AQUEOUS RING-OPENING METATHESIS POLYMERIZATIONS

Thesis by
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To my loving wife, Julie,
and daughter, Sara

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In taking a moment to reflect on the people and events that in some way influenced me, and as a result, contributed (at least indirectly) to this work, I find a long list, stretching back over a period of time. First, I would like to thank my father, who taught me that a feather can fall as fast as a brick. Those lessons influenced me more than you will ever realize. I would like to thank my mother, who taught me the virtues of hard work and patience. At least I've learned the hard work part. The Caltech community, I cannot thank enough. You have given me an opportunity to do what I have always wanted to do. I would like to thank Jody Redepenning for help with the membrane measurements, and Paul Bernhard for help with both the CV work and for providing the initial samples of $Ru(H_2O)_6(tos)_2$. Thanks also go to Dom McGrath for helpful discussions, and further samples of $Ru(H_2O)_6(tos)_2$. I would like to thank Dave Wheeler for many enlightening discussions. I would like to thank past members of the Grubbs' group, Eric Anslyn, Tim Swager, Lou Cannizzo and Wilhelm Risse, for teaching me so much. To the current members of the Grubbs' group I would like to extend both a thanks and an apology. My daily interactions with the people in the group helped to make my years here a wonderful experience. In trying to finish this work, however, I feel I have been somewhat selfish, and remiss in my community responsibilities. For this I apologize. Special thanks go to Bob Grubbs who in very subtle ways, creates a special atmosphere in which a person can learn and grow. That is a hard thing to do right, and you do it very well.

Finally, I would like to thank my wife, Julie, for all of her love and support. At the risk of sounding trite, this would not have been possible

without you. You provided both scientific and personal council, and most importantly, friendship when I needed it most.

PREFACE

Past workers in this group as well as in others have made considerable progress in the understanding and development of the ring-opening metathesis polymerization (ROMP) technique. Through these efforts, ROMP chemistry has become something of an organometallic success story. Extensive work was devoted to trying to identify the catalytically active species in classical reaction mixtures of early metal halides and alkyl aluminum compounds. Through this work, a mechanism involving the interconversion of metal carbenes and metallacyclobutanes was proposed. This preliminary work finally led to the isolation and characterization of stable metal carbene and metallacyclobutane complexes. As anticipated, these well-characterized complexes were shown to be active catalysts. In a select number of cases, these catalysts have been shown to catalyze the living polymerization of strained rings such as norbornene. The synthetic control offered by these living systems places them in a unique category of metal catalyzed reactions. To take full advantage of these new catalysts, two approaches should be explored. The first takes advantage of the unusual fact that all of the unsaturation present in the monomer is conserved in the polymer product. This makes ROMP techniques ideal for the synthesis of highly unsaturated, and fully conjugated polymers, which find uses in a variety of applications. This area is currently under intense investigation. The second aspect, which should lend itself to fruitful investigations, is expanding the utility of these catalysts through the living polymerization of monomers containing interesting functional groups. Polymer properties can be dramatically

altered by the incorporation of functional groups. It is this latter aspect which will be addressed in this work.

After a general introduction to both the ring-opening metathesis reaction (Chapter 1) and the polymerization of fuctionalized monomers by transition metal catalysts (Chapter 2), the limits of the existing living ROMP catalysts with functionalized monomers are examined in Chapter 3. Because of the stringent limitations of these early metal catalysts, efforts were focused on catalysts based on ruthenium complexes. Although not living, and displaying unusually long induction periods, these catalysts show high promise for future investigations directed at the development of catalysts for the living polymerization of functionalized monomers. In an attempt to develop useful catalysts based on these ruthenium complexes, efforts to increase their initiation rates are presented in Chapter 4. This work eventually led to the discovery that these catalysts are highly active in aqueous solution, providing the opportunity to develop aqueous emulsion ROMP systems. Recycling the aqueous catalysts led to the discovery that the ruthenium complexes become more activated with use. Investigations of these recycled solutions uncovered new ruthenium-olefin complexes, which are implicated in the activation process. Although our original goal of developing living ROMP catalysts for the polymerization of fuctionalized monomers is yet to be realized, it is hoped that this work provides a foundation from which future investigations can be launched.

In the last chapter, the ionophoric properties of the poly(7-oxanobornene) materials is briefly discussed. Their limited use as acyclic host polymers led to investigations into the fabrication of ion-permeable membranes fashioned from these materials.

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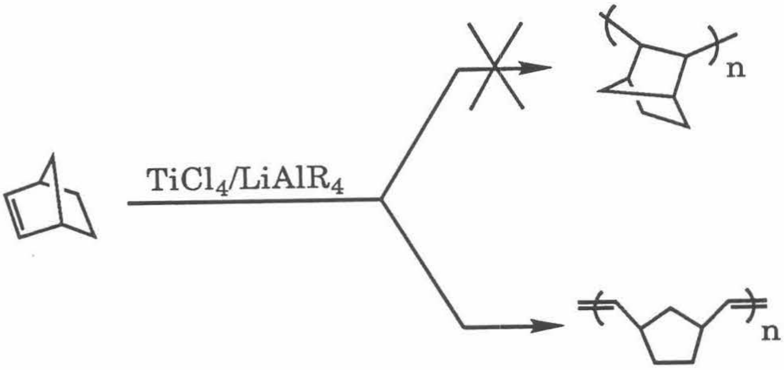
CHAPTER 1

AN INTRODUCTION TO RING-OPENING METATHESIS POLYMERIZATIONS

Abstract

The ring-opening metathesis polymerization reaction is briefly reviewed. Special emphasis is placed on the recent development of metallacyclobutane and metal alkylidene complexes which catalyze the living polymerization of norbornene. The mechanistic features possessed by these catalysts, which lend them their living characteristics, are discussed.

The ring-opening metathesis polymerization[1] (ROMP) was discovered during investigations of the Ziegler-Natta polymerization of strained cyclic olefins. Structural studies on the polymer obtained from a $TiCl_4/LiAlR_4$ catalyzed polymerization of norbornene revealed an unexpected result.[2] Instead of obtaining the fully saturated polymer expected from a coordination-insertion mechanism, the product polymer still possessed carbon-carbon double bonds, indicating that the polymerization had occurred by some ring-opening process, the mechanism of which was still undefined (Equation 1).



(1)

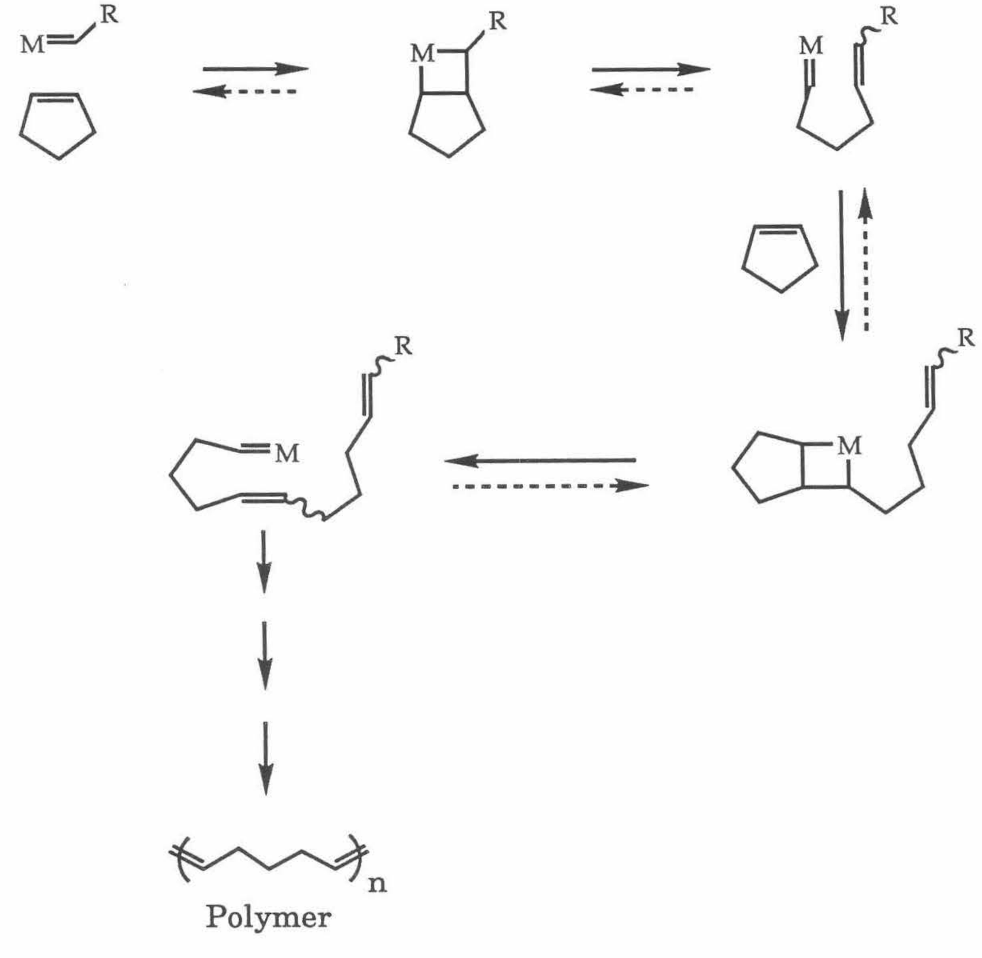
Simultaneous with, but independent of, this polymerization work, several researchers were involved in the development of the olefin metathesis reaction.[1,3] The general olefin metathesis reaction for acyclic olefins is shown in Scheme **I**.

Scheme I:

Several years elaspsed before the connection between the unusual ring-opening polymerization process and the acyclic olefin metathesis reaction was discovered. This connection was made through the discovery that $WCl_6/EtAlCl_2/EtOH$ (1/4/1) catalyzed both the ring-opening polymerization of cyclooctene[4], and the metathesis of 2-pentene.[5] Since this early period, many important discoveries have been made concerning the mechanism of the metathesis reaction.[1,6] The current basic mechanism for olefin metathesis (both for cyclic and acyclic substrates) involves the interconversion of a metal carbene and a metallacyclobutane species.[7] The formation of polymer results from the metathesis process when the two ends of the metathesized olefin remain connected together through an external ring system. The generic process for the propagation steps in the ring-opening metathesis polymerization of a cyclic olefin is shown below in Scheme **II**.

The mechanism outlined here is kept rather general. The initiation process associated with the formation of the initial carbene or metallacycle species has been omitted. These metal alkylidene or metallacyclobutane species either can be generated *in situ* [8] (as in the case of equation 1), or may be preformed and used directly as the initiating agents (*vide infra*). Termination processes which result in either the deactivation of the active end-group or its cleavage from the growing polymer chain have also been omitted from this scheme. Finally, also absent are any chain transfer processes such as "back-biting" of the active end-group into the acyclic double bonds of the polymer chains. The deletion of these features from Scheme **II** is neither an oversight, nor an attempt to oversimplify the ROMP process, but rather, results from the almost total lack of information concerning these processes for all but a small number of well-characterized

Scheme II:



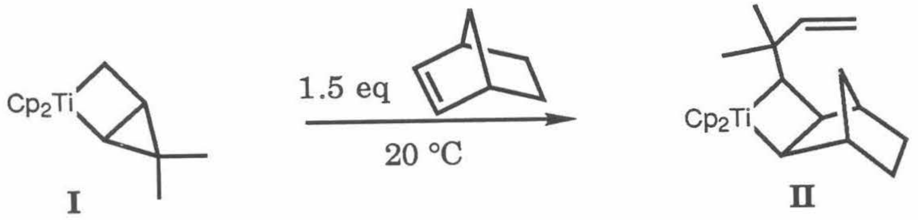
systems. It must be emphasized that the current status quo is unacceptable. It is our understanding and eventual manipulation of initiation, termination and chain transfer processes that will be paramount in the development of the next generation of well-behaved catalyst systems.

The basic mechanistic studies on the olefin metathesis reaction have provided the basis for the development of a number of sophisticated catalysts which are currently under study. Either of the two intermediates, metallacyclobutanes or metal alkylidenes, may act as the stable chain carrying species in the metathesis process. Indeed, examples of both types of complexes have been isolated and demonstrated to be active metathesis catalysts.[9] Interest in metathesis polymerizations has recently intensified following the discovery that titanacene metallacyclobutane complexes catalyze the living polymerization of norbornene.[10] Since this seminal discovery, several other living polymerization catalysts have now been reported (*vide infra*).

A living system must be free of chain termination and chain transfer steps.[11] In order to produce monodispersed polymers, certain additional criteria must be met: 1) The initiation rate must be equal to, or greater than, the propagation rate; 2) there must be only one propagating species in solution; and 3) except for the special case of a very slow depolymerization rate, the propagation steps must be irreversible. If all of the above criteria are met, then the system will be living and produce polymers whose molecular weights are characterized by a statistical Poisson distribution.[12]

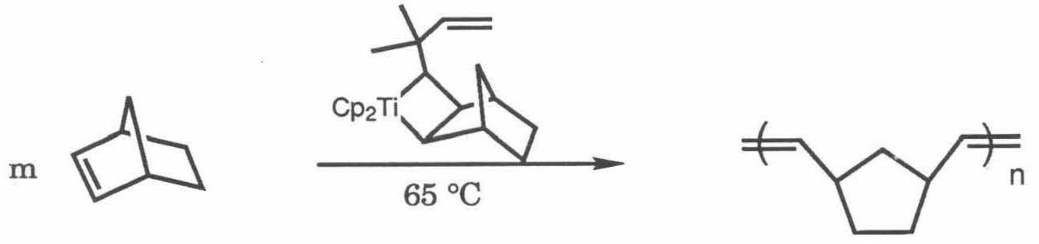
"Classical" ROMP systems, typically composed of early metal halides such as WCl_6, and alkylating reagents such as diethylaluminum chloride, fail to meet nearly all of the above listed "living" criteria. The classical systems are often plagued by one or more of the following limitations: 1) Facial back-biting steps;[13] 2) ill-defined termination steps;[14] 3) a variety of active propagating species present;[15] and 4) slow generation of the active species relative to polymerization rates.[16] All of these factors broaden the molecular weight distribution of the polymers produced. Elimination of these detrimental features for the titanacene metallacyclobutane catalysts discussed below has resulted in living systems that produce monodispersed polymers.

Thermolysis of **I** at 20 °C in the presence of norbornene affords the trisubstituted metallacyclobutane **II**[10,17] (Equation 2).



(2)

When heated to 65 °C in the presence of excess norbornene, metallacycle **II** produces the desired ring opening metathesis polymer (Equation 3).



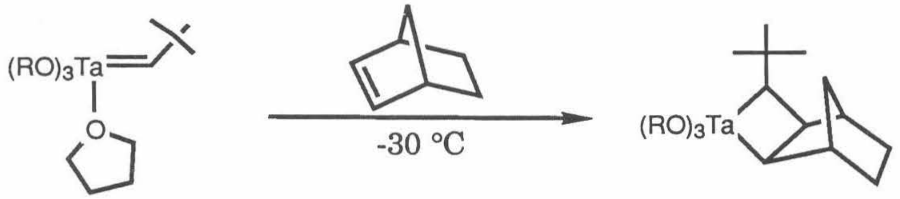
(3)

Gel permeation chromatographic analysis (GPC) of the polymer produced by the reaction of **II** with 100 equivalents of norbornene gives Mn = 21000 (vs. polystyrene standards), and a polydispersity index (PDI = M_w/M_n) of 1.08. In addition, when the molecular weight of samples obtained at intermediate conversions are plotted against % conversion, a linear plot is obtained. These results clearly indicate that this is truly a living polymerization. The stability of the titanacyclobutane end-group towards retrocleavage allows the polymerization to be stopped by cooling the reaction down, and restarted again by heating. The utility of the living titanacyclobutane-mediated polymerizations has been demonstrated not only for the synthesis of monodispersed polymers of controlled molecular weights,[10] but for the synthesis of well-designed di- and triblock copolymers[18] and in polymer end-capping processes[19] as well.

The choice of norbornene as a substrate for many of the living polymerization studies found in the literature is not coincidental. Norbornene is unique in that it possesses a very reactive strained double bond in the monomer, which is then converted into a sterically hindered unreactive double bond in the polymer. The ring strain of norbornene (27.2 Kcal/mole) is important in driving the reaction in a forward direction by suppressing depolymerization through backbiting of the penultimate double bond in the polymer chain. In addition to this, chain transfer reactions resulting from backbiting into the other acyclic double bonds in the polymer backbone are inhibited by the steric bulk provided by the adjacent cyclopentane rings. The importance of these factors is illustrated by a comparison of the above norbornene polymerization with the polymerization of slightly strained ring systems. At high monomer concentrations metallacycle **I** is effective in catalyzing the polymerization of cyclopentene, cycloheptene and cyclooctene to produce good yields of the desired ring-opened polymer.[20] In polymerizing these slightly strained monomers, however, the polydispersities of materials obtained are not as narrow as in the norbornene system (typical values range between 1.2 to

1.8). The broadened distributions observed in these polymerizations is ascribed to the introduction of a polymerization-depolymerization equilibrium into the system. This general broadening of the molecular weight distribution is anticipated by theoretical treatments, which predict a PDI = 2.0 for a reversible polymerization system that is allowed to reach equilibrium.[21] As a further consequence of the equilibrium situation established for these slightly strained rings, the molecular weight of the polymers produced shows only a small dependence on reaction time or monomer concentration.

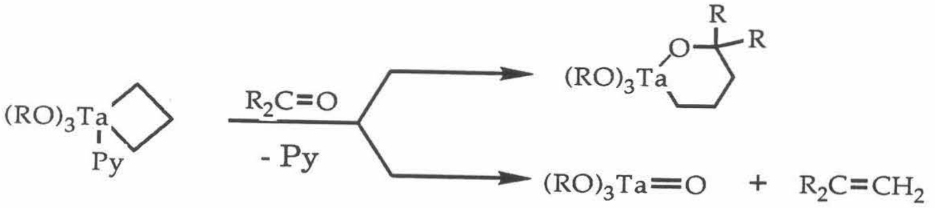
Several other reports have recently appeared concerning living ROMP systems. Metallacycle complexes analogous to the titanium system can be prepared in approximately 30% yields from the reaction of $Ta(CHtBu)(OR)_3(THF)$[22] complexes (OR = 2,6-diisopropylphenoxide (DIPP), or 2,6-dimethylphenoxide (DMP)) and norbornene at -30 °C (Equation 4).[23]



(4)

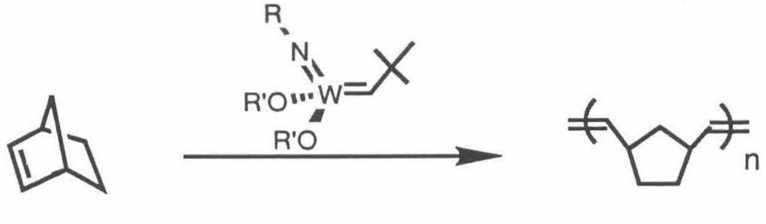
The DIPP tantalacyclobutane complexes have been shown to polymerize excess norbornene at 50 °C to yield polymer with a molecular weight proportional to the amount of monomer employed. The polydispersities of the polymers obtained at complete monomer conversion are broad, typically in the range of 1.63 to 1.95.[24] The GPC trace of the polymer obtained after only partial conversion of the monomer shows a bimodal distribution: a fraction with the expected molecular weight making up approximately 94% of the sample, and a fraction of relatively high molecular weight comprising the other 6%. The lower molecular weight fraction obtained is essentially monodispersed (i.e., PDI= 1.04 at 75% monomer conversion). These data seem to indicate that a small amount of highly active impurity is present during the reaction. Possible explanations of the broad molecular weight distributions at complete monomer conversion include the decomposition of the metallacycle end-groups at low monomer concentrations, secondary metathesis of the double bonds in the polymer chain, or a greater weight contribution in the latter stages of the reaction by the polymer fraction produced by the highly active impurity present. Evidence for the occurrence of secondary metathesis includes a very slight change in the *cis/trans* double-bond ratio of the polymer in the absence of monomer. For example, when polymers containing metallacycle end-groups are left in solution, the cis content of the polymer changes slowly from approximately 45% to 35% after five days at room temperature. In addition, the tantalacycle catalyst is known to metathesize at least 100 equivalents of *cis*-2-pentene.[24] The DMP tantallacycles are active polymerization catalysts as well. They are, however, more reactive, and as a result, not as well-behaved as the DIPP derivatives. The polydispersity of the polymer prepared using 100 equivalents was measured to be 2.71.

These tantallacycle complexes are quite reactive towards polar functional groups such as ketones and aldehydes. Two competetive reactions are observed when the tantallacycles are allowed to react with organic carbonyl groups. A Wittig type reaction via an incipient tantalum alkylidene is observed, along with a competitive direct insertion of the carbonyl into the tantallacycle to form an oxytantallacyclohexane complex (Equation 5).[24]


(5)

Kinetic analysis of the DIPP tantallacyclobutane system shows, after an initiation period, the rate of polymerization to be zero order in monomer and first order in catalyst concentration, consistent with the mechanism proposed for the titanacycle systems. The kinetic parameters calculated for these two systems are remarkably similar with $\Delta H = 24.9$ Kcal/mol, $\Delta S = 7.5$ eu, and $\Delta G_{338} = 22.4$ Kcal/mol for the tantallacycle polymerization, and $\Delta H = 27.1$ Kcal/mole, $\Delta S = 9$ eu, and $\Delta G_{338} = 24$ Kcal/mol for the titanacycle polymerization.[10]

As a complement to the stable metallacyclobutane catalysts, a series of stable alkylidene catalysts have been prepared and shown to be active, living polymerization catalysts. The complex $W(CHtBu)(NAr)(O^tBu)_2$[25] (Ar = 2,6-diisopropylphenyl) (**III**) reacts with 50-200 equivalents of norbornene in toluene at 25 °C, followed by addition of benzaldehyde as an end-capping agent, and provides polymers in which the major component has a molecular weight proportional to the number of equivalents of norbornene consumed, with dispersities of approximately 1.05 (Equation 6).


(6)

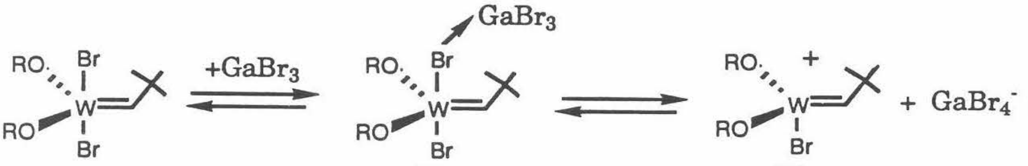
Just as was observed in the tantallacyclobutane polymerizations above, a variable amount (10-20%) of high molecular weight polymer is also produced. Again, it is thought that the high molecular weight material forms via an extremely active, as yet unidentified, tungsten-carbene species that is formed during the polymerization process. The origin of these very active impurities is unknown. Because of the extreme moisture sensitivity of **III**, it was hypothesized that a hyperactive tungsten-oxo species could be formed from the reaction between **III** and trace amounts of water in the reaction mixture. However, in control experiments using known amounts of water, the opposite was found to be true. Trace amounts of water severely deactivate **III,** leading to the formation of low rather than high molecular weight materials.[26]

Again, the living nature of this catalyst is attributed, in part, to its relative inactivity towards unactivated double bonds (i.e., the internal olefins present in the polymer backbone). Exceedingly more active yet less selective catalysts can be synthesized by modification of the alkoxide ligands on the catalyst. Substitution of the t-butoxide ligands by $-OC(CH_3)_2CF_3$ and -$-OCCH_3(CF_3)_2$ ligands[27,28] leads to increasingly more active catalysts (i.e., rapid polymerization of norbornene at -60 °C); however, the molecular weight of the polymer produced is independent of both the reaction time, as well as the equivalents of the monomer present.[25] In addition, the polydispersities typically range from 1.62 to 2.23. This attenuation of the living behavior is attributed to both a slow initiation rate relative to propagation rate and to the introduction of the secondary metathesis manifold with the double bonds along the polymer chain. The secondary metathesis theory is bolstered by two additional observations. Unlike the t-butoxide catalyst, **III**, the catalysts containing the fluorinated alkoxides are exceedingly active acyclic olefin metathesis catalysts (i.e., 1000 turnovers per minute of *cis*-2-pentene).[28] In addition, the *cis/trans* double bond ratios in the polymers formed by the fluorinated catalysts are observed to change during the course of the polymerization. This change from the kinetically determined *cis/trans* ratio (approximately 100% *cis*) towards an equilibrium ratio (approximately 20% *cis*) is a clear indication of the presence of secondary metathesis.[26]

Further synthetic utility can be introduced by changing the metal in the above alkylidene complexes from tungsten to molybdenum.[29] Molybdenum, less oxophilic than tungsten, will tolerate monomers containing mildly reactive functionality such as esters for short periods of time without appreciable catalyst deactivation. This feature allows for the rapid polymerization of olefins containing esters. For example, the polymerization of *endo,endo*-5,6-dicarbomethoxynorbornene (DCNBE) with $Mo(CH^tBu)(NAr)(O^tBu)_2$ (Ar = 2,6-diisopropylphenyl) (**IV**) has been reported to give the corresponding ring-opened polymer with molecular weights proportional to the equivalents of monomer used, and polydispersities ranging from 1.11 to 1.22.[29] It was found that **IV** would tolerate approximately 100 equivalents of DCNBE for approximately 15 minutes before deactivation became competitive.[24,29] Additional work concerning the ROMP of functionalized olefins will be covered in later chapters.

A variety of isolated pentacoordinate tungsten-carbene complexes are known to be active metathesis catalysts.[30] At least one of these systems has been proposed to be living based primarily on ^1H NMR identification of the propagating alkylidene.[31] To date, no investigation on the molecular weights and dispersity of the materials obtained has been reported which can verify the "living" claim. The solution NMR studies do confirm the mechanism of the metathesis reaction, but do not insure that all of the requisite factors are met for a living system.

$W(CH^tBu)(OCH_2tBu)_2Br_2$[31] (**V**) is a mildly active ROMP catalyst[32] that can be further activated by the addition of Lewis acids such as $GaBr_3$ to form highly active complexed (**Va**), and cationic (**Vb**) metathesis species[33] (Equation 7).



V **Va** **Vb** (7)

As evidenced by ^1H NMR, the activated catalyst mixture reacts with norbornene (or a series of methyl-substituted norbornenes) to be *partially* converted to a new carbene species.[31] From the ratio of product carbene and residual initiator carbene concentrations, it was estimated that the rate constant for propagation is at least 3 times that for initiation. This system suffers from several limitations. First, treatment with $GaBr_3$ produces an equilibrium situation in which three species are present, all of which may possess their own intrinsic activities. Second, the rate of polymerization is measurably faster than the rate of initiation. And third, a substantial amount of secondary metathesis occurs, as was evidenced by changes in both the *cis* content of the polymer and head/tail ratio of the substituted carbenes when the catalyst was left in solution (120 min at 20 °C) after consumption of the monomer.

An important extension of the $W(CH^tBu)(OCH_2{}^tBu)_2Br_2$ / $GaBr_3$ has recently been published,[34] in which the conversion of the initiating metal-carbene complex into the initial metallacyclobutane complex by the addition of a first equivalent of norbornene is directly observed at low temperature by ^{1}H NMR. Subsequent orthogonal cleavage of the metallacyclobutane and its reformation by the addition of further equivalents of norbornene are also observed. The direct observation of these primary steps may lead to a better understanding of both the kinetic and thermodynamic factors operative during these propagating steps.

The escalated development of living ROMP catalysts in recent years is evident from a chronological examination of the literature cited. Although metathesis polymerizations were discovered over a quarter century ago, the bulk of the literature concerning living systems comes from only the last two years. Clearly, this ground work should open the doors to a variety of specialized and innovative polymeric materials as the synthetic potential of these living systems is explored. Several issues still remain to be addressed. Of considerable interest, naturally, is the expansion of the domain of the living ROMP systems to include monomers other than norbornene. Although the polymerization of norbornene has provided a wealth of information used in guiding catalyst development efforts, poly(norbornene) is of little commercial interest. Several different areas are currently being examined. Many researchers would like to see the application of ROMP techniques extended to the synthesis of conducting polymers. Recently, some progress has been realized in adapting living polymerization techniques to monomers appropriate for this application. Another area of high industrial concern is the development of living catalyst systems that display tolerance towards reactive fuctional groups. Progress in this area would permit the synthesis of a host of new polymers, possessing unusual properties.

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CHAPTER 2

THE POLYMERIZATION OF FUNCTIONALIZED MONOMERS BY TRANSITION METAL CATALYSTS: AN INTRODUCTION

Abstract

The polymerization of monomers possessing polar functional groups by transition metal catalysts is reviewed. The Ziegler-Natta polymerization of functionalized vinyl monomers possessing ether, ester, halogen and amine groups is generally accompanied by catalyst deactivation processes, which result in poor yields of polymer. In the successful systems, the mechanism of polymerization is often thought to be free radical or cationic, rather than the conventional coordination-insertion mechanism observed for vinyl hydrocarbons. Limited success in the ring-opening metathesis polymerization of cyclic olefins possessing anhydride, ester, cyanide and diimide derivatives has been reported using $WCl_6/AlEt_2Cl$, or $WOCl_4/SnMe_4$ as catalysts. Again, competitive catalyst deactivation reactions limit the polymer yields obtained. Far more efficient ring-opening metathesis polymerizations are realized using the Group VIII metal catalysts. Although not as active as their early metal counterparts, the late metal catalysts display superior tolerance to functional groups. Emulsion polymerizations are discussed, with an emphasis placed on aqueous transition-metal catalyzed diene polymerizations.

INTRODUCTION

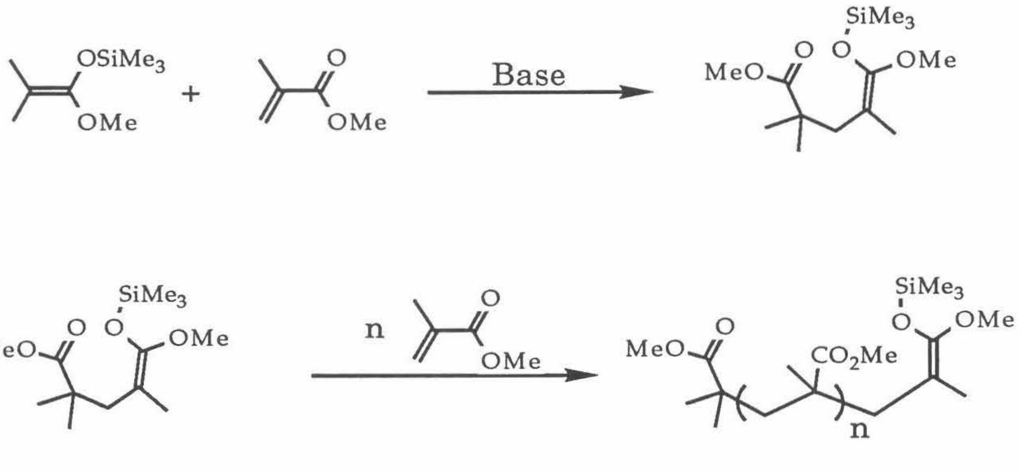
The controlled synthesis of specialized macromolecules is an extremely important area of polymer chemistry.[1] The chemical and physical properties of polymers can be modified by controlling the isomeric constitution, molecular weight and molecular weight distribution of the material.[2] More dramatic control over these and other important properties can be obtained by the selective incorporation of functional groups within the polymer's structure.[3] Permeability, compatibility, adhesion, solid-state morphology, solution rheology and glass transition and melt temperatures are all properties that can be influenced by the presence of functional groups.[3,4] For these reasons, it is desirable to develop new methods for the selective polymerization of functionalized monomers. In considering synthetic strategies for the formation of high polymers, it is ultimately more advantageous to develop chain polymerization techniques rather than step growth (condensation) techniques. This conclusion is a natural consequence of the idea that highly controlled systems will ultimately be living polymerization systems[5], which allow for the synthesis of specific molecular weight materials, di- and tri-block copolymers,[6] and specifically end-capped materials.[7] Of the three "conventional" chain polymerization techniques, radical, cationic and anionic, both cationic and anionic polymerizations can be rendered living under the appropriate reaction conditions.[5] Unfortunately, ionic polymerization techniques are among the least tolerant of monomers containing reactive functional groups.[8] For example, monomers such as chloroprene, vinyl acetate, vinyl sulfonic acid, acrylic acid, allyl alcohol, and allyl acetate can be polymerized utilizing free radical techniques; however, all of these substrates are unreactive under cationic and anionic polymerization conditions.[8] Likewise, monomers such as isobutyl vinyl ether, methyl vinyl ketone 1-vinylpyrrolidone, and allyl chloride can be polymerized using either radical or cationic methods, but not by anionic methods. Although the radical polymerizations (and selected cationic polymerizations) of the above mentioned monomers do provide polymers, not one of them is living and it is exceedingly difficult to control the molecular weight, tacticity and, where applicable, the regioselectivity of the polymers produced.[9]

Within certain limitations, however, there has been considerable success in the living polymerization of polar monomers, either through the adaptation of reaction conditions or by developing altogether new synthetic methodologies. The synthesis of poly(methyl methacrylate) provides a beautiful illustration of this progress. Despite the fact that living anionic polymerization of butadiene and styrene has been carried out commercially for some time,[10] commercial production of methacrylate polymers through anionic techniques is hampered by requisite low temperatures needed to maintain the living conditions.[11] In an effort to address this need, a fundamentally new method termed "group-transfer polymerizations" (GTP) was developed for the living polymerization of acrylate monomers.[12] Group-transfer polymerizations involve the catalyzed Michael addition of silyl ketene acetals to α,β-unsaturated esters[13] (Scheme **I**).

GTP techniques allow for the synthesis of polymers of controlled size with molecular weights as high as 50,000-100,000 at ambient temperatures. Polydispersities for these materials are typically in the range of 1.05 to 1.3 depending on the particular ester derivative employed.[12]

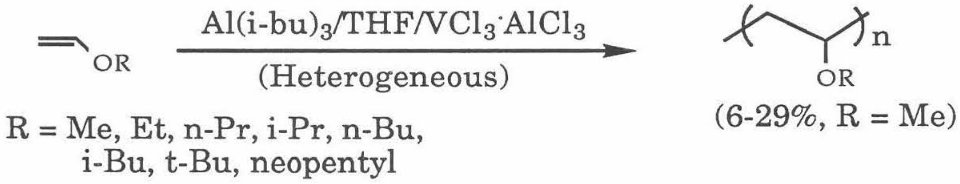
Considering the above discussion, it would be desirable to develop additional alternative chain polymerization methods that will tolerate polar functionality incorporated into the monomers. Attractive possibilities include the adaptation of transition metal polymerization catalysts such as Ziegler-Natta or ring-opening metathesis catalysts to meet these stability requirements. Stabilizing the active end-group of the growing polymer chain, using a transition metal species, should have some unique advantages over "conventional" chain polymerization methods. In addition to modulating the reactivity of the polymer end-groups, the possibility of controlling the stereoselectivity of the polymerization could be realized by manipulating the nature of the metal center and/or its ligand complement.

Scheme I:



ZIEGLER-NATTA POLYMERIZATIONS OF FUNCTIONALIZED OLEFINS

There have been several attempts to use Ziegler-Natta systems to polymerize polar monomers.[14] By and large, this has proved to be an elusive goal. The polar functional groups often react with and deactivate the catalyst systems. Because of this deactivation, yields of polymer are typically low and high catalyst-to-monomer ratios are required (values of 10 for monomer/catalyst ratios have been reported). This deactivation process is epitomized by the use of esters or alcohols to deliberately poison or otherwise attenuate the activity of various catalyst systems. In general, the few systems that have been moderately sucessful at polymerizing functionalized olefins have often been shrouded in controversy. It is asserted that for most functionalized monomers, the Ziegler-Natta mixtures act to initiate polymerization not through the conventional coordination-insertion mechanism, but through cationic, anionic or radical mechanisms. This distinction is often difficult to demonstrate unequivocally. Typically arguments for or against a particular propagation mechanism are based either on copolymerization behaviors or on comparisons of the microstructure and physical properties of the polymer produced by the Ziegler-Natta system to the authentic polymers obtained by cationic, anionic or radical polymerization methods. For example, the polymerization of vinyl ethers by Al(i-Bu)$_3$/THF/VCl$_3$·AlCl$_3$ (prepared by the reduction of 3 equivalents of VCl$_4$ with one equivalent of AlEt$_3$), has been reported[15] (Equation 1).



R = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, t-Bu, neopentyl

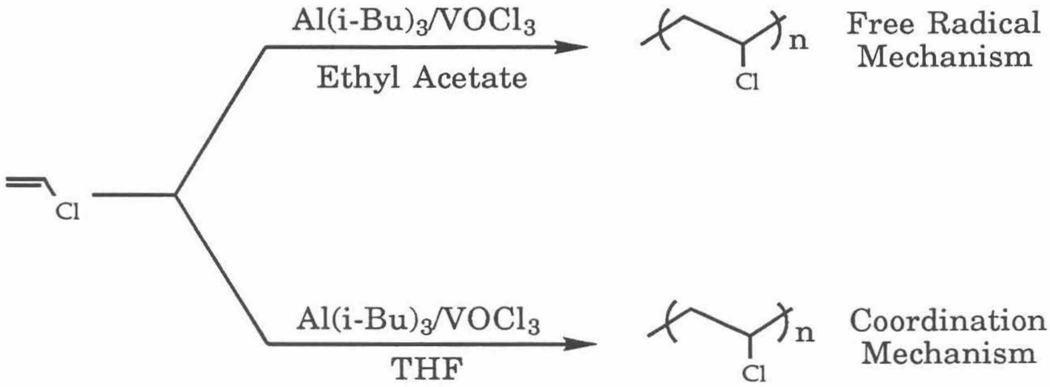
(6-29%, R = Me)

(1)

The yields of polymer are quite low, with typical values in the range of 6-29% for the polymerization of methyl vinyl ether. Given the microstructure of the polymers obtained, the propagation mechanism proposed was not a Ziegler-Natta coordination-insertion mechanism, but rather, a cationic insertion mechanism. Additional support for a cationic mechanism comes from the observation that in a copolymerization of alkyl vinyl ethers and ethylene, the rate of conversion of the vinyl ether increases in the order $AlEt_2Cl$ < $AlEtCl_2$ < $AlCl_3$, (in combination with Cp_2TiCl_2), whereas the ethylene conversion decreases simultaneously.[16]

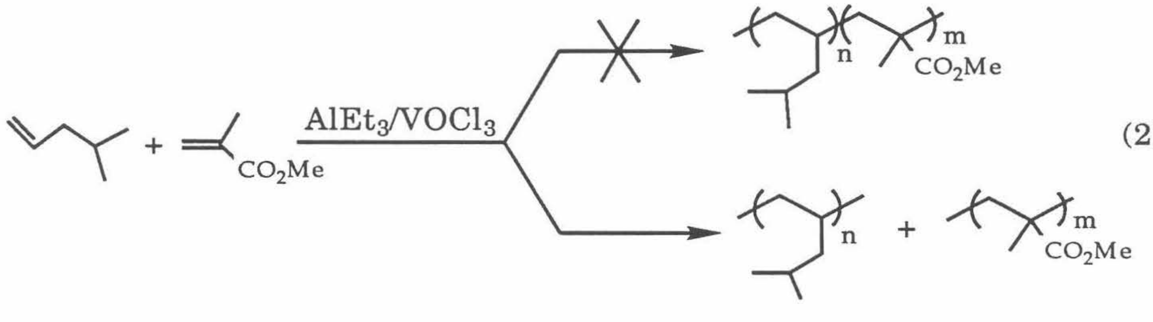
One of the most thoroughly investigated functionalized monomers for Ziegler-Natta studies is vinyl chloride.[17] For many of the catalyst mixtures studied ($AlR_3/TiCl_3$,[18] $AlEt_3/Ti(OBu)_4$/epichlorohydrin,[19] $Al(i\text{-}Bu)_2Cl/Ti(OBu)_4$,[20] $AlEtCl_2/Ti(OBu)_4$),[21] the evidence points to a radical mechanism rather than a Ziegler-Natta coordination-insertion mechanism. In support of this conclusion, when vinyl chloride is copolymerized with vinyl acetate using $VOCl_3\text{-}Al(i\text{-}Bu)_3$, the copolymer's composition was characteristic of a radical polymerization.[22] The monomer reactivity ratios[23] were measured to be $k_{11}/k_{12} = 3.74$ and $k_{22}/k_{21} = 0.033$ (1 = vinyl chloride, 2 = vinyl acetate), using the above Ziegler-Natta catalyst which compares closely with the reactivity ratios determined for a free radical process, $k_{11}/k_{12} = 2.1$ and $k_{22}/k_{21} = 0.3$. For certain catalyst systems a balance seems to exist between these two mechanisms, which under the appropriate circumstances can be shifted to favor one propagation mode over the other. For example, $Al(i\text{-}Bu)_3\text{-}VOCl_3$ with the Lewis base, ethyl acetate, produces poly(vinyl chloride) with the same kinetic and copolymer chracteristics as poly(vinyl chloride) produced from conventional radical methods.[24] By switching from ethyl acetate to THF, the kinetics and copolymerization properties deviated substantially from the radical mode behavior, and it was therefore concluded that the propagation mode switched to a coordination-insertion mechanism (Scheme II).[25]

Scheme II:



Another approach to shifting the mechanism from cationic to Ziegler-Natta is to attenuate the Lewis acidic character of the catalyst by replacing the halogen ligands with alkoxide ligands. For example, the $VOCl_3$-$AlEtCl_2$ system can be replaced with $VO(OEt)_3$-$AlEt(OEt)Cl$ to select for the Ziegler-Natta insertion mechanism.[26]

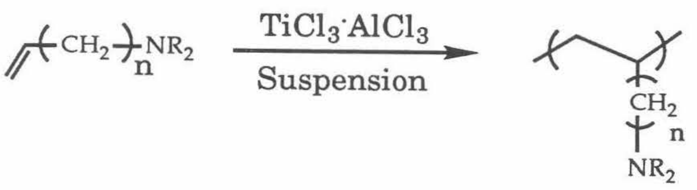
These Ziegler-Natta catalyst systems can be sufficiently complex so as to allow for the simultaneous propagation by two different reaction mechanisms. For example, it can be observed that 4-methyl-1-pentene can be "copolymerized" with methyl methacrylate using $AlEt_3/VOCl_3$.[27] Careful analysis, however, of the "copolymer" produced reveals it actually to be a mixture of homopolymers of the two components (Equation 2).



(2)

These results appear to indicate that the polymerization of the methacrylate monomers does not occur at the same site as does the α-olefin. The full mechanistic details elucidating these two pathways have not been worked out. It is known, however, that methyl methacrylate polymerized by a similar catalyst, $AlEt_2Cl/VCl_4$, gives a polymer having the the same characteristics as poly(methyl methacrylate) obtained by conventional radical methods.[28]

To increase catalyst activities and polymer yields, a basic strategy has been to select functionalized monomers that resemble, as closely as possible, conventional α-olefins. This is generally accomplished by sequestering the functional groups far from the olefin center, increasing the steric encumbrance around the functional groups, and by reducing the Lewis basicity of the heteroatoms within the functional groups. These basic principles have been demonstrated for the polymerization of ω-amino-α-alkenes by $TiCl_3 \cdot AlCl_3$ suspensions using monomer/catalyst = 10/1[29] (Equation 3).



n	R	% Yield
1	Me	0
3	Me	6
3	Et	8
3	n-Pr	99

(3)

When n=1, no polymer is obtained. When n=3, polymer is obtained, with variable yields, depending upon the R groups on the amine. When R=methyl, ethyl and n-propyl, the yields were 6, 8 and 99%, respectively. The general inactivity of these systems is illustrated by the N,N-diethyl polymerization, which required 240 hours at 60 °C to obtain an 8% yield of polymer.

The later transition metals have also been used as Ziegler-Natta catalysts. These catalysts have been primarily based on the Group VIII metals Ni, Pd, Co, Ru and Rh.[30] With a few exceptions, vinyl monomers are best polymerized by metals from the left side of the table, while diene monomers are more active with the metals from the right side of the table. (As a group, butadiene catalysts will be covered in a later section.) The lower oxophilicity of the later transition metals make them potentially interesting candidates for catalysts in the polymerization of fuctionalized monomers.[30] A few examples will be presented here. As was the case for the early metal catalysts, the polymerization mechanism, which is operative when using Group VIII metals, is often a matter of debate.

A radical propagation mechanism has also been proposed to explain the results obtained for the polymerization of vinyl monomers, using dichloro(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV) as a catalyst.[31] This catalyst, in combination with triphenylphosphine, only gave yields of less than 2% of polymers of styrene, vinyl acetate and of ethyl vinyl ether. Acrylonitrile, methl vinyl ketone and vinyl chloride produced no polymers at all using this catalyst. On the other hand, methyl methacrylate could be polymerized with yields ranging between 20 and 78%, depending on temperature and the Ru/phosphine ratio. The tacticity of the poly(methyl methacrylate), and the copolymer composition data using a methyl methacrylate-sytrene monomer feed closely paralleled the results obtained using standard radical initiators at similar temperatures.

The polymerization of vinyl monomers (acrylonitrile, methacrylonitrile, methyl acrylate) through a mechanism thought to be a coordination-insertion pathway has been reported using the stable Ru hydride, $H_2Ru(PPh_3)_4$, as a catalyst.[32] Copolymerizations of acrylonitrile with methyl acrylate using this catalyst gave copolymers with compositions that varied considerably from the compositions obtained through free radical routes. Reactivity ratios of $k_{11}/k_{12} = 4.8$ and $k_{22}/k_{21} = 0.1$ (1= acrylonitrile, 2= methyl acrylate) were obtained using these catalysts. For free radical systems, the reactivity ratios for these monomers are approximately $k_{11}/k_{12} = k_{22}/k_{21} = 1$.

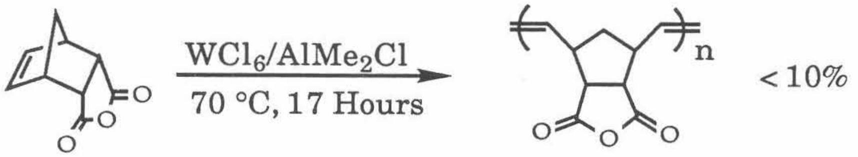
The polymerization of vinyl monomers has been reported using isolated Fe and Co alkyl species.[33] $R_2Fe(bipy)_2$ and $RCo(bipy)_2$ (R = methyl, ethyl) have been shown to be mildly active towards the polymerization of olefins with large Afrey-Price "e-values" (i.e., relatively electronegative olefins).[34] Acrylonitrile (e value 1.20), methacrylonitrile (0.81), acrolein (0.73), methyl acrylate (0.60) and methyl methacrylate (0.40) are all active toward polymerization. Vinyl chloride (0.20), vinyl acetate (-0.22), styrene (-0.80) and isobutyl vinyl ether (-1.77) were all completely inactive with both of these catalysts. Typical polymerizations are done at room temperature for several days (3-12 days) in neat monomer. The yields of polymer vary between 12-73%, depending on the monomer and reaction times.[35] Unidentified catalyst deactivation processes seem to occur at a competitive rate during these reactions, eventually killing the catalyst. The polymers obtained for most of these monomers were random, seemingly implicating a radical polymerization mechansim. However, copolymerization studies using acrylonitrile and methyl methacrylate clearly indicate that neither a free radical nor an anionic mechanism is operative. Although no direct observation of alkyl insertion into a coordinated olefin was made, all kinetic data are consistent with this mechanism.

Both the Fe and Co alkyl catalysts are limited in the types of functional groups utilized. Protic sources (alcohols, water, acids, etc.) react rapidly to protonate the alkyl group.[36] Decomposition products from the vinyl chloride experiments appear in part to be Fe(bipy)$_2$Cl$_2$, indicating C-Cl cleavage pathways. The product obtained from the reaction with vinyl acetate (VAc) was characterized as Fe(bipy)(VAc)$_2$, with the VAc ligands acting as bidentate ligands through coordination of the CO groups.[36]

RING-OPENING METATHESIS POLYMERIZATIONS OF POLAR MONOMERS

The commercial importance of bis-α,γ-substituted molecules as well as functionalized polymers has provided the impetus for the development of catalysts for the metathesis of both functionalized cyclic and acyclic substrates.[37] As in the Ziegler-Natta investigations, this work has met with mixed success. The results depend on both the catalyst and the nature of the functional groups being examined. Commonly, relatively unreactive groups such as esters are employed in these studies. Considering the number of metathesis catalysts known, surprisingly few are active when applied to functionalized substrates.[38] For instance, for the homogeneous metathesis of acyclic, unsaturated esters, virtually no catalyst systems that do not contain WCl$_6$ have been reported.[39] Of these known catalysts, the WCl$_6$/Sn(CH$_3$)$_4$ system appears to be the most effective. Other combinations (such as WCl$_6$ in combination with organoaluminum compounds), which are highly active for the metathesis of normal olefins, are almost inactive for functionalized olefins.[40] The activity of all these catalysts for the metathesis of olefins bearing functional groups is several orders of magnitude less than that observed for normal olefins.[40] The circumvention of these limitations is often attempted by using large amounts of catalyst and by limiting the investigation to monomers containing deactivated functional groups.

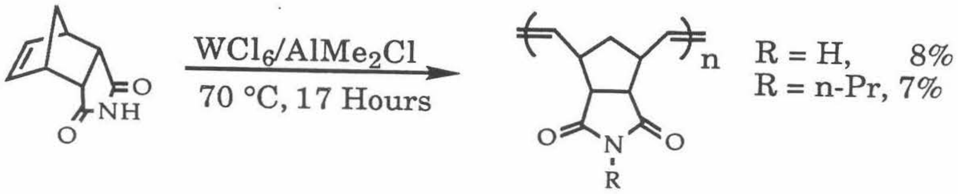
Attempts at the ring opening metathesis polymerization of *exo*-5-norbornene-2,3-dicarboxylic anhydride has been reported on several occasions[41] (Equation 4).



(4)

The yields in this reaction are quite low. In addition, the reaction conditions necessary (i.e., 70 °C, for 17 hours), are considerably more severe than would normally be used with the $WCl_6/AlMe_2Cl$ catalyst system. As a comparison, norbornene can be polymerized in minutes at room temperature using this catalyst.[42] The monomer used was the commercial Diels-Alder adduct (cyclopentadiene plus maleic anhydride), which is essentially pure *endo*-isomer (>99%). Monomer enriched in the *exo*-isomer (93%) can be obtained by running the Diels-Alder reaction under thermodynamically controlled conditions (i.e., 183 °C), and purifying it through fractional recrystallization.[43] It was found that by using this *exo*-enriched monomer, the yields of polymer could be increased to 50-60%. This finding of the greater polymerizability of the *exo*-isomer is a recurring theme observed in the polymerization of substituted norbornene derivatives. Explanations for this reactivity difference will be discussed later.

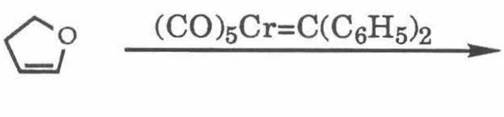
The polymerization of 5-norbornene-2,3-maleimide derivatives was also examined using the $WCl_6/AlEt_3Cl$ catalyst system.[41] (Equation 5).



(5)

As can be seen, yields of these derivatives are also quite low. For both the anhydride and the maleimide reactions, the catalyst deactivation process that occurred remains undefined. The dependence of the catalyst's reactivity on functional groups utilized is illustrated by comparing these results with the results obtained in polymerization of methyl-5-norbornene-2-carboxylate, where yields of 100% are reported using the $WCl_6/AlEt_3$ catalyst system.[41]

There has been at least one report of low yields of polymer produced from the ring-opening metathesis polymerization of the cyclic vinyl ethers 2,3-dihydrofuran and 2,3,4,5-tetrahydro-oxepin-2-yl acetate, using both $(CO)_5Cr{=}C(C_6H_5)_2$ and $(CO)_5Cr{=}C(OCH_3)C_6H_5$ catalyst systems[44] (Equations 6 and 7).

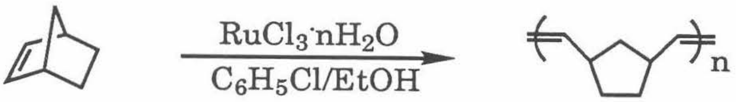


(6)

(7)

The molecular weight of the product materials varied, depending on the catalyst used. The Casey carbene, $(CO)_5Cr=C(C_6H_5)_2$, produces medium molecular weight metathesis polymer (MW =30,000 relative to polystyrene), plus a small percentage of very high molecular material (MW = 400,000), formed from what is thought to be a competing cationic mechanism. The Fisher type carbene, $(CO)_5Cr=C(OCH_3)C_6H_5$, produces only low molecular-weight oligomers (predominantly materials with a degree of polymerization 4 and 5). Using the tungsten analogues, $(CO)_5W=C(C_6H_5)_2$ or $(CO)_5W=C(OCH_3)C_6H_5$, the assumed cationic mechanism is the only process observed, as evidenced by the formation of fully saturated polymers exclusively. Extending these catalysts to other heterocyclic rings proved unsuccessful. For example, the bulk polymerization reactions of 2,5-dihydrofuran using any of the Group VI carbenes produced no polymeric materials.

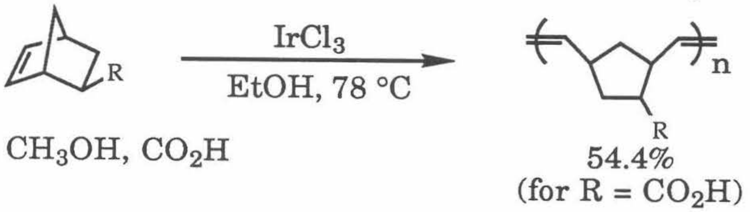
An important finding was reported in 1963, when it was discovered that $RuCl_3{\cdot}nH_2O$, $OsCl_3{\cdot}nH_2O$ and $IrCl_3{\cdot}nH_2O$ catalyzed the ring-opening metathesis polymerization of norbornene[45] (Equation 8).



(8)

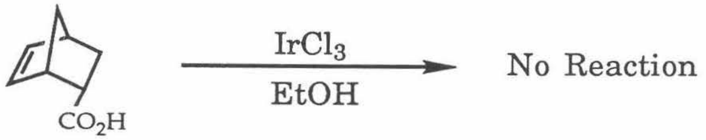
It should be noted at this time that the metal salts utilized in these polymerizations were all commercial grade compounds. It is well known that the commercial grade $RuCl_3{\cdot}3H_2O$ is an extremely impure mixture of a variety of oxochloro, hydroxocholoro, monomeric and polymeric metal species in several different oxidation states.[46] The average oxidation state of commercial "ruthenium(III) chloride" is closer to four than it is to three. Nevertheless, from our experience, this observed polymerization chemistry is consistent from one source of ruthenium to another and therefore does not appear to depend upon the presence of a particular impurity (see Chapters 3 and 4 of this work).

The reactivity order for these catalysts was found to be $Ir^{3+} > Os^{3+} > Ru^{3+}$. For example, at 80 °C, the $IrCl_3 \cdot nH_2O$ polymerized norbornene (73% yield) in 7 minutes, whereas the $RuCl_3 \cdot nH_2O$ required 6.5 hours. The overall activity of the Group VIII catalysts (ca. 50-60% yields in 6-10 hours at 80 °C) does not compare favorably with the WCl_6 catalysts (ca. 100% yields in seconds at temperatures below room temperature). The real significance of these results however, is that these polymerizations were carried out in absolute ethanol. This fact provides a clear demonstration that these Group VIII catalysts display unusual stability towards reactive functional groups. As a follow-up to this work, the polymerizations of *exo*-2-norbornene-5-carbinol and *exo*-5-norbornene-2-carboxylic acid were reported, using $IrCl_3 \cdot nH_2O$ in absolute ethanol[47] (Equation 9).



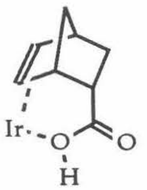
(9)

The yields of polymer in these cases were moderate. Again, the *exo*-isomers were found to be far more reactive than the *endo*-isomers. (The *endo*-acid derivative gave no polymer (Equation 10), and the *endo*-carbinol gave a 25% yield under the same conditions cited above).



(10)

The authors explained this reactivity difference by hypothesizing deactivation of the catalyst in the *endo* cases by chelation of the metal ion to the *endo* face of the monomer using the double bond and the functional group as the two bonding points.

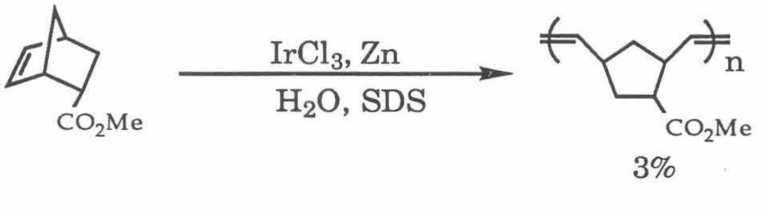


No direct proof of this deactivation mode has been reported. An alternative explanation for the *endo*/*exo* reactivity differences of substituted norbornene derivatives has been proposed by Castner and Calderon.[43] Ring-opening metathesis of an *endo,endo*-norbornene derivative results in a polymer repeat unit that consists of a five-membered ring containing four substituents on the same face. This model suggests that steric restrictions caused by both eclipsing, and transannular interactions of these substituents disfavor polymer formation.

endo exo

These Group VIII metal-catalyzed polymerizations can also be carried out in ethanol/benzene (10%) mixtures. It was reported, however, that at ethanol concentrations less than 6%, no polymerization occurs. The authors proposed that during the initiation step, the ethanol acts as a nucleophile attacking the bridgehead carbon of a π-coordinated norbornene monomer. (At that time, the carbene mechansim of olefin metathesis had not been fully established.) A full critical evaluation of this work is not possible. The authors do not discuss the catalyst concentration differences in the neat benzene reactions and the benzene/ethanol reactions. This may be an important factor, in that it is known that these Group VIII salts are *extremely* insoluble in neat benzene. Later workers showed that the alcohol may activate the Group VIII catalysts by acting as a reducing agent.

Building on this discovery, the polymerization of methyl 5-norbornene-2-carboxylate has been reported using $IrCl_3$ under aqueous emulsion conditions[48] (*vide infra*) (Equation 11).



(11)

The actual active species in any of these Group VIII catalyzed polymerizations remains unknown. There is, however, good evidence that a lower oxidation Ir species may be involved in these reactions. It was discovered that in the absence of a reducing agent, no polymer is obtained. After 20 hours at 50 °C using the indicated reducing agents, the polymer yields obtained were as follows: 2.7% with $SnCl_2$, 3.0% with powder zinc, 9.9% with ethanol, and 37% with zinc/CH_3CO_2H. It was postulated that the active metal species is an Ir^{1+} complex formed from the reduction of Ir^{3+} in the presence of the cyclic olefin. Indeed, isolated Ir^{1+} complexes such as $[IrCl(C_8H_{12})]_2$, and $[IrCl(C_6H_8)]_2$ are active toward the polymerization of norbornene.[48b]

The importance of developing high-yield, selective polymerizations of functionalized monomers can be seen from an examination of the physical properties of polynorbornene materials possessing different functional groups. Shown in Table 1 are the T_g values for several polynorbornene derivatives. As can be seen from this sampling, the physical properties of these ring-opened polymers can be adjusted over a wide range by varying the polar substituents in the polymer repeat units. A remarkable amount of work still remains to be done before the realization of reliable, well-behaved methathesis catalysts for the routine ring-opening metathesis polymerization of functionalized olefins is achieved.

EMULSION POLYMERIZATIONS

Another important issue with respect to catalytic reactions is the stability of the catalyst to common impurities found in the reaction mixtures. This issue is particularly acute for catalysts based on organometallic complexes, which are typically highly intolerant of ubiquitous impurities such as air and water.[50] The evolution of organometallic-based catalytic systems from research laboratories to full-scale, on-line industrial processes, has often been hampered by the sensitivity of the organometallic reagents.[51] In order to bring to fruition practical industrial processes based on transition metal catalysts, this issue of catalyst stability to air and water must be addressed. Although the catalyst sensitivity issue may appear unrelated to the

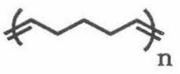
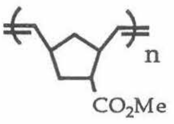
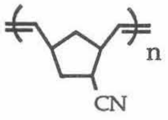
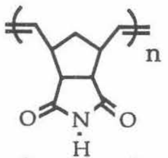
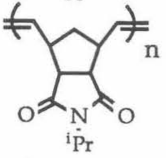
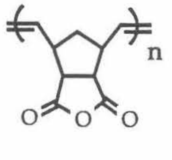
Polymer	T_g (°C)
	- 100[49]
	+ 35[49]
	+ 62[41]
	+ 114[41]
	> 250[41]
	> 200[41]
	+ 232[43]

Table 1. Various functionalized ROMP polymers and their T_g values.

polymerization of functionalized olefins, there are common threads. The features of a catalyst that lend tolerance to functional groups are very often the same features that provide stability towards impurities such as oxygen and water. By pursuing solutions to one problem, it is therefore possible to address the other problem as well. The culmination of the pursuit for robust catalysts obviously would be the development of catalysts that are stable (and active) in aqueous solution. Applied to polymerization catalysts, such a breakthrough would permit the further development of new transition metal, catalyzed aqueous-emulsion polymerization systems.

Emulsion polymerization refers to a unique process employed for some radical chain polymerizations.[52] The standard aqueous-emulsion polymerization system is composed of a water-insoluble (or partially soluble) monomer, an emulsifier and a water-soluble initiator. One example of a commercial emulsion system is the formation of a styrene-butadiene latex rubber, using sodium dodecylsulfate as a surfactant for the two monomers, with a hydroperoxide-ferrous ion, redox system as the initiator.[53] There are several distinct advantages in running a polymerization under aqueous emulsion conditions. The colloidal state of the product polymer often simplifies processing.[54] Frequently the latex can be used directly in coatings, paints and film production, without further separations or purifications. The water acts as a heat-sink during the reaction, allowing for better control over the exothermicity of polymerization.[55] Viscosity problems are eliminated when dealing with a colloidal suspension of polymer rather than the bulk polymer dissolved in solution or in the melt.[56] In addition, there is an extremely important kinetic difference when operating under emulsion conditions.[57] In a standard radical polymerization there is an inverse relationship between the polymerization rate and the polymer's molecular weight[58] (Equation 12).

$$\upsilon = \frac{k_p{}^2[M]}{2\ K_t\ R_p} \qquad (12)$$

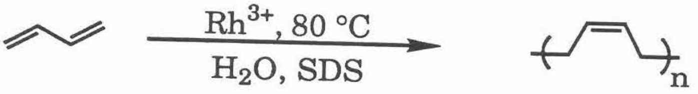
In this equation, υ is the kinetic chain length, and R_p is the rate of polymerization ($R_p = k_p[M](fk_d[I]/k_t)^{1/2}$). From a practical veiwpoint, this inverse relationship makes it extremely difficult to effect large changes in the molecular weight of the polymer. (In particular, the difficulty arises in trying to form high molecular weight polymer at rapid rates. Low molecular weight polymer can always be made by the incorporation of chain transfer agents.) The compartmentalization of the reaction under emulsion conditions acts to nullify the above inverse-rate relationship. This results in a situation wherein it is possible to simultaneously obtain high molecular weights and high polymerization rates.

Although the exact details of the emulsion polymerization process can be complex, the basic features are outlined here. When a water-insoluble (or partially soluble) monomer is dispersed in water containing a surfactant above its critical micelle concentration (CMC), the monomer is distributed between the surfactant micelles (typical concentrations are *ca.* 10^{18} micelles per ml) and monomer droplets (*ca.* 10^{11} per ml). The monomer concentration within the micelles can commonly reach 5 M. At the onset of initiation, the water-soluble initiator migrates from the aqueous phase to the more abundant micelles containing the monomer. The micelles provide a location for the reaction between hydrophobic monomer and the hydrophilic initiator. Polymerization then takes place inside these micelles with essentially one radical chain per micelle. Because of the micelle's small volume, entrance of a second radical leads to rapid termination. If the rate of production of free radicals at 50° C is about 10^{13} radicals/ml·sec,[59] then there are approximately 100,000 micelles per radical produced in a second. Therefore, there exists a very low probability of a second radical entering an active micelle. The result is that polymerization takes place at a very high rate, while the termination rate is kept quite low, allowing the formation of very high molecular weight polymer. The product polymer exists as a surfactant stabilized colloidal suspension that is typically used as is without further processing.

For obvious reasons, cationic and anionic polymerizations, as well as any other technique that propagates through water-sensitive intermediates, are not applicable to emulsion conditions. Currently, only radical emulsion processes are used commercially. This limitation has been one of the driving forces behind developing new emulsion systems.

EMULSION POLYMERIZATIONS OF BUTADIENE CATALYZED BY TRANSITION METAL COMPLEXES

Of the three common metal-catalyzed polymerizations, Ziegler-Natta, ring-opening metathesis and diene polymerizations, the latter appears to possess the greatest stability towards protic sources. The polymerization of butadiene in polar solvents was first reported in 1961 using Rh^{3+} salts.[60] It was discovered that these polymerizations could be performed in aqueous solution with an added emulsifier (sodium dodecyl sulfate, for example) (Equation 13).



(13)

This Rh-catalyzed reaction is selective for the formation of highly crystalline *trans*-1,4-polybutadiene. The activity of the catalyst shows a marked dependence on the nature of the counter ions present. Using $RhCl_3$ in 95% ethanol, no polymer was obtained after 6 hours at 80 °C, whereas the nitrate salt displays a polymerization rate of 7 g polymer/g Rh under the same conditions.

The following year, the emulsion polymerization of butadiene was reported using a number of transition metal catalysts in polar solvents.[61] It was found that the microstructure could be varied from all *trans*-1,4 (>99.5%), to high *cis*-1,4 (88%), to high 1,2-insertion (>98%), depending on the metal catalyst employed. The metal used in this study included Rh^{3+}, Rh^{1+}, Pd^{2+}, Ir^{3+}, Ru^{3+} and Co^{1+}. Molecular weights varied greatly with choice of catalyst. For example, the Pd^{2+}-catalyzed reactions produce short molecular weight oligomers (M_n = 1000-1500), while the Co^{1+} catalyst produces molecular weights of approximately 300,000.

It was discovered that the addition of 1,3-cyclohexadiene to the Rh^{3+}-catalyzed reactions increased the rate of butadiene polymerization by over a factor of 20.[62] Considering the reducing properties of 1,3-cyclohexadiene, this effect could be due to the reduction of Rh^{3+} to Rh^{1+} and stabilization of this low oxidation state by the butadiene type of ligands. With neat 1,3-cyclohexadiene, Rh^{3+} is reduced to the metallic state. These emulsion polymerizations are sensitive to the presence of Lewis basic functional groups. A stoichiometric amount of amine (based on Rh) is sufficient to inhibit polymerization completely. It was also discovered that styrene could be polymerized using the Rh^{3+} catalyst. However, the atactic nature of the polymer, along with the kinetic behavior of the reaction, indicated that a free radical process, rather than a Ziegler-Natta insertion mechanism, was operative.

There have been suggestions in the literature that the mechanisms of these metal catalyzed reactions are, in fact, either cationic[63] or free radical in nature.[62] This assessment, however, is inconsistent with all of the facts. Cationic polymerizations do have a tendency to produce high *trans*-1,4 polymer. For example, using a $TiCl_4/H_2O$ catalyst, polymer containing approximately 75% *trans*-1,4 units is obtained. However, typical cationic polymerizations are generally carried out at low temperature (-78 °C is common), to reduce the amount of insoluble, cross-linked polymer obtained. In contrast, the Rh^{3+} systems are run between +50 and +80 °C, without appreciable cross-linking occurring. In some polymerizations there does seem to be a competitive free-radical process.[64] This, however, was determined to be due to radical impurities in the surfactants used, and not due to a Rh-catalyzed reaction. In fact, Rh^{3+} was found to act as a free radical *inhibitor* for these reactions. Because of this, the free-radical mechanism was determined to be unimportant at high Rh^{3+} concentrations.[65] In addition, common free-radical inhibitors do not quench the Rh^{3+} polymerizations.[61] All of these facts point strongly to a polymerization mechanism that is substantially different from a classical free-radical or cationic mechanism.

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CHAPTER 3

THE RING-OPENING METATHESIS POLYMERIZATION OF 7-OXANORBORNENE DERIVATIVES

Abstract

The ring-opening metathesis polymerization of several 7-oxanorbornene derivatives is reported using a number of catalysts. The catalysts investigated range from preformed early metal metallacyclobutane and carbene complexes to classical Group VIII ruthenium and osmium complexes.

In general, the early transition-metal catalysts, react with, and are deactivated by, the 1,4-bridging epoxide present in this class of monomers. With $WOCl_4$, direct evidence of the interaction of the 1,4-bridging epoxide moiety with the Lewis acidic metal center is observed. Limited success, however, in polymerizing these monomers is achieved using the preformed carbene catalysts, **XV** and **XVI**. Molecular weight investigations reveal these materials actually to be low molecular weight oligomers possessing broad polydispersities. It was discovered that by switching to ruthenium- and osmium-based catalysts, high yields of high molecular weight polymers could finally be obtained.

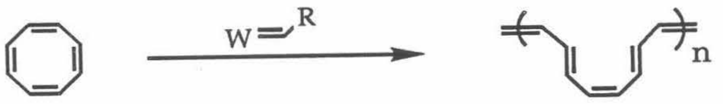
The tolerance of the Group VIII catalysts to polar groups allows for the polymerization of a number of highly functionalized monomers. The chemical modification of these highly functionalized polymers is examined. The conversion of Poly **XV** into a fully conjugated polymer, Poly **XVox**, by oxidation with DDQ, is reported. In addition, Poly **XV** can be reduced, then hydrolyzed, to form new water-soluble, synthetic polymers.

The structural characterization of these polymers is reported. The *cis/trans* ratio of the metathesized double bonds along the parent polymer's backbone is determined using ^1H and ^{13}C NMR. Polymers with *cis* contents from 95% to less than 5% have been prepared. No tacticity information is

obtained from the spectra of the unsaturated polymers. The determination of the tacticities of these polymers required elimination of their structural complexity by hydrogenating the double bonds along their backbone. The ^{13}C NMR spectra of the fully saturated polymers show resonances associated with two isomeric forms, which are ascribed to the two differing diad tacticities: isotactic and syndiotactic ring diads. Exact assignment of these two sets of resonances as the syndiotactic and isotactic diads required the resolution and polymerization of a chiral monomer, **IV***. Using the relationship that exists between the HT and HH/TT isomeric forms and the diad tacticity of a chiral polymer, (Poly **IV***), the tacticities of these 7-oxanorbornene polymers are assigned. This method shows most of these materials to be atactic, with the ruthenium catalysts displaying a slight bias towards isotactic diads. The synthesis and study of catalysts possessing chiral ligands, designed for the synthesis of high isotactic polymer, are reported.

INTRODUCTION

As outlined in Chapter 1, a number of highly active, ring-opening metathesis catalysts have recently been developed[1]. Interest in this unusual method of polymerization has intensified following the demonstration that several of these metal alkylidene[2] and metallacylobutane[3] complexes catalyze the living polymerization of strained olefins such as norbornene. The promotion of ROMP techniques from ill-defined classical systems to well-controlled living systems could reasonably be expected to open the doors to the synthesis of entire new classes of polymers. Realization of the full promise of ring-opening metathesis polymerizations as a viable synthetic technique, however, will require the resolution of several key issues. Above all, it must be demonstrated that controlled ROMP techniques may be applied successfully to monomers other than norbornene.[4] Up to this point, the polymerization of norbornene has been instrumental in uncovering the guiding principles behind the development of well-controlled metathesis catalysts. The product of these studies, polynorbornene, however, is of limited commercial interest. Little can be accomplished with polynorbornene that cannot be accomplished at less expense with poly(butadiene-*co*-sytrene) rubber materials.[5] It is therefore essential, if ROMP techniques are to make an impact in the commercial market place, that a wide range of potential monomers be examined. A good example of the application of ROMP techniques to the synthesis of unusual polymers is in the preparation of conducting polymers.[6] Ring-opening metathesis polymerizations are unique in that all of the unsaturation present in the monomers is conserved in the polymeric product. This feature makes ROMP techniques very attractive for the preparation of highly unsaturated, and fully conjugated materials. For example, through the utilization of highly active tungsten alkylidene species, polyacetylene can be formed from the direct metathesis of cyclooctatetraene[7] (Equation 1).



(1)

Another area of interest is the expansion of these highly active ROMP catalysts to the polymerization of functionalized monomers.[8] As outlined in Chapter 2, the presence of functional groups can dramatically change the properties of a polymer. Problems arise, however, in that polar functional groups will often react with and deactivate transition metal catalysts.[9] The adaptation of highly active ROMP catalysts to the polymerization of fuctionalized monomers will be of key importance in future developments of this method.

Our general goal in this work has been to examine closely the tolerance of existing ROMP catalysts toward functionalized monomers, and to apply this knowledge in the development of new, robust (but active), polymerization catalysts Ultimately, it is hoped that this project will help lay the groundwork for the development of living ROMP catalysts that are compatible with a wide range of reactive functional groups.

As a vehicle for this study, we elected to examine the ring-opening metathesis polymerization of 7-oxabicyclo[2.2.1]hept-2-ene (7-oxanorbornene) derivatives (Equation 2).


(2)

The 7-oxanorbornene system is a particularly suitable class of monomers for this study for the following reasons. First, the 1,4-bridging epoxide is a very Lewis acid-sensitive functional group (*vida infra*). Studies using 7-oxanorbornene derivatives should therefore provide a limiting threshold for a catalyst's compatibility with Lewis basic functional groups (i.e., if a particular catalyst tolerates the 1,4-bridging epoxide, then it should tolerate a number of additional functional groups as well). Second, the Diels-Alder reaction that assembles the [2.2.1] bicyclic ring system is versatile, allowing for the eventual incorporation of a large number of pendant functional groups within the same basic monomer unit. And third, poly(ethenylidene-*co*-2,5-tetrahydrofuran) (poly(7-oxanorbornene)) materials resulting from the selective metathesis polymerization of the 7-oxanorbornene monomers are of keen interest, owing to the potential for inophoric activity in these materials. Molecular model studies indicate that these poly(7-oxanorbornene) have the ability to form helical structures with all of the tetrahydrofuran oxygens facing into the interior of the helix (Figure 1).

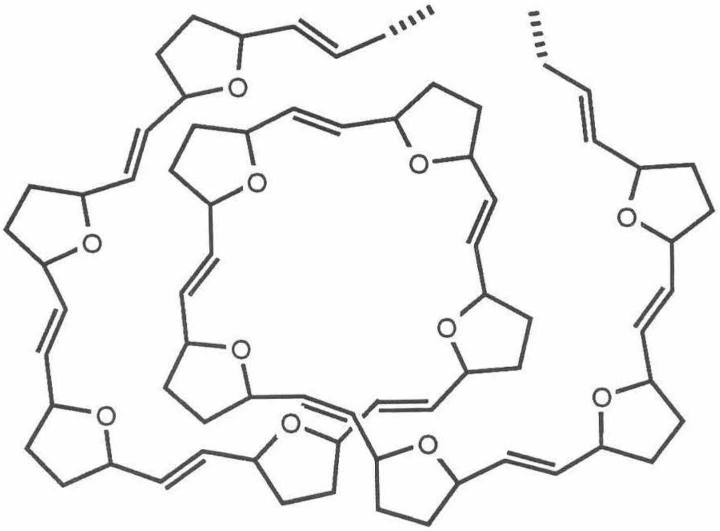


Figure 1: Proposed helical binding cavity formed from Poly(7-oxanorbornene).

This unique helical conformation may allow these polymers, when in solution, to act as useful acyclic ionophores,[10] much like their cyclic analogues, the crown ethers.[11] Polymers possessing ionophoric properties of this type have applications in a number of areas. In addition to host-guest ion-binding applications in solution,[10,11] ionophoric polymers doped with various salts are of interest for use as solid electrolytes in battery applications.[12] Finally, thin films composed of these poly(7-oxanorbornene) materials may possess oxygen-rich ionophoric channels that would enable them to act as ion-permeable synthetic membranes.[13]

RESULTS AND DISCUSSION

A. Monomer Synthesis

In the synthesis of the first test substrates, the approach was to eliminate from the monomers all heteroatom functionalities, except for the 1,4-bridging epoxide moiety. Once the stability of this group could be established under reaction conditions, other, potentially more reactive groups could be added systematically to the monomers. This approach permitted an examination of both the catalysts' compatibility with these added groups and the effects of the added functionalities on the properties of the polymers produced.

The parent compound, 7-oxabicyclo[2.2.1]hept-2-ene (7-oxanorbornene), is synthesized through a Diels-Alder reaction between furan and ethylene at high pressure and temperature[14] (118 atm., 155 °C, 16 hours) (Equation 3).

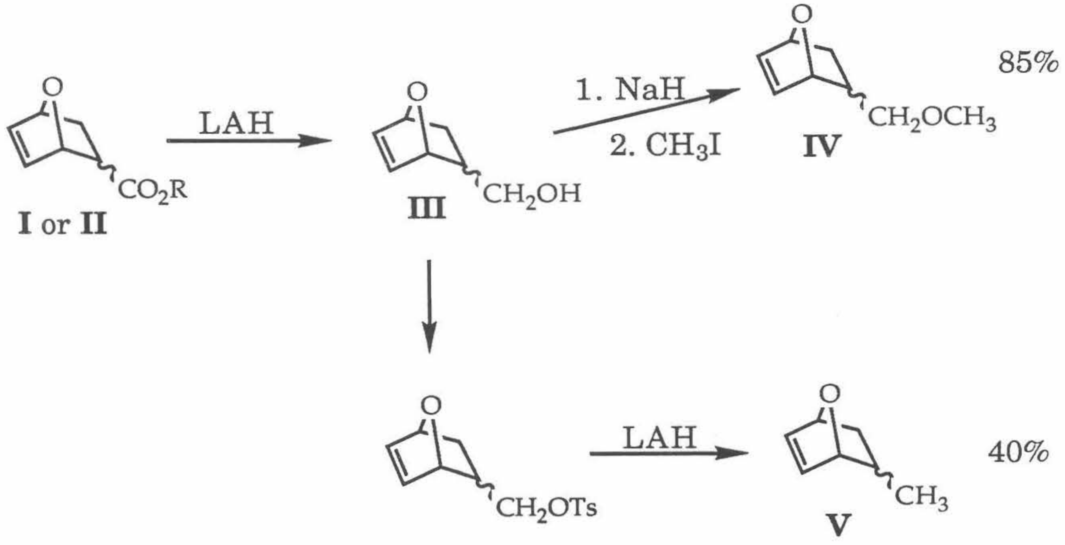
(3)

Both the aromatic nature of furan[15] as well as the strain energy of the [2.2.1] bicyclic ring system,[16] inhibit this reaction. The resulting low yields of the Diels-Alder product, *ca.* 6-10%, make the parent compound an impractical monomer for use in polymer synthesis. These limitations can be circumvented, however, by using activated dieneophiles in the Diels-Alder reaction. Members of the acrylate family can be successfully enlisted as activated dieneophiles in reactions with furan. Similarly, the otherwise slow room-temperature reactions can be catalyzed using Lewis acidic metals such as Cu^{2+} and Zn^{2+} (Equation 4).[17]

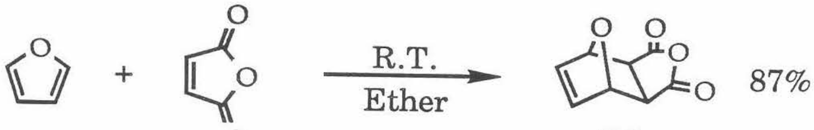
(4)

The *endo / exo* ratios are typically close to 3/1 for both derivatives. Reduction of **I** and/or **II** provides the corresponding alcohol, **III**, in good yields. The conversion of **III** to the relatively innocuous methyl ether, **IV**, can be accomplished through deprotonation and reaction of the resulting alkoxide with methyl iodide. The 5-methyl derivative, **V**, can be synthesized in approximately 40% yields through the reduction of the corresponding tosylate derivative. These reactions are summarized in Scheme **I**.

Scheme I:



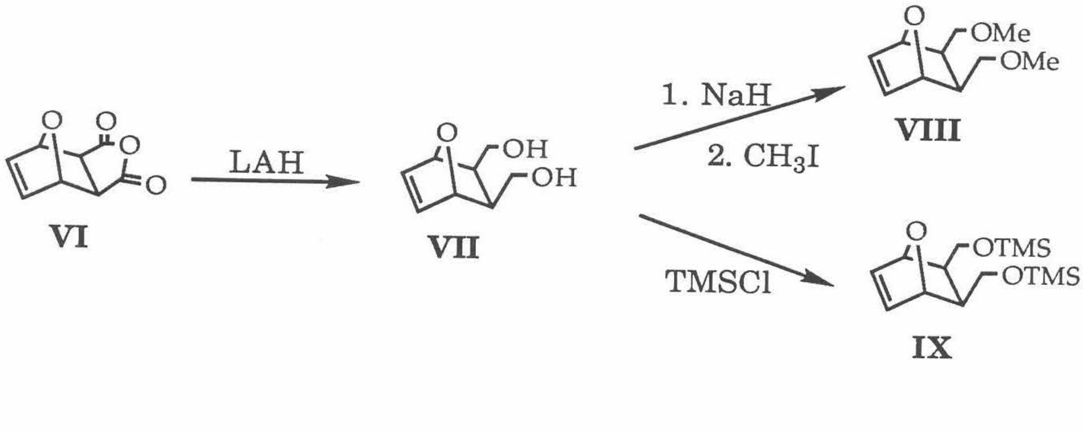
An important entry into the 7-oxanorbornene system is available through the Diels-Alder reaction of furan with maleic anhydride.[18] This reaction proceeds smoothly at room temperature to provide good yields of the adduct (Equation 5).



VI 87% (5)

Unlike Diels-Alder reactions involving cyclopentadiene, this reaction proceeds under thermodynamic, rather than kinetic control, resulting in the formation of nearly 100% of the *exo*-isomer.[19] When considering the observed ROMP reactivity differences between the *endo*- and *exo*- isomers of norbornene derivatives (see Chapter 2), this feature turned out to be an important, albeit unexpected, bonus. Anhydride **VI** can be cleanly reduced to the diol, **VII** (yields *ca.* 100%). Protection of **VII** through methylation to produce the dimethoxymethyl derivative, **VIII**, or formation of the bis(trimethylsilyl) derivative, **IX**, can be accomplished in high yields (Scheme **II**).

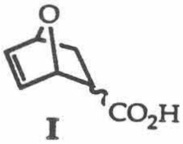
Scheme II:



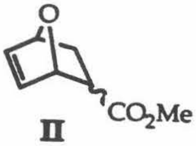
Through the same route, using 2-methyl and 2-ethylfuran, the corresponding bridgehead 1-methyl and 1-ethyl derivatives of **VIII** are also readily synthesized.

The furan-benzyne adduct, **X**, is commercially available.[20] Activated acetylenes such as dimethyl (**XI**) and diethylacetylene-1,2-dicarboxylate (**XII**) can be used as dieneophiles in reactions with furan.[21] Monomers such as **X**, **XI** and **XII** add additional unsaturation into the polymer, furnishing an opportunity to further modulate the properties of the resulting polymers.

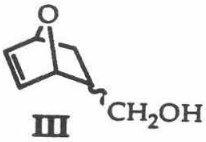
A compilation of the various 7-oxanorbornene monomers used throughout this study is provided in Table 1.



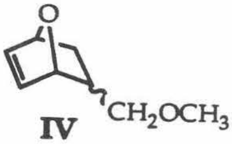
I



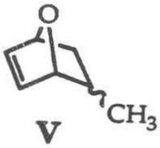
II



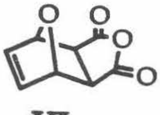
III



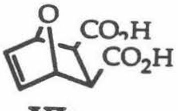
IV



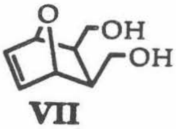
V



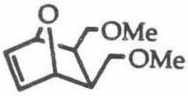
VI



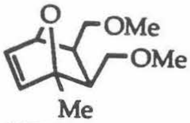
VIa



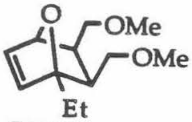
VII



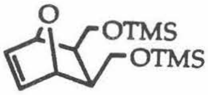
VIII



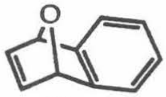
VIIIm



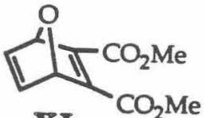
VIIIe



IX



X

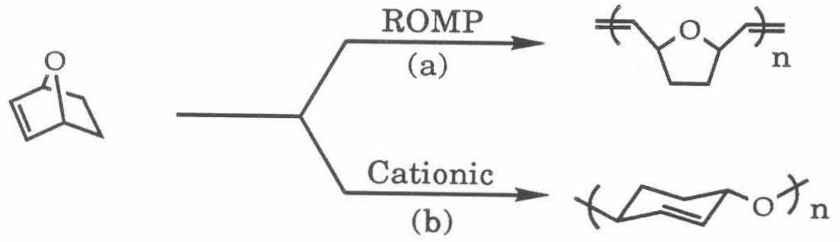


XI

Table 1: Quick reference guide to the 7-oxanorbornene monomers.

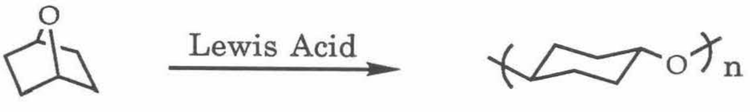
B. The Ring-Opening Metathesis Polymerization of 7-Oxanorbornene Derivatives

For the successful controlled ring-opening metathesis polymerization of the 7-oxanorbornene monomers, it is necessary to identify catalysts that will react preferentially with the olefin moiety of the monomer rather than with the 1,4-bridging epoxide (Equation 6).



(6)

The 1,4-bridging epoxide functional group can be very Lewis acid-sensitive. For example, 7-oxanorbornanes can be polymerized through a cationic ring-opening mechansim[22] (Equation 7).



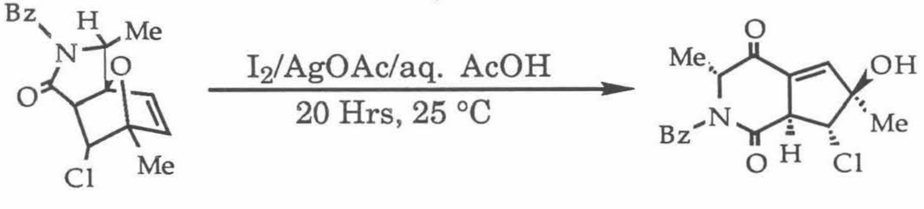
(7)

This cationic ring opening of the 1,4-bridging epoxide can be carried out between -40° and +25°C with the aid of a number of Lewis acid catalysts such as, H^+, $FeCl_3/SOCl_2$, BF_3, PF_5 and $SbCl_5$/ethylene oxide. The driving force behind this reaction is the relief of ring strain in the bicyclic monomer, which is estimated to be 13.8 Kcal/mol for the parent 7-

oxanorbornane.[23] No cationic polymerization of 7-oxanorbornenes has been reported. For two reasons, however, the cationic opening of the 1,4-bridging epoxide in 7-oxanorbornene would be expected to be even more favorable than in the saturated case. First, incorporation of the double bond in the [2.2.1] bicyclic ring system can be estimated to increase the ring strain of 7-oxanorbornene by approximately 9.6 kcal/mol.[24] Second, the cationic opening of the 1,4-epoxide in the unsaturated molecule yields a stabilized allylic cation rather than a secondary carbocation as in the saturated case.

Ring Strain: 13.8 Kcal/mol 23.4 Kcal/mol

In addition to cationic ring-opening processes, 7-oxanorbornene derivatives are also subject to cationic rearrangements catalyzed by Lewis acids. For example, skeletal rearrangements involving [1,2] cationic shifts followed by the opening of the epoxy bridge have been observed to occur in the presence of Lewis acids under mild conditions[25] (Equation 8).



(8)

1. "Classical" Tungsten(VI) Metathesis Catalysts.

Both components of the "classical" tungsten(VI) catalysts systems, the tungsten(VI) compound and the alkylating agent, possess Lewis acidic properties. Nevertheless, systems comprised of $WCl_6/Sn(CH_3)_4$, particularly $WOCl_4/Sn(CH_3)_4$, are candidates for the polymerization of monomers containing functional groups. Both of these W(VI) systems have been demonstrated to be effective for the metathesis of substrates containing polar functional groups such as esters.[8a,c,9]

When 20 equivalents of monomer **VIII** are allowed to react with a 1:1 mixture of WCl_6 and $Sn(CH_3)_4$ in chlorobenzene at room temperature, immediate decomposition of the monomer to unidentified, non-polymeric products is observed. The ^1H NMR of this reaction mixture shows multiple peaks comprising a continuous envelope from approximately 2 to 6.5 ppm. Not surprisingly, the Lewis acidity of the catalyst components appears to catalyze the decomposition of the bicyclic monomer.

In an analogous reaction using $WOCl_4/Sn(CH_3)_4$ (1:2.2), the decomposition of **VIII** is measurably slower; again, however, no polymerization is observed. The imposition of extreme conditions on reaction mixtures containing these tungsten(VI) catalysts (90 °C for 70 minutes) does not change the outcome; no polymeric products are obtained. Confirmation that reaction occurs instead between the W(VI) center and the 1,4-bridging epoxide, leading to the observed monomer decomposition, comes from the reaction of one equivalent of **VIII** with $WOCl_4$ or $WOCl_4/Sn(CH_3)_4$. Upon mixing, the initial ^1H NMR spectrum of **VIII** remains essentially unchanged except for the signal arising from the bridgehead protons, which exhibits substantial broadening (peak half-height width *ca.* 23 Hz) and downfield shift from 5.0 to 5.95 ppm (Figure 2). Over the course of 20 minutes, further decomposition to unidentified products is observed. The initial changes include new olefin resonances

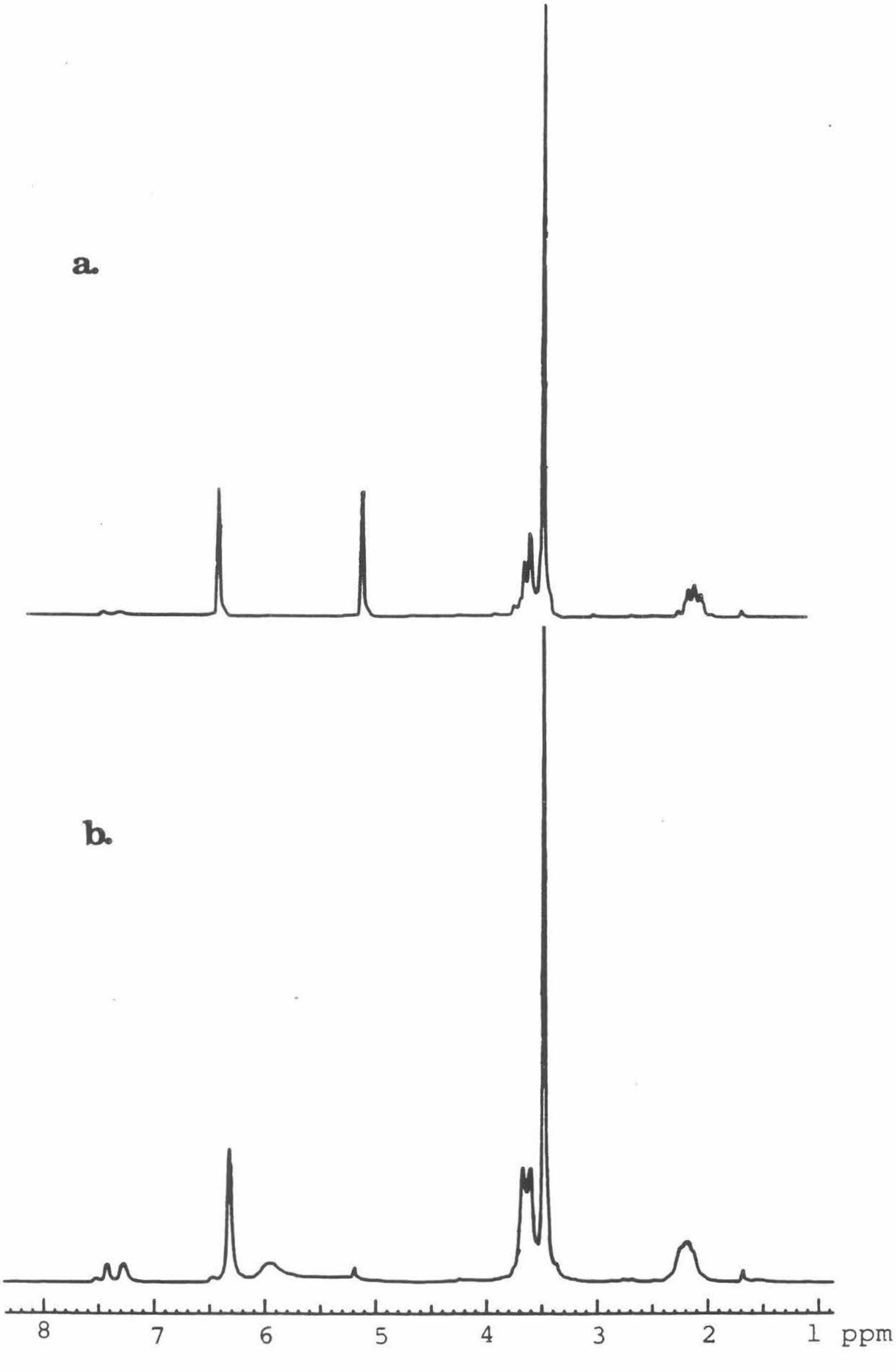
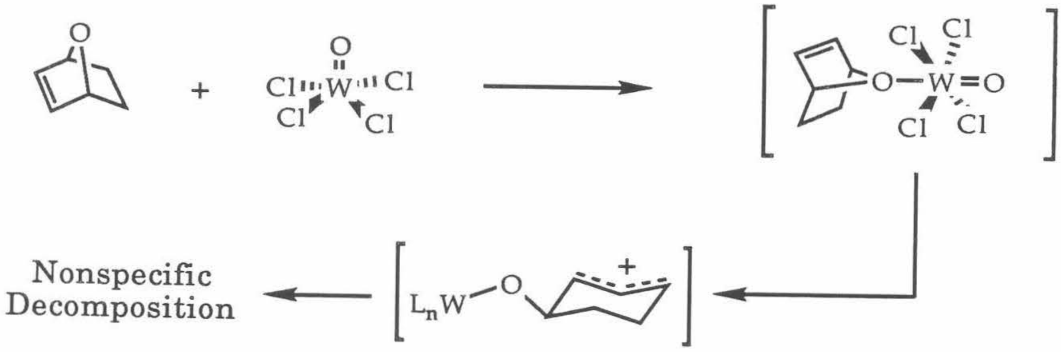


Figure 2: ^{1}H NMR spectra (C_6D_5Cl, 90 MHz) of monomer **VIII**: (a) Before addition of $WOCl_4$; and (b) after addition of $WOCl_4$.

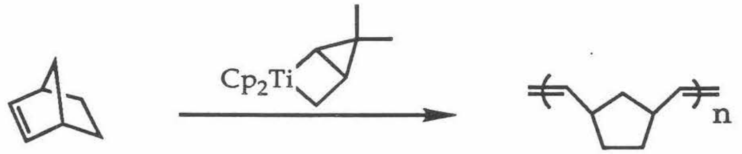
downfield from the monomer. It can be speculated that this signal is due to the substituted cyclohexene resulting from the opening of the 1,4-bridging epoxide. These initial spectra give way to a spectrum reminiscent of that observed in the WCl_6 reaction (i.e., a nearly continuous envelope of peaks from 2.0 to 6.5 ppm). Again, no polymer is formed, as evidenced by the absence of viscosity changes during the reaction, and no pentane-insoluble products are isolated through precipitation (*vida infra*). The initial changes in the NMR spectrum of **VIII** are ascribed to the coordination of the 1,4-bridging epoxide to the $WOCl_4$, where dynamic effects account for the observed broadening of the signal. This adduct subsequently undergoes non-specific decompostion (Scheme **III**).

Scheme III:



2. Titanocene Metallacyclobutanes.

Titanocene metallacyclobutanes obtained from the reaction of Tebbe reagent with olefins are attractive catalyst candidates because of their demonstrated living characteristics in the polymerization of norbornene[3a,b] (Equation 9).



(9)

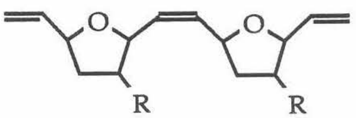
For the further development of the polymerization chemistry of titanocene metallacyclobutanes, a key concern will be the tolerance of these catalysts toward polar functional groups. Titanacycles show a wide variety of reactivities with organic reagents, including methylene transfer to organic carbonyls (aldehydes, ketones and esters)[26] (Equation 10), formation of enolates,[26a,e,27] electron transfer from activated alkyl chlorides[28] and insertion reactions with epoxides[29] (Equation 11).

(10)

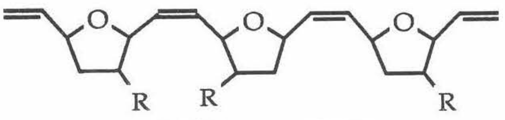
(11)

The wide scope of the reactivity displayed by titanocene metallacyclobutanes defines narrow limits to the functionalized monomers appropriate for polymerization studies.

The titanocene metallacyclobutane catalysts have additional features that may be of value in controlling the regiochemistry of the addition of non-symmetrically substituted monomers to the propagating polymer chain. The steric constraints placed on the metallacycles by the two cyclopentadienyl ligands could be used to direct the addition of monomers in a head-to-tail (HT), rather than a head-head/tail-tail (HH)/(TT) fashion.

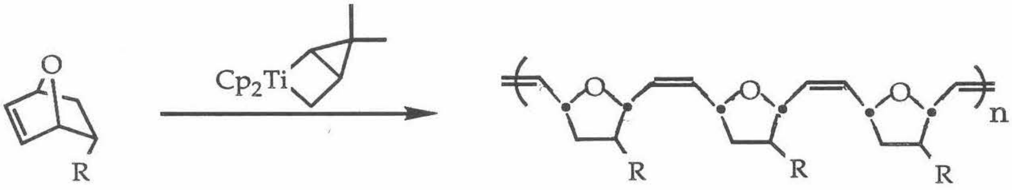


(HT)



(HH) (TT)

Mastery over the regioselectivity of the polymerization process could have even broader implications. Once (HT) selectivity can be made to dominate the course of monomer addition, it would then be possible using chiral, resolved monomers to synthesize highly regular, isotactic polymers (Equation 12). This special relationship will be discussed in more detail in the polymer characterization section.



(12)

One equivalent of monomer **VIII** reacts cleanly with metallacycle **XIII** to give the new, expected metallacyle, **XIV**, in good yield (Equation 13).

XIII **XIV** (13)

The ^{1}H NMR spectrum of this compound is consistent with the spectrum of the similar metallacycle formed from the reaction of norbornene and

XIII. No evidence of any side reaction with either the 1,4-bridging epoxide or the methyl ethers could be detected. Assuming that the [2+2] cycloaddition reaction takes place exclusively through the exo-face of the monomer's double bond, only one isomer is possible for metallacycle **XIV**. (This assumption is consistent with what is observed in the analogous reaction using norbornene).[30] However, when the nonsymmetric 5-methyl derivative, **V**, is reacted with **XIII**, four different isomers are possible. These metallacycle isomers result from the *endo*- and *exo*-methyl isomers (present in a 3:1 ratio in **V**) adding in both a *syn* and *anti* fashion to the titanium methylidene (Figure 3).

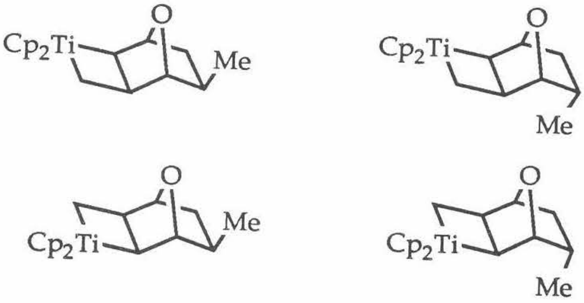
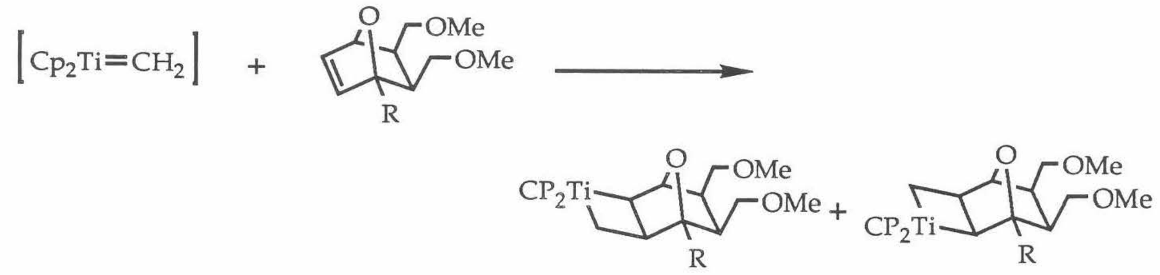


Figure 3: The four possible isomeric metallacycles resulting from the addition of *endo*/*exo*-**V** to the titanium methylidene intermediate.

If either the *exo*- or the *endo*-methyl group is capable of directing the regiochemistry of the metallacycle formation, then the expected ratio of metallacycle isomers, 3:1 *endo:exo* (each with a 1:1 ratio of *syn:anti*), will be altered. This, however, is not the case. The ^{1}H NMR spectrum of the resultant mixture of isomers from this reaction shows four methyl groups, two *endo*-methyls (0.90 and 0.97 ppm) in a 1:1 ratio, and two *exo*-methyls (1.01 and 0.98 ppm), also in a 1:1 ratio. If steric interactions between the Cp ligands and the pendant methyl group are expected to be the basis for this regioselectivity, then this result is not surprising, in that the methyl group is well removed from the cyclopentadienyl ligands during the ring-forming step. Success in controlling the regiochemistry of addition will require moving the directing group closer to the cyclopentadienyl ligands. With this in mind, both the 1-methyl and 1-ethyl-5,6-(dimethoxymethyl)-7-oxanorbornene derivatives (**VIIIm** and **VIIIe**, respectively) were synthesized. Reaction of **VIIIm** with metallacycle **XIII** gave two isomers in a 3:1 ratio, as evidenced by two sets of Cp resonances in the ^{1}H NMR spectrum (5.66, 5.26 ppm and 5.76, 5.18 ppm). As with all compounds derived from the anhydride adduct, **VI**, **VIIIm** and **VIIIe** are both *exo*-isomers. The two sets of Cp resonances are therefore assigned to the *anti* and *syn* metallacycles, respectively. When the same reaction is repeated using the larger bridgehead ethyl group as the steric controlling moiety, complete selectivity favoring the *anti* isomer is observed (Scheme **IV**).

Scheme IV:



(**XIIIm**) R = Me 3 : 1

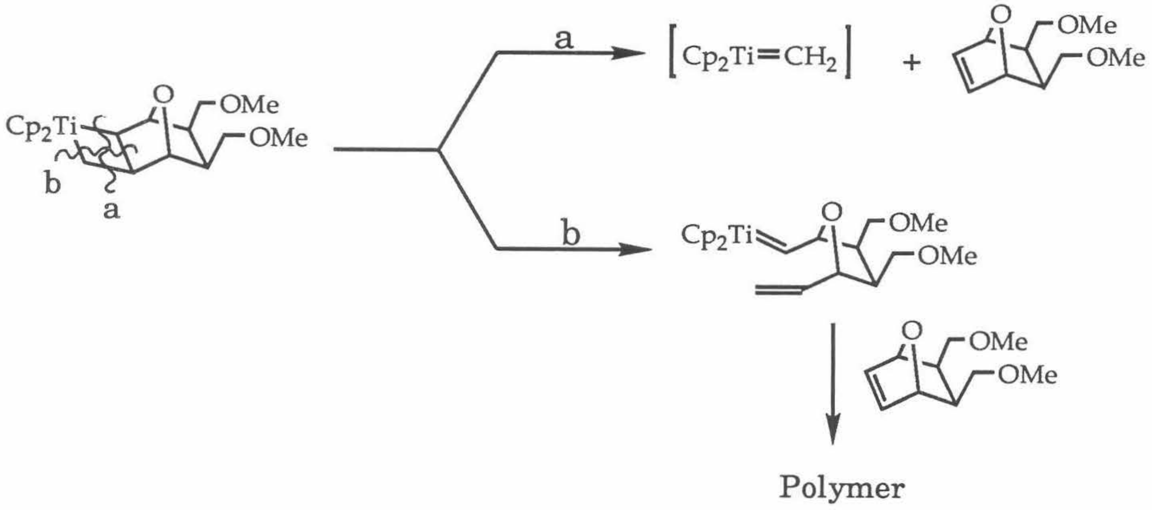
(**XIII e**) R = Et Exclusive : -

It is therefore concluded from this substituent study that if the steric constraints of the cyclopentadienyl ligands are to be used in controlling selection of (HT) diads over (HH)/(TT) diads in subsequent polymerizations, then the controlling group must be larger than methyl, and must be placed in the bridgehead position in order to exert the necessary influence.

When metallacycle **XIV** is allowed to react with excess olefin **VIII** at room temperature, no reaction takes place. Heating at 80 °C for four hours results in non-specific decomposition of the metallacycle, as evidenced by collapse of the two sharp Cp resonances at 5.64 and 5.20 ppm into a broad group of peaks from 5.5 to approximately 6.2 ppm. No polymeric materials are formed in association with the decompostion of the metallacycle. Neither does the excess olefin present appear to undergo any reaction at all during this heating process. Further studies utilizing nearly all of the 7-oxanorbornene derivatives in reaction with **XIV** at various monomer to catalyst ratios and various reaction temperatures resulted in similar observations: non-specific decomposition of the metallacycle accompanied by a complete absence of polymer formation. In addition, the 7-oxanorbornene derivatives **V** and **VIII** could not be polymerized using either metallacycle **XIII**, or the metallacycles derived from the reaction of titanocene methylidene with norbornene, and with 3,3-dimethylcyclopropene. All three of these metallacycles are known to polymerize a variety of cyclic olefins.[3a,b,31]

Scheme **V** shows the two decomposition pathways commonly observed for titanocene metallacycles. Carbene trapping experiments were performed in an attempt to determine if either of these two pathways are operative for the 7-oxametallacycles. The inability of these metallacycles to initiate polymerizations could be the failure of the initial metallacycle to undergo favorable decomposition (path (b) in Scheme **V**). The possibility also exists that the excess 7-oxanorbornene monomer present may not be reactive enough to add to the new carbene formed along path (b) in Scheme **V**.

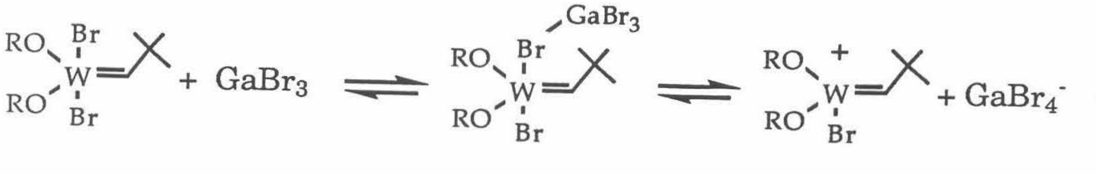
Scheme V:



In order to probe the accessibility of these two pathways to the 7-oxanorbornene metallacycles, carbonyl trapping experiments can be employed. Ketones are known to undergo rapid, Wittig-type methylene transfer reactions with the intermediate methylidene complexes in both pathways (a) and (b) to give oxo-titanocene polymers and the appropriate methylene compound. Using benzophenone, in addition to the oxo-titanocene, path (a) would yield 1,1-diphenylethylene, and path (b) would yield the other expected diphenyl substituted olefin. After 14 hours at 80 °C in the presence of excess benzophenone, metallacycle **XIV** decomposed completely. However, no titanocene-oxo compounds, nor either of the two methylene transfer products were detected. These data seem to indicate that whatever decomposition pathways may take place for these metallacycles, they do not include the intermediate methylidenes of either path (a) or (b). Further support for this assumption comes from a second experiment in which the polymerization of norbornene (an olefin in which the polymerization parameters are well documented using other metallacycles) was attempted, using metallacycle **XIV** as the catalyst. After 6 hours at 80 °C, **XIV** with 25 equivalents of norbornene produced no polymeric material. This result again indicates that the absence of polymerization chemistry is associated with the failure of the 7-oxanorbornene metallacycles to initiate by forming the required methylidene intermediates, not because of any inherent lack of reactivity in the 7-oxanorbornene monomers themselves.

3. Osborn's Catalyst $((CH_3)_3CCH_2O)_2WBr_2(CH^tBu)$.

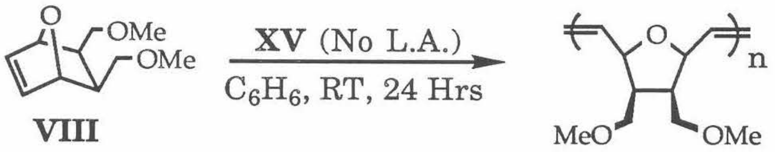
Osborn's catalyst $((CH_3)_3CCH_2O)_2WBr_2(CH^tBu)$ (**XV**), is one of a number of compounds containing the preformed neopentylidene ligand, which are known to catalyze acyclic olefin metathesis as well as the polymerization of cyclic olefins.[32] As outlined in Chapter 1, this catalyst is used in conjunction with a Lewis-acid cocatalyst such as $AlBr_3$ or $GaBr_3$.[33] It has been shown that the Lewis acid establishes an equilibrium in which it coordinates to, and then abstracts, a Br^- ligand from the coordination sphere of the tungsten center. This bromide abstraction generates a four coordinate cationic tungsten neopentylidene, which is thought to be the true active catalytic species[34] (Equation 14).



(14)

Unfortunately, all of the 7-oxanorbornene monomers are completely incompatible with the Lewis-acid cocatalyst required for the activation of **XV**. For example, when one equivalent of monomer **VIII** is added to a benzene solution of $GaBr_3$, immediate precipitation of the Lewis acid-base complex, **XIII**$\cdot GaBr_3$, is observed. It was discovered, however,during the course of these investigations that **XV** alone, without added cocatalyst, shows mild activity towards the polymerization of the 7-oxanorbornene monomers.

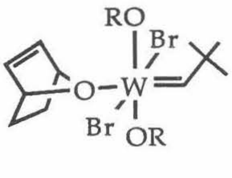
When monomer **VIII** (0.8-1.5 M) is allowed to react overnight with **XV** (ca. 0.01 M) at room temperature, the solution slowly turns from yellow to dark greenish-blue (a color often associated with tungsten oxo-species) and becomes quite viscous. Addition of this solution to pentane results in the precipitation of an off-white polymeric material later identified as the expected ring-opened metathesis polymer (Equation 15). Discussion of the full characterization of all the 7-oxanorbornene polymers will be deferred until Section C.

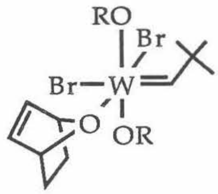


10-20% (15)

^{13}C NMR shows this polymer to have a 40:60 cis:trans ratio of double bonds along the polymer backbone. Molecular weight determinations by gel permeation chromatography (GPC) revealed this material to be a mixture of oligomers averaging between 7-9 repeat units in length. The polydispersity index (PDI), also calculated from GPC data, was approximately 1.80. In addition, the yields of polymeric material are quite low, using **XV** as a catalyst. Typical yields are often in the range of 10-20%. These observations indicate that some type of side reaction is occurring, resulting in deactivation of the catalyst. NMR experiments using only a few equivalents of monomer were performed in an attempt to better elucidate this deactivation process.

When 2-3 equivalents of monomer **VIII** are mixed with **XV** at -40 °C, no reaction is observed. The signal for the bridgehead protons, however, is considerably broadened (peak width at half-height > 14 Hz), while the remaining monomer signals remain quite sharp. (For example, the olefin proton signal in the same spectrum has a peak width at half-height of ca. 3 Hz). This broadening of the bridgehead proton resonance is interpreted as signaling coordination of the bridgehead oxygen to the metal center. The full coordination sphere around the tungsten center remains unknown. Single crystal x-ray structures performed on the analogous tungsten carbene complex $((CH_3)_3CCH_2O)_2WBr_2(\underbrace{C(CH_2)_3C}H_2)$ (**XVa**) reveal this complex (in the solid state) to be a hexacoordinate dimer held together via two tungsten-bromine bridging interactions.[35] Furthemore, the structure of $((CH_3)_3CCH_2)_2WBr_2(\underbrace{C(CH_2)_3C}H_2)\cdot GaBr_3$ (**XVb**) also shows the tungsten to be hexacoordinate, possessing two bridging bromines between the gallium and tungsten centers. In solution, it is thought that **XVa** becomes monomeric, and **XVb** ionizes to a cationic tungsten carbene and $GaBr_4^-$. It is known that **XVa** reacts with Lewis bases such as pyridine to form a hexacoordinate adduct.[35] Considering these studies, it is proposed that monomer **VIII** forms a Lewis acid-base adduct with **XV** via the 1,4-bridging epoxide in solution.





R = $CH_2C(CH_3)_3$

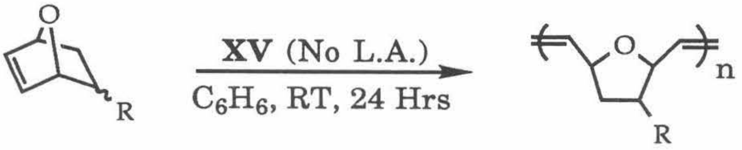
Upon warming from -40 °C, no reaction occurs until the temperature reaches *ca.* 0 °C. After approximately five minutes at this temperature, a new olefin resonance begins to appear downfield from the monomer at 6.11 ppm. This new peak is ascribed to a side reaction as it does not correspond to any of the known ring-opened polymer resonances. The chemical shift of this resonance is, however, the same as the resonance observed during the initial decomposition of monomer **VIII** by $WOCl_4$. This signal is ascribed to the substituted cyclohexene resulting from the opening of the 1,4-bridging epoxide. Upon continued warming to approximately 5 °C, polymerization begins, as evidenced by the appearance of resonances at 5.7, 4.5 and 2.3 ppm. (The remaining polymer resonances are obscured by the monomer's signals). At this point in the reaction, less than 3% of the carbene proton signal at 11.0 ppm has disappeared. No new carbene peaks, nor peaks that can be associated with a metallacyclobutane, are observed. After 15 minutes at 20 °C, approximately 25% of the carbene signal has disappeared. In addition, new resonances at 7.2 ppm begin to appear in the aromatic region of the spectrum, possibly indicating oxidation of the monomer to benzene. In subsequent experiments, it was found that warming above +40 °C can cause W^0 metal to plate out of solution. The operative temperature for this catalyst is therefore between +10° and +25 °C. At any temperature however, the deactivation reaction(s) proceed at an appreciable rate, thus limiting the polymer yield and molecular weight of the material produced.

Because the polymerization occurs simultaneously with, or is preceded by, decomposition of the catalyst, it was critical to determine whether products such as metal-oxo species resulting from the side reactions with the 7-oxanorbornene monomers are the true active species responsible for the observed polymerization. It was discovered, however, that norbornene readily polymerizes (albeit slowly), in the presence of catalyst **XV** at room temperature. The polymerization initiates immediately at room temperature, as evidenced by the presence of polynorbornene resonances and the initial disappearance of approximately 31% of the carbene signal. Unlike the 7-oxanorbornene reactions, no dramatic color changes, unidentified resonances in the aromatic or alkenyl regions of the spectrum, or any other signs of catalyst decomposition are observed. Once the initial norbornene is consumed (5 equivalents), subsequent additions of norbornene result in continued polymerization. The initial carbene signal progressively diminishes in intensity during this process. After 30 minutes, 52% of the carbene has reacted, and after one hour, 86% has been consumed. No new carbene peaks can be detected. It appears from this study that **XV** is a mildly active ROMP catalyst without any added cocatalyst.

Even at +25 °C, the rate of polymerization of **VIII** is quite low. The initial rate of polymerization for a 1.0 M monomer solution is approximately 0.9 equivalents/minute. As the catalyst is deactivated, this rate slowly decreases. After approximately 40 minutes at room temperature, no further polymerization can be detected. At this point, heating the solution to 45 °C causes the rate of polymerization to increase to approximately 0.4 equivalents/minute, before complete deactivation occurs. As mentioned previously, the addition of a Lewis-acid cocatalyst greatly increases the polymerization rate. However, because of the incompatibility of the 7-oxanorbornene monomers with the very oxophilic aluminum and gallium cocatalysts used in the literature, other reagents were sought to fill this role. The strategy adopted was that of identifying Lewis acidic compounds, which are halophilic, but not oxophilic, in their reactivity. Two types of compounds were found that met this criterion. Silver salts, such as silver tetraphenylborate, and mercury salts, such as mercuric bromide, were found to augment the rate of polymerization, without their undergoing detectable side reactions themselves with the monomer. These activated catalyst mixtures display polymerization rates of approximately 50 equivalents/minute. Furthermore, the yields of polymer can be increased from 10-20% to 70-80%, using either the **XV**/$AgBPh_4$ or the **XV**/$HgBr_2$ systems. The $HgBr_2$ cocatalyzed system is most active when run in THF, which increases the solubility of the cocatalyst. The coordinating solvent does not have a noticeable inhibitory effect on the polymerization reaction.

Problems still persist with these cocatalyzed systems. Catalyst deactivation remains a competitive process, ultimately setting limits on the yields of polymer obtained. More troubling is the fact that the cationic tungsten species generated in these activated systems are extremely difficult to remove completely from the isolated polymer. In the absence of solvent, this catalyst residue reacts very rapidly with the unsaturated polymer product, rendering it highly cross-linked.

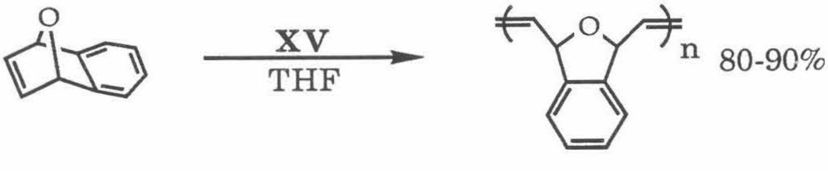
Other 7-oxanorbornene monomers similar to **VIII**, containing either pendant alkyl groups or ether groups such as **IV** and **V**, can be polymerized in the presence of **XV**. In general, these monomers show behavior similar to that of **VIII**, displaying the same catalyst deactivation processes, and hence, nearly the same yields (Equation 16).



(16)

Bridgehead substituents on the monomer seem to inhibit the polymerization. At temperatures up to +60 °C, no polymerization of **VIIIm**, containing the bridgehead methyl group, occurs, with **XV** as a catalyst. It is clear from the ^{1}H NMR of these reaction mixtures that the catalyst suffers decomposition at these temperatures, while the monomer remains unchanged.

Utilizing more reactive monomers, i.e., monomers possessing higher ring-strain energies, results in higher polymer yields. For example, rapid polymerization of monomer **X** occurs at approximately 35 °C with **XV** as the catalyst (Equation 17).



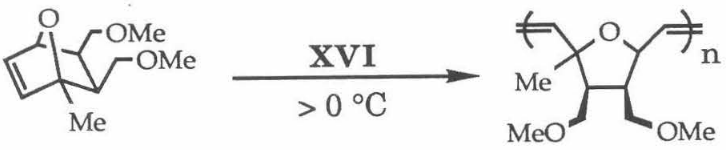
(17)

The best yields of Poly **X** are obtained when THF, rather than benzene, is used as solvent. The polymer precipitates out of either solvent as it is formed; higher molecular weight chains are obtained in THF, however, because of the polymer's enhanced solubility in that solvent.

4. Schrock's Catalyst $((CF_3)_2CH_3CO)_2W$(imido)(CH^tBu).

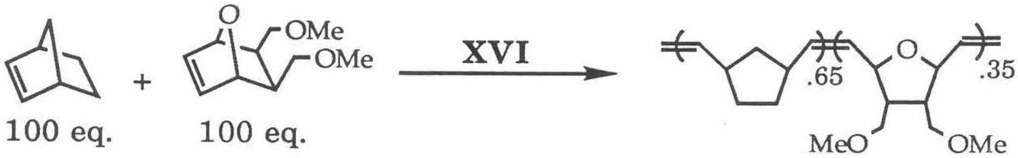
Schrock's catalyst, $((CF_3)_2CH_3CO)_2W$(imido)(CH^tBu) (imido = 2,6-diisopropyl aniline) (**XVI**) is an exceedingly active metathesis catalyst.[36] For example, **XVI** will readily polymerize norbornene at -78 °C. When two equivalents of monomer **V** are added to a solution containing **XVI** at -65 °C, the methylidene proton resonance is immediately shifted downfield by almost 0.5 ppm (8.84 to 9.31 ppm). The signal of a new carbene resulting from the metathesis of one equivalent of monomer should appear as a doublet. The shifted carbene resonance, however, remains a singlet. This shift is interpreted as arising from coordination of the monomer to the catalyst center. Unlike the broadening of the bridgehead resonances observed in the complexation of these 7-oxanorbornene monomers with **XV** and $WOCl_4$, no broadening is observed for any of the monomer signals in this system. It appears, therefore, that coordination of the monomer to **XVI** occurs through the double bond, rather than through the 1,4-bridging epoxide moiety. Upon warming to -50 °C, very slow polymerization of **V** is observed. At this point, very little of the catalyst is active. Only 4% of the initial carbene signal has disappeared, and no new carbene resonances are observed. After gradual warming to -40 °C over the course of approximately one hour, nearly all the monomer is polymerized, and approximately 84% of the original carbene has been consumed. The addition of more **V** results in further polymerization, although the rate falls off with time. Analogous results were obtained for the polymerization of **VIII**. The yields of Poly **VIII** are typically 25-35%. For both monomers, the rate of polymerization falls off with time, indicating the presence of a competitive deactivation process. By ^1H NMR, resonances at *ca.* 6.4 and 6.8 ppm, which are not associated with the ring-opened polymer, are observed to appear simultaneously during the polymerization of both **V** and **VIII**. Attempts at synthesizing polymer with a degree of polymerization greater than about 100 have all failed. These deactivating side reactions, although not as pronounced as with catalyst **XV**, nevertheless place an effective ceiling on the molecular weight as well as on the yield of polymer one can obtain.

The greater reactivity of catalyst **XVI** is illustrated by its ability to polymerize the bridgehead methyl monomer, **VIIIm**. Unlike **VIII**, which initiates polymerization with **XVI** at -55 °C, **VIIIm** does not begin to polymerize (at a very slow rate) until temperatures near -20 °C are reached. Appreciable rates of polymerization are not realized until the temperature is raised over 0 °C (Equation 18).



(18)

While compound compound **XVI** is an active polymerization catalyst for the 7-oxanorbornene monomers, these systems are *not* living, as evidenced by a measurably slow initiation rate relative to the propagation rate, and the presence of deactivating side reactions, which act to terminate the growing polymer chain. Because of these limitations, controlled block polymer synthesis cannot be accomplished using this catalyst. Random copolymers, however, of norbornene and **VIII** have been synthesized using catalyst **XVI**. When equimolar amounts (100 equivalents) of each monomer compete in the presence of **XVI**, copolymers containing approximately 65% norbornene and 35% **VIII** are obtained. The ^{13}C NMR spectra of these copolymers indicate that they are randomly assembled (Equation 19).



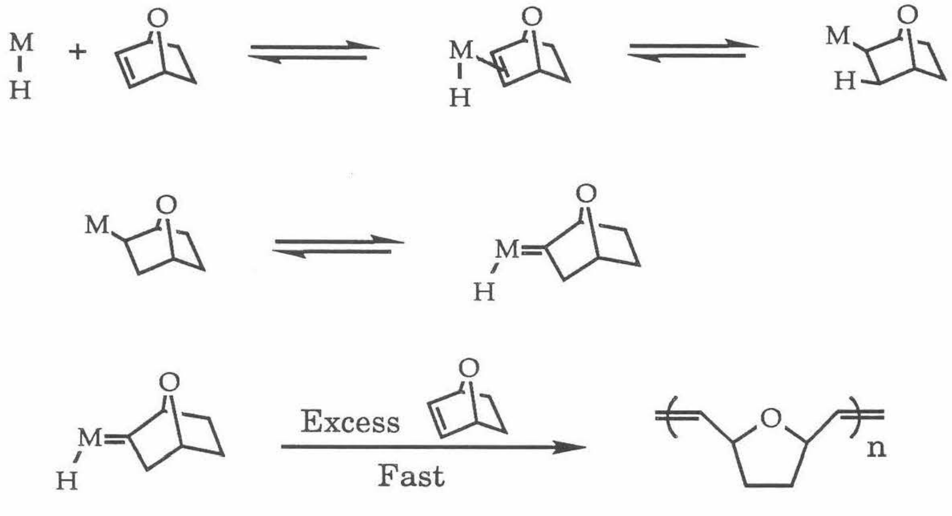
(19)

In summary, tungsten catalysts **XV** and **XVI** polymerize 7-oxanorbornene derivatives possessing alkyl or ether pendant functional groups. These catalysts are, however, subject to deactivating side reactions, which appear to be associated with coordination, and opening of the 1,4-bridging epoxide moiety. Although modest stability towards a few polar functional groups has been observed here, other, more robust catalytic systems must be indentified. Beyond the 1,4-bridging epoxide, the functional groups investigated here have been extremely limited. The polymerization of monomers containing carbonyls, or protic sources such as alcohols, phenols, carboxylic acids and amines have been completely eliminated by these studies as candidates for these early transition-metal catalysts. To reach our ultimate goal of developing sturdy, living catalysts, focus must shift from the early metal systems to investigations aimed at the understanding and development of the later transition-metal catalysts.

5. Group VIII Metal Catalysts.

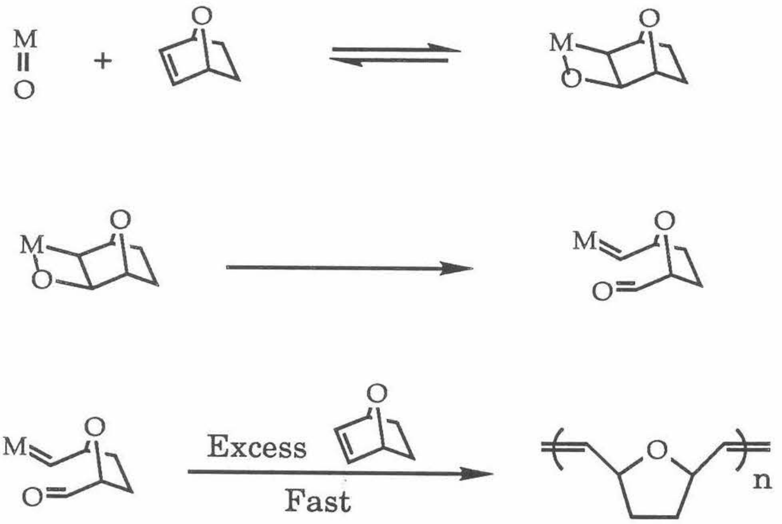
Group VIII metal compounds containing such metals as ruthenium, osmium and iridium are known to catalyze the ring-opening polymerization of cyclic olefins.[37] These polymerizations are usually preceded by an initiation period of minutes, hours, or even days, depending upon the particular monomer, catalyst and reaction conditions employed. During this initiation period, it is believed that a small amount of metal carbene is formed, which then reacts very rapidly with the cyclic olefin present. The exact nature of the initiation process that converts the metal complex precursor and the cyclic olefin to the active metal carbene, is not known. (In fact, the unstated assumption that these polymerizations occur through the metal carbene-metallacyclobutane interconversion mechanism has never been demonstrated.) Several proposals have been advanced in the literature concerning the basic steps associated with carbene formation. For example, a hydride mechanism has been proposed in which the initiating species is thought to be a small amount of metal hydride that inserts into an olefin.[38] The metal-σ complex thus produced then α-eliminates to form the metal alkylidene species (Scheme **VI**).

Scheme VI:



An alternative proposal invokes the participation of a metal oxide, that undergoes a [2+2] cycloaddition reaction with the substrate olefin to form an intermediate metalloxatane.[39] This metalloxatane then undergoes a retro [2+2] cycloaddition to form a metal carbene possessing an aldehyde end-group. Once formed, the metal carbene reacts very rapidly with the cyclic olefin present, producing the ring-opened polymer (Scheme **VII**).

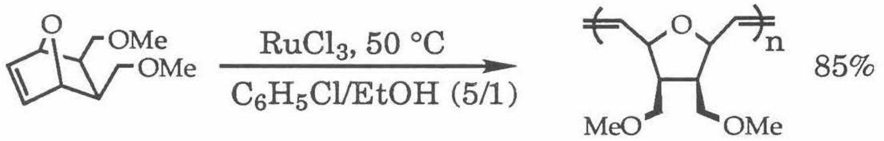
Scheme VII:



The stability of Group VIII complexes to polar functional groups in metathesis reactions is well documented (see Chapter 2). The fact that these complexes are much less oxophilic than their Group IV and V counterparts suggested that they might be excellent candidates for the polymerization of 7-oxanorbornene monomers. A comparison of the metal-oxygen bonds in Ti-O (156 Kcal/mol) and W-O (160 Kcal/mol) to that of Ru-O (110 Kcal/mol) reveals a loss of nearly 30% of bond energy in the Group VIII case.[40] This decrease in metal-oxygen bond strength aids in reducing the number of detrimental side reactions observed, by removing from these systems the large thermodynamic driving force leading to products containing metal-oxygen bonds.

As a general trend observed in the polymerization of norbornene derivatives, reactivity for the known Group VIII catalysts descends in the order Ir > Os > Ru.[37b,e] As the ring strain of the 7-oxanorbornene structure is somewhat less than norbornene, the highly active compound, $IrCl_3 \cdot nH_2O$, was selected as the catalyst of choice. The results, however, were disappointing. When 50 equivalents of monomer **VIII** were heated to 50 °C for up to three days with $IrCl_3 \cdot nH_2O$, no reaction was observed. Subsequent to this initial trial, a number of Ir^{3+} and Ir^{1+} compounds were examined; all failed to give polymer with any of the 7-oxanorbornene derivatives. No indications of any deactivation processes have been observed. The results were dramatically different, however, when the "less reactive" osmium and ruthenium complexes were utilized.

When monomer **VIII** is allowed to react with $RuCl_3 \cdot nH_2O$ at 50 °C in organic solvents, high conversion to the expected ring-opened polymer is observed (Equation 20).



(20)

For a 1 M solution of **VIII**, at 50 °C, the onset of polymerization is preceded by an initiation period lasting from 22 to 24 hours. Once initiated, the polymerization proceeds at the rate of 0.6 g polymer/hour·g catalyst. If however, rate calculations based on the molecular weight of the polymer produced as a function of time are performed (*vide infra*), it can be estimated that each active center is polymerizing at an average rate of approximately 750-1000 equivalents of monomer per minute. Thus, once initiated, these ruthenium complexes can be quite active polymerization catalysts.

In accordance with procedures outlined in the literature,[37] these polymerizations were carried out either in absolute alcohol (methanol or ethanol), or in 10-20% alcohol/benzene mixtures. Depending upon the particular 7-oxanorbornene monomer, the forming polymer may remain soluble in these organic solvents (**VIII**,**V**, norbornene), or it may precipitate (**III**, **IV**, **VII**, **X**, **XI**).

Unlike the materials produced by the tungsten catalysts **XV** and **XVI**, the polymer formed using $RuCl_3$ is high molecular weight material (M_w = 338,000, M_n = 172,000, PDI = 1.98). Figure 4 shows the results obtained from studies on the molecular weight of the polymer as a function of the number of equivalents of monomer used. From these data it can be clearly seen that these systems behave in a "classical" manner; i.e.,the molecular weight of the polymer is controlled by the rate of propagation relative to the rates of termination and chain transfer. This ratio is a fixed constant, and thus the molecular weight of the resulting polymer remains independent of the number of equivalents of monomer used.

In the presence of the catalyst $OsCl_3{\cdot}nH_2O$, rate enhancement is even more pronounced; rates of 11.5 g polymer/hour·g catalyst were obtained, as compared to 0.6 g polymer/hour·g catalyst observed for $RuCl_3$ at the same temperature. A 0.70 M solution of **VIII** in the presence of $OsCl_3{\cdot}nH_2O$ (0.12 M) at 50 °C, yielded 87% of the desired polymer after 3.25 hours. The ring-opened polymer obtained from this catalyst was badly discolored, however, and largely insoluble. Furthermore, this highly active $OsCl_3$ catalyst promoted a considerable amount of secondary chemistry on the unsaturated polymer, leading to highly cross-linked materials. Although

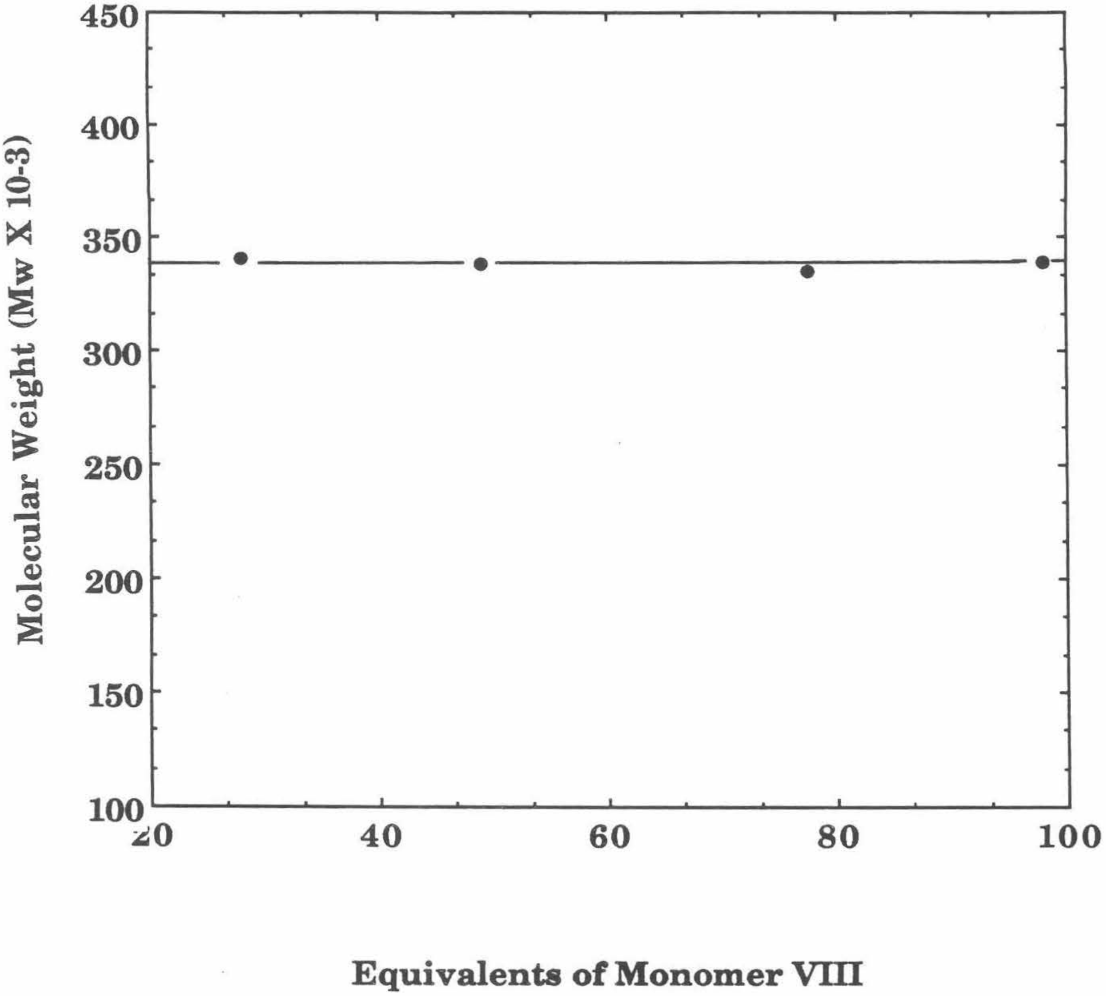


Figure 4: The molecular weight of Poly **VIII** obtained using $RuCl_3$ (0.063M in C_6H_5Cl/EtOH, 5/1), as a function of monomer concentration. (Reaction temperature, 50 °C).

various reaction conditions were employed, none were identified that served to minimize these polymer degradation processes. This secondary chemistry limited the usefulness of the osmium complexes as catalysts for the 7-oxanorbornenes. Further studies were therefore focused on the development of the ruthenium based catalysts.

The ruthenium catalyzed system is clearly not living; consequently, studies directed at controlling the molecular weights of the product polymers were focused on the addition of chain termination, or chain transfer agents to the reaction mixture. For example, carbonyl compounds such as aldehydes, ketones and even esters, are known to undergo Wittig-type reactions with transition metal carbenes [26] (Equation 21).

(21)

The efficiency of this reaction, for the tungsten and titanium catalysts, is reflected in the fact that it can be used to selectively end-cap the growing polymer chain.[41] In order to determine whether the putative intermediate ruthenium carbene species would undergo Wittig-type chemistry, a series of polymerizations were performed in the presence of varying amounts of acetone (Figure 5). As can be seen from these data, acetone has no effect whatsoever on the molecular weight of the product polymer, even when it is used as the neat solvent. It must therefore be concluded that the intermediate carbene does not engage in Wittig-type reactions. From the viewpoint of molecular weight control, this is interpreted as a negative result. On the other hand, it is a clear and unambiguous demonstration of

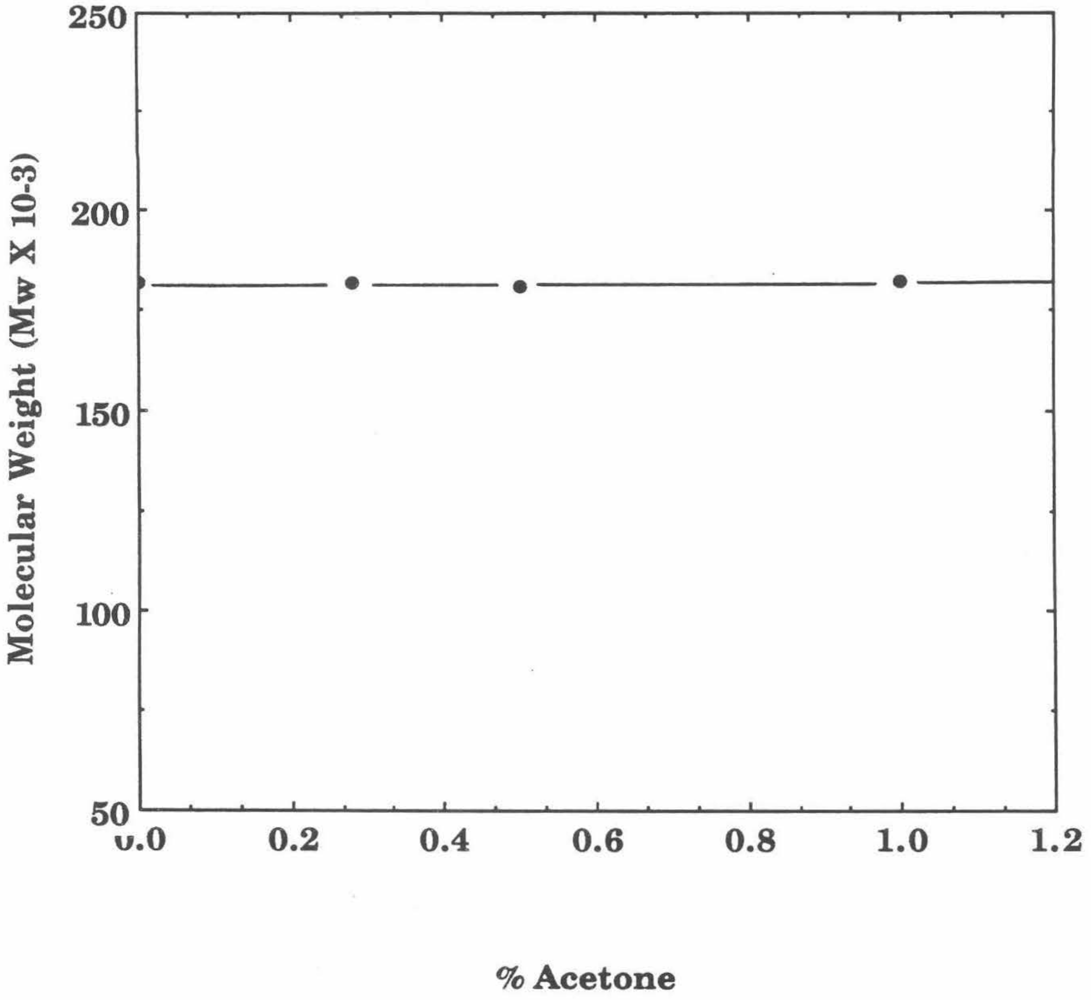


Figure 5: The molecular weight of Poly **XI** obtained using $RuCl_3$ (0.23 M in $C_6D_6/(CD_3)_2CO$), as a function of acetone concentration. (Reaction temperature, 40 °C).

the high tolerance which these ruthenium based catalysts display toward functional groups.

Modest control over the molecular weight of the product polymer has been demonstrated through the addition of acyclic olefins to the reaction mixture.[42] In metathesis polymerizations, acyclic olefins can act as chain transfer agents by end-capping the growing polymer chain and forming a new metal carbene (Equation 22).

(22)

When 2-hexene (*cis/trans* mixture) was added to the polymerization mixture, very high concentrations (relative to the monomer concentration) were necessary in order to exert even a slight effect on the molecular weight of the polymer formed (Figure 6). Surprisingly, concentrations of acyclic olefin nearly equal to the monomer concentration were required in order to begin reduce the molecular weight of the polymer. Even at a 1:1 ratio of acyclic to cyclic monomer, the molecular weight of the polymer was still quite high (M_n = 44,000). At acyclic/cyclic ratios much greater than 1.0, polymerization is inhibited. The identity of the end-groups could not be determined, even in the lowest molecular weight polymer obtained. Thus, no definitive proof exists at this juncture to show that the molecular weight reduction observed occurs via chain transfer through metathesis of the acyclic olefin. In an alternative explanation, the acyclic olefin may bind to the active catalyst, blocking coordination of cyclic monomer and thus retarding the rate of polymerization. Rates of other termination or chain transfer processes would then become more competitive,.with this inhibited

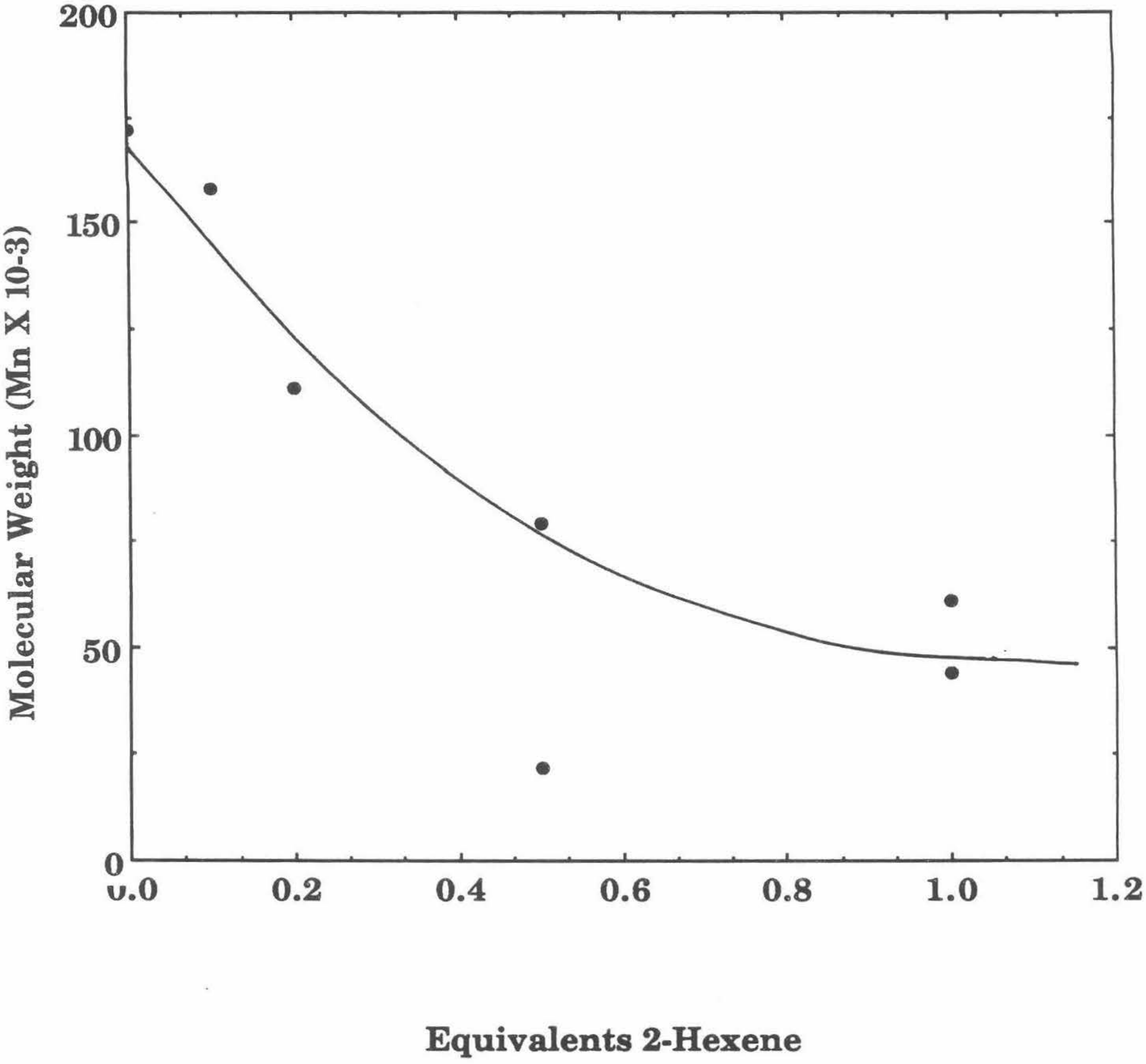


Figure 6: The molecular weight of Poly **VIII** obtained using $RuCl_3$ (0.10 M in $C_6H_5Cl/EtOH$, 1.5/1) as a function of added (*cis* / *trans*)-2-hexene. (Reaction temperature, 50 °C).

rate of propagation, resulting in a reduced molecular weight. If, indeed, the molecular weight reduction is due to acyclic olefin metathesis, then the relative rates of cyclic/acyclic olefin metathesis can be estimated to be greater than 200/1 for the intermediate ruthenium carbenes. (If another mechanism is responsible, this number then becomes an upper limit to this ratio.) The value of this ratio assumes great importance in designing new living polymerization catalysts. In principle, this number should be as large as possible, in order to minimize backbiting reactions of the carbene along the unsaturated polymer backbone. As a general rule, good living polymerization catalysts should be poor acyclic olefin metathesis catalysts. The relative indifference of these ruthenium catalysts to acyclic double bonds make them attractive as candidates for future catalyst development studies.

In an effort to better elucidate the mechanisms of initiation and propagation in these Group VIII metal-catalyzed polymerizations, approximately 30 different cationic, anionic and neutral ruthenium compounds, in oxidation states ranging from Ru^0 to Ru^{6+}, were examined. Some of these compounds are listed in Table 2. There is no special ranking implied by the sequence in which these complexes are listed. A discussion of the aqueous catalysts will be postponed until the next chapter. Table 2 should not be considered an inclusive list of ruthenium catalysts. The breadth of complexes portrayed in this collection, illustrates the universal nature of this chemistry among these Group VIII metals.

As mentioned previously, the initiating species is thought to be either a hydride or an oxide impurity that reacts with the cyclic olefin to form an active carbene. To investigate this possibility, several isolated ruthenium hydride and metal oxide complexes were examined. By and large, these

Ru Complex	Solvent(s)^a	Comments
$RuCl_3 \cdot nH_2O^b$	E, M, CB/E, B/E, C, W	Active
$RuCl_3$ (anhydrous)^c	E, W	Active, (may be heterogeneous
$OsCl_3.3H_2O$	E, M, CB/E, B/E,	Active
K_2OsO_4	!8-C-6/M^d	Inactive
$(NH_4)_2OsCl_6$	W	Active
$IrCl_3$	CB/E, E, W	Inactive
Ru(COD)^e	E, CB/E,	Active
Cp_2Ru	B,CB	Inactive
RuO_2	CB/E, E	Insol. Inactive as a heterogeneous cat.
$RuO_3(OH)_2$	18-C-6/M^d	Active
$Ru(Acac)_3$	E, M	Active
Ru Red^f	W	Active
$[Ru(NH_3)_5Cl]Cl_2$	E, M, W	Active
$[Ru(NH_3)_5OAc]OAc_2$	W	Active
$RuBr_3$	E, CB/E, B/E, W	Active
$(bipy)_3RuCl_2$	E, W	Inactive
$(bipy)_2RuCl_2$	E, W	Inactive
$Ru(NO)Cl_3$	W, E	Inactive
$Ru(NO)(NO_3)_3$	E, W	Inactive
cis$(DMSO)_4RuCl_2$	W	Active
cis$(DMSO)_4Ru(tos)_2$	W	Active
trans$(DMSO)_4RuCl_2$	W	Active
$(THT)_4RuCl_2{}^g$	W	Active
$Ru(H_2O)_6(tos)_2$	E, M, W	Active
K_2RuCl_5	18-C-6/M,^{d} W	Active
$[(C_6H_6)RuCl]_2$	M, E, W	Active
$RuHCl(PPh_3)_3$	CB, H	Active
$RuCl_2(PPh_3)_3$	CB/B	Active
Ru(TFA)^h	CB/E, B/E, E	Active
$Ru_3(CO)_{12}$	CB	Inactive
$RuCl_2(CO)_3$	CB	Inactive
$RuH_2(CO)(PPh_3)_3$	B	Inactive
$RuH(TFA)(CO)(PPh_3)_2$	B	Inactive
$RuH(OAc)(PPh_3)_3$	B	Inactive

Table 2: Group VIII complexes examined for the polymerization of the 7-oxanorbornene monomers. No ordering or ranking is implied. Notes: a) Solvents used. E=EtOH, M=MeOH, CB=C_6H_5Cl, B=C_6H_6, C=$CHCl_3$, W=H_2O. Not necessarily a comprehensive list. b) Commercial $RuCl_3$. c) Mixture of α- and β-$RuCl_3$. d) 18-Crown-6. e) Ru(COD) is an ill-defined Ru-cyclooctadiene polymer. f) Ru Red: $[Ru(NH_3)_5ORu(NH_3)_4ORu(NH_3)_5]Cl_6$. g) THT = tetrahydrothiophene. h) Ru(TFA) is an ill-defined compound with the approximate composition: $Ru_2(CF_3CO_2)_4 \cdot 3H_2O$.

studies were not enlightening. No conclusive evidence was obtained that could bolster either the proposed metal hydride or the metal oxide initiation mechanisms. Although certain of the hydride and oxide complexes were shown to be active metathesis catalysts, none of these compounds demonstrated activity superior to that of the active metal complexes which do not possess these groups. Except in a few cases, a direct comparison of activities is not possible, because a truly homologous series of complexes is not available. Ligand complements and oxidation states, factors known to influence ROMP chemistry, vary widely among these investigated ruthenium complexes. Two examples are presented below. A full discussion concerning the initation process will be presented later in Chapter 4.

If the initiation process involves the formation of a metal hydride, then catalyzing the reaction with a well-characterized ruthenium hydride should affect both the rate of initiation and the activity of the catalyst. The Ru^{2+} complex, $RuCl_2(PPh_3)_3$, is reportedly a moderately active ROMP catalyst.[39] A comparison of the activity of this complex with its hydride analogue, $RuHCl(PPh_3)_3$, was performed. The activity of each of these catalysts under identical conditions is shown in Figure 7. As can be seen, the hydride complex actually shows slightly *less* activity than does the dichloride species. In addition, the molecular weights of the two polymers are almost identical. Both of these observations indicate that in this case, no special reactivity is associated with the presence of a preformed ruthenium hydride.

It was found that the normally insoluble potassium salts of several anionic ruthenium complexes ($K_2RuO_3(OH)_2$[43] and K_2RuCl_5, for example) could be used as active polymerization catalysts, when dissolved in organic

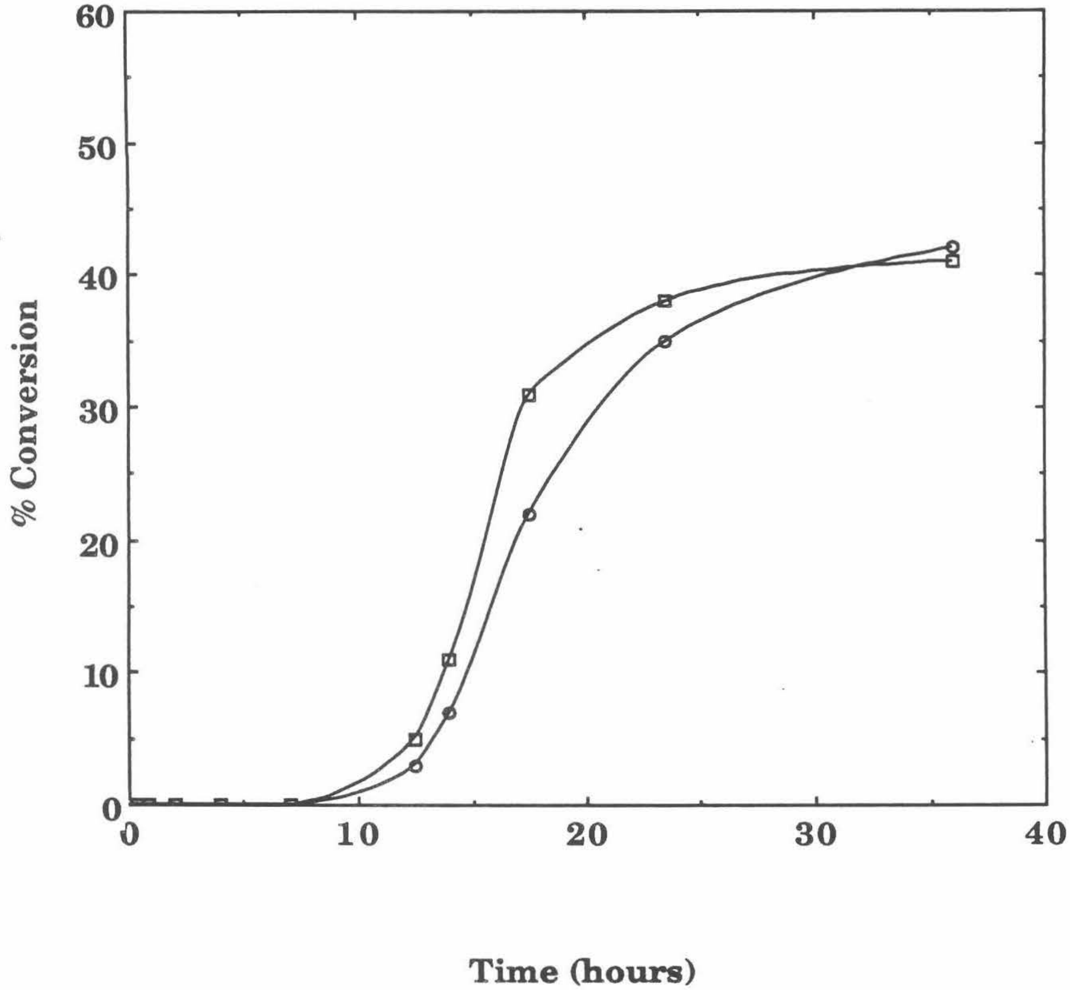
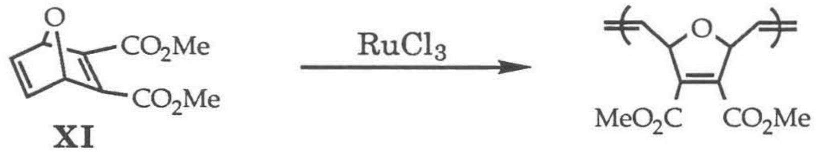


Figure 7: Comparison of the activities of RuHCl(PPh$_3$)$_3$ (0.0194 M in C$_6$D$_5$Cl) and RuCl$_2$(PPh$_3$)$_3$ (0.0198 M in C$_6$D$_5$Cl) in the polymerization of **VIII** (0.787 M) at 58 °C.

solvents using 18-crown-6. $K_2RuO_3(OH)_2$/18-Crown-6 acts as a polymerization catalyst towards monomer **VIII** (45% yield, 2 hours at 65 °C). The molecular weight of the Poly **VIII** produced using this catalyst is approximately 94,000 (M_n), with a polydispersity of 1.95. Under the same conditions, K_2RuCl_5 containing no preformed oxide moiety, requires approximately eight times as long to initiate. Under these conditions, the ruthenium-oxide species seems to be more active than the $RuCl_5^-$ species. In the proposed metal-oxide initiation mechanism, an aldehyde end-group is formed (Scheme **VI**). As evidenced by ^{1}H NMR and IR investigations of these reactions, however, no formation of organic aldehydes or carboxylic acid groups could be detected. Again, no conclusive evidence is available that implicates a metal oxide species in this initiation process. Later work revealed that under slightly different conditions, K_2RuCl_5 is a far more active catalytic species (see Chapter 4).

The tolerance which these ruthenium catalysts display towards functional groups allows for the synthesis of a wide variety of new polymers. A few examples are presented here.

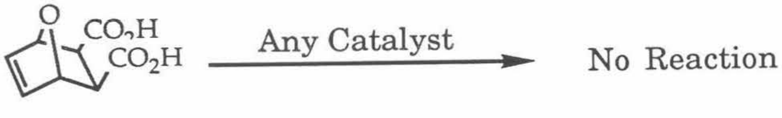
Monomer **XI**, synthesized from the Diels-Alder reaction between furan and dimethylacetylene dicarboxylate,[21] has been sucessfully polymerized using several of the ruthenium catalysts (Equation 23).



(23)

Noteworthy in this reaction is the possibility of including the ester functionality as well as the added unsaturation in the resultant polymer. The effect which the character of the monomer (presumably ring strain) has on the initiation rate is illustrated by this polymerization. The reactivity of **XI** compared to **VIII** can be seen from an examination of their respective initiation rates. The initiation time for a 1 M solution of **XI** is typically 30-35 minutes, while **VIII** initiates under the same conditions in 22-24 hours. The effect of monomer concentration on the initiation rate is illustrated in Figure 8. The initiation rate shows a strong monomer dependence at low monomer concentrations, culminating in saturation behavior at higher monomer concentrations. More qualitative monomer dependence studies show that the less reactive monomers, **IV**, **VII** and **VIII**, display the same general saturation behavior, but the extended reaction times required make accurate quantification difficult.

The additional functionality, present in Poly **XI**, suggested a new handle through which to explore the feasibility of performing chemical modifications on these preformed polymers. The general target of first choice was a new route into useful water soluble polymers,[44] through the incorporation of carboxylic acid groups into these polymers. Commencing with the most obvious route, the anhydride derivative **VI** was hydrolyzed to the corresponding diacid, **VIa**. However, all attempts at polymerizing this diacid derivative with the Group VIII catalysts failed (Equation 24).



(24)

Accordingly, polymerization of the parent anhydride, **VI**, was attempted, again with negative results (Equation 25).

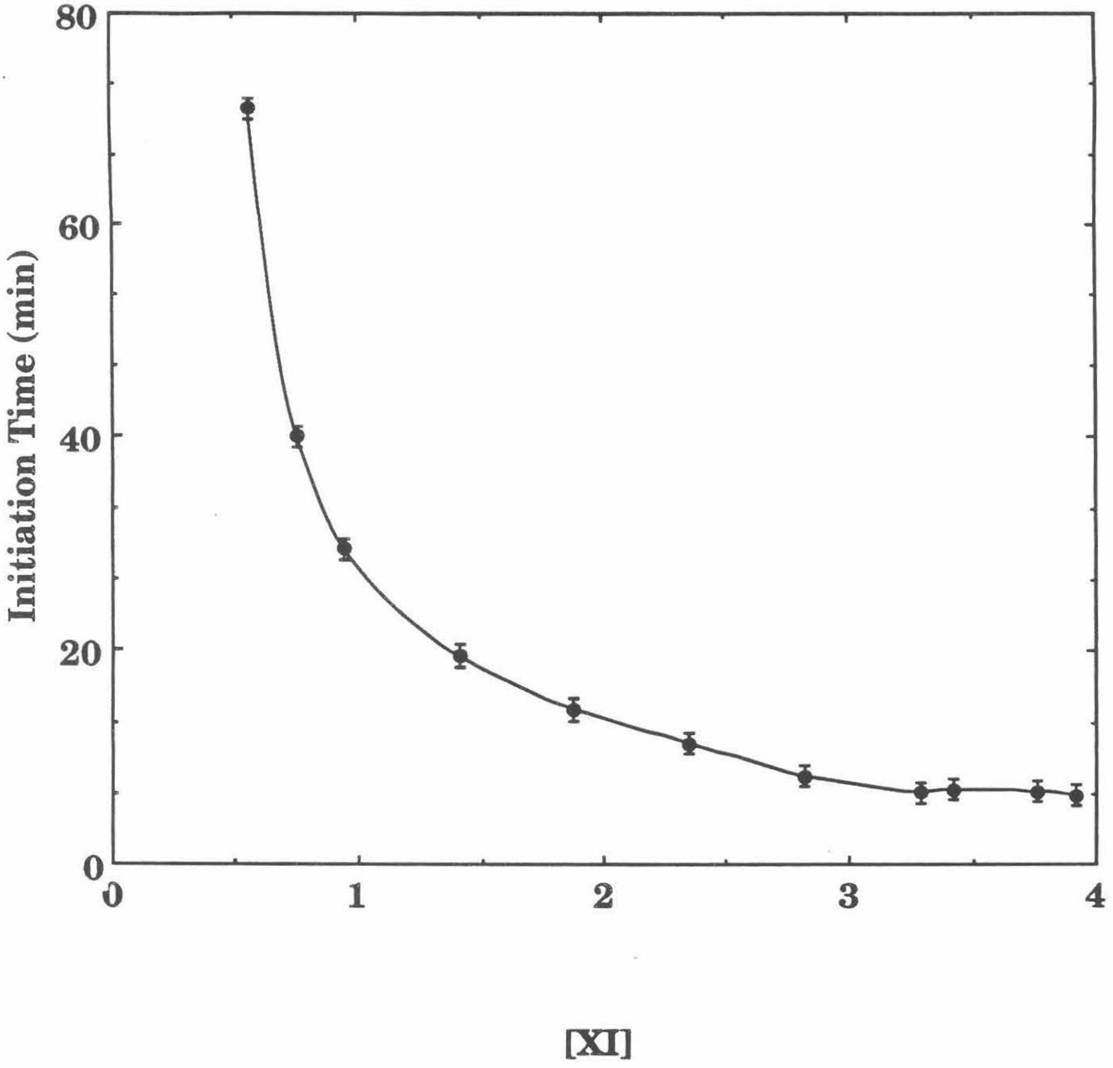
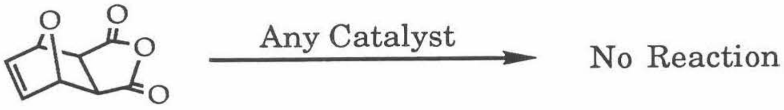


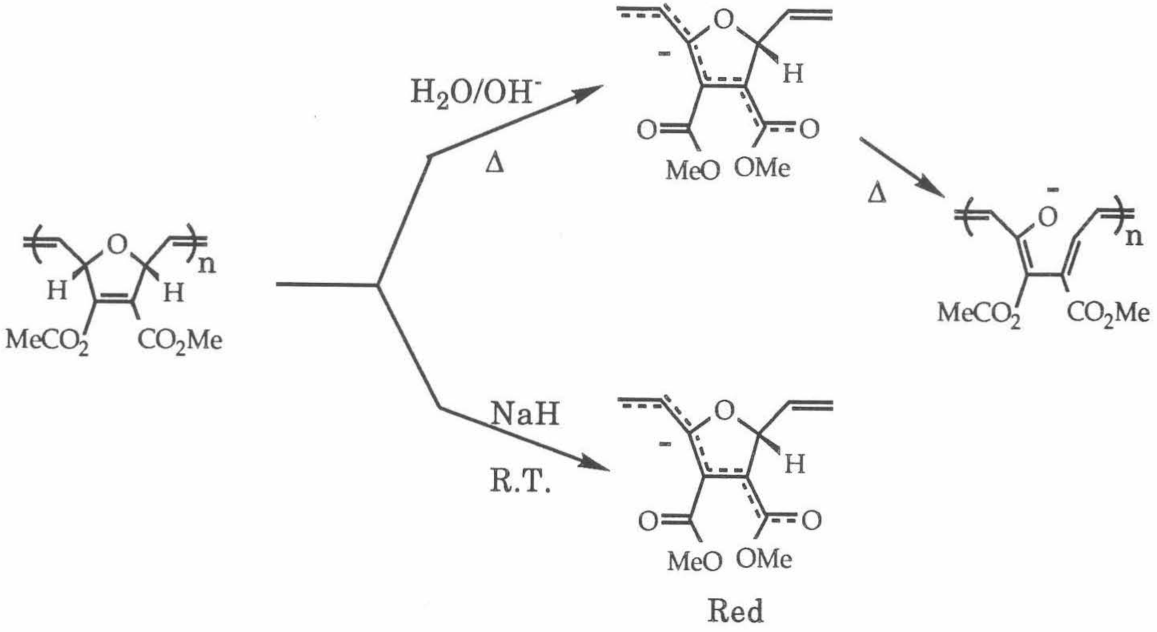
Figure 8: Initiation time (minutes) for the polymerization of **XI**, as a function of monomer concentration (mol/l). Catalyst: $RuCl_3$ (100.6 mg/ml) in CD_3OD. Temperature: 55 °C.



(25)

In light of these discouraging results, attention was turned to hydrolyzing the dimethyl esters of the preformed Poly **XI** material, as an alternate means of providing the corresponding poly diacid. Warming the polymer under acidic conditions resulted, however, in its non-specific decomposition to a discolored, intractable material. Under basic aqueous conditions, Poly **XI** undergoes side reactions to a significant degree, which degrade the material, but do not appear to cross-link it or reduce its overall molecular weight. When Poly **XI** is placed in a 5% NaOH solution, the polymer slowly dissolves and the solution turns a deep red color. The material isolated from this reaction is a rust colored, partially water-soluble polymer, which shows an increased solubility in basic solution. This material can be reversibly dissolved and reprecipitated from aqueous solution by adjusting the pH from basic to acidic, and back to basic conditions. Both ^{1}H NMR and IR evidence indicates that the original Poly **XI** undergoes partial hydrolysis of the ester groups. Accompanying the desired hydrolysis are side reactions, which appear to include a ring-opening of the 2,5-dihydrofuran ring present in the polymer's repeat unit, as evidenced by a decrease in the intensity of the polymer's ether stretch at 1240 cm^{-1}. Consistent with the observations of both ring-opening and the color change from colorless to dark red, a partial deprotonation of the allylic proton is proposed (Scheme **VIII**). Deprotonation at the allylic carbon would lead to a carbanion delocalized over six carbon centers. Ring

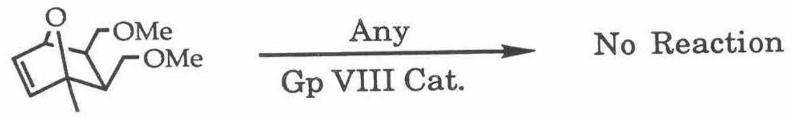
Scheme VIII:



opening of this delocalized anionic 2,5-dihydrofuran moiety would form a carbanion possessing at least one delocalized enolate anion resonance form. The enolate form of the deprotonated ring-opened polymer has four conjugated double bonds per repeat unit. The actual conjugation length along the backbone will depend, of course, on the degree of chain twisting caused by the pendant ester substituents. It is unknown whether the absorption shift to longer wavelength is due solely to the deprotonated 2,5-dihydrofuran carbanion species, or whether this proposed ring-opened enolate structure contributes as well.

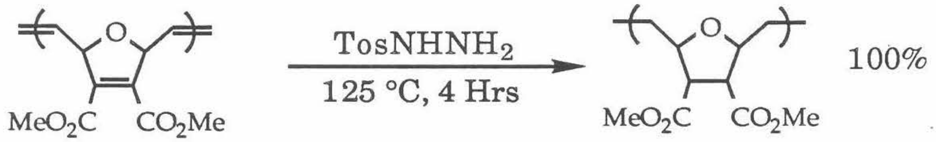
The uncomplicated deprotonation of the allylic carbon can be accomplished by reacting Poly **XI** with NaH in dry THF. In the presence of NaH, a solution of Poly **XI** slowly turns dark red over the course of two hours. Treatment of this red solution with chlorotrimethylsilane (TMSCl) results in an immediate disappearance of the red color. The ^{1}H NMR ($CDCl_3$) of the isolated polymer obtained from this treatment was unchanged except for a 17% decrease in the allylic proton signal at 5.42 ppm, and the appearance of four distinct trimethylsilyl (TMS) resonances at 0.14, 0.10, 0.05 and 0.02 ppm. From the total integration of these four resonances, it can be calculated that 22%, or a little less than one in every four repeat units, were deprotonated. This value is within reasonable agreement with the observed decrease in the allylic proton signal. The extensive decomposition (ring-opening, etc.), which occurs during the aqueous NaOH reaction, does not occur under these conditions.

In order to prepare the target diacid polymer, elimination of the allylic hydrogens was necessary. Protection of these positions by utilizing a dialkyl substituted bridgehead derivative proved unfeasible. Preliminary experiments using the bridgehead methyl derivative **VIIIm** revealed that all of the ruthenium, and the more active osmium catalysts, are completely inert with respect to monomers substituted in this fashion (Equation 26).



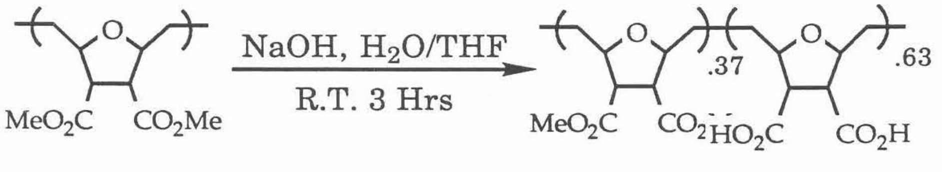
(26)

It was eventually found that the allylic hydrogens could be eliminated most efficiently in an indirect fashion, by eliminating the double bonds adjacent to them. Reduction of the double bonds in Poly **XI** was readily accomplished using p-toluenesulfonhydrazide (Equation 27).



(27)

As evidenced by both ^{13}C NMR (Figure 9) and ^{1}H NMR (Figure 10), virtually 100% conversion to the fully saturated analogue Poly **XIs**, was effected using this homogeneous hydrogenation method. This polymer, with no double bonds (and hence no allylic hydrogens), could be routinely hydrolyzed in basic aqueous/THF solution to provide the partially hydrolyzed polymer (63% hydrolysis at room temperature in three hours) (Equation 28).



(28)

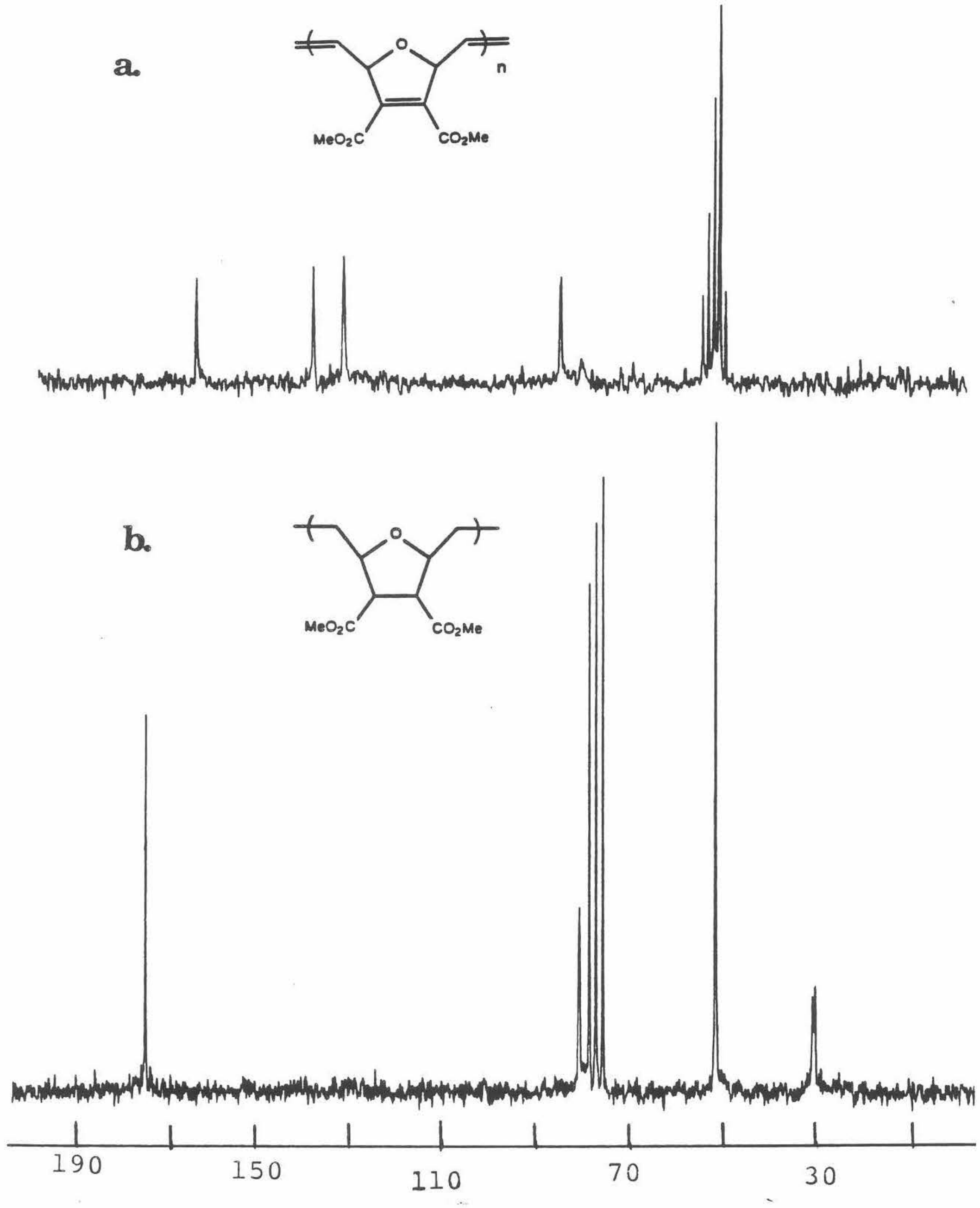


Figure 9: Comparison of ^{13}C NMR spectra; (a) unsaturated Poly **XI** (CD_2Cl_2), and (b) saturated Poly **XIs** ($CDCl_3$).

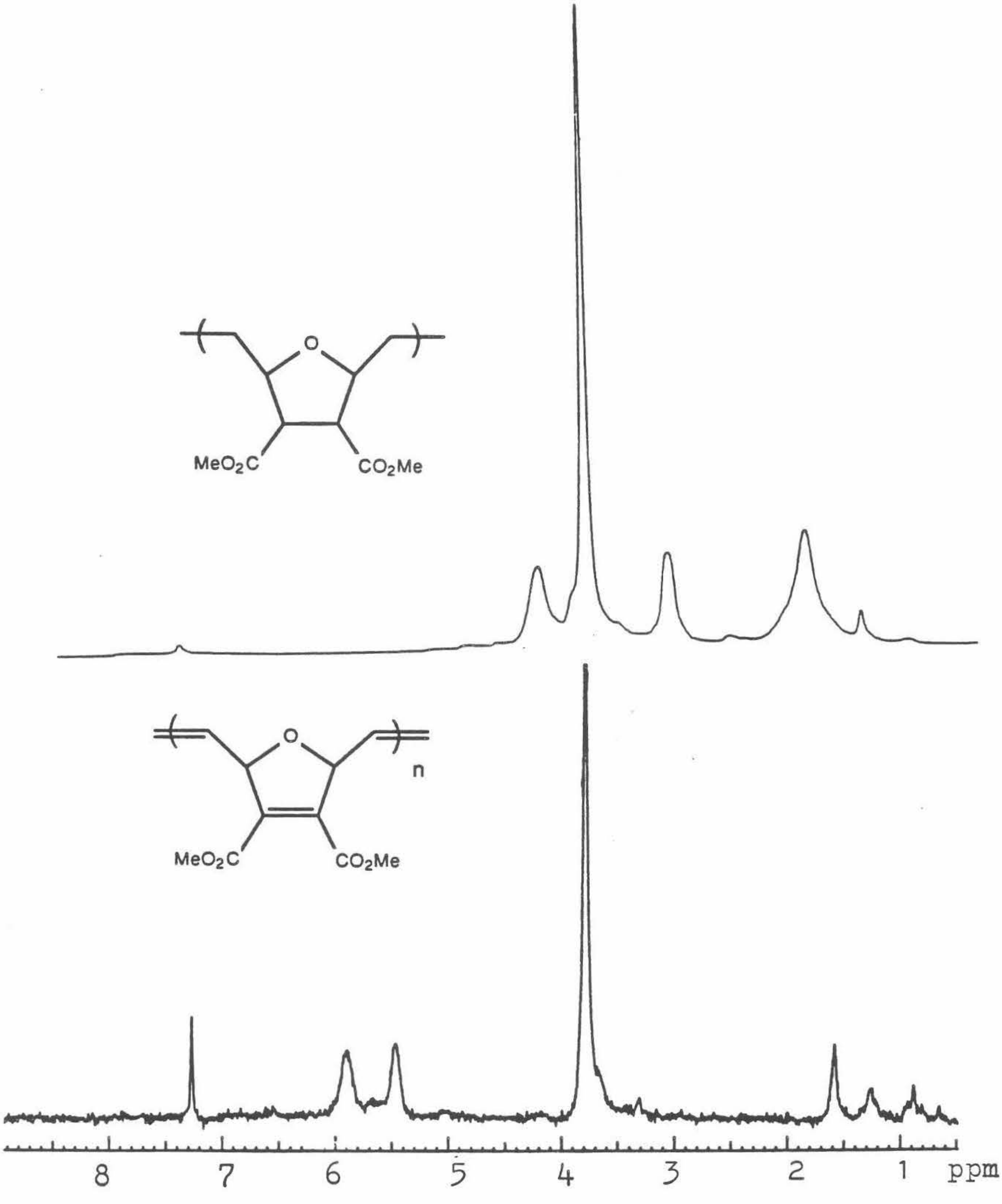


Figure 10: Comparison of ^{1}H NMR spectra ($CDCl_3$) of saturated Poly **XI** (top) and unsaturated Poly **XIs** (bottom).

Longer reaction times and higher temperatures never produced fully hydrolyzed materials.

The versatility afforded by a highly functionalized material such as Poly **XI** is exemplified not only by its ability to undergo reduction, but by the ease with which it is oxidized, as well. The added unsaturation of Poly **XI** provides an opportunity to form fully conjugated materials by oxidation of the allylic hydrogens. Fully conjugated materials such as Poly **XI**, containing the electron withdrawing ether and ester groups, are of interest for potential applications as "n-doped" electrical conducting materials.[6] In addition to modulating the band gap, the pendant ester groups provide a means for improving the solubility and tractability of these types of materials. The oxidation of Poly **XI**, (i.e., removal of the allylic hydrogens), by dichlorodicyanoquinone[45] (DDQ) in dry THF at room temperature, is signaled by a color change of the polymer solution from colorless to red over the course of approximately two hours. The intensity of the color increases with reaction time, and the color shifts from red to a dark purple over the next 24 hours. The product polymer, Poly **XIox**, obtained from this reaction after workup, is a dark-red polymer displaying a slight solubility (*ca.* 0.5-1% by weight) in CH_2Cl_2 and benzene. Through ^1H and ^{13}C NMR analysis, Poly **XIox** has been characterized as the fully unsaturated polymer resulting from removal of the allylic protons (Equation 29).

(29)

The ^1H NMR spectrum of Poly **XIox** reveals a complete disappearance of the allylic hydrogen signal at 5.58 ppm, and a shift of the olefinic protons from 5.92 ppm to a new, broad resonance between 7.7 and 6.3 ppm (Figure 11). As further evidence for this assignment, the ^{13}C NMR spectrum of this polymer shows the disappearance of the allylic carbon resonance at 86.36 ppm (CD_2Cl_2). The two olefin resonances of the parent polymer,138.22 and 131.79 ppm (CD_2Cl_2), are shifted to 143.16 and 139.26 ppm ($CDCl_3$), and are augmented by two new resonances at 154.1 and 118.1 ppm.

The efficiency of DDQ as an oxidizing agent for ROMP polymers of norbornene derivatives is normally quite poor.[46] For the 7-oxanorbornene materials, however, activation of the allylic hydrogens by the α-oxygen makes DDQ an ideal oxidizing agent. Even more rapid oxidation by DDQ is observed in 7-oxanorbornene polymers in which the abstracted hydrogens are benzylic rather than allylic.

Monomer **X** is rapidly polymerized in the presence of the ruthenium catalysts. As discussed earlier, short molecular weight oligomers obtained with catalyst **XV** are only slightly soluble. The higher molecular weight Poly **X** obtained using these ruthenium catalysts is completely insoluble. To solubilize, and hence, chemically modify Poly **X**, copolymerizations with other 7-oxanorbornene derivatives were investigated. It was found that in competition with **VIII**, the much more reactive **X** would homopolymerize, and precipitate, before substantial amounts of the less reactive monomer could be incorporated. By replacing **VIII** with **XI**, however, soluble copolymers containing **X** were synthesized. When equal amounts of **X** and **XI** are allowed to react with $RuCl_3$, a soluble copolymer, Poly (**X**-*co*-**XI**), possessing approximately 76% of the diester monomer, is obtained (Equation 30).

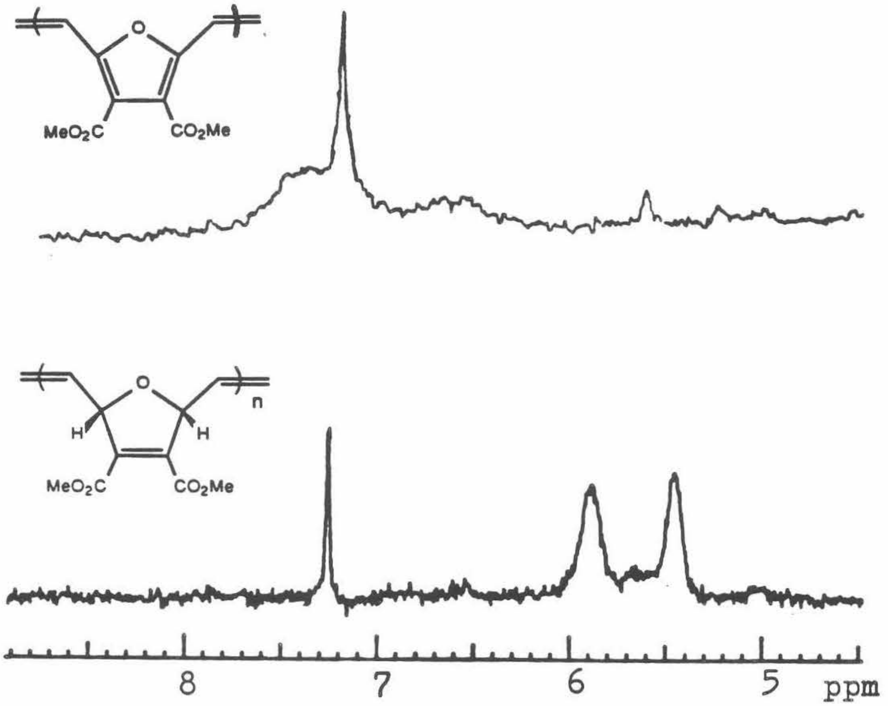
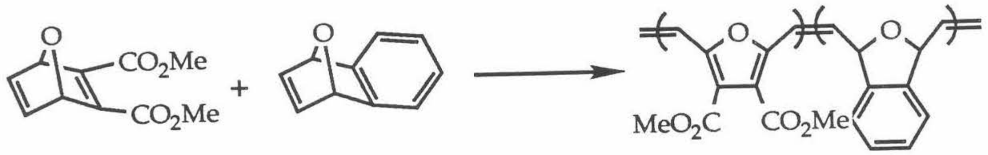


Figure 11: Comparison of the ^{1}H NMR spectra ($CDCl_3$) of the allylic and olefinic region of Poly **XI** before treatment with DDQ (bottom), and Poly **XIox** after treatment with DDQ (top).

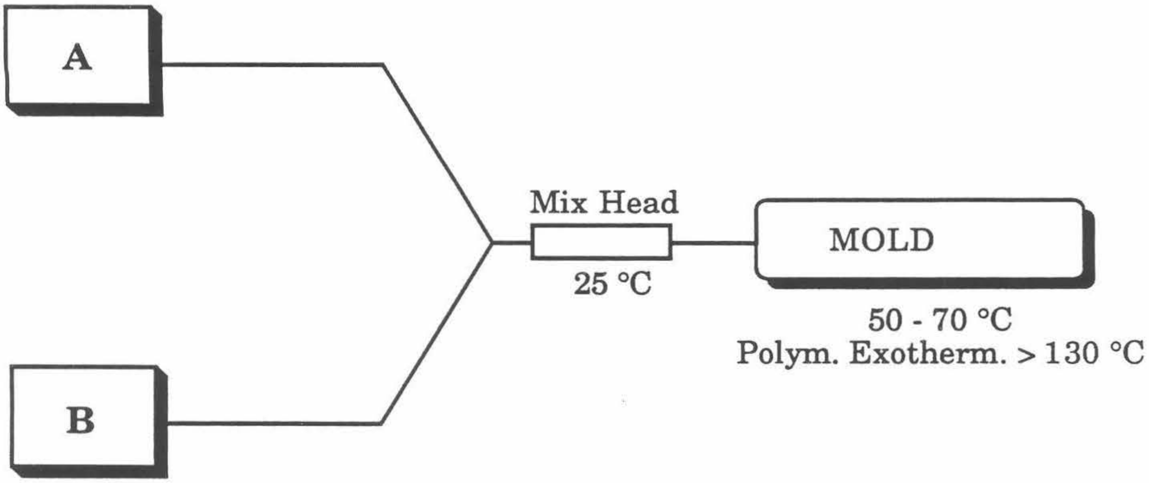


(30)

When Poly (**X**-*co*-**XI**) is allowed to react with DDQ, the solution turns red immediately, then black within 10 minutes, at room temperature. Unlike Poly **XIox**, the resulting oxidized polymer obtained from this reaction is a black, completely intractable solid.

When Poly **XIox** is exposed to I_2 vapors, the initial red polymer darkens, indicative of I_2 uptake. Both the pristine Poly **XIox** as well as the I_2 treated material form extremely brittle films which have consistently cracked before conductivity measurements could be obtained.

Reaction injection molding (RIM) reactors are typically two component systems, in which one or both of the components contain a catalyst (or cocatalyst), with no additional solvent present. The monomer and catalyst pairing is controlled in such a way so as to forestall any reaction from occurring until the two components are mixed. Once mixed (in a mold, for example), the two components are designed to react rapidly, and bulk polymerization ensues. Historically, RIM systems have been used in the formation of elastomeric polyurethanes.[47] New ring-opening metathesis polymerization RIM systems have been introduced, using the two-component catalyst, WCl_6/AlR_2Cl, to polymerize dicyclopentadiene into a highly cross-linked network[48] (Figure 12). The utility of these existing systems is presently somewhat limited by the sensitivity of the catalyst components to ubiquitous impurities such as air and water. The demonstrated stability of the ruthenium catalysts may provide the



Component **A**: WCl_6, Phenol, Benzonitrile, DCPD

Component **B**: $AlEt_2Cl$, Di-n-butyl ether, DCPD

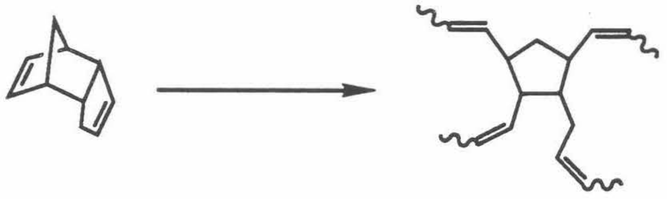
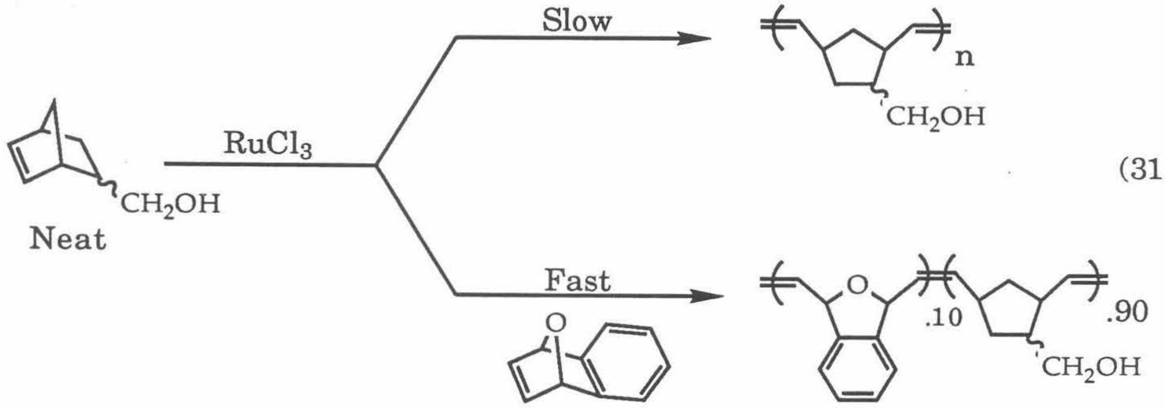


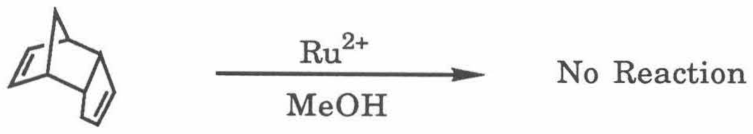
Figure 12: Schematic diagram of ring-opening metathesis polymerization RIM process for the polymerization of dicyclopentadiene.

opportunity to synthesize functionalized RIM polymers under less restrictive conditions. RIM systems are bulk (solvent-free) polymerizations; thus, a polymerizable monomer that is also capable of acting as a solvent for $RuCl_3$ is required. It was found that norbornene-5-methanol (NBOH) would dissolve small amounts of $RuCl_3$ (solutions estimated to be less than 1 X 10^{-3} M in Ru). Under these conditions, however, the bulk polymerization of NBOH is exceedingly slow. It was found, however, that when small amounts of monomer **X** (5-20%) are added, the bulk polymerization of NBOH proceeds at a rapid rate (Equation 31).



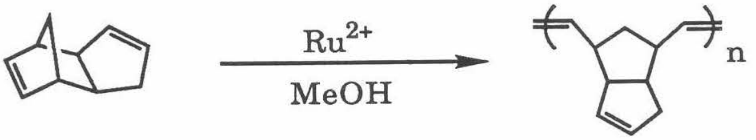
(31)

The polymers obtained in this NBOH/**X** mixture are linear, noncross-linked, rubbery materials. To investigate whether cross-links could be incorporated into these ruthenium-catalyzed systems, the polymerization of DCPD was investigated. The *endo*-DCPD was found to be completely unreactive in reactions with the ruthenium catalysts (Equation 32).



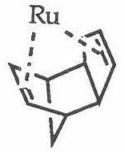
(32)

The purified *exo*-isomer, however, polymerizes readily to provide nearly quantitative yields of the ring-opened polymer (Equation 33).

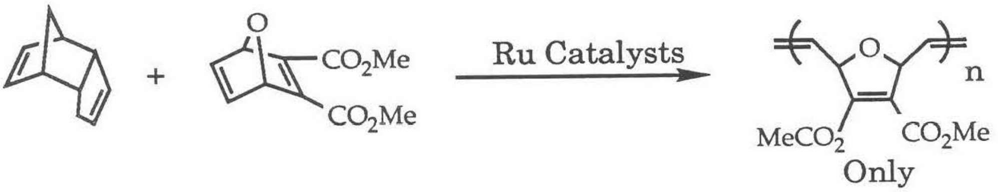


(33)

The reason for this reactivity difference is not readily apparent. It has been proposed that the *endo*-DCPD acts as a chelating group on the ruthenium centers, inhibiting further reaction of the metal.[49]



It was found, however, that when monomers **X** or **XI** were added to the *endo*-DCPD polymerization reactions, homo-polymerization of the 7-oxanorbornene monomers occurred, leaving the *endo*-DCPD untouched (Equation 34).



(34)

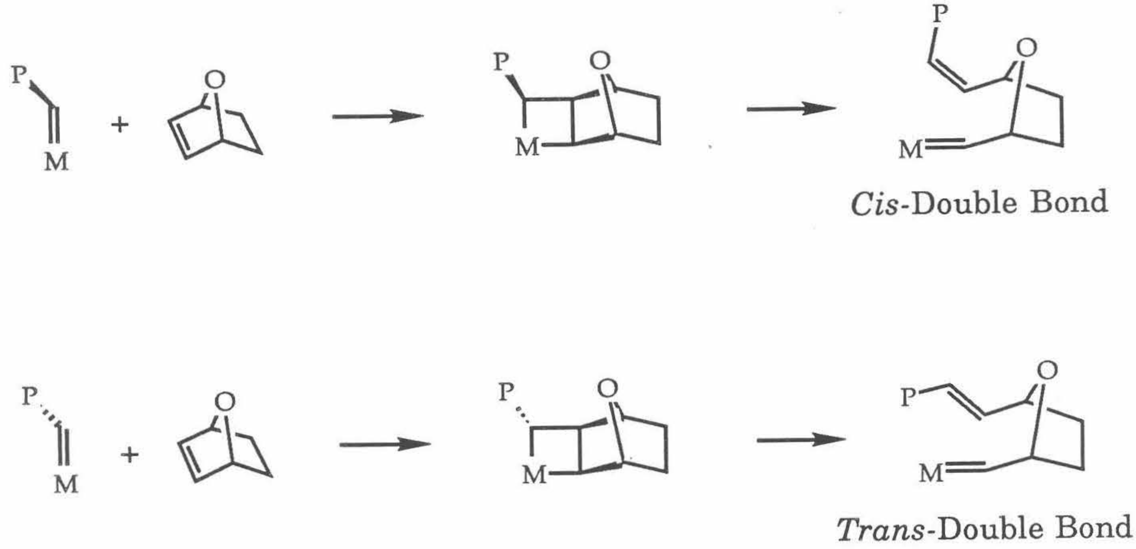
In contrast, copolymerization of the *exo*-DCPD monomer and **XI** proceeds smoothly. These results demonstrate that all of the ruthenium catalyst in the reaction mixture is not bound irreversibly by the *endo*-DCPD. Furthermore, the failure of the *endo*-DCPD to be incorporated into the growing polymer chain, after initation of the 7-oxanorbornene monomer, indicates some inherent unreactivity associated with *endo*-DCPD, which appears unrelated to the proposed chelation effects. It has been suggested that the unreativity of endo-isomers is due to the higher energy of the polymer structure formed by placing all four ring substituents on the same side of the cyclopentane repeat units.[50] Our results tend to support this argument rather than the chelation hypothesis.

Other monomers containing additional pendant olefins have also failed to polymerize. For example, 5-vinyl-2-norbornene fails to polymerize using the ruthenium catalysts. This result, however, may be due to deactivation through chelation of the catalytic center by the monomer, as evidenced by the fact that cyclic monomers polymerize in the presence of a 1:1 mixture of acyclic olefins (*vide supra*). In addition, unlike the *endo*-DCPD case, monomer **XI** fails to polymerize in the presence of 5-vinyl-2-norbornene.

C. Polymer Characterization.

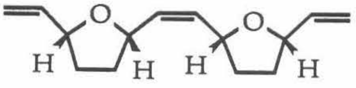
A number of isomeric variants are possible for the poly(7-oxanorbornene) materials reported here. During the polymerization of the 5,6-symmetrically substituted monomers (**VI**, **VII**, **VIII**, **XI**, etc.) the metathesized double bonds can be formed in either a *cis* or a *trans* configuration. If no isomerization occurs during the retro [2+2] process, then the determination for the formation of a *cis* or a *trans* double bond is thought to depend on the relative stereochemistry of the metallacyclobutane formation step. A cisoid addition of the bicyclic monomer relative to polymer substituent on the carbene provides a *cis*-double bond; a transoid addition provides the *trans*-double bond (Scheme **IX**).

Scheme IX:

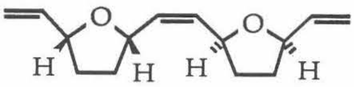


This selectivity, in turn, is thought to depend on the ligand environment of the metal. Ligands that possess a larger steric bulk relative to the polymer chain can act to block the underside of the carbene, forcing the higher energy *cis* conformation.

Two additional isomeric forms are also possible: isotactic and syndiotactic ring diads.



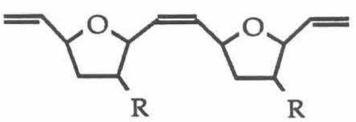
Isotactic
(*cis or trans*)



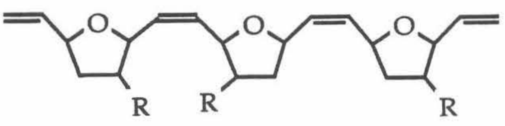
Syndiotactic
(*cis or trans*)

The relative stereochemistry of two successive rings (the tacticity) is determined by which side of the intermediate carbene the metallacycle formation occurs from. An isotactic diad results from two consecutive monomer additions from the same side of the carbene, while the syndiotactic diad results from additions to alternating sides of the carbene.

For the non-symmetrically substituted monomers (**III**, **IV**, **V**, etc.), the polymer's isomeric constitution is compounded by the possibility of head-to-tail (HT) and head-to-head/tail-to-tail (HH)/(TT) diad forms.



(HT)



(HH) (TT)

As a result of the many possible isomeric forms of poly(7-oxanorbornene), and the current lack of highly stereospecific catalysts (*vide infra*), these materials are, in general, highly amorphous, low T_g materials. With two exceptions, none of the 7-oxanorbornene polymers show signs of crystallinity. These two exceptions, Poly **X** and Poly **XI**, are similar in that irregularities that are due to endo-exo isomers at the 5,6-positions have been eliminated by the additional unsaturation present in the 7-oxanorborna-2,5-dienyl type of structures. Poly **XI** displays a T_m at *ca.* 175 °C, determined by differential scanning calorimetry (DSC) (Figure 13). Although Poly **X** gives the appearance of being partially crystalline, DSC reveals that decomposition occurs before melting (Figure 14).

The molecular weights and polydispersities of the 7-oxanorbornene polymers reported here were determined by gel permeation chromatography (GPC). The molecular weights obtained through this

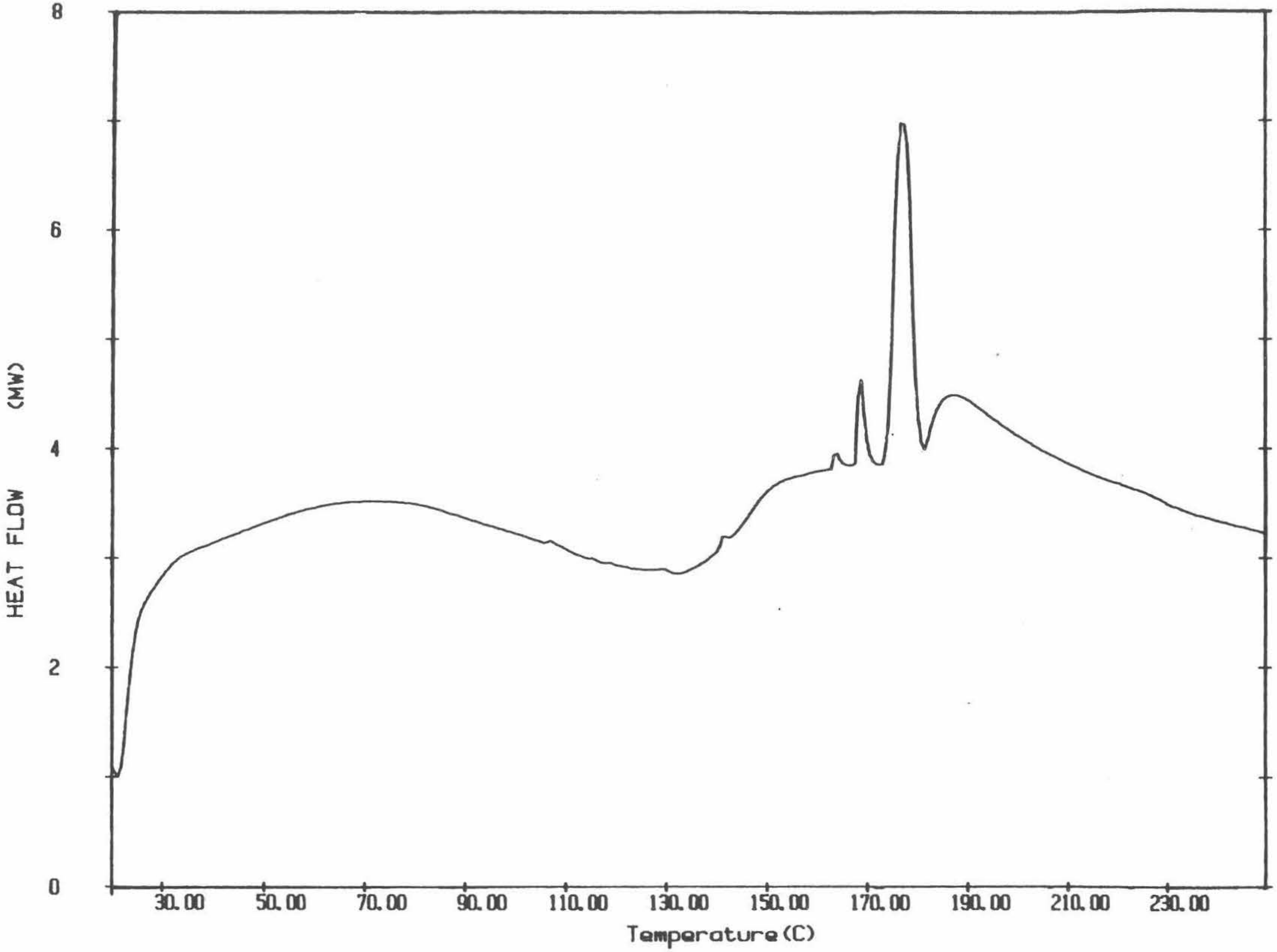


Figure 13: The DSC thermogram of poly **XI**, measured at a scan rate of 20 °C/minute.

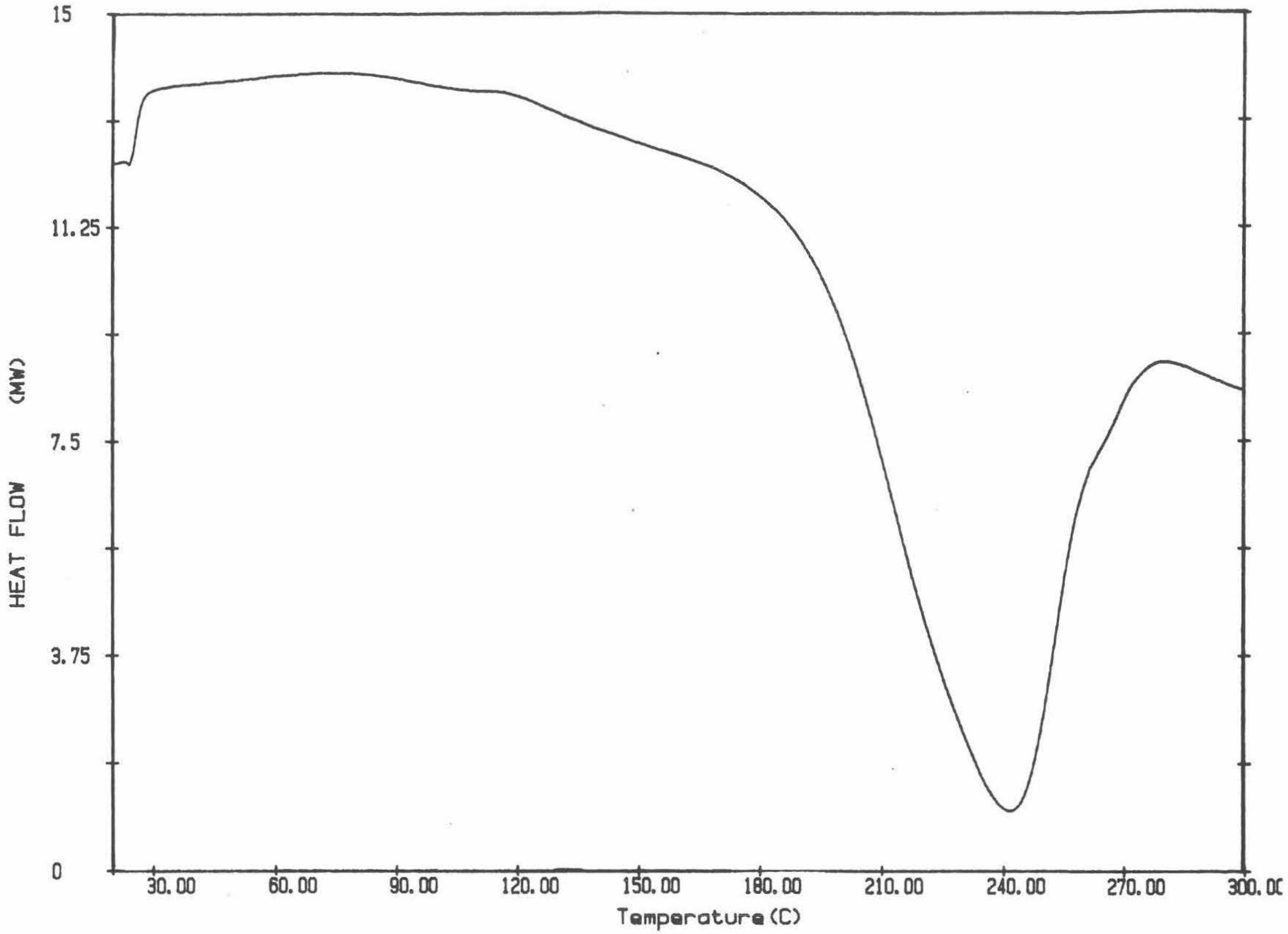


Figure 14: The DSC thermogram of poly **X**, measured at a scan rate of 10 °C/minute.

technique are calculated relative to polystyrene standards. A conversion factor that converts the relative molecular weights to actual molecular weights can be estimated by end-group analysis. A division factor of 2.3 was calculated for the 7-oxanorbornene polymers by integration of the *t*-butyl end-group of the polymers obtained using the neopentylidene catalyst, **XVI**. This value gives good agreement with the accepted value of 2 for the structurally similar polymer of norbornene. The molecular weights and polydispersities of several 7-oxanorbornene polymers obtained using different catalysts are shown in Table 3 Although none of the 7-oxanorbornene systems are living, the molecular weight can be controlled over a wide range by the choice of catalyst. For example, catalyst **XV** provides low molecular weight oligomers with an average degree of polymerization of 12-20, while some of the Group VIII catalysts provide materials with a degree of polymerization of over 5,000.

The solubilities of the 7-oxanorbornene materials vary, depending on both the nature of the pendant substituents, as well as the molecular weights. Polymers obtained from the dimethoxymethyl monomer, **VIII**, exhibit the greatest range of solubility. High molecular weight Poly **VIII** is soluble to greater than 15% in polar solvents (CH_2Cl_2, $CHCl_3$, CH_3OH, CH_3CH_2OH, $(CH_3)_2CO$, THF, etc.), and to a lesser extent (*ca.* 5%, depending on molecular weight), in non-polar solvents (CCl_4, toluene, benzene). Non-solvents for Poly **VIII** include pentane and water. In polar solvents (CH_3OH, for example), the solubility of Poly **VIII** appears to be limited only by the resulting viscosity of the solution. At room temperature, solutions of Poly **VIII** above ca. 15% become viscous gels. Changing the pendant R groups from methoxy to hydroxyl, as in Poly **VII**, dramatically decreases the solubility. Poly **VII** will swell in polar solvents (including water), but

POLYMER	CATALYST	Mw(X 10^{-3})[a]	Mn (X 10^{-3})	PDI[b]
Poly **VIII**	XV (C_6H_6 or THF)	5.84	3.24	1.81
Poly **VIII**	XVI ($C_6H_5CH_3$)	29.4	19.4	1.52
Poly **VIII**	$RuCl_3$ (C_6H_6/EtOH)	338	172	1.96
Poly **VIII**	Ru(COD)[c] (C_6H_6/EtOH)	133	77.6	1.71
Poly **VIII**	$OsCl_3$ (C_6H_6/EtOH)	416	214	1.94
Poly **VIII**	$K_2RuO_3(OH)_2$(18-Crn-6)	183	94	1.95
Poly **VIII**	$OsCl_3$ (CH_3OH)	965	792	1.22
Poly **VIII**	$RuCl_3$ (EtOH)	1120	973	1.15
Poly **VIII**	Ru(TFA)[d] (C_6H_6/EtOH)	365	184	1.98

Table 3: Molecular weights and polydispersities of various Poly(7-oxanorbornenes). Notes: a) Molecular weights given relative to polystyrene standards. b) Polydispersity index (PDI) = M_w/M_n. c) Ru(COD) is an ill-defined Ru-cyclooctadiene complex with an average oxidation state near Ru^{2+}. d) Ru(TFA) is an ill-defined compound with the approximate composition: $Ru_2(CF_3CO_2)_4 \cdot 3H_2O$.

will not form a true solution. This feature provides an efficient method for modulating the solubility properties of these materials, especially for applications in which insolubility is desirable. For example, copolymers of **VIII** and **VII** containing only a few percent of the hydroxyl monomer are almost completely insoluble. Replacement of the disubstituted monomers with the monosubstituted monomers also decreases the solubility. Poly **IV**, containing the mono-dimethoxymethyl substituent, displays a molecular weight-dependent solubility. Low molecular weight Poly **IV** obtained from catalyst **XV** is soluble in some polar solvents, while the high molecular weight materials obtained from the Group VIII catalysts, at best, only swell in polar solvents.

The good solubility of the 7-oxanorbornene materials in general allowed, in most cases, for detailed structural characterization by both solution ^{1}H and ^{13}C NMR techniques. The *cis/trans* double-bond ratios along the polymer backbone were obtained from a systematic comparison of the spectra from polymers synthesized by a number of different catalysts. To eliminate complications arising from possible HT and HH/TT isomeric diads, the symmetrically substituted Poly **VIII** was examined. The ^{1}H NMR spectra of Poly **VIII**, synthesized using three different catalysts, are shown in Figures 15, 16 and 17. The assignments of the *cis* and *trans* olefinic and allylic proton resonances were completed only after correlation with their assigned ^{13}C NMR spectra. No information concerning the tacticity of any of the 7-oxanorborene polymers could be extracted from ^{1}H NMR data.

^{13}C NMR is far more useful in assigning the *cis/trans* ratio of the 7-oxanorbornene polymers. Resonances arising from the carbons alpha to a double bond (the allylic carbons) are typically the best indicators of the *cis* or

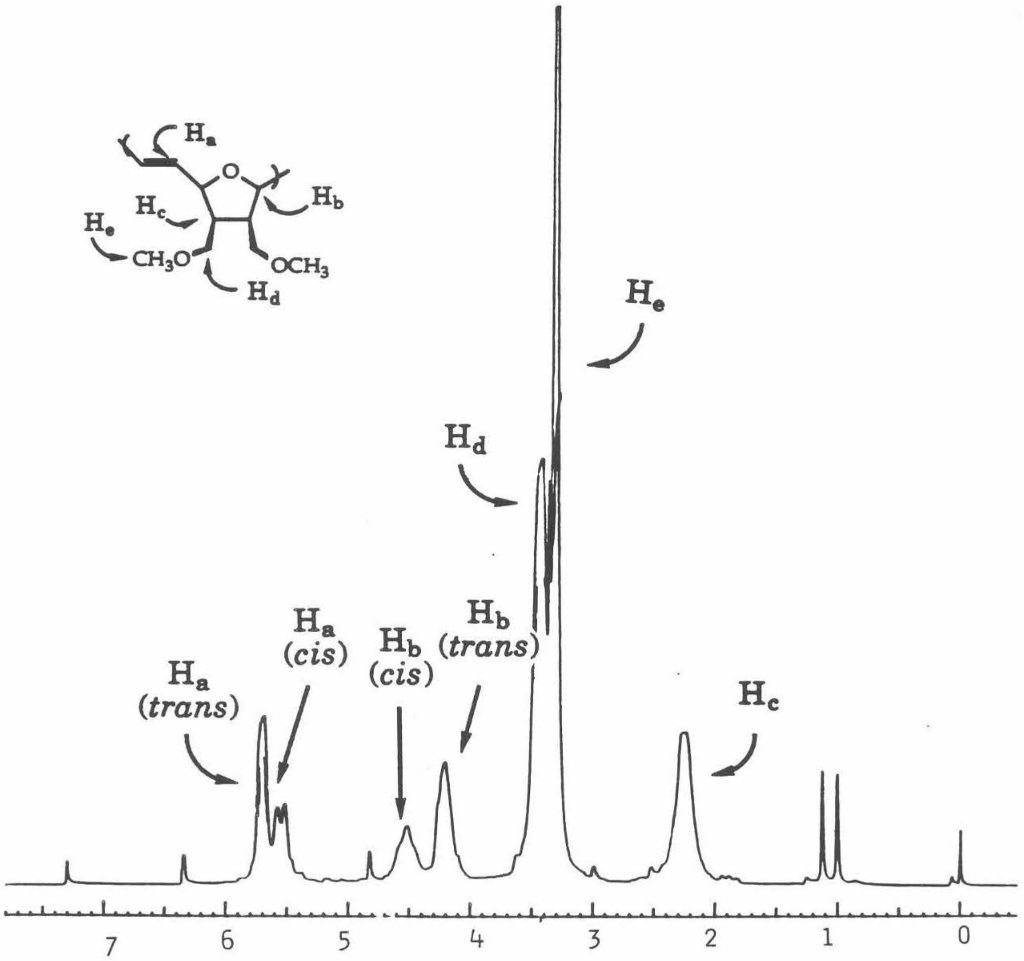


Figure 15: ^{1}H NMR spectra ($CDCl_3$) of Poly **VIII** obtained using catalyst **XV**. *Cis*/*trans* double bond ratio *ca.* 42/58.

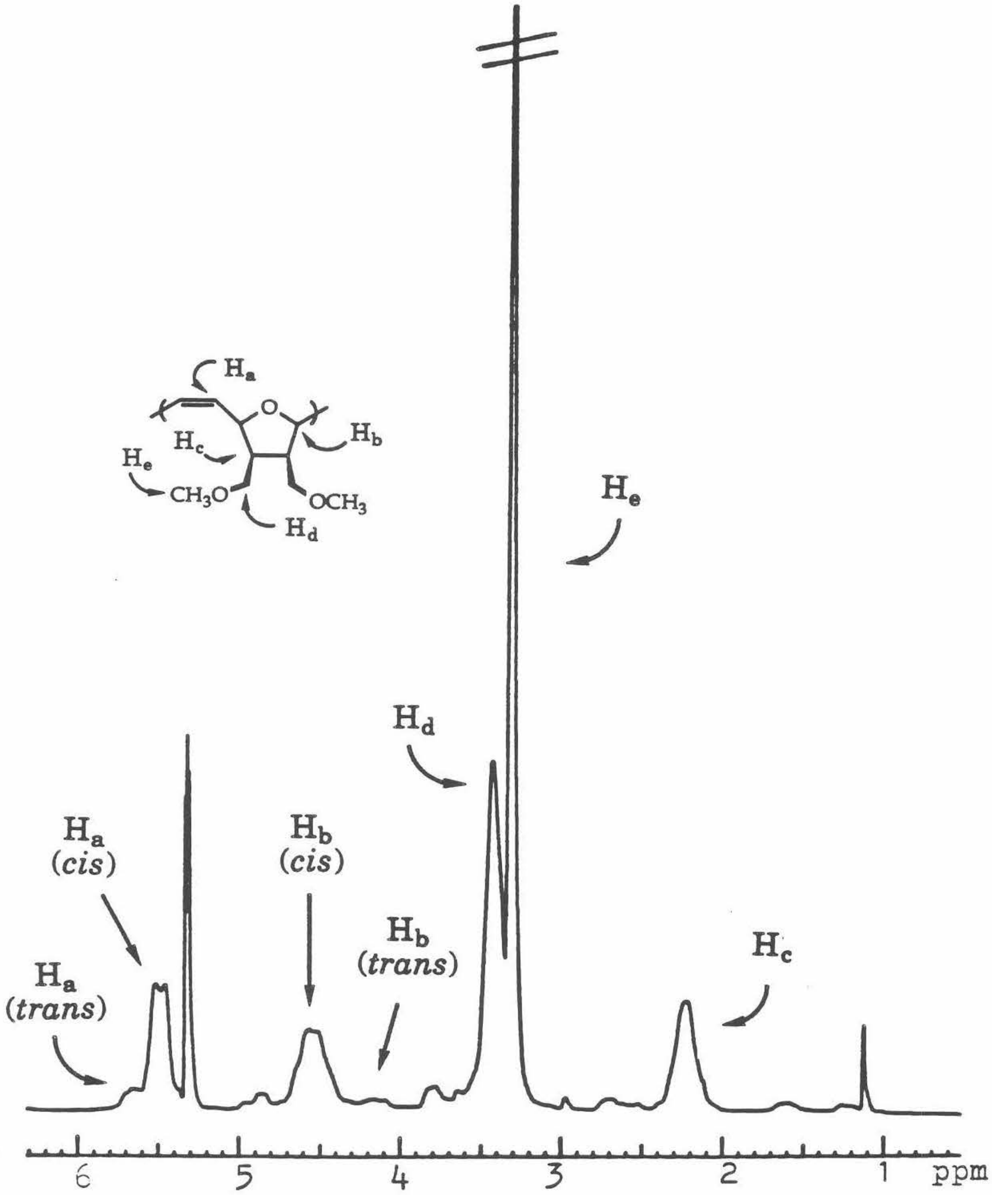


Figure 16: ^{1}H NMR spectra (CD_2Cl_2) of Poly **VIII** obtained using catalyst **XVI**. *Cis/trans* double bond ratio *ca.* 95/5.

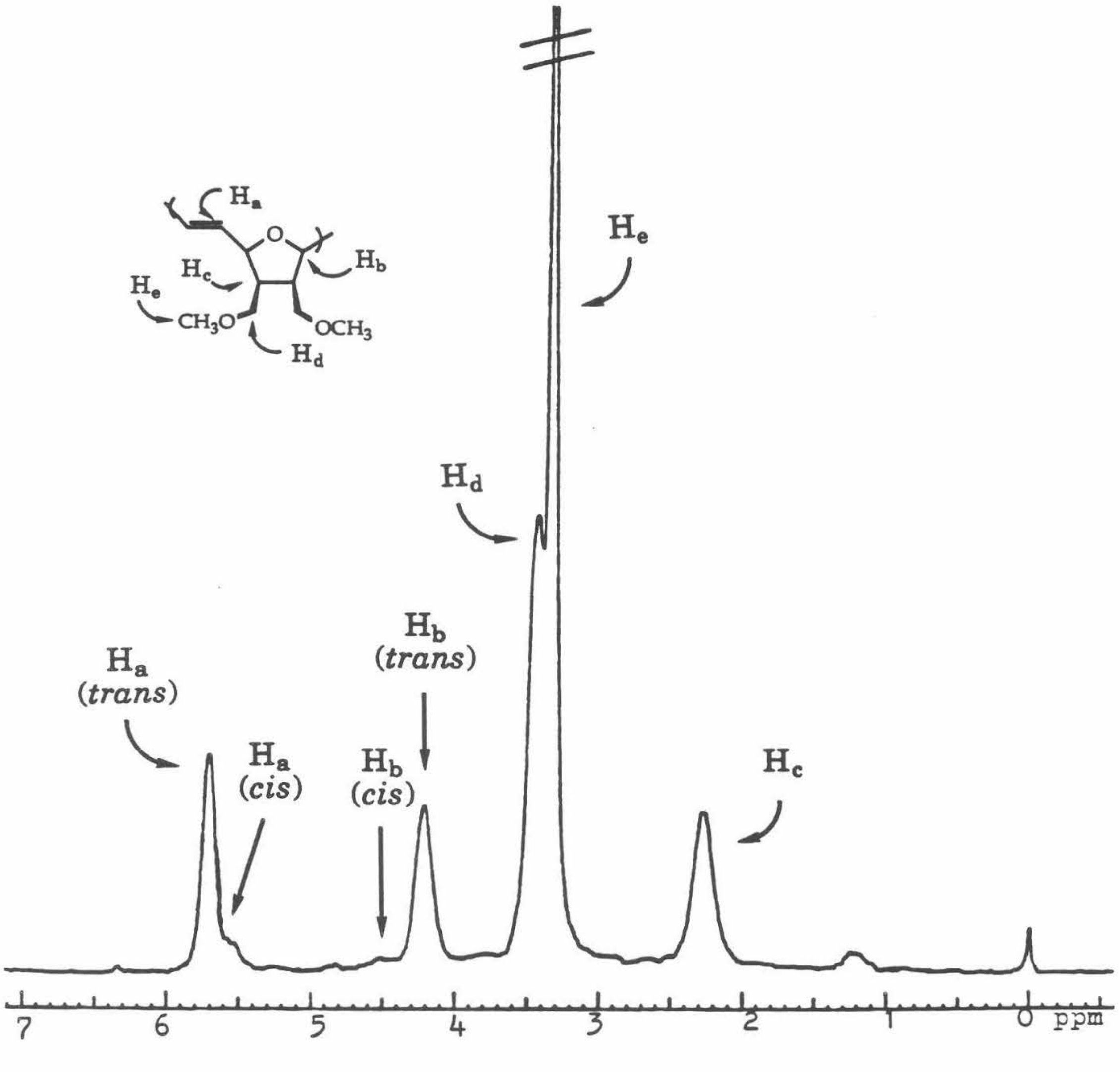


Figure 17: ^{1}H NMR spectra ($CDCl_3$) of Poly **VIII** obtained using $RuCl_3$ in C_6H_6/EtOH at 55 °C. *Cis*/*trans* double bond ratio *ca.* 5/95.

trans configuration of that bond, with a *cis*-double bond giving allylic peaks approximately 5 ppm upfield from that of the *trans*-double bond.[51] The ^{13}C NMR spectra of the same three Poly **VIII** samples are shown in Figures 18, 19 and 20. The allylic carbon (labeled C_2) appears at 81.8 ppm for the *trans*-isomer and 77.3 ppm for the *cis*-isomer. The good resolution of these peaks provides the most reliable indicator of this isomeric ratio. Figure 21 contrasts the ^{13}C NMR spectra of two extreme cases: high *cis* polymer obtained using catalyst **XVI**, and high *trans* polymer obtained using $RuCl_3{\cdot}nH_2O$. Correlation of these carbon intensities back to the proton spectra (Figures 15, 16 and 17) permits olefinic and allylic proton assignments.

The *cis*/*trans* ratios calculated from this ^{13}C NMR analysis of Poly **VIII** samples, synthesized using a variety of catalysts, are shown in Table 4. As these data indicate, the *cis*-double bond content in these polymers can be adjusted from approximately 5% to greater than 95% by choice of the appropriate catalyst. The high *cis* selectivity observed using catalyst **XVI**,[36] and the high *trans* selectivity observed using the ruthenium-based systems[52] are consistent with the results obtained for the polymerization of norbornene by these same catalysts.

The olefinic carbon resonances (labeled C_1 in Figures 18, 19 and 20), are not nearly as diagnostic. Further structural information is provided by the remaining ring carbon, (C_3). This carbon appears to be sensitive to the configuration of the double bonds on either side of the ring in which it is contained. The four resonances observed for this carbon (see Figure 18) are assigned to the four possible combinations: *cis-cis* (*cc*) (48.3 ppm), *cis-trans* (*ct*) (47.9 ppm), *trans-cis* (tc) (47.5 ppm), and *trans-trans* (*tt*) (47.2 ppm).

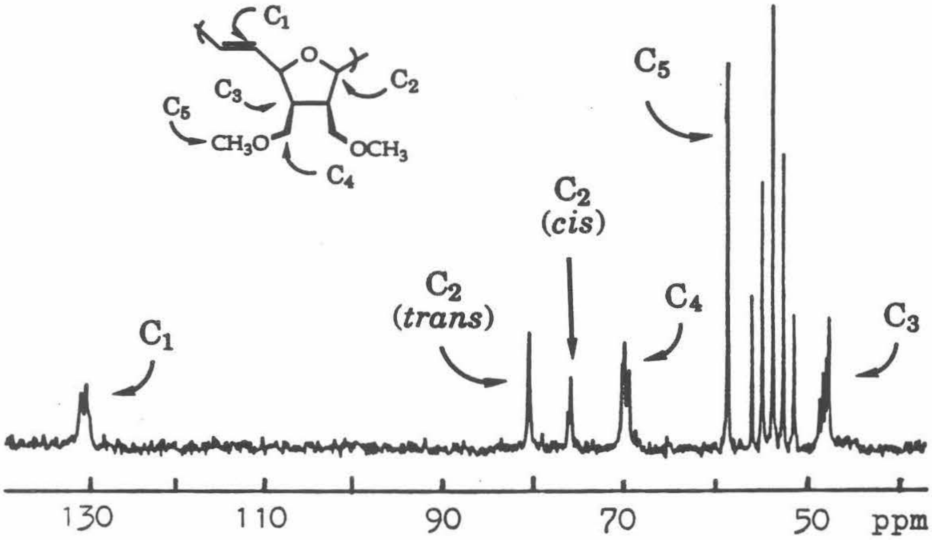


Figure 18: ^{13}C NMR spectra (CD_2Cl_2) of Poly **VIII** obtained using catalyst **XV**. *Cis/trans* double bond ratio *ca.* 42/58.

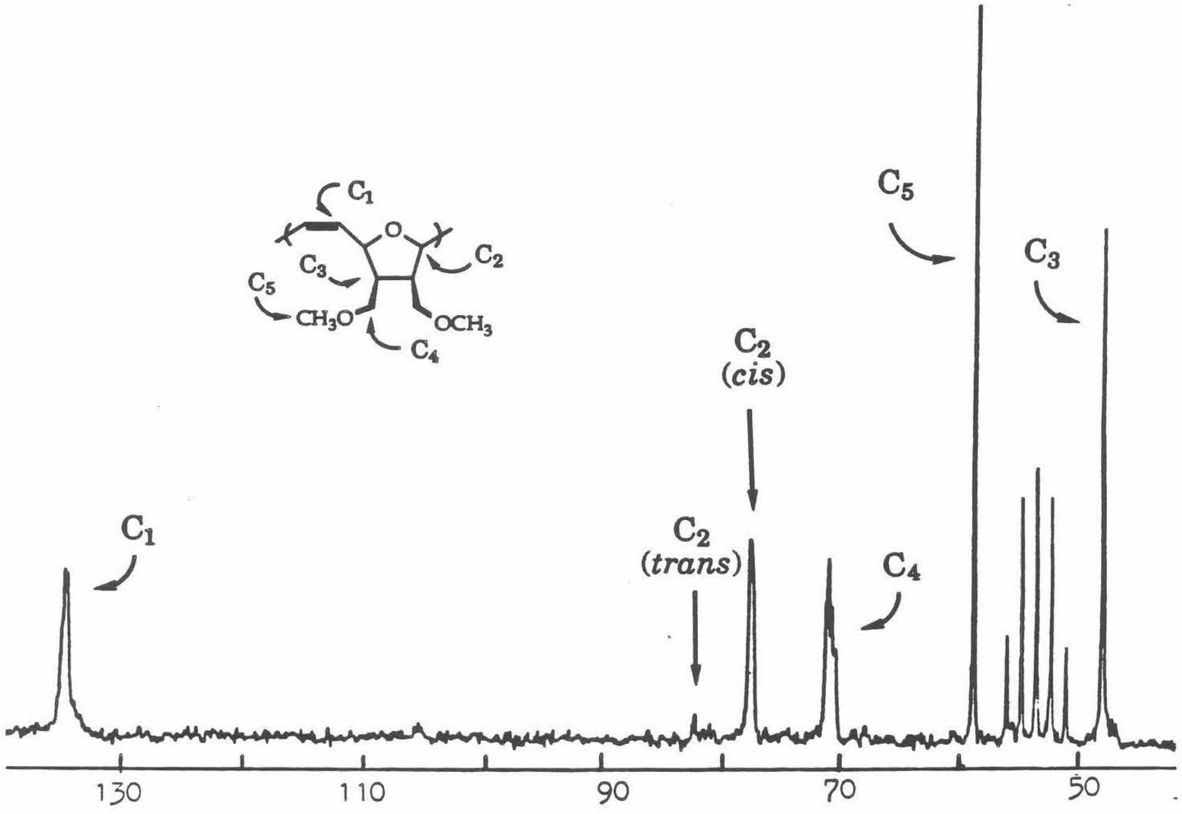


Figure 19: ^{13}C NMR spectra (CD_2Cl_2) of high *cis* Poly **VIII** obtained using catalyst **XVI**. *Cis* / *trans* double bond ratio *ca.* 95/5.

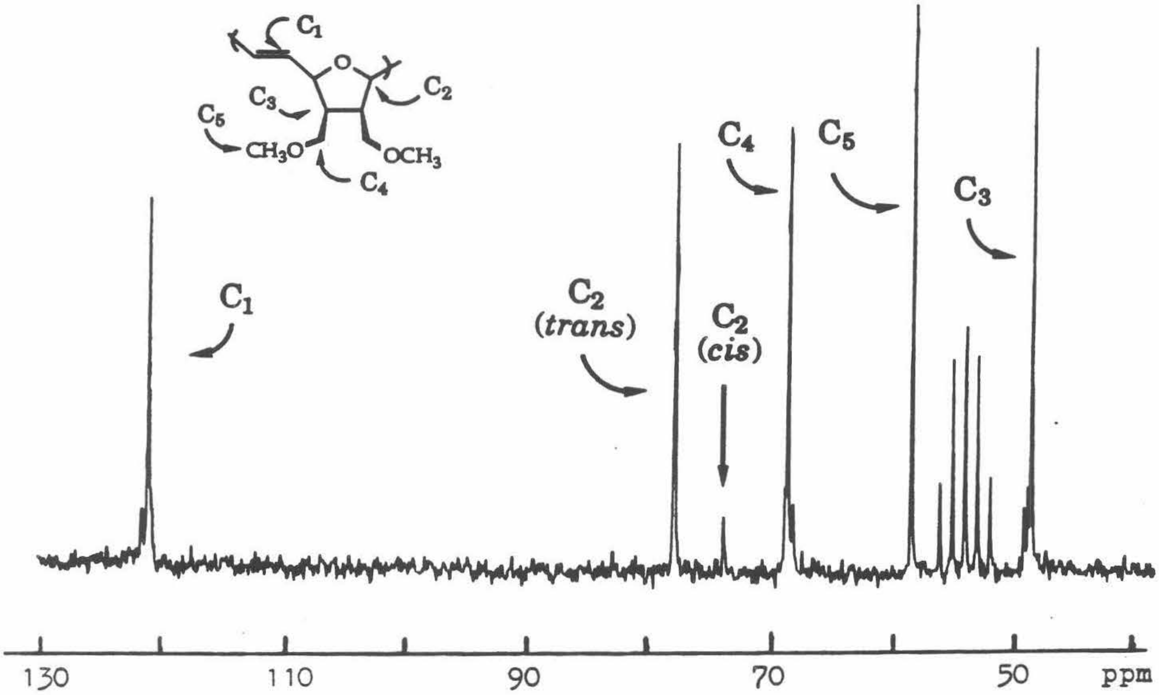


Figure 20: ^{13}C NMR spectra (CD_2Cl_2) of high *trans* Poly **VIII** obtained using $RuCl_3$ in C_6H_6/EtOH. *Cis*/*trans* double bond ratio *ca.* 5/95.

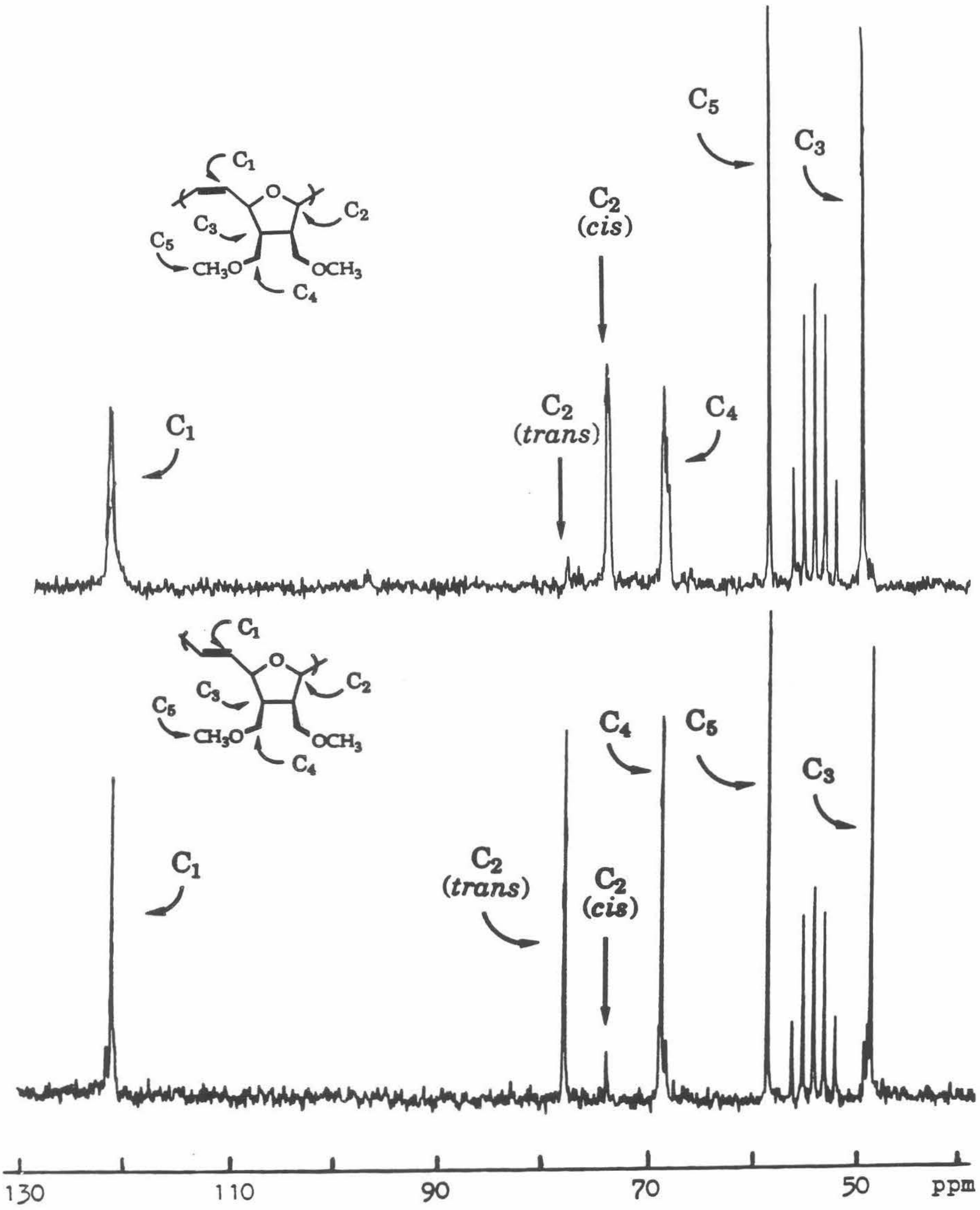


Figure 21: Comparison of ^{13}C NMR spectra (CD_2Cl_2) of high *cis* and high *trans* Poly **VIII**.

Detailed analysis of the spectra obtained from the polymers of the non-symmetrically substituted monomers is far more difficult. With the symmetrically substituted monomers, there exists the possibility of four different isomeric diads (*cis* or *trans* double bonds, either in an isotactic or syndiotactic relationship). With the non-symmetric monomers, the number of isomeric diads increases to 32. In addition to the introduction of HT and HH/TT isomers, the non-symmetric monomers obtained from the furan-acrylate Diels-Alder adducts exist as 3:1 mixtures of *endo* to *exo* isomers. As a result of these added permutations, the spectra of these polymers are correspondingly complex. For example, the ^{13}C NMR of Poly **IV** obtained using catalyst **XV** shows at least nine different resonances in the allylic carbon region of the spectrum (74 through 82 ppm).

Neither the ^{1}H nor the ^{13}C NMR spectra of the symmetrically substituted polymers (Poly **VIII** for example) appear to be sensitive to the different possible tacticities of these materials. Reduction of the double bonds with p-toluenesulfonhydrazide cleanly provides the expected saturated polymer.[53] The ^{13}C NMR spectra of these saturated polymers now reflect the presence of different isomers. Figure 22 shows the ^{13}C NMR spectra of unsaturated Poly **VIII** and the corresponding saturated polymer obtained upon reduction, Poly **VIIIs**. In the case of saturated Poly **VIIIs** (which cannot give HT, and HH/TT isomers), the only possibility for different isomers arises from differing tacticities of the diad pairs. Two types of diad pairs can exist along the polymer chain: meso (m), and racemic (r) diads. These diads, and their respective relationships to the isotactic and syndiotactic polymers, are illustrated in Scheme **X**. Note that the chirality of the adjacent allylic carbons along the chain determines whether the diads exist in a meso or racemic relationship. The chirality of these centers is fixed

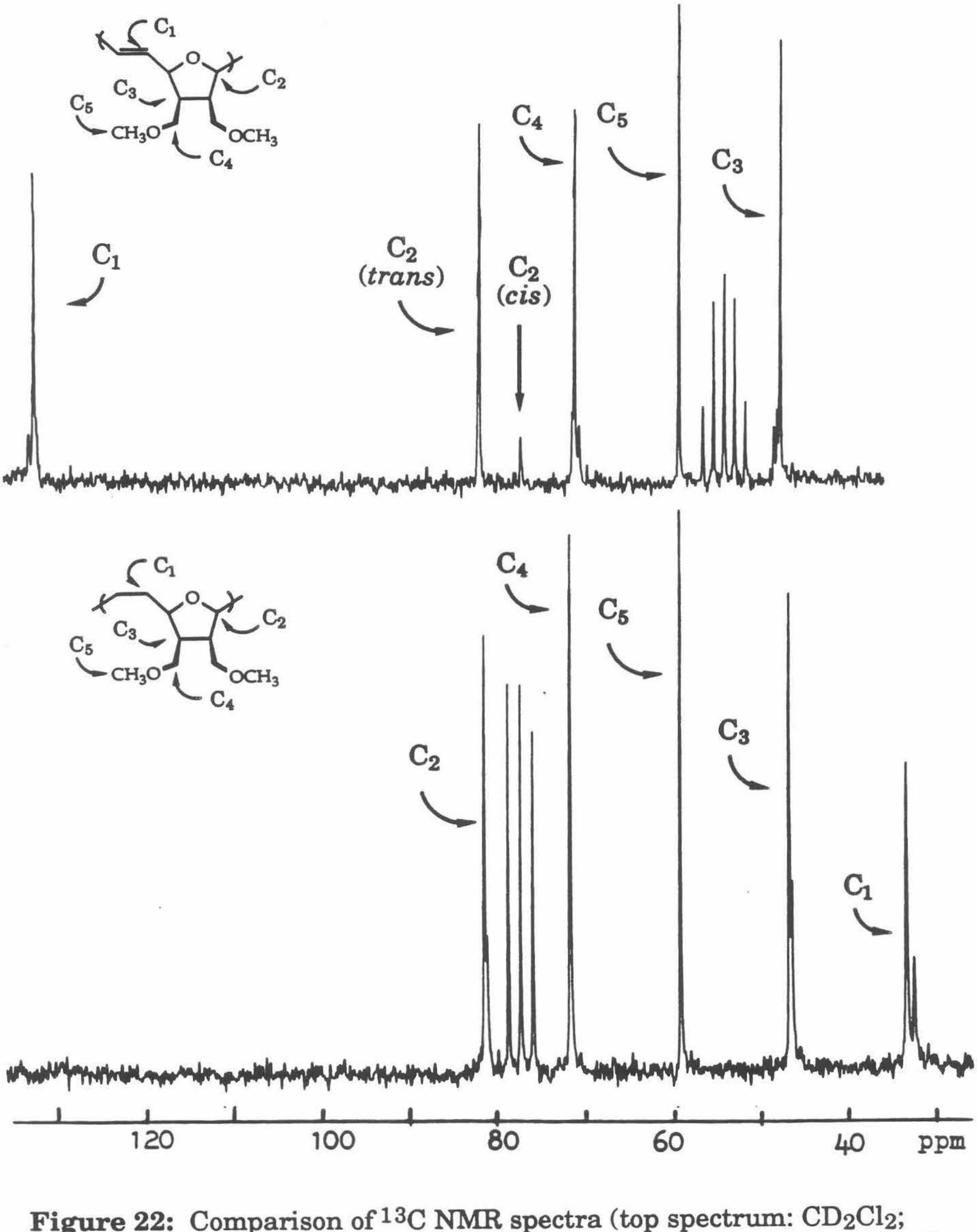
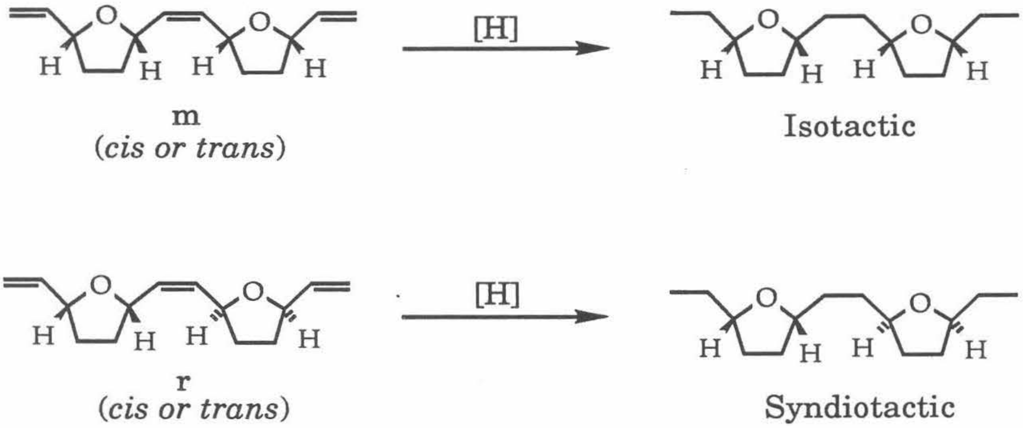


Figure 22: Comparison of ^{13}C NMR spectra (top spectrum: CD_2Cl_2; bottom spectrum: $CDCl_3$) of unsaturated (top) and saturated (bottom) poly **VIII**.

Scheme X:



before reduction of the double bonds and is not altered during this process. Therefore, the measured tacticity of the saturated polymer reflects the original tacticity of the unsaturated polymer.

Figure 23 shows the ^{13}C NMR spectra of two saturated Poly **VIII** polymers, one obtained using catalyst **XVI** and the other obtained with $RuCl_3$. Each of the carbons labeled 1, 2 and 3 appear as two sets of resonances: 32.74, 81.16 and 46.2 ppm ($CDCl_3$), and 31.90, 80.83 and 45.87 ppm ($CDCl_3$). The relative intensity of these two sets of resonances is observed to vary, depending on the catalyst initially used in the polymerization. Given that no other isomeric forms can exist for Poly **VIIIs**, these two sets of resonances are assigned as the isotactic and syndiotactic ring diads. The polymer obtained using $RuCl_3$ as a catalyst shows a 72% predominance of one type of diad over the other. In contrast, the polymer obtained using **XVI** appears to be almost atactic, i.e., approximately equal numbers of r and m diads, 45% and 55%. Given only this information, the unambiguious assignment of these two sets of resonances to either the r diad (syndiotactic polymer) or the m diad (isotactic polymer) is not possible. In order to make these assignments, the relationship between HT and HH/TT isomers, and the known r and m diads that exist for polymers composed of resolved, asymmetric monomers, is enlisted. If a polymer is composed of resolved, chiral monomers, then an HT ring sequence corresponds to an isotactic diad, and a HH/TT series corresponds to a syndiotactic diad.[54] This relationship is illustrated in Scheme **XI** for the polymer of resolved endo-(-)-5-methoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene, **IV***. It must be emphasized that this special relationship between substitution isomers and tacticity exists only for polymers comprised of resolved monomers.

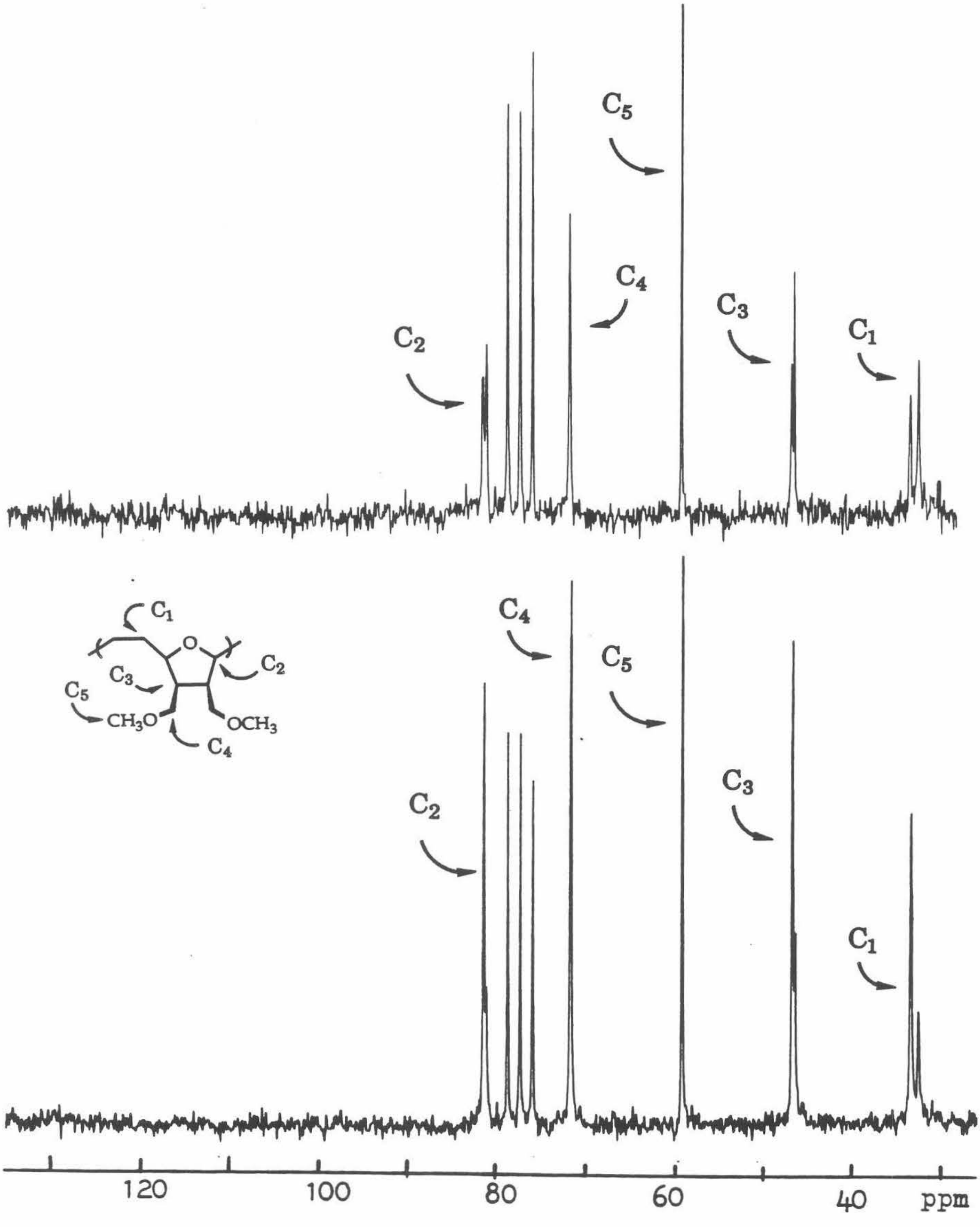
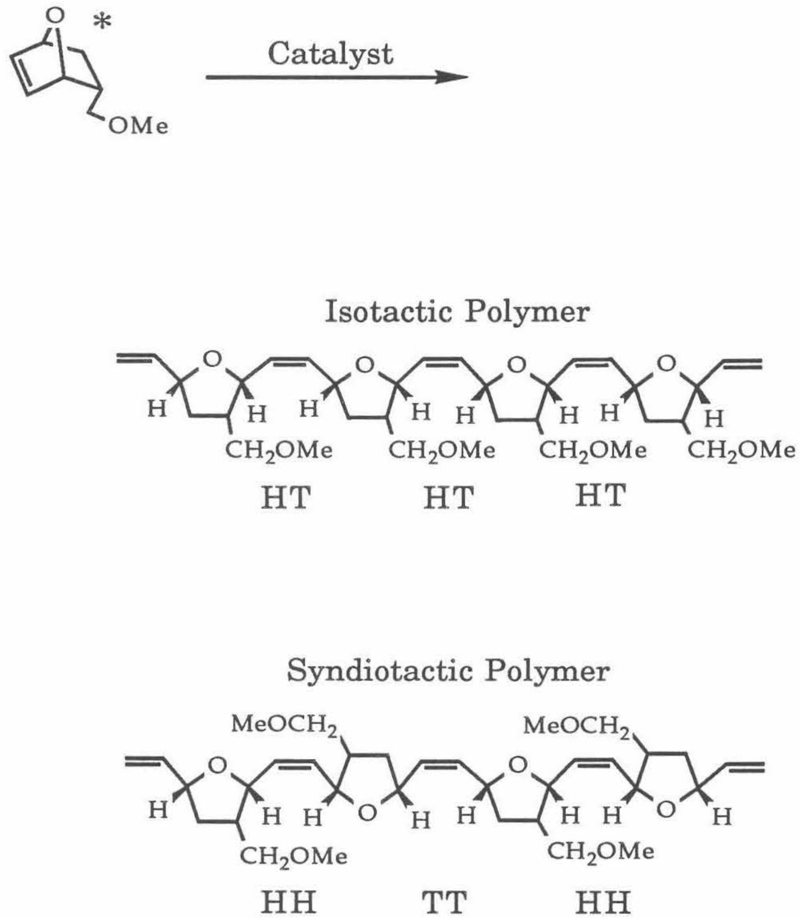


Figure 23: Comparison of ^{13}C NMR spectra of saturated poly **VIIIs** obtained using catalyst's **XVI** (top), and $RuCl_3$ (bottom).

Scheme XI:

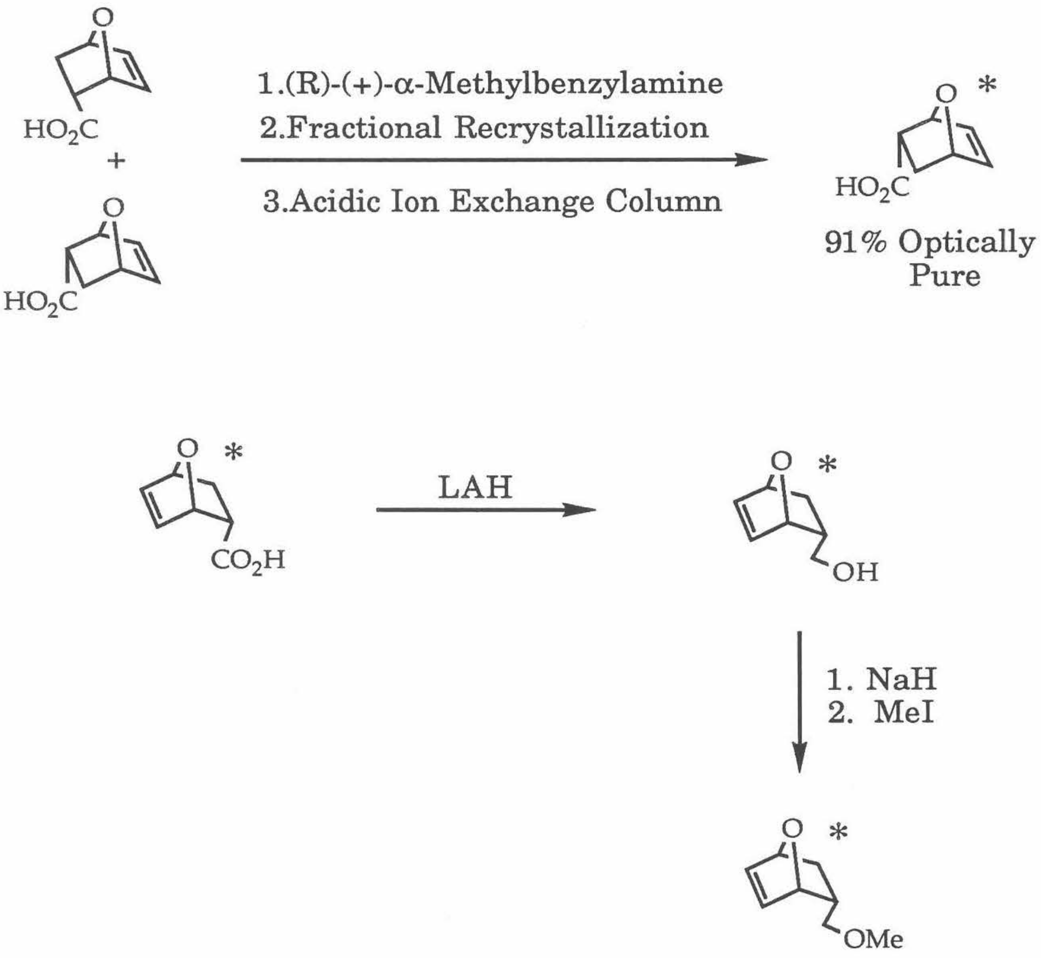


Isotactic Polymer

Syndiotactic Polymer

The resolution, and the absolute configuration of 7-oxanorbornene-2-carboxylic acid have been reported.[55] This resolution method, and further reduction to the 2-methoxymethyl deriviatve, **IV*** are illustrated in Scheme **XII**. In order to minimize the number of possible isomers, catalysts that select for either high *cis* or high *trans* polymer were employed in the polymerization of the resolved monomer. The catalyst $RuCl_3$ was chosen for its tendency to give polymers with very high *trans* content, as well as for its apparent bias towards one of the two possible tacticities, evident in the ^{13}C NMR spectra of saturated Poly **VIIIs**. Analysis of the olefinic region of the ^{13}C NMR spectrum (the most diagnostic region for this type of isomerism), then provided the HT and HH/TT isomer ratios. The exact assignment of the HT and HH/TT olefinic resonances was based on comparisons with a published spectral analysis performed on the similarly substituted poly(5-methylnorbornene).[54] Racemic Poly **IV** obtained using $RuCl_3$ shows four peaks of nearly equal intensity in the olefinic region: 133.6, 133.3, 129.8 and 129.1 ppm ($CDCl_3$). Likewise, the spectrum of the high *cis* polymer obtained using catalyst **XVI** shows four peaks: 133.7, 133.4, 129.8 and 129.1 ppm ($CDCl_3$). By analogy with poly(5-methylnorbornene), these signals may be assigned as the TH, TT, HH and HT resonances, respectively. In contrast, the spectrum of resolved Poly **IV*** obtained using $RuCl_3$ shows a 4:1 ratio of the TH and HT signals over the TT and HH signals. In the chiral polymer, the HT and TH resonances correspond to the isotactic ring diads. From this information, the dominant set of resonances observed at 81.16, 46.20 and 32.74 ppm in the ^{13}C NMR spectrum of Poly **VIIIs** obtained using $RuCl_3$ can be assigned as the isotactic ring diads. The second set of resonances, appearing at 80.83, 45.87 and 31.90 ppm are assigned to the syndiotactic diads. This assignment,

Scheme XII:


O
HO$_2$C
+
O
HO$_2$C
1.(R)-(+)-α-Methylbenzylamine
2.Fractional Recrystallization
3.Acidic Ion Exchange Column
O *
HO$_2$C
91% Optically Pure
O *
CO$_2$H
LAH
O *
OH
1. NaH
2. MeI
O *
OMe

which associates the high *trans*-selective ruthenium catalysts with formation of the isotactic diads, is consistent with the polymerization literature of substituted norbornene derivatives.[54] Table 4 details some of the tacticity data of Poly **VIII** obtained using several different catalysts. It can be concluded from these data that the existing catalysts tend to give poly(7-oxanorbornene) materials that are nearly atactic, with a slight bias towards isotactic materials in the case of the ruthenium catalysts.

Studies directed at the regiochemistry of monomer addition to the carbene, as well as the subsequent decomposition of the metallacycle to a new carbene, provide some insights into the origins of the observed stereochemistry. Scheme **XIII** illustrates this process for the formation of both a *cis*- and a *trans*-double bond, upon cleavage of the intermediate metallacycle. This scheme is based on the hypothesis that formation of a *cis*- or a *trans*-double bond is wholly determined by the relative orientation of the incoming olefin to the polymer chain on the active metal carbene. This model assumes that none of the metallacycle bonds undergo rotation during either the bond-forming or bond-breaking steps.

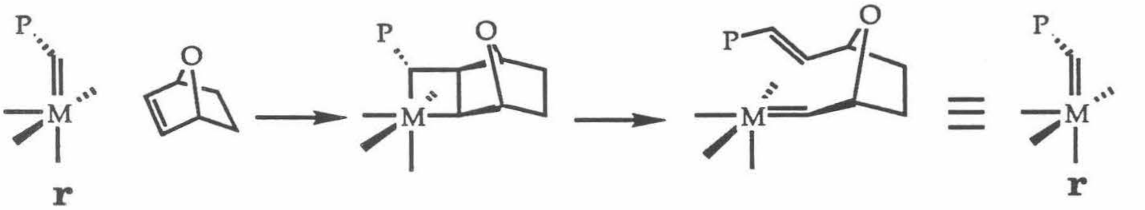
The tacticity of the polymer is dictated by the particular side of the carbene with which the incoming olefin reacts. If the olefin adds to the same side of the carbene as the previous monomer unit, an isotactic diad is produced. If the monomer adds to the opposite side relative to the last added monomer, then a syndiotactic diad is formed. This π-facial selectivity is, however, ultimately going to be determined by the side of the carbene that affords the open coordination site on the metal. Notice that formation of a *cis*- or a *trans*-double bond constitutes two different stereochemical pathways with respect to the location of the new, vacant coordination site relative to the last one (Scheme **XIII**). Following

Catalyst	% Cis Double Bonds	Diad Tacticity (r/m)
XVI	95	55/45
$K_2RuO_3(OH)_2 \cdot 18$-Crown-6	62	-
Ru Red[a]	44	-
XV	42	-
Ru(TFA)[b]	34	-
$RuCl_3$(EtOH)	34	-
$OsCl_3$ (C_6H_6/EtOH)	30	-
Ru(COD)[c]	18	50/50
$RuCl_3$(C_6H_6/EtOH)(75 °C)	12	-
$RuCl_3$(C_6H_6/EtOH)(50 °C)	3	28/72
$RuHCl(PPh_3)_3$	2	-

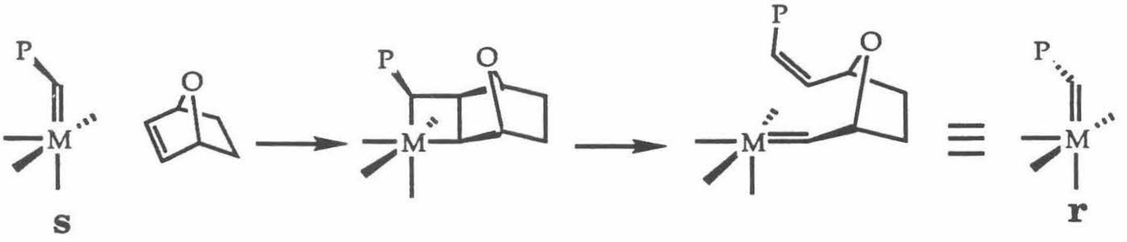
Table 4: The *cis* double-bond content and ring diad tacticity of Poly **VIII** obtained using several catalysts. Notes: a) Ru Red: $[Ru(NH_3)_5ORu(NH_3)_4ORu(NH_3)_5]Cl_6$; b) Ru(TFA) is an ill-defined compound with the approximate composition: $Ru_2(CF_3CO_2)_4 \cdot 3H_2O$; c) Ru(COD) is an ill-defined Ru-cyclooctadiene complex with an average oxidation state near Ru^{2+}.

Scheme XIII:

Trans- Addition of the Cyclic Olefin



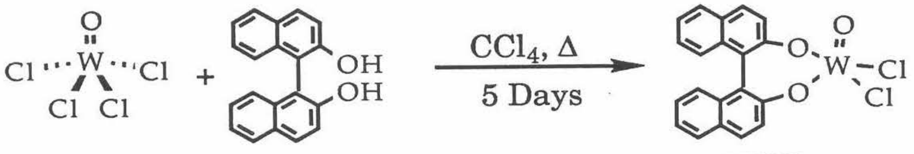
Cis- Addition of the Cyclic Olefin



P = Polymer Chain

decomposition of the metallacycle to produce a *cis*-double bond, the *enantiomer* of the original carbene is formed (i.e., the new coordination site is now on the opposite side of the carbene); when decomposition occurs to produce a *trans*-double bond, the original carbene is reinstated (i.e., the new coordination site is on the same side of the carbene). From this analysis, it follows that polymers with a high *cis* content should be syndiotactic, and polymers with a high *trans* content should be isotactic. It must be emphasized that this scheme represents only the extreme, idealized case. Any rotation of the carbene ligand, or reorganization of the ligands on the metal center, will serve to racemize these intermediates. If the rate of polymerization is fast relative to the rate of ligand reorganization, then this *cis*/syndiotactic and *trans*/isotactic correspondence will be expected. If, however, these two rates become more competitive, or if the mechanism changes (for example, prior coordination of the incoming olefin before the metallacycle undergoes the retro [2+2] cycloaddition), then this stereochemical scheme will break down. The connection between *cis*/*trans* double-bond formation and tacticity has been studied in detail.[56] Examination of the literature reveals that when a relationship does exist between *cis* and *trans* isomers of the double bonds and tacticity of the polymer, without exception, high *cis* polymers tend to be syndiotactic and high *trans* polymers tend to be isotactic.

One attractive approach to the synthesis of stereoregular ROMP materials lies in the development of catalysts containing chiral ligands. By the appropriate choice of chiral ligand, the two sides of the carbene could be rendered inequivalent, irrespective of the rate of ligand reorganization. This inequivalence should bias the process to select for reaction with one side of the carbene over the other, resulting in the formation of highly isotactic polymer. As a test of this hypothesis, a 1,1'-binaphthol derivative of $WOCl_4$ was synthesized, **XVII** (Equation 35).



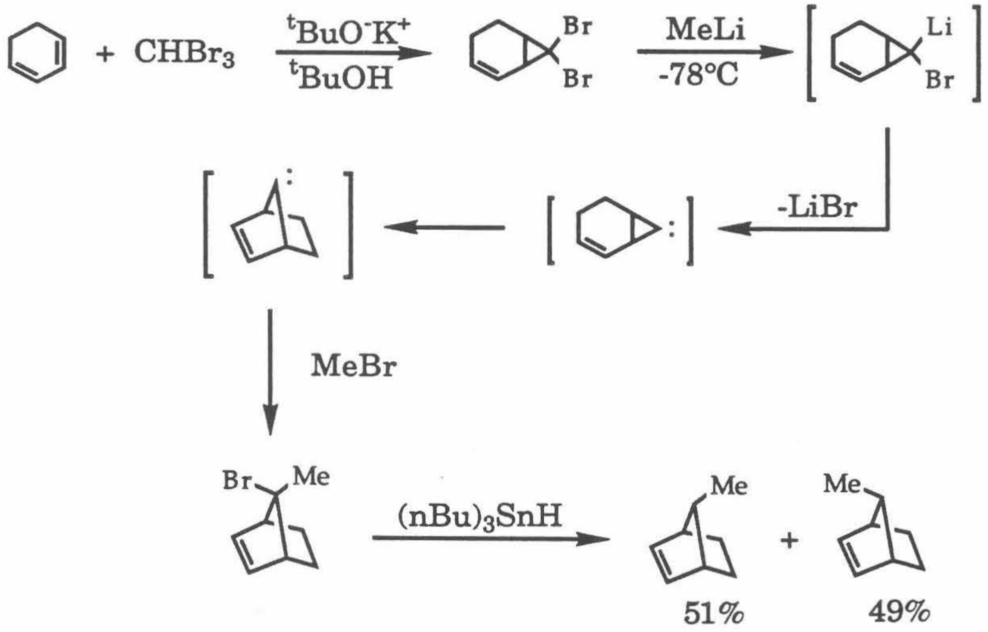
(35)

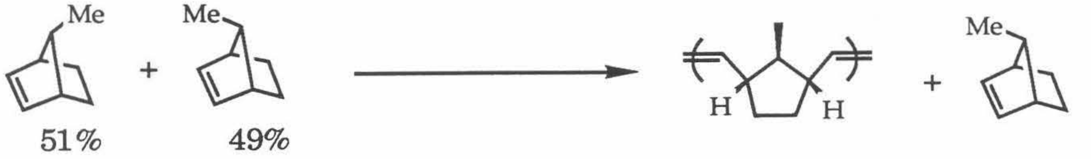
XVII

Although W(VI) catalysts have been shown to be inactive with the 7-oxanorbornene monomers, stereochemical induction by the 1,1'-binaphthol ligands can be conviently tested with norbornene derivatives such as *anti*-7-methylnorbornene. This monomer is particularly suitable in that the ^{13}C NMR spectrum of its unsaturated polymer is sensitive to polymer tacticity, thereby eliminating the need for reduction of the polymer prior to structural characterization. Following literature procedures, a 51/49 mixture of anti/syn-7-methylnorbornene was synthesized as shown in Scheme **XIV**.[57]

As with other classical W(VI) catalysts, **XVII** requires a cocatalyst, such as $Sn(CH_3)_4$. Not surprisingly, in preliminary tests using norbornene, **XVII**/$Sn(CH_3)_4$ (1:3) proved to be far less reactive than $WOCl_4/Sn(CH_3)_4$. The unsubstituted catalyst is known to polymerize norbornene rapidly below room temperature.[58] In contrast, the **XVII** system consumed less than 5% of the norbornene after 15 minutes at +40 °C. Temperatures near +50 °C were required in order to achieve a rapid rate of polymerization (*ca.* 50% conversion in 5 minutes). When 16 equivalents of the 51/49 mixture of anti/syn 7-methylnorbornene were allowed to react with **XVII**/$Sn(CH_3)_4$ (1/3), the anti-isomer was observed to polymerize slowly at 50 °C (87% conversion (anti-isomer) after 70 minutes) (Equation 36).

Scheme XIV:


+ CHBr3
tBuO-K+
tBuOH
Br
Br
MeLi
-78°C
Li
Br
-LiBr
MeBr
Br
Me
(nBu)3SnH
Me
+
Me
51%
49%



(36)

In a control experiment using $WOCl_4/Sn(CH_3)_4$, the syn-isomer was again observed to be inactive, while the anti-isomer was completely consumed in approximately 1 minute at 50 °C. Surprisingly, the ^{13}C NMR spectra of the poly(7-methylnorbornene) obtained from these two reactions showed only slight differences. The polymer obtained from the $WOCl_4$ reaction was measured to be 60% *trans*, while the **XVII** system gave a 47% *trans* polymer. From a detailed analysis of the fine structure, however, the tacticity of these two polymers appeared to be nearly identical. The *trans*-junctions in the $WOCl_4$ polymer appear to be atactic, as evidenced by resonances of equal intensity at 51.53 and 51.33 ppm, corresponding to the allylic carbons of a *trans*-double bond, existing in an isotactic and syndiotactic relationship, respectively. On the other hand, the *trans*-junctions in the **XVII** polymer appear to exert about a 10% bias towards the isotactic diads. The *cis*-junctions in both the $WOCl_4$ and **XVII** polymers appear to be highly syndiotactic. Clearly, little, if any, tacticity induction occurs by using the binaphthol ligand in this system. The explanation for this result remains unknown. It is possible that the binaphthol ligand does not lend significant steric bias to the reaction, or that the carbene lies along the pseudo C_2 rotation axis, making each face of the carbene effectively equivalent. An alternative (and simple) explanation might be that the true, active catalytic species in these reaction mixtures do not involve the binaphthol ligand. This type of complication is indicative of "classical" metathesis systems in which only a small fraction of the metal centers is actually activated. All efforts to convert **XVII** to a neopentylidene species similar to catalyst **XV** have failed. Problems arise in trying to alkylate **XVII** with neopentyl Grignard reagents. The binaphthol complex does not react with the Grigard reagents, even under conditions in which other, sterically hindered tungsten alkoxide complexes such as (2,6-diphenylphenoxy)$_2$WCl$_4$, react readily.[59] The inert nature of **XVII** towards alkylating agents, a necessary first step for carbene formation,[1] lends credence to the notion that the reactive polymerization species do not contain the binaphthol moiety.

CONCLUSION

The ring-opening metathesis polymerization of several 7-oxanorbornene derivatives has been reported using a number of catalysts. The catalysts investigated range from preformed early metal metallacyclobutane and carbene complexes to classical Group VIII ruthenium and osmium complexes.

In general, the early transition metal catalysts tend to become deactivated over the course of the polymerization, resulting in low yields of low molecular weight materials. Furthermore, the polydispersities of these materials are broad. Coordination of the monomer through the 1,4-bridging epoxide was observed using $WOCl_4$ and the carbene catalyst, **XV**. With $WOCl_4$, subsequent decomposition, which is thought to be the cationic opening of the 1,4-bridging epoxide, is observed. The utility of early metal catalysts for these functionalized monomers is limited. Under certain conditions, it may be possible to obtain living polymerizations of some of these monomers using less Lewis acidic versions of **XVI**, possessing *t*-butoxy ligands, rather than the hexafluoro-*t*-butoxy ligands used in this study.

In the case of the less oxophilic ruthenium and osmium complexes, good yields of the desired ROMP polymer are obtained. No indications of side reactions leading to catalyst deactivation are observed in these late metal systems. The tolerance which these ruthenium catalysts display towards polar substituents allows for the incorporation of a number of fuctional groups within the polymer structure. The versatility of this feature is illustrated by the facial polymerization of **XI**, and its subsequent modification to both a fully conjugated polymer, and a fully saturated, water-soluble, poly diacid material.

The unreactive nature of the ruthenium-based catalysts towards acyclic double bonds and polar functional groups makes them interesting candidates for future studies. An important future issue to address will be that of accelerating the initiation steps in these systems. Some preliminary work in this area is presented in Chapter 4.

Structural characterization of these materials was accomplished using ^1H and ^{13}C NMR. The ^1H and ^{13}C NMR spectra of the unsaturated polymers were sensitive to the *cis/trans* configuration of the double bond. No fine structure indicating the polymer tacticity could be observed in these spectra. The assignment of the diad tacticities in these polymers required hydrogenation of the polymer to the fully saturated material. The ^{13}C NMR spectra of these saturated polymers consisted of two sets of resonances arising from to the isotactic and syndiotactic ring diads. Exact assignment of the diad pairs as either syndiotactic or isotactic diads, required the synthesis and polymerization of a chiral monomer. Using the relationship that exists between the HT and HH/TT isomeric forms and the diad tacticity of a chiral polymer, the tacticities of the 7-oxanorbornene polymers were determined. Using the present stable of catalysts, the cis-double bond content in these polymers can be varied from over 95%, down to less than 5%. Similar control over the tacticity is yet to be realized. For specific applications in which the microstructure of the polymer is paramount (ionophoric applications, for example), the issue of control over tacticity must be addressed. Preliminary attempts at controlling the polymer tacticity by designing catalysts with chiral ligands have not proven fruitful. Attempts at more sophisticated methods are in order.

EXPERIMENTAL

General Procedures

All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemlog) and Linde 4A molecular sieves. All weighing of air- and/or moisture-sensitive compounds was performed in a Vacuum Atmosphere dry box under nitrogen. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6.MHz ^1H, 22.53 MHz ^{13}C) and a JEOL GX-400 (399.65 MHz ^1H, 100.67 MHz ^{13}C). Chemical shifts are referenced to residual protons on the deuterated solvents. Analytical gas chromatographic analysis (VPC) was performed on a Shimadzu GC-Mini 2 flame-ionization instrument modified for capillary use (Column: 0.24 mm X 15 m DBI) and equipped with a Hewlett-Packard Model 339A integrator. Infrared spectra were aquired on a Shimadzu IR-435 spectrometer. Samples were prepared by casting films on KBr windows. UV/vis spectra were acquired using a HP-8451A diode array spectrometer.

Gel permeation chromatography (GPC) was performed utilizing Shodex KF-803, 804, 805 and 805.4 columns with CH_2Cl_2 or THF as a solvent. The polymer was detected with a Spectroflow variable wavelength, absorbance detector and a Knauer differential refractometer. Samples for analysis were prepared between 0.2 -0.4% by weight in CH_2Cl_2 (or THF). The molecular weights were referenced to narrow dispersity polystyrene samples (Polysciences) ranging from MW = 3550 to 1,300,000.

Thermal analysis was performed on a Perkin Elmer DSC-7, TGS-2 thermogravimetric analyzer, and a 3600 data station. Scan rates are provided in the figures.

2-Carbomethoxy-7-oxabicyclo[2.2.1]hept-5-ene[60] and 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid[61], Tebbe reagent,[62] metallacycle **XIII**,[63] catalyst **XV**,[64] catalyst **XVI**,[65] $H_2Ru(CO)(PPh_3)_3$,[66] $HRu(CO)(PPh_3)_3(CF_3CO_2)$[67] were prepared according to published procedures. With the exception of hydroquinone (MCB Reagents), p-toluenesulfonyl chloride (EM Science), maleic anhydride (Mallinckrodt) and pyridine (JT Baker), all other organic chemicals were obtained from the Aldrich Chemical Company and, if not specified, used without further purification. $RuHCl(PPh_3)_3$, $[Ru(NH_3)_5Cl]Cl_2$, $Ru_3(CO)_{12}$, $RuCl_3{\cdot}nH_2O$ and $RuBr_3{\cdot}nH_2O$ were purchased from Strem. $RuCl_2(PPh_3)_3$, $(bipy)_2RuCl_2$ and $Ru(NO)(NO_3)_3$ were purchased from Johnson-Matthey/AESAR. $Ru(acac)_3$, and $(RuCl_2(CO)_3)_2$ were purchased from Aldrich Chemical Company. $K_2RuO_4{\cdot}H_2O$ and $K_2OsO_4{\cdot}H_2O$ were purchased from Alpha. $CDCl_3$ was stored over 4A molecular sieves. CH_2Cl_2 was dried over P_2O_5 and degassed on a vacuum line. Pentane was stirred over sulfuric acid, dried over calcium hydride, and vacuum-transferred from sodium benzophenone ketyl. Benzene, THF, diethyl ether, and toluene were vacuum-transferred from sodium benzophenone ketyl.

Synthesis of Exo-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride (VI). Maleic anhydride (78.8 g, 0.803 mol) was dissolved in diethyl ether (600 ml). To this solution, furan (54.7 g, 0.803 mol) was added and the resulting clear solution allowed to stir for three days, during which time the white crystalline product precipitated from solution. The precipitate was isolated by filtration, washed with cold diethyl ether and dried to yield the desired *product (101 g, 75.5%).* ^{1}H NMR ($CDCl_3$, 90 MHz) 6.55 (1 H, s), 5.43 (1 H, s), 3.19 (1 H, s) ppm.

Synthesis of Exo-7-Oxabicyclo[2.2.1]hept-2-ene-5,6-dicarbinol (VII). A 500 ml, 3-neck flask was equipped with a pressure-equalizing dropping funnel, a water-cooled reflux condenser and an overhead stirrer. The reaction vessel is charged with LAH (2.8 g, 0.074 mol) in dry THF. Anhydride **VI** (10 g, 0.060 mol) dissolved in dry THF (120 ml) is placed in the dropping funnel and added dropwise to the LAH suspension. The solution is then allowed to stir overnight. Water (3 ml), NaOH (3 ml, 15% solution), and water (9 ml) are then added slowly in sequence. The resulting white precipitate is filtered. The filtrate is concentrated (rotor-evaporated) and added to the white precipitate. This residue is placed in a Soxhlet extraction apparatus and extracted with methylene chloride for 2 days. The CH_2Cl_2 is removed (rotor-evaporated) and the remaining viscous oil dried in vacuum to yield the desired product (9.5 g, 100%). The diol obtained here can be used as is for most synthetic purposes. Further purification can be accomplished using a Kugelrohr apparatus (B.P. 120-125 °C at 0.001 torr). ^{1}H NMR ($CDCl_3$, 90 MHz) 6.42 (1 H, s), 4.69 (1 H, s), 4.06 (1 H, bs), 3.78 (2 H, m), 1.93 (1 H, m) ppm.

Synthesis of Exo-5,6-dimethoxymethyl-7-Oxabicyclo[2.2.1]hept-2-ene (VIII). A 500 ml, 3-neck flask is equipped with a pressure-equalizing dropping funnel, a water-cooled reflux condenser and a magnetic stir bar. The reaction vessel is charged with NaH (10.68 g, 0.445 mol) in dry THF (250 ml). Diol **VII** (27.8 g, 0.178 mol) is dissolved in dry THF (50 ml) and added dropwise through the dropping funnel. After complete addition of the diol, the solution was stirred for an additional half-hour to insure complete reaction.

CH_3I *(101.1* g, 0.712 mol) is then added slowly through the dropping funnel. After complete addition of the CH_3I, water is added dropwise until no further bubbling occurs. The reaction solution is then poured into diethyl ether (500 ml) and filtered. The solvent is removed at reduced pressure to yield the desired product as a clear liquid (28.0 g, 85.6%). Further purification can be accomplished using a Kugelrohr apparatus (B.P. 60-65 °C at 0.001 torr). Dry VIII is obtained by vacuum distilling (Kugelrohr apparatus) off NaH. ^1H NMR ($CDCl_3$, 90 MHz) 6.33 (1 H, s), 4.30 (1 H, s), 3.43 (2 H, m), 3.30 (3 H, s), 1.90 (1 H, s) ppm. ^{13}C NMR (Proton Decoupled) ($CDCl_3$, 22.53 MHz) 135.2, 80.18, 71.8, 58.4, 39.6 ppm. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.21; H, 8.75. Found: C, 64.82; H, 8.51.

Synthesis of Exo-5,6-Bis(Methyltrimethylsilyl)-7-Oxabicyclo[2.2.1]hept-2-ene (IX). Diol **VII** (2.3 g, 0.0147 mol) is dissolved in dry THF (25 ml). The resulting solution is then cooled to 0 °C. n-Butyl lithium (21.0 ml, 0.0336 mol, 1.6 M solution in hexane) is added slowly. After stirring 10-15 minutes at 0 °C, $(CH_3)_3SiCl$ (4.28 g, 0.0394 mol) is added via syringe. The reaction mixture is allowed to stir for 2 hours after which it is filtered through celite and the solvent evaporated under reduced pressure. The resulting yellow solution is taken up in pentane (25 ml) and again filtered. The pentane is removed under reduced pressure leaving approximately 4 ml of a yellow liquid. This liquid containing the impure product is purified using a Kugelrohr apparatus (B.P. 100-110 °C at 0.001 torr). Obtained 2.80 g (63.4%) of the desired product. ^1H NMR ($CDCl_3$, 90 MHz) 6.34 (1 H, s), 4.80 (1H, s), 3.73 (1 H, m), 3.49 (1 H, m), 2.40 (1 H, m), 0.12 (9 H, s) ppm.

Synthesis of 7-Oxabicyclo[2.2.1]hept-2-ene-5-carbinol (III). A 500 ml, 3-neck flask is equipped with a pressure-equalizing dropping funnel, a water-cooled reflux condenser and a magnetic stir bar. The reaction vessel is charged with LAH (2.0 g, 0.05 mol) in dry THF (200 ml). The methyl ester **I** (5.0 g, 0.03 mol) is dissolved in dry THF (50 ml) and added dropwise through the dropping funnel. The reaction is stirred overnight at room temperature. Water (2 ml), NaOH (2 ml, 15% solution) and water (6 ml) are added in sequence. The resulting white precipitate filtered and the filtrate concentrated under reduced pressure. The resulting residue is added to the white precipitate and the entire mass is extracted with CH_2Cl_2 for 24 hours. The CH_2Cl_2 is then removed under reduced pressure to yield the desired alcohol as a clear liquid (4.0 g, 100%). The alcohol obtained here can be used without further purification.

Synthesis of Endo/Exo-5-Methylmethoxy-7-Oxabicyclo[2.2.1]hept-2-ene (IV). This compound is synthesized in the same manner as the dimethoxymethyl derivative **VIII** presented above. Carbinol **III** (13.2 g, 0.105 mol) is reacted with NaH (3.8 g, 0.157 mol) and CH_3I (14.85 g, 0.105 mol) to yield 12.4 g (67.3%) of the desired product. (B.P. 60-65 °C at 0.001 torr). ^1H NMR ($CDCl_3$, 90 MHz) 6.25 (m), 4.87 (m), 3.32 (s), 3.25 (s), 2.85 (m), 2.45 (m), 1.90 (m), 1.22 (m), 0.68 (m) ppm. ^{13}C NMR (Proton decoupled) (C_6D_6, 22.53 MHz) 136.4, 135.9, 135.1, 132.6, 79.6, 79.5, 78.2, 77.7, 76.0, 75.5, 58.4, 38.4, 28.4 ppm.

Synthesis of 2,3-Dimethyl-7-Oxabicyclo[2.2.1]heptadiene Dicarboxylate (XI). Furan (9.6 g, 0.14 mol) is stirred with dimethylacetylene dicarboxylate (20.0 g, 0.14 mol) for two weeks to afford a near quantitative yield of the desired Diels-Alder adduct. The resulting adduct is purified using a flash chromatography column (silica gel, 40 µm, 14 cm X 5 cm), using 10% ethyl acetate/benzene as the eluent. Crude **XI** (10 g) was chromatographed using the above conditions providing 9.2 g of pure **XI** (92% isolated yield). ^{1}H NMR ($CDCl_3$, 90 MHz) 7.23 (1 H, s), 5.68 (1 H, s), 3.81 (3 H, s) ppm. ^{13}C NMR ($CDCl_3$, 22.53 MHz) 163.1, 152.9, 143.1, 84.9, 53.2 ppm. BP 100-105 °C at 0.001 torr.

Synthesis of 7-Oxabicyclo[2.2.1]hept-2-ene-5-carbinol Tosylate Ester. Carbinol **III** (7.95 g, 0.063 mol) was dissolved in dry pyridine (20 ml) and tosyl chloride (20.0 g, 0.0714 mol) is added and the reaction mixture was allowed to stir for two hours. The resulting mixture was then poured over ice (200 g) and allowed to stir for an additional hour. The aqueous solution was then extracted with CH_2Cl_2. The organic fraction was sucessively washed with water, 5% HCl, and 5% $NaHCO_3$, then evaporated under reduced pressure to yield the desired product as a yellow oil. The tosylate derivative obtained here was used without further purification.

Synthesis of 5-Methyl-7-Oxabicyclo[2.2.1]hept-5-ene (V). A 500 ml, 3-neck flask was equipped with a pressure-equalizing dropping funnel, a water-cooled reflux condenser and a magnetic stir bar. The reaction vessel was charged with LAH (3.5 g) in dry ether (100 ml). The tosylate ester (from above) (27.0 g, 0.987 mol) dissolved in dry ether (100 ml) was added slowly through the dropping funnel. After addition was complete, the resulting solution was refluxed for three hours. After cooling the reaction solution, water (4 ml), NaOH (4 ml, 15% solution) and water (12 ml) were added in sequence. The precipitate obtained was filtered and the filtrate concentrated under reduced pressure. The remaining liquid (approximately 20 ml) was passed through a column containing Alumina (Nutral, I), using pet ether as the eluent. The pet ether was distilled off and the remaining liquid washed with 5% $NaHCO_3$, and dried over Na_2SO_4. The liquid was then distilled and the product fraction boiling at 125-130 °C was collected (4.27 g, 40%). ^1H NMR ($CDCl_3$, 90 MHz) 6.30 (2 H, m), 4.74 (2 H, m), 2.05 (2 H, m), 1.12 (3 H, d (J=8.9 Hz)), 0.82 (3 H, d (J=8.9 Hz)), 0.65 (1 H, m) ppm.

Reaction of $WOCl_4$ and VIII. $WOCl_4$ (51.0 mg, 0.149 mmol) is dissolved in C_6D_5Cl and $Sn(CH_3)_4$ (26.7 mg, 0.149 mmol) is added via syringe. The resulting mixture is allowed to react for 10 minutes at room temperature, during which time the solution's color changes from orange to brown. **VIII** (27.5 mg, 0.149 mmol) is then added via syringe, and the resulting solution is monitored using ^1H NMR.

Metallacycle XIV. The metallacycles formed from the 7-oxanorbornene derivatives are all synthesized in a similar manner. A representative procedure is presented here. Metallacycle **XIII** (0.390 g, 1.57 mmol) is placed in a cold Schlenk tube under argon. Compound **VIII** (0.347 g, 1.88 mmol) is dissolved in benzene (15 ml) and added to the metallacycle via cannula. The reaction mixture is kept at 5 °C for 20 minutes, then allowed to warm to room temperature over the course of one hour. The solvent is then removed under reduced pressure. The resulting residue is washed with cold pentane (10 ml), then recrystallized from diethyl ether (20 ml) at -50 °C. The resulting red crystals are isolated and dried under vacuum to yield the desired product (0.331 g, 56%). ^1H NMR (90 MHz, C6D6) 5.68 (5H, s, Cp1), 5.23 (5H, s, Cp2), 4.50 (1H, s, bridgehead), 4.15 (1H, s, bridgehead), 3.40 (2H, m, α-H), 3.31 (4H, m, CH_2OCH_3), 3.21 (3H, s, CH_2OCH_3), 3.12 (3H, s, *CH_2OCH_3*), 3.0 (1H, m, α-H), 2.20 (2H, m, *endo*-*CH*CH_2OCH_3), 0.22 (1H, m, β-H) ppm.

Polymerizations Using Metallacycle XIV. All manipulations are carried out under dry, inert atmosphere. Metallacycle **XIV** (20 mg, 0.0810 mmol) is dissolved in 1.0 ml benzene. Monomer **V** (271.0 mg, 2.46 mmol) dissolved in 1.0 ml benzene is added to the catalyst solution via cannula. Octane (0.02 ml) is added (via syringe) as an internal standard. The resulting reaction mixture is then heated to 65 °C. Progress is monitored for 24 hours by periodically removing aliquots for capilary GC analysis. After completion of the reaction, 1.0 ml acetone is added to reaction mixture, and the product polymer precipitated by cannulating into methanol.

Polymerizations Using Catalyst XV. The 7-oxanorbornene derivatives are all polymerized using the same generalized procedure. A representative reaction is presented here. All manipulations were performed under dry, inert atmosphere. Catalyst **XV** (0.87 mg, 0.148 mmol) is dissolved in benzene (1.0 ml). To this solution, olefin **VIII** (0.681 mg, 3.7 mmol, 25 eq) dissolved in benzene (1.0 ml) is added slowly via cannula. Solution turns from yellow to blue-green over the first four hours. After 24 hours, methanol (1 ml) is added to the reaction, and the resulting solution cannulated into 50 ml pentane. The polymeric precipitate is centrifuged, and the solvent decanted off. The crude poly **VIII** is dissolved in the minimum amount of CCl_4 and precipitated again from pentane. All solvents are removed under reduced pressure to yield the expected white polymer (0.41 g, 59% yield).

Poly VIII. ^{1}H NMR (90 MHz, $CDCl_3$) 5.72 (b, *trans*-Ha), 5.58 (b, *cis*-Ha), 4.50 (b, *cis*-Hb), 4.22 (b, *trans*-Hb), 3.45 (b, $\mathit{CH_2}OCH_3$), 3.34 (b, $CH_2O\mathit{CH_3}$), 2.25 (b, Hc) ppm. ^{13}C NMR (Proton-decoupled) (CD_2Cl_2, 22.53 MHz) 133.2 (olefin), 131.1 (olefin), 81.9 (*trans*-allylic), 77.1 (*cis*-allylic), 71.2 ($\mathit{CH_2}OCH_3$), 70.9 ($\mathit{CH_2}OCH_3$), 70.3 ($\mathit{CH_2}OCH_3$), 58.9 ($CH_2O\mathit{CH_3}$), 48.5 (*cc*-$\mathit{CH}CH_2OCH_3$), 48.0 (*ct*-$\mathit{CH}CH_2OCH_3$), 47.6 (*tc*-$\mathit{CH}CH_2OCH_3$), 47.4 (*tt*-$\mathit{CH}CH_2OCH_3$) ppm. IR (Thin film) 2890 (s), 1475 (m), 1460 (m), 1390 (m), 1190 (s), 1100 (vs), 1020 (s), 963 (s) cm^{-1}.

Poly IV. ^{1}H NMR (CD_2Cl_2, 90 MHz) 5.70, 5.50, 4.70, 4.35, 4.05, 3.35, 3.30, 2.58, 2.1 ppm. ^{13}C NMR (Proton decoupled) (CD_2Cl_2, 22.53 MHz) 133.6, 133.3, 132.9, 132.2, 129.7, 129.1, 81.8, 80.3, 79.1, 76.4, 74.6, 73.4, 72.7, 58.7, 45.4, 43.2, 36.3, 35.8 ppm. IR (Thin film) 2890 (s), 1478 (m), 1450 (m), 1390 (m), 1190 (m), 1110 (vs), 1020 (s) 963 (s) cm^{-1}.

Polymerizations Using Catalyst XV/$HgBr_2$: All manipulations carried out under dry argon. Catalyst XV (31.9 mg, 0.543 mmol) and HgBr2 (113.7 mg, 0.315 mmol, 5.8 equivalents) are dissolved in THF (1.0 ml). Monomer VIII (636.2 mg, 3.45 mmol, 63.5 equivalents) (2.22 M) is added via syringe at room temperature. Within a few minutes the solution begins to become viscous, and in one hour, it is completely gelled. At this time ethanol (1.0 ml) is added, and the reaction stirred until all the polymer gel dissolves. The reaction solution is then cannulated into pentane. The polymeric precipitate is centrifuged, and the solvent decanted off. The crude poly **VIII** is dissolved in the minimum amount of CCl_4 and precipitated again from pentane. All solvents are removed under reduced pressure to yield the expected polymer (0.4976 g, 78.2 yield).

Polymerizations Using Catalyst XVI. Catalyst **XVI** (20.0 mg, 0.0252 ,mmol) is dissolved in toluene (0.5 ml) and placed in a cold bath at -40 °C. Monomer **VIII** (232 mg, 1.26 mmol, 50 eq) is dissolved in toluene (0.50 ml), cooled to -40 °C and cannulated into the catalyst solution. Over the next two hours the solution is allowed to warm to 0 °C. After 4 hours total, acetone (2 ml) is added and the solution allowed to warm to room temperature. The reaction mixture is then cannulated into pentane. The solvent is decanted off the polymeric material, and the polymer washed twice with pentane. The polymer is dissolved in the minimum amount of ethanol and precipitated by addition to pentane. The solvent is decanted off and the resulting polymer dried in vacuum to yield 112 mg (43% yield).

Poly VIII (High *cis*). ^{1}H NMR ($CDCl_3$, 90 MHz) 5.58 (b, *cis*-Ha), 4.58 (b, *cis*-Hb), 3.45 (b, CH_2OCH_3), 3.34 (b, CH_2OCH_3), 2.25 (b, Hc) ppm. ^{13}C NMR (Proton-decoupled) (CD_2Cl_2, 22.53 MHz) 133.7 (olefin), 81.8 (*trans*-allylic), 77.3 (*cis*-allylic), 71.0 (CH_2OCH_3), 70.8 (CH_2OCH_3), 70.6 (CH_2OCH_3), 58.9 (CH_2OCH_3), 48.4 (*cc*-$CHCH_2OCH_3$), 48.0 (*ct*-$CHCH_2OCH_3$), 47.6 (*tc*-$CHCH_2OCH_3$), 47.2 (*tt*-$CHCH_2OCH_3$) ppm. IR (Thin film) 2890 (s), 1475 (m), 1460 (m), 1390 (m), 1190 (s), 1100 (vs), 1018 (s), 963 (w) 730 (m). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.21; H, 8.75. Found: C, 62.42; H, 8.17.

Copolymerization of VIII and Norbornene Using XVI: Catalyst **XVI** (30.0 mg, 0.0379 mmol) is dissolved in 1.0 ml C_6H_5Cl and the resulting solution cooled to -35 °C. To this solution, **VIII** (724.1 mg, 3.93 mmol) and norbornene (370.0 mg, 3.93 mmol) dissolved in C_6H_5Cl (1.0 ml) are added via cannula. After 2 hours at -35 °C, the reaction is warmed to 0 °C and allowed to stir for an additional 20 minutes. Acetone (3 ml) is added and the solution stirred for 5 minutes before precipitating the product polymer out by addition to pentane. The polymer is dissolved in the minimum amount of $CHCl_3$ and reprecipitated by addition to pentane. The solvent is decanted off and the resulting polymer dried in vacuum to yield 285.1 mg (26.1%). ^1H NMR (90 MHz, $CDCl_3$) 5.5, 5.25, 4.45, 3.48, 3.30, 2.80, 1.80, 1.32, 0.90 ppm. ^{13}C NMR (Proton decoupled) (CD_2Cl_2, 22.53 MHz) 137.96, 133.9, 129.19, 76.9, 70.73, 70.24, 58.84, 47.76, 42.69, 38.63, 33.26, 29.76 ppm.

Polymerizations of VIII Using $RuCl_3$. The polymerizations utilizing all the ruthenium complexes are performed in a similar manner. A representative procedure is presented here. $RuCl_3$ (27.0 mg, 0.103 mmol based on $RuCl_3{\cdot}3H_2O$) is dissolved in chlorobenzene (1.45 ml) and absolute ethanol (1.0 ml). Monomer **VIII** (0.80 ml, 5.04 mmol, 48.9 eq) is then added to the catalyst mixture via syringe. The solution is degassed under vacuum, then heated at 50 °C for 4 days. The resulting viscous mixture is added to ethanol (50 ml) and centrifuged. The solution is decanted away from any insoluble catalyst residue and the solvent removed under reduced pressure. The resulting polymer is dissolved in the minimum amount of $CHCl_3$ and cannulated slowly into pentane. The solvent is decanted, and the polymer dried under vacuum to yield 684.0 mg (73.7% yield).

Poly VIII (High *trans*). ^1H NMR ($CDCl_3$, 90 MHz) 5.72 (b, Ha), 4.22 (b, Hb), 3.45 (b, CH_2OCH_3), 3.34 (b, CH_2OCH_3), 2.25 (b, Hc). ^{13}C NMR (Proton decoupled) (CD_2Cl_2, 22.53 MHz) 132. 2 (olefin), 81.9 (*trans*-allylic), 77.2 (*cis*-allylic), 71.0 ($\mathit{CH_2}OCH_3$), 58.9 ($CH_2O\mathit{CH_3}$), 48.4 (*cc*-$\mathit{CH}CH_2OCH_3$), 48.0 (*ct*-$\mathit{CH}CH_2OCH_3$), 47.7 (*tc*-$\mathit{CH}CH_2OCH_3$), 47.4 (*tt*-$\mathit{CH}CH_2OCH_3$) ppm. IR (Thin film) 2890 (s), 1475 (m), 1460 (m), 1390 (m), 1190 (s), 1100 (vs), 1018 (s), 963 (s).

Polymerization of XI Using $RuCl_3$. $RuCl_3$ (217.0 mg, 0.828 mmol) is dissolved in C_6H_5Cl (13 ml) and ethanol (5 ml). To this solution monomer **XI** (7.22 g, 34.3 mmol) (1.43 M) is added and the solution degassed under vacuum. The reaction vessel is then heated to 55 °C for one hour, after which time the viscous solution is cooled and diluted with an additional 5 ml $CHCl_3$. The polymer is then precipitated out by addition to methanol. The polymer is redissolved in the minimum amount of $CHCl_3$ and reprecipitated by addition to methanol. The methanol is decanted off and the product polymer dried under vacuum to yield 3.7 g (51.2% yield). ^1H NMR ($CDCl_3$, 90 MHz) 5.90 (b, olefin H), 5.45 (b, allylic H), 3.72 (b, methyl ester). ^{13}C NMR (Proton-decoupled) (CD_2Cl_2, 22.53 MHz) 162.78 (carboxylate C), 138.22 (olefin C), 131.79 (olefin C), 86.36 (allylic C), 52.69 ppm (methyl C). IR (Thin film): 3010 (w), 2950 (w), 1720 (vs), 1660 (m), 1440 (m) 1260 (vs), 1010 (m), 980 (m), 920 (w) cm^{-1}.

Polymerization of VIII Using $OsCl_3$. $OsCl_3$ (18.5 mg, 0.0624 mmol based on $OsCl_3 \cdot 3H_2O$) is dissolved in chlorobenzene (1.5 ml) and absolute ethanol (0.2 ml). Monomer **VIII** (533.6 mg, 2.90 mmol, 46 eq) (1.70 M) is then added to the catalyst mixture via syringe. The solution is degassed under vacuum, then allowed to stir for 11 hours. The resulting viscous mixture is added to ethanol (20 ml) and centrifuged. The solution is decanted away from any insoluble catalyst residue and the polymer is precipitated by addition to pentane. The resulting polymer is dissolved in the minimum amount of $CHCl_3$ and again cannulated slowly into pentane. The solvent is decanted, and the polymer dried under vacuum to yield 516.0 mg (96.6% yield).

Poly VIII. ^{1}H NMR ($CDCl_3$, 90 MHz) 5.72 (b, Ha), 4.22 (b, Hb), 3.45 (b, CH_2OCH_3), 3.34 (b, CH_2OCH_3), 2.25 (b, Hc). ^{13} C NMR (Proton-decoupled) (CD_2Cl_2, 22.53 MHz) 132. 2 (olefin), 81.9 (*trans*-allylic), 77.2 (*cis*-allylic), 71.0 (CH_2OCH_3), 58.9 (CH_2OCH_3), 48.4 (*cc*-$CHCH_2OCH_3$), 48.0 (*ct*-$CHCH_2OCH_3$), 47.7 (*tc*-$CHCH_2OCH_3$), 47.4 (*tt*-$CHCH_2OCH_3$) ppm. IR (Thin film) 2890 (s), 1475 (m), 1460 (m), 1390 (m), 1190 (s), 1100 (vs), 1018 (s), 963 (s).

Polymerization of XI with Varying Amounts of Acetone. Four reaction tubes were prepared: (1) $RuCl_3$ (31.0 mg), **XI** (234.6 mg), C_6D_6 (0.30 ml), EtOH (0.06 ml), $(CD_3)_2CO$ (0.0 ml, 0.0%). (2) $RuCl_3$ (42.0 mg), **XI** (315.6 mg), C_6D_6 (0.20 ml), EtOH (0.06 ml), $(CD_3)_2CO$ (0.10 ml, 28.0%). (3) $RuCl_3$ (36.1 mg), **XI** (320.6 mg), C_6D_6 (0.12 ml), EtOH (0.06 ml), $(CD_3)_2CO$ (0.18 ml, 50.0%). (4) $RuCl_3$ (20.0 mg), **XI** (285.4 mg), C_6D_6 (0.0 ml), EtOH (0.0 ml), $(CD_3)_2CO$ (0.40 ml, 100.0%). Each reaction vessel is then heated to 50 °C, for 30 minutes. The resulting Poly **XI**, is precipitated by addition of the reaction solutions to CH_3OH. Molecular weight information is obtained using GPC data collected on 0.2% polymer solutions in CH_2Cl_2.

Hydrolysis of Poly XI Using H_2O/NaOH. Poly **XI** (0.70 g) was placed in 5% NaOH (20 ml), and warmed the resulting heterogeneous mixture to 40 °C. After 20 minutes all of the polymer was observed to dissolve and the solution turned dark red. After 45 minutes, the solution was acidified with aq. HCl, and a rust colored polymer precipitated.

Reaction of Poly XI with NaH. Poly **XI** (200 mg) is dissolved in 30 ml dry THF. To this solution, 200 mg NaH is added and the resulting slurry allowed to stir at room temperature for 3 hours. During this time, the solution color turns dark red. The red polymer solution is removed from the excess NaH by cannula filtration. To this homogeneous solution, TMSCl (220 mg) is added and the solution immediately turned colorless. The solvent is removed under vacuum and the resulting polymer washed with methanol, and then dried under vacuum. ^{1}H NMR ($CDCl_3$, 90 MHz) 5.90 (b, olefin H), 5.45 (b, allylic H), 3.72 (b, methyl ester), 0.14 (TMS), 0.10 (TMS), 0.05 (TMS), 0.02 ppm (TMS).

Reduction of Poly XI using p-Toluenesulfonhydrazide. Poly **XI** (1.0 g) is suspended in p-xylene (50 ml). p-toluenesulfonhydrazide (5.5 g) added and the resulting slurry heated to 125 °C. At 80-90 °C evolution of gas (N_2) is observed. During this process, the polymer never completely goes into solution. Heating is continued for 6 hours, after which time the solution is cooled and poured into pentane. The resulting residue is washed with methanol, and the saturated polymer, poly **XIs**, dried under vacuum. ^{1}H NMR ($CDCl_3$, 90 MHz) 4.2 (1 H), 3.6 (3 H), 3.0 (1 H), 1.75 (1 H) ppm. ^{13}C NMR (Proton-decoupled) (CD_2Cl_2, 22.53 MHz) 171.62, 80.51, 51.95, 31.38, 30.93 ppm.

Hydrolysis of Poly XIs. Poly **XIs** (64.0 mg) is dissolved in a mixture of 5% NaOH (5 ml) and THF (1 ml) and allowed to stir at room temperature for 6 hours. The solution is then acidified with aqueous HCl and allowed to stand as the hydrolyzed polymer slowly precipitates out. Solution is filtered, and the polymer washed with successive portions of water, then methanol, and dried under vacuum. ^{1}H NMR (DMSO-d_6, 90 MHz) 12.2, 3.9, 3.6, 2.85, 1.8 ppm.

Reaction of Poly XI with DDQ. Poly **XI** (300 mg) is dissolved in dry THF. To this solution, DDQ (390 mg, 1.2 equivalents) is added and the resulting solution allowed to stir at room temperature. After 5 days the deep purple solution is pumped down and the resulting purple-black polymer, poly **XIox**, is dissolved in CH_2Cl_2. The insoluble hydroquinone residue is filtered off and the solvent removed under vacuum. ^1H NMR ($CDCl_3$, 90 MHz) 7.7 (broad), 3.9 ppm (broad). ^{13}C NMR (Proton-decoupled) ($CDCl_3$, 22.53 MHz) 162.39, 143.16, 139.26, 118.1, 52.37 ppm.

Monomer Dependence on Initiation Rate. The initiation time is defined as the time elapsed from initial heating of the reaction mixture until the first sign of polymer formation. The onset of polymerization can be detected in two ways. In solvents in which the polymer remains soluble (i.e., benzene/alcohol mixtures for **XI**, or neat alcohol for **VIII**), the onset of polymerization can be detected using ^1H NMR, typically by the appearance of of the olefin polymer resonances at 5.9 ppm (poly **XI**). In solvents in which the polymer is completely insoluble (i.e., alcohol for **XI**, and water for **VIII**), the onset of polymerization can be defined as the first sign of precipitate detected visually. Standard solutions of $RuCl_3$ (198.1 mg in 2.0 ml CD_3OD), and monomer (4.938 g and enough C_6D_6/CD_3OD (5/1) to bring the total volume to 5.00 ml, 4.699 M). Eleven runs are prepared using varying amounts of monomer solution, and the appropriate amount of C_6D_6/CD_3OD (5/1) added to keep the volumes constant. Before each run, a fixed amount of catalyst solution is rapidly added via syringe, the contents mixed, and the tube placed in the NMR probe at a preset temperature (55 °C). The reaction is then monitored every fourteen seconds until polymer resonances are detected.

Copolymerization of X and XI. Ru(COD) (35.5 mg) is dissolved in C_6H_5Cl (4.0 ml) and ethanol (0.5 ml). To this solution, **XI** (1.0 g, 4.76 mmol), and **X** (0.69 g, 4.79 mmol) are added, the solution degassed under vacuum, and heated to 55 °C for 4 hours. To the resulting red gel, an additional 5 ml C_6H_5Cl is added, and the polymer precipitated by addition to methanol. The solid polymer is redissolved in CHC13, and reprecipitated from methanol. The solvent is decanted off, and the polymer dried under vacuum to yield 1.57 g (92.9% yield) ^1H NMR ($CDCl_3$, 90 MHz) 7.3, 5.9, 5.6, 5.5 and 3.75 ppm. ^{13}C NMR (Proton decoupled) ($CDCl_3$, 22.53 MHz) 162.46, 140.95, 137.89, 131.39, 128.02, 122.04, 85.71, 83.95 and 52.44 ppm.

Hydrogenation of poly VIII Using p-Toluenesulfonhydrazide. Poly **VIII** (0.80 g) is dissolved in p-xylene (30 ml). To this homogeneous solution, p-toluenesulfonhydrazide (TSH) (4.63 g, 5.7 equivalents) is added and the resulting slurry heated. At 95 °C, all of the TSH goes into solution and gas evolution begins. Heating is continued for 3 hours at 110 °C, after which time the solution is cooled slightly and added slowly to rapidly stirring pentane. The resulting orange precipitate is dissolved in 15 ml $CHCl_3$, and the remaining white residue is discarded. To the CHC13 solution, silica gel (4 g) is added and the solvent removed under vacuum. The polymer, dispersed on silica gel, is loaded onto a flash chromotography column (6.5 in. X 1.5 in.) in THF/ligroin (60/40). The column is then flushed with THF/ligroin (60/40) (1000 ml) to remove tosylate impurities. The saturated polymer, poly **VIIIs**, is then eluted with neat THF (1500 ml), and the THF is removed under vacuum. If the THF used is stabilized with BHT, then the polymer obtained at this point contains the concentrated BHT. The BHT can be removed by dissolving the mixture in CHC13 and precipitating the polymer by addition to pentane. The pentane is decanted off and the poly **VIIIs** dried under vacuum to yield 731.7 g (91.4% yield). ^{1}H NMR ($CDCl_3$, 90 MHz) 3.65 (2H), 3.38 (4H), 3.30 (6H), 2.18 (2H), 1.70 (4H) ppm. ^{13}C NMR (Proton-decoupled) ($CDCl_3$, 22.53 MHz) 81.15, 80.83, 71.28, 58.67, 46.20, 45.87, 32.74, 31.98 ppm.

Synthesis of endo-(-)-5-methoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene, IV*. The resolution of 7-oxabicyclo[2.2.1]hept-2-ene-2-carboxylic acid is accomplished using (R)-(+)-α-methylbenzylamine as discribed in literature.[50] A 100 ml, 3-neck flask is equipped with a pressure-equalizing dropping funnel, a water-cooled reflux condenser and an overhead stirrer. The reaction vessel is charged with LAH (1.2 g) in dry THF (25 ml). The resolved acid (3.86 g, 0.0275 mol) (91% optically pure,$[\alpha]_D$ = -60.2°, literature, -66.4°) dissolved in dry THF (50 ml) is placed in the dropping funnel and added dropwise to the LAH suspension. The solution is then allowed to stir overnight. Water (1.5 ml), NaOH (1.5 ml, 15% solution), and water (4.5 ml) are then added slowly in sequence. The resulting white precipitate is filtered. The filtrate is concentrated (rotor-evaporated) and added to the white precipitate. This residue is placed in a Soxhlet extraction apparatus and extracted with methylene chloride for 2 days. The CH_2Cl_2 is removed (rotor-evaporated) and the remaining viscous oil dried in vacuum to yield the desired product (3.43 g, 98.8). The alcohol obtained in this fashion is carried through without further purification. A 100 ml, 3-neck flask is equipped with a pressure-equalizing dropping funnel, a water-cooled reflux condenser and a magnetic stir bar. The reaction vessel is charged with NaH (0.82 g) in dry THF (25 ml). The resolved alcohol (3.43 g, 0.0272 mol) is dissolved in dry THF (50 ml) and added dropwise through the dropping funnel. After complete addition of the diol, the solution is stirred for an additional half hour to insure complete reaction. CH_3I (8.7 g, 0.0613 mol) is then added slowly through the dropping funnel. After complete addition of the CH_3I, water is added dropwise until no further bubbling occurs. The reaction solution is then poured into diethyl ether (200 ml) and filtered. The solvent is removed at reduced pressure to yield the desired product as a clear liquid (2.98 g, 71.1%). Further purification can be accomplished using a Kugelrohr apparatus (B.P. 60-65 °C at 0.001 torr). ^1H NMR ($CDCl_3$, 90 MHz) 6.30 (m), 4.90 (m), 3.35 (s), 3.28 (s), 2.92 (m), 2.50 (m), 2.0 (m), 0.70 (m) ppm.

Synthesis of (binaphthol)$WOCl_2$. All manipulations are performed under a dry argon atmosphere. A 250 ml, 3-neck flask was equipped with a water cooled reflux condenser, a oil-bubbler and a magnetic stir-bar. The reaction vessel is charged with $WOCl_4$ (2.026 g, 5.93 mmol). A CCl_4 slurry of ± binaphthol (1.698 g, 5.93 mmol) is added slowly via cannula. Upon addition, the orange $WOCl_4$ solution turns dark purple. After complete addition, the solution is allowed to relux until no further HCl gas evolution is detected (*ca.* 7 days). During this reaction period, the atmosphere is periodically purged of HCl by drawing a vacuum over the cooled solvent, and/or by bubbling Ar vigorously through the solution. When no further HCl can be detected, the CCl4 is removed under vacuum. ^1H NMR ($CDCl_3$, 90 MHz) 7.3-6.8 (m).

Polymerization of 7-methylnorbornene Using (binaphthol)$WOCl_4$/$Sn(CH_3)_4$. A Schlenk flask is charged with (binaphthol)$WOCl_4$ (98.4 mg, 0.177 mmol) and dry benzene (5 ml) is added.

$Sn(CH_3)_4$ (0.10 ml, 129.1 mg, 0.723 mmol) is added via syringe and the reaction mixture allowed to stir at room temperature for 10 minutes. After this incubation period, 7-methylnorbornene (49/51, syn/anti) (1.032 g, 9.54 mmol) dissolved in 5.0 ml benzene is added slowly via cannula. The reaction mixture is heated to 50 °C for 2 hours. The polymer is precipitated from solution by slow addition of the reaction solution into methanol. The polymer is purified by dissolving it in the minimum amount of $CHCl_3$ and reprecipitating it from rapidly stirred methanol. ^1H NMR ($CDCl_3$, 90 MHz) 5.25 (2 H), 2.3 (1 H), 1.8 (2 H), 1.3 (2 H), 0.95 (3 H) ppm. ^{13}C NMR (Proton-decoupled) ($CDCl_3$, 22.53 MHz) 133.99, 133.80, 133.54, 51.59, 51.33, 48.67, 48.34, 47.95, 47.30, 46.39, 31.97, 31.71, 31.18, 16.69, 16.37, 16.04 ppm.

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CHAPTER 4

AQUEOUS RING-OPENING METATHESIS POLYMERIZATIONS

Abstract

During attempts to minimize the initation times of the ruthenium-catalyzed polymerizations, it was unexpectedly found that these reactions are actually cocatalyzed by water. The observation that large excesses of water in the reaction mixture do not inhibit polymerization ultimately led to the finding that the 7-oxanorbornene monomers can be polymerized in aqueous solution to provide near quantitative yields of the desired ring-opened polymer. Furthermore, the molecular weight of the material increases by a factor of four, and the polydispersities decrease from nearly 2 to 1.2 - 1.3 when these polymerizations are carried out in water.

Using norbornene as the substrate, it was found that the ruthenium catalysts can be recycled with no detectable slowing in their initiation rates. When the Ru^{3+} catalyst solutions resulting from the polymerization of **VIII** are recycled, the catalyst actually becomes more active with use. Overall, rate enhancements of nearly 8000 are measured in going from organic solvents to these recycled aqueous solutions. Ru^{3+} solutions have been recycled with **VIII** up to 14 consecutive times, without a detectable decrease in their initation rates. During efforts to uncover the reasons for this enhanced activity, it was discovered that Ru^{2+} complexes are far more active than Ru^{3+}. Furthermore, these Ru^{2+} complexes show similar increases in activity when they are recycled. When n equivalents of **VIII** are allowed to react with $Ru(H_2O)_6(tos)_2$ in D_2O, (n-1) equivalents of **VIII** are polymerized, and conversion of the catalyst to the mono-olefin adduct Ru^{2+}-**VIII** is observed. These olefin adducts display the same initiation times as do the recycled Ru^{3+} solutions. ^1H NMR investigations of the recycled Ru^{3+} solutions reveal that the same olefin complexes are formed.

The enhanced activity of these recycled solutions is ascribed to the reduction of Ru^{3+} to Ru^{2+}, and the *in situ* formation of Ru^{2+}-olefin adducts that lie along the reaction coordinate. A disproportionation of Ru^{3+} to form Ru^{2+} and Ru^{4+} is evidenced by the formation of Ru Red in reactions catalyzed by $[Ru(NH_3)_5Cl]Cl_2$.

The polymerization of **VI** using these highly active aqueous ruthenium catalysts is reported. As this polymerization is performed in water, simultaneous hydrolysis of the anhydride moiety occurs, giving the poly diacid polymer, Poly **VIa**, as the final product. Hydrogenation of this material with hydrazine provides Poly **VIas**, a close structural analogue to known antitumor and antiviral polyanionic materials.

INTRODUCTION

The Group VIII catalysts possess several characteristics that make them ideal candidates for further investigations regarding their potential as versatile living polymerization catalysts: 1) Demonstrated stability towards polar functional groups, which allows for the polymerization of a large number of monomers;[1] 2) The unreactive nature of the intermediate ruthenium carbene species towards acyclic double bonds, which suppress chain transfer through any backbiting mechanisms; and 3) Once the active catalyst centers are initiated, they can display high activities. As mentioned previously, the active centers possess turnover rates greater than 1000 equivalents of monomer per minute. The major problem, which limits the utility of these catalysts, is the exceedingly slow initiation step. Commonly, initiation periods of several hours or longer are often observed using these catalysts.[2] Once a small amount of catalyst is initiated, however, polymerization proceeds at a rapid rate. To develop practical polymerization processes using these catalysts, it becomes necessary to find ways of spurring their initiation rates. Ultimately, for the development of second generation living systems, it will be necessary to increase the rate of initiation to values equal to, or greater than, the rate of propagation.[3]

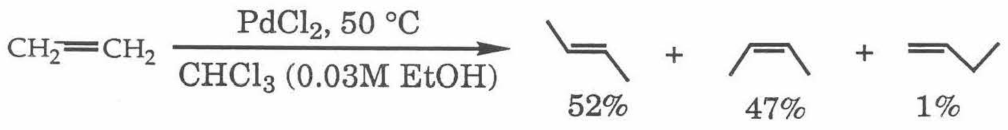
There are several examples in the literature of transition-metal, catalyzed oligomerizations and polymerizations that require activation by a cocatalyst such as oxygen, alcohols, epoxides or water. The coupled product, ethyl *trans*-but-2-enyl sulphone, is formed from the $PdCl_2$ catalyzed reaction of ethylene and sulphur dioxide[4] (Equation 1).

$$CH_2{=}CH_2 + SO_2 \xrightarrow[C_6H_6,\ 70\ °C]{PdCl_2} CH_3CH_2SO_2CH_2CH{=}CH_2 \qquad (1)$$

The reaction is cocatalyzed by the addition of small amounts of water, as indicated by the fact that no reaction occurs under rigorously anhydrous conditions. Through a Wacker-type reaction with ethylene, the water is thought to promote the reduction of Pd^{2+} to Pd^0, which is required in the catalytic cycle (Equation 2).

$$Pd\text{-}\Vert\begin{smallmatrix}CH_2\\ CH_2\end{smallmatrix} + H_2O \longrightarrow CH_3CHO + Pd^0 + HCl \qquad (2)$$

Similarly, in the dimerization of ethylene catalyzed by $PdCl_2$ in chlorinated solvents, no reaction occurs in the absence of a protic source.[5] Methanol, ethanol, isopropanol, t-butyl alcohol and water (0.02-0.10 M) all catalyze the dimerization in chloroform; the rate is essentially independent of the protic compound used (Equation 3).



(3)

However, when concentrations of alcohol in excess of 0.10 M (that is, > 1:1 ratio of ROH:$PdCl_2$) are used, catalyst deactivation occurs with formation of Pd metal. The alcohol is thought to assist in the decomposition of the initially formed $[PdCl_2(C_2H_4)]_2$ dimer to form the monomeric

$PdCl_2(C_2H_4)$ species, which then coordinate a second equivalent of ethylene, leading to coupling products.

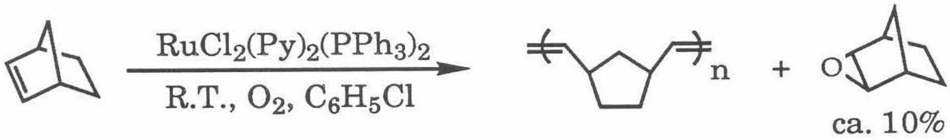
It is known that the addition of small amounts of water or oxygen activate certain Ziegler-Natta olefin polymerization systems. It was first reported that trace amounts of water added to the well-known $Cp_2TiCl_2/Al(CH_3)_3$ system gave a dramatic increase in activity, and facilitated the regulation of the molecular weight of the product polyethylene.[6] Later, especially powerful systems were obtained by the addition of water to the $Cp_2ZrR_2/Al(CH_3)_3$ system (activities as high as 2.5 X 10^7 g PE/g Zr·Hr were observed).[7] The role of water in these Ziegler-Natta systems has been linked to modification of the aluminum-alkyl component. When carefully measured aliquots of water are added to $Al(CH_3)_3$, an oligomeric compound, methyl aluminoxane, is formed. Typical repeat units in this oligomer contain aluminum atoms that still bear alkyl groups joined together by bridging oxygens. Combining preformed aluminoxanes with the transition-metal components produces Ziegler-Natta catalysts, which are the most active to date.[7] In all of these systems, water in excess of the prescribed amount quickly acts to deactivate the catalyst system.[8] For example, the $TiCl_4/AlEt_2Cl$ ethylene polymerization catalyst gives a maximum yield of polymer when 10 mole % of water (or oxygen) is added; higher mole percentages deactivate the catalyst.[9]

No aluminum-free Ziegler-Natta polymerization systems have been thus far reported which are similarly activated by oxygen or water. One report of a Group VIII transition-metal Ziegler-Natta system activated by water also contains aluminum alkyls. Both the heterogeneous $CoCl_2$-$AlEt_2Cl$, and the homogeneous $CoCl_2$-$AlEt_2Cl$-pyridine catalysts used for the selective *cis*-1,4 polymerization of butadiene are active only in the presence of small amounts of water or oxygen.[10] A 5-15 mole % of water or oxygen (based on $AlEt_2Cl$) appears to be the optimum amount required for catalyst activity. Conclusive demonstration that the activation results from the reaction of water with the $AlEt_2Cl$ is provided by control experiments. Catalyst solutions prepared by pretreating the $AlEt_2Cl$ with water before addition of the $CoCl_2$ show identical activities and selectivities as do those of catalyst solutions prepared from either the simultaneous mixing of all the components, or the prereaction of $CoCl_2$ with water. In light of the recent studies on the formation and use of aluminoxanes (*vide supra*), it would appear that analogous chemistry is probably occurring in these Co/Al systems as well.

"Classical" early metal ROMP catalysts can sometimes be activated through the addition of small amounts of anhydrous alcohols or oxygen. As with the Ziegler-Natta catalysts, a delicate balance between catalyst activation and deactivation exists in these systems as well. The $WCl_6/AlEtCl_2$ (1/4) catalyst mixture is known to be activated by the addition of exactly one equivalent of anhydrous ethanol based on tungsten.[11] Catalyst deactivation rapidly ensues if more than one equivalent of the alcohol is used. (Following polymerization, these catalysts are routinely "killed" by the addition of alcohol.) The ethanol used must be rigorously dried as even trace amounts of water can catalytically deactivate the reaction mixture. The activation of $WCl_6/Al(i\text{-bu})_3$, through the addition of one equivalent of 2,4,6-trichlorophenol, has similarly been reported.[12] An exact formula for the active species in these reactions remains elusive. The reaction of WCl_6 and alcohol is known to give a range of products, including $(RO)_3WCl_2$.[13] Indeed, several isolated metal-alkoxide complexes are known to be active catalysts.[14]

Molecular oxygen has also been implicated as an activator for a select group of ROMP catalysts. The W(0) complex, $W(CO)_3$(mesitylene), combined with $AlEtCl_2$ becomes a more active catalyst in the presence of small amounts of O_2.[15] Similar O_2 activation is seen with $ReCl_5/AlEt_3$.[16] Optimum activity is achieved using 6-10 equivalents of O_2 per Re center; at oxygen concentrations above this, the catalyst is deactivated.

Two opposing schools of thought are found in the literature, concerning the activation of the Group VIII ROMP catalysts. The first proposal begins with Ru^{2+} compounds ($Ru(PPh_3)_4Cl_2$, and $RuCl_2(Py)_2(PPh_3)_2$, for example), and oxidizes them to a higher oxidation state by means of molecular oxygen. In the alternative scenario, Ru^{3+} (or Ir^{3+}) compounds are reduced to a lower oxidation state. It has been reported that the Ru^{2+} catalyst, $RuCl_2(Py)_2(PPh_3)_2$, polymerizes norbornene nearly 100 times faster if O_2 is bubbled through the reaction mixture[17] (Equation 4).



(4)

The mechanism proposed (without any direct evidence) to account for this observation invokes a ruthenium oxide as the active species, which presumably undergoes a [2+2] cycloaddition with one equivalent of the olefin substrate to form an intermediate metallaoxetane. This intermediate then retrocleaves to provide a ruthenium carbene, which acts to initiate the polymerization. In addition to the observed polymerization, a small amount (approximately 10% conversion after 5 hours at 20 °C) of *exo*-2,3-epoxynorbornene is also formed. The isolated epoxide is also reported to act as an activating reagent, with no need for additional oxygen.

In sharp contrast to these results, several reports have appeared in which Ru^{3+} complexes are activated by the addition of reducing agents. A number of reducing agents have been examined, including H_2,[18] Mg, Zn and $SnCl_2$.[19]

RESULTS AND DISCUSSION

A. Activiation of Ruthenium(III) ROMP Catalysts.

As mentioned in Chapter 3, the ruthenium-catalyzed 7-oxanorbornene polymerizations require a somewhat lengthy initiation period. Using $RuCl_3$ as the catalyst, a 1 M solution of monomer **VIII** in a C_6H_6/EtOH (5/1) at 50 °C typically requires an initiation period between 22 and 24 hours. During the course of these $RuCl_3$ investigations, it was also noted that the initiation times as well as the polymer yields would vary substantially from run to run. The most glaringly inconsistent variable was the commercial $RuCl_3$ catalyst, which is notorious for containing numerous impurities.[20] Runs utilizing the same stock of $RuCl_3$, however, often showed differing (and lengthy) initiation periods. In addition, polymerizations using pure, well-characterized Ru^{3+} complexes (K_2RuCl_5 and $[Ru(NH_3)_5Cl]Cl_2$, etc.), still exhibited initiation periods as protracted as the commercial $RuCl_3$. In an effort to increase the initiation step and improve polymer yields, more stringent (anaerobic and anhydrous) reaction conditions were employed. Standard Schlenk line techniques were used under dry argon. Benzene is distilled from sodium benzophenone ketyl prior to use. The substrate, monomer **VIII**, was vacuum-transferred from sodium hydride. Finally, the ethanol was azeotrope-distilled with benzene, followed by distillation from hot magnesium metal.[21] Under these scrupulous conditions, however, the initiation times unexpectedly grew *more* protracted, rather than shorter, and several runs failed to give polymer altogether. After continued efforts failed to change these results, it became quite evident that water should be *included*, and not excluded from these reactions. These suspicions were confirmed when the anhydrous ethanol component was replaced with wet ethanol, and the initiation rate showed a dramatic increase. A quantitative dependence of the initiation rate on water concentration is shown in Figure 1. From these studies, it can be clearly seen that water actually acts as a cocatalyst for these ROMP reactions. In order to minimize the time required for each run, the bulk of these quantitative kinetic runs was performed using the reactive monomer **XI**. It should be emphasized, however, that this water dependence is not unique to monomer **XI**; all the other 7-oxanorbornene monomers show the same dependence on their initiation rates. As can be seen from the shape of the curve in Figure 1, the initiation rate shows saturation behavior above 7-8% H_2O. This corresponds to approximately 125-200 equivalents of water per equivalent of ruthenium at the saturation point. A small, but reproducible, deuterium isotope effect of $k_H/k_D = 1.2$ can be measured when CD_3OD/D_2O is substituted for CH_3OH/H_2O in these systems[22] (Figure 2). Without additional mechanistic information, however, full interpretation of this effect is not currently possible. A comparison of Figures 1 and 2 reveals differences in the initiation times for the blank (0% water) runs. This is to be expected if the amount of residual background water (i.e., the waters of hydration of $RuCl_3$ and residual water impurity in the methanol) differs in the two runs. As expected, regardless of the amount of water initially present, the two runs saturate to the same limiting initiation rate.

Three important points can be made from these water-dependence studies: 1) The Ru^{3+} catalyzed ROMP reactions are cocatalyzed by water. 2) This rate enhancement is not a protic- or polar-solvent effect, in that the uncatalyzed blank runs are performed in neat methanol. 3) Unlike nearly all other reactions cocatalyzed by alcohol, oxygen, or water, these reactions

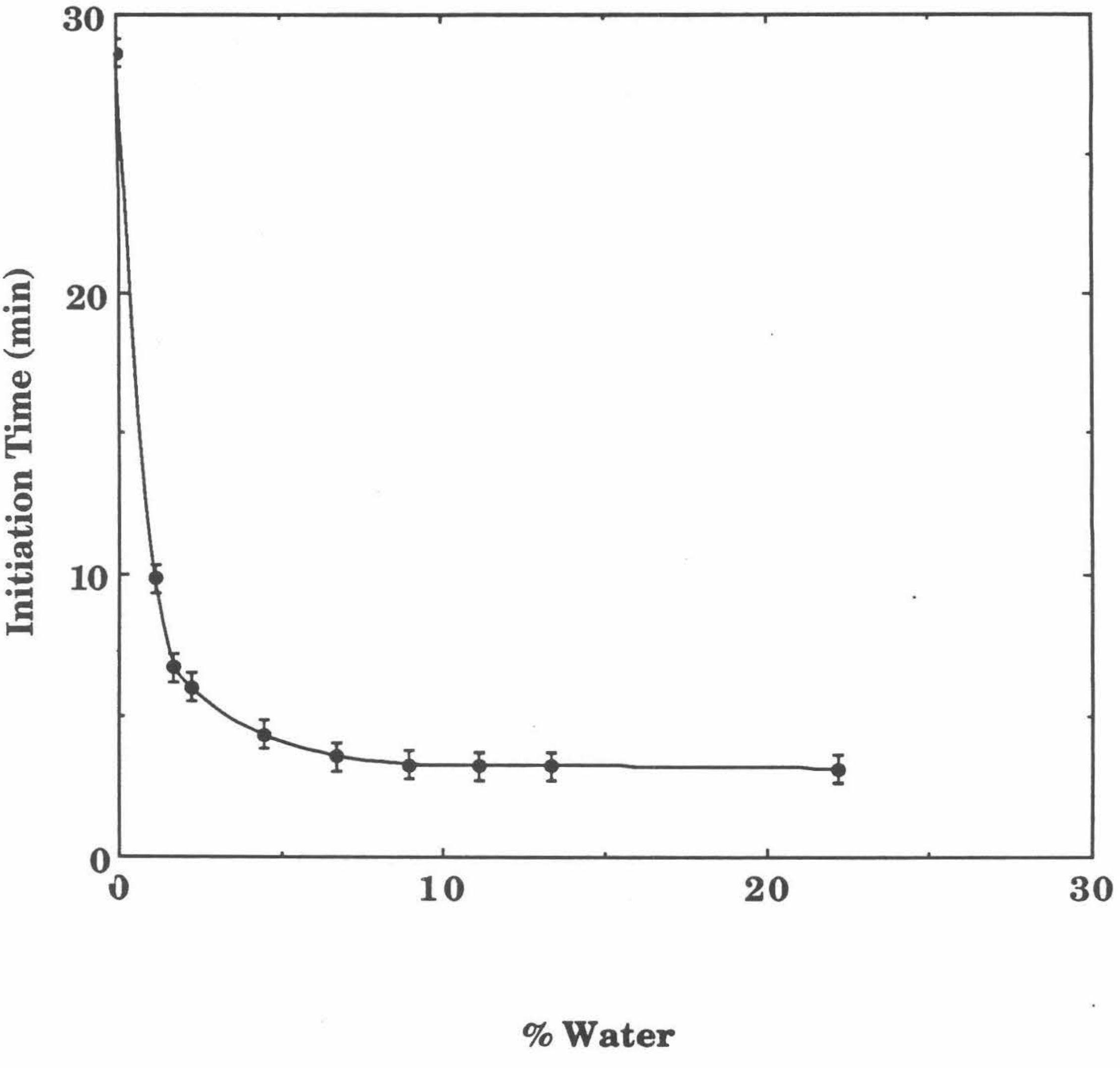


Figure 1: The initiation time (minutes) for the polymerization of **XI** (1.01 M) with $RuCl_3$ (0.081 M), as a function of water concentration in methanol at 55 °C.

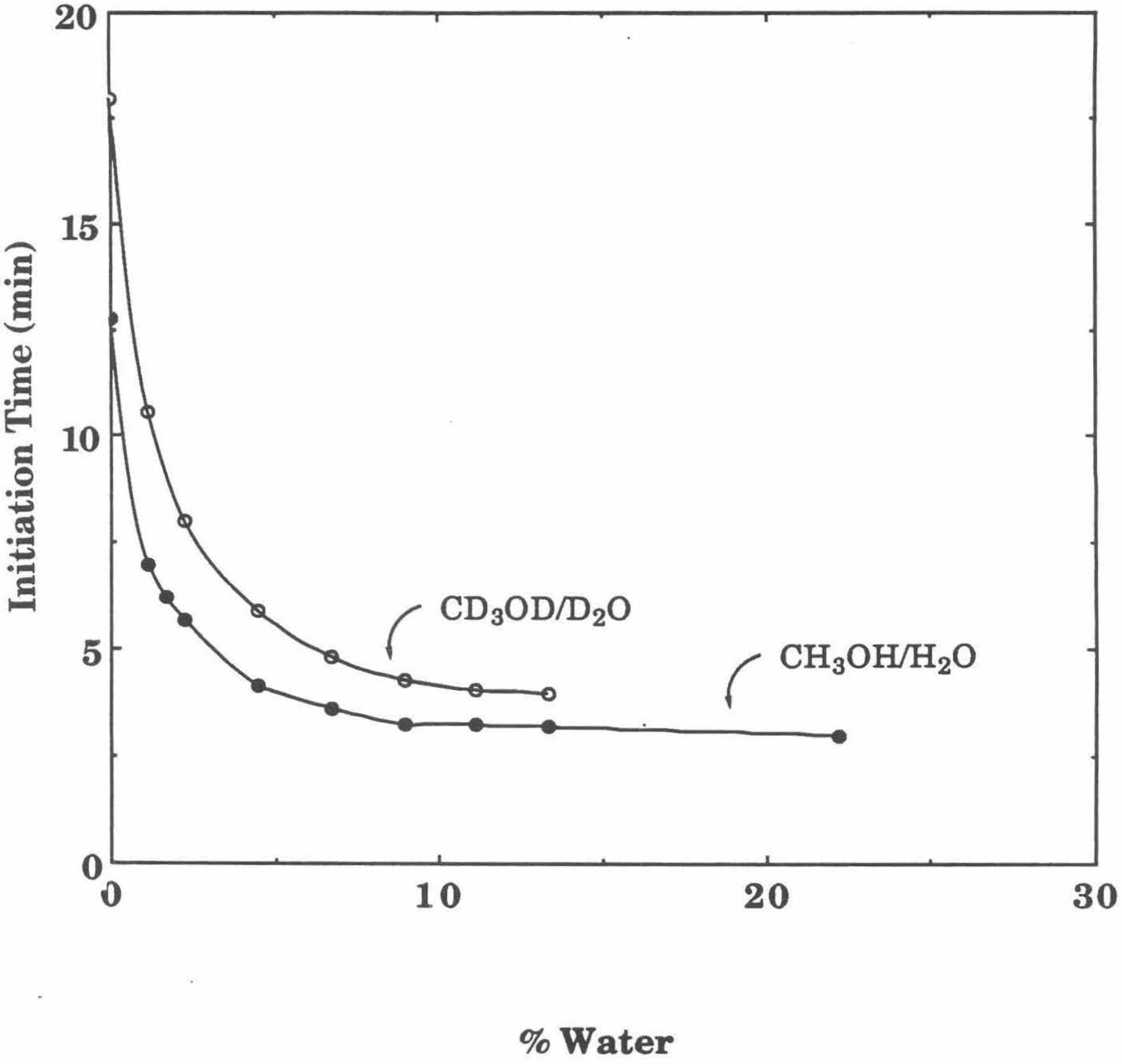


Figure 2: The initiation time (minutes) for the polymerization of **XI** (0.896 M) with $RuCl_3$ (0.0867 M), as a function of water concentration for H_2O/CH_3OH and D_2O/CD_3OD cases at 55 °C.

are not deactivated by the presence of excess water (i.e., no decrease in initiation rates is observed, even when the water concentration approaches 25%). This final observation culminated in the discovery that the polymerization of the 7-oxanorbornene monomers proceeds rapidly *in water alone* to produce the desired ROMP polymer in nearly quantitative yields. The facility of this aqueous polymerization is illustrated by the fact that the initiation period of 22-24 hours, which monomer **VIII** requires in organic solvents, is decreased to only 30-35 minutes in aqueous solution.

Table 1 shows the molecular weights and polydispersities for three samples of Poly **VIII** obtained using $RuCl_3$ in C_6H_6/EtOH (5:1), neat ethanol, and water. As can be seen from these data, conducting the polymerization in protic solution increases the molecular weight by over a factor of 4 (M_w increases from 3.38×10^5 to 1.34×10^6), and decreases the polydispersity from 1.98 to 1.23. This effect is particularly noteworthy in the case of water, where the reaction rapidly becomes heterogeneous as the polymer precipitates as it is formed. The formation of high molecular weight material under these conditions is highly unusual. In most polymerizations, low molecular weight materials result if the polymer tends to precipitate as it is formed. The difference in this case can be attributed to the solubility of the 7-oxanorbornene polymers in their respective monomers (i.e., Poly **VIII** can readily be dissolved in **VIII**). It is thought that after the initial Poly **VIII** precipitates, it begins very rapidly to incorporate monomer from the surrounding solution. The active polymer end-group then continues to propagate within the interior of the monomer-swelled polymer.

It is also important to note that this polymerization constitutes a transition-metal, catalyzed carbon-carbon bond formation reaction, which

CATALYST	SOLVENT	Mw (X 10^{-3})[a]	Mn (X10-3)	PDI
$RuCl_3 \cdot nH_2O$	C_6H_6/EtOH (5:1)	338	172	1.97
$OsCl_3 \cdot nH_2O$	C_6H_6/EtOH (5:1)	416	214	1.94
Ru(TFA)[b]	C_6H_6/EtOH (5:1)	365	184	1.98
Ru(COD)[c]	C_6H_6/EtOH (5:1)	133	78	1.71
$RuCl_3 \cdot nH_2O$	H_2O	1340	1120	1.20
$RuCl_3 \cdot nH_2O$	H_2O/Triton X-100	987	876	1.13
$RuCl_3 \cdot nH_2O$	EtOH	1120	973	1.15
$Ru(H_2O)_6(tos)_2$	H_2O	810	628	1.29
K_2RuCl_5	H_2O	952	774	1.23

Table 1: Molecular weights and polydispersities of Poly **VIII** prepared using a variety of catalysts and solvent systems. Notes: All runs at 55 °C. a) Relative to polystyrene standards. b) Ru(TFA) is an ill-defined compound with the approximate composition, $Ru_2(CF_3CO_2)_4 \cdot 3H_2O$. c) Ru(COD) is an ill-defined Ru^{2+}-cyclooctadiene complex.

occurs in aqueous media. The fact that very high molecular weight materials form under these aqueous conditions indicates that if a termination reaction involving the hydrolysis of the carbon-metal bonds is occuring in either the metallacycle or metal carbene intermediates, it has a much slower rate (by several orders of magnitude) than the rate of propagation of the polymer. (From the average corrected degree of polymerization of the Poly **VIII** obtained from these aqueous reactions, it can be estimated that approximately 2,500-2,700 turnovers occur before each termination step).

The formation of polymer possessing such narrow molecular weight distributions is unusual. Classical ROMP systems typically display molecular weight distributions of 2.0 or greater.[23] Polymers with narrow molecular weight distributions are usually obtained from living polymerization systems.[24] If these systems are living, active end-groups should be present in the polymers. Unfortunately, the very high molecular weights of these poly(7-oxanorbornene) materials make it difficult to detect the end-groups with a high degree of certainty. Using ^{1}H and ^{13}C NMR, infrared and UV/visible spectroscopy, no evidence of end-groups was detected. Experiments were performed, designed to determine whether the polymer formed under these aqueous conditions possesses active end-groups. The heterogeneous nature of this polymerization (i.e., polymer precipitation) lends some complication to this determination. Under argon, monomer **VIII** was polymerized in aqueous solution using K_2RuCl_5. The Poly **VIII** produced was removed from the catalyst solution and divided into two portions. The molecular weight of this initial polymer was determined using one portion ($M_w = 8.3 \times 10^5$). The second polymer portion was dissolved in ethanol while under argon. A second aliquot of **VIII** was then added to this polymer solution and the resulting mixture was heated to 55 °C. Within 20 minutes, the viscosity of the solution had noticeably increased, indicating polymerization of the added **VIII**. After workup, however, the polymer obtained had essentially the same molecular weight as did the original polymer ($M_w = 8.4 \times 10^5$). It must therefore be concluded that the second polymer was formed by free catalyst that was included within the matrix of the original polymer, not through continued polymerization by active end-groups on the preformed polymer. This, and other negative results obtained during similar attempts to form block copolymers, strongly suggest that these polymers contain no active end-groups. In addition, molecular weight data accumulated over time on polymers formed, using differing number of equivalents, do not show a correlation between the molecular weight and the number of equivalents used. It must therefore be concluded that although narrow molecular weight materials are obtained in protic solvents, these ruthenium-catalyzed reactions are not living. The narrow distributions and high molecular weights in these systems are thus ascribed to a fortuitous lack of facile termination steps, and to the inactivity of the propagating carbene with respect to the acyclic double bonds, which esentially eliminates chain transfer steps. Once a chain is initiated in these aqueous systems, it continues to propagate at a rapid rate in polymer particles containing high concentrations of monomer, unchecked by either chain transfer or termination steps.

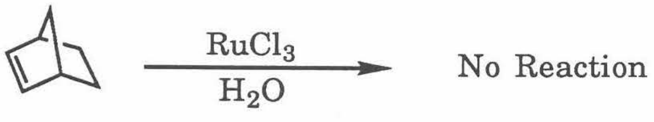
With the one exception of high concentrations of strongly coordinating ligands, these aqueous metathesis polymerizations are fairly tolerant of additives in the solution. For example, in the presence of excess Cl^- ligand (CsCl 0.15 M, 2 equivalents of Cl^- based on Ru), the polymerization of **VIII** proceeds with a normal initiation time to produce Poly **VIII** with a molecular weight equal to samples made in deionized water. The yield of polymer, however, is diminished from the near quantitative value obtained in deionized water, to only 34%. Salt concentrations much higher than this exert even more detrimental effects. If the Cl^- ion concentration is increased to 0.45 M, no polymerization occurs. When studying various polymerization effects in solutions of increasing ionic strength, caution must be used, as there is a tendency for the partially water-soluble monomers to "salt out" of the aqueous solution.

Two surfactants, one ionic, and one non-ionic, have been successfully utilized in conjunction with $RuCl_3$. Triton X-100^{TM}, a non-ionic polyether surfactant (CMC = 0.29 mM), and sodium dodecyl sulfate (SDS) (CMC = 1-2 mM) do not appear to deactivate the catalyst. Both surfactants appear to promote the formation of very high molecular weight materials possessing low polydispersities. Poly **VIII** synthesized in the presence of 0.25 M Triton X-100 displayed average molecular weights of $M_w = 9.87 \times 10^5$ and $M_n = 8.76 \times 10^5$, with a PDI = 1.13. Poly **VIII** synthesized in the presence of SDS (0.16M) possessed an even higher molecular weight ($M_w = 1.34 \times 10^6$), and a similar polydispersity.

The pH of the reaction medium was found to exert a profound effect on the initiation rates. In general, these polymerizations are inhibited in environments of both low pH (*ca.* <3), and especially high pH (*ca.* >7). The optimum pH range, as evidenced by the shortest initiation periods, is between 4 and 5. In the presence of K_2RuCl_5, monomer **VIII** (0.63 M) initiates in 243 ± 5 seconds at neutral pH. Under the same conditions, but at pH = 4.2 (5% $H_2PO_4^-$), initiation occurs in only 35 ± 5 seconds. With $RuCl_3$, the initiation rate is increased by about 66%, by lowering the pH from neutral to slightly acidc (pH = 5.3, HSO_4^-/SO_4^{2-}). The most rapid catalyst deactivation occurs in basic solutions, which appear to promote detrimental redox reactions with the metal complexes. More exact quantitative data over a large pH range are difficult to obtain because of the ambiguity introduced when using solutions containing different ionic buffer components. It is possible, and indeed likely, that common buffer components such as acetate ion may coordinate to, or react with, the ruthenium centers, thereby altering their reactivity in ways not specifically related to pH.

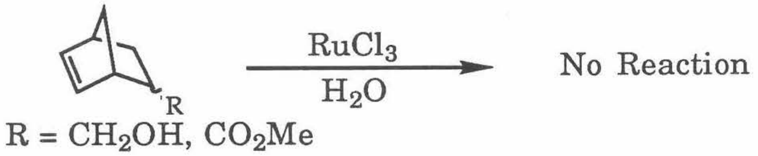
B. Aqueous Norbornene Polymerizations Initiated by the 7-Oxanorbornenes.

The the ease with which these aqueous 7-oxanorbornene polymerizations proceed is illustrated by comparison with the results obtained in parallel reactions with norbornene and norbornene derivatives. From a synthetic viewpoint, it was desirable to expand the versatility of these water-based emulsion reactions through the polymerization of other monomers. Unlike **VIII**, when norbornene is heated to 55 °C with $RuCl_3$ in aqueous solution, no reaction occurs. Extending the reaction times to over one week and increasing the reaction temperatures to 75°C, do not alter these negative results (Equation 5).



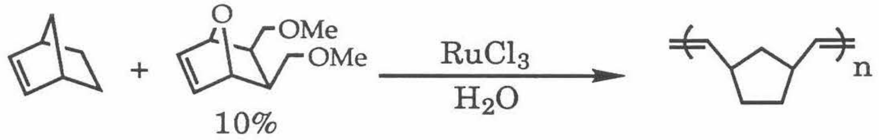
(5)

Obviously, the very poor solubility of norbornene in water contributes to this negative result. However, switching to norbornene derivatives substituted with water-solubilizing groups such as norbornene-5-methanol and 5-carbomethoxynorbornene still does not produce any polymer[25] (Equation 6).



(6)

Only after the addition of the surfactant SDS was norbornene finally induced to polymerize, albeit excruciatingly slowly, and in low yields. After *one week* at 55 °C, in the presence of SDS, a 16% yield of polynorbornene was obtained. Contrasting this result with **VIII**, which gives nearly 100% yields of polymer in 30-35 minutes, one can see the wide gulf that separates the aqueous reactivity of these two monomers. This reactivity difference can, however, be put to good use by introducing small amounts of **VIII** (*ca.* 5-10%) as an initiator for the polymerization of norbornene in an aqueous solution. When norbornene is allowed to react with $RuCl_3$ in an aqueous solution containing **VIII** (10% based on norbornene), polynorbornene is obtained in 50-60% yields (Equation 7).



(7)

According to the evidence provided by ^1H NMR, ^{13}C NMR and IR, the polynorbornene obtained in this fashion contains no detectable amounts of incorporated **VIII**. It is therefore surmised that **VIII** is present only in very small amounts as end-groups. Throughout these mixed monomer initiation systems, there appears to be an operable concentration range for the initiator, **VIII**. When the concentration of **VIII** is too low, (*ca.* < 5%), no polymerization occurs; If the concentration is too high (*ca.* >10%), homopolymerization (in low yields) of **VIII** dominates the reaction. A two-phase emulsion model can be used to describe these systems. Monomer globules of norbornene comprise one phase, while the aqueous phase contains both the $RuCl_3$ and **VIII**. Initiation occurs in the aqueous phase through reaction between the $RuCl_3$ and **VIII**. The resulting Ru complex, rendered more lipophilic by the addition of **VIII**, migrates into the norbornene globules, where homopolymerization of norbornene the proceeds. As in any of these ROMP systems, if the concentration of **VIII** is too low, no initation occurs. If, however, the concentration of **VIII** is too high, then its homopolymerization in the aqueous phase is rapid, and the Poly **VIII** formed precipitates from solution before appreciable migration into the norbornene globules can occur. This model is in agreement with the observed reactivity differences between norbornene and the 7-oxanorbornene monomers in aqueous solution. In aqueous competition experiments between **VIII** and norbornene (using SDS to minimize solubility effects), monomer **VIII** is found to be more reactive. A polymerization run with SDS using a 50/50 mixture of norbornene and **VIII**, gave a copolymer containing only 23% norbornene. This reactivity-ranking, **VIII** > norbornene, is the exact reverse of that observed using the same catalyst in organic solvents. (Copolymers obtained from 1/1 mixtures of norbornene/**VIII** in C_6H_6/EtOH are typically richer in norbornene by 10-15%). Solubility differences, even in the presence of a surfactant, cannot be ruled out as one way to account for these inverted reactivity ratios. An alternative explanation, however, was suggested by later work in which, under these polar conditions, the 7-oxanorbornenes were found to form π-complexes with the ruthenium centers far more readily than did the norbornene derivatives (*vide infra*).

C. Recycling the Aqueous ROMP Catalysts.

An important issue in any type of catalysis reaction is the degree of recyclability of the catalyst.[26] This is particularly true of transition-metal catalyzed reactions in which a considerable amount of time and money may be expended in just the catalyst preparation alone.[27] Unfortunately, the living preformed carbene and metallacycle catalysts discussed in Chapters 1 and 3, are not recyclable. Neither are the two component "classical" ROMP catalysts, such as $WCl_6/AlEt_2Cl$. It was felt, however, that these single component ruthenium catalysts may, in fact, be good candidates for recyclability studies. As a test case, the recyclability of $Ru(H_2O)_6(tos)_2$ (tos = p-toluenesulfonate)[28] in the polymerization of norbornene was examined. In methanol, the initiation time for this very active catalyst (*vide infra*) is 55 ± 5 seconds at 50 °C. The polynorbornene produced precipitates as it is formed, leaving behind the used catalyst solution. This solution was cooled down, the polymer removed, and a second aliquot of monomer was added to the catalyst solution. Upon reheating, polymerization was again observed, with the same initiation time as the first run (47 ± 5 seconds). This indentical batch of catalyst was recycled four times without any detectable loss of activity (Figure 3). It appears from this study that these ruthenium based catalysts are truly recyclable.

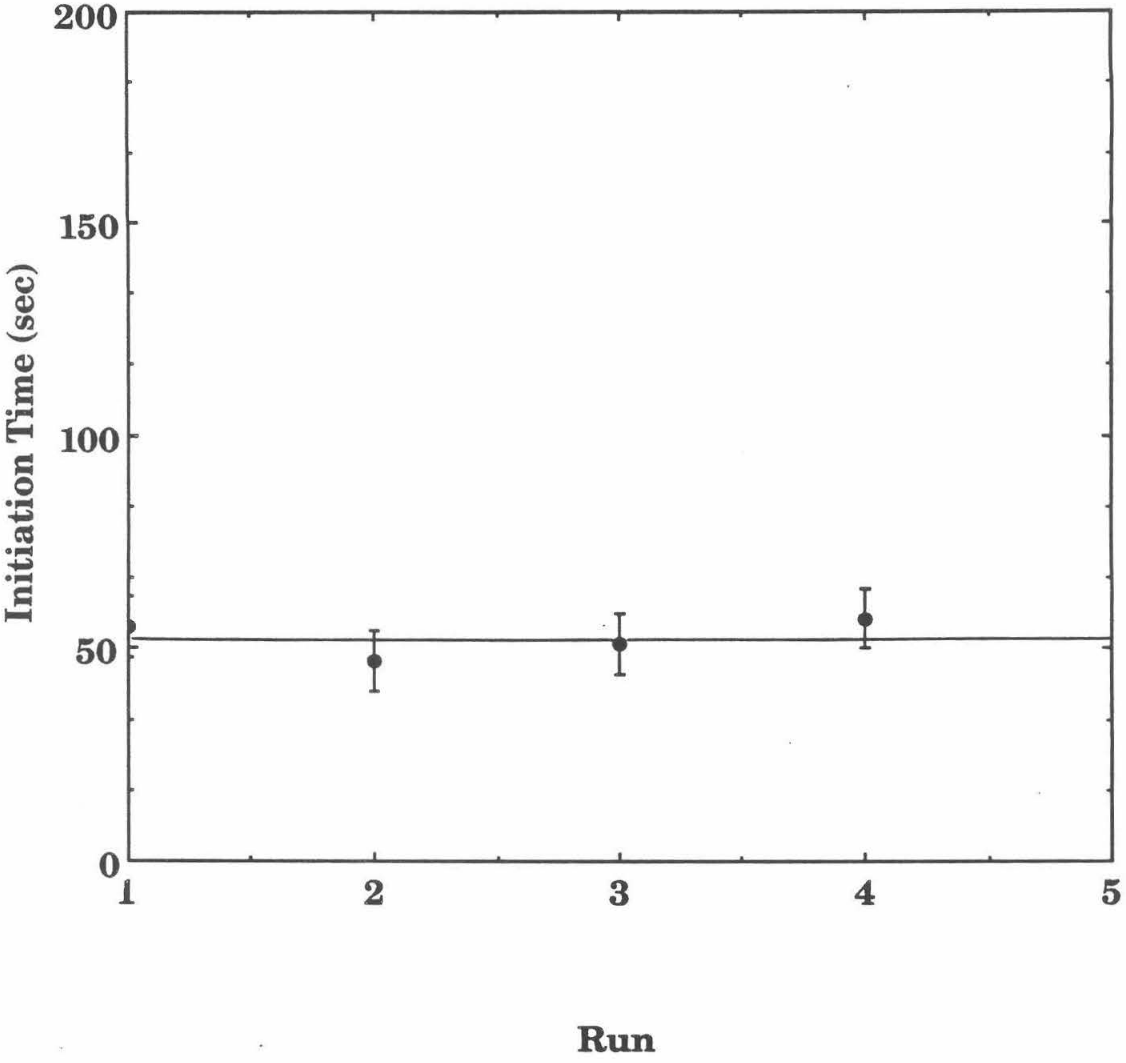


Figure 3: The initiation times (seconds) for a series of norbornene (1.02M) polymerizations in CH_3OH, using recycled $Ru(H_2O)_6(tos)_2$ (0.021M) as the catalyst at 55 °C.

Unlike the red-black organic catalyst solutions of $RuCl_3$, the aqueous solutions used in polymerizing the 7-oxanorbornenes undergo dramatic color changes during the course of the reaction. $RuCl_3$ in either organic solvents or the initial aqueous solutions has a UV/Vis spectrum, which displays a series of absorptions appearing as a broad envelope starting below 200 nm and tailing past 750 nm (Figure 4). During polymerizations of norbornene or 7-oxanorbornene derivatives in organic solvents, no major spectral changes are observed. When monomer **VIII** (1.26 M) is added to an aqueous solution of $RuCl_3$, however, and warmed to 50 °C, an intense purple color appears just before the onset of polymerization (approximately 30 minutes.) The visible spectrum of this solution has three major absorptions at 318, 488 and 561 nm (Figure 4). The formation of the purple complex(es) appears to be catalyzed by the 7-oxanorbornene monomer, with the rate of formation being dependent on the monomer's concentration. (No similar color changes result from heating aqueous solutions containing only $RuCl_3$.) The simple monomeric aquochloro ruthenium(III) complexes all have shorter wavelength absorptions. ($RuCl_4(H_2O)_2^-$, $\lambda_{max} = 269$; $RuCl_3(H_2O)_3$, $\lambda_{max} = 322$; $RuCl_2(H_2O)_4^+$, $\lambda_{max} = 376$; $RuCl(H_2O)_5^{2+}$, $\lambda_{max} = 456$ nm.)[29] Long wavelength absorptions are observed, however, for polynuclear ruthenium species. An intermediate purple ruthenium species, $\lambda_{max} = 563$ nm, has been reported, which decomposes rapidly in acidic media.[30] This complex was first proposed to be $Ru(OH)_2Cl_2(H_2O)_2$, and was later characterized as the neutral aquochloro-analogue of Ru Red, $[Ru_3O_2Cl_6(H_2O)_6]$ (Ru Purple).[31] Based on its visible spectrum, the complex corresponding to the absorption at $\lambda_{max} = 561$ nm is tentatively identified as Ru Purple. Separations on cation exchange columns confirm that it is the neutral complex. As expected from allusions in the literature to Ru

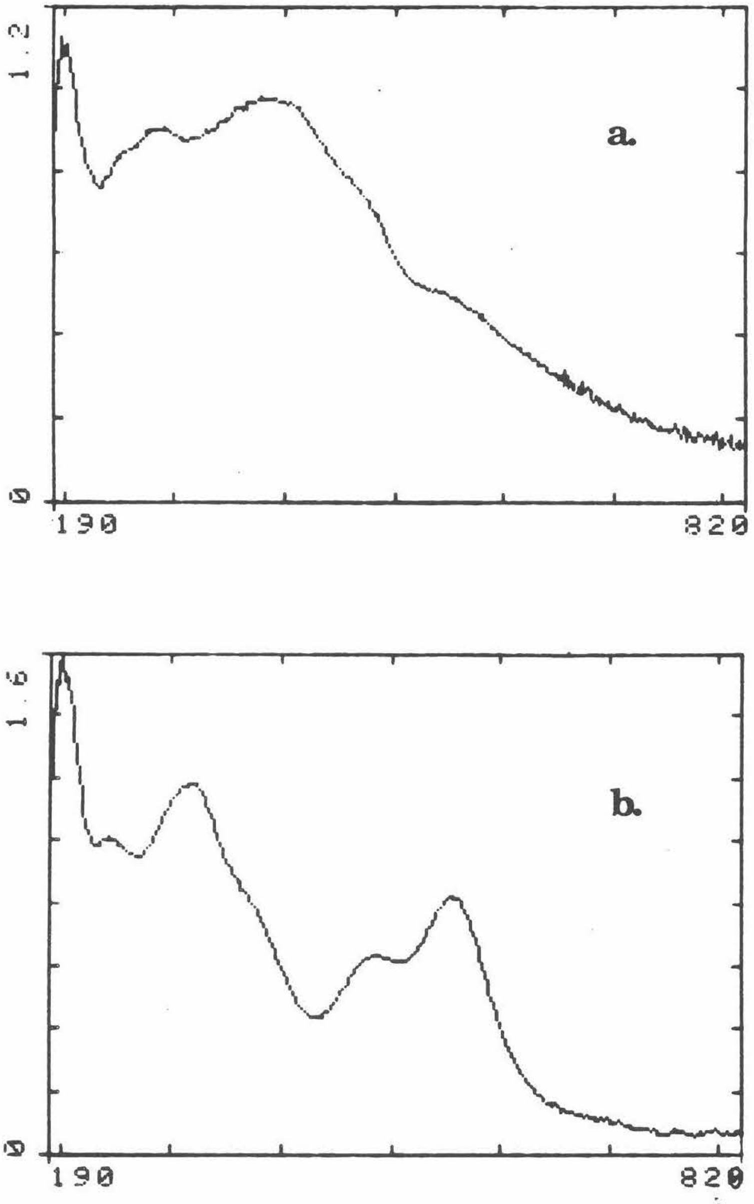


Figure 4: The UV/Vis spectra of a $RuCl_3$ in H_2O: (a) Initial; (b) obtained after polymerization of monomer **VIII**.

Purple's instability in acidic media,[30] the 561 nm absorption band disappears when these purple solutions are treated with 5% HCl.

Following the procedure outlined above for the norbornene polymerizations, the recyclability of these purple solutions resulting from the 7-oxanorbornene polymerizations were examined. A 1.05 M solution of **VIII** gave an initial initiation time of 37.5 minutes at 55 °C. Following this initiation period, the forming Poly **VIII** rapidly precipitates from the purple aqueous solution. Recycling this solution led to some surprising results. The initiation time for the second run dropped from the original 37.5 minutes down to 8.25 minutes. Recycling this catalyst solution once again, an initiation period of less than one minute was measured. By the fourth polymerization, the initiation time was reduced to only 10-12 seconds. When used in aqueous solution for the polymerization of **VIII**, these ruthenium catalysts actually become more active with use. This increase in initiation rate is shown graphically in Figure 5. "Used" $RuCl_3$ solutions have been recycled up to 14 consecutive times without a detectable change in the initiation rate. Control experiments show that heating aqueous $RuCl_3$ solutions containing no monomer actually results in a slight deactivation of the catalyst. (On two occasions, preheated $RuCl_3$ solutions failed to give any polymer at all.) Recycling the aqueous ruthenium catalysts results in a rate enhancement of nearly 8000 fold when compared with the initiation rates measured for the same polymerization in dry organic solvents.[32] The molecular weight (M_w) of the polymer obtained from a series of polymerization runs using recycled $Ru(H_2O)_6(tos)_2$ is shown in Figure 6. These data indicate that the molecular weight remains constant over repeated recyclings of the catalyst solutions. The fact that the initiation rate increases without an attendant decrease in the molecular weight, is a clear

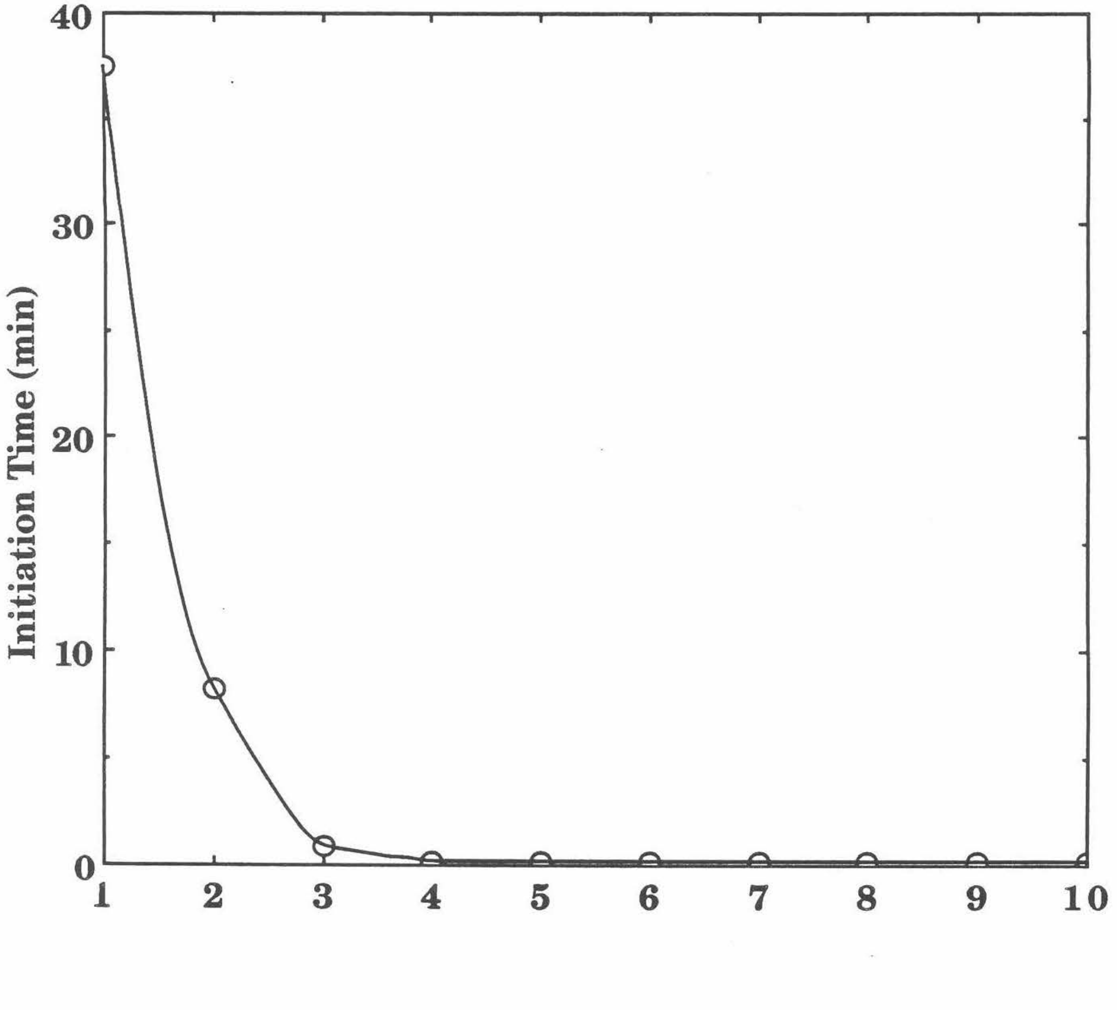


Figure 5: The initiation times (minutes) for a series of polymerizations of **VIII** (1.05M) in H_2O, using recycled $RuCl_3$ (0.099M) as the catalyst at 55 °C.

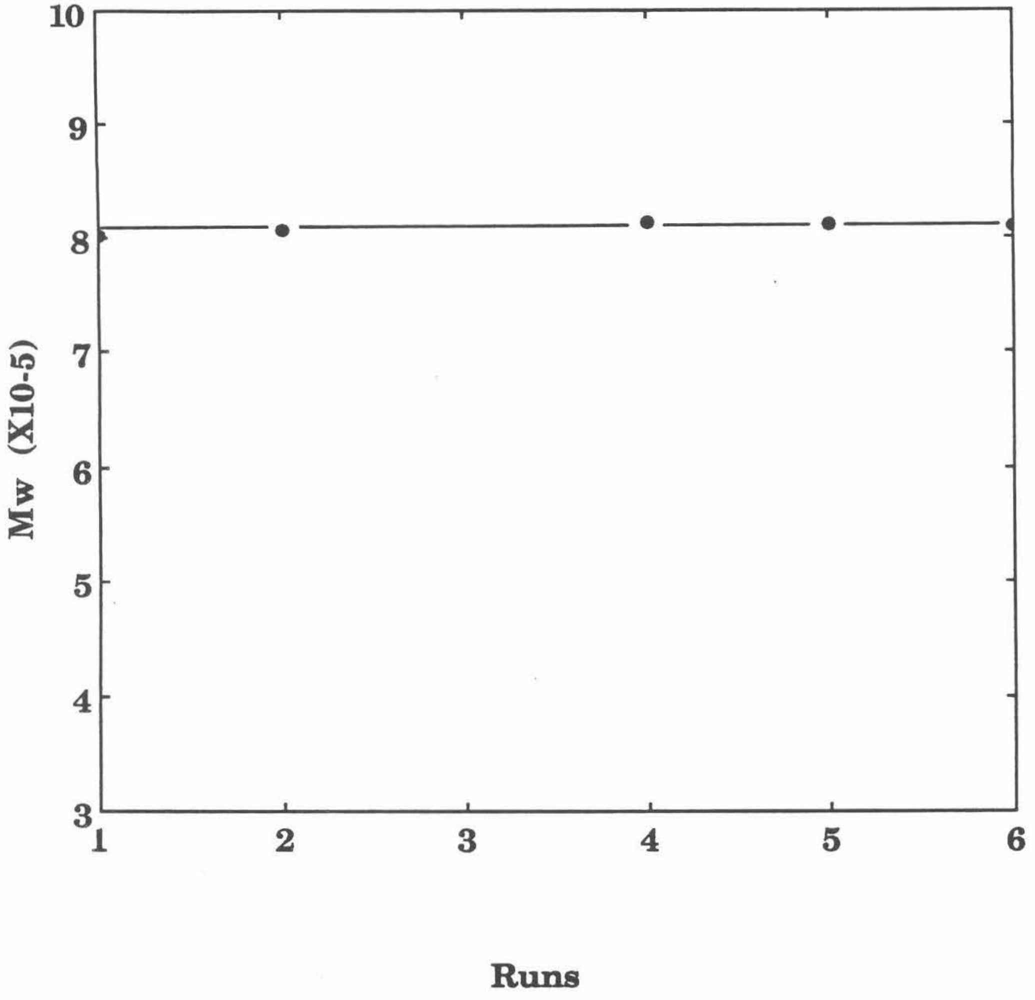


Figure 6: The molecular weights (M_w) for a series of Poly **VIII** samples obtained using recycled $Ru(H_2O)_6(tos)_2$ as the catalyst, in H_2O at 55 °C.

indication that the propagation rate is still several orders of magnitude greater than these accelerated initiation rates.

Although the initiation rate remains constant, the actual yield of polymer diminishes somewhat after repeated uses of the catalyst solution. This effect is presumably due to the continued loss of catalyst through inclusion in the product polymer, which is removed after every run. This raises an apparent contradiction: The physical loss of catalyst upon recycling affects the overall amount of polymer formed, but does not have any effect on the actual initiation time of the polymerization. Confirmation of an initiation rate independent of catalyst concentration was obtained through the appropriate kinetic runs.

Using monomer **XI**, the initiation times were measured as a function of $RuCl_3$ concentration at various fixed water levels (Figure 7). At low water concentrations (i.e., values less than the saturation level of 7-8% obtained from Figure 1), the rate of initiation increases with increasing Ru^{3+} concentration, until a maximum rate is obtained at 0.085 M. Increasing the concentration above this value actually has a deleterious effect on the rate (2.5% water curve in Figure 7). At water concentrations near the saturation value (5%), the same qualitative trend is seen; however, the effects are dampened considerably as evidenced by a decrease in the slope of the curve in both of the two regimes. At water concentrations above the saturation value (14.3%) the curve is becomes "flattened" in both regimes, exhibiting a rate essentially independent of the Ru^{3+} concentration. As these last data are collected above the water saturation concentration, this is tantamount to carrying out the reactions in pure water. It can also be seen from Figure 7 that the higher the water concentration, the faster the

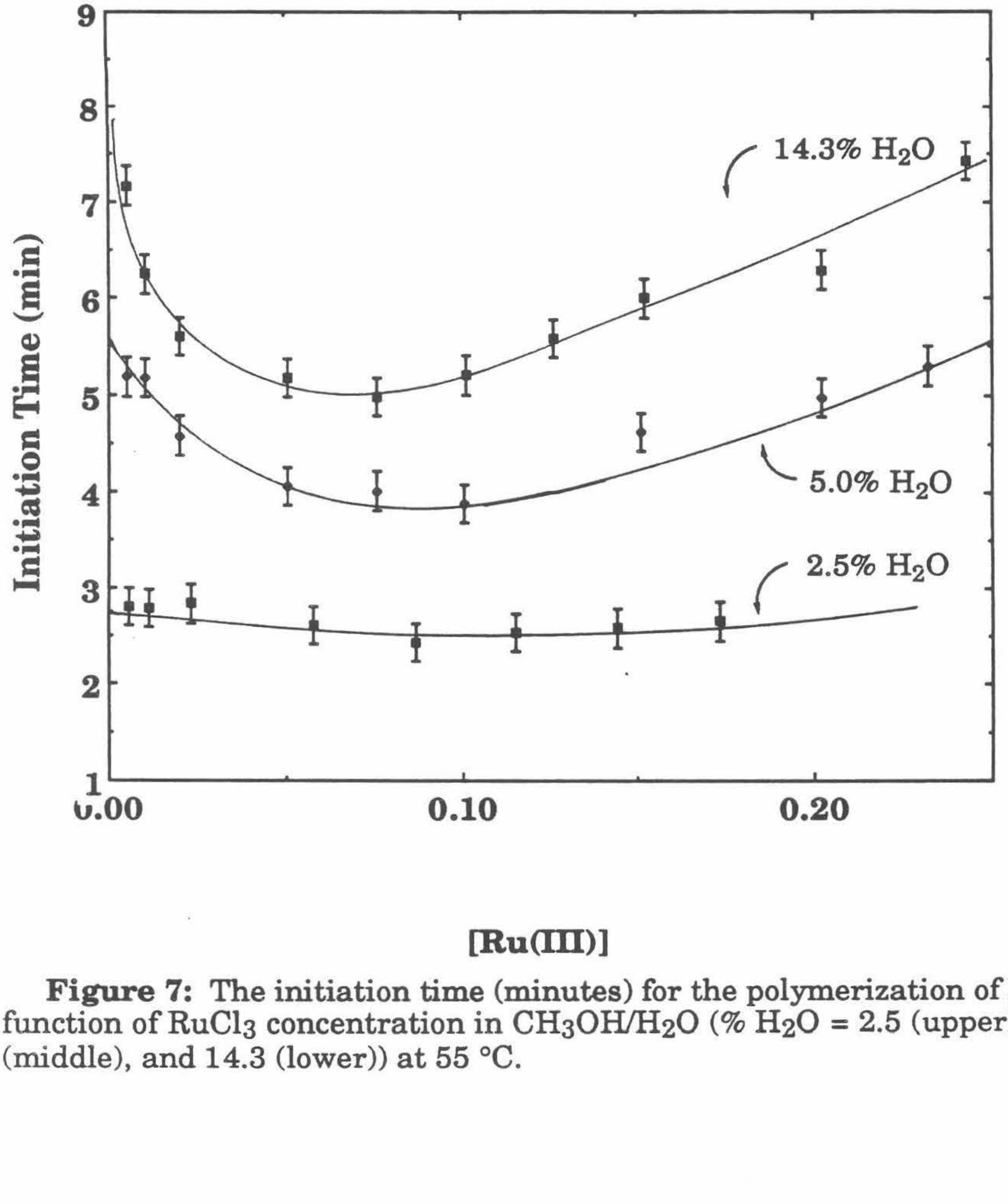


Figure 7: The initiation time (minutes) for the polymerization of **XI** as a function of $RuCl_3$ concentration in CH_3OH/H_2O (% H_2O = 2.5 (upper), 5.0 (middle), and 14.3 (lower)) at 55 °C.

rate in all of the kinetic regimes. This factor acts as an offset, generating the family of curves displayed in Figure 7.

The identification of the true active species in this complex aqueous mixture proved challenging. Cation exchange columns (Dowex 50X 2-400) provided evidence that the purple solution is actually comprised of several neutral and cationic species. (Anion exchange columns (Dowex 1X 2-400) showed no colored anionic components present in these reaction mixtures.) The neutral fraction isolated from the cation exchange column showed absorptions at 323 and 562 nm, which are assigned to $RuCl_3(H_2O)_3$ and $Ru_3O_2Cl_6(H_2O)_6$, respectively (*vide supra*). This neutral fraction typically gave initiation times with **VIII** between 4 and 5 minutes. Although more active than the original $RuCl_3$ solutions, these mixtures did not contain the most active species. Later polymerizations using well-characterized Ru^{3+} compounds exhibited very similar initiation times (*ca.* 3 minutes for K_2RuCl_5). None of the isolated fractions were able to reproduce the ultrafast initiation rates seen in the bulk recycled solution, i.e., 10-12 seconds. However, once the neutral purple fractions were recycled through a polymerization of **VIII**, they became activated and displayed these fast rates. It was noted that during these successive recycling experiments, the purple color slowly faded, leaving behind a yellow (*ca.* λ = 291 nm), but extremely active solution. In order to further investigate the origin of this rate enhancement, which resulted from recycling the catalyst, a number of well-characterized, water-soluble ruthenium complexes in various oxidation states were examined. For example, two well-characterized Ru^{3+} complexes, K_2RuCl_5 and $[Ru(NH_3)_5Cl]Cl_2$, were studied. In general, K_2RuCl_5 displays the same overall rate-enhancement behavior as does commercial $RuCl_3$, i.e., increasing activity upon successive recycling. Significant differences do exist, in that complexes comprised solely of Ru^{3+}, such as K_2RuCl_5, are far more active in the initial runs than the commercial $RuCl_3$. These initial differences are, however, quickly equalized through the recycling process, after which both systems show the same limiting initiation rates (i.e., 10-12 seconds), regardless of the original source of Ru^{3+}. This result strongly suggests that the observed polymerizations are due to chemistry of a Ru^{3+} species rather than some higher oxidation state impurity present in the $RuCl_3$. In the presence of K_2RuCl_5 (0.050 M) in H_2O, monomer **VIII** (0.50 M) displays an initial initiation time of approximately 3 minutes at 55 °C. Within the first minute of heating **VIII** with K_2RuCl_5, the orange solution (λ_{max} = 320 nm) turns dark red (UV/Vis spectrum shows long wavelength absorptions centered at approximately 520 nm). Control experiments show no color change when K_2RuCl_5 is heated in the absence of **VIII**. Following polymerization, the red color (λ = 520 nm) fades to yellow (the UV/Vis spectrum shows a new absorption at λ = 293 and the original K_2RuCl_5 absorption at 320 nm). Addition of more monomer (as little as 0.5 equivalent) to this yellow solution at room temperature causes the solution to turn red (ca. λ = 500 nm) once again. Heating this red catalyst/monomer mixture results in polymerization in approximately 10 seconds. Again, after the polymerization is completed, this red intermediate fades, leaving a yellow solution. The UV/Vis spectrum clearly shows the new absorption at λ = 293 nm increasing in intensity, and the K_2RuCl_5 absorption decreasing (λ = 320 nm). ^1H NMR studies (400 MHz, D_2O) of these red solutions formed from K_2RuCl_5 and 0.5 equivalent of **VIII** showed all of the monomer peaks paramagnetically shifted downfield (Δ_{ave} = +0.09 ppm), but no indication of any organic complex was detected.

Significant progress in uncovering the active species in these solutions was made when Ru^{2+}, rather than Ru^{3+}, species were examined. $Ru(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) was deemed an interesting candidate both because of its substitutionally labile hexa-aquo coordination sphere, and because of the convenient NMR handle provided by the tosylate counterion. Polymerization studies of **VIII** using $Ru(H_2O)_6(tos)_2$ revealed this complex to be exceedingly active. At 55 °C, with **VIII** or **XI**, initiation is quite rapid, occurring in less than one minute. Even at room temperature, the initiation of these monomers can be rapid. As was observed in the Ru^{3+} polymerizations, the recycled Ru^{2+} solutions also show enhanced activities. At room temperature, **VIII** (0.504 M), in the presence of $Ru(H_2O)_6(tos)_2$ (0.0037 M) shows an initiation time of 147 ± 5 seconds. Following polymerization, the resulting catalyst solution is yellow (λ_{max} = 294 nm). Addition of a second aliquot of **VIII** produces polymer with an initiation time of less than one minute. The high reactivity of $Ru(H_2O)_6(tos)_2$ with these monomers, coupled with the heterogeneous nature of the emulsion polymerization, makes the rate acceleration that is due to recycling difficult to quantify in these cases. It was discovered, however, that $Ru(H_2O)_6(tos)_2$ in methanol polymerizes monomer **IV** at an acceptable rate. The effect of recycling on the activity of the $Ru(H_2O)_6(tos)_2$/**IV** polymerization is shown in Figure 8. Two points should be emphasized. First, Ru^{2+} complexes are far more active than Ru^{3+} complexes. Secondly, as in the case of Ru^{3+}, the recycled Ru^{2+} catalysts become more active with use. This observation indicates that some other factor, in addition to reduction of Ru^{3+} to Ru^{2+}, is occurring during this recycling process, which serves to activate these catalyst solutions. At 55 °C, the recycled $Ru(H_2O)_6(tos)_2$ solutions show exactly the same initiation

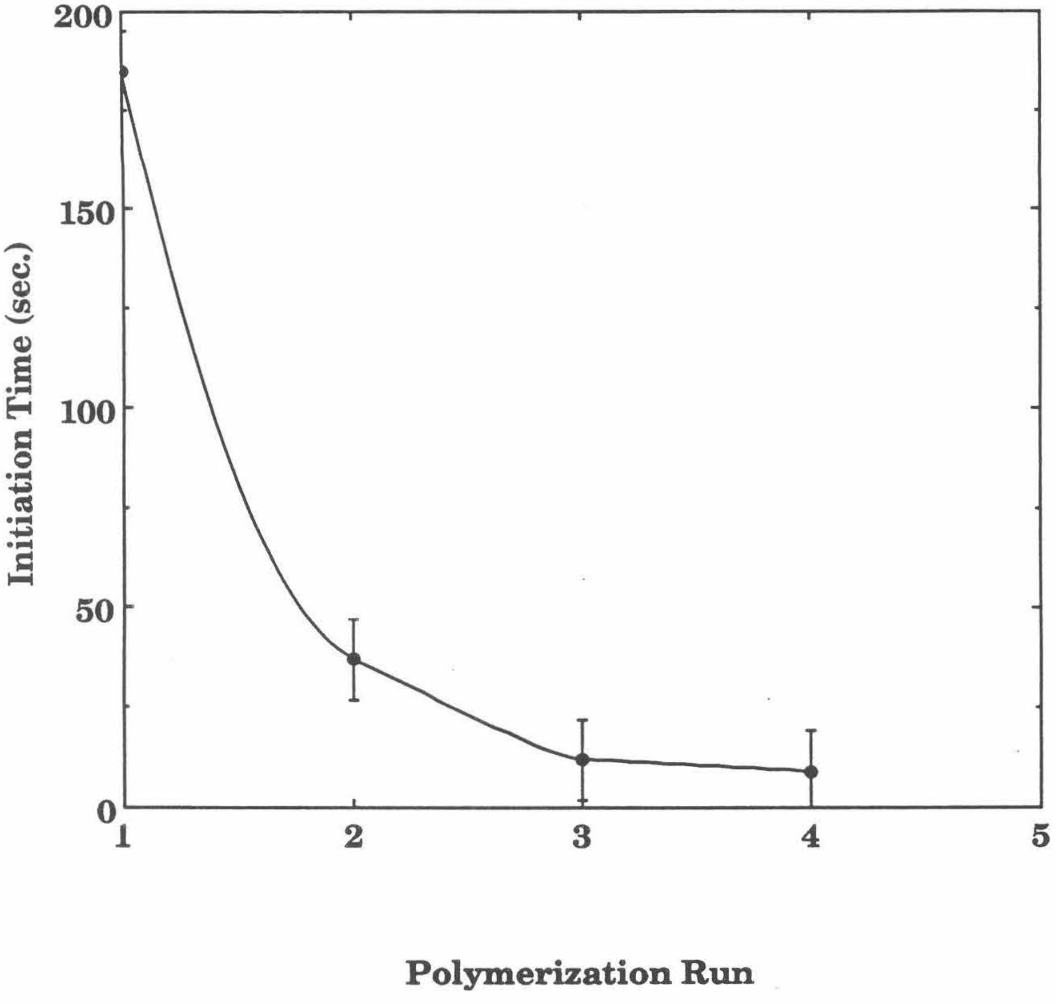
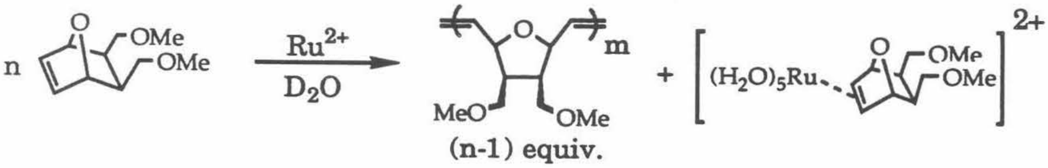


Figure 8: The initiation times (seconds) for a series of polymerizations of **IV** (0.973 M) in H_2O using recycled $Ru(H_2O)_6(tos)_2$ as the catalyst at room temperature.

times as the limiting initiation values observed, using the recycled Ru^{3+} catalysts. Just before the onset of polymerization in both the **IV** and **VIII** reactions, a red intermediate appears (λ = 285 and 411 nm), which subsequently vanishes during the polymerization. The visible spectrum of these extremely active yellow solutions (λ_{max} = 294 nm) correlates well with the most active recycled Ru^{3+} solutions (λ_{max} = 291 nm for the recycled $RuCl_3$ solution and λ_{max} = 293 nm for the recycled K_2RuCl_5 solutions).

When **VIII** (0.032 M, 0.61 equivalent based on Ru^{2+}) is allowed to react with $Ru(H_2O)_6(tos)_2$ (0.0414 M) at room temperature, no changes other than the slow disappearance of monomer are observed to occur by ^1H NMR (400 MHz, D_2O). After 40 minutes, only peaks assigned to residual monomer can be detected. Removal of the tube from the NMR probe reveals the expected polymer, and a solution identical in color to the original Ru^{2+} complex. No resonances associated with any intermediate can be detected. If, however, higher monomer concentrations are used, (0.80 M) and the reaction is heated to 55 °C for one hour, the resulting solution after polymerization is yellow (λ_{max} = 294 nm). By ^1H NMR (400 MHz, D_2O) (Figure 9), the clean conversion to a new compound, characterized as the 1:1 Ru^{2+}-**VIII** mono olefin adduct, is observed [33] (Equation 8).



(8)

This Ru^{2+}-**VIII** olefin adduct is characterized by an upfield shift of the olefinic proton signals from 6.25 to 5.08 ppm ($\Delta\delta$ = -1.17 ppm), and a downfield shift of the *endo*-proton signals from 1.77 to 2.54 ppm ($\Delta\delta$ = +0.77

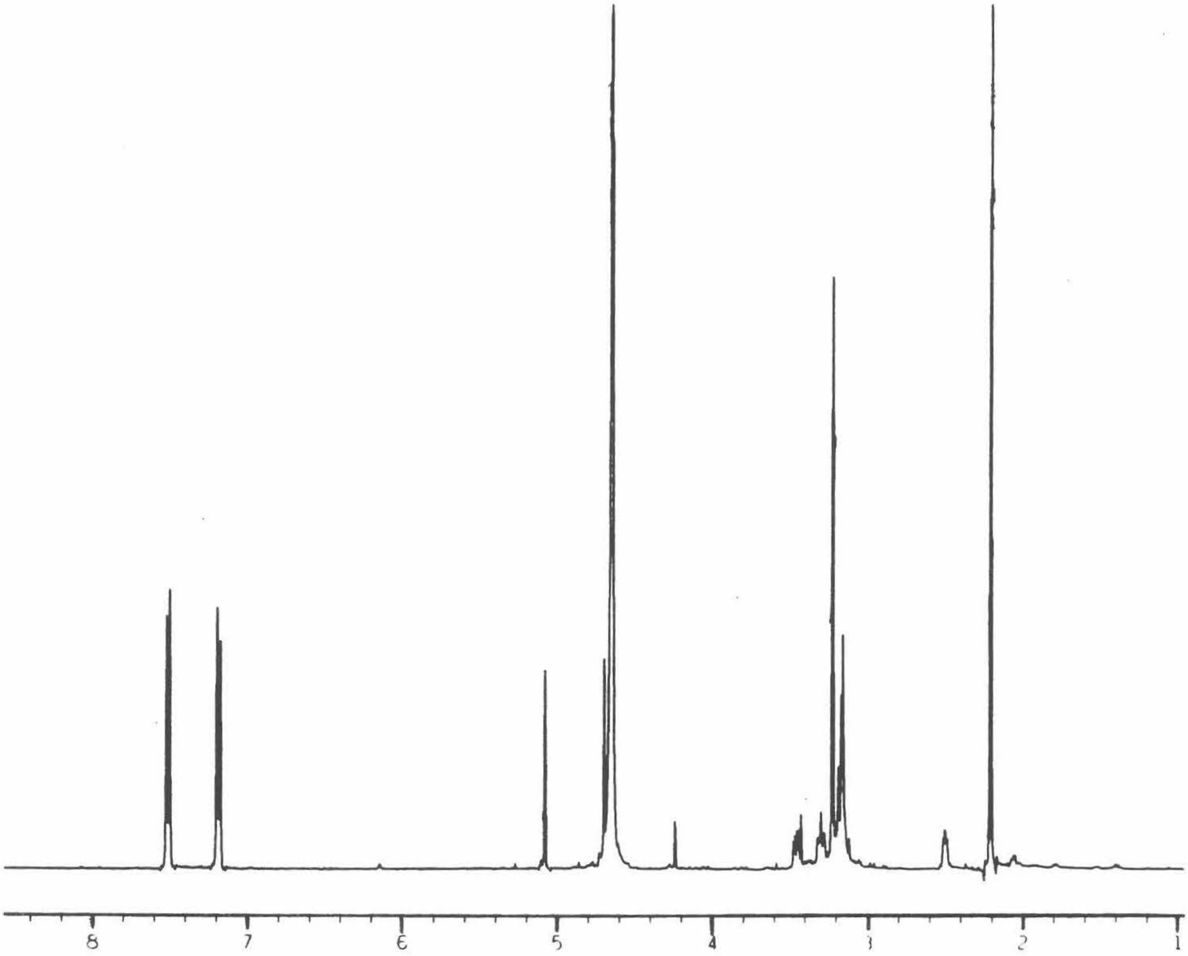
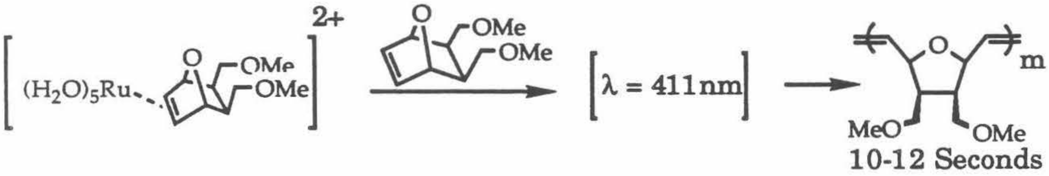


Figure 9: ^{1}H NMR (D_2O, 400 MHz) of Ru^{2+}-**VIII** generated *in situ* during the polymerization of **VIII** using $Ru(H_2O)_6(tos)_2$.

ppm). This assignment is confirmed by ^{13}C NMR, which reveals a shift of the olefinic carbons upfield from 135.16 to 84.61 ppm ($\Delta\delta$ = -50.55 ppm).[34] The complete chemical shift information is given in Table 2.

When the olefin adduct, Ru^{2+}-**VIII**, (λ_{max} = 294 nm) is allowed to react with excess monomer, polymerization is observed to occur in just under 10 seconds at 55 °C (Equation 9).



(9)

This initiation time is equal to the same limiting initiation times that are observed during the recycled Ru^{3+} polymerizations. As with the other Ru^{3+} catalysts, a red intermediate (λ_{max} = 411 nm) is observed just before the onset of polymerization. All attempts to observe this transient species by techniques other than visible spectroscopy have been unsuccessful. ^{1}H NMR at low temperatures (4.8 - 20.0 °C) of the reaction between Ru^{2+}-**VIII** (0.0526 M) and **VIII** (0.0526 M, 1 equivalent) shows no indication of the formation of any intermediates before polymerization is observed (approximately 1.5 hours at these temperatures and concentrations). This observation is consistent with the model in which only a very small amount of the Ru^{2+} is actually initiated and goes on to do the polymerization.

The red intermediate (λ_{max} = 411 nm) is more persistent when generated under an inert atmosphere (*vide infra*). Furthermore, in comparison with **VIII**, relatively long-lived red solutions can be generated during the polymerization of monomer **IV** with $Ru(H_2O)_6(tos)_2$. When used in subsequent polymerizations, these red catalyst solutions are, by far, the

		VIII		
^{1}H NMR:	**Assignment**	**Free**	**Bound**	**Δδ (ppm)**
	Olefin	6.28 (s)	5.08 (s)	-1.17
	Bridgehead	4.71 (s)	4.73 (s)	+0.02
	Methylene	3.37 (m)	3.44 (m)	+0.07
	Methyl ether	3.22 (s)	3.26 (s)	+0.04
	Endo H	1.77 (m)	2.54 (m)	+0.77
^{13}C NMR:	Olefin	135.16	84.61	-50.55
	Bridgehead	80.18	77.20	-2.98
	Methylene	71.80	71.49	-0.31
	Methyl ether	58.41	58.88	+0.47
	Methine	39.57	42.63	+3.06

Table 2: A comparison of the ^{1}H NMR (400 MHz, D_2O) and ^{13}C NMR (Proton-decoupled) (22.53 MHz, D_2O) chemical shifts of free **VIII** vs. **VIII** coordinated to $Ru^{2+}(tos)_2$. ^{13}C NMR of the olefin complex referenced to methyl signal of tosylate group: 21.25 ppm.

most active aqueous catalyst solutions yet discovered. At room temperature, using the pristine $Ru(H_2O)_6(tos)_2$ catalyst, **IV** (0.973 M), the solution turns red concurrently with initiation in 9.25 minutes. Recycling this red intermediate solution results in *the room-temperature polymerization of **IV** in just a few seconds.*

With the ^1H NMR and ^{13}C NMR resonances for the 7-oxanorbornene Ru^{2+}-olefin complexes confidently assigned, interpretation of the NMR data accumulated on the recycled Ru^{3+} systems became feasible. The ^1H NMR spectrum (D_2O) of the catalyst solution resulting from the polymerization of **VIII** with K_2RuCl_5, shows the same distinct olefin, bridgehead and *endo*-hydrogen resonances at 5.07, 4.72 and 2.58 ppm, respectively, as those observed in the Ru^{2+}-**VIII** complex. In addition, another set of resonances at 5.13, 4.75 and 2.45 ppm are also present. As Ru^{3+} is generally accepted as not forming stable olefin complexes,[20] we assign these two sets of resonances to two Ru^{2+}-olefin complexes that are generated *in situ* from Ru^{3+}. It is assumed that these two olefin complexes differ from one another in their ligand environments (i.e., maybe differing numbers of Cl^- and/or water ligands, or different geometric isomers). In an analogous fashion, the ^1H NMR spectrum (D_2O) of the catalyst solution obtained after polymerization of **VIII** with commercial $RuCl_3$ shows two sets of resonances similar to those found using K_2RuCl_5. The *in situ* formation of Ru^{2+}-olefin complexes in these catalysts solutions is corroborated by the appearance of new absorptions at $\lambda = 290\text{-}295$ nm, typical of Ru^{2+}-olefin species.[33]

The increased activity of these recycled Ru^{2+} and Ru^{3+} catalysts is attributed to: 1) The reduction of the Ru^{3+} to Ru^{2+} (when applicable); and 2) the *in situ* formation of Ru^{2+}-olefin complexes, which lie along the reaction coordinate leading to the active catalyst species. To date, no direct observation of the conversion of these olefin complexes to metal carbenes or metallacycles has been observed. The evidence that connects these olefin complexes to the observed polymerization chemistry is only circumstantial. Enhanced catalyst activity in recycled solutions is only realized under conditions in which the olefin complexes are generated. In recycled catalyst solutions in which no olefin complexes are formed, no enhanced activity is observed. These aqueous ROMP reactions that display enhanced activities seem to be the exception, rather than the rule. The only example of the former we have as yet uncovered is the Ru^{3+} or Ru^{2+} polymerizations of the 7-oxanorbornene monomers, **VIII** and **IV**, performed in aqueous solution. Examples of the latter showing no rate enhancement include the norbornene/$Ru(H_2O)_6(tos)_2$ polymerization cited earlier, and the aqueous polymerization of more reactive 7-oxanorbornene monomers containing anhydride and maleimide functional groups (*vide infra*). In addition, no rate enhancement of recycled solutions has ever been observed for polymerizations run in organic solvents. This phenomenon currently appears to be unique to prescribed aqueous 7-oxanorbornene reactions.

D. The Formation and Reactivity of the Ru^{2+}-VIII Olefin Adduct.

The observed rate enhancement of the initiation process is not the result of general Ru^{2+}-olefin complex formation, but is rather specific to the particular olefin bound. Cyclic olefin complexes, such as $Ru(H_2O)_5$(2,5-dihydrofuran)$(tos)_2$, and acyclic olefin complexes, such as $Ru(H_2O)_5$(allyl ethyl ether)$(tos)_2$, and $Ru(H_2O)_5$(diallyl ether)$(tos)_2$ have been prepared.[35] All of these type of complexes, however, show inhibited rather than enhanced initiation rates relative to the parent $Ru(H_2O)_6(tos)_2$ species. It is presumed that dissociation of the bound, spectator olefin must occur prior to formation of the 7-oxanorbornene olefin complexes.

Special kinetic factors appear to obtain, which allow for the formation of the Ru^{2+}-**VIII** complex. At low olefin concentrations, there is a large olefin dependence on the initiation rate (Figure 10). In this kinetic regime no build-up of the olefin complex occurs. At higher olefin concentrations, formation of the olefin complex is observed in water. This formation is thought to be connected with the heterogeneous nature of these aqueous polymerizations. Under the same conditions, but using methanol as the solvent, the polymer remains in solution throughout the polymerization. In this case, however, no olefin adducts are observed. In water, when polymer first forms, it precipiates out as a heterogeneous matrix, which fills the volume occupied by the solvent. The monomer, as well as unreacted metal salts, are concentrated within this matrix. At this point, it is thought that the rate of polymerization slows down, allowing for the build-up of the intermediate olefin adduct. This play-off between the rate of polymerization, and the rate of olefin complex formation, is critical in determining the yields of Ru^{2+}-**VIII**. Conversion to Ru^{2+}-**VIII** has been observed to vary from 100% down to *ca.* 30%, seemingly dependent on these competitive rates. Carrying out the polymerization at room temperature (to minimize the initial rate of polymerization), and then heating at 50 °C after the solid matrix has formed, provides near quantitative conversion of the Ru^{2+} to the olefin adduct. When the polymerization is run at higher temperatures (60 °C), the rate of polymerization is fast enough to consume too much of the monomer, precluding the quantitative formation of the

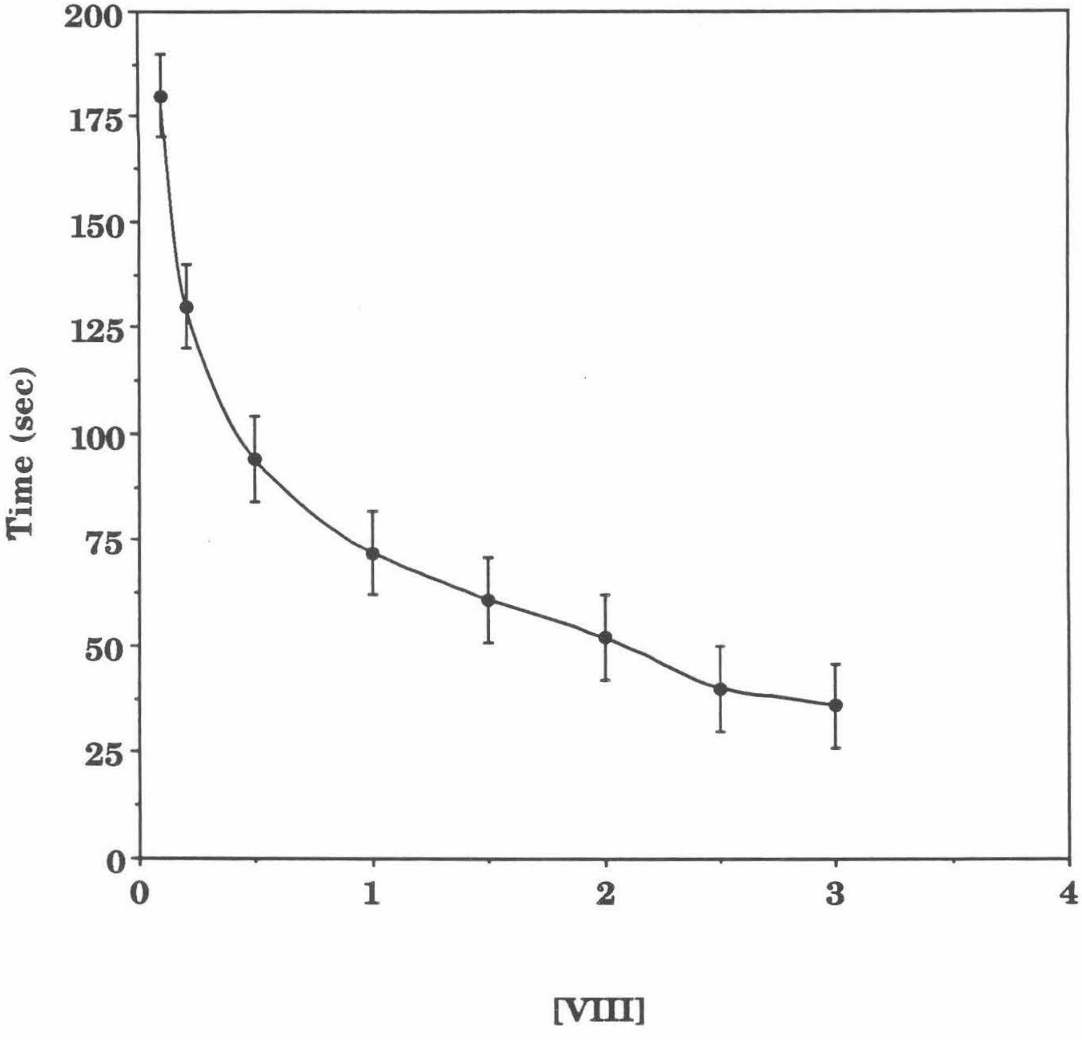
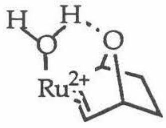


Figure 10: The initiation time (seconds) as a function of monomer concentration for the polymerization of **VIII** using $Ru(H_2O)_6(tos)_2$ (0.011 M) in D_2O.

olefin adduct. For example, when 9 equivalents (based on Ru^{2+}) of **VIII** are allowed to react with $Ru(H_2O)_6(tos)_2$ at 60 °C for 6 minutes, only 0.21 equivalent of monomer remains, and a 42.1% conversion to the olefin adduct is observed (the rest of the monomer having been converted to polymer.)

The formation of a heterogeneous matrix is not the only requirement for olefin adduct formation. Under conditions similar to those used for the formation of Ru^{2+}-**VIII**, poly(norbornene) will precipiate (from methanol), and form a similar heterogeneous matrix. However, no analogous norbornene olefin adduct is ever observed to form under these, or any other conditions. (As a result, no enhanced activity is observed for these recycled solutions.) At least two factors may be involved to account for the differences observed between these two monomers under similar conditions. It may be that the rate of conversion of olefin adduct to the active species is much faster in the case of norbornene, so that no build-up of the olefin adduct is ever observed. Alternatively, monomer **VIII** may form olefin adducts more readily than norbornene. This could arise through stabilization of the complex by chelation of the ruthenium center, using the 1,4-bridging epoxide and the olefin moiety.



At least one iron-7-oxanorbornene olefin complex, $Fe(CO)_4(\mathbf{X})$ (**X** = 1,4-epoxy-1,4-dihydronaphthalene), is known, which shows interaction between the 1,4-bridging epoxide and the carbon of the axial carbonyl ligand on the iron.[36] Currently, not enough data are available to determine the importance, if any, of these factors on olefin adduct formation.

In the absence of a reducing agent, the reduction is thought to occur through a disproportionation process (Equation 10).

$$2\,Ru^{3+} \longrightarrow Ru^{2+} + Ru^{4+} \qquad (10)$$

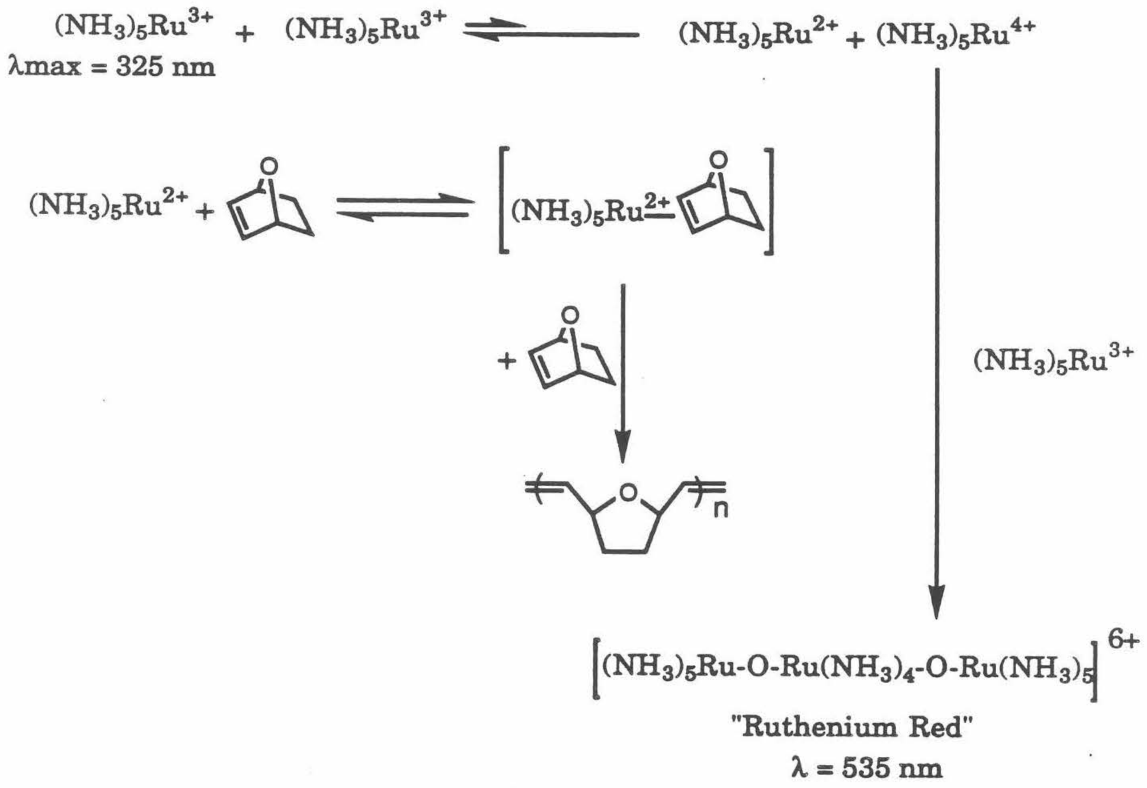
From the reduction potentials (Ru^{4+}/Ru^{3+},+0.49 V; and Ru^{3+}/Ru^{2+}, -0.11 V),[37] the equilibrium amounts of Ru^{2+} and Ru^{4+} formed through the disproportionation of a 0.01 M Ru^{3+} solution, can be estimated to be on the order of 4×10^{-7} M. This low concentration of Ru^{2+} indicates that the 7-oxanorbornene olefin may act to drive this equilbrium. In order to determine whether the proposed disproportionation is actually occurring during the initiation steps, a "Ru^{4+} trap" was incorporated into the system. It is known that Ru^{4+} generated in the presence of excess $Ru(NH_3)_5{}^{3+}$ rapidly forms the mixed valent ruthenium-oxo trimer, Ruthenium Red, $[Ru(NH_3)_5ORu(NH_3)_4ORu(NH_3)_5]^{6+}$ (λ_{max} = 532 nm with Cl^- counterions).[38] When **VIII** (0.47 M) is allowed to react with $[Ru(NH_3)Cl]^{2+}$ (0.065 M) (λ_{max} = 325 nm) at 60 °C in aqueous solution (D_2O) under argon, an intense red color (λ = 535 nm) is noted after approximately 4.5 hours. The onset of polymerization occurs virtually simultaneously with this color change. The new visible absorption at 535 nm is assigned to Ru Red. Control experiments carried out show that $Ru(NH_3)_5Cl^{2+}$ can be heated at 60 °C for more than 15 hours in the absence of olefin, with no formation of Ru Red.

Polymerizations performed with this recycled, dark-red solution display initiation times of approximately 10-15 minutes. Regardless of the number of times the red solution is recycled, the ultrafast initiations seen above are not reproduced. Consistent with the earlier analysis, no Ru^{2+}-olefin complexes are observed to form, as evidenced by ^1H NMR (400 MHz, D_2O). Using the literature extinction coefficient for Ru Red, $\varepsilon = 21{,}000$,[31] it can be calculated from the intensity of the $\lambda = 535$ nm absorption that less than 1% of the Ru^{3+} is oxidized to Ru^{4+} (0.71% and 0.94% from runs one and two, respectively). This calculated value provides an upper limit to the amount of catalyst activated.

A proposed mechanism for this disproportionation-initiation process is shown in Scheme **I**. This mechanism suggests that the disproportionation equilbrium is driven to the right by the reversible capture of Ru^{2+} by the 7-oxanorbornene olefin. Once formed, the Ru^{4+} is trapped by the excess Ru^{3+}, forming Ru Red, while the Ru^{2+}-olefin complex goes on to initiate the polymerization. The coordination of the olefin to the Ru^{2+} center is thought to be reversible under these conditions because of the absence of any olefin complex at the conclusion of the reaction. The overall disproportionation equilibrium is, however, irreversible because of the formation of Ru Red. Alternatively, the mechanism could be written with the formation of an equilibrium amount of Ru^{3+}-olefin complex, which then disproportionates with a second Ru^{3+} ion. This alternative mechanism is not considered as likely because it necessitates the invoking of a very unstable Ru^{3+}-olefin complex. Beyond the fact that there are no known Ru^{3+}-olefin complexes,[20] oxidation of Ru^{2+}-**VIII** results in the immediate dissociation of the olefin ligand (*vide infra*).

In the course of studying the $RuCl_3$-catalyzed polymerizations of **VIII**, it was discovered that the reaction initiates and propagates with very comparable rates, regardless of whether it is conducted under an atmosphere of argon or an atmosphere of air. Furthermore, the recycled

Scheme I:


$(NH_3)_5Ru^{3+}$ + $(NH_3)_5Ru^{3+}$ ⇌ $(NH_3)_5Ru^{2+}$ + $(NH_3)_5Ru^{4+}$
λmax = 325 nm
$(NH_3)_5Ru^{2+}$ +
O
$(NH_3)_5Ru^{2+}$
+
n
$(NH_3)_5Ru^{3+}$
$[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]^{6+}$
"Ruthenium Red"
λ = 535 nm

$RuCl_3$ solutions may be stored overnight under an atmosphere of air, without any appreciable loss of activity (i.e. initiation times may increase from the 10-12 second range to the 40-60 seconds range overnight). Storage over 24 hours tends to increase the initation times significantly (*ca.* 7 minutes after 48 hours); however, once reused, these solutions again become activated, displaying accelerated initiation rates. At the time, the metal-oxo mechanism was under more serious consideration, and this result was therefore not too surprising. In retrospect, however, now that more credence is placed in the Ru^{2+} mechanism, this tolerance of oxygen is actually quite unexpected. In this regard, it is important to note that while these ruthenium catalysts will tolerate oxygen over the course of several successive polymerizations, they are not entirely inert towards it. Bubbling oxygen through an aqueous $RuCl_3$ solution (0.01 M) containing **VIII** (1.05 M) for 5 minutes at room temperature, followed by 15 minutes at 55 °C, results in the appearance of the purple solution (λ = 561 nm); however, no polymerization is observed. Clearly, high concentrations of oxygen deactivate the catalyst. The deleterious effects of O_2 appear to be attenuated in the more reactive systems. Little oxygen dependence on either the initiation time, polymer yield, molecular weight or molecular weight distribution is observed for the polymerization of **VIII** or **XI**, using $Ru(H_2O)_6(tos)_2$ or $RuCl_3$. The presence of oxygen becomes more critical when a less reactive monomer or catalyst is used. For example, using the relatively unreactive $Ru(NH_3)_5Cl^{2+}$ as a catalyst, the molecular weight of Poly **VIII** is reduced by 26% (M_n = 213,000 vs. 158,000), and the polydispersity broadens by about 4% (2.70 vs. 2.80) when the reaction is run under an atmosphere of air. During the polymerization of unreactive monomers with slow initiation or propagation rates, the deactivation by O_2

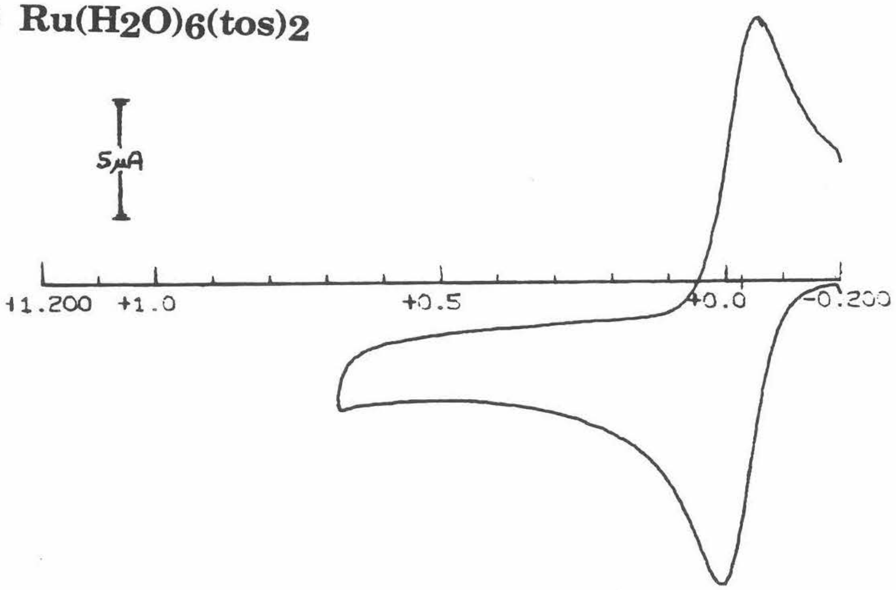
becomes a more competitive process. In examining the polymerization of the unreactive monomer, *exo*-N-methyl-7-oxanorbornene-2,3-dimaleimide, **VIa**, it was found that the yields could be improved from approximately 10-20% under air, to nearly 100% by running under argon.[39]

Notwithstanding this moderate sensitivity to oxygen, the recycled solutions from $RuCl_3$, K_2RuCl_5 and $Ru(H_2O)_6(tos)_2$ appear to be remarkably sturdy, maintaining their activity through numerous recycling steps, all performed under an atmosphere of air (over 14 recycling runs using $RuCl_3$). Insight into the origin of this robust nature is derived from an examination of the cyclic voltammogram (CV) of Ru^{2+}-**VIII**. The CV of Ru^{2+}-**VIII** shows one irreversible Ru^{2+}/Ru^{3+} oxidation couple at 1.05 V versus SSCE (Figure 11). The π-backbonding afforded by the olefin ligand in this complex serves to stabilize the Ru^{2+} oxidation state by 1.08 V, relative to the free $Ru(H_2O)_6{}^{2+}$ ion in neutral solution.[40] This stabilization accounts for the fact that aqueous solutions of Ru^{2+}-**VIII** can be used and stored for short periods under air, with no appreciable loss of catalytic activity.

E. The Role of Water in Ruthenium ROMP Reactions.

As was seen in Figures 1 and 2, water acts as a cocatalyst during the initiation steps of ROMP reactions catalyzed by $RuCl_3$. Judging by our work with several ruthenium catalysts, this appears to be a general phenomenon for Ru^{3+} complexes. In the case of reactions involving Ru^{2+} complexes, however, a different result is obtained. The initiation rates for polymerizations using Ru^{2+} as the catalyst are independent of water concentration, as can be seen in Figure 12 for the polymerization of **XI** (0.948

a) $Ru(H_2O)_6(tos)_2$



b) Ru^{2+}-**VIII**

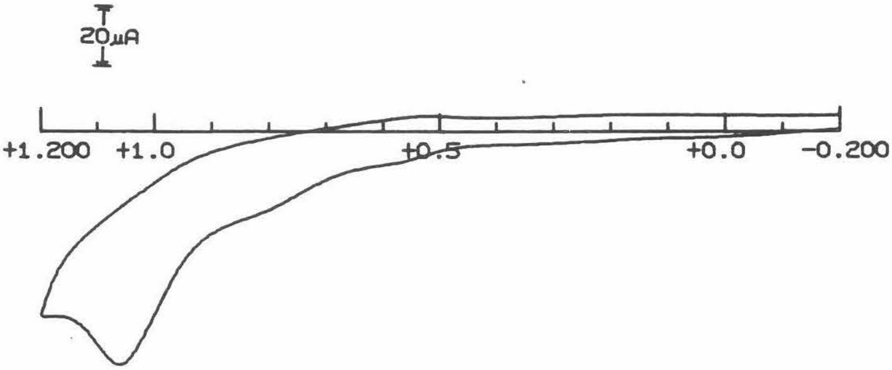


Figure 11: The cyclic voltammogram of: (a) $Ru(H_2O)_6(tos)_2$ in 0.10 M $Li(CF_3SO_3)$; and (b) Ru^{2+}-**VIII** in 0.10 M $Li(CF_3SO_3)$. Potentials are relative to SCE.

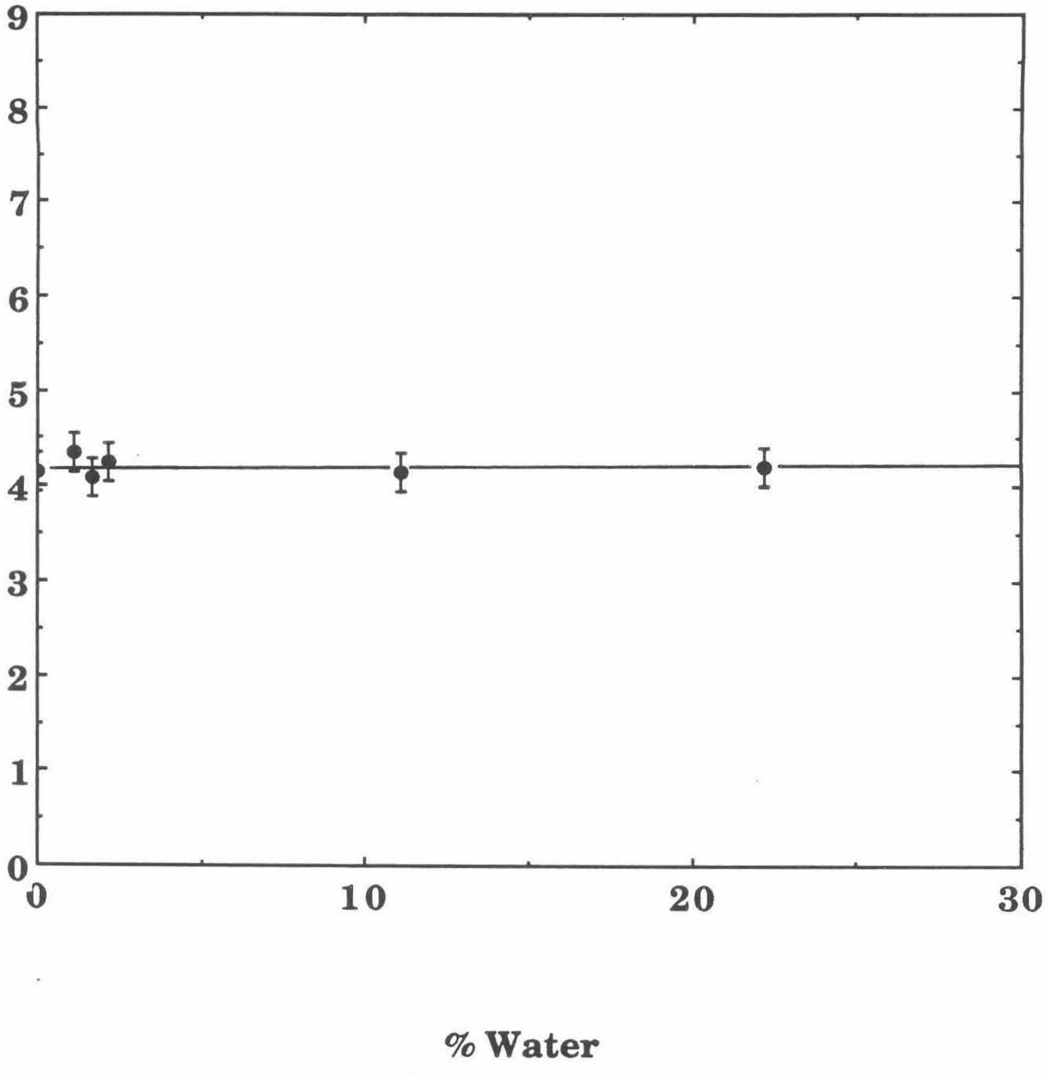


Figure 12: The initiation times (seconds) for the polymerization of **XI** (0.948 M), as a function of water concentration in methanol, using $Ru(H_2O)_6(tos)_2$ (0.0068 M) at room temperature.

M) by $Ru(H_2O)_6(tos)_2$ (0.0068 M) at 27 °C. As is true for the Ru^{3+} systems, no deactivation or inhibition is observed at high water concentrations.

A similar kinetic situation exists between these water-independent Ru^{2+} catalyzed systems, and the Ru^{3+} systems in the regime above the water-saturation limit. Both systems display initiation rates independent of the catalyst concentration (Figures 13 and 7, respectively). From the existing data, it is not possible to determine the exact role water plays in accelerating the rates of initiation in the Ru^{3+} systems. Nevertheless, it is postulated that the water serves in some capacity to facilitate the required reduction of Ru^{3+} to Ru^{2+}. Once the Ru^{2+} is generated, analogous kinetic behavior is observed for both systems.

F. Polymerizations Catalyzed Using the Preformed Olefin Adduct, Ru^{2+}-VIII:

The synthetic limits of aqueous, ruthenium catalyzed reactions can be considerably expanded by using the preformed olefin adduct, Ru^{2+}-**VIII**, as a catalyst for the polymerization of select monomers that are normally reluctant to polymerize in aqueous solution. For example, the aqueous polymerization of norbornene-5-methanol fails completely, using commercial $RuCl_3$ and the surfactant, SDS. Using the more active catalysts, K_2RuCl_5 or $Ru(H_2O)_6(tos)_2$ along with SDS, low yields (10-15%) of the polymer can be obtained (Scheme **II**). If, however, Ru^{2+}-**VIII**, generated *in situ* through the polymerization of **VIII** with K_2RuCl_5, is substituted as the catalyst, yields of over 90% of the desired ring-opened polymer are realized. Although Ru^{2+}-**VIII** proved to be very effective in this case (and others to be discussed), it has not proved to be a panacea for

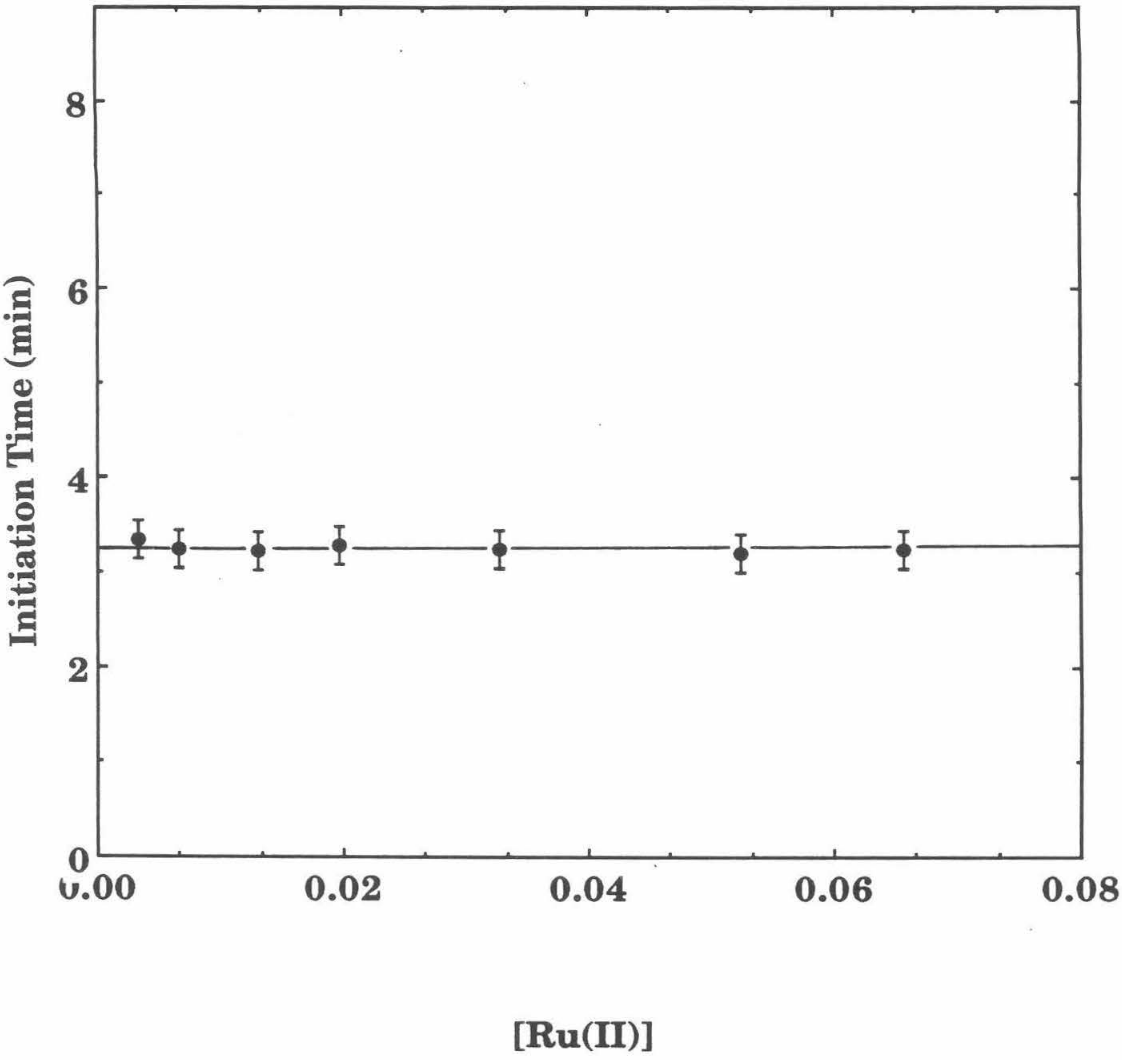
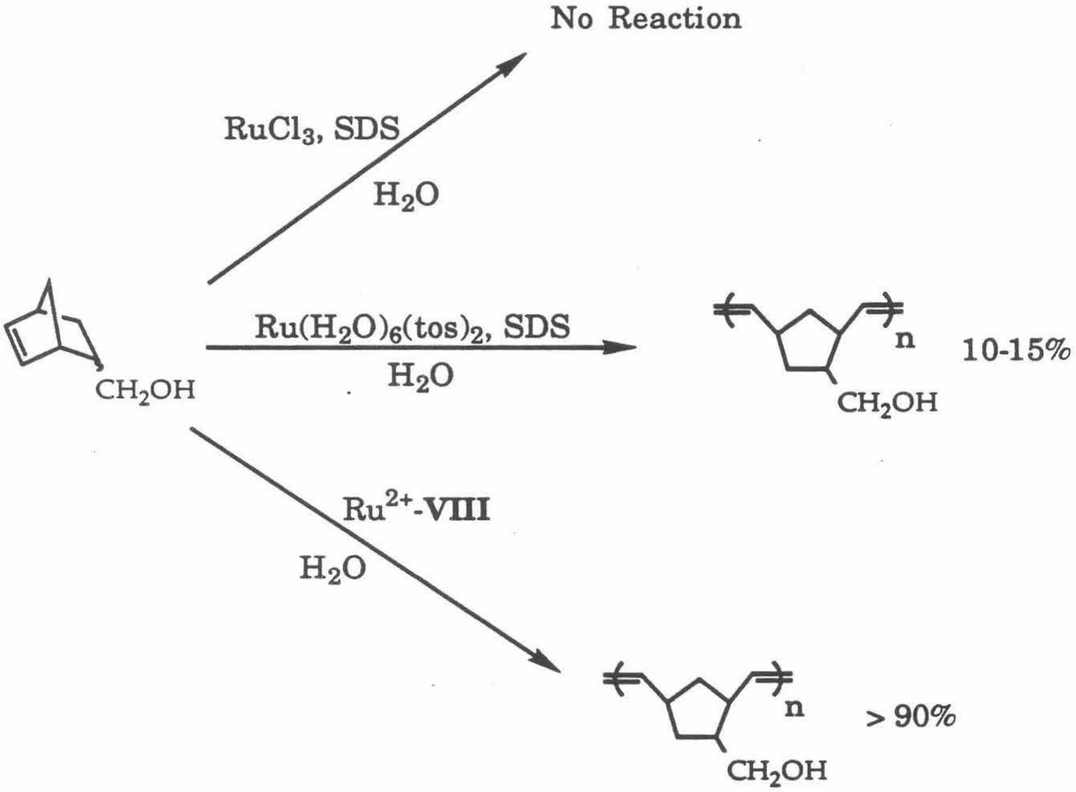


Figure 13: The initiation times (seconds) for the polymerization of **XI** (1.14 M) in methanol, as a function of $Ru(H_2O)_6(tos)_2$ concentration.

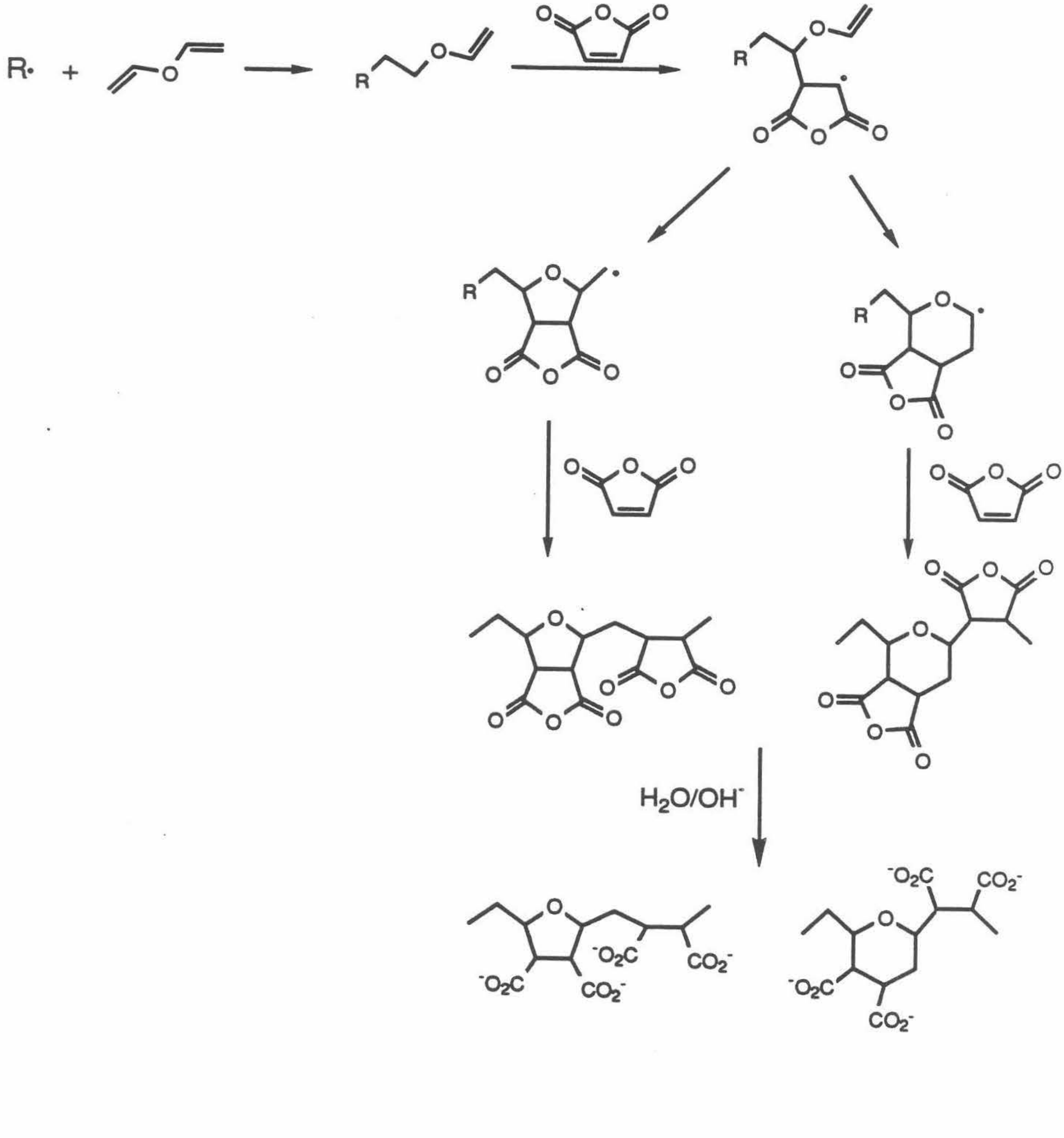
Scheme II:


No Reaction
$RuCl_3$, SDS
H_2O
$Ru(H_2O)_6(tos)_2$, SDS
H_2O
CH_2OH
n
10-15%
CH_2OH
Ru^{2+}-**VIII**
H_2O
n
> 90%
CH_2OH

initiating polymerizations in aqueous solution. Norbornene for example, fails to give polymer, using this catalyst. This result is undoubtedly due to the immiscibility of norbornene within the aqueous medium. This example underscores the importance of restricting these aqueous polymerizations to polar monomers.

Water-soluble, polyanionic materials are an important class of synthetic polymers possessing numerous industrial and medical applications.[41] One example of this class is the 2:1 copolymer produced from the free-radical polymerization of maleic anhydride : divinyl ether, DIVEMA[42] (Scheme **III**). During polymerization, cyclization occurs to form both the five-membered tetrahydrofuran ring and the six-membered pyran ring. These rings are usually formed in nearly equal quantities. The polyanionic material resulting from hydrolysis and neutralization of the polyanhydride exhibits a wide range of interesting biological activities.[42] It is an antitumor agent; it induces the formation of interferon; it has antiviral, antifungal and antibacterial activity; it is an anticoagulant and an anti-inflammatory agent; and it aids in the removal of plutonium from the liver. The copolymer is an immunostimulant, and appears to act by stimulating macrophage activity within the body. Despite this impressive list of biological activities, the advancement of these polyanionic materials in the medical research arena has been limited. This is due, in part, to the lack of selectivity involved in the synthesis of these compounds. In the free-radical process used to prepare these polyanionic materials, it is difficult to control either molecular weight or polydispersity. This lack of control is actually a pivotal issue, because the high molecular weight materials are toxic. Thus, not only are high molecular weight materials to be avoided, but samples possessing broad molecular weight distributions are equally

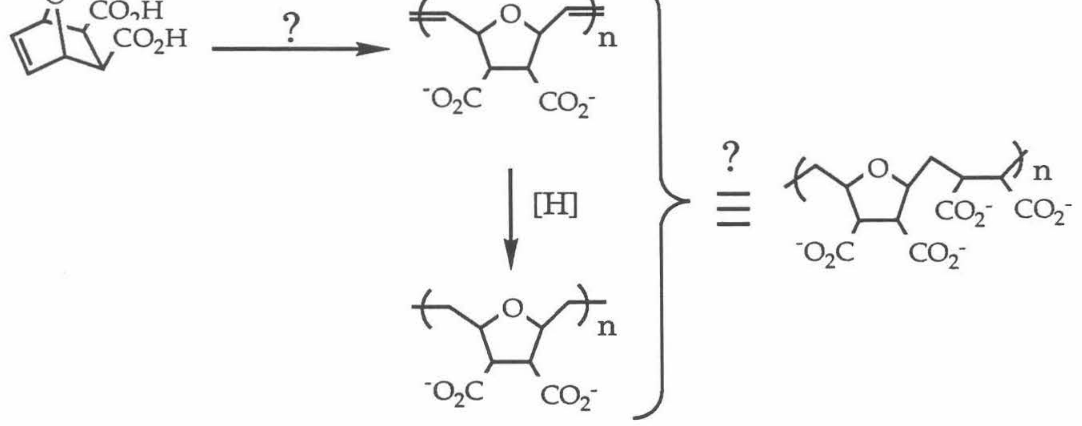
Scheme III:



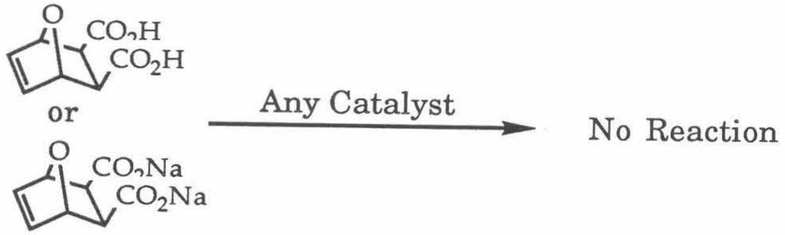
undersirable if they contain high molecular weight components. The free-radical synthesis provides little control over the regiochemistry of the cyclization steps, which leads to a random mixture of both five- and six-membered rings. In addition, the stereochemistry of the propagation steps cannot be controlled, which further complicates the composition, and thus the properties, of these materials. The reasons for developing polyanionic materials are abundant and pressing. The question is: Can new catalytic routes into polyanionic materials be envisioned, which would ultimately offer control over these key synthetic issues? In the context of this study, the question narrows and becomes: How can ROMP impact the synthesis of new, biologically interesting synthetic polymers?

Using ROMP, the most direct route into structurally similar materials is through the direct polymerization of *exo*-7-oxanorbornene-2,3-dicarboxcylic acid, **VIa**, to provide an unsaturated, structural analogue to DIVEMA. Hydrogenation of Poly **VIa** would provide the fully saturated analogue (Scheme **IV**).

Scheme IV:

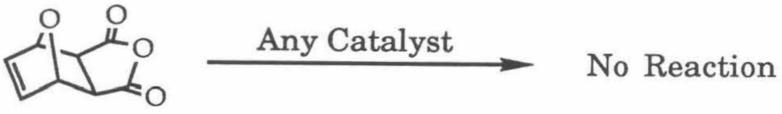


Unfortunately, our previous efforts had shown the highly functionalized monomer, **VIa**, to be completely inactive towards polymerization, using any of the ruthenium catalysts in organic solvents. Unfortunately, negative results were also obtained using the very active K_2RuCl_5, $Ru(H_2O)_6(tos)_2$ and Ru^{2+}-**VIII** catalysts in aqueous solution, with either **VIa**, or its neutralized disodium salt, **Na$_2$VIa** (Equation 11).



(11)

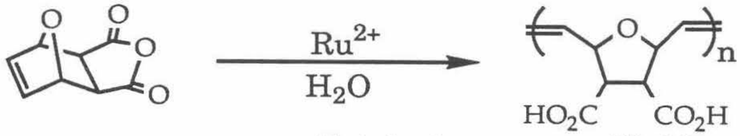
Retreating slightly, efforts were concentrated on polymerizing the anhydride, **VI**. Multiple attempts at polymerizing this monomer using ruthenium, osmium and iridium catalysts in organic solvents, all failed (Equation 12).



(12)

This result was particularly frustrating in light of the fact that the polymerization of an anhydride monomer, norbornene-2,3-dicarboxylic anhydride, had previously been demonstrated using $WCl_6/Sn(CH_3)_4$.[43] This catalyst mixture was found, however, to be completely deactivated by **VI** because of side reactions with the 1,4-bridging epoxide moiety (Chapter 3).

Good yields of the desired ROMP polymer were finally obtained when the highly active aqueous catalysts were employed. When **VI** is allowed to react with $Ru(H_2O)_6(tos)_2$ in aqueous solution at 55 °C, 10-15% yields of ROMP polymer are obtained. When carried out in water, simultaneous hydrolysis of the anhydride moiety occurs smoothly under the reaction conditions, providing the polydiacid material. When the preformed Ru^{2+}-**VIII** olefin adduct is used as the catalyst, yields greater than 70% are obtained (Equation 13).

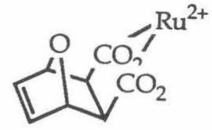


(13)

Catalyst	Yield
$Ru(H_2O)_6(tos)_2$	10-15%
Ru^{2+}-**VIII**	> 70%

For polymerizations of **VI**, a general observation is that the faster the rate of initiation, the higher the yields of polymer obtained. Recall that repetition of the above polymerization procedure using any of the aqueous catalysts and the hydrolyzed diacid monomer, **VIa**, results in catalyst deactivation. Nevertheless, in the successful anhydride polymerizations, hydrolysis is occurring to produce the diacid, and yet the polymerization proceeds. This system appears to be governed by two competing rates: the rate of polymerization (comprised of both the initiation and propagation rates), and the rate of catalyst deactivation by the diacid moiety. At high carboxylate concentrations, as would be found in reactions starting with the diacid monomer, catalyst deactivation dominates. When the reaction is begun with the anhydride monomer, however, the concentration of diacid in the reaction mixture is quite low during the critical initiation stages of the reaction, and as a result, polymerization proceeds before deactivation can occur. Using ^{1}H NMR spectroscopy, the rate of hydrolysis of the anhydride, **VI**, can be estimated under polymerization conditions (i.e., neutral water at 57 °C). Heating **VI** to 57 °C in D_2O for 15 minutes results in approximately 35% hydrolysis of the material as evidenced by the appearance of a new bridgehead proton signal at 4.16 ppm (**VI** = 4.10 ppm), and a new *endo*-proton signal at 2.39 ppm (**VI** = 2.35 ppm), both of which are assigned to the diacid form of **VI**. Recycling of the catalyst solutions resulting from the anhydride polymerizations reveal the catalyst to be completely deactivated, indicating that the catalyst is slowly killed during these runs.

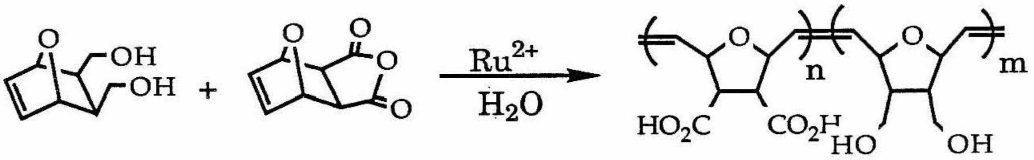
It is postulated that the deactivation process occurring in these systems involves chelation of the Ru^{2+} ion by the diacid moiety. (The acidity of the medium does not appear to be the primary factor, as it was found that solutions with pH values between 4 and 5 display the fastest initiation times.) Although no direct observation of chelation by the diacid moiety has been made, there is indirect evidence from examination of the microstructure of Poly **VIa**, which indicates that major changes have been made to the coordination sphere of the propagating species in this system. The ^{1}H NMR spectrum of Poly **VIa** (90 MHz, 2% Na_2CO_3 in D_2O, or CD_3OD) reveals a polymer with a *cis*/*trans* double bond ratio considerably different from the high *trans* content observed in all other polymers obtained using the ruthenium catalysts. From the olefin and allylic proton signals (*trans:* 5.95 and 4.72 ppm; and *cis:* 5.65 and 5.20 ppm, respectively) of Poly **VIa** prepared under these aqueous conditions, it is calculated that this polymer contains only 28% *trans*-double bonds. This number represents a nearly complete reversal when compared to the 80-95% *trans* materials, which are consistently obtained with all the ruthenium catalysts. One possible explanation is that the propagating species is a Ru center, which is mono-chelated by one equivalent of the diacid **VIa**.



If deactivation does occur by a simple chelation mechanism that blocks coordination sites required by the olefin, then the deactivated species may, in fact, be bis-chelated by two equivalents of the diacid. This deactivation process creates a situation in which the lability of the Ru^{2+} water ligands may actually be a drawback. It was discovered that the polymerization of **VI** is an isolated case in which the Ru^{3+} catalyst, K_2RuCl_5, actually performs better than the Ru^{2+} catalyst, $Ru(H_2O)_6(tos)_2$. Virtually quantitative yields of Poly **VIa** can be obtained with K_2RuCl_5. It is thought that the excess Cl^- ligands may inhibit chelating, and eventual deactivation, by the diacid monomer.

In its pristine acidic form, the solubility of Poly **VIa** in methanol and basic aqueous media is limited only by the viscosity of the resulting solution. Poly **VIa** is insoluble in acidic media. The one exception to these general solubility guidelines is the solubility of the polymer in Na_2EDTA solutions (*ca.* 0.10 M), where the pH is approximately 4.5. In neutral solution, the polymer does not form a true solution, but rather, highly viscous gels. This is actually a property peculiar to Poly **VIa**. Upon warming, Poly **VIa** present in amounts as low as 0.5 g will completely gel 120 g water (i.e. 0.4-

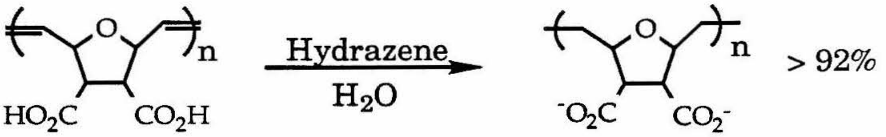
0.5% solution). In comparison, poly(acrylic acid) requires concentrations as high as 7.5% before complete gelation occurs. This unusually high gelation level is attributed to interchain hydrogen bonding between the carboxylate hydrogens and the THF oxygens. This property is reminiscent of the high modulus materials formed from mixing poly(ethyene glycol) and poly(acrylic acid).[44] The solubility and gel characteristics of Poly **VIa** can be tuned through the formation of copolymers with other 7-oxanorbornene monomers. For instance, the solubility of Poly **VIa** in basic solution can be attenuated by the incorporation of small amounts of the the diol monomer, **VII**, while organic solubility can be increased by forming copolymers with **VIII**. Copolymers of **VI** can be readily formed with **IV**, **VII** and **VIII**. In some cases, a synergistic relationship exists between the monomers. For example, using K_2RuCl_5 in aqueous solution, the initiation time for **VI** alone is 15-20 minutes, and for **VII** alone is 5-7 minutes. By combining these two monomers in a 1:1 ratio, the initiation time is cut down to only 1-2 minutes. Copolymers produced in this fashion contain nearly equal amounts of both monomers (Equation 14).



(14)

In pursuit of the saturated analogues to the bioactive polymer, DIVEMA, hydrogenation of Poly **VIa** was investigated. The solubility limitations of Poly **VIa** in suitable solvents prevented the homogenous hydrogenation by p-toluenesulfonhydrazide, which was shown to be effective in reactions with Poly **VIII**. An *in situ* hydrogenation method, based on converting the

Ru^{2+} ROMP catalyst into a hydrogenation catalyst by addition of H_2 to the reaction solution after polymerization, led only to polymer decomposition products. Limited success in hydrogenating these materials was obtained using Pd-C/H_2. In neutral water at 95 °C, where gelation was a problem, only a 2-3% conversion to the saturated polymer was evidenced by new methylene signals at 1.75 ppm (CD_3OD), and a new methine signal at 4.2 ppm. In basic solution (5% NaOH), the amount of hydrogenation was increased to 30-40%. No further changes in H_2 pressure, temperature or reaction time served to increase substantially the degree of hydrogenation of the polymer. The hydrogenated material, Poly **VIas**, containing greater than 92% saturated bonds (Figure 14) was finally obtained, using hydrazine in water (with air as the oxidant) (Equation 15).



(15)

Poly **VIa** is a highly amorphous polymer with a glass transition temperature well above room temperature. Decomposition is observed to occur before the T_g transition is detected, at temperatures greater than 150 °C. As a result, Poly **VIa** forms hard, transparent films which are slightly brittle. The flexibility and toughness of this material can be dramatically improved by forming the fully neutralized Poly **K$_2$VIa** material. On the other hand, Poly **VIas** has a subambient glass transition temperature, and as a result, is a soft, rubbery material at room temperature.

Biological testing of these new polyanionic materials is still pending.[45]

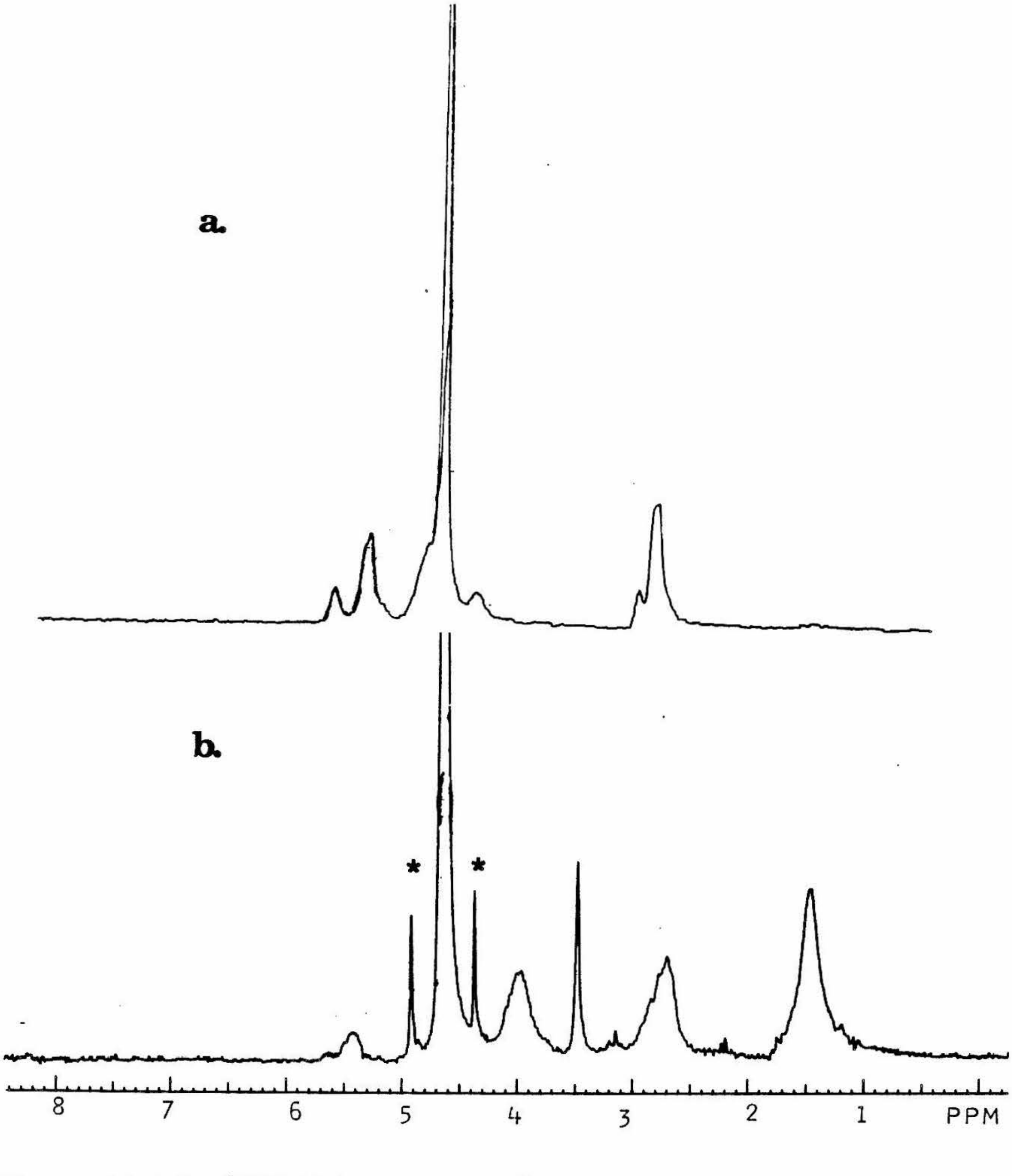


Figure 14. The ^1H NMR spectra (D_2O, 90 MHz) of (a) unsaturated Poly **VIa**; and (b) saturated Poly **VIas**.(* Denotes side bands. Resonance at 3.5 ppm is due to residual hydrazine).

CONCLUSIONS

The initiation process in Ru^{3+}-catalyzed ring-opening metathesis polymerizations was found to be cocatalyzed by water. This rate enhancement is neither a protic nor a polar solvent effect, as evidenced by the fact that the blank, non-cocatalyzed reactions are run in absolute alcohol. The observation that large excesses of water do not have a detrimental effect on the reaction led to the discovery of completely aqueous ring-opening metathesis polymerizations that provide near quantitative yields of the desired polymer. The materials obtained under these aqueous conditions have molecular weights fourfold greater than materials synthesized in non-protic solvent, and the polydispersities drop from near 2 to 1.2-1.3.

The recyclability of these single-component ruthenium catalysts was examined. It was found that not only are the Ru^{2+} and Ru^{3+} catalysts recyclable, but they actually become more active with use. In an effort to understand this observed rate enhancement, a number of ruthenium complexes in varying oxidation states were examined. Through this work, it was discovered that Ru^{2+} complexes, notably $Ru(H_2O)_6(tos)_2$, are far more active than the Ru^{3+} catalysts previously used. Like the Ru^{3+} systems, Ru^{2+} also become more active when used, and ultimately, display identical limiting initiation rates. ^1H and ^{13}C NMR investigations using $Ru(H_2O)_6(tos)_2$ revealed the formation of a Ru^{2+}-olefin complex, Ru^{2+}-**VIII**, generated *in situ* during the recycling processes. Once identified, resonances corresponding to this same complex were observed in the recycled Ru^{3+} reactions. Polymerizations catalyzed by this olefin complex display the same limiting initiation times as do the recycled catalyst solutions. The activity of these recycled catalyst solutions is ascribed to: 1) the reduction of Ru^{3+} to Ru^{2+}; and 2) the *in situ* formation of Ru^{2+}-olefin complexes that lie along the reaction coordinate. Direct observation, however, of the conversion of these olefin complexes to catalytically active species has not been accomplished.

These highly active species have been utilized for the polymerization of functionalized monomers, which have been reluctant to polymerize under aqueous conditions. Quantitative yields of the polydiacid material, Poly **VIa**, are obtained from the ruthenium-catalyzed polymerization of anhydride **VI**. The polymerization is performed in aqueous solution, resulting in simultaneous hydrolysis of the anhydride moiety. Hydrogenation of this material provides the saturated poly-diacid, which is a close structural analogue to known antiviral and antitumor agents.

EXPERIMENTAL

General Procedures

All manipulations involving air and/or moisture sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemlog) and Linde 4A molecular sieves. All weighing of air- and/or moisture-sensitive compounds was performed in a Vacuum Atmosphere dry box under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6.MHz ^{1}H, 22.53 MHz ^{13}C) and a JEOL GX-400 (399.65 MHz ^{1}H, 100.67 MHz ^{13}C). Chemical shifts are referenced to residual protons on the deuterated solvents. Infrared spectra were aquired on a Shimadzu IR-435 spectrometer. Samples were prepared by casting films on KBr windows. UV/vis spectra were aquired using a HP-8451A diode array spectrometer.

Gel permeation chromatography (GPC) was performed utilizing Shodex KF-803, 804, 805 and 805.4 columns with CH_2Cl_2 or THF as a solvent. The polymer was detected with a Spectroflow variable wavelength absorbance detector and a Knauer differential refractometer. Samples for analysis were prepared between 0.2 -0.4% by weight in CH_2Cl_2 (or THF). The molecular weights were referenced to narrow-dispersity polystyrene samples (Polysciences) ranging from MW = 3550 to 1,300,000.

Thermal analysis was performed on a Perkin Elmer DSC-7, TGS-2 thermogravimetric analyzer, and a 3600 data station. Scan rates are provided in the figures.

The 7-oxanorbornene monomers **VII, VIII** and **XI** were prepared as described in Chapter 3. Initial sample of $Ru(H_2O)_6(tos)_2$ was provided by Paul Bernhard. Later samples were prepared by Dominic McGrath, California Institute of Technology. $[Ru(NH_3)_5Cl]Cl_2$ was obtained from Strem. $RuCl_3 \cdot H_2O$ was obtained from both Strem and the Aldrich Chemical Company. K_2RuCl_5 and $(NH_4)_2OsCl_6$ were obtained from Johnson-Matthey/AESAR.

Water Concentration Dependence on Initiation Rates. The initiation time is defined as the time elapsed from the initial mixing and heating of the reaction mixture until the first sign of polymer formation. The onset of polymerization can be detected in two ways. In solvents in which the polymer remains soluble (i.e., benzene/alcohol mixtures for **XI**, or neat alcohol for **VIII**), the onset of polymerization can be detected using ^1H NMR, typically by the appearance of the olefin polymer resonances at 5.9 ppm (poly **XI**). In solvents in which the polymer is completely insoluble (i.e., alcohol for **XI**, and water for **VIII**), the onset of polymerization can be defined as the first sign of precipitate detected visually. Standard solutions of $RuCl_3$ (102.1 mg/ml CH_3OH) and monomer **XI** (1.1224 g and enough CH_3OH to bring the total volume to 2.00 ml, 2.687 M) are prepared. Ten runs are prepared using fixed amounts of monomer (0.896 M), and varying amounts of H_2O, along with the appropriate amount of added CH_3OH to keep the volumes constant. Before each run, a fixed amount of catalyst solution is rapidly added via syringe, the contents mixed, and the tube placed in the oil bath at a preset temperature (55 °C). The reaction is then monitored visually until polymer precipitate is detected. The deuterium series was run using CD_3OD and D_2O under identical conditions.

Aqueous Polymerization of VIII Using $RuCl_3$. The procedure presented here is typical of all of the aqueous ruthenium-catalyzed reactions.

Reaction times will vary, however, depending on the oxidation state and ligand sphere of the metal center. A Schlenk flask is charged with $RuCl_3$ (7.0 mg, 0.0382 mmol, based on $RuCl_3.3H_2O$) and 3.0 ml distilled water. Monomer **VIII** (0.50 ml, 580 mg, 3.15 mmol, 82 equivalents) is added via syringe and the solution degassed under vacuum. The solution is then heated to 55 °C. After 25 minutes the first polymer precipitate is noticed. Within two minutes, the solution is filled with polymer. The reaction is heated for a total of 40 minutes, after which it is cooled and the purple catalyst solution removed from the polymer via cannula. The polymer is then washed with 7-8, 10 ml portions of water. Further purification can be accomplished by dissolving the polymer in the minimum amount of ethanol, and precipitating it from a 1 M HCl solution. The polymer is washed with water (3 X 20 ml) and dried under vacuum to yield 5.72 g of poly **VIII** (98.7% yield). ^1H NMR ($CDCl_3$, 90 MHz) 5.72 (b, Ha), 4.22 (b, Hb), 3.45 (b, CH_2OCH_3), 3.34 (b, CH_2OCH_3), 2.25 (b, Hc). ^{13}C NMR (Proton-decoupled) (CD_2Cl_2, 22.53 MHz) 132. 2 (olefin), 81.9 (*trans*-allylic), 77.2 (*cis*-allylic), 71.0 (CH_2OCH_3), 58.9 (CH_2OCH_3), 48.4 (*cc*-$CHCH_2OCH_3$), 48.0 (*ct*-$CHCH_2OCH_3$), 47.7 (*tc*-$CHCH_2OCH_3$), 47.4 (*tt*-$CHCH_2OCH_3$) ppm. IR (Thin film) 2890 (s), 1475 (m), 1460 (m), 1390 (m), 1190 (s), 1100 (vs), 1018 (s), 963 (s).

Polymerization of Norbornene in Aqueous Solution Using $RuCl_3$. A Schlenk flask is charged with $RuCl_3$ (58.2 mg, 0.22 mmol) and 3.0 ml H_2O. Norbornene (0.50 g, 5.31 mmol) is added and the solution degassed under vacuum. The reaction vessel is placed in an oil bath at 52 °C. No polymer was observed to form after one week.

Polymerization of Norbornene in Aqueous SDS Solution Using $RuCl_3$. A Schlenk tube is charged with $RuCl_3$ (30 mg), SDS (100 mg) and 2.0 ml H_2O. Norbornene (205.2 mg, 2.18 mmol) is added and the solution is degassed under vacuum. The reaction vessel is placed in an oil bath at 55 °C for one week. The vessel is cooled and the solvent decanted off the polymer. The polymer is washed with water (6 X 20 ml), and ethanol (3 X 10 ml), and dried under vacuum to yield 0.033 g of polynorbornene (16% yield). ^1H NMR ($CDCl_3$, 90 MHz) 5.32, 2.4, 1.8, 1.35 ppm.

Polymerization of Norbornene in Aqueous Solution Using 10% VIII and $RuCl_3$. A Schlenk flask is charged with $RuCl_3$ (42.3 mg, 0.16 mmol) and 2.0 ml H_2O. Norbornene (322.5 mg, 3.42 mmol) and **VIII** (54 µl, 62.6 mg, 0.34 mmol, 10% based on norbornene) are added and the solution degassed under vacuum. The reaction vessel is placed overnight in an oil bath at 52 °C. The vessel is cooled and the solvent decanted off the polymer. The polymer is washed with water (6 X 20 ml), and ethanol (3 X 10 ml), and dried under vacuum to yield 175.1 mg (54.3% yield). By ^1H NMR, only resonances associated with polynorbornene are observed. ^1H NMR ($CDCl_3$, 90 MHz) 5.32, 2.4, 1.8, 1.35 ppm.

Recycling $Ru(H_2O)_6(tos)_2$/Norbornene Polymerization Solutions. A 0.45 ml reaction tube is charged with $Ru(H_2O)_6(tos)_2$ (2.3 mg, 0.0042 mmol) and 0.20 ml methanol. Norbornene (19.2 mg, 0.204 mmol) is added, and the reaction vessel placed in the oil bath at 60 °C. The reaction is then monitored visually until polymer precipitate is detected (55 seconds). The catalyst solution is carefully drawn off the polymer precipitate and added to a second reaction vessel previously charged with norbornene (18.7 mg).

This solution is then placed back into the oil bath and monitored for polymer formation (47 seconds). This recycling process is repeated a third and fourth time in an analogous fashion.

Recycling $RuCl_3$/VIII Polymerization Solutions. A 0.45 ml reaction tube is charged with $RuCl_3{\cdot}3H_2O$ (7.8 mg, 0.0297 mmol) (0.099 M) and 0.30 ml distilled water. **VIII** (50 µl, 58 mg, 0.32 mmol) (1.05 M) is added, and the reaction vessel placed in the oil bath at 55 °C. The reaction is then monitored visually until polymer precipitate is detected (37.5 minutes). The catalyst solution is carefully drawn off the polymer precipitate and placed in a second 0.45 ml reaction vessel. Extra care must be taken to compress the polymer completely in order to recover all of the catalyst solution. A blunt, solid glass rod can be used for compressing the polymer. To the used catalyst solution, a second aliquot of monomer **VIII** (50 µl, 58 mg, 0.32 mmol) is added, and the reaction vessel is then placed back into the oil bath and monitored for polymer formation (8.25 minutes). After completion of this second polymerization, the catalyst solution is withdrawn with careful compression of the polymer as outlined above. A third aliquot of **VIII** (50 µl, 58 mg, 0.32 mmol) is added, and the reaction vessel returned to the oil bath. Polymer is observed to form in 54 seconds. In the fourth run, **VIII** (50 µl, 58 mg, 0.32 mmol), polymer is observed after only 12 seconds. This recycling process is repeated a total of ten times in an analogous fashion. Occasionally, during this recycling process it becomes necessary to add small portions of water, to makeup for losses accrued during the catalyst solution recovery process. At no time is more $RuCl_3$ catalyst added. The initiation times for each run will vary slightly (usually shorter), depending on how long the solution is heated after polymer forms. In general, the longer the polymer/catalyst solution is heated, the shorter the subsequent initiation time becomes. For example, the second run has been observed to display initiation times as short as 1-2 minutes, when the previous reaction solution was heated for approximately 1 hour after the formation of polymer.

Recycling $Ru(H_2O)_6(tos)_2$/IV Polymerization Solutions. A 0.45 ml reaction tube is charged with $Ru(H_2O)_6(tos)_2$ (1.2 mg, 0.0022 mmol, 0.0054 M) and 0.40 ml D_2O. Monomer **IV** (50 µl, 60 mg, 0.39 mmol, 0.97 M) is added via syringe, and the reaction vessel placed in the oil bath at 55 °C. The reaction is then monitored visually until polymer precipitate is detected (185 seconds). The catalyst solution is carefully drawn off the polymer precipitate and added to a second reaction vessel previously charged with **IV** (50 µl, 60 mg, 0.39 mmol, 0.97 M). This solution is then placed back into the oil bath and monitored for polymer formation (37 seconds). This recycling process is repeated a third time in an analogous fashion.

$RuCl_3$ Concentration Dependence on the Initiation Rate. Standard solutions of $RuCl_3$ (105.5 mg/ml CH_3OH), and monomer **XI** (1.2244 g and enough CH_3OH to bring the total volume to 2.00 ml, 2.913 M) are prepared. Ten runs are prepared using fixed amounts of monomer (1.09 M), and H_2O (2.5% by volume), along with the appropriate amount (depending on the amount of catalyst solution to be used) of CH_3OH to keep the volumes constant. Before each run, a varying amount of standard catalyst solution is rapidly added via syringe, the contents mixed, and the tube placed in the oil bath at a preset temperature (57 °C). The reaction is then monitored visually until polymer precipitate is detected. In these ten runs, the catalyst concentration is varied from 0.00506 M to 0.243 M. A second series of runs is performed in the same manner and concentration of **XI** (1.09 M), but uses 5% H_2O in each run. Throughout ten runs, the catalyst concentration is varied from 0.00504 M to 0.232 M. A third series of runs is performed in the same manner and concentration of **XI** (1.01 M), but uses 14.3% H2O in each run. Throughout eight runs, the catalyst concentration is varied from 0.00577 M to 0.173 M.

The *in situ* Formation of Ru^{2+}-VIII During the Polymerization of VIII. An NMR tube is charged with $Ru(H_2O)_6(tos)_2$ (15,1 mg, 0.0274 mmol) and D_2O (0.40 ml). Monomer **VIII** (50 µl, 58 mg, 0.315 mmol, 11.5 equivalents) is added via syringe and the mixture kept at room temperature. During this time Poly **VIII** is observed to precipitate from solution. After 0.5 hour at room temperature, the tube is placed in an oil bath for 1.5 hours. The polymer is compressed, and the yellow solution drawn off via syringe. The ^1H NMR of this solution reveals the quantitative conversion of $Ru(H_2O)_6(tos)_2$ into Ru^{2+}-**VIII**. ^1H NMR (D_2O, 400 MHz) 7.50 (4H, d), 7.18 (4H, d), 5.07 (2H, s), 4.73 (2H, s), 3.44 (4H, m), 3.26 (6H, s), 2.54 (2H, s), 2.21 (6H, s) ppm. ^{13}C NMR (D_2O, 100.67 MHz) 143.29, 140.18, 130.17, 126.07, 84.61, 77.2, 71.49, 58.88, 42.63, 21.25 ppm (referenced to tosylate methyl peak at 21.25 ppm). UV/Vis: λ_{max} = 294 nm.

The *in situ* Formation of Ru^{2+}-VIII Using K_2RuCl_5. An NMR tube is charged with K2RuCl5 (12.0 mg, 0.0306 mmol) and 0.400 ml D_2O. Monomer **VIII** (50 µl, 58 mg, 0.315 mmol, 11.5 equivalents) is added via syringe and the tube immersed in an oil bath at 55 °C for 1.5 hours. Poly **VIII** is observed to form in 3-4 minutes. The polymer is then compressed and the yellow catalyst solution is withdrawn via syringe. The ^1H NMR spectrum of this catalyst solution shows resonances corresponding to Ru^{2+} olefin adducts. ^1H NMR (D_2O, 400 MHz) free **VIII**: 6.28 (s), 4.71 (s), 3.36 (m), 3.22 (s), 1.77 (m) ppm. Olefin Adduct(s): 5.12 (s), 5.07 (s), 4.75 (s), 4.72 (s), 3.40 (m), 2.55 (m) ppm. UV/Vis: λ_{max} = 293 nm.

Aqueous Polymerization of VIII Using $[Ru(NH_3)_5Cl]Cl_2$. All manipulations are carried out under an argon atmosphere. A Schlenk tube is charged with $[Ru(NH_3)_5Cl]Cl_2$ (15.2 mg, 0.052 mmol) (0.065 M) and 0.80 ml D_2O. The solution is vigorously degassed with Ar. Monomer **VIII** (60 µl, 69.6 mg, 0.379 mmol, 0.47 M) is added via syringe and the reaction vessel is placed in an oil bath at 60 °C. After 4.5 hours the solution begins to turn from yellow to dark purple, and polymer is observed to form. The reaction vessel is removed from the bath, the polymer compressed and the catalyst solution removed via syringe. An aliquot of this solution is diluted with D_2O and its UV/Vis spectrum measured. UV/Vis: λ = 328, 535 nm. 1H NMR shows only free **VIII**:^1H NMR (D_2O, 400 MHz) 6.28 (s), 4.71 (s), 3.36 (m), 3.22 (s), 1.77 (m) ppm.

Water Dependence on Initiation Rate Using $Ru(H_2O)_6(tos)_2$. Standard solutions of $Ru(H_2O)_6(tos)_2$ (17.0 mg, 0.0308 mmol) in 1.0 ml methanol (0.0306 M), and monomer **XI** (1.1957 g, 5.689 mmol) in 2.00 ml methanol are prepared. Eight runs are prepared using fixed amounts of monomer (0.948 M), and varying amounts of H_2O, along with the appropriate amount of added CH_3OH to keep the volumes constant. Before each run, a fixed amount of catalyst solution (final concentration, 0.0068 M) is rapidly added via syringe at room temperature. The reaction is then monitored visually until polymer precipitate is detected.

Ru^{2+} Concentration Dependence on the Rate of Initiation. Standard solutions of $Ru(H_2O)_6(tos)_2$ (29.0 mg, 0.00526 mmol, in CH_3OH, 0.131 M), and monomer **XI** (0.4809 g, 2.288 mmol, and enough CH_3OH to bring the total volume to 2.00 ml, 2.29 M) are prepared. Seven runs are prepared using fixed amounts of monomer (1.14 M), along with the appropriate amount (depending on the amount of catalyst solution to be used) of CH_3OH to keep the volumes constant. Before each run, a varying amount of standard catalyst solution is rapidly added via syringe, the contents mixed at room temperature. The reaction is then monitored visually until polymer precipitate is detected. In these seven runs, the catalyst concentration is varied from 0.00325 M to 0.0657 M.

Polymerization of Norbornene-5-methanol Using Ru^{2+}-VIII. A Schlenk tube is charged with K_2RuCl_5 (16.6 mg, 0.0423 mmol, 0.0423 M) and H_2O (1.0 ml). To this solution, monomer **VIII** (0.100 ml, 116 mg, 0.630 mmol) is added. The resulting solution is then placed in an oil bath at 55 °C for 2 hours. The resulting poly **VIII** is compressed and the catalyst solution containing Ru^{2+}-**VIII** is drawn off and placed in a new Schlenk tube. To this solution, SDS (50 mg) and norbornene-5-methanol (0.100 ml, 102.7 mg, 0.827 mmol) are added and the reaction vessel placed in the oil bath for one hour. The polymer precipitate is isolated, washed with water (4 X 5 ml) and dried under vacuum to yield 95.2 mg of poly(norbornene-5-methanol) (92.7%).

Aqueous Polymerization of VI Using Ru^{2+}-VIII. A Schlenk tube is charged with $Ru(H_2O)_6(tos)_2$ (15.5 mg, 0.0281 mmol, 0.0703 M) and H_2O (0.40 ml). To this solution, **VIII** (60 µl, 69.6 mg, 0.378 mmol, 0.944 M) is added and the reaction allowed to stir for 30 minutes at room temperature. The reaction vessel is then placed in an oil bath at 60 °C for one hour. The poly **VIII** precipitate is compressed, and the catalyst solution drawn off and placed in another Schlenk tube. To this solution, an additional 0.6 ml of water and anhydride **VI** (253.0 mg, 1.52 mmol, 1.52 M) are added, and the reaction vessel heated to 60 °C. After one hour, the Schlenk tube is removed from the oil bath, and the poly **VIa** precipitated from 1 M HCl. The polymer is then purified by dissolving in basic solution, and reprecipitating it by slow addition into 1 M HCl. The acidic solution is decanted off, and the polymer dried under vacuum to yield 188.2 mg of poly **VIa** (74.4%). ^1H NMR (CD_3OD, 90 MHz) 5.72 (*trans*-olefin H), 5.46 (*cis*-olefin H), 5.02 (allylic H), 2.90 (methine H) ppm. ^{13} C NMR (Proton-decoupled) (CD_3OD, 22.53 MHz) 174.23 (carboxylate C), 133.09 (olefin C), 82.08 (*trans*-allylic C), 78.96 (*cis*-allylic C), 54.78 (methine C) ppm.

Aqueous Polymerization of VI Using K_2RuCl_5. As a general rule, it is best to keep the monomer concentration high (between 1.5 and 2.0 M appears to be optimum), and the catalyst concentration between 0.005 - 0.01 M. Using amounts of catalyst lower than 0.005 M gives low yields of polymer, and using catalyst concentrations higher than 0.010 M makes it difficult to remove all the catalyst from the polymer. A Schlenk flask is charged with K_2RuCl_5 (28.8 mg, 0.0733 mmol, 0.0105 M), anhydride **VI** (2.00 g, 12.04 mmol, 1.72 M) and water (7.0 ml). The solution is degassed under vacuum and heated to 60 °C for 40 minutes. (Typically, after 25 minutes, the solution is too viscous to stir.) The solution is then cooled, and product polymer precipitated by slow addition to 1 M HCl. The polymer can be further purified by dissolving it in basic solution (1-2% NaOH) and reprecipitating by slow addition into aqueous HCl, the acidic solution decanted off, the polymer washed with water (5 X 25 ml) and dried under vacuum to yield 2.0 g of Poly **VIa** (100% yield). ^{1}H NMR (CD_3OD, 90 MHz) 5.72 (*trans*-olefin H), 5.46 (*cis*-olefin H), 5.02 (allylic H), 2.90 (methine H) ppm. ^{13} C NMR (Proton-decoupled) (CD_3OD, 22.53 MHz) 174.23 (carboxylate C), 133.09 (olefin C), 82.08 (*trans*-allylic C), 78.96 (*cis*-allylic C), 54.78 (methine C) ppm.

Hydrogenation of Poly VIa Using Hydrazine. A 100 ml, 3-neck flask is equipped with a reflux condenser, a gas inlet tube connected to an air line, and a magnetic stir bar. The reaction flask is charged with Poly **VIa** (892.7 mg) and 15 ml H_2O. Hydrazine hydrate, $NH_2NH_2{\cdot}H_2O$ (2.0 ml, 99%, d = 1.02 g/ml) is added. Fifteen minutes after the addition of the hydrazine, the polymer is completely dissolved in solution. Air is then vigorously bubbled through the solution for a total of 48 hours. This reaction time will vary depending on the rate of air flow. The extent of hydrogenation is periodically checked by ^{1}H NMR analysis on small aliquots removed from the reaction mixture. After sufficient hydrogenation is achieved, the polymer is recovered by evaporating the water and washing the residue in cold methanol. Integration of the residual olefinic proton signals at 5.72 and 5.46 ppm against the methine proton signals at 2.70 ppm provides the percent hydrogenation. For Poly **VIas**: ^{1}H NMR (D_2O, 90 MHz) 3.98 (2H, methine with α-oxygen), 2.70 (2H, methine with α-carboxylate group), 1.48 (4H, methylene) ppm. ^{13} C NMR (Proton decoupled) (D_2O, 22.53 MHz) 180.14

(carboxylate C), 82.14 (methine C with α-oxygen), 55.88 (methine C with α-carboxylate), 31.26 (methylene C) ppm.

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CHAPTER 5

THE IONOPHORIC PROPERTIES OF POLY(7-OXANORBORNENES)

Abstract

The ionophoric properties of the 7-oxanorbornene polymers are reported. It was found that the unsaturated poly(7-oxanorbornene) materials bind and phase transfer the larger planar aromatic dyes in which the aromatic portion is positively charged. Dyes with reversed polarity, i.e., planar aromatic anions, are not bound by these polymers. Poor discrimination is observed on comparison of differing isomeric forms of Poly **VIII**, obtained using different catalysts. It is argued that this lack of discrimination results from the inability, using the stable of existing catalysts, to prepare polymers of high isomeric purity. In solid/liquid extractions, these polymers are observed to bind Cs^+, K^+ and Na^+, but not Li^+.

Although these materials display some ionophoric properties, their ability to act as host materials in any standard phase transfer or ion-binding applications is limited. This realization led to investigations into applications more suited to polymeric materials. In pursuit of this goal, membranes were fashioned from these poly(7-oxanorbornene) materials, and the resultant permeability to ions studied. At low-concentration gradients, Poly **VIII** acts as a quasi-ideal cation membrane. From measured membrane potentials, cation transport numbers for K^+, Na^+ and Li^+ (all Cl^- salts) are calculated to be 0.84, 0.73 and 0.73, respectively. Copolymers of **VIII** and norbornene display the same behavior, yet the ideal regime is extended to much greater concentration gradients.

INTRODUCTION

Since the mid 1960's, the host-guest field of chemistry has helped build the basis of our understanding underlying the fundamentals of molecular recognition and enzymatic catalysis.[1] Pederson's seminal work in 1967, which detailed the binding of cations by cyclic crown ethers, became a cornerstone of this new field.[2] From these beginnings, a detailed understanding of the factors involved in the recognition and binding of small guest molecules by discrete host molecules has been steadily accumulating. To better model actual enzymatic systems,[3] and to facilitate many of the future applications of these ionophoric systems, it would be desirable to synthesize high molecular weight polymers possessing these specialized ionophoric properties. For example, polymeric phase-transfer agents could be designed with unusual selectivities.[4] Ionophoric polymers could be used in filtration and separation technologies[5]. Membranes could be envisioned that would selectively permit the preferential transport of one type of ion over another.[6] Coating electrodes with this type of membrane could allow for the development of new, ion-selective electrodes.[7] A goal in solid-state batteries is to develop ionophoric polymers that allow for high ion mobility when doped with ionic salts.[8] These doped polymers would then be placed between two electrodes and would act as a solid-state electrolyte. For all of these potential applications, there are surprisingly few candidate ionophoric polymers. Those that do exist are often limited by either their physical properties, or a complicated and/or unreliable synthesis. In light of the status quo in this area, it would be advantageous to develop new materials that display ionophoric properties.

The complexation and phase-transfer of cations using polymeric materials has been studied since the late 1940's.[9] Interestingly, the use of polyethyleneoxide (PEO), or lower molecular weight polyethyleneglycols (PEG), as ion complexation materials, predates the discovery of crown ethers by over 20 years.[10] The early work in this field concentrated on the development of gravimetric tests for the quantitative determination of high molecular weight PEG in solution by its precipitation with transition-metal salts.[11] The polymer most often studied was PEO or PEO capped with carboxylate end-groups. This work, however, never seemed to gain wide popularity, and remained an active area of interest to only a small segment of the polymer community. After the discovery of crown ether complexes in the 1960's,[2] a renewed interest was seen in the use of these PEO and glymes as ion-complexing agents.[12]

Crystalline complexes of PEO with potassium,[12,13] sodium[13] and mercuric chloride[14] have been reported. When methanol solutions containing sodium and potassium iodide or thiocyanate salts and PEO are evaporated, crystalline complexes possessing a stoichiometry of one metal ion per four polymer repeat units (CH_2CH_2O) are formed.[13] Using mercuric chloride, two types of crystalline complexes are observed to form: A 1:1 Hg^{2+} to repeat unit complex, and a 1:4 Hg^{2+} to repeat unit complex.[14] The structures of both of these complexes have been solved using x-ray diffraction and infrared absorption methods.[14a,b] The binding capability of these polymers is surprisingly sensitive to the nature of the repeat sequence. For example, the related polymers, poly(formal),-$(CH_2O)_n$-, and poly(oxetane), -$(CH_2CH_2CH_2O)_n$-, do not form salt complexes.[15] Unlike PEO, poly(propylene oxide), PPO, forms complexes with lithium and sodium, but not with potassium.[15]

The strong binding of ions exhibited by PEO may actually be counterproductive for some applications. In solid electrolytes and other membrane applications, ion mobility and amorphous morphology, rather than high binding constants, become the important issues.[8] PEO doped with salts such as LiTf (Tf = $CF_3SO_3^-$) have been studied as solid electrolyte materials.[15] The pristine polymer is approximately 80% crystalline with a melting point of 60 °C. The crystalline regions of some of the ion-doped polymers, however, melt above 200 °C.[13] This necessitates raising the temperature of the system considerably in order to achieve the requisite ion mobility.

These PEO complexes are unique in their ability to act as hosts when their flexible polymer chains adopt specific binding conformations in the presence of ions. A more elaborate system of this type has been synthesized, which contains THF rings along the polymer backbone[16] (Figure 1).

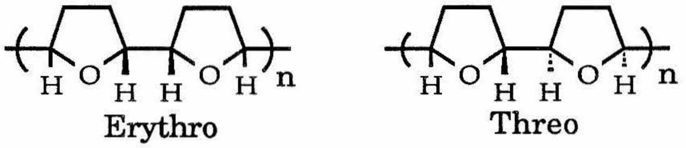


Figure 1: The threo and erythro configurations of poly(2,5-tetrahydrofuran). CPK models suggest that only the threo isomer can adopt a helical conformation.[16]

Two isomers, the threo and erythro configurations, were synthesized. Of these two isomers, only the threo polymer showed ion-binding capabilities. CPK models suggest that the threo polymer can form helical structures with the THF oxygens facing into the center, but because of steric interaction between the methine hydrogen atoms, the erythro polymer cannot.

Another class of polymeric host systems has been devised, which does not rely on the interaction of the ions with specific conformations of the main polymer chain. Polymers in this class usually possess cyclic crown ether moieties linked to the polymer chain.[17] Some examples that fall into this class are shown in Figure 2.

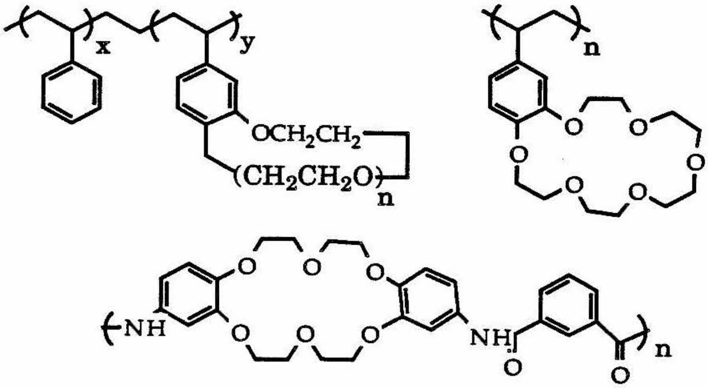
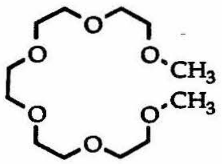
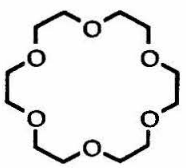


Figure 2: Polymeric ionophores possessing crown ether binding moieties.

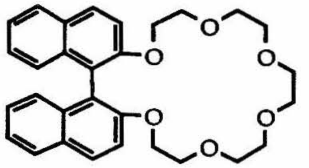
An important point concerning the relative binding ability of acyclic ionophores should be emphasized. As a general rule, acyclic ionophores are orders of magnitude less efficient in binding cations than their cyclic analogues.[18] On going from cyclic 18-crown-6 to open-chain, but similarly hexadentate, pentaethylene glycol dimethyl ether (pentaglyme), an approximate 10^4 -fold decrease in binding constants is observed for complexation of K^+ ions. A 10^3 -fold decrease is observed for Na^+ binding.[19]

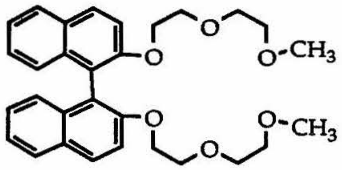


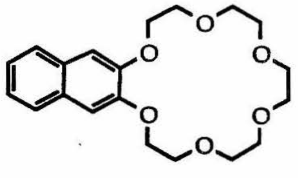


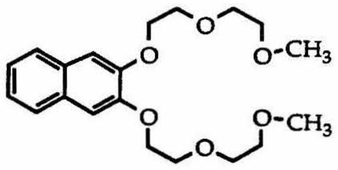
For K$^+$ (in MeOH): log K_s = 2.2 log K_s = 6.1

Although not as pronounced, this general tendency is also observed for *t*-butylammonium as guest ion in cyclic crown ethers and their corresponding glyme analogues.[20]









This difference in complex stability that can result on ring closure of the host molecule is referred to as the "macrocyclic effect."[19a,b,21] For some systems this effect has been explained in terms of entropy factors, which oppose complete enclosure of cations by acyclic ionophores.[21] Studies on macrocyclic tetraamine and tetrasulfide systems revealed that thermodynamic parameters (ΔH), coupled with ligand solvation effects, often go further in explaining the origin of the macrocyclic effect.[22]

As outlined in Chapter 3, molecular model studies indicate that the poly(7-oxanorbornene) materials reported here have the potential ability to form helical structures, with all of the tetrahydrofuran oxygens facing into the interior of the helix (Figure 3).

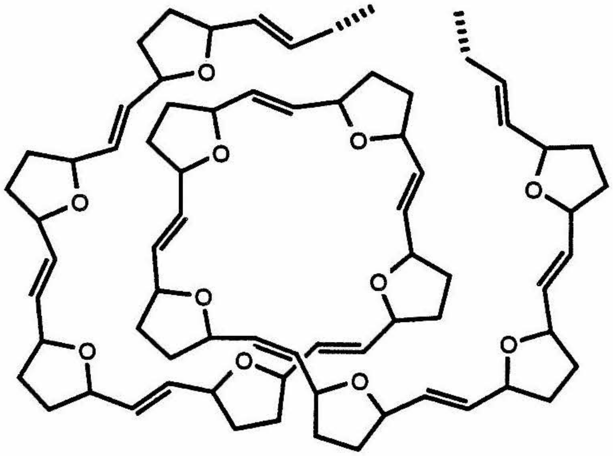


Figure 3: Proposed ion-binding cavity formed from a helical turn of poly(7-oxanorbornene).

It must be emphasized that the helical conformation represented here is an idealized situation, and any actual ionophoric character possessed by these materials could also arise from a less ordered ensemble of possible conformations. The size and characteristics of the helix are dependent upon the isomeric constitution of the polymer. Combining the configuration (*cis* or *trans*) of the double bond with the isotactic and syndiotactic diads gives rise to four different isomeric forms of poly(7-oxanorbornene): *trans*-syn, *trans*-iso, *cis*-syn and *cis*-iso. Polymer chains fashioned from CPK models give some indication of the size and ease of helix formation for each of these combinations. These sizes (oxygen-to-oxygen diameters) are only estimates of the smallest turn a particular configuration will form. The flexible nature of these acyclic materials allows them to expand or contract the dimensions of their interior, oxygen-rich cavities.

Isomeric Form	Interior Diameter (Å)	Repeat Units Per Turn
Cis-isotactic:	9-10	9-10
Trans-isotactic:	7-8	6-7
Cis-syndiotactic:	No helix possible.	
Trans-syndiotactic:	7-8	6-7

Table 1: Estimated interior diameter (oxygen to oxygen distance) of the smallest helix structure formed from the isomeric forms of poly(7-oxanorbornene).

With the exception of the *cis*-syn combination, all three remaining isomeric forms display the potential helix formation with all of the THF oxygens facing into the interior of the helix. Based on these models, the two best helices result from the *cis*-iso and *trans*-syn combinations. The models indicate that the helical conformation is very sensitive to interruptions in the uniformity of the the polymer. For example, the helix formed from the *cis*-iso sequence is completely disrupted by switching one of the diads from the isotactic to a syndiotactic relationship. On the other hand, an isotactic polymer made up of alternating *cis*- and *trans*-double bonds forms a reasonably good helix. A syndiotactic polymer with alternating *cis*- and *trans*-double bonds begins to put the pendant groups at the 3,4-positions of the ring into the interior. If these substituents are coordinating groups (such as ethers) as is the case in Poly **VIII** and Poly **IV**, this can be a useful effect. CPK models of the fully saturated polymers resulting from the hydrogenation of the parent poly(7-oxanorbornene) materials are similarly capable of adopting helical structures. These saturated helices are more flexible, and appear to form tighter turns than their unsaturated analogues.

RESULTS AND DISCUSSION

The ionophoric properties of the poly(7-oxanorbornene) materials were examined both in solution, and in the solid state. In order to study the solution behavior, host-guest extraction studies were performed. The solid state ionophoric properties of these materials were investigated through the fabrication of ion-permeable membranes.

Two types of solution phase complexation studies were performed using the 7-oxanorbornene polymers: liquid/liquid extractions of ions from an aqueous into an organic layer, and solid/liquid extractions of normally insoluble salts into organic solvents. Using both of these techniques, it can be observed that these poly(7-oxanorbornene) materials do indeed behave as ionophoric materials. The surprising feature of these materials is the extent of their flexibility, as evidenced by the wide range of cation sizes that are bound by these polymers. Cations as small as Na^+ (crystal radius = 0.93 Å) and as large as Rhodamine 6G (*ca.* 13-15 Å) have been bound by Poly **VIII**. Table 2 shows the qualitative results of aqueous/CCl_4 extractions performed on a series of polyaromatic ionic dyes comparing 18-crown-6 with Poly **VIII** obtained using catalyst **XV** (58% *trans*, unknown tacticity). In the absence of added polymer, all of these dyes are completely insoluble in CCl_4. As can be seen from these data, Poly **VIII** functions as a complement to 18-crown-6. 18-Crown-6 binds dyes composed of small cations such as sodium and large anionic organic anions (methyl orange, Rose Bengal, etc), while Poly **VIII** is selective for the binding of dyes, which are composed of small anions (Cl^-), and large planar aromatic cations such as Rhodamine 6G and Methylene Blue (MB). The ability of Poly **VIII** to phase-transfer ionic compounds into non-polar organic solvents appears to

Organic Dyes	Type	Extraction Results Poly VIII	 18-Crown-6
Methylene Blue	$Org^+ Cl^-$	Positive	Negative
Methyl Red	$Org^+ Cl^-$	Positive	Negative
Rhodamine B	$Org^+ Cl^-$	Positive	Negative
Rhodamine 6G	$Org^+ Cl^-$	Positive	Negative
Ethidium Bromide	$Org^+ Cl^-$	Positive	Negative
Methyl Orange	$Na^+ Org^-$	Negative	Positive
Rose Bengal	$Na^+ Org^-$	Negative	Positive
Eriochrome Black	$Na^+ Org^-$	Negative	Positive

Table 2: Aqueous/CCl_4 Extractions of Polyaromatic Dyes using Poly **VIII** and 18-Crown-6.

be a host-guest phenomenon, rather than being attributable to a change in the polarity of the organic phase, caused by the polymer. Solubility control experiments using CCl_4/THF and CCl_4/THF/**VIII** mixtures were run with MB. CCl_4 solutions containing 5 equivalents of THF (based on the number of THF rings present in Poly **VIII**) failed to solubilize the organic dye. Addition of monomer **VIII** to CCl_4/THF mixtures also failed to solubilize MB.

Contrary to the results obtained using the unsaturated polymers, it was found that the fully saturated polymers do not bind any dyes, regardless of their polarities. Two explanations for this result are possible. An examination of CPK models show that in addition to the the THF oxygens, the interior of the helix is lined with the double bonds of the polymer's main chain. It is thought that these unsaturated moieties play a role in the binding through favorable π –stacking interactions with the aromatic groups of the guest dye molecules. Alternatively, the saturated polymers may simply adopt solution-phase structures, which do not permit binding to occur.

Quantitative MB phase transfer experiments were performed using Poly **VIII** and Poly **IV**, both obtained from catalyst **XV**. These results are tabulated in Table 3. Included with these results are comparisons made to 18-crown-6 and the potentially helical polymer, threo-poly(2,5-tetrahydrofuran) (poly(THF)).[16] The polymer/dye ratios presented in the last column of Table 3 represent the ion saturation values obtained with these polymers (i.e., increasing the MB concentration in the aqueous phase does not increase the amount of dye bound by the polymer). From an examination of these data, a few noteworthy points can be made. In comparing the binding values obtained using Poly **VIII** and Poly **IV**, the

Host	Solvent	Absorption[b]		% MB Trans.	mg Poly/ mg Dye
		Before	After		
Poly **VIII**	CCl_4	0.69	0.51	42.6%	641
Poly **VIII**	C_6H_6	0.69	0.19	71.3%	585
Poly **IV**	C_6H_6	0.19	0.09	49.4%	1450
18-Crown-6	CCl4	0.19	0.19	0.0%	-
Poly(THF)[a]	CHCl3	-	-	83.0%	1700

Notes: a) From Reference 16. b) The aqueous MB solutions were measured before and after extraction.

Table 3: Phase transfer of Methylene Blue (MB) using Poly **VIII**, and Poly **IV** (both obtained from Catalyst **XV**), 18-Crown-6 and the helical threo-Poly(2,5-tetrahydrofuran)[a] (Poly(THF)).

former appears to be 2.5 times more efficient at binding MB. The most obvious difference between the two host materials is that Poly **VIII** possesses the two methoxymethyl substituents per repeat unit, while Poly **IV** possesses only one. As was indicated earlier, substituents in the 3,4-positions may, and undoubtably do, participate directly in the ion binding. As a secondary effect, ring substituents may also influence the binding by modulating the solubility of the polymers. Whereas Poly **VIII** displays good solubility in benzene, Poly **IV** is only partially soluble, much of the sample remaining as a swollen gel. (Solvents that are better for Poly **IV**, are also solvents for MB.) Along with solubility, ring substituents may affect binding by influencing the solution macrostructure of the host polymer. Polymers in poor solvents tend to exist in more closed spherical arrangements. These spheres may allow penetration of the ions only so far into their matrices. In very dense matrices, the surface sites may quickly saturate, preventing further ion binding.

Table 4 shows the MB extraction results obtained using different isomeric forms of Poly **VIII**.

Host Agent	% Cis	Mn (X10^{-3})	% MB Trans.	mg Polym/ mg MB (X 10^{-3})
Poly VIII	93	19.4	95.3	1.4
Poly VIII	42	3.2	81.9	1.6
Poly VIII	05	172.0	73.8	1.8
18-Crown-6	--	--	0.0	--

Table 4: Phase transfer of Methylene Blue into CCl_4 using various isomeric forms of Poly **VIII**. All runs were performed using 20 mg Poly **VIII** in 2.0 ml CCl_4 and 0.015 mg/ml MB. A comparison to 18-Crown-6 is provided.

A modest improvement of 21% in binding efficiency is observed in going from high *trans* to high *cis* Poly **VIII**. This result, however, must be qualified. Currently, the exact relationship between binding ability and the isomeric constitution of the poly(7-oxanorbornene) materials cannot be obtained unambiguously. The problem rests in the non-selective nature of the existing family of catalysts. Although catalysts are available that will select for over 95% *cis*-, or 95% *trans*-double bonds, which on the average usually provides sufficiently uniform polymer sequences to complete one turn of the helix, other variables are not held constant. Both the tacticity and the molecular weight are catalyst dependent. Until catalysts are developed that can provide perfectly stereoregular polymers of controlled molecular weight, the individual effects which each of these variables exerts on ion binding will remain unknown. This point underscores the need to develop new, more stereospecific catalysts, both for use in these, as well as in other transition metal catalyzed polymerizations.

In the liquid/liquid extractions of ionic dyes, compounds comprised of small cations such as Na^+ are not bound by the 7-oxanorbornene polymers. If, however, solid/liquid extractions are carried out using inorganic salts such as NaOH, binding is observed. This apparent contradiction is thought to arise from the different sizes of the counterions in each case. In typical cyclic host-guest complexes, both the top and bottom faces of the cation are exposed, and the anion is free to form tight ion pairs. In the complexes formed between these polymers and cations, the cations may be embedded deep within the polymeric matrix, precluding the formation of ion pairs with anything other than relatively small counterions.

Solid/liquid extractions reveal binding efficiencies for the monobasic ions in the following descending order:

$$Cs^+ \approx K^+ \quad > \quad Na^+ \quad >>> \quad Li^+$$

Cesium and potassium hydroxides dissolve more readily than does sodium hydroxide, while lithium salts do not dissolve at all. This preference for the larger ions is consistent with both the trends uncovered in liquid/liquid extractions and the conformational analysis of potential binding cavity sizes.

Through both extraction techniques, the poly(7-oxanorbornene) materials have demonstrated modest ionophoric properties. It must be concluded, however, that these ion-binding efficiencies do not approach those necessary to compete successfully with discrete cyclic hosts in any standard phase transfer or ion-binding applications. Rather, attention should be turned to devising methods of exploiting the polymeric nature of these materials in applications where low molecular weight hosts are inappropriate. One area of potential application for polymeric ionophores is that of membrane studies. The design and fabrication of ion-permeable membranes that display selectivities in ion transport would be useful for many potential analytical and separation applications.[5,6,7]

There are three general modes of ion transport across membranes, which have been identified in biological systems[23] (Figure 4). The first is termed carrier transport, where ion transport is mediated by small carrier molecules that shuttle ions from one side of the membrane to the other.[24] Examples of natural carriers in this class include monensin,[25] nigericin,[26] grisorixin,[27] alborixin,[28] and emericid.[29] By fashioning liquid/liquid membranes (i.e., two aqueous phases in a U-tube, separated by an organic phase of greater density), synthetic host molecules such as cyclic crown complexes can be induced to transport ions in this fashion.[30] The second method of transport relies on ion-selective channels that span the width of the membrane, allowing ion migration to occur through an interior hydrophilic pathway.[31] In biological systems, this is a broad class encompassing a number of intricate protein assemblies, including the H^+, Na^+, K^+, and Ca^+ active transport channels (positive ΔG), which pump these ions against a gradient fueled by ATP-driven pumps.[32,33] Examples of simpler passive transport channels (negative ΔG) include gramicidin A, a pentadecapeptide composed of alternating D- and L-amino acids, which possesses a helical conformation.[34] To mediate ion transport, it is thought that gramicidin A dimerizes in an end-to-end fashion, forming an ion

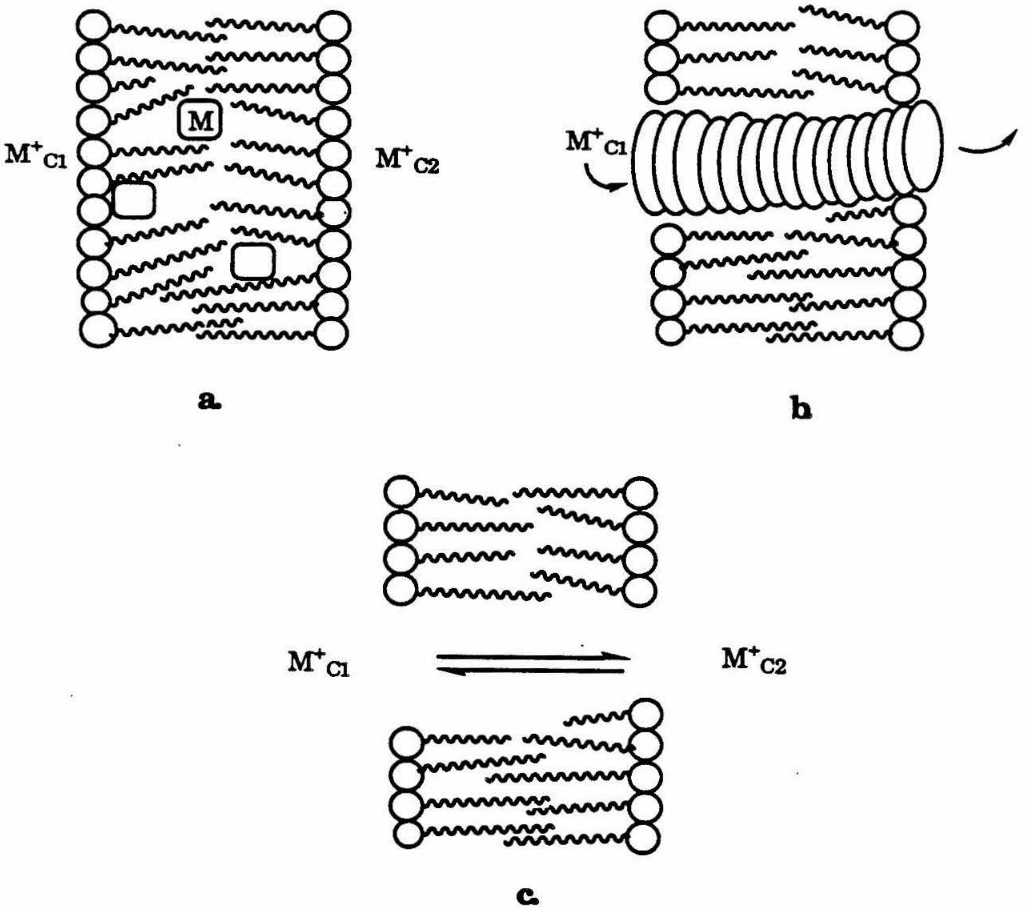


Figure 4: Three common modes of transmembrane ion transport identified in biological systems: a) Carrier transport. b) Transmembrane channels. c) Nonspecific pores. (See text for complete discussion).

channel that spans the membrane. The third and final method involves molecules that act to disrupt the integrity of the membranous structure, forming openings that allow free flow of ions through, with no permselectivity. An example in this class would be the polyene antibiotic, amphotericin B.[32]

Following demonstration of their ionophoric properties, the 7-oxanorbornene materials were tested as synthetic ion-permeable membranes using the apparatus shown in Figure 5. Solid films of polymer were cast on an inert gold grid (1000 lines/inch) to thicknesses of 50-100 μm. These polymer sheets were then sandwiched between the two concentration cells. The integrity of the membranes is tested by placing a dye solution (Methylene Blue) in one compartment and checking for any diffusion into the other compartment. By fixing the ion concentration on one side of the polymer and varying the concentration on the other, the membrane potential can be measured using two zeroed standard electrodes (SCE). If the polymer acts as an impermeable barrier, no potential will be registered. If, however, the membrane is permeable to the ions, a membrane potential will be observed. Diffusion potentials of this type obey Equation 1:[35]

$$E_{mem} = (t_+ - t_-)\, RT/F \ln C_2/C_1 \qquad (1)$$

where t_+ and t_- are the cation and anion transport numbers,[36] respectively, and C_1 and C_2 are the concentrations of ions on either side of the membrane. From the form of Equation 1, two limiting cases can be identified. If t_+ is equal to 1.0 (i.e., the membrane acts as an ideal cation permeable membrane), then in the plot of E_{mem} vs. ln C_2/C_1, a line with a positive slope of +59.2 mV (at 25 °C) will be obtained. Likewise, for an ideal

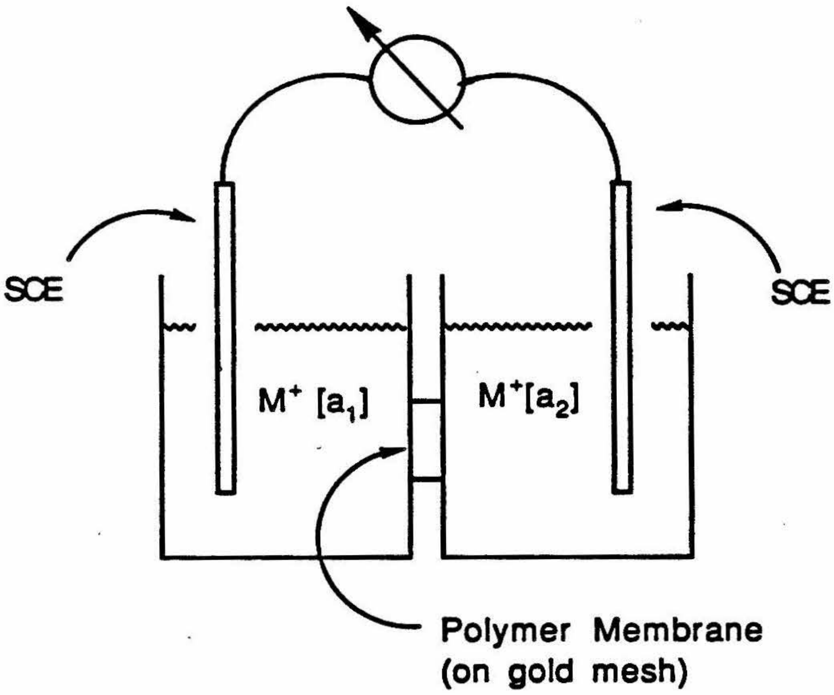


Figure 5: Ion concentration cells used to measure membrane potentials.

anion permeable membrane, $t_- = 1.0$, and the slope of the curve will equal -59.2 mV. These two extremes define the boundary conditions between which all experimental values should fall.

Films composed of Poly **VIII** do act as ion-permeable membranes, as evidenced by the generation of a membrane potential when they are placed between ion solutions of differing concentrations. The membrane potential measured is dependent on the particular cation used. Figure 6 shows the experimental potential curves measured using KCl, NaCl and LiCl with a Poly **VIII** membrane. At low ion gradients, all three ions show a linear increase in potential with increasing ion gradients. The initial positive slope of these curves indicates that ion transport is dominated by the cations. From these initial slopes, cation transport numbers for K^+, Na^+ and Li^+ (all Cl^- salts) are calculated to be 0.84, 0.73 and 0.73, respectively.

These results can be compared to results obtained using a polar but non-selective porous membrane, poly(vinylidene choride) (50 μm) (Figure 7). As can be seen from these results, ion migration through this control membrane occurs with nearly equal cation and anion transport numbers ($t_+ \approx t_-$).

Depending on the identity of the cation, a maximum membrane potential is reached, after which the slope becomes negative for increasing ion gradients. The maximum potentials for Li^+, Na^+ and K^+ are 29, 43 and 68 mV, respectively. Within the inverted regime, the cation transport numbers, t_+, are reduced from 0.84 to 0.22 (for K^+), and from 0.73 to 0.29 (for Li^+). This observed change in the slope is attributed to a change in mechanism of ion transport. At low driving gradients, the membranes act as quasi-ideal cation membranes (i.e., high cation transport numbers). During this initial stage, cations migrate through the membrane

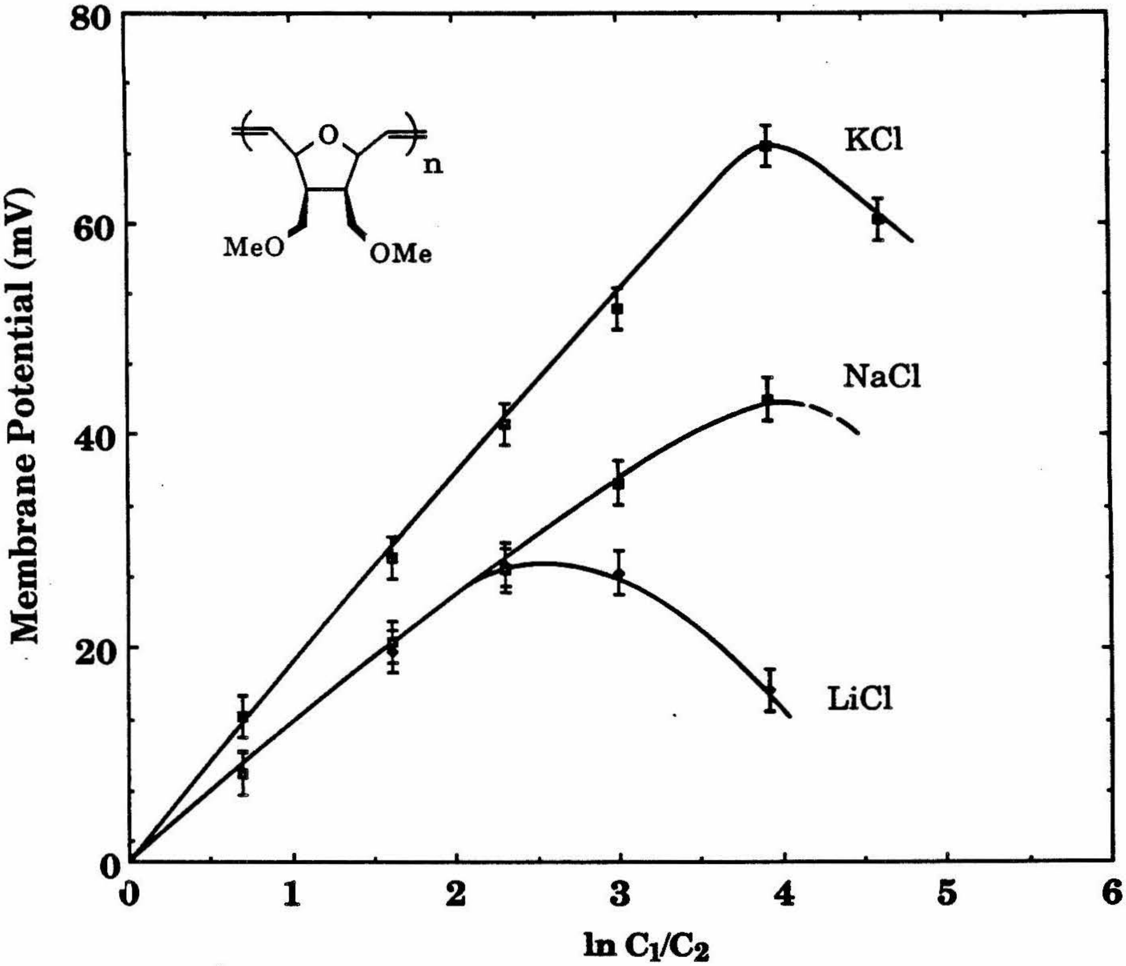


Figure 6. Membrane potential curves for the transport of KCl, NaCl and LiCl through a poly **VIII** membrane at 25 °C.

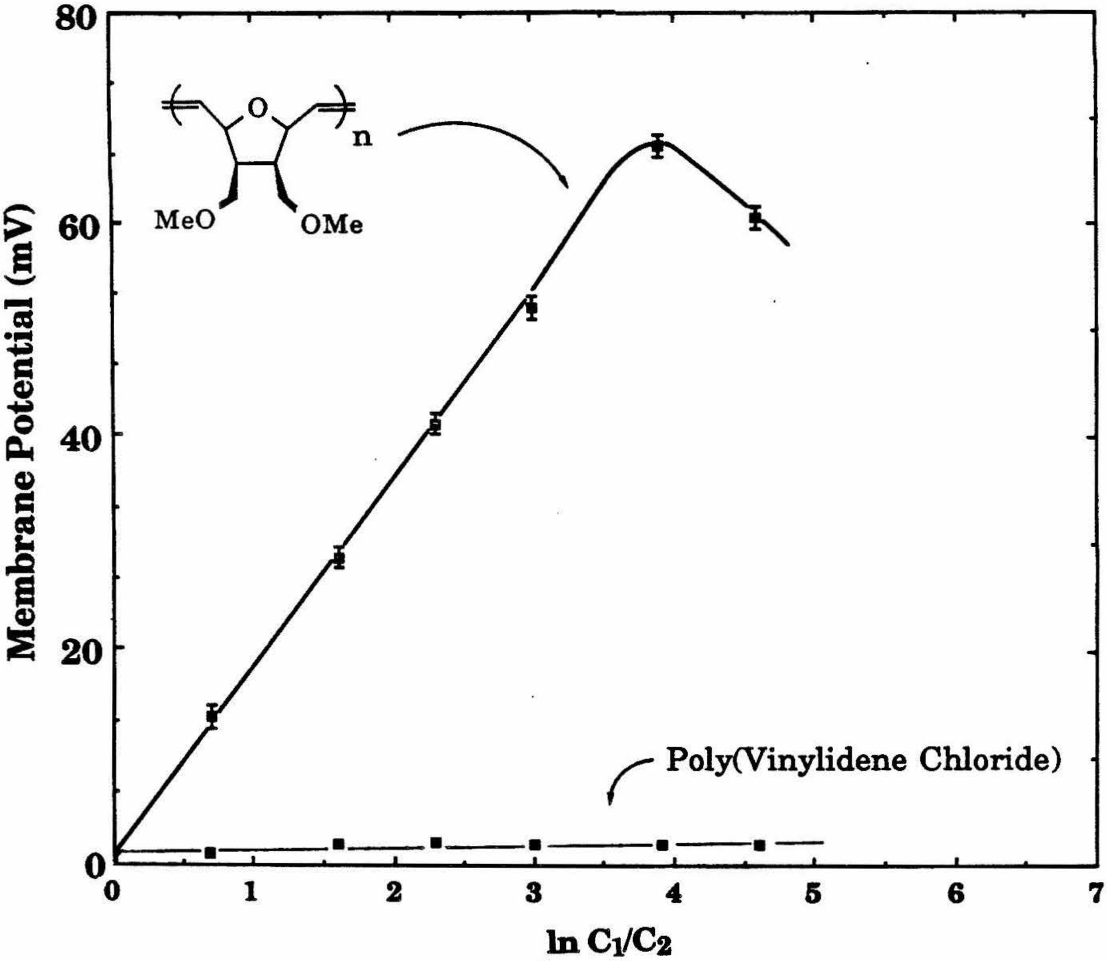


Figure 7. Membrane potential curve for the transport of KCl through a porous poly(vinylidene chloride) membrane. Also shown for reference, is the potential curve obtained using poly **VIII**.

preferentially over anions, because of the stabilization the former can obtain through coordination with both the THF rings and methoxymethyl groups. Because of this increase in internal cation concentration, the membrane acquires a net positive charge (Donnan potential).[37] As the external concentration is increased, the anions, driven by both their own concentration gradient and the newly established Donnan potential, migrate through the membrane, stabilized by the ion-pairing interactions with cations bound in the membrane. At high-concentration gradients, the anions become the dominant charge carriers, migrating through the membrane by a mechanism that is thought to involve hopping from fixed cationic site to cationic site. This results in a decrease in the membrane potential as t_- becomes a greater contributing factor. Although the carrier mechanism differs, this general inversion of the membrane potential curve at high concentration gradients is observed to occur in ion-exchange membranes such as Nafion.[38]

If this model is valid, then destabilizing the anions through structural modifications to the membranes should result in the obtainment of greater maximum potentials before breakdown occurs. Based on the proposed model of anion migration, two mechanisms for anion destabilization within the membranes can be envisioned. First, the hopping distance could be increased by increasing the distance between cation binding sites, and second, the membrane could be rendered more hydrophobic. The latter modification is based on the assumption that the anions migrating though the membrane do so with their primary spheres of hydration intact. With these goals in mind, a copolymer of norbornene (65%) and **VIII** (35%) was synthesized and fashioned into membranes. The ion permeation results for this membrane using KCl are shown in Figure 8. As can be seen from

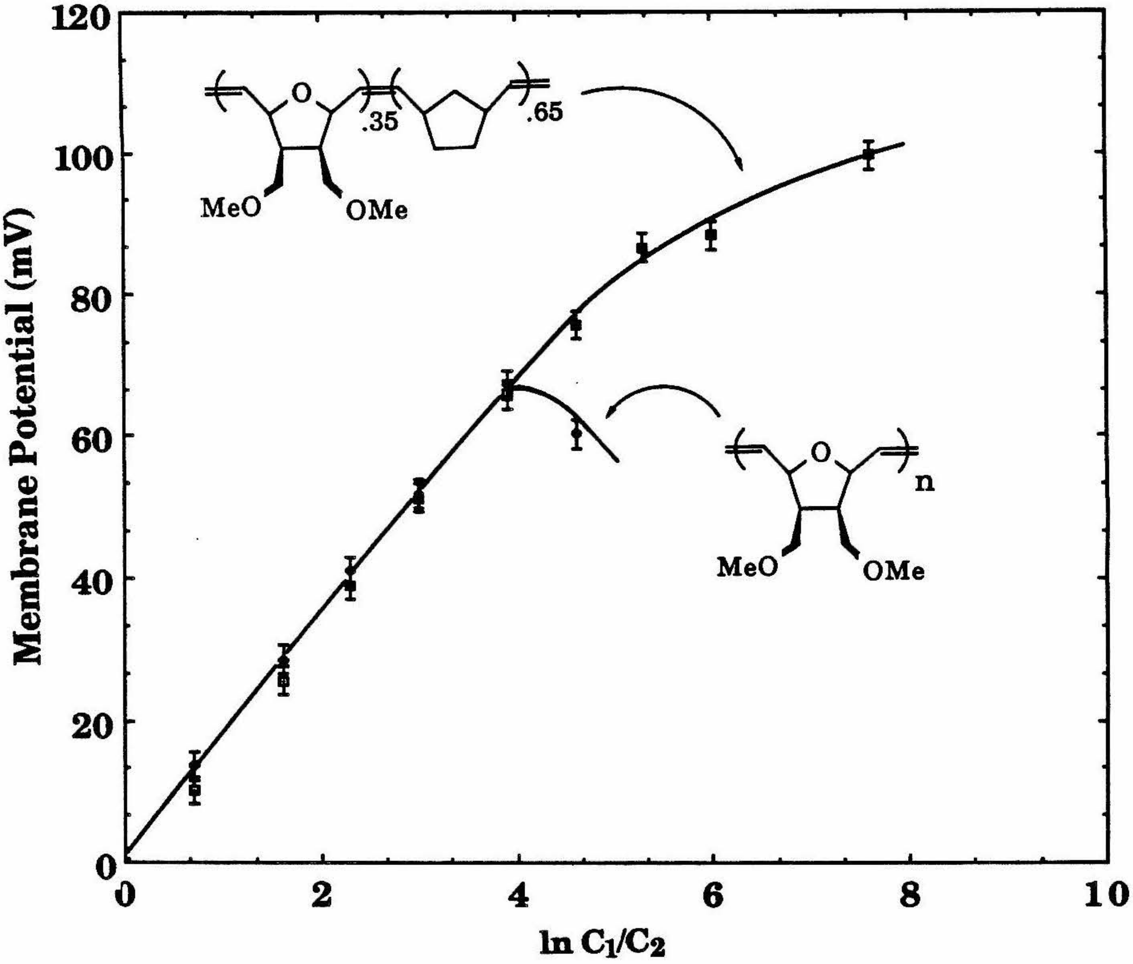


Figure 8. Membrane potential curve for the transport of KCl through membranes composed of poly **VIII**, and poly(norborene-*co*-**VIII**) (65/35).

these results, this membrane continues to behave ideally at much higher ion-concentration gradients.

The exact morphological characteristics of 7-oxanorbornene polymers that give rise to their ion permeable properties remain unclear. There appear to be oxygen rich regions within their matrices, which allow for the selective migration of cations over anions. It is, however, rather doubtful that these structures are actually the regular helical channels depicted in Figure 1. This initial analysis now appears overly optimistic. Poly **VIII** and Poly(norbornene-*co*-**VIII**) are highly amorphous materials, as evidenced by both the absence of T_m transitions in their DSC traces, and their highly elastic physical properties. A polymer possessing regular helical conformations, as depicted in Figure 3, would be expected to exhibit a more ordered morphology, and hence, a higher percentage of crystallinity. Ion migration through these membranes is therefore thought to occur through highly amorphous regions, possessing minimal order. Although amorphous materials may lack regular structures, such as oxygen-rich helices, the high flexibility inherent in their matrices favors good ion mobility. Materials possessing low T_g's are known to show enhanced ionic conductivities in solid electrolyte applications.[8] Ion migration through these membranes is therefore thought to occur through highly amorphous regions. Nevertheless, the 7-oxanorbornene membranes are ion-permeable, and in addition, show selectivity in the transport of cations over anions.

Concentration cells constructed with 7-oxanorbornene membranes can maintain their diffusion potentials over extended periods of time. This observation indicates that the potentials are generated under low ionic flux conditions. This attribute is directly analogous to many biological membranes *used in* signaling processes. For example, electrical signaling in squid axon involve changes in the available ionic concentration gradient by only 1 part in 10,000.[39] Applications arising from passive transport materials such as the poly(7-oxanorbornenes) should therefore focus on signaling, rather than on separation technologies.

CONCLUSIONS

Abeit with high host/guest ratios, the 7-oxanorbornene materials do act as ionophoric materials. Because of the adjustability of the binding cavities formed by the flexible polymer chains, cations of widely varying sizes can be complexed. Of particular interest is the observation that these materials complex large, organic dyes. This binding is specific for ionic dyes with the positive charge located on an aromatic moiety. Dyes possessing the reversed polarity are not bound. The binding of the positively charged dyes is thought to occur through interactions of the dye with the oxygens and double bonds of the polymer, as the fully saturated polymers do not act as hosts for these dyes.

The important solution morphologies of the 7-oxanorbornene polymers that give rise to these ionophoric properties is not known. Further advances in the use of 7-oxnorbornene materials as ionophoric hosts will demand the development of catalysts that display greater selectivity in the synthesis of stereoregular polymers. Using the currently available catalysts, the *cis/trans* ratios, tacticities and molecular weights of these materials cannot be varied independently of one another. This limitation currently precludes detailed structure-binding studies.

The use of 7-oxanorbornene polymers as ionophoric materials can be extended to the solid phase as well, by fashioning membranes from these materials. By measuring the membrane potentials, it can be shown that Poly **VIII** and Poly(norbornene-*co*-**VIII**) act as quasi-ideal cation membranes for the transport of K^+, Na^+ and Li^+.

EXPERIMENTAL

General Procedures

All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high-vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemlog) and Linde 4A molecular sieves. All weighing of air and/or moisture sensitive compounds was performed in a Vacuum Atmosphere dry box under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6.MHz ^{1}H, 22.53 MHz ^{13}C) and a JEOL GX-400 (399.65 MHz ^{1}H, 100.67 MHz ^{13}C). Chemical shifts are referenced to residual protons on the deuterated solvents. UV/Visible measurements were performed using a Cary 219 Spectrophotometer or HP-8451A diode array spectrometer. Fluoresence measurements were performed on a SLM Instruments Fluoresence Spectrophotometer. Membrane potentials were measured using the apparatus shown in Figure 5, equipped with an Orion 070101 pH meter and two Standard Calomel Electrodes (SCE). Gold mesh, 1000 lines/inch was obtained from Interconics Buckbee-Mears.

The poly(7-oxanorbornene) materials were synthesized as outlined in Chapters 3 and 4 of this work. Organic dyes were purchased from the Aldrich Chemical Company and used without further purification.

General Aqueous/CCl$_4$ Dye Extractions. Standard aqueous dye solutions were prepared and their concentrations determined by measuring their absorption spectra. Polymers were dissolved in either benzene or CCl$_4$ (ca. 10-20 mg polymer/ml). An aliquot of the dye solution was layered over the organic phase and shaken gently for a prescribed period of time, typically 5-10 minutes. (If shaken too vigorously, the polymer solutions easily form emulsions under these conditions). The layers are then separated and the absorbance of the aqueous phase is remeasured.

General Liquid/Solid Extractions. An efficient "yes/no" screening test is employed to determine the presence of solubilized hydroxide salts in $CHCl_3$. $CHCl_3$ solutions are made up containing polymer (10-20 mg polymer/ml), and 1,3 dinitrobenzene (*ca.* 1%), to be used as an indicator. To these solutions, one of the following solid salts is added; LiOH, NaOH, KOH or CsOH. If complexation occurs, the solution turns dark red-purple because of formation of the anionic Meisenheimer hydroxide/dinitrobenzene complex. The appropriate control experiments were run to eliminate the possibility of any spurious complexation results not mediated by the poly(7-oxanorbornene) polymers.

Membrane Potential Measurements. The apparatus shown in Figure 5 equipped with a pH meter (Orion 070101) and two SHE is used. The 7-oxanorbornene polymer is dissolved in THF (10-15% by weight). A square piece (*ca.* 0.5" X 0.5 ") of gold mesh (1000 lines/inch) is cut and placed over the side hole of one ion compartment. The polymer solution is then spread uniformly over the grid, forming a film 50-100 μm thick, and the solvent is allowed to evaporate under a stream of nitrogen. The second ion compartment is then clamped in place. Deionized water is placed in both compartments. The integrity of the membrane is checked by adding Methylene Blue (an ionic compound possessing a cation too large to diffuse through the ion channels of the membrane), to one of the compartments and checking for any slow diffusion to the other side. Membranes are typically monitored for 0.5 hour in this fashion. The two compartments are then drained and refilled with standard salt solutions of equal concentration (0.50 mM), and the voltmeter zeroed. The membrane potential is then measured as the concentration of salt is then varied on one side (1.00, 2.50, 5.00, 10.0, 25.0, 50.0, 100.0 and 200.0 mM), while the concentration on the reference side remains fixed.

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