

A Study of Sequence Distribution of Chloroprene and Methyl Methacrylate Copolymers by $^1\text{H-NMR}$

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Synopsis

The $^1\text{H-NMR}$ spectra of poly(chloroprene-methyl methacrylate) which was copolymerized with ethylaluminum dichloride (EtAlCl_2) and vanadyl trichloride (VOCl_3) were measured with the radical copolymers. The split signals of the OCH_3 and $\alpha\text{-CH}_3$ protons in the spectra were assigned to triads and pentads with methyl methacrylate as a center, respectively, and the former concentrations were in reasonable agreement with the latter concentrations in triads. Moreover, it was found that the $\alpha\text{-CH}_3$ signal was split into peaks of different tacticity when the mole fractional ratio of methyl methacrylate (MMA) to chloroprene (CP) in the copolymer was approximately 3.0 or greater.

INTRODUCTION

Masaki et al.¹ have investigated the copolymerization of CP with MMA complexed with alkylaluminum halides cocatalyzed by vanadium compounds and compared the configuration of these copolymers with that of the radical copolymers by $^1\text{H-NMR}$ spectroscopy.

Recently, the pentad sequence distribution of CP and MMA radical copolymers was estimated from the signal of the split OCH_3 protons in $^1\text{H-NMR}$ spectra shifted by the use of tris(dipivalomethanato)europium(III).²

In $^1\text{H-NMR}$ spectra of the radical copolymers with benzyl peroxide (BPO), the splitting occurs when the mole fraction of MMA in the copolymer is approximately 0.3 or greater. The split signals of the OCH_3 and $\alpha\text{-CH}_3$ protons were assigned to triads and pentads with MMA as a center, respectively. $^1\text{H-NMR}$ spectra of the copolymers of CP with MMA, which were copolymerized in the presence of EtAlCl_2 and VOCl_3 , showed splitting of the OCH_3 and $\alpha\text{-CH}_3$ signals similar to that of the radical copolymers.

When the mole fractional ratio of MMA to CP in the copolymer was approximately 3.0 or greater, the MMA $\alpha\text{-CH}_3$ signal was split into peaks of different tacticity.

The triad concentrations obtained from the OCH_3 signal were in close agreement with those calculated from copolymerization theory. The triad concentrations obtained from the signal of the $\alpha\text{-CH}_3$ protons were compared with those of the OCH_3 protons, and found to be in reasonable agreement.

EXPERIMENTAL

The conditions for all CP-MMA copolymerizations are tabulated in Table I with the values of each mole fraction in the copolymers. All $^1\text{H-NMR}$ spectra were recorded at 60°C in deuteriochloroform by the use of a Varian HA-100D spectrometer; tetramethylsilane was used as internal standard.

TABLE I
Copolymerization of Chloroprene and Methyl Methacrylate

Sample	Polymerization conditions			Mole fraction in feed		Mole fraction ^a in copolymer	
	Temp., °C	Catalyst	Conversion, wt-%	CP	MMA	CP	MMA
CM-1	60	BPO ^b	2.7	0.53	0.47	0.89	0.11
CM-2	60	BPO ^b	2.2	0.30	0.70	0.76	0.24
CM-3	60	BPO ^b	3.56	0.20	0.80	0.65	0.35
CM-4	60	BPO ^b	3.98	0.10	0.90	0.46	0.54
CM-5	60	BPO ^b	5.6	0.03	0.97	0.20	0.80
CM-6	25	EtAlCl ₂ -VOCl ₃ ^c	66.4	0.50	0.50	0.56	0.44
CM-7	25	EtAlCl ₂ -VOCl ₃ ^c	46.3	0.80	0.20	0.71	0.29
CM-8	25	EtAlCl ₂ -VOCl ₃ ^c	57.3	0.20	0.80	0.24	0.76

^a Determined by the relative areas of the methine signal in CP units and the OCH₃ signal in MMA units in the ¹H-NMR spectra. Errors = ±0.02.

^b Benzoyl peroxide.

^c Ethylaluminum dichloride-vanadyl trichloride.

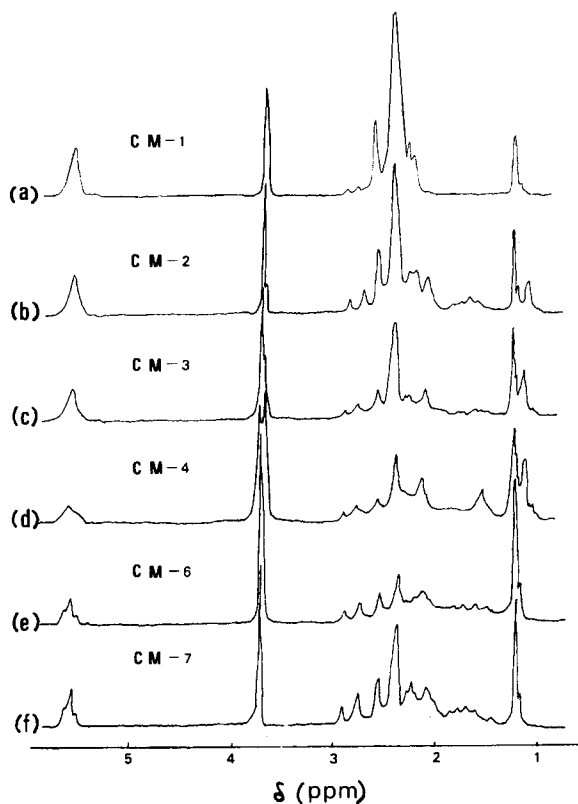


Fig. 1. ¹H-NMR spectra of CP-MMA copolymers with BPO and EtAlCl₂-VOCl₃: (a) copolymer with BPO (CP, 89 mole-%); (b) copolymer with BPO (CP, 76 mole-%); (c) copolymer with BPO (CP, 46 mole-%); (d) copolymer with BPO (CP, 46 mole-%); (e) copolymer with EtAlCl₂-VOCl₃ (CP, 56 mole-%); (f) copolymer with EtAlCl₂-VOCl₃ (CP, 71 mole-%).

RESULTS AND DISCUSSION

^1H -NMR spectra of CP-MMA copolymers with BPO and $\text{EtAlCl}_2\text{-VOCl}_3$ are shown in Figure 1. The resonance peaks of the methine and methylene protons of the CP units appear at $\delta = 5.5$ and $2.2\text{--}2.9$ ppm, respectively. On the other hand, the resonance peaks of the methine, methylene, OCH_3 , and $\alpha\text{-CH}_3$ protons of the MMA units appear at $\delta = 2.6\text{--}2.9$, $1.3\text{--}2.2$, $3.6\text{--}3.8$, and $0.8\text{--}1.3$ ppm, respectively, in Figure 1. In Figure 1, the intensity of the peak at $\delta = 2.4$ ppm, assigned to the CP-CP diad in the radical copolymer, decreases as the composition of CP and MMA in the copolymer becomes closer to equimolar, and this agrees with the experimental results reported by Yamashita et al.¹

The signal of the OCH_3 and $\alpha\text{-CH}_3$ protons in the radical copolymers were split into more than two when the mole fraction of MMA in the copolymer was approximately 0.3 or greater. The signal of the OCH_3 protons of PMMA in C_6H_6 solution was split into triads,^{3,4} but that in CDCl_3 solution was not split.⁵ Accordingly, it is thought that the signal of the OCH_3 protons in Figure 1 was split into triads by the shielding effect of chlorine.⁶

In the ^1H -NMR spectrum of the copolymer (CM-8 in Table I), the peaks of the OCH_3 protons were resolved into three with a du Pont Curve Resolver as shown in Figure 2. When the MMA unit and the CP unit are represented by M and C, the above peaks are assigned to triad sequences with MMA as a center, MMM, MMC, and CMC, from the higher field.

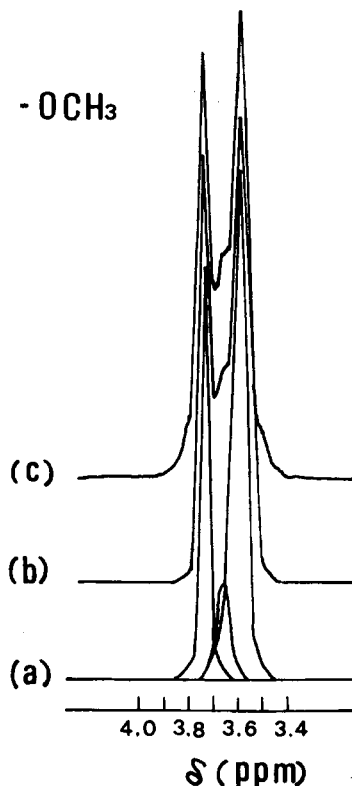


Fig. 2. ^1H -NMR spectrum of the OCH_3 protons in CP-MMA copolymer (CM-8): (a) Lorentzian components; (b) synthesized spectrum (sum of Lorentzian components); (c) observed spectrum.

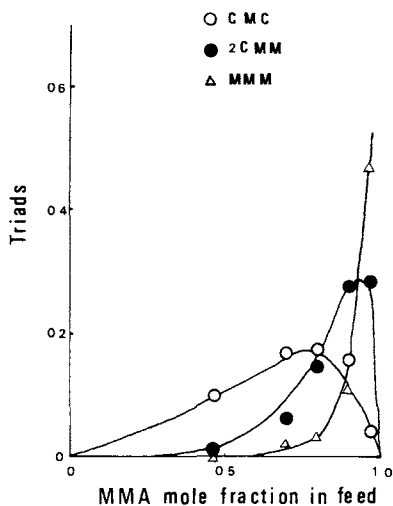


Fig. 3. More fraction of triads vs. mole fraction of MMA in monomer feed for free-radical copolymers of MMA/CP. Solid lines: calcd. from $r_C = 6.3$, $r_M = 0.116$.

In the previous paper dealing with radical copolymers, it was reported that the signal of the OCH_3 protons complexed with the shift reagent was split into six peaks assigned to the pentads, but each pentad concentration was not obtained.² In the present case, each triad concentration of the radical copolymers was obtained and compared with the theoretical concentrations.

The relative concentrations were calculated by the following equations, using each monomer reactivity of CP and MMA and each feed ratio⁷:

$$P_1(M) = 1 - P_1(C) = \frac{P_{CM}}{P_{CM} + P_{MC}} \quad (1)$$

$$P_{CM} = 1 - P_{CC} = \frac{1}{1 + r_C F} \quad (2)$$

$$P_{MC} = 1 - P_{MM} = \frac{1}{1 + r_C / F} \quad (3)$$

where P_{CM} , for example, is the probability of a CP unit being followed by an MMA unit; $P_1(M)$ and $P_1(C)$ are mole fractions of MMA and CP in the copolymer, respectively; F is the ratio of MMA/CP in the feed, and r_C and r_M are the monomer reactivity ratios of CP and MMA respectively. The monomer reactivity ratios calculated from the Fineman-Ross method were as follows: $r_C = 6.3$, $r_M = 0.116$. The theoretical triads with an MMA unit as a center are expressed as follows:

$$P_3(MMM) = P_1(M)P_{MM}^2 \quad (4)$$

$$P_3(MMC) = P_3(CMM) = P_1(M)P_{MM}P_{MC} \quad (5)$$

$$P_3(CMC) = P_1(C)P_{CM}P_{MC} \quad (6)$$

where P_3 denotes the relative concentration of the triads designated in parentheses.

In Figure 3, the observed triad concentrations are compared with the theo-

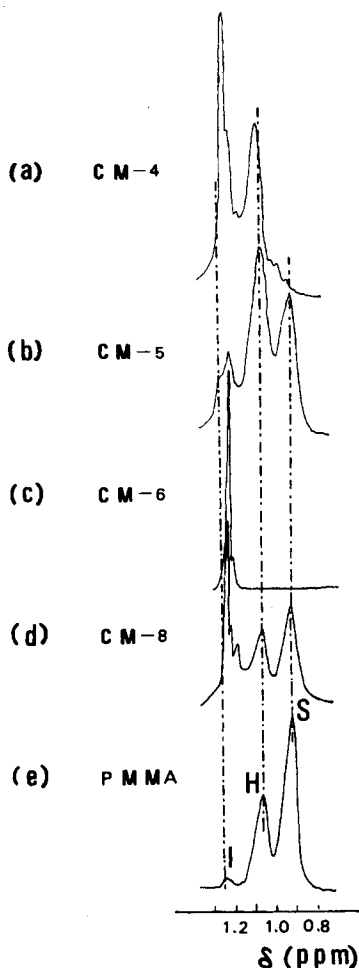


Fig. 4. $^1\text{H-NMR}$ spectra of the $\alpha\text{-CH}_3$ protons in CP-MMA copolymers with BPO (CP, 46 mole-%); (b) copolymer with BPO (CP, 20 mole-%); (c) copolymer with $\text{EtAlCl}_2\text{-VOCl}_3$ (CP, 56 mole-%); (d) copolymer with $\text{EtAlCl}_2\text{-VOCl}_3$ (CP, 24 mole-%); (e) PMMA.

retical lines calculated from eqs. (1)–(6) using $r_C = 6.3$, $r_M = 0.116$, and F , and the former agreed closely with the latter.

In Figure 4, the $^1\text{H-NMR}$ spectra of the $\alpha\text{-CH}_3$ protons of the copolymers (CM-4, CM-5, CM-6, and CM-8 in Table I) and PMMA are shown. The signal of the $\alpha\text{-CH}_3$ protons was split roughly into three peaks at $\delta = 0.86\text{--}1.00$, $1.00\text{--}1.13$, and $1.13\text{--}1.25$ ppm, but the chemical shifts of the maximum intensity of each peak, shown in Figures 4a and 4c, did not coincide with those of the syndiotactic (S), heterotactic (H), and isotactic (I) peaks of PMMA in Figure 4e. Accordingly, it is thought that the above splitting is due to the same shielding effects as in the case of OCH_3 protons. Moreover, the peaks in the lowest and the highest field were split into three at $\delta = 1.15$, 1.17 , and 1.20 ppm, and at $\delta = 0.90$, 0.94 , and 0.99 ppm, respectively; but the broad peak at $\delta = 1.00\text{--}1.13$ ppm did not split in Figure 4a.

From the above splitting, it is assumed that the split signal of the $\alpha\text{-CH}_3$

protons should not be assigned to triads, but to the pentads with an MMA as a center. These peaks were assigned intuitively to CCMCC, CCMCM, MCMCM, MMC (CMMCC + MMMCC + CMMCM + MMMCM), CMMMC, MMMMC, and MMMMM from the lower field, respectively, taking account of the shielding effect of chlorine. In Figure 4b, the peaks at $\delta = 0.91, 1.05, 1.20,$ and 1.23 ppm shifted from the peaks in Figure 4a, and the peaks at $\delta = 0.91, 1.05,$ and 1.23 ppm fit the S, H, and I peak of the PMMA in Figure 4e, respectively. This phenomenon appeared also in Figure 4d. From this result, when the mole fractional ratio of MMA to CP in the copolymer is approximately 3.0 or greater, it is thought that the MMA α -CH₃ signal was split into peaks of different tacticity.

From the signals of the OCH₃ and α -CH₃ protons, the triad and pentad concentrations were calculated by use of the Curve Resolver and are shown in Table II. In this table, the triad concentrations in the α -CH₃ protons were in reasonable agreement with those in the OCH₃ protons when the experimental errors involved in the peak area measurements are taken into consideration.

The mole fractional ratio of CP to MMA in the copolymer (CM-6 in Table I) is approximately 1.0, and the sequence distribution in Table II is only CMC in triads and predominantly CCMCC in pentads. On the other hand, the mole fractional ratio of CP to MMA in the copolymer (CM-4 in Table I) is also approximately 1.0, but the sequence distribution in Table II is more random than that in CM-6.

From this result, the copolymer (CM-6) is more alternating than the copolymer (CM-4), but the CP-CP diad exists in the former. This result agrees with the experimental result of the ozonization reaction by Masaki et al.¹

References

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