Hydrodynamic-Radius Expansion Factor of Polystyrene in Cyclohexane near the Θ Temperature

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ABSTRACT: The translational diffusion coefficient D was determined from dynamic light scattering measurements for atactic polystyrene (a-PS) in cyclohexane at various temperatures ranging from 30.0 to 45.0 °C, above and below Θ, in the range of weight-average molecular weight M_w from 1.27×10^6 to 6.40×10^6. The hydrodynamic-radius expansion factor α_H determined from D is found to deviate from the first-order perturbation theory values even for small $|\tilde{z}|$, indicating that its (first) coefficient of $\tilde{z}$ may be too large, where $\tilde{z}$ is the scaled excluded-volume parameter defined in the Yamakawa−Stockmayer−Shimada theory for the perturbed helical wormlike chain. The present data for α_H plotted against $\tilde{z}$ give a single-composite curve together with the previous ones for a-PS in toluene and in 4-*tert*-butyltoluene, confirming that the quasi-two-parameter scheme may be valid for α_H as well as for the gyration- and viscosity-radius expansion factors α_S and α_η irrespective of the solvent condition. It is also found that α_H coincides with α_η within experimental error over the whole range of $\tilde{z}$ studied.

Introduction

In this series of experimental work on the excluded-volume effects in dilute solutions of oligomers and polymers, it has been shown that a quasi-two-parameter (QTP) scheme is valid for the gyration-radius expansion factor[1−3] α_S and the viscosity-radius one[2−5] α_η; i.e., these two quantities may be expressed as functions only of the scaled excluded-volume parameter $\tilde{z}$ defined in the Yamakawa−Stockmayer−Shimada (YSS) theory[6−8] that takes account of the effects of excluded volume and chain stiffness on the basis of the helical wormlike (HW) chain model,[9,10] irrespective of the differences in chain stiffness, local chain conformation, and solvent condition. Very recently, we have also started an experimental study[11] of the hydrodynamic-radius expansion factor α_H, taking atactic polystyrene (a-PS) as a first example. It has then been found that α_H in the two good solvents toluene and 4-*tert*-butyltoluene is also a function only of $\tilde{z}$ independent of solvent condition, indicating that the QTP scheme may also be valid for α_H.

However, the situation for α_H is somewhat different from that for α_S and α_η in the following point. The observed values of α_H are appreciably smaller than the corresponding ones calculated from the Barrett equation[12] for α_H with $\tilde{z}$ in place of the conventional excluded-volume parameter z, in contrast to the results for α_S and α_η, which may be explained quantitatively by the Domb−Barrett equation[13] (for α_S^2) and approximately by the Barrett equation[14] (for α_η^3), respectively, with $\tilde{z}$ in place of z. Furthermore, the observed values of α_H and α_η agree with each other within experimental error over the whole range of $\tilde{z}$ investigated ($0.1 \lesssim \tilde{z} \lesssim 10$), being inconsistent with the Barrett prediction that α_H is definitely larger than α_η for $z > 0$. As shown in the previous paper,[11] the Barrett values[14] of α_H may partly be reconciled with our experimental results in the range of rather large $\tilde{z}$ by taking account of the possible effect of fluctuating hydrodynamic interaction.[15] However, there is still appreciable disagreement between theory and experiment in the range of small $\tilde{z}$, since the theory predicts that the effect becomes negligibly small with decreasing $\tilde{z}$. Recall that the Barrett equation for α_H is an interpolation formula constructed so that it may reproduce the first-order perturbation coefficient[16] for small z and the asymptotic form in the limit $z \to \infty$.[12] Then there arises the question of whether the first-order perturbation coefficient for α_H does or does not agree with the experimental results.

Thus, in this paper, we investigate α_H for a-PS in cyclohexane above and below the Θ temperature, 34.5 °C, in order to clarify the above point by examining the behavior of α_H in the range of small $\tilde{z}$. For this system, the binary-cluster integral β has already been determined as a function of temperature (near Θ) from the second virial coefficient A_2,[17] so that the values of z and hence $\tilde{z}$ for a given a-PS sample may readily be obtained at any temperature by the use of the values of the HW model parameters already established. We use a-PS samples with such large molecular weights ($>10^6$) that the effect of chain stiffness on $\tilde{z}$ may be sufficiently small.

Experimental Section

Materials. The a-PS samples F128a-2 and F380 used in this work are the same as those used in the previous studies of α_S,[1] α_η,[4,5] A_2 (or the interpenetration function Ψ),[18] and α_H,[11] i.e., the fractions separated by fractional precipitation from the standard samples supplied by Tosoh Co., Ltd. In the present work, two new samples designated as F288a-2 and F550-a were prepared by precipitational fractionation also from the Tosoh standard samples F-288 and F-550, respectively. All of them have a fixed stereochemical composition (the fraction of racemic diads $f_r = 0.59$) independent of weight-average molecular weight M_w.

The values of M_w obtained from static light scattering (SLS) measurements are listed in Table 1 along with those of the ratio of M_w to the number-average molecular weight M_n determined from analytical gel permeation chromatography (GPC). Here, the values of M_w for the new samples were determined from SLS measurements in cyclohexane at 34.5 °C, as described below. The value of M_w/M_n for the sample F550-a could not be determined with sufficient accuracy because of the lack of the GPC calibration curve in the necessary range. According to the supplier, the nominal value of M_w/M_n for the original sample F-550 is 1.15, and then that for F550-a must be smaller than this value. Thus, we may conclude from the values of M_w/M_n that all the samples are

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Table 1. Values of M_w and M_w/M_n for Polystyrene Samples

sample	$10^{-6}M_w$	M_w/M_n
F128a-2[a]	1.27	1.03
F288a-2	3.47	1.03
F380[b]	3.94	1.05
F550-a	6.40	

[a] M_w of F128a-2 had been determined from SLS in benzene at 25.0 °C.[5] [b] M_w of F380 had been determined from SLS in toluene at 15.0 °C.[1]

sufficiently narrow in molecular weight distribution for the present purpose.

The solvent cyclohexane was purified according to a standard procedure prior to use.

Dynamic Light Scattering. Dynamic light scattering (DLS) measurements were carried out to determine the translational diffusion coefficient D for all the samples in cyclohexane at six to eight temperatures ranging from 30.0 to 45.0 °C by the use of a Brookhaven Instruments Model BI-200SM light scattering goniometer with vertically polarized incident light of 488 nm wavelength from a Spectra-Physics Model 2020 argon ion laser equipped with a Model 583 temperature-stabilized etalon for single-frequency-mode operation. The photomultiplier tube used was an EMI 9863B/350, the output from which was processed by a Brookhaven Instruments Model BI2030AT autocorrelator with 264 channels. (An electric shutter was attached to the original detector alignment in order to monitor the dark count automatically.[19]) The normalized autocorrelation function $g^{(2)}(t)$ of the scattered light intensity $I(t)$ at time t was measured at three or four concentrations and at scattering angles θ ranging from 15 to 45°.

From the data for $g^{(2)}(t)$ thus determined at finite concentrations c, we determined D at an infinitely long time[20] at infinite dilution for each sample in the same manner as that used in the previous studies.[11,19,20] The procedure is as follows. At small c, the plot of (1/2) $\ln[g^{(2)}(t) - 1]$ against t in general follows a straight line represented by

$$(1/2)\ln[g^{(2)}(t) - 1] = \text{const} - At \quad (1)$$

with A the slope for such large t where all the internal motions of solute polymer chains have relaxed away.[20] With the slope A evaluated from the plot, we may determine the apparent diffusion coefficient $D^{(LS)}(c)$ at finite c from

$$D^{(LS)}(c) = \lim_{k\to 0} A/k^2 \quad (2)$$

where k is the magnitude of the scattering vector and is given by

$$k = (4\pi/\tilde{\lambda})\sin(\theta/2) \quad (3)$$

with $\tilde{\lambda}$ the wavelength of the incident light in the solvent. At sufficiently small c, $D^{(LS)}(c)$ may be expanded as

$$D^{(LS)}(c) = D^{(LS)}(0)(1 + k_D^{(LS)}c + ...) \quad (4)$$

so that the desired $D = D(\infty)$ (at an infinitely long time) may be determined from extrapolation of $D^{(LS)}(c)$ to $c = 0$ as

$$D = D^{(LS)}(0) \quad (5)$$

The most concentrated solution of each sample was prepared by continuous stirring at ca. 50 °C for more than 1 week. It was optically purified by filtration through a Teflon membrane of pore size 0.45 μm. The solutions of lower concentrations were obtained by successive dilution. The polymer mass concentrations c were calculated from the weight fractions with the densities of the solvent.

The values of the refractive index $\tilde{n}_0$ of pure cyclohexane at 488 nm at the required temperatures were calculated with the values of $\tilde{n}_0$ at 34.5 °C and its temperature coefficient $d\tilde{n}_0/dT$, i.e., 1.424[19] and -5.5×10^{-4} deg^{-1},[21] respectively. The values used for the viscosity coefficient η_0 of pure cyclohexane are 0.826, 0.812, 0.799, 0.786, 0.768, 0.748, 0.726, 0.704, and 0.653 cP at 30.0, 31.0, 32.0, 33.0, 34.5, 36.0, 38.0, 40.0, and 45.0 °C, respectively.[22]

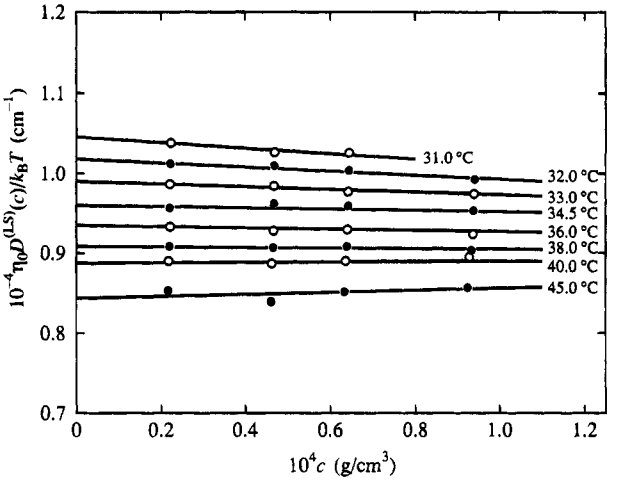

Figure 1. Plots of $\eta_0 D^{(LS)}(c)/k_BT$ against c for the a-PS sample F550-a in cyclohexane at the indicated temperatures.

Static Light Scattering. SLS measurements were carried out in cyclohexane at 34.5 °C to determine M_w of the samples F288a-2 and F550-a and to determine the mean-square radius of gyration $\langle S^2\rangle$ in cyclohexane at the same temperatures as those in the DLS measurements. A Fica 50 light scattering photometer was used for all the measurements with vertically polarized incident light of wavelength 436 nm. For a calibration of the apparatus, the intensity of light scattered from pure benzene was measured at 25.0 °C at a scattering angle of 90°, where the Rayleigh ratio $R_{Uu}(90°)$ of pure benzene was taken as 46.5×10^{-6} cm^{-1}. The depolarization ratio ϱ_u of pure benzene at 25.0 °C was found to be 0.41 ± 0.01. Scattering intensities were measured at five different concentrations and at scattering angles ranging from 15 to 142.5°. All the data obtained were analyzed by the Berry square-root plot.[23]

The test solutions were prepared in the same manner as in the case of DLS measurements.

For the refractive index increment $\partial\tilde{n}/\partial c$ at 436 nm for a-PS in cyclohexane at 34.5 °C, the result previously[17,19] reported was used. The values of $\tilde{n}_0$ of pure cyclohexane at 436 nm at the required temperatures were calculated with the literature values[23] of $\tilde{n}_0$ at 25.0 °C and its temperature coefficient $d\tilde{n}_0/dT$, i.e., 1.4328 and -5.5×10^{-4} deg^{-1}, respectively.

Results

Translational Diffusion Coefficient. Although the results are not explicitly shown here, a plot of (1/2) $\ln[g^{(2)}(t) - 1]$ against t has been found to follow a straight line over the whole range of t studied, exhibiting no curvature due to the internal motions of the chain, and the ratio A/k^2 determined from it has been found to be independent of k in the range of k studied, irrespective of the values of molecular weight, concentration, and temperature. Thus the value of $D^{(LS)}(c)$ $[=(A/k^2)_{k=0}]$ at a given finite c has been determined with sufficient accuracy (within ±0.5%) for each of the samples at any temperature examined.

Figure 1 shows plots of $\eta_0 D^{(LS)}(c)/k_BT$ against c, as an example, with the data obtained for the highest-molecular-weight sample F550-a in cyclohexane at the indicated temperatures, where η_0 is the viscosity coefficient of the solvent, k_B is the Boltzmann constant, and T is the absolute temperature. It is seen that the data points at each temperature follow a straight line, and

Table 2. Results of DLS Measurements on Polystyrene in Cyclohexane at 30.0–45.0 °C

temp, °C	$10^7 D$, cm²/s	$10^{-2}k_D^{(LS)}$, cm³/g	$10^{-2}R_H$, Å	α_H
		F128a-2		
30.0	1.16_6	−1.0	2.3_1	0.94_3
31.0	1.17_3	−0.7	2.3_4	0.95_5
32.0	1.18_1	−0.7	2.3_7	0.96_7
34.5 (Θ)	1.20_0	−0.3	2.4_5	1
36.0	1.22_0	−0.1	2.4_8	1.01_2
38.0	1.24_6	−0.1	2.5_2	1.02_9
40.0	1.28_0	0.1	2.5_5	1.04_1
45.0	1.35_8	0.2	2.6_3	1.07_3
		F288a-2		
31.0	0.73_5	−1.9	3.7_3	0.91_9
32.0	0.73_0	−1.6	3.8_3	0.94_3
34.5 (Θ)	0.72_3	−0.7	4.0_6	1
36.0	0.72_2	−0.2	4.1_9	1.03_2
38.0	0.73_9	−0.1	4.2_5	1.04_7
40.0	0.74_9	0.1	4.3_5	1.07_1
45.0	0.79_0	0.3	4.5_2	1.11_3
		F380		
32.0	0.67_1	−1.6	4.1_7	0.95_6
33.0	0.66_8	−1.2	4.2_7	0.97_9
34.5 (Θ)	0.67_3	−0.9	4.3_6	1
36.0	0.67_4	−0.9	4.4_9	1.03_0
40.0	0.69_1	0.1	4.7_2	1.08_3
45.0	0.72_0	0.3	4.9_6	1.13_8
		F550-a		
31.0	0.54_1	−3.3	5.0_7	0.91_7
32.0	0.53_7	−2.5	5.2_1	0.94_2
33.0	0.53_3	−1.7	5.3_5	0.96_7
34.5 (Θ)	0.53_1	−0.9	5.5_3	1
36.0	0.53_4	−0.8	5.6_7	1.02_5
38.0	0.53_8	−0.4	5.8_3	1.05_4
40.0	0.54_5	0.3	5.9_8	1.08_1
45.0	0.56_8	1.4	6.2_8	1.13_6

thus $D^{(LS)}(0)$ (=D) and $k_D^{(LS)}$ may be determined accurately from its ordinate intercept and slope, respectively. Similarly, we could determine D for the other samples with sufficient accuracy. The values of D and $k_D^{(LS)}$ thus obtained for a-PS in cyclohexane at various temperatures are given in Table 2 along with those of R_H calculated from the defining equation

$$R_H = k_B T/6\pi\eta_0 D \tag{6}$$

The table also includes the values of α_H calculated from the equation

$$R_H = R_{H,\Theta}\alpha_H \tag{7}$$

with the values of $R_{H,\Theta}$ for the respective samples at Θ. Equation 7 requires a comment. Strictly, α_H is defined by eq 7 with the unperturbed hydrodynamic radius $R_{H,0}$ in place of $R_{H,\Theta}$, so that for a correct determination of α_H the validity of the relation $R_{H,\Theta} = R_{H,0}$ must be confirmed experimentally. In the previous work,[11] we have already determined α_H of a-PS in good solvents following this criterion. As for the present case of a-PS in cyclohexane, the relation holds at all temperatures studied, as mentioned before.[18]

In Figure 2, the values of R_H are plotted against $1/T$, where the solid curves connect the data points smoothly. It is seen that the temperature dependence of R_H becomes more significant with increasing $1/T$ (or decreasing T) and with increasing M_w.

Mean-Square Radius of Gyration. The values of the root-mean-square radius of gyration $\langle S^2\rangle^{1/2}$ determined from SLS measurements for the a-PS samples in cyclohexane at various temperatures are given in

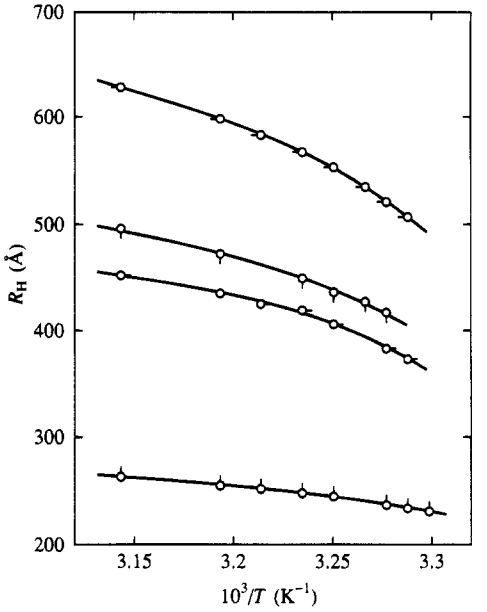

Figure 2. Plots of R_H against $1/T$ for a-PS in cyclohexane: (○, pip up) F128a-2; (○, pip right) F288a-2; (○, pip down) F380; (○, pip left) F550-a.

Table 3. Values of $\langle S^2\rangle^{1/2}$ and α_S for Polystyrene in Cyclohexane at 30.0–45.0 °C

temp, °C	$\langle S^2\rangle^{1/2}$, Å	α_S
	F128a-2	
30.0	290	0.91_8
31.0	296	0.93_7
32.0	302	0.95_6
34.5 (Θ)	316	1
36.0	322	1.01_9
38.0	330	1.04_4
40.0	336	1.06_3
45.0	349	1.10_4
	F288a-2	
31.0	475	0.90_5
32.0	494	0.94_1
34.5 (Θ)	525	1
36.0	544	1.03_6
38.0	558	1.06_3
40.0	580	1.10_5
45.0	612	1.16_6
	F380	
32.0	525	0.92_8
33.0	544	0.96_1
34.5 (Θ)	566	1
36.0	592	1.04_6
40.0	636	1.12_4
45.0	668	1.18_0
	F550-a	
31.0	622	0.85_4
32.0	657	0.90_2
33.0	688	0.94_5
34.5 (Θ)	728	1
36.0	760	1.04_4
38.0	789	1.08_4
40.0	815	1.12_0
45.0	867	1.19_1

Table 3. It also includes the values of α_S calculated from the equation

$$\langle S^2\rangle = \langle S^2\rangle_\Theta \alpha_S{}^2 \tag{8}$$

with the values of $\langle S^2\rangle_\Theta$ for the respective samples at Θ. As in the case of $R_{H,\Theta}$ mentioned above, $\langle S^2\rangle_\Theta$ may be regarded as equal to the unperturbed mean-square radius of gyration $\langle S^2\rangle_0$ in the present case. Figure 3

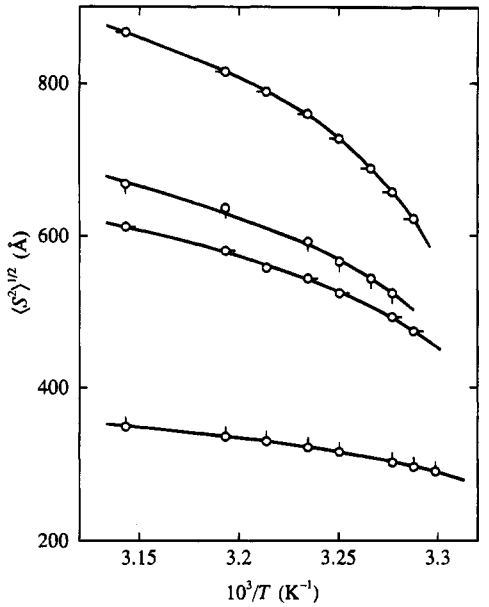

Figure 3. Plots of $\langle S^2\rangle^{1/2}$ against $1/T$ for a-PS in cyclohexane. The symbols have the same meaning as those in Figure 2.

shows plots of $\langle S^2\rangle^{1/2}$ against $1/T$ with the data given in Table 3. The solid curves connect the data points smoothly. As in the case of R_H, $\langle S^2\rangle^{1/2}$ becomes dependent on T more significantly with decreasing T and with increasing M_w.

Discussion

Relationship between α_H and α_S. Before proceeding to examine the behavior of α_H and α_S, we summarize the theoretical results for them along with α_η, for convenience.

Useful interpolation formulas for α_S^2, α_η^3, and α_H have been derived as functions of the conventional excluded-volume parameter z by Domb and Barrett,[13] by Barrett,[14] and also by Barrett,[12] respectively, which are given by

$$\alpha_S^2 = [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15} \times [0.933 + 0.067\exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \quad \text{(Domb–Barrett)} \quad (9)$$

$$\alpha_\eta^3 = (1 + 3.8\tilde{z} + 1.9\tilde{z}^2)^{0.3} \quad \text{(Barrett)} \quad (10)$$

$$\alpha_H = (1 + 6.09\tilde{z} + 3.59\tilde{z}^2)^{0.1} \quad \text{(Barrett)} \quad (11)$$

respectively, with the scaled excluded-volume parameter $\tilde{z}$ in place of z. They can reproduce the respective asymptotic forms in the limit of $\tilde{z}$ (or z) $\to \infty$, i.e.,

$$\lim_{\tilde{z}\to\infty} \alpha_S^2 = 1.54_8\tilde{z}^{0.4} \quad \text{(Domb–Barrett)} \quad (12)$$

$$\lim_{\tilde{z}\to\infty} \alpha_\eta^3 = 1.21\tilde{z}^{0.6} \quad \text{(Barrett)} \quad (13)$$

$$\lim_{\tilde{z}\to\infty} \alpha_H = 1.13_6\tilde{z}^{0.2} \quad \text{(Barrett)} \quad (14)$$

and can give the respective correct first-order perturbation coefficients,

$$\alpha_S^2 = 1 + 1.276\tilde{z} - \ldots \quad \text{(Zimm–Stockmayer–Fixman)} \quad (15)$$

$$\alpha_\eta^3 = 1 + 1.14\tilde{z} - \ldots \quad \text{(Shimada–Yamakawa)} \quad (16)$$

$$\alpha_H = 1 + 0.609\tilde{z} - \ldots \quad \text{(Stockmayer–Albrecht)} \quad (17)$$

which have been derived by Zimm, Stockmayer, and Fixman,[24] by Shimada and Yamakawa,[25] and by Stockmayer and Albrecht,[16] respectively. We note that although eq 9 has been constructed to give the correct perturbation coefficients up to the second order, its second coefficient, which is equal to 2.220, is somewhat larger than the exact value 2.082.[26]

The first-order perturbation coefficient for α_H in eq 17 has been evaluated from the Kirkwood general formula[27] for D. This D corresponds to the translational diffusion coefficient of the center of mass of the Gaussian chain at time $t = 0$. Strictly, however, the D determined from DLS measurements is the one at $t = \infty$, which corresponds to the D of the Zimm center of resistance at $t = 0$ if the preaveraged Oseen hydrodynamic interaction tensor is used. Therefore, we must use the first-order perturbation coefficient evaluated following the Kirkwood–Riseman theory,[28] in a rigorous sense. Such an evaluation has already been made by Shimada and Yamakawa[25] with the result

$$\alpha_H = 1 + 0.593\tilde{z} - \ldots \quad \text{(Shimada–Yamakawa)} \quad (18)$$

In the following comparison of the perturbation theory with the experimental results for α_H, we use eq 18 instead of eq 17.

From eqs 15, 16, and 18, we have the following linear relations between α_H and α_S and between α_η and α_S for $\tilde{z} \simeq 0$:

$$\alpha_H - 1 = 0.929(\alpha_S - 1) \quad (19)$$

$$\alpha_\eta - 1 = 0.596(\alpha_S - 1) \quad (20)$$

Now we examine the behavior of α_H and also α_η as functions of α_S. In Figure 4, the values of α_H are plotted against α_S for a-PS in cyclohexane. The unfilled circles represent the present data at various temperatures, and the triangles represent those obtained by Varma et al.[29] at 44.5 °C. They are seen to be in good agreement with each other. The figure also includes the data for α_η obtained by Miyaki[30] for a-PS in cyclohexane at various temperatures (filled circles). It is very interesting to see that the data points for α_H overlap with those for α_η within experimental error over the whole range of α_H examined. In the figure, the heavy solid and dashed curves represent the theoretical values of α_H and α_η calculated as functions of α_S from eqs 9 and 11 and from eqs 9 and 10, respectively, and the light solid and dashed straight lines represent the first-order perturbation theory values calculated from eqs 19 and 20, respectively. For $\alpha_S > 1$ (even for $\alpha_S \simeq 1$), the data points for both α_H and α_η follow the heavy dashed curve, those for α_H deviating appreciably downward from the heavy solid curve. For $\alpha_S < 1$, all the data points are located between those two curves.

α_H as a Function of $\tilde{z}$. The results in Figure 4 suggest that even the first-order perturbation theory breaks down for α_H. Thus we examine explicitly the behavior of α_H as a function of $\tilde{z}$ for a-PS in cyclohexane

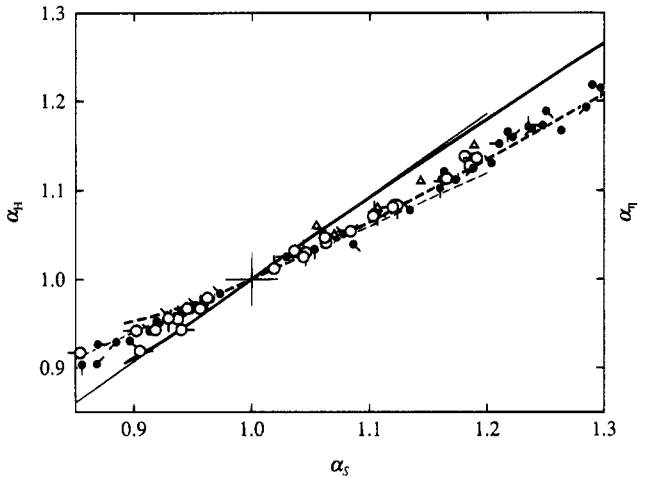

Figure 4. Plots of α_H (unfilled symbols) and α_η (filled circles) against α_S for a-PS in cyclohexane at various temperatures: (○, pip up) F128a-2 (present data); (○, pip right) F288a-2 (present data); (○, pip down) F380 (present data); (○, pip left) F550-a (present data); (△) for $2.38 \times 10^5 \leq M_w \leq 5.47 \times 10^6$ at 44.5 °C (Varma et al.);[29] (●) for $1.34 \times 10^6 \leq M_w \leq 5.68 \times 10^7$ at 30.0–55.0 °C (Miyaki).[30] The various directions of pips indicate different molecular weights. The heavy solid and dashed curves represent the values of α_H and α_η calculated from eqs 11 and 10, respectively, with eq 9, and the light solid and dashed straight lines represent the values of α_H and α_η calculated from eqs 19 and 20, respectively (see the text).

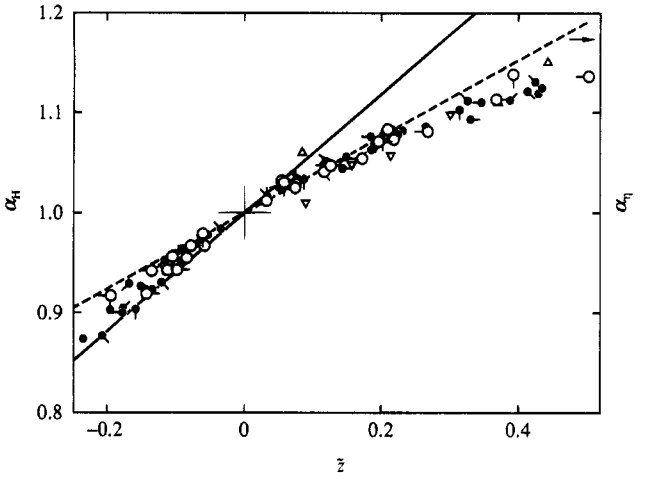

Figure 5. Plots of α_H (unfilled symbols) and α_η (filled circles) against $\tilde{z}$ for a-PS in cyclohexane at various temperatures: (▽) for $6.77 \times 10^6 \leq M_w \leq 2.06 \times 10^7$ at 36.4–38.8 °C (Vidakovic and Rondelez).[32] The other symbols have the same meaning as those in Figure 4. The solid and dashed curves represent the values of α_H and α_η calculated from eqs 18 and 16, respectively (see the text).

at various temperatures above and below Θ. Recall that for the HW chain of total contour length L, the scaled excluded-volume parameter $\tilde{z}$ is defined by

$$\tilde{z} = (3/4)K(\lambda L)z \tag{21}$$

and that the conventional excluded-volume parameter z is now given by

$$z = (3/2\pi)^{3/2}(\lambda B)(\lambda L)^{1/2} \tag{22}$$

where

$$B = \beta/a^2 c_\infty^{3/2} \tag{23}$$

with

$$c_\infty = \lim_{\lambda L \to \infty} (6\lambda \langle S^2 \rangle_0 / L) = \frac{4 + (\lambda^{-1}\tau_0)^2}{4 + (\lambda^{-1}\kappa_0)^2 + (\lambda^{-1}\tau_0)^2} \tag{24}$$

Here, λ^{-1} is the static stiffness parameter of the HW chain, κ_0 and τ_0 are the differential-geometrical curvature and torsion, respectively, of its characteristic helix taken at the minimum zero of its elastic energy, and β is the binary-cluster integral between beads with a their spacing. In eq 21, the coefficient $K(L)$ is given by

$$K(L) = \frac{4}{3} - 2.711L^{-1/2} + \frac{7}{6}L^{-1} \quad \text{for } L > 6$$
$$= L^{-1/2}\exp(-6.611L^{-1} + 0.9198 + 0.03516L) \quad \text{for } L \leq 6 \tag{25}$$

Note that L is related to the molecular weight M by the equation

$$L = M/M_L \tag{26}$$

where M_L is the shift factor defined as the molecular weight per unit contour length.

The values of the HW model parameters have been determined previously[1,31] from the mean-square optical anisotropy $\langle \Gamma^2 \rangle$ and $\langle S^2 \rangle_\Theta$ with the results $\lambda^{-1}\kappa_0 = 3.0$, $\lambda^{-1}\tau_0 = 6.0$, $\lambda^{-1} = 20.6$ Å, and $M_L = 35.8$ Å^{-1}. On the other hand, the parameter β required for the calculation of $\tilde{z}$ has been determined as a function of T from A_2 for a-PS in cyclohexane, and its values (in Å^3) per repeat unit may be calculated from[17]

$$\beta = 65(1 - \Theta/T) \quad \text{for } T \geq \Theta$$
$$= 65(1 - \Theta/T) - 610(1 - \Theta/T)^2 \quad \text{for } T < \Theta \tag{27}$$

With these values of the HW model parameters and β, we have calculated $\tilde{z}$ from eq 21 with eqs 22–26 for the a-PS samples in cyclohexane at the required temperatures. Since all the samples used in this study have large M_w, the values of $\tilde{z}$ thus calculated for them are not very different from the corresponding values of z; the absolute values of the former are smaller than those of the latter by ca. 4.8, 2.9, 2.8, and 2.2% for the samples F128a-2, F288a-2, F380, and F550-a, respectively.

In Figure 5, the values of α_H are plotted against $\tilde{z}$ with the present data for a-PS in cyclohexane at various temperatures (unfilled circles). It includes the data for α_H obtained by Varma et al.[29] from DLS measurements for a-PS samples with $2.38 \times 10^5 \leq M_w \leq 5.47 \times 10^6$ in cyclohexane at 44.5 °C (triangles up) and by Vidakovic and Rondelez[32] from sedimentation for a-PS samples with $6.77 \times 10^6 \leq M_w \leq 2.06 \times 10^7$ in cyclohexane at 36.4–38.8 °C (triangles down). The figure also includes the data for α_η by Miyaki[30] for a-PS samples with $1.34 \times 10^6 \leq M_w \leq 5.68 \times 10^7$ in cyclohexane at 30.0–55.0 °C (filled circles), for comparison. For all these literature data, $\tilde{z}$ have been calculated from eq 21 with eqs 22–26 and with the values of the HW model parameters and β given above. The solid and dashed straight lines represent the first-order perturbation theory values for α_H and α_η calculated from eqs 18 and 16, respectively. (Note that α_η has been calculated from the equation $\alpha_\eta = 1 + 0.380\tilde{z}$.) The present and literature data for α_H agree with each other within experimental error.

It is seen from Figure 5 that the first-order perturbation theory of α_H does not fit the experimental data even

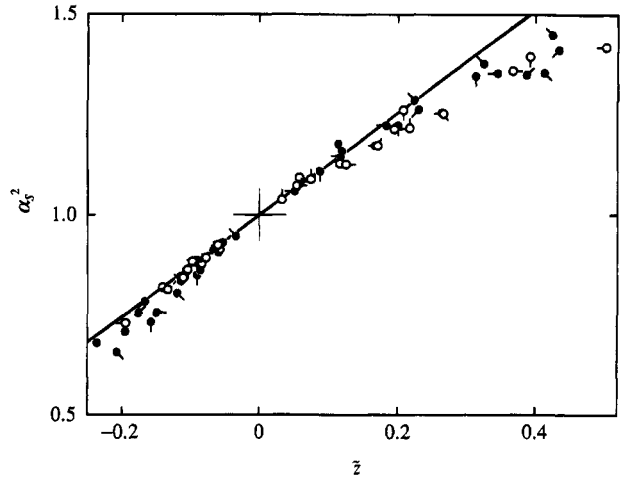

Figure 6. Plots of α_S^2 against $\tilde{z}$ for a-PS in cyclohexane at various temperatures. The symbols have the same meaning as those in Figure 4. The solid curve represents the values calculated from eq 15 (see the text).

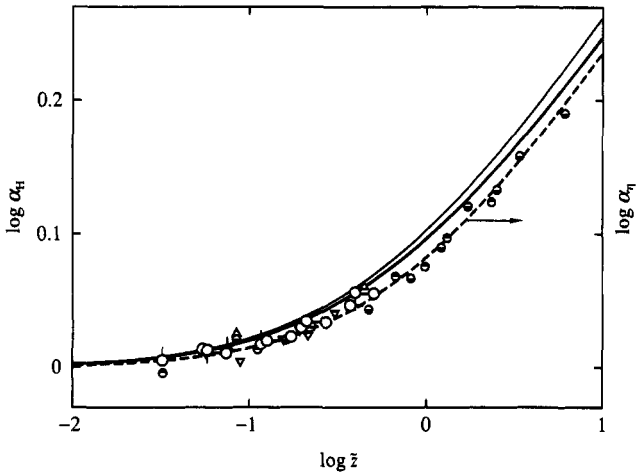

Figure 7. Double-logarithmic plots of α_H against $\tilde{z}$ for a-PS: (◒) in toluene at 15.0 °C (previous data);[11] (◓) in 4-*tert*-butyltoluene at 50.0 °C (previous data).[11] The other symbols have the same meaning as those in Figure 4. The light and heavy solid curves represent the values calculated from eqs 11 and 28, respectively (see the text). The dashed curve represents the values of α_η calculated from eq 10.

for small $|\tilde{z}|$. In contrast to this, the corresponding theory of α_η (dashed straight line) is seen to be apparently valid for α_H as well as for α_η over a rather wide range of $\tilde{z}$ ($-0.06 \lesssim \tilde{z} \lesssim 0.1$). For comparison, the values of α_S^2 are plotted against $\tilde{z}$ in Figure 6 for a-PS in cyclohexane above and below Θ, where the unfilled and filled circles represent the present data and those by Miyaki,[30] respectively, and the straight line represents the first-order perturbation theory values calculated from eq 15. As in the case of α_η, the first-order perturbation theory may explain the data over a rather wide range of $\tilde{z}$ ($-0.1 \lesssim \tilde{z} \lesssim 0.1$). Thus the behavior of α_H is quite different from that of α_η and α_S. The present finding for α_H implies that the coefficient of $\tilde{z}$ in eq 18 (or 17) may be too large.

Necessarily, as in Figure 4, the data points for α_H coincide with those for α_η within experimental error in the range of $\tilde{z}$ studied. This result is consistent with the previous ones for a-PS in the two good solvents toluene and 4-*tert*-butyltoluene and suggests that α_H almost agrees with α_η irrespective of the values of $\tilde{z}$. Figure 7 shows double-logarithmic plots of α_H against $\tilde{z}$ with the same data as those in Figure 5 along with the previous data[11] for a-PS in toluene at 15.0 °C (bottom-half-filled circles) and in 4-*tert*-butyltoluene at 50.0 °C (top-half-filled circles). The light solid curve represents the values of α_H calculated from the Barrett equation (11). The heavy solid curve represents the modified values calculated from the equation taking into account the effect of the fluctuating hydrodynamic interaction, i.e.,[15]

$$\alpha_H = \alpha_H^{(Z)} f_H \tag{28}$$

where $\alpha_H^{(Z)}$ is given by eq 11 and f_H is defined by

$$f_H = \frac{1 - \delta_{1,0}(1)}{1 - \delta_{1,0}(\alpha_S^{-1})} \tag{29}$$

with

$$\delta_{1,0}(x) = 0.12x^{0.43} \qquad (0 < x < 1) \tag{30}$$

Note that in eq 29, the ratio of the bead diameter to the effective bond length (for the Gaussian chain) has been taken as unity as in the previous papers.[11,15] On the other hand, the dashed curve represents the values of α_η calculated from eq 10. It is seen that all the data points form a single-composite curve irrespective of the solvent condition. The results confirm that α_H becomes a function only of $\tilde{z}$, or in other words, the QTP scheme may be valid for α_H as well as for α_S and α_η.

As anticipated from the results in Figure 5, the data points for α_H closely follow the dashed curve for α_η over the whole range of $\tilde{z}$ displayed. This indicates that the relation $\alpha_H \simeq \alpha_\eta$ holds experimentally, since the Barrett values (dashed curve) for α_η have been found to be able to reproduce the experimental ones.[4,11] The light solid curve deviates progressively upward from the data points with increasing $\tilde{z}$. The deviation is decreased by taking account of the effect of fluctuating hydrodynamic interaction on α_H, as shown by the heavy solid curve. However, the deviation is still somewhat large for small $\tilde{z} \lesssim 1$. This suggests that the above effect should be reconsidered more rigorously, especially in the range of small $\tilde{z}$, or that there still remains some other possible effect to be considered.

Conclusion

In this work, we have investigated α_H as a function of $\tilde{z}$ (and also α_S) for a-PS with $f_r = 0.59$ in cyclohexane at various temperatures ranging from 30.0 to 45.0 °C, using the samples with such large M_w that the effects of chain stiffness on α_H and $\tilde{z}$ may be small. It has been found that the observed values of α_H for $\tilde{z} > 0$ are appreciably smaller than the first-order perturbation theory values and those for $\tilde{z} < 0$ are larger than the latter, indicating that its (first) coefficient of $\tilde{z}$ may be too large. It has also been found that α_H coincides with α_η within experimental error even in the range of small $|\tilde{z}|$, as in the previous results[11] for a-PS in the two good solvents toluene and 4-*tert*-butyltoluene. The present and previous data for α_H plotted against $\tilde{z}$ give a single-composite curve, indicating that α_H becomes a function only of $\tilde{z}$ irrespective of the solvent condition. This confirms that the QTP scheme may be valid for α_H as well as for α_S and α_η. The single-composite curve above is close to that given by the Barrett equation[14] for α_η with $\tilde{z}$ in place of z in the range of $\tilde{z} > 0$.

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