Radical-Initiated Homo- and Copolymerizations of Methacryloyl Fluoride

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Synopsis

The kinetics of methacryloyl fluoride (MAF) homopolymerization was investigated in methyl ethyl ketone (MEK) with azobis(isobutyronitrile) as initiator. The rate of polymerization (R_p) followed the expression $R_p = k[\text{AIBN}]^{0.55}[\text{MAF}]^{1.18}$. The overall activation energy was calculated as 74.4 kJ/mol. The relative reactivity ratios of MAF(M_2) copolymerization with styrene ($r_1 = 0.083$, $r_2 = 0.14$), and methyl methacrylate ($r_1 = 0.48$, $r_2 = 0.81$) in methyl ethyl ketone were obtained. Application of the Q–e scheme (in styrene copolymerization) led to $Q = 2.22$ and $e = 1.31$. The glass transition temperature (T_g) of poly(MAF) was 90°C by thermomechanical analysis. Thermogravimetry of poly(MAF) showed a 10% weight loss of 228°C in air.

INTRODUCTION

Poly(methacryloyl chloride) (MAC) has been widely used as a starting material for many functional polymers and detailed homo- and copolymerization studies have been reported by Otsu et al.[1] and Usmanov et al.[2] Recently, Nakamura and co-workers[3] reported that poly(MAC) was a good positive electron-beam resist with a sensitivity of approximately 1×10^{-7} C/cm². However, poly(MAC) is highly susceptible to hydrolysis. Furthermore, it may react with surface hydroxyl groups present on the SiO$_2$ layer of silicon wafers.

In general, an acyl fluoride is more resistant to hydrolysis than an acyl chloride. In addition, the fluorine atom has a higher absorption coefficient at the Al–K$_\alpha$ (8.3 Å) line (i.e., 1898) than a chlorine atom. Fluoride ion is effective in part in reducing tooth decay because it is incorporated into the hydroxyapitite structure of the enamel and in part because of its bacteriacidal action. These properties suggest that poly(methacryloyl fluoride) (MAF) and its methyl methacrylate copolymer[4] would be good candidate polymers as dental materials and electron-beam or x-ray lithographic resists.[5–10]

No detailed reports have yet been published on the radical homo- and copolymerization of MAF.[4] This article describes kinetic studies of the radical polymerization of MAF, its copolymerization with vinyl monomers, and properties of the resulting polymers.

EXPERIMENTAL

Materials

Azobisisoburyronitrile (AIBN) was recrystallized from methanol.   Benzene was washed successively with concentrated sulfuric acid, dilute sodium hydroxide, and distilled water, dried over calcium chloride, and distilled.   Methyl ethyl ketone (MEK) was dried over anhydrous sodium sulfate and distilled.   The other reagents were used without further purification.
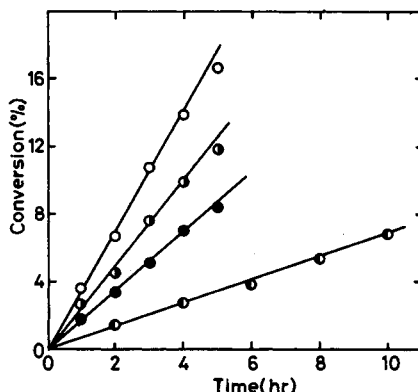

Fig. 1. Time-conversion curves for solution polymerization of MAF in MEK at (◑) 50, (●) 60, (◐) 65, and (○) 70°C. [MAF] = 1.12 mol/L; [AIBN] = 4.00 × 10⁻³ mol/L.

TABLE I
Relationship Between R_p and Initiator Concentration[a]

[AIBN] × 10³ (mol/L)	Polymerization time (h)	Yield (%)	R_p × 10⁶ (mol/L s)
1.83	5	6.43	3.45
3.67	3	5.71	5.11
7.34	2.5	6.94	7.44
11.0	1.67	5.69	9.17
18.3	1	4.67	12.5

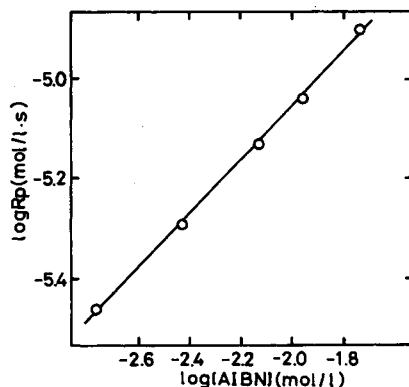[a] [MAF] = 1.12 mol/L; solvent, MEK; temperature, 60°C.

Fig. 2. Plots of log R_p vs. log [AIBN] for homopolymerization of 1.12 mol/L of MAF in MEK at 60°c.

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TABLE II

Relationship Between R_p and Monomer Concentration[a]

</div>

[MAF] (mol/L)	Polymerization time (h)	Yield (%)	$R_p \times 10^6$ (mol/L s)
0.562	8	10.6	2.08
0.842	6	8.60	3.35
1.01	4	5.56	3.90
1.69	3.1	4.98	7.52
2.25	2	3.40	10.6

[a] [AIBN] = 4.21×10^{-3} mol/L; solvent, MEK; temperature, 60°C.

Monomers

Styrene (St) and methyl methacrylate (MMA) were purified by the usual methods.

Preparation of Methacryloyl Fluoride (MAF)

This monomer was prepared according to the Howk and Jacopson procedure.[11] Methacryloyl chloride (40 g, 0.38 mol) and antimony trifluoride (60 g, 0.34 mol) were placed in a 100-mL flask, stirred at 75–80°C for 7 h, and allowed to stand overnight. The reaction mixture was distilled through a fractional column and 20–22 g (60–65%) of MAF was obtained: bp 53–55°C (lit[11] 56–58°C). IR (NaCl) 1805 (C=O), 1640 cm^{-1} (C=C); NMR (in CDCl$_3$) δ = 1.95 (s, 3H, methyl protons), δ = 5.8 (s, 1H, vinyl proton), δ = 6.4 (s, 1H, vinyl proton).

Homopolymerization of Methacryloyl Fluoride

MAF (1.0 g, 11 mmol), AIBN (6.0 mg, 3×10^{-2} mmol), and 9 mL of MEK were changed to a polymerization tube and degassed (three freeze–thaw pump cycles). The tube was sealed and heated at 65°C for 5 h, then opened, and the solution
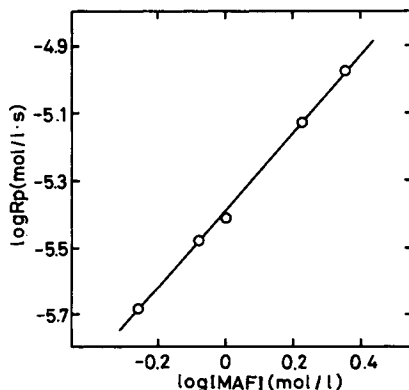

Fig. 3. Plots of log R_p vs. log [MAF] for homopolymerization of MAF in MEK at 60°C. [AIBN] = 4.21×10^{-3} mol/L.
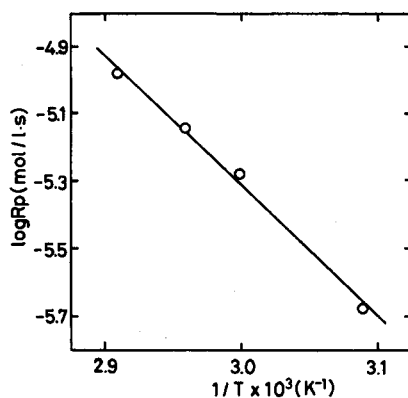
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Fig. 4. Arrhenius plot of log R_p vs. $1/T$ for homopolymerization of MAF.

was poured into excess hexane with vigorous stirring. A white polymer obtained in 14% yield exhibited $|\eta| = 0.14$ dL/g in tetrahydrofuran (THF) at 30°C.

ANAL. Calcd for C_4H_5FO: C, 54.55%; H, 5.72%. Found: C, 54.8%, H, 5.7%.

TABLE III
Copolymerization of MAF with St and MMA[a]

Monomer		Polymerization time	Copolymer	
[M_1] (mol %)	[M_2] (mol %)		Yield (%)	MAF content (mol %)
St	MAF			
0.955	0.045	5 h	4.17	0.255
0.923	0.077	5 h	4.58	0.312
0.889	0.111	3 h	4.01	0.360
0.652	0.348	3 h	6.52	0.486
0.644	0.356	1 h 5 min	2.31	0.515
0.450	0.550	3 h	8.44	0.545
0.436	0.564	1 h 30 min	4.01	0.565
0.289	0.711	3 h	9.17	0.599
0.249	0.751	2 h 1 min	5.83	0.610
0.078	0.922	3 h	7.16	0.726
0.072	0.928	3 h	7.93	0.728
0.062	0.938	3 h	8.10	0.743
MMA	MAF			
0.882	0.118	4 h 30 min	18.1	0.200
0.762	0.238	3 h	11.8	0.299
0.646	0.354	4 h	13.7	0.451
0.465	0.535	6 h	10.2	0.562
0.271	0.729	2 h 30 min	7.00	0.723
0.261	0.739	3 h	8.67	0.740
0.079	0.921	3 h	6.08	0.926

[a] [AIBN], MAF-St, 3.75×10^{-3} mol/L; MAF-St, 3.20×10^{-3} mol/L; solvent, MEK; temperature, 60°C.

Conversion of Poly(MAF) to Poly(methyl Methacrylate) (MMA)

Poly(MAF) was hydrolyzed with concentrated sulfuric acid at room temperature for three days. The solution was poured into water and the precipitated polymer was collected. The polymer was redissolved in methanol and reprecipitated from diethyl ether. The resulting poly(methacrylic acid) was converted to poly(MMA) with diazomethane in benzene and precipitated from methanol. The triad tacticity of poly(MMA) was determined by the intensity of the α-methyl signal in the ^{1}H-NMR (90 MHz) spectra measured in $CDCl_3$ at 35°C.

Kinetics

Weighed amounts of monomer, solvent, and initiator were charged into polymerization tubes and degassed at 5×10^{-3} torr by three alternate freeze–thaw cycles. 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 by pouring the solution into excess hexane, filtered, dried in vacuo at 40°C for 48 h, and weighed. The composition of the copolymer was calculated from elemental analyses.
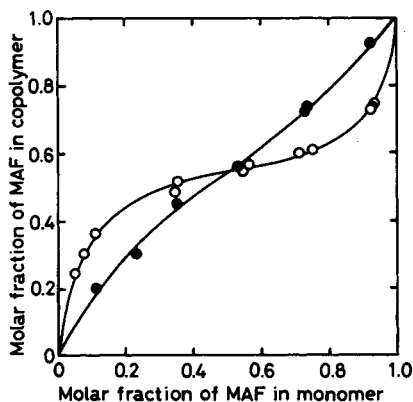

Fig. 5. Copolymerizations of MAF with St (O) and MMA (●).

TABLE IV
Copolymerization Parameters

M_1	M_2	r_1	r_2	$r_1 r_2$	Q_2	e_2
St	MAF	0.083	0.138	0.012	2.22	1.31
MMA	MAF	0.48	0.81	0.39	2.25	1.37
St[a]	MAC[b]	0.13	0.075	0.097	1.42	1.35
MMA[c]	MAC	0.25	0.65	0.16	5.08	1.75

St, $Q_1 = 1.00$, $e_1 = -0.80$; MMA, $Q_1 = 0.74$, $e_1 = 0.40$.
[a] From ref. 2 in 1,2-dichloroethane.
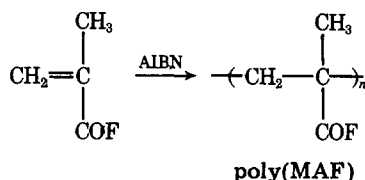[b] MAC, Methacryloyl chloride.
[c] From ref. 1 in benzene.

Measurements

The infrared (IR) spectra were recorded on a JASCO IRA-1 spectrophotometer, and the nuclear magnetic resonance (NMR) spectra on a Hitachi R-24B (60 MHz) or R-22 (90 MHz) instrument. The glass transition temperature (T_g) was determined on a Shimazu TMA-30 instrument at a heating rate 20°C/min in N_2. The thermogravimetry was performed with a Shimazu TB 20B thermal balance. The temperature range investigated was room temperature to 600°C. Viscosity measurements was made with a Ubbelode viscometer at 30°C in THF.

RESULTS AND DISCUSSION

Homopolymerization of Methacryloyl Fluoride (MAF)

Homopolymerizations were readily conducted in bulk and solution systems. MAF polymerized in both systems, but a gel polymer was obtained in bulk polymerization. In solution low yields were usually obtained (12–20%), although multiple initiations gave higher yields of soluble polymer and some gel. The homopolymer is a white solid. Films can be cast from acetone. The homopolymer is soluble in acetone, MEK, THF, and dipolar aprotic solvents; it is partially soluble in benzene and 1,2-dichloroethane and insoluble in other solvents:

$$
CH_2{=}\underset{\underset{COF}{|}}{\overset{\overset{CH_3}{|}}{C}} \quad \xrightarrow{AIBN} \quad {+}CH_2{-}\underset{\underset{COF}{|}}{\overset{\overset{CH_3}{|}}{C}}{\rightarrow}_n
$$

poly(MAF)

Kinetic Study

The solution homopolymerization of MAF in MEK was initiated with AIBN at temperatures of 50–70°C. The time-conversion curves, shown in Figure 1, were linear without an induction period. The dependence R_p on the concentrations of monomer and initiator was investigated at 60°C. Table I shows the relationship between R_p and initiator concentration. A plot of log R_p vs. log

TABLE V
Thermal Characterization of Polymers

Polymer	Mol ratio [M$_1$]/[M$_2$] in copolymer	Degradation temperature[a] (°C)	
		Initial weight loss	10% weight loss
poly(MMA)		240	260
poly(MAF)[M$_2$]		250	290
poly(MMA–MAF)	43/56	255	295
poly(ST–MAF)	47/53	250	310

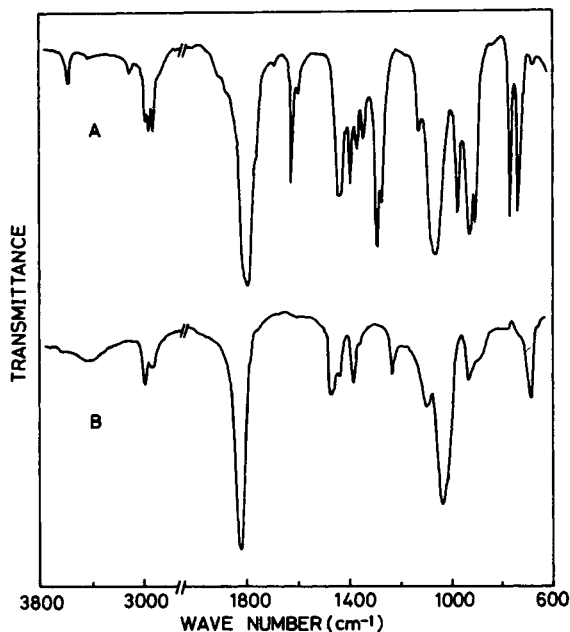[a] Observed by TG at a heating rate of 5°C min^{-1}.

Fig. 6. Infrared spectra of MAF(A) and poly(MAF) (B).

(AIBN), shown in Figure 2, is a straight line with a slope of 0.55. Table II summarizes the relationship between R_p and monomer concentration in polymerizations at 60°C. A plot of R_p vs. log (MAF) (Fig. 3) has a slope of 1.18. The rate equation for the homopolymerization of MAF in MEK may therefore be given as

$$R_p = k[AIBN]^{0.55}[MAF]^{1.18} \qquad (1)$$

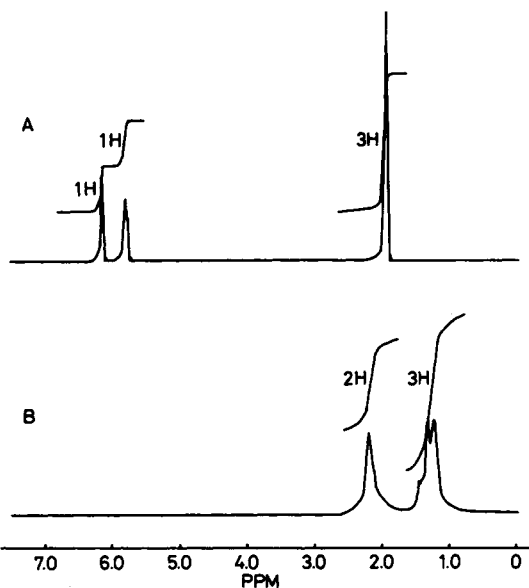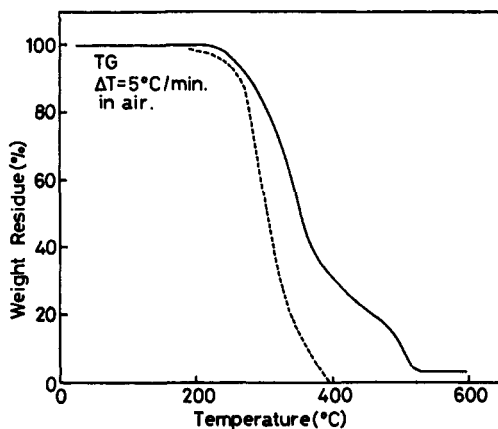Fig. 7. NMR spectra of MAF(A) and poly(MAF) (B) in CDCl$_3$.

Fig. 8. TG curves of (——) poly(MAF) and (· · ·) poly(MMA).

where k is an overall rate constant. This rate equation (1) is close to that for the homopolymerization of MAC in benzene at 60°C.[1]:

$$R_p = k[AIBN]^{0.5}[MAC]^{1.2} \tag{2}$$

The polymerization rate R_p is closely proportional to $[AIBN]^{0.5}$, but its dependence on monomer concentration exceeds first order. Such deviations from first-order kinetics are common for polymerizations in solution and can be explained in the following ways[12–14]: (a) cage effect in the initiation or (b) primary radical termination; (b) would require some departure from the observed proportionality of R_p to $[AIBN]^{0.5}$. Therefore, the cage effect seems more likely to explain the deviation of the order in monomer.

An Arrhenius plot (Fig. 4) showed the overall activation energy (E_a) as 74.4 kJ/mol. This value is smaller than that for MAC, which is 96.1 kJ/mol.[1]

Copolymerizations

Copolymerizations of MAF with styrene (St) and MMA were carried out in MEK at 60°C. The results are given in Table III. The copolymer compositions were determined by elemental analyses. The monomer–copolymer composition curves are shown in Figure 5. The monomer–copolymer composition curves are shown in Figure 5. The values of r_1 and r_2 were obtained by a nonlinear least-squares computer fit of the integrated form of the copolymer equation described earlier.[15] This study was done especially carefully for St, where several extra copolymerizations were performed at the optimized M_1/M_2 ratio.[15] $Q–e$ values for MAF, calculated from monomer reactivity ratios, are listed in Table IV, in which the corresponding values for MAC are given for comparison. As shown in Figure 5 and Table IV, the MAF–St system yielded copolymers that consisted of the two monomer units in an almost one-to-one ratio over the wide mole fraction range. The monomer reactivity ratios were $r_1 = 0.083$, $r_2 = 0.14$ for St(M_1)–MAF(M_2). Accordingly, the product r_1r_2 is $\ll 1$, which indicates a strong alternating tendency that would be reflected in the Q and e values for MAF.

The electron-withdrawing inductive effect of the fluoroformyl group is clearly manifest in the e values for MAF (1.3) versus that for MMA (0.4). The value

of the resonance parameter Q for MAF (2.2) is also significantly higher than that for MMA. It has been shown that values of Q for alkyl methacrylates correlated with the Taft δ constants for alkyl groups[16]; that is, the Q value tends to increase as δ increases. Thus the larger Q value of MAF vs. MMA is easily understood. On the other hand, it is not obvious how the Q and e values of MAF compare with those of MAC because the Q and e values of MAC (obtained from copolymerizations with St in benzene and MMA in 1,2-dichloroethane) are not in agreement (Table IV). These results may be attributed to the effect of solvents on the radical copolymerization of MAC. Similar solvent effects on the reactivity ratios for the MAF–MMA system were observed. These will be discussed in a separate article. In summary, the vinyl group in MAF tends to resemble acrylonitrile ($e = 1.20$, $Q = 0.60$), acrylamide ($e = 1.30$, $Q = 1.18$), and α-chloroacrylonitrile ($e = 1.40$, $Q = 1.72$) more than MMA.

Polymer Characterization

The homopolymer gave a satisfactory elemental analysis. Figure 6 shows the IR spectra of MAF and poly(MAF). The C=O bond stretching at 1805 cm^{-1} and C=C bond stretching at 1635 cm^{-1} were clearly observed for MAF, whereas poly(MAF) exhibited the C=O absorption at 1825 cm^{-1} and no trace of the C=C stretching was detected.

The NMR spectra of MAF (Fig. 7) consisted of a singlet for methyl protons [$\delta 1.95(3H)$] and two multiplets for the vinyl protons [$\delta 5.8(1\,H)$, $\delta 6.4(1H)$]. The NMR spectra of poly(MAF) exhibited a single peak at $\delta 2.2$ (2H) and a multiplet at $\delta 1.3(3H)$ which are assigned to the β-methylene and α-methyl protons, respectively. To obtain information on tacticity, poly(MAF) was converted to poly(MMA) by hydrolysis in sulfuric acid at 20–25°C, followed by methylation with diazomethane. The tacticity of poly(MMA) determined by ^{1}H-NMR was 21% isotactic, 45% heterotactic, and 36% syndiotactic. In the free-radical polymerization of α,α-disubstituted vinyl monomers, such as methyl methacrylate[17] (S = 58, H = 36, I = 6), syndiotactic polymers are usually obtained, but MAF gave a polymer with nearly atactic structure. This agrees with the postulate that the steric and polar interactions of the two α,α-substituents are nearly equal in the stereoregular step.[18]

The T_g, as determined by thermomechanical analysis (TMA), was 90°C. No melting point was observed for poly(MAF); TG was carried out in air at a heating rate of 5°C/min on poly(MAF) and copolymers. Figure 8 is a typical poly(MAF) thermogram; a thermogram for poly(MMA) is included for comparison. The degradation temperature for a 10% weight loss was 290°C for poly(MAF), which shows that it is somewhat more stable than poly(MMA). These and copolymer results are summarized in Table V.

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