

Synthesis of Graft Polyesters by Ring-Opening Copolymerization of Epoxy-Terminated Poly(ethylene Glycol) with Acid Anhydrides

ISAO IKEDA,* YOSHITOMO SIMAZAKI, and KIMIHIRO SUZUKI

Faculty of Engineering, Fukui University, Fukui 910, Japan

SYNOPSIS

The copolymerization of epoxy-terminated poly(ethylene glycol methyl ether) (CH₃PEG-epoxide) with phthalic anhydride catalyzed by tertiary amines was performed in *o*-dichlorobenzene at 100°C to prepare the PEG graft polyester. 4-Dimethylaminopyridine was the most favorable catalyst to give the graft polyester with relatively high molecular weight. The acidity of the reaction solution decreased and \bar{M}_n of the graft polyesters increased with reaction time. The CH₃PEG/phthalic acid ratio of the products was little affected by the kind of solvent and the reaction temperature above 100°C, but \bar{M}_n increased with lowering the polarity of solvents and with raising the temperature. Other acid anhydrides, including maleic, succinic, tetrahydrophthalic, and pyromellitic anhydride, could be copolymerized with CH₃PEG-epoxide. The number of branched CH₃PEG chains was controlled by the mixing of low molecular weight epoxide such as *n*-butyl glycidyl ether. CH₃PEG component of the graft copolymers melted and crystallized at lower temperature than the raw CH₃PEG because of the restriction on the trunk polyester chain.

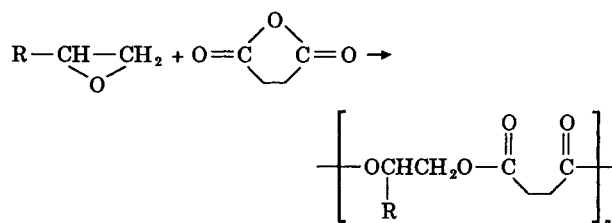
INTRODUCTION

It is well known that the polyesters can be synthesized by the ring-opening copolymerization of epoxides with acid anhydrides in the presence of various catalysts.¹⁻⁵ This method has some advantages in that the polymerization proceeds at lower temperature, in shorter reaction time, and under more conventional pressure than the synthesis of polyesters from diols and diacids. Representative epoxides, acid anhydrides, and catalysts used are as follows:

Epoxides: epichlorohydrine, *n*-butyl glycidyl ether, phenyl glycidyl ether

Acid anhydrides: maleic, succinic, phthalic, tetrahydrophthalic anhydride

Catalysts: organic and inorganic salts, tertiary amines



The reactivity of epoxides and acid anhydrides, catalyst activity, molecular weight of the copolymers, and mechanism and kinetics of the copolymerization were investigated in detail. However, no attempt has been made to synthesize the graft polyesters using the polymeric epoxides as epoxide component. Then we tried to synthesize them by the copolymerization of epoxy-terminated poly(ethyleneglycol methyl ether) (CH₃PEG-epoxide) with acid anhydrides. There are few works relating to the synthesis of graft copolymers utilizing the macromonomers having the ring-opening polymerization ability like this.⁶

A paper concerned in the PEG-grafted polyester has been reported elsewhere.⁷ In this case, acrylester-

* To whom correspondence should be addressed.

Table I Epoxidation of CH₃PEG in THF^a

Reagent of Metalation	[Reagent]	Temperature (°C)	Extent of Epoxidation (%)	
	[OH]		From GC	From HBr Reacted
NaH	1.0	40	55	72
		60	71	89
	1.5	40	118	130
		60	112	104
<i>t</i> -BuOK	1.0	40	152	85
	1.5	40	119	61

^a Reaction conditions: [CH₃PEG], 226 g/L; [ECH], 0.24 mol/L; time, 4 h.

terminated PEG was reacted with poly(ethylene terephthalate) cloth under the irradiation of electron rays.

On the other hand, the graft copolymers having the polyester graft chains has been synthesized by utilizing the copolymerization of epoxides with acid anhydrides.⁸ The photosensitive polyesters were grafted on poly(vinyl alcohol).

In this work, we investigated the reactivity of CH₃PEG-epoxide with acid anhydrides, catalyst activity, and the yield and molecular weight (\bar{M}_n) of the graft copolymers under the various reaction conditions.

EXPERIMENTAL

Materials

CH₃PEG (average MW = 1900) was purchased from Aldrich Chemical Co. and used without further purification. Phthalic anhydride (PAN) was purified by sublimation. Other acid anhydrides and catalysts were used without further purification. Epichlorohydrin (ECH) and solvents used for the copolymerization were purified by distillation over calcium hydride. Tetrahydrofuran (THF) was distilled over sodium.

Synthesis of CH₃PEG-Epoxyde

CH₃PEG 100 g dissolved in THF 400 mL was reacted with sodium hydride 1.9 g at 30°C for 2 h to sodium-metallize the terminal hydroxyl group. Then ECH 20 g was added to the solution and reacted at 40°C for 4 h. The products were precipitated in diethyl ether, filtered off, washed with diethyl ether, and dried. Then the products were dissolved in chloroform to separate sodium chloride prepared as by-product. Purified CH₃PEG-epoxyde was recovered

after twice this operation. Epoxy group in CH₃PEG-epoxyde was determined by the following method.⁹ A sample (0.1 g) dissolved in glacial acetic acid (5 mL) was reacted with 0.01*N* hydrobromic acid in glacial acetic acid solution (10 mL) at room temperature in the presence of crystal violet indicator. Then this solution was titrated to the blue-green end point with 0.01*N* sodium carbonate in glacial acetic acid solution to determine the unreacted hydrobromic acid. Epoxy group (mmol/g) was calculated from the amount of consumed hydrobromic acid.

Copolymerization of CH₃PEG-Epoxyde with PAN

Equimolar quantities of CH₃PEG-epoxyde and PAN were dissolved in a solvent and reacted at 100°C in the presence of a catalyst. Aliquots of the reaction mixture were withdrawn at intervals, dissolved in methanol, and titrated with 0.01*N* sodium hydroxide solution to determine the acid value of the solution. After the reaction the products were precipitated in

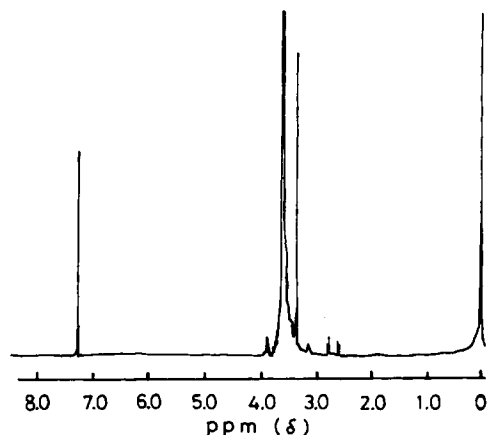


Figure 1 ¹H-NMR spectrum of CH₃PEG-epoxyde.

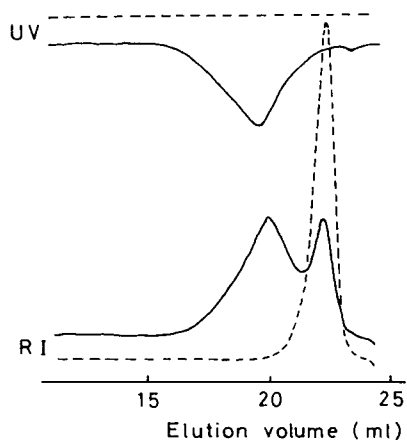


Figure 2 GPC curves of the product (—) and CH₃PEG-epoxide (---).

ethyl ether and purified by the same methods as described in the synthesis of CH₃PEG-epoxide. The ratio of CH₃PEG to phthalic acid component (CH₃PEG/PA) in the products was determined by ¹H-NMR spectra:

$$\frac{\text{CH}_3\text{PEG}}{\text{PA}} = \frac{\text{area of methoxy signal}}{\text{area of phthalic acid signal}} \times \frac{4}{3}$$

The pure graft polyesters were obtained by dialyzing the products for 2 weeks against tap water to remove the unreacted CH₃PEG-epoxide. The composition and the molecular weight of the graft copolymers

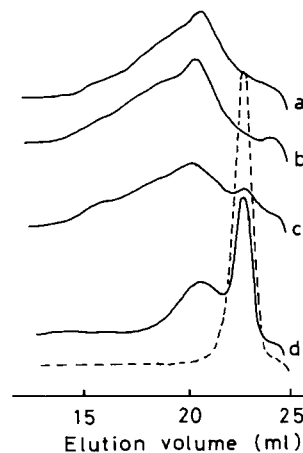


Figure 3 GPC curves of the products, quantity of DMAP (mol %): (a) 7; (b) 3; (c) 0.7; (d) 0. (---) CH₃PEG-epoxide.

were determined by ¹H-NMR spectra and GPC measurement, respectively.

Instrumental Methods

The ¹H-NMR spectra were recorded on a JEOL GX-270 spectrophotometer with TMS as an internal standard. The GPC analysis were performed using two TSK-gel columns in 10% acetonitrile aqueous solution or THF solution at 40°C after calibration with poly(ethylene oxide) or polystyrene standards, respectively. The DSC thermograms were recorded on a Shimadzu DSC-30 equipped with the cooling bath LTC-30. The rate of heating and cooling used was 5°C/min.

Table II Copolymerization of CH₃PEG-Epoxy with PAN Catalyzed by Various Catalysts^a

Catalyst	Acidity ^b (meq/g)	CH ₃ PEG/PA in Product ^c	\bar{M}_n of Graft Copolymer ^d
Triethylamine	0.16	1.44	10300
<i>N</i> -methylmorpholine	0.12	1.52	14700
Triethylenediamine	0.11	1.56	19200
4-Dimethylaminopyridine	0.06	1.54	28400
1,8-Diaza-bicyclo(5,4,0) undecene-7	—	1.69	24000
<i>N,N</i> -dimethylbenzylamine	0.18	2.63	8500
Tetra- <i>n</i> -butylammonium iodide	0.09	0.91	11300
Lithium chloride	0.13	1.16	15500
Sodium chloride	0.14	1.39	24500
Potassium chloride	0.12	1.25	28300
None	0.21	3.03	7000

^a Reaction conditions: CH₃PEG-epoxide, 1 mmol (2 g); PAN, 1 mmol (0.148 g); catalyst, 0.03 mmol; solvent (*o*-dichlorobenzene), 2 mL; temperature, 100°C; time, 24 h.

^b Starting acidity = 0.24 meq/g.

^c Determined by ¹H-NMR.

^d Determined by GPC.

Table III Copolymerization of CH₃PEG-Epoxyde with PAn with Various DMAP Concentrations^a

Quantity of DMAP (mol %)	Acidity ^b (meq/g)	\bar{M}_n of Graft Copolymer
0	0.21	7000
0.7	0.11	30100
3	0.06	28400
7	0.06	19300

^a Reaction conditions are the same as Table II.^b Starting acidity = 0.24 meq/g.

RESULTS AND DISCUSSION

Synthesis of CH₃PEG-Epoxyde

Epoxidation of CH₃PEG was performed through the alkali-metalation of hydroxy group following by the reaction with ECH. Table I shows the alkali-metalation reagents used and the extent of epoxidation. The latter was measured by both the change of ECH concentration with GC analysis and the HBr concentration added to the epoxy group. Both values were almost the same with NaH, but different with *t*-BuOK. With *t*-BuOK, it is considered that the extent of epoxidation from the change of ECH concentration became apparently larger than that from HBr method due to the anionic polymerization of ECH initiated by *t*-BuOK. With excess of NaH against the hydroxyl groups, the extent of epoxidation exhibited over 100%. CH₃PEG is known to contain about 25% the component whose end is not methylated.¹⁰ Then the epoxidation is considered to occur quantitatively in this case. The reaction temperature affected scarcely on the epoxidation.

On the reaction of hydroxyl group with ECH under the alkaline condition, it is well known that the crosslinking reaction also occurs besides the epoxidation. The GPC curves of the products prepared on this study, however, did not change compared with that of CH₃PEG. Then it is considered that the crosslinking reaction did not occur in this reaction. Figure 1 shows the ¹H-NMR spectrum of CH₃PEG-epoxyde synthesized (ethylene oxide signal at 3.6 ppm, methoxy signal at 3.4 ppm, and epoxy signals at 2.6–3.2 ppm).

Copolymerization of CH₃PEG-Epoxyde with Acid Anhydrides

Figure 2 shows a representative GPC curve of the products prepared by the copolymerization of CH₃PEG-epoxyde with PAn. Two peaks appeared on the RI curve as compared with one peak on UV

curve. The lower molecular weight peak on RI curve corresponds to the unreacted CH₃PEG-epoxyde which does not show the absorption at 254 nm. The higher molecular weight peak corresponds to the graft copolymer which shows the UV absorption. Then the molecular weight (\bar{M}_n) of the graft copolymer can be determined from UV curve by the universal calibration method. It was ascertained separately that CH₃PEG-epoxyde did not polymerize by tertiary amines. The composition of the pure graft copolymers obtained by dialyzing the products was determined by the ¹H-NMR measurement. They were consequently composed of equimolar of CH₃PEG and phthalic acid components (CH₃PEG/PA = 1.0). Then the copolymerization is considered to proceed through the following mechanism¹:

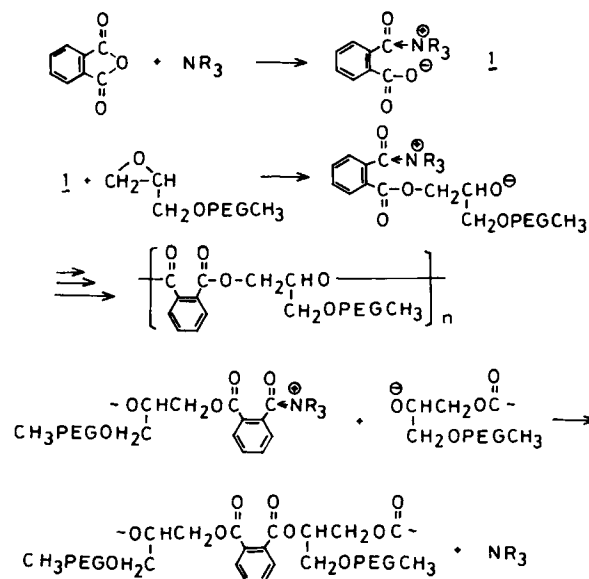
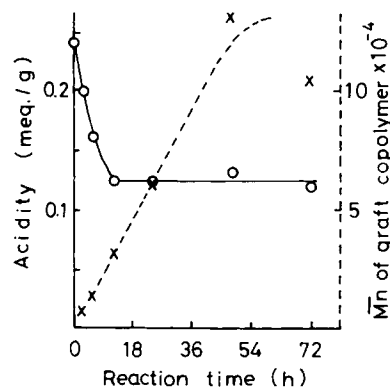
**Scheme 1****Figure 4** Time dependence of acidity (O) and \bar{M}_n of graft copolymers (X): reaction conditions are the same as Table II.

Table IV Copolymerization of CH₃PEG-Epoxy with PAN in Various Solvents at Different Temperatures^a

Solvent	Temperature (°C)	Acidity ^b (meq/g)	CH ₃ PEG/PA in Product	\bar{M}_n of Graft Copolymer
<i>m</i> -Xylene	80	0.15	1.28	14400
	100	0.06	1.09	58900
	120	0.05	1.14	193000
<i>o</i> -Dichlorobenzene	80	0.15	1.30	17800
	100	0.06	1.11	73000
	120	0.06	1.06	106000
Nitrobenzene	80	0.13	1.22	8800
	100	0.07	1.14	59000
	120	0.08	1.05	48000
	140	0.09	1.04	67000

^a Reaction conditions: CH₃PEG-epoxide, 1 mmol (2 g); PAN, 1 mmol (0.148 g); DMAP, 0.04 mmol; solvent, 2 mL; time, 24 h.

^b Starting acidity = 0.24 meq/g.

The copolymerization of CH₃PEG-epoxide with PAN was performed using various catalysts including organic and inorganic salts besides tertiary amines. Table II shows that the CH₃PEG/PA ratio of the products is above 1.0 except for tetra-*n*-butylammonium iodide. Excess of CH₃PEG component in the products is attributed to the presence of the unreacted CH₃PEG-epoxide because the pure graft copolymers were ascertained to be composed of equimolar of CH₃PEG and phthalic acid components as described previously.

Although \bar{M}_n of the graft copolymers was relatively large with DMAP and potassium chloride, the most favorable catalyst was DMAP because the inorganic salts were not soluble entirely in the organic

Table V Copolymerization of CH₃PEG-Epoxy with Various Acid Anhydrides^a

Acid Anhydride	Catalyst	Acidity ^b (meq/g)	\bar{M}_n of Graft Copolymer
Maleic	DMAP	0.13	36000
Succinic	DMAP	0.18	6100
THPA	TBAI ^c	0.04	6200
TMSB-MA	DMAP	0.04	16300
	TBAI ^c	0.04	33800
Phthalic	DMAP	0.06	28400
	TBAI ^c	0.09	11300
Pyromellitic	DMAP	0.16	12000

^a Reaction conditions: CH₃PEG-epoxide, 1 mmol (2 g); acid anhydride, 1 mmol; catalyst, 0.03 mmol; solvent (*o*-dichlorobenzene), 2 mL; temperature, 100°C; time, 24 h.

^b Starting acidity = 0.24 meq/g.

^c Tetra-*n*-butylammonium iodide.

solvents. When the copolymerization was carried out in the absence of the catalyst, the yield and \bar{M}_n of the graft copolymer were less than those for the presence of the catalyst.

Figure 3 shows the GPC curves of the raw products prepared with the various DMAP concentrations. Unreacted CH₃PEG-epoxide peak decreased with increase in the DMAP concentration and almost disappeared above 3 mol %. The peak molecular weight of the graft copolymers is almost the same for every DMAP concentration but \bar{M}_n decreased slightly with increase in the DMAP concentration as shown in Table III.

Figure 4 shows the time dependence of the acidity of the reaction solution and \bar{M}_n of the graft copolymers for batch polymerization. The acidity decreased with reaction time and leveled off above 12 h. On the other hand, \bar{M}_n of the graft copolymers increased

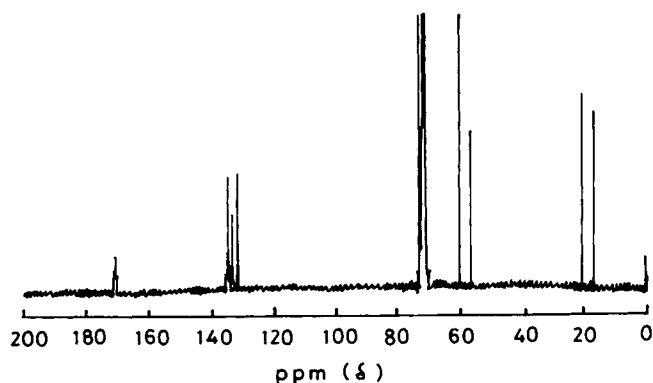
**Figure 5** ¹³C-NMR spectrum of CH₃PEG graft polyester with PAN.

Table VI Copolymerization of Mixed Epoxides with PAn^a

Epoxides		Acidity ^b (meq/g)	Graft Copolymer	
CH ₃ PEG-Epoxyde	BGE		CH ₃ PEG/PA	\bar{M}_n
0.10	0.90	0.08	0.05	14200
0.25	0.75	0.09	0.09	19200
0.50	0.50	0.09	0.21	34600
0.75	0.25	0.11	0.73	31800
1.00	0	0.13	0.95	34400

^a Reaction conditions: epoxides (CH₃-PEG-epoxyde + BGE), 2 mmol; PAn, 2 mmol (0.296 g); DMAP, 0.08 mmol; solvent (*o*-dichlorobenzene), 5 mL; temperature, 100°C; time, 24 h.

^b Starting acidity = 0.25 meq/g.

linearly until about 48 h. This is probably due to the continuous recombination between the negative and positive ends of the copolymers as shown in the polymerization mechanism. Thus the recombination reaction is considered to occur preferentially at the diminished monomer concentration.

The copolymerization was performed at various reaction temperatures in the different solvents. As shown in Table IV, the acidity and the CH₃PEG/PA ratio of the products were little affected by the kind of solvent and the reaction temperature above 100°C. However, \bar{M}_n of the graft copolymers increased with raising the reaction temperature and with lowering the polarity of solvents. Thus the recombination reaction was liable to occur at higher temperature and in the less polar solvent.

Table V shows the copolymerization of CH₃PEG-epoxyde with various acid anhydrides including

maleic, succinic, tetrahydrophthalic (THPA), 4-trimethoxysilyl-tetrahydrophthalic (TMSB-MA), phthalic and pyromellitic anhydride. All acid anhydrides used copolymerized with CH₃PEG-epoxyde to prepare the PEG graft polyesters. IR and NMR spectra revealed the characteristic peaks of acid component and ester bond besides that of CH₃PEG. The representative ¹³C-NMR spectrum of the graft polyester with PAn was shown in Figure 5. The signal of 60 ppm assigned to methoxy, 71–74 ppm to ethylene oxide, 131–135 ppm to phenyl, and 170 ppm to ester.

The low molecular weight epoxide such as *n*-butyl glycidyl ether (BGE) was added to the reaction mixture to control the number of branched CH₃PEG. As shown in Table VI, the content of CH₃PEG in the graft copolymer increased with increase in CH₃PEG-epoxyde concentration and was about one half of the starting epoxides ratio except for the higher CH₃PEG-epoxyde concentration. \bar{M}_n of the graft copolymers also increased with the CH₃PEG-epoxyde concentration and leveled off above equimolar ratio of CH₃PEG to BGE. Thus the number of branched CH₃PEG could be controlled by the mixing of BGE.

Thermal Properties of PEG Graft Polyesters

Figure 6 shows the DSC curves of the graft copolymers. On heating, the CH₃PEG component of the graft copolymers melted at lower temperature than the raw CH₃PEG. On cooling, the crystallization temperature of the CH₃PEG component was similarly lower than that of CH₃PEG. Further, the temperature lowered as \bar{M}_n of the graft copolymer increased. These results reveal that CH₃PEG chains of the graft copolymers are difficult to aggregate each other because of the restriction on the trunk poly-

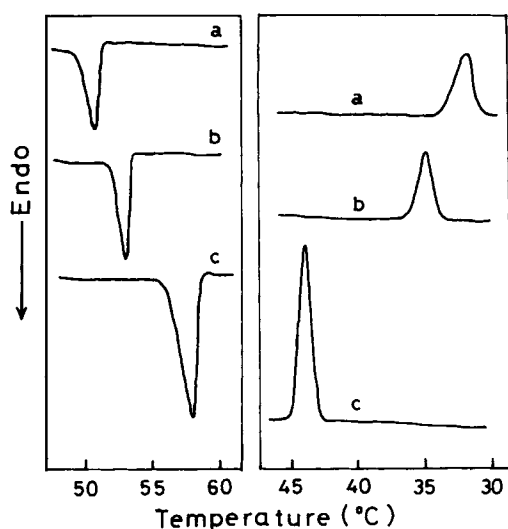


Figure 6 DSC curves of graft copolymers: (a) \bar{M}_n = 28,400; (b) \bar{M}_n = 13,600; (c) CH₃PEG-epoxyde.

ester chain and that the graft copolymers became more amorphous as \bar{M}_n increased.

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