Side Reactions in the Grafting Reaction of Living Polystyrene with Polymers Having Pendant Benzylic Halides[1]

Mikio Takaki, Ryuzo Asami,* and Yoshiyasu Kuwata

Department of Synthetic Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan. *Received August 4, 1978*

ABSTRACT: The grafting reaction of living polystyrene with polymers having benzylic halides as pendants involves as the side reaction both the monomeric and dimeric terminations of polystyryl anions. The monomeric termination is considered to be the protonation of polystyryl anions and the dimeric termination the combination between polystyryl radicals which were generated from polystyryl anions by one-electron transfer to benzylic halide groups. The extents of the terminations were evaluated on the basis of the decrease in the polymer molecules after the reaction. The termination was almost dimeric when Li^+ was used as the counterion of polystyryl anions in benzene whereas when K^+ was used it was mostly monomeric. The drastic effect of the addition of polar solvents was observed on the extent of the dimeric termination in the reaction system of polystyryllithium–poly(chloromethylstyrene)–benzene, which increased to a maximum of 67% when a minute amount of tetrahydrofuran was added to the reaction medium, but further additions suppress the dimeric termination gradually and completely. The nature of the halogen atom of the pendant benzylic halides also markedly affects the reactions and the extent of dimeric termination was higher in the order Cl < Br < I, which was as high as 70% even if K^+ was used as the counterion when benzylic iodomethyl groups were used as the pendants.

Using a method proposed previously,[2] we have been studying anionic grafting reactions of living polystyrene with some polymers having functional groups as pendants susceptible to nucleophilic addition[3] and substitution.[4] The method involves the following equation for the direct evaluation of the extent of polymer-coupling reaction, which was derived from the definition of number-average molecular weight and the fact of decrease in the number of polymer molecules after the reaction,

extent of grafting of living polystyrene, % =

$$\left\{1+\nu-\frac{(\bar{M}_n)_L+(\bar{M}_n)_B\nu}{(\bar{M}_n)_R}\right\}\times 100 \qquad (1)$$

where $(\bar{M}_n)_L$, $(\bar{M}_n)_B$, and $(\bar{M}_n)_R$ are the number-average molecular weights of the protonated living polystyrene, backbone polymer, and recovered polymer, respectively, and ν denotes the ratio of the number of molecules of backbone polymer to the number of molecules of the living polystyrene. In most cases, the degree of grafting determined from eq 1 was in good agreement with that by conventional methods.[2] However, in the case of the grafting reaction of polystyryllithium (PSt-Li) with poly(chloromethylstyrene) (P(CMS)) in benzene, the degree of grafting determined from eq 1 was somewhat higher than that evaluated by the gel permeation chromatograph (GPC) method, as reported previously.[4] This discrepancy would be ascribed to a side reaction which makes the number of polymer molecules decrease.

Such side reaction may be the dimeric termination of polystyryl anions as having been found more recently as a side reaction in the S_N reaction of PSt-Li with benzyl chloride in benzene.[1b] If the grafting reaction of PSt-Li with P(CMS) also involves the dimeric termination of polystyryl anions, the discrepancy is rather reasonable, because the dimeric termination of two molecules of living polystyrene results in the decrease of one polymer molecule in the reaction system. For the case of each grafting reaction when dimeric termination is expected to occur, eq 1 should be, therefore, modified as follows:

$$\frac{n_{LG}+n_{LD}/2}{N_L}=1+\nu-\frac{(\bar{M}_n)_L+(\bar{M}_n)_B\nu}{(\bar{M}_n)_R} \qquad (2)$$

where n_{LG}, n_{LD}, and N_L are the numbers of the molecules of living polystyrene grafted with the backbone polymer, terminated with themselves dimerically, and existing in the reaction system initially, respectively, and ν, $(\bar{M}_n)_L$, $(\bar{M}_n)_B$, and $(\bar{M}_n)_R$ are the same as in eq 1. This eq 2 will give the extent of dimeric termination of the living polystyrene (n_{LD}/N_L) if the number-average molecular weights in the right-hand side are measurable and the degree of grafting of living polystyrene (n_{LG}/N_L) in the left-hand side is obtainable by another method. Also, eq 2 will give the extent of the monomeric termination of polystyryl anions which is equal to $1-(n_{LG}+n_{LD}/2)/N_L$.

In the grafting reaction of living polystyrene with P(CMS),[4] fortunately, the degree of grafting of living polystyrene is obtainable directly from the GPC measurement as the ratio of the peak area of graft polymer to the total area of the curve of the recovered polymer mixture since the amounts of backbone polymer used in the reaction were negligibly small (<3 wt %) in comparison with that of living polystyrene and the sensitivity of the GPC detector (UV) to the polymers was considered to be almost equal. Thus, eq 2 would afford quantitative information on the side reactions which have not been clarified so far,[4-10] as well as a reasonable interpretation of the discrepancy found[4] with the extent of the grafting reaction.

Results

Side Reactions and the Application of the Method. The GPC measurements were carried out for all the polymers which have already been obtained in previous work.[4] Typical GPC curves of these polymers as shown in Figure 1 mostly have the peaks with the elution counts which correspond to the molecular weight of living polystyrene, to twice the molecular weight of living polystyrene, and to the molecular weight of graft polymer, although their peak intensities vary with reaction conditions. This fact suggests that the grafting reaction of living polystyrene with P(CMS) involves both the monomeric termination and the dimeric termination of polystyryl anions as the side reactions. The determination of the extent of each termination was difficult from the GPC curves owing to the incomplete separation of the two peaks ascribed to both the monomeric and dimeric ter-

0024-9297/79/2212-0378$01.00/0

Table I
Extents of Grafting, Dimeric Termination, and Monomeric Termination of Living Polystyrene in the Reaction with P(CMS)[a]

	living PSt		reaction			extent of reactions of LE, %			
						grafting		termination	
expt	$[\mathrm{LE}]^b \times 10^3$, mol L^{-1}	$[\mathrm{LE}]/^c$ $[\mathrm{CH_2Cl}]$	temp, °C	time, h	$(\overline{M}_\mathrm{n})_\mathrm{R}{}^d$ $\times 10^{-4}$	eq 1[e]	GPC[f]	dim.[g]	monom.[h]
	PSt-Li[i]								
L-2	3.08	0.402	23	42	9.00	75.2	56.0	38	6
L-4	3.74	0.620	23	227	7.85	71.5	52.2	39	9
L-5	4.13	0.819	23	381	7.07	68.3	45.6	45	9
	PSt-K[j]								
K-2	2.96	0.445	0	71	12.9	80.2	80.0		20
K-4	3.34	0.606	0	71	11.4	78.5	77.7	2	20
K-5	3.65	0.797	0	71	9.58	74.5	72.6	4	23

[a] These reactions were carried out in the previous study.[4] [b] Concentrations of living ends. [c] Mole ratio of living ends to chloromethyl groups. [d] Number-average molecular weight of recovered polymer. [e] Determined from eq 1 without modification for the dimeric termination of living polystyrene. [f] Determined by the GPC method. [g] Extent of dimeric termination of living ends. [h] Extent of monomeric termination of living ends. [i] In benzene. [j] In THF.

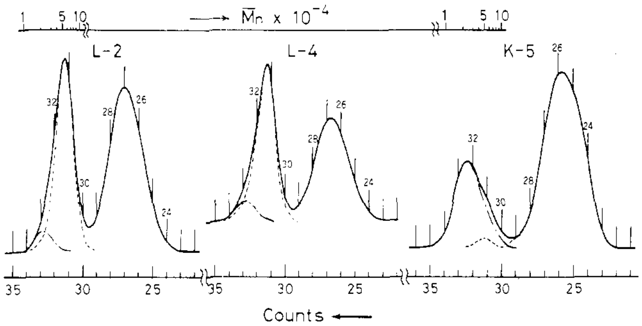

Figure 1. GPC curves of the polymers obtained in L-2, L-4, and K-5; the peaks (--- and −−−) may be ascribed to the polymer formed by the dimeric termination and the monomeric termination of living polystyrene, respectively.

minations. However, it is possible to calculate the extents of monomeric and dimeric terminations by the above method involving eq 2, and some representative results are shown in Table I. The values are closely consistent with the GPC curves in Figure 1.

Effect of Reaction Conditions on the Side Reactions and Grafting Reaction. Figures 2 and 3 show the dependence of the extents of grafting and terminations on the temperature. In the case of the reaction of PSt-Li with P(CMS), as the reaction temperature was increased the extent of the dimeric termination increased, but the extent of monomeric termination remained at a very low value. On the contrary, in the case of PSt-K, the extent of the monomeric termination increased as the reaction temperature was increased, whereas the extent of dimeric termination was not changed at a low level of 10% as shown in Figure 3.

The effect of solvent on the dimeric termination is drastic as shown in Table II. In the reaction of PSt-Li with P(CMS) in benzene, the addition of a minute amount of THF increases immediately the extent of the dimeric termination of PSt-Li with a decrease of the degree of grafting down to almost two-fifths; however, thereafter the continuous addition of more THF makes the dimeric termination decrease gradually to the minimum value of 2%. Above the mole ratio of THF added to living ends ([THF]/[LE]) of 1.58×10^3, the dimeric termination was so much suppressed that the grafting reaction takes place almost quantitatively. In the case of hexamethylphosphoric triamide (HMPA), a similar effect of polar solvent addition was observed at a low level of the ratio of [HMPA]/[LE] of ca. 10.

Table III shows the effect of the counterion of a polystyryl anion on the reaction of living polystyrene with P(CMS) in a benzene–THF mixture (THF = 50 vol %). Apparently, $\mathrm{Li^+}$ in the benzene–THF mixture suppresses both the monomeric and dimeric terminations and favors the grafting of polystyryl anions. In the case of $\mathrm{K^+}$, the reaction involves to some extent the monomeric termination.

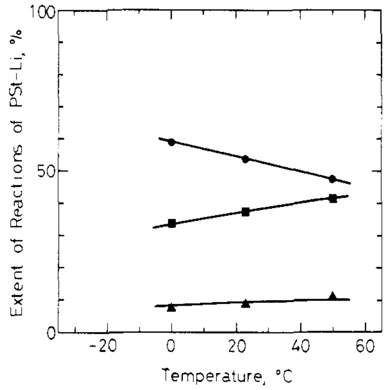

Figure 2. Dependence of the extent of the dimeric termination (■), the monomeric termination (▲), and grafting (●) on the reaction temperature in the reaction of PSt-Li with P(CMS).

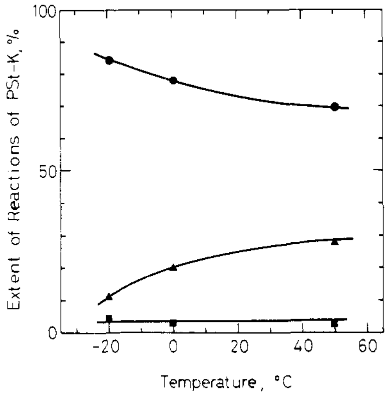

Figure 3. Dependence of the extent of the dimeric termination (■), the monomeric termination (▲), and grafting (●) on the reaction temperature in the reaction of PSt-K with P(CMS).

Figures 4 and 5 show the dependence of the extent of terminations of living polystyrene on the mole ratio of living ends to chloromethyl groups, $[\mathrm{LE}]/[\mathrm{CH_2Cl}]$, in the reaction of living polystyrene with P(CMS). As the $[\mathrm{LE}]/[\mathrm{CH_2Cl}]$ ratio was increased, the dimeric termination was increased in the case of PSt-Li whereas the monomeric termination was increased in the case of PSt-K. In Figure 4, the extent of dimeric termination exceeds the degree of

Table II
Influence of Polar Solvents on the Reaction of Living Polystyrene with P(CMS) in Benzene[a]

living PSt $[LE] \times 10^3$, mol L^{-1}	$[LE]/[CH_2Cl]$	polar solv, mol L^{-1}	[polar solv]/[b] [LE]	$(\overline{M}_n)_R \times 10^{-4}$	extent of reactions of LE, %: grafting		termination	
					eq 1	GPC	dim.	monom.
3.42	0.501	0	0	14.0	84.3	66.7	35	
		THF						
2.91	0.501	5.84×10^{-3}	2.01	5.95	62.2	28.5	67	4
2.29	0.502	9.31×10^{-3}	4.07	5.69	60.4	28.7	63	8
2.97	0.514	3.28×10^{-2}	1.10×10	5.92	62.0	30.9	62	7
2.65	0.500	5.39×10^{-2}	2.03×10	5.95	62.4	31.4	62	7
2.82	0.504	1.70×10	6.03×10	6.14	63.3	33.1	60	7
3.06	0.498	1.08	3.53×10^2	9.71	77.0	65.7	24	10
3.45	0.501	5.44	1.58×10^3	33.3	93.7	92.9	2	5
		HMPA						
2.94	0.501	3.25×10^{-2}	1.11×10	36.4	94.3	93.1	2	5
2.97	0.501	3.32×10^{-2}	1.12×10	41.8	95.1	94.0	2	4

[a] These reactions were carried out in the previous study.[4] [b] Mole ratio of polar solvent to living ends. Other explanatory notes are the same as in Table I.

Table III
Effect of Counterion on the Reaction of Living Polystyrene with P(CMS)[a]

expt	counterion	polyst. anion $[LE] \times 10^3$, mol L^{-1}	$[LE]/[CH_2Cl]$	$(\overline{M}_n)_R \times 10^{-4}$	extent of reactions of LE, %: grafting		termination	
					eq 1	GPC	dim.	monom.
C-1	Li^+	3.45	0.501	33.3	93.7	92.9	2	5
C-2	Li^+	3.46	0.504	30.6	93.1	94.3		6
C-3	K^+	3.04	0.499	12.0	79.8	78.2	3	19

[a] These reactions were carried out in the previous study;[4] solvent, benzene-THF (THF = 44 vol %); reaction temperature, 0 °C. Other explanatory notes are the same as in Table I.

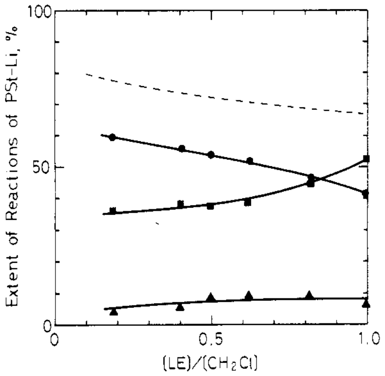

Figure 4. Relationship between the $[LE]/[CH_2Cl]$ ratio and the extent of the dimeric termination (■), the monomeric termination (▲), and grafting (●, determined by GPC method; ---, determined from eq 1) in the reaction of PSt-Li with P(CMS).

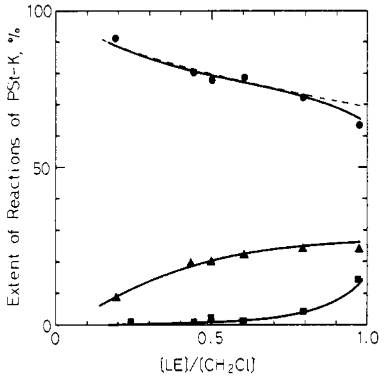

Figure 5. Relationship between the $[LE]/[CH_2Cl]$ ratio and the extent of the dimeric termination (■), the monomeric termination (▲), and grafting (●, determined by GPC method; ---, determined from eq 1) in the reaction of PSt-K with P(CMS).

grafting at $[LE]/[CH_2Cl] > 0.85$ and goes up to 53% at $[LE]/[CH_2Cl] = 1.0$.

As shown in Figure 5, the extents of grafting determined by eq 1 without any correction for the dimeric termination are in good agreement with that of grafting determined by the GPC method, suggesting the suppression of the dimeric termination in the reaction of PSt-K with P(CMS) in THF. However, in the case of the reaction of PSt-Li with P(CMS) in benzene a significant discrepancy between the values by both methods was observed owing to the dimeric termination as shown in Figure 4. In Figure 6, the number of branches per backbone and the extent of coupling chloromethyl groups are shown for both cases of PSt-Li and PSt-K where the previous data[4] calculated from eq 1 are also drawn.

Reaction with Polymers Having Pendant Benzylic Halides. In order to obtain further information on the side reactions, we carried out the reaction of living polystyrene with the polymers having pendant benzylic halides such as benzylic bromomethyl groups and benzylic iodomethyl groups. The results are summarized in Table IV. In the reaction of PSt-Li with pendant benzylic halides in benzene, the extent of the dimeric termination of PSt-Li markedly increases in the order $CH_2Cl < CH_2Br < CH_2I$, and therefore the degree of grafting decreases correspondently, whereas the extent of the monomeric termination is negligible within the experimental errors. In the case of PSt-K, the extent of dimeric termination of PSt-K increases to a great extent in the order of $CH_2Cl < CH_2Br < CH_2I$ and that of the monomeric termination decreased a little bit in the same order.

Discussion

Side Reactions and Effect of Reaction Conditions. As described above, the side reactions of living polystyrene were found to be the monomeric and dimeric terminations.

Table IV
Effect of Halogens of Pendant Benzylic Halides on the Side Reaction in the S_N Reaction with Living Polystyrene[a]

living PSt $[LE] \times 10^3$, mol L^{-1}	P(XMS) $[CH_2X] \times 10^3$, mol L^{-1}		$[LE]/[CH_2X]$	solvent	$(\overline{M}_n)_R \times 10^{-4}$	extent of reactions of LE, %: grafting, eq 1	grafting, GPC	termination, dim.	termination, monom.
PSt-Li									
3.42	P(CMS)	6.83	0.501	benzene	14.0	84.3	66.7	35	
3.23	P(BMS)[b]	6.48	0.498	benzene	7.37	69.4	46	47	7
3.42	P(IMS)[c]	6.82	0.501	benzene	6.12	62.9	29	68	3
PSt-K									
3.11	P(CMS)	6.21	0.501	THF	11.9	79.5	78.0	3	19
2.90	P(BMS)[b]	5.85	0.496	THF	6.65	62.7	39	47	14
2.91	P(IMS)[c]	5.82	0.500	THF	5.42	53.9	19	70	11

[a] Reaction temperature, 0 °C; time, 24 h. [b] Poly(bromomethylstyrene). [c] Poly(iodomethylstyrene). Other explanatory notes are the same as in Table I.

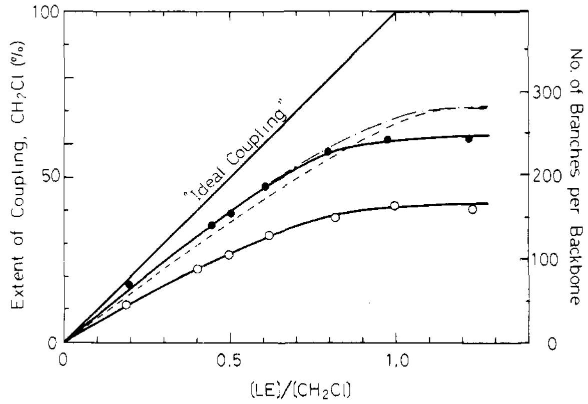

Figure 6. Relationship between the $[LE]/[CH_2Cl]$ ratio and the extent of the coupling of chloromethyl groups and the number of branches per backbone polymer in the reactions of P(CMS) with PSt-Li at 23 °C (○, determined by GPC method; ---, determined from eq 1) and PSt-K at 0 °C (●, determined by GPC method; ---, determined from eq 1).

This monomeric termination could not be the result of termination by impurities which existed adventitiously in the reaction system, since our experimental technique had been established to minimize self-termination to be less than 6% of living ends. Therefore, the most probable course of the monomeric termination must be the abstraction of a benzylic hydrogen by a polystyryl anion as is the case of the similar reaction of n-butyllithium with benzyl chloride in which the same mechanism of α-hydrogen abstraction by carbanions has been well known.[11,12] For the dimeric termination, two courses are possible in consideration of the results already reported for the similar reaction.[5,13-18] One process is the coupling reaction of living polystyrene with halogen-ended polystyrene which is formed by metal-halogen exchange, and the other one is the combination between two polystyryl radicals which are generated by one-electron transfer from polystyryl anions to halomethyl groups. However, the metal-halogen exchange would not be acceptable because the dimeric termination took place[19] even in the case of the reaction of living polystyrene with benzylic fluoromethyl groups where the fluorine atom cannot undergo the metal-halogen exchange at all.[14] Furthermore, in our preceding study[1b] of the reaction of PSt-Li with benzyl chloride which is regarded as a model reaction of this grafting reaction, the amount of bibenzyl formed was shown to be more in the case of adding benzyl chloride dropwise into the PSt-Li solution than in the case of reverse addition. This result is inconsistent with the fact that the amount of bibenzyl formed should be more in the latter case of addition than the former case if bibenzyl would be produced by the reaction of benzyl chloride with benzyl anions. Therefore, in our reaction systems the alternative process, the one-electron transfer, is more probable than the metal-halogen exchange for the dimeric termination. Although the one-electron transfer mechanism has not been amply corroborated as yet, we would like to note that the unequivocal effects of halogen, counterion, and solvent on both the monomeric and the dimeric terminations can be reasonably explained on the basis of the H abstraction and the one-electron transfer mechanisms.

As mentioned above, in the reaction of living polystyrene with pendant benzylic halides the extent of the dimeric termination of living polystyrene markedly increased in the order $CH_2Cl < CH_2Br < CH_2I$. This result is in accordance with the order of polarizability[20] of halogen series, $Cl < Br < I$ (2.28, 3.34, and 5.11, respectively), suggesting that the more polarized the halogen atom the more easily a one-electron transfer would occur from a polystyryl anion to an electron-deficient site.

The ratios of the dimeric termination to the monomeric termination are always higher in the case of PSt-Li than PSt-K to any halomethyl groups. This finding may suggest that Li^+ which is much smaller in size than K^+ will make the coordinated halogen polarize more strongly according to the well-known[21] theory of polarization which states that "the smaller is the cation, the more dense is its charge and the greater is its polarization force".

The drastic effect of the solvent shown in Table II will be explained in terms of the preferential solvation of Li^+ with polar solvents. The remarkable solvent effect of THF on the dimeric termination and grafting reaction may be attributed to various types of carbanionic species which have already been pointed out in the early work of Bywater and Worsfold.[22,23] They discovered that the lithium salts of living polystyrene are aggregated into dimers in benzene and the aggregation is completely destroyed to form PSt-Li·THF or PSt-Li·2THF when small amounts of THF are added to the solution, and by further addition of THF, Li^+ is highly solvated to form solvent-separated ion pairs or free ions. Thus, a minute amount of THF seems to make Li^+ more likely coordinate with a halogen atom because of the more ionic character of the C-Li bond in PSt-Li·THF or PSt-Li·2THF than that of the bond in PSt-Li in nonpolar solvent, enhancing the dimeric termination. On the other hand, the highly solvent-separated ion pairs and free ions would make the direct attack of polystyryl anions on the positively polarized α-carbon of a benzylic chloromethyl group easier since the highly solvated Li^+ would not be likely to coordinate with the halogen atom, and therefore the extent of grafting would be high.

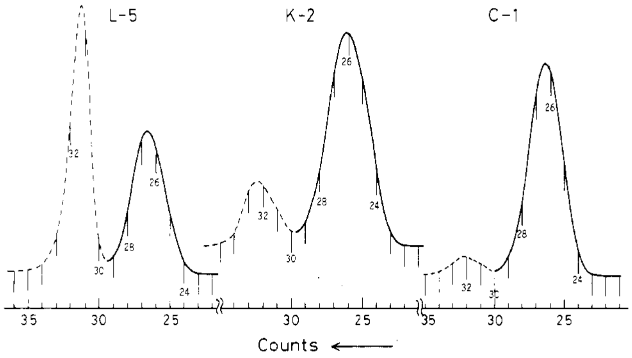

Figure 7. Comparison of the molecular weight distributions of the graft polymers obtained in L-5, K-2, and C-1.

Table V
Estimation of the Number of Branches per Backbone Polymer

expt	extent of coupling of CH_2Cl,[a] %	no. of branches per backbone[b]
L-5[c]	37.7	148
K-2[c]	35.6	141
C-1[d]	46.5	184

[a] Estimated from the extent of grafting of living ends. [b] Estimated from the extent of coupling of chloromethyl groups. [c,d] Reaction conditions and the extent of grafting of living ends are shown in Tables I and III.

Cross-Linking Reaction of Backbone Polymer. According to the mechanism of the dimeric and monomeric termination, free radicals or carbanions or carbenes may be generated on the backbone polymer, respectively. These active sites are supposed to be susceptible to cross-linking reactions. Thus, in Figure 7 the comparison of the molecular weight distributions is made for the graft polymers which were obtained in L-5, K-2, and C-1. The graft polymers of L-5 and K-2 have almost equal branches as shown in Table V whereas the graft polymer of C-1 was considered as the standard of nearly ideal grafting. The graft polymer of K-2 contains more amounts of super macromolecules than the graft polymer of L-5, although the extent of side reaction of living polystyrene in the case of K-2 is much smaller than that in the case of L-5 as shown in Table I. This fact may be attributed to the nature of the active species generated in the backbone polymer. A free radical is apt to disappear by transfer to solvent or to other compounds, but a carbanion mostly reacts with only an electrophile and a carbene reacts in a complex fashion. The extent of the intermolecular cross-linking of the active species, however, seems to be almost negligible because it was found that even the reactions involving large amounts of the terminations proceeded homogeneously all the way and did not produce any macrogel, and the polymers recovered after the reactions were all easily and completely soluble in solvents which dissolve polystyrene. The amounts of super macromolecules and macrogel formed are extremely sensitive to the extent of the intermolecular cross-linking reaction as described in the previous paper.[4] Therefore, most of the active sites on the backbone polymer, especially carbanionic species, would be lost intramolecularly, probably owing to the extremely low concentration of backbone polymer and the hindrance effect of branches already attached.

Experimental Section

The GPC curves were recorded on a Toyo Soda high-speed liquid chromatograph Model HLC 802UR (detector, UV and IR) connected with two GMH columns (2 ft × 2, Toyo Soda). THF was used as the eluent and the flow rate was 1 mL/min. The peak areas were measured by means of weighing papers cut out along the curve. The polymers submitted to the GPC measurement were those which were recovered after the reaction of living polystyrene with P(CMS),[4] poly(bromomethylstyrene) (P(BMS)), and poly(iodomethylstyrene) (P(IMS)). The reaction apparatus and the experimental procedures were the same as described in an earlier paper.[3] P(CMS), PSt-Li, and PSt-K were the same as used in the previous study.[4] P(BMS) and P(IMS) were prepared by means of a halogen–halogen exchange reaction[24] of P(CMS) with sodium bromide and potassium iodide in acetone at reflux temperature for 50 h. The number-average molecular weights of PSt-Li, PSt-K, P(BMS), and P(IMS) were 2.25×10^4, 2.47×10^4, 7.85×10^4, and 9.80×10^4, respectively. The extents of the conversion of P(CMS) to P(BMS) and P(IMS) were found to be 86.1 and 98.0% by elemental analyses. In the former case, the chloromethyl content remaining (about 14%) might be considered to have no significant effect for this reaction, because an excess amount of benzylic bromomethyl groups was reacted with that of the living polystyrene and, furthermore, the reaction of living polystyrene with benzylic chloromethyl groups is much slower than that with benzylic bromomethyl groups.

References and Notes

(1) (a) Preparation of Well-Defined Polymers by Polymer-Coupling Reaction. Part V. (b) Part IV: M. Takaki, R. Asami, and Y. Kuwata, *Polym. J.*, in press.
(2) M. Takaki and R. Asami, *Polym. J.*, **9**, 653 (1977).
(3) M. Takaki, R. Asami, and M. Mizuno, *Macromolecules*, **10**, 845 (1977).
(4) M. Takaki, R. Asami, and M. Ichikawa, *Macromolecules*, **10**, 850 (1977).
(5) T. Altares, D. P. Wyman, V. R. Allen, and K. Meyersen, *J. Polym. Sci., Part A*, **3**, 4131 (1965).
(6) S.-P. S. Yen, *Makromol. Chem.*, **81**, 152 (1965).
(7) T. Fujimoto, H. Narukawa, and M. Nagasawa, *Macromolecules*, **3**, 57 (1970).
(8) J. C. Meunier and R. Van Leemput, *Makromol. Chem.*, **142**, 1 (1971).
(9) F. Candau and E. Franta, *Makromol. Chem.*, **149**, 41 (1971).
(10) J. Pannel, *Polymer*, **12**, 558 (1971).
(11) G. L. Closs and L. E. Closs, *Tetrahedron Lett.*, **No. 24**, 26 (1960).
(12) D. F. Hoeg and D. I. Lusk, *J. Am. Chem. Soc.*, **86**, 928 (1964).
(13) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).
(14) R. G. Jones and H. Gilman, *Org. React.*, **6**, 339 (1951).
(15) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).
(16) H. R. Ward, *J. Am. Chem. Soc.*, **89**, 5517 (1967).
(17) H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967).
(18) A. F. Halasa and H. E. Adams, *J. Polym. Sci., Polym. Symp.*, **No. 30**, 169 (1970).
(19) M. Takaki, R. Asami, H. Inukai, and T. Inenaga, *Macromolecules*, following paper in this issue.
(20) J. A. A. Ketelaar, "Chemical Constitution", (Elsevier) Van Nostrand, Princeton, N.J., 1953, p 90.
(21) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry", Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963, p 195.
(22) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **40**, 1564 (1962).
(23) S. Bywater and D. J. Worsfold, *J. Phys. Chem.*, **70**, 162 (1966).
(24) R. F. Hirsch, E. Gancher, and F. R. Russo, *Talanta*, **17**, 483 (1970).