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Cyclopolymerization of α,Ω -Diepoxide with Monoepoxy Comonomer. Synthesis and Cation-Binding Property of Copolymers with Dibenzo-19-Crown-6 Units

Toyaji Kakuchi^a; Hisaho Hashimoto^b; Yasuhiro Harada^c; Toshifumi Satoh^c; Kazuaki Yokota^c

^a Division of Bioscience, Graduate School of Environmental Earth Science Hokkaido University, Sapporo, Japan ^b Department of Industrial Chemistry, Tomakomai National College of Technology, Tomakomai, Japan ^c Department of Chemical, Process Engineering Faculty of Engineering, Hokkaido University, Sapporo, Japan

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CYCLOPOLYMERIZATION OF α,ω -DIEPOXIDE WITH MONOEPSY COMONOMER. SYNTHESIS AND CATION-BINDING PROPERTY OF COPOLYMERS WITH DIBENZO-19-CROWN-6 UNITS

TOYOJI KAKUCHI*

Division of Bioscience
Graduate School of Environmental Earth Science
Hokkaido University
Sapporo 060, Japan

HISAHO HASHIMOTO

Department of Industrial Chemistry
Tomakomai National College of Technology
Nishikioka 443, Tomakomai 059-12, Japan

YASUHIRO HARADA, TOSHIFUMI SATOH, and KAZUAKI YOKOTA

Department of Chemical Process Engineering
Faculty of Engineering
Hokkaido University
Sapporo 060, Japan

ABSTRACT

Cyclopolymerizations of 5,6-benzo-1,2:9,10-diepoxy-4,7-dioxadeca-5-ene (BDD) and monoepoxy comonomers, propylene oxide (PO), epichlorohydrin (ECH), and phenyl glycidyl ether (PGE), were carried out with SnCl_4 to form gel-free copolymers with no residual epoxy groups. The copolymerization parameters were $r_1 = 1.09$ and $r_2 = 0.86$ for BDD (M_1)–PGE (M_2). In addition, 5,6:14,15-dibenzo-1,2:18,19-diepoxy-4,7-, 10,13,16-pentaaxanonadeca-5,14-diene (DDP) with PO, ECH, or PGE

were copolymerized with SnCl_4 in CH_2Cl_2 and with KOH in DMSO to form copolymers with dibenzo-19-crown-6 units. Poly[(dibenzo-19-crown-6)-*co*-PO] and poly[(dibenzo-19-crown-6)-*co*-PGE] showed lower extracting yields for alkali-metal picrates than did the homopolymer of DDP, poly(dibenzo-19-crown-6). However, poly[(dibenzo-19-crown-6)-*co*-PGE] exhibited a higher selectivity for K^+ than did the other polymers.

INTRODUCTION

Cationic cyclopolymerization of α,ω -divinylethers is one of the simplest avenues to the synthesis of polymers with crown ether units. Poly(crown ether)s have been shown to demonstrate molecular recognition in the host-guest complexation [1-5]. Excluding α,ω -divinylethers, only a few types of bifunctional monomers have been designed and synthesized for the cyclopolymerization method. Examples are α,ω -diepoxy [6-9], α,ω -diepisulfide [10], and monomers with allylic and acrylic groups [11].

Various copolymerizations of 1,6-dienes with conventional vinyl monomers have been studied. In most cases the diene cyclopolymerized and soluble polymers were obtained [12]. However, there have been limited attempts to copolymerize the dienes which lead to larger rings with the comonomers [1, 13]. We have reported the syntheses of copolymers with benzo-19-crown-6, (*S*)-binaphtho-21-crown-6, and D-manno-21-crown-6 units by copolymerizations of α,ω -divinylethers with monovinylether [14, 15]. Until recently, however, no attempt was made to elucidate the copolymerization tendency of α,ω -diepoxy in the presence of monoepoxy comonomer. It is also of interest to examine the effects of comonomer units in the resulting copolymers on the cation-binding property.

In this paper we report the cationic copolymerization of 5,6-benzo-1,2:9,10-diepoxy-4,7-dioxadeca-5-ene (BDD) with monoepoxy comonomers propylene oxide (PO), epichlorohydrin (ECH), or phenyl glycidyl ether (PGE) and the cationic or anionic copolymerizations of 5,6:14,15-dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaaxanonadeca-5,14-diene (DDP) with PO, ECH, or PGE. In addition, the cation-binding property of copolymers consisting of dibenzo-19-crown-6 and PO or PGE units was examined by the use of alkali-metal picrates.

EXPERIMENTAL

Measurements

$^1\text{H-NMR}$ spectra were recorded with a Hitachi R 90H and a Bruker MSL 400 instruments. UV spectra were recorded on a Jasco 660 UV/VIS spectrophotometer. The molecular weights of the resulting polymers were measured by gel permeation chromatography (GPC) in tetrahydrofuran on a Waters M45 high-performance liquid chromatograph equipped with three polystyrene gel columns (Shodex KF-804L). Their number-average molecular weights (M_n) were calculated on the basis of a polystyrene calibration.

Materials

Tin(IV) chloride (SnCl_4) was purified by distillation of a commercial product under reduced pressure. Potassium hydroxide (KOH), a commercial product, was used without further purification. Dichloromethane and dimethylsulfoxide (DMSO) were purified by the usual methods and distilled over calcium hydride.

Monomers

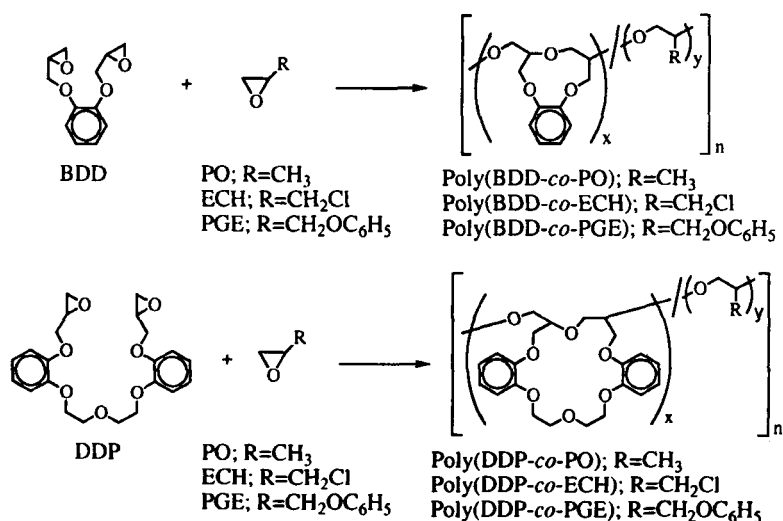
The syntheses of 5,6-benzo-1,2:9,10-diepoxy-4,7-dioxadeca-5-ene (BDD) [9] and 5,6:14,15-dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaoxonadeca-5,14-diene (DDP) [7] were reported in previous papers. Propylene oxide (PO), epichlorohydrin (ECH), and phenyl glycidyl ether (PGE) were purified by distillation of commercial products under reduced pressure.

Copolymerizations

The cationic polymerizations were carried out with SnCl_4 in dichloromethane at -30°C , and the anionic ones with KOH in DMSO at room temperature, as shown in Scheme 1. The resulting polymers were purified by reprecipitation from chloroform-methanol. The copolymer compositions were determined from the relative peak areas of the phenyl and the aliphatic protons in the $^1\text{H-NMR}$ spectra.

Cation-Binding Property

The extraction of alkali metal picrates was carried out using a procedure similar to the one developed by Pedersen [16]. A solution of polymer in dichloromethane ($[\text{crown ether units}] = 3.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) was vigorously shaken in a



SCHEME 1.

culture tube with the aqueous solution of alkali hydroxide and picric acid ([picric acid] = $7 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, [metal hydroxide] = $0.1 \text{ mol} \cdot \text{L}^{-1}$). After separating the resulting two phases, the alkali picrate extracted into the dichloromethane was indirectly determined by measuring the absorbance of picrate in the aqueous phase at 357 nm using a UV spectrophotometer.

RESULTS AND DISCUSSION

Cyclocopolymerization of α,ω -Diepoxides and Epoxy Comonomers

Table 1 lists the copolymerization results of 5,6-benzo-1,2:9,10-diepoxy-4,7-dioxadeca-5-ene (BDD) and propylene oxide (PO), epichlorohydrin (ECH), and phenyl glycidyl ether (PGE) with SnCl_4 in CH_2Cl_2 at -30°C . All the copolymerizations proceeded homogeneously, and the copolymers obtained were soluble in chloroform and THF. The copolymerization rates with ECH or PGE were much faster than that with PO. Because the GPC traces of the resulting copolymers with UV and RI detections corresponded to each other, the copolymers contain no homopolymer.

Figure 1 shows the $^1\text{H-NMR}$ spectra of the copolymers obtained from BDD with PO, ECH, and PGE. The characteristic absorption at 2.7–3.5 ppm due to the epoxy protons had completely disappeared, and thus BDD polymerized with 100% cyclization. The incorporation of comonomers with different reactivities did not inhibit the intramolecular cyclization of BDD. The polymerization of monosubstituted epoxides with a cationic initiator proceeds through ring opening at the CH-O and $\text{CH}_2\text{-O}$ bonds (α - and β -bonds) [17]. For the cationic copolymerization of BDD, the main cyclic constitutional unit in the copolymer is benzo-10-crown-3. The mole fraction of BDD units in the copolymers, which was determined by $^1\text{H-NMR}$ spectra, was 0.53 as a minimum value and increased in the order $\text{PO} < \text{ECH} < \text{PGE}$.

Figure 2 shows the copolymer composition curve for the copolymerization of BDD and PGE with SnCl_4 in CH_2Cl_2 at -30°C . The copolymerization reactivity ratios for BDD (M_1) and PGE (M_2) were estimated by use of the usual Mayo-Lewis equation and the Kelen-Tüdös method, giving $r_1 = 1.67$ and $r_2 = 0.68$. In these

TABLE 1. Cyclocopolymerization of 5,6-Benzo-1,2:9,10-diepoxy-4,7-dioxadeca-5-ene (BDD) with Propylene Oxide (PO), Epichlorohydrin (ECH), and Phenyl Glycidyl Ether (PGE)^a

Epoxy comonomer	Time	Yield, %	Mole fraction of BDD units in copolymer ^b	M_n^c
PO	15 h	20.7	0.53	5400
ECH	30 s	11.5	0.77	2700
PGE	30 s	7.4	0.86	3200

^a[BDD] = [epoxy comonomer] = $0.5 \text{ mol} \cdot \text{L}^{-1}$; [SnCl_4] = $0.05 \text{ mol} \cdot \text{L}^{-1}$; solvent, CH_2Cl_2 ; -30°C .

^bDetermined by $^1\text{H-NMR}$ spectra.

^cDetermined by GPC (polystyrene calibration).

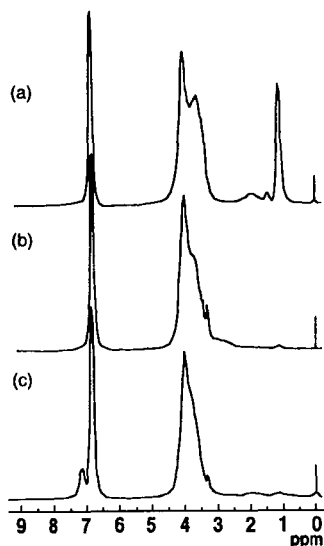


FIG. 1. $^1\text{H-NMR}$ spectra of poly(BDD-co-PO) (a), poly(BDD-co-ECH) (b), and poly(BDD-co-PGE) (c): [BDD], [PO], [ECH], [PGE], $0.5 \text{ mol}\cdot\text{L}^{-1}$; $[\text{SnCl}_4]$, $0.05 \text{ mol}\cdot\text{L}^{-1}$; solvent, CH_2Cl_2 ; -30°C .

cases the intramolecular cyclization of BDD proceeded perfectly even in a high feed ratio such as a [PGE]/[BDD] ratio of 4. The cyclopolymerization tendency of BDD in the presence of monoepoxy comonomers was high, very similar to the cationic copolymerization of α,ω -divinylether with monovinylether.

Table 2 lists the cationic and anionic copolymerization results of 5,6:14,15-dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaoxonadeca-5,14-diene (DDP) and

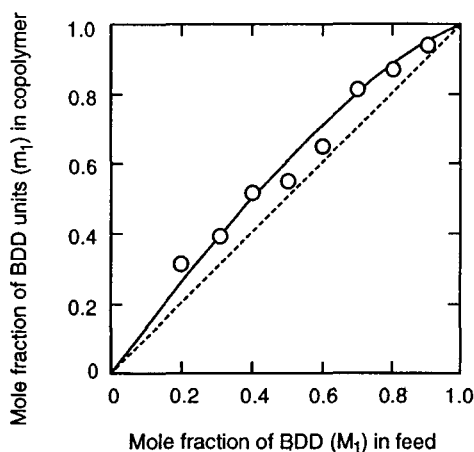


FIG. 2. Composition curve for the copolymerization of BDD and PGE with SnCl_4 in CH_2Cl_2 at -30°C .

TABLE 2. Copolymerization of 5,6:14,15-Dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene (DDP) with Propylene Oxide (PO), Epichlorohydrin (ECH), and Phenyl Glycidyl Ether (PGE)^a

Epoxy monomer (EM)	Catalyst	Solvent	Mole fraction of DDP in feed	[DDP + EM], mol · L ⁻¹	[Catalyst], mol · L ⁻¹	Time, hours	Yield, %	Mole fraction of DDP in copolymer ^b	$M_n \times 10^{-3}$ ^c
PO	SnCl ₄	CH ₂ Cl ₂	0.50	0.5	0.05	9	4	0.73	2.0
	SnCl ₄	CH ₂ Cl ₂	0.30	1.0	0.1	20	12	0.56	1.9
	KOH	DMSO	0.50	0.5	0.05	8	15	0.90	1.2
ECH	SnCl ₄	CH ₂ Cl ₂	0.50	0.5	0.05	9	20	0.89	2.3
	SnCl ₄	CH ₂ Cl ₂	0.10	2.0	0.2	25	0	—	—
	KOH	DMSO	0.50	0.5	0.05	168	0	—	—
PGE	SnCl ₄	CH ₂ Cl ₂	0.50	0.5	0.05	9	22	0.89	2.1
	SnCl ₄	CH ₂ Cl ₂	0.10	2.0	0.2	25	6	0.58	2.1
	KOH	DMSO	0.50	0.5	0.05	5	36	0.81	3.1

^a -30 °C for SnCl₄ in CH₂Cl₂; 23 °C for KOH in DMSO.

^b Determined by ¹H-NMR spectra.

^c Determined by GPC (polystyrene calibration).

PO, ECH, or PGE. The copolymerization with SnCl_4 in CH_2Cl_2 proceeded homogeneously to yield gel-free polymers, except that methanol-insoluble polymer was not obtained for a $[\text{ECH}]/[\text{DDP}]$ ratio of 9. For the copolymerization with KOH in DMSO , methanol-insoluble polymers were obtained except for the DDP -ECH system. The GPC traces of copolymers with UV detection agreed with those with RI detection.

The characteristic absorption at 2.5–3.3 ppm due to the epoxy protons completely disappeared in the $^1\text{H-NMR}$ spectra, which means that DDP polymerized with 100% cyclization. For the cationic polymerization, the main cyclic unit originating from DDP is dibenzo-19-crown-6. On the other hand, the copolymers prepared with KOH contain essentially dibenzo-19-crown-6 as cyclic constitutional units, because the ring-opening polymerization of monosubstituted epoxides with an anionic initiator occurs almost exclusively at the β -bond [17]. The compositions of the DDP unit in copolymers were larger than those in monomer feeds.

Cation-Binding Property of Copolymers with Dibenzo-19-crown-6 Units

The cation-binding property of polymeric dibenzo-19-crown-6 was estimated by one-plate extraction experiments using lithium, sodium, potassium, rubidium, and cesium picrates. Figure 3 shows the results of the extraction yields of alkali-metal picrates by poly[(dibenzo-19-crown-6) $_{0.56}$ -co-PO $_{0.44}$], poly[(dibenzo-19-crown-6) $_{0.58}$ -co-PGE $_{0.42}$], and poly(dibenzo-19-crown-6) prepared by the cationic cyclopolymerization of DDP . The extraction yields of alkali-metal picrates increased in the order $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+ \gg \text{Na}^+ > \text{Li}^+$ for each host polymer. Dibenzo-18-crown-6 shows the highest selectivity for K^+ because the diameter of the crown cavity corresponds to that of K^+ . On the other hand, the host polymers are considerably more efficient than dibenzo-18-crown-6 in binding K^+ , Rb^+ , and Cs^+ which have diameters larger than the crown cavity. This result can be explained by cooper-

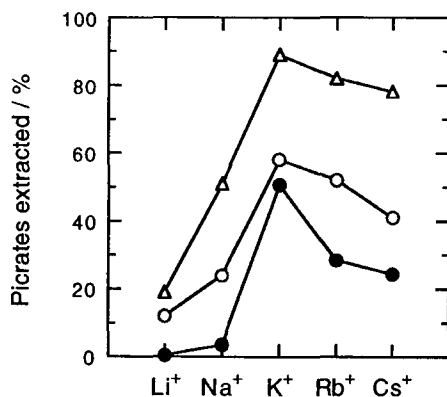


FIG. 3. Extraction yields (%) of alkali-metal picrates by poly[(dibenzo-19-crown-6) $_{0.56}$ -co-PO $_{0.44}$] (\circ), poly[(dibenzo-19-crown-6) $_{0.58}$ -co-PGE $_{0.42}$] (\bullet), and poly(dibenzo-19-crown-6) (\triangle): [crown ether units in polymer] = $3.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ in CH_2Cl_2 phase; [picric acid] = $7 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; and [metal hydroxide] = $0.1 \text{ mol} \cdot \text{L}^{-1}$ in H_2O phase.

ative coordination effects, where two neighboring crown ether rings combine with a single cation. The extraction yields for the copolymers were lower than those for the homopolymer since the comonomer units introduced into copolymers disturb the formation of 2:1 crown-cation complex.

The K^+/Na^+ , K^+/Rb^+ , and K^+/Cs^+ selectivities for poly[(dibenzo-19-crown-6)_{0.58}-co-PGE_{0.42}] were larger than those for poly(dibenzo-19-crown-6) and poly[(dibenzo-19-crown-6)_{0.56}-co-PO_{0.44}]. This result means that the PGE units in the copolymer act as steric barriers for complexation between dibenzo-19-crown-6 and cations.

CONCLUSIONS

Diepoxide-epoxide systems are generally used for commercial adhesive, resin, and paint, where diepoxy compounds act as a crosslinking component. However, the molecular-designed diepoxides were polymerized even in the presence of monoepoxy comonomer with suitable conditions to give gel-free polymers with crown ether units through a cyclopolymerization mechanism. The cation-binding properties of polymers with crown ether units change by the introduction of comonomer units. Cyclopolymerization is therefore one method for producing polymeric crown ethers whose molecular recognition properties differ from those of poly(crown ethers)s through the cyclopolymerization method.

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