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Radical Polymerization and Copolymerization of Methyl α-(Fluoroalkoxymethyl)acrylates and Characterization of Their Polymers

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RADICAL POLYMERIZATION AND COPOLYMERIZATION OF METHYL α-(FLUOROALKOXYMETHYL)ACRYLATES AND CHARACTERIZATION OF THEIR POLYMERS*

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ABSTRACT

Representatives of a new type of fluorine-containing monomer, methyl α-(fluoroalkoxymethyl)acrylates (MCFMA's), were prepared. The fluoroalkoxy groups introduced were OCH_2CF_3, $OCH_2CF_2CF_2H$, and $OCH(CF_3)_2$. All the monomers synthesized readily polymerized to number-average molecular weights of 55,000 to 110,000 at a 2 mol/L monomer concentration in dioxane using 5×10^{-3} mol/L of 2,2′-azobisisobutyronitrile at 60°C. The polymerization rate tended to decrease slightly with an increase in the size of the alkoxy group. Copolymerization of MCFMA's with styrene revealed that the fluoroalkoxymethyl group functions as an electron-attracting group depending on the number of fluorine atoms. According to thermogravimetric analysis, poly(MCFMA)'s were thermally less stable than poly(methyl methacrylate). Greater contact angles of the polymers from MCFMA's with water than poly(methyl methacrylate) were observed.

INTRODUCTION

We have reported that methyl α-(alkoxymethyl)acrylates (MCMA) including methyl α-(ethoxymethyl)acrylate (MC_2MA), radically homopolymerize rapidly de-

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*Dedicated to Professor Otto Vogl on the occasion of his 65th birthday.

spite the presence of the large α-substituent [1]. The enhanced reactivity by α-ethoxymethyl substitution toward the poly(styrene) radical has been accounted for by the electron-withdrawing character of the α-substituent [2]. However, a larger alkoxymethyl group apparently reduced the polymerization rate and the copolymerization reactivity.

These findings demonstrate the possibility that a structural change in a position remote from the carbon-carbon double bond could affect polymerization and copolymerization behavior of α-substituted acrylic monomers. Replacement of the hydrogen of the alkoxymethyl group with fluorine was expected to afford a polymerizable monomer bearing a substituent with an increased electron-attracting character.

The effects of several types of fluorine substitutions on polymerization of acrylic monomers have been examined. For ethyl α-(fluoromethyl)acrylate (EFMA), polymerizing to high molecular weight, and with a positively larger *e* value, 1.02, than that for methyl methacrylate (MMA) has been evaluated, whereas suppression of polymerization or copolymerization by the steric hindrance caused by the α-substituent has not been observed [3-5]. Methyl α-(trifluoromethyl)acrylate, for which the *e* value has been estimated to be 2.9, exhibits a relatively low ceiling temperature [6-8] because of a larger trifluoromethyl group than expected from a negatively larger Taft's steric substituent constant ($E_s = -1.61$) than that for the methyl group ($E_s = -1.24$) [2].

Copolymerizations of methacrylic esters bearing fluorine-containing ester alkyl groups have been reported. The electron-withdrawing effect of the fluoroalkyl groups through the ester linkage has been confirmed by positively enhanced *e* values [9-11], and the *Q* values for these monomers are also greater than that for methyl methacrylate (MMA) [9-12]. However, fluorine directly bound to the reacting carbon-carbon double bond behaves as a weak electron-withdrawing substituent because of the interaction of the unshared electron pair of fluorine with the π-electrons of the double bond [13]. Thus, substitution with fluorine in a polymerizable monomer results in a substantial increase in the electron-accepting character except for α-fluoroacrylates.

In the present study, methyl α-(fluoroalkoxymethyl)acrylates (MCFMA's) were synthesized. In addition to the effects of the fluoroalkoxymethyl group on the polymerization and copolymerization reactivities, the effects of fluorine substitution on the some properties of the resultant polymers are also described in this article. The monomers synthesized were methyl α-(2,2,2-trifluoroethyoxymethyl)acrylate (X = Y = H, Z = CF_3; MC_2F_3MA), methyl α-(2,2,3,3-tetrafluoro-1-propoxymethyl)acrylate (X = Y = H, Z = CF_2CF_2H; MC_3F_4MA), and methyl α-(1,1,1,3,3,3-hexafluoro-2-propoxymethyl)acrylate (X = H, Y = Z = CF_3; MC_3F_6MA):

$$CH_2{=}C(CH_2OCXYZ)COOCH_3$$

EXPERIMENTAL

Materials

MCFMA's were prepared by reaction of methyl α-(bromomethyl)acrylate [14] with the corresponding fluoroalcohols in the presence of an equimolar amount of triethylamine overnight in dioxane at room temperature. The reaction mixture was poured into a large amount of water and the organic layer was separated. The solvent and the unchanged alcohol were evaporated, and MCFMA was distilled under reduced pressure. Bp: MC_2F_4MA, 60°C/1 mmHg; MC_2F_3MA, 46°C/1 mmHg; MiC_3F_6MA, 50°C/1 mmHg.

^{1}H-NMR ($CDCl_3$): MC_2F_3MA, $\delta = 3.76$ (s, 3H, OCH_3), 3.91 (m, $J_{H\text{-}F} = 8.9$ Hz, 2H, OCH_2), 4.36 (s, 2H, CH_2O), 5.92 (t, 1H, $CH_2{=}C$), 6.36 (t, 1H, $C\underline{H}{=}C$); MC_3F_4MA, $\delta = 3.74$ (s, 3H, OCH_3), 3.90 (m, $J_{H\text{-}F} = 20.7$ Hz, 2H, OCH_2), 4.32 (s, 2H, CH_2O), 5.87 (t, 1H, $C\underline{H}{=}C$), 6.26 (tt, $J_{H\text{-}F} = 53.2$ and 5.3 Hz, 1H, CF_2H), 6.30 (t, 1H, $C\underline{H}{=}C$); MiC_3F_6MA, $\delta = 3.76$ (s, 2H, OCH_3), 4.36 (m, 1H, OCH), 4.58 (s, 2H, CH_2O), 5.96 (t, 1H, $C\underline{H}{=}C$), 6.40 (t, 1H, $C\underline{H}{=}C$). ^{13}C-NMR: MC_2F_3MA, $\delta = 51.6$ (OCH_3), 68.1 ($J_{^{13}C\text{-}F} = 33.7$ Hz, OCH), 70.5 (OCH_3), 123.9 ($J_{^{13}C\text{-}F} = 300.0$ Hz, CF_3), 126.6 ($\underline{C}H_2{=}C$), 136.1 ($CH_2{=}\underline{C}$), 165.7 ($C{=}O$); MC_3F_4MA, $\delta = 51.0$ (OCH_3), 67.3 ($J_{^{13}C\text{-}F} = 28.0$ Hz, OCH_2), 70.2 (CH_2O), 109.2 ($J_{^{13}C\text{-}F} = 32.3$ Hz, CF_2H), 115.0 ($J_{^{13}C\text{-}F} = 249.4$ and 31.9 Hz, CF_2), 126.1 ($\underline{C}H_2{=}C$), 136.2 ($CH_2{=}\underline{C}$), 165.5 ($C{=}O$): MiC_3F_6MA, $\delta = 52.6$ (OCH_3), 74.3 (CH_2O), 77.4 ($J_{^{13}C\text{-}F} = 32.2$ Hz, OCH), 122.7 ($J_{^{13}C\text{-}F} = 220.8$ Hz, CF_3), 129.4 ($\underline{C}H_2{=}C$), 136.6 ($CH_2{=}\underline{C}$), 166.7 ($C{=}O$).

Styrene (St) and MMA were distilled under reduced pressure before use. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Commercial *tert*-butyl peroxide (TBP) was distilled under reduced pressure, 50°C/90 mmHg.

Polymerization and Copolymerization

Polymerization and copolymerization of MCFMA were run in sealed tubes under vacuum. After polymerization for a desired time, the contents of the tube were poured into a large amount of *n*-hexane to precipitate the resulting polymer or copolymer.

The compositions of St-MCFMA copolymers were calculated from the intensity ratios of the resonances of the phenyl protons to those of the protons of the rest of the copolymer in their ^{1}H-NMR spectra. The compositions of MMA-MC_3F_4MA copolymers were also determined by NMR spectroscopy based on the intensity ratios of the resonances due to the protons of the difluoromethyl group to those of the two types of methoxy and methyleneoxy protons. Monomer reactivity ratios were evaluated by a nonlinear least-squares procedure [15].

Number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) were measured with a TOSO 8000 series HPLC equipped with G2000HXL, G4000HXL, G4000HXL, and G6000HXL columns, connected in this order. Tetrahydrofuran was used as the eluent, and standard poly(St) was employed for calibration.

Spectroscopy

^{1}H-NMR spectra at 60 and 400 MHz were recorded by Hitachi R24B and JEOL GX400 spectrometers, respectively. The ^{13}C-NMR spectra were recorded on a JEOL GX400 spectrometer (100 MHz) with chloroform-d_1 as solvent and tetramethylsilane as internal reference.

The ESR spectra were determined with a Bruker ESP 300 spectrometer, and the polymerization in the cavity was initiated by irradiation with a Ushio 500 W xenon lamp.

Measurements

Thermogravimetric analysis (TGA) was performed by a Shimadzu TG20 thermobalance using ca. 1.5 mg of the polymer sample at a heating rate of 10°C/min. Differential scanning calorimetory (DSC) was run using a Du Pont 1090 at a heating rate of 10°C/min. Softening temperatures of the polymers were visually measured as the temperatures where the polymer sample between slide glasses was caused to deform in a Yanagimoto Micromelting Point Apparatus.

The contact angles of water and hexadecane on the polymer film were determined by an Erma contact angle meter G-I at 23°C.

RESULTS AND DISCUSSION

Homopolymerization of MCFMA

Polymerization of MCFMA (2 mol/L) in a homogeneous solution was run in dioxane at 60°C using AIBN as an initiator. Conversion-time plots are shown in Fig. 1. Table 1 lists R_p obtained as the slope of the conversion-time relation and $\overline{M}_n$ of the resultant polymers together with those of MCMA's and poly(MCMA)'s. All the fluorine-containing monomers proceeded to polymerize to 70% conversion or above, and the effect of the ceiling temperature (T_c) was not observed. Since the size of the fluoroalkoxy groups is considered to be similar to the respective alkoxylmethyl groups, the T_c's of the α-substituted acrylates seem to be affected by not only steric factors but also by polar factors.

The R_p of MCFMA was found to increase in the order MC_3F_4MA > MC_2F_3MA > MiC_3F_6MA, and the $\overline{M}_n$ of poly(MC_2F_3MA) was higher than that of poly(MC_3F_4MA) by a factor of 1.75. Table 2 shows the results of MC_3F_4MA polymerization at higher monomer concentrations, and polymers of higher molecular weights were obtained.

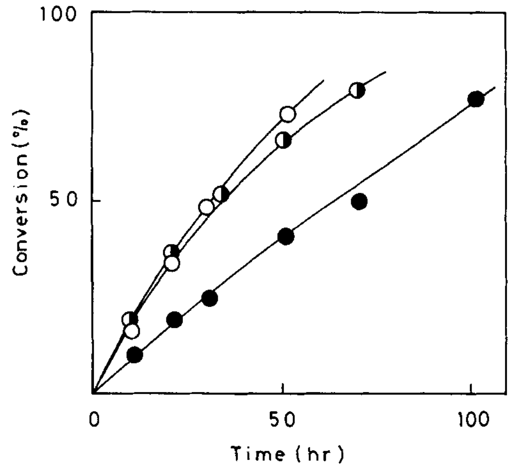

FIG. 1. Plot of conversion versus time for polymerization of MC_2F_3MA (○), MC_3F_4MA (◑), and MiC_3F_6MA (●) in dioxane at 60°C: [MCFMA] = 2.0 mol/L and [AIBN] = 5.0×10^{-3} mol/L.

TABLE 1. Polymerization of MCFMA in Dioxane at 60°C[a]

Monomer[b]	$R_p \times 10^5$, mol/L·s	$\overline{M}_n \times 10^{-4}$ [c]	$\overline{M}_w/\overline{M}_n$ [c]
MC_2F_3MA	9.2	11.0	1.80
MC_3F_4MA	10.1	6.3	1.98
MiC_3F_6MA	4.3	5.5	1.70
MC_2MA	8.5	4.2	1.92
MC_3MA[d]	6.0	3.7	1.53
MiC_3MA[e]	4.0	1.3	1.77
MMA	4.6	9.6	1.92

[a] [AIBN] = 5.0 × 10^{-3} mol/L.
[b] [MCFMA] = 2.0 mol/L.
[c] Determined by GPC.
[d] MC_3MA, methyl α-(*n*-propoxymethyl)acrylate.
[e] MiC_3MA, methyl α-(isopropoxymethyl)acrylate.

Among the MCMA monomers, R_p decreased in the order MC_2MA > MC_3MA > MiC_3MA [1]. Since the same order is expected for increasing size of the alkoxy group, steric hindrance was pointed out as one of the important factors for determining the R_p of MCMA. A faster polymerization of MCFMA than MCMA cannot be explained solely by the steric effect of the α-substituent, since the fluoroalkoxymethyl groups are expected to be as large as the respective alkoxymethyl groups. The faster propagation could be caused by an increased polar effect by the fluorine substitution.

The ESR spectrum of poly(MC_3F_4MA) was observed in a homogeneous solution at room temperature; MC_2F_3MA and MiC_3F_6MA also gave the respective propagating radicals which were detected by ESR spectroscopy under similar conditions. Figure 2 shows the 5-line spectrum of poly(MC_3F_4MA) radical with a line spacing of ca. 12.6 G, which is superimposable with that of the poly(MC_4MA) radical [1]. The fluorine substitution does not affect the splitting pattern.

Copolymerization Reactivity of MCFMA

Copolymerizations of St (M_1) with MC_2F_3MA, MC_3F_4MA, and MiC_3F_6MA (M_2) were initiated with AIBN in dioxane at 60°C. The results of the copolymeriza-

TABLE 2. Radical Polymerization of MC_3F_4MA for 2 h

[MC_3F_4MA], mol/L	[Initiator], mol/L	Temperature, °C	Conversion, %	$\overline{M}_n \times 10^{-4}$
4.46[a]	AIBN, 5.0 × 10^{-3}	60	51	22.8
5.42[b]	TBP, 2.5 × 10^{-2}	30	27	33.6

[a] Heterogeneous polymerization in benzene.
[b] Bulk polymerization with UV irradiation.

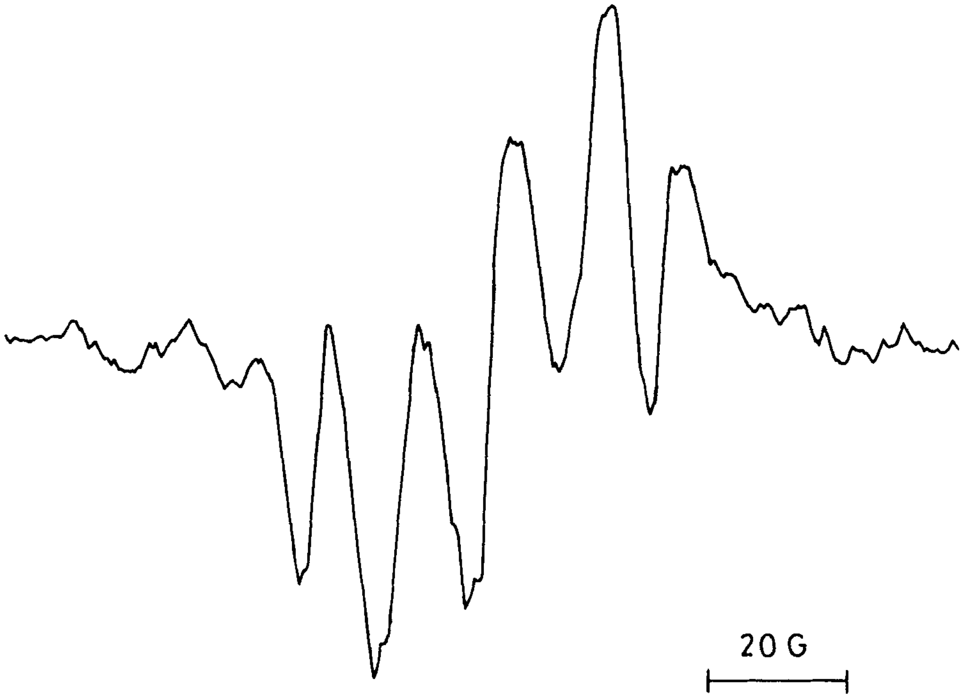

FIG. 2. ESR spectrum of poly(MC_3F_4MA) radical observed during AIBN-sensitized polymerization in dioxane initiated with UV irradiation at 25°C: [MC_3F_4MA] = 2.0 mol/L and [AIBN] = 5.0×10^{-2} mol/L.

tion are shown in Table 3, and Fig. 3 depicts the comonomer–copolymer composition curves.

The relative reactivities toward poly(St) radical, estimated as $1/r_1$, are given in the same table, and fluorine substitution is found to result in higher reactivities of MCFMA than of MCMA. Among the fluorine-containing monomers, MiC_3F_6MA bearing the most electronegative alkoxy group is more reactive than MiC_3MA by a factor of 1.8. The e value for MiC_3F_6MA, 1.25, is greater than those for MiC_3MA, 0.69, and ethyl α-(fluoromethyl)acrylate, 1.02 [3]. We can deduce that the electron-attracting power increases in the order $CH_2CF_2CF_2H < CH_2CF_3 < CH(CF_3)_2$. The Q values are similar to that of MMA, showing that the enhanced reactivity is ascribable mainly to the polar effect of the fluoroalkoxy group.

For copolymerization of MC_3F_4MA (M_2) with MMA (M_1) at 60°C, $r_1 = 1.43$ and $r_2 = 0.61$ were evaluated as shown in Fig. 3 and Table 3. The estimates of the r_1 and r_2 values, 1.28 and 0.63, using the Q and e values for MC_3F_4MA calculated from the copolymerization with St and the Q and e values for MMA are in fair agreement with the experimentally determined values. The significant steric effect of the α-substituent could not be expected in copolymerization.

The increase in the e value by fluorine substitution can be confirmed by ^{13}C-NMR spectroscopy [17]. Table 4 shows the chemical shifts of the α- and β-carbons of MCFMA and the related monomers. The chemical shifts for the α-carbon are in the range of 135.5 to 137.8 ppm. However, the resonance of the β-carbon of

TABLE 3. Copolymerization Parameters for Copolymerizations of MCFMA and MCMA (M_1) with St and MMA (M_2)

M_1	M_2	r_1	r_2	$1/r_1$	Q_2	e_2
St	MC_2F_3MA	0.26	0.20	3.8	0.97	0.92
St	MC_3F_4MA	0.37	0.17	2.7	0.70	0.87
St	MiC_3F_6MA	0.23	0.07	4.3	0.86	1.25
St	MC_2MA	0.37	0.24	2.7	0.78	0.75
St	MC_3MA	0.47	0.29	2.1	0.69	0.61
St	MiC_3MA	0.41	0.26	2.4	0.74	0.69
St	EFMA[a]	0.31	0.11	3.2	0.74	1.04
St	MMA[b]	0.52	0.46	1.9	0.74	0.40
MMA	MC_3F_4MA	1.43	0.61	0.7	0.60	0.77

[a] Ethyl α-(fluoromethyl)acrylate from Ref. 3.
[b] Ref. 16.

MC_2MA at 124.1 ppm shifts to 129.4 ppm for that of MiC_3F_6MA. The tendencies observed also indicate that the electron-withdrawing power of the fluoroalkoxy group increases in the order $CH_2CF_2CF_2H < CH_2CF_3 < CH(CF_3)_2$.

Characterization of Poly(MCFMA)

Since MCFMA's are a new series of fluorine-containing acrylic monomers, the respective polymers were characterized by solubility, thermal properties, and contact angle measurement. Solubilities of poly(MCFMA)'s are summarized in Ta-

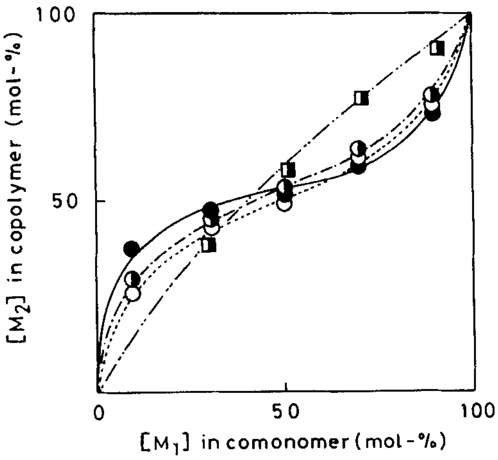

FIG. 3. Comonomer-copolymer composition curves for St (M_1)-MC_2F_3MA (○), MC_3F_4MA (◑), and MiC_3F_6MA (●) (M_2), and for MMA (M_1)-MC_3F_4MA (M_2) (◧) copolymerizations in dioxane at 60°C.

TABLE 4. Chemical Shifts of α- and β-Carbons of Carbon-Carbon Double Bond of MCFMA and MCMA in ^{13}C-NMR Spectra

Monomer[a]	Chemical shift, ppm β-Carbon	 α-Carbon
MC_2F_3MA	126.6	136.1
MC_3F_4MA	126.1	136.2
MiC_3F_6MA	129.4	136.6
MC_2MA	124.1	137.1
MC_3MA	125.3	137.4
MiC_3MA	125.0	137.8
EFMA[a]	126.7	135.6
MMA	124.0	135.5

[a] Ref. 3.

ble 5. An increase in the extent of the fluorine substitution leads to a decrease of the solubilities in *n*-hexane and benzene, and all poly(MCFMA)'s examined in which the $\overline{M}_n$'s range from 55,000 to 110,000 are soluble in methanol.

The TGA thermogram of poly(MC_2F_3MA) is shown in Fig. 4. No residue remained at 400°C, and thermal decomposition to the monomer through chain reaction is anticipated. The initial degradation temperature (T_{init}) and maximum degradation rate temperature (T_{max}) for poly(MiC_3F_6MA) together with those for poly(MC_3F_4MA) and poly(MC_2F_2MA) are summarized in Table 6. While the T_{init} and T_{max} of poly(MCFMA) are higher than those of poly(MCMA), α-alkoxymethyl and α-fluoroalkoxymethyl substitutions resulted in thermally less stable polymers than poly(MMA).

Table 6 compares the softening temperatures of the polymers, which were measured as the temperature where deformation of the sample was visually ob-

TABLE 5. Solubility of Poly(MCFMA) and Poly(MCMA) at Room Temperature[a]

Polymer	*n*-Hexane	Benzene	Chloroform	Acetone	Methanol
Poly(MC_2F_2MA)	X	O	O	O	O
Poly(MC_3F_4MA)	X	△	O	O	O
Poly(MiC_3F_6MA)	X	X	△	O	O
Poly(MC_2MA)	X	O	O	O	O
Poly(MC_3MA)	X	O	O	O	△
Poly(MiC_3MA)	X	O	O	O	X
Poly(MC_4MA)	O	O	O	O	X

[a] O = soluble, X = swollen, and △ = insoluble.

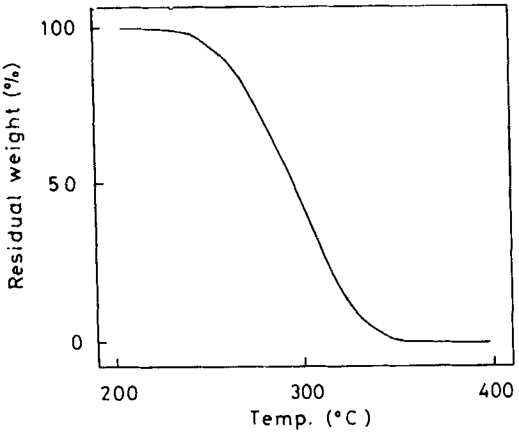

FIG. 4. TGA thermogram of poly(MC_2F_3MA).

TABLE 6. Thermal Properties of Poly(MCFMA) and Poly(MCMA)

Polymer	TGA T_{init}, °C	TGA T_{max}, °C	Softening temperature, °C	T_g, °C
Poly(MC_2F_3MA)	220	308	120-136	–
Poly(MC_3F_4MA)	223	300	110-134	–
Poly(MiC_3F_6MA)	252	329	105-117	51
Poly(MMA)	290	390	>200	104

TABLE 7. Contact Angle of Poly(MCFMA) at 23°C

Polymer	γ, mJ/cm^2	Contact angle, degree: Water	Contact angle, degree: *n*-Hexadecane
Poly(MC_2F_3MA)	35.1	90	39
Poly(MC_3F_4MA)	34.2	79	31
Poly(MiC_3F_6MA)	31.7	93	52
Poly(MMA)	42.5	77	–

served, because DSC curves of some poly(MCFMA)'s did not show clear inflections. Since the softening temperature is usually higher than T_g, the T_g's of poly(MCFMA) are likely to be lower than that of poly(MMA).

Table 7 shows the contact angles of water at 23°C. All the polymers of MCFMA showed greater contact angles than poly(MMA). The observed tendency coincides with that predicted by the surface tension (γ) calculated from contributions to parachor and molar volume except for poly(MC_2F_3MA) [18]. Probably the trifluoromethyl group in the alkoxymethyl group enhances the contact angle more than the estimate from the parachor.

CONCLUSION

MCFMA which polymerized to high molecular weight exhibited higher reactivities than MCMA in copolymerization with St. Since the bulkiness of the fluoroalkyl group could not be less than that of the corresponding alkyl group, the enhanced reactivities in polymerization and copolymerization should arise from the strong electron-attracting character of the former. Unlike MCMA polymerization, the polymerization of MCFMA at 60°C was not affected by ceiling temperature. These findings indicate that the fluoroalkyl group significantly influences the polymerization and copolymerization behavior through the CH_2O group.

Poly(MCFMA) was thermally less stable, as were the polymers from acrylic esters bearing bulkier α-substituents like poly(MCMA), than poly(MMA). All the polymers from MCFMA's seemed to show a lower T_g than that of poly(MMA). The greater contact angle of poly(MCFMA) than that of poly(MMA) is one of the characteristics of the fluoropolymers.

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REFERENCES

[1] B. Yamada, M. Satake, and T. Otsu, *Makromol. Chem.*, *192*, 2713 (1991).
[2] C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis of Chemistry and Biology*, Wiley-Interscience, New York, 1979.
[3] B. Yamada and T. Otsu, *Makromol. Chem.*, *192*, 333 (1991).
[4] S. F. Reed and M. G. Baldwin, *J. Polym. Sci.*, *A2*, 1355 (1964).
[5] J. A. Powell and R. K. Graham. *Ibid.*, *A3*, 3451 (1965).
[6] H. Ito, D. C. Miller, and C. G. Wilson, *Macromolecules*, *15*, 915 (1982).
[7] S. Iwatsuki, A. Kondo, and H. Harashima, *Ibid.*, *17*, 2473 (1984).
[8] H. Ito, B. Giese, and R. Engelbrecht, *Ibid.*, *17*, 2204 (1984).

[9] T. Narita, T. Hagiwara, and H. Hamana, *Makromol. Chem., Rapid Commun.*, *6*, 5 (1985).
[10] A. G. Pittman, B. A. Ludwig, and D. L. Sharp, *J. Polym. Sci., A-1*, *6*, 1741 (1968).
[11] A. Karpatyova, J. Barton, and O. Paleta, *Makromol. Chem., Rapid Commun.*, *8*, 621 (1987).
[12] A. Karpatyova, J. Barton, and O. Paleta, *Makromol. Chem.*, *191*, 2901 (1991).
[13] B. Yamada, T. Kontani, M. Yoshioka, and T. Otsu, *J. Polym. Sci., Polym. Chem. Ed.*, *22*, 2381 (1984).
[14] J. Villieras and M. Rambaud, *Synthesis*, p. 924 (1982).
[15] B. Yamada, M. Itahashi, and T. Otsu, *J. Polym. Sci., Polym. Chem. Ed.*, *16*, 1719 (1978).
[16] R. I. Greenly, in *Polymer Handbook*, 3rd ed. (J. Brandrup and E. H. Immergut, eds.), Wiley, 1990, p. II/153.
[17] J. J. Herman and Ph. Teyssie, *Macromolecules*, *11*, 839 (1978).
[18] D. W. van Krevelen, *Properties of Polymers*, Elsevier, 1976, Chap. 8.

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