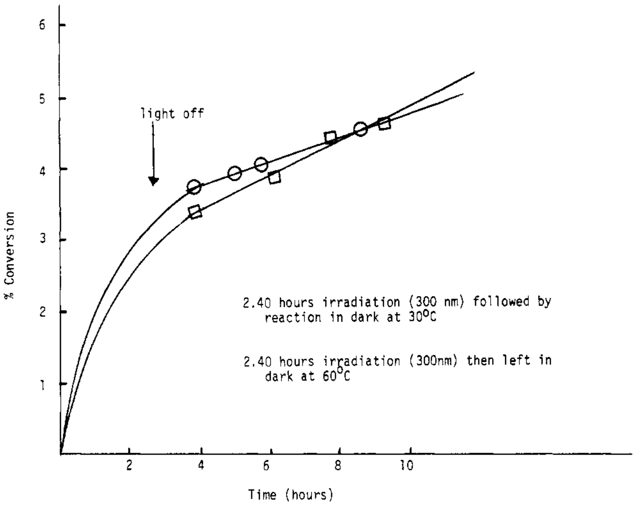

Figure 12. Photopolymerization of cyclohexene oxide initiated by **1b**.

same experimental conditions, irradiated for a specific time (2.40 h) and then transferred to a water bath at the indicated temperature for the time shown. The results show a slight increase in polymer conversion compared to that experiment where the reaction mixture is irradiated for the entire polymerization time.

A further distinction which can be made between phosphonium salts 1 in their abilities to photoinitiate free radical and/or cationic polymerization is the case where the anion is nonnucleophilic in character (e.g., SbF_6^- and PF_6^-). The salt is capable of photoinitiating both free radical and cationic polymerization when the monomer salt is irradiated at 300 nm but just free radical polymerization when the irradiation is carried out at 366 nm. At the same time, those analogous salts bearing nucleophilic anions such as $X = Br^-$ do not photoinitiate cationic polymerization due to the ability of these anions to form stable bonds and thus trap the growing cationic centers.

By selecting the proper anion and wavelength of irradiation, it is possible to carry out strictly free radical polymerization or a combination of free radical and cationic polymerization with the same photoinitiator.

Acknowledgment. The aromatic phosphonium salts used herein were first synthesized by L. Thijs. We acknowledge his work. The work was sponsored, in part, by the National Science Foundation (Grant DMR 81-03100). We are grateful for its support.

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Free Radical Copolymerization Behavior of Methyl α-(Trifluoromethyl)acrylate and α-(Trifluoromethyl)acrylonitrile: Penultimate Monomer Unit Effect and Monomer Reactivity Parameters

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ABSTRACT: Radical copolymerizations of α-(trifluoromethyl)acrylonitrile (TFMAN) or methyl α-(trifluoromethyl)acrylate (MTFMA) were carried out by using styrene (St), *p*-chlorostyrene (pClSt), and methyl methacrylate (MMA) as comonomers. The copolymerizations of the St–TFMAN, pClSt–TFMAN, and St–MTFMA systems were found to follow the penultimate model equation of the copolymerization, and the monomer reactivity ratios were calculated to be $r_1 = 0.03$ and $r_1' = 0.24$, $r_1 = 0.07$ and $r_1' = 0.63$, and $r_1 = 0.05$ and $r_1' = 0.21$, respectively. On the other hand, the copolymerizations of the MMA–TFMAN, pClSt–MTFMA, and MMA–MTFMA systems follow the conventional copolymerization equation (the terminal model equation). The Q and e values of TFMAN and MTFMA obtained are $Q = 2.5$ and $e = 3.1$ and $Q = 0.8$ and $e = 2.9$, respectively. Substituent effects of the trifluoromethyl group on the ethylene double bond are discussed.

Methyl α-(trifluoromethyl)acrylate (MTFMA) and α-(trifluoromethyl)acrylonitrile (TFMAN) were prepared[1] in 1949, and subsequently they were found to be polymerizable with free radical,[1] anionic,[2-4] and γ irradiation[5] initiations and also to be copolymerizable with common monomers such as styrene.[2,3] Recently, Ito et al.[6] described polymerization behaviors of these fluoromonomers, but they did not study their copolymerization with comono-

Table I
Copolymerization of Styrene (St, M_1) and α-(Trifluoromethyl)acrylonitrile (TFMAN, M_2)[a]

	monomer feed						copolymer			
		TFMAN			yield		elemental analysis			
run no.	St, mg	mg	mol %	time, min	mg	%	% H	% C	% N	TFMAN,[b] mol %
1	602.7	20.3	2.82	180	27.4	(4.40)	6.03	77.34	3.33	25.8
2	594.6	37.2	5.10	255	38.6	(6.11)	5.75	74.90	3.82	29.8
3	574.0	69.0	9.37	215	37.1	(5.77)	5.52	72.26	4.38	34.5
4	372.2	63.3	12.8	750	52.4	(12.1)	5.07	71.53	4.62	36.4
5	351.8	73.7	15.2	750	45.8	(10.5)	5.03	70.86	4.76	37.5
6	311.2	124.0	25.5	230	25.2	(5.79)	5.06	68.93	5.13	40.7
7	257.5	191.5	39.0	210	26.8	(5.97)	4.83	67.20	5.52	44.0
8	96.0	114.0	50.6	840	14.4	(7.98)	4.47	67.22	5.58	44.5
9	94.8	253.3	69.7	195	36.7	(10.5)	4.45	65.70	5.89	47.2
10	62.8	291.7	80.1	210	37.6	(10.6)	4.48	64.96	6.03	48.4
11		300.1	100	20[c]	0	(0)				
12[d]		391.5	100	288[c]	0	(0)				

[a] Solvent, benzene (5 mL); initiator, AIBN (0.5 mol %); temperature of polymerization, 60 °C. [b] Determined by nitrogen analysis. [c] Hours. [d] Bulk polymerization.

Table II
Copolymerization of *p*-Chlorostyrene (pClSt, M_1) and TFMAN (M_2)[a]

	monomer feed						copolymer			
		TFMAN			yield		elemental analysis			
run no.	pClSt, mg	mg	mol %	time, h	mg	%	% H	% C	% N	TFMAN,[b] mol %
13	803.7	21.5	2.97	2.5	40.8	(4.94)	4.74	63.46	1.98	19.1
14	795.3	39.0	5.32	3.5	45.9	(5.50)	4.37	62.40	2.62	25.1
15	764.0	60.1	8.26	4.0	56.1	(6.81)	4.62	61.84	2.84	27.1
16	748.5	77.3	10.6	3.0	34.9	(4.23)	4.19	61.07	3.30	31.4
17	706.5	109.0	15.0	4.5	57.8	(7.09)	3.77	60.92	3.35	31.8
18	418.4	121.7	25.0	7.8	43.5	(8.05)	3.61	59.46	3.83	36.1
19	359.0	183.2	36.9	4.0	16.0	(2.95)	3.93	58.44	4.17	39.2
20	334.8	194.9	40.0	9.0	30.1	(5.68)	3.50	57.78	4.15	39.0
21	278.3	239.8	49.7	9.0	18.6	(3.59)	3.58	56.92	4.42	41.4
22	102.8	274.2	75.3	94.0	78.8	(20.9)	3.65	55.77	5.14	47.7

[a] Solvent, benzene (5 mL); initiator, AIBN (0.5 mol %); temperature of polymerization, 60 °C. [b] Determined by nitrogen analysis.

mers other than MMA. Their monomer reactivity parameters such as Alfrey–Price's Q and e values[7] have not been estimated yet. Substituent effects of the trifluoromethyl group on the ethylene double bond have not been studied yet on the basis of the polymerization reactivity, even though its electronic substituent effects, including its Hammett and Taft constants,[8,9] were already reported by various researchers.[8–13]

In this work, radical copolymerizations of MTFMA or TFMAN were studied by using styrene (St), *p*-chlorostyrene (pClSt), and MMA as comonomers and their monomer reactivity parameters such as Q and e values were estimated. Interestingly, it was found in the copolymerizations of the MTFMA–St, TFMAN–St, and TFMAN–pClSt systems that their copolymerization behaviors are so unusual as not to obey the conventional copolymerization equation of Mayo and Lewis[14] and of Alfrey and Goldfinger[15] (terminal model equation) but as to obey the expanded copolymerization equation of Merz, Alfrey, and Goldfinger[16] (penultimate model equation).

Experimental Section

Reagents. Methyl α-(trifluoromethyl)acrylate (MTFMA) and α-(trifluoromethyl)acrylonitrile (TFMAN) were prepared according to the method of Buxton et al.[17] and were purified by fractional distillation to give fractions boiling at 104.5–104.8 °C for MTFMA (lit.[6] 104–105 °C) and at 74.5–75.0 °C for TFMAN (lit.[6] 75–77 °C), respectively. No impurity was found in their gas chromatography. MTFMA and TFMAN were dried over calcium hydride and distilled just before use. Styrene (St), *p*-chlorostyrene (pClSt) and methyl methacrylate (MMA) as comonomers, benzene as solvent, and 2,2′-azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO) as free radical initiators were purified by respective conventional methods.

Instruments. The instruments used were a Yanaco MT-2-CHN Corder for elemental analysis, a Jasco A-100 spectrophotometer for IR, a JEOL PMX 60 SI for NMR, and a Toyo Soda HLC-830D with TSK-GEL columns for GPC.

Copolymerization. Given amounts of monomers, AIBN as a free radical initiator, and benzene as a solvent were placed in an ampule, which was degassed by the freeze–thaw method and sealed. It was then placed in a bath thermostated at 60 ± 0.1 °C for the time of polymerization. The reaction mixture was poured into excess methanol to precipitate the copolymer. The copolymer was dissolved again in a small amount of chloroform and the resulting solution was poured into excess methanol to precipitate the copolymer. The copolymer was dried under reduced pressure at room temperature until constant weight. The composition of the copolymer was established by elemental analysis.

Homopolymerization of MTFMA. Given amounts of MTFMA and AIBN or BPO as free radical initiator and, if necessary, benzene as solvent were placed in an ampule. The rest of the polymerization procedure was similar to the above-mentioned copolymerization procedure. When the reaction mixture was poured into excess methanol, the polymer was obtained as a precipitate, and when the filtrate was evaporated under reduced pressure, additional product was obtained as a white powder.

Results and Discussion

Copolymerizations of α-(Trifluoromethyl)acrylonitrile with Styrene, *p*-Chlorostyrene, and Methyl Methacrylate. The results of copolymerizations of TFMAN (M_2) with St, pClSt, and MMA (M_1) in benzene at 60 °C using AIBN as radical initiator are summarized in Tables I–III, respectively. These copolymerization composition curves are shown together in Figure 1.

When TFMAN was kept in the presence of AIBN at 60 °C for 288 h, its ^1H NMR spectrum exhibited only two

Table III
Copolymerization of Methyl Methacrylate (MMA, M_1) and TFMAN (M_2)[a]

	monomer feed				copolymer						
		TFMAN			yield		elemental analysis				
run no.	MMA, mg	mg	mol %	time, h	mg	%	% H	% C	% N	TFMAN,[b] mol %
23	574.2	35.3	4.84	2.5	75.2	(12.3)	7.03	59.07	0.72	5.20
24	364.5	49.5	10.1	2.7	33.2	(8.02)	7.47	57.49	1.35	9.85
25	338.9	72.2	15.0	4.0	45.9	(11.2)	6.51	56.03	1.83	13.5
26	299.4	123.9	25.5	15	85.2	(20.1)	6.37	54.55	2.67	19.9
27	263.8	167.9	34.5	3.5	23.4	(5.42)	6.49	54.09	3.05	22.8
28	149.0	179.8	49.9	3.5	20.0	(6.08)	5.51	51.97	4.24	32.4
29	104.9	245.9	66.0	20	28.0	(7.98)	5.42	52.19	4.65	34.0
30	76.2	270.5	74.6	20	14.1	(4.07)	5.40	51.75	4.91	37.9

[a] Solvent, benzene (5 mL); initiator, AIBN (0.5 mol %); temperature of polymerization, 60 °C. [b] Determined by nitrogen analysis.

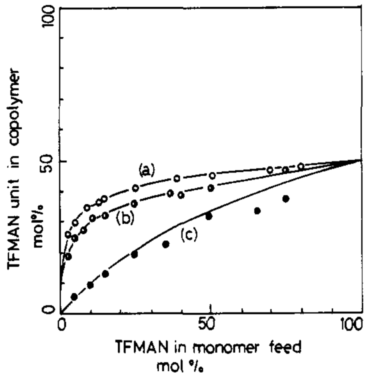

Figure 1. Copolymer composition curves for the copolymerizations of St–TFMAN (○), pClSt–TFMAN (◑) and MMA–TFMAN (●) systems in benzene at 60 °C. Solid lines a, b, and c were obtained by using $r_1 = 0.03$, $r_1' = 0.24$, and $r_2 = 0$, $r_1 = 0.07$, $r_1' = 0.63$, and $r_2 = 0$, and $r_1 = 0.92$ and $r_2 = 0$, respectively.

signals at 6.62 and 7.60 ppm, similar to that of TFMAN, and its reaction mixture was poured into excess methanol to give no precipitate. It is obvious that TFMAN does not homopolymerize via a free radical mechanism as previously reported by Ito et al.[6]

When monomer M_2 does not add to a polymer radical bearing the same terminal unit, the conventional copolymerization equation of Lewis and Mayo[14] can be reduced to the equation

$$y - 1 = r_1 x \tag{1}$$

where x is the molar ratio, $[M_1]/[M_2]$, of the two monomers in feed, and y is the molar ratio, $[m_1]/[m_2]$, of the two monomer units entering the polymers at any instant.

The results of the copolymerizations were treated according to the Kelen–Tüdös method[18] and eq 1. The plots of the Kelen–Tüdös method for these copolymerizations are illustrated in Figure 2.

For the MMA–TFMAN system, both plots of the Kelen–Tüdös method and eq 1 gave straight lines. Monomer reactivity ratios of the MMA (M_1)–TFMAN (M_2) system were calculated according to the former plot to be $r_1 = 0.92 \pm 0.06$ and $r_2 = -0.09 \pm 0.06$ and according to the latter one to be $r_1 = 0.99 \pm 0.3$. The two pairs of monomer reactivity ratios are in good agreement with each other and also close to the corresponding ones, $r_1 = 1.02$ and $r_2 = 0$, of Ito et al.[6] for the copolymerization of the same system in bulk.

Interestingly, it was found in copolymerizations of the St–TFMAN and pClSt–TFMAN systems that both plots of the Kelen–Tüdös method and eq 1 do not give straight lines, indicating that these copolymerizations do not follow the conventional copolymerization equation of Lewis and Mayo[14] and of Alfrey and Goldfinger[15] (referred to as "terminal model equation") under a prerequisite that a reactivity of a polymer radical is only determined by the terminal monomer unit. These copolymerizations could be treated satisfactorily by the expanded equation of Merz, Alfrey, and Goldfinger[16] (referred to as "penultimate model equation") under a prerequisite that a reactivity of a polymer radical is determined not only by the terminal monomer unit but also by the penultimate monomer unit. When monomer M_2 does not homopolymerize, the simplified penultimate model equation[19] is given as

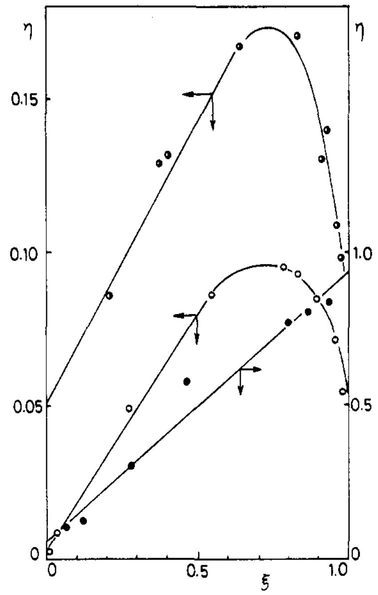

Figure 2. Kelen–Tüdös plots for the copolymerizations of St–TFMAN (○), pClSt–TFMAN (◑), and MMA–TFMAN (●) systems.

$$y - 1 = \frac{r_1' x (1 + r_1 x)}{1 + r_1' x} \tag{2}$$

and

$$r_1 = \frac{y-1}{x^2}\frac{1}{r_1'} + \frac{y-1}{x} \tag{3}$$

where x and y are the same in eq 1 and $r_1 = k_{111}/k_{112}$ and $r_1' = k_{211}/k_{212}$ are ratios of rate constants of addition of M_1 and M_2 monomers to the growing chains with terminal two monomer units $-m_1m_1\cdot$ and $-m_2m_1\cdot$, respectively. The treatments of these copolymerizations using eq 2 and 3 gave $r_1 = 0.03 \pm 0.01$ and $r_1' = 0.24 \pm 0.02$ for the St–TFMAN system and $r_1 = 0.07 \pm 0.03$ and $r_1' = 0.63 \pm 0.11$ for the pClSt–TFMAN system. The calculated plots of $y - 1$ vs. x for the copolymerizations of the St–TFMAN and pClSt–TFMAN systems using eq 2 and these found values of monomer reactivity ratios, r_1 and r_1', are illustrated in Figure 3, where these two calculated curves are

Table IV
Copolymerization of St (M_1) and Methyl α-(Trifluoromethyl)acrylate (MTFMA, M_2)[a]

	monomer feed				yield		copolymer		
		MTFMA					elemental analysis		
run no.	St, mg	mg	mol %	time, h	mg	%	% H	% C	MTFMA,[b] mol %
31		299.0	100	20	0	(0)			
32	282.2	48.2	10.3	6	13.1	(3.96)	6.22	69.33	33.8
33	264.8	68.5	14.9	5.7	19.9	(5.97)	5.96	67.44	37.1
34	233.0	117.3	25.4	6	27.6	(7.88)	5.84	65.14	41.2
35	202.0	160.2	34.9	5.9	37.1	(10.2)	5.66	64.04	43.2
36	103.2	152.1	49.9	5.3	20.9	(8.19)	5.68	62.88	45.4
37	73.4	197.2	64.5	5.8	29.9	(11.0)	5.47	61.16	48.6[c]
38	52.1	228.8	74.8	5.7	32.4	(11.5)	5.06	61.34	48.3

[a] Solvent, benzene (5 mL); initiator, AIBN (0.5 mol %); temperature of polymerization, 60 °C. [b] Determined by carbon analysis. [c] $\bar{M}_n$ = 1.9 × 10^4 determined by GPC with tetrahydrofuran as eluent and standard polystyrene as reference.

Table V
Copolymerization of pClSt (M_1) and MTFMA (M_2)[a]

	monomer feed				yield		copolymer		
		MTFMA					elemental analysis		
run no.	pClSt, mg	mg	mol %	time, h	mg	%	% H	% C	MTFMA,[b] mol %
39	404.5	11.3	2.45	9	20.3	(4.88)	4.40	65.79	10.6
40	399.5	13.4	2.93	7	18.8	(4.55)	4.49	63.94	16.3
41	387.7	33.2	7.15	9	15.8	(3.75)	4.58	61.77	23.0
42	375.1	44.1	9.57	9	21.2	(5.06)	4.58	61.62	23.5
43	351.6	70.9	15.4	9	17.8	(4.21)	4.44	59.46	30.2
44	335.8	92.3	19.8	9	28.7	(6.70)	4.46	58.88	32.1
45	313.3	113.6	24.6	9	21.7	(5.08)	4.46	57.82	35.5
46	288.4	128.7	30.2	9	24.8	(5.81)	4.29	57.50	36.5
47	246.6	178.4	39.4	7	26.0	(6.12)	4.44	56.04	41.2
48	134.5	153.8	50.7	6.5	15.1	(5.24)	4.49	55.15	44.1
49	108.4	181.8	60.1	8.2	21.0	(7.24)	4.40	54.65	45.7
50	70.5	228.2	74.4	8.5	20.1	(6.73)	4.50	53.80	48.5

[a] Solvent, benzene (5 mL); initiator, AIBN (0.5 mol %); temperature of polymerization, 60 °C. [b] Determined by carbon analysis.

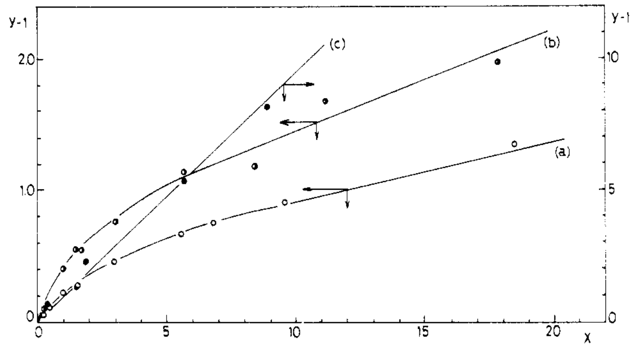

Figure 3. $y - 1$ vs. x plots for the copolymerizations of St–TFMAN (○), pClSt–TFMAN (◑), and MMA–TFMAN (●) systems. Solid lines a, b, and c were obtained by using $r_1 = 0.03$, $r_1' = 0.24$, and $r_2 = 0$, $r_1 = 0.07$, $r_1' = 0.63$, and $r_2 = 0$, and $r_1 = 0.92$ and $r_2 = 0$, respectively.

in good agreement with experimental values. Therefore, it can be concluded that the copolymerizations of the St–TFMAN and pClSt–TFMAN systems do not follow the terminal model equation but the penultimate model equation.

Copolymerization of Methyl α-(Trifluoromethyl)acrylate with Styrene, *p*-Chlorostyrene, and Methyl Methacrylate. The results of copolymerizations of MTFMA (M_2) with St, pClSt, and MMA (M_1) in benzene at 60 °C using AIBN as an initiator are summarized in Tables IV–VI, respectively. These copolymerization composition curves are shown together in Figure 4.

When MTFMA was kept in benzene in the presence of AIBN at 60 °C for 20 h and it was poured into excess methanol, no precipitate was obtained. Furthermore, when the reaction mixture was placed under reduced pressure to remove voltaile materials, no nonvolatile material stayed behind. It was concluded therefore that MTFMA is not polymerizable in benzene at 60 °C with a radical initiator. Thus, copolymerization systems containing MTFMA are to be treated satisfactorily by the simplified copolymerization eq 1 or 2.

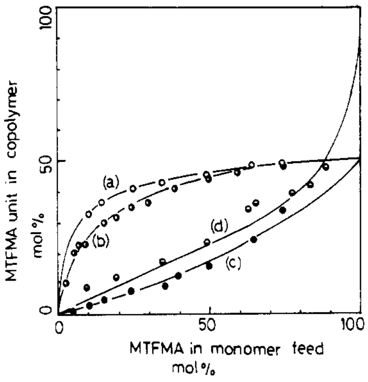

Figure 4. Copolymer composition curves for the copolymerizations of MTFMA with St (○), pClSt (◑), and MMA (●) in benzene and one for the copolymerization of MTFMA with MMA (⊖) in bulk. Solid lines a, b, c, and d were obtained by using $r_1 = 0.05$, $r_1' = 0.21$, and $r_2 = 0$, $r_1 = 0.24$ and $r_2 = 0$, $r_1 = 3.2$ and $r_2 = 0$, and $r_1 = 2.3$ and $r_2 = 0.1$, respectively.

The plots of $y - 1$ vs. x for the copolymerizations of the pClSt–MTFMA, MMA–MTFMA, and St–MTFMA systems are shown in Figure 5, where the plots for the pClSt–MTFMA and MMA–MTFMA systems give straight lines while the one for the St–MTFMA systems does not give a straight line. As for the Kelen–Tüdös treatment,

Table VI
Copolymerization of MMA (M_1) and MTFMA (M_2)[a]

	monomer feed						copolymer		
		MTFMA			yield		elemental analysis		
run no.	MMA, mg	mg	mol %	time, h	mg	%	% H	% C	MTFMA,[b] mol %
51	286.7	21.8	4.71	3	29.8	(9.66)	7.52	59.27	1.9
52	272.9	49.2	10.5	3	37.0	(11.5)	7.92	58.85	3.6
53	257.2	68.5	14.8	3	37.4	(11.5)	7.17	58.12	6.0
54	226.5	113.6	24.6	4	39.4	(11.6)	7.95	57.46	8.2
55	194.7	158.8	34.6	6.5	39.9	(11.3)	7.44	56.94	9.9
56	186.2	185.6	39.3	4	34.8	(9.36)	7.50	56.07	13.0
57	123.7	193.0	50.3	6.75	24.9	(7.86)	6.48	55.11	16.4
58	70.9	198.8	64.6	11.5	21.5	(7.97)	6.69	53.13	23.9
59	49.8	228.1	74.9	12.0	10.2	(3.67)	6.50	50.70	34.0
60	268.4	48.3	10.5	0.58	23.7	(7.48)	7.06	57.09	9.40
61	248.7	94.0	19.7	0.75	26.9	(7.85)	6.49	56.33	12.0
62	192.0	162.7	35.5	0.67	12.1	(3.41)	6.43	55.00	16.8
63	101.1	153.8	49.7	0.75	14.7	(5.77)	6.20	53.25	23.5
64	71.0	197.6	64.4	1.5	3.8	(1.41)	5.95	50.76	33.7
65	69.8	206.5	65.8	1.0	14.0	(5.07)	5.94	50.38	35.4
66	53.5	309.4	79.0	1.5	13.3	(3.66)	5.78	49.45	38.4
67	40.0	332.9	84.4	1.5	4.5	(1.21)	5.96	49.05	41.4
68	25.1	348.8	90.0	2.5	11.8	(3.16)	5.55	47.85	47.0

[a] For runs 51–59; solvent, benzene (5 mL); initiator, AIBN (0.5 mol %); temperature of polymerization, 60 °C. For runs 60–68; in bulk; initiator, AIBN (0.1 mol %); temperature of polymerization, 60 °C. [b] Determined by carbon analysis.

Table VII
Homopolymerization of MTFMA in Bulk

run no.	MTFMA, mg	initiator, mol %	temp, °C	time, h	yield, mg	conversion, %	$\bar{M}_n$[d]
69	325.4	AIBN (0.5)	60	197	40.5[a] 51.6[b]	12.4 15.9	9200 3000
70	343.5	AIBN (0.5)	60	199	54.4[a] 61.1[b]	15.8 17.8	9600 3200
71	406.7	AIBN (0.1)	60	188	41.3[a] 42.9[b]	10.2 10.5	10100 3000
72	313.8	BPO (0.5)	60	197	22.7[c]	7.23	6600

[a] Product insoluble in methanol. [b] Product soluble in methanol. [c] Product soluble in methanol but insoluble in hexane. [d] Determined by GPC with tetrahydrofuran as eluent and standard polystyrene as reference.

the former two systems gave straight lines and the last system no straight line. Thus, the copolymerizations of the pClSt–MTFMA and MMA–MTFMA systems follow the terminal model equation satisfactorily to give monomer reactivity ratios $r_1 = 0.24 \pm 0.02$ and $r_2 = 0 \pm 0.03$ and $r_1 = 3.2 \pm 0.5$ and $r_2 = 0 \pm 0.1$ at 60 °C, respectively. On the other hand, it is certain that the St–MTFMA copolymerization system does not obey the terminal model equation. The copolymerization results were analyzed by using eq 3 to give monomer reactivity ratios $r_1 = 0.05 \pm 0.01$ and $r_1' = 0.21 \pm 0.02$ at 60 °C. The copolymerization of MTFMA with St was found to follow the penultimate model equation.

In the copolymerization of the MMA–MTFMA system, it can be pointed out that the monomer reactivity ratios, r_1, in benzene of this work disagree with those in bulk ($r_1 = 2.3$ and $r_2 = 0$) found by Ito et al.[6] The results of the copolymerization in bulk are summarized in the latter half of Table VI, and the copolymerization composition curve is shown in Figure 4. The copolymerization results could be treated well according to the Kelen–Tüdös method to give the monomer reactivity ratios $r_1 = 2.3 \pm 0.2$ and $r_2 = 0.1 \pm 0.1$ at 60 °C. This value of r_1 is in good agreement with the value of Ito et al.,[6] while the value of r_2, larger than zero, disagrees with the value of zero found by Ito et al.[6] The fact that r_2 is larger than zero implies that MTFMA is homopolymerizable in bulk with a radical initiator even though its nonhomopolymerizability with a radical initiator was described by Ito et al.[6]

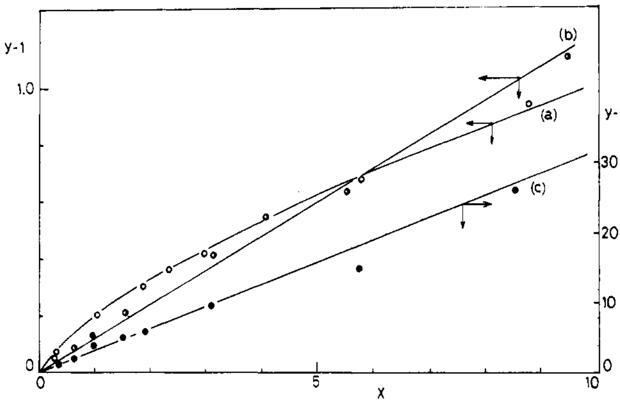

Figure 5. $y - 1$ vs. x plots for the copolymerizations of St–MTFMA (○), pClSt–MTFMA (◑), and MMA–MTFMA (●) systems. Solid lines a, b, and c were obtained by using $r_1 = 0.05$, $r_1' = 0.21$, and $r_2 = 0$, $r_1 = 0.24$ and $r_2 = 0$, and $r_1 = 3.2$ and $r_2 = 0$, respectively.

The results of the bulk polymerization of MTFMA are summarized in Table VII. MTFMA was kept in the presence of AIBN at 60 °C for 190 h, and then it was poured into excess methanol to deposit a white powdery product in 12.4% yield, which was filtered out, washed with methanol, and dried under reduced pressure. The filtrate was evaporated under reduced pressure to give another product of white powder in 15.9% yield. When BPO was used as a radical initiator instead of AIBN, a

Table VIII
Monomer Reactivity Ratios for Copolymerizations of TFMAN and MTFMA (M_2) with St, pClSt, and MMA (M_1)[a]

		penultimate model equation		terminal model equation[c]	
M_1	M_2	r_1'	r_1	r_1	r_2
St	TFMAN	0.24 ± 0.02	0.03 ± 0.01		
pClSt	TFMAN	0.63 ± 0.11	0.07 ± 0.03		
MMA	TFMAN			0.92 ± 0.06	−0.09 ± 0.06
St	MTFMA	0.21 ± 0.02	0.05 ± 0.01		
pClSt	MTFMA			0.24 ± 0.02	0 ± 0.03
MMA	MTFMA			3.2 ± 0.5	0 ± 0.1
MMA	MTFMA[b]			2.3 ± 0.2	0.1 ± 0.1

[a] Copolymerization conditions; solvent, benzene; initiator, AIBN (0.5 mol %); temperature, 60 °C. [b] Copolymerization conditions; in bulk; initiator, AIBN (0.1 mol %); temperature, 60 °C. [c] Determined by the Kelen–Tüdös method.

Table IX
Q and *e* Values of α-Substituted Acrylonitriles and Methyl Acrylates

monomer	α-substituent	*Q*	*e*	monomer	α-substituent	*Q*	*e*
TFMAN	CF_3	2.5	3.1[a]	vinylidene cyanide	CN	20.13	2.58[b]
MTFMA	CF_3	0.8	2.9[a]	methyl α-cyanoacrylate	CN	12.6	2.1[b]
acrylonitrile	H	0.60	1.20[b]	methacrylonitrile	CH_3	1.12	0.81[b]
methyl acrylate	H	0.42	0.60[b]	methyl methacrylate	CH_3	0.74	0.40[b]

[a] This work. [b] Reference 21.

product insoluble in methanol was not obtained but only a product soluble in methanol was obtained. Both soluble and insoluble products in methanol exhibited the same ^1H NMR spectra in which two broad singlet signals at 3.67 and 2.50 ppm were assigned to the methoxy and methylene protons, respectively. Both of their IR spectra similarly showed an ester carbonyl absorption at 1750 cm^{-1}, which is higher by 10 cm^{-1} than that of the monomer MTFMA. From their GPC spectra, it was found that molecular weight of the insoluble and soluble products in methanol are about 10 000 and in the range 3000–7000, respectively. It is certain that these products are homopolymers of MTFMA only with different degrees of polymerization. It can be concluded therefore that MTFMA is homopolymerizable in bulk at 60 °C with a free radical initiator even though the polymer obtained is not of high molecular weight, corresponding to the above-mentioned fact that the monomer reactivity ratio, r_2, of the copolymerization in bulk of the MMA–MTFMA system is larger than zero. The two facts, nonhomopolymerizability in benzene and homopolymerizability in bulk of MTFMA at 60 °C, allow us to presume a high equilibrium monomer concentration of MTFMA between polymerization and depolymerization to be almost as high as the monomer concentration of the monomer itself. Furthermore, in comparison of the monomer reactivity ratios of the MMA–MTFMA copolymerization between in bulk and in benzene, it was found that the r_1 in benzene is remarkably larger than the one in bulk. Since the k_{11}, the homopropagation step of MMA, is considered to be independent of a monomer concentration under those experimental conditions, the k_{12} has to be variable with a monomer concentration, indicating that an equilibrium between polymerization and depolymerization may be effective even in the cross propagation step of MTFMA to a polymer radical with the terminal MMA monomer unit as well as in the above-mentioned homopropagation step of MTFMA.

***Q* and *e* Values of TFMAN and MTFMA.** Monomer reactivity ratios obtained in copolymerizations of TFMAN and MTFMA of this work are summarized in Table VIII. Figure 6 shows the plots of ln $(r_x/Q_x) + e_x^2$ vs. e_x,[20] where Q_x and e_x are for the comonomer x and r_x is the monomer reactivity ratio of the comonomer x in the copolymerization between the monomer and the comonomer x. for the copolymerizations which follow the penultimate model equation, r_1 was preferred rather than r_1' in order to estimate *Q* and *e* values because r_1 has no repulsive influence of the penultimate monomer unit. It was found that *Q* and *e* values of TFMAN and MTFMA are $Q = 2.5$ and $e = 3.1$, and $Q = 0.8$ and $e = 2.9$, respectively.

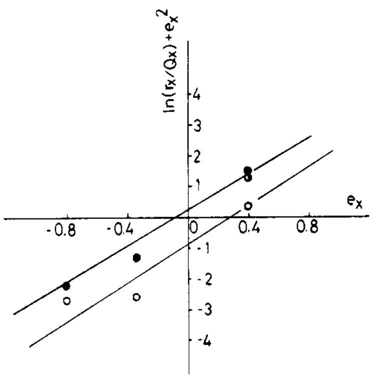

Figure 6. ln $(r_x/Q_x) + e_x^2$ vs. e_x plot for the copolymerizations of TFMAN (○) or MTFMA (in bulk (◑), in benzene (●)) with St, pClSt, and MMA.

Q and *e* values of their related monomers such as TFMAN, methacrylonitrile,[21] acrylonitrile,[21] MTFMA, MMA,[21] and methyl acrylate[21] are summarized in Table IX. It can be pointed out that the resonance stabilization effect of the trifluoromethyl group is almost equal to or a little stronger than that of the methyl group and is much weaker than that of the cyano group, whereas the polarity effect of the trifluoromethyl group is as strongly inductive electron withdrawing as that of the cyano group but that of the methyl group is electron donating.

Penultimate Unit Effect in Copolymerizations of MTFMA or TFMAN. In addition to the copolymerizations in benzene of the St–TFMAN, pClSt–TFMAN, and St–MTFMA systems, a number of copolymerization systems have been reported to follow the penultimate model equation instead of the terminal model equation. These copolymerization systems generally contain styrene and the following comonomers: fumaronitrile (14.3),[19] benzylidenemalononitrile (14.4),[23] ethyl benzylidenecyanoacetate (4.7),[24] methyl α-cyanocrotonate[25] (3.95), maleic anhydride (3.7),[19] citraconic anhydride (3.55),[19] 2,3,5-trimethyl-3-pentyl methacrylate (2.27),[26] acrylonitrile (1.5),[22] cinnamonitrile (1.4),[24] vinyl chloride (1.2),[27] where figures in parentheses refer to the ratio, r_1'/r_1, of monomer reactivity ratios regarded as a measure of the penultimate unite effect in the copolymerizations.[22] In comparison with those systems, the St–TFMAN, pClSt–TFMAN, and St–MTFMA systems were found to exhibit relatively large ratios, r_1'/r_1, of 8.0, 9.0, and 4.2, respectively. Barb[19] and Ham[22] proposed that the penultimate unit effect is attributable to dipole–dipole repulsion between polar substituent groups of the adding monomer and the penultimate monomer unit of the polymer radical in the transition state of the cross propagation steps. It is probable that polar substituent groups such as the trifluoromethyl and cyano groups in TFMAN and MTFMA may play a similar role in the penultimate unit effect because the polarity effect of the trifluoromethyl group on the monomer reactivity is considered to be as strong as that of the cyano group on the basis of the above-mentioned discussion about Q and e values for TFMAN and MTFMA as well as on the basis of a very large dipole moment of 3,3,3-trifluoropropene.[28]

On the other hand, it is certain that the copolymerizations in benzene of the MMA–TFMAN, pClSt–MTFMA, and MMA–MTFMA systems nicely follow the terminal model equation. When these systems under the terminal model equation are compared with the systems under the penultimate model equation, it is noteworthy that a great difference exists in the value of r_1 of their copolymerizations. The systems of the penultimate model equation exhibit values of r_1 close to zero while the systems of the terminal equation exhibit values of r_1 larger than zero. The low value of r_1 close to zero means a very low probability of the sequence of $-m_1m_1-$ and a high probability of the sequence of $-m_1m_2-$ in the copolymer chain; i.e., the polymer radical with the m_1 terminal unit should have an M_2 monomer unit (TFMAN or MTFMA unit) as a penultimate monomer unit, and when an M_2 monomer attacks such a polymer radical, the penultimate unit effect due to dipole–dipole repulsion is to take place frequently. When values of r_1 become larger, the polymer radical with the m_1 terminal unit should have the lower probability of finding M_2 monomer unit as a penultimate monomer unit, corresponding to the less penultimate unit effect. If experiments of copolymerizations were carried out at the monomer feed of very high concentration of M_2 and the composition of the copolymer obtained could be analyzed accurately, the penultimate unit effect would be observed. It is conceivable that the penultimate unit effect in the copolymerization is dependent upon the magnitude of the r_1. When values of the ratio r_1'/r_1 are compared among many copolymerization systems as a measure of a penultimate unit effect in copolymerization, the systems should be limited to a range of systems with similar values of r_1.

Fortunately, the copolymerizations in benzene of the St–TFMAN, pClSt–TFMAN, and St–MTFMA systems exhibit similar values of r_1. In comparison of the ratio, r_1'/r_1, it may be concluded that TFMAN with the trifluoromethyl and cyano groups as α-substituents exerts a larger penultimate unit effect than MTFMA with the trifluoromethyl and carbomethoxy groups, indicating that the cyano group is more effective in the penultimate unit effect than the carbomethoxy group. Of course, coexistence of the trifluoromethyl group and the cyano or carbomethoxy group in the monomers may play an important role in the penultimate unit effect.

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