A Study of Chloroprene and Methyl Methacrylate Radical Copolymers by 1H-NMR Spectra Shifted by the Use of Tris(dipivalomethanato)europium(III)

Tadashi OKADA, Michio IZUHARA, and Tsutomu HASHIMOTO

*Central Research Laboratory, Toyo Soda Manufacturing Co., Ltd.,
4560, Tonda, Shinnanyo-Shi, Yamaguchi-Ken, Japan.*

(Received November 19, 1973)

ABSTRACT: In 1H-nuclear-magnetic-resonance spectra of poly(chloroprene—methyl methacrylate), the signal assigned to the OCH_3 protons was split into five or six peaks by the addition of tris(dipivalomethanato)europium(III). These splittings were assinged tentatively to the methoxy protons of the central methyl methacrylate unit in the pentad sequences. The above peaks were resolved into six Lorenzian components by a curve resolver, and the fractions of the pentad sequences were obtained from the relative peak areas. Each observed concentration was in close agreement with that calculated by the copolymerization theory.

KEY WORDS Chloroprene / Methyl Methacrylate / 1H-NMR / Tris(dipivalomethanato)europium(III) / Monomer Reactivity Ratio /

The sequence distribution of monomer units in some radical copolymer systems containing methyl methacrylate has been estimated by high-resolution nuclear-magnetic-resonance (NMR) spectroscopy.[1-9] The results agree substantially with the sequence distribution predicted from the copolymerization theory.

In the 1H-NMR spectra of poly(chloprene—methyl methacrylate), the signals assigned to OCH_3 and α-CH_3 protons split into two or three peaks when the chloroprene mole fraction in the copolymer was 0.46 or less. This phenomenon agrees with the experimental results reported by Yamashita, *et al.*[10]

Recently, paramagnetic salts containing lantanides such as europium or prasseuodium have been effectively used for the investigation of polymers,[11-13] for example, the determination of the molecular weight of poly(propylene glycol) by NMR[14], and the analysis in NMR spectra of copolyesters (ethylene terephthalate—isophthalate).[15]

In this paper, the signal of the OCH_3 protons split by the addition of tris(dipivalomethanato)europium(III) to poly(chloroprene—methyl methacrylate) (CP—MMA) was assigned to the pentad sequences with an MMA unit as a center, and the observed concentrations were compared with those calculated by the copolymerization theory.

EXPERIMENTAL

All radical copolymerizations were carried out in the presence of benzoyl peroxide(BPO) at 60°C in monochlorobenzene, and their conversions were less than 10(wt%). Each conversions is tabulated in Table I. The samples

Table I. Radical copolymerization of chloroprene and methyl methacrylate[a]

Sample	Mole fraction in feed		Mole fraction[b] in copolymer		Conversion
	CP	MMA	CP	MMA	wt%
CM-1	0.90	0.10	0.98	0.02	2.3
CM-2	0.70	0.30	0.94	0.06	2.2
CM-3	0.53	0.47	0.89	0.11	2.7
CM-4	0.30	0.70	0.76	0.24	2.2
CM-5	0.20	0.80	0.65	0.35	3.56
CM-6	0.10	0.90	0.46	0.54	3.98
CM-7	0.03	0.97	0.20	0.80	5.6

[a] Polymerization conditions; total monomer of chloroprene and methyl methacrylate 20 m*l*, benzoyl peroxide 0.2 mol% based on monomers, 60°C, 1—4 hr.

[b] Determined by NMR.

for the measurements of the ¹H-NMR were prepared by dissolving 20 mg of each copolymer with 10 mg of tris(dipivalomethanato)europium (III) (Eu(DPM)₃) in 300 mg of CDCl₃. All ¹H-NMR spectra were measured at 60°C by the use of a Varian HA-100D spectrometer; tetramethylsilane was used as an internal standard.

RESULTS AND DISCUSSION

¹H-NMR spectra of CP—MMA copolymers are shown in Figure 1. The resonance peaks of methine and methylene protons of CP units appear at $\tau=4.5$ and 7.4—7.8 ppm, respectively. On the other hand, the peaks of methine,

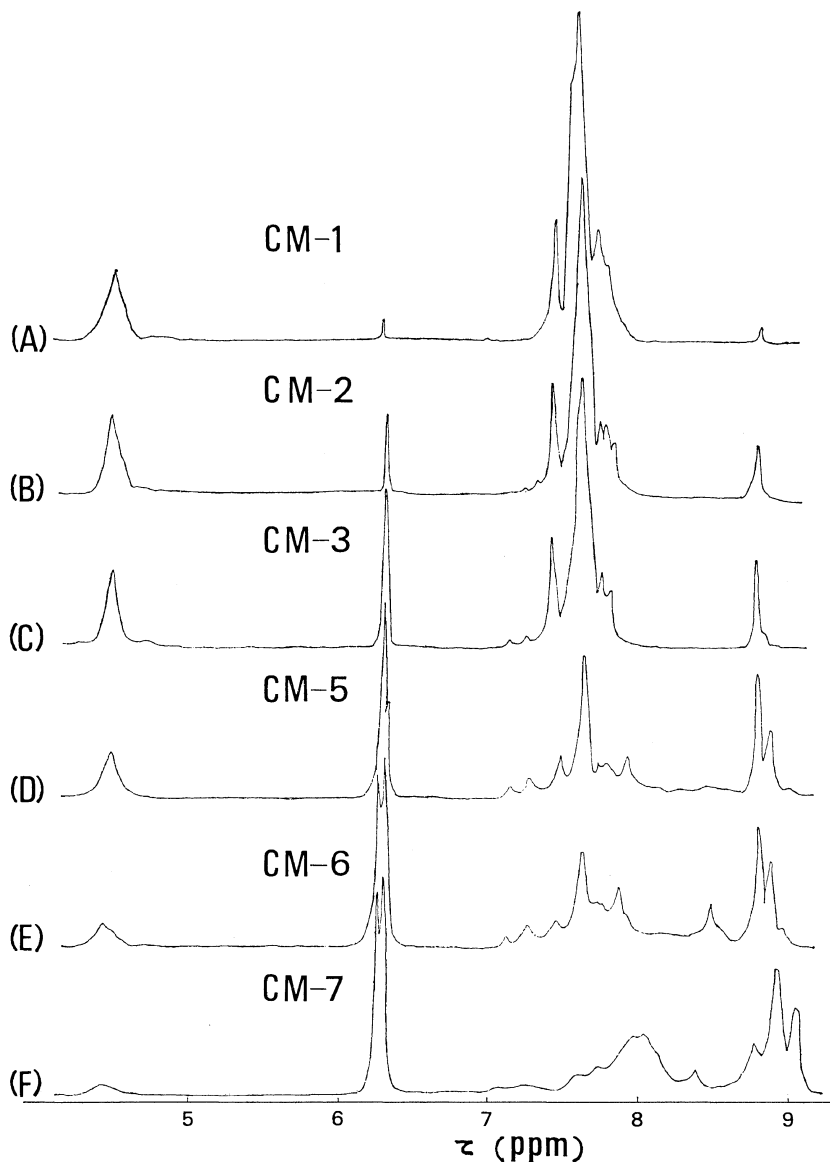**Figure 1.** ¹H-NMR spectra of poly(chloroprene—methyl methacrylate) prepared with BPO in monochlorobenzene; observed in CDCl₃ at 60°C: (A), CP in feed, 90 mol%; (B), CP in feed, 70 mol%; (C), CP in feed, 53 mol%; (D), CP in feed, 20 mol%; (E), CP in feed, 10 mol%; (F), CP in feed, 3 mol%.

methylene, and α-methyl protons of MMA units appear at $\tau=$7.1—7.4, 7.8—8.7, and 8.7—9.2 ppm, respectively. The single peak at $\tau=$6.34 ppm in Figure 1(A—D), which was assigned to the OCH₃ protons of MMA units, was separated into two peaks at $\tau=$6.34 and 6.40 ppm in Figure 1(E—F). In Figure 1, the relative intensity of the signal at $\tau=$7.6 ppm increases with the CP content in the copolymer, which suggests that the signal should be ascribed to the CP—CP diad in the copolymer. On the other hand, the signal of α-CH₃ protons in MMA units was split into three peaks with an increase in the MMA content of the copolymer. The above phenomenon agrees with the experimental results reported by Yamashita, et al.[10] The mole fractions of CP and MMA units in the copolymers shown in Table I were calculated according to the following equation:

$$\frac{(CP)}{(MMA)} = \frac{A_C}{A_M/3} \qquad (1)$$

where (CP) and (MMA) are the mole fraction of CP and MMA in the copolymers, respectively, A_C is the peak area assigned to the methine proton in CP units, and A_M is that of the OCH₃ protons in MMA units.

In Figure 2, the ¹H-NMR spectra of CP—MMA copolymer (CM-4) with and without the addition of Eu(DPM)₃ are shown. The advantage of using Eu(DPM)₃ is that the signal shifts to lower field without broadening when this reagent is complexed with the base produced in ketones, ethers, and amines in the sample.[16]

When the ¹H-NMR spectra of CP—MMA copolymers complexed with Eu(DPM)₃ are measured at 24°C, it is necessary to leave them alone for two days in order to obtain a con-

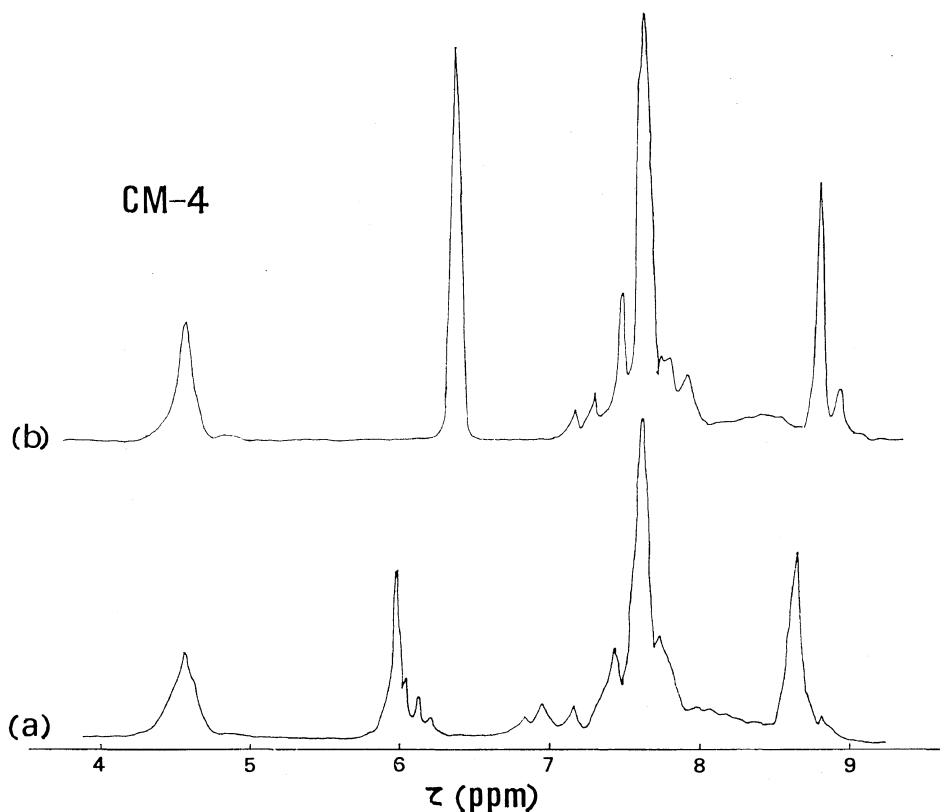**Figure 2.** ¹H-NMR spectra of CP—MMA copolymer(CM-4) prepared with BPO in monochlorobenzene; observed in CDCl₃ at 60°C: (a), with the addition of Eu(DPM)₃; (b), without the addition of Eu(DPM)₃.

stant τ value for each signal. Therefore, the above measurements were carried out after three days. The signal split by the addition of Eu(DPM)$_3$ was assigned tentatively to the OCH$_3$ protons of the central MMA unit in the pentad sequences from the following experimental results and ideas.

It is thought that the CP units in the copolymer which were prepared in CP-rich in-feed were the following four structural isomers: trans-1,4-, cis-1,4-, 1,2-, and 3,4- configurations. From the chemical shift of the methine peak in CP unit shown in Figure 1, it is suggested that the CP units in copolymers were predominantly trans-1,4-configuration.[17] Moreover, it is postulated that the trans-1,4-configuration takes three linkages: "head-to-head", "head-to-tail", and "tail-to-tail". But it was assumed that the difference of the sequences with an MMA unit as a center was more predominant than that of configurations and linkages such as the above

when the split peaks of the methyl protons in the OCH$_3$ groups complexing with Eu(DPM)$_3$ were assigned.

In Figure 3 are shown the ^{1}H-NMR spectra of the OCH$_3$ protons in CP—MMA copolymer, which was copolymerized at 25°C in the presence of ethylalminium sesquichloride (Et$_3$Al$_2$Cl$_3$) and vanadyl trichloride (VOCl$_3$); these were measured with and without the addition of Eu(DPM)$_3$. Each signal in Figure 3(B) was measured after 22 hr with the addition of Eu(DPM)$_3$, while those in Figure 3(C) were measured after three days with the same addition. In Figure 3(A), the signal of the OCH$_3$ protons was split into three peaks at $\tau=6.33$, 6.38, and 6.40 ppm by the shielding effect of chlorine.[6] When the MMA unit and the CP unit are expressed by M and C, the above split signal is assigned to the OCH$_3$ protons of the central MMA unit in the triad sequences. In Figures 3(B) and (C), the signal of the OCH$_3$ protons was split into four
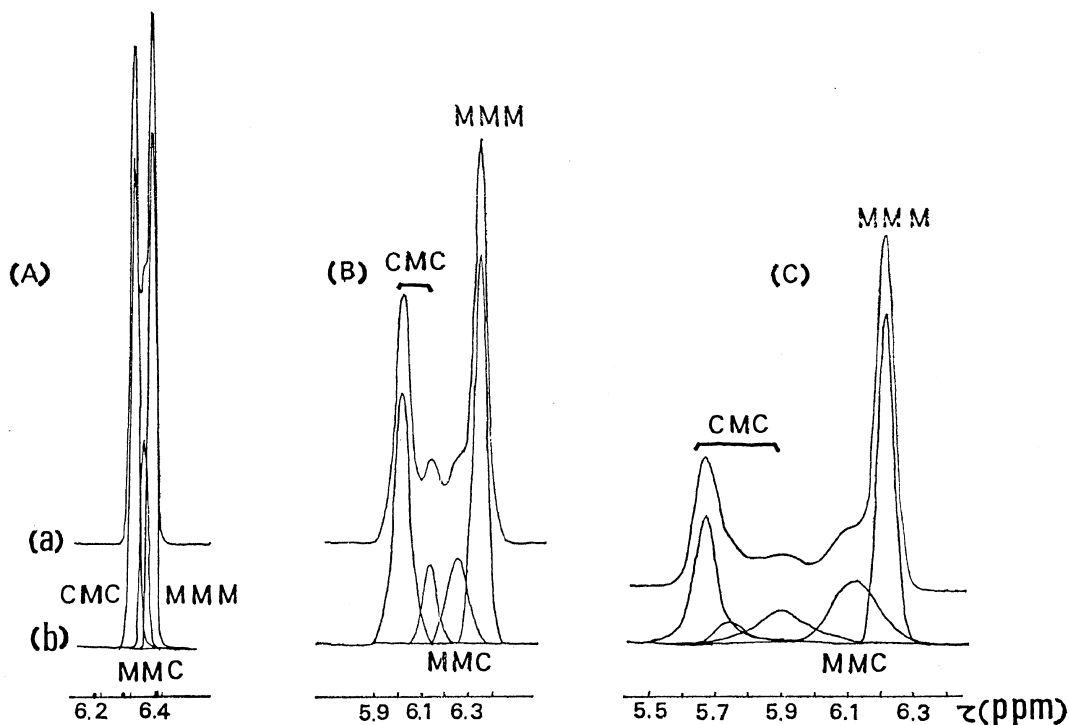

Figure 3. ^{1}H-NMR spectra of the OCH$_3$ protons in CP—MMA copolymer(MMA/CP=4 in feed) prepared with Et$_3$Al$_2$Cl$_3$—VOCl$_3$; observed in CDCl$_3$ at 60°C: (A), without the addition of Eu(DPM)$_3$; (B), after 22 hr with the addition of Eu(DPM)$_3$; (C), after three days with the addition of Eu(DPM)$_3$; (a), the observed spectra; (b), Lorentzian components resolved by a curve resolver.
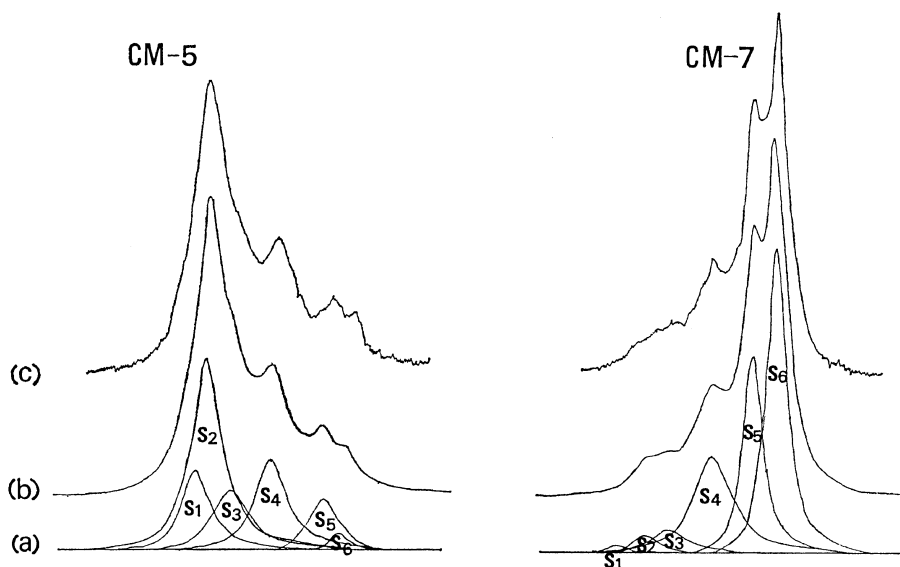
Figure 4. ¹H-NMR spectra of the OCH₃ protons in CP—MMA copolymers(CM-5 m CM-7) split by the use of Eu(DPM)₃: (a), six Lorenzian components; (b), synthesized spectra of each component in (a); (c), the observed spectra.

or five. Figures 3(Aa) and (Ab) show the observed signal of the OCH₃ protons and the Lorenzian components resolved by a curve resolver, respectively. The relative areas of the peaks in Figures 3(B) and (C) were compared with those in Figure 3(A), and the assignments were made.

The following results were obtained by the above experiment. First, the magnitude of the shifts in the signal of the OCH₃ protons split by the addition of Eu(DPM)₃ depends on the number of CP units in the sequence. Secondly, the signal of the OCH₃ protons in CP—MMA copolymer splits with the addition of Eu(DPM)₃ into the peaks assigned to the sequences longer than triads.

From the above assumption and experimental results, the assignment for the signal of the OCH₃ protons in CP—MMA copolymer (CM-4) split by the addition of Eu(DPM)₃ was carried out tentatively; that is, the splittings in Figure 2(a) were resolved into six Lorenzian peaks with a curve resolver and their assignments were postulated as follows:

$$S_1 = P_5(\text{CCMCC}) \tag{2}$$

$$S_2 = 2P_5(\text{CCMCM})$$
$$\quad + P_5(\text{MCMCM}) + 2P_5(\text{CCMMC}) \tag{3}$$

$$S_3 = 2P_5(\text{MCMMC}) \tag{4}$$

$$S_4 = 2P_5(\text{MMMCC}) + 2P_5(\text{MMMCM}) \tag{5}$$

$$S_5 = P_5(\text{CMMMC}) + 2P_5(\text{MMMMC}) \tag{6}$$

$$S_6 = P_5(\text{MMMMM}) \tag{7}$$

where S_i denotes the relative concentration of the i-th peak in NMR spectra assigned to the OCH₃ protons and P_5 the relative concentration of the pentads designated in parentheses. The above assignment for the observed peaks of the OCH₃ protons was applied to the other samples. When the concentration of S_i in eq 2—7 was estimated, the observed peaks of the OCH₃ protons were resolved with a du Pont Curve Resolver as shown in Figure 4. The observed concentration of each sample, S_i, is tabulated in Table II. However, ¹H-NMR measurements using Eu(DPM)₃ in CM-1 and CM-2 were not carried out, for the ratio of signal to noise of the peaks assigned to the OCH₃ protons in these samples was much smaller than that in the other samples.

On the other hand, the relative concentrations

T. Okada, M. Izuhara, and T. Hashimoto

Table II. Experimental and theoretical concentration of poly(chloroprene—methyl methacrylate)

Sample	Observed[a]						Calculated[b]					
	S_1	S_2	S_3	S_4	S_5	S_6	S_1	S_2	S_3	S_4	S_5	S_6
CM-1							0.016	0	0	0	0	0
CM-2							0.050	0.012	0	0	0	0
CM-3	0.071	0.038	0.005	0.005	0	0	0.076	0.038	0.002	0.002	0.001	0
CM-4	0.097	0.124	0.014	0.014	0.005	0	0.084	0.123	0.018	0.013	0.011	0
CM-5	0.051	0.163	0.047	0.062	0.033	0.007	0.063	0.171	0.042	0.049	0.033	0.004
CM-6	0.026	0.169	0.044	0.137	0.131	0.038	0.022	0.163	0.078	0.136	0.105	0.037
CM-7	0.005	0.027	0.040	0.201	0.201	0.337	0	0.044	0.046	0.210	0.185	0.311

[a] From ^{1}H-NMR spectra of OCH_3 protons in CP—MMA copolymers with the addition of $Eu(DPM)_3$.
[b] From eq 2—18, using mole fraction in feed (Table I) and $r_C=6.0$ and $r_M=0.116$.

were calculated by the following equations, using each monomer reactivity of CP and MMA and each feed ratio:[18]

$$P_1(M)=1-P_1(C)=\frac{P_{CM}}{P_{CM}+P_{MC}} \quad (8)$$

$$P_{CM}=1-P_{CC}=\frac{1}{1+r_C F} \quad (9)$$

$$P_{MC}=1-P_{MM}=\frac{1}{1+r_M/\mathsf{F}} \quad (10)$$

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

$$P_5(MMMMM)=P_1(M)P_{MM}^4 \quad (11)$$

$$P_5(CMMMM)=P_5(MMMMC)=P_1(M)P_{MM}^3 P_{MC} \quad (12)$$

$$P_5(CMMMC)=P_1(C)P_{MM}^2 P_{MC}P_{CM} \quad (13)$$

$$P_5(MMMCM)=P_5(MCMMM)$$
$$=P_1(M)P_{MM}^2 P_{MC}P_{CM} \quad (14)$$

$$P_5(CMMCM)=P_5(MCMMC)$$
$$=P_1(M)P_{MM}P_{MC}^2 P_{CM} \quad (15)$$

$$P_5(CCMMM)=P_5(MMMCC)$$
$$=P_1(M)P_{MM}^2 P_{MC}P_{CC} \quad (16)$$

$$P_5(MCMCM)=P_1(M)P_{MC}^2 P_{CM}^2 \quad (17)$$

$$P_5(CCMCC)=P_1(C)P_{CC}^2 P_{MC}P_{CM} \quad (18)$$

The pentad concentrations calculated from eq 8—18 using $r_C=6.0$, $r_M=0.116$, and each F, were summed into S_i in eq 2—7 for comparison with the observed S_i; their values are tabulated in Table II.

CONCLUSION

When $Eu(DPM)_3$ was added to CP—MMA copolymers, the signal of the OCH_3 protons in MMA units shifted to lower field and split into six. These six peaks were assigned to pentad sequences with an MMA unit as a center. In the case of these assignments, it was presumed that the magnitude of the shift depended on the number of CP units in the sequence. Each observed concentration was in close agreement with that calculated by the copolymerization theory.

REFERENCES

1. F. A. Bovey, *J. Polym. Sci.*, **62**, 197 (1962).
2. Y. Kato, N. Ashikari, and A. Nishioka, *Bull. Chem. Soc. Japan*, **37**, 1630 (1964).
3. H. J. Harwood and W. M. Ritchey, *J. Polym. Sci., Part B*, **3**, 427 (1965).
4. K. Ito and Y. Yamashita, *ibid., Part B*, **3**, 625 (1965).

5. K. Ito and Y. Yamashita, *ibid.*, *Part A–1*, **4**, 631 (1966).
6. K. Ito, S. Iwase, and Y. Yamashita, *Macromol. Chem.*, **110**, 233 (1967).
7. U. Johnsen and K. Kolbe, *ibid.*, **116**, 173 (1968).
8. J. Guillot, A. Guyot, and P. Q. Tho, *J. Macromol. Sci.*, **A2**, 1303 (1968).
9. E. Klesper, *J. Polym. Sci.*, *Part B*, **6**, 313 (1968); *Part B*, **7**, 661, 727 (1969).
10. A. Masaki, M. Yasui, and I. Yamashita, *J. Macromol. Sci.*, **A6**(7), 1285 (1972).
11. J. E. Guillet, I. R. Peat, and W. F. Reynolds, *Tetrahedron Lett.*, **38**, 3493 (1971).
12. H. Yuki, K. Hatada, T. Hasegawa, Y. Terawaki, and H. Okuda, *Polymer J.*, **3**, 645 (1972).
13. S. Amiya, I. Ando, and R. Chujo, *ibid.*, **4**, 385 (1973).
14. F. F. -L. -Ho, *Polymer Lett.*, **9**, 491 (1971).
15. R. Chujo, K. Koyama, I. Ando, and Y. Inoue, *Polymer J.*, **3**, 394 (1972).
16. C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).
17. R. C. Ferguson, *J. Polym. Sci.*, *Part A*, **2**, 4735 (1964).
18. K. Ito and Y. Yamashita, *ibid.*, *Part A*, **3**, 2165 (1965).