Macromolecules

Volume 26, Number 2 January 18, 1993

Acyclic Diene Metathesis (ADMET) Polymerization. Synthesis of Unsaturated Polycarbonates

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Received May 22, 1992; Revised Manuscript Received August 10, 1992

ABSTRACT: The first acyclic diene metathesis (ADMET) polymerization of carbonate containing monomers using the molybdenum catalyst, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$ is reported. Bis(1-hexenyl) carbonate, bis(1-pentenyl) carbonate, bis(1-butenyl) carbonate, and 4,4′-isopropylidenebis(phenyl 1-butenyl carbonate) successfully undergo ADMET homopolymerization. These polymerizations are initiated under bulk conditions and are continued in solution to produce poly(5-decenyl carbonate), poly(4-octenyl carbonate), poly(3-hexenyl carbonate), and poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxycarbonyl-1,6-hex-3-enylene), respectively. No metathesis activity is observed for bis(1-propenyl) carbonate due to a negative neighboring group effect. This effect involves either the coordination of the carbonyl oxygen to the metal center or simply the polarization of the double bond such that the intermediates of the metathesis process are not favored. All polymer structures were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy. Number-average molecular weights were determined by end-group analysis and vapor pressure osmometry. Synthesis, characterization, and the general limitations of this polymerization are discussed.

Introduction

Acyclic diene metathesis (ADMET) polymerization has been established as a viable synthetic route to high molecular weight unsaturated polymers and copolymers containing various functionalities if certain synthesis rules are obeyed.[1-12] The synthesis of polymers via ADMET chemistry was not possible until the discovery that Lewis acid-free catalyst systems were required to avoid competing vinyl addition chemistry.[4,5] The polymers that result from ADMET chemistry are perfectly linear and free from branching and other defects. They are pure in that no other repeat unit is present and the end groups are well-defined.

Commercial methods of preparing polycarbonates involve either an ester interchange route carried out as a two-stage melt polymerization process or a phosgene reaction carried out in a basic solution (Figure 1).[13] Recently the ring-opening polymerization of carbonate-containing macrocycles has been reported as a route to various functionalized polycarbonates (Figure 2).[14] Polycarbonates have found many commercial applications involving packaging, structural foam, and transparent glasses.

The metathesis of carbonyl-containing compounds has received attention in the past.[13,15] Until the development of Lewis acid-free metathesis catalyst systems, however, the metathesis of unsaturated compounds containing the carbonyl functionality had been unsuccessful due to the

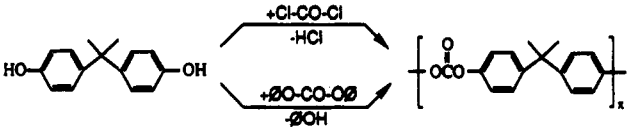

Figure 1. Conventional syntheses of polycarbonates.

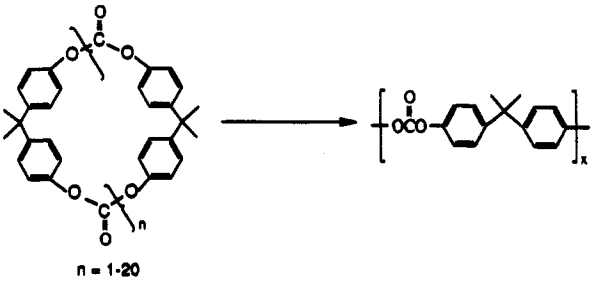

Figure 2. Polycarbonates synthesized via ring-opening polymerization.

rapid poisoning of the catalyst system.[16-20] Only low conversions were observed, and thus highly reactive classical homogeneous metathesis catalyst systems such as WCl_6–$SnMe_4$ and $WOCl_4$–$SnMe_4$ have seen only limited success in the metathesis of unsaturated esters and WCl_6–$Me_3Al_2Cl_3$ in the metathesis of unsaturated ketones. Heterogeneous catalyst systems based on Re_2O_7/Al_2O_3–$SnMe_4$ also have been used in the attempted metathesis of unsaturated esters and ketones; however, as in the case for previous homogeneous catalyst systems, conversions

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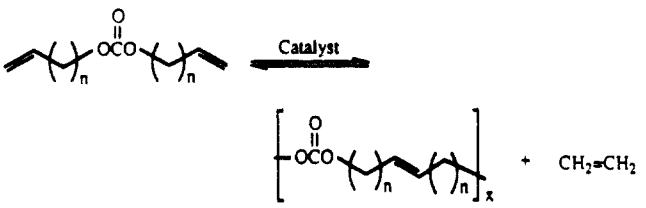


Figure 3. ADMET polymerization of alkyl carbonate diolefins.

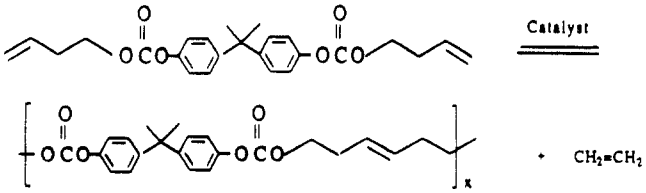


Figure 4. ADMET polymerization of monomer containing the Bisphenol A unit.

are less than the necessary >99% required for successful step polymerization chemistry.[13,15] Consequently, high polymers do not form. Recently we have reported the successful ADMET polymerization of ester- and ketone-containing monomers.[10-12]

This paper reports the successful ADMET polymerization of carbonate-containing monomers using the molybdenum-based catalyst Mo(CHCMe$_2$Ph)(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCCH$_3$(CF$_3$)$_2$]$_2$. Simple alkyl monomers have been used to define the synthesis rules of the ADMET polymerization of monomers containing the carbonate functionality (Figure 3). A polymer containing the Bisphenol A linkage was also synthesized, demonstrating the polymerization of a highly functionalized carbonate monomer (Figure 4).

Experimental Section

Monomer syntheses were performed under a dry argon atmosphere using standard Schlenk techniques. Toluene and pentane were extracted with cold, concentrated sulfuric acid followed by basic potassium permanganate. Tetrahydrofuran (THF), pentane, and toluene were distilled from potassium benzophenone ketyl. Mo(CHCMe$_2$Ph)(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCCH$_3$(CF$_3$)$_2$]$_2$ was prepared according to literature methods.[18] All other solvents and reagents were purged with argon and used without further purification.

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a Varian XL-200 (200 MHz) spectrometer. NMR data are listed as parts per million downfield from TMS. Obvious multiplicities and routine coupling constants are not listed. Spectra are obtained in $CDCl_3$ unless otherwise noted. IR data were recorded on a Perkin-Elmer 281 infrared spectrometer. Gel permeation chromatography (GPC) analyses were carried out with the use of coupled Phenomenex Phenogel 5 500- and 5000-Å columns, a Waters Associates differential refractometer, and a Perkin-Elmer LC-75 spectrophotometric detector on polymer samples 0.1–0.3% w/v in THF. The GPC columns were calibrated versus commercially available polystyrene samples ranging from 910 to 1.10 × 10^6. Vapor pressure osmometry was carried out with the use of a Wescam 233 molecular weight apparatus at 50 °C on polymer samples ranging from 8 to 18 g/L in toluene. Differential scanning calorimetry (DSC) was carried out using a Du Pont DSC 2910 differential scanning calorimeter. Thermogravimetric analysis (TGA) was carried out using a Du Pont Hi-Res TGA 2950 thermogravimetric analyzer. Elemental analyses are by Atlantic Microlab, Inc., Atlanta, GA.

Bis(1-hexenyl) Carbonate (1). 5-Hexen-1-ol (10.0 g, 0.0998 mol), dimethyl carbonate (4.047 g, 0.0449 mol), and LiH (0.020 g, 0.00252 mol) were all added to a dry-argon-purged 100-mL round-bottomed flask equipped with a flash distillation apparatus. Methanol was then distilled from the mixture under argon until no more methanol was recovered. The flash distillation apparatus was then replaced by a standard fractional distillation apparatus and the fractional distillation continued under vacuum. The product was then stirred over CaH_2 overnight, after which the mixture was filtered under argon over a Celite bed with the aid of dry pentane. The pentane was then stripped off of the mixture which was then vacuum transferred into a round-bottomed storage flask equipped with a Rotaflow stopcock and molecular sieves as a colorless oil (6.61 g, 65%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.40–1.55 (m, 2 H), 1.64–1.77 (m, 2 H), 2.04–2.17 (q, 2 H), 4.10–4.20 (t, 2 H), 4.93–5.09 (m, 2 H), 5.72–5.88 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.1, 137.9, 114.5, 67.5, 32.9, 27.8, 24.7; IR (neat, KBr) 2925, 1750, 1640, 1260 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.93; H, 9.83.

Bis(1-pentenyl) Carbonate (2). The preparation of **2** from 4-penten-1-ol (10 g, 0.1161 mol), dimethyl carbonate (4.706 g, 0.0522 mol), and LiH (0.02 g, 0.00252 mol) was analogous to the procedure for **1**, yielding the product as a colorless oil (6.21 g, 60%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.72–1.84 (p, 2 H), 2.10–2.21 (p, 2 H), 4.10–4.20 (t, 2 H), 4.96–5.11 (m, 2 H), 5.72–5.89 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.0, 137.0, 115.1, 67.0, 29.5, 27.5; IR (neat, KBr) 2960, 1750, 1645, 1260 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.76; H, 9.10.

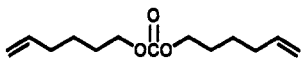
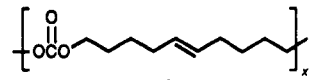
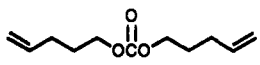
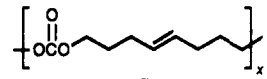
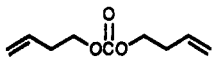
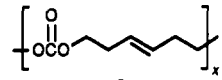
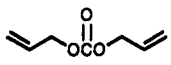
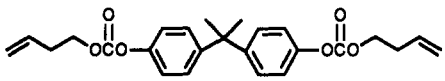
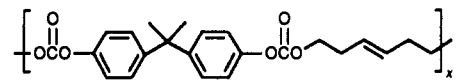
Bis(1-butenyl) Carbonate (3). The preparation of **3** from 3-buten-1-ol (10.0 g, 0.1387 mol), dimethyl carbonate (5.62 g, 0.0624 mol), and LiH (0.02 g, 0.00252 mol) was analogous to the procedure for **1**, yielding the product as a colorless oil (7.0 g, 66%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 2.39–2.48 (m, 2 H), 4.14–4.23 (t, 2 H), 5.08–5.20 (m, 2 H), 5.72–5.88 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 154.8, 133.1, 117.3, 66.5, 32.7; IR (neat, KBr) 2970, 1750, 1645, 1260 cm^{-1}. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.56; H, 8.26.

Bis(1-propenyl) Carbonate (4). The preparation of **4** from allyl alcohol (10.0 g, 0.1722 mol), dimethyl carbonate (6.97 g, 0.0775 mol), and LiH (0.02 g, 0.00252 mol) was analogous to the procedure for **1**, yielding the product as a colorless oil (5.51 g, 50%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 4.53–4.63 (m, 2 H), 5.18–5.40 (m, 2 H), 5.80–6.02 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 154.8, 131.5, 118.7, 60.4; IR (neat, KBr) 2950, 1750, 1650, 1260 cm^{-1}. Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.03; H, 7.10.

4,4′-Isopropylidenebis(phenyl 1-butenyl carbonate) (5). 4-Buten-1-ol (4.94 g, 0.0686 mol) and pyridine (5.42 g, 0.0686 mol) were added to a dry 250-mL Schlenk tube and stirred under argon at 0 °C in 50 mL of dry THF. 4,4′-Isopropylidenediphenol bis(chloroformate) (10.0 g, 0.0286 mol) dissolved in 50 mL of dry THF was then added dropwise via an addition funnel, after which the mixture was allowed to stir for an additional 2 h at room temperature. The solvent was then removed in vacuo, resulting in a thick yellow oil. The oil was then dissolved in enough toluene to allow transfer by pipet to a 6-in. silica gel column (100–200 mesh) and the product eluted using a toluene–hexane (1/1) solvent. The solvent was then removed in vacuo and the resulting colorless opaque oil left under vacuum for an additional 8 h to remove any excess 4-buten-1-ol and pyridine. The oil was then dissolved in enough toluene to allow effective stirring in CaH_2 overnight. The mixture was then filtered under argon through a Celite bed with the aid of dry toluene. The toluene was then removed in vacuo, resulting in the product as a colorless, opaque oil (8.3 g, 68%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.58–1.75 (s, 3 H), 2.41–2.59 (q, 2 H), 4.22–4.35 (t, 1 H), 5.08–5.25 (m, 2 H), 5.71–5.96 (m, 1 H), 7.0–7.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 153.8, 149.0, 148.0, 133.3, 127.9, 120.5, 117.9, 67.7, 42.5, 33.0, 30.9. IR (neat, KBr) 2975, 1770, 1640, 1250 cm^{-1}. Anal. Calcd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.64. Found: C, 70.80; H, 6.66.

Poly(5-decenyl carbonate) (6). In a drybox under a nitrogen atmosphere the molybdenum catalyst (0.012 g, 2.209 × 10^{-5} mol) was weighed into a Schlenk tube equipped with a stopcock followed by **1** (2.0 g, 8.8 × 10^{-3} mol). Rapid evolution of ethylene was evident, and the reaction was allowed to stir until the reaction mixture thickened, after which 2 mL of toluene was added. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional 8 h. The reaction mixture which was then diluted

Table I
Polymerization of Acyclic Unsaturated Carbonates

monomer	polymer
 1	 6
 2	 7
 3	 8
 4	no reaction
 5	 9

with benzene (50 mL) and extracted with a sodium carbonate solution (3 × 50 mL) followed by water. The benzene fraction was then slowly added to a stirring solution of methanol, precipitating the polymer as a white solid which was isolated via centrifugation. A vacuum was then applied to the polymer for a period of 24 h, resulting in the product as a white powder (1.6 g, 93%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.25–1.51 (p, 2 H), 1.51–1.75 (p, 2 H), 1.88–2.10 (m, 2 H), 4.0–4.18 (t, 2 H), 5.28–5.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.4, 130.2, 129.6, 67.8, 32.0, 28.1, 25.7. IR (film, KBr) 2900, 1745, 1260 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 65.85; H, 9.11.

Poly(4-octenyl carbonate) (7). The preparation of 7 from the catalyst (0.0132 g, 2.52 × 10^{-5} mol) in the Schlenk tube was analogous to the procedure for 6 with 2 (2.0 g, 1.01 × 10^{-2} mol) to yield poly(4-octene)carbonate as an opaque, highly viscous oil (1.46 g, 85%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.60–1.82 (p, 2 H), 1.95–2.18 (m, 2 H), 4.0–4.2 (t, 2 H), 5.30–5.51 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.3, 129.8, 67.3, 28.6, 28.4. IR (film, KBr) 2950, 1750, 1360 cm^{-1}. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.59; H, 8.29.

Poly(3-hexenyl carbonate) (8). The preparation of 8 from the catalyst (1.53 × 10^{-2} g, 2.94 × 10^{-5} mol) in the Schlenk tube was analogous to the procedure for 6 with 3 (2.0 g, 1.18 × 10^{-2} mol) to yield poly(3-hexene)carbonate as a white solid (1.57 g, 94%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 2.22–2.48 (m, 2 H), 4.0–4.2 (t, 2 H), 5.45–5.60 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.1, 128.1, 67.2, 31.9. IR (film, KBr) 2960, 1745, 1260 cm^{-1}. Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 57.49; H, 7.23.

Attempted Polymerization of 4. Catalyst (0.020 g, 3.84 × 10^{-7} mol) and 4 (1.0 g, 7.04 × 10^{-3} mol) were reacted in a procedure analogous to the synthesis of 6. Upon addition of the monomer to the catalyst there was no apparent evolution of ethylene, and after 3 h ^{1}H NMR revealed only unreacted starting material.

Poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxycarbonyloxy-1,6-hex-3-enylene) (9). Monomer 5 (2.0 g, 4.71 × 10^{-3} mol) and toluene (2 mL) were mixed together to allow efficient stirring of the monomer and then added to a Schlenk tube preloaded with catalyst (0.010 g, 1.92 × 10^{-5} mol). Rapid evolution of ethylene was evident, and the reaction was allowed to stir until the reaction mixture thickened, after which 2 mL of toluene was added. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional 8 h. Benzene (50 mL) was then added to dilute the reaction mixture, which was then extracted with a sodium carbonate solution (3 × 50 mL) followed by water. The benzene fraction was then slowly added to a stirring solution of methanol, precipitating the polymer as a pale yellow solid which was isolated via centrifugation. A vacuum was then applied to the polymer for a period of 24 h, resulting in the product as a pale yellow solid (1.76 g, 94%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.55–1.80 (s, 3 H), 2.38–2.64 (m, 2 H), 4.16–4.38 (t, 2 H), 5.54–5.72 (m, 1 H), 7.0–7.38 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 153.7, 149.0, 148.0, 128.2, 127.9, 120.5, 67.9, 42.5, 31.9, 30.9. IR (film, KBr) 2970, 1770, 1240 cm^{-1}. Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 67.99; H, 6.21.

Dilute-Solution Polymerization of 5. The polymerization was analogous to the procedure for the synthesis of 9, however, 5 (1.0 g, 2.36 × 10^{-3} mol) was dissolved in 10 mL of toluene before the addition of catalyst.

Results and Discussion

This is the first example of the ADMET polymerization of carbonate-containing monomers. In order to establish the synthesis rules and conditions for the polymerization of these carbonate monomers, a study was undertaken to determine the number of methylene spacers required to allow a successful ADMET polymerization. A summary of the monomers studied and the polymers formed is found in Table I.

ADMET Chemistry and the Negative Neighboring Group Effect. Table I lists the unsaturated carbonate monomers with various numbers of methylene spacers between the carbonate group and the olefin used in this research. The polymerization of the linear alkyl carbonate 3 demonstrates that monomers with as few as two methylene spacers between the carbonate functionality and the olefin polymerize successfully using the molybdenum catalyst. The polymerization proceeds rapidly at room temperature and exhibits no evidence of chain transfer or branching in either the ^{1}H NMR or ^{13}C NMR as well as the optimal MWD (molecular weight distribution) of 2.0. These polymerizations demonstrate the ability to rapidly synthesize high molecular weight unsaturated polycarbonates. By comparison, the alkyl carbonate 4, in which only one methylene spacer is present, shows no evidence of metathesis.

The number of methylene spacers between the carbonate functionality and the olefin is a factor in these polymerizations. This observation agrees with similar studies of monomers containing the ether and the ester functionalities.[6,9] The phenomenon of needing two methylene spacers between the functionality and the olefin has been termed the negative neighboring group effect.[9]

Table II
Molecular Weight Data for Unsaturated Polycarbonates

polymer	% trans	$\bar{M}_n$	$\bar{X}_n$	MWD
6	94	11 700[a]	52	2.0[c]
7	83	8 600[b]	51	1.8[c]
8	89	8 200[b]	58	2.0[c]
9		15 800[a]	40	1.9[c]

[a] Determined by NMR end-group analysis. [b] Determined by VPO. [c] Determined using an unprecipitated reaction mixture.

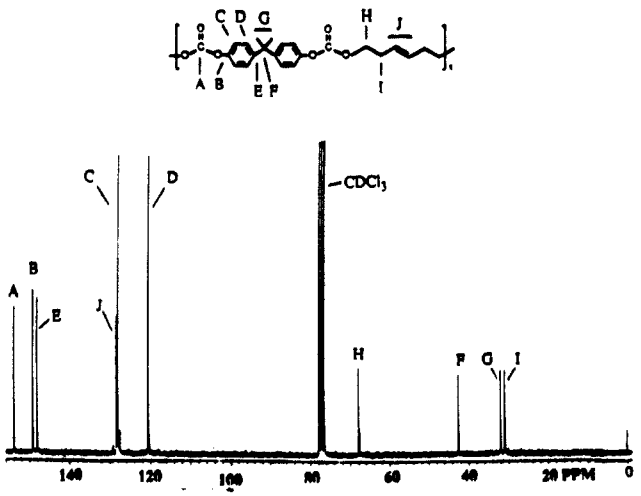


Figure 5. 50-MHz ^{13}C NMR spectrum of polymer 9.

Polymer Characterization and Molecular Weight Analysis. Table II contains the molecular weight and structural data for polymers 6–9. In all cases, the oligomers were found to be perfectly linear and pure as demonstrated by the ^{13}C NMR for polymer 9 in Figure 5. The trans/cis ratio found in polymers 6–8 was similar to that observed in other ADMET polymers. This ratio for polymer 9 could not be determined since the cis signal overlaps with the aromatic region in the ^{13}C NMR spectrum.

In the case of polymer 9 evidence of lower molecular weight cyclics was observed both in the GPC trace and in the thermal analysis. A polymerization of monomer 5 in a dilute solution enhanced the formation of cyclics. The major product was again high molecular weight polymer; however, significant fractions of low molecular weight compounds were also evident (Figure 6). The ^1H and ^{13}C NMR spectra of this material revealed the absence of vinyl end groups. These end groups are easily observed in ADMET polymerizations up to a degree of polymerization of approximately 50 for linear chains, implying that the lower molecular weight fractions are likely cyclics.

Thermal Analysis. The thermogravimetric analysis (TGA) data are shown in Table III. Polymers 6–8 exhibited a large initial weight loss in a single step. Polymer 9 showed an initial weight loss at 75 °C; however, only 5% weight loss was observed up to 275 °C, at which time a large weight loss was observed (Figure 7). The reason for this initial weight loss is presumably due to the presence of lower molecular weight cyclics which are decomposing at lower temperatures than the high molecular weight chains.

The differential scanning calorimetry (DSC) data are shown in Table IV. No T_g is observed for polymers 6 and 8 above −100 °C. Polymer 7 showed a T_g at −58 °C for a 5 °C/min ramp rate. No other transitions were observed between +150 and −100 °C for this polymer, however, due to the slow kinetics of crystallization. Polymer 9 was measured between −100 and 60 °C (Figure 8). The initial heating cycle showed a clear T_m (ΔH of 4.9 J/g). The second and subsequent heating cycles show a reproducible but smaller T_m (ΔH of 1.5 J/g) due to the slow kinetics of

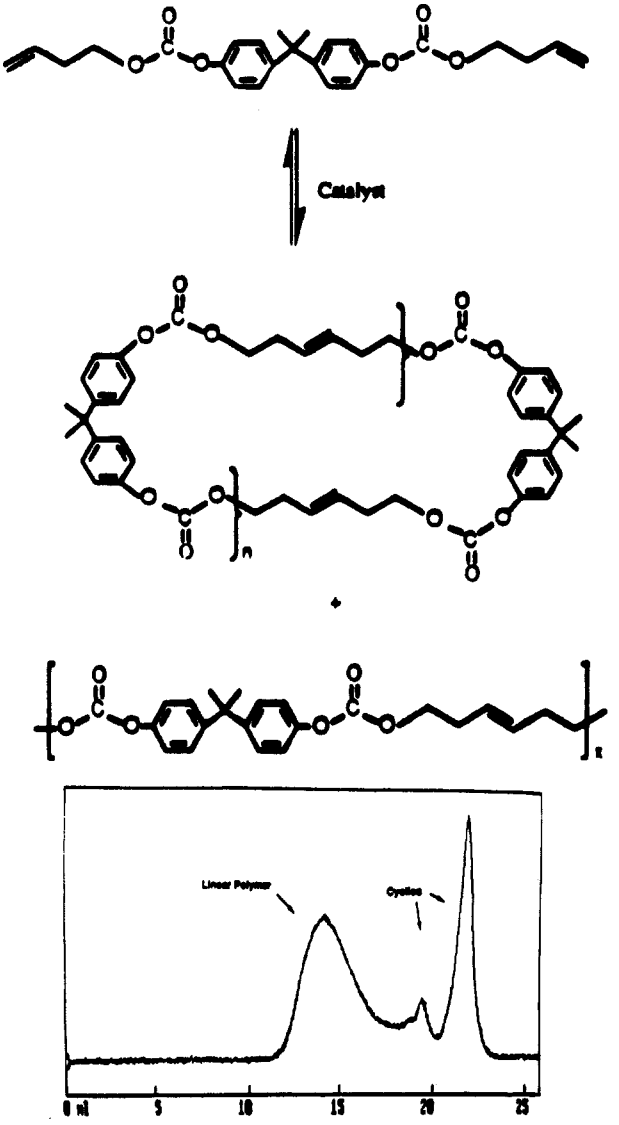


Figure 6. GPC of the solution polymerization of monomer 5.

Table III
Thermogravimetric Analysis Data for Unsaturated Polycarbonates[a]

	onset (°C)		90% wt loss (°C)	
polymer	air	nitrogen	air	nitrogen
6	222	230	455	360
7	235	271	445	414
8	222	255	495	460
9	70	75	490	445

[a] All values were obtained at a 5 °C/min heating rate.

crystallization or possibly a trace amount of cyclics not removed in the purification step. The T_g appeared at −36 °C in the initial heating cycle. In the second and all subsequent heating cycles the T_g reproducibly appeared at −38 °C.

Conclusions

Acyclic diene metathesis (ADMET) polymerization offers a viable route for the synthesis of pure unsaturated polycarbonates. The use of the highly active, Mo-based, Lewis acid-free alkylidene catalyst provides a clean route to unsaturated polycarbonates with known vinyl end groups. The polymerizability of a monomer is limited by the number of methylene spacers between the carbonate functionality and the olefin, a phenomenon which we term the negative neighboring group effect. Further investigation into the nature of the negative neighboring group

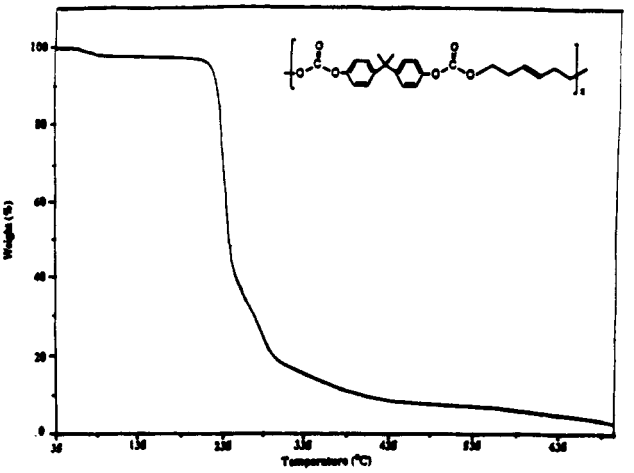


Figure 7. TGA of polymer **9** (heating rate of 5 °C/min under a N_2 purge).

Table IV
Differential Scanning Calorimetry Data for Unsaturated Polycarbonates

polymer	T_m (°C)	T_c (°C)	T_g (°C)
6	77.8[a]	57.5[a]	
7			-58.0[b]
8	42.2[a]	31.5[a]	
9	29.5[a]		-21.9[a]

[a] Values obtained at 20, 10, and 5 °C/min and then extrapolated back to 0 °C/min. [b] Values determined from a 5 °C/min cycle.

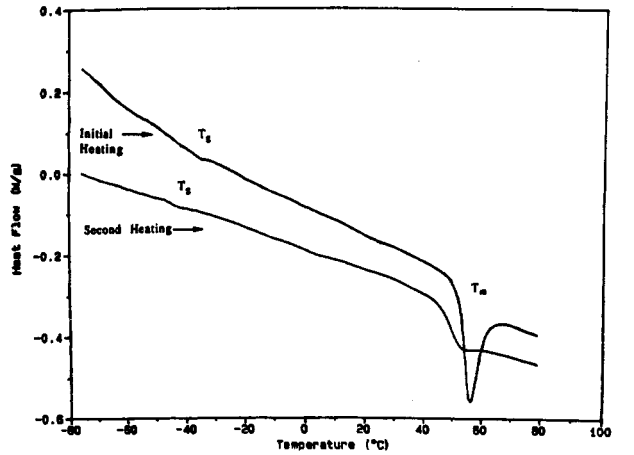


Figure 8. DSC of polymer **9** (heating rate of 20 °C/min).

effect as well as the polymerization of monomers containing other polar functionalities is currently being pursued.

Acknowledgment. We thank the National Science Foundation (Grant DMR-8912026) and the University Research Initiative Program (Grant N00014-86-G-0224) as conducted by DARPA and the Naval Research Office for their support of this work. We also are very thankful to A. S. Gamble and J. M. Boncella for helpful discussions.

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Registry No. **1**, 144634-71-9; **2**, 144634-72-0; **3**, 85120-17-8; **4**, 15022-08-9; **5**, 144634-73-1; **6** (homopolymer), 144634-76-4; **7** (homopolymer), 144634-77-5; **8** (homopolymer), 144634-78-6; **9** (homopolymer), 144634-79-7; 5-hexen-1-ol, 821-41-0; dimethyl carbonate, 616-38-6; 4-penten-1-ol, 821-09-0; 3-buten-1-ol, 627-27-0; allyl alcohol, 107-18-6; 4,4′-isopropylidenediphenol bis(chloroformate), 2024-88-6.