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Dilute-Solution Properties and Temperature Dependence of Unperturbed Chain Dimensions for Poly(*p-tert*-butylstyrene)

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ABSTRACT: The temperature coefficient of chain dimensions for poly(*p-tert*-butylstyrene) (PtBS) has been determined from intrinsic viscosity measurements over the temperature range 10.9–65.0 °C in three chemically similar Θ solvents. The value of $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = -1.87\ (\pm 0.3) \times 10^{-3}\ \mathrm{K}^{-1}$ is larger than the value of $-1.1 \times 10^{-3}\ \mathrm{K}^{-1}$ previously established for polystyrene (PS). Some comments are also made regarding specific solvent influences on unperturbed chain dimensions, based on available data for PtBS and PS.

Introduction

In this paper we present a study of the effect of temperature on the unperturbed dimensions of poly(*p-tert*-butylstyrene) (PtBS). PtBS is an ideal polymer for such dilute-solution studies because linear materials with narrow molecular weight distributions are readily prepared by anionic polymerization.

For substituted polystyrenes, Mark[1] has predicted via rotational isomeric state (RIS) models that relatively small para substituents, such as chloro and methyl groups, should have a minor effect on chain dimensions as compared to those of the parent polystyrene chain. More recent RIS calculations by Bahar et al.[2] for poly(*p*-chlorostyrene) have fortified Mark's findings. In addition, experimental studies on poly(*p*-methylstyrene)[3,4] and poly(*p*-chlorostyrene)[4–7] have further confirmed these predictions. In contrast, for PtBS the very bulky and approximately spherical *tert*-butyl group is known[8–10] to lead to enhancement of the characteristic ratio (C_∞)[11] relative to polystyrene and its *p*-chloro and *p*-methyl derivatives.

Likewise, insofar as the temperature coefficient of chain dimensions ($\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$, where $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end distance) is concerned, small para substituents are again predicted to have a negligible influence.[1,2] Information is also available on this parameter from an experimental standpoint, with small negative and small positive values of $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ being reported[7] in a variety of Θ media for poly(*p*-chlorostyrene). Experiment yields[12] a value of $-1.1 \times 10^{-3}\ \mathrm{K}^{-1}$ for the temperature coefficient of polystyrene under conditions where specific solvent effects are minimized. This result is in good agreement with theory.[13,14]

In the following, $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ is evaluated for a series of well-defined PtBS samples from intrinsic viscosity measurements conducted in a series of chemically similar Θ solvents. Intrinsic viscosities in the thermodynamically good solvents cyclohexane and benzene are also presented and discussed. Comparisons are made with previously published data on dilute PtBS solutions.

Experimental Section

The *p-tert*-butylstyrene monomer was obtained from Scientific Polymer Products. The supplier claimed 95% para substitution, and this was confirmed by NMR. This material was stirred and degassed over calcium hydride on a high-vacuum line followed by distillation. The collected monomer was then exposed to dibutylmagnesium (Lithium Corp.), distilled into evacuated ampules with breakseals, and stored at −78 °C until use; no monomer was stored for more than 3 days.

Polymerizations were conducted in sealed, evacuated (ca. 10^{-6} mmHg) vessels.[15] *sec*-Butyllithium was used as initiator. Either benzene or cyclohexane was used as solvent, and purification was conducted by methods described elsewhere.[15] Conversions were nearly quantitative after 24 h at 25 °C. Degassed methanol was used to achieve termination.

Molecular weight characterization involved a combination of size exclusion chromatography (SEC), low-angle laser light scattering (LALLS), and membrane osmometry (MO). For SEC a Waters 510 pump was used in conjunction with a Waters 410 differential refractometer. Two Waters "Linear Ultrastyragel" columns were used in series with tetrahydrofuran as the mobile phase.

LALLS experiments were performed in cyclohexane at 25 °C with the Chromatix KMX-6 unit (λ_0 = 633 nm; $\mathrm{d}n/\mathrm{d}c$ = 0.129 mL g^{-1} (ref 9)). MO experiments involved the use of the Mechrolab Model 501 instrument in toluene at 37 °C.

Θ solvents used for viscosity measurements were obtained from Alfa or Aldrich. Analysis of these materials, 3-nonanol, 2-octanol, 1-hexanol, and 1-nitropropane, by gas chromatography indicated that all were >99.5% pure. Cyclohexane (Aldrich, HPLC grade), toluene (Fisher, ACS certified), and benzene (Fisher, spectrograde) were used as received.

Θ temperature determinations in 3-nonanol and 1-hexanol involved studies of phase equilibria (Shultz–Flory plots);[16] the Θ temperature of 32.7 °C in 2-octanol was previously reported.[9]

Results and Discussion

Molecular characteristics of the PtBS samples are presented in Table I. Two samples from previous work[9] are described, along with nine new materials. Although higher molecular weight samples exhibit somewhat larger polydispersity ratios than do lower molecular weight samples, all materials are sufficiently narrow in distribution for the present purposes.

Intrinsic viscosities and Huggins coefficients are presented in Table II. $[\eta]$ value for the good solvent cyclohexane is plotted as a function of $\bar{M}_\mathrm{w}$ in Figure 1; data from previous studies[8–10] are also included. Generally very good agreement is seen between the different sets of data. For data of this work and ref 9, no discernible effect of temperature (25 versus 35 °C) on $[\eta]$ values in cyclohexane is observed. The two lowest molecular weight samples have higher $[\eta]$ values than expected based on higher molecular weight species. This effect is anticipated at low $\bar{M}_\mathrm{w}$ values[17–19] and may be attributed, at least in part, to deviations from Gaussian statistics observed even in Θ solvent at low molecular weights.[20–22] Combining the data of this work with those from ref 9 (and ignoring samples

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Table I
Molecular Characteristics of PtBS Chains

sample	$\bar{M}_w \times 10^{-5}$ [a]	$\bar{M}_n \times 10^{-5}$ [b]	$\bar{M}_w/\bar{M}_n$ [c]	$\bar{M}_w/\bar{M}_n$ [d]	$\bar{M}_z/\bar{M}_w$ [d]
1	0.126	0.116	1.09	1.05	1.05
4	0.310	0.281	1.10	1.06	1.06
2	0.346	0.315	1.10	1.07	1.06
200[e]	1.57	1.44	1.09	1.08	1.09
250[e]	1.75	1.62	1.08	1.08	1.08
5	1.96	1.87	1.05	1.08	1.09
3	6.59			1.17	1.14
6	9.46			1.12	1.10
7	15.0			1.22	1.10
8	17.4			1.17	1.08
13	24.0			1.12	1.10

[a] LALLS. [b] Membrane osmometry. [c] Absolute measurements. [d] SEC. [e] Reference 9.

with $M < 2.7 \times 10^4$) yields the Mark–Houwink–Sakurada (M–H–S) parameters given in Table III.

Excellent agreement is observed between our $[\eta]$ data in benzene and those of Kucukyavuz and Kucukyavuz,[8,10] and, as with cyclohexane, a decrease in slope is observed at very low molecular weights. Linear regression analysis of data for the ten highest molecular weight samples yields the power law parameters reported in Table III. The slightly larger M–H–S exponent for benzene suggests that this is a somewhat better solvent for PtBS than is cyclohexane. Below ca. 7×10^5 in molecular weight (see Table II) $[\eta]$ values in cyclohexane are slightly larger than those in benzene, although these differences are probably not outside experimental error.

M–H–S parameters for the three Θ solvents are presented in Table III. The values in 2-octanol at 32.7 °C are in excellent agreement with those reported previously for this system.[9] The M–H–S exponents found in all three solvents are slightly less than 0.5, indicating that the Θ temperatures were slightly underestimated in each case.

Evaluation of unperturbed chain dimensions requires correction for deviations from the actual Θ state, since the intercept K is very sensitive to small changes in a. It has recently been shown[23] that the Burchard–Stockmayer–Fixman (B–S–F)[24,25] relationship is adequate for determining unperturbed dimensions below the Θ temperature (for M–H–S exponents as low as 0.386, if molecular weights are not too high). This expression is given as

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

where B is a function of Flory's interaction parameter, molar volume of solvent, and polymer specific volume, Φ_0 is Flory's[26] hydrodynamic constant (taken as 2.5×10^{21}), and K_Θ is the unperturbed chain dimension. From K_Θ, $\langle r^2\rangle_0$ can be evaluated from[27]

$$K_\Theta = \Phi(\langle r^2\rangle_0/\bar{M}_w)^{3/2} \tag{2}$$

This, in turn, allows the calculation of C_∞ from[11]

$$C_\infty \equiv \lim_{N\to\infty} \frac{\langle r^2\rangle_0}{Nl^2} \tag{3}$$

where N is the number of main-chain bonds and l is the average bond length (1.53×10^{-8} cm). Values of K_Θ and C_∞ are listed in Table IV.

The value of 12.6 for C_∞ at 32.7 °C is in accord with the value of 12.3 previously reported for determinations under the same conditions and in 1-nitropropane at 31 °C.[9] Kucukyavuz and Kucukyavuz[8,10] have reported a slightly higher value of 13.4 based on both viscosity and light scattering results in 1-nitropropane at 31 °C. However, correction of their viscosity data via the B–S–F approach, which was not done in their work, yields $C_\infty = 12.1$—a result that is in accord with the present findings. These authors[10] have recently criticized the application of the B–S–F procedure below the Θ temperature, suggesting that it leads to underestimation of K_Θ. Suffice it to note that, as mentioned above, recent and extensive data on the poly(α-methylstyrene)/cyclohexane Θ system[23] have confirmed the validity of the B–S–F approach well below the Θ regime. Correct values of K_Θ are extracted from data obtained as much as 16 °C below Θ. Recent viscosity data published by Gundert and Wolf[28] for the polyisobutylene/ethyl heptanoate system also extrapolate to the correct K_Θ value even when measurements are done 18 °C below Θ. Thus, this suggestion[10] is not supported by experiment.

The same authors also claim[10] that the M–H–S parameters for the PtBS/1-nitropropane Θ system remain unchanged over the range 31–47 °C (although only data at 31 °C were actually shown in the paper). This is a remarkable finding, as it is well-known that chain dimensions are very sensitive to temperature in the vicinity of Θ.[26,29] Consequently, we decided to try to reproduce this result. For PtBS-6 ($\bar{M}_w = 946\,000$), $[\eta]$ values of 0.456, 0.505, and 0.549 dL g^{-1} and k_H values of 0.82, 0.65, and 0.57 were found at temperatures of 29, 37, and 45 °C, respectively. Clearly, as temperature is increased, $[\eta]$ increases substantially while k_H decreases. Further strong evidence of the sensitivity of chain dimensions of PtBS in 1-nitropropane to temperature is also found by examining the second virial coefficient (A_2) and radius of gyration (R_G) data of Kucukyavuz and Kucukyavuz (Table II of ref 8). Here, R_G is observed to increase strongly with temperature, while A_2 goes from positive values above 31 °C, to zero values at 31 °C, to negative values below 31 °C. Thus, their recent claim[10] of lack of coil shrinkage or expansion for PtBS near Θ cannot be supported.

The temperature coefficient is obtained from the data of Table IV from

$$\frac{d \ln \langle r^2\rangle_0}{dT} = \frac{2}{3}\frac{d \ln K_\Theta}{dT} \tag{4}$$

The value of $d \ln \langle r^2\rangle_0/dT$ thus derived is $-1.87\ (\pm 0.3) \times 10^{-3}$ K^{-1}. This value for PtBS is substantially larger than the value of $-1.1\ (\pm 0.2) \times 10^{-3}$ K^{-1} reported[12] for polystyrene of similar tacticity.[30]

The potential hazards inherent in the determination of the temperature coefficient must be mentioned. The relatively small magnitude of this parameter makes its accurate evaluation rather difficult. When the B–S–F method is applied to treatment of the $[\eta]$ data obtained under Θ or near-Θ conditions for the same polymer samples, the error involved (generally at least 5%) in the determination of $\bar{M}_w$ cancels out insofar as a relative comparison of K_Θ values is concerned. Thus, the relevant source of error is in the determination of $[\eta]$—only about 2% in the present case. The potential role of specific solvent effects should also be recognized. C_∞ for polystyrene is known to vary by as much as ca. 10% in different solvents at a given temperature.[12,31-34] The choice of a series of chemically similar (higher alcohol) Θ solvents is expected to minimize or eliminate the impact of the specific solvent effect on the value of $d \ln \langle r^2\rangle_0/dT$ derived. The use of this approach previously with polystyrene[12] yielded both chain dimensions and temperature coefficients in agreement with theory.[13,14]

It is seen from this work that both C_∞ and $d \ln \langle r^2\rangle_0/dT$ for PtBS are larger than for the parent polystyrene (C_∞

Table II
Intrinsic Viscosities[a] and Huggins Coefficients of PtBS Samples

		cyclohexane 25 °C		benzene 35 °C		3-nonanol 10.9 °C		2-octanol 32.7 °C		1-hexanol 65.0 °C	
sample	$\bar{M}_w \times 10^{-5}$	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H
1	0.126	0.079	0.90	0.075	0.91						
4	0.310	0.143	0.57								
200[b]	1.57	0.447	0.32	0.434	0.43	0.237	0.85	0.220	1.21	0.210	0.69
250[b]	1.75	0.479	0.32	0.461	0.40						
5	1.96	0.531	0.33			0.257	0.99	0.243	0.88	0.230	0.75
3	6.59	1.24	0.32	1.23	0.37	0.478	0.76	0.450	0.79	0.382	0.89
6	9.46	1.66	0.28	1.67	0.31	0.570	0.72	0.527	1.06	0.451	1.28
7	15.0	2.35	0.34	2.46	0.31						
8	17.4	2.53	0.27	2.64	0.30	0.738	0.77	0.715	0.75	0.642	0.88
13	24.0	3.32	0.30			0.909	0.79	0.840	0.87	0.812	1.29

[a] In dL g^{-1}. [b] Values for cyclohexane are from measurements performed at 35 °C.[9]

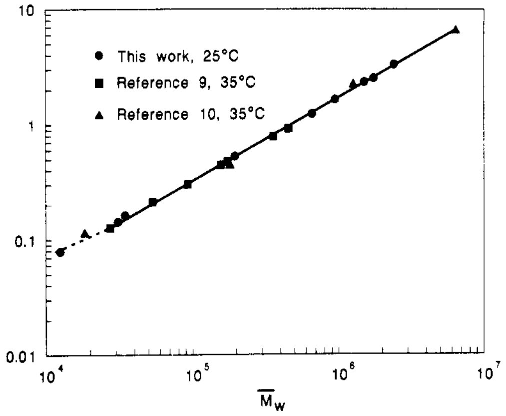

Figure 1. Mark-Houwink-Sakurada plot for PtBS in cyclohexane.

Table III
Mark-Houwink-Sakurada Parameters for PtBS in Various Solvents

solvent	temp, °C	$K \times 10^4$, dL g^{-1}	a
cyclohexane	25, 35	0.852	0.717
benzene	35	0.658	0.739
3-nonanol	10.9	6.65	0.490
2-octanol	32.7	6.08	0.492
1-hexanol	65.0	6.47	0.480

Table IV
Unperturbed Parameters for PtBS

solvent	temp, °C	$K_\Theta \times 10^4$, dL g^{-1}	C_∞
3-nonanol	10.9	5.95	13.1
2-octanol	32.7	5.57	12.6
1-hexanol	65.0	5.11	11.9

Table V
Unperturbed Dimensions for PtBS Derived from Measurements in Moderate to Good Solvents

solvent	temp, °C	$K_\Theta \times 10^4$, dL g^{-1}	ref
1,4-dioxane	25	5.92	9
1,4-dioxane	38	5.63	9
tetrahydrofuran	30	5.75	9
benzene	35	5.82	10, this work
cyclohexane	25, 35	5.77	9, 10, this work

Table VI
Intrinsic Viscosities of PtBS-250 in Toluene at Various Temperatures

temp, °C	$[\eta]$, dL g^{-1}	k_H
15	0.475	0.36
20	0.478	0.34
22	0.480	0.33
25	0.474	0.38
27	0.481	0.33
30	0.471	0.37
35	0.472	0.37
40	0.474	0.36

= 10.0–10.7 and d ln $\langle r^2 \rangle_0/\mathrm{d}T = -1.1 \times 10^{-3}$ K^{-1} [12,31,32]). It is clear that the presence of the large and spherical *tert*-butyl substituent results in substantially different conformational characteristics for PtBS as compared to PS. No RIS model has yet appeared for PtBS chains; it is hoped that the present results will stimulate such developments.

In Table V unperturbed chain dimensions estimated via the B–S–F approach[24,25] for data obtained in good to moderate solvents are presented. For dioxane (moderate solvent) treatment of data from ref 9 yields $K_\Theta = 5.92 \times 10^{-4}$ and 5.63×10^{-4} dL g^{-1} at 25 and 38 °C, respectively. These data tend to support the negative temperature coefficient reported above for PtBS. In the thermodynamically good solvents (tetrahydrofuran, benzene, and cyclohexane) only data for molecular weights between 27 000 (the break point in Figure 1) and 196 000 are used, since downward curvature is observed at higher molecular weights in each of the B–S–F plots for these good solvents. K_Θ values of ca. 5.8×10^{-4} dL g^{-1} are obtained in these solvents. These values are in very good accord with those reported above for dioxane but are slightly larger than those found in the Θ solvents 2-octanol and 1-nitropropane at about the same temperature.[9] The common feature of the solvents in Table V is their cyclic nature. Thus, as found previously for polystyrene,[34,35] it appears that cyclic solvents promote large values of unperturbed chain dimensions relative to acyclic solvents. Orofino[35] has suggested that acyclic solvents allows the chain to take on conformations that require segment–segment interactions that cannot be achieved in cyclic solvents. The results of Table V suggest that solvent polarity is, however, unimportant at least for the present system. The relative importance of polarity versus geometry, which was previously questioned,[34] appears to be answered by the present results. Additional work involving Θ solvents of varying polarity and geometry would, however, be required for more definitive conclusions to be drawn.

Finally, we feel obliged to comment on "conformational transitions" reported[36] for the PtBS/toluene system in the vicinity of 30 °C. This transition was reportedly observed via both $[\eta]$ and dn/dc determinations for two samples of PtBS having different molecular weights, with the strongest effect being seen for a sample with $\bar{M}_w = 1.8 \times 10^5$. We therefore decided to measure $[\eta]$ in toluene as a function of temperature for PtBS-250, which has $\bar{M}_w = 1.75 \times 10^5$. Our results are presented in Table VI and Figure 2. No evidence of a conformational transition is observed in these data. Averaging the $[\eta]$ values obtained at eight temperatures over the range 15–40 °C yields $[\eta]$

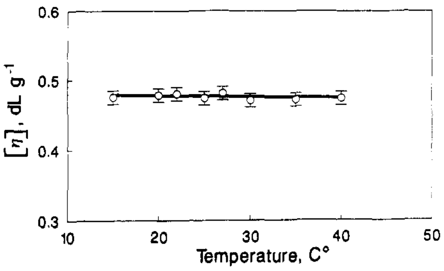

Figure 2. Plot of [η] versus temperature for sample PtBS-250 in toluene. Error bars correspond to ±2% in the values of [η].

= 0.476 ± 0.004 dL g^{-1}, where the error indicated is the standard deviation. Values of k_H are also effectively constant, ranging from 0.33 to 0.38. Use of a conservative error estimate of ±2% in [η] yields the error bars used in Figure 2. No deviation from linearity would be evident even if error bars of ±1% were used.

Conversely, values of [η] ranging between about 1.1 and 2.4 dL g^{-1} are reported over the same temperature range for a sample with essentially the same molecular weight (1.8×10^5) in ref 36. Not only are we unable to confirm or rationalize the claimed[36] "conformational transitions", we are also at a loss to explain why their [η] values are ca. 2–5 times as large as the values in Table VI. Suffice it to note that our [η] values (Table VI) are in agreement with [η] values determined in the other good solvents benzene and cyclohexane at this molecular weight (see Figure 1). Furthermore, K_Θ values given in Figure 3 of ref 36 suggest C_∞ values of ca. 40–50, in strong disagreement with results presented above and earlier.[8-10] Thus, the claimed[36] conformational transition for the PtBS/toluene system is not observed in our laboratory. It should be emphasized that the PtBS samples used in both cases were prepared by anionic polymerization and thus have low polydispersities and similar tacticities.

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References and Notes

(1) Mark, J. E. *J. Chem. Phys.* **1972**, *56*, 458.
(2) Bahar, I.; Baysal, B. M.; Erman, B. *Macromolecules* **1986**, *19*, 1703.
(3) Tanaka, G.; Imai, S.; Yamakawa, H. *J. Chem. Phys.* **1970**, *52*, 2639.
(4) Kuwahara, N.; Ogino, K.; Kasai, A.; Ueno, S.; Kaneko, M. *J. Polym. Sci., Part A* **1965**, *3*, 985.
(5) Noguchi, Y.; Aoki, A.; Tanaka, G.; Yamakawa, H. *J. Chem. Phys.* **1970**, *52*, 2651.
(6) Mohite, R. B.; Gundiah, S.; Kapur, S. L. *Makromol. Chem.* **1968**, *116*, 280.
(7) Izumi, Y.; Miyake, Y. *Polym. J.* **1973**, *4*, 205.
(8) Kucukyavuz, Z.; Kucukyavuz, S. *Eur. Polym. J.* **1978**, *14*, 867.
(9) Mays, J. W.; Ferry, W. M.; Hadjichristidis, N.; Funk, W. G.; Fetters, L. J. *Polymer* **1986**, *27*, 129.
(10) Kucukyavuz, S.; Kucukyavuz, Z. *Polym. Commun.* **1990**, *31*, 35.
(11) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(12) Mays, J. W.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2231.
(13) Abe, A. *Polym. J.* **1970**, *1*, 232.
(14) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(15) Morton, M.; Fetters, L. J. *Rubber Chem. Technol., Rubber Rev.* **1975**, *48*, 359.
(16) Shultz, A. R.; Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 4760.
(17) Altares, T.; Wyman, D. P.; Allen, V. R. *J. Polym. Sci., Part A* **1964**, *2*, 4533.
(18) Bianchi, U.; Dalpiaz, M.; Patrone, E. *Makromol. Chem.* **1964**, *80*, 112.
(19) Fox, T. G.; Kinsinger, J. B.; Mason, H. F.; Schuele, E. M. *Polymer* **1962**, *3*, 71.
(20) Huber, K.; Bantle, S.; Lutz, P.; Burchard, W. *Macromolecules* **1985**, *18*, 1461.
(21) Einaga, Y.; Koyama, H.; Konishi, T.; Yamakawa, H. *Macromolecules* **1989**, *22*, 3419.
(22) Konishi, T.; Yoshizaki, T.; Saito, T.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1990**, *23*, 290.
(23) Lindner, J. S.; Hadjichristidis, N.; Mays, J. W. *Polym. Commun.* **1989**, *30*, 174.
(24) Burchard, W. *Makromol. Chem.* **1960**, *50*, 20.
(25) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.
(26) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(27) Fox, T. G.; Flory, P. J. *J. Phys. Colloid Chem.* **1949**, *53*, 197.
(28) Gundert, F.; Wolf, B. A. *J. Chem. Phys.* **1987**, *87*, 6156.
(29) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(30) Information on the tacticity of anionically produced PtBS is presented in ref 8 as 55% syndiotactic. This result is almost identical with the 56% syndiotactic content found for anionically produced polystyrene (Sato, H.; Tanaka, Y.; Hatada, K. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1667). Thus, the presence of the bulky *tert*-butyl group has no apparent effect on the tacticity of the polymer obtained, at least insofar as anionic polymerizations based on the lithium counterion are concerned.
(31) Abdel-Azim, A.-A. A.; Huglin, M. B. *Polymer* **1983**, *24*, 1429.
(32) Abdel-Azim, A.-A. A.; Huglin, M. B. *Eur. Polym. J.* **1982**, *18*, 735.
(33) Orofino, T. A.; Ciferri, A. *J. Phys. Chem.* **1964**, *68*, 3136.
(34) Bohdanecky, M.; Berek, D. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 275.
(35) Orofino, T. A. *J. Chem. Phys.* **1966**, *45*, 4310.
(36) Al-Ghezawi, N.; Kucukyavuz, Z.; Kucukyavuz, S. *J. Polym. Sci., Polym. Lett. Ed.* **1990**, *28*, 111.

Registry No. *p-tert*-Butylstyrene (homopolymer), 9053-30-9.