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Radical-Initiated Homo- and Copolymerization of α-Fluoroacrylamide "Living" Radicals in a Homogeneous System

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ABSTRACT: The kinetics of α-fluoroacrylamide (FAA) homopolymerization has been investigated in dimethyl sulfoxide (Me_2SO), using azobis(isobutyronitrile) (AIBN) as an initiator. The rate of polymerization (R_p) could be expressed by $R_p = [AIBN]^{0.95}[FAA]^{1.1}$. This abnormal rate dependence on the initiator concentration was interpreted on the basis of a unimolecular termination mechanism. The presence of "living" propagation radicals was observed by ESR and their concentration increased linearly with time. The overall activation energy was calculated to be 97.8 kJ/mol. The relative reactivity ratios in FAA (M_2) copolymerizations with methyl methacrylate ($r_1 = 2.10$, $r_2 = 0.16$) were obtained. Applying the Q–e scheme led to $Q = 0.54$ and $e = 1.45$ for FAA. The glass transition temperature (T_g) of poly(FAA) was observed to be 211 °C by thermomechanical analysis (TMA). Dehydrofluorination of poly(FAA) occurred at 270–275 °C.

Introduction

As a part of a continuing research program on the structure–reactivity relationships exhibited by vinyl monomers, in both their radical-initiated homo- and copolymerizations, the polymerization behavior of the vinyl monomers containing fluorine has been investigated in our laboratories.[1,2] Fluorine's small size and large electronegativity make it an interesting substituent to study at the radical center. Furthermore, an α fluorine cannot stabilize a radical center by resonance because it cannot expand its octet of valence-shell electrons. This leads to lower polymerization reactivities when compared to such α substituents as –CN, –COOR, –COR, etc. This is illustrated below where the Alfrey–Price Q–e values are shown for a series of substituted ethylenes. In general, high Q values correspond to high monomer reactivity.

	$CH_2{=}CHF$	$CH_2{=}CHCN$	$CH_2{=}CHCO_2Et$	$CH_2{=}CHCOPh$
Q	0.025	0.60	0.52	2.9
e	−0.82	1.20	0.22	0.66

In an earlier paper, we reported kinetic studies of the radical-initiated homo- and copolymerization of methyl α-fluoroacrylate (MAF).[1] That investigation revealed that the introduction of an α fluorine increases the e value but does not affect the Q value. This finding apparently reflected a fundamental characteristic of fluorine.

Many reports have been published on the polymerization of acrylamide, methacrylamide, and their N-substituted compds. However, no detailed studies exist of the radical polymerization of α-halogenated acrylamides.

In this paper, we describe the synthesis and kinetic studies of the radical-initiated polymerization of α-fluoroacrylamide (FAA) as well as the characterization of the resulting polymer. In addition, the reactivity of this monomer in copolymerizations with methyl methacrylate will also be discussed. The substituent effect of the α fluorine is elucidated.

Experimental Section

Materials. α,α-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Dimethyl sulfoxide was distilled from calcium hydride. Methyl methacrylate (MMA) was purified by the usual method.[3] The other reagents were used without further purification.

Preparation of Ethyl α-Fluoroacrylate. To a 1-L three-neck flask equipped with a mechanical stirrer, thermometer, condenser, and dropping funnel were added sodium hydride (20 g, 50% oil) and freshly distilled diethyl oxalate (61.3 g, 0.42 mol) dissolved in 300 mL of diethyl ether. To this mixture were added ethyl α-fluoroacetate (2 g) and a few drops of anhydrous ethanol. The mixture was refluxed until the evolution of hydrogen began and the mixture became a faint yellow. The remaining ethyl α-fluoroacetate (36 g) was added at a rate such that the reaction mixture continued to reflux gently due to the heat of reaction. Reflux was maintained 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 aqueous 5% Na_2CO_3 and then with saturated aqueous NaCl. The ether layer was dried ($MgSO_4$) and distilled under reduced pressure. The fraction boiling at 51–52 °C/80 mmHg was collected: lit.[4] bp 82–84 °C; yield 24.5 g (52%); IR (NaCl) ν(C=O) 1740, ν(C=C) 1660, ν(C—F) 1180 cm^{-1}; NMR ($CDCl_3$) δ 1.3 (t, 3 H), 4.2 (q, 2 H), 5.1 (q, J = 8 Hz, J = 3 Hz), 5.6 (q, $J_{H,F}$ = 36 Hz, J = 3 Hz, 1 H).

α-Fluoroacrylamide (FAA). Ethyl α-fluoroacrylate (22.6 g, 0.19 mol) was dissolved in 80 mL of ethanol and the solution was cooled with an external ice–water bath. A slow stream of ammonia gas was passed through this solution for 3 h with stirring. The solvent was evaporated and the residue was crystallized from toluene to give white plates: yield, 11.6 g (83%); mp 115–117 °C (lit.[5] mp 115–116 °C); IR (KBr) ν(N—H) 3370, 3200, ν(C=O) 1680, ν(C=C) 1650, ν(C—F) 1220 cm^{-1}; NMR (in $Me_2SO\text{-}d_6$) δ 5.4 (q, J = 40 Hz, J = 3 Hz, 1 H), 5.0 (q, J = 8 Hz, J = 3 Hz, 1 H), 7.4 (br s, 2 H).

Solution Polymerization of FAA. α-FAA (2 g, 0.018 mol), AIBN (2 mg, 1.2×10^{-5} mol), and Me_2SO (20 mL) were charged into a polymerization tube followed by degassing. The tube was sealed and heated at 50 °C for 26 h. The tube was opened and the viscous solution was diluted with Me_2SO (40 mL). The polymer was then precipitated by dropwise addition of the Me_2SO

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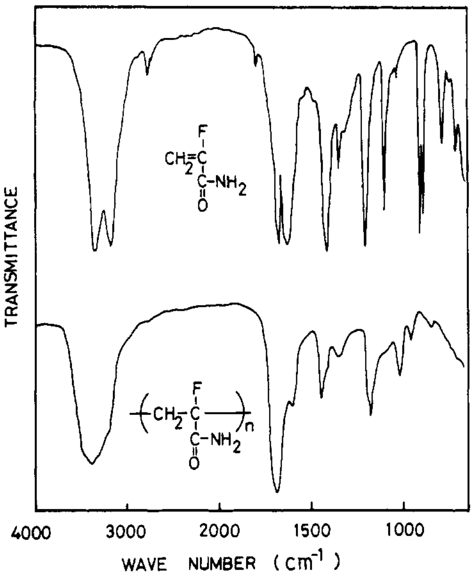


Figure 1. Infrared spectra of FAA (NaCl) and poly(FAA) (film).

solution into excess methanol with vigorous stirring. A white fibrous polymer was obtained (99%), exhibiting $[\eta]$ = 2.4 dL/g in Me_2SO at 30 °C. IR (film) ν(N—H) 3350, 3180, ν(C=O) 1690 cm^{-1}. NMR (in CF_3COOH) δ 7.1 (2 H), 2.9 (2 H). Anal. Calcd for C_3H_4NOF: N, 15.72. Found: N, 15.3.

Kinetics. Weighed amounts of FAA, Me_2SO, and AIBN were charged into polymerization tubes, degassed by three alternate freeze–pump–thaw cycles, sealed, and placed in a thermostated bath for selected times. Next, the tubes were removed and the polymer was precipitated into excess methanol, filtered, dried in vacuo at 60 °C for 48 h, and weighed.

Measurements. The IR spectra were recorded on a Jasco IRA-1 spectrophotometer and the NMR spectra on a Hitachi R-24B (60 MHz) instrument. The glass transition temperature was determined on a Shimadzu TMA-30 instrument at a heating rate of 20 °C/min in nitrogen. Differential thermal analysis (DTA) and thermogravimetry (TG) were performed with a Shimadzu DT-20 instrument and TG-20B thermal balance, respectively. The ESR spectra were obtained by using a JEOL JES FE-3X spectrometer employing 100-kHz modulation and a frequency of 9.1 GHz. Sample temperature was controlled with a Model ES-VT-3A controller and a Model ES-UCT-2AX variable-temperature accessory. The absolute concentration of radicals was determined after double integration by comparison with the ESR spectrum of 2,2-diphenyl-1-picrylhydrazyl (DPPH).

Results and Discussion

Homopolymerization of α-Fluoroacrylamide (FAA). Fluoroacrylamide (FAA) was prepared by the reactions shown in Scheme I.

Scheme I

$$FCH_2COOC_2H_5 + C_2H_5OOCCOOC_2H_5 \xrightarrow[Et_2O]{NaH} C_2H_5OOCCOC^{-}FCOOC_2H_5Na^{+} + EtOH \xrightarrow[\text{then reflux 15 min}]{\text{paraformaldehyde}\\ \text{0–5 °C}} CH_2{=}CFCOOC_2H_5 + C_2H_5OOCCOO^{-}Na^{+}$$

$$CH_2{=}CFCOOC_2H_5 + NH_3 \rightarrow \underset{\text{FAA}}{CH_2{=}CFCONH_2} + C_2H_5OH$$

Solution polymerizations were easily carried out with AIBN as the initiator. The homopolymer is a white solid, and transparent films of poly(α-fluoroacrylamide) can be cast from Me_2SO solutions. Poly(FAA) is insoluble in many organic solvents but is soluble in trifluoroacetic acid at room temperature and in Me_2SO on heating. This solubility behavior is very different from that of polyacrylamide, which is very soluble in water.

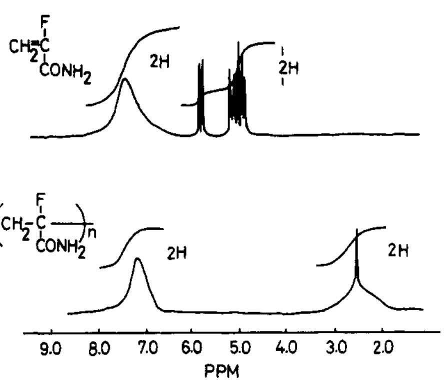


Figure 2. NMR spectra of FAA in $Me_2SO\text{-}d_6$ and poly(FAA) in CF_3COOH at 30 °C.

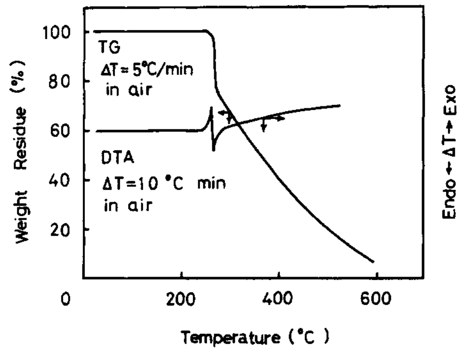
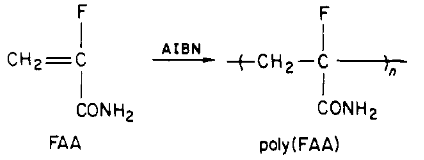


Figure 3. TGA and DTA traces for poly(FAA).



$$\underset{\text{FAA}}{CH_2{=}\overset{\overset{\large F}{|}}{\underset{\underset{\large CONH_2}{|}}{C}}} \xrightarrow{\text{AIBN}} \underset{\text{poly(FAA)}}{\left(CH_2-\overset{\overset{\large F}{|}}{\underset{\underset{\large CONH_2}{|}}{C}}\right)_n}$$

Homopolymer Characterization. The homopolymer gave a satisfactory elemental analysis. The IR spectra of FAA and poly(FAA) are shown in Figure 1. The characteristic N–H bond stretching at 3370 and 3200 cm^{-1}, the C=O bond stretching at 1680 cm^{-1}, and the C=C bond stretching at 1650 cm^{-1} are clearly observed for the monomer, whereas poly(FAA) exhibited the broad N–H bond stretching at 3390 cm^{-1} and the C=O bond stretching at 1690 cm^{-1} while no trace of a C=C bond stretching was detected. The NMR spectrum of FAA (Figure 2) in $Me_2SO\text{-}d_6$ at 30 °C consists of a broad peak for the amide protons at δ 7.4 (2 H) and two quartets for the vinyl protons at δ 5.4 (J = 40 Hz, J = 3 Hz) and δ 5.0 (J = 8 Hz, J = 3 Hz). The NMR spectrum of poly(FAA) in CF_3COOH (Figure 2) exhibited broad peaks at δ 7.1 (2 H) and δ 2.9 (2 H), which were assigned to the amide and methylene protons, respectively.

The glass transition temperature (T_G) of poly(FAA) was observed at 211 °C by thermomechanical analysis (TMA) in N_2. This temperature is substantially higher than the T_g value reported for poly(acrylamide) of 165 °C.[6] Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out in air at heating rates of 5 and 10 °C/min, respectively. Thermograms are shown for the homopolymer in Figure 3. DTA of poly(FAA) exhibited a first exothermic peak at 270 °C followed by an endothermic peak at 275 °C, which correlated well with an initial weight loss temperature in the TG curve. The rapid weight loss, observed at 270–275 °C in the TG curve, amounted to 24% of the weight of poly(FAA). This value

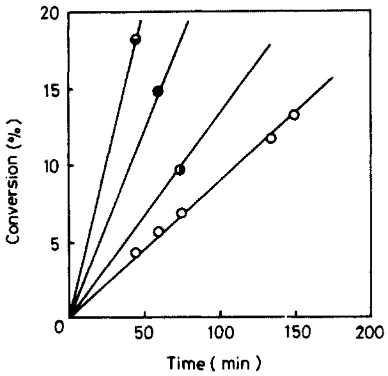


Figure 4. Time–conversion curves for the solution polymerization of FAA at various temperatures: (○) 50 °C; (◑) 55 °C; (●) 60 °C; (⊖) 65 °C. [FAA] = 0.5 mol/L. [AIBN] = 1.52×10^{-4} mol/L. Solvent: Me_2SO.

Table I
Relationship between R_p and Initiator Concentration[a]

[AIBN] × 10^4, mol/L	polymn time, min	yield, %	$R_p \times 10^6$, mol/(L·s)	$[\eta]_{inh}$,[b] dL/g
3.04	45	10.2	18.89	5.2
2.28	60	9.3	12.88	5.7
1.52	90	9.1	8.43	5.5
0.76	135	7.9	4.88	5.8
0.30	210	5.0	1.98	

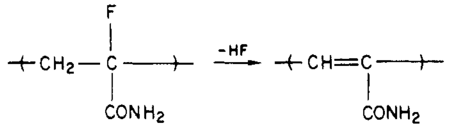
[a] [FAA] = 0.5 mol/L. Solvent: Me_2SO. Polymerization temperature: 50 °C. [b] Measured at 30 °C in Me_2SO.

Table II
Relationship between R_p and Monomer Concentration[a]

[FAA], mol/L	polymn time, min	yield, %	$R_p \times 10^6$, mol/(L·s)
1.0	60	5.3	14.79
0.75	70	6.7	12.02
0.50	90	8.8	8.13
0.25	150	13.4	3.72
0.10	300	23.7	1.32

[a] [AIBN] = 1.52×10^{-4} mol/L. Solvent: Me_2SO. Polymerization temperature: 50 °C.

is in excellent agreement with the calculated value (22.5%) of the weight loss which would occur on dehydrofluorination of poly(FAA). This interpretation is further supported by the following results:



$$-\!\!\left[CH_2-\overset{F}{\underset{CONH_2}{C}}\right]\!\!- \xrightarrow{-HF} -\!\!\left[CH{=}\underset{CONH_2}{C}\right]\!\!-$$

(a) Heating poly(FAA) films at 270–280 °C under nitrogen for 1 h gave black films due to the formation of conjugated double bonds. (b) In the IR spectrum of thermally treated film, the characteristic absorption band of C–F bond stretching became very weak while the N–H bond stretching and the C=O bond stretching were unchanged.

Kinetic Studies. The solution homopolymerization of FAA in Me_2SO was initiated with AIBN at temperatures from 50 to 65 °C. The time–conversion curves, shown in Figure 4, were linear and without an induction period. The dependence of the rate of polymerization (R_p) on the concentration of monomer and initiator concentration was investigated at 50 °C. Table I shows the relationship between R_p and initiator concentration. A plot of log R_p against log [AIBN], shown in Figure 5, is a straight line with a slope of 0.95. Table II summarizes the relationship between R_p and monomer concentration in polymerizations at 50 °C. A plot of log R_p vs. log [FAA] (Figure 6) has a slope of 1.1. The rate equation for the homopolymerization of FAA in Me_2SO may be given, therefore, as

$$R_p = k[\mathrm{AIBN}]^{0.95}[\mathrm{FAA}]^{1.1}$$

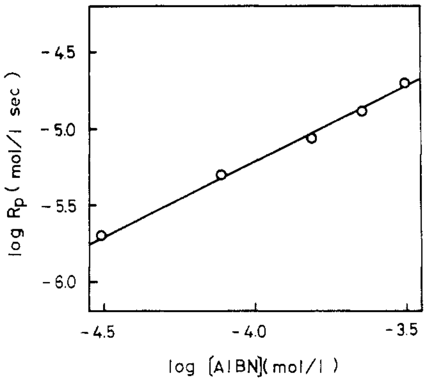


Figure 5. Plot of log R_p vs. log [AIBN] for the homopolymerization of FAA in Me_2SO at 50 °C. [FAA] = 0.5 mol/L.

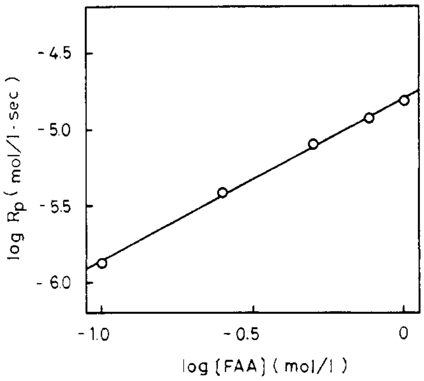


Figure 6. Plot of log R_p vs. log [FAA] for the homopolymerization of FAA in Me_2SO at 50 °C. [AIBN] = 1.52×10^{-4} mol/L.

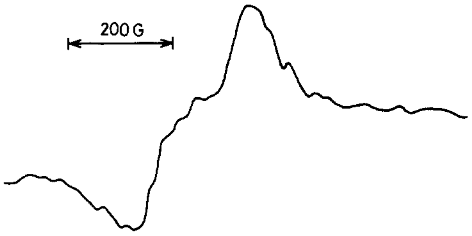


Figure 7. ESR spectrum of the living propagation radicals.

The polymerization rate is almost proportional to $[\mathrm{FAA}]^{1.0}$, but the dependence on initiator concentration exceeds one-half order and is nearly first order. It is well-known that the dependence of R_p on initiator concentration becomes close to first order in some heterogeneous polymerizations,[7] since most of the growing chains terminate via a unimolecular mechanism. The presence of "living" or trapped nonterminated radicals in polymerized systems also has been demonstrated by ESR measurements.[8] Since FAA polymerization proceeded homogeneously, the presence of chain-end radicals that were unable to react (either by dimerization or disproportionation) at first seemed unlikely. However, if they were present, that would account for the observed rate equation. Thus, ESR measurements were carried out at −120 °C to elucidate the termination mechanism. The ESR spectrum (Figure 7) was obtained from an FAA polymerization solution. It shows a broad signal with a g value of about 2.003 and two hyperfine structures. The hyperfine splitting is about 200 G ($=10^{-4}$ T). This large value is characteristic of the fluorine atom of a C–F fragment. Therefore, the

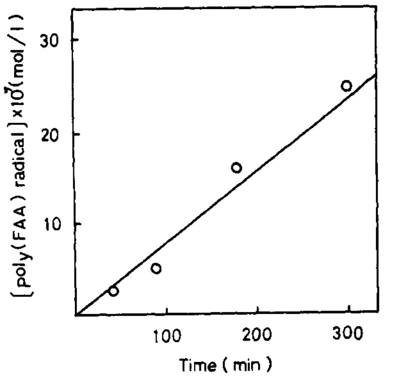


Figure 8. Relationship between polymerization time and the concentration of poly(FAA) radicals. [FAA] = 0.5 mol/L; [AIBN] = 1.52×10^{-4} mol/L. Solvent: Me_2SO. Polymerization temperature: 50 °C.

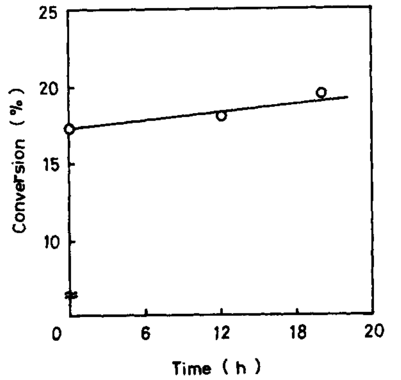
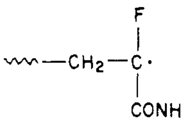


Figure 9. Change in polymer yield with time during the postpolymerization at room temperature after prior polymerization at 50 °C for 2 h. [FAA] = 0.5 mol/L; [AIBN] = 3.04×10^{-4} mol/L.

observed ESR spectrum is assigned to the following polymer radical, 1.



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Remarkably, this ESR signal also was observed even after samples were allowed to stand for 1 week at room temperature. Thus, these "living radicals" were quite stable and resistant to dimerization and disproportionation. The concentration of the living propagation radicals was determined by comparison with the ESR spectrum of DPPH in dilute Me_2SO solution. The variation in the concentration of radical 1 was measured at various polymerization times by cooling the solutions from +50 to −120 °C and obtaining their ESR spectra. The concentration of the observed living radicals increased linearly with time during polymerization (Figure 8). Furthermore, under the reaction conditions these living radicals do not seem to participate in propagation at temperatures of 50 °C. The number-average degree of polymerization in most radical-initiated vinyl addition polymerizations is inversely dependent on the radical concentration. However, as can be seen from Table I, the inherent viscosities of the FAA polymers obtained (hence their molecular weights) were approximately constant as the initiator concentration was varied. In addition, as seen in Figure 9, postpolymerization was extremely slow at room temperature, although a relatively high concentration of propagating radicals remained available to initiate further growth of the polymer chains when more monomer was added.

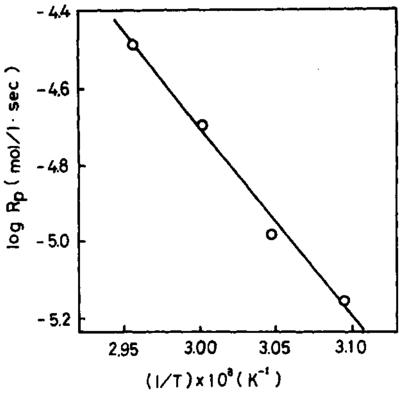


Figure 10. Plot of log R_p vs. $1/T$ for polymerization of FAA.

Table III
Copolymerization of FAA with Methyl Methacrylate[a]

MMA (M_1), mol %	FAA (M_2), mol %	polymn time, min	copolymn yield, %	FAA content,[b] mol %
0.800	0.200	270	4.0	0.120
0.701	0.299	240	5.1	0.155
0.604	0.396	210	4.7	0.196
0.505	0.495	180	3.8	0.237
0.437	0.563	180	4.6	0.293
0.399	0.601	180	5.1	0.317
0.206	0.794	150	3.9	0.525
0.142	0.858	180	5.6	0.632
0.105	0.895	120	4.1	0.675

[a] [AIBN] = 1.38×10^{-4} mol/L. Solvent: Me_2SO. Copolymerization temperature: 50 °C. [b] FAA content of the copolymer.

From these results, the abnormal rate dependence on the initiator concentration can be explained on the basis of a unimolecular termination mechanism. The reason the living radicals exist in solution is most likely due to the poor solubility of high molecular weight poly(FAA) in Me_2SO solutions. When the growing polymeric radicals reach a molecular weight where they verge on insolubility in Me_2SO they become tightly coiled. Thus two such radical centers cannot easily react with one another.

Figure 10 shows the Arrhenius plot of R_p vs. $1/T$ from which the overall activation energy E_a is estimated to be 97.8 kJ/mol. In the presence of an initiator, the overall activation energy for a unimolecular termination mechanism is given by

$$E_a = E_d + E_p - E_t$$

where E_d, E_p, and E_t are the activation energies for the initiation, propagation, and termination steps, respectively. When the literature[9] value for E_d of 128 kJ/mol (in benzene) is used, the value for $E_p - E_t$ for FAA polymerization in Me_2SO is −30.2 kJ/mol. This finding indicates that the termination step has a very high activation energy. Therefore the propagating radicals become living radicals as molecular weight increases.

Copolymerization. Copolymerizations of FAA with MMA were carried out in Me_2SO at 50 °C. Results are given in Table III. The copolymer compositions were determined by nitrogen analyses. The monomer copolymer composition curve is shown in Figure 11. The reactivity ratio values, r_1 and r_2, were obtained by the Kelen–Tüdös method.[10] Defining FAA as M_2, the ratios were determined as $r_1 = 2.1$ and $r_2 = 0.16$. The reactivity of FAA can be illustrated by considering the inverse of its monomer reactivity ratio ($1/r$). The value of $1/r_2$ is 6.3, thus the FAA radical reacts preferentially with MMA. The Q–e values for FAA, calculated from the reactivity ratios,

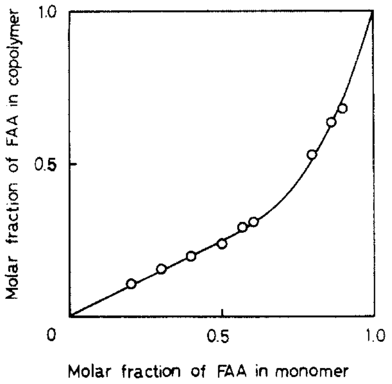


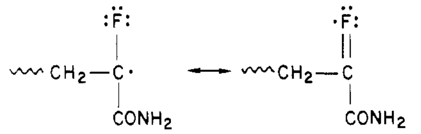
Figure 11. Copolymerization of FAA with MMA.

Table IV
Copolymerization Parameters[a]

M_1	M_2	r_1	r_2	r_1r_2	Q_2	e_2
MMA	FAA	2.10	0.16	0.336	0.54	1.45
	AM[b]				1.1	1.2
	MAM[c]				1.4	1.2

[a] MMA: $Q = 0.74$; $e = 0.40$. [b] Acrylamide. [c] Methacrylamide.

are listed in Table IV where the corresponding Q–e values for acrylamide (AM) and methacrylamide (MAM) are shown for comparison. The strong inductive effect of the α fluorine is clearly manifest in the e value for FAA (1.45) vs. that for acrylamide (1.2) or methacrylamide (1.2). On the other hand, the value of Q for FAA (0.54) is substantially smaller than that of either acrylamide (1.1) or methacrylamide (1.4). This is the same trend that is observed by comparing the Q values of methyl methacrylate and methyl α-fluoroacrylate.[1] The Q value for methyl α-fluoroacrylate (0.47)[1] is smaller than that of MMA (0.74). The Q value is related to the resonance stability of the monomer's corresponding radical. The α-fluorine is ineffective in stabilizing the radical **1a**. This is illustrated by resonance structure **1b** which places nine electrons in fluorine's outer shell. Other factors, such as fluorine's strong electron-withdrawing inductive effect, would also destabilize electron-deficient radical **1**.



1a **1b**

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