Transport Coefficients of Oligo- and Poly(dimethylsiloxane)s in Dilute Solutions. The Draining Effect

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ABSTRACT: The translational diffusion coefficient D and intrinsic viscosity $[\eta]$ of oligo- and poly(dimethylsiloxane)s (PDMS) were examined, especially regarding their molecular-weight dependence, in the range of weight-average molecular weight M_w from 2.37×10^2 to 1.12×10^6 in bromocyclohexane at 29.5 °C (Θ). A study was also made of $[\eta]$ in methyl ethyl ketone at 20.0 °C (Θ). It is found that $DM_w^{1/2}$ decreases and $[\eta]/M_w^{1/2}$ increases with increasing M_w, and none of them becomes a constant independent of M_w even for such large M_w that the ratio of the mean-square radius of gyration to M_w is independent of M_w. This anomalous behavior may be considered the so-called "draining effect". This is believed to be the first observation of the effect for a long flexible polymer. For the oligomers of very low M_w, $[\eta]$ in bromocyclohexane becomes negative as in the case of polyisobutylene in isoamyl isovalerate and in benzene studied previously. Thus the data for $[\eta]$ were treated following the procedure proposed therein. The results for both D and $[\eta]$ may be almost quantitatively explained by the transport theory of the helical wormlike touched-bead model with values of the model parameters unambiguously determined. From the model parameters obtained, the PDMS chain is found to assume the local conformation with retention of large helical portions in dilute solution as in the case of the poly(methyl methacrylate) chain. The value of the static stiffness parameter λ^{-1} is almost the same as that of atactic polystyrene, so that the PDMS chain may be regarded as stiffer than usually considered. The value of the hydrodynamic diameter d_b of the bead is found to be appreciably small compared to those for the other flexible polymers studied previously. A rather detailed discussion of these results is given.

Introduction

In a previous paper,[1] we have studied the mean-square electric dipole moment $\langle \mu^2 \rangle$ of poly(dimethylsiloxane) (PDMS) over a wide range of molecular weight M, including the oligomers of very low M. It has been demonstrated that the dependence of $\langle \mu^2 \rangle$ on M may well be explained by the corresponding theory[2] on the basis of the helical wormlike (HW) chain model,[3,4] with a proper set of values of the model parameters, i.e., the constant curvature κ_0 and torsion τ_0 of the characteristic helix, the static stiffness parameter λ^{-1}, and the shift factor M_L. Thus the values of the reduced parameters $\lambda^{-1}\kappa_0$ and $\lambda^{-1}\tau_0$ and the product $\lambda^{-1}M_L$ have been determined with sufficient accuracy. Recall that the values of λ^{-1} and M_L cannot in principle be determined separately from the analysis of the molecular weight dependence of $\langle \mu^2 \rangle$ alone. In this paper, the study of dilute solution properties of PDMS initiated in the previous paper[1] is extended to the translational diffusion coefficient D and intrinsic viscosity $[\eta]$ in Θ solvents. From the analysis of their molecular weight dependence, we estimate not only λ^{-1} and M_L separately but also the hydrodynamic diameter d_b of the PDMS chain.

The parameter λ^{-1} thus determined gives a measure of *static* stiffness of the PDMS chain. The notion that the PDMS chain is very flexible has been widely accepted, based on the fact that the glass transition temperature of PDMS is extremely low[5] and also its bulk modulus is very small.[6] However, these properties refer to those in the bulk, so that it is not adequate to conclude from them that the single isolated PDMS chain in dilute solution is very flexible. The present analysis suggests that the PDMS chain is rather stiff in this static sense.

Several experimental results have already been reported in the literature for D and $[\eta]$ of PDMS in the unperturbed Θ state: D and $[\eta]$ in bromocyclohexane at 28 °C (Θ)[7-10] and $[\eta]$ in methyl ethyl ketone (MEK) at 20 °C (Θ).[9] Some of them have revealed deviations from the proportionality relations $D \propto M^{-1/2}$ and $[\eta] \propto M^{1/2}$, in contradiction to the common notion that the relations should hold for unperturbed long flexible chains.[11] Thus it has often been claimed that the PDMS chain exhibits "anomalous" behavior in the transport processes in dilute solution, or, in other words, the excluded-volume effect does not disappear even in the Θ state above. In contrast to this, Horská et al.[10] have ascribed the "anomaly" to badness of the experimental data, supporting the above common notion, although their results are not conclusive either.

In our recent study of steady-state transport coefficients of flexible polymers with sufficiently high M,[12] the quantities $DM^{1/2}$ and $[\eta]/M^{1/2}$ of PDMS in bromocyclohexane at 29.5 °C (Θ) have been found to depend on M even for such large M that the ratio of the mean-square radius of gyration $\langle S^2 \rangle$ to M is independent of M, indicating in our opinion that the so-called "draining effect" does exist. In order to make the conclusion more definite, in the present paper we pursue further the discussion of the problem on the basis of experimental data over a wider range of M, including the oligomer region.

Uncertainty still remains in the Θ temperature of the bromocyclohexane solution of PDMS; the above value 28 °C, which has been determined from viscosity measurements,[13] is somewhat lower than the value 29 °C determined from light-scattering measurements.[14,15] Thus, in the present study, we have also determined the Θ temperature of this solution before measurements of the transport coefficients. (We note that the value of Θ determined here has already been used in ref 12.)

In anticipation of the results, we note that the intrinsic viscosities for the oligomer samples of PDMS with very low M in bromocyclohexane become negative as in the case of the oligomer samples of polyisobutylene (PIB) in isoamyl isovalerate (IAIV) and in benzene.[16] The procedure proposed therein[16] for an analysis of data for such a case on the basis of the HW chain is applied to that of the present data for $[\eta]$. As for D, any anomalous behavior

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like the negative intrinsic viscosity has not been observed. Thus the validity of the above procedure may be examined by a comparison of the values of $d_{\rm b}$ determined from $[\eta]$ and D.

Experimental Section

Materials. Most of the PDMS samples used in this work are the same as those used in the previous studies,[1,12] i.e., fractions separated from the commercial samples supplied from Toshiba Silicone Co., Ltd., named Low Boil Fractions, 5CS, TSF451-10, TSF451-100, TSF451-500, TSF451-50M, and TSE200A. The samples with weight-average molecular weights $M_{\rm w} < 700$ had been separated by fractional distillation under reduced pressure, those with $700 < M_{\rm w} < 5 \times 10^3$ by preparative gel permeation chromatography (GPC), and the others with higher $M_{\rm w}$ by fractional precipitation.

The first and second fractions from the fractional distillation had been identified with the monomer and dimer, respectively, from the number of kinds of protons determined by ^{1}H NMR spectroscopy.[1] The xth fraction designated as ODMSx (x = 3–7) had been identified with the (monodisperse) x-mer by analytical GPC with the monomer and dimer as standards.[1] Thus the values of $M_{\rm w}$ for these fractions had been calculated from their chemical formulas. The values of $M_{\rm w}$ for the sample in the range of $700 < M_{\rm w} < 900$ and of the ratio of $M_{\rm w}$ to the number-average molecular weight $M_{\rm n}$ for all the samples had also been determined by analytical GPC. The values of $M_{\rm w}$ of the other samples with $M_{\rm w} > 900$ had been obtained from static light scattering (SLS) measurements as stated below.

The solvent bromocyclohexane (Tokyo Kasei Kogyo Co.; 98% purity) used for SLS, dynamic light scattering (DLS), and viscosity measurements was purified by distillation under reduced pressure in a dry nitrogen atmosphere after dehydration with sodium carboxide anhydride. The other solvents, toluene used for SLS measurements and methyl ethyl ketone (MEK) used for viscosity measurements, were purified according to standard procedures.

Static Light Scattering. SLS measurements were carried out to determine $M_{\rm w}$ of the samples with $M_{\rm w} > 900$ and also the Θ temperature of bormocyclohexane solutions. The values of $M_{\rm w}$ were determined for all those samples in toluene at 25.0 °C and for some of them with $M_{\rm w} > 3 \times 10^4$ also in bromocyclohexane at Θ. For the determination of Θ, the second virial coefficient A_2 was measured for the three fractionated samples PDMS20, PDMS40, and PDMS110 along with the original whole sample TSE200A at several temperatures ranging from 20 to 45 °C.

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 scattering angle 90° at 25.0 °C, where the Rayleigh ratio $R_{\rm Uu}(90°)$ of pure benzene was taken as 46.5×10^{-6} cm^{-1}. The depolarization ratio $\rho_{\rm u}$ of pure benzene at 25.0 °C was determined to be 0.41 ± 0.01 by the method of Rubingh and Yu.[17] Scattering intensities were measured at five different concentrations and at scattering angles ranging from 30 to 150°. The data obtained were treated by the Berry square-root plot.[18] In the present case, corrections for the optical anisotropy were unnecessary since the degree of depolarization was negligibly small.

The most concentrated solution of each sample was prepared gravimetrically and made homogeneous by continuous stirring at 35–40 °C for 10–15 h. It was optically purified by filtration through a Teflon membrane of pore size 0.10–0.45 μm. The solutions of lower concentrations were obtained by successive dilution. The weight concentrations of the test solutions were converted to the polymer mass concentrations c by the use of the densities of the solvents.

The refractive index increment $\partial n/\partial c$ was measured at 436 nm by the use of a Shimadzu differential refractometer for PDMS samples in toluene at 25.0 °C and in bromocyclohexane at 29.5 °C. For the toluene solutions, $\partial n/\partial c$ increases from -0.112_9 to -0.103_6 cm^3/g as $M_{\rm w}$ is increased from 1.14×10^3 to 3.19×10^4, and it becomes constant for higher $M_{\rm w}$. The value of $\partial n/\partial c$ for the bromocyclohexane solution is -0.093_6 cm^3/g for $M_{\rm w} > 3 \times 10^4$.

Dynamic Light Scattering. DLS measurements were carried out to determine D for the 15 samples ODMS2 through PDMS6 in bromocyclohexane at 29.5 °C (Θ), 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 9893B/350, the output from which was processed by a Brookhaven Instruments Model BI2030AT autocorrelator with 264 channels. A minor modification has been made of the detector alignment as described elsewhere.[12] The normalized autocorrelation function $g^{(2)}(t)$ of scattered light intensity $I(t)$ at time t was measured at four or five concentrations and at scattering angles ranging from 10 to 110°. All the test solutions were prepared in the same manner as in the case of SLS measurements except for the calculation of c of the solutions of the oligomer samples with $M_{\rm w} \lesssim 900$, for which use was made of the densities of the solutions instead of the solvent. The solution density was measured with a pycnometer of the Lipkin–Davison type.

For each sample, D was determined from the data for $g^{(2)}(t)$ in the same manner as in previous studies.[12,19] Although the method is rather familiar at the present time, there still seems to be some confusion about the determination of D, or about the relation between D and the first cumulant Γ. Thus it is pertinent to reconsider it in some detail. The confusion seems to be concerned with the time scales on which DLS measurements are carried out, along with the definition of D. The conventional translational diffusion coefficient D is defined as the limiting value $D(\infty)$ of the time-dependent translational diffusion coefficient $D(t)$ at $t \rightarrow \infty$. The latter may be explicitly defined by

$$D(t) = \langle |\mathbf{R}_{\rm G}(t) - \mathbf{R}_{\rm G}(0)|^2 \rangle / 6t \qquad (1)$$

where $\mathbf{R}_{\rm G}(t)$ is the vector position of the center of mass of a polymer chain at time t. Note that the translational diffusion coefficient in general depends on t because of the coupling between translational and internal motions of the chain and that $D(t)$ attains a constant value $D(\infty)$ after all the internal motions have relaxed away.

The autocorrelation function $g^{(2)}(t)$ at infinite dilution is related to the dynamic structure factor $S(k,t)$ for a single polymer chain by the equation

$$\frac{1}{2} \ln[g^{(2)}(t) - 1] = \text{const} + \ln[S(k,t)/S(k,0)] \qquad (2)$$

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

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

with θ the scattering angle and $\tilde{\lambda}$ the wavelength of the incident light in the solvent. The second term on the right-hand side of eq 2 may be written in the form

$$\ln[S(k,t)/S(k,0)] = -k^2 t D(t)[1 + \mathcal{O}(k^2)] \qquad (4)$$

The (*theoretical*) first cumulant Γ defined from the initial derivative of ln $S(k,t)$ with respect to t may then be given by

$$\Gamma \equiv -[\mathrm{d} \ln S(k,t)/\mathrm{d}t]_{t=0} = -k^2 D(0)[1 + \mathcal{O}(k^2)] \qquad (5)$$

The quantity Γ thus defined is related to $D(0)$.

In practice, however, we can only measure a chain of numbers of photons arriving at a detector at (identical) finite time intervals, each being the sampling time δ, which depends on the efficiency of the photomultiplier and the correlator used. (For example, δ should be set larger than 0.1 μs in the case of our DLS apparatus.) Thus the quantity $g^{(2)}(t)$ actually obtained is the autocorrelation function of time-average scattered light intensity at the time interval δ, and therefore the *experimental* first cumulant Γ_δ is not exactly equivalent to Γ, where

$$\Gamma_\delta \equiv -\lim_{\substack{t \to 0 \\ (t > \delta)}} \frac{1}{2} \mathrm{d} \ln[g^{(2)}(t) - 1]/\mathrm{d}t \qquad (6)$$

with the experimentally observed values of $g^{(2)}(t)$. If the time interval δ is much longer than the longest relaxation time of internal motions, e.g., the relaxation time of the first normal mode for the Gaussian chain (or spring-bead) model given by[11,20]

$$\tau_1 = M\eta_0[\eta]/0.586RT\lambda_1 \qquad (7)$$

with η_0 the solvent viscosity, R the gas constant, T the absolute temperature, and λ_1 (=4.04) the corresponding reduced Zimm eigenvalue,[11,21] then Γ_δ becomes a limiting constant value Γ_∞ defined by

$$\Gamma_\infty \equiv -[\mathrm{d}\ln S(k,t)/\mathrm{d}t]_{t=\infty} \qquad (8)$$

From eq 8 with eq 4, Γ_∞ is seen to be related to $D(\infty)$ by

$$\Gamma_\infty = -k^2D(\infty) + \mathcal{O}(k^4) \qquad (9)$$

If the change in $D(t)$ at small t is not observable, so that $\ln[g^{(2)}(t) - 1]$ is linear in t and the following relation holds

$$\Gamma_\delta = \Gamma_\infty \qquad \text{with } \delta \gg \tau_1 \qquad (10)$$

as has usually been considered,[22,23] then $D(\infty)$ may be determined from the (experimental) first cumulant Γ_δ. (Even in such a case, we should pay due attention to the difference between the theoretical and experimental first cumulants.)

However, the situation becomes rather complicated if the plot of $(1/2)\ln[g^{(2)}(t) - 1]$ against t does not follow a straight line at small t, as shown in Figure 2 of ref 12 for the atactic polystyrene (a-PS) sample with $M_w = 7.32 \times 10^5$ in cyclohexane at 34.5 °C (Θ) at scattering angle 30°. In that case (of large M_w), Γ_δ is definitely different from Γ_∞, and it is the latter that is required for the determination of $D(\infty)$. For this purpose, we must analyze the data for $g^{(2)}(t)$ at large t, i.e., in the range of $t \gg \tau_1$, where the plot follows a straight line. In practice, we analyze the data in the range of $t > 10\tau_1$. We note that the value of $10\tau_1$ is smaller than the smallest δ of our DLS apparatus for the PDMS samples with $M_w \lesssim 5 \times 10^4$.

Actually, we deal with the data at finite concentrations, although sufficiently low, and their part at large t can be represented by the equation

$$\frac{1}{2}\ln[g^{(2)}(t) - 1] = \mathrm{const} - At \qquad (11)$$

Here the coefficient A becomes equal to Γ_∞ only in the limit of $c \to 0$. Thus, instead of estimating Γ_∞ directly, we first obtain A from eq 11 with the data for $g^{(2)}(t)$ at finite c and then determine the apparent diffusion coefficient $D^{(\mathrm{LS})}(c)$ at finite c from

$$D^{(\mathrm{LS})}(c) = \lim_{k\to 0} A/k^2 \qquad (12)$$

At sufficiently low concentrations, $D^{(\mathrm{LS})}(c)$ may be expanded as

$$D^{(\mathrm{LS})}(c) = D(1 + k_D{}^{(\mathrm{LS})}c + ...) \qquad (13)$$

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

$$D = D^{(\mathrm{LS})}(0) \qquad (14)$$

The values of the refractive index at a wavelength of 488 nm and the viscosity coefficient η_0 of bromocyclohexane at 29.5 °C, which are required for the analysis of the DLS data, are 1.499 and 1.97 cP, respectively.

Viscosity. Viscosity measurements were carried out for the 15 samples ODMS2 through PDMS6 in bromocyclohexane at 29.5 °C (Θ) and for all the samples in MEK at 20.0 °C (Θ). Viscosities of the solutions of several high-molecular-weight samples in bromocyclohexane were also measured at 28.0 and 26.0 °C. For the measurements, we used a viscometer of the Ubbelohde type and a specially designed (four-bulb) spiral capillary viscometer of the suspended-liquid type.

The flow time was measured to a precision of 0.1 s, and the test solutions were maintained at a constant temperature within ±0.005 °C during the measurement. Density corrections were made in the calculations of the concentration c and also of the relative viscosity η_r from the flow times of the solution and solvent. The data obtained for the specific viscosity η_{sp} and η_r were treated as usual by the Huggins and Fuoss–Mead plots to determine $[\eta]$.

Table I. 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
ODMS2	2.37×10^2	2	1.00
ODMS3	3.11×10^2	3	1.00
ODMS4	3.85×10^2	4	1.00
ODMS5	4.59×10^2	5	1.00
ODMS7	6.08×10^2	7	1.00
ODMS10	8.15×10^2	9.8	1.00
ODMS14[a]	1.14×10^3	14.2	1.01
ODMS18	1.39×10^3	17.5	1.01
ODMS24	1.90×10^3	24.4	1.03
ODMS35	2.67×10^3	34.8	1.02
ODMS71	5.37×10^3	71.2	1.06
PDMS1	8.26×10^3	110	1.05
PDMS2	2.21×10^4	297	1.08
PDMS3	3.19×10^4 (3.22×10^4)[b]	429	1.08
PDMS6	5.90×10^4	794	1.08
PDMS20	1.83×10^5 (1.85×10^5)	2470	1.05
PDMS40	3.84×10^5 (3.86×10^5)	5180	1.06
PDMS70	6.46×10^5 (6.60×10^5)	8710	1.07
PDMS90	9.28×10^5 (9.14×10^5)	12500	1.07
PDMS110	1.12×10^6 (1.14×10^6)	15100	1.08

[a] M_w's of ODMS14 through PDMS110 were determined from LS measurements in toluene. [b] The figures in parentheses represent the values in bromocyclohexane.

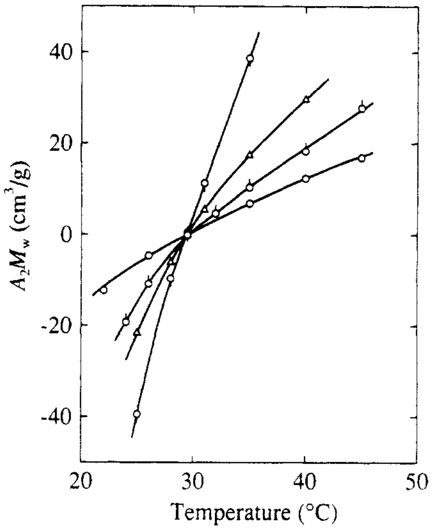

Figure 1. Plots of A_2M_w against temperature for the PDMS samples in bromocyclohexane: ○, PDMS20; ȯ, PDMS40; ọ, PDMS110; △, the whole sample TSE200A.

Results

Molecular Weights and Their Distributions. The values of M_w, the weight-average degree of polymerization x_w, and the ratio of M_w to M_n are summarized in Table I. (We note that the sample PDMS6 has not been used previously.[1,12]) The values of M_w determined from SLS measurements for several high-molecular-weight samples in the two solvents, i.e., toluene and bromocyclohexane, are in good agreement with each other. Note that the samples ODMSx (x = 2–7) are completely monodisperse. The molecular weight distributions for the other samples may be regarded as sufficiently narrow.

Θ Temperature of Bromocyclohexane Solutions. Figure 1 shows plots of A_2M_w against temperature for the three samples PDMS20, PDMS40, and PDMS110 and also the original whole sample TSE200A in bromocyclohexane. It is seen that A_2 vanishes at almost the same temperature independent of M_w, leading to the conclusion that the Θ temperature is 29.5 °C for bromocyclohexane solutions of PDMS. This value of Θ is rather in good agreement with the value 29.0 °C determined by Schultz et al.[14,15] from

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

sample	$10^7 D$, cm^2/s	$k_D^{(LS)}$, cm^3/g
ODMS2	42.1	0.2_2
ODMS3	40.3	-0.2_4
ODMS4	36.8	-0.6_6
ODMS5	32.6	-0.5_7
ODMS7	28.0	-0.7_1
ODMS10	21.8	-0.4_6
ODMS14	18.6	-1.2_9
ODMS18	16.1	-1.2_0
ODMS24	13.5	-1.0_5
ODMS35	12.2	-2.0_0
ODMS71	7.78	-2.4_6
PDMS1	5.96	-2.9_3
PDMS2	3.89	-5.9_1
PDMS3	3.17	-6.8_3
PDMS6	2.34	$-12._9$
PDMS20[a]	1.25	$-20._8$
PDMS40	0.850	$-32._8$
PDMS70	0.639	$-50._0$
PDMS90	0.536	$-59._1$
PDMS110	0.480	$-68._8$

[a] The values of D of PDMS20 through PDMS110 have been reproduced from ref 12.

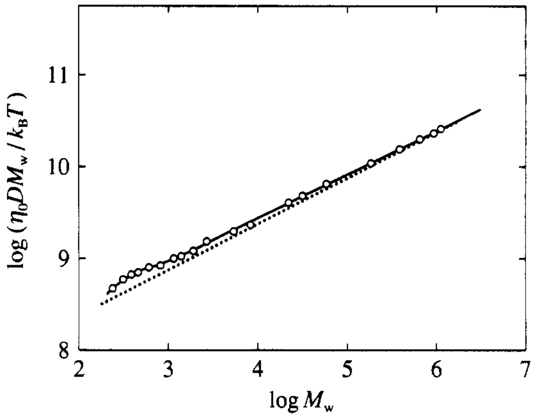

Figure 2. Double-logarithmic plots of $\eta_0 D M_w / k_B T$ against M_w for PDMS in bromocyclohexane at 29.5 °C. The dotted straight line has a slope of 0.5.

Table III. Results of Viscometry on Oligo- and Poly(dimethylsiloxane)s in Bromocyclohexane at 29.5 °C and in MEK at 20.0 °C

	bromocyclohexane (29.5 °C)		MEK (20.0 °C)	
sample	[η], dL/g	k'	[η], dL/g	k'
ODMS2	−0.0111		0.0045	
ODMS3	−0.0073		0.0067	
ODMS4	−0.0042		0.0084	
ODMS5	−0.0026		0.0099	
ODMS7	0.0009		0.0125	0.96
ODMS10	0.0041		0.0153	0.93
ODMS14	0.0094	1.26	0.0206	0.82
ODMS18	0.0125	0.97	0.0233	0.70
ODMS24	0.0174	0.62	0.0278	0.66
ODMS35	0.0228	0.65	0.0340	0.60
ODMS71	0.0398	0.55	0.0521	0.54
PDMS1	0.0554	0.53	0.0678	0.48
PDMS2	0.0981	0.65	0.116	0.43
PDMS3	0.118	0.76	0.140	0.44
PDMS6	0.181	0.68	0.208	0.36
PDMS20[a]	0.339	0.60	0.396	0.45
PDMS40	0.518	0.71	0.582	0.50
PDMS70	0.709	0.56	0.797	0.52
PDMS90	0.851	0.58	0.976	0.56
PDMS110	0.954	0.63	1.10	0.57

[a] The values of [η] of PDMS20 through PDMS110 in bromocyclohexane at 29.5 °C have been reproduced from ref 12.

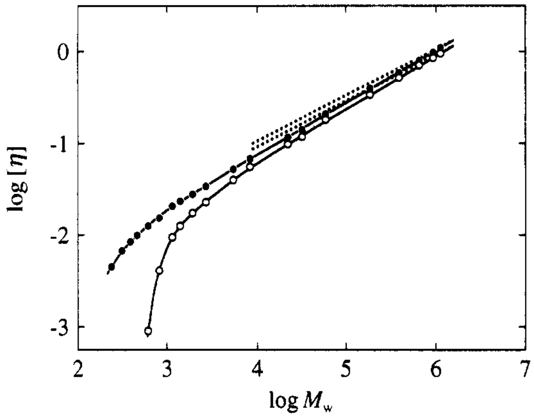

Figure 3. Double-logarithmic plots of [η] (in dL/g) against M_w for PDMS: ○, in bromocyclohexane at 29.5 °C; ●, in MEK at 20.0 °C. The dotted straight lines have a slope of 0.5.

SLS measurements but is somewhat higher than the value 28.0 °C by Haug and Meyerhoff[13] from viscosity measurements, although the latter has often been used in recent studies of the transport properties.[7-10]

Translational Diffusion. The values of D and $k_D^{(LS)}$ for all the samples studied are given in Table II. The values of D for the five samples with the highest M_w, i.e., PDMS20 through PDMS110, have been reproduced from ref 12, and those of $k_D^{(LS)}$ for these samples are the results determined there (although not reported).

Figure 2 shows double-logarithmic plots of $\eta_0 D M_w / k_B T$ (in cm^{-1}) against M_w, where k_B is the Boltzmann constant. The solid curve connects these data points smoothly, and the dotted line indicates its asymptotic straight line of slope $^1/_2$. The data points do not follow the latter straight line even in the range of high M_w examined; the behavior is quite unusual, differing from that of most of typical flexible polymers in the unperturbed state. The present finding is in qualitative coincidence with the literature data, although the latter are somewhat fragmental. As M_w is decreased, the data points deviate upward progressively from the straight line and follow an S-shaped curve at very small M_w.

Viscosity. Intrinsic viscosity data for all the PDMS samples in the two Θ solvents are summarized in Table III along with the values of the Huggins coefficient k'. The latter values for ODMS2 through ODMS10 in bromocyclohexane and for ODMS2 through ODMS5 in MEK have been omitted from the table since they become extraordinarily large for vanishingly small [η] even if the Huggins plot itself has a finite, normal slope, as in the case of the oligomer samples of PIB in the previous study.[16] The values of [η] for the five samples with the highest M_w, i.e., PDMS20 through PDMS110, in bromocyclohexane have been reproduced from ref 12, and those of k' for these samples are the results determined there (although not reported). As mentioned in the Introduction, [η] is negative for ODMS2 through ODMS5 in bromocyclohexane.

Figure 3 shows double-logarithmic plots of [η] (in dL/g) against M_w with the data in bromocyclohexane at 29.5 °C (Θ) (unfilled circles) and in MEK at 20.0 °C (Θ) (filled circles). Here, we have used the values of M_w listed in the second column of Table I. The data for ODMS2 through ODMS5 in bromocyclohexane cannot be plotted in the figure. The solid curves connect the data points smoothly, and the dotted lines indicate their respective asymptotic straight lines of slope $^1/_2$. The values of [η] in bromocyclohexane are smaller than those in MEK over the whole range of M_w. The ratio of [η] in bromocyclohexane to that in MEK is ca. 0.87 for $M_w \gtrsim 5 \times 10^4$ and becomes smaller with decreasing M_w. The data points for the two

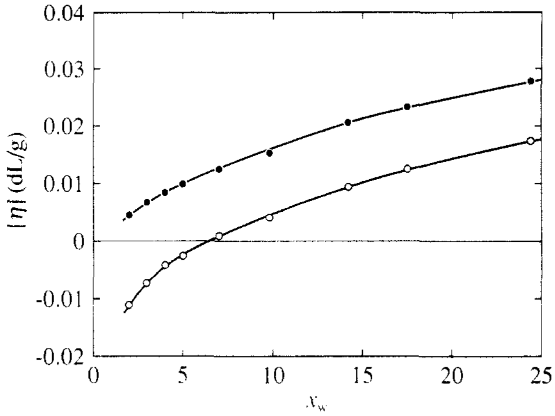

Figure 4. Plots of $[\eta]$ against x_w for ODMS samples: ○, in bromocyclohexane at 29.5 °C; ●, in MEK at 20.0 °C.

Table IV. Results of Viscometry on Poly(dimethylsiloxane)s in Bromocyclohexane at 26.0 and 28.0 °C

	26.0 °C		28.0 °C	
sample	$[\eta]$, dL/g	k'	$[\eta]$, dL/g	k'
PDMS6	0.178	0.65	0.180	0.62
PDMS20	0.328	0.78	0.334	0.74
PDMS70	0.631	0.84	0.666	0.72
PDMS110	0.837	0.80	0.892	0.72

solvents do not follow the respective asymptotic straight lines as in the case of D but deviate downward from them, the behavior differing again from that of most of flexible polymers in the unperturbed state. These results also agree qualitatively with the literature data mentioned in the Introduction. The deviations become large with decreasing M_w, especially in bromocyclohexane.

In order to examine the dependence of $[\eta]$ on x_w at small x_w, including the negative $[\eta]$, its values are plotted against x_w in Figure 4, in which the symbols have the same meaning as in Figure 3. It is seen that the difference between the values of $[\eta]$ in the two solvents is almost independent of x_w for $x_w \gtrsim 4$ (in its range displayed). This result is quite similar to those for PIB in IAIV and in benzene,[16] as stated in the Introduction.

The values of $[\eta]$ obtained for four high-molecular-weight samples in bromocyclohexane at 26.0 and 28.0 °C are listed in Table IV along with those of k'.

Discussion

Analysis of D on the Basis of the HW Model. For the HW touched-bead model with the total number N of beads or the total contour length $L = Nd_b$ with d_b the diameter of the bead, the quantity $\eta_0 D M_w/k_B T$ may be written in the form[19]

$$\eta_0 D M_w/k_B T = (M_L/3\pi) f_D(\lambda L; \lambda^{-1}\kappa_0, \lambda^{-1}\tau_0, \lambda d_b) \qquad (15)$$

where the function f_D is given by eq 6 of ref 19 and may be evaluated numerically by the use of the interpolation formula for the mean reciprocal end-to-end distance of the chain as given in the Appendix of ref 24. The function f_D satisfies the following relation:

$$\lim_{\lambda L \to \infty} f_D(\lambda L)/(\lambda L)^{1/2} = (6^{1/2}/2) c_\infty^{-1/2} \rho_\infty \qquad (16)$$

with

$$c_\infty = \frac{4 + (\lambda^{-1}\tau_0)^2}{4 + (\lambda^{-1}\kappa_0)^2 + (\lambda^{-1}\tau_0)^2} \qquad (17)$$

and with ρ_∞ (=1.505) being the coil limiting value of the ratio ρ of the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ to the hydrodynamic radius $R_H = k_B T/6\pi\eta_0 D$.

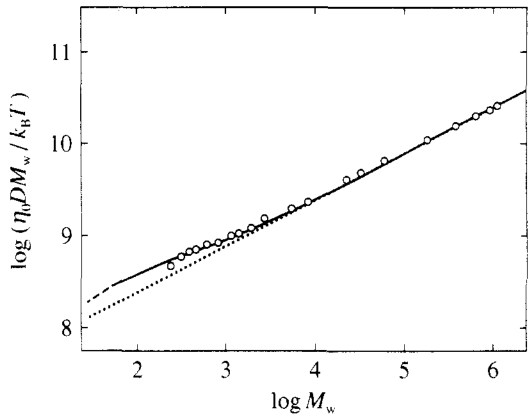

Figure 5. Double-logarithmic plots of $\eta_0 D M_w/k_B T$ against M_w for PDMS in bromocyclohexane at 29.5 °C. The solid curve represents the best-fit HW theoretical values for $N \geq 2$, with the dashed line segment connecting the values for $N = 1$ and 2. The dotted straight line has a slope of 0.5.

As already mentioned in the Introduction and shown in the Results, any anomalous behavior like the negative intrinsic viscosity has not been observed for D. This is also guaranteed by the definition of D as given by eq 1. Thus we analyze the data following the procedure used in the previous study,[19] the basic equations being given by

$$\log(\eta_0 D M_w/k_B T) = \log f_D(\lambda L) + \log M_L - 0.975 \qquad (18)$$

$$\log M_w = \log(\lambda L) + \log(\lambda^{-1} M_L) \qquad (19)$$

The quantities M_L and $\lambda^{-1}M_L$ (and therefore λ^{-1} and M_L) may be estimated from a best fit of double-logarithmic plots of the theoretical f_D against λL for properly chosen values of $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, and λd_b to that of the observed $\eta_0 D M_w/k_B T$ against M_w, so that we may in principle determine the five parameters $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, λ^{-1}, M_L, and d_b. However, in the present analysis, for simplicity, we assume that $\lambda^{-1}\kappa_0$ and $\lambda^{-1}\tau_0$ are the same as those estimated previously[1] from the analysis of the data for $\langle \mu^2 \rangle$ in cyclohexane at 25.0 °C, i.e., $\lambda^{-1}\kappa_0 = 2.6$ and $\lambda^{-1}\tau_0 = 0$, and determine the remaining three parameters λ^{-1}, M_L, and d_b.

Figure 5 shows double-logarithmic plots of $\eta_0 D M_w/k_B T$ against M_w for PDMS in bromocyclohexane at 29.5 °C. The unfilled circles represent the present (and previous[12]) experimental values, and the solid curve represents the best-fit theoretical values calculated for $N \geq 2$ from eqs 18 and 19 with eq 15 with $\lambda d_b = 0.05$, $\log M_L = 1.255$, and $\log(\lambda^{-1}M_L) = 2.747$, with the dashed line segment connecting those values for $N = 1$ and 2. The dotted line indicates the asymptotic straight line of slope $^1/_2$. It is seen that the agreement between theory and experiment is rather good. In particular, the observed results at large M_w and in the oligomer region are quantitatively reproduced by the theory, although the agreement is not complete in the intermediate region. The values of the HW model parameters thus determined are listed in the first row of Table V.

Effects of Specific Interactions on $[\eta]$. It has been found that $[\eta]$ is negative for the four oligomer samples ODMS2 through ODMS5 in bromocyclohexane, as in the case of PIB oligomers in IAIV and in benzene.[16] Such anomalous behavior may be regarded as arising from specific interactions between polymer and solvent molecules and can never be treated molecular-theoretically within the framework of classical hydrodynamics. Thus

Table V. Values of the HW Model Parameters

polymer (f_r)	solvent	temp, °C	$\lambda^{-1}\kappa_0$	$\lambda^{-1}\tau_0$	λ^{-1}, Å	M_L, Å^{-1}	d_b, Å	obsd quantity
PDMS	bromocyclohexane	29.5	2.6	0	31.0	18.0	1.6	$\langle\mu^2\rangle$,[a] D
			2.6	0	25.5	20.6	2.0	$\langle\mu^2\rangle$,[a] $[\eta]$
	MEK	20.0	2.6	0	28.0	20.6	2.0	$\langle\mu^2\rangle$,[a] $[\eta]$
a-PS (0.59)	cyclohexane	34.5	3.0	6.0	23.5	42.6	10.1	$\langle\Gamma^2\rangle$,[b] $[\eta]$[c]
			3.0	6.0	27.0	35.0	9.5	$\langle\Gamma^2\rangle$,[b] D[d]
a-PMMA (0.79)	acetonitrile	44.0	4.5	2.0	45.0	38.6	7.2	$[\eta]$[e]
	n-butyl chloride	40.8	4.5	2.0	45.0	38.6	7.9	$[\eta]$[e]
PIB	isoamyl isovalerate	25.0	0		12.7	24.1	6.4	$[\eta]$[f]

[a] See ref 1. [b] See ref 27; $\langle\Gamma^2\rangle$, mean-square optical anisotropy. [c] See ref 28. [d] See ref 19. [e] See ref 26. [f] See ref 16.

it is convenient to reproduce briefly the recipe for treating this problem[16] before we make an analysis of the present data on the basis of the HW touched-bead (classical hydrodynamic) model.

According to the classical hydrodynamic theory of the model, its intrinsic viscosity $[\eta]_C$ may be written in the form[25]

$$[\eta]_C = [\eta]_{KR} + [\eta]_E \tag{20}$$

where $[\eta]_{KR}$ and $[\eta]_E$ are the Kirkwood–Riseman and Einstein intrinsic viscosities, respectively, the latter being given by

$$[\eta]_E = 5\pi N_A d_b^{\,3}/12M_b \tag{21}$$

with N_A Avogadro's number and M_b ($=M/N$) the molecular weight of the bead. An additional (negative) term η^* is then introduced in order to take account of the effects of the specific interactions. Thus the observed $[\eta]$ may be written in the form

$$[\eta] = [\eta]_C + \eta^* \ (\eta^* \le 0) \tag{22}$$

If we assume that this modification applies only to the term $[\eta]_E$ (not to $[\eta]_{KR}$), then η^* must be independent of M, so that

$$\lim_{M\to\infty} ([\eta]/[\eta]_C) = 1 \tag{23}$$

Although the (negative) quantity η^* thus introduced may in principle be estimated from an analysis of experimental data in one solvent, an unequivocal estimation is actually very difficult and some additional assumptions are required. In the case of PIB,[16] we have further assumed that the difference between the values of $[\eta]$ in the two solvents IAIV and benzene arises from that in η^*, since $[\eta]$ for large M_w in the two solvents were found to be identical with each other. In the present case, $[\eta]$ has been found to depend on solvent even in the range of large M_w, indicating that there is a possibility of the dependence of the unperturbed chain dimension or the coil limiting value Φ_∞ of the Flory–Fox factor Φ, or both, on solvent. Then it does not seem very reasonable to apply the same assumption. However, if $[\eta]_C$ depends appreciably on solvent through them in the range of small M_w (or x_w) as displayed in Figure 4, then the difference in $[\eta]$ must depend appreciably on M_w there. As seen from Figure 4, however, this is not the case, the situation for small M_w being similar to the case of PIB. Thus, as far as the range of small M_w is concerned, we simply again adopt the same assumption on $[\eta]$ as before to write

$$\begin{aligned}\Delta\eta &\equiv [\eta]_{(1)} - [\eta]_{(2)} \\ &= \eta_{(1)}{}^* - \eta_{(2)}{}^*\end{aligned} \tag{24}$$

where the subscripts (1) and (2) refer to the solvents MEK and bromocyclohexane, respectively. It is then found that $\Delta\eta$ for the present case is 0.0115 dL/g as an average value for the seven samples ODMS4 through ODSM24.

Analysis of $[\eta] - \eta^*$ on the Basis of the HW Model. Now $[\eta]_C$ for the HW touched-bead model with the total number N of beads may be written in the form[25]

$$[\eta]_C = (1/\lambda^2 M_L) f_\eta(\lambda L;\ \lambda^{-1}\kappa_0,\ \lambda^{-1}\tau_0, \lambda d_b) \tag{25}$$

where the function f_η is defined by

$$f_\eta(\lambda L) = \lambda^{-1} M_L [\tilde{\eta}]_C \tag{26}$$

with $[\tilde{\eta}]_C$ being the $[\eta]_C$ measured in units of $(\lambda^{-1})^3$ and being given by eq 15 with eqs 17 and 27 of ref 25. It satisfies the following asymptotic relation

$$\lim_{\lambda L\to\infty} f_\eta(\lambda L)/(\lambda L)^{1/2} = c_\infty^{\,3/2}\Phi_\infty \tag{27}$$

(with $\Phi_\infty = 2.870 \times 10^{23}$ mol^{-1}).

The basic equations for an analysis of the dta for $[\eta]$ are given by

$$\log [\eta]_C = \log f_\eta(\lambda L) - \log(\lambda^2 M_L) \tag{28}$$

along with eq 19. Thus the quantities $\lambda^2 M_L$ and $\lambda^{-1} M_L$ may then be estimated from a best fit of double-logarithmic plots of the theoretical f_η against λL for properly chosen values of $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, and λd_b to those of the "observed" $[\eta]_C = [\eta] - \eta^*$ against M_w with properly chosen η^*, so that we may in principle determine the six parameters $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, λ^{-1}, M_L, d_b, and η^*. As in the case of D, however, we assume that $\lambda^{-1}\kappa_0$ and $\lambda^{-1}\tau_0$ are the same as those determined from $\langle\mu^2\rangle$, i.e., $\lambda^{-1}\kappa_0 = 2.6$ and $\lambda^{-1}\tau_0 = 0$,[1] and determine the remaining four parameters λ^{-1}, M_L, d_b, and η^*.

We analyze the present data in the two Θ solvents simultaneously by the curve fitting under the condition that $\Delta\eta = 0.0115$ dL/g. Before doing this, a remark should be made on the difference in $[\eta]$ observed in the range of large M_w. As mentioned above, it may be due to the dependence of the unperturbed chain dimension or Φ_∞, or both, on solvent. In the previous study of $[\eta]$ for atactic poly(methyl methacrylate) (a-PMMA) in two Θ solvents,[26] it has been found from the data for $[\eta]$ and $\langle S^2\rangle$ that the difference in $[\eta]$ comes from that in Φ_∞. For the present case, however, $\langle S^2\rangle$ in MEK cannot be determined from SLS measurements since $\partial n/\partial c$ is negligibly small for this system. Thus, in this study, we simply assume that the unperturbed chain dimensions, and therefore the parameters λ^{-1} and M_L, are different with the same value of Φ_∞ in the two solvents.

Figure 6 shows double-logarithmic plots of $[\eta] - \eta^*$ ($= [\eta]_C$) against M_w for PDMS. The unfilled and filled circles represent the experimental values in bromocyclohexane at 29.5 °C (Θ) with $\eta^* = -0.0115$ dL/g and in MEK at 20.0 °C (Θ) with $\eta^* = 0$. The solid curves represent the respective best-fit theoretical values calculated for $N \ge 2$ from eqs 28 and 19 with eq 25 with $\lambda d_b = 0.08$, $\log(\lambda^{-1} M_L) = 2.720$, and $\log(\lambda^2 M_L) = -1.500$ for the case of the bromocyclohexane solutions and with $\lambda d_b = 0.07$, $\log(\lambda^{-1} M_L) = 2.760$, and $\log(\lambda^2 M_L) = -1.580$ for the case

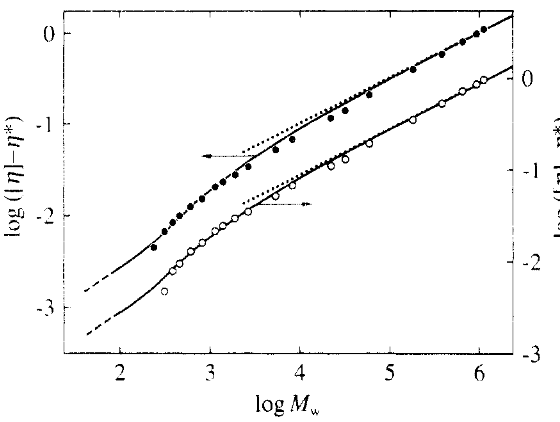

Figure 6. Double-logarithmic plots of $[\eta] - \eta^*$ (in dL/g) against M_w for PDMS: ○, in bromocyclohexane at 29.5 °C ($\eta^* = -0.012$ dL/g); ●, in MEK at 20.0 °C ($\eta^* = 0$). The solid curves represent the respective best-fit HW theoretical values for $N \geq 2$, with each dashed line segment connecting the values for $N = 1$ and 2.

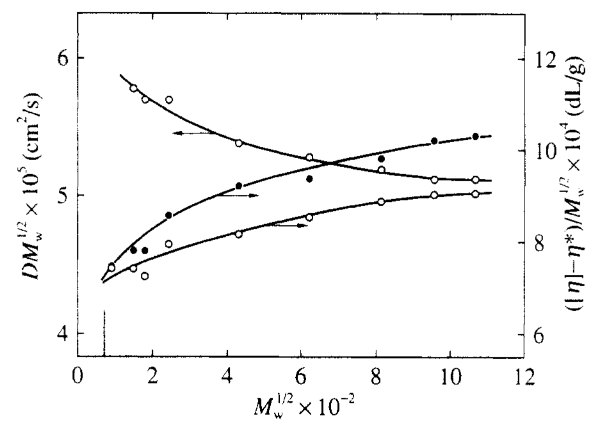

Figure 7. Plots of $DM_w^{1/2}$ and $([\eta] - \eta^*)/M_w^{1/2}$ against $M_w^{1/2}$ for PDMS: ○, in bromocyclohexane at 29.5 °C ($\eta^* = -0.012$ dL/g); ●, in MEK at 20.0 °C ($\eta^* = 0$). The vertical line segment indicates the lower bound of M_w above which the HW theoretical values of the ratio $\langle S^2\rangle/M_w$ for PDMS become independent of M_w.

of the MEK solutions. The dashed line segments connect the respective theoretical values for $N = 1$ and 2, and the dotted lines indicate the respective asymptotic straight lines of slope $^1/_2$. As in Figure 5, the theoretical curves may represent the observed values reasonably well, although the former are less significantly S-shaped than the latter. The values of the model parameters thus determined for PDMS in bromocyclohexane and MEK are listed in the second and third rows of Table V, respectively.

HW Model Parameters. In Table V are summarized the values of the HW model parameters determined for PDMS. For comparison, it also includes the results obtained similarly for a-PS (with the fraction of racemic diads $f_r = 0.79$),[19,27,28] a-PMMA (with $f_r = 0.79$),[26] and PIB.[16] The three sets of values of λ^{-1}, M_L, and d_b for PDMS are rather in good agreement with one another. Any of its values of M_L is somewhat smaller than the value 25.5 Å^{-1} corresponding to the chain fully extended to the all-*trans* conformation. The radius ρ and pitch h of its characteristic helix are estimated from the values of $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, and λ^{-1} to be ca. 11 and 0 Å, respectively. The former is considerably large compared to that of a-PS and almost comparable in magnitude to that of a-PMMA,[29] indicating that the PDMS chain in dilute solution assumes the local conformation with retention of large helical portions as suggested before.[1] It is important to see that the value of λ^{-1} for PDMS is almost comparable to that for a-PS and significantly larger than that for PIB, although smaller than that for a-PMMA. Thus it may be said that the PDMS chain is rather stiff in a static sense, in contradiction to the common notion as mentioned in the Introduction.

The values of d_b obtained from D and $[\eta]$ for PDMS in bromocyclohexane are nearly close to each other. This result may justify the above treatment of $[\eta]$ in which η^* is incorporated to consider the specific interactions between solute and solvent molecules. It is also important to see from the table that the value of d_b for PDMS is appreciably small compared to those of the other polymers. This indicates that the PDMS chain behaves hydrodynamically as a very thin chain. The chemical structure of the repeat unit of PDMS is similar to that of PIB, the $Si(CH_3)_2$ group and O atom of the former corresponding to the $C(CH_3)_2$ and CH_2 groups of the latter, respectively. Although the difference between the O atom and CH_2 group in size may possibly cause a slight decrease in the mean hydrodynamic thickness of the PDMS chain compared to the PIB chain, the former may be expected to have almost the same value of d_b as the latter. In contradiction to this expectation, however, the value of d_b of the former is only about one-third of that of the latter. The difference may partly arise from that between the two chains in the preferred local chain conformation such that the PDMS chain prefers the all-*trans* conformation, while the PIB chain takes the conformation close to the 8_3 helix, as deduced from the values of M_L and as discussed previously.[16] Note that the HW chain contour is taken along the successive Si (or O) atoms for the former in the all-*trans* conformation and along the helix axis for the latter. Thus the effective hydrodynamic thickness of the former around the HW contour may be considered to be smaller than that of the latter. Further, from Figures 5 and 6, the single bead of the HW touched-bead model is found to correspond to about half of the repeat unit of the PDMS chain. On the other hand, in the case of PIB, the single bead corresponds to its three successive repeat units or so. Another possible and more important source of the small d_b for PDMS may be that the hydrodynamic nonslip boundary condition on the bead surface cannot necessarily be valid for this chain. Finally, we note that Bohdanecký et al.[30] have also obtained the small diameter for this chain from an analysis of transport data on the basis of the wormlike cylinder model,[31] and given a similar discussion.

Draining Effects. Figure 7 shows plots of $DM_w^{1/2}$ and $([\eta] - \eta^*)/M_w^{1/2}$ against $M_w^{1/2}$. The unfilled and filled circles represent the experimental values in bromocyclohexane at 29.5 °C and in MEK at 20.0 °C, respectively, and the solid curves connect the data points smoothly. The vertical line segment indicates the value of M_w above which the HW theoretical values of $\langle S^2\rangle/M_w$ calculated with the model parameters listed in Table V become almost independent of M_w. It is seen that $DM_w^{1/2}$ increases and $([\eta] - \eta^*)/M_w^{1/2}$ decreases with decreasing M_w even in the range of M_w where the static property such as $\langle S^2\rangle$ exhibits the Gaussian coil behavior in the unperturbed state. Since the Θ temperature has been unambiguously determined for the bromocyclohexane solutions of PDMS, we may conclude that this anomalous behavior should be regarded as the so-called *draining effect* as far as the bromocyclohexane solutions are concerned. As has usually been the case, by the term draining effect, we simply mean that, for flexible polymers at Θ, the ratio $[\eta]/M_w^{1/2}$ decreases from a constant value with decreasing M_w. (We note, however, that, in general, $[\eta]/M_w^{1/2}$ or $([\eta] - \eta^*)/M_w^{1/2}$ deviates either downward or upward from the asymptotic constant with decreasing M_w, depending on the value of the ratio d_b/λ^{-1}.) In this connection, we note that Edwards et al.[32]

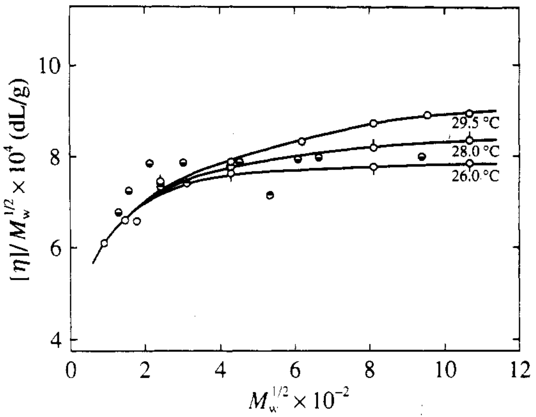

Figure 8. Plots of $[\eta]/M_w^{1/2}$ against $M_w^{1/2}$ for PDMS in bromocyclohexane: ○, present data at 29.5 °C; ȯ, present data at 28.0 °C; ọ, present data at 26.0 °C; ◒, data at 28.0 °C by Zilliox et al.[9]; ◓, data at 28.0 °C by Horská et al.[10]

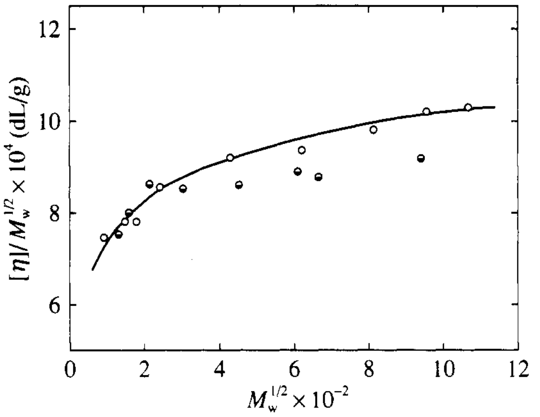

Figure 9. Plots of $[\eta]/M_w^{1/2}$ against $M_w^{1/2}$ for PDMS in MEK at 20.0 °C: ○, present data; ◒, data by Zilliox et al.[9]

have claimed that the draining effect exists for short PDMS chains. However, their results are quite different from ours, showing that $DM_w^{1/2}$ is independent of M_w for $M_w > 800$ ($x_w > 10$).

In order to clarify the confusing situation of the literature results for $[\eta]$ stated in the Introduction, the present data (unfilled circles) for PDMS in bromocyclohexane at 29.5, 28.0, and 26.0 °C are plotted in the form of $[\eta]/M_w^{1/2}$ vs $M_w^{1/2}$ in Figure 8 and compared with those obtained at 28.0 °C by Zilliox et al.[9] and by Horská et al.[10] The results of Semlyen et al.[7,8] are not included, since they are limited to the range of relatively small M_w. The data points by Zilliox et al. follow a horizontal line for $M_w \gtrsim 5 \times 10^4$ but exhibit an unnatural break at $M_w \simeq 5 \times 10^4$. One of the two values by Horská et al. is small compared to the others, although they claim that $[\eta]/M_w^{1/2}$ is constant at 28.0 °C. Thus they regard the temperature 28.0 °C as the (hydrodynamical) Θ point according to the common notion as far as the above data are concerned. Although this Θ temperature was first reported by Haug and Meyerhoff[13] and has often been used, we do not know the reason why it is preferred to the Θ temperature 29.0 °C determined by Schultz et al.[14,15] (including Haug himself) from SLS measurements. In contrast to the above data, the present results show that the ratio $[\eta]/M_w^{1/2}$ still exhibits the draining effect at 28.0 °C and becomes almsot independent of M_w at 26.0 °C at least in the range of $M_w > 1.8 \times 10^5$. Thus we may say that the "Θ behavior" of $[\eta]$ is observed at a temperature definitely different from the one at which A_2 vanishes, for the bromocyclohexane solution.

In Figure 9 are compared the present data for $[\eta]$ in MEK at 20.0 °C with those obtained by Zilliox et al.[9] Their data again exhibit an abnormal break in $[\eta]/M_w^{1/2}$ at $M_w \simeq 5 \times 10^4$. They are systematically lower than ours for $M_w \gtrsim 5 \times 10^4$. However, both show that $[\eta]/M_w^{1/2}$ depends on M_w over the whole range of M_w examined. In summary, we may conclude that the "Θ behavior" of $[\eta]$ of PDMS cannot be observed at the Θ temperature defined thermodynamically and that this arises from the draining effect.

Concluding Remarks

We have been able to determine separately the static stiffness parameter λ^{-1} and the shift factor M_L for PDMS from the analyses of the data for D and $[\eta]$ in the Θ solvents. With them combined with the values of the other model parameters, the HW theory may well explain the observed molecular-weight dependence of D and $[\eta]$. The value of λ^{-1} obtained for PDMS is almost the same as that for a-PS, indicating that the PDMS chain is not so flexible as expected from the bulk properties, e.g., the glass transition temperature and the bulk modulus. These quantities reflect the mobility of rather small portions of polymer chains in the bulk, so that they depend not only on the kinetics of those portions but also on the interactions with the surrounding chains. Then they do not necessarily have direct correlation with the *static* stiffness, as mentioned in the Introduction, nor with the *dynamic* stiffness as defined from the correlation times for, for instance, dielectric and magnetic relaxation and fluorescence depolarization for the single polymer chain.[33] Previously, we have shown semiempirically that for a variety of flexible polymer chains, such as polyether, polyvinyl, and α-substituted polyvinyl chains, there exists a rather strong positive correlation between these two kinds of chain stiffness.[33] Thus, considering their values of λ^{-1}, the PDMS chain might be expected to have the dynamic stiffness of the same order of magnitude as the a-PS chain, although the chemical structure of PDMS is different from those of the above polymers. Unfortunately, however, any data that enable us to estimate the dynamic stiffness of this kind of the PDMS chain are not available at present.

The negative $[\eta]$ observed for the oligomer samples in bromocyclohexane may well be treated according to the procedure proposed in the previous study.[16] The value of the bead diameter d_b thus determined from $[\eta]$ is rather in good agreement with that determined from D, justifying the validity of the procedure employed for the analysis of $[\eta]$. The value of d_b thus determined is found to be appreciably small compared to those for the other flexible polymers studied in our laboratory. It is for the first time that the so-called *draining effect* has been found in the present (and previous[12]) work for a typical flexible polymer like PDMS. The analysis of such data on the basis of the HW transport theory leads inevitably to small values of λd_b and d_b. Considering the fact that the theory has worked rather well for a number of polymers, we must accept the present result for d_b of PDMS as real. Its smallness suggests that the nonslip boundary condition on the bead surface may break down for this chain. This indicates that its intermolecular interactions are rather weak, thus possibly leading to its low glass transition temperature and bulk modulus.

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