Second and Third Virial Coefficients for Polyisobutylene in Cyclohexane

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ABSTRACT: Light scattering measurements were made on cyclohexane solutions of 10 polyisobutylene (PIB) fractions ranging in weight-average molecular weight M_w from 2.6×10^4 to 1.4×10^7 at 25 °C to determine the molecular weight dependence of the second virial coefficient A_2, the third virial coefficient A_3, and the z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$. Zero-shear intrinsic viscosities were also determined as a function of M_w. For M_w higher than 7×10^4, A_3 and $\langle S^2 \rangle_z$ vary as $M_w^{0.6}$ and $M_w^{1.19}$, respectively, and the factor g defined by $A_3/A_2^2M_w$ increases with increasing M_w. The interpenetration function Ψ and g plotted against the cube of the radius expansion factor, α_s^3, are almost superimposed on the respective relations known for polystyrene in benzene. As α_s^3 increases, Ψ gradually decreases to an asymptotic value of 0.22–0.24, while g increases to 0.45–0.50. It is found that no available theory can explain the molecular weight dependence of A_3 for the two typical flexible polymers, though the g vs α_s^3 relation predicted early by Stockmayer and Casassa happens to come close to the experimental curve for $\alpha_s^3 > 2$.

Introduction

In our previous work,[1,2] it was found from light scattering measurements that the third virial coefficient A_3 of polystyrene in benzene varies in proportion to $M_w^{0.6}$ for M_w higher than 2×10^5 and that, in the same M_w region, the reduced third virial coefficient g defined by $A_3/A_2^2M_w$ increases monotonically with increasing M_w. Here, as usual, M_w and A_2 denote the weight-average molecular weight and the second virial coefficient, respectively. Apparently, similar studies on other polymer + solvent systems are needed to see whether these findings are common to long flexible chains in good solvents. Thus, in the present work, with polyisobutylene (PIB) in cyclohexane at 25 °C chosen as such a system, light scattering experiments were performed to determine A_2 and A_3 as functions of M_w.

The PIB fractions prepared in this study covered a broad range of M_w from 2.6×10^4 to 1.4×10^7. The M_w value of 1.4×10^7 was the largest among those[3-8] so far reported for this polymer. Thus we also determined z-average mean-square radii of gyration $\langle S^2 \rangle_z$ and zero-shear intrinsic viscosities $[\eta]$ for the PIB fractions in cyclohexane, hoping to establish their asymtotic behavior at high molecular weight. In this connection, we note that, although PIB is known as a typical flexible polymer, published $\langle S^2 \rangle_z$ data in the solvent are yet limited to those reported early by Matsumoto et al.[4] The results obtained for A_2, A_3, $\langle S^2 \rangle_z$, and $[\eta]$ are compared with literature data for the same system[4,5,7] or the polystyrene + benzene system,[1,2] and the chain length dependence of A_2 and A_3 is discussed in relation to the two-parameter theory.

Experimental Section

Samples. Three commercial PIB samples were used. Two of them (higher molecular weight samples) were Enjay's Vistanex L-80 and L-300 stored in our laboratory, and the other (lower molecular weight sample), designated below as S, was obtained from Scientific Polymer Products, Inc. From these samples 10 fractions were prepared by fractionation as described below.

Samples L-80 and L-300 were each separated into seven parts using the Θ column elution method with benzene as the solvent. The experimental procedures were essentially the same as those employed by Matsumoto et al.[4] The middle parts were fractionated again by the same method to obtain 3–5 fractions from each. Appropriate fractions, designated A-22, A-42, A-62 (from L-80), P-32, P-53, and P-62 (from L-300), were chosen from many fractions extracted in this way. The first three fractions were further fractionally precipitated with benzene as the solvent and methanol as the precipitant to remove lower and higher molecular weight portions. The fractions thus obtained were designated A-22B4, A-42B3, and A-62B1 and were used for the present study, along with fractions P-32, P-53, and P-62. These six fractions were reprecipitated from benzene solutions into acetone and dried in vacuo for about 1 week.

Sample S was fractionated by the column method with a benzene–methanol mixture instead of pure benzene as the eluent; the composition of methanol in the mixture was adjusted so that the solution became turbid at about 23 °C. However, a larger portion of the polymer tended to elute at a lower temperature, and the column method seemed less effective for a lower molecular weight sample. Thus, after this method had been repeated, the fractions obtained were subjected to fractional precipitation in benzene–methanol mixtures. In this way, four fractions, designated below as S-111B, S-112B, S-114B, and S-14B, were prepared. They were freeze-dried from cyclohexane solutions after being reprecipitated from benzene solutions into methanol.

Light Scattering. Intensities of light scattered from cyclohexane solutions of PIB were measured at 25 °C on a Fica 50 light scattering photometer in an angular range from 22.5 or 30 to 150°; for the two highest molecular weight fractions P-53 and P-62, the measurement was made from 15 to 41° at intervals of 2.0 or 2.5°. Vertically polarized incident light of 436-nm wavelength was used for seven lower molecular weight fractions and that of 546 nm for the others. Benzene at 25 °C was used to calibrate the apparatus. Its Rayleigh ratio was taken to be 46.5×10^{-6} cm^{-1} for 436 nm and 16.1×10^{-6} cm^{-1} for 546 nm,[9] and its depolarization ratio was determined to be 0.41 and 0.40 for 436 and 546 nm, respectively, by the method of Rubingh and Yu.[10]

Test solutions were prepared as follows. First, a given PIB fraction was mixed with cyclohexane by stirring for 2–7 days in an air bath thermostated at 30 °C; for the two highest molecular weight fractions, very gentle stirring was applied to prevent the polymer from degradation. The solution was then diluted with the solvent to a series of polymer concentrations. In this way, seven solutions of different concentrations were prepared for each fraction. They were optically clarified by the method established in this laboratory (see, for example, ref 11). The cyclohexane used was fractionally distilled after being refluxed over sodium for more than 4 h.

The polymer mass concentration c in each solution was calculated from the solute weight fraction, with the solution

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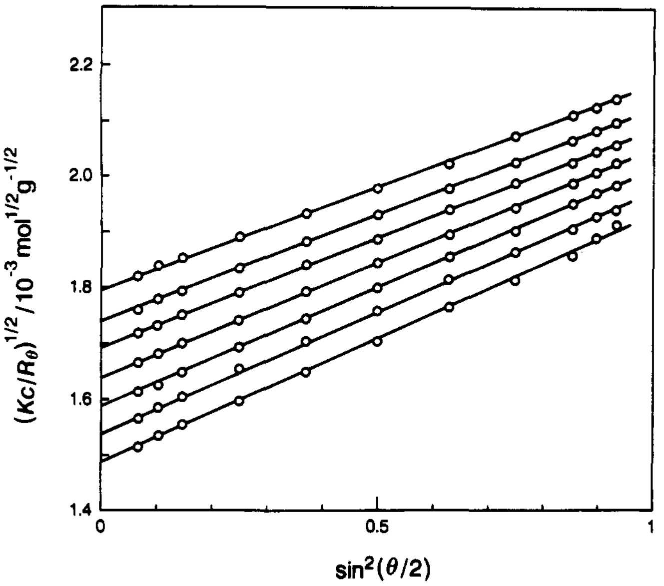

Figure 1. Angular dependence of the scattering intensity for PIB fraction A-22B4 in cyclohexane at 25 °C. The polymer concentrations are 9.755×10^{-4}, 8.301×10^{-4}, 6.954×10^{-4}, 5.523×10^{-4}, 4.170×10^{-4}, 2.803×10^{-4}, and 1.440×10^{-4} g cm^{-3} from top to bottom.

density approximated by the solvent density. This approximation introduced errors of less than 0.5% in the values of A_2 and A_3 for all fractions studied. The highest c studied by light scattering was about 2×10^{-2} g cm^{-3} (see Figure 3).

Excess refractive indices for PIB in cyclohexane at 25 °C were measured at concentrations below 2×10^{-2} g cm^{-3} using a modified Schulz–Cantow type differential refractometer and a double-beam differential refractometer (Otsuka Electronics, DRM-1020). The results for the specific refractive index increment were 0.0991 and 0.0966 cm^3 g^{-1} at 436 and 546 nm, respectively, independent of c in the range examined. These values agreed closely with 0.0987 cm^3 g^{-1} (at 436 nm) and 0.0961 cm^3 g^{-1} (at 546 nm) obtained by Tong et al.[12] Matsumoto et al.[4] reported a slightly larger value of 0.1008 cm^3 g^{-1} at 436 nm.

Viscometry. Zero-shear intrinsic viscosities for the three highest molecular weight fractions in cyclohexane at 25 °C were determined by a low-shear four-bulb capillary viscometer of the Ubbelohde type. For the other fractions, a conventional capillary viscometer was used.

Results

Data Analysis. Figure 1 illustrates the angular dependence of $(Kc/R_\theta)^{1/2}$ for fraction A-22B4 in cyclohexane at 25 °C. Here, K is the optical constant and R_θ is the reduced scattering intensity at scattering angle θ. From the zero-angle values of Kc/R_θ (i.e., Kc/R_0) obtained by extrapolation for the fraction and those similarly obtained for other fractions, plots of $S(c_1,c_2)$ vs $c_1 + c_2$ were constructed according to the expression of Bawn et al.[13] (originally derived for osmotic pressure)

$$S(c_1,c_2) \equiv [(Kc/R_0)_{c=c_2} - (Kc/R_0)_{c=c_1}]/(c_2 - c_1) = 2A_2 + 3A_3(c_1 + c_2) + 4A_4(c_1^2 + c_1c_2 + c_2^2) + \ldots \quad (1)$$

where A_4 denotes the fourth virial coefficient and c_1 and c_2 denote different c values. The resulting Bawn plots are shown in Figure 2. The plotted points for each fraction fall on a straight line, allowing separate determination of A_2 and A_3. We note that when contributions from A_4 to $S(c_1,c_2)$ are not negligible, a Bawn plot should bend or even show splits.[14]

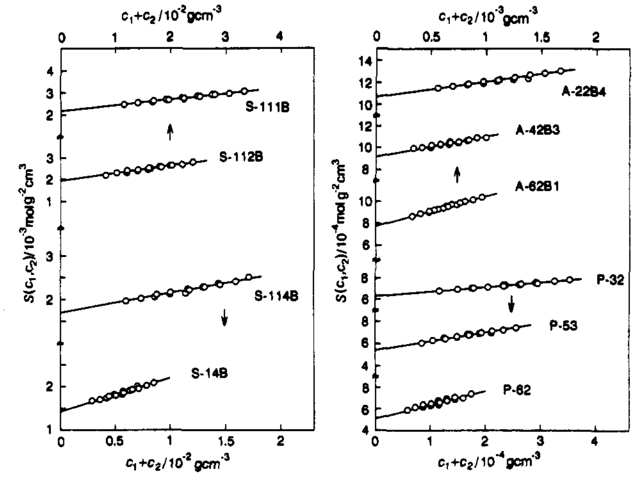

Figure 2. Plots of $S(c_1,c_2)$ vs $c_1 + c_2$ for PIB fractions in cyclohexane at 25 °C. $S(c_1,c_2)$ data for pairs of neighboring c_1 and c_2 in a series of polymer concentrations are omitted, since they were not very accurate (see eq 1).

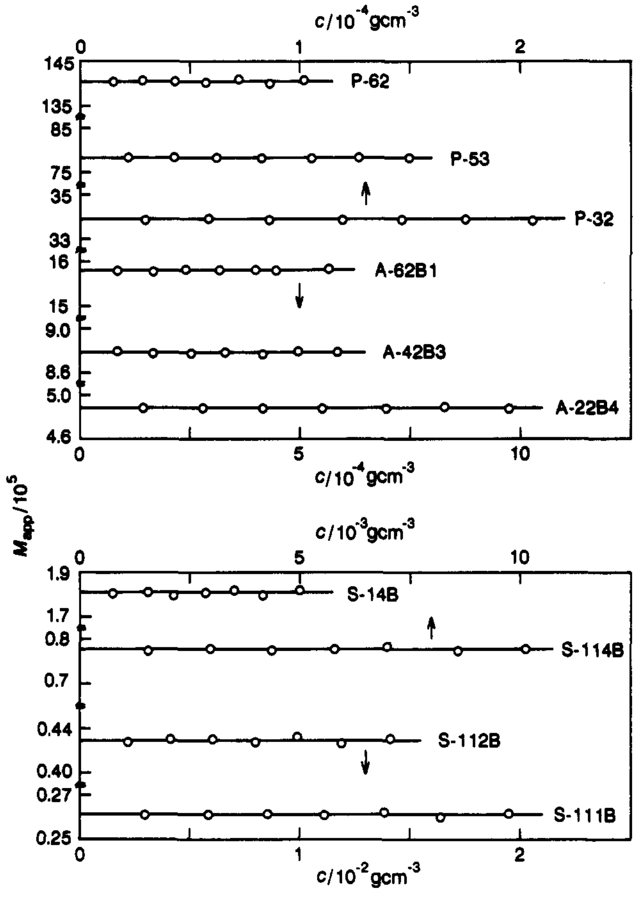

Figure 3. Plots of M_{app} vs c for PIB fractions in cyclohexane at 25 °C. M_{app} is defined by eq 2.

With A_2 and A_3 thus evaluated, we calculated M_{app} defined by

$$M_{app} = [(Kc/R_0) - 2A_2c - 3A_3c^2]^{-1} \quad (2)$$

as a function of c for each fraction. Figure 3 shows that the plots of M_{app} vs c constructed are essentially horizontal for any fractions and thus permit unambiguous extrapolation of M_{app} to $c = 0$. The intercepts give M_w for the respective fractions.

The values of M_w, A_2, and A_3 determined are summarized in Table I, along with those of $\langle S^2 \rangle_z^{1/2}$ obtained by Berry's square-root plot[15] (for fraction S-114B, $\langle S^2 \rangle_z^{1/2}$ was

Table I
Results from Light Scattering Measurements on PIB Fractions in Cyclohexane at 25 °C

fraction	$M_w \times 10^{-5}$	$A_2 \times 10^4$, mol g^{-2} cm^3	$A_3 \times 10^2$, mol g^{-3} cm^6	$\langle S^2\rangle_z^{1/2}$, nm	M_w/M_n[a]
S-111B	0.261	10.6	0.88		
S-112B	0.429	9.55	1.1_5		1.08
S-114B	0.777	8.40	1.5_0	$11._6$	1.10
S-14B	1.81	7.05	2.6	18.7	1.09
A-22B4	4.88	5.30	4.7	33.4	1.10
A-42B3	8.78	4.55	6.3	47.6	1.09
A-62B1	15.8	3.85	9.2	66.8	
P-32	33.9	3.13	$14._0$	107	
P-53	78.3	2.68	27	177	
P-62	141	2.54	42	252	

[a] From gel permeation chromatography.

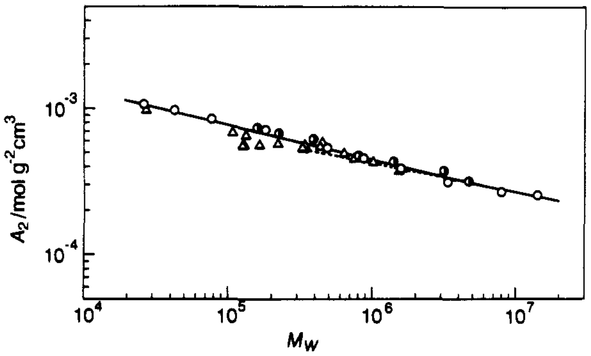

Figure 4. Molecular weight dependence of A_2 for PIB in cyclohexane: (○) this work; (◐) Matsumoto et al.;[4] (△) Fetters et al.[7]

evaluated by the method described elsewhere[16]). The last column of this table presents ratios of the weight-average to number-average molecular weight, M_w/M_n, estimated from gel permeation chromatography in chloroform.

Molecular Weight Dependence of Virial Coefficients. The molecular weight dependence of A_2 for PIB in cyclohexane is illustrated in double-logarithmic form in Figure 4, in which the data of Matsumoto et al.[4] (at 25 °C) and Fetters et al.[7] (at 23 °C) are also shown for comparison. The solid curve fitting our data points is almost linear with a slope of −0.24 for M_w below 2×10^6 and slightly bends upward for higher M_w. The indicated dashed line, which is almost tangential to this curve for $M_w > 2 \times 10^6$, has a slope of −0.20. This exponent is the asymptotic value predicted by two-parameter theories.[17] The data of Matsumoto et al. appear slightly above the solid line but give the exponent −0.23 close to our value of −0.24. On the other hand, those of Fetters et al. deviate downward from the line for M_w below 4×10^5, yielding an exponent of about −0.20.

Figure 5 shows that A_3 for PIB in cyclohexane increases almost in proportion to $M_w^{0.6}$ over the entire range of molecular weight studied. This exponent of 0.6 agrees with that obtained previously[1,2] for polystyrene in benzene for M_w above 2.5×10^5. We note that it is the asymptotic value expected from the two-parameter theory.

The values of g calculated from the data of A_2, A_3, and M_w in Table I are plotted against log M_w in Figure 6. It can be seen that g stays at about 0.28 up to $M_w \sim 2 \times 10^5$ and then gradually increases to 0.45–0.50 with increasing M_w. This behavior of g is also similar to what we observed previously[2] for polystyrene in benzene in the region of M_w above 10^5. A quantitative comparison between g of the two polymers is deferred to the Discussion section.

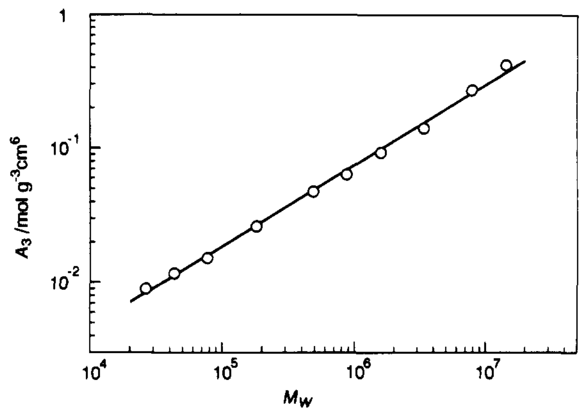

Figure 5. Molecular weight dependence of A_3 for PIB in cyclohexane at 25 °C. The slope of the straight line is 0.6.

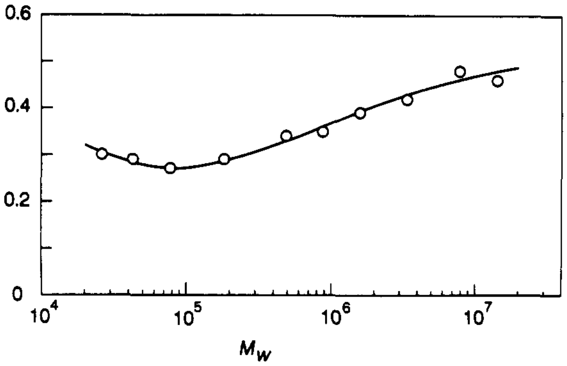

Figure 6. Molecular weight dependence of g for PIB in cyclohexane at 25 °C.

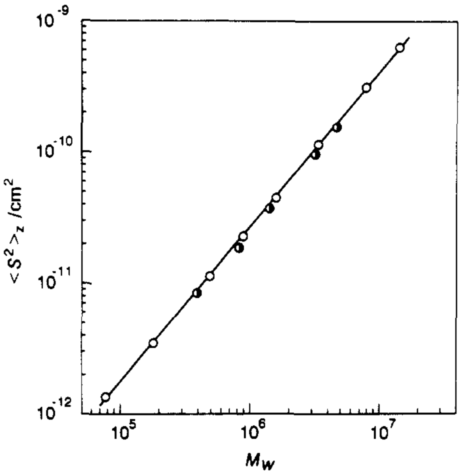

Figure 7. Molecular weight dependence of $\langle S^2\rangle_z$ for PIB in cyclohexane at 25 °C: (○) this work; (◐) Matsumoto et al.[4]

Molecular Weight Dependence of $\langle S^2\rangle_z$ and [η]. The values of $\langle S^2\rangle_z$ in Table I are plotted double-logarithmically against M_w in Figure 7, together with the data of Matsumoto et al.[4] Our data points are fitted by a straight line with slope 1.19 (±0.01) throughout the entire range of M_w indicated. This slope is to be expected for long flexible chains with large excluded volume.[18] It perfectly agrees with the exponent determined for polystyrene in benzene by Miyaki et al.[11] from their own $\langle S^2\rangle_z$ data and those of Yamamoto et al.[19] and Fukuda et al.[20] covering a very wide range of M_w from 1.8×10^5 to 5.7×10^7. The PIB data of Matsumoto et al. appear systematically below ours, but the slope 1.17 reported by them does not differ much from 1.19.

The values of [η] and k' (Huggins' constant) determined for all PIB fractions in cyclohexane at 25 °C are presented in Table II, and these [η] data are compared with those

Table II
Results from Viscosity Measurements on PIB Fractions in Cyclohexane at 25 °C

fraction	$[\eta] \times 10^{-2}$, cm^3 g^{-1}	k'
S-111B	0.276	0.39
S-112B	0.379	0.36
S-114B	0.592	0.36
S-14B	1.07	0.36
A-22B4	2.32	0.38
A-42B3	3.56	0.38
A-62B1	5.32	0.38
P-32	9.46	0.35
P-53	18.3	0.38
P-62	27.4	0.35

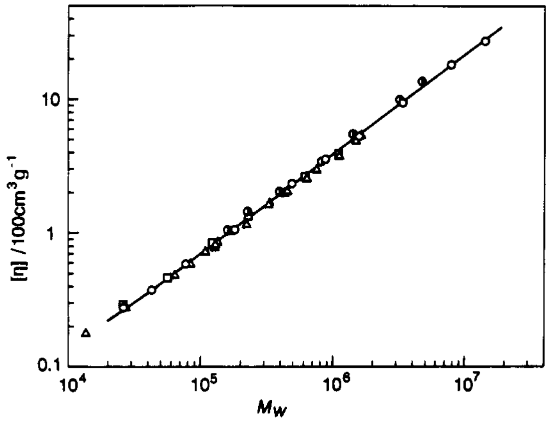

Figure 8. Molecular weight dependence of $[\eta]$ for PIB in cyclohexane at 25 °C: (○) this work; (◑) Matsumoto et al.;[4] (□) Gundert and Wolf;[5] (△) Fetters et al.[7]

of Matsumoto et al.,[4] Gundert and Wolf,[5] and Fetters et al.[7] in Figure 8. As a whole, the four data sets agree with one another. The curve drawn to fit our data points has a slope of 0.75 for $M_w > 7 \times 10^4$, which is also in substantial agreement with 0.76 reported by Matsumoto et al. and 0.74 by Fetters et al.

Discussion

Interpenetration Function. The second virial coefficient is usually discussed in terms of the interpenetration function Ψ defined by[17]

$$\Psi = \frac{A_2 M^2}{4\pi^{3/2} N_A \langle S^2 \rangle^{3/2}} \tag{3}$$

where N_A is Avogadro's constant. We calculated Ψ from the data of M_w, A_2, and $\langle S^2 \rangle_z^{1/2}$ in Table I. The unfilled circles in Figure 9 show the resulting Ψ values plotted against α_s^3, the cube of the radius expansion factor ($\alpha_s^2 = \langle S^2 \rangle_z / \langle S^2 \rangle_{0z}$, with $\langle S^2 \rangle_{0z}$ being the value of $\langle S^2 \rangle_z$ in the Θ state). We have evaluated[21] α_s using the experimental relation $\langle S^2 \rangle_{0z}/M_w = 9.52 \times 10^{-18}$ cm^2 in isoamyl isovalerate, reported by Matsumoto et al.[4] The graph includes the Ψ data of these authors for PIB in cyclohexane (the half-filled circles) and also those of Yamamoto et al.,[19] Fukuda et al.,[20] and Miyaki et al.[11,23] for polystyrene in benzene (the filled circles with or without pip). The unfilled and filled circles are fitted by the single solid curve indicated, being consistent with the prediction from the two-parameter theory that Ψ should be a universal function of α_s. The asymptotic value of Ψ for large α_s appears to lie between 0.22 and 0.24. The half-filled circles deviate upward from the solid curve. This deviation reflects the small differences in both A_2 and $\langle S^2 \rangle_z$ between our data and Matsumoto's, observed in Figures 4 and 7.

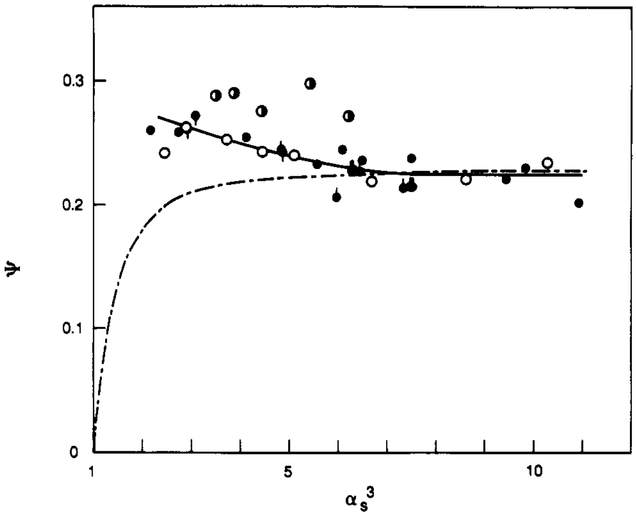

Figure 9. Plots of Ψ vs α_s^3 for PIB in cyclohexane (○, present data; ◑, ref 4) and polystyrene in benzene (●, refs 11 and 23; ●, ref 19; ●, ref 20). Dot–dash line, Barrett's theory.[24]

The dot-dash line in Figure 9 represents Barrett's theory[24]

$$\Psi = (z/\alpha_s^3)(1 + 14.3z + 57.3z^2)^{-0.2} \tag{4}$$

combined with the Domb–Barrett expression[25] for α_s:

$$\alpha_s^2 = \left[1 + 10z + \left(\frac{70\pi}{9} + \frac{10}{3}\right)z^2 + 8\pi^{3/2}z^3\right]^{2/15}[0.933 + 0.067 \exp(-0.85z - 1.39z^2)] \tag{5}$$

Here, z is the familiar excluded-volume parameter. Satisfactory agreement is observed between the dot–dash and solid curves for α_s^3 greater than 6. Equation 4, when combined with the asymptotic relation[11,26] $\alpha_s^2 = 1.53z^{2/5}$ derived from computer simulation data, yields an asymptotic Ψ of 0.235,[18,24] which is close to the above estimate (0.22–0.24) for the two typical flexible polymers.

However, with a decrease in α_s^3, the theoretical curve declines, while the experimental one rises. A similar opposite trend of Ψ at relatively large α_s has already been observed for poly(D-β-hydroxybutyrate)[27] as well as for polystyrene.[23] The present PIB data provide additional evidence for this serious discrepancy. As discussed by Fujita and Norisuye,[28] the observed opposite trend may be ascribed primarily to the fact that eq 4 with eq 5 predicts a molecular weight dependence of A_2 weaker than that represented by $A_2 \propto M^{-0.2}$, while the experimental A_2 for PIB (that for polystyrene as well) has a stronger dependence (see Figure 4). We should add that, in contrast to the dot–dash line sharply declining to zero, Ψ for low molecular weight polystyrene in toluene[29,30] rises first gradually and then sharply as α_s approaches unity.

Reduced Third Virial Coefficient. We have found that the molecular weight dependence of A_3 and g for PIB in cyclohexane is quite similar to that for polystyrene in benzene. For a quantitative comparison, the values of g for the two systems are plotted against α_s^3 in Figure 10. For fractions whose $\langle S^2 \rangle_z$ data are unavailable, we have estimated α_s by extrapolating the empirical relations $\alpha_s^2 = 0.206 M_w^{0.19}$ for PIB and $\alpha_s^2 = 0.167 M_w^{0.19}$ for polystyrene;[11,23] the former was obtained from our data in Figure 7 and the $\langle S^2 \rangle_{0z}$ data of Matsumoto et al. Because of the extrapolation, the abscissa values below 2 are inaccurate, but their accuracy is immaterial in the discussion below.

The plotted points for the two polymers approximately fall on a single curve, at least, in the region of α_s^3 above 2, as indicated by a solid line. This finding is consistent

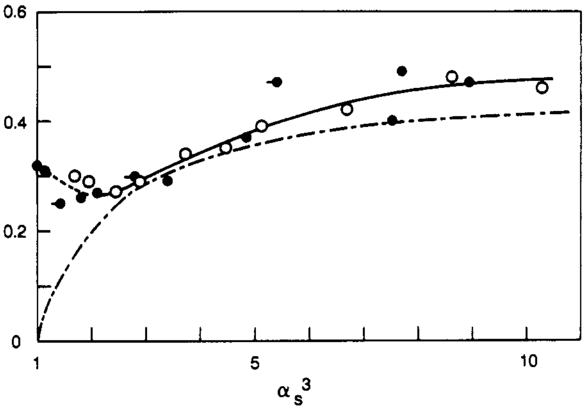

Figure 10. Plots of g vs α_s^3 for PIB in cyclohexane (○) and polystyrene in benzene (-●, ref 1; ●, ref 2). Dot–dash line, Stockmayer and Casassa's theory.[34]

with the requirement of the two-parameter theory. The solid curve rises with increasing α_s and appears to level off at 0.45–0.50. This leveling-off value of g is close to 0.44, evaluated by Knoll et al.[31] and des Cloizeaux and Noda,[32] for good solvent systems on the basis of the first-order ϵ expansion in the renormalization group method. However, this agreement should be accepted with reservation until a higher order calculation becomes available. Further, as noted previously,[2,14] all the renormalization group calculations[31-33] so far made fail to explain why g for a good solvent system depends on M. On the other hand, the two-parameter theories worked out early by Stockmayer and Casassa,[34] Koyama,[35] and Yamakawa[36] all predict g to increase monotonically with increasing M.

The dot–dash line in Figure 10 represents the g vs α_s^3 relation predicted by Stockmayer and Casassa, who combined their smoothed-density theory for g (as a function of z/α_s^3) with the original Flory equation[37] for α_s, i.e., $\alpha_s^5 - \alpha_s^3 = 2.60z$. This line comes close to the solid curve for $\alpha_s^3 > 2$. However, as α_s approaches unity, it sharply declines to zero, while the experimental g stays at about 0.3 or even goes up after passing through a shallow minimum. This sharp contrast is similar to what has been observed for Ψ.[30]

As was shown by Miyaki and Fujita,[38] the original Flory equation used by Stockmayer and Casassa is a good approximation to either PIB in cyclohexane or polystyrene in benzene for $\alpha_s^3 > 2$, so that the observed agreement between the solid and dot–dash curves in Figure 10 may be taken as that in g itself. However, this agreement must be due to a compensation of the errors in both A_2 and A_3 that the Stockmayer–Casassa smoothed-density theory involves, because the Flory–Krigbaum theory[39] for A_2 based on the same smoothed-density model fails to describe A_2 for flexible polymers. In other words, the Stockmayer–Casassa theory should be invalid for A_3, though it almost quantitatively explains the ratios of A_3 to $A_2^2M_w$ for the two typical flexible polymers in the region of α_s^3 above 2. Koyama's theory[35] is essentially the same as the Stockmayer–Casassa theory, while Yamakawa's theory[36] based on the differential-equation approach gives g values that are too large.

In conclusion, none of the available theories can explain the observed molecular weight dependence of A_3 for PIB in cyclohexane and polystyrene in benzene. Even qualitatively, there exists a serious discrepancy in g between our experiments and the two-parameter theory when α_s is approached to unity by lowering the molecular weight in a given good solvent. The discrepancy is similar to what is known for Ψ, indicating that the current two-parameter theory for A_3 overlooks something important, as is the case with that for A_2.

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