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but since

$$\int_0^1 P(\phi) \ln P(\phi)\, d\phi = 0.14$$

so

$$\Delta G = N_d kT\left(\frac{f-1}{f}\right)(\ln V_B - 0.14)$$

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Synthesis and Polymerization of Methyl α-Fluoroacrylate

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ABSTRACT: Methyl α-fluoroacrylate (MFA) has been synthesized and both homopolymerized and copolymerized by bulk, solution, and emulsion methods. The reaction of methyl α-chloroacetate with KF gave methyl α-fluoroacetate, which was treated successively with dimethyl oxalate, NaH, paraformaldehyde, and sodium methoxide to yield MFA. The kinetics of MFA homopolymerization and copolymerization has been investigated in acetonitrile, using azobis(isobutyronitrile) (AIBN) as an initiator. The rate of polymerization (R_p) could be expressed by $R_p = k[\text{AIBN}]^{0.6}[\text{MFA}]^{1.1}$. The overall activation energy was calculated to be 73.6 kJ/mol. Thermogravimetric analysis of poly(methyl α-fluoroacrylate) showed a 10% weight loss at 350 °C in N_2. The glass transition temperature (T_g) of poly(methyl α-fluoroacrylate) was observed to be 128 °C by thermomechanical analysis. The relative reactivity ratios of MFA (M_1) copolymerizations with styrene ($r_1 = 0.15$, $r_2 = 0.62$) and methyl methacrylate ($r_1 = 0.36$, $r_2 = 1.17$) were obtained. Applying the Q, e scheme (in styrene copolymerizations) led to $Q = 0.47$ and $e = 0.73$ for MFA. This value of Q is less than the values of Q for the chlorine and bromine analogues.

The necessity for manufacturing very fine patterns of submicron size on integrated circuit devices has increased.[1] Electron-beam[2,3] and X-ray[4,5] lithography offer higher resolution than the conventional UV method. Such fabrications require resists which are sensitive to an electron beam or X-rays. Resist polymers which degrade by chain scission to give lower molecular weight materials are called positive resists. Those that cross-link upon irradiation are

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known as negative resists. A good positive resist should undergo the highest possible number of chain scissions per unit of absorbed radiation dose.

It is known that the introduction of an electron-withdrawing or electronegative substituent at the quaternary carbon may increase the radiation degradation susceptibility of α-substituted acrylate polymers. Helbert et al. reported[6,7] that poly(methyl α-chloroacrylate) (PMCA) degraded by chain scission more readily than poly(methyl methacrylate) (PMMA). However, PMCA also undergoes significant linking ($G_x \simeq 0.7$), which results, presumably, from dissociative electron capture of the α chlorine.[7] The electron affinities of chlorine and fluorine, when bonded to carbon, are about equal, but the C–F bond strength is greater than that of the C–Cl bond. This suggested that poly(methyl α-fluoroacrylate) (PMFA) might not undergo dissociative electron capture. Therefore, the G_x value of PMFA might be significantly lower than the 0.7 value of PMCA.[7] Thus, poly(methyl α-fluoroacrylate) (PMFA) was considered a good candidate polymer for electron-beam and X-ray resist studies.

However, except for a few patents[8] no reports have been published on the synthesis of MFA and its polymerization. We now report the successful preparation of MFA, its homopolymerization, and its copolymerization with vinyl monomers. Kinetic studies of the radical homopolymerization of MFA are also described.

Experimental Section

Materials. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Acetonitrile was purified by distillation from phosphorus pentoxide. The other reagents were used without further purification. The monomers, styrene (St), methyl methacrylate (MMA), and methacrylonitrile (MCN), were purified by usual methods.

Preparation of Methyl α-Fluoroacetate. (a) Into a 500-mL three-necked, round-bottomed flask, fitted with a mechanical stirrer and distilling head, were added freshly distilled acetamide (35 g), methyl α-chloroacetate (108 g, 1 mol), and potassium fluoride (75.4 g, 1.3 mol, dried at 120 °C for 1 day). The mixture was heated with stirring. The color of the mixture gradually darkened. After refluxing began, a small amount of methanol was distilled. The temperature at the distilling head then rose to 100 °C and stayed at 100–108 °C during the reaction, which required about 2 h. During this time, methyl α-fluoroacetate distilled from the reaction vessel and was collected. At the end of the reaction, the temperature fell gradually to 70 °C. The crude distillate weighed 75 g. After two redistillations, 60 g (65%) of methyl α-fluoroacetate was obtained; bp 103–105 °C [lit.[9] bp 104–105 °C]. Key IR bands are observed at 3050, 2960, 2860, 1765, 1440, 1390, 1370, 1295, 1225, 1000, 970, 890, 845, 785, and 690 cm^{-1}. The NMR spectrum ($CDCl_3$) showed methylene protons at δ 4.81 (d, J_{F-H} = 48 Hz, 2 H) and methyl protons at δ 3.78 (s, 3 H).

(b) To a solution of 2 g of 18-crown-6 in 100 mL of acetonitrile was added 13 g of KF. After the heterogeneous system was stirred for 30 min, 10 mL of methyl α-chloroacetate was added and the resulting mixture was refluxed with stirring. The extent of conversion of methyl α-chloroacetate was followed by measuring the yield of methyl α-fluoroacetate by gas chromatography (GC). *Caution*! Methyl α-fluoroacetate is highly toxic! All operations should be carried out in an efficient hood.

Preparation of Methyl α-Fluoroacrylate. To a 1-L three-necked flask equipped with a mechanical stirrer, thermometer, condenser, and dropping funnel were added sodium hydride (20 g) and freshly distilled dimethyl oxalate (49.4 g, 0.42 mol) dissolved in 300 mL of diethyl ether. To this mixture were added methyl α-fluoroacetate (2 g) and a few drops of anhydrous methanol. The mixture was refluxed until the evolution of hydrogen began and the mixture became a faint yellow. The remaining methyl α-fluoroacetate (34.8 g) was added at a rate such that the reaction mixture continued to reflux gently due to the heat of reaction. After this, refluxing was continued for an additional 3 h. Then paraformaldehyde (12 g, 0.41 mol) was added at 0–5 °C and the mixture was brought slowly to the boiling point, where it was maintained for 15 min. After cooling, the reaction mixture was poured into a mixture of 100 mL of diethyl ether and 400 mL of water, and the ether layer was separated. The aqueous phase was again extracted with 100 mL of ether, and the combined ether layers were washed with 100 mL of aqueous 5% Na_2CO_3, followed by washing successively with aqueous NaCl and water. The ether layer was dried ($MgSO_4$) and distilled under reduced pressure. The fraction boiling at 30–46 °C (100 mmHg) was redistilled. Polymerization-grade methyl α-fluoroacrylate [12.5 g (30%)] was collected at 32–33 °C (65 mmHg) [lit.[2] bp 90.5–91.8 °C (765 mmHg)]. Key IR bands are observed at 3160, 3090, 3020, 2970, 2860, 1750, 1655, 1440, 1395, 1325, 1205, 1165, 990, 945, 905, 840, and 790 cm^{-1}. The NMR spectrum ($CDCl_3$) showed methyl protons at δ 3.75 (s, 3 H) and vinyl protons at δ 5.18 (q, 1 H, J = 6 Hz) and δ 5.65 (q, 1 H, J = 35 Hz, J = 3.6 Hz).

Homopolymerization of Methyl α-Fluoroacrylate. Bulk Polymerization. MFA (2 g, 19 mmol) and AIBN (0.005 g, 3.0 × 10^{-5} mol) were charged into a polymerization tube, followed by degassing (three vacuum freeze–thaw cycles) and sealing. After 24 h of heating at 60 °C, the tube was cooled and then opened, and the resulting clear solid block was dissolved in acetonitrile. The polymer was purified by repeated reprecipitations from acetonitrile into methanol, filtration, and drying in vacuo at 40 °C for 24 h to give 1.6 g (80%) of PMFA, which exhibited [η] = 5.0 dL/g in acetonitrile at 30 °C.

Solution Polymerization. MFA (2 g, 19 mmol), azobis(isobutyronitrile) (0.005 g, 3 × 10^{-5} mol), and dry acetonitrile were charged into a polymerization tube, followed by degassing (three freeze–thaw–pump cycles). The tube was sealed and heated at 60 °C for 24 h. The tube was opened and the solution was diluted with acetonitrile. The polymer was precipitated by dropwise addition of the acetonitrile solution to excess methanol with vigorous stirring. A tough white fibrous polymer was obtained (1.6 g, 80%), exhibiting [η] = 2.4 dL/g in acetonitrile at 30 °C.

Emulsion Polymerization. Into a 100-mL three-necked flask, fitted with a condenser, thermometer, nitrogen inlet, and magnetic stirrer, were placed 25 mL of distilled and degassed water, sodium lauryl sulfate (0.1 g, 3.5 × 10^{-4} mol), and $K_2S_2O_8$ (0.016 g, 5.9 × 10^{-5} mol). Nitrogen was passed through the mixture for 30 min. Then methyl α-fluoroacrylate (10 g, 0.096 mol) was added and the reaction mixture was heated at 50 °C with vigorous magnetic stirring for 24 h, under a slow stream of nitrogen. The resulting latex was coagulated by pouring into rapidly stirring methanol. The polymer was filtered and dried in vacuo overnight at 40 °C to give 9 g (90%) of PMFA with [η] = 5.0 dL/g in acetonitrile at 30° C. The IR spectrum exhibited $\tilde{\nu}_{CO}$ at 1770 and 1750 cm^{-1}. Anal. Calcd: C, 46.16; H, 4.84; F, 18.25. Found: C, 46.08; H, 4.84; F, 17.71.

Copolymerization of Methyl α-Fluoroacrylate with Methyl Methacrylate. Distilled and degassed water (100 mL), sodium lauryl sulfate (0.4 g, 1.38 × 10^{-3} mol), and $K_2S_2O_8$ (0.06 g, 2.22 × 10^{-4} mol) were placed in a 250-mL three-necked flask under nitrogen. After a 30-min nitrogen purge, a mixture of MFA (20 g) and MMA (20 g) was added, followed by heating at 50 °C for 24 h with vigorous magnetic stirring. The resulting copolymer latex was coagulated by pouring the reaction mixture into rapidly stirring methanol (500 mL). The precipitate was filtered and dried in vacuo for 24 h at 40 °C to give 39 g of copolymer (98%) exhibiting [η] = 5.1 dL/g in acetonitrile at 30 °C. Fluorine analysis (9.12%) indicated the MFA/MMA ratio was 46/54.

Kinetics. Weighed amounts of monomer, solvent, and initiator were charged into tubes. The tubes were degassed at 5 × 10^{-3} torr by three freeze–thaw cycles; liquid nitrogen was used as freezing medium. After the tubes were sealed, they were placed in a constant-temperature bath for specified times. After removal from the bath, the polymer was precipitated in a rapidly stirred large excess of methanol. The polymer was filtered, dried in vacuo at 40 °C for 48 h, and weighed. The composition of the copolymers was calculated from elemental carbon analyses.

Measurements. The infrared spectra were recorded on a JASCO IRA-1 spectrophotometer, the ultraviolet spectra on a Hitachi Model 100-60 spectrophotometer, and the NMR spectra on a Hitachi R-24B (60 MHz) instrument. Membrane osmometry (MOSM) was performed with a Wescan Model 230 osmometer at 28 °C, using acetonitrile solvent.

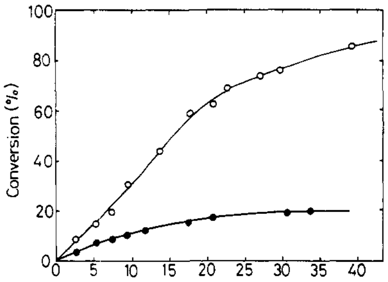


Figure 1. Time-conversion curve of methyl α-fluoroacetate in the halogen-halogen exchange of methyl α-chloroacetate with KF in (○) 0.757 and (●) 0.0757 mmol of 18-crown-6. Methyl α-chloroacetate, 11.4 mmol.

Viscosity measurements were made with a Ubbelohde-type viscometer at 30 °C and were run in acetonitrile.

Results and Discussion

Methyl α-fluoroacrylate (MFA) was prepared by the reactions shown in Scheme I.

Scheme I

$$ClCH_2COOCH_3 + KF \xrightarrow[\text{in } CH_3CONH_2]{120\text{–}125\ °C} FCH_2COOCH_3 + KCl$$

$$ClCH_2COOCH_3 + KF \xrightarrow[\text{18-crown-6 in } CH_3CN]{\text{reflux}} FCH_2COOCH_3 + KCl$$

$$FCH_2COOCH_3 + CH_3OOCCOOCH_3 \xrightarrow[Et_2O]{NaH}$$

$$CH_3OOCCO\bar{C}FCO_2CH_3Na^+ \xrightarrow[\text{then reflux 15 min}]{\text{paraformaldehyde } 0\text{–}5\ °C} \xrightarrow{CH_3ONa} CH_2{=}CFCO_2CH_3\ (MFA) + CH_3OOCCOONa$$

Two methods were employed to prepare methyl α-fluoroacetate. Conventionally, replacement of halogen by fluorine is carried out in high-boiling polar solvents by using anhydrous potassium fluoride. As described by Ernst et al.,[10] methyl α-chloroacetate was converted to methyl α-fluoroacetate by heating with anhydrous KF in acetamide in 60% yield. Another convenient method uses a crown ether to solubilize alkali-metal halides in dipolar and nonpolar aprotic solvents. The reagent was prepared by dissolving 18-crown-6 in dry acetonitrile and then adding dry KF. After the heterogeneous system was stirred for 30 min, methyl α-chloroacetate was added and the resulting mixture was refluxed with stirring. Figure 1 shows the time-conversion curve of methyl α-fluoroacetate in the chloride-fluoride exchange reaction of methyl α-chloroacetate with KF. The reaction was almost complete after 40 h.

Attempts to prepare MFA according to the patent literature[8] were not satisfactory, so that method was improved. Methyl α-fluoroacetate reacted with dimethyl oxalate in the presence of NaH in diethyl ether to give the sodium salt of methyl (methoxyoxalyl)fluoroacetate. Without isolation, this salt was condensed with paraformaldehyde to afford MFA in 30% yield.

It's NMR spectrum consisted of a singlet for the methyl protons at δ 3.75 (3 H) and two quartets for the vinyl protons at δ 5.18 (J = 6 Hz, J = 3 Hz) and δ 5.65 (J = 35 Hz, J = 3.6 Hz) (Figure 2). The IR spectrum had a carbon-carbon double-bond absorption at 1655 cm^{-1} and a strong ester carbonyl absorption at 1750 cm^{-1} (Figure 3).

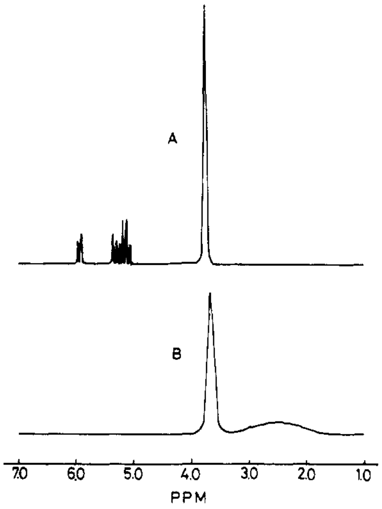


Figure 2. NMR spectra of (A) MFA and (B) PMFA in $CDCl_3$ with internal Me_4Si reference.

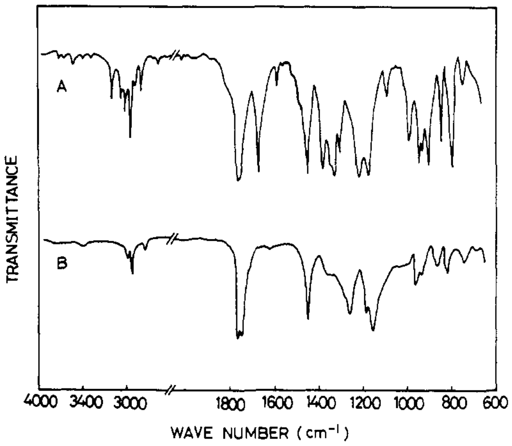


Figure 3. Infrared spectra of (A) MFA (NaCl) and (B) PMFA (film).

Table I
Homopolymerization of Methyl α-Fluoroacrylate (MFA)[a]

polymn method	amt of MFA, g	initiator	initiator amt, mg	T, °C	yield, g	[η],[b] dL/g
bulk	2	AIBN	5	60	1.6 (80)[c]	5.0
solution[d]	2	AIBN	5	60	1.6 (80)	2.4
emulsion[e]	10	$K_2S_2O_8$	16	60	9.0 (90)	5.0

[a] Polymerization time, 24 h. [b] In acetonitrile. [c] % yield given in parentheses. [d] Acetonitrile was used as solvent. [e] Sodium lauryl sulfate (0.1 g) was used as an emulsifier.

Polymerization of Methyl α-Fluoroacrylate. Homopolymerizations were conducted in bulk, solution, and emulsion systems. MFA polymerized quite readily under each of these conditions. The experimental conditions and polymerization results are given in Table I.

$$CH_2{=}C(F)CO_2CH_3 \rightarrow \underset{PMFA}{-[CH_2C(F)(CO_2CH_3)]-_n}$$

The intrinsic viscosity of PMFA in acetonitrile at 30 °C was 5.0 dL/g, when $\bar{M}_n$ = 250 000 (determined by membrane osmometry).

Copolymerizations of MFA with MMA and MCN were carried out in emulsion systems, using sodium lauryl sulfate as an emulsifier. The results are summarized in Table II. The copolymer compositions were calculated from elemental analyses.

Table II
Emulsion Copolymerization of MFA with Methyl Methacrylate (MMA) and Methacrylonitrile (MCN)[a]

monomer (amt, g)		amt of $K_2S_2O_8$ initiator, g	T, °C	time, h	yield, g	$[\eta]$,[b] dL/g	M_1/M_2 mol ratio in copolym	$10^{-5}\overline{M}_n$[c]
M_1	M_2							
MFA (10)	MMA (30)	0.05	40	64	29 (73)[d]	5.2	22/78	6.0
MFA (20)	MMA (20)	0.06	50	24	39 (98)	5.0	46/54	6.5
MFA (30)	MMA (10)	0.06	50	24	38 (95)	6.0	63/37	16.0
MFA (10)	MCN (30)	0.05	50	24	39 (98)	5.8	16/84	10.0
MFA (17)	MCN (23)	0.06	50	28	20 (50)	3.0	20/80	
MFA (27)	MCN (13)	0.06	50	26	37 (93)	6.0	57/43	

[a] Sodium lauryl sulfate (0.4 g) was used as emulsifier. [b] At 30 °C in acetonitrile. [c] Measured by membrane osmometry at 28 °C in acetonitrile. [d] % yield given in parentheses.

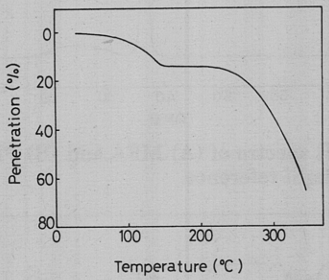


Figure 4. TMA of PMFA. ΔT = 20 °C/min.

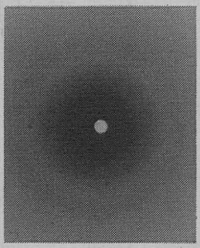


Figure 5. X-ray diffraction pattern of PMFA.

The homopolymer and copolymers are white solids. Films of each can be cast from acetonitrile. The homopolymer is readily soluble in acetonitrile, chloroform, dichloromethane, dioxane, and dipolar aprotic solvents. It is insoluble in acetone, tetrahydrofuran, benzene, and methanol.

Polymer Characterization. The homopolymer gave a satisfactory elemental analysis. Figure 3 shows the infrared spectra of MFA and PMFA. PMFA exhibited two carbonyl absorption peaks at 1770 and 1750 cm^{-1}, and no trace of the C=C stretching peak was detected. According to Bellamy and Williams,[11] the double carbonyl absorption for α-halo esters is indicative of rotational isomerism. Furthermore, Lenz et al.,[12] reported that two carbonyl absorptions, at 1742 and 1772 cm^{-1}, of poly(methyl α-chloroacrylate) correlated very well with dyad tacticity. Therefore double carbonyl absorptions of PMFA indicate that it may be the syndiotactic polymer. The NMR spectrum exhibited a single peak at δ 3.68 (3 H) and a broad peak at δ 2.0–2.9 (2 H), as shown in Figure 2.

The glass transition temperature (T_g) of PMFA was determined by thermomechanical analysis (TMA), as shown in Figure 4. Two-step penetration occurred at 128 and 295 °C. The former penetration was assigned to the T_g, while the latter was assigned to the degradation temperature. This may be compared to the reported T_g value for poly(methyl α-chloroacrylate) of about 150 °C.[12] A melting point of PMFA was not observed, in agreement with the X-ray diffraction pattern of PMFA, which showed very little crystalline structure (Figure 5).

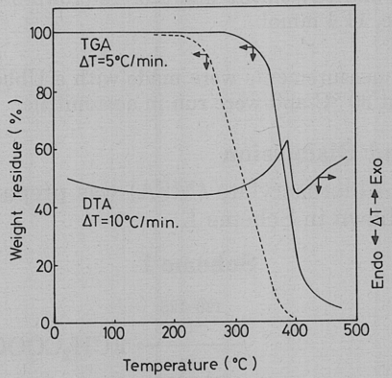


Figure 6. TGA and DTA curves of (—) PMFA and (---) PMMA.

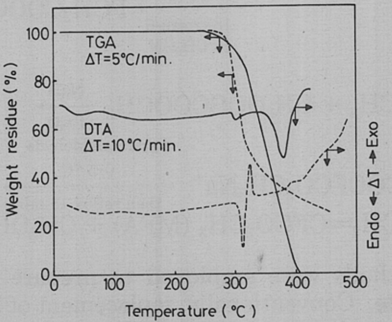


Figure 7. TGA and DTA curves of (—) P(MFA–MMA) and (---) P(MFA–MCN).

Table III
Thermal Characterization of Polymers

polym	M_1/M_2 mole ratio in copolym	degradn temp,[a] °C
PMMA		260
PMFA		350
P(MFA–MMA)	22/78	305
P(MFA–MMA)	46/54	315
P(MFA–MMA)	63/37	340
P(MFA–MCN)	16/84	290
P(MFA–MCN)	20/80	295
P(MFA–MCN)	57/43	305

[a] In N_2. Temperature at which 10% weight loss was observed by TGA.

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were carried out in N_2 at heating rates of 5 and 10 °C/min, respectively, on PMFA, P(MFA–MMA), and P(MFA–MCN). Typical thermograms are shown for the homopolymer in Figure 6 and for copolymers in Figure 7. The DTA curves of PMFA exhibited an initial exotherm at about 320 °C, which correlated well with TGA, confirming that the initial weight loss occurred at about this temperature. The degradation temperature for 10% weight loss was 350 °C, and after rapid degradation, a small amount of residue remained up

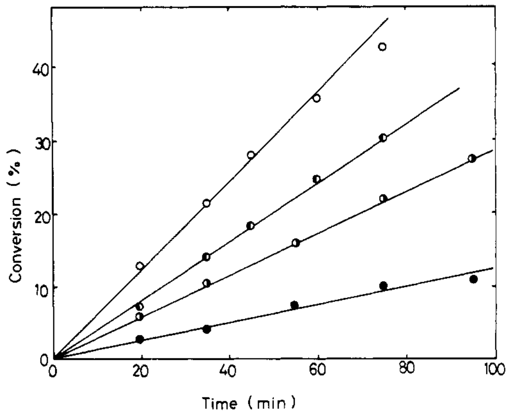


Figure 8. Time–conversion curves for solution polymerization of MFA at (●) 50, (◑) 60, (◐) 65, and (○) 70 °C. [MFA] = 8.92 × 10^{-1} (50 °C), 9.11 × 10^{-1} (60 °C), 9.29 × 10^{-1} (65 °C), and 9.32 × 10^{-1} mol/L (70 °C); [AIBN] = 8.30 × 10^{-4} mol/L; solvent acetonitrile.

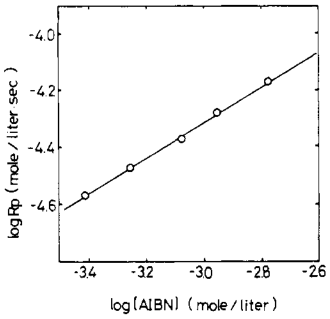


Figure 9. Plot of log R_p vs. log [AIBN] for homopolymerization of MFA in acetonitrile at 60 °C. [MFA] = 8.32 × 10^{-1} mol/L.

Table IV
Relationships between R_p and Initiator Concentration[a]

10^3 × [AIBN], M	polymn time, min	% yield	$10^5 R_p$, mol/(L·s)
1.69	20	9.78	6.78
1.12	20	7.80	5.34
0.842	30	9.24	4.27
0.562	30	7.34	3.39
0.393	41	8.05	2.72

[a] [MFA] = 8.32 × 10^{-1} mol/L, solvent acetonitrile, temperature 60 °C.

to 500 °C. This may be compared to the TGA curve of the less stable poly(methyl methacrylate), where no residue remained.

More rapid degradations were observed with increasing MMA contents in P(MFA–MMA) copolymers, and residues were not observed. The initial degradation temperature decreased with increasing MCN contents in P(MFA–MCN) copolymers. The percentage residue also increased with increasing MCN composition. These results are summarized in Table III.

Kinetic Study. The solution polymerization of MFA in acetonitrile was initiated with AIBN at temperatures from 50 to 70 °C. The time–conversion curves are shown in Figure 8. This polymerization was linear with time and without an induction period. Table IV shows the relationships between R_p and initiator concentration at 60 °C.

A plot of log R_p against log [AIBN] is shown in Figure 9. The slope of the observed least-squares-fit straight line is 0.6. Table V shows the relationship between R_p and monomer concentration in the polymerization at 60 °C. A plot of log R_p against log [MFA] (Figure 10) has a slope of 1.1. The rate equation for the homopolymerization of MFA in acetonitrile may be given, therefore, as eq 1, where

$$R_p = k[\text{AIBN}]^{0.6}[\text{MFA}]^{1.1} \quad (1)$$

k is an overall rate constant. Equation 1 is close to that expected for the normal vinyl free-radical polymerization mechanism.

Table V
Relationships between R_p and Monomer Concentration[a]

[MFA], M	polymn time, min	% yield	$10^5 R_p$, mol/(L·s)
0.365	20	14.5	4.39
0.686	20	16.3	9.31
0.982	20	17.2	14.0
1.27	20	16.6	17.7
1.55	20	18.1	23.3

[a] [AIBN] = 9.61 × 10^{-3} mol/L, solvent acetonitrile, temperature 60 °C.

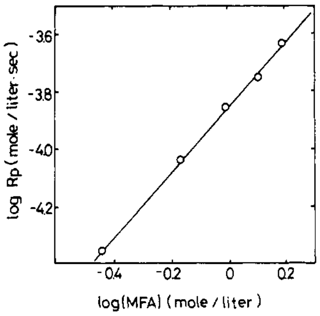


Figure 10. Plot of log R_p vs. log [MFA] for homopolymerization of MFA in acetonitrile at 60 °C. [AIBN] = 9.61 × 10^{-3} mol/L.

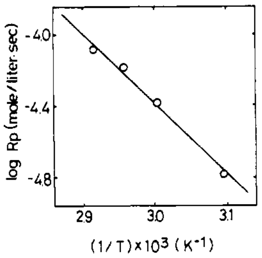


Figure 11. Plot of log R_p vs. $1/T$ for polymerization of MFA.

Figure 11 shows an Arrhenius plot of R_p vs. $1/T$. From the slope of this plot the overall activation energy E_a is estimated to be 73.6 kJ/mol. In the presence of an initiator, for a normal kinetic scheme the overall activation energy is given by eq 2, where E_d, E_p, and E_t are the activation energies for the initiation, propagation, and termination steps, respectively.

$$E_a = E_d/2 + [E_p - (E_t/2)] \quad (2)$$

Using the literature value for E_d of 128 kJ/mol,[13] we calculate a value for $[E_p - (E_t/2)]$ for MFA in acetonitrile of 9.6 kJ/mol. This may be compared with a literature value of $[E_p - (E_t/2)]$ for MMA of 17.2 kJ/mol.[14]

Copolymerizations. The copolymerizations of MFA with styrene and methyl methacrylate were carried out in acetonitrile at 60 °C. The results are given in Table VI.

The copolymer composition was determined by elemental analyses. The monomer–copolymer composition curves are shown in Figure 12. The values of r_1 and r_2 were obtained by the nonlinear, least-squares-fitting technique of Tidwell and Mortimer[15,16] which we have advocated previously.[17] Q and e values for MFA, calculated from monomer reactivity ratios, are listed in Table

Table VI
Copolymerizations of MFA with Styrene and Methyl Methacrylate[a]

[monomer], mol %		polymn time, h	copolym yield, %	MFA content, mol %
St	MFA			
0.883	0.117	5	5.95	0.140
0.701	0.299	4	6.47	0.290
0.510	0.490	3	5.16	0.433
0.331	0.669	4	7.95	0.518
0.134	0.866	3	7.95	0.644

[monomer], mol %		polymn time, min	copolym yield, %	MFA content, mol %
MMA	MFA			
0.852	0.148	60	7.35	0.118
0.713	0.287	40	5.83	0.238
0.517	0.483	60	9.54	0.366
0.315	0.685	20	4.67	0.518
0.158	0.842	20	6.03	0.708

[a] [AIBN] = 6.09×10^{-3} mol/L, solvent acetonitrile, temperature 60 °C.

Table VII
Copolymerization Parameters[a]

M_1	M_2	r_1	r_2	r_1r_2	Q_2	e_2
St	MFA	0.62	0.15	0.093	0.47	0.73
MMA	MFA	1.17	0.36	0.42	0.92	1.3
St[b]	MCA[c]	0.25	0.30	0.075	2.0	0.77
St[b]	MBA[d]				4.5	1.2

[a] St, $Q = 1.00$, $e_1 = -0.80$; MMA, $Q_1 = 0.74$, $e_1 = 0.40$.
[b] From ref 10. [c] MCA = methyl α-chloroacrylate.
[d] MBA = methyl α-bromoacrylate.

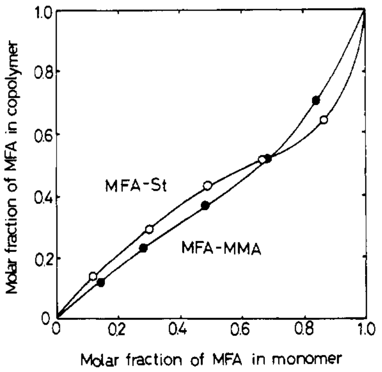


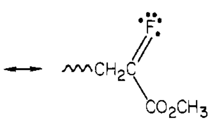
Figure 12. Copolymerization of MFA with St and MMA: (○) MFA-St; (●) MFA-MMA.

VII, where the values for α-chloro- and α-bromoacrylate are shown for comparison.[18]

Ito et al.[19] reported that the relation between log Q and λ_{max} of vinyl monomers is linear; that is

$$\log Q = -10.88 + (5.175 \times 10^{-2})\lambda_{max} \quad (3)$$

Using $\lambda_{max} = 203$ nm for MFA in methanol in eq 3, the Q value was calculated to be 0.42, which agreed well with 0.47 obtained from the styrene copolymerizations. Examination of relative e values for MFA ($e = 0.73$), methyl α-chloroacrylate ($e = 0.77$), and methyl α-bromoacrylate ($e = 1.2$) reveals that e increases with increasing atomic number of the halogen. This order is surprising since the electron-withdrawing inductive effects of the halogen series (F > Cl > Br) would predict the e values would be in just the opposite order. The reason for this order in e values is unknown. The Q values also increase in the order F < Cl < Br. Since Q is related to the resonance stability of the monomer's corresponding radical 1, this treatment argues



1a 1b

that the α fluorine stabilizes the acrylate radical less than chlorine or bromine. The contribution of hybrid structure **1b** is not favorable since **1b** places nine electrons in fluorine's outer shell. The other halogens might more readily accommodate nine electrons by expanding their valence shell through d orbitals. Other factors, such as fluorine's strong −I inductive effect would also destabilize radical 1 relative to its Cl and Br analogues. Thus 1 is not as stable as its bromine and chlorine analogues.

Electron-induced reactions in polymers are nonspecific and similar to the thermally induced reactions. The thermal sensitivity of a resist polymer is frequently proportional to its electron sensitivity.[3] Since copolymers of MFA with MMA and MCN were less thermally stable than PMFA, they were anticipated to exhibit higher electron sensitivities. Radiation degradation studies of PMFA and MFA copolymers with MMA and MCN have now been performed. PMFA was found to degrade predominantly by cross-linking.[20] Remarkably, copolymers of MFA and MMA degrade predominantly by chain scission and exhibit higher G_s values than pure poly(methyl methacrylate) despite the fact PMFA degrades by cross-linking.[20] Thus, MFA/MMA copolymers can be used as positive electron-beam resists while the PMFA homopolymer cannot be used in this fashion.

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