클로로프렌과 글리시딜메타크릴레이트 공중합체의 합성 및 물성

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Synthesis and Properties of Poly(chloroprene-co-glycidylmethacrylate)

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요 약: 벤젠을 용매로 하여 클로로프렌(CP)과 글리시딜메타크릴레이트(GMA) 공중합체를 라디칼 용액중합으로 합성하였다. 합성된 공중합체는 FT-IR과 ¹H-NMR spectrophotometers 및 DSC(differential scanning calorimetry)를 이용하여 특성결정을 하였다. DSC 분석결과 이 공중합체는 무정형이었고, 유리전이 온도는 −16.4℃이었다. 공중합체의 단량체 상대반응성비는 r_1(CP)은 3.85이었고, r_2(GMA)는 0.19이었다. 얻어진 공중합체의 열적 안정성과 내광성을 각각 열중량분석법(thermogravimetry)과 Fade-o-meter를 이용하여 특성을 결정하였다. 얻어진 공중합체의 열적 안정성은 폴리클로로프렌(CR)에 비해 약간 감소하였으나, 자외선이나 열에 노출시켰을 때 CR에 비해 상당히 양호한 내광성을 나타내었다.

Abstract: A copolymer of chloroprene(CP) and glycidylmethacrylate(GMA)(poly(CP-co-GMA)) was prepared by radical solution copolymerization in benzene. The copolymer was characterized by FT-IR and ¹H-NMR spectrophotometers, and differential scanning calorimetry(DSC). DSC analysis showed that the copolymer was amorphous and had glass transition temperature of about −16.4℃. The monomer reactivity ratios were given as r_1(CP) = 3.85 and r_2(GMA) = 0.19 in the copolymerization of CP and GMA. Thermal stability and the light resistance of the copolymer were measured using a thermogravimetric analyzer(TGA) and Fade-o-meter, respectively. It was found that the copolymer showed slightly lower thermal stability than that of polychloroprene(CR), while the copolymer showed fairly better light resistance under the environmental conditions both exposed to U. V. light and heat.

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INTRODUCTION

Polychloroprene(CR) is one of important synthetic rubbers and as such its chemical structures and physical properties have been investigated extensively.[1~6] However, its poor heat resistance and weatherability limit the outdoor use of the material and its blends. To improve the poor performances, copolymers and graft copolymers of chloroprene and a second monomer have been prepared.[7~12] In our earlier reports, we synthesized and characterized copolymers of chloroprene(CP) and maleic anhydride(MAH), ethylmethacrylate (EMA), or isobutylmethacrylate(iBMA).[13~15]

In this work, we obtained a copolymer of chloroprene and glycidylmethacrylate. The copolymer was characterized with IR and ^{1}H-NMR spectroscopies. To determine monomer reactivity ratios, radical solution copolymerizations of CP and GMA were carried out in the presence of AIBN as an initiator in benzene at 50℃, and their conversions were adjusted to be less than 10%. The glass transition temperature and the average molecular weight of the poly(chloroprene-co-glycidylmethacrylate) were measured by differential scanning calorimetry(DSC) and gel permeation chromatography, respectively.

Thermal stability and the light resistance of the copolymer were investigated using a thermogravimetric analyzer(TGA) and a fade-o-meter, respectively.

EXPERIMENTAL

Materials. Glycidylmethacrylate(Aldrich) and benzene(Aldrich) were purified by the standard methods. 2,2'-Azobisisobutyronitrile(AIBN) was purified by recrystallization in dehydrated ethanol. 3,4-Dichloro-1-butene(DCB)(Aldrich), tetrahydrofurfuryl alcohol(THFA)(Aldrich) and sodium hydroxide(NaOH)(Junsei) were used as received without further purifications.

Synthesis of Polychloroprene and Polyglycidylmethacrylate. Chloroprene(CP) was prepared by reacting DCB in aqueous solution of sodium hydroxide in the presence of THFA at 60℃ by the same method described as in our previous work.[13]

The polychloroprene(CR) and polyglycidylmethacrylate(PGMA) were obtained in a glass ampoule by polymerizing 0.2 mole of CP or GMA with 0.2 mole% of AIBN as an initiator at 50℃ in 100 ml of benzene for 10 hours.

After reaction, the reaction mixture was poured into a large amount of methanol. The product of CR or PGMA recovered from methanol was dried under vacuum at 30℃ to remove all volatiles.

Synthesis of Poly(chloroprene-co-glycidylmethacrylate)(poly(CP-co-GMA)). The copolymer of chloroprene and glycidylmethacrylate was obtained by the same method as described for CR. For the determination of monomer reactivity ratios, a series of polymerizations in which the feed ratio was varied for CP(M_1) to GMA(M_2) in benzene (ranged from 0.43 to 2.33) yielded copolymers ; 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 mole of chloroprene and 0.20 mole of GMA were polymerized with 0.2 mole% AIBN as an initiator at 50℃ in benzene.

Measurements

Molecular weight : The molecular weights of polymers were measured by gel permeation chromatography(GPC ; Water 244) using PS standards. THF was used as an effluent.

Glass transition temperature : The glass transition temperature(T_g) was measured using a differential scanning calorimetry(DSC ; DuPont 2100). The thermograms of polymers were obtained at a heating rate of 10℃/min. The T_g value was taken as the initial onset of the change of slope in the DSC curve on the second run.

Thermogravimetric analysis : Thermal stabilities of polymers were examined with a Shimadzu-DT 30A TGA instrument as a scanning rate of 15℃/min in air.

Light resistance : The light resistances of polymers were determined using Fade-o-Meter(Atlas)

(at 60℃ and 65% R. H.) and color difference meter(ND-101 DP). The film specimens were cast from THF solution(ca. 3 wt.%) on a nonyellowing urethane-coated hiding paper. The films were slowly dried at room temperature and then kept under vacuum until they reached constant weight. The cross-sectional area of the films was 3×5 cm^2 and the thickness was 35 μm. The color difference (ΔE) of the samples after exposing to U. V. was calculated using the Hunter-Schofield equation.[13] In order to investigate the light resistance of samples exposed to heat, some of the samples had been exposed to heat at 100℃ for 24 hrs in a thermal aging oven before placing into the Fade-o-meter.

RESULTS AND DISCUSSION

Characterization. Poly(chloroprene-co-glycidylmethacrylate)(poly(CP-co-GMA)) was identified by FT-IR spectroscopy(Mattson Galaxy series 60 30). The FT-IR spectrum of poly(CP-co-GMA) was illustrated in Fig. 1. The FT-IR spectrum of poly(CP-co-GMA) exhibited characteristic peaks of stretching vibration of vinyl C-H bond at 3020 and 3100 cm^{-1}. The peaks of epoxy groups for the poly (CP-co-GMA) appeared at 1100~1200 cm^{-1}. The
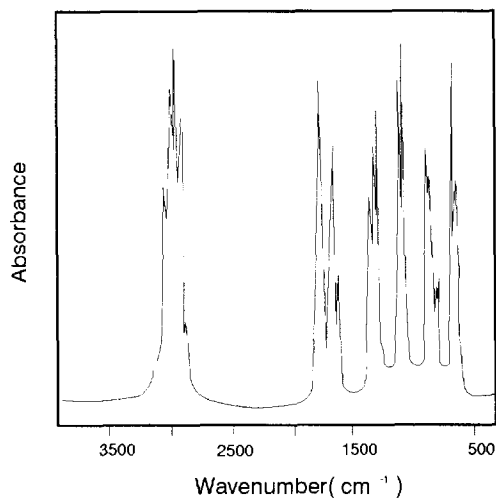
peaks of C-Cl bond, C=O bond and C=C double bond appeared at 600~800, 1750, and 1660 cm^{-1}, respectively.

The molecular weight of poly(CP-co-GMA) was determined as $\overline{M}_n=45,600$, $\overline{M}_w=74,200$. In this case, the copolymer has the composition ratio of 1/1 by weight in feed ratio. This copolymer was used for the investigation of thermal stability and light resistance as well as for the determination of glass transition temperature. The molecular weights of CR and PGMA were summarized in Table 1.

Fig. 2 shows DSC thermograms of CR, PGMA and poly(CP-co-GMA). The T$_g$'s of homopolymers were 63.7℃ and −45.7℃ for PGMA and CR, respectively. The copolymer had T$_g$ of −16.4℃, which was higher by about 36.4℃ than that of CR. The CR exhibited a melting peak around at 52.8℃ but the copolymer did not show any melting peak, meaning that the CR had some degree of crystalli-

Table 1. 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
PGMA	77,000	126,400	1.64
poly(CP-co-GMA)	45,600	74,200	1.63

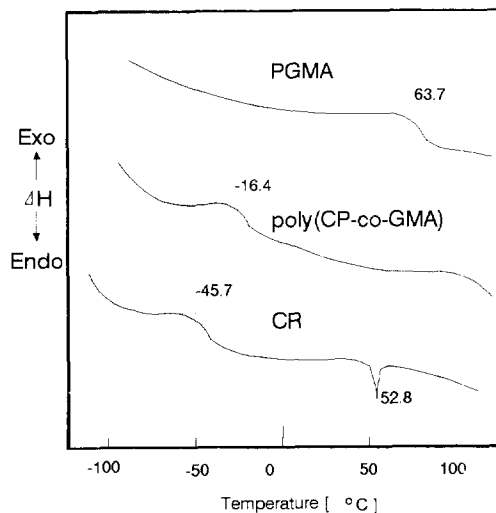**Fig. 1.** FT-IR spectrum of poly(CP-co-GMA).

Fig. 2. DSC thermograms of various samples.

nity whereas the copolymer was amorphous.

Monomer Reactivity Ratios. To determine monomer reactivity ratios, all radical copolymerization of CP and 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, [GMA]/[CP], were varied from 0.43 to 2.33.

The compositions of poly(CP-co-GMA) were determined by using ^{1}H-NMR spectroscopy(Bruker 300 CW). Fig. 3 shows ^{1}H-NMR spectra of CR and PGMA. The resonance peaks of the methine and methylene protons of CR appeared at $\delta = 5.1 \sim$ 5.5 and $2.0 \sim 2.8$ ppm, respectively. It is seen that the CR has 1,4-addition structure. Those of -OCH$_2$-, -CH-O-, -O-CH$_2$, methylene and -CH$_3$ protons of PGMA were appeared at $\delta = 3.5 \sim 4.2$, $3.2 \sim 3.4$, $2.6 \sim 2.9$, $1.8 \sim 2.4$ and $0.8 \sim 1.4$ ppm, respectively.
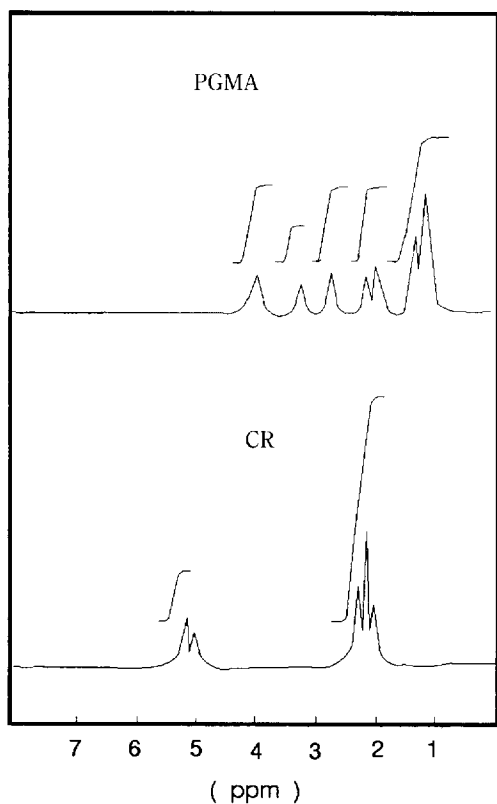
Fig. 4 illustrates a typical ^{1}H-NMR spectrum of poly(CP-co-GMA) having the composition of 50/50 CP/GMA by weight % in feed ratio.

The copolymer compositions were estimated from the integrated area ratios of the resonance peaks due to =CH- of CP and -CH$_3$ protons of GMA for the copolymers having various compositions. The mole fractions of CP and GMA, thus obtained, were tabulated in Table 2. The Finneman-Ross plot in copolymerization of CP(M_1) and GMA (M_2) was shown in Fig. 5. The monomer reactivity ratios were determined as r_1(CP) = 3.85 and r_2 (GMA) = 0.19 in the copolymerization of CP and GMA.

The Q-e values of GMA for the copolymerization of CP and GMA were calculated based on the Q-e scheme of the copolymerization of styrene(Q = 1.
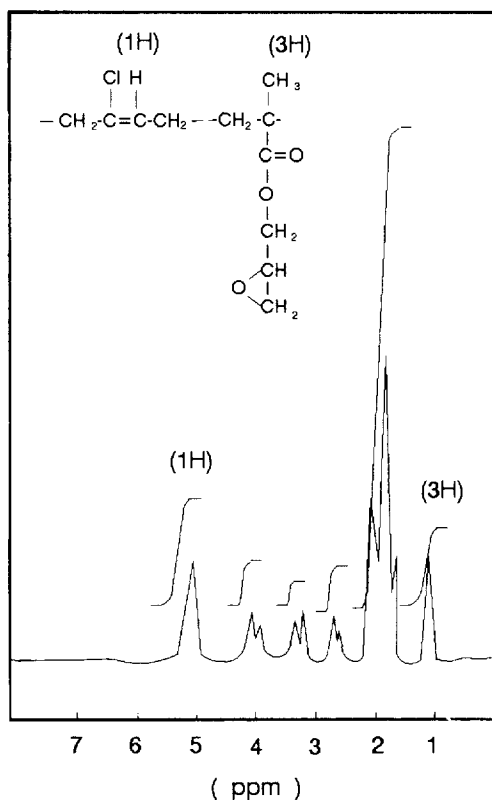
Fig. 3. ^{1}H-NMR spectra of CR and PGMA.(Benzene-D$_6$)

Fig. 4. Typical ^{1}H-NMR spectrum of the poly(CP-co-GMA) having 50/50 CP/GMA composition by weight % in feed ratio.(Benzene-D$_6$)

Table 2. Determination of Monomer Reactivity Ratios for the Copolymerization of CP(M_1) and GMA(M_2)

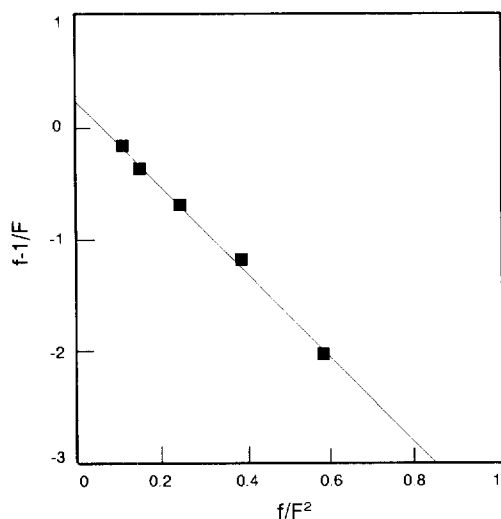| Sample	$F=$ $[M_2]/[M_1]$	$f=$ m_2/m_1	F^2	$f\text{-}1$	$(f\text{-}1)/F$	f/F^2
CG-1	0.43	0.11	0.89	−0.89	−2.070	0.590
CG-2	0.67	0.17	0.45	−0.83	−1.239	0.378
CG-3	1.00	0.24	1.00	−0.76	−0.760	0.240
CG-4	1.50	0.37	2.25	−0.63	−0.420	0.164
CG-5	2.33	0.56	5.43	−0.44	−0.189	0.103

Fig. 5. Finneman-Ross plot for the copolymerization of chloroprene($r_1=3.85$) and glycidylmethacrylate($r_2=0.19$) at 50℃.

Table 3. Copolymerization Parameters

M_1	M_2	r_1	r_2	$r_1 \cdot r_2$	Q_2	e_2
ST	CP	−	−	0.93	9.08	0.14
CP	GMA	3.85	0.19	0.73	1.68	−0.24

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

0, e=−0.8) with chloroprene(Q=9.08, e=0.14),[17] and listed in Table 3.

Properties

Thermal stability : Fig. 6 shows TGA curves of CR, poly(CP-co-GMA) and PGMA. It is observed that the thermal stability of polymers decreases in the order CR>poly(CP-co-GMA)>PGMA. As shown in Fig. 6, the residual weight at 400℃ of the
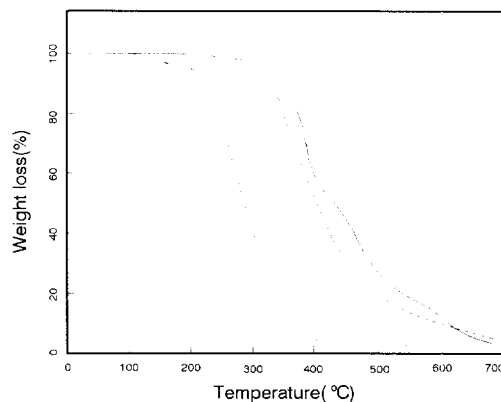

Fig. 6. TGA curves of PGMA, poly(CP-co-GMA) and CR. Heating, 15℃/min in air, —— : CR, − ·· − : poly (CP-co-GMA), ---- : PGMA.

copolymer is 57%, whereas those of CR and PGMA are 63% and 3%, respectively. It should be noted that the copolymer shows relatively good thermal stability comparable to that of CR, even though the CR shows slightly better thermal stability than the copolymer.

Of interesting is, however, the fact that thermal degradation of the copolymer follows simple inverse-sigmoidal kinetics unlike CR, whereas two-stage degradation kinetics arround 400~500℃ was observed for CR due to dehydrochlorination.

Light Resistance : The weathering of polymers is very important regarding their long-term properties. Several primary causes of deterioration of polymers include sunlight, temperature, moisture and pollutants.[18] There are several experimental techniques to test weather resistivity of materials. We applied the accelerated weathering test to compare the light resistance of materials, *viz.* Fade-o-Meter.

The light resistance of samples was semi-quantitatively expressed in term of color difference (ΔE) with National Beaureau of Standards Units. The color difference theories imply that the smaller ΔE means better light resistance.[18~22] The samples were exposed in the Fade-o-Meter for measurements of light resistance for 30 through 180 minutes.

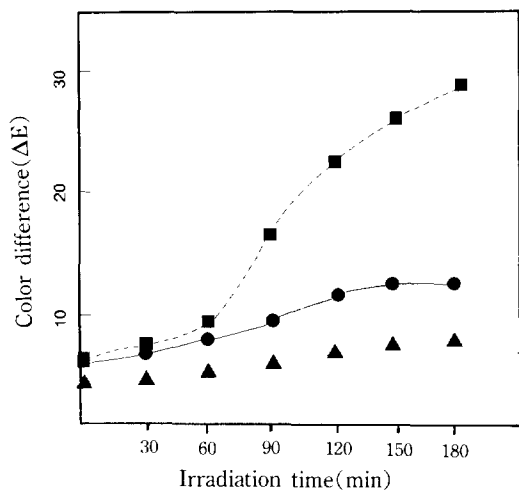Fig. 7 shows light resistances of CR, PGMA and

Fig. 7. Color difference change against irradiation time for three different samples without heat pretreatment, —■— : CR, —●— : poly(CP-co-GMA), —▲— : PGMA.
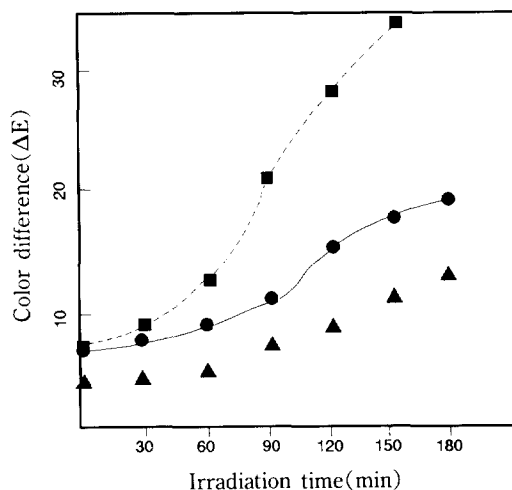

Fig. 8. Color difference change against irradiation time for three different samples after exposure to heat(100℃) in thermal aging oven for 24 hrs., —■— : CR, —●— : poly(CP-co-GMA), —▲— : PGMA.

poly(CP-co-GMA) after exposure to U. V. light. The light resistance of the copolymer was much improved compared to that of CR due to the introduction of glycidylmethacrylate, while CR possessed inherently yellowing property in outdoor uses because of its allylic chlorine content. ΔE is almost constant as a function of time up to 180 minutes for PGMA. This fact implies that the copolymer might be stabilized to U. V. light because allylic chlorine content is decreased due to the presence of glycidylmethacrylate in the polymer chain.

The light resistance of CR, PGMA and poly(CP-co-GMA) after exposure to heat(100℃) is illustrated in Fig. 8. The light resistance of copolymer under the thermal aging condition was superior to that of CR due to the stabilizing role of glycidymethacrylate to heat as well as U. V. light. Careful examination of the two figures reveals that the yellowing property of CR is more severe for the samples exposed to heat than non heat-treated ones whereas the copolymer shows considerable anti-yellowing property under even severe environmental condition.

CONCLUSIONS

In this work, the copolymer of chloroprene(CP) and glycidylmethacrylate(GMA) was synthesized and characterized. The basic properties such as thermal stability and light resistance were discussed.

1. The monomer reactivity ratios were given as $r_1(CP) = 3.85$ and $r_2(GMA) = 0.19$ in the copolymerization of CP and GMA.

2. The copolymer, poly(CP-co-GMA) was amorphous and has glass transition temperature of $-16.4℃$.

3. The thermal stability of poly(CP-co-GMA) was comparable to that of CR.

4. Poly(CP-co-GMA) showed fairly better light resistance with exposed both to U. V. light and heat at 100℃.

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