Anionic Grafting Reaction of Living Polystyrene with Poly(*p*-vinylstyrene oxide) and Its Styrene Copolymer[1]

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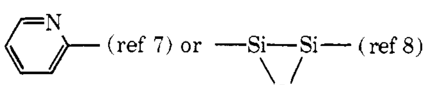
ABSTRACT: Poly(*p*-vinylstyrene oxide) and its styrene copolymers were treated with living polystyrene, and their usefulness as a backbone polymer was investigated under various reaction conditions for the preparation of a well-defined graft polymer. As the amount of living polystyrene is increased, the number of branches is also increased but the extent of grafting of living polystyrene decreased. A significant increase of the extent of grafting is observed by the addition of a large amount of polar solvents. The effect of Li^+ as the counterion in the living polystyrene on the grafting is greater than that of K^+. The grafting reaction is more or less hindered by the branches already grafted to the backbone polymer when the backbone polymer is poly(*p*-vinylstyrene oxide). The extent of grafting of living polystyrene is 62% or lower in a Li^+–benzene (counterion–solvent) system or a K^+–tetrahydrofuran system, but a high extent of grafting (81%) was attained in a Li^+–tetrahydrofuran/benzene system.

In the preceding paper,[2] we described a method for evaluating the extent of the polymer-coupling reaction by the determination of the number-average molecular weight of the recovered polymer. Using this method, we have been studying the polymer-coupling reaction by means of addition, substitution, or condensation. It is our purpose to evaluate systematically and quantitatively the usefulness of prepolymers for the preparation of well-defined polymers and at the same time to determine the functional groups which couple stoichiometrically with other prepolymers. Consequently, we hope to develop our study to get well-defined polymers, e.g., well-defined block or cross-linked or graft polymers, etc. First of all, we have tried the anionic grafting reaction of living polymers with a multifunctional backbone polymer.

Since the pioneering work of Gallot et al.[3,4] on the anionic grafting reaction of living polymer with poly(methyl methacrylate) or poly(vinyl chloride) was reported, many grafting reactions have been studied for the preparation of well-defined graft polymers. In these studies living polymers have been grafted with various multifunctional backbone polymers by means of nucleophilic addition or nucleophilic substitution using R-Cl,[5] $-COOCH_3$,[6]



(ref 7) or (ref 8)

groups as the functional groups of the backbone polymers. However, most of the studies have been made with emphasis on the physical properties of the graft polymer obtained, and only a few studies have been done from the viewpoint of organic synthesis of graft polymers and from the viewpoint of the systematic and quantitative evaluation of the backbone polymer.

In order to prepare a well-defined graft polymer, it is necessary to find out the best combination of a backbone polymer and a living polymer and to control the number of branches in such a combination, with the consideration of the effect of reaction conditions in detail.

In this paper, we dealt with the anionic grafting reaction of living polystyrene with poly(*p*-vinylstyrene oxide) and its copolymers with styrene which contain the pendant epoxide ring as the functional group that is susceptible to nucleophilic addition. The coupling reactivities of these prepolymers were investigated under various reaction conditions.

Experimental Section

Materials. Polystyrylpotassium used in the grafting reaction was prepared by polymerization of styrene with cumylpotassium in tetrahydrofuran (THF), and polystyryllithium was prepared by polymerization of styrene with *n*-butyllithium in benzene. Poly(*p*-vinylstyrene oxide) and its styrene copolymers used as backbone polymers were obtained by homopolymerization and copolymerization of *p*-vinylstyrene oxide (synthesized according to the method of Tanimoto et al.[9]) with styrene using α,α'-azobisisobutyronitrile as an initiator. The backbone polymers were purified first by several reprecipitations from a benzene–methanol system and finally by freeze drying under high vacuum of about 10^{-5} mm Hg. The purified backbone polymer was dissolved, in situ, with a solvent which was distilled in the presence of sodium–benzophenone complex under high vacuum. The composition of the copolymers, number-average molecular weights, and abbreviations for the living polystyrenes and the backbone polymers are given in Table I. The epoxide ring contents of the resulting copolymers were determined by the HCl–pyridine method.[10] The homo- and copolymers were also identified by means of NMR and IR spectroscopy. Benzene and THF were purified by the usual methods and distilled in the presence of the sodium–benzophenone complex under high vacuum. The other reagents used in this experiment were purified by the usual methods.

Grafting Reaction. All operations were carried out in a high vacuum system (ca. 10^{-5} mm Hg). The grafting reaction was carried out in the apparatus as shown in Figure 1. The sealed glass reactor and the ampules for the prepolymer solutions were first treated with dilute hydrofluoric acid and finally rinsed with distilled water and dried. In order to eliminate the last traces of organic compound, these parts were heated to a high temperature that would barely deform the glass tubing before assembling. The parts were assembled as in Figure 1 and this apparatus was then linked to a vacuum line, evacuated, and sealed off. The living polymer and the backbone polymer solutions were then introduced separately into the sealed glass reactors A and B, respectively, by crushing the respective break-seals. The empty ampules of living polystyrene and backbone polymer were washed with condensed solvent by cooling the ampules with dry ice–methanol. When the whole apparatus attained a fixed temperature, the living polystyrene solution was added to the backbone polymer solution quickly by upturning side A of the reactor. The prepolymer solutions were mixed completely within a few seconds by upturning side A and side B of the reactor alternatively. After a desired period of reaction, a small amount of methanol was introduced through break-seal (BS) in order to terminate the reaction. The gross polymer in the reaction mixture was precipitated by pouring the mixture into a large amount of methanol and then filtered and dried in vacuo at room temperature for 50–70 h.

The optical cell (C) is joined to the sealed glass reactor if the measurement of optical density of living polystyrene solution is desired.

Evaluation of the Extent of Grafting. The extent of grafting of living polystyrene was evaluated from the following equation[2]

$$\text{Extent of grafting of living polystyrene, \%} = \left\{1+\nu-\frac{(\overline{M}_n)_B\nu+(\overline{M}_n)_L}{(\overline{M}_n)_R}\right\}\times 100 \qquad (1)$$

where $(\overline{M}_n)_L$, $(\overline{M}_n)_B$, and $(\overline{M}_n)_R$ are the number-average molecular weights ofthe terminated living polystyrene, backbone polymer, and recovered polymer, respectively, and ν originally denotes the ratio of the number of molecules of backbone polymer to the number of molecules of the living polystyrene but is also the same as the mole ratio. The moles of backbone polymer and living polystyrene were obtained by dividing the weights of the fed backbone polymer and

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

Prepolymer	Abbreviation	Composition (St/*p*-VSO)[a]	$\overline{M}_n \times 10^{-4}$
Polystyrylpotassium	PSt-K		2.51
Polystyryllithium	PSt-Li		2.41
Poly(*p*-vinylstyrene oxide)[b]	P(VSO)		0.873
p-Vinylstyrene oxide–styrene copolymer	P(VSO-S)$_{4.4}$	4.40	4.40
p-Vinylstyrene oxide–styrene copolymer	P(VSO-S)$_{10.6}$	10.6	3.04

[a] Mole ratio of styrene to *p*-vinylstyrene oxide in copolymer. [b] NMR spectrum indicated that the purity of *p*-vinylstyrene oxide was above 95%.

living polystyrene by their number-average molecular weights, respectively. The extent of the grafting reaction of the epoxide ring was estimated from the value of the extent of grafting of the living polystyrene.

Measurement and Characterization. The number-average molecular weights of the prepolymers and the recovered polymer were determined by the osmotic pressure measurement in toluene at 37 °C using a Knauer membrane osmometer, but the number-average molecular weight of poly(*p*-vinylstyrene oxide) was determined by the vapor pressure osmometry using a Hitachi Perkin-Elmer 115 osmometer because of its relatively low molecular weight. The intrinsic viscosities of the polymers were determined in toluene at 30.0 °C using a Ubbelohde type viscometer. Gel permeation chromatograms were measured in THF using a Shimazu GPC-1A with a three-column system (10^4, 10^5; and 10^6 Å). Fractional precipitation was carried out as follows. Four-hundred milligrams of a sample was dissolved in 40 mL of benzene and to this mixture 17 mL of methanol (a slightly smaller amount than that required for homopolystyrene precipitation) was added with stirring. This mixture was warmed until it was homogeneous and allowed to cool slowly to separate into two layers, of which the supernatant layer was removed. Further processes were carried out by the usual method. Turbidimetric titration was performed as follows. To 18 mL of a polymer solution of definite concentration (11.7 ± 0.2 mg/dL; solvent, benzene) in a 50 mL Erlenmeyer flask (having a glass stopcock) was added dropwise, with stirring by a magnetic stirrer, 10 mL of isopropyl alcohol so that the solution was close to the precipitating point. Then, an increment (0.5–1.0 mL) of isopropyl alcohol was added dropwise with stirring, and the solution was warmed until the turbidity of the solution disappeared. It was then cooled slowly to ca. 30 °C. A part of this cooled solution was placed in an optical cell (quartz) having an optical path of 1.0 cm. The cell was then inserted into the cell compartment (kept at 25 °C) of a Hitachi Model 124 spectrophotometer equipped with a recorder. The optical density at 350 nm was measured by recorder tracing at the saturation. Further addition of isopropyl alcohol and the measurements of the optical density were repeated until the total isopropyl alcohol added was ca. 30 mL. The turbidity was calculated from the following equation

$$\text{turbidity, \%} = \frac{D/C}{D_f/C_f} \times 100$$

where D = optical density of the individual solution; D_f = optical density of the solution where all polymers are assumed to be aggregated; C = polymer concentration of the individual solution; C_f = polymer concentration of the solution where all polymers are assumed to be aggregated.

Results and Discussion

Coupling Reactivity of the Prepolymers. The grafting reaction of living polystyrene with the backbone polymer containing pendant epoxide ring proceeded homogeneously. During the reaction, the red color ascribed to the living polystyrene decreased gradually and finally disappeared when the mole ratio of living end to epoxide ring ([LE]/[EP]) was smaller than unity, and the increase in viscosity of the reaction mixture was observed unequivocally. The recovered polymer was easily soluble in solvents such as THF, benzene, and other solvents which dissolve polystyrene. Tables II and III show the reaction conditions and the results of the reactions. The relations between the extent of grafting and [LE]/[EP] are shown in Figures 2 to 4, where the horizontal thick line of 100% extent of grafting (Figures 2 and 3) or the oblique thick line (Figure 4) represent the ideal case without producing homopolystyrene.

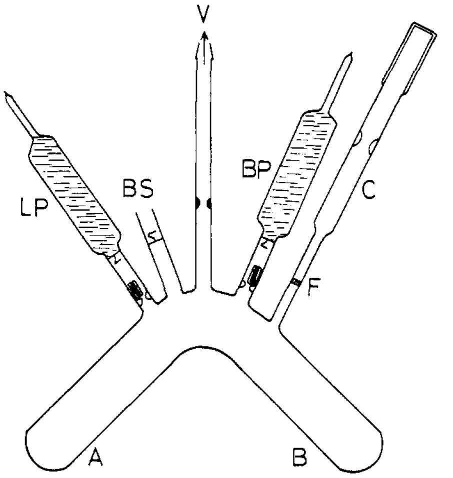


Figure 1. *Apparatus for the grafting reaction.* A and B, reactor; LP, solution of living polystyrene; BS, break-seal; BP, solution of backbone polymer; F, filter; C, optical cell; V, to vacuum line.

Figures 2 and 3 show the usefulness of the prepolymers as precursors or as backbone polymers for the preparation of well-defined graft polymers; they also show the dependency of the extent of grafting of living polystyrene on the [LE]/[EP] ratio. Figure 4 may be referred to for the controlling of the number of branches per backbone.

From these plots as well as from the results in Tables II and III, the following are obvious. (1) The extent of grafting of living ends does not exceed 62% under the reaction conditions shown in Tables II and III. (2) As the amount of living ends is increased, the number of branches of the backbone polymer also increases, but the extent of grafting of the living polystyrene decreases. (3) The difference in the extent of grafting between poly(*p*-vinylstyrene oxide) and its styrene copolymer was evident when the [LE]/[EP] ratio exceeds 0.5. The fact that the extent of grafting of living polystyrene did not exceed 62% may be ascribed to a side reaction in which the living polystyrene has been protonated since the color of living polystyrene completely disappeared when the [LE]/[EP] ratio was smaller than unity. Since a high degree of grafting has been shown even at low values of [LE]/[EP], the side reaction assumed to have occurred is probably not due to the impurities which may be contained in the backbone polymer. Two kinds of reactions were suggested to have taken place competitively in the course of the reaction. One is the addition of the attacking carbanion to the α or β C atom of the epoxide ring with the formation of graft polymer, and the other is the abstraction of an α or β H atom in the epoxide ring by the carbanion, protonating the living end. As the reaction proceeds, the latter reaction may predominate over the former, because the former may be subject to steric hindrance. The hindering effect of the branches which are already grafted to the backbone polymer has been pointed out by Ishizu et al.[11,12] in the reaction of living polystyrene with chloromethylated polystyrene. Also, the solubility of the alcoholate resulting from the coupling may have some effect on the steric hindrance. The hindering effect of the branches shown in Figure

Table II
Anionic Grafting Reaction of PSt-K with P(VSO), $P(VSO\text{-}S)_{4.4}$, and $P(VSO\text{-}S)_{10.6}$[a]

Expt No.	Backbone $[EP]^b \times 10^3$, mol L^{-1}	PSt-K $[LE]^c \times 10^3$,	[LE]/[EP]	$(\overline{M}_n)_R{}^d \times 10^{-4}$	Extent of grafting, % LE[e]	EP[f]
	P(VSO)					
SOK-1	16.2	3.16	0.192	5.12	60.6	11.6
-2	8.40	4.26	0.507	5.88	61.0	30.9
-3	4.30	3.10	0.721	3.93	38.5	27.8
-4	3.48	3.55	1.02	3.44	29.0	29.6
-5	2.26	3.99	1.50	3.40	27.3	41.0
	$P(VSO\text{-}S)_{4.4}$					
SOK-6	10.9	2.16	0.198	6.04	60.9	12.1
-7	6.76	3.34	0.494	6.37	61.8	30.5
-8	4.94	3.90	0.789	5.89	58.0	45.8
	$P(VSO\text{-}S)_{10.6}$					
SOK-9	4.85	3.66	0.755	5.46	57.2	43.2

[a] Solvent, THF; reaction time, 48 h; reaction temperature, 20 °C. [b] Concentration of epoxide ring. [c] Concentration of living end. [d] Number-average molecular weight of recovered polymer. [e] Extent of grafting reaction of living end. [f] Extent of grafting reaction of epoxide ring which was estimated from the extent of grafting reaction of living end.

Table III
Anionic Grafting Reaction of PSt-Li with P(VSO), $P(VSO\text{-}S)_{4.4}$, and $P(VSO\text{-}S)_{10.6}$[a]

Expt No.	Backbone $[EP] \times 10^3$, mol L^{-1}	PSt-Li $[LE] \times 10^3$, mol L^{-1}	[LE]/[EP]	$(\overline{M}_n)_R \times 10^{-4}$	Extent of grafting % LE	EP
	P(VSO)					
SOL-1	16.4	3.29	0.201	5.06	61.5	12.4
-2	8.95	4.46	0.498	5.72	60.7	30.2
-3	4.51	3.22	0.714	4.98	54.0	38.6
-4	3.73	3.67	0.948	4.48	48.0	45.5
-5	2.88	4.17	1.45	3.90	39.3	57.0
	$P(VSO\text{-}S)_{4.4}$					
SOL-6	7.13	3.62	0.508	5.77	59.1	30.0
-7	5.84	4.01	0.687	5.72	58.5	39.3
-8	4.38	4.47	1.02	5.51	56.6	57.7
-9	3.16	4.86	1.54	5.19	53.7	82.6
	$P(VSO\text{-}S)_{10.6}$					
SOL-11	11.4	2.28	0.200	4.95	61.5	12.3
-12	7.20	3.60	0.500	5.46	60.5	30.3
-13	5.94	4.00	0.673	5.46	59.3	39.9
-14	4.51	4.44	0.984	5.46	58.2	57.3
-15	3.45	4.78	1.39	5.19	55.1	76.6

[a] Solvent, benzene; reaction time, 48 h; reaction temperature, 20 °C.

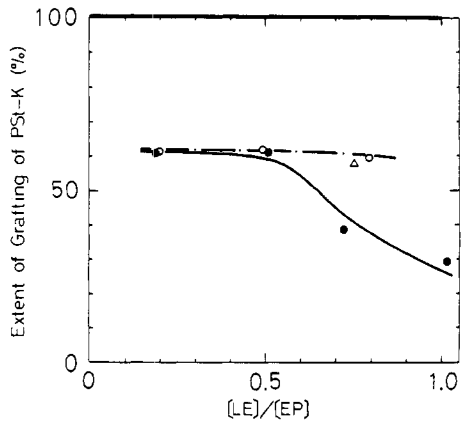


Figure 2. Relationship between extent of grafting of PSt-K and [LE]/[EP] ratio in the reaction of PSt-K with P(VSO) (●), $P(VSO\text{-}S)_{4.4}$ (○), and $P(VSO\text{-}S)_{10.6}$ (△).

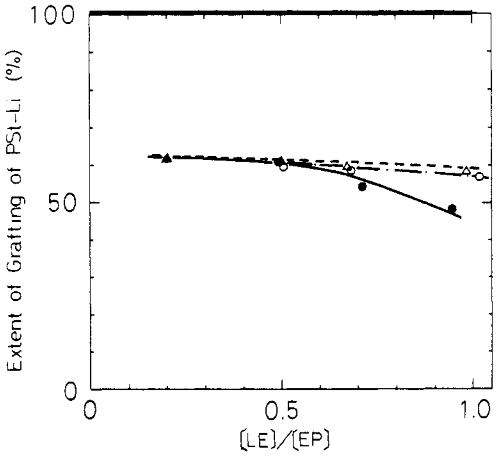


Figure 3. Relationship between extent of grafting of PSt-Li and [LE]/[EP] ratio in the reaction of PSt-Li with P(VSO) (●), $P(VSO\text{-}S)_{4.4}$ (○), and $P(VSO\text{-}S)_{10.6}$ (△).

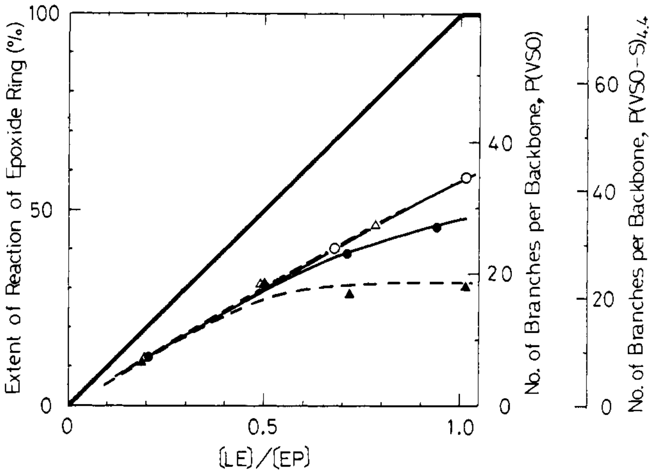


Figure 4. Relationship between extent of grafting reaction of epoxide ring and [LE]/[EP] ratio in the reaction: PSt-K vs. P(VSO) (▲); PSt-K vs. $P(VSO\text{-}S)_{4.4}$ (△); PSt-Li vs. P(VSO) (●); PSt-Li vs. $P(VSO\text{-}S)_{4.4}$ (○).

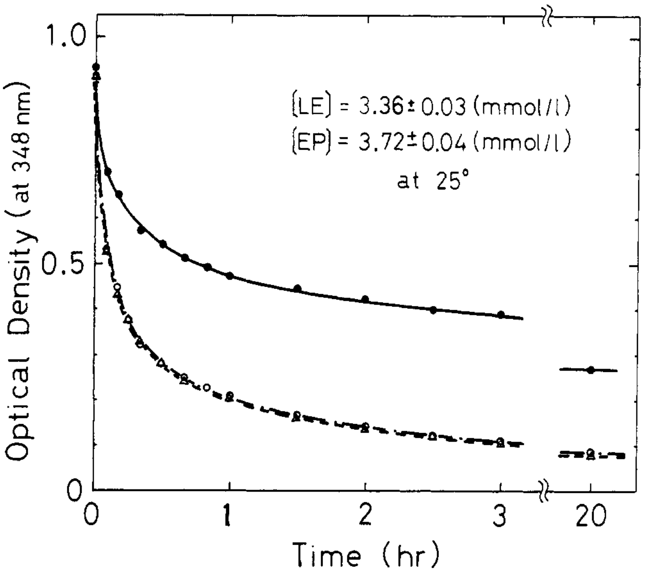


Figure 5. Optical density change with the passage of time in the reactions of PSt-K with P(VSO) (●), $P(VSO\text{-}S)_{4.4}$ (○), and $P(VSO\text{-}S)_{10.6}$ (△).

5, and the increase in solubility of the alcoholate caused by the addition of a polar solvent (Table IV), will be discussed later. As can be seen in Figures 2 and 3, at high values of [LE]/[EP], the descending slope of the curves for polystyrylpotassium is much steeper than that of the curve for polystyryllithium. This finding shows that R-OK is less soluble than R-OLi in these solvents. Therefore, in the former case a shrunken form of the backbone polymer makes the polymer molecule compact and epoxide groups less reactive.

Effect of Reaction Conditions. It has been indicated that the extent of grafting is dependent on the [LE]/[EP] ratio. Hence, at a constant value of [LE]/[EP], the comparison of the intrinsic viscosities of the polymers obtained under various reaction conditions should give information on the effect of these conditions.

The coupling reactivity of polystyryllithium in the grafting reactions increased gradually as the amount of THF increased as shown in Table IV. No remarkable difference of the extent of coupling was observed by addition of a small amount of THF in pure benzene in spite of the presumable change of the form of the active center such as detected by Bywater and Worsfold[13,14] and Morton[15] in propagation reaction of polystyryllithium. It was also determined that the effect of addition of polar solvents on the extent of grafting does not depend on the identity of the polar solvents but on the amount of polar solvent. The amount would have bearing on the solubility of the backbone polymer. Therefore, it is suggested that the addition of THF hardly affects the reactivity of polystyryllithium but does affect that of the backbone polymer. This result is in contrast to the result of the coupling reaction between living polystyrene and poly(chloromethylstyrene).[16] The increase of the extent of grafting due to the addition of polar solvent may be ascribed to the increase in solubility of the alcoholate resulting from the grafting reaction. Presumably, the expanded chain of backbone polymer makes it easier for the living end to couple with the epoxide ring.

The effect of temperature on the grafting reaction is shown in Table V for the cases of polystyryllithium and polystyrylpotassium. Although the effect is not significant, it can be seen that the lower the temperature the higher is the extent of grafting.

Table VI clearly shows that Li^+ is more favorable than K^+ for the grafting reaction in benzene–THF (THF = 54 vol %). There are two reasons to be considered for the cause of the counterion effect. One is, as described above, the solubility of the alcoholate resulting from the coupling reaction and the

Table IV
Effect of Polar Solvents on the Grafting Reaction of PSt-Li with P(VSO) in Benzene[a]

Expt No.	Polar solvent [P.sol],[b] mol L^{-1}	PSt-Li [LE] × 10^3, mol L^{-1})	P(VSO) [EP] × 10^3, mol L^{-1}	[LE]/[EP]	[P.sol]/[LE]	$[\eta]_R$,[c] dL g^{-1}	$[\eta]_R/[\eta]_L$[d]
	THF						
SOL-21	3.58×10^{-3}	3.57	7.14	0.500	1.00	0.240	1.45
-22	4.59×10^{-2}	3.99	7.94	0.503	1.15×10	0.242	1.46
-23	6.62	2.70	5.43	0.497	2.45×10^3	0.289[e]	1.74
-24	6.63	2.70	5.42	0.498	2.46×10^3	0.270	1.63
	HMPA[f]						
SOL-26	3.58×10^{-2}	3.85	7.64	0.504	9.30	0.242	1.46
	TMEDA[g]						
SOL-31	3.78×10^{-2}	3.84	7.70	0.499	9.84	0.239	1.44
SOL-2	0	4.46	8.95	0.498	0	0.236	1.42

[a] Reaction time, 48 h; reaction temperature, 20 °C. [b] Indicates the concentration of polar solvent. [c] Intrinsic viscosity of recovered polymer. [d] $[\eta]_L$ indicates the intrinsic viscosity of the terminated living polystyrene and is equal to 0.166 dL/g in the case of PSt-Li; $[\eta]_R/[\eta]_L$ is regarded as a measure of the extent of grafting because the ratio of PSt-Li to P(VSO) was constant, and the amount of P(VSO) was negligibly small compared to that of living polystyrene. [e] $(\overline{M}_n)_R = 10.4 \times 10^4$. Extent of grafting reaction: LE, 80.8%; EP, 40.2%. [f] Hexamethylphosphoramide. [g] *N,N,N′,N′*-Tetramethylethylenediamine.

Table V
Effect of Temperature on the Grafting Reaction of Living Polystyrene with P(VSO)[a]

Living PSt $[LE] \times 10^3$, mol L^{-1}	P(VSO) $[EP] \times 10^3$, mol L^{-1}	[LE]/[EP]	Reaction temp, °C	$[\eta]_R$, dL g^{-1}	$[\eta]_R/[\eta]_L$
PSt-Li[b]					
4.47	8.93	0.501	75	0.225	1.36
4.48	8.92	0.502	40	0.233	1.40
4.46	8.95	0.498	20	0.236	1.42
PSt-K[c]					
4.26	8.55	0.498	60	0.222	1.31
4.65	8.46	0.550	18	0.236	1.39
4.25	8.54	0.498	−78	0.246	1.45

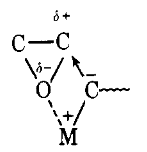
[a] Reaction time, 48 h, except 72 h for the experiment of the last column. [b] In benzene; $[\eta]_L = 0.166$ dL/g. [c] In THF; $[\eta]_L = 0.170$ dL/g.

Table VI
Effect of Counterion on the Grafting Reaction of Living Polystyrene with P(VSO)[a]

Counterion	Polyst$^-$ [b] $[LE] \times 10^3$, mol L^{-1}	P(VSO) $[EP] \times 10^3$, mol L^{-1}	[LE]/[EP]	$[\eta]_R$, dL g^{-1}	$[\eta]_R/[\eta]_L$
Li^+	2.70	5.43	0.497	0.289[c]	1.74
Li^+	2.70	5.42	0.498	0.270	1.63
K^+	2.60	5.21	0.499	0.221	1.30
K^+	2.66	5.30	0.502	0.236	1.39

[a] Reaction time, 48 h; reaction temperature, 20 °C; solvent, THF–benzene (THF = 54 vol %). [b] Polystyryl anion; $[\eta]_L$ of PSt-Li = 0.166 dL/g, $[\eta]_L$ of PSt-K = 0.170 dL/g.

other is the strength of the coodination of the counterion to the O atom of the epoxide ring. As can be seen in the following scheme, the stronger the coodination of the counterion to the O atom of the epoxide ring, the more electropositive becomes the C atom of the epoxide ring. This makes the nucleophilic addition of the carbanion easier.



This agrees with the generally accepted idea[17] that the coodination of a metal atom to the ring oxygen is the first step in the ring-opening polymerization of epoxides with organometallic compounds.

In order to study the hindering effect of the branches on the surrounding epoxide ring and the steric hindrance caused by the lower solubility of the alcoholates, the decay of the optical density at 348 nm ascribed to polystyrylpotassium was followed for the reaction of polystyrylpotassium with poly(*p*-vinylstyrene oxide) and its styrene copolymers. From the results shown in Figure 5, it can be seen that the epoxide groups of poly(*p*-vinylstyrene oxide) are less reactive than those of the styrene copolymers, whereas the reactivities of the epoxide groups of the two styrene copolymers are almost equal. This result suggests that the reactivity of the epoxide ring was decreased by the hindering effect of the branches already coupled to the neighboring epoxide ring. The effect of the steric hindrance would be pronounced because of the less solubility of the alcoholate. However, these difficulties almost disappear if the backbone polymer consists of more than 4.4 styrene units on the average between the adjacent *p*-vinylstyrene oxide units. Similar results can also be seen in Figures 2 and 3, where the curves obtained by plotting the extent of grafting of living polystyrene against [LE]/[EP] begin to slope downwards at [LE]/[EP] = 0.5 in the case of the reaction of living polystyrene with poly(*p*-vinylstyrene oxide), whereas the plots are almost horizontal in the case of the reaction of living polystyrenes with its styrene copolymers.

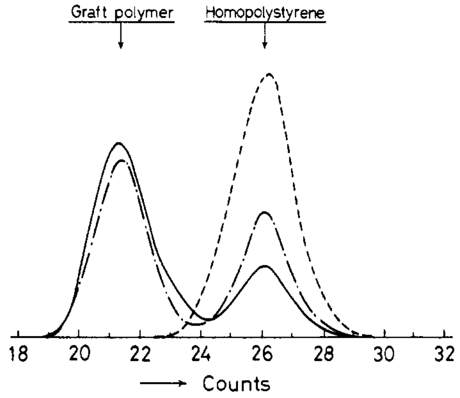


Figure 6. GPC profiles of the polymers obtained in Ex SOK-2 (– – –) and Ex SOL-23 (—), and terminated living polystyrene used in the grafting reaction (- - -).

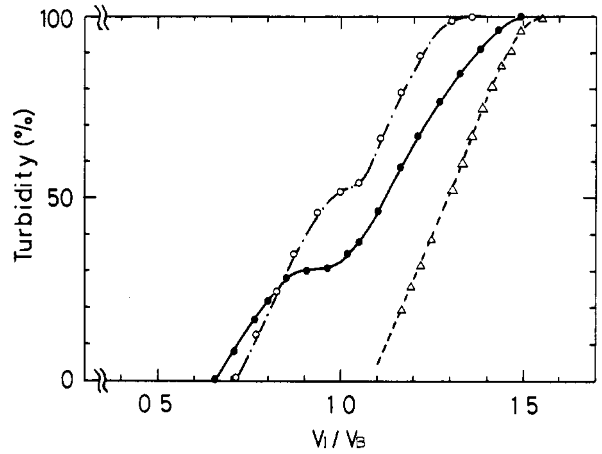


Figure 7. Turbidimetric titration curves for the polymers obtained in Ex SOL-1 (○) and Ex SOL-5 (●), and terminated living polystyrene used in the grafting reaction (△). V_I is the total volume of isopropyl alcohol added and V_B is the volume of benzene used as solvent.

One can increase the maximum extent of grafting about the 62% shown in Figures 2 and 3, under certain reaction conditions. For example, an 80.8% grafting of living polystyrene was obtained when a mixture of THF and benzene (THF = 54 vol %) was used as solvent and Li^+ as the counterion (Tables IV and VI).

Characterization of the Products. The gel permeation chromatograms (GPC) of the polymers obtained in Exs SOK-2 and SOL-23 showed two peaks (Figure 6). The elution count of the peak on the right agrees with that of living polystyrene terminated without grafting, while that of the peak on the left seems to be a little larger than that expected from the molecular weight of graft polymer estimated from the extent of coupling. However, this disagreement may be reasonable as in view of results reported by Kato et al.[18] for the case of graft polymers having very close branches. Therefore, the peak of low molecular weight polymer may be ascribed to the uncoupled living polystyrene, and that of high molecular weight polymer to the graft polymer. Furthermore, since the amount of backbone polymers used in the graftig reactions is negligibly

Table VII
Fractionation Results of Recovered Polymer (Ex. SOL-5)

	Weight		No.-average molecular weight $\overline{M}_n \times 10^{-4}$	
	mg	%		
Fraction I (Homopolystyrene)	252	63.0	2.61	(2.41[a])
Fraction II (Graft polymer)	145	36.3	38.3	(82.9[b])

[a] Of terminated living polystyrene used in this grafting reaction, for reference. [b] Of graft polymer which is expected from the extent of coupling of epoxide ring, for reference.

small compared with that of living polystyrene, the ratio of the area of the peak of the graft polymer to total area of the two peaks may indicate the extent of coupling of living polystyrene. The extent of coupling so determined for Exs SOK-2 and SOL-23 is 59.7 and 76.5%, respectively.

The turbidimetric titration curves of the polymers obtained in Exs SOL-1 and SOL-5 have a clear inflection point as shown in Figure 7 so that both parts before and after this point can be distinguished easily. The part before the inflection corresponds to the graft polymer and may also represent the extent of grafting (Ex SOL-1, 53%; Ex SOL-5, 31%) for the same reason given in the discussion of the GPC data. The part after the inflection corresponds to the uncoupled living polystyrene.

Table VII shows the results of the fractional precipitation. In a single fractionation, the number-average molecular weight of fraction I was approximately equal to that of the living polystyrene used. On the other hand, the number-average molecular weight of fraction II was about half of that of the graft polymer ($\overline{M}_n = 82.9 \times 10^4$) estimated from the extent of coupling of epoxide ring (57%). However, the discrepancy may be explained by taking into account 3.5 wt % of uncoupled living polystyrene ($\overline{M}_n = 2.47 \times 10^4$) in the graft polymer. Therefore, the fractionation seems to have been carried out satisfactorily, and the weight percent of fraction II (36.3%) should be approximately equal to the extent of grafting of living polystyrene because, as mentioned above, the amount of backbone polymer used was negligibly small compared with that of living polystyrene.

In the GPC and the turbidimetric titration curves, the graft polymer and the uncoupled living polystyrene were distinguished easily owing to the great difference in their molecular weight which arose from the high degree of coupling. The same reason may be given for the easy separation of the respective polymers in the fractional precipitation and for the good agreement[2] of the extent of grafting calculated from eq 1 with that determined by the above characterizations.

References and Notes

(1) Preparation of Well-Defined Polymers by Polymer-Coupling Reaction. Part II. Part I: M. Takaki and R. Asami, to be published.
(2) M. Takaki and R. Asami, Part I, to be published.
(3) G. Finaz, Y. Gallot, P. Rempp, and J. Parrod, *J. Polym. Sci.*, **58**, 1363 (1962).
(4) Y. Gallot, P. Rempp, and J. Parrod, *J. Polym. Sci., Polym. Lett. Ed.*, **1**, 329 (1963).
(5) For example, J. Pannell, *Polymer*, **12**, 558 (1971).
(6) For example, G. A. Andreeva and A. A. Korotov, *Vysokomol. Soedin.*, **12**, 95 (1970).
(7) A. B. Gosnell, J. A. Gervasi, D. K. Woods, and V. Stannett, *J. Polym. Sci., Part C*, 611 (1969).
(8) E. Papirer and V. T. Nguyen, *J. Polym. Sci., Polym. Lett. Ed.*, **10**, 167 (1972).
(9) S. Tanimoto, C, Nakashima, and R. Oda, *Nippon Kagaku Zasshi*, **86**, 860 (1965).
(10) E. C. Dearborn, R. M. Fuoss, A. K. Mackenzie, and R. G. Shepherd, *Ind. Eng. Chem.*, **45**, 2715 (1953).
(11) K. Ishizu, T. Fukutomi, and T. Kakurai, *Polym. J.*, **7**, 228 (1975).
(12) K. Ishizu, T. Fukutomi, and T. Kakurai, *Nippon Kagaku Kaishi*, 534 (1975).
(13) S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **40**, 1564 (1962).
(14) S. Bywater and D. J. Worsfold, *J. Phys. Chem.*, **70**, 162 (1966).
(15) M. Morton, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **5**, 1092 (1964).
(16) Part III: M. Takaki, R. Asami, and M. Ichikawa, *Macromolecules*, following paper in this issue.
(17) P. Ehrlich and E. D. Graham, *J. Polym. Sci.*, **45**, 243 (1960).
(18) T. Kato, A. Itsubo, Y. Yamamoto, T. Fujimoto, and M. Nagasawa, *Polym. J.*, **7**, 123 (1975).

Coupling Reaction between Living Polystyrene and Poly(chloromethylstyrene)[1]

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ABSTRACT: The coupling reaction between living polystyrene and poly(chloromethylstyrene), P(CMS), was investigated with emphasis on the coupling reactivity of P(CMS) as a multifunctional backbone polymer for the preparation of well-defined polymer. The backbone polymer was prepared by the radical polymerization of commercially available chloromethylstyrene. High extent of coupling (>80%) is attained in tetrahydrofuran/benzene (44/56 vol %) mixture with Li^+ as the counterion and at low values of the mole ratio of living ends to chloromethyl groups, [LE]/[CH_2Cl], in the case of K^+. The extent of side reactions is large at high values of [LE]/[CH_2Cl] or in a P(CMS)–poly(styryllithium)–benzene system. The solvent, the counterion, and the reaction temperature all affect the extent of coupling mainly by changing the ionic character of the living polystyrene.

A chloromethyl group of benzylic type is one of the functional groups that has often been used for the preparation of well-defined polymers such as star and graft polymers by means of nucleophilic substitution with living polymers. For the preparation of star polymers, tri(chloromethyl)benzene,[2] tetra(chloromethyl)benzene,[3,4] hexa[*p*-(chloromethyl)phenyl]benzene,[5] and chloromethylated polystyrene (low degree of polymerization)[3] have been used as the multifunctional centers. For graft polymers, i.e., comb-shaped polymers, only chloromethylated polystyrene[3,6-12] has been used.

Altares et al.[3] treated poly(styryllithium) (PSt-Li) with tetra(chloromethyl)benzene or chloromethylated polystyrene