

Synthesis of Graft Polyethers by Ring-Opening Copolymerization of Epoxy-Terminated Poly(ethylene glycol) with Epoxides

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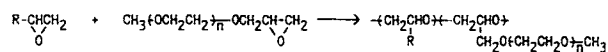
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SYNOPSIS

The copolymerization of epoxy-terminated poly(ethylene glycol methyl ether) (CH₃PEG-epoxide) with low molecular weight epoxides such as phenyl glycidyl ether (PGE) was carried out to prepare the PEG graft polyethers. Potassium *tert*-butoxide was the most favorable catalyst used to obtain the graft polyethers. The apparent number-average molecular weight (\bar{M}_n) of the graft polyethers decreased with increase in PGE concentration because PGE acted as both solvent and comonomer. The composition of the graft polyethers (PGE/CH₃PEG), however, increased with increase in PGE concentration and was almost consistent with the feed ratio of the two monomers. The graft polyethers whose composition was over 10 were insoluble in water. The \bar{M}_n of the graft polyethers was little affected by the reaction temperature, but more affected by the presence of solvent. Besides PGE, *n*-butyl glycidyl ether and styrene oxide were effective as comonomers. CH₃PEG-epoxide hardly polymerized in *tert*-butyl alcohol. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Macromonomers having an end-group capable of ring-opening polymerization are much fewer than those having a double-bond end group capable of radical polymerization. Kobayashi et al. synthesized the poly(ethylene oxide) macromonomer having a ring-opening polymerizable 2-oxazoline group and copolymerized with 2-phenyl-2-oxazoline to prepare the well-defined graft copolymer.¹ We synthesized the poly(ethylene glycol methyl ether) macromonomer having an epoxy end group (CH₃PEG-epoxide) and copolymerized with acid anhydrides to prepare PEG graft polyesters as described in a previous article.² The present article deals with the synthesis of PEG graft polyethers by the copolymerization of CH₃PEG-epoxide with low molecular weight epoxides:



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The effects of reaction conditions on the molecular weight and the composition of graft copolymers were investigated.

Block copolymers of propylene oxide and ethylene oxide are well-known examples of the copolymerization between epoxides.^{3,4} They are commercially used as aqueous surfactants.

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,² where the hydroxyl group of CH₃PEG was sodium-metallized with sodium hydride and reacted with epichlorohydrine (ECH). Epoxides such as phenyl glycidyl ether (PGE), *n*-butyl glycidyl ether (BGE), styrene oxide (SO), ECH, and glycidyl methacrylate (GMA) were purified by distillation over calcium hydride. Catalysts such as potassium *tert*-butoxide (*t*-BuOK), sodium methoxide (CH₃ONa), tetra-*n*-butylam-

monium iodide ($n\text{-Bu}_4\text{NI}$) and triethylenediamine (TEM) were commercial catalysts and used without further purification. Solvents such as m -xylene, o -dichlorobenzene, $tert$ -butyl alcohol ($t\text{-BuOH}$), nitrobenzene, and dimethyl sulfoxide (DMSO) were commercial guaranteed solvents.

Copolymerization of CH_3PEG -epoxide with Epoxides

A mixture of dried CH_3PEG -epoxide, epoxide such as PGE, and catalyst such as $t\text{-BuOK}$ was introduced in a test tube and reacted at 100°C under a nitrogen atmosphere. A solvent such as DMSO was used in some experiments. After the reaction, methyl alcohol was added to the solution to terminate the reaction and to dissolve the reaction mixture. The products were precipitated by adding ethyl ether to the concentrated solution and purified by twice repetition of the dissolution and the precipitation. The apparent number-average molecular weight (\overline{M}_n) and the ratio of PGE component to CH_3PEG (PGE/ CH_3PEG), i.e., the composition of the products,

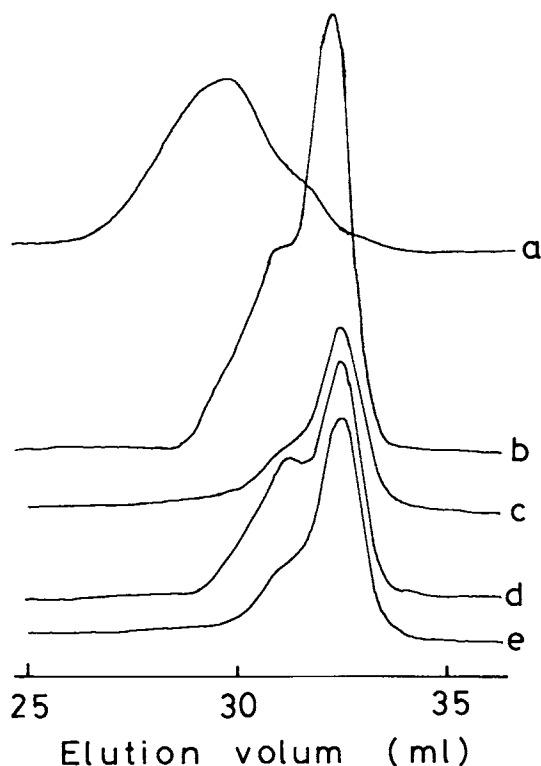


Figure 1 GPC (RI) curves of the products: catalyst (a) $t\text{-BuOK}$; (b) CH_3ONa ; (c) $n\text{-Bu}_4\text{NI}$; (d) TEM; (e) none. Reaction conditions: CH_3PEG -epoxide, 1 mmol (2 g); PGE, 9 mmol (1.2 mL); catalyst, 1 mmol; temperature, 100°C ; time, 24 h.

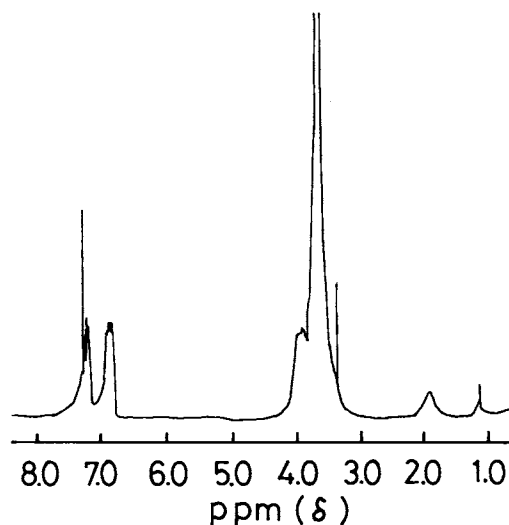


Figure 2 ^1H -NMR spectrum of graft polyether of CH_3PEG -epoxide with PGE (in CDCl_3).

were determined by gel permeation chromatography (GPC) equipped with UV and RI detectors.⁵

Polymerization of CH_3PEG -Epoxide

Polymerization of CH_3PEG -epoxide catalyzed by $t\text{-BuOK}$ was carried out at 100°C under a nitrogen atmosphere in the presence or the absence of $t\text{-BuOH}$ as the solvent. The products were treated as same as were the products of the copolymerization.

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 the calibration with poly(ethylene oxide).

RESULTS AND DISCUSSION

Copolymerization of CH_3PEG -Epoxide with Epoxides

Copolymerization of CH_3PEG -epoxide with PGE was carried out with various catalysts such as $t\text{-BuOK}$, CH_3ONa , $n\text{-Bu}_4\text{NI}$, and TEM. RI curves of the products are shown in Figure 1. The appearance of the component having a higher molecular weight than that of CH_3PEG -epoxide was

Table I Copolymerization of CH₃PEG–Epoxide with PGE at Various *t*-BuOK Concentrations^a

<i>t</i> -BuOK (mmol)	\overline{M}_n	$\overline{M}_w/\overline{M}_n$	PGE/CH ₃ PEG
0	2,700	1.24	0
0.10	13,400	1.18	4.5
0.25	9,000	1.32	8.4
0.50	8,300	1.27	6.9
1.00	9,400	1.43	10.6

^a Reaction conditions: CH₃PEG–epoxide, 1 mmol (2 g); PGE, 9 mmol (1.2 mL); temperature, 100°C; time, 24 h.

clearly recognized with *t*-BuOK. Further, the peak of unreacted CH₃PEG–epoxide was not recognized in this case. This component was ascertained as a copolymer from the fact that it was not a homopolymer of CH₃PEG–epoxide, as the absorption at 254 nm was recognized as corresponding to the RI curve (CH₃PEG–epoxide did not show the absorption at this wave length) and that the ¹H-NMR spectrum of the product showed the signals of the phenyl group and the ethylene oxide group at 6.8–7.4 and 3.4–3.8 ppm, respectively (Fig. 2). A large amount of CH₃PEG–epoxide remained unreactive with the other catalysts, though a slight increase in molecular weight was recognized with CH₃ONa and TEM. A *t*-BuOK representative catalyst of an anionic ring-opening polymerization of epoxides was also the most appropriate catalyst on this copolymerization because unreacted CH₃PEG–epoxide was hardly recognized on the copolymerization under various reaction conditions. The effectiveness of *t*-BuOK as catalyst in this reaction can be attributed to the strong nucleophilicity of this compound.

The effect of the *t*-BuOK concentration on the \overline{M}_n and the composition (PGE/CH₃PEG) of the graft copolymers was examined. With *t*-BuOK concentration over 0.25 mmol, they were almost constant and PGE/CH₃PEG of the copolymer was al-

most consistent with the feed ratio (9.0) of two monomers as shown in Table I.

Table II shows the effect of PGE concentration on \overline{M}_n and PGE/CH₃PEG of the graft copolymers. The \overline{M}_n of the copolymer decreased with increase in PGE concentration. This may be due to the role of PGE acting as both solvent and comonomer, i.e., it is considered that many kinds of copolymers were prepared with lower PGE concentration because of the great polymerization ability of CH₃PEG–epoxide, as described later, whereas the complicated reactions were suppressed in the presence of a large amount of PGE. Then, the molecular weight distribution of the products would become narrower with high PGE concentration, as shown in Figure 3. PGE/CH₃PEG of the copolymer increased with increase in PGE concentration and was almost consistent with the feed ratio of two monomers, i.e., the grafting efficiency of CH₃PEG–epoxide was over 80% in every PGE concentration. Thus, the composition of copolymer can be controlled by the control of PGE concentration. The solubility of graft copolymers to water was examined. The copolymer prepared at a PGE concentration of 4 mmol was soluble, but those of 9 and 19 mmol were insoluble in water. The degree of swelling (represented by g water/g copolymer) of the copolymer with a PGE concentration of 9 mmol was larger than that of copolymer with 19 mmol, as shown in Table II. These are attributed to the hydrophobicity of the poly(PGE) component in the copolymers. The PGE/CH₃PEG of the copolymers did not change at all before and after the swelling treatment. This shows that the purification method of the products described in the Experimental section is adequate.

Copolymerization of CH₃PEG–epoxide with PGE was carried out in various solvents such as DMSO, nitrobenzene, *t*-BuOH, *o*-dichlorobenzene, and *m*-xylene. As shown in Table III, the \overline{M}_n and the PGE/CH₃PEG of the copolymers were independent of the dielectric constant of the solvents. The largest \overline{M}_n and the nearest PGE/CH₃PEG value to the feed

Table II Copolymerization of CH₃PEG–Epoxide with PGE at Various PGE Concentrations^a

PGE (mmol)	\overline{M}_n	$\overline{M}_w/\overline{M}_n$	PGE/CH ₃ PEG	Grafting Efficiency of CH ₃ PEG–Epoxide (%)	Degree of Swelling (g Water/g Copolymer)
4	20000	1.93	4.1	100	Soluble
9	9400	1.43	10.6	84	8.4
19	6500	1.27	23.5	81	3.3

^a Reaction conditions: CH₃PEG–epoxide, 1 mmol (2 g); *t*-BuOK, 1 mmol; temperature, 100°C; time, 24 h.

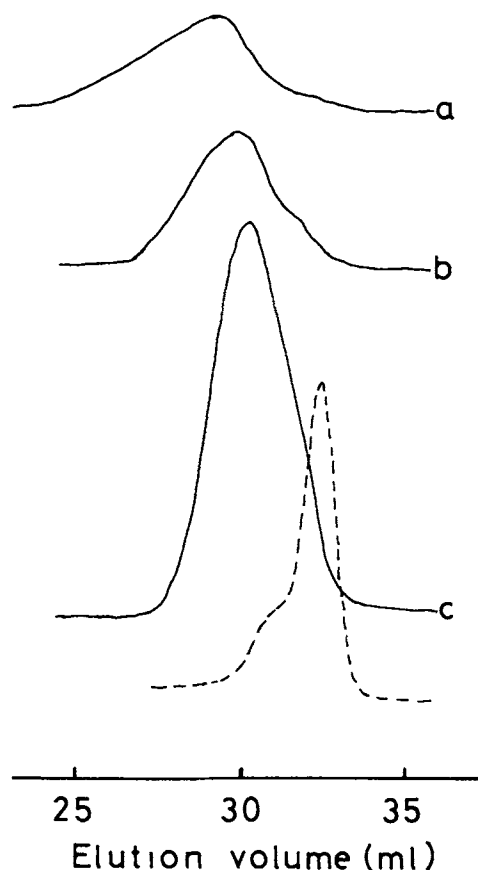


Figure 3 GPC (RI) curves of the products prepared at various PGE concentrations (solid line) and CH₃PEG-epoxide (dotted line): PGE concentration (a) 4 mmol; (b) 9 mmol; (c) 19 mmol.

ratio (9.0) of two monomers were obtained with the copolymerization in DMSO.

The rate of copolymerization was investigated at 40 and 100°C in DMSO. As shown in Figure 4, the conversion of PGE increased with reaction time and reached 93% after 8 h at 40°C, whereas it reached

Table III Copolymerization of CH₃PEG-Epoxyde with PGE in Various Solvents^a

Solvent	ϵ	\bar{M}_n	\bar{M}_w/\bar{M}_n	PGE/ CH ₃ PEG
<i>m</i> -Xylene	2.4	3800	1.26	11.8
<i>o</i> -Dichlorobenzene	9.9	7000	1.22	12.9
<i>t</i> -Butyl alcohol	11.4	5200	1.19	5.0
Nitrobenzene	34.8	4400	1.20	7.1
Dimethyl sulfoxide	45.0	7300	1.27	10.5

^a Reaction conditions: CH₃PEG-epoxide, 1 mmol (2 g); PGE, 9 mmol (1.2 mL); *t*-BuOK, 0.25 mmol; solvent, 2 mL; temperature, 100°C; time, 24 h.

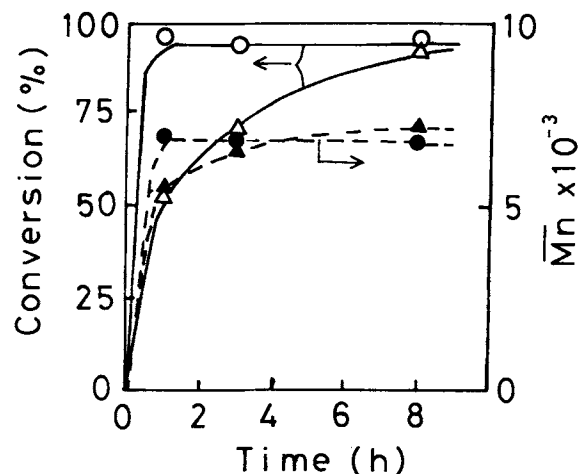


Figure 4 Effect of reaction temperature on the rate of copolymerization (solid line) and \bar{M}_n of graft copolymer (dotted line): temperature (○, ●) 100°C; (△, ▲) 40°C. Reaction conditions: CH₃PEG-epoxide, 1 mmol (2 g); PGE, 9 mmol (1.2 mL); *t*-BuOK, 1 mmol; DMSO, 2 mL.

over 90% within 1 h at 100°C. The \bar{M}_n of the copolymer showed a similar tendency and was almost same at 40 and 100°C after 3 h, i.e., 6700. When the copolymerization was carried out in the absence of solvent, the \bar{M}_n of the copolymers was in the range of 10,100 to 9100 at 60–120°C. Thus, the \bar{M}_n of the copolymer was little affected by the reaction temperature, but more affected by the presence of solvent.

Besides PGE, BGE and SO were effective as a comonomer, as shown in Table IV. The \bar{M}_n of copolymers was almost same with BGE and one-half with SO compared with that of PGE. Graft copolymers were seldom prepared with ECH and GMA.

Polymerization of CH₃PEG-Epoxyde

Polymerization of CH₃PEG-epoxide catalyzed by *t*-BuOK was carried out to examine the ability of

Table IV Copolymerization of CH₃PEG-Epoxyde with Various Epoxydes^a

Epoxyde	\bar{M}_n	\bar{M}_w/\bar{M}_n
PGE	9,400	1.43
BGE	10,400	1.30
SO	5,400	1.28
ECH	2,700	1.45
GMA	2,200	1.18

^a Reaction conditions: CH₃PEG-epoxide, 1 mmol (2 g); epoxide, 9 mmol; *t*-BuOK, 1 mmol; temperature, 100°C; time, 24 h.

homopolymerization. In the absence of solvent, the reaction mixture solidified (maybe due to the formation of cross-linking) after 2 h under the same conditions as those of the copolymerization. On the other hand, in the polymerization in *t*-BuOH, the reaction mixture did not solidify within 24 h and the product having about twice as large an \overline{M}_n as that of CH₃PEG was prepared. Thus, it is considered that the side reaction owing to the large reactivity of CH₃PEG-epoxide was suppressed by the role of PGE as both solvent and comonomer on the copolymerization.

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