

Characterization of Chloroprene and Maleic Anhydride Copolymer by ^{13}C -NMR Spectroscopy and Pyrolysis GC/MS

WON-JEI CHO,* CHI-HOON CHOI, and CHANG-SIK HA

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

SYNOPSIS

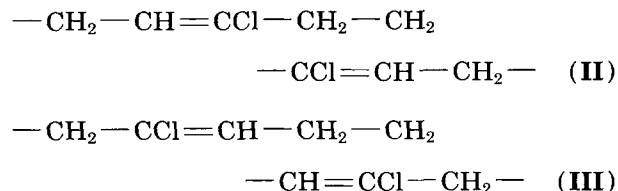
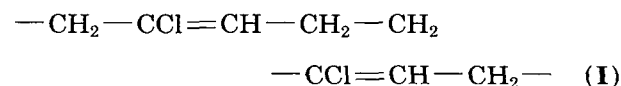
The radical copolymerizations of chloroprene (CP) and maleic anhydride (MAH) were carried out with AIBN in 1,4-dioxane at 60°C. The monomer reactivity ratios were estimated as $r_1(\text{CP}) = 0.38$ and $r_2(\text{MAH}) = 0.07$. Microstructures in the copolymer of chloroprene (CP) and maleic anhydride (MAH) were investigated by 75.4 MHz ^{13}C - and 300 MHz ^1H -NMR spectroscopies. Resonances were assigned to the monomer sequence dyads CC, CM, and MC (C = chloroprene, M = maleic anhydride). Well resolved fine structure in the ^{13}C -NMR spectra showed that 1,2- and 3,4-structural chloroprene units were negligible in the copolymer. The pyrolysis characterization of the copolymer was also investigated by the pyrolysis gas chromatography mass spectrometry (GC/MS). The fragments of CP and MAH monomers and CP-MAH hybrid dimer, CO, and CO_2 were identified after pyrolysis of the copolymer. © 1994 John Wiley & Sons, Inc.

Keywords: poly(chloroprene-co-maleic anhydride) • characterization • monomer reactivity ratios • microstructure • monomer sequence dyads • ^{13}C -NMR spectroscopy • pyrolysis GC/MS

INTRODUCTION

^1H -NMR and ^{13}C -NMR spectra have found increased use in the characterization of polymers.^{1,2} Especially, Brame and Kahn^{3,4} stressed that ^{13}C -NMR analysis could provide detailed information on the microstructure of chloroprene homopolymers and copolymers.

The microstructure of polychloroprene (CR) has received considerable attention.⁵⁻¹³ It has been recognized that CR possesses conformations such as *cis*-1,4, *trans*-1,4, 1,2-, and 3,4-structural chloroprene units and for each conformation, head-to-tail addition (I), head-to-head addition (II), and tail-to-tail addition (III) are possible.^{5,6} It was reported that among those structures formed from chloroprene monomer, *trans*-1,4 conformation is most frequently found in CR.



Although a few articles have reported on the microstructures of copolymers containing chloroprene,¹³⁻¹⁸ no article is published on the microstructure of the copolymer of chloroprene and maleic anhydride in open literature.

In this work, chloroprene monomer (CP) was synthesized from 3,4-dichlorobutene and copolymerization was carried out from the monomer and maleic anhydride (MAH) with AIBN as the initiator at 60°C in 1,4-dioxane. The reactivity ratios, r_1 and r_2 , in the copolymerization of CR and MAH were determined by the Kelen-Tüdös method. Microstructure of the copolymer was determined at the dyad level by using 300 MHz ^1H -NMR and 75.4 MHz ^{13}C -NMR spectroscopies. The pyrolysis behavior of the copolymer was also examined by the pyrolysis gas chromatography mass spectrometry (GC/MS) from the degradation fragments.

* To whom all correspondence should be addressed.

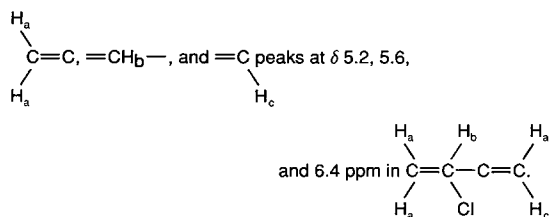
EXPERIMENTAL

Materials

Maleic anhydride, 1,4-dioxane, and toluene (Junsei) were used after being purified by the standard methods. 2-2'-Azobisisobutyronitrile (AIBN) was used after recrystallization in dehydrated ethanol. 3,4-Dichloro-1-butene and tetrahydrofurfuryl alcohol (Aldrich) were used as received without further purification.

Chloroprene

Chloroprene monomer (CP) was prepared by reacting 3,4-dichloro-1-butene and an aqueous solution of sodium hydroxide in the presence of tetrahydrofurfuryl alcohol and hydroquinone at 55°C. The product was distilled in argon gas under reduced pressure (25°C/160 mmHg). The purity of CP was confirmed to be 99.8% by gas chromatography (Varian 3300) and the identification of CP was accomplished by infrared (Perkin-Elmer 1330) and ¹H-NMR (Bruker 300CW) spectroscopies (analysis; IR (KBr, cm⁻¹); 3020 (stretching vibration of vinyl C—H bond), 1650 (C=C double bond), 600 and 670 (C—Cl bond); ¹H-NMR (Bruker 300CW) (CCl₄):



CP was used as soon as possible after distillation because it was polymerized slowly during storage, even at low temperature.

Copolymerization

Polymerization was proceeded in a glass ampoule. 1,4-Dioxane was used as a diluent for copolymerization. In a typical experiment, CP (22.125 g, 0.25 mol) and maleic anhydride (MAH) (24.5125 g, 0.25 mol) were radically polymerized with an initiator, AIBN (0.2053 g, 1.25×10^{-3} mol) at $60 \pm 0.1^\circ\text{C}$ in 1,4-dioxane (100 mL). After 50 min, the reaction mixture was poured into a large amount of toluene. The copolymer, recovered from toluene, was under vacuum at ambient temperature to remove all volatiles. For reactivity tests, four different mol ratios in feed were used; the monomer mol ratios in feed $[\text{MAH}](M_2)/[\text{CP}](M_1)$ ranged from 0.42–1.50. Conversion was adjusted below 10%.

Polychloroprene (CR) was also prepared by the same method as described for the copolymerization.

Characterization

Polychloroprene and the copolymer [poly(CP-co-MAH)] of CP with MAH were characterized by infrared spectroscopy (Perkin-Elmer 1330). Copolymer analysis was made by ¹H-NMR (Bruker 300CW) and ¹³C-NMR (JEOL JNM-FX60) spectrophotometers. Intrinsic viscosities of polymers were measured in acetone with a Cannon-Fenske viscometer (#50) at $25 \pm 0.01^\circ\text{C}$. The structure of the copolymer was identified by IR spectrophotometer. IR (KBr, cm⁻¹); 3020 (stretching vibration of =C—H bond), 1855 and 1775 (C=O group of anhydride), and 1660 (C=C double bond). The copolymer was soluble in acetone, methyl ethyl ketone, and tetrahydrofuran, but insoluble in carbon tetrachloride and ethyl acetate. The composition and the intrinsic viscosity of the copolymers are listed in Table I. The copolymer having a 1 : 1 mol ratio in feed was used for the microstructure analyses throughout this article.

Table I. Compositions, Intrinsic Viscosities, and Glass Transition Temperatures of Poly(CP-co-MAH)s^a

Samples	Mol Ratio in Feed [MAH] (M_2)/[CP] (M_1)	Mole Ratio in Copolymer [MAH] (m_2)/[CP] (m_1)	$[\eta]$ (dL/g)	T_g ($^\circ\text{C}$)
CR	—	—	0.81	−43
CM-1	1.50	1.50	0.52	3
CM-2	1.00	1.28	0.51	7
CM-3	0.67	1.14	0.57	11
CM-4	0.42	1.10	0.46	13

^a Obtained from the copolymerizations of CP and MAH using 0.25 mol % of AIBN in 1,4-dioxane at 60°C for 2 h.

Thermal properties of polymers were measured by using a thermogravimetric analyzer (TGA; DuPont 9900) and differential scanning calorimetry (DSC; Perkin-Elmer DSC7). Thermal analyses were performed under nitrogen gas at a heating rate of 10°C/min. The copolymer has glass transition temperatures of 3–13°C, which is higher by 46–56°C than that of CR. The glass transition temperatures of the copolymers increased as the composition of maleic anhydride increased (see also Table I).

Pyrolysis gas chromatography mass spectrometry (GC/MS). The gas chromatography (GC; Varian 3300) was coupled to a Varian MAT 112-S mass spectrometer (MS). A pyroprobe (Chemical Data System, Inc. Model 120) and hydrogen generator (Canberre Ind. Inc.; Model 7526) were used to obtain the GC/MS data.

RESULTS AND DISCUSSION

Monomer Reactivity

Reactivity ratios of monomers in the copolymerization of CP and MAH were determined by using the Kelen-Tüdös method. The 300 MHz ^1H -NMR spectrophotometer was utilized in the quantitative analysis of poly(CP-co-MAH) prepared from four different mol ratios of MAH to CP in feed (from 0.42–1.50). The copolymer composition was assayed from peak areas of the methylene protons in the CP unit and the methine protons in the MAH units.

A typical ^1H -NMR spectrum of copolymer of CP and MAH (Sample CM-3) is shown in Figure 1. The peak at δ 5.69 was used to measure the content of CP, which was attributed to the $-\text{CH}=\text{}$ group in CP. The total amount of both components in the copolymer was measured using the lines appearing over the range of δ 2.0 to 3.5 ppm, attributed to the different kinds of CH_2 and $\text{C}-\text{H}$ groups present in the copolymer. The two sets of lines used in the measurement are well separated from each other. Then, the copolymer composition was obtained by the following relationships from the area measurements of these two sets of lines, which were basically similar as those described for the copolymer of 2-chlorobutadiene-1,3 and 2,3-dichlorobutadiene-1,3 by Brame and Khan:¹³

$$kI_1 = [\text{CP}]$$

$$kI_2 = 4[\text{CP}] + 2[\text{MAH}]$$

where k is a proportionality constant, I_1 is the integrated intensity of the line at δ 5.69, and I_2 is the

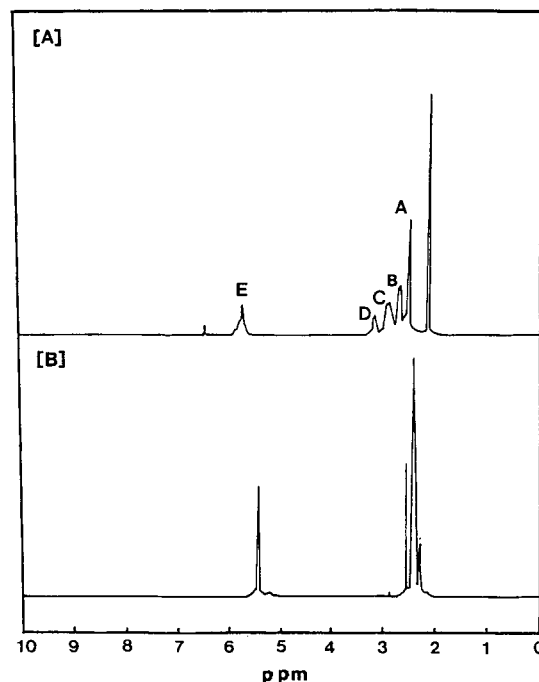


Figure 1. ^1H -NMR spectra of (A) poly(CP-co-MAH) prepared with AIBN in 1,4-dioxane and (B) CR (in THF-d_8).

integrated intensity of the lines covering the range from δ 2.0–3.5, and $[\text{CP}]$ and $[\text{MAH}]$ are mol fractions of CP and MAH, respectively. Table II summarizes the results.

In Table II, the parameters for the Kelen-Tüdös calculation are also listed. The reactivity ratios are given as 0.38 for $r_1(\text{CP})$ and 0.07 for $r_2(\text{MAH})$. This data shows that CP and MAH copolymerize in an alternate manner and that MAH has little tendency to homopolymerize under these conditions.

^{13}C -NMR

Considerable complexity in ^{13}C -NMR spectral assignments is introduced from a chemical shift sensitivity to both the comonomer sequence arrangements and possible configurational arrangements for any given sequence. In general, previous literature assignments have been based on comparisons to chemical shifts calculated through reference polymers.

Comparisons of ^{13}C -NMR chemical shifts of the copolymer with the ^{13}C -NMR spectra observed for CR are presented in Figure 2. The assignments to carbon types have been performed in an analogous manner as described in past polymer literature, but we have adopted the same nomenclature for the copolymer as suggested by Kahn and Brame for CR.¹³

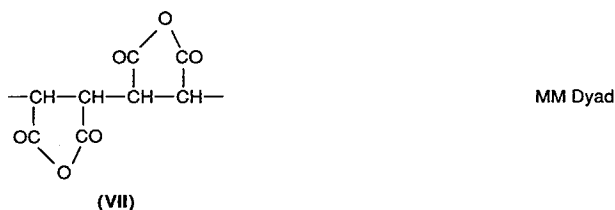
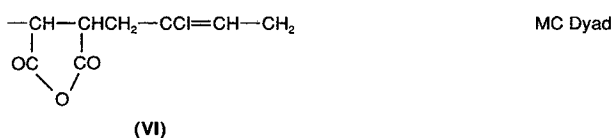
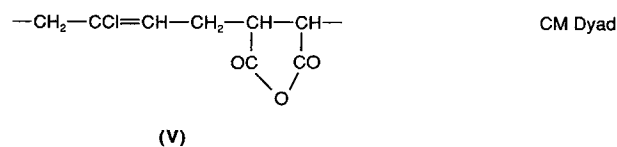
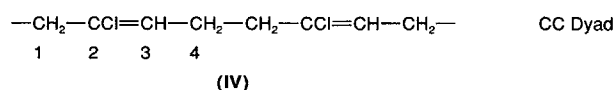
Table II. Determination of Monomer Reactivity Ratios for the Copolymerization of CP (M_1) and MAH (M_2) with AIBN at 60°C [AIBN], 1.25×10^{-3} M, $\alpha = \sqrt{F_{\min} \times F_{\max}} = 1.905^a$

Exp. No.	$X = [M_2]/[M_1]$	$Y = m_2/m_1$	X^2	$Y - 1$	$F = X^2/Y$	$G = \frac{X(Y - 1)}{Y}$	$\alpha + F$	$\eta = G/(\alpha + F)$	$\xi = F/(\alpha + F)$
1	1.50	1.50	2.25	0.50	1.50	0.50	2.28	0.22	0.66
2	1.00	1.28	1.00	0.28	0.78	0.22	1.57	0.14	0.50
3	0.67	1.14	0.45	0.14	0.39	0.08	1.18	0.07	0.33
4	0.42	1.10	0.19	0.00	0.19	0.00	0.97	0.00	0.19

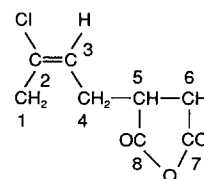
^a Kelen-Tüdös equation. $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$; $r_1(\text{CP}) = 0.38$, $r_2(\text{MAH}) = 0.07$.

The peaks appearing in the high-field region (25–50 ppm) may be confidently assigned to aliphatic carbons, while the chemical shifts of the peaks appearing in the low-field region in the 120–140 ppm range are consistent with those of unsaturated carbons.

The assignments are given in dyad form for the copolymer, since dyad statistics can account for all the lines assigned in this region to CR, and their reactivity values tell that the copolymer has almost ideal alternating structure. Dyad structures were assigned as follows:



The monomer sequences in question are CC, CM, and MC dyads, where C represents a CP unit and M represents a MAH unit. The presence of the MM dyad (VII) is neglected in this assignment, since there is a minimal possibility of MM structure from the monomer reactivity ratio. Carbons of the compounds (V) were numbered as follows:



As shown in Table II and Figure 2, C_1 and C_4 carbons in the CM dyad shifted down-field from the line of the same carbons in the CC dyad (IV) because of the deshielding effect due to $\text{C}=\text{O}$ bonding to the C_5 and C_6 carbons in the case of the CM dyad. In the CC dyad, the shift of the C_1 carbon down-field by the amount of about 5 ppm from the line of

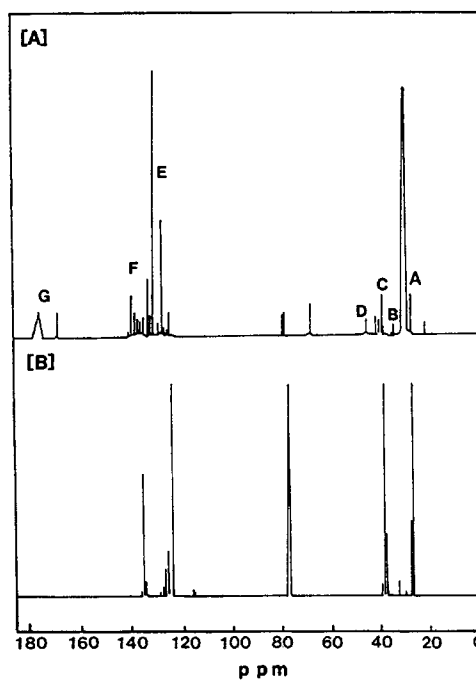


Figure 2. ^{13}C -NMR spectra of (A) poly (CP-co-MAH) prepared with AIBN in 1,4-dioxane and (B) CR (in THF-d_8).

Table III. Summary of ^{13}C -NMR Data for poly(CP-co-MAH)

Absorption	Carbon	Integration	Sequence Type	Observed Chemical Shift (ppm)
A	C_4		CC dyad	27.48
B	C_1		CC dyad	33.69
C	C_1, C_4	2	CM and MC dyads	39.82
D	C_5, C_6	1	CM and MC dyads	45.09
E	C_3	1	CM, MC, and CC dyads	128.92
F	C_2	1	CM, MC, and CC dyads	135.39
G	C_7, C_8	2	CM and MC dyads	174.09

the C_4 carbon, adjacent to the $-\text{CCl}=\text{}$ group in the polymer, can be explained by the "gamma" effect of chlorine. The peaks around 135 ppm, assigned to C_2 carbon, indicate the influence of $-\text{Cl}$ atom. Several peaks around 129 ppm, assigned to the C_3 carbon, exhibit the effect of a neighboring sequence type. The peaks appearing at 174 ppm are due to C_7 and C_8 carbons. The chemical shifts of the peak are consistent with those of carbons in poly(styrene-co-maleic anhydride).^{19,20}

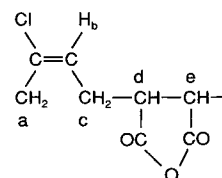
A summary of frequencies and assignments for the major lines is given in Table III. The 1,2 and 3,4-additions in polychloroprene were not detected.

The interpretation was also made by comparison with the detailed results of Khan and Brame⁴ on the copolymers of CP and methylmethacrylate (MMA), in which various kinds of CP sequences were determined from the analysis of ^{13}C -NMR spectra of different copolymers prepared using different concentrations of Lewis acids. They determined all six possible triads of monomeric units as individual peaks in the methylene region first by ^1H -NMR and then by ^{13}C -NMR studies of the copolymer.

^1H -NMR

The microstructure of the copolymer was also established by ^1H -NMR spectroscopy (Fig. 1) and Table IV summarizes the results. Characteristic

peaks were observed at $\delta = 2\text{--}3.5$ ppm and $\delta = 5.7$ ppm in the spectra of the copolymer. The down-field peak was ascribed to the olefinic proton vicinal to the chlorine in CP, whereas peaks around 2–3.5 ppm were assigned other protons. For convenience, protons of the compounds were assigned as follows:



The H_a proton within the CC dyad was observed at 2.44 ppm like that in CR, whereas the protons within CM or MC dyads were shifted down-field from the line of the CH_2 carbon because of the presence of $\text{C}=\text{O}$ group. The H_a proton was shifted more down-field than the H_c proton because of the deshielding effect of chlorine within the $-\text{CCl}=\text{}$ group. In the case of H_d and H_e protons, a single peak at 3.1 ppm was reported due to the stronger effect of substituted $\text{C}=\text{O}$ rather than to the effect of sequence type.²¹ The results of ^{13}C -NMR spectra could be supported by comparing those with the ^1H -NMR signals of the copolymer.

Thermogravimetry

Thermogravimetry curves obtained at $10^\circ\text{C}/\text{min}$ (under N_2 atmosphere) for CR and poly(CP-co-

Table IV. Summary of ^1H -NMR Data for poly(CP-co-MAH)

Absorption	Hydrogen	Integration	Sequence Type	Observed Chemical Shift (ppm)
A	H_a	4	CC dyad	2.44
B	H_c	2	CM and MC dyads	2.63
C	H_a	2	CM and MC dyads	2.81
D	H_d, H_e	2	CM and MC dyads	3.07
E	H_b	1	CM, MC, and CC dyads	5.69

MAH) are shown in Figure 3. Two stages of reaction can be distinguished in the breakdown of the copolymer. The decomposition temperatures and the weight residue % of CR and poly(CP-co-MAH)s having different mol ratios are summarized in Table V. The first stage at 150°C is ascribed to the decomposition of CO or CO₂ gas from maleic anhydride, whereas the second stage at 360°C is due to the dehydrochlorination reaction.²²

The traditional radical chain model for the mechanism of vinyl polymer degradation involves three types of processes: (1) initiation reactions by which radicals are formed, (2) chain propagation reactions that produce scission of the polymer backbone, and (3) termination reactions that remove chain-propagating radicals from the system.

Initiation may result from labile linkages already existing in the polymer. If such initiation is followed by a depropagation (unzipping) to low molecular weight fragments, then the rate of volatilization will decrease continuously as the reaction proceeds. On the other hand, if the chain breaks come about more or less randomly, either because of random initiation or more commonly because of β -scission of radicals formed on the polymer backbone by hydrogen ab-

straction (transfer), most early fragments will be too large to volatilize, but the rate will increase with conversion as greater numbers of smaller fragments lose weight. If new labile linkages, such as unsaturated end groups, are formed from transfer and disproportionation reactions, the rate of initiation will increase. Thus, in only a few cases of polymer degradation, such as of poly(tetrafluoroethylene) (PTFE), the weight-loss kinetics conform reasonably close to the simple n th order kinetic models. The kinetics of degradation by TG are beyond the scope of this article and not described here. It is thought from the TG curves, however, that the degradation fragments can give some information about the microstructure of the copolymer, thus the pyrolysis/GC mass spectroscopic studies have been made for the degradation fragments.

Pyrolysis GC/MS

An investigation into the nature of the fragment species in the copolymer after pyrolysis was also made using the pyrolysis GC/MS (PGC) technique.^{23,24} Pyrolysis GC/MS has made great strides toward being a powerful tool in the structural char-

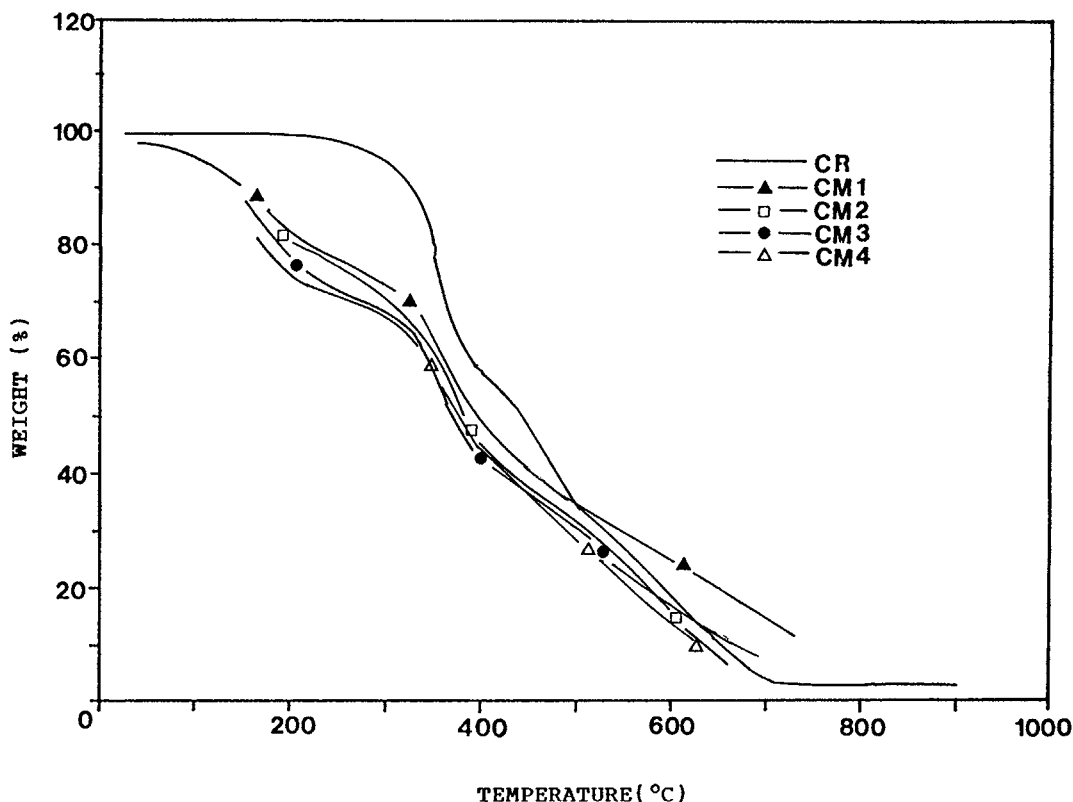


Figure 3. TGA curves of various samples; heating rate, 10°C/min (N₂ atmosphere).

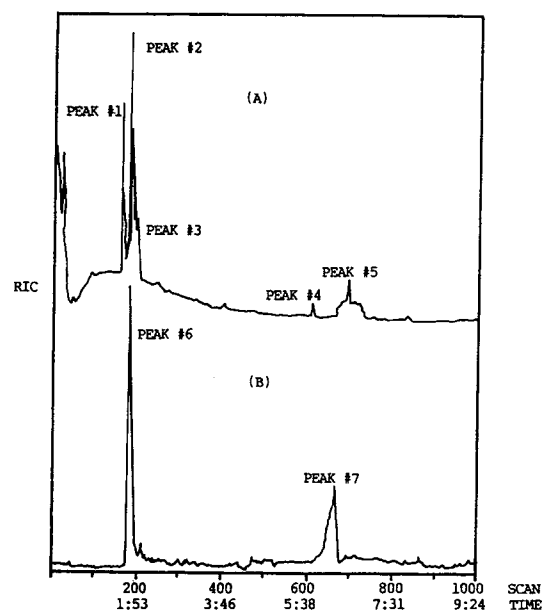
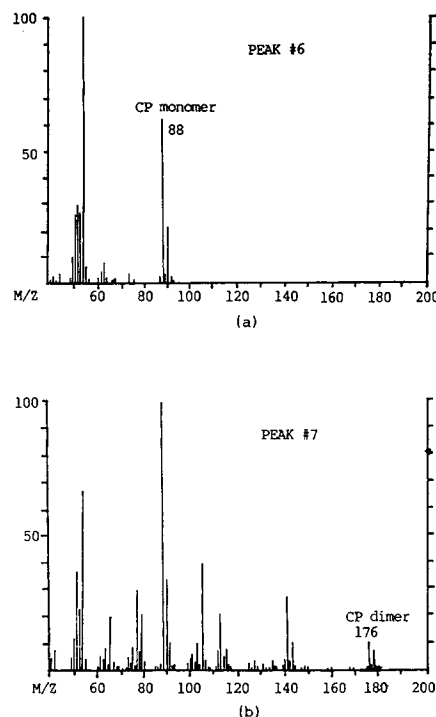
Table V. Decomposition Temperatures and Weight Residues of Various Samples

Sample	Decomposition Temperature (°C)		Weight Residue (%)	
	A Stage ^a	B Stage ^b	A Stage	B Stage
CR	—	360	99	57
CM-1	163	364	82	48
CM-2	149	368	80	44
CM-3	151	359	76	42
CM-4	136	364	74	42

^a Temperature range of A stage: 30–200°C.^b Temperature range of B stage: 200–400°C.

acterization of polymers. The structural information obtained by pyrolysis GC/MS is sometimes unique and complementary to that obtained by conventional spectroscopic methods such as IR and NMR. In this work the pyrolysis GC/MS was applied for complementary characterization of microstructures in poly(CP-co-MAH). Pyrolysis of the sample was performed up to 1000 scans.

Figure 4 shows a typical pyrogram of the copolymer. The identification was carried out primarily by a directly coupled GC-MS system. It can be seen that the pyrogram of the copolymer is different from that of CR. For CR, one can speculate that the two characteristic peaks, denoted as peak 6 and 7, re-

**Figure 4.** Pyrograms from PGC/MS analysis of poly(CP-co-MAH) (A) and CR (B).**Figure 5.** Mass pyrograms for CR: (a) peak #6 and (b) peak #7.

spectively, are assigned to CP monomer and dimer, respectively. The mass spectra of CR, shown in Figure 5, proves the speculation. From the TG curves (Fig. 3) and pyrograms (Fig. 4), one can see that the degradation follows a depolymerization mechanism due to the dehydrochlorination reaction. It was stated above that the copolymer has CM, MC, and CC dyad from ¹³C-NMR analyses. Preliminary evidence indicated that hybrid peaks such as CM, MC dyads were not observed on the pyrogram of CR. However, on the pyrogram of the copolymer we can see various kinds of hybrid peaks, which reflect the existence of junctions of different monomer units.

It may be assumed from the microstructural analyses that a CP monomer, MAH monomer, and CP-MAH hybrid dimer are produced after decomposition from CM and MC dyads, and CP monomer and dimer are produced after decomposition of the CC dyad. Figure 6 shows the mass spectra of poly(CP-co-MAH). It is seen that the anhydride group is removed from maleic anhydride in the form of CO and CO₂ (peak 1). The decomposition of CP dimer occurred in peak 4 as in the case of CR. These results clearly show that there exists a CC dyad in the copolymer. The peak 5 is assigned to the MAH monomer. There exists no MAH dimer. Table VI

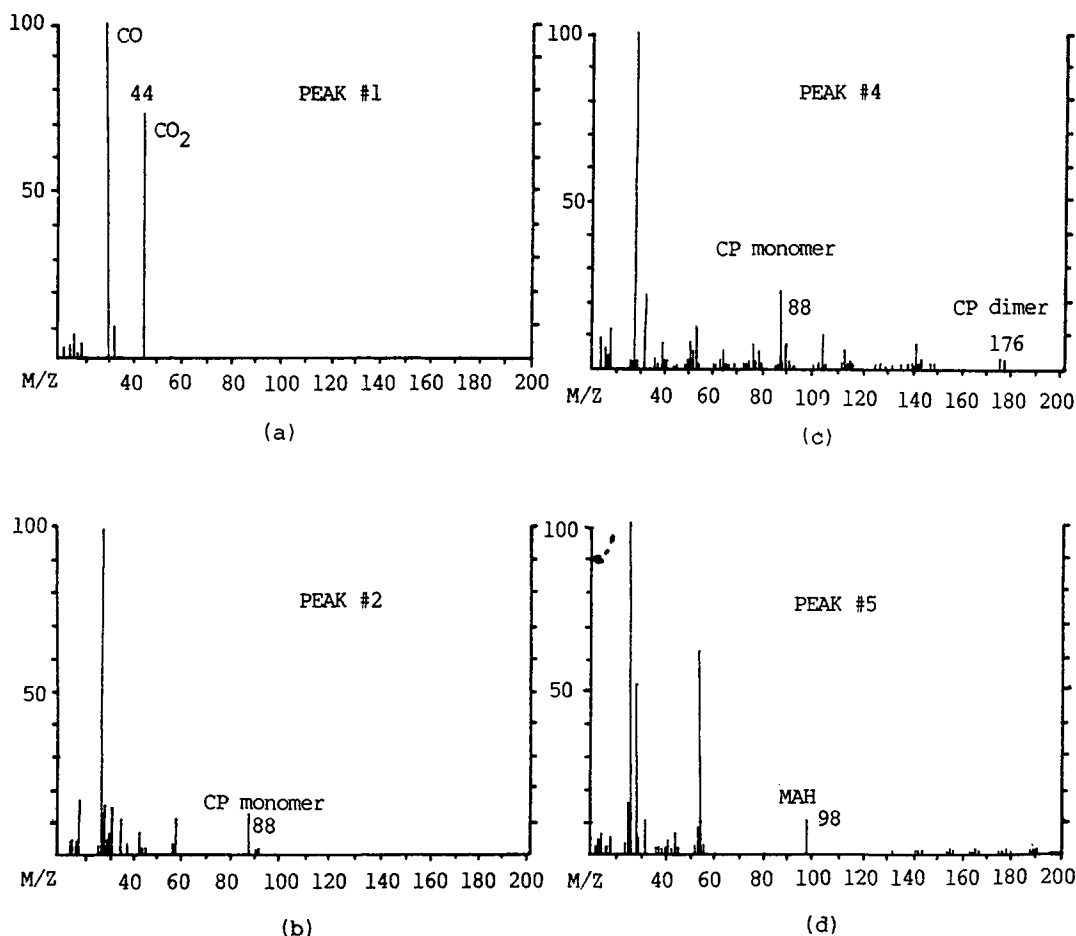


Figure 6. Mass pyrograms for poly(CP-co-MAH): (a) peak #1, (b) peak #2, (c) peak #4, and (d) peak #5.

summarizes the observed results from the pyrograms of the poly(CP-co-MAH).

CONCLUSIONS

The radical copolymerizations of chloroprene (CP) and maleic anhydride (MAH) were carried out with

AIBN in 1,4-dioxane at 60°C. The monomer reactivity ratios were estimated as $r_1(\text{CP}) = 0.38$ and $r_2(\text{MAH}) = 0.07$ using the Kelen-Tüdös method. Microstructures in the copolymer of chloroprene (CP) and maleic anhydride (MAH) were investigated by 75.4 MHz ^{13}C -, and 300 MHz ^1H -NMR spectroscopy. Resonances were assigned to the monomer sequence dyads CC, CM, and MC (C = chloroprene, M = maleic anhydride) in this study, based on previous assignments in literature on the chemical shifts calculated through reference polymer, polychloroprene. The ^{13}C -NMR data was supported by ^1H -NMR spectral results.

The TG curves implied that the degradation fragments can give some information about the microstructure of the copolymer. Thus, the fragments of the copolymer after pyrolysis were also analyzed by using the pyrolysis gas chromatography mass spectrometry (GC/MS) technique to obtain complementary structural information along with the conventional spectroscopic methods.

Table VI. Pyrolysis Products Obtained from Poly(CP-co-MAH) and CR

Peak No.	Assignment
1	Carbon monoxide, carbon dioxide
2	Carbon monoxide, hydrogen chloride, chloroprene monomer
3	Hydrogen oxide, carbon monoxide
4	Chloroprene dimer
5	Maleic anhydride
6	Chloroprene monomer
7	Chloroprene dimer

Well resolved fine structure in the ^{13}C -NMR spectra showed that 1,2- and 3,4-units were negligible in the copolymer. It was suggested from the microstructural analyses that the copolymer contains CM, MC, and CC dyads. The presence of the MM dyad was neglected in this assignment from the monomer reactivity ratios.

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