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# Depolarized Rayleigh Scattering from Short-Chain Polystyrene in a Θ-Solvent

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ABSTRACT: Five different polystyrene samples with a narrow molecular weight distribution were investigated in dilute solution in bicyclohexyl by depolarized light scattering using interferometric techniques. Bicyclohexyl was found to be a Θ-solvent at 61 °C. The chain length of the polystyrene samples varied from approximately 10 to 100 monomer units. We investigated the temperature range from 20 to 90 °C whereby the solution concentrations were in the nonoverlap region ($c[\eta] \ll 1$). The depolarized Rayleigh spectra were well-represented by a single Lorentzian line shape which was assigned to the overall reorientational motion of the chains. The reorientational relaxation times fit to the modified Stokes–Einstein–Debye relation, yielding hydrodynamic volumes of the oligomers. The reorientation motion of polystyrene in bicyclohexyl reflects, with increasing molecular weight, a tendency to coil formation of the molecules beginning at a nominal molecular weight of 2000. Using the Perrin relation we were able to calculate the axial ratios of the oligomers at the Θ-point assuming a prolate ellipsoid of revolution.

## I. Introduction

Dynamic depolarized light scattering is a convenient and well-established experimental method to study reorientational dynamics in simple molecular liquids[1–6] as well as in polymer systems.[7–14] However, experimental investigations of small oligomeric chains are rather less. Due to the intermediate region of short polymer chains, the rotational dynamics in dilute solutions are influenced by the transition from a rigid molecule to a flexible coil.

In polymer systems several relaxation processes are reflected in the polarizability time correlation function $C_{\text{aniso}}(t)$. Depending on the accessible time scale we know (i) the overall rotation of the molecules as a whole, (ii) the coupled main-chain torsions,[15,16] (iii) the conformational transitions,[17] and (iv) the local motions of optically anisotropic side groups.[18] Due to the presence of all these modes, in certain cases, the depolarized Rayleigh spectrum may have a complex shape depending on $C_{\text{aniso}}(t)$.

The influence of any collision-induced contribution to the depolarized scattering spectrum is a very complicated and theoretically unsolved problem. For polymeric systems one assumes that the collision-induced polarizability fluctuations contribute to a broad background in the low-frequency window considered by interferometric techniques. The coupling of rotational and collisional dynamics may be neglected due to the different time scales of motion.

The coherent character of the Rayleigh scattering leads to spectral line shapes depending on both single particle motions and possible correlated collective motions of molecular pairs in nondiluted solutions. Thus, the general form of $C_{\text{aniso}}(t)$, neglecting collison-induced contributions, can be written as[1]

$$C_{\text{aniso}}(t) = \sum_i \langle \mathrm{Tr}\,[\beta_i(0)\,\beta_i(t)] \rangle + \sum_{i \neq j} \langle \mathrm{Tr}\,[\beta_i(0)\,\beta_j(t)] \rangle \tag{1}$$

with $\beta_i$ the traceless anisotropic polarizability tensor of the $i$th subunit in laboratory-fixed coordinates. The brackets denote an ensemble average where the first term includes the self part. The summation over all pairs of molecules in the second term indicates the distinct part. Thus, the spectral distribution for the depolarized scattered light of a macromolecular solution in an optically isotropic solvent is given by the Fourier transform of the time correlation function of the total anisotropic polarizability fluctuation in the scattering volume.[1]

$$I_{\text{VH}}(\omega) \propto \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, e^{i\omega t} C_{\text{aniso}}(t) \tag{2}$$

The indices V and H indicate the different polarization directions of the incident and scattered electric field, respectively, and $\omega$ is the cycle frequency.

For sufficient small chains the diffusive molecular rotation is well-separated from the other above-mentioned dynamic processes, and in many cases the overall reorientation is the main shaping mechanism of the depolarized spectral intensity.[7–14]

For low molecular weight polystyrene (PS) samples ($M_{\text{w}} < 10\,000$) in dilute solutions of $CCl_4$, Bauer, Brauman, and Pecora could describe the depolarized Rayleigh spectra by a single Lorentzian line shape and assigned the halfwidth to the overall reorientation motion.[7]

Carpenter and Skolnick used a simple theoretical model to calculate the depolarized Rayleigh spectrum of dilute polymer solutions.[14] They have shown that the spectral band shape, obtained with VH polarization geometry, is dominated by the overall molecular rotation and consists of a single Lorentzian if the degree of polymerization $z$ is sufficiently small so that internal modes do not contribute significantly to the scattered intensity.

$$I_{\text{VH}}(\omega) \propto \frac{\Gamma}{\Gamma^2 + \omega^2} \tag{3}$$

$\Gamma$ is the half-width at half-height (hwhh) of a single Lorentzian given by[1]

$$\Gamma = \frac{j_2}{g_2}\frac{1}{2\pi}(q^2 D_{\text{t}} + 6 D_{\text{r}}) \tag{4}$$

The ratio $j_2/g_2$ reflects the influence of dynamic and static orientational pair correlations of the anisotropic scatters.

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$D_t$ is the translational and $D_r$ the rotational diffusion coefficient of the solute, and $q$ is the wave vector of the scattered light. In the case of the polystyrene solutions considered here, the spectrum is not affected by the translational diffusion because $q^2D_t \ll 6D_r$. Thus, the collective reorientational relaxation time $\tau_{1s}$ is given by[19,20]

$$\tau_{1s} = \frac{g_2}{j_2}\frac{1}{6D_r} = \frac{g_2}{j_2}\tau_{or} \tag{5}$$

where $\tau_{or}$ is the single-particle reorientational relaxation time. If the solution concentration is sufficiently low, neither static nor dynamic orientational pair correlations contribute to the spectrum and the ratio $g_2/j_2$ equals 1.

Reorientational relaxation times show a viscosity–temperature dependence described by the modified Stokes–Einstein–Debye (SED) equation

$$\tau_{or} = \tau_0 + V_m\frac{\eta}{kT}fC \tag{6}$$

where $\tau_0$ is an empirical time reached at zero viscosity and/or infinite temperature. $V_m$ is the molecular volume of the rotation particle. $k$ is the Boltzmann constant, $T$ the absolute temperature, and $\eta$ the dynamic shear viscosity of the fluid. The parameters $f$ and $C$ are responsible for the shape and boundary conditions during the reorientation motion in the liquid. Thus, the molecular volume $V_m$ is related to the hydrodynamic volume by

$$V_h = V_m fC \tag{7}$$

For small molecules several hydrodynamic models were tested to describe the rotational diffusion in liquids.[21-24] The reorientation of macromolecules in solution consisting of small solvent molecules is well-described under "stick" conditions, indicating that the first solvent shells are sticking on the particle surface during the rotational motion. In such cases $C$ takes the value 1. The hydrodynamic friction is determined by the shape factor $f$. Assuming the shape of the rotating molecule as a prolate ellipsoid, Perrin derived an expression[25] whereby $f$ depends on the axial ratio $p = b/a \leq 1$.

$$f(p) = \frac{2}{3}(1-p^4)\left(\frac{(2p^2-p^4)}{(1-p^4)^{1/2}}\ln\left\{\frac{1+(1-p^2)^{1/2}}{p}\right\} - p\right)^{-1} \tag{8}$$

In order to obtain hydrodynamic volumes, we fitted the SED equation to the experimental reorientational relaxation times.

Using eqs 7 and 8, we calculated the axial ratios for the PS samples under study assuming stick conditions during the reorientational motion in bicyclohexyl (BCH) around the Θ-point.

## II. Experimental Section

The spectra were obtained by a conventional light scattering instrument. The light source was an argon ion laser, Spectra Physics Model 171, operating at 488-nm single-frequency mode. The depolarized scattered light at $\varphi = 90°$ was frequency-analyzed by a piezoelectrically scanned planar Fabry–Perot interferometer (FPI) RC110 from Burleigh Instruments. We recorded three FPI orders of which the first order was taken as the instrumental function. The finesse was typically between 40 and 70 at different free spectral changes (FSR). A stabilization system DAS 1 (Burleigh Instruments) was used for drift stabilization and data acquisition. For data analysis the spectra were transferred to a Hewlett Packard 9000/300 computer. The experimental spectra were fitted by an interactive convolute-and-fit procedure based on the modified Marquardt algorithm. The half-widths Γ were reproducible to better than 10%.

**Table I**
**Probe Specification of the PS Standards and Experimental Parameters**

| $M^a$ | batch no. | $\langle M\rangle_w{}^b$ | $\langle M\rangle_w/\langle M\rangle_n{}^b$ | mass % PS | solvent | FSR, GHz |
|---|---|---|---|---|---|---|
| 800 | 61 004 | 826 | 1.14 | 3, 5, 7, 10, 12 | $CCl_4$ | 2.2 |
| 800 | 61 004 | 826 | 1.14 | 2, 4, 6, 8, 10 | BCH | 2.1, 1.5 |
| 1200[c] | | | 1.08 | 9.2 | BCH | 1.5 |
| 2000 | 61 222 | 2111 | 1.06 | 2.4 | BCH | 2.1 |
| 4000 | 61 100 | 3600 | 1.06 | 1.8 | BCH | 2.1 |
| 9000 | 80 314 | 9100 | 1.06 | 1.1 | BCH | 2.1 |
| 17500 | 41 220 | 20400 | 1.04 | | | |
| 35000 | 80 317 | | 1.06 | | | |
| 50000 | 60 917 | 53700 | 1.06 | | | |
| $2 \times 10^6$ | | $2 \times 10^6$ | 1.06 | | | |

[a] Nominal weight of the PS standard. [b] Determined by Pressure Chemical Co. using intrinsic viscosity (±5%). [c] Polymer Laboratories, Ltd.; $\langle M\rangle_p = 1200$.

**Table II**
**Physical Properties of the PS Solutions in BCH at Θ-Temperature**

| $M$ | $c$, mg/mL | $\rho$, g/mL | $\eta$, cP | $[\eta]_\Theta$, cm³/g |
|---|---|---|---|---|
| 800[a] | 86.6 | 0.8679 | 2.04 | 1.24 ± 0.15 |
| 1200 | 79.8 | 0.8690 | 2.14 | 0.83 ± 0.23 |
| 2000 | 20.4 | 0.8543 | 1.94 | 3.41 ± 0.23 |
| 4000 | 15.3 | 0.8566 | 1.94 | 3.93 ± 0.44 |
| 9000 | 9.3 | 0.8609 | 1.90 | 5.92 ± 0.17 |
| 17500 | | | | 9.50 ± 0.17 |
| 35000 | | | | 10.10 ± 0.40 |

[a] Solution with 10% PS 800 in BCH.

Anionic polymerized atactic polystyrene standards from Pressure Chemical Co., Pittsburgh, PA, and from Polymer Laboratories, Ltd., U.K., with narrow molecular weight distributions were used. The nominal molecular weights of the investigated polystyrene samples are listed in the first column of Table I. The polymer specifications characterized by Pressure Chemical Co. and the experimental parameters, chosen for our light scattering experiments, are also displayed in Table I.

BCH from Jansen Chimica, Beerse, Belgium, was vacuum-distilled ($bp_{14Torr}$ = 109–111 °C). Carbon tetrachloride of spectroscopic purity from Aldrich Chemie, Steinheim, FRG, was used without further purification.

To remove dust, the PS solutions were filtered into quadratic glass cuvettes through a 0.22-μm Millipore filter. The investigated temperature range was between 20 and 90 °C. The sample temperature was controlled to better than ±0.25 K. The viscosities were measured with an Ubbelohde capillary viscometer (Fa. Schott, FRG). We use the following standard PS samples: $M$ = 9000, 35 000, 50 000, and 2 000 000. The Θ-temperature of the system PS–BCH was determined by monitoring the intensity of the transmitted and the scattered light as a function of temperature and concentration (Table II). Approaching the critical temperature from above, the transmitted intensity displays in a very narrow temperature range a marked decrease while the scattered intensity is strongly amplified by critical opalescence. We therefore determined for each PS standard sample the critical phase separation temperature as a function of concentration. The curves display as maximum critical temperature $T^{cr}_{max}$ which was inserted in the Schultz–Flory equation:[26]

$$\frac{1}{T^{cr}_{max}} = \frac{1}{T_\Theta} + \frac{b}{T_\Theta\langle M\rangle_w{}^{1/2}} \tag{9}$$

We found $T_\Theta$ = 61 ± 2 °C. This information on the Θ-temperature of the polymer was used to qualitatively characterize the solute–solvent interaction for the short-chain molecules.

BCH has a very high boiling point, which allows us to study a large temperature range. On the other hand, we have chosen BCH for its solution properties and its low depolarized scattered intensity. Figure 1 shows two interferometric orders of the depolarized Rayleigh spectrum of pure BCH recorded with a FSR of 49.5 GHz. At the much smaller FSR, which we selected for measuring the solutions, the spectrum of the solvent appears as

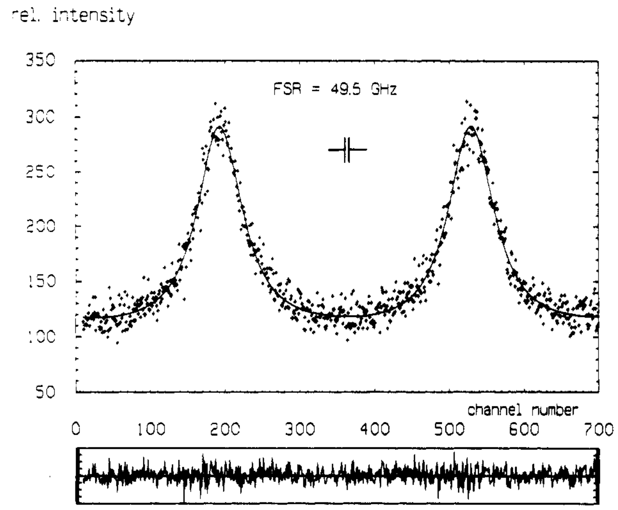

**Figure 1.** Depolarized Rayleigh spectrum of pure BCH recorded with two FPI orders at 60 °C. The solid line represents the theoretical curve of the fitted single Lorentzian. In the lower window the deviation between the experimental data points (+) and the Lorentzian is shown. The half-width of the instrumental function is indicated.

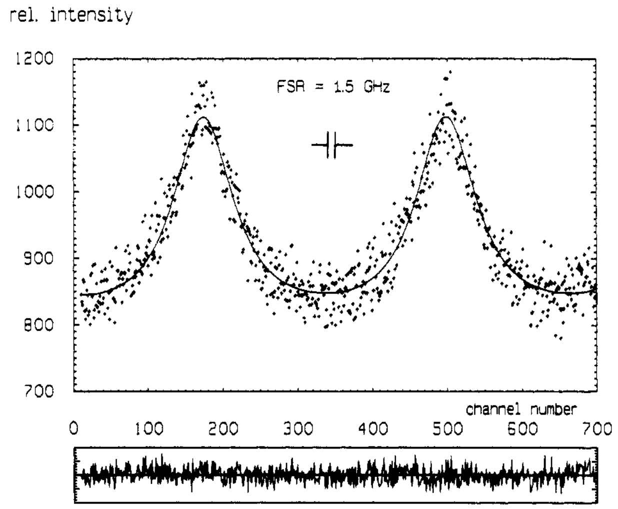

**Figure 2.** Depolarized Rayleigh spectrum of 10% PS 800 in BCH solution recorded with two FPI orders at 62 °C. The lower window shows the deviation between experimental data points and the fitted single Lorentzian. The symbols used have the same meaning as in Figure 1.

an unresolved broad background. Figures 2 and 3 display the spectra obtained from solutions of two different PS samples fitted with single Lorentzians.

## III. Results and Discussion

A single Lorentzian could be fitted to all the depolarized Rayleigh spectra. In Tables III and IV we show the obtained half-widths as a function of the concentration from solutions of the PS 800 sample in BCH and in $CCl_4$ at constant temperature. Thus, it is possible to study the viscosity dependence at the same temperature of this short-chain oligomer by changing the concentration and/or the solvent.

In Figure 4 the reorientational relaxation times obtained from $\Gamma$ have been plotted versus the ratio $\eta/T$ by using the corresponding solution viscosity. In this representation we plotted also the results from the temperature-dependent measurements of the 10% PS 800 solution in BCH. It is obvious that in the investigated temperature and viscosity range the hydrodynamic boundary conditions are identical. From the slope of the fitted equation (SED) we find an effective hydrodynamic reorientation volume

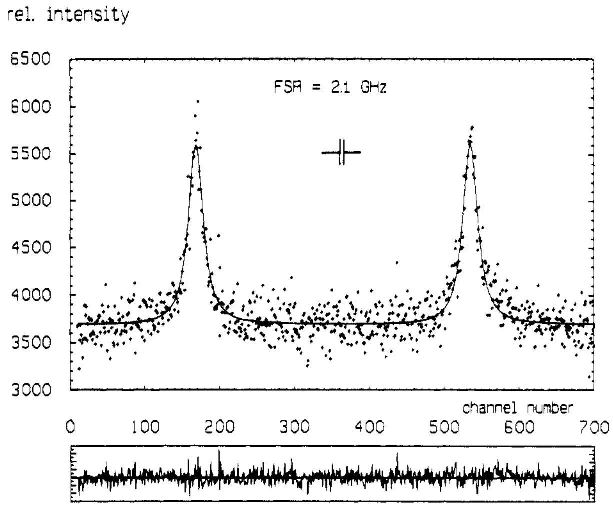

**Figure 3.** Depolarized Rayleigh spectrum of 1.1% PS 9000 in BCH solution recorded with two FPI orders at 63 °C. The lower window shows the deviation between experimental data points and the fitted single Lorentzian. The symbols used have the same meaning as in Figure 1.

**Table III**
**Experimental Results from PS 800 Solutions in BCH at 24 °C with FSR = 2.1 GHz**

| mass % PS 800 | $\Gamma_{hwhh}$, GHz | $\tau_{or}$, ns | $\eta/T \times 10^3$, cP/K |
|---|---|---|---|
| 3 | 109 | 1.46 | 13.01 |
| 5 | 100 | 1.58 | 13.53 |
| 7 | 94 | 1.69 | 14.81 |
| $10^a$ | 88 | 1.80 | 15.29 |

[a] The spectrum is measured at 25.7 °C with FSR = 1.5 GHz.

**Table IV**
**Experimental Data for the PS 800 Solution in $CCl_4$ at 23 °C and FSR = 2.2 GHz**

| mass % PS 800 | $\Gamma_{hwhh}$, GHz | $\tau_{or}$, ps | $\eta/T \times 10^3$, cP/K |
|---|---|---|---|
| 4.4 | 267 | 595 | 4.05 |
| 6.0 | 258 | 615 | 4.53 |
| 7.9 | 245 | 650 | 5.17 |
| 10.5 | 178 | 900 | 6.19 |

of approximately 1500 Å$^3$ which turned out not to be affected by the nature of the solvent, the concentration, and the temperature.

The experimental results for the PS solutions in BCH are represented in Table V. By fitting eq 6 to the relaxation times at different temperatures, we found a linear behavior using the solution viscosities at their corresponding temperatures (see Figure 5). The slopes obtained for different molecular weights agree well with the increasing hydrodynamic volumes of the reorientating PS chains. They have to be understood as average values because temperature effects on the molecular shapes are unknown but assumed here to be small for the short chains. The hydrodynamic volumes $\langle V\rangle_h$ are compared with the molecular volumes of the PS samples in Table VI. For the low molecular weight samples we obtain hydrodynamic volumes roughly twice as large as the molecular volumes. At higher molecular weights the ratio $\langle V\rangle_h/\langle V\rangle_m$ drastically decreases. This behavior of $\langle V\rangle_h/\langle V\rangle_m$ clearly indicates that at small values of $\langle M\rangle_w$ the molecule is more elongated than at larger values of $\langle M\rangle_w$. This conclusion is also supported by the axial ratios displayed in column 4 of Table VI. The above-mentioned observations suggest that all the spectra were obtained in a concentration range where polymer overlap could be safely excluded, as can be also estimated from the data of Table II.

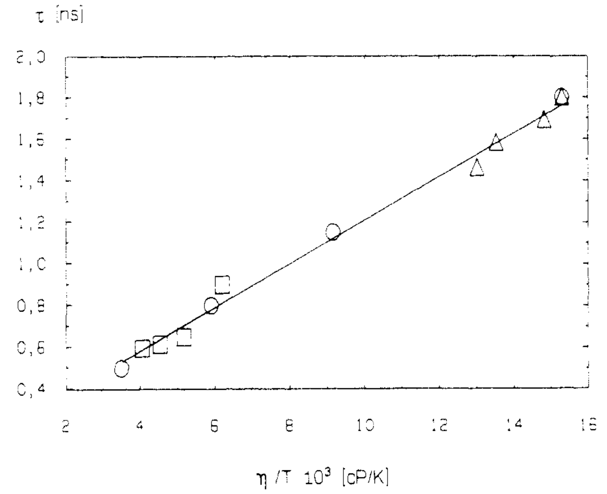

**Figure 4.** Reorientation times of PS 800 as a function of $\eta/T$. The plot includes (a) solutions in BCH at 24 °C at different concentrations (△), (b) solutions in $CCl_4$ at 23 °C at different concentrations (□), and (c) 10% solutions in BCH at different temperatures (○).

**Table V**
**Experimental Results from the Temperature-Dependent Depolarized Rayleigh Spectra and Viscosity Measurements of Five PS Samples with Narrow $\langle M\rangle_w$ Distribution in BCH Solution**

| $M$ | $T$, °C | $\tau_{or}$, ps | $\eta/T \times 10^3$, cP/K |
|---|---|---|---|
| 800 (10%) | 25.7 | 1800 | 15.29 |
| | 44.5 | 1150 | 9.14 |
| | 62.2 | 800 | 5.89 |
| | 86.0 | 500 | 3.49 |
| 1200 (9.2%) | 25.7 | 3030 | 15.44 |
| | 44.5 | 2040 | 9.42 |
| | 62.2 | 1330 | 6.17 |
| | 86.0 | 920 | 3.74 |
| 2000 (2.4%) | 21.0 | 4970 | 15.54 |
| | 35.9 | 3100 | 10.47 |
| | 50.2 | 2220 | 7.39 |
| | 63.6 | 1550 | 5.48 |
| 4000 (1.8%) | 21.0 | 7190 | 15.14 |
| | 35.9 | 4740 | 10.30 |
| | 63.6 | 2340 | 5.47 |
| | 82.1 | 1950 | 3.78 |
| 9000 (1.1%) | 21.0 | 9830 | 15.29 |
| | 35.9 | 6700 | 10.29 |
| | 64.2 | 3250 | 5.30 |
| | 82.1 | 2400 | 3.66 |

In Figure 6 we plotted the effective hydrodynamic volume of each sample reduced with the mean degree of polymerization $\langle z\rangle$ versus its molecular weight. We observe a strong increase of this quantity with increasing $\langle M\rangle_w$ for the PS samples with $M_w \leq 2000$. In this low molecular weight region the molecules presumably grow, forming rather elongated stiff chains. This leads to an increasing value of the effective hydrodynamical volume required by the monomeric units during the tumbling motion of the molecule. However, a further increase of the chain length leads to a decrease of the effective hydrodynamic volume. This indicates that the average shape of the longer chains becomes increasingly compact with $\langle M\rangle_w$ tending toward a coil in the high molecular weight limit. This limit is obviously approached at $\langle M\rangle_w \geq 9100$ as is suggested by the plateau in Figure 6 and the axial ratio of 1 in Table VI.

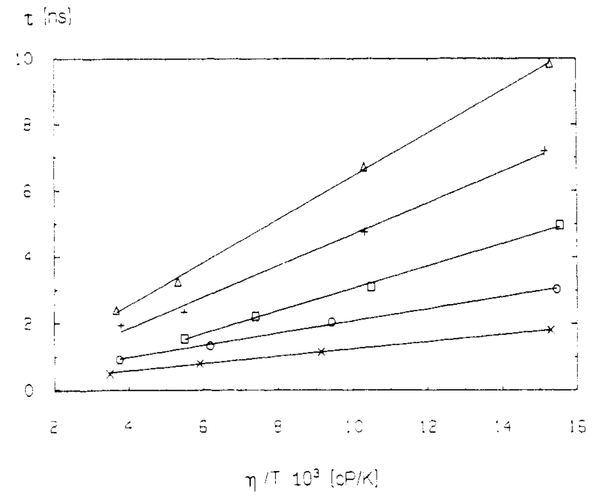

**Figure 5.** Stokes–Einstein–Debye plot for five polystyrene samples, PS 800 (×), PS 1200 (○), PS 2000 (□), PS 4000 (+) and PS 9000 (△) in BCH solution.

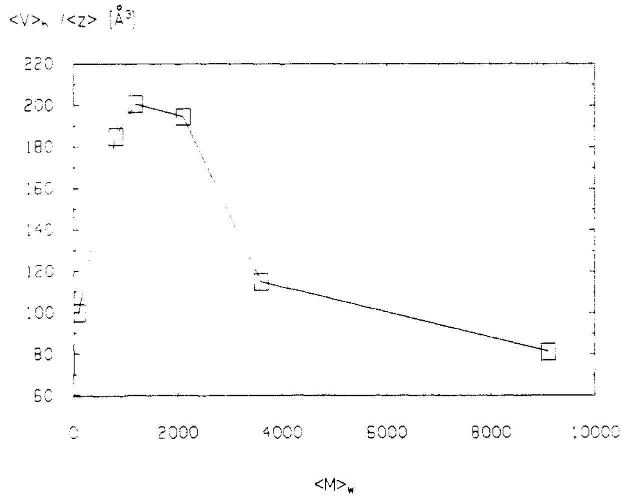

**Figure 6.** Effective reduced hydrodynamic volumes $\langle V\rangle_h/\langle z\rangle$ of toluene and five PS samples in BCH solution versus molecular weight.

**Table VI**
**Hydrodynamic Properties from the Rotational Diffusion Coefficient of Polystyrene in the Θ-Solvent Bicyclohexyl**

| $M$ | $\langle V\rangle_h$, Å³ | $\langle V\rangle_m$,[a] Å³ | $b/a$(prolate)[b] |
|---|---|---|---|
| 92[c] | 100 | 103.1 | |
| 800 | 1480 ± 50 | 827 | 0.38 |
| 1200 | 2410 ± 90 | 1240 | 0.40 |
| 2000 | 3890 ± 270 | 2380 | 0.41 |
| 4000 | 4020 ± 190 | 3720 | 0.41 |
| 9000 | 7140 ± 310 | 9410 | ≈1.0 |

[a] Calculated using van der Waals volume increments[27] with the volume of a monomer unit of 103.4 Å³. [b] $p$ is calculated by numerical solution of eq 8 using $f(p)$ under stick boundary conditions in eq 7. [c] Values for toluene; $V_h$ taken from ref 21.

## IV. Conclusion

Depolarized Rayleigh spectra of five low molecular weight polystyrene samples in dilute solution in bicyclohexyl, a Θ-solvent at 61 °C, have been obtained. The spectra fit well to single Lorentzian line shapes which were assigned to the overall reorientation motion of the highly anisotropic polystyrene.

The relaxation times at different molecular weights scale with the viscosity in agreement with the Stokes–Einstein–Debye equation. The obtained hydrodynamic volumes $V_h$, reduced to a simple monomer unit, show a maximum at $\langle M\rangle_w \approx 2000$, apparently reflecting increasing coiling with increasing chain length. Also the axial ratios, calculated using the Perrin relation for a prolate shape, increase with increasing molecular weight. This corresponds to the same behavior as obtained from the hydrodynamic volumes. At $\langle M\rangle_w = 9100$ the axial ratio

$p$ is nearly 1 due to the more spherical shape of the chain. The results are interpreted in terms of a crossover from a linear shape of low $\langle M\rangle_w$ molecules to increasingly compact shapes with increasing values of $\langle M\rangle_w$. In fact, we use the ratio $\langle V_h\rangle/\langle V_m\rangle$ as a kind of "compactness indicator" for the reorienting molecules. A dynamic crossover which bears an interesting analogy to our static crossover has been observed[28] in dielectric studies of similar polymer chains with increasing $\langle M\rangle_w$. In a study of the reorientation of alkane chains, however, we came to the conclusion that the distinction between static and dynamic effects is rather complicated since it depends on the time scale of the latter.[29]

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**Registry No.** PS, 9003-53-6; bicyclohexyl, 92-51-3.