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Acyclic Diene Metathesis (ADMET) Segmented Copolymers

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ABSTRACT: A series of segmented copolymers was synthesized via acyclic diene metathesis (ADMET) chemistry by copolymerizing either an aliphatic carbonate hard segment diene or an aromatic ester hard segment diene with a telechelic oligomer soft segment diene of either poly(tetramethylene oxide) or polyisobutylene. The thermal behavior of these copolymers was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The data show that these unsaturated copolymers are semicrystalline, thermally stable materials which exhibit phase separation between the hard and soft phases. The carbonate copolymers were hydrogenated to yield saturated counterparts which display an increase in melting temperature when compared with their unsaturated analogues while maintaining approximately the same glass transition temperature. In some cases hydrogenation also led to the appearance of two melting endotherms.

Introduction

Segmented copolymers are an important class of block copolymers that combine the properties of two different homopolymers. Segmented polymers can range in properties from toughened thermoplastics to thermoplastic elastomers depending on the nature of the hard and soft segments found in the polymer backbone and their relative weight percent.

Segmented copolymers are a type of copolymer architecture synthesized from the *step-growth* copolymerization either of two different end-reactive oligomers or by the combination of an oligomer with a comonomer or monomers such that the second segment backbone is grown as the polymerization proceeds. The result is a copolymer chain containing several short blocks (segments) of the two component homopolymer backbones. Chemistry of this nature cannot be accomplished using chain polymerization techniques, for not only is it impractical to grow such short blocks (hard and soft segments) via a chain procedure, doing so would demand highly precise and repetitive living polymerization monomer additions.

Acyclic diene metathesis (ADMET) is potentially useful in this sort of chemistry. It operates by an equilibrium step-growth polymerization mechanism that produces high polymer via the condensation of monomers bearing terminal olefin functionality. ADMET chemistry has been used to polymerize a variety of functional and hydrocarbon α,ω-diene monomers provided certain monomer structure/reactivity guidelines are met.[1−4] Keeping these structure/reactivity guidelines in mind, ADMET polymerization and copolymerization of several oligomeric α,ω-dienes has been realized.[5−8] To date, α,ω-diene oligomers with poly(tetramethylene) oxide,[6,7] polyisobutylene,[8,9] and polysiloxane[10] backbones have been successfully utilized in ADMET chemistry to build a variety of segmented copolymer structures.

Neither the carbonate functionality nor the ester functionality is new to the segmented copolymer field or to metathesis chemistry. Hydroxyl-capped aliphatic polycarbonates or polyesters have been used as the soft segment in polyurethane segmented copolymers, and several other combinations including polyester−polycarbonate segmented copolymers are known.[11,12] Segmented polyether−ester copolymers, such as Du Pont's Hytrel, have been commercially known since the early 1970s. Polyisobutylene−polyester block copolymers[13−16] and polycarbonate−polyisobutylene block copolymers [17] have also been reported.

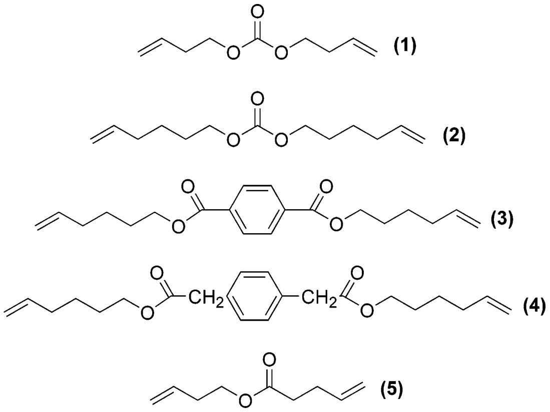

Figure 1. Carbonate diene comonomers bis(3-butenyl) carbonate (**1**) and bis(5-hexenyl) carbonate (**2**) and ester diene comonomers bis(3-hexenyl) terephthalate (**3**), bis(1-hexenyl)-phenylenediacetate (**4**), and 3-butenyl 4-pentenoate (**5**).

The acyclic diene metathesis polymerization of dienes bearing both carbonate as well as ester functionality have been described previously. Patton demonstrated that a bisphenol A based diene carbonate as well as aliphatic carbonate dienes with two to four methylene spacers between the carbonate functionality and the reacting olefin are amenable to ADMET polymerization.[18] Patton also used ADMET chemistry to polymerize ester-functionalized dienes.[19]

Herein we describe the synthesis of a series of segmented copolymers from the ADMET copolymerization of a diene comonomer bearing either ester or carbonate functionality (Figure 1) along with an α,ω-diene telechelic oligomer, either poly(tetramethylene oxide) (Figure 2) or polyisobutylene (Figure 3), to create a variety of segmented copolymer combinations. The resulting segmented copolymers were studied by ther-

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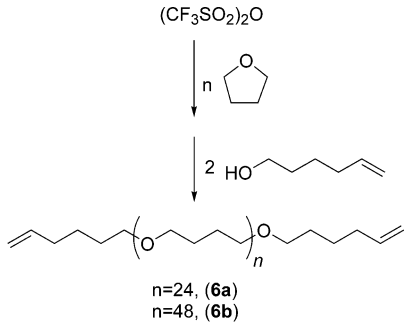

Figure 2. Synthesis of poly(tetramethylene oxide) telechelic oligomer dienes **6a** and **6b**.

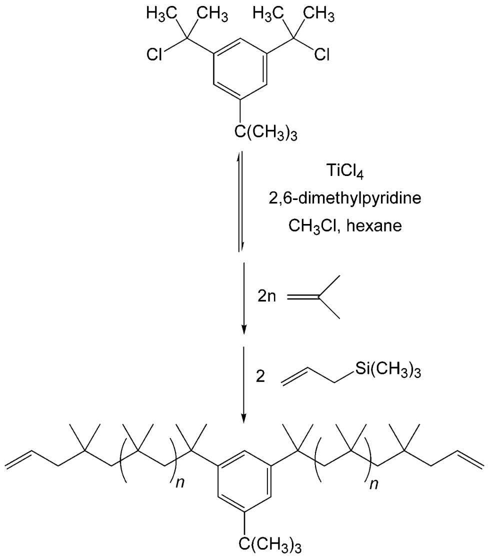

Figure 3. Synthesis of polyisobutylene telechelic oligomer dienes **7a** and **7b**.

mogravimetric analysis to measure their thermal stability and by differential scanning calorimetry both to examine the crystalline nature of these materials and to provide an indication of the degree of phase separation of the component segments.[6]

Results and Discussion

Monomers and Telechelic Oligomer Dienes. Five diene monomers bearing carbonate or ester functionality were synthesized as the hard segment monomers for this study (Figure 1). The monomers bis(3-butenyl) carbonate (**1**) and bis(5-hexenyl) carbonate (**2**) were chosen for the synthesis of the polycarbonate hard segments, monomers which were synthesized by a modification of published synthesis procedures.[18] Dimethyl carbonate was condensed with either 3-buten-1-ol or 5-hexen-1-ol in the presence of sodium metal to make **1** or **2**, respectively. The ester functional monomers were synthesized via standard esterification methods. The bis(5-hexenyl) terephthalate (**3**) was synthesized according to the literature procedure by the reaction of terephthaloyl chloride with 5-hexen-1-ol,[19] while the bis(5-hexenyl) phenylene diacetate (**4**) was synthesized from the condensation of 1,4-phenylenediacetic acid with 5-hexen-1-ol. The 3-butenyl 4-pentenoate (**5**) was kindly provided by M. Watson in our laboratory.

Telechelic oligomeric dienes both of poly(tetramethylene oxide), with $M_n = 1800$ (**6a**) and 3600 (**6b**), and polyisobutylene, with $M_n = 1700$ (**7a**) and 3100 (**7b**) were synthesized for use as soft segments in these copolymers. Poly(tetramethylene oxide) telecehlic oligomer dienes were synthesized by cationic ring-opening polymerization of tetrahydrofuran initiated by triflic anhydride, in a modification of the method described by Smith and Hubin.[20] The growing poly(tetramethylene oxide) was capped with 5-hexen-1-ol to obtain the terminal olefin end groups (Figure 2). Isobutylene polymerization was performed in the Storey Research Laboratory using a dicumyl dichloride diiniator and $TiCl_4$/lutidine system developed by Storey and coworkers.[21−24] Diene end group functionalization of the polyisobutylene oligomer was achieved by capping with allyltrimethylsilane (Figure 3). Molecular weight data for the telechelic oligomer dienes is summarized in Table 1.

Table 1. Molecular Weight of Parent Telechelic Oligomers

telechelomer oligomeric diene	type[a]	DP	M_n (NMR)	M_n (GPC) (vs PS stds.)[d]	M_w/M_n	functionality
6a	THF	25	1800[b]	3900	1.11	1.95
6b	THF	46	3600[b]	7400	1.07	1.95
7a	IB	24	1700[c]	1800	1.15	1.94
7b	IB	50	3100[c]	3200	1.12	1.95

[a] THF designates poly(tetramethylene oxide) backbone; IB designates poly(isobutylene) backbone. [b] Integration of OCH_2 to olefin end groups. [c] Integration of aromatic H to olefin end groups. [d] Determined by GPC relative to polystyrene standards.

Table 2. Segment Combinations of Diene Monomers and Telechelic Oligomer Dienes Made and Studied in This Work

		hard segment	soft segment telechelomer oligomeric diene		
	monomer	6a	6b	7a	7b
1	bis(5-butenyl) carbonate	8	9	12	13
2	bis(5-hexenyl) carbonate	10	11	14	15
3	bis(5-hexenyl) terephthalate	16		19	
4	bis(1-hexenyl) phenylene diacetate	17			
5	4-butenyl pentenoate	18			

ADMET Copolymerizations. The various combinations of comonomers and telechelic oligomer dienes described in this work are summarized in Table 2. All the combinations of hard segment comonomers and soft segment telechelic oligomer dienes led to ADMET polymer chemistry under mild reaction conditions. This result is surprising in that the possible incompatibility of such monomers and oligomeric dienes might suggest heterogeneous polymerization conditions. Nonetheless, these polymerizations proceeded smoothly with the rapid release of ethylene, typical of ADMET polycondensation. The diene oligomers, either poly(tetramethylene oxide) (**6**) or polyisobutylene (**7**), were copolymerized in a 1:1 w/w ratio with either **1** or **2** to give a total of eight different carbonate-based segmented copolymers, **8**−**15**. For the ester-based segmented copolymers, poly(tetramethylene oxide) telechelic oligomer diene (**6a**) was copolymerized in a 1:1 w/w ratio with comonomers **3**, **4**, and **5**, and polyisobutylene telechelic oligomer diene (**7a**) was copolymerized in a 1:1 w/w ratio with comonomer **3** to give a total of four different ester-containing segmented copolymers, **16**−**19**. The ADMET reactions for these copolymerizations are shown in Figures 4 and 5.

Copolymerizations were performed on a 0.6−1.4 g scale using the Grubbs first-generation ruthenium benzylidene metathesis catalyst.[25,26] The carbonate-

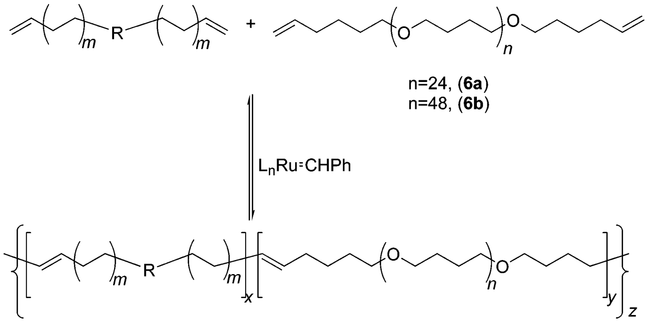

Figure 4. ADMET copolymerization of α,ω-dienyl poly(tetramethylene oxide) (**6**) with a functionalized diene monomer to synthesize segmented copolymers. R = generic representation of carbonate or ester functional group within monomer.

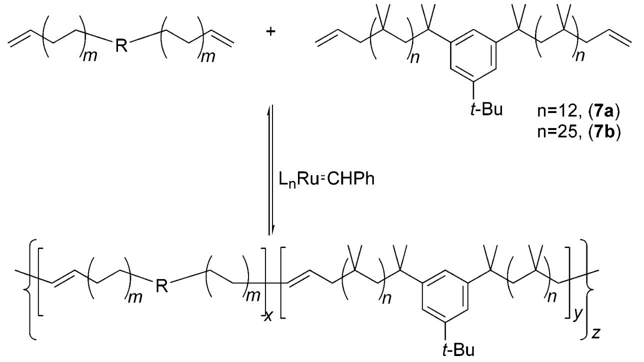

Figure 5. ADMET copolymerization of α,ω-dienyl poly(isobutylene) (**7**) with a functionalized diene monomer to synthesize segmented copolymers. R = generic representation of carbonate or ester functional group within monomer.

containing copolymers were all soft white solids. The terephthalate–poly(tetramethylene oxide) copolymer (comprised of **3** + **6a**) was a soft white solid, while the phenylene diacetate–poly(tetramethylene oxide) copolymer (comprised of **4** + **6a**) was a soft, tacky material, and the butenyl pentenoate–poly(tetramethylene oxide) copolymer (comprised of **5** + **6a**) was a sticky viscous liquid. The copolymerization of polyisobutylene telechelic oligomer diene (**7a**) with bis(5-hexenyl) terephthalate (**3**) gave a soft waxy solid. For the samples that were not to be hydrogenated, the crude ADMET reaction product was dissolved in chloroform and exposed to 50/50 silica gel/alumina to aid in removal of the catalyst.

Hydrogenation. The carbonate-containing copolymers were hydrogenated using the tandem ADMET–hydrogenation method described by Watson et al.[27,28] This procedure is especially convenient in that the homogeneous first-generation Grubbs catalyst first induces ADMET polymerization, after which it is converted to a heterogeneous hydrogenation catalyst via the addition of silica gel. The remnants of the Ru metathesis catalyst that adhere to silica are highly active for hydrogenation; further, the catalyst/silica can be easily filtered. Thus, after ADMET polymerization is complete, 0.3 g of crude reaction product was dissolved in toluene along with 0.25 g of silica gel and exposed to 120 psi hydrogen at 90 °C for 48 h to give **8H** to **15H**. The silica gel was then filtered off and the toluene evaporated to yield the hydrogenated copolymer.

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

Table 3. Summary of Molecular Weight Data for Segmented Copolymers[a]

copolymer	hard segment–soft segment combination	M_n (g/mol)	M_w (g/ mol)	M_w/M_n
	carbonate copolymers			
8	**6a** + **1**	7 000	13 100	1.88
9	**6b** + **1**	6 000	10 000	1.75
10	**6a** + **2**	9 600	15 200	1.59
11	**6b** + **2**	10 500	21 800	2.07
12	**7a** + **1**	4 000	7 300	1.83
13	**7b** + **1**	5 100	15 400	3.02
14	**7a** + **2**	5 700	10 600	1.9
15	**7b** + **2**	10 000	22 000	2.07
	ester copolymers			
16	**6a** + **3**	15 000	29 000	2.0
17	**6a** + **4**	23 000	39 000	1.7
18	**6a** + **5**	24 000	32 000	1.4
19	**7a** + **3**	14 300	22 900	1.7

[a] Determined by GPC relative to polystyrene standards.

Molecular weight data is summarized in Table 3 and indicates molecular weights (M_n) in the range of 5000–24000 vs polystyrene standards, with polydispersities (M_w/M_n) close to the ideal 2.0 for equilibrium step-growth polymerization.

Integration of the terminal olefin end groups by ^{1}H NMR indicated that the ADMET polymerization is less complete for the copolymerizations involving polyisobutylene telechelic oligomers than for the polyether telechelic oligomer diene when exposed to similar reaction conditions and time. One explanation of this reactivity difference is the greater steric bulk imparted by the gem-dimethyl near the reacting olefin of the polyisobutylene telechelic oligomer. It was also found that the copolymerizations involving bis(3-butenyl) carbonate (**1**) were much slower than those with bis(5-hexenyl) carbonate (**2**). Polymerizations with **1** showed incomplete conversion even after several days of exposure to catalyst and vacuum. Homopolymerization of the carbonate diene monomers, **1** and **2**, confirmed that the butenyl carbonate monomer is less reactive than hexenyl carbonate to ADMET polymerization. Apparently the close proximity of the carbonate functional group drives the dynamic catalyst complex equilibrium further toward the intramolecular complex, thereby slowing the kinetics of ADMET polymerization. This effect of functional group–olefin proximity on ADMET monomer reactivity has been described previously.[4]

Thermal Analysis of the Carbonate Segmented Copolymers. Thermal gravimetric analysis of the segmented carbonate- and ester-containing copolymers is summarized in Table 4; weight loss was monitored as the polymers were heated from 40 to 700 °C under a nitrogen atmosphere. The polyisobutylene copolymers appear to be slightly more thermally stable, with carbonate copolymers showing 50% weight loss in the range of 369–414 °C and ester copolymers showing 50% weight loss in the range of 385–421 °C. No significant effect on thermal stability was observed between the two lengths of either the polyisobutylene or polyether oligomer used in this study. All of the copolymers synthesized in this work display sufficient thermal stability to make them potentially useful materials.

Differential scanning calorimetry was employed both to examine the crystalline nature of these new segmented copolymers and to provide an estimate of the degree of hard segment/soft segment phase separation within them, since the presence of distinct thermal

Table 4. Thermogravimetric Analysis of Segmented Copolymers[a]

copolymer type	parent monomer−telechelomer combination	onset (°C)	50% weight loss (°C)	90% weight loss (°C)
	carbonate			
8	**6a** + **1**	320	369	413
9	**6b** + **1**	294	398	430
10	**6a** + **2**	381	414	441
11	**6b** + **2**	384	409	438
12	**7a** + **1**	365	409	435
13	**7b** + **1**	355	405	432
14	**7a** + **2**	368	410	438
15	**7b** + **2**	366	414	440
	ester			
16	**6a** + **3**	397	421	451
17	**6a** + **4**	394	418	454
18	**6a** + **5**	345	385	415
19	**7a** + **3**	378	409	433

[a] Scanning rate 20 °C/min.

Table 5. Differential Scanning Calorimetry Thermal Transitions for Parent Ether, Isobutylene, Carbonate, and Ester Soft Segment and Hard Segment Homopolymers[a]

homopolymer	T_g (°C)	T_m (°C)	Δ*H* (J/g)
homopolymer of telechelic oligomeric diene **6a** or **6b**	−93	25	
homopolymer of telechelic oligomeric diene **7a** or **7b**	−70		
homopolymer of hard segment monomer **1**	(−58)[b]	42	47.2
homopolymer of hard segment monomer **2**	(−62)[b]	77	46.2
homopolymer of hard segment monomer **3**		110	
homopolymer of hard segment monomer **4**		35	
hompolymer of hard segment monomer **5**	−15	−9	

[a] Scanning rate 20 °C/min. Data collected on second heating cycle. [b] Weak transition.

transitions corresponding to each parent homopolymer can be an indication of phase separation present in the copolymer material. For example, the polyether soft segments are expected to display a T_g at −90 °C as well as a melting endotherm around 25 °C on the second heating scan, while the polyisobutylene soft segments are expected to have a glass transition temperature of −70 °C with no T_m. These thermal transitions are evident in the homopolymers of each of the soft phases; data for these isobutylene, ester, and ether homopolymers are summarized in Table 5. This table displays the thermal data for the hard segment homopolymers as well.

By comparison, thermal data were obtained for two of the unsaturated copolymers employing the hexenyl carbonate segment as well as for all four of the ester-containing copolymers. The observed thermal data for the carbonate- and ester-containing copolymers is summarized in Tables 6 and 7, respectively.

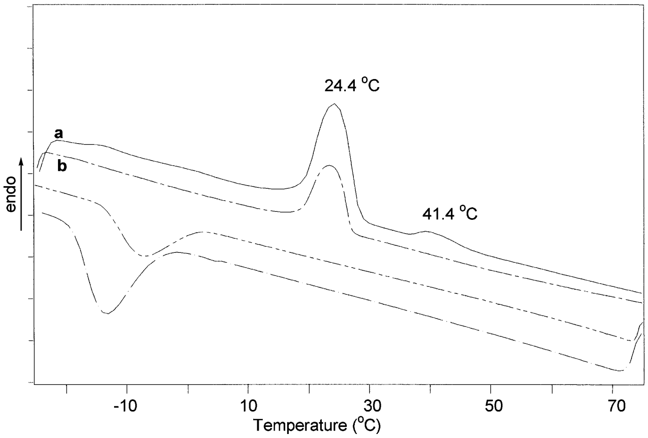

Figure 6. DSC thermogram of polyether−polycarbonate segmented copolymer **9** (comprised of **6b** + **1**). First (a) and second (b) heating scan, 20 °C/min.

First, it is important to note that virtually all of these segmented ADMET copolymers crystallize, one with a melting endotherm as high as 111 °C. Three unsaturated carbonate segmented copolymers fail to crystallize, possibly due to a slower rate of crystallization. Each of the polymers display similar behavior, however, often exhibiting a T_g for the soft phase and one or melting endotherms for the hard phase. The DSC thermogram for carbonate segmented copolymer **9**, comprised of poly(tetramethylene oxide) (**6b**) and bis(butenyl) carbonate (**1**), is shown in Figure 6. On the first scan of a sample of copolymer **9** that has stood at room temperature for several days, a small peak is observed at 41 °C, which corresponds to the polycarbonate hard segment. In subsequent scans, this higher melting peak disappears and only the dominant peak around 24 °C is observed. These results indicate that while phase separation is not evident on the time scale of the DSC scanning, the segments of copolymer **9** do have the potential to phase separate under the appropriate annealing conditions.

The polyether−carbonate segmented copolymer **11**, comprised of poly(tetramethylene oxide) (**6b**) and bis(hexenyl carbonate) (**2**), also shows a significant T_m at 23 °C; a very weak peak at 19 °C is present only on the first scan. The dominant T_m is slightly depressed from the expected melting point for the polyether homopolymer, and also the T_g observed at −75 °C is elevated from the T_g of the **6b** homopolymer; both observations suggest some degree of mixing between the soft and hard polyether−carbonate phases, which is typical for many segmented copolymer systems.

The polyisobutylene−carbonate segmented copolymer **15** (comprised of telechelic oligomer **7b** and comonomer

Table 6. Differential Scanning Calorimetry Analysis of Carbonate Segmented copolymers, before and after hydrogenation[a]

	unsaturated carbonate segmented copolymer			carbonate segmented copolymer after hydrogenation				
copolymers	T_g	T_m	Δ*H* (J/g)	H_2 T_g	H_2 T_{m1}	Δ*H* (J/g)	H_2 T_{m2}	Δ*H* (J/g)
8 (**6a** + **1**)	−65	23	62.4	−77	22	81.8	34[d]	
9 (**6b** + **1**)	−65	24, (41.4)[c]	38.7	−74	24	68.1	45[d]	15.9
10 (**6a** + **2**)	−70	14	42.0	−74	15	52.1	36	31.8
11 (**6b** + **2**)	−76	(19),[b,c] 23[b]	51.1	−76	25	55.4	46	36.8
12 (**7a** + **1**)	−66			−64	(7)[c]	12.0	50	33.1
13 (**7b** + **1**)	−65			−74			46	19.1
14 (**7a** + **2**)	−65			−66			48	35
15 (**7b** + **2**)	−66	(14),[c] 38	3.9	−65			48	25.9

[a] Data obtained on second heating scan at 20 °C/min. [b] These T_m's for copolymer **11** were barely observable. [c] Only observed on first heating scan. [d] Very weak transition appearing as a shoulder on primary melting peak.

Table 7. Differential Scanning Calorimetry Analysis of Ester Segmented Copolymers[a]

unsaturated ester segmented copolymer	T_g (°C)	T_m 1 (°C)	T_m 2 (°C)	ΔH (J/g)
16 (**6a** + **3**)	−78		88[b]	9.6
17 (**6a** + **4**)	−64	24		4.5
18 (**6a** + **5**)	−93[c]	15		43
19 (**7a** + **3**)	−73		111	31.1

[a] Data obtained on second heating scan at 20 °C/min. [b] Additionally, small peaks at 20 (0.8 J/g) and 78 °C (1.0 J/g) were also observed when scanned at 10 °C/min. [c] Very weak T_g transition.

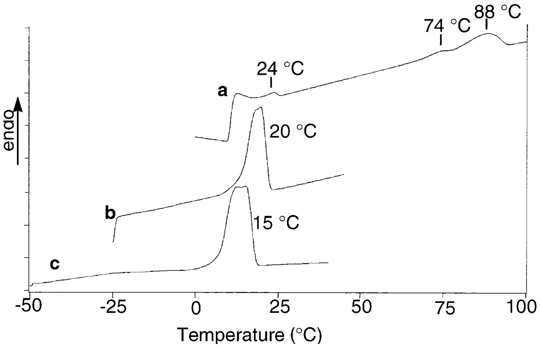

Figure 7. DSC thermograms of the polyether−ester segmented copolymers: (a) copolymer **16** (comprised of **6a** + **3**); (b) copolymer **17** (comprised of **6a** + **4**); (c) copolymer **18** (comprised of **6a** + **5**) (heating rate 10 °C/min).

2) shows thermal behavior consistent with a greater degree of phase separation. The glass transition temperature appears at −65 °C, which is only slightly higher than expected for pure polyisobutylene homopolymer, and the melting peak observed at 38 °C is only slightly lower than the expected 40 °C for pure poly(bis(hexenyl) carbonate) segments. This is a well phase-separated material. Combination with the less polar polyisobutylene segments facilitates phase separation of the carbonate segments, allowing the unsaturated carbonate segments to recrystallize more easily. As with the carbonate−ether segmented copolymer **11**, a first scan weak melting endotherm is observed at 14 °C for copolymer **15**. It is difficult to determine whether these two peaks correlate to a similar melt-depressed mixed poly(bis(hexenyl) carbonate) phase.

The polyether/polyester segmented ADMET copolymers appear to phase segregate less well, giving conflicting results. DSC thermograms for the polyether/polyester segmented copolymers heated either at 20 or 10 °C/min are displayed in Figure 7. The poly(ether−terephthalate) copolymer (**16**) shows a melting endotherm for the **6a** soft polyether segment at 24 °C, virtually identical to the melting point for its homopolyether equivalent; thus, the soft phase can be regarded as relatively pure. However, the polyester hard segment shows a broad melt at 88 °C rather than the single sharp melting point at 110 °C that would correspond to a well phase-separated polyester segment. This observation is likely a manifestation of phase mixing in the hard segment. It is important to note that phase mixing in one segment only is viable and known in other systems, so this result is not completely surprising. What is unusual, however, is the thermal response on subsequent heating cycles. On the second heating scan (scan a), while the T_m for the polyether is hardly visible (but still at 24 °C), the hard segment melting peak splits into two endotherm peaks at 88 and 74 °C. Further, these two endotherms remain during subsequent heating scans. The soft phase glass transition temperature for this copolymer (not shown in Figure 7) is observed at−78 °C when heated at 20 °C/min from a quenched melt. This value is slightly higher than the expected −90 °C T_g for the polyether homopolymer. These results suggest that *the semicrystalline and amorphous regions of the soft polyether phases have different levels of purity.* The crystalline region of the polyether segment is relatively pure (T_m of 24 °C as noted above), while the amorphous region of the soft segment is mixed. Another way to view the morphology is to state that three phases exist in the bulk material, including an ester-rich phase (T_m = 88 °C), an ether-rich phase (T_m = 24 °C), and a mixed interfacial phase with an intermediate melting point.

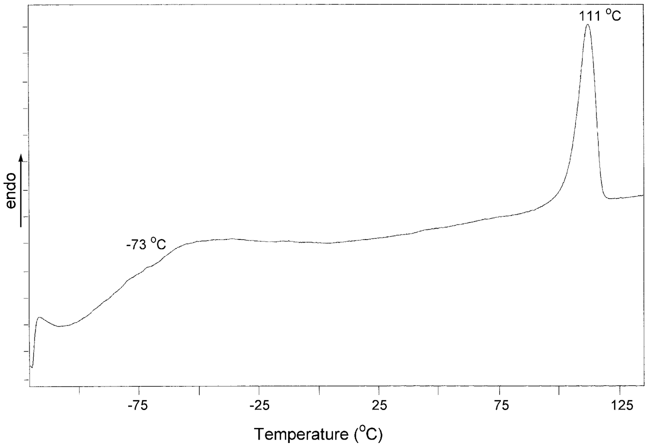

Figure 8. DSC thermogram of the polyisobutylene−ester segmented copolymer copolymer **19** (comprised of **7a** + **3**) (heating rate 20 °C/min).

The ester−ether segmented copolymer **17** (combining **6a** with **4**) shows a single melting endotherm at 20 °C, which is suppressed from the expected T_m of either parent homopolymer (Figure 7, scan b). This indicates significant melting point depression resulting from mixing of the ester and ether segments. The ester−ether copolymer **18** also shows a broad melting endotherm at 15 °C, which is intermediate to the melting points of the parent segments (Figure 7, scan c). Apparently these segmented copolymers are phase mixed but not to the point of eliminating hard segment crystallization completely.

Figure 8 shows the polyisobutylene segmented polyester copolymer equivalent (when compared with Figure 7, scan a) to be much better phase separated. Both possess the bis(hexenyl) terephalate hard segment; note the high T_m for this segment in the isobutylene copolymer at 111 °C and the distinct T_g at −73 °C. Both phases are relatively pure and well phase separated in this material, an observation which is consistent with the expected decrease in compatibility of ester-based segments with the nonpolar polyisobutylene backbone vs the more polar polyether backbone.

Thermal Analysis of Hydrogenated Carbonate-Containing Segmented Copolymers. Further thermal analysis was performed on the hydrogenated analogues of the carbonate segmented copolymers. Qualitatively, the hydrogenated polymers all were less soft in nature than their unsaturated analogues at room temperature, likely the result of transforming the double bonds along the polymer backbone to more regular and compact methylene units. This “firming” effect is also observed more quantitatively by noting the changes in

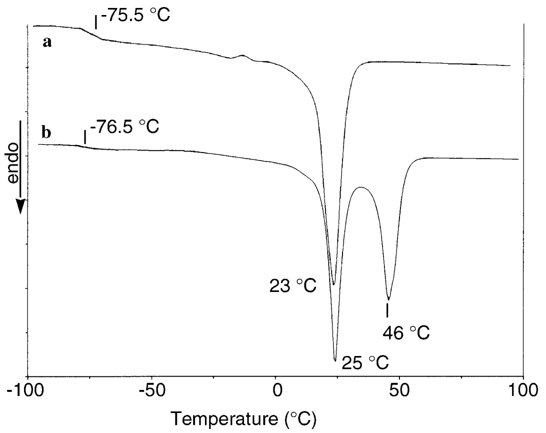

Figure 9. DSC thermogram of polycarbonate–polyether segmented copolymer **11** (comprised of **6b** + **2**) (a) before hydrogenation and (b) after hydrogenation, showing the effect of hydrogenation on melting point of carbonate segments (second scan, 20 °C/min)

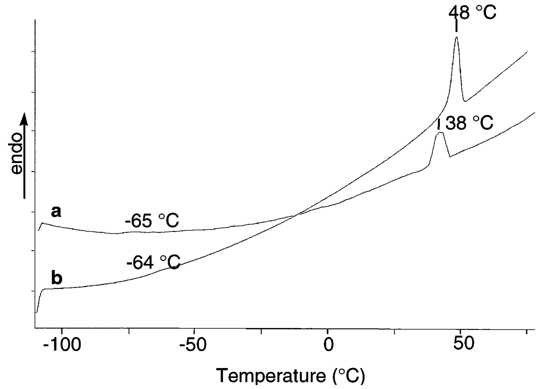

Figure 10. DSC thermogram of polycarbonate–polyisobutylene segmented copolymer **15** (comprised of **7b** + **2**) (a) before hydrogenation and (b) after hydrogenation, showing the effect of hydrogenation on melting point of carbonate segments (second scan, 20 °C/min).

melting point. All but one copolymer displayed melting points that correlate to hydrogenated carbonate homopolymer, in addition to the expected transitions of the parent telechelic oligomer dienes.

The effect of hydrogenation is illustrated by the DSC curves for the carbonate-containing segmented copolymers **11** and **15**, for which thermal data was collected for both the unsaturated and the hydrogenated copolymers. In the case of polycarbonate/polyether copolymer **11** (Figure 9), hydrogenation leaves the glass temperature for the soft segment oligomer essentially unchanged; a T_g from −73 to −76 °C suggests the soft phase is pure for both the unsaturated and hydrogenated versions, since that is the T_g for the pure polyether homopolymer. Note that no melting endotherm is visible for the unsaturated polycarbonate hard segment (scan a, Figure 9). Hydrogenation of copolymer **11** changes this situation significantly. The saturated carbonate segment readily crystallizes (scan b, Figure 9), and the heating scan now shows two melting transitions, one at 25 °C (characteristic of the polyether soft segment T_m) and the other at 46 °C (for the saturated carbonate hard segment). The hydrogenated version of copolymer **11** is a well phase separated system.

Enhanced phase separation is already evident in the unsaturated versions of the polycarbonate/polyisobutylene ADMET segmented copolymers. Note that the unsaturated polyisobutylene-based copolymer **15** displays a melting peak at 38 °C, consistent with a moderately phase-separated unsaturated carbonate segment (Figure 10). Phase separation of copolymer **15** further improves upon hydrogenation. Upon hydrogenation of **15**, the melting peak corresponding to the hydrogenated carbonate segments both increases to 48 °C and appears slightly sharper than in the unsaturated copolymer.

This T_m at 48 °C for the saturated polycarbonate segments in **15** corresponds nicely with the new melting transition at 46 °C observed for the hydrogenated polycarbonate segments in copolymer **11**.

Conclusions

Accessing segmented copolymer architectural arrays is indeed possible using equilibrium step polymerization metathesis polycondensation chemistry. Several segmented copolymers have been synthesized possessing polycarbonate or polyester hard segments in combination with polyisobutylene and polytetramethylene oxide soft segments; each of these segmented copolymers has been characterized in terms of primary structure. Thermogravimetric analysis of these materials shows them to possess adequate thermal stability; DSC analysis demonstrates the hard segment within most of them readily crystallizes. Phase separation between the hard and soft segments occurs, where the degree of phase separation appears to be a function both of segment miscibility (or lack thereof) and crystallization propensity of the hard segment. In addition, hydrogenation of the carbonate-based copolymers leads to increased phase separation of the component segments. The potential utility of this new class of segmented copolymers warrants further attention.

Experimental Section

Spectra for ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were obtained on a Varian Gemini-Series NMR superconducting spectrometer system. All NMR data were generated in $CDCl_3$ as the solvent, and peaks are listed in ppm downfield from tetramethylsilane. 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 a light scattering detector. Preparatory HPLC was performed on a Rainan Dynamax system equipped with Dynamax 60 Å silica preparative column and Dynamax spectophotometer 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 or 20 °C/min, as indicated. Both TGA and DSC were interfaced to a TAC7/DX thermal analysis controller. Some DSC were kindly run at Eastman Chemical Co. on a TA Instruments Universal V2.5D at 20 °C/min. For all DSC data, samples were heated above their melting point and cooled, and then data was collected for the second heating and cooling scan unless otherwise indicated.

The Grubbs first-generation catalyst $RuCl_2(P(C_6H_{11})_3)_2CHPh$ was prepared according to published procedures.[25] Diethyl ether, tetrahydrofuran, toluene, and pentane were distilled from sodium/potassium alloy. 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. Triflic anhydride was freshly distilled before use, and 5-hexen-1-ol and *n*-hexane were distilled from calcium hydride and stored over 4 Å molecular sieves. Titanium tetrachloride and anhydrous 2,6-dimethyl pyridine were used as received. Isobutylene and methyl chloride were dried by passage through a column packed with BaO and $CaCl_2$. The initiator, 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl) benzene, was prepared in three steps from 5-*tert*-butyl isophthalic acid, according to published procedures.[21] Isobutylene was polymerized by Chris Curry by the cationic inifer method described by Storey and co-workers at the University of Southern Mississippi and using the facilities and expertise of the Storey research group.[21,22] The terminal olefin functionality was introduced by quenching the polymerizations with 7 mol equiv of allyltrimethylsilane per chain end.[23]

Synthesis of Bis(3-butenyl) Carbonate (1). 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 was 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 cm^{-1}; ^1H NMR 2.44 (m, 4H), 4.18 (t, 4H), 5.12 (m, 4H), 5.8 (m, 2H); ^{13}C NMR 154.8, 133.1, 117.1, 66.5, 32.7.

Synthesis of Bis(5-hexenyl) Carbonate (2). 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 was 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%; IR (C═O) 1750 cm^{-1}; ^1H 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}C NMR 166.0, 138.2, 134.1, 129.1, 115.1, 65.5, 33.2, 27.8, 25.2.

Synthesis of 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. Bis(5-hexenyl) terephthalate (**3**) was prepared according to published procedures.[19] The 3-butenyl 4-pentenoate (**5**) was prepared by M. Watson from 3-buten-1-ol and 4-pentenoic acid.

Synthesis of Bis(5-hexenyl)phenylene Diacetate (4). Phenylene diacetate (3.0 g, 0.016 mol) was dissolved in 75 mL of 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 was collected into the Dean−Starke trap. The progress of the reaction was monitored by GC, and after 24 h 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 and then calcium hydride. Distillation followed by preparatory-scale HPLC yielded **4** as a colorless oil. Isolated yield 68%. Anal.Calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found C, 73.42; H, 8.68. IR (C═O) 1735 cm^{-1}; ^1H 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_2), 5.77 (m, 2H, ═CH), 7.24 (s, 4H, ArH); ^{13}C NMR 171.5, 138.3, 132.9, 129.4, 114.7, 64.8, 41.1, 33.2, 28.0, 25.1.

Synthesis of α,ω-Dienyl Poly(tetramethylene oxide) (M_n = 1800) (6a). Dry, degassed tetrahydrofuran (36.0 mL, 0.44 mol) was placed in a Schlenk flask and cooled to −13 °C with a benzonitrile slush bath. Triflic anhydride (1.0 mL, 5.9 × 10^{-3} mol) was added all at once by syringe. The reaction was maintained at −13 °C and stirred for 25 min, and then the polymerization was quenched by rapidly adding 5 mL (0.04 mol) of 5-hexen-1-ol. The reaction was allowed to warm to room temperature and stirred 12 h. Solvent was evaporated to reduce the volume by one-half, and 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 diethyl ether 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. Calcd for $C_{112}H_{222}O_{26}$: H, 11.27; C, 67.77. Found: H, 11.27; C, 67.31. Dp ≈ 25, M_n ≈ 1700 by ^1H NMR, mp = 25, 35 °C; ^1H NMR 1.42 (m, 4H), 1.60 (s, 98H, CH_2), 1.81 (m, 4H), 2.07 (q, 4H), 3.41 (s, 102H, 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).

Synthesis of α,ω-Dienyl Poly(tetramethylene oxide) (M_n = 3600) (6b). The synthesis of the larger molecular weight poly(tetramethylene oxide) oligomer is identical to that described above with the exception of reaction time. After adding the triflic anhydride (1.0 mL, 5.9 × 10^{-3} mol) to 36 mL of tetrahydrofuran at −13 °C, as above, the reaction was allowed to stir for 45 min before quenching with 5-hexen-1-ol. After three precipitations and drying under vacuum, the oligomer was obtained as a soft white powder. Anal. Calcd for $C_{204}H_{406}O_{49}$: C, 67.25; H, 11.23. Found: C, 66.54; H, 11.20. Dp ≈ 48, M_n ≈ 3600 by ^1H NMR, 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).

ADMET Copolymerizations. The Grubbs first-generation ruthenium catalyst was used for these polymerizations. ADMET copolymerizations of the telechelic oligomer diene with diene monomers were performed on a 0.4−0.7 g scale following the usual ADMET polymerization procedure, employing vacuum with stirring for 4−6 days.[26] Upon completion of the ADMET polymerizations, the product was dissolved in chloroform and filtered through a plug of 50/50 silica gel/alumina. For hydrogenations 0.3 g of the reaction product, still containing the Ru catalyst, was dissolved in toluene along with 0.25 g of silica gel. This mixture was then exposed to 120 psi hydrogen at 90 °C for 48 h.

Copolymerization of 1 with 6a To Make 8. The polymerization procedure described above was used to copolymerize 0.79 g (4.64 × 10^{-3} mol) of bis(3-butenyl) carbonate plus 0.79 g (4.16 × 10^{-4} mol) of ether telechelic oligomer diene, **6a,** using 0.01 g of ruthenium benzylidene. After stirring for 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); ^1H 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_2), 5.50 (br, 2.1H, ═CH), 5.60 (br m, 0.1H, end ═CH); ^{13}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 1 with 6b To Make 9. The polymerization procedure described above was used to copolymerize 0.46 g (2.70 × 10^{-3} mol) of bis(3-butenyl) carbonate plus 0.46 g (1.28 × 10^{-4} mol) of **6b** using 0.01 g of ruthenium benzylidene. After stirring for 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 though a plug of silica/alumina. IR (C═O) 1745 cm^{-1}; ^1H NMR ($CDCl_3$) 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_2), 5.5 (br, 2H, ═CH), 5.60 (br m, 0.1H, end ═CH); ^{13}C NMR ($CDCl_3$) 155.1, 128.1, 127.2, 70.6 (THF), 67.2, 66.9, 31.9, 26.9, 26.5 (THF).

Copolymerization of 2 with 6a To Make 10. The polymerization procedure described above was used to copolymerize 0.95 g (4.20 × 10^{-3} mol) of bis(5-hexenyl) carbonate plus 0.95 g (5.0 × 10^{-4} mol) of **6a**. After stirring for 7 days, one-half of the light yellow reaction mixture was dissolved in toluene and hydrogenated while the other half was dissolved in chloroform and filtered through a plug of alumina. Hydrogenation gave a soft, waxy solid. IR (C═O) 1745 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.41 (m, 4H), 1.59 (br s, 15H, (THF + C2), 1.98 (m, 4H), 3.37 (s, 11H, THF), 4.08 (t, 4H), 5.35 (br s, 2H); ^{13}C NMR (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 2 with 6b To Make 11. The polymerization procedure described above was used to copolymerize 0.54 g (2.39×10^{-3} mol) of bis(5-hexenyl) carbonate plus 0.54 g (1.50×10^{-4} mol) of **6b** using 0.01 g of ruthenium benzylidene. IR (C═O) 1747 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.40 (p, 4H), 1.60 (br s, 16H, THF), 1.98 (br m, 4H), 3.38 (12H, THF), 4.10 (t, 4H), 5.36 (br m, ═CH); ^{13}C NMR (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 1 with 7a To Make 12. The polymerization procedure described above was used to copolymerize bis(3-butenyl) carbonate (0.35 g, 2.39×10^{-4} mol) and **7a** (0.40 g, 2.06×10^{-4} mol) using 0.01 g of ruthenium benzylidene. After stirring for 18 days, the polymerization was terminated, though NMR showed end groups still remained. IR (C═O) 1747 cm^{-1}; ^{1}H NMR (CDCl$_3$) 0.79 (s), 1.00 (d), 1.10 (br s, 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 ═CH$_2$), 5.52 (br, 2H, ═CH), 5.83 (m, 2.1H, end ═CH), 7.17 (s, 3.1 H, ArH); ^{13}C NMR (CDCl$_3$): 148.9, 148.5, 136.1, 129.7, 127.9, 121.2, 120.1, 116.7, 59.7 (*C*Me$_2$), 59.1, 58.6, 55.7, 50.3, 38.9, 37.9 (CH$_2$), 35.4, 34.8, 32.3, 32.0, 31.6, 31.2 (CH$_3$), 30.9, 30.7, 29.1, 28.1, 25.6

Hydrogenated: ^{1}HNMR (CDCl$_3$) 0.79 (s), 1.00 (d), 1.10 (br s, CH$_3$), 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 1 with 7b To Make 13. The polymerization procedure described above was used to copolymerize bis(3-butenyl) carbonate (0.55 g, 3.23×10^{-3} mol) and **7b** (0.55 g, 1.77×10^{-4} mol) using 0.01 g of ruthenium benzylidene. After stirring for 18 days, the polymerization was terminated, though NMR showed end groups still remained. IR (C═O) 1745 cm^{-1}; ^{1}H NMR 0.79 (s), 1.00 (d), 1.10 (br s, CH$_3$), 1.31−1.37 (m), 1.41 (s, CH$_2$), 1.84 (s), 2.04 (d), 2.40 (m, 4H), 4.13 (t, 4H), 5.21 (m, H, end ═CH$_2$), 5.5 (br, 2H, ═CH), 5.60 (br m, 0.1H, end ═CH), 7.17 (s, Ar); ^{13}C NMR 155.1, 149.0, 148.5, 136.1, 121.2, 120.1, 116.7, 59.5 (*C*Me$_2$), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1, 37.8 (CH$_2$), 35.4, 32.3, 31.6, 31.2 (CH$_3$), 31.0, 30.7, 29.1, 25.6.

Copolymerization of 2 with 7a To Make 14. The polymerization procedure described above was used to copolymerize 0.48 g (2.12×10^{-4} mol) of bis(5-hexenyl) carbonate plus 0.48 g (2.87×10^{-4} mol) of **7a** using 0.01 g of ruthenium benzylidene. After stirring for 11 days, the reaction was terminated. IR (C═O) 1745 cm^{-1}; ^{1}HNMR (CDCl$_3$) 0.79 (s), 0.98 (m), 1.10 (s, CH$_3$), 1.31−1.37 (m), 1.41 (s, 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}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 (*C*Me$_2$), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1, 37.8 (CH$_2$), 35.4, 32.3, 31.6, 31.2 (CH$_3$), 31.0, 30.7, 29.1, 25.6.

Copolymerization of 2 with 7b To Make 15. The polymerization procedure described above was used to copolymerize 0.30 g (9.65×10^{-5} mol) of poly(isobutylene) **7b** plus 0.30 g (1.33×10^{-3} mol) of bis(5-hexenyl) carbonate using 0.01 g of ruthenium benzylidene. After stirring for 16 days, the reaction was terminated by hydrogenation and workup. IR (C═O) 1745 cm^{-1}; ^{1}HNMR (CDCl$_3$) 0.79 (s), 0.99 (m), 1.00 (s), 1.10 (br s, CH$_3$), 1.31−1.37 (m), 1.41 (br s, 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}C NMR (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 (*C*Me$_2$), 59.0, 58.6, 55.8, 50.3, 39.0, 38.1, 37.8 (CH$_2$), 35.4, 32.3, 31.6, 31.2 (CH$_3$), 31.0, 30.7, 29.1, 25.6.

Copolymerization of 3 with 6a To Make 16. The terephthalate monomer **3** (0.72 g, 2.18×10^{-3} mol) and ether telechelic oligomer diene **6a** (0.722 g, 4.2×10^{-4} mol) were weighed into a vacuum flask and stirred together until homogenized. The ruthenium catalyst (0.005 g) was added, and the reaction was moved to a Schlenk line and warmed to 60 °C. The reaction was stirred for 48 h, and 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 cm^{-1}; ^{1}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}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 4 with 6a To Make 17. The phenylene diacetate monomer **4** (1.0 g, 2.18×10^{-3} mol) and **6a** (1.0 g, 4.2×10^{-4} mol) were weighed into a vacuum flask and stirred together until homogenized. The ruthenium catalyst (0.005 g) was added, and the reaction was moved to a Schlenk line with an oil bath at 60 °C. The reaction was stirred for 48 h. 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^{-1}; ^{1}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 (br s, ═CH), 7.23 (s, 4H, ArH); ^{13}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 5 with 6a To Make 18. The aliphatic ester monomer **5** (0.75 g, 5.2×10^{-3} mol) and **6a** (0.72 g, 4.2×10^{-4} mol) were weighed into a vacuum flask and stirred together until homogenized. The ruthenium catalyst (0.005 g) was added, and the reaction was moved to a Schlenk line with an oil bath. The reaction was stirred for 48 h. 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^{-1}; ^{1}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); ^{13}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 3 with 7a To Make 19. The terephthalate monomer **3** (0.46 g, 1.18×10^{-3} mol) and **7a** (0.46 g, 2.8×10^{-5} mol) were weighed into a vacuum flask and stirred together until homogenized. The ruthenium catalyst (0.01 g) was mixed in, and the reaction was moved to a Schlenk line and warmed to 60 °C. The reaction was stirred for 5 days, and 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 cm^{-1}; ^{1}H NMR 0.80 (s), 1.00 (d), 1.10 (s, CH$_3$), 1.31−1.37 (m), 1.41 (s, CH$_2$), 1.52 (m, 4H E), 18−2.2 (m E + IB), 4.31 (t, 4HE), 5.43 (m, 1H, ═CH), 7.17 (s, 3 Ar), 8.09 (br s, 4H, ArH); ^{13}C NMR 165.8, 134.2, 129.5, 121.2, 120.1, 65.5, 59.5 (CMe$_2$), 59.0, 58.8, 58.6, 38.9, 38.1, 37.8 (CH$_2$), 32.2, 31.6, 31.2 (CH$_3$), 30.7, 29.4, 29.2, 28.6, 25.9.

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