Excluded-Volume Effects on the Intrinsic Viscosity of Oligomers and Polymers of Styrene and Isobutylene

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ABSTRACT: The intrinsic viscosity [η] was determined for atactic polystyrene (a-PS) in toluene at 15.0 °C in the range of weight-average molecular weight M_w from 2.66×10^2 to 3.84×10^6 and for polyisobutylene (PIB) in *n*-heptane at 25.0 °C in the range of M_w from 1.12×10^2 to 1.76×10^6. These solvents and temperatures have been chosen so that the values of [η] for the unperturbed a-PS and PIB chains in given good solvents may coincide with the respective values of $[\eta]_0$ in cyclohexane at 34.5 °C (Θ) and in isoamyl isovalerate at 25.0 °C (Θ). It is then found that the viscosity–radius expansion factor α_η thus determined correctly is a function only of the radius expansion factor α_S in a first approximation, in contrast to literature data. When plotted against the conventional excluded-volume parameter z, the present data for α_η do not form a single-composite curve as yet, depending on the chain stiffness. However, the data form such a curve when plotted against the scaled excluded-volume parameter $\tilde{z}$ defined in the Yamakawa–Stockmayer–Shimada theory for the wormlike and helical wormlike chains with excluded volume. Thus a *quasi*-two-parameter scheme may be regarded as valid for α_η as well as for α_S. It is also pointed out that the relation between α_η and $\tilde{z}$ (or z) is still worth deriving theoretically.

Introduction

In the preceding paper,[1] we have studied the expansion factor α_S determined from the mean-square radius of gyration $\langle S^2 \rangle$ for atactic polystyrene (a-PS) in a good solvent toluene over a wide range of molecular weight, including the oligomer region. This is a start of our reinvestigation of the excluded-volume effects in dilute polymer solutions from a new point of view beyond the framework of the two-parameter theory[2] to give an explanation to many experimental findings inconsistent with its prediction. It has been shown that the results obtained for α_S may well be explained by the Yamakawa–Stockmayer–Shimada (YSS) theory,[3-5] which assumes that α_S is a function only of the scaled excluded-volume parameter $\tilde{z}$ that takes account of the effects of excluded volume and chain stiffness on the basis of the Kratky–Porod (KP) wormlike chain[6] and the helical wormlike (HW) chain.[7,8] The implication is that a *quasi*-two-parameter scheme may be regarded as valid for α_S. Thus, in the present paper, we proceed to make a study of the viscosity–radius expansion factor α_η determined from the intrinsic viscosity [η] for a-PS and also polyisobutylene (PIB).

Now the breakdown of the two-parameter theory of α_η has already been pointed out by Miyaki and Fujita,[9] who have shown that for these polymers in various solvents α_η is not a function of only α_S or the conventional excluded-volume parameter z. This leads us to a reconsideration of the problem with respect to at least two points: (1) determination itself of $\alpha_\eta{}^3$ as the ratio of [η] to its value $[\eta]_\Theta$ in an appropriate Θ solvent at the Θ temperature and then (2) reanalysis of data for α_η in terms of the scaled parameter $\tilde{z}$ instead of z.

The first point is under the same idea as the reconsideration of a determination of α_S made in the preceding paper. That is, we must choose a pair of Θ and good solvents so that the value of $[\eta]_\Theta$ may be identical with the *unperturbed* value that [η] would have if the excluded-volume interaction were absent in that good solvent at a given temperature. In practice, this can be done by using values of $[\eta]_\Theta$ and [η] of the oligomers without intramolecular excluded-volume interaction, as done in the preceding work. Thus, for a-PS, we have chosen toluene at 15.0 °C and cyclohexane at 34.5 °C as good and Θ solvents, respectively. In the case of PIB, we have another difficulty in the choice of its Θ solvent. It is known that there are specific interactions between solute and solvent molecules such that [η] is negative for the oligomers with very low molecular weights in its Θ solvents benzene and isoamyl isovalerate (IAIV).[10] Such an effect must be removed from the observed $[\eta]_\Theta$, but, fortunately, its contribution may be neglected in IAIV except for very low molecular weights. Thus, for PIB, we choose IAIV at 25.0 °C (Θ) as a Θ solvent. The good solvent then chosen is *n*-heptane at 25.0 °C.

Having determined correctly α_η, the second point is worth examining as a next step, although there may also be an effect of partial drainage on α_η. The reason is that it has been shown that the effect of chain stiffness on α_S remains rather large even for very large molecular weights.[1] Then the determination of the parameter $\tilde{z}$ (and also z) requires values of the HW model parameters along with the excluded-volume strength B. It is reasonable to adopt the former values obtained previously from $[\eta]_\Theta$,[10,11] while the latter should be determined from $\langle S^2 \rangle$, as done in the preceding work for a-PS in toluene. Thus, in the present work, a similar determination of B is also made for PIB in *n*-heptane.

Experimental Section

Materials. All the a-PS samples used in this work are the same as those used in the previous studies of the mean-square optical anisotropy $\langle \Gamma^2 \rangle$,[12] $[\eta]_0$,[11] the unperturbed mean-square radius of gyration $\langle S^2 \rangle_0$,[13] $\langle S^2 \rangle$,[1] the transport factors ρ and Φ for long flexible chains,[14] and the translational diffusion coefficient D,[15] i.e., the fractions separated by preparative gel permeation chromatography (GPC) or fractional precipitation from the standard samples supplied by Tosoh Co., Ltd. They are sufficiently narrow in molecular weight distribution and have a fixed stereochemical composition (the fraction of racemic diads $f_r = 0.59$) independent of molecular weight. The values of the weight-average molecular weight M_w obtained from analytical GPC or light scattering (LS) measurements and the weight-average degree of polymerization x_w calculated from them are given in Table I along with those of the ratio of M_w to the number-average molecular weight M_n determined from analytical GPC.

All the PIB samples used in this work are the same as those used in the previous studies of $[\eta]_0$[10] and ρ and Φ.[14] Their detailed

Table I
Values of M_w, x_w, and M_w/M_n for Atactic Oligo- and Polystyrenes

sample	M_w	x_w	M_w/M_n
OS2[a]	2.66×10^2	2	1.00
OS3	3.70×10^2	3	1.00
OS4	4.74×10^2	4	1.00
OS5	5.78×10^2	5	1.00
OS6	6.80×10^2	5.98	1.00
OS8	9.04×10^2	8.13	1.01
A1000-b[b]	1.48×10^3	13.7	1.02
A2500-a′	1.78×10^3	16.6	1.04
A2500-a	2.27×10^3	21.3	1.05
A2500-b	3.48×10^3	32.9	1.07
A5000-3	5.38×10^3	51.2	1.03
F1-2	1.01×10^4	96.6	1.03
F2[c]	2.05×10^4	197	1.02
F4	4.00×10^4	384	1.02
F10	9.73×10^4	935	1.02
F20	1.91×10^5	1840	1.02
F40	3.59×10^5	3450	1.01
F80	7.32×10^5	7040	1.01
F128-2	1.32×10^6	12700	1.05
F380	3.84×10^6	36900	1.05

[a] M_w's of OS2 through OS8 had been determined from GPC.[11,12] [b] M_w's of A1000-b through F1-2 had been determined from LS in methyl ethyl ketone at 25.0 °C.[11,12] [c] M_w's of F2 through F380 had been determined from LS in cyclohexane at 34.5 °C,[1,13,14] except for F20, for which it had been determined from LS in toluene at 15.0 °C.[1]

Table II
Values of M_w, x_w, and M_w/M_n for Oligo- and Polyisobutylenes

sample	M_w	x_w	M_w/M_n
OIB2[a]	1.12×10^2	2	1.00
OIB4	2.24×10^2	4	1.00
OIB11	6.41×10^2	11.4	1.01
OIB14	7.92×10^2	14.1	1.01
OIB18[b]	1.01×10^3	18.0	1.02
OIB22	1.25×10^3	22.2	1.02
OIB26	1.47×10^3	26.2	1.02
OIB32	1.81×10^3	32.2	1.04
PIB1	8.73×10^3	155	1.10
PIB2	1.66×10^4	295	1.08
PIB3	2.79×10^4	496	1.07
PIB5	4.85×10^4	863	1.06
PIB9	8.55×10^4	1520	1.08
PIB13	1.30×10^5	2310	1.09
PIB40[c]	4.22×10^5	7510	1.09
PIB60	6.34×10^5	11300	1.06
PIB80	8.19×10^5	14600	1.09
PIB180	1.76×10^6	31300	

[a] M_w's of OIB2 through OIB14 had been determined from GPC.[10] [b] M_w's of OIB18 through PIB13 had been determined from LS in n-heptane at 25.0 °C.[10] [c] M_w's of PIB40 through PIB180 had been determined from LS in IAIV at 25.0 °C.[10,14]

characteristics are described in the previous paper.[10] Those with $M_w > 5 \times 10^3$ are the fractions separated by fractional precipitation from the commercial samples of Enjay Chemical Co., named Vistanex LM-MS, L-80, and L-200. The oligomer samples with $5 \times 10^2 < M_w < 5 \times 10^3$ are the fractions separated by preparative GPC from the original samples prepared by living cationic polymerization and then subjected to dehydrochlorination to remove the terminal chlorine atom. They have fixed chemical structures at their chain ends independent of M_w, and there is no disorder in their chain sequences such as branching and dislocation of the methyl side groups. The dimer sample OIB2 is a mixture prepared by mixing 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene of Aldrich Chemical Co. in the ratio 96:4 to match its chain end structures with those of the other oligomers. The tetramer sample OIB4 is the commercial tetraisobutylene of Tokyo Kasei Kogyo Co. The values of M_w, x_w, and M_w/M_n are summarized in Table II. From the results for the ratio M_w/M_n, the molecular weight distributions of these samples may be regarded as sufficiently narrow.

The solvents toluene and n-heptane used for viscosity and LS measurements were purified according to standard procedures.

Viscosity. Viscosity measurements were carried out for all the a-PS and PIB samples in toluene at 15.0 °C and in n-heptane at 25.0 °C, respectively, and also for the four highest-molecular-weight samples of the former in toluene at 30.0 °C in order to examine the temperature dependence. We note that these solvents are good and medium for a-PS and PIB, respectively. Viscosity measurements were also made for the a-PS samples F20 and F380 in cyclohexane at 34.5 °C. We used conventional capillary viscometers of the Ubbelohde type except for the oligomer samples of a-PS and PIB with small values of $[\eta]$, for which four-bulb spiral capillary viscometers of the same type were employed. Viscosities for the highest-molecular-weight samples of a-PS and PIB were measured at very low shear rate by using four-bulb spiral capillary viscometers so that the non-Newtonian effect might be ignored. The effect was not detected for the other samples. In all the measurements, the flow time was measured to a precision of 0.1 s, keeping the difference between flow times of the solvent and solution larger than ca. 20 s. The data obtained were treated as usual by the Huggins and Fuoss–Mead plots to determine $[\eta]$ and the Huggins coefficient k'.

The test solutions were prepared by continuous stirring at room temperatures for ca. 1 day for a-PS in toluene and at 20–50 °C for 1–3 days for PIB in n-heptane. The polymer mass concentrations c (in g/cm^3) were calculated from the weight fractions with the densities of the solutions. Density corrections were made in the calculation of the relative viscosity from the flow times of the solvent and solution for both a-PS and PIB. The densities of the solvent and solution were measured with a pycnometer of the Lipkin-Davison type.

Light Scattering. LS measurements were carried out to determine $\langle S^2 \rangle$ of the four highest-molecular-weight samples of PIB in n-heptane at 25.0 °C and also of the four highest-molecular-weight samples of a-PS in toluene at 30.0 °C in order to examine the temperature dependence. A Fica 50 light-scattering photometer was used for all the measurements with vertically polarized incident light of wavelength 436 nm. For a calibration of the apparatus, the intensity of light scattered from pure benzene was measured at 25.0 °C at a scattering angle of 90°, where the Rayleigh ratio $R_{Uu}(90°)$ of pure benzene was taken as 46.5×10^{-6} cm^{-1}. The depolarization ratio ρ_u of pure benzene at 25.0 °C was found to be 0.41 ± 0.01. Scattering intensities were measured at five different concentrations and at scattering angles ranging from 30 to 150°. The data obtained were analyzed by the Berry square-root plot.[16]

The most concentrated solutions of each sample were prepared in the same manner as in the case of viscometry. They were optically purified by filtration through a Teflon membrane of pore size 0.45 μm. The solutions of lower concentrations were obtained by successive dilution. The polymer mass concentrations c were calculated from the weight fractions with the densities of the solvents.

Results

Intrinsic Viscosity of Atactic Oligo- and Polystyrenes. The values of $[\eta]$ for all the a-PS samples in toluene at 15.0 °C are summarized in Table III along with those of the Huggins coefficient k'. (The results in toluene at 30.0 °C are given in the Discussion, for convenience.) The former (unfilled circles) are double-logarithmically plotted against M_w in Figure 1. In the table and figure, the previous results (filled circles in the figure) for the same a-PS samples in cyclohexane at 34.5 °C (Θ) have been reproduced from refs 11, 13, and 14, for reference. As already reported in the preceding paper,[1] the data for the oligomer samples in these two solvents coincide with each other for $578 \le M_w \le 2270$, indicating that the unperturbed chain dimensions and conformations of a-PS are the same under the two solvent conditions. It has actually been confirmed that the values of $\langle S^2 \rangle$ in toluene at 15.0 °C agree with those in cyclohexane at Θ in the oligomer region for M_w

Table III
Results of Viscometry on Atactic Oligo- and Polystyrenes in Toluene at 15.0 °C and in Cyclohexane at 34.5 °C (Θ)

	toluene (15.0 °C)		cyclohexane (34.5 °C)[a]	
sample	[η], dL/g	k'	[η], dL/g	k'
OS2	0.0185	0.93	0.0149	1.3
OS3	0.0234	0.90	0.0192	1.2
OS4	0.0260	0.83	0.0247	0.91
OS5	0.0275	0.87	0.0274	0.89
OS6	0.0291	0.86	0.0293	0.84
OS8	0.0318	0.90	0.0326	0.87
A1000-b	0.0368	0.69	0.0370	0.96
A2500-a′	0.0393	0.85	0.0408	0.94
A2500-a	0.0449	0.69	0.0450	0.89
A2500-b	0.0548	0.79	0.0543	0.93
A5000-3	0.0694	0.71	0.0659	0.81
F1-2	0.103	0.52	0.0900	0.67
F2	0.156	0.44	0.123	0.63
F4	0.248	0.40	0.172	0.58
F10	0.467	0.36	0.273	0.54
F20	0.756	0.36	0.380	0.53
F40	1.18	0.35	0.512	0.62
F80	1.97	0.34	0.734	0.63
F128-2	2.91	0.35	0.981	0.58
F380	7.05	0.34	1.75	0.66

[a] Reproduced from refs 11, 13, and 14 except for F20 and F380 (present work).

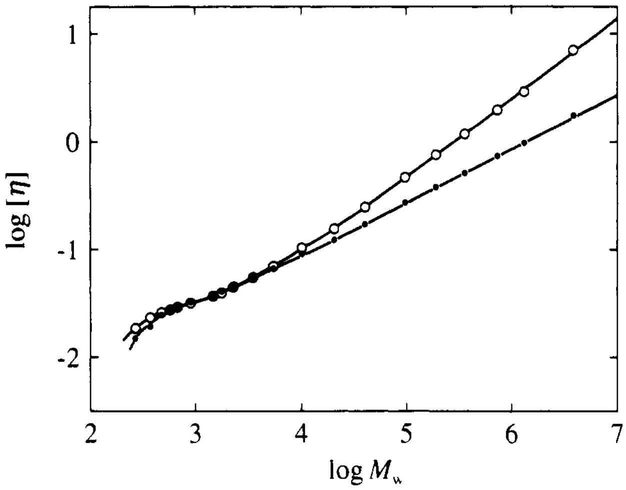

Figure 1. Double-logarithmic plots of [η] (in dL/g) against M_w for a-PS: (○) in toluene at 15.0 °C; (●) in cyclohexane at 34.5 °C (Θ).

< 1780. Thus we may also calculate α_η for a-PS in toluene at 15.0 °C by the use of the values of [η]$_\Theta$ in cyclohexane at Θ. It is seen from Figure 1 that the difference between the values of [η] in the two solvents, i.e., the excluded-volume effect on [η] (in toluene), becomes appreciable for $M_w > 5380$ or for $x_w \gtrsim 50$. This critical value of x_w for the onset of the effect on [η] is larger than the corresponding value ca. 20 estimated from α_S.

The difference between the values of [η] in toluene and in cyclohexane in the very low oligomer region for $M_w \leq 474$ may rather be regarded as arising from that in the chain-end effect, so that we ignore it in the present discussion.

Table IV
Results of Viscometry on Oligo- and Polyisobutylenes in n-Heptane at 25.0 °C and in IAIV at 25.0 °C (Θ)

	n-heptane (25.0 °C)		IAIV (25.0 °C)[a]	
sample	[η], dL/g	k'	[η], dL/g	k'
OIB2	0.0027		-0.0145	
OIB4	0.0158	0.89	0.0071	
OIB11	0.0319	0.84	0.0301	0.77
OIB14	0.0341	0.82	0.0338	0.73
OIB18	0.0375	0.81	0.0369	0.65
OIB22	0.0412	0.75	0.0410	0.59
OIB26	0.0445	0.78	0.0439	0.59
OIB32	0.0490	0.69	0.0482	0.69
PIB1	0.119	0.61	0.108	0.51
PIB2	0.174	0.45	0.141	0.55
PIB3	0.232	0.38	0.180	0.51
PIB5	0.330	0.41	0.241	0.52
PIB9	0.471	0.40	0.318	0.46
PIB13	0.615	0.39	0.396	0.50
PIB40	1.34	0.40	0.709	0.56
PIB60	1.80	0.38	0.882	0.63
PIB80	2.17	0.38	0.998	0.60
PIB180	3.78	0.37	1.46	0.73

[a] Reproduced from refs 10 and 14.

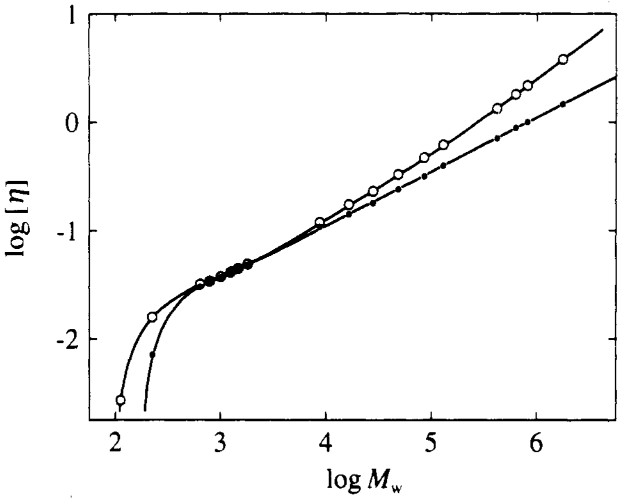

Figure 2. Double-logarithmic plots of [η] (in dL/g) against M_w for PIB: (○) in n-heptane at 25.0 °C; (●) in IAIV at 25.0 °C (Θ).

Intrinsic Viscosity of Oligo- and Polyisobutylenes. The results from viscometry on PIB in n-heptane at 25.0 °C are summarized in Table IV. It also includes the previous results[10,14] in IAIV at 25.0 °C (Θ), for reference. Figure 2 shows double-logarithmic plots of [η] (unfilled circles) and [η]$_\Theta$ (filled circles) against M_w. It is seen that, for $M_w < 641$ ($x_w \lesssim 11$), [η] in n-heptane decreases steeply with decreasing M_w as well as [η]$_\Theta$ in IAIV, indicating the existence of the effect of specific interactions between solute and solvent molecules. The difference between the values of [η] in the two solvents in this oligomer region may be regarded as arising from those in both effects of specific interactions and chain ends, and we exclude this region from the present discussion. As noted previously,[10] the former effect becomes negligibly small for $M_w > 600$ for the IAIV solutions. This may be considered also the case with the n-heptane solutions.

As also seen from Figure 2, there is good agreement between the values of [η] in the two solvents for $792 < M_w < 1810$, in which range the excluded-volume effect may be neglected. Then this leads to the conclusion that the unperturbed chain dimensions of PIB are the same under the two solvent conditions. We note that the agreement has not been confirmed with respect to $\langle S^2 \rangle$, since small-angle X-ray scattering measurements are not feasible for PIB in IAIV because of the extremely low excess electron density.[10] Thus we may calculate α_η for PIB in n-heptane at 25.0 °C by the use of the values of [η]$_\Theta$ in IAIV at Θ.

The difference between the values of [η] in the two solvents for larger M_w, i.e., the excluded-volume effect on [η] (in n-heptane) is seen to become appreciable for $M_w >$ ca. 2000 or for $x_w \gtrsim 36$. We note that this critical value of x_w corresponds to the value 6.5 of the reduced contour length, which is close to the corresponding value 5.4 for

Table V
Values of $\langle S^2\rangle^{1/2}$ and $\langle S^2\rangle_0^{1/2}$ for Polyisobutylene in *n*-Heptane at 25.0 °C and in IAIV at 25.0 °C (Θ)

sample	*n*-heptane (25.0 °C) $\langle S^2\rangle^{1/2}$, Å	IAIV (25.0 °C)[a] $\langle S^2\rangle_0^{1/2}$, Å
PIB40	262	206
PIB60	324	247
PIB80	389	284
PIB180	606	415

[a] The values of $\langle S^2\rangle_0$ are the unpublished results[10] already obtained in the determination of M_w except for that of PIB60 reproduced from ref 14.

Table VI
Values of α_η^3 and α_S^3 for Atactic Oligo- and Polystyrenes in Toluene at 15.0 °C and for Oligo- and Polyisobutylenes in *n*-Heptane at 25.0 °C

a-PS			PIB		
sample	α_η^3	α_S^3	sample	α_η^3	α_S^3
OS5	1.00		OIB14	1.01	
OS6	0.993		OIB18	1.02	
OS8	0.975		OIB22	1.00	
A1000-b	0.995	0.948[a]	OIB26	1.01	
A2500-a′	0.963	1.02	OIB32	1.02	
A2500-a	0.998	1.05	PIB1	1.10	
A2500-b	1.01	1.08	PIB2	1.23	
A5000-3	1.05	1.23	PIB3	1.29	
F1-2	1.14	1.23	PIB5	1.37	
F2	1.27	1.30	PIB9	1.48	
F4	1.44	1.66	PIB13	1.55	
F10	1.71		PIB40	1.89	2.06
F20	1.90	2.32	PIB60	2.04	2.26
F40	2.30	2.89	PIB80	2.17	2.57
F80	2.68	3.44	PIB180	2.59	3.11
F128-2	2.97	4.31			
F380	4.03	5.60			

[a] The values of α_S^3 for a-PS have been reproduced from ref 1.

a-PS estimated from the above critical value of x_w. (For the critical reduced contour length, see ref 4.)

Mean-Square Radius of Gyration of Polyisobutylene. The values of $\langle S^2\rangle^{1/2}$ determined from LS measurements for the PIB samples with $M_w \geq 4.22 \times 10^5$ in *n*-heptane at 25.0 °C are given in Table V along with those of $\langle S^2\rangle_0^{1/2}$ in IAIV at 25.0 °C (Θ). (The results for a-PS in toluene at 30.0 °C are given in the Discussion, for convenience.) The latter values for the samples PIB40, PIB80, and PIB180 are the unpublished results already obtained in the determination of their M_w,[10] except for that of PIB60 reproduced from ref 14. From the results for $\langle S^2\rangle_0^{1/2}$, we obtain $\langle S^2\rangle_0/x_w$ = 5.53 Å^2 on the average. The value 5.35 Å^2 of $\langle S^2\rangle_0/x_w$ determined by Matsumoto et al.[17] is ca. 3% smaller than the present value. In this connection, we note that their Θ temperature for the IAIV solution is ca. 3 °C lower than ours.

According to the conclusion derived in the preceding subsection, we may also calculate α_S for PIB in *n*-heptane at 25.0 °C by the use of the above values of $\langle S^2\rangle_0$ in IAIV at Θ.

Discussion

Relation between α_η^3 and α_S^3. In Table VI are summarized the values of α_η^3 calculated from the equation

$$[\eta] = [\eta]_\Theta \alpha_\eta^3 \tag{1}$$

for the a-PS samples in toluene at 15.0 °C and for the PIB samples in *n*-heptane at 25.0 °C with the values of $[\eta]$ (and $[\eta]_\Theta$) given in Tables III and IV, respectively. It

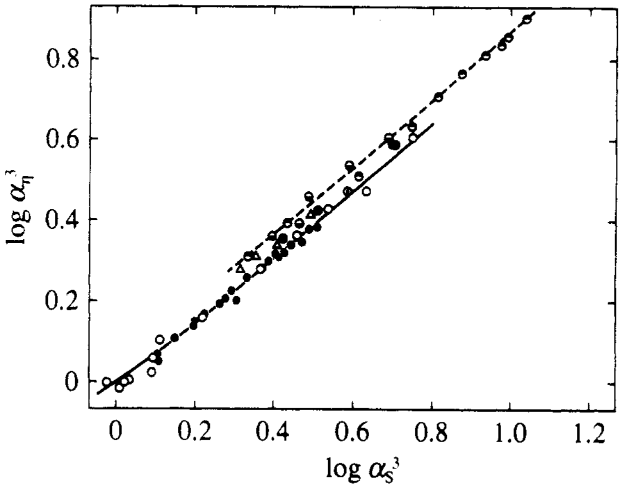

Figure 3. Double-logarithmic plots of α_η^3 against α_S^3 for a-PS and PIB: (○) a-PS in toluene at 15.0 °C (present data); (⊙) a-PS in toluene at 30.0 °C (present data); (●) a-PS ($M_w > 10^7$) in cyclohexane at various temperatures (36.0–55.0 °C) (Miyaki);[19] (◓) a-PS in benzene at 25.0 °C (Miyaki et al.);[18,19] (◒) a-PS in benzene at 30.0 °C (Yamamoto et al.);[20] (△) PIB in *n*-heptane at 25.0 °C (present data).

includes the values of α_S^3 calculated from the equation

$$\langle S^2\rangle = \langle S^2\rangle_0 \alpha_S^2 \tag{2}$$

for the latter system with the values of $\langle S^2\rangle^{1/2}$ and $\langle S^2\rangle_0^{1/2}$ given in Table V and also the results for the former reproduced from the preceding paper.[1] Figure 3 shows double-logarithmic plots of α_η^3 against α_S^3 (unfilled circles and triangles). In the figure are also plotted the literature data for a-PS, i.e., Miyaki et al.'s data[18,19] (top-half-filled circles) in benzene at 25.0 °C, Yamamoto et al.'s data[20] (bottom-half-filled circles) in benzene at 30.0 °C, and Miyaki's data[19] (filled circles) for very high molecular weight samples with $M_w > 10^7$ in cyclohexane at various temperatures ranging from 36.0 to 55.0 °C. It is seen that the data points for the benzene solutions of a-PS follow a curve (dashed) distinctly separated from those for the other systems, in contrast to the two-parameter theory prediction, as pointed out by Miyaki and Fujita.[9] On the other hand, the data sets for the toluene (unfilled circles) and cyclohexane (filled circles) solutions of a-PS form a single-composite curve (solid), and the data points (triangles) for PIB in *n*-heptane are located between the two curves.

It is believed that the definite split of the log α_η^3 vs log α_S^3 plot for a-PS in benzene from the others is related to the inadequacy of the usual determination of α_η and α_S with the values of $[\eta]_\Theta$ and $\langle S^2\rangle_0$ in cyclohexane at 34.5 °C (Θ), the latter probably being not identical with the respective unperturbed values in the good solvent. This is the reason why we have paid special regard to a determination of α_η and α_S. For a-PS, we have confirmed that the values of $[\eta]_\Theta$ and $\langle S^2\rangle_0$ obtained in cyclohexane at Θ and used for the determination of α_η and α_S agree with those of the unperturbed chains in toluene at 15.0 °C, as mentioned above and also in the preceding paper.[1] For PIB, the agreement has been confirmed for $[\eta]_\Theta$ but not for $\langle S^2\rangle_0$, as mentioned above.

In order to demonstrate the situation more explicitly, the results for $\langle S^2\rangle$ and $[\eta]$ obtained for the four highest-molecular-weight samples of a-PS in toluene at 30.0 °C are given in Table VII along with the results in toluene at 15.0 °C. Then we have also determined α_η and α_S for them at 30.0 °C with these values and the values of $[\eta]_\Theta$ and $\langle S^2\rangle_0$ in cyclohexane at Θ, respectively. The results

Table VII
Values of $\langle S^2\rangle^{1/2}$ and $[\eta]$ for Atactic Polystyrene in Toluene at 30.0 and 15.0 °C

	$\langle S^2\rangle^{1/2}$, Å		$[\eta]$, dL/g	
sample	30.0 °C	15.0 °C[a]	30.0 °C	15.0 °C
F40	231	238	1.16	1.18
F80	349	363	1.95	1.97
F128-2	501	520	2.91	2.91
F380	947	984	6.80	7.05

[a] Reproduced from ref 1.

Table VIII
Values of the HW Model Parameters Determined from $[\eta]_\Theta$ for Atactic Polystyrene and Polyisobutylene

polymer (f_r)	solvent	temp, °C	$\lambda^{-1}\kappa_0$	$\lambda^{-1}\tau_0$	λ^{-1}, Å	M_L, Å^{-1}	ref
a-PS (0.59)	cyclohexane	34.5	3.0	6.0	23.5	42.6	11
PIB	IAIV	25.0	0		12.7	24.1	10

are shown by the center-filled circles in Figure 3. They are seen to shift definitely toward the dashed curve for a-PS in benzene. This is mainly due to the temperature dependence of $\langle S^2\rangle$, as seen from Table VII; the values of $\langle S^2\rangle$ at 30.0 °C are ca. 7% smaller than those at 15.0 °C, while the temperature dependence of $[\eta]$ is much smaller. Thus we may conclude that the deviation of the data points for a-PS in benzene from those for the other systems arises from the inadequacy in the determination of α_η and α_S, as mentioned above.

Having determined correctly the expansion factors, it is now important to see that the relation between $\alpha_\eta{}^3$ and $\alpha_S{}^3$ for a-PS in toluene at 15.0 °C is consistent with that for a-PS in cyclohexane down to a region of very small $\alpha_S{}^3$, i.e., $\alpha_S{}^3 < 1.1$. This is a striking finding if we consider the fact that the effect of chain stiffness on α_S still exists for the present samples (in toluene) but may be regarded as negligible for the latter with $M_w > 10^7$ (in cyclohexane). As suggested in the preceding paper,[1] for a-PS in toluene α_S may be expressed as a function only of the scaled excluded-volume parameter $\tilde{z}$. The above finding implies that this is also the case with α_η. Thus it is worthwhile to examine the behavior of α_η as functions of the conventional excluded-volume parameter z and also $\tilde{z}$ in more detail. Before doing this, it is necessary to establish the values of the model parameters.

Model Parameters. We make an analysis of data on the basis of the HW chain with excluded volume. In the unperturbed state, it may be described in terms of four model parameters:[7,8] the constant curvature κ_0 and torsion τ_0 of its characteristic helix taken at the minimum zero of its elastic energy, the static stiffness parameter λ^{-1}, and the shift factor M_L as defined as the molecular weight per unit contour length. For the present treatment of α_η, for which we have not developed an HW theory, it is reasonable to adopt the values of these HW model parameters determined previously from $[\eta]_\Theta$ for a-PS[11] and PIB.[10] The results have been reproduced in Table VIII.

For a determination of z and $\tilde{z}$, an additional parameter, i.e., the excluded-volume strength B (or reduced strength λB), is required. The latter may be determined from a comparison of experimental data for α_S with the YSS theory.[3-5] It is therefore convenient to again reproduce necessary equations. For the HW chain of total contour length L, it assumes the Domb–Barrett expression[21] for $\alpha_S{}^2$, i.e.

$$\alpha_S{}^2 = [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15}[0.933 + 0.067\exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \quad (3)$$

Table IX
Values of the Reduced Parameter λB Determined from $\langle S^2\rangle$ for Atactic Polystyrene and Polyisobutylene

polymer (f_r)	solvent	temp, °C	λB
a-PS (0.59)	toluene	15.0	0.26[a]
a-PS[b]	cyclohexane	55.0	0.031
		50.0	0.024
		45.0	0.016
		40.0	0.0087
		38.0	0.0056
		36.0	0.0030
PIB	*n*-heptane	25.0	0.083

[a] Reproduced from ref 1. [b] From ref 19.

with

$$\tilde{z} = (3/4)K(\lambda L)z \quad (4)$$

in place of the parameter z, which is defined in the YSS theory by

$$z = (3/2\pi)^{3/2}(\lambda B)(\lambda L)^{1/2} \quad (5)$$

where

$$B = \beta/a^2c_\infty{}^{3/2} \quad (6)$$

with β the binary cluster integral between beads with a their spacing and

$$c_\infty = \lim_{\lambda L\to\infty}(6\lambda\langle S^2\rangle_0/L) = \frac{4 + (\lambda^{-1}\tau_0)^2}{4 + (\lambda^{-1}\kappa_0)^2 + (\lambda^{-1}\tau_0)^2} \quad (7)$$

In eq 4, the coefficient $K(L)$ is given by

$$K(L) = \frac{4}{3} - 2.711L^{-1/2} + \frac{7}{6}L^{-1} \qquad \text{for } L > 6$$
$$= L^{-1/2}\exp(-6.611L^{-1} + 0.9198 + 0.03516L) \qquad \text{for } L \leq 6 \quad (8)$$

Recall that L is related to the degree of polymerization x by the equation

$$L = xM_0/M_L \quad (9)$$

with M_0 the molecular weight of the repeat unit.

We have already determined the reduced parameter λB for a-PS in toluene at 15.0 °C in the preceding paper.[1] The result has been reproduced in Table IX. In order to make a similar determination for PIB in *n*-heptane at 25.0 °C, the present values of $\alpha_S{}^2$ are double-logarithmically plotted against x_w in Figure 4. As in the analysis of $[\eta]_\Theta$,[10] we represent the PIB chain by the KP model, considering the fact that the conformation close to the 8_3 helix of pitch 18.60 Å taken in the crystalline state is locally preserved also in dilute solutions. Since the KP chain is a special case of the HW chain with $\kappa_0 = 0$, eq 7 reduces to

$$c_\infty = 1 \quad (10)$$

and the value of τ_0 is of no significance in this case. Further, we assign M_L the value 24.1 Å^{-1} corresponding to the above conformation, as given in Table VIII. For λ^{-1}, we then obtain, instead of the value 12.7 Å in Table VIII, the value 14.0 Å from the present average value 5.53 Å for $\langle S^2\rangle_0/x_w$. In Figure 4, the solid curve represents the best-fit HW (KP) theoretical values calculated from eq 3 with eqs 4, 5, 8, and 9 with these values of the model parameters along with $\lambda B = 0.083$. This value of λB thus determined is given in Table IX.

In order to analyze the data[19] for a-PS in cyclohexane at various temperatures, the results obtained similarly are

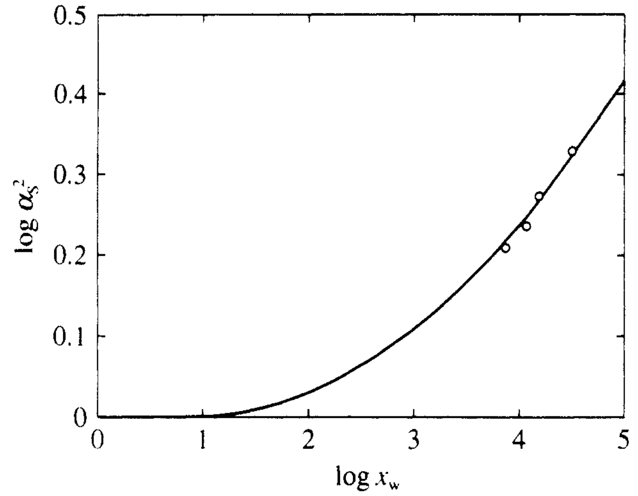

Figure 4. Double-logarithmic plots of α_S^2 against x_w for PIB in n-heptane at 25.0 °C. The solid curve represents the best-fit YSS theory values.

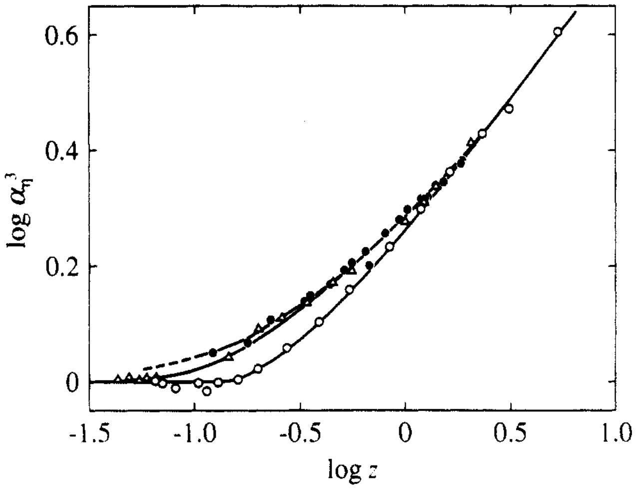

Figure 5. Double-logarithmic plots of α_η^3 against z for a-PS and PIB: (○) a-PS in toluene at 15.0 °C (present data); (●) a-PS ($M_w > 10^7$) in cyclohexane at various temperatures (36.0–55.0 °C) (Miyaki);[19] (△) PIB in n-heptane at 25.0 °C (present data).

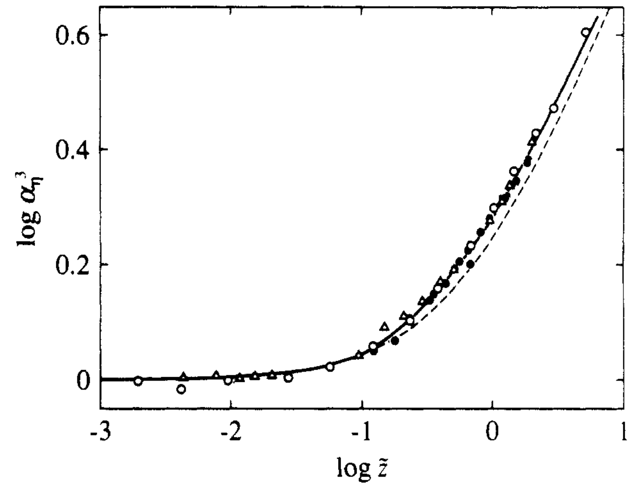

Figure 6. Double-logarithmic plots of α_η^3 against $\tilde{z}$ for a-PS and PIB. The symbols have the same meaning as those in Figure 5. The dashed curve represents the values calculated from eq 11.

also summarized in Table IX. (We note that the dependence on temperature of $\langle S^2\rangle_0$ for this system may be neglected in its range studied, as shown in a forthcoming paper.)

α_η^3 as a Function of z. We first examine the behavior of α_η^3 as a function of z. Figure 5 shows double-logarithmic plots of α_η^3 against z for the present data for a-PS in toluene at 15.0 °C (unfilled circles) and PIB in n-heptane at 25.0 °C (triangles) and also for the literature data[19] for a-PS in cyclohexane at various temperatures (filled circles). Here, the values of z have been calculated from eq 5 with eq 9 with the values of λ^{-1} and M_L given in Table VIII and those of λB given in Table IX. The solid curves connect the data points smoothly.

The curve for the filled circles may be considered to represent a relation between α_η^3 and z that must be predicted by the two-parameter theory, since it refers to the data for such high molecular weights that the coefficient $K(L)$ given by eq 8 almost takes its coil limiting value $^4/_3$. Despite the fact that we have paid special regard to the determination of α_η, the two lower curves still deviate downward from this (limiting) curve with decreasing z or M_w, in accord with the finding by Miyaki and Fujita[9] as mentioned in the Introduction. For a-PS in toluene, the deviation occurs already for considerably large values of z and α_η^3 approaches unity extremely rapidly with decreasing z. On the other hand, for PIB in n-heptane, the deviation is less appreciable, although α_η^3 again becomes unity at finite z. The approach of α_η^3 to unity at finite z corresponds to the similar behavior of α_S^2 discussed in the preceding paper. Thus these results are believed to arise from the effect of chain stiffness, the stiffness as represented by λ^{-1} being larger for a-PS than for PIB. It is then interesting and important to examine whether α_η^3 is or is not a function only of the scaled parameter $\tilde{z}$.

α_η^3 as a Function of $\tilde{z}$. Figure 6 shows double-logarithmic plots of α_η^3 against $\tilde{z}$ for the same data as in Figure 5. The values of $\tilde{z}$ have been calculated from eq 4 with eq 8 and with the above values of z. It is seen that the data points for all the systems form a single-composite curve as indicated by the solid line, irrespective of the differences in chain stiffness, local chain conformation, and excluded-volume strength. [Note that the slight discrepancy between the data points for PIB in n-heptane and those for a-PS in toluene at 15.0 °C and in cyclohexane found in Figure 3 completely disappears in Figure 6. This may probably be an accident arising from the fact that it is canceled out by the differences between the values of the HW model parameters λ^{-1} and M_L (from $\langle S^2\rangle_0$) used for the determination of λB and those (from $[\eta]_\Theta$) used for the calculation of $\tilde{z}$.] Thus, from the results obtained in Figures 3 and 6, we may conclude that α_η is also a function only of the parameter $\tilde{z}$ in a first approximation.

In this connection, it is interesting to note that Barrett[22] has derived a closed expression for α_η as a function of z. If we replace his z by $\tilde{z}$ as in the case of α_S, then we have

$$\alpha_\eta^3 = (1 + 3.8\tilde{z} + 1.9\tilde{z}^2)^{0.3} \tag{11}$$

In Figure 6, the dashed curve represents the values calculated from eq 11. The observed values cannot be well explained by this theory in the range of large $\tilde{z}$. It is evident that this is due to the incorrectness of his original equation itself for large z. However, the good agreement between theory and experiment for small $\tilde{z}$ suggests the adequacy of the replacement of z by $\tilde{z}$, since his original equation must be correct for small z.

Conclusion

We have determined $[\eta]$ for a-PS in toluene at 15.0 °C and for PIB in n-heptane at 25.0 °C over a wide range of M_w, including the oligomer region. These temperatures have been chosen so that the unperturbed values of $[\eta]$ may be identical with the values of $[\eta]_\Theta$ in cyclohexane and in IAIV, respectively, and thus we have determined correctly the viscosity–radius expansion factor α_η. It is then found that α_η is a function only of the radius expansion factor α_S in a first approximation, in contrast to the literature data. However, when plotted against the conventional excluded-volume parameter z, the present data for α_η do not form a single-composite curve as yet; the plot exhibits a downward deviation from the two-parameter theory prediction, depending on the chain stiffness. As was expected, however, the data form a single-composite curve when plotted against the scaled excluded-volume parameter $\tilde{z}$, so that the *quasi*-two-parameter scheme may be regarded as valid for α_η as well as for α_S. This also implies that there is no effect of partial drainage on α_η if it is not observed in $[\eta]_\Theta$.[10,11] The single-composite curve above cannot be well explained by, for instance, the Barrett theory with $\tilde{z}$ in place of z except for small $\tilde{z}$. Thus the relation between α_η and $\tilde{z}$ (or z) is still worth deriving theoretically. Before doing this, it is necessary to further confirm the present conclusion using some other flexible polymers. In this spirit, a similar study is now in progress for atactic oligo- and poly(methyl methacrylate)s and oligo- and poly(dimethylsiloxane)s.

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