On the "Universal Constants" ρ and Φ of Flexible Polymers

Toshiki Konishi, Takenao Yoshizaki, and Hiromi Yamakawa*

Department of Polymer Chemistry, Kyoto University, Kyoto 60601, Japan

Received April 23, 1991; Revised Manuscript Received June 3, 1991

ABSTRACT: The translational diffusion coefficient D, intrinsic viscosity $[\eta]$, and mean-square radius of gyration $\langle S^2 \rangle$ were determined for several high molecular weight samples of atactic polystyrene in cyclohexane at 34.5 °C and in *trans*-decalin at 21.0 °C, of atactic poly(methyl methacrylate) (a-PMMA) in acetonitrile at 44.0 °C and in *n*-butyl chloride at 40.8 °C, of polyisobutylene in isoamyl isovalerate at 25.0 °C, and of poly(dimethylsiloxane) (PDMS) in bromocyclohexane at 29.5 °C, all these temperatures being the respective Θ temperatures. With the data obtained, the ratio ρ of $\langle S^2 \rangle^{1/2}$ to the hydrodynamic radius defined from D and the ratio (Flory–Fox factor) Φ of the hydrodynamic volume defined from $[\eta]$ to $\langle S^2 \rangle^{3/2}$ were calculated. The results are the following. For PDMS, ρ decreases and Φ increases with increasing weight-average molecular weight M_w in the range of such large M_w that $\langle S^2 \rangle / M_w$ is independent of M_w, indicating that the so-called "draining effect" exists. For the other polymers, ρ and Φ are independent of M_w in such a range of M_w, as was expected. However, their values (with polydispersity corrections), including the asymptotic values for PDMS, seem rather universal within experimental error except for a-PMMA in acetonitrile. A detailed theoretical discussion of the results is also given.

Introduction

Long ago, Flory[1] presented a version that concerns the universality in steady-state transport processes in dilute polymer solutions. It may be stated as follows: The ratio of the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ to the hydrodynamic radius defined from the translational diffusion coefficient D, now designated by ρ, and also the so-called Flory–Fox factor Φ, now defined as the ratio of the hydrodynamic volume defined from the intrinsic viscosity $[\eta]$ to $\langle S^2 \rangle^{3/2}$, are universal constants for long unperturbed flexible polymer chains (without excluded volume). Here, by "long unperturbed" we mean chains such that the ratio of $\langle S^2 \rangle$ to the molecular weight M is independent of M. This version is consistent with the classical hydrodynamic theories of Kirkwood and Riseman[2,3] and of Zimm[4] for long enough Gaussian chains in the nondraining limit with the preaveraging of hydrodynamic interaction (HI)[5] and has been widely accepted for a long time. However, some objections to it have been presented during the past decade.

On the theoretical side, in 1980 Zimm[6] carried out Monte Carlo evaluation of D and $[\eta]$ for Gaussian chains with nonpreaveraged or fluctuating HI in the rigid-body ensemble approximation and found that the Kirkwood–Riseman–Zimm values[2-4] of ρ and Φ are about 13 and 12% too high, respectively. Subsequently, Fixman[7,8] has derived the decrease in ρ below the Kirkwood value 1.505, depending on the local structure and hence the stiffness of the chain, by introducing constraints on bond lengths and angles, or equivalently internal friction, in the chain with fluctuating HI. Recently, Yamakawa and Yoshizaki[9] have obtained a similar result on the basis of the helical wormlike (HW) chain with partially fluctuating (orientation-dependent) HI.

On the other hand, experimentally, significant advances have been made in the dynamic light scattering technique to facilitate an accurate determination of D. The values of ρ thus found for several polymer–Θ solvent systems[10,11] are about 1.3 and in rather good agreement with Zimm's Monte Carlo value,[6] while the value 1.16 found for atactic poly(methyl methacrylate) (a-PMMA)[12] is considerably small, indicating that ρ is not a universal constant. As for Φ, a vast amount of experimental data have been reported so far, but they are less accurate than those for ρ; the results from different laboratories scatter appreciably even for the same polymer–solvent system. Thus it is difficult to draw a definite conclusion about the nonuniversality of Φ from the literature data. Very recently, however, we have found that the values of Φ for a-PMMA with the fraction of racemic diads $f_r = 0.79$ in two Θ solvents differ by about 9% from each other, the difference being beyond experimental error.[13]

Under these circumstances, it is necessary and important to reexamine experimentally the universality of ρ and Φ on the basis of their values obtained in the same laboratory from static and dynamic light scattering and viscosity measurements for as many polymer–solvent systems as possible, using well-characterized samples for which polydispersity corrections can be made rather accurately. This is the main purpose of the present paper. The polymer–Θ solvent systems we have investigated are the following: atactic polystyrene (a-PS) with $f_r = 0.59$ in cyclohexane at 34.5 °C and in *trans*-decalin at 21.0 °C, a-PMMA with $f_r = 0.79$ in acetonitrile at 44.0 °C and in *n*-butyl chloride at 40.8 °C, polyisobutylene (PIB) in isoamyl isovalerate at 25.0 °C, and poly(dimethylsiloxane) (PDMS) in bromocyclohexane at 29.5 °C. The results indicate clearly the nonuniversality, and a rather detailed theoretical discussion of them is given in the Discussion section.

It is pertinent to make here a preliminary remark on the determination of D from the observed (normalized) autocorrelation function of scattered light intensity $g^{(2)}(t)$. It is usually done from the slope of the plot of $\ln (g^{(2)} - 1)$ against t. For large M, because of the coupling between the translational and internal motions of the chain, D in general depends on time t and the plot is slightly concave upward for small t even at small magnitude of the scattering vector. Indeed, this nonlinear region can be observed with a recent dynamic light scattering apparatus with high precision. However, the value of D we desire is the one at an infinitely long time, and therefore we must suppress some data for small t. A criterion for this suppression is also discussed.

Experimental Section

Materials. The four a-PS samples used in this work are those obtained from the original standard ones F-40, F-80, F-128, and F-288 supplied from Tosoh Co., Ltd. The sample from F-128, which is designated F128-2, is the same as that used before in the determination of f_r,[14] the sample designated F288-a is a fraction separated from F-288 by fractional precipitation, and the remaining two were obtained from F-40 and F-80 by reprecipitation just for purification. These three original samples may be regarded as having the same value of f_r (=0.59) as F-128 and also those used in previous studies,[14-16] since they were synthesized by the same method (anionic polymerization with *n*-butyllithium as an initiator). For the sake of confirmation, f_r of F-40 was determined from ^{13}C NMR and found to be 0.58. The spectrum was taken for its 1,2-dichlorobenzene solution containing benzene-d_6 for a signal lock at 120 °C as before by the use of a JEOL JNM GX-400 spectrometer. The standard sample F-20 was also used only for the determination of the refractive index increment.

The three a-PMMA samples used in this work are the same as those used in the studies of $\langle S^2\rangle$[17] and $[\eta]$,[13] i.e., the fractions separated by fractional precipitation from the original samples prepared by radical polymerization.

Three of the four PIB samples used, PIB40, PIB80, and PIB180, are the same as those used in the study of $[\eta]$,[18] i.e., the fractions from the commercial samples of Enjay Chemical Co., named Vistanex L-80 and L-200. The remaining additional one is another fraction from L-80.

Four of the five PDMS samples used, PDMS20, PDMS40, PDMS70, and PDMS110, are the same as those used in the studies of the mean-square electric dipole moment[19] and transport coefficients,[20] which are fractions from the commercial samples of Toshiba Silicone Co., Ltd., named TEF451-50M and TSE200A. The remaining additional one is another fraction from TSE200A.

The ratio of the *z*-average molecular weight M_z to the weight-average molecular weight M_w and that of $M_w{}^{1/2}$ to the weight-average square-root molecular weight $(M^{1/2})_w$, both of which are necessary for polydispersity corrections, were determined by analytical gel permeation chromatography (GPC).

The solvents *trans*-decalin (Tokyo Kasei Kogyo Co.; 99% purity), isoamyl isovalerate (IAIV) (Tokyo Kasei Kogyo Co.; 99% purity), and bromocyclohexane (Tokyo Kasei Kogyo Co.; 98% purity) used for static and dynamic light scattering (SLS and DLS) and viscosity measurements were purified by distillation under reduced pressure in a dried nitrogen atmosphere. Before the distillation, *trans*-decalin was first dried with calcium chloride anhydride and then passed through a silica gel column, IAIV was dried with potassium carboxide anhydride, and bromocyclohexane was dried with sodium carboxide anhydride. The purity of each solvent after distillation was examined by gas chromatography, and it was found to contain no detectable impurity (i.e., the cis component for *trans*-decalin, isoamyl alcohol and/or isovaleric acid for IAIV, and cyclohexanol for bromocyclohexane). The treatment of purified *trans*-decalin required special care, since the residual water, if any, has great influences on solution properties. In order to keep its quality unchanged during the course of all measurements, the whole amount of purified *trans*-decalin was once stocked in a flask after distillation and then divided into small amounts necessary for each measurement to reserve in sealed flasks filled with dried nitrogen gas.

The other solvents cyclohexane, acetonitrile (CH_3CN), and *n*-butyl chloride (*n*-BuCl) used for SLS, DLS, and viscosity measurements and benzene for SLS measurements were purified according to standard procedures. The solvent 1,2-dichlorobenzene and the internal signal lock reagent benzene-d_6 used for NMR measurements were of reagent grade.

Static Light Scattering. SLS measurements were carried out to determine M_w and the *z*-average mean-square radius of gyration $\langle S^2\rangle_z$ for all the a-PS samples in cyclohexane at 34.5 °C (Θ) and the three of them with the lowest M_w in *trans*-decalin at Θ, for the additional PIB sample ($M_w = 6.34 \times 10^5$) in IAIV at 25.0 °C (Θ), and for the additional PDMS sample ($M_w = 9.14 \times 10^5$) in bromocyclohexane at 29.5 °C (Θ) and also to determine the Θ temperature of *trans*-decalin solutions of a-PS. We also determined M_w for the two a-PS samples with the lowest M_w in benzene (at 25.0 °C). For the determination of Θ, the second virial coefficient A_2 was measured for three a-PS samples at several temperatures ranging from 17 to 35 °C.

A Fica 50 light scattering photometer was used for all the measurements with vertically polarized incident light of wavelength 436 nm as before.[18] The data obtained were analyzed by the Berry square-root plot.[21] For the present cases, corrections for optical anisotropy were unnecessary.

The most concentrated solutions of the samples were prepared by continuous stirring in the dark at ca. 50 °C for 7 days for a-PS in cyclohexane, at ca. 50 °C for 4 days for a-PS in *trans*-decalin, at room temperatures for 1 day for a-PS in benzene, at ca. 50 °C for 3 days for PIB in IAIV, and at 35–40 °C for 15 h for PDMS in bromocyclohexane. (Complete dissolution of each polymer was confirmed from flow times.) These solutions were optically purified by filtration through a Teflon membrane of pore size 0.45 μm. (From flow times, the filtration was confirmed to cause neither change in polymer concentration nor chain scission.) All solutions of lower concentrations were obtained by sequential dilution. The weight concentrations of test solutions were determined gravimetrically and converted to mass concentrations c by the use of the densities of the solvents.

The values of the solvent density we used are 0.7653 g/cm^3 for cyclohexane at 34.5 °C, 0.8691 g/cm^3 for *trans*-decalin at 21.0 °C, 0.8737 g/cm^3 for benzene at 25.0 °C, 0.8504 g/cm^3 for IAIV at 25.0 °C, and 1.3236 g/cm^3 for bromocyclohexane at 29.5 °C, and also the values of the refractive index we used for them at a wavelength of 436 nm are 1.428, 1.480, 1.520, 1.420, and 1.503, respectively.

The refractive index increment $\partial n/\partial c$ was measured at 436 nm for the a-PS standard sample F-20 in *trans*-decalin at 21.0 °C (Θ) (see the Results section) by the use of a Shimadzu differential refractometer and was determined to be 0.138 cm^3/g. The values of $\partial n/\partial c$ we used for the other polymer–solvent systems are 0.181 cm^3/g for a-PS in cyclohexane at 34.5 °C,[22] 0.110 cm^3/g for PIB in IAIV at 25.0 °C,[18] and −0.094 cm^3/g for PDMS in bromocyclohexane at 29.5 °C.[20]

Dynamic Light Scattering. DLS measurements were carried out to determine D for the three a-PS samples with the lowest M_w in cyclohexane at 34.5 °C and in *trans*-decalin at 21.0 °C, for the two a-PMMA samples with the lowest M_w in CH_3CN at 44.0 °C and in *n*-BuCl at 40.8 °C, for the three PIB samples with the lowest M_w in IAIV at 25.0 °C, and for all the five PDMS samples in bromocyclohexane at 29.5 °C (all these temperatures being the respective Θ temperatures).

For all measurements, we used a Brookhaven Instruments Model BI-200SM light scattering goniometer with vertically polarized incident light of wavelength 488 nm 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 (PMT) used was an EMI 9863B/350, the output of which was processed by a Brookhaven Instruments Model BI2030AT autocorrelator with 264 channels. The dark count was 300–500 cps for the operation at room temperatures. In order to monitor the dark count automatically, the detector alignment was equipped with an electric shutter before the PMT. It was also equipped with a diffusing filter just before the shutter. The normalized autocorrelation function $g^{(2)}(t)$ of scattered light intensity $I(t)$, i.e.

$$g^{(2)}(t) = \langle I(0)\, I(t)\rangle / \langle I(0)\rangle^2 \qquad (1)$$

was measured at four or five different concentrations and at scattering angles ranging from 30 to 150°.

Test solutions were prepared in the same manner as in the case of SLS measurements except for the a-PMMA samples. The most concentrated solution of each of them in CH_3CN was prepared by continuous stirring in the dark at ca. 50 °C for 1 day. Preparation of that in *n*-BuCl required much care, and this was done according to the procedure described previously.[13] The values of the solvent density we then used for the determination of c are 0.7557 g/cm^3 for CH_3CN at 44.0 °C and 0.8637 g/cm^3 for *n*-BuCl at 40.8 °C.

Now the correlation function $g^{(2)}(t)$ experimentally determined at infinite dilution is related to the dynamic structure factor $S(k,t)$, which is defined as the Fourier transform of the autocorrelation function of the polymer segment density function, by the equation

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

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

Table I
Values of M_w, M_z/M_w, and $M_w^{1/2}/(M^{1/2})_w$ for Atactic Polystyrene, Atactic Poly(methyl methacrylate), Polyisobutylene, and Poly(dimethylsiloxane) Samples

polymer (f_r)	sample code	$10^{-6}M_w$	solvent	M_z/M_w	$M_w^{1/2}/(M^{1/2})_w$
a-PS (0.59)	F40	0.359	cyclohexane	1.01	1.00
		0.367	*trans*-decalin		
	F80	0.732	cyclohexane	1.01	1.00
		0.703	*trans*-decalin		
	F128-2	1.32	cyclohexane	1.03	1.01
		1.29	*trans*-decalin		
	F288-a	3.52	cyclohexane	1.03	1.00
a-PMMA (0.79)	Mr4	0.361	CH_3CN	1.06	1.01
		0.347	*n*-BuCl		
	Mr8	0.758	CH_3CN	1.04	1.01
		0.783	*n*-BuCl		
	Mr28	2.83	CH_3CN		
		2.83	*n*-BuCl		
PIB	PIB40	0.422	IAIV	1.08	1.01
	PIB60	0.634		1.05	1.01
	PIB80	0.819		1.09	1.01
	PIB180	1.76			
PDMS	PDMS20	0.185	bromocyclohexane	1.05	1.01
	PDMS40	0.386		1.06	1.01
	PDMS70	0.660		1.07	1.01
	PDMS90	0.914		1.07	1.01
	PDMS110	1.14		1.08	1.01

light in the solvent. The constant term on the right-hand side of eq 2 arises from the finiteness of the scattering volume and detector area and also of the sampling time, and it vanishes for an ideal scattering apparatus with vanishing scattering volume and detector area and with vanishing sampling time. The second term may be written in the form

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

for such small k that k^{-1} is much greater than the average polymer chain dimension.

As explicitly shown in eq 4, the translational diffusion coefficient D in general depends on t for the chain having internal degrees of freedom. After all the internal motions relax away, $D(t)$ becomes a constant independent of t. It is what we desire and is designated by $D(\infty)$. Except for very small t, eq 2 with eq 4 may then be rewritten in the form

$$\frac{1}{2}\ln\,[g^{(2)}(t) - 1] = \text{constant} - At \qquad (5)$$

A similar equation holds at finite concentrations c unless c is large. Thus the desired $D(\infty)$ may be determined from

$$D(\infty) \equiv D = \lim_{\substack{k\to 0\\ c\to 0}} A/k^2 \qquad (6)$$

with the values of A obtained from the plots of the quantity on the right-hand side of eq 5 against t for various values of k and c according to eq 5 (see the Results section).

The values of the refractive index we used at a wavelength of 488 nm are 1.424 for cyclohexane at 34.5 °C, 1.476 for *trans*-decalin at 21.0 °C, 1.337 for CH_3CN at 44.0 °C, 1.397 for *n*-BuCl at 40.8 °C, 1.415 for IAIV at 25.0 °C, and 1.499 for bromocyclohexane at 29.5 °C. The values of the viscosity we used for them to calculate ρ from D are 0.768, 2.07, 0.285, 0.362, 1.33, and 1.97 cP, respectively. We note that the former values were calculated from interpolation of those at wavelengths of 436 and 546 nm and that the latter values except for cyclohexane were determined from flow times using the literature values for this solvent as a standard.

Viscosity. Viscosity measurements were carried out for all the a-PS samples in cyclohexane at 34.5 °C and the three of them with the lowest M_w in *trans*-decalin at 21.0 °C, for the additional PIB sample ($M_w = 6.34 \times 10^5$) in IAIV at 25.0 °C, and for the additional PDMS sample ($M_w = 9.14 \times 10^5$) in bromocyclohexane at 29.5 °C (all these temperatures being again the respective Θ temperatures). For the measurements, we used two viscometers of the Ubbelohde type and two specially designed (four-bulb) spiral capillary viscometers 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 measurements. In the measurements for PIB in IAIV and PDMS in bromocyclohexane, the surface of the water in a thermostat was covered with liquid paraffin to remove the possible effects of moisture. 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, except for the case of PIB in IAIV, for which the solution and solvent had the same density independent of c within experimental error. The solution density was measured with a picnometer of the Lipkin–Davison type; the values were available from the previous measurements except for a-PS in *trans*-decalin.

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 $[\eta]$. However, the case of a-PS in cyclohexane requires a remark. In this case, both the plots were concave upward at very low concentrations, indicating that adsorption of polymer molecules on the capillary wall occurred. Thus we used the spiral capillary viscometer of a larger capillary diameter (1.2 mm) and carried out measurements at higher concentrations (0.001–0.009 g/cm^3) for a-PS than for the other polymers in order to minimize the effect of the adsorption.

Results

Molecular Weights and Their Distributions. The values of M_w, M_z/M_w, and $M_w^{1/2}/(M^{1/2})_w$ for all the samples used in this work are given in Table I. The values of these two ratios for the a-PMMA and PIB samples with the highest M_w, i.e., Mr28 and PIB180, could not be determined with sufficient accuracy because of the lack of the GPC calibration curve in the necessary range. The values of M_w for each sample of a-PS and a-PMMA in their respective two Θ solvents are in good agreement with each other. We note that, for the a-PS samples F40 and F80, those also agree well with the values 3.57×10^5 and 7.23×10^5 in benzene, respectively. Polydispersity corrections for ρ and Φ are made in a later subsection with the values of the above two ratios in the fifth and sixth columns of the table, although they indicate that the molecular weight distributions of the samples are rather sufficiently narrow.

Θ Temperature of *trans*-Decalin Solutions of a-PS. Figure 1 shows plots of A_2M_w against temperature for the three a-PS samples F40, F80, and F128-2 in *trans*-decalin. It is seen that A_2 vanishes nearly at the same temperature independent of M_w, leading to the conclusion that the Θ temperature is 21.0 °C for *trans*-decalin solutions of a-PS with $f_r = 0.59$. This value of Θ is to be compared with the literature values: 21.3 °C by Berry et al.,[21] 23.8 °C by Inagaki et al.,[23] 20.4 °C by Fukuda et al.,[24] 21.2 °C by

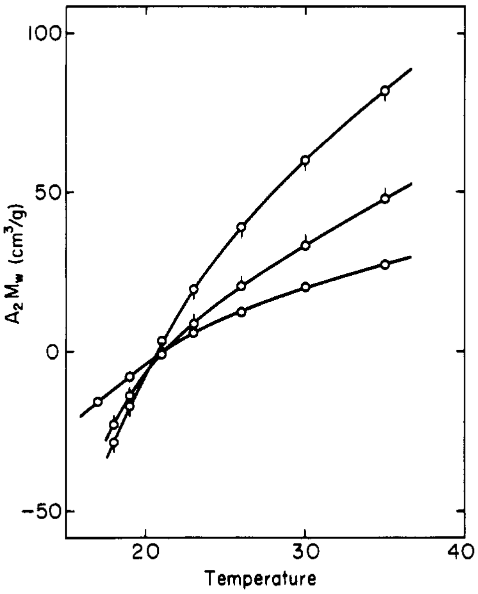

Figure 1. Plots of A_2M_w against temperature for a-PS samples in *trans*-decalin: ○, F40; ȯ, F80; ϙ, F128-2.

Nakata et al.,[25] 20.5 °C by Nose and Chu,[26] and 23.0 °C by Nakamura et al.[27] The results are seen to scatter rather appreciably. This had first led us to choose diethyl malonate as another Θ solvent (other than cyclohexane) for a-PS, which solutions had already been studied by Orofino and Mickey[28] and by Bohdanecký and Berek.[29] However, for this system, we had found that the flow time had become shorter and shorter during viscosity measurements and concluded, from the analytical GPC diagram for the recovered sample, that chain scission had occurred. Finally, therefore, we chose *trans*-decalin as another Θ solvent despite the scatter of the literature values of Θ, which may be regarded as arising partly from the possible small difference in solvent quality.

Mean-Square Radius of Gyration. The values of $\langle S^2\rangle_z$ and $\langle S^2\rangle_z/M_w$ for all the samples are given in the second and third columns of Table II, respectively. The values for all the a-PMMA samples in CH_3CN and in *n*-BuCl have been reproduced from refs 17 and 13, respectively, those for the PIB samples PIB40, PIB80, and PIB180 are the unpublished results already obtained in the determination of their M_w,[18] and those for the PDMS samples PDMS40, PDMS70, and PDMS110 are the results for which the details are reported elsewhere.[20] For each system, the ratio $\langle S^2\rangle_z/M_w$ is seen to be almost independent of M_w in its range studied, so that the chain may be regarded as long enough for the present discussion of ρ and Φ. It is also seen that the values for this ratio for a-PS are definitely larger in cyclohexane than in *trans*-decalin, and similarly those for a-PMMA are slightly larger in CH_3CN than in *n*-BuCl, indicating that the unperturbed chain dimension depends more or less on solvent.

Now we should compare the present results for $\langle S^2\rangle_z/M_w$ with its literature values. It is well-known that the Zimm plot tends to overestimate it, and therefore we cite only the values determined from the Berry square-root plot as adopted here.

For a-PS in cyclohexane, the value 7.78×10^{-18} cm^2 as the mean of the present values is somewhat larger than the corresponding value 7.6×10^{-18} cm^2 by Berry[21] but definitely smaller than the value 8.4×10^{-18} cm^2 determined long ago in our laboratory[30] and also the values 8.31×10^{-18} cm^2 by Miyaki et al.[22] and 8.33×10^{-18} cm^2 by Miyaki.[31] However, a comparison of the present estimate with our previous one and Berry's may be inappropriate since the procedures of calibrating light scattering photometers are different. The difference between our present and Miyaki's values[31] is probably due to the difference in molecular weight distribution. (Indeed, these two values agree with each other to within 1% after polydispersity corrections.) The value 8.31×10^{-18} cm^2 by Miyaki et al.,[22] which was determined by the "asymptote" method,[32] is the monodisperse value the ratio would have if the sample were completely monodisperse, and therefore it must, in general, be smaller than values for polydisperse samples, but it is larger than the present and even some of his own polydisperse values.[31] This is unphysical and indicates that the asymptote method is not valid, probably because of the breakdown of the Debye scattering function for the a-PS chain.

For a-PS in *trans*-decalin, the value 7.39×10^{-18} cm^2 as the mean of the present values is smaller than the corresponding values 7.6×10^{-18} cm^2 by Berry,[21] 7.86×10^{-18} cm^2 by Fukuda et al.,[24] and 9.48×10^{-18} cm^2 by Nose and Chu.[26] A comparison with Berry's value may again be inappropriate. The difference between the present value and that by Fukuda et al. is probably due to the difference in molecular weight distribution. The reason for the relatively large value by Nose and Chu is not clear. At any rate, it should be noted that the experimental accuracy is worse for a-PS in *trans*-decalin than in cyclohexane.

For a-PMMA in *n*-BuCl, recall that our values are remarkably larger than those by Schulz and Kirste.[33] The possible reason for this was already discussed.[13,17] For PIB in IAIV, which had been studied also by Matsumoto et al.,[34] we do not cite their result since their Θ temperature is ca. 3 °C lower than ours. For PDMS, a comparison is made elsewhere.[20]

Translational Diffusion Coefficient. Figure 2 shows a plot of $(1/2)\ln[g^{(2)}(t) - 1]$ against t for the data for the a-PS sample F80 in cyclohexane at 34.5 °C, which were obtained at the lowest concentration c ($=4.095 \times 10^{-4}$ g/cm^3) and at the smallest scattering angle θ ($=30°$). It is seen that $g^{(2)}(t)$ can be determined with sufficient accuracy at such a low concentration. For this case, the value of $\langle S^2\rangle_z k^2$ calculated with the value of $\langle S^2\rangle_z$ given in Table II is 0.0521 and is much smaller than unity. For such small $\langle S^2\rangle_z k^2$, the relaxation due to internal motions of the chain is in general difficult to observe, and then the plot is expected to follow a straight line. However, the plot obtained is seen to be slightly concave upward for $t < 0.05$ ms, and, indeed, this may be regarded as arising from the dependence of D on t due to the coupling between the translational and internal motions of the chain.

Thus, for the determination of $D(\infty)$, we must adopt data only at such large t that the internal motions have relaxed away. For convenience, we chose as an appropriate lower limit of such t the time $10\tau_1$, where τ_1 is the relaxation time of the first normal mode for the Gaussian chain, i.e., the spring-bead (SB) model, and is given in the nondraining limit by[4,5]

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

with η_0 the solvent viscosity, R the gas constant, T the absolute temperature, and λ_1' the corresponding reduced eigenvalue. With the Zimm value 4.04 of λ_1',[5,35] we have $\tau_1 = 6.8\ \mu$s for the present case. In the figure, the arrow indicates the value of $t = 10\tau_1$, and the solid line is a best fit straight line with the value 1403 s^{-1} of A determined by the least-squares method for the data for $t > 10\tau_1$. We note that the data for $t < 10\tau_1$ give the value 1576 s^{-1} of A, which is ca. 12% larger than the above value.

Figure 3 shows plots of values of A/k^2 thus determined against k^2 for the same system as above, the points

Table II

Values of $\langle S^2\rangle_z$, $\langle S^2\rangle_z/M_w$, D_z, $D_zM_w^{1/2}$, $[\eta]$, and $[\eta]/M_w^{1/2}$ for Atactic Polystyrene, Atactic Poly(methyl methacrylate), Polyisobutylene, and Poly(dimethylsiloxane) Samples in Θ Solvents

sample code	$10^{12}\langle S^2\rangle_z$, cm²	$10^{18}\langle S^2\rangle_z/M_w$, cm²	$10^7 D_z$, cm²/s	$10^4 D_zM_w^{1/2}$, cm²/s	$[\eta]$, cm³/g	$10^2[\eta]/M_w^{1/2}$, cm³/g
			a-PS/Cyclohexane (34.5 °C)			
F40	2.79	7.77	2.25	1.35	51.2	8.55
F80	5.78	7.90	1.57	1.34	73.4	8.58
F128-2	10.2	7.73	1.17	1.34	98.1	8.54
F288-a	27.1	7.70			162	8.63
			a-PS/*trans*-Decalin (21.0 °C)			
F40	2.61	7.11	0.812	0.492	47.3	7.81
F80	5.25	7.47	0.585	0.490	64.5	7.69
F128-2	9.78	7.58	0.425	0.483	91.2	8.03
			a-PMMA/CH_3CN (44.0 °C)			
Mr4	2.43	6.74	6.84	4.11	33.3	5.54
Mr8	5.02	6.62	4.73	4.12	47.3	5.43
Mr28	18.9	6.69			96.2	5.72
			a-PMMA/*n*-BuCl (40.8 °C)			
Mr4	2.25	6.48	5.25	3.09	34.1	5.79
Mr8	5.11	6.52	3.58	3.17	52.7	5.96
Mr28	18.6	6.56			100	5.94
			PIB/IAIV (25.0 °C)			
PIB40	4.25	10.1	1.06	0.689	70.9	10.9
PIB60	6.10	9.62	0.855	0.681	88.2	11.1
PIB80	8.06	9.84	0.752	0.681	99.8	11.0
PIB180	17.2	9.77			146	11.0
			PDMS/Bromocyclohexane (29.5 °C)			
PDMS20			1.25	0.538	33.9	7.88
PDMS40	3.39	8.78	0.850	0.528	51.8	8.34
PDMS70	5.85	8.86	0.639	0.519	70.9	8.73
PDMS90	8.31	9.09	0.536	0.512	85.1	8.90
PDMS110	10.0	8.77	0.480	0.512	95.4	8.94

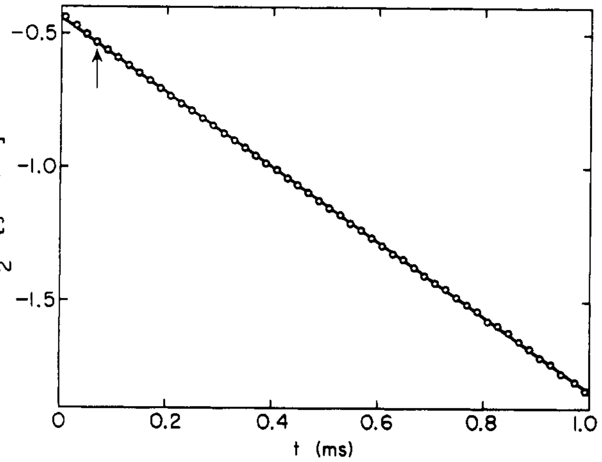

Figure 2. Plot of (1/2) ln $[g^{(2)}(t) - 1]$ against t for a-PS sample F80 in cyclohexane at 34.5 °C (c = 4.095 × 10^{-4} g/cm³, θ = 30°). The arrow indicates $t = 10\tau_1$, and the straight line has a slope of $-A$.

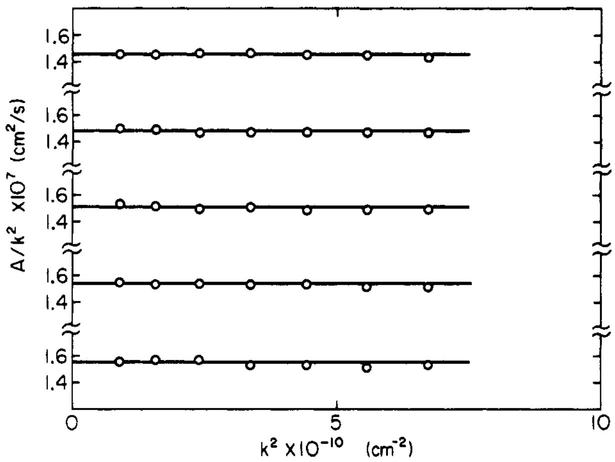

Figure 3. Plots of A/k^2 against k^2 for a-PS sample F80 in cyclohexane at 34.5 °C. The polymer mass concentrations c are 1.714 × 10^{-3}, 1.402 × 10^{-3}, 1.064 × 10^{-3}, 6.685 × 10^{-4}, and 4.095 × 10^{-4} g/cm³ from top to bottom.

representing the values at c = 1.714 × 10^{-3}, 1.402 × 10^{-3}, 1.064 × 10^{-3}, 6.685 × 10^{-4}, and 4.095 × 10^{-4} g/cm³ from top to bottom. In the range of k^2 displayed, A/k^2 is seen to be almost independent of k, so that we adopt as the value of $(A/k^2)_{k=0}$ at each finite c the mean value represented by the horizontal line. Then the values of $(A/k^2)_{k=0}$ at finite c are extrapolated to $c = 0$ in order to evaluate D at $c = 0$ from the ordinate intercept. Figure 4 shows such plots for the three a-PS samples indicated in cyclohexane at 34.5 °C. Similarly, we have been able to determine D for all the systems with sufficient accuracy. The value of D thus determined is the z average, which we designate by D_z as usual.

The values of D_z and $D_zM_w^{1/2}$ are given in the fourth and fifth columns of Table II, respectively. For large M_w ($\langle S^2\rangle_z k^2 \gtrsim 1$), the contribution of internal motions to $g^{(2)}(t)$ is so large that the plot as in Figure 2 becomes linear only at large t and the determination of its slope A is very difficult. Thus we have not determined D for the samples F288-a, Mr28, and PIB180. It is seen that $D_zM_w^{1/2}$ is independent of M_w except for PDMS, for which it decreases with increasing M_w. A comparison of the present results with literature values is made later with respect to ρ.

Intrinsic Viscosity. The values of $[\eta]$ and $[\eta]/M_w^{1/2}$ for all the samples are given in the sixth and seventh columns of Table II, respectively. The former values for all the a-PMMA samples and the PIB samples PIB40, PIB80, and PIB180 have been reproduced from refs 13 and 18, respectively, and those for the PDMS samples PDMS20, PDMS40, PDMS70, and PDMS110 are the results for which the details are reported elsewhere.[20] It is seen that $[\eta]/M_w^{1/2}$ is independent of M_w except for PDMS, for which it increases with increasing M_w, that the values of $[\eta]$ for a-PS are definitely larger in cyclohexane

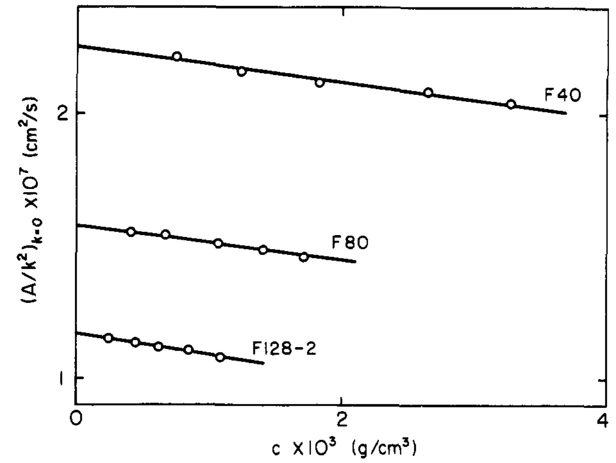

Figure 4. Plots of $(A/k^2)_{k=0}$ against c for the a-PS samples indicated in cyclohexane at 34.5 °C.

than in *trans*-decalin as in the case of $\langle S^2\rangle_z$, and that the values of $[\eta]$ for a-PMMA are smaller in CH$_3$CN than in n-BuCl, although the values of its $\langle S^2\rangle_z$ in these two Θ solvents do not differ very appreciably. A comparison of the present results with literature values is made later with respect to Φ.

ρ and Φ. The factors ρ and Φ are explicitly defined as

$$\rho = \langle S^2\rangle^{1/2}/R_H \qquad (8)$$

$$\Phi = V_H/\langle S^2\rangle^{3/2} \qquad (9)$$

In eq 8, R_H is the hydrodynamic radius defined from D as

$$R_H = k_B T/6\pi\eta_0 D \qquad (10)$$

with k_B the Boltzmann constant, and in eq 9, V_H is the hydrodynamic volume defined from $[\eta]$ as

$$V_H = M[\eta]/6^{3/2} \qquad (11)$$

The values of ρ and Φ calculated from eqs 8–11 with the values of $\langle S^2\rangle_z$, D_z, and $[\eta]$ obtained are given in the second and third columns of Table III, respectively. No appreciable dependence of them on M_w is seen except for PDMS.

Now we make polydispersity corrections to the above values of ρ and Φ for a quantitative discussion. Their corrected (monodisperse) values, which we designate by ρ(cor'd) and Φ(cor'd), respectively, may be calculated from

$$\rho(\text{cor'd}) = [M_w/(M^{1/2})_w M_z^{1/2}]\rho \qquad (12)$$

$$\Phi(\text{cor'd}) = [M_z^{3/2}/(M^{1/2})_w M_w]\Phi \qquad (13)$$

In the derivation of these equations, we have assumed that $\langle S^2\rangle$, D, and $[\eta]$ for homogeneous polymers are proportional to M, $M^{-1/2}$, and $M^{1/2}$, respectively, and used the relation $(M^{-1/2})_z = (M^{1/2})_w/M_w$ and also the fact that the observed value of $[\eta]$ for a polydisperse sample is the weight average. Although D_z and $[\eta]$ are not exactly proportional to $M_w^{-1/2}$ and $M_w^{1/2}$, respectively, for PDMS, as noted above, the effects may be regarded as small. The values of ρ(cor'd) and Φ(cor'd) calculated from eqs 12 and 13 with the values of M_z/M_w and $M_w^{1/2}/(M^{1/2})_w$ listed in Table I are given in the fourth and fifth columns of Table III, respectively. It is seen that the correction is larger for Φ than for ρ (as is well-known) and also that there is no appreciable dependence on M_w of ρ(cor'd) and Φ(cor'd) except for PDMS. Thus, except for it, we adopt their mean values as the values for long unperturbed chains, which we designate particularly by ρ_∞ and Φ_∞, respectively.

Table III
Values of ρ, Φ, ρ(cor'd), and Φ(cor'd) for Atactic Polystyrene, Atactic Poly(methyl methacrylate), Polyisobutylene, and Poly(dimethylsiloxane) Samples in Θ Solvents

sample code	ρ	$10^{-23}\Phi$, mol^{-1}	ρ(cor'd)	$10^{-23}\Phi$(cor'd), mol^{-1}
		a-PS/Cyclohexane (34.5 °C)		
F40	1.28	2.68	1.27	2.74
F80	1.28	2.63	1.27	2.68
F128-2	1.27	2.70	1.25	2.85
F288-a		2.75		2.88
		a-PS/*trans*-Decalin (21.0 °C)		
F40	1.27	2.80	1.26	2.86
F80	1.29	2.58	1.28	2.63
F128-2	1.28	2.61	1.26	2.76
		a-PMMA/CH$_3$CN (44.0 °C)		
Mr4	1.31	2.15	1.29	2.35
Mr8	1.30	2.17	1.28	2.32
Mr28		2.25		
		a-PMMA/n-BuCl (40.8 °C)		
Mr4	1.24	2.39	1.22	2.61
Mr8	1.28	2.43	1.26	2.59
Mr28		2.41		
		PIB/IAIV (25.0 °C)		
PIB40	1.33	2.33	1.29	2.63
PIB60	1.29	2.52	1.27	2.72
PIB80	1.30	2.43	1.26	2.78
PIB180		2.45		
		PDMS/Bromocyclohexane (29.5 °C)		
PDMS40	1.39	2.18	1.36	2.38
PDMS70	1.38	2.26	1.34	2.54
PDMS90	1.37	2.20	1.34	2.45
PDMS110	1.34	2.34	1.30	2.67

The results are given in the fourth and fifth columns of Table IV except in the last row (for PDMS).

In the case of PDMS, ρ(cor'd) and Φ(cor'd) depend on M_w as well as $D_z M_w^{1/2}$ and $[\eta]/M_w^{1/2}$, and therefore we must evaluate ρ_∞(cor'd) and Φ_∞(cor'd) by extrapolation to $M_w = \infty$. However, this is difficult since the values of ρ(cor'd) and Φ(cor'd) rather scatter. These asymptotic values may instead be obtained more accurately by calculating them from eqs 8–11 with the asymptotic values of $D(\text{cor'd})M_w^{1/2}$ and $[\eta](\text{cor'd})/M_w^{1/2}$ along with the value of $\langle S^2\rangle(\text{cor'd})/M_w$, where the corrected D, $[\eta]$, and $\langle S^2\rangle$ are the respective values for a monodisperse sample having the molecular weight M_w, and may be calculated from

$$D(\text{cor'd}) = [M_w^{1/2}/(M^{1/2})_w]D_z \qquad (14)$$

$$[\eta](\text{cor'd}) = [M_w^{1/2}/(M^{1/2})_w][\eta] \qquad (15)$$

$$\langle S^2\rangle(\text{cor'd}) = (M_w/M_z)\langle S^2\rangle_z \qquad (16)$$

Since it is known that the first-order corrections to the asymptotic forms of D and $[\eta]$ are of order $M^{-1/2}$,[5,36] the above asymptotic values may be obtained by extrapolation to $M_w^{-1/2} = 0$ of plots of $D(\text{cor'd})M_w^{1/2}$ and $[\eta](\text{cor'd})/M_w^{1/2}$ against $M_w^{-1/2}$. This is shown in Figure 5. The results are 5.00×10^{-5} cm²/s and 9.80×10^{-2} cm³/g, respectively. We also have the value 8.29×10^{-18} cm² of $\langle S^2\rangle(\text{cor'd})/M_w$ as the mean of its four values. The values of ρ_∞(cor'd) and Φ_∞(cor'd) thus calculated are given in the last row of Table IV.

It is seen from Table IV that the values of ρ_∞(cor'd) and Φ_∞(cor'd) for a-PS in the two Θ solvents do not differ, while those for a-PMMA definitely differ beyond experimental error. Thus it is concluded that the difference between the values of $[\eta]$ in the two Θ solvents is due to

Table IV
Values of ρ_∞(cor'd) and Φ_∞(cor'd) for Atactic Polystyrene, Atactic Poly(methyl methacrylate), Polyisobutylene, and Poly(dimethylsiloxane) Samples in Θ Solvents

polymer (f_r)	solvent	temp, °C	ρ_∞(cor'd)	$10^{-23}\Phi_\infty$(cor'd), mol^{-1}
a-PS (0.59)	cyclohexane	34.5	1.26 ± 0.01	2.79 ± 0.08
	trans-decalin	21.0	1.27 ± 0.01	2.75 ± 0.09
a-PMMA (0.79)	CH_3CN	44.0	1.29 ± 0.02	2.34 ± 0.06
	n-BuCl	40.8	1.24 ± 0.02	2.60 ± 0.06
PIB	IAIV	25.0	1.27 ± 0.01	2.71 ± 0.06
PDMS	bromocyclohexane	29.5	1.28 ± 0.02	2.79 ± 0.04

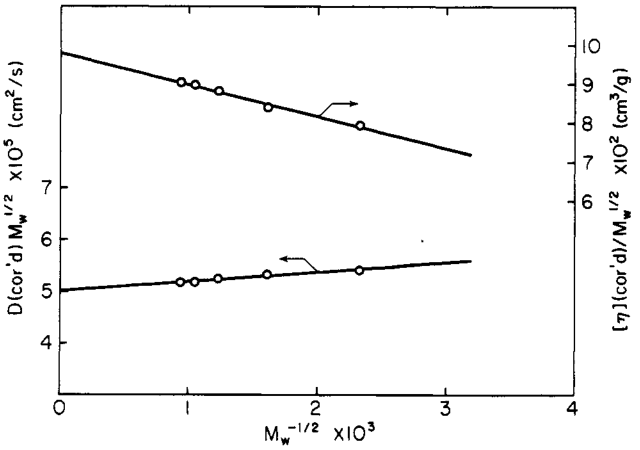

Figure 5. Plots of D(cor'd)$M_w^{1/2}$ and $[\eta]$(cor'd)$/M_w^{1/2}$ against $M_w^{-1/2}$. The data points (unfilled circles) are extrapolated to $M_w^{-1/2} = 0$ following the respective straight lines.

the difference in $\langle S^2\rangle_z$ for a-PS but to that in Φ for a-PMMA. (For the latter, $\langle S^2\rangle_z$ is somewhat larger in CH_3CN than in *n*-BuCl, although $[\eta]$ is smaller in CH_3CN.)

Finally, we compare the present results with literature values. For a-PS, the value of ρ_∞(cor'd) in cyclohexane agrees well with the value 1.27 by Schmidt and Burchard,[10] and that in *trans*-decalin also agrees well with the value 1.28 by Tsunashima et al.[37] but not with the value 1.43 by Nose and Chu.[26] The value of Φ_∞(cor'd) in cyclohexane is ca. 10% larger than the corresponding value 2.55 × 10^{23} by Miyaki et al.[22] This difference is mainly due to the difference in $\langle S^2\rangle$(cor'd), as mentioned in the previous subsection. For a-PMMA in *n*-BuCl, the value of ρ_∞(cor'd) is rather close to those for the other polymers but appreciably larger than the value 1.16 by ter Meer et al.[12] This difference may be regarded as arising from the fact that the Θ temperature 34.5 °C adopted by them, which was determined by Schulz and Kirste,[33] is lower than ours, as discussed previously.[13]

Discussion

Nonuniversality. In this paper, we have reexamined experimentally the Flory version concerning the universality in polymer transport processes. The results are summarized as follows.

First, in the case of PDMS, there is dependence of $DM^{1/2}$ and $[\eta]/M^{1/2}$ on M even for such a long unperturbed chain that $\langle S^2\rangle/M$ is independent of M; ρ decreases and Φ increases with increasing M in such a range of M. This behavior of ρ and Φ is nothing else than the so-called "draining effect" in the Kirkwood–Riseman language,[2] and it may possibly be observed for hydrodynamically thin chains, or more exactly for the case of the small ratio of the chain diameter to the chain stiffness.[36,38] Indeed, the PDMS chain is hydrodynamically thin, as shown later, and we believe that this is the first clear observation of the draining effect for flexible chains. Second, however, the values of ρ_∞ and Φ_∞ for the four polymers studied seem universal within experimental error except for a-PMMA in CH_3CN, as seen from Table IV. For this polymer, ρ and Φ clearly depend on the kind of Θ solvent. In this connection, we note that Hirao et al.[39] have recently reported a similar dependence of Φ on solvent for poly(1-phenyl-1-propyne) in cyclohexane at 36 °C (Θ) and in toluene at 25 °C.

Theoretical Discussion. Now we give a theoretical discussion of the above results. The molecular weight dependence of ρ and Φ as observed in the case of PDMS may be explained theoretically in terms of the draining effect as mentioned above. Therefore, attention is given to the asymptotic values ρ_∞ and Φ_∞, and in this subsection, we suppress the subscript ∞, for simplicity.

We first consider ρ. The theory of ρ recently developed[9] on the basis of the discrete HW chain[40] with (partially) fluctuating HI is suitable for the present discussion, and it is therefore convenient to begin by giving its brief description. Consider the chain composed of N identical rigid subbodies, each with translational and rotatory friction coefficients ζ_t and ζ_r, connected with fixed bond length a. Suppose that they are located on the continuous HW chain contour of total length L, which is defined in terms of the four model parameters: the constant curvature κ_0 and torsion τ_0 of its characteristic helix, the stiffness parameter λ^{-1}, and the shift factor $M_L = M/L$.[40,41] For sufficiently large N, ρ may then be expressed as[9]

$$\rho = \rho^{(Z)}(1 - \delta_0 - \delta_1) \tag{17}$$

where $\rho^{(Z)}$ is the Zimm value with preaveraged HI; i.e.[4]

$$\rho^{(Z)} = 1.479 \tag{18}$$

δ_0 is the relative decrease in ρ below $\rho^{(Z)}$ at $t = 0$ due to the constraints,[40] and δ_1 is the additional relative decrease at $t = \infty$ due to the coupling between the translational and internal motions. The correction term δ_0 has been found to be very small (~0.02 at most) and almost independent of the HW model parameters above and also of ζ_t and ζ_r and has been simply put $\delta_0 = 0.02$. The term δ_1 is given by

$$\delta_1 = 0.2635 r_1 a (c_\infty N \lambda^{-1} \Delta s)^{-1/2} \sum_{k=1}^{N} S_k (\lambda_k^{B})^{-1} \tag{19}$$

with $\Delta s = L/N = M/M_L N$ and with

$$r_1 = \zeta_t / 3\pi\eta_0 a \tag{20}$$

$$c_\infty = [4 + (\lambda^{-1}\tau_0)^2]/[4 + (\lambda^{-1}\kappa_0)^2 + (\lambda^{-1}\tau_0)^2] \tag{21}$$

where we note that a is uniquely related to Δs. In eq 19, the factor S_k represents the magnitude of the coupling between the translational and kth internal modes, and λ_k^B is the (approximate) kth eigenvalue of the mobility tensor multiplied by ζ_t. Recall that λ_k^B is a function of the HW model parameters and also ζ_t, but we do not reproduce their explicit forms, for simplicity. Thus the theory predicts that ρ is not a universal constant since δ_1 depends on the HW model parameters even in the limit of $N \to \infty$. Its HW theoretical values are calculated later.

Table V
Values of the HW Model Parameters for Atactic Polystyrene, Atactic Poly(methyl methacrylate), Polyisobutylene, and Poly(dimethylsiloxane)

polymer (f_r)	solvent	temp, °C	$\lambda^{-1}\kappa_0$	$\lambda^{-1}\tau_0$	λ^{-1}, Å	M_L, Å^{-1}	d_b, Å
a-PS (0.59)	cyclohexane	34.5	3.0[a]	6.0[a]	22.5[b]	36.7[b]	10.1[c]
	trans-decalin	21.0	(3.0)	(6.0)	21.4	(36.7)	(10.1)
a-PMMA (0.79)	CH_3CN	44.0	4.0[d]	1.1[d]	57.9[d]	36.3[d]	7.2[e]
	n-BuCl	40.8	4.0[d]	1.1[d]	57.9[d]	36.3[d]	7.9[e]
PIB	IAIV	25.0	0[f]		12.7[f]	24.1[f]	6.4[f]
PDMS	bromocyclohexane	29.5	2.6[g]	0[g]	25.5[h]	20.6[h]	2.0[h]

[a] See ref 14. [b] See ref 16. [c] See ref 15. [d] See ref 17. [e] See ref 13. [f] See ref 18. [g] See ref 19. [h] See ref 20.

For the SB model with (partially) fluctuating HI, we have also derived a similar expression for ρ,[9] which is given by eq 17 with $\delta_0 = 0$ and with

$$\delta_1 = 0.2635 r_1 N^{-1/2} \sum_{k=1}^{N} S_k (\lambda_k^{\mathrm{B}})^{-1} \text{ (SB)} \tag{22}$$

where r_1 is given by eq 20 but with the effective bond length a and with the translational friction coefficient ζ_t of the bead and λ_k^{B} is a function of r_1. If the Stokes law is assumed for ζ_t, we have $r_1 = d_b/a$ with d_b the diameter of the bead. Then δ_1 becomes a function of d_b/a, so that ρ is again not a universal constant even for the SB model (Gaussian chain) with large N.

Next we consider Φ. Its theoretical evaluation has not been carried out as yet on the basis of the HW chain with fluctuating HI. However, this has already been done by Fixman and Pyun[42,43] on the basis of the SB model. In the zeroth order (or diagonal) approximation, which is good enough for the present discussion, their result may be written in the form

$$\Phi = (3\pi)^{-1/2} N_A h \sum_{k=1}^{N} \{k^2 + (4h/\pi^2)[I_1(k) + I_2(k)]\}^{-1} \text{ (SB)} \tag{23}$$

where N_A is Avogadro's number, h is the draining parameter defined by

$$h = (3N/4\pi)^{1/2} r_1 \tag{24}$$

and $I_1(k)$ is given by

$$I_1(k) = \pi k^{1/2}\left[\pi k C(\pi k) - \frac{1}{2}S(\pi k)\right] \tag{25}$$

with $S(x)$ and $C(x)$ the Fresnel integrals defined by

$$\begin{Bmatrix} S \\ C \end{Bmatrix}(x) = (2\pi)^{-1/2}\int_0^x t^{-1/2}\begin{Bmatrix} \sin \\ \cos \end{Bmatrix} t \, dt \tag{26}$$

In eq 23, $I_2(k)$ is also a function only of k and represents the contribution arising from the fluctuating part of HI, but we do not reproduce its explicit form, for simplicity. We note that, if I_2 is suppressed, eq 23 gives Φ in the Hearst version.[44] For very large N, the relative contribution of terms with large k to the sum of eq 23 is small, and only several with small k make a contribution to Φ. The term k^2 may then be neglected compared to the term $(4h/\pi^2)(I_1 + I_2)$, and Φ becomes independent of h, i.e., d_b/a. Thus Φ is a universal constant for the Gaussian chain in the limit of $N \to \infty$ in contrast to ρ.

It is then instructive to rewrite eq 22 for δ_1 for the SB model in the Fixman–Pyun notation and compare it with eq 23 for Φ. If we use the expression for λ_k^{B} in the Hearst version, it reads

$$\delta_1 = 0.2635(4\pi/3)^{1/2}\pi^2 h \sum_{k=1}^{N} (S_k/N^3)[k^2 + (4h/\pi^2) I_1(k)]^{-1} \text{ (SB)} \tag{27}$$

where $I_1(k)$ is given by eq 25. Equation 27 is similar to eq 23 in form except for the factor S_k/N^3, but because of this factor, the relative contribution of terms with large k to the sum of eq 27 remains finite in the limit of $N \to \infty$, so that δ_1 depends on d_b/a.

From the above discussion, it is now clear that the observed nonuniversality of Φ for a-PMMA cannot be explained theoretically on the basis of the Gaussian chain and even of the HW chain, if the HW theory is completed, as far as we take the limit of $N \to \infty$. A possible explanation is the following. There may be a balance between the local chain conformation and hydrodynamic chain thickness (relative to λ^{-1}), leading to the apparent constancy of Φ, although not universal, over a wide range of large and finite M. (Recall that Φ increases with increasing M for very thin chains.) Unfortunately, however, it is almost impossible to evaluate Φ for finite N on the basis of the HW chain with fluctuating HI. We only note that the situation (low Φ) for a-PMMA in CH_3CN may be similar to that in the case of stiff chains. (See the Concluding Remarks section.)

Comparison with the HW Theoretical Values for ρ_∞. Having shown theoretically that ρ_∞ is not a universal constant, it is interesting to make a comparison of its observed values with the HW theoretical ones. The values of the HW model parameters necessary for this theoretical calculation are listed in Table V. For a-PS in cyclohexane, λ^{-1} and M_L were determined from $\langle S^2 \rangle$[16] using the values of $\lambda^{-1}\kappa_0$ and $\lambda^{-1}\tau_0$ from the mean-square optical anisotropy,[14] and d_b was determined from $[\eta]$.[15] For a-PS in *trans*-decalin, we have the experimental data only for $\langle S^2 \rangle$ for very high molecular weight samples. Thus, assuming that all the model parameters other than λ^{-1} are independent of solvent and therefore that the ratio of λ^{-1} in *trans*-decalin to that in cyclohexane is identical with the corresponding ratio of $\langle S^2 \rangle$, we have calculated the value of λ^{-1} in *trans*-decalin using the respective mean values 7.39×10^{-18} and 7.78×10^{-18} cm^2 of $\langle S^2 \rangle_z / M_w$ in these solvents. For a-PMMA, the parameters other than d_b were determined from $\langle S^2 \rangle$ in CH_3CN[17] and d_b was determined from $[\eta]$ in the two Θ solvents.[13] For PIB, all the parameters were determined from $[\eta]$.[18] For PDMS, the values of λ^{-1}, M_L, and d_b are those determined from $[\eta]$[20] using the values of $\lambda^{-1}\kappa_0$ and $\lambda^{-1}\tau_0$ from the mean-square electric dipole moment.[19] (The PDMS chain is seen to be very thin, having small d_b, as already noted.)

The theoretical values of ρ_∞ calculated from eqs 17–21 with the HW model parameters in Table V are given in Table VI along with the observed values. We note that we have taken account of the effect of hydrodynamic chain thickness by simply putting the parameter r_1 equal to the ratio of d_b of each polymer to that of a-PS (10.1 Å); i.e., $r_1 = 0.713$ for a-PMMA in CH_3CN, 0.782 for a-PMMA in *n*-BuCl, 0.634 for PIB, and 0.198 for PDMS, assuming $r_1 = 1$ for a-PS.

It is seen that the theoretical values are larger than the observed ones but do not appreciably differ from each other. This is consistent with the experimental results except for a-PMMA. For this polymer, the theory again fails to explain the appreciable difference between the

Table VI
Comparison with the HW Theoretical Values for ρ_∞

polymer (f_r)	solvent	temp, °C	ρ_∞ obsd	ρ_∞ calcd
a-PS (0.59)	cyclohexane	34.5	1.26	1.35
	trans-decalin	21.0	1.27	1.35
a-PMMA (0.79)	CH_3CN	44.0	1.29	1.34
	n-BuCl	40.8	1.24	1.34
PIB	IAIV	25.0	1.27	1.36
PDMS	bromocyclohexane	29.5	1.28	1.37

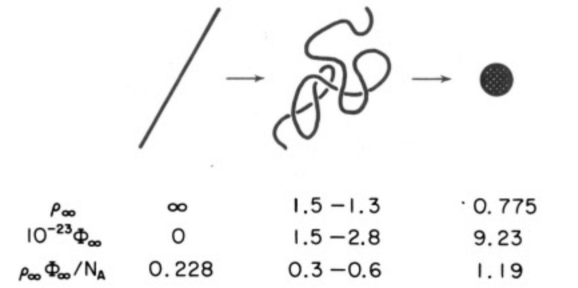

Figure 6. Conformational change from a long rod to a sphere through a random coil with their values of ρ_∞, Φ_∞, and $\rho_\infty\Phi_\infty/N_A$.

observed values in the two solvents; the situation may be similar to that in the case of Φ.

Concluding Remarks

We have shown that ρ_∞ and Φ_∞ are not necessarily universal for a-PMMA, which is stiff-chain-like (with relatively large λ^{-1}). Thus it is interesting to examine their dependence on the global chain conformation. Figure 6 illustrates the conformational change from a long rigid rod to a rigid sphere through a random coil with their values of ρ_∞, Φ_∞, and $\rho_\infty\Phi_\infty/N_A$. For the rod, these values have been calculated from the expressions for D and $[\eta]$ without the preaveraging of the HI tensor[5] with the relation $\langle S^2\rangle = L^2/12$, and for the sphere, they have been calculated from the Stokes and Einstein formulas with the relation $\langle S^2\rangle = 3d^2/20$ with d the diameter. For the random coil, the possible ranges of observed values are given. The upper bound for ρ_∞ corresponds to the case of typical stiff chains like poly(*n*-hexyl isocyanate) (PHIC) and DNA, for which we have previously[9] estimated ρ_∞ using the experimental data obtained by Murakami et al.,[45] by Record et al.,[46] and by Godfrey and Eisenberg.[47] (For stiff chains, the theoretical ρ_∞ is equal to $\rho^{(Z)}$.[9]) The lower bound corresponds to the case of flexible chains including the present ones. On the other hand, the lower bound for Φ_∞ corresponds to the result for PHIC[45] and the upper bound to the case of flexible chains. It is seen that the changes in ρ_∞, Φ_∞, and $\rho_\infty\Phi_\infty$ are consistent with the conformational change above, the change of the product $\rho_\infty\Phi_\infty$ being rather insensitive. It is also important to note that, for stiff chains (in the coil limit), Φ_∞ is small ($\sim 1.5 \times 10^{23}$) and does not seem to have reached its true asymptotic limit.

The fact that Φ_∞ for a-PMMA in CH_3CN is smaller than those for the other (flexible) polymers may cast some doubt that there is intra- and/or intermolecular association. However, if so, the global conformation becomes close to the sphere, and the scheme of Figure 6 tells us that Φ_∞ must then be larger than ca. 2.8×10^{23}. Thus this possibility may be denied. (The good agreement between M_w's in the two Θ solvents and a good solvent denies intermolecular association.[13,17])

Acknowledgment. This research was supported in part by a Grant-in-Aid (01430018) from the Ministry of Education, Science, and Culture, Japan.

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter XIV.
(2) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(3) Kirkwood, J. G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 649; *J. Polym. Sci.* **1954**, *12*, 1.
(4) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(5) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(6) Zimm, B. H. *Macromolecules* **1980**, *13*, 592.
(7) Fixman, M. *J. Chem. Phys.* **1984**, *80*, 6324; **1986**, *84*, 4085.
(8) Fixman, M. *Faraday Discuss.* **1987**, *No. 83*, 199; *J. Chem. Phys.* **1988**, *89*, 2442.
(9) Yamakawa, H.; Yoshizaki, T. *J. Chem. Phys.* **1989**, *91*, 7900.
(10) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 211 and references cited therein.
(11) Tsunashima, Y.; Hirata, M.; Nemoto, N.; Kajiwara, K.; Kurata, M. *Macromolecules* **1987**, *20*, 2862.
(12) ter Meer, H.-U.; Burchard, W.; Wunderlich, W. *Colloid Polym. Sci.* **1980**, *258*, 675.
(13) Fujii, Y.; Tamai, Y.; Konishi, T.; Yamakawa, H. *Macromolecules* **1991**, *24*, 1608.
(14) Konishi, T.; Yoshizaki, T.; Shimada, J.; Yamakawa, H. *Macromolecules* **1989**, *22*, 1921.
(15) Einaga, Y.; Koyama, H.; Konishi, T.; Yamakawa, H. *Macromolecules* **1989**, *22*, 3419.
(16) Konishi, T.; Yoshizaki, T.; Saito, T.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1990**, *23*, 290.
(17) Tamai, Y.; Konishi, T.; Einaga, Y.; Fujii, M.; Yamakawa, H. *Macromolecules* **1990**, *23*, 4067.
(18) Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules*, in press.
(19) Yamada, T.; Yoshizaki, T.; Yamakawa, H., to be submitted for publication in *Macromolecules*.
(20) Koyama, H.; Yamada, T.; Yoshizaki, T.; Einaga, Y.; Yamakawa, H., to be submitted for publication in *Macromolecules*.
(21) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.
(22) Miyaki, Y.; Einaga, Y.; Fujita, H.; Fukuda, M. *Macromolecules* **1980**, *13*, 588.
(23) Inagaki, H.; Suzuki, H.; Fujii, M.; Matsuo, T. *J. Phys. Chem.* **1966**, *70*, 1718.
(24) Fukuda, M.; Fukutomi, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 871.
(25) Nakata, M.; Higashida, S.; Kuwahara, N.; Saeki, S.; Kaneko, M. *J. Chem. Phys.* **1976**, *64*, 1022.
(26) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590.
(27) Nakamura, Y.; Norisuye, T.; Teramoto, A. *Polym. Prepr., Jpn.* **1990**, *39*, 4019.
(28) Orofino, T. A.; Mickey, J. W., Jr. *J. Chem. Phys.* **1963**, *38*, 2512.
(29) Bohdanecký, M.; Berek, D. *Makromol. Chem., Rapid. Commun.* **1985**, *6*, 275.
(30) Yamamoto, A.; Fujii, M.; Tanaka, G.; Yamakawa, H. *Polym. J.* **1971**, *2*, 799.
(31) Miyaki, Y. Ph.D. Thesis, Osaka University, Osaka, Japan, 1981.
(32) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(33) Schulz, G. V.; Kirste, R. *Z. Phys. Chem.* **1961**, *30*, 171.
(34) Matsumoto, T.; Nishioka, N.; Fujita, H. *J. Polym. Sci., A-2* **1972**, *10*, 23.
(35) Zimm, B. H.; Roe, G. M.; Epstein, L. F. *J. Chem. Phys.* **1956**, *24*, 279.
(36) Yamakawa, H.; Fujii, M. *Macromolecules* **1973**, *6*, 407; **1974**, *7*, 128.
(37) Tsunashima, Y.; Nemoto, N.; Kurata, M. *Macromolecules* **1983**, *16*, 1184.
(38) Yamakawa, H. *J. Chem. Phys.* **1970**, *53*, 436.
(39) Hirao, T.; Teramoto, A.; Sato, T.; Norisuye, T.; Masuda, T.; Higashimura, T. *Polym. J.*, in press.
(40) Yamakawa, H. In *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*; Nagasawa, M., Ed.; Elsevier: Amsterdam, 1988; p 21.
(41) Yamakawa, H. *Annu. Rev. Phys. Chem.* **1984**, *35*, 23.
(42) Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3831.
(43) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3838.
(44) Hearst, J. E. *J. Chem. Phys.* **1962**, *37*, 2547.
(45) Murakami, H.; Norisuye, T.; Fujita, H. *Macromolecules* **1980**, *13*, 345.
(46) Record, M. T., Jr.; Woodbury, C. P.; Inman, R. B. *Biopolymers* **1975**, *14*, 393.
(47) Godfrey, J. E.; Eisenberg, H. *Biophys. Chem.* **1976**, *5*, 301.

Registry No. PS, 9003-53-6; PMMA, 9011-14-7; PIB, 9003-27-4; IAIV, 659-70-1; CH_3CN, 75-05-8; *n*-BuCl, 109-69-3; *trans*-decalin, 493-02-7; bromocyclohexane, 108-85-0; cyclohexane, 110-82-7.