Dilute solution properties of poly(4-hydroxystyrene)

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Light-scattering and viscosity measurements have been carried out on dilute solutions of poly(4-hydroxystyrene) (PHS) fractions, which were obtained by hydrolysis of poly(4-acetoxystyrene) (PAS). The Mark–Houwink–Sakurada equations were determined in dioxane, tetrahydrofuran, isobutyl acetate and ethyl propionate at 25°C. The unperturbed dimension and the thermodynamic interaction parameters for PHS in various solvents were also determined and compared with those previously obtained for PAS. It was concluded that the hindrance potential of rotation around the C–C bond in the main chain of PHS is influenced more than expected solely from the volume effect of side groups, but it is within the same range found for other polar *para*-substituted polystyrenes. Also, it was found that in contrast to the PAS–solvent system there are significant energetic and entropic interactions between segments of PHS and solvent molecules, arising from the presence of a hydroxyl group in the side chain.

(Keywords: poly(4-hydroxystyrene); poly(4-acetoxystyrene); light scattering; unperturbed dimension; thermodynamic interaction parameter)

INTRODUCTION

Recently poly(4-hydroxystyrene) (PHS) has received much attention as a multifunctional polymer with a number of specialized applications. For example, the polymer cures epoxy resins by yielding crosslinking structures[1] which have various advantages over conventional epoxies with respect to thermal stability, flammability and chemical resistance. Besides many patents and reports on utilization of the polymer, there are several fundamental research reports[2–8] on the preparation and polymerization of this polymer. Many reports on the copolymer containing 4-hydroxystyrene as a functional polymer have also been published. For example, Overberger *et al.*[9] reported on cooperative effects in the esterolytic action of a copolymeric catalyst consisting of 4(5)-vinyl imidazole and 4-hydroxystyrene, and Ledwith *et al.*[10] found that phenolic groups in poly(acrylonitrile-*co*-4-hydroxystyrene) afford useful attachment sites protecting amino acid at the first stage in solid-phase peptide synthesis. Nakamura *et al.*[2,11–14] reported on studies of thermoanalysis of PHS and homologous polymers, and of copolymers of 4-hydroxystyrene and 4-acetoxystyrene which were obtained by partial or complete hydrolysis of poly(4-acetoxystyrene) (PAS). Nakamura *et al.*[13] found that the glass transition temperature T_g of PHS is much higher than that of PAS, and that T_g increases with increase of the degree of hydrolysis of PAS, and decreases with the addition of a small amount of water to PHS and/or partially hydrolysed PAS. They explained that these facts have been attributed to hydrogen bond formation between hydroxyl groups of the side chains.

Solution properties of this copolymer will change with the composition of 4-hydroxystryene and 4-acetoxystyrene owing to the strong polarity and the possibility of hydrogen bond formation of hydroxyl groups. From this point of view, it is important to study the solution properties of the respective homopolymers, PAS and PHS. We reported the solution properties of PAS in the preceding paper[15], but for the latter polymer there has been no report except a brief description on solubility and limiting viscosity numbers in some solvents by Danusso *et al.*[7] In this paper the fundamental solution properties of PHS including solubility in various kinds of diluent were reported, and compared with those of PAS.

EXPERIMENTAL

Materials

PHS fractions were prepared by complete hydrolysis of PAS fractions. Polymerization and fractionation of the parent polymer, PAS, were described in the previous paper[15], whose hydrolysis was carried out with almost the same procedure as described by Tanaka and Senju[4]. Each of the fractions was dissolved in dioxane, and subsequently aqueous 0.8 M sodium hydroxide solution was added with stirring at room temperature. 2,6-Di-t-butylphenol (0.15%) was used as antioxidant to prevent the polymer from undergoing an appreciable gelation reaction between phenol groups, and the air in the reaction vessel was substituted with a nitrogen atmosphere. The resulting mixture was added slowly with stirring into a large excess of dilute aqueous hydrochloric acid. The recovered polymer was dried in a vacuum oven

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to constant weight, and the i.r. spectra of these samples were observed with a Hitachi infra-red spectrophotometer, type EDI-G2, and were in good agreement with those of PHS reported by Danusso[7].

All the solvents and other materials used were of reagent grade, and purified according to the standard procedures except those used for solubility tests.

Measurements

Light-scattering measurements were carried out on fractions of PHS in dioxane at 25 ± 0.1°C with a Fica 50 light-scattering photometer using vertically polarized light of wavelength 436 nm. The experimental details were the same as those described in the previous paper[15]. Measurements of refractive-index increment were carried out in dioxane at 25 ± 0.1°C using a Shimadzu differential refractometer DR-3. The result obtained for 436 nm light was 0.197 ml g^{-1}. Observed scattering data were treated by the method of Zimm.

Viscosity measurements were carried out with an Ubbelohde type viscometer in a water bath controlled within ±0.01°C at the desired temperature. Both shear rate and kinetic energy corrections were negligible. The limiting viscosity number, $[\eta]$, was determined by the Huggins plot and the Fuoss–Mead plot when necessary.

Densities of polymer solution and solvent were measured with an Anton Paar densimeter type DMA60-DMA602HT. Temperature fluctuations at each measurement were controlled within ±0.005°C over the range of 6.4–60°C. The apparatus constant was determined from the densities of redistilled water and air.

Solubility tests for PHS were carried out by the method of Izumi and Miyake as before[15]; a polymer sample, PHS18-2, and each of the test liquids were shaken in sealed glass tubes at iced water (L), room (R) and high (~70–90°C) (H) temperatures, and the solubility was observed in each temperature range.

RESULTS AND DISCUSSION

Solubilities

The results are summarized in *Table 1* where symbols '+', '−' and '±' denote the polymer soluble, insoluble and swollen, respectively, and a letter 'N' diluents frozen at the temperature range. PHS are soluble in aliphatic alcohols, and insoluble in non-polar solvents such as aliphatic and aromatic hydrocarbons. Some of these results are in contrast to those for PAS; PAS is insoluble in aliphatic alcohols and soluble in benzene. However, there are many common solvents for both polymers such as ketones, esters, pyridines and dioxane.

Molecular weight dependence of $\langle S^2\rangle_z^{1/2}$ *and* A_2

Table 2 summarizes the values of the weight-average molecular weight, M_w, the z-average root-mean-square radius of gyration, $\langle S^2\rangle_z^{1/2}$, and the second virial coefficient, A_2, obtained by light-scattering measurements in dioxane at 25°C. *Figures 1* and *2* show log–log plots of $\langle S^2\rangle_z^{1/2}$ against M_w and of A_2 against M_w for PHS in dioxane at 25°C, together with those for PAS in the same conditions[15] for comparison. The straight lines in each figure were drawn by the least squares method, where the two suspicious, points of lowest molecular weight in *Figure 2* were disregarded. They are represented by:

$$\langle S^2\rangle_z^{1/2}=3.26\times10^{-9}M_w^{0.55}$$

$$A_2=9.74\times10^{-2}M_w^{-0.38}$$

As apparently seen from both figures, dioxane is a better solvent for PHS than for PAS. The second virial coefficients of PHS in dioxane are enormously large in the whole range of molecular weight when compared with those of PAS, and the exponent γ in $A_2\propto M_w^{-\gamma}$ is larger than that ($=0.23$) of PAS[15] and also those ($=0.15$–0.2) frequently reported for other ordinary linear polymer–solvent systems. Further, the values of the dimensionless ratio $A_2M_w/[\eta]$ for PHS fractions, which behaves like the interpenetration function Ψ, were found to be too high (>200), compared with the usually expected value of 100–150[17]. It seems that there are strong polymer–polymer interactions in this system.

Mark–Houwink–Sakurada equations

The limiting viscosity numbers for PHS in dioxane, tetrahydrofuran (THF), isobutyl acetate and ethyl propionate at 25°C are summarized in *Table 3*. The Mark–Houwink–Sakurada equations calculated using the least squares method were respectively as follows:

$$[\eta]=2.03\times10^{-4}M_w^{0.66}\quad\text{in dioxane}$$

$$[\eta]=3.72\times10^{-4}M_w^{0.60}\quad\text{in THF}$$

$$[\eta]=5.94\times10^{-4}M_w^{0.53}\quad\text{in isobutyl acetate}$$

$$[\eta]=6.37\times10^{-4}M_w^{0.52}\quad\text{in ethyl propionate}$$

Judging from the indices of M_w in the above equations, isobutyl acetate and ethyl propionate are close to the theta solvent. However, we have failed to determine the theta state in these solvents from phase separation experiments. When the $[\eta]$–M_w relationship of PHS in dioxane at 25°C is compared with those of PAS and polystyrene reported in the previous paper[15], dioxane is a better solvent for PHS than for PAS, but a poorer one than for polystyrene.

On the whole, the $[\eta]$–M_w relationships for PHS are quite normal for a random coiled polymer and did not show any peculiarities which might be expected to occur from the strong hydrogen bonding interaction and/or the gelation reaction between phenol groups.

Estimation of unperturbed dimension

According to the theory of Flory and Fox[18–20], the constant K_Θ is related to the unperturbed mean-square end-to-end distance $\langle R^2\rangle_0$ by:

$$K_\Theta=\Phi_0(\langle R^2\rangle_0/M)^{3/2}\qquad(1)$$

where M is the molecular weight of polymer and Φ_0 the universal constant. Since the theta solvent for PHS was not yet found in these experiments, the value of K_Θ was indirectly estimated by the extrapolation methods based on the two-parameter theories. The Stockmayer–Fixman equation[21] is:

$$[\eta]/M^{1/2}=K_\Theta+0.51\Phi_0BM^{1/2}\qquad(2)$$

Table 1 Solubility tests for the PHS18-2–diluent system at low (L), room (R) and high (H) temperatures[a]

Diluents	L	R	H	Diluents	L	R	H
Pentane	–	–	–	Pentyl acetate	+	+	+
Hexane	–	–	–	Isopentyl acetate	+	+	+
Dodecane	–	–	–	Methyl propionate	+	+	+
Bromoethane	–	–	–	Ethyl propionate	+	+	+
1-Chlorobutane	–	–	–	Propyl propionate	±	±	±
Dichloromethane	–	–	–	Isopropyl propionate	±	±	±
1,1-Dichloroethane	–	–	–	Butyl propionate	±	±	–
1,2-Dichloroethane	–	–	–	Isobutyl propionate	±	±	–
Dibromoethane	N	–	–	Isopentyl propionate	±	±	–
Chloroform	–	–	–	Hexyl propionate	±	±	–
Bromoform	–	–	–	Dimethyl sulphoxide	N	+	+
1,1,1-Trichloroethane	–	–	–	Carbon disulphide	–	–	–
Tetrachloromethane	–	–	–	Butylamine	+	+	+
1,1,2,2-Tetrachloroethane	–	–	–	Triethylamine	–	–	–
1,1,2,2-Tetrabromoethane	–	–	–	Formamide	+	+	+
Tetrachloroethylene	–	–	–	Ethylenediamine	+	+	+
Pentachloroethane	–	–	–	*N*,*N*-Dimethylformamide	+	+	+
Methanol	+	+	+	*N*,*N*-Dimethylacetamide	+	+	+
Ethanol	+	+	+	Acetonitrile	+	+	+
1-Propanol	+	+	+	3-Hydroxylpropiononitrile	+	+	+
2-Propanol	+	+	+	Nitromethane	–	–	–
2-Methyl-1-propanol	+	+	+	Nitroethane	–	–	–
2-Methyl-2-propanol	+	+	+	Cyclohexane	N	–	–
1-Butanol	+	+	+	Methylcyclohexane	–	–	–
2-Butanol	+	+	+	Cyclohexanol	+	+	+
3-Methyl-1-butanol	+	+	+	Cyclohexanone	+	+	+
2-Methyl-2-butanol	+	+	+	Benzene	–	–	–
1-Pentanol	+	+	+	Toluene	–	–	–
2-Pentanol	+	+	+	Ethylbenzene	–	–	–
2-Ethyl-1-hexanol	+	+	+	Cumene	–	–	–
Allyl alcohol	+	+	+	Xylene	–	–	–
1,2-Ethanediol	+	+	+	Chlorobenzene	–	–	–
1,3-Butanediol	+	+	+	Bromobenzene	–	–	–
1,5-Pentanediol	+	+	+	Dichlorobenzene	–	–	–
Glycerol	+	+	+	Benzyl chloride	–	–	–
Diethyl ether	–	–	–	3-Methylphenol	–	–	–
2-Butoxyethanol	+	+	+	Anisole	–	–	–
Bis(2-hydroxylethyl) ether	+	+	+	Phenyl acetate	–	±	+
3,6-Dioxa-1-octanol	+	+	+	Phenyl propionate	±	±	±
3,6-Dioxa-1-decanol	+	+	+	Benzyl alcohol	+	+	+
3,6-Dioxa-1,8-octanediol	+	+	+	2-Phenylethanol	+	+	+
Acetaldehyde	+	+	+	Benzyl acetate	+	+	+
Acetone	+	+	+	Benzyl propionate	±	±	+
Butanone	+	+	+	Acetophenone	+	+	+
2-Pentanone	+	+	+	Methyl benzoate	+	+	+
3-Pentanone	+	+	+	Ethyl benzoate	+	+	+
4-Methyl-2-pentanone	+	+	+	Aniline	–	–	–
2,4-Dimethyl-3-pentanone	±	±	±	3,3′-Dimethylbenzidine	–	–	–
2-Hexanone	+	+	+	1-Bromonaphthalene	–	–	–
5-Methyl-2-hexanone	+	+	+	1,2,3,4-Tetrahydronaphthalene	–	–	–
2-Heptanone	+	+	+	Decahydronaphthalene	–	–	–
3-Heptanone	+	+	+	Furfuryl alcohol	+	+	+
2,6-Dimethyl-4-heptanone	±	±	±	2-Furaldehyde	+	+	+
2-Octanone	+	+	+	Tetrahydrofuran	+	+	+
3-Nonanone	±	±	±	1,4-Dioxane	N	+	+
Formic acid	–	–	–	Pyridine	+	+	+
Acetic acid	N	+	+	2-Methylpyridine	+	+	+
Butyric acid	±	±	±	3-Methylpyridine	+	+	+
Ethyl formate	+	+	+	4-Methylpyridine	+	+	+
Ethyl acetate	+	+	+	2-Ethylpyridine	+	+	+
Propyl acetate	+	+	+	5-Ethyl-2-methylpyridine	+	+	+
Isopropyl acetate	+	+	+	Piperidine	+	+	+
1-Methylpropyl acetate	+	+	+	Morpholine	+	+	+
Butyl acetate	+	+	+	Water	–	–	–
Isobutyl acetate	+	+	+				

[a] See text for meaning of symbols

where B is a constant for a polymer–solvent system at a particular temperature and is related to the binary cluster integral. One of the more recent refinements of the two-parameter theory has been discussed by Tanaka[22] and expressed as:

$$([\eta]/M^{1/2})^{5/3} = K_\Theta^{5/3} + 0.627\Phi_0 K_\Theta^{2/3} B M^{1/2} \qquad (3)$$

Plots of $[\eta]/M_w^{1/2}$ and of $([\eta]/M_w^{1/2})^{5/3}$ against $M_w^{1/2}$ for PHS in dioxane, THF, isobutyl acetate and ethyl propionate at 25°C are shown in *Figures 3* and *4*.

Tanaka has reported that $([\eta]/M^{1/2})^{5/3}$, rather than $[\eta]/M^{1/2}$, should be linear in $M^{1/2}$ for most polymer–solvent systems. Though the linearity of both plots does not differ so much in *Figures 3* and *4*, the agreement of the

Table 2 Light-scattering data for PHS in dioxane at 25°C

Fraction	$10^{-4}M_w$	$10^6\langle S^2\rangle_z^{1/2}$ (cm)	10^4A_2 (ml mol g^{-2})
4-4	3.81	1.37	35.6
19-5	9.74	2.04	30.9
4-2	15.3	2.34	10.3
19-4	24.2	2.85	7.16
19-3	57.1	4.44	6.94
16-2	97.1	6.59	4.93
19-2	133	7.36	4.47
16-2′	216	9.71	3.50
13-3	266	10.1	3.01
16-1′	340	12.3	2.75
13-2	583	15.6	2.66

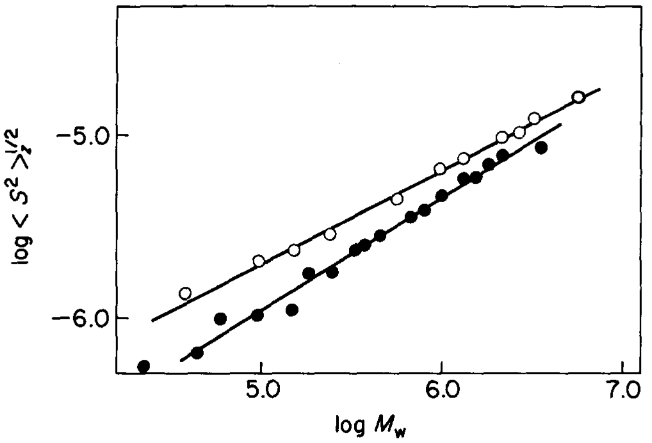

Figure 1 Double logarithmic plots of $\langle S^2\rangle_z^{1/2}$ against M_w for PHS fractions (○) and PAS fractions[15] (●) in dioxane at 25°C

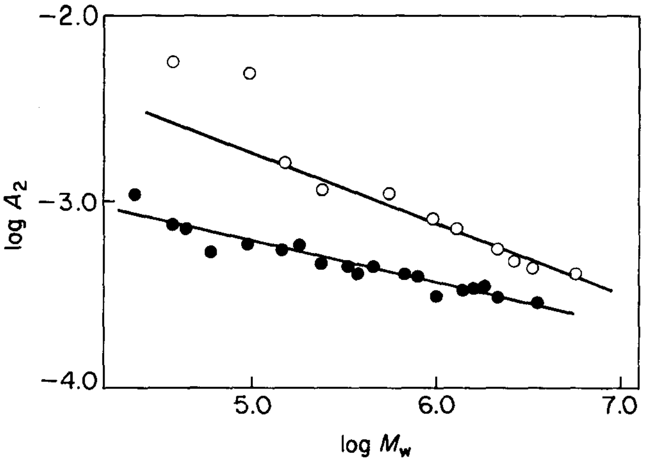

Figure 2 Double logarithmic plots of A_2 against M_w for PHS fractions (○) and PAS fractions[15] (●) in dioxane at 25°C

extrapolated values at $M=0$ in different solvents is better in the Tanaka plot. The values of $K_{\Theta w}$ estimated from the intercept of each line are shown in *Table 4*.

The $K_{\Theta w}$ values thus obtained were corrected for the molecular weight heterogeneity of fractions as before[15], because the parent polymer PAS and the scheme of its fractionation were the same as those described in the previous paper[15], and additionally the degradation of polymer was found to be negligible during hydrolysis. The corrected values of K_Θ are listed in *Table 4*, and its mean value was calculated to be $(8.83 \pm 0.30)\times 10^{-4}$ dl g^{-1}. The unperturbed chain dimensions expressed as $(\langle R^2\rangle_0/M)^{1/2}$, the characteristic ratio C_∞ and the steric factor σ (defined as the ratio of the unperturbed end-to-end distance $\langle R^2\rangle_0^{1/2}$ to $\langle R^2\rangle_{0f}^{1/2}$ of the hypothetical chain with free internal rotation around skeletal bonds) were calculated to be $(6.75 \pm 0.07)\times 10^{-9}$ cm, 11.5 ± 0.3 and 2.40 ± 0.03, respectively. Here the value of Φ_0 was regarded as 2.87×10^{21} mol^{-1}.

The σ value of PHS is comparable to or higher than that ($=2.37$) of PAS estimated earlier[15], in spite of the fact that the former polymer apparently holds the geometrically smaller pendant group. The relationship between the values of σ and molar volume V_x of the

Table 3 Limiting viscosity numbers $[\eta]$ for PHS in various solvents at 25°C

	$[\eta]$ (dl g^{-1})			
Fraction	Dioxane	THF	Isobutyl acetate	Ethyl propionate
4-4	0.221	0.209	0.166	0.165
19-5	0.385	–	0.249	0.245
4-2	0.548	0.478	0.335	0.344
19-4	0.708	0.588	0.415	0.408
19-3	1.32	1.09	0.667	0.685
16-2	1.78	1.44	0.860	0.862
19-2	2.19	1.76	1.07	1.07
16-2′	2.92	2.32	1.35	1.31
13-3	3.51	2.78	1.45	1.37
16-1′	4.04	3.28	1.76	1.75
13-2	6.30	5.38	2.60	2.92

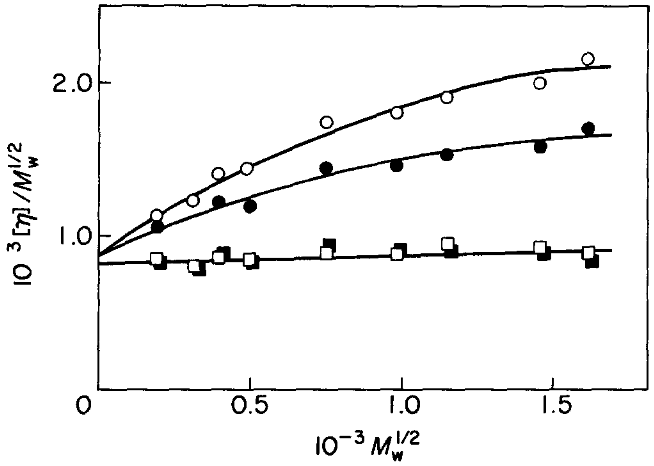

Figure 3 Stockmayer–Fixman plots for PHS at 25°C in dioxane (○), THF (●), isobutyl acetate (□) and ethyl propionate (■)

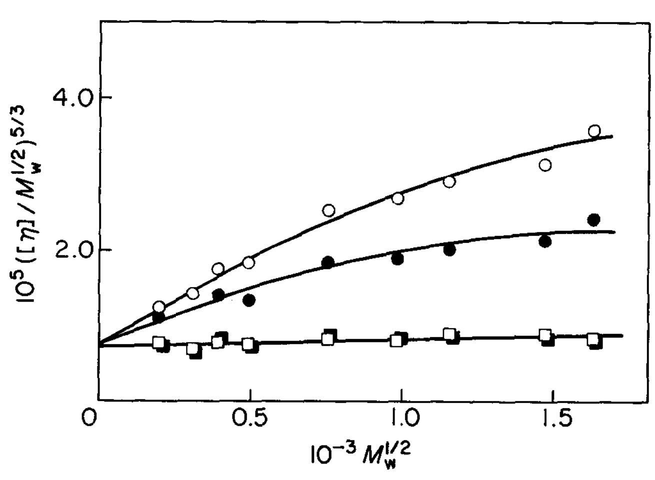

Figure 4 Tanaka plots for PHS in various solvents at 25°C. The symbols have the same significance as those in *Figure 3*

Table 4 Molecular parameters of PHS obtained by two methods

	Stockmayer–Fixman method					Tanaka method				
Solvent	$10^4K_{\Theta w}$	10^4K_Θ	σ	C_∞	$10^{29}B$	$10^4K_{\Theta w}$	10^4K_Θ	σ	C_∞	$10^{29}B$
Ethyl propionate	8.27	8.58	2.38	11.3	3.37	8.27	8.58	2.38	11.3	4.76
Isobutyl acetate	8.37	8.69	2.39	11.4	4.35	8.35	8.67	2.39	11.4	6.22
THF	9.00	9.34	2.45	12.0	90.0	8.41	8.73	2.39	11.4	94.8
Dioxane	9.00	9.34	2.45	12.0	129	8.41	8.73	2.39	11.4	145

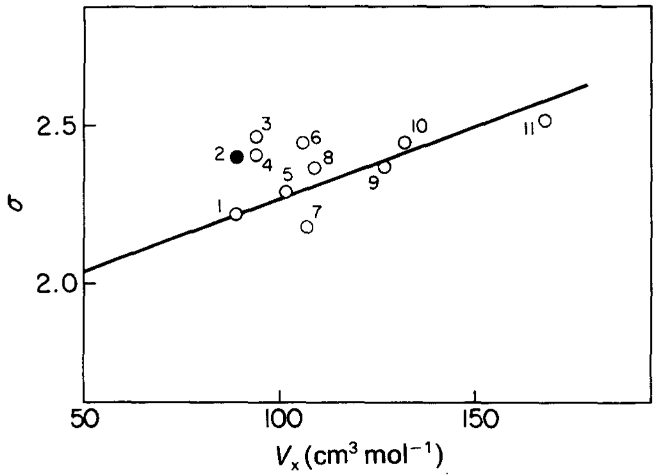

Figure 5 Plots of the steric factor σ against the molar volume V_x of each side group for *para*-substituted polystyrenes and their closely related compounds: (1) polystyrene[23–26]; (2) PHS; (3) poly(3-fluorostyrene)[27]; (4) poly(4-fluorostyrene)[27]; (5) poly(4-chlorostyrene)[16]; (6) poly(4-bromostyrene)[28]; (7) poly(4-methylstyrene)[29,30]; (8) poly(4-methoxystyrene)[31]; (9) PAS[15]; (10) poly(2-vinylnaphthalene)[32]; (11) poly(4-cyclohexylstyrene)[33]

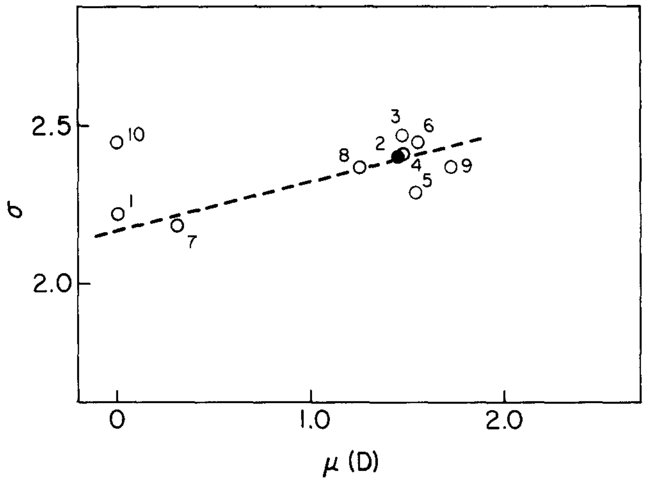

Figure 6 Plots of the steric factor σ against the dipole moment μ of each side group[39,40]. The significance of the arabic numbers is found in *Figure 5*

polymer side chain is displayed in *Figure 5* for *para*-substituted polystyrenes and some of their closely related compounds, where the full line represents the relation established for the poly(vinylaromatic) series by Iwama *et al.*[34] As shown in this figure, the full circle for PHS deviates upwards a little from the full line, together with some of the other polar polystyrene derivatives.

It has been reported that, besides V_x, the σ value is affected by the dipole–dipole (electrostatic) interaction between side chains[35] and/or of the others[36]. Concerning the electrostatic interaction, Fort *et al.*[37] studied the effect of the hydroxyl group in the side chain of poly(2-hydroxyethyl methacrylate) and concluded that the steric factor is approximately comparable to the values for some other methacrylates with less polar side groups. Stejiskal *et al.*[38] studied the same problem and concluded, on the contrary, that the steric factor of poly(2-hydroxyethyl methacrylate) is higher than that of poly(2-methoxyethyl methacrylate). They attributed this to the difference of polarity between hydroxyl and methoxyl groups. Kuwahara *et al.*[33] reported that the chain conformation of poly(*p*-substituted styrene) is not affected by the electrostatic interaction of side groups.

The σ values in *Figure 5* were plotted against the dipole moment μ of the side group in *Figure 6*. The points at $\mu \simeq 0$ indicate that the σ value depends on the value of V_x primarily. But for polar polymers a small increase of σ is shown on increasing the μ value, and also the full circle for PHS in this figure belongs to a group of points for other polar polystyrene derivatives. It is seen in *Figure 5* that the σ value approaches the full line by changing the group at the *para*-position of polystyrene from a hydroxide group in PHS to a methoxide group in poly(4-methoxystyrene). We may conclude that the σ value is somewhat affected by the electrostatic interaction, in addition to the geometrical volume interaction between side groups.

Evaluation of thermodynamic interaction parameters

The thermodynamic interaction parameters in some solvents were estimated by measuring the temperature variation of limiting viscosity numbers for several PHS and PAS fractions. *Figure 7* shows the limiting viscosity numbers of PHS16-1′, measured in dioxane, dimethylformamide (DMF), 4-methyl-2-pentanone, 2-propanol, isobutyl acetate and ethyl propionate, as a function of temperature. Such relationships are also shown in *Figure 8* on a fraction of PAS1-2 (used in ref. 15) in dioxane, DMF, 4-methyl-2-pentanone and benzene. The temperature coefficients of $[\eta]$ for PAS are positive in all solvents measured, whereas those for PHS are evidently the opposite.

The viscosity–radius expansion factor α_η is defined by:

$$\alpha_\eta^3 = [\eta]/[\eta]_\Theta \qquad (4)$$

where

$$[\eta]_\Theta = K_\Theta M^{1/2} \qquad (5)$$

and α_η^3 was expanded in terms of the excluded-volume parameter z by Kurata and Yamakawa[41] as follows:

$$\alpha_\eta^3 = 1 + C_1 z - \ldots \qquad (6)$$

where z is defined by:

$$z=(2\bar{v}_2^2/N_A V_1)(M/4\pi\langle S^2\rangle_0)^{3/2}\psi_1(1-\Theta/T)M^{1/2} \quad (7)$$

with $\bar{v}_2$ the specific volume of the polymer, V_1 the molar volume of the solvent, N_A the Avogadro number, $\langle S^2\rangle_0$ the unperturbed mean-square radius of gyration of a linear flexible polymer, ψ_1 the entropy parameter, and Θ the Flory temperature.

Various values of the coefficient C_1 in equation (6) have been proposed by many investigators[41-45]. In this work, we adopt the equation proposed by Tanaka[22] as:

$$\alpha_\eta^5=1+1.90z \quad (8)$$

From equations (7) and (8) the following equation can be derived:

$$(\alpha_\eta^5-1)/M^{1/2}=1.90(2\bar{v}_2^2/N_A V_1)(M/4\pi\langle S^2\rangle_0)^{3/2}\psi_1(1-\Theta/T) \quad (9)$$

Figures 9 and *10* show plots of $(\alpha_\eta^5-1)/M^{1/2}$ against $1/T$ for PHS and PAS in each solvent shown above. Values of ψ_1 and Θ were calculated from each intercept and slope of the lines in these figures. The enthalpy parameter κ_1 and the excess free energy parameter χ_1 were obtained from the following relations:

$$\kappa_1=\psi_1\Theta/T \quad (10)$$

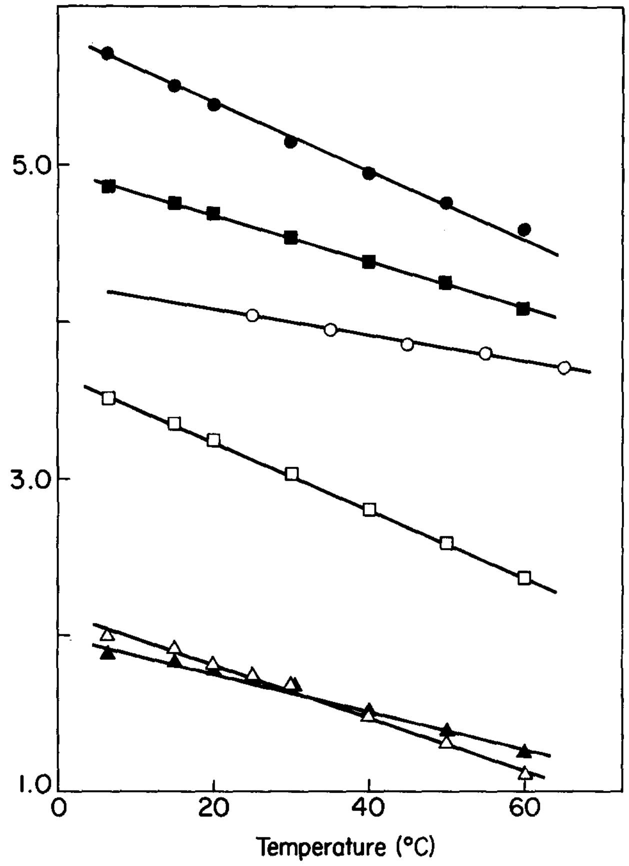

Figure 7 Temperature dependence of $[\eta]$ for PHS16-1′ in dioxane (○), DMF (●), 4-methyl-2-pentanone (□), 2-propanol (■), isobutyl acetate (△) and ethyl propionate (▲)

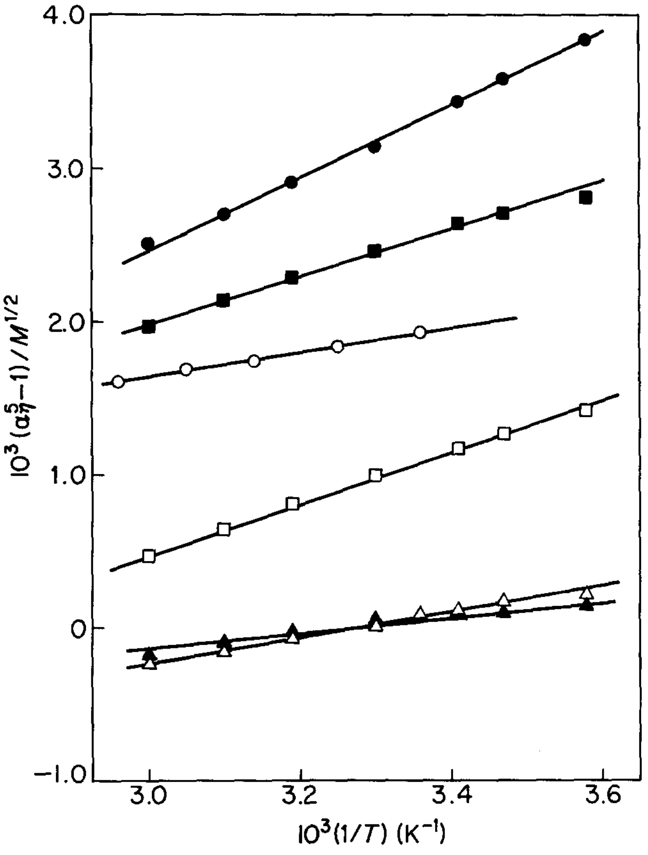

Figure 9 Plots of $(\alpha_\eta^5-1)/M^{1/2}$ against $1/T$ for PHS16-1′ in various solvents. The symbols have the same significance as those in *Figure 7*

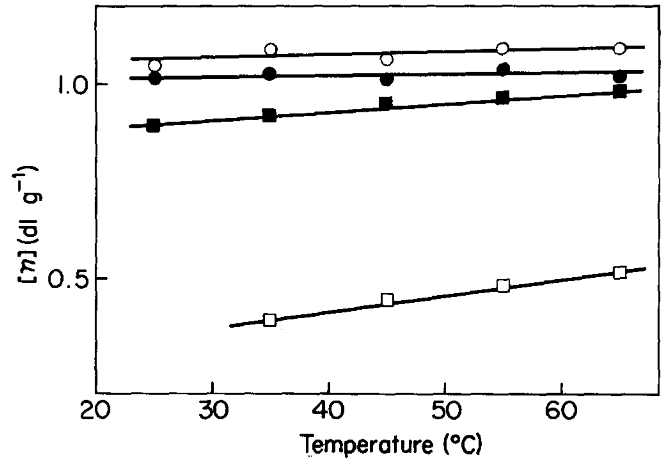

Figure 8 Temperature dependence of $[\eta]$ for PAS1-2 in dioxane (○), DMF (●), 4-methyl-2-pentanone (□) and benzene (■)

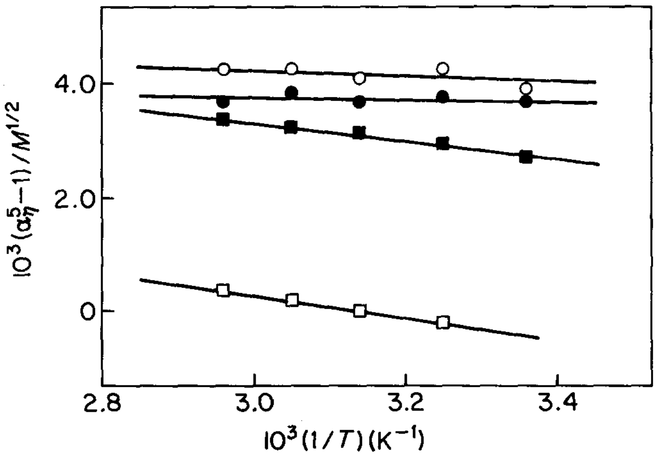

Figure 10 Plots of $(\alpha_\eta^5-1)/M^{1/2}$ against $1/T$ for PAS1-2 in various solvents. The symbols have the same significance as those in *Figure 8*

Table 5 Thermodynamic interaction parameters for dilution of PHS and PAS in various solvents

PHS				PAS			
Solvent	$10^2\psi_1$	$10^2\kappa_1$	χ_1	Solvent	$10^2\psi_1$	$10^2\kappa_1$	χ_1
Dioxane	-1.5	-5.3	0.46	Dioxane	9.7	3.5	0.44
DMF	-7.9	-14	0.44	DMF	4.1	0.3	0.46
4-Methyl-2-pentanone	-14	-18	0.46	4-Methyl-2-pentanone	11	11	0.50
2-Propanol	-4.8	-9.6	0.45	Benzene	10	6.7	0.47
Isobutyl acetate	-8.8	-8.9	0.50				
Ethyl propionate	-5.8	-5.9	0.50				

and

$$\chi_1 = 0.5 + \kappa_1 - \psi_1 \qquad (11)$$

The evaluated values of ψ_1, κ_1 and χ_1 for PHS and PAS are summarized in *Table 5*. The values of κ_1 indicate that the energetic interaction is endothermic in all PAS–solvent systems, but contrarily, exothermic in PHS–solvent systems. The ψ_1 parameters are very small in both PAS- and PHS–solvent systems when compared with the theoretical value 0.5. Moreover, the ψ_1 values for PHS–solvent systems are smaller than those for PAS–solvent systems (and even negative). These results indicate that there is a stronger fixation of solvent molecules to polymer coils in all PHS–solvent systems observed in this work.

In the case of PHS, it may be concluded that the hydroxyl group introduced at the *para*-position of the side chain does influence the hindrance potential to internal rotation around C–C bonds in the main chain, but it is within the same range found for some other polar *para*-substituted polystyrenes. Also, there exist strong thermodynamic interactions in solution of PHS, arising from hydrogen bond formation between polymer and solvent molecules.

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