

ACYCLIC DIENE METATHESIS (ADMET) SEGMENTED COPOLYMERS

By

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Measured against that which we desire,  
our knowledge is clearly limited,  
and if in this context we regard ourselves as children,  
then we know that we are growing.

Justus Liebig

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## KEY TO ABBREVIATIONS

A,B	generic repeat units or segments in a copolymer
C1	bis(3-butenyl) carbonate
C2	bis(5-hexenyl) carbonate
Cy	cyclohexyl, C <sub>6</sub> H <sub>11</sub>
DD	1,9-decadiene
E1	bis(5-hexenyl) terephthalate
E2	bis(5-hexenyl) phenylene diacetate
E3	3-butenyl 4-pentenoate
<i>i</i> -Pr	isopropyl (C <sub>3</sub> H <sub>7</sub> )
L <sub>n</sub>	generic ligands about a transition metal
Me	methyl CH <sub>3</sub>
OTf	triflate, O <sub>3</sub> SCF <sub>3</sub>
Ph	phenyl C <sub>6</sub> H <sub>5</sub>
PIB1	α,ω-dienyl polyisobutylene with M <sub>n</sub> =1700
PIB2	α,ω-dienyl polyisobutylene with M <sub>n</sub> =3100
PIB3	α,ω-dienyl polyisobutylene with M <sub>n</sub> =5800
PTHF1	α,ω-dienyl poly(tetrahydrofuran) with M <sub>n</sub> =1800
PTHF2	α,ω-dienyl poly(tetrahydrofuran) with M <sub>n</sub> =3600
PTHF3	α,ω-dienyl poly(tetrahydrofuran) with M <sub>n</sub> =1700

- R generic alkyl group
- U1 bis(5-hexenyl) 1,4-phenylenedicarbamate
- U2 bis(5-hexenyl) methylene bis(4-phenylenecarbamate)
- U3 bis(5-hexenyl) 4-methyl-1,3-phenylenedicarbamate
- X,Y generic functional groups (eg. groups that can react with each other to form a link between monomers in step-growth polymerization)

Abstract of Dissertation Presented to the Graduate School  
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## ACYCLIC DIENE METATHESIS (ADMET) SEGMENTED COPOLYMERS

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Chairman: Professor Kenneth B. Wagener  
Major Department: Chemistry

A series of segmented copolymers was synthesized by using acyclic diene metathesis (ADMET) to copolymerize  $\alpha,\omega$ -dienyl polyether or polyisobutylene telechelic oligomers with  $\alpha,\omega$ -diene comonomers possessing ester, carbonate, or urethane functionality. The  $\alpha,\omega$ -diene telechelomers were synthesized by cationic polymerization of tetrahydrofuran and isobutylene, capping with 5-hexen-1-ol and allyltrimethylsilane, respectively. Polyisobutylene telechelomers were copolymerized with decadiene, bis(5-hexenyl) terephthalate, bis(3-butenyl) carbonate, bis(5-hexenyl) carbonate, bis(5-hexenyl) methylene-*p*-diphenylenedicarbamate, and 2,4-bis(5-hexenyl)tolylene dicarbamate. Poly(tetramethylene oxide) telechelomers were copolymerized with bis(5-hexenyl) terephthalate, bis(5-hexenyl) phenylene diacetate, 3-butenyl 4-pentenoate, bis(3-butenyl) carbonate, bis(5-hexenyl) carbonate, bis(5-hexenyl) methylene-*p*-

diphenylene dicarbamate, and 2,4-bis(5-hexenyl)tolylene dicarbamate. In each case conversion was good, with the number average molecular weight increasing to approximately 20000 to 30000 g/mol, and in most cases only negligible unreacted parent oligomer could be detected.

Differential scanning calorimetry (DSC) was used to study the thermal behavior of the segmented copolymers. Segmented copolymers of polyisobutylene with ester or carbonate comonomers showed both a  $T_g$  near  $-70$  °C, corresponding to polyisobutylene, and a melting point that correlated to the homopolymer of the second segment. Segmented copolymers of polyisobutylene with decadiene showed intermediate phase separation. Segmented copolymers of poly(tetramethylene oxide) with decadiene had been shown previously by Brzezinska to have two melting points at 25 and 55 °C, indicating immiscibility of the polyether and polyoctenamer segments. However, copolymers of poly(tetramethylene oxide) with ester, carbonate, and urethane comonomers gave materials showing some degree of phase miscibility, as indicated by multiple melting points, and in some cases an increase in the  $T_g$  of poly(tetramethylene oxide). Segmented copolymers of poly(tetramethylene oxide) with the more flexible esters, bis(5-hexenyl) phenylene diacetate and butenyl pentenoate, as well as the two carbonate comonomers gave materials showing an intermediate melting point, indicating a high degree of miscibility of the two segments. The more rigid terephthalate as well as the two urethane monomers gave copolymers that appeared to have an intermediate degree of phase separation. Hydrogenation of the carbonate copolymers and the decadiene-polyisobutylene copolymers led to an increase in the melting points of these materials.

## CHAPTER 1 INTRODUCTION

In the quest for new, high-performance polymers, the novel *arrangement* of standard monomers or repeat units can be as significant as the invention of new monomers.<sup>1,2</sup> Drawing from the variety of possible polymer architectures along with the wide range of different mechanisms available for assembling monomers to polymers, a myriad of macromolecular structures are available to today's polymer chemist.

### Block, Segmented and Graft Copolymers

Block, graft, and segmented copolymers are related types of copolymers, similar in that there are distinct lengths of two or more homopolymer backbones incorporated into one copolymer macromolecule.<sup>1-11</sup> Using the nomenclature of "A" and "B" to refer to different homopolymer chains, diblock, terblock, segmented (multiple blocks), and graft copolymers are depicted in **Figure 1-1**. Block and segmented copolymers are characterized by two or more polymer chains joined covalently in an *end-to-end* fashion. Block copolymers typically have fewer, longer chains and are synthesized by chain polymerization methods, while segmented copolymers have several shorter chains in each macromolecule and are synthesized by step-growth mechanisms, as described below.<sup>4-5</sup>



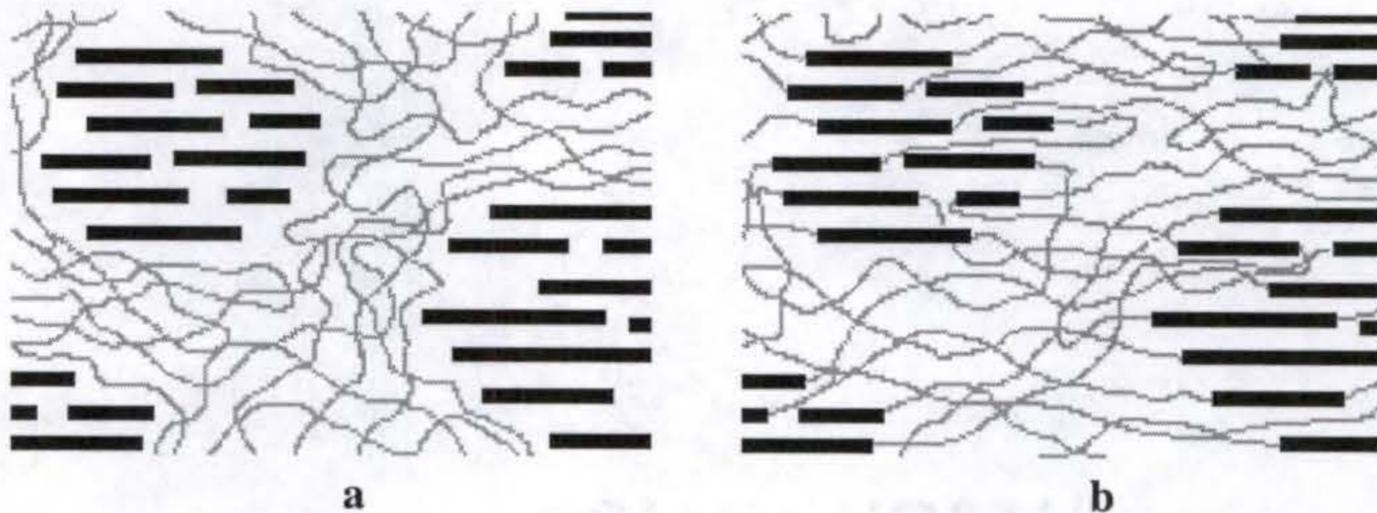
homopolymer or the corresponding random and alternating copolymers.<sup>4,5,8,9</sup> For example, while random and alternating copolymers typically have thermal transitions that are intermediate to the two parent polymers, the thermal behavior of block copolymers reflects that of each parent polymer, rather than an average of the two. With certain compositions, the mechanical and rheological properties can be greatly different from either parent homopolymer. These unique properties are a result of the phase separation, which arises from the sequenced arrangement of monomers in block copolymers.<sup>8</sup>

### Phase Separation in Polymer Blends

The mixing of two homopolymers to make a polymer *blend* is one of the simplest ways to alter the bulk properties of a polymer.<sup>11-16</sup> However, in order for a mixture of two species to be miscible, the Gibbs free energy of mixing,  $\Delta G_{\text{mix}}$ , must be negative (**Equation 1-1**). The mixing of small molecules is aided by an increase in entropy. However, due to their large size, polymers gain little or no entropy when mixed, which results in a positive  $\Delta G_{\text{mix}}$  unless a very negative enthalpy of mixing can offset this unfavorable entropy.<sup>14</sup> Mixtures of polymers, polymer blends, are therefore miscible only in a few cases, usually requiring secondary interactions such as hydrogen bonding between the two polymer chains to produce a more favorable  $\Delta H_{\text{mix}}$ .

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad \text{(Equation 1-1)}$$

This positive  $\Delta G_{\text{mix}}$ , which is typically observed, results in a demixing of the two components into domains within the bulk material.<sup>14</sup> (Figure 1-2a) Phase separation can affect both the optical and mechanical qualities of the bulk blended material. The interfacial boundaries between domains represent weak points in the material, and the more distinct the two parent homopolymers, the less interfacial cohesion holds these differing domains together.



**Figure 1-2.** Phase separation in a) polymer blends compared with b) segmented copolymers.

### Phase Separation in Block Copolymers

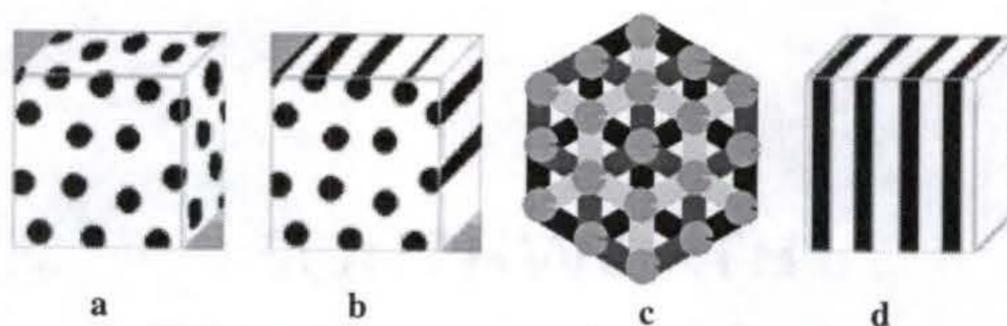
The tendency for phase separation is also present in block copolymers, since these types of polymers are composed of distinct sequences of two parent homopolymers within each macromolecular chain. However, the nature of phase separation observed in block copolymers is slightly different than that observed for the corresponding blend.<sup>14,17</sup> The differing blocks still prefer to separate into domains, but at

the same time the covalent bonds between the blocks prevent *complete* phase separation as would occur with the corresponding blend. (**Figure 1-2b**) This drive toward demixing coupled with the molecular connectivity between blocks, leads to *microphase separation* in block and segmented copolymers. The covalent bonding holding the different blocks together tends to reduce the size of the phase separated domains on the order of  $10^{-2}$   $\mu\text{m}$ , and creates connectivity at the interface between domains. As a result, block copolymers do not make the sacrifice in overall mechanical strength that is observed with polymer blends.

Microphase separation can lead to unique bulk properties for block copolymer materials. Within each microscopic domain, the polymer resembles the bulk parent homopolymer. Thermal characteristics, as well as other properties characteristic of the parent polymer can be retained in the copolymer, while rheological properties can be quite unique.<sup>8,10,14</sup>

The size and nature of the phase separation are influenced by the miscibility of the two blocks, as well as by the lengths and relative volumes of the two species. Temperature and pressure also influence the tendency for phase separation, and it should be noted that not all block copolymers exhibit phase separation.<sup>10</sup> Generally, for shorter blocks, such as in segmented copolymers, the domains tend to be smaller, and below a certain block length phase mixing will be less disfavored. Often for segmented copolymers, the domain size is smaller than the wavelength of light, so these materials can be transparent unlike many polymer blends. The influence of the relative volume of the

components on phase separation has been studied in depth.<sup>15-20</sup> The general morphologies for a two component system at differing relative volume percent is depicted in **Figure 1-3**. Domains of the minor component take on differing forms within a matrix of the major component or *continuous phase*, such that the interfacial area between the two is minimized. With increasing amount, the minor component, A, forms spherical then cylindrical domains. Further increasing the proportion of A, a tetrapodal bicontinuous double diamond lattice morphology has been observed to occur in some systems between the rod and column morphologies.<sup>19,20</sup> As the two components A and B approach nearly equal proportions, a layered, lamellae, morphology is observed, and further increasing the proportion of A leads to phase inversion with A becoming the continuous phase. Phase separation for block copolymers consisting of more than two different component blocks has also been studied, but is beyond the scope of this discussion.



**Figure 1-3.** Primary modes of phase separation in two-component block copolymer system: **a)** spherical; **b)** cylindrical (rods); **c)** bicontinuous double diamond; **d)** lamellae (layered).

### Analysis of Phase Separated Materials

There are many analytical techniques available for studying heterogeneous and phase separated polymer materials.<sup>1,15,20-22</sup> Traditional polymer analyses, such as gel permeation chromatography (GPC) can provide information on the molecular weight and distribution of the copolymer. Depending on the method of synthesis, a bimodal peak is often observed for block copolymers by GPC corresponding to a fraction of low molecular weight homopolymer species in addition to the copolymer.<sup>4</sup>

Information can also be gained about the size and shape of the phase separated domains. Small angle X-ray scattering (SAXS) can be used to elucidate the size of the domains, particularly for copolymers in which one or both of the component polymers is crystallizable or in cases where the morphology is in a very ordered matrix.<sup>22-24</sup> Light scattering and neutron scattering can also be useful in providing information about the phase separation.

Electron microscopy is perhaps the most compelling method for studying microphase separated materials, as this technique can provide an actual image of the size and shape of morphological features.<sup>24</sup> Scanning electron microscopy (SEM) can provide information on the surface structure, while transmission electron microscopy (TEM) can be used to elucidate the bulk structure of a material. TEM usually requires selective "staining" of one component of the material to impart a contrast in the electron densities between the two blocks. Osmium tetroxide or ruthenium tetroxide are two common stains that selectively react with the double bonds such as those of alkenes and carbonyls.

Differential thermal analysis (DSC, DTA, DMA) can also provide information on phase separated materials, and these methods require less expertise and sample preparation than electron microscopy methods.<sup>21,24</sup> The greater the degree of phase separation in the material, the more distinctly the thermal transitions corresponding to homopolymers will be retained in the copolymer. Thermal analysis can be used to detect both  $T_g$  and  $T_m$ , so copolymers of all combinations of crystallizable and amorphous blocks can be studied.

#### Applications of Phase Separated Copolymer Materials

The phenomenon of phase separation can impart interesting and useful bulk properties to copolymers, making these useful both as materials themselves and as agents in modifying the properties of other homopolymers. Block and segmented copolymers are usually more expensive to synthesize than homopolymers, so their use is mainly in specialty applications or as additives to commodity polymers. The combination of soft and hard blocks can give properties ranging from toughened, impact resistant thermoplastics to thermoplastic elastomers as described in detail below. Other specialty applications include uses which require the combination of certain properties of each parent homopolymer are desired. For example, the hydrophobicity of one homopolymer could be combined with the toughness and chemical resistance of a second homopolymer.<sup>4</sup>

### Thermoplastic elastomers

One of the most important applications of phase separated block copolymers is as thermoplastic elastomers.<sup>4,8,9,14</sup> A thermoplastic elastomer is a material that can be reversibly elongated when tension is applied, but unlike *thermoset* elastomers such as vulcanized natural rubber, these materials can be melted and processed. Thermoplastic elastomers require at least three blocks in each polymer chain.<sup>4</sup> For block copolymers, this requires a terblock copolymer with central blocks of a highly amorphous, low  $T_g$ , "soft," polymer flanked by blocks of a glassy (high  $T_g$ ) or crystalline, "hard," polymer. Segmented copolymers, with their multiple short blocks, can also behave as thermoplastic elastomers, and a classic example is the poly(urethane-ether) or poly(ester-ether) segmented copolymers (e.g. Lycra<sup>TM</sup> and Hytrel<sup>TM</sup>).<sup>25-28</sup>

The  $T_g$  or  $T_m$  of the "hard" block parent polymer needs to be above the use temperature of the material, yet low enough to allow for melt processing. The "soft" parent polymer is an amorphous polymer with a low  $T_g$ , such as polybutadiene, polyisoprene, or polyisobutylene or a semicrystalline polymer with a low melting point such as an aliphatic polyether.<sup>23-25</sup> The relative proportion of hard and soft phases is also important in achieving elastomeric behavior, where the continuous phase needs to be amorphous, and typically volume proportions of 20-40% hard phase are used. The chains of the amorphous continuous phase can slip past each other, allowing the material to elongate, but the hard domains act as physical anchors, preventing the soft phase chains from stretching beyond the point of recovery. These physical crosslinks are thermally reversible, allowing the material to be melted and easily processed, whereas in

traditional thermoset rubbers the crosslinks are chemical, and heating does not melt these materials.

#### Modifiers and compatibilizing agents

Segmented copolymers can also serve as compatibilizing agents.<sup>8-9</sup> Commodity polymers are often blended with other polymers, plasticizers, or other additives to modify the properties of the parent material. However, these additives can be immiscible with the polymer for reasons mentioned above, often compromising the mechanical strength and optical clarity of the material.

Segmented copolymers can help to homogenize polymer blends.<sup>12</sup> One approach is to mix the homopolymer with a copolymer in which one of the blocks is compatible with the homopolymer and the second component acts as a modifier. Another approach employs block copolymers as macromolecular "surfactants" in homogenizing a mixture of two dissimilar homopolymers. The blocks or segments are chosen such that each favors one of the polymers being mixed. Phase separation may still occur in the bulk material, but the added covalent bonding between segments of the block copolymer not only reduces domain size, but helps to retain the physical strength of the material by adding extra connectivity throughout the material.

## Coatings and adhesives

Segmented copolymers are an important component of many coatings and adhesives.<sup>1,29</sup> Again, the ability to combine the distinct compositions and properties of two different homopolymers into a single macromolecule chain allows these unique properties. Theoretically, segmented copolymers can be tailored according to substrate and surface quality desired. One component favors adhesion to the substrate while the other segment either favors adhesion to a different substrate or has the surface quality desired for a coating.

## Synthesis of Block and Segmented Copolymers

The synthesis of block and segmented copolymers requires controlled polymerization methods.<sup>2-4,30</sup> Several options are possible, yet each has its limitations on the possible combinations of homopolymer blocks.

### Sequential Monomer Addition Method

The synthesis of block and segmented copolymers can be divided into two general approaches. The first involves the sequential addition of monomers in a well-controlled or living chain polymerization.<sup>30-35</sup> This method is suited to the formation of diblock and terblock copolymers, giving controlled and predictable polymer structures, molecular weights, and weight distributions. Many ring-opening or chain polymerizations, such as anionic, cationic, transition metal coordination, and controlled radical polymerization



Another limitation to the sequential addition method is that the monomers used for each block must both be active toward the same polymerization mechanism. However, studies in "propagation transformation" have shown that monomer reactivity does not always have to be a limitation.<sup>30,36-40</sup> Propagation transformation involves changing the nature of the active end of a growing polymer *in situ* before adding a second monomer to grow the second block of the copolymer. Endo and coworkers have reduced the cationic endgroup of polymerizing ethylene oxide to an anionic site capable of initiating methyl methacrylate or caprolactone.<sup>36-37</sup> Grubbs and coworkers have switched from ring-opening metathesis polymerization (ROMP) to Ziegler-Natta polymerization by reacting the growing transition metal alkylidene with an alcohol to give the metal-alkyl species, which can initiate polymerization ethylene.<sup>38</sup> Block copolymers of polynorbornene with polyethylene have been made by this approach. Additionally, Guo and coworkers performed radical to cationic transformation polymerization. The radical chain end of AIBN-initiated *p*-methoxystyrene was transformed *in situ* to a cationic center capable of polymerizing cyclohexene oxide by  $\text{Ph}_2\text{I}^+\text{PF}_6^-$ .<sup>39</sup>

#### Reaction of End-Functionalized Oligomers

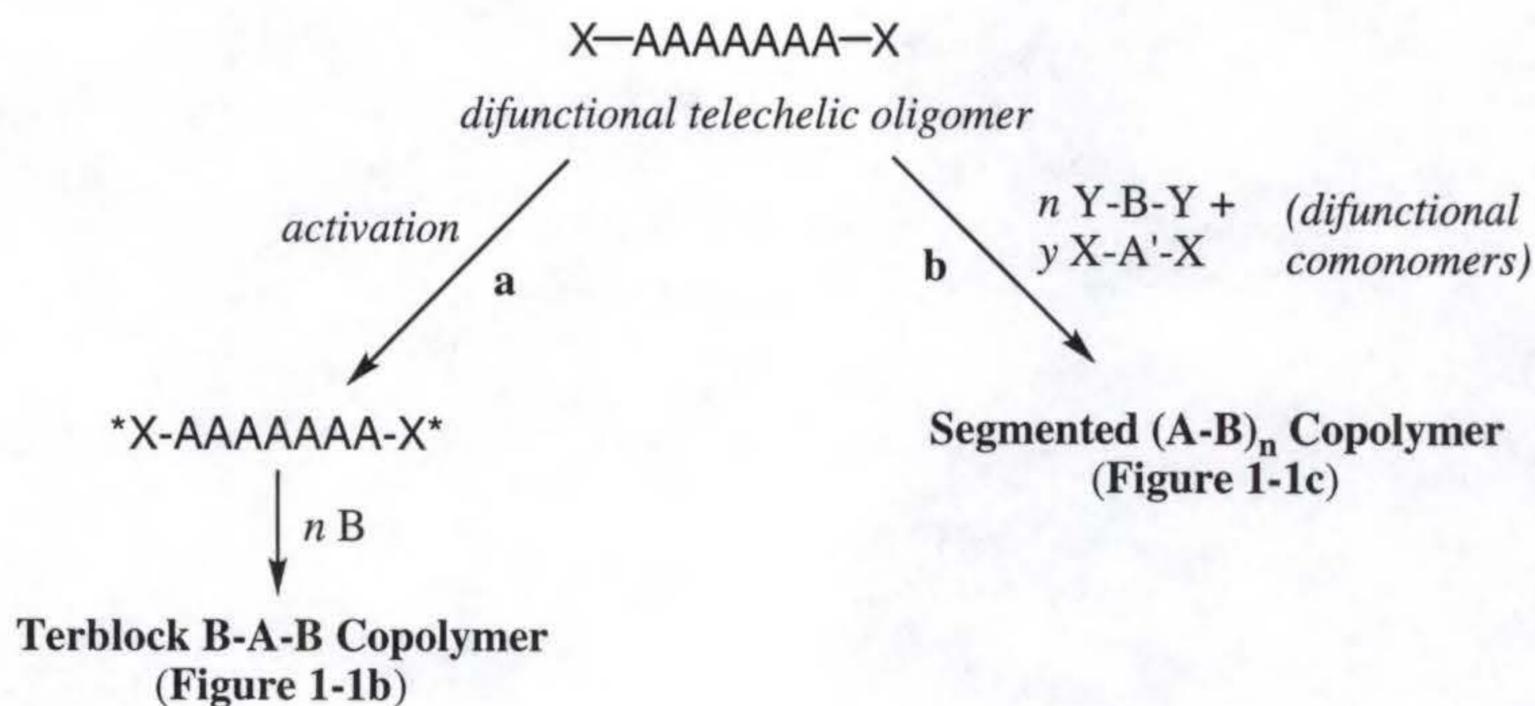
An assortment of block and segmented copolymers can be made by starting with an oligomer in which one or both ends are capped with an appropriate functional group.<sup>3,30</sup> The oligomer is typically grown by chain methods, and a number of scenarios are possible for the synthesis of these end-functionalized, *telechelic*, oligomers.<sup>3,30</sup> Functionalization of one end of the oligomer can be achieved by using either an initiator *or*

a capping agent that possesses the desired functionality. Telechelic oligomers functionalized at both ends,  $\alpha,\omega$ -telechelic oligomers, are best made by using a diinitiator then terminating polymerization with a functionalized capping agent. These could also be made by using a functionalized capping agent in addition to a functionalized initiator. This route would also allow the creation of  $\alpha,\omega$ -heterofunctionalized oligomers, but these are beyond the scope of this discussion.

The functional group of a telechelic oligomer can be activated to form an initiator for the chain polymerization of another monomer, which can provide an additional route to obtaining diblock and terblock copolymers of monomers that are reactive toward a different polymerization mechanism (**Figure 1-5a**). An example is the ROMP-group transfer radical polymerization (GTRP) block copolymers studied by Matyjaszewski and coworkers.<sup>40</sup> Polynorbornene is capped with 4-chloromethyl benzaldehyde, to give a benzylchloride endgroup, which, upon activation by various transition metals, creates an initiating site for the group transfer polymerization of methyl methacrylate.

The most common route to segmented, or multi-block, copolymers is by the copolymerization of an  $\alpha,\omega$ -difunctional telechelic oligomer along with difunctional comonomers in a step-growth process (**Figure 1-5b**).<sup>27,28</sup> These difunctional oligomers function essentially as large monomers in step-growth polymerizations. As in all step-growth polymerizations, the polymer chain is built through a series of coupling reactions, and the growth of high molecular weight, linear polymer requires careful control of the

stoichiometry of perfectly difunctional monomers such that none of the reactants is in excess and serves as a chain limiter.



**Figure 1-5.** Synthesis of block copolymers from a telechelic oligomer. **a)** Initiation of a second chain polymerization; **b)** incorporation in step-growth polymerization with difunctional comonomers.

Thus, by replacing a portion of one difunctional monomer by a stoichiometrically equivalent amount of an oligomer possessing the same difunctionality, a copolymer can be formed with oligomer segments incorporated periodically along the backbone of the original step-polymer backbone. The two most common examples of these are the poly(ester-ether) and the poly(urethane-ether) segmented copolymers derived from the copolymerization of  $\alpha,\omega$ -hydroxyl telechelic poly(oxytetramethylene) along with a glycol (ethylene glycol or 1,4-butane diol) and terephthaloyl chloride or diisocyanates, respectively.<sup>27-28</sup>

### Limitations in the Synthesis of Segmented Copolymers

With the numerous potential applications for segmented copolymers, it can be envisioned that segmented copolymers could be tailor-made according to the particular combination of compatibilities desired. However, even given the variety of methods known for making block copolymers, there remain limitations on the block combinations that can be achieved. If chain polymerization is used, both monomers must be reactive toward the same mechanism except for a few specialized cases mentioned above. Methods for coupling two end-reactive polymers or for using step-growth techniques require careful control of stoichiometry and functionality.

The synthesis of perfectly difunctional telechelic oligomers requires a diinitiated polymerization and high-yielding capping reaction to place the desired functionality on the end of the polymer chain. However, few polymerizations lend themselves to the synthesis of perfectly difunctional  $\alpha,\omega$ -telechelomers. Further, the reactivity of the capping reagent toward selectively terminating the polymerization is dependant on the polymerization mechanism used to grow the oligomer.

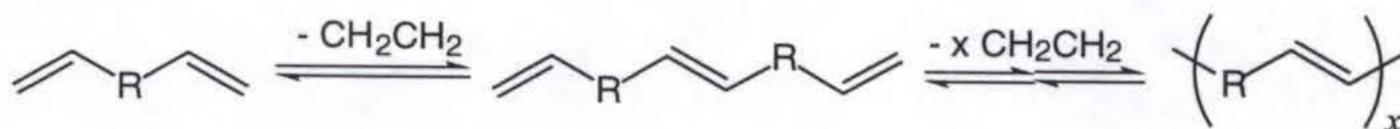
### ADMET Segmented Copolymers

The synthesis of segmented copolymers is also subject to the practical limitations of step polymerization. Monomer and telechelic oligomer must be perfectly difunctional or the molecular weight will be reduced due to chain termination by monofunctionalized species.<sup>1</sup> Furthermore, if the polymerization is of the  $XX + YY$  type, in which an X

functionality can only react with a Y functionality, then stoichiometry balance between the two functional groups is also crucial in achieving high molecular weight, as an excess of either functionality will again act as a chain limiter. Acyclic diene metathesis (ADMET) polymerization, has the potential to overcome some of these limitations in stoichiometry and backbone combinations.<sup>41</sup>

### General Features of Acyclic Diene Metathesis Polymerization

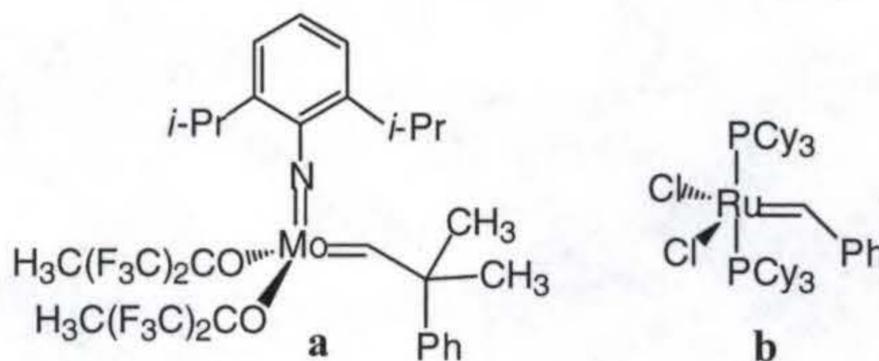
As mentioned above, segmented copolymers are produced by step-growth polymerization methods. Acyclic diene metathesis (ADMET) polymerization is a step growth, condensation polymerization mechanism that was developed in the Wagener group and has been used to polymerize a number of  $\alpha,\omega$ -diene functionalized monomers (**Figure 1-6**).<sup>42-43</sup> In the presence of an appropriate catalyst, olefin reacts with olefin to form the polymer linkages, obviating the stoichiometry issues inherent in XX + YY step systems. Polymer can be formed from the reaction of a single diene monomer. Furthermore, in ADMET *copolymerizations*, the stoichiometry of the two monomers can be varied over all ranges without limiting the molecular weight.



**Figure 1-6.** ADMET conversion of generic diene monomer to unsaturated polymer.

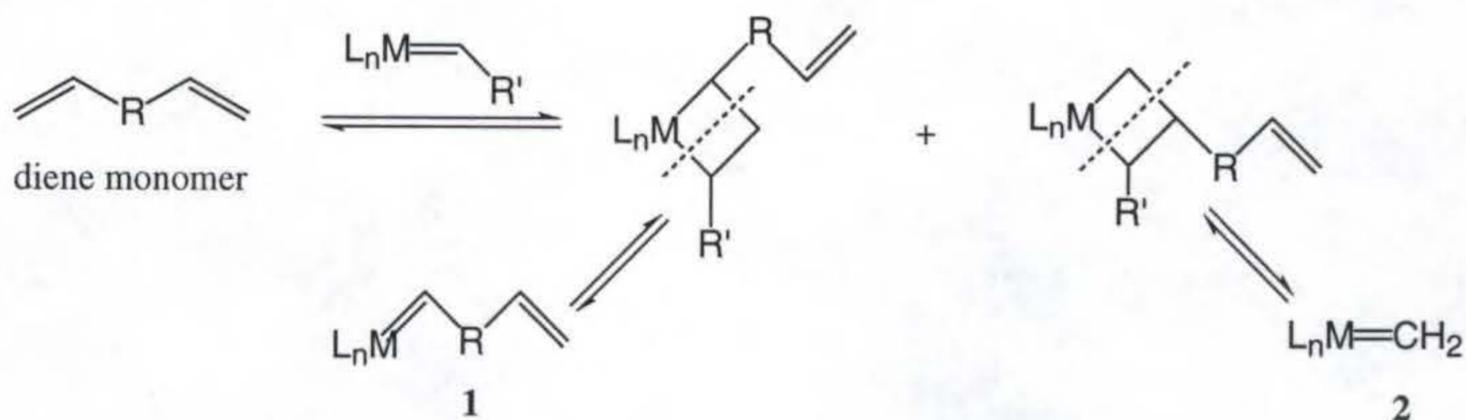
### Mechanistic Features of ADMET Chemistry

ADMET is a variation of the olefin metathesis reaction.<sup>41</sup> Olefin metathesis is mediated by certain transition metal alkylidene complexes, and two common ones are illustrated in **Figure 1-7**.<sup>46-49</sup> The alkylidene can be pre-formed as in the well-defined Schrock tungsten and molybdenum systems and the Grubbs ruthenium complexes,<sup>44-47</sup> or it can be generated *in situ*.<sup>48-49</sup> Strained cyclic olefins can undergo ring-opening metathesis polymerization (ROMP) and acyclic dienes can undergo either ring closing metathesis (RCM) reactions or step-growth polymerization (ADMET) depending on the diene and reaction conditions.<sup>41</sup>



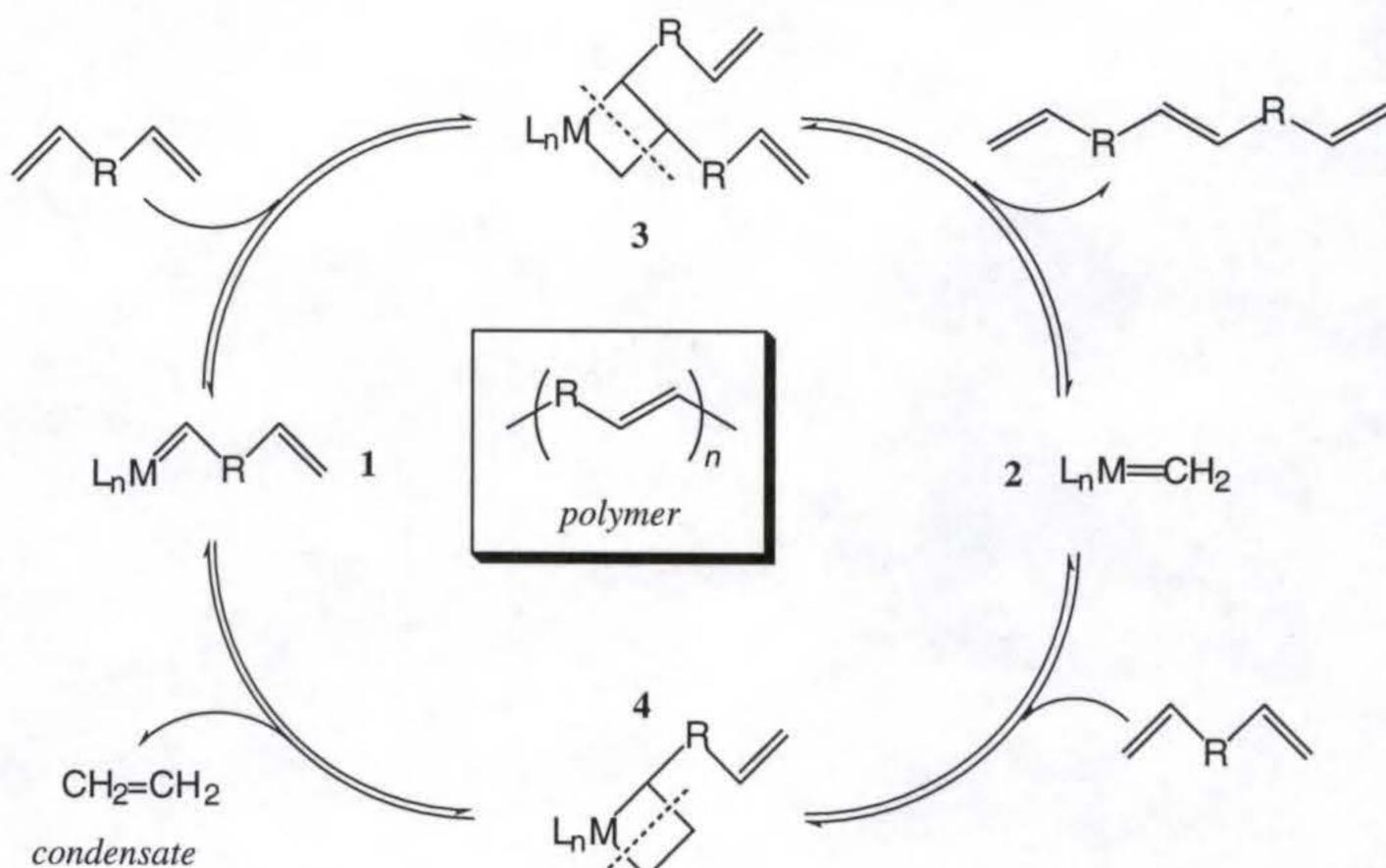
**Figure 1-7.** Two common well-defined alkylidene catalysts for ADMET polymerization. **a)** Schrock molybdenum and **b)** Grubbs ruthenium catalysts (Cy=C<sub>6</sub>H<sub>11</sub>)

The olefin metathesis reaction can be used to generate polymers in a step-growth fashion by employing diene monomers, and the reaction may be easily driven toward polymer by using terminal diene monomers such that the condensate is ethylene. The mechanism for ADMET polymerization is illustrated below and can be viewed in two steps, beginning with olefin coordination to the original metal alkylidene. (**Figure 1-8**)



**Figure 1-8.** Two regiochemical possibilities for reaction of catalyst precursor with monomer

Two metallocyclobutane species are formed, depending on the regiochemistry of olefin addition. Productive cleavage of the metallacyclobutanes gives two new alkylidenes, **1** and **2**, which enter the catalytic cycle. (**Figure 1-9**) Starting from the methylidene, **2**, olefin adds to form a metallacyclobutane **4**, which cleaves to give alkylidene **1**. A second monomer coordinates and forms metallacyclobutane **3**. Productive cleavage of this ring forms a link between the two monomer units while regenerating methylidene **2**. The dimer formed can enter the catalytic cycle on subsequent cycles. As with other step-growth polymerizations, polymer is built as the result of a series of coupling reactions, and high molecular weight polymer is only achieved after high conversion of the reactive olefin groups.



**Figure 1-9.** The catalytic cycle for ADMET polymerization showing productive reactions that lead to polymer formation.

### The Scope of ADMET

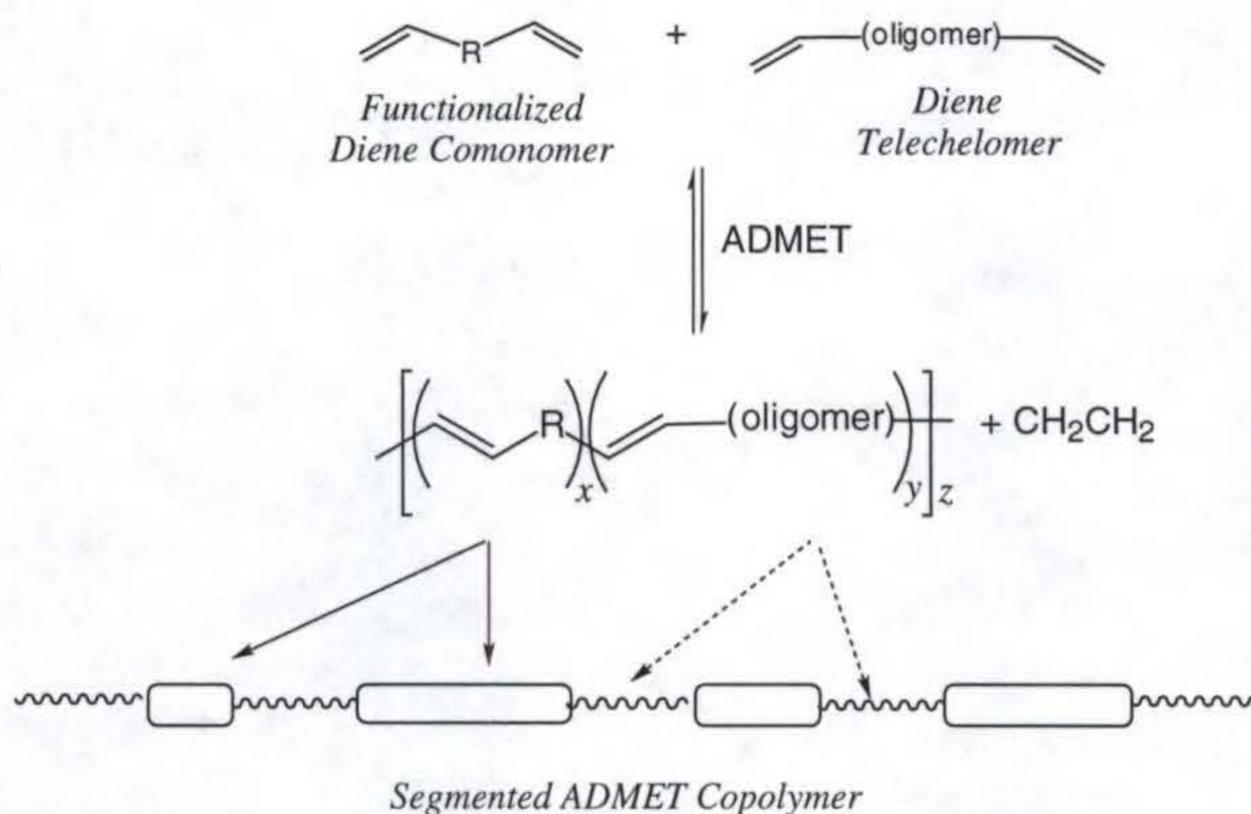
Since the discovery of ADMET as a viable route to forming polymer from diene monomers, the scope of this polymerization has been explored.<sup>41,50-52</sup> Diene monomers containing a variety of different functional groups, including a variety of different atoms such as oxygen, sulfur, silicon, germanium, phosphorous and nitrogen, have been successfully polymerized by ADMET techniques. However, a few guidelines must be followed to ensure successful ADMET polymerization. Studies have shown that the reacting olefin must be spaced at least two methylenes away from any functional group.<sup>53</sup> Sterics are also a factor, and substitution of the internal carbon of the metathesizing olefin prohibits metathesis.<sup>54</sup> Furthermore, metathesis is hindered for internal olefins or olefins

with substitution on the carbon alpha to the double bond.<sup>55</sup> Heeding these restrictions, a number of functional groups have been found to be amenable to ADMET polymerization, including ester, carbonate, siloxane, boronate, alcohol, and amine groups. The several reviews have summarized the breadth of ADMET, and the references therein may be consulted for specific details.<sup>50-52</sup>

Many diene monomers are accessible through relatively straightforward syntheses, making ADMET attractive as a route to a variety of polymer backbones not attainable by other means. Furthermore, ADMET has seen recent application in the formation of tailored polymer backbone structures.<sup>50</sup>

#### Producing Segmented Copolymers by ADMET

Given the versatility of ADMET polymerization for small diene monomers, it is reasonable that ADMET may likewise be amenable to the polymerization of macrodienes. Further, ADMET copolymerization of an  $\alpha,\omega$ -dienyl telechelic oligomer along with known diene monomers could provide a route to the synthesis of segmented copolymers. The general approach to ADMET segmented copolymers is illustrated in **Figure 1-10**, which shows the condensation of a macrodiene with a small molecule diene comonomer to make a copolymer with a segmented structure.<sup>56-60</sup> Alternately a single monomer could be used and that is the approach of Qiao and Baker. The ADMET homopolymerization of short  $\alpha,\omega$ -pentenyl glymes produced produced segmented ether-ethylene copolymers.<sup>61-63</sup>

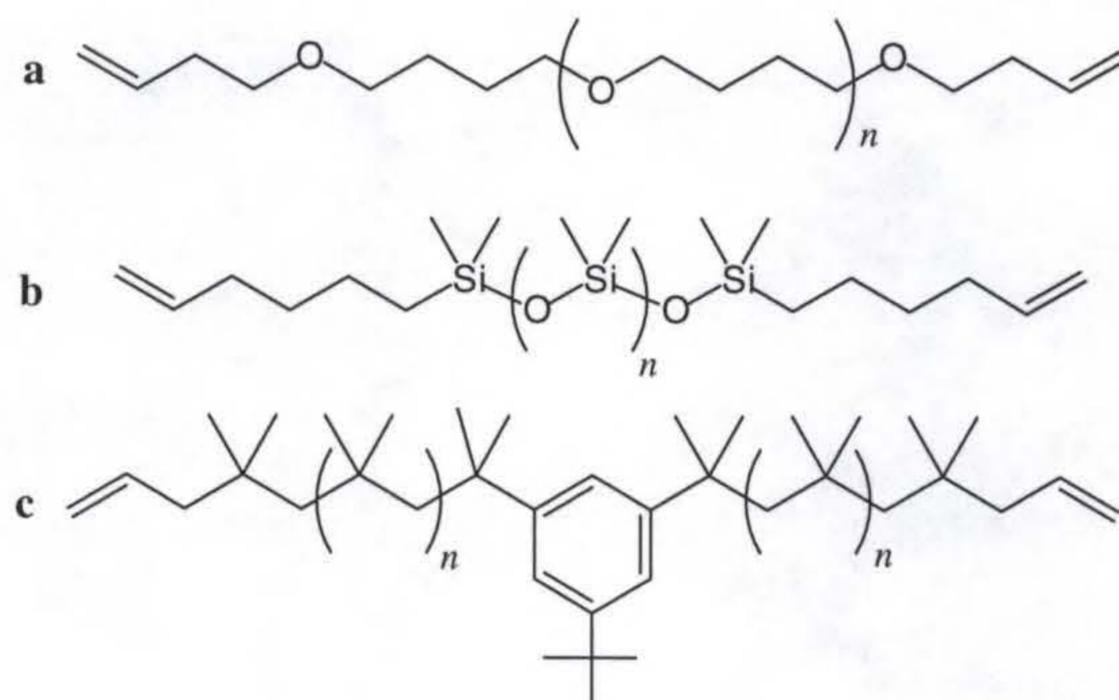


**Figure 1-10.** Synthesis of ADMET segmented copolymers-the essence of this study.

The key to using ADMET to make segmented copolymers lies in the ability to synthesize  $\alpha,\omega$ -diene telechelic oligomers and in the reactivity of these diene telechelomers toward olefin metathesis with the catalysts used for ADMET polymerization. Theoretically, if the same steric and electronic restrictions known for small molecule dienes are observed, then the olefin functionality in of an  $\alpha,\omega$ -diene telechelomer should be reactive toward ADMET polymerization.

To date, three  $\alpha,\omega$ -diene telechelic oligomers, poly(oxytetramethylene), polysiloxane, and polyisobutylene have been synthesized and all three were found to be reactive toward ADMET polymerization (**Figure 1-11**).<sup>56-60</sup> These telechelic oligomer provide three very different backbone structures and different corresponding properties,

and their use in segmented copolymers could lead to unique combinations not possible by other polymerization routes.



**Figure 1-11.** Diene telechelic oligomers. **a)** Poly(oxytetramethylene); **b)** Poly(dimethyl siloxane); **c)** Poly(isobutylene).

Brzezinska and coworkers studied the copolymerization of  $\alpha,\omega$ -dienyl poly(tetramethylene oxide) with decadiene to generate segmented copolymers.<sup>56-58</sup> The copolymerization of  $\alpha,\omega$ -dienyl poly(oxytetramethylene) and polyisobutylene telechelic oligomers with carbonate, ester, and urethane-functionalized diene comonomers is the essence of the research described herein.<sup>59-60</sup> Additionally, the ADMET reactivity and copolymerization of the polyisobutylene telechelomer with decadiene was studied. Although the ester, carbonate, and urethane functionalities were chosen for this study of segmented ADMET copolymers, theoretically any diene monomer could be incorporated

with these or other diene telechelomers to form additional combinations of segments, provided the diene functionality is amenable to ADMET chemistry.

The syntheses of poly(tetramethylene oxide) and polyisobutylene  $\alpha,\omega$ -dienyl telechelomers are discussed in Chapter 2. The reactivity of polyisobutylene toward metathesis chemistry and its copolymerization with decadiene are discussed in Chapters 2 and 3, respectively. It was shown that the polyether and polyisobutylene  $\alpha,\omega$ -dienyl telechelomers could indeed be incorporated into copolymers with the ester, carbonate, and urethane monomers, and these copolymers are discussed in Chapters 4, 5, and 6, respectively. Experimental details for this study are described in Chapter 7.

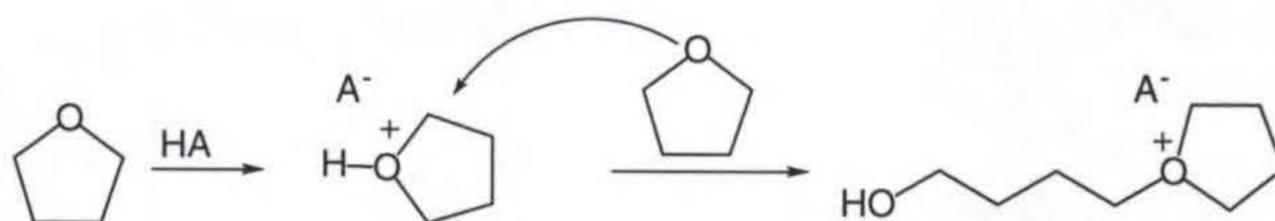
The structures of the copolymers were verified by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and IR spectroscopy, as well as gel permeation chromatography (GPC). Furthermore, the thermal behavior of these copolymers was studied by differential scanning calorimetry and thermogravimetric analysis.

## CHAPTER 2 SYNTHESIS AND CHARACTERIZATION OF DIENE TELECHELOMERS

As mentioned in Chapter 1, the key to ADMET segmented copolymers lies in the synthesis and reactivity of  $\alpha,\omega$ -diene functionalized telechelic oligomers. Two such telechelomers were chosen for this study, poly(tetramethylene oxide) and polyisobutylene. Each was synthesized by cationic polymerization followed by controlled termination with a suitable capping agent bearing the olefin functionality.

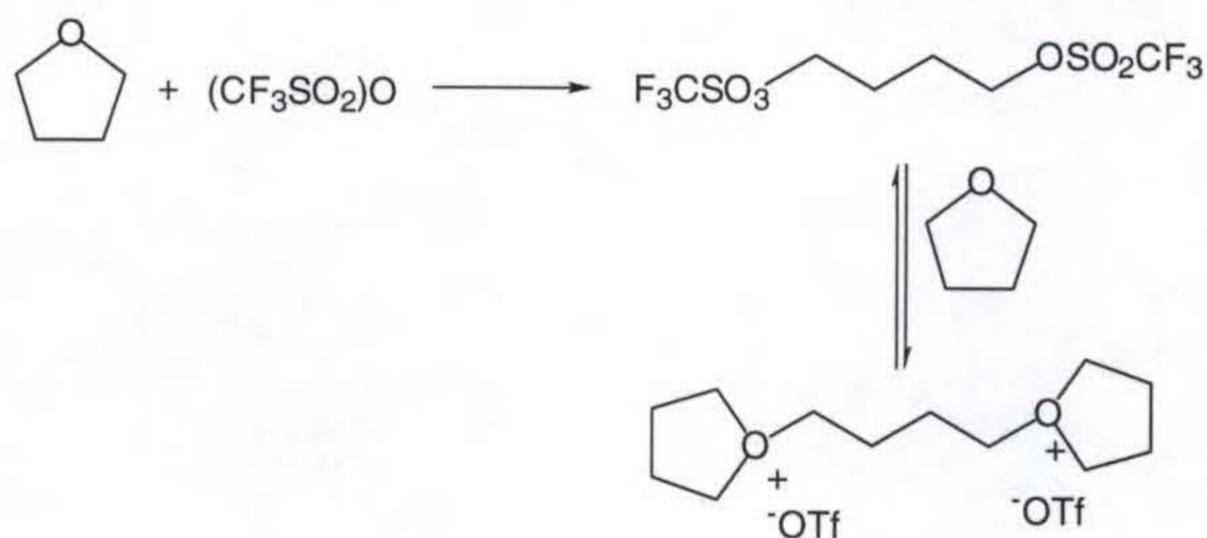
### Poly(tetramethylene oxide) $\alpha,\omega$ -Dienyl Telechelomers

Strong protonic acids, such as trifluoromethanesulfonic acid, can be used to initiate the ring-opening polymerization of cyclic ethers such as tetrahydrofuran.<sup>33,64-65</sup> Initiation involves protonation of tetrahydrofuran to form a secondary oxonium ion. Nucleophilic attack of monomer at either carbon alpha to the oxonium ion opens the first ring, reforming a tertiary oxonium ion (**Figure 2-1**).



**Figure 2-1.** Initiation of tetrahydrofuran polymerization with protonic acid, HA.

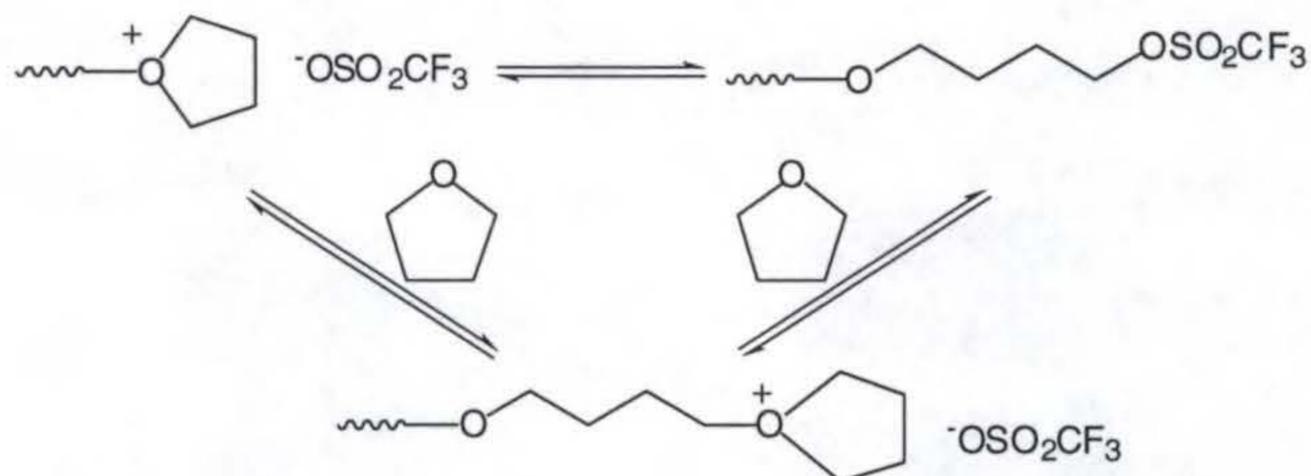
The corresponding anhydrides and esters of strong protonic acids can likewise initiate polymerization of cyclic ethers.<sup>33-34</sup> Triflic anhydride is a particularly interesting initiator, because it acts as a *di*initiator for cyclic ethers, growing the polymer chain from a central point with two identical ends, as illustrated in **Figure 2-2**.



**Figure 2-2.** Diinitiation with triflic anhydride to produce two propagating ends.

Propagation proceeds through oxonium and ester end groups, rather than the more reactive carbenium species, which reduces the propensity for side reactions. During the polymerization, the oxonium end groups are subject to nucleophilic attack by monomer, ether groups within the polymer chain, and counterion. In the polymerization of tetrahydrofuran with triflate as the counterion, the combination of counterion with chain end is a reversible reaction, and both the oxonium and the covalent ester species are active toward nucleophilic attack by monomer (**Figure 2-3**). Reaction with polymer is also reversible in these polymerizations, but since these chain transfer reactions lead to the formation of cyclics (through intramolecular backbiting) or chain scrambling (through intermolecular reactions), the molecular weight distribution can be broadened if these reactions compete with propagation. To minimize the amount of nonproductive

reactions, the polymerization is best performed with high concentrations of monomer and at lowered temperatures.

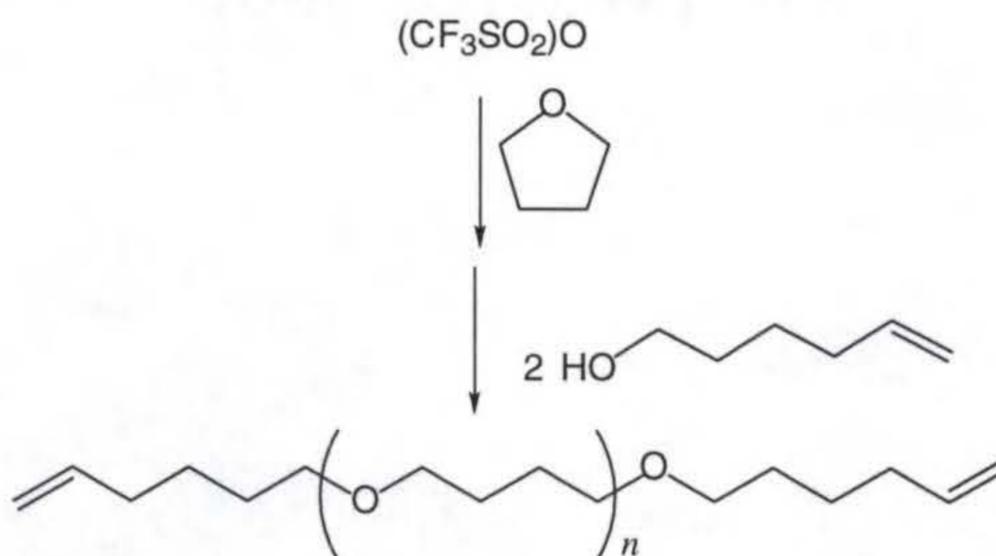


**Figure 2-3.** Equilibrium between oxonium and ester endgroups.

Quenching this polymerization with water yields the dihydroxyl terminated polyether. However, other nucleophiles such as alcohols, Grignard reagents, or alkali metal reagents can also be used to terminate the polymer chain, and the use of a functionalized nucleophile imparts functionality to the polymer chain end.<sup>33,66</sup>

#### Synthesis of $\alpha,\omega$ -Dienyl Poly(tetramethylene oxide) Telechelomers

The diene functionalized polyether telechelomers used for this study were synthesized from the triflic anhydride initiated ring-opening polymerization of tetrahydrofuran followed by capping with 5-hexen-1-ol (**Figure 2-4**).



**Figure 2-4.** Diene functionalized poly(tetramethylene oxide).

A summary of the molecular weight data for the three polyether telechelomers synthesized for this study is given in **Table 2-1**. The values for  $M_n$  obtained by GPC relative to polystyrene standards are a little over twice those determined by endgroup analysis. The functionality,  $F$ , was determined by comparing the integration of terminal olefin signals to signals arising from OH endgroup, which were undetectable in **PTHF1** and **PTHF2**.

**Table 2-1.** Poly(tetramethylene oxide) telechelomers synthesized.

Telechelomer	$X_n$	$M_n$ NMR <sup>a</sup> g/mol	$M_n$ GPC <sup>b</sup> g/mol	$M_w/M_n$	F
<b>PTHF1</b>	25	1900	3900	1.11	>1.94
<b>PTHF2</b>	46	3600	7400	1.07	>1.94
<b>PTHF3</b>	21	1700	3800	1.7	1.94

a. Integration of internal  $\text{CH}_2$  to olefin endgroups.

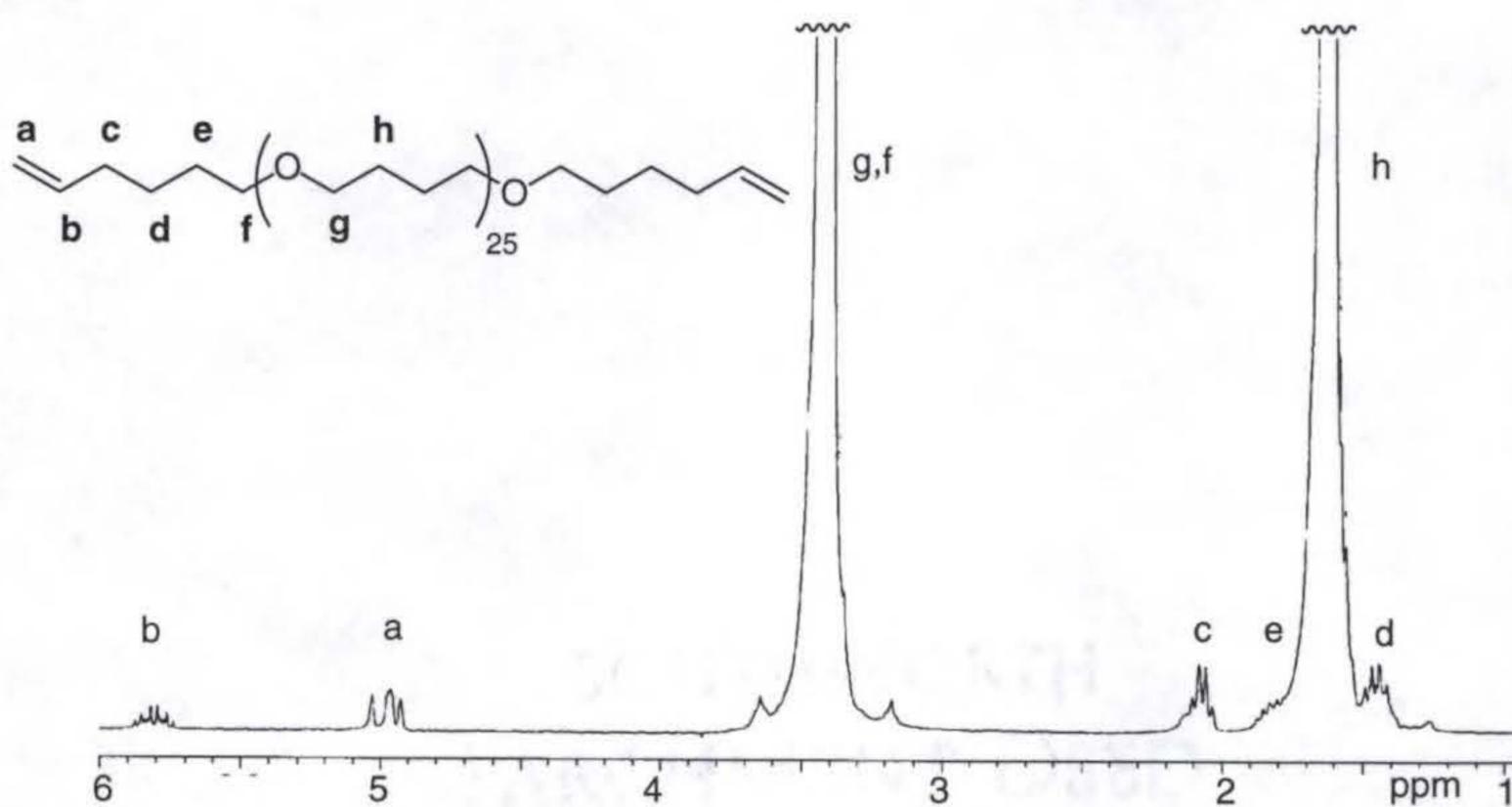
b. Molecular weight relative to polystyrene standards.

The poly(tetramethylene oxide) used for the polymerizations with ester monomers described in Chapter 4, **PTHF3**, was kindly provided by Krystyna Brzezinska. Brzezinska polymerized tetrahydrofuran at room temperature in methylene chloride, using triflic anhydride as the initiator.<sup>57</sup> After proceeding for 12 hours at room temperature, 5-hexenol was added to terminate the polymerization, thereby generating the diene functionalized telechelomer.

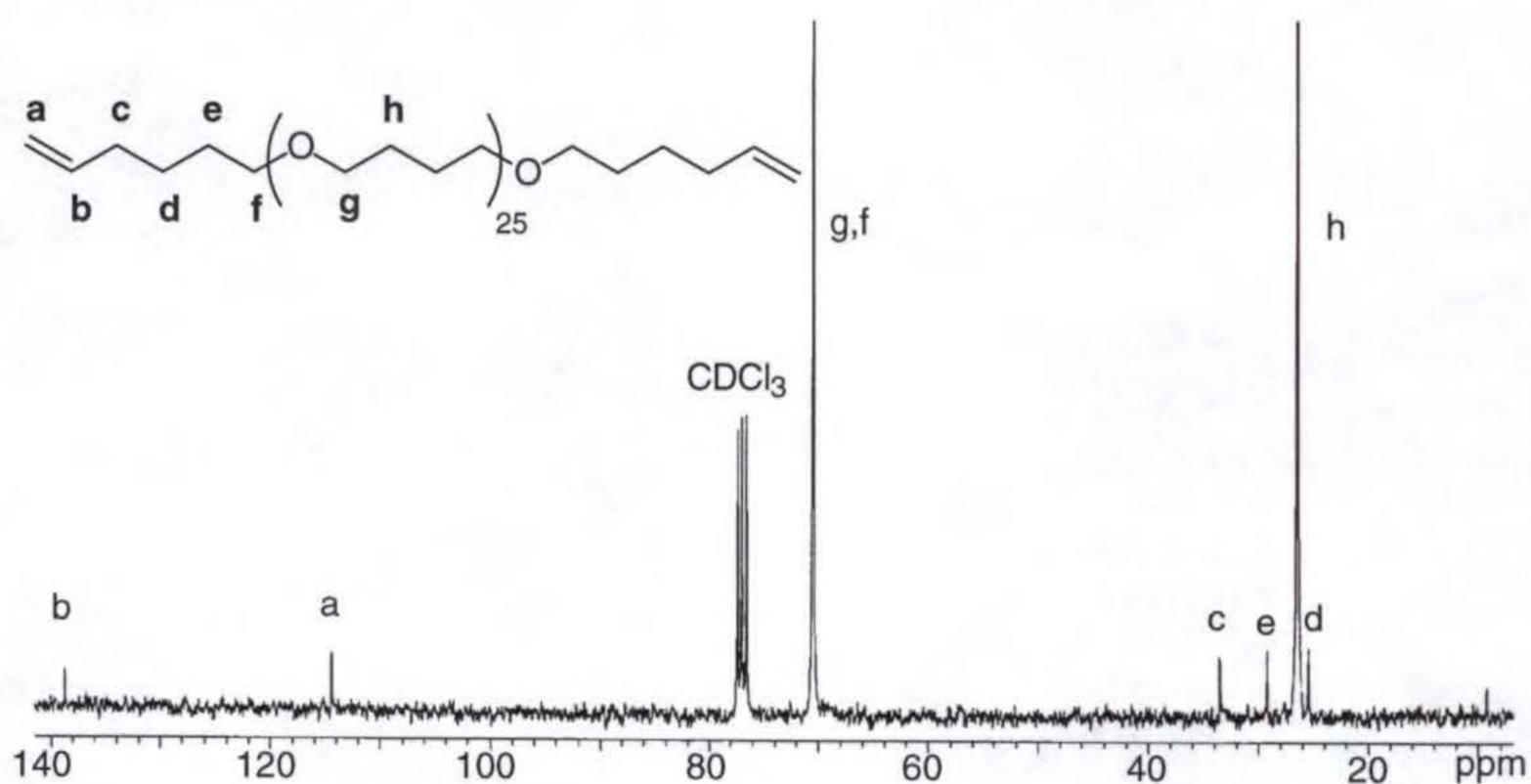
All subsequent poly(tetramethylene oxide) telechelomers were synthesized by an alternate method based on that of Smith and Hubin.<sup>66,68</sup> Rather than using a solvent, triflic anhydride was added to neat, chilled tetrahydrofuran. In the Brzezinska method, the polymerization is allowed to reach equilibrium, and the relative concentrations of monomer and initiator determine the resulting molecular weight of the oligomer. However, by performing the polymerization in the bulk, at low temperatures, and with a fixed amount of monomer and initiator, the molecular weight becomes a function of time. The polymerization is purposely allowed to only proceed to a very low degree of conversion, and on this time frame the polymerization approaches livingness. Indeed the molecular weight distributions of **PTHF1** and **PTHF2** were narrower than **PTHF3**.<sup>57</sup>

Telechelomers used for the work described in Chapters 5 and 6 were synthesized by adding 1.0 mL triflic anhydride to 36.0 mL tetrahydrofuran chilled to  $-13\text{ }^{\circ}\text{C}$ . Reaction for 25 minutes gave  $M_n=1800$  (**PTHF1**), while reaction for 45 minutes increased the molecular weight to  $M_n=3600$  (**PTHF2**). As above, the polymerizations were terminated by adding 5-hexenol. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra for **PTHF1** are

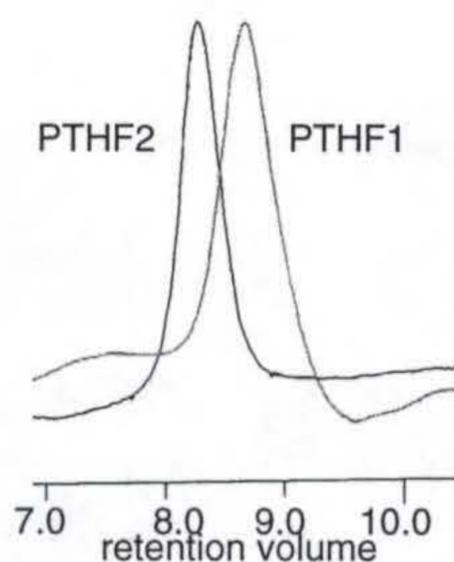
shown in **Figure 2-5** and **Figure 2-6**, respectively, and the GPC chromatograms for **PTHF1** and **PTHF2** are shown in **Figure 2-7**.



**Figure 2-5.**  $^1\text{H}$  NMR of **PTHF1** telechelomer.



**Figure 2-6.**  $^{13}\text{C}$  NMR of **PTHF1** telechelomer.



**Figure 2-7.** GPC of poly(tetramethylene oxide) telechelomers. **PTHF1:**  $M_n=1800$ ,  $PDI=1.11$ ; **PTHF2:**  $M_n=3600$ ,  $PDI=1.07$ .

### Polyisobutylene $\alpha,\omega$ -Dienyl Telechelomers

Polyisobutylene is an amorphous, rubbery polymer used in elastomers and for gas barrier applications.<sup>1,68</sup> This polymer is attractive as a soft phase for segmented and block copolymers because it is an amorphous, hydrocarbon polymer with a  $T_g$  of between  $-67$  and  $-73$  °C.

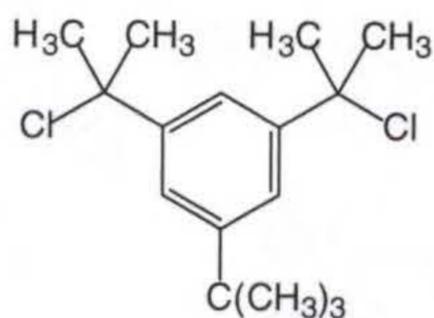
Isobutylene is a monomer that can only be polymerized by cationic routes.<sup>1</sup> Chain transfer events are prevalent in classical cationic polymerizations, so in order to obtain control over the polymerization, systems employing Lewis acid catalysts are used to mediate the reactivity of the propagating cationic site.<sup>3,33</sup> Lewis acids such as  $BCl_3$  or  $TiCl_4$  in the presence of a chloride initiator are most commonly used to polymerize isobutylene in a controlled fashion. Under certain conditions, initiation, transfer, and

termination reactions can be controlled, and this has been termed the *iniferter* or *inifer* method.<sup>2-3</sup>

### Inifer Method for Polymerizing Isobutylene

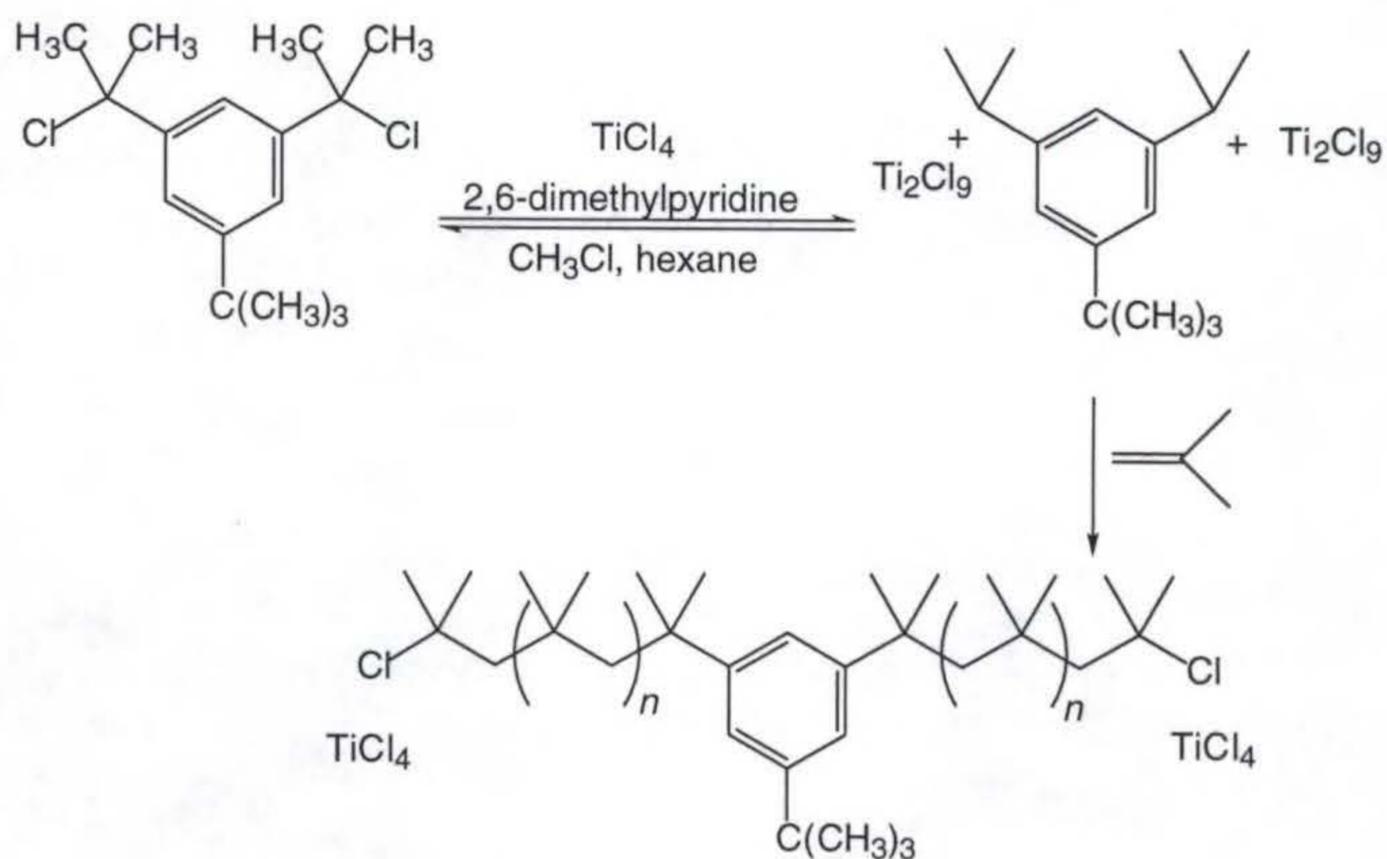
The titanium activated system developed by Kennedy and used extensively by Storey was used to synthesize three  $\alpha,\omega$ -dienyl polyisobutylene samples of differing molecular weights.<sup>69-73</sup> This system is attractive not only because it provides a clean, controlled polymerization with narrow molecular weight distributions, but also because it allows for capping of the polymer with allyl trimethylsilane to give terminal olefin end groups.<sup>3,69</sup>

The inifer method involves the use of a chloride functionalized species that can form a carbenium species when activated with a Lewis acid. Many such initiators, both aromatic and aliphatic, and mono-, di-, and tri-functionalized in chloride have been developed. Difunctionalized initiators, such as 5-*tert*-butyl dicumyl chloride, can initiate polymer growth from two sites on a central headgroup, allowing the formation of difunctional telechelic oligomers (**Figure 2-8**).<sup>70-71</sup> The *tert*-butyl group meta to the initiating groups is necessary to block electrophilic aromatic substitution on the aromatic ring after the first addition of monomer, which would result in an indanyl structure.<sup>3</sup>



**Figure 2-8.** Blocked dicumyl chloride initiator used for polymerization of isobutylene.

Titanium tetrachloride activates the chloride functionality of the initiator, and establishes an equilibrium between a weak covalent chlorine-carbon bond and a tight ion pair between the carbocation chain end and a dimeric titanium anion,  $\text{Ti}_2\text{Cl}_9^-$  (**Figure 2-9**). Titanium tetrachloride is unique compared to other Lewis acid polymerization catalysts in that it is more reactive as its dimer.<sup>73,77</sup> This equilibrium between dormant covalent species and contact ion pair mediates the polymerization, reducing chain transfer and other side reactions. Isobutylene can insert into this activated chain end, but the close proximity of the bulky titanium counterion hinders other reactions.



**Figure 2-9.** Polymerization of isobutylene using the *t*-butyl-dicumyl chloride initiator, and  $\text{TiCl}_4$  cocatalyst.

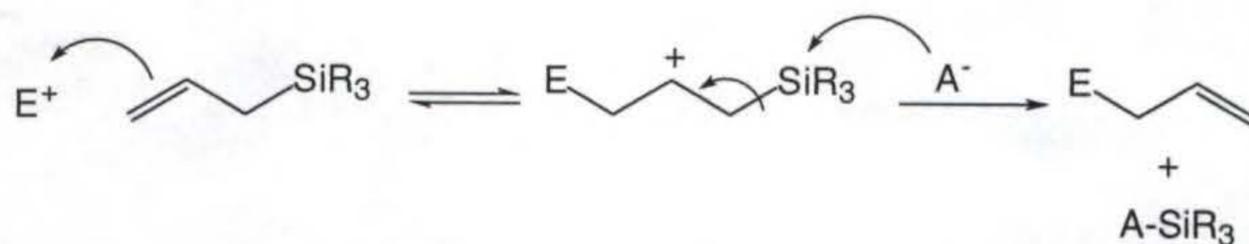
Titanium tetrachloride is necessary to activate the chloride bonds of the initiator, but this compound is also extremely reactive toward the trace amounts of water that are in the reaction medium, even under normal drybox conditions. The reaction of  $\text{TiCl}_4$  with water produces  $\text{HCl}$ , which can also initiate polymerization of isobutylene, so a hindered base, such as 2,6-dimethylpyridine, is added to the system to scavenge  $\text{HCl}$ . The function of this base is twofold. In addition to preventing unwanted initiation by  $\text{HCl}$ , it is believed that this base interacts with the titanium to mediate the nucleophilicity of the counterion species. Some studies have indicated a reduction in chain transfer and termination events upon adding pyridine and substituted pyridines. The propagation rate is slowed, but narrower molecular weight dispersity can be achieved.<sup>78-79</sup>

Side reactions are also minimized by conducting the polymerization at  $-80\text{ }^{\circ}\text{C}$ . The activation energy for chain transfer events is higher than for propagation, so the polymerization is actually faster when run at very low temperatures. Indeed, at this temperature, the polymerizations are complete in a matter of seconds or minutes. At  $-80\text{ }^{\circ}\text{C}$ , and with the appropriate amounts of initiator, activator, and Lewis base, side reactions are minimized such that this system approaches livingness. The low temperature also facilitates the handling of the isobutylene and solvent, methyl chloride, which are gases at room temperature.

#### Functionalization with Allyl trimethyl Silane

Controlled termination of olefins polymerized by the inifer technique is not as straightforward as for the ring-opening polymerizations of the cyclic ethers described above. Addition of most nucleophiles, such as water or alcohols, yields the chloride terminated polymer because the nucleophile attacks the Lewis acidic titanium species rather than reacting with the carbenium end of the growing polymer chain. However, reaction is possible between the growing polymer chain end and allyltrimethyl silane or other allyl transfer agents.<sup>69</sup> The overall result is the transfer of an allyl group to the end of the polymer chain with trimethylsilyl chloride formed as a side product.

There is no detailed report on the mechanism for the allyl group transfer.<sup>3,69</sup> It is allyl silanes as well as allyl germanes and stannanes can transfer an allyl group to electrophilic species (**Figure 2-10**).<sup>80</sup>

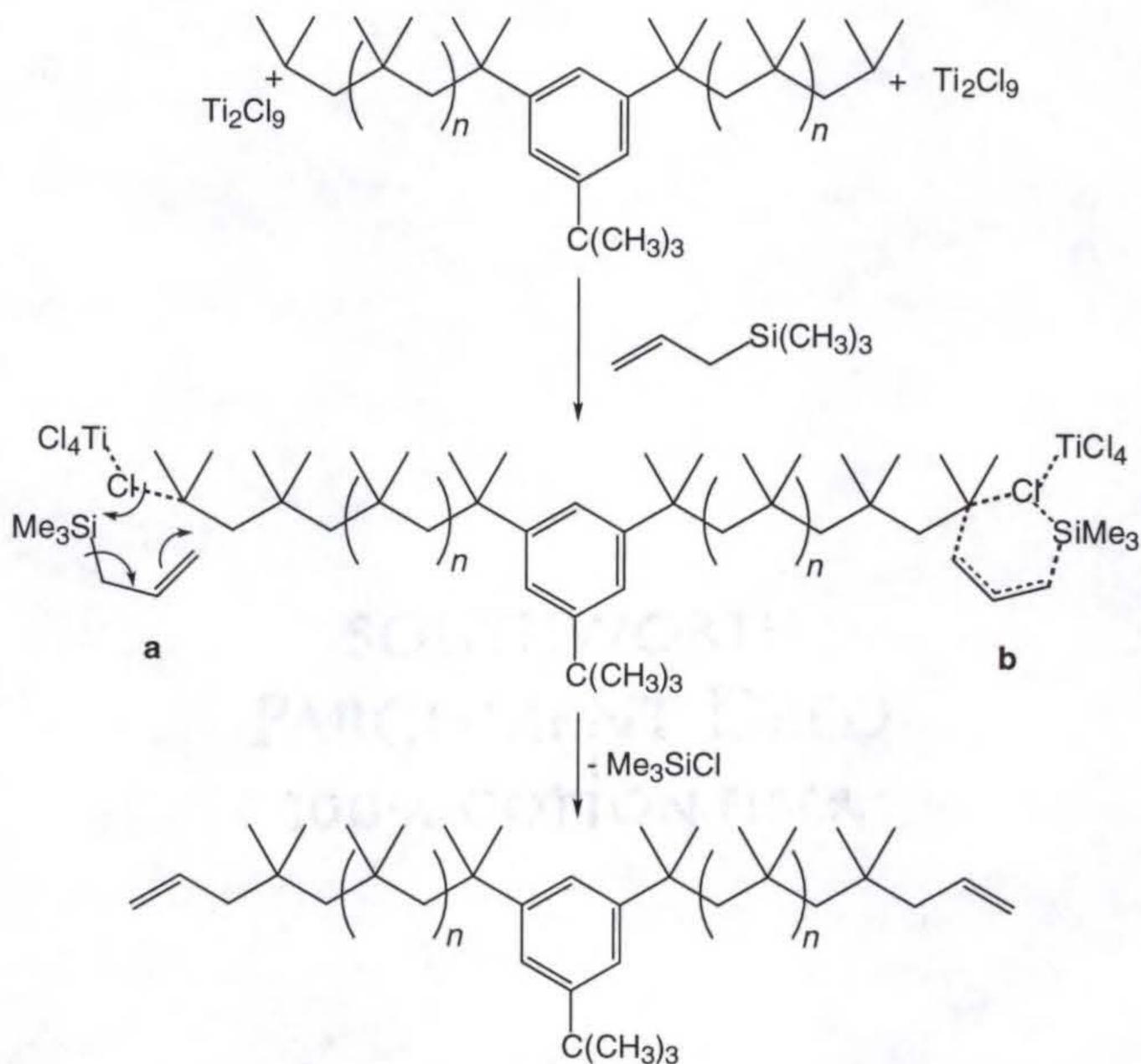


**Figure 2-10.** Reaction of electrophilic center with allylsilane followed by demetallation.

Titanium tetrachloride is used to facilitate the reaction of allyltrimethylsilane to carbonyl compounds by coordinating to the carbonyl oxygen,<sup>80</sup> and  $\text{TiCl}_4$  activates the polymer chain end toward reaction with electron rich species.

However, there is also the possibility that the titanium tetrachloride plays a more involved role. There is evidence that there is some degree of alkene monomer coordination to titanium when  $\text{TiCl}_4$  is used as the catalyst in cationic polymerization, although the extent of olefin coordination and its effect on polymerization has not been elucidated. Therefore interaction of the allyltrimethylsilane with the Lewis acidic titanium is not unreasonable. Further, it is known that transition metal allyl complexes can be formed from the combination of allyltrimethylsilane with the metal chloride.<sup>84-85</sup> If a titanium allyl complex were to form, there is ample evidence that this species could transfer the allyl group to the polymer chain end. It has been demonstrated that the use of allyl borane, allyl aluminum, or cyclopentadienyl aluminum species as activators in cationic alkene polymerization results in allyl or cyclopentadienyl terminated polymer, respectively.<sup>81-83</sup> It is therefore difficult to determine the degree of involvement of  $\text{TiCl}_4$  in the allylation without performing a mechanistic study of this reaction. The simple and generally accepted mechanism for end-capping the polyisobutylene with allyltrimethyl

silane is the direct attack of the allyl with the activated carbon center via a six membered transition state as illustrated in **Figure 2-11**.

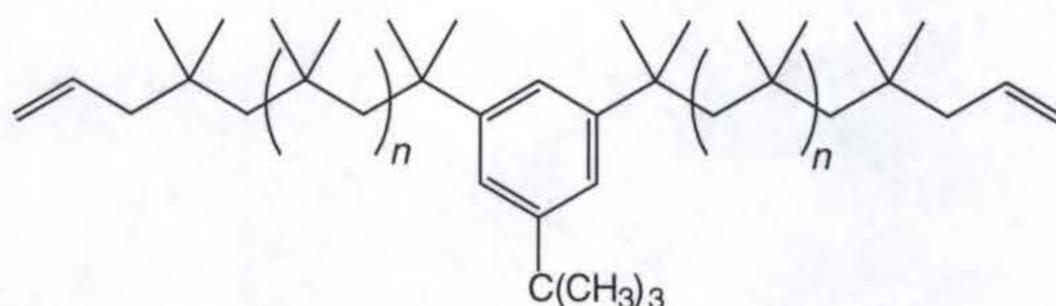


**Figure 2-11.** Capping polyisobutylene with allyl trimethylsilane.

### Synthesis of $\alpha,\omega$ -Dienyl Polyisobutylene

The inifer method allows for well-controlled polymerization of isobutylene and endcapping to obtain terminal olefin groups. These olefin end groups can be used as is or

reacted further to generate other end-functionality on these telechelic oligomers. Three polyisobutylene telechelomers with three different molecular weights were synthesized using the inifer method and allylation described above (**Figure 2-12**).



**Figure 2-12.**  $\alpha,\omega$ -Dienyl polyisobutylene synthesized for this study. ( $n=12, 25, 49$ )

The molecular weight data are summarized in **Table 2-2** and the GPC curves for the three samples are shown in **Figure 2-13**. There is actually good agreement between the molecular weight determined by light scattering, NMR integration, and that determined relative to polystyrene standards. The telechelomers produced were of narrow molecular weight distribution and by  $^1\text{H}$  NMR integration of the terminal olefin groups vs. the three aromatic protons indicates that the functionality,  $F$ , is close to 2.0.

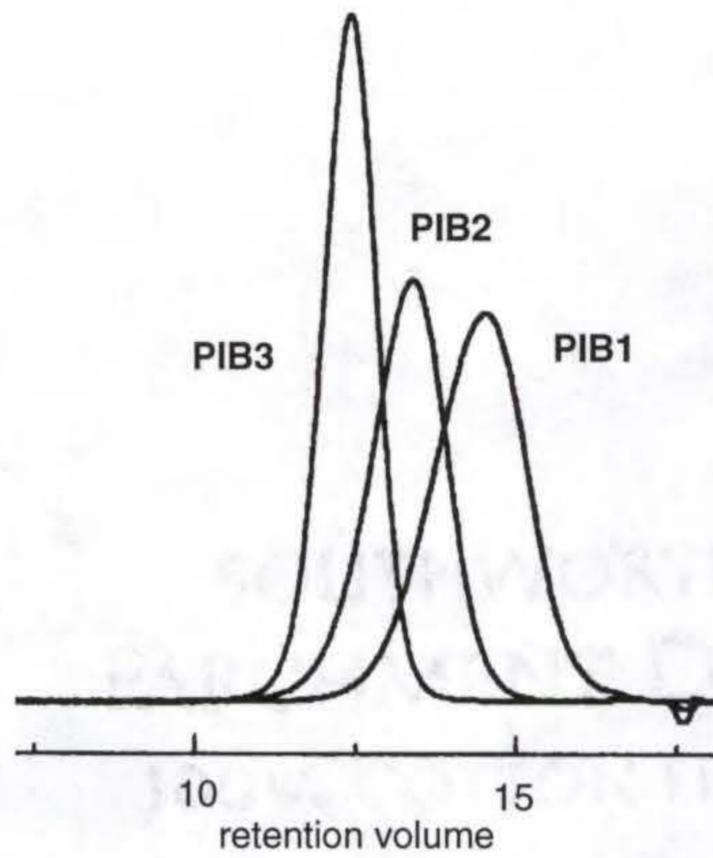
**Table 2-2.** Polyisobutylene telechelomers synthesized.

Telechelomer	IB units ( $2n$ )	$M_n$ NMR <sup>a</sup> g/mol	$M_n$ GPC <sup>b</sup> g/mol	$M_n$ GPC <sup>c</sup> g/mol	$M_w/M_n$	$F^a$
PIB1	24	1700	1700	1800	1.15	1.94
PIB2	50	3100	3100	3200	1.12	1.95
PIB3	98	5800	5800	5900	1.03	2.0

a. Integration of aromatic H to olefin endgroups.

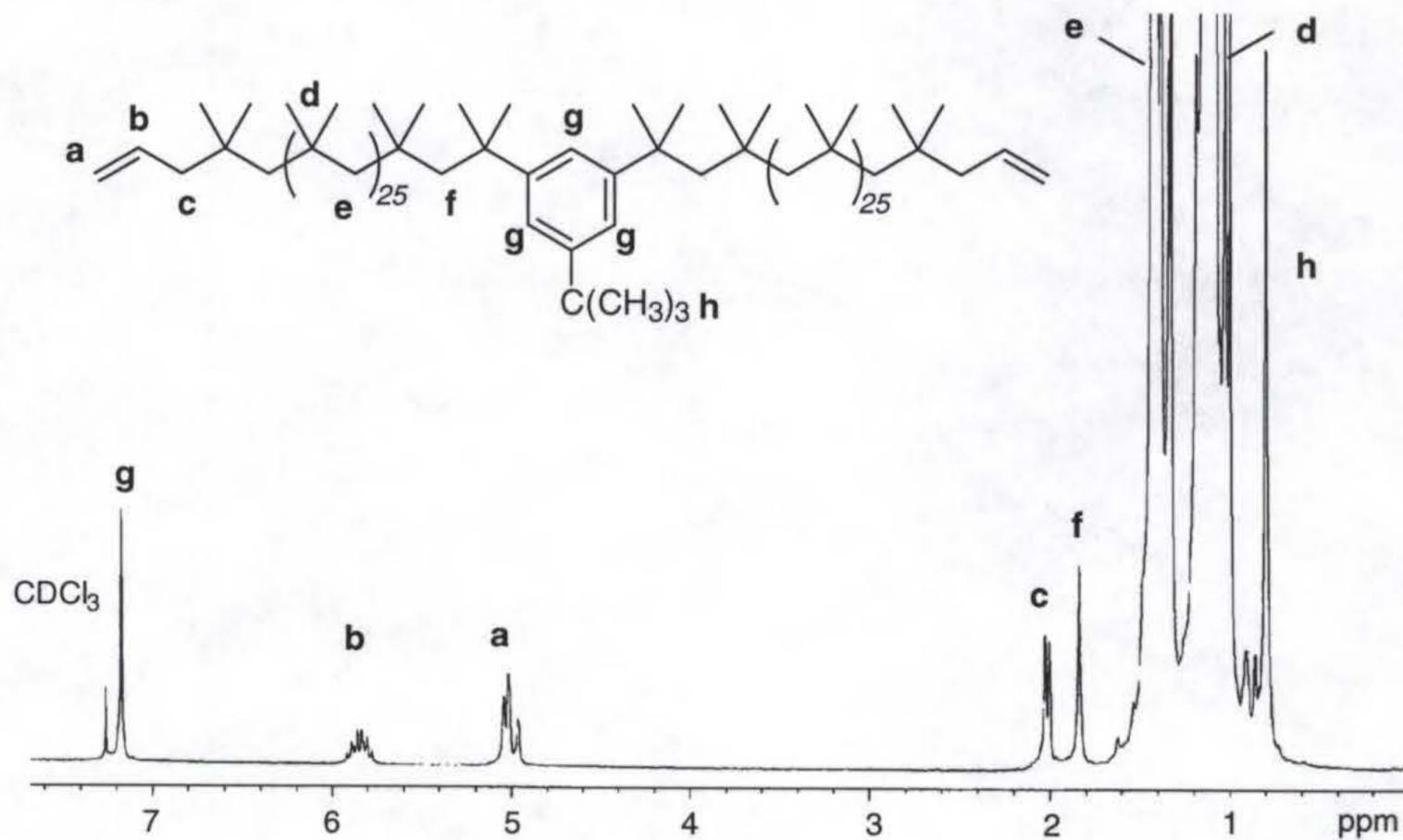
b. Molecular weight by light scattering.

c. Molecular weight relative to polystyrene standards.

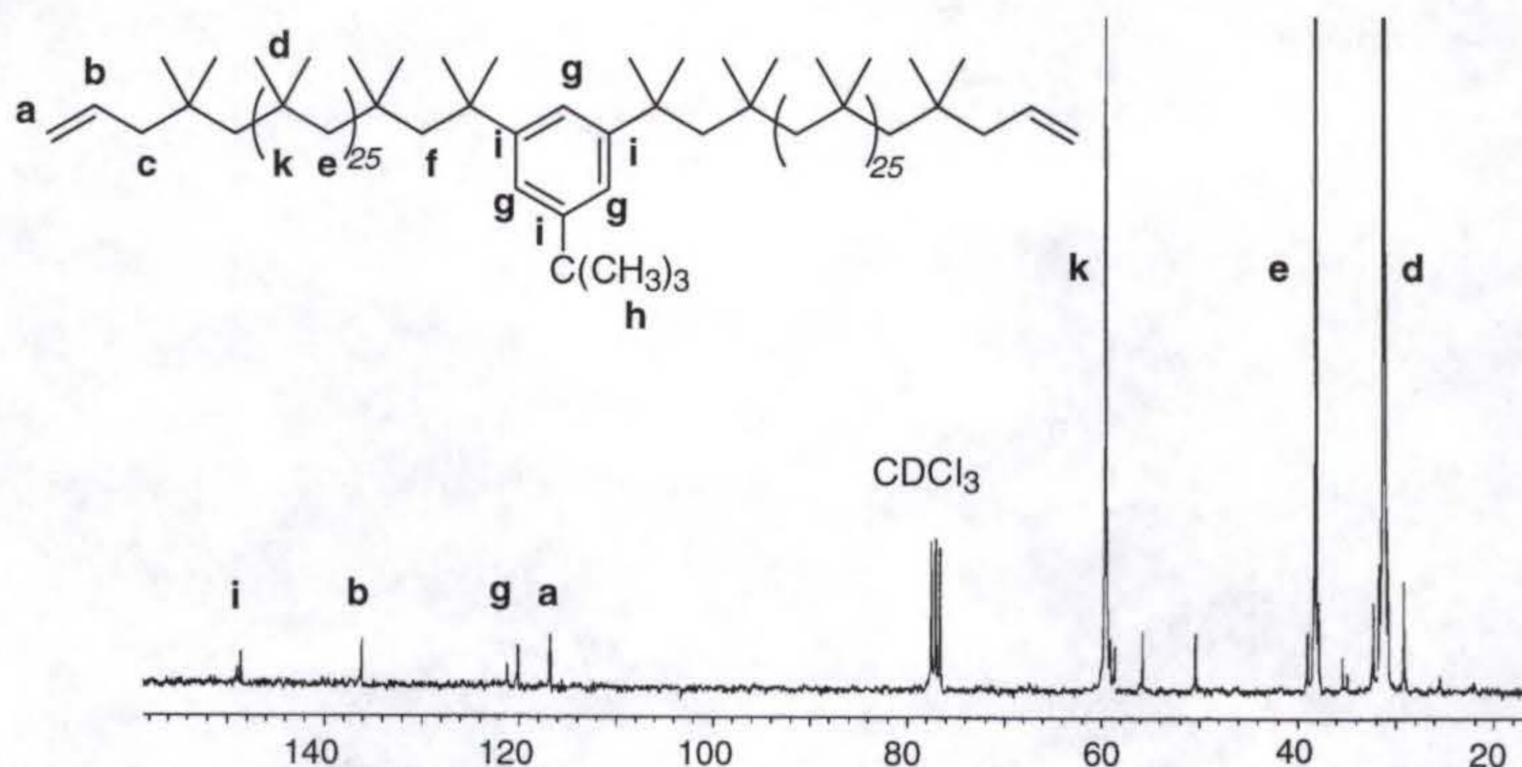


**Figure 2-13.** GPC of PIB telechelomers: **PIB1** ( $M_n=1700$ ); **PIB2** ( $M_n=3100$ ); **PIB3** ( $M_n=5800$ )

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are shown below in **Figure 2-14** and **Figure 2-15**, respectively.



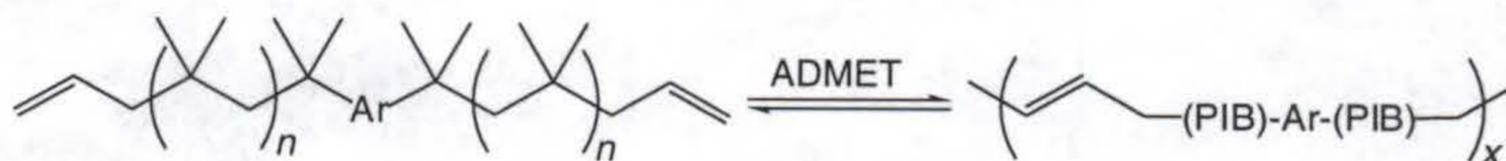
**Figure 2-14.**  $^1\text{H}$  NMR of **PIB2** telechelomer.



**Figure 2-15.**  $^{13}\text{C}$  NMR of PTHF2 telechelomer.

### Metathesis Reactivity of $\alpha,\omega$ -Dienyl Polyisobutylene

The shortest oligomer ( $M_n \sim 1700$ ) was used to obtain an estimate of the reactivity of the terminal allyl groups toward the ruthenium and molybdenum metathesis catalysts. Metathesis polymerization of the alkene terminated polyisobutylene generates a polymer consisting of polyisobutylene segments interrupted periodically by 2-butenyl units as well as the aromatic initiating fragment associated with each chain (**Figure 2-16**).



**Figure 2-16.** ADMET polymerization of  $\alpha,\omega$ -dienyl polyisobutylene telechelomers.

Polymerizations were conducted using both Schrock's molybdenum  $((\text{Mo}(\text{NC}_6\text{H}_3-2,6-i\text{-Pr})(\text{OCCH}_3(\text{CF}_3)_2)_2(\text{CHC}(\text{CH}_3)_2\text{C}_6\text{H}_5))$  and Grubbs's ruthenium  $((\text{Ru}(\text{P}(\text{C}_6\text{H}_{11})_3)_2\text{Cl}_2(\text{CHPh}))$  alkylidene catalysts, **Figure 1-7**. ADMET polymerizations were conducted in the bulk with 1:200 catalyst to monomer ratio under vacuum. The ruthenium reactions were begun at 40 °C for 24 hours then warmed to 75 °C for two additional days. The molybdenum catalyst is generally faster than the ruthenium systems, but one drawback of the molybdenum catalyst is its lower tolerance toward heating, so these reactions were performed at 40 °C for 3 days. Conversion was estimated by  $^1\text{H}$  NMR end-group analysis and gel permeation chromatography and is summarized in **Table 2-3**.

**Table 2-3.** Molecular weight data for metathesis conversion of polyisobutylene telechelomers.(g/mol).

Telechelomer	Ruthenium		Molybdenum	
	$^1\text{H}$ NMR <sup>a</sup>	GPC <sup>b</sup>	$^1\text{H}$ NMR <sup>a</sup>	GPC <sup>b</sup>
PIB(1700)	16,000	17,000	15,000	16,000

a. Molecular weight calculated from ratio of terminal to internal endgroups.

b. Molecular weight vs. polystyrene standards.

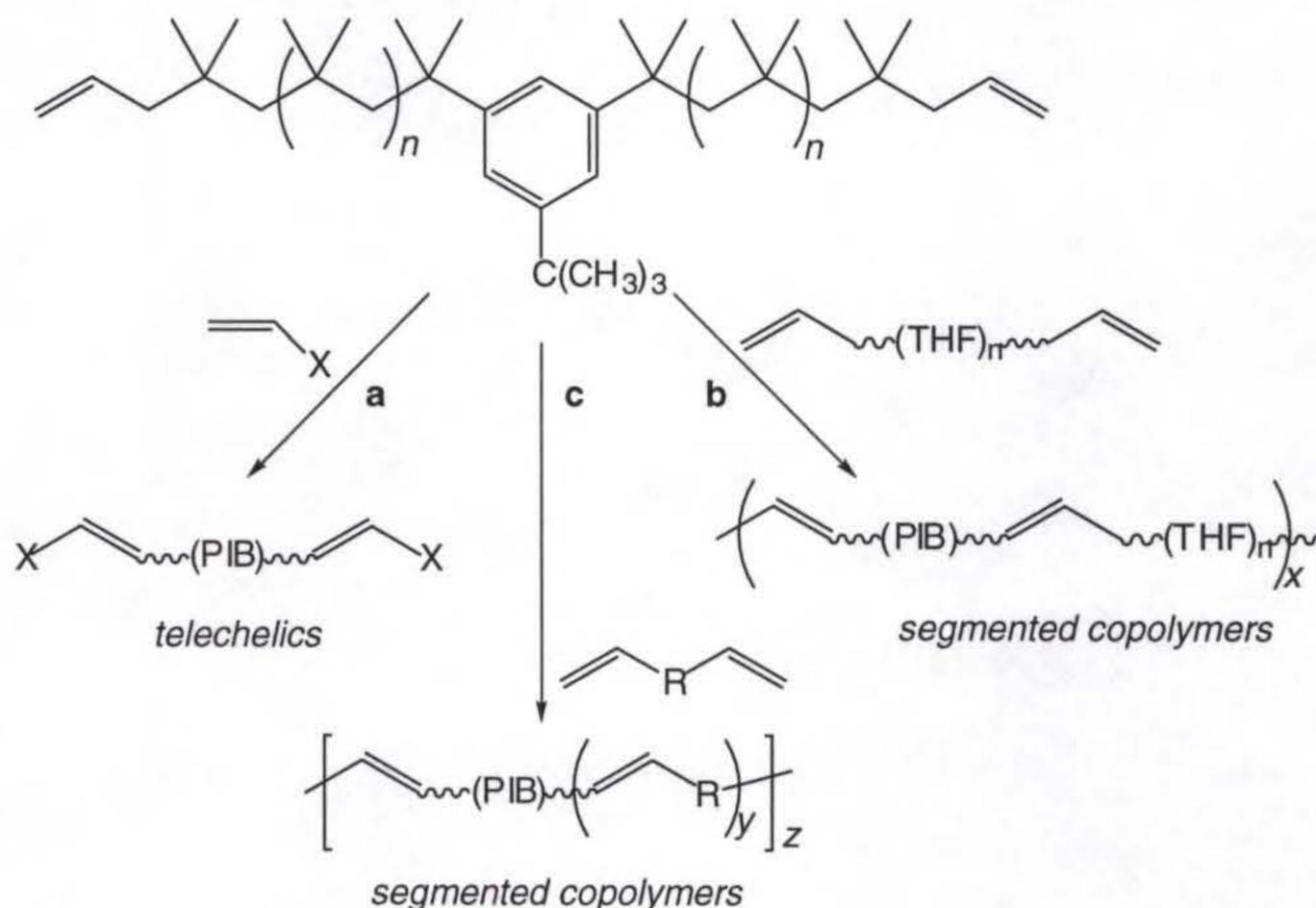
Metathesis polymerization of the polyisobutylene telechelomers is slow compared to many of the small diene monomers typically used in ADMET polymerization, and this reduced reactivity could be attributed to a number of factors. Firstly the concentration of reacting olefin groups is small due to the large size of the telechelomers. This situation can be related to a step polymerization at high conversions.

Catalyst plus two polymer end groups must find each other for each new connection to occur. Further, the polyisobutylene oligomers are very viscous materials as opposed to the liquid monomers typically used in ADMET polymerization, which may also hinder the required convergence of olefin groups and the reactive catalyst sites. Additionally, the steric influence of the methyl groups on the carbon  $\beta$  to the reacting olefin could slow olefin metathesis. Studies by Konzelman and Wagener have shown that placing bulky substituents near the metathesizing olefin hinders metathesis.<sup>55</sup> Another factor that could slow the metathesis polymerization of these telechelomers arises from polyisobutylene's low gas permeability. Polyisobutylene is such a good barrier to air that it is used as liner material in tires and inflated balls.<sup>65</sup> If the ethylene that is given off in the metathesis reaction is trapped and kept in close proximity to the catalyst, it could re-enter the catalytic cycle in depolymerizing reactions with the growing polymer.

#### Perspectives on PIB Telechelomers for Tailored Polymers

Both the molybdenum and ruthenium catalysts were effective toward the metathesis conversion of the polyisobutylene telechelomers. Under the reaction conditions used, polymerization was not complete, as conversion of this telechelomer appears to be slower than that of many small molecule aliphatic diene monomers due to a number of contributing factors described above. Subsequent metathesis reactions with these telechelomers will need to be conducted for longer reaction times and higher temperatures, if possible, to achieve adequate conversion.

Despite their slowed reactivity, the ability of  $\alpha,\omega$ -dienyl polyisobutylene to undergo metathesis reactivity opens the door to many possible uses for these telechelomers (**Figure 2-17**). For example, olefin metathesis chemistry could be used to introduce new endgroups to these oligomers by reaction with an excess of functionalized mono-olefin capping agents. Further, metathesis could be used to couple these polyisobutylene telechelomers with diene telechelomers of a differing backbone (e.g. the poly(tetramethylene oxide) telechelomers described above), and this reaction would produce a segmented copolymer.



**Figure 2-17.** Some of the possibilities for metathesis conversion of  $\alpha,\omega$ -dienyl polyisobutylene telechelomers. **a)** end-functionalization **b)** reaction with other diene telechelomers **c)** reaction with diene comonomers.

Alternatively, copolymerization of these  $\alpha,\omega$ -dienyl polyisobutylene telechelomers with small molecule diene monomers could also lead to segmented

copolymers, and this is the approach explored in the subsequent chapters of this dissertation. Copolymerization with decadiene is discussed in Chapter 3, while Chapters 4-6 present copolymerization with carbonate, ester, and urethane functionalized diene comonomers to produce several new segmented copolymers.

### CHAPTER 3

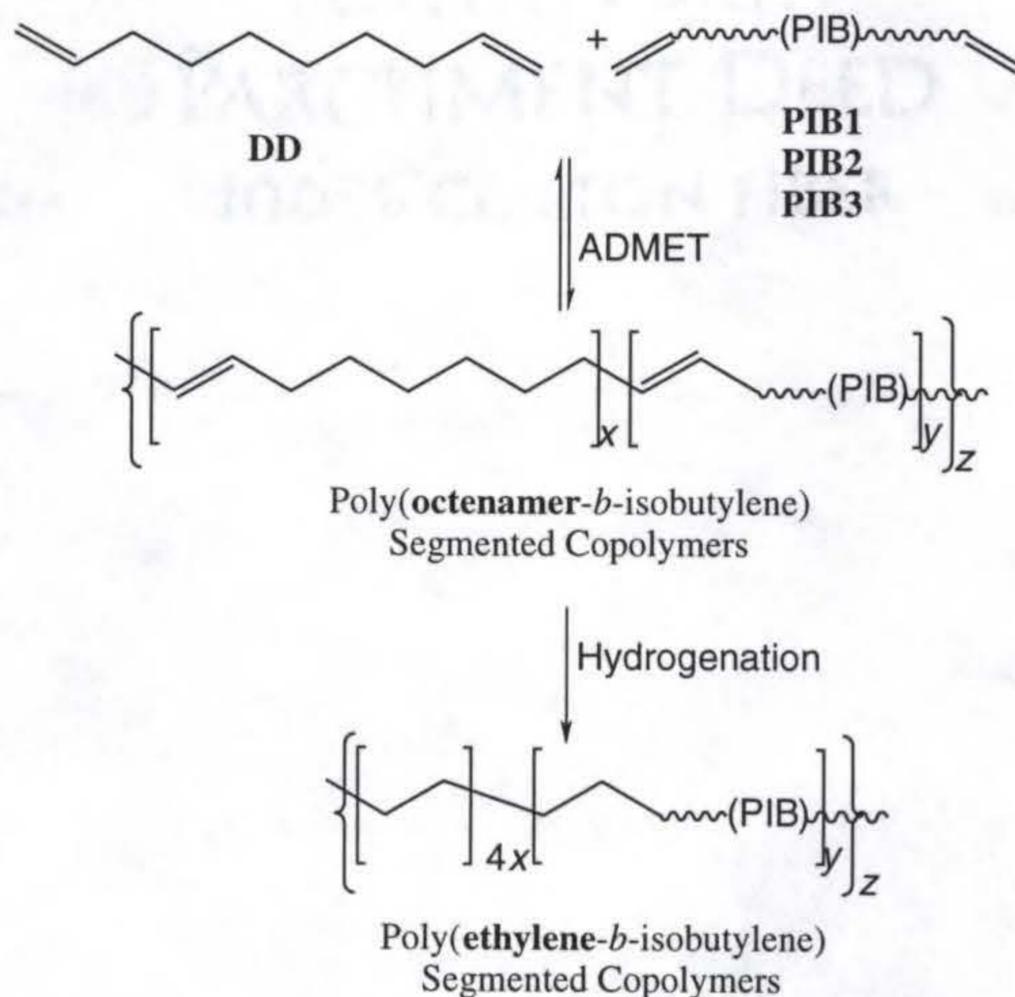
## COPOLYMERIZATION OF POLYISOBUTYLENE WITH DECADIENE

Decadiene is the benchmark monomer for acyclic diene metathesis polymerization. Not only was this the first monomer utilized in ADMET polymerization,<sup>43</sup> but it has been used to determine the reactivity of new catalysts<sup>47-48,86</sup> as well as to study the kinetics of ADMET polymerization.<sup>87</sup> Further, it was the successful copolymerization of decadiene with poly(tetramethylene oxide) diene telechelomers that initiated the research effort in ADMET segmented copolymers.<sup>57</sup>

The copolymerization of decadiene with the polyisobutylene telechelomers would create segmented copolymers in which both blocks are aliphatic hydrocarbon chains. However, it is the hydrogenated analogs of these polyoctenamer-isobutylene segmented copolymers, which approximate segmented polyethylene-isobutylene structures, that are particularly interesting. Although alternating copolymers of isobutylene-ethylene have been reported, to date no chain polymerization mechanism has been able to generate copolymers of ethylene and isobutylene arranged as blocks.<sup>88-89</sup>

### Synthesis of Segmented Copolymers of Decadiene and Polyisobutylene

Nine different segmented copolymers were synthesized from the copolymerization of diene polyisobutylene with decadiene. The unsaturated poly(isobutylene-octenamer) copolymers were then hydrogenated using the methods developed by Watson and coworkers<sup>90</sup> to give the nine corresponding saturated polymers, which approximate a poly(isobutylene-ethylene) segmented structure (**Figure 3-1**).



**Figure 3-1.** Copolymerization of polyisobutylene with decadiene followed by hydrogenation.

Polyisobutylene diene oligomers with parent molecular weights of 1700 (**PIB1**) 3100 (**PIB2**) and 5800 (**PIB3**) were copolymerized in three different ratios with decadiene. The proportions used are abbreviated as 1:2, 1:4, and 1:6, which refer to the target compositions of the final copolymer containing one octenamer unit per every two,

four, or six isobutylene repeat units, respectively. Upon hydrogenation each octenamer repeat unit is converted to four ethylene repeat units, which changes the proportions of hard phase repeat unit with respect to isobutylene repeat units, as summarized in **Table 3-1**. However, to avoid confusion, the copolymers will be referred throughout this text as 1:6, 1:4, and 1:2 for the same copolymer sample both before and after hydrogenation.

**Table 3-1.** Target proportions of octenamer and isobutylene in copolymers, and the calculated conversion of these proportions in terms of ethylene repeat units upon hydrogenation.

Poly(octenamer-IB) copolymer	After hydrogenation	
	mol ethylene : mol IB	wt ethylene: wt IB
mol octenamer : mol IB		
1:6	2:3	1:3
1:4	1:1	1:2
1:2	2:1	1:1

#### Molecular Weight Analysis of Decadiene-PIB Segmented Copolymers

The unsaturated copolymers containing a largest fraction of polyisobutylene (1:6) were sticky, viscous materials, resembling the parent polyisobutylene, and even after hydrogenation, these remain very soft and tacky and transparent. The 1:4 copolymers based on **PIB2** and **PIB3** were soft, tacky semisolids and remained soft translucent to transparent tough rubbery substances upon hydrogenation. A higher

degree of conversion was achieved with the **PIB1** 1:4 polymerization, which was a resilient soft solid. The 1:2 copolymers were soft, waxy translucent materials, and hydrogenation yielded soft white powders. Upon hydrogenation all materials became more firm and the 1:4 and 1:2 became noticeably less soluble in common organic solvents.

Much like the homopolymerizations of polyisobutylene described in Chapter 2, the copolymerizations of decadiene with polyisobutylene telechelomers were slow, although improved molecular weight was achieved by allowing the reactions to proceed for at least 7-10 days. Upon copolymerization the molecular weights of the resulting copolymers increased relative to the parent homopolymer, and in each case there was only negligible unreacted parent oligomer as detected by GPC of the filtered reaction product prior to precipitation. Molecular weight data is summarized in **Table 3-2** and indicates that copolymers of modest molecular weight (up to 22,000 vs. polystyrene standards) were obtained in all but one case. The polydispersity ( $M_w/M_n$ ) of the copolymers was found to be lower than the expected 2.0 for step-growth polymerization, but is still broader than the parent telechelomer.

Molecular weight was measured only for the unsaturated polyoctenamer-polyisobutylene copolymers due to the reduced solubility of the materials after hydrogenation. The 1:2 and 1:4 copolymers were insoluble in chloroform or other common solvents at room temperature, precluding gel permeation chromatography or NMR analysis at room temperature. However, while some studies have shown a change in the hydrodynamic volume of an unsaturated polymer after hydrogenation,<sup>62</sup> other

studies have shown that the hydrogenation procedure has little effect on the molecular weight of the polymer.<sup>53</sup>

**Table 3-1.** Summary of molecular weight data for decadiene-PIB segmented copolymers.

Copolymer (ratio wt:wt)	$M_n$ $\times 10^3$ g/mol	$M_w$ $\times 10^3$ g/mol	$M_w/M_n$
PIB1-DD (2:1)	20	36	1.8
PIB2-DD (2:1)	14	20	1.4
PIB3-DD (2:1)	20	26	1.3
PIB1-DD (4:1)	35	47	1.4
PIB2-DD (4:1)	22	29	1.4
PIB3-DD (4:1)	22	29	1.5
PIB1-DD (6:1)	21	29	1.5
PIB2-DD (6:1)	23	34	1.5
PIB3-DD (6:1)	28	37	1.6

#### Thermal Analysis of Decadiene-PIB Segmented Copolymers

Thermal gravimetric analysis (TGA) of the segmented copolymers is summarized in **Table 3-2**. The thermal stability of the copolymers in nitrogen is comparable to that of the respective homopolymers, with all copolymers showing 50 % weight loss in the range of 410-425 °C. The length of the oligomer produced no significant effect on thermal weight stability.

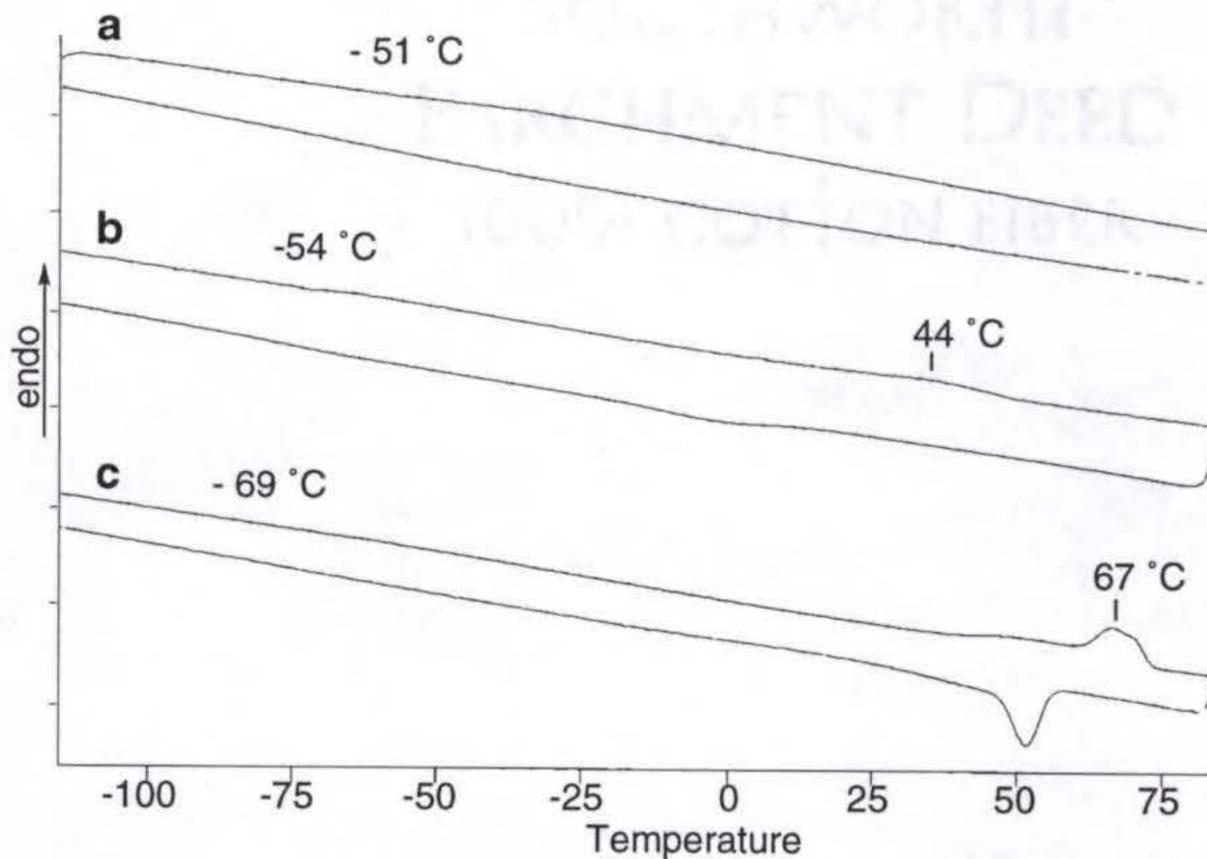
**Table 3-2.** Thermal gravimetric analysis of decadiene-PIB segmented copolymers: Temperatures of onset, 50%, and 90% weight loss. 20 °C/min.

Copolymer (wt ratio)	Onset °C	50% °C	90% °C
PIB1-DD (2:1)	380	410	434
PIB2-DD (2:1)	392	417	438
PIB3-DD (2:1)	381	410	434
PIB1-DD (4:1)	381	426	458
PIB2-DD (4:1)	384	412	436
PIB3-DD (4:1)	394	410	435
PIB1-DD (6:1)	378	409	431
PIB2-DD (6:1)	382	412	436
PIB3-DD (6:1)	387	415	438

Differential scanning calorimetry was used to study the phase separation in the copolymers both before and after hydrogenation, and **Figures 3-2** through **3-6** show some of the trends that were observed. The 1:6 copolymers, which contain the largest fraction of polyisobutylene, are amorphous, sticky materials displaying only a glass transition temperature near the expected  $-70$  °C corresponding to polyisobutylene. Increasing the proportion of decadiene in the polymerization led to the formation of soft waxes for the 1:4 copolymer and finally soft white solids for the 1:2 copolymers, which displayed melting points corresponding to their polyoctenamer segments.

As illustrated in **Figure 3-2**, as the proportion of decadiene is increased, the product changes from an amorphous material to a more solid semicrystalline material. For the copolymers with **PIB1**, the 1:6 copolymer is a viscous liquid. Increasing the

proportion of decadiene to 1:4 gives a soft wax with a melting point of 44 °C. Further increasing the amount of decadiene gives a copolymer with a melting point close to that expected for a decadiene homopolymer.



**Figure 3-2.** DSC trace showing the effect of proportion of hard phase on unsaturated PIB-octenamer copolymers: copolymers of **PIB1** with a) 1:6, b) 1:4, and c) 1:2 proportions of octenamer.

The effect of increasing the amount of hard phase is also reflected in the change in glass transition temperature. The samples with the lowest proportion of polyoctenamer, are completely amorphous with the glass transition temperature elevated from that of the polyisobutylene homopolymer. Presumably there is too little polyoctenamer to be able to separate into crystalline domains. However, the increase in the soft phase  $T_g$  is consistent with mixing of the amorphous polyoctenamer with the amorphous polyisobutylene. The introduction of these less flexible segments could have an overall stiffening of the bulk material, similar to what is observed for commercial polyester-ether

segmented copolymers upon varying the proportions of hard and soft segments.<sup>28</sup> As the amount of polyoctenamer increases, the two components are able to phase separate into crystalline and amorphous domains. With less polyoctenamer present in the soft phase, the glass transition temperature decreases, approaching that of the PIB homopolymer. Similar results are observed for the other copolymer combinations, and these are summarized in **Table 3-3**.

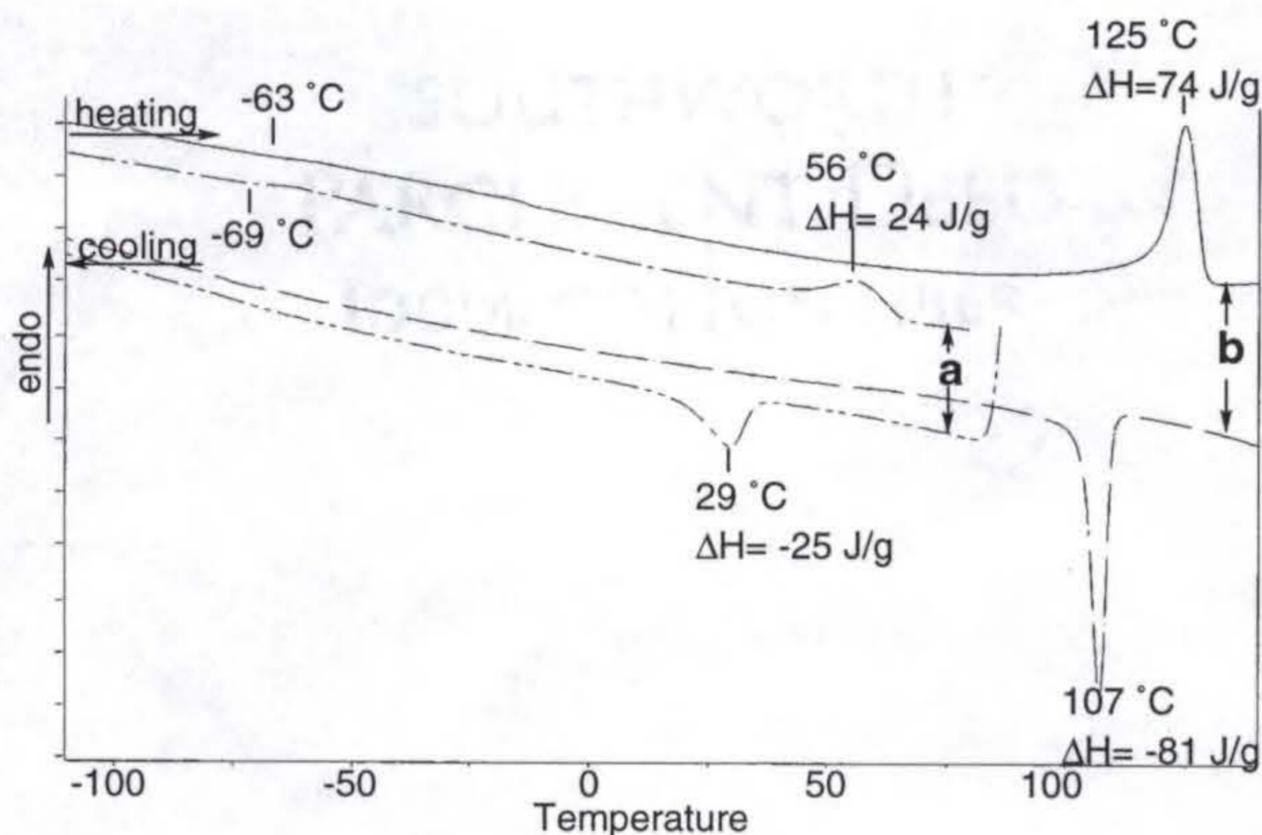
**Table 3-3.** Differential scanning calorimetry analysis of decadiene-PIB segmented copolymers. Data from second heating scan at 20 °C/min.

Copolymer (wt ratio)	T <sub>g</sub> °C	T <sub>m</sub> (°C) onset/peak	T <sub>g</sub> after H <sub>2</sub> °C	T <sub>m</sub> after H <sub>2</sub> onset/peak
PIB1-DD (2:1)	-69	62 / 67		
PIB2-DD (2:1)	-69	60 / 67		
PIB3-DD (2:1)	-69	48 / 56	-63	120 / 125
PIB1-DD (4:1)	-54	44	-60	88
PIB2-DD (4:1)	-54	--	-59	85 / 100
PIB3-DD (4:1)	-68	36	-64	120
PIB1-DD (6:1)	-51	--	-53	--
PIB2-DD (6:1)	-59	--	-60	--
PIB3-DD (6:1)	-66	--	-62	--

#### Hydrogenation of Segmented Copolymers

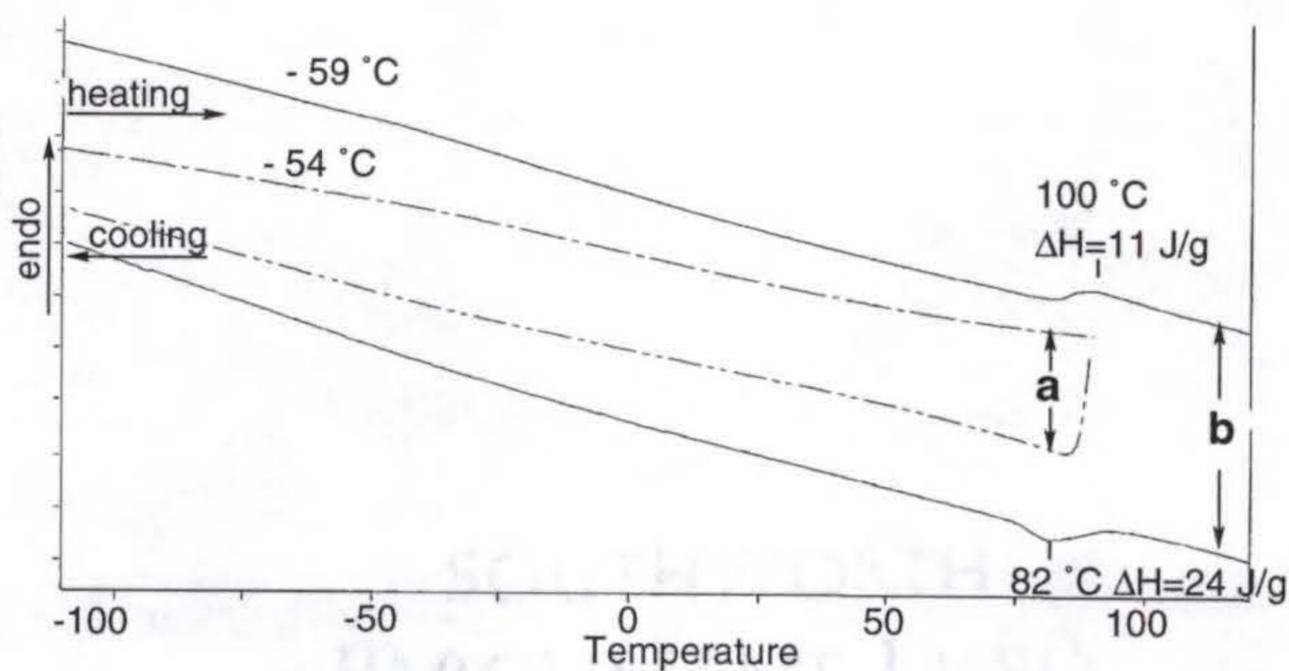
Hydrogenation of the segmented copolymers effectively converts the polyoctenamer segments to polyethylene segments. In each case an increase in the

melting point of these segments was observed upon hydrogenation, while the  $T_g$  remains essentially unchanged. The effect of hydrogenating the copolymers is illustrated with the copolymer of **PIB3** with 2:1 decadiene (DD) (**Figure 3-3**) and with **PIB2** with decadiene 1:4 (**Figure 3-4**). Upon hydrogenating the 2:1 **PIB3**/DD copolymer, not only is the melting point elevated from 56 °C to 125 °C, but also the enthalpy associated with this transition increases.



**Figure 3-3.** DSC trace showing the effect of hydrogenation on melting point: a) **PIB3**/DD 2:1 before hydrogenation and b) after hydrogenation.

Hydrogenation has an even more pronounced effect in the case of the 4:1 **PIB2**/DD copolymer, which displays only a glass transition temperature for the unsaturated copolymer. Upon hydrogenation, a weak melting endotherm appears at 100 °C.

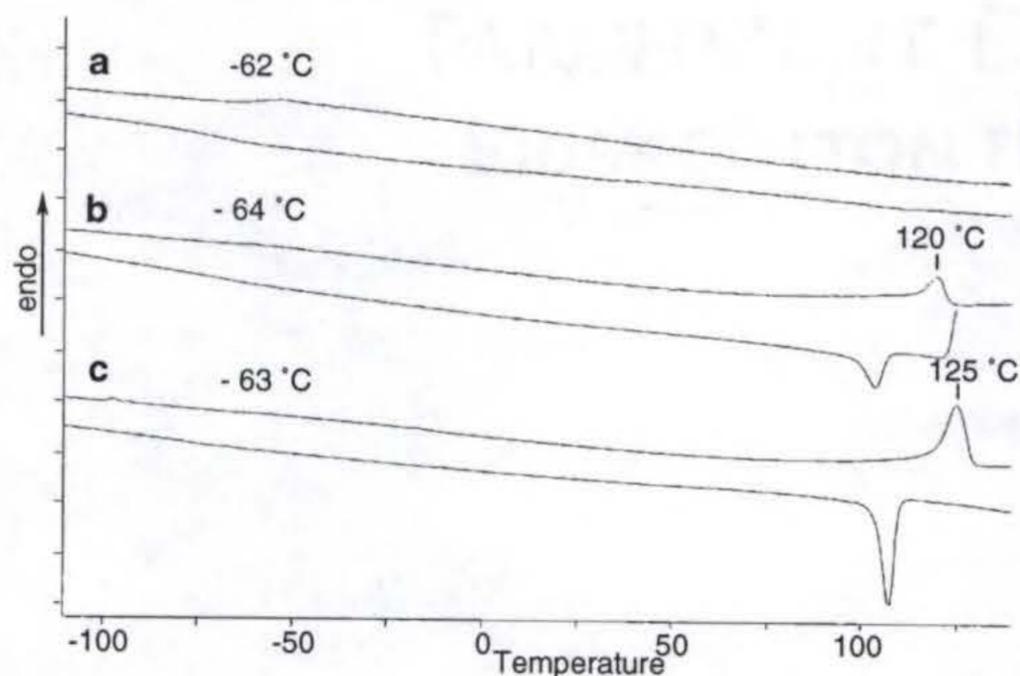


**Figure 3-4.** DSC trace showing the effect of hydrogenation on melting point: a) PIB2/DD 4:1 before hydrogenation and b) after hydrogenation.

Similar results are observed with the other copolymers upon hydrogenation. The melting points of the hydrogenated polyoctenamer segments are much lower than that of high molecular weight linear polyethylene, which is in the range of 135-140 °C. This depression from the expected melting point may be due to either incomplete hydrogenation or to the short length of the polyethylene segments. If the segment length is very short, as would be expected for a segmented copolymer, then the polymer chains will not form the same type of crystal morphology as long-chain polyethylene.

The effect of hard phase proportion observed with the polyoctenamer/polyisobutylene copolymers is also seen their saturated analogs. **Figure 3-5** shows the hydrogenated copolymers of **PIB3** with the three different proportions of hard phase. The copolymers with the highest proportion of PIB remain amorphous, even after hydrogenation. However, decreasing the amount of PIB reveals a

melting point for the polyethylene segments which increases with increasing incorporation of hard phase. With the highest incorporation of ethylene segment, a melting point is observed at 125 °C.



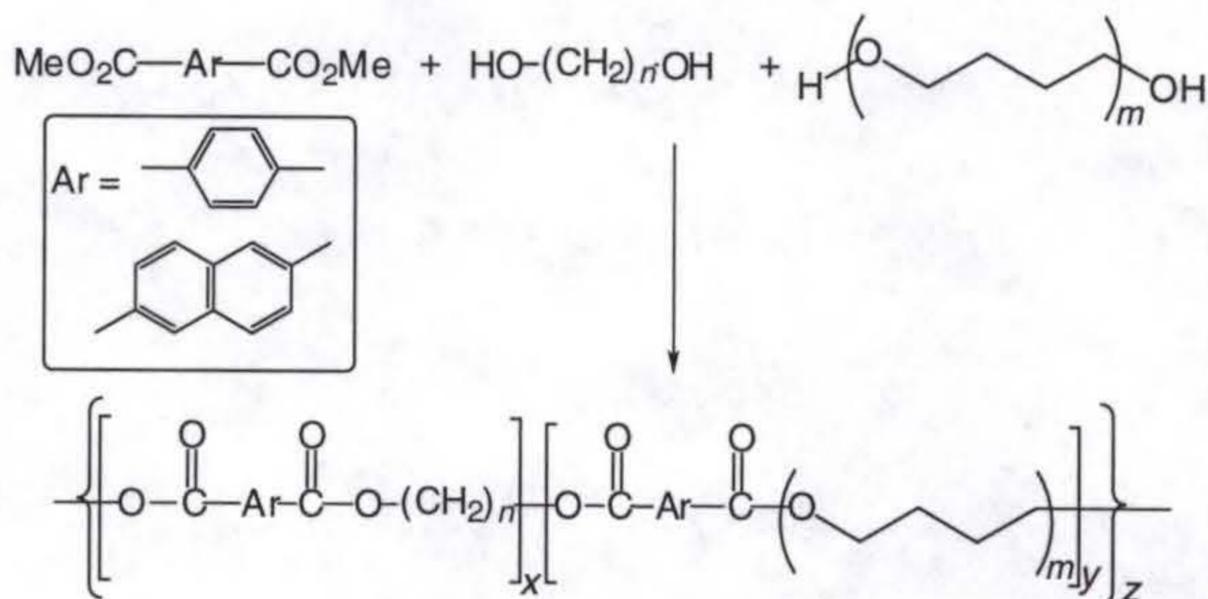
**Figure 3-5.** DSC trace showing the effect of proportion of hard phase for hydrogenated copolymers: Saturated copolymers of **PIB3** with **a)** 1:6; **b)** 1:4; and **c)** 1:2 to octenyl repeat unit.

Despite the fact that both segments are composed of hydrocarbon parent polymers, the data for both the PIB-polyoctenamer and the PIB-polyethylene copolymers indicates that by incorporating a high enough proportion of hard segment, a copolymer with thermal properties consistent with phase separation can be obtained.

Most of the copolymers obtained were too low in molecular weight to be useful as materials. However, the **PIB1/DD** 1:4 demonstrated that with high enough molecular weight, these polyisobutylene-ethylene copolymers could be potentially interesting materials.

CHAPTER 4  
SEGMENTED ESTER COPOLYMERS

Segmented polyether-ester copolymers, such as Du Pont's Hytrel™, have been commercially known since the early 1970's.<sup>28</sup> These polymers are typically based on aromatic ester repeat units such as ethylene or butylene terephthalates or 2,6-naphthalene dicarboxylates combined with soft polyethers, such as poly(tetramethylene oxide) or poly(ethylene oxide). (Figure 4-1).



**Figure 3-1.** General scheme for synthesis of commercial poly(ester-ether) segmented copolymers.  $m=13$ ;  $n=2,4$ .

The rigid, crystalline carboxylate segments impart high melting points and good thermal stability to these copolymers. Segmented ester-ether copolymers range from toughened thermoplastics to thermoplastic elastomers depending on the weight percent of

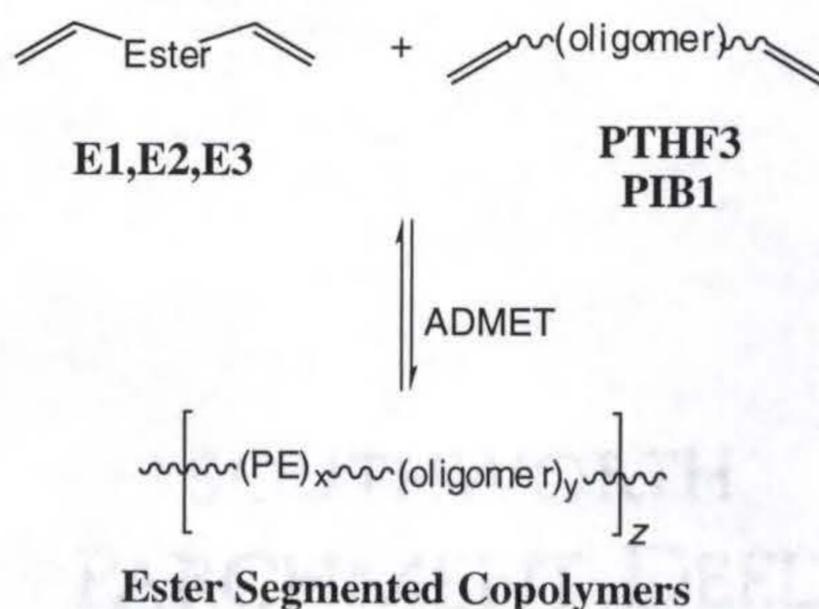
ester to ether. The noncrystalline portions of the polyester are incorporated into the amorphous soft phase along with the polyether, allowing some copolymers with up to 50 % ester to show elastomeric behavior.

### Synthesis of Ester ADMET Segmented Copolymers

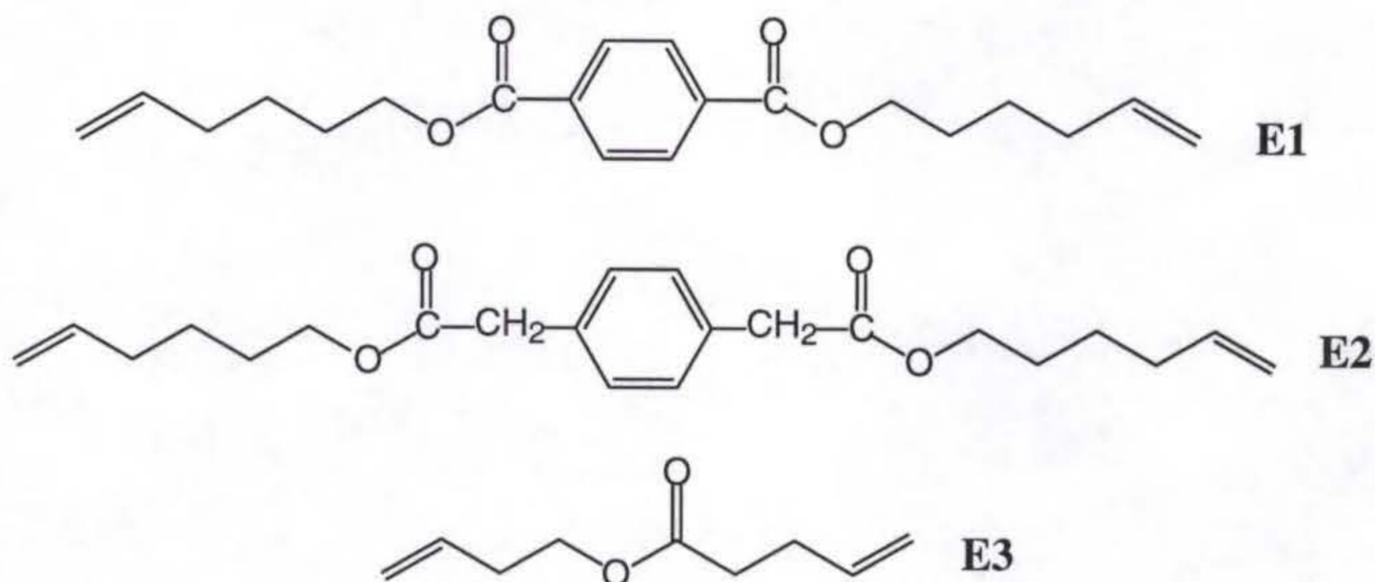
Ester dienes are not new to ADMET chemistry.<sup>91</sup> Patton and Wagener studied the viability of the ester functionality in ADMET monomers and found that terephthalate dienes as well as aliphatic esters are reactive toward metathesis chemistry provided the functionality is separated by at least two methylene units from the metathesizing olefin.

For this study, three ester diene monomers were copolymerized with polyisobutylene **PIB1** and poly(tetramethylene oxide) **PTHF3** diene telechelic oligomers to make four different segmented copolymers (**Figure 4-2**). The polyisobutylene diene oligomers with parent molecular weights of 1700 (**PIB1**) and poly(tetramethylene oxide) oligomers with molecular weights of 1700 (**PTHF3**) were used, and the synthesis of these telechelomers is described in Chapter 2.

The monomers, shown in **Figure 4-3**, were synthesized via standard esterification methods. The bis(5-butenyl) terephthalate (**E1**) was synthesized according to the literature procedure by the reaction of terephthaloyl chloride with 5-hexen-1-ol,<sup>91</sup> while the bis(5-hexenyl) phenylene diacetate (**E2**) was synthesized from the condensation of 1,4-phenylene diacetic acid with 5-hexen-1-ol. The 3-butenyl 4-pentenoate (**E3**) was kindly provided by M. Watson.



**Figure 4-2.** Synthesis of carbonate segmented copolymers. (PE) = polyester segment, (oligomer) = polyether or polyisobutylene segment.

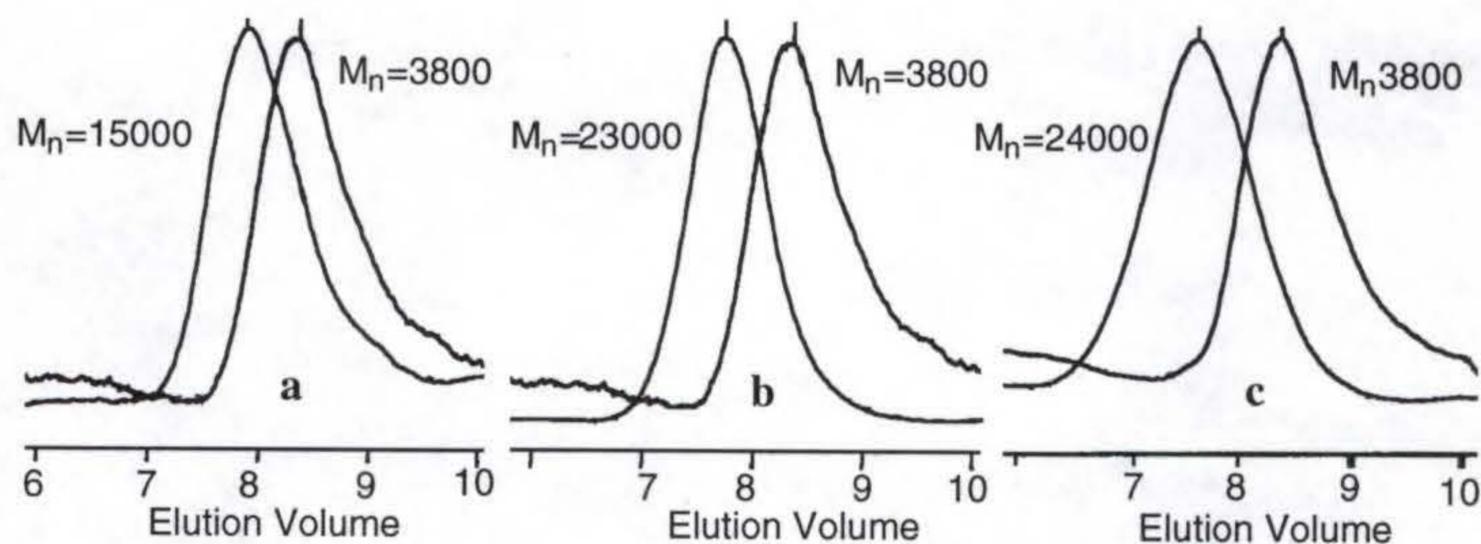


**Figure 4-3.** Ester monomers used to make segmented copolymers.

Poly(tetramethylene oxide) (PTHF1) diene telechelomer was copolymerized in a 1:1 wt:wt ratio with bis(5-hexenyl) terephthalate, **E1**, bis(1-hexenyl)phenylene diacetate, **E2**, and 3-butenyl 4-pentenoate, **E3**. The terephthalate copolymer was a soft white solid, while the phenylene diacetate copolymer was a soft, tacky material, and the butenyl pentenoate copolymer was a sticky viscous liquid. Polyisobutylene telechelomer (**PIB1**) was copolymerized with bis(5-hexenyl) terephthalate, **E1** to give a soft waxy solid.

### Molecular Weight Analysis of Ester Segmented Copolymers

The molecular weight of the resulting copolymers increases relative to the parent telechelomers in each case with negligible unreacted parent oligomer as detected by GPC, and the chromatograms comparing parent telechelomer to final copolymer are shown in **Figure 4-4** and **Figure 4-5** for the THF and PIB copolymers, respectively. Molecular weight data is summarized in **Table 4-1** and indicates that copolymers of modest molecular weight ( $M_n$  in the range of 15,000 to 24,000 vs. polystyrene standards) were obtained in each case. The polydispersity ( $M_w/M_n$ ) of the copolymers was found to approach 2.0 which is consistent for step-growth polymerization.



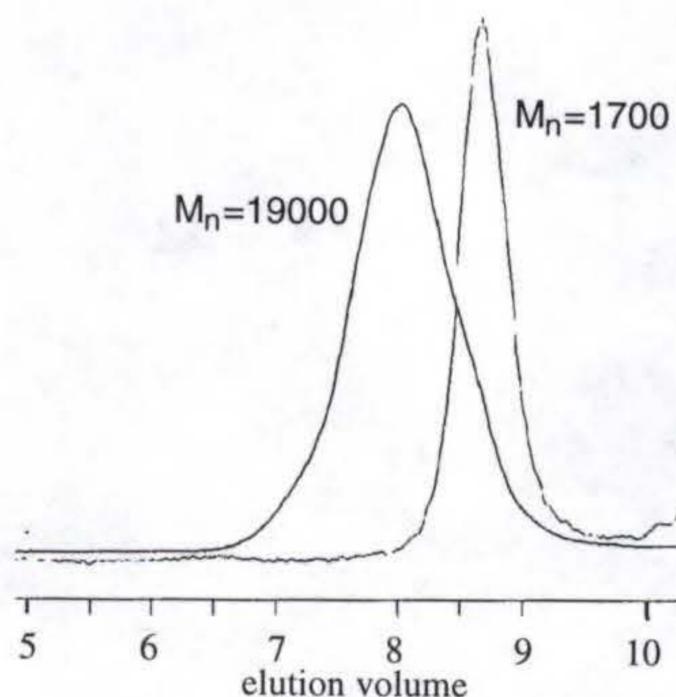
**Figure 4-4.** GPC of poly(tetramethylene oxide) oligomer before and after copolymerization with a) **E1**; b) **E2**; and c) **E3**. ( $M_n$  value vs. polystyrene standards.)

**Table 4-1.** Summary of molecular weight data for ester segmented copolymers.<sup>a</sup>

Copolymer	$M_n$ $\times 10^3$ g/mol	$M_w$ $\times 10^3$ g/mol	$M_w/M_n$
PTHF1-E1	15	29	2.0
PTHF1-E2	23	39	1.7
PTHF1-E3	24	32	1.4
PIB1-E1	19	32	1.7

<sup>a</sup>Molecular weight vs. polystyrene standards.

Polymerization using the polyisobutylene oligomer appeared to proceed more slowly than those using the polyether telechelomer, and this decreased reactivity of polyisobutylene diene is discussed in Chapter 2. Integration of the terminal to internal olefin end groups by <sup>1</sup>H NMR confirms that the polymerization is less complete for the copolymerizations using polyisobutylene.

**Figure 4-5.** GPC of PIB1 telechelomer before and after copolymerization with E1.

### Thermal Analysis of the Ester Segmented Copolymers

Thermal gravimetric analysis (TGA) data for the segmented copolymers under nitrogen atmosphere are summarized in **Table 4-2**. The polymers have varied thermal stabilities with 50 % weight loss in the range of 385-420 °C.

**Table 4-2.** TGA data for ester segmented copolymers.<sup>a</sup>

Copolymer	Onset (°C)	50% (°C)	90 % (°C)
PTHF1-E1	397	421	451
PTHF1-E2	394	418	454
PTHF1-E3	345	385	415
PIB1-E1	378	409	433

<sup>a</sup> heating at 20 °C/min under nitrogen atmosphere

Differential scanning calorimetry was used to study the phase separation of the copolymers. The polyether segments should display  $T_g$  at  $-90$  °C as well as a melting endotherm around  $25$  °C on the second heating scan while the polyisobutylene has a glass transition temperature near  $-70$  °C. The transitions of the parent isobutylene, ester and ether homopolymers are summarized in **Table 4-3**.

The observed thermal data for the *copolymers* is summarized in **Table 4-4**. The DSC thermograms for the polyether/polyester segmented copolymers heated at  $20$  °C/min or  $10$  °C/min for did not show the melting endotherms that would be expected if the material were completely phase separated (**Figure 4-6**).

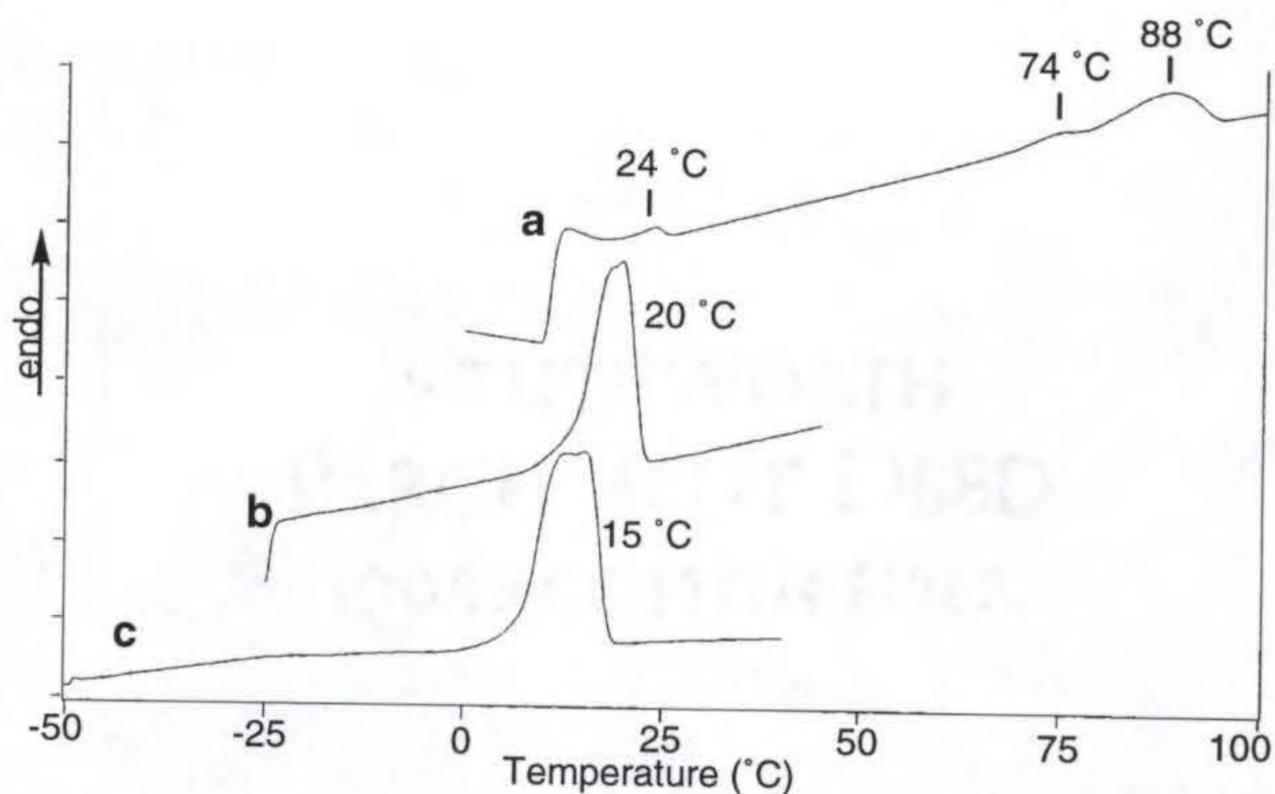
**Table 4-3.** Thermal transitions for parent ether, isobutylene, and ester homopolymers<sup>a</sup>

Ester homopolymer	T <sub>g</sub>	T <sub>m</sub>
PTHF1	-93 °C	25 °C
PIB	-70 °C	--
E2	--	110 °C
E3	--	35 °C
E4	-15 °C	-9 °C

<sup>a</sup>Scanning rate 20 °C/min. Data collected on second heating cycle.

The poly(ether-terephthalate) copolymer showed the expected melting endotherm for the **PTHF3** segment at 24 °C. However, rather than a single sharp melting point at 110 °C that would correspond to a phase-separated polyester segment, a melting peak at 103 °C was observed on the first heating scan, which split into two lower temperature endotherms at 88 and 74 °C on subsequent heating scans. Additionally, a glass transition was observed at -78 °C for this polymer when heated at 20 °C from a quenched melt, and this is slightly higher than the expected -90 °C for the polyether homopolymer.

These results suggest a certain degree of mixing between the polyester and polyether segments. It can be rationalized that three phases exist in the bulk material, including an ester-rich phase (T<sub>m</sub>=88 °C), and ether-rich phase (T<sub>m</sub>=24 °C), and a mixed interfacial phase with an intermediate melting point. As mentioned in Chapter 1, the sharpness of the boundaries between two phases varies depending on the nature, length, and proportion of the two components.



**Figure 4-6.** DSC's for polyether-ester copolymers. **a)** PTHF3+E1; **b)** PTHF3+E2; **c)** PTHF3+E3. Heating rate 10 °C/min.

The copolymers of poly(tetramethylene oxide) with the more flexible ester monomers behave similarly. The **E2** copolymer showed a  $T_g$  at  $-64$  °C with a single melting endotherm at 20 °C, while the copolymer with 3-butenyl 4-pentenoate, **E3**, displays a  $T_g$  at  $-93$  °C and single melting peak at 15 °C. The convergence of the expected melting peaks for the ester and ether segments is consistent with phase mixing of the polyether and polyester segments to give an intermediate melting point. Additionally, the  $T_g$  for the **E1** and **E2** copolymers is higher than that of the polyether homopolymer, and this is consistent with phase mixing of amorphous portions of the polyester into the amorphous polyether phase to give an intermediate  $T_g$ .

These observations of the thermal behavior for these copolymers are consistent with data that is observed in the commercial polyether-ester copolymers.<sup>28</sup> For many of the commercial systems it is observed that the noncrystalline portions of the polyester

are incorporated into the soft phase along with the polyether segments, and increasing the amount of hard phase ester leads to an increase in not only the  $T_m$  but also the  $T_g$  upon. Therefore, it is reasonable to assume that a similar effect will be observed in the ADMET generated polyether-ester copolymers. This indicates that the ADMET segmented ether-ester copolymers are phase mixed to differing extents, thus leading toward an averaging of the thermal transitions of the two components. A small amount of phase mixing leads to melting point depression for the **E1** segments when combined with the polyether, while phase mixing seems to be even greater for the more flexible **E2** and **E3** copolymers.

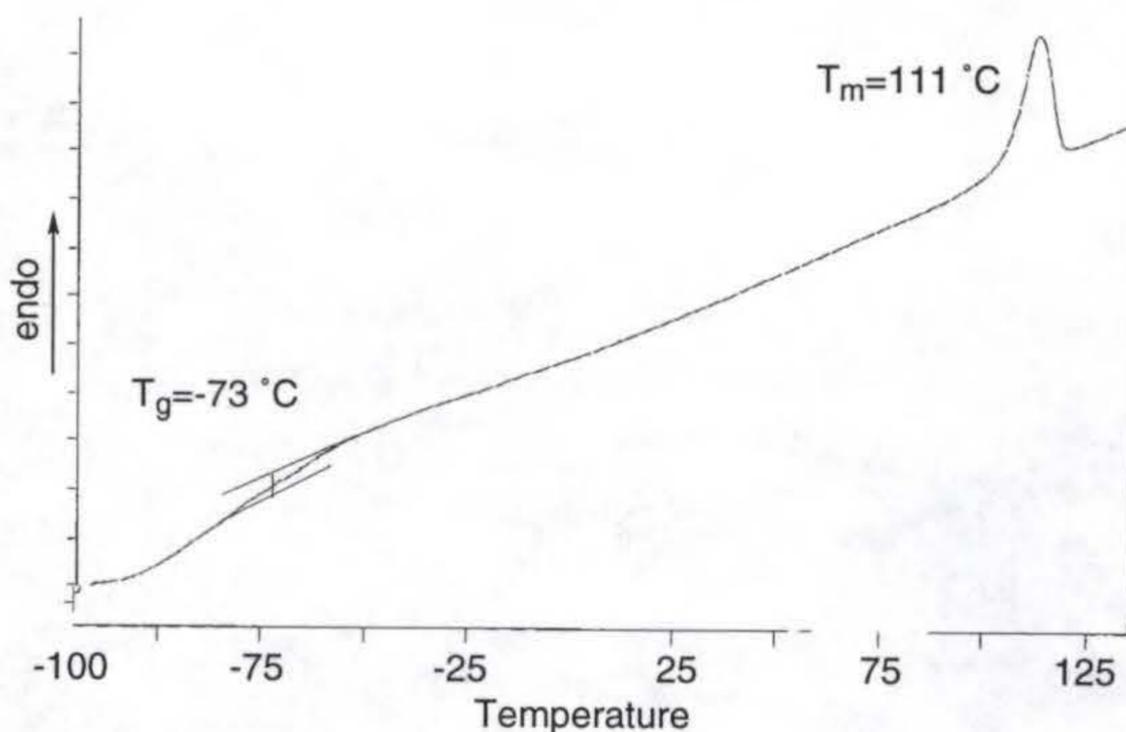
**Table 4-4.** DSC analysis of ester segmented copolymers.

Copolymer	$T_g$	$T_m$ 1	$T_m$ 2
<b>PTHF1-E1</b>	-78 °C <sup>a</sup>	20 °C <sup>a</sup>	78 °C <sup>a</sup> 103 °C <sup>a</sup>
<b>PTHF1-E2</b>	-64 °C <sup>a</sup>	24 °C	--
<b>PTHF1-E3</b>	-93 °C	15 °C	--
<b>PIB1-E2</b>	-73 °C	--	111 °C

<sup>a</sup>Scanning rate 20 °C/min. Data collected on second heating cycle.

<sup>b</sup>Scanning rate 10 °C/min. Data collected on second heating cycle.

Thermal analysis of the polyisobutylene segmented ester copolymer showed the expected glass transition at -73 °C for the polyisobutylene segments along with the expected melting point for the respective polyester segments (**Figure 4-6**).



**Figure 4-6.** DSC for polyisobutylene **PIB1** copolymer with **E1**. Heating rate 20 °C/min.

The sharpness and temperature of the melting peak are combined with the low  $T_g$ , are consistent with a high degree of phase *separation* for these polyisobutylene/polyester copolymers, which is in contrast to what was observed for the polyether segmented copolymers. The differing behavior of the two sets of segmented copolymers can be correlated to the polarity of their parent homopolymers. Both the polyether and the polyester contain polar groups along their backbone and it is reasonable to suggest that these could participate in secondary dipole-dipole interactions that would facilitate the enthalpy of mixing of the two segments. However, polyisobutylene is a purely hydrocarbon backbone and would be expected to be less miscible with the polar polyester segments.

## CHAPTER 5 SEGMENTED CARBONATE COPOLYMERS

Carbonates are another common class of step-growth polymers, with the aromatic polycarbonates based on bisphenol A as important thermoplastic materials. The use of carbonates in segmented copolymers is not as extensive as that of esters or urethanes. Hydroxyl-capped aliphatic polycarbonates have been used as the soft segment in polyurethane segmented copolymers, and polyester-polycarbonate segmented copolymers are also commercially known.<sup>92</sup>

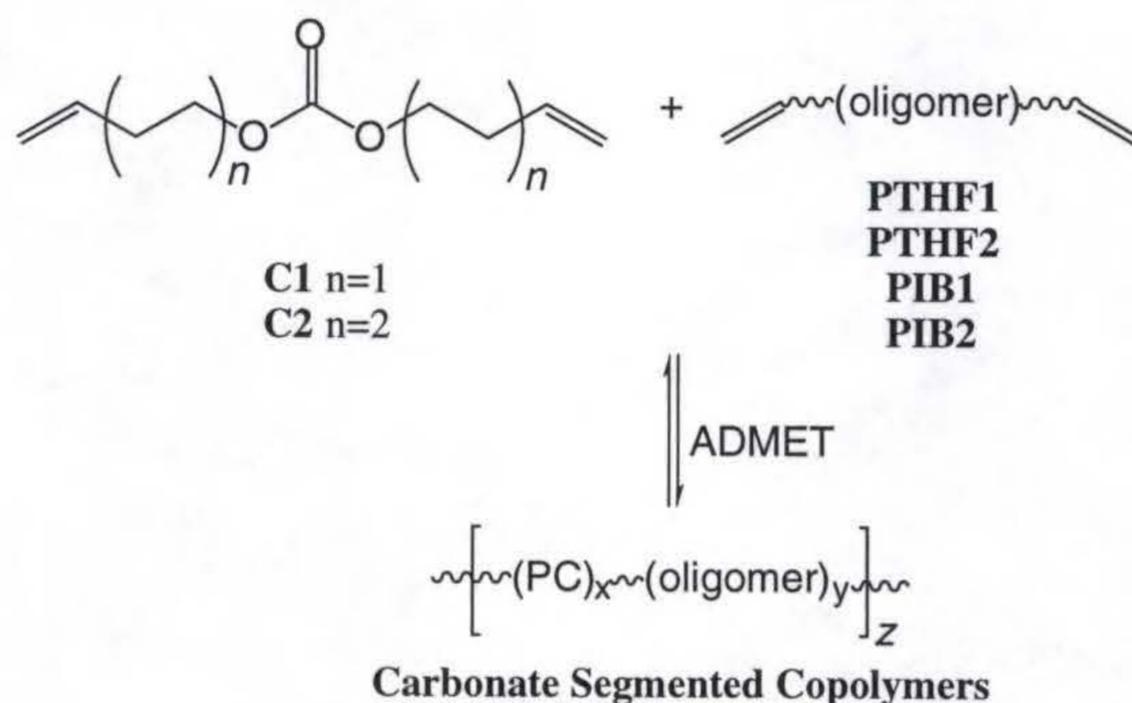
Carbonates are not new to ADMET chemistry, as Patton and coworkers demonstrated that aliphatic carbonate dienes with two to four methylene spacers between the carbonate functionality and the reacting olefin are amenable to ADMET polymerization.<sup>93</sup> Patton also explored the ADMET polymerization of a diene monomer whose homopolymerization gave an alternating bisphenol-A/3-hexenyl copolycarbonate structure.

### Synthesis of Carbonate ADMET Segmented Copolymers

For the synthesis of ADMET segmented polycarbonates, the monomers bis(3-butenyl) carbonate (**C1**) and bis(5-hexenyl) carbonate (**C2**) were chosen. The

carbonate monomers were synthesized by a modification of the published synthesis.<sup>93</sup> Dimethyl carbonate was condensed with either 3-buten-1-ol or 5-hexen-1-ol in the presence of sodium metal to make **C1** and **C2**, respectively.

Diene telechelomers of polyisobutylene, with  $M_n=1700$  (**PIB1**) and 3100 (**PIB2**), as well as poly(tetramethylene oxide), with  $M_n=1800$  (**PTHF1**) and 3600 (**PTHF2**), were used. These diene oligomers were copolymerized in a 1:1 wt:wt ratio with either **C1** or **C2** to give a total of eight different carbonate segmented copolymers (**Figure 5-1**).



**Figure 5-1.** Synthesis of carbonate segmented copolymers. (PC) = polycarbonate segment, (oligomer) = polyether or polyisobutylene segment.

### Molecular Weight Analysis of Carbonate Segmented Copolymers

Upon copolymerization the molecular weight of the resulting copolymers increases relative to the parent homopolymer in each case as measured by GPC.

Molecular weight data is summarized in **Table 5-1** and indicates modest molecular weights ( $M_n$  in the range of 25,000 vs. polystyrene standards) with polydispersities ( $M_w/M_n$ ) approximately 2 were found for the copolymers, which is consistent for step-growth polymerization.

**Table 5-1.** Summary of molecular weight data for carbonate segmented copolymers.<sup>a</sup>

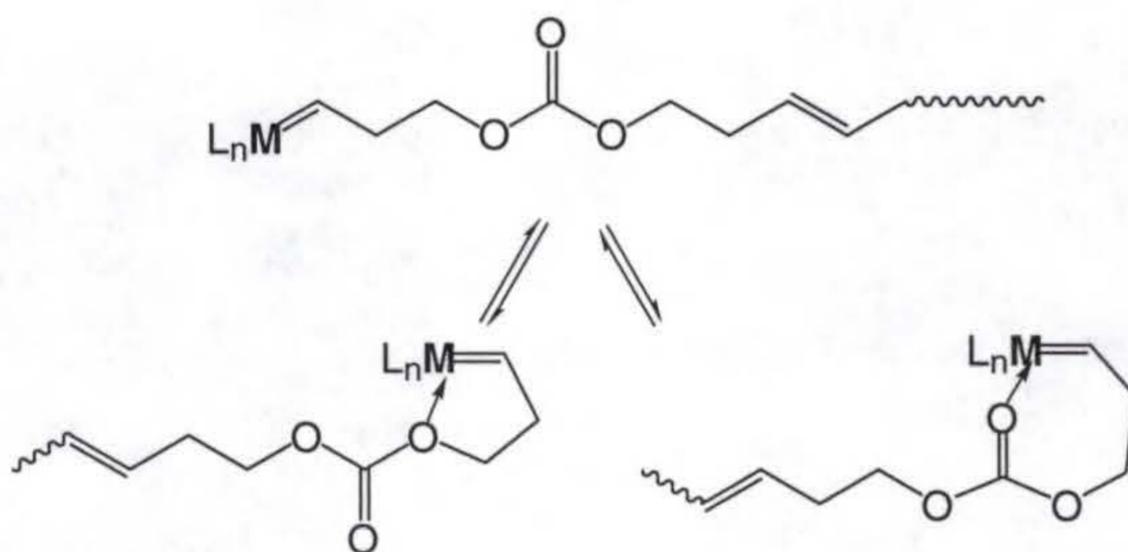
Copolymer	$M_n$ $\times 10^3$ g/mol	$M_w$ $\times 10^3$ g/mol	$M_w/M_n$
PTHF1-C1	7	13	1.88
PTHF2-C1	6	10	1.75
PTHF1-C2	9	19	2.11
PTHF2-C2	11	16	1.47
PIB1-C1	4	8	1.93
PIB2-C1	5	11	2.37
PIB1-C2	8	14	1.76
PIB2-C2	10	22	2.07

a. Determined by GPC relative to polystyrene standards

Polymerizations using polyisobutylene oligomer appeared to proceed more slowly than those using the polyether telechelomer, as discussed previously. Integration of the terminal olefin end groups by  $^1\text{H}$  NMR confirms the polymerization is less complete for these copolymerizations. It was also found that the copolymerizations involving bis(3-butenyl) carbonate were much slower than those with bis(5-hexenyl) carbonate. These showed incomplete conversion even after several days of exposure to

catalyst and vacuum. Homopolymerization of each of these carbonate monomers confirmed that the butenyl carbonate monomer is less reactive than hexenyl carbonate to ADMET polymerization.

Although this reactivity difference is not addressed in the original work concerning the ADMET polymerization of carbonate monomers, it is reasonable to suggest that the growing chain end derived from the bis(3-butenyl) carbonate is more prone to chelation to the transition metal catalyst to give a favorable 5 or 7 membered ring as shown in **Figure 5-2**. The observation of hindered or prohibited ADMET polymerization by polar functional groups close to the metathesizing double bond has been referred to as the "negative neighboring group effect."<sup>28-30</sup>



**Figure 5-2.** Potential chelation of C1 carbonate functionality to catalyst during ADMET polymerization.

### Thermal Analysis of the Carbonate Segmented Copolymers

Thermal gravimetric analysis of the segmented carbonate copolymers under nitrogen atmosphere is summarized in **Table 5-2**. The polyisobutylene copolymers appear to be slightly more thermally stable, with all copolymers showed 50 % weight loss in the range of 370-410 °C. The length of the oligomer showed no significant effect on thermal stability.

**Table 5-2.** Thermal gravimetric analysis of carbonate segmented copolymers.

<b>Copolymer</b>	<b>Onset (°C)</b>	<b>50 % (°C)</b>	<b>90% (°C)</b>
<b>PTHF1-C1</b>	320	369	413
<b>PTHF2-C1</b>	294	398	430
<b>PTHF1-C2</b>	381	414	441
<b>PTHF2-C2</b>	384	409	438
<b>PIB1-C1</b>	365	409	435
<b>PIB2-C1</b>	355	405	432
<b>PIB1-C2</b>	368	410	438
<b>PIB2-C2</b>	366	414	440

Differential scanning calorimetry was used to provide an indication of the phase separation of the copolymers. As discussed previously, the presence of distinct phase transitions corresponding to each parent homopolymer can be an indication of phase separation in the material.

Differential thermal analysis was obtained for two of the unsaturated copolymers employing the **C2** carbonate segment. The polyether-carbonate copolymer shows three melting endotherms on the first scan, including the two expected for a first scan of poly(tetramethylene oxide) as well as a small peak at 19 °C. This additional peak could be due to phases containing polycarbonate segments that are unable to recrystallize on the timescale of the experiment. The stronger melting transition is slightly depressed from the expected melting point for the polyether homopolymer, indicating a simple melting point depression occurring from phase mixed polyether-carbonate (**Table 5-3**).

The polyisobutylene copolymer with **C2** shows thermal behavior consistent with a greater degree of phase separation. The  $T_g$  for the polyisobutylene is slightly higher than PIB homopolymer, and the melting peak observed at 38 °C is slightly lower than the 40 °C for the homopolycarbonate. Once again a weak melting endotherm is observed at 14 °C only on the first scan. It is difficult to determine whether this peak can be correlated to the peak at 19 °C observed for the polyether-**C2** copolymer.

**Table 5-3.** Differential scanning calorimetry analysis of carbonate segmented copolymers, before and after hydrogenation. Data obtained on second heating scan at 20 °C/min. (Temps in °C,  $\Delta H$  in J/g)

Copolymer	Unsaturated Copolymer			After Hydrogenation				
	T <sub>g</sub>	T <sub>m</sub>	$\Delta H$ J/g	H <sub>2</sub> T <sub>g</sub>	H <sub>2</sub> T <sub>m1</sub>	$\Delta H$ J/g	H <sub>2</sub> T <sub>m2</sub>	$\Delta H$ J/g
poly C1	-57°	45°	(47.2J)					
poly C2	--	39°	(46.2J)					
PTHF1-C1	-65°	23	(62.4J)	- 77°	22°	(81.8J)	34 <sup>b</sup>	
PTHF2-C1	-- <sup>c</sup>	24	(43.0J)	-74°	24°	(68.1J)	45 <sup>b</sup>	(15.9J)
PTHF1-C2	-70°	14	(42.0J)	-74°	15°	(52.1J)	36°	(31.8J)
PTHF2-C2	-76	(19°) <sup>a</sup> , 23°	(51.1J)	- 76°	25°	(55.4J)	46°	(36.8J)
PIB1-C1	-66	--		- 64°	(7°) <sup>b</sup>	(12.0J)	50°	(33.1J)
PIB2-C1	?	?		-65°	--		46°	(19.1J)
PIB1-C2	-65	--		-66°	--		48°	(35J)
PIB2-C2	-66	(14°) <sup>a</sup> , 38°	(3.9J)	-64°	--		48°	(31.2J)

a. Only observed on first heating scan.

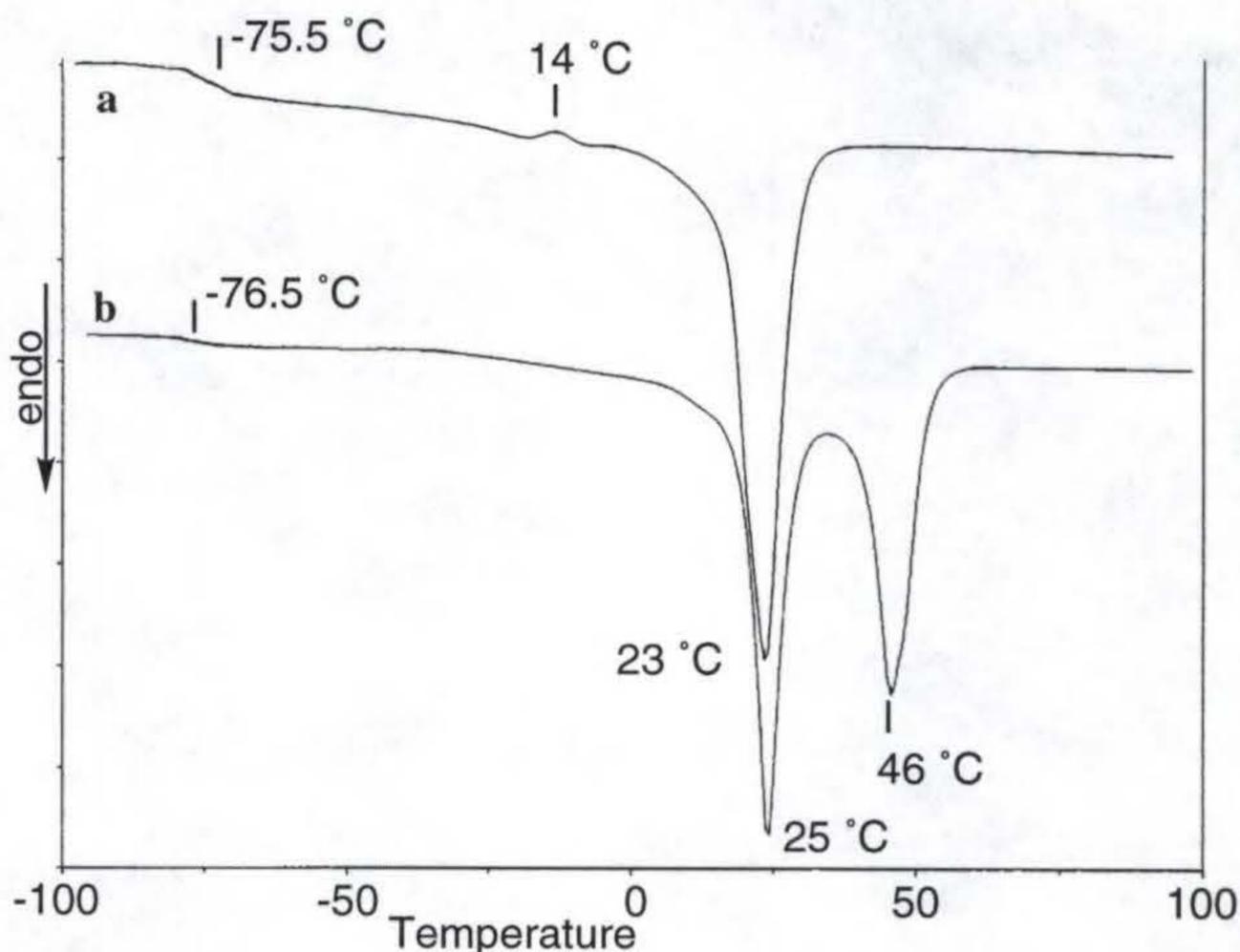
b. Very weak transition appearing as shoulder on primary melting peak.

c. No observable T<sub>g</sub> above -15 °C

Further thermal analysis was performed on the hydrogenated analogs of the carbonate copolymers. Hydrogenation of the copolymers has a firming effect on the materials, similar to what is seen for the PIB/decadiene copolymers. All but one copolymer displayed melting points that correlate to hydrogenated carbonate in addition to the expected transitions of the parent telechelomers.

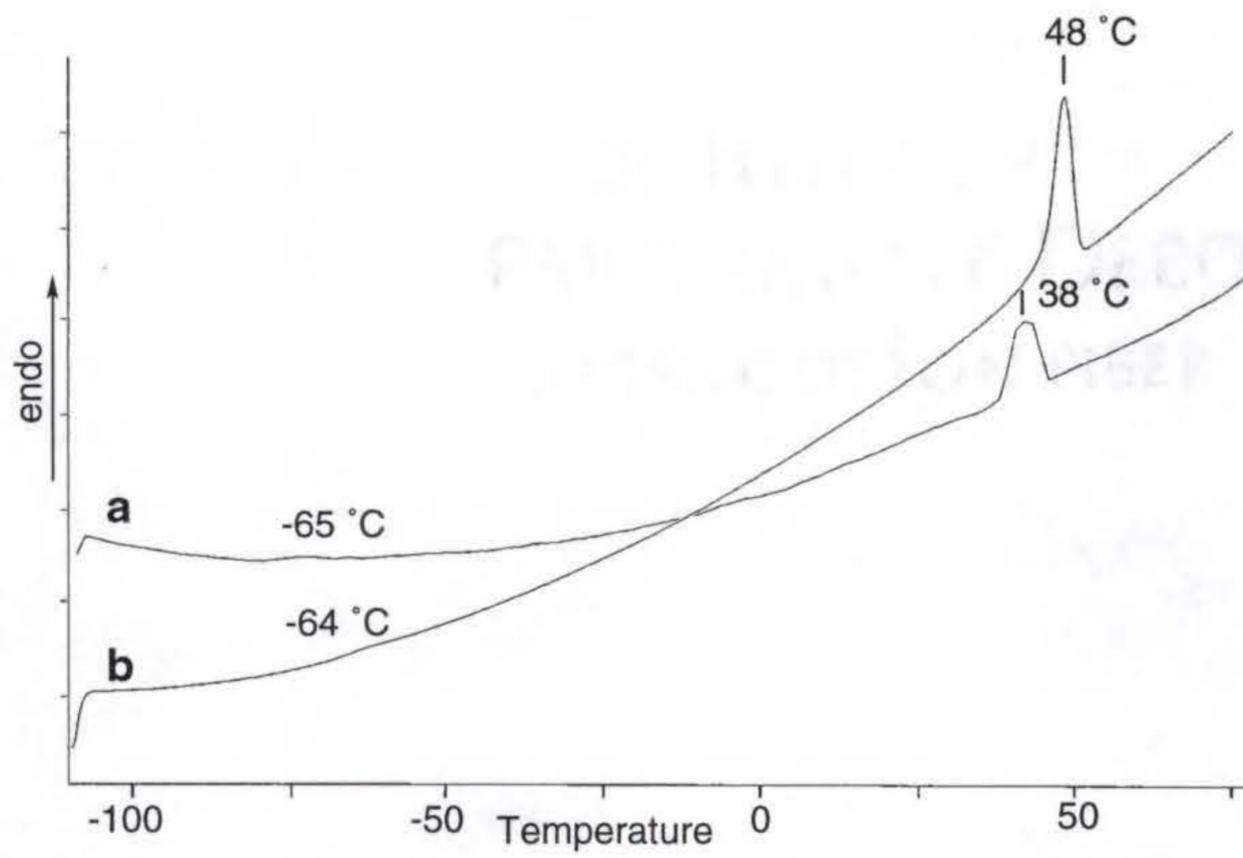
The effect of hydrogenation is illustrated with the **PTHF2/C2** and **PIB2/C2** copolymers, for which thermal data was collected for both the unsaturated and the hydrogenated copolymers (**Figure 5-4** and **Figure 5-5**). Hydrogenation appears to lead

to greater phase separation, even with the polyether. After hydrogenation, the saturated carbonate segment readily crystallizes, and two peaks are seen on the heating scans at 25 °C (polyether) and 46 °C (saturated carbonate).



**Figure 5-3.** Effect of hydrogenation on melting point: Copolymer of **PTHF2/C2** a) before hydrogenation and b) after hydrogenation.

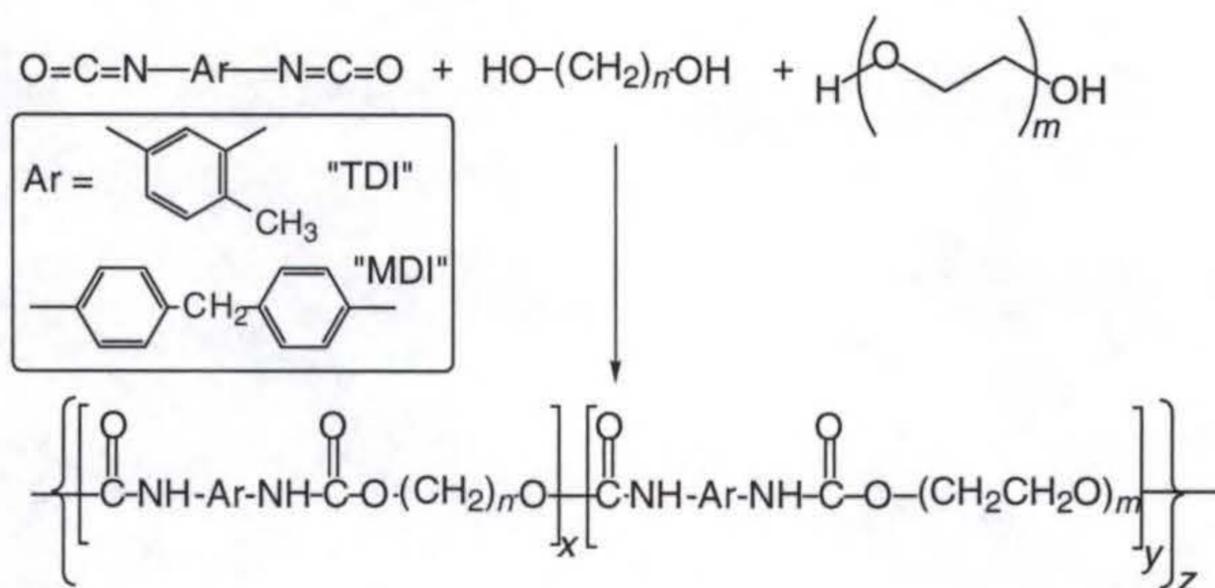
By comparison, the **PIB2/C2** copolymer does display a consistent melting peak for the unsaturated carbonate segment. This implies that the unsaturated carbonate is able to recrystallize more easily when it has a higher degree of phase separation, as would be expected when combined with the hydrocarbon PIB component vs. the more polar polyether. Upon hydrogenation the carbonate melting peak increases from 38 °C to 48 °C, nicely matching the melting transition observed for the **PTHF2/C2** copolymer.



**Figure 5-4.** Effect of hydrogenation on melting point: Copolymer of **PIB2/C2**  
**a)** before hydrogenation and **b)** after hydrogenation.

CHAPTER 6  
SEGMENTED URETHANE COPOLYMERS

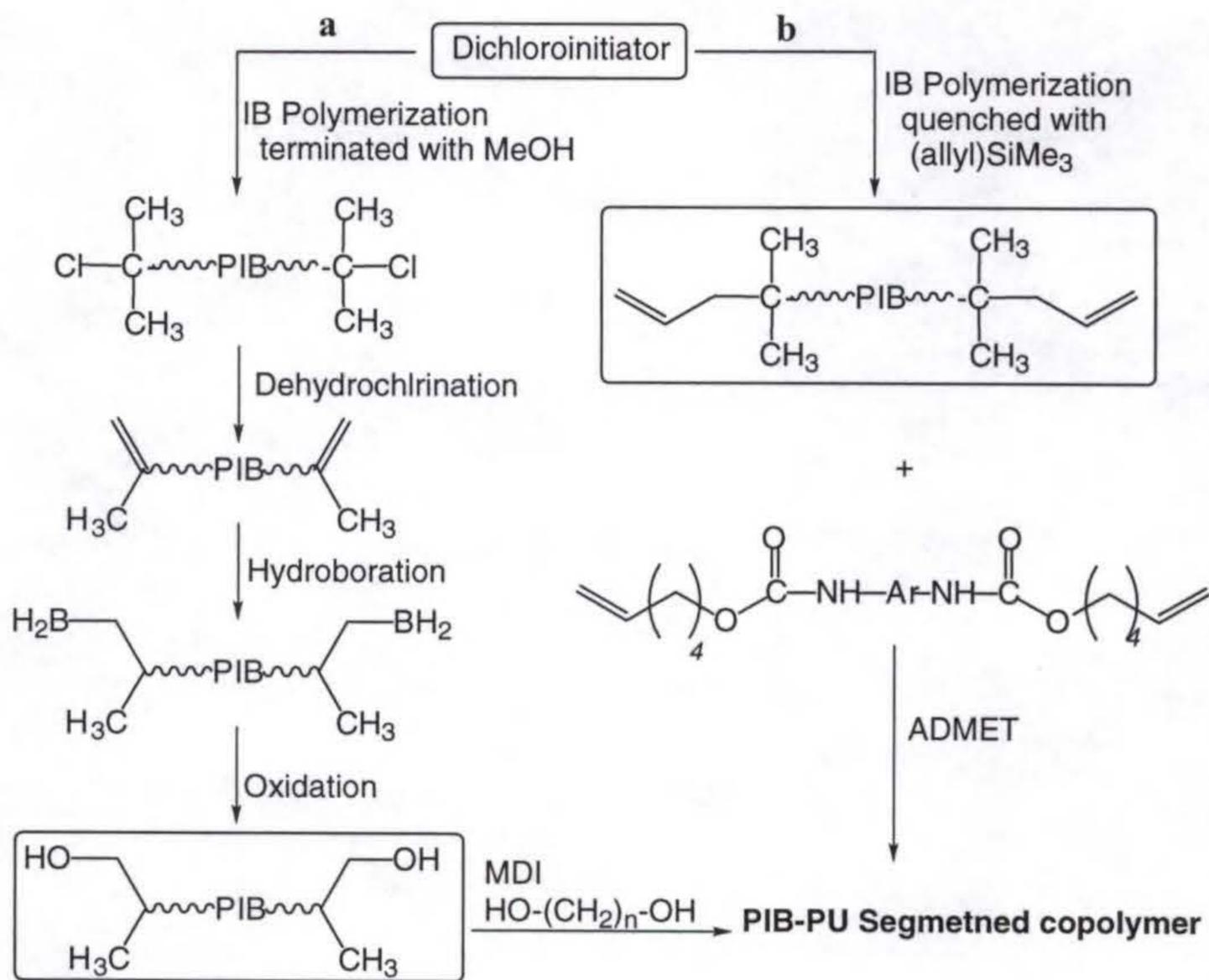
Segmented urethane-ether copolymers are well known as thermoplastic elastomers, with Lycra™ as the classic example.<sup>27,68</sup> Segmented poly(urethane-ether)s are synthesized from the copolymerization of diisocyanates along with diols and an  $\alpha,\omega$ -dihydroxyl polyether (**Figure 6-1**).



**Figure 6-1.** General synthesis of aromatic poly(urethane-ether) segmented copolymer

Polyurethane-isobutylene copolymers are also known, and using polyisobutylene offers some advantages over polyether as the soft segment.<sup>29</sup> The polyisobutylene imparts greater stability towards hydrolysis, oxidation, chemicals, and thermal degradation, as well as offering good barrier and damping ability over a wide temperature range. Poly(urethane-isobutylene)s are made from the condensation of  $\alpha,\omega$ -hydroxyl

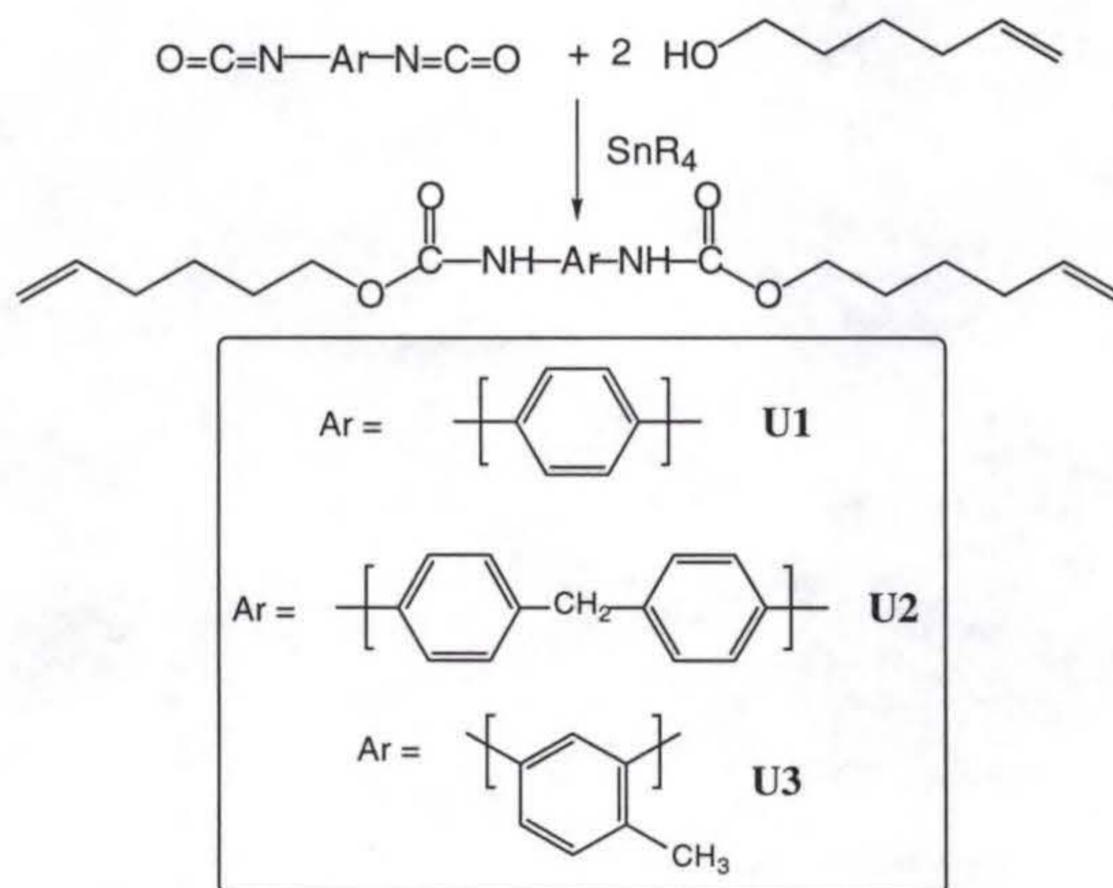
polyisobutylene with diisocyanates and small glycols. However, the synthesis of the dihydroxyl polyisobutylene telechelomer is a multistep process, as there is no direct way to introduce the hydroxyl functionality onto polyisobutylene. Allyl-capped polyisobutylene can be synthesized by simply quenching the polymerization with allyltrimethyl silane. ADMET condensation of allyl-PIB with  $\alpha,\omega$ -dienyl urethanes would offer poly(urethane-isobutylene) segmented copolymers in a total of only three steps as opposed to the five steps using the traditional method. A comparison of the two approaches is shown in **Figure 6-2**.



**Figure 6-2.** Comparison of **a)** traditional method for the synthesizing PIB-PU segmented copolymers vs. **b)** ADMET approach.



phenylene diisocyanate, methylene-*p*-diphenylene diisocyanate, and tolyene-2,4-diisocyanate, respectively. Each urethane diene is a solid, which distinguishes these monomers from the traditional liquid diene monomers studied for ADMET polymerization. The *p*-phenylene dicarbamate, **U1**, has a melting point too high to be amenable to ADMET polymerization, while **U2** and **U3** melted near 70 °C and 90 °C respectively. The phenylene dicarbamate monomer (**U1**) did not polymerize under the conditions used, so this monomer was not used for further investigation. The melt-homopolymerization of **U2** and **U3** proceeded with poor conversion. However, copolymerization with the poly(tetramethylene oxide) oligomer seemed to facilitate mixing of the monomer with catalyst.



**Figure 6-4.** Urethane monomers tested for ADMET segmented copolymers.

Molecular Weight Analysis of Urethane Segmented Copolymers

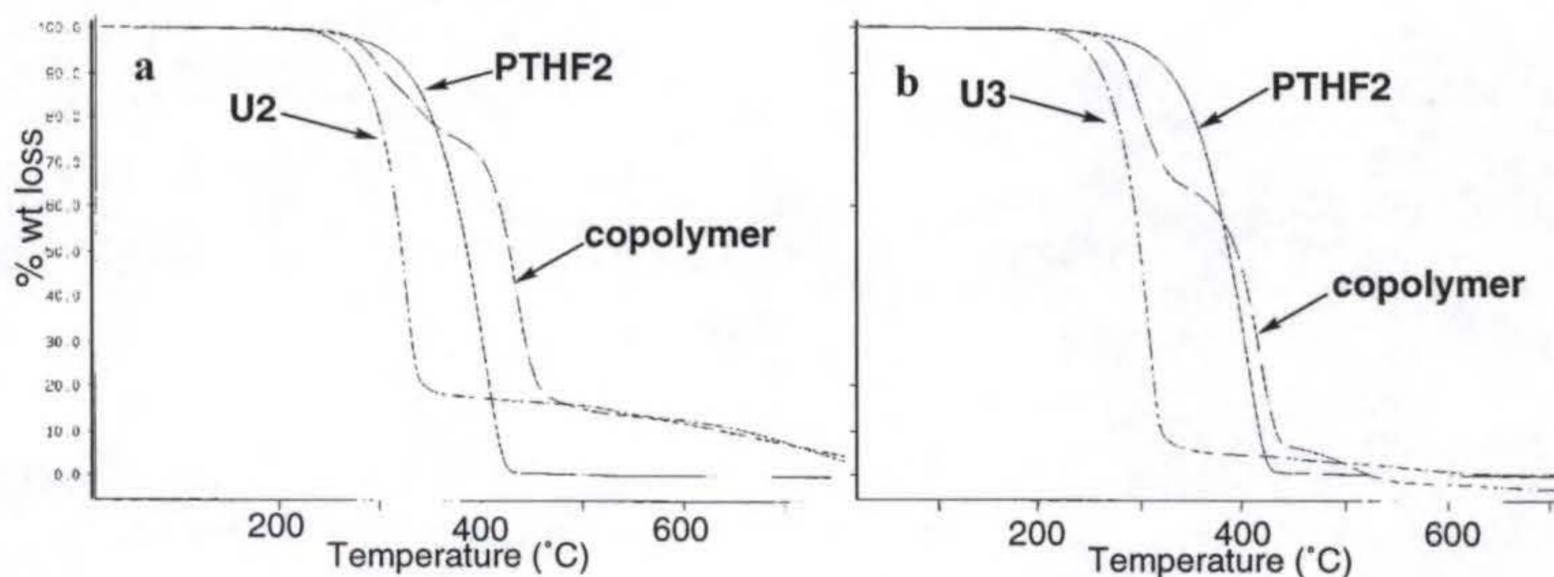
Poly(oxytetramethylene) (PTHF2) and polyisobutylene (PIB1) diene telechelomers were copolymerized to target a ratio of 6 IB units to 1 urethane repeat in the final copolymer. Upon copolymerization the molecular weight of the resulting copolymers increases relative to the parent in each case with negligible unreacted parent oligomer as detected by GPC. Molecular weight data is summarized in **Table 6-1** and indicates copolymers of modest molecular weight (in the range of 25,000 to 30,000 vs. polystyrene standards) were obtained in each case. The polydispersity ( $M_w/M_n$ ) of the copolymers was found to be slightly greater than 2.0, and is in the range which is consistent for step-growth polymerization. The broader distribution is probably due to the decreased metathesis reactivity of the urethane, particularly in the reactions with polyisobutylene where the molten urethane monomer is insoluble in the polyisobutylene. The solid urethane monomers were, however, able to dissolve in the melted poly(tetramethylene oxide) at 60 °C allowing for better mixing of the two reacting species.

**Table 6-1.** Summary of molecular weight data for urethane segmented copolymers.

Copolymer	$M_n$ $\times 10^3$ g/mol	$M_w$ $\times 10^3$ g/mol	$M_w/M_n$
PTHF2-U2	30	59	2.0
PTHF2-U3	29	56	1.94
PIB1-U2	25	49	2.03
PIB1-U3	26	50	2.0

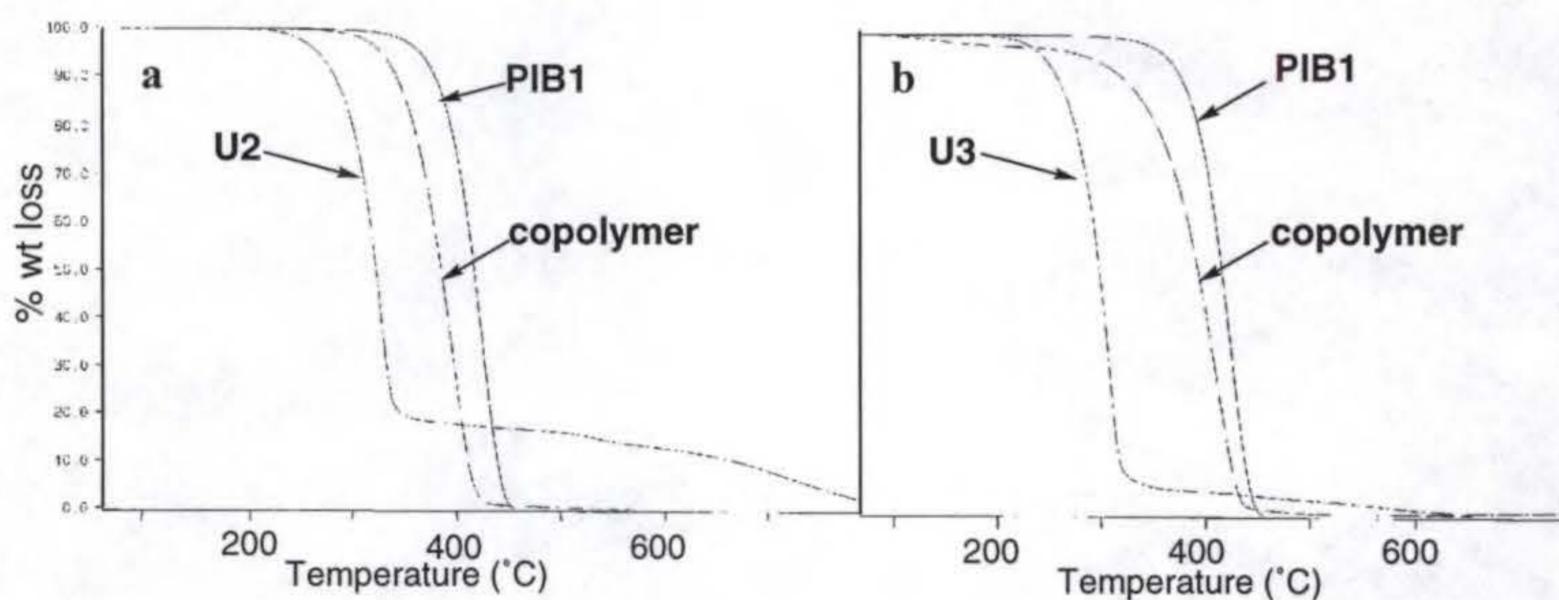
### Thermal Analysis of the Urethane Segmented Copolymers

As with the previously discussed systems, thermal analysis gave an indication of the thermal stability and degree of phase separation of the polyurethane segmented copolymers. Thermal gravimetric analysis of the segmented copolymers under nitrogen atmosphere is summarized in **Table 6-2**. The urethane-ether copolymers show interesting thermogravimetric behavior. The TGA scans showing the urethane monomer, poly(tetramethylene oxide) telechelomer, and the copolymer of the two for both ether-urethane copolymers are shown below (**Figure 6-5**). Rather than the relatively sharp decrease in weight as observed for the other segmented copolymers studied, decomposition of the ether-urethanes appears to occur in two stages, with the weight loss trailing off gradually above 450 °C.



**Figure 6-5.** TGA thermograms of poly(ether-urethane) copolymers. **a)** PTHF2/U2 copolymer; **b)** PTHF2/U3 copolymer. (20 °C/min, Nitrogen)

The polyisobutylene copolymers appear to be slightly more thermally stable, with all copolymers losing 50 % of their weight in the range of 390-395 °C (Figure 6-6). However, this resemblance to the thermal stability of the polyisobutylene homopolymer could be merely due to the very low incorporation of urethane into the copolymer.



**Figure 6-6.** TGA thermograms for polyisobutylene urethane segmented copolymers: a) PIB1/U2 copolymer; b) PIB1/U3 copolymer. (20 °C/min, Nitrogen)

**Table 6-2.** Thermal gravimetric analysis of urethane segmented copolymers.

Copolymer	Onset (°C)	50 % (°C)	90 % (°C)
PTHF2-U2	372	391	403
PTHF2-U3	384	395	407
PIB1-U2	387	392	404
PIB1-U3	389	396	408

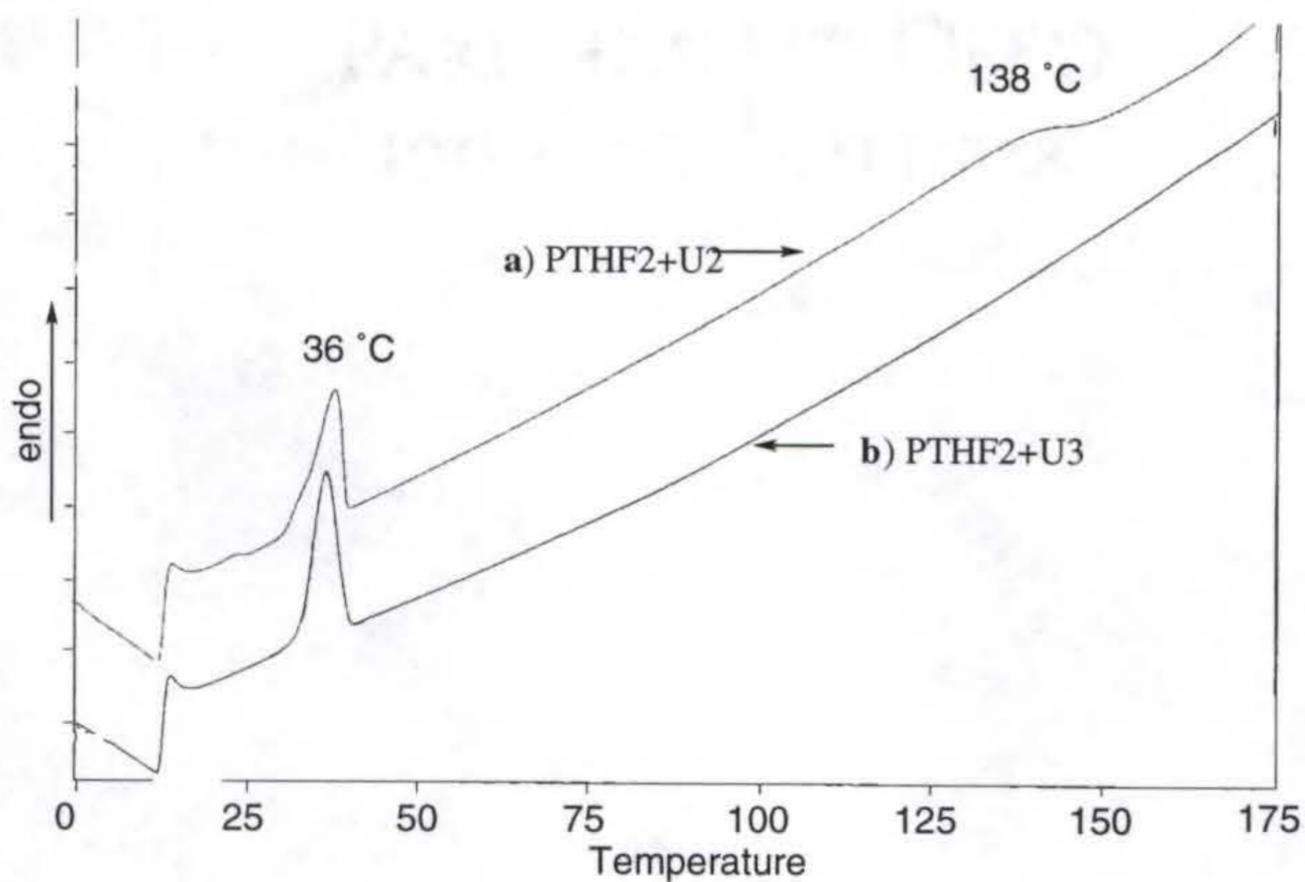
Differential scanning calorimetry was used to provide an indication of the phase separation of the copolymers. As discussed previously, the presence of distinct phase

transitions corresponding to each parent homopolymer can be an indication of phase separation of the two segments in the bulk polymer. The observed thermal data for the urethane copolymers are summarized in **Table 6-3**. The data reflect the first heating scan because no melting peaks corresponding to the urethane segments were observed on the second heating scan. Unfortunately, suitable samples of the homopolymers of the urethanes were not able to be obtained via ADMET polymerization, so the expected melting points of the urethane segment are unknown. The polyether/polyurethane segmented copolymers each showed the expected first-scan melt of the polyether at 36 °C. The **U2** based copolymer shows a weak melting endotherm at 138 °C, which disappeared upon subsequent scans, while the **U3** ether copolymer showed no detectable melting endotherm above 36 °C even on the first scan (**Figure 6-6**). The copolymers with polyisobutylene showed no observable melting peaks between 20 °C and 150 °C, and this is perhaps due to the low incorporation of urethane into the copolymers after workup.

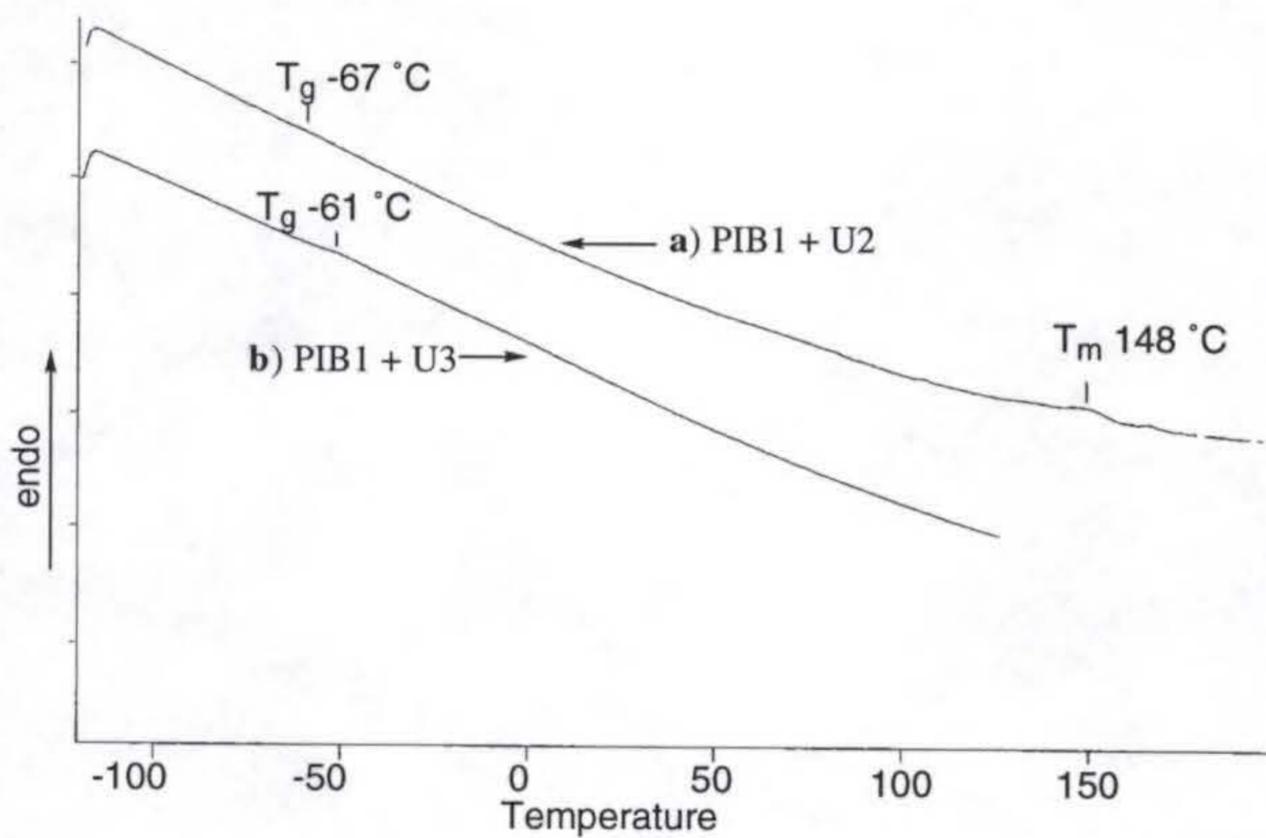
**Table 6-3.** DSC thermal transitions for urethane segmented copolymers at 20 °C/min.<sup>a</sup>

Copolymer	T <sub>g</sub> (°C)	T <sub>m1</sub> (°C)	T <sub>m2</sub> (°C)
PTHF2-U2	--	36 °C	138 °C
PTHF2-U3	--	36 °C	--
PIB1-U2	-67 °C	--	148 °C
PIB1-U3	-61 °C	--	--

a. Data obtained from first heating cycle.



**Figure 6-6.** First heating scan thermogram for polyether-polyurethane copolymers. a) PTHF2 + U2; b) PTHF2 + U3.



**Figure 6-7.** First heating scan thermogram for polyisobutylene-polyurethane copolymers. a) PIB1 + U2; b) PIB1 + U3

The observed DSC data are difficult to interpret with this limited amount of data, and comparison of samples with a higher incorporation of urethane would be helpful. However, bulk ADMET polymerization of these solid urethane monomers is problematic. Homopolymerization only proceeded to low conversion, especially in the case of U2 which melts at 90 °C. The Grubbs catalyst is not stable over the long reaction times at this temperature required. The copolymerizations with the polyether seemed to perform better, as the molten poly(tetramethylene oxide) is able to dissolve the urethane monomers. The polyisobutylene copolymerizations were never able to be completely homogenized even after stirring several days. One possible approach to facilitating the polymerization of these and high-melting ADMET monomers is to add a small amount of a high-boiling plasticizer, such as diphenyl ether, to the polymerization mixture. This would help to liquify the solid monomer and would keep the viscosity lower throughout the polymerization.

## CHAPTER 7 EXPERIMENTAL PROCEDURES

### General Experimental Procedures

Spectra for  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) were obtained on a Varian Gemini-Series NMR superconducting spectrometer system. All NMR data were generated in  $\text{CDCl}_3$  as the solvent, and peaks are listed in ppm downfield from tetramethyl silane. Infrared (IR) data were recorded neat, using KBr plates on a Perkin Elmer 281 infrared spectrometer. Low and high resolution mass spectrometry was recorded on a Finnigan 4500 Gas Chromatography/Mass Spectrometer using either electron or chemical ionization conditions. Elemental Analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Gel Permeation Chromatography (GPC) was performed on a Waters and Associates model 590 chromatograph using a Phenomenex mixed bed column and chloroform as the eluent at a flow rate of 1.0 mL/min. Peaks were detected using both a Waters Associates differential refractometer and a Perkin Elmer LC-75 spectrophotometric detector (250 nm), and calibrated with polystyrene standards. Molecular weights of the three polyisobutylene telechelic oligomers were additionally determined by GPC with light scattering detector.

Preparatory HPLC was performed on a Rainan Dynamax system equipped with Dynamax 60 Å silica preparative column and Dynamax spectrophotometer set at 254 nm.

Thermal Gravimetric Analysis (TGA) was performed on a Perkin Elmer TGA7 as a heating rate of 20 °C/min up to 800 °C. Differential Scanning Calorimetry (DSC) was performed on a Perkin Elmer DSC7 at heating rates of 10 °C/min or 20 °C/min, as indicated. Both TGA and DSC were interfaced to a TAC7/DX thermal analysis controller. Some DSC were run on a TA Instruments Universal V2.5D at 20 C/min. Samples were heated above their melting point, cooled, then data was collected for the second heating and cooling scan unless otherwise indicated.

The Grubbs catalyst,  $\text{RuCl}_2(\text{P}(\text{C}_6\text{H}_{11})_3)_2\text{CHPh}$ <sup>46</sup> and the Schrock molybdenum catalyst  $(\text{Mo}(\text{NC}_6\text{H}_3\text{-2,6-}i\text{-Pr})(\text{OCCH}_3(\text{CF}_3)_2)_2\text{CHC}(\text{CH}_3)_2\text{C}_6\text{H}_5)$ <sup>44</sup> were prepared according to published procedures. Toluene and pentane were treated with concentrated sulfuric acid prior to drying over sodium/potassium alloy. Diethyl ether, toluene, and pentane were distilled from sodium/potassium alloy.

#### Synthesis of $\alpha,\omega$ -Dienyl Telechelic Oligomers

The diene telechelomers used for this study were synthesized by cationic polymerization of tetrahydrofuran or isobutylene followed by capping with 5-hexen-1-ol or allyltrimethyl silane, respectively.

Poly(tetramethylene oxide) Telechelomers

Poly(oxytetramethylene) oligomers were synthesized by cationic ring-opening polymerization of tetrahydrofuran initiated by triflic anhydride. Tetrahydrofuran was dried over sodium/potassium amalgam and freshly distilled before use. Triflic anhydride was freshly distilled before use, and 5-hexen-1-ol was distilled from calcium hydride.

Synthesis of  $\alpha,\omega$ -dienyl poly(tetramethylene oxide) ( $M_n=1800$ ) (PTHF1).

Dry, degassed tetrahydrofuran (36.0 mL, 0.44 mol) was placed in a Schlenk flask and cooled to  $-13\text{ }^\circ\text{C}$  with a benzonitrile slush bath. Triflic anhydride (1.0 mL,  $5.9 \times 10^{-3}$  mol) was added all at once by syringe. The reaction was maintained at  $-13\text{ }^\circ\text{C}$  and stirred for 25 minutes, then the polymerization was quenched by rapidly adding 5 mL (0.04 mol) 5-hexen-1-ol. The reaction was allowed to warm to room temperature and stirred 12 hours. Solvent was evaporated to reduce the volume in half, then the reaction mixture was precipitated into methanol that contained 5 % w:v sodium bicarbonate to yield a white solid. The solid was collected by filtration and redissolved in chloroform and reprecipitated in methanol twice more to ensure complete removal of the triflic acid. The precipitate was dried under vacuum to give a soft white powder. Anal. Calc. for  $\text{C}_{112}\text{H}_{222}\text{O}_{26}$ : 11.27 %H, 67.77 %C. Found: 11.27 %H, 67.31 %C.  $D_p \sim 25$   $M_n \sim 1700$  by  $^1\text{H}$  NMR, mp = 25, 35  $^\circ\text{C}$ ;  $^1\text{H}$  NMR 1.42 (m, 4H), 1.60 (s, 98H,  $\text{CH}_2$ ), 1.81 (m, 4H), 2.07 (q, 4H), 3.41 (s, 102H,  $\text{OCH}_2$ ), 4.97 (m, 4  $=\text{CH}_2$ ), 5.80 (m, 2= $\text{CH}$ );  $^{13}\text{C}$  NMR 138.7 ( $=\text{CH}$ ), 114.4 ( $\text{CH}_2$ ), 70.5 ( $\text{OCH}_2$ ), 33.5 ( $\text{CH}_2$ ), 29.2 ( $\text{CH}_2$ ), 26.4 ( $\text{CH}_2$ ), 25.4 ( $\text{CH}_2$ ).

Synthesis of  $\alpha,\omega$ -dienyl poly(tetramethylene oxide) ( $M_n = 3600$ ) (PTHF2).

The synthesis of the larger poly(oxytetramethylene) oligomer is identical to that described above with the exception of reaction time. After adding the triflic anhydride (1.0 mL,  $5.9 \times 10^{-3}$  mol) to 36 mL tetrahydrofuran at  $-13$  °C, the reaction was allowed to stir for 45 minutes before quenching with 5-hexen-1-ol. After three precipitations, and drying under vacuum, the oligomer was obtained as a soft white powder. Anal. Calc. for  $C_{204}H_{406}O_{49}$  : 67.25 %C, 11.23 %H; Found: 66.54 %C, 11.20 %H;  $D_p \sim 48$   $M_n \sim 3600$  by  $^1H$  NMR,  $M_n \sim$ , PDI  $\sim 1.10$  by GPC. mp = 25, 35 °C;  $^1H$  NMR 1.42 (m, 4H), 1.60 (s, 200H,  $CH_2$ ), 1.81 (m, 4H), 2.07 (q, 4H), 3.41 (s, 202H,  $OCH_2$ ), 4.97 (m, 4 = $CH_2$ ), 5.80 (m, 2= $CH$ );  $^{13}C$  NMR 138.7 (=CH), 114.4 ( $CH_2$ ), 70.5 ( $OCH_2$ ), 33.5 ( $CH_2$ ), 29.2 ( $CH_2$ ), 26.4 ( $CH_2$ ), 25.4 ( $CH_2$ ).

Polyisobutylene Telechelomers

Isobutylene was polymerized cationically using the inifer method described by Storey and coworkers, using the facilities and expertise of the Storey research group.<sup>72</sup> The initiator, 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl) benzene, was prepared in three steps from 5-*t*-butyl isophthalic acid, according to published procedures.<sup>70-71</sup> *n*-Hexane was freshly distilled from calcium hydride. Titanium tetrachloride and anhydrous 2,6-dimethyl pyridine were used as received. Isobutylene and methylchloride were dried by passage through a column packed with BaO and  $CaCl_2$ . Polymerizations were

conducted under a nitrogen atmosphere drybox equipped with an integral heptane bath cooled to  $-80\text{ }^{\circ}\text{C}$  by a recirculating methanol chiller and liquid nitrogen coils regulated with a temperature controller. A 40/60 v:v mixture of n-hexane and methylchloride was used as the solvent to give fixed concentrations of 1.0 M isobutylene and  $2.5 \times 10^{-3}$  M lutidine. Reactions were quenched with 7 molar equivalents of allyltrimethyl silane per chain end.<sup>69</sup>

$\alpha,\omega$ -Dienyl polyisobutylene ( $M_n=1700$ ) (PIB1)

A three neck 1-liter flask was equipped with an overhead mechanical stirrer and chilled to  $-80\text{ }^{\circ}\text{C}$ . To the flask were added sequentially, 5-*tert*-butyl-1,3-bis (2-chloro-2-propyl) benzene (*t*-Bu-*m*-DCC) (4.955 g,  $1.725 \times 10^{-2}$  mol), condensed methyl chloride (131.5 mL), condensed isobutylene (28.2 mL, 0.356 mol), chilled hexane (197.3 mL), then 2,6-dimethyl pyridine (0.1 mL). After the reaction mixture had equilibrated for 30 minutes at  $-80\text{ }^{\circ}\text{C}$ , titanium tetrachloride (37.9 mL) was added all at once by syringe to the reaction mixture, which turned a yellow-orange color. The polymerization was complete in seconds and allyltrimethylsilane (38.2 mL, 0.241 mol) was added to quench the reaction. After stirring 15 minutes, the reaction was removed from the drybox and chilled anhydrous methanol (90 mL) was added to the cloudy, peach-colored reaction mixture to quench the titanium chloride. The reaction was allowed to warm to room temperature and the volatile solvents evaporated from the product. The polymer solution was washed with 5% HCl, then with water and the hexane layer dried over magnesium sulfate. The solvent was removed *in vacuo* to yield a colorless, viscous material.

$M_n \sim 1670$ ; Anal. Calc. for  $(C_{22}H_{34})(C_4H_8)_{24}$ : 86.15 %C, 13.85 %H; Found: 86.14 %C, 13.86 %H.  $^1H$  NMR 0.79 (s), 1.00 (d), 1.10 (s,  $CH_3$ ), 1.31-1.37 (m), 1.41 (s,  $CH_2$ ), 1.84 (s), 2.04 (d, 4H,  $CH_2-CH=$ ), 5.01 (m, 4H,  $=CH_2$ ), 5.84 (m, 2H,  $=CH$ ), 7.17 (s, 3H, Ar);  $^{13}C$  NMR 149.0, 148.5, 136.1, 121.2, 120.1, 116.7, 59.5 ( $CH_2$ ), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1, 37.8 ( $CMe_2$ ), 35.4, 32.3, 31.6, 31.2 ( $CH_3$ ), 31.0, 30.7, 29.1.

$\alpha,\omega$ -Dienyl polyisobutylene ( $M_n=3100$ ) (PIB2)

**PIB2** was prepared in an analogous manner as described above using 3.1805 g ( $1.107 \times 10^{-2}$ ) *t*-Bu-*m*-DCC, 197.3 mL condensed methyl chloride, 42.3 mL (0.535 mol) condensed isobutylene, 296.0 mL chilled hexane, and 0.15 mL 2,6-dimethyl pyridine. After the reaction mixture had equilibrated for 30 minutes at  $-80$  °C, titanium tetrachloride (24.3 mL) was rapidly added by syringe to the reaction mixture, which turned a yellow-orange color. The polymerization was complete in seconds and allyltrimethylsilane (24.6 mL, 0.155 mol) was added to quench the reaction. After stirring 15 minutes, the reaction was worked up as described above. After drying over magnesium sulfate, the hexane was removed *in vacuo* to yield a colorless, viscous material.  $M_n \sim 3110$ ; Anal. Calc. for  $(C_{22}H_{34})(C_4H_8)_{50}$ : 85.91 %C, 14.09 %H; Found: 85.90 %C, 14.10 %H;  $^1H$  NMR 0.79 (s), 1.00 (s), 1.10 (s,  $CH_3$ ), 1.31 (s), 1.37 (s), 1.41 (s), 2.04 (d, 4H,  $CH_2-CH=$ ), 5.01 (m, 4H,  $=CH_2$ ), 5.84 (m, 2H,  $=CH$ ), 7.17 (s, 3H, Ar);  $^{13}C$  NMR 149.0, 148.5, 136.1, 121.2, 120.1, 116.7, 59.5 ( $CH_2$ ), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1, 37.8 ( $CMe_2$ ), 35.4, 32.3, 31.6, 31.2 ( $CH_3$ ), 31.0, 30.7, 29.1.

$\alpha,\omega$ -Dienyl polyisobutylene ( $M_n=5800$ ) (PIB3).

PIB3 was prepared in an analogous manner as described above using 2.084 g ( $7.251 \times 10^{-3}$ ) *t*-Bu-*m*-DCC, 263.1 mL condensed methyl chloride, 56.3 mL (0.713 mol) condensed isobutylene, 394.7 mL chilled hexane, and 0.21 mL 2,6-dimethyl pyridine. After the reaction mixture had equilibrated for 30 minutes at  $-80$  °C, titanium tetrachloride (15.9 mL) was rapidly added by syringe to the reaction mixture, which turned a yellow-orange color. The polymerization was complete in seconds and allyltrimethylsilane (16.1 mL, 0.101 mol) was added to quench the reaction. After stirring 15 minutes, the reaction was worked up as described above. After drying over magnesium sulfate the hexane was removed *in vacuo* to yield a colorless, viscous material.  $M_n \sim 5820$ ; Anal. Calc. for  $(C_{22}H_{34})(C_4H_8)_{98}$ : 85.78 %C, 14.22 %H; Found: 85.77 %C, 14.23 %H;  $^1H$  NMR 0.79 (s), 1.00 (s), 1.10 (s,  $CH_3$ ), 1.31 (s), 1.37 (s), 1.41 (s), 2.04 (d, 4H,  $CH_2-CH=$ ), 5.01 (m, 4H,  $=CH_2$ ), 5.84 (m, 2H,  $=CH$ ), 7.17 (s, 3H, Ar);  $^{13}C$  NMR 149.0, 148.5, 136.1, 121.2, 120.1, 116.7, 59.5 ( $CH_2$ ), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1, 37.8 ( $CMe_2$ ), 35.4, 32.3, 31.6, 31.2 ( $CH_3$ ), 31.0, 30.7, 29.1.

Synthesis of Diene Monomers

Ester, carbonate and urethane diene monomers were synthesized. Some of the monomers had been previously synthesized and some were new monomers for the ADMET repertoire, as indicated below.

### Ester Diene Monomers

Terephthaloyl chloride (fresh bottle) and phenylene diacetic acid were used as received. The alcohols, 5-hexen-1-ol, and 3-buten-1-ol, were dried over calcium hydride and distilled prior to use. The 3-butenyl 4-pentenoate (**E3**) was prepared by Mark Watson from 3-buten-1-ol and 4-pentenoic acid. Bis(5-hexenyl) terephthalate (**E1**) was prepared according to published procedures.<sup>91</sup>

### Bis(5-hexenyl) phenylene diacetate (**E2**)

Phenylene diacetate (3.0 g, 0.016 mol) was dissolved in 75 mL toluene in a 100 mL round bottom flask equipped with a Dean-Starke apparatus. A catalytic amount of concentrated sulfuric acid (5 drops) was added in addition to 5-hexen-1-ol (10.0 mL, 0.0416). The reaction was heated to reflux, and the water byproduct collected into the Dean Starke trap. The progress of the reaction was monitored by GC, and after 24 hours the reaction mixture was washed with saturated sodium bicarbonate, then 1 M sodium hydroxide, and finally with water. The toluene layer was dried over magnesium sulfate, then calcium hydride. Distillation followed by preparatory scale HPLC yielded **E2** as a colorless oil. (Isolated yield 68%) Anal Calc for C<sub>22</sub>H<sub>30</sub>O<sub>4</sub>: 73.71 %C, 8.44 %H; Found 73.42 %C, 8.68 %H; IR (C=O) 1735 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.41 (p, 4H), 1.63 (p, 4H), 2.04 (q, 4H), 3.59 (s, 4H), 4.09 (t, 4H), 4.97 (m, 4H, =CH<sub>2</sub>), 5.77 (m, 2H, =CH), 7.24 (s, 4H, ArH); <sup>13</sup>C NMR 171.5, 138.3, 132.9, 129.4, 114.7, 64.8, 41.1, 33.2, 28.0, 25.1.

### Carbonate Diene Monomers

Bis(1-butenyl)carbonate (**C1**) and bis(1-hexenyl) carbonate (**C2**) were synthesized by a modification of the published procedure.<sup>93</sup> Dimethyl carbonate, 5-hexen-1-ol, and 3-buten-1-ol were dried over calcium hydride and distilled prior to use. Sodium metal spheres were rinsed with pentane before use.

#### Bis(3-butenyl) carbonate (**C1**)

Dimethyl carbonate (5.0 g, 0.056 mol) and 3-buten-1-ol (8.8 g, 0.122 mol) were weighed into a 50 mL round bottom flask equipped for distillation under an argon blanket. Sodium metal (0.02 g) was added and the reaction heated to reflux. Methanol was distilled from the reaction mixture and the progress of the reaction was monitored by GC. The remaining oil was distilled and further purified by preparatory scale HPLC. (Isolated yield 67%) IR (C=O) 1750  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 2.44 (m, 4H), 4.18 (t, 4H), 5.12 (m, 4H), 5.8 (m, 2H);  $^{13}\text{C}$  NMR 154.8, 133.1, 117.1, 66.5, 32.7.

#### Bis(5-hexenyl) carbonate (**C2**)

Dimethyl carbonate (5.0 g, 0.056 mol) and 5-buten-1-ol (12.2 g, 0.122 mol) were weighed into a 50 mL round bottom flask equipped for distillation under an argon blanket. Sodium metal (0.02 g) was added and the reaction heated to reflux. Methanol was distilled from the reaction mixture and the progress of the reaction was monitored by GC.

The remaining oil was distilled and further purified by preparatory scale HPLC. (Isolated yield 71%) bp= 79 °C(0.8 mmHg); IR (C=O) 1750  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.50 (p, 4H), 1.70 (p, 4H), 2.12 (q, 4H), 4.15 (t, 4H), 5.0 (m, 4H), 5.8 (m, 2H);  $^{13}\text{C}$  NMR 166.0, 138.2, 134.1, 129.1, 115.1, 65.5, 33.2, 27.8, 25.2.

### Urethane Diene Monomers

Dibutyltin dilaurate, 1,4-phenylene diisocyanate, methylene di-*p*-phenylene diisocyanate, and tolyene 2,4-diisocylate were used as received. The unsaturated alcohol, 5-hexen-1-ol was dried over calcium hydride and distilled prior to use.

### Bis(5-hexenyl)1,4-phenylene dicarbamate (U1)

Phenylene diisocyanate (2.5 g,  $1.56 \times 10^{-2}$  mol) was dissolved in 20 mL diethyl ether at room temperature under Schlenk conditions. A catalytic amount of dibutyl tin dilaurate (1 drop,  $\sim 0.02$  mL,  $3.38 \times 10^{-5}$  mol) was added, then a solution of 5-hexen-1-ol (4.2 mL,  $3.5 \times 10^{-2}$  mol) in 20 mL diethyl ether was added dropwise to the isocyanate solution over the course of 30 min. The reaction was stirred 24 hours then the ether removed *in vacuo*. The product was recrystallized from ether/pentane to give a beige solid. (Isolated yield 65 %); Calc for  $\text{C}_{20}\text{H}_{28}\text{O}_4\text{N}_2$ : 66.64 %C, 7.83 %H; IR (C=O) 1696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.49 (p, 4H), 1.68 (p, 4H), 2.08 (q, 4H), 4.16 (t, 4H), 4.99 (m, 4H), 5.79 (m, 2H), 6.65 (brs, NH); 7.30 (s, 4H, Ar);  $^{13}\text{C}$  NMR 153.8, 138.3, 133.5.1, 119.6, 114.8, 65.1, 33.2, 28.3, 25.1.

Bis(5-hexenyl) methylene diphenylene dicarbamate (U2)

**U2** was synthesized in an analogous manner as described above from the reaction of 3.91 g ( $1.56 \times 10^{-2}$  mol) methylene-di-*p*-phenylene diisocyanate and 4.2 mL ( $3.5 \times 10^{-2}$  mol) 5-hexen-1-ol. After stirring 24 hours, the ether removed *in vacuo*. The product was recrystallized from ether/pentane to give a white solid. The product formed needle-like crystals as observed by polarized optical microscopy.  $T_m = 76-79$  °C; (Isolated yield 72 %); Calc for  $C_{27}H_{34}O_4N_2$ : 71.97 %C, 7.61 %H; Found 72.10 %C, 7.58 %H, 6.31 %N; IR (C=O) 1713, 1694  $cm^{-1}$ ;  $^1H$  NMR 1.45 (p, 4H), 1.54 (p, 4H), 2.04 (q, 4H), 3.84 (s, 2H, Ar-CH<sub>2</sub>-Ar); 4.12 (t, 4H), 4.95 (m, 4H), 5.76 (m, 2H), 6.56 (s, 2NH), 7.07 (m, 2ArH), 7.23 (m, 2ArH);  $^{13}C$  NMR 153.7, 138.3, 136.2, 135.9, 129.4, 118.8, 114.8, 65.1, 40.5, 33.3, 28.3, 25.1.

Bis(5-hexenyl) 4-methyl-1,3-phenylenedicarbamate (U3)

**U3** was synthesized in an analogous manner as described above from the reaction of 2.22 mL ( $1.56 \times 10^{-2}$  mol) toluene-2,4-diisocyanate with 4.2 mL ( $3.5 \times 10^{-2}$  mol) 5-hexen-1-ol. After stirring was stirred 24 hours the ether removed *in vacuo*. The product was recrystallized from ether/pentane to give a beige solid. The product formed flat diamond and fan-like crystals as observed by polarized optical microscopy  $T_m = 66-69$  °C; (Isolated yield 75 %); Calc for  $C_{21}H_{30}O_4N_2$ : 67.36 %C, 8.07 %H; Found 67.20 %C, 8.07 %H, 7.57 %N; IR (C=O) 1703  $cm^{-1}$ ;  $^1H$  NMR 1.49 (p, 4H), 1.66 (p, 4H), 2.08 (q, 4H), 2.17 (s, 3H, Ar-CH<sub>3</sub>); 4.15 (t, 4H), 4.97 (m, 4H, =CH<sub>2</sub>), 5.79 (m, 2H, =CH), 6.42 (s,

<sup>1</sup>H, NH), 6.74 (s, 1H, NH), 7.06 (d, 1H, Ar), 7.24 (m, 1H, Ar), 7.75 (s, 1H); <sup>13</sup>C NMR 153.7 (C=O), 138.3 (=CH), 136.7 (Ar-N), 136.2 (Ar-N), 130.7 (Ar-H), 121.8 (Ar-Me), 114.8 (=CH<sub>2</sub>), 114.2 (Ar-H), 110.9 (Ar-H btwn NH) 65.2 (OCH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 28.3(CH<sub>2</sub>), 25.1 (CH<sub>2</sub>), 16.9 (Ar-CH<sub>2</sub>).

### Synthesis of Segmented Copolymers

ADMET polymerizations were begun in an argon atmosphere drybox in flasks equipped with a high vacuum valve. Catalyst to diene ratio was approximately 1:200 to 1:400. Grubbs ruthenium benzylidene catalyst was used unless otherwise indicated. Generally reactions were begun at ambient temperature and periodic vacuum then heated under full vacuum as the reaction became more viscous. Polymerizations ensued for 7 to 21 days before either hydrogenating or terminating by dissolving in chloroform and filtering through a plug of 50:50 silica gel/alumina.

### Polyisobutylene/Decadiene Segmented Copolymers

Polyisobutylene oligomers were copolymerized with decadiene in three different proportions (to target 1:2, 1:4, and 1:6 molar repeat unit ratio of octenamer to isobutylene in the product copolymer) to make a total of 9 polymers as summarized in Chapter 2. Ruthenium catalyzed ADMET polymerization and hydrogenation were performed in tandem.

The polymers were hydrogenated using the method developed by Watson.<sup>53</sup> In a typical procedure, 0.3 g crude polymer mixture (still containing the ruthenium catalyst) was dissolved in 10 mL toluene along with 0.15 g 100-mesh silica gel in a glass pressure tube. The vessel was charged with 120 psi hydrogen and stirred at 90 °C for 48 hours. Completeness of hydrogenation was determined by <sup>1</sup>H NMR when the polymer was soluble in chloroform.

#### Copolymerization of PIB1 with decadiene 1:6

**PIB1** (0.36 g,  $2.16 \times 10^{-4}$  mol) and decadiene (0.15 g,  $1.08 \times 10^{-3}$  mol) were weighed into a vacuum flask equipped with a Teflon valve. After mixing the monomers together for 5 minutes, 0.01 g ruthenium catalyst was added to the monomer mixture. The polymerization was moved to a schlenk line and periodic vacuum applied for 24 hours until the reaction became very viscous. The flask was then moved to vacuum line equipped with an oil diffusion pump and an oil bath at 70 °C. The reaction was monitored periodically by <sup>1</sup>H NMR and after stirring 8 days the polymerization was dissolved in chloroform and filtered through alumina and silica. Evaporation of the solvent yielded a viscous clear material. <sup>1</sup>H NMR 0.79 (s, 12H), 1.00 (m, 10H), 1.10 (s, 90H, CH<sub>3</sub>), 1.12 (s, 4H), 1.31 (s, 4H), 1.37 (s, 60H, CH<sub>2</sub>), 1.40 (d 16H), 1.81 (s, 4H), 2.0 (brs 17H), 5.39 (br m 10H), 7.17 (s, 3 Ar); <sup>13</sup>C NMR: 148.9, 148.5, 132.9, 131.4, 130.3, 129.9, 127.1, 126.5, 121.1, 120.1, 59.5 (CMe<sub>2</sub>), 59.0, 58.6, 56.0, 49.5, 39.0, 38.1, 37.8 (CH<sub>2</sub>), 35.4, 32.3, 31.6, 31.2 (CH<sub>3</sub>), 31.0 (CH<sub>2</sub>), 30.7, 29.1, 28.5; After hydrogenation:

$^1\text{H}$  NMR: 1.0 – 2.0 (vbr m, 220 H), 7.18 (s, 3H);  $^{13}\text{C}$  NMR: 130.3 (Ar), 59.5 (PIB  $\text{CH}_2$ ), 38.1 ( $\text{CMe}_2$ ), 32.6, 31.2 ( $\text{CH}_3$ ), 29.7 (PE  $\text{CH}_2$ ), 29.0.

Copolymerization of **PIB2** with decadiene 1:6.

**PIB2** (0.44 g,  $1.41 \times 10^{-4}$  mol) and decadiene (0.18 g,  $1.30 \times 10^{-3}$  mol) were copolymerized as described above to give a clear viscous material.  $^1\text{H}$  NMR 0.79 (s, 12H), 0.9-1.5 (brm, 230 H), 1.81 (s, 4H), 2.0 (brs 17H), 5.39 (br m 6H), 7.17 (s, 3 Ar);  $^{13}\text{C}$  NMR: 148.9, 148.5, 132.9, 131.4, 130.3, 129.9, 127.1, 126.5, 121.1, 120.1, 59.5 ( $\text{CMe}_2$ ), 59.0, 58.6, 56.0, 49.5, 39.0, 38.1, 37.8 ( $\text{CH}_2$ ), 35.4, 32.3, 31.6, 31.2 ( $\text{CH}_3$ ), 31.0 ( $\text{CH}_2$ ), 30.7, 29.1, 28.5; After hydrogenation:  $^1\text{H}$  NMR 1.0 – 2.0 (vbr m, 249 H), 7.18 (s, 3H);  $^{13}\text{C}$  NMR: 130.3 (Ar), 59.5 (PIB  $\text{CH}_2$ ), 38.1 ( $\text{CMe}_2$ ), 32.6, 31.2 ( $\text{CH}_3$ ), 29.7 (PE  $\text{CH}_2$ ), 29.0.

Copolymerization of **PIB3** with decadiene 1:6.

**PIB3** (0.43 g,  $7.39 \times 10^{-5}$  mol) and decadiene (0.17 g,  $1.23 \times 10^{-3}$  mol) were copolymerized as described above to give a clear viscous material.  $^1\text{H}$  NMR 0.79 (s, 12H), 0.9-1.5 (brm, 260 H), 1.81 (s, 4H), 2.0 (brs 17H), 5.39 (br m 10H), 7.17 (s, 3 Ar);  $^{13}\text{C}$  NMR: 148.9, 148.5, 132.9, 131.4, 130.3, 129.9, 127.1, 126.5, 121.1, 120.1, 59.5 ( $\text{CMe}_2$ ), 59.0, 58.6, 56.0, 49.5, 39.0, 38.1, 37.8 ( $\text{CH}_2$ ), 35.4, 32.3, 31.6, 31.2 ( $\text{CH}_3$ ), 31.0 ( $\text{CH}_2$ ), 30.7, 29.1, 28.5; After hydrogenation:  $^1\text{H}$  NMR 1.0 – 2.0 (vbr m, 300 H), 7.18

(s, 3H);  $^{13}\text{C}$  NMR: 130.3 (Ar), 59.5 (PIB  $\text{CH}_2$ ), 38.1 ( $\text{CMe}_2$ ), 32.6, 31.2 ( $\text{CH}_3$ ), 29.7 (PE  $\text{CH}_2$ ), 29.0.

#### Copolymerization of PIB1 with decadiene 1:4

**PIB1** (0.29 g,  $1.74 \times 10^{-4}$  mol) and decadiene (0.18 g,  $1.30 \times 10^{-3}$  mol) were copolymerized as described above to give a somewhat translucent semisolid.  $^1\text{H}$  NMR 0.79 (s, 12H), 0.98-1.20 (br m, 110H), 1.20-1.40 (br m, 90H), 1.0 (br s, 16H), 1.81 (s, 4H), 2.0 (brs 11H), 5.39 (br m 10H), 7.17 (s, 3 Ar);  $^{13}\text{C}$  NMR: 130.3 (Ar), 59.5 (PIB  $\text{CH}_2$ ), 38.1 ( $\text{CMe}_2$ ), 32.6, 31.2 ( $\text{CH}_3$ ), 29.7 (PE  $\text{CH}_2$ ), 29.0.

#### Copolymerization of PIB2 with decadiene 1:4.

**PIB2** (0.26 g,  $8.36 \times 10^{-5}$  mol) and decadiene (0.16 g,  $1.16 \times 10^{-3}$  mol) were copolymerized as described above to give a viscous semisolid.  $^1\text{H}$  NMR 0.80 (s, 4H), 0.9–2.0 (vbr m, 460 H), 5.39 (br m 13H), 7.18 (s, 3H);  $^{13}\text{C}$  NMR: 130.3 (Ar), 59.5 (PIB  $\text{CH}_2$ ), 38.1 ( $\text{CMe}_2$ ), 32.6, 31.2 ( $\text{CH}_3$ ), 29.7 (PE  $\text{CH}_2$ ), 29.0.

#### Copolymerization of PIB3 with decadiene 1:4.

**PIB3** (0.45 g,  $7.73 \times 10^{-5}$  mol) and decadiene (0.28 g,  $2.03 \times 10^{-3}$  mol) were copolymerized as described above to give a viscous semisolid.  $^1\text{H}$  NMR 0.79 (s, 12H), 0.9-1.5 (brm, 700 H), 1.81 (s, 4H), 2.0 (brs 17H), 5.39 (br m 35 H), 7.17 (s, 3 Ar);  $^{13}\text{C}$  NMR: 130.3 (Ar), 59.5 (PIB  $\text{CH}_2$ ), 38.1 ( $\text{CMe}_2$ ), 32.6, 31.2 ( $\text{CH}_3$ ), 29.7 (PE  $\text{CH}_2$ ), 29.0.

Copolymerization of **PIB1** with decadiene 1:2

**PIB1** (0.39 g,  $2.34 \times 10^{-4}$  mol) and decadiene (0.48 g,  $3.47 \times 10^{-3}$  mol) were copolymerized as described above to give a soft white solid.  $^1\text{H}$  NMR 0.79 (s, 12H), 0.9-1.5 (brm, 480 H), 1.81 (s, 4H), 2.0 (brs 17H), 5.39 (br m 35 H), 7.17 (s, 3 Ar);  $^{13}\text{C}$  NMR: 130.3 (Ar), 59.5 (PIB  $\text{CH}_2$ ), 38.1 ( $\text{CMe}_2$ ), 32.6, 31.2 ( $\text{CH}_3$ ), 29.7 (PE  $\text{CH}_2$ ), 29.0.

Copolymerization of **PIB2** with decadiene 1:2.

**PIB2** (0.41 g,  $1.32 \times 10^{-4}$  mol) and decadiene (0.50 g,  $3.62 \times 10^{-3}$  mol) were copolymerized as described above to give a soft translucent waxy material.  $^1\text{H}$  NMR 0.79 (s, 12H), 0.9-1.5 (br s 650 H), 1.80 (s, 4H), 2.0 (brs 17H), 5.39 (br m 34H), 7.17 (s, 3 Ar);  $^{13}\text{C}$  NMR: 130.3 (Ar), 59.5 (PIB  $\text{CH}_2$ ), 38.1 ( $\text{CMe}_2$ ), 32.6, 31.2 ( $\text{CH}_3$ ), 29.7 (PE  $\text{CH}_2$ ), 29.0.

Copolymerization of **PIB3** with decadiene 1:2.

**PIB3** (0.42 g,  $7.22 \times 10^{-5}$  mol) and decadiene (0.52 g,  $3.67 \times 10^{-3}$  mol) were copolymerized as described above to give a soft wax.  $^1\text{H}$  NMR: 0.79 (s, 12H), 0.9-1.5 (brm, 820 H), 1.80 (s, 4H), 2.0 (brs 16H), 5.39 (br m 54H), 7.17 (s, 3 Ar);  $^{13}\text{C}$  NMR: 130.3 (Ar), 59.5 (PIB  $\text{CH}_2$ ), 38.1 ( $\text{CMe}_2$ ), 32.6, 31.2 ( $\text{CH}_3$ ), 29.7 (PE  $\text{CH}_2$ ), 29.0.

### Ester Segmented Copolymers

Copolymerizations of the ester diene monomers with polyisobutylene and poly(tetramethylene oxide) telechelomers were performed on a 0.4 to 0.7 g scale as indicated above, with polymerizations proceeding for 4-6 days. These copolymers were not hydrogenated.

#### Copolymerization of **E1** with **THF1**

The terephthalate monomer, **E1**, (0.72 g,  $2.18 \times 10^{-3}$  mol) and **THF1** (0.722 g,  $4.2 \times 10^{-4}$  mol) were weighed into a vacuum flask, and stirred together until homogenized. The ruthenium catalyst (0.005 g) was added and the reaction moved to a schlenk line with and warmed to 60 °C. The reaction was stirred for 48 hours, then the reaction mixture was dissolved in chloroform and filtered through a plug of silica gel. The solvent was evaporated to yield a soft white solid. IR (C=O)  $1721 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR 1.52 (p, 4H), 1.61 (THF), 1.78 (m, 4H), 2.07 (q, 4H), 3.41 (THF), 4.33 (t, 4H), 5.43 (m, =CH), 8.10 (s, 4H, ArH);  $^{13}\text{C}$  NMR 165.8, 134.1, 130.3, 129.5, 70.6 (THF), 65.4, 32.1, 28.1, 26.5 (THF), 25.9.

#### Copolymerization of **E2** with **THF1**

The phenylene diacetate monomer, **E2**, (1.0 g,  $2.18 \times 10^{-3}$  mol) and **THF1** (1.0 g,  $4.2 \times 10^{-4}$  mol) were weighed into a vacuum flask, and stirred together until homogenized. The ruthenium catalyst (0.005 g) was added and the reaction moved to a schlenk line with an

oil bath at 60 °C. The reaction was stirred for 48 hours. The reaction mixture was dissolved in chloroform and filtered through a plug of silica gel. The solvent was evaporated to yield a soft solid. IR (C=O) 1736 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.37 (p, 4H), 1.61 (p, 4H+ THF), 1.99 (q, 4H), 3.41 (THF), 3.58 (s, 4H), 4.07 (t, 4H), 5.36 (brs, =CH), 7.23 (s, 4H, ArH); <sup>13</sup>C NMR 171.5, 132.9, 130.2, 129.4, 70.6 (THF), 64.8, 41.0, 32.0, 28.0, 26.5 (THF), 25.7.

#### Copolymerization of E3 with THF1

The aliphatic ester monomer, **E1**, (0.75 g, 5.2x10<sup>-3</sup> mol) and **THF1** (0.72 g, 4.2x10<sup>-4</sup> mol) were weighed into a vacuum flask, and stirred together until homogenized. The ruthenium catalyst (0.005 g) was added and the reaction moved to a schlenk line with an oil bath. The reaction was stirred for 48 hours. The reaction mixture was dissolved in chloroform and filtered through a plug of alumina. The solvent was evaporated to yield a viscous liquid. IR (C=O) 1738 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.37 (m, end THF H), 1.61 (s, THF), 1.99 (q, 4H end THF), 2.32 (m, 6H), 3.39 (THF), 4.06 (t, 2H), 5.46 (br s, =CH); <sup>13</sup>C NMR 172.9, 131.1, 129.4, 128.2, 127.4, 126.5, 70.6 (THF), 63.7, 34.1, 31.9, 31.8, 27.8, 26.5 (THF), 22.8.

#### Copolymerization of E1 with PIB1

The terephthalate monomer, **E1**, (0.46 g, 1.18x10<sup>-3</sup> mol) and **PIB** (0.46 g, 2.8x10<sup>-5</sup> mol) were weighed into a vacuum flask, and stirred together until homogenized. The

ruthenium catalyst (0.01 g) was mixed in, and the reaction moved to a schlenk line with and warmed to 60 °C. The reaction was stirred for 5 days, then the reaction mixture was dissolved in chloroform and filtered through a plug of alumina. The solvent was evaporated to yield a soft beige solid. IR (C=O) 1721  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 0.80 (s), 1.00 (d), 1.10 (s,  $\text{CH}_3$ ), 1.31-1.37 (m), 1.41 (s,  $\text{CH}_2$ ), 1.52 (m, 4H E), 1.8-2.2 (m E+IB), 4.31 (t, 4HE), 5.43 (m, 1H, =CH), 7.17 (s, 3 Ar), 8.09 (br s, 4H, ArH);  $^{13}\text{C}$  NMR 165.8, 134.2, 129.5, 121.2, 120.1, 65.5, 59.5 ( $\text{CMe}_2$ ), 59.0, 58.8, 58.6, 38.9, 38.1, 37.8 ( $\text{CH}_2$ ), 32.2, 31.6, 31.2 ( $\text{CH}_3$ ), 30.7, 29.4, 29.2, 28.6, 25.9.

### Carbonate Segmented Copolymers

Copolymerizations of the carbonate diene monomers with polyisobutylene and poly(oxytetramethylene) telechelomers were performed on a 0.6 to 1.4 g scale following the procedure described above. The Grubbs ruthenium benzylidene was used, and after polymerization, 0.3 g product was dissolved in toluene and along with 0.25 g silica gel and exposed to 120 psi hydrogen at 90 °C for 48 hours. The remaining product was dissolved in chloroform and filtered through a plug of 50/50 silica gel/alumina.

### Copolymerization of C1 with PTHF1

The polymerization procedure described above was used to copolymerize 0.79 g ( $4.64 \times 10^{-3}$  mol) bis(3-butenyl) carbonate plus 0.79 g ( $4.16 \times 10^{-4}$  mol) **PTHF1** using 0.01 g ruthenium benzylidene. After stirring 7 days at 70 °C, 0.3 g of the amber reaction mixture

was dissolved in toluene and hydrogenated, while the other half was dissolved in chloroform and filtered through a plug of alumina/silica. Hydrogenation gave a waxy, colorless opaque solid. IR 1745 (C=O);  $^1\text{H}$  NMR: 1.42 (br), 1.54 (s, 14H, THF), 1.81 (br), 2.07 (br), 2.40 (br, 4H), 3.41 (s, 12H, THF), 4.14 (t, 4H), 5.21 (m, 0.2H, end =CH<sub>2</sub>), 5.50 (br, 2.1H, =CH), 5.60 (brm, 0.1H, end =CH);  $^{13}\text{C}$  NMR: 154.9, 133.3, 132.7, 131.9, 127.9, 127.0, 124.6, 124.3, 123.7, 70.4 (THF), 68.2, 67.3, 66.9, 66.7, 32.1, 31.7, 29.0, 26.7, 26.3 (THF), 25.7.

#### Copolymerization of C1 with PTHF2

The polymerization procedure described above was used to copolymerize 0.46 g ( $2.70 \times 10^{-3}$  mol) bis(3-butenyl) carbonate plus 0.46 g ( $1.28 \times 10^{-4}$  mol) **PTHF2** using 0.01 g ruthenium benzylidene. After stirring 20 days at 70 °C, 0.3 g of the reaction mixture was dissolved in toluene and hydrogenated, while the remaining product was dissolved in chloroform and filtered through a plug of silica/alumina. IR (C=O) 1745  $\text{cm}^{-1}$   $^1\text{H}$  NMR (CDCl<sub>3</sub>) 1.61 (s, 13H, THF), 2.40 (br m, 4H), 3.40 (s, 12H); 4.12 (t, 4H); 5.21 (m, 0.2H, end =CH<sub>2</sub>), 5.5 (br, 2H, =CH), 5.60 (brm, 0.1H, end =CH);  $^{13}\text{C}$  NMR: (CDCl<sub>3</sub>) 155.1, 128.1, 127.2, 70.6 (THF), 67.2, 66.9, 31.9, 26.9, 26.5 (THF).

#### Copolymerization of C2 with PTHF1

The polymerization procedure described above was used to copolymerize 0.95 g ( $4.20 \times 10^{-3}$  mol) bis(5-hexenyl) carbonate plus 0.95 g ( $5.0 \times 10^{-4}$  mol) **PTHF1**. After

stirring 7 days, half the light yellow reaction mixture was dissolved in toluene and hydrogenated, while half was dissolved in chloroform and filtered through a plug of alumina. Hydrogenation gave a soft, waxy solid. IR (C=O)  $1745\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ ) 1.41 (m, 4H), 1.59 (brs, 15H, (THF+C2)); 1.98 (m, 4H), 3.37 (s, 11H, THF), 4.08 (t, 4H); 5.35 (br s, 2H);  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ ) 155.3, 130.6, 130.1, 129.5, 128.8, 70.5 (THF), 67.7, 67.3, 32.2, 31.9, 29.1, 28.5, 28.1, 28.0, 26.6, 28.4 (THF), 25.6, 25.5.

#### Copolymerization of C2 with PTHF2

The polymerization procedure described above was used to copolymerize 0.54 g ( $2.39 \times 10^{-3}$  mol) bis(5-hexenyl) carbonate plus 0.54 g ( $1.50 \times 10^{-4}$  mol) **PTHF2** using 0.01 g ruthenium benzylidene. IR (C=O)  $1747\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.40 (p, 4H), 1.60 (br s, 16H, THF), 1.98 (brm, 4H), 3.38 (12H, THF), 4.10 (t, 4H), 5.36 (br m, =CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 155.3, 130.1, 129.6, 70.5 (THF), 67.7, 31.9, 28.0, 26.4 (THF), 25.6, 25.5.

#### Copolymerization of C1 with PIB1

The polymerization procedure described above was used to copolymerize bis(3-butenyl) carbonate (0.35g,  $2.39 \times 10^{-4}$  mol) and **PIB1** (0.40 g,  $2.06 \times 10^{-4}$  mol) using 0.01 g ruthenium benzylidene. After stirring 18 days the polymerization was terminated, though NMR showed end-groups still remained. IR (C=O)  $1747\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.79 (s), 1.00 (d), 1.10 (brs,  $\text{CH}_3$ ), 1.78, 1.31- 1.41 (m), 1.83 (s), 2.00 (d), 2.4 (m, 4H), 4.13 (t, 4H), 5.01 (m, 4H, end = $\text{CH}_2$ ), 5.52 (br, 2H, =CH), 5.83 (m, 2.1H, end =CH), 7.17 (s, 3.1

H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 148.9, 148.5, 136.1, 129.7, 127.9, 121.2, 120.1, 116.7, 59.7 (CMe<sub>2</sub>), 59.1, 58.6, 55.7, 50.3, 38.9, 37.9 (CH<sub>2</sub>), 35.4, 34.8, 32.3, 32.0, 31.6, 31.2 (CH<sub>3</sub>), 30.9, 30.7, 29.1, 28.1, 25.6

Hydrogenated: ;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) 0.79 (s), 1.00 (d), 1.10 (brs, CH<sub>3</sub>), 1.21 (s), 1.41 (m, 4H), 1.43 (m, H), 1.84 (s), 2.00 (m, 4H), 4.12 (t, 4H), 7.17 (s, 7H, ArH).

#### Copolymerization of C1 with PIB2

The polymerization procedure described above was used to copolymerize bis(3-butenyl) carbonate (0.55g,  $3.23 \times 10^{-3}$  mol) and **PIB2** (0.55 g,  $1.77 \times 10^{-4}$  mol) using 0.01 g ruthenium benzylidene. After stirring 18 days the polymerization was terminated, though NMR showed end-groups still remained. IR (C=O)  $1745 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR 0.79 (s), 1.00 (d), 1.10 (brs, CH<sub>3</sub>), 1.31-1.37 (m), 1.41 (s, CH<sub>2</sub>), 1.84 (s), 2.04 (d), 2.40 (m, 4H), 4.13 (t, 4H), 5.21 (m, H, end =CH<sub>2</sub>), 5.5 (br, 2H, =CH), 5.60 (brm, 0.1H, end =CH), 7.17 (s, Ar);  $^{13}\text{C}$  NMR 155.1, 149.0, 148.5, 136.1, 121.2, 120.1, 116.7, 59.5 (CMe<sub>2</sub>), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1, 37.8 (CH<sub>2</sub>), 35.4, 32.3, 31.6, 31.2 (CH<sub>3</sub>), 31.0, 30.7, 29.1, 25.6.

#### Copolymerization of PIB1 with C2

The polymerization procedure described above was used to copolymerize 0.48 g ( $2.12 \times 10^{-4}$  mol) bis(5-hexenyl) carbonate plus 0.48 g ( $2.87 \times 10^{-4}$  mol) **PIB1** using 0.01 g ruthenium benzylidene. After stirring 11 days the reaction was terminated. IR (C=O)

1745  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) 0.79 (s), 0.98 (m), 1.10 (s,  $\text{CH}_3$ ), 1.31-1.37 (m), 1.41 (s,  $\text{CH}_2$ ), 1.65 (br m, 4H, C2), 1.81 (s), 2.01 (br m, 4H, C2), 4.11 (t, 4H, C4), 5.40 (br, 2.44H, =CH), 7.16 (s, 0.44H, Ar);  $^{13}\text{C NMR}$  155.3, 148.9, 148.5, 136.1, 131.5, 130.1, 129.6, 128.8, 127.9, 121.2, 120.1, 116.7, 59.5 ( $\text{CMe}_2$ ), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1, 37.8 ( $\text{CH}_2$ ), 35.4, 32.3, 31.6, 31.2 ( $\text{CH}_3$ ), 31.0, 30.7, 29.1, 25.6.

### Copolymerization of **PIB2** with **C2**

The polymerization procedure described above was used to copolymerize 0.30 g ( $9.65 \times 10^{-5}$  mol) poly(isobutylene) plus 0.30 g ( $1.33 \times 10^{-3}$  mol) bis(5-hexenyl) carbonate using 0.01 g ruthenium benzyldiene. After stirring 16 days, the reaction was terminated by hydrogenation and workup. IR ( $\text{C=O}$ ) 1745  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.79 (s), 0.99 (m), 1.00 (s), 1.10 (brs,  $\text{CH}_3$ ), 1.31-1.37 (m), 1.41 (brs,  $\text{CH}_2$ ), 1.66 (m, 5H), 1.81 (s), 2.01 (m, 4H, C2), 4.11 (t, 4H), 5.38 (br m, 2H, =CH), 7.17 (s, 0.25H, Ar);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): 155.3, 148.9, 148.5, 136.1, 131.5, 130.1, 129.6, 128.8, 127.9, 121.2, 120.1, 116.7, 59.5 ( $\text{CMe}_2$ ), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1, 37.8 ( $\text{CH}_2$ ), 35.4, 32.3, 31.6, 31.2 ( $\text{CH}_3$ ), 31.0, 30.7, 29.1, 25.6

### Urethane Segmented Copolymers

Two urethane monomers, bis(5-hexenyl)methylene-1,4-diphenylene dicarbamate (**U2**) and bis(5-hexenyl)toluene 1,3-dicarbamate (**U3**) were copolymerized with **PIB1** and

with **PTHF2**, in ADMET polymerizations as described above. The ratio of the two was such to give approximately 5 THF or IB repeat units per 1 urethane repeat unit.

#### Copolymerization of U2 with PTHF2

The solid reactants, **PTHF2** (0.30g,  $8.33 \times 10^{-5}$  mol) and **U2** (0.25 g,  $5.56 \times 10^{-4}$  mol) were mixed together with 0.01 g ruthenium catalyst. The reaction was warmed to 80 °C, but chunks of the urethane monomer remained. After stirring 4 days, the reaction mixture was dissolved in chloroform and filtered through alumina. Evaporation gave hard pink solid. Precipitation into methanol was unsuccessful at removing the residual catalyst. IR (C=O)  $1713 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR 1.45 (br, 4H), 1.61 (br s, 51H, THF), 2.05 (br m, 4H), 3.40 (s, 46H, THF), 3.87 (s, 2H, Ar-CH<sub>2</sub>-Ar); 4.13 (s, 4H), 4.40 (br, 3.3H, =CH), 6.59 (br, 2NH), 7.07 (br d, 2ArH), 7.23 (d, 2ArH);  $^{13}\text{C}$  NMR 153.7 (C=O), 138.3, 136.2, 135.9, 129.4, 118.8, 70.6 (THF), 65.1, 40.5, 33.3, 28.3, 26.5 (THF), 25.1

#### Copolymerization of U3 with PTHF2

The solid reactants, **PTHF2** (0.40g,  $1.11 \times 10^{-4}$  mol) and **U3** (0.31 g,  $8.29 \times 10^{-4}$  mol) were mixed together with 0.01 g ruthenium catalyst. The reaction was warmed to 60 °C to give a homogeneous, bubbling liquid. After stirring 4 days, the reaction mixture was dissolved in chloroform and filtered through alumina. Evaporation gave soft beige solid. Precipitation into methanol was unsuccessful at removing the residual catalyst. IR (C=O)  $1703 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR 1.42 (br s4, 4H), 1.61 (br s, 28H, THF), 2.02 (br s, 4H), 2.16 (s, 3H,

Ar-CH<sub>3</sub>); 3.40 (br s, 25 H, THF), 4.14 (br s, 4H), 5.39 (br s, 2.4H, =CH), 6.43 (br s, 1H, NH), 6.74 (br, 1H, NH), 7.04 (br s, 1H, Ar), 7.26 (s, 2H, Ar), 7.73 (br s, 1H); <sup>13</sup>C NMR 153.7 (C=O), 138.3 (=CH), 136.7 (Ar-N), 136.2 (Ar-N), 130.7 (Ar-H), 121.8 (Ar-Me), 114.2 (Ar-H), 110.9 (Ar-H), 70.5 (THF), 65.2 (OCH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 28.3(CH<sub>2</sub>), 26.5 (THF), 25.1 (CH<sub>2</sub>), 16.9 (Ar-CH<sub>2</sub>).

### Copolymerization of U2 with PIB1

**PIB1** (0.18 g,  $1.11 \times 10^{-4}$  mol) and **U2** (0.20 g,  $4.40 \times 10^{-4}$  mol) were weighed into a vacuum flask. The solid urethane monomer remained as solid chunks in the viscous PIB, even after stirring for several minutes, so 0.5 mL toluene was added to aid mixing. Catalyst (0.01 g) was added to the flask and the reaction was heated to 80 °C while applying periodic vacuum. After several hours the reaction became more homogeneous, but some solids still remained throughout the reaction. After stirring 10 days, chloroform was added to the reaction mixture, which did not all dissolve, and the chloroform solution was filtered through alumina. Evaporation of the solvent yielded a viscous grey semisolid. IR (C=O) 1713 cm<sup>-1</sup>; <sup>1</sup>H NMR: 0.6-1.6 (m, 790H), 1.84 (s, 18H), 2.04 (brd 16H), 2.20 (s, 1H), 3.84 (s, 2H, Ar-CH<sub>2</sub>-Ar); 4.15 (br t, 2H), 4.95 (m, 3.5H end =CH<sub>2</sub>), 5.25-5.5 (m, 10H =CH), 5.76 (m, 2H end =CH), 6.56 (br, 1NH), 7.07-7.2 (m, 15H); <sup>13</sup>C NMR: 155, 148.9, 148.5, 136.1, 129.8, 128.7, 121.1, 120.1, 117.8, 59.7, 59.5 (PIB C), 59.2, 59.0, 58.5, 55.9, 49.1, 42.5, 38.9, 38.1 (PIB CH<sub>2</sub>), 37.9, 37.8, 35.9, 35.6, 34.8, 32.3, 31.6, 31.2 (PIB CH<sub>3</sub>), 30.98, 30.7, 29.2, 28.9.

Copolymerization of U3 with PIB1

PIB1 (0.48 g,  $2.88 \times 10^{-4}$  mol), U3 (0.30 g,  $8.02 \times 10^{-4}$  mol), and 0.5 mL toluene were added to a vacuum flask, and stirred for several minutes until mostly homogenized. Ruthenium catalyst (0.01 g) was added and the reaction was warmed to 70 °C with periodic vacuum. After stirring 8 days, the reaction mixture was dissolved in chloroform and filtered through alumina to give a brown viscous liquid upon evaporation. IR (C=O)  $1703 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR 0.79, (s), 0.8-1.5 (m, H), 1.61 (br, s), 1.84 (s), 1.98-2.14 (m, 4H), 2.17 (s, 3H, Ar-CH<sub>3</sub>); 4.15 (br s, 4H), 5.00 (m, H, end =CH<sub>2</sub>), 5.36-5.6 (m, 2H, end =CH), 5.81 (m, 2H, end =CH), 6.42-6.6 (br, 1H, NH), 7.06 (br s, 1H, Ar), 7.17 (s, 3 Ar), 7.24 (br, H, Ar), 7.75 (br, 1H);  $^{13}\text{C}$  NMR 153.7 (C=O), 149.0, 148.5, 138.3 (=CH), 136.7, 136.2, 130.7, 121.8 (Ar-Me), 121.2, 120.1, 114.2, 110.9, 65.2 (OCH<sub>2</sub>), 59.5 (PIB C), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1 (PIB CH<sub>2</sub>), 37.8, 35.4, 33.2 (CH<sub>2</sub>), 31.2 (PIB CH<sub>3</sub>), 30.7, 28.93, 25.1 (CH<sub>2</sub>), 16.9 (Ar-CH<sub>2</sub>).

## CHAPTER 8 SUMMARY

This research described in this dissertation extends the scope of ADMET segmented copolymers stemming from the initial poly(tetramethylene oxide)-polyoctenamer segmented copolymers first synthesized by Brzezinska. A series of segmented copolymers was synthesized by acyclic diene metathesis (ADMET) copolymerization of  $\alpha,\omega$ -dienyl polyether and polyisobutylene telechelomers with  $\alpha,\omega$ -diene comonomers. Both new and known diene monomers were combined in new ways in the synthesis of a variety of segmented copolymers, with the urethane diene monomers, butenyl pentenoate, bis(1-hexenyl)phenylene diacetate, and  $\alpha,\omega$ -dienyl polyisobutylene being used for the first time in ADMET chemistry.

Polyisobutylene telechelomers were copolymerized with decadiene, bis(5-hexenyl) terephthalate, bis(3-butenyl) carbonate, bis(5-hexenyl) carbonate, bis(5-hexenyl) methylene bis(1,4-diphenylenecarbamate), and 1,3-bis(5-hexenyl) 4-methyl-1,3-phenylenedicarbamate. Poly(tetramethylene oxide) telechelomers were copolymerized with bis(5-hexenyl) terephthalate, bis(5-hexenyl) phenylene diacetate, 3-butenyl 4-pentenoate, bis(3-butenyl) carbonate, bis(5-hexenyl) carbonate, bis(5-hexenyl) methylene bis(1,4-diphenylenecarbamate), and 1,3-bis(5-hexenyl)

4-methyl-1,3-phenylenedicarbamate. In each case an increase in molecular weight to 20000 to 30000 g/mol could be eventually attained. However, polymerizations involving polyisobutylene telechelomers and bis(3-butenyl) carbonate required several days to achieve appreciable molecular weight, and factors that may contribute to this decreased reactivity are discussed in Chapter 2 and Chapter 5, respectively.

Differential scanning calorimetry was performed on many of the segmented copolymers to study the degree of phase separation in the bulk material. Segmented copolymers of polyisobutylene with decadiene, ester, carbonate, or urethane comonomers tended to show both a  $T_g$  close to  $-70\text{ }^\circ\text{C}$  and a melting point approaching that of the homopolymer of the second segment. This is consistent with a high degree of phase separation between the segments. Segmented copolymers of poly(tetramethylene oxide) with decadiene had been shown previously by Brzezinska to be well phase separated. However it was shown herein that copolymers of this polyether with ester, carbonate, and urethane comonomers give materials showing varying degrees of phase miscibility. Copolymers utilizing the more flexible esters, bis(5-hexenyl) phenylene diacetate and 3-butenyl 4-pentenoate, as well as the hexenyl carbonate comonomers gave materials showing a single intermediate melting point, which indicates a high degree of miscibility between the two segments. The more rigid bis(5-hexenyl) terephthalate, the hydrogenated carbonates, and the MDI-based urethane monomers gave segmented copolymers that appeared to have an higher degree of phase separation with the polyether. In all cases hydrogenation seems to increase the propensity for phase separation, as well as increasing the melting point and degree of crystallinity

The binding of one's graduate research into a dissertation is by no means an indication that the study is complete. The work described herein serves to open the door to ADMET segmented copolymers as well as to an array of different, tailored architectures. The number of diene monomers available to ADMET polymerization makes ADMET segmented copolymerization an attractive means for the combination of different polymer backbones, and the combinations described herein serve as a mere sampling of the many other combinations that should be possible. Further, the  $\alpha,\omega$ -dienyl telechelomers for ADMET polymerization are not limited to those used for this study or mentioned in Chapter 1. Theoretically any living or well-controlled polymerization that can be diinitiated and selectively terminated with an appropriate capping agent bearing the olefin functionality can be used to yield new  $\alpha,\omega$ -dienyl telechelomers. As mentioned earlier, providing the guidelines on the sterics and functionality about the metathesizing double bond are met, there is no reason to suspect that any new diene telechelomers would not likewise be reactive toward ADMET chemistry. With the synthesis of new  $\alpha,\omega$ -dienyl telechelomers and their combination with the different small molecule diene monomers, ADMET could provide an almost endless array of segment combinations, many of which may not be possible by other standard polymerization methods.

This study was designed to expand the scope of ADMET segmented copolymers, with a focus on the synthesis of some new segmented materials. The morphology of these copolymers was studied by DSC to provide information about phase separation in

the materials, given the combinations and proportions used. However, the observation of thermal transitions can only provide a preliminary indication of phase separation and morphology. Electron microscopy (TEM or SEM) or surface analysis (AFM) of these systems would be necessary to verify and elaborate on the speculated microphase morphology of these systems. Electron microscopy gives information on the degree of phase separation and the size and shape of the domains, which, as described in Chapter 1, can be quite complex and be dependant on many variables. ADMET generates unsaturated polymers, and for segmented copolymers, the segments arising from the smaller diene monomer will contain a higher density of these unsaturated sites than the segments arising from the pre-formed telechelomer. Therefore, even for hydrocarbon copolymers such as the PIB/polyoctenamer copolymers described Chapter 3, ADMET segmented copolymers should lend themselves nicely to segment-selective staining with  $\text{OsO}_4$  or  $\text{RuO}_4$ . Furthermore, the segmented copolymers containing ester, carbonate, and urethane segments provide additional staining sites at the carbonyl functionality.

As mentioned in Chapter 1, the morphology of block copolymers is influenced by the relative volumes of the two component blocks and also the lengths of these blocks. The study described in Chapter 3 with the decadiene-polyisobutylene gave a preliminary indication of the effect of soft and hard phase proportion and length of soft phase. These copolymers were sticky, viscous materials with the higher amount of polyisobutylene becoming more solid upon increasing the amount of decadiene comonomer. The ratio of telechelomer to comonomer was chosen at 1:1 wt:wt for the other copolymers of this study, but other proportions are equally accessible. As mentioned in Chapter 1,

ADMET has the advantage of not requiring a certain stoichiometry of telechelomer to comonomer since both bear the same reacting olefin functionality. Further, the procedures described for the synthesis of the polyisobutylene and poly(tetramethylene oxide) telechelomers can be easily adapted to provide oligomers with a range of different lengths in addition to the molecular weights chosen for this study.

Finally, there is a materials element to these ADMET segmented copolymers that, although beyond the scope of this study, is nonetheless just as interesting and significant. As mentioned in Chapter 1, segmented copolymers have the potential to serve many applications as specialty materials. Provided a large enough molecular weight can be achieved, ADMET segmented copolymers could potentially serve any of the applications mentioned in Chapter 1. For example, on a qualitative level, the copolymerization of **PIB1** with decadiene in a 1:4 ratio gave a somewhat stretchy material. Dynamic mechanical analysis could be employed to *quantitatively* reveal the effect of segment identity, length, and proportion on the rheological properties of these segmented copolymers. This would be particularly interesting for the combinations of segments that are not available by other synthetic methods.

Thus this study has opened the door to a new facet of designed ADMET polymers. With a virtually endless array of potential segment combinations from both known and yet to be discovered telechelomers and diene comonomers, the area of ADMET segmented copolymers should provide ample opportunity in further researching both the synthetic as well as the materials aspects of these polymers.

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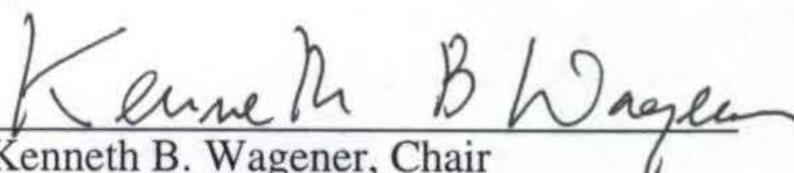
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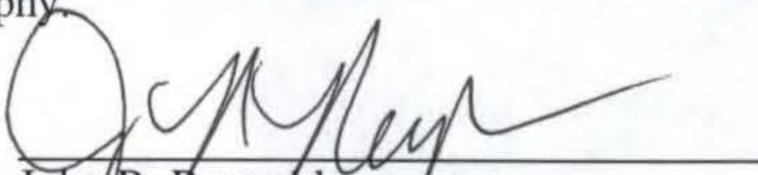
## BIOGRAPHICAL SKETCH

Debra Tindall was born on April 12, 1972, in Kingsport, Tennessee, the daughter of Bill and Judy Tindall. She grew up in Kingsport with her parents and older sister, Cindy. Debra graduated from Sullivan South High School in the top ten of her class, then went on to Furman University in Greenville, South Carolina. At Furman, Debra pursued a degree in chemistry while continuing to indulge her artistic and athletic interests. She took numerous classes in the art department and was invited to participate in the Senior Art Show. Debra was also active on the fencing and rowing teams as well as the chemistry softball team. During her college summers, Debra conducted research at Eastman Chemical Company, the University of Minnesota, and Brown University as part of NSF-REU programs. Debra graduated from Furman *summa cum laude* with a Bachelor of Science degree in chemistry in May 1994. She then began graduate school at the University of Florida under the guidance of Professor Kenneth B. Wagener where she studied organic/polymer chemistry. After five long years of studying, research, and an occasional road race or art class, Debra received her Ph.D. in May 1999. Coming full circle, she returned to Kingsport, Tennessee with her two cats, Chessie and Katie, to start work in the Cellulose Esters group at Eastman Chemical Company.

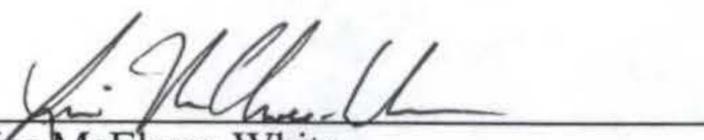
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Kenneth B. Wagener, Chair  
Professor of Chemistry

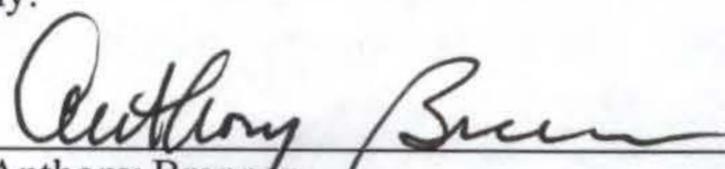
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John R. Reynolds  
Professor of Chemistry

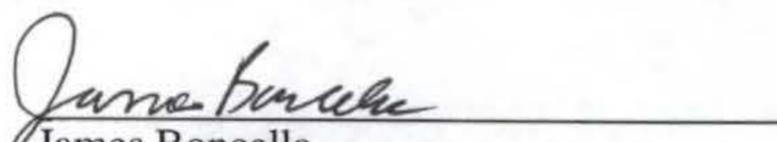
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Anthony Brennan  
Associate Professor of Materials Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

  
James Boncella  
Associate Professor of Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences, and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1999

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Dean, Graduate School

