

Syntheses of Copolymers of Chloroprene with Ethylmethacrylate and Glycidylmethacrylates

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SYNOPSIS

Chloroprene (2-chloro-1,3-butadiene; CP) was prepared by dehydrochlorination of 3,4-dichloro-1-butene (DCB) in aqueous solution of sodium hydroxide in the presence of tetrahydrofurfuryl alcohol (THFA) at 60°C. The copolymers of CP with ethylmethacrylate (EMA) and glycidylmethacrylate (GMA) were prepared by radical solution polymerization in benzene. The copolymers, poly(CP-co-EMA) and poly(CP-co-GMA), were characterized by FT-IR and ¹H-NMR spectrophotometers and differential scanning calorimetry (DSC). It was observed that the copolymers were amorphous and had glass transition temperatures of about -34.5 and -16.4°C, respectively. The monomer reactivity ratios were given as $r_1(\text{CP}) = 2.14$ and $r_2(\text{EMA}) = 0.18$ in the copolymerization of CP and EMA, and as $r_1(\text{CP}) = 4.02$ and $r_2(\text{GMA}) = 0.12$ in copolymerization of CP and GMA, respectively. For comparison, the graft copolymers of EMA or GMA onto CR (poly(CR-*g*-EMA) and poly(CR-*g*-GMA)) were also prepared. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polychloroprene (CR) is one of the most commonly used synthetic rubbers in the rubber industries because of the high mechanical strength, good resistance to hydrocarbon oils and polar solvents and chemicals, adequate low-temperature behavior, and compatibility with other rubbers. However, its poor heat resistance and weatherability limit the outdoor use.¹⁻⁵

Recently, modification of CR by copolymerization with other second monomers has been the subject of ongoing work in this laboratory in order to make improvements in the poor performance of CR. For example, we have previously prepared the copolymers of chloroprene with maleic anhydride or isobutylmethacrylates.⁶⁻⁸

In this work, we obtained copolymers of chloroprene (CP) and two different alkylmethacrylates (AMA), i.e., ethylmethacrylate (EMA) and glycidylmethacrylate (GMA). The copolymers were

characterized with FT-IR and ¹H-NMR spectroscopies. To determine monomer reactivity ratios, radical solution copolymerizations of CP and EMA or GMA were carried out in the presence of 2,2'-azobisisobutyronitrile (AIBN) as an initiator in benzene at 50°C, and their conversions were adjusted to be less than 10%. The glass transition temperatures and the average molecular weights of the poly(chloroprene-co-ethylmethacrylate) and poly(chloroprene-co-glycidylmethacrylate) were measured by differential scanning calorimetry (DSC) and gel permeation chromatography, respectively. For comparison, the graft copolymers of EMA or GMA onto CR were also prepared.

EXPERIMENTAL

Materials

Ethylmethacrylate (Aldrich), glycidylmethacrylate (Aldrich), and benzene (Junsei) were purified by the standard methods. (AIBN) and benzoylperoxide (BPO) were purified by recrystallization in dehydrated ethanol. 3,4-Dichloro-1-butene (DCB) (Aldrich), tetrahydrofurfuryl alcohol (THFA) (Ald-

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rich) and sodium hydroxide (NaOH) (Junsei) were used as received without further purifications.

Synthesis of Chloroprene (2-chloro-1,3-Butadiene)

Chloroprene (CP) was prepared by reacting DCB in aqueous solution of sodium hydroxide in the presence of THFA at 60°C by the same method described as in our previous work.⁶⁻⁸ The mole ratio of DCB/NaOH/THFA/H₂O was 1/1.3/1.5/1.5. The product of the dehydrochlorination of DCB was filtered to remove sodium chloride, and supernatant was dried with CaCl₂ and distilled in argon under reduced pressure and the fraction, collected at 25°C and 160 mmHg, was retained for copolymerization. The purity of chloroprene was confirmed to be 99.5% by gas chromatography and the yield of chloroprene was 85%. Chloroprene was used as soon as possible after distillation because it polymerizes slowly during storage, even at low temperature.

The structure of chloroprene was confirmed by IR spectrophotometry (Perkin-Elmer 1330) and ¹H-NMR spectroscopy (Bruker 300 CW). The IR spectrum of chloroprene exhibited characteristic peaks of stretching vibration of vinyl C—H bond at 3020 and 3100 cm⁻¹, whereas the characteristic peaks of stretching vibration of vinyl C—H bond disappeared at 2950 and 2990 cm⁻¹. The ¹H-NMR (CCl₄) spectrum of chloroprene showed =CH₂ and =CH— peaks at δ = 5.2, 5.6, and 6.4 ppm, whereas the characteristic peaks of DCB was shown at δ = 3.6

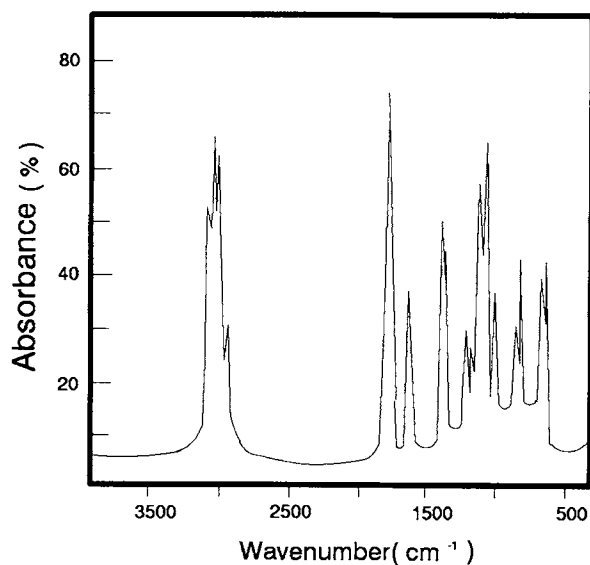


Figure 1 FT-IR spectrum of poly(CP-co-EMA).

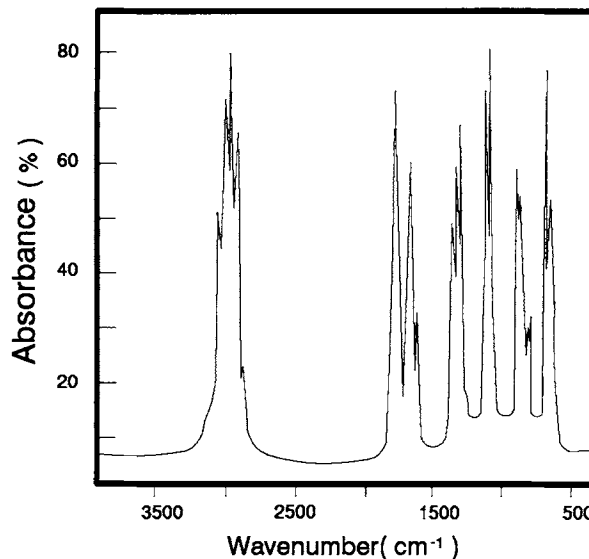


Figure 2 FT-IR spectrum of poly(CP-co-GMA).

and 4.5 ppm due to —CH₂Cl and —CHCl, respectively.

Synthesis of Polychloroprene and Polyalkylmethacrylates

The polychloroprene (CR) was obtained in a glass ampoule by polymerizing 0.2 mol of CP with 0.2 mol % of AIBN as an initiator at 50°C in benzene for 10 h.

After reaction, the reaction mixture was poured into a large amount of methanol. The product recovered from methanol was dried under vacuum at 30°C to remove all volatiles. Polyethylmethacrylate (PEMA) and polyglycidymethacrylate (PGMA) were synthesized by the same method as described for CR.

Syntheses of Poly(Chloroprene-co-Alkylmethacrylates)

The copolymers of chloroprene and alkylmethacrylate, viz. EMA and GMA, were obtained by the same method as described for CR. For the determination of monomer reactivity ratios, a series of copolymers were prepared in which the feed ratio was varied for CP (*M*₁) to EMA (*M*₂) or GMA (*M*₂) in benzene (0.43–2.33).

Copolymerization was adjusted to make conversion below 10% by controlling reaction time. To make a copolymer with *M*₁/*M*₂ = 1, for example, 0.20 mol of chloroprene and 0.20 mol of EMA or

Table I Average Molecular Weights of Various Samples

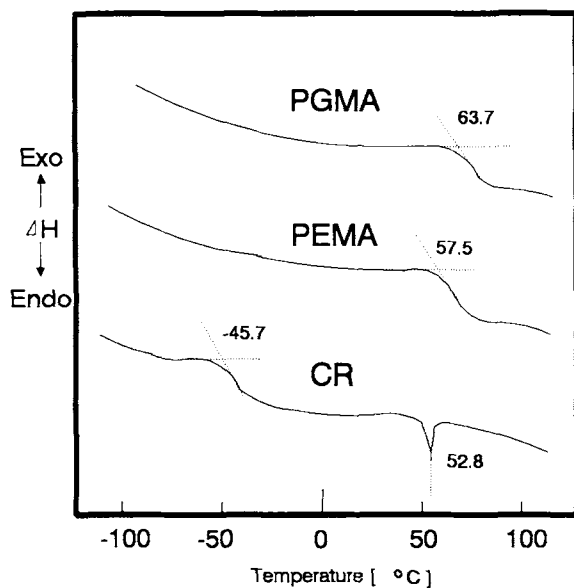
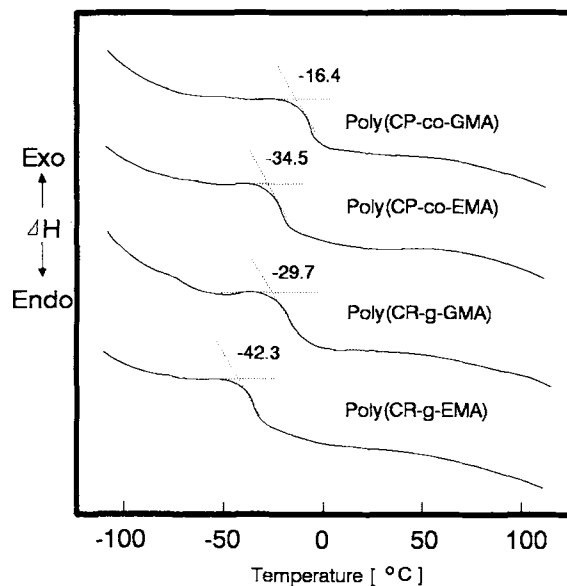
Samples	Average Molecular Weight		
	\overline{M}_n	\overline{M}_w	$\overline{M}_w/\overline{M}_n$
CR	81,000	194,000	2.40
PEMA	80,000	143,000	1.79
poly(CR- <i>g</i> -EMA)	74,000	140,000	1.89
poly(CP-co-EMA)	58,300	71,000	1.22
PGMA	77,000	126,400	1.64
poly(CR- <i>g</i> -GMA)	63,000	128,000	2.03
poly(CP-co-GMA)	45,600	74,200	1.63

GMA were radically copolymerized with 0.2 mol % AIBN as an initiator at 50°C in benzene.

Synthesis of Poly(Chloroprene-*g*-Alkylmethacrylates)

The graft copolymerizations of EMA and GMA onto CR were carried out in glass tubes: 1 g of CR was dissolved in benzene: 0.20 mol of EMA or GMA were dissolved in benzene and then added to 0.20 mol of BPO. The tube was sealed after charging with argon and the reaction was carried out at 70°C for 10 h. The precipitates from methanol was filtered and dried in vacuum to constant weight.

The FT-IR spectra of poly(chloroprene-*g*-ethylmethacrylate) [poly(CR-*g*-EMA)] and poly(chloroprene-*g*-glycidylmethacrylate) [poly(CR-*g*-

**Figure 3** DSC thermograms of homopolymers.**Figure 4** DSC thermograms of the copolymers and the graft copolymers.

GMA)] exhibited characteristic peaks of C=O bond at 1750 cm^{-1} , C=C double bond at 1660, and C—Cl bond at 600–800 cm^{-1} . The peaks of epoxy groups for the poly(CR-*g*-GMA) were appeared at 1100–1200 cm^{-1} .

Measurement

The molecular weights of homopolymers and copolymers having 1/1 composition of CP and AMA by weight were measured by gel permeation chromatograph (GPC) using polystyrene (PS) standards. THF was used as an eluent.

The glass transition temperatures (T_g) were measured using a differential scanning calorimetry (DSC; DuPont 2100). The thermograms of CR, PEMA, PGMA, poly(CP-co-EMA), poly(CP-co-

Table II Glass Transition Temperatures of Homopolymers, Copolymers, and Graft Copolymers

Samples	T_g (°C)
CR	-45.7
PEMA	57.5
PGMA	63.7
poly(CP-co-EMA)	-34.5
poly(CP-co-GMA)	-16.4
poly(CR- <i>g</i> -EMA)	-42.3
poly(CR- <i>g</i> -GMA)	-29.7

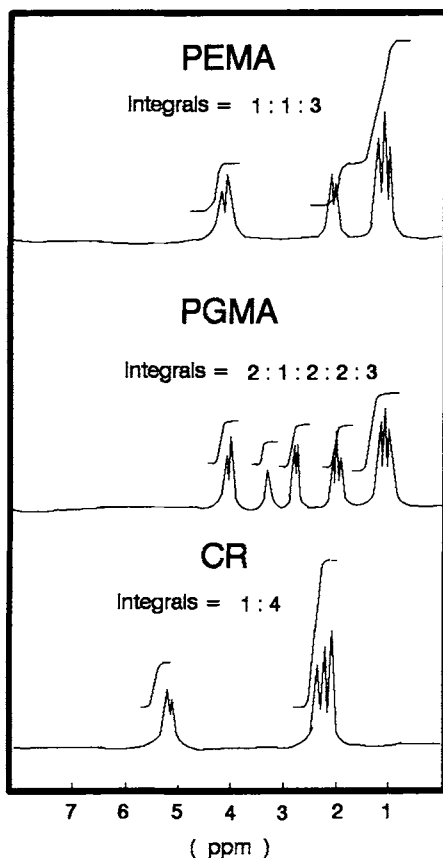


Figure 5 $^1\text{H-NMR}$ spectra of CR, PGMA, and PEMA.

GMA), poly(CR-*g*-EMA), and poly(CR-*g*-GMA) were obtained at a heating rate of $10^\circ\text{C}/\text{min}$. The T_g value was taken as initial onset of the change of slope in the DSC curve on the second run.

RESULTS AND DISCUSSION

Characterization

Poly(chloroprene-co-ethylmethacrylate) [poly(CP-co-EMA)] and poly(chloroprene-co-glycidylmethacrylate) [poly(CP-co-GMA)] were identified by

FT-IR spectroscopies (Mattson Galaxy series 6030). The FT-IR spectra of poly(CP-co-EMA) and poly(CP-co-GMA) are illustrated in Figures 1 and 2, respectively. The FT-IR spectra of poly(CP-co-EMA) and poly(CP-co-GMA) exhibited characteristic peaks of stretching vibration of vinyl C—H bond at 3020 and 3100 cm^{-1} . The peaks of C—Cl bond, C=O bond, and C=C double bond were appeared at $600\text{--}800$, 1750 , and 1660 cm^{-1} , respectively. The peaks of epoxy group for poly(CP-co-GMA) were observed at $1100\text{--}1200\text{ cm}^{-1}$.

The molecular weights of poly(CP-co-EMA) and poly(CP-co-GMA) was determined as $\overline{M}_n = 58,300$, $\overline{M}_w = 71,000$ and $\overline{M}_n = 45,600$, $\overline{M}_w = 74,200$, respectively. In Table I, the molecular weights of CR, PEMA, PGMA, poly(CP-co-EMA), poly(CP-co-GMA), poly(CR-*g*-EMA), and poly(CR-*g*-GMA) are listed. In this case, the copolymers have the composition ratio of 1/1 by weight in feed.

Figure 3 shows DSC thermograms of CR, PEMA, and PGMA. The T_g 's of homopolymers were -45.7 , 63.7 , and 57.5°C for CR, PGMA, and PEMA, respectively. The CR exhibited also a melting peak around at 52.8°C .

Figure 4 shows DSC thermograms of the copolymers, poly(CP-co-EMA) and poly(CP-co-GMA), and the graft copolymers, poly(CR-*g*-EMA) and poly(CR-*g*-GMA). The copolymers, poly(CP-co-EMA) and poly(CP-co-GMA), have T_g of -34.5 and -16.4°C , respectively, which are higher by about 13 and 30°C than that of CR. The CR exhibited a melting peak around 52.8°C , but the copolymers did not show any melting peaks, meaning that the CR has some degree of crystallinity whereas the copolymers are amorphous.

This kind of thermal characteristics of a chloroprene-containing copolymer was also observed in the case of poly(chloroprene-co-maleic anhydride).⁶ The graft copolymers, poly(CR-*g*-EMA) and poly(CR-*g*-GMA), showed T_g of -42.3 and -29.7°C , which are higher by about 3.4 and 16°C than that of CR. The glass transition temperatures of the co-

Table III Determination of Monomer Reactivity Ratios for the Copolymerization of CP (M_1) and EMA (M_2)

Sample	$F = [M_2]/[M_1]$	$f = m_2/m_1$	F^2	$F - 1$	$(f - 1)/F$	f/F^2
CE-1	0.43	0.18	0.185	-0.82	-1.90	0.97
CE-2	0.67	0.27	0.449	-0.73	-1.09	0.60
CE-3	1.00	0.37	1.00	-0.63	-0.63	0.37
CE-4	1.50	0.52	2.25	-0.48	-0.32	0.23
CE-5	2.33	0.75	5.43	-0.25	-0.11	0.14

Table IV Determination of Monomer Reactivity Ratios for the Copolymerization of CP (M_1) and GMA (M_2)

Sample	$F = [M_2]/[M_1]$	$f = m_2/m_1$	F^2	$F - 1$	$(f - 1)/F$	f/F^2
CG-1	0.43	0.099	0.185	-0.90	-2.093	0.535
CG-2	0.67	0.145	0.449	-0.855	-1.270	0.322
CG-3	1.00	0.25	1.00	-0.75	-0.750	0.250
CG-4	1.50	0.41	2.25	-0.59	-0.393	0.182
CG-5	2.33	0.61	5.43	-0.39	-0.167	0.112

polymers were higher than those of the graft copolymers and CR. Table II summarizes the results.

Monomer Reactivity Ratios

To determine monomer reactivity ratios, all radical copolymerizations of CP and EMA or GMA were carried out in the presence of AIBN as an initiator in benzene at 50°C, and their conversions were adjusted to be less than 10%. The monomer ratios in feed, $[EMA]/[CP]$ or $[GMA]/[CP]$, were varied from 0.43 to 2.33.

The compositions of poly(CP-co-EMA) and poly(CP-co-GMA) were determined by using $^1\text{H-NMR}$ spectroscopy (Bruker 300 CW). Figure 5 shows $^1\text{H-NMR}$ spectra of CR, PEMA, and PGMA. The resonance peaks of the methine and methylene protons of CR appeared at $\delta = 5.1\text{--}5.5$ and $2.0\text{--}2.8$

ppm, respectively. Those of OC_2H_5 , methylene and $-\text{CH}_3$ protons of PEMA were appeared at $\delta = 3.8\text{--}4.2$, $2.0\text{--}2.8$, and $0.8\text{--}1.3$ ppm, and those of $-\text{OCH}_2-$, $-\text{CH}-\text{O}-$, $-\text{O}-\text{CH}_2$, methylene and $-\text{CH}_3$ protons of PGMA were appeared at $\delta = 3.5\text{--}4.2$, $3.2\text{--}3.4$, $2.6\text{--}2.9$, $1.8\text{--}2.4$, and $0.8\text{--}1.4$, respectively. The $-\text{CH}_3$ protons appeared in PEMA and PGMA were used to determine the copolymer compositions.

From the integrated areas at the resonance peaks due to $-\text{CH}_3$ protons in CR/PEMA and CR/PGMA mixtures having various compositions, calibration curves were obtained to determine compositions of poly(CP-co-EMA) and poly(CP-co-GMA). The mole fractions of CP and EMA or GMA, thus obtained, are tabulated in Tables III and IV. From the data, the Fineman-Ross plots in copo-

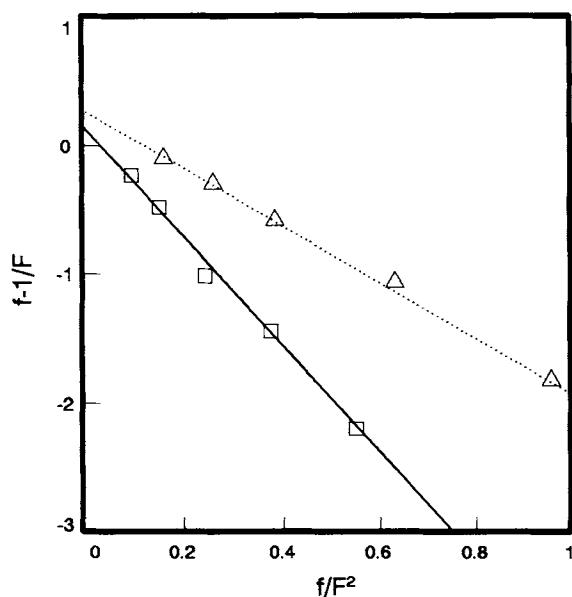


Figure 6 Fineman-Ross plots for the copolymerizations of chloroprene and alkylmethacrylate at 50°C: (Δ) poly(CP-co-EMA); (\square) poly(CP-co-GMA).

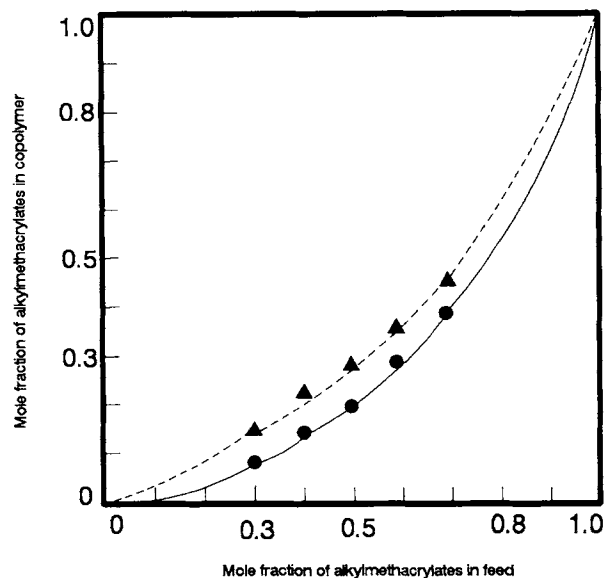


Figure 7 Mole fractions of alkylmethacrylates in copolymer and in feed for the copolymerizations of alkylmethacrylates with chloroprene: (\blacktriangle) poly(CP-co-EMA); (\bullet) poly(CP-co-GMA).

Table V Copolymerization Parameters

M_1	M_2	r_1	r_2	r_1/r_2	Q_2	e_2
ST	CP	—	—	0.93	9.08	0.14
CP	EMA	2.14	0.18	0.39	1.70	-0.64
CP	GMA	4.02	0.12	0.48	1.95	-0.71

ST, styrene; $Q = 1.00$; $e = 0.8$; CP, 2-chloro-1,3-butadiene; $Q_1 = 9.08$; $e_1 = 0.14$.

lymerization of CP (M_1) and EMA (M_2) or CP (M_1) and GMA (M_2) could be drawn, as shown in Figure 6. The monomer reactivity ratios are determined as $r_1(\text{CP}) = 2.14$ and $r_2(\text{EMA}) = 0.18$ in the copolymerization of CP and EMA, and $r_1(\text{CP}) = 4.02$ and $r_2(\text{GMA}) = 0.12$ in the copolymerization of CP and GMA, respectively.

The relative monomer reactivity ratio for GMA in the copolymerization with CP was smaller than that for EMA. This result may be due to the steric hindrance of bulkier GMA than EMA. Figure 7 shows the relationship of the mole fraction in copolymers and the mole fraction in feeds. This result means that the conversions of GMA are relatively less than that of EMA because of the lower reactivity of GMA than that of EMA with CR.

By definition, the Q - e scheme is based on the copolymerization of styrene ($Q = 1.0$, $e = -0.8$) with chloroprene ($Q = 9.08$, $e = 0.14$).⁹ The Q - e values of EMA and GMA for the copolymerization of CR and alkylmethacrylates, EMA and GMA, are listed in Table V. GMA's $|e|$ value is larger than that for EMA, reflecting the electron withdrawing inductive effect of the epoxy group, and thus the Q value of the resonance parameter for GMA is larger than that for EMA.

CONCLUSION

In this work, the copolymers of chloroprene with two different alkylmethacrylates, EMA and GMA,

or poly(CP-co-EMA) and poly(CP-co-GMA), were prepared by radical solution copolymerization and characterized by FT-IR and ¹H-NMR spectroscopies and T_g behaviors. For comparison, the graft copolymers of EMA or GMA onto CR were also prepared. The monomer reactivity ratios were given as $r_1(\text{CP}) = 2.14$ and $r_2(\text{EMA}) = 0.18$ or $r_1(\text{CP}) = 4.02$ and $r_2(\text{GMA}) = 0.12$ in the copolymerizations of CP and EMA and CP and GMA, respectively. The copolymers, poly(CP-co-EMA) and poly(CP-co-GMA), were amorphous with glass transition temperatures of -34.5 and -16.4°C , whereas the graft copolymers have T_g of -42.3 and -29.7°C , respectively.

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