Preparation and Polymerization of p-Fluoromethylstyrene

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ABSTRACT: p-Fluoromethylstyrene (p-FMS) was prepared by means of a halogen—halogen interconversion reaction of p-chloromethylstyrene with potassium fluoride in the presence of a phase-transfer catalyst. As p-FMS is increasingly purified, it becomes less stable and undergoes the polycondensation of benzylic-type fluoromethyl groups. However, p-FMS was stable when traces of a basic solvent were added to it. Thus, in the presence of a small amount of acetonitrile, the homopolymerization of the monomer and the copolymerization with styrene (St) were carried out at 60°C using α,α'-azobisisobutyronitrile as an initiator. The radical copolymerization of p-FMS with methyl methacrylate (MMA) takes place without any polycondensation even in the absence of a basic solvent, owing to the weak basicity of MMA itself. Monomer reactivity ratios of p-FMS (M_A) with St and MMA (M_B) are $r_A=1.3$, $r_B=0.44$ and $r_A=0.84$, $r_B=0.30$, respectively. The polymers obtained were found to be stable both in solid state and in basic solvents.

KEY WORDS   Halogen—Halogen Interconversion / p-Fluoromethyl-styrene / Basic Solvent / Radical Polymerization / Monomer Reactivity Ratio /

Although the chloromethylation of polystyrene has been performed mostly for the preparation of polymers having benzylic-type chloromethyl groups, recently the homo- and copolymerization[1,2] of chloromethylstyrene (CMS), which is now commercially available, were recommended to obtain the well-defined polymers. However, no reports have been published on the synthesis of polymers containing fluoromethyl groups by either the fluoromethylation of polystyrene or the polymerization of fluoromethylstyrene monomers.

In the recent literature,[3] it has been shown that the chlorine of organic chlorides can be successfully replaced by fluorine in the presence of a phase-transfer catalyst. As the application of this method, we have carried out the halogen—halogen interconversion reaction of p-CMS with potassium fluoride in the presence of the catalyst.

The present study deals with the preparation of p-FMS and its radical homopolymerization and copolymerization with vinyl monomers.

EXPERIMENTAL

Materials

Commercial potassium fluoride (KF) and commercial cetyltrimethylammonium bromide (CTMAB), a phase-transfer catalyst, were used without further purification. p-Chloromethylstyrene (p-CMS) was prepared by the method described in another paper.[2] Methyl methacrylate (MMA), styrene (St), and α,α'-azobisisobutyronitrile (AIBN) used in the copolymerizations were purified by the usual methods.

Procedures

Preparation of p-FMS from p-CMS. In a 500-ml three-necked round-bottom flask were placed 60 g of p-CMS, 186 g of KF, 11.8 g of CTMAB, which is essential to this kind of

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reaction,[3-5] 70 ml of toluene, 105 ml of water, and a small amount of p-tert-butylcatechol. The mixture was stirred vigorously and heated in an oil bath of 120°C (temp of the mixture, 113°C). In order to avoid prolonged heating of the reaction mixture, the extent of conversion of p-CMS was followed by measuring the residual p-CMS with gas chromatography (GC). When the extent of conversion reached a maximum, stirring was stopped and the hot mixture was allowed to separate into two layers. The lower aqueous layer was removed from the flask by a siphon while the layer was hot. The yield of p-FMS was found to increase to some extent when the aqueous solution was renewed in the course of the reaction. The organic compounds contained in the aqueous layer removed were extracted with ether and added to the organic layer. The organic layer was washed several times with water containing sodium sulphate, dried over sodium sulphate, and poured into methanol to separate the polymer formed during the interconversion reaction. After the solvent was evaporated and small amounts of hexamethylphosphoric triamide (HMPA) and p-tert-butylcatechol were added to its residue, the mixture was distilled under a reduced pressure (7.0 mmHg), giving 26 g of p-FMS as a fraction of 45.5°C. $n_D^{20} = 1.5347$. $d_4^{20} = 1.22$. Fluorine content was 13.7% (calcd, 13.95%). In the receiving flask, a small amount of potassium carbonate was placed beforehand. HMPA and potassium carbonate were added in order to stabilize the fluoromethyl groups, as will be described later.

Polymerization. The homopolymerization of p-FMS and its copolymerization with St were carried out as described in another paper,[2] with the exception that acetonitrile was added to p-FMS before the polymerization as a stabilizer.

Analysis and Measurements

The composition of the copolymers was determined mostly by NMR analysis. Some of these results were checked by elemental analyses of those copolymers and the coincidence was satisfactory. NMR spectra were recorded using a Hitachi R-20B (60 MHz) spectrometer. IR spectra were obtained on a spectrometer of Model IRA-1 of JASCO. Gel-permeation chromatograms (GPC) were measured in tetrahydrofuran (THF) using a Toyo Soda HLC-802UR with two GHM columns.

RESULTS AND DISCUSSION

Preparation of p-FMS
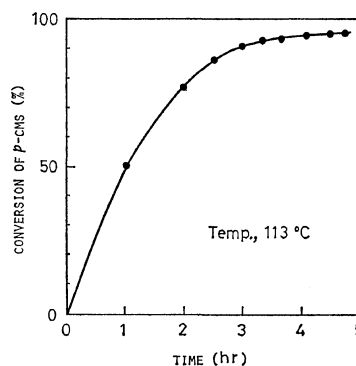
Table I summarizes the results of the halogen—

Figure 1. Time—conversion curve of p-CMS in the halogen—halogen interconversion of p-CMS with potassium fluoride. The extent of conversion of p-CMS was obtained from residual p-CMS determined by GC.

Table I. Halogen—halogen interconversion reaction of p-CMS with potassium fluoride[a]

p-CMS			KF		CTMAB[b]		Toluene, ml	H₂O, ml	Time, hr	p-FMS[c] yield, %
g	mol		g	mol	g	mol				
34	0.223		106	1.82	6.7	0.018	40	60	4	18
60	0.393		186	3.20	11.8	0.032	70	105	6	26
60	0.393	{1st	170	2.93	11.0	0.030	70	100	1}[d]	39
		{2nd	170	2.93	6.5	0.018	—	70	4}	

[a] Reaction temp, 113°C.
[b] CTMAB, cetyltrimethylammonium bromide.
[c] bp, 62.5°C/9.5 mmHg; 45.5°C/7.0 mmHg.
[d] The aqueous solution was renewed in the course of the reaction.
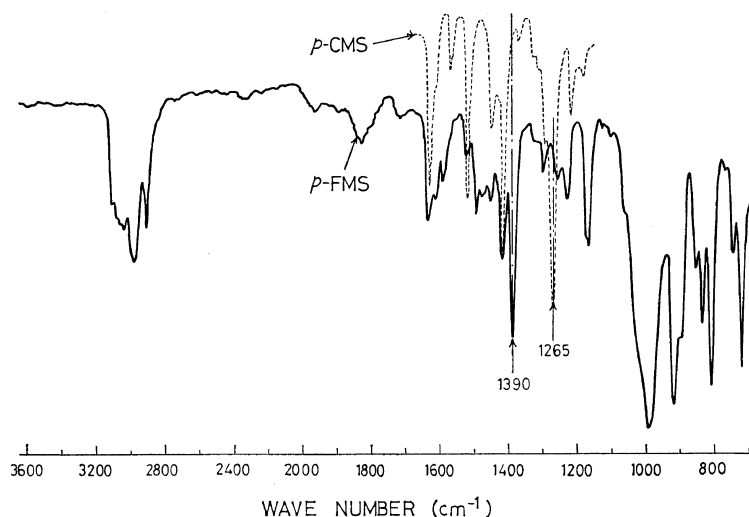
WAVE NUMBER (cm⁻¹)

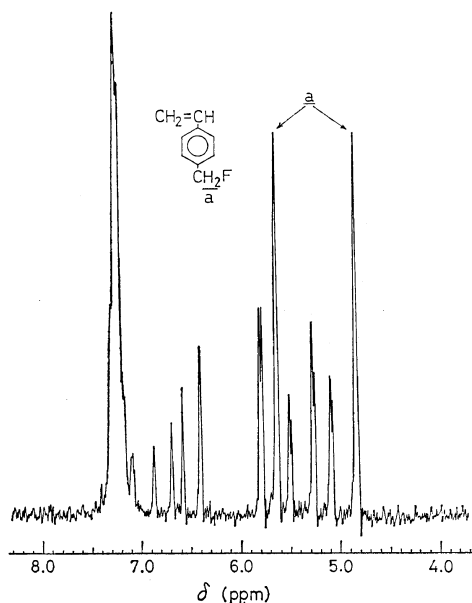**Figure 2.** Infrared spectra of *p*-FMS (——) and *p*-CMS (- - -).

Figure 3. NMR spectrum of *p*-FMS (*ca.* 5% in CCl₄).

halogen interconversion reaction of *p*-CMS with KF in the presence of CTMAB as a catalyst. Figure 1 shows the relation between reaction time and the extent of conversion of *p*-CMS which was obtained from the residual *p*-CMS determined by GC. Although the extent of conversion of *p*-CMS is above 90%, the yield

of *p*-FMS is appreciably lower. The low yield of isolated *p*-FMS may be due to the high reaction temperature, which causes the thermal polymerization of vinyl groups in the course of the interconversion reaction and is indispensable to this reaction.[3] The favorable reaction time is found to be 4—6 hr from Table I and Figure 1 under these reaction conditions.

The GC of *p*-FMS prepared by the above method showed a single peak. In the IR spectrum of *p*-FMS (Figure 2), the –CH₂Cl peak at 1265 cm⁻¹ gave place to the –CH₂F peak at 1390 cm⁻¹. Figure 3 shows the NMR spectrum (CCl₄) of *p*-FMS, where the phenyl, vinyl, and fluoromethyl proton signals appeared at $\delta = 7.27$, 5.08—6.88, and 5.22 (doublet, $J_{H-F} = 47$ Hz), respectively. The ratio of the peak areas was 4.0 : 4.0 : 3.01 : 2.0.

It was found that *p*-FMS is an extraordinarily labile monomer and less stable as it is more purified. In most cases, when no stabilizer was used, the distillate of *p*-FMS polymerized almost explosively, with evolution of heat and fumes during distillation. Even if such polymerization did not take place during the distillation, the distilled *p*-FMS kept at room temperature suddenly polymerized after an induction period of a few hours. This polymerization reaction was found to be a polycondensation of Friedel—Crafts-type which was reported in an early ref

6 and was confirmed by our recent study[7] on the non-catalyzed polymerization of benzyl fluoride and its related reactions. However, we found that the fluoromethyl group of p-FMS was made stable for a long time in the presence of a small amount of HMPA, THF, acetonitrile, or basic inorganic compounds such as potassium carbonate, whereas benzene, nitrobenzene, and nitromethane were not effective. This suggests that the basicity of these substances was responsible for the stabilization of p-FMS. Now it is understood that the strong basicity of CTMAB stabilized the produced p-FMS during the halogen—halogen interconversion reaction even at a high temperature of 113°C. Accordingly, we would like to suggest that it is important for the storage of this monomer to add a small amount of a basic solvent or potassium carbonate to the monomer.

Homopolymerization of p-FMS

As expected from the preceding discussion, no sooner had the ampoule containing pure p-FMS and 1 wt % of AIBN been immersed in a thermostat kept at 60°C than p-FMS polymerized explosively and the polymer filled up the ampoule. This polymer is insoluble in THF, benzene, and N,N-dimethylformamide. The insolubility of the polymer is obviously due to the gelation reaction, where both the polycondensation of benzylic-type fluoromethyl groups and the addition polymerization of vinyl groups take place simultaneously. However, as described above, only the vinyl polymerization of p-FMS took place at a moderate rate, even at 60°C, when a small amount of basic solvent was added to p-FMS as a stabilizer. In this study, acetonitrile was used as the basic solvent

by reason of the fact that the chain-transfer constant of styryl radical to the solvent is relatively low ($C_s = 2.45 \times 10^{-5}$ at 60°C[8]). The results of the homopolymerization of p-FMS are given in Table II. The polymer thus obtained was soluble in solvents which dissolve polystyrene, such as THF, benzene, N,N-dimethylformamide, etc. In the NMR spectrum of poly(p-fluoromethylstyrene), PFMS, two broad peaks at $\delta = 6.97$ and 6.48 ppm (phenyl protons), a doublet peak at 5.21 ppm ($J_{H-F} = 47$ Hz), (fluoromethylene protons), and a broad peak at $\delta = 1.5$ ppm (methylene and methyn protons) appeared and assigned (Figure 4). The ratio of the peak areas was 4.0 : 2.0 : 3.1, suggesting that only the addition polymerization of the vinyl group of p-FMS took place.

When PFMS was kept in its solid state, the pendant fluoromethyl groups of PFMS were stable, i.e., the IR spectrum of the polymer did not change at room temperature even after three months. Also, the polymer was stable in a
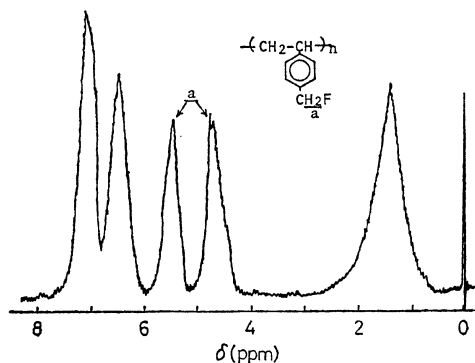

Figure 4. NMR spectrum of poly(p-flouoromethyl-styrene) (ca. 5% in CCl₄—CDCl₃ mixture).

Table II. Homopolymerization of p-FMS[a]

p-FMS, g	AIBN, mg	Benzene, ml	Acetonitrile, ml	Time, hr	Polymer	
					Yield, %	$M_n \times 10^{-4}$ [b]
2.0	21	2.0	0	1	95[c]	—
0.5	11	0.5	0.2	20	51	6.4
3.2	38	2.0	1.0	23	83	3.1[d]

[a] Temp, 60°C.
[b] Based on GPC, calibrated with standard polystyrene.
[c] Gelation.
[d] Fluorine content: found, 13.6%; calcd, 13.95%.

Table III. Radical copolymerization of p-FMS with St[a]

No.	p-FMS (M_A), mmol	St (M_B), mmol	Mol fract of M_A in feed	Time, min	Conversion, %	M_n[b] $\times 10^{-5}$	Mol fract of M_A in copolymerization
S- 1	2.57	16.3	0.136	45	6.4	—	0.26
S- 2	3.93	12.9	0.233	45	4.8	1.4	0.34
S- 3	5.99	12.1	0.331	40	6.8	—	0.46
S- 4	7.93	11.1	0.417	50	5.6	2.0	0.53
S- 5	9.22	10.4	0.470	40	7.6	—	0.58
S- 6	10.7	7.52	0.587	50	8.5	—	0.68
S- 7	11.9	5.30	0.692	40	6.8	2.0	0.75
S- 8	13.1	5.07	0.721	35	7.7	—	0.78
S- 9	12.0	3.28	0.785	50	7.6	1.4	0.84
S-10	13.2	1.74	0.883	40	11.0	—	0.93

[a] Temp, 60°C; initiator, AIBN (0.5 wt %); acetonitrile, 5 wt % of an amount of p-FMS.
[b] Based on GPC, calibrated with standard polystyrene.

basic solvent or a hydrocarbon solvent containing a small amount of a basic solvent. However, when the polymer was dissolved in purified benzene, the polymer solution gradually became turbid and then turned into a jelly-like mass after a day or less.

Copolymerization with St or MMA

The radical copolymerization of p-FMS (M_A) with St (M_B) was performed in the presence of a small amount of acetonitrile. The results are given in Table III. The Fineman—Ross plots gave a straight line and the reactivity ratios, r_A and r_B, were estimated to be 1.3 and 0.44, respectively. By the use of these reactivity ratios, the composition curve for the copolymerization was drawn as shown in Figure 5. The experimental plots are in close agreement with the calculated composition curve.

In the radical copolymerization of p-FMS with MMA, only the vinyl copolymerization took place without any polycondensation of the fluoromethyl group, even in the absence of any basic solvent. This suggests that a week basicity of MMA itself is enough to supress the polycondensation. Thus the copolymerization of p-FMS (M_A) with MMA (M_B) was carried out without the addition of a basic solvent. The copolymerization results are summarized in Table IV. The reactivity ratios estimated from the Fineman—Ross plots are $r_A=0.84$ and $r_B=0.30$. The composition curve obtained from these values agrees with the experimental plots (Figure 5). It is also noted that the composition curve for the
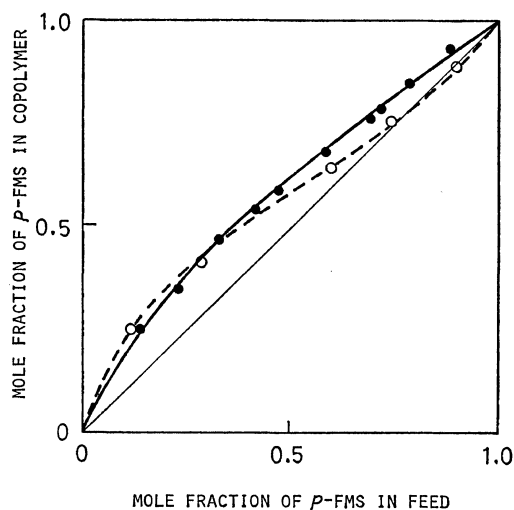

Figure 5. Composition curves for the copolymerization of p-FMS (M_A) with St (M_B) and p-FMS (M_A) with MMA (M_B) by AIBN at 60°C. M_B (St): ●, experimental; ——, calculated from $r_A=$ 1.3 and $r_B=0.44$. M_B (MMA): ○, experimental; - - -, calculated from $r_A=0.84$ and $r_B=0.30$.

copolymerization of p-FMS with MMA is similar in trend to that of p-CMS with MMA.

The copolymerization parameters are listed in Table V. The copolymerization reactivities of p-FMS with St or MMA are a little larger than those of p-CMS with St or MMA. The Alfrey—Price Q value of p-FMS is somewhat larger than that of p-CMS. In the case of copolymerization with St, the e value of p-FMS is

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Table IV. Radical copolymerization of p-FMS with MMA[a]

No.	p-FMS (M_A), mmol	MMA (M_B), mmol	Mol fract of M_A in feed	Time, hr	Conversion, %	$M_n{}^b \times 10^{-5}$	Mol fract of M_A in copolymerization
M-1	2.13	16.8	0.113	1	0.15	6.5	0.21
M-2	4.56	11.0	0.293	2	4.98	—	0.44
M-3	9.22	6.15	0.600	2	5.72	1.4	0.64
M-4	11.3	4.05	0.736	2	7.81	—	0.76
M-5	14.2	1.66	0.895	2	7.93	1.4	0.89

[a] Temp, 60°C; initiator, AIBN (0.5 wt %); bulk.
[b] Based on GPC, calibrated with standard polystyrene.

Table V. Copolymerization parameters

M_A	M_B	r_A	r_B	$r_A r_B$	Q	e	ref
p-FMS	St	1.3	0.44	0.59	1.3	−0.07	This paper
CMS	St	1.1	0.69	0.79	0.98	−0.31	2
p-FMS	MMA	0.84	0.30	0.25	1.5	−0.77	This paper
CMS	MMA	0.76	0.37	0.28	1.3	−0.73	2

larger than of p-CMS. This is reasonable when the order of electronegativity of halogens is considered. However, in the case of copolymerization with MMA, the above relation is reversed; moreover, the e value of p-FMS is much smaller than that obtained for the copolymerization with St. This suggests an interaction between a fluoromethyl group and a methoxycarbonyl group, since a fluoromethyl group is stabilized by MMA.

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