Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Radical Copolymerizability of Acrylamide Derivatives with Methyl Vinyl Ketone

Natsuki Yamashita[a]; Kazuyukiikezawa[a]; Shin-Ichirou Ayukawa[a]; Toshihisa Maeshima[a]
[a] Department of Applied Chemistry Faculty of Science and Engineering, Kinki University, Higashi-Osaka, Japan

To cite this Article Yamashita, Natsuki , Kazuyukiikezawa, Ayukawa, Shin-Ichirou and Maeshima, Toshihisa(1984) 'Radical Copolymerizability of Acrylamide Derivatives with Methyl Vinyl Ketone', Journal of Macromolecular Science, Part A, 21: 5, 615 — 629

To link to this Article: DOI: 10.1080/00222338408056576

URL: http://dx.doi.org/10.1080/00222338408056576

J. MACROMOL. SCI.–CHEM., A21(5), pp. 615-629 (1984)

Radical Copolymerizability of Acrylamide Derivatives with Methyl Vinyl Ketone

NATSUKI YAMASHITA, KAZUYUKI IKEZAWA,
SHIN-ICHIROU AYUKAWA, and TOSHIHISA MAESHIMA

Department of Applied Chemistry
Faculty of Science and Engineering
Kinki University
Kowakae, Higashi-Osaka, 577 Japan

ABSTRACT

Radical copolymerization of methyl vinyl ketone (MVK, M_1) with acrylamide (AAm) and its derivatives, such as methacrylamide (MAAm) and N,N'-dimethylacrylamide (DMAAm), was carried out in dioxane or ethanol using α,α'-azobisisobutylonitrile as the initiator at 60°C under vacuum. The monomer reactivity ratios found in dioxane were as follows: $r_1 = 1.06$, $r_2 = 6.41$ for the MVK-AAm system; $r_1 = 0.29$, $r_2 = 3.05$ for the MVK-MAAm system; and $r_1 = 0.95$, $r_2 = 0.26$ for the MVK-DMAAm system. The r_1 and r_2 values obtained in ethanol were as follows: $r_1 = 0.88$, $r_2 = 1.18$ for the MVK-AAm system; and $r_1 = 0.37$, $r_2 = 2.04$ for the MVK-MAAm system. Q_2 and e_2 values of AAm derivatives in dioxane were estimated to be 3.03 and 1.04 for MAAm and 2.15 and 1.11 for DMAAm, respectively. The Q_2 and e_2 values of MAAm in ethanol were estimated to be 2.67 and 1.21, respectively. Based on these results, the alternating copolymerizability depends on the interaction of monomer-monomer, and the strong solvent effect depends on the radical copolymerization of the AAm derivatives.

0022-233X/84/2105-0615$3.50/0

INTRODUCTION

Since the solvent effect on radical polymerization was reported by Ito and Otsu [1], various reports have been made on this study. In particular, Saini et al. [2] found the solvent effect on radical copolymerization of acrylamide (AAm) with styrene and methyl methacrylate.

We have investigated the anionic polymerizability of acrolein (AL), methyl vinyl ketone (MVK), methyl methacrylate, and several AAm derivatives induced by a pyridine-water mixture or imidazole [3-5]. An interaction between AL and AAm derivatives was found [6].

On the other hand, the radical copolymerization of AL (M_1) with AAm (M_2) was investigated by Schulz et al. [7], and the monomer reactivity ratios were reported as $r_1 = 1.69$ and $r_2 = 0.21$. We have also reported on the free-radical copolymerizabilities of AL (M_1) with methacrylamide (MAAm) and N,N-dimethylacrylamide (DMAAm) [8]. The monomer reactivity ratios obtained were as follows: $r_1 = 0.62$, $r_2 = 0.12$ for the AL-MAAm system; $r_1 = 0.95$, $r_2 = 0.26$ for the AL-DMAAm system. All of these values indicate alternating copolymerizability. These facts also suggest the presence of an interaction between AL and AAm derivatives, in analogy with the results on anionic copolymerization.

This investigation was performed to reveal the radical copolymerizability of methyl vinyl ketone with AAm derivatives.

EXPERIMENTAL

Materials

Methyl vinyl ketone (MVK) was prepared in the manner described in a previous article [5]. AAm and MAAm were purified by recrystallization from benzene. DMAAm was purified by distillation. Dioxane and ethanol for the polymerization solvent and α,α'-azobisisobutylnitrile (AIBN) for the radical initiator were purified in the usual way.

Polymerization Methods

Free-radical copolymerization of MVK (M_1) with AAm derivatives (M_2) was carried out in dioxane or ethanol by using AIBN at 60°C in a sealed tube. The required amounts of the monomers, the initiator, and the solvent were placed into the tube. The tube was sealed after degassing by repeated freezing and thawing cycles. Copolymerization was stopped below 10% conversion. The reaction mixture was poured into a large amount of precipitant, and the precipitate was filtered off and dried in vacuo to constant weight.

Copolymer compositions were determined by elementary analysis. The monomer reactivity ratio was determined by the Fineman-Ross method [9]. These Q-e values were determined by using the Alfrey-Price equation [10].

Analyses

The elementary analysis of copolymers was estimated with a Yanagimoto CHN Corder MT-2. Infrared (IR) spectroscopy was measured with a KBr disk using a Nihonbunkou IRA-1 spectrophotometer.

RESULT AND DISCUSSION

Copolymerization Results of MVK-AAm System

Radical copolymerizations of MVK (M_1) with AAm (M_2) were carried out in dioxane and ethanol at 60°C (Tables 1 and 2). These polymers, obtained as white powders, were soluble in formic acid and dimethylsulfoxide.

The IR spectra of the copolymers (Fig. 1, c and c') have several characteristic absorption bands [5] of poly-MVK: $-CH_2-$ chain at 3000-2890 cm^{-1} and $>C=O$ group at 1710-1690 cm^{-1}. The absorption bands of the $-CONH_2$ (amide I) group of the AAm unit were also observed at 1660 cm^{-1}.

The monomer reactivity ratio was determined from Fineman-Ross plots (Figs. 2 and 3). These monomer-copolymer composition curves are summarized in Fig. 4. In Fig. 4 the experimental values agree well with the calculated curve. It is interesting to note that a difference between dioxane and ethanol is clear in the copolymerization curves. The experimental data show a strong influence of the solvents on these copolymerizations.

Copolymerization Results of MVK-MAAm System

Radical copolymerizations of MVK (M_1) with MAAm (M_2) were carried out in dioxane and ethanol (Tables 3 and 4). The IR spectra for the MVK-MAAm system is shown in Fig. 5. They show that the copolymers are constituted of the polymer units of MVK (3000-2850, 1700, 1350 cm^{-1}) and MAAm (1650 cm^{-1}).

The r_1 and r_2 values were obtained from the results of Fineman-Ross plots (Figs. 6 and 7). Monomer-copolymer composition curves are shown in Fig. 8. These results indicate solvent effects on radical polymerization.

TABLE 1. Copolymerization[a] Results of MVK (M_1) with AAm (in dioxane)

Charged composition MVK (mol%)	Polymerization time (min)	Conversion (%)	Elementary analysis (%)			Incorporated ratio of MVK (mol%)
			C	H	N	
100	26	7.4	67.43	8.88	0.00	100
80	30	10.1	63.56	8.61	3.55	67
60	14	8.1	56.18	7.67	9.26	32
50	12	8.2	54.18	7.50	11.45	22
40	10	7.6	52.34	7.39	13.45	14
20	6	6.5	48.02	7.27	15.53	7
0	4	6.7	46.42	7.33	17.33	0

[a] Copolymerization conditions: Total monomers, 1.80 mol/L; AIBN, monomer/100; solvent, dioxane; 60°C.

TABLE 2. Copolymerization[a] Results of MVK (M_1) with AAm (in dioxane)

Charged composition MVK (mol%)	Polymerization time (min)	Conversion (%)	Elementary analysis (%)			Incorporated ratio of MVK (mol%)
			C	H	N	
100	36	7.6	67.95	8.64	0.00	100
80	32	8.1	65.27	8.40	2.35	78
60	28	7.9	62.10	8.44	5.31	55
50	24	5.6	59.72	7.88	7.13	44
40	20	4.3	57.82	7.87	8.55	37
20	6	1.5	51.86	7.26	12.26	20
0	3	6.7	47.16	6.82	18.43	0

[a] Copolymerization conditions: Total monomers, 1.80 mol/L; AIBN, monomer/100; solvent, ethanol; 60°C.

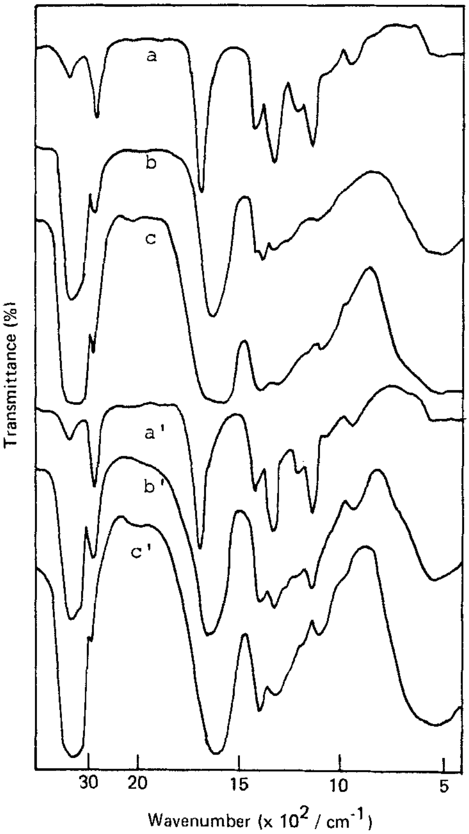


FIG. 1. IR spectra of poly-MVK (a), poly-AAm (b), and MVK-AAm copolymer (c) in dioxane; and of poly-MVK (a'), poly-AAm (b'), and MVK-AAm copolymer in ethanol.

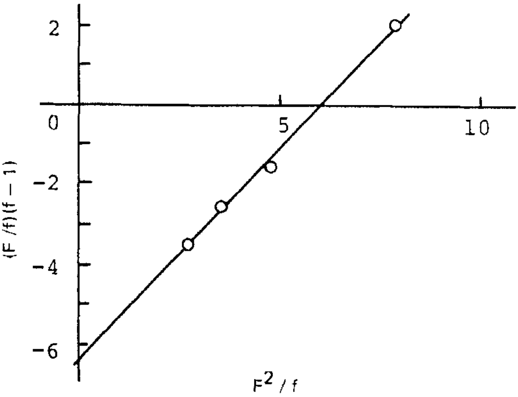


FIG. 2. Fineman-Ross plot of copolymerization of MVK (M_1) with AAm (in dioxane).

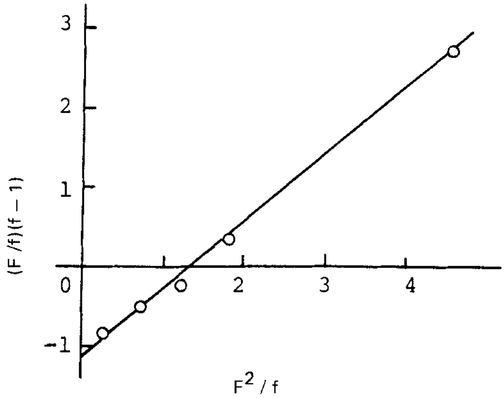


FIG. 3. Fineman-Ross plot of copolymerization of MVK (M_1) with AAm (in ethanol).

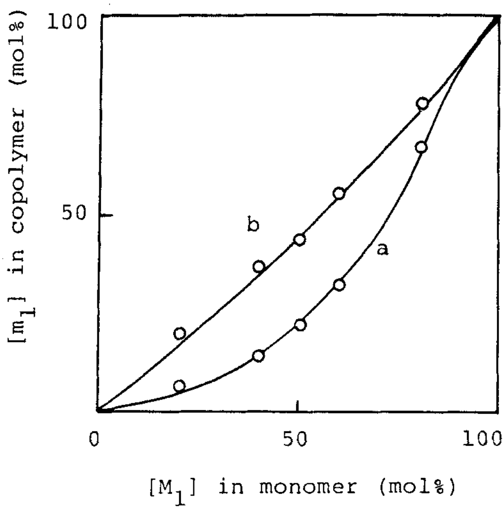


FIG. 4. Monomer-copolymer composition curves of copolymerization of MVK (M_1) with AAm (a, in dioxane; b, in ethanol).

TABLE 3. Copolymerization[a] Results of MVK (M_1) with MAAm (in dioxane)

Charged composition MVK (mol%)	Polymerization time (min)	Conversion (%)	Elementary analysis (%)			Incorporated ratio of MVK (mol%)
			C	H	N	
100	26	7.4	67.43	8.80	0.00	100
80	20	4.9	63.70	8.83	4.48	55
60	14	4.0	55.76	8.11	7.53	33
50	12	4.3	57.60	8.59	9.30	23
40	10	4.7	56.73	8.17	10.52	17
20	8	5.8	54.33	8.31	12.42	8
0	14	5.7	50.11	8.45	14.36	0

[a] Copolymerization conditions: Total monomers, 1.80 mol/L; AIBN, monomer/100; solvent, dioxane; 60°C.

TABLE 4. Copolymerization[a] Results of MVK (M_1) with MAAm (in dioxane)

Charged composition MVK (mol%)	Polymerization time (min)	Conversion (%)	Elementary analysis (%)			Incorporated ratio of MVK (mol%)
			C	H	N	
100	36	7.6	67.95	8.64	0.00	100
80	21	4.4	64.11	8.71	3.60	62
60	17	3.1	60.71	8.72	6.25	42
50	13	2.3	57.89	7.89	8.00	31
40	9	2.6	56.81	8.09	9.60	22
20	5	1.6	54.00	7.95	11.45	13
0	7	1.9	49.32	8.04	14.53	0

[a] Copolymerization conditions: Total monomers, 1.80 mol/L; AIBN, monomer/100; solvent, ethanol; 60°C.

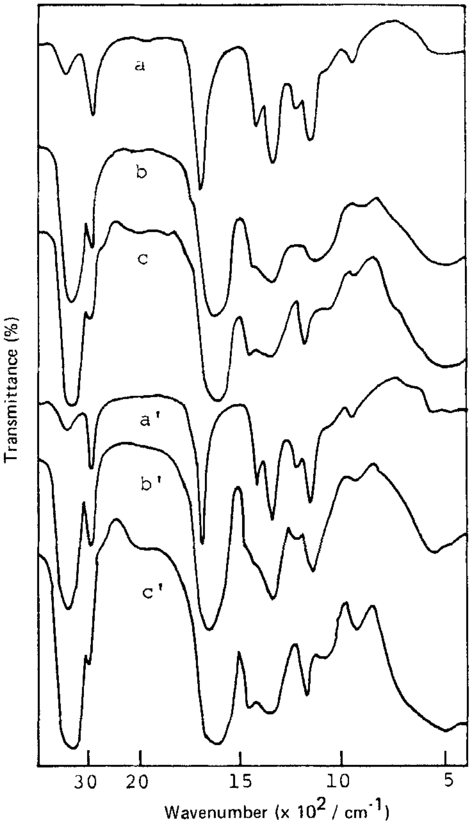


FIG. 5. IR spectra of poly-MVK (a), poly-MAAm (b), and MVK-MAAm copolymer (c) in dioxane; and of poly-MVK (a'), poly-MAAm (b'), and MVK-MAAm copolymer in ethanol.

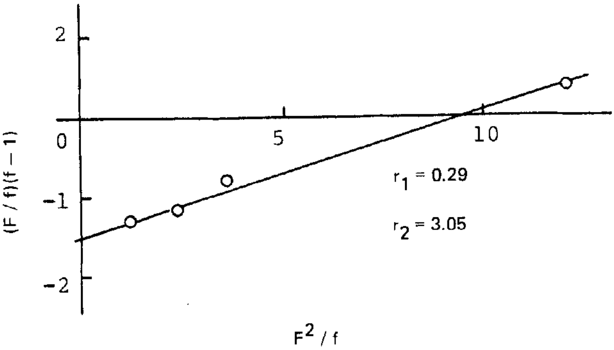


FIG. 6. Fineman-Ross plot of copolymerization of MVK (M_1) with MAAm (in dioxane).

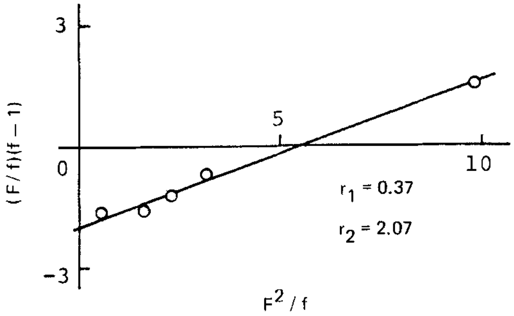


FIG. 7. Fineman-Ross plots of copolymerization of MVK (M_1) with MAAm (in ethanol).

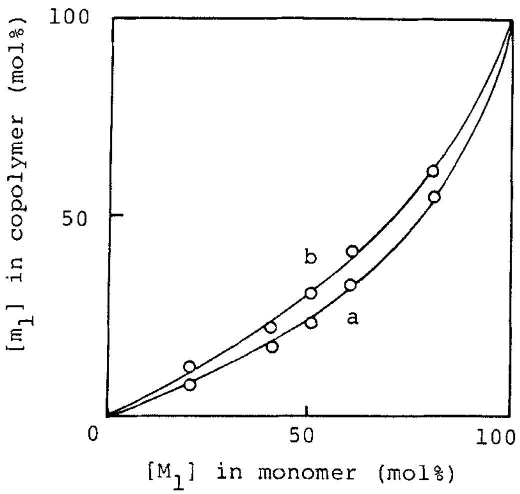


FIG. 8. Monomer-copolymer composition curves of copolymerization of MVK (M_1) with MAAm (a, in dioxane; b, in ethanol).

Copolymerization Results of MVK-DMAAm System

Copolymerizations of MVK (M_1) with DMAAm were carried out in dioxane at 60°C (Table 5). These copolymers are insoluble in ethanol.

The IR spectra of the copolymer (Fig. 9) have characteristic absorption bands that depend on MVK (2870, 1700, 1350 cm^{-1}) and DMAAm (1610 cm^{-1}).

The Fineman-Ross plots and the monomer-copolymer composition curves are shown in Figs. 10 and 11, respectively.

TABLE 5. Copolymerization[a] Results of MVK (M_1) with DMAAm (in dioxane)

Charged composition MVK (mol%)	Polymerization time (min)	Conversion (%)	Elementary analysis (%)			Incorporated ratio of MVK (mol%)
			C	H	N	
100	26	7.4	67.43	8.88	0.00	100
80	22	4.7	64.92	9.00	3.08	65
60	20	4.5	63.17	9.14	5.93	41
50	18	2.4	62.60	9.19	7.13	32
40	16	3.8	60.80	9.23	7.77	28
20	14	4.0	59.57	9.24	10.33	23
0	2	2.7	56.57	8.77	12.84	0

[a] Copolymerization conditions: Total monomers, 1.80 mol/L; AIBN, monomer/200; solvent, dioxane; 60°C.

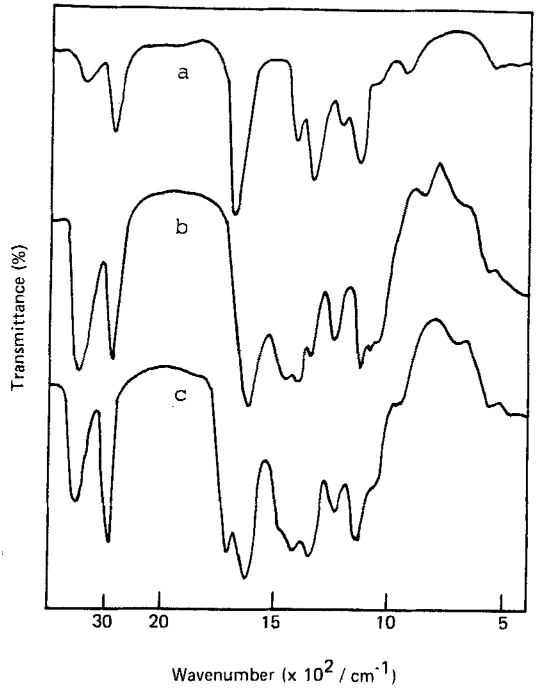


FIG. 9. IR spectra of poly-MVK (a), poly-DMAAm (b), and MVK-DMAAm copolymer (c) in dioxane.

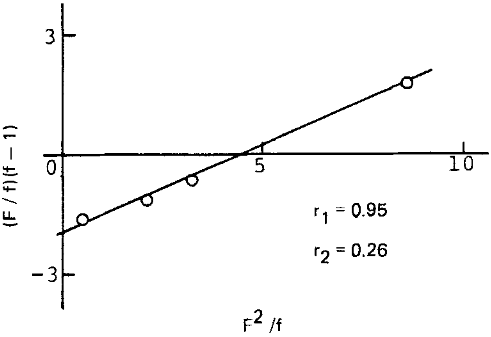


FIG. 10. Fineman-Ross plot of copolymerization of MVK (M_1) with DMAAm (in dioxane).

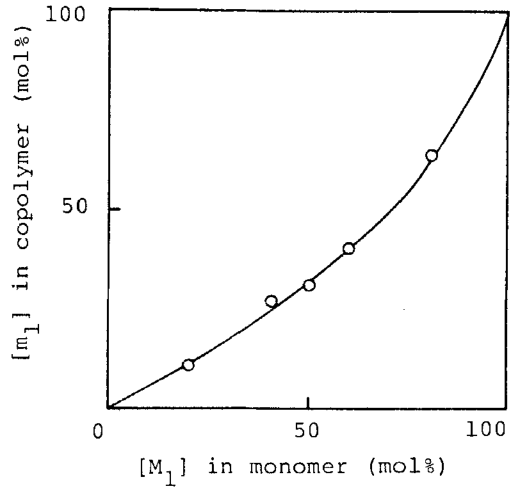
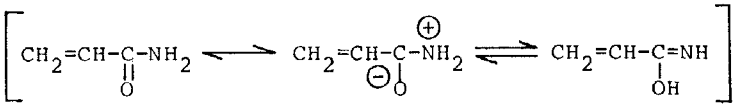


FIG. 11. Monomer-copolymer composition curve of copolymerization of MVK (M_1) with DMAAm (in dioxane).

Copolymerization Parameters

The copolymerization parameters of these results are summarized in Table 6, together with the parameters of the AL-AAm derived copolymerization system from a previous report [8]. In these results the alternating copolymerizability is clearly indicated for the AL-AAm derived copolymerization system. These interesting results may be explained by the effects of monomer-monomer or monomer-polymer on interaction [8]. The high values of r_1r_2 in for MVK-AAm derived systems indicate a low tendency of the monomers to alternate. Therefore, the interaction between MVK and AAm derivatives may be absent in radical copolymerization. On the other hand, it is interesting to note that the effect of solvent in this study was clearly found. Such strong solvent effects on the radical copolymerization of AAm has been reported by Saini et al. [2]. The result of our study may also be explained by a displacement of the following equilibrium:



$$\left[CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}NH_2 \longleftrightarrow CH_2{=}CH{-}\underset{\ominus O}{C}{-}\overset{\oplus}{NH_2} \rightleftharpoons CH_2{=}CH{-}\underset{OH}{C}{=}NH \right]$$

brought about by solvents with different dielectric constants and polarities.

TABLE 6. Copolymerization Parameters (by AIBN)

M_1	M_2	Q_2	e_2	r_1	r_2	r_1r_2
AL[a]	AAm[d]	1.18	1.30	1.69	0.21	0.35
	MAAm[e]	0.59	-0.88	0.62	0.12	0.07
	DAAm[e]	0.53	-0.54	0.95	0.26	0.25
MVK[b]	AAm	-	-	1.06	6.41	6.79
	MAAm	3.03	1.04	0.29	3.05	0.88
	DAAm	2.15	1.11	0.95	0.26	0.83
MVK[c]	AAm	-	-	0.88	1.18	1.04
	MAAm	2.67	1.21	3.37	2.04	0.76

[a] In DMF at 50°C.
[b] In dioxane at 60°C.
[c] In ethanol at 60°C.
[d] Data by Schulz et al. [7].
[e] By our unpublished data [8].

REFERENCES

[1] T. Itou and T. Otsu, J. Macromol. Sci.–Chem., A3, 197 (1963).
[2] G. Saini, A. Leoni, and S. Franco, Makromol. Chem., 144, 235 (1971).
[3] N. Yamashita, S. Morita, and T. Maeshima, J. Macromol. Sci.–Chem., A12(9), 1261 (1978).
[4] S. Morita, H. Inoue, N. Yamashita, and T. Maeshima, Ibid., A16(5), 1003 (1981).
[5] N. Yamashita, H. Inoue, and T. Maeshima, J. Polym. Sci., Polym. Chem. Ed., 17, 2739 (1979).
[6] S. Morita, K. Ikezawa, H. Inoue, N. Yamashita, and T. Maeshima, J. Macromol. Sci.–Chem., A17(9), 1495 (1982).
[7] R. C. Schulz, E. Kaiser, and W. Kern, Makromol. Chem., 58, 160 (1962).
[8] N. Yamashita, K. Ikezawa, S. Morita, Y. Kawabe, and T. Maeshima, Unpublished.
[9] M. Fineman and S. D. Ross, J. Polym. Sci., 5, 269 (1950).
[10] J. Alfrey and C. C. Price, Ibid., 2, 101 (1947).

Accepted by editor September 30, 1983
Received for publication October 28, 1983