Synthesis and Properties of Poly(acrylic Acid) with Uniform Poly(methyl Methacrylate) Side Chains

Hong-Quan Xie[a]; Guo-Cai Xu[a]; Jen-She Guo[a]

[a] Department of Chemistry, Huazhong University of Science and Technology, Wuhan, People's Republic of China

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SYNTHESIS AND PROPERTIES OF POLY(ACRYLIC ACID) WITH UNIFORM POLY(METHYL METHACRYLATE) SIDE CHAINS

HONG-QUAN XIE,* GUO-CAI XU, and JEN-SHE GUO

Department of Chemistry
Huazhong University of Science and Technology
Wuhan, 430074, People's Republic of China

ABSTRACT

Copolymerization of the poly(methyl methacrylate) (PMMA) macromer with acrylic acid in dimethylformamide solution was studied using AIBN as initiator. The copolymers were purified by extractions with toluene and methanol successively and characterized with IR, ^{1}H NMR, and TEM. The graft copolymers exhibit good emulsifying properties which change with pH and behave as a good compatibilizer for the blending of epichlorohydrin rubber with poly(vinyl chloride) or PMMA. The addition of approximately 3% graft copolymer to the blends evidently improves their mechanical properties and causes the two T_g's to become closer. The blends of PMMA with epichlorohydrin rubber at a weight ratio of 6/4 with the addition of 2–4% graft copolymer show the mechanical properties of a thermoplastic elastomer.

INTRODUCTION

Polymers with uniform side chains were first obtained by Milkovich [1] using the macromer technique. Ito et al. [2] synthesized poly(methyl methacrylate) (PMMA) macromer through radical polymerization in the presence of thioglycollic acid, followed by reaction of the carboxylic acid end-group with glycidyl methacrylate. Recently, we reported the copolymerization of PMMA macromer with butyl acrylate [3] and the terpolymerization of PMMA macromer with butyl acrylate and acrylic acid, the products of which were neutralized with metallic ions to form ionomers [4].

This paper deals with the copolymerization of PMMA macromer with acrylic acid and studies the product properties of poly(acrylic acid) with uniform PMMA side chains, in order to get an amphiphilic copolymer to be used as both an emulsifying agent and a compatibilizer for polymer blending.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was purified by washing with 20% NaOH and water successively, followed by distillation over CuCl under reduced pressure. AIBN was purified by crystallization from ethanol and vacuum-dried. Thioglycollic acid was purified by distillation under reduced pressure. Acrylic acid (AA) was dried over 4A molecular sieve and distilled over CuCl under reduced pressure. Chemically pure benzene and dimethylformamide (DMF) were dried by standing over a 4A molecular sieve overnight. Glycidyl methacrylate was synthesized by neutralization of methacrylic acid with 20% NaOH, followed by reaction with epichlorohydrin at 85 °C using benzyl triethyl ammonium chloride as catalyst. After azeotropic distillation of water, the product was purified by vacuum distillation and kept in a refrigerator before use. All the other reagents were chemically pure and used as received.

Synthesis of PMMA Macromers

Radical polymerization of MMA was carried out in benzene under nitrogen atmosphere using AIBN as initiator and a different amount of thioglycollic acid as chain transfer agent at 65 °C for 12 h, to obtain prepolymers with different molecular weight, which were then purified by precipitation in benzene with methanol [2, 5]. The yield was about 60%. Carboxylic acid end-groups of the prepolymer were determined by titration in acetone with absolute ethyl alcohol solution of KOH using methanolic solution of phenolphthalein as indicator. The purified prepolymer was then reacted in xylene with glycidyl methacrylate (GMA) at a molar ratio of GMA/COOH=2 using N,N-dimethyl benzylamine as catalyst at 139°C under nitrogen atmosphere for 8 h. The macromer thus obtained was purified by precipitation in benzene with methyl alcohol. Efficiency of the reaction between the prepolymer and GMA was determined to be nearly 100% by titration of the remaining carboxylic acid end-groups in the macromer. ^{1}H NMR spectrum of the macromer showed the presence of double bonds at 5.5 and 6 δ.

Copolymerization of the PMMA Macromer with AA

AA and AIBN were added to the DMF solution of PMMA macromer and copolymerization was carried out at 60°C under a nitrogen atmosphere. The copolymerization was terminated with 1% aqueous solution of p-hydroxyphenol. After evaporation of the solvent, the crude product was vacuum-dried to a constant weight. The crude products were extracted successively with toluene and methanol at room temperature for 24 h each three times, to remove the unreacted PMMA

macromer and poly(acrylic acid) respectively. Conversion of AA and the macromer (or grafting efficiency) can be calculated as follows:

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

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

The efficiency of purification was ascertained by extractions of a mixture of PMMA macromer and poly(acrylic acid) and also by determination of the acidity of the toluene extract of the crude graft copolymer.

Characterization and Testing

The molecular weights of the macromers were determined by a Knauer VPO apparatus using $CHCl_3$ as solvent. IR spectra of the copolymers were obtained with PE-580B spectrophotometer using a KBr disk coated with the copolymer. ^{1}H NMR spectra of the copolymers were recorded with XL-200 NMR spectrometer using deuterated dimethyl sulfoxide (DMSO) as solvent and tetramethylsilane as internal standard. Microphotographs of the lead ion neutralized copolymer and blends of the copolymer with PVC were taken by a TEM-100 CXII transmission electron microscope. DSC curves of the blends were obtained with PE DSC-4 differential scanning calorimeter combined with a computer at a heating rate of 20°C/min and a sample weight of ca. 5 mg.

Emulsifying properties of the copolymers are represented by emulsifying volume, determined as follows. The copolymer was dissolved in 10 mL DMSO and then added to a mixture of 30 mL toluene and 60 mL water. The mixture was shaken thoroughly for several minutes and poured into a measuring cylinder. Overnight, the system separated into two layers. The emulsifying volume is taken as the total volume of the organic solvents plus water minus the volume of the lower water layer after separation.

Blending of epichlorohydrin rubber (ECHR, molecular weight 6×10^5) with poly(vinyl chloride) (PVC, XJ-2 type) was carried out on a hot mill at 130°C for 20 min, after PVC powder was mixed with 2% tribasic lead phosphate and 3% lead stearate as stabilizer on a hot mill. Blending of ECHR with PMMA (molecular weight 4.2×10^5) was also carried out on a hot mill, but at 125°C for 10 min.

The tensile strength and ultimate elongation of the blends with or without the addition of the copolymer used as compatibilizer were determined on a DL-250 tensile tester at 25 ± 2°C with an extension rate of 250 mm/min after the sample had been hot-pressed at 150–160°C and cut into specimens.

RESULTS AND DISCUSSION

Copolymerization of the PMMA Macromer with AA

Since only DMF, DMSO, and dioxane were reported to be able to dissolve PMMA, AA, and P(MMA-AA), they were tested as the solvent for copolymerization of the PMMA macromer and AA. The results are listed in Table 1. DMF seems to be the most suitable solvent among them. When dioxane was used as the

TABLE 1.   Effect of Polymerization Solvent on Grafting Efficiency

Solvent	Grafting efficiency (%)	Conv. of AA (%)
DMF	84.6	98.0
DMSO	82.0	93.1
Dioxane	62.3	105[a]

[a]This is due to the PAA complexed strongly with dioxane, which cannot be completely evaporated out during drying.

Polymerization conditions: M_n of PMMA macromer = 6 × 10^3, AA/macromer = 2.65 (w/w), AIBN = 0.2%, concentration = 0.24 g/mL, 60°C, 10 h.
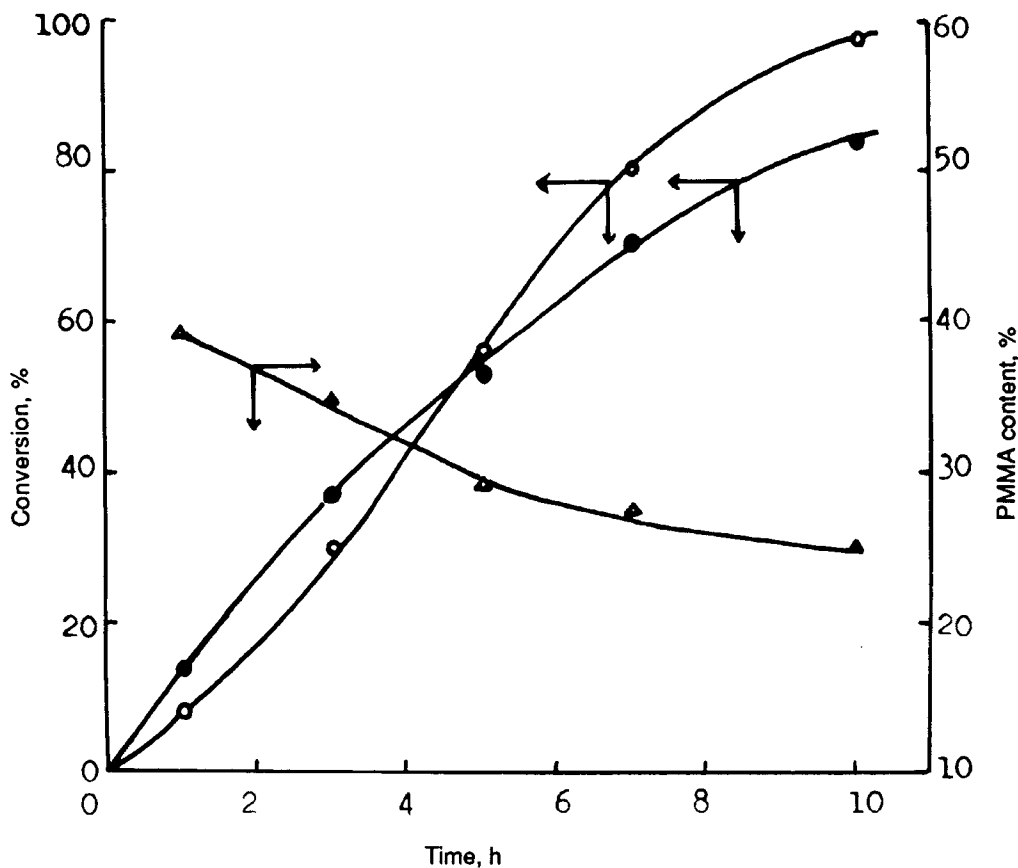

FIG. 1.   Conversion rate of PMMA macromer and AA and change of PMMA content of the product versus copolymerization time: ○, AA; ●, macromer. Polymerization conditions are the same as those in Table 1, except time.
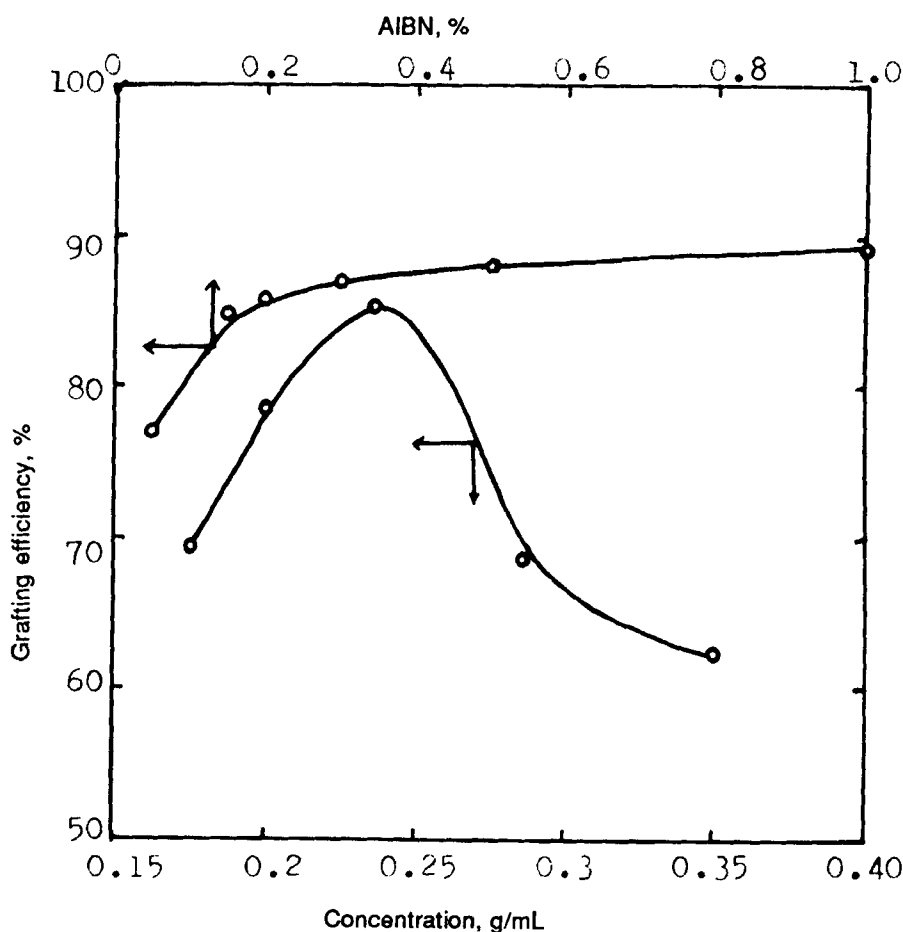
FIG. 2.   Effects of concentration of macromer plus AA and amount of initiator on grafting efficiency in the copolymerization of PMMA macromer with AA. Polymerization conditions are the same as those in Table 1, except M_n of the macromer is equal to 4×10^3.

polymerization solvent, the copolymer separated out and the polymerization system became heterogeneous; thus the grafting efficiency was greatly reduced. Besides, dioxane, which complexes strongly with PAA, cannot be completely separated from the copolymer, so sometimes the conversion of AA may exceed 100%.

Figure 1 shows the copolymerization rates of both the PMMA macromer and AA. At first, the conversion rate of the macromer was higher than that of AA. Gradually the conversion rate of the macromer became reduced until the conversion of AA 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 AA at the beginning of copolymerization. With increasing conversion, the viscosity of the polymerization system gradually increased, resulting in a more difficult diffusion of the macromer and a lowering of the reaction probability of the macromer.

Figure 2 indicates that by increasing the amount of the initiator used, grafting efficiency increased rapidly at lower AIBN concentration. This is because the active centers increased with an increase of initiator, resulting in a decrease of the molecu-
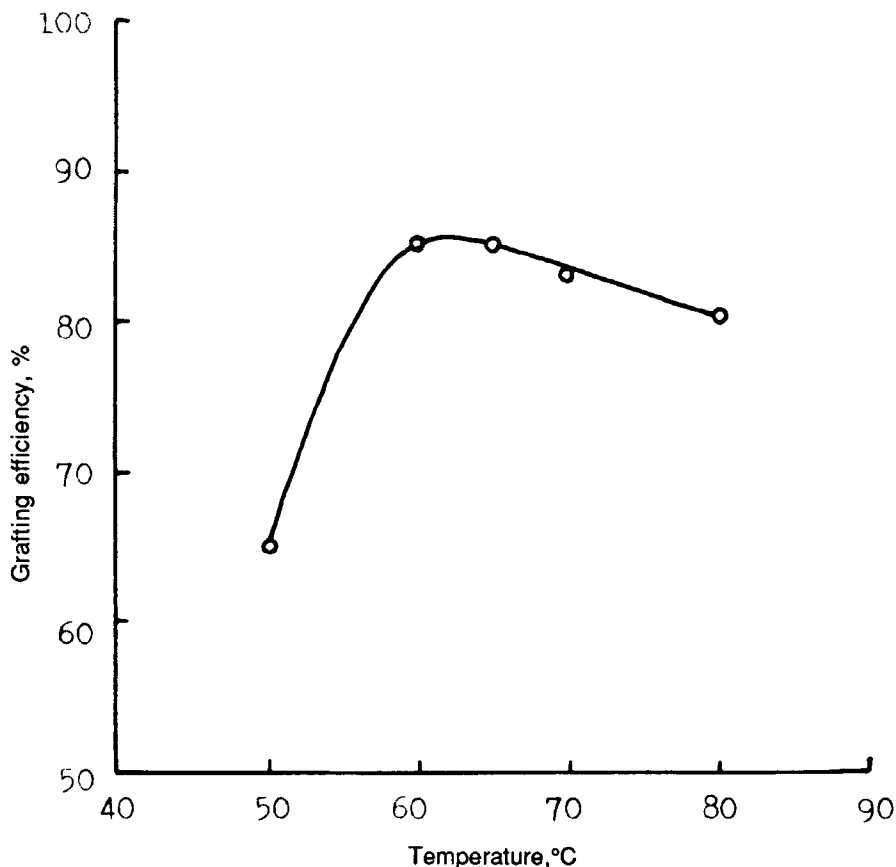
FIG. 3.   Effect of copolymerization temperature on the grafting efficiency. Polymerization conditions are the same as those in Fig. 2.

lar weight of active chains and also of the viscosity of the polymerization system. Lower viscosity is favorable to an increase in grafting efficiency. This is more evident at lower concentration. Figure 2 also shows a maximum in the relationship between grafting efficiency and the total concentration of the macromer and monomer at fixed AIBN concentration. This can be explained as follows: If the concentration is too high as copolymerization proceeds, the very high viscosity of the polymerization system will restrict the motion of active chains and macromers, thereby decreasing the grafting efficiency. However, if the concentration is too low, more impurities are present in the copolymerization system, inducing termination of the more active macromer and reducing the grafting efficiency.

It is interesting to note that there is also a maximum in the relationship between grafting efficiency and copolymerization temperature (Fig. 3). This is quite different from copolymerization of macromer with monomers other than acrylic acid [3, 6] in a hydrocarbon solution. It may probably be due to the fact that DMF solvent can associate with AA through hydrogen bonding, thus lowering the reactivity of AA and enhancing the conversion of the macromer. The hydrogen
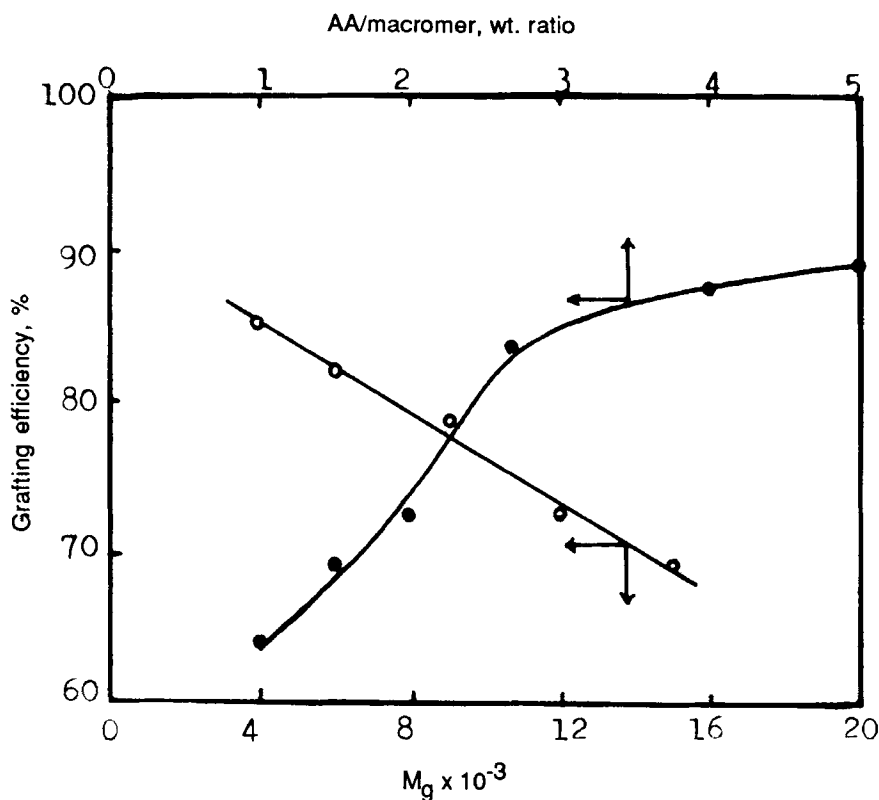
AA/macromer, wt. ratio

FIG. 4.   Effect of molecular weight of PMMA macromer and charging ratio of AA/ PMMA macromer on the grafting efficiency.

bonds may dissociate at higher temperature; therefore, the reactivity of AA increased as compared with the macromer.

Grafting efficiency decreases with increasing molecular weight of the macromer and with decreasing charging ratio of monomer to macromer, as shown in Fig. 4. The former case may be due to more difficult diffusion and larger steric hindrance of the macromer with higher molecular weight, which makes the reaction between active centers and macromer less probable. The latter case is probably due to an increase of viscosity of the polymerization system containing more macromers, and also due to the difficulty of homopolymerization of the macromer.

Characterization of the Purified Copolymers

The IR spectrum of the purified copolymer shows the characteristic peak at 1730 cm^{-1} for the carbonyl group of ester, a peak at 1440 cm^{-1} for the methyl ester, and peaks at 1150–1250 cm^{-1} for C—O vibration as well as a peak at 1690 cm^{-1} for the carbonyl group of the carboxylic acid dimers and a peak at 910 cm^{-1} for the OH group of the carboxylic acid.

From the ^{1}H NMR spectrum of the purified copolymer the peaks may be assigned as follows (Fig.5):
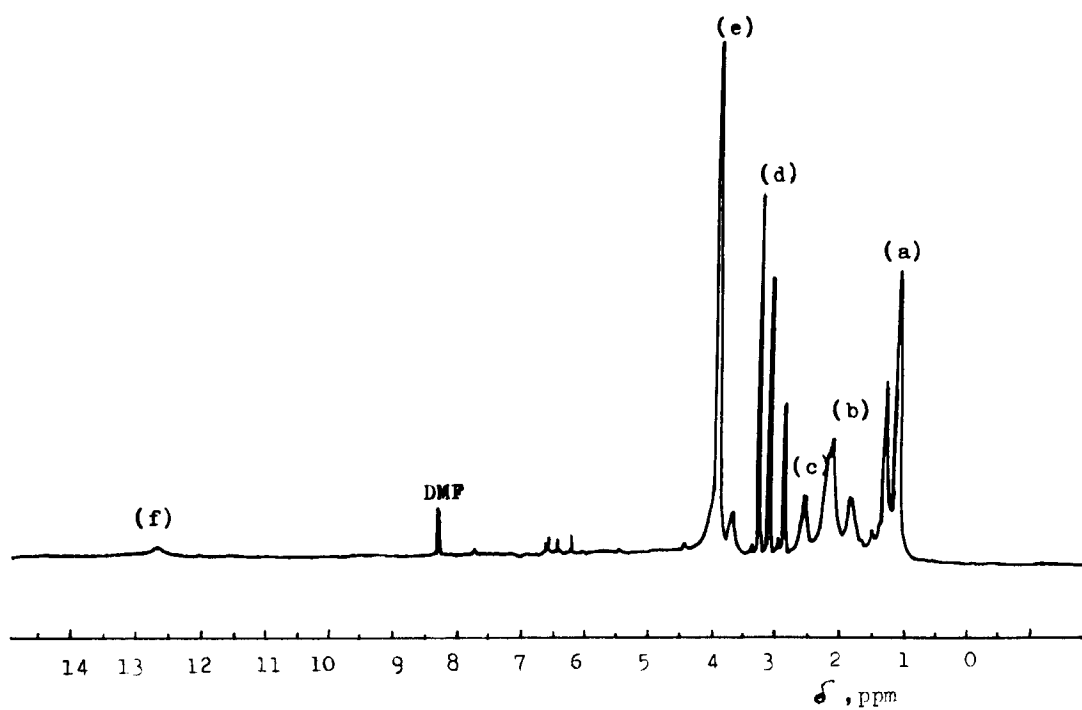
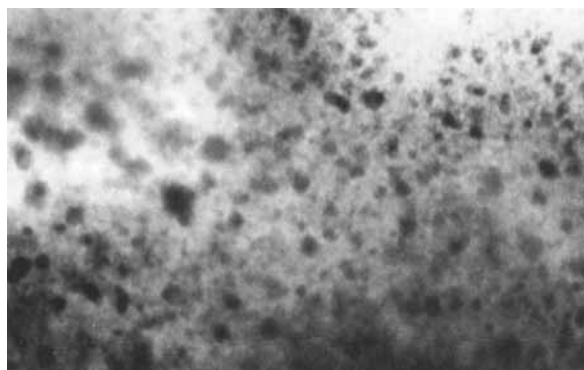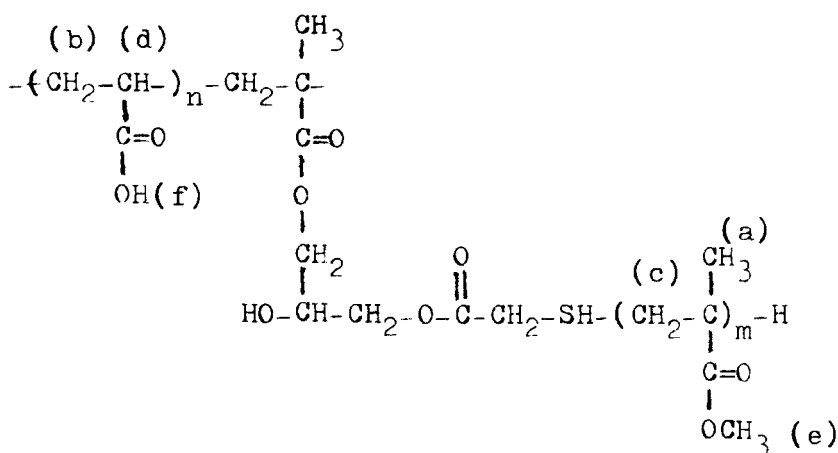FIG. 5. ^{1}H NMR spectrum of the purified graft copolymer.

FIG. 6.   TEM microphotograph of the lead ion neutralized graft copolymer (79,000×).

$$-\left(CH_2-\underset{\underset{OH\,(f)}{\overset{\displaystyle |}{C=O}}}{\overset{(b)\quad(a)}{CH}}-\right)_n-CH_2-\overset{CH_3}{\underset{\overset{\displaystyle |}{C=O}}{\overset{\displaystyle |}{C}}}-$$

(b) (a) CH_3

$-(CH_2-CH-)_n-CH_2-C-$

|C=O |C=O

OH(f)   O

          CH_2 O   (c) CH_3 (a)

HO-CH-CH$_2$-O-C-CH$_2$-SH-(CH_2-C)$_m$-H

          C=O

          OCH_3 (e)

where $\delta_a = 1.0,\ 1.2,\ \delta_b = 1.8,\ 2.0,\ \delta_c = 2.5,\ \delta_d = 3.2,\ \delta_e = 3.7,\ 3.9,\ \delta_f = 12.6$. Only a small peak for proton of carboxylic acid was detected because of the existence of hydrogen bonds. $\delta = 2.8,\ 3.0$, and 8.2 are due to the protons of DMF solvent included in the sample.

Microphotography of the lead ion neutralized copolymer showed three phases: large bright regions for the PMMA glassy domains, black spots for the lead ionic

TABLE 2. Effect of PAA Content and Amount of the Graft Copolymer[a] on Emulsifying Volume

PAA content (%)	Weight of copolymer added (g)	Emulsifying volume (mL)
67.0	0.1	27
	0.2	30
	0.3	33
	0.5	36
	0.3[b]	42
73.8	0.1	36
	0.2	38
	0.3	40
	0.5	45
	0.3[b]	48
79.0	0.1	37
	0.3	42
	0.5	49
	0.3[b]	54

[a]The graft copolymerization was synthesized from PMMA macromer with $M_n = 6 \times 10^3$.

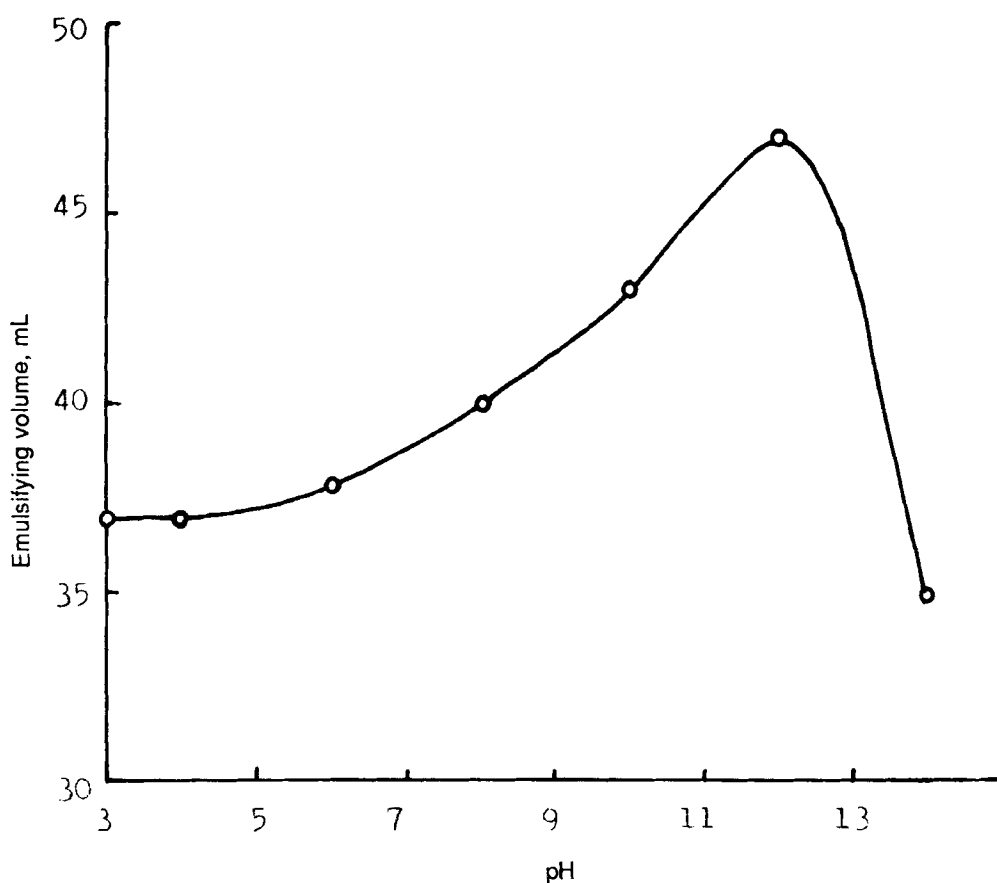[b]The graft copolymer was first neutralized with NaOH.

FIG. 7.   Effect of pH on emulsifying volume.

clusters, and the continuous dark phase of poly(acrylic acid) containing lead ions (Fig. 6).

Properties of the Graft Copolymers

Since the copolymers contain both the hydrophilic AA main chain and the hydrophobic PMMA grafts, they are amphiphilic and can emulsify oil/water system. Table 2 shows the property of graft copolymer in emulsifying the toluene/water system and indicates that emulsifying volume increases with PAA content or amount of the copolymer used. These effects are due to the increase in quantity of emulsifying centers. Emulsifying volume increases with pH up to pH 12, but decreases for excess NaOH added, as shown in Fig. 7. The former fact is attributed to the neutralization of COOH groups and destruction of hydrogen bonds, resulting in an increase of emulsifying centers; the latter is due to the presence of excess strong electrolyte, which destroys the emulsion. The emulsion is quite stable for cycling between room temperature and −20°C and on warming at 50°C for 3 days. When the graft copolymer is used as the emulsifier for emulsion polymerization of
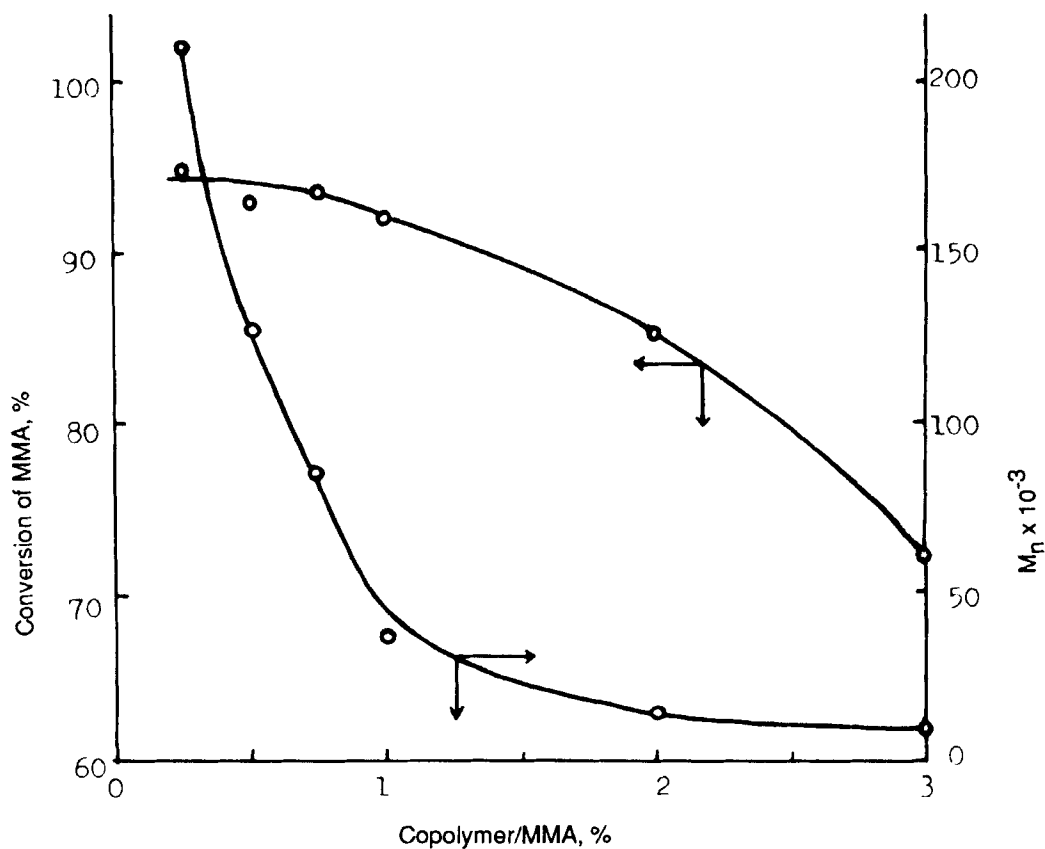
FIG. 8.   Effect of amount of the graft copolymer used as emulsifier in the polymerization of MMA on conversion of MMA and molecular weight of the product.

TABLE 3.   Mechanical Properties of the PVC/ECHR Blends Versus Amount of the Graft Copolymer[a] Added as Compatibilizer

Graft copolymer added (%)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	3.5	55	3
0.5	4.1	70	4
1	6.3	100	6
2	7.5	115	6
3	14.2	120	10
4	10.3	165	10
5	7.0	120	8
3[b]	10.3	65	5

[a]The graft copolymer was synthesized from PMMA macromer with M_n = 1.2 × 10⁴.

[b]The graft copolymer was neutralized with lead ion.

TABLE 4.   Effect of the Graft Copolymer[a] on Mechanical
Properties of PVC/ECHR Blends with Different Compositions

PVC/ ECHR (wt. ratio)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
3/7	0.5	715	70
4/6	1.5	420	43
5/5	2.9	160	13
6/4	7.7	150	10
7/3	14.2	120	10
8/2	24.2	55	2

[a]Weight percent of the graft copolymer based on the blend = 3%.
The graft copolymer was obtained from PMMA macromer with M_n =
1.2×10^4.

MMA, oil-soluble AIBN can be used as the initiator. The copolymer acts not only as emulsifier, but also as molecular weight regulator, as shown in Fig. 8. However, the polymerization product precipitated out at the latter stage of polymerization.

The graft copolymer can be used as a compatibilizer for the blending of ECHR with PVC or PMMA. When ECHR was blended with PVC alone, the tensile strength and ultimate elongation were low. However, if about 3% graft copolymer was added to the blend (PVC/ECHR = 7/3), the mechanical properties of the blends were improved considerably and the blends behaved like toughened plastics, as shown in Table 3. But if the graft copolymer was used at more than 4% of the blend, the tensile strength decreased. At a fixed amount of the graft copolymer (3%) added, the blends seem to exhibit good mechanical properties when the weight ratio of PVC/ECHR is larger than 6/4 (Table 4). The improvement of mechanical properties of the blend by the graft copolymer may be attributed to some compati-
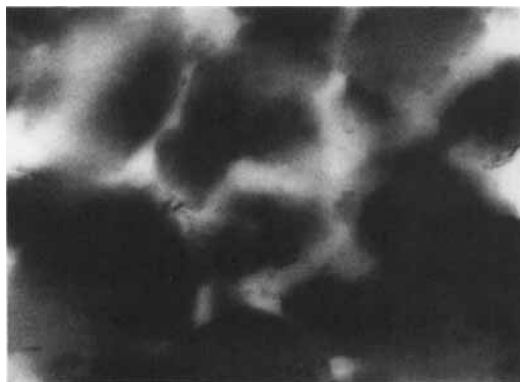

FIG. 9.   TEM microphotograph of the PVC/ECHR blend with the addition of the graft copolymer as compatibilizer (45,000 ×).

TABLE 5.   Mechanical Properties of PMMA/ECHR Blends[a] with
or Without the Graft Copolymer[b] Added as Compatibilizer

Graft copolymer/ blend (wt%)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	5.9	90	—
0.5	8.2	155	2
1	9.2	185	4
2	9.9	210	8
3	13.4	245	15
4	10.7	220	8
5	8.2	200	8

[a]PMMA/ECHR (wt ratio) = 6/4.
[b]The graft copolymer was obtained from PMMA macromer with M_n = 1.2 × 10^4.

bility of PMMA grafts with PVC and the hydrogen bonding between the PAA main chain with ECHR. The DSC curve shows the T_g's of the blend containing 3% graft copolymer are −14.6°C and +88°C, which are somewhat different from the T_g's of ECHR (−18°C) and PVC (+89°C). The inward shift of T_g's denotes that the graft copolymer enhances the compatibility of ECHR and PVC.

If the graft copolymer was first neutralized with lead ions and then used as compatibilizer, the tensile strength and ultimate elongation of the PVC/ECHR (7/3) blend decreased, but were still higher than those of the blend without compatibilizer (see Table 3). This implies that the hydrogen bond interaction is stronger than the ion-dipole interaction.

Microphotography of the blend (PVC/ECHR = 7/3) containing 3% graft copolymer indicates dark particles of PVC separated by a bright phase of ECHR (Fig. 9). Since PVC was first mixed with 5% lead compounds, it may appear dark under TEM, and since ECHR is more viscous than PVC at 130°C, ECHR may surround the PVC particles. The interface between the two phases seems obscure, owing to the presence of the graft copolymer as compatibilizer.

When ECHR was blended with PMMA alone at a weight ratio of 4/6, the mechanical properties appeared poor. But if 2–4% graft copolymer was added as a compatibilizer, the blends behaved like thermoplastic elastomers with ultimate elongation larger than 200% and permanent set smaller than 20% (Table 5). T_g's of the blend containing 3% graft copolymer were shown by DSC curve to be 6.5°C and 30.2°C, which indicates a large inward shift of T_g's compared to those of the individual homopolymers. Obviously, the improvement of mechanical properties is due to the good miscibility of PMMA grafts with PMMA and the hydrogen bonding interaction between PAA main chains and ECHR.

CONCLUSION

Copolymerization of the PMMA macromer with AA can be carried out homogeneously in DMF solution. Grafting efficiency increased with increasing amount of initiator or charging ratio of monomer to macromer and with decreasing molecu-

lar weight of the macromer. A maximum exists in the relationship between grafting efficiency and copolymerization temperature or the total concentration of the macromer and monomer. The purified copolymers were shown by IR, ^{1}H NMR, or TEM to be multiphase graft copolymers. The graft copolymers exhibit good emulsifying properties, which change with pH and behave as a good compatibilizer for the blending of epichlorohydrin rubber with PVC or PMMA.

ACKNOWLEDGMENT

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