Unperturbed dimension of poly(4-acetoxystyrene) measured in good and theta solvents

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(Received 16 November 1984; revised 19 December 1984)

In order to obtain the additional data concerning the unperturbed dimension of poly-4-substituted styrene, light scattering measurements are performed on the twenty-two fractions with molecular weight of (0.91–352) $\cdot 10^4$ of poly(4-acetoxystyrene) in dioxan at 25°C, from which the molecular weight obtained was found easily to be evaluated with the gel permeation chromatography using THF. Phase separation experiments for this polymer indicate that the theta state is attained in isopropyl acetate at 19.7°C and butyl acetate at 26.8°C. By making viscosity measurements at that state, the value of K_Θ is directly evaluated as $5.4 \cdot 10^{-4}$ dl g^{-1}. The limiting viscosity number is also obtained in good solvents, THF and dioxan, at 25°C and constants of the Mark–Houwink–Sakurada equation in each solvent are determined. Further, approximately the same K_Θ as above is obtained from these data with the Stockmayer–Fixman plot. The calculated value of steric factor, 2.37, on this polymer may be plausible, compared with those of polyvinylaromatic derivatives.

(Keywords: poly(4-acetoxystyrene); unperturbed dimension; light scattering; theta solvent; viscosity)

INTRODUCTION

Poly(4-acetoxystyrene) (PAS) is one of the polystyrene derivatives with nearly non-polar *para*-substituents, and it can be hydrolysed to poly(4-hydroxystyrene) (PHS). Though the latter polymer has been investigated by several workers[1–3] in order to have more characteristic properties arising from the presence of polar, phenolic hydroxyl groups, e.g., as new materials with industrial importance or as model compounds of lignin[4–6], little is known about the former, PAS, which has solely appeared in some papers[7,8] as a starting material for PHS in most cases. Therefore no report on the dilute solution properties not only of a copolymer of 4-acetoxystyrene and 4-hydroxystyrene but also of either homopolymer has been published. Meanwhile, Kuwahara *et al.*[9,10] reported that the chain conformation of poly-4-substituted styrene was not affected by the electrostatic interaction of the side group, but only by its molar volume. In this paper, the unperturbed dimension of PAS was investigated in two non-theta and two theta solvents by light scattering and viscometry to obtain the additional data concerning this.

EXPERIMENTAL

Material

The monomer of 4-acetoxystyrene, kindly supplied from Dr Furukawa of Maruzen Oil Co. Ltd., was fractionally distilled under reduced pressure of a nitrogen atmosphere with 0.01% 1,1-diphenyl-2-picrylhydrazyl as an inhibitor, of which the middle portion (b.p. 65°C/0.1 mm) was used for polymerization. All the solvents and other materials were of reagent grade, and purified according to the standard procedures except those used for solubility tests.

Polymerization and fractionation

As shown in *Table 1*, radical polymerization of 4-acetoxystyrene was carried out under various conditions by ways of solution polymerization in benzene with 2,2′-azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) as an initiator, and of suspension polymerization in 2% aqueous gelatin solution with AIBN, as well as by thermal polymerization without any initiator, in the usual manner. Gelatin was used as a suspension stabilizer, and the air in a polymerization flask or ampoule was replaced by nitrogen in all polymerizations. After a given time, the prepared polymers were poured into a large amount of appropriate non-solvent such as methanol or water to stop the reaction, washed thoroughly and dried in a vacuum oven at ~60°C. The infra-red spectra from films of prepared sampls were in good agreement with those reported by Danusso *et al.*[7]

Of them, three samples labelled PAS 1, PAS 3, PAS 10 in *Table 1*, were successively divided into 6–10 fractions for this study, by the fractional precipitation method with 2-butanone and methanol as a solvent–nonsolvent system at 30°C, some of which were further subfractionated into two parts for the following measurements (see *Table 3*). After purification by being repeatedly dissolved in 2-butanone and reprecipitated with methanol, all the fractions were dried in a vacuum oven to constant weight.

Solubility tests

The polymer and test liquids were shaken in sealed glass tubes[11] and the solubility was observed in the temperature range of about 0–90°C.

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0032-3861/85/081175-06$03.00

Table 1 Polymerization of 4-acetoxystyrene under various conditions

Sample code	Monomer (g)	Solvent		Stabilizer		Initiator		Time (h)	Temp. (°C)	Yield (g)	$[\eta]^a$ (dl g^{-1})	$M_w^b/10^4$
			(ml)		(g)		(g)					
PAS 1	100	—		—		—		12	95	40	0.780	49.1
PAS 3	100	Benzene	450	—		AIBN	0.498	39	65	40	0.190	6.3
PAS 4	100	Benzene	400	—		AIBN	0.250	44	65	60	0.470	23.7
PAS 5	80	Benzene	350	—		BPO	0.400	117	65	20	0.200	6.3
PAS 6	100	Benzene	135	—		AIBN	0.200	41	65	85	0.470	20.9
PAS 7	100	Benzene	135	—		AIBN	0.050	119	65	25	0.620	30.4
PAS 8	100	Benzene	100	—		AIBN	0.100	424	45	91	1.29	105
PAS 10	131	Water	900	Gelatin	20	AIBN	0.276	326	55	62	1.37	90.0
PAS 11	100	Water	200	Gelatin	4	AIBN	2.000	325	45	84	3.20	–
PAS 12	100	Water	200	Gelatin	4	AIBN	1.500	326	45	72	3.48	462
PAS 13	100	Water	200	Gelatin	4	AIBN	1.000	326	45	80	4.02	487
PAS 14	100	Water	200	Gelatin	4	AIBN	0.500	326	45	89	5.00	–
PAS 16	100	Water	200	Gelatin	4	AIBN	1.500	72	65	62	1.92	164
PAS 17	100	Water	200	Gelatin	4	AIBN	2.001	72	65	68	1.68	137
PAS 18	100	Water	200	Gelatin	4	AIBN	3.004	72	65	79	1.54	99.1
PAS 19	100	Water	200	Gelatin	4	AIBN	4.001	48	65	84	1.40	107

[a] Measured in dioxane at 25.0°C by viscometry
[b] Measured in dioxane at 25.0°C by light scattering

Light-scattering

Light scattering measurements were made at 25±0.1°C by a Fica 50 light-scattering photometer with vertically polarized light of 436 nm in wavelength. Optical purification of solution and solvent was made by the centrifugation with 33 500 G for three hours using a Marusan centrifugator Model 50B-CFS-3, and they were directly transferred into a light scattering cell with a pipette which had been cleaned by rinsing with fresh splash of acetone in the special columns proposed by Thurmond[12]. Measurements were made for four or five solution concentrations and at scattering angles of 30–142.5°. The observed intensities of scattered light were analysed with the well-known double extrapolation method of Zimm.

The specific refractive index increment d*n*/d*c* was measured with a Shimadzu differential refractometer DR-3, calibrated with aqueous potassium chloride solutions.

Viscosity

Viscosity measurements were made in a water bath controlled within ±0.01°C at a desired temperature with Ubbelohde-type dilution viscometers. All solutions and solvents were filtered through sintered glass filters G-3 prior to measurements. The initial solution concentrations of 0.15–1.0 g dl^{-1} were used according to the molecular weight of the fractions measured and were determined by the weighing method. The data at four to five concentrations were extrapolated linearly to infinite dilution by both Huggins and Kraemer plots, to obtain a common intercept giving the limiting viscosity number $[\eta]$. In no case were kinetic energy corrections necessary.

Phase separation

Phase separation temperature on several polymer fractions was measured with sealed thick glass capillary-tubes containing the solution ranging from 0.5 to 7.0 wt%, according to the method by Cowie *et al.*[13]

Gel permeation chromatography (g.p.c.)

Measurements of g.p.c. were carried out with a modified Model 1000/S/401 type instrument of Waters Associates, and a combination of μStyragel columns of 10^5 nm, 10^4 nm, 10^3 nm, and 10^6 nm was utilized. The flow rate of THF and toluene as eluents was 1.0 ml min^{-1}. In each measurement, 200 μl of the sample solution with concentration of 0.1–0.2 g dl^{-1} was injected.

RESULTS AND DISCUSSION

Solubility of PAS for liquids

In *Table 2* are summarized the results of solubility tests on a sample, PAS 4, for various liquids at iced-water (L), room (R) and high (~70–90°C) (H) temperatures respectively, where a symbol of 'plus' denotes the polymer soluble, and the letter N diluents frozen. Roughly it is noticed from the table that ketones, esters, amines, halogenated and aromatic compounds are solvents and aliphatic alcohols, ethers and hydrocarbons are non-solvents for this polymer.

Light scattering and g.p.c.

As given in *Table 3*, the weight-average molecular weights M_w of each fraction of PAS used in this investigation were determined by light scattering measurements in dioxan, selected as a solvent, at 25°C together with their *z*-average mean-square radius of gyration $\langle S^2 \rangle_z$ and second virial coefficient A_2. Here the observed value of d*n*/d*c* was 0.139 ml g^{-1} for PAS under that condition.

In order to ascertain the estimated values M_w and further to know the distribution widths of the fractions, g.p.c. experiments were performed in THF. According to the method proposed by Benoit *et al.*[14], a universal calibration curve of $[\eta]M_w$ against elution volume V_e was previously made up with the monodisperse standard polystyrene (PS) of Pressure Chemicals Co. in THF and toluene, as shown in *Figure 1*. The data for each fraction of PAS obtained by using the above M_w and the $[\eta]$ measured in THF at 25°C by viscometry were also plotted with filled circles. They are found to satisfy the calibration curve practically. This indicates both the values of M_w from light scattering and g.p.c. may approximately coincide with each other. Additionally their polydispersity index, M_w/M_n, analysed from g.p.c. data was also shown in the third column of *Table 3*, where M_n is the number-average molecular weight.

Table 2 Solubility tests for the PAS 4-diluent system at each low (L), room (R) and high (H) temperature

Diluents	L	R	H	Diluents	L	R	H	Diluents	L	R	H	Diluents	L	R	H
Pentane	–	–	–	Bis(2-hydroxyethyl)				Methyl propionate	+	+	+	Phenol	N	N	+
Dodecane	–	–	–	ether	–	–	–	Ethyl propionate	+	+	+	3-Methylphenol	+	+	+
Bromoethane	+	+	+	3,6-Dioxa-1-octanol	+	+	+	Propyl propionate	–	±	+	Anisole	+	+	+
1-Bromopropane	–	+	+	3,6-Dioxa-1-decanol	–	–	±	Isopropyl propionate	–	–	–	Phenyl acetate	+	+	+
1-Bromobutane	–	–	±	3,6-Dioxa-1,8-				Butyl propionate	–	–	–	Phenyl propionate	+	+	+
1-Chlorobutane	–	–	–	octanediol	–	–	–	Isobutyl propionate	–	–	–	Benzyl alcohol	+	+	+
Bromoethylene	N	+	+	Acetaldehyde	+	+	+	Isopentyl propionate	–	–	–	Phenetyl alcohol	+	+	+
Dichloromethane	+	+	+	Acetone	+	+	+	Hexyl propionate	–	–	–	Benzyl acetate	+	+	+
1,1-Dichloroethane	+	+	+	2-Butanone	+	+	+	Ethyl dodecanoate	–	–	–	Benzyl propionate	+	+	+
1,2-Dibromoethane	N	+	+	3-Methyl-2-butanone	+	+	+	Methyl methacrylate	+	+	+	Acetophenone	+	+	+
1,2-Dichloroethane	+	+	+	2-Pentanone	+	+	+	Carbon disulphide	–	–	–	Methyl benzoate	+	+	+
Bromoform	+	+	+	4-Methyl-2-pentanone	–	+	+	Dimethyl sulphoxide	N	+	+	Ethyl benzoate	+	+	+
Chloroform	+	+	+	3-Pentanone	±	+	+	Ethylamine	+	+	+	Methyl salicylate	+	+	+
1,1,1-Trichloroethane	+	+	+	2,4-Dimethyl-3-				Ethylenediamine	+	+	+	Benzoyl chloride	+	+	+
Tetrachloromethane	–	–	–	pentanone	–	–	–	2,2′,2″-Nitrilo-				Aniline	+	+	+
1,1,2,2-Tetrabromo-				2-Hexanone	+	+	+	triethanol	N	–	–	2-Methylaniline	+	+	+
ethane	±	±	+	5-Methyl-2-hexanone	–	±	+	Formamide	–	–	–	*N*,*N*-Dimethylaniline	±	+	+
1,1,2,2-Tetrachloro-				2-Heptanone	–	+	+	*N*,*N*-Dimethyl-				Decahydro-			
ethane	+	+	+	3-Heptanone	–	+	+	formamide	+	+	+	naphthalene	–	–	–
Tetrachloroethylene	–	–	–	4-Heptanone	–	–	+	*N*,*N*-Dimethyl-				1-Bromonaphthalene	–	+	+
Pentachloroethane	+	+	+	2,6-Dimethyl-4-				acetamide	+	+	+	1-Chloronaphthalene	+	+	+
Methanol	–	–	–	heptanone	–	–	–	Acetonitrile	+	+	+	Pyridine	+	+	+
Ethanol	–	–	–	2-Octanone	–	±	+	3-Hydroxy-				2-Methylpyridine	+	+	+
1-Propanol	–	–	–	3-Nonanone	–	–	–	propiononitrile	–	–	–	3-Methylpyridine	+	+	+
2-Propanol	–	–	–	Formic acid	+	+	+	Nitromethane	+	+	+	2-Ethylpyridine	+	+	+
2-Methyl-1-propanol	–	–	–	Acetic acid	N	+	+	Nitroethane	+	+	+	5-Ethyl-2-methyl-			
2-Methyl-2-propanol	–	–	–	Propionic acid	+	+	+	Cyclohexane	N	–	–	pyridine	+	+	+
1-Butanol	–	–	–	Butyric acid	–	–	+	Methylcyclohexane	–	–	–	Piperidine	+	+	+
2-Buranol	–	–	–	Acrylic acid	+	+	+	Cyclohexanol	N	–	–	4-Methylpyridine-N-			
2-Methyl-2-butanol	–	–	–	Methacrylic acid	N	–	+	Cyclohexanone	+	+	+	oxide	+	+	+
1-Pentanol	–	–	–	Dichloroacetic acid	+	+	+	Benzene	+	+	+	Furfuryl alcohol	+	+	+
2-Pentanol	–	–	–	Ethyl formate	+	+	+	Toluene	±	±	+	2-Furaldehyde	+	+	+
2-Ethyl-1-hexanol	–	–	–	Ethyl acetate	+	+	+	Ethylbenzene	–	–	–	Tetrahydrofuran	+	+	+
2-Propen-1-ol	–	–	±	Propyl acetate	+	+	+	1,2-Dimethylbenzene	–	–	–	1,4-Dioxan	N	+	+
1,2-Ethanediol	–	–	–	Isopropyl acetate	+	+	+	1,4-Dimethylbenzene	–	–	–	2,2-Dimethyl-1,3-			
1,2-Propanediol	–	–	–	1-Methylpropyl				Bromobenzene	+	+	+	dioxolan-4-methanol	–	–	–
1,3-Butanediol	–	–	–	acetate	–	±	+	Chlorobenzene	+	+	+	Morpholine	+	+	+
1,5-Pentanediol	–	–	–	Butyl acetate	+	+	+	1,2-Dichlorobenzene	+	+	+	Petroleum ether	–	–	–
Glycerol	N	–	–	Isobutyl acetate	–	±	+	1,2,4-Trichloro-				Paraffin oil	–	–	–
Diethyl ether	–	–	–	Pentyl acetate	–	–	±	benzene	+	+	+	Ligroin	–	–	–
2-Butoxyethanol	–	–	±	Isopentyl acetate	–	–	–	Benzyl chloride	+	+	+	Water	–	–	–

Table 3 Light-scattering data for PAS in dioxan at 25°C

Fraction	$M_w \times 10^{-4}$	M_w/M_n*	$\langle S^2\rangle_z \times 10^{12}$ (cm^2)	$A_2 \times 10^4$ (ml mol g^{-2})
1–2	67.3	1.65	12.4	2.56
1–3	37.8	1.39	6.21	2.46
1–4	24.4	1.14	2.95	3.12
1–5	15.0	1.46	1.10	3.43
1–6	3.80	1.57	–	–
3–2	9.55	1.40	1.04	3.65
3–4	5.98	1.39	0.781	3.29
3–6	4.47	1.19	0.403	4.48
3–7	3.71	1.16	–	4.69
3–8	2.32	1.24	0.291	6.94
3–9	1.42	1.13	–	6.85
3–10	0.91	1.13	–	–
10–1	352	1.71	78.2	1.81
10–2	219	2.23	59.4	1.89
10–3	184	–	48.7	2.18
10–4	155	1.55	33.6	2.06
10–5–1	166	–	34.8	2.07
10–5–2	101	1.72	21.4	1.95
10–6	80.5	–	14.7	2.51
10–7–2	45.8	1.29	7.99	2.83
10–8–1	33.5	1.29	5.41	2.77
10–8–2	18.4	1.48	3.10	3.71

*Determined by g.p.c., using THF as the solvent and based on the polystyrene standard

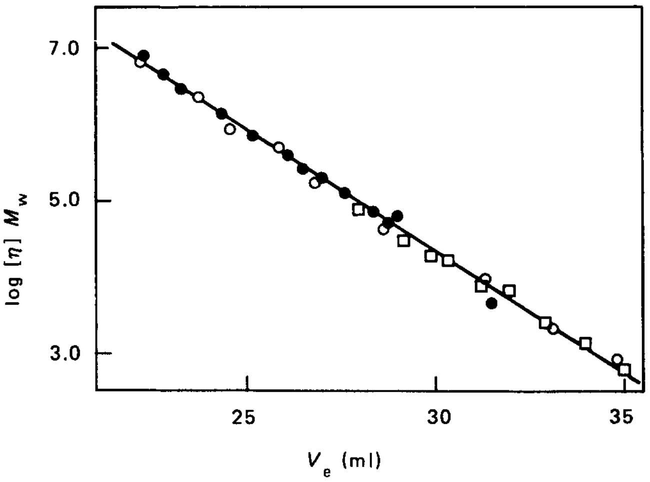

Figure 1 Calibration curve of $[\eta]\cdot M_w$ against elution volume V_e, obtained from monodisperse polystyrene of Pressure Chemicals in THF (○) and toluene (□) and the plot observed for PAS in THF (●)

Relationships of $\langle S^2\rangle_z$ *and* A_2 *vs.* M_w *in dioxan at 25°C*

The values of $\langle S^2\rangle_z^{1/2}$ and A_2 obtained in dioxan at 25°C, were plotted against the M_w on double-logarithmic

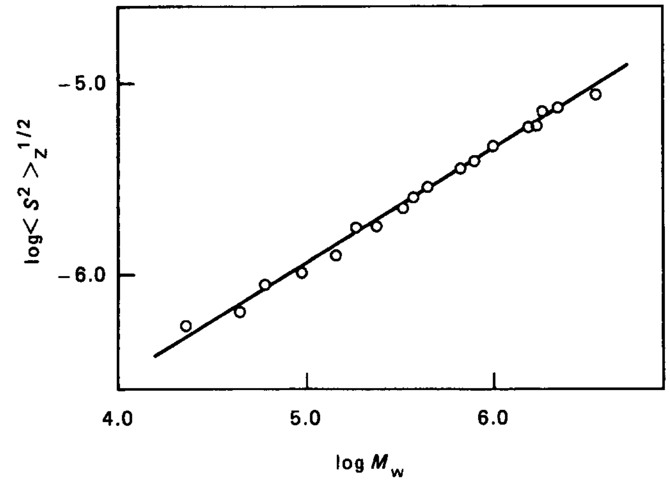

Figure 2 Double-logarithmic plots of $\langle S^2\rangle_z^{1/2}$ against M_w for PAS fractions in dioxan at 25°C

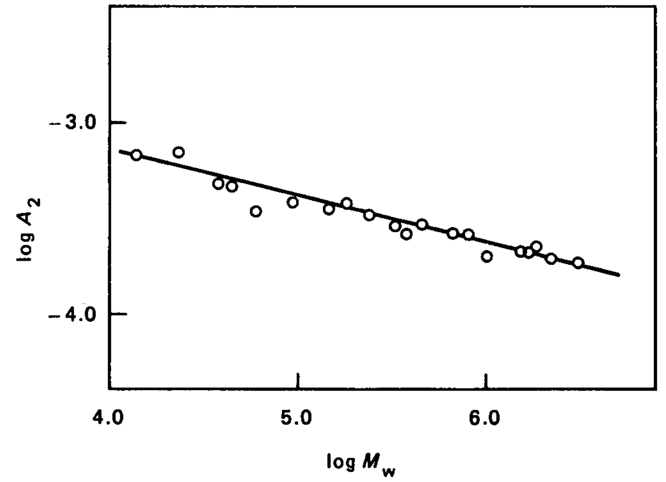

Figure 3 Double-logarithmic plots of A_2 against M_w for PAS fractions in dioxan at 25°C

scales in *Figures 2* and *3*. Least-squares fitting gave the following two relations:

$$\langle S^2\rangle_z^{1/2}=1.15\times10^{-9}M_w^{0.60}$$

$$A_2=5.66\times10^{-3}M_w^{-0.23}$$

from which it is found that dioxan is an intermediate or good solvent for PAS, and that the indices of M_w in these equations seem to be normal, i.e., similar to those frequently reported for polystyrene derivatives and many other ordinary linear polymers.

Search for the theta condition on PAS

From the above solubility tests and further tentative phase separation experiments the two solvents, isopropyl acetate (IPA) and butyl acetate (BA), were selected and the precipitation temperatures T_p were determined in these solvents at concentration c of each PAS fraction with molecular weight M. As an example, *Figure 4* depicts a phase diagram in IPA. After the asymptotic value of these curves was taken as the critical temperature, T_c, of each fraction in each solvent, the equation of Schultz–Flory[15] was applied to calculate the theta temperature Θ as follows:

$$1/T_c=(1/\Theta)(1+b/M^{1/2}) \qquad (1)$$

where b is a constant. From the intercepts of each straight line on the ordinate in *Figure 5*, the value of Θ for this polymer was determined as 19.7°C for IPA and 26.8°C for BA.

Relationships between $[\eta]$ *and* M_w

Besides THF mentioned above, the viscosity measurements were also performed in dioxan at 25°C, IPA at 19.7°C and BA at 26.8°C. The resulting plots of log $[\eta]$ vs. $\log M_w$ are shown in *Figure 6*, where a common straight line was drawn for the points plotted with open and filled squares, for they were regarded approximately as the same within possible experimental errors. The

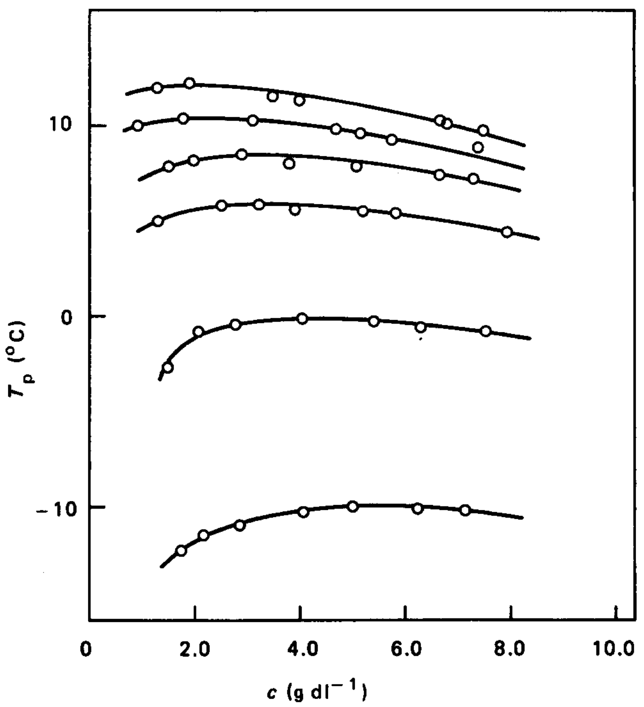

Figure 4 Phase diagrams for several PAS fractions in isopropyl acetate

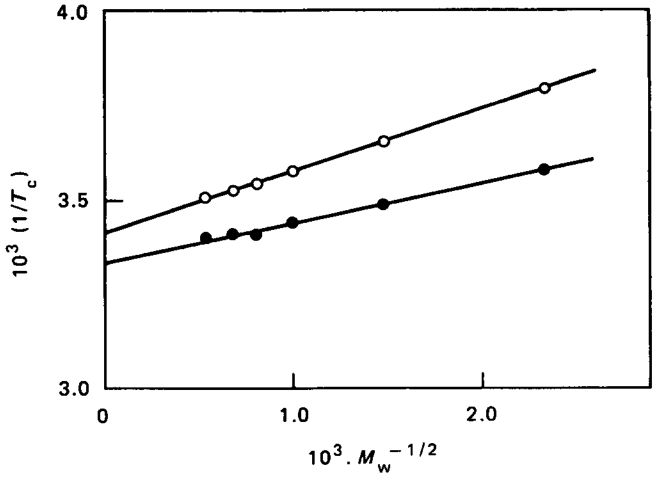

Figure 5 Plots of reciprocals of critical precipitation temperature T_c^{-1} against $M_w^{-1/2}$ for PAS fractions in isopropyl acetate (○) and butyl acetate (●)

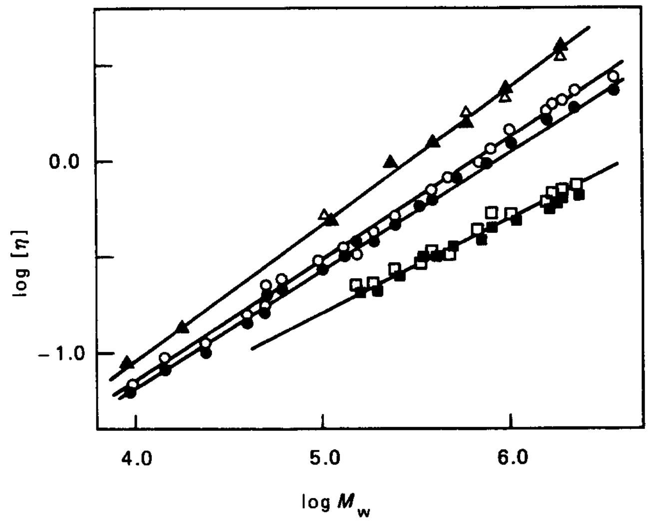

Figure 6 Double-logarithmic plots of $[\eta]$ against M_w for PAS fractions in dioxan (○) at 25°C, THF (●) at 25°C, isopropyl acetate (□) at 19.7°C, butyl acetate (■) at 26.8°C, and for monodisperse polystyrene of Pressure Chemicals in dioxan (△) at 25°C and THF (▲) at 25°C

resulting familiar Mark–Houwink–Sakurada equations, $[\eta]=KM^a$, were over a very wide range of molecular weight respectively as follows:

$[\eta]=1.67\times10^{-4}M_w^{0.65}$	in dioxan at 25°C
$[\eta]=1.75\times10^{-4}M_w^{0.64}$	in THF at 25°C
$[\eta]=5.20\times10^{-4}M_w^{0.50}$	in IPA at 19.7°C and in BA at 26.8°C

For comparison our data on the aforementioned PS of Pressure Chemicals measured in dioxan and THF at 25°C, were also plotted with open and filled triangles in the Figure and the following equation holds; e.g.,

$$[\eta]=1.27\times10^{-4}M_w^{0.71} \quad \text{for PS in THF at 25°C}$$

It is apparent from the indices of M_w in these equations that dioxan and THF are intermediate or fairly good solvents for PAS but poorer than PS, and that IPA and BA are substantially Θ-solvents at respective temperatures.

Estimation of the unperturbed dimension on PAS

The Mark–Houwink–Sakurada equation at the theta state is expressed by:

$$[\eta]_\Theta = K_\Theta M^{0.5} \tag{2}$$

where the subscript Θ denotes at the theta state. Furthermore K_Θ is connected to the unperturbed end-to-end dimension $\langle R^2\rangle_0$ as:

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

Here Φ_0 is Flory's universal constant at that state. Therefore the value of K_Θ for PAS was found directly to be $5.20\cdot10^{-4}$ dl g^{-1}, as comprehensible from the above data at theta states; i.e., in IPA at 19.7°C and BA at 26.8°C.

However, the K_Θ value can also be estimated with several indirect or extrapolation methods using the limiting viscosity number-molecular weight data in non-theta solvents. The Stockmayer–Fixman plot[16] of them was used here, which has very often been applied to many kinds of polymer. The equation is:

$$[\eta]/M^{1/2} = K_\Theta + 0.51\Phi_0 B M^{1/2} \tag{4}$$

where B is the long-range interaction parameter. *Figure 7* shows the plots of $[\eta]/M_w^{1/2}$ against $M_w^{1/2}$ for PAS in dioxan and THF at 25°C, together with those in IPA and BA at respective temperatures. These plots gave a set of lines with a common intercept, though there is a little ambiguity because of drawing with rather large downward curvature in good solvents and therefore the B value may not be referred to here. This implies that implicitly the same K_Θ value as above is estimated from the indirect method irrespective of the nature of solvent used.

Assuming the Schulz–Zimm type distribution function[17] for each fraction, the obtained value of K_Θ was corrected to be $5.4\cdot10^{-4}$ dl g^{-1} for molecular weight heterogeneity with an average value of 1.42 of the M_w/M_n already given in *Table 3*. Hence using $\Phi_0=2.87\cdot10^{21}$ in c.g.s. units the unperturbed dimension of PAS was calculated by equation (3) as:

$$(\langle R^2\rangle_0/M)^{1/2}=5.73\times10^{-9}$$

Thus the steric factor σ $(=(\langle R^2\rangle_0/\langle R^2\rangle_{0f})^{1/2})$ and the characteristic ratio $C_\infty(=[(K_\Theta/\Phi_0)^{2/3}(M_0/2\cdot l^2)]_{n\to\infty})$ for PAS were calculated as 2.37 and 11.2 respectively, where M_0 is the monomer molecular weight, l is the bond length (i.e., 0.154 nm for a C–C bond), n is the total number of backbone bonds and $\langle R^2\rangle_{0f}$ stands for the mean-square end-to-end distance of the model chain with hypothetically free rotation around backbone bonds.

The result of $\sigma=2.37$ for PAS may be plausible as compared with those of polystyrene (2.22),[18] poly(4-chlorostyrene) (2.18–2.29),[18–21] poly(4-methylstyrene) (2.17–2.19),[9,22] poly(4-methoxystyrene) (2.37),[23] poly(2,4-dimethylstyrene) (2.35),[24] poly(2-vinylnaphthalene) (2.45)[25] and poly(4-cyclohexylstyrene) (2.52),[10] since this σ value for PAS lies near to the line for polyvinyl-aromatic series in Figure 3 of ref. 21, plotted against the molar volume of side group V_x (=127 cm^3 mol^{-1} for PAS), which serves as a rough measure of the steric hindrance caused by the side groups.

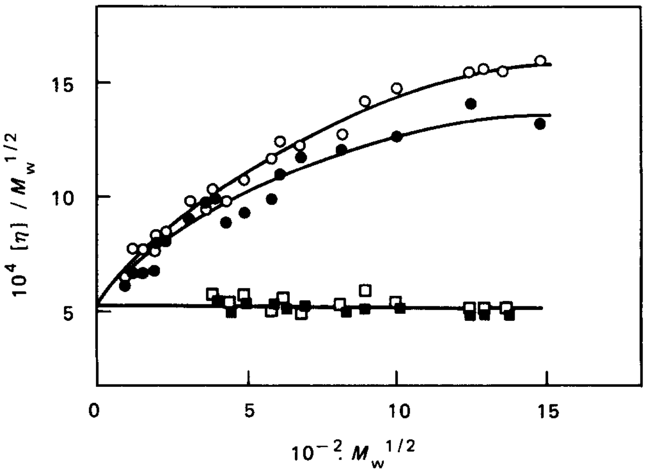

Figure 7 Stockmayer–Fixman plots for PAS in various solvents. The symbols have the same significance as those in *Figure 6*

REFERENCES

1 Danusso, F., Ferruti, P. and Marabelli, C. G. *Chim. Ind. (Milan)* 1965, **47**, 493
2 Kato, M. *J. Polym. Sci. A-1* 1969, **7**, 2405
3 Yoshida, H., Nakamura, K. and Kobayashi, Y. *Polym. J.* 1982, **14**, 855
4 Tanaka, H. and Senju, R. *Mokuzai Gakkai Shi* 1970, **16**, 394
5 Hatakeyama, T., Nakamura, K. and Hatakeyama, H. *Polymer* 1978, **19**, 593
6 Nakamura, K., Hatakeyama, T. and Hatakeyama, H. *Polymer* 1981, **22**, 473
7 Danusso, F., Ferruti, P. and Crespi, A. M. *Chim. Ind. (Milan)* 1965, **47**, 55
8 Nakamura, K., Hatakeyama, T. and Hatakeyama, H. *Polymer* 1983, **24**, 871
9 Kuwahara, N., Ogino, K., Kasai, A., Ueno, S. and Kaneko, M. *J. Polym. Sci. A* 1965, **3**, 985
10 Kuwahara, N., Ogino, K., Komura, M., Iida, N. and Kaneko, M. *J. Polym. Sci. A-2* 1966, **4**, 173
11 Izumi, Y. and Miyake, Y. *Polym. J.* 1972, **3**, 647
12 Thurmond, C. D. *J. Polym. Sci.* 1952, **8**, 607
13 Cowie, J. M. G., Maconnachie, A. and Ranson, R. J. *Macromolecules* 1971, **4**, 57
14 Benoit, H., Grubisic, Z., Rempp, P., Decker, D. and Zilliox, J. G. *J. Chim. Phys.* 1966, **63**, 1507
15 Shultz, A. R. and Flory, P. J. *J. Am. Chem. Soc.* 1952, **74**, 4760
16 Stockmayer, W. H. and Fixman, M. *J. Polym. Sci. C* 1963, **1**, 137
17 Zimm, B. H. *J. Chem. Phys.* 1948, **16**, 1099
18 Kurata, M. and Stockmayer, W. H. *Fortschr. Hochpolym. Forsch.* 1963, **3**, 196
19 Kubo, K., Ogino, K. and Nakagawa, T. *Nippon Kagaku Zasshi* 1967, **88**, 1254
20 Hernandez-Fuentes, I. and Prolongo, M. G. *Eur. Polym. J.* 1979, **15**, 571
21 Izumi, Y. and Miyake, Y. *Polym. J.* 1973, **4**, 205
22 Tanaka, G., Imai, S. and Yamakawa, H. *J. Chem. Phys.* 1970, **52**, 2639
23 Imanishi, Y., Higashimura, T. and Okamura, S. *Kobunshi Kagaku* 1965, **22**, 241
24 Chen, C. S. H. and Stamm, R. F. *J. Polym. Sci.* 1962, **58**, 369
25 Utracki, L. A. and Simha, R. *Makromol. Chem.* 1968, **117**, 94