

Synthesis of Graft Poly(ester ether) by Ring-Opening Copolymerization of Epoxy-Terminated Poly(ethylene glycol) with Lactones

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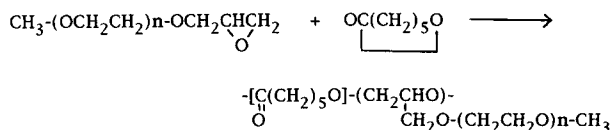
SYNOPSIS

The copolymerization of epoxy-terminated poly(ethylene glycol methyl ether) (CH₃PEG-epoxide) with lactones such as ϵ -caprolactone (CL) was carried out to prepare the PEG graft poly(ester ether). The methanol-insoluble part of the reaction product was considered to be the graft copolymer. The graft copolymer was prepared using potassium *tert*-butoxide or sodium methoxide as a catalyst. The apparent number-average molecular weight (\bar{M}_n) of the graft copolymers increased with an increase in CL concentration and a decrease in the dielectric constant of the solvents. β -Propiolactone (PL) and δ -valerolactone (VL) were also copolymerized with CH₃PEG-epoxide as well as was CL. The apparent composition of the graft copolymers (lactone units/CH₃PEG) was greater than the feed ratio of the two monomers in all cases. On the other hand, the composition of copolymers prepared with the copolymerization of low molecular weight epoxides such as phenyl glycidyl ether with VL was almost consistent with the feed ratio of the two monomers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

We have reported on the ability of epoxy-terminated poly(ethylene glycol methyl ether) (CH₃PEG-epoxide) as a macromonomer capable of anionic copolymerization.^{1,2} Thus, poly(ethylene glycol) (PEG) graft polyesters or polyethers were prepared when it was copolymerized with acid anhydrides or epoxides, respectively. In the present article, it was copolymerized with lactones such as β -propiolactone (PL), δ -valerolactone (VL), and ϵ -caprolactone (CL).

The copolymerization of CH₃PEG-epoxide with CL catalyzed by potassium *tert*-butoxide (*t*-BuOK) is considered to proceed by the following equation:



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Although there are many articles relating to the synthesis of poly(ether ester) or poly(ester ether), most of them are block copolymers.³⁻⁵ Zhu et al. synthesized random copolymers of ethylene oxide and lactide using triethylaluminum-water as a catalyst.⁶ These copolymers are expected to be biodegradable materials.

EXPERIMENTAL

Materials

CH₃PEG (average MW = 1900) was purchased from Aldrich Chemical Co. and used without further purification. CH₃PEG-epoxide was synthesized as described in the previous article,¹ where the hydroxyl group of CH₃PEG was sodium-metallized with sodium hydride and reacted with epichlorohydrin. Low molecular weight epoxides, such as allyl glycidyl ether (AGE), glycidyl methacrylate (GMA), and phenyl glycidyl ether (PGE), and lactones, such as PL, VL, and CL, were purified by distillation over calcium hydride. Catalysts such as triethylenediamine (TEM), 4-dimethylaminopyridine (DMAP),

t-BuOK, and sodium methoxide (CH₃ONa) were commercial catalysts and used without further purification. Solvents such as *m*-xylene, *tert*-butanol, and dimethyl sulfoxide (DMSO) were commercial guaranteed solvents.

Copolymerization of CH₃PEG–Epoxide with Lactones

A mixture of dried CH₃PEG–epoxide, lactone such as CL, and catalyst such as *t*-BuOK, was dissolved in *tert*-butanol and reacted at 40°C under a nitrogen atmosphere. After the reaction, methanol was added to the solution to terminate the reaction and to dissolve the reaction mixture on heating. The products were precipitated by adding ethyl ether to the concentrated solution and purified by repetition of the dissolution and the precipitation twice. Then, the purified products were separated into methanol-soluble and -insoluble parts. The apparent number-average molecular weight (\bar{M}_n) and the ratio of the CL component to CH₃PEG (CL units/CH₃PEG), i.e., the apparent composition of the each part, were determined by GPC and ¹H-NMR, respectively. The composition was calculated using the following equation:

CL units/CH₃PEG

$$= \frac{\text{Area of methylene signal (4.1 ppm) of PCL}}{\text{Area of ethylene oxide signal (3.65 ppm) of CH}_3\text{PEG}} \times 90$$

Copolymerization of Low Molecular Weight Epoxides with VL

A mixture of epoxide such as PGE, VL, and TEM was dissolved in *tert*-butanol and reacted at 40°C for 24 h under a nitrogen atmosphere. After the reaction, the products were precipitated by adding ethyl ether to the reaction mixture, washed repeatedly with ethyl ether, and dried. \bar{M}_n and the composition (VL units/epoxide) of the copolymer were determined in a similar manner as with CH₃PEG–epoxide.

Instrumental Methods

The ¹H-NMR spectra were recorded on a JEOL GX-270 spectrophotometer with TMS as the internal standard. The GPC analysis was performed using a TOSOH HLC-803D liquid chromatograph equipped

with G2000H8 and G4000H8 columns in THF at 40°C after calibration with poly(ethylene oxide).

RESULTS AND DISCUSSION

Copolymerization of CH₃PEG–Epoxide with CL

Confirmation of Copolymerization

The copolymerization of CH₃PEG–epoxide with CL catalyzed by *t*-BuOK was carried out in *tert*-butanol at 40°C. The products were fractionated into methanol-soluble and -insoluble parts because methanol is a good solvent of CH₃PEG–epoxide but is not a solvent for PCL. Their representative GPC curves are shown in Figure 1. Although the methanol-soluble part consisted of a mixture of unreacted CH₃PEG–epoxide and the product had higher molecular weight than that of CH₃PEG–epoxide, the methanol-insoluble part consisted of only the component of high molecular weight. A ¹H-NMR spectrum of the methanol-insoluble part showed a signal for ethylene oxide groups of CH₃PEG at 3.65 ppm besides signals for PCL at 1.4, 1.65, 2.3, and 4.1 ppm as shown in Figure 2. From these results, the methanol-insoluble part was considered to be the graft copolymer although it would contain some CL homopolymer. The separation of pure graft copolymer

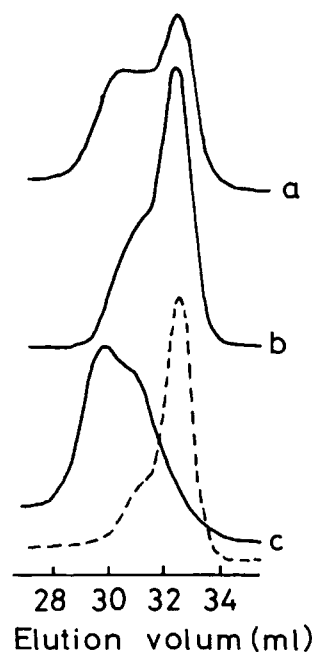


Figure 1 GPC (RI) curves of the (a) crude product and (b) methanol-soluble and (c) methanol-insoluble part of the product. Dotted line is that of CH₃PEG–epoxide.

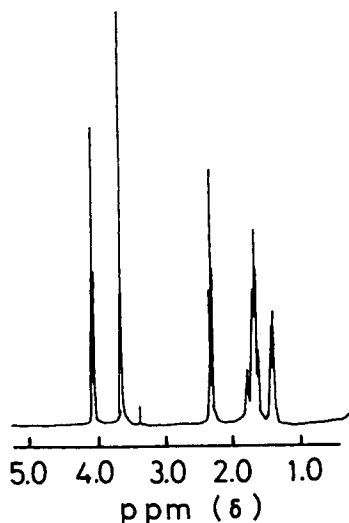


Figure 2 $^1\text{H-NMR}$ spectrum of graft poly(ester ether) of $\text{CH}_3\text{PEG-epoxide}$ with CL (in CDCl_3).

and CL homopolymer was difficult due to their similar solubility in some solvents.

Effect of Catalyst on \bar{M}_n and Composition of Graft Copolymer

The copolymerization of $\text{CH}_3\text{PEG-epoxide}$ with CL was carried out with various catalysts such as TEM , DMAP , $t\text{-BuOK}$, and CH_3ONa in $t\text{-butanol}$ at 40°C . As shown in Table I, methanol-insoluble fractions were not formed with amines, whereas they were formed with alkoxides such as $t\text{-BuOK}$ and CH_3ONa . Although the \bar{M}_n of the methanol-insoluble part was almost same with both catalysts, the composition ($\text{CL units}/\text{CH}_3\text{PEG}$) with CH_3ONa was much larger than that with $t\text{-BuOK}$. Moreover, it was much larger than the feed ratio of the two monomers (9.0) in both cases, unlike the copoly-

Table I Copolymerization of $\text{CH}_3\text{PEG-Epoxide}$ with CL in $t\text{-Butanol}$ by Various Catalysts^a

Catalyst	Conversion of CL (%)	Methanol-insoluble Part	
		\bar{M}_n	CL Units/ CH_3PEG
TEM	63	—	—
DMAP	37	—	—
$t\text{-BuOK}$	100	5900	60
CH_3ONa	100	4600	119

^a Reaction conditions: $\text{CH}_3\text{PEG-epoxide}$, 1 mmol (2 g); CL , 9 mmol (0.96 mL); catalyst, 0.4 mmol; $t\text{-butanol}$, 3 mL; temperature, 40°C ; time, 4 h.

merization of $\text{CH}_3\text{PEG-epoxide}$ with acid anhydrides and with epoxides. From these results, and the fact that measured \bar{M}_n was smaller than the MW calculated from the composition, it is considered that CL homopolymer was contained in the methanol-insoluble part in both cases and that its amount with CH_3ONa was more than with $t\text{-BuOK}$. This may be due to the greater ability for anionic polymerization of CL compared with that of $\text{CH}_3\text{PEG-epoxide}$. The \bar{M}_n of methanol-soluble fractions was almost the same as that for $\text{CH}_3\text{PEG-epoxide}$.

Copolymerization in Various Solvents

The copolymerization of $\text{CH}_3\text{PEG-epoxide}$ with CL catalyzed by $t\text{-BuOK}$ was carried out in various solvents such as $m\text{-xylene}$, $t\text{-butanol}$, DMSO , and a mixed solvent of $t\text{-butanol}$ and DMSO (1 : 1 v/v) at 40°C . As shown in Table II, methanol-insoluble fractions were not formed in DMSO and the mixed solvent of $t\text{-butanol}$ and DMSO , whereas they were formed on copolymerization in $m\text{-xylene}$ and $t\text{-butanol}$, which had a relatively lower dielectric constant. Though the composition of methanol-insoluble fractions with $m\text{-xylene}$ and $t\text{-butanol}$ were almost same, the \bar{M}_n with $m\text{-xylene}$ was larger than that with $t\text{-butanol}$. Thus, the \bar{M}_n of the graft copolymer depended on the dielectric constant of the solvents. It is considered that \bar{M}_n of the copolymers became larger in the solvents having a lower dielectric constant because the chain-transfer reaction hardly occurred in these solvents. The products prepared in the solvents having a relatively higher dielectric constant are considered to dissolve in methanol due to their lower \bar{M}_n .

Table II Copolymerization of $\text{CH}_3\text{PEG-Epoxide}$ with CL in Various Solvents^a

Solvent	Conversion of CL (%)	Methanol-insoluble Part	
		\bar{M}_n	CL Units/ CH_3PEG
$m\text{-Xylene}$	100	14,700	56
$t\text{-Butanol}$	100	5,900	60
$t\text{-Butanol}$ + DMSO (1 : 1 v/v)	100	—	—
DMSO	32	—	—

^a Reaction conditions: $\text{CH}_3\text{PEG-epoxide}$, 1 mmol (2 g); CL , 9 mmol (0.96 mL); $t\text{-BuOK}$, 0.4 mmol; solvent, 3 mL; temperature, 40°C ; time, 4 h.

Table III Copolymerization of CH₃PEG–Epoxide with CL in *tert*-Butanol at Various CL Concentrations^a

CL Concentration (mmol)	Conversion of CL (%)	Methanol-insoluble Part	
		\bar{M}_n	CL Units/CH ₃ PEG
1	9	—	—
4	8	—	—
9	100	5,900	60
19	100	11,300	176

^a Reaction conditions: CH₃PEG–epoxide, 1 mmol (2 g); *t*-BuOK, 4 mol % for total monomers; temperature, 40°C; time, 4 h.

Effect of CL Concentration on \bar{M}_n and Composition of Graft Copolymer

The copolymerization of CH₃PEG–epoxide with CL catalyzed by *t*-BuOK was carried out at various CL concentrations in *tert*-butanol at 40°C. As shown in Table III, methanol-insoluble fractions were not formed at lower CL concentration where the molar ratio of CL to CH₃PEG–epoxide was less than 4.0, whereas they were formed at higher CL concentrations where the molar ratio was more than 9.0. Both \bar{M}_n and the composition of the methanol-insoluble fraction increased with an increase in monomer concentration. However, the products are considered to contain much CL homopolymer because its \bar{M}_n is smaller than is the MW derived from calculation based on the composition as described before.

Copolymerization of CH₃PEG–Epoxide with Other Lactones

The copolymerization of CH₃PEG–epoxide with PL and VL catalyzed by *t*-BuOK was carried out in *tert*-

Table IV Copolymerization of CH₃PEG–Epoxide with Various Lactones in *tert*-Butanol^a

Lactone	Conversion of Lactone (%)	Methanol-insoluble Part	
		\bar{M}_n	Lactone Units/CH ₃ PEG
PL	100	980	280
VL	90	2900	134
CL	100	5900	60

^a Reaction conditions: CH₃PEG–epoxide, 1 mmol (2 g); lactone, 9 mmol; *t*-BuOK, 0.4 mmol; *tert*-butanol, 3 mL; temperature, 40°C; time, 4 h.

Table V Copolymerization of Low Molecular Weight Epoxides with VL^a

Epoxide	Conversion of VL (%)	Copolymer	
		\bar{M}_n	VL Units/Epoxide
AGE	5	1100	—
GMA	86	1900	12
PGE	84	1700	9

^a Reaction conditions: epoxide, 1 mmol; VL, 9 mmol; TEM, 4 mmol; *tert*-butanol, 3 mL; temperature, 40°C; time, 24 h.

butanol at 40°C to compare their reactivity with that of CL. As shown in Table IV, PL and VL formed graft copolymers having higher lactone composition values than those for CL. However, since the \bar{M}_n of graft copolymers with PL and VL was smaller than that with CL, it is apparent that they contained much homopolymer of lactones even if the difference of their unit molecular weights were taken into consideration. Thus, the ability for anionic polymerization of PL and VL is larger than that of CL.

Copolymerization of Low Molecular Weight Epoxides with VL

The copolymerization of low molecular weight epoxides such as AGE, GMA, and PGE with VL catalyzed by TEM was carried out in *tert*-butanol at 40°C. As shown in Table V, the composition of copolymers was almost consistent with the feed ratio of two monomers (9.0). From this result, it was apparent that the ability of polymerization of CH₃PEG–epoxide was less than that of low molecular weight epoxides under these reaction conditions.

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Received February 23, 1994

Accepted March 3, 1994