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Excluded-Volume Effects on the Intrinsic Viscosity of Oligo- and Polystyrenes. Solvent Effects

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ABSTRACT: The viscosity-radius expansion factor α_η of atactic polystyrene (a-PS) with the fraction of racemic diads $f_r = 0.59$ was reinvestigated mainly in order to resolve a deviation of literature experimental data for α_η^3 of a-PS in benzene at 25.0 °C from a universal curve in the log α_η^3 vs log α_S^3 plot established for other polymer–solvent systems, where α_S is the (gyration-)radius expansion factor. For this purpose, the intrinsic viscosity $[\eta]$ was determined for a-PS in benzene at 25.0 °C, in methyl ethyl ketone (MEK) at 35.0 °C, and in *trans*-decalin at 21.0 °C (Θ) in the range of weight-average molecular weight M_w from 5.78×10^2 to 3.84×10^6, and also the mean-square radius of gyration $\langle S^2 \rangle$ in these solvents in the range of M_w from 3.59×10^5 to 3.84×10^6. The values of $[\eta]$ of oligostyrene samples in these three solvents, for which the excluded-volume effect was negligible, were confirmed to agree approximately with each other. The (double-logarithmic) plots of α_η^3 against α_S^3 for a-PS in benzene at 25.0 °C and in MEK at 35.0 °C were found to follow the universal curve above, if the values of $[\eta]_\Theta$ and $\langle S^2 \rangle_0$ of a-PS in *trans*-decalin at Θ instead of those in cyclohexane at Θ are used as reference standards to calculate α_η^3 and α_S^2, respectively. It was also found that the data for α_η^3 of a-PS in various solvents form a single-composite curve when plotted against the scaled excluded-volume parameter $\tilde{z}$ defined in the Yamakawa–Stockmayer–Shimada theory based on the helical wormlike chain model. Thus the present results confirm the previous conclusion that the *quasi*-two-parameter scheme may be regarded as valid for α_η as well as for α_S irrespective of the differences in chain stiffness, local chain conformation, and solvent condition.

Introduction

In previous papers[1,2] of this series, we have investigated the gyration- and viscosity-radius expansion factors α_S and α_η for atactic polystyrene (a-PS) and polyisobutylene (PIB) over a wide range of molecular weight M, including the oligomer region. We have explicitly demonstrated that α_η becomes a function only of α_S when they are determined correctly by choosing properly a good and Θ solvent pair so that the unperturbed values of the mean-square radius of gyration $\langle S^2 \rangle$ and the intrinsic viscosity $[\eta]$ in that good solvent may coincide with those in the Θ state, i.e., $\langle S^2 \rangle_0$ and $[\eta]_\Theta$, respectively, taken as the reference standards. In practice, combinations of toluene at 15.0 °C and cyclohexane at 34.5 °C (Θ) and of *n*-heptane at 25.0 °C and isoamyl isovalerate at 25.0 °C (Θ) were adopted for a-PS and PIB, respectively. It has also been found that α_η as well as α_S may be expressed as functions only of the scaled excluded-volume parameter $\tilde{z}$ defined in the Yamakawa–Stockmayer–Shimada (YSS) theory[3–5] that takes account of the effects of excluded volume and chain stiffness on the basis of the helical wormlike (HW) chain,[6,7] including the Kratky–Porod wormlike chain[8] as its special case. The implication is that a *quasi*-two-parameter scheme may be regarded as valid for both α_S and α_η.

Before the above work, Miyaki and Fujita[9] had pointed out that the two-parameter theory[10] of α_η breaks down. Their findings for a-PS are summarized as follows: (1) in the log α_η^3 vs log α_S^3 plot, the experimental data in benzene exhibit a definite split from those in other solvents, e.g., cyclohexane at various temperatures, and (2) when double-logarithmically plotted against the conventional excluded-volume parameter z, the data for α_η^3 in different solvents do not form a single-composite curve; i.e., the data for the benzene and methyl ethyl ketone (MEK) solutions deviate significantly downward from those for the cyclohexane solutions, especially at small z (or M). As for the first point, we have confirmed that when compared at fixed α_S^3, their results for α_η^3 of a-PS in benzene deviate upward from our data in toluene at 15.0 °C, which are in good agreement with their data in cyclohexane, and suggested that the discrepancy is related to the inadequacy of the usual determination of α_η and α_S with the value of $[\eta]_\Theta$ and $\langle S^2 \rangle_0$ in cyclohexane at 34.5 °C (Θ).[2] Actually, the results for a-PS in toluene at 30.0 °C have been found to shift toward those in benzene, since the values of $[\eta]_\Theta$ and $\langle S^2 \rangle_0$ in cyclohexane at Θ used for the calculation of α_η and α_S agree with those for the unperturbed chains in toluene at 15.0 °C but not with those at 30.0 °C. In this connection, we note that the unperturbed dimension of a-PS has long been recognized to depend on the solvent and temperature.[11–13] For the second point, we have also found that the plots of log α_η^3 vs log z for a-PS in toluene at 15.0 °C and PIB in *n*-heptane at 25.0 °C deviate downward from the "two-parameter theory prediction" represented by the results for a-PS with very large M in cyclohexane, depending on chain stiffness. As stated above, however, the same data form a single-composite curve when plotted against $\tilde{z}$. Thus, the second point above may be considered to arise from the effect of chain stiffness.

The object of the present work is to confirm the validity of the quasi-two-parameter scheme for α_η of a-PS in various solvents, including benzene and MEK. For this purpose, we reinvestigate α_η and α_S of a-PS in benzene and in MEK by choosing a proper Θ solvent and then determining them correctly. In this work, we try to use *trans*-decalin at 21.0 °C as another Θ solvent for a-PS instead of cyclohexane at 34.5 °C. The reason for this is that the values of $[\eta]$ of a-PS in the oligomer region, where the excluded-volume effect may be neglected, are lower in benzene at 25.0 °C than in cyclohexane at Θ except for the dimer and trimer,[14] while in the coil limit the values of $[\eta]_\Theta$ in *trans*-decalin at Θ are lower than those in cyclohexane at Θ,[15] so that the values in the former Θ solvent may be expected to be closer to the unperturbed values in benzene than those in the latter.

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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
OS5[a]	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-a	1.23×10^3	11.3	1.03
A2500-a′ [b]	1.78×10^3	16.6	1.04
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
F4[c]	4.00×10^4	384	1.02
F10	9.73×10^4	935	1.02
F40	3.59×10^5	3450	1.01
F80	7.32×10^5	7040	1.01
F80a-2	7.32×10^5	7040	1.03
F128-2	1.32×10^6	12700	1.05
F128a-2	1.27×10^6	12200	1.03
F380	3.84×10^6	36900	1.05

[a] M_w's of OS5 through OS8 had been determined from GPC.[16] [b] M_w's of A2500-a′ through F1-2 had been determined from LS in MEK at 25.0 °C.[14,16] [c] M_w's of F4 through F380 had been determined from LS in cyclohexane at 34.5 °C[1,15,17] except for F80a-2 and F128a-2, for which they were determined from LS in benzene at 25.0 °C in this work.

Experimental Section

Materials. Most of the a-PS samples used in this work are the same as those used in the previous studies of the mean-square optical anisotropy $\langle \Gamma^2 \rangle$,[16] $[\eta]_\Theta$,[14] $\langle S^2 \rangle_0$,[17] the transport factors ρ and Φ for long flexible chains,[15] the translational diffusion coefficient D,[18] $\langle S^2 \rangle$,[1] and $[\eta]$,[2] i.e., the fractions separated by preparative gel permeation chromatography or fractional precipitation from the standard samples supplied by Tosoh Co., Ltd. The additional samples A1000-a, F80a-2, and F128a-2 used in this work are also fractions separated similarly from the Tosoh standard samples. The two of them, F80a-2 and F128a-2, may be regarded as the same as F80 and F128-2, respectively. All the samples 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, the weight-average degree of polymerization x_w, and the ratio of M_w to the number-average molecular weight M_n are listed in Table I. It also includes the values of M_w determined from the present light scattering (LS) measurements for the sample A1000-a in cyclohexane at 34.5 °C and for F80a-2 and F128a-2 in benzene at 25.0 °C. As seen from the values of M_w/M_n, all the samples are sufficiently narrow in molecular weight distribution.

The solvents benzene and MEK were purified according to standard procedures prior to use. The solvent *trans*-decalin was also thoroughly purified and treated with special care following the procedure described before.[15] It was found to contain no detectable impurity, especially the *cis* component, from an examination by gas chromatography.

Viscosity. Viscosity measurements were carried out for almost all the samples in *trans*-decalin at 21.0 °C (Θ) and in MEK at 35.0 °C and for the samples with $M_w \geq 4.00 \times 10^4$ also in benzene at 25.0 °C. We used conventional capillary viscometers of the Ubbelohde type except for the oligomer samples with $M_w \leq 5.38 \times 10^3$ in MEK, the sample F380 in all three solvents, and F128a-2 in benzene, for which four-bulb spiral capillary viscometers of the same type were employed. Viscosities of the latter two samples in these solvents were then measured at very low shear rate so that the non-Newtonian effect might be ignored. This 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 test solutions were maintained at a constant temperature within ±0.005 °C during the measurements. 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 temperature for ca. 1 day for a-PS in benzene and in MEK and at ca. 50 °C for 4 days for a-PS in *trans*-decalin. 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. 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 $\langle S^2 \rangle$ (and also M_w) of the three samples F380, F128a-2, and F80a-2 in benzene at 25.0 °C and in *trans*-decalin at 21.0 °C and of the four samples F380, F128a-2, F80a-2, and F40 in MEK at 35.0 °C. Measurement was also made for the sample A1000-a in cyclohexane at 34.5 °C to determine its M_w. A Fica 50 light-scattering photometer was used for all the measurements with vertically polarized incident light of wavelength 436 nm, except for the sample F380 in benzene for which the incident light of wavelength 546 nm was employed to determine its rather large value of $\langle S^2 \rangle$. 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 to seven different concentrations and at scattering angles ranging from 30 to 150°, except for F380 in all three solvents and F128a-2 in benzene. For the latter cases, the intensities were measured at 10–12 scattering angles ranging from 20 to 45 or 65°. For the sample A1000-a, the intensities were measured at eight different concentrations with polarized and unpolarized incident light to make corrections for optical anisotropy. All the data obtained were analyzed by the Berry square-root plot.[19]

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 or 0.10 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.

The refractive index increment $\partial n/\partial c$ measured with a Shimadzu differential refractometer at 436 nm for the sample A1000-a in cyclohexane at 34.5 °C is 0.1765 cm^3/g. The values of $\partial n/\partial c$ at 436 nm used for a-PS in the other solvents are 0.1094 cm^3/g in benzene at 25.0 °C,[20] 0.2321 cm^3/g in MEK at 35.0 °C,[21] and 0.138 cm^3/g in *trans*-decalin at 21.0 °C.[15]

Results

Intrinsic Viscosity. The values of $[\eta]$ for all the samples determined in benzene at 25.0 °C, in MEK at 35.0 °C, and in *trans*-decalin at 21.0 °C (Θ) are summarized in Table II along with those of the Huggins coefficient k'. It also includes the values obtained previously for the same samples in benzene at 25.0 °C[14] and in *trans*-decalin at Θ.[15] Figure 1 shows double-logarithmic plots of the ratio $[\eta]/M_w^{1/2}$ against M_w for the results in benzene (unfilled circles), in MEK (circles with vertical bar pip), and in *trans*-decalin (triangles). The previous results for the same a-PS samples in cyclohexane at 34.5 °C (Θ) (filled circles) have been reproduced from refs 14, 15, and 17, for reference. The figure also includes the literature data by Miyaki[22] (circles with pip) and by Nakamura[23] (inverse triangles) for a-PS samples of the same source (from the Tosoh standard samples) in the same solvents and at the same temperatures. Their data for each system are in good agreement with the present ones. The solid and dashed curves connect the data points smoothly (the latter for the cyclohexane solutions).

It is seen that the data points in *trans*-decalin are definitely lower than those in cyclohexane, the coil limiting value of $[\eta]/M_w^{1/2}$ for the former being ca. 7% smaller than that for the latter. In the oligomer region where the excluded-volume effect may be neglected, the values of $[\eta]/M_w^{1/2}$ in benzene and in MEK are definitely smaller than those in cyclohexane at Θ, as mentioned for the former

Table II. Results of Viscometry on Atactic Oligo- and Polystyrenes in *trans*-Decalin at 21.0 °C (Θ), in MEK at 35.0 °C, and in Benzene at 25.0 °C

	trans-decalin (21.0 °C)		MEK (35.0 °C)		benzene (25.0 °C)	
sample	[η], dL/g	k'	[η], dL/g	k'	[η], dL/g	k'
OS5[a]	0.0261	0.96			0.0264	0.82
OS6[a]	0.0283	0.95	0.0274	1.00	0.0280	0.82
OS8[a]	0.0321	0.84	0.0294	0.94	0.0307	0.81
A1000-a	0.0359	1.01	0.0335	0.90		
A2500-a′ [a]	0.0398	1.10	0.0372	0.79	0.0384	0.77
A2500-b[a]	0.0533	0.81	0.0513	0.76	0.0550	0.71
A5000-3[a]	0.0658	0.75	0.0629	0.71	0.0695	0.58
F1-2[a]	0.0877	0.72	0.0864	0.62	0.102	0.54
F4	0.164	0.61	0.182	0.51	0.256	0.39
F10	0.257	0.55	0.307	0.46	0.479	0.37
F40[b]	0.473	0.57	0.681	0.43	1.25	0.35
F80[b]	0.645	0.60				
F80a-2			1.06	0.43	2.07	0.35
F128-2[b]	0.912	0.62				
F128a-2			1.52	0.39	3.11	0.34
F380	1.66	0.65	3.32	0.40	7.32	0.35

[a] The data in benzene at 25.0 °C have been reproduced from ref 14. [b] The data in *trans*-decalin at 21.0 °C have been reproduced from ref 15.

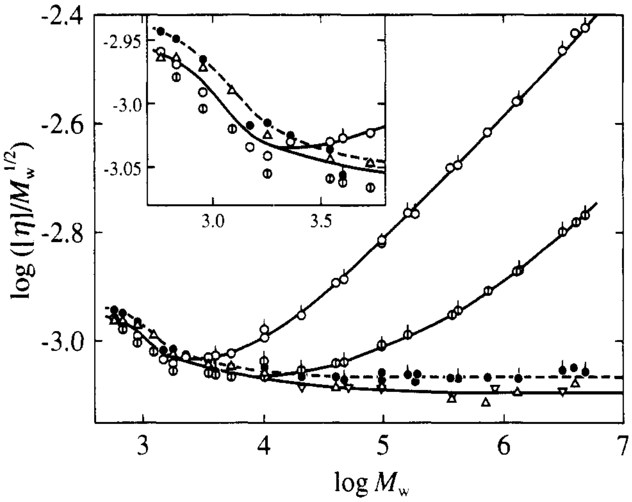

Figure 1. Double-logarithmic plots of $[\eta]/M_w^{1/2}$ ($[\eta]$ in dL/g) against M_w for a-PS: (○) in benzene at 25.0 °C (present data); (ȯ) in benzene at 25.0 °C (Miyaki);[22] (⦶) in MEK at 35.0 °C (present data); (⦶̇) in MEK at 35.0 °C (Miyaki);[22] (△) in *trans*-decalin at 21.0 °C (Θ) (present data); (▽) in *trans*-decalin at 21.0 °C (Θ) (Nakamura);[23] (●) in cyclohexane at 34.5 °C (Θ) (previous data);[14,15,17] (●̇) in cyclohexane at 34.5 °C (Θ) (Miyaki).[22] The solid and dashed curves connect the data points smoothly.

Table III. Results of Light Scattering Measurements on Atactic Polystyrene in *trans*-Decalin at 21.0 °C (Θ), in MEK at 35.0 °C, and in Benzene at 25.0 °C

	trans-decalin (21.0 °C)		MEK (35.0 °C)		benzene (25.0 °C)	
sample	$M_w \times 10^{-4}$	$\langle S^2 \rangle^{1/2}$, Å	$M_w \times 10^{-4}$	$\langle S^2 \rangle^{1/2}$, Å	$M_w \times 10^{-4}$	$\langle S^2 \rangle^{1/2}$, Å
F40[a]	36.7	162	37.1	193	35.7	239
F80[a]	70.3	229			73.1	372
F80a-2	72.3	230	73.9	283	73.2	372
F128-2[a]	129	313				
F128a-2	124	302	128	390	127	518
F380	396	561	402	747		1040

[a] The data in *trans*-decalin at 21.0 °C have been reproduced from ref 15, and those for F40 and F80 in benzene at 25.0 °C are unpublished results (see the text).

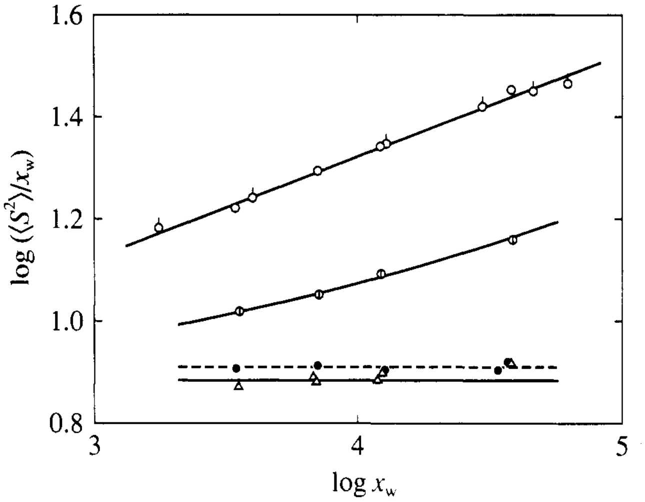

Figure 2. Double-logarithmic plots of $\langle S^2 \rangle / x_w$ ($\langle S^2 \rangle$ in Å^2) against x_w for a-PS. The symbols have the same meaning as those in Figure 1. For the *trans*-decalin and cyclohexane solutions at Θ, $\langle S^2 \rangle / x_w$ means $\langle S^2 \rangle_0 / x_w$. The solid and dashed lines connect the data points smoothly (the latter for the cyclohexane solutions).

in the Introduction. In this region the values of $[\eta]/M_w^{1/2}$ in *trans*-decalin at Θ are rather close to those in benzene and in MEK. The data for the pentamer and hexamer in *trans*-decalin at Θ and in benzene at 25.0 °C coincide with each other. Then these results lead to the conclusion that the unperturbed dimensions of the a-PS chain in benzene and in MEK are definitely different from those in cyclohexane at Θ but may be regarded as nearly identical with those in *trans*-decalin at Θ. Thus, in this work we calculate α_η for a-PS in benzene at 25.0 °C and in MEK at 35.0 °C by the use of the values of $[\eta]_\Theta$ in *trans*-decalin at Θ. It is seen that the excluded-volume effect on $[\eta]$ becomes appreciable for $M_w \gtrsim 2 \times 10^3$ in benzene at 25.0 °C and for $M_w \gtrsim 10^4$ in MEK at 35.0 °C.

Mean-Square Radius of Gyration. The values of $\langle S^2 \rangle^{1/2}$ determined from LS measurements for the a-PS samples with $M_w \geq 3.57 \times 10^5$ in benzene at 25.0 °C, in MEK at 35.0 °C, and in *trans*-decalin at 21.0 °C (Θ) are given in Table III along with those of M_w determined simultaneously. It also includes the previous results by Konishi et al.[15] for the samples F40, F80, and F128-2 in *trans*-decalin at Θ and for F40 and F80 in benzene at 25.0 °C. (The latter data are unpublished results already obtained in the determination of their M_w.)

Figure 2 shows double-logarithmic plots of the ratio $\langle S^2 \rangle / x_w$ against x_w for the results in benzene at 25.0 °C (unfilled circles), in MEK at 35.0 °C (circles with vertical bar), and in *trans*-decalin at Θ (triangles). It also includes the previous results in cyclohexane at Θ (filled circles),[1,15] for reference, and the literature data in benzene at 25.0 °C by Miyaki (unfilled circles with pip).[22] Here, for the *trans*-decalin and cyclohexane solutions at Θ, $\langle S^2 \rangle / x_w$ means $\langle S^2 \rangle_0 / x_w$. The solid and dashed lines connect the data points smoothly (the latter for the cyclohexane solutions). The data points for the *trans*-decalin solutions are clearly seen to be lower than those for the cyclohexane solutions except for the sample F380; the adopted value of $\langle S^2 \rangle_0 / x_w$ of a-PS in *trans*-decalin at Θ is ca. 6% smaller than that in cyclohexane at Θ. This result corresponds to that for $[\eta]_\Theta / M_w^{1/2}$ shown in Figure 1. As in the case of α_η, we calculate α_S for a-PS in benzene at 25.0 °C and in MEK at 35.0 °C by taking the values of $\langle S^2 \rangle_0$ in *trans*-decalin at Θ as reference standards.

It is seen from Figure 2 that Miyaki's data for the benzene solutions coincide quantitatively with the present ones. Recall here that his value[22] 8.68 Å^2 of $\langle S^2 \rangle_0 / x_w$ of a-PS (in the range of x_w displayed) in cyclohexane at Θ is ca. 7% larger than our corresponding value 8.13 Å^2 (dashed

Table IV. Values of α_η^3 and α_S^3 for Atactic Oligo- and Polystyrenes in MEK at 35.0 °C and in Benzene at 25.0 °C

	MEK (35.0 °C)		benzene (25.0 °C)	
sample	α_η^3	α_S^3	α_η^3	α_S^3
OS5			1.01	
OS6	0.968		0.989	
OS8	0.916		0.956	
A1000-a	0.933			
A2500-a′	0.935		0.965	
A2500-b	0.962		1.03	
A5000-3	0.956		1.06	
F1-2	0.985		1.16	
F4	1.11		1.56	
F10	1.19		1.86	
F40	1.44	1.69	2.64	3.21
F80				4.29
F80a-2	1.65	1.86	3.18	4.23
F128a-2	1.67	2.15	3.41	5.05
F380	2.00	2.36	4.41	6.37

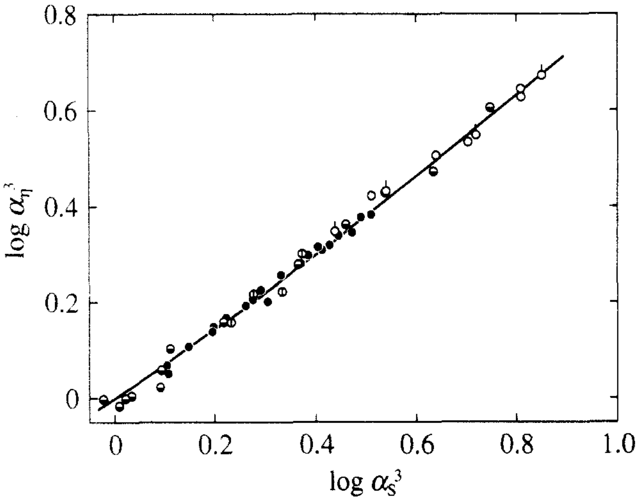

Figure 3. Double-logarithmic plots of α_η^3 against α_S^3 for a-PS: (◒) a-PS in toluene at 15.0 °C;[2] (●) a-PS ($M_w > 10^7$) in cyclohexane at various temepratures (36.0–55.0 °C) (Miyaki).[22] The other symbols have the same meaning as those in Figure 1. The solid curve connects the data points smoothly.

line of Figure 2), as previously mentioned.[1,15] However, we note that Nakamura and Norisuye[24] of the same laboratory have recently obtained the results for this system which are consistent with ours.

Discussion

Relation between α_η^3 and α_S^3. In Table IV 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 benzene at 25.0 °C and in MEK at 35.0 °C, with the results given in Table II, and the value of α_S^3 calculated from the equation

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

for the same systems, with the results given in Table III. These values of α_η^3 are double-logarithmically plotted against α_S^3 in Figure 3 (unfilled circles and circles with vertical bar). It also includes Miyaki's data[22] (unfilled circles with pip) in benzene at 25.0 °C, which have been recalculated by taking the values of $[\eta]_\Theta/M_w^{1/2}$ and $\langle S^2 \rangle_0/x_w$ in *trans*-decalin at Θ determined in this work as reference standards. In the figure we have also reproduced the previous results[2] (bottom-half-filled circles) for a-PS in toluene at 15.0 °C and Miyaki's results[22] (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 all the data points for different solvent systems form a single-composite curve. The split of the data for the benzene solutions found in Figure 3 of ref 2 and in Figure 10 of ref 9 disappears completely in Figure 3. This is just what was expected; the split is due to the calculations of α_η and α_S with the inadequate values of $[\eta]_\Theta$ and $\langle S^2 \rangle_0$. However, we must note that the rather large values (8.68–9.15 Å^2) of $\langle S^2 \rangle_0/x_w$ of a-PS in cyclohexane at Θ by Miyaki et al.,[22,25] which were taken as the references in the calculation of α_S, are in part responsible for the above discrepancy; if we use the value 8.13 Å^2 of $\langle S^2 \rangle_0/x_w$ (dashed line of Figure 2) instead of their own values, then the discrepancy becomes small, although it does not completely disappear. Thus we reconfirm that, at least for a-PS, α_η becomes a function only of α_S irrespective of the solvent used and the molecular weight range examined, if α_η and α_S are correctly determined. This leads to the expectation that the quasi-two-parameter scheme for α_η and α_S, which has been verified in the previous work[1,2] for a-PS in toluene at 15.0 °C and for PIB in *n*-heptane at 25.0 °C, may be valid for a-PS also in benzene and in MEK. In the following, this point is examined.

Model Parameters. In order to analyze the present data for α_η on the basis of the HW chain with excluded volume, we need the values of the model parameters. The HW model parameters[6,7] are the following four: the constant differential–geometrical 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. In addition, for the perturbed chain we must determine the excluded-volume strength B (or reduced strength λB). In the previous work,[2] we have adopted the values of the four HW model parameters for a-PS determined from $[\eta]_\Theta$ in cyclohexane at Θ: $\lambda^{-1}\kappa_0 = 3.0$, $\lambda^{-1}\tau_0 = 6.0$, $\lambda^{-1} = 23.5$ Å, and $M_L = 42.6$ Å^{-1}. In this work, however, we redetermine them from $[\eta]_\Theta$ in *trans*-decalin at Θ, in accordance with the calculation of α_η. We assume that the values of $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, and M_L are the same as the above values and that the difference between the values of $[\eta]_\Theta/M_w^{1/2}$ in *trans*-decalin and cyclohexane at Θ arises from the difference in λ^{-1}. Then we have $\lambda^{-1} = 22.4$ Å in *trans*-decalin at Θ.

Now the reduced excluded-volume strength λB may be determined from a comparison of experimental data for α_S with the YSS theory,[3-5] as done previously.[1,2] Thus, for convenience, we summarize the necessary basic equations. For the HW chain of total contour length L, the theory assumes the Domb–Barrett expression[26] for α_S^2, i.e.,

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

with

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

in place of the parameter z, which is now defined by

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

where

$$B = \beta/a^2 c_\infty^{3/2} \tag{6}$$

with β the binary-cluster integral between beads with a

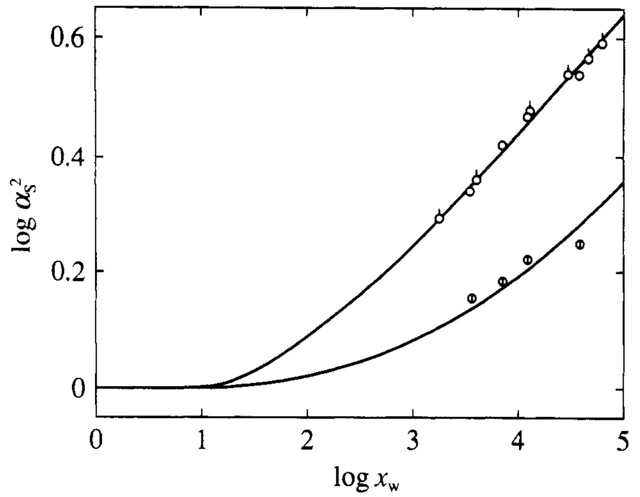

Figure 4. Double-logarithmic plots of α_S^2 against x_w for a-PS. The symbols have the same meaning as those in Figure 1. The solid curves represent the best-fit YSS theory values (see the text).

their spacing and

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

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

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

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

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

with M_0 the molecular weight of the repeat unit of a given real chain.

For a comparison between the experimental and theoretical values of α_S, we must again redetermine the HW model parameters to fit the data for $\langle S^2\rangle_0/x_w$ in *trans*-decalin at Θ (except for that for F380). Here, we change again only the value of λ^{-1}, by assuming that the values of the other parameters are the same as those previously determined from $\langle S^2\rangle_0/x_w$ in cyclohexane at Θ. The value of λ^{-1} thus redetermined is 19.4 Å. (The values of $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, and M_L are 3.0, 6.0, and 35.8 Å^{-1}, respectively.) In Figure 4, the present values of α_S^2 for a-PS in benzene at 25.0 °C (unfilled circles) and in MEK at 35.0 °C (circles with vertical bar) are double-logarithmically plotted against x_w, and the solid curves represent the best-fit YSS theoretical values calculated from eq 3 with eqs 4, 5, 8, and 9 with these values of the HW model parameters, along with $\lambda B = 0.33$ and 0.060 for the benzene and MEK solutions, respectively. Thus these are the desired results for λB.

Test of the Quasi-Two-Parameter Scheme. 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 a-PS in benzene at 25.0 °C (unfilled circles) and in MEK at 35.0 °C (circles with vertical bar), where the values of z have been calculated from eqs 5 and 9. It also includes Miyaki's data[22] (circles with pip) for the same solvent systems and the previous results[2] (bottom-half-filled circles) in toluene at 15.0 °C. The solid and dashed curves connect the data points smoothly (the latter for the toluene solutions). The dotted curve represents the "two-parameter theory prediction" determined from the data for a-PS with very large M_w (>10^7) in cyclohexane at various temperatures.[2,22]

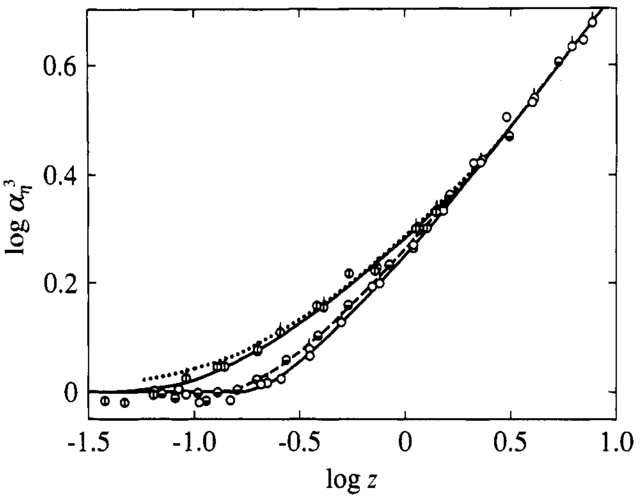

Figure 5. Double-logarithmic plots of α_η^3 against z for a-PS. The symbols have the same meaning as those in Figure 3. The solid and dashed curves connect the data points smoothly. The dotted curve represents the values for a-PS (with $M_w > 10^7$) in cyclohexane at various temperatures (36.0–55.0 °C) (Miyaki).[22]

As found previously,[2] the plots do not form a single-composite curve but give separate curves depending on the solvent condition even if α_η is determined correctly. The curves for the benzene and MEK solutions deviate downward from the dotted curve with decreasing z (or M_w). For the benzene solutions, the deviation occurs at very large z as in the case of the toluene solutions, and α_η^3 approaches unity extremely rapidly (even more rapidly than for the toluene solutions) as z is decreased. For the MEK solutions, the deviation is less significant but α_η^3 again becomes unity at finite z. At any rate, it is now evident that such deviations from the two-parameter theory (dotted curve of Figure 5), which depend on the polymer and solvent, arise from the effect of chain stiffness, as already discussed in the previous paper.[2] In particular, it is interesting to see that for a-PS in benzene log α_η^3 increases almost linearly with log z over a wide range of z, indicating that the validity of the Houwink–Mark–Sakurada relation for this system over a wide range of M_w ($\gtrsim 10^5$) as seen from Figure 1 is partly due to the effect of chain stiffness.

Next we examine the behavior of 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 those in Figure 5, where the values of $\tilde{z}$ have been calculated from eqs 4, 5, and 8. As in the case of Figure 3, the split of the data for the benzene solutions as found in the literature[9] and also in Figure 5 disappears in Figure 6. This is also the case with the MEK solutions. The implication is that α_η^3 of a-PS becomes a function only of $\tilde{z}$ irrespective of the solvent condition. Thus the deviations[9] of the data for α_η^3 of a-PS in benzene and in MEK from the two-parameter theory prediction may be regarded as arising partly from the effect of chain stiffness and partly from the inadequacy of the calculation of α_η and α_S mentioned above.

Conclusion

In this work, we have reinvestigated α_η as a function of α_S and also of $\tilde{z}$ for a-PS in benzene at 25.0 °C and in MEK at 35.0 °C. Here, the values of α_η and α_S have been calculated by taking $[\eta]_\Theta$ and $\langle S^2\rangle_0$ in *trans*-decalin at Θ as reference standards instead of those in cyclohexane at Θ, on the basis of the present finding that the former $[\eta]_\Theta$

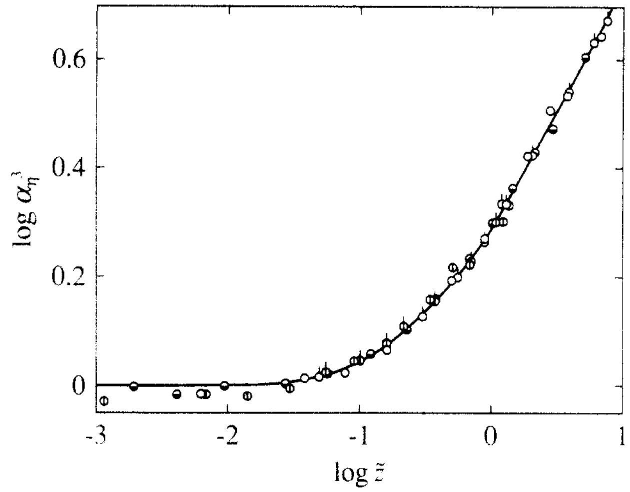

Figure 6. Double-logarithmic plots of α_η^3 against $\tilde{z}$ for a-PS. The symbols have the same meaning as those in Figure 3. The solid curve connects the data points smoothly.

is closer to [η] in the above good solvents than the latter in the oligomer region where the excluded-volume effect may be neglected. It is then found that α_η is a function only of α_S irrespective of the solvent condition. Thus it may be concluded that the split of the log α_η^3 vs log α_S^3 plot for a-PS in benzene from that for the other solvent systems as found in the literature[2,9] arises partly from the inadequate choice of the cyclohexane solution at Θ as the reference to the benzene solution of a-PS. We most note that the split also arises partly from the somewhat too large values of $\langle S^2 \rangle_0 / x_w$ obtained by Miyaki et al.[22,25] for a-PS in cyclohexane at Θ.

It is again found that when plotted against z, the data for α_η for various solvent conditions do not form a single-composite curve because of the effect of chain stiffness even if α_η is determined correctly. In particular, this effect on α_η remains significant up to large M_w ($\simeq 10^6$) for a-PS in benzene at 25.0 °C. However, the data form a single-composite curve when plotted against $\tilde{z}$, as was expected. In summary, the present results confirm the previous conclusion that the quasi-two-parameter scheme may be regarded as valid for α_η as well as for α_S irrespective of the differences in chain stiffness, local chain conformation, and solvent condition (or excluded-volume strength).

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