Synthesis and Properties of Amphiphilic Copolymers of Butyl Acrylate and Methyl Methacrylate with Uniform Polyoxyethylene Grafts

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ABSTRACT: Amphiphilic copolymers of butyl acrylate (BA) and methyl methacrylate (MMA) with uniform polyoxyethylene (PEO) grafts were synthesized by the copolymerization of BA and MMA with a methacrylate-terminated PEO macromer in benzene with azobisisobutyronitrile as an initiator. The effects of various copolymerization conditions on the grafting efficiency and molecular weight of the copolymers, as well as the effect of the copolymerization time on the conversions of the macromer and the monomers, were reported. The copolymers, with uniform PEO grafts, were purified by successive extractions with water and ether/acetone (3/7) to remove unreacted macromer and ungrafted copolymers of MMA and BA, respectively. The purified graft copolymers were characterized with IR, ^{1}H-NMR, membrane osmometry, gel permeation chromatography, and differential scanning calorimetry. The highest grafting efficiency was about 90%, and molecular weight of the copolymers varied around 10^5. The average grafting number of the copolymer was about 10. A study of the crystalline properties, emulsifying properties, phase-transfer catalytic ability, and mechanical properties of the graft copolymers showed that the emulsifying volume decreased with the increasing molecular weight of the PEO grafts but increased with the PEO content. The conversion of potassium phenolate in the Williamson solid–liquid reaction obviously increased with an increasing PEO content of the graft copolymers. The crystallinity of the graft copolymers increased with the PEO content of the graft copolymers or the molecular weight of the macromer used. The copolymers, prepared under certain conditions, behaved as thermoplastic elastomers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2982–2988, 2003

Key words: graft copolymers; amphiphiles; macromonomers; phase transfer catalysis; elastomers

INTRODUCTION

Amphiphilic copolymers, especially those containing polyoxyethylene (PEO) as hydrophilic segments, have been the subject of numerous studies.[1–3] PEO-containing amphiphilic copolymers can be used as emulsifiers, surface-active agents, antistatic agents, phase-transfer catalysts, solid polymer electrolytes after complexation with alkali salts, and so forth.

It is interesting to prepare graft copolymers with uniform PEO grafts as amphiphilic polymers via the macromer technique because they exhibit various good properties.[3] Milkovich[4] first developed the method of synthesizing copolymers with uniform grafts with the macromer technique. Rempp and coworkers[5,6] reported the synthesis of PEO macromers through the anionic polymerization of ethylene oxide (EO), either with alkali metal alcoholate as the initiator

and methacryloyl chloride as the terminating agent or with an alkali metal unsaturated alcoholate as the initiator and alkyl chloride as the terminating agent. Ito and coworkers[7,8] synthesized PEO macromers with potassium tertiary butoxide as the initiator and methacryloyl chloride or *p*-vinyl benzyl chloride as the terminating agent and studied their reactivity in copolymerizations with styrene. However, the synthetic method for PEO macromers with an alkali metal alcoholate as the initiator has several disadvantages: it requires 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 relatively small. Since Cabasso and Silkha[9] revealed that with potassium naphthalide and dimethyl sulfoxide (DMSO) as the initiator system, living PEO anions could be obtained in a monoanionic form, Xie et al.[10] improved the method of synthesizing PEO macromers through the anionic polymerization of EO in DMSO with a tetrahydrofuran (THF) solution of potassium naphthalide as an initiator, followed by termination with methacryloyl chloride. The molecular weights of the macromers varied from 2×10^3 to 1.2×10^4, with a weight-

average molecular weight/number-average molecular weight ratio (M_w/M_n) of 1.07–1.12. The macromers were shown by UV, IR, and ^{1}H-NMR to have one double bond in the molecule. Xie et al.[11] also studied the copolymerization of the PEO macromer, synthesized by the improved method, with methyl methacrylate (MMA), butyl acrylate (BA), or styrene in benzene with azobisisobutyronitrile (AIBN) as an initiator[10] and some properties of the products. Wesslen and Wesslen[12] prepared amphiphilic graft copolymers by the radical solution polymerization of a methacrylate-terminated PEO macromer with acrylate or methacrylate comonomers and studied the critical micelle concentrations and surface tensions. Recently, we reported the synthesis, characterization, and properties of graft copolymers of ethyl acrylate with uniform PEO grafts.[13] However, the amphiphilic graft copolymers of ethyl acrylate, poly(butyl acrylate), poly(methyl methacrylate (PMMA), or polystyrene with uniform PEO grafts behave either like plastics or like soft resins.

This article deals with the copolymerization of the PEO macromer with BA and MMA for the preparation of an amphiphilic and thermoplastic elastomer. The effects of copolymerization conditions on the grafting efficiency (GE) and molecular weight of the graft copolymers, as well as the average grafting number (N_g) and characterization of purified poly(butyl acrylate-co-methyl methacrylate) [P(BA-co-MMA)] with uniform PEO grafts, are reported. Various properties, including the crystallinity, emulsifying properties, phase-transfer catalyst properties, and mechanical properties of the graft copolymers are also reported.

EXPERIMENTAL

Materials

Commercial EO was treated with KOH and CaH_2 successively, distilled into purified toluene or a cold trap, and stored in a refrigerator. Analytical-reagent (AR) THF was distilled over ferrous sulfate and dried with CaH_2. AR DMSO was dried with CaH_2 for 48 h and distilled under reduced pressure; the distillate at 85–87°C and 25 mmHg was collected. Chemically pure (CP) BA or MMA was washed successively with 10% NaOH and water, dried with anhydrous $CaCl_2$, and then distilled over CuCl. CP benzene was dried overnight with 4-Å molecular sieves. CP AIBN was recrystallized from ethanol. α-Methacryloyl chloride was prepared by the reaction of CP 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 the reaction of 14 g of CP naphthalene and 5.1 g of potassium chips in 70 mL of dried THF with stirring under a nitrogen atmo-

sphere for 3–4 h, followed by time in a refrigerator. The upper dark green solution was taken out when potassium naphthalide was used. The content of potassium naphthalide in the solution was determined by titration of the hydrolyzed liquor with a 0.1N HCl solution, with methyl orange as the indicator.

Other reagents, such as toluene, ethyl ether, acetone, p-hydroxyphenol, potassium phenolate, and n-butyl bromide, were CP.

Synthesis of the PEO macromer

The PEO macromer was synthesized as follows.[10] A THF solution of potassium naphthalide with a concentration of about 2.5 mol of potassium napthalide/L was added dropwise into 100 mL of a DMSO solution with 0.6 mol of EO until the light yellow color ceased to disappear. Then, the required amount of the THF solution of potassium naphthalide was injected with a syringe. The mixture was cooled in an ice bath so that the reaction temperature remained below 30°C for 2 h. The reaction was kept at 30°C for 6 h. The reaction solution became dark yellow. The reaction was terminated by the injection of 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, reprecipitated with ethyl ether, filtered, and vacuum-dried to a constant weight.

Copolymerization of the PEO macromer with BA and MMA

A certain amount of the dried macromer was dissolved in benzene. Then, BA, MMA, and AIBN were added to it. The copolymerization was carried out at 65°C under a nitrogen atmosphere with stirring for a certain time. Then, a small amount of p-hydroxyphenol was added to terminate the copolymerization. The solvent was evaporated. After vacuum drying to a constant weight, the product was extracted with water three times for the removal of the unreacted PEO macromer and was extracted with ethyl ether/acetone (3/7 v/v) three times, each for 24 h, for the removal of the copolymer of BA and MMA. The conversion of the PEO macromer and the GE and conversion of the monomers was calculated with the following equations:

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

$$\text{Conversion of the monomers}(\%)$$
$$= (\text{Crude product} - \text{Macromer charged})$$
$$\times 100/\text{Monomers charged}$$

Characterization

The number-average molecular weights of the macro-mers (M_{ng}'s) were measured with a Knauer vapor pressure osmometry (VPO) instrument with chloroform as the solvent. The gel permeation chromatography (GPC) curve of the copolymer or the macromer was obtained with an LC-4A type apparatus with THF as the eluent. The M_n values of the copolymers were determined with a Bruss membrane osmometer with dimethylformamide as the solvent. The PEO content of the copolymer was calculated from the oxygen content as determined from an elemental analysis with a CHN-600 elemental analysis apparatus. IR spectra were taken with a PE-580B spectrophotometer. The sample was dissolved in chloroform and coated on KBr crystals. The ^{1}H-NMR spectrum was recorded with an XL-200 NMR spectrometer with CDCl$_3$ as a solvent and tetramethylsilane as an internal standard. The melting point was found from differential scanning calorimetry (DSC) curves with a PE DSC-4 differential scanning calorimeter combined with a computer at a heating rate of 20°C/min and with a sample weight of about 5 mg.

Measurement of the crystallinity by wide-angle X-ray diffraction (WAXD)

The crystallinity (X_c) was measured by WAXD with a Rigaku 3015 apparatus at a scanning rate of 2°/min. X_c was calculated according to a published method.[15]

Measurement of the emulsifying volume

The copolymer was dissolved in 30 mL of benzene, and then 150 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 and water minus the volume of the lower layer after separation.

Phase-transfer catalysis property in the williamson reaction

Toluene (40 mL), *n*-butyl bromide (2 mL), and a certain amount of the copolymer were added to a bottle containing potassium phenolate (1.0 g, accurately weighed). After N$_2$ purging, the system was heated at 90°C for 4 h with stirring. After the reaction, toluene was evaporated, and 50 mL of distilled water was added. The precipitated copolymer was filtered and washed. The unreacted potassium phenolate in the filtrate and washing solution was titrated with standard HCl, with methyl red as an indicator, to deter-
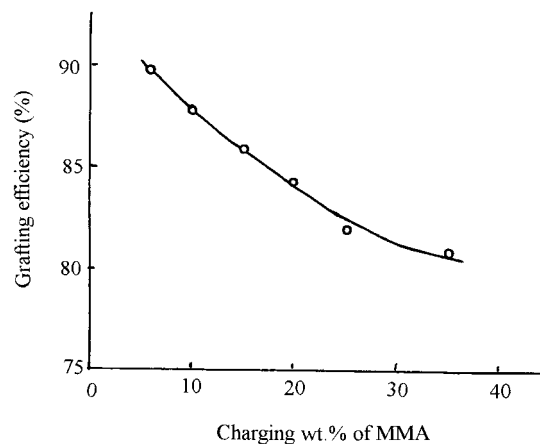

Figure 1 Effect of the charging weight percentage of MMA on the GE (charging weight percentage of the PEO macromer with a molecular weight of 6010 = 30%; AIBN concentration = 0.15%; temperature = 65°C; time = 12 h).

mine the conversion of potassium phenolate into butyl phenolate.

Measurement of the mechanical properties

The mechanical properties of the graft copolymers were determined on a DL-250 tensile tester with a stretching rate of 250 mm/min after compression molding at 150°C under a hot press. The permanent set was measured as the elongation percentage 3 min after the specimen was broken and reunited.

The apparent crosslink density (V_α) was calculated as follows:[16]

$$V_\alpha = \sigma(RT)^{-1}(\lambda - \lambda^{-2})^{-1}$$

where σ is the tensile strength and λ is the extension ratio.

RESULTS AND DISCUSSION

Effects of the copolymerization conditions on the GE and molecular weight of the graft copolymers

The molecular weights of the PEO macromers were determined by VPO to be in the range of 2×10^3 to 8×10^3, and their molecular weight distribution (M_w/M_n) was determined by GPC to be 1.08–1.12. This coincides with our former results,[10] which also showed that the macromers had one double bond in the molecule according to UV, IR, and ^{1}H-NMR.

The effect of the charging percentage of MMA on the GE is shown in Figure 1. The GE of the macromer diminished with an increasing charging percentage of MMA. This can be explained by the reactivity ratios. Because the macromer was difficult to homopolymerize on account of its steric hindrance, r for the macromer approached zero, whereas r_{BA} was 0.37 and r_{MMA}
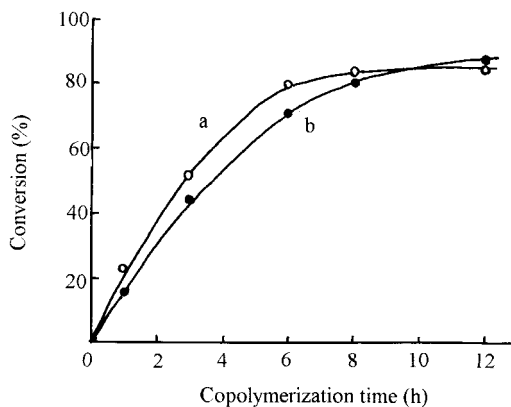
Figure 2 Conversions of (a) the macromer and (b) the monomers versus the copolymerization time (the copolymerization conditions in Figure 1 apply here, except for BA/MMA = 5/2).

TABLE I
Effect of Copolymerization Time on PEO Content, M_{nc}, and the-N_2, of the Graft Copolymers

Time (h)	PEO content (%)	$M_{nc} \times 10^{-5}$	N_g
1	39.8	1.54	10.2
3	34.8	1.72	10.0
6	32.4	1.81	9.8
8	29.9	19.2	9.6
12	28.3	20.0	9.4

The copolymerizattion conditions were the same as in Figure 2.

was 1.81;[17] in other words, MMA was easier to homopolymerize than copolymerize with the macromer and BA. Therefore, the more MMA there was, the less reaction there was between the macromer and the monomers, and this resulted in decreasing GE. Therefore, the charging weight ratio of BA to MMA was chosen to be 7/3 in the following experiments

Figure 2 shows that the conversions of the monomers and the macromer versus time increased abruptly at first and then slowly. At the initial stage, the conversion of the macromer was higher than that of the monomers, whereas at the later stage, the conversion of the monomers was higher than that of the macromer. This phenomenon implies that the terminal methacrylate double bonds of the macromer were more reactive than the acrylate double bonds of BA. At the initial stage of copolymerization, the viscosity of the copolymerization system was comparatively low, and the diffusion of the macromer was easier. As the copolymerization proceeded, the viscosity increased because of the conversion of the macromer into the copolymer, and this hindered the diffusion of the macromer and reduced the reaction probability of the macromer at the lowered concentration. Therefore, at the later stage of copolymerization, the conversion of the monomers exceeded that of the macromer.

Table I shows that with increasing copolymerization time, the PEO content of the graft copolymer decreased, whereas the molecular weight of the graft copolymer increased. This can be interpreted as follows. With increasing conversion, the viscosity of the polymerization system increased, and this enhanced the shielding of the active centers and prevented chain termination, resulting in an increase of the molecular weight of the copolymer. The increased viscosity restricted the diffusion of the macromer much more seriously than that of the monomers, causing a decrease of the PEO content of the copolymer. This also

demonstrates that at the initial stage, the macromer copolymerized more quickly than the monomers, whereas at the later stage, the conversion of the monomers exceeded that of the macromer.

Figure 3 indicates that with an increasing amount of the initiator (AIBN), GE increased significantly at first and then gradually, whereas the molecular weight of the graft copolymer decreased significantly at first and then gradually. This can be explained as follows: the number of active centers increased with an increasing amount of the initiator and the amount of the monomer distributed to the active centers diminished, so the molecular weight of the graft copolymer formed was lowered and the viscosity of the polymerization system decreased; this was favorable to the diffusion of the macromer and resulted in increasing GE.

Figure 4 illustrates that GE decreased gradually with M_{ng}. This might have been due to more difficult diffusion and larger steric hindrance of the macromer with a higher molecular weight; this made the reaction between active centers and the macromer less probable.

GE obviously decreased with an increasing charging weight percentage of the macromer, as also shown
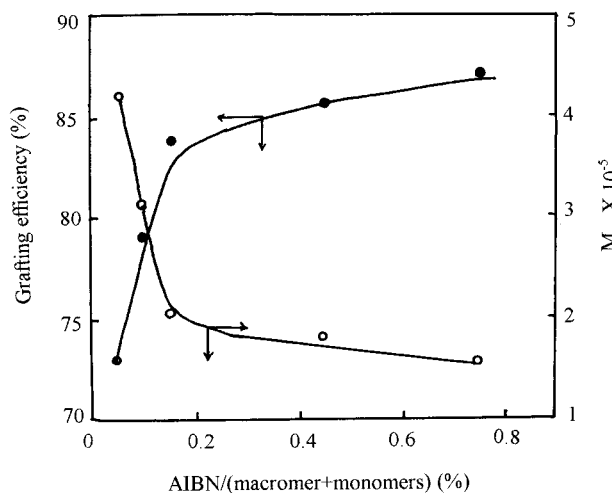

Figure 3 Effect of the amount of AIBN on the GE and molecular weight of the graft copolymer (the copolymerization conditions in Fig. 2 apply here, except for time = 14 h).
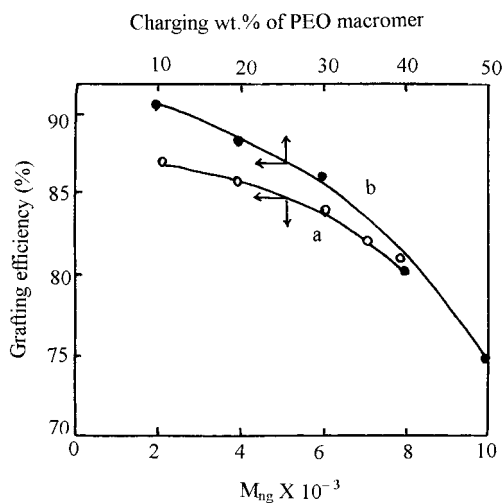
Figure 4 Effect of the molecular weight of the macromer and the charging weight ratio of the macromer to the monomers on the GE (the copolymerization conditions in Figure 2 apply here, except for time = 14 h and, for curve b, molecular weight of the macromer = 3900).

in Figure 4, probably because the initial viscosity of the copolymerization system increased with the macromer content, which made the diffusion of the macromer more difficult and reduced the collision probability of active centers with the macromer. This may also be due to the difficulty of the homopolymerization of the macromer due to its high steric hindrance.

Characterization of the purified graft copolymer with uniform PEO grafts

The crude product obtained from the copolymerization of the macromer with BA and MMA was purified by extractions at room temperature with water for the removal of the unreacted PEO macromer and with ethyl/acetone (3/7 v/v) for the removal of copolymer of BA and MMA. The efficiency of the purification by extractions was proven by the GPC curve of the purified graft copolymer, which exhibited only one peak without a shoulder, as shown in Figure 5.

The IR spectrum of the purified graft copolymer showed characteristic absorptions at 1120, 1730, and 1160–1260 cm^{-1} for C—O—C ether groups, carbonyl
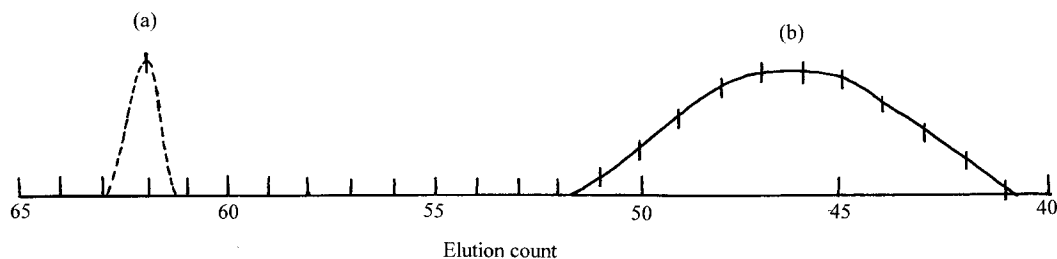

Figure 6 ^{1}H-NMR spectrum of purified P(BA-*co*-MMA)-*g*-PEO with a charging weight ratio of BA/MMA/macromer = 49/21/30 during synthesis.

groups, and ester groups of primary alcohol, respectively, and absorption peaks at 940–960, 1450–1470, and 2830–2870 cm^{-1} for butyl groups (CH$_3$, CH$_3$O, and CH$_2$O groups, respectively).

The ^{1}H-NMR spectrum (Fig. 6) of the purified graft copolymer exhibited peaks at δ = 0.8–1.0 for protons of CH$_3$ and CH$_2$ of butyl ester, δ = 1.35 for protons of methyl groups, δ = 1.49 for protons of CH$_2$ groups in the main chain, δ = 3.3 for protons of CH groups in the main chain, δ = 3.5 for protons in —CH$_2$CH$_2$O— (oxyethylene), δ = 3.85 for protons of CH$_2$O groups in butoxy groups, and δ = 4.1 for protons of OCH$_3$ groups of the methoxy groups.

These two spectra demonstrated that the purified graft copolymer was indeed composed of PEO and poly(BA-*co*-MMA) segments.

Structural parameters of the purified graft copolymers

Because the molecular weights of the graft copolymer and the uniform grafts, which were equal to that of the macromer, could be measured by membrane osmometry and VPO, respectively, N_g of the graft copolymer could be calculated according to the following equation: $N_g = M_{nc} \times W_g/M_{ng}$, where W_g represents the weight fraction of the PEO grafts in the copolymer (calculated according to the elemental analysis) and M_{nc} and M_{ng} represent the number-average molecular

Figure 5 GPC curves of (a) the macromer and (b) purified P(BA-*co*-MMA)-*g*-PEO with a charging weight ratio of BA/MMA/macromer = 49/21/30 during synthesis.
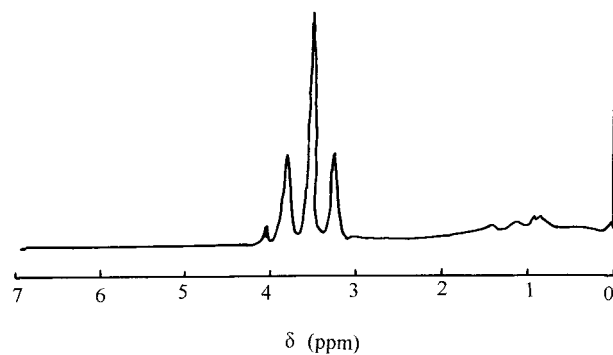
TABLE II
X_c of the Graft Copolymers Determined via WAXD

Charging weight percentage of the PEO macromer	M_{ng}	X_c (%)
70	6010	49.5
60	7050	24.6
60	6010	22.4
45	6010	17.0
28	6010	0

TABLE III
Emulsifying Volume (EV) of the Graft Copolymers

Copolymer (g)	Molecular weight of the macromer	PEO content (%)	EV (mL)
0.1	2100	35.1	33.1
0.2	2100	35.1	40.2
0.3	2100	35.1	48.3
0.2	3950	35.5	37.0
0.2	6010	34.9	35.2
0.2	7050	35.0	33.8
0.2	6010	30.2	32.6
0.2	6010	40.1	41.3
0.2	6010	45.2	46.0

weights of the purified copolymer and the macromer, respectively.

Table I lists the N_g values of some samples of graft copolymers obtained at different copolymerization times and shows that N_g of the graft copolymers decreased from 10.2 to 9.4 for polymerization times from 1 to 12 h.

Crystallinity of the purified graft copolymer

The DSC curve of the purified graft copolymer showed an endothermic peak from 35 to 60°C with the maximum at 49.4°C, which represented the melting of PEO crystals in the graft copolymer. The melting point was lower than that of the EO homopolymer. This implies that the main chain of P(BA-co-MMA) might have restricted the crystallization of PEO because of the good compatibility of PMMA and PEO. 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 X_c values are shown in Table II. The data indicate that the graft copolymers possessed a PEO crystallinity of 0–50%. X_c obviously increased with the PEO content of the graft copolymer and also with the molecular weight of the PEO grafts in the graft copolymer.

Emulsifying properties of the graft copolymers

Because the graft copolymers contained both the hydrophilic PEO grafts and the hydrophobic P(BA-co-MMA) backbone, they were amphiphilic and were able to emulsify the benzene/water system. Table III indicates that with increasing amounts of the copolymer, the emulsifying volume, which represented the emulsifying properties, increased because of the increase in the number of emulsifying centers. The emulsion type remained unchanged as an oil-in-water type.

The same table also shows that at fixed PEO and copolymer contents, the smaller the molecular weight was of the PEO grafts, the larger the emulsifying volume was. This might be due to the increase in the number of emulsifying centers formed by the increasing number of PEO grafts.

Phase-transfer catalysis properties in the williamson reaction

Because the PEO grafts had the function of complexing alkali metallic ions, the graft copolymer containing PEO grafts could act as phase-transfer catalysts in the Williamson solid–liquid reaction.[12] The phase-transfer catalyst properties of the copolymer in the Williamson reaction between solid potassium phenolate and liquid n-butyl bromide could be represented by the increased conversion of potassium phenolate. In Table IV, it is shown that almost no reaction occurred in the absence of the graft copolymer. The conversion of potassium phenolate increased with the amount of the copolymer added to the Williamson reaction. The result indicates that the graft copolymer could complex the potassium ions of the phenolate and transfer them from the solid to an organic solution, enhancing the reaction between potassium phenolate and n-butyl bromide. The phase-transfer catalytic effect increased with the PEO content of the graft copolymer, probably because of the increased complexation of potassium ions; this resulted in a higher conversion of potassium

TABLE IV
Phase-Transfer Catalyst Property of the Graft Copolymers in the Williamson Reaction

Copolymer (wt. % on KPh)[a]	PEO content (%)	Conversion of KPh (%)
0	0	4.1
20.6	34.9	81.5
20.5	30.2	76.0
20.5	34.9	80.9
20.5	40.1	85.5
20.5	45.2	87.0
10.3	34.9	72.2
30.9	34.9	84.0
50.1	34.9	91.2
20.5[b]	34.9	80.1

[a] KPh represents potassium phenolate.
[b] Reused.

TABLE V
Effect of the Charging Weight Percentage and Molecular Weight of the PEO Macromer on Mechanical Properties of the Graft Copolymers[a]

Molecular weight of macromer	Charging weight of macromer	σ^b (MPa)	ε (%)	δ (%)	$V_\alpha \times 10^4$ (mol/mL)
2100	28	2.16	490	27	1.74
3950	28	2.25	455	22	2.03
6010	28	3.14	400	16	3.17
7050	28	3.33	380	14	3.61
7900	28	3.82	350	12	4.46
7050	21	2.84	445	19	2.56
7050	28	3.33	380	14	3.61
7050	35	3.92	300	12	5.41
7050	40	4.02	350	12	6.93
7050	45	4.21	200	12	9.81

[a] A weight ratio of BA/MMA = 7/3 was used in the copolymerization with the PEO macromer.
[b] σ, ε, and δ represent the tensile strength, ultimate elongation, and permanent set, respectively

phenolate. The graft copolymer could be recovered and used again with its phase-transfer catalytic activity almost unchanged, as indicated in Table IV.

Mechanical properties of the graft copolymers

The copolymers of BA or ethyl acrylate with uniform PEO grafts appeared to be quite soft, with low tensile strengths, whereas the copolymers of MMA with uniform PEO grafts behaved as plastics. However, the copolymers of MMA and BA with uniform PEO grafts behaved like thermoplastic elastomers under certain conditions, as shown in Table V. With the increase in the molecular weight of the macromer or PEO grafts, the tensile strength increased, whereas the ultimate elongation and the permanent set diminished. This fact is related to the increase of V_α (Table V), which was attributed to the crystalline domains formed by the PEO grafts. The shorter the PEO grafts were, the lower the crystallinity was and, therefore, the more difficult the formation was of the crystalline domains, which acted as physical crosslinks; this resulted in a lowered tensile strength. Although the tensile strength of the graft copolymer was not so high, its ultimate elongation was higher than 200%, and its permanent set was less than 30%. The last two characteristics, together with its repeat processability for at least five times by hot pressing, indicate that it behaved like a thermoplastic elastomer.

With an increasing charging weight percentage of PEO or the PEO content of the graft copolymer, the tensile strength increased, whereas the ultimate elon-

gation decreased. At the same time, V_α obviously increased. This fact was ascribed to the increase in the number of crystalline domains and physical crosslinks due to the increase of uniform PEO grafts.

CONCLUSIONS

In the copolymerization of the PEO macromer with BA and MMA, the GE decreased with an increasing charging weight percentage of MMA or the macromer as well as the molecular weight of the PEO macromer, but it increased with an increasing amount of the initiator. The conversion of the macromer was higher than that of the monomers at the initial stage of copolymerization but became lower at the later stage. The PEO content of the graft copolymer and N_g decreased with the copolymerization time, whereas the molecular weight of the graft copolymer increased with the copolymerization time. The molecular weight of the graft copolymer varied in the range of $1-5 \times 10^5$, and N_g could reach about 10. The purified graft copolymer was characterized by GPC, IR, and ^{1}H-NMR. The graft copolymer could emulsify benzene/water systems and act as a phase-transfer catalyst in the Williamson reaction with 85–90% conversion of potassium phenolate. The graft copolymer showed crystallinity values of 0–50%. At a charging weight ratio of BA/MMA = 7/3 and a charging weight percentage of the macromer of 20–45%, the graft copolymer exhibited thermoplastic elastomer behavior.

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