Polymer Bulletin 30, 235–242 (1993)

Polymer Bulletin

Radical polymerization of fluoroalkyl 2-fluoroalkoxy methacrylate to new type of fluorine containing polymer

Bunichiro Yamada*, Shinji Tagashira, and Takayuki Otsu

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

Summary

Fluoroalkyl 2-fluoroalkoxymethylacrylates as 1,1-disubstituted ethylenic monomers were synthesized from methyl 2-hydroxymethylacrylate as a starting compound. These monomers readily polymerized to high molecular weight despite considerable steric hindrance expected. Electron withdrawing character of the fluoroalkyl groups rendered these monomers as much stronger electron accepting monomers than methyl methacrylate in copolymerization. The polymers obtained were characterized by thermal stability, glass transition temperature, and contact angle of the polymer film to water.

Introduction

Recently, polymerizable 1,1-disubstituted ethylenes bearing bulky substituents have drawn attention despite considerable steric hindrance expected. Among them, variety of alkyl 2-(substituted methyl)acrylates [1-6] which are difunctionally substituted ethylenic monomers have been derived from alkyl 2-hydroxymethylacrylate [7]. We have pointed out the presence of boundary of acceleration and suppression of the polymerization between ethyl 2-fluoromethylacrylate and ethyl 2-chloromethylacrylate [8] as well as methyl methacrylate (MMA) and methyl 2-ethylacrylate [9]. Furthermore, replacement of the chlorine in the substituent of the 2-chloromethylacrylate by bromine leads to reluctance of polymerization and copolymerization [8], and alternatively, the 2-bromomethylacrylate undergoes exclusively addition-fragmentation reaction in the polymerization with styrene (St) and methyl methacrylate (MMA) [10]. Methyl 2-phenoxymethylacrylate [4] which has a relatively low ceiling temperature has been shown to take place polymerization and the addition-fragmentation reaction simultaneously [11,12]. Such structural changes at the remote position from the reacting carbon-carbon double bond dramatically influence polymerization behavior of 1,1-disubstituted ethylenic monomers.

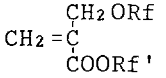
While methyl 2-alkoxymethylacrylates (MCMA's) exhibit different polymerization reactivities dependent on the carbon number of the alkoxy group, enhanced copolymerization reactivity of MCMA with St and MMA arising from the electron withdrawing character of the alkoxymethyl group has been noted [6]. Methyl 2-fluoroalkoxymethylacrylates (MCFMA's) bearing stronger electronegative groups than the alkoxymethyl group as the 2-substituent have been prepared by Mathias et

---

*Corresponding author

al. [13] and us [14] independently. These monomers polymerize rapidly, and the resulting polymers exhibited characteristics expected for fluoropolymers. Considering the higher polymerization and copolymerization reactivities of MCFMA than MCMA, we expected that the monomer with fluorine substitution to a higher extent such as fluoroalkyl 2-fluoroalkoxymethylacrylates (DCFMA's), which are stronger electron accepting monomers than MCFMA, polymerize readily to a new type of fluorine containing polymers.

In the present work, 2,2,2-trifluoroethyl 2-(2,2,2-trifluoroethoxymethyl)acrylate (DC_2F_3MA), 2,2,3,3-tetrafluoro-1-propyl 2-(2,2,3,3-tetrafluoro-1-propoxymethyl)acrylate (DC_3F_4MA), 2,2,3,3-tetrafluoro-1-propyl 2-(2,2,2-trifluoroethoxymethyl)acrylate ($C_3F_4C_2F_3MA$), and 2,2,2-trifluoroethyl 2-(2,2,3,3-tetrafluoro-1-propoxymethyl)acrylate ($C_2F_3C_3F_4MA$) were synthesized and polymerized with an expectation as highly polymerizable 2-substituted acrylate bearing a bulky and electronegative group:



$$CH_2=\underset{COORf'}{\overset{CH_2ORf}{C}}$$

Rf = Rf' = CH_2CF_3 (DC_2F_3MA)
Rf = Rf' = $CH_2CF_2CF_2H$ (DC_3F_4MA)
Rf = CH_2CF_3, Rf' = $CH_2CF_2CF_2H$ ($C_3F_4C_2F_3MA$)
Rf = $CH_2CF_2CF_2H$, Rf' = CH_2CF_3 ($C_2F_3C_3F_4MA$)

Experimental

DCFMA's were prepared by reaction of the 2-fluoroalkoxymethylacryloyl chloride with fluoroalcohol. The acryloyl chloride was synthesized by the reaction of 2-fluoroalkoxymethylacrylic acid which was synthesized by alkaline hydrolysis of MCFMA with thionyl chloride. Structures of DCFMA's were verified by ^1H- and ^{13}C-NMR spectroscopy. ^1H-NMR (400 MHz, $CDCl_3$) : DC_2F_3MA, δ = 3.90(q, 2H, OCH_2), 4.38(s, 2H, CH_2O), 4.56(q, 2H, $COOCH_2$), 6.06(s, 1H, CH=C), and 6.48 ppm (s, 1H, CH=C); DC_3F_4MA, δ = 3.89(t, 2H, OCH_2), 4.33(s, 2H, CH_2O), 4.58(t, 2H, $COOCH_2$), 5.88(tt, 1H, CF_2H), 5.92(tt, 1H, CF_2H), 6.00(s, 1H, CH=C), and 6.45 ppm(s, 1H, CH=C); $C_3F_4C_2F_3MA$, δ = 3.89(q, 2H, OCH_2), 4.37(s, 2H, CH_2O), 4.58 (tt, 2H, $COOCH_2$), 5.88(tt, 1H, CF_2H), 6.04(s, 1H, CH=C), and 6.45 ppm(s, 1H, CH=C); $C_2F_3C_3F_4MA$, δ = 3.89(tt, 2H, OCH_2), 4.33(s, 2H, CH_2O), 4.56(q, 2H, $COOCH_2$), 5.92(tt, 1H, CF_2H), 6.02(s, 1H, CH=C), and 6.47ppm(s, 1H, CH=C). ^{13}C-NMR (100 MHz, $CDCl_3$): DC_2F_3MA, δ = 60.66(q, $COO\underline{C}H_2$), 68.34(q, OCH_2), 70.33(s, CH_2O), 122.97(q, CF_3), 123.90(q, CF_3), 129.21(s, $\underline{C}H_2=C$), 134.90(s, $CH_2=\underline{C}$), and 163.70 ppm(s, C=O); DC_3F_4MA, δ = 59.87(t, $COO\underline{C}H_2$), 67.69(t, OCH_2), 70.38(s, CH_2O), 109.29 (tt, CF_2), 109.50(tt, CF_2), 114.15(tt, CF_2H), 114.99(tt, CF_2), 129.19(s, $\underline{C}H_2=C$), 135.00(s, $CH_2=\underline{C}$), and 163.87 ppm(s, C=O); $C_3F_4C_2F_3MA$, δ = 59.90(t, $COO\underline{C}H_2$), 68.28(q, OCH_2), 70.38 (s, CH_2O), 109.48(tt, CF_2), 114.13(tt, CF_2H), 123.88(q, CF_3), 129.18(s, $CH_2=\underline{C}$), 134.99(s, $\underline{C}H_2=C$), and 163.87 ppm(s, C=O); $C_2F_3C_3F_4MA$, δ = 60.71(q, 36.5 Hz, $COO\underline{C}H_2$), 67.81(t, OCH_2), 70.38(s, CH_2O), 109.26(tt, CF_2), 114.96(tt, CF_2H), 122.94(q, CF_3), 129.38(s, $CH_2=\underline{C}$), 134.86(s, $\underline{C}H_2=C$), and 163.68 ppm(s, C=O). Commercially available MMA, St, and isobutyl vinyl ether (IBVE) were distilled before use. The polymerizations and copolymerizations in dioxane were run in sealed tubes and

2,2'-azobisisobutyronitrile (AIBN) recrystallized from methanol was used as an initiator. After polymerization for a certain time, the contents of the ampoule were poured into hexane to precipitate the polymer or copolymer. Overall rate of the polymerization (R_p) was determined from the weight of the polymer isolated.

Copolymer compositions were calculated from fluorine analysis by combustion method [15] and from the intensity ratio of the resonances due to the aromatic and methyleneoxy protons in the ^{1}H-NMR spectra of the copolymer of DCFMA with St. The compositions of the copolymers with MMA and IBVE were also determined by using the intensity of the resonances of the methoxy and methineoxy protons in the ^{1}H-NMR spectra. Monomer reactivity ratios, r_1 and r_2, were evaluated by a non-linear least squares procedure [16].

Number and weight average molecular weight ($\bar{M}_n$ and $\bar{M}_w$) was measured by a TOSO 8000 series HPLC equipped with GPC columns and tetrahydrofuran as solvent. Light scattering measurement was carried out with an Otsuka DLS-700 photometer and dioxane was used as solvent. Thermogravimetric analysis (TGA) was done using a Shimadzu TG20 thermobalance and ca. 1.5 mg of polymer sample was heated in nitrogen atmosphere at a heating rate of 10°C/min, and initial temperature of degradation (T_{init}) and maximum degradation rate temperature (T_{max}) were determined. Glass transition temperature (T_g) was measured by Rigaku 8230B differential scanning calorimeter at a heating rate of 10°C/min. Contact angle of polymer film to water was measured at 25°C by a Erma contact angle meter G-I. Surface tension of polymer was estimated according to additivity of paracohl [17,18].

Results and discussion

Polymerization and copolymerization

Polymerizing MCMA and MCFMA, we have shown faster polymerization of these monomers than MMA [6,14]. Although the polymerizations of some MCMA's suffered from suppression due to relatively low ceiling temperatures resulting in diminish of the polymerization rate as the conversion raised [6], all the MCFMA's polymerized smoothly up to high conversions [14]. R_p's of DCFMA and MCFMA monomers at the initial stage of the polymerization are compared in Table 1. Although the GPC measurement showed lower molecular weight of poly(DCFMA) than poly(MMA), faster polymerization could not give lower molecular weight according to the standard kinetics of radical polymerization. $\bar{M}_n$ determined by GPC given in Table 1 seems to be too low when compared with $\bar{M}_w$ from the light scattering measurement. Slower polymerization of DC_3F_4MA than the other DCFMA's could be ascribable to reduction of R_p by steric hindrance to a some extent.

The ^{13}C-NMR spectra of DCFMA and poly(DCFMA) exhibited the polymer formation by cleavage of the carbon-carbon double bond. Resonances due to the carbons of the double bond of DCFMA at ca. 129 and 135 ppm disappeared in the spectra of the polymers, and the methylene and quaternary carbons in the main chain of poly(DCFMA) showed the resonances at ca. 42 and 50 ppm, respectively.

Table 1. Polymerization of DCFMA in dioxane at 60°C: [Monomer] = 2.0 mol/L and [AIBN] = 5 mmol/L

Monomer	$R_p \times 10^5$ (mol/L·s)	Polymer	
		$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
DC_2F_3MA	7.6	5.1	1.86
DC_3F_4MA	5.4	2.0	1.60
$C_3F_4C_2F_3MA$	10.9	3.4	1.92
$C_2F_3C_3F_4MA$	8.1	2.3[a]	1.92
MC_2F_3MA[b]	9.2	11.0	1.80
MC_3F_4MA[b]	10.1	6.3	1.98
MMA	4.6	9.6	1.92

a) $\bar{M}_w = 5 \times 10^5$ by light scattering measurement.
b) Ref. 14.

From the copolymer composition relations for the copolymerizations of DC_2F_3MA (M_1) with St and MMA (M_1) depicted in Fig. 1, r_1, r_2, Q_2, and e_2 were evaluated as summarized in Table 2. In the same table, r_1 and r_2 for the copolymerizations of other DCFMA's and their Q and e values are also shown. DCFMA exhibited higher reactivity than MCFMA bearing the corresponding fluoroalkoxymethyl group. As anticipated from the electronegative character of the fluoroalkyl group in each monomer, the value of e for DCFMA is apparently greater than that for MCFMA.

Narita et al. [19] have reported that the e values of 2,2,2-trifluoroethyl acrylate and methacrylate are greater than those of the methyl esters (e = 0.60 and 0.40) by 0.53 and 0.58, respectively. Similarly, the increase in e value

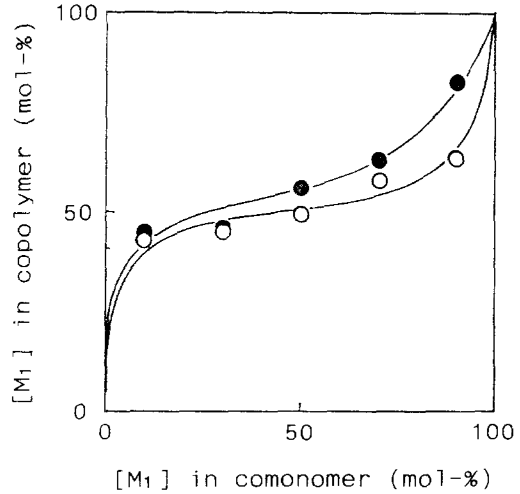


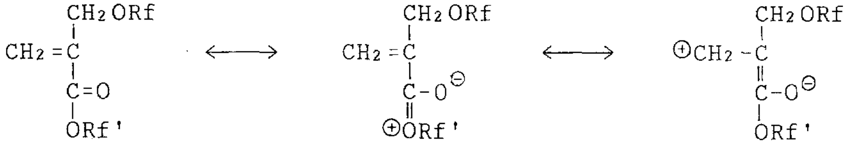
Fig. 1. Copolymer composition curves for copolymerizations of DC_2F_3MA (M_2) with St (○) and MMA (M_1) (●): $[M_1] + [M_2]$ = 2.0 mol/L and [AIBN] = 5.0 mmol/L. Curves are drawn for r_1 = 0.11 and r_2 = 0.05, and r_1 = 0.35 and r_2 = 0.04.

Table 2. Copolymerization parameters for copolymerization of DCFMA (M_2) with St and MMA (M_1) at 60°C

M_1	M_2	r_1	r_2	$1/r_2$	Q_2	e_2
St	DC_2F_3MA	0.11	0.05	9.1	1.50	1.46
St	$C_3F_4C_2F_3MA$	0.09	0.08	11.1	1.81	1.43
St	DC_3F_4MA	0.22	0.07	4.5	0.87	1.26
St	$C_2F_3C_3F_4MA$	0.14	0.06	7.1	1.25	1.37
MMA	DC_2F_3MA	0.35	0.04	2.9	4.86	2.45
MMA	DC_3F_4MA	0.80	0.05	1.3	1.92	2.22

by replacement of the methyl group of MC_2F_3MA (e = 0.92) with the trifluoroethyl group as the ester alkyl group leading to DC_2F_3MA (e = 1.46) is estimated to be 0.54. The tetrafluoropropyl group as a part of the 2-substituent and the ester alkyl group also bring about increases in e value. The increase in e value by replacement of the ethoxy group of methyl 2-ethoxymethylacrylate (e = 0.75) by the trifluoroethoxy group leading to MC_2F_3MA (e = 0.92) is 0.17. The difference in e value between methyl 2-ethoxymethylacrylate and DC_2F_3MA, 0.71, is in agreement with the summation of 0.54 and 0.17.

The greater increment in e value by the trifluoroethyl group as the ester alkyl group can be explained by a decrease and increase in contributions of the resonance structures of II and III, respectively, among the resonance structures of DFCMA, I, II, and III:



I II III

A larger Q value for DC_2F_3MA than MC_2F_3MA can also be accounted for by larger contribution of III arising from a decrease in contribution of II. The changes in the Q and e values by replacement of the methyl or ethyl group by the tetrafluoropropyl group can be interpreted similarly. The e value for DC_3F_4MA is smaller than that for DC_2F_3MA, indicating that the trifluoromethyl (CF_3) group in the trifluoroethyl group exhibits stronger electron withdrawing character than the tetrafluoroethyl (CF_2CF_2H) group in the tetrafluoropropyl group. Although larger e values for DCFMA's than MCFMA's can also be expected from larger chemical shifts of the 2-carbons of the former in ^{13}C-NMR spectra, an empirical equation predicting the e value derived [20] was not applicable to DCFMA and MCFMA.

The Q_2 and e_2 values calculated from the copolymerizations with MMA (M_1) are not agree with those from the copolymerization with St. These tendencies may imply that the steric interaction of the methyl and carbomethoxy groups of

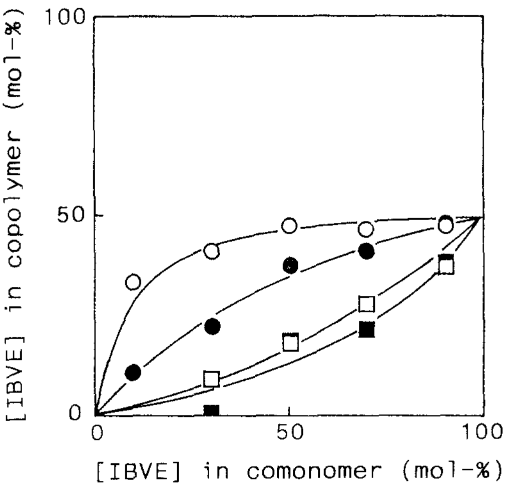


Fig. 2. Copolymer composition curves for copolymerizations of DC_2F_3MA (○), DC_3F_4MA (●), MC_2F_3MA (□), and MC_3F_4MA (■) with IBVE (M_1) in dioxane at 60°C: $[M_1] + [M_2] = 4.0$ mol/L and [AIBN] = 5.0 mmol/L

MMA and poly(MMA) radical with the 2-substituents of the fluoro-monomers and their polymer radicals in propagation can be anticipated, and polymerization and copolymerization of 1,1-disubstituted ethylene are likely to be readily susceptible to steric hindrance.

In accordance with the positively enhanced e value, the copolymerization of DC_2F_3MA (M_2) with IBVE (M_1) showed a highly alternating tendency ($r_1 = 0$ and $r_2 = 0.14$) as depicted in Fig. 2 unlikely to the copolymerization of MC_2F_3MA ($r_1 = 0$ and $r_2 = 3.82$). Apparently, electron withdrawing character arising from the fluorine substitution rendered the copolymerization of DC_2F_3MA and IBVE with the highly alternating tendency. Random propagations occurred in the copolymerizations of MC_2F_3MA (M_2) with IBVE (M_1) and MC_3F_4MA (M_2) with IBVE (M_1) ($r_1 = 0$ and $r_2 = 5.42$). Although DC_3F_4MA was also expected to be an electron accepting monomer in the copolymerization with IBVE (M_1), the alternating tendency observed was not so high ($r_1 = 0$ and $r_2 = 0.89$) in conformity with the lower e value given in Table 2.

Characterization of Polymer

Since new type of fluorine containing polymers were obtained, some characteristics of these polymers were examined. Tables 3 and 4 show solubility and thermal properties of the fluoropolymers. All the polymers from DCFMA were soluble in methanol as well as poly(MCFMA) [14]. This phenomenon could arise from an increase in polar interaction of the fluoroalkyl group with methanol. Acetone and dioxane which was used as solvent for the polymerization and copolymerization of DCFMA dissolved polymers of DCFMA.

Table 3. Solubility of poly(DCFMA)$^{a)}$

Polymer	n-Hexane	Benzene	Chloroform	Acetone	Methanol
DC$_2$F$_3$MA	X	X	X	O	O
DC$_3$F$_4$MA	X	S	S	O	O
C$_2$F$_3$C$_3$F$_4$MA	X	X	X	O	O
C$_3$F$_4$C$_2$F$_3$MA	X	X	X	O	O

a) O: Soluble, S: Swollen, X: Insoluble

Table 4. Thermal properties of poly(DCFMA)

Polymer	T_g (°C)	TGA (°C)	
		T_{init}	T_{max}
DC$_2$F$_3$MA	50	201	250
DC$_3$F$_4$MA	40	248	299
C$_3$F$_4$C$_2$F$_3$MA	53	243	261
C$_2$F$_3$C$_3$F$_4$MA	58	216	258
MC$_2$F$_3$MA	59	220$^{a)}$	308$^{a)}$
MC$_3$F$_4$MA	36	223$^{a)}$	329$^{a)}$
MMA	127$^{b)}$	245$^{b)}$	296,380$^{b)}$

a) Ref. 14. b) Ref. 21.

Table 5. Contact angle and surface tension of poly(DCFMA)

Polymer	Contact angle (degree)	Surface tension$^{a)}$ (mJ/m^2)
DC$_2$F$_3$MA	95	33.0
DC$_3$F$_4$MA	90	32.4
C$_3$F$_4$C$_2$F$_3$MA	92	32.6
C$_2$F$_3$C$_3$F$_4$MA	92	32.6
MC$_2$F$_3$MA	92	35.1
MC$_3$F$_4$MA	90	34.2
MMA	77$^{b)}$	42.5

a) Calculated from the additivity in refs. 17 and 18.
b) Ref. 14.

Poly(DCFMA)'s exhibited T_g in the range of 40 to 58°C which are apparently lower and higher than those for poly(MMA)(127°C) [21] and poly(methyl acrylate)(around 20°C) [22], respectively, and all the polymers prepared were thermally less stable than poly(MMA) as confirmed by TGA as shown in Table 4. Contact angles of poly(DCFMA) films to water, which are significantly higher than that of poly(MMA) film, are similar to those of poly(MCFMA) as shown in Table 5. It is supposed that the polymers have sufficient amount of the fluoroalkyl group to occupy the surface of the film as pointed out by Iwatsuki et al. [23] for copolymers of fluoroalkyl 2-fluoroalkylacrylates.

In summary, DCFMA's polymerized readily to high molecular weight, and electron withdrawing character of the fluoroalkyl group as the ester alkyl group and a part of the 2-substituent enhanced reactivity in copolymerizations with St and MMA. High alternating tendency in the copolymerization with IBVE is noted. The stronger electron withdrawing character of the trifluoroethyl group than the tetrafluoropropyl group was clearly observed in the copolymerizations. Characterization of poly(DCFMA) revealed that the fluoroalkyl group as the ester alkyl group does not affect remarkably the solubility, T_g, TGA, and the contact angle.

References

1) Reed, S. F. and Baldwin, M. G., *J. Polym. Sci.*, **A2**, 1355 (1964).
2) Powell, J. A. and Graham, R. K., *J. Polym. Sci.*, **A3**, 3451 (1965).
3) Warren, S. C. and Mathias, L. J., *J. Polym. Sci.: Part A: Polym. Chem.*, **28**, 1637 (1990).
4) Lenz, R. W., Saunders, K., Balakrishnan, T., and Hatada, K., *Macromolecules*, **12**, 392 (1979).
5) Sato, T., Morita, N., Tanaka, H., and Ota, T., *Makromol. Chem.*, **191**, 2599 (1990).
6) Yamada, B., Satake, M., and Otsu, T., *Makromol. Chem.* **192**, 2713 (1991).
7) Hoffmann, H. M. R. and Rabe, J. *Angew. Chem., Int. Ed. Eng.*, **22**, 795 (1983).
8) Yamada, B. and Otsu, T., *Makromol. Chem.* **192**, 333 (1991)
9) Chikanishi, K. and Tsuruta, T., *Makromol. Chem.*, **81**, 198 (1965).
10) Yamada, B., Kobatake, S., and Otsu, T., *Polym. J*, **24**, 281 (1992).
11) Yamada, B., Satake, M., and Otsu, T., *Polym. J.*, **24**, 563 (1992).
12) Yamada, B., Kobatake, S., Satake, M., and Otsu, T., *J. Polym. Sci.: Part A: Polym. Chem.* in press.
13) Jariwala, C. P., Sundell, P. G., Hoyle, C. E., and Mathias, L. J., *Macromolecules*, **24**, 6352 (1991).
14) Yamada, B., Satake, M., and Otsu, T., *J. M. S.-Pure Appl. Chem.*, **A29**, 533 (1992).
15) Schoniger, W., *Mikrochim. Acta*, **1956**, 869.
16) Yamada, B., Itahashi, M., and Otsu, T., *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1719 (1978).
17) Van Krevelen, D. W., "*Properties of Polymers*", 2nd Ed, Elsevier, 1976.
18) Rabek, J. F., "*Experimental Methods in Polymer Chemistry*", Wiley, 1980.
19) Narita, T., Hagiwara, T., and Hamana, H., *Makromol. Chem., Rapid Commun.* **6**, 5 (1985).
20) Herman, J. J. and Teyssie, Ph., *Macromolecules,* **11**, 839 (1978).
21) Matsumoto, A., Tanaka, S., and Otsu, T., *Macromolecules*, **24**, 4017 (1991).
22) Peyser, P., "*Polymer Handbook*", 3rd Ed., Brandrup, J. B. and Immergut, E. H., Ed., Wiley, New York, 1989, p. VI/209.
23) Iwatuski, S., Kondo, A., and Sakai, Y., *Nippon Kagaku Kaishi*, **1985**, 1884.

Accepted January 18, 1993 S