Hybrid Copolymerization of Alkyl Vinyl Ethers with Glycidyl Ethers

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Synopsis

Homopolymerization and copolymerization experiments of isobutyl and dodecyl vinyl ether with propylene oxide, and some glycidyl ethers have been carried out by using both conventional cationic initiators (BF_3, $BF_3 \cdot OEt_2$) and 4-chlorophenyldiazonium tetrafluoborate as cationic photoinitiator. Conventional polymerization experiments performed under vacuum at low and room temperature gave rise to a mixture of the two homopolymers, indicating that the epoxide and vinyl ethers are incompatible with respect to chemical reactivity and that apparently no hybrid copolymerization occurs. Analogous results were obtained in parallel photoinitiated polymerization experiments.

INTRODUCTION

During the last two decades considerable efforts have been devoted to the development of photocurable materials to be used in coating applications as their use could solve the economic and ecological problems related to the use of the traditional products.[1,2] Even if many such materials already find industrial application, not all the problems connected with their use have been solved. In particular, materials having very good mechanical properties like poly(ester)s, poly(amide)s, and poly(epoxide)s cannot be used unless functionalized with olefinic double bonds, as curing generally occurs by a photoinitiated radical polymerization.

It seemed therefore interesting to establish if materials such as epoxides, which are known to polymerize cationically,[3] could be conveniently used as photocurable coatings in the presence of a cationic photoinitiator. Moreover, as it is well known that addition of wax gives a glossy finish to conventional coating, we thought it was possible that photopolymerization of epoxides with long chain alkyl vinyl ethers could afford the same result without incurring the problems connected with additive migration.

The study of copolymerization of heterocycles with vinyl monomers, usually referred to as hybrid copolymerization, could be very useful in both modifying the physicochemical properties of polymeric materials derived from heterocyclic monomers and clarifying the copolymerization mechanism of monomers having different intrinsic reactivities. Alkyl vinyl ethers in fact can be polymerized by a cationic mechanism, the propagating species being carbenium ions. Most heterocycles can also be polymerized in the presence of cationic initiators, but

the accepted mechanism[4-6] assumes that in the propagating species the positive charge is located on the heteroatom and that propagation itself occurs by the nucleophilic attack of the monomer heteroatom on the carbon atom in the α position to the positive charge according to the scheme:
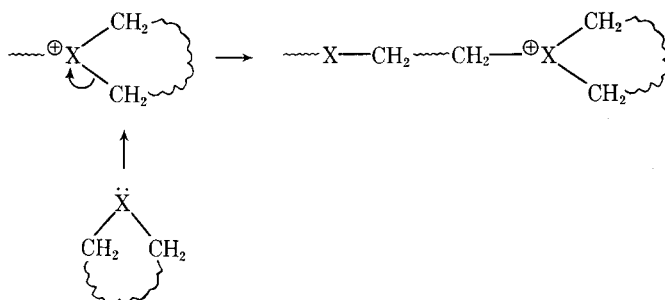
At present, however, it is not yet clear if, in the case of strained heterocycles like epoxides, propagation occurs via oxonium or carbenium ions[7] and it is still debatable if either both of them or a cation having an intermediate character act as active species.[8]

In order to obtain quasirandom copolymers, the rates of homo and cross-propagation reactions of the two comonomers must be of the same order of magnitude,[9] but this condition is not generally satisfied in the case of hybrid copolymerization as vinyl monomers are usually much more reactive than heterocycles. Accordingly, copolymerization of styrene with β-propiolactone[10,11] and 3,3-dichloromethyloxetane[12] gives only mixtures of the corresponding homopolymers whereas copolymerization of styrene with more reactive heterocycles such as 1,3-dioxolane,[13] trioxane,[14] and various epoxides[15] affords true copolymers. Block copolymers are obtained when epichlorohydrin[16] and 1,3-dioxepane[17] are polymerized with isobutyl vinyl ether, which is more reactive than styrene toward cationic initiation. To the best of our knowledge, however, data are not available on the copolymerization of alkyl vinyl ethers with glycidyl ethers.

In the present paper we wish to report on the results obtained in the conventional cationic copolymerization of alkyl vinyl ethers such as isobutyl vinyl ether (BVE) and dodecyl vinyl ether (DVE) with epoxy derivatives such as propylene oxide (PO), p-cresyl glycidyl ether (CGE), benzyl glycidyl ether (BGE), and bisphenol "A" diglycidyl ether (PGE):

BVE   DVE   PO   BGE

$$CH_2-CH-CH_2$$

CGE PGE
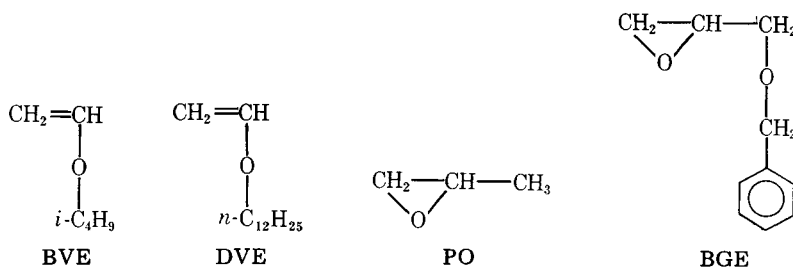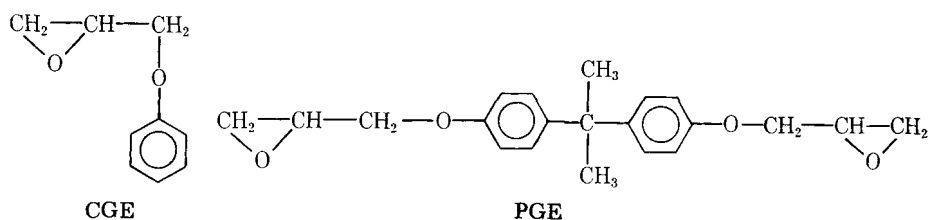
Some preliminary experiments of cationic photoinitiated homo- and copolymerization of the above monomers are also reported. Great interest, in fact, has been recently focused on a new series of cationic photoinitiators based on onium salts, which have been demonstrated to possess a high efficiency in the cationic polymerization of oxyheterocyclic compounds through the *in situ* formation of Brönsted acids.[18] In our investigation, however, we thought it more convenient to use a diazonium salt capable of giving rise, under irradiation, to a Lewis acid such as BF_3, which in turn was used as initiator in parallel experiments of conventional cationic polymerization of alkyl vinyl ethers and epoxides.

EXPERIMENTAL

Monomers

Bisphenol "A" Diglycidyl Ether[19] **(PGE).** A mixture of 111 g (0.50 mol) of bisphenol "A" [2,2-di(4-hydroxyphenyl)propane] and 197 g (2.14 mol) of epichlorohydrin were heated at 55°C; then a solution of 39 g (0.97 mol) of NaOH in 390 mL of water was added under stirring and the temperature kept at 55°C for 2 h. After cooling the organic layer was separated, and excess epichlorohydrin was removed under vacuum. A solution of 50 g (1.25 mol) of NaOH in 130 mL of water was added to the residue dissolved in 160 mL of acetone and 25 mL of water, and the mixture was heated at 65°C for 1.5 h. After cooling the organic layer was washed with water, dried over sodium sulfate, and distilled to yield 143 g (62.5%) of product having bp 240°C/0.5 mm.

^{1}H-NMR (CCl$_4$): δ 6.8 (m, 8 H, aromatic protons), 4.0 (m, 4 H, CH$_2$—O), 3.1 (m, 2 H, epoxy CH), 2.6 (m, 4 H, epoxy CH$_2$), and 1.6 ppm (s, 6 H, CH$_3$).

IR (liquid film): 3050, 3040, 2960, 2925, 2880, 1510, 1460, 1250, 1195, 1040, 910, 830, and 770 cm^{-1}.

***p*-Cresyl Glycidyl Ether**[20] **(CGE).** By following the procedure reported above and starting from 50.0 g of *p*-cresol, 55.2 g (72.8%) of product having bp 97°C/2 mm were obtained.

^{1}H-NMR (neat): δ = 6.8 (m, 4 H, aromatic protons), 3.8 (m, 2 H, CH$_2$—O), 3.2 (m, 1 H, epoxy CH), 2.6 (m 2 H, epoxy CH$_2$), and 2.2 ppm (s, 3 H, CH$_3$).

IR (liquid film): 3060, 3030, 3000, 2920, 2870, 1580, 1510, 1450, 1280, 1240, 1040, 920, 820, and 770 cm^{-1}.

Benzyl Glycidyl Ether (BGE). 354 g (3.85 mol) of epichlorohydrin were slowly added over 6 h to a mixture of 1041 g (9.64 mol) of benzyl alcohol and 10 mL of 96% H$_2$SO$_4$ heated at 70°C and then BaCO$_3$ was added to neutrality. The mixture was left at 70°C 3 h more, and after cooling the precipitate was filtered off and the filtrate distilled under vacuum; 157 g of product having bp 87°C/0.5 mm were obtained. After dissolution in 700 mL of diethyl ether the product was

slowly added to a solution of 170 g (4.25 mol) of NaOH in 300 mL of water. The organic layer, washed with water and dried over sodium sulfate, after removal of the solvent was distilled to yield 41.0 g of product having bp 93°C/0.4 mm.

^{1}H-NMR (neat): δ 7.2 (s, 5 H, aromatic protons), 4.4 (s, 2 H, benzylic protons), 3.4 (m, 2 H, CH$_2$—O), 3.0 (m 1 H, epoxy CH), and 2.6 ppm (m 2 H, epoxy CH$_2$).

IR (liquid film): 3060, 3030, 3000, 2920, 2850, 1600, 1450, 1380, 1250, 1160, 1090, 910, 800, 740, and 690 cm^{-1}.

Dodecyl Vinyl Ether (DVE) (bp 74°C/0.3 mm) was prepared in 27% yield by direct vinylation of 1-dodecanol according to Reppe.[21]

^{1}H-NMR (neat): δ 6.4 (2d, 1 H, one vinyl proton), 4.0 (2d, 1 H, one vinyl proton), 3.9 (2d, 1 H, one vinyl proton), 3.6 (t, 2 H, CH$_2$—O), 1.4 (s, 20 H, methylene groups), and 0.9 ppm (t, 3 H, methyl group).

IR (liquid film): 3120, 3080, 2920, 2850, 1645, 1600, 1470, 1200, 1070, 960, 810, and 720 cm^{-1}.

Isobutyl Vinyl Ether (BVE) and Ethyl Vinyl Ether (EVE). The commercial products were distilled over Na/K under dry nitrogen.

Propylene Oxide (PO). The commercial product was distilled over CaH$_2$ under dry nitrogen.

Catalysts

4-Chlorophenyldiazonium Tetrafluoborate.[22] To 31.8 g (0.25 mol) of 4-chloroaniline in 126 mL of 18% HCl cooled at 0°C, a solution of 18.3 g (0.26 mol) of sodium nitrite in 37.5 mL of water and a solution of 38.0 g (0.35 mol) of sodium tetrafluoborate in 75 mL of water were slowly added in that order. The resulting solution was stirred at 0°C for 2 h. The precipitate, washed with water at 0°C, methanol, and diethyl ether, was dried under vacuum to yield 47.3 g (83.6%) of product as yellow crystals.

TABLE I
Homopolymerization of CGE, BGE, PO, BVE, and DVE in the Presence of Cationic Catalysts

Run	Monomer (type)	Catalyst (type)	Molar ratio monom./catal.	Temp (°C)	Duration (h)	Conv. (%)
C1	CGE	BF$_3$	30	−78	48	55.7
C2				20	96	90.7
B1	BGE	BF$_3$	30	−78	20	83.1
B2				20	24	80.1
P1[b]				−78	24	0.0
P2[b]	PO	EtAlCl$_2$	30	20	720	5.7
P3[b]		BF$_3$·OEt$_2$		130	8	49.3
I1			50	−90	24	24.5
I2				−78	4	57.1
I3	BVE	BF$_3$	250	20	3	64.8
I4[c]				0	6	90.3
D1	DVE	BF$_3$	50	−45	5	89.3
D2				20	8	96.8

The table header "Polymerization conditions[a]" spans the Monomer, Catalyst, Molar ratio, Temp, and Duration columns.

[a] 8 mmol of monomer in 5 mL of dichloromethane if not otherwise stated.
[b] In toluene (5 mL).
[c] In nitrobenzene (5 mL).

TABLE II

Fractionation of Poly(glycidyl Ether)s and Poly(alkyl Vinyl Ether)s by Extraction with Boiling Methanol[a]

| Polymer | | Fraction 1 | | | Fraction 2 | | |
Type	Run	wt %	$\overline{M_n} \times 10^{-3}$ [b]	$\overline{DP_n}$	wt %	$\overline{M_n} \times 10^{-3}$ [b]	$\overline{DP_n}$
Poly(cresyl	C1	82	0.80	5	18	7.5	46
glycidyl ether)	C2	96	1.00	6	4	3.3	24
Poly(benzyl	B1	100	0.60	4	0	—	—
glycidyl ether)	B2	66	0.85	5	34	4.2	26
	I1	4	0.72	7	96	13.0	130
Poly(isobutyl	I2	1	0.63	6	99	12.0	120
vinyl ether)	I3	5	0.56	6	95	11.0	110
	I4	9	0.44	4	91	5.1	51
Poly(dodecyl	D1	0	—	—	100	12.4	59
vinyl ether)	D2	0	—	—	100	20.0	95

[a] Fraction 1: soluble in boiling methanol; Fraction 2: residue to the extraction with boiling methanol.

[b] Determined by osmometry in 1,2-dichloroethane at 37°C.

Boron Trifluoride (BF$_3$) was obtained by thermal decomposition at 160°C under vacuum of 4-chlorophenyldiazonium tetrafluoborate.[23] The decomposition product was purified from 4-chloro-1-fluorobenzene by cooling at −78°C and then trapped at the liquid nitrogen temperature. The product was purified by repeated sublimations and then stored under vacuum at 77°K. The dosing was accomplished by measuring the pressure of BF$_3$ after expansion through a known volume of the vacuum line.

Boron Trifluoride Etherate (BF$_3$·OEt$_2$) and Ethyl Aluminum Dichloride (EtAlCl$_2$). The commercial products were purified by distillation at reduced pressure.

Polymerization Experiments

Polymerization experiments with BF$_3$ were carried out in glass vials connected to a vacuum line equipped with metal valves. Measured quantities of solvents and monomers were distilled into the reaction ampole cooled at 77°K. Before adding BF$_3$ the reaction mixture was melted and thoroughly mixed. The ampule was then sealed under vacuum and allowed to stand at the desired temperature under vigorous stirring. In the case of polymerizations initiated by BF$_3$·OEt$_2$ and EtAlCl$_2$ all the necessary operations were carried out in glass vials sealed under dry nitrogen.

Polymerization products were recovered by adding cold ammoniacal methanol to the reaction mixture and the coagulated polymers were then dried to a constant weight under vacuum at 50°C.

Photoinitiated Polymerization

A mixture of monomer(s) (1.0 g) and 4-chlorophenyldiazonium tetrafluoborate (0.05 g) was placed in a petri dish (Φ = 5 cm) and irradiated for 5 min with a 1500-W Xenon lamp. Polymerizations were interrupted by adding 5 mL of ammoniacal methanol.

Copolymerization of Propylene Oxide (PO) with Isobutyl Vinyl Ether (BVE) and Ethyl Vinyl Ether (EVE)

Run	Comonomer	Catalyst	Molar ratio comon. s/cat.	Temp (°C)	Duration (h)	Conv[b] (%)
			Polymerization conditions[a]			
PI1	BVE	$BF_3 \cdot OEt_2$	60	−78	24	12.4
PI2	BVE	$EtAlCl_2$	15	20	720	7.5
PE1	EVE	$BF_3 \cdot OEt_2$	60	−78	24	14.1

[a] PO (6 mmol) and alkyl vinyl ether (6 mmol) in toluene (10 mL).

[b] Evaluated as (weight of polymer/weight of comonomer mixture) × 100; mainly constituted by poly(propylene oxide).

Polymer Characterization

IR Spectra were recorded by a Perkin-Elmer Model 225 spectrophotometer on liquid film or polymer films cast from chloroform solution.

^{1}H-NMR Spectra were recorded on a Varian T-60 Spectrometer by using TMS as internal standard.

Molecular Weights $(\overline{M_n})$ were determined at 37°C on polymer solutions in 1,2-dichloroethane by using a vapor pressure osmometer Mechrolab Model 301 A.

Gel Permeation Chromatography (GPC) measurements were performed on polymer solutions in chloroform by a Perkin-Elmer Model 601 chromatograph equipped with RI detector and three columns (VIT-X-5150, VIT-X-648, and styragel 500A) connected in series. The operational conditions were: solvent chloroform, column temperature 25°C, flow rate 1.0 mL/min. Quantitative calculations were not feasible due to the lack of suitable standards for calibration; as a consequence the GPC traces were examined only qualitatively.

Cleavage of Polymeric Benzyl Ethers

Anhydrous HBr was obtained by reaction of bromine with tetrahydronaphthalene[24] and directly bubbled into the reaction vessel.

Poly(benzyl Glycidyl Ether). Dry gaseous HBr was bubbled for 3 h into a solution of 0.70 g of poly(BGE) (run B2, fraction 1) in 100 mL of toluene. The precipitated polymer was washed with water, dissolved in ethanol, and precipitated into a large excess of n-pentane. 0.32 g of polymeric product were obtained.

^{1}H-NMR (methanol d_4): δ 4.8 (s, 1 H, OH), 3.7 (m, 1 H, CH), 3.6 and 3.4 ppm (2m, 4 H, CH_2).

Poly(benzyl Glycidyl Ether-co-Isobutyl Vinyl Ether). Dry gaseous HBr was bubbled for 3 h in a solution of 1.51 g of a sample of poly(BGE-co-BVE) containing 40% mol of BVE monomeric units (run BI3, fraction 2) in 100 mL of toluene; 0.54 g of toluene insoluble product having ^{1}H-NMR and IR spectra identical to those of polyglycidol were obtained. The toluene solution, evaporated to dryness under vacuum, left 0.51 g of residue which was identified as poly(BVE).

TABLE IV

Copolymerization of p-Cresyl Glycidyl Ether (CGE) with Isobutyl Vinyl Ether (BVE) in the Presence of BF_3

| Run | CGE (mmol) | Molar ratio CGE/BVE | Polymerization conditions[a] | | | | Conv[b] (%) | Polymeric product | |
			Molar ratio comon. s/cat.	Solvent (mL)	Temp (°C)	Duration (h)		BVE units (mol%)	$\bar{M}_n \times 10^{-3}$ [c]
CI1	10	0.3	50	24	−78	13	65.4	78.2	1.7
CI2					20		61.9	79.5	2.5
CI3	20	1.0	130	7	−78	24	86.7	48.0	7.7
CI4					20		86.4	53.4	3.7
CI5	30	3.0	50	2	−45	16	78.6	25.3	1.3
CI6				4	−35	24	94.9	28.8	1.0
CI7				2	20	17	85.2	18.1	1.1
CI8[d]			250	0	−20	16	75.0	39.6	1.2
CI9[d]	20	1.0	250	0	20	24	78.1	42.1	1.0
CI10[e]			50	7	0	15	71.7	52.7	6.0

[a] In dichloromethane if not otherwise stated.
[b] Evaluated as (weight of polymer/weight of comonomer mixture) × 100.
[c] Determined by osmometry in 1,2-dichloroethane.
[d] In bulk.
[e] In nitrobenzene.

SOLARO ET AL.

TABLE V
Fractionation of Copolymers of p-Cresyl Glycidyl Ether (CGE) with Isobutyl Vinyl Ether (BVE) by Extraction with Boiling Methanol[a]

| | | Fraction 1 | | | Fraction 2 | |
| | | BVE units[b] | | | BVE units[b] | |
Run	wt %	(mol %)	$\overline{M_n} \times 10^{-3}$ [c]	%-weight	(mol %)	$\overline{M_n} \times 10^{-3}$ [c]
CI1	35	28	0.45	65	97	2.3
CI2	44	44	0.55	56	100	4.0
CI3	65	15	1.10	35	90	20.0
CI4	68	20	0.80	32	100	10.0
CI5	49	20	0.60	51	30	2.0
CI6	65	17	0.55	35	48	1.7
CI7	57	15	0.75	43	22	1.6
CI8	70	19	0.30	30	76	3.3
CI9	80	20	0.20	20	100	4.3
CI10	72	39	0.60	28	81	20.0

[a] Fraction 1: soluble in boiling methanol; Fraction 2: residue to the extraction with boiling methanol.

[b] Determined by ^{1}H-NMR.

[c] Determined by osmometry in 1,2-dichloroethane at 37°C.

RESULTS AND DISCUSSION

Homopolymerization Experiments

In order to compare the physicochemical properties of the polymeric products obtained in copolymerization experiments with those of the corresponding homopolymers, the investigated monomers were homopolymerized under the same experimental conditions adopted in the corresponding copolymerization experiments (Table I). The polymeric product thus obtained were fractionated according to the solubility in boiling methanol (Table II).

p-Cresyl Glycidyl Ether (CGE) was polymerized in CH_2Cl_2 solution in the presence of gaseous BF_3 at $-78°C$ and $+20°C$ (runs C1 and C2). The polymeric
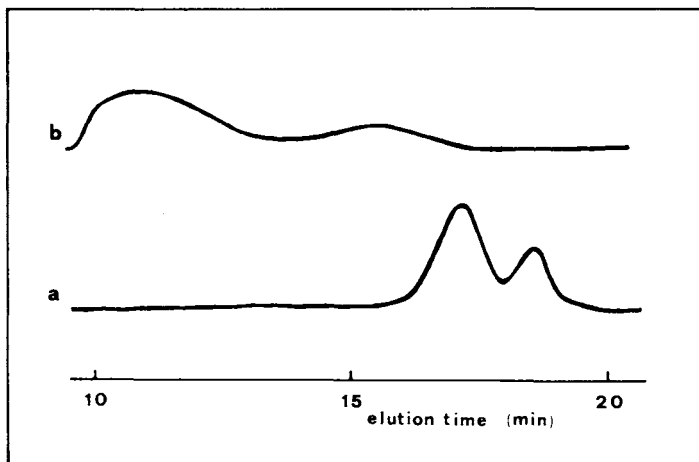

Fig. 1. GPC typical traces of copolymerization products of p-cresyl glycidyl ether (CGE) with isobutyl vinyl ether (BVE): (a) fraction soluble in methanol (run CI3) containing 15% BVE; (b) fraction insoluble in methanol (run CI3) containing 90% BVE.

TABLE VI
Copolymerization Experiments of Bisphenol A Diglycidyl Ether (PGE) with Isobutyl Vinyl
Ether (BVE)

		Polymerization conditions[a]				
Run	PGE (mmol)	Molar ratio PGE/BVE	Catalyst	Molar ratio comon. s/cat.	Duration (h)	Conv[b] (%)
AI1	6.4	0.32	$EtAlCl_2$	41	48	36.4
AI2	7.7	0.38	$BF_3 \cdot OEt_2$	27	72	83.6

[a] In 40 mL of toluene at $-78°C$.
[b] Evaluated as (weight of polymer/weight of comonomer mixture) $\times$ 100.

products thus obtained were characterized by a rather low molecular weight ($\simeq$ 1000) and only the polymer prepared at lower temperature contained a significant amount (about 20% by weight) of product insoluble in boiling methanol having $\overline{M_n}$ 7500.

Benzyl Glycidyl Ether (BGE) was polymerized in CH_2Cl_2 solution in the presence of gaseous BF_3 at $-78°C$ and $+20°C$ (runs B1 and B2). In both cases conversion was larger than 80%, the product obtained at lower temperature being completely soluble in boiling methanol while the polymer prepared at $20°C$ contained an insoluble fraction (34%) having $\overline{M_n}$ 4200.

Propylene Oxide (PO) was polymerized in toluene solution either in the presence of $EtAlCl_2$ at $-78°C$ and $+20°C$ (runs P1 and P2) or at $130°C$ in the presence of $BF_3 \cdot OEt_2$ (run P3). A significant amount of polymeric product was obtained only at $130°C$ while at lower temperature very low conversions were observed.

Isobutyl Vinyl Ether (BVE) was polymerized at temperatures between $-90°C$ and $+20°C$ in the presence of gaseous BF_3 either in CH_2Cl_2 (runs B1–B3) or in nitrobenzene (run B4). By increasing the temperature from $-90°C$ to $+20°C$ conversion to polymeric product increases from 24% to 65% and correspondingly the average degree of polymerization ($\overline{DP_n}$) decreases from 130 to 110. Even lower $\overline{DP_n}$ (51) and higher conversion (90%) were observed when nitrobenzene was used as solvent.

Dodecyl Vinyl Ether (DVE) was polymerized in CH_2Cl_2 in the presence of gaseous BF_3 at $-45°C$ and $+20°C$ (runs D1 and D2). The polymeric products obtained in high yields (>90%) resulted completely insoluble in boiling methanol.

Copolymerization Experiments

Propylene oxide was copolymerized in toluene solution either with isobutyl vinyl either in the presence of $BF_3 \cdot OEt_2$ at $-78°C$ and in the presence of $EtAlCl_2$ at $20°C$ (Table III, runs PI1 and PI2) or with ethyl vinyl ether in the presence of $BF_3 \cdot OEt_2$ at $-78°C$ (run PE1). In all cases very low conversions (<15%) to polymeric product were observed, and this was mainly constituted by the homopolymer of PO, as shown by ^{1}H-NMR. This result, as already observed in other cases of hybrid copolymerization,[25,26] can be explained by assuming that PO forms stable complexes with the catalyst, which can slowly add only to heterocyclic monomers, thus acting as an inhibitor of the polymerization of alkyl vinyl ethers.

SOLARO ET AL.

TABLE VII
Copolymerization Experiments of Benzyl Glycidyl Ether (BGE) with Isobutyl Vinyl Ether
(BVE) in the Presence of BF_3

| | Polymerization conditions[a] | | | | |
Run	BGE (mmol)	Molar ratio BGE/BVE	Solvent (mL)	Temp (°C)	Conv[b] (%)
BI1	7.3	0.3	1.8		93.0
BI2	7.3	0.9	1.7	−78	83.0
BI3	22.1	3.0	3.8		70.0

[a] In dichloromethane, molar ratio comonomers/catalyst = 25, duration 24 h.

[b] Evaluated as (weight of polymer/weight of comonomer mixture) × 100.

Ten copolymerization runs of p-cresyl glycidyl ether with isobutyl vinyl ether were carried out in the presence of gaseous BF_3 in the temperature range −78−+20°C (Table IV, runs CI1–CI10). In all cases the polymeric products, obtained in fairly high yields (>60%), contained structural units derived from both comonomers. By fractionation according to the solubility in boiling methanol two fractions were obtained (Table V). The presence, at least for molar ratios CGE/BVE ≤ 1.0 (runs CI1–CI4 and CI8–CI10), of a residue of relatively high molecular weight constituted almost exclusively of units derived from BVE, unequivocally demonstrates that the copolymerization of the two monomers is not a statistical one. On the other hand, the presence of a soluble fraction containing structural units derived from both comonomers does not allow one to exclude the formation of copolymer macromolecules.

In order to clarify this last point, four copolymer samples (runs CI3 and CI4, fractions 1 and 2), and for comparison two samples of the corresponding homopolymers were analyzed by GPC. While in the case of the homopolymers only one peak is present in the chromatogram, elution of the copolymerization products gives rise in all cases to two rather well-resolved peaks (Fig. 1). The bimodal distribution of molecular weights very likely indicates the formation of a mixture of the two homopolymers, as the presence of two catalytic species with different activity does not seem feasible under the reported copolymerization conditions.

BVE was copolymerized with the diglycidyl ether of bisphenol "A" (PGE), a bifunctional monomer having chemical structure, and presumably reactivity, similar to CGE. Polymerization experiments were carried out at −78°C in the presence of either $EtAlCl_2$ or $BF_3 \cdot OEt_2$ (Table VI, runs A1 and A2). The polymeric products, obtained in 36% and 84% yields, respectively, contained a fraction soluble in chloroform constituted by the homopolymer of BVE. However, it is not possible to evaluate the chemical composition of the insoluble fraction due to its crosslinked structure.

Finally, benzyl glycidyl ether (BGE) was copolymerized with BVE in CH_2Cl_2 at −78°C in the presence of gaseous BF_3 by using molar ratios BGE/BVE between 0.3 and 3.0 (Table VII, runs B1–B3) and the polymeric products, obtained in high yields (>70%), were fractionated according to the solubility in methanol and n-hexane. In all cases three fractions were obtained: one soluble in methanol constituted by poly(BGE), one soluble in n-hexane mainly constituted by poly(BVE), and one soluble in both solvents, which contained almost equimolar amounts of units derived from both the comonomers (Table VIII).

TABLE VIII
Fractionation of Copolymers of Isobutyl Vinyl Ether (BVE) with Benzyl Glycidyl Ether (BGE) by Extraction with Boiling Solvents[a]

Run	Fraction 1			Fraction 2			Fraction 3		
	wt %	BGE units[b] (mol %)	$\overline{M}_n \times 10^{-3}$ [c]	wt %	BGE units[b] (mol %)	$\overline{M}_n \times 10^{-3}$ [c]	wt %	BGE units[b] (mol %)	$\overline{M}_n \times 10^{-3}$ [c]
BI1	9	100	1.6	34	46	0.95	57	0	20.0
BI2	9	100	4.5	57	71	0.50	34	0	18.0
BI3	45	100	1.6	49	60	0.65	6	18	3.5

[a] Fraction 1: soluble in methanol, insoluble in n-hexane; Fraction 2: soluble in both methanol and n-hexane; Fraction 3: insoluble in methanol, soluble in n-hexane.

[b] Determined by NMR.

[c] Determined by osmometry in 1,2-dichloroethane at 37°C.

It is well known that poly(benzyl vinyl ether) can be quantitatively and selectively debenzylated by action of gaseous HBr while under the same experimental conditions no modification occurs in poly(BVE).[24] A sample of poly(BGE) was reacted with dry HBr at room temperature and cleavage at the level of the benzyl group occurred quantitatively as determined by ^{1}H-NMR. When the same reaction was carried out on the copolymerization product of BGE with BVE (run BI3, fraction 2), it was possible to fractionate the reaction product in two portions: one soluble in n-hexane constituted by poly(BVE) and one soluble only in methanol and having a ^{1}H-NMR spectrum identical to that of the product obtained by debenzylation of poly(BGE). This last result unequivocally demonstrates that, in the cationic copolymerization of alkyl vinyl ethers with alkyl or aryl glycidyl ethers, only a mixture of the two homopolymers is obtained.

Photoinitiated Polymerization

Results analogous to those previously presented were obtained in photoinitiated polymerization experiments carried out on both glycidyl and vinyl ethers and on their mixtures having different chemical composition, by using 4-chlorophenyldiazonium tetrafluoborate as BF_3 source under irradiation by a 1500-W Xenon lamp. While in the case of diepoxides an insoluble film is obtained, in all the other cases (vinyl ethers and monoepoxides) soluble polymer films are formed. These resulted in the case of copolymerization experiments, constituted by a homogeneous blend of the corresponding homopolymers, thus indicating that a cationic photopolymerization process takes place in open systems.

Apparently, despite the temperature increase of the comonomer bulk due to the presence of a rather powerful lamp placed at 15-cm distance from the liquid films, no thermal or photochemical process, leading to covalent binding between polyhydrocarbon and polyether chains, seems to take place.

As a conclusion of the reported investigation, it can be stressed that the polymerization of mixtures of glycidyl ethers and alkyl vinyl ethers, both under conventional and photinitiated cationic conditions, does occur without any mutual inhibition effect on the propensity of the two functionally different monomers to react with cationic species.

Although, in all the considered cases, polymeric products were isolated in fairly high yield, no real copolymer macromolecules of the two different comonomers were obtained, in contrast to the hybrid copolymerization claimed to have taken place between some unsaturated and heterocyclic monomers under conventional cationic conditions.

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