First Cumulant of the Dynamic Structure Factor for Flexible Polymers. Excluded-Volume Effects

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ABSTRACT: The first cumulant $\Omega(k)$ of the dynamic structure factor as a function of the magnitude k of the scattering vector was determined from dynamic light scattering (DLS) measurements for an atactic polystyrene (a-PS) sample with the weight-average molecular weight $M_w = 8.04 \times 10^6$ in toluene at 15.0 °C, an atactic poly(methyl methacrylate) (a-PMMA) sample with $M_w = 1.31 \times 10^7$ in acetone at 25.0 °C, an atactic poly(α-methylstyrene) (a-PαMS) sample with $M_w = 5.46 \times 10^6$ in toluene at 25.0 °C, and a polyisobutylene (PIB) sample with $M_w = 6.63 \times 10^6$ in *n*-heptane at 25.0 °C. It was also determined for the a-PS and a-PαMS samples in cyclohexane in the vicinity of the respective Θ temperatures (34.5 and 30.5 °C). The translational diffusion coefficient D was also determined from DLS measurements for the a-PS, a-PMMA, a-PαMS, and PIB samples in the same solvent conditions mentioned above. From a comparison of the present data with the previous ones for all the samples in the respective Θ temperatures, it is found that the observed dimensionless coefficient C of the k^4-term in the expansion of $\Omega(k)$ does not almost depend on excluded volume, as predicted by the Tanaka–Stockmayer first-order perturbation theory of C, being in good agreement with the theoretical value for the Gaussian chain with nonpreaveraged hydrodynamic interaction. Further, it is found that the excluded-volume effect is very small on the quantity $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ over the whole range of k^2 examined, where $\langle S^2 \rangle$ is the mean-square radius of gyration. Their first-order perturbation theory of the height of the plateau in the k^3-region, however, cannot explain the behavior of the present experimental data. The disagreement between theory and experiment may be regarded as arising from the fact that the theory based on the Gaussian chain model cannot take proper account of effects of chain stiffness and local chain conformation.
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In recent years, we have made a series of experimental studies of effects of chain stiffness and local chain conformation on the first cumulant $\Omega(k)$ of the dynamic structure factor as a function of the magnitude k of the scattering vector for both flexible and semiflexible polymers in the unperturbed (Θ) state.[1–3] It has then been concluded that the universality predicted by the Gaussian chain theory[4–6] for the plot of $\eta_0 \Omega(k)/k_B T k^3$ against $\langle S^2 \rangle^{1/2} k$ cannot be realized for flexible polymers even with very high molecular weights ($\simeq 10^6$–10^7), and that the height of the plateau in the k^3-region depends on chain stiffness and local chain conformation, as predicted by the helical wormlike (HW) chain theory,[7,8] where η_0 is the solvent viscosity, k_B the Boltzmann constant, T the absolute temperature, and $\langle S^2 \rangle$ the mean-square radius of gyration. In this paper, we further proceed to make an experimental study of the excluded-volume effects on $\Omega(k)$.

Now there have been rather many theoretical and experimental investigations on the excluded-volume problem of $\Omega(k)$. On the theoretical side, Benmouna and Akcasu[9,10] first evaluated it for flexible polymers

in good solvents on the basis of the blob model,[11] giving attention to the height of the plateau, and then Tanaka and Stockmayer[12] carried out its conventional first-order perturbation calculation[13] with the use of the Akcasu–Gurol formula.[6] However, most of experimental investigations[14–18] which followed these theoretical ones were motivated by the problem raised by Benmouna and Akcasu concerning the height of the plateau, and overlooked the conclusion derived by Tanaka and Stockmayer that the excluded-volume effect on the dimensionless coefficient C of the k^4-term in the expansion of $\Omega(k)$ is very small. Thus the main purpose of the present paper is to examine experimentally the validity of this interesting prediction. This is compatible with our procedure of analyzing experimental data made so far with respect to the excluded-volume effects on dilute polymer solutions. We also examine the k^3-region.

For the present purpose, we use atactic polystyrene (a-PS), atactic poly(methyl methacrylate) (a-PMMA), atactic poly(α-methylstyrene) (a-PαMS), and polyisobutylene (PIB) samples, each with the highest molecular weight of all used in our previous experimental

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studies. Further, dynamic light scattering (DLS) measurements are carried out not only in good solvents but also in the vicinity of the Θ temperatures for a-PS and a-PαMS.

EXPERIMENTAL

Materials

The a-PS sample F850-a, the a-PMMA sample Mr127, the a-PαMS sample AMS550, and the PIB sample PIB660 are the same as those used in the previous studies of $\Omega(k)$ in their respective Θ solvents.[1,2] The sample F850-a is a fraction separated by fractional precipitation from the original standard sample F850 supplied by Tosoh Co., Ltd., and has the value of the fraction of racemic diads $f_r = 0.59$. The sample Mr127 (with $f_r = 0.79$) is a fraction separated by fractional precipitation from the original sample prepared by radical polymerization in bulk at $60\,°C$ with azobis(isobutyronitrile) as an initiator. The sample AMS550 (with $f_r = 0.70$) is a fraction separated by fractional precipitation from the original sample prepared by living anionic polymerization in tetrahydrofuran with *sec*-butyllithium as an initiator at $-40\,°C$. The sample PIB660 is a fraction separated from the commercial sample of Aldrich Co., named 18,149-8, by the Θ column elution method followed by fractional precipitation.

In Table I are given the values of the weight-average molecular weight M_w previously[1,2,19] determined from static light scattering measurements for the four samples in their respective Θ solvents, *i.e.*, in cyclohexane at $34.5\,°C$ (Θ) for a-PS, in acetonitrile at $44.0\,°C$ (Θ) for a-PMMA, in cyclohexane at $30.5\,°C$ (Θ) for a-PαMS, and in isoamyl isovalerate (IAIV) at $25.0\,°C$ (Θ) for PIB. We note that although the values of the ratio of M_w to the number-average molecular weight M_n for these samples could not be determined from analytical gel permeation chromatography (GPC) with sufficient accuracy because of the lack of the GPC calibration curve in the necessary range of M_w, their molecular weight distribution

Table I. Values of M_w for Polystyrene, Poly(methyl methacrylate), Poly(α-methylstyrene), and Polyisobutylene

Sample	Solvent condition	M_w
a-PS (F850-a)[a]	Cyclohexane, $34.5\,°C$ (Θ)	8.04×10^6
a-PMMA (Mr127)[a]	Acetonitrile, $44.0\,°C$ (Θ)	1.31×10^7
a-PαMS (AMS550)[b]	Cyclohexane, $30.5\,°C$ (Θ)	5.46×10^6
PIB (PIB660)[c]	IAIV, $25.0\,°C$ (Θ)	6.63×10^6

[a]The values of M_w for F850-a and Mr127 have been reproduced from ref 2. [b]The value of M_w for AMS550 has been reproduced from ref 19. [c]The value of M_w for PIB660 has been reproduced from ref 1.

may be considered as narrow ($M_w/M_n \lesssim 1.1$) as other samples previously[1,2] used.

The solvents toluene and cyclohexane for a-PS and a-PαMS, acetone for a-PMMA, and *n*-heptane for PIB were purified according to standard procedures prior to use.

Dynamic Light Scattering

DLS measurements were carried out to determine the translational diffusion coefficient D for F850-a in toluene at $15.0\,°C$, Mr127 in acetone at $25.0\,°C$, AMS550 in toluene at $25.0\,°C$, and PIB660 in *n*-heptane at $25.0\,°C$, and also for F850-a in cyclohexane at various temperatures ranging from 31.0 to $45.0\,°C$ and AMS550 in cyclohexane at 35.0, 40.0, and $45.0\,°C$. Measurements were also carried out to determine $\Omega(k)$ for all the samples in the same solvent conditions as those in the cases of D. For all the measurements, a Brookhaven Instruments model BI-200SM light scattering goniometer was used with vertically polarized incident light of wavelength $\lambda_0 = 488\,nm$ from a Spectra-Physics model 2020 argon ion laser equipped with a model 583 temperature stabilized etalon for a single-frequency-mode operation. The photomultiplier tube used was EMI 9893B/350, the output from which was processed by a Brookhaven Instruments model BI-2030AT or BI-9000AT Digital Correlator. (An electric shutter was attached to the original detector alignment in order to monitor the dark count automatically.) The method of data analysis for D is the same as that described in a previous paper.[20] As for $\Omega(k)$, the CONTIN method[21] was employed as before.[1,2]

For the determination of D for each sample, the normalized autocorrelation function $g^{(2)}(t)$ of the scattered light intensity was measured at five concentrations and at scattering angles θ ranging from 13 to $26°$. For the determination of $\Omega(k)$, $g^{(2)}(t)$ was measured at $\theta = 20, 25, 30, 60, 90, 120,$ and $150°$ for F850-a in toluene and for Mr127 in acetone, at $\theta = 30, 45, 60, 90, 120,$ and $150°$ for AMS550 in toluene and for PIB660 in *n*-heptane, at $\theta = 20, 25, 30, 45, 60, 90, 120,$ and $150°$ for F850-a in cyclohexane, and at $\theta = 30, 45, 60, 90, 120,$ and $150°$ for AMS550 in cyclohexane. These measurements for each sample were carried out at the same concentrations as those in the case of the determination of D. The sampling times adopted for the determination of D were $120–180\,\mu s$ for F850-a in toluene, $50–80\,\mu s$ for Mr127 in acetone, $100\,\mu s$ for AMS550 in toluene and PIB660 in *n*-heptane, $60–150\,\mu s$ for F850-a in cyclohexane, and $100\,\mu s$ for AMS550 in cyclohexane. For the determination of $\Omega(k)$, two measurements with different sampling times were carried out for each solution at each angle in order to cover a wide range of time and to

check its possible dependence on the choice of the sampling time. The sampling times so adopted were 0.3–70 μs for F850-a in toluene, 0.2–50 μs for Mr127 in acetone, 0.5–20 μs for AMS550 in toluene and for PIB660 in n-heptane, 0.5–90 μs for F850-a in cyclohexane, and 0.5–20 μs for AMS550 in cyclohexane.

The most concentrated solutions of the samples were prepared gravimetrically and then made homogeneous by continuous stirring at *ca.* 50 °C for 7–10 d in cyclohexane and for 2–3 d in the good solvents. They were optically purified by filtration through a Teflon membrane of pore size 1.0 μm. The solutions of lower concentrations were obtained by successive dilution, adding the solvents optically purified by filtration through a Teflon membrane of pore size 0.1 μm. The weight concentrations of the test solutions were converted to the polymer mass concentrations c by the use of the densities of the solutions. The values of the refractive index n_0 of the solvent used at a wavelength of 488 nm are 1.514 for toluene at 15.0 °C, 1.361 for acetone at 25.0 °C, 1.506 for toluene at 25.0 °C, 1.390 for n-heptane at 25.0 °C. The values of n_0 for cyclohexane at 488 nm at the required temperatures were calculated with the values of n_0 at 34.5 °C and its temperature coefficient dn_0/dT, *i.e.*, 1.424 and -5.5×10^{-4} deg^{-1},[22] respectively. The values of η_0 used are 0.626 cP for toluene at 15.0 °C, 0.306 cP for acetone at 25.0 °C, 0.552 cP for toluene at 25.0 °C, and 0.392 cP for n-heptane at 25.0 °C. The values of η_0 used for cyclohexane are 0.818, 0.812, 0.799, 0.786, 0.768, 0.761, 0.748, 0.726, 0.704, and 0.653 cP at 30.5, 31.0, 32.0, 33.0, 34.5, 35.0, 36.0, 38.0, 40.0, and 45.0 °C, respectively.

RESULTS

Translational Diffusion Coefficient

The values of D determined in this study are given in the third column of Table II along with those previously determined for a-PS in cyclohexane at 34.5 °C (Θ),[2] a-PMMA in acetonitrile at 44.0 °C (Θ),[2] a-PαMS in cyclohexane at 30.5 °C (Θ),[1] and PIB in IAIV at 25.0 °C (Θ).[1] For later convenience, in its fourth column are also given the values of $\langle S^2 \rangle^{1/2}$ previously determined for a-PS[2] in cyclohexane at 34.5 °C (Θ) and in toluene at 15.0 °C, a-PMMA[2] in acetonitrile at 44.0 °C (Θ) and in acetone at 25.0 °C, a-PαMS[19] in cyclohexane at 30.5 °C (Θ) and in toluene at 25.0 °C, and PIB[1] in IAIV at 25.0 °C (Θ) and in n-heptane at 25.0 °C.

First Cumulant

The first cumulant $\Omega(k)$ (as a function of the magnitude k of the scattering vector) defined as the initial

Table II. Values of D and $\langle S^2 \rangle$ for Polystyrene, Poly(methyl methacrylate), Poly(α-methylstyrene), and Polyisobutylene

Sample	Solvent	Temp. (°C)	$10^8 D$ (cm^2/s)	$10^{-2} \langle S^2 \rangle^{1/2}$ (Å)
a-PS (F850-a)	Cyclohexane	31.0	4.8$_4$	
		32.0	4.7$_3$	
		33.0	4.6$_9$	
		34.5 (Θ)	4.6$_6$[a]	8.2$_2$[a]
		36.0	4.6$_5$	
		38.0	4.7$_0$	
		40.0	4.7$_4$	
		45.0	5.0$_0$	
	Toluene	15.0	3.2$_8$	15.$_3$[b]
a-PMMA (Mr127)	Acetonitrile	44.0 (Θ)	11.$_2$[a]	9.3$_9$[a]
	Acetone	25.0	6.2$_6$	16.$_4$[b]
a-PαMS (AMS550)	Cyclohexane	30.5 (Θ)	5.7$_4$[c]	6.0$_9$[d]
		35.0	5.8$_9$	
		40.0	6.1$_2$	
		45.0	6.4$_7$	
	Toluene	25.0	5.1$_2$	11.$_4$[d]
PIB (PIB660)	IAIV	25.0 (Θ)	2.6$_7$[c]	8.0$_0$[c]
	n-Heptane	25.0	6.1$_3$	12.$_8$[e]

[a] The values of D and $\langle S^2 \rangle^{1/2}$ for a-PS in cyclohexane at 34.5 °C (Θ) and for a-PMMA in acetonitrile at 44.0 °C (Θ) have been reproduced from ref 2. [b] The values of $\langle S^2 \rangle^{1/2}$ for a-PS in toluene at 15.0 °C and for a-PMMA in acetone at 25.0 °C were determined in ref 2, although they were not reported there. [c] The value of D for a-PαMS in cyclohexane at 30.5 °C (Θ) and those of D and $\langle S^2 \rangle^{1/2}$ for PIB in IAIV at 25.0 °C (Θ) have been reproduced from ref 1. [d] The values of $\langle S^2 \rangle^{1/2}$ for a-PαMS in cyclohexane at 30.5 °C (Θ) and in toluene at 25.0 °C have been reproduced from ref 19. [e] The value of $\langle S^2 \rangle^{1/2}$ for PIB in n-heptane at 25.0 °C was determined in ref 1, although it was not reported there.

decay rate of the dynamic structure factor $S(k,t)$ (as a function of k and time t), *i.e.*, $\Omega(k) \equiv -[d \ln S(k,t)/dt]_{t=0}$ may be written in terms of the normalized autocorrelation function $g^{(2)}(t)$ of the scattered light intensity observed in DLS measurements as follows,

$$\Omega(k) = -\left[\frac{d}{dt} \left\{ \frac{1}{2} \ln[g^{(2)}(t) - 1] \right\} \right]_{t=0} \quad (1)$$

We note that k is related to the scattering angle θ by

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

with $\tilde{\lambda}$ the wavelength of the incident light in the solvent.

As in the case of the previous studies of Ω for flexible and semiflexible polymers,[1–3] the initial slope of $(1/2) \ln[g^{(2)}(t) - 1]$ at each θ for each test solution has been determined by extrapolating the data to $t = 0$ by the use of the Fortran program package CONTIN[21] supplied by Brookhaven Instruments. Then the values of the initial slope so determined at finite concentrations at each θ for each sample have
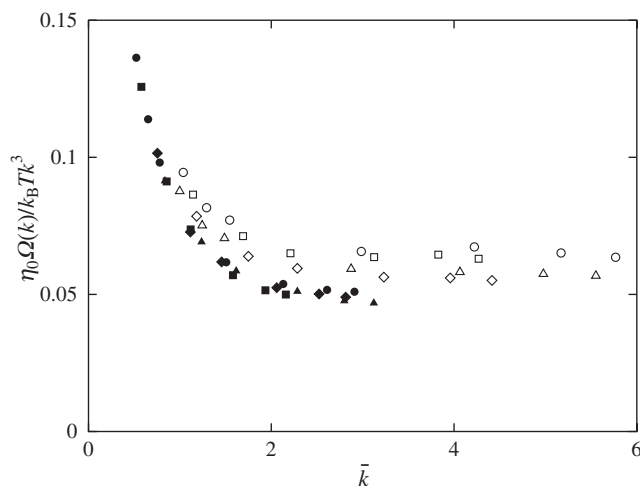
Figure 1. Plots of $\eta_0\Omega(k)/k_B Tk^3$ against the reduced magnitude $\bar{k}$ of the scattering vector for a-PS (circle), a-PMMA (triangle), a-PαMS (square), and PIB (diamond). The unfilled symbols represent the present experimental values in the good solvents: toluene at 15.0 °C, acetone at 25.0 °C, toluene at 25.0 °C, and *n*-heptane at 25.0 °C for a-PS, a-PMMA, a-PαMS, and PIB, respectively. The filled symbols represent the previous experimental values[1,2] in the Θ conditions: cyclohexane at 34.5 °C, acetonitrile at 44.0 °C, cyclohexane at 30.5 °C, and IAIV at 25.0 °C for a-PS, a-PMMA, a-PαMS, and PIB, respectively.

Figure 2. Plots of $\eta_0\Omega(k)/k_B Tk^3$ against the reduced magnitude $\bar{k}$ of the scattering vector for a-PS (circle) and a-PαMS (square), both in cyclohexane, in the vicinity of the respective Θ temperatures. The unfilled circles with pip up, right, down, and left represent the present experimental values for a-PS at 36.0, 38.0, 40.0, and 45.0 °C, respectively, and the filled ones with pip up, right, and down represent those at 33.0, 32.0, and 31.0 °C, respectively. The unfilled squares with pip up, right, and down represent the present experimental values for a-PαMS at 35.0, 40.0, and 45.0 °C, respectively. The filled circles and squares without pip have the same meaning as those in Figure 1, *i.e.*, a-PS in cyclohexane at 34.5 °C (Θ) and a-PαMS in cyclohexane at 30.5 °C (Θ), respectively.
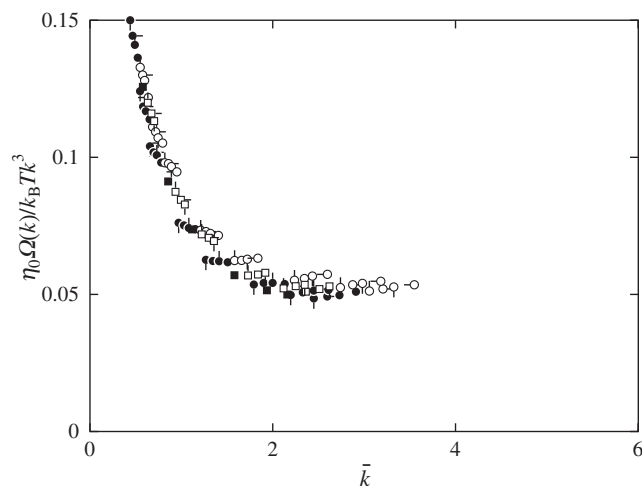
been linearly extrapolated to $c = 0$ to determine Ω at infinite dilution.

Figure 1 shows plots of $\eta_0\Omega(k)/k_B Tk^3$ against the reduced magnitude $\bar{k}$ of the scattering vector defined by

$$\bar{k} \equiv \langle S^2 \rangle^{1/2} k \qquad (3)$$

i.e., the so-called universal plots. The unfilled circles, triangles, squares, and diamonds represent the present experimental values for a-PS in toluene at 15.0 °C, a-PMMA in acetone at 25.0 °C, a-PαMS in toluene at 25.0 °C, and PIB in *n*-heptane at 25.0 °C, respectively, and the filled circles, triangles, squares, and diamonds represent the previous ones for a-PS in cyclohexane at 34.5 °C (Θ),[2] a-PMMA in acetonitrile at 44.0 °C (Θ),[2] a-PαMS in cyclohexane at 30.5 °C (Θ),[1] and PIB in IAIV at 25.0 °C (Θ),[1] respectively. In the figure, the values of $\bar{k}$ for the data points have been calculated from eq 3 with the observed values of $\langle S^2 \rangle^{1/2}$ given in the fourth column of Table II. It is seen that the excluded-volume effect moves the data point at given k (or θ) to the lower right for small $\bar{k}$ and to the upper right for large $\bar{k}$, this trend being consistent with the literature data.[14–18]

Figure 2 shows plots of $\eta_0\Omega(k)/k_B Tk^3$ against $\bar{k}$ for a-PS and a-PαMS, both in cyclohexane, in the vicinity of the respective Θ temperatures. The unfilled circles with pip up, right, down, and left represent the present experimental values for a-PS at 36.0, 38.0, 40.0, and

45.0 °C, respectively, and the filled ones with pip up, right, and down represent those at 33.0, 32.0, and 31.0 °C, respectively. The unfilled squares with pip up, right, and down represent the present experimental values for a-PαMS at 35.0, 40.0, and 45.0 °C, respectively. The filled circles and squares without pip represent the previous[1,2] values at the respective Θ temperatures, and have the same meaning as those in Figure 1. In the figure, the values of $\bar{k}$ for the data points at temperatures other than Θ have been calculated from eq 3 with the values of $\langle S^2 \rangle^{1/2}$ evaluated as follows.

We have previously constructed empirical interpolation formulas for the (effective) binary-cluster integral β as a function of T for a-PS[7,23] and a-PαMS,[24] both in cyclohexane, in the vicinity of the respective Θ temperatures, which are given by (β in Å[3])

$$\beta = 72\tau \qquad \text{for } \tau \geq 0$$
$$= 72\tau - 350\tau^2 \quad \text{for } \tau < 0 \quad \text{(a-PS)} \qquad (4)$$

$$\beta = 66\tau \qquad \text{for } \tau \geq 0$$
$$= 66\tau - 830\tau^2 \quad \text{for } \tau < 0 \quad \text{(a-PαMS)} \qquad (5)$$

with

$$\tau = 1 - \Theta/T \qquad (6)$$

We note that the numerical coefficients in eqs 4 have been reestimated from the results in ref 24. With the value of β calculated from the above equations for a-PS or a-PαMS in cyclohexane at given T ($\simeq \Theta$), we may calculate $\langle S^2 \rangle$ from the following HW theory equations[7] with the observed value of $\langle S^2 \rangle_0$ at the Θ temperature given in the fourth column of Table II.

The quantity $\langle S^2 \rangle$ may be written in the form,

$$\langle S^2 \rangle = \langle S^2 \rangle_0 \alpha_S{}^2 \qquad (7)$$

where the gyration-radius expansion factor α_S as a function of the (intramolecular) scaled excluded-volume parameter $\tilde{z}$ may be given by the Domb–Barrett equation[25] for $\tilde{z} \geq 0$ and by the first-order perturbation theory equation[7,13] for $\tilde{z} < 0$,

$$\alpha_S{}^2 = [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15}$$
$$\times [0.933 + 0.067 \exp(-0.85\tilde{z} - 1.39\tilde{z}^2)]$$
$$\text{for } \tilde{z} \geq 0$$
$$= 1 + 1.276\tilde{z} - \cdots \qquad \text{for } \tilde{z} < 0 \quad (8)$$

The parameter $\tilde{z}$ is defined by the (original) excluded-volume parameter z multiplied by a correction factor, *i.e.*,

$$\tilde{z} = \frac{3}{4}K(\lambda L)z \qquad (9)$$

where the coefficient $K(\lambda L)$ as a function of the total contour length L of the HW chain divided by the (static) stiffness parameter λ^{-1} represents the effect of chain stiffness on the intramolecular excluded-volume effect and is given by

$$K(L) = \frac{4}{3} - 2.711L^{-1/2} + \frac{7}{6}L^{-1} \qquad \text{for } L > 6$$
$$= L^{-1/2} \exp(-6.611L^{-1} + 0.9198 + 0.03516L)$$
$$\text{for } L \leq 6 \quad (10)$$

The parameter z is defined in terms of the HW model parameters by

$$z = (3/2\pi)^{3/2}(\lambda B)(\lambda L)^{1/2} \qquad (11)$$

with B the excluded-volume strength defined by

$$B = \frac{\beta}{a^2 c_\infty{}^{3/2}} \qquad (12)$$

where a is the distance between the adjacent beads composing the HW chain, which is usually set equal to the HW contour length corresponding to the repeat unit, *i.e.*, $a = M_0/M_L$ with M_0 the molecular weight of the repeat unit and M_L the shift factor as defined as the molecular weight per unit HW contour length, and c_∞ is defined by

$$c_\infty = \frac{4 + (\lambda^{-1}\tau_0)^2}{4 + (\lambda^{-1}\kappa_0)^2 + (\lambda^{-1}\tau_0)^2} \qquad (13)$$

with κ_0 and τ_0 the constant differential-geometrical curvature and torsion of the characteristic helix associated with the HW chain.

The values of the HW model parameters $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, λ^{-1}, and M_L and also that of M_0 used in the calculation of $\langle S^2 \rangle$ are 3.0, 6.0, 20.6 Å, 35.8 Å^{-1}, and 104, respectively, for a-PS[7] and 3.0, 0.9, 46.8 Å, 39.8 Å^{-1}, and 118, respectively, for a-PαMS.[26] We note that M_w has been converted to L by the use of the relation $L = M_w/M_L$.

It is seen from Figure 2 that the trend of the data point at given k (or θ) in the vicinity of the Θ temperature is consistent with that in Figure 1.

DISCUSSION

Small k Region

Following the formulation of the dynamic structure factor on the basis of the HW chain model,[7,8] its first cumulant $\Omega(k)$ may be written in the form,

$$\Omega(k) = Dk^2[1 + \rho^{-1}F(k)] \qquad (14)$$

where ρ^{-1} is the reduced hydrodynamic radius defined by $\rho^{-1} = R_H/\langle S^2 \rangle^{1/2}$ with R_H the hydrodynamic radius, which is defined by $R_H = k_B T/6\pi\eta_0 D$. The quantity $F(k)$ on the right-hand side of eq 14 is a function of k dependent on the HW model parameters, *i.e.*, chain stiffness and local chain conformation, but the detailed expression for it is not necessary for the present purpose. For small k, $\Omega(k)$ may be expanded in even powers of k and the term $\rho^{-1}F(k)$ may then be written in the form,

$$\rho^{-1}F(k) = C\langle S^2 \rangle k^2 + \mathcal{O}(k^4) \qquad (15)$$

We note that all theoretical expressions derived for $\Omega(k)$ may be written in the form of eq 14 with eq 15 irrespective of the polymer chain model adopted and the approximations used. The explicit expressions for D (or R_H), $F(k)$, and therefore C depend on the model and also on the approximations.

From eq 14 with eq 15, we have

$$[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2 = F(k)/\rho\langle S^2 \rangle k^2$$
$$= C + \mathcal{O}(k^2) \qquad (16)$$

It is then seen that the coefficient C may be determined as the intercept by extrapolation to $k^2 = 0$ from data for $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ plotted against k^2, which may be evaluated only from experimentally observed values of $\Omega(k)$, D, and $\langle S^2 \rangle$. As emphasized by Stockmayer and coworkers,[27,28] C may therefore be considered to be an interesting quantity, although only a few experimental studies have been made.

The first-order perturbation result for C obtained by Tanaka and Stockmayer[12] for the Gaussian chain by
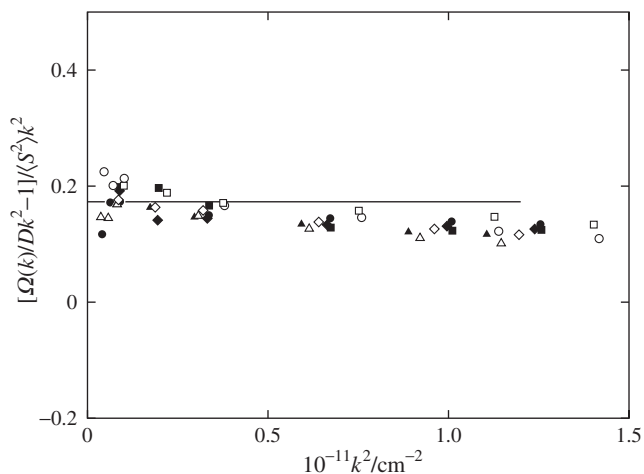
Figure 3. Plots of $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ against k^2. The symbols have the same meaning as those in Figure 1. The horizontal line segment indicates the unperturbed theoretical value 13/75 of the intercept (see the text).

Figure 4. Plots of $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ against k^2. The symbols have the same meaning as those in Figure 2. The horizontal line segment indicates the unperturbed theoretical value 13/75 of the intercept (see the text).
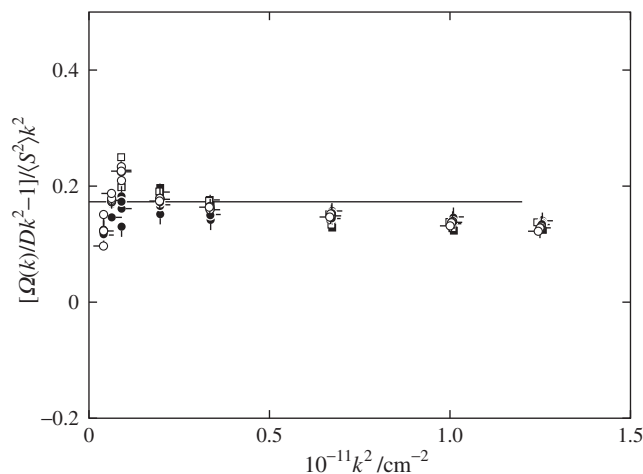
an application of the Akcasu–Gurol formula[6] with nonpreaveraged hydrodynamic interaction may be written in the quasi-two-parameter (QTP) scheme[7] (using $\tilde{z}$ in place of z) as

$$C = \frac{13}{75}(1 + 0.000494\tilde{z} + \cdots) \qquad (17)$$

This indicates that the excluded-volume effect on C is very small at least for small $\tilde{z}$.

Figure 3 shows plots of $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ against k^2 for a-PS in cyclohexane at 34.5 °C (Θ) (filled circle) and in toluene at 15.0 °C (unfilled circle), a-PMMA in acetonitrile at 44.0 °C (Θ) (filled triangle) and in acetone at 25.0 °C (unfilled triangle), a-PαMS in cyclohexane at 30.5 °C (Θ) (filled square) and in toluene at 25.0 °C (unfilled square), and PIB in IAIV at 25.0 °C (Θ) (filled diamond) and in *n*-heptane at 25.0 °C (unfilled diamond). Here, the values of $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ have been calculated from the observed values of $\Omega(k)$ shown in Figure 1 and those of D and $\langle S^2 \rangle$ given in the third and fourth columns, respectively, of Table II. The horizontal line segment indicates the unperturbed theoretical value 13/75 of the intercept C given by eq 17 with $\tilde{z} = 0$ (without the excluded-volume effect). It is seen that there is no appreciable excluded-volume effect on the quantity $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ over the range of k^2 examined within experimental error even in this case of large excluded volume, and that the observed values of the intercept C are in rather good agreement with its unperturbed theoretical value. We note that in the plots of this kind, experimental errors become large as k^2 is decreased to 0.

Figure 4 shows similar plots for a-PS and a-PαMS, both in cyclohexane, in the vicinity of the respective

Θ temperatures. The symbols have the same meaning as those in Figure 2. Here, the values of $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ have been calculated from the observed values of $\Omega(k)$ shown in Figure 2 and those of D given in the third column of Table II along with the values of $\langle S^2 \rangle$ calculated in the same manner as that described in the RESULTS section. As expected from Figure 3, the excluded-volume effect is very small not only on the intercept C but also on $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ over the range of k^2 examined also in this case of small excluded volume.

From Figures 3 and 4, it may be concluded that the excluded-volume effect on the intercept C is very small if any, and that its unperturbed theoretical value 13/75 seems to be in rather good agreement with the observed values. Further, we emphasize that the interesting experimental finding is that the excluded-volume effect is very small also on the quantity $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ over the whole range of k^2 examined in the present study.

It should be noted here that the above successful agreement between theory and experiment does not necessarily confirm the validity of the Akcasu–Gurol formula itself. The reason for this is that the formula has two inherent difficulties: (1) it cannot take account of constraints (on, for instance, bond lengths and bond angles) in a polymer chain but is valid only for the Gaussian chain, and (2) it is the formula for the *mathematical* initial time derivative of the dynamic structure factor, which does not directly corresponds to $\Omega(k)$ *actually* observed (at $t = \infty$). However, the present results indicate that these difficulties do not cause any serious errors in the evaluation of the intercept C.

Large k Region

Finally, we examine the excluded-volume effect on the height of the plateau in the k^3-region. In this region, it is convenient to write $\Omega(k)$ in the form,[7,8]

$$\eta_0\Omega(k)/k_BTk^3 = (1/6\pi)[\rho/\bar{k} + F(\bar{k})/\bar{k}] \quad (18)$$

The Gaussian chain theory[4-6] predicts that $\eta_0\Omega(k)/k_BTk^3$ in this region for flexible polymers with very large molecular weights becomes a constant independent of polymer–solvent pair. On the other hand, experimental data[1,2] exhibit slight but appreciable differences in the height, as predicted by the HW theory. According to the QTP scheme for the intramolecular excluded-volume effects,[7] however, we assume that the ratio $[\eta_0\Omega(k)/k_BT]/[\eta_0\Omega(k)/k_BT]_0$ of the perturbed to the unperturbed value of the height is a function only of $\tilde{z}$, and compare the experimental data with the Tanaka–Stockmayer first-order perturbation result for the height, which may be written in the QTP scheme as

$$[\eta_0\Omega(k)/k_BT]/[\eta_0\Omega(k)/k_BT]_0$$
$$= 1 + 2.11\tilde{z}\bar{k}_0^{-1} + \cdots \quad (19)$$

where $\bar{k}_0$ is given by eq 3 with $\langle S^2 \rangle_0^{1/2}$ in place of $\langle S^2 \rangle^{1/2}$.

Figure 5 shows plots of $[\eta_0\Omega(k)/k_BT]/[\eta_0\Omega(k)/k_BT]_0$ at $\theta = 150°$ against $\tilde{z}\bar{k}_0^{-1}$ for a-PS and a-PαMS, both in cyclohexane, in the vicinity of the respective Θ temperatures. The symbols have the same meaning as those in Figure 2. The ratios have been calculated from the values of $\eta_0\Omega(k)/k_BTk^3$ at $\theta = 150°$ shown in Figure 2. We note that a negligibly small temperature dependence of the refractive index n_0 of pure cyclohexane in the vicinity of the Θ temperature has
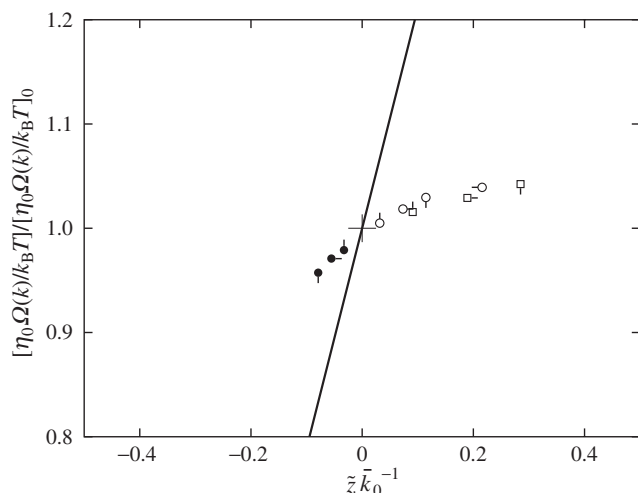
been ignored. The value of $\tilde{z}$ for each data point has been calculated from eqs 4–6 and 9–13 with the HW model parameters given in the RESULTS section. The straight line represents the first-order perturbation theory values calculated from eq 19. It is seen that the data points for the two polymers form a single-composite curve, whose slope at $\tilde{z}\bar{k}_0^{-1} = 0$ is remarkably different from the theoretical prediction. The disagreement between theory and experiment may be regarded as arising from the fact that the Tanaka–Stockmayer first-order perturbation calculation based on the Gaussian chain model cannot take account of effects of chain stiffness and local chain conformation, which may possibly become more important in such a range of large k.

CONCLUDING REMARKS

The first cumulant $\Omega(k)$ of the dynamic structure factor as a function of the magnitude k of the scattering vector has been determined for the a-PS sample with $M_w = 8.04 \times 10^6$ in toluene at $15.0°C$, the a-PMMA sample with $M_w = 1.31 \times 10^7$ in acetone at $25.0°C$, the a-PαMS sample with $M_w = 5.46 \times 10^6$ in toluene at $25.0°C$, and the PIB sample with $M_w = 6.63 \times 10^6$ in n-heptane at $25.0°C$. It has been also determined for the a-PS and a-PαMS samples in cyclohexane in the vicinity of the respective Θ temperatures (34.5 and 30.5 °C). From a comparison of the present data so obtained with the previous ones for all the samples in the respective Θ temperatures, it has been found that the observed dimensionless coefficient C of the k^4-term in the expansion of $\Omega(k)$ does not almost depend on excluded volume, as predicted by the Tanaka–Stockmayer first-order perturbation theory of C, being in good agreement with the theoretical value for the Gaussian chain with nonpreaveraged hydrodynamic interaction. Further, it has been found that the excluded-volume effect is very small on the quantity $[\Omega(k)/Dk^2 - 1]/\langle S^2 \rangle k^2$ over the whole range of k^2 examined in the present study.

The excluded-volume effect on the height of the plateau in the k^3-region has been also examined. In this region, however, the first-order perturbation theory cannot explain the behavior of the present experimental data. The disagreement between theory and experiment may be regarded as arising from the fact that the theory based on the Gaussian chain model cannot take proper account of effects of chain stiffness and local chain conformation. It is then very interesting to treat theoretically both effects of these and excluded volume on the height of the plateau (still within the framework of the Akcasu–Gurol formulation). We will consider this problem in a forthcoming paper.

Figure 5. Plots of $[\eta_0\Omega(k)/k_BT]/[\eta_0\Omega(k)/k_BT]_0$ at $\theta = 150°$ against $\tilde{z}k_0^{-1}$ for a-PS and a-PαMS, both in cyclohexane, in the vicinity of the respective Θ temperatures. The straight line represents the first-order perturbation theory values.[12]

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