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AN IMPROVED SYNTHETIC METHOD FOR PREPARING POLYOXYETHYLENE MACROMERS AND A STUDY OF THEIR COPOLYMERIZATION WITH ALKYL ACRYLATES

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ABSTRACT

Polyoxyethylene macromers were synthesized by polymerization of ethylene oxide in dimethylsulfoxide by using potassium naphthalide in tetrahydrofuran as initiator, followed by termination with methacryloyl chloride. Potassium naphthalide is more active as an initiator than sodium naphthalide. The initiator in this case was confirmed to be of the monoanionic type. The molecular weight of the macromers can be varied from 2×10^3 to 1.2×10^4 with $M_w/M_n = 1.07$ – 1.12 . The macromers were characterized by UV, IR, and ^1H NMR, and copolymerized with butyl acrylate, methyl acrylate, or methyl methacrylate. The grafting efficiency can reach about 90%. The graft copolymers were purified by extractions and characterized by GPC, IR, and a Bruss membrane osmometer. The average grafting number of the copolymers varied from 10 to 15.

INTRODUCTION

Rempp [1] and Masson [2], and their coworkers reported the synthesis of polyoxyethylene (PEO) macromers through anionic polymerization of ethylene oxide (EO), either by using alkali alcoholate as the initiator and

methacryloyl chloride as the terminating agent or by using unsaturated alkali alcoholate as the initiator and alkyl chloride as the terminating agent. Ito et al. [3, 4] synthesized PEO macromers by using potassium tertiary butoxide as the initiator and methacryloyl chloride as the terminating agent, and then studied their reactivity in copolymerization with styrene. They [4] also studied the reactivity of PEO macromers, obtained upon termination with *p*-vinyl benzyl chloride, in copolymerization with styrene in different solvents. However, the above synthetic method for PEO macromers using an alkali alcoholate as the initiator possesses several disadvantages; it needs relatively long reaction times; solubility of an alkali alcoholate in most solvents is rather low; and the molecular weight range of the PEO macromers that can be obtained is small.

Bawn et al. [5] mentioned the preparation of living PEO anions by using potassium *t*-butoxide as the initiator and dimethylsulfoxide (DMSO) as the solvent, and they pointed out that the real initiator was the reaction product: dimethylsulfonium anion. Cabasso and his coworkers [6] revealed that upon using potassium naphthalide and DMSO as the initiator system, living PEO anions can be obtained and, according to the molecular weight of the products, the polymerization was monoanionic. The polymerization rate is comparatively high. However, synthesis of PEO macromers using this initiator has not yet been reported. Our work deals with an improved method of synthesizing PEO macromers using potassium naphthalide in tetrahydrofuran as the initiator, DMSO as the solvent, and methacryloyl chloride as the terminating agent. The macromers obtained were characterized and copolymerized with butyl acrylate, methyl acrylate, or methyl methacrylate in benzene using AIBN as the initiator. Thus we were able to examine macromer reactivity under different polymerization conditions and also determined the average grafting number of the copolymers obtained.

EXPERIMENTAL

Materials

A.R. dimethylsulfoxide was dried with CaH_2 for 48 h and distilled; the distillate at $85\text{--}87^\circ\text{C}/25\text{ mmHg}$ was collected. Commercial ethylene oxide (EO) was treated with KOH and CaH_2 successively, then distilled into purified toluene or into a cold trap and stored in a refrigerator. A.R. tetrahydrofuran (THF) was distilled over ferrous sulfate and dried with

CaH₂. C.P. *n*-butyl acrylate (BA), methyl acrylate (MA) or methyl methacrylate (MMA) was washed successively with 10% NaOH and water, dried with anhydrous Na₂SO₄, and then distilled over CuCl; the distillate collected at 48–49°C/25 mmHg was kept under nitrogen atmosphere in a refrigerator until used. C.P. benzene was dried overnight with 4A Molecular Sieves. C.P. azobisisobutyronitrile (AIBN) was recrystallized from ethanol.

Preparation and Analysis of Potassium Naphthalide

Naphthalene (14 g) and 5.1 g potassium chips were put into 70 mL dried THF, stirred under nitrogen atmosphere for 3–4 h, and then kept in a refrigerator. The upper dark green solution was taken out when the potassium naphthalide was used. The content of potassium in the solution was determined by titration of the hydrolyzed liquor with 0.1 N HCl solution, using methyl orange as indicator.

Preparation of α -Methacryloyl Chloride

C.P. α -methacrylic acid was reacted with an equivalent amount of sulfonyl chloride under stirring at 65°C for 10 h. The product was distilled under reduced nitrogen pressure over CuCl with the distillate collected at 50–52°C/35 mmHg.

Synthesis of PEO Macromers

EO (0.6 mol) was dissolved in 100 mL DMSO. Under nitrogen atmosphere, the THF solution of potassium naphthalene was dropped in via syringe until the light yellow color ceased to disappear. The required amount of THF solution of potassium naphthalide was injected by means of a syringe. The mixture was cooled in an ice bath in order to keep the reaction temperature below 30°C for 2 h. Then the reaction was maintained at 30°C for 6 h. The reaction solution became dark yellow. The reaction was terminated by injecting excess α -methacryloyl chloride into the system and kept at 30°C for 4 h. The product was precipitated and washed with ethyl ether. The precipitate was dissolved in chloroform and reprecipitated with ethyl ether, filtered, and vacuum dried to constant weight.

Characterization of the PEO Macromer

The number-average molecular weight (\bar{M}_n) and molecular weight distribution were measured with a Knauer VPO apparatus by using chloroform as the solvent and with a LC-4A liquid chromatographic apparatus by using THF as the eluent, respectively. IR and UV spectra were taken with a PE-580B spectrophotometer and a Specord UV-Vis spectrophotometer, respectively. The $^1\text{H-NMR}$ spectrum was recorded with a XL-200 (200 MHz) spectrometer.

Copolymerization of the PEO Macromer with Alkyl Acrylate

A certain amount of the dried macromer was dissolved in benzene, and butyl acrylate (or methyl acrylate or methyl methacrylate) and AIBN were added. Copolymerization was carried out at 60–70°C under nitrogen atmosphere with stirring for a certain time. Then a small amount of hydroquinone was added to terminate the copolymerization. The solvent was evaporated. After vacuum drying to constant weight, the product was extracted with water three times to separate out the unreacted PEO macromer and extracted with ethyl ether or ethyl ether/acetone (3/7 by volume) three times to separate out the homopolymer of BA or of MA or MMA, respectively. Conversion of the PEO macromer and the grafting efficiency (G.E.) can be calculated according to the following equation:

$$\text{G.E., \%} = \frac{(\text{macromer charged} - \text{macromer unreacted})}{\text{macromer charged}} \times 100$$

% Conversion of MA, BA, or MMA =

$$\frac{(\text{crude product} - \text{macromer charged})}{\text{MA (BA, or MMA)}} \times 100$$

Characterization of the Purified Graft Copolymer

The GPC curve of the copolymer was obtained by using a LC-4A type apparatus with THF as the eluent. IR spectra were recorded on a PE-580B spectrophotometer by using KBr pellets. The number-average molecular weights of the copolymers were determined by using a Bruss membrane osmometer with THF as the solvent. The PEO content was calculated from the oxygen content as determined from elemental analysis.

RESULTS AND DISCUSSION

Synthesis of PEO Macromers

The polymerization of EO in DMSO initiated by potassium naphthalide, as carried out by us, is somewhat different from that used by Cabasso et al. [6]. They first reacted the THF solution of potassium naphthalide with DMSO before adding it to a DMSO solution of EO, while we added a THF solution of potassium naphthalide directly to the DMSO solution of EO.

First-order kinetics for the polymerization of EO was found, as shown in Fig. 1. Conversion of EO at 30°C after 6.7 h reached 98%. When \bar{M}_n

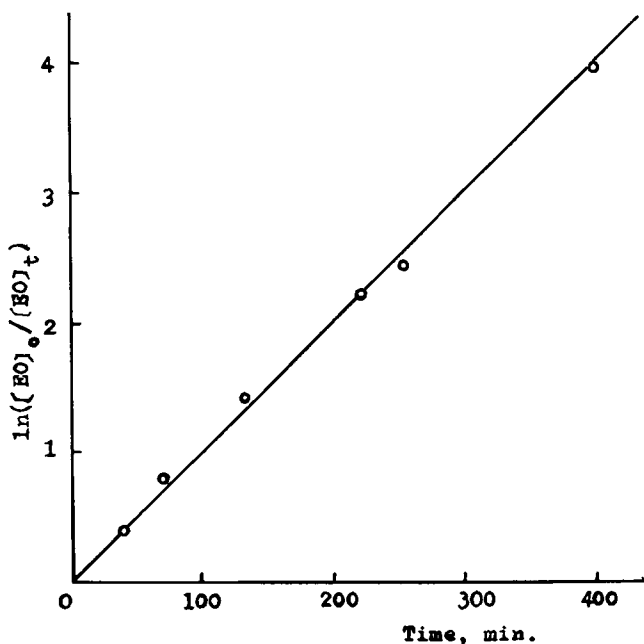


FIG. 1. First-order kinetics for the polymerization of EO initiated with potassium naphthalene in DMSO: $K/EO = 4.15 \times 10^{-3}$.

of the polyoxyethylene samples was plotted versus conversion, a straight line passing through the origin was obtained, as shown in Fig. 2, which demonstrates "living" polymerization.

The polymerization rates of EO in DMSO by sodium naphthalide and potassium naphthalide are compared in Table 1. It can be seen that rate of polymerization initiated by potassium naphthalide is higher than that using sodium naphthalide as initiator. This is similar to anionic polymerizations catalyzed by alkali metal where the activity increases with the electropositive nature of the metal.

The \bar{M}_n values of PEO, as determined by VPO, are close to the \bar{M}_n calculated under the hypothesis of monoanionic initiator, i.e., about half the value based on dianionic initiators as summarized in Table 2. This shows that potassium naphthalide in a DMSO solution of EO is not a dianionic initiator but a monofunctional initiator.

It is well known that the reactivity of an alkoxide anion is far less than that of a carbanion. In the reaction with methacryloyl chloride the alkoxide anion can only react with the acid chloride function but not with the double bond. Hence it is possible to obtain high termination efficiency.

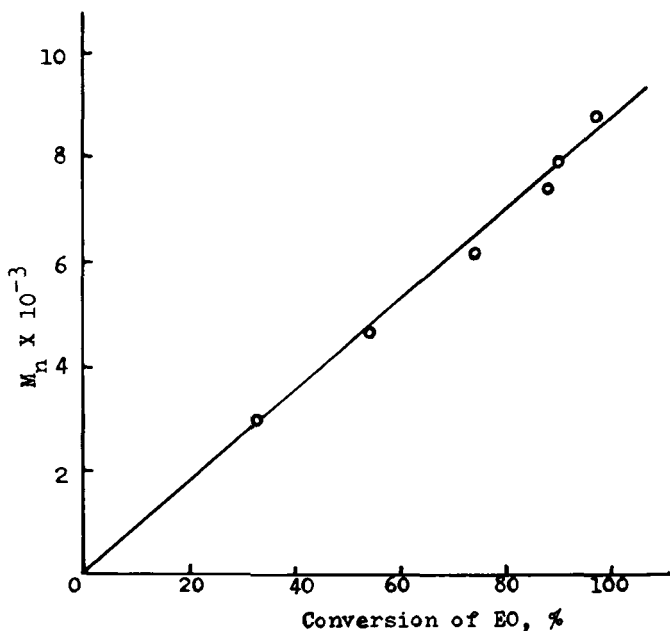


FIG. 2. Plot of M_n of PEO versus conversion.

TABLE 1. Comparison of Polymerization Rate of EO Initiated with Sodium Naphthalide and with Potassium Naphthalide in DMSO^a

	Initiator			
	Potassium naphthalide		Sodium naphthalide	
Polymerization time, h	5.5	12	5.5	12
% Conversion	78.6	96.7	36.9	68.0

^aInitiator/EO = 2.4×10^{-3} .

We tried to measure the double bond content of the PEO macromer by means of UV spectrophotometry by using absolute ethyl alcohol as solvent and a mixture of MMA and PEO as a standard for the purpose of comparison. It is necessary to determine first whether or not the dimethyl group is present at the end of the PEO chain. No absorption peak was

TABLE 2. Effect of Potassium Naphthalide Concentration on the Molecular Weight of PEO Obtained^a

Concentration of potassium naphthalide, mol/L	$\bar{M}_n \times 10^{-3}$		
	(VPO)	^b	^c
0.100	2.2	2.6	5.2
0.050	4.0	5.3	10.6
0.035	7.0	7.5	15.0
0.025	9.1	10.6	21.2
0.020	12.0	13.2	26.4

^aPolymerization conditions: concentration of EO = 6.0 mol/L, 30°C, 8 h, DMSO as solvent.

^bMolecular weight of PEO calculated according to monoanionic initiator.

^cMolecular weight of PEO calculated according to dianionic initiator.

found at 210 nm in the UV spectrum of PEO prior to termination with methacryloyl chloride, while a strong absorption peak appears at 207 nm for the macromer after termination.

From the plot of absorption intensity versus concentration, knowing the M_n of the PEO macromers (determined by VPO), the relative mol% of double bonds in the PEO macromer or terminating efficiency can be calculated according to the following equation:

$$\text{Double bonds, mol\%} = C_0 \times M_n \times 100 / (C_s \times 100.1)$$

where 100.1 is the molecular weight of MMA, C_0 is the concentration of the MMA (weight/volume) corresponding to the calibration curve, and C_s is the real concentration of the macromer. It can be noted from Table 3 that the mol% of double bonds is mostly higher than 94% and that the molecular weight of PEO macromers does not exert any serious influence on the double bond content. The double bond content cannot reach 100% due to the reaction of PEO anions with impurities in the termination reaction. The double bond content measured by this method seems higher than the grafting efficiency estimated from the conversion of the macromer upon copolymerization with alkyl acrylate. The grafting efficiency of the macromer is usually below 95%.

TABLE 3. Relative Mol% of Double Bonds in PEO Macromer Determined by UV Spectrophotometry

C_s , mg/mL	$C_0 \times 10^3$, mg/mL	$\bar{M}_n \times 10^{-3}$ [VPO]	Double bonds, mol%
0.17	7.6	2.2	98
0.41	9.6	4.0	94
0.76	10.3	7.0	95
0.97	10.3	9.1	97
1.12	8.9	12.0	95

Characterization of the PEO Macromers

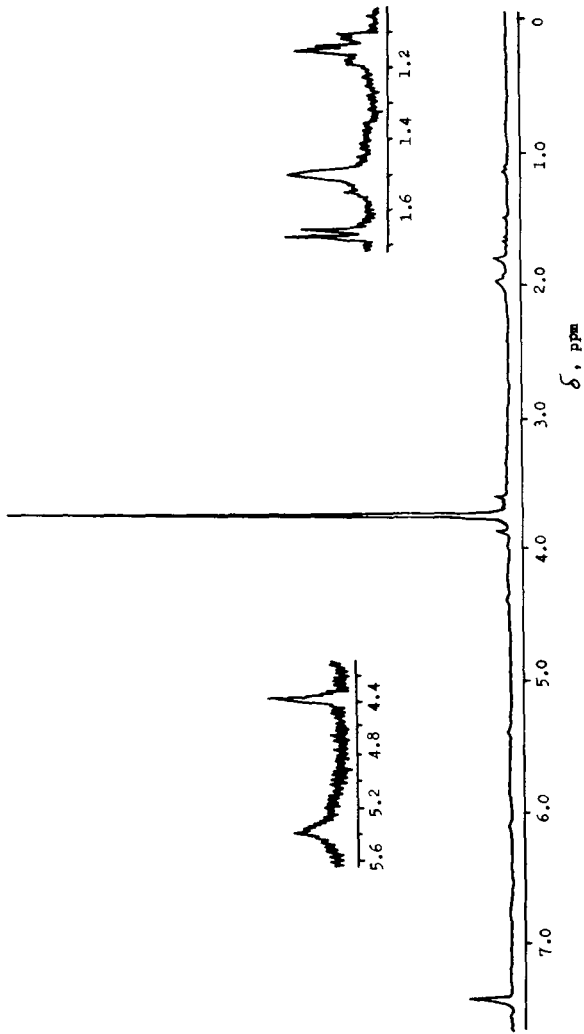
Table 4 lists the number-average weight molecular weight of the PEO macromers determined by VPO and their polydispersity indices \bar{M}_w/\bar{M}_n , determined by GPC, in comparison with those of polystyrene macromers obtained by polymerization of styrene initiated with *n*-butyl lithium-THF. It can be seen that the molecular weight distribution of PEO macromer is slightly broader than that of the styrene macromer, yet it is still narrow. The same table indicates that \bar{M}_w/\bar{M}_n of the PEO macromer is not directly related to their molecular weight.

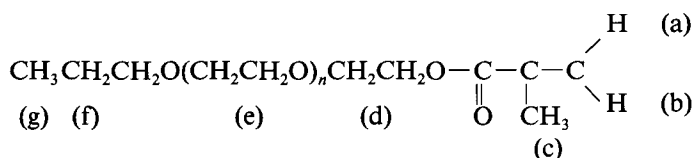
IR spectra of both the PEO macromer and the OH-containing PEO before termination with methacryloyl chloride were compared. Both samples show absorption peaks at 2900 and 1120 cm^{-1} , which denote the vibration of CH_2 and $\text{C}-\text{O}-\text{C}$, respectively. The difference is a broad peak occurring at 3450 cm^{-1} , characteristic for OH vibration in the IR spectrum of the PEO terminated protonically. The IR spectrum of the macromer exhibits peaks at 1730 and 1640 cm^{-1} which are characteristic of the absorption of $\text{C}=\text{O}$ and $\text{C}=\text{C}$, respectively. Neither the PEO macromer nor the PEO terminated protonically shows the presence of naphthalene or benzene ring in their IR spectra. This demonstrates that in our system EO is not initiated by dianionic initiator from potassium naphthalide.

From the $^1\text{H-NMR}$ spectrum of the PEO macromer (Fig. 3), the peaks may be assigned as follows:

TABLE 4. Number-Average Molecular Weight and Molecular Weight Distribution of the PEO Macromers

Macromers	$\bar{M}_n \times 10^{-3}$ [VPO]	\bar{M}_w/\bar{M}_n (GPC)
PEO-1	2.2	1.09
PEO-2	4.0	1.10
PEO-3	7.0	1.07
PEO-4	12.0	1.12
PS	10.7	1.04

FIG. 3. $^1\text{H-NMR}$ spectrum of the PEO macromer in C_6D_6 .



where $\delta_a = 5.4$, $\delta_b = 6.1$, $\delta_f = 1.5-1.68$, $\delta_d = 4.4$, $\delta_e = 3.75$, $\delta_c = 2.0$, and $\delta_g = 1.15$.

No peaks of protons of DMSC ($\delta = 2.6$) or of naphthalene can be detected except the peak arising from the solvent C_6D_6 . This also indicates that the initiator is neither dimsyl anion nor dianionic potassium naphthalide. Probably the initiator is methyl anion formed by the reaction between potassium and dimethylsulfoxide.

Further study is needed to clarify the initiation mechanism. However, both IR and $^1\text{H-NMR}$ spectra confirm the presence of double bonds in the PEO macromer.

Copolymerization Rate of the PEO Macromer with MA

Figure 4 shows the copolymerization rates of both the macromer terminated with a methacryl group and MA. At the beginning, the conversion rate of the macromer was higher than that of MA, but after a certain time the conversion of MA exceeded that of the macromer. This is due to the higher reactivity of the methacryloyl group of the macromer than that of the acryloyl group of MA at the beginning of reaction. With an increase in conversion, the viscosity of the polymerization solution gradually increased, resulting in more difficult diffusion of the macromer. Thus the conversion rate of the macromer became lower than that of MA at a later stage. The PEO content in the copolymer decreased with increasing conversion, as shown in the same figure. This can be interpreted as follows: With increasing conversion, viscosity of the polymerization system increased. The increased viscosity restricts the diffusion of the macromer much more seriously than that of the MA monomer, thus causing the decrease of PEO content of the copolymer.

No gel was formed in the copolymer, and this also confirms that the PEO macromer is monofunctional.

Effects of Copolymerization Conditions

Table 5 and Fig. 5 indicate that in the copolymerization of the PEO macromer with MMA or BA, grafting efficiency increases and molecular

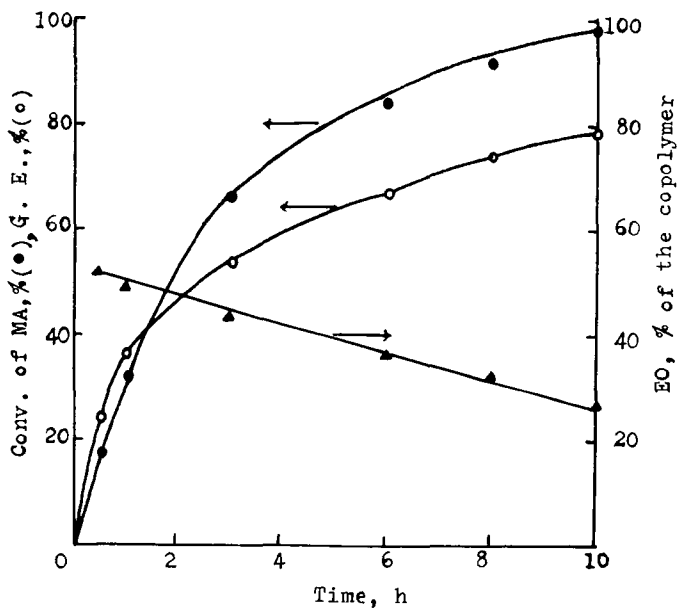


FIG. 4. Conversion rate of MA (●) and PEO (○) macromer and change of copolymer composition versus copolymerization time.

TABLE 5. Effect of Amount of Initiator on Grafting Efficiency and Molecular Weight of Copolymers (\bar{M}_{nc})^a

Amount of AIBN used, w%	G.E., %	$\bar{M}_{nc} \times 10^{-5}$
0.15	78.4	2.15
0.30	79.7	1.81
0.50	81.3	0.98

^aPolymerization conditions: \bar{M}_n of PEO macromer = 2.2×10^3 , macromer/MMA = 3/7 (w/w), 69°C, 10h.

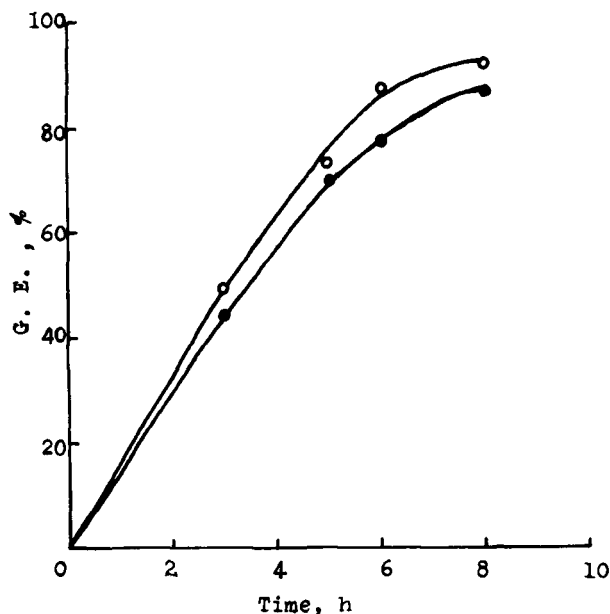


FIG. 5. Effect of amount of initiator on grafting efficiency in the copolymerization of PEO macromer with BA. Amount of AIBN used: (○) 1%, (●) 0.5%.

weight of the copolymer decreases with increasing amount of AIBN used. This is simply due to the fact that the concentration of active centers increases with an increase in AIBN, resulting in a decrease in molecular weight of the copolymer and viscosity of the solution. The latter helps increase grafting efficiency.

In the copolymerization of PEO macromer with BA, a maximum is observed in the relation between grafting efficiency and concentration (Fig. 6). This result can be explained as follows: If the concentration is too high, the very high viscosity of the polymerization system as copolymerization proceeds will restrict the motion of active chains and macromers, thus decreasing the grafting efficiency. However, if the concentration is too low, more impurities are present in the copolymerization system, thereby inducing termination of the more active macromer and reducing the grafting efficiency.

Figure 6 also shows that the molecular weight of the copolymer increases with concentration. This result is expected since the kinetic chain length is usually proportional to the monomer concentration.

In the copolymerization of the macromer with BA, the molecular

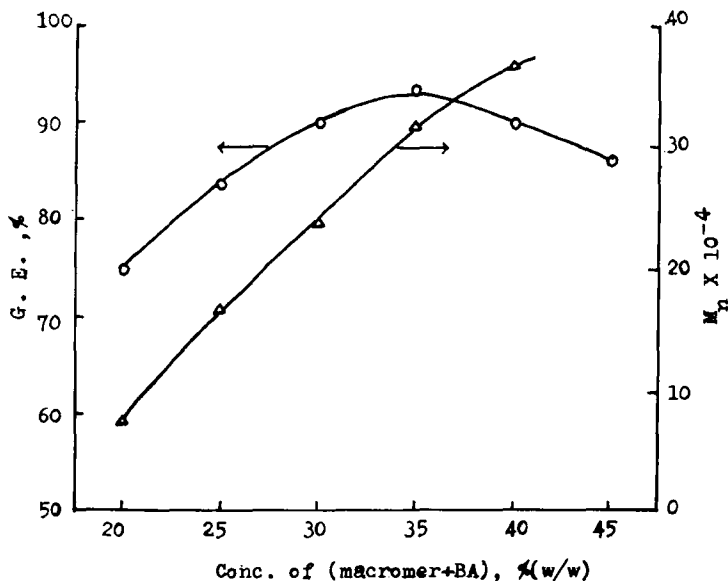


FIG. 6. Effect of total concentration of BA and PEO macromer on the grafting efficiency (○) and molecular weight (△) of copolymer.

weight of the copolymer decreases with increasing reaction temperature as illustrated in Fig. 7. This result is attributed to the fact that increasing the temperature will increase the decomposition rate of initiator. At the same time, the higher temperature and lower viscosity of the reaction may increase termination. Figure 7 also shows a decrease in grafting efficiency with an increase in the macromer/monomer ratio which is probably also related to the increase of viscosity.

Purification and Characterization of the Graft Copolymer

The crude product of the copolymerization contains homopolymer of alkyl acrylate, unreacted PEO macromer, and the graft copolymer. The homopolymer of alkyl acrylate and unreacted PEO macromer can be separated from the graft copolymer by means of water extractions and ethyl ether or ethyl ether/acetone mixture extractions as described in the Experimental section.

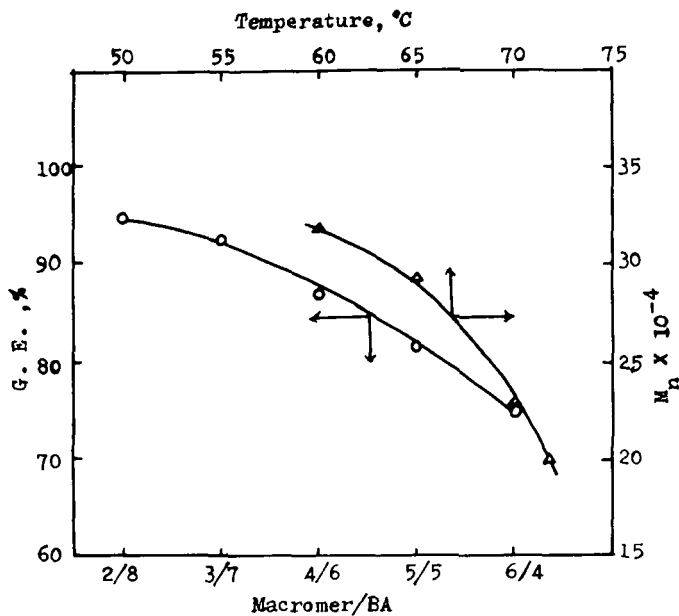


FIG. 7. Effect of charging ratio of PEO macromer/BA on grafting efficiency (○) and effect of copolymerization temperature on molecular weight (△) of the copolymer.

The GPC curve of the purified graft copolymer of the PEO macromer and MA shows that after extraction and purification, the macromer can be completely removed from the graft copolymer.

The IR spectrum of the purified PBA-*g*-PEO copolymer showed a characteristic peak at 1120 cm^{-1} for the C—O—C ether group, a peak at 2920 cm^{-1} for the methylene group, a peak at 1730 cm^{-1} for the carbonyl group, two peaks at 940 and 960 cm^{-1} for the butyl group, and peaks at 1165 and 1265 cm^{-1} for the C—O—C of the ester. This indicates that the copolymers are composed of EO and BA units.

Since the molecular weight of the macromer (M_{ng}) and the copolymer (M_{nc}) can be determined by VPO and membrane osmometry, respectively, and the weight fraction of the PEO in the copolymer (W_g) can be determined by elemental analysis as indicated in the Experimental section, the average grafting number (N_g) can be calculated by

$$N_g = (M_{nc} W_g) / M_{ng}$$

Table 6 shows that the grafting number of PBA-*g*-PEO and PMMA-*g*-PEO varies between 10 and 15, and N_g decreases gradually with an increase of conversion of the PEO macromer. This is coincident with the different polymerization rates of the macromer and monomer at different stages, as stated above.

CONCLUSION

Polyoxyethylene macromers with molecular weight from 2×10^3 to 1.3×10^4 and $\bar{M}_w/\bar{M}_n = 1.07$ – 1.12 can be obtained by the polymerization of ethylene oxide in DMSO by using potassium naphthalide in THF as initiator, followed by termination with methacryl chloride. The macromers were shown by UV, IR, and ^1H NMR to have one double bond in the molecule. The macromers can be copolymerized with butyl acrylate, methyl acrylate, or methyl methacrylate to give grafting efficiencies of approximately 90%. The average grafting number of the purified copolymers varied from 10 to 15.

TABLE 6. Grafting Numbers of the PMMA-*g*-PEO or PBA-*g*-PEO Copolymers

Comonomer	$\bar{M}_{ng} \times 10^{-3}$	$\bar{M}_{nc} \times 10^{-4}$	$W_g, \%$	N_g	Conversion of macromer, %
BA	6.21	30.0	30.1	14.5	—
BA	6.21	19.1	38.7	11.9	—
MMA	2.20	5.9	49.3	13.2	37.8
MMA	2.20	6.5	43.6	12.9	57.9
MMA	2.20	7.0	37.8	12.0	71.8
MMA	2.20	9.8	23.7	10.6	81.3

ACKNOWLEDGMENT

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