Ruthenium Mediated Olefin Metathesis: Materials with Controlled Microstructure and Functionalization

Thesis by

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For my Family,

and in Memory of my Grandmothers

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Abstract. Methylcyclopentene and cyclooctadiene were copolymerized via ring opening metathesis polymerization (ROMP) mediated by the well-defined complex $(PCy_3)_2Cl_2Ru{=}CHPh$ to produce materials with controlled microstructure and functionalization. The copolymer (COD/3-MCP) composition (10-80 methyls/1000 carbons) and melting point (T_m) (65 - 110°C) were controlled by comonomer feed ratio. Polymerizations performed in the presence of chain transfer agent (CTA) *cis*-2-butene-1,4-diacetate provided telechelic copolymers with controlled chain length (M_n 1500-3500 g/mol), and ^{13}C NMR spectra were used to assign polymer microstructure. The ruthenium carbene was converted *in situ* to an active olefin hydrogenation catalyst. The effectiveness of this methodology depends on polymer microstructure, solvent, temperature, pressure and additives. Methylene chloride is the best solvent for hydrogenation (200°C, 800 psi H_2, Olefin/Ru $\approx$ 2000). The structure/property relationships of this family of materials was investigated by numerous methods. The number of backbone methyl branches had a significant effect on the melt transition temperature and enthalpy and zero shear viscosity. There was not a demonstrable effect on the energy of activation of flow. However, preliminary rheo-optical measurements indicate a strong dependence of the stress-optic coefficient on methyl branch.

The regiospecific and irreversible reaction of ruthenium carbenes $(PR_3)_2Cl_2RuCHR'$ (R = PPh_3 or PCy_3, R' = Ph, $CHCPh_2$, $(CH_2)_4CH_3$ or polynorbornene) with electron rich vinyl ethers (EtOCH=CHR, R = H, CH_3, $(CH_2)_5CH_3$, CH_2Ph or Ph) was also investigated. These reactions were monitored by ^1H NMR spectroscopy and kinetic data was obtained under pseudo first order conditions ([vinyl ether]$_0$/[Ru]$_0$ 10/1). The half lives ($t_{1/2}$) for this reaction were calculated from the observed kinetic data for [vinyl ether] = 0.15 M. ^1H NMR data indicates that the observed metathesis was regiospecific and irreversible yielding a heteroatom stabilized alkylidene species ($L_nRu{=}CHOEt$). Ruthenium catalysts possessing electron rich alkyl phosphines were more reactive towards each substrate. Coordination of a heteroatom from the polymer backbone (poly(cyclobutene) with pendant amide or ether groups) significantly inhibited metathesis at all temperatures. The analogous triphenylphosphine derivatives were less reactive and $(PPh_3)_2Cl_2RuCH(C_7H_{10})_n$ reacts only with ethyl vinyl ether at 20°C. At 40°C metathesis was observed with other less hindered substrates.

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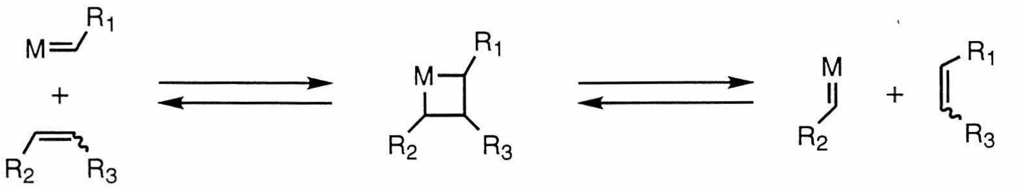
Chapter 1

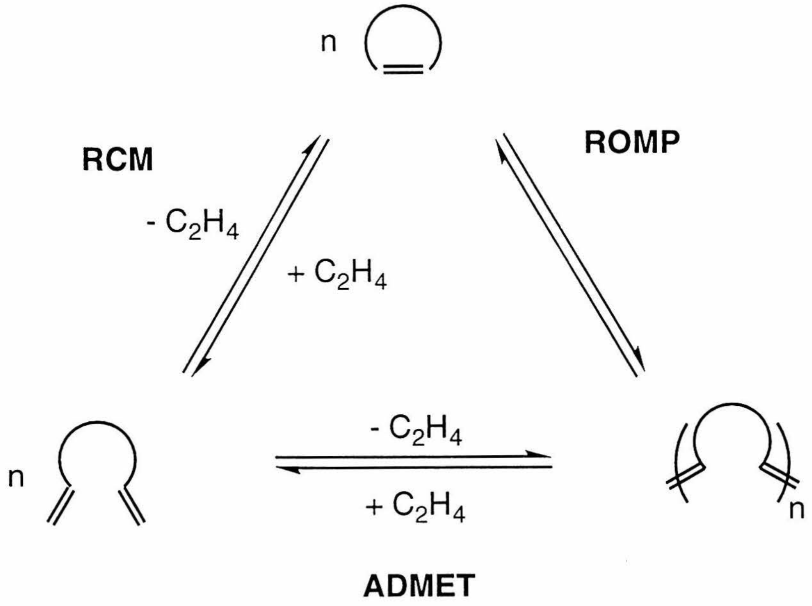
Introduction.

Olefin metathesis is an interesting and synthetically useful reaction,[1] in which there is a net exchange of olefin substituents. The transformation proceeds via the reversible formation of a metallacyclobutane[2] which then undergoes either degenerate cleavage to form starting materials or productive cleavage for the formation of a new carbon carbon double bond and a new metal carbon bond (Eq. 1). Recently, olefin cross-metathesis has been utilized to synthesize unsymmetric functionalized olefins.[3]



(1)

In addition to these cross metathesis reactions, olefin metathesis has been exploited for a variety of reactions including ring closing metathesis (RCM),[4-6] ring opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET) (Scheme 1).



Scheme 1: Olefin Metathesis.

Initially, ROMP was the most widely utilized reaction for metathesis initiators. Ill-defined heterogeneous systems have been used for commercial production of polynorbornene, polyoctenamer and polydicyclopentadiene.[7] These classic systems are generally comprised of an early transition metal halide or oxide which are activated by and alkylaluminum reagent. Norbornene is polymerized using $RuCl_3$/HCl in butanol and the resultant polymer can absorb 5-10 times its mass of oil to form elastomeric materials good for shock insulators and viscoelastic layer dampers. DCPD has been reaction injection molded (RIM) using a mixture of WCl_6/$WOCl_4$ and other additives. Commercial products include golf cart bumpers, snowmobile facia and industrial corrosion resistant parts. Compared to the variety of multi-component systems, there are relatively few well defined single component carbenes that are active towards olefin metathesis (Figure 1).[1]

Many of these complexes have bulky ligands, and in fact the carbene substituents are often also sterically bulky. This structural requirement prevents bimolecular decomposition of the carbene. In the case of titanocylobutanes, the metallacycle is lower in energy than the carbene and can be isolated and characterized.[8] Titanacylclobutanes also polymerize norbornene in a living fashion.[9]

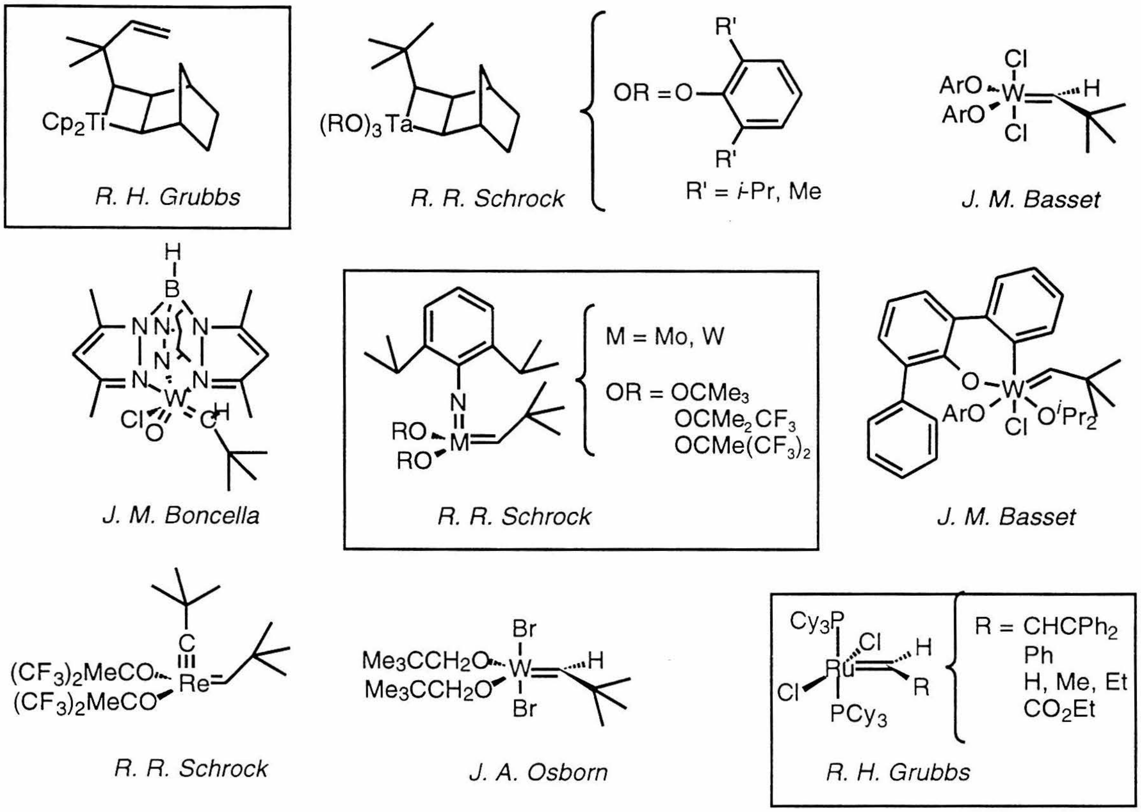
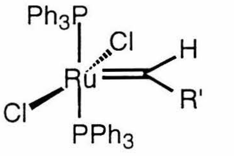


Figure 1. Single Component Metathesis Initiators

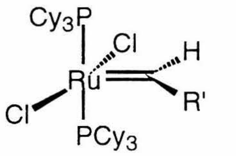
The development of new catalysts was focused on several goals: increased activity, stability and functional group tolerance. The most active are molybdenum and tungsten alkylidenes with hexaflouro alkoxy substituents.[10-13] These catalysts will catalyze ring closing metathesis to form tri- and tetra-substituted olefins.[14,15] The activity of these catalysts has been modified not only by varying the alkoxide ligands, but also by the addition of an exogenous Lewis base. The latter methodology was used to effect the living polymerization of cyclobutenewhich after hydrogenation affords monodisperse polyethylene.[16] One drawback to the early transition metal complexes is that their syntheses are multi-step, require rigorously pure reagents and are very sensitive to air and moisture. Furthermore, although these complexes are very active, they are not stable in solution for prolonged periods of time and have very limited tolerance for functional groups. Specifically, molybdenum carbenes react with aldehydes and tungsten reacts with aldehydes and ketones to form the corresponding metal-oxo species which are not metathesis active. Less sterically hindered early transition metal carbenes have been synthesized recently.[17] Complexes with chiral ligands have also been synthesized for stereoselective ring closing metathesis.[18,19]

A major advancement in this field occurred with the development of the new and improved ruthenium (II) carbenes.[20-22]

R = (a) $CHCPh_2$
(b) Ph



(1a,b)



(2a,b)

These catalysts are air and moisture stable and react exclusively with olefins in the presence of most functional groups. These ruthenium complexes are less active than $MNAr(OC(CF_3)_2CH_3)_2{=}CHR$ (M = Mo, W),[23] but they exhibit far greater synthetic utility. The first isolated ruthenium (II) carbene (**1a**) is only active towards highly strained cycloalkenes. Substitution of the triphenylphosphine ligands with more electron rich phosphines (tricyclohexyl phosphine) enhances activity and stability and (**2a-b**) ring open low strained cycloolefins and react with acyclic olefins.

Historically, the most studied metathesis reactions have been polymerizations. Metathesis polymerization is an inherently entropically disfavored equilibrium process (Table 1). The polymerization is driven by the relief of ring strain,

Table 1. Thermodynamics *trans*-polymers vis ROMP of cyclic olefins[1,24,25]

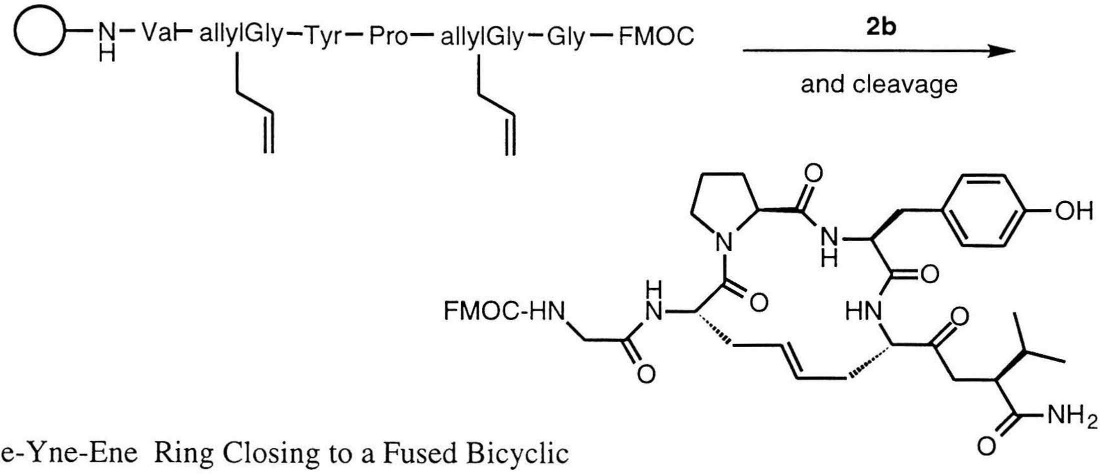
Monomer	$-\Delta H^\circ$ kJ mol^{-1}	$-\Delta S^\circ$ J K^{-1}mol^{-1}	$-\Delta G^\circ$ kJ mol^{-1}
cyclobutene[a]	121	52	105
cyclopentene	20	46	6.3
cyclohexene	2	28	-7.3
cycloheptene	20	17	14
cyclooctene	22	2	20
1,5-cyclooctadiene	33	5	24
norbornene[b]	62	50	47

[a] *cis* polymer [b] 55% *cis* polymer

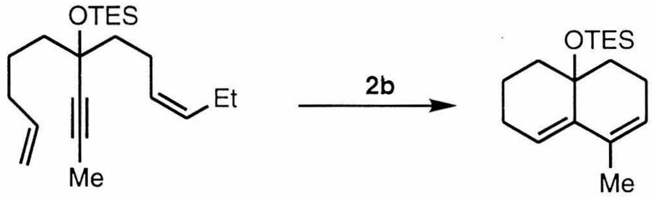
not by differences between double/single bond energies as is typical in typical Ziegler Natta processes. ROMP has been utilized to make photo- and electroluminescent polymers,[26-29] liquid crystalline polymers,[30,31] telechelic polymers,[32-34] glycopolymers[35] and other macromolecules with biological applications.[36] Hydrolytically degradable polymers[37] have also been synthesized, and metathesis has been used to degrade polymers with olefins in the backbone.[38,39]

Recently, there has been a renewed interest in the field of ring closing metathesis[40,41] (Scheme 2) including applications toward amino acid analogs,[42] and natural products.[43,44] Template directed ring closings to form crown ethers[45] and catenanes[46] have also been demonstrated.

Ring Closing of Peptide



Ene-Yne-Ene Ring Closing to a Fused Bicyclic



Scheme 2. Ring Closing Metathesis.

New reaction topologies have been developed including ene-yne-ene ring closing to form fused and spiro bicyclics[47] and tandem ring opening/closing reactions.[48] Metathesis has been used ring close the pendant vinyl groups of poly(1,2-butadiene) to make cyclopolymer.[49]

A final area of exciting research is in water soluble catalysts[50] and reactions in aqueous media. Living polymerizations[51] and ring closing metathesis[52] have both been done in aqueous media.

This thesis describes several ways of using these well defined ruthenium catalyst systems to synthesize new polymeric materials with tailorable properties. Chapter two describes the synthesis of polyethylene/polypropylene copolymer analogs. The addition of a chain transfer agent provides a synthesis of telechelic EP copolymers. A notable feature of this study is that a ruthenium carbene complex is used for both monomer synthesis and polymerization. Furthermore, the ruthenium carbene can be converted *in situ* to an active olefin hydrogenation catalyst. Characterization of the polymers and the effect of methyl branching is also presented. Chapter three describes reactions to selectively cleave the metal center from the polymer terminus while transferring a new carbon fragment. The accompanying appendices briefly describe the synthesis of several monomers for ROMP and the use of metathesis catalysts to synthesize and end-functionalize poly(3,3-dimethylcyclobutene). Finally, the last appendix describes a safe and convenient method for the purification of common organic solvents.

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Chapter 2

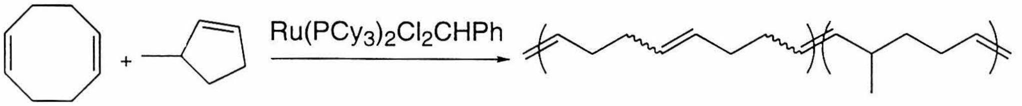
Synthesis and Characterization of Methylcyclopentene and Cyclooctadiene Copolymers.

Abstract. A new series of ethylene/propylene (EP) copolymers has been prepared. The well-defined ruthenium complex, $(PCy_3)_2Cl_2Ru{=}CHPh$ was used to synthesize methylcyclopentene (MCP), copolymerize MCP and cyclooctadiene (COD) and to generate *in situ* and active hydrogenation catalyst. The copolymer (COD/MCP) composition (10-80 methyls/1000 carbons) and melting point (T_m) (65 - 110°C) were controlled by comonomer feed ratio. Polymerizations were also performed in the presence of chain transfer agent (CTA) *cis*-2-butene-1,4-diacetate. This procedure provided telechelic copolymers with controlled chain length and monomer incorporation. The molecular weight of the telechelics (M_n 1500-3500 g/mol) was controlled by the ratio of [monomer]/[CTA]. The ^{13}C NMR spectra were used to assign polymer microstructure by comparison with calculated spectra and hydrogenated samples of poly(4-methylcyclopentene). The ruthenium carbene was converted *in situ* to an active olefin hydrogenation catalyst. The effectiveness of this methodology depends on polymer microstructure, solvent, temperature, pressure and additives. Methylene chloride is the best solvent for hydrogenation and at 200°C and 800 psi H_2, polymers are completely hydrogenated (Olefin/Ru $\approx$ 2000).

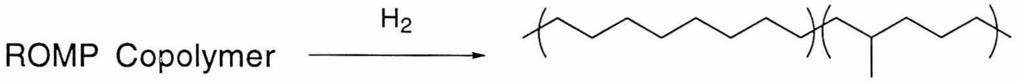
This synthetic route is a convenient method for the preparation of polymers with controlled composition and molecular weight. The structure/property relationships of this family of materials was investigated by numerous methods. It was determined that the number of backbone methyl branches had a significant effect on the melt transition temperature and enthalpy and zero shear viscosity. There was not a demonstrable effect on the energy of activation of flow. Preliminary rheo-optical measurements indicate a strong dependence of the stress-optic coefficient on methyl branch content.

Introduction

This chapter will focus on the synthesis and characterization of a family of ethylene/propylene (EP) copolymers prepared via the ring opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene and 3-methylcyclopentene (Eq. 1). This molecular architecture is not generally available through typical polymerization methodologies. Subsequent hydrogenation affords the saturated copolymers (Eq. 2). Structurally, these materials are analogous to random EP copolymers made by Ziegler Natta methods.



(1)



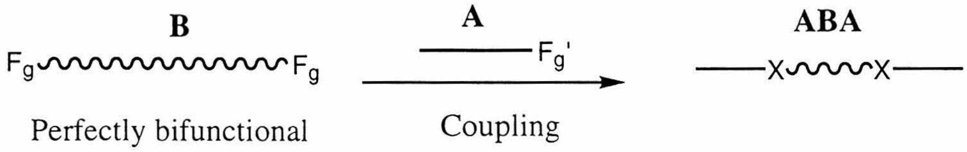
(2)

Polyethylene/Polypropylene
Copolymer

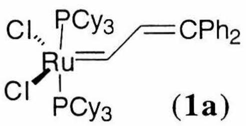
Linear polyethylene (HDPE) has a melting point of 135°C. The decreased crystallinity of EP copolymers (EPM) results in lower melting temperatures and shrinkage and therefore increases the processability of these materials compared to pure polyethylenes. EPM's are a member of the specialty elastomer family with an approximated worldwide production capacity of 10^6 metric tons. These elastomeric materials recover their shape after > 50% strain is released and their entropically derived equilibrium modulus increases with temperature. These materials have numerous uses including cable insulators and sealants.[1]

The present synthetic approach allows for the rational control of both the number of branches and the molecular weight of the desired polymers. For many Ziegler-Natta catalysts, the amount of branching and degrees of polymerization are related to catalyst structure and activity. Current metathesis polymerization methods allow for the independent control of these two structural parameters for investigations of structure/property relationships.

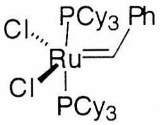
Another advantage of this synthetic approach is that it is easily adapted to the synthesis of telechelic polymers. Telechelic polymers are macromolecules with functional groups situated at each chain end.[2,3] These polymers serve as efficient macromolecular reagents in coupling reactions to give multiblock copolymers, star polymers, or segmented polymer networks.



For example, telechelic polymers are used to make thermoplastic triblock polymers (e.g., styrene-butadiene-styrene, Kraton.®[4] Telechelic polymers are classically prepared using conventional syntheses, such as step growth and anionic polymerizations. Recently, catalyst systems utilized in living polymerizations have been modified for the synthesis of telechelic polymers. In particular, the development of well-defined, functional group tolerant ruthenium metathesis catalysts (**1a** and **1b**)[5-7] has dramatically expanded the range of available telechelic polymers.[8]

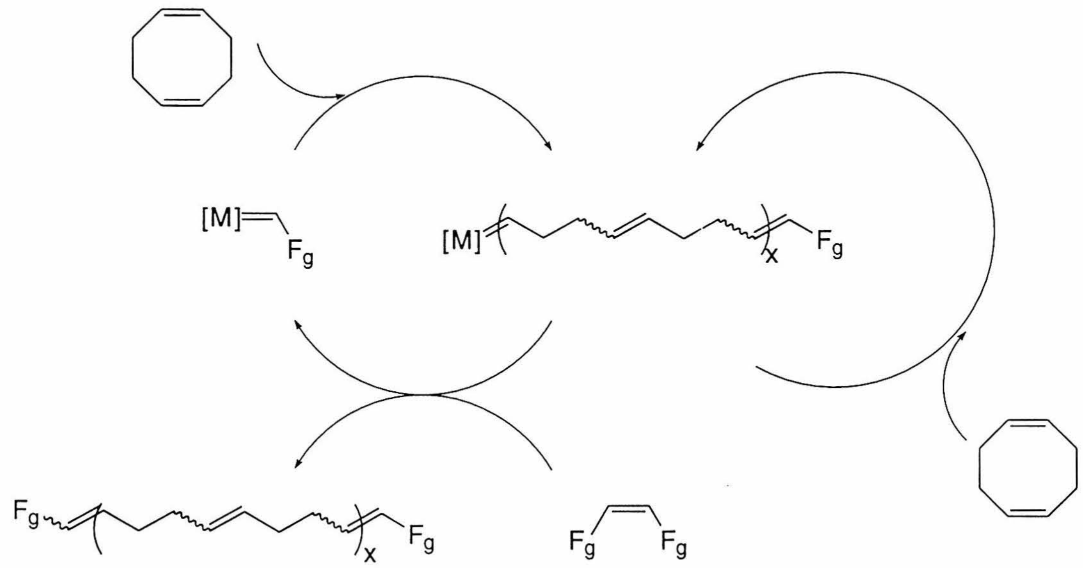


(1a)



(1b)

A variety of metathesis based processes have been employed for the preparation of telechelics including the selective hydrolytic degradation of a ROMP copolymer.[9] Another route to these materials is metathesis degradation of an unsaturated polymer with a difunctional acyclic olefin.[10-13] A related process is the ring-opening metathesis polymerization (ROMP) of a cyclic olefin in the presence of an olefinic chain-transfer agent (Scheme 1).[14-19]



Scheme 1. Synthesis of Telechelics via ROMP and Chain Transfer.

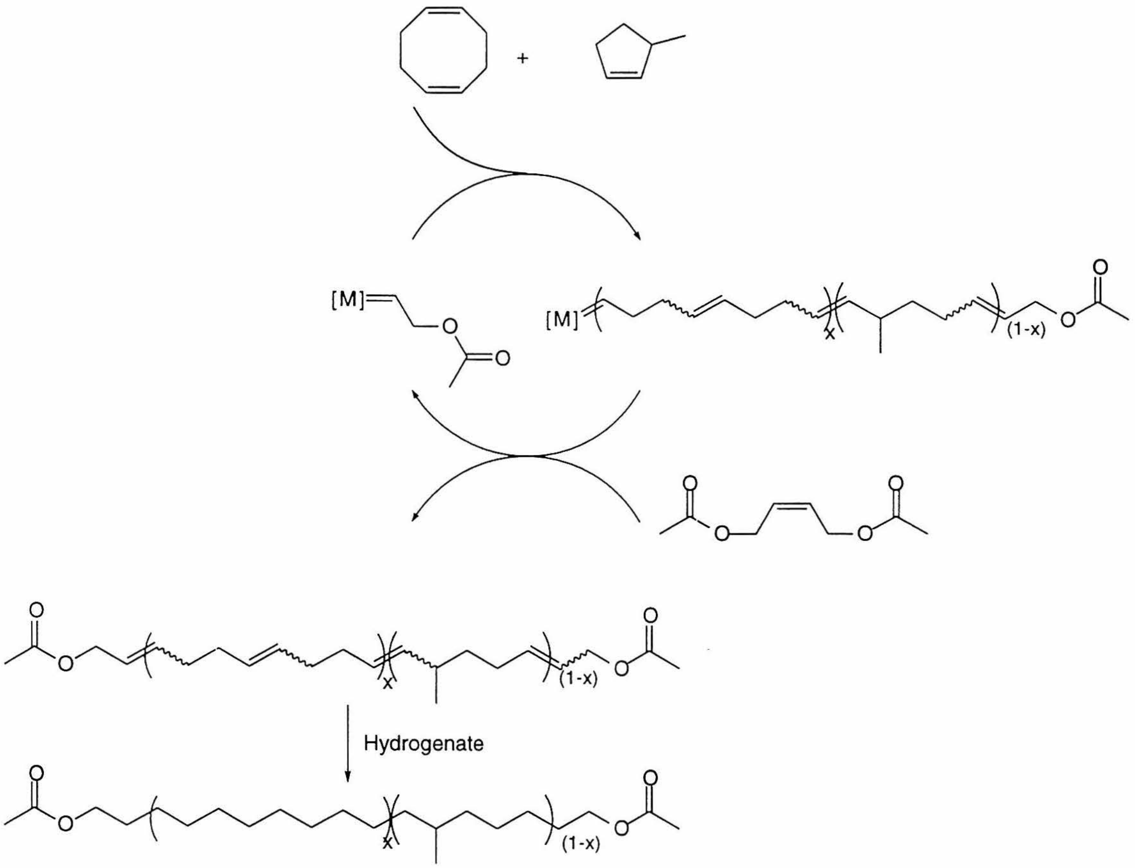
Telechelic polymers with olefinic endgroups have also been synthesized via acyclic diene metathesis (ADMET).[20,21] In general, metathesis polymerization methods can utilize a wider range of monomers and reaction conditions compared to conventional syntheses.

Metathesis initiators have recently been utilized for the synthesis of perfectly linear and bifunctional hydroxytelechelic polybutadiene (HTPBD).[17-19] This synthetic route allows for control of polymer molecular weight and also avoids the branching and functional group variability produced by radical polymerizations.[22-26] HTPBD is an industrially important amorphous polymer that is frequently used as a macromonomer in the synthesis of hydrolytically stable polyurethanes.[27-29] Hydrogenation of HTPBD gives hydroxytelechelic polyethylene (HTPE), a highly crystalline polymer with a melting point (T_m) as high as 125°C.[3,19] Introduction of methyl groups to the polymer backbone affords a route to ethylene-propylene telechelic copolymers. As with the non-telechelic analogs, the pendant methyl groups affect polymer properties such as crystallinity, glass transition temperature (T_g) and refractive index. For the synthesis of polyurethanes, hydroxytelechelic ethylene-propylene polymers (HTEP) have several advantages compared to HTPBD. Most significantly, the chemical stability of the saturated EP polymers is greatly improved.

Table 1. Relative Rates of Reactivity of Ozone with Hydrocarbon Polymers

Polymer	**K_1(L/Mole-sec)**
cis-Polyisoprene	440,000
cis-Polybutadiene	60,000
Polystyrene	.3
Polypropylene	.08
Polyethylene	.046
Polyisobutene	.012

Unsaturated polymers are susceptible to environmental degradation by ozone attack and UV promoted processes (Table 1).[30] Saturated EP polymers are dramatically more stable and exhibit enhanced mechanical stability. Compared to hydrogenated 1,4-polybutadiene, HTEP is more processable due to the decreased crystallinity.[31] Methodology developed for the synthesis of HTEP will allow for the design of new polymers with controlled methyl content and hence tailorable physical and mechanical properties (Scheme 2). In this chapter, the use of discrete ruthenium carbene complexes for the copolymerization of 1,5-cyclooctadiene and methyl-substituted cycloolefins will be discussed. Both high molecular weight and telechelic EP polymers were synthesized and characterized.



Scheme 2. Synthesis of Telechelic EP Copolymers.

The synthesis of the EP copolymers highlighted a challenge in convenient polymer hydrogenation. Two of the most common methods of hydrogenation are heterogeneous palladium catalysts and homogeneous (and stoichiometric) diimides. Palladium supported on $CaCO_3$ has been widely utilized for hydrogenating olefins in polymer backbones,[32,33] but does have some disadvantages. Investigations of the hydrogenation of poly(vinylethylene) with supported Pd indicated that initially, the olefinic groups of the polymer are adsorbed on the surface of the heterogeneous catalyst. After approximately 85% hydrogenation the polymer desorbs.[34] Furthermore, the palladium (and support) must be separated from the polymer. And due to the low Pd loading, the mass of the catalyst (and support) may be larger than the substrate further complicating polymer purification.

The solubility of polyethylene and EP in common solvents is very low at room temperature, and neither high temperature nor high pressure filtrations are very practical on the laboratory scale for isolating polyethylene. Diimides have been used for the hydrogenation of polymer backbones.[35] At high temperatures, *p*-toluenesulfonyl hydrazide undergoes decomposition to form the reactive diimide N_2H_2. This reaction requires 1-2 equivalents of diimide and is not convenient for batch or large scale reactions.[36]

It is widely reported that ruthenium complexes including $RuCl_2(PPh_3)_3$ are active olefin hydrogenation catalysts.[36] Recent investigation demonstrated that ruthenium hydrides with cyclohexyl phosphine are isolable, and are in fact efficient hydrogenation catalysts.[37,38] For instance, during the synthesis of $(PCy_3)_2Ru(H)Cl(H_2)_2$, the evolved cyclooctadiene is hydrogenated (Eq 3).

$$[CODRuCl_2]_x + 2PCy_3 + NEt_3 \xrightarrow[H_2]{sec\text{-}BuOH} (PCy_3)_2Ru(H)(Cl)(H_2)_2 + HNEt_3Cl + C_8H_{16} \qquad (3)$$

Recent work in our laboratory has demonstrated that when carbene complex (**1b**) is under an atmosphere of dihydrogen, toluene is evolved and both $Ru(H)_2Cl_2(PCy_3)_2$ and $Ru(H)(H_2)Cl(PCy_3)_2$ are observed in addition to the starting carbene.[39] (After 1 hour at 50˚C, the hydride species are each present in approximately 10% and the remaining 80% is starting material.) This chapter describes our investigations to convert the ruthenium carbene *in situ* to an active olefin hydrogenation catalyst. There have been recent reports utilizing activated silica gel as a cocatalyst/support for the *in situ* hydrogenation of polymers generated by ADMET.[21]

In addition to characterizing the polymers by GPC, NMR and DSC, rheological and rheo-optical measurements of the EP polymers were also performed. The zero shear viscosity and activation energy of flow were measured. Preliminary results for the determination of the effect of methyl branching on the stress-optic coefficient are also presented.

Results and Discussion

Part I. Monomer Synthesis.

In order to incorporate methyl substituents into the polymer chain, a methyl-substituted, strained cycloolefin monomer must be employed in the copolymerization reaction. The ruthenium initiators (**1a**) and (**1b**) do not ring-open tri-substituted olefins, rendering 1-methyl cycloalkenes unsuitable monomers for these reactions. Furthermore, large scale polymer synthesis requires either commercial availability or an efficient synthesis of the monomer. Since ring closing metathesis (RCM) of α,ω-dienes is an attractive strategy for the synthesis of cyclic olefins,[40] we set out to synthesize methyl-substituted cyclopentenes using this methodology. We first investigated the RCM of diethyl diallylmalonate (**2**) as a precursor to 4-methylcyclopentene (4-MCP) (Figure 1). The complex $Cl_2(PCy_3)_2Ru{=}CHCHPh_2$ (**1a**)[5] when dissolved in neat (**2**) closes the diene to the cycloolefin (**3**) nearly quantitatively when the reaction is carried out under vacuum for several days.

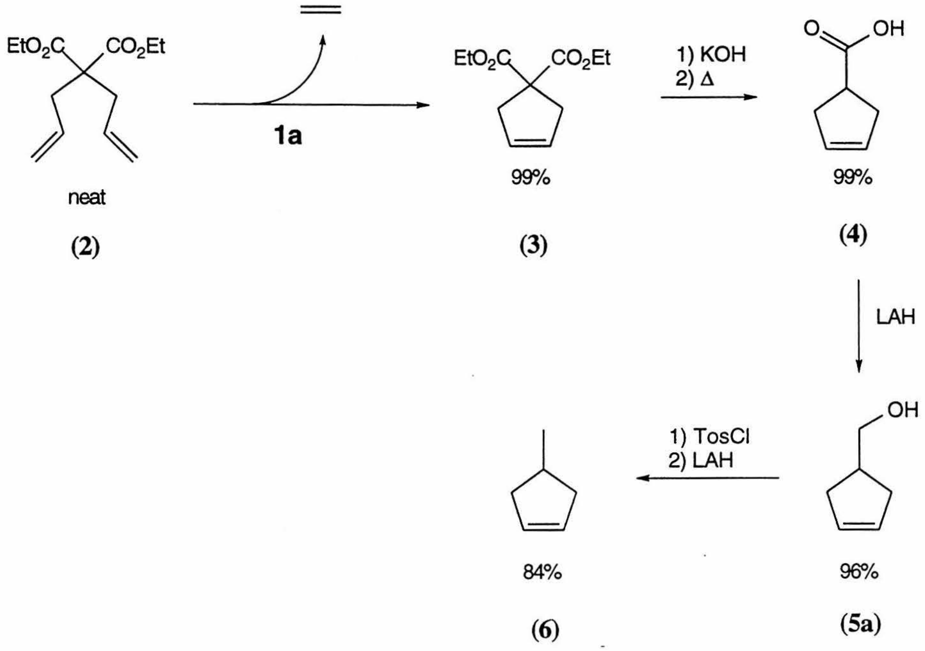


Figure 1. Synthesis of 4-Methylcyclopentene.

Subsequent hydrolysis, decarboxylation and reduction yields the alcohol (**5a**) in 96% yield from (**4**). Conversion to the tosylate and reduction with $LiAlH_4$ yields the 4-MCP (**6**) in an overall yield of 84%.

Using a modified version of the synthesis recently reported by Nugent and Feldman,[41] we synthesized (*R*)-(+)-3-methylcyclopentene (3-MCP) from the commercially available, *technical grade* compound (-)-β-citronellene (**7**) (Figure 2).

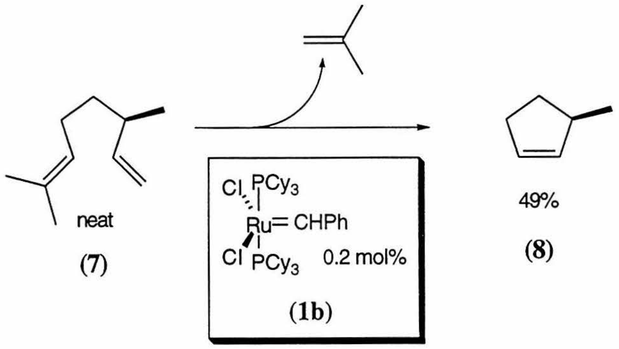


Figure 2. Synthesis of (R)-(+)-3-Methylcyclopentene.

Complex $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1b**)[6,7] was dissolved in neat citronellene and immediately heated to 90°C. The desired product, (*R*)-(+)-3-methylcyclopentene, was collected by distillation as the reaction proceeded. This transformation proceeds with retention of methyl group absolute configuration. After removal of the isobutylene byproduct by refluxing, (**8**) was obtained in 49% yield. The remaining of the undistilled material in the reaction flask was 1-isopropylidene-2,3-dimethylcyclopentane, an impurity found in citronellene.[42]

Part II. ROMP of Methylcyclopentene and Cyclooctadiene.

Homopolymerization of 4-methylcyclopentene (6) and 3-methylcyclopentene (8). There is precedent for the ring-opening metathesis polymerizations of methylcyclopentene, but only one case used isomerically pure monomer, [43] the others were mixtures of olefins.[44-47] Both 3-MCP and 4-MCP were polymerized with (**1b**). Neat polymerization of each monomer affords polymer in approximately 60% isolated yield. Because metathesis polymerization is an equilibrium process driven by the relief of ring strain, monomers such as cyclopentenes which have low ring strain have correspondingly high equilibrium monomer concentrations and are not completely ring opened.[8] The reversible conversion of 3-methylcyclopentene to polymer can be followed by ^1H NMR. A 4.5M solution of 3-MCP (50% monomer, 50% CD_2Cl_2) reaches 30% conversion at room temperature after 1 hour. The sample was then cooled to 0°C and allowed to equilibrate for 12 hours. ^1H NMR at 0°C indicated 60% conversion to polymer. The sample was then heated to 40°C, and after 1 hour the sample contained only 10% polymer. More detailed quantitative analysis concerning the equilibrium monomer concentration and ceiling temperature as well as computer modeling will be reported separately. [48]

Telechelic Copolymer Synthesis. A series of telechelic polymers was synthesized (Figure 3), and the polymer composition and molecular weight were assigned based on ^1H NMR spectral analysis. The polymer composition was controlled by the ratios of COD:3-MCP and of monomer:CTA.

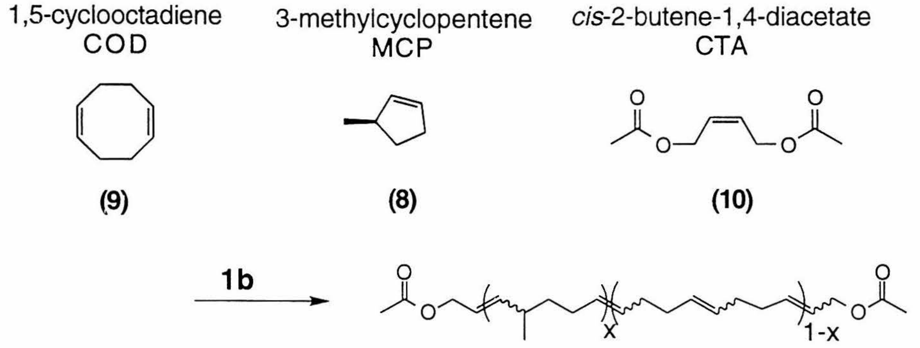


Figure 3. Synthesis Telechelic MCP/COD Copolymers.

In a typical reaction, 1.5 mg (0.018 mmol) of the ruthenium metathesis initiator (**1b**) (dissolved in 50μl benzene) was added to a mixture of 800μl of 1,5-cyclooctadiene (COD, 6.5 mmol, **9**), 180μl of 3-methylcyclopentene (3-MCP, 1.6 mmol, **8**) and 130μl of acetate protected diol (CTA, 0.82 mmol, **10**) ([cyclic olefin]/[catalyst] 4000; [cyclic olefin]/[CTA] 10). After 24h at room temperature the polymerization was terminated by the addition of excess ethyl vinyl ether (20μl). The polymer was precipitated into methanol, washed with methanol and vacuum dried. In all cases, the polymers were clear viscous oils.

One of the inherent advantages to this strategy is that experimental parameters can be rationally varied to control the polymer structure and composition. The effects of comonomer feed ratio, ratio of chain transfer to monomer, and reaction temperature on the chemical and physical properties of the resultant polymers were investigated. The monomer feed was systematically varied from 20-50 mol% 3-MCP, and the polymer composition, degree of polymerization and yield were determined. The fraction of 3-methylcyclopentene in the polymerization feed is *directly proportional* to its incorporation in the polymer backbone. Notably, the relationship between monomer feed and incorporation remains linear when the concentration of the chain transfer agent and therefore the molecular weight is varied (Figure 4).

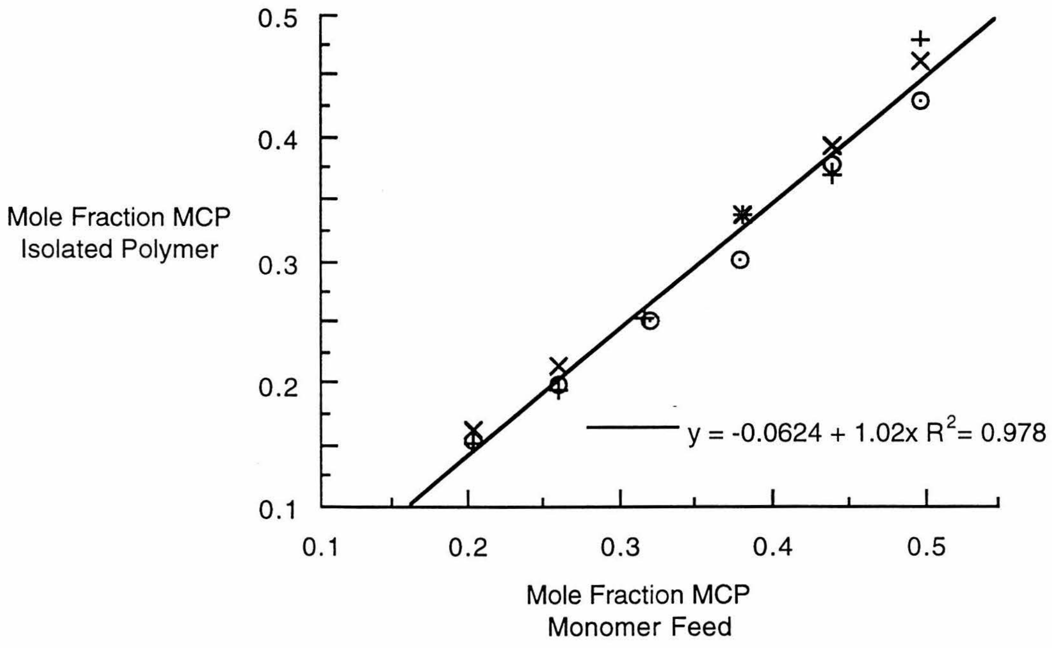


Figure 4. Polymer Composition vs. Monomer Feed

Samples were polymerized at room temperature for 24 hours.

Furthermore, the degree of polymerization is constant over the range of comonomer feeds (Table 2). Cyclooctadiene and methylcyclopentene have relatively high equilibrium monomer concentrations and polymerizations proceed to higher conversions when performed neat.[49]

Table 2. Degree of Polymerization with Varying Monomer Feed[a]

Mole Fraction 3-MCP	0.50	0.44	0.38	0.32	0.26	0.20
Degree Polymerization	20.0	19.6	19.5	19.6	19.5	19.8

[a] $\frac{[8]+[9]}{[10]} = 10$; Samples were polymerized 24h at 25°C; X_n calculated from ^{1}H NMR.

Since varying the monomer feed ratios changes the monomer concentrations, the yields of isolated polymers are dependent on monomer feed. The isolated yield of polymer was highest for polymers with high COD content (Table 3).

The amount of acyclic olefin (CTA) relative to the monomer is used to control the molecular weight. If all the chain transfer agent is incorporated, then the degree of polymerization may be calculated according to equation 4. Although not all the chain transfer agent was consumed (40-60% was incorporated as determined by ^{1}H NMR), the degree of polymerization varied linearly with the concentration of CTA (Figure 5).[50] The amount of chain transfer agent present (5-20%) did not change the relative incorporation of COD and 3-MCP. Furthermore, the comonomer ratio did not effect the incorporation of chain transfer agent. At higher relative concentrations of chain transfer agent, (lower molecular weight polymers), the concentration of the cyclic monomers is decreased, and as expected, the yield of isolated polymer decreases (Table 3).

$$\text{Degree Polymerization} = \frac{[\text{Cyclic Monomer}]}{[\text{Chain Transfer}] + [\text{Catalyst}]} \qquad (4)$$

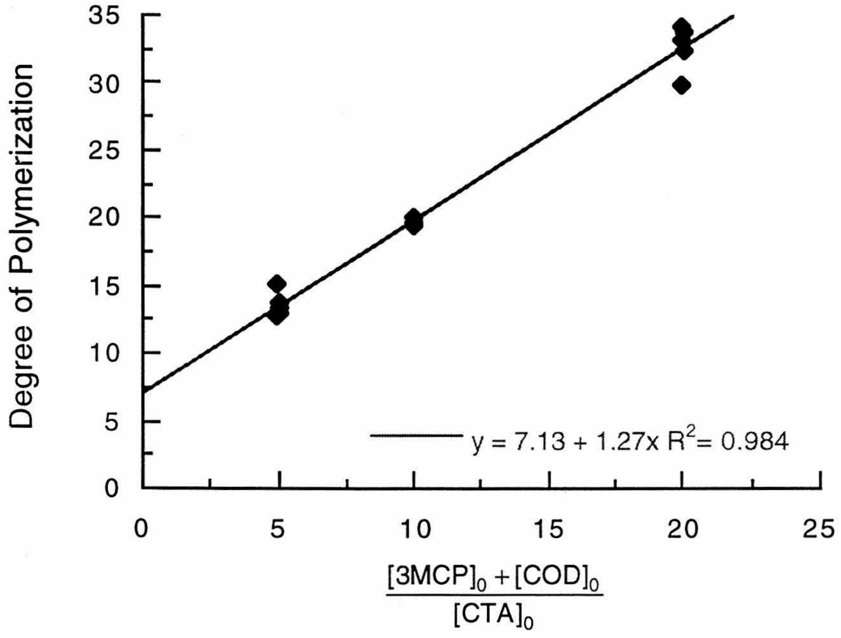


Figure 5. [CTA] vs. Degree Polymerization.

The polymerization temperature affects both the rates of reaction and the equilibrium monomer concentrations. Therefore, the degree of polymerization, monomer incorporation, and yield are all affected by the reaction temperature. At higher temperatures, more of the chain transfer agent is incorporated resulting in a decrease of the degree of polymerization (Table 4). Another interesting effect of temperature is the relative amounts of 3-MCP and COD incorporated into the polymer.

Table 3. Summary of Telechelic Syntheses

	Reaction Feed			Characterization of Olefinic Polymer					Hydrogenated Polymer	
Entry	$\frac{[\mathbf{9}]_0+[\mathbf{8}]_0}{[\mathbf{1b}]_0}$	$\frac{[\mathbf{9}]_0+[\mathbf{8}]_0}{[\mathbf{10}]_0}$	$\frac{[\mathbf{9}]_0}{[\mathbf{9}]_0+[\mathbf{8}]_0}$	Yield	$\frac{[\mathbf{9}]}{[\mathbf{9}]+[\mathbf{8}]}$ a	M_n ^{1}HNMR^b	M_n GPC^c	PDI^c	M_n GPC^c	PDI^c
1	4490	20.1	0.80	76	0.84	3,690	5410	2.06	4410	1.81
2	4470	20.0	0.74	84	0.79	3,230	4570	2.01	4640	1.90
3	4460	*	0.68	71	0.73	4,490	5860	2.24	8750	2.03
4	4490	20.1	0.62	62	0.66	3,390	4590	2.19	5760	2.03
5	4470	20.0	0.56	78	0.61	3,520	4460	2.16	6000	1.90
6	4460	19.9	0.50	67	0.54	3,360	4380	2.14	7400	1.79
7	4490	10.0	0.80	74	0.84	2,230	2930	1.85	3010	1.63
8	4470	10.0	0.74	70	0.80	2,170	2820	1.81	2980	1.75
9	4470	10.0	0.68	71	0.75	2,160	2960	1.82	3340	1.80
10	4470	10.0	0.62	68	0.70	2,130	2870	1.79	4030	1.71
11	4470	10.0	0.56	56	0.62	2,090	2820	1.78	4110	1.74
12	4460	10.0	0.50	50	0.57	2,110	2970	1.77	4670	1.69
13	4410	5.0	0.80	50	0.85	1,570	1990	1.74	2490	1.48
14	4400	5.0	0.74	53	0.81	1,510	1720	1.63	2660	1.50
15	4380	5.0	0.68	47	0.75	1,470	1920	1.65	2920	1.50
16	4420	5.0	0.62	41	0.66	1,540	1890	1.61	3250	1.52
17	4400	5.0	0.56	38	0.63	1,520	1980	1.62	3250	1.39
18	4380	5.0	0.50	28	0.52	1,620	2340	1.47	4980	2.06

[a] Mole fraction of COD incorporated into the polymer determined by ^{1}H NMR.

[b] M_n calculated from the integration of ^{1}H NMR as described in the experimental section.

[c] GPC calibrated with polystyrene samples; 60°C toluene as the eluent.

Table 4. Effect of Temperature on Polymer Composition[a]

Temperature	Time	Yield	3-MCP mole fraction incorporated	Degree of Polymerization
0°C	16h	8.3%	0.36	37.3
25°C	16h	68%	0.18	20.9
55°C	16h	62%	0.10	17.6
25°C/55°C	16h/8h	74%	0.15	15.6

[a] Ruthenium was dissolved in minimal (50μl) benzene and added to a solution of cyclooctadiene, 3-methylcyclopentene and chain transfer agent ([COD]/[MCP] = 4). Reactions were terminated by the addition of excess ethyl vinyl ether. $\frac{[8]}{[8]+[9]} = 0.25$; $\frac{[8]+[9]}{[10]} = 10$.

At room temperature, the polymer composition is approximately the same as the polymerization feed. At low conversation, polymerizations conducted at 0°C favors incorporation of methylcyclopentene. At elevated temperatures, the yield of polymer is not decreased substantially, but the amount of 3-MCP incorporated decreases. In order to most efficiently react the chain transfer agent and still incorporate 3-MCP, an aliquot of a sample polymerized at room temperature was subsequently heated to 40°C without terminating the polymerization or adding more catalyst. The modest decrease in the observed molecular weight is consistent with a higher degree of CTA incorporation, and the methyl content of the polymer backbone was intermediate to the polymers formed at the two reaction temperatures.

High Molecular Weight Polymers. The synthesis of high molecular weight polymers was also investigated. Initial experiments were performed under similar conditions to the telechelics, but the absence of solvent was problematic. The resultant polymers were higher molecular weight (M_n 20-40 K), and the reaction mixtures were highly viscous. Furthermore upon addition of solvent, it took several hours to obtain a homogenous solution. The reactions can be performed in the presence of solvent, but the incorporation of methylcyclopentene is dramatically diminished (Figure 6).

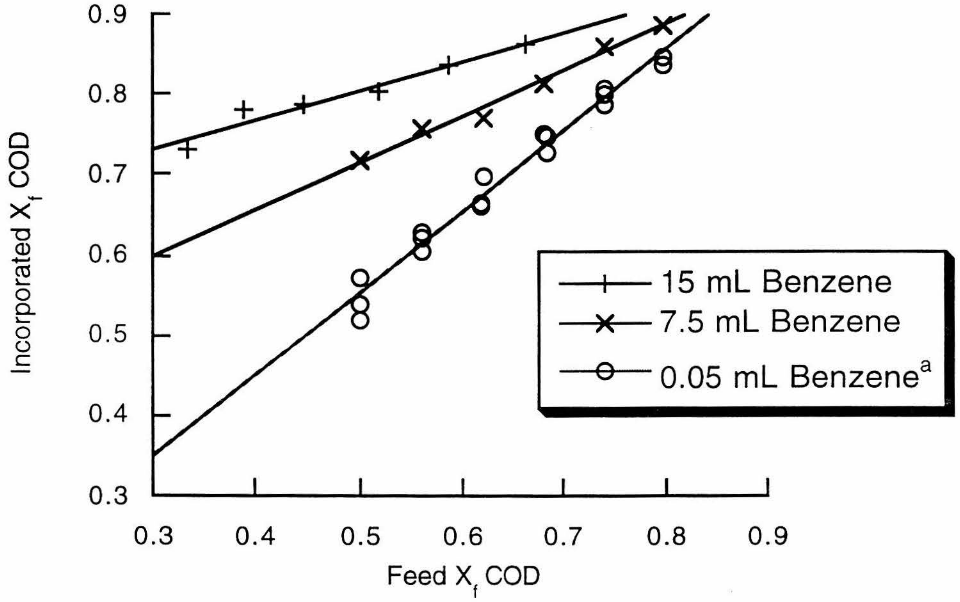


Figure 6. Effect of Concentration on Copolymer Composition.

[a] Telechelic polymers were synthesized with 0.05 mL benzene and 0.04 - 0.13 mL chain transfer agent. The incorporation of COD fits lines with slopes of 1.01, 0.58 and 0.36 for reactions run with 0.05, 7.5 and 15 mL of benzene respectively.

Although the incorporation of methylcyclopentene is dramatically decreased when the reactions are done more dilute, the fraction of incorporation is linearly dependent on methylcyclopentene concentration (Figure 7).

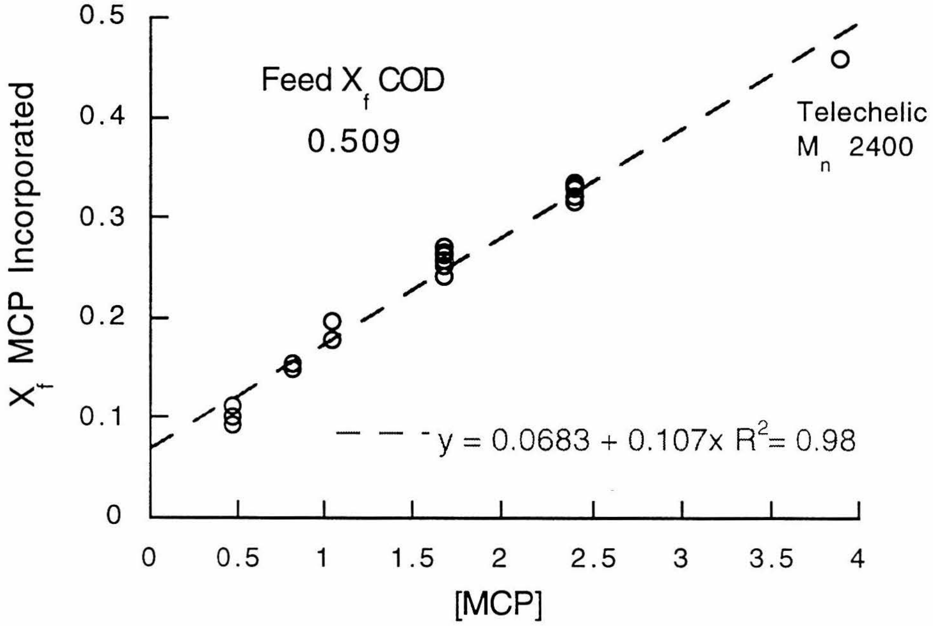


Figure 7. MCP Incorporation vs. Concentration

For the telechelics, minimal solvent was used to dissolve the catalyst (0.9 g monomer, 0.050 mL benzene), and the incorporation of methylcyclopentene was approximately the feed ratio. For instance, when the feed was 50% MCP, the copolymer was nearly 50% MCP. As solvent is added to the reaction mixture, 1.0 - 10mL the incorporation of methylcyclopentene decreased to 30-10%. A variety of reaction conditions were examined in order to synthesize high molecular weight polymers. In general, increasing the methylcyclopentene content of the copolymer resulted in both lower yields and a lower degree of polymerization.

Furthermore, the high viscosity of the reaction mixture greatly slowed the polymerization reaction. Presumably, this is due to the slow rate of diffusion of the monomer to the reactive chain end. In fact, when the polymerization was quenched after 24 hours, the sample with the highest catalyst loading had the highest molecular weight and the sample with minimal catalyst had the lowest molecular weight. After 72 hours, the expected relationship of monomer/catalyst ratio was observed (Table 5): increasing the ratio of monomer to catalyst actually increased the molecular weight.

Table 5. Effect of Polymerization Time on Molecular Weight

Olefin/Ru	X_fCOD	M_n	Olefin/Ru	X_fCOD	M_n
2020	0.42	23.6	2290	0.52	28.6
4040	0.46	17.2	4570	0.57	35.2
1960	0.70	41.8	2220	0.74	40.6
3920	0.73	17.3	4440	0.77	57.9
2160	0.86	40.0	2450	0.88	54.5
4330	0.87	22.2	4910	0.89	73.4
Polymerized 24 hours.			Polymerized 72 hours.		

Although the reaction should proceed to equilibrium faster if the reaction viscosity is decreased, diluting the reaction drastically decreases both the yield and the incorporation of methylcyclopentene. Heating the reaction to increase the polymerization rate and/or decrease the viscosity is not possible because at elevated temperatures, 3-methylcyclopentene is not significantly polymerizable. Another complication of these studies was the presence of small amounts of terminal olefin. Commercially available 1,5-cyclooctadiene contains 1.5 % 4-vinyl-1-cyclohexene. Upon distillation, the 4-vinyl-1-cyclohexene was not initially detected by GPC (0.8% solution in hexanes). Further examination of higher concentration solutions (4% in hexanes) showed the presence of 0.1% 4-vinyl-1-cyclohexene. Further distillation reduced the 4-vinyl-1-cyclohexene to 0.0024%. Repurification of the cyclooctadiene afforded slightly higher molecular weight polymers,[51] but not samples with M_n >100K. The 3-methylcyclopentene also had to be redistilled as the GC showed trace amounts of citronellene contamination from the ring closing reaction.

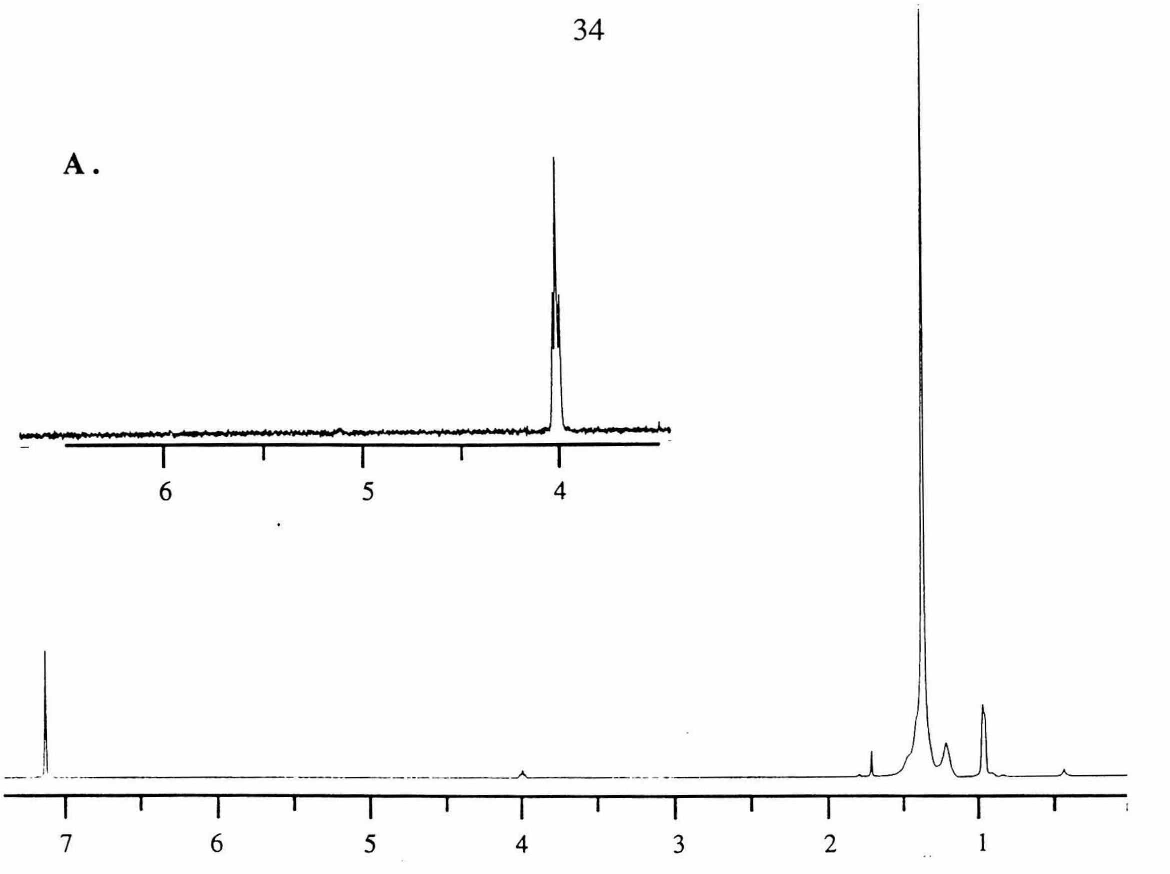
The copolymerization of *cis*-cyclooctene and 3-methylcyclopentene did yield several polymers of higher molecular weight (Table 6), but the utility of this approach was somewhat limited. The more saturated polymer backbone resulted in higher viscosity and lower solubility in methylene chloride which compounded the challenge of incorporating methylcyclopentene Attempts to increase the methyl content of the polymers generally resulted in decreased yield and the molecular weights limited to M_n's of approximately 70K. A second complication is that COE/MCP copolymers appear to have discernibly different microstructures than the COD/MCP analogs (*vide infra).*

Table 6. Synthesis of COE/MCP Copolymers

Olefin/Ru	X_f COE Feed	X_f COE Incorp	Yield	M_n	M_w
4100	0.62	0.81	72	110,400	207,700
2060	0.63	0.8	69	133,400	255,300
3370	0.46	0.63	50	62,600	129,100
2900	0.30	0.44	46	72,700	164,400
3160	0.22	0.31	25	70,600	155,800

Part III (A). Hydrogenations Mediated by Palladium

Hydrogenation of Telechelic Polyolefins. The polymers prepared in this study were readily hydrogenated using palladium on carbon black. For polymers with higher methyl content, the hydrogenations were facile at at room temperature under one atmosphere of hydrogen. For polymers with few methyl groups (< 50/1000C) on the backbone, the hydrogenated polymers have limited solubility at room temperature and therefore could not be completely hydrogenated under these conditions. In order to increase the efficiency of hydrogenation, reactions were performed at elevated temperatures and pressure (60°C and 60 psig H_2 in cyclohexane). The polymers were isolated in over 90% yield after separation of the supported palladium from the polymer solution by filtration. The quantitative hydrogenation of the polymer backbone is evident by the lack of olefinic resonances in the ^{1}H NMR (Figure 8). Interestingly, the acetate groups remain on the polymer termini. Resonances corresponding to both head-to-head and head-to-tail incorporation of methylcyclopentene units were observed in the ^{13}C NMR. The highly reactive diimide N_2H_2 also efficiently mediates the hydrogenation of the polymer backbone.[35] The diimide is generated by the thermal decomposition of *p*-toluenesulfonyl hydrazide. This methodology requires the generation of an excess of diimide and this highly exothermic reaction is not ideal for large scale hydrogenations. Copolymers of cyclooctene and methylcyclopentene were also prepared and hydrogenated.[52] The ^{13}C NMR resonances indicate more head-to-head and head-to-tail incorporation of 3-methylcyclopentene units which indicates the COE/MCP copolymers may be blockier than the COD/MCP analogs (Figure 9).



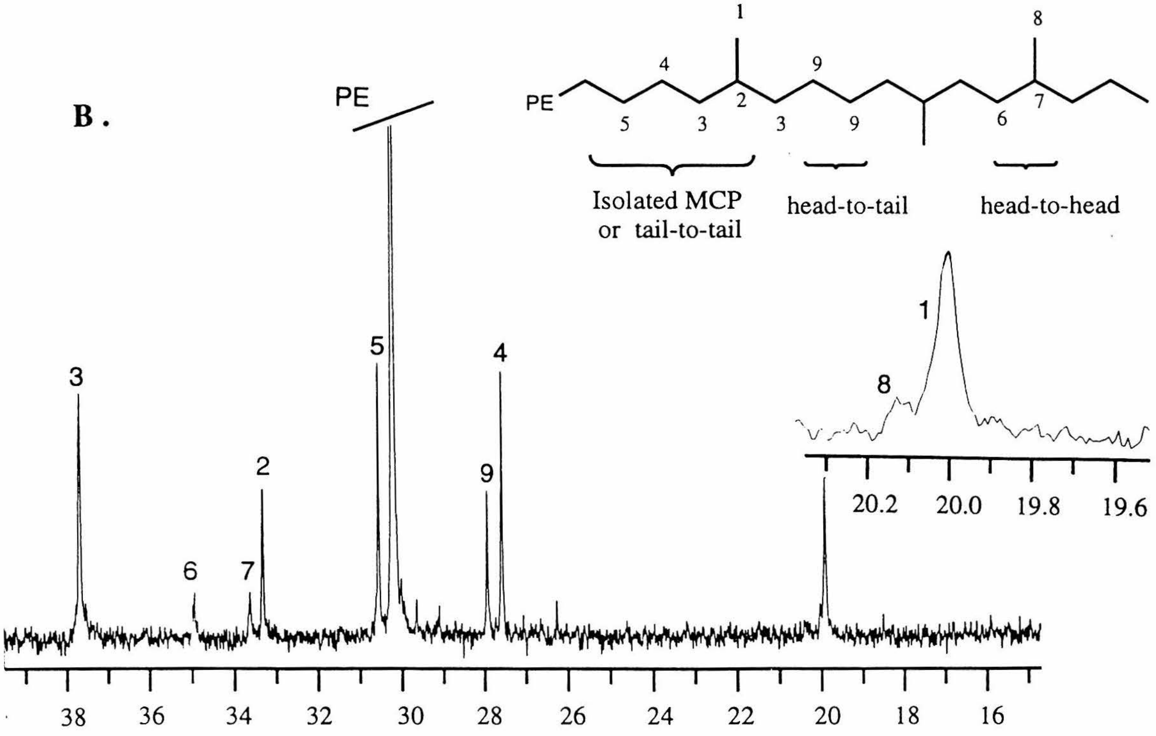


Figure 8. ^{1}H NMR (A) and ^{13}C NMR (B) of Hydrogenated COD/MCP Copolymer

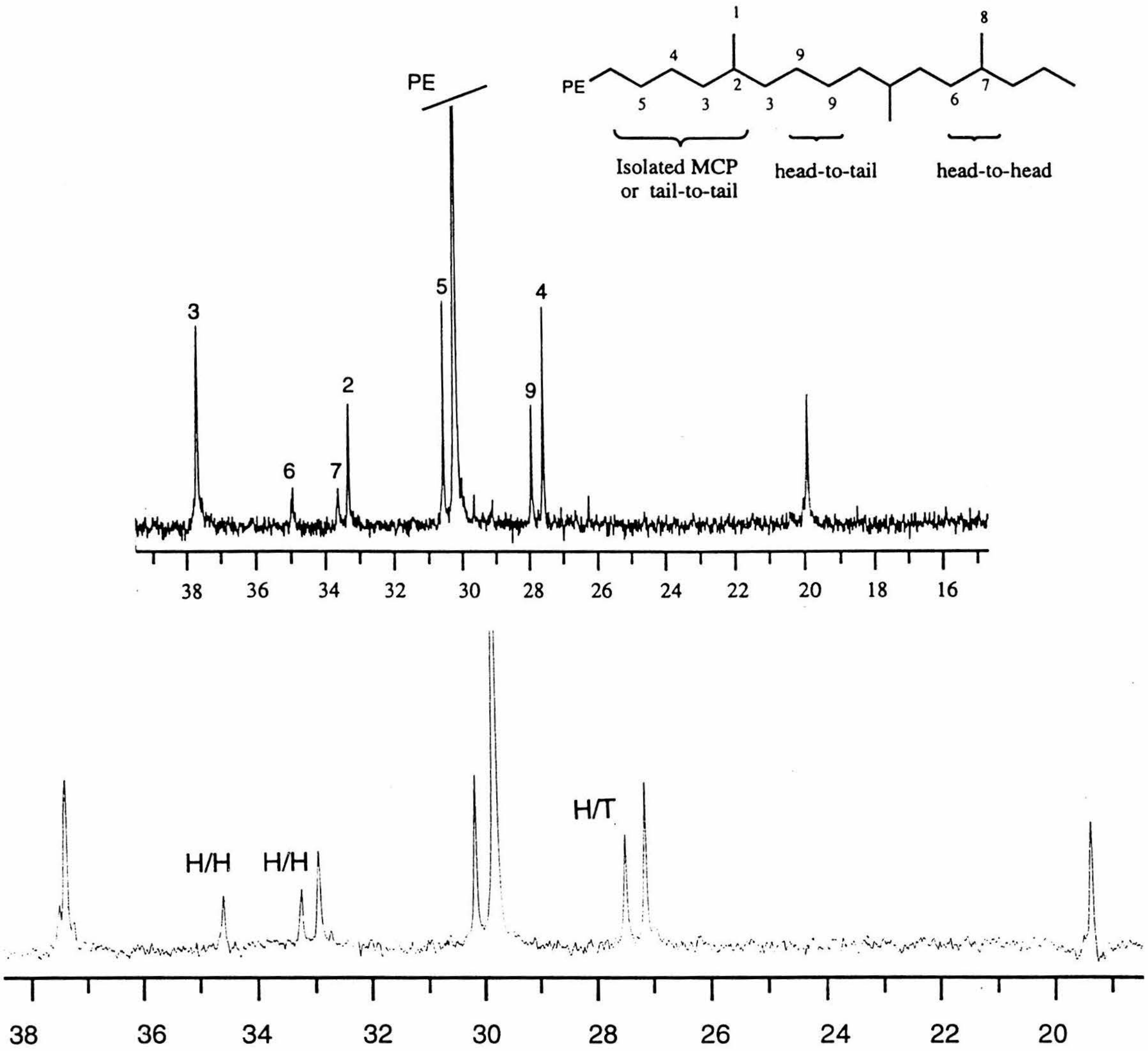


Figure 9. ^{13}C NMR of Hydrogenated COE/MCP Copolymer

Part III (B). ***Ruthenium Mediated Hydrogenations.*** The viability of generating ruthenium hydrides *in situ* for the hydrogenation of olefins was investigated using commercially available olefinic substrates. Small molecule substrates and (**1b**) were dissolved in deuterated solvent (C_6D_6 or CD_2Cl_2) and heated to 60-80°C under 95 psi H_2 pressure in a Parr stainless steel high pressure reactor. After 15 h the reaction mixture was transferred to an NMR tube, and the product mixture analyzed by ^1H and ^{13}C NMR (Table 7).

Table 7. Hydrogenation of Small Molecules[a]

Substrate	Olefin/catalyst	PPh_3	Hydrogenated	Comments
1-pentene	130	no	100%	carbene persisted
1-pentene	120	yes	> 95%	small amount of octene carbene persisted
cis-2-pentene	90	no	< 10%	isomerization cis/trans and positional ethylidene and propylidene observed
cis-2-pentene	90	yes	< 3%	no isomerization
cyclohexene	170	no	< 3%	
cyclohexene	170	yes	< 3%	carbene persisted
diallyldiethylmalonate	130	no	< 3%	(ring closed first)
diallyldiethylmalonate	130	yes	< 3%	(ring closed first) carbene persisted

[a] Concentration of Ru 0.04 M; 60 ° C; 95 psi H_2

Although 1-pentene was efficiently hydrogenated under these conditions, hydrogenation of internal or cyclic olefins were not complete. The presence of added triphenyl phosphine stabilized the starting carbene complex, but afforded no increase in hydrogenation activity. Excess phosphine also stabilized (**1b**) in the absence of olefinic substrates. When the complex was dissolved in C_6D_6 or CD_2Cl_2, and held at 60°C and 95 psi H_2 pressure for 5 h there was complete decomposition of (**1b**) while in the presence of 2 equivalents of PPh_3, some carbene could still be observed by ^1H NMR.

Once we established that is was possible to generate a hydrogenation catalyst *in situ*, we investigated the hydrogenation of a model polymer system. The polybutadiene utilized in these studies contained both internal and terminal olefins (20-25% 1,2-; 10-25% cis; 50-60% trans) which provided qualitative information about relative reactivities. Under most conditions we investigated, partial hydrogenation of polybutadiene was observed (Table 8).

Table 8. Hydrogenation of Polybutadiene

Olefin/Ru	Pressure	Temperature	Solvent	Additive	Hydrogenation
170	120 psi[a]	80°C	CH_2Cl_2		65% (>95% vinyl)
130	120 psi[a]	80°C	CH_2Cl_2	PPh_3	10% internal 100% vinyl
480	500 psi[b]	80°C	CH_2Cl_2		86%
550	500 psi[b]	80°C	CH_2Cl_2	TEA[c]	none
440	500 psi[d]	110°C	toluene		31%
520	500 psi[d]	110°C	toluene	TEA[c]	44%

[a] 15 hours. [b] 9 hours. [c] 50 eq. [d] 6 hours.

Generally, terminal olefin hydrogenation was facile and proceeded nearly to completion. Internal olefins were less reactive and hydrogenation was inhibited by the presence of an exogenous bases. In methylene chloride (120 psi, 80°C, 15 h), polybutadiene was 65% hydrogenated, including 95% of the terminal olefins. Addition of PPh_3 changed the selectivity of hydrogenation, and 100% of the terminal olefin was hydrogenated compared to only 10% of the backbone olefins. In methylene chloride, triethylamine did not promote hydrogenation. Hydrogenation was less efficient in toluene, but triethylamine seemed to have a modest promoting effect in that solvent.

After demonstrating the hydrogenation of polymer backbones, we investigated the efficacy of metathesis polymerization of cyclooctadiene and subsequent *in situ* hydrogenation (Table 9) In all cases, the polymer backbone was partially hydrogenated. Due to the insolubility of the hydrogenated polymer (polyethylene) in methylene chloride, hydrogenation does not proceed to completion.

Table 9. Hydrogenation of Poly(COD)[a]

Olefin/Ru	Pressure	Temperature	Solvent	Additive	Hydrogenation
560	65 psi[b]	25°C	CH_2Cl_2		20%
121	65 psi[b]	25°C	CH_2Cl_2		40%
260	500 psi[c]	120°C	CH_2Cl_2		57%
340	500 psi[c]	120°C	CH_2Cl_2	TEA[d]	>99%
340	500 psi[c]	120°C	toluene		38%
250	500 psi[c]	120°C	toluene	TEA[e]	48%

[a] Ruthenium complex (**1b**) was added to COD (1mL) and 5mL solvent and stirred for one hour. 20 mL solvent were added (under H_2 balloon) and subsequently pressurized in reactor. [b] 12 hours [c] 11 hours [d] 15 eq. [e]13 eq

After demonstrating the viability of using the complex (**1b**) for both metathesis and for generating a hydrogenation catalysts *in situ*, we investigated the synthesis and hydrogenation of COD/MCP copolymers. In efforts to improve the efficiency of hydrogenation, a variety of higher boiling solvents were investigated including chlorinated solvents such as dichloroethane and solvents known to dissolve polyethylene such as trichlorobenzene (Table 10). Furthermore, it was determined that addition of 20-50 equivalents of ethyl vinyl ether did not perceptibly affect the hydrogenation. When the

Table 10. Effect of Solvent on MCP/COD Copolymer Hydrogenation

Polymerized	24 h	**1,2-Dichlorobenzene** (Olefin/Ru: 990-1200)
Hydrogenated	11 h	All conditions 10-20%
180 psi	140°C	
		1,2,4-Trichlorobenzene (Olefin/Ru: 930-1130)
Polymerized	24 h	Without TEA 3-10 % hydrogenated
Hydrogenated	11 h	With TEA and no CTA 24%
180 psi	125°C	With TEA and CTA <10%
Polymerized	11 h	**1,2-Dichloroethane** (Olefin/Ru: 1240)
Hydrogenated	11 h	All conditions 25-35%
180 psi	85°C	
Polymerized	24 h	**Dichloromethane** (Olefin/Ru: 1150)
Hydrogenated	20 h	Most conditions 50-60%
180 psi	95°C	TEA and not CTA: 87%
		(Olefin/Ru: 1240)
Polymerized	10 h	**1,2,4-Trichlorobenzene** 5 %
Hydrogenated	9 h	**1,2-Dichloroethane** 18%
180 psi	85°C	**Dichloromethane** 45%
Polymerized	22 h	**Dichloromethane** (Olefin/Ru: 1250)
Hydrogenated	23 h	Average 6 reactions 85%
180 psi	95°C	
		50/50 mixture 1,2-Dichlorobenzene/CH_2Cl_2
Polymerized	25 h	(Olefin/Ru: 1200) 40-60%
Hydrogenated	16 h	
180 psi	85°C	

reaction is not quenched with ethyl vinyl ether, the carbene species remains active upon dilution.[53] Quenching the carbene is important to preserve the polymer structure and molecular weight. Copolymerizations were performed with and without chain transfer agent to determine whether or not the acetate groups interfered with the hydrogenations. Reactions were also performed with and without triethylamine (3 eq.). Usually, six experiments were conducted side by side, and the average results are summarized in Table 10.

Although a wide range of reactions conditions were very promising for polymer hydrogenation, there were no discernible trends in the data. Methylene chloride appeared to be the best solvent for hydrogenation, but analysis of the effects of additives was more difficult. The presence of either chain transfer agent or triethylamine usually effected the degree of hydrogenation by less than 10%. Several other additives were tested including HCl (0.8eq. in anhydrous ether) which had a negligible effect on hydrogenation yield. Predictably, dichlorotoluene completely inhibited hydrogenation activity. It is known that dichlorotoluene reacts with $Ru(H)_2(H_2)_2(PCy_3)_2$ in the presence of olefins to form carbenes.[37] Finally, we decided to investigate hydrogenations at higher pressures. Cyclooctadiene was polymerized in the presence of 2-pentene (0.05 eq, to lower the molecular weight) and subsequently hydrogenated at 400 psi (Table 11).

Table 11. Hydrogentions of Poly(COD) at High H_2 Pressure[a]

Solvent	% Hydrog.
CH_2Cl_2	>99%!!
C_6H_5Cl	64%
C_6H_5Cl/TEA	61%
C_6H_5Cl/HCl	61%

[a] 400 psi, 110°C, 7 hours Olefin/Ru : 1760

Higher pressure does improve the efficiency of hydrogenation. Methylene chloride appears to be the best solvent for hydrogenation despite the poor solubility of the product polymer. Increasing the pressure to 800 psi did not improve the hydrogenation yield in chlorobenzene (55-70%). Similarly, a mixture of chlorobenzene and methylene chloride provided hydrogenation yields of 60-75%. Although methylene chloride is the best solvent for hydrogenation, the efficiency of the reaction appears to be solubility limited. Side by side reaction at several olefin/catalyst ratios yielded very similar degrees of hydrogenation (yields 60-99%) (Table 12).

Table 12. Effect of Catalyst Loading on Poly(COD) Hydrogenation[a]

Run	Olefin/Ru	Hydrogenation	Conditions
1	3300	60%	3 runs 10 mL CH_2Cl_2
2a	1630	83	5mL CH_2Cl_2
2b	815	62	
2c	540	60	
3a	1650	99	10 mL CH_2Cl_2
3b	830	99	
3c	550	99	
4a	1530	42	10 mL CH_2Cl_2/5 mL toluene
4b	760	72	
4c	510	48	

[a] 0.8 g COD, 110°C, 500 psi H_2, 24 hours

Numerous reaction conditions were investigated, including higher temperatures (135 - 200 °C) and pressures (800 - 1000 psi) (Table 13). Although higher pressures tended to improve the hydrogenation yield, reactions performed at elevated temperatures (180 - 200°C) resulted in consistently higher hydrogenation yields, generally greater than 90%.

Table 13. High Temperature Hydrogenation of MCP/COD Copolymers[a]

	Olefin/Ru	yield	% Hydrogenated
65°C[a,b]	1360	64	78
1000 psi	680	69	81
	450	70	83
130°C[a,b]	1740	80	96
850 psi	870	81	>99
	580	83	99
180-200°C[b,c]	2280	47	94
800 psi	1140	31[d]	92
	760	68	96
200°C[a,e]	1870	40	95
800 psi	930	59	99
	750	65	95

[a] Polymerized 24 hours, hydrogenated 24 hours. [b] 25 mL CH_2Cl_2 [c] Polymerized 12 hours, hydrogenated 12 hours. [d] incomplete recovery of sample [e] 10 mL CH_2Cl_2/20 mL toluene

Utilizing the higher temperature reaction conditions a series of MCP/COD copolymers were then synthesized, quenched with ethyl vinyl ether, and submitted to hydrogenation conditions (200°C, 800 psi H_2). (For representative syntheses, see the Appendix to this chapter.) As before, there was no residual odor of either monomer. The only exception was when a large excess of monomer (olefin/catalyst ratio $\approx$ 20,000) was used. Although some polymer hydrogenation was observed, undoubtedly with catalyst loadings < 0.1% poisoning effects could be significant. At these higher temperatures, all hydrogenations were nearly quantitative (Ru/Olefin up to 8000), but in some instances trace residual olefin resonances (δ 5.5 ppm) were observed in the ^1H NMR. The presence of residual olefin (< 1%) could not be correlated to catalyst loading or polymer composition.

The resonances did not appear to be an artifact of data collection and could not be attributed to a tri-substituted olefin. (Isomerization of the double bond to a methyl group would afford a tri-substituted olefin, but the observed resonance is not that observed in partially hydrogenated polyisoprene samples (δ 5.35 ppm).) Allowing the reaction to proceed for 48 - 72 hours provided quantitatively hydrogenated samples.

In light of these interesting results, we investigated the hydrogenation of the trisubstituted olefin in polyisoprene (Table 14). The hydrogenation system is indeed active towards trisubstituted olefin, but reactions did not proceed to completion. Methylene chloride again enhanced reactivity, and using toluene as a cosolvent greatly diminished the observed hydrogenation.

Table 14. Hydrogenation of Polyisoprene.

Entry	Olefin/Ru	% Hydrogenated	Conditions
1a	105	87	20 mL CH_2Cl_2
1b	220	65	200°C 500 psi
1c	520	89	
2a	100	44	10 mL C_7H_8/
2b	200	13	10 mL CH_2Cl_2
2c	410	36	200°C 600 psi
3a	110	92	20 mL CH_2Cl_2
3b	250	97	200°C 800 psi
3c	610	97	

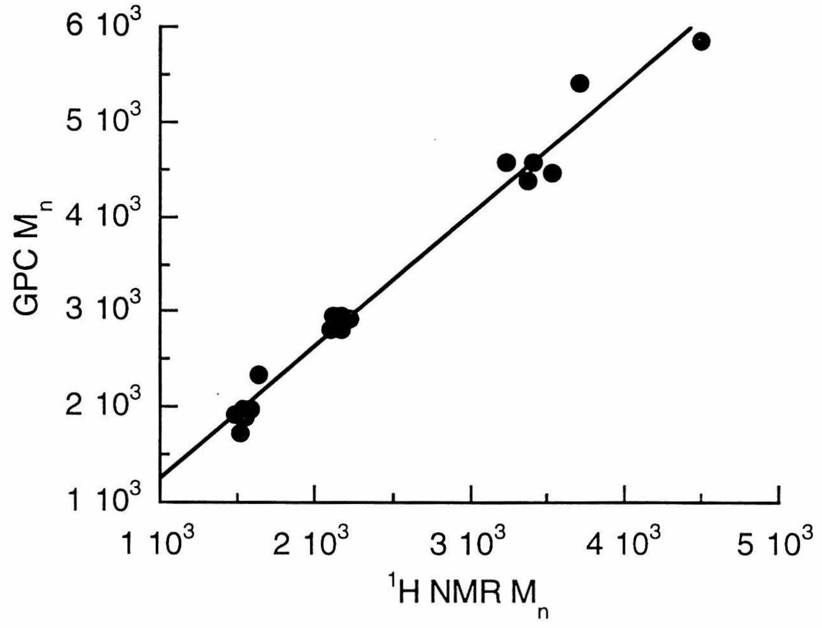
Polyisoprene (0.5 g) was dissolved, (**1b**) was added and the mixture was heated and under H_2 pressure 24 h.

Part IV. Physical Characterization of Copolymers.

Molecular Weight Determination. Both the molecular weight (M_n) and composition (COD/3-MCP) of the telechelic polyolefins were calculated from the ^1H NMR spectra as described in the experimental section. The molecular weight (relative to polystyrene) and PDI of each polymer was also characterized using GPC (60°C toluene). For the polyolefins, the GPC determined number average molecular weights correlated well with those obtained from the endgroup analysis (Figure 10A).

The elution volume (hydrodynamic radii) of the polymers was similar over the range of backbone compositions. After hydrogenation, the apparent molecular weight by GPC is strongly dependent on the number of methyl groups on the polymer backbone (Figure 10B), because the hydrodynamic radii of the polymers become more sensitive to the methyl groups along the backbone. Increasing the number of methyl groups in the polymer backbone strongly increased its hydrodynamic volume and estimated molecular weight. The theoretical polydispersity for equilibrium polymerizations is 2.0, and the observed polydispersities were between 1.5 and 2.0 (Table 3).

A



B

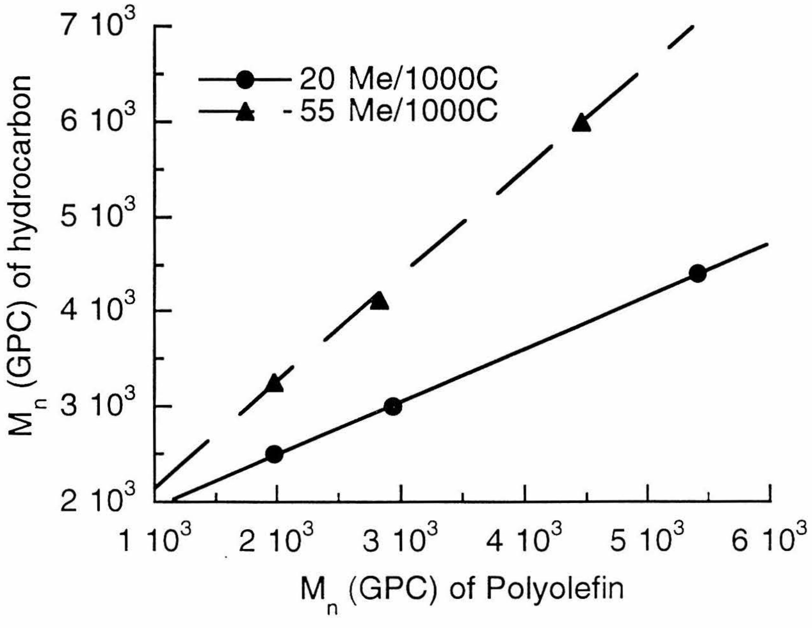


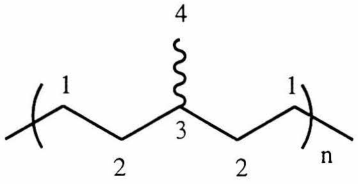
Figure 10A. Comparison of Molecular Weights Determined by GPC and End Group Analysis.

Figure 10B. Effect of Branching on Apparent Molecular Weight.

A. Polymer M_n calculated from ^1H NMR vs GPC for polymers with 20-80 methyl groups/1000 carbons.

B. GPC's for polyolefin and hydrocarbon at two polymer compositions: For 20 Me/1000C, slope = 0.56: For 55 Me/1000C, slope 1.11.

Characterization of hydrogenated polymers. The double bond of 4-methylcyclopentene is symmetrically located, and metathesis affords a regioregular polymer with a methyl group every five carbons of the backbone. The hydrogenated polymer has four main ^{13}C resonances and the endgroups can also be assigned with DEPT experiments confirming the assignments.



1 28.0 ppm
2 37.2 ppm
3 31.9 ppm
4 20.0 ppm

If 3-methylcyclopentene is polymerized in a regioregular fashion, the hydrogenated polymers should be identical. In contrast to previously reported polymerization's,[43] the metathesis polymerization of 3-MCP with ruthenium metathesis initiator was also not regioregular between 0-55°C. Furthermore, polymerization with early transition metathesis catalysts were not regioregular. The copolymerization of COD and 3-MCP affords a polymer where 3-MCP monomers were sequentially incorporated in the polymer backbone (Figure 8B). Both head-to-head and head-to-tail insertions of 3-MCP were observed (assignments are in the experimental section).

The melting transitions (T_m) of the polymers were determined by differential scanning calorimetry (DSC). The observed DSC behavior was reproducible with no apparent hysteresis, and each sample was scanned 3-4 times. There was strong correlation observed between the methyl content and T_m of both the telechelic polymers (Table 15) and the higher molecular weight EP copolymers (Table 16). Entries 10-11 of Table 16 are polymers prepared from COE/MCP copolymerization. The DSC's of the resultant polymer is independent of which comonomer was polymerized with MCP. The glass transitions were not observed in the DSC traces.

Table 15. Melting Points of Telechelic EP Copolymers[a]

Entry Number	MCP/[b] Chain	COD/[b] Chain	Me/ 1000 C	T_m[c]	J/g
1	6	29	20	108	150
2	6	24	26	103	133
3	12	31	35	99	119
4	11	22	48	92	81
5	13	21	54	77	41
6	15	18	73	70	39
7	3	17	21	105	151
8	4	16	27	101	128
9	5	15	34	*98*	108
10	6	14	42	*98*	
11	7	12	55	77	60
12	9	11	64	74	
13	2	11	22	104	149
14	2	10	29	101	130
15	3	10	38	100	
16	5	9	48	96	50
17	5	9	58	90	
18	7	8	70	65	30

[a] For entries 1-6, $M_n \approx 3500$; Entries 7-12 $M_n \approx 2200$; Entries 13-18 $M_n \approx 1500$.

[b] Average number of monomer units incorporated based on the polymer composition and molecular weight.

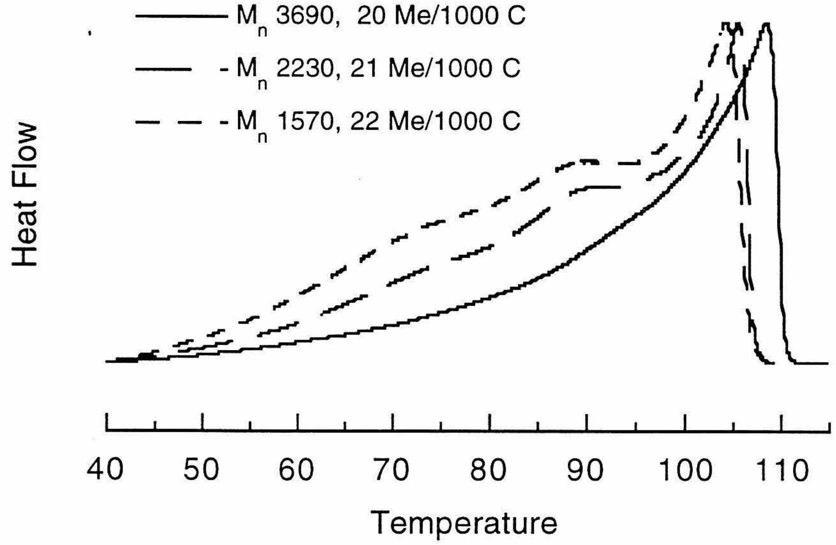
[c] The reported T_m is the peak temperature. The onset temperature was difficult to identify because the melt transitions were broad.

Table 16. Melting Points of Selected EP Coolymers.

Entry Number	Me/ 1000C	T_m[a]	J/g
1	86	64	25
2	73	72	35
3	61	80	52
4	51	88	69
5	41	95	80
6	34	101	93
7	26	106	105
8	19	112	121
9	12	118	133
10	26	106	106
11	92	61	24

[a] The reported T_m is the peak temperature. The onset temperature was difficult to identify because the melt transitions were broad.

Within each series of polymers, the enthalpy of the transition systematically decreased with increasing methyl content. This phenomenon is reasonably a consequence of decreased efficiency of crystal packing. (The melt enthalpies of the telechelics and high MW EP copolymers can not be directly compared due to an uncorrectable drift in instrument calibration.) Within the series of telechelic polymers, the melting transitions of the lower molecular weight samples were broader than polymers with higher molecular weights and the T_m's were slightly depressed(Figure 10).



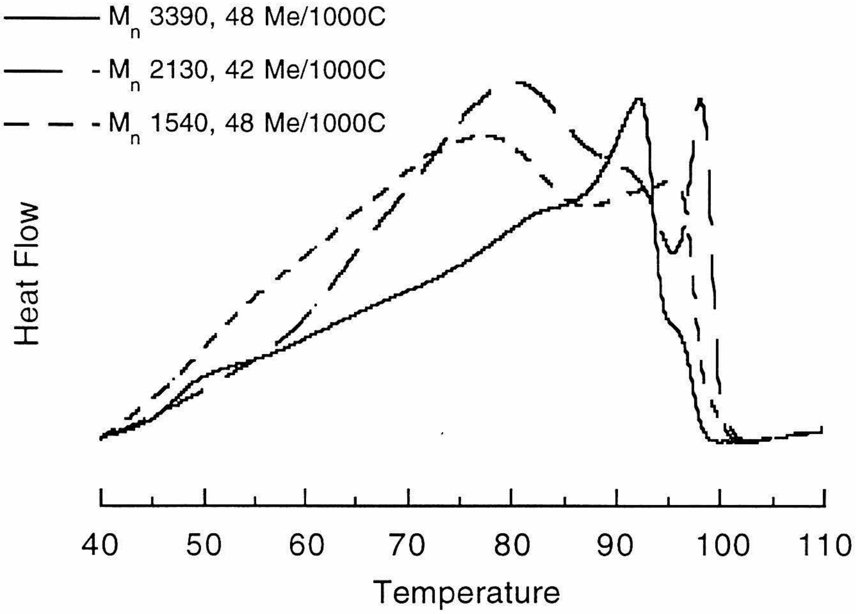


Figure 11. DSCs of Telechelic EP Copolymers.

Interestingly, several of the telechelic polymers exhibited multiple transitions in the DSC traces. For a polymer with an average of 42 methyls/1000C, and a M_n of 2130, there is an average of 5.9 methyls per polymer chain (Table 15). Because the incorporation of methylcyclopentene units is approximately random, it is statistically likely that some low molecular weight chains have no methyl groups and are highly crystalline. For higher molecular weight samples no secondary melting transitions were observed (Figure 11).

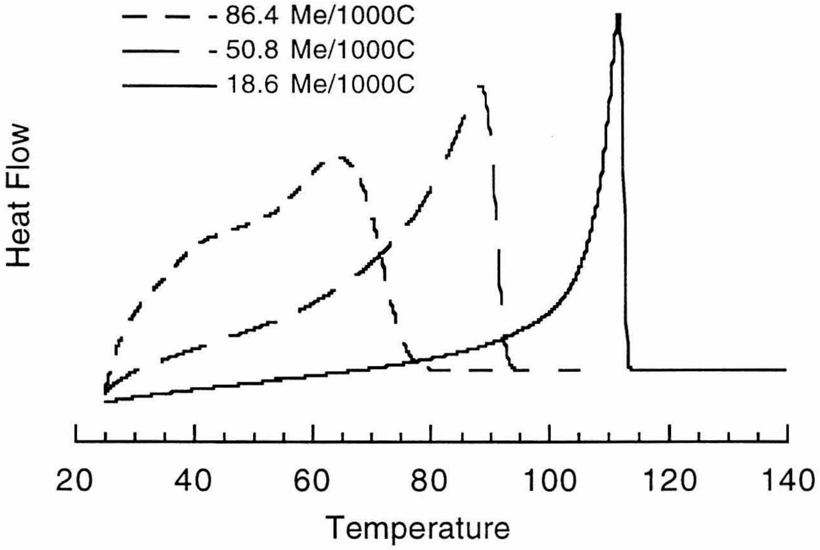


Figure 12. DSCs of High Molecular Weight EP Copolymers.

The melting points of these new EP polymers were compared with the known melting points of branched polyethylenes (Figure 12).[54] The literature values were for commercially available polyethylenes with methyl branches, including Marlex® and Epolene.® Both the telechelic copolymers and the higher molecular weight samples demonstrated melt behavior similar to the literature reports of branched PE.

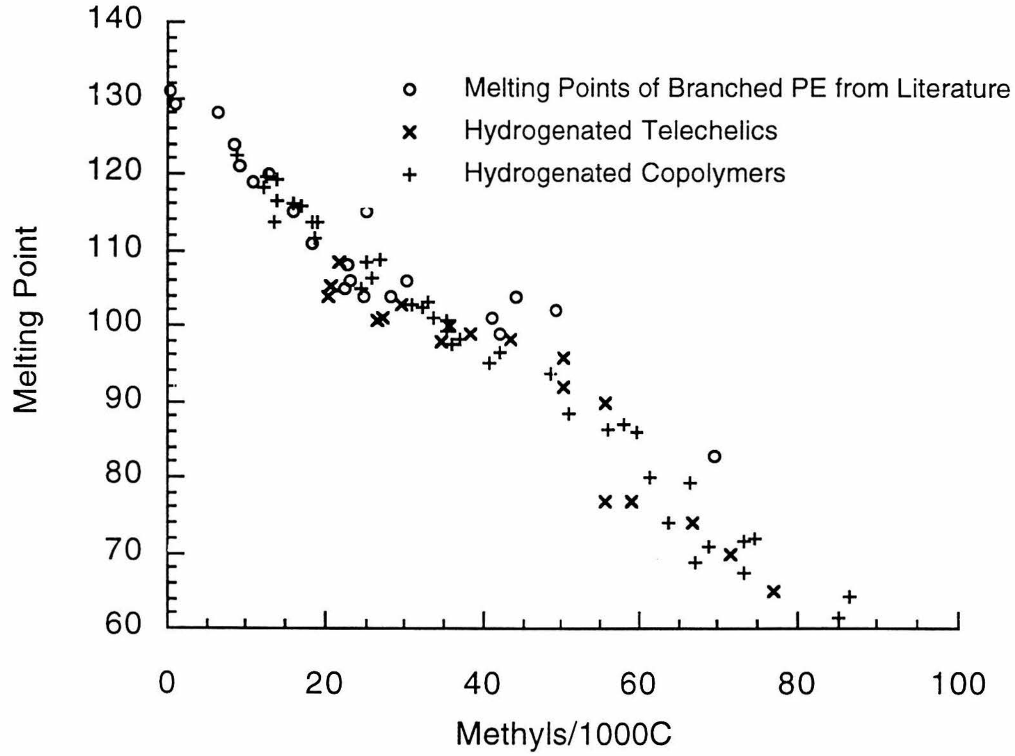


Figure 12. Melting Points of Branched Polyethylenes.

Part V. Characterization by Rheometry and Rheo-optical Methods.

Rheology is the study of the deformation and flow of materials. The flow properties of polymers are very important for many processing methodologies including injection molding and extrusion. The description of polymer flow is complex because polymers may behave as both a solid and a liquid depending on the timescale of the induced perturbation and corresponding relaxation. For example, polysiloxane (silly putty) flows under the force of gravity, but bounces when impacted quickly. The description of polymer flow requires the consideration of two components: a purely viscous fluid and a perfect elastic spring. For a purely viscous fluid, all applied energy is dissipated through molecular motions (flow) and displacement is proportional to the force applied. A perfect elastic component stores all applied energy (straining of bond angles and lengths), and when the force is removed there is no net displacement. There are several qualitative models of polymer behavior based on the consideration of these components in series (Maxwell Element) and in parallel (Voigt-Kelvin Element).[55,56]

Many common rheological measurements are based on shear (2-dimensional) deformation. A known force/area is applied (shear stress, τ), and the displacement is measured (shear strain, γ) (Figure. 14). Viscosity (η) is a measurement of the resistance to flow and is defined in terms of the shear stress and the rate of straining (*vide infra)*. Unlike Newtonian fluids, polymer melts and solutions are aligned under shear stresses and the viscosity actually decreases as the shear rate increases (*pseudoplastic behavior,* shear thinning).

Shear Stress	τ	Force/Area (dyne/cm^2)
Shear Strain	γ	dx/dy (dimensionless)

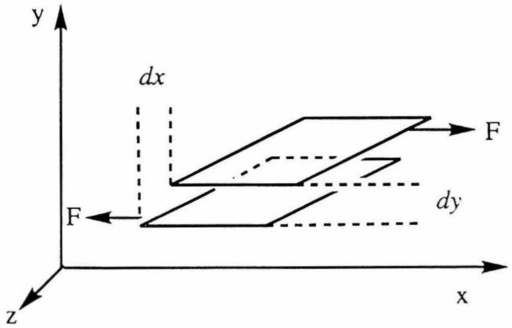


Figure 14. Diagram of Shear Stress and Strain.

Shear deformation can be exploited by many experimental techniques. The relaxation behavior of a polymer is often probed by imparting a strain (displacement) and following the relaxation to equilibrium (x-axis is time). Alternatively, the force necessary to impart a known strain on a certain timescale can be measured (x-axis is frequency). These experiments describe 3 distinct regions of polymer behavior. When a polymer chain is stressed, molecular anisotropic orientation results, and that stress is relaxed through molecular motion. Fast relaxations occur on very short timescales and small distances (glassy state, no flow); At intermediate timescales there is disentangling of chains (rubbery state); Long timescales correspond to slow relaxations and flow (terminal region). Analogously, when measuring the force necessary to impart a known strain, the x-axis is reversed (Figure 15).

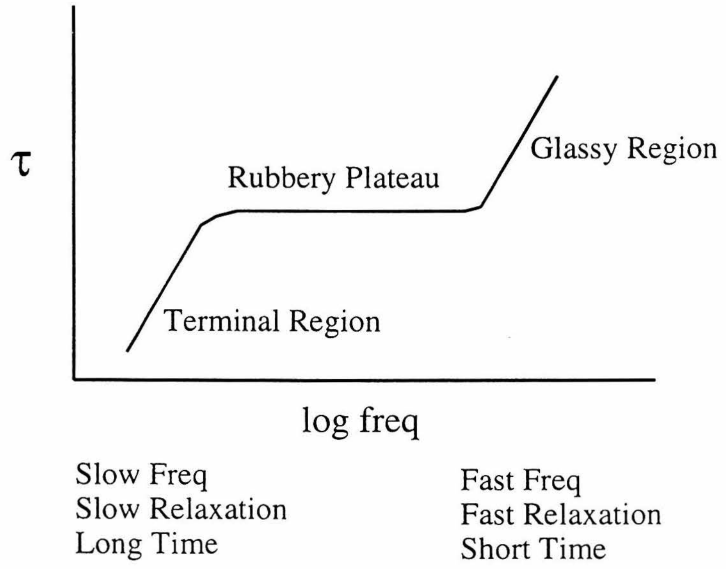
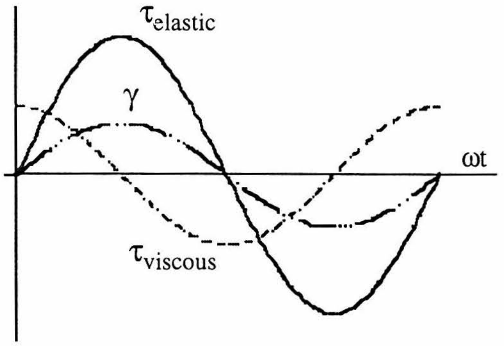


Figure 15. Representation of Relaxation Spectrum

In order to evaluate the effects of methyl branching and molecular weight on the flow behavior of polyethylene/polypropylene copolymers, we utilized parallel plate rheometry with oscillating shear. Oscillating shear takes advantage of the fundamentally different response of the viscous and elastic elements. Applying strain (γ) to an elastic element causes stress (τ) in the same direction, but straining a viscous element actually corresponds to stress orthogonal to the displacement. When a polymer sample is subjected to oscillating shear strain, the measured stress is out of phase with the applied strain (Figure. 16)



$\tau_{elastic}$ is in phase with the applied strain

$$\tau_{elastic} \propto G\gamma\sin(\omega t)$$

$$\tau_{viscous} \propto \dot{\gamma}\,\eta = \eta\omega\gamma\cos(\omega t)$$

stress is 90° out of phase with strain
liquid isn't compressed
displacement is ⊥

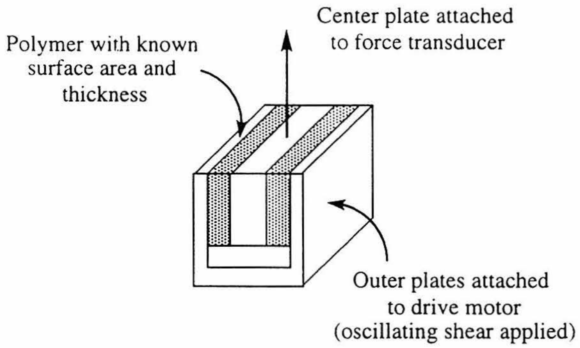
Viscoelastic materials exhibit intermediate response

Figure 16. Sinusoidal Deformation.

The term modulus is used to describe the relationship between stress and strain under many different experimental of conditions. For example, Young's Modulus is the ratio of tensile stress and elongation (uniaxial straining of a solid). Complex shear modulus (G*) is a function of angular frequency ω and is the sum of the in-phase and out-of-phase components (Eq. 5)

$$G^*(\omega) = G'(\omega) + iG''(\omega) \qquad (5)$$

The in-phase portion is known as the storage modulus G' (Eq. 6) because after one full cycle, no net work is done. The out-of-phase portion is the loss modulus G" (Eq. 7) because the applied force is dissipated as heat. (Strain is applied sinusoidally, and in the first 1/4 cycle, the in-phase element stores the energy while the viscous element dissipates the energy (proportional to η). In the second 1/4 revolution, the elastic element recovers the stored energy while the viscous element dissipates the energy.)



Calculate phase difference between the applied strain and observed stress.

In-Phase: (6)

Storage Modulus

$$G' = \tau'/\gamma'$$

Out of Phase: (7)

Loss Modulus

$$G'' = \tau''/\gamma''$$

Figure 17. Experimental Apparatus Used for Mechanical Analysis.

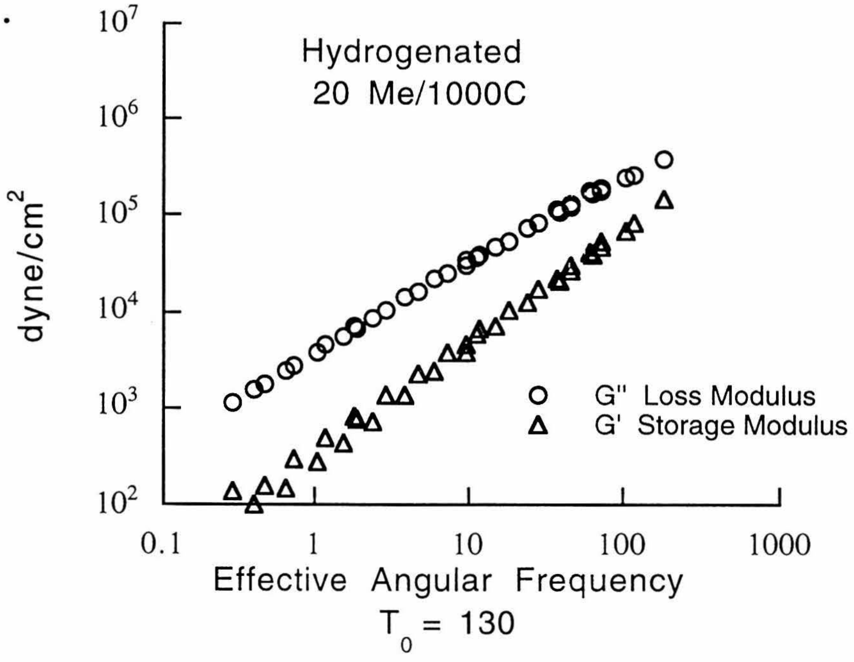
A further consideration when performing rheological experiments is the mechanical limitations of the instrument (Figure 17). The experimentally accessible frequency range is $\omega = 10^{-1} - 10^{2}$ rads^{-1} however, invoking the theory of time-temperature superposition can increase the available effective frequency range. Consider a relaxation which occurs at a certain time t_x at a given temperature. When the sample is cooled, the same relaxation would take longer and analogously, at higher temperatures the relaxation would occur more quickly.[55,56] The relationship between the time-temperature superposition coefficients (a_T) and the reference temperature is often given by the Williams-Landel-Ferry (WLF) equation (Eq. 8).[57] The reference temperature T_0 is usually close to the glass transition temperature, and the coefficients C_1 and C_2 are empirically determined.

$$\log(a_T) = \frac{-C_1 * (T - T_0)}{C_2 + T - T_0} \qquad (8)$$

When plotting storage and loss modulus, the x-axis is the apparent frequency $\omega(a_T)$ ($a_T = 1$ at T_0). The temperature dependence of a_T is well represented for $T < T_g + 150$, and for these experiments data could only be collected above well above the T_g ($T > T_g + 200$). In this temperature range, the relationship of a_T and temperature fit and Arrhenius form (*vide infra*) and the data was empirically shifted to a convenient T_0 within the range of temperatures investigated.[58]

Initial experiments were done on samples with M_n of 20K. At this molecular weight, it is estimated that there are only 10-15 entanglements per chain,[57] and at accessible frequencies and temperatures no disentangling relaxations could be observed (terminal region exclusively) (Figure 17). The plateau region would only be observed at higher frequencies. Higher frequencies were not possible due to mechanical limitations, and the sample could not be characterized at temperatures lower than the crystallization temperature. Characterizing melt polyethylene is challenging because the useful temperature region is somewhat limited due its high crystallinity. Furthermore the coefficient of viscosity is small which restricts the frequencies available by time-temperature superpositions (smaller magnitude a_T).[59] For example, a typical time-temperature coefficient for an EP copolymer for (T_0 - 10) shifts the frequency by a factor of 1.2. In comparison, the WLF time-temperature coefficients of polybutadiene, polyurethane, polystyrene and PMMA are 9.7, 17.8, 24.0 and 128.[57] In order to observe a larger temperature range, the modulus of several samples were measured before hydrogenation (Figure 18). These are not crystalline at room temperature, and they were shifted to a lower temperature. Homopolymers of MCP and COD were also examined but were also in the terminal region under comparable conditions.

A.



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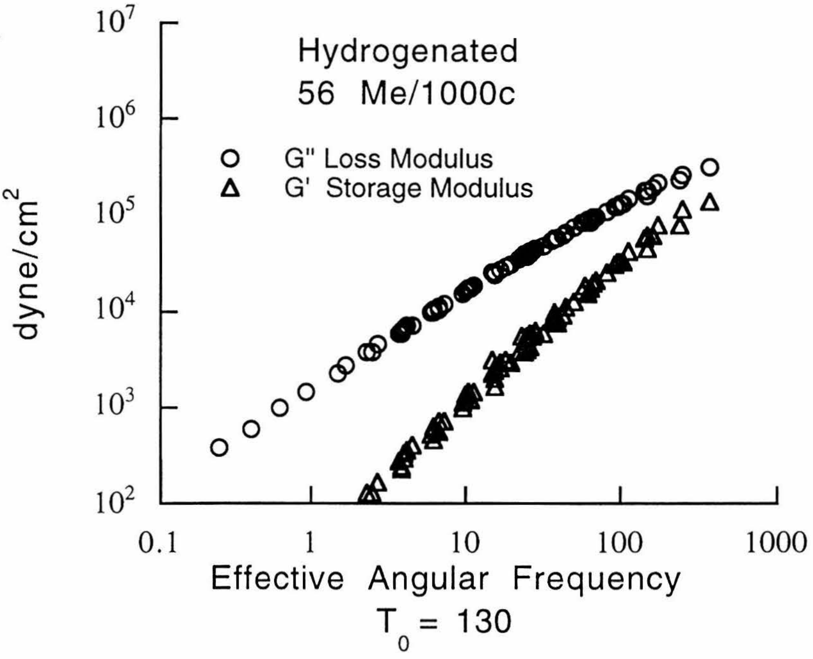
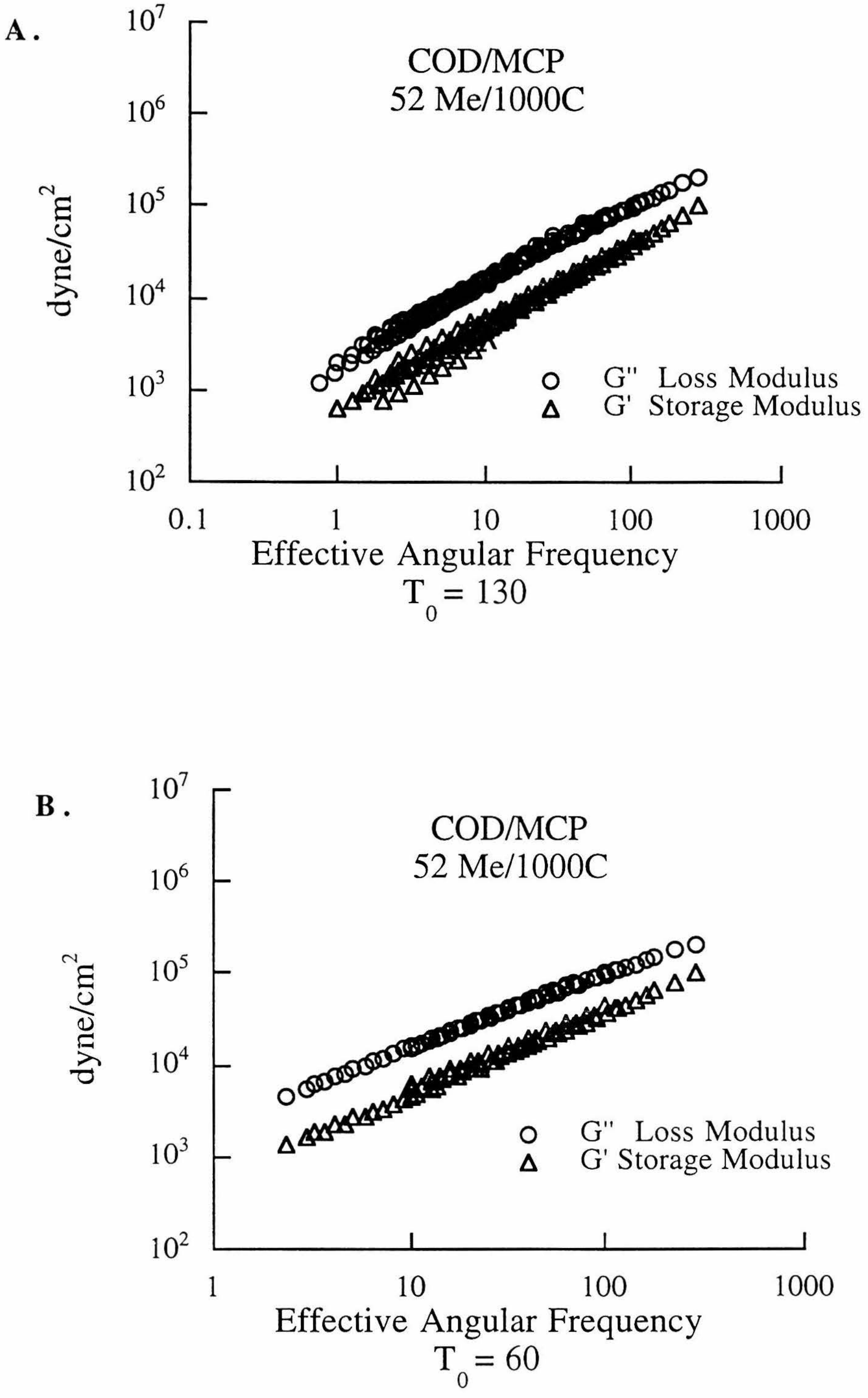


Figures 18A,B. Storage and Loss Moduli of Hydrogenated EP Copolymers



Figures 19A,B. Storage and Loss Moduli of Unsaturated ROMP Copolymers.

Although these samples did not provide insight into the entangled behavior of these polymers, the low frequency data could be used to determine the zero shear viscosity (η_0). The steady state flow viscosity at very small shear rates is dependent both on molecular weight and structural factors. Viscosity is defined as the applied stress (force/area) divided by the rate of strain (Eq. 9). The zero shear viscosity is the limit of the loss modulus divided by frequency as the frequency approaches zero (Eq. 12). The zero shear viscosity as a function of temperature is plotted for several polymers with different methyl content (Figure 20).

$$\eta = \tau / \dot{\gamma} \qquad (\text{force} \bullet \text{sec/cm}^2) \qquad (9)$$

$$\tau'' = G''\gamma'' \qquad (\text{force/cm}^2) \qquad (10)$$

$$\dot{\gamma} = d\gamma/dt \qquad (\text{sec}^{-1}) \qquad (11)$$

$$\eta_0 = \lim_{\omega \to 0} (G''/\omega) \qquad (12)$$

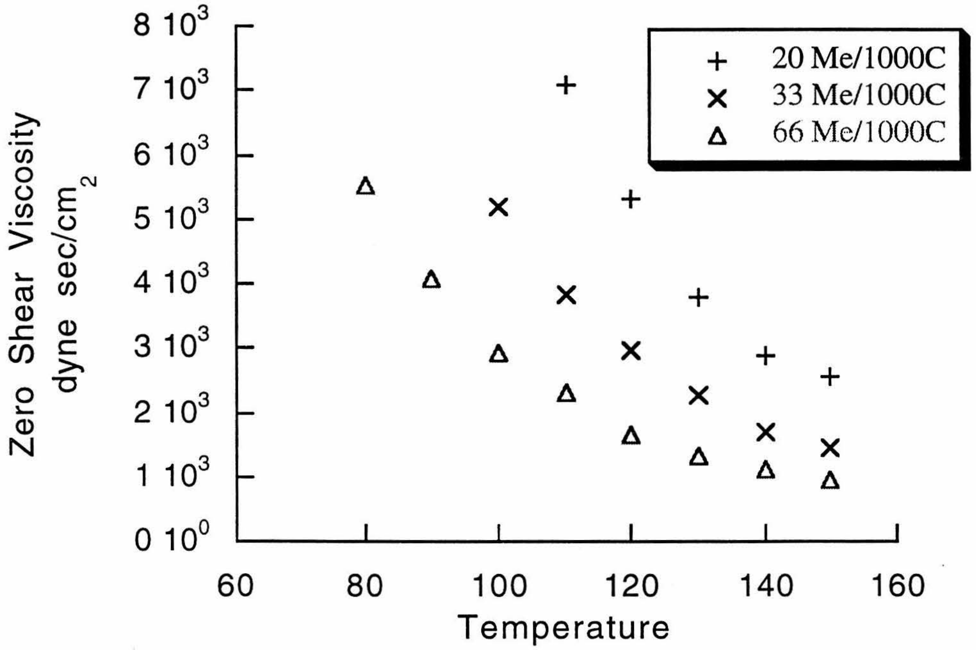


Figure 20. Zero Shear Viscosity of Saturated EP Copolymers

The hydrogenated polymers and the parent unsaturated materials have dramatically different properties at room temperature, i.e. the hydrogenated polymers are crystalline and the parent polymers are viscous oils. Above the melting temperature, the polymers have very similar zero shear viscosity. The viscosity of polyethylene with only 6% methyl branching is actually similar to an unsaturated polymer (Figure 21).

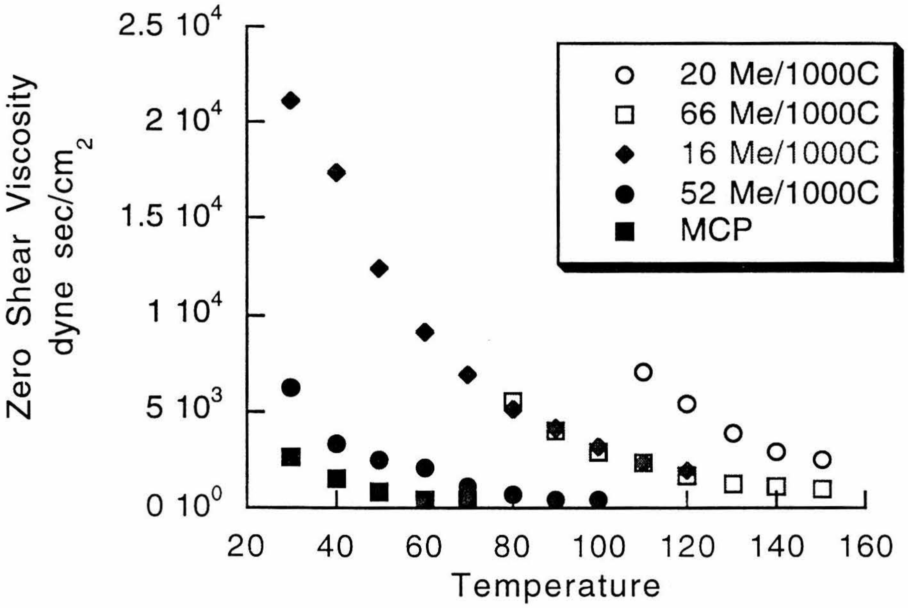


Figure 21. Zero Shear Viscosity of Saturated and Unsaturated Copolymers.

Open symbols represent hydrogenated samples, and solid symbols represent unsaturated polymers.

In order to observe the plateau region of the storage and loss modulus, higher molecular weight polymers needed to be prepared and characterized. Lower molecular weight polymers relax more quickly than their higher molecular weight analogs. As the polymer chain length is increased, the number of entanglements increases, which corresponds to broader plateau regions and longer relaxation times. Several model polyethylene samples which were prepared by addition polymerization of polyethylene were rheologically characterized to determine the approximate molecular weight necessary to observe the plateau region of the modulus. The crossover between terminal and rubbery behavior was observed for polyethylene with M_n of 51.4 K (PDI 2.1, 4 Methyls/1000 C)

(Figure 22). Only the plateau region was observed for M_n of 107 K (PDI 2.4, 5 Methyls/1000 C) (Figure. 23A) and for slightly higher molecular weight sample with narrower PDI and more branching (M_n 116 K, PDI 2.2, 8 Me/1000C) the crossover of storage and loss modulus was closely approached (Figure. 23B).

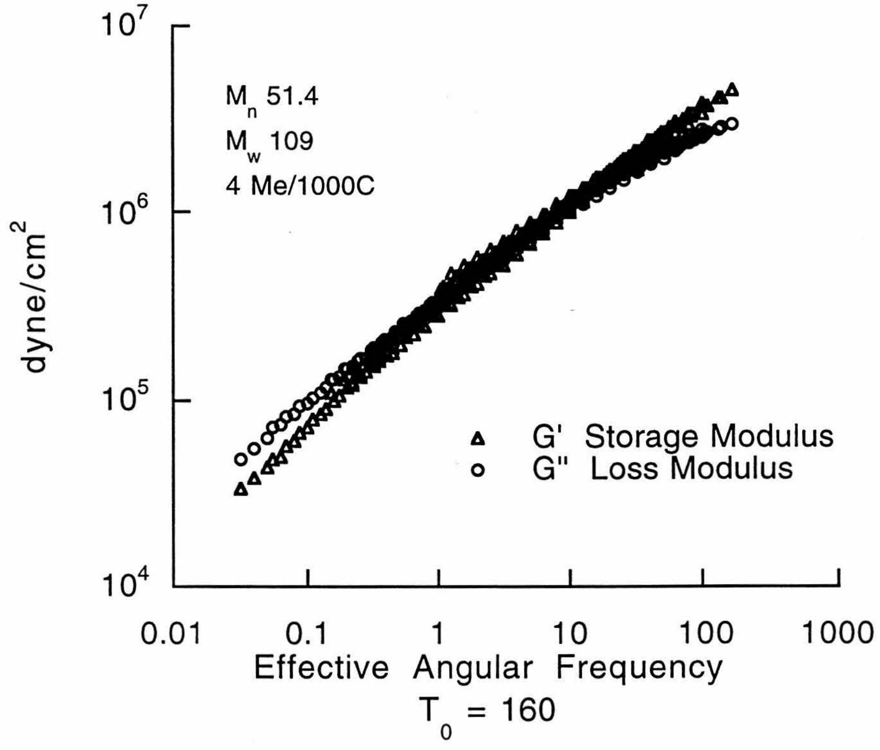
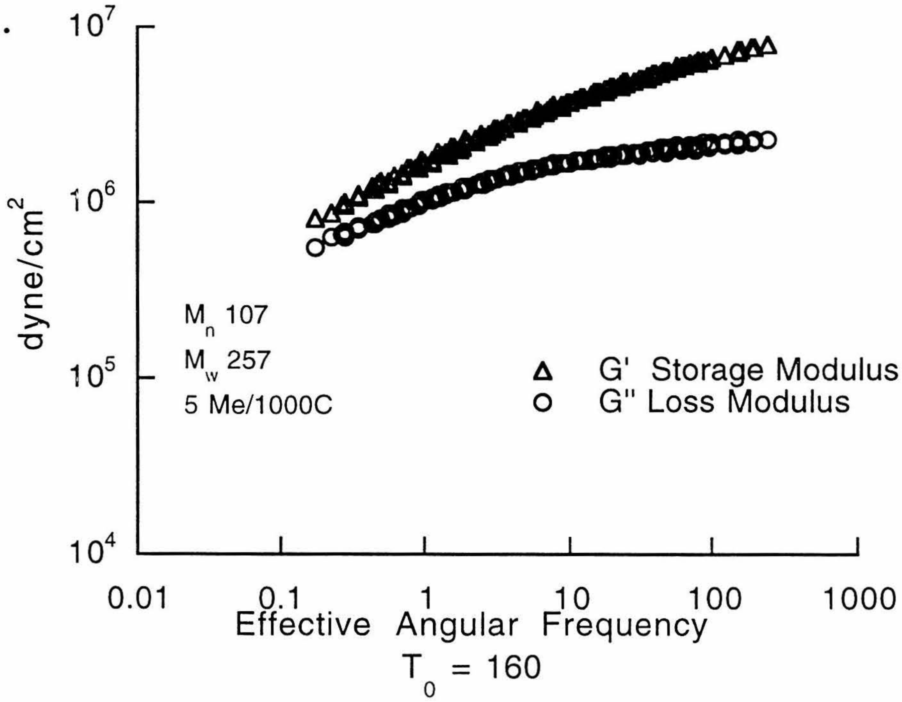


Figure 22. Crossover of Strorage and Loss Moduli.

A.



B.

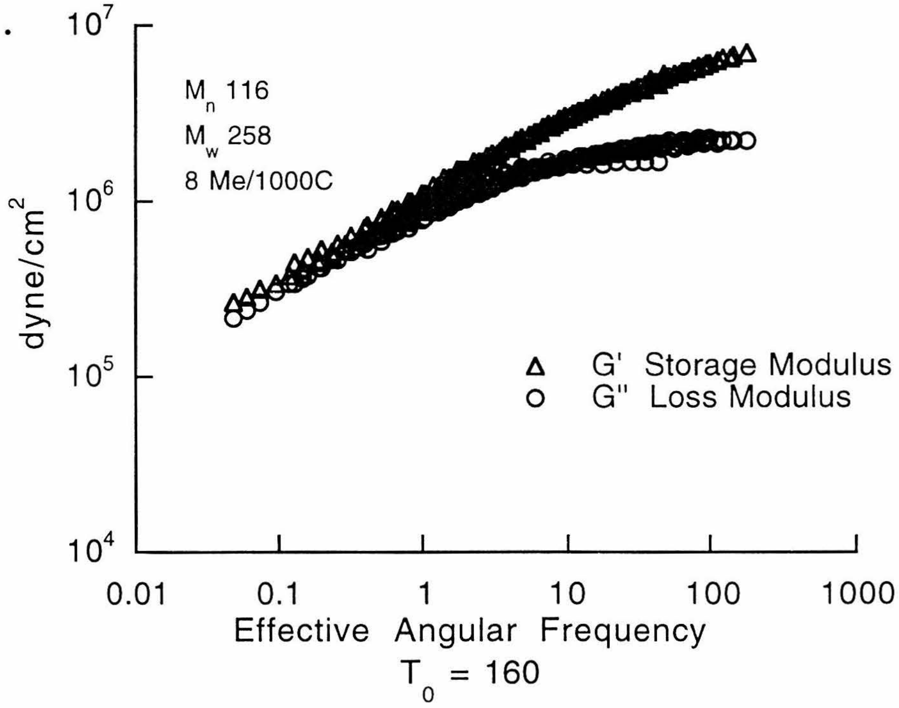


Figure 23A,B. Moduli of Model Polymers in Plateau Region.

The examination of these model polymers indicated that an M_n of 40-150 K would display behavior in the plateau region and a range of crossover points (G' = G"). (Rheological testing of addition polymers with M_n 16 K gave similar results to those prepared by metathesis polymerization/hydrogenation.) Additionally, the flow activation energy of these samples was calculated from the time temperature superposition coefficients (Eq. 13) (R is universal gas constant).

$$E_a = \frac{\ln (a_T) * R}{(1/T - 1/T_0)} \qquad (13)$$

These data fit to an activation energy of 6.7 kcal/mol which agrees well with the a reported values of 6.4-6.7 kcal/mole for HDPE (13.0 kcal/mole for LDPE)[60] (Figure24).

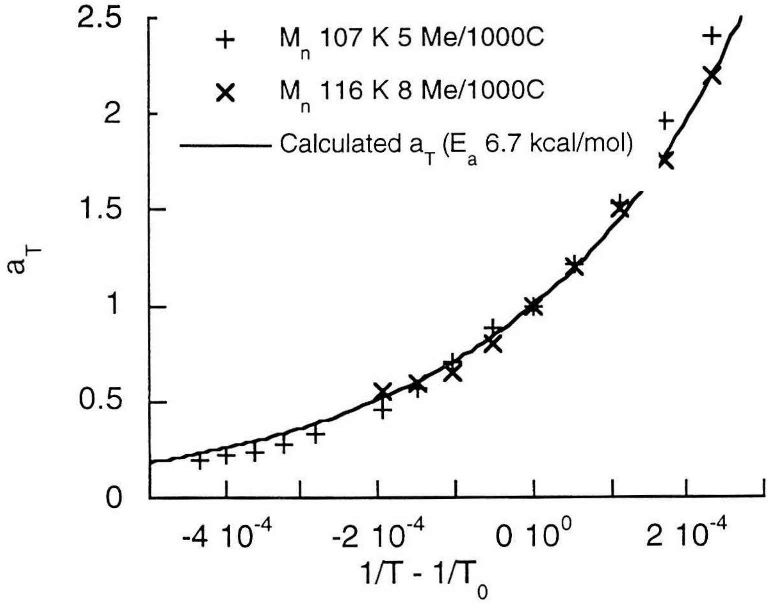


Figure 24. Exponential Fit of Time Temperature Coefficients of Model Polymers (T_0 = 160).

Higher molecular weight COD/MCP copolymers were synthesized and hydrogenated. The molecular weights of these samples were determined relative to polystyrene prior to hydrogenation. Although the saturated model polymers were also characterized relative to polystyrene, the molecular weights could not be directly compared. The molecular weights were determined by size exclusion chromatography and the hydrodynamic volumes of saturated and unsaturated polymers are very different. Furthermore, the hydrodynamic volume of saturated polymers is very sensitive to methyl branching on the polymer backbone (*vide supra*). Samples with M_n's near 30 K (25 - 75 branches) were in the plateau region (Figure 26). Similarly, the higher molecular weight samples (70 K, 35 branches) also demonstrated terminal region behavior (Figure. 25). The flow activation energy was comparable to the previously characterized samples (Figure 27).

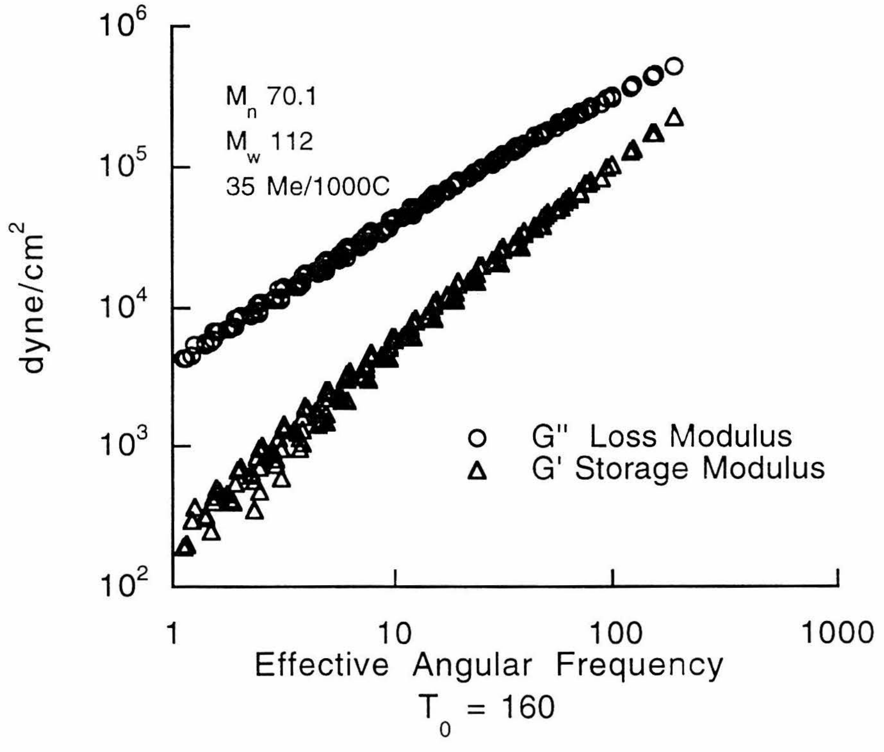


Figure 25. Storage and Loss Modulus of EP Copolymer (M_n, 70K).

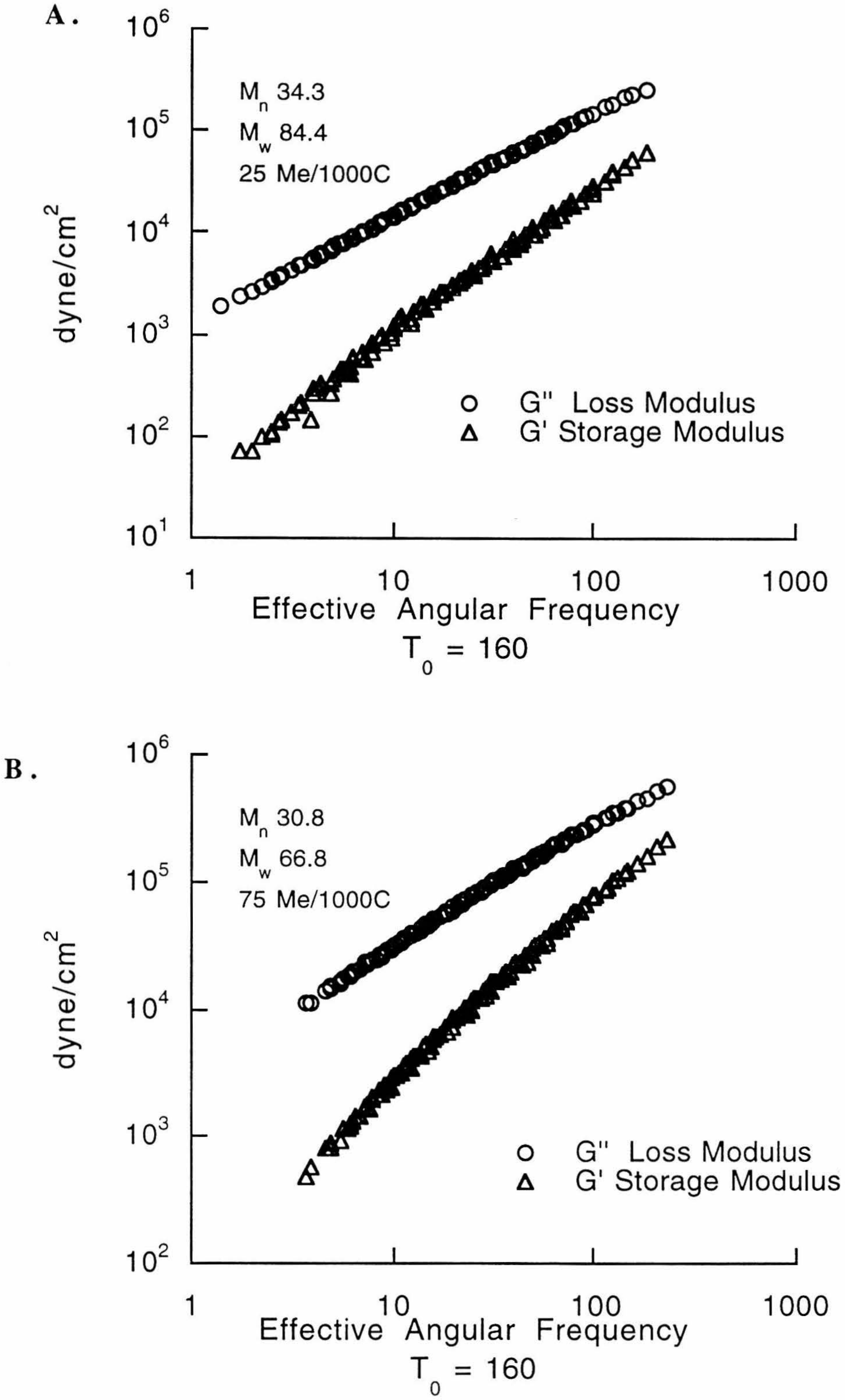


Figure 26A,B. Storage and Loss Modulus of EP Copolymer (M_n, 30K).

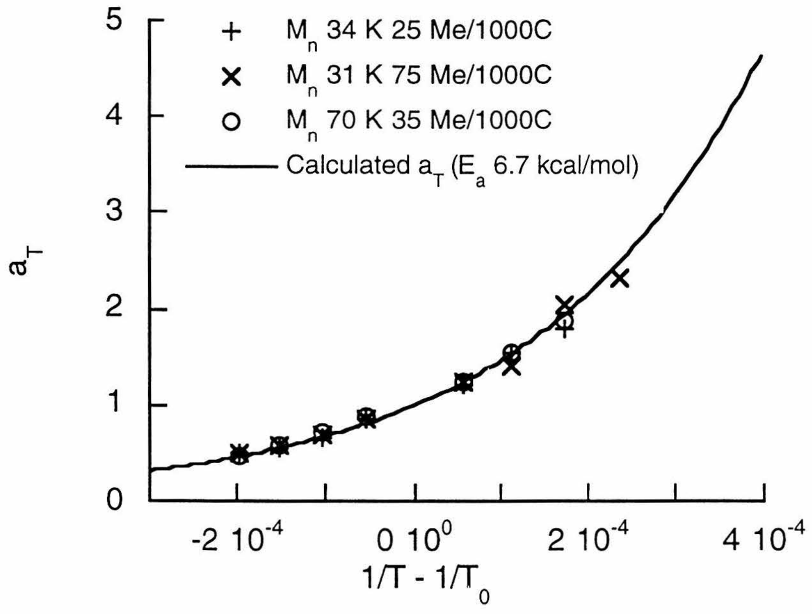


Figure 27. Exponential Fit of Time Temperature Coefficients of EP Copolymers (T_0 = 160).

Samples with molecular weights over 100 K were synthesized *via* the copolymerization of cyclooctene and methylcyclopentene. The crossover into the plateau region could be observed in these samples. Although both samples had similar methyl content and PDI, the difference in molecular weight significantly shifted the crossover point (Figure 28). It was determined at this point that parallel plate rheometry would not permit us to deconvolute the subtle effects of methyl branching on the polymer behavior from the more pronounced effects of molecular weight and polydispersity.

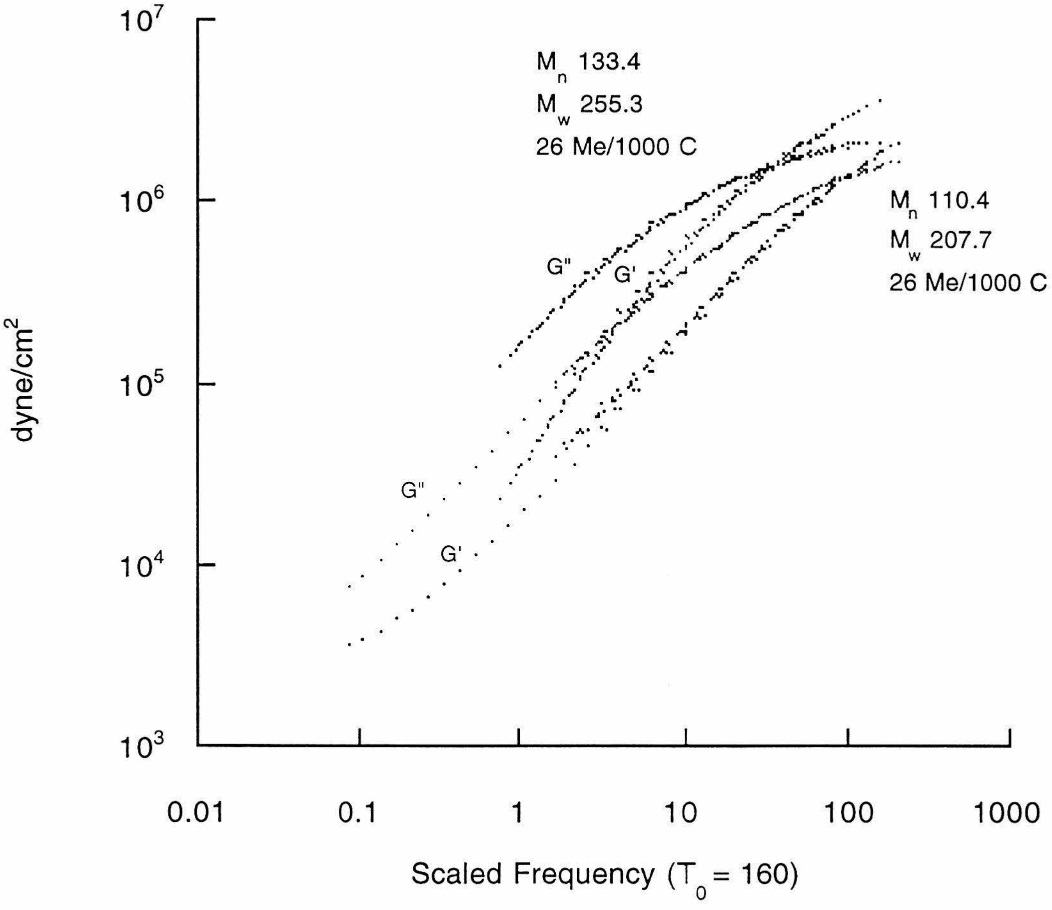


Figure 28. Crossover Region of EP Copolymer.

Rheo-optical Characterization.[61]

Rheo-optical methods of polymer characterization are extremely sensitive to changes in both the molecular structure and orientation of polymers.[62,63] Thus, these methods are ideal for discerning the differences among the various EP copolymers in this study. Rheo-optical characterizations combine mechanical and optical measurements such as light scattering or birefringence. Some differences between mechanical and optical characterization are highlighted in Table 17. The major drawbacks of optical methods include the necessity of suitable optical properties (transparency, freedom from contaminants) and the more complicated experimental configuration and analysis.

Table 17. Comparison of Mechanical and Optical Methodologies.

Rheological (Mechanical)	**Rheo-optical**
• Measures dissipation/storage of energy • Very sensitive to MW/PDI • Both sample and instrument subject to mechanical forces.	• Measures an optical quantity which directly correlates with molecular orientation and shape • Not molecular weight dependent • Measured quantity decoupled from applied field (extreme sensitivity)

When light propagates through a non-absorbing (and non-scattering) medium, its speed is reduce to υ, which is slower than the speed of light *in vacuo* (c). The ratio of these speeds is the refractive index (n) (Eq. 14).

$$c/\upsilon = n \qquad (14)$$

The change in speed results in changes in both the wavelength and propagation direction at the interface of two materials with different refractive indices (refraction). When the material is anisotropic, the value of n will depend on the relative orientation of the light (polarization) to the molecular axes. The dependence of refraction on orientation results in birefringence (double refraction). When the anisotropy arises from molecular alignment, flow birefringence is measured. Form birefringence arises from phase separation or microstructures at a larger scale such as lamellae of block copolymers. For polymers under shear, very slight perturbations from equilibrium produce a measurable birefringence. An exaggerated schematic of the approach is shown in Figure 29.

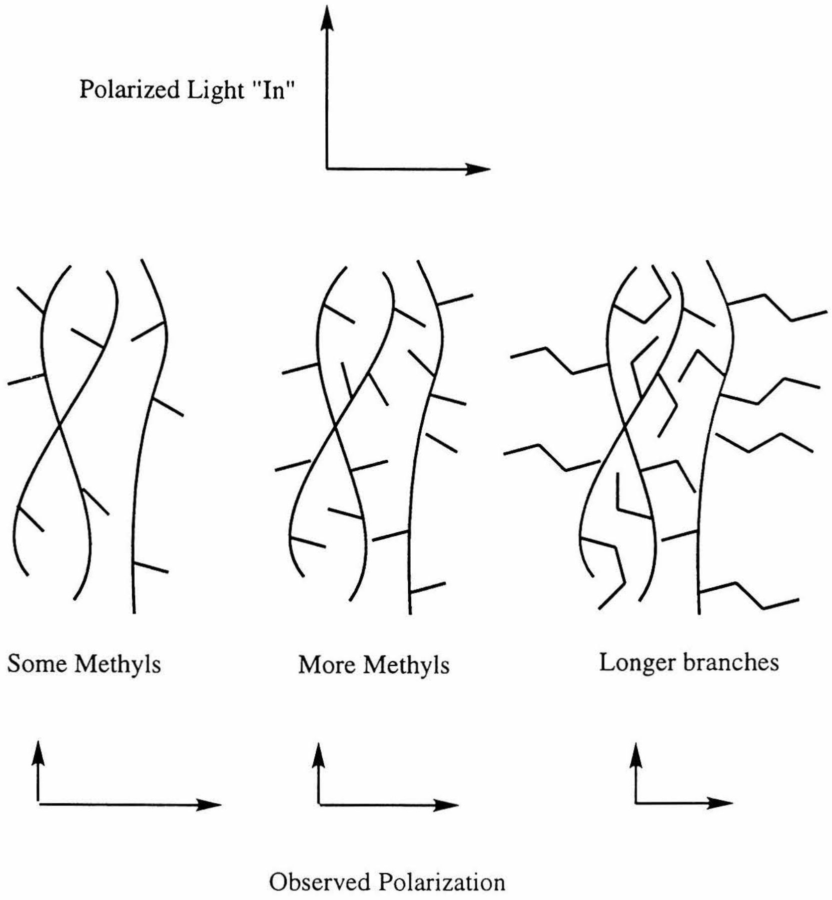


Figure 29. Illustration of Stress Optic Experiment.

The stress-optical coefficient (*C*) is often used when discussing flow birefringence. It assumes that for a given polymer undergoing flow, the stress tensors and the index of refraction tensor are related by the proportionality constant *C* (stress-optic coefficient). For flexible homopolymer melts, the stress-optical coefficient relationship is almost universal, and values of *C* are independent of shear rate (even in the shear thinning regime), molecular weight and molecular weight distribution. The ratio *C* is strongly dependent on the monomer unit(s) (polymer backbone) and slightly dependent on temperature and wavelength. Importantly, *C* is independent of time after the onset of shear. The magnitude of the measured birefringence depends on both the degree of molecular orientation (proportional to stress) and the difference in refractive index along the axes. (The difference in refractive index reflects the polarizability anisotropy of the monomer unit.) Schematics of the sample flow cell and optical train are provided (Figure. 30, 31).[64]

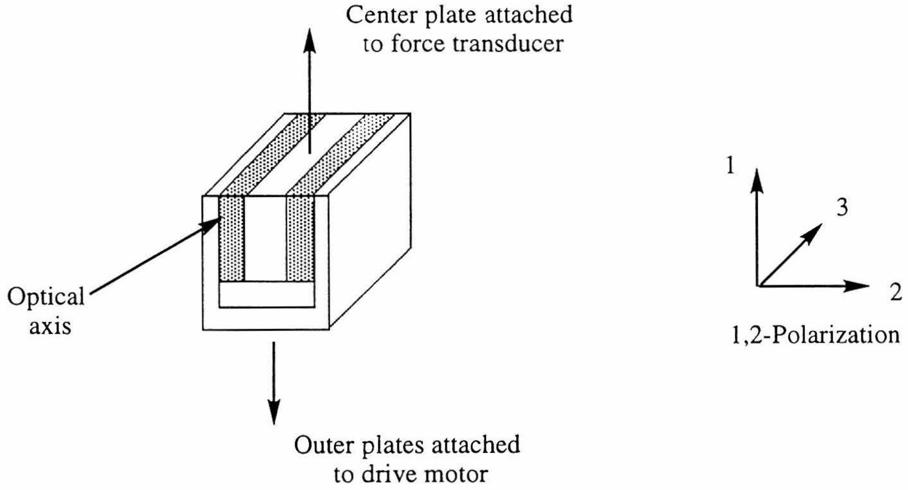


Figure 30. Sample Flow Cell.

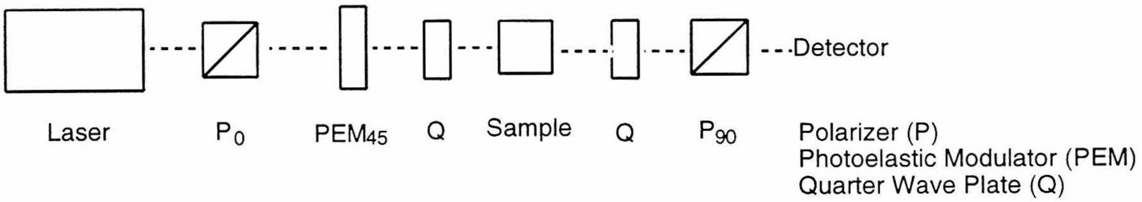


Figure 31. Schematic of Optical Train.

The sample flow cell is very similar to the configuration utilized in oscillating shear rheometry. Storage and loss modulus (G', G") are measured by the same method as previously described. The optical train consists of a laser (He/Ne, λ = 632.8 nm), a polarizer (0°), a photoelastic modulator (200 KHz) and a quarter wave plate followed by the flow cell, a quarter wave plate, a polarizer (90°) and then a CCD detector. The photoelastic modulator provides the carrier signal for data acquisition, and the quarter wave plates retard the polarization such that zero birefringence provides zero signal. Optical data is acquired at 200 KHz and 400 KHz.

Using the experimental configuration described, the difference in the refractive indices of the two axes is measured (Δn). Simultaneously, the stress tensors of each axis are also measured ($\Delta\sigma$).[62] The stress-optic coefficient can be expressed as the ratio of these differences or of the complex birefringence (B*) and modulus (G*) (Eq. 15).[64] Although birefringence and modulus are frequency dependent, the stress-optic ratio C is independent of frequency (Figure 32).

$$C = \frac{\Delta n}{\Delta\sigma} = \frac{|B^*|}{|G^*|} \tag{15}$$

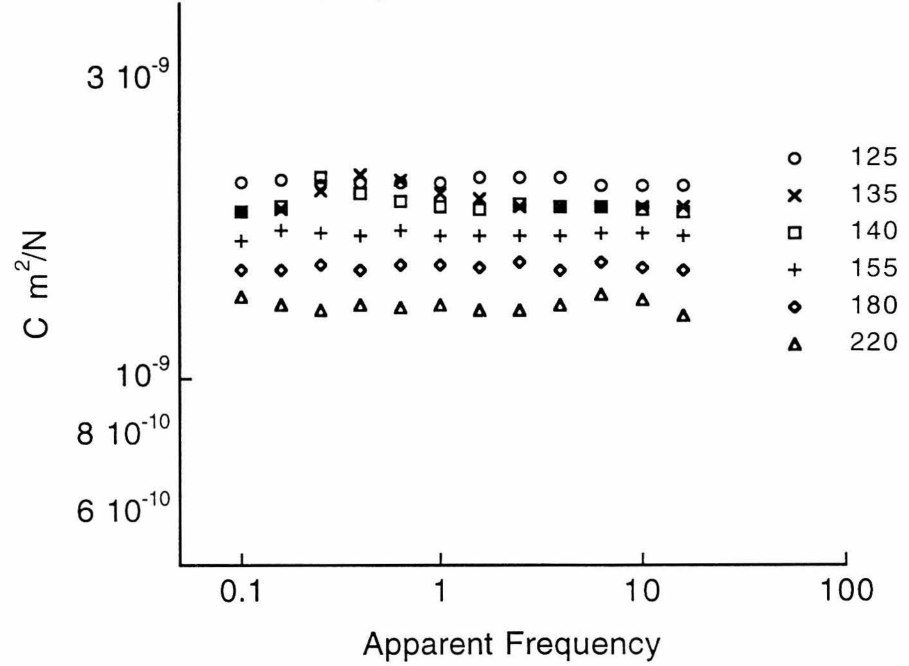


Figure 32. Stress Optic Coefficient vs. Frequency for EP Copolymer (35Me/1000C).

There is an expression relating *C* to the optical anisotropy of the polymer and the temperature (Eq. 16). The constant A is independently determined for different polymer backbones, and includes topological parameters as well as a factor to describe the difference in polarization of the two axes.

$$C = \frac{A*(n^2+2)^2}{T*n} \qquad \text{(Eq. 16)}$$

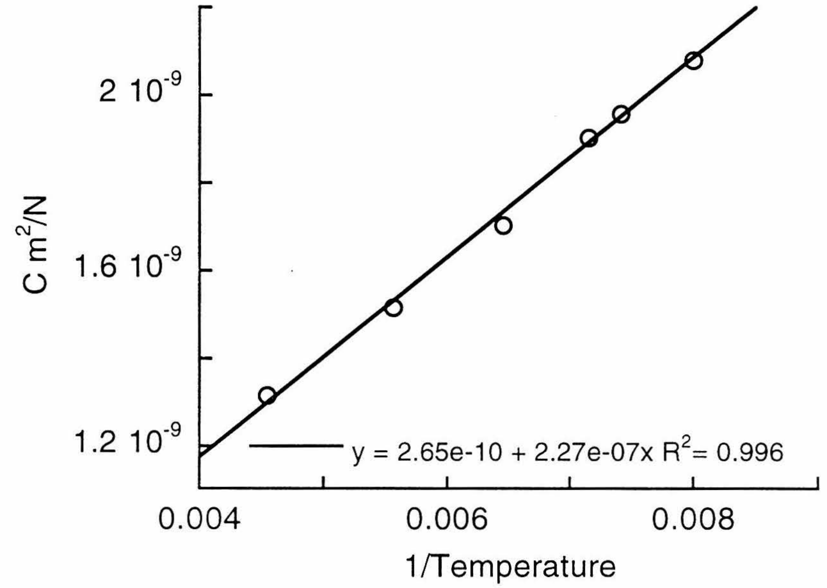


Figure 33. Stress Optic Coefficient vs. Inverse Temperature.

It is expected, that polymers with an increased number of branches (or increased length of branches) would have smaller stress optic coefficients. Preliminary results confirm this trend (Table 18), and further characterization is ongoing. The observed *C*'s are slightly smaller than reported in literature (HDPE, 2.4 e^{-9}, LDPE 2.0 e^{-9}, PP 0.9 e^{-9}),[62] but it is not clear if there are differences in sample purity or instrument calibration. At the current time, these samples can not be compared to commercially available longer branched polyethylenes[65] because these samples contain additives. The changes in molecular polarizability prevent a direct comparison.

Table 18. Selected Stress Optic Coefficients for EP Copolymers

Methyls/1000C	M_n	Temp. °C	*C*
35	40,600	155	1.72e-9
35	40,600	180	1.51e-9
12	71,200	170	1.72e-9

Conclusions

A new versatile methodology for the synthesis of EP polymers utilizing a well-defined organometallic initiator has been developed. Cyclooctadiene and methylcyclopentene are efficiently copolymerized in the presence of a difunctional chain transfer agent to produce bifunctional telechelic copolymers. The reaction feed provides straightforward control of the polymer composition and molecular weight. The polyolefins are easily hydrogenated to give a series of EP polymers, and the melting points of the polymers decrease with higher methyl incorporation into the polymer backbone. The functional group tolerant metathesis catalyst ($(PCy_3)_2Cl_2RuCHPh$) provides a unique opportunity in the design and synthesis of well-defined EP telechelic polymers. In addition to telechelic polymers, higher molecular weight analogs were also synthesized. After metathesis polymerization, the ruthenium carbene is converted to and active olefin hydrogenation catalyst *in situ*. At 200° C and 800 psi H_2, polymers are completely hydrogenated (Olefin/Ru $\approx$ 2000). While methylene chloride appears to be essential for efficient hydrogenation of polymer substrates, the unreacted monomer appeared to be more easily hydrogenated. Under milder reaction conditions (temperature and/or pressure) and with all solvents, no residual monomer was detected. Finally, the saturated polymers were characterized by size exclusion chromatography, NMR, thermal and rheological methods. Mechanical data has provided zero shear viscosity data and flow activation energies. Samples were also characterized by rheo-optical methods. The effect of methyl branching on the flow birefringence was determined.

Experimental Section.

Materials and Equipment. All reactions with organometallic compounds were carried out under dry nitrogen or argon using a Vacuum Atmospheres drybox or standard vacuum line/Schlenk techniques. Solvents were purified by methods described previously.[66]

NMR spectra were recorded on either a GE QE-300 Plus (^{1}H, 300.10 MHz; ^{13}C, 75.49 MHz) spectrometer or JEOL GX-400 (^{1}H, 399.65 MHz; ^{13}C, 100.40 MHz). Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane and referenced to residual protio solvent. Optical rotations were measured on a Jasco DIP-360 polarimeter with 1 dm cell. Gas Chromatographic analyses were performed on an HP-5890 Series II Gas Chromatograph with and SE-30 capillary column. Gel permeation chromatography (GPC) analyses of saturated polymers were carried out with a Waters 150-C ALC/GPC instrument equipped with a differential refractometer and Waters Ultrastyragel 105,104,103, 500Å columns in series; the columns were eluted with toluene at 65°C and were calibrated using Shodex S-series polystyrene standards. Unless otherwise specified, all other GPC analyses were performed in methylene chloride and were obtained on an HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 micron linear mixed bed columns and a Knauer differential refractometer. The molecular weights were calibrated using calibrated using Shodex S-series polystyrene standards. DSC measurements were made on a Perkin Elmer DSC 7 thermal analyzer at a heating rate of 10°C/min from 20 to 150°C.

Rheological measurements were performed on a Rheometrics RSA II utilizing a parallel plate configuration. Stainless steel plates (12.7 x 15.9 mm) were used. The plate gap was determined both by preparing and weighing PDMS samples and using Fila Gauge (gap size ≈ 0.4mm). Experiments were performed in the linear region of the stress/strain curve with strain rates from 0.2 - 100% and frequency range of 100 - 0.10 rad•sec^{-1}.

Rheo-optical measurements were performed on a Rheometrics RSA II utilizing a parallel plate configuration. Stainless steel plates with T-support. The gap size (≈ 0.4mm) was measured using a Fila Gauge. The optical train consisted of a laser (He/Ne, $\lambda = 632.8$ nm), a polarizer (0°), a photoelastic modulator (45°, 200 KHz) and a quarter wave plate followed by the flow cell, a quarter wave plate, a polarizer (90°) and then CCD detector.

cis, *cis*-1,5-Cyclooctadiene (99+%) was obtained from Aldrich and was purified by distillation to remove traces of 4-vinyl-1-cyclohexene. Diethyl diallylmalonate (Aldrich, 98%), (-)-β-citronellene (Fluka, 90%, $[\alpha]^{20}{}_{D} = -7.7°$ ($c = 9.3$, $CHCl_3$), ca. 72% ee), *p*-toluenesulfonyl chloride (Aldrich 99+%), *p*-toluenesulfonhydrazide (Aldrich 97%) and triisopropylamine (Aldrich 98%) were used as received. *cis*-1,4-Bisacetoxy-2-butene (**10**),[19] $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1a**) [6,7] and $Cl_2(PCy_3)_2Ru{=}CHCHPh_2$ (**1b**)[5] were synthesized as described in the literature. Palladium 10% on carbon (Aldrich) and cyclohexane (Aldrich) were used as received.

4-Methylcyclopentene (6). To diethyl diallylmalonate (80g, 0.333 mol) in a 250 mL round-bottomed flask under argon was added a solution of $Cl_2(PCy_3)_2Ru{=}CHCHPh_2$ (**1**) (250 mg, 2.70 x 10^{-4} mol; 5 mL benzene). The flask was evaporated (10^{-3} Torr) for 36 h to remove ethylene (with no loss of product). The reaction flask was then back-filled with argon and fitted with a water-cooled distillation head. The crude reaction mixture was distilled (0.25 Torr, 63-75°C) to give 3-cyclopentene-1,1-dicarboxylic acid, diethyl ester (**3**); 70.0 g, 99% yield. The spectroscopic properties matched those reported in the literature. Hydrolysis and decarboxylation was performed according to literature procedure[67] to give 3-cyclopentene-1-carboxylic acid, (**4**), 36.6 g, 99% yield. Reduction to the alcohol was accomplished by adding (**4**) in 200 mL of dry THF to a solution of

$LiAlH_4$ (32g, 0.843 mol; 600 mL THF) at 0°C over 30 min. The mixture was allowed to warm to room temperature and react overnight, then quenched with 50 mL of DI water, followed by 50 mL of an aqueous 1M NaOH solution. The suspension was filtered over a coarse frit, then washed with 1 l of diethyl ether and filtrate concentrated by rotary evaporation. The resulting colorless oil was vacuum distilled (100°C) to give cyclopentene-3 methanol, (**5a**), 31.5 g, 96% overall yield from diethyl diallylmalonate. This alcohol (**5a**, 10.65 g, 0.108 mol) was converted to the tosylate by dissolving in pyridine (250 mL) with *p*-toluenesulfonyl chloride (24 g, 0.126 mol) at 0°C and allowing to react overnight. The reaction was poured onto 100g of ice and neutralized with 1M HCl. The reaction was extracted with 3 x 150 mL CH_2Cl_2. The organic layer was washed twice with DI H_2O (100 mL) then dried over Na_2SO_4 and rotary evaporated to yield a crystalline solid (**5b**) 25.9 g, 95% yield. Tosylate (**5b**) (25.9 g, 0.103 mol) was dissolved in dry diglyme (100 mL) and added *via* addition funnel to a solution of $LiAlH_4$ (5.6 g, 0.148 mol; 200 mL diglyme) at 0°C over 20 min under argon. The mixture was allowed to warm to room temperature and was stirred overnight. Using a solvent trap cooled with liquid nitrogen, 30 mL of volatiles were removed from the reaction flask by vacuum, which were shown by ^1H NMR to contain the product and diglyme. This colorless liquid was distilled (1 atm, 70-73°C) to give (**6**) 7.80 g, 88% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 1.00 (J = 6.9 Hz, 3 H), 1.8-1.95 (m, 2H), 2.25-2.45 (m, 1H), 2.45-2.55 (m, 2H), 2.6-2.8 (m, 1H), 5.63 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.78, 31.68, 40.86, 129.79. Anal. Calcd. for C_6H_{10}: C, 87.73; H, 12.27. Found C, 87.66; H, 12.37.

(R)-(+)-3-Methylcyclopentene (8). In a 100 mL round-bottomed flask, (-)-β-citronellene (42 g 0.304 mol) was degassed by three freeze-pump-thaw cycles. Under a stream of argon, $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1b**) (530 mg 6.44×10^{-4} mol) was added to the solid. A water-cooled distillation head was placed on the flask, and the reaction solution was heated to 90°C. Over 1 hour, 24.5 g of a colorless liquid was collected. The product was refluxed for 2 h in a 100 mL round-bottomed flask fitted with a water-cooled condenser to remove isobutylene, then distilled (1 atm, 72-75°C) to give (**7**) 12.2 g, 49% yield. The spectroscopic properties matched those reported in the literature: ^1H NMR (300 MHz, $CDCl_3$) δ 1.00 (J = 6.9 Hz, 3 H), 1.2-1.4 (m, 1H), 2.0-2.15 (m, 1H), 2.2-2.45 (m, 2H), 2.6-2.8 (m, 1H), 5.6-5.75 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.96, 31.94, 32.12, 39.91, 129.56, 136.96. $[\alpha]^{20}_D = +126.4°$ (c = 5.1, $CHCl_3$), lit. $[\alpha]^{20}_D = +167.4°$ (c = 5.23, $CHCl_3$);[41] ca. 76% ee. Anal. Calcd. for C_6H_{10}: C, 87.73; H, 12.27. Found C, 87.19; H, 12.52.

Polymer Synthesis. Telechelic Polyolefin: In a typical reaction, 1.5 mg (0.0018 mmol) of the ruthenium metathesis catalyst (**1b**) (dissolved in 50μl benzene) was added to a mixture of 800μl of COD, (6.5 mmol, 0.706 g) 180μl of 3-MCP (1.6 mmol, 0.136 g) and 130μl of CTA (0.82 mmol, 0.140). (Cyclic monomer/catalyst = 4500; cyclic monomer/CTA = 10). After 24h the polymerization was terminated by the addition of excess ethyl vinyl ether (20μl, 0.3 mmol). The polymer was precipitated and washed with methanol and then vacuum dried (0.73g, 74% yield). In all cases, the polymers were clear viscous oils.

^1H NMR olefinic broad peak 5.49 ppm; endgroup 2 doublets (c/t) 4.60 ppm (6.6 J_{HH}), 4.46 ppm (5.5 J_{HH}) ratio 1/3.25; allylic 2.11 ppm; homoallylic 1.37 ppm; methyl 0.97 (d, 6.0 J_{HH}) ppm.

Polymer Hydrogenation. *Using tosylhydrazide.* Polyolefin(4-methylcyclopentene) (0.24g, 4.4 mmol olefin) was dissolved in 15 mL p-xylene and 2.0 mL of tri-*n*-butyl amine. Tosylhydrazide (1.8g, 8.8 mmol) was added and the mixture was heated at reflux for 3h. The polymer was precipitated by the addition of acetone.

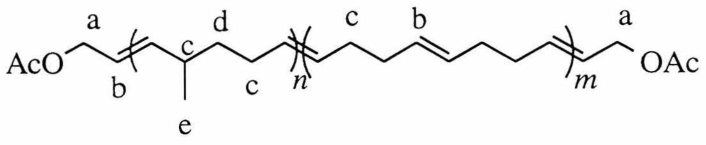
Using palladium supported on carbon. The polyolefin (400 mg) was dissolved in 15 mL cyclohexane and 40 mg of 10% Pd/C was added.[68] The vial was placed in a Parr Reactor under 60 psi H_2 and heated to 60°C for 12h. The palladium was removed by filtration through Celite with 80°C toluene as eluent . After concentration (5 mL) the polymer was precipitated into methanol and isolated in over 90% yield. All samples were white, and varied from waxy to powdered dependent on the polymer composition.

^{1}H NMR endgroup 4.00 (t, 6.4 Hz) backbone 1.36 ppm. ^{13}C NMR major peak 30.12; 37.60*(3)*, 34.89*(6)*, 33.58*(7)*, 33.28*(2)*, 30.53*(5)*, 27.95*(9)*, 27.60*(4)*, *20.14 (8?)*, 20.02*(1)*

Via the in situ generation of an active ruthenium hydrogenation catalyst. After polymerizing 1.0 - 1.5g MCP/COD with 0.2 - 5 mL solvent, ethyl vinyl ether was added and enough solvent to bring total volume to 20 mL. (Initially, this was done under an H_2 balloon, but this precaution was not necessary.) Reaction vessels were placed in Parr stainless steel reactor. (Rebuilt 2L rated with 250 psi gauge or 1L rated to 2000 psi)

The degree of hydrogenation of polymers and most small molecules was calculated from ^{1}H NMR integrations. In the case of 1- or 2-pentene, the ^{13}C NMR spectra was taken to confirm the presence of pentane, butane and hexane.

<u>Calculation of Polyolefin Composition and Molecular Weight .</u> The ^{1}H NMR spectra are used to calculate the relative incorporation of methylcyclopentene and cyclooctadiene as well as the molecular weight of the polymer (**A**). An average COD/MCP ratio is calculated comparing by the relative intensities of the methyl group (e) and homoallylic protons (d) of



A

the ring opened methylcyclopentene (5H) to both the olefinic (b) and allylic (c) protons of the backbone. The integration of (d) and (e) was set to a single MCP unit (d + e = 5).

With $n = 1$ and m is simply the ration of COD to MCP (COD/MCP). The intensity of the allylic resonance: $c = (3n + 8m) = 3 + 8*(\mathrm{COD/MCP})$

$$\mathrm{COD/MCP} = (c - 3)/8 \qquad (2)$$

Integration of the olefinic signal: $b = 2n + 4m = 2 + 4*(\mathrm{COD/MCP})$

$$\mathrm{COD/MCP} = (b - 2)/4 \qquad (3)$$

The polymer composition (mole fraction of each monomer) is calculated from the average of Eq. (2) and (3). The distinct chemical shift of the endgroup is integrated relative to the backbone protons to calculate the number average molecular weight (equation 4). [69]

$$\frac{4}{2 + 2 * n + 4 * m} = \frac{a}{b} \qquad (4)$$

Molecular weights of all samples were also measured by GPC relative to polystyrene standards.

Appendix to Chapter 2.

Table A1. Representative Syntheses of EP Copolymers[a]

Entry	Ole/ Ru	MCP conc	X_f Feed COD	X_f Incorp COD	Yield	Hydrog	M_n $x10^{-3}$	M_w $x10^{-3}$	T_g
1a	2800	.82	.509	.851	37	100	8.5	14.4	
1b	1400	.82	.509	.846	42	100	6.4	12.9	
1c	700	.82	.509	.845	47	100	5.9	11.8	
1d	2800	.47	.509	.908	25	>99	4.6	7.6	
1e	1400	.47	.509	.898	27	>99	5.1	8.1	
1f	700	.47	.509	.889	32	100	5.5	8.7	
2a	690	.82	.509	.831	55	100	9.1	13.9	
2b	620	.94	.422	.808	50	100	7.0	10.3	
2c	560	1.06	.329	.765	43	100	5.2	7.5	
2d	500	1.19	.228	.704	59	100	3.1	4.5	
2e	430	1.29	.121	.592	30	100	1.7	2.3	
2f	370	1.44	0	--	48	>99	0.68	0.86	
3a	2400	2.40	.509	.666	55	>99	10.4	19.8	
3b	2400	1.67	.509	.748	50	100	8.4	15.9	
3c	2400	1.04	.509	.823	43	100	7.2	12.8	
3d	1200	2.40	.509	.677	60	100	8.6	16.9	
3e	1200	1.67	.509	.733	--	100	7.7	15.9	
3f	1200	1.04	.509	.804	50	100	6.0	11.7	
4a	2330	2.40	.509	.667	54	>99	10.7	20.0	
4b	4650	2.40	.509	.684	54	90	9.8	19.8	
4c	23260	2.40	.509	.679	48	5	9.2	52.2	
4d	2330	1.67	.509	.737	66	100	9.2	16.8	
4e	4650	1.67	.509	.743	27	84	9.1	17.2	
4f	23260	1.67	.509	.59	39	6	7.6	14.5	

Table A1 Continued

Entry	Ole/ Ru	MCP conc	X_f Feed COD	X_f Incorp COD	Yield	Hydrog	M_n $x10^{-3}$	M_w $x10^{-3}$	T_g
5a	1980	2.40	.509	.669	45	98	54.2	103	
5b	3950	2.40	.509	.684	41	79	51.0	101	
5c	7910	2.40	.509	.669	-	-	37.6	88.6	
5d	1980	1.67	.509	.729	28	98	40.9	70.9	
5e	3950	1.67	.509	.743	-	-	44.9	88.0	
5f	7900	1.67	.509	.747	-	-	37.4	77.4	
6a	1050	2.40	.509	.644	68	#5	37.3	78.1	
6b	950	2.79	.422	.571	58	1-27	29.8	68.8	
6c	850	3.21	.329	.483	68	?	27.4	53.8	
6d	760	3.65	.228	.346	59	?	25.4	47.6	
6e	660	4.11	.119	.245	46	?	14.2	26.0	
6f	570	4.60	0	0	-	?	2.7	3.8	
7a	1400	1.67	.509	.761	62	>99	8.7	15.8	103
7b	1480	1.44	.577	.802	50	>99	11.1	21.8	109
7c	1550	1.21	.645	.814	56	100	34.3	84.4	109
7d	1620	0.99	.711	.857	46	100	39.5	77.6	114
7e	1700	0.76	.777	.902	32	100	23.9	49.4	120
7f	1770	0.54	.854	.932	-	>99	28.6	57.0	123
8a	2320	1.27	.689	.512	56	100	30.8	66.8	72
8b	2540	1.78	.597	.556	55	100	28.4	67.3	79
8c	2750	2.23	.526	.604	59	100	30.1	68.4	87
8d	2960	2.63	.470	.661	61	100	34.5	84.1	94
8e	3180	2.99	.425	.745	35	100	70.1	112	101
8f	3439	3.30	.388	.813	69	100	36.8	85.9	110
9a[a]	4070	3.54	.347	.553	55	>99	-	-	69
9b	3700	2.05	.571	.740	60	100	27.8	57.5	98
9c	3730	1.07	.762	.857	64	>99	-	-	-
9d	8340	3.23	.347	.543	50	100	28.2	52.0	71
9e	7400	1.84	.571	.768	56	>99	29.4	58.6	-
9f	7460	0.96	.762	.861	60	>99	41.2	73.1	-

Table A1 Continued

Entry	Ole/ Ru	MCP conc	X_f Feed COD	X_f Incorp COD	Yield	Hydrog	M_n $\times 10^{-3}$	M_w $\times 10^{-3}$	T_g
10a	2020	3.68	.307	.421	61	100	23.6	58.1	-
10b	1960	2.05	.571	.702	69	100	41.8	88.0	96
10c	2160	1.02	.780	.862	87	100	40.0	82.9	114
10d	4040	3.35	.307	.457	28	100	17.2	57.4	61
10e	3920	1.84	.571	.733	54	100	17.3	70.0	98
10f	4330	0.92	.780	.872	62	100	22.2	87.9	116
11a	2490	2.45	.400	.596	53	100	9.8	52.9	86
11b	1960	1.42	.571	.766	63	100	43.7	87.6	103
11c	2160	0.71	.780	.895	72	100	40.6	88.5	114
11d	4980	2.3	.400	.618	46	100	7.20	18.2	86
11e	3920	1.31	.571	.817	52	100	16.3	31.3	105
11f	4330	0.66	.780	.893	36	100	20.3	42.0	120
12a	2290	2.45	.307	.520		100	28.6	71.1	67
12b	2220	1.42	.571	.745		100	40.6	84.3	99
12c	2450	0.71	.780	.878		100	54.5	104.7	116
12d	4580	2.63	.307	.572		100	35.2	89.0	74
12e	4440	1.53	.571	.774		100	57.9	116.7	103
12f	4910	0.77	.780	.894		100	73.4	136.6	117

Table A1 Continued

Entry	Ole/ Ru	MCP conc	X_f Feed COD	X_f Incorp COD	Yield	Hydrog	M_n $x10^{-3}$	M_w $x10^{-3}$	T_g
13a	1950	3.68	.307	.451	43	100	56.8	122.7	64
13b	2030	3.31	.372	.520	50	100	65.3	134.5	72
13c	2110	2.95	.437	.585	58	100	63.8	130.1	80
13d	2190	2.58	.504	.647	64	100	62.0	131.4	88
13e	2270	2.21	.571	.710	73	100	65.2	138.2	95
13f	2330	1.84	.640	.756	69	100	74.0	165.0	101
13g	2410	1.47	.709	.810	74	100	79.5	161.4	106
13h	2490	1.10	.780	.859	68	100	67.5	144.4	112
13i	2570	0.74	.852	.906	79	100	71.2	151.6	118

[a] Unless otherwise noted, reactions were polymerized, quenched with ethyl vinyl ether, diluted with 20 mL CH_2Cl_2 and pressurized to 800 psi at 200°C for 24 hours. Runs 1a-11f were polymerized for 24 hours. 12a-f were polymerized 72 hours. 13a-f were polymerized 24 hours. 9a-f were hydrogenated for 60 hours. 10a-13f were hydrogenated 48-72 hours.

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(51) Homopolymers of cyclooctadiene (COD/Ru ≈ 2000) went from M_n 50K to 80K.

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(68) When the hydrogenated polymer is soluble in cyclohexane, bubbling hydrogen through the solution at lower temperatures also affords complete hydrogenation.

(69) Using the average (m/n) calculated from equations 2 and 3, the average number of methylcyclopentenes per chain is solved for.

$$n = \frac{4 * b - 2 * a}{a * (2 + 4 * (m / n))}$$

Chapter 3.

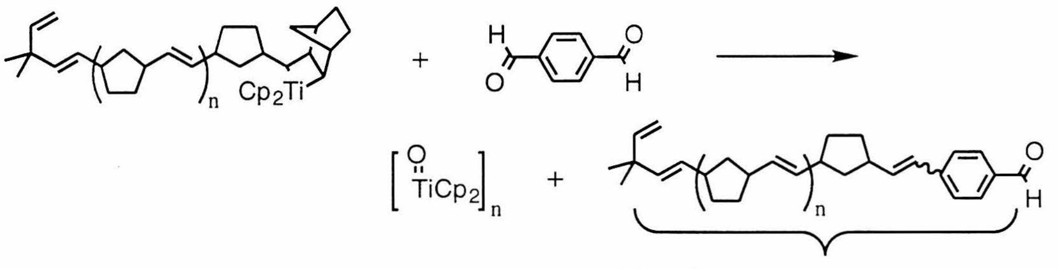
Reaction of Ruthenium Carbenes with Vinyl Ethers.

Abstract The regiospecific and irreversible reaction of ruthenium carbenes $(PR_3)_2Cl_2RuCHR'$ (R = PPh_3 or PCy_3, R' = Ph, $CHCPh_2$, $(CH_2)_4CH_3$ or polynorbornene) with electron rich vinyl ethers (EtOCH=CHR, R = H (**3**), CH_3 (**4**) $(CH_2)_5CH_3$ (**5b**), CH_2Ph (**6b**) or Ph (**7b**)) was investigated. A series of substituted vinyl ethers with varying steric properties were synthesized and reacted with metathesis active ruthenium carbenes. These reactions were monitored by ^1H NMR spectroscopy and kinetic data was obtained under pseudo first order conditions ($[\text{vinyl ether}]_0/[Ru]_0$ 10/1). The half lives ($t_{1/2}$) for the metathesis reactions were calculated from the observed kinetic data for [vinyl ether] = 0.15 M. ^1H NMR data indicates that the observed metathesis was regiospecific and irreversible yielding a heteroatom stabilized alkylidene species (L_nRu=CHOEt). Ruthenium catalysts possessing electron rich phosphines were more reactive and underwent metathesis with each substrate. $(PCy_3)_2Cl_2RuCH(CH_2)_4CH_3$ (**2d**) reacts too rapidly with (**3**) and (**4**) to obtain kinetic data. At 20°C $t_{1/2}$ <1.5 min. and 2.2 min. for (**5b**), and *cis*- (**6b**) respectively. At 40°C, the calculated half lives are <0.5 min., 8.9 min. and 37.6 min. for *cis*- (**6b**), *trans*- (**6b**) and *cis*- (**7b**) respectively. Coordination of a heteroatom from the polymer backbone (poly(cyclobutene) with pendant amide or ether groups) significantly inhibited metathesis even at elevated temperatures. The ruthenium complexes with triphenylphosphine ligands were less reactive and $(PPh_3)_2Cl_2RuCH(C_7H_{10})_n$ (**1c**) reacts only with (**3**) at 20°C ($t_{1/2}$ 5.8 min.). At 40°C metathesis was observed with (**3**), (**4**), (**5**) and *cis*- (**6b**) with calculated $t_{1/2}$ of 4.0 min., 7.2 min., 14.8 min. and 33.7 min. respectively. Metathesis with *trans*- (**6b**) occurred on the same time scale as decomposition and no reaction with *cis*- (**7b**) was observed.

Introduction

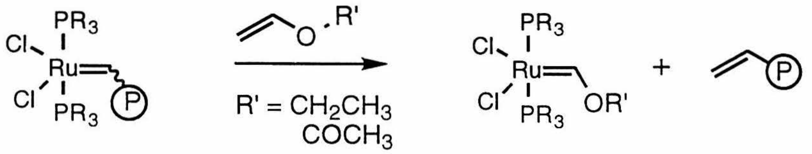
Rational control of molecular architecture is one of the ultimate goals in polymer science. Living polymerizations, i.e. where no chain transfer or chain termination occurs, provide several routes to polymeric materials of predictable and tunable structure. One synthetic approach for the efficient synthesis of well defined diblock and triblock copolymers is the consecutive addition of different monomers.[1-9] A second approach is to change the mechanism of polymerization by the controlled termination of a living polymerization followed by a second initiation and polymerization sequence.[10,11]

Living ring-opening metathesis polymerizations (ROMP) is one methodology for controlled structure.[1-4] There are several examples of block copolymer synthesis by sequential monomer addition[12,13] and control of morphologies for new materials.[14] Metathesis initiators have also been used in syntheses of copolymers via a change of mechanism.[15,16] Early transition metal carbenes are highly oxophilic and undergo a Wittig type reaction (Eq. 1).[4,17,18] Norbornene was polymerized with a titanacylcobutane initiator and endcapped with terephthaldehyde.[15] Subsequent group transfer polymerization of a silyl enol ether (and hydrolysis to poly(vinyl alcohol)) afforded a block copolymer not accessible from a single polymerization method.



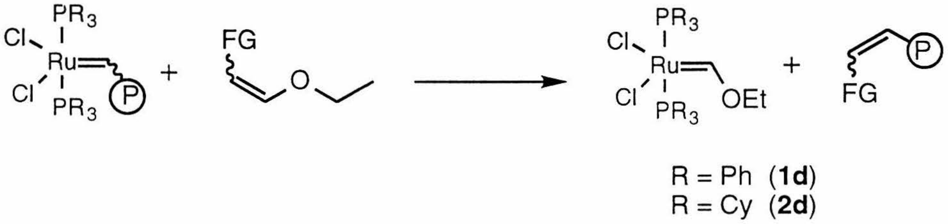
(1)

Recently developed well defined ruthenium based catalysts are very functional group tolerant,[19-21] and preferentially react with olefins while in the presence of numerous functionalities. Notable exceptions to this trend are the reactions with vinyl ethers or vinyl acetates (Eq. 2).



(2)

Reaction with these electron rich olefins is quantitative and regiospecific and the resulting ruthenium Fischer like carbenes are stable in solution for days even in the presence of strained olefins such as norbornene. Termination of the propagating polymer chain with ethyl vinyl ether or vinyl acetate transfers a methylene group to the polymer chain end. This functionality limits future modification of the polymer termini. Therefore, it is desirable to develop a methodology which will allow the introduction of a functional group of greater synthetic utility (Eq. 3).

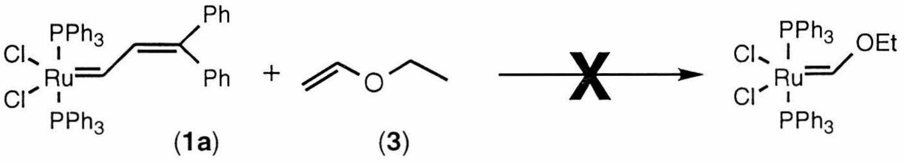


(3)

To this end, this chapter describes the reactivity of sterically demanding vinyl ethers with various ruthenium based carbene species.

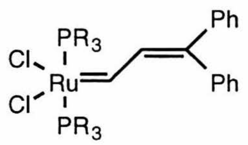
Results and Discussion.

The intent of the investigation, was to determine conditions which would irreversibly cleave the propagating ruthenium carbene from a polymer chain, and trap the metal center in an unreactive form. Initial investigations of the reaction of ruthenium initiators (**1a**) with ethyl vinyl ether yielded no new observable carbene (Eq. 4).[22]

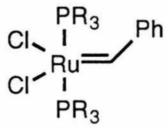


(4)

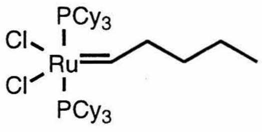
Is well known however that (**1a**) is stabilized by the conjugated diphenyl vinyl group with the related carbene (**1b**) being much more reactive. Although the rate of propagation is necessarily identical for (**1a**) and (**1b**), the rates of initiation of (**1b**) is 3 orders of magnitude faster.[21] A similar reactivity pattern was observed for the (**2a**) and (**2b**).[21]



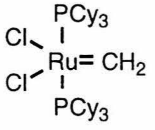
(**1a**) R = Ph
(**2a**) R = Cy



(**1b**) R = Ph
(**2b**) R = Cy

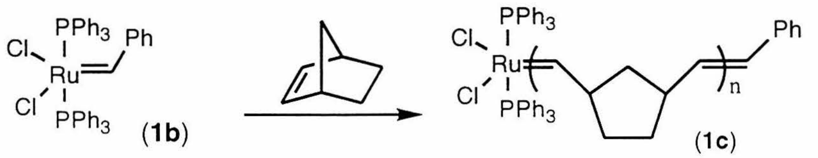


(**2c**)



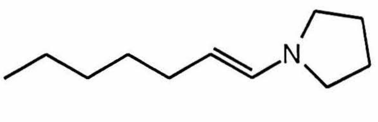
(**2e**)

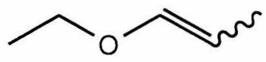
Therefore, in order to better model the termination of polymerizations, we surveyed the reactivity of benzylidene based ruthenium carbenes. In the case of the triphenylphosphine based benzylidene catalysts, the carbene was initiated with 10 equivalents of norbornene (**1c**) (Eq. 5). The cylcohexyl derivative (**2b**) was not completely initiated under the same conditions, therefore the more reactive pentylidene derivative (**2c**)[21] was independently synthesized and used for the kinetic studies.



(**1b**) (**1c**) (5)

We began our investigation of the reactivity of carbenes towards several electron rich olefins[22] including N-1-heptenyl pyrrolidine and commercially available 1-ethyl-1-propenyl vinyl ether (**4**).

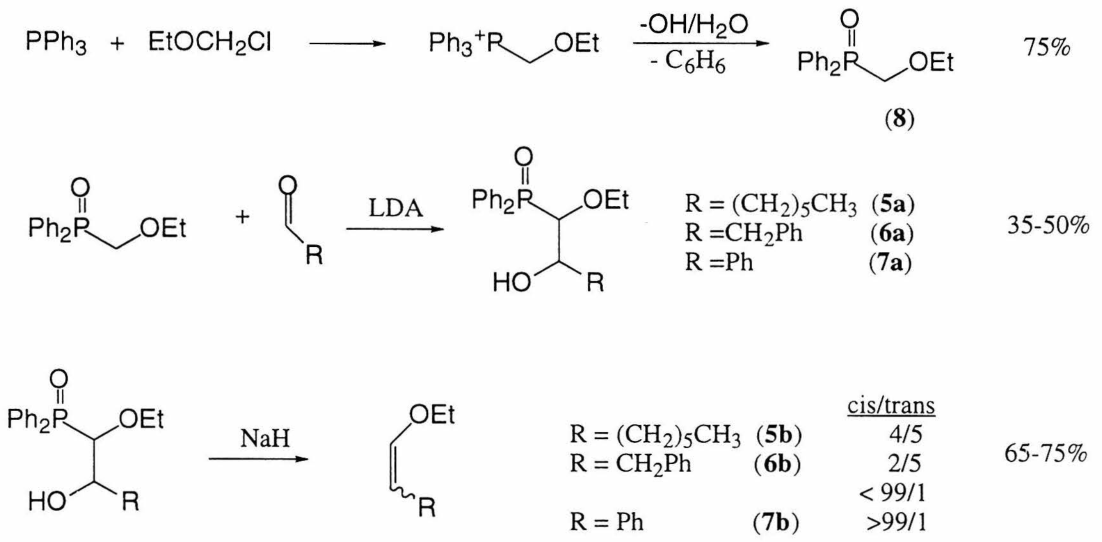




(**4**)

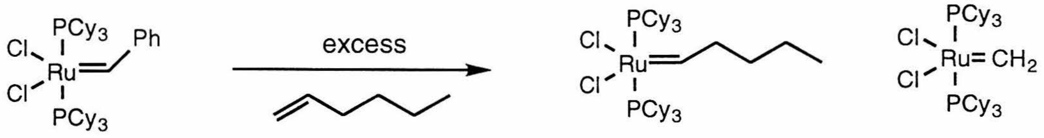
Analogous to the reactivity of (**1a**) with ethyl vinyl ether, neither the eneamine nor ethyl propenyl ether cleanly (or completely) reacts to form a new carbene. In contrast, 1-ethyl-1-propenyl ether react cleanly and completely with (**2a**) in 2.5 h 40°C to give a new carbene species at δ14.5 ppm. Although reaction of (**2a**) with the eneamine cleanly provides a new carbene peak at δ13.7 ppm, the reaction does not proceed to completion. Subsequent experiments focused on a the reactivity of substituted vinyl ethers. The longer chain octenyl vinyl ether (**5b**), phenethyl vinyl ether (**6b**) and benzyl vinyl ether (**7b**) were synthesized via the Horner Wittig reaction (Scheme 1).[23]

Scheme 1. Synthesis of Vinyl Ethers.



Reaction of triphenylphosphine and chloromethyl ethyl ether affords ethoxymethyldiphenylphosphine oxide (**8**). Condensation with an aldehyde yields a diphenyl phosphinoyl alcohol (**5a-7a**). The ensuing elimination of diaryl phosphinic acid yields vinyl ethers (**5b-7b**). In some cases (**6a**, **7a**) the phosphinoyl alcohol was fractionally recrystallized to diastereomeric purity. The elimination of phosphinic acid from racemic (**6a**) occurs with net retention of configuration to provide exclusively *trans*- (**6b**). Eliminations from a mixture of diastereomers provided *cis/trans* mixtures of the vinyl ethers. These types of substrates could be easily substituted to incorporate other functionalities for polymer modification.

In all of the following cases, the reactions are regiospecific and *no methylidene was observed.* Previous experiments indicate that for the metathesis of terminal olefins (propene, n-butene and n-hexene), the thermodynamic product is the methylidene $((PCy_3)_2Cl_2RuCH{=}CH_2)$ (**2e**) (Eq. 6).[21]



(6)

(**2b**) (**2c**) (**2e**)

kinetic product

thermodynamic product

In contrast, methylidene was never observed during the reaction of ethyl vinyl ether. Analogously, metathesis with the other vinyl ethers exclusively resulted in the ethoxy substituted carbene (**1d** or **2d**). Therefore, the reaction of the ruthenium center with the vinyl ether is either regiospecific and irreversible or the methylidene is significantly more reactive towards vinyl ether than the starting carbene. The results of this investigation and known reactivity trends support the former scenario. Kinetic studies were performed under pseudo-first order conditions with an approximate 10-15 fold excess of vinyl ether and monitored to at least 3 half lives. Unless otherwise stated, the rate constants were calculated from 3 or more runs. All concentrations were calculated from ^1H NMR integrations. Relaxation delays of at least delays of at least three times t_1 were used to avoid saturation effects.

Tricyclohexylphosphine Ruthenium Carbenes.

The cyclohexyl phosphine alkyl carbene is very active and reacts completely with several of the vinyl ether substrates at 20°C. The starting carbene peak of (**2c**) is observed at 20.0 ppm in C_6D_6. Complete formation a new carbene (**2d**) (s, 14.55 ppm). is observed within 2 minutes of the addition of either ethyl vinyl ether (**3**) or ethyl propenyl ether (**4**). Kinetic data was obtained because the reactions were too rapid. Reactions with sterically demanding vinyl ethers (9.5 eq) (**5b**) and (**6b**) are slower, but proceed to completion at 20°C in 5 and 10 minutes respectively (Fig 1).

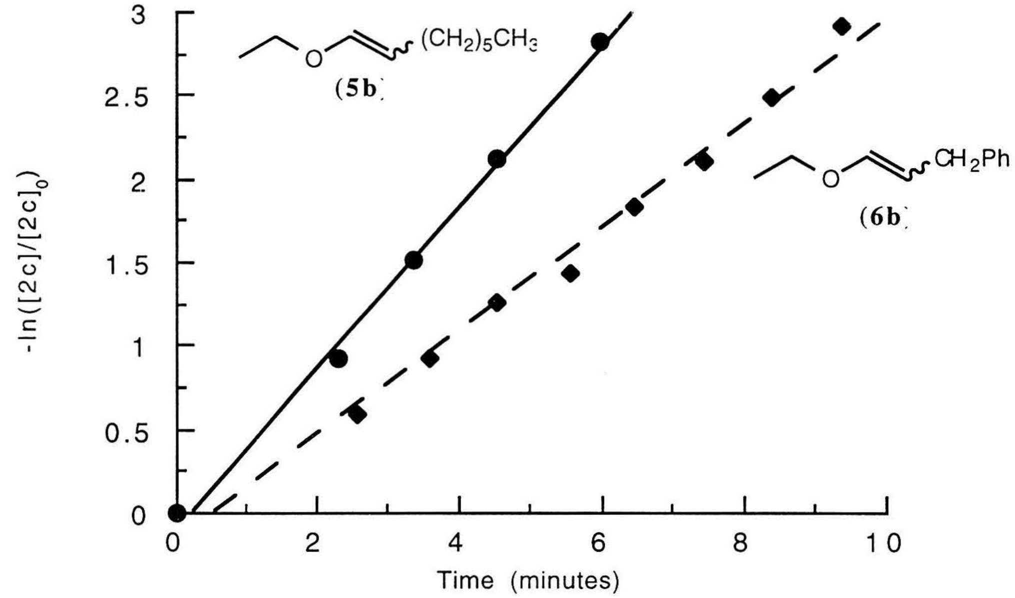


Figure 1. Reaction of $(PCy_3)_2Cl_2Ru{=}CH(CH_2)_4CH_3$ with vinyl ethers (**5b**) and (**6b**) at 20°C in C_6D_6. (**5b**) 9.6 eq. *cis* isomer (15.3 c+t): $k_{obs} = -0.0726 + 0.481(t)$ $r^2 = 0.996$; (**6b**) 9.5 eq. *cis* isomer (20 c+t): $k_{obs} = -0.146 + 0.311(t)$ $r^2 = 0.989$

A *cis/trans* mixture of (**6b**) (4.2 eq *cis*; 15.2 eq. total) reacts rapidly at 40°C and is complete in under 7 minutes. Interestingly, the independently synthesized *trans* isomer of (**6b**) is much less reactive (Figure 2), which is consistent with previous observations.[24-27] The sluggish reactivity of *trans*-(**6b**) suggests that reaction of the *cis* isomer dominates the observed reaction of (**2c**) with the *cis/trans* mixture of (**6b**) at 40°C. Metathesis with benzyl vinyl ether (**7b**) (15.5 eq) is significantly slower but remains first order to 90% conversion (Fig 2). The half lives of metathesis with vinyl ether to obtain (**2d**) were estimated from the observed rate constants (Table 1) (pseudo first order conditions; [vinyl ether] = 0.15 M).

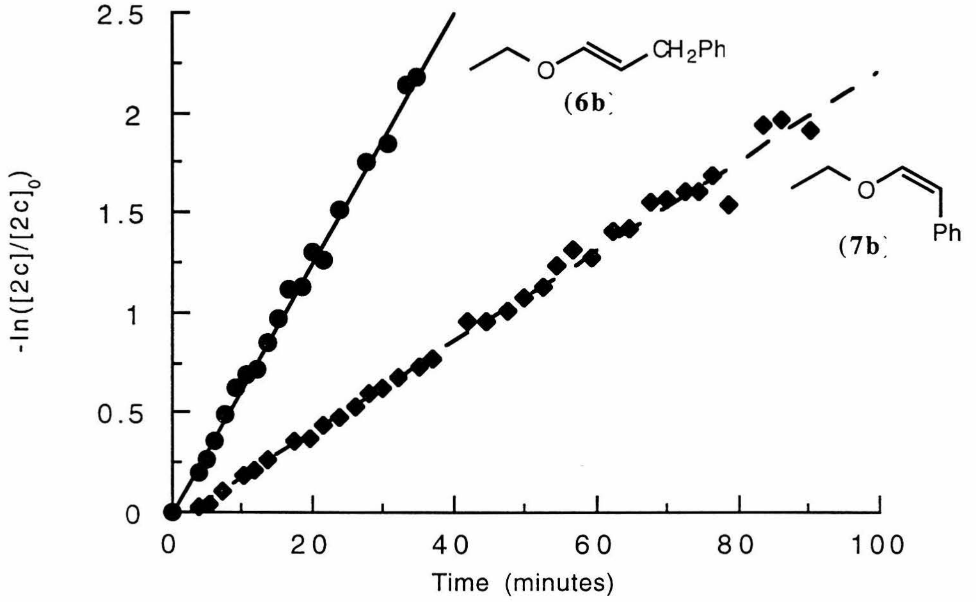


Figure 2. Reaction of $(PCy_3)_2Cl_2Ru{=}CH(CH_2)_4CH_3$ with vinyl ethers *trans*- (**6b**) and *cis*- (**7b**) at 40°C in C_6D_6. (**6b**) 15.1 eq. *trans* isomer; $k_{obs} = -3.31e\text{-}4 + 0.631(t)$ $r^2 = 0.996$; (**7b**) 15.5 eq. *cis* isomer; $k_{obs} = -0.0451 + 0.0227(t)$ $r^2 = 0.993$

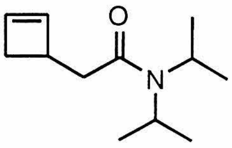
Table 1. Reactions of $(PCy_3)_2Cl_2Ru{=}CH(CH_2)_4CH_3$ (1d).

Vinyl Ether	Temp	Calculated $t_{1/2}$[a]	k	Std Dev
5b	20	<1.5 min	>3[c]	
6b (cis)	20	2.2 min	2.09	.0107
6b (cis)	40	<0.5 min	>9[c]	
6b (trans)	40	8.9 min	0.516	.067
7b	40	37.6 min	0.123	.0893

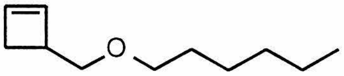
[a] The $t_{1/2}$ was calculated for a pseudo first order rate law where [Ru] = 0.015 M; 10 equivalents vinyl ether (0.15M). $t_{1/2} = \ln(2)/k_{obs}$ $k_{obs} = k(0.15M)$

[b] rate constant in $M^{-1}min^{-1}$ $k = k_{obs}/[ve]$ [c] estimated from single run

After establishing the utility of vinyl ethers for cleaving the living chain end from a alkyl carbene, we were interested in a related system where metathesis activity is retarded by intramolecular chelation of a substrate heteroatom. After initiation with (**2c**), living polymerizations of (**9**) and (**10**)



(**9**)



(**10**)

proceed with intramolecular heteroatom chelation and concomitant loss of one equivalent of phosphine.[28] The reaction of (**5b**, 13 eq. *cis*) with (**2c**) initiated with (**9**) at 40°C afforded less than 5% (**2d**) after 30 minutes. The ether cyclobutene (**10**) proceeded to only 15% conversion after 60 minutes at 40°C (9.8 eq. *cis* **5b**). The intramolecular coordination of the heteroatom containing side group significantly decreases the rate of polymerization[28] and prevents efficient metathesis with the sterically demanding vinyl ether (**5b**).

Triphenylphosphine Ruthenium Carbenes.

Triphenylphosphine substituted ruthenium carbenes reacts much more slowly than the corresponding cyclohexyl derivatives. In fact, no new carbene is observed from the reaction of the highly conjugated diphenyl vinylidene (**1a**) and ethyl vinyl ether.[22] The uninitiated phenyl carbene (**1b**) does not react completely with ethyl vinyl ether, but resonances attributable to new carbene (**1d**) (t, 14.40 ppm, 6.4 J_{HP}) were observed. The initial rate constant was estimated at 0.4 $M^{-1}min^{-1}$, but the carbene signals begin to disappear before complete conversion to (**1d**). In contrast, initiation of (**1b**) with norbornene with subsequent addition of ethyl vinyl ether (20°C) affords complete conversion to the new carbene (**1d**) in 20 minutes (Figure 3). The metathesis at 40°C is more facile, and is complete in less than 10 minutes (Figure 3).

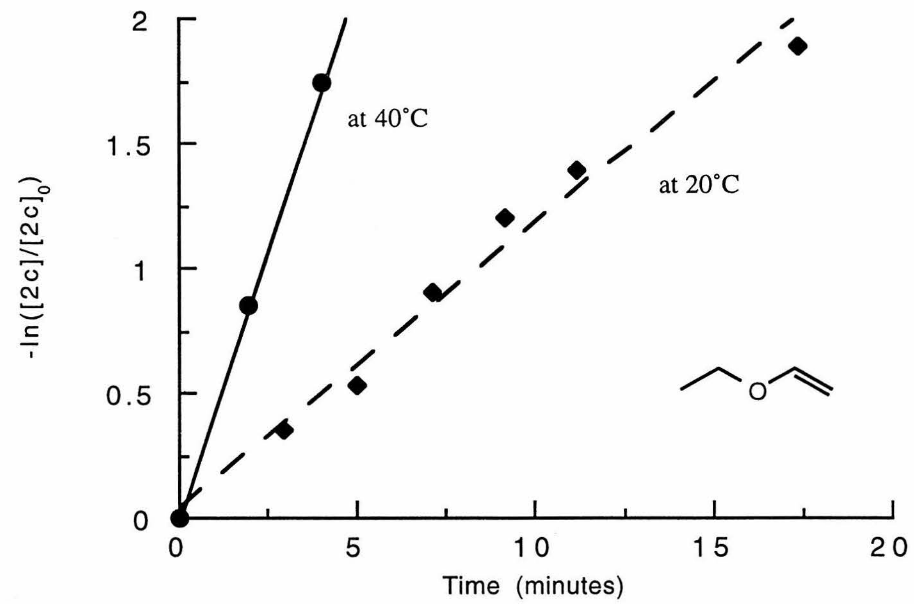


Figure 3. (**1b**) was completely initiated with 20 eq. norbornene in C_6D_6 before addition of (**3**). 21.0 eq. at 40°C: $k_{obs} = -7.54e\text{-}3 + 0.436(t)$ $r^2 = 0.999$; 15.5 eq. at 20°C: $k_{obs} = -0.0446 + 0.113(t)$ $r^2 = 0.982$

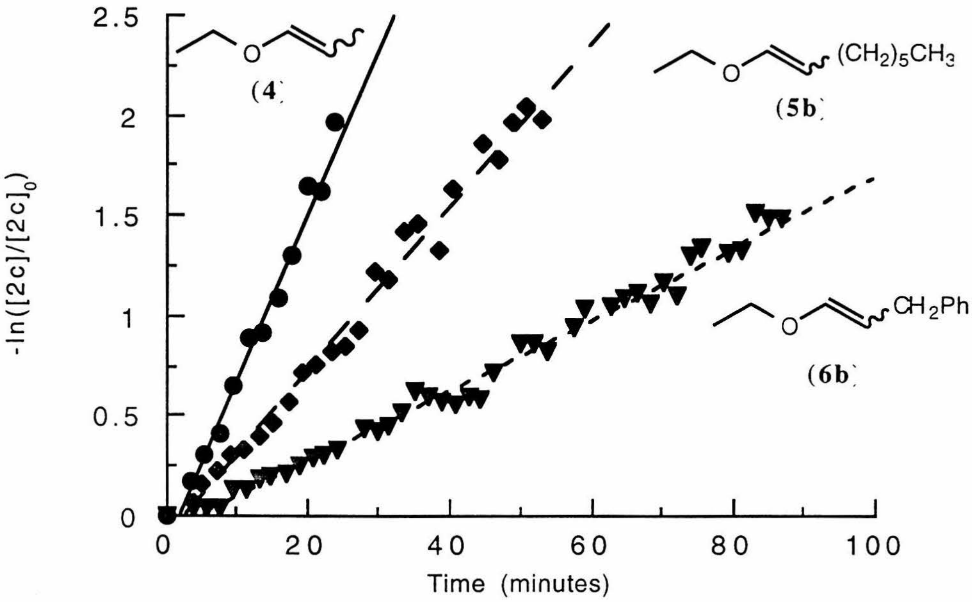


Figure 4. (**1b**) was completely initiated with 20 eq. norbornene in C_6D_6 before addition of (**4-6b**). Reactions were monitored at 40°C. (**4**) 13.2 eq. *cis* (17.7 c+t); $k_{obs} = -0.119 + 0.0825(t)$ $r^2 = 0.982$; (**5b**) 9.6 eq. *cis* (15.3 c+t); $k_{obs} = -0.0892 + 0.0412(t)$ $r^2 = 0.986$; (**6b**) 9.7 eq. *cis* (20.4 c+t); $k_{obs} = -0.0742 + 0.0178(t)$ $r^2 = 0.988$

The more sterically demanding vinyl ethers (**4-7b**) did not undergo metathesis with (**1c**) at 20°C but the ethoxy carbene (**1d**) was generated at 40°C using (**5b**) and (**6b**) (Fig 4). The estimated half lives (pseudo first order, [vinyl ether] = 0.15 M) approximately doubled for each increase in the sterics of the vinyl ether EtOCH=CHR, R= H, CH_3, $(CH_2)_5CH_3$, CH_2Ph (Table 2). There was no observable reaction of (**1c**) with *trans-* (**6b**) or (**7b**). The conjugated triphenylphosphine ruthenium carbenes (**1a**-**b**) do not react completely with any of the acyclic vinyl ethers. The initiated (unconjugated) carbene (**1c**) does undergo facile metathesis with ethyl vinyl ether at 20°C and (**4**, **5b**, and *cis-* **6b**) at 40°C. More sterically demanding vinyl ethers do not undergo complete metathesis with (**1c**).

Table 2. Reactions of $(PPh_3)_2Cl_2Ru{=}CH(C_7H_{10})_n$ (2d).

Vinyl Ether	Temp	Calculated $t_{1/2}$[a]	k[b]	Std Dev
3	20	5.8 min	0.791	.0248
3	40	4.0 min	1.15[c]	
4	40	7.2 min	0.6421	.0421
5b	40	14.8 min	0.3120	.0291
6b	40	33.7 min	0.1371	.0232

[a] The $t_{1/2}$ was calculated for a pseudo first order rate law where [Ru] = 0.015 M; 10 equivalents vinyl ether (0.15M]). $t_{1/2} = \ln(2)/k_{obs}$ $k_{obs} = k(0.15M)$

[b] rate constant in $M^{-1}min^{-1}$ $k = k_{obs}/[ve]$

[c] estimated from single run

Conclusions.

We have demonstrated the efficient chain termination of ruthenium based polymerizations. The cyclohexyl phosphine derivatives are more reactive than the corresponding aryl phosphine carbenes. Furthermore, the initiated carbenes were significantly more reactive than the conjugated starting carbenes. The cyclohexylphosphine carbene (**2c**) underwent metathesis with all surveyed vinyl ethers, but the aryl phosphine derivative (**1c**) reacted only with the less sterically demanding substrates (**3**), (**4**), (**5b**), and (*cis*- **6b**). In all observed cases the reaction of a vinyl ether with a ruthenium carbene followed the reactivity pattern of: EtOCH=CHR; R = H > CH_3 > *cis*- CH_2Ph > *trans*-CH_2Ph > *cis*-Ph. Prior to this investigation, cleavage of a ruthenium center from a propagating chain end was limited to that of a methylene transfer to the polymer terminus. We have demonstrated the transfer of large and more structurally complex substituents to a growing polymer chain. Furthermore, we have developed a straightforward synthetic route to a family of vinyl ether based on a parent aldehyde.

Experimental Section.

Materials and Equipment. All reactions with organometallic compounds were carried out under dry nitrogen or argon using a Vacuum Atmospheres drybox or standard vacuum line/Schlenk techniques. NMR spectra were recorded on a JEOL GX-400 (^{1}H, 399.65 MHz; ^{13}C, 100.40 MHz; ^{31}P, 161.85 MHz). Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane and referenced to residual protio solvent. Phosphorus shifts are referenced to an external 85% H_3PO_4 standard.

Ruthenium carbenes[20] and cyclobutenes[28] were synthesized as described in literature. Norbornene was vacuum transferred from sodium. Solvents were purified by methods described previously.[29] Triphenylphosphine and chloromethyl ether were used as received. Diisopropyl amine, heptaldehye, benzaldehyde and acetaldehyde were distilled before use.

Syntheses of (**5**)-(**8**) modified from literature procedures.[23]

Ethoxymethyldiphenylphosphine Oxide (**8**). Triphenylphosphine (48g, 183 mmol) and chloroethyl ether (19.0g, 1.25eq) were heated in 200 mL dry benzene at 50°C for 72h. The white precipitate of ethoxymethyltriphenylphosphinium chloride was filtered off and washed with ether. This was heated in 100 mL of 30 wt% with sodium hydroxide water for 3h, and the benzene was distilled off. After cooling, the product was extracted into chloroform (3 X 80mL) and dried by rotary evaporation. After recrystallization from ethylacetate 36g of (**5**) was isolated. A second crop of crystals (10g) was collected for an overall yield of 92%. *^{31}P NMR:* 27.57 ppm; *^{1}H NMR:* 1.06 ppm (t, 6.8 Hz, 3H); 3.54 (q of d, 6.96 Hz, 2.26 Hz, 2H); 4.19 ppm (d of d, 6.6 Hz, 2.2Hz, 2H). *^{13}C NMR:* 14.87, 68.57, 69.46, 69.52, 69.62, 128.43, 128.54, 131.06, 131.44, 131.53, 132.05. Calculated MH$^+$ 261.104443; found 261.106804.

1-Diphenylphosphinoyl-1-ethoxyoctane-2-ol. **(5a)** Diisopropyl amine (2.65g, 26.2 mmol) was cooled to -78°C in 100mL of THF and n-Butyl lithium (15 mL, 24.0 mmol) was added. The solution was warmed to 0°C and ethoxymethyldiphenylphosphine oxide (**5**) (5.0g,19.2 mmol) dissolved in 20 mL dry THF was added via cannula. Heptaldehyde (2.6g, 23.0 mmol) was dissolved in 10 mL THF and added via cannula to the cooled solution. The solution was warmed to room temperature and then added to 200 mL of saturated ammonium chloride. The mixture was extracted with ether (3 X 100mL). The ether layers were combined, dried with magnesium sulfate and dried by rotary evaporation. After column chromatography (15/85 ethylacetate/petroleum ether) and crystallization the product was obtained in 53% yield (3.8g) as a mixture of diastereomers. *^{31}P NMR:* 33.11, 29.71 ppm. *^{1}H NMR:* 1.0 (m, 3H); 1.17-1.20 (m, 3H); 1.89-1.34 (m, 8H); 3.28,3.69 (m, 2H)(diastereomeric OCH_2);..3.5 (d, **??**) 3.34-3.40 (m) diastereomeric 1H (HOC<u>H</u>R); 3.95 (d of d 5.84, 8.8 Hz, 1H); 4.07 (q, 1H); 4.14-4.16 ppm (m,1H); 4.52 (bs, 1H); 7.44-7.5 (m, 6H); 7.63-7.76 (m, 6H); 7.79-7.87 (m, 4H); 7.96-8.03 (m, 2H); 8.17-8.24 (m, 2H). *^{13}C NMR:* 14.0, 15.27, 22.54, 25.21, 25.81, 28.97, 29.33, 31.63, 31.76, 33.56, 33.66, 34.00, 34.06, 69.62, 69.68, 69.92, 69.97, 71.21, 71.73, 81.57, 81.7, 82.42, 82.55, 128.21, 128.29, 128.40, 128.48, 128.60, 131.12, 131.26, 131.35, 131.96, 132.04, 132.13, 132.56, 132.65. Calculated MH^+ 375.208909; found 375.210006.

1-Diphenylphosphinoyl-1-ethoxyoctane-3-phenyl-propan-2-ol **(6a)**. Diisopropyl amine (4.2g, 41.9 mmol) was cooled to -78°C in 100mL of THF and n-Butyl lithium (38.4 mmol) was added. The solution was warmed to 0°C and ethoxymethyldiphenylphosphine oxide (**5**) (8.0g, 30.5 mmol) dissolved in 30 mL dry THF was added via cannula. Acetaldehyde (4.4g, 36.6 mmol) was dissolved in 10 mL THF and added via cannula to the cooled solution. The solution was warmed to room temperature and then added to 200 mL of saturated ammonium chloride. The mixture was extracted with ether (3 X 100mL). The ether layers were combined, dried with magnesium sulfate and dried by rotary evaporation. After crystallization from ethyl acetate/hexanes, the product was obtained in 40% yield (4.7g) as a mixture of diastereomers. In an subsequent synthesis, 10 % of the crude product did not redissolve in diethyl ether yet was identified as pure (**6a**). Based on the subsequent elimination product (trans) it has been assigned as a mixture of (S,R) and (R, S) diastereomers. *^{31}P NMR:* 31.90 ppm *^{1}H NMR:* 1.03 (t, 6.96 H, 3H); 2.74, 3.04 diasteromeric CH_2Ph (vicinal J_{HH} 2 Hz, 9.15 Hz, geminal J_{HH} 13.8 Hz, 2H); 3.10-3.17 (m, 1H); 3.52-3.59 (m, 1H); 3.98 (d of d, 3.98 Hz, 2- 6 Hz, 1H); 4.20-4.27 (m, 2H); 7.17-7.28 (m, 5H); 7.43-7.58 (m, 6H); 7.80-7.85 (m, 2H); 8.04-8.09 (m, 2H). *^{13}C NMR:* 15.20, 39.74(d),69.76, 69.78, 72.63, 72.67, 81.49, 82.34, 126.10, 128.09, 128.22, 128.34, 128.40, 128.52, 129.40, 131.17, 131.26, 131.73, 132.06, 132.38, 132.46, 132.67, 138.39. Calculated MH^+ 381.161958; found 381.163892.

2-Diphenylphosphinoyl-2-ethoxyoctane-1-phenyl-ethan-1-ol (**7a**). Diisopropyl amine (2.65g, 26.2 mmol) was cooled to -78°C in 100mL of THF and n-Butyl lithium (15 mL, 24.0 mmol) was added. The solution was warmed to 0°C and ethoxymethyldiphenylphosphine oxide (**5**) (5.0g,19.2 mmol) dissolved in 20 mL dry THF was added via cannula. Benzaldehyde (2.4g, 23.0 mmol) was dissolved in 10 mL THF and added via cannula to the cooled solution. The solution was warmed to room temperature and then added to 200 mL of saturated ammonium chloride. The mixture was extracted with ether (3 X 100mL). The ether layers were combined, dried with magnesium sulfate and dried. After crystallization from ethyl acetate the product was obtained in 35% yield (1.2g). *^{31}P NMR:* 30.52 ppm. *^{1}H NMR:* 0.84 ppm (t, 6.96 Hz, 3H); 2.92-3.06 (m, 2H); 4.17 ppm (m, 1H); 4.31 (d, 5.16 Hz, 1H); 5.23 (m, 1H); 7-8 ppm (m, 15H). *^{13}C NMR:* 15.01,69.91, 69.97, 71.95, 82.83, 83.67, 126.26, 127.40, 127.91, 128.04, 128.16, 128.60, 128.71, 131.07, 131.16, 131.77, 131.86, 132.07, 140.88, 140.97. Calculated MH$^+$ 367.146308; found 367.146385.

(5b) *1-Ethoxyoct-1-ene***.** 1-Diphenylphosphinoyl-1-ethoxyoctane-2-ol (**6a**) (3.75g, 10.0 mmol) was dissolved in 30 mL dry THF, and NaH (0.30g, 13.0 mmol) was added. After filtering over celite the THF was evaporated and the product was distilled under vacuum and obtained in 60% yield (0.90 g) as a mixture of isomers cis/trans 5/3.
mixture of isomers (39% trans (J_{HH} 12.44 Hz), 61% cis (J_{HH} 6.24 Hz)). d=0.798 g/mL *^{1}H NMR:* *trans isomer:* 0.86 ppm (t, 6.6 Hz 3H); 1.22-1.3 (m, 13H); 3.70 ppm (q, 6.96 Hz 2H); 4.74 ppm (m, 1H); 6.19 ppm (d, 12.44 Hz, 1H); *cis isomer:* 0.86 ppm (t, 6.6 Hz 3H); 1.22-1.3 (m, 13H); 3.75 ppm (q, 6.96 Hz 2H); 4.32 (q, 6.96 Hz, 1H); 5.90 ppm (d, 6.24 Hz, 1H); *^{13}C NMR:* 14.07, 14.78, 15.24, 22.65, 23.94, 27.76, 28.69, 28.93, 29.81, 30.73, 31.74, 64.57, 67.40, 104.42, 107.22, 144.42, 144.42, 145.87. Calculated MH$^+$ 156.151415; found 156.151834.

(6b) *3-Ethoxy-1-phenylprop-2-ene* *or* *1-Ethoxy-3-Phenylprop-1-ene.* 1-Diphenylphosphinoyl-1-ethoxyoctane-3-phenyl-propan-2-ol (**6b**) (1.80g, 4.7 mmol) was dissolved in 30 mL dry THF, and NaH (0.28g, 11.8 mmol) was added. After filtering over celite the THF was evaporated and the product was distilled under vacuum and obtained in 65% yield (0.50 g) as a mixture of isomers (cis/trans: 1.1/1). The pure trans isomer was similarly obtained from diastereomerically pure (**6b**). d =0.93 g/mL *^{1}H NMR:* 1.39 ppm (t, 6.96 Hz, 3H); 3.37 ppm (d, 7.32 Hz, 2H); 3.84 (q, 6.96 Hz, 2H); 5.05 (d of t, 12.44 Hz, 7.32 Hz, 1H); 6.46 (d, 12.44 Hz, 1H); 7.39-7.42 (m, 3H); 7.39-7.42 (m, 2H). *^{13}C NMR:* 14.74, 34.05, 64.60, 102.85, 125.86, 128.46 (doublet??), 141.66, 147.08. Calculated MH$^+$ 162.104465; found 162.102976.

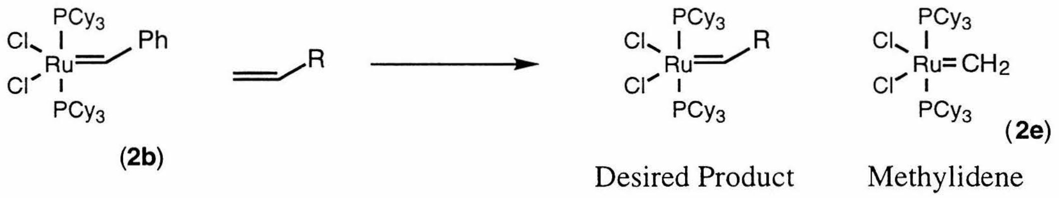
(7b) *1-Phenyl-2-Ethoxyethylene.* 2-Diphenylphosphinoyl-2-ethoxyoctane-1-phenyl-ethan-1-ol (**6c**) (1.20g, 3.3 mmol) was dissolved in 30 mL dry THF, and NaH (0.100g, 4.1 mmol) was added. After filtering over celite the THF was evaporated and the product was distilled under vacuum and the cis vinyl ether was obtained in 75% yield (0.36 g). d=1.019 g/ mL *^{1}H NMR:* 1.37 ppm(t, 6.96 Hz, 3H); 3.99 ppm (q, 6.96 Hz, 2H); 6.21 ppm (d, 6.96 Hz, 1H); 5.22 ppm (d, 7.32 Hz, 1H); 7.14 (t, 7.5 Hz, 1H); 7.29 ppm (m, 2H); 7.60 ppm (d, 7.32 Hz, 2H); *^{13}C NMR:* 15.39, 69.04, 105.49, 125.55, 128.09 (2 overlap), 136.07, 146.46. Calculated MH^+ 148.08815; found 148.088917.

Kinetics of Chain Termination by Vinyl Ether. Fresh stock solutions of the ruthenium carbenes (0.015-0.020M in CD_2Cl_2) were prepared in a dry box and the 5 mm NMR tubes were sealed in an inert atmosphere. Complete initiation of (**1c**) to (**1d**) was confirmed by ^{1}H NMR before the addition of vinyl ether. The vinyl ethers were stored in screw cap vials equipped with a Teflon liner cap. By the spectrometer (equilibrated to the appropriate temperature), the vinyl ethers were added via gas-tight syringe to the ruthenium carbene solution. All runs were repeated 3 or more times. A long pulse delay (5 sec) was used during data acquisition to prevent signal saturation. The kinetics were monitored by the disappearance of the initial carbene and appearance of the new signal and followed for at least 3 half lives. The relative concentrations were determined from the integration of the ^{1}H resonances of the starting and product carbenes. Kinetic data for the reaction were fit by least-squares methods to equation (4).

$$-\ln\frac{[\mathbf{1c}]}{[\mathbf{1c}]+[\mathbf{1d}]} = k_{obs}(\text{time}) \qquad (4)$$

Appendix to Chapter 3: Ruthenium Carbenes Dimerize α-Olefins.

One method for functionalizing polymer terminii is the selective cleavage of the metal center from the polymer. Alternatively, the initiation of a living polymerization may be performed with functionalized carbene. Functionalized carbenes are easily synthesized by the reaction of benzylidene catalyst (**2b**) with an α-olefin (Eq. i), but one limitation of this approach is the formation the methylidene (**2e**) which is difficult to separate from the desired product.

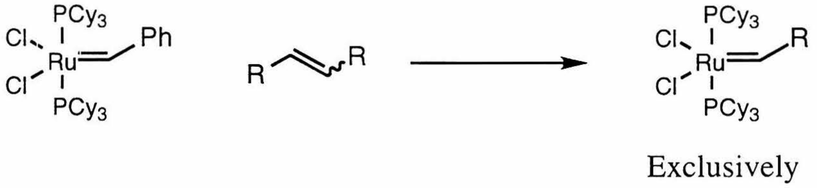


(i)

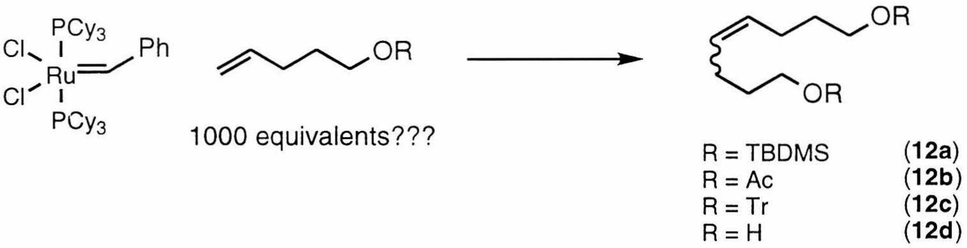
The reaction of (**2b**) of 5-penten-1-ol has been reported.[21.24] Under similar reaction conditions, (**2b**) was dissolved in CH_2Cl_2 (0.4 M) and cooled to -78°C, a solution of α-olefin C_5H_9OR (R = TBDMS (**11a**), Ac (**11b**) and Tr (**11c**)) (1.0 M, 12 eq.) was added via cannula and the reaction mixture was warmed to room temperature. After removeing the solvent *in vacuo,* the residue was washed with methanol. If the reaction was incomplete (as determined by ^1H NMR), another aliquot of α-olefin was added. Although on a small scale $Ru(PCy_3)_2Cl_2{=}CH(CH_2)_3OR$ (R = TBDMS) was isolated without any methylidene, scale-up afforded the desired product contaminated with both methylidene (3%) and residual starting material (3%). Similarly, synthesis of

$Ru(PCy_3)_2Cl_2{=}CH(CH_2)_3OR$ (R = OAc) afforded the desired product with residual starting material (5%) and methylidene (3%).

Formation of the methylidene may be avoided by the reaction the ruthenium center with an internal olefin (Eq. iii). Subsequently the synthesis of symmetric internal olefins via metathesis dimerization (Eq. iv) was investigated.



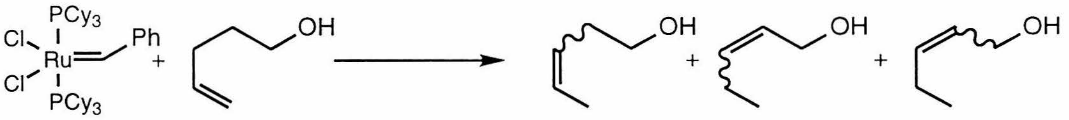
(iii)



R = TBDMS **(12a)**
R = Ac **(12b)**
R = Tr **(12c)**
R = H **(12d)**

(iv)

The dimerization of C_5H_9OR (R = TBDMS) proceeded to completion (60°C, 24h, 1500 eq.). Monitoring the dimerization of 5-penten-1-ol by ^1H NMR again indicated the disappearance of the terminal olefin, but peak integration indicated that the olefin was being isomerized to a mixture of internal olefins (Eq. v).



(v)

The trityl protected alcohol is crystalline and the dimerization was performed in CH_2Cl_2 rather than neat. The reaction proceeds to 66% conversion under these unoptimized conditions. The complex $Ru(PCy_3)_2Cl_2{=}CH(CH_2)_3OAc$ (**11b**) was synthesized by reaction with the α-olefin (3.5% methylidene), and it was demonstrated to initiate the polymerization of cyclooctadiene. Despite the independent synthesis and reaction of (**11b**), this complex was apparently not active for the dimerization of α-olefin under these condition. More recently, it has been demonstrated that reaction under neat conditions and high vacuum (60 mtorr) affords a wide variety of symmetrically substituted olefins.[30] Removal of trace ethylene is important for improving the yield of cross metathesis. The symmetric internal olefin (**12a**) was reacted with (**2b**) to cleanly afford the new carbene (**11a**) with no other carbenes detectable by ^{1}H NMR. This was used to initiate the polymerization of cyclooctadiene and the functionalized olefin was observed by ^{1}H NMR. Substrates such as (**11a**) can initiate living polymerizations of monomers such as cyclobutenes[28] to afford perfectly monofunctional polymers.

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Appendix 1
Synthesis of Cyclooctene Monomers

Appendix 2

Synthesis of Controlled Structure Polyenes as Substrates for Model Cascade Reactions

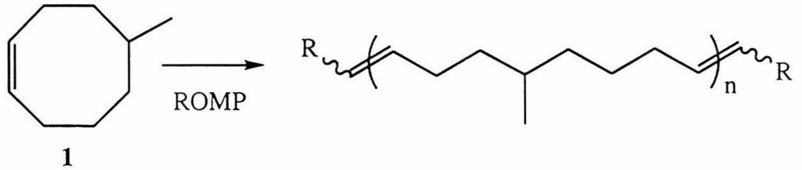
Appendix 3
Safe and Convienent Procedure for Solvent Purification

Appendix 1: Synthesis of Cyclooctene Monomers

Several new cyclooctenes were synthesized with substitution at C-5 (X = CN, COOH, CH_2OH). Several routes were investigated for the synthesis of 5-methylcyclooctene, but the product was never isolated cleanly.

Introduction

The ring opening metathesis polymerization (ROMP) of functionalized cyclooctenes offers a route to a variety of polymeric structures with differing properties. One monomer of particular interest is 5-methyl cyclooctene because it offers a new route to ethylene/propylene copolymers (EP rubbers).[1] The ring opening metathesis homopolymerization of substituted cyclooctenes avoids the difficulty of controlling relative reactivities of different monomers (Eq. 1) . Another advantage of cyclooctene is the presence of easily hydrogenated disubstituted olefins in the backbone. Hydrogenation of tertiary olefins of poly(isoprene) is much more difficult to accomplish with acceptable efficiency.



1

Eq. 1

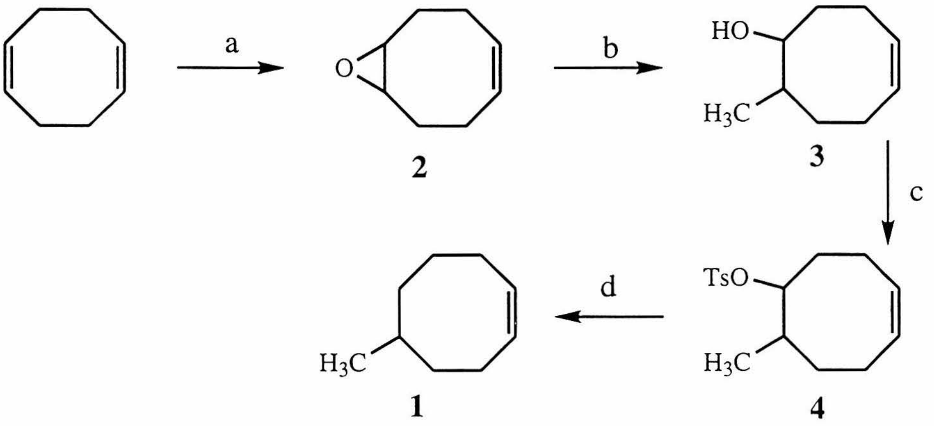
We were interested in preparing 5-methyl cyclooctene on a multigram scale from 1,5-cyclooctadiene. Thus, the synthesis must consist of a few, relatively high yielding steps which are amenable to scale-up. Furthermore, an efficient purification process has to be developed to yield extremely pure monomer.[2,3] One challenging aspect of the synthesis of this monomer is the unusual reactivity of cyclooctene. Cationic or radical reactions at the

4 or 5 positions of cyclooctene result in significant formation of bicyclics.[3,4] For example, treatment of 5-iodocyclooctene with lithium dimethyl cuprate yields [3.3.0] bicyclooctene in greater than 25% yield.[4]

Results and Discussion

Our first synthetic route to **1** is shown in Scheme 1. The epoxidation was done with excess 1,5-cyclooctadiene (1,5-COD). The mono epoxide was easily separated from 1,5-COD and diepoxycyclooctane by column chromatography. The ring opening of the epoxide proceeded in modest yield. Using fresh CuI stored in anhydrous conditions, and MeMgBr, **2** was isolated in 60% yield. The tosylation proceeded smoothly in dry pyridine, and the product was recrystallized. However, the displacement of the tosylate proved to be problematic.

Scheme 1. The Synthesis of 5-Methylcyclooctene via Epoxidation.

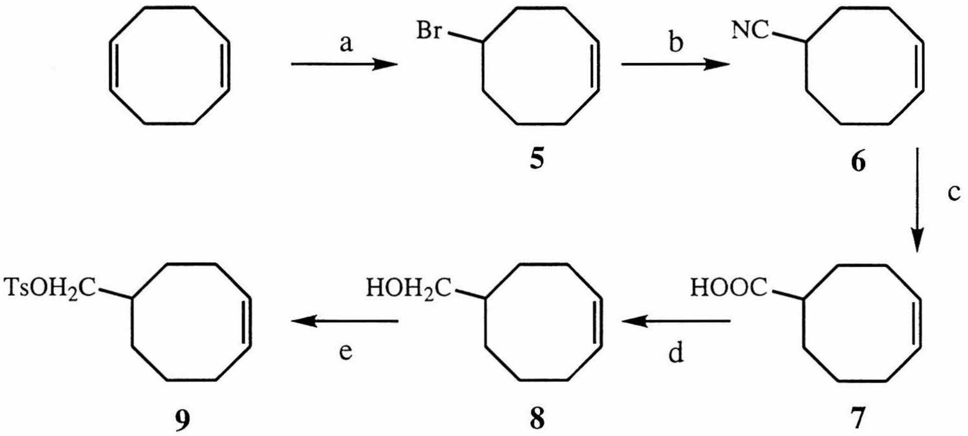


a) MCPBA in $CHCl_3$ b) CH_3MgBr, CuI, THF, 12 h
c) TsCl, pyridine, 25° C, 24 h d) DME Zn/Na reflux 3 h.

Neither $LiAlH_4$ nor $(C_2H_5)_3BHNa$ afforded methylcyclooctene. NaI/Zn reduction successfully removed the tosylate. The ^1H NMR spectrum of the product mixture contained the characteristic doublet of **1**, but GC analysis indicated that it was actually a mixture of several compounds, and the major product was 40%. Presumably, there was significant bicyclic product formation. Efficient conversion of the α-branched secondary tosylate to the desired alkane was not possible, therefore an alternative route to substituted cyclooctenes was proposed and is outlined in Scheme 2.

The second route to methyl cyclooctene offered another important advantage in that each intermediate was itself an interesting substrate for ROMP. The resulting hydrogenated polymers are regular terpolymers of butadiene, ethylene and a vinyl monomer. Alternating terpolymers are not synthetically accessible through other routes.

Scheme 2. The Synthesis of 5-Methylcyclooctene via 5-Bromocyclooctene.



a) HOBr, CH_3COOH b)NaCN/DMSO 90° C, 3 h c) $KOH/H_2O/H_2O_2$, H_3PO_4
d) $LiAlH_4$/THF, 0° C, 10 min e) TsCl pyridine. 24 h

Bromination of 1,5-COD proceeded smoothly with HBr in CH_3COOH. Cyanide substitution proceeded in only 50% yield. When the reaction was done as concentrated as possible, there is some improvement; but other cyanide salts, the presence of crown ethers, and a variey of reaction temperatures did not improve the yield. The carboxylation was straightforward, and the reduction was quantitative. The tosylation proceeded in moderate (50%) yield; however, an efficient method for the reduction of the tosylate to the desired cyclooctene was not found. $LiAlH_4$ appeared to partially react to give methyl cyclooctene.

The ^{1}H NMR spectrum of the crude reaction mixture included the characteristic doublet of **1**, but only in low conversion, and the product could not be isolated cleanly.

Conclusions

Several interesting monomers were synthesized which have been polymerized.[5] The cyclooctene ring is very susceptible to bicylic formation, and this complicated the attempts to reduce the tosylates to 5-methylcyclooctene. To date, we have not yet developed a viable synthesis of 5-methylcyclooctene amenable to scale-up and purification.

Experimental Section.

5,6-Epoxycyclooctene (**2**). MCPBA (62g, 60% Aldrich, 0.22 mol) dissolved in 100 mL chloroform was added dropwise over 2 h to a solution of 1,5-cyclooctadiene (28g, 0.26 mol) in 200 mL chloroform, and stirred overnight. The solution was cooled to 0° C and the mcba was filtered off. After chromatoagraphy, 16 g (60%) was isolated. ^{1}H NMR($CDCl_3$) δ 5.6(t, 2H), δ 3.0(t 3H) δ1.75-2.5 (m, 8H).

2-Methyl-5-cyclooctenol (**3**). CuI is light sensitive and the reaction flask was covered with foil. CuI (0.53g, 28 mmol) in 35 mL THF was cooled to -40° C and (**2**) (1.7g, 14 mmol) was added. The solution was warmed to 0° C and after 1 hour was added to H_2SO_4/ice water solution, and extracted with ether (3 x 60 mL) After chromatography 1.2 g (60%) were recovered. ^{1}H NMR($CDCl_3$) δ 2.5-2.75 (m, 2H), δ 3.6 (m, 1H), δ 1.3-2.5 (m, 9H), δ 0.98 (d, 3H, J_{HH} 7 Hz).

2-Methyl-5-cyclooctene tosylate.(**4**) Compund **3** (4.4g, 31.4 mmol) was dissolved in 80 mL dry pyridine, and *p*-toluene sulfonyl chloride (6.3g, 33 mmol) was added. The solution was stirred overnight at room temperature, added to ice water/HCl solution, and extracted with ether (3 x 75 mL). The combined organics were washed with copper sulfate solution to remove trace pyridine, dried over $MgSO_4$, and the volatiles removed *in vacuo*.

The oil was recrystallized form ethyl acetate/hexanes to afford 7.7g (83% yield) of a colorless solid ^{1}H NMR($CDCl_3$) δ 7.8 (d, 2H), δ 7.35 (d, 2H), δ 5.5-5.75 (m, 2H), δ 4.5-4.65 (m,1H), δ 2.45 (s, 3H), δ 2.4-1.25 (m, 9H), δ 0.88 (d, 3H).

5-Methylcyclooctene (**1**). Tosylate (**4**) (0.54g, 1.83 mmol), NaI (1.37g, 9.15 mmol), and Zn (1.2g, 18.3 mmol) were refluxed in 10 mL DME for 3 hours. The Zn was removed by filtration, and the solution was added to water and extracted with pentane (3 x 15). Crude yield was 55%. NMR($CDCl_3$) δ 5.8-5.6 (m,2H), δ 2.5-1.2 (m, 11H), δ 1.0 (d,3H).

5-Bromocyclooctene (**5**)*: 30% HBr in acetic acid (97.0 g, 0.36 mol) was added dropwise over 30 minutes to a stirring 0° C solution of 1,5-cyclooctadiene (42.7 g, 0.4 mol), stirred 24 hours, and poured ice-water (300 ml), extracted with diethyl ether (5 x 50 ml.), and washed with saturated $NaHCO_3$ (5 x 100 ml.). Ether layers were dried with magnesium sulfate and solvent removed in vacuo yielding an orange oil. After chromatography 50 g (**5**) (74% yield) were isolated. ^{1}H NMR ($CDCl_3$) δ 1.3–2.9 (m, 10 H), 4.0-4.55 (m, 1 H), 5.3-5.9 (m, 2 H).

5-Cyanocyclooctene (**6**): Compound **5** (8g, 40 mmol) was dissolved in 5 mL DMSO and was added dropwise to a 90° C solution of NaCN (4.6g, 2.2 eq) in 30 mL DMSO, and heated at 100° C for 3 h. The reaction mixture was then poured into water, extracted with ether (3x20mL), dried over $MgSO_4$ and the volatiles removed *in vacuo*. Yield = 2.7 g 90% crude yield 50% yield after chromatography.^{13}C NMR ($CDCl_3$): δ 23.22, 24.89, 26.82, 28.02, 29.21, 31.99, 123.18, 128.84, 130.51.

4-Cyclooctene carboxylic acid (**7**): Compund **6** (3.4g, 25 mmol) in 60 mL of 30% KOH in water and 12 mL of 40% H_2O_2 were stirred at 50° C for 1 h and subsequently refluxed for 15 h. The reaction mixture was cooled to RT, poured into 40% phosphoric acid and set aside for several h. The product was extracted with ether (6x50 mL), dried over $MgSO_4$,

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* prepared by M. A. Hillmyer and W. R. Laredo

concentrated *in vacuo*, and then recrystallized from 50mL ether. Yield = 2.6 g (70% yield).^{13}C NMR ($CDCl_3$): δ 24.07, 25.91, 27.81, 29.28, 31.45, 43.24, 129.50, 130.64, 184.21.

4-Cyclooctenemethyl alcohol (**8**): 17 mL of 1M $LiAlH_4$ was added to a 0° C solution of (**7**) (2.6g 16.9 mmol) in 20 mL THF and stirred for 30 minutes. The reaction mixture was poured onto ice water and extracted with ether. After drying with $MgSO_4$ and concentration *in vacuo*, 2.3 g (93% yield) was recovered. ^{13}C NMR ($CDCl_3$): δ 24.391, 25.26, 25.56, 27.82, 29.30, 31.55, 40.168, 67.59, 68.38, 129.66, 129.95.

4-Cyclooctenemethyl tosylate (**9**). Compound **8** (2.3g, 16.4 mmol) was dissolved in 40mL of dry pyridine, and *p*-tosylchloride (3.1g, 16.5 mmol) was added. The solution was stirred overnight at room temperature, added to ice water/HCl solution, and extracted with ether (3 x 30 mL). The combined organics were washed with copper sulfate solution to remove trace pyridine, dried over $MgSO_4$, and the volatiles removed *in vacuo*. Yield = 2.4g (50 %). ^{13}C NMR ($CDCl_3$): δ 21.39, 23.90, 25.53, 27.41, 29.15, 31.04, 36.74, 75.74, 127.60, 129.45, 129.62, 130.05, 132.90, 144.46.

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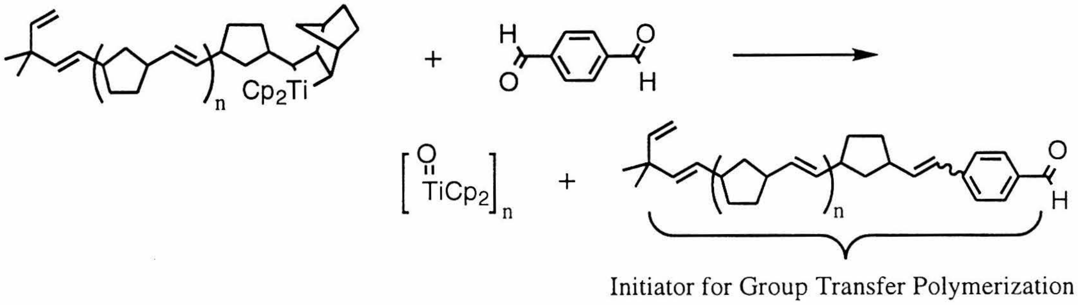
Appendix 2. Synthesis of Controlled Structure Polyenes as Substrates for Model Cascade Reactions

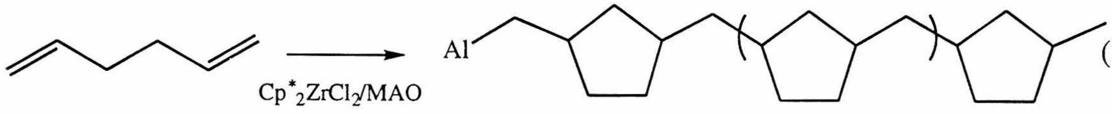
Rational control of molecular architecture is one of the ultimate goals in polymer science. Living polymerizations provide several advantages in the synthesis of materials with predictable and tunable structures. One advantage of living systems is the ability to transform the living chain end into a site for future synthetic manipulations. There are several examples of the controlled termination of a living polymerization followed by a second initiation and polymerization sequence.[1,2] Metathesis initiators have also been used in syntheses of copolymers via a change of mechanism.[3,4] Early transition metal carbenes are highly oxophilic and undergo a Wittig type reaction (Eq. 1).[5-7] Norbornene was polymerized with a titanacylcobutane initiator and endcapped with terephthaldehyde.[3] Subsequent group transfer polymerization of a silyl enol ether (and hydrolysis to poly(vinyl alcohol)) afforded a block copolymer not accessible from a single polymerization method.



(1)

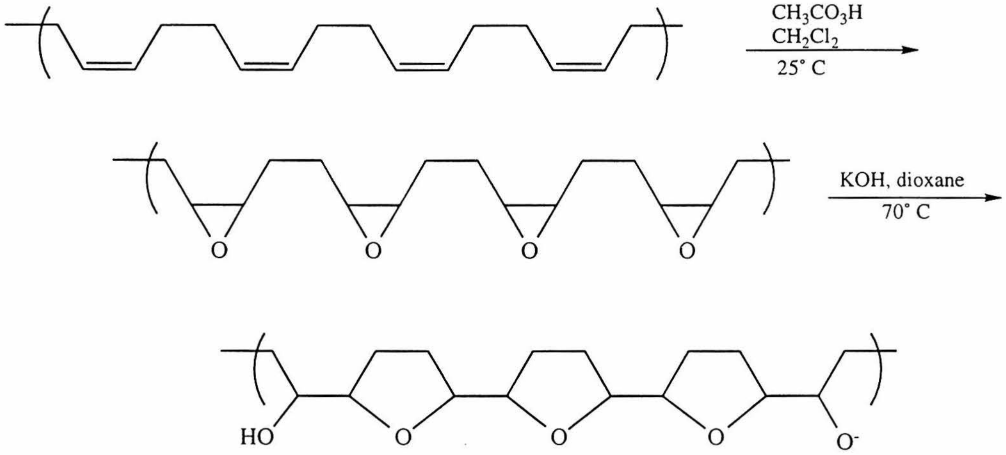
Initiator for Group Transfer Polymerization

When the cyclopolymerizaiton of 1,5-hexadiene with $Cp^*_2ZrCl_2$ and MAO cocatalyst is performed at low temperature, chain transfer to aluminum is the exclusive mechanism of chain termination (Eq. 2).[8] Subsequent exposure to air results in an alcohol terminated polymer



(2)

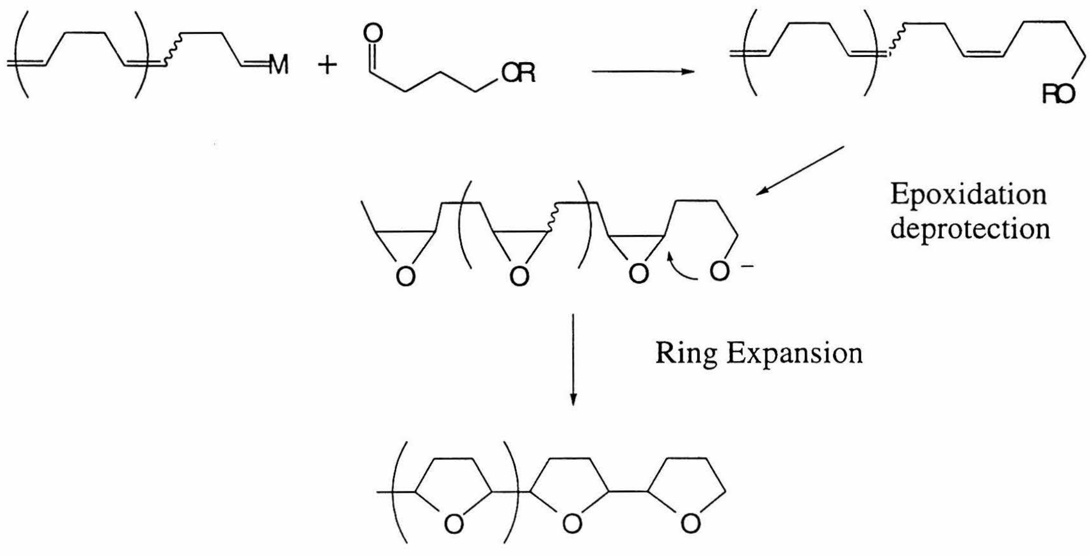
Another case where this approach may be useful is in the synthesis of poly-2,5-THF. One synthetic route is the epoxidation of 1,4-polybutadiene followed by ring expansion (Scheme 1).[9,10] Under these conditions, nucleophilic addition/ring opening of the epoxide (initiation) is a random process and is the rate controlling step in the ring expansion.



Scheme 1. Synthesis of Poly(2,5-tetrahydrofurandiyl) from Polybutadiene

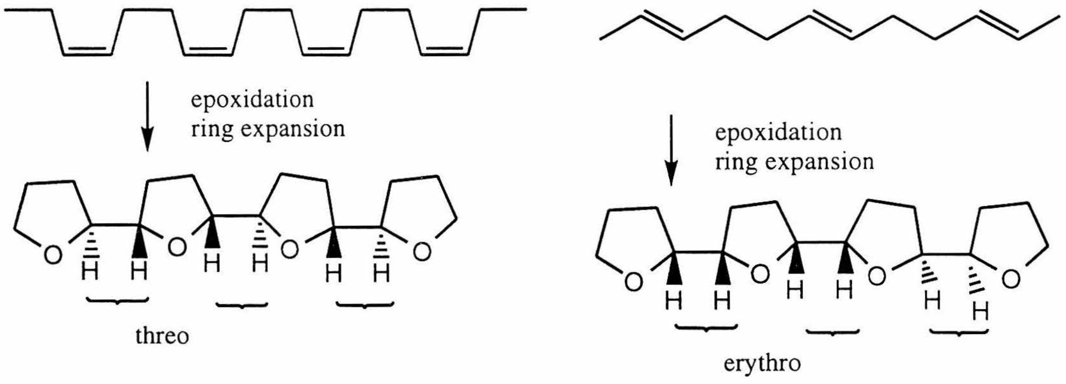
Ring expansion proceeds in one direction along the chain until a defect is encountered (usually a pendant vinyl group). The ring expansion generally proceeds in approximately 75% yield.

A series of cyclobutenes have been polymerized by ROMP,[11-14] and the selective functionalization of the chain terminus can be achieved by reaction with the appropriate aledehyde. It is possible that the chain terminus could than be used to initiate a cascade of ring expansions (Scheme 2).



Scheme 2. Synthesis Poly(2,5-THF) via Controlled Initiation.

When choosing cyclobutene monomers to investigate, we began our investigations with 3,3-dimethylcyclobutene because the ROMP polymerization afforded polymer with high *cis* content.[12] This microstructure was preferred because *cis*-polybutadiene affords a flexible coiled structure with interesting ion-binding properties. *Trans*-polybutadiene affords an extended and rigid structure (Fig 1).



cis-polybutadiene: threo

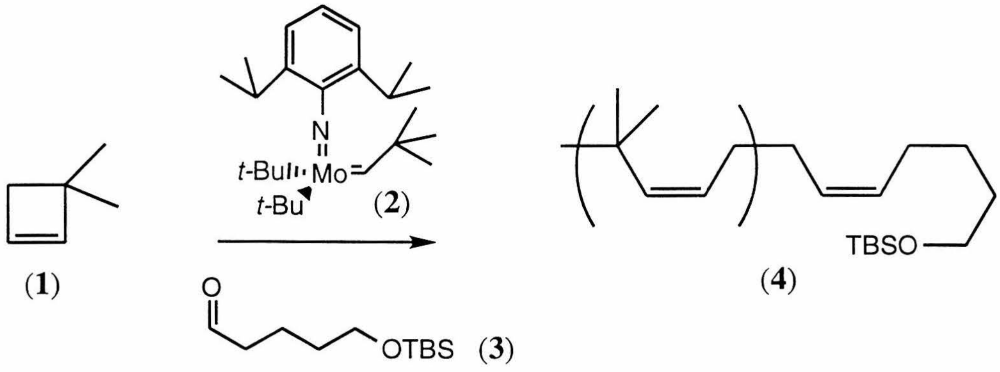
flexible coiled, ion-binding

trans-polybutadiene: erythro

rigid extended structure.

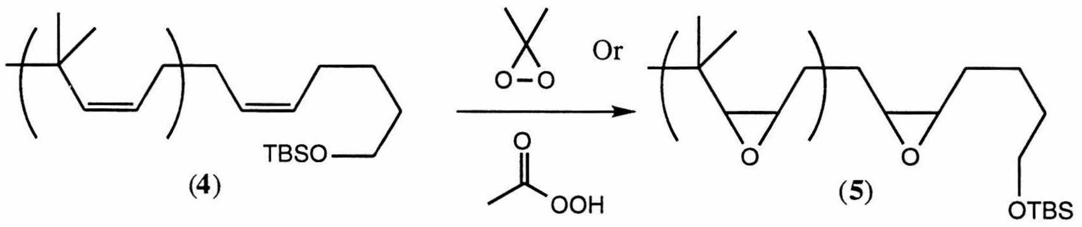
Figure 1. Stereochemistry of Polybutadiene/Poly(2,5-THF)

Polymerization of 3,3-dimethylcylcobutene (**1**) with the molybedenum initiator (**2**) proceeded smoothly and was quenched with aldehyde (**3**) and afforded polymer (**4**) (Eq. 3). The terminating agent was prepared from 1-hexenol. Protection with TBS followed by ozonolysis afforded the silyl ether desired pentaldehyde (**3**). Endgroup analysis of the polymer (**4**) by ^{1}H and ^{13}C NMR indicated the presence of the desired terminal functionality.



(3)

Dimethyldioxirane was prepared via the addition of Oxone ($2KHSO_5 \bullet KHSO_4 \bullet K_2SO_4$) to a mixture of acetone, water and $NaHCO_3$.[15,16] Distillation (with a dry ice trap) afforded a 0.04 M solution of dimethydioxirane. The polymer was then dissolved in methylene chloride, and approximately 2 equivalents of dioxirane were added at 0°C and the solution was warmed to room temperature (Eq. 4). The progress of the reaction was monitored by ^{1}H NMR. Aliquots from the reaction were removed periodically and the disappearance of the olefinic resonances were monitored. Addition of 2-3 aliquots of dioxirane over several days afforded completely epoxidized backbone. The epoxidation could also be efficiently merdiated by peracetic acid.



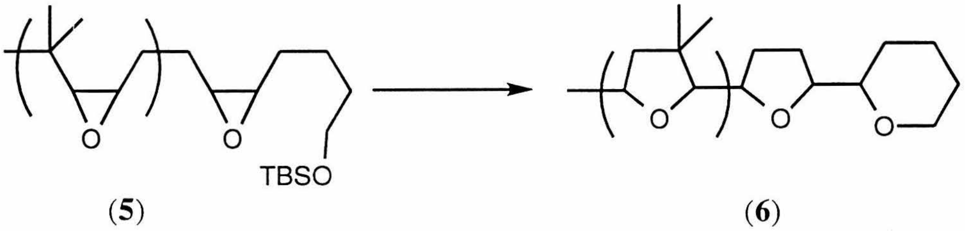
(4)

Thermal analysis of the polymers demonstrated a shift in glass transition temperature after epoxidation (Table 1). The change in molecular weight relative to polystyrene reflects changes in the solution coiling of the polymer backbone (hydrodynamic volume) in addition to the increased molar weight of the polymer.

Table 1. Physical Characterization of Polymers.

Sample	M_n	M_w	T_g
(**4**)	6,600	9,200	-30.5°C
(**5**)	4,300	8,900	-9.1°C

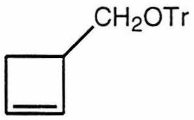
Ring expansion was attempted several times by the *in situ* deprotection of the TBS-alcohol with $N(Bu)_4^+F^-$ to form the poly(2,5-tetrahydrofurandiyl) analog (**6**) (Eq. 5). Ring expansion of the epoxides was incomplete and the changes in the backbone could not be conclusively assigned to (**6**).



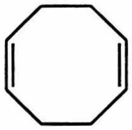
(5)

One potential source of these problems could be that the polymer actually was highly *trans* in contrast to the previously assignment.[17] The initiation step in the cascade reaction is to form a tetrahydropyran (Eq. 5). To eliminate the possibility of ring closure being kinetically limiting, the corresponding C4 aldehyde (which would initiate the cascade by forming a 5-membered ring) was also synthesized and used to functionalize the polymer terminus. Unfortunately, these polymers also failed to ring open/cascade sucessfully. A complex mixture of products was obtained in all cases. The precursor polymers (both polyene and polyepoxide) were well-defined and had assignable spectra. However the cascade reaction was not well behaved. This could be due to either polymer conformation or kinetically accessible side reactions.

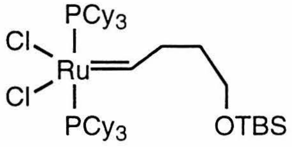
Several other monomers were briefly investigated. The cylcobutene derivative (**7**) was prepared according to literature procedure[18] and polymerized with (**2**). Unfortunately, this polymer could not be completely epoxidized by dimethyldioxirane or peracetic acid.



(7)



(**8**)



(**9**)

Cyclooctadiene (**8**) was also polymerized (with Mo(NR)(OC(CH_3)(CF_3)$_2$)$_2$CHR) and quenched with a functionalized aldehyde. Alternatively, COD could be polymerized with the functionalized rutheium initiator (**9**). Poly(cyclooctadiene) was successfully epoxidized (with peracetic acid) and some ring expansion was observed. The ring expansion did not appear to occur in a controlled fashion and was did not proceed to completion.

Experimental Section.

Synthesis of (**3**). 1-Hexen-6-ol (10 mL, 83 mmol) and imidazole (13.6g, 2.4 eq.) were dissolved in DMF (30 mL), TBSCl (15 g, 1.2eq.) was added and the reaction was stirred at room temperature then heated at 50°C for 1.5 h. The reaction mixture was poured into H_2O and extracted with hexanes. After distillation the TBS protected alcohol was cleanly isolated in 90% yield. (^{13}C NMR 138.8, 114.3, 63.0, 33.5, 32.3, 25.9, 25.1, 18.3, -5.3.) The α-olefin (3.1 g, 14.4 mmol) was dissolved in 250 mL chloroform and ozonized for 30 minutes. The reaction was quenched with triphenyl phosphine and purified by column chromatography.

^{1}H NMR 9.56 (1H, s), 3.418 (2H, t, 2.7 Hz), 2.25 (2H, t, 5.8 Hz), 1.52 (2H, m), 1.48 (2H, M), 1.35 (s, 9H), -1.16 (s, 6H) ^{13}C NMR 202.3, 62.4, 43.4, 32.0, 25.8, 18.5, 18.1, -5.5.

Polymerization Conditions. A solution of (**2**) in benzene was added to a monomer solution (**1**, 0.7 M) (monomer/catalyst 60/1) and stirred for 30 minutes. The reaction was quenched by the addition of aldehyde (5 eq.). The polymer was precipitated into methanol and isolated in 85-95% yield.

^{1}H NMR 5.2-5.3 (2H, m), 1.91 (2H, d, 6.6Hz), 0.91 (6H, s) endgroup visible as small triplet δ 3.6. ^{13}C NMR 142.5, 122.4, 46.3, 36.0, 27.1

Epoxidation by Dimethyldioxirane. The polymer was dissolved in methylene chloride (0.5 M), and approximately 2 equivalents of dimethyldioxirane (0.04 M) were added at 0°C and the solution was warmed to room temperature. The progress of the reaction was monitored by ^{1}H NMR. Aliquots from the reaction were removed periodically and the disappearance of the olefinic resonances were monitered. Addition of 2-3 aliquots of dioxirane over several days afforded completely epoxidized backbone.

Epoxidation by Peracetic Acid. The polymer (**4**) was dissolved in CH_2Cl_2 (0.3 M) and 2 equivalents of peracetic acid (32 wt% in acetic acid) and 2 equivalents of NaOAc were added. Aliquots of peroxide needed to be several times to afford complete hydrogenation. The reaction mixture was stirred overnight then added to water and extracted with methylene chloride.

^{1}H NMR epoxides (2H) at 2.87 (d, 5.7 Hz) and 2.46 (d, 13.2 Hz) in a ration of 6:5, broad methylene at 1.44-1.51 ppm (2H), 2 methyl peaks at 0.94 (d, 5.4 Hz), 0.88 (d, 3.6 ppm); ^{13}C NMR 65.54, 65.49, 51.74, 42.71, 42.67, 33.47, 33.44, 24.17, 24.10, 23.35, 23.24, 22.98, 22.93, 22.88, 22.83

Attempted Cascade Reactions. The polymer was dissolved in DME and KF (and 18crown6) or $N(Bu)_4{}^+F^-$ was added and the reaction stirred at room temperature. The polymer was isolated after precipitaion into methanol.

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Safe and Convenient Procedure for Solvent Purification

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Summary: This contribution describes a general method for the purification of solvents for use with air and moisture sensitive reactions. This procedure provides a nonhazardous alternative to distillations and vacuum transfers and does not require undue supervision or cooling, yet allows for the rapid collection of large quantities of extremely pure solvents on demand. Solvents are rigorously degassed in 18 L reservoirs and passed through two sequential purification columns. Protic contaminants are removed with activated alumina, while a supported copper catalyst is used to remove trace oxygen from hydrocarbons. The purification system is interfaced with either a glove box or Schlenk manifold for the anhydrous / anaerobic collection of solvents. Solvents purified by this method and tested with stock solutions of sodium benzophenone ketyl or titanocene dichloride / zinc dust are free of oxygen at least to the ppm level. Furthermore, this system may be used for the in-line purification of gases and is easily scaled down to provide a convenient method for the purification of deuterated solvents or other reagents.

Introduction

Current methods for the purification of organic solvents include distillation and vacuum transfer from dehydrating/deoxygenating reagents such as sodium benzophenone ketyl, $LiAlH_4$, NaK alloy, and CaH_2.[1,2] Because of the extreme reactivity of the reagents, these procedures pose very serious explosion and fire hazards; this is true not only during the purification procedure but also when the spent materials are quenched for disposal. Distillations pose an especially dangerous fire hazard because of the presence of hot flammable vapors and heat/spark sources. Vacuum transfers are somewhat safer than distillation procedures, but are not convenient for high-boiling solvents or for purifying large volumes of solvent (>1 L). The procedure described herein provides a nonhazardous alternative that does not require undue supervision or cooling, yet allows for the rapid collection of large quantities of extremely pure solvents on demand. Stock solutions of sodium benzophenone ketyl or titanocene dichloride/zinc dust may be used to qualitatively assess the O_2 and protic contaminants. Coulometric methods are also available to test for water at the ppm level.[3] Solvents purified by this method are free of oxygen at least to the ppm level.

Purification System

General Outline. Solvent reservoirs are sparged and pressurized with nitrogen (5−50 psig), and the solvent is passed through the two sequential purification columns. For all solvents, the first column is activated alumina, which removes polar impurities such as water, peroxides, and inhibitors (e.g., BHT). The second optional column is either another activated alumina column or a column of supported copper catalyst (Q-5), which removes trace O_2 to the ppm levels. If rigorously olefin-free hydrocarbon solvents are required, standard methods must be used to remove the olefins prior to use.[1,2] We have found that when HPLC grade reagents are used, upward of 400 L of solvent can be purified before regeneration of a set of columns is necessary. After column exit and before collection, the purified solvent is passed through an in-line filter (2−15 μm). Several collection systems have been developed. Two procedures include a Schlenk manifold for degassing and evacuating the void volume between the purification system and collection vessel. To avoid the construction of a vacuum system, the solvent may be plumbed directly into a dry box, dispensed directly into reaction flasks, or collected in receiving flasks (≥1 L) equipped with an oil bubble and septum port.

Detailed Description. Solvent reservoirs (18 L) may be rented prefilled with anhydrous solvent or purchased from Aldrich.[4] Reservoirs are filled with HPLC grade solvent on site. The accompanying columns (1−4 L capacity) are available from Whitey or may be constructed from stainless steel pipe, weld caps, and NPT nipples. LaRoche A-2 alumina (12 × 32) and Engelhard CU-0226S (formerly known as Q-5 reactant, a commercially available scavenger) are used as column packing. All tubing is $^{1}/_{4}$ in. stainless steel with $^{1}/_{4}$ in. stainless Swagelok fittings. Sample hardware is listed in the Experimental Procedures section. Quick connects and valves used with ethereal and halogenated solvents must have Kalrez or Teflon O-rings for long term operations.

A schematic diagram of the assembled system is shown in Figure 1. (**CAUTION!!** The setup in Figure 1 should be grounded to eliminate a spark source.) To maintain anaerobic and anhydrous conditions, the volume between the bellows valve and collection vessel is evacuated and back-filled with nitrogen several times. The collection vessel is under static vacuum before

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(4) Solvents available in Kilo-Lab cylinders include acetonitrile, benzene, diethyl ether, dimethoxyethane, heptane, hexane, methylene chloride, pentane, tetrahydrofuran, and toluene. Empty cylinders are also available. Kilo-Lab cylinders are rated for 240 psi and have fusible plugs for overpressure situations.

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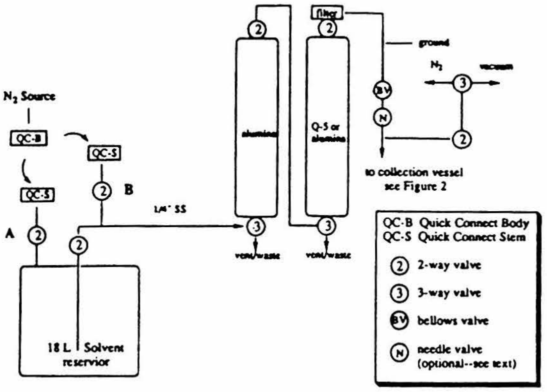

Figure 1. Solvent purification system. Degassing: Pressurize at B, vent to hood from A. Purging tubing with N_2: Pressurize at B, vent to the three-way valve. Purification/collection: Pressurize at A.

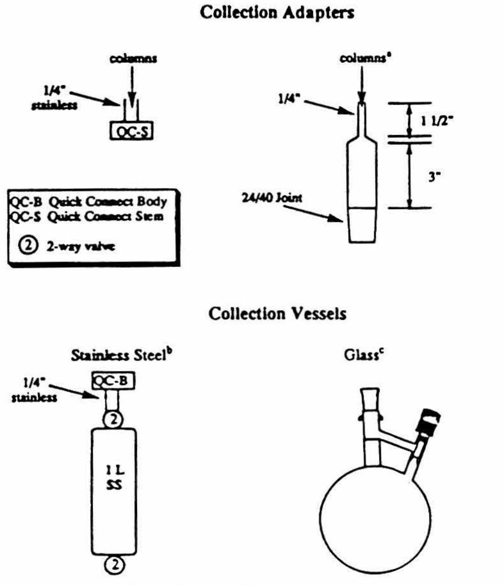

Figure 2. Collection adapters/vessels for use with Schlenk manifold. (a) A 24/40 adapter may be constructed of Pyrex or stainless steel and attached to the collection system with $^1/_4$ in. Swagelok fittings. Teflon ferrules are used with glass adapters. (b) To aid in rapid draining of solvent in the glove box, a quick connect stem is attached to the top of the stainless steel vessel. (c) 1 L Straus flasks (Kontes 213210-1000) are ideal for solvent collection and storage.

opening the bellows valve. (In applications where the pressure exceeds 10 psig, a bellows valve and needle valve should be used in series.) Two types of collection vessels that may be used are shown in Figure 2. Stainless steel cylinders are convenient when there is a dry box available for draining and sealing the vessels. Glass collection vessels are convenient for use with a Schlenk line. (**CAUTION!!** Glass should not be used when the pressure exceeds 5 psig.) Installation of the vacuum manifold can be avoided by directly plumbing the solvent into a dry box. To maintain an air-tight seal into the dry box, the stainless steel tubing is fed through a drilled-out $^1/_4$ in. Ultra-Torr fitting. To prevent the unattended accidental delivery of solvent in the box, an air-actuated ball valve with foot pedal control is installed between the columns and glove box (Figure 3).

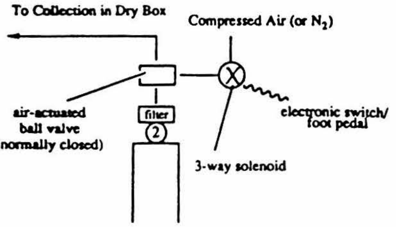

Figure 3. Air-actuated control of solvent flow. (a) To open air-actuated ball valve: Depression of the foot pedal energizes the solenoid, which pressurizes and opens the air-actuated ball valve. To close ball valve: Disengagement of the foot pedal deenergizes/vents the solenoid, and the ball valve closes via a spring return.

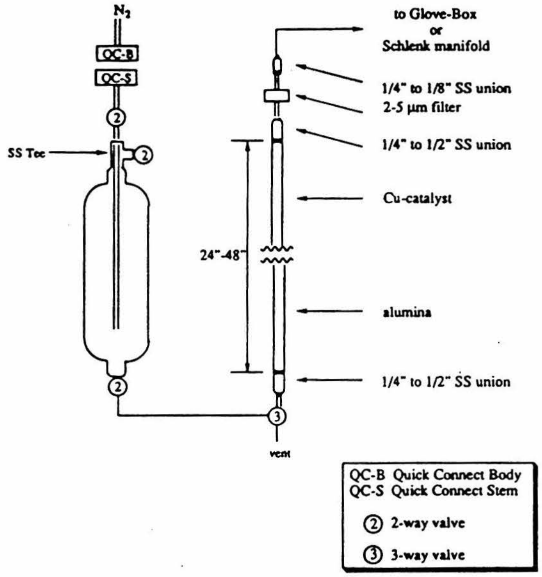

Figure 4. Small scale purification system.

A scaled-down version of this system can be used to purify small volumes of solvents, deuterated solvents, or frequently used reagents. The system can be built analogously to the preceding one by utilizing $^1/_8$ in. tubing and a single smaller column (Figure 4). The reagent reservoir is a 1 L stainless steel sample cylinder. The dip-tube used for degassing is constructed from $^1/_4$ in. stainless steel tubing and a drilled-through $^1/_4$ in. Swagelok $^1/_4$ in. male NPT adapter. Stainless steel tubing ($^1/_2$ in.) is used as the purification column, which is packed with alumina and the supported Cu catalyst.

Experimental Procedures

Column Activation. The columns are packed with A-2 alumina or Q-5 reactant (supported copper redox catalyst) with plugs of glass wool at each end. Columns are heated[5] with a one- or two-zone heating mantle,[6] and the temperature is monitored with thermocouples. Alumina columns are activated at 375 °C for 6–8 h with a constant nitrogen purge

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[5] Care should be taken during the activation step to prevent water vapor in the vent gas from condensing and running back into the column.

(approximately 2−25 L/min). The Q-5-packed columns are heated to 200 °C with a nitrogen purge (ca. 2−3 h), followed by activation with 5% hydrogen in nitrogen (ca. 25 L/min for 1−2 h); the temperature should not exceed 250 °C. Columns are cooled under nitrogen flow. The two-way valves recommended herein are not rated for the high temperatures of the exit gas and should be attached during nitrogen flow when the columns are cooled.[7] The columns are then isolated from the atmosphere and installed in the purification system.

Reservoir Installation. The entire system is purged with nitrogen through valve B prior to the first use of the columns (Figure 1). The two three-way valves at the bottom of the columns allow this to be done stepwise, so that air and moisture are not allowed to enter the activated columns. The solvent is degassed for 20 min with nitrogen through B while outlet A is vented to a hood. The nitrogen feed is then switched to A, and the tubing between the reservoir and columns is purged with a small amount of solvent before the solvent is introduced to the columns. The tubing between the reservoir and column is purged each time the solvent reservoir is changed or refilled. When the solvent is introduced into a dry, freshly activated alumina column, the column can become warm due to the heat of absorption.

Solvent Collection. When the purification system is in line with a glove box, solvent is collected by opening a two-way valve in the globe box while simultaneously opening the air-actuated ball valve. When a Schlenk manifold is used, the system is kept under dynamic vacuum (Figure 1: 2 open, 3 to vacuum) when not in use, and the collection vessel is attached under nitrogen purge (2 open, 3 to N_2). Prior to collection, the vessel and void volume are evacuated/back-filled three times, and the collection vessel is left under static vacuum (2 closed). To collect solvent, BV and N are opened. Although stainless steel vessels may be completely filled, glass vessels should only be filled to three-fourths capacity to avoid over pressurization. When collection is finished, the vessel is back-filled with nitrogen (2 open, 3 to N_2), and the collection vessel is sealed and removed from the adapter under inert gas purge. The adapter is evacuated and the residual solvent is collected in the N_2 trap of the Schlenk manifold. The solvent may then be tested for trace protic contaminants and O_2.

One or two drops of benzophenone ketyl in THF (without residual Na) are added to a small portion of solvent (3−5 mL) in the glove box. The persistence of a dark purple color indicates good solvent quality. If a glove box is not available, the solvent may be tested in a similar manner by using Ar-flushed syringes or cannulas. Solvents should be tested once the system is first constructed and each time the solvent reservoir is refilled. Solvents purified by these methods have been used in this laboratory in the synthesis of a variety of air and moisture sensitive compounds with no observed decrease in the purity or yield of the products.

Column Regeneration. When column performance deteriorates, the columns are removed from the purification system, blown dry of solvent, and disassembled, and the spent packing is disposed.[8] Reactivation is not recommended since it is difficult to remove all solvent residue, and upon heating they may react to form higher molecular weight products. Alumina columns that have been used to purify ethers should be washed with aqueous ferrous sulfate to destroy peroxides before disposal.[1] The packing material of columns used to purify gases can be reused by regeneration in the same manner in which they were initially activated. However, flammable gases need to be purged from the columns first.

Sample hardware: 18 L cylinders, outlet valves, and dip tubes, Aldrich Z14,888-1, Z14,886-5, and Z15,164-5, respectively; heating mantles from Glas-Col or LabGlas; 1 L cylinders, Whitey 304L-HDF4-1L-3.785L; three-way ball valves, Whitey SS-43XS4; two-way ball valves, Whitey SS 43S4; bellows valve, Nupro SS-4BG; in-line filters, Nupro SS-4FW-15; needle valve, Nupro SS-4H; quick connects (Swagelok), SS-QC4-D-400 and SS-QC4-B-400; QC series with Kalrez O-rings or QT series quick connects for ethereal and halogenated solvents; air-actuated valve, SS-42S4-131CS; three-way solenoid, ASCO 8314; foot pedal, HITREADLITE HT-52-S; nitrogen inlet flare fitting adapter for Kilo-Lab cylinders, SS-400-A-4ANF. Inexpensive 18 L cylinders equipped with all necessary valves are available from McMaster-Carr (refrigerant recovery cylinder No. 17305K74).

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(6) Heating tape may also be used. For large columns at least two heating zones are needed with separate thermocouples and controls. We found it convenient to wrap the thermocouple between the column and heating mantle.

(7) Valves rated for higher temperatures are available at approximately 3 times the cost of the valves suggested (high-temperature two-way valve for use with hydrocarbons, Whitey 83KS4, with halogenated and ethereal solvents, Nupro SS-4BG). If these valves are used, they may be installed before column activation, and the columns may be cooled under dynamic nitrogen pressure with the exit valves closed.

(8) Any disposal practice must be in compliance with all federal, state/provincial, and local laws and regulations.