(9) See, for example: Ditto, S. R.; Card, R. J.; Davis, P. D.; Neckers, D. C. *J. Org. Chem.* **1979,** *44,* 894.
(10) Searle, R.; Williams, J. L. R.; Doty, J. C.; DeMeyer, D. C.; Merrill, S. H.; Laakso, T. M. *Makromol. Chem.* **1967,** *107,* 246.
(11) Millar, J. R. *J. Chem. Soc.* **1960,** 1311.
(12) Ranby, B.; Rabek, F. J. "Photodegradation, Photooxidation and Photostabilization of Polymers"; Wiley: New York, 1976.
(13) See, for example: Neckers, D. C. "Mechanistic Organic Photochemistry"; Reinhold, New York, 1967.
(14) Hammond, G. S.; Moore, W. M.; Foss, R. P. *J. Am. Chem. Soc.* **1961,** *83,* 2789.
(15) Tinnemans, A. H. A.; Neckers, D. C. *J. Org. Chem.* **1977,** *42,* 2374.
(16) Walling, C.; Gibian, M. J. *J. Am. Chem. Soc.* **1965,** *87,* 3413.

Copolymerization of Ethyl Glycidate with Cyclic Ethers by Organometallic Initiators

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ABSTRACT: Ethyl glycidate (EG) was copolymerized with propylene oxide (PO), 1-butene oxide (BO), and oxetane by organoaluminum initiators to produce high molecular weight polyethers with pendant ester groups. The ternary initiator system $AlEt_3/H_2O/AcAc$ (1/0.3/0.5) gave the best results with PO and BO, yielding polymers of η_{inh} 0.6–4.3 dL/g containing up to 4 mol % of EG units. EG was relatively unreactive in these copolymerizations; the concentration of EG in the copolymer was always significantly less than that in the feed, and increased EG feed concentrations depressed both the rate of polymerization and the product molecular weight. Oxetane copolymers containing ca. 1 mol % of EG units were obtained with η_{inh} 0.7–1.0 dL/g, along with oligomeric products, using a similar initiator system. Conversion of these polyethers into novel ionomers was demonstrated: treatment of the ester with NaOH gave the polymeric sodium salt, which was further converted to the free acid by reaction with glacial acetic acid in dioxane.

Introduction

The incorporation of ionic groups into organic polymers can produce remarkable effects on physical and mechanical properties.[1] Particularly successful has been the preparation of polyolefin ionomers containing pendant metal carboxylate groups. Despite the technical and commerical success of these materials, though, there remain unanswered significant questions concerning the solid-state morphologies of ion-containing polymers; ionic groups could be embedded in a nonpolar hydrocarbon matrix to aggregate, or "cluster", and, in fact, evidence for cluster formation has been obtained through infrared and X-ray techniques.[2,3]

But what if the polymer backbone (polymer "matrix") can interact more favorably with ("solvate") the ionic groups? What kinds of morphologies and physical properties will then be observed? One means of providing this kind of solvation is to incorporate into the polymer backbone heteroatoms (or "donor" atoms) which interact strongly with metal cations. In particular, one might expect the incorporation of oxygen atoms into the chain to accomplish this, by analogy to the solvation of metal cations by crown ethers. Ionization may then affect polymer properties in a manner quite different from that observed in olefin polymers. In order to investigate this possibility, we have undertaken the preparation of polyethers with pendant carboxylate groups and, in particular, we have focused on the preparation of homopolymers and copolymers of ethyl glycidate (EG).[4-9] Ethyl glycidate was previously shown to polymerize with an aluminum alkyl/water initiator system to a crystalline homopolymer.[10] The initiator system which was the basis of this paper was reported in detail in a separate communication.[11] Carboxyl-modified polyethers were also made by substitution reactions on polyethers, particularly on polymers and copolymers of epichlorohydrin.[12]

In recent papers, we have described the copolymerization of EG with trioxane[4-7] and tetrahydrofuran,[8,9] using cationic initiators. The preparation of low molecular weight EG homopolymer by cationic polymerization has also been reported.[8,9] In all of these experiments, EG was found to be a rather unreactive monomer, probably as a result of the electron-withdrawing inductive effect of the carboethoxy group. The adverse effect of the electron-withdrawing group of the epoxy ring and its effect in copolymerization have been reported in the unfavorable copolymerization of epichlorohydrin with ethylene oxide.[13] EG was incorporated into poly(oxymethylenes) (POM) via bulk, solution, or gas-phase techniques, and terpolymerization with trioxane and 1,3-dioxolane was also accomplished, but in all cases, the resulting polymers contained only low percentages of carboxylate groups. In copolymerization with THF, an interesting 1:2 EG–THF copolymer was formed under conditions precluding THF homopolymerization, indicating that homopropagation of EG is very slow under cationic conditions.[9]

In the present paper, we report the copolymerization of EG with several oxiranes and with oxetane, using organometallic initiators. Conversion of the resulting copolymers to the salt and acid forms is also described briefly.

Experimental Section

Materials. Ethyl glycidate (EG) was prepared from ethyl acrylate by the method of Emmons and Pagano[14] and stored in vacuum-sealed ampules at room temperature in the dark. Before use, ethyl glycidate was dried overnight over freshly activated molecular sieves.

Other monomers were twice distilled from CaH_2 under dry nitrogen and used immediately: propylene oxide (PO) (bp 34 °C), 1-butene oxide (BO) (bp 63 °C), epichlorohydrin (ECH) (bp 116

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Table I
Copolymerization of Ethyl Glycidate by $AlEt_3/H_2O/AcAc$ Initiator[a]

no.	comonomer[b]	[EG], mol %	polymn time, days	% yield	η_{inh}, dL/g	EG in copolymer, mol %
1	PO		4	63	4.6	
2	PO	5	14	82	3.9	0.4
3	PO	10	14	59	2.6	0.8
4	PO	20	21	38	2.9	1.8
5	PO	30	31	35	0.89	3.3
6	BO	5	10	43	3.9	0.5
7	BO	10	10	29	4.3	0.9
8	BO	20	28	33	2.8	3.2
9	BO	30	38	28	0.64	3.7
10	ECH	20	gel			
11	PGE	10	gel			
12	IBO	5	no polymer			
13	IBO	10	no polymer			
14	oxetane[c]	5	7 days at 55 °C	55	0.74	0.7
15	oxetane[c]	10	14 days at room temp	39	1.0	1.0

[a] Initiator concentration 2 mol %, 1:0.3:0.5 $AlEt_3/H_2O/AcAc$, room temperature unless otherwise noted. [b] PO = propylene oxide, BO = 1-butene oxide, ECH = epichlorohydrin, PGE = phenyl glycidyl ether, IBO = isobutylene oxide. [c] 1/0.5/0.5 $AlEt_3/H_2O/AcAc$.

°C), isobutylene oxide (IBO) (bp 52 °C). Phenyl glycidyl ether [bp 91 °C (3 mm)] and oxetane (bp 46 °C) were distilled from CaH_2 immediately before use.

Triethylaluminum was obtained as a 15% solution in *n*-heptane and was used as received. Acetylacetone (AcAc) was distilled [bp 53 °C (42 mm)] and stored in the dark until use.

Benzene was twice distilled from sodium, under dry nitrogen. Dioxane was distilled from CaH_2, under dry nitrogen.

Measurements. Infrared spectra were recorded on a Hitachi EPI G31 spectrophotometer. Samples were deposited on NaCl from benzene solution or were prepared as thin smears on NaCl. NMR spectra were recorded at 220 MHz on a Varian HR-220 spectrometer.

Inherent viscosity measurements were carried out at 30 °C, in benzene, using a modified Ubbelodhe viscometer with a glass frit for filtration of the sample solutions. Sample concentration was 0.5 g/dL.

Initiator Preparation ($AlEt_3/H_2O/AcAc$) (1/0.3/0.5). A dry, nitrogen-filled flask with a side arm was charged with 10 mL of a 15% w/v solution of $AlEt_3$ (13.1 mmol) in *n*-heptane and fitted with a pressure-equalizing addition funnel. The flask was then cooled in ice–water while a mixture of 0.07 mL of H_2O (3.9 mmol) and 10 mL of dry ether was added via the funnel, with stirring, over a period of 20 min. Addition of this mixture caused formation of a white precipitate. AcAc (0.67 mL, 6.6 mmol) in 10 mL of dry ether was then added in a similar fashion, maintaining cooling and nitrogen flow. The faintly yellow solution was allowed to warm to room temperature overnight and was then stored in the dark at −20 °C until use.

Polymerizations. Given below are the general procedures used in polymerization experiments; specific experiments are listed in Table I.

Polymerization under Nitrogen. A dry, nitrogen-filled polymerization tube was charged with benzene, monomers, and catalyst, cooled in dry ice–ethanol, and sealed under nitrogen. All transfers were made with nitrogen-filled syringes. The polymerization mixture was allowed to stand at room temperature for the desired period, and then the tube was cooled in dry ice–ethanol and opened. The tube contents were dissolved in 100–150 mL of benzene, and the benzene solution was washed with 120-mL portions of 0.1 N HCl and water (twice). The benzene was then removed by freeze-drying, and the yield and inherent viscosity of the polymer were determined.

Vacuum Technique. A polymerization reactor fitted with a side arm with a stopcock was flamed out and cooled under vacuum. PO and benzene were transferred to the reactor by trap-to-trap distillation. The reactor was filled with nitrogen, EG and initiator were introduced from dry syringes, and the reactor was sealed under vacuum. After the desired polymerization time at room temperature, the polymer was isolated and characterized as above.

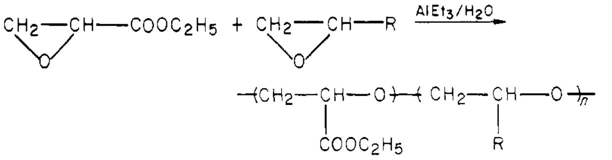
Hydrolysis of Ethyl Glycidate/Propylene Oxide Copolymer. A sample (500 mg) of a copolymer containing ca. 1 mol % EG was dissolved in 40 mL of dioxane. A 4 N aqueous solution of NaOH (6.25 mL, 1.00 g of NaOH) was then added, causing some turbidity in the reaction mixture. Nitrogen was bubbled through the mixture for 15 min, and the reaction flask was then fitted with a reflux condenser and immersed in an oil bath at 120 °C. The mixture was heated under a nitrogen blanket, with vigorous stirring, for 1 h. After the mixture was cooled to room temperature, the polymer was recovered by portionwise addition of the reaction mixture to 250 mL of gently stirred distilled water, filtered, and washed with three 25-mL portions of distilled water. Drying for 2 days at 56 °C (0.02 mm) over P_2O_5 gave 370 mg (74%) of white, elastic polymer. The ester stretching vibration at 1740 cm^{-1} was completely absent and was replaced by the carboxylate C=O stretching band at 1610 cm^{-1}.

Preparation of the Acid Form of Ethyl Glycidate/Propylene Oxide Copolymer. The sodium salt prepared as described above (200 mg) was dissolved in 5 mL of dioxane with vigorous stirring. Nitrogen was bubbled through the mixture for 1 h, and 0.5 mL of acetic acid was added via syringe. The colorless, homogeneous mixture was stirred under nitrogen, at room temperature, for 2.5 h. The polymer was recovered by portionwise addition of the reaction mixture to 125 mL of rapidly stirred distilled water; the polymer was then transferred to fresh distilled water and kneaded with a spatula. The white elastic polymer was then dried [56 °C (0.02 mm), P_2O_5] to a constant weight, yield 188 mg (94%). The acid C=O stretching vibration at 1735 cm^{-1} was prominent, but a small absorption at 1610 cm^{-1} remained.

Results and Discussion

Copolymerization of EG with several cyclic ethers by organometallic initiators gave high molecular weight polyethers with pendant ester groups. These polyethers serve as intermediates in the preparation of novel ionomer systems: they can be converted to sodium salts by reaction with NaOH and then to the polymeric acids by further treatment with glacial acetic acid.

Copolymerization of Ethyl Glycidate. The results of copolymerization of EG with several cyclic ethers, using $AlEt_3/H_2O/AcAc$ initiator systems, are summarized in Table I (eq 1). These $AlEt_3$ initiators were found to be most useful in these copolymerizations; $ZnEt_2/H_2O$, $ZnEt_2/CH_3NO_2$, $FeCl_3$/PO and Al(O-*i*-Pr)$_3$ were used with less success, as described below. All copolymerizations were carried out in sealed tubes, under nitrogen or vacuum and at room temperature unless noted otherwise in Table I. Also listed in Table I is a "control" homopolymerization of propylene oxide (experiment no. 1) used to provide a



$$CH_2\text{—}CH\text{—}COOC_2H_5 + CH_2\text{—}CH\text{—}R \xrightarrow{AlEt_3/H_2O} \text{—}(CH_2\text{—}\underset{COOC_2H_5}{CH}\text{—}O)\text{—}(CH_2\text{—}\underset{R}{CH}\text{—}O)_n\text{—} \quad (1)$$

R = CH_3, C_2H_5, CH_2Cl, CH_2—O—Ph

check on initiator activity and polymerization technique.

Six comonomers were used in these experiments: propylene oxide (PO), 1-butene oxide (BO), epichlorohydrin (ECH), phenyl glycidyl ether (PGE), isobutylene oxide (IBO), and oxetane. Primary attention was focused on copolymerizations with PO or BO with EG (experiments 2–9), for which a range of monomer feed compositions was investigated; column 6 of Table I gives the inherent viscosities of these copolymers. It is clear from these data that very high molecular weight copolymers were obtained. For example, an inherent viscosity of 3.9 dL/g (experiments 2 and 6) corresponds to a molecular weight of approximately 10^6, based on the viscosity–molecular weight relations for homopolymers of PO and BO.[15] Molecular weights of some of the copolymers were checked by gel permeation chromatography in order to verify the results of the viscosity determination; in all cases the two techniques were in good agreement with data known for copolymers of PO and BO with functional comonomers. From the GPC data we have all indications that the copolymers are true copolymers and not mixtures of homopolymers, and the molecular weight distribution shows polydispersity normally expected from such copolymers. These copolymers were colorless elastomers, and at these high molecular weights, the materials were quite tough.

EG is quite unreactive in these copolymerizations. This is indicated by the copolymer compositions given in the last column of Table I and by the observed decreases in polymerization rate and product molecular weight as the feed content of EG was increased. The composition data indicate that the copolymers obtained were very poor in EG content as compared to the EG content of the monomer feed mixture; for example, with 30 mol % EG in the feed, an EG/PO copolymer containing only 3–4 mol % of EG units was obtained.

Because the content of EG in the copolymers was so low, it was difficult to obtain precise values of copolymer compositions. The most sensitive technique proved to be measurement of the intensity of the ester carbonyl absorption at 1740 cm^{-1} in the infrared spectrum. Figure 1 shows the infrared spectrum of an EG/PO copolymer prepared with 20 mol % of EG in the monomer feed mixture (experiment 4). The C═O stretching absorption is unmistakable, and that it is not a result of oxidation of the polymer was proven by the complete absence of such an absorption in the spectrum of PO homopolymer, even after 2 months of storage. The intensity of the 1740-cm^{-1} band (relative to that at 1450 cm^{-1}) increased essentially linearly with the EG feed concentration.

The ratio of absorption intensity at 1740 cm^{-1} to that at 1450 cm^{-1} was thus used to determine relative copolymer compositions. Absolute compositions were obtained from the 220-MHz ^{1}H NMR spectrum of one copolymer from each series; i.e., the IR technique was "calibrated" by using 220-MHz ^{1}H NMR spectroscopy. Figure 2 shows the ^{1}H NMR spectrum which corresponds to the IR spectrum in Figure 1 (copolymer no. 4). The methyl protons of the carboethoxy group of EG appear as a triplet at 1.23 ppm; although the signal is weak, it is cleanly resolved from the PO methyl doublet at 1.1 ppm. By careful integration of the spectrum, the EG content of the copolymer was determined to be 3.3 mol %. The compositions of the other EG/PO copolymers were then determined from their infrared spectra, and a similar procedure was used for BO and oxetane copolymers.

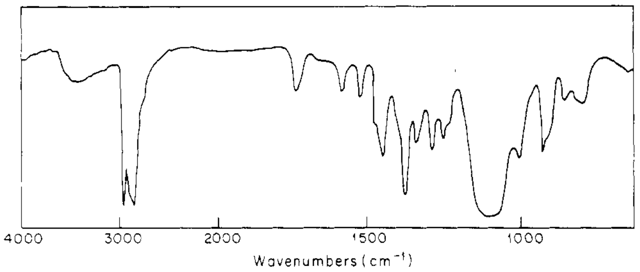


Figure 1. Infrared spectrum of a copolymer of EG and PO, prepared with 20 mol % EG in the monomer feed mixture (experiment 4 in Table I).

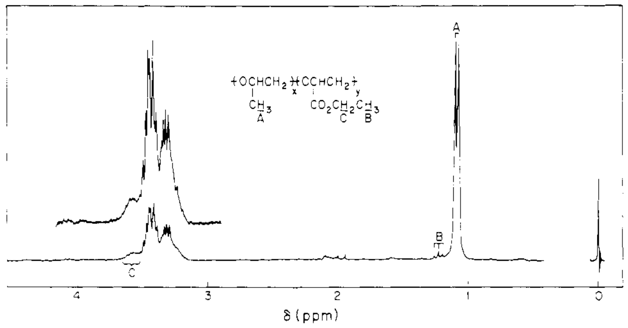


Figure 2. 220-MHz ^{1}H NMR spectrum of a copolymer of EG and PO, prepared with 20 mol % EG in the monomer feed mixture (experiment 4 in Table I).

Copolymerization of EG with three additional oxiranes was investigated briefly. Copolymerizations with ECH and with PGE produced significant fractions of benzene-insoluble polymers. It seems likely that this was a result of crystallization of a stereoregular polymer fraction in each case, but we did not pursue this point. It is known that both ECH and PGE form substantial fractions of crystalline isotactic homopolymers with modified organoaluminum initiators similar to that employed in this work.[9] These results indicate unfavorable copolymerizations of EG with ECH and PGE. We did not observe any polymer formation in an attempted copolymerization of EG and IBO using the $AlEt_3/H_2O/AcAc$ (1/0.3/0.5) initiator. Successful homopolymerization of IBO by organometallic initiators has been reported.[16,17]

Copolymerization of EG with oxetane was accomplished by using an $AlEt_3/H_2O/AcAc$ (1/0.5/0.5) initiator system (experiments 14 and 15). Although the use of organoaluminum initiators in oxetane polymerization has not been extensive, using these systems, Vandenberg and Robinson[18,19] have reported successful copolymerizations of oxetane with a variety of oxiranes and Koinuma and Hirai[20] have prepared aliphatic polycarbonates. EG was found not to be very reactive in copolymerization with oxetane; the copolymers produced were very poor in EG compared to the monomer feed mixture. The copolymers were obtained as white, leathery solids, with molecular weights of approximately 50 000, based on inherent viscosity measurements.[8] Copolymerization was accompanied by the formation of sublimable colorless needles, whose ^{1}H NMR spectrum (δ 1.7, quintet, 2 H; δ 3.4, triplet, 4 H) is precisely that expected for a cyclic oligomer of oxetane. Rose has reported that polymerization of oxetane by BF_3 is accompanied by formation of cyclic tetramer,[21] whose melting point (70 °C) agrees well with that which we ob-

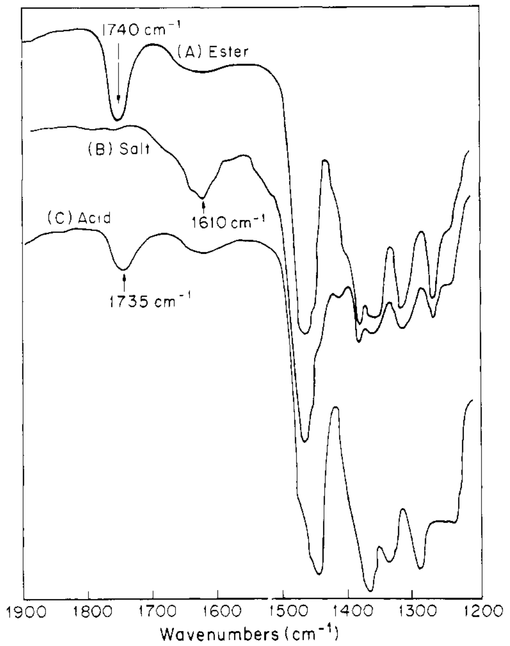
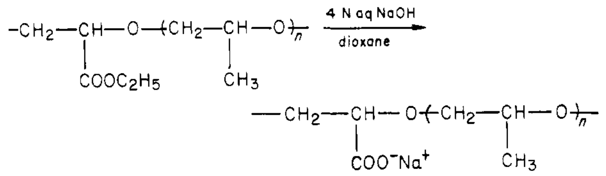


Figure 3. Infrared spectra of a copolymer of EG and PO: (A) as prepared; (B) after treatment with NaOH in aqueous dioxane; (C) after further treatment with acetic acid in dioxane.

served for our byproduct (73–76 °C). The copolymerization systems using organoaluminum initiators thus seem to involve two types of catalyst sites, coordination[11] and cationic. The production of cyclic tetramer from oxetane is taken to indicate the latter catalyst nature.

Homopolymerization of EG was also attempted with $ZnEt/H_2O$, $ZnEt_2/CH_3NO_2$, $Al(O\text{-}i\text{-}Pr)_3$ and $AlEt_3/H_2O/AcAc$ initiators, but only the $AlEt_3$ system produced any homopolymer. The other initiators, including the $FeCl_3/PO$ system, were also ineffective in copolymerization of EG with ethylene oxide or PO.

Analysis of Copolymers. Selected polyethers containing pendant carboethoxy groups were treated with NaOH in aqueous dioxane to produce the polymeric sodium salts (eq 2). Heating of the turbid reaction mixture



$$-CH_2-\underset{\displaystyle COOC_2H_5}{\underset{|}{CH}}-O-\!\!\left(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O\right)_{\!n}\!- \xrightarrow[\text{dioxane}]{\text{4 N aq NaOH}} -CH_2-\underset{\displaystyle COO^-Na^+}{\underset{|}{CH}}-O\!\left(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O\right)_{\!n}\!- \quad (2)$$

for 1 h at reflux was sufficient to prepare a polymer that was completely without the 1740-cm^{-1} ester carbonyl absorption in the infrared spectrum (Figure 3B). The ester band was replaced by a new absorption at 1610 cm^{-1}, due to the carboxylate anion of the sodium salt. Treatment of the sodium salt with excess acetic acid in homogeneous solution in dioxane then provided the free acid form of the copolyether. As shown in Figure 3C, the IR spectrum of the free acid shows the carboxyl band at 1735 cm^{-1}, along with a small absorption at 1610 cm^{-1}, probably due to residual carboxylate. These IR spectral changes are in excellent agreement with those observed in earlier work on EG/trioxane copolymers.[6]

Conclusions

Polyethers with pendant carboethoxy groups may be prepared by copolymerization of EG with oxiranes and with oxetane, using organometallic initiators. The most effective initiators appear to be modified $AlEt_3$ systems, which produce copolymers of very high molecular weight. EG is rather unreactive in these copolymerizations, and the copolymers obtained in this way are poor in ethyl glycidate, compared to the monomer feed. Conversion of the copolymers to novel polyether ionomers can be accomplished by hydrolysis of the carboethyoxy groups with aqueous sodium hydroxide. Characterization of the physical and mechanical properties of these new materials will be reported separately.

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References and Notes

(1) R. H. Rees, British Patent 1011981 (1966).
(2) W. J. MacKnight, L. W. McKenna, B. E. Read, and R. S. Stein, *J. Phys. Chem.*, **72**, 1192 (1968).
(3) B. W. Delf and W. J. MacKnight, *Macromolecules*, **2**, 309 (1969).
(4) K. V. Martin and O. Vogl, U. S. Patent 3284411 (1966).
(5) K. V. Martin, U.S. Patent 3316218 (1968).
(6) L. DeMejo, W. J. MacKnight, and O. Vogl, *Polymer*, **19**, 959 (1978).
(7) L. DeMejo, W. J. MacKnight, and O. Vogl, *Polym. J.*, 11, 15 (1979).
(8) D. Tirrell, O. Vogl, T. Kobayashi, S. Kobayashi, and T. Saegusa, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20**(1), 794 (1979).
(9) T. Saegusa, T. Kobayashi, S. Kobayashi, S. Lund-Couchman, and O. Vogl, *Polym. J.*, 11, 463 (1979).
(10) E. J. Vandenberg, U.S. Patent 3106549 (1963).
(11) E. J. Vandenberg, *J. Polym. Sci., Part A-1*, 525 (1969).
(12) E. J. Vandenberg, U.S. Patent 3417036 (1967).
(13) E. J. Vandenberg, *Pure Appl. Chem.*, **48**, 300 (1976).
(14) W. D. Emmons and A. S. Pagano, *J. Am. Chem. Soc.*, **77**, 89 (1955).
(15) J. Brandrup and E. M. Immergut, Eds., "Polymer Handbook", 2nd ed., Wiley, New York, 1975, pp iv–24.
(16) E. J. Vandenberg, *J. Polym. Sci.*, **47**, 486 (1960).
(17) S. Kambara and A. Takahashi, *Makromol. Chem.*, **58**, 226 (1962).
(18) E. J. Vandenberg, *J. Polym. Sci.—Polym. Chem. Ed.*, **10**, 329 (1972).
(19) E. J. Vandenberg and A. E. Robinson, *ACS Symp. Ser.*, **No. 6**, 101 (1975).
(20) H. Koinuma and H. Hirai, *Makromol. Chem.*, **178**, 241 (1977).
(21) J. B. Rose, *J. Chem. Soc.*, 542 (1956).