Hydrodynamic Properties of Polystyrene in Dilute *n*-Butyl Chloride Solution

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ABSTRACT: Dilute-solution hydrodynamic properties of polystyrene in *n*-butyl chloride were studied by photon correlation spectroscopy and intrinsic viscosity [η] measurements. *n*-Butyl chloride is found to be of moderate solvating power for polystyrene. Chain dimensions estimated from [η] values via the Burchard–Stockmayer–Fixman approach are in accord with values reported previously in other chloroalkanes but are considerably smaller than values found in cyclohexane. The role of specific solvent effects on unperturbed chain dimensions is discussed.

Introduction

Hydrodynamic radii of near-monodisperse polystyrenes in *n*-butyl chloride have recently been reported[1] over a range of molecular weights and temperatures. For even the highest molecular weight studied (1×10^5), no coil expansion (excluded-volume effect) was observed based on comparison to hydrodynamic radii measured under Θ conditions (cyclohexane, 35 °C) by the same group.[2,3] These results would suggest that *n*-butyl chloride serves as a Θ solvent for polystyrene. However, the additional observation was made[1] that the hydrodynamic radii of polystyrenes in *n*-butyl chloride showed no variation with temperature from 5 to 75 °C. This was of interest, since chain dimensions are known to exhibit a strong dependence on temperature in the vicinity of Θ.

In the present study, we have reinvestigated the polystyrene/*n*-butyl chloride system using a combination of photon correlation spectroscopy (PCS) and intrinsic viscosity experiments. Measurements have been conducted over the temperature range 10–50 °C and over the molecular weight range 10^4 to 6.8×10^5. The role of solvent geometry on polystyrene chain dimensions is also discussed.

Experimental Section

Near-monodisperse polystyrenes were obtained from Waters Associates, Pressure Chemical Co., and Polymer Laboratories. The *n*-butyl chloride was purchased from Aldrich (HPLC grade), analyzed by gas chromatography (ca. 99.9% pure), and used as received.

Molecular weight characterization involved a combination of low-angle laser light scattering (LALLS), size exclusion chromatography (SEC), and, in some cases, membrane osmometry. LALLS measurements were conducted in toluene at 25 °C using the Chromatix KMX-6 photometer, operating at a wavelength (λ) of 632.8 nm. The refractive index increment (dn/dc) under these conditions was measured with the Chromatix KMX-16 unit as 0.107 mL g^{-1}. Membrane osmometry measurements were also conducted in toluene (37 °C) using the Wescan Model 230 instrument.

SEC results were generated in tetrahydrofuran at 30 °C using a Waters Model 510 pump, Waters Model 410 refractometer, and two Waters "mixed-bed" linear Ultrastyragel columns (porosity of 10–10^5 nm). Twenty-microliter injections of ca. 0.2% solutions were employed; the flow rate of the mobile phase was maintained at 1.0 mL min^{-1}.

Intrinsic viscosities and Huggins coefficients were measured with Ubbelohde dilution viscometers which yielded solvent flow times >120 s. Huggins' equation[4] was used in treating the data, which were obtained for solutions where the relative viscosity was ≤1.6. All solvents and solutions were freed of particulates by filtration directly into the viscometer using Acrodisc CR membrane filters with 1.0-μm nominal porosity. Thermal control was maintained to within ±0.02 °C with a water bath and a Fisher Scientific heater/circulator. Flow times were reproducible to ±0.1 s.

The light-scattering data were taken on a Brookhaven apparatus using a BI2030 correlator. The photomultiplier tube was Model 9863/B350 from Thorn EMI. The laser was a Spectra Physics Series 2000 argon ion laser, and laser power at $\lambda = 488$ nm ranged from 25 to 100 mW depending on the scattering efficiency of the solutions. Care was taken to ensure that the correlator was not clipped while data were taken to prevent distortion of the correlation function. Data were analyzed by the method of cumulants[5,6] to second order. Temperature control was achieved with a circulating-water bath, with the control being ±0.1 °C.

In dilute-solution scattering, dust removal is essential both in the index-matching fluid and the sample itself. In our apparatus, decalin was used as the index-matching fluid and was filtered with a 0.2-μm filter and a peristaltic pump. The solutions on which the scattering was done were filtered with a closed-loop filtration system using a valveless metering pump (1.0 mL/min) and a 0.2-μm Acrodisc CR membrane filter. The solution flowed through the pump, into the filter, into the scattering cell, out of the scattering cell, into a small reservoir that serves as a solvent and polymer solution injection point, and back into the pump to complete the loop. The filtration system, which required about 5 mL to complete the loop, was used in the following way. It was first filled with 5 mL of solvent which was then circulated in the loop for 15–20 min at 1 mL min^{-1} until all the dust was removed. A small amount of stock solution was then injected into the loop through a septum and circulated for ca. 20 min until all the dust was removed and the solution was thoroughly mixed. This system is a duplicate of a system that has been in operation for some time.[7]

Results and Discussion

Molecular characteristics of the polystyrene samples are presented in Table I. Both SEC results and absolute measurements of $\bar{M}_n$ and $\bar{M}_w$ confirm their near-monodisperse nature. Intrinsic viscosities and Huggins coefficients measured at 10, 25, and 50 °C are listed in Table II. Excellent agreement is observed between values obtained at the two lower temperatures. Values at 50 °C are slightly smaller for a given molecular weight sample. This difference appears to be outside of the experimental error which we estimate at ±2%.

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Table I
Molecular Characteristics of Polystyrenes

$\bar{M}_w \times 10^{-3}$ [a]	$\bar{M}_n \times 10^{-3}$ [b]	$\bar{M}_w/\bar{M}_n$ [c]	$\bar{M}_z/\bar{M}_w$ [c]
9.7		1.03	1.03
19.6	19.1	1.03	1.03
37.0	35.5	1.04	1.03
50.0	49.5	1.04	1.02
111	108	1.03	1.03
254	235	1.07	1.07
392	350	1.11	1.07
675		1.08	1.06

[a] LALLS. [b] Membrane osmometry. [c] SEC.

Table II
Intrinsic Viscosities (mL g^{-1}) and Huggins Coefficients for Polystyrene in *n*-Butyl Chloride

	10 °C		25 °C		50 °C	
$\bar{M}_w \times 10^{-3}$	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H
9.7	8.8	0.72	8.8	0.68	8.3	0.82
19.6	12.3	0.63	12.4	0.58	11.9	0.61
37.0			18.6	0.49	17.8	0.54
50.0			21.7	0.50	21.1	0.51
111			38.8	0.44	37.6	0.46
254			66.4	0.39	64.7	0.41
392			87.8	0.39	84.4	0.42
675	124	0.37	124	0.38	121	0.42

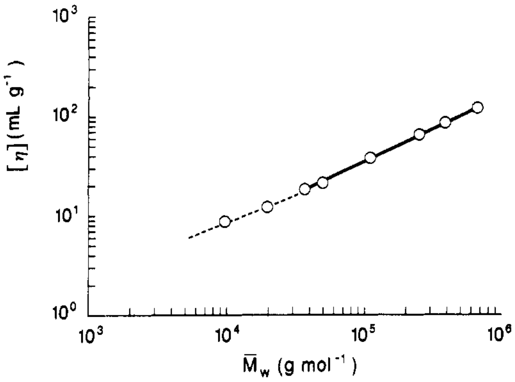

Figure 1. Mark–Houwink–Sakurada plot for polystyrene in *n*-butyl chloride at 25 °C.

Table III
Diffusion Coefficients and Equivalent Sphere Radii for Polystyrene in *n*-Butyl Chloride at 25 °C

$\bar{M}_w \times 10^{-3}$	$D_0 \times 10^7$, [a] cm^2 s^{-1}	R_h, nm	R_v, nm	R_v/R_h
9.7			2.38	
19.6			3.38	
37.0			4.78	
50.0	10.3	4.97	5.56	1.12
111	6.96	7.36	8.80	1.20
254	4.29	11.95	13.9	1.16
392	3.48	14.7	17.6	1.20
675	2.42	21.2	23.7	1.12

[a] Negative values of the diffusion virial coefficient k_d were obtained at lower molecular weights, while a positive value was obtained at the highest molecular weight. The same trend was previously found for flexible chains in moderate solvents.[12-14]

Table IV
Viscometric and Hydrodynamic Coil Expansion Factors for Polystyrene in *n*-Butyl Chloride at 25 °C

$\bar{M}_w \times 10^{-3}$	α_η [a]	α_h [b]
9.7	1.02	
19.6	1.01	
37.0	1.04	
50.0	1.05	1.00
111	1.11	1.00
254	1.16	1.07
392	1.18	1.06
675	1.21	1.16

[a] $[\eta]_\Theta = 8.47 \times 10^{-2}\bar{M}_w^{1/2}$.[18] [b] $R_{h,\Theta} = 2.22 \times 10^{-2}\bar{M}_w^{1/2}$.[18]

Figure 1 shows the plot of ln $[\eta]$ versus ln $\bar{M}_w$ obtained at 25 °C. Data for molecular weights ≥37 000 yield[8,9]

$$[\eta] = 1.74 \times 10^{-2}(\pm 0.002)\bar{M}_w^{0.662(\pm 0.012)} \text{ (mL g}^{-1}) \quad (1)$$

This equation may be compared with the corresponding result at 50 °C ($M \geq 37\,000$)

$$[\eta] = 1.62 \times 10^{-2}(\pm 0.002)\bar{M}_w^{0.665(\pm 0.010)} \text{ (mL g}^{-1}) \quad (2)$$

Huggins coefficients in Table II also show little variation with temperature.

Translational diffusion coefficients D_0, obtained by extrapolation of measured diffusion coefficients for several polymer concentrations at 25 °C to infinite dilution, are listed in Table III. Hydrodynamic radii R_h, calculated as

$$R_h = \frac{kT}{6\pi\eta_0 D_0} \quad (3)$$

where k is Boltzmann's constant, T is temperature, and η_0 is solvent viscosity,[10] and viscometric radii R_v, where[11]

$$R_v = ([\eta]M)^{1/3}(10/3\pi N_A)^{-1/3} \quad (4)$$

and N_A is Avagadro's number, are also tabulated (Table III). Hydrodynamic and viscometric radii, respectively, lead to the power laws

$$R_h = 1.21 \times 10^{-2}(\pm 0.002)\bar{M}_w^{0.554(\pm 0.02)} \text{ (nm)} \quad (5)$$

and

$$R_v = 1.36 \times 10^{-2}(\pm 0.001)\bar{M}_w^{0.556(\pm 0.004)} \text{ (nm)} \quad (6)$$

where in eq 6 molecular weights <37 000 are omitted.[8]

The value of R_v are, on average, 16% larger than R_h values for the same sample. Theory[15,16] predicts R_v/R_h values of 1.13 and 1.23 for self-avoiding and unperturbed coils, respectively. Our average value falls between these two predictions. Since the power law exponents in eqs 1, 2, 5, and 6 provide strong evidence that *n*-butyl chloride is a moderate solvent for polystyrene, this result might be anticipated. R_v/R_h values of ca 1.15 have also been found for some other flexible chains in thermodynamically moderate solvents.[13,14,17]

The previous study by Maa and Chen[1] had revealed no indication of an excluded-volume effect for this polymer/solvent system up to $M = 1 \times 10^5$, based on a comparison between R_h values measured in both *n*-butyl chloride and cyclohexane at the 35° Θ state. These findings seem surprising in view of the power law exponents reported in this work. However, in Table IV we list chain expansion factors calculated based on both $[\eta]$ (as $\alpha_\eta = ([\eta]/[\eta]_\Theta)^{1/3}$) and R_h (as $\alpha_h = R_h/R_{h,\Theta}$). Here the Θ-condition values are derived from extensive and well-documented literature data for the polystryene/cyclohexane system.[18] Our results for R_h confirm the findings of Maa and Chen[1] with regard to absence of chain expansion effects on R_h when $M \leq 10^5$. Excluded-volume effects on R_h are, however, noted at higher molecular weights. α_η is more sensitive to chain expansion; i.e., expansion is detected at lower molecular weights. It must be noted in this regard that K_Θ for polystyrene is known to be ca. 8% larger in cyclohexane than in 1-chloro-*n*-undecane at about the same temperature.[19] Such specific solvent effects are well documented,[19,24] and clearly the comparison of results in *n*-butyl chloride to unperturbed dimensions in a chloroalkane would be more appropriate and also lead to measurable chain expansion at lower molecular weights. Unfortunately, this can only be done at present with data

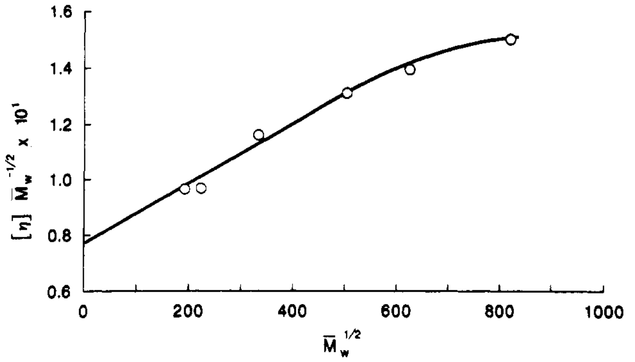

Figure 2. BSF plot for estimation of unperturbed dimensions of polystyrene in *n*-butyl chloride at 25 °C.

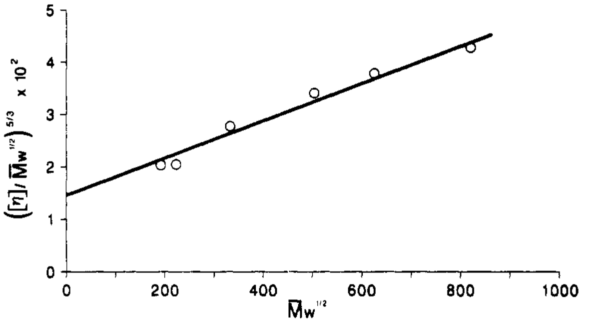

Figure 3. Tanaka plot for estimation of unperturbed dimensions. Notice that, unlike the BSF plot (Figure 2), this plot is linear even for the largest excluded volumes investigated.

for $[\eta]$ since R_h values have not been reported for the polystyrene/1-chloro-*n*-undecane system. Calculation using the data from ref 18 results in an increase of about 3% in α_η values. It should also be noted that several recent studies on the R_h–$\bar{M}_w$ behavior of polymer/good solvent systems have found a gradual transition from Gaussian to excluded-volume behavior as $\bar{M}_w$ is increased.[25]

Maa and Chen[1] have, with justification based on their data, which were limited to lower molecular weights, questioned the importance of a specific solvent effect. In Figures 2 and 3 we have plotted our viscosity data at 25 °C in the forms suggested by Burchard, Stockmayer, and Fixman[26,27] (BSF plot) and Tanaka,[28] respectively. The intercept of such plots allows an estimation of unperturbed chain dimensions.[29] K_Θ values of 7.7×10^{-2} mL g^{-1} are obtained from both plots, in excellent agreement with the value reported previously for 1-chloro-*n*-decane at 32.8 °C ($K_\Theta = 7.75 \times 10^{-2}$ mL g^{-1}) but smaller than the value of 8.37×10^{-2} mL g^{-1} reported in the same paper for the polystyrene/cyclohexane system.[19]

Finally, we note that Maa and Chen[1] found no dependence of R_h on temperature over the range 5–75 °C. Our viscosity data in Table II tend to support this claim, with, as noted above, perhaps a small decrease in chain dimensions being noted at 50 °C. In addition, R_h measurements on the highest molecular weight sample of this work ($\bar{M}_w = 6.75 \times 10^5$) yielded values of 21.3, 21.2, and 21.7 nm at 10, 25, and 40 °C respectively. These values are identical within experimental error (±3%) and support the previously cited finding of Maa and Chen[1] with regard to a lack of measurable temperature effect on chain dimensions.

In summary, *n*-butyl chloride is of moderate solvating power for polystyrene. Our results show unequivocally that *n*-butyl chloride is far from a Θ solvent for polystyrene at any of the temperatures investigated.[30] Chain dimensions estimated from $[\eta]$ values via the BSF and Tanaka[26-28] approaches are in accord with those reported previously in other chloroalkanes at about the same temperature.[19] These results fortify the previous findings[19-24] with regard to specific solvent effects on chain dimensions. The lack of measurable excluded-volume effects on R_h at low molecular weights ($\bar{M}_w \leq 10^5$) is believed to be partially due to specific solvent effects and also, possibly, due in part to gradual crossover behavior of R_h.[25] Thus, the polystyrene/*n*-butyl chloride system does not exhibit anomalous behavior.

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(30) This is not a surprising result in view of Θ temperatures previously reported for polystyrene in other chloroalkanes (see refs 19, 23, and 24).

Registry No. Polystyrene (homopolymer), 9003-53-6; *n*-butyl chloride, 109-69-3.