Excluded-Volume Effects on the Transport Coefficients of Oligo- and Poly(dimethylsiloxane)s in Dilute Solution

Ken Horita, Nobuo Sawatari, Takenao Yoshizaki, Yoshiyuki Einaga, and Hiromi Yamakawa*

Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan

Received February 13, 1995; Revised Manuscript Received April 19, 1995[⊗]

ABSTRACT: The translational diffusion coefficient D and intrinsic viscosity $[\eta]$ of oligo- and poly(dimethylsiloxane)s (PDMS) were determined in toluene at 25.0 °C in the range of weight-average molecular weight M_w from 1.08×10^3 to 1.12×10^6 for the former and from 5.33×10^2 to 1.12×10^6 for the latter. The hydrodynamic- and viscosity-radius expansion factors α_H and α_η were then determined from the values of the hydrodynamic radius R_H defined from D and those of $[\eta]$ corrected for the specific interaction between polymer and solvent molecules, respectively, with the use of the corresponding values of $R_{H,0}$ and $[\eta]_0$ for the unperturbed PDMS chain in toluene at 25.0 °C. Here, the latter values were obtained by multiplying the previous values of $R_{H,\Theta}$ and $[\eta]_\Theta$ in bromocyclohexane at Θ by respective proper factors that take account of the solvent dependence of the bead diameter and may be calculated by the use of the helical wormlike (HW) chain theory. The results show that both α_H and α_η become functions only of the scaled excluded-volume parameter $\tilde{z}$ defined in the Yamakawa–Stockmayer–Shimada theory for the HW chain with excluded volume, being consistent with the previous results for atactic polystyrene. This implies that the quasi-two-parameter scheme may be valid for α_H and α_η irrespective of the differences in polymer species and solvent condition and, moreover, that there is no draining effect on α_H and α_η, although it is significant for the unperturbed PDMS chain. It is again found that the Barrett equation overestimates α_H. This disagreement between theory and experiment may be semiquantitatively explained by the Yamakawa–Yoshizaki theory, which takes account of the possible effect of fluctuating hydrodynamic interaction on α_H.

Introduction

In this series of experimental work on the excluded-volume effects in dilute solutions of oligomer and polymers, we have already studied the gyration-radius expansion factor α_S for atactic polystyrene (a-PS),[1] atactic poly(methyl methacrylate) (a-PMMA),[2] and isotactic poly(methyl methacrylate) (i-PMMA),[3] the viscosity-radius expansion factor α_η for a-PS,[4,5] polyisobutylene (PIB),[4] a-PMMA,[2] and i-PMMA,[3] and the hydrodynamic-radius expansion factor α_H for a-PS.[6] It has been shown that a quasi-two-parameter (QTP) scheme is valid for α_S and α_η; i.e., these quantities may be expressed as functions only of the scaled excluded-volume parameter $\tilde{z}$ defined in the Yamakawa–Stockmayer–Shimada (YSS) theory[7-9] that takes account of the effects of excluded-volume and chain stiffness on the basis of the helical wormlike (HW) chain,[10,11] irrespective of the differences in chain stiffness, local chain conformation, and solvent condition. For a-PS,[6] it has then been found that α_H as a function of $\tilde{z}$ does not depend on solvent condition, indicating that the QTP scheme may be valid for α_H at least for a given polymer, but its validity has not yet been completely confirmed. Thus, in the present paper, we proceed to make a study of α_H along with α_η for poly(dimethylsiloxane) (PDMS) in order to confirm this.

As found in our previous study of the transport coefficients, i.e., the intrinsic viscosity $[\eta]_\Theta$ and translational diffusion coefficient D_Θ, of PDMS in the unperturbed (Θ) state,[12] their behavior is rather strange in the following two points: (1) The so-called *draining effect* exists in them and (2) $[\eta]$ becomes negative for oligomers with very small molecular weight M. We note that, to the best of our knowledge, the former is observed only for PDMS, while the latter is observed also for some other polymers, e.g., n-alkanes[13] and PIB,[14] and is not characteristic of PDMS. These points require some remarks.

First, if the draining effect exists in the unperturbed Gaussian chain, the total frictional force exerted by the chain on its surrounding solvent becomes smaller than that in the nondraining limit, so that the values of $[\eta]_\Theta$ and the hydrodynamic radius $R_{H,\Theta}$ ($\propto D_\Theta^{-1}$) determined from D_Θ must become smaller than the respective values in that limit.[15] Then the relations $[\eta]_\Theta \propto M^{1/2}$ and $R_{H,\Theta} \propto M^{1/2}$ hold only asymptotically in the limit of large M (in the nondraining limit) and the exponents of M become larger than $^1/_2$. In fact, $[\eta]_\Theta/M^{1/2}$ and $D_\Theta M^{1/2}$ for PDMS have been found to depend appreciably on M even for such large M that the ratio of the unperturbed mean-square radius of gyration $\langle S^2\rangle_\Theta$ to M is independent of M (see Figure 7 of ref 12). For the perturbed Gaussian chain, Freed and co-workers[16,17] have developed the (polymer) renormalization group theory which predicts that both α_η and α_H have smaller values than the nondraining-limiting values in the range of large (conventional) excluded-volume parameter z. This prediction implies that the QTP scheme breaks down; i.e., α_η and α_H as functions of $\tilde{z}$ depend on the degree of draining, so that their observed values plotted against $\tilde{z}$ do not give respective single-composite curves. Thus the validity of their theory may be examined by comparing values of α_η and α_H for PDMS as functions of $\tilde{z}$ with the single-composite curves previously obtained for a-PS,[4,5] PIB,[4] a-PMMA,[2] and i-PMMA,[3] for which no evidence of the draining effect has been found.[2,3]

Second, in the previous analysis of $[\eta]_\Theta$ for PIB[14] and PDMS[12] at Θ, which becomes negative for oligomers with very small M, we have converted the observed $[\eta]_\Theta$ to the "corrected intrinsic viscosity", which may be directly compared with the polymer classical hydrodynamic theories, by subtracting the contribution η^* (<0)

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

Table 1. Values of M_w, x_w, and M_w/M_n for Oligo- and Poly(dimethylsiloxane)s

sample	M_w	x_w	M_w/M_n
ODMS6	5.33×10^2	6	1.00
ODMS7	6.07×10^2	7	1.00
ODMS8	6.81×10^2	8	1.00
ODMS13	1.08×10^3	13.4	1.01
ODMS18[a]	1.39×10^3	17.5	1.01
ODMS22	1.73×10^3	22.2	1.04
ODMS35a	2.70×10^3	35.3	1.05
ODMS71	5.37×10^3	71.2	1.06
PDMS1a	8.97×10^3	120	1.05
PDMS2	2.21×10^4	297	1.08
PDMS3	3.19×10^4	429	1.08
PDMS6	5.90×10^4	794	1.08
PDMS20	1.83×10^5	2470	1.05
PDMS40	3.84×10^5	5180	1.06
PDMS70	6.46×10^5	8710	1.07
PDMS90	9.28×10^5	12500	1.07
PDMS110	1.12×10^6	15100	1.08

[a] M_ws of ODMS18 through PDMS110 except for ODMS22, ODMS35a, and PDMS1a had been determined from SLS in toluene at 25.0 °C.[12]

from specific interactions between solute and solvent molecules from the observed $[\eta]_\Theta$. The quantity η^* for a given polymer may depend on solvent, so that due attention must be paid to the difference in it between the Θ and good solvents used in order to determine α_η correctly, especially in the oligomer region.

For the determination of α_η and also of α_H, we must also take into consideration the solvent dependence of the hydrodynamic thickness of the polymer chain. Such dependence has already been found in the previous studies of α_η for a-PMMA[2] and i-PMMA,[3] although its consideration has not been necessary there since α_η for large M has been treated. In anticipation of the results, the hydrodynamic radius R_H for PDMS in the good solvent toluene used in the present study is somewhat larger than that in the Θ solvent bromocyclohexane used in the previous study even in the oligomer region where the excluded-volume effect on R_H may be neglected. This indicates that the hydrodynamic chain thickness depends appreciably on solvent also for PDMS. Thus, in the present work, we calculate both α_H and α_η correctly by taking into account also this dependence.

Experimental Section

Materials. More than half of the PDMS samples used in this work are the same as those used in the previous studies of the transport factors ϱ and Φ,[18] the mean-square electric dipole moment $\langle\mu^2\rangle$,[19] the intrinsic viscosity $[\eta]_\Theta$,[12] and the translational diffusion coefficient D_Θ,[12] i.e., the fractions separated from the commercial samples supplied by Toshiba Silicone Co., Ltd., named 5CS, TSF451-10, TSF451-100, TSF451-500, TSF451-50M, and TSE200A.

In the present work, seven new samples with weight-average molecular weight $M_w < 10^4$ designated as ODMS6, ODMS7, ODMS8, ODMS13, ODMS22, ODMS35a, and PDMS1a were prepared by separation also from the commercial samples of Toshiba Silicone Co., Ltd. Of these, the first three samples were separated by fractional distillation under reduced pressure from TSF451-5, the next three samples by preparative gel permeation chromatography (GPC) from TSF451-10 and the residue of the distillation of TSF451-5, and the last one by fractional precipitation from TSF451-100. All the samples have a methyl group at one end of the chain and a trimethylsilyl group at the other.

The values of 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 1. From GPC measurements, the new oligomer samples ODMS6, ODMS7, and ODMS8 were found to be completely monodisperse. Thus the values of their molecular weights were calculated from their chemical formulas. The values of M_w for the other new samples were determined from static light scattering (SLS) measurements in toluene at 25.0 °C, as described below. As seen from the values of M_w/M_n, all the samples are sufficiently narrow in molecular weight distribution.

The solvent toluene was purified according to a standard procedure prior to use.

Static Light Scattering. SLS measurements were carried out in toluene at 25.0 °C to determine M_w of the samples ODMS13, ODMS22, ODMS35a, and PDMS1a. A Fica 50 light-scattering photometer was used for all the measurements with vertically polarized incident light of wavelength 436 nm. For 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 $R_{\mathrm{Uu}}(90°)$ 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 5–7 different concentrations and at scattering angles ranging from 30 to 142.5°. All the data obtained were analyzed by the Berry square-root plot.[20] Corrections for the optical anisotropy were not made since its effect was negligibly small, as described previously.[12]

The most concentrated solution of each sample was prepared by continuous stirring at room temperature for ca. 1 day, preventing it from being exposed to light. It was 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 solutions. The densities of the solvent and solutions were measured with a pycnometer of the Lipkin–Davison type.

The value of the refractive index increment $\partial n/\partial c$ measured with a Shimadzu differential refractometer at 436 nm were -0.112_0, -0.108_9, -0.106_2, and -0.103_8 cm^3/g for ODMS13, ODMS22, ODMS35a, and PDMS1a, respectively, in toluene at 25.0 °C.

Dynamic Light Scattering. DLS measurements were carried out to determine the translational diffusion coefficient D for all the samples except for ODMSx with $x = 6$, 7, and 8 in toluene at 25.0 °C by the use of a Brookhaven Instruments Model BI-200SM light-scattering goniometer with vertically polarized incident light of 488 nm wavelength from a Spectra Physics Model 2020 argon ion laser equipped with a Model 583 temperature-stabilized etalon for single-frequency-mode operation. The photomultiplier tube used was EMI 9863B/350, the output from which was processed by a Brookhaven Instruments Model BI2030AT autocorrelator with 264 channels. (An electric shutter was attached to the original detector alignment in order to monitor the dark count automatically.[18]) The normalized autocorrelation function $g^{(2)}(t)$ of the scattered light intensity $I(t)$ at time t was measured at four or five concentrations and at scattering angles θ ranging from 15 to 50°.

From the data for $g^{(2)}(t)$ thus determined at finite concentrations c, we determined D at an infinitely long time[12] at infinite dilution for each sample in the same manner as that used in the previous studies.[6,12,18,21,22] The procedure is as follows. At small c, the plot of $(1/2)\ln[g^{(2)}(t) - 1]$ against t in general follows a straight line represented by

$$(1/2)\ln[g^{(2)}(t) - 1] = \mathrm{const} - At \tag{1}$$

with A the slope for such large t that all the internal motions of solute polymer chains have relaxed away.[12] With the slope A evaluated from the plot, we may determine the apparent diffusion coefficient $D^{(\mathrm{LS})}(c)$ at finite c from

$$D^{(\mathrm{LS})}(c) = \lim_{k\to 0} A/k^2 \tag{2}$$

where k is the magnitude of the scattering vector and is given by

$$k = (4\pi/\tilde{\lambda})\sin(\theta/2) \tag{3}$$

Table 2. Results of DLS Measurements on Oligo- and Poly(dimethylsiloxane)s in Toluene at 25.0 °C and in Bromocyclohexane at 29.5 °C (Θ)

	toluene, 25.0 °C			bromocyclohexane, 29.5 °C (Θ)[a]		
sample	$10^7 D$, cm²/s	$k_D^{(LS)}$, cm³/g	R_H, Å	$10^7 D_\Theta$, cm²/s	$k_D^{(LS)}$, cm³/g	$R_{H,\Theta}$, Å
ODMS13	60.2	−0.39	6.6			
ODMS18	51.7	−0.49	7.7			
ODMS22	46.0	−0.38	8.6			
ODMS35a	36.6	−0.19	10.8			
ODMS71	25.1	0.31	15.8	7.78	−2.46	14.5
PDMS1a	19.2	0.92	20.6			
PDMS2	11.7	3.20	33.9	3.89	−5.91	28.9
PDMS3	9.48	5.15	41.8	3.17	−6.83	35.5
PDMS6	6.69	9.72	59.2	2.34	−12.9	48.1
PDMS20	3.54	31.1	112	1.25	−20.8	90.0
PDMS40	2.34	52.1	169	0.850	−32.8	132
PDMS70	1.70	83.3	232	0.639	−50.0	176
PDMS90	1.40	108	283	0.536	−59.1	210
PDMS110	1.24	123	319	0.480	−68.8	234

[a] The results have been reproduced from ref 12.

with $\tilde{\lambda}$ the wavelength of the incident light in the solvent. At sufficiently small c, $D^{(LS)}(c)$ may be expanded as

$$D^{(LS)}(c) = D^{(LS)}(0)(1 + k_D^{(LS)}c + ...) \tag{4}$$

so that the desired $D = D(\infty)$ (at an infinitely long time) may be determined from extrapolation of $D^{(LS)}(c)$ to $c = 0$ as

$$D = D^{(LS)}(0) \tag{5}$$

The test solutions were prepared in the same manner as in the case of SLS measurements.

The values of the refractive index at 488 nm and the viscosity coefficient η_0 used are 1.505_6 and 0.5516 cP,[23] respectively, for pure toluene at 25.0 °C.

Viscosity. Viscosity measurements were carried out for all the samples except for ODMS18 in toluene at 25.0 °C. We used conventional capillary and four-bulb spiral capillary viscometers of the Ubbelohde type. In all the measurements, the flow time was measured to a precision of 0.1 s, keeping the difference between those of the solvent and solution larger than ca. 20 s. The test solutions were maintained at 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 in the same manner as in the case of SLS measurements. Density corrections were made in the calculations of c and also of the relative viscosity from the flow times of the solution and solvent.

Results

Translational Diffusion Coefficient. The values of D and $k_D^{(LS)}$ obtained for all the PDMS samples in toluene at 25.0 °C are given in Table 2 along with the values of R_H calculated from the defining equation

$$R_H = k_B T / 6\pi\eta_0 D \tag{6}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η_0 is the viscosity coefficient of the solvent. It also includes the previous results[12] for the same samples in bromocyclohexane at 29.5 °C (Θ).

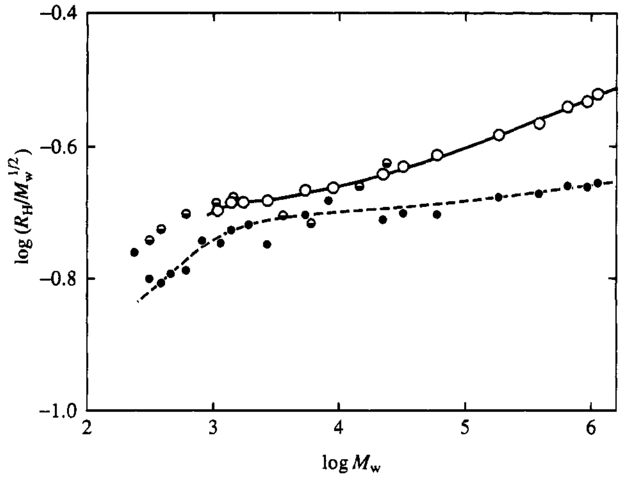

Figure 1. Double-logarithmic plots of $R_H/M_w^{1/2}$ (R_H in Å) against M_w for PDMS: (○) in toluene at 25.0 °C; (◒) in toluene at 25.0 °C (Edwards et al.);[24] (●) in bromocyclohexane at 29.5 °C (Θ) (previous data).[12] The solid and dashed curves connect our data points smoothly.

Figure 1 shows double-logarithmic plots of $R_H/M_w^{1/2}$ (R_H in Å) against M_w for PDMS in toluene at 25.0 °C (unfilled circles). It includes the results for $R_{H,\Theta}$ previously[12] obtained for PDMS in bromocyclohexane at Θ (filled circles) and also the literature data obtained by Edwards et al.[24] for PDMS in toluene at 25 °C (bottom-half-filled circles) by the classical boundary-spreading technique, for comparison. We note that the latter data are not the results at infinite dilution but at small finite concentrations (at ca. 1.3 wt%) and that they are plotted using the values of M_n determined by GPC instead of those of M_w. The solid and dashed curves connect our data points smoothly (the latter for the bromocyclohexane solutions).

It is seen that Edwards et al.'s data for $M_n \lesssim 1.5 \times 10^3$ are rather smoothly connected to the present data in toluene at 25.0 °C, although their data for higher M_n scatter remarkably. The values of R_H in toluene are larger than those of $R_{H,\Theta}$ in bromocyclohexane at Θ over the whole range of M_w examined. The difference is significant even in the oligomer region for $M_w \lesssim 10^3$, where the excluded-volume effect on α_H may be considered negligible. (This value 10^3 of M_w corresponds to the value ca. 1.8 of the reduced contour length λL, if the values of the HW model parameters given below are used, and this value of λL is comparable to or smaller than the critical value for the onset of the excluded-volume effects on α_S and α_η.[1-5]) This result implies that the hydrodynamic chain thickness (bead diameter) has different values in the two solvents toluene and bromocyclohexane. Thus we cannot calculate α_H correctly for PDMS in toluene by the use of the values of $R_{H,\Theta}$ in bromocyclohexane as the reference standards.

Intrinsic Viscosity. The results for the intrinsic viscosity $[\eta]$ and the Huggins coefficient k' for all the PDMS samples in toluene at 25.0 °C are summarized in Table 3 along with those previously[12] obtained for the same samples in bromocyclohexane at 29.5 °C (Θ). Figure 2 shows double-logarithmic plots of $[\eta]/M_w^{1/2}$ ($[\eta]$ in dL/g) against M_w with the present data for PDMS in toluene at 25.0 °C (unfilled circles) along with the previous ones[12] in bromocyclohexane at Θ (filled circles) and in methyl ethyl ketone (MEK) at 20.0 °C (Θ) (filled triangles). It also includes the literature data obtained by Zilliox et al.[25] for PDMS in toluene at 35.0 °C (top-half-filled circles), by Brzezinski et al.[26] in toluene at 25.0 °C (right-half-filled circles), by Dodgson and Semlyen[27] in toluene at 25.0 °C (bottom-half-filled circles), and by Barry[28] in toluene at 20.0 °C (left-half-filled circles), for comparison. The solid and dashed curves connect our data points smoothly (the latter for the bromocyclohexane and MEK solutions).

Table 3. Results of Viscometry on Oligo- and Poly(dimethylsiloxane)s in Toluene at 25.0 °C and in Bromocyclohexane at 29.5 °C (Θ)

	toluene, 25.0 °C		bromocyclohexane, 29.5 °C (Θ)[a]	
sample	$[\eta]$, dL/g	k'	$[\eta]_\Theta$, dL/g	k'
ODMS6	0.00757	2.06		
ODMS7	0.00907	1.45	0.0009	
ODMS8	0.0103	1.20		
ODMS13	0.0161	0.79		
ODMS22	0.0241	0.64		
ODMS35a	0.0324	0.62		
ODMS71	0.0538	0.43	0.0398	0.55
PDMS1a	0.0764	0.39		
PDMS2	0.140	0.36	0.0981	0.65
PDMS3	0.175	0.37	0.118	0.76
PDMS6	0.279	0.37	0.181	0.68
PDMS20	0.625	0.37	0.339	0.60
PDMS40	1.05	0.37	0.518	0.71
PDMS70	1.56	0.37	0.709	0.56
PDMS90	2.03	0.36	0.851	0.58
PDMS110	2.35	0.36	0.954	0.63

[a] The results have been reproduced from ref 12.

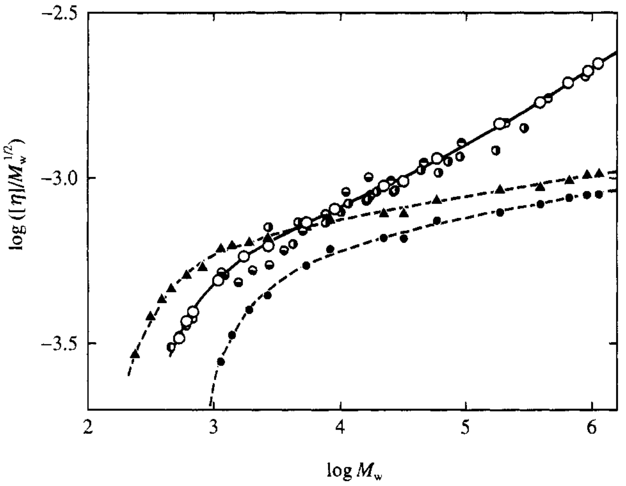

Figure 2. Double-logarithmic plots of $[\eta]/M_w^{1/2}$ ($[\eta]$ in dL/g) against M_w for PDMS: (○) in toluene at 25.0 °C; (●) in bromocyclohexane at 29.5 °C (Θ) (previous data);[12] (▲) in MEK at 20.0 °C (Θ) (previous data);[12] (◓) in toluene at 35.0 °C (Zilliox et al.);[25] (◑) in toluene at 25.0 °C (Brzezinski et al.);[26] (◒) in toluene at 25.0 °C (Dodgson and Semlyen);[27] (◐) in toluene at 20.0 °C (Barry).[28] The solid and dashed curves connect our data points smoothly.

It is seen that the data of Dodgson and Semlyen have the M_w dependence of $[\eta]$ remarkably different from the present and other literature results. (We note that Dodgson and Semlyen have not determined unequivocally the values of M_w since they have determined M_w by GPC.) The data of the other groups agree with each other fairly well except for those for the two highest-molecular-weight samples by Brzezinski et al., indicating that for PDMS in toluene $[\eta]$ does not appreciably depend on temperature. For $M_w \gtrsim 10^4$, the values of $[\eta]$ in toluene become progressively larger than those of $[\eta]_\Theta$ in bromocyclohexane and in MEK at Θ with increasing M_w because of the excluded-volume effect, while for lower M_w, they are intermediate between the values of $[\eta]_\Theta$ in the two Θ solvents. This suggests that the specific interaction between polymer and solvent molecules discussed before[12,14] has a significant effect also on $[\eta]$ in toluene, as observed previously[12] for $[\eta]_\Theta$ in bromocyclohexane and in MEK. Thus, for a correct determination of α_η, we must remove its contribution from the observed $[\eta]$, in addition to the consideration of the effect of the solvent dependence of the bead diameter found above for R_H, as mentioned in the Introduction.

Table 4. Values of $\langle S^2\rangle^{1/2}$ and α_S for Poly(dimethylsiloxane) in Toluene at 25.0 °C

sample	$\langle S^2\rangle^{1/2}$, Å[a]	α_S
PDMS20	165	(1.29)[b]
PDMS40	250	1.36
PDMS70	338	1.40
PDMS90	411	1.43
PDMS110	465	1.47

[a] The values of $\langle S^2\rangle^{1/2}$ have been determined from the SLS data which had already been obtained in ref 12. [b] The value of α_S for PDMS20 has been calculated with the value 0.0888 Å^2 of $(\langle S^2\rangle_\Theta/M_w)_\infty$.[18]

Discussion

Gyration-Radius Expansion Factor α_S. Before evaluating α_H and α_η, we first determine values of α_S for several high-molecular-weight PDMS samples in toluene at 25.0 °C and also that of the reduced excluded-volume strength λB from them. In Table 4 are given the values of the root-mean-square radius of gyration $\langle S^2\rangle^{1/2}$ for the five samples determined from the SLS data which had already been obtained in ref 12. A remark must then be made on the determination of α_S from them. In the previous studies of α_S,[1-3] we gave particular attention to its correct determination by choosing properly a pair of good and Θ solvents so that the values of the unperturbed mean-square radius of gyration $\langle S^2\rangle_0$ in that good solvent may coincide with those of $\langle S^2\rangle_\Theta$ in the Θ solvent taken as reference standards. The coincidence of the former with the latter was then confirmed by comparing the values of $\langle S^2\rangle$ in the good and Θ solvents in the oligomer region where the excluded-volume effect may be negligible. For PDMS, however, the same procedure cannot be applied, since small-angle X-ray scattering measurements are not feasible for a determination of $\langle S^2\rangle$ of the oligomer samples. Thus, in the present work, we calculate α_S for the above samples in toluene at 25.0 °C by using the values of $\langle S^2\rangle_\Theta^{1/2}$ previously[18] obtained for the same samples in bromocyclohexane at Θ as the reference standards, assuming that the relation $\langle S^2\rangle_0 = \langle S^2\rangle_\Theta$ holds for this pair of good and Θ solvents. The values of α_S thus obtained are also listed in Table 4.

Corresponding to the calculation of α_S, we calculate α_η^3 (tentatively) for the same samples in toluene at 25.0 °C with the values of $[\eta]$ and those of $[\eta]_\Theta$ in bromocyclohexane at Θ given in Table 3 (in which the latter data have been reproduced from ref 12), considering the fact that the above-mentioned effects of the specific interaction between polymer and solvent molecules and of the solvent dependence of the bead diameter on α_η may become negligibly small for such large M_w. (A more rigorous calculation of α_η which takes account of these effects is given below.)

Figure 3 shows double-logarithmic plots of α_η^3 against α_S^3 with the results thus obtained for PDMS in toluene at 25.0 °C (unfilled circles). It includes the previous data for a-PS in toluene at 15.0 °C (bottom-half-filled circles),[4] in benzene at 25.0 °C (right-half-filled circles),[5] in MEK at 35.0 °C (left-half-filled circles),[5] in 4-*tert*-butyltoluene at 50.0 °C (top-half-filled circles),[6] and also the literature data[29] for a-PS in benzene at 25.0 °C (right-half-filled circles with pip) and in cyclohexane at 36.0−55.0 °C (filled circles), for comparison. The solid curve connects the data points for a-PS smoothly.

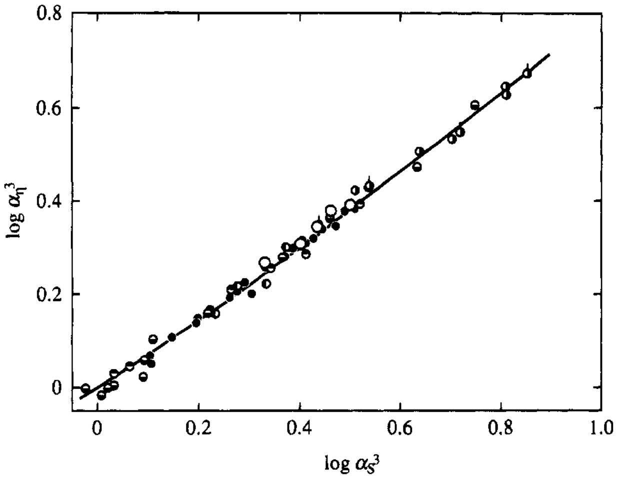

Figure 3. Double-logarithmic plots of α_η^3 against α_S^3: (○) for PDMS in toluene at 25.0 °C; (◒) for a-PS in toluene at 15.0 °C (previous data);[4] (◑, no pip) for a-PS in benzene at 25.0 °C (previous data);[5] (◑, pip up) for a-PS in benzene at 25.0 °C (Miyaki);[29] (◐) for a-PS in MEK at 35.0 °C (previous data);[5] (◓) for a-PS in 4-*tert*-butyltoluene at 50.0 °C (previous data);[6] (●) for a-PS in cyclohexane at 36.0–55.0 °C (Miyaki).[29] The solid curve connects the data points for a-PS smoothly.

It is seen that the present data for PDMS are consistent with those for a-PS (the solid curve) within experimental error. This indicates that the above assumption and neglect of the two effects are valid, so that α_S and α_η may be correctly determined for these high-molecular-weight samples. Recall that it has already been established[2–6] that if the values of α_S and α_η are correctly calculated, the plots as in Figure 3 form a single-composite curve independent of a polymer–solvent system. The results in Figure 3 also indicate that there is no draining effect on α_η for PDMS as well as for the other polymers a-PS, PIB, and a- and i-PMMAs[2–6] despite the fact that such an effect has been found for PDMS in the unperturbed state.[12] Note that this effect must cause a progressive decrease in α_η from the value corresponding to the above single-composite curve with increasing α_S (or M_w), if any, as mentioned in the Introduction.

Now we determine the value of λB for PDMS in toluene at 25.0 °C from α_S. For this purpose, the values of α_S^2 are double-logarithmically plotted against x_w in Figure 4 with the data given in Table 4. The solid curve represents the best-fit YSS theory values calculated from the Domb–Barrett equation[30] for α_S^2 with $\tilde{z}$ in place of z, i.e.,

$$\alpha_S^2 = [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15} \times [0.933 + 0.067\exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \quad (7)$$

Recall that for the HW chain of total contour length L, $\tilde{z}$ is defined by

$$\tilde{z} = (3/4)K(\lambda L)z \quad (8)$$

and that z is now given by

$$z = (3/2\pi)^{3/2}(\lambda B)(\lambda L)^{1/2} \quad (9)$$

where

$$B = \beta/a^2 c_\infty^{3/2} \quad (10)$$

with

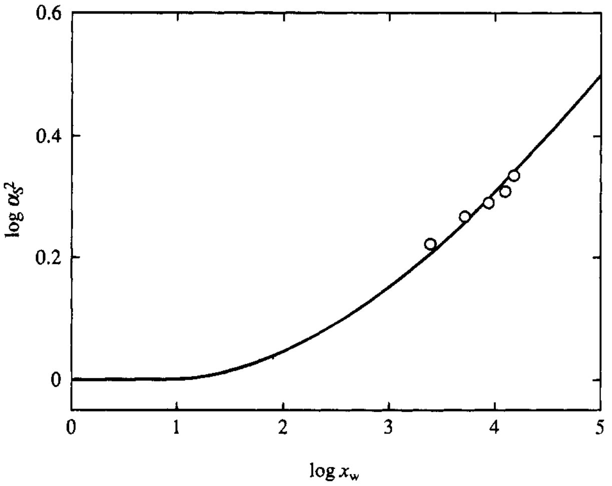

Figure 4. Double-logarithmic plots of α_S^2 against x_w for PDMS in toluene at 25.0 °C. The solid curve represents the best-fit YSS theory values (see the text).

$$c_\infty = \lim_{\lambda L \to \infty}(6\lambda\langle S^2\rangle_0/L) = \frac{4 + (\lambda^{-1}\tau_0)^2}{4 + (\lambda^{-1}\kappa_0)^2 + (\lambda^{-1}\tau_0)^2} \quad (11)$$

Here, λ^{-1} is the static stiffness parameter of the HW chain, κ_0 and τ_0 are the differential-geometrical curvature and torsion, respectively, of its characteristic helix taken at the minimum zero of its elastic energy, and β is the binary-cluster integral between beads with a their spacing. In eq 8, the coefficient $K(L)$ is given by

$$K(L) = \frac{4}{3} - 2.711L^{-1/2} + \frac{7}{6}L^{-1} \quad \text{for } L > 6$$
$$= L^{-1/2}\exp(-6.611L^{-1} + 0.9198 + 0.03516L) \quad \text{for } L \le 6 \quad (12)$$

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

$$L = xM_0/M_L \quad (13)$$

where M_0 is the molecular weight of the repeat unit of a given real chain and M_L (=M/L) is the shift factor as defined as the molecular weight per unit contour length. We here adopt the values of λ^{-1} and M_L previously[12] determined from $[\eta]_\Theta$, i.e., λ^{-1} = 25.5 Å and M_L = 20.6 Å^{-1}. The value of λB thus determined from the curve fitting in Figure 4 is 0.14.

Evaluation of the Hydrodynamic- and Viscosity-Radius Expansion Factors. As mentioned above, we cannot use the values of $R_{H,\Theta}$ in bromocyclohexane at Θ as reference standards to calculate α_H because of the solvent dependence of the bead diameter of the PDMS chain. Thus we must obtain the values of $R_{H,0}$ for the unperturbed PDMS chain in toluene at 25.0 °C by circumventing this difficulty. For this purpose, we resort to the HW theory of the translational diffusion coefficient D_0 for the unperturbed chain. For the HW touched-bead model with the total number N (=L/d_b) of beads with d_b the bead diameter, the quantity $\eta_0 D_0 M_w/k_B T$ may be written in the form[22]

$$\eta_0 D_0 M_w/k_B T = (M_L/3\pi)f_D(\lambda L;\lambda^{-1}\kappa_0,\lambda^{-1}\tau_0,\lambda d_b) \quad (14)$$

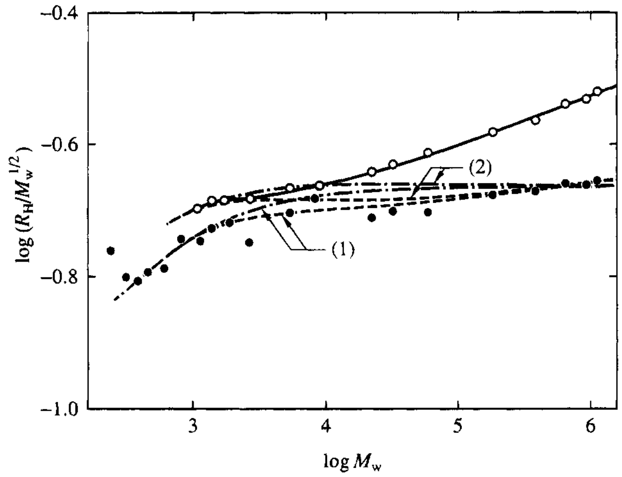

Figure 5. Double-logarithmic plots of $R_H/M_w^{1/2}$ (R_H in Å) against M_w for PDMS. The symbols have the same meaning as those in Figure 1. The solid curve and the dashed curve (1) connect the data points smoothly (the latter for the bromocyclohexane solutions). The chain curves (1) and (2) represent the HW theory values of $R_{H,0}$ in bromocyclohexane and in toluene, respectively. The dashed curve (2) represents the values of $R_{H,0}$ in toluene used as reference standards to calculate α_H (see the text).

where the function f_D is given by eq 6 of ref 22 and may be evaluated numerically by the use of the interpolation function for the mean reciprocal end-to-end distance of the chain as given in the Appendix of ref 31. It satisfies the relation

$$\lim_{\lambda L\to\infty} f_D(\lambda L)/(\lambda L)^{1/2} = (6^{1/2}/2)c_\infty^{-1/2}\varrho_\infty \qquad (15)$$

with ϱ_∞ (=1.505) being the coil-limiting value of the ratio ϱ of $\langle S^2\rangle_0^{1/2}$ to $R_{H,0}$.

Figure 5 shows double-logarithmic plots of $R_H/M_w^{1/2}$ (R_H in Å) against M_w. The present and previous data for PDMS in toluene at 25.0 °C (unfilled circles) and in bromocyclohexane at Θ (filled circles), respectively, are reproduced from Figure 1, and the solid curve and the dashed curve (1) are the same as those in Figure 1. The chain curve (1) represents the best-fit HW theory values for $R_{H,\Theta}$ in bromocyclohexane calculated from eqs 6 and 14 with $\lambda^{-1}\kappa_0 = 2.6$, $\lambda^{-1}\tau_0 = 0$, $\lambda^{-1} = 31.0$ Å, $M_L = 18.0$ Å^{-1}, and $\lambda d_b = 0.045$. Here, the same values as those previously[12] determined from D_Θ have been used for the four basic HW model parameters $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, λ^{-1}, and M_L, but the value of λd_b has been changed from the previous one, 0.05, to attain better agreement between theory and experiment in the oligomer region. The chain curve (2) represents the HW theory values for $R_{H,0}$ calculated also from eqs 6 and 14 with the same values of the basic HW model parameters but with the value 0.070 of λd_b. This value of λd_b has been determined so that the theoretical curve may fit the data points for R_H for the three lowest-molecular-weight samples in toluene, for which the excluded-volume effect may be negligible. The values of d_b obtained from the above values of λd_b are 2.2 and 1.4 Å for PDMS in toluene and in bromocyclohexane, respectively. The former is ca. 57% larger than the latter but still small compared to the values for other flexible polymers.

As mentioned above, the values of $\langle S^2\rangle_0$ and therefore of the basic HW model parameters of the PDMS chain in the two solvents may be considered to agree with each other, so that only the values of the hydrodynamic chain thickness represented by d_b must be different in the two solvents (if there were no excluded-volume effect in toluene). Thus the HW theory values represented by the chain curve (2) itself may be regarded as the values for $R_{H,0}$ in toluene if the chain curve (1) reproduces well the dashed curve (1). Unfortunately, however, the chain curve (1) cannot completely reproduce the dashed curve (1) in the intermediate range of M_w displayed, as stated previously.[12] Then, considering that the HW theory may give the correct ratio of $R_{H,0}$ in toluene to $R_{H,\Theta}$ in bromocyclohexane, we regard the former as having the value equal to the interpolated (smoothed) one of the latter [the dashed curve (1)] multiplied by the ratio of the HW theoretical value in toluene [the chain curve (2)] to that in bromocyclohexane [the chain curve (1)]. The values thus obtained for $R_{H,0}$ are represented by the dashed curve (2) in the figure.

Table 5. Values of α_H for Oligo- and Poly(dimethylsiloxane)s in Toluene at 25.0 °C

sample	α_H	sample	α_H
ODMS13	1.00	PDMS3	1.13
ODMS18	1.01	PDMS6	1.17
ODMS22	1.01	PDMS20	1.23
ODMS35a	1.00	PDMS40	1.27
ODMS71	1.04	PDMS70	1.33
PDMS1a	1.05	PDMS90	1.34
PDMS2	1.10	PDMS110	1.36

In Table 5 are given the values of $\alpha_H = R_H/R_{H,0}$ determined for PDMS in toluene at 25.0 °C from the values of R_H in Table 2 and those of $R_{H,0}$ corresponding to the dashed curve (2) in Figure 5. We note that the dashed curve (2) fits very well the data points for the five highest-molecular-weight samples in bromocyclohexane at Θ and that the values of α_H for them in Table 5 then agree with those calculated with the values of $R_{H,\Theta}$ in Table 2 within 1%.

Now we proceed to evaluate α_η. We first estimate values of η^* for PDMS in bromocyclohexane at Θ and in toluene at 25.0 °C and then evaluate unperturbed values $([\eta] - \eta^*)_0$ in toluene from the values of $([\eta] - \eta^*)_\Theta$ in bromocyclohexane at Θ along the same line as in the above evaluation of $R_{H,0}$ on the basis of the corresponding HW theory.[32]

In the previous study of $[\eta]_\Theta$ of PDMS,[12] η^* in bromocyclohexane at Θ was estimated to be −0.0115 dL/g, assuming that the hydrodynamic thickness of the PDMS chain has the same value in the two Θ solvents bromocyclohexane and MEK [at 20.0 °C (Θ)] and that η^* vanishes in MEK. In the present study, we estimate η^* in toluene and also reestimate it in bromocyclohexane, taking account of the theoretical requirement that the values of the hydrodynamic chain thickness determined from D_Θ and $[\eta]_\Theta$ in the same solvent must be the same. That is, the values of η^* for PDMS in the two solvents are determined so that the values of $[\eta] - \eta^*$ for the oligomer samples may coincide with the HW (classical hydrodynamic) theoretical values $[\eta]_C$ calculated with $d_b = 1.4$ and 2.2 Å in bromocyclohexane and in toluene, respectively.

For the HW touched-bead model, $[\eta]_C$ may be written in the form[32]

$$[\eta]_C = (1/\lambda^2 M_L) f_\eta(\lambda L; \lambda^{-1}\kappa_0, \lambda^{-1}\tau_0, \lambda d_b) \qquad (16)$$

where the function f_η is defined by

$$f_\eta(\lambda L) = \lambda^{-1} M_L [\bar{\eta}]_C \qquad (17)$$

with $[\bar{\eta}]_C$ being the $[\eta]_C$ measured in units of $(\lambda^{-1})^3$ and

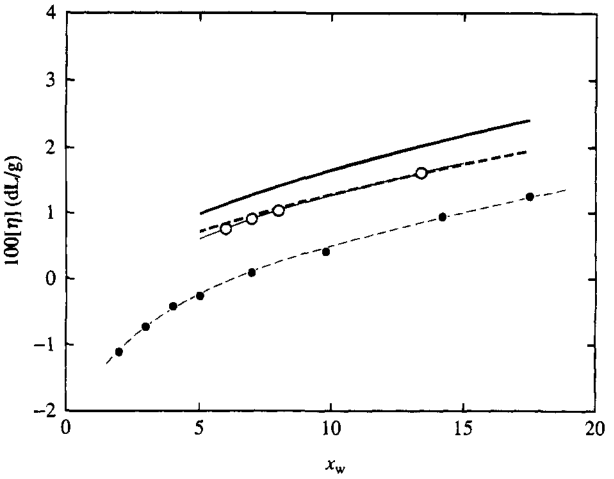

Figure 6. Plots of $[\eta]$ against x_w for PDMS oligomers. The symbols have the same meaning as those in Figure 1. The light solid and dashed curves connect the data points, unfilled and filled circles, respectively. The heavy solid and dashed curves represent the HW theory values of $[\eta]_C$ for $d_b = 2.2$ and 1.4 Å, respectively (see the text).

being given by eq 15 with eqs 17 and 27 of ref 32. It satisfies the following asymptotic relation

$$\lim_{\lambda L \to \infty} f_\eta(\lambda L)/(\lambda L)^{1/2} = c_\infty^{3/2}\Phi_\infty \tag{18}$$

with Φ_∞ (=2.870 × 10^{23} mol^{-1}) being the coil-limiting value of the Flory–Fox factor Φ.

Figure 6 shows plots of $[\eta]$ against x_w. The unfilled circles represent the present experimental values determined for the samples ODMSx with x = 6, 7, 8, and 13 in toluene, the filled circles represent the values previously[12] determined for the samples ODMSx with x = 2, 3, 4, 5, 7, 10, 14, and 18 in bromocyclohexane at Θ, and the light solid and dashed curves connect the respective data points smoothly. (Note that the samples ODMSx with x = 2, 3, 4, 5, 10, 14, and 18 have not been used in the present study.) The heavy solid and dashed curves represent the HW theoretical values calculated from eq 16 with $\lambda^{-1}\kappa_0 = 2.6$, $\lambda^{-1}\tau_0 = 0$, $\lambda^{-1} = 25.5$ Å, and $M_L = 20.6$ Å^{-1} and with $\lambda d_b = 0.085$ and 0.055 (d_b = 2.2 and 1.4 Å) for the former and latter, respectively. We note that in these calculations we have used the values of λ^{-1} and M_L previously[12] determined from $[\eta]_\Theta$ but not from D_Θ. Then, for PDMS in toluene, η^* is found to be −0.0038 dL/g as an average of the differences between the four values of $[\eta]$ in toluene (unfilled circles) and the corresponding theoretical values (corresponding points on the heavy solid curve). As for PDMS in bromocyclohexane, it is found to be −0.0078 dL/g as an average of the differences between the four values of $[\eta]$ for the samples ODMSx with x = 7, 10, 14, and 18 in bromocyclohexane (the right four filled circles) and the corresponding theoretical values (corresponding points on the heavy dashed curves). This value of $|\eta^*|$ in bromocyclohexane is somewhat smaller than the previous value mentioned above.

The values of $([\eta] - \eta^*)/M_w^{1/2}$ evaluated by the use of those of η^* thus determined for PDMS in the two solvents are double-logarithmically plotted against M_w in Figure 7. The unfilled and filled circles represent the values in toluene 25.0 °C and in bromocyclohexane at Θ, respectively, and the solid curve and the dashed curve (1) connect them smoothly, respectively. The difference between the values for the oligomers in the two solvents is due to that in the hydrodynamic chain thickness. We evaluate $([\eta] - \eta^*)_0$ in toluene by adopting the same maneuver as in the above evaluation of $R_{H,0}$, i.e., by setting its value equal to the interpolated (smoothed) value of $([\eta] - \eta^*)_\Theta$ in bromocyclohexane [the dashed curve (1)] multiplied by the ratio of the HW theoretical value in toluene [the heavy solid curve in Figure 6] to that in bromocyclohexane [the heavy dashed curve in Figure 6]. We note that the HW theory cannot give completely exact values for $([\eta] - \eta^*)_0$ nor $R_{H,0}$ in toluene. The values of $([\eta] - \eta^*)_0/M_w^{1/2}$ thus determined are represented by the dashed curve (2) in Figure 7.

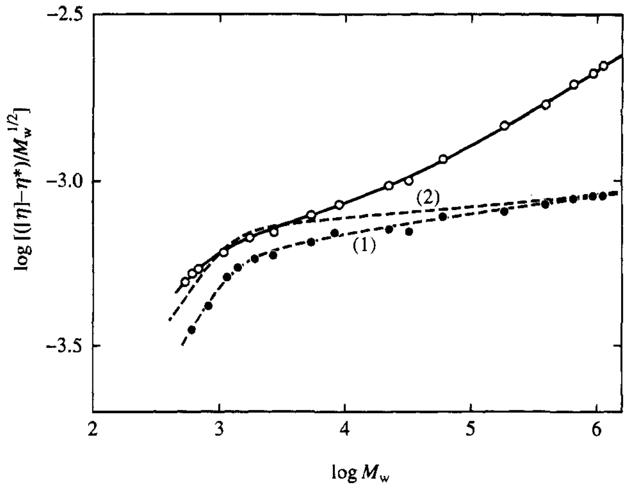

Figure 7. Double-logarithmic plots of $([\eta] - \eta^*)/M_w^{1/2}$ against M_w for PDMS. The symbols have the same meaning as those in Figure 1. The solid curve and the dashed curve (1) connect the data points smoothly (the latter for the bromocyclohexane solutions). The dashed curve (2) represents the values of $([\eta] - \eta^*)_0/M_w^{1/2}$ in toluene used as reference standards to calculate α_η^3 (see the text).

Table 6. Values of α_η^3 for Oligo- and Poly(dimethylsiloxane)s in Toluene at 25.0 °C

sample	α_η^3	sample	α_η^3
ODMS13	0.98	PDMS6	1.42
ODMS22	0.96	PDMS20	1.72
ODMS35a	0.96	PDMS40	1.94
ODMS71	1.04	PDMS70	2.18
PDMS1a	1.10	PDMS90	2.33
PDMS2	1.22	PDMS110	2.43
PDMS3	1.25		

In Table 6 are given the values of α_η^3 determined for PDMS in toluene at 25.0 °C as the ratio of $[\eta] - \eta^*$ with the $[\eta]$ values given in Table 3 and $\eta^* = -0.0038$ dL/g to $([\eta] - \eta^*)_0$ with its values given by the dashed curve (2) in Figure 7. We note that the dashed curve (2) fits the data points fairly well for the four highest-molecular-weight samples in bromocyclohexane at Θ and that the values of α_η^3 for them in Table 6 then agree with those calculated with the values of $[\eta]_\Theta$ in Table 3 within 5%.

Hydrodynamic-Radius Expansion Factor α_H. Of the values of α_H given in Table 5, those for the five highest-molecular-weight samples are double-logarithmically plotted against α_S (unfilled circles) in Figure 8. It also includes the previous data[6] for a-PS in toluene at 15.0 °C (bottom-half-filled circles) and in 4-*tert*-butyltoluene at 50.0 °C (top-half-filled circles), for comparison. The dotted curve represents the values calculated from the Barrett equation[33] for α_H with $\tilde{z}$ in place of z,

$$\alpha_H = (1 + 6.09\tilde{z} + 3.59\tilde{z}^2)^{0.1} \tag{19}$$

and eq 7 for α_S^2. Very recently, Yamakawa and

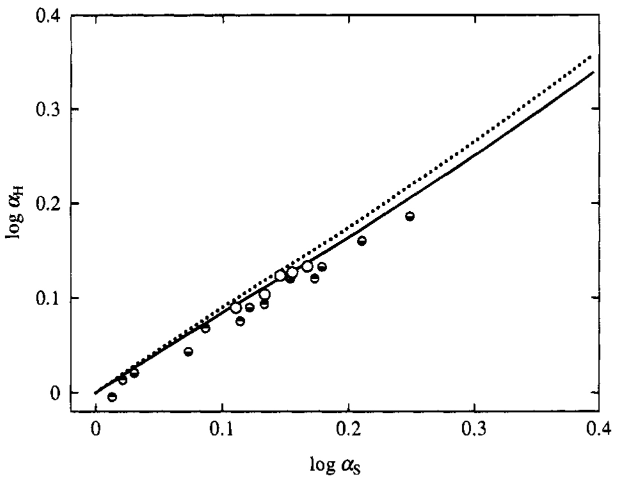

Figure 8. Double-logarithmic plots of α_H against α_S: (○) for PDMS in toluene at 25.0 °C; (◒) for a-PS in toluene at 15.0 °C (previous data);[6] (◓) for a-PS in 4-*tert*-butyltoluene at 50.0 °C (previous data).[6] The solid and dotted curves represent the values calculated from eqs 20 and 19, respectively (see the text).

Yoshizaki[34] have evaluated theoretically the possible effect of fluctuating hydrodynamic interaction on α_H on the basis of the Gaussian chain. Equation 19 may then be corrected as

$$\alpha_H = \alpha_H^{(Z)} f_H \tag{20}$$

where $\alpha_H^{(Z)}$ is given by eq 19, and f_H is defined by

$$f_H = \frac{1 - \delta_{1,0}(1)}{1 - \delta_{1,0}(\alpha_S^{-1})} \tag{21}$$

with

$$\delta_{1,0}(x) = 0.12x^{0.43} \qquad (0 < x < 1) \tag{22}$$

Note that in eq 21, the ratio of the bead diameter to the effective bond length (for the Gaussian chain) has been taken as unity as in the previous papers.[6,34] The solid curve in Figure 8 represents the values calculated from eq 20 with eqs 19 (for $\alpha_H^{(Z)}$), 21, and 22 and with eq 7 for α_S.

It is seen that the present data points for PDMS in toluene form a single-composite curve together with the previous ones for a-PS in toluene and in 4-*tert*-butyltoluene. Thus we may conclude that α_H becomes a function only of α_S irrespective of the differences in polymer species and solvent condition. This implies that there is no draining effect also on α_H, as anticipated from the same conclusion for α_η derived above. However, all the data points are located below the dotted curve over the whole range of α_S (or M_w) examined, as already pointed out previously.[6] The disagreement between theory and experiment is diminished by taking account of the effect of fluctuating hydrodynamic interaction on α_H, as shown by the solid curve, which shifts progressively downward from the dotted one with increasing α_S and approaches the data points.

Figure 9 shows double-logarithmic plots of α_H against $\tilde{z}$ for PDMS in toluene at 25.0 °C (unfilled circles) with the data in Table 5. Here, the values of $\tilde{z}$ have been calculated with the values of λ^{-1} and M_L previously[12] determined from $[\eta]_\Theta$ and that of λB determined above from α_S. This figure includes the same data for a-PS (half-filled circles) as those in Figure 8, for comparison. The light solid curve represents the values of α_H calculated from eq 19, and the heavy solid curve represents those calculated from eq 20 with eqs 7, 19 (for $\alpha_H^{(Z)}$), 21, and 22. On the other hand, the dashed curve represents the values of α_η^3 calculated from the Barrett equation[35] with $\tilde{z}$ in place of z,

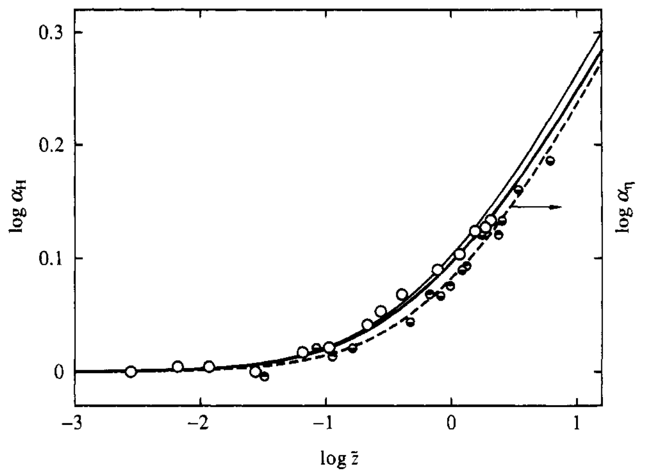

Figure 9. Double-logarithmic plots of α_H against $\tilde{z}$. The symbols have the same meaning as those in Figure 8. The heavy and light solid curves represent the values calculated from eqs 20 and 19, respectively (see the text). The dashed curve represents the values of α_η calculated from eq 23.

$$\alpha_\eta^3 = (1 + 3.8\tilde{z} + 1.9\tilde{z}^2)^{0.3} \tag{23}$$

All the data points for PDMS and a-PS in Figure 9 seem to form a single-composite curve irrespective of the differences in polymer species and solvent condition within experimental error, indicating that α_H becomes a function only of $\tilde{z}$, or, in other words, the QTP scheme may be valid for α_H as well as for α_S and α_η.[1-5] Strictly, the present data points for PDMS are located somewhat above the previous ones for a-PS for $0.2 \lesssim \tilde{z} \lesssim 1$. However, this discrepancy need not be considered very significant, since the ambiguity in the values of α_H for PDMS is somewhat larger than that for a-PS owing to the rather complicated procedure of determining the present values.

As anticipated from the results in Figure 8, the light solid curve deviates upward from the data points for large $\tilde{z}$. However, the heavy solid curve is seen to become closer to the data points with increasing $\tilde{z}$. As discussed previously,[6] this result indicates that the use of the Barrett equation for α_H itself is inappropriate. As also found in the previous work,[6] the present data points for PDMS along with the previous ones for a-PS seem to follow the dashed curve which represents the relation between log α_η and log $\tilde{z}$ except in the intermediate range of M_w studied for the former.

Viscosity-Radius Expansion Factor α_η. The values of α_η^3 for PDMS in toluene in Table 6 are double-logarithmically plotted against $\tilde{z}$ in Figure 10 (unfilled circles) with the same values of $\tilde{z}$ as those in Figure 9. It also includes the previous results[4-6] for a-PS in toluene at 15.0 °C (bottom-half-filled circles), in benzene at 25.0 °C (right-half-filled circles with and without pip), in MEK at 35.0 °C (left-half-filled circles), and in 4-*tert*-butyltoluene at 50.0 °C (top-half-filled circles), for comparison. The solid curve represents the theoretical values calculated from eq 23.

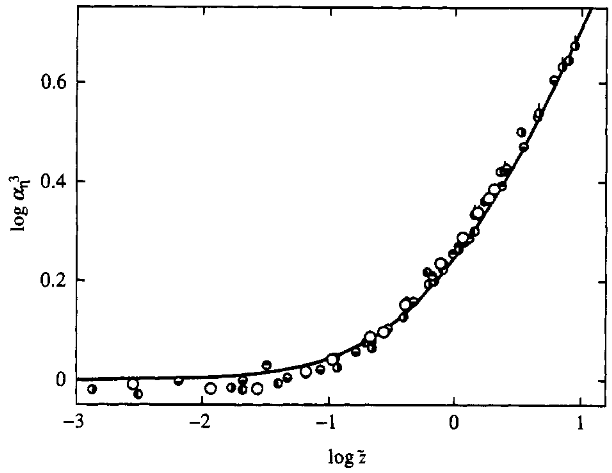

Figure 10. Double-logarithmic plots of α_η^3 against $\tilde{z}$. The symbols have the same meaning as those in Figure 3. The solid curve represents the values calculated from eq 23.

It is seen that the present data points for PDMS together with the previous ones for a-PS form a single-composite curve. This result reconfirms that α_η is a function only of $\tilde{z}$, or, in other words, the QTP scheme is valid for α_η, irrespective of the differences in polymer species and solvent condition (excluded-volume strength) and also that there is no draining effect on α_η.

Concluding Remarks

In this work, we have investigated the hydrodynamic- and viscosity-radius expansion factors α_H and α_η as functions of $\tilde{z}$ (and also of α_S) for PDMS in toluene at 25.0 °C. It has been found that R_H in this solvent is larger than $R_{H,\Theta}$ in bromocyclohexane at Θ even in the oligomer region where the excluded-volume effect may be negligible, indicating that the bead diameter d_b of the PDMS chain depends appreciably on solvent. In addition, the specific interaction between polymer and solvent molecules has been found to have a significant effect on $[\eta]$ in toluene, as observed previously[12] in bromocyclohexane. These facts make it impossible to evaluate α_H and α_η for PDMS in toluene by the use of the values of $R_{H,\Theta}$ and $[\eta]_\Theta$ directly measured in the Θ solvent taken as the reference standards. Thus, in the present paper, we have estimated $R_{H,0}$ and $[\eta]_0$ for the unperturbed PDMS chain in toluene at 25.0 °C as functions of M_w by multiplying the values of $R_{H,\Theta}$ and $[\eta]_\Theta$ in bromocyclohexane at Θ by the proper factors that represent the effects of the solvent dependence of d_b and may be calculated by the use of the HW theory. Then we have obtained the correct values of α_H and α_η from the results for R_H directly determined and those for $[\eta]$ corrected for the specific interaction above.

It has been shown that the present data points for α_H and α_η as functions of $\tilde{z}$ for PDMS form single-composite curves together with the respective data previously[4-6] obtained for a-PS over the whole range of M_w studied. This implies that the QTP scheme may be valid for α_H as well as for α_η irrespective of the differences in polymer species and solvent condition. The present results clearly show that there is no draining effect on α_H and α_η for PDMS as in the case of other flexible polymers studied so far,[2-5] despite the fact that the draining effect is significant for PDMS in the unperturbed state.[12] We note that the ambiguity in the values of α_H and α_η determined for PDMS in this work is somewhat larger than that for the other polymers studied so far[2-6] because of the rather complicated procedure of determining them. For sufficiently large M_w, however, it is still so small that the above (previous) conclusion may be unaltered.

The present results for PDMS give the values of α_H smaller than those calculated from the Barrett equation,[33] confirming the previous results[6] for a-PS. It has been found that the Yamakawa–Yoshizaki theory[34] which takes account of the possible effect of fluctuating hydrodynamic interaction on α_H may explain the observed results semiquantitatively.

References and Notes

(1) Abe, F.; Einaga, Y.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1993**, *26*, 1884.
(2) Abe, F.; Horita, K.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1994**, *27*, 725.
(3) Kamijo, M.; Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1995**, *28*, 1095.
(4) Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1993**, *26*, 1891.
(5) Horita, K.; Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1993**, *26*, 5067.
(6) Arai, T.; Abe, F.; Yoshizaki, T.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1995**, *28*, 3609.
(7) Yamakawa, H.; Stockmayer, W. H. *J. Chem. Phys.* **1972**, *57*, 2843.
(8) Yamakawa, H.; Shimada, J. *J. Chem. Phys.* **1985**, *83*, 2607.
(9) Shimada, J.; Yamakawa, H. *J. Chem. Phys.* **1986**, *85*, 591.
(10) Yamakawa, H. *Annu. Rev. Phys. Chem.* **1984**, *35*, 23.
(11) Yamakawa, H. In *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*; Nagasawa, M., Ed.; Elsevier: Amsterdam, 1988; p 21.
(12) Yamada, T.; Koyama, H.; Yoshizaki, T.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1993**, *26*, 2566.
(13) Rempp, P. *J. Polym. Sci.* **1957**, *23*, 83.
(14) Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1991**, *24*, 4423.
(15) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971; Chapter 6.
(16) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley-Interscience: New York, 1987.
(17) Douglas, J. F.; Freed, K. F. *Macromolecules* **1994**, *27*, 6088.
(18) Konishi, T.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1991**, *24*, 5614.
(19) Yamada, T.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1992**, *25*, 1487.
(20) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.
(21) Dehara, K.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1993**, *26*, 5137.
(22) Yamada, T.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1992**, *25*, 377.
(23) Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. H.; Pimentel, G. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*; Carnegie Press: Pittsburgh, 1953.
(24) Edwards, C. J. C.; Stepto, R. F. T.; Semlyen, J. A. *Polymer* **1980**, *21*, 781.
(25) Zilliox, J. G.; Roovers, J. E. L.; Bywater, S. *Macromolecules* **1975**, *8*, 573.
(26) Brzezinski, J.; Czlonkowska-Kohutnicka, Z.; Czarnecka, B.; Kornaś-Calka, A. *Eur. Polym. J.* **1973**, *9*, 733.
(27) Dodgson, K.; Semlyen, J. A. *Polymer* **1977**, *18*, 1265.
(28) Barry, A. J. *J. Appl. Phys.* **1946**, *17*, 1020.
(29) Miyaki, Y. Ph.D. Thesis, Osaka University, 1981.
(30) Domb, C.; Barrett, A. J. *Polymer* **1976**, *17*, 179.
(31) Yamakawa, H.; Yoshizaki, T. *J. Chem. Phys.* **1983**, *78*, 572.
(32) Yoshizaki, T.; Nitta, T.; Yamakawa, H. *Macromolecules* **1988**, *21*, 165.
(33) Barrett, A. J. *Macromolecules* **1984**, *17*, 1561.
(34) Yamakawa, H.; Yoshizaki, T. *Macromolecules* **1995**, *28*, 3604.
(35) Barrett, A. J. *Macromolecules* **1984**, *17*, 1566.

MA950182V