Partial Alkali Metalation of Poly(*p*-hydroxystyrene) and Poly(*p*-hydroxystyrene-*co*-styrene) and the Solubility of the Resulting Polymer in Tetrahydrofuran

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ABSTRACT: The partial alkali metalation of poly(*p*-hydroxystyrene) (PHS) and poly(*p*-hydroxystyrene-*co*-styrene) P(HS-*co*-S) with alkali metal naphthalene (M-Naph) was carried out to obtain a solution of the metalated polymer. The value for $\{[OM]/[OH]_0\}_{tur}$ was determined as the ratio of pendant metal phenolates ($-\text{C}_6\text{H}_4\text{OM}$; M = Li, Na, and K) to the initial pendant phenols when the titration of a PHS or P(HS-*co*-S) solution with M-Naph begins to give a turbid solution and/or a polymer precipitation. The value of $\{[OM]/[OH]_0\}_{tur}$ was found to depend on the counter cation (M^+); *i.e.*, the solubility of partially-metalated P(HS-*co*-S) was in the order $OK \approx ONa < OLi$. Also, the solubility of P(HS-*co*-S)-Na increased with an increase in the styrene content of the copolymer. The plot of $\{[ONa]/[OH]_0\}_{tur}$ vs. the concentration of P(HS-*co*-S) was linear and "intrinsic" $\{[ONa]/[OH]_0\}_{tur}$ was found to be 0.70. These results can be interpreted in terms of solubility parameter. The polymer which was once precipitated at a high $[OM]/[OH]_0$ ratio became soluble again by hydrolysis with acid or by dilution with a THF solution of PHS or P(HS-*co*-S).

KEY WORDS Poly(*p*-hydroxystyrene) / Poly(*p*-hydroxystyrene-*co*-styrene) / Alkali Metal Naphthalene / Alkali Metalation / Solubility Parameter /

Poly(*p*-hydroxystyrene) (PHS) and poly(*p*-hydroxystyrene-*co*-styrene) P(HS-*co*-S) were treated with alkali metals such as Li, Na, and K in order to prepare a polymer having alkali metal phenolate as pendants (PHS-M, P(HS-*co*-S)-M). Although it is well known that phenol readily reacts with alkali metal forming alkali metal phenolate, no reaction of PHS or P(HS-*co*-S) with alkali metal took place in THF under the heterogeneous condition. The homogeneous metalation which was performed using alkali metal naphthalene (M-Naph) gave PHS-M or P(HS-*co*-S)-M and it revealed that with an increase in the degree of metalation of pendant phenols, the solubility of the resulting polymer was remarkably decreased and the phase separation of the metalated polymer took place.

In this study, the change in solubility caused by copolymer composition and by the degree of metalation of the pendant phenols was investigated and is discussed qualitatively in terms of the solubility parameter. Also, our aim in the meta-

lation of PHS and P(HS-*co*-S) is the use of resulting polymers as multifunctional couplers, *i.e.*, backbone polymers in the grafting reactions with living polytetrahydrofuran (PTHF), as was shown to be the high coupling reactivity¹ of phenoxide ions with propagating species of living PTHF molecules. Thus, emphasis has been placed on the critical extent of metalation of P(HS-*co*-S) in the homogeneous conditions, since this value corresponds to the maximum number of grafted branches of the backbone polymer which can be attained in grafting reactions with living PTHF under appropriate conditions. Grafting reactions with living PTHF will be dealt in the following paper.²

EXPERIMENTAL

Materials

The PHS used was obtained by the radical polymerization of *p*-hydroxystyrene (*p*-HS) prepared by the base-catalyzed hydrolysis of *p*-

Table I. Compositions and number-average molecular weights (M_n) of the polymers used

Polymer		Composition (St/ <i>p</i> -HS) ^a	$M_n \times 10^{-4}$
Poly(<i>p</i> -hydroxystyrene)	PHS	—	0.85 ^b
Poly(<i>p</i> -hydroxystyrene- <i>co</i> -styrene)	P(HS- <i>co</i> -S ₅)	5.40	12.7 ^c
"	P(HS- <i>co</i> -S ₁₁)	11.2	9.14 ^c
"	P(HS- <i>co</i> -S ₁₉)	19.2	6.02 ^c

^a Mole ratios of styrene to *p*-hydroxystyrene in the copolymers were determined by ultraviolet spectra (UV).^b Based on GPC.^c Determined by the osmotic-pressure measurement.

acetoxystyrene (Maruzen Petrochemical Co.), with α, α -azobisisobutyronitrile (AIBN) in benzene (50 vol%) at 60°C. The poly(*p*-hydroxystyrene-*co*-styrene)s employed were prepared in the following manner. *p*-Acetoxystyrene was copolymerized with styrene under the same conditions as in homopolymerization. Each of the copolymers was fractionated into five fractions by the addition of methanol to a 1% polymer solution in benzene. The third fractions which were shown to be most monodisperse by gel-permeation chromatography (GPC) were hydrolyzed with NaOH in dimethyl sulfoxide. The infrared (IR) spectra of the hydrolyzed copolymers had no absorption at 1770 cm⁻¹ due to acetoxyl groups. The mole ratios of styrene to *p*-HS in the copolymers were spectroscopically determined by the calibration curve of styrene units vs. *p*-HS units ($\epsilon_{\max} = 1.8 \times 10^3$ at $\lambda_{\max} = 281$ nm). The compositions of the copolymers and the molecular weights of the homopolymer and copolymers are listed in Table I along with their abbreviations. Lithium-, sodium-, and potassium-naphthalenes (Li, Na-, and K-Naph) were prepared by the usual method. Tetrahydrofuran (THF) as a solvent was purified according to the conventional anionic-polymerization technique.

Measurement

The number-average molecular weights of the copolymers were determined by osmotic-pressure measurement in toluene at 37°C, using a Knauer membrane osmometer. Gel-permeation chromatograms were measured in THF using a Toyo Soda HLC-802UR with two GHM columns (2 ft $\times$ 2, Toyo Soda).

Determination of $\{[OM]/[OH]_0\}_{\text{tur}}$

By using a titration device shown in Figure 1, the value of $\{[OM]/[OH]_0\}_{\text{tur}}$ was determined as the fraction of pendant metal phenolates to the initial pendant phenols at which the titration of a PHS or P(HS-*co*-S) solution with M-Naph begins to show a turbid solution and/or a polymer precipitation.

This device was evacuated on a high vacuum line (ca. 10⁻⁵ mmHg) and sealed off from the line. First, a PHS or P(HS-*co*-S) solution in ampule P was transferred to reaction vessel R and ampule P was rinsed by cooling with dry ice-methanol. After the polymer solution became ambient in temperature, an M-Naph solution in ampule M was introduced to the buret part B, and stopcock C (high vacuum stopcock; ACE, Glass Inc. #8192-03) was released slowly with this device, being inclined so that

Figure 1. Titration device for the determination of a value of $\{[OM]/[OH]_0\}_{\text{tur}}$. Symbols are shown in text.

several drops of the M-Naph solution could fall into pocket A. In this manner, deactivated M-Naph, which was formed to a small extent by contact with teflon surface of the stopcock, was removed. After the device was put into a vertical position, the stopcock was released again so that the M-Naph solution could drop slowly and constantly into the polymer solution with stirring by stirrer S. This titration was stopped when the solution became turbid.

RESULTS

The reaction of PHS and P(HS-co-S) with M-Naph proceeded homogeneously and very rapid in THF at a low mole ratio of M-Naph to hydroxyl groups, but as the ratio was increased, the reaction

mixture became turbid and almost all of the polymer molecules were precipitated by the addition of equimolar M-Naph to the hydroxyl groups, with the exception of P(HS-co-S₁₉).

The solubility of a partially-metalated P(HS-co-S) is expected to be correlated with its counter cation. Actually, as shown in Table II, the value of $\{[OM]/[OH]_0\}_{tur}$ is greatly dependent on the counter cation; *i.e.*, the solubility of P(HS-co-S₅)-M is of the order $K^+ \approx Na^+ < Li^+$. Furthermore, the cation of M-Naph affected the phase separation behavior of the resulting polymer. In the case of K-Naph, almost all the polymer molecules were precipitated immediately at the value of $\{[OK]/[OH]_0\}_{tur}$. However, in the cases of Li-Naph and Na-Naph, the reaction mixture was slightly turbid at the value of $\{[OM]/[OH]_0\}_{tur}$ and then became milky white after

Table II. Values of $\{[OM]/[OH]_0\}_{tur}$ in the reactions of P(HS-co-S₅) with M-Naph^a

	M-Naph		P(HS-co-S ₅)		$\{[OM]/[OH]_0\}_{tur}^c$	Remarks
	Concn	Vol ^b	[OH] ₀	Vol		
	mmol l ⁻¹	ml	mmol l ⁻¹	ml		
Li-Naph	10.6	3.84	14.0	5.90	0.57	Turbid after 20—30 min
Na-Naph	11.5	2.10	14.0	4.80	0.36	Turbid after 3—6 min
"	11.5	2.15	14.0	4.25	0.39	"
K-Naph	10.7	2.35	14.0	4.83	0.37	Polymer precipitated immediately

^a Solvent, THF; temp, room temp (*ca.* 23°C).

^b Minimum volume of an M-Naph solution at which polymer begins to precipitate.

^c Phase separation did not occur below this value of $\{[OM]/[OH]_0\}_{tur}$.

Table III. Values of $\{[ONa]/[OH]_0\}_{tur}$ in the reactions of Na-Naph with PHS and P(HS-co-S)₅^a

Exptl no.		Polymer soln			Na-Naph		$\{[ONa]/[OH]_0\}_{tur}$
		[Polymer]	[OH] ₀		[Na]	Vol ^b	
		g l ⁻¹	mmol l ⁻¹	ml	mmol l ⁻¹	ml	
1	PHS	9.85	82.0	4.05	10.4	1.00	0.03 ₁
2	P(HS-co-S ₅)	9.56	14.0	4.80	11.5	2.10	0.36
3	P(HS-co-S ₁₁)	9.37	7.32	4.89	10.4	2.58	0.76
4	P(HS-co-S ₁₉)	10.6	5.00	5.00	10.4	2.64	(1.10) ^c

^a Solvent, THF; temp, room temp.

^b Minimum volume of a Na-Naph solution in which the polymer begins to precipitate.

^c Reaction mixture is completely homogeneous and pale-green owing to Na-Naph.

20—30 minutes in the former case and after 3—6 minutes in the latter case.

The values of $\{[\text{ONa}]/[\text{OH}]_0\}_{\text{tur}}$ were determined in the reactions of Na-Naph with PHS and P(HS-co-S)s. The results are shown in Table III. The solubility of P(HS-co-S)-Na was found to depend on the composition of the copolymers. In the case of PHS, the value of $\{[\text{ONa}]/[\text{OH}]_0\}_{\text{tur}}$ was as low as 0.031 whereas in the case of P(HS-co-S₁₉), the solution showed no precipitate even when an excess of Na-Naph was added to the hydroxyl groups. From these values of $\{[\text{ONa}]/[\text{OH}]_0\}_{\text{tur}}$ and the compositions of the copolymers, the number of monomer units per O-Na bond necessary for the resulting polymer to remain in solution was estimated. Also from these results, the number of O-Na bonds per 100 monomer units ($\{\text{ONa}/100 \text{ monomer units}\}_{\text{tur}}$) at which the phase separation of the resulting polymer begins to occur could be estimated. In Figure 2, $\{\text{ONa}/100 \text{ monomer units}\}_{\text{tur}}$ is plotted against the composition of the copolymer. In a reaction of P(HS-co-S) with Na-Naph, Figure 2 predicts that if a plotted point of the number of O-Na bonds per 100 monomer units against the St/*p*-HS mole ratio in P(HS-co-S) lies on below the curve, the homogeneity of the solution will be maintained, and if the point lies on the curve or above the curve, the metalated polymer will be insoluble. In fact, the metalated polymer was soluble in THF in the case of Exptl no. 4 (in Table III) giving the point marked by an asterisk in Figure 2.

In Figure 3, the values of $\{[\text{ONa}]/[\text{OH}]_0\}_{\text{tur}}$ are plotted against the polymer concentration in the reaction of Na-Naph with P(HS-co-S₅). It is clearly shown that these values depend on the polymer concentration. The plot of $\{[\text{ONa}]/[\text{OH}]_0\}_{\text{tur}}$ vs. polymer concentration showed a straight line and the value of $\{[\text{ONa}]/[\text{OH}]_0\}_{\text{tur}}$ extrapolated to zero concentration, *i.e.*, “intrinsic” $\{[\text{ONa}]/[\text{OH}]_0\}_{\text{tur}}$ was 0.70. This value and the composition of P(HS-co-S₅) suggest that the non-metalated monomer units are more necessary than the 8.1 units per O-Na bond at least for P(HS-co-S₅) to remain in solution.

DISCUSSION

The solubility parameter has been shown to be useful as an explanation for the solubility phenomena qualitatively. Hansen³ proposed that the

Figure 2. Plot of St-*p*-HS (mol mol⁻¹) in P(HS-co-S) vs. $\{\text{ONa}/100 \text{ monomer units}\}_{\text{tur}}$ at which the phase separation of the resulting polymer begins to occur in the reactions of Na-Naph with PHS and P(HS-co-S)s. The polymer concentrations at the values of $\{[\text{ONa}]/[\text{OH}]_0\}_{\text{tur}}$ were 6.7—7.9 g l⁻¹. Asterisk mark is explained in the text.

Figure 3. Dependence of $\{[\text{ONa}]/[\text{OH}]_0\}_{\text{tur}}$ on the polymer concentration in the reaction of P(HS-co-S₅) with Na-Naph.

Hildebrand solubility parameter,⁴ the overall parameter (δ_0), must be expressed by δ_d , δ_p , and δ_h as in the following equation,

$$\delta_0^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

where δ_d , δ_p , and δ_h correspond to dispersion forces, polar forces, and hydrogen bonding, respectively. In this study, δ_d , δ_p , and δ_h are considered to participate mainly with styrene units, metalated *p*-hydroxystyrene units, and *p*-hydroxystyrene units,

respectively. Consequently, a metalated PHS should have the highest value for δ_p and, thus, have the highest solubility parameter for δ_o . A solvent which dissolves the metalated PHS should thus have a very high solubility parameter. In fact, the metalated PHS was insoluble in THF with a solubility parameter⁵ of 9.2 but soluble in water with a solubility parameter⁵ of 24.5.

The effect of the counter cation on the value of $\{[OM]/[OH]_0\}_{tur}$ may be ascribed to the difference in ionic character which increases in the order of $Li-O < Na-O < K-O$, as is well known. That is, the conversion of O-H bonds to O-Na or O-K bonds must involve a greater increase in the δ_o value than that of the O-H bonds to O-Li bonds. Accordingly, it is easily seen that P(HS-co-S)₅-K and -Na are less soluble than P(HS-co-S)₅-Li in THF whose solubility parameter is relatively small.

The decrease in the value of $\{[ONa]/[OH]_0\}_{tur}$ with an increase in *p*-HS content in P(HS-co-S) may be interpreted as follows. The solubility parameters⁵ of benzene and phenol are 9.2 and 14.5, and are the pendant moieties of a styrene unit and a *p*-HS unit, respectively. These values suggest that the solubility parameter of *p*-HS units in P(HS-co-S) is substantially larger than that of styrene units, *i.e.*, the higher the *p*-HS content in P(HS-co-S), the larger is the solubility parameter of the P(HS-co-S). Therefore, in the case of P(HS-co-S) with a high *p*-HS content, a small extent of metalation would

make the solubility parameter of the metalated P(HS-co-S) so different from that of THF that the metalated P(HS-co-S) becomes insoluble in THF.

The polymer which was once precipitated in THF owing to a high $[OM]/[OH]_0$ ratio was still insoluble after the addition of a large amount of THF. However, the insoluble polymer became soluble by the addition of a small amount of a PHS or P(HS-co-S) solution as the ratio of $[OM]/[OH]_0$ was reduced. The insoluble polymer became instantaneously soluble by hydrolysis with acid such as acetic acid or aqueous hydrochloric acid. The GPC curve of the hydrolyzed P(HS-co-S)-M coincided with that of the polymer before the metalation. This fact implies that the metalation does not involved side reactions such as a scission of a main chain and intermolecular cross-linking reaction.

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