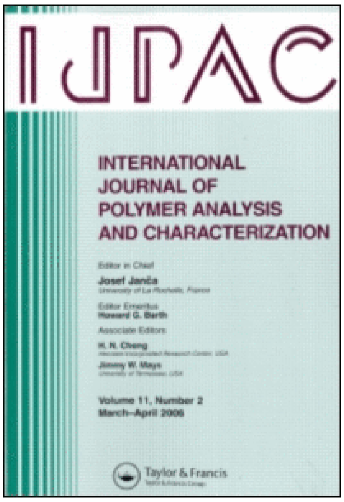

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Hydrodynamic Properties of Polystyrene in Alkyl Acetates

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Viscometry and dynamic light scattering experiments on nineteen narrow molecular weight distribution polystyrene samples ($M_w = 2{,}800 - 1{,}582{,}000$) were carried out in methyl, ethyl, propyl and butyl acetate. The scaling equations between the intrinsic viscosity or the diffusion coefficient and the weight average molecular weight are reported. By comparing the results the influence of the esterified alkyl group of the solvent on the hydrodynamic properties of the polystyrene was studied.

Keywords: Polystyrene; Hydrodynamic properties; Viscometric radius; Hydrodynamic radius; Viscometry; Dynamic light scattering

INTRODUCTION

Major advances have been accomplished in understanding the hydrodynamic behavior of flexible polymers,[1] because on the one hand improved theoretical techniques (numerical simulations, renormalization group theory approaches, *etc.*) for the prediction of polymer chain statistics and dynamics have been developed[2–11] and on the other hand extensive experimental data on the dilute solution properties of linear chains have been collected.[12]

The most important parameter determined experimentally is the size of the polymer chain in solution. The size can be expressed either as

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radius of gyration, R_g, or viscometric, R_v, hydrodynamic, R_h and thermodynamic radius R_T. R_v, R_h and R_T are the radii of a hard sphere having the same intrinsic viscosity, diffusion coefficient and excluded volume respectively with the macromolecular chain. Theoretical predictions[6, 13] and experimental results[14, 15] show that the different radii exhibit power scaling laws against the molecular weight having the following form:

$$R \sim M^{\nu} \tag{1}$$

where ν is a characteristic exponent. In the case of a θ-solvent (Gaussian coil) $\nu = 0.5$, whereas in good solvents ν increases to the asymptotic value $\nu = 0.588$.

Polystyrene, PS is probably the most extensively studied polymer due to its commercial importance and the availability of nearly monodisperse samples covering a wide range of molecular weights. Static and dynamic properties have been reported in many solvents of different quality, such as tetrahydrofuran,[16-21] benzene,[22-27] ethylbenzene,[19, 28, 29] toluene,[16, 30-33] butanone-2,[34] *n*-butyl chloride,[35] carbon tetrachloride,[36, 37] cyclohexane,[31, 38-40] trans-decalin[41-43] *etc.*

In this paper the hydrodynamic properties of PS in methyl, ethyl, *n*-propyl and *n*-butyl acetate, MAc, EAc, PAc and BAc respectively are reported. Samples covering a broad range of molecular weights were studied by dilute solution viscometry and dynamic light scattering, DLS.

EXPERIMENTAL

Narrow molecular weight distribution polystyrene standards were obtained from Pressure Chemical Co. and Toyo Soda Co. The solvents MAc, EAc, PAc and BAc were refluxed over CaH_2 for at least 24 hours and were distilled just prior to use. Tetrahydrofuran, THF, was purified over Na.

The polydispersities of the samples were obtained by size exclusion chromatography, SEC, using a modular instrument consisting of a Waters Model 510 pump, a Waters Model U6K sample injector, a Waters Model 401 differential refractometer, and a set of 4 μ-Styragel columns with a continuous porosity range from 10^6 to 10^3 Å. The columns were housed in an oven thermostated at 40°C. THF was the carrier solvent at a flow rate of 1 ml/min.

Static light scattering measurements were performed in THF in order to verify the molecular weights given by the supplier. A Chromatix KMX-6 low angle laser light scattering, LALLS photometer at 25°C equipped with a 2 mW He-Ne laser operating at $\lambda = 633$ nm was used. The equation describing the concentration, c, dependence of the reduced intensity is

$$Kc/\Delta R_\theta = 1/M_w + 2A_2c + \cdots \tag{2}$$

where K is a combination of optical and physical constants, including the refractive index increment, dn/dc, and the excess Rayleigh ratio of the solution over that of the solvent, ΔR_θ, M_w is the weight average molecular weight, and A_2 is the second virial coefficient. Stock solutions were prepared, followed by dilution with solvent to obtain solutions with lower concentrations. All the solutions were clarified by filtering through 0.22 μm pore size nylon filters directly into the scattering cell.

Refractive index increments in THF at 25°C were measured with a Chromatix KMX-16 refractometer operating at 633 nm. The dn/dc values for all samples having M_w higher than 10,000 was equal to 0.189 ml/g. For the samples with M_w around 10,000 slightly lower dn/dc values were obtained ($dn/dc = 0.187$ ml/g).

Dynamic light scattering measurements were conducted with a Series 4700 Malvern system composed of a PCS5101 goniometer with a PCS stepper motor controller, a Cyonics variable power Ar^+ laser, operating at 488 nm, a PCS8 temperature control unit, a RR98 pump/filtering unit and a 192 channel correlator for the accumulation of the data. The correlation functions were analyzed by the cumulant method and the CONTIN software. Measurements were carried out at 90°. The angular dependence of the ratio Γ/q^2, where Γ is the decay rate of the correlation function and q is the scattering vector, was not very important for all samples. Apparent translational diffusion coefficients at zero concentration, $D_{o,\mathrm{app}}$ were measured using the equation:

$$D = D_o(1 + k_D c) \tag{3}$$

where k_D is the coefficient of the concentration dependence of the diffusion coefficient:

$$k_D = 2A_2M - k_f - u_2 \tag{4}$$

where A_2 is the second virial coefficient, M the molecular weight, k_f the frictional virial coefficient and u_2 the partial specific volume of the polymer.

Hydrodynamic radii at infinite dilutions, R_h, were calculated by aid of the equation:

$$R_h = kT/6\pi\eta_s D_o \tag{5}$$

where k is the Boltzmann's constant, T the absolute temperature and η_s the viscosity of the solvent.

Viscometric data were analyzed using the Huggins equation:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c + \cdots \tag{6}$$

and the Kraemer equation

$$\text{In}\eta_r/c = [\eta] + k_K[\eta]^2 c + \cdots \tag{7}$$

where η_r, η_{sp} and $[\eta]$ are the relative, specific and intrinsic viscosities respectively, k_H and k_K the Huggins and Kraemer constants, respectively. Virtually identical intrinsic viscosities were obtained by the two methods when k_H was lower than 0.5. In the case where k_H is higher than 0.5 the Kraemer equation gave slightly higher $[\eta]$ values. The results from the Huggins equation were used for the analysis. All the measurements were carried out at 25°C using Cannon-Ubbelohde dilution viscometers with a Schott-Geräte AVS 410 automatic flow timer. Viscometric radii were calculated from the equation

$$R_v = (3/10\pi N_A)^{1/3}([\eta]M_w)^{1/3} \tag{8}$$

where M_w is the weight average molecular weight determined by light scattering measurements.

RESULTS AND DISCUSSION

The molecular characteristics of the polystyrenes, measured by LALLS in THF and SEC are given in Table I. The samples have

TABLE I Molecular characteristics of the PS samples

M_w[a]	M_w[b]	I[c]
2500	2800[c]	1.07
4000	4000[c]	1.06
9000	10000	1.06
10000	10200	1.07
20000	16700	1.04
25000	20000	1.03
30300	26700	1.03
33000	35000	1.06
40000	40000	1.05
45000	44000	1.05
52000	50000	1.06
90000	84800	1.04
95000	100000	1.06
233000	252600	1.06
390000	378900	1.10
600000	571900	1.10
758500	734700	1.05
900000	842800	1.10
1800000	1582000	1.13

[a] Molecular weight given by the supplier.
[b] By LALLS in THF at 25°C.
[c] By SEC.

weight average molecular weights covering the range from 2.8×10^3 up to 1.6×10^6 and exhibit narrow molecular weight distributions.

The $\log[\eta]$ *versus* $\log M_w$ and the $\log Do$ *versus* $\log M_w$ plots for PS in MAc are given in Figure 1, whereas the viscometry and DLS data are reported in Table II.

The data can be described by the following equations:

$$[\eta] = 7.01 \times 10^{-2} M_w^{0.499} \text{ (corr. coef.} = 0.998) \tag{9}$$

$$Do = 2.38 \times 10^{-4} M_w^{-0.488} \text{ (corr. coef.} = 0.998) \tag{10}$$

The corresponding viscometric and hydrodynamic radii derived from the above equations scale with the molecular weight according to the equations:

$$R_v = 2.24 \times 10^{-2} M_w^{0.499} \text{ (corr. coef.} = 0.999) \tag{11}$$

$$R_h = 2.51 \times 10^{-2} M_w^{0.488} \text{ (corr. coef.} = 0.998) \tag{12}$$

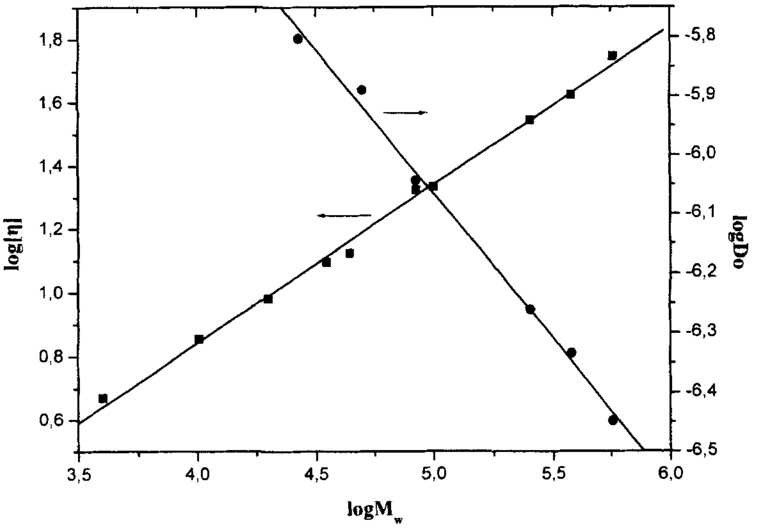

FIGURE 1 Log [η] *versus* log M_w (■) and log *Do versus* log M_w (•) for PS in MAc.

It is obvious from these results that MAc is a θ-solvent for PS. In a previous study[44] concerning the static and dynamic properties of a PS sample having $M_w = 1.8 \times 10^5$ in MAc it was reported that the θ-temperature, defined as the temperature where $A_2 = 0$, is equal to 43°C, whereas the upper critical solution temperature is 14°C and the lower critical solution temperature is 143°C. Consequently it was concluded that the θ-region is quite broad but is shrinked by increasing the molecular weight of the sample.

The data obtained in MAc are comparable with those observed in cyclohexane at 34.5°C, which is a θ-solvent for PS.[12,31,38–40] It is noted that the k_H values are higher than 0.5 for all samples as is expected for a θ-solvent and that the double logarithmic plot between intrinsic viscosity and molecular weight (Fig. 1) is linear in the whole molecular weight range. Furthermore the k_D values are negative for all samples as a consequence of the very low A_2 values observed in theta solvents (Eq. 4). The R_v/R_h ratio is very close to unity in agreement with previous observations in cyclohexane at 34.5°C.

The viscometry and DLS results for PS in EAc are reported in Table III and the plots describing the dependence of log [η] and log *Do* with the log M_w are shown in Figure 2.

TABLE II Hydrodynamic properties of PS in Methyl Acetate

M_w[a]	$[\eta]$, ml/g	k_H	R_v, nm	$Do \times 10^7$, cm^2/s	k_D, cm^3/g	R_h, nm	R_v/R_h
4000	4.67	1.36	1.44				
10200	7.14	1.10	2.26				
20000	9.59	1.05	3.12				
26700			3.64[b]	15.77	−8.0	3.80	0.96
35000	12.4	0.91	4.10			4.17[c]	0.98
44000	13.3	1.06	4.52			4.66[c]	0.97
50000			4.98[b]	12.90	−15.4	4.64	1.07
84800	21.0	0.87	6.55	9.06	−18.8	6.62	0.99
100000	21.5	0.85	6.98			6.96[c]	1.00
252600	34.9	0.96	11.2	5.48	−40.3	10.9	1.02
378900	41.9	0.88	13.6	4.62	−53.5	13.0	1.05
571900	55.8	0.86	17.2	3.56	−82.7	16.8	1.02

[a] By LALLS.
[b] Values calculated using Eq. (11).
[c] Values calculated using Eq. (12).

TABLE III Hydrodynamic properties of PS in Ethyl Acetate

M_w[a]	$[\eta]$, *ml/g*	k_H	R_v, *nm*	$Do \times 10^7$, cm^2/s	k_D, cm^3/g	R_h, *nm*	R_v/R_h
4000	5.13	0.72	1.48				
10200	8.50	0.78	2.39				
26700			3.85[b]	14.27	– 10.2	3.59	1.07
35000	13.8	0.66	4.24			4.21[c]	1.01
44000	16.9	0.65	4.90			4.74[c]	1.03
84800			7.10[b]	8.30	– 22.2	6.17	1.15
100000	27.8	0.42	7.61			7.29[c]	1.04
252600			12.6[b]	4.38	6.2	11.8	1.07
378900	62.1	0.62	15.5	3.42	12.4	15.0	1.03
571900	90.0	0.58	20.1	2.85	13.8	18.2	1.11
734700	91.7	0.53	22.0	2.52	20.8	20.3	1.08
842800	108	0.51	24.3	2.30	21.9	22.3	1.09
1582000	150	0.49	33.5	1.77	31.1	28.9	1.16

[a] By LALLS.

[b] Values calculated using Eq. (15).

[c] Values calculated using Eq. (16).

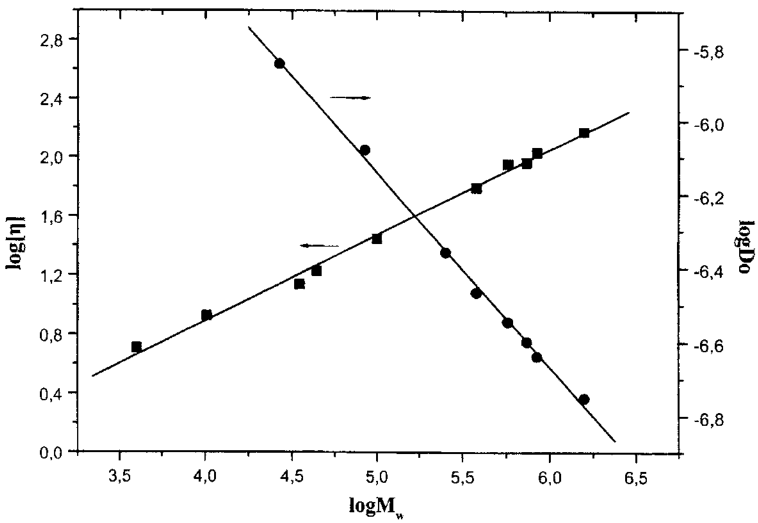

FIGURE 2 Log $[\eta]$ *versus* log M_w (■) and log Do *versus* log M_w (•) for PS in EAc.

The data in Table III can be represented by the equations:

$$[\eta] = 3.79 \times 10^{-2} M_w^{0.579} \text{ (corr. coef. = 0.997)} \qquad (13)$$

$$Do = 3.08 \times 10^{-4} M_w^{-0.526} \text{ (corr. coef. = 0.999)} \qquad (14)$$

The following scaling relations concerning the viscometric and hydrodynamic radii can be extracted from these results:

$$R_v = 1.81 \times 10^{-2} M_w^{0.526} \text{ (corr. coef. = 0.999)} \qquad (15)$$

$$R_h = 1.66 \times 10^{-2} M_w^{0.526} \text{ (corr. coef. = 0.999)} \qquad (16)$$

In a previous study[45] the dependence of the R_h values from the molecular weight of the PS in EAc at 25°C was concluded to follow the equation:

$$R_h = 1.39 \times 10^{-2} M_w^{0.542 \pm 0.019} \qquad (17)$$

This result is in good agreement with Eq. (16) having in mind that in the previous study only high molecular weight samples ($7.06 \times 10^5 \leq M_w \leq 6.77 \times 10^6$) were used.

The exponents in Eqs. (13) and (14) clearly demonstrate that EAc is a moderate solvent for PS at 25°C. The plots of Figure 2 are linear in the whole range of molecular weights examined. In general it is observed that the low molecular weight chains assume extended conformations approaching wormlike behavior thus leading to a substantial decrease in the exponent of the equation relating the $[\eta]$ with the M_w.[46,47] This behavior is not followed in this case, since EAc has only a moderate solvating power for PS. High values of the Huggins coefficients were observed specially for the lower molecular weights. This behavior is associated with both the moderate solvating power of EAc and the deviation from the Gaussian behavior in the case of the short chains.

A characteristic behavior was observed with the diffusion virial coefficient k_D. The sign of k_D was changed from negative at low molecular weights to positive at higher molecular weights. This behavior has been previously reported for PS.[34,48,49] As shown by Eq. (4) the k_D values reflect both thermodynamic and hydrodynamic contributions. Since the partial specific volume of the polymer, u_2 is very small the change of the sigh from negative to positive demonstrate the increasing importance of the thermodynamic contribution with increasing molecular weight.

The R_v/R_h ratio varies slightly with the molecular weight and the average value is 1.08 ± 0.05. In both good (toluene) and θ-solvent (cyclohexane at 34.5°C) it was reported that $R_v/R_h = 1.03 \pm 0.05$.[31] In ethylbenzene, another good solvent for PS the same ratio was equal to 1.18 ± 0.07[12] and was slightly increasing with molecular weight. A similar behavior was observed in CCl_4 with the ratio being 1.19 ± 0.05.[36] In the moderate solvent *n*-butyl chloride a ratio $R_v/R_h = 1.16 \pm 0.04$[35] was reported. It is obvious from these results that the ratio R_v/R_h is sensitive to both the nature of the solvent and the polymer. The theory predicts values equal to 1.0 for hard spheres, 1.13 for self-avoiding coils and 1.23 for unperturbed coils.[50–52] It is well known that the intrinsic viscosity radius reflects both static and dynamic contributions, since $[\eta] \sim R_G^2 R_h$, where the radius of gyration R_G is more sensitive to the larger dimension of a nonspherical molecule and R_h is a pure hydrodynamic parameter. Therefore the different R_v/R_h values reflect changes in shape of the polymer coil.

Small R_v/R_h values are associated with rather spherical coils, whereas larger values correspond to more elliptical species.

The data concerning the viscometric and DLS results for PS in PAc and BAc are given in Tables IV and V respectively, whereas the double logarithmic plots showing the dependence of the $[\eta]$ and Do with the molecular weight of the PS samples in these solvents are given in Figures 3, 4.

The scaling relationships derived from these data are the following:

Propyl Acetate

$$[\eta] = 3.09 \times 10^{-2} M_w^{0.610} \text{ (corr. coef.} = 0.999) \qquad (18)$$

$$Do = 2.12 \times 10^{-4} M_w^{-0.521} \text{ (corr. coef.} = 0.998) \qquad (19)$$

$$R_v = 1.72 \times 10^{-2} M_w^{0.535} \text{ (corr. coef.} = 0.999) \qquad (20)$$

$$R_h = 1.86 \times 10^{-2} M_w^{0.521} \text{ (corr. coef.} = 0.998) \qquad (21)$$

Butyl Acetate

$$[\eta] = 3.36 \times 10^{-2} M_w^{0.606} \text{ (corr. coef.} = 0.999) \qquad (22)$$

$$Do = 1.40 \times 10^{-4} M_w^{-0.506} \text{ (corr. coef.} = 0.996) \qquad (23)$$

$$R_v = 1.75 \times 10^{-2} M_w^{0.535} \text{ (corr. coef.} = 0.999) \qquad (24)$$

$$R_h = 2.29 \times 10^{-2} M_w^{0.506} \text{ (corr. coef.} = 0.996) \qquad (25)$$

It is clear from these results that PAc and BAc are moderate solvents for PS but both are slightly better solvents than EAc. A similar behavior was observed as in the case of EAc. The plots of Figures 3 and 4 are linear for the whole range of molecular weights, the k_H coefficient is higher than 0.5 for the low molecular weight samples and the k_D values change sign from negative to positive with increasing molecular weight. The R_v/R_h ratio is equal to 1.12 and 1.13 for PAc and BAc respectively and depends slightly on the molecular weight of the sample.

TABLE IV Hydrodynamic properties of PS in *n*-Propyl Acetate

M_w[a]	$[\eta]$, *ml/g*	k_H	R_v, *nm*	$Do \times 10^7$, *cm²/s*	k_D, *cm³/g*	R_h, *nm*	R_v/R_h
2800	4.16	1.78	1.22				
4000	5.26	1.08	1.49				
10000	8.24	0.88	2.35				
16700	11.2	0.84	3.09				
26700	14.7	0.83	3.96	10.80	−17.9	3.66	1.13
40000	20.5	0.44	5.06			4.64[c]	1.09
84800	28.5	0.58	7.26	5.86	−10.4	6.76	1.09
252600			13.4[b]	3.07	10.9	12.9	1.04
378900	75.3	0.46	16.5	2.56	14.0	15.4	1.08
560000			20.5[b]	2.20	21.1	18.0	1.14
571900	106	0.51	21.2	2.13	33.3	18.6	1.16
734700	110	0.47	22.2	1.86	41.8	21.3	1.11
842800	128	0.46	25.8	1.69	45.1	23.4	1.12
1582000	195	0.40	36.6	1.34	47.0	29.5	1.29

[a] By LALLS.
[b] Values calculated using Eq. (20).
[c] Value calculated using Eq. (21).

TABLE V Hydrodynamic properties of PS in *n*-Butyl Acetate

M_w[a]	$[\eta]$, *ml/g*	k_H	R_v, *nm*	$Do \times 10^7$, cm^2/s	k_D, cm^3/g	R_h, *nm*	R_v/R_h
2800	4.22	1.07	1.23				
4000	5.56	0.87	1.52				
10000	8.79	0.60	2.40				
16700	11.4	0.76	3.11				
26700	16.2	0.48	4.09	8.86	−7.1	3.64	1.17
84800	30.0	0.51	7.39	4.19	13.9	7.70	0.98
252600			13.6[b]	2.40	18.2	13.4	1.01
378900	78.5	0.36	16.8	2.08	24.1	15.5	1.09
571900	109	0.56	21.5	1.71	28.8	18.8	1.16
734700	113	0.36	23.6	1.50	31.3	21.6	1.10
842800	132	0.44	26.0	1.40	40.6	23.0	1.16
1582000	209	0.39	37.4	1.11	54.8	29.1	1.34

[a] By LALLS.

[b] Values calculated using Eq. (24).

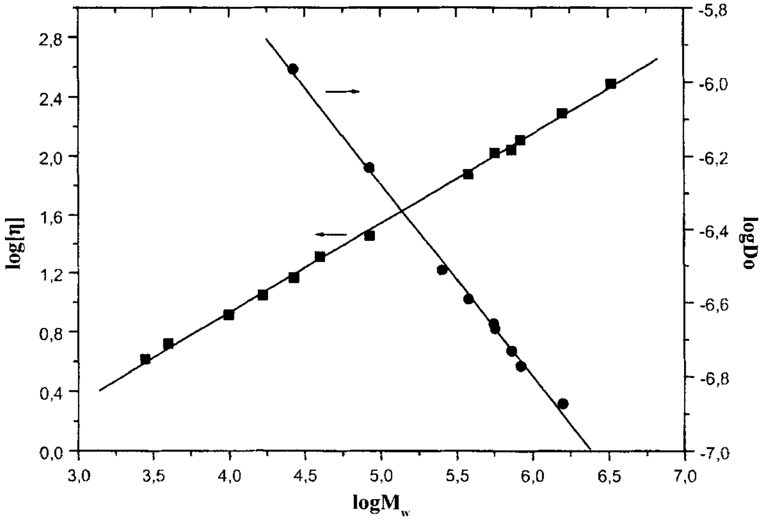

FIGURE 3 Log[η] *versus* logM_w (■) and log *Do versus* logM_w (•) for PS in PAc.

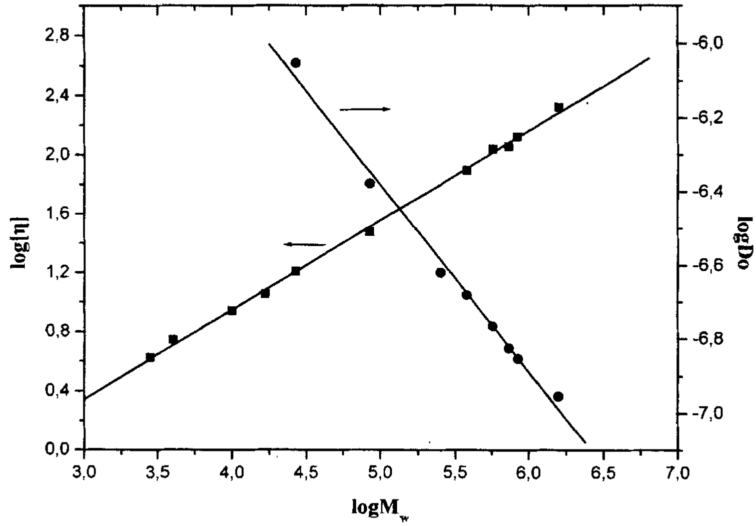

FIGURE 4 Log[η] *versus* logM_w (■) and log *Do versus* logM_w (•) for PS in BAc.

CONCLUSIONS

The dilute solution hydrodynamic properties for near-monodisperse PS in MAc, EAc, PAc and BAc at 25°C were studied by viscometry and dynamic light scattering. It was found that MAc is a θ-solvent, whereas EAc, PAc and BAc are moderate solvents for PS. The $\log[\eta]$ *versus* $\log M_w$ and $\log Do$ *versus* $\log M_w$ plots were linear for the whole range of molecular weights studied. In the case of MAc the k_H values were higher than 0.5 and k_D values negative for all samples. For the other solvents k_H values higher than 0.5 were obtained for the lower molecular weights and the k_D values changed sign from negative to positive with increasing molecular weight. The R_v/R_h ratio was found to depend slightly on the nature of the solvent and the polymer reflecting changes in the shape of the macromolecular coil.

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