Dilute solution properties of poly(*p*-t-butylstyrene)

A. George, W. W. Wilson and J. S. Lindner
Department of Chemistry and Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, Mississippi, MS 39762, USA

and J. W. Mays*
Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294, USA
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The dilute solution properties of poly(*p*-t-butylstyrene) (PtBS) in cyclohexane, a good solvent, and 2-octanol, a theta solvent, are reported. The polymers are narrow-molecular-weight-distribution samples produced by an anionic polymerization process and span more than two orders of magnitude of molecular weight. The techniques used to study solutions of PtBS include static and dynamic light scattering, solution viscometry, and size exclusion chromatography. The results are compared with those obtained from other polymer/solvent systems and with predictions from various theories.

(Keywords: poly(*p*-t-butylstyrene); solution properties; light scattering)

INTRODUCTION

The dilute solution behaviour of high-molecular-weight poly(*p*-t-butylstyrene) (PtBS) samples with narrow-molecular-weight distributions, in both a good solvent and a theta solvent, is reported. The PtBS samples were prepared by controlled anionic polymerization and encompass a molecular-weight range of more than two orders of magnitude. The methods used to study these materials include dynamic light scattering (DLS), static light scattering (SLS), low-angle laser light scattering (LALLS), dilute solution viscometry, and size exclusion chromatography (s.e.c.). Although several previous studies of the solution properties of PtBS have been published[1–5], the present paper reports, for the first time, translational diffusion coefficients for this polymer. These data, combined with other pertinent measured parameters, allow an insight into the molecular-weight dependence and the excluded-volume dependence of PtBS solutions. In addition, the behaviour of PtBS is compared to the properties exhibited by other flexible polymer chains and with various theoretical expectations.

EXPERIMENTAL

The anionic polymerization procedures employed in preparing linear PtBS specimens with narrow-molecular-weight distributions have been described previously[2,5]. Polydispersities were examined in tetrahydrofuran using a Waters Associates s.e.c. instrument. In some instances, a membrane osmometer (Hewlett-Packard 503) was used to provide a direct measure of the number-average molecular weight, M_n. Coupling of the results obtained for M_n with values obtained for the weight-average molecular weight, M_w, as determined by light scattering (see below), yielded polydispersity ratios, M_w/M_n, which were in good agreement with those derived from the s.e.c. measurements[2,5].

LALLS experiments were conducted in cyclohexane (Aldrich HPLC grade) using a Chromatix KMX-6 instrument; measurements were carried out at room temperature (~22°C). The refractive index increment, d*n*/d*c*, was determined as 0.129 ml g^{-1} under the same conditions ($\lambda = 632.8$ nm) using a Chromatix KMX-16 differential refractometer. This instrument was also used to measure d*n*/d*c* for PtBS in 2-octanol, giving a value of 0.126 ml g^{-1} at 33°C. All solvents and solutions were filtered through either 0.2 or 0.45 μm pore-size filters directly into the scattering cell. The LALLS data were analysed using square-root plots[6].

Solvents and solutions for both the SLS and DLS measurements were clarified by closed-loop filtration[7,8]. SLS experiments were conducted in cyclohexane and 2-octanol using a Wyatt Technology Dawn Model F photometer. This instrument used a 5 mW He–Ne laser for the incident light source at 632.8 nm, a cylindrical scattering cell having a solution volume of approximately 0.2 ml, and a series of photodiodes arranged about the cell to simultaneously detect the scattered intensity at 15 different scattering angles over the range from ~7.1 to 143.4°. Calibration of the photometer was carried out using poly(α-methylstyrene) with a molecular weight of 20 100 g mol^{-1} as the polymer standard. Normalization of the photometer, i.e. determining the relative responses for the 15 detectors, was performed in both cyclohexane and 2-octanol, using a low-molecular-weight (~30 000 g mol^{-1}) PtBS sample

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* To whom correspondence should be addressed

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in each solvent. Data analysis was performed by using the method of Zimm[9] which led to values for M_w, the osmotic second virial coefficient, A_2, and, in the case of the higher-molecular-weight polymers, the z-average radius of gyration, $R_{G,z}$. Some of the data points obtained at the lowest angles were omitted from the analysis of the scattering diagrams. For example, in *Figure 1*, detectors 4–15 ($\theta = 29.3$–$143.4°$) were employed, while in *Figure 2*, detectors 2–15 ($\theta = 15.7$–$143.4°$) were used. Non-linearity at the lower angles is thought to be due to stray light. Dust, if present, would be observed to radically increase the scattering at the lower angles, thus resulting in a strong downward curvature in the extrapolated data, i.e. the values of A_2 and $R_{G,z}$ would increase and non-linear fits, instead of the linear fits used in all of the scattering diagrams, would be required. Kim and Cotts[10] also observed instrumental artifacts at these lower angles when using this instrument.

DLS experiments were conducted on the custom-built instrument described previously[11], with the measurements confined to a scattering angle of 20°. Temperature control ($\pm 0.1°$C) was achieved by the circulation of water through a copper coil inserted in a vat containing toluene as the index-matching fluid. Experiments using cyclohexane as the solvent were performed at 30°C, while the 2-octanol studies were carried out at 32.7°C. The scattered light was detected by an RCA C31034 photomultiplier tube, used in conjunction with a Fluke 415B power supply. The signal was amplified by a Pacific AD-6 discriminator and routed to a Brookhaven BI-2030AT digital correlator.

The data obtained were analysed by a second-order cumulant fit[12,13]:

$$b^{1/2}\frac{\ln(g'(\tau))}{B} = \ln(b^{1/2}) - \Gamma(\tau) + \frac{\mu_2(\tau)}{2} \qquad (1)$$

where τ is the time delay, $g'(\tau)$ is the electric field correlation function, B is the baseline (determined by calculation or from the eight channels delayed in τ), b is an optical constant, Γ is the decay constant, and μ_2 is the second moment of the decay-constant distribution. Values of the apparent, z-average[12] diffusion coefficient D_{APP} (the z-subscript is omitted) were obtained from

$$\Gamma = D_{APP}\boldsymbol{q}^2 \qquad (2a)$$

with the scattered wave vector, $\boldsymbol{q}$, given by

$$\boldsymbol{q} = \frac{4\pi n_0}{\lambda_0}\sin\frac{\theta}{2} \qquad (2b)$$

In equation (2b) n_0 is the solvent refractive index, λ_0 is the incident wavelength *in vacuo* (632.8 nm) and θ is the scattering angle. Second moment values were typically less than 0.1 but showed some increases for samples PtBS-11 (0.14), PtBS-500 (0.15) and PtBS-60 (0.13) (all average values). The larger average value for PtBS-11 is consistent with the larger molecular weight of this sample. In any case, values of approximately 0.1 are typical of low-polydispersity unimodel size distributions and seem to fortify the results obtained from the s.e.c. measurements.

Translational z-average diffusion coefficients, D_0, were determined from the measured values of D_{APP} obtained at various concentrations, c, according to:

$$D_{APP} = D_0(1 + k_d c + \cdots) \qquad (3)$$

where k_d, the diffusion virial coefficient, is given by

$$k_d = 2A_2M - k_f - v_2 \qquad (4)$$

In equation (4), k_f is the frictional virial coefficient, and v_2 is the partial specific volume of the polymer. The hydrodynamic radius, R_H, was calculated from the D_0 values by using the Stokes–Einstein equation:

$$R_H = \frac{kT}{6\pi\eta_0 D_0} \qquad (5)$$

where k is the Boltzmann constant, T is the absolute temperature, and η_0 is the solvent viscosity at the temperatures used, i.e. 7.78×10^{-4} and 4.45×10^{-3} N s m^{-2} for cyclohexane at 30°C and 2-octanol at 32.7°C, respectively[14].

Intrinsic viscosities, $[\eta]$, and Huggins coefficients, k_H, were measured with an Ubbelohde dilution viscometer, using the experimental procedures reported previously[2,5].

RESULTS AND DISCUSSION

Scattering diagrams for the sample PtBS-8 in the good solvent, cyclohexane, and in the theta solvent, 2-octanol, are given in *Figure 1*. Molecular characteristics of the PtBS samples, derived from light scattering and s.e.c. experiments, are presented in *Table 1*. Although some increase in polydispersity is observed on going from low to high molecular weights, the polydispersities of these PtBS samples are similar to those exhibited by

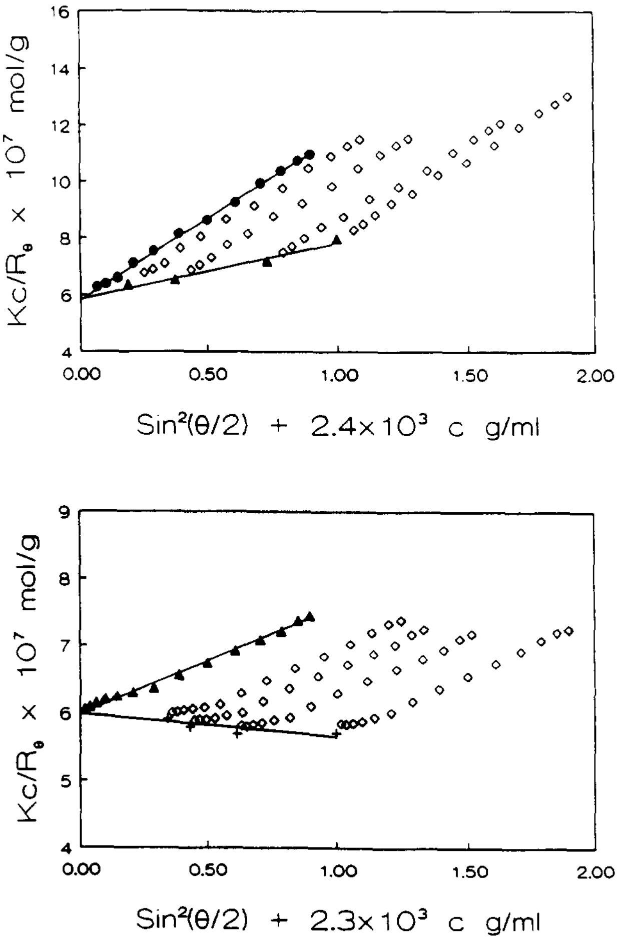

Figure 1 Scattering diagrams for the sample PtBS-8 in cyclohexane at 25°C (upper plot) and in 2-octanol at 32.7°C (lower plot). The small negative second virial coefficient observed in 2-octanol indicates that the solvent quality is slightly poorer than at θ

Table 1 Molecular characteristics of the PtBS samples using light scattering and s.e.c. experiments

	SLS				S.e.c.	LALLS	
Sample	$M_w (\times 10^{-5})$	A_2 ($\times 10^4$) (ml mol g^{-2})	$R_{G,z}$ [a] (nm)	$R_{G,z}$ [b] (nm)	M_w/M_n	$M_w (\times 10^{-5})$	A_2 ($\times 10^4$) (ml mol g^{-2})
PtBS-60	0.487	8.0	–	–	1.05	0.535	6.7
PtBS-120	0.912	5.7	–	–	1.06	0.929	5.1
PtBS-250	1.63	4.4	–	–	1.08	1.75	4.6
PtBS-300	3.83	3.5	–	–	1.10	3.58	3.5
PtBS-500	4.99	3.2	29.7	17.4	1.11	4.55	3.2
PtBS-6	9.63	2.7	42.9	22.3	1.12	9.46	2.2
PtBS-8	17.0	2.4	60.1	30.7	1.17	17.4	2.1
PtBS-13	23.5	2.5	73.9	38.6	1.12	24.0	1.7
PtBS-11	74.1	1.6	149	–	1.11[c]	75.5[c]	–

[a] Measured in cyclohexane
[b] Measured in 2-octanol
[c] Obtained from s.e.c.–LALLS using a measured d*n*/d*c* value of 0.141 ml g^{-1} for PtBS in THF at 633 nm and 25°C

commercial polystyrene standards with similar molecular weights. Thus, polydispersity effects, which should be small, are not considered in the following discussion.

Close agreement is observed between the M_w and (in most instances) the A_2 values obtained using the two different light scattering procedures. Consequently, in the subsequent analyses average values of M_w and A_2 are employed; these combined data lead to the following power law relationship:

$$A_2 = 1.71 \times 10^{-2} M_w^{-0.30} \qquad (6)$$

Equation (6) is similar to the relationship previously established[2] between the A_2 and M_n values obtained from osmometry experiments in toluene (another good solvent) at 37°C, i.e.

$$A_2 = 1.68 \times 10^{-2} M_n^{-0.32} \qquad (7)$$

The exponents of equations (6) and (7) are consistent with those previously reported for other styrene polymers in good solvents[11,15–18].

$R_{G,z}$ results are shown as a function of M_w in *Figure 2*. The following power law expressions, equations (8) and (9), are obtained for solutions in cyclohexane and 2-octanol, respectively:

$$R_{G,z} = 1.31 \times 10^{-2} M_w^{0.589} \qquad (8)$$

$$R_{G,z} = 2.73 \times 10^{-2} M_w^{0.491} \qquad (9)$$

The exponent in the case of cyclohexane is in very close agreement to that predicted by theory, i.e. 0.588[19], while the value of 0.491 confirms that 2-octanol at 32.7°C is, within experimental error, a theta solvent for PtBS.

The results of intrinsic viscosity measurements are presented in *Table 2*. The $[\eta]$ values lead to the power laws

$$[\eta] = 8.30 \times 10^{-3} M_w^{0.719} \qquad (10)$$

and

$$[\eta] = 5.28 \times 10^{-2} M_w^{0.501} \qquad (11)$$

in cyclohexane and 2-octanol, respectively. The Huggins coefficients are typical of those observed experimentally in both good and theta solvents for other linear flexible polymer chains[20], with average values of approximately 1/3 and 1 being observed for cyclohexane and 2-octanol, respectively.

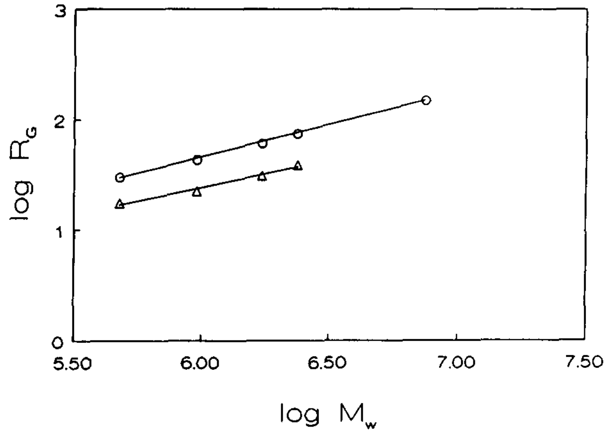

Figure 2 Radii of gyration (in nm) *versus* the weight-average molecular weight for PtBS samples in cyclohexane (○) and in 2-octanol (Δ)

Table 2 Intrinsic viscosities and Huggins coefficients of the PtBS samples

		Cyclohexane[a]		2-Octanol[b]	
Sample	$M_w (\times 10^{-5})$	$[\eta]$ (ml g^{-1})	k_H	$[\eta]$ (ml g^{-1})	k_H
PtBS-60	0.511	21.2	0.45	12.3	1.24
PtBS-120	0.921	30.3	0.41	16.3	1.11
PtBS-250	1.69	47.9	0.32	22.1	1.08
PtBS-300	3.71	79.2	0.28	31.6	1.11
PtBS-500	4.77	92.8	0.25	33.9	1.16
PtBS-6	9.55	166	0.28	52.7	1.06
PtBS-8	17.2	253	0.27	71.5	0.75
PtBS-13	23.8	332	0.30	84.0	0.87
PtBS-11	74.8	725	0.30	–	–

[a] Data were obtained at either 25 or 35°C. Previous findings (see ref. 5) have shown that this small temperature difference has a negligible effect on the $[\eta]$ values for PtBS in this solvent
[b] Data obtained at 32.7°C

Values for D_0, k_d and R_H are presented in *Table 3*. Excellent linearity was observed in the plots of D_{APP} against *c* (see *Figure 3*), and the values of D_0 and k_d were taken from the intercept and slope, respectively (see

Table 3 Results obtained from DLS experiments on different PtBS samples

		Cyclohexane			2-Octanol		
Sample	$M_w(\times10^{-5})$	D_0 ($\times10^7$) ($cm^2 s^{-1}$)	k_d ($cm^3 g^{-1}$)	R_H (nm)	D_0 ($\times10^7$) ($cm^2 s^{-1}$)	k_d ($cm^3 g^{-1}$)	R_H (nm)
PtBS-60	0.511	4.81	15	5.95	1.06	−29	4.75
PtBS-120	0.921	3.81	25	7.51	0.867	−24	5.80
PtBS-250	1.69	2.68	35	10.7	0.625	−45	8.05
PtBS-300	3.71	1.75	73	16.3	0.462	−68	10.9
PtBS-500	4.77	1.40	97	20.4	0.376	−137	13.4
PtBS-6	9.55	0.967	175	29.6	0.279	−177	18.0
PtBS-8	17.2	0.665	253	43.0	0.202	−312	24.9
PtBS-13	23.8	0.586	333	48.8	0.163	−333	30.7
PtBS-11	74.8	0.292	668	97.9	–	–	–

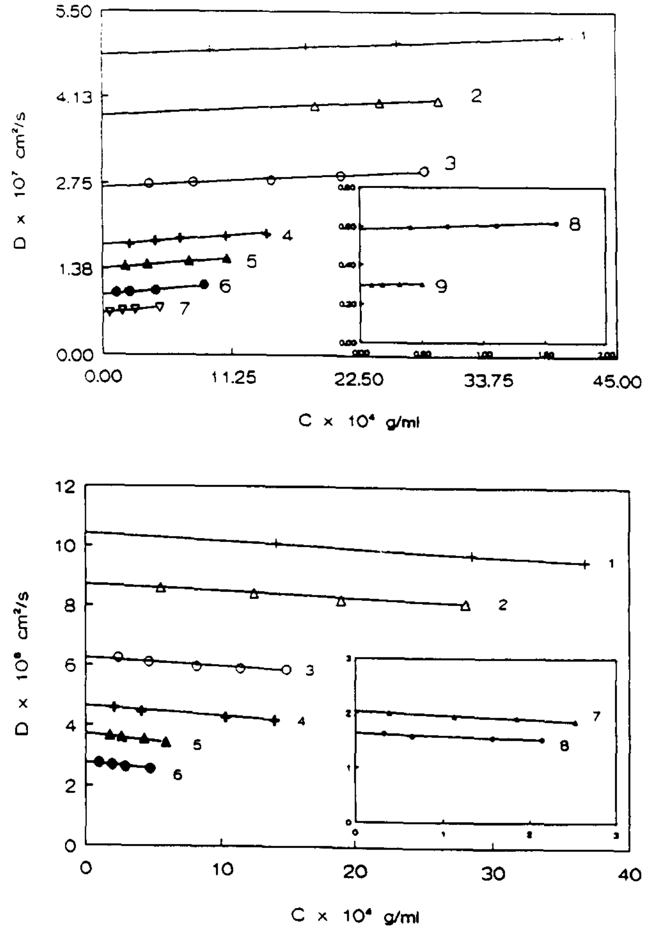

Figure 3 Plots of the apparent diffusion coefficient *versus* solute concentration for PtBS samples in cyclohexane (upper plot) and in 2-octanol (lower plot): (1) PtBS-60; (2) PtBS-120; (3) PtBS-250; (4) PtBS-300; (5) PtBS-500; (6) PtBS-6; (7) PtBS-8; (8) PtBS-13; (9) PtBS-11

equation (3)). The variation of D_0 with M_w is shown in *Figure 4*. These power laws appear to be strictly linear over the range of molecular weights studied and lead to the expressions

$$D_0 = 2.55\times10^{-4}M_w^{-0.572} \qquad (12)$$

and

$$D_0 = 2.22\times10^{-5}M_w^{-0.488} \qquad (13)$$

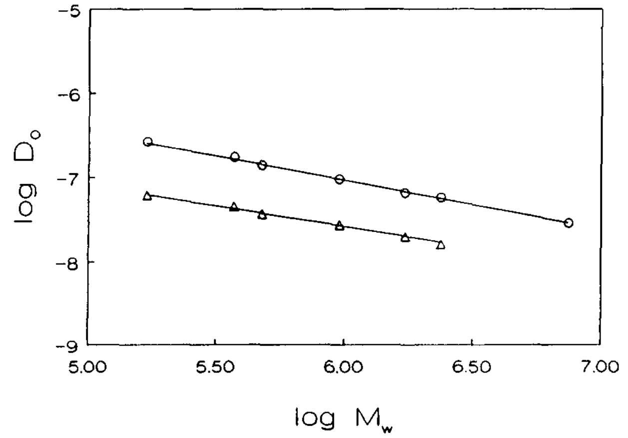

Figure 4 Power law plot of the translational diffusion coefficient (in $cm^2 s^{-1}$) *versus* the molecular weight, measured in cyclohexane (○) and in 2-octanol (△)

for cyclohexane and 2-octanol solutions, respectively. The corresponding power law relationships between R_H and M_w, in cyclohexane and 2-octanol, respectively, are

$$R_H = 1.12\times10^{-2}M_w^{0.572} \qquad (14)$$

and

$$R_H = 2.29\times10^{-2}M_w^{0.487} \qquad (15)$$

The k_d values in *Table 3* are positive in cyclohexane, a good solvent, and negative in the theta solvent, 2-octanol. The magnitude of k_d increases with increasing molecular weights in both of the solvents. This is typical, and well-established, behaviour for k_d. The frictional virial coefficients, k_f, may be calculated from the k_d values (using equation (4)) by assuming that $v_2 \simeq 1\ cm^3\ g^{-1}$. The exact value of v_2 is not necessary, as this term has only a very minor impact on the calculation. The reduced frictional virial coefficient, k_f^*, may then be obtained from

$$k_f^* = k_f[M/(N_A V_H)] \qquad (16)$$

where N_A is the Avogadro constant and V_H is the hydrodynamic volume, i.e. $(4/3)\pi R_H^3$. The values of k_f^* are presented in *Table 4*. Those shown for cyclohexane appear to be independent of the molecular weight; the average value of 5.4 is similar to those reported previously for a variety of flexible polymer chain/good solvent systems, where k_f^* is seen to vary between ~4.5 and 7[11,21–25]. Theoretical studies[6,26,27] predict values of 6.4 to 7.2 in good solvents; our results are only in moderate agreement with these predictions. The k_f^* values under theta conditions increase with increasing M_w; a similar dependence on M_w was recently noted[25] for poly(isobutylene) in a theta solvent.

From the data given in *Tables 1–3* a number of ratios can be calculated. One goal of this present work is to compare the present findings with other experimental and theoretical values. The parameters are Π, defined as

$$\Pi = (A_2 M)/[\eta] \tag{17}$$

ρ, defined as

$$\rho = R_{G,z}/R_H \tag{18}$$

the Flory–Fox parameter, ϕ, given by

$$\phi = [\eta]M/(6^{3/2}R_{G,z}^3) \tag{19}$$

the interpenetration function, Ψ, given by

$$\Psi = A_2 M^2/(4\pi^{3/2} N_A R_{G,z}^3) \tag{20}$$

and the Flory–Mandelkern–Scheraga parameter, β, defined as

$$\beta = (M[\eta]/100)^{1/3}/[f] \tag{21}$$

where $[f] = 6\pi R_H$. Values of these solution parameters, obtained for PtBS in both cyclohexane and 2-octanol, are presented in *Table 5*. None of these parameters exhibit, within experimental error, any dependence on M_w. Consequently, the following discussion involves only the average values and their reported standard deviations.

Table 4 Values of the reduced frictional virial coefficients obtained for PtBS samples in cyclohexane and 2-octanol

		k_f^*	
Sample	$M_w(\times 10^{-5})$	Cyclohexane	2-Octanol
PtBS-60	0.511	5.7	5.3
PtBS-120	0.921	6.3	4.3
PtBS-250	1.69	6.3	5.6
PtBS-300	3.71	6.3	7.6
PtBS-500	4.77	4.6	10.7
PtBS-6	9.55	4.4	11.4
PtBS-8	17.2	4.6	13.7
PtBS-13	23.8	5.4	10.8
PtBS-11	74.8	5.4	–

Average values of ρ, ϕ and β for PtBS in the theta solvent 2-octanol are similar to those found for other flexible polymer chains at the theta condition. The ρ value of 1.26 is in good agreement with the well-established result of 1.28 for polystyrene in cyclohexane[28]. Although there is some scatter in the experimental results for the Flory–Fox parameter, the mean value, $2.61 \pm 0.46 \times 10^{23}$, is in agreement with the results of the Monte Carlo simulation of Zimm[29], as well as with the range of values recently reported by Yamakawa and co-workers[30]. Under theta conditions the value of 2.23×10^6 for the Flory–Mandelkern–Scheraga parameter β is in good agreement with the theoretical result, i.e. 2.15×10^6, reported by Douglas and Freed[31,32] and also with the values calculated by Barrett[33] and Oono[34].

As discussed in earlier works (see refs. 11 and 25) the values of all of the solution parameters, with the exception of Ψ, the interpenetration function, can be employed to ascertain the relative extent of the hydrodynamic interaction (draining) of the system. This assignment is possible since the flow field will be altered, thus giving rise to changes in friction which are manifested in the viscosity and in the frictional coefficient (or in R_H or D). The quantity Ψ does not depend on either [f] or [η]. The average value for Ψ of 0.22 (see *Table 5*) is in agreement with the theoretical value of 0.219 obtained by Oono[34], and, within experimental error, the result of 0.24 given by Barrett[33]. The present experimental value is somewhat smaller than the value of 0.268 which was theoretically derived by Douglas and Freed[31,32]. It has been indicated[35] that Oono's value may be underestimated, but nonetheless the experimental value of 0.22 is generally consistent with available theoretical estimates.

The average Π value of 1.61 in the good solvent cyclohexane is larger than the theoretical (least draining) values of 1.10, 1.17 and 1.20, reported by Douglas and Freed[31,32], Barrett[33] and Oono[34], respectively. It is also larger than values normally observed for other polymer/good solvent systems[36], although the recent

Table 5 Solution parameters obtained for PtBS samples in 2-octanol and cylohexane

		2-Octanol			Cyclohexane				
Sample	$M_w(\times 10^{-5})$	ρ	$\phi\ (\times 10^{-23})$	$\beta\ (\times 10^{-6})$ $(\mathrm{mol}^{-1/3})$	Ψ	Π	$\phi\ (\times 10^{-23})$	ρ	$\beta\ (\times 10^{-6})$ $(\mathrm{mol}^{-1/3})$
PtBS-60	0.511	–	–	2.06	–	1.78	–	–	1.97
PtBS-120	0.921	–	–	2.26	–	1.64	–	–	2.14
PtBS-250	1.69	–	–	2.20	–	1.59	–	–	2.14
PtBS-300	3.71	–	–	2.38	–	1.64	–	–	2.16
PtBS-500	4.77	1.30	2.09	2.16	0.21	1.64	1.15	1.46	1.98
PtBS-6	9.55	1.24	3.09	2.34	0.22	1.44	1.37	1.45	2.09
PtBS-8	17.2	1.23	2.89	2.28	0.23	1.56	1.36	1.40	2.01
PtBS-13	23.8	1.26	2.37	2.18	0.22	1.51	1.33	1.51	2.17
PtBS-11	74.8	–	–	–	0.20	1.65	1.12	1.52	2.05
Average		1.26	2.61	2.23	0.22	1.61	1.27	1.47	2.08
Standard deviation		±0.03	±0.46	±0.10	±0.01	±0.10	±0.12	±0.05	±0.08

study of poly(ethylene oxide) in water by Selser and co-workers yields an average value of 1.88[37]. The present value (1.61) is slightly larger than the value of 1.43 reported previously[11] for poly(α-methylstyrene) in toluene, or the result reported for polystyrene in toluene of 1.41[38,39], or the value of 1.54 reported for polystyrene in THF[40].

The results for the Flory–Fox parameter ϕ in the good solvent (cyclohexane) do not appear to depend on the solute molecular weight, and have an average value of 1.27×10^{23}. The ratio ϕ/ϕ_0 of 0.49 is smaller than any of the recent theoretical values[31–34]; these range between 0.66 and 0.87 in the least draining limit. Thus, the present result suggests the presence of draining.

The average value for ρ of 1.47 is in good agreement with previous reports for polystyrene and poly(α-methylstyrene)[11]. The average value for β (2.08×10^6) is in accord with the predicted value of 2.16×10^6 determined by Douglas and Freed[31,32] for a flexible non-draining polymer chain in a good solvent. However, our measured value is smaller than the theoretical values suggested both by Barrett (2.4×10^6)[33] and by Oono (2.36×10^6)[34].

In general, the bulk of the results for PtBS in cyclohexane indicate that the solution properties are strongly affected by draining or hydrodynamic interaction. This result is similar to those obtained for polystyrene[38,39] and poly(α-methylstyrene)[11] in toluene and may reflect the influence of the substituent t-butyl group. Further studies on substituted styrene chains are needed in order to attempt correlations of the substituent group to the solution properties.

It is possible to estimate errors for the experimental observables. Such errors will depend on the complexity of the experimental protocols and will affect the calculated ratios, ρ, Π, β, ϕ and ψ. Assuming errors of 5% from all static scattering results, of 3% from measurement of D_0, and 2% for the intrinsic viscosity, it is calculated that the parameters Ψ and ϕ (with $R_{G,z}^3$) will exhibit errors approaching 20%. Alternatively, ρ, Π and β will yield errors of approximately 10%. For these parameters, therefore, a consideration of quite conservative estimates of errors still indicates enhanced solvent permeation through the polymer coil.

CONCLUSIONS

Solution properties are reported for nine narrow-distribution samples of poly(*p*-t-butylstyrene) in a good solvent, cyclohexane, and in a theta solvent, 2-octanol. Power law exponents in the relationships derived for A_2, $R_{G,z}$, $[\eta]$ and D_0 in the two solvents are consistent with previous work on PtBS and also with solution studies on other styrene polymers. In cyclohexane, the solution parameters ρ, Π and ϕ, appear to be strongly influenced by the draining (hydrodynamic interaction) effect.

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