

Solvent Effects on Radical Homo- and Copolymerizations of Methacryloyl Fluoride

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Synopsis

The effect of solvent in homo- and copolymerizations of methacryloyl fluoride (MAF) was investigated in various aromatic solvents. In these solvents, there is a significant effect on the rate of polymerization, on the tacticity of the resulting poly(methacryloyl fluoride), and on the copolymerization of MAF with methyl methacrylate (MMA). The equilibrium constants between MAF and aromatic solvents were determined from NMR spectroscopic measurements. These results indicated that the solvent effect on the MAF polymerization stems from changes in reactivity of MAF induced by the strong MAF-solvent interaction as well as stabilization of the MAF radical by solvents. Copolymerization of MAF with both *p*-methoxystyrene (MSt) and *p*-nitrostyrene (NSt) was also studied.

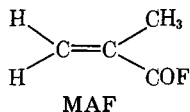
INTRODUCTION

Many reports have been published on the effect of solvent on the radical homo- and copolymerizations of vinyl monomers. The rates of homopolymerizations and the values of monomer reactivity ratios frequently vary in different solvents.

Bamford and Brumby,¹ Yamamoto and Hirota,² and Kamachi et al.³ independently measured the rate constants in the polymerization of methyl methacrylate (MMA) in aromatic solvents and observed that both the rate of polymerization (R_p) and the rate constant of propagation (k_p) decreased in the following order: benzonitrile > anisole > chlorobenzene > fluorobenzene > benzene. Bamford and Brumby¹ and Kamachi et al.³ explained this variation in terms of the formation of an electron donor-acceptor complex. On the other hand, Yamamoto and Hirota² concluded that R_p was more largely influenced by the effect of viscosity of the monomer-solvent mixtures in the termination step. They supported this view because only small changes of k_p were observed when comparing those solvents.

Previously, we reported a kinetic study of the radical polymerization of methacryloyl fluoride (MAF).⁴ MAF was found to be a strongly electron-deficient monomer.⁴ Also, copolymerization of MAF with styrene (St) yielded copolymers with a one-to-one monomer ratio over a wide mole fraction range. This

strong alternating tendency was attributed to an interaction of MAF and St. MAF is a stronger electron acceptor than MMA. Therefore, a larger solvent effect was expected than that observed in the polymerization of MMA.



This article describes the effect of solvent on the radical-initiated homo- and copolymerizations of MAF.

EXPERIMENTAL

Materials

Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Benzene was purified by washing sequentially with sulfuric acid, water, aqueous sodium hydrogen carbonate solution, and water, followed by drying (CaCl_2) and distillation. Anisole was dried over sodium wire and distilled. Benzonitrile was distilled from calcium hydride. Nitrobenzene was distilled from phosphorus pentoxide. Methyl ethyl ketone (MEK) was dried over anhydrous sodium sulfate and distilled. The other reagents were used without further purification.

Monomers

Methyl methacrylate (MMA) was purified by the usual methods. MAF was prepared as described in a previous article.⁴ It was purified by passing through a column of neutral aluminum oxide, drying (anhydrous MgSO_4), and distillation. *p*-Methoxystyrene (MSt) or *p*-nitrostyrene (NSt) was synthesized in 30 and 88% yield from *p*-methoxycinnamic acid or *p*-nitrocinnamic acid, respectively.

MSt: b.p. $39^\circ\text{C}/0.18$ mm Hg (literature⁵ $46^\circ\text{C}/0.5$ mm Hg). IR (NaCl) 1625 cm^{-1} ($\text{C}=\text{C}$); NMR (in CDCl_3) $\delta = 3.7$ (s, 3H), $\delta = 5.0$ (q, 1H), $\delta = 5.45$ (q, 1H), $\delta = 6.5$ (q, 1H), $\delta = 6.95$ (m, 4H).

NSt: b.p. $64^\circ\text{C}/0.08$ mm Hg (literature⁶ $77^\circ\text{C}/2$ mm Hg). IR (NaCl) 1600 cm^{-1} ($\text{C}=\text{C}$); NMR (in CDCl_3) $\delta = 5.35$ (d, 1H), $\delta = 5.75$ (d, 1H), $\delta = 6.65$ (q, 1H), $\delta = 7.7$ (m, 4H).

Homo- and Copolymerization

Weighed amounts of monomer, solvent, and initiator were changed into polymerization tubes, followed by degassing via three alternate freeze-pump-thaw cycles. After sealing, the tubes were placed in a constant temperature bath ($60 \pm 0.1^\circ\text{C}$) for specified times. After removal from the bath, the polymers were precipitated in excess methanol, filtered, dried *in vacuo* at 60°C for 48 h, and weighed. The composition of the copolymer was calculated by the elemental analysis of carbon or nitrogen content.

TABLE I
Rate of Homopolymerization of MAF in Various Solvents^a

Solvent	Yield (%)	$R_p \times 10^6$ (mol/L·s)
MEK (10 mL)	6.62	4.69
MEK (5 mL) + benzene (5 mL)	5.96	4.23
MEK (5 mL) + anisole (5 mL)	6.95	4.93
MEK (5 mL) + benzonitrile (5 mL)	7.14	5.06

^a [MAF] = 1.25 mol/L. [AIBN] = 3.88×10^{-3} mol/L. Polymerization time, 4 h; polymerization temperature, 60°C.

Measurements

The IR spectra were recorded on a JASCO IRA-1 spectrophotometer, and the NMR spectra on a Hitachi R-24B (60 MHz) or a Hitachi R-22 (90 MHz) instrument.

RESULTS AND DISCUSSION

Dependence of MAF's Homopolymerization Rate (R_p) on Aromatic Solvents

Homopolymerizations of MAF were carried out using AIBN as an initiator in the 1:1 MEK and aromatic solvent solutions. MEK was used because poly-(MAF) was insoluble in pure aromatic solvents. As shown in Table I, the R_p of MAF follows the order: benzonitrile > anisole > benzene. The difference in R_p upon varying the solvent was smaller than was expected. This probably occurs because MEK is a strong donor solvent and competes with aromatic solvents to form complexes with MAF. The order of the solvent effect was same to that observed in the polymerization of MMA.¹⁻³ This can be explained in the following way. First, the reactivity of MAF is influenced by the interaction with solvents. Second, the reactivity of the growing radical is influenced by solvents.

Interaction between MAF and Solvents

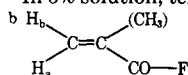
In order to clarify the interaction between MAF and solvents, the chemical shifts ($\Delta\delta$) of β -olefinic protons of MAF were measured at 30°C in each solvent. Since cyclohexane is an inert solvent, it was used as an internal reference. The results, given in Table II, show that donor solvents, such as anisole and benzene, caused upfield shifts and the acceptor solvents, benzonitrile and nitrobenzene, caused downfield shifts. The large chemical shift changes were observed in both *cis*- and *trans*-olefinic protons.

The stoichiometry of solvent/MAF complexes was determined by the continuous variation method of Job using NMR data. NMR spectra were taken for several MAF/aromatic solvent ratios in cyclohexane. A plot of molar fraction of MAF in benzene versus the chemical shifts of MAF's vinyl protons is shown

TABLE II
Chemical Shifts of the Olefinic Protons of MAF in Various Solvents^a

C ₆ H ₅ —X	H _a (Hz) ^b	H _b (Hz) ^b	Δδ _{H_a—H_b}
—OCH ₃	354.0	321.5	32.5
—H	345.5	306.5	37.0
—CN	368.5	349.5	19.0
—NO ₂	370.5	351.5	19.0

^a In 5% solution; temperature, 30°C; cyclohexane was used as internal reference.



in Figure 1. The maximum shift was observed at an MAF mole fraction of 0.5 indicating the formation of 1:1 complex between MAF and benzene. Therefore, we assumed that the complex between formation MAF and other solvents is 1:1. Equilibrium constants (K) were estimated from NMR spectroscopic measurements using the following equation:⁷

$$1/\Delta = 1/K \cdot \Delta_0 \cdot [D]_0 + 1/\Delta_0 \quad (1)$$

Here, Δ is the observed chemical shift for the olefinic protons in the specific solvent system relative to that in cyclohexane. Δ_0 is the shift of the neat interacting species relative to that in cyclohexane. $[D]_0$ is the concentration of the solvent. As a typical example, the chemical shifts of the olefinic protons of MAF in various concentrations of benzene are shown in Table III, and a plot of eq. (1) is shown in Figure 2. $1/K \cdot \Delta_0$ is the slope of the line obtained by plotting $1/\Delta$ against $1/[D]_0$. The intercept is $1/\Delta_0$. From the values of slope and intercept, the value of K was obtained as 0.10–0.11 L/mol. These values of K for MAF with benzene, anisole, benzonitrile, nitrobenzene, MEK, and styrene are summarized in Table IV. It is clear from the large equilibrium constants that MAF strongly

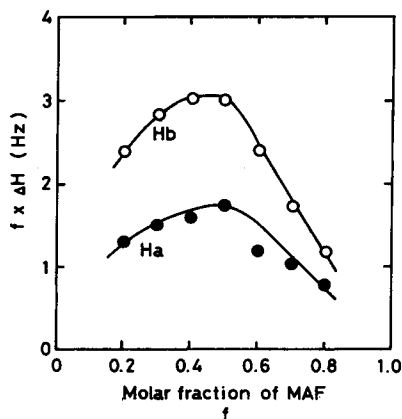
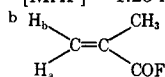


Fig. 1. Plots of molar fraction of MAF against chemical shifts of MAF's vinyl protons in benzene at 30°C. (●) H_a is *trans* to methyl and (○) H_b is *trans* to COF.

TABLE III
Chemical Shift of the Olefinic Proton of MAF at Various Concentrations of Benzene^a

Solvent	[Benzene] (mol/L)	H _a ^b (Hz)	H _b ^b (Hz)	Δδ _a ^c (Hz)	Δδ _b ^c (Hz)
Cyclohexane	0	363.5	340.0	—	—
Benzene (50%)	5.00	351.5	319.0	12.0	21.0
Benzene (70%)	7.00	348.5	314.0	15.0	26.0
Benzene (90%)	9.00	346.6	310.5	17.0	29.5

^a [MAF] = 1.25 mol/L; temperature, 30°C; cyclohexane was used as internal reference.



^c Δδ = δH(cyclohexane) - δH(benzene).

interacts with donor molecules. The strong interaction between MAF and solvents suggests that the interaction between the chain-propagating MAF radical and these solvents is even stronger.

Solvent Effect on the Tacticity of Poly(MAF)

The strong interaction between the propagating MAF radical or monomer with solvents should influence the tacticity of the resulting polymers. The triad tacticities of poly(MAF), prepared at 60°C using AIBN initiation in several solvents, were calculated from NMR spectra and they are summarized in Table V. In the free-radical polymerization of α,α-disubstituted vinyl monomers, such as MMA (I = 6, H = 36, S = 58), syndiotactic polymers are usually obtained, but MAF gave a polymer of highly heterotactic structure. The probabilities of triad tacticity are described by the single parameter:

$$P_i = \sigma^2, P_h = 2\sigma(1 - \sigma), P_s = (1 - \sigma)^2$$

The P_s , P_h , and P_i show the probability of forming syndiotactic, heterotactic, and isotactic triads, respectively. σ denotes the probability of isotactic monomer

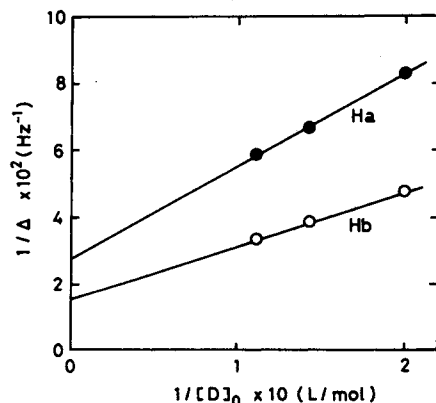


Fig. 2. Plots of $1/\Delta$ against $1/[D]_0$ for the complex of MAF with benzene. (●) H_a; (○) H_b.

TABLE IV
 Equilibrium Constant (K)^a

Acceptor	Donor	K (L/mol)
MAF(H_a)	benzene	0.10
MAF(H_b)	benzene	0.11
MAF(H_a)	anisole	0.11
MAF(H_b)	anisole	0.08
MAF(H_a)	benzonitrile	≈ 0
MAF(H_b)	benzonitrile	≈ 0
MAF(H_a)	nitrobenzene	≈ 0
MAF(H_b)	nitrobenzene	≈ 0
MAF(H_b)	MEK	0.15
MAF(H_a)	St	0.10

^a [MAF] = 1.25 mol/L; temperature, 30°C; cyclohexane was used as internal reference.

placement during polymerization. A plot of this relationship with experimentally determined points is shown in Figure 3. The value of σ calculated in benzene is closed to 0.5 which means a heterotactic polymer is obtained. Several plots did not lie on a theoretical line. This implies that the polymer's configuration sequence deviates from Bernoullian. This deviation can be explained by postulating an interaction between the propagating MAF radical (or monomer MAF) with solvent in the stereoregulating step.

Copolymerization of MAF with MMA

As we described above, there is a strong interaction between MAF and donor solvents. This finding led to a study of the copolymerization of MAF. One would expect to observe a significant solvent effect on the reactivity ratios for an MAF-comonomer pair.

We used MMA as the comonomer because a large interaction existed between MAF and St as described above. Copolymerizations of MAF with MMA were carried out in anisole, benzene, benzonitrile, and nitrobenzene at 60°C. The composition-conversion results are summarized in Table VI. Copolymer compositions were determined by elemental analyses. The monomer-copolymer composition curves are shown in Figures 4-7. Values of r_1 and r_2 were obtained by a nonlinear, least-squares fitting of the integrated form of the copolymer equation developed by Tidwell and Mortimer,^{8,9} which we have adapted into

 TABLE V
 Tacticity of Poly(MAF) Obtained in Several Solvents

Solvent	Isotactic P_i (%)	Heterotactic P_h (%)	Syndiotactic P_s (%)	σ
Anisole	26	39	35	0.41
Benzene	28	42	30	0.45
MEK	21	45	34	0.42
1,2-Dichloroethane	16	43	41	0.36

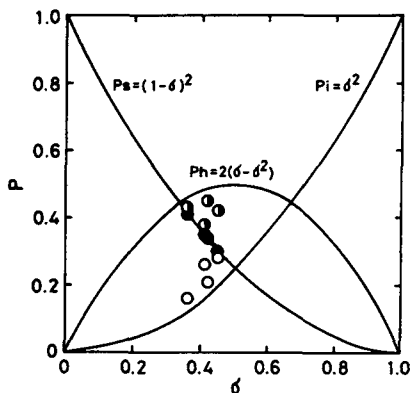


Fig. 3. Probabilities P_i , P_s , P_h of formation for isotactic, syndiotactic, and heterotactic triads, respectively. $i(\circ)$ peaks; $s(\bullet)$ peaks; $h(\odot)$ peaks.

computer programs and advocated previously.¹⁰ Q and e values for MAF, calculated from these monomer reactivity ratios, are listed in Table VII.

Alfrey-Price Q and e values for MAF were calculated on the assumption that the Qe values for MMA are independent of the nature of the solvent. This assumption is backed by the fact that K values for MMA-solvent complex formation are so small that, if they exist, they cannot be detected by the NMR technique described earlier. As shown in Figures 4-7 and Table VII, it is evident that the solvents used in the copolymerizations affected copolymer compositions considerably. The reactivity ratios, especially r_2 , were significantly changed.

Several interpretations have been proposed for the solvent dependence of reactivity ratios. Cameron and Esslemont¹¹ and Bonta et al.¹² studied on the solvent effect for the copolymerizations of St/methacrylonitrile or St/MMA, respectively. A direct correlation was found between the propagating radical's reactivity toward monomers and the dielectric constant of the solvent employed. They have explained their results in terms of polarization of the growing radicals

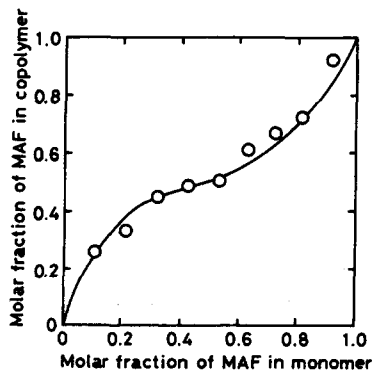


Fig. 4. Copolymerization of MAF with MMA in anisole.

TABLE VI
 Copolymerization of MAF with MMA in Aromatic Solvents^a

Monomer		Polymer- ization time (h)	Copolymer	
MMA [M ₁] (mol %)	MAF [M ₂] (mol %)		Yield (%)	MAF content (mol %)
In anisole				
0.888	0.112	2.0	13.0	0.260
0.787	0.213	2.0	8.75	0.337
0.679	0.321	2.5	10.2	0.451
0.573	0.427	2.5	9.93	0.489
0.468	0.532	2.5	9.38	0.507
0.369	0.631	2.5	8.75	0.616
0.277	0.723	2.5	7.34	0.671
0.184	0.816	3.0	6.49	0.723
0.085	0.915	3.0	4.97	0.926
In benzene				
0.942	0.058	2.0	10.3	0.099
0.880	0.120	2.5	11.6	0.240
0.831	0.169	2.0	9.56	0.260
0.755	0.245	2.5	9.80	0.318
0.712	0.288	2.5	9.63	0.395
0.611	0.389	2.5	8.44	0.433
0.553	0.447	2.5	8.03	0.470
0.448	0.552	2.5	7.12	0.526
0.251	0.749	2.5	5.46	0.634
0.150	0.850	2.5	4.82	0.723
0.039	0.961	3.0	4.67	0.943
In benzonitrile				
0.879	0.121	2.0	16.1	0.260
0.781	0.219	2.0	14.8	0.337
0.676	0.324	2.5	16.6	0.451
0.573	0.427	2.5	15.0	0.507
0.480	0.520	2.5	13.4	0.544
0.379	0.621	2.5	12.4	0.634
0.279	0.721	2.5	10.7	0.722
0.201	0.799	3.0	11.2	0.792
0.094	0.906	3.0	9.16	0.926
In nitrobenzene				
0.777	0.223	2.0	6.02	0.260
0.668	0.332	2.5	8.01	0.376
0.565	0.435	2.5	8.01	0.470
0.462	0.538	2.5	7.88	0.562
0.367	0.633	2.5	7.43	0.634
0.169	0.831	3.0	8.21	0.792
0.076	0.924	3.0	6.91	0.843

^a [AIBN = 2.90×10^{-3} mol/L; temperature, 60°C.

by the electron-donating or electron-withdrawing character of its functional groups.

Recently, Madruga et al.¹³ studied solvent effects on the radical-initiated MMA/St copolymerization in aromatic solvents. The changes in the reactivity

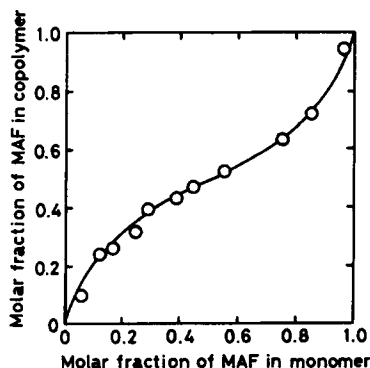


Fig. 5. Copolymerization of MAF with MMA in benzene.

ratios were reversed. Taking into account the behavior of both monomers in their respective homopolymerizations, Madruga argued that the reactivity of MMA radicals toward MMA monomer increases when the solvent dielectric constant increases. In contrast, the reactivity of the styryl radical toward styrene decreases with an increase in solvent dielectric constant. However, data shown in Table VII indicate that no relationship exists for the reactivity ratios versus the solvent dielectric constants for the MMA/MAF system.

Bamford and Brumby¹ and Kamachi et al.¹⁴ found that the rate of propagation in homopolymerizations of MMA or phenyl methacrylate (PMA) decreased with increasing the availability of π electrons in aromatic solvents. Therefore, we plotted the values of Q (determined for MAF in copolymerizations with MMA, Table VII) against the Hammett σ values of substituents attached to the phenyl ring of the aromatic solvents employed. Figure 8 shows that a crude linear relationship exists. That is, the value of Q obtained for MAF in these copolymerizations increases as the availability of π electrons in aromatic solvent nucleus increased.

The above results suggest a cause of the solvent effect. Most of the effect could be attributed to either: (a) changes in the monomer reactivity induced by the monomer-solvent interaction or (b) changes in the reactivity of the propagating

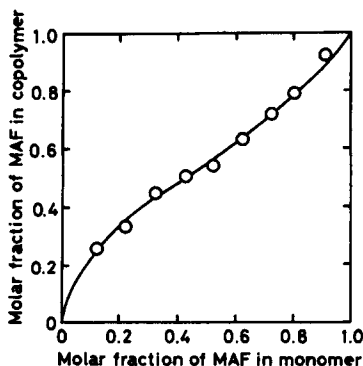


Fig. 6. Copolymerization of MAF with MMA in benzonitrile.

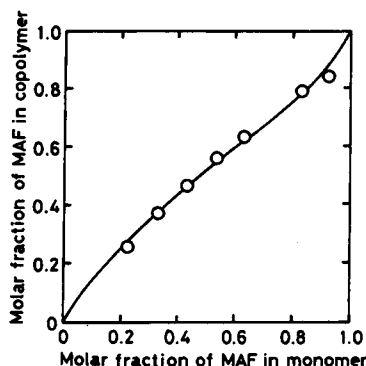


Fig. 7. Copolymerization of MAF with MMA in nitrobenzene.

radical induced by the radical-solvent interaction. A solvent effect on r_2 means that a change in the ratio k_{22}/k_{21} occurs where k_{22} and k_{21} are the rate constants for addition of MAF and MMA monomers, respectively, to the MAF radical. If the propagating MAF radical's reactivity is influenced by solvent, this variation in reactivity might be approximately equally manifest in the addition of $\sim\text{MAF}\cdot$ to MMA and MAF. Thus, one can speculate that a variation in monomer's reactivity [cause (a) above] is the major contributor to the solvent effect. However, this explanation is speculative because the inherent reactivities of both the complexed and uncomplexed monomers will be different and one cannot predict what relative contributions these two forms of the monomer will make to the overall process. The kinetic role of both complexed and uncomplexed monomer are difficult to unravel. Attempts to more rigorously analyze solvent effects by this type of analysis would involve an approach similar to the analysis of copolymerizations proceeding by a mixture of the terminal and charge-transfer mechanisms.¹⁰

Copolymerization of MAF with *p*-Methoxystyrene(MSt) or *p*-Nitrostyrene (NSt)

As we have stated above, MAF is in equilibrium with an MAF-solvent complex in aromatic solvents such as anisole and benzene. So, we expected that the interaction between MAF and MSt would be relatively large thereby yielding 1:1 copolymers regardless of the composition of the monomer feed. On the other

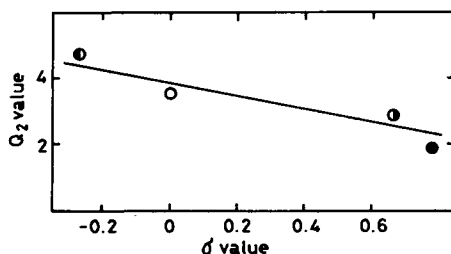


Fig. 8. Plots of the Q values determined for MAF against the Hammett σ values for the substituents on the aromatic solvents.

TABLE VII
Copolymerization Parameters^a

M ₁	M ₂	r ₁	r ₂	r ₁ r ₂	Q ₂	e ₂	Solvent
MMA	MAF	0.48	0.28	0.13	4.74	1.82	anisole
MMA	MAF	0.37	0.37	0.13	3.56	1.82	benzene
MMA	MAF	0.39	0.87	0.34	2.89	1.44	benzonitrile
MMA	MAF	0.57	0.65	0.37	1.93	1.39	nitrobenzene

^a MMA: Q₁ = 0.74, e₁ = 0.40

hand, formation of a MAF–NSt complex is unlikely. Copolymerizations of MAF and MSt were carried out in MEK at 60°C. Copolymerizations of MAF with NSt also were carried out for comparison. The copolymer compositions were determined by elemental analyses of their carbon and nitrogen content, respectively. The results are given in Table VIII.

The monomer–copolymer composition curves are shown in Figure 9. The values of r_1 and r_2 were obtained by the nonlinear least-squares method mentioned above.^{8–10} Q - e values for MAF, calculated from monomer reactivity ratios, are shown in Table IX. As shown in Figure 9 and Table VIII, the MAF–MSt system yielded nearly 1:1 copolymers over the wide range of feed compositions as expected. The monomer reactivity ratios were $r_1 = 0.017$, $r_2 = 0.11$ for MSt(M₁)–MAF(M₂). Copolymerizations of MAF with NSt showed a normal

TABLE VIII
Copolymerization of MAF with MSt or NSt^a

Monomer		Polymer- ization time (h)	Copolymer	
[M ₁] (mol %)	[M ₂] (mol %)		Yield (%)	MAF content (mol %)
MSt	MAF			
0.799	0.201	1.0	1.73	0.498
0.698	0.302	1.0	2.47	0.486
0.595	0.405	1.5	5.17	0.502
0.500	0.500	1.5	6.10	0.526
0.403	0.597	1.5	6.92	0.549
0.391	0.609	3.0	13.4	0.553
0.296	0.704	1.6	6.69	0.549
0.199	0.801	1.6	7.66	0.591
0.123	0.877	1.6	7.44	0.642
NSt	MAF			
0.799	0.201	4.2	5.86	0.257
0.703	0.297	4.0	4.85	0.310
0.592	0.408	4.0	5.00	0.331
0.569	0.431	3.0	3.52	0.392
0.500	0.500	4.0	5.29	0.402
0.477	0.523	4.0	4.89	0.440
0.392	0.608	4.0	5.18	0.450
0.359	0.641	4.0	4.96	0.478
0.279	0.721	4.6	5.49	0.542
0.185	0.815	4.6	5.57	0.595
0.099	0.901	5.0	5.98	0.703

^a [AIBN] = 2.90×10^{-3} mol/L; solvent, MEK; temperature, 60°C.

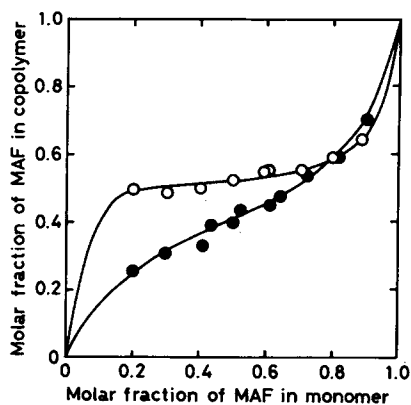


Fig. 9. Copolymerization of MAF with MSt (O) or NSt (●).

TABLE IX
Copolymerization Parameters^a

M ₁	M ₂	r ₁	r ₂	r ₁ r ₂	Q ₂	e ₂
MSt	MAF	0.017	0.11	0.0018	5.03	1.41
NSt	MAF	0.091	0.15	0.091	4.84	1.94

^a MSt = *p*-methoxystyrene: $Q_1 = 1.36$, $e_1 = -1.11$. NSt = *p*-nitrostyrene: $Q_1 = 1.63$; $e_1 = 0.39$.

monomer-copolymer composition curve. The alternation observed in the MSt-MAF system might be interpreted as due either to the preferential polymerization of a MSt-MAF donor-acceptor pair complex¹⁰ or by the usual arguments based on ionic stabilization of the MSt-MAF transition states ($\sim\text{M}_1\text{---M}_2$ or $\sim\text{M}_2\text{---M}_1$).

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