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Dynamic Light Scattering from Regular Star-Branched Molecules[†]

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ABSTRACT: The conformational and dynamic behavior of polystyrene star molecules with 3, 12, and 18 arms has been studied by means of dynamic and static light scattering. Measurements have been carried out in cyclohexane at 34.5 °C and in toluene at 20 °C. The g ($\equiv\langle S^2\rangle_b/\langle S^2\rangle_l$) and h ($\equiv R_{hb}/R_{hl}$) factors were determined in both solvents by comparison of the properties of branched and linear chains. In addition the ρ ($\equiv\langle S^2\rangle^{1/2}/R_h$) parameters were obtained from the combined measurements of the radius of gyration $\langle S^2\rangle^{1/2}$ and the hydrodynamic radius R_h. The g and h factors have nearly the same values in both solvents, with the exception of the 18-arm star, where $g_\Theta > g$ and $h_\Theta > h$. Furthermore, the experimental data are larger than predicted by theory, and the deviations appear to increase with increasing number of arms. This effect is taken as evidence for a perturbation of Gaussian statistics of a single chain by the presence of the others. The ρ values were found to be 14–25% lower than expected from theory. In the good solvent this ρ parameter is about 20% larger than in the Θ-solvent. The three parameters g, h, and ρ also show a chain length dependence. The increase of g and h with decreasing $\bar{M}_w$ is explained by a chain expansion due to the high segment density, which becomes more effective for short arms. This result is in qualitative agreement with a recent theory by Daoud and Cotton. The increase of ρ at lower $\bar{M}_w$ indicates an increasing influence of the free-draining term. The effect of excluded volume is represented by the factor $g(\alpha) = \alpha_{Sb}^2/\alpha_{Sl}^2$, where α_{Sb} and α_{Sl} are the chain expansion factors of the branched and linear chains, respectively. The curve $g(\alpha)$ as a function of $\bar{M}_w$ shows a minimum at about $\bar{M}_w = 1.5 \times 10^5$. In this region $\alpha_{Sb} \simeq 1$; the star molecule is already in the Θ-solvent considerably stretched and the excluded volume has no further effect. For the linear chains α_{Sl} is still appreciably larger than those of the linear chains. The second virial coefficients were found to be smaller than those of the linear chains. The effect is, however, less pronounced than predicted by theory.

In previous papers the properties of regular star molecules were compared with those of the corresponding linear chains.[4,6,9–16] In many cases the common static light scattering technique has been applied for determining the mean square radii of gyration and the decrease of the Θ-temperature with increasing arm number and decreasing arm molecular weight, respectively. The arm chain length of many of the prepared star molecules was in a region which is no longer appropriate for a determination of $\langle S^2\rangle$ by light scattering, and therefore the products were characterized by intrinsic viscosity, $[\eta]$, measurements. Unfortunately, the relation between $\langle S^2\rangle$ and $[\eta]$ is complicated by hydrodynamic interactions, which up to now appear not to be fully understood.

A further study of the simple star-branched structures remains an interesting subject as a consequence of several recent developments. The first results from the high standard reached in the anionic linking reaction by which the preparation of well-defined stars with 8, 12, or 18 arms is now possible.[11,12,16] Secondly, new measurement methods of high precision, as, for instance, dynamic light scattering, have been recently developed and thus allow the detection of rather small deviations from the theoretically predicted behavior.

In this paper we report on combined static light scattering (SLS) and dynamic light scattering (DLS) measurements from 3-, 12- and 18-arm near-monodisperse polystyrene (PS) star molecules in dilute solution of a Θ-solvent and a good solvent. These measurements gave us data of the translational diffusion coefficient or hydrodynamic radius in addition to the quantities mentioned above. The theory for the hydrodynamic radius can be treated mnore rigorously than that of intrinsic viscosity, and for this reason a better understanding of the effect of hydrodynamic interaction can be anticipated.[17]

Experimental Section

The construction and handling of the light scattering apparatus, which allows the simultaneous recording of the SLS and DLS, were published elsewhere.[18] A krypton Kr AT 165 laser (Spectra Physics) was used as light source (647.1 nm). Cylindrical glass cells with a diameter of 10 mm, used as scattering cells, were placed in the center of a refractive index matching bath with toluene as the liquid. The scattered light was evaluated by an autocorrelator (Malvern K 7023) with 96 channels, of which 72 were used for the time correlation function (TCF). The last 20 channels are delayed by 164 sample times and yield the base line, which in all measurements was compared with the calculated "far point".

Toluene and cyclohexane were distilled over Na wire. The polymer solutions were clarified by centrifugation of the scattering cells in a swinging bucket rotor, applying the floating technique.[19]

The dn/dc values of the polystyrene stars in toluene and cyclohexane were determined with the Chromatix laser differential refractometer KMX-16, operating at 633 nm. In toluene at 20 °C the measurements yielded a value of dn/dc = 0.103 cm^3/g for nearly all the star-branched molecules. Only the low molecular weight samples PS 9-12 (dn/dc = 0.098 cm^3/g and PS 6-12 (dn/dc = 0.100 cm^3/g) exhibit significant deviations from this value. In cyclohexane at 34.5 °C we measured dn/dc = 0.157 cm^3/g for the 12-arm stars and dn/dc = 0.163 cm^3/g for the 3-arm stars. The toluene values are in accord with those presented elsewhere.[20]

The polystyrene stars were prepared by following the general procedures outlined elsewhere.[9,11,12] The initiator was purified *sec*-butyllithium. Benzene was the polymerization solvent. Prior to linking the linear arms into the star-shaped structure, we reacted the active centers with several units of butadiene in order to facilitate the linking reaction.[9,10] Before the addition of the linking agent a small amount of solution was removed from the glass reactor, the active centers were quenched with methanol, and the linear polystyrene was isolated by freeze-drying. The linking agents were the chlorosilanes CH_3SiCl_3 (Petrarch), $Si(CH_2CH_2SiCl_3)_4$, and $(Cl_3SiCH_2CH_2)_3SiCH_2CH_2Si(CH_2CH_2SiCl_3)_3$. The preparation of the dodeca- and octadecachlorosilanes has been previously described.[11,12]

Preliminary characterization of the polystyrene stars and their constituent arms was done with membrane osmometry, when feasible, size exclusion chromatography, and low-angle laser light scattering. For the latter measurements, the Waters 150C and Chromatix KMX-6 instruments were combined. The Waters 150C instrument was equipped with a five-column μ-Styragel set having a porosity range of 10^6 to 5×10^2 Å. The carrier solvent was tetrahydrofuran at a flow rate of 1 mL min^{-1}. All of the samples were found to have near-monodisperse molecular weight distributions ($\bar{M}_z/\bar{M}_w$ and $\bar{M}_w/\bar{M}_n < 1.1$) following the removal of unlinked arms via fractionation.

[†] In honor of Walter H. Stockmayer, mentor, friend, and continuing source of inspiration.

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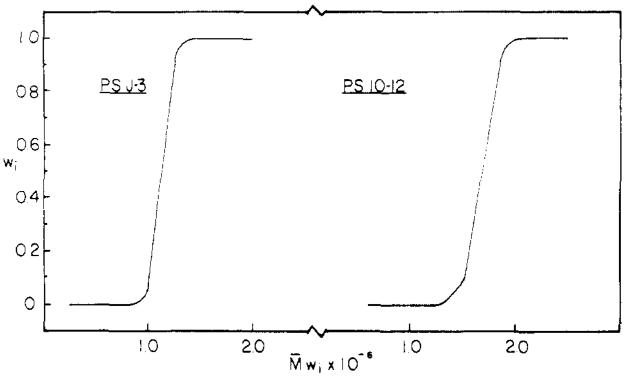

Figure 1. Cumulative molecular weight distributions for the PS J-3 and PS 10-12 polystyrene stars.

The combination of the Waters 150C instrument with the Chromatix KMX-6 low-angle laser light scattering instrument allows the evaluation of the cumulative molecular weight distributions of the star polystyrenes. Representative distributions (Figure 1) show that these star-branched polystyrenes possess essentially uniform degrees of branching. Similar results have also been reported[16] for the 18-arm polystyrene used in this work.

Results

Linear PS has a Θ-temperature in cyclohexane of 34.5 °C. Most of our measurements on three 3-arm stars, six 12-arm stars, and one 18-arm star were carried out in cyclohexane at 34.5 °C and in toluene at 20 °C. In a recent paper Bauer et al.[14] reported Θ-temperature depressions for 8- and 12-arm polyisoprene (PI) stars. They noticed a drop of about 12 °C for the lowest molecular weight 12-arm star with arm molecular weight $\bar{M}_{nb} = 5 \times 10^3$, which became increasingly smaller with increasing $\bar{M}_{nb}$ and approached a plateau for $\bar{M}_{nb} = 5 \times 10^4$, where the Θ-temperature depression was less than 1.5 °C.

To check this effect for PS star molecules, we carried out temperature-dependent measurements of the SLS and DLS with two 12-arm stars PS 4-12 ($\bar{M}_w = 4.67 \times 10^5$, $\bar{M}_{n,arm} = 3.9 \times 10^4$) and PS 10-12 ($\bar{M}_w = 1.69 \times 10^6$, $\bar{M}_{n,arm} = 1.4 \times 10^5$). The temperature dependence of A_2 for PS 4-12 is shown in Figure 2a. Accordingly the sample has a Θ-temperature of 29 °C. For the high molecular weight stars a Θ-temperature of 34 °C was observed.

Panels b and c of Figure 2 show the results of hydrodynamic radii R_h and the radii of gyration $S \equiv \langle S_2\rangle^{1/2}$ for the PS 4-12 sample. The hydrodynamic radius is defined by eq 5. Only a slight decrease in R_h is obtained in the temperature region of 7 °C below Θ despite a marked change in A_2. The experimental error for S for the low molecular weight 12-arm star is much higher than for R_h, but within this region of error no variation with temperature was observed. The drop of the Θ-temperature for sample PS 10-12 is less than 1 °C and here also no significant change in dimensions was observed. Therefore the Θ-temperature depression for the low molecular weight star can be considered to be of minor relevance for the determination of the conformational properties—at least with regard to the accuracy of the present instrument.

The interpretation of the SLS is common practice and will not be discussed here. In our DLS we used the homodyne technique, where a TCF of the scattering intensity $\langle i(0)i(t)\rangle = G_2(t)$ is recorded. This TCF is for dilute solutions and is related to the TCF of the electric field[21]

$$g_1(t) \equiv \langle E(0)E^*(t)\rangle/[E(0)] \tag{1}$$

as follows:

$$G_2(t) = A + Bg_1(t)^2 \tag{2}$$

where A and B are constant factors and $E(0)$ and $E(t)$ are the electric scattering fields at time zero and a delay time t. In all cases we observed a single-exponential decay of

$$\left(\frac{B}{A}\right)^{1/2} g_1(t) = \left(\frac{G_2(t)}{G_2(\infty)} - 1\right)^{1/2} \cong \left(\frac{B}{A}\right)^{1/2} e^{-\Gamma t} \tag{3}$$

as a function of time. The decay constant Γ is called the first cumlant, which is related to the translational diffusion coefficient D by[22,23]

$$\Gamma = Dq^2(1 + C\langle S^2\rangle q^2 - ...) \tag{4}$$

where $q = (4\pi/\lambda) \sin (\theta/2)$ with θ the scattering angle and λ the wavelength in the medium. The reduced first cumulant Γ/q^2 is, in general, a function of the scattering angle. In the present case, however, no angular dependence of Γ/q^2 was observed. The application of the Stokes–Einstein relationship allows an effective hydrodynamic radius to be determined from the translational diffusion coefficient by the following equation:

$$D = \frac{kT}{6\pi\eta_0 R_h} \tag{5}$$

where η_0 is the solvent viscosity.

The diffusion coefficient is, in general, concentration dependent and can for dilute solutions with $c < c^*$ be described by

$$D(c) = D(1 + k_D c) \tag{6}$$

where c^* is the overlap concentration.[24,25]

Equation 4 suggests a plot of the reduced first cumulant Γ/q^2 against q^2 and extrapolation toward $q^2 = 0$; the intercept is $D(c)$. This value has then to be plotted against the concentration and extrapolated for $c \rightarrow 0$.

In none of the investigated star molecules was an angular dependence observed, although the SLS yielded a significant angular distribution for the higher molecular weights, which was evaluated by the use of Zimm plots. Some samples exhibited a noticeable upturn of the angular envelope. In these cases we made also a plot of $(Kc/\Delta R_\theta)^{1/2}$ against q^2 (Berry plot),[26] by which the Zimm plot became transformed into a straight line. This plot allowed a more reliable extrapolation toward zero angle.[23] Mostly, however, the curvature in the Zimm plots was very slight.

Figure 3 shows, as an example, the angular dependence of the SLS of the 3-arm star PS J-3 in cyclohexane at 34.5 °C and in toluene at 20 °C. In Figure 4 the k_D values of

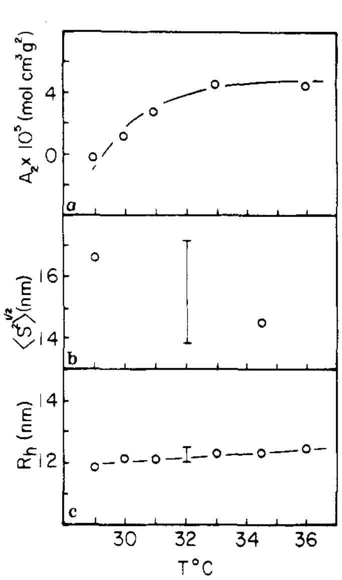

Figure 2. Temperature-dependent measurements on A_2, $\langle S^2\rangle^{1/2}$, and R_h for sample PS 4-12 in cyclohexane. The bars indicate the experimental error.

Table I
Molecular Weight $\bar{M}_w$, Mean Square Radius of Gyration $\langle S^2 \rangle$, Diffusion Coefficient D, and Hydrodynamic Radius R_h of Polystyrene Star Molecules in Toluene at 20 °C and in Cyclohexane at 34.5 °C and the Second Virial Coefficient in Toluene

			toluene				cyclohexane		
sample	f^a	$\bar{M}_w \times 10^{-3}$	$A_2 \times 10^4$, mol·cm³·g⁻²	$\langle S^2 \rangle$, nm²	$D \times 10^7$, cm²·s⁻¹	R_h, nm	$\langle S^2 \rangle$, nm²	$D \times 10^7$, cm²·s⁻¹	R_h, nm
PS A-3	3	12.4	10.1		14.9_6	2.4_3		11.7_3	2.5_5
PS I-3	3	920	2.7_9	1390	1.2_7	28.1	488	1.4_7	20.4
PS J-3	3	1190	2.7_9	1830	1.1_3	32.2	762	1.2_8	23.4
PS 9-12	12	55	4.9_8		7.4_6	4.8_7		6.6_1	4.5_8
PS 6-12	12	149	3.7_0	110	4.4_0	8.2_5	137	4.0_4	7.4_4
PS 4-12	12	467	2.0_9	320	2.3_9	15.2	240	2.4_2	12.4
PS 5-12	12	808	1.8_2	548	1.7_9	20.7	219	1.8_5	16.3
PS 7-12	12	1110	1.7_2	930	1.4_7	24.7	420	1.6_1	18.7
PS 10-12	12	1690	1.6_2	1300	1.2	30.5	392	1.3_5	22.3
18-PS1	18	8770 8800^b	0.7_4	5430 4800^b	0.480	64.2	1689 1600^b	0.62_1	48.3

[a] f denotes star functionality, which is derived from the ratio of star and arm molecular weights. Within experimental error, the star polystyrenes used in this work had the functionalities listed. [b] Reference 16; via static light scattering.

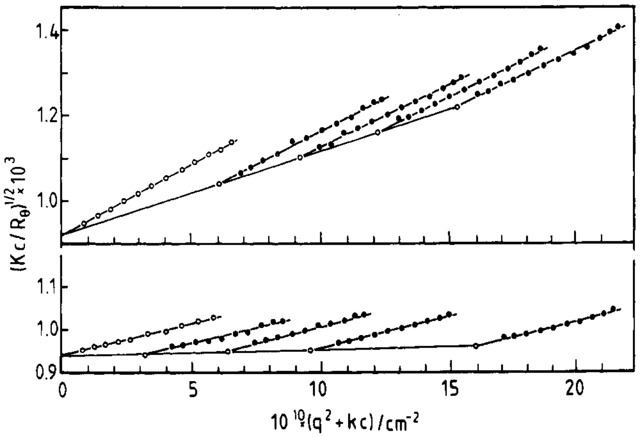

Figure 3. Berry plots in toluene at 20 °C (above) and cyclohexane at 34.5 °C (below) of one of the 3-arm stars (PS J-3).

the investigated star molecules are compared with the respective behavior of the linear chains.[27-31] A complete list of $\bar{M}_w$, A_2, $\langle S^2 \rangle$, R_h, and D is given in Table I.

The experimental error in the mean square radius of gyration for the higher molecular weights was 5–10% and amounts up to 30% for the PS 6-12 sample. The corresponding error in the diffusion coefficient was always less than 2%.

The dilute solution properties are usually interpreted in terms of the two shrinking factors g and h based on the mean square radii of gyration of the branched and linear chain at the same molecular weight

$$g \equiv \langle S^2 \rangle_b / \langle S^2 \rangle_l \tag{7}$$

and on the respective hydrodynamic radii at the same molecular weight

$$h \equiv R_{hb}/R_{hl} \tag{8}$$

As long as the chain conformation of an arm in an f-star molecule is not perturbed by the presence of the other $f - 1$ arms, the g and h factors must show values smaller than unity. Equations were derived by Zimm and Stockmayer[1] and by Stockmayer and Fixman[3] for molecules in Θ-solvents (i.e., $A_2 = 0$).

$$g = (3f - 2)/f^2 \tag{9}$$

$$h = \frac{f^{1/2}}{2 - f + 2^{1/2}(f - 1)} \tag{10}$$

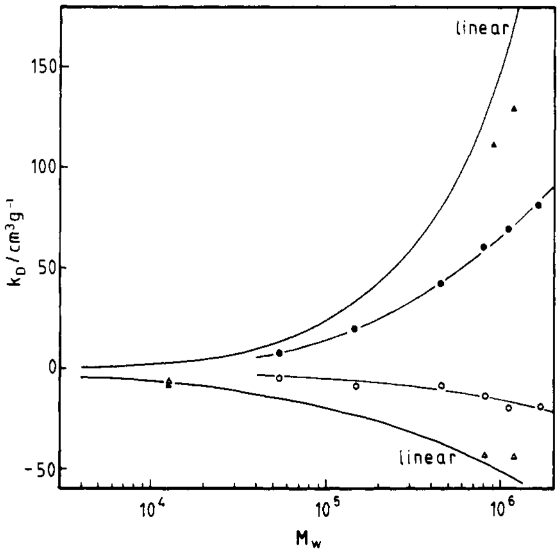

Figure 4. Experimental k_D values of the stars in toluene ((▲) 3-arm; (●) 12-arm) and cyclohexane ((△) 3-arm; (○) 12-arm) in comparison with the behavior of linear chains (upper and lower lines).[27-31]

Panels a and b of Figure 5 show the dependence on f according to these two equations and the experimental results of the star molecules obtained from measurements in cyclohexane at 34.5 °C and toluene at 20 °C. In Figure 5a we have also used results from earlier studies[9,10,14] for PS stars and PI stars. For the determination of the g and h factors, the corresponding quantities of the linear chains are required. The $\langle S^2 \rangle$ values of PS in toluene have been taken from a relationship by Raczek,[32] while the relationship for R_h was established by our own DLS measurements[27,28] on anionic linear PS in a molecular weight range from 3×10^4 to 2×10^6. Details will be published elsewhere.[27] The corresponding relationship for the linear PS in cyclohexane were taken from Schmidt and Burchard.[33]

The properties of star molecules can be characterized also by a dimensionless quantity

$$\rho \equiv \langle S^2 \rangle^{1/2}/R_h \tag{11}$$

This parameter ρ has the advantage that two quantities $\langle S^2 \rangle^{1/2}$ and R_h can be obtained directly from our combined light scattering measurement, and reference to linear

Table II
ρ Ratios and Molecular Shrinking Factors g and h (Eq 7 and 8) in Comparison with Theoretical Predictions Based on Eq 9 and 10 and Monte Carlo (MC) Calculations[35]

		g				h			ρ	
sample	f	C_6H_{12}	MC	eq 9	C_7H_8	C_6H_{12}	eq 10	C_7H_8	C_6H_{12}	C_7H_8
	2^a			1.000			1.000		1.27	1.56
PS A-3	3					0.99_2		0.97_2		
PS I-3	3	0.63_1			0.71_2	0.92_9		0.93_9	1.08	1.33
PS J-3	3	0.76_1	0.83	0.77_7	0.69_0	0.93_7	0.94_7	0.92_7	1.18	1.33
	4		0.67	0.62_5			0.89_2			
	6		0.50	0.44_5			0.79_8			
	8		0.40	0.34_4			0.72_5			
	9		0.36	0.30_9			0.69_5			
PS 9-12	12					0.84_7		0.83_0		
PS 6-12	12	1.1			0.9	0.84_2	0.86	0.79_0	1.57	1.27
PS 4-12	12	0.61_2			0.36_8	0.79_2		0.75_2	1.25	1.18
PS 5-12	12	0.32_2			0.32_7	0.79_2		0.74_6	0.91	1.13
PS 7-12	12	0.45_0			0.38_1	0.77_5		0.74_0	1.10	1.23
PS 10-12	12	0.27_6		0.23_6	0.32_3	0.74_9	0.62_3	0.73_0	0.89^d	1.18
18-PS1	18	0.22_9 $(0.22_8)^b$		0.16_0	0.19_0 $(0.20_3)^b$	0.71_2 $(0.76)^{b,c}$	0.52_8	0.58_3 $(0.68)^{b,c}$	0.85^d	1.15

[a] Linear polystyrene. [b] Reference 16. [c] Based on sedimentation velocity coefficients. [d] These values are close to the theoretical value of 0.77_5 for hard spheres. These findings are in accord with parallel observations reported in ref 16.

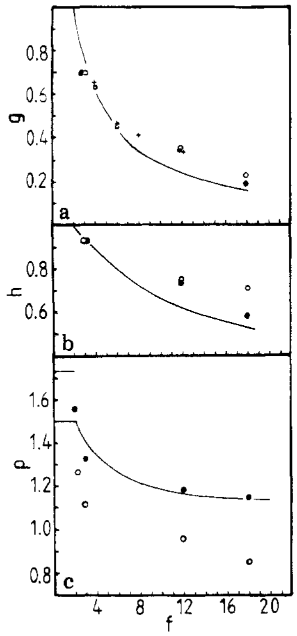

Figure 5. g, h, and ρ as a function of f. The continuous lines are calculated with eq 9, 10, and 12, respectively. The experimental data from measurements in toluene and cyclohexane are represented by filled and unfilled circles, respectively. The plots, in addition, contain literature data of PS in cyclohexane[9,10] (□) and PI in dioxane[13,14] (+).

standards, as in the case of g and h, is no longer required. The dependence of ρ on the number of arms was calculated for unperturbed stars:[22]

$$\rho = \left(\frac{3f-2}{f\pi}\right)^{1/2} \frac{8[2-f+2^{1/2}(f-1)]}{3f} \qquad (12)$$

The theoretically predicted dependence on f is shown in Figure 5c together with data of measurement. The ρ parameters in good solvent have been calculated only for linear chains.[34-36]

Equations 9, 10, and 12 contain no molecular weight dependencies, which is a consequence of the assumed Gaussian subchain statistics. Since this assumption is not justified for chains in a good solvent, we determined the g, h, and ρ parameters for the six available 12-arm stars.

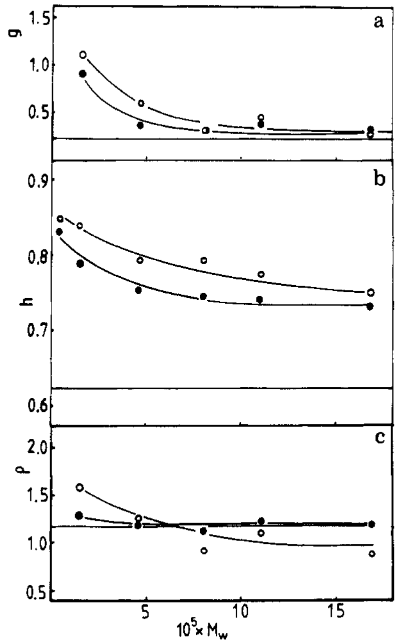

Figure 6. Dependence of g, h, and ρ on $\bar{M}_w$ of the 12-arm stars in toluene (●) and cyclohexane (○). The predicted values of the eq 9, 10, and 11 are indicated by the lines parallel to the abscissa.

A clear molecular weight dependence is observed for the samples in toluene, as expected, but also in cyclohexane (Figure 6a–c). Similar results have also been observed for 8-, 12-, and 18-arm polyisoprenes[37] in non ideal and ideal solvents. The values at the largest molecular weights were taken for the plots in Figure 5a–c. The various values for g, h, and ρ are given in Table II.

Finally, we determined the second virial coefficients of the star molecules. They are shown in Figure 7 in comparison to the molecular weight dependence of A_2 for linear PS, where the results of Berry,[26] Bawn and Wajid,[38] Bantle, Schmidt, and Burchard,[18] and Huber and Burchard[27] were used.

Discussion

The results of this investigation may be summarized as follows:

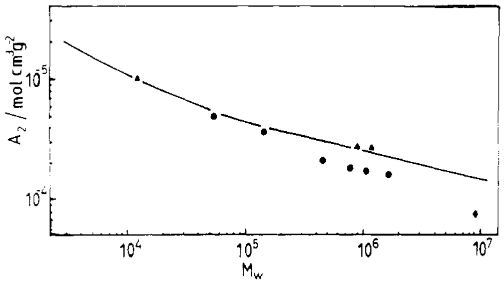

Figure 7. Plot of log A_2 vs. log $\bar{M}_w$. The continuous line gives the experimental curve of linear PS. The symbols denote (▲) 3-arm stars, (●) 12-arm stars, and (♦) 18-arm stars.

1. The experimental g values at the Θ-point are, within the limits of error, the same as for the molecules in a good solvent except that of the star with 18 branches.

2. Up to an arm number of $f = 6$, good agreement of g with theory is found.[9,10] At $f > 6$, g shows deviations from theory toward larger values, a trend which has been observed elsewhere.[14] In other words, the shrinking of $\langle S^2 \rangle$ is less than predicted by theory under the assumption that the individual star arms remain undisturbed by the presence of the others.

3. Similar deviations from theory are observed for the hydrodynamic shrinking factor h.

4. The deviations of h are less pronounced in the good solvent both for the 12-arm stars and for the 18-arm star.

5. A considerable depression of the experimental ρ values under Θ-conditions was found. This deviation from theory seems to increase slightly with the arm number f.

6. The second virial coefficients for the 12- and 18-arm stars are lower than for the linear chains of the same molecular weight. For short arms the A_2 values of the stars approach the relationship of the linear chains.

The deviations in g and h may be interpreted as follows. The assumption that the attached chains preserve their unperturbed dimensions is apparently valid only for stars with 6 or less arms. If the star has 8 or more arms, the conformation of an arm becomes increasingly perturbed by the presence of the other arms, simply because of an overcrowding of segments near the star center. In fact, Monte Carlo calculations of star molecules on the basis of self-avoiding walks on a lattice by several authors[39-41] reveal similar deviations from the Gaussian behavior when the arm number is larger than 4. The g values calculated by Mazur and McCrackin[39] are given in Table II. Calculations for the hydrodynamic radii $\langle 1/R_h \rangle^{-1}$ have not been performed.

The molecular weight dependence of g and h indicates that the geometric and hydrodynamic shrinking becomes smaller or vanishes with decreasing molecular weight. The following arguments may serve as an explanation. In the star molecule there exists a core of a very high segment density which near the center will approach close sphere packing. Linear chains in the bulk can still realize Gaussian unperturbed conformations since both chain ends can move freely. In a star molecule, however, f chains are fixed at a common junction point; thus, for this reason, the Gaussian chain statistics can no longer be realized and the chain must stretch out. Such extension opposes the shrinking of the star dimensions calculated under the assumption that the arms are not disturbed by the presence of the others. The chain expansion is not uniform since near the star center the self-avoiding effect is strong while near the periphery the segment density is small and consequently the self-avoiding effect is low. Eventually, for long arms, ideal chain behavior will become possible under Θ-solvent conditions. This consideration leads to the conclusion that the effect of stretching has more influence for short arms than for the longer ones, and for very short chains the chain stretching may overcompensate the shrinking due to branching. This seems to be the case for the lowest molecular weight PS 9-12 star although one has to keep in mind the rather high experimental error in that region.

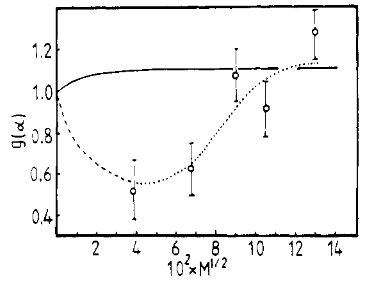

Figure 8. $g(\alpha)$ as a function of $\bar{M}_w^{1/2}$. The continuous line is a theoretical curve, the dashed one is calculated under the assumption of $\alpha_{S_b} \sim 1$, and the dotted line is an interpolated curve, obtained from the smoothed experimental curves of S as a function of $\bar{M}_w$.

The behavior of the g and h factors of the stars in a good solvent is governed by two effects: (i) the shrinking due to branching and (ii) the chain expansion due to the excluded volume effect. We thus may conveniently write

$$g = \frac{\langle S^2 \rangle_s}{\langle S^2 \rangle_l} = \frac{\langle S^2 \rangle_{0s} \alpha_s^2}{\langle S^2 \rangle_{0l} \alpha_l^2} = g_\Theta g(\alpha) \tag{13}$$

and

$$h = \frac{R_{hb}}{R_{hl}} = h_\Theta \frac{\alpha_{hb}}{\alpha_{hl}} = h_\Theta h_\alpha \tag{14}$$

where g_Θ and h_Θ are the shrinking factors of the stars, in the Θ-solvent discussed above.

The factor $g(\alpha)$ can be calculated on the basis of common theories on excluded volume. Following Yamakawa, we can for a very good solvent use the generalized Flory relationship

$$\alpha_S^5 - \alpha_S^3 = K_f z = K_f k' M^{1/2} \tag{15}$$

where for linear chains $K_1 = 1.276$ and for the 12-arm stars $K_{12} = 1.770$. In the above equation we have used

$$z = \left(\frac{3}{2\pi b^2} \right)^{3/2} \beta N^{1/2} \tag{16}$$

with β the cluster integral (excluded volume) of a segment, b the effective bond length, and N the number of segments in the chain. Since β can be assumed to have the same value in the linear and star-branched chain, the proportionality factor k' can be obtained from the experimental relationship of $\alpha_S^5 - \alpha_S^3$ as a function of $M^{1/2}$ of linear polystyrene in toluene. Our own measurements in toluene at 20 °C yielded

$$k' = 0.0040 \tag{17}$$

We then calculated for the 12-arm stars the $M^{1/2}$ dependence of $\alpha_S^5 - \alpha_S^3$ using $K_{12} = 1.770$ in eq 15 and derived from the two relationships of the linear and 12-arm star molecules the ratio

$$g(\alpha) = \alpha_S^2 / \alpha_{Sl}^2 \tag{18}$$

at the same $\bar{M}_w$.

This function is shown as the continuous line in Figure 8. One notices that $g(\alpha)$ is slightly molecular weight dependent at low $\bar{M}_w^{1/2}$ but approaches a plateau above $\bar{M}_w^{1/2} = 300$ with a value of $g(\alpha) = 1.1$. All measured star molecules had $\bar{M}_w^{1/2} > 300$, and therefore we should observe a total shrinking factor g which is about 10% higher than the corresponding value in the Θ-solvent. The more pronounced expansion of the star molecules compared to that of a linear chain is the consequence of the higher segment density in the star molecule, by which the probability of contacts between segments is enhanced.

The experiments indeed show an increase for g of that magnitude for the highest molecular weight of the 12-arm stars; but for the lower molecular weights a continuous decrease well below the theoretical curve is obtained. For the lowest molecular weight we find $\alpha_{S_b}^2 \cong 1$, i.e., no expansion of the arms under the influence of the excluded volume, while for a linear chain of the same arm length the excluded volume is, with $\alpha_{S_l}^2 = 1.7$, still effective. In other words the short arms already under Θ-conditions are so largely stretched out that the excluded volume has no additional effect. For very long chains, on the other hand, the segment volume and the corresponding overcrowding in space plays no essential role and the theoretically predicted increase of $g(\alpha)$ is obtained as a result of the excluded volume effect. The dashed line was calculated under the assumption that $\alpha_{S_b} = 1$ in that region while for the linear chains α_{S_l} is still larger than unity and only gradually approaches this value. For very short chains $g(\alpha) \rightarrow 1$, since in both the linear and branched chains the excluded volume effect is no longer effective.

Our results generally correspond with the predictions of the simplified model of Daoud and Cotton.[42] These authors divide star molecules into three domains: (i) at large radii from the center they assume essentially the same excluded volume behavior as linear chains have at comparable low concentration; (ii) at medium radii from the center they assume complete shielding of the excluded volume effect, i.e., $\alpha_S = 1$; and (iii) near the center they assume a core of close segment packing. In fact, region i of the Daoud model may be recognized for the highest molecular weight (the dashed line). In the region between these limits we have contributions from all three domains of the Daoud–Cotton model, contributions which are difficult to separate.

The molecular weight dependence of the hydrodynamic shrinking factor h shows, as expected, similar behavior to g. Although h still decreases slightly with molecular weight, the high accuracy of the measurements shows clearly that the theoretical value, indicated by the horizontal line, will never be approached. The larger values of h may be due to the same reasons as discussed for the g factor, but there may be also an additional effect which results from the hydrodynamic interaction between the segments. This suspicion is confirmed when the expansion of $\alpha_h = R_h/R_{h\Theta}$ of the hydrodynamic radius in toluene is inspected. While in the limit of long arms $\alpha_{S_b}^5 - \alpha_{S_b}^3 > \alpha_{S_l}^5 - \alpha_{S_l}^3$, we find for the hydrodynamic expansion the opposite behavior, i.e., $\alpha_{hb}^5 - \alpha_{hb}^3 < \alpha_{hl}^5 - \alpha_{hl}^3$, as is shown in Figure 9. Clearly, the excluded volume has less effect on the hydrodynamic radius in the star molecules than it has on the geometric radius of gyration.

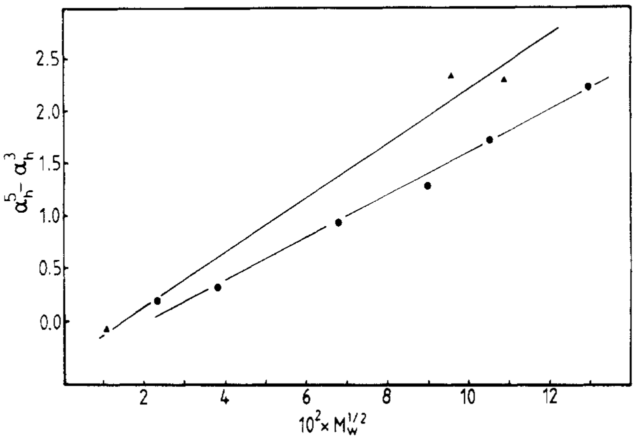

Figure 9. $\alpha_h^5 - \alpha_h^3$ as a function of $\bar{M}_w^{1/2}$. The data of the 12-arm (●) and 3-arm stars (▲) are compared with the experimental behavior of linear PS, which is represented by the upper line.

The hydrodynamic interaction increases with the segment density and causes an increase of R_h in addition to the chain stretching discussed already for $\langle S^2 \rangle$. In good solvents the segment density is lowered and the hydrodynamic interaction is thus weakened. The hydrodynamic radius now becomes governed by two counteracting effects: (i) the geometric expansion due to the excluded volume and (ii) the decrease of the hydrodynamically effective sphere radius as a result of the decreasing segment density; i.e., the solvent penetrates deeper into the coiled molecule. The described effect is particularly acute for the 18-arm star.

Concerning the ρ parameter, three effects have to be discussed: (i) the chain length dependence, (ii) the dependence on the number of arms, and (iii) the influence of the solvent power.

The ρ parameter is experimentally derived from the translational diffusion coefficient D and the radius of gyration $\langle S^2 \rangle^{1/2}$ for the same molecule

$$\rho = \frac{6\pi\eta_0}{kT} D \langle S^2 \rangle^{1/2} \tag{11'}$$

Inserting in this equation the relationship for the radius of gyration and the diffusion coefficient of the regular star molecules in the unperturbed state, one obtains, if the effect of free draining is taken into account[22,43]

$$\rho = \frac{b}{af}\left(\frac{3f-2}{6N}\right)^{1/2} + \frac{8}{3}\,\frac{(2-f) + 2^{1/2}(f-1)}{(\pi f)^{1/2}}\left(\frac{3f-2}{f^2}\right)^{1/2} \tag{19}$$

where a is the hydrodynamic radius of an individual monomer and b the effective bond length; in particular, for $f = 12$ we have

$$\rho = \frac{b}{a}(0.198/N^{1/2}) + 1.16 \tag{20}$$

For sufficiently long arms the effect of the free-draining term becomes negligibly small, but for short chains the first term has an additional effect, and ρ should increase with decreasing M, which is, in fact, observed qualitatively for the Θ-solvent but not for the good solvent. However, in order to describe the observed increase quantitatively, we have to assume $b/a = 45$ and $b/a = 43$ for the two lowest molecular weights, which correspond to quite unrealistically low values for the hydrodynamic radius of one repeating unit. We thus come to the conclusion either that the Kirkwood general diffusion equation does not describe correctly all of the effects of the hydrodynamic interaction or that the non-Gaussian chain behavior of the short chains contains in the nondraining term a certain chain length dependence.

For very long chains, on the other hand, the effect of mutual perturbation of the arms becomes negligible, and in this limit we should observe a ρ value of 1.16, while experimentally 0.96 is found. As already mentioned, a lower limiting value is found also for the linear chains, an

Table III
Values for C_f and K_f for Different Degrees of Branching f

f	C_f	K_f
1	2.865	1.276
3	3.279	1.298
12	11.585	1.770
18	19.543	2.054

observation which fortifies our doubt regarding the Kirkwood approximation for the hydrodynamic interaction.

In order to discuss the effect of the solvent power, we can write

$$\rho = \rho_\Theta \alpha_S / \alpha_\mathrm{h} \tag{21}$$

Experimentally, we found for long chains of comparable length, i.e., DP(arm) of 2×10^3 to 3×10^3, $\alpha_S/\alpha_\mathrm{h} = 1.35$, 1.23, 1.19, and 1.20 for $f = 18$, 12, 3, and 1, respectively. These data seem to indicate an increase of $\alpha_S/\alpha_\mathrm{h}$ with the number of arms. Akcasu et al.[34] have calculated ρ on the basis of the blob concept; together with eq 21 and $\rho_\Theta = 8/3\pi^{1/2}$ one obtains for large linear chains

$$\alpha_S \alpha_\mathrm{h} = \frac{18\pi^{1/2}}{8} \Big/ [(1 - \nu)(2 - \nu)][3\pi(1 + \nu)(1 + 2\nu)]^{1/2}] \tag{22}$$

which yields with the observed exponents of $\nu_\mathrm{h} = 0.58$[28] (R_h vs. $\bar{M}_\mathrm{w}$) and $\nu_S = 0.595$[32] ($\langle S^2 \rangle^{1/2}$ vs. $\bar{M}$,w) $\alpha_S/\alpha_\mathrm{h} = 1.18$ and 1.22, respectively. These values lie well within the experimental error of the observed quantity. Raczek[32] has carried out measurements on linear PS chains in toluene to much higher molecular weights, i.e., DP $\sim 1.5 \times 10^5$, and found in the limit of the highest molecular weight $\alpha_S/\alpha_\mathrm{h} = 1.30$. Apparently, the ratio $\alpha_S/\alpha_\mathrm{h}$ increases still in the range of DP = 1×10^3 to 1.5×10^5. This fact has to be kept in mind when the large value of $\alpha_S/\alpha_\mathrm{h}$ for the 18-arm star is considered.

In conclusion, we note the measurements concerning the second virial coefficient A_2. In two different papers Casassa[44] and Candau, Rempp, and Benoit[45] calculated a decrease of A_2 with increasing f. In the theory of Casassa this decrease is given by the equation

$$(A_{2_\mathrm{b}}/A_{2_\mathrm{l}}) = [h_0(\bar{z})]_\mathrm{b}/[h_0(\bar{z})]_\mathrm{l} \tag{23}$$

where A_{2_b} and A_{2_l} are used at the same $\bar{M}_\mathrm{w}$ and

$$h_0(\bar{z}) = \frac{1}{2C_f\bar{z}} \ln (1 + 2C_f\bar{z}) \tag{24}$$

with $\bar{z} = z/\alpha_S^3$. The expansion factor and z parameter in turn are related as shown in eq 15.

Equations 24 and 15 hold for linear and star-branched polymers, where, however, the constants K_f and C_f depend on the number of arms, f. Their values are given in Table III.

Figure 10 shows the experimental points and the theoretical curves of $A_{2_\mathrm{b}}/A_{2_\mathrm{l}}$ as a function of the z parameter for $f = 3$, 12, and 18 calculated from eq 23, 24, and 15 with the constants of Table III. In all cases we find the experimental points being shifted toward higher values, a trend supported by results presented elsewhere.[46] At present, we are not able to give a conclusive interpretation of this systematic shift. A rather trivial explanation would be too low a curve for A_2 of the linear chains, which is used as the standard. Although the accuracy in measuring A_2 is fairly low, it has to be emphasized that our own measurements with linear chains agree satisfactorily with literature data.[26,38]

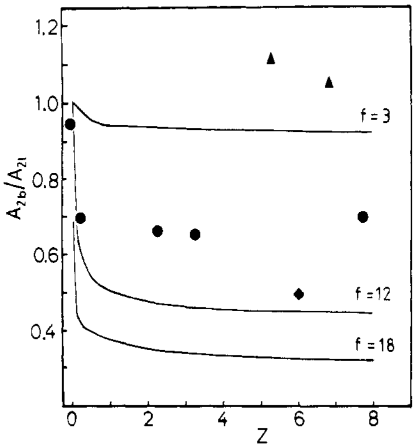

Figure 10. Ratio $A_{2\mathrm{b}}/A_{2\mathrm{l}}$ of 18-, 12-, and 3-arm stars as a function of z predicted by the theory of Casassa in comparison with our experimental results ((♦) 18-arm, (●) 12-arm, (▲) 3-arm stars).

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Registry No. Polystyrene (homopolymer), 9003-53-6.

References and Notes

(1) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(2) Benoit, H. *J. Polym. Sci.* **1953**, *11*, 507.
(3) Stockmayer, W. H.; Fixman, M. *Ann. N.Y. Acad. Sci.* **1953**, *57*, 334.
(4) Morton, M.; Helminiak, T. E.; Gadkari, S. D.; Bueche, F. *J. Polym. Sci.* **1962**, *57*, 471.
(5) Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19.
(6) Bauer, B. J.; Fetters, L. J. *Rubber Chem. Technol.* **1978**, *50*, 407. Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 89.
(7) Zelinski, R. P.; Wofford, C. F. *J. Polym. Sci., Part A-1* **1965**, *3*, 93.
(8) Gervasi, J. A.; Gosnell, A. B. *J. Polym. Sci., Part A-1* **1966**, *4*, 1391.
(9) Roovers, J. E. L.; Bywater, S. *Macromolecules* **1972**, *5*, 385.
(10) Roovers, J. E. L.; Bywater, S. *Macromolecules* **1974**, *7*, 443.
(11) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978**, *11*, 668.
(12) Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1980**, *13*, 191.
(13) Hadjichristidis, N.; Roovers, J. E. L. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521.
(14) Bauer, B. J.; Hadjichristidis, N.; Fetters, L. J.; Roovers, J. E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2410.
(15) Roovers, J. E. L.; Toporowski, P. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1907.
(16) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.
(17) Stockmayer, W. H. "Fluid Mechanics"; Gordon and Breach: London, 1976.
(18) Bantle, S.; Schmidt, M.; Burchard, W. *Macromolecules* **1982**, *15*, 1604.
(19) Dandliker, W. B.; Krautt, J. *J. Am. Chem. Soc.* **1956**, *78*, 2380.
(20) Hadjichristidis, N.; Fetters, L. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2163.
(21) Berne, B. J.; Pecora, R. "Dynamic Light Scattering"; Wiley: New York, 1976.
(22) Burchard, W.; Schmidt, M.; Stockmayer, W. H. *Macromolecules* **1980**, *13*, 580, 1265.
(23) Burchard, W. *Adv. Polym Sci.* **1983**, *48*, 1.
(24) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1970.
(25) Graessley, W. W. *Polymer* **1980**, *21*, 258.
(26) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.
(27) Huber, K.; Burchard, W., in preparation.
(28) Huber, K. Diploma Thesis, Freiburg, 1982.
(29) Jones, G.; Caroline, D. *J. Chem. Phys.* **1979**, *37*, 187.

Macromolecules **1984**, *17*, 548–553

(30) Han, C. C.; McCrackin, F. L. *Polymer* **1979**, *20*, 427.
(31) King, T. A.; Knox, A.; McAdam, J. D. G. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 44*, 195.
(32) Raczek, J. Ph.D. Thesis, Mainz, 1980.
(33) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 210.
(34) (a) Benmouna, M.; Akcasu, A. Z.; Daoud, M. *Macromolecules* **1980**, *13*, 1703. (b) Akcasu, A. Z.; Han, C. C. *Ibid.* **1979**, *12*, 276.
(35) Yamakawa, H. J. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(36) Tanaka, G.; Stockmayer, W. H. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 6401.
(37) Hadjichristidis, N.; Nerger, D.; Fetters, L. J., in preparation.
(38) Bawn, C. E. H.; Wajid, M. A. *J. Polym. Sci.* **1957**, *12*, 109.
(39) Mazur, J.; McCrackin, F. *Macromolecules* **1977**, *10*, 326.
(40) Kajiwara, K.; Burchard, W. *Macromolecules* **1982**, *15*, 660.
(41) Kolinski, A.; Sikorski, A. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3147.
(42) Daoud, M.; Cotton, J. P. *J. Phys. (Paris)* **1982**, *43*, 531.
(43) Kirkwood, J. G. *J. Polym. Sci.* **1954**, *12*, 1.
(44) Casassa, E. F. *J. Chem. Phys.* **1962**, *37*, 2176.
(45) Candau, F.; Rempp, P.; Benoit, H. *Macromolecules* **1972**, *5*, 627.
(46) Qian, R.; Yin, Q.; Cao, T.; Fetters, L. J. *Kexue Tongbao* **1983**, *6*, 354.

Light Scattering from Ternary Solutions. 1. Dilute Solutions of Polystyrene and Poly(methyl methacrylate)

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ABSTRACT: The Flory–Huggins interaction parameter χ_{12} between unlike polymers in dilute ternary solutions of polystyrene, poly(methyl methacrylate), and bromobenzene was evaluated by light scattering conducted under the special condition that we call an "optical Θ state". In this state, the scattering components relevant to the polymer–solvent interactions exactly cancel each other, and this permits observation of the heteropolymer interaction only. Measurements were made for several blends of the polymers, covering a wide range of molecular weight. In all the cases examined, the concentration envelope of the Zimm plot was represented by a straight line extending to a remarkably high concentration. It was thus possible to evaluate χ_{12} with high precision, despite its small magnitude (typically, of the order of 10^{-3}). It was established that χ_{12} decreases with an increase in molecular weight. The observed trend of χ_{12} was shown to be nearly quantitatively consistent with dilute solution theories. It seems that χ_{12} becomes concentration dependent above a certain, relatively high concentration and that this characteristic concentration is molecular weight dependent.

Introduction

Quantitative discussion of the polymer–polymer interaction in a ternary solution of two polymers 1 and 2 and a solvent has usually involved determining the phase diagram to calculate the Flory–Huggins interaction parameter χ_{12} between the two polymers.[1-3] The phase diagram approach, however, is tedious and may not always provide accurate results.[3] Moreover, it is basically incapable of providing information off the loci of the binodals. As is well-known, the Flory–Huggins solvent–polymer interaction parameter χ_{0i}, where the subscript 0 denotes the solvent and i the polymer, depends on both the molecular weight and concentration of the polymer.[4-6] The few previous studies on ternary solutions imply that χ_{12} also depends on either or both of them.[2,3] In order to establish these dependencies and comprehensively understand the behavior of a ternary solution, it is necessary to evaluate χ_{12} as a function of molecular weight and of concentration continuously from the dilute limit up to the region of phase separation.

The light scattering method in principle meets this requirement. There have been several interesting light scattering studies. Notably, Scholte[5,6] has accurately determined χ_{0i} of binary solutions by this method. He also studied the spinodal of polystyrene (PS)–cyclohexane systems, showing the advantage of this method.[6] The spinodal approach was later used by van den Esker and Vrij[3] to investigate PS–polyisobutylene (PIB)–toluene ternary solutions. They chose toluene as solvent because PIB scatters little light in it, and this offered a certain advantage in their later analysis.[7] This technique of optically masking one of the polymer components has been commonly employed to study ternary solutions[8-10] as well as block copolymer solutions.[11-15]

A dilute ternary solution study by light scattering originates from the work of Stockmayer and Stanley,[16] who investigated mixtures of PS and poly(methyl methacrylate) (PMMA) in a solvent giving large refractive index increments (of the same sign) to the polymers. More systematic work along this line has been reported by Kratochvil et al.,[17,18] who evaluated the second virial coefficient between unlike polymers. As opposed to one's intuitive expectation, this parameter was found to decrease as the value of χ_{12}, calculated according to Krause's procedure,[19] increases, an unexplained result.

Generally, it is difficult to precisely determine χ_{12}, especially in dilute solution. The effects of polymer–solvent interactions are usually so large that they are likely to mask the relatively small contribution from a polymer–polymer interaction. The report of Hyde and Tanner[8] on the PS–PIB–cyclohexane system clearly indicates the difficulty of this kind. According to concentrated solution studies,[1,3] χ_{12} of this system is expected to be positive, possibly of the order of 10^{-2}. However, the dilute solution work could show only that it is zero with estimated error limits from 10^{-2} to as large as 10^{-1}.

In a previous note,[20] we have proposed a light scattering method that may overcome the difficulty and simplify experiments. It is based on the use of a solvent in which the refractive index increments of the two polymers are opposite in sign so that the scattering components relevant to polymer–solvent interactions cancel each other. It should be possible in this way to observe the polymer–polymer interaction selectively.

In this work, we apply this technique to dilute ternary solutions of PS and PMMA. To our knowledge,[16,21] this

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