Dynamic Depolarized Light Scattering by Oligo- and Poly(α -methylstyrene)s in Dilute Solution

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(Received July 30, 2004; Accepted September 9, 2004; Published January 15, 2005)

ABSTRACT: The power spectrum J_Γ of the excess depolarized component of scattered light was determined from frequency-domain dynamic depolarized light scattering measurements for 10 samples of atactic oligo- and poly(α -methylstyrene)s (a-P α MS), each with the fraction of racemic diads $f_r = 0.72$, in the range of weight-average degree of polymerization x_w from 2 to 67.1 in cyclohexane at 30.5 °C (Θ). It is found that, as in the cases of atactic polystyrene (a-PS), atactic poly(methyl methacrylate) (a-PMMA), and isotactic (i-) PMMA, J_Γ may be well represented in terms of a single Lorentzian independently of x_w , and that the relaxation time τ_Γ as defined as the reciprocal of the half-width at half-maximum of J_Γ evaluated at infinite dilution increases with increasing x_w and levels off to its asymptotic value in the limit of $x_w \rightarrow \infty$, being consistent with the theoretical prediction on the basis of the helical wormlike (HW) chain model. A comparison is made of the present data for τ_Γ with the HW theory, and it is shown that the theory may explain satisfactorily the data in the range of $x_w \gtrsim 10$, although semiquantitatively. For $x_w \lesssim 10$, the rigid sphere model having the radius equal to the apparent root-mean-square radius of gyration of the HW chain may give a good explanation of τ_Γ . From a comparison of the present results for τ_Γ for a-P α MS with previous ones for a-PS and a- and i-PMMA, it is shown that there is good correlation between static and dynamic chain stiffness, the latter being defined as the ratio of the relaxation time associated with the local motion of the long chain to that of its isolated repeat unit (monomer), as predicted by the HW theory. [DOI 10.1295/polymj.37.7]

KEY WORDS Poly(α -methylstyrene) / Dynamic Depolarized Light Scattering / Spectrum of Depolarized Scattered Component / Helical Wormlike Chain / Dynamic Chain Stiffness /

In a new framework of polymer solution science on the basis of the helical wormlike (HW) chain model,^{1,2} we have recently made a series of experimental studies^{3–6} of dilute solution behavior of atactic oligo- and poly(α -methylstyrene)s (a-P α MS) in the unperturbed Θ state. Specifically, we have determined the mean-square radius of gyration $\langle S^2 \rangle$,³ mean-square optical anisotropy $\langle \Gamma^2 \rangle$,⁴ scattering function,⁵ and steady-state transport coefficients⁶ in cyclohexane at 30.5 °C (Θ),³ using well-fractionated a-P α MS samples with the fraction of racemic diads f_r regulated to be 0.72 ± 0.01 .⁷ The results obtained have been analyzed to show that the a-P α MS chain has rather large chain stiffness and strong helical nature like the atactic poly(methyl methacrylate) (a-PMMA) chain with $f_r = 0.79$.^{1,8} Here, by the term “helical nature,” we mean that the chain tends to retain large and clearly distinguishable helical portions in dilute solution.¹

In the present and following⁹ papers, we proceed to make a study of dynamical properties of a-P α MS and its oligomers at Θ . We have already investigated as those properties the spectrum J_Γ of the (excess) depolarized scattered component, spin-lattice relaxation time T_1 , and nuclear Overhauser enhancement NOE

for atactic polystyrene (a-PS),¹⁰ a-PMMA,¹¹ and isotactic (i-) PMMA.¹² The conclusions derived from an analysis of experimental data for them within the framework of the dynamic theory^{1,13–15} of the (unperturbed) HW chain are the following. First, J_Γ may be well represented in terms of a single Lorentzian, and the relaxation time τ_Γ defined by the reciprocal of the half-width at half-maximum (HWHM) of J_Γ increases with increasing weight-average degree of polymerization x_w and levels off to its asymptotic value in the limit of $x_w \rightarrow \infty$, the results being consistent with the dynamic HW theory prediction.^{1,13} Second, T_1 and NOE are closely correlated with τ_Γ . Third, the dynamic HW theories^{1,13–15} may explain semiquantitatively the dependences on x_w of these three properties for $x_w \gtrsim 10$ except for NOE for a-PS, while the rigid sphere model with a single, proper relaxation time is valid for them for smaller x_w . Fourth, as far as the above three polymers are concerned, there is good correlation between dynamic and static chain stiffness, as predicted by the HW theory.^{1,15} Thus the main purpose of the present and following papers is to examine whether the above conclusions are also valid for a-P α MS.

In the present paper, we carry out frequency-

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domain dynamic depolarized light scattering (LS) measurements to determine J_{Γ} for a-P α MS and its oligomers in cyclohexane at 30.5 °C (Θ) by the use of a Fabry–Perot (FP) interferometer in the manner established in previous papers,^{10–12} and then examine the behavior of τ_{Γ} as a function of x_w . Results of nuclear magnetic relaxation measurements and their analysis are reported in the following paper.⁹

EXPERIMENTAL

Materials

All the a-P α MS samples used in this work are the same as those used in the previous study of $\langle \Gamma^2 \rangle$,⁴ *i.e.*, fractions separated by preparative gel permeation chromatography (GPC) or fractional precipitation from the original samples prepared by living anionic polymerization.^{3,7} We note that the initiating chain end of each polymerized sample is a *sec*-butyl group and the other end is a hydrogen atom.

The values of the weight-average molecular weight M_w determined from ^1H and ^{13}C NMR spectra, by analytical GPC, or from (static) LS measurements (in cyclohexane at 30.5 °C), x_w estimated from M_w , the ratio of M_w to the number-average molecular weight M_n determined by analytical GPC,^{3,6} and f_r determined from ^1H and ^{13}C NMR spectra^{3,7} are given in Table I. Although f_r of the samples OAMS4–OAMS10 could not be determined because of the complexity of their ^1H NMR spectra, they may be regarded as having almost the same value of f_r ($0.71 \lesssim f_r \lesssim 0.73$) as OAMS3 or OAMS13 with $M_w = 1.60 \times 10^3$ (which is not used in this work), since the samples OAMS3–OAMS13 are fractions from one original sample.⁷ As seen from the values of f_r , all the samples except OAMS2 have the fixed stereochemical composition $f_r = 0.72 \pm 0.01$. As previously⁶ mentioned, the difference in f_r between the sample OAMS2 and the others may be regarded as arising from that in reaction mechanism; *i.e.*, f_r of the former is determined by the

termination reaction with methanol, while those of the latter are determined (mainly) by the propagation reaction. As seen from the values of M_w/M_n , all the samples are very narrow in molecular weight distribution.

The solvent cyclohexane used for dynamic depolarized LS measurements was purified according to a standard procedure prior to use.

Dynamic Depolarized Light Scattering

The photometer used for all dynamic depolarized LS measurements is the same as that used in the previous studies,^{4,10–12,16,17} *i.e.*, a Brookhaven Instruments Model BI-200SM goniometer with a minor modification of its light source part and with a detector alignment previously assembled to incorporate an FP interferometer in it. It has been described in detail in a previous paper,¹⁶ and therefore we here only give its short sketch (see Figure 1 of ref 16).

Vertically polarized 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 was used as a light source. It was made highly vertically (v) polarized by passing through a Gran–Thompson (GT) prism with an extinction ratio smaller than 10^{-5} . The scattered light was measured at a scattering angle of 90°. Its horizontal (H) component, *i.e.*, the depolarized (Hv) component, which was extracted from the total scattered light intensity by the use of the same GT prism as above, was analyzed with a Burleigh Instruments Model RC-110 FP interferometer equipped with a Model RC-670 pair of plane mirrors with a flatness of $\lambda/200$ and a reflectivity of 97.5%. The intensity of the Hv component filtered through the FP interferometer was measured by an EMI 9893B/350 photomultiplier (PM) tube. A pinhole of diameter 100 μm was used as a spatial filter, which was placed between the interferometer and the PM tube. All the measurements were carried out by the single passing as in the previous studies.^{10–12}

As before,^{10–12} the transmittance $T(\omega)$ of the FP interferometer was determined by measuring the polarized component of the light intensity scattered from a solution of an a-PS sample with $M_w = 7.32 \times 10^5$ in methyl ethyl ketone at the concentration $c \simeq 1 \times 10^{-3} \text{ g/cm}^3$ and at 30.5 °C following the procedure of Ouano and Pecora.¹⁸

In the present study, the free spectral range (FSR) of the interferometer (*i.e.*, the distance between the mirrors) was changed from 4.71×10^{10} to $8.66 \times 10^{11} \text{ rad/s}$ depending on the width of J_{Γ} in order to attain an appropriate resolution. As in the previous studies,^{10–12} the value δ of FSR for each setting was determined by the use of the ^4He hyperfine structure

Table I. Values of M_w , x_w , M_w/M_n , and f_r for atactic oligo- and poly(α -methylstyrene)s

Sample	M_w	x_w	M_w/M_n	f_r
OAMS2	2.94×10^2	2	1	0.56
OAMS3	4.12×10^2	3	1	0.73
OAMS4	5.30×10^2	4	<1.01	
OAMS5	6.48×10^2	5	<1.01	
OAMS6	7.66×10^2	6	<1.01	
OAMS8	1.04×10^3	8.29	1.01	
OAMS10	1.27×10^3	10.3	1.01	
OAMS19	2.27×10^3	18.7	1.07	0.72
OAMS38	4.57×10^3	38.2	1.07	0.72
OAMS67	7.97×10^3	67.1	1.04	0.72

interval of 1.0 cm^{-1} at 587.5 nm associated with the $2^3\text{P}-3^3\text{D}$ transition for $3 \times 10^{11} \lesssim \delta \lesssim 9 \times 10^{11}\text{ rad/s}$ and of the Brillouin shift $\Delta\omega_{\text{B}}$ of $3.53 \times 10^{10}\text{ rad/s}$ in the Rayleigh–Brillouin spectrum of pure benzene at 25.0°C at 1 atm for $10^{11} \lesssim \delta \lesssim 3 \times 10^{11}\text{ rad/s}$. For $\delta \lesssim 10^{11}\text{ rad/s}$, the distance between the mirrors was directly measured.

Measurements were carried out on solutions of all the samples in cyclohexane at 30.5°C (Θ). The most concentrated solution of each sample in cyclohexane was prepared gravimetrically and made homogeneous by continuous stirring at *ca.* 50°C for 1–2 d. This solution and the solvent were optically purified by filtration through a Teflon membrane of pore size 0.1 or $0.45\text{ }\mu\text{m}$. The solutions of lower concentrations were obtained by successive dilution. The weight concentrations of the test solutions were converted to the solute mass concentrations c (in g/cm^3) by the use of the densities of the solutions.

Before and after each measurement on the solution or solvent, the transmittance of the FP interferometer was determined in the manner as described above. In the present measurements, the finesse could be kept at 30–60 during a single measurement, which took *ca.* 40 min.

RESULTS

In each frequency-domain measurement of the intensity I_{Hv} of the depolarized (Hv) component of the light scattered from a test solution by the use of the FP interferometer, an apparent spectrum $I_{\text{Hv,ap}}(\Delta\omega_{\text{ap}})$ is observed as a function of the difference $\Delta\omega_{\text{ap}}$ between the angular frequencies ω of the peak of the transmittance $T(\omega)$ of the FP interferometer and of the incident light. The spectrum $I_{\text{Hv,ap}}(\Delta\omega_{\text{ap}})$ so observed may be represented by a convolution integral of $T(\omega)$ and the true spectrum $I_{\text{Hv}}(\Delta\omega)$ as a function of the difference $\Delta\omega$ between ω 's of the scattered and incident light waves, *i.e.*, the integral of $T(\Delta\omega - \Delta\omega_{\text{ap}})I_{\text{Hv}}(\Delta\omega)$ over $\Delta\omega$.^{10,19} Further, $I_{\text{Hv}}(\Delta\omega)$ is in general composed of the intrinsic depolarized spectrum $J_{\Gamma}(\Delta\omega)$ due to the solute a-P α MS and that due to the solvent molecule. Fortunately, in the present case, the optical anisotropy of the solvent cyclohexane is very small compared to that of the solute a-P α MS as in the previous case of a-PS in cyclohexane or carbon tetrachloride,¹⁰ so that $I_{\text{Hv}}(\Delta\omega)$ may be equated to $J_{\Gamma}(\Delta\omega)$. Then, assuming that J_{Γ} (I_{Hv} in the present case) may be represented by a linear combination of several (practically six) Lorentzians and using $T(\omega)$ experimentally determined, the coefficient (weight) and the HWHM of each Lorentzian may be determined by numerical deconvolution of $I_{\text{Hv,ap}}$.^{10–12}

As in the cases of a-PS¹⁰ and a- and i-PMMA,^{11,12}

the HWHMs of the six Lorentzians so determined for each test solution were found to be the same, indicating that J_{Γ} may be fitted by a single Lorentzian. We then determine the (apparent) relaxation time τ_{Γ} defined by the reciprocal of the HWHM of J_{Γ} thus determined, which is just the HWHM of the single Lorentzian in the present case. Figure 1 shows plots of τ_{Γ} against c for all a-P α MS samples in cyclohexane at 30.5°C (Θ). Each plot follows a straight line and the value of τ_{Γ} at infinite dilution may be determined from its intercept.

The values of τ_{Γ} so obtained at infinite dilution are given in Table II along with those of the reduced relaxation time $k_{\text{B}}T\tau_{\Gamma}/\eta_0$ with k_{B} the Boltzmann constant, T the absolute temperature, and η_0 the solvent

Figure 1. Plots of τ_{Γ} against c for all a-P α MS samples in cyclohexane at 30.5°C (Θ).

Table II. Values of τ_{Γ} and $k_{\text{B}}T\tau_{\Gamma}/\eta_0$ for atactic oligo- and poly(α -methylstyrene)s in cyclohexane at 30.5°C at infinite dilution

Sample	τ_{Γ} (ns)	$k_{\text{B}}T\tau_{\Gamma}/\eta_0$ ($\text{\AA}^3$)
OAMS2	0.032_0	$1.6_4 \times 10^2$
OAMS3	0.073_6	$3.7_7 \times 10^2$
OAMS4	0.098_8	$5.0_6 \times 10^2$
OAMS5	0.14_0	$7.1_5 \times 10^2$
OAMS6	0.15_9	$8.1_4 \times 10^2$
OAMS8	0.27_8	$1.4_2 \times 10^3$
OAMS10	0.46_7	$2.3_9 \times 10^3$
OAMS19	1.0_6	$5.4_2 \times 10^3$
OAMS38	1.5_0	$7.6_7 \times 10^3$
OAMS67	1.6_6	$8.4_9 \times 10^3$

viscosity. The latter reduced values have been calculated from the former with the value 0.818 cP of η_0 for cyclohexane at 30.5 °C. As discussed in the previous papers,^{10–12} the reduced relaxation time $k_B T \tau_\Gamma / \eta_0$ must be independent of solvent condition if the motions of the small molecules or the motional units in the polymer chain may be described in the diffusion limit and if the local chain conformation does not depend on that condition. In the previous study of a-PS,¹⁰ the values of $k_B T \tau_\Gamma / \eta_0$ for cumene, which may be regarded as corresponding to the monomer (repeat unit) of a-P α MS as well as of a-PS, in cyclohexane at 34.5 °C and in carbon tetrachloride at 25.0 °C have been found to agree well with each other, leading to the conclusion that the dynamics that governs τ_Γ may be described in the diffusion limit for solutions of a-PS in cyclohexane. This may also be the case with a-P α MS.

Figure 2 shows plots of $k_B T \tau_\Gamma / \eta_0$ at infinite dilution against the logarithm of x_w for a-P α MS in cyclohexane at 30.5 °C (Θ). In the figure, the solid and dashed curves represent the theoretical values for the HW model and the rigid sphere model, respectively, which are obtained and discussed in the next (DISCUSSION) section. As in the cases of a-PS¹⁰ and a- and i-PMMA,^{11,12} the reduced relaxation time $k_B T \tau_\Gamma / \eta_0$ increases with increasing x_w and seems to level off in the limit of $x_w \rightarrow \infty$, the result being consistent with the HW theory.¹³ We have estimated its asymptotic value in this limit to be *ca.* $8.5 \times 10^3 \text{ Å}^3$ from the observed value $8.49 \times 10^3 \text{ Å}^3$ of $k_B T \tau_\Gamma / \eta_0$ for the sample OAMS67 with the largest x_w , which is appreciably smaller than the corresponding value $2 \times 10^4 \text{ Å}^3$ for a-PMMA,¹¹ appreciably larger than the one $4 \times 10^3 \text{ Å}^3$ for a-PS,¹⁰ and slightly larger than

Figure 2. Plots of $k_B T \tau_\Gamma / \eta_0$ at infinite dilution against the logarithm of x_w for a-P α MS in cyclohexane at 30.5 °C (Θ). The solid and dashed curves represent the theoretical values for the HW model and the rigid sphere model, respectively.

the one $8 \times 10^3 \text{ Å}^3$ for i-PMMA.¹²

DISCUSSION

HW Theory

In order to make a comparison of the present results of depolarized LS measurements with the (dynamic) HW theory,^{1,13} it is convenient to begin by giving its brief explanation. The model used is the discrete HW chain^{1,20} such that it is composed of N identical rigid subbodies, each with the translational and rotatory friction coefficients ζ_t and ζ_r , joined successively with bonds of fixed length a , and that the orientation of each subbody with respect to its predecessor is described by the potential energy of the original continuous HW chain. Therefore, the basic model parameters for the former are the same as those for the latter, *i.e.*, the constant differential-geometrical curvature κ_0 and torsion τ_0 of the characteristic helix of the latter taken at the minimum zero of its elastic energy and the static stiffness parameter λ^{-1} .

For the single discrete HW chain so defined, the power spectrum $J_\Gamma(\Delta\omega)$ of the depolarized component of the light scattered from it as a function of the difference $\Delta\omega$ between the angular frequencies of the scattered and incident light waves may be written in the form^{1,13}

$$J_\Gamma(\Delta\omega) = \sum_{k \text{ odd}} \sum_{j=-2}^2 A_k^j \frac{\tau_{2,k}^j}{1 + (\Delta\omega \tau_{2,k}^j)^2} \quad (1)$$

where

$$\tau_{2,k}^j = 1/\lambda_{2,k}^j \quad (2)$$

$$A_k^j = \frac{12\pi}{(N+1)} B_k^j \cot^2 \left[\frac{\pi k}{2(N+1)} \right] \quad (3)$$

with

$$B_k^j = (8\pi^2)^{-1} \left| \sum_{j'=-2}^2 \alpha_2^{jj'} R_{2,k}^{jj'} \right|^2 \quad (4)$$

In eq 2, $\lambda_{2,k}^j$ are the eigenvalues of the matrix representation of the diffusion operator associated with the subspace (of full Hilbert space) spanned by the basis set with the “total angular momentum quantum number” $L = 2$ and the number of “excited” subbodies $n = 1$. Specifically, $J_\Gamma(\Delta\omega)$ is the Fourier–Laplace transform of a linear combination of the basic time-correlation functions associated with that subspace. We use the augmented eigenvalues $\lambda_{2,k}^j$ given by eq 25 of ref 15 (or eq 49 of ref 13) which takes partly into account the interactions with the complementary subspace. Thus $\lambda_{2,k}^j$ may readily be calculated for given values of N and the six model parameters introduced above: κ_0 , τ_0 , λ^{-1} , a , ζ_t , and ζ_r . (Of course,

the absolute temperature T should also be specified.) In eq 4, α_2^j are the spherical tensor components of the polarizability tensor affixed to the subbody, and $R_{2,k}^{ij}$ is the transformation matrix associated with the eigenvalue problem of the above-mentioned matrix and is given by eq 40 of ref 13. We note that $R_{2,k}^{ij}$ depends on the parameters κ_0 , τ_0 , and λ^{-1} . As explicitly shown in the previous theoretical paper,¹³ Lorentzians only with very small k make contribution to J_Γ because of the factor $\cot^2[\cdot \cdot \cdot]$ involved in the amplitude A_k^j given by eq 3, and moreover, only those belonging to one or two branches (j) of the eigenvalue spectrum ($\lambda_{2,k}^j$) make contribution because of the factor B_k^j given by eq 4. The resultant J_Γ may therefore be represented practically in terms of a single Lorentzian. This is consistent with the previous and present experimental results.

Dependence of τ_Γ on x_w

Now we proceed to make a comparison of the present data for τ_Γ with the HW theory. In Figure 2, the solid curve represents the HW theoretical values of τ_Γ given as the reciprocal of the HWHM of J_Γ calculated from eqs 1 and 2 with the values of the (static) model parameters determined from $\langle S^2 \rangle$,³ i.e., $\lambda^{-1}\kappa_0 = 3.0$, $\lambda^{-1}\tau_0 = 0.9$, $\lambda^{-1} = 46.8 \text{ \AA}$, and $\lambda a = 0.063$ ($a = 2.95 \text{ \AA}$), those of the (dynamic) parameters, i.e., $r_1 \equiv \zeta_t/3\pi\eta_0 a = 1.0$ and $r_2 \equiv \zeta_r/a^2\zeta_t = 8.0$, and those of the components of the polarizability tensor α of the subbody (repeat unit) expressed in the localized Cartesian coordinate system affixed to it, which are the same as those previously⁴ used to calculate $\langle \Gamma^2 \rangle$ and are given by

$$\alpha = \text{diag}(1.40, 2.47, -3.87) \text{ \AA}^3 \quad (\text{a-P}\alpha\text{MS}) \quad (5)$$

where N has been set equal to x_w . Recall that $\langle \Gamma^2 \rangle$ is equal to the integral of J_Γ over the whole range of $\Delta\omega$ at zero scattering angle.^{1,13}

We note that the above value of λa has been calculated from eq 9.14 of ref 1 (or eq 22 of ref 20) with the value 0.0634 of $\lambda\Delta s = \lambda M_0/M_L$, where M_0 is the molecular weight of the repeat unit and is taken to be 118 for a-PαMS and M_L is the shift factor as defined as the molecular weight per unit contour length and has been determined to be $39.8 \text{ \AA}^{-1}$ for a-PαMS.³ We also note that the above values of r_1 and r_2 are the same as those previously used for a-PS¹⁰ and a- and i-PMMA.^{11,12} If we assume as in the previous studies^{10–12} that the subbody is an oblate spheroid having the rotation axis of length a and the diameter d , then d is calculated to be $11 \text{ \AA}$ from eq 10.18 with eqs 10.19, 6.A.47, and 6.A.48 of ref 1 (or eqs 35–38 of ref 21) with the above values of a , r_1 , and r_2 . This value of d is in good agreement with the value $11 \text{ \AA}$ previously¹⁵ estimated from the chemical structure of syndio-

tactic PαMS (with $f_r = 1.0$), indicating that the above values of r_1 and r_2 are reasonable.

In Figure 2, we have omitted the HW theoretical values for $x_w \lesssim 10$ since the block-diagonal approximation^{1,22} adopted in that theory breaks down in the range of such small N . The theoretical asymptotic value of $k_B T \tau_\Gamma / \eta_0$ in the limit of $x_w \rightarrow \infty$ is $2.07 \times 10^4 \text{ \AA}^3$ and is *ca.* 2.4 times as large as the experimental value *ca.* $8.5 \times 10^3 \text{ \AA}^3$. As in the cases of a- and i-PMMA,^{11,12} agreement between theory and experiment is only semiquantitative and is not so good as in the case of a-PS.¹⁰

As in the previous studies of a-PS¹⁰ and a- and i-PMMA,^{11,12} we consider τ_Γ for the rigid sphere model¹ having the radius equal to the apparent root-mean-square radius of gyration $\langle S^2 \rangle_s^{1/2}$ of the HW chain and having a cylindrically symmetric polarizability tensor. It may be given by

$$\tau_\Gamma = 4\pi\eta_0 \langle S^2 \rangle_s^{3/2} / 3k_B T \quad (6)$$

We note that $\langle S^2 \rangle_s^{1/2}$ is defined as the coefficient of the squared scattering vector k^2 in the expansion of the scattering function determined from small-angle X-ray scattering measurements and may be regarded as the mean-square radius of gyration of the excess electron density. Thus it may be given by

$$\langle S^2 \rangle_s = \langle S^2 \rangle + S_c^2 \quad (7)$$

where $\langle S^2 \rangle$ is the (usual) mean-square radius of gyration of the HW chain contour of total length L and is given by eq 5 of ref 3 (or eq 4.83 of ref 1 in units of λ^{-1}) and S_c is the (effective) radius of gyration of the cross section of the excess electron density distributed around the chain contour and has already been evaluated to be $\sqrt{10.7} \text{ \AA}$ for a-PαMS.³ The values of τ_Γ calculated from eq 6 with eq 7 are represented by the dashed curve in Figure 2. We note that the contour length L of the HW chain has been converted to x_w by the use of the relation $x_w = M_L L / M_0$. The dashed curve may reproduce satisfactorily the data points for $x_w \lesssim 10$ as in the cases of a-PS¹⁰ and a- and i-PMMA.^{11,12}

Comparison with Other Flexible Polymers

Finally, in this subsection we compare the present results for a-PαMS with the previous ones for a-PS¹⁰ and a- and i-PMMA.^{11,12} Figure 3 shows double-logarithmic plots of $\tau_\Gamma / \tau_\Gamma^0$ against x_w for a-PαMS in cyclohexane at 30.5°C (Θ) (unfilled circles), a-PS in cyclohexane at 34.5°C (Θ) (filled circles), a-PMMA in acetonitrile at 44.0°C (Θ) (filled triangles), and i-PMMA in acetonitrile at 28.0°C (Θ) (filled inverted triangles), where τ_Γ^0 is the τ_Γ of the monomer (isolated repeat unit), i.e., $\tau_\Gamma^0 = 0.00607 \text{ ns}$ for a-PαMS (cumene) in cyclohexane at 30.5°C , 0.00562 ns for a-

Figure 3. Double-logarithmic plots of $\tau_\Gamma/\tau_\Gamma^0$ against x_w , where τ_Γ^0 is the τ_Γ of the isolated monomer: (○) present data for a-PαMS in cyclohexane at 30.5 °C (Θ); (●) previous data for a-PS in cyclohexane at 34.5 °C (Θ);¹⁰ (▲) previous data for a-PMMA in acetonitrile at 44.0 °C (Θ);¹¹ (▼) previous data for i-PMMA in acetonitrile at 28.0 °C (Θ).¹² The heavy solid, dashed, dot-dashed, and dotted curves represent the respective HW theoretical values, and the light curves represent the respective theoretical values for the rigid sphere model.

PS (cumene) in cyclohexane at 34.5 °C,¹⁰ 0.0019₃ ns for a-PMMA (methyl isobutylate) in acetonitrile at 44.0 °C,¹¹ and 0.0023₆ ns for i-PMMA (methyl isobutylate) in acetonitrile at 28.0 °C.¹² The above value 0.0060₇ ns of τ_Γ^0 in cyclohexane at 30.5 °C has been calculated from the value 0.0056₂ ns previously¹⁰ determined in cyclohexane at 34.5 °C by assuming that the reduced relaxation time $k_B T \tau_\Gamma^0 / \eta_0$ is independent of T . As previously noted,^{11,12} the values of the reduced relaxation time $k_B T \tau_\Gamma^0 / \eta_0$ are 31.1 and 29.6 Å³ for cumene and methyl isobutylate, respectively, and are in good agreement with each other.

The asymptotic value $\tau_{\Gamma,\infty}/\tau_\Gamma^0$ of the ratio $\tau_\Gamma/\tau_\Gamma^0$ in the limit of $x_w \rightarrow \infty$ represents the degree of restriction on the rotational motion of the isolated motional unit (monomer) due to its incorporation into the long enough polymer chain and may be regarded as a measure of “dynamic chain stiffness” (associated with J_Γ).^{1,15} The heavy solid, dashed, dot-dashed, and dotted curves represent the HW theoretical values of τ_Γ for a-PαMS, a-PS, a- and i-PMMA, respectively, divided by the respective observed ones of τ_Γ^0 , and the light curves represent the respective theoretical values for the rigid sphere model.

Although the values of the ratio $\tau_\Gamma/\tau_\Gamma^0$ for a-PαMS, a-PS, a- and i-PMMA are close to each other in the oligomer region with very small x_w , they deviate from each other with increasing x_w . In the limit of $x_w \rightarrow \infty$, the value of the ratio for a-PαMS is intermediate between those for a-PMMA and a-PS, and is slightly

larger than that for i-PMMA, reconfirming our previous conclusion^{1,15} that there is good correlation between the dynamic and static chain stiffness. We note that the values of λ^{-1} are 20.6 Å (a-PS) < 38.0 Å (i-PMMA) < 46.8 Å (a-PαMS) < 57.9 Å (a-PMMA).¹ Considering the fact that the HW theoretical values have been calculated by the use of the values of the HW model parameters determined from the equilibrium property $\langle S^2 \rangle$ along with the proper values of the dynamic parameters, it may be concluded that the dynamic HW theory may explain well the difference in $\tau_{\Gamma,\infty}/\tau_\Gamma^0$ among a-PαMS, a-PS, a- and i-PMMA, although agreement between theory and experiment is only semiquantitative except for a-PS.

CONCLUDING REMARKS

The power spectra J_Γ of the excess depolarized component of the light scattered from a-PαMS in cyclohexane at 30.5 °C (Θ) were determined from frequency-domain dynamic depolarized LS measurements following the data-processing procedure previously developed in order to extract J_Γ from observed spectra. Then it has been found that J_Γ may be well represented in terms of a single Lorentzian independently of x_w , and that the relaxation time τ_Γ defined by the reciprocal of the HWHM of J_Γ increases with increasing x_w and levels off to its asymptotic value in the limit of $x_w \rightarrow \infty$ as in the previous cases of a-PS¹⁰ and a- and i-PMMA,^{11,12} being consistent with the theoretical prediction on the basis of the HW chain model. From a rather detailed analysis of the present data, it has been shown that the HW theory may explain semiquantitatively the observed dependence of τ_Γ (or J_Γ) on x_w over that range of x_w for which the theory is applicable, *i.e.*, for $x_w \gtrsim 10$, while the rigid sphere model^{1,10–12} having the radius equal to the apparent root-mean-square radius of gyration $\langle S^2 \rangle_s^{1/2}$ of the HW chain may reproduce well the data for $x_w \lesssim 10$. From a comparison of the present results for a-PαMS with the previous ones for a-PS and a- and i-PMMA, it has also been shown that the dynamic chain stiffness¹ defined as the ratio of the relaxation time associated with the local motion of the long chain to that of its isolated repeat unit (monomer) is well correlated with the static chain stiffness λ^{-1} , as predicted by the HW theory.

In the following paper,⁹ we make a nuclear magnetic relaxation study of a-PαMS in a similar spirit.

Acknowledgment. This research was supported in part by the 21st century COE program “COE for a United Approach to New Materials Science” from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

REFERENCES

1. H. Yamakawa, "Helical Wormlike Chains in Polymer Solutions," Springer, Berlin, 1997.
2. H. Yamakawa, *Polym. J.*, **31**, 109 (1999).
3. M. Osa, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **33**, 4828 (2000).
4. H. Kojo, M. Osa, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **36**, 6570 (2003).
5. Y. Ohgaru, M. Sumida, M. Osa, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **33**, 9316 (2000).
6. I. Suda, Y. Tominaga, M. Osa, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **33**, 9322 (2000).
7. M. Osa, M. Sumida, T. Yoshizaki, H. Yamakawa, K. Ute, T. Kitayama, and K. Hatada, *Polym. J.*, **32**, 361 (2000).
8. Y. Tamai, T. Konishi, Y. Einaga, M. Fujii, and H. Yamakawa, *Macromolecules*, **23**, 4067 (1990).
9. M. Osa, H. Ueda, T. Yoshizaki, and H. Yamakawa, *Polym. J.*, **37**, 14 (2005).
10. Y. Takaeda, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **27**, 4248 (1994).
11. Y. Takaeda, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **28**, 682 (1995).
12. Y. Naito, N. Sawatari, Y. Takaeda, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **30**, 2751 (1997).
13. T. Yoshizaki and H. Yamakawa, *J. Chem. Phys.*, **99**, 9145 (1993).
14. H. Yamakawa and M. Fujii, *J. Chem. Phys.*, **81**, 997 (1984).
15. H. Yamakawa, T. Yoshizaki, and M. Fujii, *J. Chem. Phys.*, **84**, 4693 (1986).
16. Y. Takaeda, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **26**, 3742 (1993).
17. Y. Takaeda, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **28**, 4167 (1995).
18. A. C. Ouano and R. Pecora, *Macromolecules*, **13**, 1167 (1980).
19. T. Yoshizaki, Y. Takaeda, and H. Yamakawa, *Macromolecules*, **26**, 6891 (1993).
20. H. Yamakawa and T. Yoshizaki, *J. Chem. Phys.*, **75**, 1016 (1981).
21. T. Yoshizaki and H. Yamakawa, *J. Chem. Phys.*, **81**, 982 (1984).
22. H. Yamakawa, T. Yoshizaki, and J. Shimada, *J. Chem. Phys.*, **78**, 560 (1983).