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Scattering Function of Syndiotactic Poly(methyl methacrylate) in Dilute Solution

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ABSTRACT: The scattering function was measured for a syndiotactic poly(methyl methacrylate) (s-PMMA) sample with the fraction of racemic diads $f_r = 0.92$ and weight-average molecular weight $M_w = 3.76 \times 10^4$ in acetonitrile at 44.0 °C (Θ) for the magnitude k of the scattering vector smaller than 1 Å^{-1} by the use of the same point-focusing small-angle X-ray scattering (SAXS) camera as used in a previous SAXS study of atactic (a-)PMMA samples with $f_r = 0.79$. Supplementary measurements were also carried out on the same s-PMMA sample in benzene at 25.0 °C. As in the case of a-PMMA, the Kratky plots of the present data for s-PMMA in the two solvents do not exhibit the second maximum and minimum, or oscillation, as observed by Kirste and Wunderlich in the range of $k \gtrsim 0.4$ Å^{-1}, being consistent with the theoretical prediction on the basis of the helical wormlike chain. A rather detailed comparison of the present data for s-PMMA in acetonitrile with the previous corresponding ones for a-PMMA shows that the relative value of the first maximum of the Kratky plot compared to the first minimum is larger for the former than for the latter. This may be regarded as arising from the fact that the helical nature of PMMA chains becomes more remarkable with increasing f_r.

Introduction

In a previous small-angle X-ray scattering (SAXS) study of the scattering function P_s for atactic oligo- and poly(methyl methacrylate)s (a-PMMA) with the fraction of racemic diad $f_r = 0.79$ in the unperturbed Θ state (in acetonitrile at 44.0 °C),[1] it has been shown that its Kratky plot does not exhibit the second maximum and minimum, or oscillation, as observed by Kirste and Wunderlich[2,3] for syndiotactic (s-)PMMA, which is considered to have $f_r \simeq 0.9$, in the range of the magnitude of the scattering vector $k \gtrsim 0.4$ Å^{-1}. Our experimental result above is rather consistent with the theoretical prediction[4] on the basis of the helical wormlike (HW) chain[5,6] and therefore has resolved the problem, which had for a long time been bothering us, that the HW model cannot predict the above remarkable oscillation observed by Kirste and Wunderlich despite the fact that it may give a good explanation of other static and steady-state transport properties. Although their s-PMMA sample has f_r somewhat larger than our a-PMMA samples, we have not considered this to be a main source of the difference between our and their data in the above range of k but regarded it as arising mainly from the difference between the SAXS apparatuses and also that between the data processing procedures. Note that they used a Kratky camera with the desmearing procedure, while we have determined P_s directly by the use of a point-focusing camera.

As already noted in the previous paper,[1] however, the rotational isomeric state model[7] does predict that the Kratky plot for a- (and s-) PMMA in the range of large k exhibits oscillation for $f_r \gtrsim 0.8$, with it becoming more remarkable with increasing f_r.[8–10] Thus, in order to confirm our previous conclusion stated above, it is desirable to carry out measurements on an s-PMMA sample having the same f_r as that of Kirste and Wunderlich by the use of the same SAXS apparatus that we have used in the previous study.[1] In the present study, we do this and examine the dependences on f_r of the behavior of the Kratky plot in such a range of k and also of the first maximum and minimum of the plot that appear for smaller k.

Experimental Section

Materials. The s-PMMA sample used in this work is a fraction separated by fractional precipitation using chloroform as a solvent and methanol as a precipitant from a commercial sample 28300-4 of Polymer Laboratories Ltd. prepared by anionic polymerization. Its initiating chain-end group is fluorene, and the other end is a hydrogen atom. The nominal values of the weight-average molecular weight M_w and the ratio of M_w to the number-average molecular weight M_n are 3.4×10^4 and 1.17, respectively. The ratio M_w/M_n was estimated to be 1.12 for the fractionated test sample by analytical gel permeation chromatography with the use of our calibration curve determined for the a-PMMA with $f_r = 0.79$.

The solvents acetonitrile used for light scattering (LS) and SAXS measurements and benzene used for SAXS measurements were purified according to standard procedures.

^{1}H NMR. ^{1}H NMR spectra of α-methyl protons of the sample were recorded on a JEOL JMN GX-280 spectrometer at 270.05 MHz. The spectrum was taken in deuterated chloroform at 55 °C using a radio-frequency pulse angle of 45° with a pulse repetition time of 57 s. The chemical shifts δ referring to the proton of residual (impurity) chloroform were converted to the TMS scale.

Light Scattering. LS measurements were carried out to determine M_w of the sample and also the Θ temperature of acetonitrile solutions. M_w was determined in acetonitrile at 45.0 °C. For the determination of Θ, the second virial coefficient A_2 was measured for the sample at several temperatures ranging from 35 to 55 °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 a scattering angle of 90° at 25.0 °C, where the Rayleigh ratio $R_{\mathrm{Uu}}(90°)$ of pure benzene was taken as 46.5×10^{-6} cm^{-1}. The depolarization ratio ρ_u of pure benzene at 25.0 °C was determined to be 0.41 ± 0.01 by the method of Rubingh and Yu.[11] Scattering intensities were measured at five different concentrations and at scattering angles ranging from 30 to 150°. The data obtained were treated by the

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Berry square-root plot[12] and also by the Bawn plot.[13,14] In the present case, corrections for the optical anisotropy were unnecessary since the degree of depolarization was negligibly small.

The most concentrated solution of the sample was prepared gravimetrically and made homogeneous by continuous stirring at 50 °C for 2 days. It was optically purified by filtration through a Teflon membrane of pore size 0.45 μm. The solutions of lower concentrations were obtained by successive dilution. The weight concentrations of the test solutions were converted to the polymer mass concentrations c by use of the density of the solvent.

The refractive index increment $\partial n/\partial c$ for the sample in acetonitrile at 45.0 °C was measured at 436 nm by the use of a Shimadzu differential refractometer. The result is 0.146_5 cm^3/g.

Small-Angle X-ray Scattering. As in the previous SAXS studies,[1,15] all measurements were carried out by the use of a point-focusing camera of overall length 6 m in the High-Intensity X-ray Laboratory of Kyoto University. A detailed specification of this camera has already been given elsewhere,[16] and its brief description has been given in the previous paper.[15] Thus we here note only a few points proper to the present work.

In this work, the Mo Kα line of wavelength λ_0 = 0.711 Å was used as the incident beam by eliminating other lines with a Zr foil of 50-μm thickness. The distance from a sample cell to a detector (two-dimensional position-sensitive proportional counter) was ca. 640 mm as before,[1,15] so that intensity measurements could be carried out in the range of k up to ca. 1 Å^{-1}. The temperature of the sample cell was kept constant at 44.0 ± 0.2 °C for the acetonitrile solutions and at 25.0 ± 0.1 °C for the benzene solutions. The excess scattering intensity in the range of $k \gtrsim 0.5$ Å^{-1} was very small. Therefore, in order to diminish statistical errors in this range, the intensities scattered from each solution and the solvent were accumulated for ca. 12 and 6 h, respectively. The measurements on the solvent were made before and after every measurement on the solution.

As in the previous studies,[1,15] the two-dimensional data thus obtained for a solution of solute mass concentration c (in g/cm^3) were first corrected for the detector sensitivity and then averaged over polar angles in the detector plane to obtain the scattering intensity $I_{\rm obs}(k,c)$ as a function of k, which is explicitly defined by

$$k = (4\pi/\lambda_0)\sin(\theta/2) \qquad (1)$$

with θ the scattering angle. From the observed intensity $I_{\rm obs}$, we evaluate the reduced intensity $I_{\rm R}(k,c)$ defined by

$$I_{\rm R}(k,c) = I_{\rm obs}(k,c)/AI_0 \qquad (2)$$

where A is the transmittance of a given sample solution and I_0 is the intensity of the incident beam monitored by the intensity scattered from a polyethylene film placed in front of the detector. The excess reduced scattering intensity $\Delta I_{\rm R}(k,c)$ is then obtained as the reduced scattering intensity from the solution $I_{\rm R,soln}(k,c)$ minus that from the solvent $I_{\rm R,solv}(k)$ [$=I_{\rm R,soln}(k,0)$] as follows,

$$\Delta I_{\rm R}(k,c) = I_{\rm R,soln}(k,c) - I_{\rm R,solv}(k) \qquad (3)$$

Results

Molecular Weight and Stereochemical Composition. The value of $M_{\rm w}$ of the s-PMMA sample determined from LS measurements in acetonitrile at 45.0 °C is 3.76 × 10^4. The difference between this value and the nominal value (3.4 × 10^4) for the commercial sample may be mainly due to the fractionation.

Figure 1 shows a ^{1}H NMR spectrum of α-methyl protons of the s-PMMA sample. The assignments of the peaks to the three kinds of triads, i.e., mm, mr, and rr with m and r indicating the meso and racemic diads, respectively, have been made on the basis of the ^{1}H NMR spectra obtained by Chûjô et al.[17] for PMMA, as shown in the figure. The relative intensities of the three peaks for mm, mr, and rr are 0.01_4, 0.13_8, and 0.84_8, respectively, and $f_{\rm r}$ is evaluated to be 0.92 from these values, assuming that the triad distributions in the sample are Bernoullian as in the case of a-PMMA.[18]

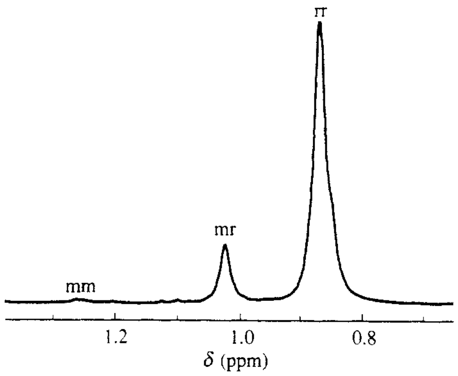

Figure 1. ^{1}H NMR spectrum of α-methyl protons of the s-PMMA sample.

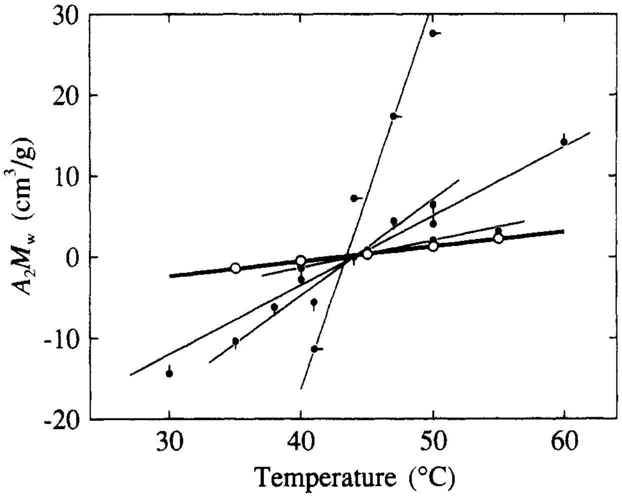

Figure 2. Plots of $A_2M_{\rm w}$ against temperature for the s-PMMA sample in acetonitrile along with those for a-PMMA samples studied previously:[19] (○) for the s-PMMA sample; (●) for an a-PMMA sample (MM5) with $M_{\rm w}$ = 5.16 × 10^4; (●) for an a-PMMA sample (MM19′) with $M_{\rm w}$ = 1.91 × 10^5; (●) for an a-PMMA sample (Mr4) with $M_{\rm w}$ = 3.61 × 10^5; (●) for an a-PMMA sample (Mr19) with $M_{\rm w}$ = 1.90 × 10^6.

Θ Temperature. Figure 2 shows plots of $A_2M_{\rm w}$ against temperature for the s-PMMA sample in acetonitrile. The unfilled circles represent the present data, which follow the indicated thick straight line. For comparison, the previous data[19] for four a-PMMA samples with $M_{\rm w}$ = 5.16 × 10^4, 1.91 × 10^5, 3.61 × 10^5, and 1.90 × 10^6, named MM5, MM19′, Mr4, and Mr19, respectively, have also been reproduced in the figure (filled circles with or without pip).

It is seen from the figure that A_2 vanishes at 43.0 °C for the present data for s-PMMA. Although this temperature is somewhat lower than the Θ temperature 44.0 °C determined previously from the above data for a-PMMA reproduced, it may be concluded that the Θ temperature for s-PMMA with $f_{\rm r}$ = 0.92 in acetonitrile is actually identical with that for a-PMMA with $f_{\rm r}$ = 0.79 since the experimental error for $A_2M_{\rm w}$ is not small for the present sample with rather small $M_{\rm w}$. Thus all the SAXS measurements in acetonitrile were carried out at 44.0 °C.

Scattering Function. The excess reduced scattering intensity $\Delta I_{\rm R}(k,c)$ introduced in the Experimental Section, which may be determined directly from SAXS measurements at finite mass concentration c, may be related to the normalized scattering function $P_{\rm s}$ as follows:[1,15]

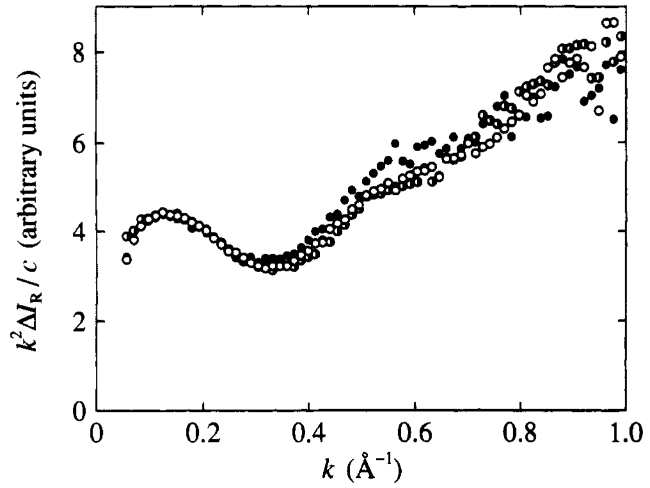

Figure 3. Plots of $k^2\Delta I_R/c$ against k for the s-PMMA sample in acetonitrile at 44.0 °C: (○) c = 0.0974 g/cm^3; (◑) c = 0.0808 g/cm^3; (●) c = 0.0599 g/cm^3.

$$\frac{Kc}{\Delta I_R(k,c)} = \frac{1}{M_w P_s(k)} + 2A_2 Q(k)\, c + \mathcal{O}(c^2) \tag{4}$$

where K is the optical constant, A_2 is the second virial coefficient, and Q represents the intermolecular interference.[20] Note that P_s and Q become unity at $k = 0$. From eq 4, we obtain

$$\frac{\Delta I_R(k,c)}{K M_w c} = P_s(k) - 2A_2 M_w [P_s(k)]^2 Q(k)\, c + \mathcal{O}(c^2) \tag{5}$$

We may then evaluate P_s by extrapolating the ratio $\Delta I_R(k,c)/KM_wc$ to $c = 0$ if the values of K and M_w are known. In the limits of $k \rightarrow 0$ and $c \rightarrow 0$, we have from eq 4

$$K = [\Delta I_R(0,c)/c]_{c=0}/M_w \tag{6}$$

Thus, as noted in the previous papers,[1,15] K may be evaluated experimentally if the value of $[\Delta I_R(0,c)/c]_{c=0}$ is determined for a sample whose M_w is known.

The quantity $[\Delta I_R(0,c)/c]_{c=0}$ may be determined experimentally for those oligomer samples for which the Berry square-root plot[12] against k^2 follows a straight line in such a range of large k as measured with the present SAXS apparatus, and, in fact, we have done this in the previous SAXS studies of oligomers and polymers of styrene[15] and of methyl methacrylate.[1] For the present case, however, this is impossible since measurements were not carried out for oligomer samples. Thus we consider P_s only on a relative scale.

Figure 3 shows plots of $k^2\Delta I_R(k,c)/c$ against k for the s-PMMA sample in acetonitrile at various c at 44.0 °C. The ordinate quantity corresponds to the (relative-scale) Kratky function $F_s(k)$ defined by

$$F_s(k) = M_w k^2 P_s(k) \tag{7}$$

(at finite concentrations), so that the above plots correspond to the Kratky plot. In the figure, the unfilled, right-half-filled, and filled circles represent the values at c = 0.0974, 0.0808, and 0.0599 g/cm^3, respectively. It is seen that the plot is almost independent of c in the range of k displayed as in the previous case of a-PMMA,[1] so that we adopt the values of $\Delta I_R(k,c)/c$ at the highest concentration as those of the (relative-scale) scattering function P_s for the single polymer chain at infinite dilution. We note that for a-PS in cyclohexane at 34.5 °C, the Kratky plot depends appreciably on c in the range of $k \gtrsim 0.1$ Å^{-1}, in contrast to the present case of s-PMMA.

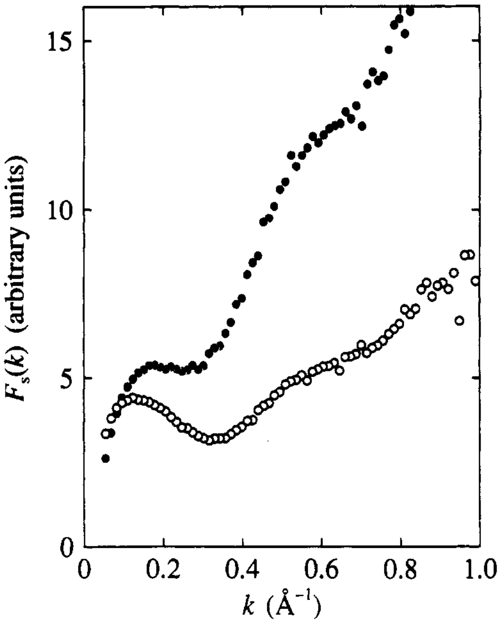

Figure 4. Plots of (relative-scale) $F_s(k)$ against k for the s-PMMA sample in acetonitrile at 44.0 °C (○) and in benzene at 25.0 °C (●).

As for the benzene solutions, we carried out measurements at c = 0.0551 and 0.0335 g/cm^3 and also found that the Kratky plot is independent of c as in the case of the acetonitrile solutions, although we do not show the results explicitly. Thus, also for the benzene solutions, $\Delta I_R(k,c)/c$ at the higher concentration is adopted as (relative-scale) P_s.

Figure 4 shows plots of (relative-scale) $F_s(k)$ against k for the s-PMMA sample in acetonitrile at 44.0 °C (unfilled circles) and in benzene at 25.0 °C (filled circles). Here, the data for the benzene solution require some comments. Although the measurements in the two solvents were carried out for the same sample under the same apparatus condition, the observed values of (relative-scale) $F_s(k)$ in them cannot be compared directly. The optical constant in eq 4 or 5 may be written explicitly in the form

$$K = \phi'_A (\Delta z_e)^2 \tag{8}$$

where ϕ'_A is a constant independent of polymer and solvent and Δz_e is the mole number of effective electrons per unit gram of the solute polymer and is given by

$$\Delta z_e = (n_2/M_0) - (v_2 \rho_0 n_1/M_s) \tag{9}$$

In eq 9, n_2 and M_0 are the number of electrons and the molecular weight per repeat unit of the polymer, respectively, v_2 is the partial specific volume of the polymer, ρ_0 is the density of the solvent, and n_1 and M_s are the number of electrons and the molecular weight of the solvent molecule, respectively. Thus, the difference between the values of Δz_e in the two solutions must be taken into account for the above comparison. The values of Δz_e may be calculated to be 0.208 and 0.155 mol/g for the acetonitrile and benzene solutions, respectively, from eq 9 with n_2 = 54 and M_0 = 100 g/mol and with v_2 = 0.82 cm^3/g, ρ_0 = 0.7554 g/cm^3, n_1 = 22, and M_s = 41 g/mol for the former and with v_2 = 0.818 cm^3/g, ρ_0 = 0.8737 g/cm^3, n_1 = 42, and M_s = 78 for the latter. Then the values of (relative-scale) F_s for the benzene solution shown in Figure 4 have been

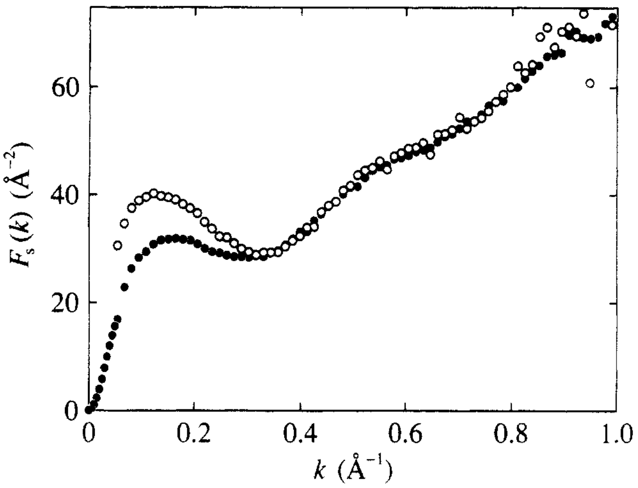

Figure 5. Comparison of the data for s-PMMA with those for a-PMMA in acetonitrile at 44.0 °C: (○) present data for the s-PMMA sample; (●) previous data for an a-PMMA sample (MM1) with $M_w = 1.09 \times 10^4$.[1]

calculated by multiplying the directly experimentally determined ones by the ratio of $(\Delta z_e)^2$ for the acetonitrile solution to that of the benzene solution.

Discussion

Comparison with a-PMMA. Now we make a comparison of the present SAXS data for (relative-scale) F_s for s-PMMA with the previous ones for a-PMMA.[1] Figure 5 shows plots of $F_s(k)$ against k for the s-PMMA sample (unfilled circles) and for an a-PMMA sample (MM1) with $M_w = 1.09 \times 10^4$ (filled circles),[1] both in acetonitrile at 44.0 °C. We note that the data for a-PMMA for $k \gtrsim 0.05$ Å^{-1} were obtained by the use of the same SAXS camera as used in the present study, and those for $k \lesssim 0.05$ Å^{-1}, by the use of a Kratky camera with the desmearing procedure, by which P_s and therefore F_s for small k may be determined with sufficient accuracy. Although the data for both samples for $k \gtrsim 0.05$ were taken with the same camera, they cannot be compared directly with each other since the polyethylene films used for the minitor of the intensity in the present and previous measurements are different. Thus we have multiplied the present data for P_s by a proper constant factor so that they agree with those for a-PMMA as a whole for $k \gtrsim 0.4$ Å^{-1}, i.e., for k larger than the value corresponding to the first minimum of F_s.

As seen from the figure, the Kratky plots for the s- and a-PMMA for $k \gtrsim 0.4$ Å^{-1} agree almost completely with each other and do not exhibit oscillation, confirming our previous conclusion.[1] It is also interesting to see that the relative value of the first maximum compared to the first minimum is larger for s-PMMA than for a-PMMA. This may be regarded as arising mainly from the fact that the helical nature of PMMA chains becomes more remarkable with increasing f_r.

Solvent Effects. It is seen from Figure 4 that for s-PMMA, for $k \gtrsim 0.4$ Å^{-1}, F_s exhibits no oscillation in benzene at 25.0 °C as well as in acetonitrile at 44.0 °C and also that, for $k \gtrsim 0.2$ Å^{-1}, it is substantially larger in the former solvent system than in the latter. This is probably due to the fact that the effective diameter of the cross section of the excess electron density distribution in the s-PMMA chain is smaller in benzene than in acetonitrile because of the smaller contrast Δz_e between the polymer and solvent in the electron density in the former. For $k \lesssim 0.1$ Å^{-1}, F_s is somewhat smaller in benzene. The reason for this is clearly that the mean-square radius of gyration $\langle S^2 \rangle$ of the s-PMMA chain is somewhat larger in benzene than in acetonitrile because of the excluded-volume effect. Recall that the coefficient of the k^2 term of P_s and therefore that of the k^4 term of F_s are proportional to minus $\langle S^2 \rangle$. The most remarkable difference between the shapes of F_s in benzene and in acetonitrile is that the ratio of the (first) maximum to the minimum is smaller in the former. This may be regarded as arising partly from the fact that the helical nature of the chain is somewhat weakened by the excluded-volume effect, which tends to extend its helical portion preserved in dilute solution, and partly from the fact that its effective diameter is smaller in benzene (see Figure 8 of ref 1 and Figure 9 of ref 10).

Conclusion

It has been shown that even for s-PMMA with $f_r = 0.92$ the Kratky plot does not exhibit the second maximum and minimum, confirming the previous conclusion[1] that the difference between our data for a-PMMA with $f_r = 0.79$ and those obtained by Kirste and Wunderlich[2,3] for s-PMMA with $f_r \gtrsim 0.9$ does not arise from the difference in f_r but from the difference between the SAXS apparatuses and also that between the data processing procedures. More important to us is the fact that the result that the Kratky plot for a- or s-PMMA with large f_r never exhibits oscillation in the range of $k \gtrsim 0.4$ Å^{-1} is consistent with the theoretical prediction on the basis of the HW model. This resolves completely our problem mentioned in the Introduction.

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