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

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ABSTRACT: Previously unknown unsaturated polyethers from acyclic, ether-containing dienes have first been obtained via acyclic diene metathesis (ADMET) polymerization in the presence of the catalyst W(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-Pr_2)[$OCMe(CF_3)_2$]$_2$. Polymer yields are high, and number-average molecular weights up to $\bar{M}_n$ = 15 000–18 000 are observed. Structural assignments of the polymers are based on ^{13}C NMR and ^1H NMR spectroscopy, IR spectroscopy, and elemental analysis. The polymerizability of the ether-containing α,ω-diene appears to be a function of the distance between the ether oxygen and the metathesizing double bond in the monomer. An ether-containing diene has also been copolymerized with 1,9-decadiene.

Introduction

Recently acyclic diene metathesis (ADMET) polymerization has been reported as a useful equilibrium step propagation, condensation scheme, where this research had successfully employed linear acyclic hydrocarbon dienes as monomers (Figure 1).[1-5] Acyclic diene metathesis (ADMET) expands metathesis polymerization beyond the very successful ring-opening metathesis (ROMP) reaction,[6-11] and, thus far, this chemistry has produced high molecular weight hydrocarbon linear homopolymers[1] and random copolymers.[2] The utility of ADMET chemistry for the polymerization of dienes containing silyl,[12] aromatic,[13] and ester[14] functional groups also is being investigated. In this paper, we report the first synthesis of unsaturated polyether polymers via ADMET polycondensation techniques (Figure 2). There are no reports in the literature on the condensation polymerization of α,ω-dienes containing ether functional groups, and few reports exist on model compound metathesis (without polymerization) reactions of acyclic vinyl ethers.[15-18] None of these reported model reactions is high yielding.

Experimental Section

Materials. The catalyst W(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-Pr_2)-[$OCMe(CF_3)_2$]$_2$ was synthesized according to published procedures.[19,20] Due to the very sensitive nature of the catalyst, all monomers, reagents, and solvents used in conjugation with this catalyst had to be >99% pure. Divinyl ether (from Johnson Matthey Co., Inc.) and diallyl ether (from Aldrich Chemical Co., Inc.) were dried over calcium hydride for 48 h, degassed several times, and then vacuum transferred into a flask with a single aliquot (20 mg) of catalyst for 15 min. These purified monomers then were transferred into a break-seal ampule and sealed under high vacuum. Three additional α,ω-diene ethers of the structure $CH_2{=}CH(CH_2)_nO(CH_2)_nCH{=}CH_2$ (n = 2–4) were synthesized as previously reported.[21] The structures of the monomers were confirmed by their ^1H and ^{13}C NMR, elemental analysis, and mass spectrometry (Table I).

These monomers, as well as the 1,9-decadiene (Aldrich Chemical Co., Inc.) used in the copolymer work, were purified by the same method as described above. Each monomer was transferred into a sodium-mirrored flask equipped with a Teflon stopcock. The monomers then were transferred under vacuum to the break-seal ampules and sealed under high vacuum (10^{-6} mbar).

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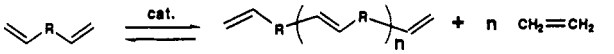

Figure 1. Acyclic diene metathesis (ADMET) polymerization.

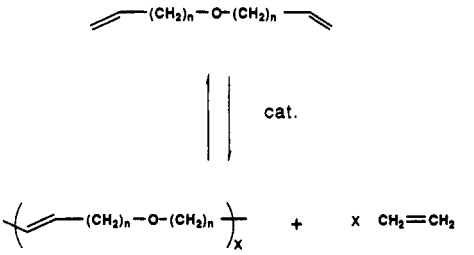

Figure 2. Acyclic diene metathesis (ADMET) polymerization of α,ω-unsaturated ether monomers.

Polymerization Procedure. The general procedure used to perform acyclic diene metathesis (ADMET) polymerization is described elsewhere.[1] Polymerizations were conducted in bulk with 20 mg of catalyst and 1.0 g of monomer. All reactions were performed under reduced pressure starting at room temperature and then increasing to 50 °C to drive the reaction to completion. After 48 h, the reactions were quenched by exposure to the atmosphere. The polymers were dissolved in toluene and subsequently precipitated in methanol.

Characterization. 200-MHz ^1H NMR and 50-MHz ^{13}C NMR spectra for all polymers were obtained with a Varian XL Series NMR superconducting spectrometer system, and all spectra were taken at room temperature in $CDCl_3$. Elemental analysis of products was done by Atlantic Microlab, Inc., Atlanta, GA. Infrared analyses were performed by using a Perkin-Elmer 1600 FTIR spectrophotometer. Vapor-pressure osmometry was done with a Wescan Model 233, molecular weight apparatus. Size-exclusion chromatography data were obtained by using a Waters Associates liquid chromatograph apparatus equipped with an RI detector. THF was used as solvent in the SEC work, and two μ-Styragel columns, 10^2 and 10^3 Å, were used in series. A constant flow rate of 1 mL/min was maintained, and the instrument was calibrated by using polystyrene standards.

Results and Discussion

Homopolymerization of Ether-Containing α,ω-Dienes by Acyclic Diene Metathesis (ADMET) Chemistry. Acyclic diene metathesis (ADMET) polymerization is an equilibrium step propagation condensation type reaction,[1,22] where the production and removal of ethylene (for α,ω-dienes) drives the polymerization. We have found that previously unknown unsaturated polyethers can be synthesized by this technique if appropriate methylene "spacer" units are placed between the ether

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Table I
Characterization Data for the Monomers CH_2=$CH(CH_2)_nO(CH_2)_nCH$=CH_2 (n = 2-4)

monomer n	elem anal. theory, %	elem anal. found, %	mol wt theory (found)[a]	^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz), $CDCl_3$ (ppm)
2	C = 76.19 H = 11.11	C = 76.28 H = 11.14	126.20 (-)	^{1}H NMR: δ 5.70-5.92 and 5.02-5.17 (CH_2=CH-), 3.33-3.45 (-CH_2OCH_2-), 2.25-2.39 (-CH_2-) ^{13}C NMR: δ 134.33 and 116.6 (CH_2=CH-), 70.00 (-CH_2OCH_2-), 36.48 (-CH_2-)
3	C = 77.92 H = 11.69	C = 77.81 H = 11.73	154.25 (155.14)	^{1}H NMR: δ 5.05-5.90 and 4.92-4.97 (CH_2=CH-), 3.37-3.43 (-CH_2OCH_2-), 2.06-2.17 (CH_2=$CHCH_2$-), 1.62-1.73 (-CH_2-) ^{13}C NMR: δ 138.22 and 114.47 (CH_2=CH-), 70.04 (-CH_2OCH_2-), 30.27 (CH_2=$CHCH_2$-), 28.97 (-CH_2-)
4	C = 79.12 H = 12.09	C = 78.96 H = 12.10	182.31 (183.17)	^{1}H NMR: δ 5.67-5.75 and 4.8-4.98 (CH_2=CH-), 3.29-3.36 (-CH_2OCH_2), 1.94-2.01 (CH_2=$CHCH_2$-), 1.33-1.55 (-CH_2CH_2-) ^{13}C NMR: δ 138.78 and 114.39 (CH_2=CH-), 70.79 (-CH_2OCH_2-), 33.54 (CH_2=$CHCH_2$-), 29.26 and 25.57 (-CH_2CH_2-)

[a] Determined from the parent peak in mass spectrometry.

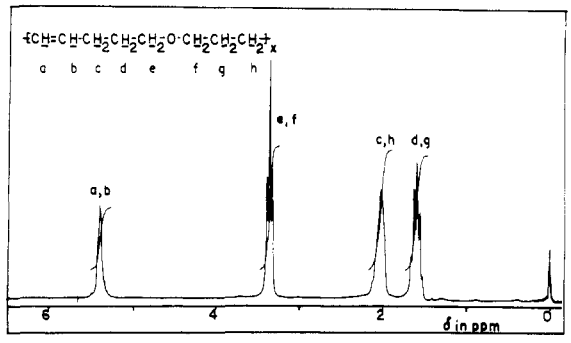

Figure 3. ^{1}H NMR (200-MHz) spectrum in $CDCl_3$ of the unsaturated polyether-[CH=CH$(CH_2)_3$O$(CH_2)_3$]$_x$.

oxygen and the polymerizing vinyl functional group. In order to observe the influence of the distance between the oxygen and the double bond on the ADMET polymerization, we used a series of acyclic ether-containing α,ω-dienes with an increasing number of methylene groups between ether oxygen and the metathesizing double bond (see Figure 2), ranging from the case where no spacer is present (n = 0) to as many as four methylene spacers (n = 4). The following results were observed.

Divinyl ether (n = 0) and diallyl ether (n = 1) do not polymerize by using standard conditions for ADMET polymerization. Di-3-butenyl ether (n = 2) does release ethylene slowly, yet only low molecular weight products are generated. However, the ether-containing α,ω-dienes, di-4-pentenyl ether (n = 3) and di-5-hexenyl ether (n = 4), polymerize readily under the conditions employed, and new, thermally stable unsaturated polyethers are generated. Thus, the yield of unsaturated polyethers decreases with a decreasing number of methylene spacer groups in the monomer, which seems to be typical for the olefin metathesis of unsaturated ethers. These results are in good agreement with Ast's[15] work concerning the attempted metathesis reactions involving unsaturated vinyl ether model compounds.

Several side products of the reaction between the catalyst W(CH-t-Bu)(N-2,6-C_6H_3-i-Pr_2)[OCMe$(CF_3)_2]_2$ and the monomer diallyl ether (mole ratio = 1:3) were observed by ^{1}H and ^{13}C NMR spectroscopy. It may be that the allyl group and the ether oxygen in diallyl ether are coordinated to the metal center, since this type of interaction has been

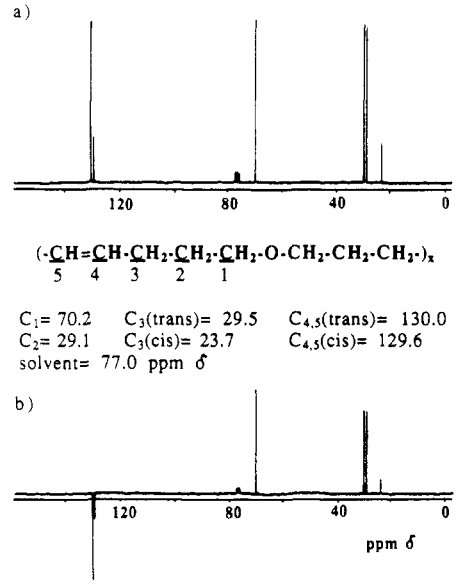

Figure 4. ^{13}C NMR (50-MHz) spectrum (a) and the APT ^{13}C NMR spectrum (b) of the unsaturated polyether, -[CH=CH-$(CH_2)_3$O$(CH_2)_3$]$_x$.

observed by Schrock[23] in the attempted metathesis of ester-containing olefins. For example, when methyl acrylate, was reacted with W(CH-t-Bu)(N-2,6-C_6H_3-i-Pr_2)[OCMe$_2$-$(CF_3)]_2$, a stable metallacyclobutane complex formed in which the carbonyl oxygen atom was bound to the tungsten.[23] These results suggest that coordination of the ester group, and perhaps other functionalities such as ether groups, can significantly alter the activity of the catalyst itself. An interaction between the double bond and the ether oxygen with the catalyst metal may result in blocking of the metathesis reaction and perhaps even partial destruction of the catalyst. According to the results reported in this paper, this effect may be particularly important when the heteroatom is separated from the olefin by less than three methylene spacer groups.

These reactions were done under bulk polymerization conditions using Schrock's catalyst.[19,20] The monomer to catalyst ratio was rather high, 200:1, for most polymerizations, and all polymerizations were done starting first at room temperature under reduced pressure. The tem-

Table II
Polymerization of the Acyclic Sym Unsaturated Ethers $CH_2{=}CH(CH_2)_nO(CH_2)_nCH{=}CH_2$ (n = 3,4) in Bulk, 50 °C, 48 h

		polymer elem anal.			
monomer n	yield, %	theory, %	found, %	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]
3	96	C = 76.19 H = 11.11	C = 7605 H = 11.11	18 000	1.73
4	99	C = 77.92 H = 11.69	C = 77.63 H = 11.72	15 000	1.99

[a] Vapor pressure osmometry. [b] GPC (calibration for polystyrene standards).

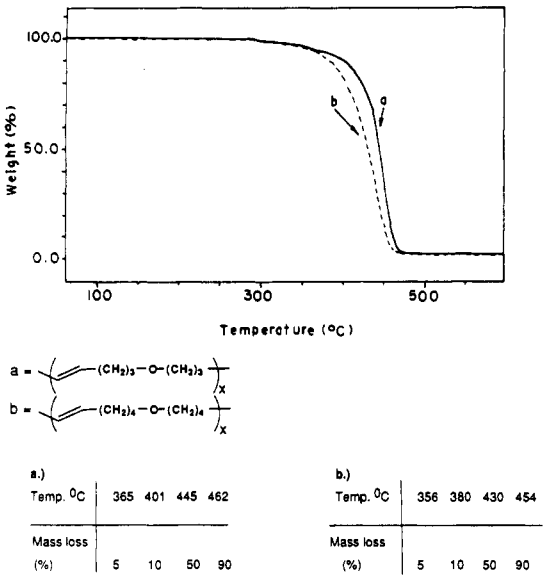

Figure 5. TGA curves of the polyethers $+CH{=}CH(CH_2)_nO(CH_2)_n+_x$ in air with (a) n = 3 and (b) n = 4. Heating rate: 20 °C/min.

perature then was increased to 50 °C to drive the reaction to completion. During the polymerization of each of the two monomers containing more than two methylene spacers, pure ethylene was evolved (as determined by GC/MS spectrometry), and the reaction mixture gradually became more viscous. No accompanying reactions were observed.

The ^{1}H NMR spectrum (Figure 3) of the polymer $+CH_2{=}CH(CH_2)_3O(CH_2)_3+_x$ demonstrates that a perfectly linear, unsaturated polyether is the exclusive product in this ADMET polymerization. The signal at 5.39 ppm corresponds to the internal olefinic protons. Figure 4a shows the ^{13}C NMR spectra for this polymer and indicates that a high degree of stereochemical purity is present (80% trans). The APT ^{13}C NMR spectrum (Figure 4b) clearly delineates the difference between methine and methylene carbon atoms.

The results shown in Table II indicate that high molecular weight polymer forms in high yield. The elemental analyses reflect precisely the values that are calculated for the polymer structure, which again verifies the purity of the reaction itself. The results obtained from ^{13}C and ^{1}H NMR and IR spectroscopy, in combination with the elemental analyses confirm the structural assignment of these two polymers. Vapor-pressure osmometry measurements give number-average molecular weight values of 18 000 and 15 000 (see Table II), which are in agreement with end-group analysis using ^{1}H NMR. The polydispersities of 1.73 and 1.99, determined by size-exclusion chromatography, indicate that the polymers were produced by a step propagation type polymerization, which is consistent with the ADMET polymerization mechanism.

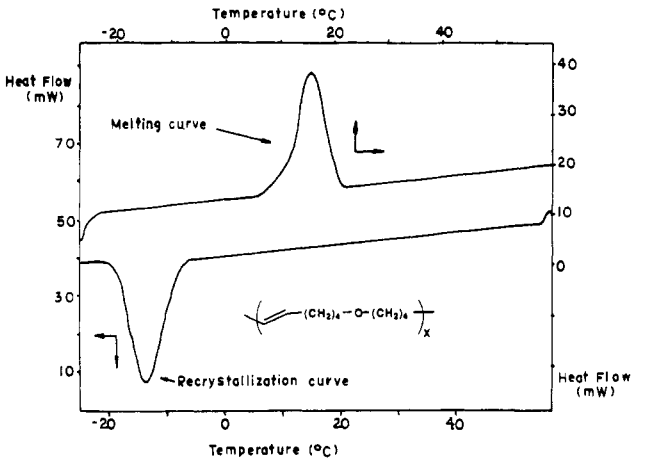

Figure 6. Differential thermal analysis of the polyether $+CH{=}CH(CH_2)_4O(CH_2)_4+_x$: (a) melting curve, (b) recrystallization curve. Scanning rate: 20 °C/min.

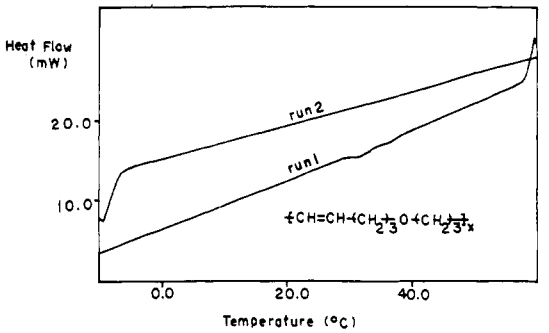

Figure 7. Differential thermal analysis of the polyether $+CH{=}CH(CH_2)_3O(CH_2)_3+_x$. Scanning rate: 5–20 °C/min.

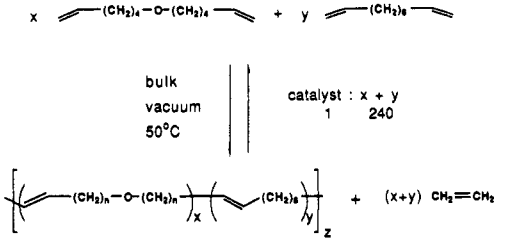

Figure 8. Acyclic diene metathesis (ADMET) copolymerization.

Surprisingly, these unsaturated polyethers display a high degree of thermal stability, as measured by thermogravimetric analysis. For example, poly(oxyethylene) and poly(oxytetramethylene) show onsets of weight loss well below 300 °C. By comparison, the onset of weight loss for both new unsaturated polyethers (n = 3 and n = 4) is above 350 °C (Figure 5). These are excellent values for polyethers. The explanation for this enhanced thermal stability is not obvious; however, it may be due to extensive cross-linking of the sites of unsaturation, which appear in each and every repeat unit in these new polyethers.

The melting behavior of these two unsaturated polyethers is dependent upon the number of methylene spacers present in the repeat unit. Apparently, at least four methylene spacers are required to generate a polymer that displays meltable crystals near or above room temperature. The four methylene spacer polymer shows a melting point of 16 °C and a recrystallization temperature of −14 °C (Figure 6). By comparison, no melting or recrystallization is observed for the polymer possessing three methylene spacers (Figure 7), regardless of the heating or cooling rate.

Table III
Copolymerization of CH_2=$CH(CH_2)_4O(CH_2)_4CH$=CH_2 and CH_2=$CH(CH_2)_6CH$=CH_2 Initiated with W(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-Pr_2)[$OCMe(CF_3)_2$]$_2$ in Bulk, 50 °C, 48 h

monomer feed of 1,9-decadiene/ether	yield, %	repeat unit ratio[a] (octenamer/ether)	elem anal. theory, %	elem anal. found, %	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[c]
1.8	94	1.95	C = 83.36 H = 12.29	C = 83.10 H = 12.23	6000	1.74

[a] Determined by integration of the ^{1}H NMR signals at 3.37 and 5.37 ppm (Figure 11). [b] Vapor-pressure osmometry. [c] GPC (calibration for polystyrene standards).

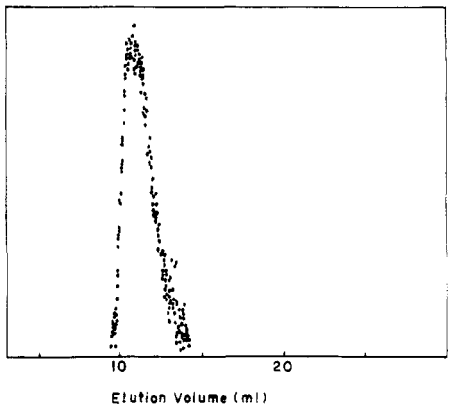

Figure 9. GPC curve of the copolymer $\{CH{=}CH(CH_2)_4O(CH_2)_4\}_x\{CH{=}CH(CH_2)_6\}_y$.

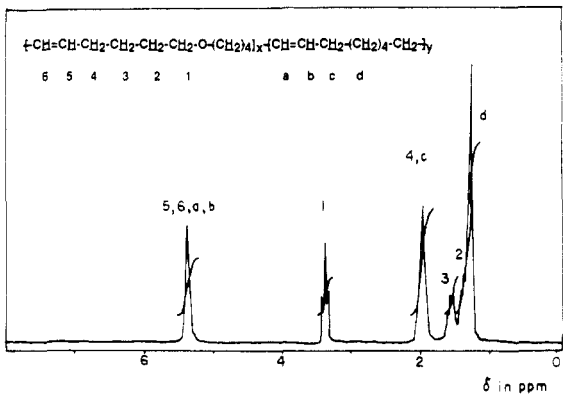

Figure 10. ^{1}H NMR spectrum of the copolymer $\{CH{=}CH(CH_2)_4O(CH_2)_4\}_x\{CH{=}CH(CH_2)_6\}_y$.

Copolymerization Behavior of Di-5-hexenyl Ether and 1,9-Decadiene. Both of these monomers have been shown to homopolymerize smoothly, so their copolymerization was expected to occur readily as well. This is in fact the case. Figure 8 illustrates that the copolymerization produces only copolymer and ethylene, and, as before, the ethylene produced is analytically pure as shown by GC/MS. The size-exclusion chromatogram of the copolymer (Figure 9) illustrates that a copolymer in fact is produced, rather than a blend. An analysis of the ^{1}H NMR data (Figure 10), particularly the signals at 3.37 and 5.37 ppm, provides the ratio of polyoctenamer to polyether repeat units in this copolymer. These data show that the composition of the copolymer is dictated by the monomer feed ratios (see Table III). This result is consistent with any equilibrium step polymerization and is confirming evidence for the step nature of the copolymerization scheme.

Results shown in Table III indicate that copolymer forms in high yield. Elemental analysis data also agree with a copolymer consisting of the ratio of ether and octenamer repeat units as provided by the monomer feed.

Figure 11 shows the ^{13}C NMR spectra for the copolymer, where the region at 129–131 ppm confirms formation of

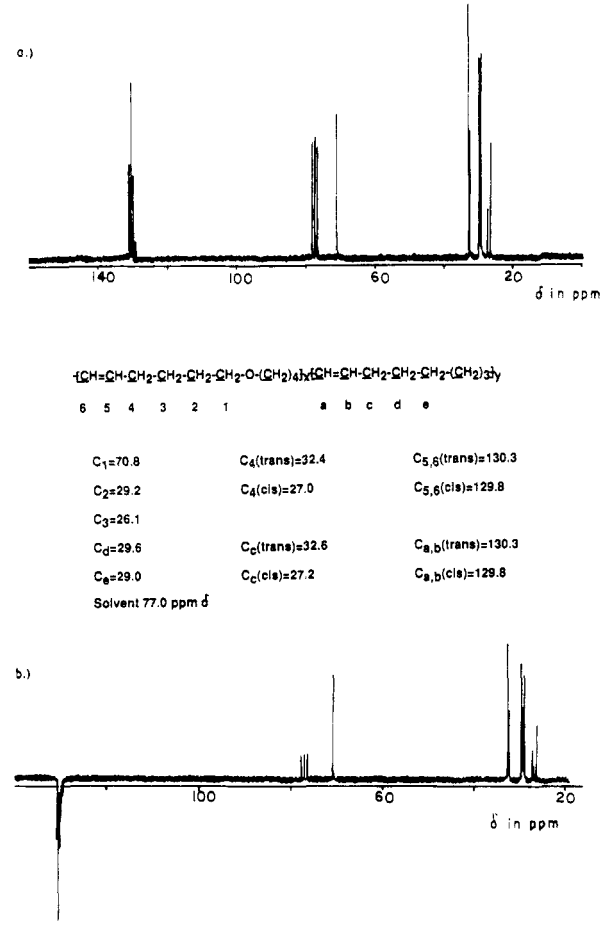

Figure 11. ^{13}C NMR spectrum of the copolymer $\{CH{=}CH(CH_2)_4O(CH_2)_4\}_x\{CH{=}CH(CH_2)_6\}_y$.

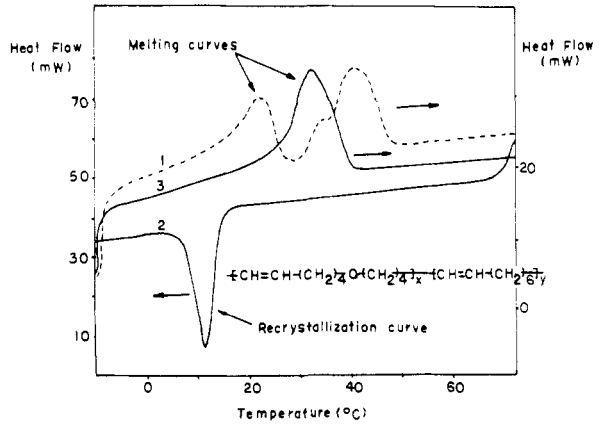

Figure 12. Differential thermal analysis of the copolymer $\{CH{=}CH(CH_2)_4O(CH_2)_4\}_x\{CH{=}CH(CH_2)_6\}_y$: (1) initial melting curve, (2) recrystallization curve, (3) second melting curve. Scanning rate: 20 °C/min.

the copolymer. While the ^{13}C NMR spectrum for each homopolymer possesses only two signals (cis and trans stereochemistry) in this region,[1] the spectrum for the

copolymer exhibits six signals (Figure 11) due to the presence of additional linkages in the copolymer. Figure 12 illustrates the thermal behavior of the copolymer $\{CH{=}CH(CH_2)_4O(CH_2)_4\}_x\{CH{=}CH(CH_2)_6\}_y$ both in terms of its heating and cooling characteristics. The DSC of the copolymer shows two initial endotherms, $T_m(1) = 20$ °C and $T'_m(1) = 40$ °C. After recrystallization, $T_{recr} = 11$ °C, followed by reheating, only one endotherm was observed ($T_m(3) = 31$ °C). This endotherm was apparent after further recrystallization cycles. Introducing an unsaturated ether repeat unit into the backbone of polyoctenamer decreases its melting temperature from 52 °C for 77% trans polyoctenamer[24] to 31 °C without destroying the copolymer ability to recrystallize.

Conclusions

The syntheses of two unsaturated polyether homopolymers and one copolymer have been accomplished by acyclic diene metathesis (ADMET) polymerization chemistry. The synthesis rules associated with the formation of unsaturated polyethers are becoming clear, where the use of sufficiently long methylene spacer moieties precludes intramolecular poisoning of the metal present in the catalyst. While these unsaturated homo- and copolyethers exhibit predictable crystallization/recrystallization behavior, they display a surprisingly high degree of thermal stability. Consequently, they may become quite useful materials. We continue to investigate the effect of monomer structure on the ADMET polymerizability of ether-containing monomers.

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