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Acyclic Diene Metathesis (ADMET) Polymerization. Thermal, Ultraviolet, and Chemical Modification of ADMET Polyethers

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Introduction

It has been shown that acyclic diene metathesis (ADMET) chemistry can produce high molecular weight linear unsaturated polyethers in high yield and with a high degree of stereochemical purity (80% trans)[1] (Figure 1). These polyethers have a double bond in each repeat unit available for secondary reactions, thermal, UV, and chemical modification. In this paper, we report cross-linking and chemical modification reactions by epoxidation and conversion of epoxides to chlorohydrin groups.

Experimental Section

Materials. All chemicals used were purchased from Aldrich Chemical Co. and, if not otherwise stated, used without further purification.

Monomers. Bis(4-pentenyl) ether, $CH_2{=}CH(CH_2)_3O(CH_2)_3CH{=}CH_2$, and bis(5-hexenyl) ether, $CH_2{=}CH(CH_2)_4O(CH_2)_4CH{=}CH_2$, were synthesized as previously reported.[1] The structures of the monomers were confirmed by their ^1H and ^{13}C NMR, elemental analysis, and mass spectrometry.[1]

Polymerization Procedure. The catalyst, $[(CF_3)_2CH_3CO]_2(NAr)W{=}CHC(CH_3)_3$, was synthesized by known methods.[4] In order to ensure the absence of oxygen and absolute dryness, monomers were degassed a few times, dried over calcium hydride, and then transferred to a sodium-mirrored flask. The general procedure to perform metathesis polymerization was described in our first paper.[1] The monomer to catalyst ratio was 200:1. All polymerizations were done starting first at room temperature under reduced pressure. The temperature then was increased to 50 °C in order to drive the reaction to completion. During the polymerization pure ethylene was evolved (as determined by GC/MS). After 48 h, the reactions were terminated by exposure to the atmosphere. The polymers were dissolved in toluene and subsequently precipitated in methanol and then dried under vacuum.

UV Irradiation. UV irradiation without a photoinitiator was carried out in quartz ampules in air, using a preparative photochemical reactor (Rayonet Type RS, New England Ultraviolet Co.) with a low-pressure, quartz, mercury-vapor lamp (250 nm). Ultraviolet irradiation, with benzophenone as the photoinitiator, was carried out in an open vessel. Solutions of the polymer in benzene with the desired amount of benzophenone (6–14%) were vacuum dried in the vessel until the weight was constant. The UV lamp used was a black light, long-wave ultraviolet (365 nm) Spectroline Model B-100 (Spectronics Co.).

Thermal Cross-Linking. Cross-linking of the unsaturated polyethers was carried out in the ampules at 156, 199, and 255 °C for different times ranging from 12 to 300 min in air.

Gel Content. The amount of insoluble products (percent gel content) was measured after the cross-linking reaction. The polymer was cut into thin slices and added to an excess of benzene and held at 35 °C for 24 h. After extraction, the gel was washed with acetone and vacuum dried overnight at 35 °C. The gel content was taken as the weight percent of insoluble network polymer in the sample.

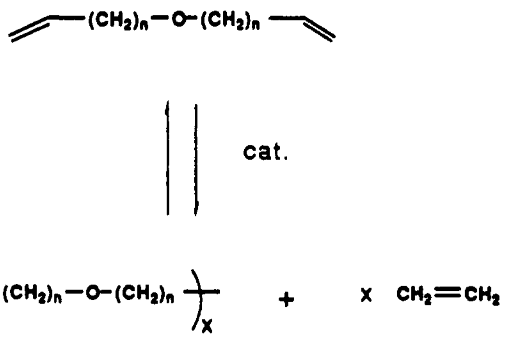

Figure 1. Acyclic diene metathesis (ADMET) polymerization of the symmetrical unsaturated polyethers ($n > 3$).

Epoxidation of the Polymer $[-CH{=}CH(CH_2)_4O(CH_2)_4-]_x$. The procedure to perform the epoxidation reaction has been described elsewhere.[6,7] In a typical reaction, intended to yield 50 mol % modification of double bonds, a sample of the polymer (1.163 g, 6.34×10^{-3} mol of monomeric units) was dissolved in chloroform (30 mL). The 3-chloroperbenzoic acid (purity 60% by assay; 0.5508 g, 3.19×10^{-3} mol of peroxide) was dissolved in chloroform (20 mL) and added dropwise to the polymer solution at room temperature. The reaction vessel was then stoppered and left overnight in the dark. The epoxidized polymer was precipitated in methanol, washed, and dried under vacuum.

Epoxide Titration. An accurately weighed epoxidized polymer was dissolved in dry benzene, and the solution was titrated with a solution of HBr in glacial acetic acid (2×10^{-2} mol L^{-1}) with crystal violet as the indicator. Elem anal. Calcd for 50 mol % epoxidation: C, 74.07; H, 11.11; O, 14.82. Found: C, 74.27; H, 11.26; O, 14.47 (calculated by difference).

Conversion of Epoxides to Chlorohydrin Groups. The epoxide groups on the modified polyethers were converted to chlorohydrin units by adding a 200% excess (based on epoxide content) of concentrated HCl to a solution of the epoxidized polyether in THF at room temperature. The modified polyethers were isolated by precipitation in methanol, washed, and dried under vacuum. Elem anal. Calcd for 50 mol % conversion to chlorohydrin groups: C, 66.67; H, 10.28; Cl, 9.72. Found: C, 66.80; H, 10.41; Cl, 9.76.

Characterization. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) 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 analyses of products were performed by Atlantic Microlab, Inc., Atlanta, GA. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer. Vapor-pressure osmometry was done with a Wescan Model 233 molecular weight apparatus. Size-exclusion chromatography was obtained using a Waters Associates liquid chromatograph apparatus with an RI detector. THF was used as the 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 using polystyrene standards. UV irradiation was carried out in quartz ampules using a Rayonet Type RS preparative photochemical reactor (New England Ultraviolet Co.) and a black light, long-wave ultraviolet (365 nm) Spectroline Model B-100 (Spectronics Co.; 110–120 V, 60 Hz, 3.3 A) lamp.

Results and Discussion

The unmodified unsaturated polyethers, $[-CH{=}CH(CH_2)_nO(CH_2)_n-]_x$ ($n = 3$ or 4), synthesized by acyclic diene metathesis polymerization,[1] are described in Table I. By utilizing the sites of unsaturation in the polymer chain, cross-linking and chemical modification of these ADMET polyethers have been affected.

Previously, Hocker et al. reported[2,3] the preparation of the unsaturated polyether $[-OCH{=}CHCH_2CH_2-]_x$ by the ring-opening metathesis polymerization of 2,3-dihydrofuran using chromium carbene catalysts. They noted that this polymer underwent cross-linking in the presence

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Table I
Characterization of the Symmetrical Unsaturated Polyethers, $[-CH{=}CH(CH_2)_nO(CH_2)_n-]_x$, Synthesized by ADMET, in Bulk (50 °C, 48 h)

	elem anal.			
polymer (n)	calcd	found	M_n[a]	M_w/M_n[b]
3	C = 76.19 H = 11.11	C = 76.05 H = 11.11	18 000	1.73
4	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).

Table II
Photo-Cross-Linking[a] of the Symmetrical Unsaturated Polyethers, $[-CH{=}CH(CH_2)_nO(CH_2)_n-]_x$, without Additives, 50 °C, in Bulk

polymer (n)	time, min	gel content, wt	polymer (n)	time, min	gel content, wt
3	30	16.0	4	80	9.0
3	60	10.5	4	250	34.0
3	120	18.0	4	400	32.0
3	240	22.7	4	1440	30.0
3	553	29.0			

[a] UV (250-nm) irradiation; sample thickness, ~0.3–0.4 mm; distance from the UV lamp to the sample, 7 cm.

Table III
Photo-Cross-Linking[a] of the Symmetrical Unsaturated Polyether $[-CH{=}CH(CH_2)_4O(CH_2)_4-]_x$ with Benzophenone as the Photoinitiator, 75 °C, in Bulk

time, min	benzophenone, wt %	gel content, wt %	time, min	benzophenone, wt %	gel content, wt %
30	6.0	54	45	10.8	93
30	10.8	87	15	14.0	>80

[a] UV (365-nm) irradiation; sample thickness, ~0.3–0.4 mm; distance from the UV lamp to the sample, 10 cm.

Table IV
Thermal Cross-Linking on the Symmetrical Unsaturated Polyether $[-CH{=}CH(CH_2)_4O(CH_2)_4-]_x$ in Bulk

temp, °C	time, min	gel content, wt %	temp, °C	time, min	gel content, wt %
156	17	2.2	199	240	95.0
156	133	14.5	255	12	41.0
156	300	92.0	255	30	57.0
199	18	38.0	255	60	82.0
199	150	94.0			

of a catalyst residue and air or moisture. We have performed a similar cross-linking but under more controlled conditions using several techniques.

Photo-Cross-Linking of the Symmetrical Unsaturated Polyethers. We have studied photo-cross-linking of symmetrical unsaturated polyethers with and without additives. The gel content was measured for the sample after irradiation (see the Experimental Section). The data in Table II demonstrate the dependence of the gel content on the irradiation time when not using a photoinitiator. Gel contents of about 30% were obtained from both unsaturated polyethers upon extended irradiation.

When a photoinitiator is added, UV cross-linking of the unsaturated polyethers can be optimized, giving a higher gel content after shorter irradiation times (Table III). The photoinitiator, benzophenone, forms radicals by abstracting hydrogen in the excited state. To initiate cross-linking of the unsaturated polyethers, it is essential that these radicals be able to abstract hydrogen from unsaturated polyether chains or add to double bonds with sufficient efficiency to produce macroradicals. The data in Table III demonstrate the dependence of the gel content on the benzophenone concentration. The UV cross-linking of the symmetrical unsaturated polyethers was carried out at 75 °C, which is above the melting point of the polymer.[1] To obtain a gel content of around 90% after 30 min, 10.8 wt % benzophenone is needed. Thus, the presence of a photoinitiator allows faster and more complete cross-linking than can be achieved for pure polymer.

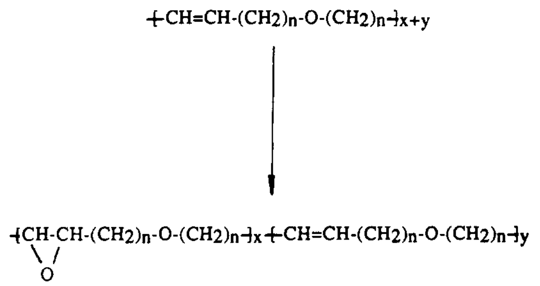

Figure 2. Epoxidation of the symmetrical unsaturated polyethers, $[-CH{=}CH(CH_2)_nO(CH_2)_n-]_x$, where n = 3 or 4.

Thermal Cross-Linking. We have found that the unsaturated polyethers can also be cross-linked thermally. The gel contents of the cross-linked polymer, determined from the residual weight after extraction with benzene (see the Experimental Section), are listed in Table IV. At the temperatures used for these experiments, two reactions are possible: cross-linking and degradation. However, the reaction rate of cross-linking is apparently much faster at temperatures of 156–255 °C than the rate of degradation. This is in agreement with previous TGA experiments in which no weight loss was observed until the temperature reached 300 °C.[1] In the samples treated at 255 °C for 1 h, the amount of gel formed reached 82%.

Chemical Modification of the Symmetrical Unsaturated Polyethers. Epoxidation and Conversion to Chlorohydrin Groups. The epoxidation of the symmetrical unsaturated polyethers was accomplished with 3-chloroperbenzoic acid (CPBA) (Figure 2) using the same procedure as for the epoxidation of *cis*-1,4-polybutadiene.[6,7] The epoxidation of the ring-opening metathesis polymerization product of deltacyclene has been described recently.[8] However, only 10–15% of the olefins could be epoxidized by CPBA before polymer decomposition occurred. Up to 50% of the olefins in the ADMET polyethers were epoxidized with no apparent decomposition. The epoxidized polymers were characterized by elemental analysis, IR, and ^1H and ^{13}C NMR spectroscopy and also by elemental analysis and HBr titration.

The ^1H NMR spectrum of the partially epoxidized polyether is shown in Figure 3. The signals at 2.75 and 3.20 ppm can be attributed to trans and cis protons H^a, in the epoxidized unit $-CH_2^{b}\overline{CH^{a}CH^{a}O}CH_2^{b}-$. The addition is stereospecific; i.e., a trans polymer gives a trans epoxide and a cis polymer a cis epoxide. No selectivity is apparent for the epoxidation of cis relative to trans olefins. H^b protons give the signal at 1.52 ppm, which is partially covered by the $-CH_2-$ signals from the polymer. The signal at 5.39 ppm corresponds to the remaining internal olefinic protons. In the ^{13}C NMR spectrum of the partially epoxidized polyether $[-CH{=}CH(CH_2)_4O(CH_2)_4-]_x$, new signals were found at 58.57 and 56.96 ppm, which can be attributed to the trans and cis H^a protons in the epoxidized unit, respectively. The signals at 130.0 ppm and 129.6 ppm correspond to the internal olefinic protons.

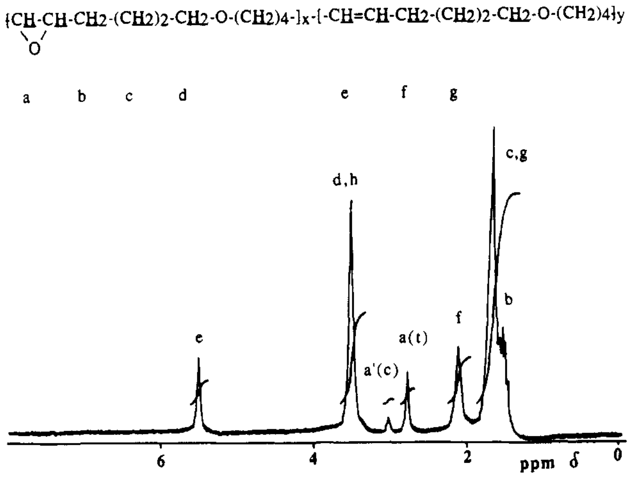

Figure 3. ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of the polymer $[-CHCHO(CH_2)_4O(CH_2)_4-]_x[-CH{=}CH(CH_2)_4O(CH_2)_4-]_y$ containing 51 mol % epoxide groups.

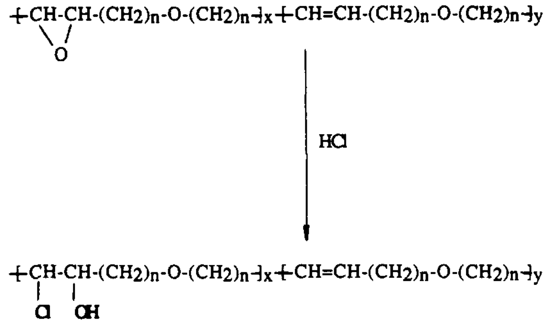

Figure 4. Chlorohydrination of the epoxidized polyether, $[-CHCHO(CH_2)_nO(CH_2)_n-]_x[-CH{=}CH(CH_2)_nO(CH_2)_n-]_y$ (n = 3 or 4).

Table V
Epoxidation of the Symmetrical Unsaturated Polyethers, $[-CH{=}CH(CH_2)_nO(CH_2)_n-]_x$, with 3-Chloroperbenzoic Acid in $CHCl_3$, 25 °C

	epoxide group, %		
polymer (n)	calcd[a]	^{1}H NMR[b]	HBr titration[c]
3	19.3	19.0	18.2
4	50.3	51.0	50.0

[a] Calculated from the epoxidation reaction (Figure 2). [b] Calculated from the ^{1}H NMR spectrum by integration of the signals at 2.75 and 3.20 ppm (trans and cis protons H^a in the epoxidized unit $-CH_2CH^aCH^aOCH_2-$) and from the signal at 5.39 ppm (internal olefinic protons). [c] See the Experimental Section.

These values are in agreement with data from the ^{13}C NMR study of epoxidized 1,4-polyisoprene and 1,4-polybutadiene.[6,9] Analysis of the partially epoxidized unsaturated polyethers by several methods (Table V) indicates that the epoxidation with CPBA was quantitative. The elemental analysis agrees precisely with the values that were calculated for the partially epoxidized polymer (see the Experimental Section). Also, the results obtained from ^{1}H and ^{13}C NMR and IR spectroscopy confirm the structural assignment of these modified polyethers.

The epoxide groups on the modified polyethers (Figure 4) were converted to chlorohydrin units by adding a 200% excess (based on epoxide content) of concentrated HCl to a THF solution of the epoxidized polyether at room temperature.

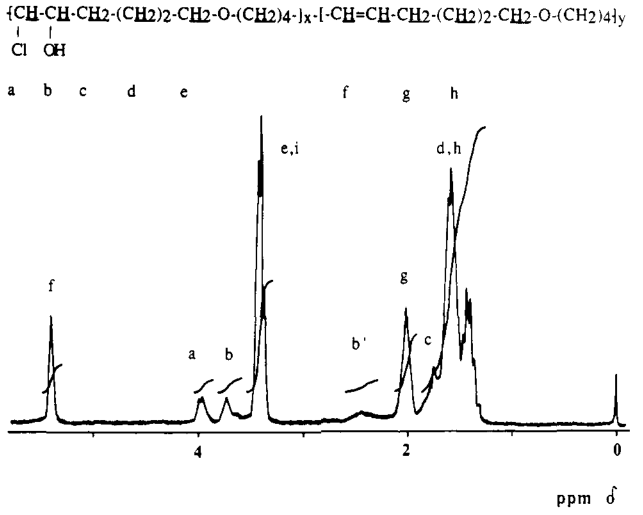

Figure 5. ^{1}H NMR (200-MHz) spectrum of the modified symmetrical unsaturated polyether, $[-C(Cl)HC(OH)H(CH_2)_4O(CH_2)_4-]_x[-CH{=}CH(CH_2)_4O(CH_2)_4-]_y$, in $CDCl_3$, at room temperature, containing 50 mol % chlorohydrin groups.

Table VI
Epoxide Groups Converted to Chlorohydrin

chlorohydrinated polymer (n)	chlorohydrin group, %	
	calcd	found
3	19.3	19.0
4	50.3	50.3

[a] Calculated from the ^{1}H NMR spectrum.

After reaction with HCl, the ^{1}H NMR (Figure 5) signals at 2.75 and 3.20 ppm, characteristic of the epoxide group, disappeared, to be replaced by two new signals at 3.92 and 3.72 ppm. These new peaks can be attributed to protons on carbon atoms with Cl and OH groups, respectively. The ^{13}C NMR spectrum displayed two new signals at 68.6 and 74.5 ppm, corresponding to the carbon atoms bearing OH and Cl substituents, respectively.

Analysis of the chlorohydrinated polyethers (Table VI) together with results from ^{1}H and ^{13}C NMR and IR spectroscopy and elemental analysis (see the Experimental Section) demonstrates that the conversion of the epoxide to chlorohydrin is also quantitative.

Conclusion

It is clear from these preliminary results that there is a great potential for the modification of the unsaturated polymers synthesized by ADMET. The olefinic groups can be cross-linked either thermally or photochemically. They can also be quantitatively modified by epoxidation and subsequent conversion of epoxides to chlorohydrin groups. Further characterization of the polyether gels and the chemically modified polyethers is currently being investigated and will be reported separately.

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References and Notes

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Registry No. $CH_2{=}CH(CH_2)_3O(CH_2)_3CH{=}CH_2$ (homopolymer), 139071-10-6; $CH_2{=}CH(CH_2)_4O(CH_2)_4CH{=}CH_2$ (homopolymer), 135311-00-1; 3-chloroperbenzoic acid, 937-14-4; benzophenone, 119-61-9.