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

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ABSTRACT: Anionically polymerized six-arm star polystyrene samples with weight-average molecular weights M_w of 5.6×10^4−3.2×10^6 were studied by light scattering and viscometry in cyclohexane at different temperatures to determine their *z*-average mean-square radii of gyration ($\langle S^2\rangle_z$), second and third virial coefficients (A_2 and A_3), and intrinsic viscosities ($[\eta]$). The values of A_3 at the Θ point (34.5 °C), where those of A_2 were essentially zero for $M_w > 10^6$, were about 5×10^{-4} cm^6 mol g^{-3} and yielded 4×10^{-45} cm^6 for the ternary cluster integral. The data for $\langle S^2\rangle_z$ and A_2 at Θ were in line with previous perturbation calculations taking into account ternary cluster interactions, but the (residual) ternary effects on these properties were not very significant, at least, for $M_w > 10^6$. The expansion factor $\alpha_S{}^2$ for $\langle S^2\rangle$ and that for $[\eta]$ plotted against the conventional excluded-volume parameter for $M_w > 1 \times 10^6$ came close to the known relations for both linear and four-arm star polystyrenes of high molecular weight in cyclohexane. On the other hand, the relation between Ψ (the interpenetration function) and $\alpha_S{}^3$ for the six-arm star polymer appeared far above that for the linear chain and appreciably above that for the four-arm star chain at temperatures above Θ. These experimental results for $\alpha_S{}^2$ and Ψ were quantitatively described by the interpolation formulas constructed in previous work.

Introduction

The present work is concerned with excluded-volume effects on the mean-square radius of gyration $\langle S^2\rangle$, second virial coefficient A_2, third virial coefficient A_3, and intrinsic viscosity $[\eta]$ of six-arm star polystyrene in cyclohexane near the Θ point. It is an extension of our previous light scattering and viscometric studies[1] on cyclohexane solutions of four-arm star polystyrene, for which the following conclusions were derived from data analysis and some theoretical calculations (see ref 2 for a good solvent system).

(1) The binary cluster approximation breaks down for A_3 at and near the Θ point, but it holds for $\langle S^2\rangle$ and A_2, as is the case with linear chains,[3] if the binary cluster integral is replaced by a linear combination of the binary and ternary cluster integrals. (2) The relation between $\alpha_S{}^2$ (the expansion factor for $\langle S^2\rangle$) and z (the conventional excluded-volume parameter) and that between $\alpha_\eta{}^3$ (the expansion factor for $[\eta]$) and z for molecular weights higher than 8×10^5 are almost the same as those[4,5] known for linear polystyrene in cyclohexane near the Θ point. On the other hand, the interpenetration function Ψ plotted against $\alpha_S{}^3$ (>1) appears significantly above that for the linear chain, reflecting the difference in molecular architecture. (3) These $\alpha_S{}^2$ vs z and Ψ vs $\alpha_S{}^3$ relations are satisfactorily described by the interpolation formulas constructed.

The present study was undertaken to see whether the above conclusions apply to six-arm star polystyrene in cyclohexane. To this end, we prepared seven narrow-distribution samples of the star polymer ranging in weight-average molecular weight M_w from 5.6×10^4 to 3.2×10^6 and made light scattering and viscosity measurements on them. The data obtained for A_2, A_3, $\langle S^2\rangle_z$ (*z*-average $\langle S^2\rangle$), and $[\eta]$ are analyzed below.

Experimental Section

Polymer Samples. Seven samples of six-arm star polystyrene were synthesized by the anionic polymerization of styrene in benzene at 35 °C with 1,2-bis(trichlorosilyl)ethane as the coupling agent. *sec*-Butyllithium was used to initiate the polymerization of styrene. After 12 h, a small amount of the reaction mixture was removed for use in characterization of the linear precursor. At this stage, i.e., before the addition of the coupler to the remainder, styryllithium ends were converted to isoprenyllithium groups by the addition of 1−6 equiv of isoprene since the coupling reaction of polystyrene having styryllithium groups is known to produce only four-arm star chains by steric hindrance.[6]

The samples thus prepared were fractionally precipitated with toluene/methanol mixtures at fixed temperatures (for three lower molecular weight samples) or cyclohexane at varying temperatures (for the rest) to remove incomplete star chains including linear precursor molecules and also to narrow the molecular weight distribution. The procedure was repeated until gel permeation chromatography (GPC) in chloroform showed a single sharp peak for each six-arm star sample; use was made of a Tosoh HLC SC-8010 with a UV-8010 detector and three columns, TSK-GEL G1000HxL, G4000HxL, and G5000HxL, connected in series. The purified samples were designated as 6S10, 6S17, 6S36, 6S85, 6S190, 6S260, and 6S570 according to the molecular weight ($\times 10^{-3}$) of the arm (the linear precursor before coupling). The ratio of M_w for each star polymer sample to that for its arm was 6 ± 0.3 when determined by light scattering in benzene. (We wish to report light scattering data for benzene solutions in a forthcoming paper.) The weight-average to number-average molecular weight ratios for samples 6S17, 6S36, 6S85, 6S190, and 6S260 were estimated by GPC to be less than 1.04, using the calibration curve constructed with the light scattering molecular weights for the seven samples.

Light Scattering. Light scattering measurements were made at different temperatures T between 15 and 55 °C on a Fica-50 light scattering photometer with vertically polarized incident light of 436 and 546 nm wavelengths in an angular range from 30° to 150°. Intensity data at 546 nm were used to determine M_w, A_2, and A_3, since, as remarked previously,[1,7] the attenuation of light by scattering, absorption, and multiple scattering was not always negligible at 436 nm, giving rise to small errors in A_2 at and near the Θ point where A_2 is vanishingly small. Data at 436 nm were used for the deter-

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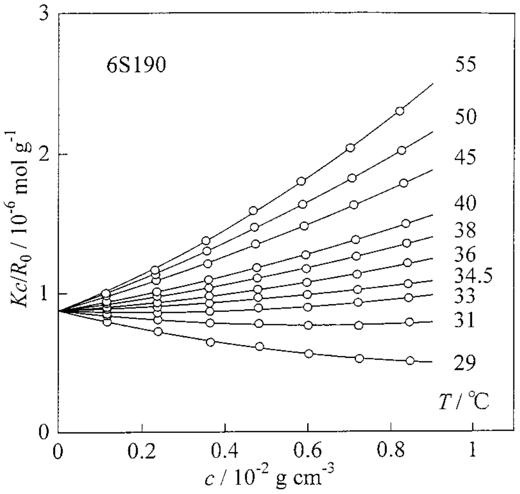

Figure 1. Concentration dependence of Kc/R_0 for six-arm star polystyrene 6S190 in cyclohexane at the indicated temperatures.

mination of $\langle S^2 \rangle_z$. The apparatus was calibrated with benzene at 25 °C as the reference liquid, whose Rayleigh ratio at 436 and 546 nm were taken to be 46.5×10^{-6} and 16.5×10^{-6} cm^{-1}, respectively.[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 were measured for sample 6S10 at 20, 30, 40, and 50 °C in the range of c below 4.5×10^{-2} g cm^{-3}, with the result that

$$\rho = 0.77849 + 0.286_3 c \quad (\mathrm{g\ cm^{-3}};\ 20\ °\mathrm{C})$$

$$\rho = 0.76898 + 0.293_3 c \quad (\mathrm{g\ cm^{-3}};\ 30\ °\mathrm{C})$$

$$\rho = 0.75938 + 0.298_2 c \quad (\mathrm{g\ cm^{-3}};\ 40\ °\mathrm{C})$$

$$\rho = 0.75009 + 0.300_4 c \quad (\mathrm{g\ cm^{-3}};\ 50\ °\mathrm{C})$$

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

The specific refractive index increment $\partial n/\partial c$ of six-arm star polystyrene in cyclohexane was determined at 20, 30, 40, and 50 °C and at $c \leq 4.0 \times 10^{-2}$ g cm^{-3} using a modified Schulz–Cantow type differential refractometer. It was independent of c in that range but dependent slightly on molecular weight at any T examined. The $\partial n/\partial c$ values at 436 and 546 nm were found to be represented by

$$\partial n/\partial c = 0.1679 + 4.73 \times 10^{-4} T\ (°\mathrm{C}) + 1.75 \times 10^2/M_\mathrm{w} \quad (\mathrm{cm^3\ g^{-1}};\ 436\ \mathrm{nm})$$

$$\partial n/\partial c = 0.1575 + 4.56 \times 10^{-4} T\ (°\mathrm{C}) + 2.66 \times 10^2/M_\mathrm{w} \quad (\mathrm{cm^3\ g^{-1}};\ 546\ \mathrm{nm})$$

Viscometry. Intrinsic viscosities for all samples in cyclohexane were determined as functions of T by conventional capillary viscometers of the Ubbelohde type. In evaluation of the relative viscosity, the difference between the solvent and solution densities were taken into account.

Results

Virial Coefficients. Figure 1 illustrates the concentration dependence of Kc/R_0 for sample 6S190 at the indicated temperatures, where K is the optical constant and R_0 the excess reduced scattering intensity at zero angle. These data were analyzed using the Bawn plot[9] of $S(c_1,c_2)$ vs $c_1 + c_2$ based on the equation

$$S(c_1,c_2) \equiv \frac{(Kc/R_0)_{c=c_2} - (Kc/R_0)_{c=c_1}}{c_2 - c_1} = 2A_2 + 3A_3(c_1 + c_2) + \ldots \qquad (1)$$

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 have been 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.

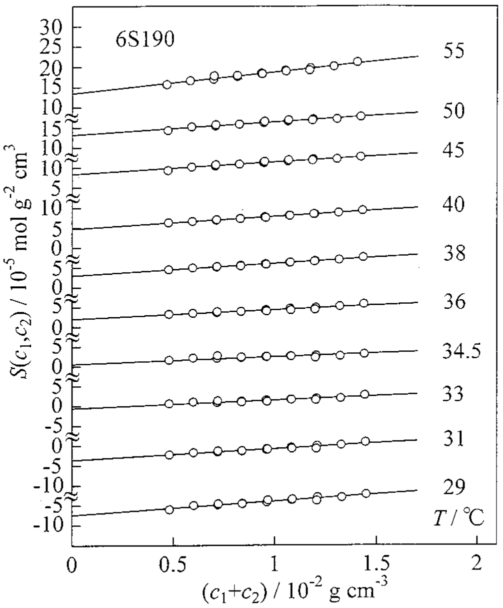

Figure 2. Plots of $S(c_1,c_2)$ vs $c_1 + c_2$ for sample 6S190 in cyclohexane at the indicated temperatures.

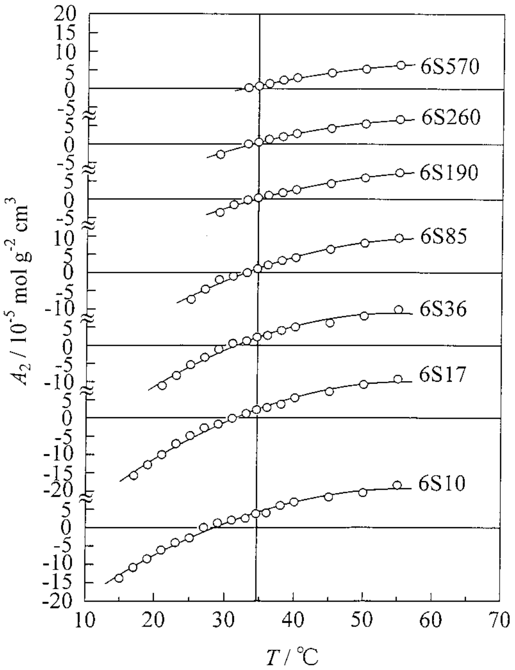

Figure 3. Temperature dependence of A_2 for six-arm star polystyrene samples in cyclohexane. The vertical line indicates 34.5 °C (the Θ temperature).

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

sample	$10^{-4}\cdot M_w$	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}
6S10	5.59	3.8	5.1		0.137	
6S17	9.62	2.2	3.5		0.187	
6S36	21.0	2.3	2.8		0.250	
6S85	50.1	1.0	5.5	$14._4$	0.398	4.5
6S190	116	0.3	6.0	21.5	0.588	4.7
6S260	148	0.5	5.6	24.9	0.655	4.3
6S570	320	0.7	8.3	37.0	1.004	4.3

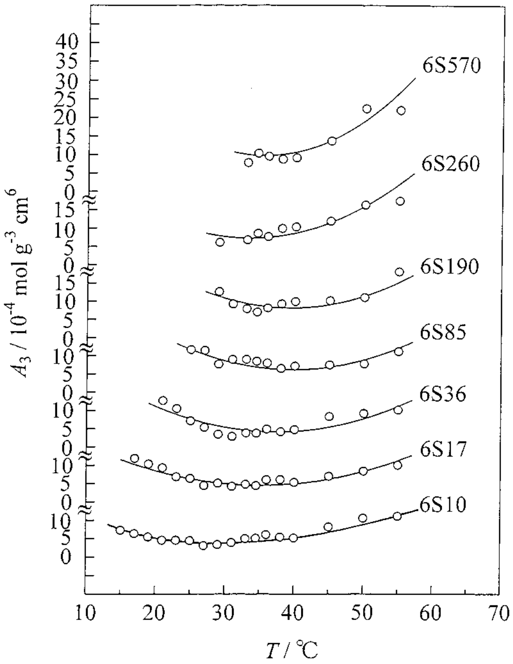

Figure 4. Temperature dependence of A_3 for six-arm star polystyrene samples in cyclohexane.

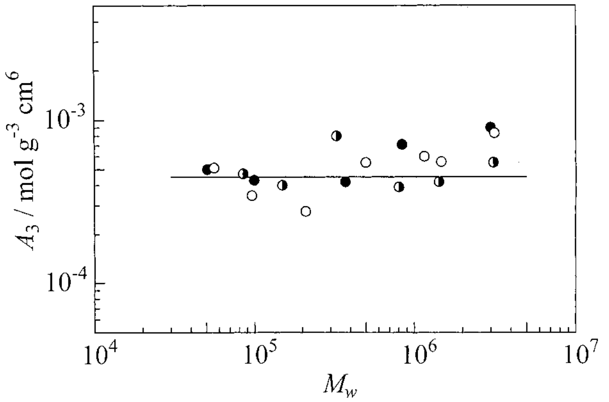

Figure 5. Molecular weight dependence of A_3 for six-arm star polystyrene (○), four-arm star polystyrene[1] (◑), and linear polystyrene[11] (●) in cyclohexane at 34.5 °C.

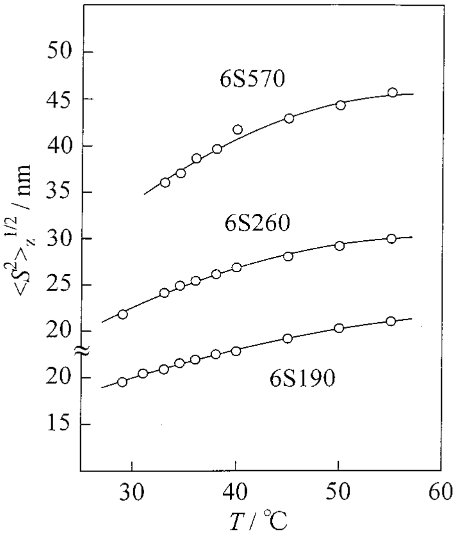

Figure 6. Temperature dependence of $\langle S^2\rangle_z^{1/2}$ for six-arm star polystyrene samples in cyclohexane.

The molecular weight of each sample was determined by extrapolating to $c = 0$ the apparent molecular weight M_{app} [$\equiv (Kc/R_0 - 2A_2c - 3A_3c^2)^{-1}$] calculated with the values of A_2 and A_3. The plots of M_{app} vs c were all horizontal over the concentration range studied. The values of M_w thus obtained at different T agreed within ±4% for any samples.

The second virial coefficients for the seven samples are plotted against T in Figure 3. Those for the three highest molecular weights become almost zero at 34.5 °C (see also Table 1), so that the Θ temperature for six-arm star polystyrene in cyclohexane may be determined as 34.5 °C, the same temperature as that for linear and four-arm star polystyrenes. Note that the Θ point is defined as the temperature at which A_2 for high molecular weight vanishes. As M_w decreases, A_2 at this temperature increases, being consistent with the earlier observation by Roovers and Bywater[10] for six-arm star polystyrene in cyclohexane.

Figure 4 shows that the curve of A_3 vs T for each sample is parabolic with a broad positive minimum around Θ. This behavior of A_3 is quite similar to what was observed for linear flexible polymers[11−13] and four-arm star polystyrene[1] in Θ solvents. We note that such positive minima of A_3 for linear polymers have been explained theoretically as due to ternary cluster effects.[14] The molecular weight dependence of A_3 for six-arm star polystyrene at 34.5 °C is shown in Figure 5, along with that for linear[11] and four-arm star[1] polystyrenes in the same solvent. The values of A_3 for the three polymers are almost constant in the indicated M_w range, scattering around 4.5 × 10^{-4} cm^6 mol g^{-3}. The data of A_2 and A_3 at 34.5 °C are presented in Table 1, along with those of M_w (the mean of the values at different T for each sample).

Radius of Gyration. Infinite-dilution values of Kc/R_θ at scattering angle θ, i.e., $(Kc/R_\theta)_{c=0}$, were obtained by extrapolation of $(Kc/R_\theta - 2A_2c - 3A_3c^2)$ at fixed θ to $c = 0$,[12] 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 6 depicts the temperature dependence of $\langle S^2\rangle_z^{1/2}$ thus obtained for the three highest molecular weight samples 6S190, 6S260, and 6S570.

Figure 7 shows that our $\langle S^2\rangle_z$ data (the larger unfilled circles) at Θ appear somewhat above those of Roovers and Bywater[10] (the smaller unfilled circles) for the same system. Since our samples are essentially monodisperse, the discrepancy cannot be attributed to the polydispersity and remains to be seen. The figure includes Miyaki's data[4,15] for linear polystyrene and our previous data[1] for four-arm star polystyrene under the same solvent conditions. Comparison of the data sets clearly shows that, as the number of arms increases at a fixed M_w, $\langle S^2\rangle_z$ decreases. The straight line fitting the present data is expressed by

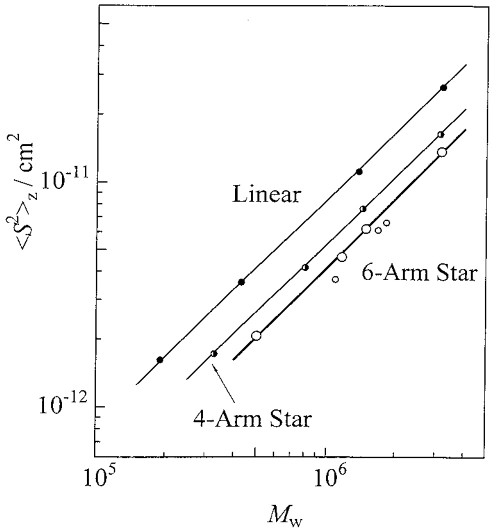

Figure 7. Molecular weight dependence of $\langle S^2\rangle_z$ for six-arm star polystyrene (○, this work; ○, Roovers and Bywater[10]), four-arm star polystyrene[1] (◑), and linear polystyrene[4,15] (●) in cyclohexane at the Θ temperature.

$$\langle S^2\rangle_z = 4.1 \times 10^{-18} M_w \quad \text{(six-arm star)} \tag{2}$$

in units of cm^2. Using the relation $\langle S^2\rangle_z = 8.35 \times 10^{-18} M_w$ (cm^2) for linear polystyrene, i.e., the uppermost straight line in the figure, we obtain 0.49 for the ratio g_S of $\langle S^2\rangle_z$ for six-arm star polystyrene to that for the linear polymer with the same molecular weight in cyclohexane at Θ. This ratio is slightly higher than the Gaussian chain value 0.444 calculated from the equation of Zimm and Stockmayer[16]

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

where the subscript 0 signifies the unperturbed state and f denotes the arm number. The g_S value 0.46 derived from Roovers and Bywater's data[10] is closer to this Gaussian chain value. It is known that experimentally determined g_S values for star polymers with $f > 6$ in Θ solvents are systematically larger than those calculated from eq 3.[17,18]

Intrinsic Viscosity. Figure 8 shows the temperature dependence of $[\eta]$ for the seven samples of six-arm star polystyrene in cyclohexane. The values at the Θ temperature are again compared with the literature data for linear,[4,19] four-arm star,[1] and six-arm star[10] polystyrenes in Figure 9. As is the case with $\langle S^2\rangle_z$, $[\eta]$ lowers with increasing arm number. The straight line for the six-arm star polymer is represented by

$$[\eta] = 5.5 \times 10^{-2} M_w^{0.50} \quad \text{(6-arm star)} \tag{4}$$

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[4] to obtain a value of 0.63 for the ratio g_η of $[\eta]$ for six-arm star polystyrene to that for linear polystyrene. This value is close to those (0.62−0.63) reported by Douglas et al.[17] for six-arm star polymers in the Θ state, but all these are significantly smaller than the value 0.705 predicted by the Zimm−Kilb theory.[20]

The Flory viscosity factor defined by

$$\Phi = \frac{[\eta] M_w}{6^{3/2} \langle S^2\rangle_z^{\,3/2}} \tag{5}$$

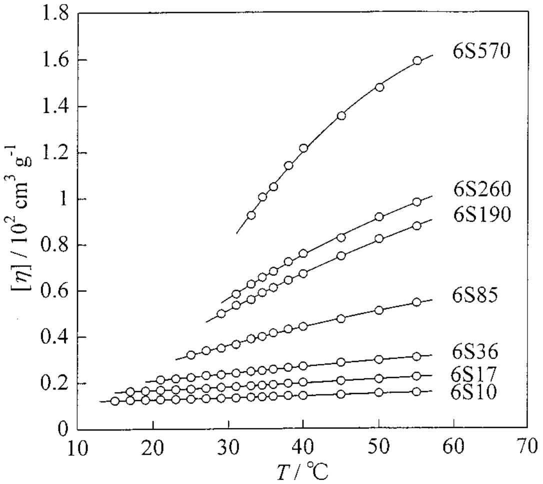

Figure 8. Temperature dependence of $[\eta]$ for six-arm star polystyrene samples in cyclohexane.

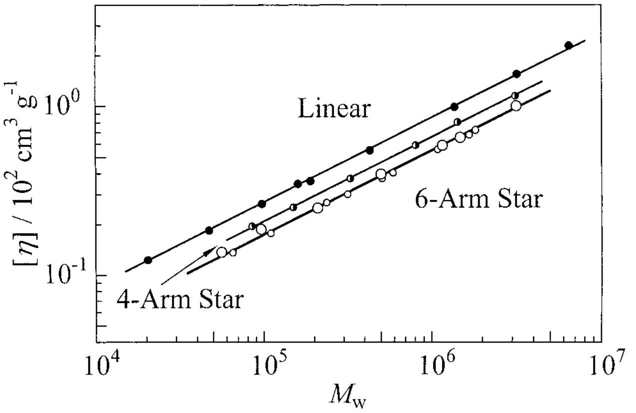

Figure 9. Molecular weight dependence of $[\eta]$ for six-arm star polystyrene (○, this work; ○, Roovers and Bywater[10]), four-arm star polystyrene[1] (◑), and linear polystyrene[4,19] (●) in cyclohexane at the Θ temperature.

was calculated for samples 6S85, 6S190, 6S260, and 6S570 at 34.5 °C to obtain a mean of 4.5 × 10^{23} mol^{-1}, which is smaller than the value (5.1−5.8) × 10^{23} mol^{-1} obtained by Roovers and Bywater[10] for the same system. These Φ values are much larger than what is known for linear[3,21] and four-arm star[1] polystyrenes ((2.5−2.8) × 10^{23} and (3.6−3.8) × 10^{23} mol^{-1}, respectively) in cyclohexane at Θ, 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, as is the case for linear and four-arm star polystyrenes, A_3 for six-arm star polystyrene in cyclohexane at Θ remains positive. Thus, the binary cluster approximation to it breaks down. If the ternary cluster integral β_3 is incorporated in the single contact approximation, A_3 for any long bead chains is expressed by

$$A_3 = \frac{N_A{}^2 n^3}{3M^3} \beta_3 \tag{6}$$

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 5. Taking one bead as the monomer unit, we obtain $\beta_3 = 4 \times 10^{-45}$ cm^6 for the three polymers in cyclohexane from the A_3 data in the figure. With this β_3 value, we here examine effects of ternary cluster interactions on A_2 and $\langle S^2\rangle$ of six-arm star polystyrene at the Θ point. It should be noted that such effects were negligible for four-arm star polystyrene.[1]

The perturbation theory for A_2 of Gaussian star polymers with f uniform arms is written as[22]

$$A_2 = \frac{N_A n^2}{2M^2}\left\{\beta + \frac{4\sqrt{f}}{\sqrt{n}}[(f-1)(2-\sqrt{2})-2]\left(\frac{3}{2\pi b^2}\right)^{3/2}\beta_3 + ...\right\} \qquad (7)$$

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 parentheses vanishes at Θ, but the second one remains nonzero unless the molecular weight is infinitely high. Using $\beta_3 = 4 \times 10^{-45}$ cm^6 and $b = 7.2 \times 10^{-8}$ cm (obtained from $\langle S^2\rangle_z = 8.35 \times 10^{-18} M_w$ cm^2 for linear polystyrene), we find that the contribution of the latter term to A_2 (for $f = 6$) is less than 1.0×10^{-5} cm^3 mol g^{-2} for the three highest molecular weight samples and hardly distinguishable from zero experimentally. However, it is 1.3×10^{-5} cm^3 mol g^{-2} for 6S85 and increases to 3.9×10^{-5} cm^3 mol g^{-2} as the molecular weight further decreases to 5.6×10^4 (sample 6S10). These residual ternary cluster contributions are quite close to the measured A_2 values in Table 1, but the excellent agreement may be fortuitous because the effect of arm ends is not considered in eq 7. The present analysis shows that the binary cluster approximation with the effective cluster integral essentially holds for A_2 of the six-arm star polystyrene chain if M_w is higher than 10^6.

With the Gaussian model, we previously calculated $\langle S^2\rangle$ up to the order of β_2 and β_3. The result[1] reads

$$\langle S^2\rangle = \langle S^2\rangle_0\left[1 + K_f z + K'_f\left(\frac{3}{2\pi b^2}\right)^3\beta_3 + ...\right] \qquad (8)$$

where K_f and K'_f are known functions of f (K_f is due originally to Berry and Orofino[23]), $\langle S^2\rangle_0$ 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

$$z = \left(\frac{3}{2\pi b^2}\right)^{3/2}\beta\sqrt{n} \qquad (9)$$

The third term in the square brackets of eq 8, which is independent of n, remains nonzero at the Θ point. For six-arm star polystyrene in cyclohexane, this residual ternary cluster term is 0.11 when estimated with the above values of β_3 and b. Interestingly, this small ternary contribution explains the discrepancy between the experimental and Gaussian g_S values observed above. At present, however, we are not confident of whether this discrepancy in g_S arises entirely from ternary cluster interactions, since no information is available about interarm interactions in the central portion of the chain.

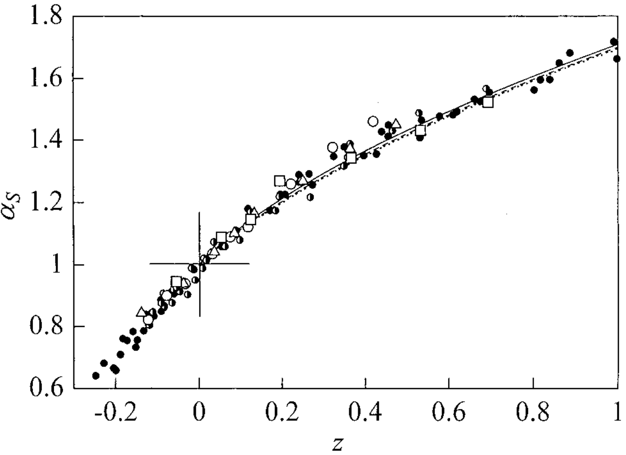

Figure 10. Plots of $\alpha_S{}^2$ vs z for six-arm star polystyrene (○, 6S190; △, 6S260; □, 6S570), four-arm star polystyrene[1] (◑), and linear polystyrene[4] (●) in cyclohexane. The solid, dashed, and dotted lines represent eq 11 for $f = 6$, 4, and 2, respectively.

In short, eqs 7 and 8 are in line with our A_2 and $\langle S^2\rangle_z$ data at Θ, but the residual ternary contributions to these properties are rather small and may be ignored in a fairly good approximation in discussing the expansion factors and the interpenetration function for high molecular weight samples of six-arm star polystyrene in cyclohexane. It should be noted that for stars with larger f these equations predict more pronounced ternary contributions to A_2 and $\langle S^2\rangle$.

Expansion Factors. If the molecular weight is higher than a certain value, both $\alpha_S{}^2$ and $\alpha_\eta{}^3$ may be treated approximately in the conventional two-parameter scheme[21,24] corresponding to the coil limit of the quasi-two-parameter theory[3] for the helical wormlike chain. In this limit, these expansion factors should be universal functions of z. We previously estimated such a molecular weight to be roughly 8×10^5 for four-arm star polystyrene.[1] This value corresponds to 1.2×10^6 for the six-arm star polymer, so that the analysis below is confined to the three highest molecular weight samples (see Table 1).

We constructed a plot of $\alpha_S{}^2$ vs z using the $\langle S^2\rangle_z$ data in Figure 6 and the empirical relation[4,5]

$$\beta = 72 \times 10^{-24}\left(1 - \frac{\Theta}{T}\right) \quad (\mathrm{cm}^3) \qquad (10)$$

for linear polystyrene in cyclohexane at $T > \Theta$. The result is shown with unfilled symbols in Figure 10, along with the relations similarly obtained from Miyaki's data[4] (filled circles) for linear polystyrene ($1.3 \times 10^6 \le M_w \le 5.6 \times 10^7$) and from our previous data[1] (half-filled circles) for four-arm star polystyrene ($8.0 \times 10^5 \le M_w \le 3.1 \times 10^6$) in the same solvent. It can be seen that the $\alpha_S{}^2$ vs z relations for the three types of polystyrene are not different from one another in the z range studied.

The previously proposed interpolation expression[1] of $\alpha_S{}^2$ for regular star polymers is

$$\alpha_S{}^2 = (1 + 5.56K_f z + 10.62z^{20/9})^{0.18} \qquad (11)$$

which was derived by combining the first-order perturbation theory[23] and the asymptotic relation[25] in the limit of infinite z; for $f = 2$, 4, and 6, $K_f = 1.276$, 1.342, and 1.449, respectively. We note that the values of $\alpha_S{}^2$

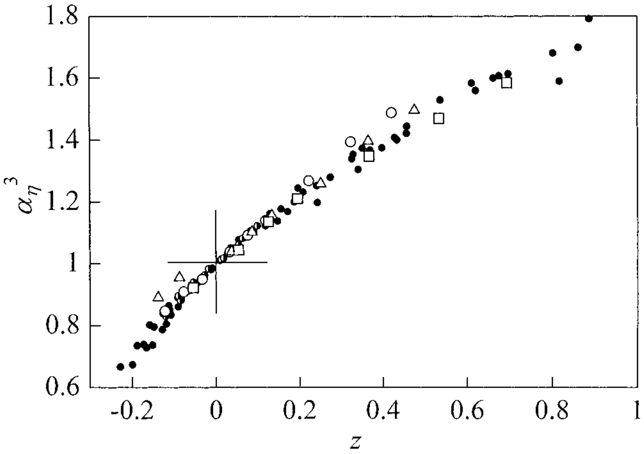

Figure 11. Plots of $\alpha_\eta{}^3$ vs z for six-arm star polystyrene (○, 6S190; △, 6S260; □, 6S570), four-arm star polystyrene[1] (◑), and linear polystyrene[4] (●) in cyclohexane.

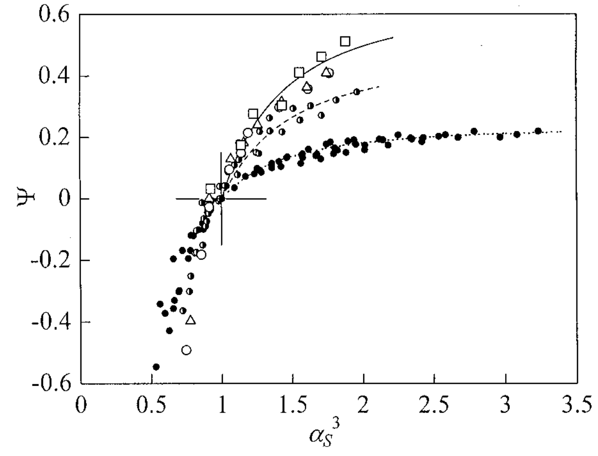

Figure 12. Plots of Ψ vs $\alpha_S{}^3$ for six-arm star polystyrene (○, 6S190; △, 6S260; □, 6S570), four-arm star polystyrene[1] (◑), and linear polystyrene[4] (●) in cyclohexane. The solid, dashed, and dotted lines represent the values calculated from eqs 11 and 13 for six-arm star ($f = 6$), four-arm star ($f = 4$), and linear ($f = 2$) polystyrenes, respectively.

calculated from eq 11 for $f = 2$ and from the familiar Domb–Barrett equation[26] agree within 1.3% for $z > 0$. The solid, dashed, and dotted lines in Figure 10 represent eq 11 for $f = 6$, 4, and 2, respectively. They come close to one another and closely fit the experimental points for the star and linear polymers, leading to the conclusion that eq 11 satisfactorily describes the z dependence of $\alpha_S{}^2$ for the three types of high molecular weight polystyrene in cyclohexane near (but above) Θ.

Figure 11 shows the $\alpha_\eta{}^3$ vs z relations for six-arm star, four-arm star,[1] and linear[4] polystyrenes in cyclohexane. No substantial difference is seen among the relations for the three types of polymer, though the $\alpha_\eta{}^3$ data for the four-arm star chain are limited to small z.

Interpenetration Function. In Figure 12, Ψ data for high molecular weight samples of six and four-arm[1] star and linear[4] polystyrenes in cyclohexane are plotted against $\alpha_S{}^3$, where Ψ is defined by

$$\Psi = \frac{A_2 M^2}{4\pi^{3/2} N_A \langle S^2\rangle^{3/2}} \qquad (12)$$

When compared at the same $\alpha_S{}^3$ (above Θ), Ψ is the highest for the six-arm star chain and becomes lower with decreasing f. This remarkable f dependence of Ψ may be considered to reflect a higher segment density in chains with larger f.

The solid, dashed, and dotted lines in Figure 12 represent the Ψ values calculated from our interpolation equation[1]

$$\Psi = \frac{z}{(\alpha_S{}^3 g_{S0})^{3/2}}\left[1 + 5C_f z + \frac{0.0411}{(\Psi^* g_{S0}{}^{3/2})^5} z^2\right]^{-0.2} \qquad (13)$$

and eq 11 for $f = 6$, 4, and 2, respectively. Here, C_f is the first-order perturbation coefficient[27] for A_2 (5.390, 3.873, and 2.865 for $f = 6$, 4, and 2, respectively), and Ψ^* is the value of Ψ in the limit of $z \to \infty$ (0.64, 0.46, and 0.235 for $f = 6$, 4, and 2, respectively).[28–30] The agreements between theory and experiment for six-arm star, four-arm star, and linear polystyrenes in Figure 12 are satisfactory, explaining the large difference in Ψ among the polymers.

Conclusions

The present data of $\langle S^2\rangle_z$, A_2, A_3, and $[\eta]$ for six-arm star polystyrene samples with M_w of 5.6×10^4–3.2×10^6 in cyclohexane at different temperatures have been compared with the known results for four-arm star and linear polystyrenes in the same solvent. The difference in molecular architecture among the three polymers manifests itself in the interpenetration function Ψ and Flory's viscosity factor, whereas no substantial difference appears in the Θ point (i.e., the temperature where $A_2 = 0$ for high molecular weight) and the magnitude of the ternary cluster integral at Θ. Although ternary cluster effects on $\langle S^2\rangle$ and A_2 of the six-arm star chain are not always negligible, these properties for $M_w > 10^6$ can practically be treated in the binary cluster approximation. The relations between $\alpha_S{}^2$ and z and between $\alpha_\eta{}^3$ and z for such high molecular weights are also essentially the same for the three types of polystyrene. Another important conclusion is that the interpolation formulas constructed in previous work almost quantitatively describe the z dependences of $\alpha_S{}^2$ and Ψ for the three polymers with high molecular weights.

References and Notes

(1) Okumoto, M.; Terao, K.; Nakamura, Y.; Norisuye, T.; Teramoto, A. *Macromolecules* **1997**, *30*, 7493.
(2) Okumoto, M.; Nakamura, Y.; Norisuye, T.; Teramoto, A. *Macromolecules* **1998**, *31*, 1615.
(3) Yamakawa, H. *Helical Wormlike Chains in Polymer Solutions*; Springer: Berlin, 1997.
(4) Miyaki, Y. Ph.D. Thesis, Osaka University, 1981.
(5) Miyaki, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.
(6) Watanabe, H.; Yoshida, H.; Kotaka, T. *Macromolecules* **1988**, *21*, 2175.
(7) Terao, K.; Okumoto, M.; Nakamura, Y.; Norisuye, T.; Teramoto, A. *Macromolecules* **1998**, *31*, 6885.
(8) Deželić, Gj.; Vavra, J. *Croat. Chem. Acta* **1966**, *38*, 35.
(9) Bawn, C. E. H.; Freeman, R. F. J.; Kamaliddin, A. R. *Trans. Faraday Soc.* **1950**, *46*, 862.
(10) Roovers, J. E. L.; Bywater, S. *Macromolecules* **1974**, *7*, 443.
(11) Nakamura, Y.; Norisuye, T.; Teramoto, A. *Macromolecues* **1991**, *24*, 4904.
(12) Akasaka, K.; Nakamura, Y.; Norisuye, T.; Teramoto, A. *Macromolecules* **1994**, *269*, 363.
(13) Nakamura, Y.; Inoue, N.; Norisuye, T.; Teramoto, A. *Macromolecules* **1997**, *30*, 631.
(14) Norisuye, T.; Nakamura, Y. *Macromolecules* **1994**, *27*, 2054.
(15) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(16) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.

(17) Douglas, J. F.; Roovers, J.; Freed, K. F. *Macromolecules* **1990**, *23*, 4168.

(18) Grest, G. S.; Fetters, L. J.; Huang, J. S.; Richter, D. *Adv. Chem. Phys.* **1996**, *94*, 67.

(19) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2103.

(20) Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19.

(21) Fujita, H. *Polymer Solutions*; Elsevier: Amsterdam, 1990.

(22) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 3089.

(23) Berry, G. C.; Orofino, T. A. *J. Chem. Phys.* **1964**, *40*, 1614.

(24) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.

(25) Shida, K.; Kimura, M.; Kawazoe, Y.; Ohno, K.; Nakamura, Y. *Macromolecules* **1998**, *31*, 2343.

(26) Domb, C.; Barret, A. *J. Polym.* **1976**, *17*, 361.

(27) Casassa, E. F. *J. Chem. Phys.* **1962**, *37*, 2176.

(28) Ohno, K.; Shida, K.; Kimura, M.; Kawazoe, Y. *Macromolecules* **1996**, *29*, 2269.

(29) Rubio, A. M.; Freire, J. J. *Macromolecules* **1996**, *29*, 6946.

(30) Barrett, A. J. *Macromolecules* **1985**, *18*, 196.

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