Excluded-Volume Effects in Star Polymer Solutions: Four-Arm Star Polystyrene in Cyclohexane near the Θ Temperature

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ABSTRACT: Light scattering and viscosity measurements were made on anionically polymerized four-arm star polystyrene samples with weight-average molecular weights M_w of 8.5 × 10^4 to 3.1 × 10^6 in cyclohexane at different temperatures to determine the mean-square radius of gyration $\langle S^2 \rangle$, the second and third virial coefficients (A_2 and A_3), and the intrinsic viscosity. The values of A_3 at the Θ point (34.5 °C), where A_2 for any sample was essentially zero, were about 5×10^{-4} cm^6 mol g^{-3} and yielded a value of 4×10^{-45} cm^6 for the ternary cluster integral. It was shown that although the binary cluster approximation breaks down for A_3 near Θ, it holds for $\langle S^2 \rangle$ and A_2, as is the case with linear chains, if the binary cluster integral is replaced by a linear combination of the binary and ternary cluster integrals. The expansion factor $\alpha_S{}^2$ for $\langle S^2 \rangle$ and that for the intrinsic viscosity plotted against the excluded-volume parameter z in the coil limit for $M_w > 8 \times 10^5$ came close to the known relations for linear polystyrene of high molecular weight in cyclohexane. On the other hand, the relation between the interpenetration function Ψ and $\alpha_S{}^3$ for the star polymer appeared far above that for the linear chain at temperatures above Θ. These experimental results for $\alpha_S{}^2$ and Ψ were quantitatively explained by the interpolation formulas constructed in this work.

Introduction

Much work has been done on dilute solutions of star polymers,[1,2] but our understanding of excluded-volume effects in those polymers is still far below the level that has been reached for linear chains. Indeed, little is as yet known about the validity of the binary cluster approximation to dilute-solution properties and about the behavior of the radius and viscosity expansion factors and the interpenetration function even for four-arm star polymers in the vicinity of the Θ point.

The present work was undertaken to explore these by light scattering and viscosity measurements on four-arm star polystyrene samples with weight-average molecular weights M_w of 8.5 × 10^4 to 3.1 × 10^6 in cyclohexane at different temperatures. Use of the polystyrene + cyclohexane system is advantageous in that the experimental results obtained for $\langle S^2 \rangle_z$ (the z-average mean square radius of gyration), A_2 (the second virial coefficient), A_3 (the third virial coefficient), and $[\eta]$ (the intrinsic viscosity) of the star polymer can be compared with precise data[3−6] available for the linear chain. In order to discuss $\langle S^2 \rangle_z$ and A_2 in quantitative terms, some theoretical calculations were also performed in this work.

Experimental Section

Samples. Three samples of four-arm star polystyrene, 4S77, 4S184, and 4S662, were kindly furnished by Professor Hiroshi Watanabe of the Institute for Chemical Research, Kyoto University. These samples had been synthesized by anionic polymerization and shown to have almost uniform arm lengths.[7] However, when examined by gel permeation chromatography (GPC), each sample exhibited a small subpeak (less than 1% by area) corresponding to the arms produced by degradation of the star polymer during long-time storage. Therefore, the samples were purified several times by fractional precipitation and GPC. The samples thus obtained had no sub-peak on their chromatograms and thus contained no imperfect star molecules. These samples from 4S77, 4S184, and 4S662 were designated as 4S77′, 4S184′, and 4S662′, respectively.

In addition to them, we synthesized three samples of four-arm star polystyrene by anionic polymerization in the manner reported by Watanabe et al.[7] A six-functional reagent was used as the coupler, but two coupling sites (Si−Cl bonds) were left unreacted by steric hindrance.[7] Upon exposure to air, hydroxyl groups are likely to be generated from these Si−Cl bonds, but they may not affect solution properties when each arm is sufficiently long. The samples obtained were purified by successive fractional precipitation to remove the precursor linear chains contained and designated as 4S22, 4S39, and 4S384. The ratio of M_w for each star polymer to that for its arm (the precursor linear polymer before coupling) was 4 ± 0.2 when determined by light scattering. The weight-average to number-average molecular weight ratios for the star polymer samples were estimated by GPC to be less than 1.03 for 4S39, 4S77′, and 4S184′ and 1.06 for 4S384.

Light Scattering. Light scattering measurements were made on a Fica-50 light scattering photometer with vertically polarized incident light of 436-nm wavelength in an angular range from 15 to 150°. The apparatus was calibrated with benzene at 25 °C as the reference liquid, whose Rayleigh ratio at 436 nm was taken to be 46.5×10^{-6} cm^{-1}.[8] Seven solutions of different polymer concentrations were studied for each sample. The polymer mass concentration c was calculated from the gravimetrically determined weight fraction of the solute with the solution density ρ.

Densities of cyclohexane solutions of sample 4S77′ were measured at 25, 30, and 40 °C in the range of c below 3×10^{-2} g cm^{-3}, with the result that

$$\rho = 0.77384 + 0.277_5 c \quad (\text{g cm}^{-3};\ 25\ ^\circ\text{C})$$

$$\rho = 0.76900 + 0.280_3 c \quad (\text{g cm}^{-3};\ 30\ ^\circ\text{C})$$

$$\rho = 0.75970 + 0.286_0 c \quad (\text{g cm}^{-3};\ 40\ ^\circ\text{C})$$

Necessary values at other temperatures were obtained by interpolation or extrapolation.

The specific refractive index increment $\partial n/\partial c$ of four-arm star polystyrene in cyclohexane was determined at 25, 30, 35, and 40 °C for $c \lesssim 2.5 \times 10^{-2}$ g cm^{-3} using a modified Shulz−Cantow

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type differential refractometer. It depended slightly on molecular weight at any temperature T examined. The $\partial n/\partial c$ values at 436 nm were found to be represented by

$$\partial n/\partial c = 0.1646 + 4.70 \times 10^{-4} T\ (°\mathrm{C}) + 1.50 \times 10^{2} M_{\mathrm{w}}^{-1}\ (\mathrm{cm}^3\ \mathrm{g}^{-1})$$

After the completion of the present light scattering measurement, Terao et al.[9] found in their work on concentrated solutions that the attenuation of light by scattering, absorption, and multiple scattering cannot always be ignored for cyclohexane solutions of polystyrene. Close examination revealed that for 436-nm wavelength, these effects give rise to small errors (less than 10^{-5} cm^3 mol g^{-2}) in A_2 near the Θ point where A_2 is vanishingly small. Though M_{w}, $\langle S^2\rangle_z$, and A_3 (even at Θ) were free from the effects, we corrected our raw scattering data according to Terao et al.'s procedure, which is briefly described below.

Terao et al.[9] expressed the reduced excess scattering intensity R_θ at scattering angle θ as

$$R_\theta = R_{\theta,\mathrm{app}} \exp(2.303\gamma lc + \tau l) - f(\theta)\tau^2 \tag{1}$$

by considering the above-mentioned effects. Here, $R_{\theta,\mathrm{app}}$ is the apparent (or measured) reduced scattering intensity at θ, γ is the absorbance of light, l is the inner diameter of the cylindrical cell used, τ is the turbidity, and $f(\theta)$ is a certain function of θ associated with multiple scattering; for our system, $l = 2.2$ cm, $f(\theta) = 0.07 + 0.09 \sin\theta$ (cm), and $\gamma = 0.16$ cm^2 g^{-1} at 436 nm.[9] The turbidity may be related to R_{90} (the value of R_θ at $\theta = 90°$) for vertically polarized incident light by

$$\tau = 8\pi R_{90}/3 \tag{2}$$

provided that the angular dependence of R_θ is negligibly small. Substitution of this equation together with experimental $R_{90,\mathrm{app}}$ and c into eq 1 for $\theta = 90°$ allows us to determine τ for the solution considered. We may then get R_θ as a function of θ from eq 1 with this τ and the experimental $R_{\theta,\mathrm{app}}$. For long chains, the right-hand side of eq 2 must be multiplied by $(1 + \Delta)$, where Δ represents the effect of the angular dependence of R_θ. The factor $(1 + \Delta)$ was 1.045 when evaluated for the Gaussian four-arm star with $\langle S^2\rangle^{1/2} = 40$ nm (this radius corresponds to the one for the highest molecular weight studied in this work). However, the values of R_θ calculated from eq 1 with this factor taken into account did not differ more than 1% from those evaluated by use of eq 2. In particular, the difference was less than 0.1% for R_0 (the zero-angle value of R_θ), with which the present correction is primarily concerned. Thus, the R_θ values corrected with eqs 1 and 2 were used for our data analysis.

Viscometry. Intrinsic viscosities were measured by conventional capillary viscometers of the Ubbelohde type.

Results

Virial Coefficients. Figure 1 illustrates the concentration dependence of Kc/R_0 for sample 4S184′ at the indicated temperatures, where K denotes the optical constant. These data were analyzed using the Bawn plot[10,11] of $S(c_1,c_2)$ vs $c_1 + c_2$ based on the equation

$$S(c_1,c_2) \equiv \frac{(Kc/R_0)_{c=c_2} - (Kc/R_0)_{c=c_1}}{c_2 - c_1} = 2A_2 + 3A_3(c_1 + c_2) + \ldots \tag{3}$$

where $(Kc/R_0)_{c=c_1}$ and $(Kc/R_0)_{c=c_2}$ denote the values of Kc/R_0 at different concentrations c_1 and c_2, respectively. The Bawn plots constructed are shown in Figure 2, where the data for pairs of neighboring c_1 and c_2 in a series of polymer concentrations are omitted, since they were less accurate. The plotted points at each T follow a straight line whose intercept and slope permit us to determine A_2 and A_3, respectively. Similar plots for six samples at 34.5 °C (34 °C for three samples) are displayed in Figure 3.

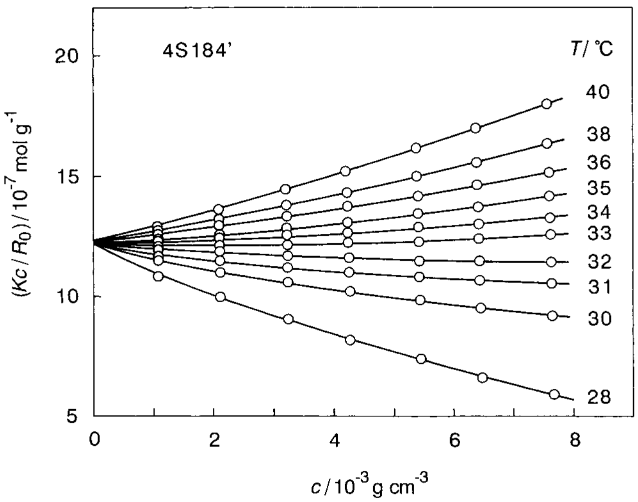

Figure 1. Concentration dependence of Kc/R_0 for four-arm star polystyrene 4S184′ in cyclohexane at indicated temperatures.

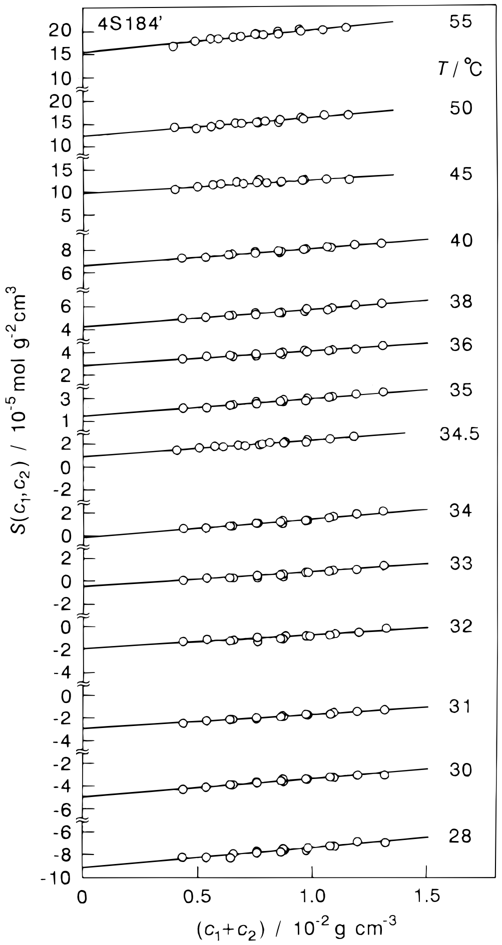

Figure 2. Plots of $S(c_1,c_2)$ vs $c_1 + c_2$ for 4S184′ in cyclohexane at indicated temperatures.

The molecular weight of each sample was determined as described elsewhere.[11] Namely, the apparent molecular weight M_{app} defined by $M_{\mathrm{app}} = [Kc/R_0 - 2A_2c - 3A_3c^2]^{-1}$ was calculated with the values of A_2 and A_3 and then extrapolated to $c = 0$. The values of M_{w} thus obtained at different T agreed within ±1.9% for any sample. The data for M_{w}, A_2, and A_3 at 34.5 °C are

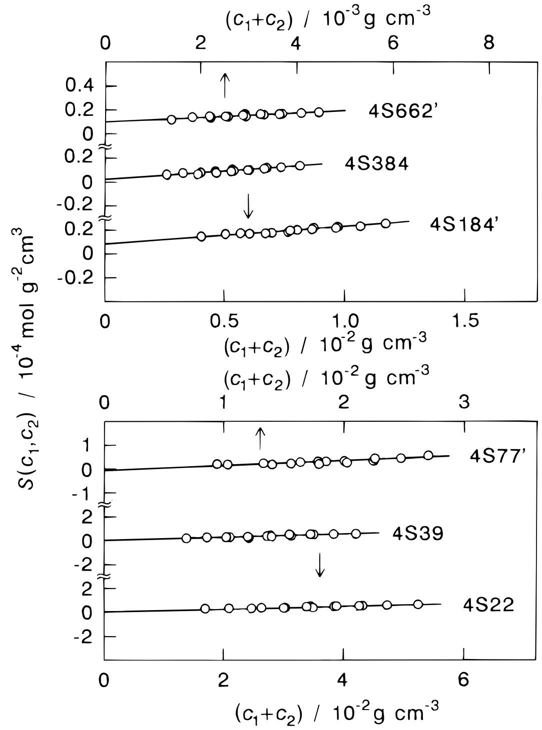

Figure 3. Plots of $S(c_1,c_2)$ vs $c_1 + c_2$ for cyclohexane solutions of samples 4S662′, 4S384, and 4S184′ at 34.5 °C and samples 4S77′, 4S39, and 4S22 at 34 °C.

Table 1. Results from Light Scattering and Viscosity Measurements on Four-Arm Star Polystyrene Samples in Cyclohexane at 34.5 °C

sample	$10^{-4}M_w$	10^5A_2, cm^3 mol g^{-2}	10^4A_3, cm^6 mol g^{-3}	$\langle S^2\rangle_z^{1/2}$, nm	$10^{-2}[\eta]$, cm^3 g^{-1}	$10^{-23}\Phi$, mol^{-1}
4S22	8.50	0.3	4.7		0.196	
4S39	15.5	0.5	4.0		0.253	
4S77′	32.9	−0.2	8.0	$13._1$	0.376	3.7_4
4S184′	80.5	0.5	3.9	20.4	0.589	3.8_0
4S384	143	0.2	4.2	27.6	0.806	3.7_3
4S662′	312	0.2	5.5	40.5	1.149	3.6_7

summarized in Table 1; the values for samples 4S22, 4S39, and 4S77′ are the interpolated ones.

The second virial coefficients for the six samples are plotted against T in Figure 4. They are seen to become identically zero at 34−35 °C. In fact, all the A_2 values at 34.5 °C are essentially zero without discernible variation with M_w. Thus, the Θ temperature for four-arm star polystyrene in cyclohexane may be determined as 34.5 °C, the same temperature as that for linear polystyrene. Our Θ agrees with Strazielle and Helz's result[12] for a sample with $M_w = 3.12 \times 10^5$ but is slightly higher than that (32.5−33 °C) reported by Roovers and Bywater[13] for samples with $M_w = 9.33 \times 10^4$ and 1.52×10^5. The last group obtained a much lower temperature of 29.2 °C for $M_w = 5.02 \times 10^4$. This is most likely due to the effect of chain (or arm) ends on A_2, as is the case for linear polystyrene with $M_w < 2 \times 10^4$.[14-19]

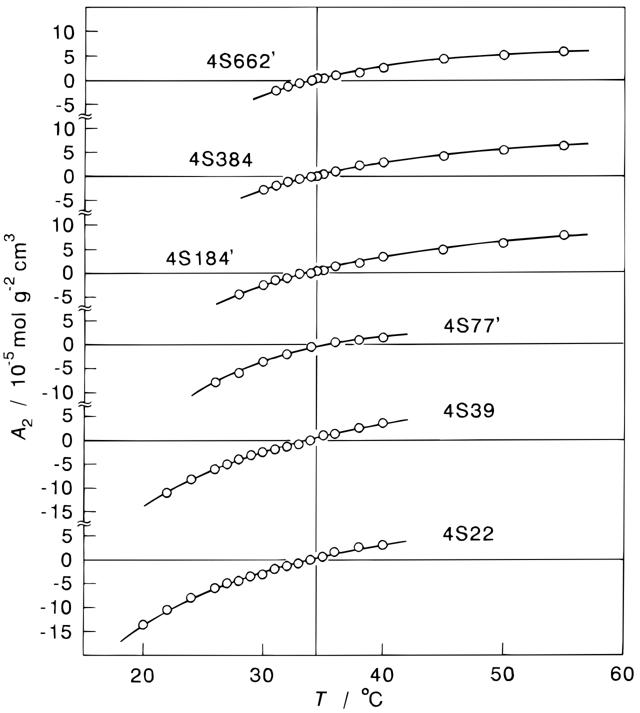

Figure 4. Temperature dependence of A_2 for four-arm star polystyrene samples in cyclohexane. The thin vertical line shows 34.5 °C (the Θ temperature).

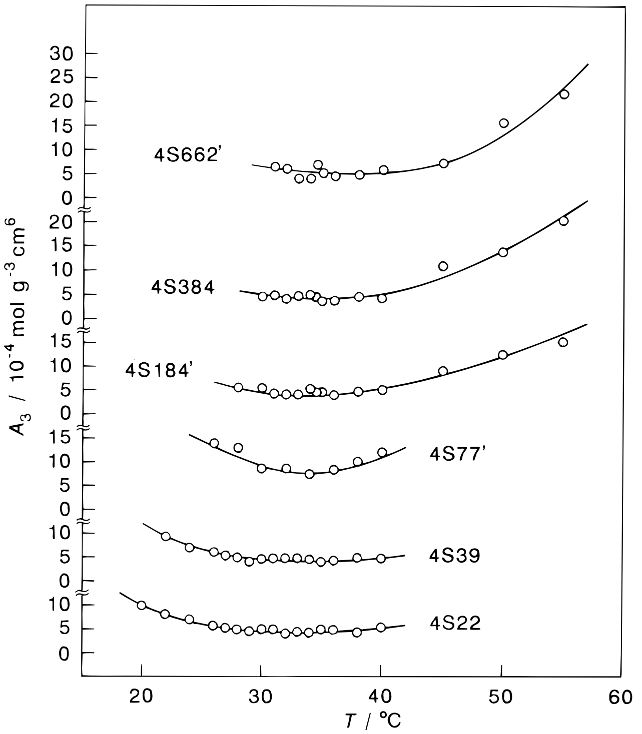

Figure 5. Temperature dependence of A_3 for four-arm star polystyrene samples in cyclohexane.

Figure 5 depicts the temperature dependence of A_3. The curve for each sample is parabolic with a broad positive minimum around Θ and the minimum becomes shallower as M_w decreases. These features are similar to what was observed for linear flexible polymers in Θ solvents.[6,19,20] We note that those features for the latter class of polymers have been explained theoretically as due to remarkable ternary cluster effects.[21] The molecular weight dependence of A_3 for four-arm star polystyrene at 34.5 °C is shown in Figure 6 (unfilled circles), along with that for linear polystyrene in the same solvent (filled circles).[6] The values of A_3 for both polymers are almost constant in the indicated M_w range, scattering around 4.5×10^{-4} cm^6 mol g^{-3}.

Radius of Gyration. Values of $(Kc/R_\theta)_{c=0}$ were obtained by extrapolation of $(Kc/R_\theta - 2A_2c - 3A_3c^2)$ at fixed θ to $c = 0$,[20] and radii of gyration were evaluated from the initial slopes of $(Kc/R_\theta)_{c=0}{}^{1/2}$ vs $\sin^2(\theta/2)$ plots. Figure 7 depicts the temperature dependence of $\langle S^2\rangle_z{}^{1/2}$ thus obtained for the three highest molecular weight samples 4S184′, 4S384, and 4S662′.

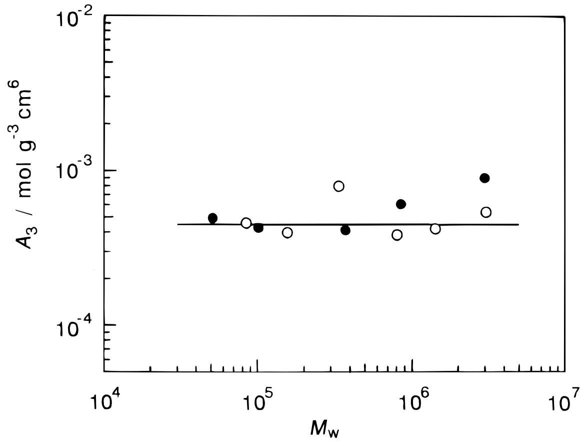

Figure 6. Molecular weight dependence of A_3 for four-arm star polystyrene (unfilled circles) and linear polystyrene[6] (filled circles) in cyclohexane at 34.5 °C.

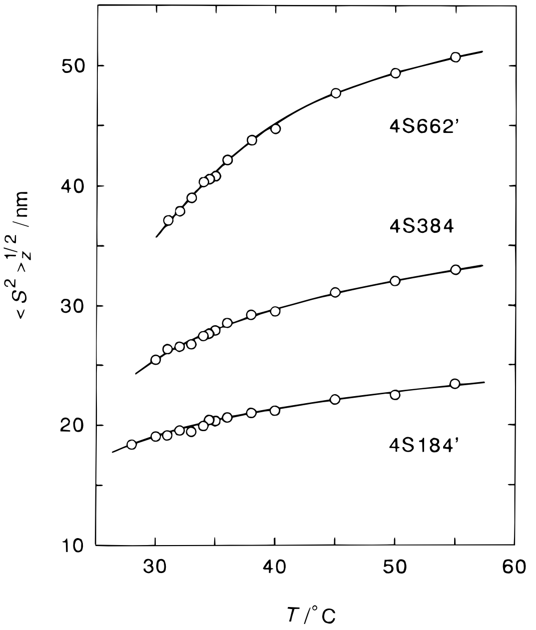

Figure 7. Temperature dependence of $\langle S^2\rangle_z^{1/2}$ for four-arm star polystyrene samples in cyclohexane.

Our $\langle S^2\rangle_z$ data at Θ are compared with those of Berry[22] and Roovers et al.[13,23] in Figure 8, in which Miyaki's data[3,4] for linear polystyrene under the same solvent condition are included. The straight line fitting the present data is expressed by

$$\langle S^2\rangle_z = 5.3 \times 10^{-18} M_w \quad \text{(star)} \tag{4}$$

in units of cm^2. If the relation $\langle S^2\rangle_z = 8.35 \times 10^{-18}\, M_w$ (cm^2) for linear polystyrene, i.e., the upper straight line in the figure, is used, the ratio g_S of $\langle S^2\rangle_z$ for four-arm star polystyrene to that for linear polystyrene in cyclohexane at Θ is evaluated as 0.63. This is very close to the Gaussian chain value 0.625 obtained from the equation of Zimm and Stockmayer[24]

$$g_{S0} = (3f - 2)/f^2 \tag{5}$$

where the subscript 0 signifies the unperturbed state and f denotes the arm number. A similarly close ratio of 0.65 was reported by Hadjichristidis and Roovers[25] for four-arm star polyisoprene in dioxane (32.5 °C).

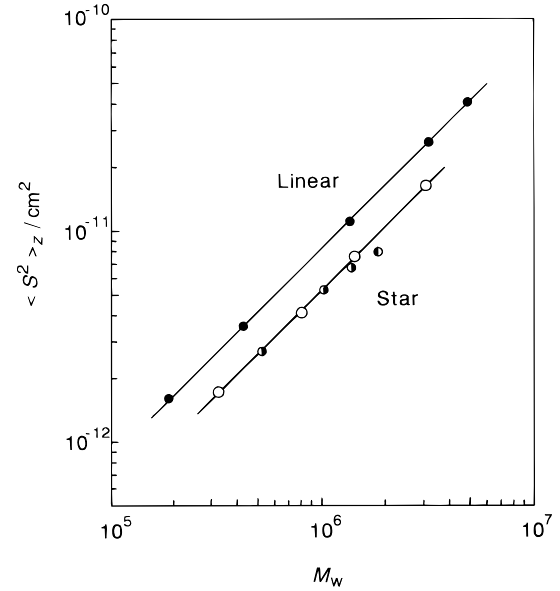

Figure 8. Molecular weight dependence of $\langle S^2\rangle_z$ for four-arm star polystyrene (○, this work; ◐, Berry;[22] ◑, Roovers et al.[13,23]) and linear polystyrene (●, Miyaki et al.[3,4]) in cyclohexane at the Θ temperature.

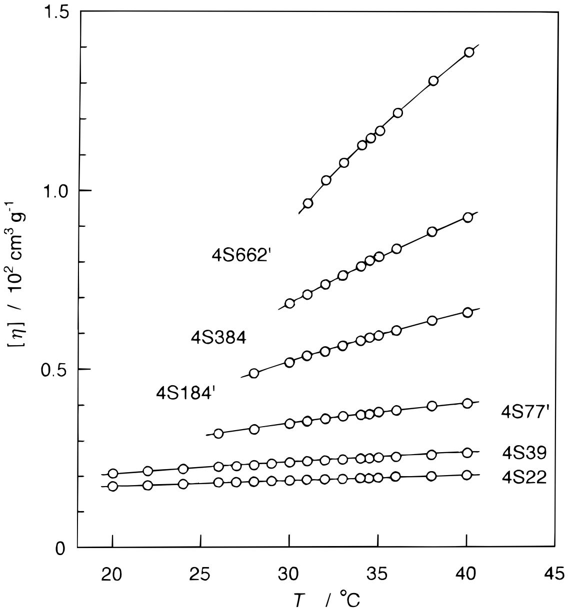

Figure 9. Temperature dependence of $[\eta]$ for four-arm star polystyrene samples in cyclohexane.

Intrinsic Viscosity. Figure 9 shows the temperature dependence of $[\eta]$ for the six samples of four-arm star polystyrene in cyclohexane. The values at the Θ temperature are again compared with the literature data for four-arm star[12,26] and linear polystyrenes[3,27] in Figure 10. The straight line for the star polymer is represented by

$$[\eta] = 6.6 \times 10^{-2} M_w^{\ 0.50} \quad \text{(star)} \tag{6}$$

in units of cm^3 g^{-1}. This is combined with the relation $[\eta] = 8.8 \times 10^{-2}\, M_w^{\ 0.50}$ (cm^3 g^{-1}) for the linear polymer[3,27] to obtain a value of 0.75 for the ratio g_η of $[\eta]$ for four-arm star polystyrene to that for linear polystyrene. This value is close to those (0.76−0.77) reported by Douglas et al.[2] for four-arm star polymers in the Θ state, but all these are significantly smaller than the value 0.824 predicted by the Zimm−Kilb theory.[28] Hence, g_η for long flexible star polymers in the unperturbed state remains to be investigated theoretically.

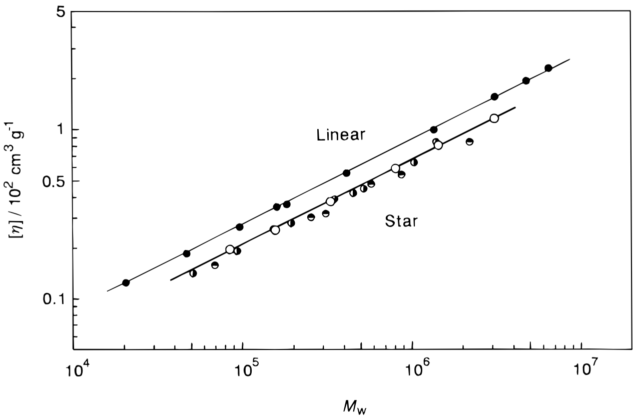

Figure 10. Molecular weight dependence of $[\eta]$ for four-arm star polystyrene (○, this work; ◑, Roovers and Bywater,[13] ◓, Strazielle and Herz[12]) and linear polystyrene (●, Miyaki et al.[3,27]) in cyclohexane at the Θ temperature.

The Flory viscosity factor defined by

$$\Phi = \frac{[\eta]M_w}{6^{3/2}\langle S^2\rangle_z^{\,3/2}} \tag{7}$$

was calculated for samples 4S77′, 4S184′, 4S384, and 4S662′ at 34.5 °C to obtain an average value of 3.6×10^{23} mol^{-1}, which is in substantial agreement with the value 3.7×10^{23} mol^{-1} obtained earlier by Roovers and Toporowski.[23] for the same system. These Φ values are much larger than what is known for linear polystyrene in cyclohexane, reflecting the difference in molecular architecture. Our numerical results for $\langle S^2\rangle_z$, $[\eta]$, and Φ at 34.5 °C have been presented in the fifth to seventh columns of Table 1.

Discussion

Ternary Cluster Effects. We have found that A_3 for four-arm star polystyrene in cyclohexane at Θ remains positive. This reveals the breakdown of the binary cluster approximation to it. If the ternary cluster integral β_3 is incorporated in the *single* contact approximation, A_3 for any long bead chains is expressed by

$$A_3 = \frac{{N_A}^2 n^3}{3M^3}\beta_3 \tag{8}$$

where N_A is the Avogadro constant, n is the number of beads in one chain, and M is the molecular weight. This equation predicts A_3 at Θ to be independent of molecular weight and chain architecture, being consistent with the behavior observed for star and linear polystyrenes in Figure 6. Applying eq 8 to the A_3 data in the figure (with one bead taken as the monomer unit), we obtain $\beta_3 = 4 \times 10^{-45}$ cm^6 for both polymers in cyclohexane. With this β_3 value, we here examine effects of ternary cluster interactions on A_2 and $\langle S^2\rangle$ of four-arm star polystyrene.

The perturbation theory for A_2 of Gaussian star polymers with f uniform arms is written as[29]

$$A_2 = \frac{N_A n^2}{2M^2}\left\{\beta + \frac{4\sqrt{f}}{\sqrt{n}}[(f-1)(2-\sqrt{2})-2]\left(\frac{3}{2\pi b^2}\right)^{3/2}\beta_3 + \ldots\right\} \tag{9}$$

where β is the effective binary cluster integral defined by the sum of β_2 (the binary cluster integral) and $C\beta_3$, with C being a constant for a given system, and b is the bead spacing. The first term in the braces vanishes at Θ, but the second term remains nonzero unless the molecular weight is infinitely high. Using $\beta_3 = 4 \times 10^{-45}$ cm^6 and $b = 7.3 \times 10^{-8}$ cm (obtained from eq 4), we find that the contribution of the latter term to A_2 (for $f = 4$) is -6×10^{-6} cm^3 mol g^{-2} for the lowest molecular weight sample 4S22. This value is hardly beyond the experimental uncertainty, and thus the residual ternary cluster term has no substantial effect on A_2 in the molecular weight range studied here.

With the Gaussian model, we have calculated $\langle S^2\rangle$ up to the order of β_2 and β_3. The result reads

$$\langle S^2\rangle = \langle S^2\rangle_0\left[1 + K_f z + K_f'\left(\frac{3}{2\pi b^2}\right)^3\beta_3 + \ldots\right] \tag{10}$$

where

$$K_f = \frac{6}{f^{1/2}(3f-2)}\left\{\frac{67}{315} + \frac{268\sqrt{2}-67}{315}(f-1) + \frac{202\sqrt{2}-276}{45}(f-1)(f-2)\right\} \tag{11}$$

$$K_f' = \frac{6}{3f-2}\left\{-\frac{13\pi}{24} - \frac{13\pi}{8}(f-1) + \left[\frac{101}{45} + \frac{103}{54}\pi - \frac{14}{5}\sqrt{3}\right](f-1)(f-2) + \left[\frac{104}{9} - \frac{32}{27}\pi - 4\sqrt{3}\right](f-1)(f-2)(f-3)\right\} \tag{12}$$

$\langle S^2\rangle_0$ is the unperturbed mean-square radius of gyration, i.e., $g_{S0}nb^2/6$, and z is the excluded-volume parameter defined (with the effective binary cluster integral) by

$$z = \left(\frac{3}{2\pi b^2}\right)^{3/2}\beta\sqrt{n} \tag{13}$$

Equation 11 is due originally to Berry and Orofino.[30]

The third term in the square brackets of eq 10, which is independent of n, remains nonzero at the Θ point. For four-arm star polystyrene in cyclohexane, however, this residual ternary cluster term is only 1.5×10^{-2} when estimated with the above values of β_3 and b.

In short, the residual ternary cluster contributions to A_2 and $\langle S^2\rangle$ are insignificant for four-arm star polystyrene in cyclohexane, and the binary-cluster approximation with β in place of β_2 must hold for these properties, as is the case for linear flexible polymers. It is probably pertinent to note, however, that as eqs 9 and 10 with eq 12 predict, the residual ternary contributions to A_2 and $\langle S^2\rangle$ can be significant for stars with larger f.

Expansion Factors. According to recent studies by Yamakawa and co-workers,[31-36] the quasi-two-parameter theory[37-39] based on the helical wormlike (HW) chain model quantitatively describes data of $\alpha_S{}^2$ (the expansion factor for $\langle S^2\rangle$) and $\alpha_\eta{}^3$ (the expansion factor for $[\eta]$) for linear flexible polymers with a single parameter $\tilde{z}$, which is called the scaled excluded-volume parameter and related to the conventional excluded-volume parameter z by $\tilde{z} = (3/4)K(\lambda L)z$. Here, λ^{-1} is the stiffness parameter, L is the contour length of the HW chain, and $K(\lambda L)$ is given by $K(\lambda L) = (4/3) - 2.711(\lambda L)^{-1/2} + (7/6)(\lambda L)^{-1}$ for $\lambda L > 6$. In the coil limit, $K(\lambda L)$ approaches 4/3 and $\tilde{z}$ becomes equal to z; note that though z here has to be expressed in terms of the HW parameters (see eq 5 of ref 32), it is equivalent to the one defined by eq 13.

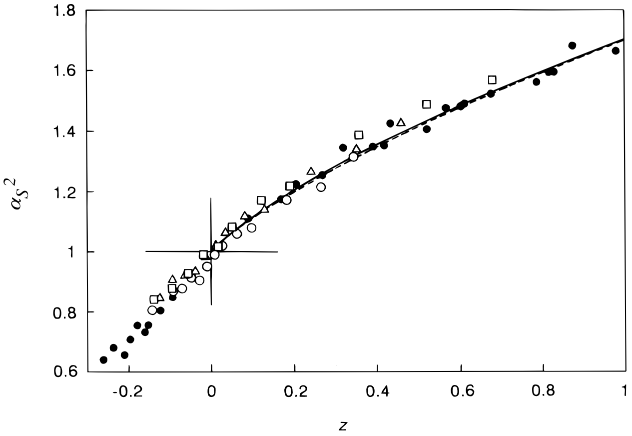

Figure 11. Plots of α_S^2 vs z for four-arm star polystyrene (○, 4S184′; △, 4S384; □, 4S662′) and linear polystyrene[3] (filled circles) in cyclohexane. The solid and dashed lines represent eq 17 for $f = 4$ and 2, respectively.

For star polymers, no expression for $K(\lambda L)$ or, more correctly, $(3/4)K(\lambda L)$ representing the stiffness effect is as yet available. If L is taken as the contour length from the end of one arm to that of another arm, i.e., as the total length of two arms, $K(\lambda L)$ for the linear portion of four-arm star polystyrene is estimated to be 1.22 for the total molecular weight of 80.5 × 10^4 (sample 4S184′) in cyclohexane, using M_L (the molar mass per unit contour length) = 358 nm^{-1} and λ^{-1} = 2.06 nm for linear polystyrene.[32] This $K(\lambda L)$ value is only 8.5% smaller than the coil limiting value, suggesting that the stiffness effect on the intramolecular excluded-volume parameter is not very significant for four-arm star polystyrene with $M_w > 8 \times 10^5$.

On the basis of the above consideration, we constructed a plot of α_S^2 vs z using the $\langle S^2\rangle_z$ data in Figure 7 and the empirical relations[40]

$$\beta = 72 \times 10^{-24}\left(1 - \frac{\Theta}{T}\right) \qquad (\text{cm}^3;\ \text{for } T > \Theta) \qquad (14)$$

for linear polystyrene in cyclohexane. The result is shown with unfilled symbols in Figure 11, along with the relation (filled circles) similarly obtained from Miyaki's data for linear polystyrene ($1.3 \times 10^6 \le M_w \le 5.6 \times 10^7$) in the same solvent. It can be seen that the α_S^2 vs z relations for star and linear polystyrenes are not different from each other in the z range studied.

Very recently, Shida et al.[41] showed from Monte Carlo simulations that α_S^2 for star polymers with very long uniform arms can be represented by the same asymptotic law as that for linear chains,[4] i.e.,

$$\alpha_S^{\ 2} = 1.53z^{2/5} \qquad (15)$$

We combined this relation with the first-order perturbation equation

$$\alpha_S^{\ 2} = 1 + K_f z + ... \qquad (16)$$

with the aid of the Domb–Barrett function[42] for linear chains to obtain the interpolation formula

$$\alpha_S^{\ 2} = (1 + 5.56K_f z + 10.62z^{20/9})^{0.18} \qquad (17)$$

This equation with $f = 2$ gives α_S^2 values that agree with those calculated from the Domb–Barrett equation[42] within 1.3% for $z > 0$. The solid and dashed lines in Figure 11 represent eq 17 for $f = 4$ and 2, respectively.

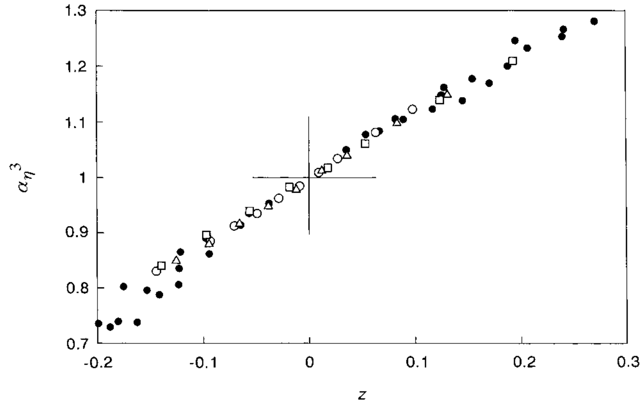

Figure 12. Plots of α_η^3 vs z for four-arm star polystyrene (○, 4S184′; △, 4S384; □, 4S662′) and linear polystyrene[3] (filled circles) in cyclohexane.

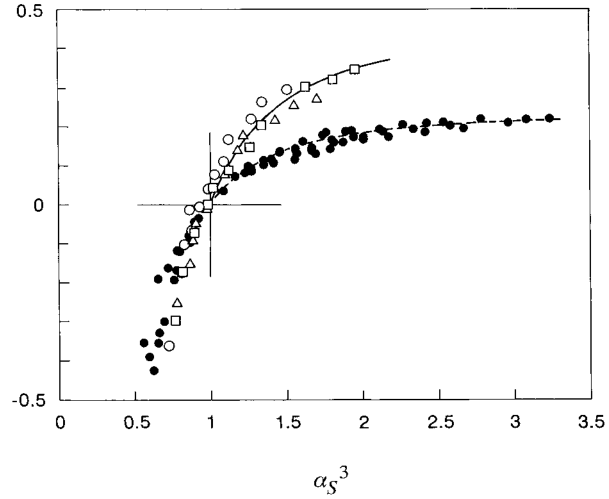

Figure 13. Plots of Ψ vs α_S^3 for four-arm star polystyrene (○, 4S184′; △, 4S384; □, 4S662′) and linear polystyrene[3] (filled circles). The solid and dashed lines represent the values calculated from eqs 17, 19, and 23 for four-arm star ($f = 4$) and linear ($f = 2$) polystyrenes, respectively.

The former is seen to fit the plotted points for four-arm star polystyrene.

Figure 12 shows the α_η^3 vs z relations for star and linear[3] polystyrenes in cyclohexane. No substantial difference is seen between the relations for the two types of polystyrene, though the present α_η^3 data are limited to small z.

Interpenetration Function. In Figure 13, Ψ data for four-arm star and linear polystyrenes in cyclohexane are plotted against α_S^3, where Ψ is defined by

$$\Psi = \frac{A_2M^2}{4\pi^{3/2}N_A\langle S^2\rangle^{3/2}} \qquad (18)$$

In the region of $\alpha_S^3 > 1$, Ψ for the star polymer is significantly larger than that for the linear polymer. The data points for 4S184′ (the unfilled circles) appear slightly above those for the other star samples of higher molecular weight. Although this may be due to the effect of chain stiffness, we consider no such effect in the ensuing analysis, again confining ourselves to the coil limit of the HW chain.

In this limit, eq 18 is written in terms of the familiar $h(z)$ function as

$$\Psi = (z/\alpha_S^{\ 3})h(z)/g_{S0}^{\ 3/2} \qquad (19)$$

with g_{S0} given by eq 5. For very small z, $h(z)$ of star polymers is given by[43]

$$h(z) = 1 - C_f z + ... \tag{20}$$

with

$$C_f = \frac{32}{15 f^{1/2}}[7 - 4\sqrt{2} + (f-1)(17\sqrt{2} - 9\sqrt{3} - 8) + (f-1)^2(9\sqrt{3} - 6\sqrt{2} - 7)] \tag{21}$$

For very large z, on the other hand, there must exist a certain asymptotic value of Ψ (for a given f), i.e.,

$$\Psi^* = \lim_{z \to \infty} \Psi \tag{22}$$

By combining eqs 20 and 22 in such a way that $h(z)$ for $f = 2$ with $\Psi^* = 0.235$ agrees with Barrett's function,[44] we constructed an interpolation equation for $h(z)$. The result reads

$$h(z) = \left[1 + 5C_f z + \frac{0.0411}{(\Psi^* g_{S0}{}^{3/2})^5} z^2\right]^{-0.2} \tag{23}$$

which allows $h(z)$ to be calculated as a function of z if Ψ^* is available from Monte Carlo computations.

The solid and dashed lines in Figure 13 represent the values computed from eqs 23 and 17 for $f = 4$ and $f = 2$, respectively, using $\Psi^* = 0.44$ for $f = 4$ (refs 45 and 46) and $\Psi^* = 0.235$ for $f = 2$. The agreements between theory and experiment for both four-arm star and linear polystyrenes in Figure 13 are satisfactory, explaining the large difference in Ψ between the polymers.

Conclusions

We have determined $\langle S^2 \rangle_z$, A_2, A_3, and $[\eta]$ for four-arm star polystyrene samples with M_w of 8.5×10^4 to 3.12×10^6 in cyclohexane at different temperatures and compared them with the known results for linear polystyrene in the same solvent. Although the difference in molecular architecture between the two polymers manifests itself in the interpenetration function Ψ and Flory's viscosity factor, no substantial difference appears in the Θ temperature and the magnitude of the ternary cluster integral at Θ. Further, the binary cluster approximation holds for $\langle S^2 \rangle_z$ and A_2 of the star polymer, as is the case with the linear polymer, if the binary cluster integral is replaced by the effective one. For $M_w > 8.5 \times 10^5$ the relations between $\alpha_S{}^2$ and z (the excluded-volume parameter in the coil limit) and between $\alpha_\eta{}^3$ vs z are also essentially the same for the two polymers. The z dependencies of $\alpha_S{}^2$ and Ψ for the star polymer are quantitatively described by the interpolation formulas constructed in this work.

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