Polymer Bulletin 44, 309–316 (2000)

Polymer Bulletin

Solution properties of polymacromonomers consisting of polystyrene

4. Translational diffusion coefficient in cyclohexane at the Θ temperature

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Received: 8 February 2000/Accepted: 18 February 2000

Summary

Dynamic light scattering measurements have been made on 14 samples of a polymacromonomer consisting of polystyrene with 15 styrene side-chain units in cyclohexane at 34.5°C (the theta point) to determine the translational diffusion coefficient D as a function of molecular weight. The dependence of D on the main-chain length is analyzed on the basis of the wormlike chain by taking into account the end effect arising from side chains near the main-chain ends. The model parameters describing this dependence, i.e., the Kuhn segment length (11.5 ± 1.5 nm), the linear mass density (5600 ± 700 nm^{-1}), the diameter (5.2 ± 0.5 nm), and the end-effect parameter δ (2.5 ± 0.3 nm), are close to those determined previously from $\langle S^2\rangle_z$ (the z-average mean-square radius of gyration) and $[\eta]$ (the intrinsic viscosity), leading to the conclusion that the wormlike chain model is capable of consistently explaining $\langle S^2\rangle_z$, $[\eta]$, and D of the polymacromonomer in the Θ solvent.

Introduction

Although polymacromonomers, a new class of regular comb polymers, are now known to behave like semiflexible chains in solution (1-3), unequivocal determination of their stiffness or conformational characteristics is still a subject matter. Wintermantel et al. (1,2) reported that measured z-average mean-square radii of gyration $\langle S^2\rangle_z$ and intrinsic viscosities $[\eta]$ for such a polymer consisting of the poly(methyl methacrylate) backbone and polystyrene (PS) side chains in toluene, a good solvent, are not consistently explained by the current theories (4-6) for the wormlike chain (7), a typical model for semiflexible chains, yielding different values for the Kuhn segment length. In contrast to this, we recently found that these theories are capable of quantitatively describing $\langle S^2\rangle_z$ and $[\eta]$ for two series of polymacromonomer samples consisting only of PS and having 15 and 33 styrene side chain residues (polymacromonomers F15 and F33) in cyclohexane at 34.5°C (8-10), the Θ temperature, if end effects arising from the contribution of side chains near the main-chain ends to the polymacromonomer contour are taken into consideration. Undoubtedly, the absence of intramolecular excludedvolume effect in the Θ solvent made our analysis less equivocal.

The present paper reports a dynamic light scattering (DLS) study undertaken to see whether data of the translational diffusion coefficient D, another important physical property, for the polymacromonomer F15 in cyclohexane at the Θ point are consistent with the above finding from static light scattering and viscometry. The experimental results for D and their analysis based on the unperturbed wormlike chain are presented below.

Experimental

Samples

The previously investigated samples (9), F15-1, F15-2, ..., F15-14, of the F15 polymacromonomer with known weight-average molecular weights M_w were used for the present study (see Figure 1 in ref. 8 or 9 for the chemical structure of the polymer). The weight-average to number-average molecular weight ratios $M_\mathrm{w}/M_\mathrm{n}$ previously determined by gel permeation chromatography were in the range between 1.05 and 1.10 for F15-2, F15-3, ..., F15-13. The side chain length distribution, examined for the precursor (α-benzyl-ω-hydrogen polystyrene) by a MALDI-TOF spectrometer, was characterized by $M_\mathrm{w}/M_\mathrm{n}$ of 1.09. The molecular weight of our macromonomer was 1.65×10^3 (9).

Dynamic Light Scattering

DLS experiments were carried out for the 14 samples in cyclohexane at 34.5°C using an ALV/DLS/SLS-5000 light scattering photometer with an ALV/5000E/WIN correlator. Vertically polarized incident light of wavelength 488 nm (argon ion laser) or 532 nm (YAG laser) was used. The refractive index n_0 of the solvent was taken as 1.423 at 488 nm and 1.421 at 532 nm. Test solutions and the solvent were filtered (with 0.5 μm Millipore filters) directly into light scattering cells capable of being spun in a centrifuge. They were then centrifuged in a Sorvall RC-5C centrifuge for about 30 min.

The normalized autocorrelation function $g^{(2)}(t)$ of scattered light intensity at time t was determined at four polymer mass concentrations c (for each sample) and at scattering angles θ ranging from 30 to 90°. It is related to the first cumlant Γ by

$$\frac{1}{2}\ln\left[g^{(2)}(t)-1\right]=\text{constant}-\Gamma\, t+O\left(t^2\right) \tag{1}$$

and the desired D is determined from

$$D = \lim_{\substack{k \to 0 \\ c \to 0}} \Gamma / k^2 \qquad (2)$$

Here, k denotes the magnitude of the scattering vector defined by $k = (4\pi n_0/\lambda_0)\sin(\theta/2)$, with λ_0 being the wavelength of the incident light in vacuum.

Results

Figure 1 illustrates the plots of $\ln[g^{(2)}(t)\text{-}1]$ against k^2t for the highest molecular weight sample F15-1 at c = 1.151 X 10^{-3} g cm^{-3} and at the indicated scattering angles. The data points at each θ follow a straight line in the indicated range of k^2t. The values of Γ/k^2 determined from the slopes were essentially independent of k for any samples, allowing accurate evaluation of $(\Gamma/k^2)_{k\to 0}$, i.e., the zero-angle value of Γ/k^2. The resulting $(\Gamma/k^2)_{k\to 0}$ values plotted against c are shown for the two highest and three lowest molecular weight samples in Figure 2. The values of D obtained from the indicated lines and from similar straight lines for the other samples are summarized in Table I, along with those of M_w determined by static light scattering in part 2 (9). Figure 3 illustrates the

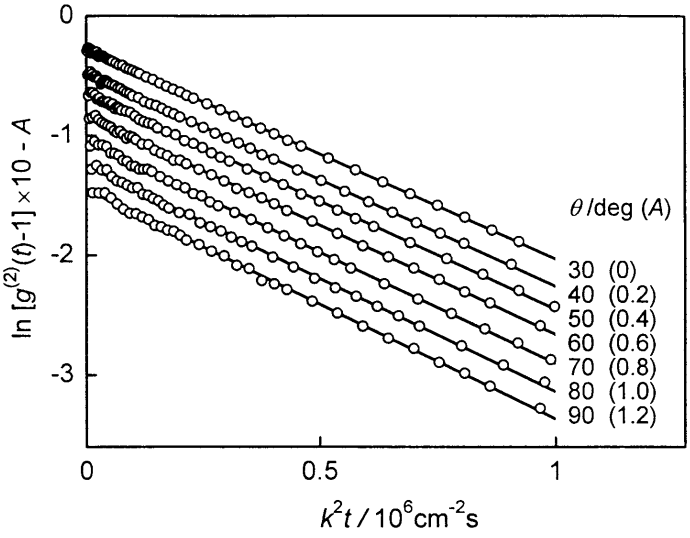

Figure 1. Plots of $\ln[g^{(2)}(t)\text{-}1]$ vs. k^2t ($c = 1.151 \times 10^{-3}$ g cm^{-3}) for polymacromonomer sample F15-1 in cyclohexane at 34.5°C. The ordinate values at a given θ are shifted by $-A$. Wavelength, 488 nm.

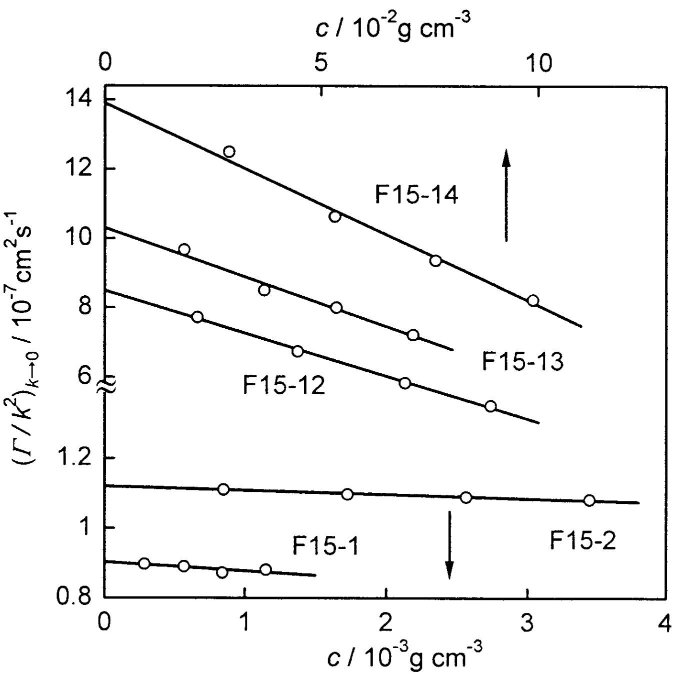

Figure 2. Concentration dependence of $(\Gamma/k^2)_{k\to 0}$ for samples F15-1, F15-2, F15-12, F15-13, and F15-14 in cyclohexane at 34.5°C.

molecular weight dependence of D for the polymacromonomer in cyclohexane at Θ (34.5°C). The curve fitting the data points is convex upward with a slope of - 0.49 for $M_w > 1 \times 10^6$ and - 0.34 for $M_w < 6 \times 10^4$. The former exponent is close to the Gaussian chain value - 0.5.

Table I. Molecular Weights and Diffusion Coefficients for Polymacromonomer Samples in Cyclohexane at 34.5°C

Sample	$M_w/10^{4\,a}$	$D/10^{-7}\text{cm}^2\text{s}^{-1}$	Sample	$M_w/10^{4\,a}$	$D/10^{-7}\text{cm}^2\text{s}^{-1}$
F15-1	647	0.903	F15-8	25.2	4.21
F15-2	404	1.12	F15-9	17.5	4.91
F15-3	225	1.57	F15-10	12.3	5.74
F15-4	123	2.04	F15-11	6.14	7.61
F15-5	82.2	2.57	F15-12	4.74	8.49
F15-6	60.9	3.00	F15-13	2.60	10.3
F15-7	38.1	3.49	F15-14	1.08	13.9

[a] Taken from ref. 9

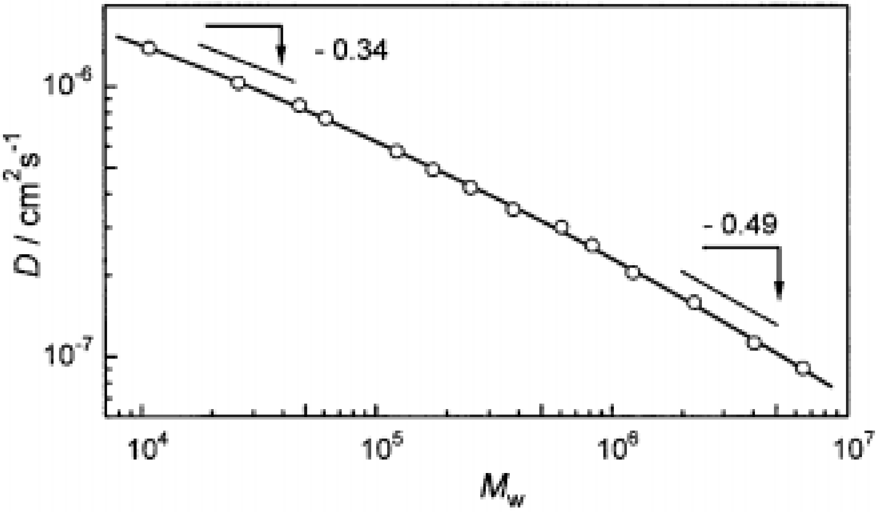

Figure 3. Molecular weight dependence of D for the F15 polymacromonomer in cyclohexane at 34.5°C.

Discussion

Analysis

We analyze the present D data on the basis of the Yamakawa-Fujii theory (11) for the translational friction coefficient of an unperturbed wormlike cylinder (with the familiar Einstein relation), but for low molecular weights we use Norisuye et al.'s theory (12) for short wormlike cylinders with hemisphere caps since the Yamakawa-Fujii theory ignores the contribution from the cylinder ends. Both theories contain three parameters, the contour length L, the Kuhn segment length λ^{-1}, and the cylinder diameter d. The first parameter is related to the molecular weight M by $L = M/M_L$, with M_L being the linear mass density of the chain. For our polymacromonomer with low M_w, however, side chains near the main-chain ends should contribute toward apparently increasing L (see Figure 3 of ref 10). Denoting this contribution by δ, we have

$$L = M / M_L + \delta \tag{3}$$

This end effect, i.e., the effect of δ, on $[\eta]$ of the polymacromonomer was remarkable for M_w below 10^5 (10).

A curve-fitting procedure was employed for our analysis with two of the four parameters (λ^{-1}, M_L, d, and δ) fixed to the values (9,10) previously determined from $[\eta]$ (or $\langle S^2\rangle_z$) data (see Table II). Namely, λ^{-1} and M_L, for example, were estimated for the given values of d and δ, and the estimation was extended to all cases of other fixed parameter pairs. It should be noted that more than two parameters cannot uniquely be determined from the present D data. Except for the case in which λ^{-1} and M_L are assumed to be known, all the cases gave equally close agreements between theory and experiment. However, the estimated values for each parameter slightly differed depending on the choice of the parameter pair, so that their mean was taken as the desired value. We note that the effect of δ on the D - M relation was appreciable for $M < 10^5$ but not as remarkable as that on the $[\eta]$ - M relation (10).

The parameters thus obtained are presented in Table II, along with our previous estimates from $\langle S^2\rangle_z$ and $[\eta]$, and the calculated and experimental D values are compared in Figure 4, in which the solid lines for M above and below 1.2 X 10^5 refer to the theories of Yamakawa and Fujii (11) and Norisuye et al. (12), respectively, and their left end at M = 1.51 X 10^4 corresponds to the sphere limit of $L = d$. These curves smoothly connect and closely fit the data points down to this limit. Since the

Table II. Wormlike-Chain Parameters for the Polymacromonomer F15 in Cyclohexane at 34.5°C.

method	d / nm	λ^{-1}/nm	$M_L/10^3\text{nm}^{-1}$	δ/nm
$\langle S^2\rangle_z$ [a]	—	9.5	6.2	—
$[\eta]$ [a]	4.7	9.5[b]	6.3	2.2
D	5.2±0.5	11.5±1.5	5.6±0.7	2.5±0.3

[a] refs. 9 and 10 [b] Assumed

parameters from D are fairly close to those from $[\eta]$ and $\langle S^2\rangle_z$, we may conclude that the three properties of the polymacromonomer in cyclohexane at the Θ point are consistently explained by the wormlike chain. The backbone stiffness of this polymer, expressed by λ^{-1} of about 10 nm (Table II), is five times higher than that of the linear PS chain (5), and the values of M_L ($\approx$ 6000 nm^{-1}) and d ($\approx$ 5 nm) are compatible with the chemical structure of the polymacromonomer, as discussed previously (9,10). In particular, this d is about twice as large as the calculated end-to-end distance (2.4 nm) of each side chain (10). In regard to the subtle difference between the parameters from D and $[\eta]$ (or $\langle S^2\rangle_z$), the following remarks may be pertinent.

The two dashed lines (joined at M = 1.5 X 10^5) in Figure 4 represent the D values calculated from the theories of Yamakawa and Fujii (for M > 1.2 X 10^5) and Norisuye et al. (for M < 1.2 X 10^5) using the parameters from $[\eta]$. Their upward deviation from the data points or the solid lines, at least, for high molecular weights is very likely due to the inaccuracy of the former theory for long wormlike chains since the present $(\lambda M_L)^{1/2}$ value determining the coil limiting behavior of the polymacromonomer is 16 % larger than that from $\langle S^2\rangle_z$ or $[\eta]$. This degree of disagreement often observed for long flexible chains (5) is responsible for the above finding that no good agreement between the theoretical and experimental D is obtained when λ^{-1} and M_L from $\langle S^2\rangle_z$ or $[\eta]$ are used in the analysis; note that, although the $[\eta]$ theory of Yoshizaki et al. (6) in the coil limit is not accurate either, it happened to give $(\lambda M_L)^{1/2}$ consistent with the

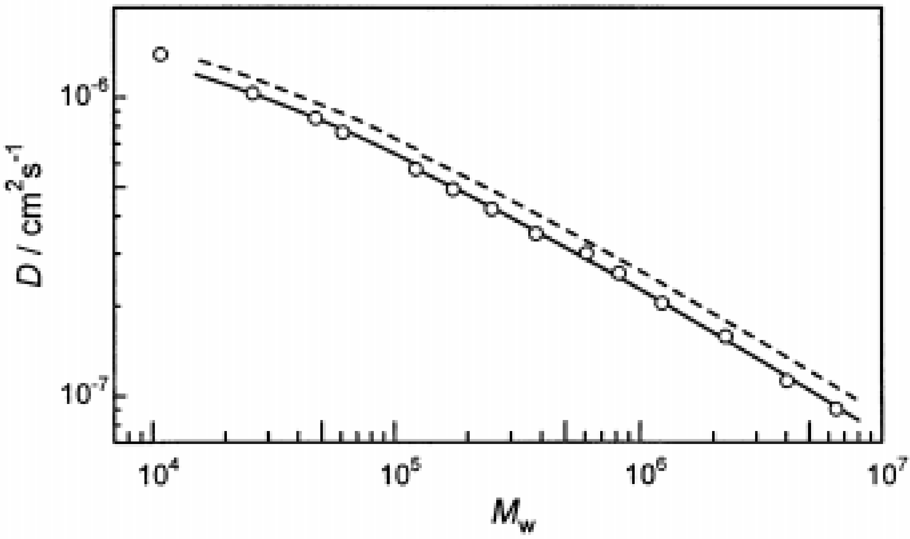

Figure 4. Comparison between the measured D for the polymacromonomer F15 in cyclohexane at 34.5℃ and the theoretical solid curves (Yamakawa and Fujii's theory (11) for $M > 1.2\times10^5$ and Norisuye et al.'s (12) for $M < 1.2\times10^5$) for the unperturbed wormlike chain with λ^{-1} = 11.5 nm, M_L = 5600 nm^{-1}, d = 5.2 nm, and δ = 2.5 nm. The dashed lines represent the theoretical values calculated with the parameters from $[\eta]$.

chain dimensions for our thick polymer molecule. The small deviation of the dashed line for $M < 10^5$ may be attributed to our simplified treatment of side chain effects near the main-chain ends or to certain shortcomings of the current polymer hydrodynamic theories themselves (5,6,11,12) and does not seem to impair the applicability of the wormlike chain to the polymacromonomer.

Reduced Hydrodynamic radius

The circles in Figure 5 show the values of the reduced hydrodynamic factor ρ^{-1} [= $k_B T/6\pi\eta_0 D\langle S^2\rangle_z^{1/2}$] for our polymacromonomer in cyclohexane, calculated from the data in Table I and our previous $\langle S^2\rangle_z$ data (9), where $k_B T$ has the usual meaning and η_0 denotes the solvent viscosity. This hydrodynamic factor is essentially independent of M_w in the range examined, exhibiting behavior similar to that of unperturbed long flexible chains rather than thin stiff chains (5).

The curve in Figure 5 represents the theoretical ρ^{-1} values computed for the wormlike chain with λ^{-1} = 10.5 nm, M_L = 5900 nm^{-1} (both the means of the parameter from $\langle S^2\rangle_z$ and D), d = 5.2 nm, and δ = 2.5 nm from the Yamakawa-Fujii theory and the expression for the unperturbed mean-square radius of gyration $\langle S^2\rangle$ (4):

$$\lambda^2\langle S^2\rangle = \frac{\lambda L}{6} - \frac{1}{4} + \frac{1}{4\lambda L} - \frac{1}{8(\lambda L)^2}\left[1-\exp(-2\lambda L)\right] \qquad (3)$$

We note that the effect of side chains on $\langle S^2\rangle$ (9) and that of δ on D is negligible in the M_w range concerned here. Though the curve appears somewhat below the data points

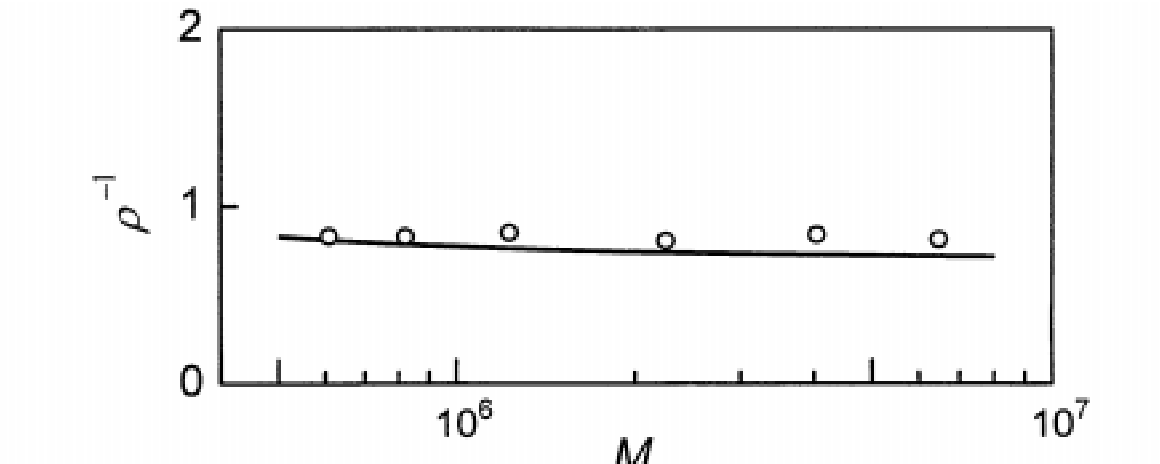

Figure 5. Comparison between the theoretical and experimental ρ^{-1} for the polymacromonomer F15 in cyclohexane at 34.5°C (see the text for the parameters used for the calculation).

because of the small discrepancy between the parameters from D and $\langle S^2 \rangle_z$, the agreement between theory and experiment is not bad. This confirms that D and $\langle S^2 \rangle_z$ for our polymacromonomer in the Θ solvent is consistently explained by the wormlike chain model.

Conclusion

We determined translational diffusion coefficients covering a broad range of M_w for a series of polymacromonomer samples consisting of 15 styrene side chain residues in cyclohexane at 34.5°C (a Θ solvent) by dynamic light scattering, and analyzed them on the basis of the wormlike chain. The data are described fairly satisfactorily by the current theories (11,12) for this model when the end effect arising from side chains near the main-chain ends is considered. Within the accuracy of the theories, the estimated parameters are consistent with those determined previously from $\langle S^2 \rangle_z$ and $[\eta]$. Hence, the wormlike chain model allows a consistent explanation of $\langle S^2 \rangle_z$, $[\eta]$, and D for the polymacromonomers in the Θ solvent.

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