This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Copolymerization of Polymethyl Methacrylate Macromers with *n*-Butyl Acrylate and Mechanical Properties of the Graft Copolymers

Hong-Quan Xie[a]; Shi-Biao Zhou[a]
[a] Department of Chemistry, Huazhong University of Science and Technology Wuhan, People's Republic of China

To cite this Article Xie, Hong-Quan and Zhou, Shi-Biao(1990) 'Copolymerization of Polymethyl Methacrylate Macromers with *n*-Butyl Acrylate and Mechanical Properties of the Graft Copolymers', Journal of Macromolecular Science, Part A, 27: 4, 491 — 507

To link to this Article: DOI: 10.1080/00222339009349571

URL: http://dx.doi.org/10.1080/00222339009349571

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. MACROMOL. SCI.—CHEM., A27(4), pp. 491–507 (1990)

COPOLYMERIZATION OF POLYMETHYL METHACRYLATE MACROMERS WITH *n*-BUTYL ACRYLATE AND MECHANICAL PROPERTIES OF THE GRAFT COPOLYMERS

HONG-QUAN XIE and SHI-BIAO ZHOU

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

ABSTRACT

The copolymerization of polymethyl methacrylate (PMMA) macromer with butyl acrylate in benzene was studied. The PMMA macromer was obtained by radical polymerization in the presence of thioglycollic acid as a chain transfer agent, followed by termination with glycidyl methacrylate. The copolymerization rate and effects of various copolymerization conditions, such as molecular weight of macromer, charging ratio of macromer to monomer, amount of initiator, kind of solvent, concentration, and copolymerization temperature, on grafting efficiency and molecular weight of copolymer were investigated. The copolymers were purified by fractional precipitation. The purified copolymers with uniform PMMA grafts were characterized by GPC, IR, UV, and DSC. Structural parameters of the copolymers were determined by VPO and membrane osmometry. Average grafting number per chain decreases with an increase of conversion. Measurement of mechanical properties of the copolymers shows that both molecular weight and the content of the macromer affect mechanical properties of the copolymer, and within a certain range they behave like a thermoplastic elastomer.

INTRODUCTION

Since Milkovich developed the method of preparing copolymers with uniform grafts by using the macromer technique, the synthesis of polystyrene, polyoxyethylene, and polymethyl methacrylate (PMMA) macromers and their copolymerization have been studied extensively. Milkovich and Chiang [1] reported the synthesis of polystyrene macromers through termination of living polystyrene anions with methacryloyl chloride and their copolymerization with butyl acrylate and ethyl acrylate. Rempp [2] summarized the synthesis methods and copolymerization of the polyoxyethylene macromers. Several methods for the synthesis of the PMMA macromer have been published. Ito and coworkers [3] obtained polystearyl methacrylate macromer through free radical polymerization by using thioglycollic acid as the chain transfer agent, followed by reaction with glycidyl methacrylate. Bonardi et al. [4] used thioglycol as the chain transfer agent in preparing macromers of dodecyl methacrylate, followed by reaction with methacryloyl chloride. Albrecht and Wunderlich [5] reported the copolymerization of methacrylic acid with the PMMA macromers obtained by a similar method. Lutz et al. [6] synthesized the PMMA macromer with a narrow molecular weight distribution through the anionic polymerization of MMA at low temperature and then direct deactivation of carbanions with *p*-vinyl or *p*-isopropenyl benzyl bromide. Cacioli and coworkers [7] obtained the PMMA macromers by using methyl azoisobutyrate as the initiator and tetraphenylporphyrin as the chain transfer agent, and they studied their copolymerization with ethyl acrylate, MMA, styrene, or acrylonitrile.

This paper deals with a detailed study of the copolymerization of PMMA macromers obtained by radical polymerization with *n*-butyl acrylate in benzene, characterization of the purified copolymers, and also studies of their mechanical properties in order to obtain a thermoplastic elastomer with PMMA aggregates as physical crosslinks and without double bonds in the chains.

EXPERIMENTAL

Materials

n-Butyl acrylate (BA) and MMA were purified and dried as usual. AIBN was purified by recrystallization from ethyl alcohol and vacuum dried. Thioglycollic acid was purified by distillation under reduced pressure. C.P. *N,N'*-Dimethyl benzylamine was used without purification. C.P. Benzene was 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 with 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.

Synthesis of PMMA Macromers

Radical polymerization of MMA was carried out in benzene under a nitrogen atmosphere by using azobisisobutyronitrile (AIBN) as the initiator and different amounts of thioglycollic acid as the chain transfer agent at 65°C for 12 h in order to obtain prepolymers with different molecular weights, which were then purified by precipitation in benzene with methyl alcohol. The yield was about 60%. Carboxyl end groups of the prepolymer were determined by titration in acetone with an absolute ethyl alcohol solution of KOH while using a methanolic solution of phenolphthalein as the indicator. The purified prepolymer was then reacted in xylene with glycidyl methacrylate (GMA) at a molar ratio of GMA/COOH = 2 by using *N,N'*-dimethyl benzylamine as the catalyst at 139°C under a nitrogen atmosphere for 8 h. The macromer thus obtained was purified by precipitation in benzene with methyl alcohol. The efficiency of the reaction between prepolymer and glycidyl methacrylate was determined to be nearly 100% by titration of the remaining carboxyl end groups in the macromer.

Copolymerization of the PMMA Macromer with *n*-Butyl Acrylate (BA)

BA and AIBN were added to the benzene solution of PMMA macromer, and copolymerization was carried out at 64°C under a nitrogen atmosphere. The reaction was terminated with a 1% methanol solution of *p*-methoxy-phenol. The solvent was stripped off with boiling water, and the product was vacuum dried to constant weight.

The crude product was dissolved in *n*-butanol at 65°C, then cooled to 0°C, at which temperature the homopolymer of MMA was precipitated out. After filtration and washing of the precipitate, methanol was dropped into the mixture of filtrate and washings with stirring up to a volume ratio of methanol/(butanol + methanol) equal to 0.5–0.6. The precipitated product is the graft copolymer. The homopolymer of BA can be obtained as a precipitate by further dropping methanol into the filtrate up to a volume ratio of methanol/(butanol + methanol) equal to 0.7–0.9.

Conversion of the macromer into copolymer or the grafting efficiency (G.E.) can be calculated by the following equation, utilizing the data obtained from GPC or fractional precipitation:

$$\begin{aligned}\text{G.E. \%} &= (\text{macromer charged} - \text{macromer unreacted}) \times 100/\text{macromer charged}\\ &= \text{peak area of copolymer} \times 100/\text{peak area of (copolymer + macromer)}\end{aligned}$$

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

% BA copolymerized = % conversion of BA − % homopolymer of BA

% PMMA content in the copolymer = macromer charged × G.E. × 100/(macromer charged × G.E. + BA charged × % BA copolymerized)

Characterization and Testing

The molecular weights of the PMMA macromers and the graft copolymer were determined with a Knauer VPO apparatus by using $CHCl_3$ as the solvent and with a Bruss membrane osmometer by using tetrahydrofuran as the solvent, respectively. Molecular weight distribution was measured by GPC on a liquid chromatographic apparatus (LC-4A) with a differential refractive index detector by using tetrahydrofuran as the eluent.

IR spectra of the copolymers were taken with a PE-580B spectrophotometer by using a KBr disk coated with the copolymer. UV spectra were recorded by a Specord UV-Vis by using a copolymer solution in 95% ethanol. Glass transition temperatures of the copolymers were measured with a PE DSC-4 apparatus combined with a computer, employing a heating rate of 20°C/min and a sample weight of about 10 mg.

Mechanical properties of the copolymers were determined on a DL-250 tensile tester with a stretching rate of 250 mm/min after compression molding at 150–170°C under a hot press. Permanent set was measured as percent elongation after the specimen was broken and reunited after 3 min.

RESULTS AND DISCUSSION

Copolymerization Rate of the PMMA Macromer with BA

When copolymerization of the prepolymer with BA in benzene was tried, with AIBN as the initiator, the product precipitated in *n*-butanol at 0°C was the same as the original prepolymer with respect to amount and molecular weight. This demonstrates that no copolymerization occurred with the prepolymer containing no terminal double bonds.

Figure 1 shows the copolymerization rates of both the macromer and BA. At the beginning, the conversion rate of the macromer was higher than that of BA. The difference between the two rates gradually became smaller until the conversion of BA exceeded that of the macromer. This was due to the higher reactivity of the methacryloyl group of the macromer than that of the acryloyl group of BA at the beginning of the reaction. With an increase of conversion, the viscosity of the polymerization solution gradually increased, resulting in a more difficult diffusion of the macromer and a lowering of the reaction probability of the macromer. Thus,

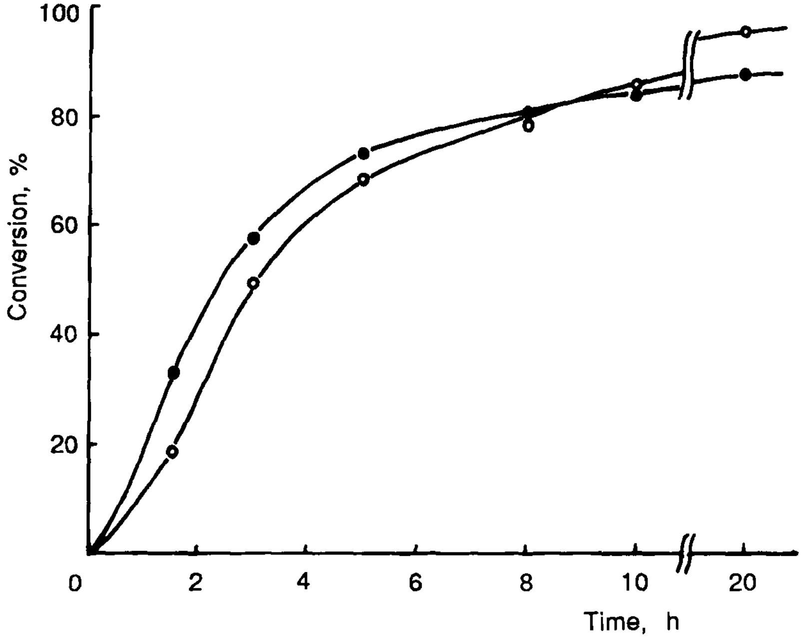

FIG. 1. Comparison of copolymerization rates of the macromer and butyl acrylate: (○) BA, (●) the macromer with $M_n = 1.02 \times 10^4$.

the conversion rate of the macromer became lower than that of BA in the later stage.

Table 1 illustrates the effect of the molecular weight of the PMMA macromers on the conversion rate of the macromer in copolymerization with BA. Note that the molecular weight of the macromer exerts little influence on the polymerization rate.

The content of PMMA in the copolymer decreased and the number-average molecular weight of the copolymer increased with increasing conversion, as shown in Fig. 2. This can be interpreted as follows: With increasing conversion, the viscosity of the polymerization system increased, which enhanced the shielding of the active centers and prevented chain termination, thus resulting in an increase of molecular weight of the copolymer. The increased viscosity restricts the diffusion of the macromer much more seriously than that of the BA monomer, hence causing a decrease of the PMMA content of the copolymer.

TABLE 1. Conversions of the Macromer and Butyl Acrylate versus Copolymerization Time[a]

	A[b]		B[c]	
Time, h	Conversion of the macromer, %	Conversion of BA, %	Conversion of the macromer, %	Conversion of BA, %
1.5	32.5	19.0	30.0	17.0
3.0	61.0	50.0	59.5	50.5
5.0	72.5	69.0	70.5	71.4
8.0	80.0	79.5	78.8	82.0
10.0	83.5	87.0	82.0	88.7

[a] Conditions of polymerization: Macromer/BA = 1/3 (w/w), AIBN/(BA + macromer) = 0.15% (w/w), (macromer + BA)/benzene = 1/4 (w/w), 66.5°C.

[b] M_n of the macromer = 5.6×10^3.

[c] M_n of the macromer = 1.68×10^4.

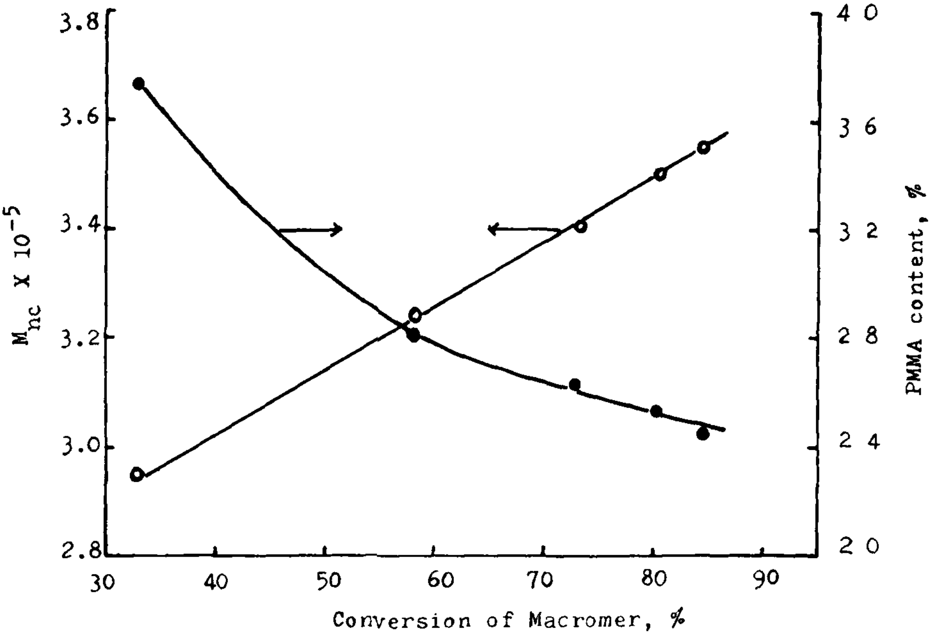

FIG. 2. Change of molecular weight and PMMA content of the copolymer vs conversion of the macromer.

Effects of Copolymerization Conditions

1. Effect of Amount of Initiator Used

Table 2 indicates that by increasing the amount of AIBN used, grafting efficiency increased and molecular weight of the copolymer decreased. This is because the active centers increased with an increase of AIBN, resulting in a decrease of the molecular weight of the copolymer and also of the viscosity of the polymerization system. Lower viscosity is favorable to an increase in grafting efficiency.

2. Effect of Kind and Amount of the Solvent Used

As summarized in Table 3, toluene seems to be worse than benzene or cyclohexanone as a polymerization solvent. This is probably because the hydrogen

TABLE 2. Effect of Amount of Initiator on Grafting Efficiency and Molecular Weight of Copolymers[a]

AIBN/(macromer + BA), %	G.E., %	$M_{nc} \times 10^{-5}$
0.03	77.2	5.50
0.06	79.8	4. 85
0.15	82.5	3.20
0.55	83.0	2.05
1.00	83.4	1.15

[a] Conditions of polymerization: Macromer/BA = 1/3 (w/w), M_n of macromer = 1.15×10^4, (macromer + BA)/benzene = 1/3 (w/v), 64°C, 10 h.

TABLE 3. Effect of Kind of Solvent on Grafting Efficiency and Molecular Weight of Copolymers[a]

Solvent	G.E., %	$M_{nc} \times 10^{-5}$
Benzene	84.3	5.30
Cyclohexanone	83.7	5.20
Toluene	80.8	4.74

[a] Conditions of polymerization: Macromer/BA = 1/3 (w/w), M_n of macromer = 1.37×10^4, (macromer + BA)/solvent = 1/3 (w/v), AIBN/(BA + macromer) = 0.06% (w/v), 64°C, 16 h.

atoms in the methyl group of toluene have a tendency to take part in chain termination in radical polymerization, thus reducing the molecular weight of the copolymer and also the grafting efficiency due to termination of the more active macromer.

There exists a maximum in the relationship between grafting efficiency and the amount of solvent used, i.e., concentration, as indicated in Fig. 3. 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. Maximum grafting efficiency appears at a higher concentration for macromers with a lower molecular weight because a macromer with a lower molecular weight will exhibit the same viscosity at a higher concentration.

Figure 3 also shows that the molecular weight of the copolymer increases with concentration up to a certain limit because the kinetic chain length is usually

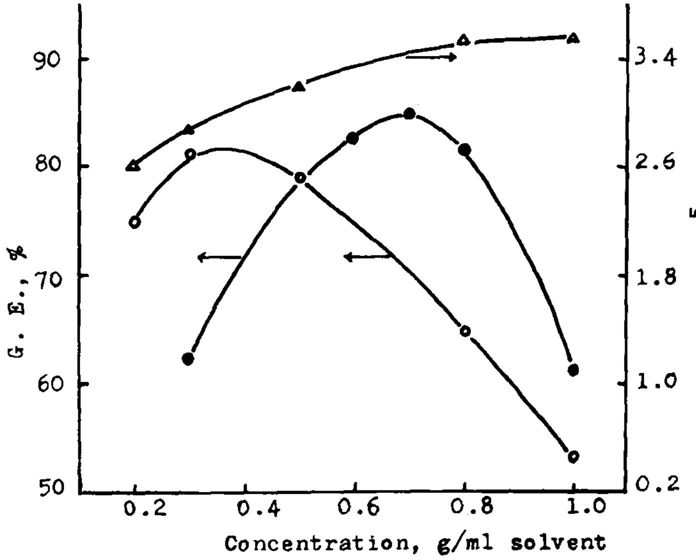

FIG. 3. Grafting efficiency and molecular weight of the copolymers vs concentration of the monomers and molecular weight of the macromer: (○) $M_{ng} = 1.6 \times 10^4$, (●) $M_{ng} = 7.5 \times 10^3$.

proportional to the monomer's concentration and fewer impurities are present at a higher concentration.

3. Effect of Copolymerization Temperature

Mobility of the macromers and their reaction probability increases with increasing temperature of copolymerization. This results in improved grafting efficiency, as illustrated in Fig. 4, even though the molecular weight of the copolymer decreases. The latter phenomenon is attributed to the fact that with increasing temperature, the decomposition rate of the initiator increases. The resulting increase in active centers produces a lower molecular weight copolymer. At the same time, the viscosity of the copolymerization system is reduced with increasing temperature, resulting in an increase in the availability of active centers which are readily terminated.

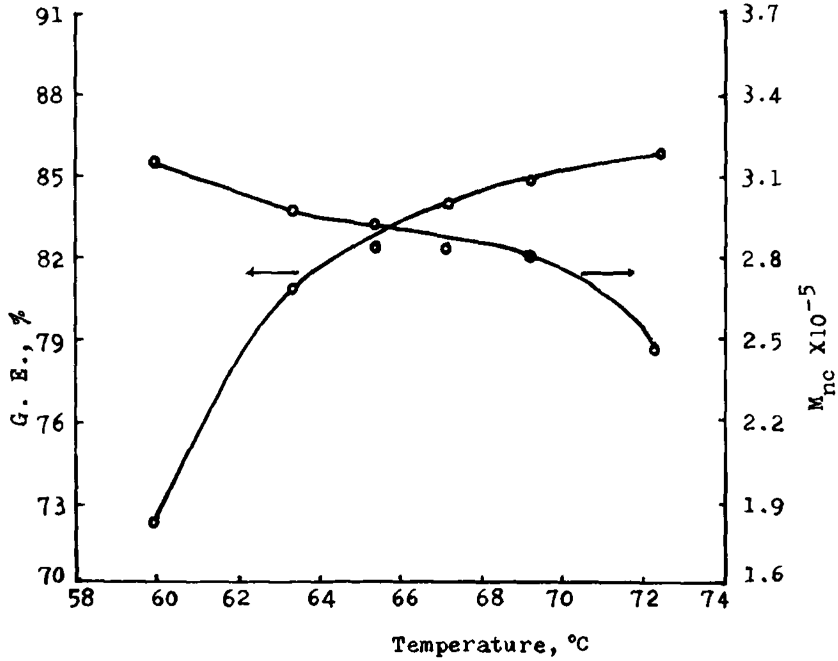

FIG. 4. Effect of copolymerization temperature on grafting efficiency and molecular weight of the copolymer.

4. Effect of Molecular Weight of the Macromer

Figure 5 shows that grafting efficiency decreases with increasing molecular weight of the macromer. This may be due to more difficult diffusion and larger steric hinderance of the macromer with higher molecular weight, which makes the reaction between active centers and the macromer less probable. However, the molecular weight of the copolymer increases with increasing molecular weight of the macromer used.

5. Effect of the Charging Ratio of Macromer to Monomer by Weight

Figure 6 shows that grafting efficiency decreases with an increase of the charging ratio of macromer to monomer, probably due to an increase of viscosity of the polymerization system containing more macromers, which reduces diffusion and reaction of the macromer, and also due to the difficulty of homopolymerization of the macromer.

The same figure illustrates that the molecular weight of the copolymer increases with the charging ratio. This is because a higher viscosity of the polymerization

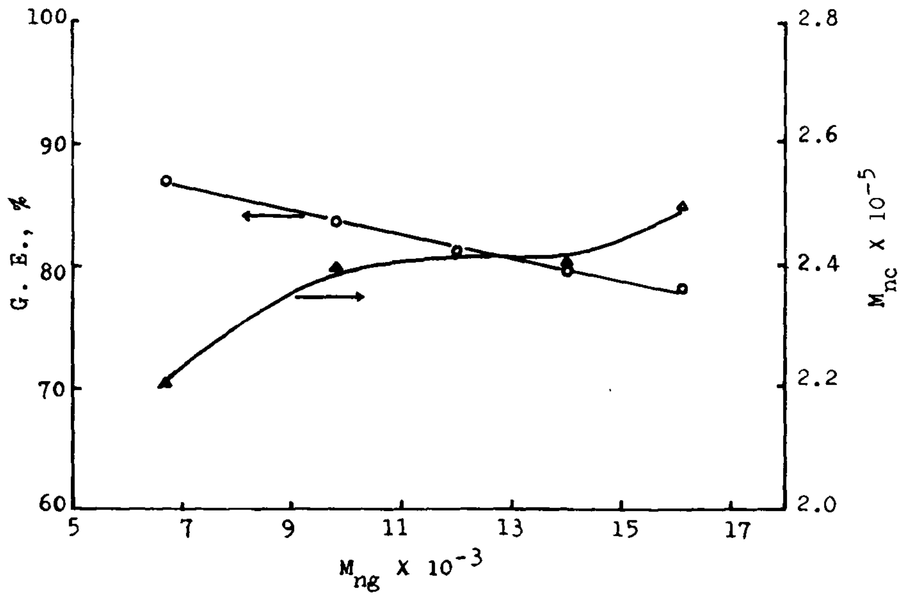

FIG. 5. Effect of molecular weight of the macromer on grafting efficiency and molecular weight of the copolymers.

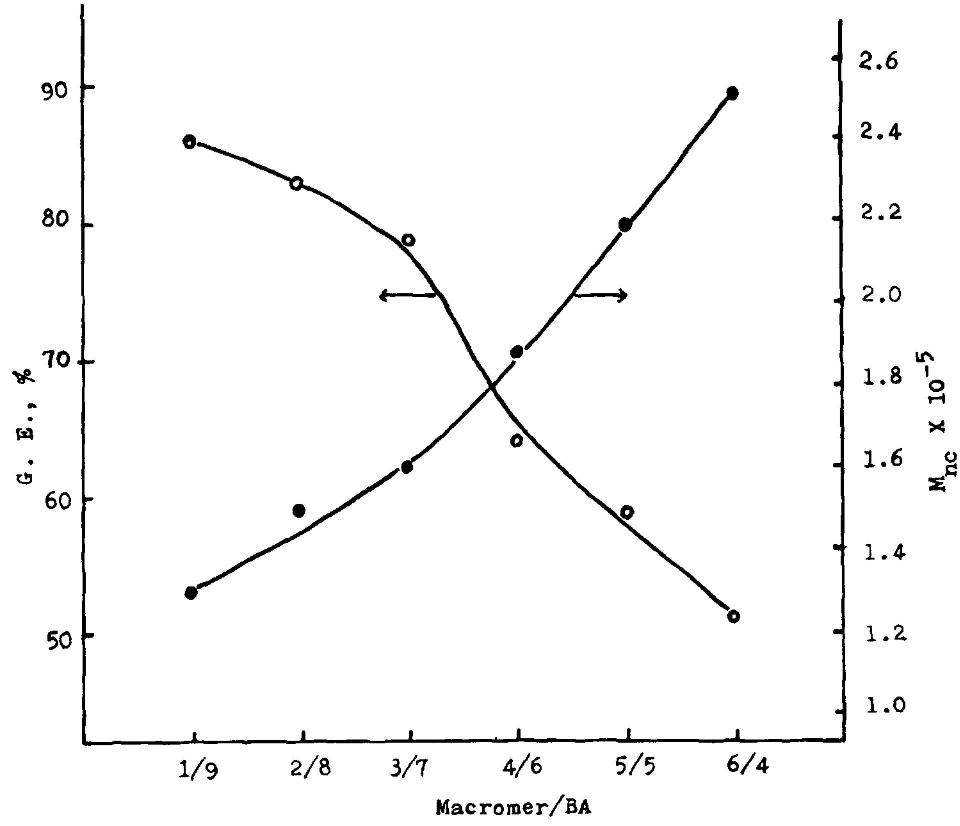

FIG. 6. Effect of charging weight ratio of macromer/butyl acrylate on grafting efficiency and molecular weight of the copolymers.

system containing more macromers has a greater tendency to shield the active centers and prevents them from chain transfer or termination, and also because relatively more macromer is copolymerized in the product.

Purification of the Graft Copolymers

The crude product of copolymerization contains homopolymer of BA, unreacted PMMA macromer, and the graft copolymer. The homopolymer of BA and unreacted PMMA macromer can be separated from the graft copolymer by means of fractional precipitation as described in the Experimental section.

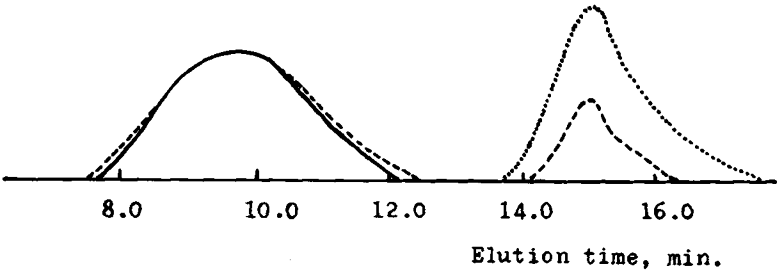

FIG. 7. GPC curves of the macromer and the copolymer before and after purification: (· · ·) the macromer, (– –) unpurified copolymer, and (——) purified copolymer.

Figure 7 shows GPC curves of the crude product of copolymerization before and after purification. It can be seen that after two purifications the macromer can be thoroughly removed from the graft copolymer. No methacryloyl group can be detected by UV spectrophotometry at 208 nm (Fig. 8).

Structural Parameters of the Purified Copolymers with Uniform PMMA Grafts

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 PMMA in the copolymer (W_g) can be calculated as indicated in the Experimental section, the average grafting number (N_g) can be calculated by

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

Table 4 indicates that with an increase of conversion of macromer, N_g decreases gradually. This is coincident with different polymerization rates of the macromer and monomer at different stages.

Characterization of the Purified Graft Copolymers

The IR spectrum of the graft copolymer in Fig. 9 shows a characteristic peak at 1730 cm^{-1} for the carbonyl group, a multipeak at 2920–2980 cm^{-1} for methyl and methylene groups, two peaks at 940 and 960 cm^{-1} for the butyl ester, and a peak at 1165–1265 cm^{-1} for the C–O vibration.

From DSC curves of the copolymer (Fig. 10), two glass transition temperatures (T_g's) can be noted, namely –45 and +94°C, indicating phase separation in the

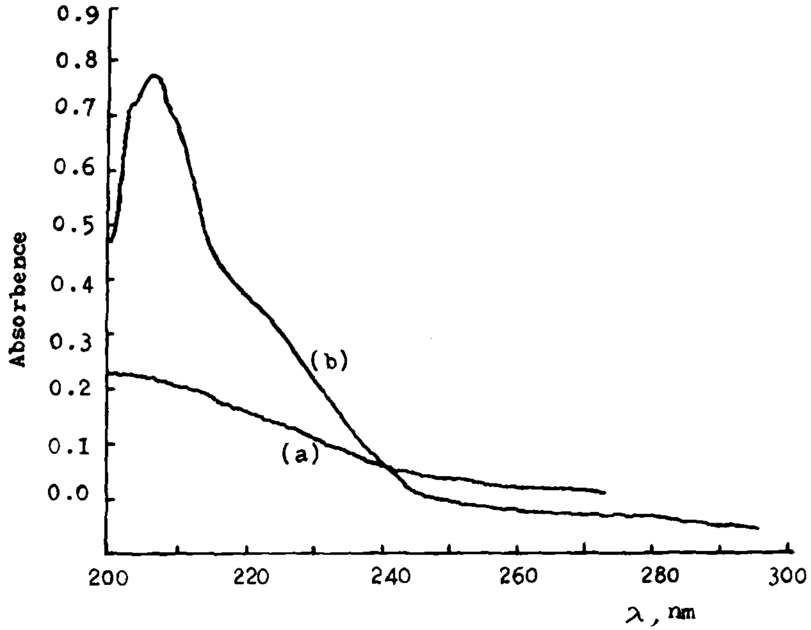

FIG. 8. UV spectrum of the purified copolymer (a) and the macromer (b).

TABLE 4. Change of Average Grafting Number with Conversion[a]

Conversion of macromer, %	W_g, %	$M_{nc} \times 10^{-5}$	N_g
33.0	37.3	2.95	10.79
58.0	28.1	3.24	8.93
73.5	26.3	3.40	8.77
80.5	25.5	3.50	8.75
84.5	24.6	3.55	8.56

[a] Conditions of polymerization: M_n of macromer = 1.02×10^4, macromer/BA = 1/3 (w/w), AIBN/(macromer + BA) = 0.15% (w/w), (BA + macromer)/benzene = 1/4 (w/v), 66.5°C.

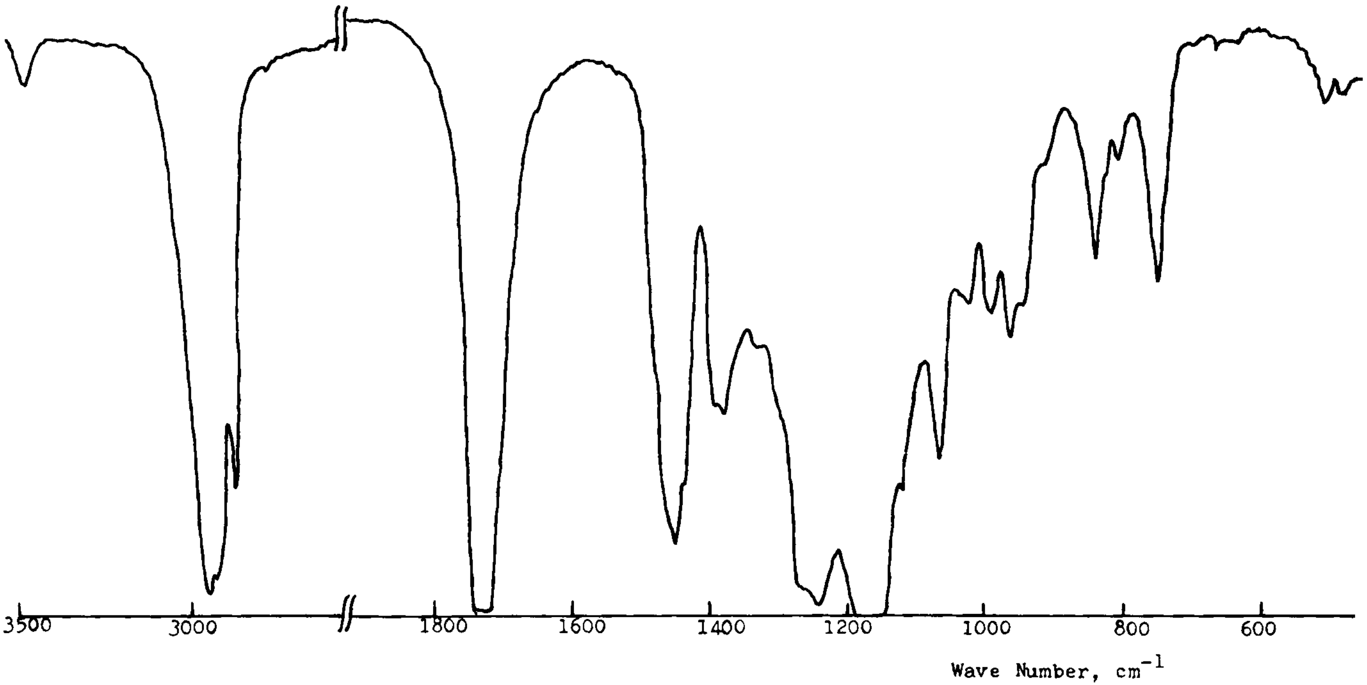

FIG. 9. IR spectrum of the purified copolymer.

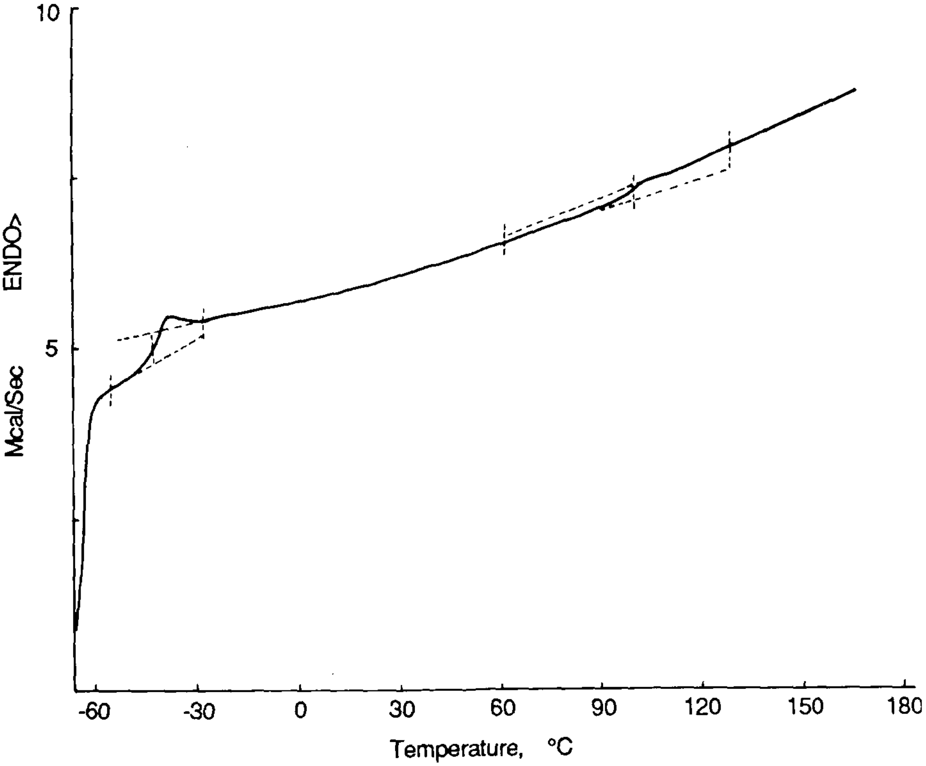

FIG. 10. DSC curve of the purified copolymer.

graft copolymer. However, T_g's for the homopolymers of BA and MMA are at −52 and +105°C, respectively. This implies that the two T_g's shift toward each other in the graft copolymer, which means that partial compatibilization between PMMA and PBA occurred in the copolymer.

Mechanical Properties of the Graft Copolymers

Table 5 lists the mechanical properties of the graft copolymers versus the molecular weight of macromer used in copolymerization. It can be seen that with increasing molecular weight of the macromer, the tensile strength of the copolymer increased while ultimate elongation and permanent set decreased. When M_n of the macromer is less than 5×10^3, the tensile strength seems rather low. This

TABLE 5. Relation between Mechanical Properties of the Copolymers and Molecular Weight of the Macromers (M_{ng})[a]

$M_{ng} \times 10^{-3}$	Tensile strength, MPa	Ultimate elongation, %	Permanent set, %
4.5	3.3	620	30
10.1	4.8	565	23
13.7	5.3	495	17
18.9	5.8	470	16
22.4	6.1	460	16

[a] Conditions of polymerization: Macromer/BA = 1/3 (w/w), AIBN/(BA + macromer) = 0.15% (w/w), (macromer + BA)/benzene = 1/3 (w/v), 64°C, 10 h.

may be because very short PMMA grafts cannot from domains efficiently. The higher the molecular weight of the macromer used, the more efficient the formation of domains by PMMA grafts, resulting in an increase of physical crosslinks.

When the molecular weight of the macromer is kept constant, the tensile strength of the copolymer increases and the ultimate elongation decreases with increasing PMMA content of the copolymer, as indicated in Table 6. Permanent set exhibits a minimum at 33% PMMA content. When the PMMA content of the copolymer is less than 16%, the mechanical properties are rather poor, possibly because the number and size of the domains formed by PMMA grafts, and hence the physical crosslinks, are not large enough. In the range of 20–40% PMMA content, the copolymers behave like a thermoplastic elastomer with higher tensile strength and ultimate elongation and low permanent set. Above 50% PMMA content, the very large permanent set of the product indicates that the copolymer behaves rather like a toughened plastic than a thermoplastic elastomer. This is due

TABLE 6. Effect of PMMA Content on Mechanical Properities of the Copolymers[a]

PMMA, %	$M_{nc} \times 10^{-5}$	Tensile strength. MPa	Ultimate elongation, %	Permanent set, %
15.6	1.34	3.1	690	38
20.2	1.52	4.5	630	29
33.3	1.60	6.0	575	17
38.5	1.88	6.3	350	32
56.0	2.19	6.1	270	>50

[a] $M_{ng} = 1.6 \times 10^4$.

to the occurrence of a phase inversion; in other words, the PMMA aggregate changes from domains into a continuous phase while PBA changes from a continuous phase into domains.

ACKNOWLEDGMENT

The financial support of this research by the National Natural Science Foundation Committee of China is gratefully acknowledged.

REFERENCES

[1] G. O. Schulz and R. Milkovich, *J. Appl. Polym. Sci., 27,* 4773 (1982).
[2] P. Rempp, *Plaste Kautsch., 28,* 365 (1981).
[3] K. Ito, N. Usami, and Y. Yamashita, *Macromolecules, 13,* 216 (1980).
[4] C. Bonardi, B. Boutevin, Y. Pietrasanti, and M. Taha, *Makromol. Chem., 186,* 261 (1985).
[5] K. Albrecht and W. Wunderlich, *Agnew. Makromol. Chem., 145–146,* 89 (1986).
[6] P. Lutz, P. Masson, G. Beinert, and P. Rempp, *Polym. Bull., 12,* 79 (1984).
[7] P. Cacioli, D. G. Hawthorne, R. L. Laslett, E. Rizzardo, and D. H. Solomon, *J. Macromol. Sci.—Chem., A23,* 839 (1986).

Received February 22, 1989
Revision received August 7, 1989