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Polymerization of Methyl α-(Trifluoromethyl)acrylate and α-(Trifluoromethyl)acrylonitrile and Copolymerization of These Monomers with Methyl Methacrylate

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ABSTRACT: Methyl α-(trifluoromethyl)acrylate (MTFMA) and α-(trifluoromethyl)acrylonitrile (TFMAN) have been successfully anionically homopolymerized by pyridine initiation. Typical anionic initiators for methyl methacrylate (MMA) polymerizations gave rise to complications such as attack on the trifluoromethyl moiety. While radical polymerizations of these monomers failed, both of the monomers have been copolymerized with MMA (M_2) by benzoyl peroxide (BPO) initiation, and monomer reactivity ratios have been determined: $r_{\mathrm{MTFMA}} = 0$ and $r_{\mathrm{MMA}} = 2.36$; $r_{\mathrm{TFMAN}} = 0$ and $r_{\mathrm{MMA}} = 1.02$. Mechanistic explanations of the monomer reactivities are presented.

Introduction

Radiation-sensitive polymers have found wide use in microelectronic fabrication processes as resists. Poly(methyl methacrylate) (PMMA), the most widely used electron beam and deep UV resist, possesses a number of desirable processing characteristics but lacks sensitivity sufficient to allow high production throughput.

Incorporation of an electron-withdrawing group into the PMMA structure has been shown to cause an increase in radiation degradation sensitivity. For example, Helbert et al.[1-3] Chen et al.,[4] and Lai et al.[5,6] observed that poly(methyl α-chloroacrylate) degraded by chain scission more easily than PMMA, but at the same time suffered from a significant cross-linking component. Copolymers of methyl α-fluoroacrylate with MMA have been found by Pittman and co-workers[7,8] to be about twice as sensitive to γ radiation as PMMA, although the homopolymer predominantly cross-linked. Incorporation of a halogenated alkyl group into the ester side chain of acrylate polymers has also been reported to provide a significant increase in sensitivity over PMMA.[7-13] We have found[14] that introduction of a trifluoromethyl group in the α position of the acrylate polymer enhances the chain degradation sensitivity while elminating cross-linking reactions even in homopolymers of methyl α-(trifluoromethyl)acrylate (MTFMA) and α-(trifluoromethyl)acrylonitrile (TFMAN) in contrast to the α-halogenated acrylate homopolymers above. Helbert et al.[9] and Pittman et al.[10] also reported the enhanced sensitivity of copolymers of MTFMA and TFMAN with MMA or methacrylonitrile.

Polymerization of MTFMA and TFMAN by free radical initiation has been claimed by Dickey,[15] but attempts in our laboratory and by Anspon et al.[16] to repeat Dickey's work were successful. We have, however, found that both MTFMA and TFMAN can be anionically homopolymerized[14] and now report these polymerizations as well as radical copolymerizations of these monomers with MMA. Lithographic work will be reported elsewhere. As mentioned earlier, while we were preparing this paper, Helbert et al.[9] and Pittman et al.[10] reported that the copolymers of MTFMA and TFMAN with MMA exhibited high degradation susceptibility and electron beam sensitivity. However, homopolymerizability of these monomers and their copolymerization behaviors have not been discussed before.

Experimental Section

Preparation of Methyl α-(Trifluoromethyl)acrylate.[17] Methyl α-(trifluoromethyl)acrylate (MTFMA) was synthesized by a modification of the method of Buxton et al.[17] Direct methanolysis of the cyanohydrin of 1,1,1-trifluoroacetone gave methyl α-hydroxy-α-(trifluoromethyl)propionate in ca. 70% yield. The α-hydroxyl group was esterified by treating the propionate with acetic anhydride, triethylamine, and 4-(dimethylamino)pyridine in dichloromethane to give methyl α-acetoxy-α-(trifluoromethyl)propionate in ca. 75% yield. Pyrolysis of the ester acetate yielded MTFMA in ca. 62% yield. After ether extraction of the crude pyrolysis product, MTFMA was purified by fractional distillation and purity assayed by gas chromatography (GC). Fractions purer than 99.5% were used for all polymerizations: bp 104–105 °C (lit.[17] bp 103.8–105 °C); ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.80 (CH_3O), 6.40 and 6.67 (CH_2); ^{13}C NMR (20 MHz, $CDCl_3$) δ 53.2 (CH_3O); 122.2 (CF_3) ($J_{CF} = 274$ Hz), 133.2 (CH_2) ($J_{CF} \simeq 5$ Hz), 133.2 (αC), ($J_{CF} \simeq 50$ Hz), 162.7 (C=O).

Preparation of α-(Trifluoromethyl)acrylonitrile.[17] The above cyanohydrin was acetylated and the resulting cyanoacetate was pyrolyzed in ca. 74% yield to give α-(trifluoromethyl)acrylonitrile (TFMAN). Purification was achieved by fractional distillation, and fractions with purity greater than 99.5% (GC) were used for all polymerization experiments: bp 75–77 °C [lit.[17] bp 75.9–76.2 °C (759 mm)]; ^{1}H NMR (60 MHz, neat) δ 6.62 and 6.70 (CH_2); ^{13}C NMR (20 MHz, $CDCl_3$) δ 112.2 (CN), 115.4 (αC) ($J_{CF} \simeq 40$ Hz), 120.3 (CF_3) ($J_{CF} = 272.5$ Hz), 138.4 (CH_2) ($J_{CF} = 3.8$ Hz).

Radical Homopolymerization Experiments. Radical polymerization of MTFMA was attempted under several conditions as detailed in Table I, but all failed. MTFMA (1.617 g, 1.05×10^{-2} mol) and azobis(isobutyronitrile) (AIBN, 1.43 mg, 0.1 mol % to monomer) were placed in a dry polymerization tube, and the tube was degassed and sealed under vacuum. The mixture was allowed to stand at 60 °C for 5 days. No polymerization occurred. Initiation by benzoyl peroxide (BPO) did not produce polymer. γ-Ray radiation (10 Mrd) over 24 h in bulk at −27 °C and in toluene at −78 °C was not effective. Radical polymerization of TFMAN with BPO at 60 °C was also unsuccessful (Table III).

Radical Copolymerization. Radical copolymerizations of MTFMA and TFMAN with MMA (M_2) were carried out in bulk with BPO as an initiator at 60 °C (Tables II and IV, respectively). The copolymerizations were terminated at relatively low conversion. The copolymer formed was dissolved in chloroform, precipitated in methanol, isolated by filtration, and dried at 40–50 °C under vacuum. The composition of the copolymers was determined by elemental analysis and by ^{1}H and ^{13}C NMR.

Reactivity Ratio Determination. Monomer reactivity ratios (r_1 and r_2) for MTFMA, TFMAN, and MMA were determined by the Kelen–Tüdös linear method[18] based on the differential copolymer composition equation. Copolymer compositions of the radical copolymerization products were obtained from elemental analyses (MTFMA–MMA) or ^{1}H NMR (TFMAN–MMA).

Anionic Polymerization. Anionic polymerizations were carried out in vacuo under scrupulously anhydrous conditions. Ampules were throughly dried by intermittent flaming under high vacuum. Solvents (tetrahydrofuran, toluene, *n*-hexane and diethyl ether) were dried by refluxing over CaH_2 followed by distillation and were stored over CaH_2. A known amount of solvent was placed in a dry ampule connected to a break seal under nitrogen flow, CaH_2 was added, and the tube was sealed while the contents

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Table I
Radical and Anionic Polymerizations of Methyl α-(Trifluoromethyl)acrylate

polymn no.	MTFMA feed, g or mL	initiator	solvent	temp, °C	time, h	yield, mg	
						insol[a]	sol[b]
	1.617[h]	AIBN (0.1)[j]		60	144	0	
	1.456[h]	BPO (0.1)		60	144	0	
	0.904[h]	γ-ray (10 Mrd)		−25 to −5	24	0	
	1.483[h]	γ-ray (10 Mrd)	toluene (5.0)[k]	−78 to −40	24	0	
1	0.5[i]	*n*-BuLi (2.0)	toluene (1.0)	−78	16	1	2
				0	16		
4	0.5[i]	$^{+}Na^{-}(MeSt)_4^{-}Na^{+}$ (1.0)	THF (1.1)	−78	69	12	11
				0	48		
5	0.5[i]	*n*-BuLi/18-crown-6 (2.0)	toluene (0.5)	−78	72	20[c]	21[d]
7	0.5[i]	PhMgBr (1.6)	toluene (0.5)	0	74	0	trace
9	0.5[i]	*n*-BuLi/18-crown-6 (1.6)	toluene (0.5)	0	111	0	trace
18[e]	5.0[i]	*n*-BuLi/18-crown-6 (2.0)	toluene (5.0)	−78 to −35	144	4	
24[e]	5.0[i]	*n*-BuLi/18-crown-6 (1.5)	toluene (7.5)	−78 to −60	192	8	
32[e]	3.0[i]	*n*-BuLi/18-crown-6 (5.0)	THF (4.0)	−78	168	8	
55	0.5[i]	pyridine (5.7)		0	20.5[f]	187[g]	

[a] Methanol-insoluble fraction. [b] Methanol-soluble fraction. [c] $\overline{M}_n = 2.91 \times 10^4$; $\overline{M}_w = 4.04 \times 10^4$. [d] $\overline{M}_n = 2.37 \times 10^3$; $\overline{M}_w = 3.01 \times 10^3$. [e] Monomer crystallized during polymerization. [f] Mixture solidified in 1 h. [g] $\overline{M}_n = 1.72 \times 10^4$; $\overline{M}_w = 2.23 \times 10^4$. [h] Grams. [i] Milliliters. [j] Mol % in parentheses. [k] Milliliters in parentheses.

Table II
Radical Copolymerization of Methyl α-(Trifluoromethyl)acrylate (MTFMA, M_1) and Methyl Methacrylate (MMA, M_2)[a]

polymn no.	MTFMA feed, g	MMA feed, g	mole fraction of MTFMA in feed	time	copolymer yield, g (%)	mole fraction of MFTMA in copolymer	
	0.85	0.55	0.50	5[g]	0.717 (51)[b]	0.23[c]	0.25[f]
	1.30	0.39	0.66	4[g]	0.674 (40)[d]	0.36[c]	0.38[f]
	3.70	0.56	0.81	3[g]	1.02 (24)[e]	0.45[c]	0.44[f]
M63	0.295	0.722	0.21	120[h]	0.112 (11.0)	0.13[f]	
M66	0.426	0.700	0.28	65[h]	0.034 (3.0)	0.14[f]	
M62	0.505	0.525	0.39	90[h]	0.025 (2.4)	0.16[f]	
M64	0.626	0.421	0.49	90[h]	0.024 (2.3)	0.23[f]	
M61	0.716	0.343	0.58	90[h]	0.024 (2.3)	0.23[f]	
M65	0.894	0.198	0.75	130[h]	0.031 (2.8)	0.31[f]	

[a] [BPO] = 0.1 mol %, temp = 60 °C, bulk. [b] $\overline{M}_n = 1.05 \times 10^5$, $\overline{M}_w = 3.32 \times 10^5$. [c] ^{13}C NMR. [d] $\overline{M}_n = 1.06 \times 10^5$, $\overline{M}_w = 2.42 \times 10^5$. [e] $\overline{M}_n = 7.65 \times 10^4$, $\overline{M}_w = 1.95 \times 10^5$. [f] Carbon analysis. [g] Days. [h] Minutes.

Table III
Radical and Anionic Polymerizations of α-(Trifluoromethyl)acrylonitrile

polymn no.	TFMAN feed, g or mL	initiator	solvent	temp, °C	time	yield, g
	1.0[d]	BPO (0.1)[f]		60	4 days	0
22[a]	0.5[e]	*n*-BuLi/18-crown-6 (1.2)	toluene (0.5)[g]	−78	1 h	0.260
44[a]	1.0[e]	*n*-BuLi/18-crown-6 (1.2)	THF (1.0)	−78	4 h	0.203
46[b]	0.5[e]	(CaH_2)		room temp	>1 month	0.465
54[c]	0.48[e]	BPO (5.0)		60	10 days	0
		pyridine		room temp	ca. 1 min	0.627

[a] Polymer immediately precipitated when the reagents were mixed. [b] The monomer polymerized to a clear, hard solid while being dried on CaH_2 at room temperature in a tube sealed under high vacuum. [c] The monomer vigorously polymerized when a drop of pyridine was added to the radical polymerization mixture at room temperature. [d] Grams. [e] Milliliters. [f] Mol %. [g] Milliliters.

were frozen at liquid nitrogen temperatures. Degassing was repeated until evolution of hydrogen gas ceased. The ampule was then melted off the vacuum line. *n*-Butyl bromide (*n*-BuBr), bromobenzene (PhBr), and the monomers were dried in the same fashion. Pyridine was dried over molecular sieves (3 Å) and further dried over sodium hydroxide pellets under high vacuum. α-Methylstyrene and tetrahydrofuran (THF) used in the tetramer dianion synthesis were further dried over a sodium mirror under high vacuum. *n*-Butyllithium (*n*-BuLi) was synthesized by the reaction of *n*-BuBr with metallic lithium in *n*-hexane. The lithium bromide that precipitated during the reaction was removed by filtration. The resulting *n*-BuLi solution (1 M in *n*-hexane) was then distributed under nitrogen flow into ampules connected to a break seal. The ampules were melted off the vacuum line after degassing and stored. Phenylmagnesium bromide (PhMgBr) was synthesized by the reaction of PhBr with magnesium turnings in diethyl ether and distributed in a similar manner. α-Methylstyrene (αMeSt) tetramer dianion $^{+}Na^{-}(\alpha MeSt)_4^{-}Na^{+}$ was synthesized by the reaction of αMeSt with an oil-free sodium mirror in THF. The red solution (1 M in THF) was distributed under high vacuum through a sintered glass filter into calibrated ampules connected to a break seal. 18-Crown-6 was purified by recrystallization from hexanes. Transfer of the reagents and polymerization were carried out under high vacuum. The monomer and solvent were introduced into a polymerization ampule by distillation in vacuo simply by crushing the break seals with a glass-coated iron bar. The initiator solution was allowed to flow into the polymerization ampule by crushing the initiator ampule break seal in vacuo, and complete addition of the initiator was achieved by refluxing the solvent.

.Table IV
Radical Copolymerization of α-(Trifluoromethyl)acrylonitrile (TFMAN, M_1) and Methyl Methacrylate (MMA, M_2)[a]

polymn no.	mole fraction of TFMAN in feed	time	copolymer yield, %	mole fraction of TFMAN in copolymer			
				^{1}H NMR[b]	anal.		
					C	H	N
	0.50	4 days	66.2		0.35	0.36	0.34
	0.19	100 min	4.8		0.16	0.18	0.16
	0.40	125 min	1.7		0.29	0.27	0.25
	0.58	170 min	1.6		0.59	0.40	0.28
I56	0.18	2.2 h	6.7[d]	0.22[c]	0.20	0.20	0.14
I57	0.30	3.0 h	7.7[e]	0.23	0.25	0.25	0.24
I58	0.39	3.5 h	6.6[f]	0.28	0.29	0.27	0.27
I59	0.50	4.3 h	7.4[g]	0.31	0.33	0.31	0.30
I60	0.60	4.8 h	5.6[h]	0.33	0.34	0.29	0.34
I61	0.70	5.0 h	4.7[i]	0.41	0.37	0.38	0.36
I62	0.80	7.0 h	3.5	0.65[c]			
I63	0.90	7.0 h	0.8	0.45			

[a] [BPO] = 0.1 mol %, temp = 60 °C, bulk. [b] Measured in pyridine-d_5. [c] Measured in $CDCl_3$; errors large due to impurities in the solvent. [d] $\overline{M}_n = 2.91 \times 10^5$, $\overline{M}_w = 5.20 \times 10^5$. [e] $\overline{M}_n = 2.54 \times 10^5$, $\overline{M}_w = 4.08 \times 10^5$. [f] $\overline{M}_n = 2.23 \times 10^5$, $\overline{M}_w = 3.40 \times 10^5$. [g] $\overline{M}_n = 2.03 \times 10^5$, $\overline{M}_w = 2.90 \times 10^5$. [h] $\overline{M}_n = 1.53 \times 10^5$, $\overline{M}_w = 2.55 \times 10^5$. [i] $\overline{M}_n = 1.27 \times 10^5$, $\overline{M}_w = 2.16 \times 10^5$.

Polymerization was terminated by adding cold methanol to the polymerization ampule at the polymerization temperature. The resulting mixture was dissolved in dichloromethane and then poured into a large excess of stirred methanol containing a small amount of hydrochloric acid. The polymer was reprecipitated in methanol, isolated by filtration, and dried in vacuo at 38 °C. The methanol-soluble fraction was recovered by concentration of the mother liquor to dryness, followed in some cases by precipitation in hexane.

Measurements. NMR spectra were recorded on Varian T-60 (^{1}H), Varian CFT-20 (^{1}H and ^{13}C), and IBM NR-80 (^{19}F) spectrometers. Gel permeation chromatography (GPC) was performed with a Waters Model 150 chromatograph equipped with six μ-Styragel columns. Measurements were made at 30 and 40 °C in THF (PMTFMA and copolymers). Combustion analyses were performed by Childers Laboratories, Milford, N.J., and by Chemical Analytical Services, University of California, Berkeley, Calif.

Results and Discussion

Radical Polymerization. In the Introduction it was noted that Anspon's attempt[16] to polymerize MTFMA failed in spite of Dickey's claim.[15] Our attempts to repeat Dickey's work were also unsuccessful (Table I). It is very surprising that Dickey listed Lewis acids as effective initiators for the polymerization of this and related monomers, since no other effective cationic homopolymerization of acrylate or methacrylate monomers has been reported. Since, as shown in Tables II and IV, radical copolymerizations of MMA with MTFMA and TFMAN have proceeded normally, the observation that the fluorinated monomers will not homopolymerize must be explained in terms of the low reactivity of the monomers themselves and/or the radicals derived from them rather than the possible inhibition by impurities or unique terminating mechanisms.

In order to study the reactivity of MTFMA and TFMAN, copolymerizations of the fluorinated monomers (M_1) with MMA (M_2) were carried out (Tables II and IV). The copolymerizations were terminated at low conversions in order to allow use of the differential form of the copolymerization equation. The initial and final feed ratios of the comonomers were confirmed to be indistinguishable by monitoring the reaction mixture by GC. The experimental conditions therefore warrant the use of the differential equation instead of the integrated form. The copolymer compositions were determined by combustion elemental analysis (MTFMA–MMA) or by ^{1}H NMR (TFMAN–MMA) and the monomer reactivity ratios (r_1 and r_2) were obtained by the Kelen–Tüdös linear method.[18] For MTFMA the values determined are $r_1 = 0$ and $r_2 = 2.36$ and for TFMAN they are $r_1 = 0$ and $r_2 = 1.02$.

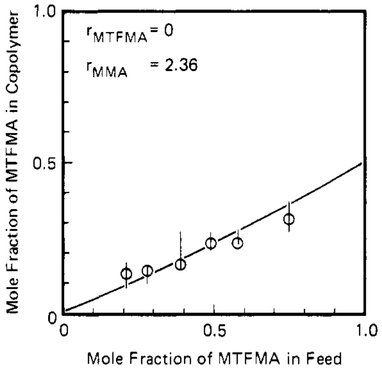

Figure 1. Copolymer composition vs. monomer feed of MTFMA and MMA. Vertical lines represent errors involved in elemental analysis.

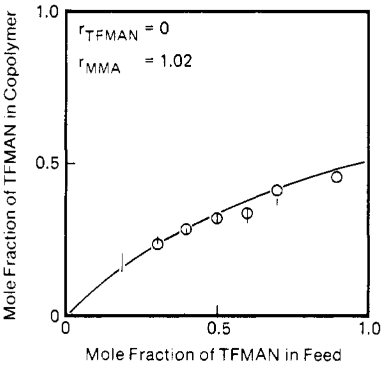

Figure 2. Copolymer composition vs. monomer feed of TFMAN and MMA. Vertical lines represent errors involved in elemental analysis, and circles represent mole fraction of TFMAN in copolymer determined by ^{1}H NMR integration measured in pyridine-d_5.

The reactivity ratio $r_1 = 0$ for MTFMA and TFMAN means that these monomers do not self-propagate ($k_{11} = 0$) and indicates that Dickey's reported homopolymerization of MTFMA and TFMAN is suspect.[15] The copolymer composition curves for MTFMA–MMA and TFMAN–MMA are presented in Figures 1 and 2, respectively. The figures indicate that a very high M_1 con-

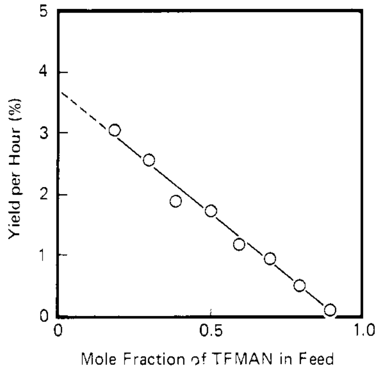

Figure 3. Relationship between yield per hour and mole fraction of TFMAN in feed of copolymerization with MMA. [BPO] = 0.1 mol %, bulk, at 60 °C.

tent in the feed would produce a copolymer with almost 1:1 alternation and that copolymers with greater than 50% M_1 could not be obtained under these conditions.

The lower reactivity of TFMAN is evidenced also by the decreasing yield and molecular weight of the copolymer with increasing TFMAN in the feed (Table IV). The yield per hour (approximate propagation rate), as demonstrated in Figure 3, linearly decreases with the increase in the mole fraction of TFMAN in the feed, revealing that the propagation of the TFMAN homopolymerization is essentially zero.

Monomer reactivity has been generally interpreted in terms of resonance stabilization (Q) and polarity (e) (Alfrey–Price Q–e scheme),[19] the latter of which has been shown to be linearly related to the Hammett substituent constant σ.[20] By summarizing the polymerization data for varieties of vinyl monomers, Tsuruta[20,21] proposed general criteria for reactivity: monomers with e values between 1.7 and −1.0 ($0.7 > \sigma > -0.1$) readily undergo radical polymerization, and monomers with e greater than 1.7 ($\sigma > 0.7$) and with e values smaller than −1.0 ($\sigma < -0.1$) have tendencies to undergo anionic and cationic polymerizations, respectively, rather than radical polymerization. Though there are a few exceptions,[22] the Tsuruta criteria generally hold. According to the additivity of e values proposed by Otsu et al.,[23] the e values of MTFMA and TFMAN can be calculated as follows:

$$e_{CH_2=C(CF_3)(CO_2CH_3)} = e_{CH_2=CH(CO_2CH_3)} + 2.4\sigma_{CF_3} = 0.6 + 2.4 \times 0.54 = 1.9$$

$$e_{CH_2=C(CF_3)(CN)} = e_{CH_2=CH(CN)} + 2.4\sigma_{CF_3} = 1.2 + 2.4 \times 0.54 = 2.5$$

The high polarity of MTFMA and TFMAN generated by the strong inductive electron-withdrawing effect of the CF_3 group would therefore be expected to result in low reactivity toward radical homopolymerization in these fluorinated monomers.

The low radical polymerizability of these fluorinated monomers seems to be consistent with analogues studied by others for which reactivity ratios in copolymerization with MMA (M_2) are reported as follows:

$$CH_2{=}C(CH_2F)(CO_2Et){:}^{24} \quad r_1 = 0.51,\ r_2 = 1.05$$

$$CH_2{=}CF(CO_2CH_3){:}^{25} \quad r_1 = 0.36,\ r_2 = 1.17$$

In addition, methyl α,β,β-trifluoroacrylate[26] has been reported to show only meager radical polymerization.

In contrast to the examples above, trifluoromethyl-substituted olefins such as 3,3,3-trifluoropropene and 2-methyl-3,3,3-trifluoropropene do exhibit radical polymerization,[27] while the parent hydrocarbons do not polymerize by radical initiation. Here, the high electron density at the double bond (highly negative e) is reduced by introduction of the electron-withdrawing CF_3 group to such an extent that radical homopolymerization can occur.

Electron-deficient monomers generally possess high reactivity toward radicals. Giese et al.[28] have clearly demonstrated the high reactivity of olefins containing electron-withdrawing substituents toward alkyl radicals which have a nucleophilic character and have also shown that copolymerization Q,e parameters and the reactivity toward a cyclohexyl radical are linearly related.[29] One would expect then that MTFMA and TFMAN would be more reactive than MMA toward electron-rich alkyl radicals. In polymerization, however, the reactivity of the polymer radical plays an important role in kinetics and is known to contribute more strongly to the propagation rate (k_p) than the reactivity of the monomer. Yokota et al.[30] have indicated, by studying the relative reactivities of alkyl methacrylate polymer radicals toward MMA and of alkyl methacrylate toward PMMA radical, that the polar effect of the alkyl group on the polymer radical is about 2.5 times greater than that of the monomer. It would be very difficult for the highly electron-deficient MTFMA and TFMAN radicals to add to the highly electron-deficient MTFMA and TFMAN monomers ($k_{11} \approx 0$), which is consistent with our observation that $r_1 = 0$.

The significantly higher reactivity of MMA toward the PMMA radical than MTFMA ($r_2 = 2.36$) appears to be contradictory, but this fact might be explained at least in part by steric effects. Even though the CF_3 group is not much bulkier than the CH_3 group, the difference in size may be sufficient to explain the low reactivity of MTFMA relative to MMA. Tsuruta et al.[31] have noted in copolymerization studies of methyl α-alkylacrylates with styrene that the reactivity does not depend on the polar effect of the α-alkyl group but does depend strongly on the steric effect. The importance of the steric effect in polymerization of methyl α-alkylacrylates was also pointed out by Cameron et al.[32]

By comparing the $1/r_2$ values of the two copolymerization systems, it is revealed that TFMAN is 2.3 times more reactive than MTFMA toward PMMA radical, which is consistent with its higher polarity and smaller steric hindrance.

Linear relationships between vinyl monomer reactivity and NMR chemical shifts and between monomer e values and chemical shifts have been well established.[33-39] The β carbon (133.2 ppm) and β protons (6.40 and 6.67 ppm) of MTFMA absorb at much lower field than the corresponding resonances of MMA, reflecting the lower electron density in the C=C bond due to the strong electron-withdrawing effect of the CF_3 group. The β-carbon (138.4 ppm) and β-proton (6.62 and 6.70 ppm) resonances of TFMAN appear still further downfield, consistent with the higher e value of the monomer.

Anionic Polymerization. Since radical homopolymerization of the monomers failed and vinyl monomers with very positive e values have been shown to readily undergo anionic polymerization, anionic initiators were tested as shown in Table I. We were further encouraged to conduct these experiments by the report that low-conversion, low molecular weight homopolymers of α-(trifluoromethyl)vinyl acetate ($e = 1.51$) had been obtained by pyridine initiation[40] while isopropenyl acetate itself did not undergo anionic polymerization. It is also known that the transition state of radical polymerizations is more strongly affected by steric effects than that of anionic polymerizations as evidenced by the successful anionic homopolymerization of methyl α-n-butylacrylate.[41] We have found that anionic homopolymerization of MTFMA and TFMAN does occur, especially when pyridine is used as an initiator.

As shown in Table I, the anionic intiators such as *n*-BuLi and PhMgBr, typically employed for MMA polymerization, produced only a small amount of polymeric and oligomeric materials from MTFMA. The meager polymerization of MTFMA could be ascribed to one of several factors, including termination by coordination of the initiator counterion and/or fluorine abstraction by either the initiator or the polymer anion.

It has been suggested that anionic polymerizations of MMA[42] and methyl isopropenyl ketone[43] suffer from pseudotermination due to the cyclic coordination of the growing end and the penpenultimate carbonyl function to the counterion. This phenomenon was suspected to be responsible for the low yield and oligomer formation in MTFMA polymerizations initiated with metal alkyls. According to ^{1}H FT NMR integration, the methanol-insoluble fraction of polymn no. 1 (Table I) is a polymeric material and the methanol-soluble fraction is a mixture of monomer and dimer attached to the *n*-butyl residue. The methanol-insoluble fraction of polymn no. 4 has three MTFMA units on each side of the α-MeSt tetramer while the methanol-soluble fraction has one MTFMA unit on each end of the tetramer. When 18-crown-6 was added to the *n*-BuLi initiator system, the yield was greatly increased. GPC analysis has indicated that both the methanol-insoluble and soluble fractions from the crown ether reactions are polymeric ($\bar{M}_w = 4.04 \times 10^4$ and 3.01×10^3, respectively). One is thus tempted to conclude that the above-mentioned pseudotermination might well be present in the nonpolar solvent and even to some extent in THF.

Another possible explanation for the slow polymerization of MTFMA could involve chain termination by fluorine elimination. In order to study this possibility, ^{19}F NMR studies were made on the polymers and oligomers. Fluorine resonances other than CF_3 were not detected. The CF_3 absorption was rather complex due, at least in part, to the sequence and configuration differences, but fluorine termination does not appear to be operative. The ^{19}F NMR study, however, does not necessarily eliminate the possibility of the attack of the initiator on the CF_3 moiety. In fact, Buxton et al.[17] have reported that the CF_3 group is remarkably labile toward aqueous alkali, especially when the fluorine atoms are allylic. Henne et al.[44] also noted when studying the base-catalyzed addition of alcohols to 3,3,3-trifluoropropene that extensive attack on the fluorinated group took place, providing products such as 3-ethoxy-3,3-difluoropropene, even though some of the expected addition to the C=C bond did occur. In addition, sodium naphthalene and the conditions employed for the anionic polymerization of styrene fail to produce a polymer of α-(trifluoromethyl)vinyl acetate, but the weaker base pyridine successfully initiates the polymerization.[40] These observations together with our successful polymerization of MTFMA by pyridine initiation (no. 55) might indicate that the strongly basic anionic initiators attack the CF_3 moiety faster than the C=C bond. Our poorer polymer yields at higher temperature (0 °C, no. 7 and 9) may support this mechanistic explanation. Large-scale preparations with *n*-BuLi/18-crown-6 (no. 18, 24, and 32) failed, mainly due to the crystallization of the MTFMA monomer (mp ca. −20 °C), which occurred even with higher dilution, at higher temperature, and at higher initiator concentration.

The successful initiation of MTFMA polymerization with pyridine to produce a high polymer ($\bar{M}_n = 1.72 \times 10^4$) in a good yield (ca. 40%) is of interest, because pyridine is not strong enough to initiate the polymerization of MMA. Therefore, MTFMA must be more reactive than MMA toward anionic initiators owing to its higher *e* value due to the electron-withdrawing effect of the CF_3 group. However, the polymerization of MTFMA suffers from the above-mentioned side reaction when alkyl alkali metal initiators are employed.

In contrast to the meager polymerizations of MTFMA with *n*-BuLi/18-crown-6, the analogous TFMAN exhibited spontaneous polymerization under the same conditions. Polymerization was so fast that the dissolving and mixing of the reagents were incomplete when the polymer precipitated as a rigid solid, preventing the monomer from reacting further. The products were very faintly colored, indicative of slight concurrent cyclization through the CN groups. At this moment, we do not have a satisfactory explanation for the observation that TFMAN is readily polymerized under conditions with which MTFMA is very difficult to polymerize. Absence of pseudotermination and steric hindrance in TFMAN polymerization might be part of the reason.

TFMAN was also readily homopolymerized by pyridine initiation after an unsuccessful attempt at radical homopolymerization. One drop of pyridine was added to the monomer at room temperature and resulted in vigorous polymerization with heat evolution (no. 54). The polymer purified by precipitation was yellow due to considerable cyclization at elevated temperature.

^{1}H NMR Spectra. The methoxy ^{1}H NMR absorptions of the MTFMA–MMA copolymers are interesting. The signals are composed of two main resonances, possibly due to the slight difference in chemical shifts of the CH_3O group of the two monomer units. There are poorly resolved shoulders between the main peaks, which might be indicative of sequential and/or configurational information. The former is more likely, since the methoxyl signal of PMMA does not show splitting due to tacticity in $CDCl_3$.[45] We are continuing to explore high-field NMR spectra of these interesting polymers.

The methoxy ^{1}H NMR resonances of the TFMAN–MMA copolymers dissolved in deuterated pyridine also split into more than two peaks. The relative intensities change greatly with the copolymer composition. Sequential and/or configurational information might be obtained by analyzing higher field NMR spectra.

Conclusions

1. MTFMA and TFMAN do not undergo radical homopolymerization under conventional conditions.
2. MTFMA and TFMAN copolymerize with MMA by BPO initiation. The reactivity ratios determined are $r_{\mathrm{MTFMA}} = 0$, $r_{\mathrm{MMA}} = 2.36$ and $r_{\mathrm{TFMAN}} = 0$, $r_{\mathrm{MMA}} = 1.02$.
3. MTFMA shows only meager anionic polymerization when alkyl alkali metal initiators are used due to the preferential attack of the initiators on to the CF_3 moiety of the monomer.
4. In contrast, TFMAN can be readily homopolymerized by initiation with *n*-BuLi/18-crown-6.
5. Both MTFMA and TFMAN readily undergo homopolymerization by anionic initiation with pyridine.

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(46) **Note Added in Proof**: After this paper had been submitted for publication, we found a Japanese patent (Japan. Koka: Tokkyo Koho 96825, 1978) describing enhanced electron beam sensitivity of copolymers of MMA with vinyl monomers containing halogens including MTFMA. However, the homopolymerization of MTFMA and TFMAN is not discussed in the patent.

Halato-Telechelic Polymers. 4. Synthesis and Dilute-Solution Behavior

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ABSTRACT: Halato-telechelic polymers (HTP) result from the complete ionization of both ends of telechelic prepolymers. Their behavior in nonpolar solvents is characterized by a very abrupt increase of viscosity at increasing concentration, so that gel formation is noted at concentrations as low as 1.5 g·dL^{-1}. The nature of the ion pairs, polarity of the medium, and temperature influence significantly the gel formation and prove its electrostatic origin. The depressive effect of any polar additive on the gelation requires drastic conditions in the synthesis of reproducible materials. In this respect, an efficient synthetic pathway has been proposed. The influence of molecular weight and end-to-end distance of the prepolymer shows the determinant role played by the polymeric backbone on the ion aggregation process.

Introduction

In the past 2 decades, ion-containing polymers have attracted increasing attention, thanks to the dramatic modifications induced in the properties of polymeric materials by strongly interacting ions. A large range of potential applications is, of course, the primary source of this interest.[1] Books and reviews published recently give an excellent outline of their synthesis, structure, properties, and applications.[2-6]

Network glasses and polyelectrolytes have been known for a long time, whereas ionomers are now also recognized as very attractive materials. They consist of mainly nonpolar polymeric backbones carrying pendant ionizable groups (carboxylate or sulfonate), more or less randomly distributed along them. As a typical example, polyethylene-based ionomers are commercially available from DuPont under the trade name Surlyn. They can be processed on conventional equipment for plastics and offer improved properties in comparison to the corresponding base polymer.[4,5]

Eisenberg has paid attention to the role played by the strong coulombic interactions in controlling the supermolecular structure of ionomers. In media of low dielectric constant, the ionic groups can aggregate not only into multiplets but also into clusters, depending on the ion content.[5,7] Multiplets contain a few ion pairs, whereas clusters consist of 30–100 ion pairs, including some polymeric chains; they are responsible for a multiphase structure in ionomers. Rheological behavior, X-ray and neutron diffraction, electron microscopy, and NMR, IR,

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