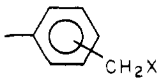
Reaction of Living Polystyrene with Poly(*p*-fluoromethylstyrene) and Its Styrene Copolymer[1]

Mikio Takaki, Ryuzo Asami,* Hiroshi Inukai, and Tsutomu Inenaga

Department of Synthetic Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan. *Received August 3, 1978*

ABSTRACT: The reaction of living polystyrene with poly(*p*-fluoromethylstyrene) (P(FMS)) and its styrene copolymers (P(FM-S)) was carried out under various reaction conditions as one of a series of studies on the preparation of well-defined polymers. This reaction involves the grafting reaction, the monomeric termination, and the dimeric termination of living polystyrene, being greatly affected by reaction conditions. For example, the grafting reaction of polystyryllithium (PSt-Li) takes place almost quantitatively in a tetrahydrofuran–benzene medium whereas the monomeric termination of PSt-Li occurred exclusively in benzene. When P(FMS) was used as the backbone polymer, the degree of grafting was dependent on the mole ratio of living ends to fluoromethyl groups ([LE]/[CH_2F]) larger than 0.5, and at [LE]/[CH_2F] = 1.15 the "grafting density" of P(FMS) went up to 71% though 38% of PSt-Li gave homopolystyrene. In the case of P(FMS-S), however, the degree of grafting was independent of the mole ratio and an amount of homopolystyrene formed was as small as 10% or less.

A number of efforts have been made by many investigators to find out a quantitative coupling reaction between two prepolymers for the preparation of well-defined polymers such as graft, comb-shaped, and star-type polymers. We also have been studying various polymer-coupling reactions for the same purpose, and recently have reported on the coupling reaction between living polystyrene and poly(chloromethylstyrene)[2] instead of chloromethylated polystyrene.[3-10] These reactions of living polystyrene with benzylic chloromethyl groups have been found to involve side reactions to some extent, which were revealed to be the monomeric and dimeric termination of living polystyrene in the previous papers.[1b,11] Also, the experimental results of the coupling reactions of living polystyrene with pendant benzylic halides such as



X = Cl, Br, and I

have shown that the extent of side reactions was in the following order: chloride < bromide < iodide.[1b] This fact prompted us to investigate the reaction of living polystyrene with polymer having benzylic fluoromethyl groups as the pendants, with the expectation of the improvement in the extent of coupling.

As will be described in this work, the coupling reactivity of poly(*p*-fluoromethylstyrene) with living polystyrene is, however, not always in accord with the order expected above. Namely, being greatly affected by reaction conditions, the coupling reaction of polystyryllithium with fluoromethyl groups changed from almost no coupling to stoichiometrical one. In the present study, the variety of the reaction of the polymers containing benzylic fluoromethyl groups as the pendants will be demonstrated.

Experimental Section

Materials and Coupling Reaction. Poly(*p*-fluoromethylstyrene) (P(FMS)) was obtained by homopolymerization of *p*-fluoromethylstyrene (*p*-FMS, prepared by the method reported previously[12]) and its styrene copolymers (P(FMS-S) by copolymerization of *p*-FMS with styrene in the presence of 5 wt % acetonitrile to *p*-FMS using α,α'-azobis(isobutylnitrile) as an initiator. Each of the polymers was fractionated into five fractions by previous method,[2] and the third fractions were used as the backbone polymers. In the H^1 NMR spectrum of P(FMS) thus obtained, two broad peaks at δ = 6.48 and 6.97, a doublet peak at 5.21 ($J_{H\text{-}F}$ = 47 Hz), and a broad peak at 1.5 were observed and were assigned to phenyl, fluoromethyl, and methylene and methine protons, respectively. The ratio of the peak areas was 4.0:2.0:3.1. These polymers are stable enough both in a solid state and in a basic solvent (e.g., tetrahydrofuran (THF), acetonitrile, *N*,*N*-dimethylformamide), and even in a hydrocarbon medium if it contains a trace of such a basic solvent; however, they are labile in pure benzene solution, i.e., the polymer solution gradually became turbid and then turned into a jelly-like mass after a day or less.[12] The backbone polymer solutions were prepared in THF or in benzene, according to the reported procedures[2] except for the addition of a few drops of THF to 10 mL of benzene used for freeze drying. When the polymer solution was prepared in benzene, it was immediately submitted to the reaction after the preparation, because of the instability of the backbone polymer in benzene as mentioned above. Polystyryllithium and polystyrylpotassium used as a precursor were prepared by the same method as described in a previous paper.[13] The composition of the copolymers, number-average molecular weights, and abbreviations for the precursors and the backbone polymers are given in Table I.

Table I
Abbreviation, Composition, and Number-Average Molecular Weight ($\overline{M}_n$) of the Prepolymers

prepolymer	abbreviation	composition (St/p-FMS)[a]	$\overline{M}_n \times 10^{-4}$
polystyryllithium	PSt-Li		2.70
polystyrylpotassium	PSt-K		2.63
poly(*p*-fluoromethylstyrene)	P(FMS)	*b*	3.05
p-fluoromethylstyrene–styrene copolymer	$P(FMS\text{-}S)_{5.1}$	5.10	4.14
p-fluoromethylstyrene–styrene copolymer	$P(FMS\text{-}S)_{22.5}$	22.5	7.20

[a] Mole ratio of styrene to *p*-fluoromethylstyrene in copolymer which was determined by elemental analysis. [b] Fluorine content: found, 13.6%; calcd., 13.95%.

The reaction apparatus and the experimental procedures employed in this study were the same as described previously.[13]

Measurement and Evaluation of the Extent of Reactions. The number-average molecular weights of the prepolymers and the recovered polymers after the reactions were determined by the osmotic pressure measurement in toluene at 37 °C using a Knauer membrane osmometer. Gel permeation chromatograms were obtained previously.[1b] The rate of the reaction of PSt-K with the backbone polymers was measured by spectroscopic method by use of the same reaction apparatus as described previously,[13] viz., the decay of optical density of 348 nm ascribed to PSt-K was followed by a Hitachi Model 220 spectrophotometer.

The extent of the grafting reaction, the monomeric termination, and the dimeric termination of living polystyrene were evaluated by the same method as described in the preceding paper.[1b] The degree of coupling of fluoromethyl groups in the backbone polymer

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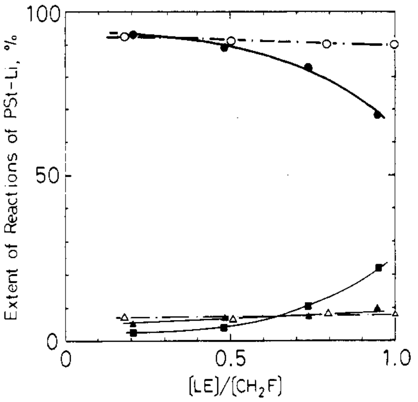

Figure 1. Dependence of the extent of the grafting reaction (○, ●), the monomeric termination (△, ▲), and dimeric termination (■) of PSt-Li on the [LE]/[CH_2F] ratio in the reaction of PSt-Li with P(FMS) (●, ■, △) or P(FMS-S)$_{5.1}$ (○, △).

was estimated from the degree of grafting of living polystyrene determined by the GPC method.[1b]

Results

The reactions of living polystyrene with P(FMS) or P(FMS-S) were observed to proceed always homogeneously and were shown to involve the grafting reaction, the monomeric termination, and the dimeric termination of living polystyrene. Table II shows the results of some reactions under typical reaction conditions. The reactions of PSt-Li with the backbones in benzene (e.g., LFS-2′ and LFS-5′) proceeded rapidly and the yellow color ascribed to PSt-Li disappeared within the time of mixing, but the extent of grafting of PSt-Li was as low as about 10%, i.e., the monomeric termination of PSt-Li took place predominantly. However, when these reactions were carried out in a THF–benzene medium (THF = 50 vol %, unless otherwise noted), the rate of the reactions was slowed down to some extent whereas the degree of grafting was almost quantitative. Also, the reactions are affected by such reaction conditions as the mole ratio of living ends to fluoromethyl groups ([LE]/[CH_2F]), the distance between adjacent fluoromethyl groups, and the counterion of polystyryl anion as shown in Tables II and III, as well as by the temperature as shown in Table IV.

The dependence of the extent of reactions on the [LE]/[CH_2F] ratio is shown in Figure 1 as to the reaction of PSt-Li with P(FMS) and P(FMS-S)$_{5.1}$ in a THF–benzene mixture. When P(FMS-S)$_{5.1}$ was used as the backbone polymer, the degree of grafting of PSt-Li was as high as 90% or more and independent of the ratio. However, in the case of P(FMS), the degree of grafting considerably decreased and the extent of the dimeric termination of PSt-Li increased, when the value of [LE]/[CH_2F] exceeded 0.5. Figure 2 shows the dependence of the extent of reactions on the [LE]/[CH_2F] ratio as to the reaction of PSt-K with P(FMS) or P(FMS-S)$_{5.1}$ in THF. When P(FMS-S)$_{5.1}$ was used as the backbone, the degree of grafting of PSt-K was about 60% and was independent of the ratio. In the case of P(FMS), the degree of grafting of PSt-K decreased as the [LE]/[CH_2F] ratio increased. Furthermore, the extent of monomeric termination became larger than that of grafting at the range of [LE]/[CH_2F] > 0.6. In these reaction systems, the extent of dimeric termination of PSt-K was negligibly small over the range of [LE]/[CH_2F] ratio from 0.2 to 1.0.

Figure 3 shows the plots of the extent of coupling reaction of fluoromethyl groups against the [LE]/[CH_2F] ratio in the optimum reaction system, i.e., PSt-Li–P(FMS) or P(FMS-S)$_{5.1}$–THF/benzene mixture. The curve for P(FMS-S)$_{5.1}$ is very close to the ideal coupling line that represents an ideal case without any side reactions. However, the curve for P(FMS) deviates remarkedly from the ideal coupling line when the [LE]/[CH_2F] ratio exceeds 0.5 and the extent of coupling seems to converge to ca. 75%, where the branches calculated from the extent of coupling are still as many as 164 per backbone polymer molecule.

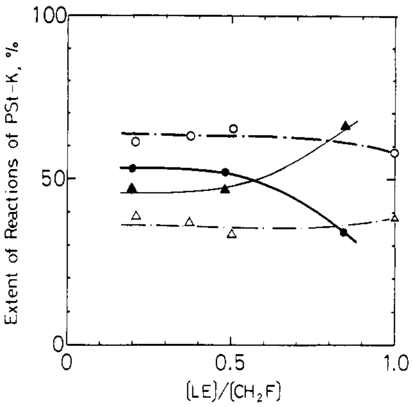

Figure 2. Dependence of the extent of the grafting reaction (○, ●) and the monomeric termination (△, ▲) on the [LE]/[CH_2F] ratio in the reaction of PSt-K with P(FMS) (●, ▲) or P(FMS-S)$_{5.1}$ (○, △).

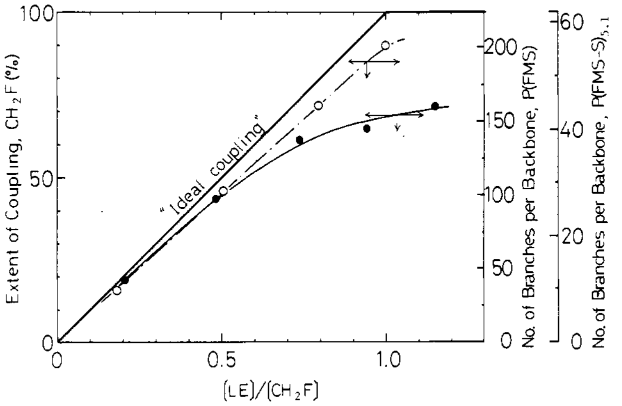

Figure 3. Relationship between the [LE]/[CH_2F] ratio and the extent of coupling of fluoromethyl groups and the number of branches per backbone polymer molecule in the reaction of PSt-Li with P(FMS) (●) or P(FMS-S)$_{5.1}$ (○) in a THF–benzene medium.

The effect of the counterion of polystyryl anion was investigated and the results are shown in Table III. The degree of grafting is much higher with Li^+ than with K^+, and in the latter the termination of the polystyryl anion is mostly monomeric.

The reaction of PSt-K with P(FMS-S)$_{5.1}$ was carried out over the temperature range from −78 to 23 °C and the results are shown in Table IV. The rate of the reaction was slowed down at lower temperature; for example, in KFS-T-2 (at −78 °C) the red color ascribed to polystyryl anions faded apparently but did not disappear completely even for 125 h. As concerns the extent of reactions, the lower the temperature the higher the extent of dimeric termination of PSt-K, while both the degree of grafting and the monomeric termination of PSt-K decrease as the temperature is lowered.

Discussion

Hindering Effect on the Degree and the Rate of Grafting. As described in previous papers,[2,13] the decrease in the degree of grafting with an increase in the [LE]/[CH_2F] ratio is interpreted in terms of the hindering effect[7,8] of the branches which are already attached to the backbone polymer. As shown in Figures 1 and 2, no hindering effect is recognizied on the extent of grafting in

Table II: Anionic Grafting Reaction of Living Polystyrene with P(FMS) and P(FMS-S)$_{5.1}$ under Various Reaction Conditions

expt	living PSt [LE]^a × 10^3, mol L^{-1}	backbone [CH$_2$F]^b × 10^3, mol L^{-1}	[LE]/[CH$_2$F]	solvent	reaction temp, °C	reaction time, h	$(\overline{M}_n)_R$^{c} × 10^{-4}	extent of reactions of LE, %: grafting eq 1^d	grafting GPC^e	termination dim.^{f}	termination monom.^{g}	extent of coupling of CH$_2$F,^{h} %
	PSt-Li	P(FMS)										
LF-2	2.11	10.3	0.205	THF/Bz^i	0	20	30.6	94	93	2	5	19
LF-12	4.63	4.01	1.15	THF/Bz^i	0	163	10.8	75	62	26	12	71
		P(FMS-S)$_{5.1}$										
LFS-2′	2.15	8.72	0.247	Bz	23	20	2.90	3	10^j		90	
LFS-5′	3.22	6.45	0.499	Bz	23	20	3.05	8	18^j		82	
LFS-2	1.81	10.0	0.181	THF/Bz^i	23	20	16.4	93	92	3	5	17
LFS-5	3.32	6.60	0.503	THF/Bz^i	23	20	24.5	93	92	3	5	46
LFS-10	4.42	4.43	0.998	THF/Bz^i	23	50	24.8	91	90	2	8	90
	PSt-K	P(FMS)										
KF-2	2.03	10.2	0.199	THF	23	44	5.12	50	53	0	47	11
KF-8	4.07	4.84	0.841	THF	23	170	3.74	30	34	0	66	29
		P(FMS-S)$_{5.1}$										
KFS-2	1.96	9.43	0.208	THF	23	23	5.91	59	61	0	39	13
KFS-10	4.17	4.16	1.00	THF	23	124	6.49	60	58	4	38	58

[a] Concentrations of living ends. [b] Concentrations of fluoromethyl groups. [c] Number-average molecular weight of recovered polymer. [d] Determined from eq 1 in the preceding paper.[1b] [e] Estimated by GPC. [f] Dimeric termination of living polystyrene. [g] Monomeric termination of living polystyrene. [h] Estimated from the degree of grafting of living ends estimated by GPC. [i] THF–benzene mixture (THF = 50 vol %). [j] In the GPC curve, the parts of graft polymer and dimerically terminated PSt-Li were indistinguishable.

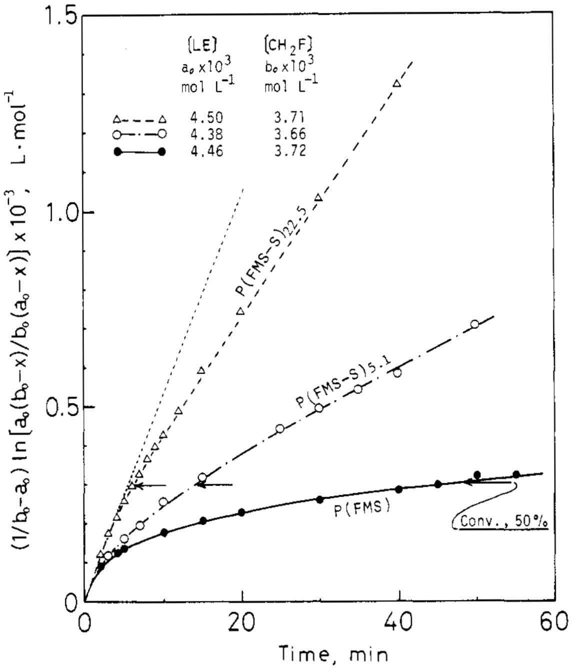

Figure 4. Second-order plots for the reactions of PSt-K with P(FMS) (●), P(FMS-S)$_{5.1}$ (○), and (FMS-S)$_{22.5}$ (△) at 26 °C.

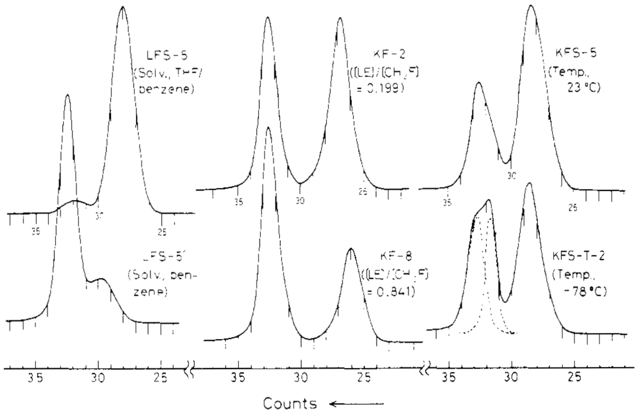

Figure 5. GPC curves of polymers obtained under various reaction conditions; the peaks of them can be ascribed to the polymers produced by the grafting reaction (<30 counts), the dimeric termination (ca. 31.5 counts), and the monomeric termination (ca. 32.5 counts) of living polystyrene as previously reported.[1b]

the P(FMS-S)$_{5.1}$-PSt-Li or PSt-K systems, and this suggests that the sixth fluoromethyl group from the coupled one would be free from such steric hindrance. In the P(FMS)–PSt-Li system, the degree of grafting begins to decrease as the [LE]/[CH$_2$F] ratio comes close to 0.5 as shown in Figure 1, showing that just adjacent fluoromethyl groups would be subject to the hindrance. However, in the P(FMS)–PSt-K system, the degree of grafting is only just above 50% which begins to decrease again as the ratio comes close to 0.5 as shown in Figure 2, showing that the fluoromethyl group four units apart from the coupled one would be subject to the hindrance. The second-order plots of the reactions of PSt-K with P(FMS), P(FMS-S)$_{5.1}$, and P(FMS-S)$_{22.5}$ are shown in Figure 4. It clearly can be seen that these plots are not straight lines and deviate from the dotted straight line calculated for the second-order reaction. These deviations, showing the depression of the rate of the reactions, became much greater as the contents of FMS in the backbone polymers increased. Even in the case of P(FMS-S)$_{22.5}$ the rate began to decrease at an early stage of the reaction,

Table III
Effect of Counterion on the Reaction of Living Polystyrene with P(FMS-S)$_{5.1}$ [a]

expt	counter-ion	polystyryl anion [LE] × 10^3, mol L^{-1}	P(FMS-S)$_{5.1}$ [CH_2F] × 10^3, mol L^{-1}	[LE]/[CH_2F]	$(\overline{M}_n)_R \times 10^{-4}$	extent of reactions of LE, %: grafting eq	grafting GPC	termination dim.	termination monom.
LFS-C-1	Li^+	3.22	6.60	0.503	24.5	93	91	3	6
KFS-C-2	K^+	1.63	3.22	0.506	7.15	65	63	4	33

[a] Solvent: THF–benzene (THF = 50 vol %); reaction temperature, 23 °C; reaction time, 20 h. Other explanatory notes are the same as in Table II.

Table IV
Influence of Temperature on the Reaction of PSt-K with P(FMS-S)$_{5.1}$

expt	PSt-K [LE] × 10^3, mol L^{-1}	P(FMS-S)$_{5.1}$ [CH_2F] × 10^3, mol L^{-1}	[LE]/[CH_2F]	reaction temp, °C	reaction time, h	$(\overline{M}_n)_R \times 10^{-4}$	extent of reactions of LE, %: grafting eq	grafting GPC	termination dim.	termination monom.
KFS-5	3.22	6.42	0.502	23	23	7.46	67	66	2	32
KFS-T-1	3.26	6.35	0.513	0	33	7.74	68	63	10	27
KFS-T-2	3.29	6.27	0.525	−78	128	6.65	62	51	22	27[a]

[a] Maybe contains homopolystyrene produced by the protonation of unreacted PSt-K with terminant of the reaction, methanol, because the red color of the reaction mixture had remained until the reaction was terminated. Other explanatory notes are the same as in Table II.

about 50% of the extent of reaction. This decrease of the rate of the reaction unequivocally arises from steric hindrance of the branch polymer attached, and it will be concluded that the rate-determining step of the reaction has changed to the diffusion process of the living ends.

Owing to the hindering effect of branches, there seems to be a limit to the number of branches capable of being attached to a backbone polymer molecule. Actually, the curve for P(FMS) in Figure 3 appears to saturate in the range of the [LE]/[CH_2F] ratio greater than 1.2. Thus, the maximum "grafting density" (the number of branches per 100 monomer units) is estimated to be about 75%. This value must be the highest one which has been obtained so far.

Wide Variety of the Reaction. The striking feature of the reaction between these prepolymers is the fact that the reaction is so pronouncedly affected by the reaction conditions. The S_N mechanism was almost completely changed to other mechanisms in the extreme case. Namely, as shown above, in the case of PSt-Li it is nearly quantitatively grafted with the fluoromethyl group in a THF–benzene mixture whereas in benzene the monomeric termination of PSt-Li takes place exclusively resulting in a low extent of coupling. PSt-K is mostly grafted with P(FMS) in the range of [LE]/[CH_2F] < 0.6, but the monomeric termination of PSt-K is the main reaction in the range of [LE]/[CH_2F] > 0.6. Also, the dimeric termination of PSt-K was negligible at 23 °C whereas it increased markedly at −78 °C. Furthermore, the change of the counterion of polystyryl anion from Li^+ to K^+ leads to a considerable increase of the monomeric termination. This variety of the reaction is also unequivocally shown in the GPC curves in Figure 5. The peak intensities of polymers produced by the grafting reaction, monomeric termination, and dimeric termination are in good agreement with the extents of each reaction shown in Table II which were determined according to the method described in the preceding paper.[1b] In general, the reaction of living polystyrene with benzylic fluoromethyl groups involves monomeric termination to a higher extent than the reaction of living polystyrene with poly(chloromethylstyrene).[2] These results could be ascribed to the higher electronegativity of the fluorine with a large electron-withdrawing inductive effect which decreases the electron density on the α-hydrogens as well as the α-carbon. Also, the counterion, solvent, or reaction temperature plays an important role in these reactions. As was discussed in the preceding study,[1b] therefore, the reaction seems to proceed mostly through a coordination between the counterion and the fluorine atom which may vary with various factors such as solvation, ionic radium, and other electronic properties of the counterion, temperature, and polarizability of fluorine atom. Only in the case of the PSt-Li–THF/benzene system does the reaction with fluoromethyl groups seem to proceed via a direct attack on a positively polarized α-carbon of a benzylic fluoromethyl group by a polystyryl anion which is separated far from Li^+ by THF molecules.[14]

The termination reactions of living polystyrene with benzylic fluoromethyl groups seem basically similar to those of living polystyrene with benzylic chloromethyl groups as described in the preceding paper.[1b] The monomeric termination of living polystyrene may be protonation, and the dimeric termination seems to be the combination between polystyryl radicals formed as a consequence of one-electron transfer from a polystyryl anion to a fluoromethyl group.

References and Notes

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