Excluded-Volume Effects in Star Polymer Solutions: Four-Arm Star Polystyrene in Benzene

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Received December 2, 1997; Revised Manuscript Received January 12, 1998

ABSTRACT: Radii of gyration, second and third virial coefficients, and intrinsic viscosities have been determined by light scattering and viscometry for four-arm star polystyrene samples with weight-average molecular weights M_w of 9.1×10^4 to 3.1×10^6 in benzene at 25 °C. They are compared with typical data for linear polystyrene in the same solvent to establish the ratios of the respective properties of the star chain to those of the linear chain at high M_w. The relation between the radius expansion factor and the excluded-volume parameter z for $M_w > 3 \times 10^5$ comes close to the known relation for the linear polymer in the coil limit and is described by the previously proposed interpolation formula. On the other hand, the viscosity expansion factor vs z plot appears significantly below that for linear polystyrene, the difference remaining to be explained theoretically. The values obtained for the interpenetration function are in the range between 0.43 and 0.46 and about 1.8 times as large as those for the linear polymer. They agree closely with recent Monte Carlo simulation data, but their comparison with the previously constructed interpolation expression suggests that, as in the case for linear flexible polymers, the effect of chain stiffness on the second virial coefficient needs to be considered for M_w below 10^6.

Introduction

Recently, we investigated 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 four-arm star polystyrene in cyclohexane near the Θ point and drew the following conclusions from data analysis and some theoretical calculations.[1] (1) The binary cluster approximation breaks down for A_3 at and near Θ, but it holds for $\langle S^2 \rangle$ and A_2, as is the case with linear chains,[2] if the binary cluster integral is replaced by a linear combination of the binary and ternary cluster integrals. (2) For molecular weights higher than 8×10^5, the relations between the expansion factor $\alpha_S{}^2$ for $\langle S^2 \rangle$ and the excluded-volume parameter z (in the coil limit of the quasi-two-parameter scheme[2]) and between the expansion factor $\alpha_\eta{}^3$ for $[\eta]$ and z are almost the same as those known 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 $\alpha_S{}^3 > 1$) appears far above that for the linear polymer system, reflecting the difference in molecular architecture. (3) The interpolation formulas constructed for $\alpha_S{}^2$ and Ψ satisfactorily describe the z-dependence of $\alpha_S{}^2$ and the $\alpha_S{}^3$ dependence of Ψ near the Θ point.

In the present work, we extended the light-scattering and viscosity measurements to benzene solutions, i.e., a good solvent for four-arm star polystyrene. The purpose is 2-fold. One is to determine the ratio of each of the measured $\langle S^2 \rangle_z$ (the z-average $\langle S^2 \rangle$), A_2, A_3, and $[\eta]$ for the star polymer in the good solvent to that for the linear chain, for which precise data are available. The other is to examine whether our interpolation formulas[1] mentioned above are capable of describing $\alpha_S{}^2$ and Ψ data in a region of large z.

Experimental Section

Polymer Samples. The previously investigated samples[1] of four-arm star polystyrene, 4S22, 4S39, 4S77′, 4S184′, 4S384, and 4S662′, were used for the present study. To these were added two samples, 4S34 and 4S171, furnished by Professor Hiroshi Watanabe of the Institute for Chemical Research, Kyoto University. These samples were purified by fractional precipitation to eliminate a small amount of linear chains produced during long-time storage. The resulting samples from 4S34 and 4S171 were designated as 4S34′ and 4S171′, respectively. Their weight-average to number-average molecular weight ratios were less than 1.03 when estimated by gel permeation chromatography.

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}.[3]

Seven solutions of different polymer concentrations were prepared for a given sample. The polymer mass concentration c in each solution was calculated from the weight fraction of the solute with the solution density approximated by the solvent density. This approximation did not introduce errors greater than 0.3% in the values of A_2 and A_3.

The specific refractive index increment $\partial n/\partial c$ in benzene at 25 °C and 436 nm was measured for all the four-arm star polystyrene samples using a modified Schulz−Cantow differential refractometer. It slightly increased with increasing M_w and was represented by

$$\partial n/\partial c = -120/M_w + 0.1075 \ (\mathrm{cm^3\,g^{-1}})$$

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

Results

Analysis of Light-Scattering Data. Excess reduced scattering intensities R_θ at finite scattering angles θ were extrapolated to $\theta = 0$ to obtain R_0 (i.e., R_θ at $\theta = 0$), with the aid of the square-root plot[4] of $(Kc/R_\theta)^{1/2}$ vs $\sin^2(\theta/2)$ for all samples except the highest

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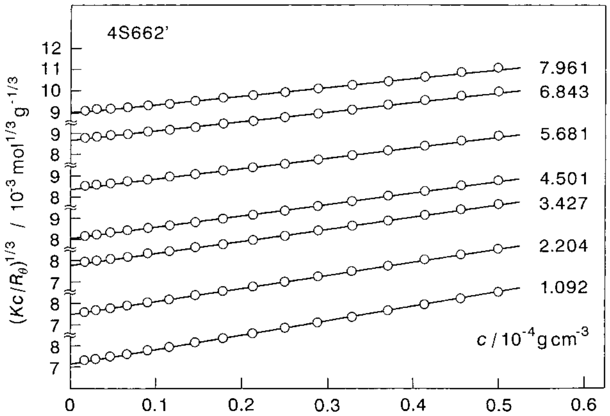

Figure 1. Plots of $(Kc/R_\theta)^{1/3}$ vs $\sin^2(\theta/2)$ for four-arm polystyrene sample 4S662′ in benzene at 25 °C.

molecular weight one, 4S662′, where K denotes the optical constant. This type of plot for 4S662′ bent upward for $\sin^2(\theta/2)$ larger than 0.3 at any c studied and the extrapolation for the sample was facilitated by plotting $(Kc/R_\theta)^{1/3}$ against $\sin^2(\theta/2)$. Figure 1 shows that the resulting cube-root plots at a series of c are essentially linear, allowing accurate determination of Kc/R_0. The following remark provides a theoretical basis for this procedure.

The intramolecular interference factor $P(\theta)$ for a Gaussian star chain composed of f identical arms is given by[5,6]

$$P(\theta) = \frac{2}{x} + \frac{f}{x^2}\left\{(f-3) - 2(f-2)\exp\left(-\frac{x}{f}\right) + (f-1)\exp\left(-\frac{2x}{f}\right)\right\} \qquad (1)$$

with

$$x = \frac{Nb^2}{6}\left(\frac{4\pi}{\lambda}\right)^2 \sin^2(\theta/2)$$

where N is the total number of bonds with length b in the chain and λ the wavelength of light in the scattering medium. For small x, eq 1 gives

$$P(\theta)^{-1/p} = 1 + \frac{3f-2}{3pf^2}x + \frac{1}{36p^2f^4}[3(6-p)f^2 - 6(p+4)f + 8(p+1)]x^2 + \ldots \qquad (2)$$

When the third term on the right-hand side of eq 2 vanishes, the plot of $P(\theta)^{-1/p}$ vs x and hence that of $(Kc/R_\theta)^{1/p}$ vs $\sin^2(\theta/2)$ follow the initial tangent over the widest angle. For $f = 4$, this condition is satisfied when p equals 25/8, a value close to 3.

The data for Kc/R_0 obtained were analyzed by the Bawn plot,[7] i.e., the plot of $S(c_1,c_2)$ vs $c_1 + c_2$ based on the equation[8]

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

where $(Kc/R_0)_{c=c_i}$ denotes the value of Kc/R_0 at $c = c_i$ (i = 1, 2). The Bawn plots constructed are shown in Figure 2. The data points for each sample follow a straight line, whose intercept and slope give A_2 and A_3, respectively.

Table 1. Results from Light-Scattering and Viscosity Measurements on Four-Arm Star Polystyrene in Benzene at 25 °C

sample	$M_w \times 10^{-4}$	10^4A_2, cm^3 mol g^{-2}	10^2A_3, cm^6 mol g^{-3}	$\langle S^2\rangle_z^{1/2}$, nm	$10^{-2}[\eta]$, cm^3 g^{-1}
4S22	9.14	4.85	0.73		0.308
4S34′	15.3	4.20	0.95	11.9 ± 0.7	0.472
4S39	16.2	4.15	0.95	12.2 ± 0.7	0.461
4S77′	34.3	3.38	1.25	18.6	0.772
4S171′	80.9	2.77	2.3	31.1	1.48
4S184′	85.2	2.73	2.1	32.2	1.60
4S384	147	2.36	3.3	44.2	2.42
4S662′	314	1.92	5.0	69.2	4.21

The virial coefficients thus determined were used to calculate the apparent molecular weight M_{app} [$\equiv(Kc/R_0 - 2A_2c - 3A_3c^2)^{-1}$] as a function of c. The plot of M_{app} vs c constructed for each sample was horizontal, giving the desired weight-average molecular weight M_w.

The z-average mean-square radius of gyration was determined from the initial slope of the square-root or the cube-root plot at $c = 0$; the infinite-dilution values of Kc/R_θ were obtained by extrapolation of $(Kc/R_\theta)^{1/2}$ plotted against c. The numerical results of M_w, A_2, A_3, and $\langle S^2\rangle_z$ are summarized in Table 1, along with those of $[\eta]$.

Molecular Weight Dependence of $\langle S^2\rangle_z$, A_2, A_3, and $[\eta]$. Figure 3 compares the molecular weight dependence of $\langle S^2\rangle_z$ for four-arm star polystyrene (unfilled circles) with that for linear polystyrene[9] (filled circles), both in benzene. The straight line fitting the plotted points for the star polymer is represented by

$$\langle S^2\rangle_z = 8.9 \times 10^{-19} M_w^{1.19} \text{ (in cm}^2\text{)} \qquad (4)$$

This line is parallel to that for linear polystyrene represented by $\langle S^2\rangle_z = 1.4_7 \times 10^{-18} M_w^{1.19}$ (cm^2), giving 0.61 as the ratio g_S of $\langle S^2\rangle_z$ for the star polymer to that for the linear polymer of the same molecular weight, i.e., $g_S = \langle S^2\rangle_z(\text{star})/\langle S^2\rangle_z(\text{linear})$. This ratio agrees substantially with those of 0.58 by Berry[10] and 0.62 by Roovers et al.[11,12] for polystyrene in toluene. All these ratios in the good solvents are quite close to our previous value 0.63 for the same polymer in cyclohexane at the Θ point and also to the theoretical value 0.625 for four-arm Gaussian stars (see eq 9). This proximity is consistent with the predictions from renormalization group theory[12,13] and Monte Carlo simulations.[14,15]

The molecular weight dependences of A_2 and A_3 for four-arm star polystyrene in benzene at 25 °C are shown in Figures 4 and 5, respectively, where the literature data[8,9,16,17] for linear polystyrene in the same solvent are included. In the former figure, the data for either polystyrene can be fitted approximately by a straight line with a slope −0.25 in the molecular weight range indicated and yield 0.89 for the ratio $A_2(\text{star})/A_2(\text{linear})$. In the latter figure, the curves fitting the data points for the respective polymers are essentially linear and parallel with slope 0.6 for M_w above 2×10^5, giving the ratio $A_3(\text{star})/A_3(\text{linear})$ a value of 0.85 in the high molecular weight region.

Figure 6 shows the reduced third virial coefficients Γ ($=A_3/A_2{}^2M_w$) for four-arm star and linear[8,17] polystyrenes in benzene. When compared at the same M_w, Γ for the star chain is larger than that for the linear chain. This may be a special case of Burchard's general

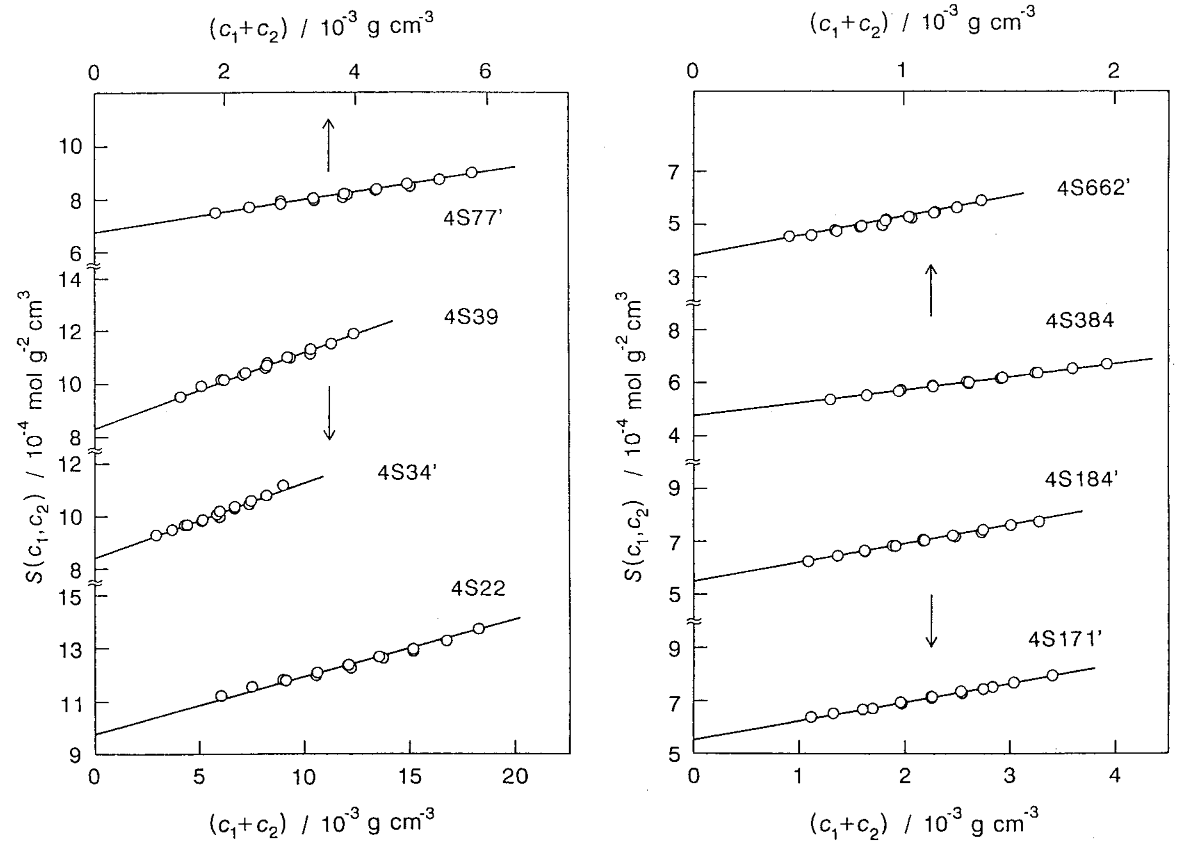

Figure 2. Bawn plots for the indicated samples of four-arm star polystyrene in benzene at 25 °C. The data for pairs of neighboring c_1 and c_2 in a series of polymer concentrations are omitted, since they were less accurate.

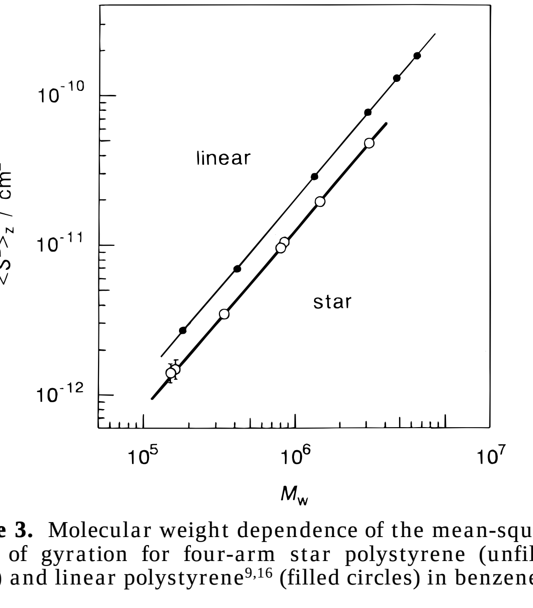

Figure 3. Molecular weight dependence of the mean-square radius of gyration for four-arm star polystyrene (unfilled circles) and linear polystyrene[9,16] (filled circles) in benzene at 25 °C.

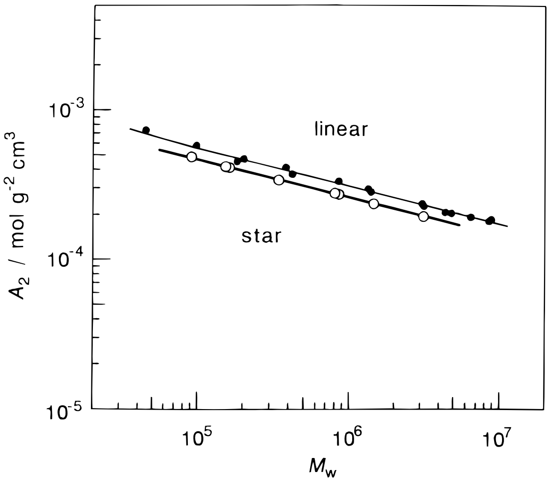

Figure 4. Molecular weight dependence of the second virial coefficient for four-arm star polystyrene (unfilled circles) and linear polystyrene[9,16,17] (filled circles) in benzene at 25 °C.

deduction[18] that Γ increases with increasing f toward the value 0.625 for rigid spheres. However, the Γ values in the figure change significantly with M_w. As is the case for linear polystyrene (see also ref 19), our Γ in the range of M_w between 2×10^5 and 3×10^6 increases in proportion to $M_w^{0.1}$ since $A_2 \propto M_w^{-0.25}$ and $A_3 \propto M_w^{0.6}$ in that range.

The molecular weight dependence of $[\eta]$ for four-arm star polystyrene in benzene is illustrated in Figure 7, which includes the data of Strazielle and Herz[20] for the same system and those for linear polystyrene in benzene.[16,21] The data for the star polymer can be represented by

$$[\eta] = 5.6_2 \times 10^{-5} M_w^{0.75}\ (10^2\ \mathrm{cm^3\ g^{-1}}) \qquad (5)$$

Using the relation $[\eta] = 8.2 \times 10^{-5} M_w^{0.75}$ for linear polystyrene in benzene, we obtain a value of 0.69 for the ratio g_η [$\equiv[\eta](\mathrm{star})/[\eta](\mathrm{linear})$], which is appreciably smaller than our previous value 0.75 in cyclohexane at the Θ point.[1] Such differences in g_η between good and Θ solvents are known for various star polymers.[12]

Values of the Flory viscosity factor Φ [$=[\eta]M_w/(6\langle S^2\rangle_z)^{3/2}$] were calculated to be $(2.8 \pm 0.1) \times 10^{23}$ mol^{-1}

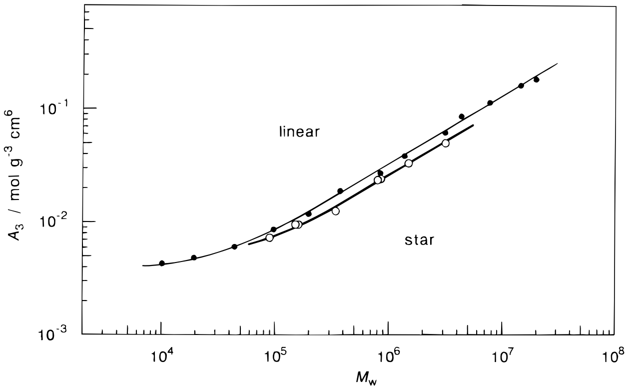

Figure 5. Molecular weight dependence of the third virial coefficient for four-arm star polystyrene (unfilled circles) and linear polystyrene[8,17] (filled circles) in benzene at 25 °C.

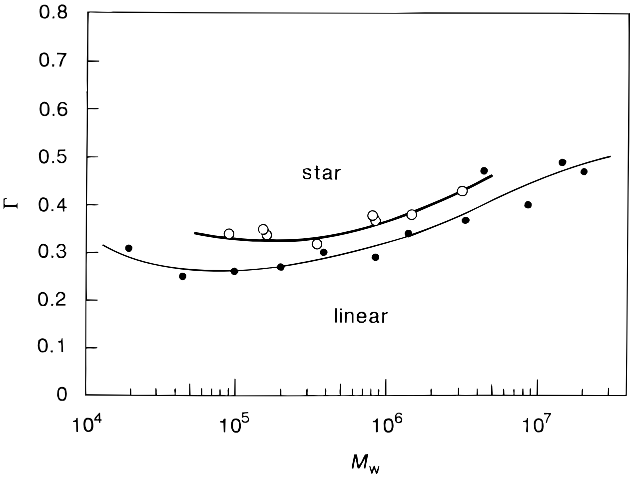

Figure 6. Molecular weight dependence of the reduced third virial coefficient ($\equiv A_3/A_2{}^2M_w$) for four-arm star polystyrene (unfilled circles) and linear polystyrene[8,17] (filled circles) in benzene at 25 °C.

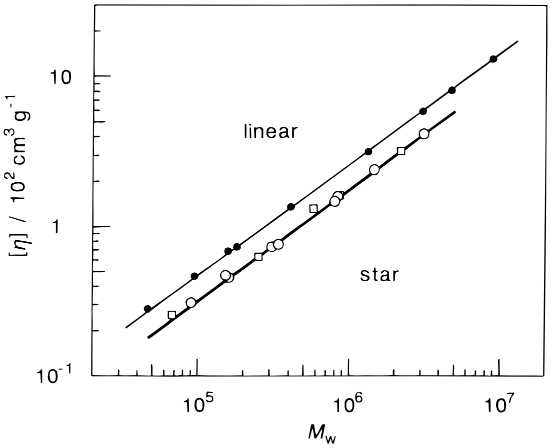

Figure 7. Molecular weight dependence of intrinsic viscosity for four-arm star polystyrene (unfilled circles, present data; squares, Strazielle and Herz[20]) and linear polystyrene[16,21] (filled circles) in benzene at 25 °C.

from the data in Table 1. Note that since $[\eta] \propto M_w{}^{0.75}$ and $\langle S^2\rangle_z \propto M_w{}^{1.19}$ for our system, Φ is almost independent of M_w in the limited range from 1.53×10^5 to 3.14×10^6. Our Φ of 2.8×10^{23} mol^{-1} is somewhat smaller than Roovers and Toporowski's values[11] of $(2.9-3.6) \times 10^{23}$ mol^{-1} in toluene. The recent Monte Carlo simulation value[15] of $2.9_5 \times 10^{23}$ mol^{-1} (in the limit of $N \to \infty$) is close to ours.

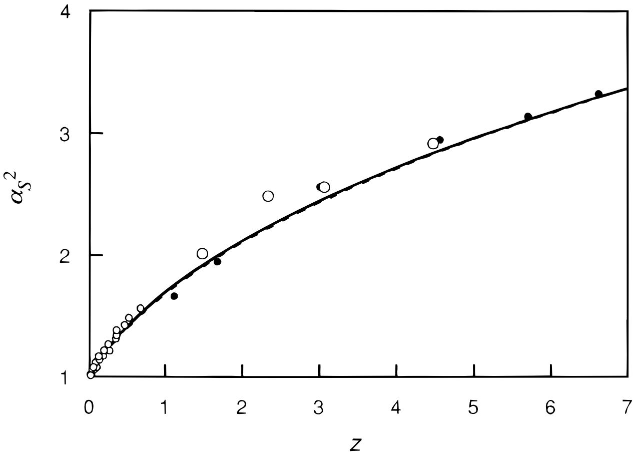

Figure 8. Plots of $\alpha_S{}^2$ against z for four-arm star polystyrene in benzene (larger unfilled circles), four-arm star polystyrene in cyclohexane[1] (smaller unfilled circles), and linear polystyrene in benzene[9,16] (filled circles). The solid and dashed lines represent eq 7 for $f = 4$ and 2, respectively.

Discussion

Expansion Factors. As discussed previously,[1] both $\alpha_S{}^2$ and $\alpha_\eta{}^3$ for four-arm star polystyrene may be treated approximately in the conventional two-parameter theory[22,23] corresponding to the coil limit of the quasi-two-parameter scheme[2] for the helical wormlike chain, provided that M_w is higher than 8×10^5. In this limit, these expansion factors should be universal functions of z defined by

$$z = \left(\frac{3}{2\pi b^2}\right)^{3/2} \beta N^{1/2} \qquad (6)$$

where β is the binary-cluster integral for the interaction between a pair of beads (hereafter we take the monomeric unit as one bead).

With Miyaki's β value of 3.0×10^{-23} cm^3 for linear polystyrene in benzene[9,16] and our previous $\langle S^2\rangle_z$ data for four-arm star polystyrene in cyclohexane at the Θ temperature (34.5 °C), we calculated $\alpha_S{}^2$ and z for our samples with $M_w > 3 \times 10^5$ in benzene.[24] The resulting relation is shown by larger unfilled circles in Figure 8, along with the previously determined relation for the star polymer in cyclohexane near the Θ point (smaller unfilled circles) and that for the linear polymer in benzene (filled circles). It can be seen that the plotted points for the two polymers in benzene come close to each other, as was found previously for cyclohexane solutions.

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

$$\alpha_S{}^2 = (1 + 5.56K_f z + 10.62 z^{20/9})^{0.18} \qquad (7)$$

which was derived by combining the first-order perturbation theory[26] and the asymptotic relation[15] in the limit of infinite z; for $f = 2$ and 4, $K_f = 1.276$ and 1.342, respectively (the expression[26] for the first-order perturbation coefficient K_f is lengthy and omitted here). We note that the values of $\alpha_S{}^2$ calculated from eq 7 for $f = 2$ and from the familiar Domb–Barrett equation[27] agree within 1.3% for $z > 0$.

The solid line in Figure 8 represents eq 7 for $f = 4$. It closely fits the experimental points for the star polymer in benzene as well as those in cyclohexane.[1] Thus, we

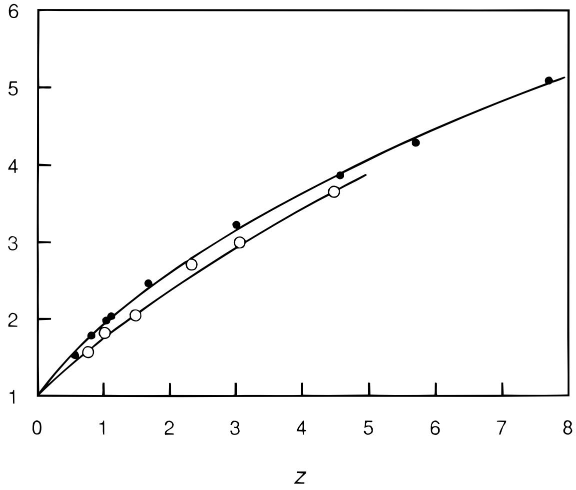

Figure 9. Plots of $\alpha_\eta{}^3$ against z for four-arm star polystyrene in benzene (unfilled circles) and linear polystyrene in benzene[16] (filled circles). Curves represent empirical fits.

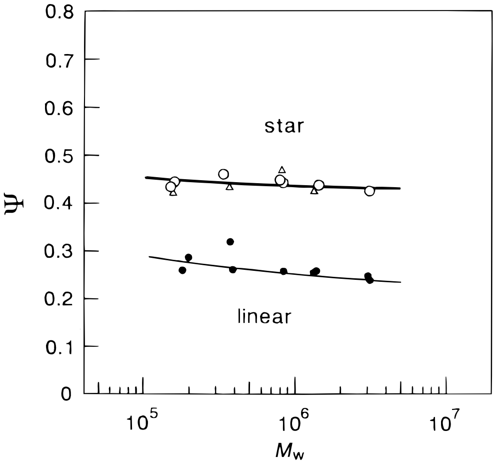

Figure 10. Molecular weight dependence of interpenetration function for four-arm star polystyrene in benzene (unfilled circles), four-arm star polybutadiene in cyclohexane[12] (triangles), and linear polystyrene in benzene[9,12,16,17] (filled circles).

may conclude that the proposed expression satisfactorily describes the z-dependence of $\alpha_S{}^2$ for four-arm star polystyrene of high molecular weight over a broad range of z. The dashed line, which represents eq 7 for $f = 2$, comes very close to the solid line, being consistent with our finding that the $\alpha_S{}^2$ vs z relations for the star and linear polymers are almost the same. It should be noted that the smoothed density model[28] and blob[29] theories fail to predict this fact.

The $\alpha_\eta{}^3$ vs z relations for four-arm star and linear polystyrenes in benzene are compared in Figure 9, where, as in the case for $\alpha_S{}^2$, the $[\eta]$ data in cyclohexane at the Θ point have been used for the unperturbed intrinsic viscosities in benzene. The data points (the unfilled circles) for the star polymer appear systematically below those for the linear polymer (the filled circles). This difference in $\alpha_\eta{}^3$ between the two polymers is a direct consequence of the smaller g_η in benzene than in cyclohexane at the Θ point and offers theorists a challenging problem. In this connection, we note that no such difference was observed in cyclohexane at different temperatures where z was smaller than 0.2.[1]

Interpenetration Function. Figure 10 shows that our values of Ψ for four-arm star polystyrene in benzene (the unfilled circles) are in the range between 0.43 and 0.46 and appear to depend very weakly on M_w (Ψ is defined by $A_2 M_w{}^2/4\pi^{3/2} N_A \langle S^2\rangle_z{}^{3/2}$, with N_A being the Avogadro constant). They are close to the reported values (the triangles) for four-arm star polybutadiene in cyclohexane (at 25 °C),[12] a good solvent; the data reported in the early 1970s[10,30,31] are omitted in the figure because they considerably scatter. The Ψ values for star polystyrene are about 1.8 times as large as those (the filled circles) for linear polystyrene,[9,16] reflecting a higher segment density in star chains.

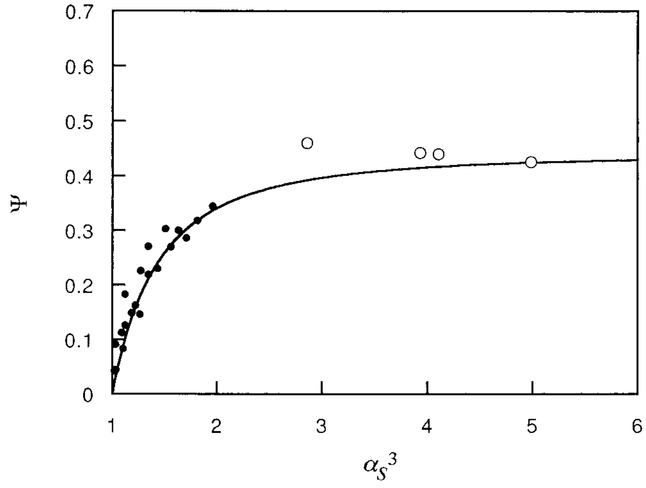

Figure 11. Plots of Ψ vs $\alpha_S{}^3$ for four-arm star polystyrene in benzene (unfilled circles) and in cyclohexane[1] (filled circles). The curve represents eq 8 with eq 7 for $f = 4$.

The renormalization group theory of Douglas and Freed[13] predicts for four-arm star chains in the good solvent limit a Ψ value of 0.53, which is significantly larger than the above experimental values. Recent Monte Carlo simulations give 0.43 (ref 32) and 0.44 (ref 33), being in good agreement with our experiment.

The unfilled and filled circles in Figure 11 show the Ψ data plotted against $\alpha_S{}^3$ for four-arm star polystyrene in benzene and in cyclohexane, respectively. The curve in the figure represents the values calculated from the interpolation equation[1]

$$\Psi = \frac{z}{(\alpha_S{}^2 g_{S0})^{3/2}}\left[1 + 5C_f z + \frac{0.0411}{(\Psi^* g_{S0}{}^{3/2})^5}\, z^2\right]^{-0.2} \qquad (8)$$

and eq 7 for $\alpha_S{}^2$ with $f = 4$. Here, C_f is the first-order perturbation coefficient[34] for A_2 (3.873 for $f = 4$), Ψ^* is the value of Ψ in the limit of $z \to \infty$ (0.44 for $f = 4$),[33] and g_{S0} (the value of g_S in the Θ state) is given by[35]

$$g_{S0} = (3f - 2)/f^2 \qquad (9)$$

The benzene data tend to deviate systematically above the curve with decreasing $\alpha_S{}^3$. This behavior of experimental Ψ is very similar to what has been observed for linear flexible polymers in good solvents,[9,19,23,36-38] and may be ascribed primarily to the effect of chain stiffness on A_2.[2,38,39]

Conclusions

We have determined $\langle S^2\rangle_z$, A_2, A_3, and $[\eta]$ as functions of M_w for four-arm star polystyrene in benzene, a good solvent, and established the ratios of the respective properties to those of the linear chain from comparison with typical data for linear polystyrene in the same solvent. Detailed analyses of $\alpha_S{}^2$, $\alpha_\eta{}^3$, and Ψ (the interpenetration function) have led to the following conclusions.

1. The relation between α_S^2 and z (the conventional excluded-volume parameter) for $M_w > 3 \times 10^5$ is almost the same as that for linear polystyrene in benzene and is satisfactorily described by our interpolation formula[1] previously constructed.

2. On the other hand, the α_η^3 vs z relation for the star polymer comes significantly below that for the linear chain.

3. The values of Ψ, which lie in the range between 0.43 and 0.46, agree substantially with Monte Carlo simulation results.[32,33] Though the previous interpolation formula[1] fairly well reproduces the Ψ data, it tends to deviate downward with decreasing α_S^3 below 4. This is probably due to the effect of chain stiffness on A_2.

Acknowledgment. We thank Professor Hiroshi Watanabe of the Institute for Chemical Research of Kyoto University, who kindly gave us four-arm star polystyrene samples.

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MA971757M