Functionalized Polymers via Ring-Opening Metathesis Polymerization

Thesis by
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Acknowledgments

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It is now time for the customary few words of thanks to Bob, Professor Grubbs Himself. Bob has elevated laissez-faire to an art form. He gave me a lot of rope and I damn near hung myself. I learned a lot in the five-and-a-quarter years I spent in Bob's lab, I also struggled a lot and cried not a few times. Bob seems to have an inexhaustible supply of patience with his students and faith that it will all work out. It didn't seem very likely there for a few years, but I admit Bob was right again. It all worked out again.

It is also customary to mention one's friends in the acknowledgments. This is one custom I will forgo. I loved being at Caltech, but I refuse to produce a list of my friends. I refuse to be quite that trite. There are things that do not belong in print, and among them are one's emotional ties. I do apologize to those group members who plodded through the above heartfelt, technically related acknowledgments to see which friends I would mention. On second thought HAH! I don't apologize at all.

It is customary also to thank those who proofread this work, and that I do gladly. Randy Lee, Marc Hillmyer and Greg Fu each proofread a chapter of this thesis, under significant time pressure. Their comments were instrumental in figuring out what it was I meant to say in the first place.

Abstract

The first chapter describes the use of ring-opening metathesis polymerization (ROMP) for the synthesis of poly(sulfones) from functionalized 7-oxanorbornenes. Tungsten and molybdenum alkylidenes as well as ruthenium salts were used to generate polymers with varied backbone geometric- and stereo-isomerism. These poly(sulfones) exhibit clean mass loss under both oxidative and inert atmospheres. Thermal gravimetric analysis was used to investigate these poly(sulfones), as well as other 7-oxanorbornene polymers. Comparison of ether, amide and acid derivitized polymers indicates that clean thermolysis is observed when the polymer contains the following features: an oxygen of the tetrahydrofuran ring, a second ring fused to the tetrahydrofuran ring, a high proportion of *trans*-to-*cis* bonds, an atactic backbone, and the sulfone group. Product studies indicate that the mechanism of decomposition under an argon atmosphere involves initial loss of sulfur dioxide. Based on comparison of thermal analysis data of olefinic and saturated polymers, oxidative attack at the olefin backbone is postulated as the first step in degradation under ambient atmosphere.

In the second chapter of this thesis, the use of living poly(*exo*-dicyclopentadiene) and living poly(norbornene) in reactions with a telechelic dialdehyde to form triblock co-polymers by coupling of reactive end groups is detailed. A reagent-specific degradation reaction prevented the isolation of triblock co-polymers from excess homopolymer, although gel-permeation chromatographs indicate that the coupling takes place with good efficiency. The successful use of poly(styrene-co-vinylbenzaldehyde) as a scavenging reagent for ROMP polymers is also reported.

Several small projects are discussed in the third chapter. The most important topic is the ionophoric behavior of ROMP poly(ethers). Monomers and polymers containing amines, thiophenes and methanesulfonyl groups are also discussed. The methanesulfonyl-derivitized ROMP polymer exhibits clean, uncatalyzed, elimination of methanesulfonic acid at 220 °C, which has implications for precursor polymers currently under study.

Table of Contents

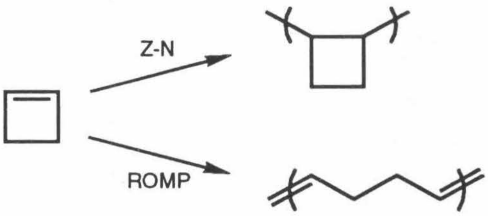
Chapter 1:

The Synthesis and Properties of Poly(Sulfones) from ROMP.

Introduction

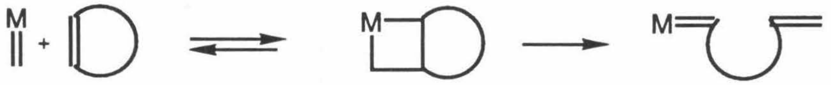
Ring-Opening Metathesis Polymerization

The conversion of cyclic olefins to unsaturated polymers via metal catalysis was discovered during the exploration of metal salt/olefin reactivity that was spurred by the discovery of Ziegler-Natta polymerization. Certain metal salts, when reacted with cyclic olefins, afford polymers with the same degree of unsaturation as the monomers. Ziegler-Natta polymerization, on the other hand, gives polymers with no unsaturation. Cyclobutene, for instance, may be polymerized in either fashion (eq. 1).[1]



(1)

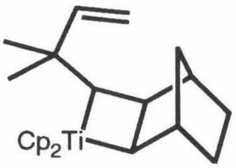
The mechanism of Ring-Opening Metathesis Polymerization (ROMP) is well established.[2] The metal center rests in one of two forms, a metal-alkylidene or a metallacyclobutane. The metal-alkylidene reacts with a cyclic olefin to form a metallacyclobutane, which may cleave in either degenerate (reforming starting materials) or productive fashion. Productive cleavage yields a new carbon-carbon double bond, which becomes part of the growing polymer chain, and a new metal-alkylidene (eq. 2). This new alkylidene goes on to react with another cyclic olefin, propagating the polymerization. Productive cleavage is favored by relief of ring strain as in the polymerization of norbornene, or by controlling equilibrium conditions, as in the polymerization of cyclopentene.



(2)

The earliest ROMP catalysts, referred to as classical catalysts, were ill-defined mixtures generally consisting of a metal salt and a Lewis acid co-catalyst. In these systems, the metallacyclobutanes and metal-alkylidenes are inferred rather than observed. Research in the area of classical catalysts continues, with efforts focused on increasing their activity and tolerance. Classical systems based on tungsten oxytetrachloride are currently used in the commercial manufacture of ROMP polymers.

Well defined catalysts have been isolated as metallacyclobutanes, which must be heated to induce cleavage and generate the active alkylidene. The titanacyclobutane, **1**, was the first such metallacyclobutane to be isolated. It was generated from the reaction of a protected alkylidene and an olefin.[3]



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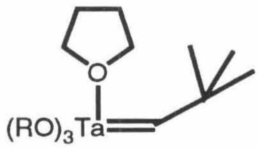
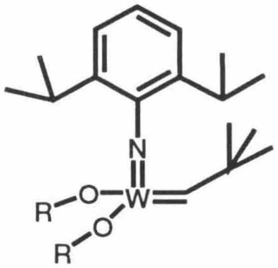
Other active catalysts were isolated as the metal-alkylidene, such as the tantalum-alkylidene **2**[4] and the family of tungsten-alkylidenes **3abc.**[5]



R = diisopropylphenyl

2

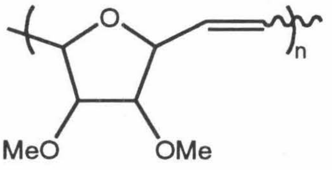


a) R = $C(CH_3)_3$
b) R = $C(CH_3)_2CF_3$
c) R = $CCH_3(CF_3)_2$

3abc

These examples, as well as most classical catalysts, effect the polymerizations of only hydrocarbon-containing monomers, limiting the applicability of ROMP.

Recently, catalysts have been developed which are tolerant of functional groups. Novak and Grubbs[6] discovered that the classical system "$RuCl_3$"/H_2O, which had been reported as a poor catalyst for hydrocarbon monomers,[7] was remarkably efficient in the polymerization of the 7-oxanorbornene derivative which gives **4**. These authors expanded this result to include the salts K_2RuCl_5 and $tos_2Ru(H_2O)_6$ and broadened the scope of the polymerization to related 7-oxanorbornenes such as the anhydride which is polymerized and hydrolyzed simultaneously to give **5**.[8]



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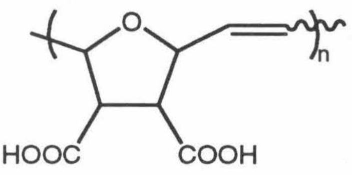

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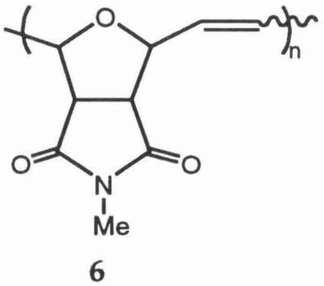
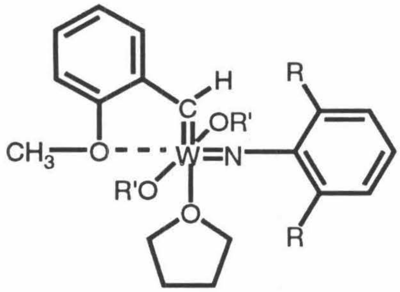
Aqueous ruthenium-catalyzed polymerization of 7-oxanorbornenes was also used in the synthesis of a high T_g material, **6**.[9]



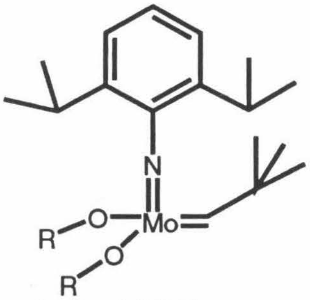
6

These successes with functionality-tolerant classical ROMP catalysts were followed by the development of functionality-tolerant well defined catalysts: a family of tungsten *o*-methoxybenzylidenes, **7abc**[10] and a family of molybdenum-alkylidenes, **8abc**.[11] A series of ester and cyano-containing 7-oxanorbornenes and their 7-methylene counterparts were polymerized by **8b**.[12] The 7-oxanorbornene derivatives were observed to polymerize faster than the 7-methylene derivatives.



a) R = H   R' = $C(CH_3)(CF_3)_2$
b) R = Me
c) R = *i*-Pr

7abc



a) R = $C(CH_3)$
b) R = $C(CH_3)_2(CF_3)$
c) R = $C(CH_3)(CF_3)_2$

8abc

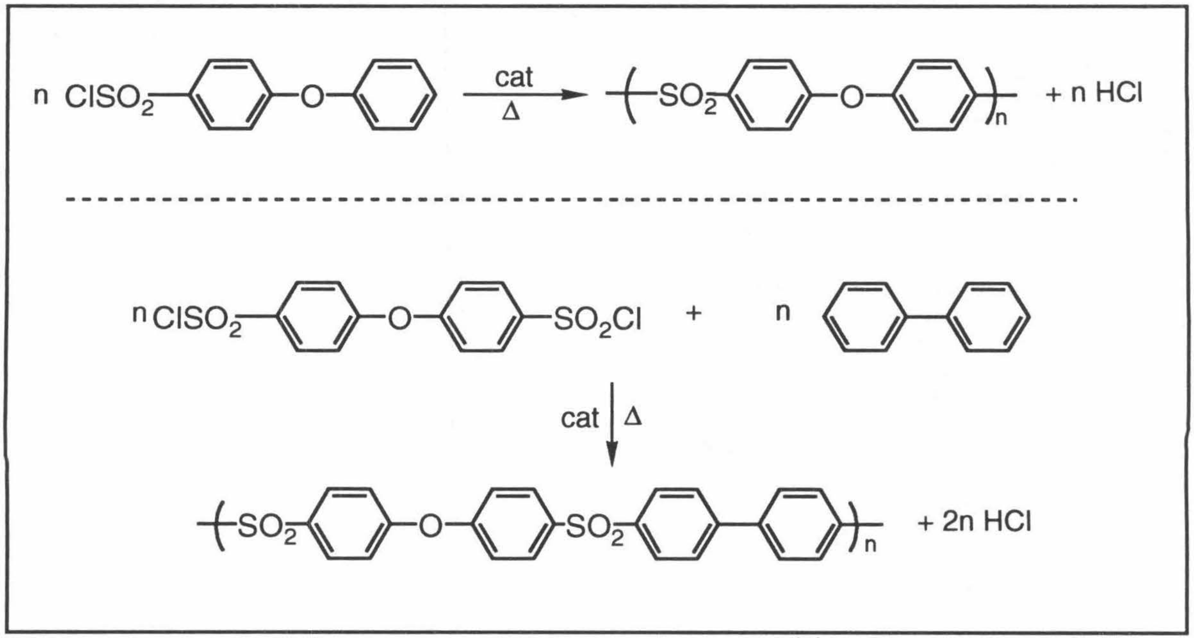
Encouraged by these results, we attempted and herein report the synthesis of polymeric sulfones using ROMP. Poly(sulfones) are a diverse group of polymers whose synthesis and properties are outlined below to provide context and motivation for the research described in this chapter.

Poly(sulfones)

Polymers containing the sulfone group have been known for several decades. Sulfone containing polymers can be classified into three broadly-defined groups: poly(arylsulfones), poly(olefinsulfones) and polymers with sulfones in the side-chains. A brief summary of each of these groups will be presented, with emphasis on the syntheses of these polymers and their thermal stability and decomposition characteristics.

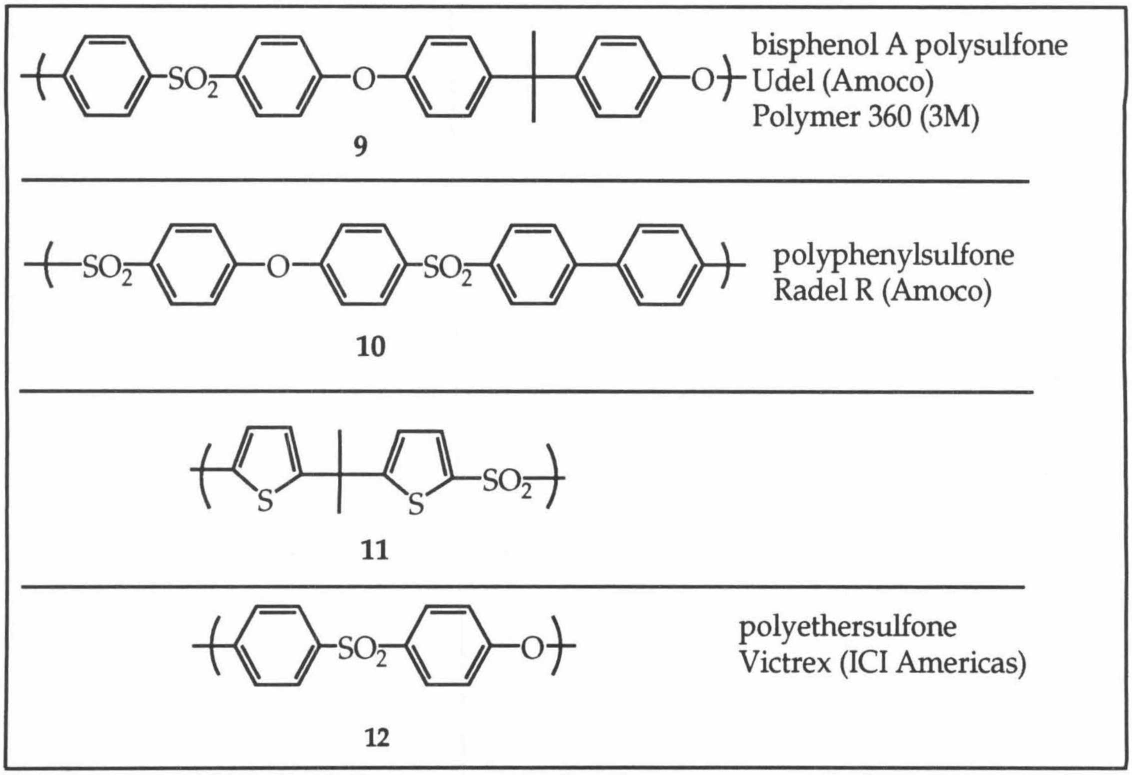
Poly(arylsulfones)

Poly(arylsulfones) are broadly defined as polymers that contain the sulfone group, *para*-linked aromatic rings and perhaps other groups in the backbone of the polymer, such as ether or dimethylmethylene. Poly(arylsulfones) were introduced in the 1960's, and were of interest because of their strength and thermal stability.[13] A typical synthesis of a poly(arylsulfone) is outlined in Scheme 1. Figure 1 provides structures and common and trade names for the poly(arylsulfones) discussed here.



Scheme 1: A Typical Synthesis of a Poly(arylsulfone)[14]

The thermal degradation properties of bisphenol A polysulfone, **9**, were reported by Gesner and Kelleher[15] in 1968. In the absence of light, **9** is stable to oxidative attack up to 140 °C. The mechanism of thermal, or dark, decomposition was not pursued, but the free-radical photo-decomposition was explored in detail. Gillham *et al.*[16] discussed the thermal properties of **10**, and Bringer and Morneau[17] reported a similar material of ill-defined structure. Compound **10** and similar materials are stable to 500 °C, with the onset of degradation at the T_g, 550 °C. Degradation is complete in air, but not in nitrogen. The pyrolysis products were reported: bisphenyl, biphenylether, phenol, and benzene are major products and dibenzofuran is a minor product. No discussion of the mechanism of decomposition was, however, presented, nor was a source of hydrogen, a necessary reactant in the decomposition reaction, suggested. More recently, Choi and co-workers introduced the thiophene-linked polysulfones **11**, which lack a T_g and degrade at lower temperatures than conventional poly(arylsulfones).[18] Sasuga *et al.* studied the electron beam resistance of a number of aromatic polymers, and found the poly(arylsulfones) **9** and **12** to be less stable to radiation than other aromatic polymers such as poly(imide), poly(ether-ether-ketone), poly(etherimide) and poly(arylate). This lack of stability was attributed to the propensity for SO_2-C bond homolysis leading to chain scission.[19]


9
bisphenol A polysulfone
Udel (Amoco)
Polymer 360 (3M)

10
polyphenylsulfone
Radel R (Amoco)

11

12
polyethersulfone
Victrex (ICI Americas)

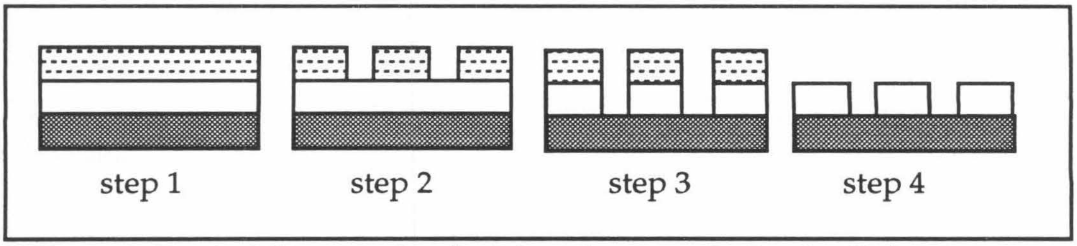
Figure 1: Common and Trade Names for Some Poly(arylsulfones)

Although poly(arylsulfones) were originally designed as high performance materials for harsh environments, they have demonstrated utility in other applications. Compound **9**, for example, has found extensive use as a gas separation membrane.[20] There is also interest in the use of poly(arylsulfones) as orthopedic implants; *in vitro* compatibility studies have shown promise.[21]Poly(arylsulfone) Co-polymers

Poly(arylsulfones) have been included as part of graft and block copolymers. Some recent examples are described here. Tingerthal *et al.*[22] used poly(arylsulfone)/ poly(phenyleneoxide) block copolymers with very small blocks (M_n ~3000) in fundamental studies of polymer miscibility. Auman *et al.*[23] demonstrated the synthesis of alternating block co-polymers of poly(arylethersulfone) and poly(dimethylsiloxane) by hydrosilation of α,ω-olefin terminated poly(arylethersulfones). These authors were able to vary the composition of these polymers, and thus vary the thermal transitions of the poly(arylethersulfone). Poly(arylsulfones) have also been incorporated into block co-polymers for membrane applications, where the poly(arylsulfone) provides strength and a softer block provides permeability.[24] Using a variation of this strategy, Nagase *et al.*[25] reported polydimethylsiloxane grafted onto poly(arylsulfones). These materials combined the strength of poly(arylsulfones) with the permeability of poly(dimethylsiloxane) to generate membranes with enhanced gas transport properties.

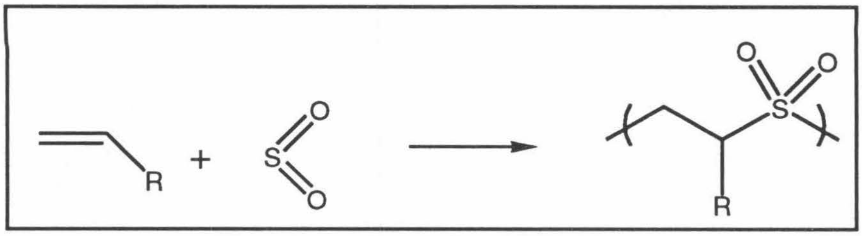
Poly(olefin sulfones)

Interest in poly(olefinsulfones) focuses on their use as resists. A resist is formed by creating a pattern in an insulating layer that contacts a semiconductor using a process called micro-lithography. A simple resist system is illustrated in Scheme 2: the solid layer on the bottom is a semiconductor (such as silicon) the white section is an insulator, (commonly silicon dioxide), and the dashed region is the resist. The resist, which is often a polymer, is spin-coated onto the insulating layer, giving the structure illustrated in step 1. In step 2, called developing, a pattern is created in the resist by exposure of some areas to radiation; the irradiated sections have a marked solubility difference from the non-irradiated sections. Consequently, one of the sections is dissolved away leaving the desired pattern. Step 3 is the transfer of the pattern to silicon dioxide, a process called etching. This is often accomplished with hydroflouric acid, although oxygen plasma is used as well. Finally, in step 4, called stripping, the rest of the resist is removed. The key features of a resist are (1) sensitivity to the radiation source so small amounts of radiation can be used, (2) good resolution (i.e., the edges of the image are sharp not ragged) and (3) resistance to swelling in the developing solvent. The radiation can cause solubility differences in two ways: in a negative resist the irradiated part becomes insoluble, for example, by crosslinking; in a positive resist, the irradiated section becomes soluble by, for example, chain scission.



Scheme 2: Typical Strategy for the Manufacture of a Device Using a Resist

Sulfur dioxide co-polymerizes with α-olefins in a thermally reversible process giving perfectly alternating vinyl addition co-polymers as shown in Scheme 3. Ceiling temperatures for these polymerizations range between 5 - 90 °C.[26] These polymers are useful as resists because the carbon-sulfur bonds homolyze readily with electron beam radiation leading to a high rate of backbone scission. Electron beam radiation is particularly useful because the wave length is very small. The resolution of a feature made by the resist process is limited by the wavelength of the impending radiation, thus, beams having smaller wavelengths can generate resolved features of smaller sizes. Parameters for micro-lithography using poly(1-butene sulfone) have been optimized to yield a highly sensitive resist process.[27] Volatile product studies of radiation-induced decomposition show an SO_2 to olefin ratio greater than one, and minor organic products (1-3%) that are attributable to cleavage of side chains before backbone scission occurs, or independant reactions of organic free-radicals at chain termini.[28]



Scheme 3: Alternating Poly(olefinsulfones)

Bowden et al.[29] used poly(2-methyl-1-pentene sulfone) as a solubility inhibitor in a Novolac positive resist formulation. Novolac resins are phenolic oligomers that are soluble in organic solvents and aqueous bases. The blend of poly(2-methyl-1-pentene sulfone) and novolac is insoluble. When the polymer blend is irradiated, however, the poly(2-methyl-1-pentene sulfone) undergoes chain scission, and the novolac becomes soluble. The sensitivity and contrast of this novolac system are excellent: submicron features were created using this resist. In addition, poly(olefinsulfones) resists are not suitable for the harsh dry etching conditions required for Very Large Scale Integrated (VLSI) devices, but this polymer blend is. By using a polymer blend, this system takes advantage of the high sensitivity toward radiation of poly(olefinsulfones) and the robust nature of the Novolac resin.

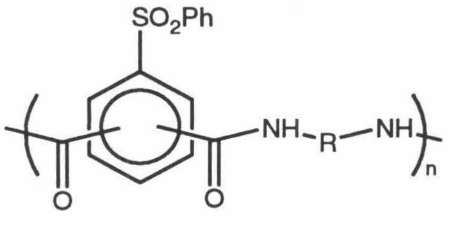
Poly(olefinsulfones) are not stable under dry (e.g. oxygen plasma) etching conditions. Kilichowski and Pampalone[30] used another approach to increase the stability of their reisist, in this case to overcome the dry etching limitation of poly(olefinsulfones). They co-polymerized vinyltrialkylsilanes with sulfur dioxide to make resists with good resistance to O_2 plasma etching. The alkylsilanes on the outer surface of the resist were oxidized to silicon dioxide which protected the underlying layer of polymer.

Arnold *et al.*[31] used the facile olefin/sulfur dioxide co-polymerizations to effect polymerizations of relatively unreactive vinyl mesogens, creating liquid-crystalline polymers. Although thermal depolymerization occurs with these polymers, correct choice of mesogen yielded polymers with liquid-crystalline phase transitions below the ceiling temperature of the poly(olefinsulfone) backbone.

Poly(olefinsulfones) are also bio-compatible and permeable to gases. Specifically the hexadecene-sulfur dioxide co-polymer is elastomeric and has the highest gas permeability of the polymers in the C_8-C_{18} α-olefin co-polymer series. The permeable hexadecene-sulfur co-polymer is cast on microporous polypropylene, which provides mechanical strength. Used this way, the hexadecene-sulfur dioxide copolymer has been successfully used as a hemodialysis membrane in test animals.[32]

Polymers with Sulfone Groups as Side-Chains

Sulfone groups have been introduced as side chains on a wide variety of polymer backbones.[33] A few examples where the effects of substitution on thermal stability are considered will be discussed here. Adduci and Brunea[34] prepared a series of poly(isophthalamides) and poly(terephthalamides) substituted on the aromatic ring with phenyl sulfone, **13**. They report T_gs in the range 100 - 200 °C. These values are 60-150 °C lower than the unsubstituted polymers. The phenylsulfone-substituted polymers also showed a lower thermal stability than the parent polymers, presumably due to carbon-sulfur bond homolysis. Onset of decomposition occurs from 380 to 410 °C. Conversely, Cameron and Chishti[35] reported an increase in both T_g and thermal stability when ArSCl is added across the double bond in poly(*cis*--1,4-butadiene) followed by oxidation to yield **14**. They report T_gs of 125 and 136 and onsets of decomposition at 285 and 289 °C for phenyl and tolyl sulfone side chains, respectively. The phenylsulfone group introduced a weakness, presumably C-SO_2 bond homolysis, relative to the parent polymer. The addition of arylsulfones to poly(*cis*-1,4-butadiene) across the double bond increases thermal stability. The C-SO_2 bond is thermally stable relative to oxidation of olefins, but unstable relative to aryl C-H bonds, thus arylsulfones increase the thermal stability of **14** relative to poly(butadiene), but decrease the thermal stability of **13** relative to its parent polymer.



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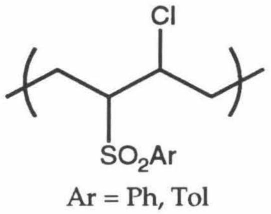

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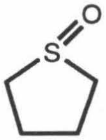
Results and Discussion

The ROMP synthesis of poly(sulfones) was undertaken in order to create a material with the radiation sensitivity of the poly(olefinsulfones) used as electron beam resists. Based on the stabilities of other ROMP polymers, we expected their new polymers to have greater thermal stability than conventional poly(olefinsulfones.) The ability to sucessfully subject monomeric sulfones to ROMP would expand the variety of materials currently available via this mechanism, that is, the very polar sulfone repeat unit is expected to significantly affect the solid phase inter-chain interactions that are responsible for a polymer's mechanical integrity. Success in creating a new ROMP polymer with either radiation sensitivity or unusual (for a ROMP polymer) mechanical properties, or other useful properties would expand the characteristics available for incorporation into block co-polymers. The synthesis of potential ROMP monomers appeared straightforward, and functionality-tolerant ROMP catalysts had recently been developed. Initial screening of catalyst tolerance was expanded to include sulfide **15** or the sulfoxide **16** as well as the model sulfone **17**.

15



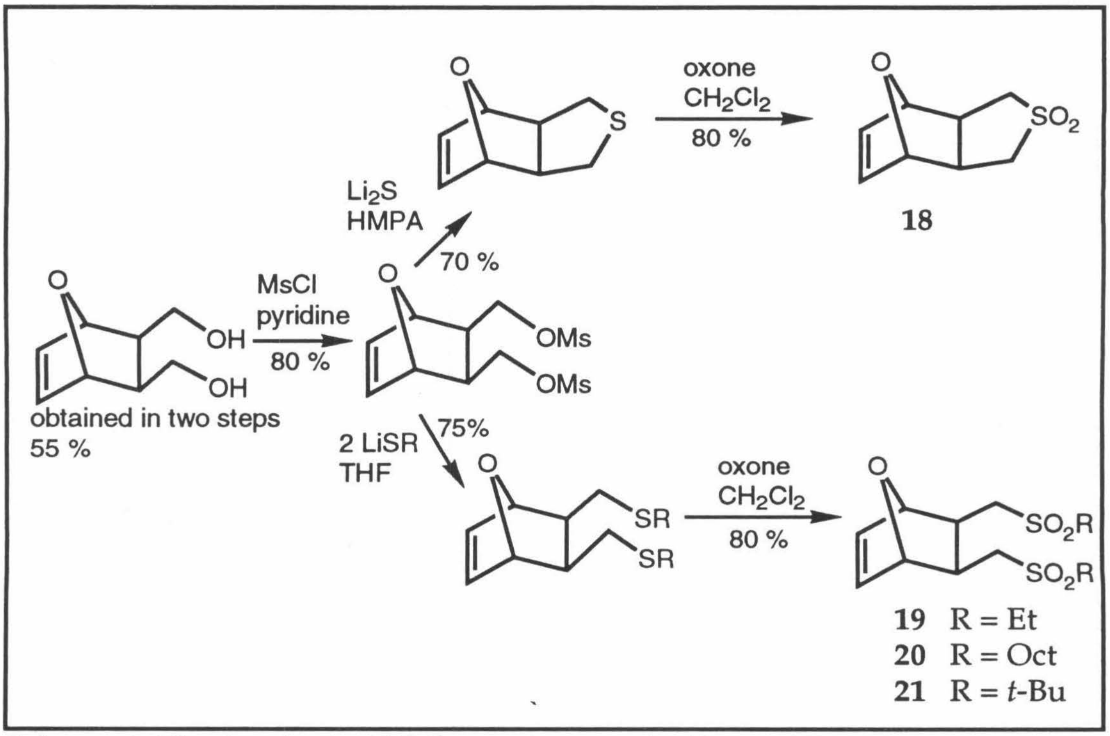
16

17

We attempted to make by ROMP in the presence of the above test molecules. Polymerization did not proceed in the presence of the sulfoxide or the sulfide. The lone pairs on sulfur are thought to complex strongly to ruthenium and interfere with catalysis. Polymerization in the presence of sulfone **17** proceeded smoothly however, and the synthesis of sulfone-functionalized 7-oxanorbornenes was undertaken.

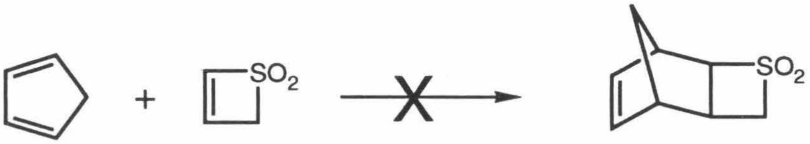
Synthesis of the Monomers

Monomers used in the polymeric sulfones were the cyclic sulfone **18,** and the bis(alkylsulfones) **19, 20** and **21**. These monomers can be synthesized in five steps, with twenty-five percent overall yield as shown in Scheme **4**.



Scheme 4: The Synthesis of 7-Oxanorbornenylsulfones

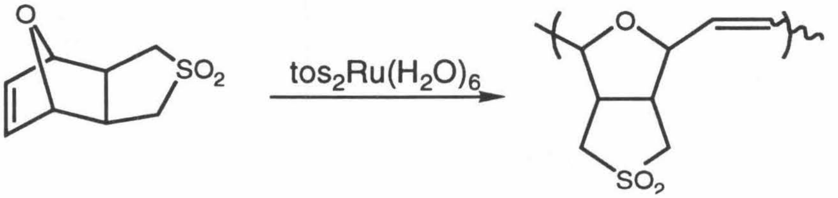
We believed that it might be possible to synthesize the cyclic sulfone **18** by the Diels-Alder reaction between furan and butadiene sulfone. Even catalyzed with $LiClO_4$[36], however, this reaction does not occur. Nor does the reaction between cyclopentadiene and thiete-1,2-dioxide (**22**) which would have provided another interesting monomer (**23**), proceed with $LiClO_4$ catalysis.



22 **23** (3)

Polymerization with Ruthenium Salts

The ruthenium salts $RuCl_3$ and K_2RuCl_5 do not effect polymerization of **18**. Catalysis with the more active[37], $tos_2Ru(H_2O)_6$, however produces greater than ninety-five percent yield of a white amorphous solid, identified by ^1H NMR as the ring-opened polymer, **18-Ru**.

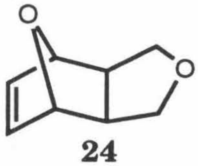


(4)

18 **18-Ru**

The optimum conditions for successful $tos_2Ru(H_2O)_6$-mediated polymerizations of **18** are demanding and not entirely straightforward in terms of solvent, atmosphere and temperature. We found that the solvents for polymerization can be water, methanol, ethanol or dimethylformamide (DMF). DMF is useful for NMR studies because the resultant polymers remain in solution. Unexpectedly, the polymerization in DMF is faster than that in water or alcohol. This does not appear to be caused by greater numbers of active catalysts in DMF, as demonstrated by a systematic investigation of the ruthenium-catalyzed synthesis of the polymer **4** in which we held the monomer-to-catalyst ratio and overall concentration steady while varying ratios of DMF and water. The molecular weights and polydispersity indices were the same for each solvent combination. This result suggests strongly that the same number of catalysts were active in the two solvents

In typical polymerizations of **18**, the reaction mixture is purged with argon during dissolution of monomer and catalyst. We have found that the ruthenium-catalyzed polymerizations to form the malemide **6** and the acid **5**, as well as the sulfone **18-Ru** require anaerobic conditions, but the ether monomers **4** and **24** will polymerize under aerobic conditions.



24

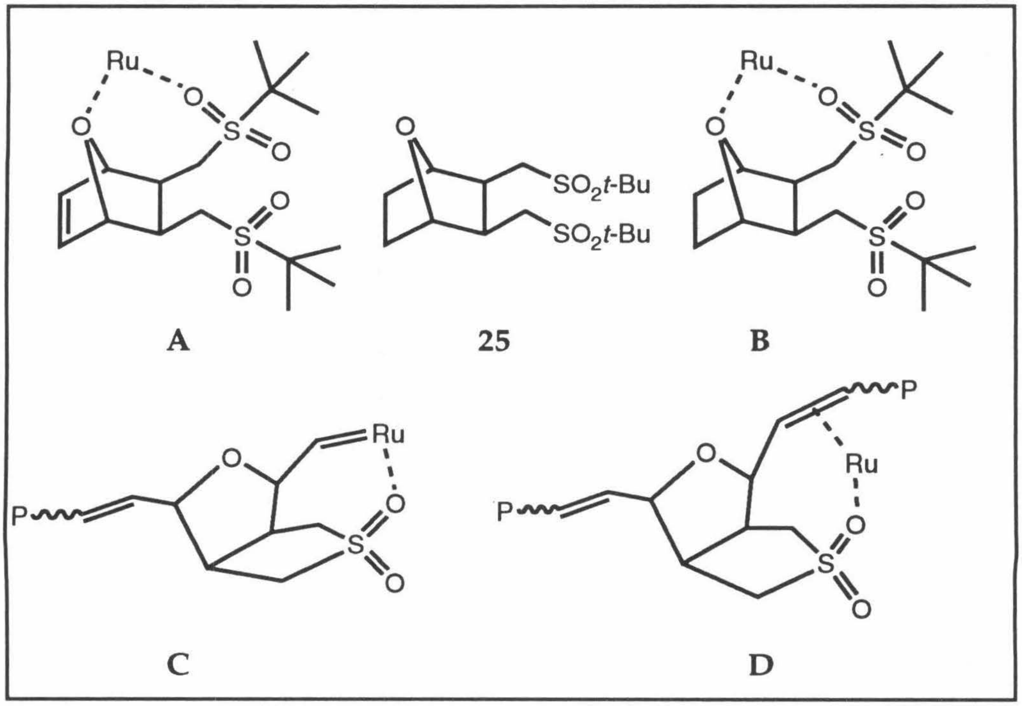
The required temperature for the formation of **18-Ru** is unusual -- room temperature. All other ruthenium-catalyzed polymerizations require 50-65 °C.

Finally, synthesis of **18-Ru** requires a 10:1 monomer to catalyst ratio. In the polymerization to form **4**, the molar ratio of metal salt to monomer is approximately 1:100 for successful polymerziations. Even at this level, it is estimated that << 1% of the catalyst is active.[38] When the monomer **18** is combined with 0.01 equivalents of $tos_2Ru(H_20)_6$, no polymerization is observed over a period of days; the reaction mixture, which begins red, and becomes yellow in successful polymerizations, turns green. One explanation of these results is that the metal center and the monomer **18** react in some fashion, other than ROMP, which causes the ROMP activity of the catalyst to be slowed or partially eliminated. The existence and nature of this interaction is still unkown, although several experiments, described below, have been performed in an attempt to better understand the $tos_2Ru(H_20)_6$-**18** system.

The pathway between the ruthenium salt and the active metathesis catalyst(s) formed *in situ* is unknown. However, the chemistry of $tos_2Ru(H_2O)_6$ and acyclic olefins has been studied in some detail; a ruthenium-hydride mechanism has been implicated in the isomerization of homo-allyl alcohol,[39] although the relationship between the olefin-isomerization mechanism and the metathesis-initiation mechanism has not been established. The salt $tos_2Ru(H_20)_6$ forms olefin complexes with several monomers as well as acyclic olefins, and the initiation process may begin with the ruthenium-olefin complex. Previous work in this group has indentified the ruthenium olefin complex of **4** in solution after polymerization is complete.[8] This complex can be isolated quantitatively. In an effort to determine whether this ruthenium-olefin complex might be a rest state of the precursor, or an uninvolved spectator species, we sought to follow the ruthenium-catalyzed polymerization of **18** by NMR and search for the previously unobserved active species. Herein we report the first example of a $tos_2Ru(H_2O)_6$ polymerization that is observable by NMR. The ruthenium olefin-complex comprises 30 % of the ruthenium present, determined by integration relative to the tosylate anion. This complex is observable in the first hour; its concentration does not detectably change over the duration of the polymerization (six hours). No active carbene complexes are seen by NMR (we would expect such a resonance between 8 and 20 ppm, and only the residual proteo DMF signal is seen in that region). The active species is present only in undetectable amounts, which is consistent with the estimate for **4** that << 1% of ruthenium is active. We cannot draw any conclusions from these data about the role of the ruthenium olefin complex in the polymerization.

Poisoning of the ruthenium center by the sulfone might occur during any of the potential intermediates leading to the catalytic species, or on the catalytically active species itself. The small fraction of ruthenium centers that become active catalysts (<< 1%) with well-behaved monomers precludes investigating the poisoning mechanism directly. We performed several experiments in an attempt to investigate this poisoning indirectly.

One reasonable poisoning mechanism involves the coordination of a ruthenium intermediate by the sulfone moiety, followed by further reaction of the monomer. Since the sulfone **17** does not inhibit the polymerization of **4**, the coordination might involve cooperative binding using both the 7-oxa position and the sulfone group or groups, as illustrated by structures **A** and **B** in Scheme 5. The inability of compound **25** to inhibit the polymerization of **4** does not support this hypothesis. Another possibility is for the olefin to be involved.



Scheme 5: Some Possible Coordination Modes for Ruthenium and Sulfone Monomers and Polymers

For instance, complexation might involve the nascent polymer, as shown in **C** of Scheme 5. In this scenario, the rate of initiation is not affected, but the rate of propagation is slowed. Another possibility is complexation of ruthenium atoms by segments of the polymer chain removed from the catalytic center, shown in **D** of Scheme 5.

A simple explanation is a trace amount of impurity. The monomer is made from precursors containing functional groups known to inhibit polymerization; trace amounts of starting materials could conceivably poison a catalyst. The fact that multiple batches of both catalyst and monomers have exhibited the same behavior argues against this explanation, although both were synthesized from the same route every time. Another argument against the impurity theory is that well-defined tungsten and molybdenum catalysts polymerize sulfone monomers at monomer-to-catalyst ratios of 100:1. The unusual monomer-to-catalyst ratio appears to be ruthenium-specific. Since the monomer **18** is not stable in the gas phase, it was analyzed by reverse-phase high pressure liquid chromatography, which shows one peak only, and elemental analysis. Within the limits of modern analytical techniques, the material is pure.

Another attempt to support chelation as an initial poisoning step involved digesting the monomer with, in seperate experiments, an equivalent iron (II) chloride or an equivalent of magnesium chloride, then adding the catalyst. If the monomer did coordinate strongly to metals, occupying the site on the monomer before addition of the ruthenium salt should competitively decrease the amount of poisoning. Pre-digestion of the monomer with salts did not afford polymerization of the monomer at ratios of monomer to catalyst reactions greater than 5:1. This result argues that chelation of the iniating species (thus decreasing k_i) or catalyst precursor does not occur.

It is also possible that the retro-Diels-Alder products of sulfone monomers might poison the polymerizations. The fact that the polymerization of **18** is inhibited by temperatures greater than ambient supports such a mechanism. However, no support for this mechanism was found when the compound **21** and its hydrogenated analog, **24**, were sealed in NMR tubes and allowed to stand at room temperature for two weeks. No retro-Diels-Alder products were observed in the NMR ; the spectra were unchanged. Furthermore, an attempt to inhibit polymerization of **4** with sulfolene itself, a retro-Diels-Alder product of **18**, was unsuccessful. In light of these results, a simple explanation identifying retro-Diels-Alder products of the sulfone monomers as catalyst poisons appears untenable.

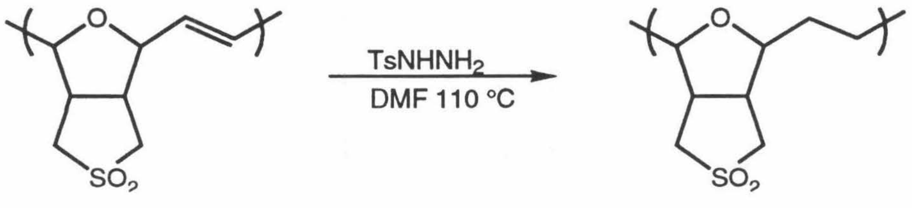
The above attempts to elucidate the mechanism of catalyst poisoning were unsuccessful. The studies suggest, however, that the poisoning might occur via intramolecular inhibition of propagation (*vide supra*). A better understanding of this poisoning mechanism might come with further elucidation of the events leading to the formation of the ruthenium-carbene in aqueous systems.

Synthesis and Characterization of Poly(sulfones) from ROMP

The polymer **18-Ru** is soluble in DMF (dimethylformamide) and dimethylsulfoxide, and sparingly soluble in N-methylpyrrolidinone. The dissolved polymer can be recovered by precipitation and is identical by NMR before and after dissolution, indicating that no irreversible interactions occur between the polymer and these strongly coordinating solvents. As precipitated, the material is a soft white solid which crumbles when handled.

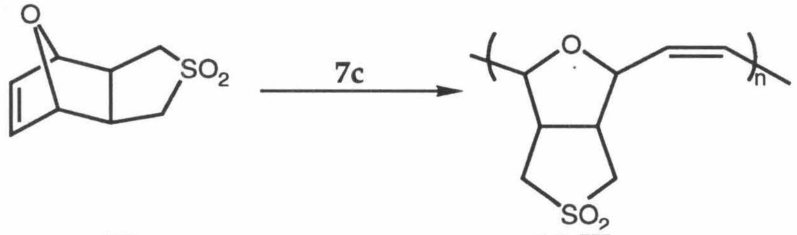
Although the monomer to catalyst ratio was low in these polymerizations, all detectable catalyst residue was removed.[40] GPC analysis of this material in DMF at 80 °C relative to poly(ethylene oxide) standards indicated an M_n of 77,800, and an M_w of 189,000, showing a broad distribution ($M_w/M_n = 2.4$) of high molecular weight material. Analysis by ^{1}HMNR spectra indicate 70 % of the olefins in the backbone of the polymer are *trans*, as is common for ROMP polymerizations catalyzed by ruthenium salts. Analysis by ^{13}C NMR support this observation, but do not suggest any stereoregularity in the backbone, as would be present in syndio- or isotactic polymers. The stereochemistry of ruthenium-catalyzed **4** has been thoroughly investigated, and the polymer is atactic.[41] Inspection of the ^{1}H NMR spectrum of the hydrogenated **18-Ru'** (*vida infra*) and comparison with the spectra of **4** of known tacticities indicates that **18-Ru** is also atactic.

The backbone of the polymer **18-Ru** can be hydrogenated to give the fully saturated polymer **18-Ru'** in quantitative yield (eq.n 5). **18-Ru'** has M_n of 101,000 and M_w of 260,000, (by GPC in DMF at 80 °C, relative to poly(ethylene oxide) standards). Since hydrogenation of the backbone significantly increases the degrees of freedom around the backbone carbon atoms, it increases the flexibility of the backbone. Hydrogenation should, therefore, also alter the hydrodynamic radius of the polymer. GPC works on a size-exclusion principle, and is a direct measure of hydrodynamic radii, not of molecular weights or chain lengths. The GPC data for **18-Ru'** cannot therefore, be expected to be the same as the data for **18-Ru.** We can conclude from the GPC data only that these chains are on the same order of magnitude. When isolated in the same way as **18-Ru**, by precipitation from DMF into methanol, the polymer **18-Ru'** is a hard plug. It does not crumble, nor does it exhibit any obvious elasticity. This qualitative increase in mechanical strength is also attributable to the increase in degrees of freedom in the backbone: more flexible backbones may allow better packing in the solid state and more entanglement of the polymer chains.



18-Ru **18-Ru'** (5)

The family of tungsten catalysts **7abc** were investigated for activity with the sulfone monomer **18**. At room temperature in a nitrogen dry box, **7b** and **7c** polymerized **18** in 85 % yield using a 100:1 monomer to catalyst ratio. The catalyst **7a** does not effect the polymerization. The steric bulk of the dimethyl- and diisopropylarylimido groups in **7b** and **7c** probably protect the metal center from attack by polar functionalities, while the phenylimido group does not protect the metal center. The mode of attack on **7a** has not been investigated beyond examination by ^{1}H NMR, which was uninformative. These sulfones represent the first example of monomers where well-defined tungsten catalysis proved more tolerant of functionality than ruthenium.



18 **18-W** (6)

The polymer formed by **7c, 18-W** has greater than 90% cis double bonds (from ^{1}H NMR analysis). No information is available about the tacticity of **18-W**, but in all cases where the tacticities of tungsten-catalyzed 7-oxanorbornene polymers has been investigated, the polymers are syndiotactic.[41] Analysis of the polymer **18-W** by GPC (in DMF at 80 °C versus poly(ethylene oxide standards) shows an M_n of 21,900 and an M_w of 54,000, which, as in the case of **18-Ru**, is a broad distribution of molecular weights ($M_w/M_n = 2.5$). Because of the difference in the ratio of *cis* to *trans* double bonds the conformation of the polymer backbone in **18-W** is different than that of **18-Ru** and the molecular weights cannot be compared directly. Polymer **18-W** has a different appearance than **18-Ru**. Isolated in the same way, by dissolving the initially formed polymer in DMF and precipitating into methanol, the tungsten-catalyzed polymer **18-W**, is yellowish, transparent and brittle, while the original ruthenium-catalyzed polymer is soft, white, and opaque.

The molybdenum catalysts **8b** and **8c** also efficiently polymerize sulfone monomers. Monomer **18** can be converted to the polymer **18-Mo** in good yield. The data for **18-Mo** are similar to those for **18-W**, as shown in Table 1.

Table 1: Comparison of the Properties of **23** Made by Three Catalysts.

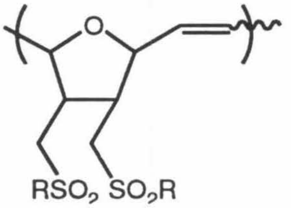
	yield	M/C[a]	M_n[b]	M_w	M_w/M_n	cis/trans[c]
18-Ru	95	5:1	77,800	189,000	2.4	30/70
18-W	85	117:1	21,900	54,000	2.5	90/10
18-Mo	83	101:1	23,200	102,000	4.4	80/20

[a] Molar ratio of monomer to catalyst . [b] Molecular weight data are from GPC in DMF relative to poly(ethylene oxide) standards. [c] From integration of ^{1}H NMR resonances.

The cyclic polymer **18-Mo** is similar in appearance to **18-W** as well as in spectroscopic properties. It is clear, yellowish and hard to break. It precipitates from methylene chloride during polymerization, and can be purified by reprecipitation from DMF into methanol. Any remaining catalyst residues are are not detectable.[42] Analysis by NMR indicates that the olefins in the backbone of this polymer are 80 % *cis*, the tacticity is unknown, but expected, by analogy to known poly(7-oxanorbornene) polymers, to be syndiotactic. The exact tacticity of **18-Mo** is currently under investigation. The polymer **18-Ru** has a high percentage of *trans* double bonds, which give it an extended conformation relative to the polymers **18-W** and **18-Mo** which are high in *cis* content and should thus be more twisted and kinked. Accordingly, a higher apparent molecular weight would be expected for **18-Ru** even for the same number of repeat units. Whether the observed molecular weight difference is due to this difference alone, or is combined with a real difference in the number of repeat units is not known. The clarity and hardness of **18-W** and **18-Mo** might be attributable to a high *cis* content as well. The hardness might be attributable to the more kinked or bent backbone which might be more entangled.

The polydispersity of **18-Mo** is strikingly high for a ROMP polymer. Both the tungsten *ortho*-methoxybenzylidene **7c** and the molybdenum neophylidene **8b** are relatively active catalysts; precipitation of polymer is observed within half an hour. The ruthenium-catalyzed polymerization is much slower, with precipitation observed only after several hours. In ROMP systems, a large distribution of molecular weights indicates an initiation rate that is slower or on the same order as propagation; thus, chains that initiate early propagate and grow a polymer chain to a significant length before other catalyst centers initiate. The activity of the tungsten *ortho*-methoxybenzylidene **7c** is moderated by the presence of an equivalent of tetrahydrofuran and the coordination of the oxygen atom from the *ortho*-methoxybenzylidne. These Lewis bases might slow the rate of initiation, bringing the relative rates more in line with those of a living system and lowering the PDI. The polymerizations of **18** are almost certainly not living, the precipitation of polymer from the reaction mixture and the observation of significant amounts of unreacted neophylidene and ortho-methoxybenzylidene rule out the possibility of a living system.

A series of bis(alkylsulfone)-containing monmers were synthesized and polymerized with molybdenum in an attempt to modify the thermal and



19-Mo R= Et
20-Mo R= Oct
21-Mo R = t-Bu

solubility properties of ROMP sulfones. The data for the polymerization of these monomers are summarized in Table 2.

Table 2: Data for the Polymerization of Sulfone Monomers by Catalyst **8b**.

polymer	yield	M/C[a]	M_n[b]	M_w	M_w/M_n	cis/trans[c]
18-Mo	83	101:1	23,200	102,000	4.4	80/20
19-Mo	53	67:1	16,600	30,300	1.8	-[d]
20-Mo	70	102:1	219,700	1,877,300	8.6	70/30
21-Mo	88	74:1	60,8000	91,100	1.5	60/40

[a] Molar ratio of monomer to catalyst . [b] Molecular weight data are from GPC in methylene chloride relative to poly(styrene standards), except data for **18-Mo**, which are from GPC in DMF relative to poly(ethylene oxide) standards. [c] From integration of ^{1}H NMR resonances. [d]High temperatature ^{1}H NMR data not yet available for this polymer.

The bis(alkylsulfone) polymers are all soluble in conventional solvents such as methylene chloride, chloroform and tetrahydrofuran, as well as in DMF and dimethylsulfoxide. They are purified by passing dilute methylene chloride solutions of the polymer through a plug of silica gel, followed by concentration and precipitation into methanol. The ethyl **19-Mo**, and the *t*-butyl **21-Mo** derivitives are similar to **18-Mo** in appearance; they are hard, clear yellowish solids. The low yield of **19-Mo** is in agreement with the observation that solid precipitates out of the polymerization reaction; the supernatant is collected and the desired polymer precipitated from the supernatant. The insoluble portion of the polymerization mixture might be cross-linked polymer. The octyl polymer **20-Mo** is a white, fibrous and brittle material as precipitated from methylene chloride. Solutions of this polymer are qualitatively more viscous that those of the other linear sulfone derivatives; the reaction mixture holds its shape in the vial almost instantaneously on mixing monomer and catalyst. There are several explanations for the occurrence of high molecular weight and high viscosity in this system. The polymerization may naturally give very high molecular weight polymers and this may be the sole cause of the viscosity. In another scenario, the quickly thickening reaction mixture causes a heterogeneous distribution of catalyst and monomers which terminates some catalyst ends early while allowing those in monomer-rich areas to continue polymerizing, thus giving a broad distribution of molecular weights. The GPC trace of **20-Mo** supports this explanation; it is tri-modal. The two large peaks are of lower molecular weight, the third peak is small, broad and of very high molecular weight.

Another monomer in this series, the bis(benzylsulfone) has been synthesized, but we were not able to purify it. Attempted with recrystallization, flash chromatography, and preparative HPLC, all efforts to purify failed, often producing material less pure than the crude reaction mixture. An attempt to polymerize the crude reaction mixture failed as well.

Polymerization Attempts with Thiete-1,1-dioxide.

Success in the polymerization of 7-oxanorbornenyl sulfones lead us to consider the polymerization of thiete-1,1-dioxide[43] i.e., the conversion of **22** to **26**. The ROMP of this monomer would have lead to a polymer similar to the poly(olefinsulfones), especially after hydrogenation. Since **26** would have been a ROMP monomer, it would have been a candidate for block-co-polymerization. Another interesting feature of polymers derived from **22** is their potential degradation properties. While **26** is similar to the poly(olefinsulfones), it should degrade into small organic fragments with the formula C_3H_4, allene or methyl acetylene. Hydrogenated, the polymer should form propylene upon elimination. However, **22** will not polymerize via any of the ruthenium catalysts nor the well-defined catalysts **7c**, **8b** or **8c**. There are at least two possible explanations for this lack of ROMP reactivity. First, the electron-withdrawing nature of the sulfone, which in this case is adjacent to the olefin, renders it relatively electron-poor. Second, the rather large size of the sulfone group, which in this case is very close to the olefin, might prevent approach of the olefin to the metal alkylidene. It is possible that both of these effects are operating synergistically. Sulfur is also much larger than carbon, lessening the ring strain: thiete-1,1-dioxide, **22** should be less strained than cyclobutene itself.

22 **26**

(7)

Thermal Analysis of Ruthenium-Catalyzed Sulfone Polymers

The polymer **18-Ru** is a white, amorphous solid, soluble in DMSO and DMF. It does not exhibit a glass transition by Differential Scanning Calorimetry (DSC), although an endotherm at 210 °C is observed on initial heating, which is attributed to crosslinking. The behavior of **18-Ru** in Thermal Gravametric Analysis (TGA) is more interesting. In ambient atmosphere, the onset of mass loss occurs at 230 °C, proceeding to 100 %

mass loss by 450 °C. Under inert (Ar) atmosphere onset occurs at 440 °C with complete loss by 520 °C.

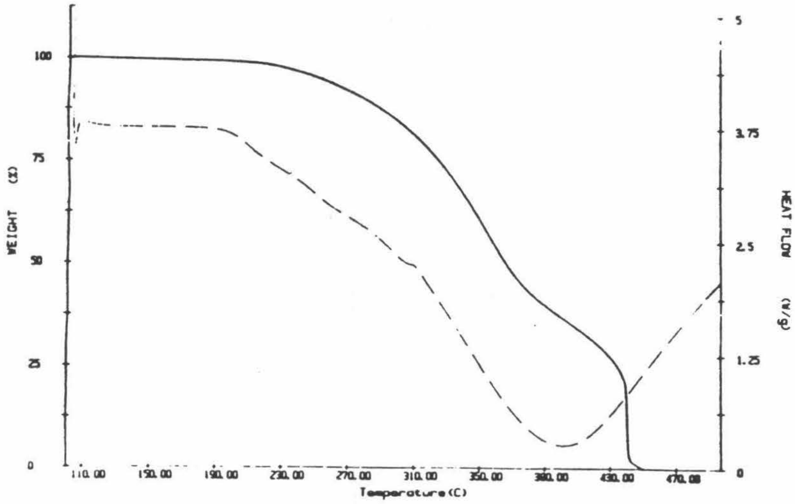


Figure 6: TGA and DSC of **18-Ru**.

As shown in Figure 2, the process is initially exothermic, as bonds are being broken, and then endothermic, presumably due to boil off of the organic fragments. The fully saturated polymer **18-Ru'** exhibits 100 % mass loss on heating as well. The T_ds for this material are 440 °C under air and 470 °C under Ar.

The structural components of **18-Ru** and the hydrogenated analog **18-Ru'** that give rise to no-ash degradation were investigated. The functional group dependence of no-ash degradation was investigated by subjecting other ruthenium-polymerized 7-oxanorbornene polymers to TGA up to 700 °C. The results of these studies are summarized in Table 3. Other than the sulfones, only one polymer, **6**, showed clean mass loss, which for this polymer occurs only under air.

Whether the oxygen of the terahydrofuan ring is required for clean degradations of polymers of this type is not known because the 7-methylene analogs of these polymers are currently synthetically inaccessible.[44] All examples of clean degradation, **18-Ru**, **18-Ru'** and **6** have a second ring fused to the tetrahydrofuran ring of the backbone. This feature is not sufficient for clean degradation, as the ether polymer **24-Ru** does not cleanly thermalyze. Hydrogenation of the backbone of the polymer **18-Ru** to **18-Ru'** raises the onset temperature in air, but does not significantly change the onset temperature in Ar. This suggests that different mechanisms are operative in air and Ar, and that the aerobic mechanism is associated with the olefinic backbone. Specifically, we believe oxidative attack at the olefin occurs during oxidative degradation, while thermal loss of sulfur dioxide by carbon-sulfur bond homolysis occurs during inert atmosphere degradation.

Table 3: Air and Ar T_d and Mass Loss for Several Ruthenium-Polymerized Poly(7-oxanorbornenes).

	Air		Ar	
	T_d (°C)	loss (%)	T_d (°C)	loss (%)
18-Ru	230	100	440	100
18-Ru'	440	100	470	100
6 (maleimide)	370	100	400	80
24 (ether)	375	75	440	85
4 (ether)	430	85	400	85
5 (acid)	230	55	230	55

There are several possible roles the sulfone group might play in polymer degradation. It is apparent that at least under an inert atmosphere, sulfur dioxide is liberated as a first step (*vide infra*). The sulfur dioxide gas might, however, be present during the rest of the degradation at least partially entrapped in the polymer matrix. The presence of sulfur dioxide might facilitate the decomposition of the remaining organic fragments. Another possibility is that the sulfur dioxide itself may not have any role beyond the initial carbon-sulfur bond homolysis. For example, sulfur dioxide might simply provide a cleaner degradation pathway than that available to other 7-oxanorbornene polymers.

In order to test the effect of sulfur dioxide during thermolysis, two polymers that did not contain sulfones (e.g., **4** and **6**) were subjected to TGA in a sulfur dioxide stream. The results of these analyses suggested definite reactivity between the gas and the polymer. The ether polymer **4** has a lower T_d in an inert atmosphere than it does in either an oxidative (oxygen) or reductive (sulfur dioxide) atmosphere. This observation suggests that for this polymer, a high T_d might result from reactions within the polymer, yielding highly cross-linked material. Analysis by TGA of the highly oxidized poly(acid) **6** shows no difference under oxygen and argon atmospheres, but mass loss begins almost immediately under a sulfur dioxide stream leaving slightly more residue, which is consistent with a high degree of gas-polymer reactivity. Although these results suggest a definite role for gaseous sulfur dioxide in the degradation of **6** we are unable (perhaps unwilling) to propose a mechanism for this interaction. We simply note here that the highly oxidized polymer **6** is degraded more readily under the reducing atmosphere of sulfur dioxide than under the inert atmosphere of argon. Sulfur dioxide reduces the highly oxidized polymer by some obscure mechanism, and thus lowers the T_d.

Table 4: TGA in Air, Ar and SO_2 for Two Ruthenium-Polymerized Poly(7-oxanorbornenes)

	Air		Ar		SO_2	
	T_d	% loss	T_d	% loss	T_d	% loss
4 (ether)	430	85	400	85	550	90
6 (acid)	230	55	230	55	< 100	60

Examination of the products formed from the degradation of **18-Ru** and **18-Ru'** were undertaken. Analysis by IR of the volatiles from the thermolysis of **18-Ru** collected in a gas-phase cell in early stages of degradation ($T \leq 500$ °C) show only sulfur dioxide. Analysis by ^{1}H NMR of the volatiles from later stages of the degradation of **18-Ru** are difficult to interpret: the data show mostly aliphatic peaks; however, some olefinic and aldehydic resonances can also be detected. Pyrolysis-GC/MS analysis of both **18-Ru** and **18-Ru'** showed sulfur dioxide as the major product. Identified organic pyrolysis products of **18-Ru** were mostly aromatic molecules with nine or fewer carbons, including styrene, ethyl benzene, 2,3-dimethylfuran, methyl styrene, benzoic acid, benzaldehyde, and acetophenone. These molecules are very common in the pyrolysis products of polymers; their presence suggests that there is no unusual or characteristic degradation pathway. Fewer reaction products were identified in the GC/MS of the **18-Ru'**, however the pyrolysis of **18-Ru'** did produce some larger molecular weight species (molecular ion > 200).

Thermal Analysis of Molybdenum-Catalyzed Sulfone Polymers

Three sulfone polymers **18-Mo**, **19-Mo**, **20-Mo** and **21-Mo** were subjected to TGA under air and argon; the results from these studies are below in Table 5. Under an atmosphere of argon, where we postulate that loss of sulfur dioxide is the first step, the organic group bound to the sulfone influences the T_d. The polymer **18-Mo** has the highest T_d, and all the bis(alkylsulfone) polymers have significantly lower T_ds. This observation can be rationalized if we consider that every carbon-sulfone bond homolysis event in the degradation of **18-Mo** creates an organic radical still bound to the polymer backbone. In contrast, some of the homolysis events in the bis(alkylsulfone)-containing polymers create small organic ethyl, octyl or *t*-butyl radicals which are free to enter the gas phase and start mass loss. We believe that the bis(alkylsulfone) polymers lose mass as soon as homolysis occurs, while **18-Mo** does not lose mass until much later. The bis(*t*-butylsulfone)-containing polymer **21-Mo** has a lower T_d than the other bis(alkylsulfones)-containing polymers. This is consistent with the fact that the 3° *t*-butyl radical is more stable than the 1° ethyl and octyl radicals and we believe carbon-sulfur bond homolysis to be the first step in thermal degradation.

Table 5: TGA Data for a Family of ROMP Poly(sulfones).

	Air		Ar	
	T_d (°C)	loss (%)	T_d (°C)	loss (%)
18-Mo	356	100	402	82
19-Mo	293	93	314	85
20-Mo	245	99	312	91
21-Mo	280	100	286	85

Comparison of the Thermal Analysis Properties of Polymer **18** Generated by Three Different Catalysts

The polymer **23** has been made with three catalysts: the $tos_2Ru(H_2O)_6$, the tungsten *ortho*-methoxybenzylidene **7c**, and the molybdenum neophylidene **8b**. The polymer **18-Ru** shows the most dramatic change in T_d under different atmospheres, and is the only polymer to degrade cleanly under argon. The ratio of *cis* to *trans* olefins in the polymer backbone is an obvious difference between **18-Ru** (predominately *trans*) and **18-Mo** and **18-W** (both predominately *cis*). The tacticities of **18-Mo** and **18-W** are unknown, although some tacticity is expected, while **18-Ru** is atactic; tacticity may influence the cleanness of degradation, however this effect cannot be separated from the effect of the *cis*/*trans* ratio. The possibility of catalyst residues affecting the degradation properties must also be considered.

Tungsten was detected in a sample of **18-W**, and while the level of ruthenium in the sample of **18-Ru** was below the threshold for detection, that threshold is high: 100-200 ppm. The polymer **18-Mo** is the only material we are confident is catalyst-free (< 10-20 ppm), and it exhibits a retention of mass similar to **18-W**, the only polymer we are confident is not catalyst-free. Any effect of catalyst residue is more involved than the simple absence or presence of metal-containing compounds. The *cis/trans* ratio shows the clearest correlation with the difference in the amount of mass left after degradation, although there is not enough information on the degradation mechanism in general to allow us to propose a mechansim for this effect.

Table 6: TGA Data for the Polymer **23** from Three Different Catalysts.

		Air		Ar	
	% cis	T_d (°C)	loss (%)	T_d (°C)	loss (%)
18-Ru	30	230	100	440	100
18-W	90	303	100	460	80
18-Mo	70	356	100	402	80

Exploration of Potential Applications

Before examining the radiation properties of polymer **18-Ru**, the material was subjected to Thermal Mechanical Analysis (TMA) to determine whether the material flowed significantly. Radiation-induced reactivity might be useful in a resist for microlithography, but a resist must not creep; that would blur the image created by exposure to radiaiton. Fortunately, there was no detectable flow between room temperature and 200 °C. Other promising features are that the polymer forms films and can be spin-cast from DMF.

Preliminary radiation experiments were performed to test **18-Ru** for potential use in lithography. An exposed sample of the polymer was subjected to 25 Mrads γ radiation. The exposed sample did not show any difference in appearance, nor was it soluble in simple organic solvents, which might have suggested scission of the polymer backbone. Analysis by X-ray fluorescence showed a 6 % loss of sulfur indicating that sulfur-carbon bond homolysis probably did occur, but resulted in cross-linking instead of chain scission. Examination by TGA of exposed and unexposed samples showed some differences; the exposed sample began losing weight at relatively low temperatures (ca 100 °C) although the magnitude of this loss was small. The onset of substantial degradation occurred at slightly lower temperatures for the exposed polymer than for the unexposed polymer. In addition, mass loss for the exposed sample was not complete by 525 °C; mass loss for the unexposed polymer was complete at this temperature. These data are consistent with initial radiation induced-bond homolysis generating sulfur dioxide followed by crosslinking. It might be possible to use this reactivity to crosslink the irradiated areas, making them insoluble and thus generating a negative reisist. The bis(alkylsulfone) polymers are particularly attractive for this application because they are readily soluble in a variety of solvents.

The material **18-Ru** was also tested for its ability to undergo clean thermolysis on the surface of several different materials. Complete mass loss was observed on only two surfaces: platinum and silicon dioxide. Polymers thermolyzed in an oxidizing atmosphere from glass, silinized glass, gold, titanium, nickel, brass, stainless steel, silicon, and aluminum left some residue. These observations suggest that there might be some limitations on the use of these polymers as binders for ceramics processing.

Conclusions

The monomer **18** is readily polymerized by the tungsten *ortho*-methoxybenzylidene **7c** and the molybdenum neophylidene **8b**. Polymerization of **18** can be effected by $tos_2Ru(H_2O)_6$ only with a 10:1 monomer to catalyst ratio, which may be due to complexation of metal centers by the nascent polymer chain, or by segments of the polymer distant from the active catalyst. The polymer **18-Ru** has a high proportion of *trans*-olefins in the backbone of the polymer, and is soft and opaque, while **18-W** and **18-Mo** have high proportions of *cis* double bonds and are hard and clear. All polymers from **18** have M_n in the tens of thousands (relative to poly(ethyleneoxide)) and are soluble in DMF and DMSO. Polydispersities for **18-Ru** and **18-W** are ca. 2.5, while the PDI for **18-Mo** is 4.4. None of these systems are living.

Monomers containing two alkyl sulfone side chains were synthesized and polymerized with molybdenum neophylidene **8b**. The bis(ethylsulfone) **19-Mo** and the bis(*t*-butylsulfone) **21-Mo** are similar to **18-Mo**; the bis(octylsulfone) **20-Mo** is different in appearance, being an opaque, fibrous and brittle material, and is different in molecular weight, having a substatially higher M_n and M_w. These polymers are readily soluble in methylene chloride, chloroform and tetrahydrofuran; the octyl derivitive **20-Mo** forms viscous solutions.

The polymers **18-Ru** and **18-Ru'** thermolyze cleanly under atmospheres of argon and air. Six polymers thermolyze cleanly only under an atmosphere of air: the ruthenium-catalyzed maleimide **6**, and the sulfones **18-W, 18-Mo, 19-Mo, 20-Mo**, and **21-Mo**. *Key features in the thermolysis of 18-Ru might be the oxygen of the tetrahydrofuran ring, the second ring fused to the* *tetrahydrofuran ring, the high proportion of trans-to-cis bonds, the lack of stereoregularity in the backbone, and the sulfone moiety.* The mechanism of decomposition under an argon atmosphere involves initial loss of sulfur dioxide, as shown by product studies. We propose that carbon-sulfur bond homolysis as the first step in inert-atmosphere degradation. The lower T_ds of the bis(alkylsulfones) are consistent with this proposal. We propose that degradation under ambient atmosphere occurs by a separate mechanism: oxidative attack on the olefin backbone, which is consistent with the relative T_ds of **18-Ru** and **18-Ru'** under ambient and argon atmospheres.

Initial radiation studies indicate loss of sulfur without any indication of backbone scission. TGA suggests some crosslinking might occur, and we suggest that these materials, especially the bis(alkylsulfone) polymers, might be useful as negative-tone resists.

Experimental

General Procedures. All manipulations involving air- and/or moisture sensitive compounds were carried out using standard Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å sieves. Solids were transferred and stored in a N_2-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a Jeol GX-400 (399.65 MHz ^1H, 100.40 MHz ^{13}C) or a GE QE-300 (300.19985 MHz ^1H, 75.492893 MHz ^{13}C). Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. ^1H-^{13}C INEPT Spectra were recorded on the JEOL GX-400 NMR Spectrometer, operating at the frequencies listed above. The ^1H decoupler 90° and ^{13}C 90° pulse widths were measured on a sample of 1:1 to chloroform : acetone-d_6 as described by Derome[45] and by searching for the 180° null, respectively, and were typically 41 and 10.5 ms, respectively on the 5mm $^1H/^{13}C$ prove. The fixed delays were set for J_{CH} = 150-155 Hz. Infrared spectra were obtained on a Perkin-Elmer 1600 Series FT-IR; samples were neat on AgCl plates unless otherwise described. Analytical HPLC was performed using a Waters 600E HPLX System with a Beckman Ultrasphere ODS (C_{18}, 5 m) reverse-phase HPLC column, 4.6 mm x 250 mm, and a Waters 994 Programmable Photodiode Detecter. GPC analyses were carried out on an HPLC system consisting of an Altex Model 110A pump operating at 1.0 mL/min, a Rheodyne Model 7125 injector with a 100 mL injection loop, through either three Shodex Styragel columns (KF 803, KF 804 and KF 805) or an American Polymer Standards 10 mm mixed-bed column, and two detectors (Knauer Differential-Refractomer and Kratos Spectroflow 757 UV detector operating at 325 nm). Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7 and thermogravametric analysis was accomplished on a Perkin-Elmer TGA-2. Thermal Mechanical Analysis was carried out on Perkin Elmer TMA-3 apparatus. Pyrollysis GC/MS was performed by Phil Kehoe of the Eastman Kodak Company, Rochester, NY. Exposure to γ radiation and the accompanying X-ray fluorescence studies were performed by Jim Hansen of Bell Labs, Murray Hill, NJ.

Materials. Catalyst $tos_2Ru(H_2O)_6$ was prepared according to literature procedures.[46] K_2RuCl_5 was purchased from Aesar ; $RuCl_3{\cdot}nH_2O$ was purchased from Strem; both were used as received. The tungsten catalysts

7abc were provided by L. K. Johnson, the molybdenum catalysts **8b** and **8c** were provided by V. P. Conticello and G. C. Fu , respectively, all of this laboratory. Monomer synthesis and polymerization of **4** were carried out according to literature procedure.[8] The polymers **5** and **6** were provided by M. A. Hillmyer and J. E. Barrett of this lab. Monomer synthesis and polymerization of **24** were carried out as described in Chapter 3 of this thesis.

Screening of Ruthenium Catalysts for Sulfur Tolerance. The sulfide **15**, sulfoxide **16** and sulfone **17** were purchased from Aldrich chemicals and distilled prior to use. Screening reactions were carried out with potassium ruthenate or ruthenium tosylate; the successful polymerization of **4** indicated a tolerance for that functionality. Two polymerization solutions were prepared with the monomer, water and catalyst. In separate trials, sulfide, sulfoxide and sulfone were added to a reaction mixture and the other was left as a control. The presence of polymer indicated no inhibition.

Synthesis of *exo*-2,3-dimethansulfonyloxymethyl-7-oxabicyclo-[2.2.1]-hept-5-ene. The diol, *exo*-2,3-dihydroxymethyl-7-oxabicyclo-[2.2.1]-hept-5-ene (20.31 g, 0.133 moles) was dried in THF over sieves. The solvent was removed and the diol was dissolved in 60 mL pyridine (distilled from CaH_2). Under a stream of Ar, a 2 L, three neck flask equipped with addition funnel, mechanical stirrer and Ar inlet/ thermometer adapter was charged with 17.3 mL (0.267 moles) methanesulfonyl chloride (used as received from Kodak) and 50 mL pyridine. This was cooled to -10 °C with dry ice/acetone. The diol solution was added dropwise over 2 hr, keeping the reaction temperature under 10 °C. The reaction was allowed to stir 1.5 hr, and then 1.25 L of an ice-cold 1.75 M HCl solution was added quickly. The mixture was allowed to stir 0.5 hr, then the solid product was collected by vacuum filtration and washed twice with cold water. The solids were then dissolved in chloroform, dried over magnesium sulfate and filtered. The volume of solvent was reduced, and the product was recrystallized from boiling chloroform to give 25 g (60 %) of a brown granular solid. ^{1}H NMR δ (ppm) 6.43 (s, olefin, 2H); 4.88 (s, bridgehead, 2H); 4.35 (m, methylene, 4H); 3.05 (s, methyl, 6H); 2.18 (m, methine, 2H). ^{13}C NMR δ (ppm) 135, 80, 69, 40, 36.

Synthesis of *exo*-10-oxa-6-sulfatricyclo-[4.3.0.1^{3,9}]-dec-1-ene. In the drybox, *exo*-2,3-dimethansulfonyloxymethyl-7-oxa-2.2.1-bicyclohept-5-ene, (15 g, 48 mmoles) and lithium sulfide, anhydrous (6.04 g, 144 mmoles) were weighed into a 250 mL Schlenk flask, which was transferred to a Schlenk line.. DMSO (150 mL, distilled from sieves) was added. The flask was sealed, brought to 100 °C with stirring, and left at 70 °C stirring, for 3 days. To the cooled reaction mixture was added 40 mL hexanes and 40 mL brine. The aqueous layer was washed 3 x 40 mL hexanes. The organics were combined, dried over magnesium sulfate, filtered and the solvent was removed. The solids were dried under vacuum overnight. The product (3.99 g, 54 %) was used as obtained. ^{1}H NMR (DMSO-d_6) δ (ppm) 6.36 (s, olefin, 2H); 4.60 (s, bridgehead, 2H); 2.87, 2.60 (m, methylene, 4H); 2.62 (s, methine, 2H).

Synthesis of *exo*-10-oxa-6-(dioxasulfa)tricyclo-[4.3.0.1^{3,9}]-dec-1-ene. **18**. Oxone (23.8g, 39 mmoles) was dissolved in 100 mL water. The sulfide *exo*-10-oxa-6-sulfatricyclo-[4.3.0.1^{3,9}]-dec-1-ene (4.0 g, 26 mmoles) was dissolved in 150 mL methanol and cooled with an ice bath. The oxone solution was added to the stirring sulfide and the resulting white slurry was allowed to stir 4 hr. The reaction mixture was then diluted with 250 mL water and extracted 3 x

250 mL chloroform. The organics were combined, dried over magnesium sulfate and the solvent removed. The resulting white solids were dried under vacuum overnight to give 4.4 g (79 %) of sulfone ^{1}H NMR δ (ppm) 6.37 (s, olefin, 2H); 4.73 (s, bridgehead, 2H); 3.30, 2.73 (m, methylene, 4H); 2.45 (m, methine, 2H). Analysis calc % C 51.6, % H 5.42; found % C 51.5, % H 5.18. Reverse-Phase HPLC was carried out with isocratic 50/50 ethyl acetate/hexane, a 20 mL injection volume and the UV/vis detector set at 246 and 300 nm.

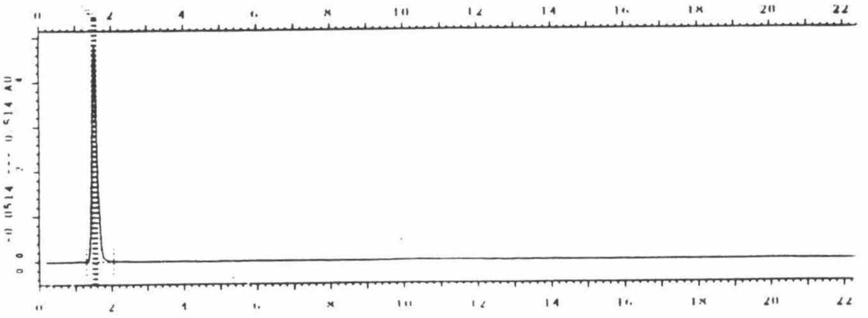


Figure 5. Reverse-Phase HPLC Trace of **18.**

<u>Synthesis of *exo*-2,3-di(*t*-butylsulfamethyl)-7-oxabicyclo-[2.2.1]-hept-5-ene.</u>
Fresh THF (90 mL) was syringed into a 500 mL schlenk flask under Ar. 1,1-dimethylethane thiol (5.8 g, 64 mmole) was added via syringe and the solution cooled to 0 °C. A hexane solution of *n*-butyl lithium (36 mL, 1.8 M) was added via syringe and the mixture was stirred for 30 min, then, under Ar flow, 10 g (32 mmoles) of the solid 2,3-dimethansulfonyloxymethyl-7-oxa-2.2.1-bicyclohept-5-ene was added all at once. The reaction was allowed to warm to room temperature while stirring overnight. The reaction mixture was poured into a seperatory funnel containing 200 mL each diethyl ether and water. The aqueous layer was washed 3 x 100 mL ether, the organics were combined, dried over $MgSO_4$ and evaporated to yield 7.0 g (73 %) of

crude sulfide, which was oxidized without further purification. ^{1}H NMR ($CDCl_3$) δ (ppm) 6.31 (s, olefin, 2H); 4.83 (s, bridgehead, 2H); 2.83, 2.47 (m, methylene, 4H); 1.70 (m, methine, 2H); 1.29 (s, methyl, 18H).

Synthesis of *exo*-2,3-di(ethylsulfamethyl)-7-oxabicyclo-[2.2.1]-hept-5-ene. This compound was prepared as for 2,3-di(*t*-butylsulfamethyl)-7-bicyclo-[2.2.1]-hept-5-ene. ^{1}H NMR ($CDCl_3$) δ (ppm) 6.35 (s, olefin, 2H); 4.88 (s, bridgehead, 2H); 2.78 (m, methylene, 2H); 2.53 (q, $SC\underline{H}_2CH_3$, 6H); 2.42 (m, methylene, 2H); 1.76 (m, methine, 2H); 1.23 (t, $SCH_2C\underline{H}_3$, 18H).

Synthesis of *exo*-2,3-di(octylsulfamethyl)-7-oxabicyclo-[2.2.1]-hept-5-ene. This compound was prepared as for 2,3-di(*t*-butylsulfamethyl)-7-bicyclo-[2.2.1]-hept-5-ene. ^{1}H NMR ($CDCl_3$) δ (ppm) 6.41 (d, J_{HH} = 0.61 Hz, olefin, 2H); 5.06 (d, J_{HH} = 0.59 Hz, bridgehead, 2H); 3.19, 2.85, 2.99 (all m, overlapping methylenes α-to-SO_2, 8H); 2.38 (m, methine, 2H); 1.79 (m, internal methylene of octyl, 4H); 1.40 (m, internal methylene of octyl, 4H); 1.24(m, internal methylene of octyl, 16H); 0.84 (t, J_{HH} = 6.63 Hz, methyl, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm) 135.7, 82.5, 53.9, 52.4, 34.6, 31.6, 28.9, 28.8, 28.3, 22.5, 21.7, 14.0.

Synthesis of *exo*-2,3-di(ethylsulfonylmethyl)-7-oxabicyclo-[2.2.1]-hept-5-ene, **19**. Prepared as for *exo*-2,3-di(*t*-butylsulfonylmethyl)-7-oxabicyclo-[2.2.1]-hept-5-ene, **21**. ^{1}H NMR ($CDCl_3$) δ (ppm) 6.45 (s, olefin, 2H); 5.08 (s, bridgehead, 2H); 3.24 (m, methylene, 2H); 3.04 (q, $SC\underline{H}_2CH_3$, 6H); 2.93 (m, methylene, 2H); 2.43 (m, methine, 2H); 1.43 (t, $SCH_2C\underline{H}_3$, 18H). ^{13}C NMR ($CDCl_3$) δ 135 (olefin); 83 (bridgehead); 52 ($\underline{C}H_2CH_3$); 48 (CH_2); 35 (CH ring); 6.5 ($CH_2\underline{C}H_3$).

Synthesis of *exo*-2,3-di(octylsulfonylmethyl)-7-oxabicyclo-[2.2.1]-hept-5-ene, **20**. Prepared as for *exo*-2,3-di(*t*-butylsulfonylmethyl)-7-oxabicyclo-[2.2.1]-hept-5-ene, **21**. ^{1}H NMR ($CDCl_3$) δ (ppm) 6.41 (s, olefin, 2H); 5.06 (s, bridgehead, 2H); 3.2-2.8 (m, overlapping methylenes, 8H); 2.38 (m, *endo*-methine, 2H); 1.79 (m, β-methylene on octyl chain, 4H); 1.4-1.0 (m, five internal methylenes from octyl chain, 20H); 0.84 (t, methyl, 6H). ^{13}C NMR (CDCl3) δ (ppm) 135.7 (olefin); 83.5 (bridgehead); 53.9, 52.4 (methylenes); 34.6, 31.6, 28.9, 28.8, 28.3, 22.5, 21.7, (methine and octyl chain, unassigned); 14.0 (methyl).

Synthesis of *exo*-2,3-di(*t*-butylsulfonylmethyl)-7-oxabicyclo-[2.2.1]-hept-5-ene, **21**. The sulfide, 2,3-di(*t*-butylsulfamethyl)-7-oxabicyclo-[2.2.1]-hept-5-ene. (7.0 g, 23. mmoles) was dissolved in 150 mL methanol and the solution chilled to 0 °C; 43 g Oxone (70 mmole) was dissolved in 200 mL water, then poured into the chilled sulfide solution. The reaction mixture was allowed to stir and warm to room temperature over four hours. The resulting slurry was diluted with 250 mL water and washed 3 x 250 mL chloroform. The organics were dried over $MgSO_4$ and rotovapped to dryness, yielding 7.0g (82 %) of product. The product was further purified by flash chromatography in 100 % ethyl acetate. ^{1}H NMR in $CDCl_3$ δ (ppm) 6.46 (s, olefin, 2H); 5.04 (s, bridgehead, 2H); 3.33, 2.88 (m, methylene, 4H); 2.50 (m, methine, 2H); 1.41 (s, methyl, 18 H). ^{13}C in $CDCl_3$ δ 135.9 (olefin); 83.4 (bridgehead); 59.8; (methylene); 46.1 (quatenary carbon); 34.7 (methine); 23.3 (methyl). IR solid on AgI cm^{-1} 2990 (C-H stretch); 1477 (C-H scissor); 1282 (SO_2 asymmetric stretch) 1106 (SO_2 symmetric stretch).

Ruthenium-Catalyzed Polymerization of **18**. Monomer **18** (1.57 g, 8.45 mmole) and $tos_2Ru(H_2O)_6$ (0.377 g, 0.726 mmole) were placed in a flask and subjected to three pump fill cycles, and then dissolved in 90 mL degassed water. After three days the white precipitate was collected by centrifuge and washed 3 x 90 mL water, 90 mL ethanol, 90 mL diethyl ether. The crude polymer was dried *in vacuo* to yield 1.46 g (93.1 %) of solid. The polymer can be further purified by dissolving it in dimethyl formamide and precipitating into water, or by soxhlet extraction with tetrahydrofuran. ^1H NMR (DMSO-d_6) δ (ppm) 4.99 (br s, *trans*-olefin, 1.4 H); 4.78 (br d, *cis*-olefin, 0.6 H); 3.63 (br s, *cis*-α-to-oxygen); 3.31 (br s, *trans*-α-to-oxygen); 2.49 (br s, methylene, partially under DMSO); 2.22 (br d, methylene, 2H); 1.84 (br s, methine, 2 H). ^{13}C NMR (DMSO-d_6) δ (ppm) 133-132 (*cis*-olefins); 131-130 (*trans*-olefins); 82.5-84 (*trans*-α-to-oxygen); 78-80 (*cis*-α-to-oxygen); 51 (methylene); 43-45 (methine). (^{13}C NMR assignments aided by INEPT.)

Ruthenium-Catalyzed Polymerization of **21**. Polymerization of **21** was performed in the manner described above for **18**.

Synthesis of *exo*-10-oxa-6-(dioxasulfa)Tricyclo-[4.3.0.$1^{3,9}$]-decane.
This compound was prepared according to literature methods[47] from **18.** ^1H NMR (CH_2Cl_2) δ (ppm) 4.28 (m, bridgehead, 2H); 3.14, 2.76, 2.65 (m, exocyclic methylene and *endo*-methine, 6H); 1.77, 1.55 (m, norbornane methylene, 4H). ^{13}C NMR δ (ppm) 80.3, 52.3, 43.8, 28.9.

Synthesis of 2,3-*exo*-di(*t*-butylsulfonyl methyl)-7-oxabicyclo-[2.2.1]-heptane, **24**. This compound was prepared according to literature methods[#] from **21**. ^1H NMR (CH_2Cl_2) δ (ppm) 4.60 (d, bridgehead, 2H); 3.17, 2.89 (m, exocyclic methylene, 4H); 2.68 (s, *endo*-methine, 2H); 1.74, 1.62 (m, norbornane methlyene, 4H); 1.39 (s, methyl, 18H).

Examining the Ability of **24** to Inhibit Ruthenium ROMP. To test the ability of **24** to inhibit ruthenium catalyzed polymerizations, a stock solution of the monomer for **4** in water was made, to which a small amount of $tos_2Ru(H_2O)_6$ was added. The solution was split in half, and **24** was added to one, the other was reserved as control, and both were heated to 60 °C overnight. The resulting polymers were dissolved in and reprecipitated from THF. The polymer samples were identical by ^1H NMR and GPC.

Pre-Chelation of Metal Salts by the Monomer **21**. To test pre-chelation, four runs were set up based on 20 mg **21** each. The monomer and magnesium chloride were dissolved together, purged and shaken one hour before the ruthenium was added. After addition the mixtures were shaken overnight. Polymer was observed in run A and D only. A parallel experiment was run with iron (II) chloride, showing polymerization only in the absence of iron.

	eq. monomer	eq. $MgCl_2$	eq Ru II
A	1	1	1
B	1	1	.5
C	1	1	.25
D	1	0	1

Attempt to Observe Retro-Diels-Alder in Monomer **21**. The attempt to observe retro-Diels-Alder chemistry in the monomers was undertaken by dissolving known amounts of **21** and **24** (as a control) each with hexamethyl benzene as standard in dichlromethane-d_2, degassing and sealing off the

NMR tube under vacuum. An initial set of spectra were obtained, with integration, and another set of spectra was obtained after two weeks. There was no change in either pair of spectra.

Polymerization of **18** with Tungsten *o*-methoxybenzylidene **7c** to form **18-W**. In a typical experiment, **18** (140 mg, 641 mmoles) and catalyst **7c** (8.6 mg, 5.47 mmoles) were weighed out in the dry box and dissolved in 2 mL dry CH_2Cl_2. Polymer was observed in ~ 20 min. The yellow material, which appears crystalline, was collected by centrifugation. The polymer **18-W** was dissolved in DMF and precipitated into acetone three times before collecting, yielding 123 mg (87.9 %). ^1H NMR (DMF-d_7) δ (ppm) 4.99 (br, *trans*-olefin, 0.18 H); 4.78 (br, *cis*-olefin, 1.72 H); 3.63 (br *cis*-α-to-oxygen, 1.72 H); 3.31 (br *trans*-α-to-oxygen, 0.18 H); 2.49, 2.22 (br, methylene, 4 H); 1.84 (br, methine, 2 H). ^{13}C NMR δ (ppm) 132 (*cis*-olefin); 130 (*trans*-olefin); 83 (*trans*-α-to-oxygen); 79(*cis*-α-to-oxygen); 51 (CH_2); 44.5 (methine).

Polymerization of **18** with Molybdenum Neophylidene **8b** to form **18-Mo.** In the dry box, monomer **18** (1.03g, 5.53 mmoles) was dissolved in two mL CH_2Cl_2. The catalyst (36 mg, 0.055 mmole) was dissolved in 0.5 mL CH_2Cl_2 and added to the monomer solution. After 24 hours, the precipitate was centrifuged down and collected. The material was dissolved in DMF and precipitated into methanol three times and dried under vacuum, yielding 951 mg (89 %) of yellowish transparent polymer. ^1H NMR (DMF-d_7) δ (ppm) 4.99 (br, *trans*-olefin, 0.34 H); 4.83 (br, *cis*-olefin, 1.66 H); 3.67 (br *cis*-α-to-oxygen, 1.66 H); 3.32 (br *trans*-α-to-oxygen, 0.34 H); 2.43, 2.26 (br, methylene, 4 H); 1.88 (br, methine, 2 H). ^{13}C NMR (DMF-d_7) δ (ppm) 132 (*cis*-olefin); 130 (*trans*-olefin); 83 (*trans*-α-to-oxygen); 79 (*cis*-α-to-oxygen); 50 (CH_2); 44(methine).

Polymerization of **19** with Molybdenum Neophylidene **8b** to form **19-Mo.** In the dry box the monomer (59 mg, 200 mmoles) and the catalyst (2.0 mg, 3.0 mmoles) were dissolved in 0.5 mL CH_2Cl_2 each and combined at room temperature. After one hour, some precipitate was observed, which was filtered from the solution, and would not redissolve. The filtrate was added to methanol and the polymer collected and reprecipitated twice, yielding 31.3 mg (53 %) fine off-white powder. GPC in methylene chloride, relative to polystyrene M_n = 16 600, M_w = 30 300, PDI 1.8. NMR

Polymerization of **20** with Molybdenum Neophylidene **8b** to form **20-Mo.** In the dry box, the monomer **20** (1.02 g, 2.14 mmoles) was dissolved in two mL CH_2Cl_2. The catalyst (14 mg, 0.021 mmoles) was dissolved in 0.5 mL CH_2Cl_2 and added to the catalyst solution. The solution became viscous immediately. After twenty-four hours, the solution was treated with BHT, diluted to 100 mL, and passed through silica gel to remove catalyst residue. The concentrated filtrate (25 mL) was precipitated into methanol, and the precipitate was collected and dried overnight, yielding 679. mg of a fluffy white solid (70 %). GPC in methylene chloride: ^{1}H NMR (DMF-d_7, 80 °C) δ (ppm) 5.95, 5.90 (br, trans-olefin, 0.58 H); 5.71 (br, *cis*-olefin, 1.42 H); 4.97, 4.93 (br, *cis*-α-to-oxygen, 1.42 H); 4.57, (v. br, *trans*-α-to-oxygen, 0.58 H); 3.48, 3.17 (br, CH_2 α-to-SO_2, 8H); 2.95 (br, *endo*, methine partially obscured by DMF); 1.85 (br, CH_2 of octyl, 4H); 1.50 (br, CH_2 of octyl, 4H); 1.35 (br, CH_2 of octyl, 16H); 0.92 (br, CH_3, 6H). ^{13}C NMR (DMF-d_7 80 °C) δ (ppm) 135-133 (olefin); 83-82 (*trans*-α-to-oxygen); 79-78 (*cis*-α-to-oxygen); (CH_2Cl_2, 25 °C) 55 ($SO_2\underline{C}H_2(CH_2)_6CH_3$); 52-48 ($CH_2$ on ring); 43-40 (methine); 32, 29.3, 28.6, 27.1, 22.8, 21.9 (octyl chain); 14.0 (methyl).

Polymerization of **21** with Molybdenum Neophylidene **8b** to form **21-Mo.** In the dry box, the monomer (161 mg, 441 mmoles) and the catalyst (4 mg, 6 mmoles) were dissolved in 0.5 mL CH_2Cl_2 each and combined at room temperature. After one hour, the solution was treated with BHT and precipitated into methanol. The polymer was redissolved and precipitated twice, yielding 143 mg (88 %) of white solid. GPC in methylene chloride, relative to polystyrene, Mn = 60 800, Mw = 91 100, PDI 1.5. ^{1}H NMR (DMF-d_7) δ (ppm) 6.08 (br, trans-olefin, 0.72 H); 5.90 (br, *cis*-olefin, 1.28 H); 5.241 (br *cis*-a-to-oxygen, 1.28 H); 4.75 (br *trans*-α-to-oxygen, 0.72 H); 3.68 3.00 (br, methylene, 4H); 1.8-1.4 (br, *t*-butyl and *endo*-methine, 20H). ^{13}C NMR (DMF-d_7) δ (ppm) 133 (olefin); 83 (*trans* α-to-oxygen); 78 (*cis*-α-to-oxygen); 60 (CH_2); 42 (methine); 24 (CH_3) The quatenary carbon of the *t*-butyl group was not observed.

Hydrogenation of **18** to **31**. The polymer (0.300 g, 1.61 mmoles monomer) was dissolved in 25 mL dry DMF by stirring overnight. The solution was purged with Ar, and *p*-toluenesulfonhydrazine was added as a solid. The reaction mixture was sealed, and heated to 110 °C overnight. The cooled reaction mixture was transferred to a centrifuge tube and treated with 20 mL distilled water, precipitating the polymer. The mixture was centrifuged, the supernatant pipetted off and the polymer solid was washed twice more with water and twice with THF (40 mL each). The solid was dried under vacuum overnight and the solid plug of polymer removed (0.285 g, 94%). ^{1}H NMR δ (ppm) 3.73 (br s, 2H, α-to-oxygen); 2.44, 2.14 (br m, methylene, 4H); 1.67 (br s, tertiary, 2H); 0.78 (pseudo t, 4H, backbone). ^{13}C NMR (DMF-d_7) δ (ppm) 84 (backbone methine); 52 (ring methylene); 44 (ring methine); 31.5 (backbone methylene). IR (cm^{-1}) 1300, asymmetric S=O stretch; 1112.5, symmetric S=O stretch.

Generation and Collection of Pyrollysis Gases for IR and NMR Studies. The polymer was placed on a platinum coated watch glass in the bottom of a large-mouthed, o-ring sealed vessel, which was evacuated and heated to 300 °C. Gases were collected in a liquid-nitrogen cooled NMR tube, or nipple on a gas-phase IR cell. Watch glasses (25 mm diameter) were washed for five minutes each in trichloroethylene, methanol and acetone. They were then coated with 500 Å chromium, under 10 mTorr argon, with a sputtering power of 300 watts. Then 500 Å platinum was applied under 5 mTorr argon and a sputtering power of 300 watts. The base pressure for the apparatus was 3 x 10 $^{-7}$ Torr.

Thermolysis from Various Surfaces. Samples of gold, titanium, nickel, brass, stainless steel silicon, glass, silanized glass, platinum and silicon coated with silicon dioxide were loaded with samples of polymer 18 in a Thermolyne Type 1400 furnace, which was heated to 700 °C for two hours. Residue was observed on the samples of gold, titanium, nickel, brass, stainless steel silicon, glass, silanized glass, while the silicon coated with silicon dioxide and platinum samples were ash-free.

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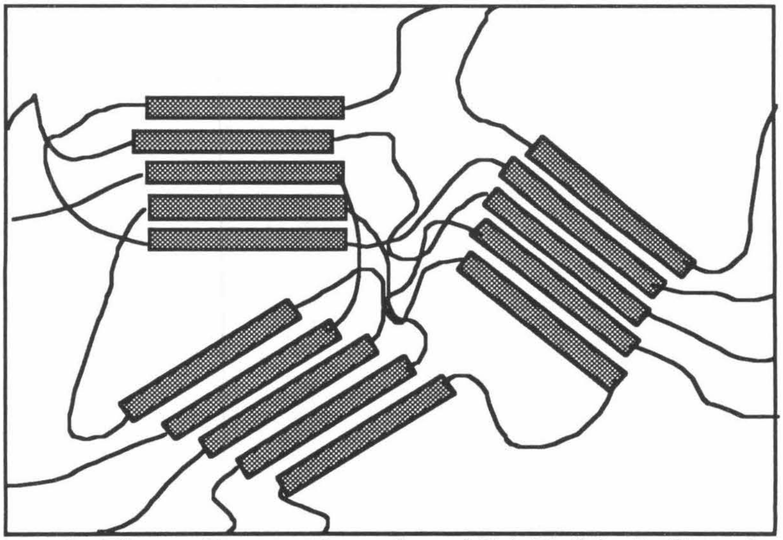
Chapter 2

The Synthesis of Triblock Co-polymers via Coupling of Reactive End Groups.

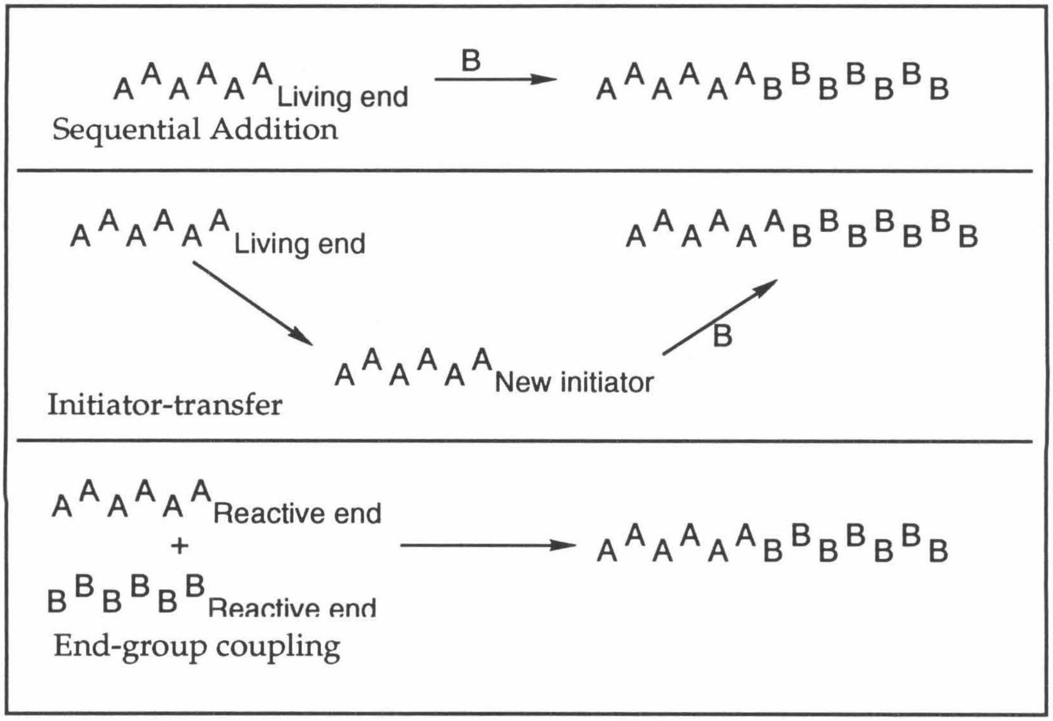
Introduction

The distinctive feature of block co-polymers is phase separation on a very small scale. Block co-polymers often contain immiscible polymers, for instance poly(styrene) and poly(butadiene). The solid mass of polymer will in fact be an interconnected network of homo-polymer micro-domains (Scheme 1). In truly phase-separated block co-polymers, each of the constituent blocks will show the thermal transitions of the homopolymer. Thermoplastic elastomers can be made by using a high T_g (hard) and a low T_g (soft) block. The micro-domains of the hard polymer serve as physical cross-links, making the material tough, while the soft blocks, which are above their T_g, are elastomeric. Other elastomers can be toughened by chemical crosslinks (vulcanized rubber, for instance), but they cannot be processed after crosslinking. Above the T_g of the hard segment, the hard segment becomes soft, and above a certain critical temperature the phases mix. Under these conditions the material can be processed. On cooling, the phase separation occurs again, and the thermoplastic regains its initial strength.



Scheme 1: Phase-Separation of an ABA Triblock Co-polymer.

Block co-polymers can be synthesized by several techniques including addition of a new monomer to a living polymer (sequential addition), conversion of a living end to an initiator for a new polymerization mechanism (initiator-transfer), and reaction of two preformed polymers with reactive end-groups (end-group coupling). All three techniques have been demonstrated with ROMP polymers.

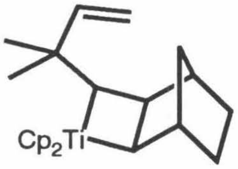


Scheme 2: Methods for the Synthesis of Block Co-polymers.

Block Co-Polymers From ROMP

Titanacyclobutane **1**, one of the early living ROMP catalysts, has been used to create block co-polymers via sequential addition. Sequences of fifty repeat units were synthesized using the monomers norbornene, benzonorbornadiene, 6-methylbenzonorbornadiene, and *endo*- and *exo*-

dicyclopentadiene.[1] Electro-active block co-polymers[2] and nano-clusters of platinum and palladium[3] have also been synthesized by sequential addition methods using catalyst **2**. The utility of these methods is limited by the types of monomer that are polymerized in a living fashion by ROMP catalysts. To date, these are limited to hydrocarbons, fluorinated hydrocarbons,[4] and metal-derivatized norbornenes.



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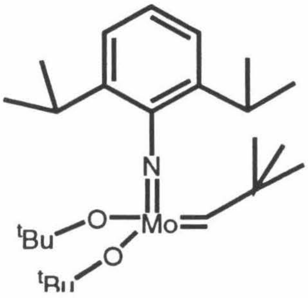
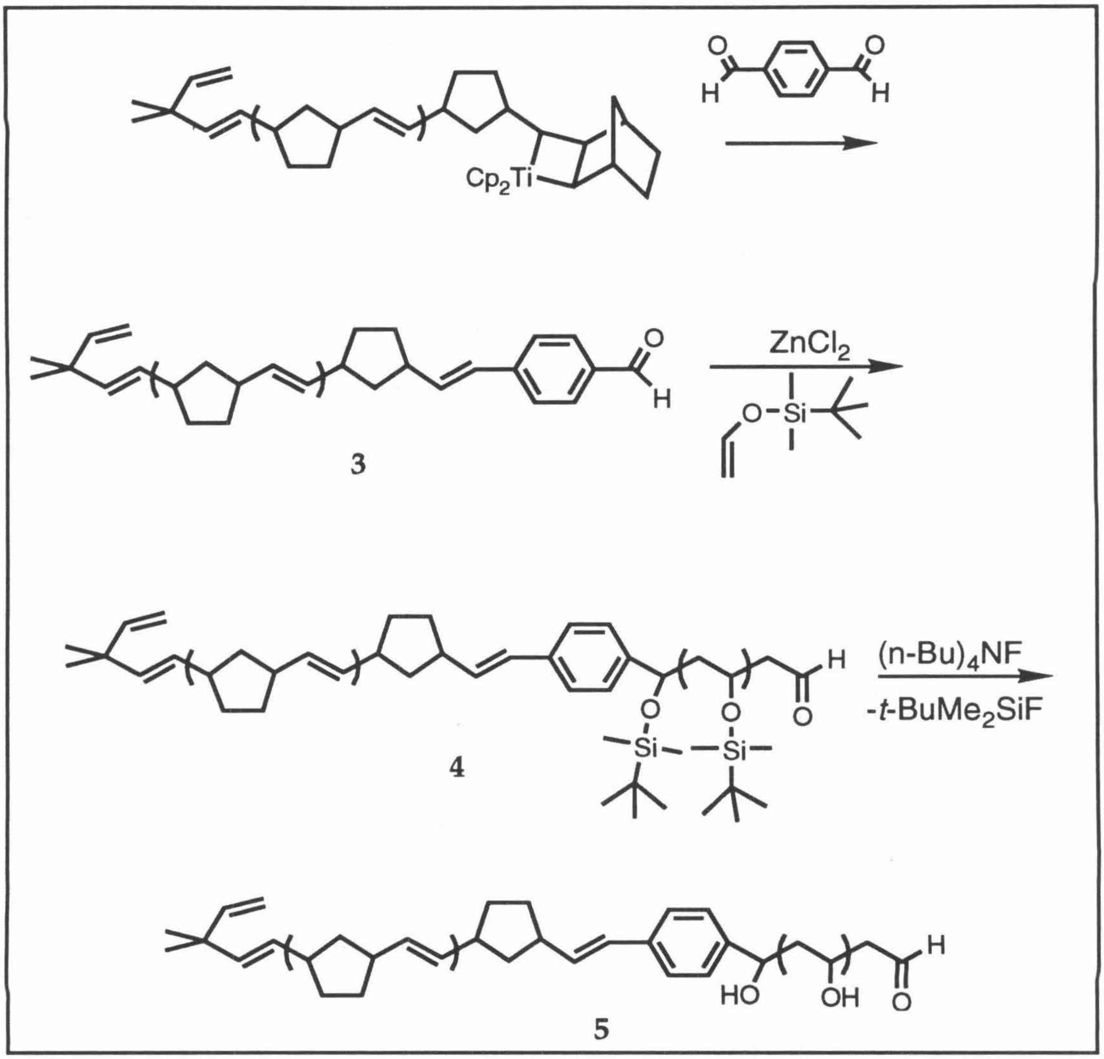


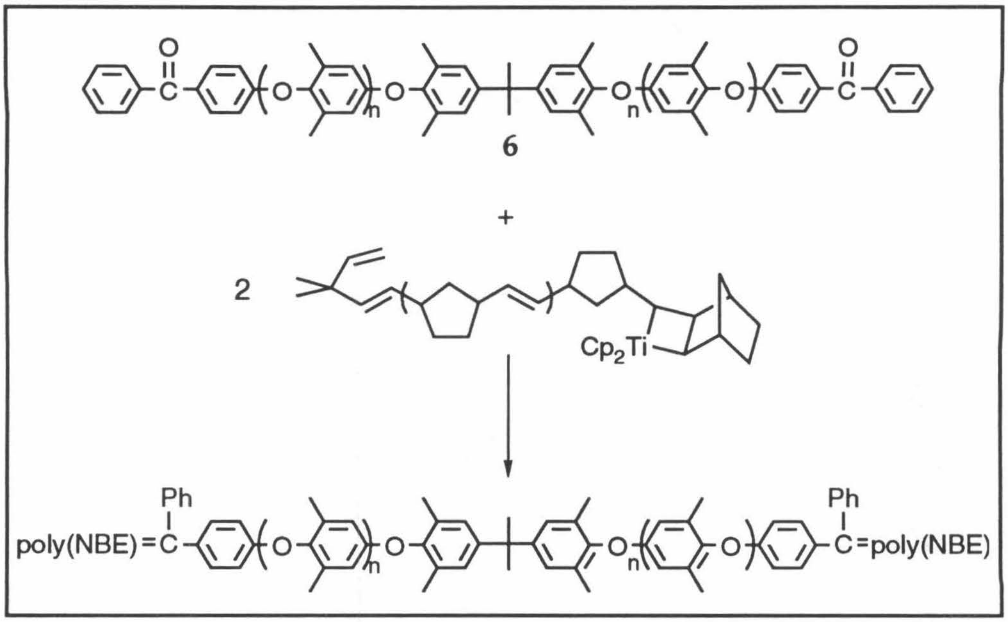
2

There has been one report of the initiator-transfer method of forming block co-polymers being used with a ROMP polymer.[5] As shown in Scheme 3, the living end of a ROMP polymer was treated with terephthaldehyde, giving polymer **3**, which was then treated with zinc chloride and (*t*-butyldimethyl)silyl vinyl ether. Aldol-group transfer polymerization[6] then occurs, forming poly(norbornene-*b*-((*t*-butyldimethyl)silyl vinyl ether), **4**. This polymer was hydrolyzed to give poly(norbornene-*b*-vinyl alcohol) **5**, an amphiphilic polymer with potential applications as an emulsifier, flocculant, wetting agent, foam stabilizer, and stabilizer for polymer blends.



Scheme 3: Initiator-Transfer Method of Synthesizing Block Co-Polymers using ROMP and Group-Transfer Polymerization.

Formation of a triblock co-polymer by using the living end of ROMP polymers as a reactive end has also been reported once.[7] In this synthesis, the preformed poly(arylether) **6** was endcapped with a ketone and treated with a living polymer (Scheme 4.)



Scheme 4: Demonstration of the Reactive End-Group Method of Block Co-Polymer Synthesis Using Living ROMP Polymers as One Reactive End Group.

Other Examples of Reactive End Group Syntheses of Block Co-Polymers

The challenges associated with the synthesis of block co-polymers via reactive end groups are not specific to ROMP polymers; polymers formed by anionic, cationic, poly(ester)- and urethane-formation mechanisms have been used in reactive end-group syntheses of block co-polymers, and the problems are the same as for a ROMP system. The fundamental problem with end-group coupling reactions is kinetic. The reactions that are used to couple end groups are thermodynamically favorable, and both fast and efficient on small molecules. Coupling reactions are by nature second order (eq. 1):

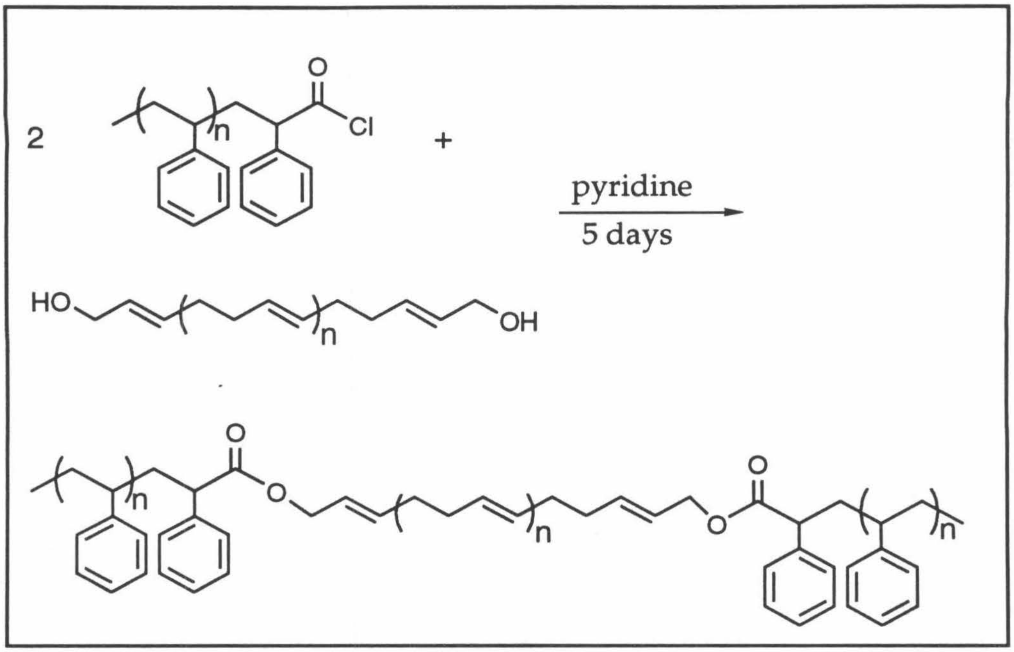
$$\text{rate} = k_c[A][B], \tag{1}$$

where k_c is the rate constant for the coupling reaction and A and B are the reactive end-groups. The concentration of end-groups is small in the beginning of the reaction and the rate is slow, but since the reaction is second order, the decrease in the rate is controlled by the product *of [A] and [B]. If* the reaction is run with one equivalent of each reactive end-group ([A] = [B]), the rate will decrease according to the square of the concentration of either reactant measured alone (eq. 2):

$$\text{rate} = k_c[A]^2. \tag{2}$$

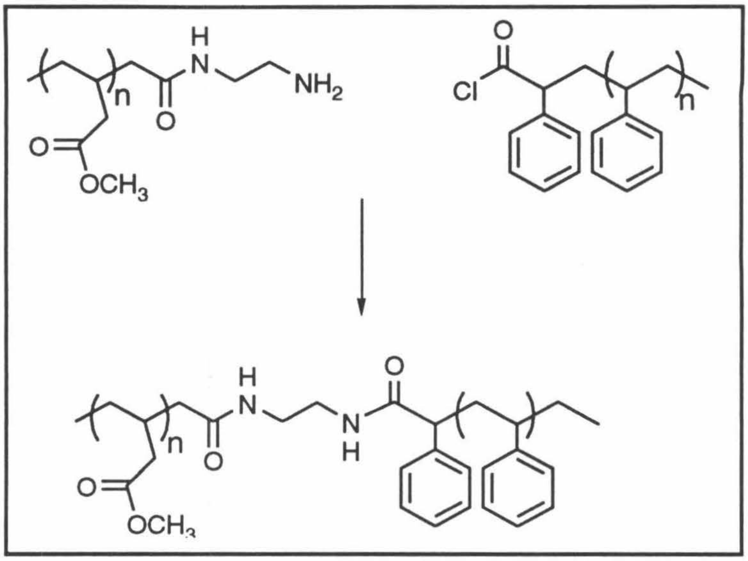
For small-molecule processes, a sluggish reaction can be run in a concentrated solution, but this is complicated by the viscous nature of polymer solutions. In polymer reactions a balance must be found between increasing the necessarily small concentration of end groups and making a solution that is too viscous for good mobility of the end groups. These problems are manifested by the long reaction times (days) reported for several coupling reactions. A brief survey of the synthesis of triblock co-polymers via coupling reactions follows. Where possible, the efficiency of the reaction and the specific reaction conditions are outlined.

Pinazzi et al. reported the use of acid chloride-terminated poly(styrene) and hydroxyl-terminated poly(isoprene) and poly(butadiene) (Scheme 5) in the synthesis of block co-polymers. Unfortunately, the end-group functionality was never above 90%, and the triblock co-polymers were contaminated with unreacted homopolymers. The length of time for this reaction is particularly long, five days.



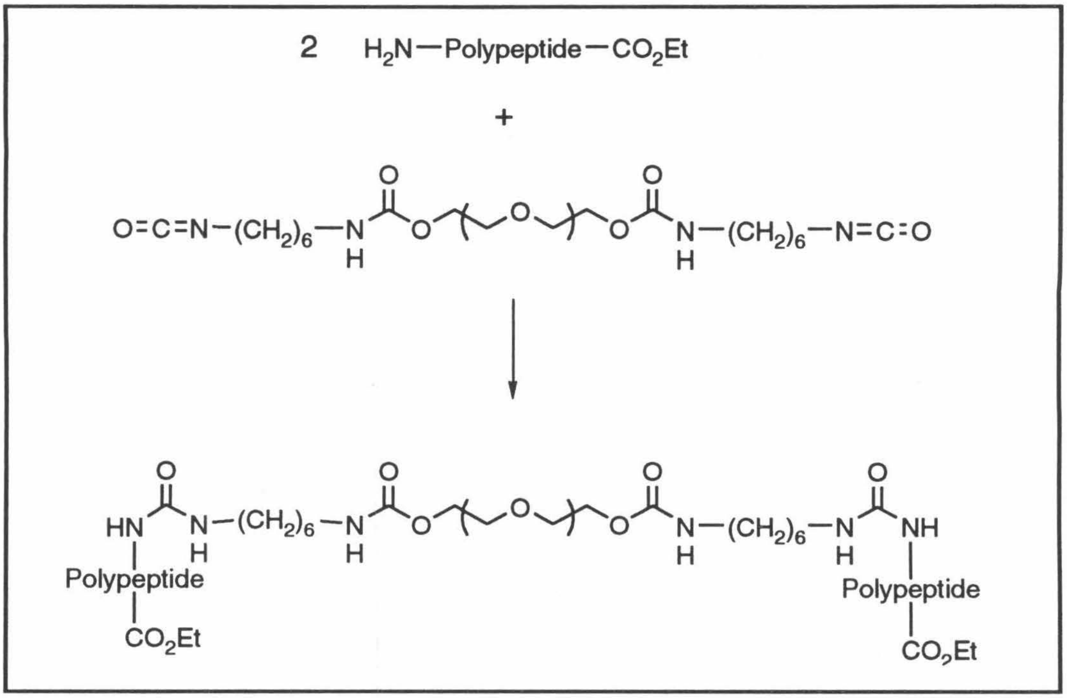
Scheme 5: End-group Coupling by Reaction of Terminal Acid Chlorides with Terminal Hydroxy Groups.

A similar approach was reported by Ikada et al. (Scheme 6).[8] They reported low yields due to a loss of acyl chloride end-groups. Because the co-polymer had different solubility properties than either homopolymer, they were able to purify the block co-polymer. No experimental details were reported for this reaction.



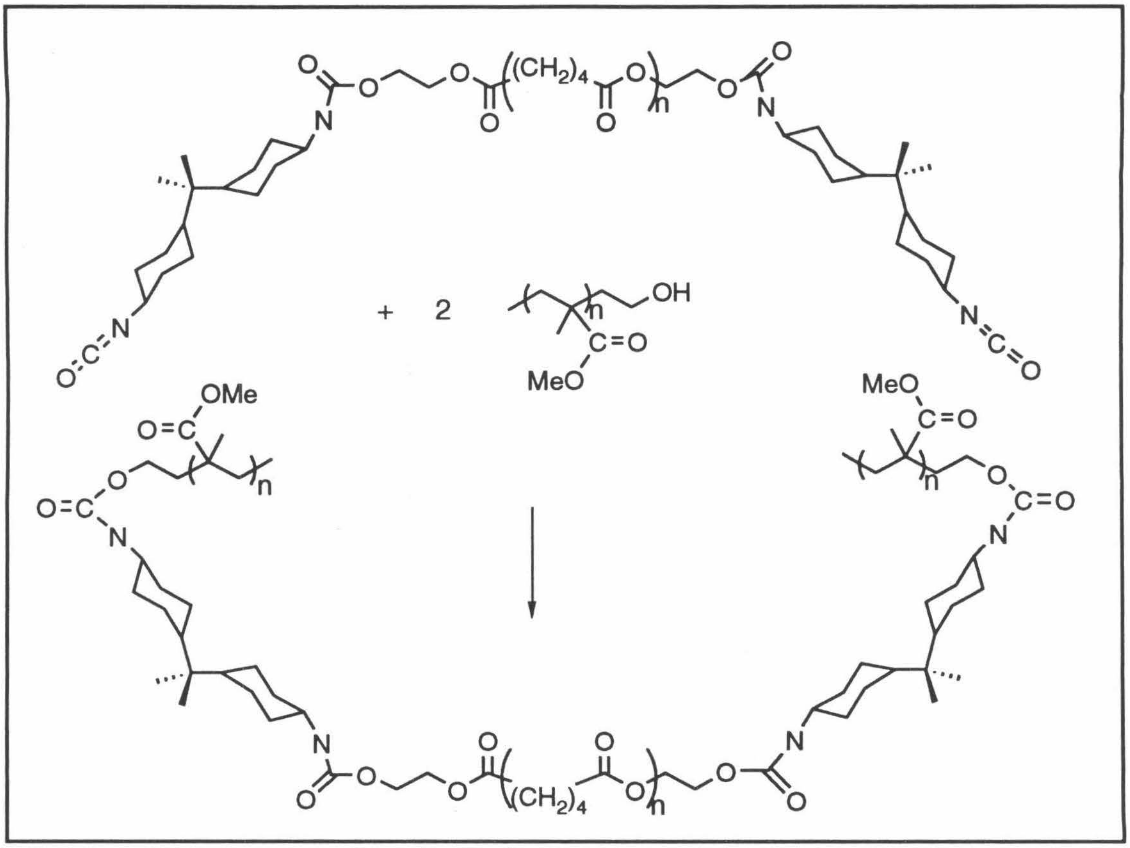
Scheme 6: End-Group Coupling by Formation of Amides from a Terminal Acid Chloride and a Terminal Amine.

Synthetic polypeptides have been incorporated into a triblock co-polymer by Leonhardt et al.[9] As shown in Scheme 7, they treated hydroxy-terminated poly(ethyleneoxide) with an excess of hexamethylenediisocyanate to synthesize the isocyanate-terminated telechelomer. This was in turn treated with a synthetic polypeptide, the amine terminus of which reacted with the isocyanate to form the triblock co-polymer. Unfortunately, the GPC traces of the pre-polymers are multi-modal, precluding a straightforward analysis of the coupling efficiency. The coupling reaction was run in a 1 millimolar solution, but no reaction times are given.



Scheme 7: Use of Hexamethylenediisocyanate to Couple Telechelic Poly(ethyleneoxide) to a Synthetic Polypeptide.

Using a similar approach, Grezlak and Wilkes[10] treated a hydroxyl-terminated polyester made via condensation polymerization with an excess of bis(4,4'-bisisocyanatocyclohexyl)methane (Scheme 8). This isocyanate-terminated polyester was treated with two equivalents of hydroxy-terminated poly(methylmethacrylate). The reaction mixture was 10% polymer by weight in benzene and the reaction was allowed to proceed for eight days at 65 °C. GPC analysis was somewhat complicated by the broad molecular weight and low M_n of the polyester prepolymer. Although the reaction clearly proceeded well, it is not clear that the reaction proceeded quantitatively.



Scheme 8: Diisocyanate Coupling of a Condensation Polyester and Poly(methylmethacrylate).

The first unequivocal demonstration of clean coupling to form a triblock co-polymer was achieved by Richards et al.,[11] who titrated a 0.01 M solution of living poly(THF) cation at 0 °C with a 10-15% by weight solution of living poly(styrene) anion. The persistence of the characteristic red color of the poly(styrene) anion was taken as the end point. GPC analysis showed clean coupling, as shown in Figure 1. Unfortunately, the same techniques failed to effect a clean synthesis of poly(α-methylstyrene)-*b*-poly(THF)-*b*-poly(α-methylstyrene). Richards et al.[12] reported a 20 % coupling efficiency for this reaction and attributed this poor yield to proton transfer from the living poly(THF) cation to the living poly(α-methylstyrene) anion, giving an olefin-terminated poly(THF) and a hydrogen-terminated poly(α-methylstyrene) as side products.

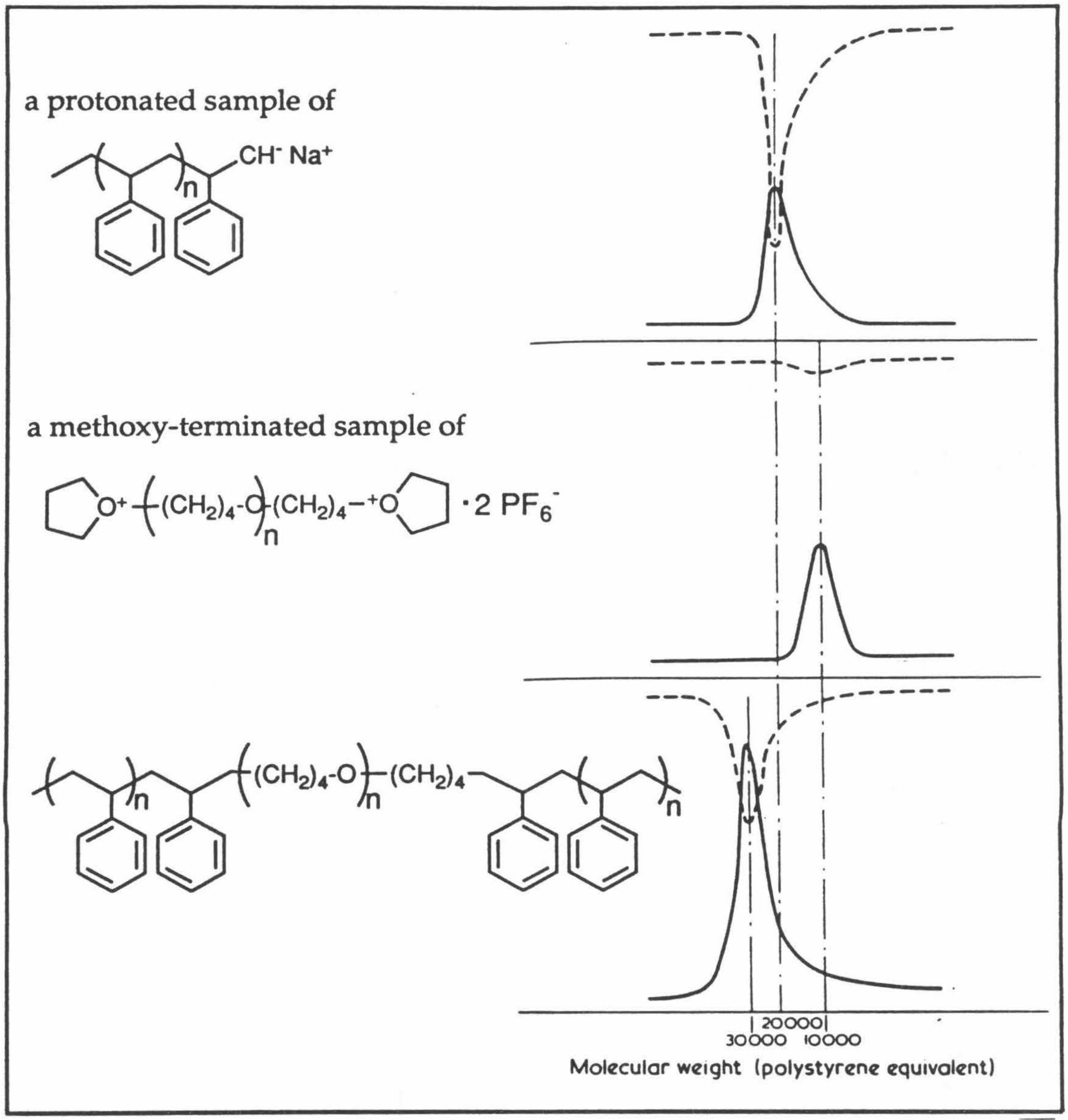


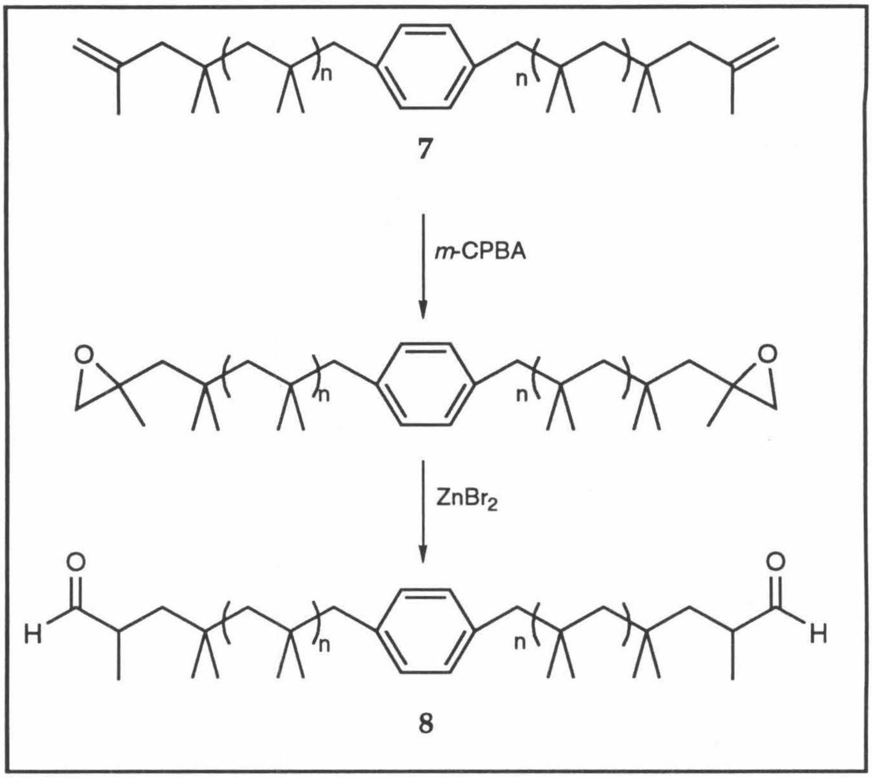
Figure 1: GPC Traces Demonstrating Clean Coupling Between Living Poly(styrene) and Difunctional Living Poly(THF).

More recently, Chien et al.[13] constructed the same triblock co-polymer using a diisocyanate. Hydroxy-terminated poly(THF) was treated with bis(4,4'-isocyanatophenyl)methane. A 20 % excess of hydroxy-capped poly(styrene) was added to the telechelic isocyanate, and the mixture was heated at 100 °C for eight hours. GPC traces show a qualitatively good yield of triblock, contaminated with the excess poly(styrene).

Paulus et al. proposed localizing the end groups of imisicble polymer chains at a solvent interface. This should increase the rate and efficiency of coupling reactions by dramatically increasing the effective concentraton of the reactive end groups. They suggested using quaternization of a secondary amine with an alkyl halide as the coupling mechansim. Preliminary studies on the effects the end-group of the polymers have on the interface were published in 1987,[14] but unfortunately no work on the co-polymerizations themselves has been published to date.

Results and Discussion

We attempted, the synthesis of a triblock co-polymer via end-group coupling of separately synthesized hard and soft blocks. The soft block, poly(isobutylene), is purchased as a telechelomer with olefin end-groups. Poly(isobutylene) used in these experiments is made via living cationic polymerization with a di-functional initiator and the reaction is terminated such that the end groups are olefins, giving the structure **7**. This is cleanly converted to the dialdehyde **8** in two steps: epoxidation and rearrangement (Scheme 8). The functionality of the olefinic telechelomer, as purchased, is 2.0 ± 0.1, and this is maintained during the conversion of the olefins to aldehydes, as determined by ^{1}H NMR analysis.



Scheme 9: Conversion of Poly(isobutylene) Di-olefin Telechelomer into the Di-aldehyde Telechelomer.

The desired hard block is poly(*exo*-dicyclopentadiene), made via ROMP. Poly(*exo*-dicyclopentadiene) has a T_g of 108 °C. In initial experiments, poly(norbornene), which has a relatively low T_g of 38 °C, was used instead of poly(*exo*-dicyclopentadiene) to conserve the monomer *exo*-dicyclopentadiene, which must be synthesized by rearrangement of *endo*-dicyclopentadiene.

Based on the previously reported success of titanacyclobutane-endcapped poly(norbornene) and poly(*exo*-dicyclopentadiene) in the synthesis of triblock co-polymers[7] (Scheme 4) we attempted the analogous reaction with poly(isobutylene) which was end-functionalized with aldehydes, **8**. Accordingly, living poly(norbornene) was synthesized with the titanacyclobutane **1**, a catalyst which requires heating for both initiation and propagation. The reaction must be stopped, by cooling to room temperature, before all monomer is consumed; the propagating titanium-alkylidene is not stable in the absence of excess catalyst. The preformed poly(norbornene) with active titanacyclobutane ends was heated to 60 °C for twelve hours with a stoichiometric amount of **8**. The reaction must be heated to generate the titaniumalkylidene that is the active species in carbonyl olefination. Simultaneous reactions with terephthaldehyde and benzaldehyde were run on aliquots of the same living polymer solution as controls. GPC traces of the reaction products from the reaction with **8** and the control experiments are shown in Figure 2. These results were consistent for several sets of reactions.

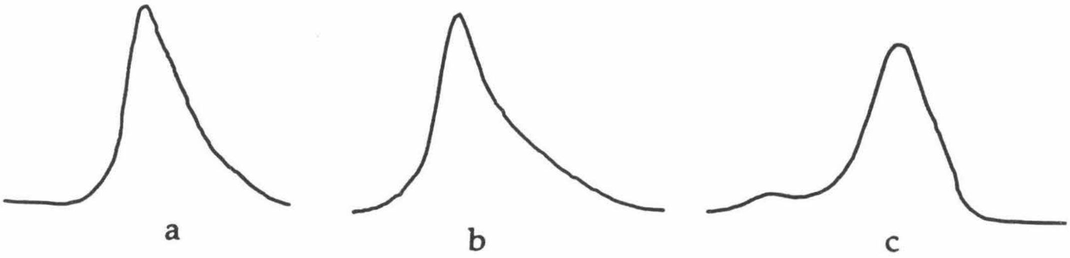


Figure 2: GPC Traces for the Reaction of Living Titanacyclobutane-endcapped Poly(norbornene) with a) Benzaldehyde, b) Terephthaldehyde and c) **8**.

The consistently poor results obtained with the same system that Risse and Grubbs had used successfully with an aryl ketone-endcapped polymer prompted us to investigate the stability of the aliphatic aldehyde endgroup. Accordingly, the aldehyde-endcapped polymer was dissolved in dry, degassed toluene-d_8[15] , and sealed in an NMR tube. After acquiring an initial spectrum, the sample was heated to 65°C for twenty-four hours, and another spectrum was acquired. As shown in Figure 3, significant amounts of the aldehyde end group were lost over 24 hours at 65 °C in clean solvent. These results prompted us to consider another catalyst, one that is in the active carbene form at room temperature and will not require heating for olefination.

The living and synthetically accessible molybdenum catalyst **2** was the clear choice. While catalyst **2** is not active towards ketones, it does olefinate aldehydes at room temperature. Furthermore, the living molybdenum-alkylidene polymer end-group is stable in the absence of excess monomer, which simplifies the experimental procedure. Following the procedure of Murdzek et al.,[16] the living poly(norbornene) was synthesized in benzene solution (2.8 millimolar) in the dry box. A solution of known concentration of **8** was added to the polymerization mixture after thirty minutes. Parallel reactions with terephthaldehyde and benzaldehyde were also run. After three hours, the **8** and terephthaldehyde reactions were quenched with an excess of benzaldehyde. A set of typical GPC traces is shown in Figure 3. The terephthaldehyde consistently reacts more efficiently with the poly(norbornene)-Mo than does **8**.

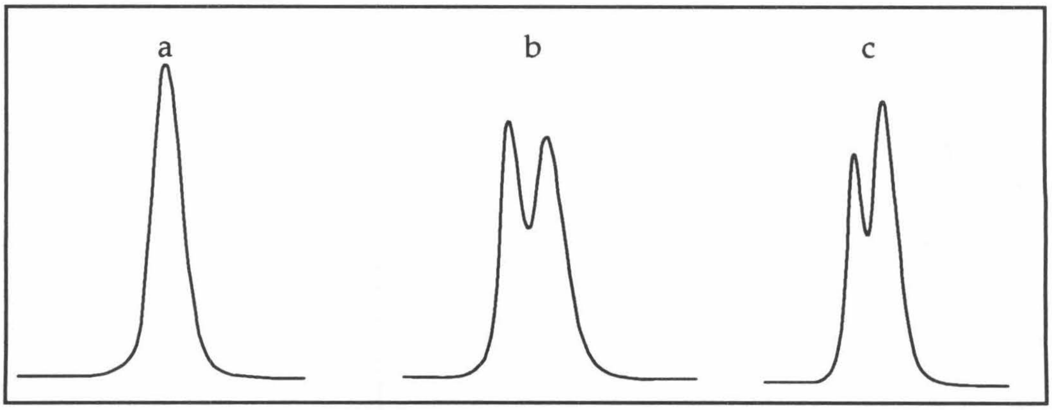


Figure 3: GPC Traces of the Endcapping Reaction Between Living Poly(norbornene) with a) Benzaldehdye b) Terephaldehyde and c) **8**.

Conditions were optimized for the reaction of poly(norbornene)-Mo and terephthaldehyde. The conversion did not exceed 75% until the reaction mixture was placed in a sonicator. Optimum conditions for the reaction are sonication at room temperature for six hours (keeping the temperature low requires cooling the sonicator), with 200 equivalents of norbornene relative to molybdenum. The maximum yield of the coupling reaction with terephthaldehyde was 85%; however typical values remained near 75-80%.

The GPC chromatograms are somewhat ambiguous. The high molecular weight peak is triblock co-polymer alone. However, the center or B block is so short ($M_n = 1350$) that AB diblocks with unreacted or decomposed aldehydes are indistinguishable from unreacted A blocks or A blocks with decomposed end-groups. The percent conversions that are reported here are not strict percent conversions, but the ratio of triblock to both diblock and unreacted A block.

The optimized conditions for poly(norbornene) and terephthaldehyde were transferred to reactions with living poly(*exo*-dicyclopentadiene) and **8**. Under these conditions, the reaction with **8** gave 50 % coupling, while a parallel reaction with terephthaldehyde gave 75 %. The reaction with **8** was repeated, holding the temperature in the sonicator at 30, 40 and 50 °C. Yields were consistently 50 ± 5 %.

Unfortunately, both aldehydes and living ends are unstable over a time scale of days, and yields did not improve after a few hours had passed. In several reactions, unreacted aldehydes were observed in the final reaction mixture, indicating that the probelm may lie with the living polymers, not the aldehydes.

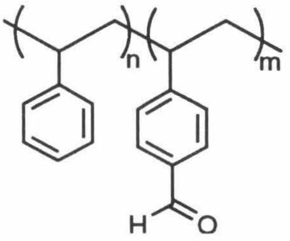
The kinetics can be manipulated to increase the reaction rate, however. Using a large excess of one reagent, living poly(*exo*-dicyclopentadiene), will keep the concentration of poly(*exo*-dicyclopentadiene) essentially constant, and the reaction will be pseudo-first order (eq. 3):

$$\text{rate of olefination} = k'[\mathbf{8}], \tag{3}$$

where k' = k[living poly(*exo*-dicyclopentadiene)]. The rate of reaction will only decrease linearly over the time of the reaction, instead of by a power of two. This may speed the desired reaction sufficiently so that the quenching of aldehyde endgroups is quantitative. If this strategy works, the reaction mixture will contain some fraction of triblock co-polymer and unreacted living ends, but no unreacted aldehyde groups.

The initial indication that this strategy had merit came when two reactions, one with a stoichiometric amount of **8** and one with half the stoichiometric amount, were run and analyzed simultaneously. As in previous reactions, only 50% coupling was observed in the stoichiometric reaction. However, the same ratio of triblock to unreacted poly(norbornene) and diblock was observed with the reaction in which only 50% of the stoichiometric amount of aldehyde was present. These data indicate that all or most of the available aldehyde groups had reacted, leaving only the excess A block.

The task remaining, then was to separate the triblock co-polymer and the unreacted A block. To do this, we again took advantage of the Wittig-like olefination reaction. The random co-polymers **9** (poly(styrene-*co*-vinylbenzaldehyde)) are reported in the literature.[17] The aldehyde monomer was synthesized by two routes and polymerized according to published procedures. The monomer was initially synthesized by reduction of vinylbenzoic acid with lithium aluminum hydride, followed by oxidation with pyridinium chlorochromate. The monomer was purified by flash chromatography and vacuum distillation. Polymers made with this monomer reacted with all living polymer in solution, as indicated by TLC analysis. The polymer **9** does not move on TLC in benzene solution, but poly(norbornene) moves with the solvent front; TLC and flash chromatography are useful to separate the polymer mixtures on analytical and preperative scales, respectively. The polymer **9** is used in a hundred-fold excess of aldehyde: the poly(styrene-*co*-vinylbenzaldehyde-*g*-norbornene) created this way is a smear near the baseline of the TLC, reflecting the distribution of polar and non-polar, grafted, groups in the sample. The success of this method, however, is dependant on the source of monomer. If the monomer is synthesized by another route, hexammine oxidation of *p*-chloromethylstyrene,[18] the polymerization proceeds as expected, but the reaction to form poly(styrene-*co*-vinylbenzaldehyde-*g*-*exo*-dicyclopentadiene) does not proceed cleanly. Some amount of poly(norbornene) is left in the reaction mixture. This is attributed to the presence of impurities either in the monomer, or from the hexammine reaction. When a 100 fold excess of aldehyde is used in the reaction, less than a percent of reactive impurity can kill a significant portion of the living ends before graft-forming olefination can occur.



9

The experimental procedure for the use of **9** involved making the living poly(*exo*-dicyclopentadiene) in the dry box, and adding either half or a quarter an equivalent of **8** (based on aldehyde functionality). The reaction mixture was then sonicated at a controlled temperature and for a prescribed time. A control batch of living polymer was subjected to sonication without any aldehyde present to ensure the reaction conditions themselves were not causing any degradation of the living polymer. After sonication with **8**, a hundred equivalents of **9** (based on aldehyde) was added to a portion of the living polymer treated with **8**, and the rest of the living polymer was quenched with an excess of benzaldehyde. The control reaction was also treated with a hundred equivalents of **9**. The reaction mixtures containing **9** were then sonicated for four hours. Complete reaction of **9** with the control reaction is indicated by an absence of poly(*exo*-dicyclopentadiene) in a TLC. Figure 4 shows GPC traces for a typical set of reactions. This reaction has been run at 40 and 65 °C for two hours and at 65 °C for one hour. The results are indentical[19] under the above conditions: for half an equivalent of **8**, the reaction proceeds 40-50 %, for one quarter an equivalent, the reaction proceeds 20-25 %. These results suggest the poor yields reported for one equivalent to be the result of insufficient <u>living</u> poly(*exo*-dicyclopentadiene).

The reaction mixtures shown in GPC traces IIA and IIB have been treated with **9**, removing all <u>living</u> poly(*exo*-dicyclopentadiene). In each case a control reaction was treated with **9**, which cleanly removed <u>all</u> poly(*exo*-dicyclopentadiene). What is left appears in Figure 4: a triblock co-polymer, now the major component, and a shorter polymer which must be either poly(*exo*-dicyclopentadiene) with an unreactive ("dead") end group or diblock co-polymer. ^{1}H NMR analysis of this mixture does not show any unreacted

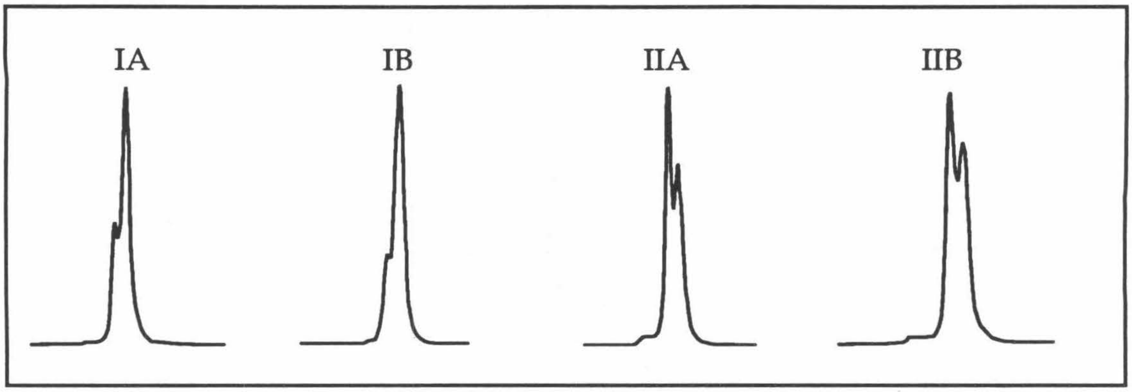


Figure 4: GPC Traces from Reaction of A (Two-fold) and B (Four-Fold) Excess of Living Poly(exo-Dicyclopentadiene) with **8**. (IA and IB are Before Treatment with **9**, IIA and IIB are After Treatment with **9**.)

aldehydes, so any diblock co-polymer present contains poly(isobutylene) without an aldehyde end group.

The yields of triblock co-polymer in GPC traces IA and IB and the absence of unreacted aldehyde in the ^{1}H NMR suggest that the aldehyde functionality is reacting in high yields, if not quantitatively. The most likely identity of the low molecular weight fraction is poly(*exo*-dicyclopentadiene) that has undergone a molybdenum-alkylidene decomposition reaction. The reaction conditions alone do not cause molybdenum-alkylidene decomposition: in control experiments the living poly(*exo*-dicyclopentadiene) reacts quantitatively with **9**. The most likely conclusion is that there is an unidentified, but competitive side reaction that destroys the living end of poly(*exo*-dicyclopentadiene). That side reaction is not present in the reaction of terethphaldehyde, which consistently reacts in 70-80 % yield.

The purity of **8** has been checked by ^{1}H NMR, GPC and TLC. No unidentified impurity[20] has been detected, which neither confirms nor dismisses the possibility of an impurity. Several batches of **8** have been made and used. All batches that were used showed the correct ratio of aldehyde to aromatic peaks; no difference in reactivity was noted.

Conclusions

The reaction between living poly(*exo*-dicyclopentadiene) and **8** appears to be limited only by the supply of living poly(*exo*-dicyclopentadiene). Unfortunately, the living end of poly(*exo*-dicyclopentadiene) decomposes in an unidentified fashion in the reaction mixture, contaminating the triblock co-polymer with forty percent poly(*exo*-dicyclopentadiene) homopolymer. The decomposition reaction appears to be reagent specific. Diblock synthesis with terephthaldehyde proceeds to an extent that unreacted living polymer is observable but not quantifiable (conversion ~ 80 %). Quantitative reaction occurs between **9** and living poly(*exo*-dicyclopentadiene), even after living poly(*exo*-dicyclopentadiene) has been sonicating at 65 °C for two hours.

Although **8** appears to be a poor canditate for the synthesis of ABA triblock co-polymers from ROMP, we have outlined the parameters for successful reactions of living poly(*exo*-dicyclopentadiene) with aldehydes. Sonication at 65 °C for no more than six hours are the optimal conditions. The use of **9** as a scavenging reagent for unreacted living molybdenum alkyldenes has been sucessfully demonstrated. We hope to apply these results to other more amenable systems in the future.

Experimental

General Procedures. All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å sieves. Solids were transferred and stored in a N_2-filled

Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a Jeol GX-400 (399.65 MHz ^1H, 100.40 MHz ^{13}C). Proton chemical shifts are referenced to internal residual solvent protons. GPC analyses were carried out on an HPLC system consisting of an Altex Model 110A pump operating at 1.0 mL/min, a Rheodyne Model 7125 injector with a 100 mL injection loop, or on a home-built unit consisting of either three Shodex Styragel columns (KF 803, KF 804 and KF 805) or an American Polymer Standards 10 mm mixed-bed column, and two detectors (Knauer Differential-Refractomer and Kratos Spectroflow 757 UV detecter operating at 325 nm). Sonication was accomplished in a Branson 5260 cleaning bath; temperature was controlled by placing a coil in the bath, through which cooled water was circulated by a VWR 1140 recirculating bath.

Materials. The catalyst **1** was synthesized according to published procedures,[21] while the catalyst **2** was purchased from Strem Chemicals and used as recieved. Benzene was vacuum-transferred from sodium benzophenone and methylene chloride was vacuum transferred from calcium hydride. Norbornene was vacuum distilled from sodium. *Exo*-dicyclopentadiene was provided by J. S. Moore of this lab. The di-olefin end-capped poly(isobutylene) was purchased from Akron Cationic Polymer Development Corporation, Akron, OH, and used as received. Terephthaldehyde was purchased from Aldrech Chemicals and purified according to published procedures.[22] Vinylbenzoic acid, lithium aluminum hydride and pyridinium chlorochromate were purchased from Aldrich

Chemicals and used as received. Silica Gel 60 and reagent-grade hexanes and ethyl acetate for chromatography were purchased from EM Science.

Synthesis of **8**. The diolefin polymer (1.47 g, 1.088 mmole) was dissolved in 5 mL methylene chloride, freeze-pump-thaw degassed three times and maintained under argon. *m*-CPBA (3.76 g, 10.9 mmole) was dissolved in 15 mL methylene chloride, similarly degassed and cooled to 0 °C. The polymer solution was added by cannula to the cooled *m*-CPBA solutuion. The reaction was allowed to warm to room temperature and stirred for four hours. Hexanes (40 mL) were added to the reaction mixture and the combined organics were extracted with 2 x 20 mL water, 2 x 20 mL 15 % sodium hydroxide and 4 x 20 mL water. The organics were dried over anhydrous magnesium sulfate, rotovapped and dried *in vacuo*. The resulting yellow oil was not characterized, but dissolved in 10 mL benzene, to which 0.1 g $ZnBr_2$ was added. The solution was sealed in a heavy-wall Köntes tube and heated at 90 °C for ten minutes. The resulting solution was diluted with 10 mL benzene and filtered through a plug of silica. The bulk of benzene was removed under vacuum, but traces remained. Due to the thermally unstable nature of the aldehyde endgroup (*vide supra*) the remaining traces of solvent were not removed, but measured by integration of ^1H NMR resonances. Yields of **8** were typically > 90 %. The polymer was stored in benzene solutions, the concentration of which was determined by integration of ^1H NMR resonances in methylene chloride. Concentrations were typically near 0.02 M in polymer chain, 0.04 M in aldehyde end groups. ^1H NMR spectra were acquired with a five second delay to allow the polymer chain and the aldehyde end group to relax. Assignment of ^1H NMR resonances for the polymer are not clear, except for the aldehyde at 9.2 ppm and the internal *p*-

substituted benzene at 7.2 ppm. A typical spectrum is reproduced (figure 5) in lieu of attempting to list and assign the resonances in the aliphatic region.

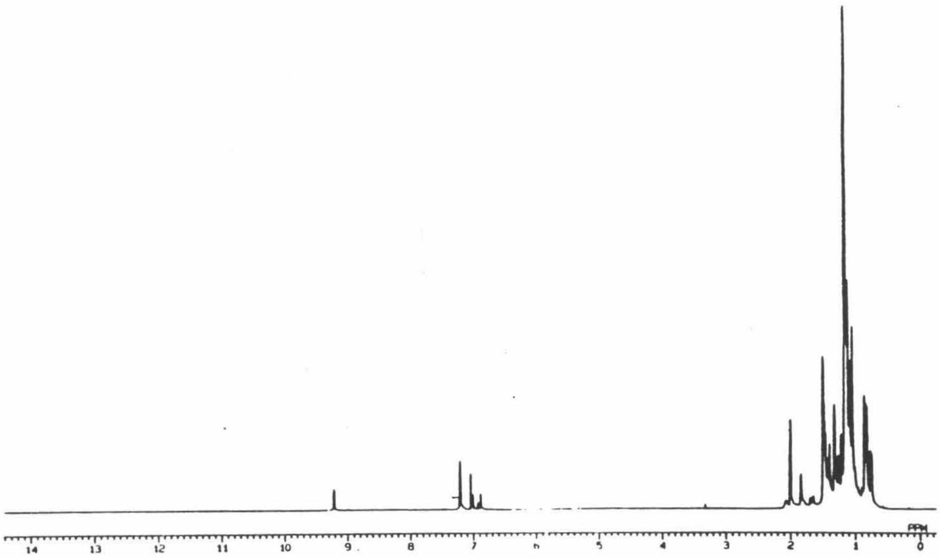


Figure 5: 1H NMR Spectrum of **8** in Methlyene Chloride -d_2.

Synthesis of 4-Vinylbenzyl Alcohol. Vinylbenzoic acid (4.5 g, 30.4 mmole) was dissolved in 100 mL fresh THF and added dropwise over 1 hr to a slurry of lithium aluminum hydride (1.7 g, 45.6 mmol) in 100 mL THF stirring at 0 °C. The reaction was complete by TLC one hour after addition was complete, and was quenched with 2 mL water, 2 mL 15 % sodium hydroxide, 6 mL water added in turn, dropwise. The reaction was diluted with 100 mL ether, and filtered. The solvent was removed to yield a yellow oil which was purified by flash chromatography ($R_f = 0.6$ in 25 % hexane in ethyl acetate). The final product was a yellow oil, 2.1g, 51 %. ^{1}H NMR (CD_2Cl_2) δ (ppm) 7.4 (d, 2H); 7.2 (d, 2H); 6.7 (q, 1H); 5.8 (d, 1H); 5.3 (d, 1H); 4.7 (s, 2H).

Synthesis of 4-Vinylbenzaldehyde. Vinylbenzyl alcohol (1 g, 7.45 mmole) was dissolved in 50 mL methylene chloride and added in one portion to a slurry of pyridinium chlorochromate (3.21 g, 14.9 mmole) in 50 mL methylene chloride stirring at room temperature. After 1 hr the reaction was complete by TLC and the reaction mixture was filtered through a silica gel plug and rotovapped to yield a bright yellow oil. This was purified by flash chromatography (Rf = 0.7 in 25 % ethyl acetate in hexanes) to give a pale yellow oil. The oil was vacuum transferred to remove inhibitors and stored in the freezer under argon. 0.224 g (24 %). ^{1}H NMR data agrees with published data.[17]

Polymerization of 4-Vinylbenzaldehyde to form **9**. The polymerization was carried out according to published procedures, and spectroscopic data were in agreement with those in the literature.[17]

Titanium End-Group Coupling Reactions. Titanacyclobutane end-group coupling reactions were carried out according to published procedures.[6]

Molybdenum End-Group Coupling Reactions. In a typical reaction, **2** was dissolved in benzene at a concentration of 1 mg/mL. The monomer was dissolved in half as much benzene as was used for the catalyst solution. The monomer was added to the catalyst; after thorough mixing, the mixture was distributed to teflon-capped vials in 1.5 mL aliquots (~ 1 mg catalyst per vial). The aldehyde stock solutions in benzene were stored in the dry box freezer and thawed immediately before use. Aldehydes were measured out and used in the dry box with 10-100 μL gas-tight syringes. Reactions for sonication were firmly capped with teflon-lined screw caps; the caps were secured with electrical tape before placing the vials in the temperature-equilibrated sonicator. After the prescribed reaction time, the tape was removed from the vials and they were taken back into the dry box.

Work-up of Co-polymers without using **9**. Any remaining living polymer was quenched with an excess of benzaldehyde (typically five drops per mg of catalyst). Reaction mixtures were then treated with BHT before exposure to the atmosphere. The polymer was precipitated (methanol for poly(norbornene) and diethylether for poly(*exo*-dicyclopentadiene)) and dried under vacuum. The polymer was dissolved in GPC solvent and passed through a plug of silica to remove catalyst residues before using a micro-pore filter to remove particulates.

Work-up of Co-polymers using **9**. An excess (100-fold) of **9** was weighed and dissolved in dry, degassed dichloromethane. This solution was passed through a plug of activated alumina directly into the reaction mixture. The vial was again removed from the dry box, the cap secured with electrical tape, and the mixture sonicated. The reaction mixture was subjected to standard flash chromatography in benzene. The fractions containing ROMP polymers were treated with BHT, rotovapped and dried *in vacuo*. These polymers were redissolved in GPC solvents and filtered to remove particulates.

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[19] Identical within error, which is estimated to be ± 10%.

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Chapter 3

Four Functionalized 7-Oxanorborne Systems.

General Introduction and Outline of Chapter

This chapter is a collection of small projects. Two of these projects were taken to their logical conclusion, and two are left with unexplored potential. Each project is presented separately, with its own introduction, results and discussion, and conclusion sections, while the experimentals are gathered at the end. Figures, compounds, references etc. are numbered consecutively throughout the chapter.

The first section is a follow-up of work on ionophoric membranes from ROMP polymers that was published as a Communication. We designed and synthesized several new polymers, designed to tailor the membrane transport behavior. We found that none of our new polymers transported ions; unfortunately, the known polymer did not behave as expected either. The sub-chapter on membrane transport details our initial goals for the project, the difficulties we encountered and our final understanding of the system.

The section on poly(amines) describes several approaches, by no means exhausted, to making poly(amines). The poly(amines) project was part of the exploratory work undertaken in the wake of Novak's aqueous polymerization coup -- the sulfones discussed in chapter one came out of the same period of exploration. The poly(amines) were abandoned in favor of pursuing these poly(sulfones). As detailed in this sub-chapter, there are even better catalysts for poly(amines) now, and still many opportunities for the synthesis of interesting monomers.

The thiophenes project is discussed next. A three-step synthesis to a monomer that is a thiophene fused to norbornene is outlined. The first step was non-trivial, and the third did not work at all. The initial steps lead to a molecule that is interesting in its own right.

The final section describes recent results with the polymerization and initial characterization of a methanesulfonate-derivitized polymer. This polymer has promise as a precursor for several applications, and has thermal properties with bearing on conducting polymer projects currently underway in our group.

The Synthesis and Membrane Transport Properties of Ether-Substituted 7-Oxanorbornenes.

Introduction

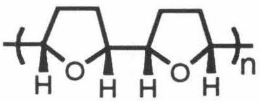
Membrane Transport

Polymeric membranes can transport small molecules from one side to the other. Transport mechanisms in porous materials are via channels, and any separation is based on size exclusion. Densely packed amorphous polymers transport and separate on a solution/diffusion mechanism, where the permeant dissolves into the polymer and then diffuses through the material to the other side. The driving force for this is either a concentration gradient or physical pressure. From a design perspective, the polymer must provide some stabilization to the permeant to enable the initial dissolution, but too much stabilization approaches complexation and will be detrimental to diffusion. Other concerns include sufficient empty space in the native polymer to accommodate the permeant molecules with out gross distortion of the membrane. Permeants that are good solvents for the polymer will swell the material. While separation is still obtained, these materials are often too soft (gel-like) to be efficient membranes, and their transport kinetics are complicated.[1]

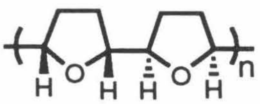
There are limits on the physical nature of a polymer used in separation membranes. Crystalline polymers are not suitable for use as membranes since permeation disturbs crystal packing forces. Glassy polymers are also unsuitable for liquid separations; they do not have sufficient mobility of polymer chains to allow transport of ions. The amorphous polymers used must be strong in thin sheets, and processable into hollow fibers. The successful applications to date include reverse osmosis to purify water, usually using cellulose acetate membranes, hemodialysis which also often uses cellulose acetate polymers, and gas separations, which employ a wide variety of polymers. The way in which polymers are cast into membranes is an additional complication. Casting determines the performance of the membrane in ways that are not understood, making membrane casting more of a black art than a science, and hindering attempts to infer structure-property relationships.

Ionophores

The classic examples of ionophores are crown ethers. The synthetic utility of these non-ionic molecules derives from their ability to coordinate to small cations and transport the cation and the accompanying anion to an organic phase. Linear polymeric analogs to crown ethers, such as polyethylene oxide, also complex cations and are being investigated as solid electrolytes.[2] A more constrained polymer **1**, with THF rings in the polymer backbone complexed ions only in the threo conformation. Only the CPK model of the threo polymer could form a helix, suggesting that the threo polymer has a helical nature when complexing ions.[3] Polymers with pendant crown ethers have also been synthesized.[4]



erythro-1



threo-1

Ionophoric ROMP Polymers

As reported by Novak and Grubbs,[5] the polymer **poly(2)** exhibited ionophoric behavior in three ways. As a dissolved polymer, **poly(2)** enabled the dissolution of sodium, potassium and lithium hydroxides in chloroform.

Poly(2) also mediated the extraction of five cationic dyes from water into carbon tetrachloride, although it was ineffective in the extraction of anionic dyes. The contrast between the dissolution of solid metal hydroxides and the inability of the polymer to extract dyes with the same metal cation suggests that these are different phenomena. The most important demonstration of ionophoric behavior, however, was the preferential transport of cations through a membrane made of **poly(2)**. This preferential transport was detected using the apparatus sketched in Figure 1. Initially, the concentrations in the cells are equal; then the concentration in one cell is gradually increased. As the concentration difference (the driving force) increases, more of the cation is transported, building up an electric potential, called the Donnan potential, which is measured on a voltmeter.

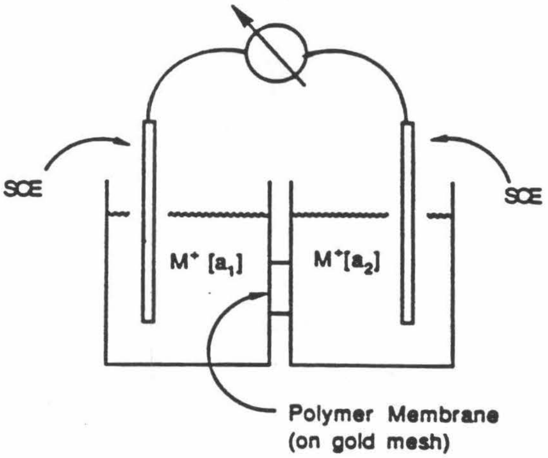
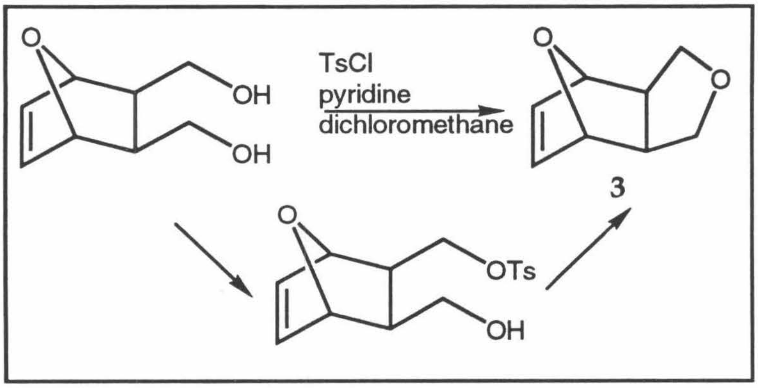


Figure 1: Apparatus for Detecting Donnon Potentials in Polymer Membranes

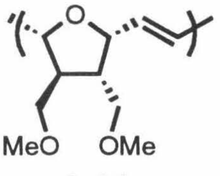
Results and Discussion

The ionophoric behavior of **poly(2)** was reported by Novak.[5] In an attempt to modify the ionophoric behavior of the membranes, several other ether monomers were made and polymerized. The cyclic ether **3** was synthesized according to Figure 1 in an attempt to create a more strongly binding polymer. The monomer **3** polymerized with aqueous ruthenium catalysis under ambient atmosphere, at 55 °C (identical conditions to those used for **poly(2)**.)

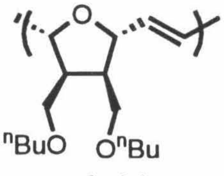


Scheme 1: Synthesis of Monomer **3**

The newly-synthesized **poly(3)** failed to exhibit Donnan behavior under conditions in which **poly(2)** had shown Donnan behavior. The material was an effective barrier, showing high resistivities. This suggested to us that a more open, linear structure was necessary for transport. Seeking to create a polymer with a more open structure than **poly(3)**, the monomer **4** was synthesized and polymerized to form **poly(4)**. Since plasticized polymers often function better as membranes, it was thought that the butoxy-methyl polymer poly(**5**) would be a naturally plasticized material and therefore a better membrane. Monomer (**5**) was accordingly synthesized and polymerized. Both **4** and **5** polymerized under the conditions described above for the polymerization of **2**.



poly(4)



poly(5)

Unfortunately, the polymer **poly(4)**, also failed to exhibit Donnan behavior. Although the impermeable nature of **poly(3)** could be explained, polymer **poly(4)**, by analogy to the known **poly(2)** should have exhibited selective transport. We reasoned that the substituents on **poly(2)** would need more open space to rotate around the carbon-carbon and carbon-oxygen bonds than **poly(3)** which has fewer degrees of rotational freedom. The *trans* nature of **poly(4)** creates an irregular structure, and all the degrees of freedom found in **poly(2)** are retained. The inability of **poly(4)** to transport cations was puzzling and lead to the reconstruction of published experiments[6] and a subsequent reinvestigation of the ionophoric behavior of **poly(2)**.

Initial attempts to reproduce the extraction of dyes and the Donnan potential with **poly(2)** failed. The extraction of dyes experiment was reproducible only with low molecular weight oligomers (M_n ~ 10). This can be attributed to the inability of high molecular weight polymers to enter the aqueous phase and complex the dye molecule. The difficulties encountered with membrane transport experiments were not as easily understood.

The polymers in our initial attempts at demonstrating Donnan behavior were made with aqueous polymerization catalysts; they were high molecular weight (~ 200 000 vs polystyrene) and clean. The published experiments were done using oligomers from Osborne's catalyst in a chlorobenzene/ ethanol mixture. These materials were low molecular weight (M_n ~ 10) and difficult to purify since the catalyst was soluble in organic solvents. Neither polymers made according to the Osborne's catalyst procedure, nor polymers from aqueous polymerization doped with metal ions exhibited Donnan behavior.

Casting conditions can vary the behavior of the membranes greatly and are difficult to control or document accurately. Working from conversations with previous workers, casting was tried from THF/dioxane mixtures, instead of the THF solution previously used. Any solvents trapped in the membrane would plasticize the polymer, which is known to increase flux. No effect was seen using polymer from Osborne's catalyst and varying THF/dioxane mixtures.

In some polymer systems, certain casting conditions will lead to the formation of asymmetric membranes; unfortunately these conditions are not *a priori* predictable. It was possible that the membranes used in either the original study or the new studies, but not both, were asymmetric. This difference would account for the difference in transport behavior. Asymmetric membranes have two sections, a thin dense skin, in which the solution/diffusion mechanism operates, and a larger porous structure that provides mechanical strength. Scanning Electron Microscopy was used to look for asymmetry. The results of these experiments were inconclusive; the membranes are too thin and fragile to cross-section cleanly. SEM did provide a thickness of 7 μm for a representative membrane.

The lack of an explanation lead to extensive rechecking of the equipment, including exchanging components. The entire apparatus was tested with a commercial ion-exchange membrane, Spectra-por. Donnan behavior was easily and reproducibly observed, as shown in Figure 3. Experiments with Pt electrodes showed high resistance across **poly(2)**, and significantly less with Spectra-por, indicating that resistance measured with Pt electrodes is a good measure of communication across membranes.

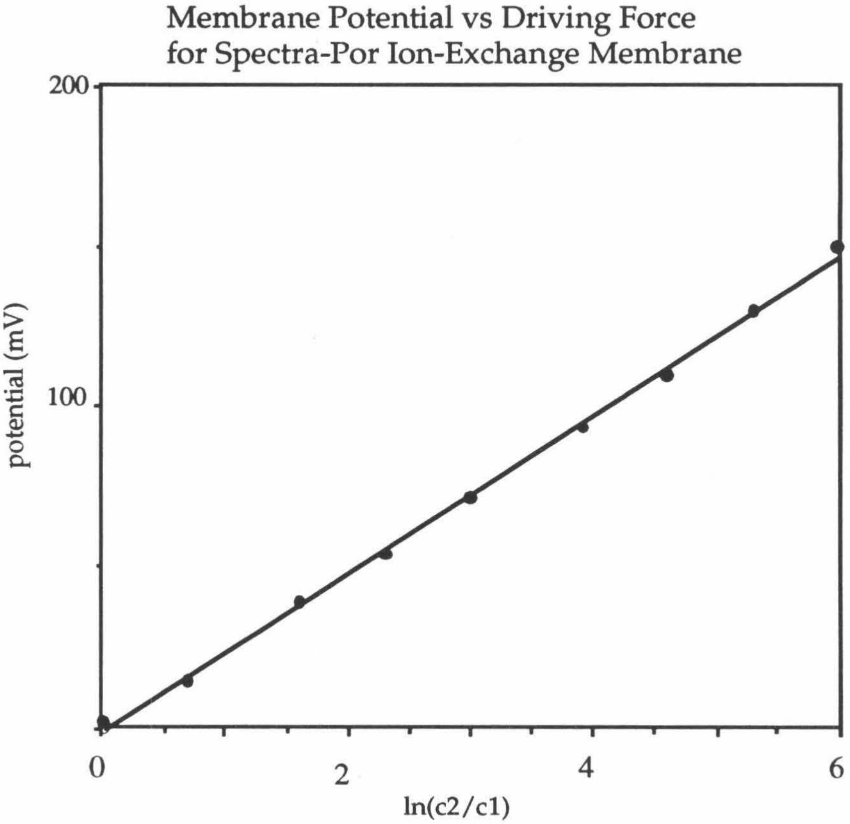


Figure 2: Donnan Behavior of Spectra-Por Ion Exchange Membrane

Concern that the thickness of the membranes was impeding transport of cations across the membrane and causing the very high resistance lead to a series of measurements of thickness (measured by absorbance) vs resistance. Seventy-five membranes were made: two were sacrificed for SEM experiments, ten membranes had leaks, and eight registered a resistance too large to measure. Data for the remaining fifty-five membranes are graphed in Figure 3. All points except the one in parentheses can be explained using two cases. In the first case, all is as expected, resistance and thickness are related. This corresponds to a uniformly thick and dense membrane. In the second case, the resistance remains low even for thick membranes. This suggests the membranes are not uniformly thick; small areas of very thin membranes lower the resistance, without changing the absorbence. Four membranes were tested for, and exhibited Donnan behavior over a few increases in driving force (difference in concentrations in cell one and cell two).

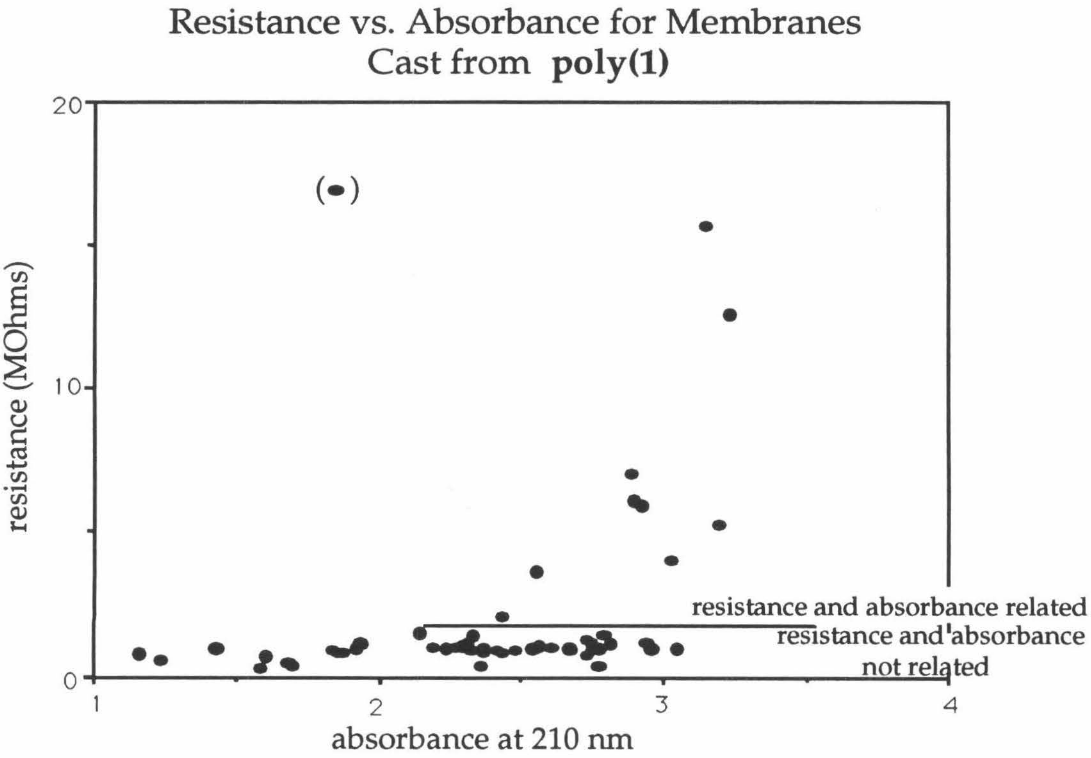
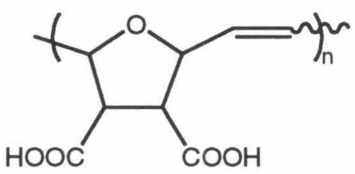


Figure 3: Resistence vs. Absorbance

Conclusion

Although we still do not understand what serendipitous conditions of membrane formation caused **poly(2)** to transport ions, we have reproduced the general result of earlier work. The initial goal of this project, to pursue structure/property relationships and design polymers with enhanced ionophoric character, was abandoned. The widely varying behavior of the same polymer sample under apparently identical casting conditions caused us to question our ability to interpret any results we might obtain.

Several other existing ROMP polymers are good candidates for membrane transport, should, for instance, a permeable block in a block co-polymer ever be desired. The polymeric acid **6** is an obvious choice for ion-exchange membranes. Crosslinking conditions for this material are under investigation.[7] The functionalized polymers **7** and **8** may show transport of cations, water or gases, by analogy to known materials. **7** is a particularly attractive alternative since it forms good strong films.



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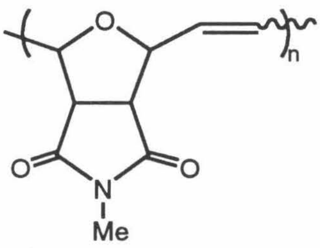
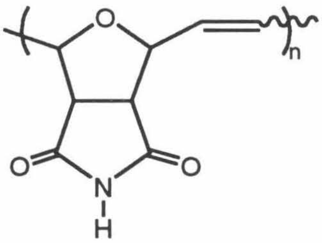


7



8

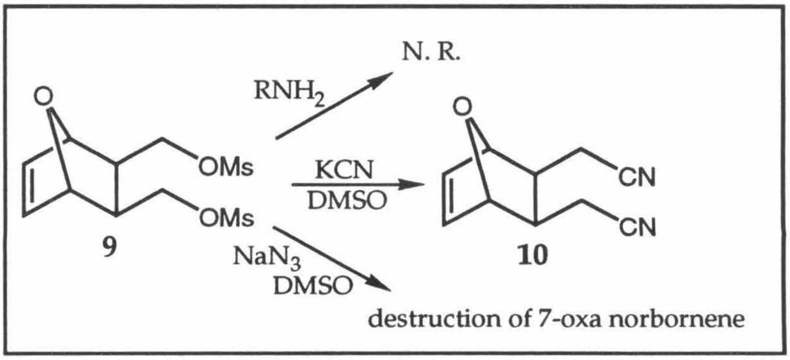
Polymeric Amines

Introduction

We sought to make poly(amines) for use as catalyst support polymers or as transition-metal sponges and, quaternized, as poly(cations). Several synthetic approaches were tried.

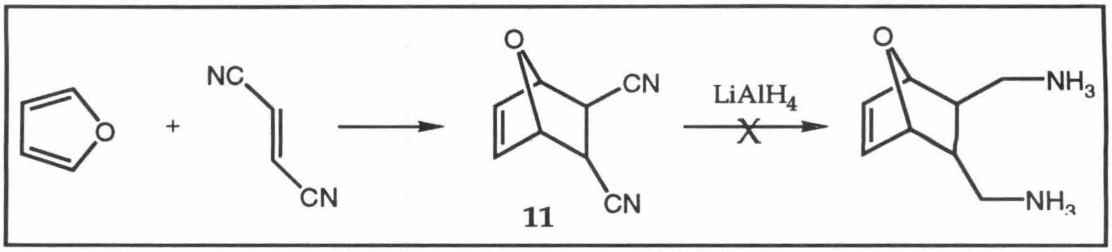
Results and Discussion

The mesylate **9** was treated with three nitrogen nucleophiles shown in Scheme 2: potassium cyanide, sodium azide and both *i*-propyl amine and ethyl amine. The amines did not react at all. Sodium azide reacted in DMSO at 40 °C to destroy the norbornene ring, but was unreactive at room temperature with lithium iodide added in catalytic amounts, it was also unreactive with acetone as solvent under similar conditions. Potassium cyanide in DMSO at 75 °C with catalytic dimethylaminopyridine yielded 71 % of the desired nitrile.



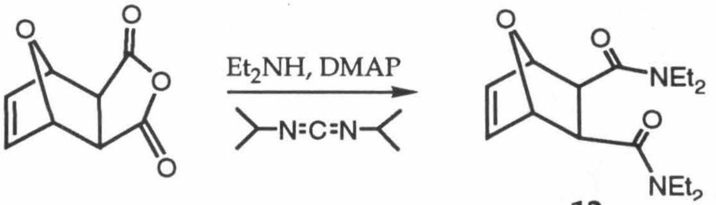
Scheme 2: The Reaction of Nitrogen Nucleophiles with the Dimesylate **9**

A *trans*-nitrile without the 2,3-methylene, **10**, is more simply made by the reaction of fumaronitrile with furan. This was reduced by $LiAlH_4$ in an attempt to make the *trans*-diamine, as shown in Scheme 3. However, the norbornene structure was destroyed in the reaction. The nitrile **10** has since been polymerized itself.[8]



Scheme 3: Attempted Reduction of a 7-Oxanorbornene Nitrile.

Another approach, reacting sodium azide with the maleic acid-furan diels-alder adduct, destroyed the norbornene structure. However, reaction of diethylamine with the maleic anhydride diels-alder adduct, with DMAP and 1,3-diisopropylcarbodiimide yielded **12** the expected amide (eq 1). Although the reaction appeared clean by NMR, the material was not isolated from the reaction by products. Reduction of this monomer would have given the diammine.

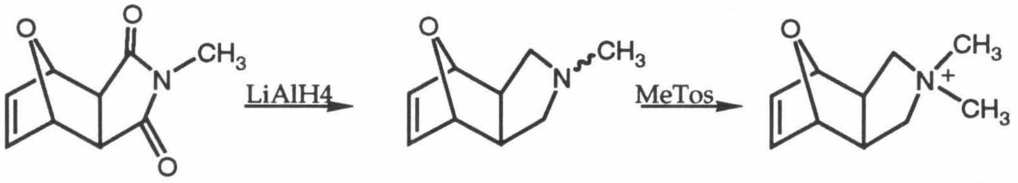


12

(1)

Other workers[9] in this group have had some success in the polymerization of quaterized nitrogen. Reduction of **7** with $LiAlH_4$ gives the amine **13**, which can not be polymerized by $tos_2Ru(H_2O)_6$ (tos = *para*-toluenesulfonate).

Addition of methyl tosylate to the amine followed by quaternization yielded **14** (eqn 2), which is polymerized by tos$_2$Ru(H$_2$O)$_6$.

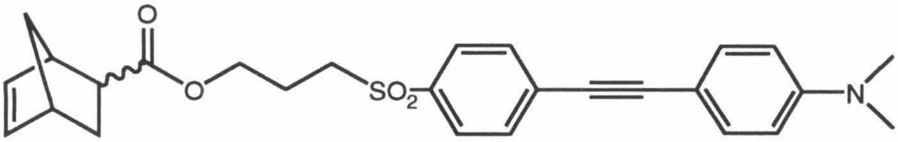


(2)

7 **13** **14**

Conclusion

While the polymerization of **14** is a promising result, the ability of a molybdenum-neophylidene to polymerize norbornenes with chromophores such as **15**[10] suggests that we can now polymerize ammines without protecting them. There are also promising ruthenium catalysts currently under development[11] that may allow the direct polymerization of amines.



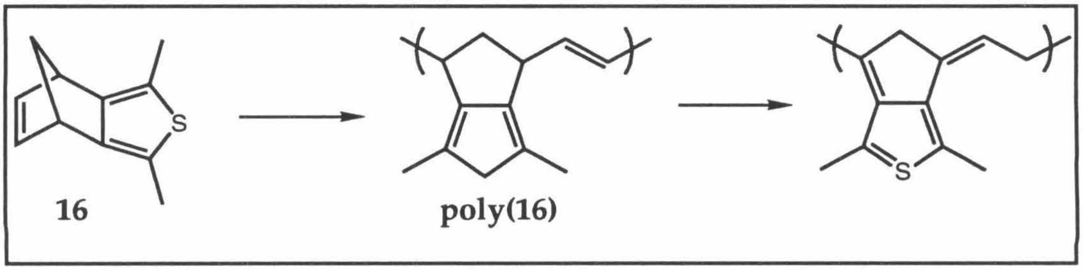
15

The prospects for the creation of poly(amines) are even greater now than when this project was undertaken, and there is motivation for a strong synthetic effort.

Polythiophenes from ROMP

Introduction

The goal of this project was the synthesis of thiophenes fused to the back of a norbornene structure, as in Scheme 4. Monomers of the type **16** would polymerize to give a polymer **poly(16)** with one thiophene per repeat unit, one synthetic step from conjugation. This would serve two purposes. First, the iodine doped polymer, **poly(16)** could conduct only through the chain hopping mechanism, but would have no through-bond conductivity mechanism available. Consequently, the conductivity of this polymer would give a base-line conductivity. Second, treatment of **poly(16)** with DDQ. or other H-atom abstraction reagent could potentially give a conducting band.

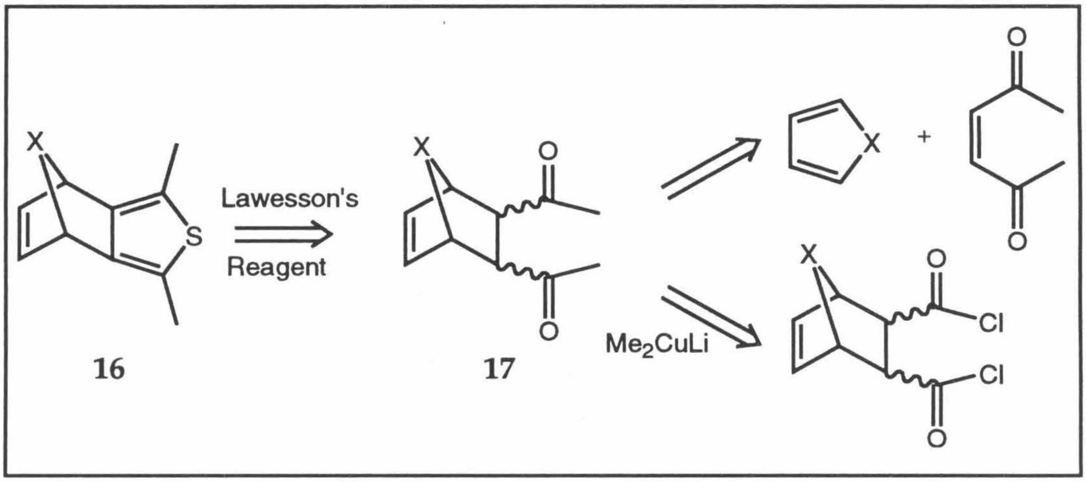


Scheme 4: ROMP Poly(thiophenes)

Thiophene does not inhibit the polymerization of **1** with ruthenium; the presence of a thiophene moiety on the monomer is not expected to interfere with ROMP.

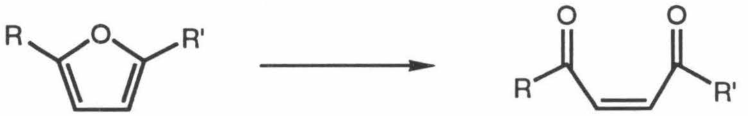
Results and Discussion

The synthetic route to the monomer **16** is sketched below. The final, and key, step involves treatment of a 2,3-di(methylketone)-bicyclohept-5-ene, **17**, with Lawesson's Reagent. Lawesson's Reagent is reported to form 2,5-disubstituted thiophenes from a variety of ene-1,4-diones.[12] The dimethylketone **17** could be approached either by Diels-Alder with cyclopentadiene and an ene-dione, or by reaction of methyl cuprate with 2,3-dicarboxylic acid-bicyclohept-5-ene. Substrates for both of these reactions were accessible; thus encouraged by the literature, the synthesis of **17** was undertaken.



Scheme 5: Synthetic Routes to Norbornenyl Thiophenes

Methyl cuprate does not effect the transformation of the di(acid chloride) to the desired diketone; no products with the 7-oxanorbornene structure are detected. Oxidative opening of substituted furans proved more fruitful (eqn 3). Both the ene-dione **18** and the aldehyde/ketone **19** were synthesized by this method. Several approaches to the oxidative opening have been reported in the literature and were attempted. Photooxidation using Rose Bengal and O_2 was attempted[13] as was reaction with ceric ammonium nitrate.[14] Peracetic acid was finally used successfully,[15] although this reaction also failed if the peracid was not fresh. The use of *m*-CPBA has also been reported,[16] but the peracetic acid route was satisfactory and the *m*-CBPA route was not attempted, nor was the reported conversion of 1,4-bisketone alkanes to 1,4-bisketone alkenes via SeO_2 attempted.[17]



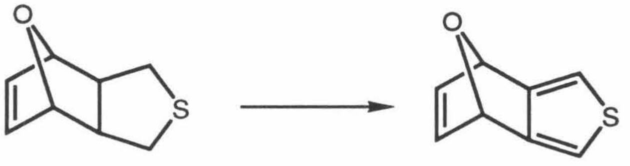
R = Me R' = Me**18**
R = Et R' = H **19**

(3)

The ene-dicarbonyls **18** and **19** undergo Diels-Alder reaction with cyclopentadiene cleanly in refluxing tetrahydrofuran, yielding the desired 2,3-disubstituted norbornenes.

A model reaction of the third step, the treatment of 1,4-hexanedione with Lawesson's Reagent reacts smoothly, as reported in the literature, to give 2,5-dimethylthiophene. When the 2,3-di(methylketone)-bicyclohept-5-ene is used as the substrate however, the reaction does not proceed smoothly. No products containing the norbornene structure were identified in the reaction products, which consisted mainly of a tar. It may be significant that although reactions of Lawesson's Reagent with olefinic substrates to form thioketones have been reported,[18] no reactions with olefinic substrates to form thiophenes have been reported. What is more worrisome is the absence of reports of tetrasubstituted thiophenes being formed by the action of thiophenes. One example of a 2,3-di(methylketone)-2.2.2-bicylooct-5-ene being converted by H_2S to the corresponding fused-ring thiophene has been reported.[19] However, while the reactions of both 2.2.2 and 2.2.1 systems are discussed throughout this paper, the synthesis of the 2.2.1 fused thiophene molecule is not reported. It is possible that the strain inherent in a 2.2.1-fused thiophene system must be in place before the thiophene is formed.

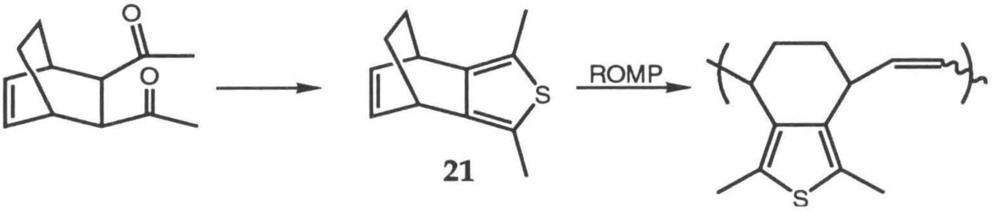
There are several synthetic routes that might circumvent this problem by starting with a preformed, fused five-membered ring, the most obvious of which is the conversion of the sulfide **20**, the synthesis of which is discussed in Chapter 1, to the thiophene (eq 4). This does not allow easy entre´ into thiophenes alkylated at the 2 and 5 positions, but might be a reasonable approach to the parent polymer.



20

(4)

Since 2,2,2-systems also undergo ROMP, and the thiophene substituted-2,2,2-bicyclooctene, **21** has been reported, the synthesis and polymerization of **21** (eq 5) might be a good route to ROMP poly(thiophenes).



21

(5)

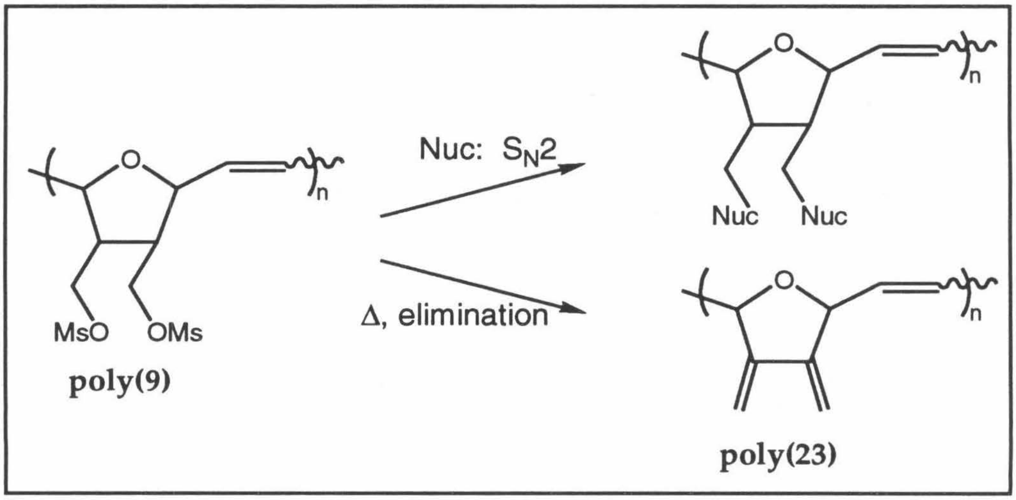
Conclusion

While the route to norbornenyl thiophenes via Lawesson's reagent did not succeed, there are still several viable approaches to poly(thiophenes) via ROMP.

Poly(dimesylate): a Precursor Polymer

Introduction

Polymers with reactive side-groups are useful for graft co-polymers and post modification of the chain. This poly(mesylate) **poly(9)** is particularly attractive because it has two modes of reactivity as synthesized (Scheme 6).



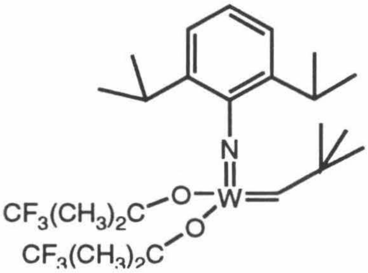
Scheme 6: Expected Reactivity of **Poly(9)**.

The nucleophilic substitution approach to functionalizing this polymer might be particularly useful for the amines discussed above, and for sulfides. The opening of the bicyclic ring eliminates quite a bit of steric hindrance, which is thought to be responsible for the slow reactivity observed with the monomer **9**. The presence of a polymer chain may well compensate for the relative openness of the cyclopentane in some cases, but in others the difference may be useful. Hydrolysis of the mesylate to the alcohol would give a water soluble, hydrogen-bonding polymer. The insertion of a block of mesylate in a co-polymer, followed by hydrolysis, would lead to an amphiphillic polymer.

The second mode of reaction, elimination, leaves a diene in the appropriate conformation for Diels-Alder reactions. As activated dieneophiles often contain polar, water soluble and biologically active groups, this might be an entry to polymeric drugs.

Results and Discussion

The monomer precursor **9**, does not polymerize with the aqeous ruthenium systems. It does, however, polymerize with the molybdenum neophylidene **22** in



22

dichloromethane in a nitrogen drybox. The polymer precipitates out of solution, and is purified by dissolution in dimethylformamide and precipitation into methanol. The purified polymer is an off-white, fluffy solid isolated in 80 % yield. The solid is identified as a ROMP polymer by ^1H NMR, which also reveals the predominately *cis* nature of the backbone olefins. The distribution of molecular weights is broad: $M_n = 39{,}600$, $M_w = 202{,}000$ giving $M_w/M_n = 5.1$. A broad molecular weight distribution is not unexpected when the polymer precipitates from solution during the polymerization.

The solid polymer **poly(8)** has been subjected to thermal gravimetric analysis and the thermogram is shown below as Figure 4. The loss of methanesulfonic acid is proposed as the cause of mass loss. This polymer loses mass in an extrodinarily clean fashion, and at a very low temperature. Onset of mass loss is at 220 °C, a temperature easily reached in solution. The onset of mass loss is visually observable: a cloud of smoke rises from the sample at the same time the spike is recorded. The apparent rise in mass is associated with the dramatic way the gases leave the polymer sample--the TGA balance pan is pushed down by the force of exiting masses, giving the appearance of mass gain.

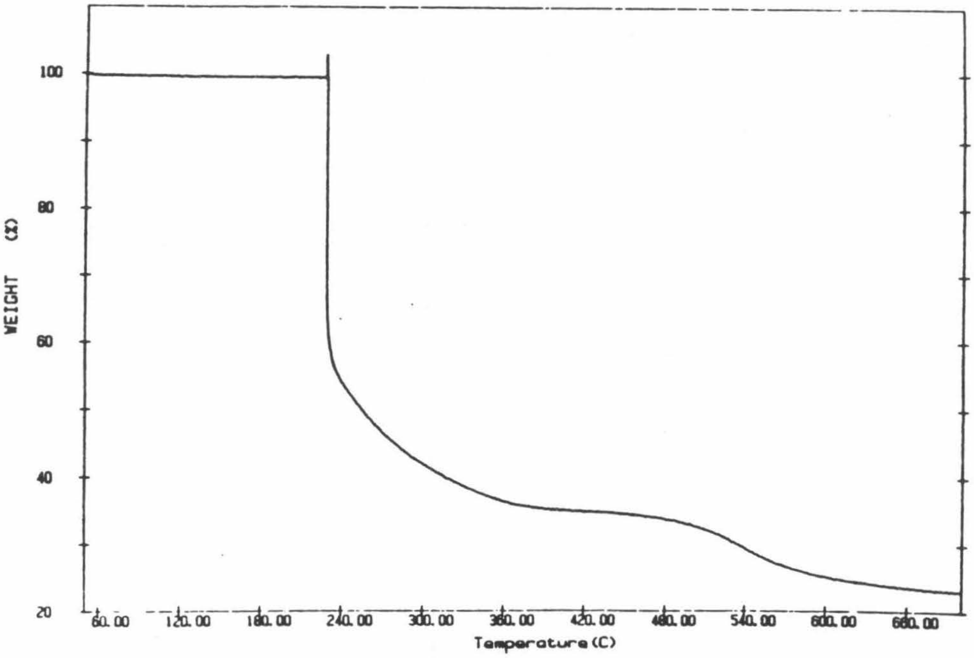
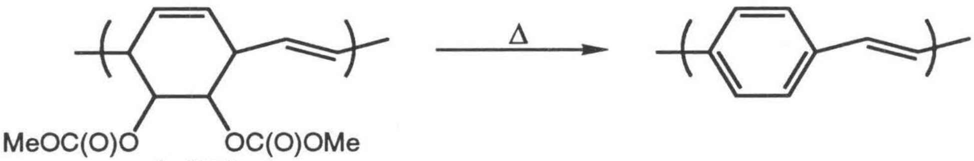


Figure 4: Thermogravimetric Analysis of **poly(8)**.

Conclusion

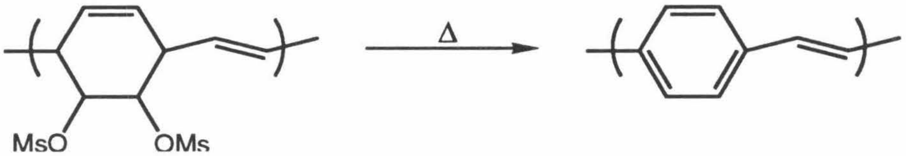
From TGA the poly(diene) **poly(23)** is accessible at reasonable temperatures (~ 220 °C) and hence could be generated in solution and derivitzed with dieneophiles *in situ*. Hydrogenation of the backbone would reduce the possiblility of crosslinking or other side reactions with backbone olefins.

The suddenness of mass loss and the low-temperature onset of this polymer has significance for precursor polymers currently under study in our group.[20] The onset of mass loss from the poly(*para*-phenylenevinylene) precursor carbonate **poly(23)** to form poly(phenylenevinylene) (eqn 6) is 265 °C, and loss is not as quick. Lower temperatures of thermolysis reduce unwanted side reactions: derivitization of the monomer to the mesylate may lower the onset of decomposition. We might expect the onset of mass loss for **poly(24)** to be lower than the onset for **poly(9)** due to the driving force present when an aromatic moiety is created (eq 7).



poly(23)

(6)



poly(24)

(7)

Experimental

General Procedures. _ All manipulations involving air- and/or moisture sensitive compounds were carried out using standard Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å sieves. Solids were transferred and stored in a N_2-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner and a Dri-Cold Freezer.

Instrumentation.

NMR spectra were recorded on a Jeol GX-400 (399.65 MHz ^{1}H, 100.40 MHz ^{13}C) or a GE QE-300 (300.19985 MHz ^{1}H, 75.492893 MHz ^{13}C). Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are reference to the carbon signal of the deuterated solvents. GPC analyses in methylene chloride were carried out on an HPLC system consisting of an Altex Model 110A pump operating at 1.0 mL/min, a Rheodyne Model 7125 injector with a 100 mL injection loop, through either three Shodex Styragel columns (KF 803, KF 804 and KF 805) or an American Polymer Standards 10 mm mixed-bed column, and two detectors (Knauer Differential-Refractomer and Kratos Spectroflow 757 UV detector operating at 325 nm). GPC analysis in DMF were carried out by American Polymer Standards. Thermogravametric analysis was accomplished on a Perkin-Elmer TGA-2. UV/vis measurements were carried out with a HP 8451A UV/vis spectrometer.

Synthesis of *exo*-6,10-dioxatricyclo-[4.3.0.1^{3,9}]-dec-1-ene, **3**. The diol 2,3-di(hydroxymethyl)-7-oxabicyclo-[2.2.1]-hept-1-ene (6 g, 39.4 mmole) was weighed into a round bottom flask equipped with a stir bar and dissolved in 100 mL of dichloromethane. Toluenesulfonyl chloride (7.52 g, 39.4 mmole) was dissolved in pyridene (9.53 mL, 118.2 mmole) and dichloromethane (100 mL) and the solution was added dropwise to the stirring solution of diol. The reaction mixture was allowed to reflux for 24 hours, after which the reaction mixture was washed three times each with 1 N NaOH and 1 N HCl. The dichloromethane solution was dried over magnesium sulfate and the solvent removed by rotary evaporation. The product was obtained as a white solid by crystallization from 50/50 dichloromethane/pentane in approximately 30 % yeild (ca 2 g). ^{1}H NMR ($CDCl_3$) δ (ppm) 6.43 (s, olefin, 2H); 4.78 (s, bridgehead, 2H); 3.95, 3.64 (m, methylene, 2H); 2.50 (m, methine, 2H).

Polymerization of **3**. A small amount (~ 1 mg) of ruthenium trichloride was placed in a small culture tube and dissolved in 2 mL methanol. The monomer **3**, (0.1 g) was added and dissolved. Two drops of water were added to the reaction mixture and the tube was placed in a 50 °C oil bath overnight. The polymer precipitated from the reaction mixture, and was removed as a white plug. The polymer was dissolved in dichloromethane and gently washed with 2 x 10 mL 0.2 M Na_2EDTA and 2 x 10 mL water and precipitated with methanol. The polymer was dissolved in dichloromethane and precipitated into methanol three times, after which the polymer was dried under vacuum. ^{1}H NMR (CD_2Cl_2) δ (ppm) 5.8 (br, *trans*-olefin); 5.6 (br, *cis*-olefin); 4.3 (br, *cis*-bridgehead); 4.0-3.7 (br, methylene); 3.4 (br, *trans*-bridgehead); 2.65 (br, methine). (Fully coupled) ^{13}C NMR (CD_2Cl_2) δ (ppm) 132 (m, olefin); 86,87 (d, methine); 71 (t, methylene); 32 (m, bridgehead). IR (neat film) 2955,2855 (s, C-H stretching), 1624 (s, C=C stretching), 1020 (s, br, C-O stretching).

Synthesis of Bicylco[2.2.1]-*erans*2,3-di(methoxymethyl)-7-oxa-hept-1-ene, **4**,was carried out according to the method reported by Novak[4] for the monomer **2**. ^{1}H NMR ($CDCl_3$) δ (ppm) 6.40 (d, olefin, 1H); 6.27 (d, olefin, 1H); 4.92 (d, bridgehead, 1H); 4.75 (s, bridgehead, 1H); 3.45 (m, $1/2$ methylene 1H); 3.34 (s, methoxy, 3H); 3.31 (m, $1/2$ methylene, 1H); 3.29 (m, $1/2$ methylene, 1H), 3.27 (s, methoxy, 3H), 2.95 (m, $1/2$ methylene, 1H), 1.91 (m, methine, 1H), 1.32 (m, methine, 1H).

Synthesis of Bicylco[2.2.1]-*exo*-2,3-di(butoxymethyl)-7-oxa-hept-1-ene, **5**,was carried out according to the method reported by Novak[4] for the monomer **2**. ^{1}H NMR ($CDCl_3$) δ (ppm) 6.33 (s, olefin, 2H); 4.80 (s, bridgehead, 2H); 3.50 (m, $1/2$ methylene, 2H); 3.40 (t, butyl group: α methylene, 4H), 3.25 (m, $1/2$ methylene, 2H), 1.84 (m, methine, 2H), 1.53 (m, butyl group: β methylene, 4H), 1.34 (m, butyl group: γ methylene, 4H), 0.88 (t, methyl, 6H).

Ionophore Experiments

Syntheses, extraction and initial Donnan experiments with **poly(2)** were carried out according to procedures outlined by Novak.[4] The Spectra/Por I-S Membrane was purchased from Spectrum and used as received.

The membranes cast for the absorbance vs. resistance measurements were cast on gold foil over holes drilled in quartz plates. The membranes were allowed to dry at least twelve hours before measuring absorbance at 210 nm. Five sequential absorbance readings were collected, the mean of which was used in an attempt to average out the effects of scattering caused by the gold grid. The quartz plates were placed between the plexiglass cells, sealed with Apiezon M grease. The cells were held together with a large D clamp. Lithium chloride solution, (0.1 mM) was placed in each cell, the bubbles next to the membrane were gently removed by suction with a Pasteure pipette, and the Pt electrodes were placed in the cells. The electrode leads were shorted, and then allowed to drift to a reading for one minute, after which the leads were again shorted. Five readings one minute apart were taken in this way, and the results averaged to give a resistance reading. If the resistance was anomously low, or at the end of the sequence, methyl orange was added to one cell to check for leaks. In no cases of anomously low resistance was a leak not detected.

sample	absorbance	resistance(MΩ)	drift	comments
65.0	1.42			overload
65.2	1.58	0.3		
65.4	2.77	0.4		
65.6	2.36	0.4		
65.8	1.69	0.4		
70	1.3			overload
70.2	1.24	0.53		Donnan for two points, failed
70.4	1.68	0.43		3 reads, fail
70.6	1.4			leak
70.8	1.01			leak
85.0	1.1			leak
85.2	1.6	0.714		2 reads, failed in Donnan
85.4	1.45			leak
85.6	1.5			broke
85.8	1.16	0.78		2 reads, then leak
97.0	2.96	0.94	-0.02	Donnan, leveled off in 2 points
97.2	2.2	1	-0.4	3 reads, leak
97.4	2.55	3.6	-4	
97.6				sacrificed for SEM
97.8				sacrificed for SEM
123.0	2.94	1.18	-0.15	
123.2	2.43	2.09	-3.53	
123.4	2.84			leak
123.6	2.89	7.06	-0.47	
123.8	2.52			overload
148.0	1.96			leak
148.2	2.48	0.914		
148.4	2.46			overload

148.6	3.23	1.26	
148.8	2.54		
248.0	3.29		overload
248.2	3.214		leaked
248.4	3.128		overload
248.6	3.087	5.25	
248.8	3.14		overload
258.0	2.135	1.506	
258.2	3.152	1.569	
258.4	2.928	5.98	
258.6	2.326	1.392	
258.8	1.848	1.693	
262.0	2.305	1.155	
262.2	2.781	0.934	
262.4	2.771	0.94	
262.6	1.426	0.922	
262.8	3.047	0.932	
266.0	1.871	0.85	
266.2	3.028	4.04	
266.4	2.746	0. 87	
266.6	2.672	0 .892	
266.8	2.538	0.925	
268.0	2.665	0.9.39	
268.2	2.428	0.857	
268.4	2.192	0.998	
268.6	2.318	0.91	
268.8	1.915	0.925	
170.0	2.675	0.965	
170.2	1.831	0.914	
170.4	2.291	1.06	
170.6	2.813	1.14	
170.8	2.75	1.12	
172.0	2.555	1.04	
172.2	2.402		overload
172.4	2.323	0.917	
172.6	2.731	1.25	
172.8	2.408	0.905	
174.0	3.4		very unstable
174.2	2.733	0.766	
174.4	1.856	0.841	
174.6	2.367	0.861	
174.8	1.931	1.13	
182.0	2.233	0.957	
182.2	2.603	0.981	
182.4	2.789	1.428	
182.6	2.367	0.975	
182.8	2.9	6.124	

Synthesis of **10**. The mesylate **8** (2 g, 6.4 mmole), potassium cyanide (0.713 g, 19.2 mmole) dimethylaminopyridine (< 10 mg) were weighed out in the hood and placed in a 100 mL flask, to which was added 40 mL DMSO that had been stored over sieves. The reaction mixture was purged during dissolution and then heated to 68 °C overnight. After cooling the dark-orange reaction mixture, 50 mL saturated brine was added and the aqeous mixture extracted 6 x 25 mL ethyl acetate. The combined organics were back extracted with 2 x 25 mL brine and 1 x 25 mL H_2O, dried and rotovapped, yeilding 0.80 g (71%) brown oil. The material was purified by flash chromatography; the desired product has a low R_f and stains blue with anisaldehyde on TLC. ^1H NMR δ (ppm) 6.40 (s, olefin, 2H); 4.69 (s, bridgehead, 2H); 4.08, 3.82 (m, methylene, 4H); 1.96 (m, methine, 2H).

Synthesis of **12**. The Diisopropylcarbodiimide (3.53 mL, 23 mmoles), diethylamine (6.2 mL 60 mmoles, distilled from CaH_2) and dimethylaminopyridine (0.184g, 1.5 mmoles) were dissolved in 25 mL CH_2Cl_2. The Diels-Alder adduct of maleic anhydride and furan (2.5 g, 15 mmoles) was added portionswise to the reaction. After thirty minutes the reaction mixture was filtered through a plug of silica and rotovapped to yeild white crystals and an orange oil. Recrystallization from water and a minimum of ethanol gave white crystals of diisopropyl urea and a brown oil, containing the desired amide, identified by its ^1H NMR (ppm) 6.45 (s, olefin, 2H); 5.17 (s, bridgehead,2H); 3.67 (q, $CH_3C\underline{H}_2$, 4H); 2.73 (s, endo, 2H); 1.18 (t, $C\underline{H}_3CH_2$, 6H). Distillation of the amide gave white crystals of 1,2-(N, N-diethylamido)ethene, the retro-Diels Alder product of the desired amido-substituted 7-oxanorbornene.

Synthesis of **17**. The enedione **18** (1g, 8.92 mmoles) was dissolved in 25 mL THF and cooled to 0 °C. The freshly cracked pentadiene (0.71g, 10.7 mmoles) was added dropwise from a pipette. The reaction was allowed to warm to room temperature overnight. ^{1}H NMR δ (ppm) 6.17 (s, olefin, 2H), 3.36 (s, methine, 2H); 3.15 (s, bridgehead, 2H); 1.44 1.56 (m, 7-methylene, 2H).

Synthesis of **18**. The oxidation was carried out according to literature procedures.[12] ^{1}H NMR δ (ppm) 6.27 (s, olefin, 2H); 2.30 (s, methyl, 6H).

Synthesis of **19**. The oxidation was carried out according to literature procedures.[13] ^{1}H NMR δ (ppm) 9.75 (d, $J_{H\text{-}H}$ = 7 Hz, aldehyde 1H); 6.87 (d, $J_{H\text{-}H}$ = 16 Hz, olefin, 1H); 6.76 (dd $J_{H\text{-}H}$ = 7 Hz, $J_{H\text{-}H}$ = 16 Hz, olefin, 1H); 2.72 (q, $J_{H\text{-}H}$ = 7 Hz, methylene, 2H); 1.13 (t, $J_{H\text{-}H}$ = 7 Hz, methyl, 3H). IR (neat on NaCl plate) 3365 (s, aldehyde C-H stretch), 2980-2731 (s, alkane an dalkene C-H stretch), 1789-1695 (s, carbonyl). λ_{max} = 222 nm.

Polymerization of **9**. The monomer (0.5g, 1.6 mmole) was dissolved in 20 mL methylene chloride, and the catalyst (21mg, 0.032 mmole) was dissolved in 1 mL methylene chloride and added to the monomer solution. The mixture was shaken to mix: cloudiness was observed within twenty minutes of mixing, but the reaction was allowed to proceed overnight. The polymer precipitated out of solution and was collected by centrifugation and dried *in vacuo*. The solids were dissolved in DMF and precipitated into methanol. The precipitated polymer was collected by filtration and again dried *in vacuo*, giving 394 mg (79%) of an off white solid polymer. ^{1}H NMR (DMF-d_7) δ (ppm) 5.90 (br s, *trans*-olefin, 0.4H); 5.70 (br s, *cis*-olefin, 1.6H); 4.9-4.3 (br m, methylene and methine α-to-oxygen); 3.27 (m, methyl, 6H); 2.65 (br s, methine, 2H). ^{13}C NMR (DMF-d_7) δ (ppm) 135-133 (olefin); 83, 77 (methine α-to-oxygen); 69-67 (methylene); 47-45 (methine); 37 (methyl).

Notes and References

[1] These are the so-called case II or non-Fickian systems. A good general description of the theoretical models used to describe both Fickian and non-Fickian systems, as well as transport in glassy polymers is given by Aminabhavi, T. M.; Aithal, U. S.; Shukla, S. S. *JMS-Rev. Macromol.Chem. Phys.* **1988**, *C28*, 421.

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