Synthesis, Characterization, and Properties of Amphiphilic Poly(ethyl acrylate) with Uniform Polyoxyethylene Grafts

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ABSTRACT: Amphiphilic copolymers of ethyl acrylate (EA) with uniform polyoxyethylene (PEO) grafts were synthesized by copolymerization of EA with methacrylate terminated PEO macromer in benzene using azobisisobutyronitrile as the initiator. The effects of the molecular weight of the macromers, the charging weight ratio of the macromer to EA, the total monomer concentration, and the amount of initiator on the grafting efficiency (GE) were reported as was the molecular weight of the copolymers. The highest GE reached to above 90% and the molecular weight of the copolymers varied from $(5-15) \times 10^4$. The reactivity ratio of EA with the macromer was determined to be 0.83. The graft copolymers were purified with extractions and the purified products were characterized with IR, ^{1}H-NMR, gel permeation chromatography, differential scanning calorimetry, and membrane osmometry. The average grafting number of the copolymer varied from 2 to 11. The glass-transition temperature of the poly(EA) in the copolymer was increased because of the partial compatibility of the two components. The crystalline property, emulsifying property, and dilute solution viscosity of the graft copolymers, as well as ionic conductivity of their complexes with alkali metal salts, were studied. The emulsifying volume decreased with the increasing molecular weight of the PEO grafts. The addition of NaOH to the emulsion affected the emulsifying volume only slightly, whereas the addition of HCl changed the oil in water type emulsion into a water in oil type. The conductivity of the $LiClO_4$ complex of the copolymer with an oxyethylene/Li ratio of 20 reached 3.7×10^{-5} S/cm at 27°C. The lower the crystallinity of the complex, the higher was the conductivity. The dilute solution viscosity showed the existence of intramolecular microphase separation. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 903–912, 2001

Key words: polyoxyethylene; graft copolymer; polyacrylate; amphiphilic polymer; macromer

INTRODUCTION

Recent research of amphiphilic copolymers has aroused great interest, especially for those containing poly(ethylene oxide) (polyoxyethylene or PEO) as hydrophilic segments.[1–3] The PEO-containing amphiphilic copolymers can be used as emulsifiers, surface active agents, antistatic agents, phase transfer catalysts, solid polymer electrolytes after complexing with alkali salts, and so forth.

It was of interest to prepare graft copolymers with uniform PEO grafts as amphiphilic polymers, because they exhibited good properties.[3] Milkovich[4] first developed the method of synthesizing copolymers with uniform side chains using the macromer technique. Rempp et al.[5,6] reported

the synthesis of PEO macromers through anionic polymerization of EO by using either an alkali metal alcoholate as the initiator and methacryloyl chloride as the terminating agent or an alkali metal unsaturated alcoholate as the initiator and alkyl chloride as the terminating agent. Ito et al.[7,8] synthesized PEO macromers by using potassium tertiary butoxide as the initiator and methacryloyl chloride or *p*-vinyl benzyl chloride as the terminating agent and studied their reactivity in copolymerization with styrene. However, the synthetic method for PEO macromers using an alkali metal alcoholate as the initiator possesses several disadvantages: it needs relatively long reaction times, the solubility of an alkali metal alcoholate in most solvents is rather low, and the molecular weight range of the PEO macromers that can be obtained is small. Xie et al.[9] improved the method of synthesizing PEO macromers through anionic polymerization of EO in dimethyl sulfoxide using a tetrahydrofuran (THF) solution of potassium naphthalide as the initiator, followed by termination with methacryloyl chloride. The molecular weight of the macromers can be varied from 2×10^3 to 1.2×10^4 with a polydispersity index (M_w/M_n) of 1.07–1.12. Xie et al. studied copolymerization of the PEO macromer, which was synthesized by the improved method, with methyl methacrylate (MMA), butyl acrylate, or styrene in benzene using azobisisobutyronitrile (AIBN) as an initiator,[9] and some properties of the products.[10,11] Wesslen and Wesslen[12] prepared amphiphilic graft copolymers by radical solution polymerization of MA terminated PEO macromer with acrylate or MA comonomers and studied critical micelle concentrations and surface tensions.

This article deals with the effects of synthetic conditions on the grafting efficiency (GE), molecular weight, reactivity ratio, average grafting number, and characterization of poly(ethyl acrylate) (PEA) with uniform PEO grafts. The crystallinity, emulsifying properties, viscosity in dilute solution, and conductivity of its complexes with alkali metal salts were studied.

EXPERIMENTAL

Materials

Commercial EO was treated with KOH and CaH$_2$ successively, then distilled into purified toluene or into a cold trap and stored in a refrigerator.

Analytical reagent grade THF was distilled over ferrous sulfate and dried with CaH$_2$. Analytical reagent grade dimethyl sulfoxide (DMSO) was dried with CaH$_2$ for 48 h and distilled under reduced pressure; the distillate was collected at 85–87°C and 25 mmHg. Chemically pure EA was washed successively with 10% NaOH and water, dried with anhydrous CaCl$_2$, and then distilled over CuCl. Chemically pure benzene was dried overnight with 4-Å molecular sieves. Chemically pure AIBN was recrystallized from ethanol. α-Methacryloyl chloride was prepared by reacting chemically pure α-methacrylic acid with an equivalent amount of sulfonyl chloride under stirring at 65°C for 8 h. The product was distilled under reduced nitrogen pressure over CuCl. Potassium naphthalide was prepared by reacting 14 g of chemically pure naphthalene and 5.1 g of potassium chips in 70 mL of dried THF with stirring under a nitrogen atmosphere for 3–4 h, followed by storing 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 0.1N HCl solution using methyl orange as the indicator.

The other reagents, such as benzene, toluene, acetonitrile, ethyl ether, acetone, chloroform, LiClO$_4$, and KSCN, were chemically pure.

Synthesis of PEO Macromers

PEO macromer was synthesized as follows[9]: the THF solution of potassium naphthalide was added dropwise into 100 mL DMSO solution of 0.6 mol EO until the light yellow color ceased to disappear. Then the required amount of the 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.

Copolymerization of PEO Macromer with EA

A certain amount of the dried macromer was dissolved in benzene. Then EA and AIBN were

added to it. Copolymerization was carried out at 60–70°C under a 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 3 times to remove the unreacted PEO macromer and extracted with ethyl ether/acetone (3/7 v/v) 3 times, each for 24 h, to remove the homopolymer of EA. Conversion of the PEO macromer or the GE and conversion of EA can be calculated according to the following equations:

$$GE (\%) = (\text{macromer charged}$$
$$- \text{macromer unreacted}) \times 100/\text{macromer charged}$$

$$\text{Conversion of EA } (\%)$$
$$= (\text{crude product} - \text{macromer charged})$$
$$\times 100/\text{EA charged}$$

Characterization

The number-average molecular weights of the macromers (M_{ng}) were measured with a Knauer vapor pressure osmometer by using chloroform as the solvent. The gel permeation chromatography (GPC) curve of the copolymer was obtained by using an LC-4A type apparatus with THF as the eluent. The number-average molecular weights of the copolymers were determined by using a Bruss membrane osmometer with dimethylformamide (DMF) as the solvent. The PEO content of the copolymer was calculated from the oxygen content as determined from elemental analysis using a CHN-600 elemental analysis apparatus. IR spectra were taken with a PE-580B spectrophotometer. The sample was dissolved in chloroform and coated on a KBr crystal. The ^{1}H-NMR spectrum was recorded with an EM-360 (60 MHz) spectrometer using CDCl3 as the solvent and tetramethyl silane as the internal standard. The glass-transition temperature (T_g) and melting point were found from differential scanning calorimetry (DSC) curves using a PE DSC-4 DS calorimeter combined with a computer at a heating rate of 20°C/min and a sample weight of about 10 mg. The crystallinity (X_c) was measured by wide angle X-ray diffraction (WAXD) using a Rigaku 3015 apparatus with a scanning rate of 2°C/min. The crystallinity was calculated according to a published method.[13]

Determination of Intrinsic Viscosity of Graft Copolymer

The intrinsic viscosity [η] of the diluent solution of the copolymer was determined with an Ubbelohde viscometer at four different concentrations (C) below 0.5 g/100 mL at a certain temperature using toluene as the solvent. This was followed by extrapolating η_{sp}/C and ln η_r/C at different concentrations to zero concentration. The intercept of the two lines was at zero concentration, and the intercept value was taken as [η].

Measurement of Emulsifying Volume

The copolymer was dissolved in 30 mL of benzene and then 70 mL of water was added. The mixture was shaken thoroughly for several minutes and then poured into a cylinder with a cover. Overnight the system separated into two layers. The emulsifying volume was taken as the total volume of the benzene solution plus the water minus the volume of the lower layer after separation.

Preparation of Alkali Metal Salt Complex of Copolymer and Measurement of Its Conductivity

Complexes of the copolymers with alkali metal salts were prepared thus: 0.6 g of copolymer was weighed accurately and dissolved in dried acetonitrile. A measured volume of acetonitrile solution of the alkali metal salt, which was dried previously at 160°C, was added to the copolymer solution with stirring. After evaporation, the complex was dried thoroughly in a vacuum desiccator over P_2O_5 for more than 1 day. The complex was hot pressed in a die into pellets (about 2-mm thickness and 14-mm diameter), sandwiched between two thin aluminum disks at 80°C, and then kept in a vacuum desiccator with fresh P_2O_5 for 1 day. The ac conductivity was measured with a DDS-11 conductometer using copper disk electrodes operated at a frequency of 1100–1200 Hz. Before measurement the sample was equilibrated with P_2O_5 in the conductivity cell for 1 day. The determination was repeated once more. Usually, no further change in conductivity at room temperature was observed.

RESULTS AND DISCUSSION

Effects of Copolymerization Conditions on GE and Molecular Weight of Graft Copolymers

Figure 1 illustrates that increasing the molecular weight of the macromer (M_{ng}) gradually de-
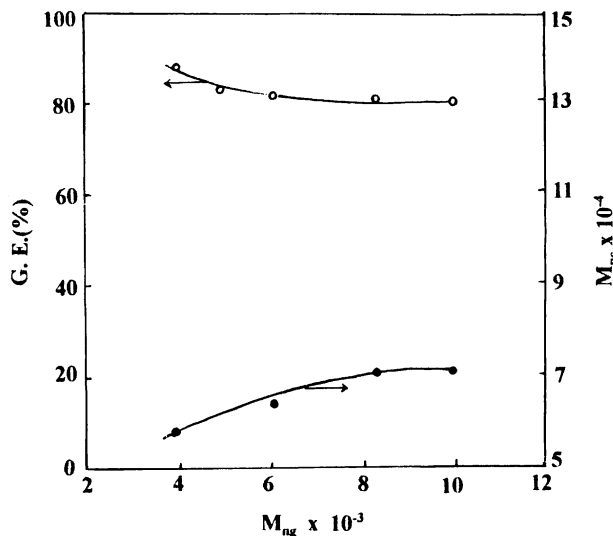
Figure 1 The effect of the molecular weight of the macromer on the grafting efficiency and molecular weight of the graft copolymer (macromer/EA = 3/7 w/w, total monomer concentration = 25 g/100 mL benzene, AIBN = 0.15%, 60°C, 24 h).

creases the GE whereas the molecular weight of the graft copolymer increases gradually. When the molecular weight of the macromer is higher than 8000, the GE and molecular weight of the copolymer are almost constant. This implies that the reactivity of the macromer with higher molecular weight is not dependent on its length. The increase of the molecular weight of the copolymer with increasing molecular weight of the macromer is due to the fact that as the viscosity of the copolymerization system increases with the increasing molecular weight of the macromer, the rate constant of the chain termination diminishes more quickly than the rate constant of the chain propagation, resulting in the increasing molecular weight of the copolymer. On the other hand, copolymerization of one molecule of macromer with a molecular weight much higher than that of EA raises the molecular weight of the copolymer more markedly.

The GE obviously decreases with the charging weight ratio of macromer/EA, as shown in Figure 2, probably because the initial viscosity of the copolymerization system increases with the macromer content, which causes the diffusion of macromer to be more difficult and reduces the collision probability of active centers with the macromer. Figure 2 denotes that a minimum value of the molecular weight of the copolymer occurs at a charging weight ratio of macromer/EA of 60/40.

This may be ascribed to the reason that the increase of viscosity of the polymerization system, which is due to the increase of macromer concentration, makes the diffusion of both the macromer and active centers more difficult. The low diffusion rate of the macromer reduces the molecular weight of the copolymer, because less macromer is copolymerized with the monomer, whereas at too high macromer concentration the difficult diffusion of active centers besides the macromer avoids the chain transfer and termination, thus increasing the life of active centers, resulting in the rise in the molecular weight of the copolymer.

Figure 3 shows that the GE increases with the total monomer (macromer plus EA) concentration at first and then decreases. A maximum value occurs at about 30 g/100 mL benzene. This is attributed to the fact that an increase in total monomer concentration within a certain range enhances the collision probability between active chains and the macromer and diminishes the probability of chain transfer to the solvent, thus increasing the conversion of the macromer or GE. However, when the total monomer concentration is too high, the viscosity of the polymerization system increases obviously and the mobility of the macromer molecules is reduced more evidently than that of the monomer, thereby reducing the copolymerization of the macromer, resulting in a reduction of the GE. The molecular weight of the graft copolymer increases with increasing total
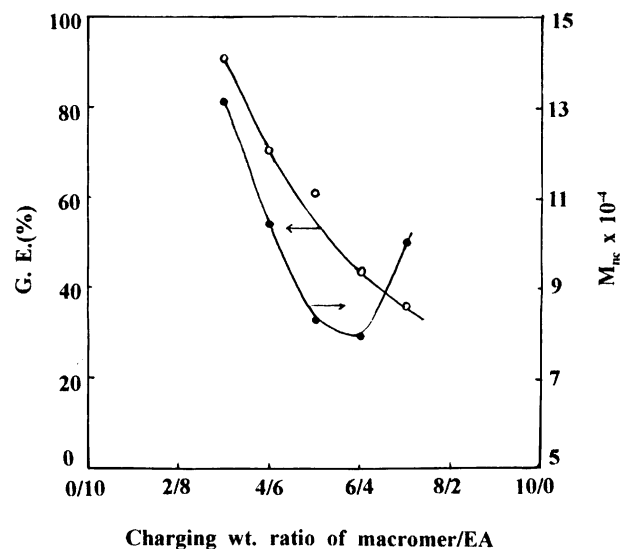

Figure 2 The effect of the charging weight ratio of macromer/EA on the grafting efficiency and molecular weight of the graft copolymer. The same conditions as Figure 1 were used, except M_{ng} = 3300.
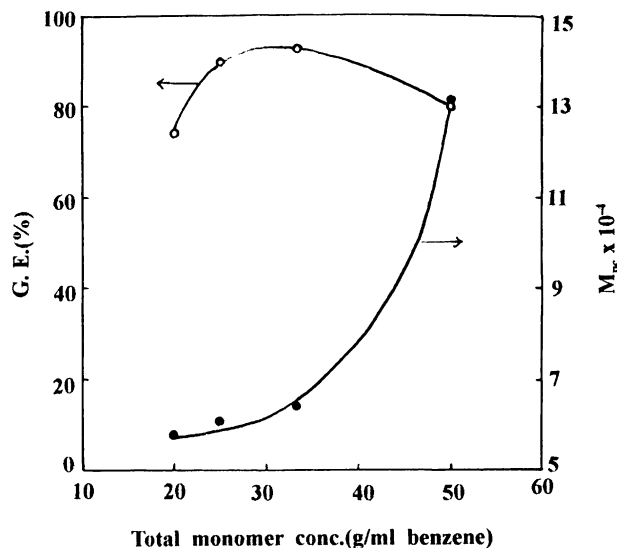
Figure 3 The effect of the total monomer concentration on the grafting efficiency and molecular weight of the graft copolymer (macromer/EA = 3/7 w/w, M_{ng} = 3300, AIBN = 0.15%, 60°C, 24 h.)

Figure 4 The effect of the amount of AIBN on the grafting efficiency and molecular weight of the graft copolymer. The same conditions as Figure 3 were used, except that the total monomer concentration was 50 g/100 mL benzene.

monomer concentration, as shown in Figure 3. This is coincident with the increase of the kinetic chain length with increasing monomer concentration.

Figure 4 indicates that with an increasing amount of initiator (AIBN) the GE increases gradually whereas the molecular weight of the graft copolymer decreases evidently. This is because the number of active centers increases with increasing initiator amount and the amount of monomer distributed to the active centers diminishes. Thus, the molecular weight of the graft copolymer formed is lowered and the viscosity of the polymerization system decreases, which is favorable to the diffusion of the macromer, resulting in increasing GE.

Estimation of Reactivity Ratio of EA in Copolymerization with Macromer

Figure 5 shows that the conversions of EA and the macromer versus time both increase abruptly at first and then slowly. At the initial stage the conversion of the macromer is higher than that of the monomer (EA), whereas at the later stage the conversion of EA is higher than that of the macromer. This phenomenon implies that the terminal MA double bonds of the macromer are more reactive than the acrylate double bonds of EA. At the initial stage of copolymerization the viscosity
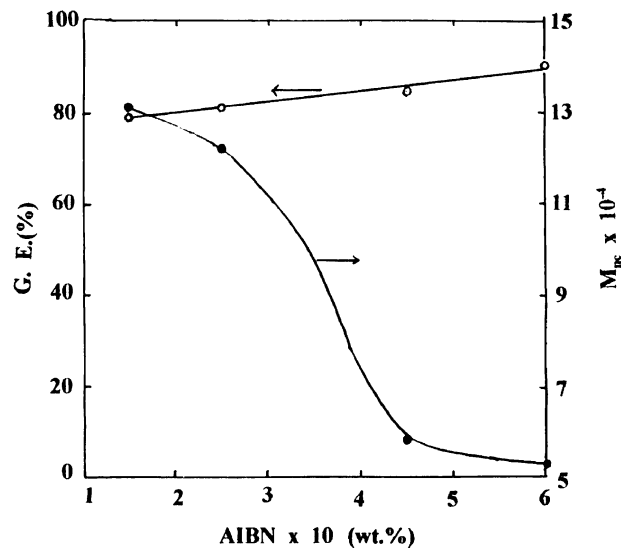
of the copolymerization system is comparatively low and the diffusion of the macromer is easier. As the copolymerization proceeds the viscosity increases because of the conversion of macromer into copolymer, which hinders the diffusion of the macromer and reduces the reaction probability of the macromer at lowered concentration. Thus, at the later stage of copolymerization conversion of EA exceeds that of the macromer.
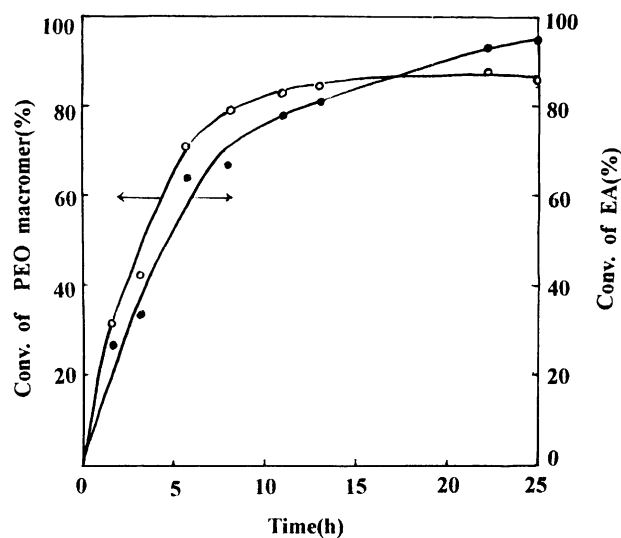

Figure 5 The conversions of the macromer and EA versus the copolymerization time.

Table I   Reactivity Ratio (r_2) of EA in Copolymerization with PEO Macromer at Different Conversions

| Copolym. Time (h) | Conversion of (%) | | r_2 |
	Macromer	EA	
1.6	30.9	26.5	0.833
5.7	70.7	64.1	0.834
10.9	82.9	77.0	0.832
22.2	87.0	92.3	1.260

Table II   Efficiency of Extraction of Polymer Mixture with Water and Ethyl Ether/Acetone (3/7 v/v)

| Extraction Times | Weight Extracted Out (g) | |
	PEO Macromer	PEA
1	1.8864	1.8144
2	0.0913	0.1530
3	0.0207	0.0311
4	0.0014	0.0011
Total	1.9998	1.9996

The sample polymer was a mixture of 2 g PEA and 2 g PEO macromer used for the extraction test.

Because the macromer is quite difficult to homopolymerize because of its steric hindrance, the r_1 is usually assumed to be zero and the reactivity ratio (r_2) of the monomer EA may be estimated according to the simplified Kennedy equation:

$$r_2 = \ln(1 - P_2)/\ln(1 - P_1)$$

where P_1 and P_2 are the conversions of the macromer and monomer, respectively. Table I lists the r_2 values calculated from the conversions of the macromer and monomer at different copolymerization times. It can be seen that the r_2 stays constant at about 0.83 for both conversions below 80%, but it rises to 1.26 after the conversion of EA and the PEO macromer reach over 90 and 85%, respectively. The latter phenomenon is due to the increased viscosity, which hinders the copolymerization of EA with the macromer. According to the literature,[14] the r_2 for EA in copolymerization with MMA is 0.47, which is less than that for EA in the copolymerization with the macromer. This fact can be interpreted as follows: the double bonds of EA are more difficult to copolymerize with the terminal MA double bonds of the macromer than with those of MMA, which is due to the larger steric hindrance of the macromer and higher viscosity of the copolymerization system, containing the macromer. Thus, the k_{21} of EA in the copolymerization with the macromer is smaller than that in the copolymerization with MMA, resulting in a larger r_2 value in the former case.

Characterization of Purified Graft Copolymer with Uniform PEO Grafts

The crude product obtained in the copolymerization of the macromer with EA was purified by extractions at room temperature with water to remove the unreacted PEO macromer and with ethyl/acetone (3/7 v/v ratio) to remove the homopolymer of EA. The efficiency of the purification by extractions was proved by the data listed in Table II. It can be noted that when 2 g of macromer and 2 g of homopolymer of EA were mixed together and extracted with water and ethyl ether/acetone (3/7), after three extractions with water nearly all the PEO macromer was extracted out; however, after three extractions with ethyl ether/acetone (3/7 v/v) almost all the homopolymer of EA was extracted out. The GPC curve of the purified graft copolymer exhibited only one peak without a shoulder.

The IR spectrum (Fig. 6) of the purified graft copolymer shows the characteristic absorptions at 1120, 1730, 1160–1260, and 2900 cm^{-1} for C—O—C ether groups, carbonyl groups, ester groups of primary alcohol, and CH$_2$ groups, respectively.

The ^{1}H-NMR spectrum (Fig. 7) of the purified graft copolymer exhibits peaks at 3.90–4.27 and 1.13–1.35δ for protons in —OCH$_2$CH$_3$ (ester) groups, 3.63δ for protons in —CH$_2$CH$_2$O— (oxy-
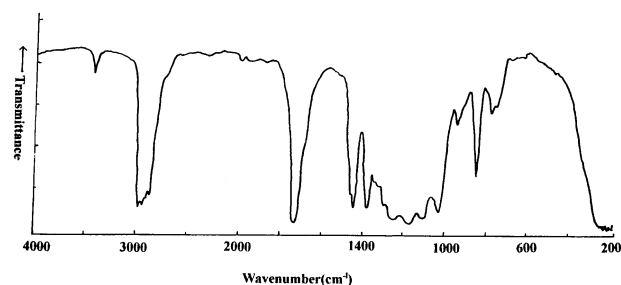
Figure 6 The IR spectrum of the purified PEA-*g*-PEO.
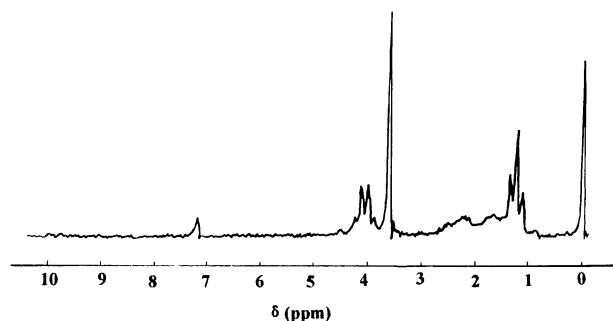
Figure 7   The ^{1}H-NMR spectrum of the purified PEA-*g*-PEO.

Table III   Structural Parameters of Graft Copolymers

M_{ag}	$M_{ac} \times 10^{-4}$	W_g	N_g
3,300	13.1	0.271	10.7
3,300	10.0	0.253	7.7
3,300	7.9	0.262	6.3
3,300	5.8	0.267	4.7
3,300	6.1	0.240	4.4
3,300	5.8	0.296	5.2
3,300	6.4	0.222	4.3
10,020	7.1	0.283	2.0
6,100	6.4	0.230	2.4
3,890	7.1	0.266	4.9

ethylene), and a small peak at 7.23δ for protons of a small amount of chloroform impurity in the solvent.

These two spectra demonstrate that the purified graft copolymer is indeed composed of PEO and PEA segments.

Structure Parameters of Purified Graft Copolymers

The molecular weights of the graft copolymer and the uniform grafts, which are equal to that of the macromer, can be measured by a membrane osmometer and vapor pressure osmometer, respectively. The average grafting number (N_g) of the graft copolymer can be calculated according to the following equation:

$$N_g = M_{nc} \times W_g/M_{ng}$$

where W_g represents the weight fraction of PEO grafts in the copolymer calculated according to the elemental analysis and M_{nc} and M_{ng} represent the number-average molecular weights of the purified copolymer and the macromer, respectively.

Table III lists the average grafting number of different samples of graft copolymers and shows that the N_g of the graft copolymers varies from 2 to 11 for different molecular weights of macromers and copolymers. The different samples were obtained under different synthetic conditions. It can be noted that the higher the charging molecular weight of the macromer (M_{ng}) the less is the N_g.

Crystallinity of Purified Graft Copolymer

The DSC curve (Fig. 8) of the purified graft copolymer illustrates an endothermic peak at 63.9°C

that represents the melting of PEO crystals in the graft copolymer. There is also a deflection at −9°C on the DSC curve, which denotes the T_g of PEA in the graft copolymer. This T_g is higher than that of pure PEA (−22°C). The difference may be ascribed to partial compatibility between the PEA backbone and PEO grafts.

A WAXD diagram of PEO showed two peaks at $2\theta = 19$ and 23. The graft copolymer containing uniform PEO grafts also exhibited these two diffraction peaks but with relatively lower intensity. The calculated crystallinities (X_c) are shown in Table IV. The data indicate that the copolymer possesses a PEO crystallinity of about 47.8% whereas that of the PEO macromer is in the range of 88–92%, which is dependent on the molecular weight of the PEO macromer.

Table IV shows that when the graft copolymer was complexed with LiClO$_4$ or KSCN, the crystallinity of the PEO decreased. LiClO$_4$ exerts a larger influence on lowering the crystallinity of PEO than KSCN at the same molar ratio of EO/metal. The higher the molar ratio of EO/Li or the less the amount of alkali salt used in forming the complex, the higher was the crystallinity.
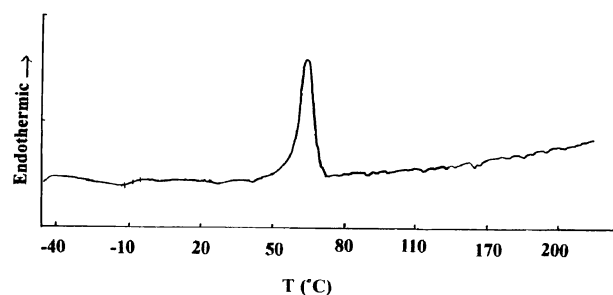

Figure 8   The DSC curve of the purified PEA-*g*-PEO.

Table IV Crystallinity (X_c) of Graft Copolymer and Its Complexes Determined Via WAXD

Sample	Molar Ratio		X_c (%)
	EO/Li	EO/K	
PEA-g-PEO			47.8
PEA-g-PEO/LiClO$_4$	20		16.3
PEA-g-PEO/LiClO$_4$	40		21.0
PEA-g-PEO/KSCN		20	17.2

The PEO content of the graft copolymer was 59.2% (M_{ng} = 3300).

Emulsifying Properties of Graft Copolymers

Because the graft copolymer contains both the hydrophilic PEO grafts and the hydrophobic PEA backbone, they are amphiphilic and are able to emulsify oil with water. Table V indicates that increasing the copolymer amount increases the emulsifying volume, which represents the emulsifying properties, because of the increase of emulsifying centers. The emulsion type remains unchanged as the O/W type.

Table V also shows that at a fixed PEO content and amount of the copolymer, the smaller the molecular weight of the PEO grafts, the larger is the emulsifying volume. This may be due to the increase of emulsifying centers, which are formed by the increasing number of PEO grafts. It is of interest to note that the emulsifying volume increases with the decrease of the difference of the solubility parameters ($\Delta\delta$) between the nonpolar solvents (δ_1) and PEA ($\delta_2 = 9.2$–9.4). The less the

$\Delta\delta$, the less is the mixing enthalpy and the less the mixing free energy, which favors the spontaneous dissolution of PEA backbones in the organic solvent, thus enhancing the emulsifying properties.

It can be seen from Table VI that addition of NaOH as an electrolyte diminishes the emulsifying volume slightly, because the emulsifier based on the amphiphilic graft copolymer is nonionic. But addition of HCl reduces the emulsifying volume more seriously than NaOH, probably because H$^+$ can interact with lone pair electrons of the ether groups of the PEO grafts, thus weakening the association between hydrophilic PEO grafts and water molecules, which results in changing the emulsion type from O/W to water in oil (W/O). When the toluene/water volume ratio was changed from 30/70 to 70/30, the emulsion type was also changed from O/W to W/O, as shown in Table VI. Ostwald[15] pointed out in his theory that the emulsion type is related to the volume ratio of two phases: when the water phase is <26 vol % only a W/O type emulsion can be formed, but when the water phase is >74 vol % only an O/W type emulsion can be formed.

Conductivity of Complexes of Graft Copolymer with Alkali Metal Salts

It is well known that PEO can be complexed with alkali metal salt to form ion-conducting materials. However, pure PEO possesses high crystallinity, which reduces the ion transportation below the melting point of PEO. One of the aims for

Table V Effects of Graft Copolymer Concentration, Molecular Weight of Grafts, and Different Oil Phase on Emulsifying Volume

Graft Copolymer Concn (g/mL)	M_{ng}	Oil Phase	Solu. Parameter (δ_1)	Emul. Vol. (mL)
0.0044	3300	Toluene	8.9	41.0
0.0022	3300	Toluene	8.9	40.0
0.0011	3300	Toluene	8.9	38.0
0.0005	3300	Toluene	8.9	36.0
0.0022	3890	Toluene	8.9	38.5
0.0022	4960	Toluene	8.9	37.5
0.0022	6100	Toluene	8.9	37.0
0.0022	3300	Ethylbenzene	8.8	38.0
0.0022	3300	Isopropylbenzene	8.86	39.0
0.0022	3300	Xylene	9.0	41.0

The PEO content of the graft copolymers varied from 25 to 28%; all the emulsions were oil/water type.

Table VI   Effect of Electrolytes on Emulsifying Volume and Emulsion Type

Volume of (mL)		HCl (mmol)	NaOH (mmol)	Emul. Vol. (mL)	Emul. Type
Toluene	Water				
30.0	70.0			40.0	O/W
30.0	70.0	0.362		35.0	W/O
30.0	70.0		0.362	39.5	O/W
70.0	30.0			39.0	W/O

The PEO content of the graft copolymer was 26.7% (M_{ag} = 3300); the concentration of the graft copolymer was 0.0022 g/mL.

synthesizing PEA with uniform PEO grafts is to increase the conductivity of PEO used as a solid polymer electrolyte by lowering the crystallinity of PEO and enhancing the film-forming properties of PEO.

Figure 9 illustrates the Arrhenius plot of conductivity for complexes of PEA-*g*-PEO with LiClO$_4$ or KSCN. The complex of PEA-*g*-PEO with LiClO$_4$ at an EO/Li molar ratio of 20 exhibits conductivity higher than that of PEA-*g*-PEO at an EO/Li molar ratio of 40. The conductivity of the LiClO$_4$ complex with an EO/Li molar ratio of 20 reaches 3.7×10^{-5} S/cm at 27°C, which is obviously higher than that of pure PEO at the same EO/Li

ratio. In the latter case the σ is only 10^{-7} S/cm. The reason why the conductivity of the LiClO$_4$ complex of the copolymer is higher at an EO/Li molar ratio of 20 than that at 40 or than that of pure PEO is due to the lower crystallinity of the complex at an EO/Li molar ratio of 20, as indicated in Table IV. The complex of the graft copolymer with KSCN shows conductivity lower than the complex with LiClO$_4$ at the same molar ratio of EO/metal of 20 at the temperature below the melting point of PEO. As mentioned above, LiClO$_4$ can lower the crystallinity of PEO more effectively than KSCN at ambient temperature. Thus, the conductivity of the former complex is higher than that of the latter complex at ambient temperature.
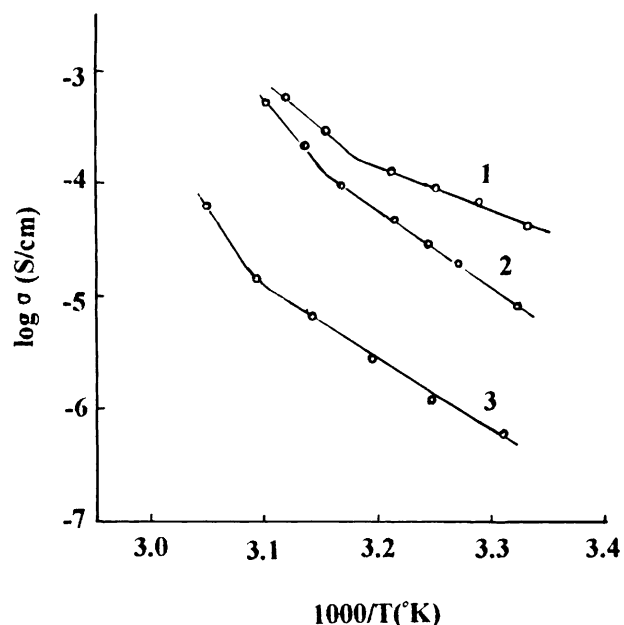
Dilute Solution Properties of Graft Copolymer

Figure 10 shows the change of the intrinsic viscosity [η] of the dilute solution of the graft copolymer in toluene with temperature (T) in the range of 25–70°C. It indicates an initial rising value of [η] with temperature and a discontinuity in [η] at 40°C. This is followed by a sharp fall in [η] to a minimum value and then by a further rise after passing through the minimum. The peak in the [η] versus the T curve marks the change from the intramolecular phase separated form to a random conformation. With the increase of temperature, each type of segment gradually extends, resulting in the increase of [η]. After 40°C the intramolecular phase separation changes to an intramolecular blend, resulting in a decrease in [η]. When the temperature increases further, the intramolecular blend is gradually broken due to the intensive macromolecular chain motion and the chains extend again, leading to the increase of [η]. This intramolecular phase separation indicates that microphase separation exists in the graft copolymer.
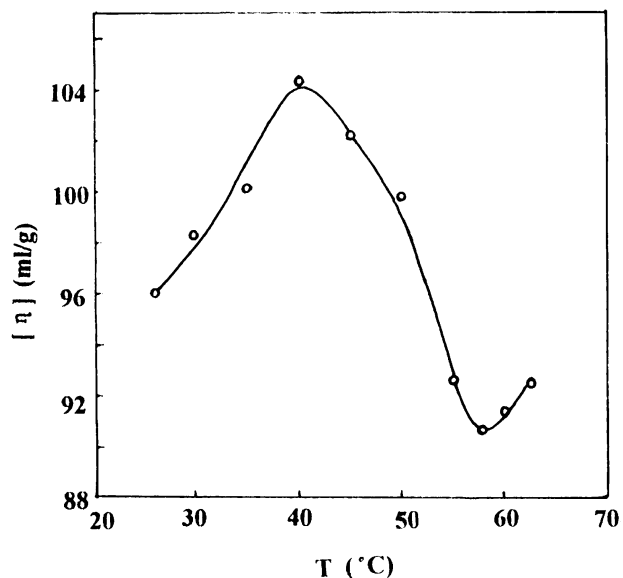

Figure 9   The change of conductivity of alkali metal salt complexes of PEA-*g*-PEO versus temperature: PEA-*g*-PEO/LiClO$_4$ at EO/Li = 20/1 (curve 1), PEA-*g*-PEO/KSCN at EO/K = 20/1 (curve 2), and PEA-*g*-PEO/LiClO$_4$ at EO/Li = 40/1 (curve 3).

Figure 10 The change of the $[\eta]$ of the toluene solution of PEA-*g*-PEO versus the temperature.

Girolamo and Urwin[16] also formerly indicated that the intramolecular phase separation phenomenon existed for polyisoprene-*b*-styrene in cyclohexane solution.

CONCLUSION

The effects of various synthetic conditions on the GE and molecular weight of the copolymer were studied. The highest GE reached above 90% and the molecular weight of the copolymers varied from (5 to 15) $\times$ 10^4. The reactivity ratio of EA with the macromer was determined to be 0.83. A mixed solvent of ethyl ether/acetone in a 3/7 volume ratio was found to be an effective solvent for separating the homopolymer of EA from the graft copolymer. The average grafting number of the copolymers varied from 2 to 11. Partial compatibility existed between the PEA and PEO segments, because the T_g of the copolymer was higher than that of the pure PEA, which was indicated by the DSC curve. The emulsifying volume decreased with the increasing molecular weight of the PEO grafts. The addition of NaOH to the emulsion affected the emulsifying volume only slightly whereas addition of HCl not only decreased the emulsifying volume but also changed the O/W type emulsion into a W/O type. The conductivity of the LiClO$_4$ complex at 27°C reached 3.7×10^{-5} S/cm at an EO/Li molar ratio of 20 and decreased at an EO/Li molar ratio of 40, which was related to the crystallinity of the complex. The dilute solution viscosity of the copolymer with uniform PEO grafts exhibited an intramolecular phase separation phenomenon including a maximum $[\eta]$ and a minimum $[\eta]$ within 25–70°C.

REFERENCES

1. Velichkova, R. S.; Christova, D. C. Progr Polym Sci 1995, 20, 819.
2. Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjchristidis, N. Adv Polym Sci 1998, 135, 1.
3. Xie, H. Q.; Xie, D. Prog Polym Sci 1999, 24, 275.
4. Milkovich, R. Polym Prepr 1980, 21, 40.
5. Rempp, P.; Masson, P.; Vargas, J. S.; Franta, E. Plast Kautsch 1981, 28, 365.
6. Masson, P.; Beinert, G.; Franta, E.; Rempp, P. Polym Bull 1982, 7, 17.
7. Ito, K.; Tsuchida, H.; Hayashi, A.; Kitano, T.; Yamade, E.; Matsumoto, T. Polym J 1985, 17, 827.
8. Ito, K.; Tsuchida, H.; Kitano, T. Polym Bull 1986, 15, 425.
9. Xie, H. Q.; Liu, J.; Li, H. J Macromol Sci Chem 1990, A27, 725.
10. Xie, H. Q.; Liu, J.; Xie, D. Eur Polym J 1989, 25, 1119.
11. Xie, H. Q.; Xie, D.; Liu, J. Polym Plast Technol Eng 1989, 28, 355.
12. Wesslen, B.; Wesslen, K. B. J Polym Sci Polym Chem Ed 1992, 30, 355.
13. Xie, H. Q.; Zhou, P. G. In Multicomponent Polymer Materials; Paul, D. R., Sperling, C. H., Eds.; Advances in Chemistry Series 211; American Chemical Society: Washington, DC, 1986; p 139.
14. Brandrup, J.; Immergut, E. H. Polymer Handbook, 2nd ed.; Wiley: New York, 1975.
15. Ostwald, W. Kolloid Z 1910, 6, 103.
16. Girolamo, M.; Urwin, J. R. Eur Polym J 1971, 7, 693.