Solution properties and chain flexibility of poly(*p*-tert-butylstyrene)

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The dilute solution properties of anionically synthesized poly(*p*-tert-butylstyrene) (PtBS) were studied in tetrahydrofuran, cyclohexane 1,4-dioxane, 1-nitropropane and 2-octanol. Cyclohexane and tetrahydrofuran are good solvents for PtBS, 1,4-dioxane is of intermediate solvent power, and 1-nitropropane and 2-octanol are theta solvents. The unperturbed dimension results show PtBS to be a more extended chain than polystyrene. These observations are interpreted in light of rotational isomeric state (RIS) models for polystyrene and poly(*p*-chlorostyrene) and experimental data available for polystyrene and its substituted derivatives.

(Keywords: poly(*p*-tert-butylstyrene); intrinsic viscosities; unperturbed chain dimensions)

INTRODUCTION

Rotational isomeric state (RIS) theory[1] has been successfully applied to the study of polystyrene chain conformations[2–6]. Also, Mark[7] has applied RIS models to the study of poly(*p*-chlorostyrene) conformations. Mark concluded that nonbulky para substituents should have negligible effects on the chain flexibility relative to the parent polystyrene, since energetically favourable conformations for polystyrene are those which minimize steric (and other) interactions between already bulky phenyl groups. Experimental results for poly(*p*-chlorostyrene)[8–12], poly(*p*-methylstyrene)[12,13], and other parasubstituted styrene polymers[14–17] support Mark's[7] conclusions.

In this work, the solution properties and unperturbed dimensions of poly(*p*-tert-butylstyrene) (PtBS) are reported. This work constitutes only the second report of solution properties of PtBS; our results are in essential agreement with those of Kucukyavuz and Kucukyavuz[17]. The unperturbed dimensions of PtBS are of interest because of the bulky nature of the t-butyl group particularly since RIS calculations have not yet been applied to the topic of the unperturbed dimensions of PtBS.

p-tert-Butylstyrene may be subjected to controllable anionic polymerization. Consequently, polymers of narrow molecular weight distribution and linear structure may be obtained. Well-defined polymers are necessary for a meaningful study of polymer unperturbed dimensions.

EXPERIMENTAL

PtBS samples were synthesized using anionic polymerization and high vacuum techniques[18]. Polymerizations were initiated with purified sec-butyllithium at room temperature. Benzene was used as the solvent. Essentially complete conversion was obtained after 12 h. The active centres were terminated with degassed methanol and the polymers then precipitated in methanol.

The polydispersity of the samples was measured using size-exclusion chromatography (SEC). Both Waters Ana-Prep and 150C instruments were used with a differential refractive index detector. The measurement temperature was 30°C with tetrahydrofuran (THF) as the solvent. A seven column Styragel set (total length of 28 feet) with a continuous porosity range of 2×10^3 to 5×10^6 Å was used in the Ana-prep instrument while the 150C was equipped with a 6 μ-Styragel column having a porosity range of 10^2 to 10^6 Å. The flow rate was 1 ml min^{-1}. The measured polydispersities $\bar{M}_w/\bar{M}_n$ are given in *Table 1*. The $\bar{M}_w/\bar{M}_n$ ratios from SEC measurements are in good agreement with those determined by low-angle laser light scattering and membrane osmometry. All measures of polydispersity indicated that the polymers used here are nearly monodisperse.

Solvents used for dilute solution measurements were reagent grade materials. Further purification by drying and distillation was carried out before use. Solvent purity was checked by gas chromatography and found to be nearly 100%.

The weight-average molecular weights ($\bar{M}_w$) were measured using the Chromatix KMX-6 low-angle photometer at 25°C in cyclohexane, with a laser source at 633 nm. The

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Table 1 Molecular characteristics of poly(*p*-tert-butylstyrene)

	PtBS sample						
	30	60	120	200	250	300	500
$\bar{M}_w \times 10^{-4}$ (g mol^{-1})	2.74	5.35	9.29	15.7	17.5	35.8	45.5
$\bar{M}_n \times 10^{-4}$ (g mol^{-1})	2.46	4.94	8.80	14.4	16.2	34.9	42.8
$A_2 \times 10^4$ (ml mol g^{-2})	6.26	5.37	4.95	3.77	4.22	2.74	2.58
$\bar{M}_w/\bar{M}_n$	1.11	1.08	1.06	1.09	1.08	1.03	1.06
$\bar{M}_z/\bar{M}_w$ (SEC)	1.05	1.05	1.06	1.09	1.08	1.10	1.11
$\bar{M}_w/\bar{M}_n$ (SEC)	1.05	1.05	1.06	1.08	1.08	1.10	1.11
$[\eta]^{30°C}_{THF}$ (dl g^{-1})	0.131	0.214	0.310	0.457	0.481	0.806	0.932
k_H	0.41	0.27	0.28	0.28	0.31	0.29	0.28
$[\eta]^{38°C}_{1,4\text{-dioxane}}$ (dl g^{-1})	0.127	0.212	0.303	0.447	0.479	0.792	0.928
k_H	0.40	0.45	0.41	0.32	0.32	0.28	0.25
$[\eta]^{25°C}_{1,4\text{-dioxane}}$ (dl g^{-1})	–	–	0.226	–	0.331	0.542	0.619
k_H	–	–	0.44	–	0.42	0.38	0.36
$[\eta]^{25°C}_{1,4\text{-dioxan}}$ (dl g^{-1})	–	–	–	0.294	0.313	0.489	0.554
k_H	–	–	–	0.46	0.53	0.47	0.47
$[\eta]^{31°C}_{NO_2Pr}$ (dl g^{-1})	0.088	0.123	0.164	0.206	0.222	0.319	0.341
k_H	1.07	0.84	0.79	0.88	0.72	0.69	0.65
$[\eta]^{32.7°C}_{2\text{-octanol}}$ (dl g^{-1})	–	0.123	0.163	0.206	0.221	0.316	0.339
k_H	–	1.24	1.11	1.21	1.08	1.11	1.16

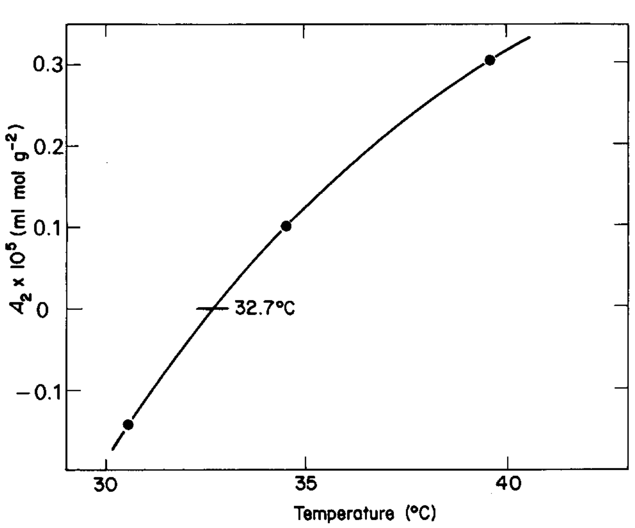

Figure 1 Variation of the second virial coefficient with temperature for PtBS-60 in 2-octanol

d*n*/d*c* value, measured with a Chromatix KMX-16 refractometer, was 0.129 ± 0.002 ml g^{-1}. The number-average molecular weights ($\bar{M}_n$) were obtained in toluene at 37°C using a Hewlett-Packard 503 membrane osmometer with S and S-08 membranes. Values of $\bar{M}_w$ and $\bar{M}_n$ are given in *Table 1*. Second virial coefficients (A_2) from membrane osmometry measurements are also given.

The theta (θ) temperature of PtBS in 2-octanol, defined as the temperature at which $A_2 = 0$, was determined by light scattering with a Sofica photometer using unpolarized light at 436 nm. The concentration dependence of scattering intensity was used to derive second virial coefficients as a function of temperature (*Figure 1*). The theta temperature was found to be 32.7°C.

Dilute solution viscosities were measured in 2-octanol at 32.7°C, the measured theta temperature, using Cannon–Ubbelhode semimicro viscosmeters having negligible kinetic energy corrections. Intrinsic viscosities ($[\eta]$) were obtained by extrapolating plots of η_{sp}/c vs. c and $\ln\eta_r/c$ vs. c to zero concentration. Intrinsic viscosities were also measured in 1-nitropropane at 31°C, the near-theta condition reported by Kucukyavuz and Kucukyavuz[17]. In addition, the intrinsic viscosities were also measured in 1,4-dioxane, tetrahydrofuran and cyclohexane. These values and the respective Huggins coefficients (k_H) are given in *Table 1*.

Information regarding the tacticity of anionically synthesized PtBS is not available at this time. It is likely that the tacticity is similar to that of anionically synthesized polystyrene[19], i.e., a random distribution with a probability of racemic dyads of *ca.* 0.56.

RESULTS AND DISCUSSION

Constants from Mark–Houwink–Sakurada (M–H–S) equations for PtBS in various solvents are given in *Table 2*. These values are based on linear regression analysis of data for $\bar{M}_w$ and $[\eta]$ (in dl g^{-1}) given in *Table 1*. Correlation coefficients are in all cases greater than 0.999. Clearly, the value of $\alpha = 0.48_8$ for 2-octanol at 32.7°C indicates that the viscosity measurements were carried out slightly below theta conditions. In the case of 1-nitropropane viscosities, $\alpha = 0.48_9$, again indicating that $[\eta]$ was measured at slightly below theta state. *Figure 2* shows the log$[\eta]$–log $\bar{M}_w$ plots for PtBS in the solvents used in this work. The M–H–S constants reported here for 1-nitropropane and cyclohexane are in agreement with the data of Kucukyavuz and Kucukyavuz[17] who obtained

$$[\eta]^{31°C}_{1\text{-nitropropane}} = 6.1 \times 10^{-4} \bar{M}_w^{0.49} \text{ and}$$

$$[\eta]^{35°C}_{\text{cyclohexane}} = 9.9 \times 10^{-5} \bar{M}_w^{0.71}$$

The dependence of the osmotic second virial coefficient on molecular weight is shown below. The relationship

$$A_2(\text{ml mol g}^{-2}) = 1.68 \times 10^{-2}\, \bar{M}_n^{-0.32}$$

Table 2 Mark–Houwink–Sakurada constants for poly(*p*-tert-butylstyrene)

Solvent	Temperature (°C)	$K \times 10^4$ (dl g^{-1})	α
Tetrahydrofuran	30.0	1.0_4	0.70_0
Cyclohexane	35.0	1.1_1	0.69_4
1,4-dioxane	25.0	2.1_4	0.60_4
1,4-dioxane	38.0	1.4_3	0.64_4
1-nitropropane	31.0	6.0_0	0.48_9
2-octanol	32.7	6.1_0	0.48_8

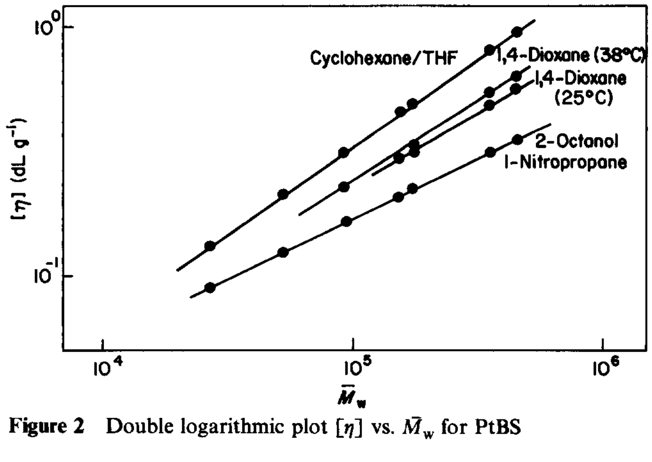

Figure 2 Double logarithmic plot $[\eta]$ vs. $\bar{M}_w$ for PtBS

was obtained in toluene at 37°C. The value of the exponent is only slightly smaller than the limiting value of -0.25 predicted by Casassa and Berry[20]. This value is similar to behaviour previously observed[21–24] for polystyrene in good solvents.

Flory's[1] characteristic ratio C_∞ is defined as

$$C_\infty \equiv \lim_{n\to\infty}\left[\frac{\langle r^2\rangle_0}{nl^2}\right]=\left[\frac{\langle r^2\rangle_0 \bar{M}_w^{-1}}{\frac{n'}{M}l^2}\right]$$

where $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end distance, n is the number of main chain bonds, n' the number of bonds per monomer unit, and l is the average bond length (1.53 Å). The mean square end-to-end distance is available from intrinsic viscosity values under theta conditions using Flory's[25,26] equation

$$K_\theta=\phi(\langle r^2\rangle_0/\bar{M}_w)^{3/2}$$

where $K_\theta=[\eta]_\theta/\bar{M}_w^{1/2}$ and $\phi=2.5\times10^{21}$.[14,27–31] Clearly, decreasing values of the characteristic ratio indicate increasing chain flexibility since $C_\infty=1$ for a freely jointed chain.

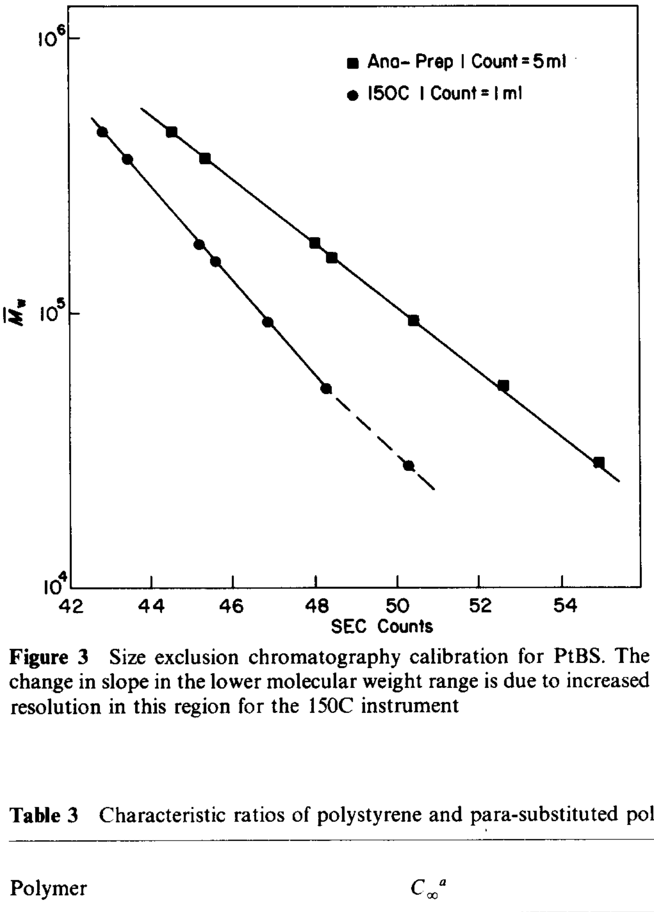

Figure 3 Size exclusion chromatography calibration for PtBS. The change in slope in the lower molecular weight range is due to increased resolution in this region for the 150C instrument

When intrinsic viscosity values under theta conditions are not available, unperturbed dimensions can be estimated from intrinsic viscosities measured under non-theta conditions using various extrapolation procedures. Perhaps the most useful and commonly employed extrapolation procedure is that due to Burchard[32] and Stockmayer and Fixman[33]. The B–S–F relation is given as

$$[\eta]/\bar{M}_w^{1/2}=K_\theta+0.51B\phi M_w^{1/2}$$

where B is a function of Flory's interaction parameter, polymer specific volume, molar volume of solvent and Avogadro's number. The B–S–F treatment of the near-theta temperature data obtained in 1-nitropropane and 2-octanol yields a K_θ of $5.4_2\times10^{-4}$ dl g^{-1}. Calculation yields a value of 12.3 for the characteristic ratio. The validity of the measured PtBS molecular weights is fortified by the consistent calibrations obtained by combining the absolute values of $\bar{M}_w$ and the SEC peak retention volumes for each sample (*Figure 3*).

Kucukyavuz and Kucukyavuz[17] report 13.4 for the PtBS characteristic ratio from intrinsic viscosities in 1-nitropropane at 31°C. However, these authors failed to correct their data for deviations from the actual theta state. Since their quoted M–H–S parameters in 1-nitropropane are virtually identical to ours, application of the B–S–F method to their data would lead to a characteristic ratio in agreement with our value of 12.3. Unfortunately, since the necessary $[\eta]$ values are not given in their paper, we cannot include their results in this calculation. Kucukyavuz and Kucukyavuz[17] also measured $\langle S^2\rangle_{oz}$ for two PtBS samples by light scattering in nitropropane at 31°C and obtained, after heterogeneity corrections, a characteristic ratio of 13.6.

Table 3 Characteristic ratios of polystyrene and para-substituted polystyrenes

Polymer	C_∞[a]	Method[b]	Measurement temperature (°C)	Reference(s)
Polystyrene	10.7–11.1	VT	34.5	34–36
Poly(*p*-methylstyrene)	10.8	VT	16.4	13
Poly(*p*-methylstyrene)	10.4	VG	30.0	12
Poly(*p*-chlorostyrene)	11.1	VG, LSG	30.0	8
Poly(*p*-chlorostyrene)	11.7[c]	VT	33.0	10
Poly(*p*-chlorostyrene)	~10.3	VG	30.0	9, 11, 12
Poly(*p*-bromostyrene)	13.4	VT, LST	26.3	14
Poly(*p*-bromostyrene)	12.5	VG, LSG	30.0	8
Poly(*p*-fluorostyrene)	11.6	VT	25.0	15
Poly(*p*-cyclohexylstyrene)	14.1	VG, LSG	30.0	12
Poly(*p*-tert-butylstyrene)	13.4, 13.6	LST, VT	31.0	17
Poly(*p*-tert-butylstyrene)	12.3	VT	31.0, 32.7	this work

[a] The value of ϕ was taken as 2.5×10^{21} for the interpretation of the intrinsic viscosity data

[b] The terminology is taken from the 'Polymer Handbook' (Eds. J. Brandrup and E. H. Immergut), J. Wiley and Sons, 2nd edn., New York, 1975, IV–4

VT = intrinsic viscosity under θ or near θ conditions
LST = light scattering under θ or near θ conditions
VG = intrinsic viscosity in good solvents
LSG = light scattering in good solvents

[c] Data were very scattered

Additional data regarding the characteristic ratio for PtBS are not available at this time. Clearly, PtBS is a more extended chain than polystyrene, where this parameter is calculated to be 10.7–11.1[34–36] at 34.5°C in cyclohexane. Experimental results for other *p*-substituted polystyrenes are given in *Table 3*. Notice that, in general, as the size of the substituent increases, the characteristic ratio also increases. The presence of small substituents such as $-CH_3$ or $-Cl$ impart negligible changes relative to polystyrene.

These observations are in agreement with RIS theory. As Mark[7] has pointed out, the presence of small para substituents, such as $-Cl$, should have negligible effects on C_∞. The reason for this is that conformations in which p-C_6H_4Cl groups are close enough for strong steric or electrostatic interactions are already largely excluded due to steric repulsions between already bulky phenyl groups. Therefore, only in the case of very large substituents, such as the bromo, cyclohexyl or t-butyl groups, are hindrances to internal rotation significantly different from those present in the parent polystyrene.

In closing, we point out that values of the Huggins coefficient followed established trends. We found $k_H \leqslant 0.4$ in cyclohexane and tetrahydrofuran while larger values were found under near-theta conditions (*Table 1*). These latter results are at least in qualitative accord with the theory of Peterson and Fixman[37] but contradict other available theoretical predictions[38–43].

An influence of the type of theta-solvent on the magnitude of k_H is also evident (*Table 1*). This effect has, to the best of our knowledge, not been previously observed experimentally nor examined theoretically. We are unable at this time to explain or rationalize this finding.

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