First Cumulant of the Dynamic Structure Factor for Polymers in Θ Solvents. Effects of Chain Stiffness and Local Chain Conformation

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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 two atactic poly(α-methylstyrene) (a-PαMS) samples with weight-average molecular weights $M_w = 3.22 \times 10^6$ and 5.46×10^6 in cyclohexane at $30.5\,°C$ (Θ) and for one polyisobutylene (PIB) sample with $M_w = 6.63 \times 10^6$ in isoamyl isovalerate at $25.0\,°C$ (Θ). The translational diffusion coefficient was also determined from DLS measurements for the a-PαMS sample with the larger M_w and for the PIB sample in the same solvent conditions. The mean-square radius of gyration $\langle S^2 \rangle$ was determined from static light scattering measurements for the PIB sample. From a comparison of the present data for a-PαMS and PIB along with the previous ones for atactic polystyrene and poly(n-hexyl isocyanate) with the helical wormlike chain theory, it may be concluded that the universality predicted by the Gaussian chain theory 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 M_w ($\simeq 10^6$–10^7), and that the height of the plateau in the k^3-region depends on chain stiffness and local chain conformation, where η_0 is the solvent viscosity, k_B the Boltzmann constant, and T the absolute temperature. [DOI 10.1295/polymj.38.153]
KEY WORDS Poly(α-methylstyrene) / Polyisobutylene / Dynamic Light Scattering / Dynamic Structure Factor / First Cumulant / Helical Wormlike Chain /

Recently, experimental studies have been made of the behavior of 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 dilute solution.[1,2] For typical flexible polymers such as atactic polystyrene (a-PS) and atactic poly(methyl methacrylate) (a-PMMA) with very high molecular weights in the respective Θ solvents, cyclohexane at $34.5\,°C$ and acetonitrile at $44.0\,°C$,[1] it has been found that the so-called universal plots of $\eta_0 \Omega(k)/k_B T k^3$ against $\langle S^2 \rangle^{1/2} k$ for these polymers are appreciably, although slightly, deviated from each other in the range of large k, 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. For semiflexible polymers, for example, poly(n-hexyl isocyanate) (PHIC) in n-hexane at $25.0\,°C$,[2] on the other hand, it has been found that the behavior of the plot depends remarkably on chain stiffness. Such behavior of these experimental results have been shown to be consistently explained by the helical wormlike (HW) chain theory,[3,4] leading to the conclusion that the plot depends on chain stiffness and local chain conformation in contradiction to the prediction by the Gaussian chain theory.[5–7] In this paper, we further make a similar study of $\Omega(k)$ for atactic poly(α-methylstyrene) (a-PαMS) and polyisobutylene (PIB)

in Θ solvents in order to confirm the previous conclusion.

It is convenient to make here a remark on the conformational characteristics of the present two polymer chains which have been found from an analysis of their dilute solution properties on the basis of the HW chain model.[3,8,9] The value of the static stiffness parameter λ^{-1} for the a-PαMS chain is $46.8\,\text{Å}$, which is more than two times as large as the value $20.6\,\text{Å}$ for a-PS, and moreover, it tends to retain as large helical portions in dilute solution as the a-PMMA chain. On the other hand, the value of λ^{-1} for the PIB chain is $15.3\,\text{Å}$, which is the smallest of the ones for all the polymers we have investigated so far. We may therefore examine effects of chain stiffness and local chain conformation on the behavior of $\Omega(k)$ for a variety of flexible polymers.

EXPERIMENTAL

Materials

The two a-PαMS samples AMS320 and AMS550 used in this work are the same as those used in previous studies of the gyration-, viscosity-, and hydrodynamic-radius expansion factors[10,11] and the second and third virial coefficients,[12,13] *i.e.*, fractions separated by fractional precipitation from the original sam-

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Table I. Values of M_w, M_w/M_n, $\langle S^2 \rangle^{1/2}$ and R_H for poly(α-methylstyrene) and polyisobutylene

Sample	M_w	M_w/M_n	$10^{-2}\langle S^2 \rangle^{1/2}$ (Å)	$10^{-2}R_H$ (Å)
	a-PαMS in Cyclohexane at 30.5 °C (Θ)			
AMS320[a]	3.22×10^6 (3.24×10^6)[b]	1.05	4.6_5	3.6_8
AMS550[a]	5.46×10^6 (5.56×10^6)		6.0_9	4.7_4
	PIB in IAIV at 25.0 °C (Θ)			
PIB660	6.63×10^6 (6.49×10^6)		8.0_0	6.1_5

[a]The values of M_w and $\langle S^2 \rangle^{1/2}$ for AMS320 and AMS550, and also of R_H for AMS320 have been reproduced from refs 9, 10, and 21. [b]The values of M_w in parentheses represent those determined from SLS measurements for a-PαMS in toluene at 25.0 °C, which have been reproduced from ref 10, and for PIB in *n*-heptane at 25.0 °C.

ples prepared by living anionic polymerization. We note that the initiating chain end of each a-PαMS sample is a *sec*-butyl group and the other end is a hydrogen atom. The values of the fraction of racemic diads f_r are 0.73 and 0.70 for AMS320 and AMS550, respectively.[10,14] The one PIB sample PIB660 used is a fraction newly separated from the commercial sample of Aldrich Co., named 18,149-8, by the Θ column elution method[15,16] with benzene as a solvent followed by fractional precipitation with benzene as a solvent and methanol as a precipitant.

The solvent cyclohexane for a-PαMS was purified according to a standard procedure. The solvent isoamyl isovalerate (IAIV) for PIB was purified by distillation under reduced pressure after dehydration with potassium carbonate.

Static Light Scattering

Static light scattering (SLS) measurements were carried out to determine the weight-average molecular weight M_w and $\langle S^2 \rangle$ for the PIB sample PIB660 in IAIV at 25.0 °C (Θ) and also its M_w in *n*-heptane at 25.0 °C. A Fica 50 light-scattering photometer was used for all the measurements with vertically polarized incident light of wavelength 436 nm. For a calibration of the apparatus, the intensity of light scattered from pure benzene was measured at 25.0 °C at a scattering angle of 90°, where the Rayleigh ratio $R_{Uu}(90°)$ of pure benzene was taken as 46.5×10^{-6} cm^{-1}.[17] The depolarization ratio ρ_u of pure benzene at 25.0 °C was found to be 0.41 ± 0.01. Scattered intensities were measured at six different concentrations and at scattering angles θ ranging from 17.5 to 55°. All the data obtained were analyzed by the Berry square-root plot.[18]

The most concentrated solutions of PIB660 in IAIV and in *n*-heptane were prepared gravimetrically and then made homogeneous by continuous stirring at *ca.* 50 °C for 7 d and 3 d, respectively. 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 M_w and $\langle S^2 \rangle^{1/2}$ so determined for PIB660 are given in Table I along with those for AMS320 and AMS550 determined previously[9,10] in cyclohexane at 30.5 °C (Θ) and also in toluene at 25.0 °C. For each sample, the values of M_w with and without parentheses represent the values in its good and Θ solvents, respectively, and are seen to be in good agreement with each other within experimental error. We note that the ratio of M_w to the number-average molecular weight M_n could be determined from analytical gel permeation chromatography (GPC) only for AMS320, its value being given in the third column of Table I. Although the values of M_w/M_n for the other samples could not be determined with sufficient accuracy because of the lack of the GPC calibration curve in the necessary range of M_w, their molecular weight distributions may be considered as narrow ($M_w/M_n \lesssim 1.1$) as that of AMS320.

Dynamic Light Scattering

Dynamic light scattering (DLS) measurements were carried out to determine the translational diffusion coefficient D for AMS550 in cyclohexane at 30.5 °C (Θ) and for PIB660 in IAIV at 25.0 °C (Θ). Measurements were also carried out to determine $\Omega(k)$ for all the a-PαMS and PIB samples in the respective Θ solvents. 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-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.[19] As for $\Omega(k)$, the CONTIN method[20] 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 θ ranging from 18 to 26°. For the determination of $\Omega(k)$, it was measured at 30, 45, 60, 90, 120, and 150° for all the samples. 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 100 μs for AMS550 and 100–200 μs for PIB660. 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 0.5–20 μs for AMS320 and AMS550 and 1.0–100 μs for PIB660.

The most concentrated solutions of AMS320 and AMS550 in cyclohexane were prepared gravimetrically and made homogeneous by continuous stirring at *ca.* 50 °C for 7 d. The test solutions of AMS320 and AMS550 and also of PIB660 were prepared in the manner mentioned in the last subsection. The values of the refractive index at 488 nm and of η_0 used are 1.426 and 0.818 cP, respectively, for cyclohexane at 30.5 °C and 1.415 and 1.33 cP, respectively, for IAIV at 25.0 °C.

RESULTS

Translational Diffusion Coefficient

The values of D determined in this study are $5.7_4 \times 10^{-8}$ cm²/s for the a-PαMS sample AMS550 in cyclohexane at 30.5 °C (Θ) and $2.6_7 \times 10^{-8}$ cm²/s for the PIB sample PIB660 in IAIV at 25.0 °C (Θ). The values of the hydrodynamic radius R_H calculated from the defining equation

$$R_H = k_B T / 6\pi \eta_0 D \qquad (1)$$

with the above values of D are given in the fifth column of Table I along with that previously determined for AMS320 in cyclohexane at 30.5 °C.[21]

The ratio $\rho = \langle S^2 \rangle^{1/2} / R_H$ may be evaluated to be 1.29 and 1.30 for AMS550 and PIB660, respectively, using the values of $\langle S^2 \rangle^{1/2}$ and R_H given in the fourth and fifth columns, respectively, of Table I. The value 1.29 of ρ for AMS550 agrees well with the previous ones[21] 1.26–1.29 determined for a-PαMS in the range of $4 \times 10^5 \lesssim M_w \lesssim 3 \times 10^6$, including AMS320, and

the value 1.30 for PIB660 also with the previous ones[19] 1.29–1.33 determined for PIB in the range of $4 \times 10^5 \lesssim M_w \lesssim 2 \times 10^6$. It may then be concluded that both the present SLS and/or DLS measurements for the samples AMS550 and PIB660 with rather large M_w could be carried out successfully.

First Cumulant

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

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

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

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

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,[1,2] the initial tangent 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[20] supplied by Brookhaven Instruments. Then the values of the initial slope so determined at finite concentrations at each θ for each sample have been linearly extrapolated to $c = 0$ to determine Ω at infinite dilution. In Table II are given the values of $\Omega(k)$ and $\eta_0\Omega(k)/k_B T k^3$ so determined.

DISCUSSION

Nonuniversality—Effects of Chain Stiffness and Local Chain Conformation

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

$$\bar{k} \equiv \langle S^2 \rangle^{1/2} k \qquad (4)$$

i.e., the so-called universal plot. The unfilled circles with pip up and down represent the present experimental values for the a-PαMS samples AMS320 and AMS550, respectively, in cyclohexane at 30.5 °C (Θ), and the filled circles those for the PIB sample PIB660 in IAIV at 25.0 °C (Θ). For comparison, there are also shown the previous results for a-PS[1] with $M_w = 6.40 \times 10^6$ (square with pip up) and 8.04×10^6 (square with pip down) in cyclohexane at 34.5 °C (Θ) and for PHIC[2] with $M_w = 1.04 \times 10^5$ (unfilled triangle), 3.63×10^5 (filled triangle), and 7.71×10^5

(unfilled inverted triangle) in *n*-hexane at 25.0 °C. In the figure the heavy curves represent the HW theoretical values, and the light ones the theoretical values for the Kratky–Porod (KP) wormlike chain model.[3] They are discussed in the next subsection.

Table II. Values of $\Omega(k)$ and $\eta_0\Omega(k)/k_BTk^3$ for poly(α-methylstyrene) in cyclohexane at 30.5 °C (Θ) and Polyisobutylene in IAIV at 25.0 °C (Θ)

Sample	θ (deg)	$10^{-3}k$ (Å^{-1})	$\Omega(k)$ (s^{-1})	$\eta_0\Omega(k)/k_BTk^3$
AMS320	30	0.950	$7.0_3 \times 10^2$	0.160
	45	1.405	$1.5_6 \times 10^3$	0.110
	60	1.836	$2.7_8 \times 10^3$	0.087_6
	90	2.596	$6.2_4 \times 10^3$	0.069_6
	120	3.179	$1.0_1 \times 10^4$	0.061_1
	150	3.546	$1.3_0 \times 10^4$	0.056_8
AMS550	30	0.950	$5.5_3 \times 10^2$	0.126
	45	1.405	$1.3_0 \times 10^3$	0.091_2
	60	1.836	$2.3_4 \times 10^3$	0.073_7
	90	2.596	$5.1_1 \times 10^3$	0.057_0
	120	3.179	$8.4_8 \times 10^3$	0.051_5
	150	3.546	$1.1_4 \times 10^4$	0.050_0
PIB660	30	0.943	$2.6_3 \times 10^2$	0.102
	45	1.394	$6.1_0 \times 10^2$	0.072_8
	60	1.822	$1.1_6 \times 10^3$	0.061_9
	90	2.576	$2.7_8 \times 10^3$	0.052_5
	120	3.156	$4.8_8 \times 10^3$	0.050_2
	150	3.520	$6.6_1 \times 10^3$	0.049_0

It is seen that there are slight but appreciable differences in the height of the k^3-region (the plateau region) in the plot between the three flexible polymers, and moreover, that the order of the height (a-PαMS < PIB < a-PS) is not correlated with that of the magnitude of λ^{-1} [PIB (15.3 Å) < a-PS (20.6 Å) < a-PαMS (46.8 Å)]. Such differences may then be regarded as arising from that in local chain conformation as well as in chain stiffness. As for PHIC, whose λ^{-1} value (840 Å in *n*-hexane[22]) is one order of magnitude larger than those for the three flexible polymers, the plots deviate appreciably upward from those for the latter three. Further, the plots for the three PHIC samples deviate appreciably from each other, while those for the two samples of each of a-PαMS and a-PS form a single-composite curve within experimental error. Such characteristics of the plots for PHIC may be considered to arise from very large chain stiffness. The present experimental results seem to confirm the previous conclusion that the universality in the k^3-region cannot be realized because of the effects of chain stiffness and local chain conformation. In the next subsection, we further discuss this difference in the behavior of the plot on the basis of the HW (and KP) theory.

Comparison with the HW Theory

We begin by giving a short sketch of the (discrete) dynamic HW chain model (and also of the KP chain as its special case).[3] It is composed of N identical rigid subbodies joined successively with bonds of fixed
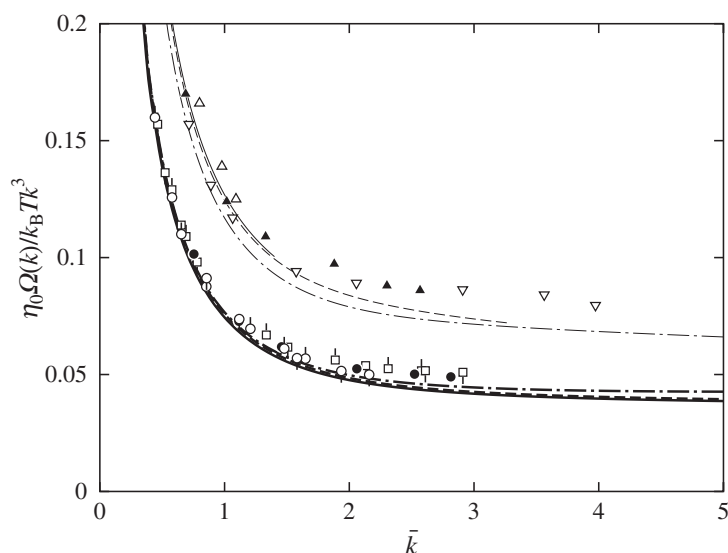

Figure 1. Plots of $\eta_0\Omega(k)/k_BTk^3$ against the reduced magnitude $\bar{k}$ of the scattering vector. The unfilled circles with pip up and down represent the present experimental values for the a-PαMS samples AMS320 and AMS550, respectively, in cyclohexane at 30.5 °C (Θ), and the filled circles those for the PIB sample PIB660 in IAIV at 25.0 °C (Θ). Also are shown the results for a-PS[1] with $M_w = 6.40 \times 10^6$ (square with pip up) and 8.04×10^6 (square with pip down) in cyclohexane at 34.5 °C (Θ) and for PHIC[2] with $M_w = 1.04 \times 10^5$ (unfilled triangle), 3.63×10^5 (filled triangle), and 7.71×10^5 (unfilled inverted triangle) in *n*-hexane at 25.0 °C. The heavy solid, dashed, and dot-dashed curves represent the HW theoretical values for a-PαMS, PIB, and a-PS, respectively, and the light solid, dashed, and dot-dashed curves represent the KP theoretical values for the PHIC samples with the smallest through largest M_w, respectively (see the text).

length a, where their centers are located nearly on the contour of the continuous HW chain of length L and each subbody has translational and rotatory friction coefficients ζ_t and ζ_r. Specifically, the pair potential between successive two subbodies is chosen so that the static behavior of the dynamic model becomes identical with that of the continuous HW chain.[3] The latter is an elastic wire model with both bending and torsional energies. In particular, for flexible chains, the bending and torsional force constants associated with the two kinds of elastic energies may be set equal to each other. The HW chain may then be described in terms of the static stiffness parameter λ^{-1} (equal to the bending force constant multiplied by $2/k_B T$) and the constant differential-geometrical curvature κ_0 and torsion τ_0 of the characteristic helix, *i.e.*, the regular helical form taken by the contour of the chain at the minimum zero of its total elastic energy along with the shift factor M_L as defined as the molecular weight per unit contour length. A special case of the HW chain with $\kappa_0 = 0$ but with the two (different) force constants is the *generalized* KP chain, which is the model for most of stiff (or semiflexible) chains (with large λ^{-1}). If the torsion of the chain is not considered, the generalized KP chain is identical with the *original* KP chain (with $\kappa_0 = 0$ and with vanishing torsional force constant) and the parameter τ_0 does not appear. In what follows, therefore, both the original and generalized KP chains are referred to simply as the KP chain. The number of subbodies N in the discrete model is related to L by $L = N\Delta s$, where Δs is the contour length per subbody and is uniquely related to a. (In the case of flexible polymers, the subbody is chosen as a repeat unit of a given polymer chain.)

Now, for the dynamic HW chain (without excluded volume) such that each subbody has an isotropic scatterer, the dimensionless quantity $\eta_0 \Omega(k)/k_B T k^3$ may be written in the form[3,4]

$$\eta_0 \Omega(k)/k_B T k^3 = (1/6\pi)[\rho/\bar{k} + F(\bar{k})/\bar{k}] \quad (5)$$

where $F(\bar{k})$, which is given by eq 10.66 of ref 3, may be expressed in terms of the solutions of the eigenvalue problem associated with the diffusion operator appearing in the coarse-grained version of the diffusion equation,[3] along with $\langle S^2 \rangle$ and the mean-square end-to-end distance of the HW chain, which are given by eqs 4.83 and 4.82, respectively, of ref 3. The dimensionless quantity $F(\bar{k})$ as a function of $\bar{k}$ depends on the dimensionless parameters $\lambda^{-1}\kappa_0$, $\lambda^{-1}\tau_0$, $\lambda\Delta s$ (or λa), N, $r_1 = \zeta_t/3\pi\eta_0 a$, and $r_2 = \zeta_r/a^2\zeta_t$ and may be evaluated numerically.

In Figure 1, the heavy solid and dashed curves represent the HW theoretical values calculated from eq 5 for a-PαMS and PIB, respectively. In the calculation

we have used the parameter values $\lambda^{-1}\kappa_0 = 3.0$, $\lambda^{-1}\tau_0 = 0.9$, and $\lambda^{-1} = 46.8$ Å for a-PαMS[9] and $\lambda^{-1}\kappa_0 = 1.0$, $\lambda^{-1}\tau_0 = 0$, and $\lambda^{-1} = 15.3$ Å for PIB,[8] which have been determined experimentally from an analysis of the M_w dependence of the unperturbed or perturbed $\langle S^2 \rangle$. The subbody corresponds to a repeat unit of a given polymer chain, as mentioned above, and then the values of $\lambda\Delta s$ have been taken to be 0.0634 and 0.175 for a-PαMS and PIB, respectively, which have been calculated using the relation $\Delta s = M_0/M_L$ with the respective values 118 and 56 of the molecular weight M_0 of the repeat unit and the respective values 39.8 and 20.9 Å^{-1} of M_L for a-PαMS[9] and PIB.[8] Further, we have chosen r_1 and r_2 to be 1 and 10, respectively, which may be of reasonable order, and $N + 1$ to be 10^4, which corresponds to the limit of the capacity of the computer used. As for ρ, we have used the present experimental values 1.27_5 and 1.30 for a-PαMS and PIB, respectively, the former value being the mean of values obtained for the two a-PαMS samples AMS320 and AMS550.

In Figure 1 are also shown the HW theoretical values for the a-PS (heavy dot-dashed curve) and the KP theoretical values for the three PHIC samples (light solid, dashed, dot-dashed curves for the samples with the smallest through largest M_w, respectively), which have been reproduced from Figure 2 of ref 1 and from Figure 3 of ref 2, respectively.

It is seen from the figure that the HW (and KP) theory may correctly predict the order of the height of the plateau in the k^3-region for the three flexible polymers (a-PαMS < PIB < a-PS) and also the dependence of $\eta_0 \Omega(k)/k_B T k^3$ on M_w for the PHIC, although all the theoretical curves deviate somewhat downward from the corresponding data points and agreement between theory and experiment is not completely quantitative. The qualitative agreement between theory and experiment for the three flexible polymers indicates that there is very little doubt that the height of the k^3-region for flexible polymers with very large M_w depends slightly on both chain stiffness and local chain conformation and therefore that the universality cannot in general be realized. For semiflexible polymers, whose conformational behavior cannot be described by the Gaussian chain statistics, the height of $\eta_0 \Omega(k)/k_B T k^3$ is much larger than that for flexible polymers in the large k region, as predicted by the theory.

CONCLUSIONS

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 two a-PαMS samples in cyclohexane at 30.5 °C (Θ) and the one

PIB sample in IAIV at 25.0 °C (Θ). From a comparison of the present data for a-PαMS and PIB along with the previous ones for a-PS and PHIC with the HW (and KP) theory, we have reconfirmed the conclusion that the universality predicted by the Gaussian chain theory for the plot of $\eta_0 \Omega(k)/k_{\mathrm{B}} T k^3$ 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.

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