Synchrotron Small-Angle X-ray Scattering from Polystyrene Polymacromonomers in Toluene

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ABSTRACT: Synchrotron small-angle X-ray scattering (SAXS) measurements have been made on toluene solutions of six polystyrene polymacromonomer samples having a fixed side chain length of 15 styrene residues and ranging in the polymerization degree of the main chain N_w from 6.5 to 106 (in weight average) at 25 °C. The z-average mean-square radii of gyration $\langle S^2 \rangle_z$ from the present SAXS and previous light scattering as a function of N_w and the particle scattering functions $P(\theta)$ in the form of $k^2P(\theta)$ against k (the magnitude of the scattering vector) are compared with theoretical values for three models: (a) the wormlike cylinder with a uniform cross section, (b) the wormlike chain with Gaussian density distribution within the cross-sectional plain, and (c) the touched-bead comb with wormlike main and side chains. Theoretical curves for the models (a) and (b) equally fit the data points for $\langle S^2 \rangle_z$ and $k^2P(\theta)$ (for $k < 1 \text{ nm}^{-1}$) with a set of model parameters consistent with that describing the previously determined N_w -dependence of intrinsic viscosity in toluene, but the latter model explains the $P(\theta)$ behavior up to a slightly larger k . The model (c) allows similarly good fits to $\langle S^2 \rangle_z$ and better fits to $k^2P(\theta)$ over a wider k range if the Kuhn segment length of each side chain and the bead diameter are adjusted to values much larger than those expected for an isolated polystyrene molecule. The decoupling approximation to $P(\theta)$ invoked in the literature is also examined for the models (a) and (b).

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Dilute-solution studies^{1–9} revealed that polymacromonomer molecules have considerably high stiffness in solution and can be modeled by the Kratky-Porod (KP) wormlike chain.¹⁰ Analyses of hydrodynamic properties such as the intrinsic viscosity $[\eta]$ and the translational diffusion coefficient D generally give information on the chain diameter d , but as was pointed out previously in relation to the estimation of d , available hydrodynamic theories involve a few problems in their accuracy (see ref 11). Thus, for the purpose of deducing geometrical features of polymacromonomer side chains, we commenced small-angle X-ray scattering (SAXS) experiments^{11,12} on cyclohexane solutions of low molar mass polystyrene polymacromonomer F15 (with 15 styrene residues in each side chain) at the theta point 34.5 °C using a laboratory scale apparatus.¹² The result showed that the measured z-average mean-square radii of gyration $\langle S^2 \rangle_z$ and particle scattering functions $P(\theta)$ for k (the magnitude of the scattering vector) smaller than 1 nm^{-1} are essentially consistent with the structural information derived from $[\eta]$ and D on the wormlike cylinder model. With regard to the structural feature of the side

chains, however, this uniform cylinder can be a coarse-grained model, at least, for low molecular weight samples.

In the present study, we made synchrotron SAXS measurements on F15 polymacromonomer samples in toluene (a good solvent) at 25 °C hoping to find a molecular model relevant to the cross-sectional structure of the comb polymer molecule. Use of the high-intensity X-ray source was essential to raise the accuracy of intensity data for $k > 1 \text{ nm}^{-1}$ where the previous cyclohexane data from our own apparatus were not very accurate. The $\langle S^2 \rangle_z$ data and scattering curves obtained are compared with theoretical values calculated for a few different models including the wormlike cylinder. The work reported here includes theoretical considerations of the decoupling approximation invoked by Rathgeber *et al.*¹³ and Zhang *et al.*¹⁴ in recent small-angle neutron scattering studies on comb-branched polymer and polymacromonomer solutions. These authors concluded that measured scattering curves are explained by the product of the scattering function for the wormlike chain contour and that for the cross sectional plain based on a Gaussian function

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Table I. Weight-average molecular weights, degrees of polymerization, and ratios of weight- to number-average molecular weight for polymacromonomer F15 samples (reproduction from ref 5)

Sample	$M_w/10^5$	N_w	M_w/M_n
F15-9	1.75	106	1.10
F15-10	1.23	745	1.10
F15-11	0.614	37.2	1.08
F15-12	0.474	28.7	1.09
F15-13	0.260	15.8	1.09
F15-14	0.108	6.5	—

for the radial distribution of side chain segments. Our discussion on the validity of the decoupling approximation (presented in the Appendix) utilizes $P(\theta)$ for cylindrical wormlike chains calculated elsewhere¹⁵ without resort to the approximation.

EXPERIMENTAL

Polymer Samples

Six polymacromonomer samples, F15-9–F15-14, were chosen from a series of F15 samples prepared previously.⁵ This polymacromonomer consists of the polystyrene main chain and side chains of 15 (weight average value) styrene residues connected to the para position of every phenylene group of the main chain. The weight-average molecular weights M_w , weight-average degrees of polymerization N_w , and weight-to number-average molecular weight ratios M_w/M_n of the samples are given in Table I. The M_w and M_w/M_n values had been determined by static light scattering and size-exclusion chromatography, respectively.⁵

SAXS Measurements

Synchrotron SAXS experiments on toluene solutions of the polymacromonomer samples were carried out at a beam line BL40B2 in the synchrotron facility, SPring8 (Proposal No. 2002B0112-NL2-np and 2005B0088). A monochronized X-ray beam of 1.5 nm wavelength was exposed for 4 min to each solution in a quartz capillary cell (1.5 mm diameter) placed in a capillary holder whose temperature was kept at 25 °C (± 0.1 °C) by circulation of temperature-regulated water. The scattered X-ray from the solution was detected on an imaging plate (IP) as a two dimensional image. The distance from the capillary to IP was set to be 1000 mm, which was confirmed by the powder diffraction pattern of lead stearate. The desired intensities $I(\theta)$ were obtained as a function of scattering angle θ by integration of intensities over a narrow angular range between $\theta - \Delta\theta$ and $\theta + \Delta\theta$ with $\Delta\theta = 0.005^\circ$. Four solutions with different poly-

Figure 1. SAXS data for polymacromonomer sample F15-10 in toluene obtained from a laboratory system (panel a, $c = 0.116$, 0.0881, 0.0603, and 0.0315 g cm⁻³ from top to bottom; exposure time 6 h) and from the synchrotron facility (panel b, $c = 0.0546$, 0.0429, 0.0292, and 0.0143 g cm⁻³ from top to bottom; exposure time 4 min).

mer mass concentrations c were prepared for each sample. The solvent intensity also measured was subtracted from $I(\theta)$ for each solution to evaluate the excess scattering intensity $\Delta I(\theta)$.

Figure 1 compares $k^2[c/\Delta I(0)]/[c/\Delta I(\theta)]$ obtained from a laboratory scale SAXS system¹² (a) and the synchrotron facility (b) for sample F15-10 in toluene, where $[c/\Delta I(0)]$ denotes $[c/\Delta I(\theta)]$ extrapolated to $\theta = 0$. In spite of the longer exposure time (6 h) and higher polymer concentrations in the former experiment, the data points in panel (a) considerably scatter. This is due to weak scattering signals available from the laboratory system.

The scattering intensities at each θ were extrapolated to $c = 0$ by use of the square-root plot, *i.e.*, $[c/\Delta I(\theta)]^{1/2}$ vs. c , to obtain $[c/\Delta I(\theta)]_{c=0}^{1/2}$. Figure 2 shows $[c/\Delta I(\theta)]_{c=0}^{1/2}$ plotted against k^2 for each sample (“ $c = 0$ ” is omitted in the figure). The initial slope and intercept ($[c/\Delta I(0)]_{c=0}^{1/2}$ at $k = 0$) of each plot give $\langle S^2 \rangle_z$. The particle scattering function was evaluated from $[c/\Delta I(0)]_{c=0}/[c/\Delta I(\theta)]_{c=0}$.

RESULTS

Figure 3 shows that the data of $\langle S^2 \rangle_z$ (the unfilled symbols) from the present SAXS and previous light scattering measurements on F15 samples in toluene⁵ (at 15 °C) are smoothly connected and that the molecular weight dependence becomes very weak as M_w de-

Figure 2. Plots of $[c/\Delta I(\theta)]^{1/2}$ against k^2 for indicated polystyrene polymacromonomer samples in toluene.

Figure 3. Molecular weight dependence of $\langle S^2 \rangle_z$ for polystyrene polymacromonomer F15 in toluene (unfilled circles, present SAXS at 25°C; unfilled triangles, previous light scattering at 15°C) and in cyclohexane at 34.5°C (filled triangles, previous light scattering;⁵ filled circles, previous SAXS¹¹). The thick solid and dashed lines represent the theoretical values in toluene for the wormlike cylinder and its centroid, respectively, and the thin solid and dashed lines, the corresponding theoretical values in cyclohexane. The theoretical values for the touched-bead comb model in toluene are shown by the dot-dashed line, which almost overlaps the thick solid curve. See the text for the model parameters used for the calculations.

Table II. Numerical values for the dimensional parameters of F15 polystyrene polymacromonomer in toluene determined from SAXS measurements

Sample	$\langle S^2 \rangle_z / \text{nm}^2$	d / nm	$\langle r_c^2 \rangle^{1/2} / \text{nm}$
F15-9	50	5.5	2.1
F15-10	27	5.1	1.9
F15-11	13	5.1	1.9
F15-12	10.0	4.8	1.9
F15-13	6.0	4.6	1.8
F15-14	3.7	3.9	1.6

creases below 10^5 . This figure includes our previous light scattering⁵ and SAXS¹¹ results for cyclohexane solutions of F15 at the theta point. The $\langle S^2 \rangle_z$ values are systematically larger in the good solvent than in the theta solvent (the indicated lines are explained in the next section). Numerical data of $\langle S^2 \rangle_z$ from the present SAXS study are summarized in the second column of Table II.

The Kratky plots of $k^2 P(\theta)$ against k for all the samples studied are shown in Figure 4a and b. As is the case for cyclohexane solutions,¹¹ each curve has a broad maximum which is typical of thick polymer chains.

DISCUSSION

Radius of Gyration

The mean-square radius of gyration $\langle S^2 \rangle$ of a cylindrical wormlike (or KP) chain is expressed by¹⁶

$$\langle S^2 \rangle = \langle S^2 \rangle_{\text{KP}} + \langle r_c^2 \rangle \quad (1)$$

with the mean-square radius of gyration of the cross section $\langle r_c^2 \rangle$ given by $d^2/8$, where d is the chain diameter. In the above equation, $\langle S^2 \rangle_{\text{KP}}$ denotes $\langle S^2 \rangle$ for the centroid of the chain. It is given by the familiar Benoit-Doty expression¹⁷ as a function of L (the contour length) and λ^{-1} (the Kuhn segment length) if no intramolecular excluded-volume effect is significant. Taking into account the apparent contribution δ of side chains near the main-chain ends to L , we have

$$L = M_w / M_L + \delta \quad (2)$$

with M_L being the molar mass per unit contour length. Thus, without excluded-volume effect, the molecular weight dependence of $\langle S^2 \rangle$ for the cylinder model is determined by four parameters, λ^{-1} , M_L , d , and δ . According to our previous analysis⁵ of light scattering $\langle S^2 \rangle_z$ data ($M_w > 3.8 \times 10^5$) based on the Yamakawa-Stockmayer-Shimada scheme^{18–20} with the Domb-Barrett equation²¹ for the radius expansion factor α_S , excluded-volume effects on $\langle S^2 \rangle_z$ for the F15 polymer in toluene are appreciable only for M_w above 10^6 . In this high M_w region, one additional parameter B (the

Figure 4. (a) Scattering functions for samples F15-9, F15-10, and F15-11 in toluene at 25 °C compared with theoretical curves. Solid lines, cylindrical wormlike chain with uniform cross section; dashed lines, wormlike chain with Gaussian density distribution in the cross-sectional plane; thin dot-dashed line, wormlike comb without chain thickness; thick dot-dashed line, wormlike touched-bead comb with chain thickness. See the text and Table II for the model parameters used for the calculations. (b) Scattering functions for samples F15-12, F15-13, and F15-14 in toluene at 25 °C compared with theoretical curves. The lines have the same meaning as that in Figure 4a.

excluded-volume strength) is needed for the evaluation of α_S .

The thick solid line closely fitting the toluene data

in Figure 3 represents the theoretical values for the uniform cylinder model computed with the previous parameters from light scattering⁵ ($\lambda^{-1} = 16 \text{ nm}$, $M_L = 6200 \text{ nm}^{-1}$, and $B = 4.5 \text{ nm}$) and the newly estimated ones ($d = 5.0 \text{ nm}$ and $\delta = 2.3 \text{ nm}$). This d of 5.0 nm is the mean of the values determined from the present $P(\theta)$ data for samples F15-9–F15-13 (see the next subsection), while δ has been estimated so that the calculated $\langle S^2 \rangle$ curve gives the closest agreement with the experimental data. In actuality, these two parameters coincide with those determined from $[\eta]$.⁶ The thick dashed line calculated for $d = \delta = 0$ fits only the light scattering data (the unfilled triangles) and deviates remarkably downward from the SAXS data. The result from our previous analysis for cyclohexane solutions¹¹ is also shown by the thin solid curve (calculated for $\lambda^{-1} = 9.5 \text{ nm}$, $M_L = 6200 \text{ nm}^{-1}$, $B = 0$, $d = 4.7 \text{ nm}$, and $\delta = 2.2 \text{ nm}$) and the thin dashed curve (for $d = \delta = 0$). The quantitative agreement between the solid lines and the experimental data in the respective solvents demonstrates that in the cylinder model, the consideration of d and δ is essential for analyses of $\langle S^2 \rangle_z$ of polymacromonomer F15 for $M_w < 3 \times 10^5$ or $N_w < 200$ and indeed allows a consistent explanation of the $\langle S^2 \rangle_z$ and $[\eta]$ data over a broad range of M_w from 1.1×10^4 to 6.5×10^6 .

For further comparison, we computed $\langle S^2 \rangle$ for a comb-branched polymer model (see the Appendix of ref 11) in which wormlike touched-bead side chains of contour length L_s ($= 3.92 \text{ nm}$ for F15¹¹) and Kuhn segment length λ_s^{-1} ($= 6 \text{ nm}$) are linked to the wormlike touched-bead main chain (of contour length M_w/M_L and Kuhn segment length λ^{-1}) by universal joints. In this computation, the thickness of all the sub-chains was taken into account by addition of $3d_b^2/20$ (in place of $d^2/8$ in eq 1)¹⁶ to $\langle S^2 \rangle$ of the comb chain with d_b (the bead diameter) $= 3 \text{ nm}$, and the values of α_S were assumed to be the same as those in the cylinder model mentioned above. The λ_s^{-1} value of 6 nm used was estimated by the analysis of $P(\theta)$ in the next subsection and the d_b value was chosen so as to give the closest fit to the data points. The dot-dashed curve representing the calculated result in Figure 3 almost overlaps the solid line and thus can hardly be seen. In other words, the agreement between theory and experiment is as good as that in the cylinder model. However, the d_b value of 3 nm is too large compared to the expected value (about 1 nm) for the polystyrene molecule^{16,22} (the discussion is deferred to the next subsection). As for the effect of d_b , the $\langle S^2 \rangle_z$ data for cyclohexane solutions were previously¹¹ analyzed in an erroneous way. Their re-analysis shows that a d_b of 2 nm leads to a good fit to the filled symbols (not shown for clarity). This value also seems too

large, but it is close to what was estimated previously¹¹ from $P(\theta)$.

Scattering Function

Recently, we made a theoretical calculation of $P(\theta)$ for the wormlike chain with a circular cross section¹⁵ of diameter d according to the scheme of Nagasaka *et al.*,²³ in which $P(\theta)$ is formally written as

$$P(\theta) = \frac{2}{(\lambda L)^2} \int_0^{\lambda L} (\lambda L - t) I(k; t) dt \quad (3)$$

with

$$I(k; t) = \sum_{n, n_0, n_t=0}^{\infty} (-1)^n \begin{pmatrix} 2n & 2n_0 & 2n_t \\ 0 & 0 & 0 \end{pmatrix}^2 (4n+1) \times [(4n_t+1)(4n_0+1)]^{1/2} F_{n_0}(k) F_{n_t}(k) I_{n, n_t}(k; t) \quad (4)$$

In this equation, $(\cdot \cdot \cdot)$ denotes the Wigner 3- j symbol, $I_{n, n_t}(k; t) (= \langle j_{2n}(kr) P_{2n}(\cos \Theta) P_{2n_t}(\cos \theta) \rangle')$ in ref 15) is a function of n , n_t , k , and t (the contour distance), and $F_n(k)$ is given by

$$F_n(k) = 2\pi(4n+1)^{1/2} \frac{(2n-1)!!}{(2n)!!} \int_0^{\infty} j_{2n}(kr) \rho(r) r dr \quad (5)$$

where $j_n(x)$ is the spherical Bessel function of the n th order and $\rho(r)$ is the normalized electron density at a distance r from the center in the cross-sectional plain.

For a uniform cylinder, $\rho(r)$ is given by

$$\rho(r) = \begin{cases} 4/\pi d^2 & (0 \leq r \leq d/2) \\ 0 & (r > d/2) \end{cases} \quad (6)$$

for which explicit expressions of $F_n(k)$ for small n are given as $F_n(kd)$ in the Appendix of ref 15. We consider another electron density distribution given by the Gaussian function

$$\rho(r) = \frac{1}{\pi \langle r_c^2 \rangle} \exp(-r^2 / \langle r_c^2 \rangle) \quad (7)$$

In this case, $F_n(k)$ may be calculated numerically. In our comparison with the $P(\theta)$ data, d or $\langle r_c^2 \rangle$ is regarded as an unknown with the other parameters (for the wormlike cylinder) fixed to the values describing the $\langle S^2 \rangle_z$ data.

The solid and dashed lines in Figure 4 show the calculated scattering functions for the wormlike chains with uniform and Gaussian cross-section profiles, respectively. Though both of these curves closely fit the data points for k below 1 nm^{-1} , those for the latter profile give slightly better fits. This is consistent with what was found by Rathgeber *et al.*¹³ and Zhang *et al.*,¹⁴ but, as mentioned in the Introduction, these groups invoked the decoupling approximation in their

analyses. We discuss the validity of this approximation in the Appendix.

The estimated d and $\langle r_c^2 \rangle^{1/2}$ for all the samples are summarized in the third and fourth columns, respectively, of Table II. These parameters decrease slightly with lowering M_w , but except for F15-14, they are roughly constant (within $\pm 10\%$). The values of $\langle r_c^2 \rangle$ are fairly close to those of $d^2/8$, which is the mean-square radius of the uniform, circular cross section. In this connection, we note that the analysis of $\langle S^2 \rangle$ data based on the Gaussian cross-section profile can equally be made by eq 1.

Rathgeber *et al.*¹³ showed that the scattering curve for a comb polymer with the number of residues in each side chain smaller than 50 is explained by a wormlike chain with $\rho(r)$ that is proportional to $r^{-4.5}$ and has a cutoff at the side-chain end. However, such a profile fails to explain our experimental data. The main and side chains of Rathgeber *et al.*'s polymer are different in chemical structure and have wider distribution in length. Thus, their conclusion should not be generalized to other brush-like polymers.

Finally, we compare the $P(\theta)$ data with the theoretical values for the comb-branched polymer model mentioned in the previous subsection. Considering the thickness of every sub-chain in the touched-bead model,²⁴ we have

$$P(\theta) = 9 \left(\frac{2}{kd_b} \right)^6 [\sin(kd_b/2) - (kd_b/2) \cos(kd_b/2)]^2 P_0(\theta) \quad (8)$$

where $P_0(\theta)$, the particle scattering function for the wormlike comb composed of infinitely thin sub-chains, can be calculated from eqs 3 and 4 for $n = n_0 = n_t = 0$ with $I_{0,0}(k; t)$ given in ref 15 (see also the Appendix of ref 11). With λ^{-1} , M_L , and L_s fixed to 16 nm , 6200 nm^{-1} , and 3.92 nm , respectively, we searched for values of λ_s^{-1} and d_b allowing the closest agreement between theory and experiment.

The fitting results are illustrated for the highest and lowest molecular weight samples (F15-9 and F15-14) in Figure 4a and 4b, respectively. In the former, the thick dot-dashed curve calculated for $\lambda_s^{-1} = 6 \text{ nm}$ and $d_b = 3.6 \text{ nm}$ almost completely overlaps the data points (and thus can hardly be seen), whereas the thin dot-dashed curve for $\lambda_s^{-1} = 6 \text{ nm}$ and $d_b = 0$ appears far above the data points, indicating the significant contribution of the sub-chain thickness to $P(\theta)$. In the latter, the dot-dashed line computed for $\lambda_s^{-1} = 3 \text{ nm}$ and $d_b = 2.2 \text{ nm}$ fits the data points up to $k = 1.9 \text{ nm}^{-1}$ where both solid and dashed curves fail. For the other samples, fits were as good as that of the thick dot-dashed line for F15-9 when the same λ_s^{-1} value of 6 nm and a d_b of $2.9\text{--}3.2 \text{ nm}$ (close to 3 nm from $\langle S^2 \rangle_z$) were chosen.

This λ_s^{-1} value, much larger than the Kuhn segment length (2 nm) for an isolated polystyrene chain, coincides with what was estimated previously¹¹ to explain $\langle S^2 \rangle_z$ and $P(\theta)$ data for the F-15 polymer in cyclohexane. As was pointed out in that paper, it yields an average diameter of 5.8 nm if the root-mean-square end-to-end distance for the contour length $2L_s$ is equated to the diameter. This diameter is comparable to the d values (4.6–5.5 nm) based on the uniform cylinder model (Table II), suggesting that the side chains of the F15 polymacromonomer are somewhat stiffened and hence more extended than the isolated polystyrene molecule. We note that this was also case in cyclohexane ($d = 4.7$ – 5.1 nm).¹¹ The other parameter d_b decreases from 3.6 to 2.2 nm with decreasing N_w . Namely, it appears to approach the value (*ca.* 1 nm) expected for the polystyrene chain. However, such N_w -dependent behavior of too large d_b must be taken to reveal certain shortcomings of the model. Thus, the present comb model seems less adequate than the wormlike chain with either uniform or Gaussian density distribution in the cross-sectional plain, although it allows close fits to the $P(\theta)$ data in toluene as well as in cyclohexane¹¹ over a wider range of k .

CONCLUDING REMARKS

The measured $\langle S^2 \rangle_z$ and $P(\theta)$ for polystyrene polymacromonomer F15 (with M_w ranging from 1.08×10^4 to 1.75×10^5) in toluene (a good solvent) have been compared with theoretical predictions based on the three models: (a) the wormlike cylinder with a uniform cross section, (b) the wormlike chain with Gaussian density distribution within the cross-sectional plain, and (c) the touched-bead comb with wormlike main and side chains. The conclusions from this comparison and some related remarks may be summarized as follows.

1. The model (a) allows both $\langle S^2 \rangle_z$ and $P(\theta)$ ($k < 1 \text{ nm}^{-1}$) to be quantitatively explained by $\lambda^{-1} = 16 \text{ nm}$, $M_L = 6200 \text{ nm}^{-1}$, $d = 5.0 \text{ nm}$, and $\delta = 2.3 \text{ nm}$, *i.e.*, by essentially the same parameter set as that describing $[\eta]$ data⁶ for the polymer in toluene.
2. When the electron density distribution is taken to be Gaussian [the model (b)], the agreement in $P(\theta)$ is somewhat improved (up to a k of 1.2 nm^{-1}). This was found earlier by Rathgeber *et al.*¹³ and Zhang *et al.*¹⁴ on the decoupling approximation. This approximation is not bad if d or $\langle r_c^2 \rangle^{1/2}$ is adjusted (see the Appendix).
3. Much closer agreements can be reached between the experimental and theoretical $P(\theta)$ with the model (c) if λ_s^{-1} (the Kuhn segment length of each side chain) and d_b (the bead diameter) are adjusted to 6 and 2.2–3.6 nm, respectively. However, since the d_b

values in this range are much larger than that expected for the polystyrene chain, without some improvement this model does not seem useful.

The unfavorable situation with the present comb model is attributable partly to the universal joint assumed for the linkage between each side chain and the main chain. Although the λ_s^{-1} value of 6 nm must be somewhat overestimated due to this assumption, it strongly suggests that the side chains in the F15 polymacromonomer should be more extended than the isolated polystyrene chain. On the other hand, no reasonable interpretation can be made for d_b that decreases from 3.6 to 2.2 nm with a decrease in the number of side chains. This trend is far more conspicuous than what was observed previously for the same F15 samples in cyclohexane (the theta solvent),¹¹ in which d_b from $P(\theta)$ was insensitive to N_w , being in the range between 2.0 and 2.5 nm. This contrast may be taken to suggest that side chain–side chain interactions have something to do with the seemingly unreasonable d_b values. Those interactions are known to stiffen the main chain (more remarkably in good solvents),²⁵ but their effect on the spatial distribution of side chain segments is left unexplored. Evidently, a more elaborate comb model should deserve to be devised for clarification of conformational features of polymacromonomer side chains.

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APPENDIX

This appendix is to give a warning to use of the decoupling approximation in analyses of scattering functions. In this approximation, $P(\theta)$ is expressed by a product of $P_0(\theta)$ and the scattering function for the cross-sectional plain $P_{cs}(\theta)$

$$P(\theta) = P_0(\theta) \times P_{cs}(\theta) \quad (\text{A-1})$$

with $P_{cs}(\theta)$ given by²⁶

$$P_{cs}(\theta) = \left[2\pi \int_0^\infty \rho(r) J_0(kr) r dr \right]^2 \quad (\text{A-2})$$

Here, $J_n(x)$ is the Bessel function of the n -th order. As is well known, $P_{cs}(\theta)$'s for the uniform and Gaussian electron density profiles in the cross-sectional plain are given by $[2J_1(kd/2)/(kd/2)]^2$ and $\exp(-k^2 \langle r_c^2 \rangle / 2)$, respectively. It should be noted that eq 8 for the touched-bead comb is free from the decoupling approximation.

Figure A. Comparison between theoretical values for cylindrical wormlike chains with (dashed lines) and without (solid lines) decoupling approximation for $L/d = 10$ and indicated λd values. The dot-dashed lines represent the values in the decoupling approximation (eqs A-1 and A-2) with eq A-3.

Figure A illustrates theoretical $(kL)^2 P(\theta)$ vs. kL for the cylindrical wormlike chains with $L/d = 10$ and $\lambda d = 0.01, 0.1, 1$, and 10 . The solid lines were calculated from eqs 3–5 and the dashed lines, from eq A-1 with eq A-2 [see the Discussion section for $P_0(\theta)$]. It is seen that the dashed line, close to the corresponding solid line for $\lambda d < 0.1$, deviates downward for larger λd . Thus, the decoupling approximation underestimates d for $\lambda d > 0.1$ and becomes poorer with increasing chain flexibility for fixed d . We find, however, that, as indicated by dot-dashed lines in the figure, the values from eqs A-1 and A-2 come close to the solid lines when d_{app} given by the following equation is substituted for d .

$$d_{\text{app}}/d = 0.80 + 0.20 \exp(-2.0\lambda d) \quad (\text{A-3})$$

Thus, the chain diameter estimated on the decoupling approximation may be corrected with this relation although resort to the approximation is undesirable. We note that eq A-3 is a good approximation for $L/d \geq 2.5$, $\lambda d \leq 10$, and $kd \leq 10$. This equation is also applicable to the Gaussian profile if we replace d and d_{app} by $8^{1/2} \langle r_c^2 \rangle^{1/2}$ and $8^{1/2} \langle r_c^2 \rangle_{\text{app}}^{1/2}$, respectively, where $\langle r_c^2 \rangle_{\text{app}}$ means the apparent $\langle r_c^2 \rangle$ estimated on the decoupling approximation.

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