Macromolecules 1991, *24,* 6686–6689

Analysis of Solution Properties of Polystyrene in 2-Butanone in the Framework of the Hard-Sphere Model

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Received July 8, 1991; Revised Manuscript Received August 30, 1991

ABSTRACT: The hydrodynamic properties of near-monodisperse polystyrene (PS) in 2-butanone have been studied by photon-correlation spectroscopy and viscometry. The derived translational diffusion coefficients D_0 and intrinsic viscosities $[\eta]$, along with literature data for the second virial coefficient A_2, have been used to calculate the corresponding equivalent sphere radii: R_H, R_V, and R_T (hydrodynamic, viscometric, and thermodynamic radii, respectively). Various ratios of these radii and ratios of the equivalent sphere radii with the radius of gyration R_G have been used to test theoretical predictions of dilute-solution behavior for linear chains. Of particular note is the observed strong variation of the ratio R_V/R_H with the specific nature of the polymer/solvent system. We tentatively attribute this behavior to crossover effects and, possibly, to changes in the average shape of the chain (from more spherical to more elliptical) brought about by specific polymer–solvent interactions.

Introduction

Several studies of the behavior of polystyrene (PS) in 2-butanone have already appeared.[1-7] In general, good agreement is noted between various workers insofar as the dependence of the second virial coefficient (A_2)[1-3,6] and the intrinsic viscosity $([\eta])$[1-3,6] on molecular weight is concerned. Conversely, substantially different results for the molecular weight dependence of the translational diffusion coefficient (D_0) have been noted.[4-7]

In this work, we report a photon-correlation spectroscopy (PCS) study of the diffusion behavior of high molecular weight, near-monodisperse PS standards, covering nearly 2 orders of magnitude in molecular weight, in 2-butanone at 25 °C. Intrinsic viscosities are also reported as a function of temperature.

Experimental Section

Polystyrene standards were purchased from Polymer Laboratories, Pressure Chemical Co., Toya Soda Co., and Waters Associates. Characterization methods employed in our laboratories for evaluating weight-average molecular weight $(\bar{M}_W)$, number-average molecular weight $(\bar{M}_N)$, and polydispersity ratios have been recorded previously.[8,9] Briefly, $\bar{M}_W$ values were measured using the Chromatix KMX-6 low-angle laser light scattering (LALLS) unit in toluene ($dn/dc = 0.107$ at $\lambda = 633$ nm). $\bar{M}_N$ values were measured using a Mechrolab Model 501 membrane osmometer in toluene. Polydispersities were evaluated using a Waters size-exclusion chromatography (SEC) system. The 2-butanone solvent (ACS Certified, Fisher Scientific) was dried over 4-Å molecular sieves before use.

A Brookhaven Instruments goniometer and Model BI2030 AT correlator, a Thorn EMI Model 9863/B350 photon-counting tube, and a Spectra-Physics argon ion ($\lambda = 488$ nm) laser (Series 2000) were employed for the PCS experiments. Laser powers of ca. 50 mW were used; at least three correlation functions were taken for each of four or more concentrations, which were clarified using a closed-loop filtration system with 0.2-μm filters. Temperature was controlled at 25.0 ± 0.1 °C; filtered decalin was used as the index matching and thermostating fluid. Measurements were confined to a scattering angle of 30°. Measured and calculated base lines agreed to within 0.02%, and second moment values were less than 0.1. Literature values[10] for the physical constants of 2-butanone at 25 °C were used.

Intrinsic viscosities and Huggins coefficients were derived via linear regression analysis using Huggins equation for data where the relative viscosity, η_r, varied between about 1.5 and 1.1. Solvent and solutions were filtered through 1.0-μm filters directly into the viscometers. Ubbelohde viscometers having very long flow times and, consequently, negligible kinetic energy corrections were used. Temperature control was within ±0.02 °C, and flow times for a given solution were reproducible to well within 0.1 s.

Results and Discussion

Molecular weights and polydispersity ratios for the PS standards are presented in Table I. In subsequent analysis, these samples are considered to be monodisperse due to their very narrow molecular weight distributions.

Results from PCS and intrinsic viscosity experiments are summarized in Table II. The reported D_0 and k_d values were determined from the intercept and slopes of linear plots of the apparent diffusion coefficient (D) versus concentration. Typical plots are shown in Figure 1. The combined results for D_0 and $\bar{M}_W$ lead to the following equation (Figure 2)

$$D_0 = 4.58 \times 10^{-4} \bar{M}_W^{-0.55_7} \tag{1}$$

while the $[\eta]$ values of Table II lead to the Mark–Houwink–Sakurada (MHS) equation (Figure 3).

$$[\eta] = 2.59 \times 10^{-2} \bar{M}_W^{0.61_3} \tag{2}$$

Equation 2 is in accord with results from a number of prior studies,[1-3,6] where experiments were conducted over the temperature range of 22–30 °C. Intrinsic viscosity results as a function of temperature (Table III) indicate a very weak temperature influence on dilute-solution parameters, an observation previously recorded by Outer, Carr, and Zimm.[1] Conversely, the diffusion behavior of

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0024-9297/91/2224-6686$02.50/0

Table I
Molecular Characteristics of PS Standards

$\bar{M}_W \times 10^{-4}$	$\bar{M}_N \times 10^{-4}$	$\bar{M}_W/\bar{M}_N$[a]	$\bar{M}_Z/\bar{M}_W$[a]
302		1.15	1.17
178		1.13	1.10
135		1.10	1.09
86.7		1.12	1.08
41.3	37.9	1.08	1.07
20.6	18.5	1.04	1.05
9.80	9.62	1.03	1.02
6.80		1.03	1.03
3.70	3.59	1.04	1.03

[a] Via SEC.

Table II
Hydrodynamic Properties of PS in 2-Butanone at 25 °C

$\bar{M}_W \times 10^{-4}$	$D_0 \times 10^7$, cm² s⁻¹	k_d, mL g⁻¹	$[\eta]$, mL g⁻¹	k_H
302	1.14	187	249	0.34
178			174	0.44
135	1.82	121	150	0.40
86.7	2.18	35.6	111	0.39
41.3	3.39	14.1	69.7	0.45
20.6	4.84	1.88	45.0	0.47
9.80	7.81	−25.2	29.3	0.46
6.80			24.0	0.29
3.70	13.2	−37.9	16.8	0.34

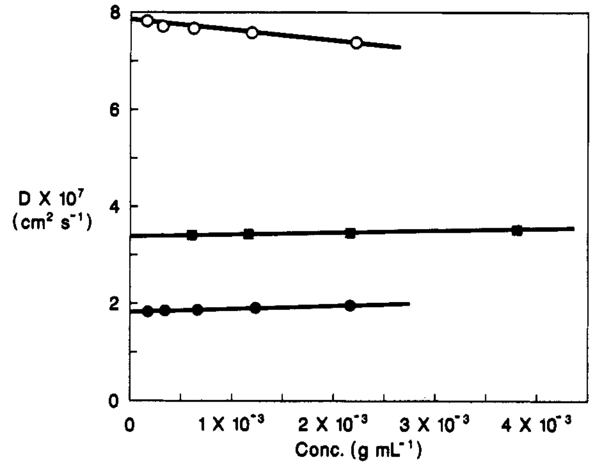

Figure 1. Apparent diffusion coefficients as a function of concentration for PS in 2-butanone at 25 °C: (●) $M_W = 1.35 \times 10^6$; (■) $M_W = 4.13 \times 10^5$; (○) $M_W = 9.80 \times 10^4$.

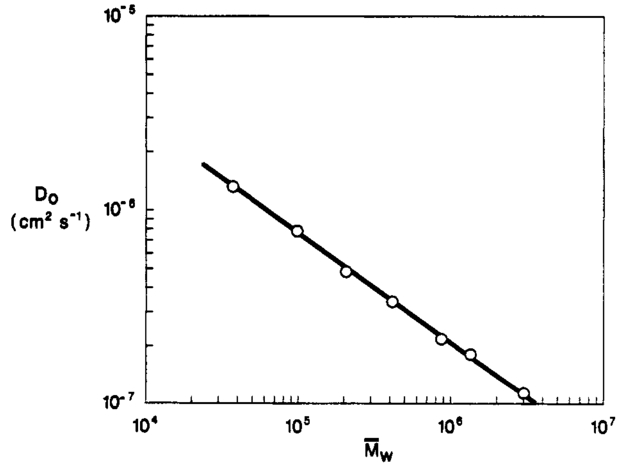

Figure 2. Dependence of the translational diffusion coefficient D_0 on molecular weight.

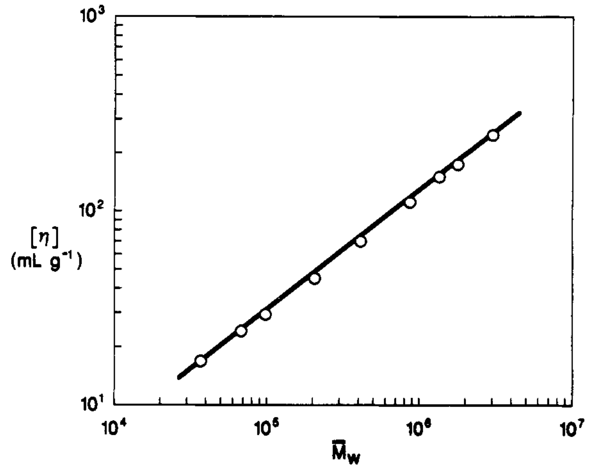

Figure 3. Variation of the intrinsic viscosity with molecular weight for PS in 2-butanone at 25 °C.

Table III
Temperature Dependence of $[\eta]$ and k_H[a]

	50 °C		5 °C	
$\bar{M}_W \times 10^{-4}$	$[\eta]$, mL g⁻¹	k_H	$[\eta]$, mL g⁻¹	k_H
86.7	107	0.38	111	0.40
67.5	94.0	0.41	95.9	0.37
25.4	52.2	0.44	54.6	0.40
20.6	45.3	0.34	46.1	0.45
10.2			30.8	0.30
9.80	28.7	0.38		
5.00	18.8	0.54	19.9	0.35

[a] The results for $[\eta]$ lead to the equations $[\eta] = 2.53 \times 10^{-2}\bar{M}_W^{0.612}$ and $[\eta] = 2.93 \times 10^{-2}\bar{M}_W^{0.603}$ at 50 and 5 °C, respectively.

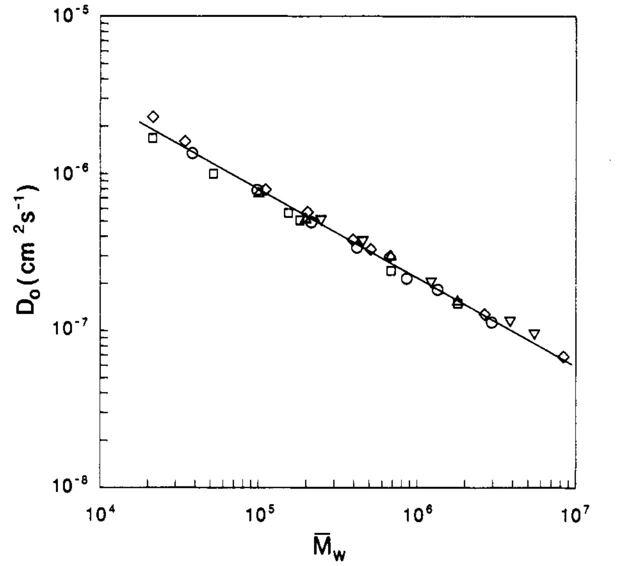

Figure 4. Combined data on the translational diffusion coefficient as a function of molecular weight for PS in 2-butanone at 25 °C. Symbols are as follows: (○) this work; (△) ref 7; (▽) ref 6; (□) ref 4; (◇) ref 5.

PS in 2-butanone has been quite controversial, as noted above. In Figure 4 our D_0 values are plotted along with results from four previous studies.[4-7] From these 31 data points, corrected where necessary to 25 °C, we calculate a power law in good agreement with eq 1:

$$D_0 = 4.14 \times 10^{-4}\bar{M}_W^{-0.54_5} \tag{3}$$

In general, the data of King and co-workers[5] and Varma et al.[6] lie above the line corresponding to eq 3, while the D_0 values of Ford et al.[4] are slightly smaller than predicted based on eq 3. Our data are in excellent accord with those of Kok et al.[7]

Several of the prior studies[4,5,7] report a change in sign of the diffusion virial coefficient k_d from negative at low molecular weights to positive at higher molecular weights.

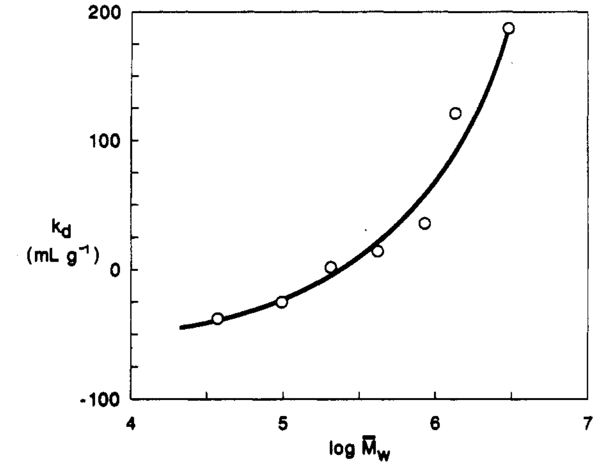

Figure 5. Molecular weight dependence of k_d. Note the crossover from negative to positive values of k_d at ca. 2 × 10^5.

Table IV
Radii[a] and Size Ratios of PS of 2-Butanone

$M_W \times 10^{-4}$	R_H	R_V	R_T[b]	R_G[c]	R_G/R_H	R_G/R_V	R_G/R_T	R_V/R_H
302	50.7	49.2	39.4	69.7	1.37	1.42	1.77	0.97
178		36.6	28.9	51.5		1.41	1.78	
135	31.8	31.8	24.6	44.0	1.38	1.38	1.79	1.00
86.7	26.5	24.8	18.9	34.1	1.29	1.38	1.80	0.94
41.3	17.1	16.6	12.3	22.3	1.30	1.34	1.81	0.97
20.6	11.9	11.4	8.15					0.96
9.80	7.40	7.69						1.04
6.80		6.37						
3.70	4.38	4.62						1.05

[a] In nanometers. [b] From ref 1. [c] From ref 6.

Such an effect is also noted in our work (Figure 5), with the crossover occurring at ca. 2 × 10^5. As is well-known, k_d values reflect both thermodynamic and hydrodynamic contributions[11]

$$k_d = 2A_2M - k_f - \upsilon_2 \tag{4}$$

where M is molecular weight, k_f is the frictional virial coefficient, and υ_2 is the partial specific volume of the polymer. As King et al.[5] have pointed out, the change from negative to positive k_d values reflects the increasing importance of the thermodynamic contribution with increasing molecular weight, since υ_2 is very small and independent of M. Unlike k_d, the k_H values of Table II are essentially constant.

From the D_0 values of Table II equivalent sphere hydrodynamic radii, R_H, may be calculated from

$$R_H = kT/6\pi\eta_0D_0 \tag{5}$$

where k is the Boltzmann constant, T is absolute temperature, and η_0 is the viscosity of the solvent. Similarly, the equivalent sphere viscometric radius, R_V, can be calculated from the $[\eta]$ values since[12]

$$R_V = (10/3\pi N_A)^{-1/3}([\eta]M)^{1/3} \tag{6}$$

where N_A is Avogadro's number. R_H is the radius of a solid sphere with the same diffusion coefficient of the polymer, whereas R_V is the radius of a hard sphere which exhibits the same intrinsic viscosity. Values of R_H and R_V are tabulated in Table IV. Also tabulated are values of the thermodynamic radius, R_T[11]

$$R_T = (16/3\pi N_A)^{-1/3}(A_2M^2)^{1/3} \tag{7}$$

which corresponds to the radius of a hard sphere with the same excluded volume as the polymer coil, and values of the radius of gyration, R_G. The data of Outer, Carr, and Zimm[1] on well-fractionated free-radically produced PS are utilized for the necessary A_2 values. It should be noted that these A_2 values are in accord with the A_2 results of Oth and Desreux[3] and Varma et al.[6] The R_G results of these latter authors are the only available data obtained on anionically produced samples.

The data of Table IV yield the following molecular weight dependencies for the various radii:

$$R_H = 1.26 \times 10^{-2}\bar{M}_W^{0.55_7} \tag{8}$$

$$R_V = 1.60 \times 10^{-2}\bar{M}_W^{0.53_7} \tag{9}$$

$$R_G = 1.37 \times 10^{-2}\bar{M}_W^{0.57_2} \tag{10}$$

$$R_T = 6.19 \times 10^{-3}\bar{M}_W^{0.58_7} \tag{11}$$

The exponents of eqs 8 and 9 are typical of those observed for polymers in thermodynamically moderate solvents, while the R_G power law exponent 0.572 is only slightly smaller than the theoretical good solvent value of 0.588.[13] This behavior is consistent with earlier observations[14-16] that the crossover from Θ condition to good solvent behavior occurs more gradually for hydrodynamic radii than for the static radius R_G. The strong molecular weight dependence for R_T (eq 11) is also a result of the vanishing excluded-volume effect as molecular weight is reduced.

The ratios of these various radii are also of interest. A very recent theory[17] gives the size ratios for linear unperturbed chains as

$$R_G^\circ{:}R_V^\circ{:}R_H^\circ{:}R_T^\circ = 1{:}0.836{:}0.778{:}0$$

and for nondraining good solvents as

$$R_G{:}R_V{:}R_H{:}R_T = 1{:}0.805{:}0.777{:}0.710$$

2-Butanone is of moderate thermodynamic quality for PS, based on both the magnitude of A_2 and the various measures of polymer size. Our average value of R_G/R_H = 1.33 is in agreement with the theoretical value[17] of 1.29 corresponding to a good solvent. Also, the experimental findings for the R_G/R_V and R_V/R_H ratios (1.39 and 0.99, respectively) are in reasonable accord with theoretical predictions of 1.24 for R_G/R_V and 1.04 for R_V/R_H in good solvents.[17]

Roovers and Toporowski[18] have previously reported that R_V/R_H = 1.03 ± 0.05 for PS in both good (toluene) and Θ solutions. The present findings are in agreement with this suggestion. Previously, however, for PS in another thermodynamically moderate solvent, n-butyl chloride, we found R_V/R_H = 1.16 ± 0.04.[19] Furthermore, for the system poly(α-methylstyrene)/n-butyl chloride (another polymer/moderate solvent system) we find R_V/R_H = 1.18 ± 0.01.[20] In addition, for linear polybutadiene in good and Θ solvents R_V/R_H values of 1.17 and 1.13, respectively, have recently been reported by Roovers and Martin,[21] whereas Fetters and co-workers[22] have found R_V/R_H = 1.05 ± 0.03 for polyisobutylene in good, moderate, and Θ solvents. Clearly, these findings suggest that the parameter R_V/R_H, which would be unity for a true hard sphere, is much more sensitive to the nature of the polymer and solvent than previously considered. We find it surprising that the ratio of these two measures of hydrodynamic size varies so widely, but it must be noted that specific solvent influences on unperturbed chain dimensions are not negligible.[8,9,23,24] Differences in crossover behavior of various parameters (noted above) perhaps plays a major role in causing this effect. Also, the varying R_V/R_H ratios

Table V
Fractional Virial Coefficients for PS in 2-Butanone

$\bar{M}_w \times 10^{-4}$	k_f	k_f^*
302	229	2.10
135	104	1.73
86.7	124	2.29
41.3	76.7	2.51
20.6	50.8	2.46

may reflect a change in shape of the polymer coil. Smaller R_V/R_H values may correspond to more spherical coils, with larger values corresponding to more elliptical species. This is possible since the intrinsic viscosity reflects both static and dynamic contributions ($[\eta] \sim R_G^2R_H$),[16] while R_H is a purely hydrodynamic term, and since R_G is most sensitive to the larger dimension of nonspherical objects. The potential influences of polydispersity, solvent quality, chain stiffness, and draining on the magnitude of R_V/R_H cannot be ruled out. According to Douglas et al.,[17] however, the influence of solvent quality should be marginal for nondraining coils.

Finally, values of k_f calculated from eq 4 (assuming $\nu_2 = 0.9$) and values of the reduced frictional coefficient k_f^*

$$k_f^* = k_f(M/N_AV_H) \qquad (12)$$

where the hydrodynamic volume $V_H = {}^4/_3\pi R_H^3$, are given in Table V. The average value of $k_f^* = 2.22$ is in excellent agreement with the theoretical value of 2.23 for unperturbed coils.[25] Much larger values of 7.16 are predicted[11,25] for both hard spheres and self-avoiding coils. Since 2-butanone is not a Θ solvent for PS, perhaps the rather small k_f^* values are a reflection of a nonspherical shape, although we are not aware of any k_f^* values for ellipsoids. If k_f^* values for ellipsoids are expected to be smaller than those for spheres, for a given polymer/solvent system small k_f^* values and large R_V/R_H values could go hand-in-hand.

In order to gain additional insight into this problem, we are planning experiments to explore the influence of both the solvent quality and chemical structure on the R_V/R_H parameter.

Acknowledgment. J.W.M. is grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation, through an NSF-EPSCoR grant, for support of this research. We thank Dr. Jeff Lindner for helpful discussions.

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Registry No. PS (homopolymer), 9003-53-6; $H_3CC(O)CH_2CH_3$, 78-93-3.