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NOTE

First Cumulant of Polymacromonomers Consisting of Polystyrene

Yoshimura Tomoaki and Nakamura Yo*

Department of Polymer Chemistry, Kyoto University, Katsura, Kyoto 615-8510, Japan

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Introduction

Polymacromonomers, whose molecule has a main chain covered by dense side chains, are sometimes called "bottle-brush polymers" or "brushlike polymers" and known to behave as stiff chains.[1−7] Recent dilute-solution studies on polymacromonomers consisting of polystyrene showed that the mean-square radius of gyration $\langle S^2 \rangle$,[8−11] the scattering function,[12−14] the intrinsic viscosity $[\eta]$,[10,11,15] and the hydrodynamic radius R_H,[11,16,17] which reflect the global conformation or motion, can be described by the theories for the cylindrical wormlike chain model. On the other hand, local properties of polymacromonomers have not been studied yet. It seems important to see whether such properties can be explained by the same model or not.

The first cumulant $\Omega(k)$ of the dynamic structure factor, measured by the dynamic light scattering technique, is available to study local motions of polymer chains, where k denotes the magnitude of the scattering vector. It is known that the reduced first cumulant defined by $\eta_0\Omega(k)/k_BTk^3$ approaches a constant for $\langle S^2 \rangle^{1/2}k > 1$ for the Gaussian chain,[18−20] where η_0 means the solvent viscosity, k_B the Boltzmann constant, and T the absolute temperature. The existence of a plateau of $\eta_0\Omega(k)/k_BTk^3$ plotted against $\langle S^2 \rangle^{1/2}k$ was confirmed by studies on solutions of high molecular weight polystyrene (PS) in theta solvents, although the plateau value was smaller than the theoretical values for the Gaussian model with and without the preaveraging approximation of the hydrodynamic tensor.[21,22]

Yoshizaki et al.[23] carried out a more precise calculation based on the helical-wormlike chain model[24] and showed that the plateau height depends on the local conformation of the polymer. The theory successfully explained the experimental data for PS,[25] poly(methyl methacrylate),[25] poly(α-methylstyrene),[26] polyisobutylene,[26] and poly(hexyl isocyanate);[27] the $\eta_0\Omega(k)/k_BTk^3$ values for the former four flexible polymers were rather close to each other, but those for the last stiff polymer were much larger than the others. It is intriguing to see if $\Omega(k)$ for polymacromonomers is close to the flexible chain or stiff chain values.

Here, we make dynamic light scattering measurements to determine $\Omega(k)$ for polystyrene polymacromonomers in cyclohexane at 34.5 °C (theta solvent) and toluene at 15.0 °C (good solvent). Experimental values for $\eta_0\Omega(k)/k_BTk^3$ are compared with theoretical values based on the wormlike chain model. For this purpose, the experimental data for large $\langle S^2 \rangle^{1/2}k$ range are essential. Thus, we choose polymer samples with long main-chain length, which have large $\langle S^2 \rangle$.

Experimental Section

The polymacromonomer samples, which have polystyrene structure in both main and side chains, with relatively high degree of polymerization of main chain (denoted by N) had been chosen from previously studied F33,[9,15] F65,[10] and F110,[11] whose weight-average degrees of polymerization of side chain (denoted by n) are 33, 65, and 113, respectively. Weight-average molecular weights M_w for these samples determined in the previous studies are summarized in Table 1 along with n and N which was calculated from M_w divided by the molecular weight of the macromonomer.

Reagent grade solvents (Wako Chemical Co.) were fractionally distilled after refluxing 5 h over sodium metal. Each polymer sample was mixed with the solvent and stirred for 12 h at the room temperature or at 50 °C for toluene and cyclohexane solutions, respectively. For each sample, five solutions with different mass concentration c less than 2.5×10^{-4} g cm^{-3} were prepared. They were optically clarified passing through double layer of Teflon filter with 0.1 μm pore size.

Dynamic light scattering measurements were made on a Brookhaven BI-200SM instrument equipped with BI-9000AT correlator and Nd:YVO$_4$ laser (Spectra Physics, Millennia IIs, 2 W) with 532 nm wavelength at scattering angles $\theta = 30°$, 45°, 60°, 90°, 120°, and 150° to obtain the normalized autocorrelation function $g^{(2)}(t)$. Solution temperature was kept at 34.5 and 15.0 °C for cyclohexane and toluene solutions, respectively. The sampling time was taken to be 1−5 μs.

Results and Discussion

The absolute value of the initial slope of (1/2) $\ln[g^{(2)}(t) - 1]$ plotted against t for each solution with the mass concentration c was equated to the apparent first cumulant $\Omega(k,c)$, which was weakly dependent on c. Thus, the measured $\Omega(k,c)$ values were extrapolated to $c = 0$ to obtain $\Omega(k)$. By extrapolating $\Omega(k)/k^2$ to $k^2 = 0$, we obtained the translational diffusion coefficient D, which essentially agreed with those determined in the previous studies.[11,16,17] Calculated R_H values from $k_BT/6\pi\eta_0 D$ with D obtained are given in Table 1 along with the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ previously studied and the ratio of $\langle S^2 \rangle^{1/2}$ to R_H (denoted by ρ).

The reduced first cumulant for all the polymacromonomer samples in cyclohexane at 34.5 °C is plotted against $\langle S^2 \rangle^{1/2}k$ by the unfilled symbols in Figure 1. For linear polystyrene in the same solvent, it is known that $\eta_0\Omega(k)/k_BTk^3$ hardly depends on M_w, and experimental data for different M_w make almost a composite curve if M_w is more than 10^6.[21] Similar behavior can be seen for the polymacromonomers' $\eta_0\Omega(k)/k_BTk^3$ when the data for F33-1 and F33-2 or F110-1 and F110-2 in Figure 1 are compared. Another point to note is that the data points for polymacromonomers with different side chain length come close instead of the large difference of the stiffness parameter λ^{-1} and the diameter d (see Table 2).

The filled symbols in Figure 1 show $\eta_0\Omega(k)/k_BTk^3$ for polymacromonomer F110-1 and F110-2 in toluene at 15.0 °C. It can be seen that the difference between $\eta_0\Omega(k)/k_BTk^3$ values for F110 in good (toluene) and theta (cyclohexane) solvents is almost

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*Corresponding author. E-mail: yonaka@molsci.polym.kyoto-u.ac.jp.

Table 1. Properties of Polymacromonomer Samples in Cyclohexane (CH) at 34.5 °C and Toluene (Tol) at 15.0 °C

sample	solvent	n	$10^{-6}M_w$	$10^{-3}N$	$\langle S^2\rangle^{1/2}$/nm	R_H/nm	ρ
F33-1	CH	33	10.6[a]	3.08	54.5[a]	43.1	1.26_5
F33-2	CH	33	7.50[a]	2.24	44.9[a]	36.6	1.22_7
F65-2	CH	65	4.23[b]	0.624	28.1[b]	23.8	1.18_1
F110-1	CH	113	13.0[c]	1.10	52.5[c]	40.9	1.28_4
F110-2	CH	113	10.2[c]	0.864	42.9[c]	36.8	1.16_6
F110-1	Tol	113	13.0[c]	1.10	65.0[c]	49.1	1.32_4
F110-2	Tol	113	10.2[c]	0.864	51.1[c]	42.7	1.19_7

[a] Reference 8. [b] Reference 10. [c] Reference 11.

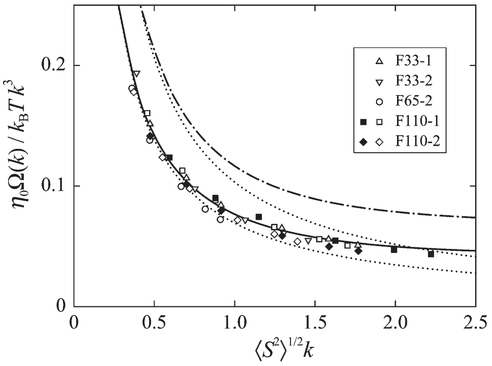

Figure 1. Reduced first cumulant for polystyrene polymacromonomers plotted against $S^{21/2}k$; triangles up, F33-1; triangles down, F33-2; circles, F65-2; squares, F110-1; diamonds, F110-2. Unfilled and filled symbols represent the data for cyclohexane and toluene solutions, respectively. Solid and dot-dashed lines show calculated values from eq 1 for linear polystyrene and poly(hexyl isocyanate), respectively. Dotted lines are drawn to indicate the contribution from the first term in the square brackets of eq 1.

invisible being different from linear polymer systems, in which the excluded-volume effect on the reduced first cumulant is significant.[28] This must be ascribed to the reduced contour lengths λL of F110-1 and F110-2 (1.87 and 1.48, respectively) smaller than the value (about 3) at which the excluded-volume effect on the chain dimension starts to appear.

According to the theory of Yoshizaki et al.,[23] $\eta_0\Omega(k)/k_BTk^3$ for the touched-bead helical wormlike chain is written as

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

Here, $\bar{k}$ denotes $\langle S^2\rangle^{1/2}k$ and $F(\bar{k})$ is the term reflecting the internal motion of the polymer chain. The first term in the square brackets in eq 1 is the contribution from the translational motion and may be calculated theoretically. However, it is known that the theoretical ρ for infinitely long flexible polymers is 10−20% larger than experimental values.[29] Hence, we use experimental ρ in Table 1 instead of the theoretical one for the calculation of $\eta_0\Omega(k)/k_BTk^3$.

The solid line in Figure 1 represents the theoretically calculated values by the above eqation to represent the experimental data for linear polystyrene (PS) with molecular weight $M = 1.0 \times 10^6$ in cyclohexane at 34.5 °C[25] (the parameters for the calculation are the same as those used in ref 25). The data points for the polymacromonomers come close to this line. On the other hand, the dot-dashed line calculated to represent the experimental values[27] for poly(hexyl isocyanate) (PHIC) with $M = 7.7 \times 10^5$ in hexane at 25.0 °C (the parameters for the calculation are the same as those used in ref 27) is much higher than the data points. The dotted lines in Figure 1 represent the values calculated from the first term in the square brackets in eq 1, showing that the contribution of this term is larger than that of the other term, corresponding to the difference between the solid/dot-dashed line and the dotted line, and that the dotted line for PS is closer to the data points for the polymacromonomers than that for PHIC. Thus, the polymacromonomers' $\eta_0\Omega(k)/k_BTk^3$ coming close to the solid line is primarily due to the ρ values in Table 1 closer to the PS value (1.305)[25] than the PHIC value (1.945).[27]

Table 2. Molecular Parameters for Polystyrene Polymacromonomers

sample	solvent	M_L/nm^{-1}	λ^{-1}/nm	d/nm	δ/nm
F33[a]	CH	13 500	22	10	4
F65[b]	CH	26 000	36	15	6
F110[c]	CH	45 500	80	24	5
F110[c]	Tol	45 500	155	26	5

[a] Reference 8. [b] Reference 10. [c] Reference 11.

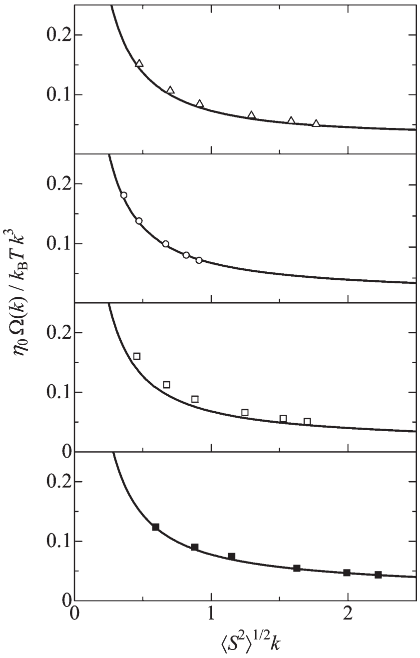

Figure 2. Comparison between calculated (solid lines) and observed (symbols) reduced first cumulant: F33-1 in cyclohexane at 34.5 °C (CH), F65-2 in CH, F110-1 in CH, and F110-1 in toluene at 15.0 °C, from top to the bottom.

For the wormlike chain model, $F(\bar{k})$ is a function of the contour length L and the bead diameter d_b both divided by λ^{-1}. The first parameter for the polymacromonomer samples may be calculated from[15]

$$L = M_w/M_L + \boldsymbol{\delta} \qquad (2)$$

Here, δ means the apparent contribution of side chains near the main-chain ends to the main chain contour. The second parameter d_b may be related to the chain diameter d by $d/d_b = 0.861$.[30] Values of M_L, λ^{-1}, d, and δ determined in previous studies are summarized in Table 2, which were used for the present calculation.

Comparison of experimental $\eta_0\Omega(k)/k_BTk^3$ for F33-1, F65-2, and F110-1 in cyclohexane and F110-1 in toluene with the theoretical one is illustrated in the different panels of Figure 2. The almost perfect fits of the solid lines to the experimental data show that the theory successfully explains the internal motion of polymacromonomer chains as well as the global one, which is reflected by ρ. Thus, we confirm again that the wormlike chain is a quite suitable model for polymacromonomer molecules.

Although not shown in Figure 2, the calculated line for linear PS (solid line in Figure 1) comes close to the solid lines in the figure. If we calculate λd for the polymacromonomers from Table 2, they are in the range 0.17−0.46 and close to the PS value (0.46), but much larger than the PHIC value (0.035). At the same $\langle S \rangle^{1/2}k$, the reduced $\Omega(k)$ is insensitive to λL but remarkably changed with λd. As the result, $\eta_0\Omega(k)/k_BTk^3$ for the polymacromonomers takes very close values to those for PS.

If the main-chain stiffness of polymacromonomer molecules could be increased without changing d and L, the reduced $\Omega(k)$ might increase and finally cease to have the plateau since the chain stiffness accelerates the relaxation process as is the case for PHIC. However, to obtain higher stiffness, the polymer must have longer side chains, which may increase d and reduce $\Omega(k)$ because of the enhanced friction. By the compensation of these two effects, the reduced $\Omega(k)$ values for polymacromonomers with different side-chain length almost agree.

In the present analyses, we only considered the main-chain dynamics because the polymacromonomers studied have main chains much longer than the side chains. To detect much faster side-chain motions, different techniques may be required.

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