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Small-angle X-ray scattering from bisphenol A polycarbonate in tetrahydrofuran. Molecular characteristics and excluded-volume effects

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Small-angle X-ray scattering measurements have been made on six fractions of bisphenol A polycarbonate with weight-average molecular weights M_w of 2.3×10^3–1.3×10^4 in tetrahydrofuran at 25°C using a new type of apparatus equipped with an imaging plate detector. The z-average radii of gyration $<S^2>_z^{1/2}$ and the particle scattering functions obtained are analysed on the basis of current theories for the worm-like chain, along with previous data for $<S^2>_z$ (from light scattering on high molecular weight samples) and the intrinsic viscosity $[\eta]$. Excluded-volume effects on $<S^2>_z$ and $[\eta]$, which are significant for M_w above 10^4, are taken into account by the quasi-two-parameter (QTP) theory for the worm-like or helical worm-like chain. It is found from the analysis that all the properties examined are explained consistently by the worm-like chain whose contour is characterized by a Kuhn segment length of 3.0 nm and a linear mass density of 240 nm^{-1}. In particular, the theory of Yoshizaki *et al.* for $[\eta]$ of an unperturbed worm-like chain combined with the QTP theory is found to describe the molecular weight dependence of Flory's viscosity factor over the entire range of M_w examined, i.e. from 2.3×10^3 to 4.7×10^5. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Recently, we constructed a small-angle X-ray scattering (SAXS) apparatus equipped with an imaging plate detector, and demonstrated its usefulness for laboratory-scale experiments on polymer solutions by measuring the z-average mean-square radius of gyration $<S^2>_z$ and the particle scattering function $P(\theta)$ for polystyrene in cyclohexane and toluene[1]. This apparatus requires no desmearing procedure, directly giving desired scattering intensities as a function of scattering angle. In the present work, the SAXS experiment was extended to poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene), usually referred to as bisphenol A polycarbonate (PC), in tetrahydrofuran (THF), a good solvent, to determine the molecular characteristics of the polymer with the Kratky–Porod (KP) worm-like chain[2] as the model. Though PC is flexible, no theta solvent suitable for measurements is known[3].

In a previous study, Maeda and Norisuye[3] estimated the KP model parameters for PC in THF by analysing intrinsic viscosity ($[\eta]$) data[3,4] for samples of low molecular weight on the basis of the theory of Yoshizaki *et al.*[5] for unperturbed KP chains, but they assumed a relation between the partial specific volume and the hydrodynamic chain diameter. Apparently, the estimated model parameters build not only on this assumption, but also on the accuracy of the current viscosity theory for flexible chains. In view of such uncertainty, it seemed significant to see whether SAXS data of $<S^2>_z$ and $P(\theta)$ for PC samples of low molecular weight lead to a conclusion consistent with that derived from $[\eta]$.

In this short paper, our SAXS data are analysed together with previous data[3,4] for $<S^2>_z$ (from light scattering) and $[\eta]$ by relevant theories. Excluded-volume effects on $<S^2>_z$ and $[\eta]$ are taken into account in the recent scheme of the quasi-two-parameter theory[6–8] for the KP chain or more generally the helical worm-like (HW) chain[9].

EXPERIMENTAL

Samples and preparation of solutions

Six PC samples, M-7, M-8, M-9, M-10, M-11 and M-13, were chosen for the present SAXS study from the previously investigated samples[3] whose z-average to weight-average molecular weight ratios were 1.01–1.12. Viscosity measurements on these chosen samples in THF at 25°C gave essentially the same $[\eta]$ values as those[3] reported previously, indicating that no degradation had taken place during the storage of the samples.

Each test sample was dried *in vacuo* for more than 24 h before use. Its solutions were prepared by mixing the weighed amount of the polymer with THF. The polymer mass concentration c was calculated from the polymer weight fraction and the solution density. The THF used was fractionally distilled after being made free from peroxides with ferrous sulfate and dehydrated with calcium hydride.

SAXS measurements

Intensities of X-ray scattered from PC in THF at 25°C were measured on the previously constructed SAXS apparatus[1]. The X-ray beam generated from the copper rotating anode of a Rigaku RU-200 X-ray generator (40 kV–150 mA) was monochronized with a graphite plate to the Kα line (wavelength $\lambda_0 = 0.154$ nm), passed through three pinhole slits and irradiated on the test solution in a quartz-glass capillary cell (1.5 mm in diameter). The scattered beam was detected on an imaging plate (IP) as a

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two-dimensional image, which was processed with an IP reading system (Rigaku R-AXIS DS) to obtain scattered intensities at intervals of 0.05 mm on the image. The desired scattering intensity I_θ was obtained as a function of scattering angle θ by integrating intensities over a narrow angular range from $\theta - \Delta\theta$ and $\theta + \Delta\theta$ with $\Delta\theta = 0.01°$, 0.02° or 0.04°. As shown previously[1], no significant error is introduced in $< S^2 >^{1/2}$ (of less than 10 nm) and $P(\theta)$ if $\Delta\theta < 0.042°$.

Three to six solutions with different polymer concentrations (0.014–0.15 g cm^{-3}) were measured for each sample. Intensity data were accumulated for 8 or 10 h; the measurement on sample M-11 was extended to 20 h, but only a little bettered data quality. The solvent intensity was measured before and after the measurement of every solution and its mean was subtracted from I_θ for the solution to obtain the excess scattering intensity ΔI_θ at θ. The resulting data for $c/\Delta I_\theta$ were extrapolated to infinite dilution using the square-root plot of $(c/\Delta I_\theta)^{1/2}$ *versus* c, but those for $\theta > 2.8°$ were discarded because ΔI_θ values were too small to be extrapolated with reasonable accuracy. Thus, our analysis of $P(\theta)$ does not go into the local conformation of PC.

RESULTS

Figure 1 illustrates the scattering function for sample M-11 in the form of the Kratky plot of $k^2P(\theta)$ against the magnitude k of the scattering vector defined by $k = (4\pi/\lambda_0)\sin(\theta/2)$. The curve fitting the data points monotonically rises with increasing k.

Figure 2 shows plots of $P(\theta)^{-1/2}$ *versus* k^2 at relatively low scattering angles for all the samples studied. The values of $<S^2>_z^{1/2}$ evaluated from the slopes of the indicated straight lines are presented in *Table 1*, along with those of the weight-average molecular weight M_w determined previously[3] from sedimentation equilibrium.

The measured $< S^2 >_z$ values should contain the contributions from the finite chain thickness. However, when estimated on the basis of the expression of Konishi *et al.*[10] for discrete or continuous chains, these contributions were found to be negligible (within experimental error) even for the lowest molecular weight studied here. Hence, the $<S^2>_z^{1/2}$ data given in *Table 1* can be regarded as those associated with the contour of the PC chain.

The second virial coefficients A_2 were evaluated from the plots of zero-angle values of $(c/\Delta I_\theta)^{1/2}$ *versus* c with the aid of the M_w values in *Table 1*. The estimated A_2 increased from 1.5×10^{-3} (for sample M-7) to 6.2×10^{-3} mol $\mathrm{g}^{-2}\,\mathrm{cm}^3$ (for sample M-13) with decreasing molecular weight.

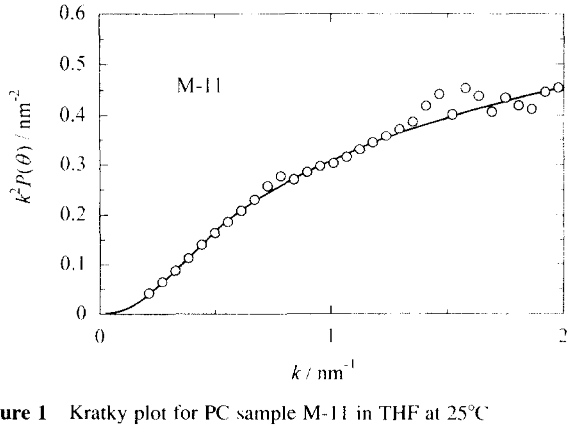

Figure 1 Kratky plot for PC sample M-11 in THF at 25°C

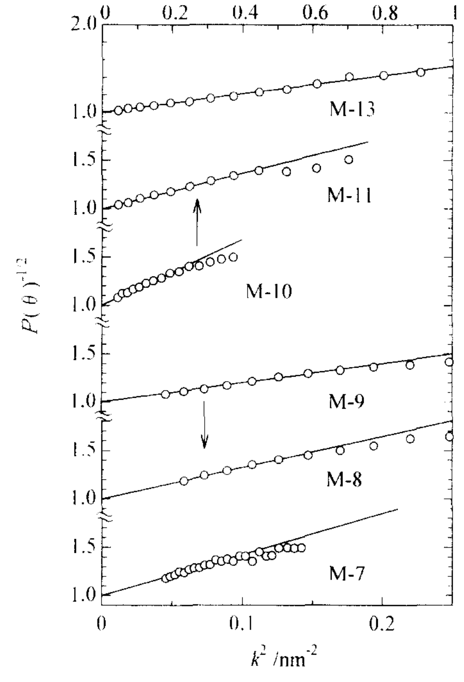

Figure 2 Angular dependence of $P(\theta)^{-1/2}$ for PC samples in THF at 25°C

Table 1 Radii of gyration from SAXS measurements on PC samples in THF at 25°C

Sample	$10^{-3}M_w$ [a]	$<S^2>_z^{1/2}$ (nm)
M-7	13.1	5.1
M-8	9.80	4.4
M-9	6.48	3.5
M-10	5.68	3.2
M-11	3.42	2.3
M-13	2.31	1.8

[a] Taken from Ref. [3]

DISCUSSION

Radius of gyration

The unperturbed mean-square radius of gyration $< S^2>_0$ for the centroid of the KP chain is expressed by[11]

$$< S^2 >_0 = \frac{L}{6\lambda} - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^3 L} - \frac{1}{8\lambda^4 L^2}[1 - \exp(-2\lambda L)] \tag{1}$$

where λ^{-1} and L are the Kuhn segment length and the contour length of the chain, respectively. The latter is related to the molecular weight M by

$$L = \frac{M}{M_L} \tag{2}$$

with M_L being the molar mass per unit contour length of the chain.

Adopting the Domb–Barrett function[12] for the radius expansion factor $\alpha_s ([= (< S^2 > / < S^2 >_0)^{1/2}]$ in the quasi-two-parameter (QTP) scheme[6–8] for the KP or HW bead chain, we have

$$\alpha_s^2 = \left[1 + 10\tilde{z} + \left(\frac{70\pi}{9} + \frac{10}{3}\right)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3\right]^{2/15} \times [0.933 + 0.067\exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \tag{3}$$

where $\tilde{z}$ is the scaled excluded-volume parameter defined by

$$\tilde{z} = (3/4)K(\lambda L)z \tag{4}$$

with

$$K(\lambda L) = (4/3) - 2.711(\lambda L)^{-1/2} + (7/6)(\lambda L)^{-1} \text{ for } \lambda L > 6 \tag{5}$$

$$= (\lambda L)^{-1/2}\exp[-6.611(\lambda L)^{-1} + 0.9198 + 0.03516\lambda L] \quad \text{for } \lambda L \leq 6$$

$$z = (3/2\pi)^{3/2}\lambda B(\lambda L)^{1/2} \tag{6}$$

In equation (6), B denotes the excluded-volume strength defined by $B = \beta/a^2$ (for the KP chain), with β and a being the binary cluster integral and the bead spacing, respectively. As can be seen from the above equations, $< S^2 >$ for a given M is determined by λ^{-1}, M_L and B.

The previous analysis[3] suggested that excluded-volume effects on $[\eta]$ for PC in THF are not very significant for M_w below 10^4. Based on this, the present $< S^2 >_z^{1/2}$ data for $M_w < 10^4$ were first analysed by the method of Murakami *et al.*[13], i.e. by use of the linear plot of $(M_w/ < S^2 >_z)^{1/2}$ *versus* M_w^{-1}; note that equation (1) can be approximated by[13]

$$(M/ < S^2 >_0)^{1/2} = (6\lambda M_L)^{1/2} + \frac{(3M_L)^{3/2}}{(2^{3/2}\lambda^{1/2}M)} \tag{7}$$

provided $\lambda L > 2$, and that the slope and intercept of the plot give λ^{-1} and M_L. It was found, however, that the plot bent slightly downward for $M_w^{-1} < 1.7 \times 10^{-4}$ owing to small excluded-volume effects on $< S^2 >_z$. The values of λ^{-1} and M_L were, therefore, estimated in reliance on the data points for the two lowest molecular weights, with the result that $\lambda^{-1} = 3.0$ nm and $M_L = 240$ nm^{-1}. With these values, B was then determined to be 0.22 nm so that the QTP theory expressed by equations (1)–(6) gives the closest agreement with the $< S^2 >_z^{1/2}$ data from the previous light scattering[3,4] and present SAXS experiments.

Figure 3 shows that the theoretical solid curve calculated for $\lambda^{-1} = 3.0$ nm, $M_L = 240$ nm^{-1} and $B = 0.22$ nm closely fits the data points for $< S^2 >_z^{1/2}$ over the entire range of molecular weight examined. The dashed line, which represents the theoretical values for the unperturbed KP chain ($B = 0$), stays quite close to the solid curve in the region of molecular weight below 6×10^3, its deviation from the latter curve being only 1.6% at $M = 5.68 \times 10^3$ (sample M-10) and 0.8% at $M = 3.42 \times 10^3$ (sample M-11). Thus, excluded-volume effects on $< S^2 >_z$ of PC in THF may be considered almost completely negligible below $M_w = 4 \times 10^3$.

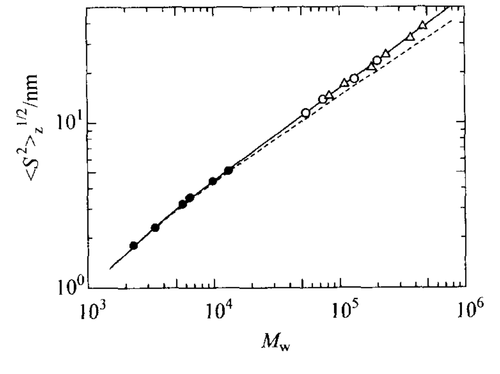

Figure 3 Comparison between the theoretical and experimental radii of gyration for PC in THF at 25°C: (●) present SAXS data; (○) light scattering data of Maeda and Norisuye[3]; (△) light scattering data of Tsuji *et al.*[4]; (———) theoretical values for the perturbed KP chain with $\lambda^{-1} = 3.0$ nm, $M_L = 240$ nm^{-1} and $B = 0.22$ nm; (– – –) theoretical values for the unperturbed KP chain ($B = 0$)

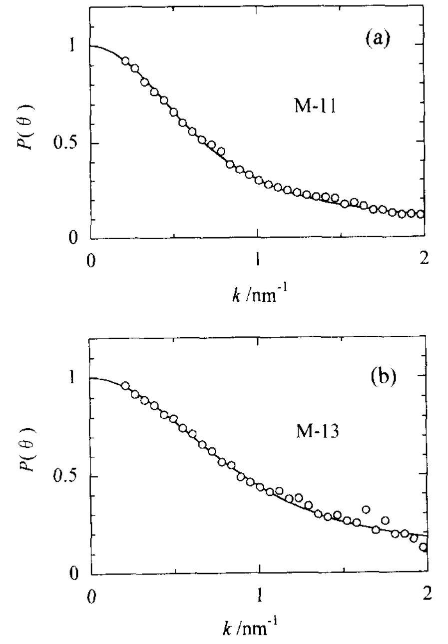

Figure 4 Comparison between the theoretical and experimental scattering functions for PC samples M-11 (a) and M-13 (b) in THF at 25°C. The curves represent the values calculated for the unperturbed KP chains[15] with: (a) $L = 14.2$ nm and $\lambda^{-1} = 3.1$ nm; and (b) $L = 9.6$ nm and $\lambda^{-1} = 2.9$ nm

Our λ^{-1} value of 3.0 nm does not differ much from that of 3.18 nm estimated from $[\eta]$ with the relation $\bar{v}$ (the partial specific volume) $= \pi N_A d_b^2/(6M_L)$ by Maeda and Norisuye[3], who forced the theory of Yoshizaki *et al.*[5] for the intrinsic viscosity $[\eta]_0$ of an unperturbed KP touched-bead chain to fit data for $M_w < 10^4$. Here, N_A is the Avogadro constant and d_b is the diameter of one bead. The slightly larger λ^{-1} value by Maeda and Norisuye may be owing to the neglect of small excluded-volume effects on $[\eta]$ in the range of M_w between 6×10^3 and 10^4 (see *Figure 3* and also Figure 6 of Ref. [3]). On the other hand, the M_L value of 241 nm^{-1} obtained by these authors is in almost perfect agreement with ours (240 nm^{-1}), indicating that the above relation for $\bar{v}$ happens to be a good approximation to PC in THF. We note that these M_L values are very close to that of 244 nm^{-1} calculated from crystallographic data[14] for PC.

Particle scattering function

The circles in *Figure 4a* and *b* show the $P(\theta)$ data for the two lowest molecular weight samples M-11 and M-13 for which intramolecular excluded-volume effects are negligible. For their comparison with the available theory[15] of $P_0(\theta)$ for the centroid of the unperturbed KP chain these data have to be corrected for the chain thickness, but no rigorous way of the correction is as yet known. If use is made of the conventional relation[16,17] $P(\theta) = P_0(\theta)\exp[-(kd)^2/16]$ for straight cylinders of diameter d and if d of the PC chain is taken as 0.57 nm (corresponding to a d_b value[3] of 0.77 nm), the ratio of $P(\theta)/P_0(\theta)$ is estimated to be 0.92 at $k = 2$ nm^{-1}. This correction factor lowers $P(\theta)$ only by 0.010–0.015 at $k = 2$ nm^{-1} where the experimental $P(\theta)$ for either sample is as small as 0.1–0.2. Thus, the difference between $P(\theta)$ and $P_0(\theta)$ may be ignored in the present analysis.

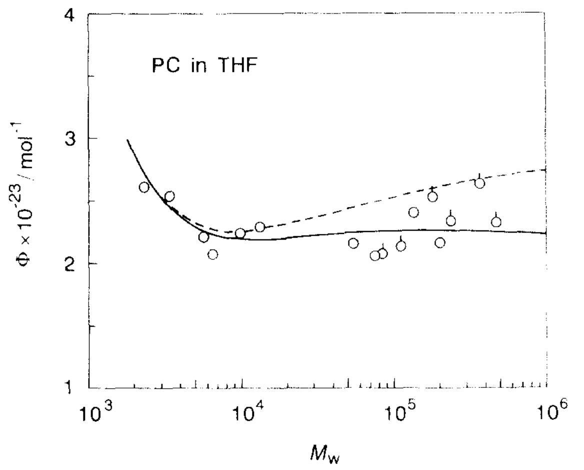

Figure 5 Molecular weight dependence of Flory's viscosity factor for PC in THF at 25°C (see the text for the symbols). The solid line represents the theoretical values for the perturbed KP chain with $\lambda^{-1} = 3.0$ nm, $M_L = 240$ nm^{-1}, $d_b = 0.77$ nm and $B = 0.22$ nm. The dashed line refers to the unperturbed state

The curves in *Figure 4a* and *b* represent the theoretical $P_0(\theta)$ values for the unperturbed KP chains[15] with $L = 14.2$ nm and $\lambda^{-1} = 3.1$ nm (for sample M-11) and $L = 9.6$ nm and $\lambda^{-1} = 2.9$ nm (for sample M-13). The values of L for the respective samples have been calculated from M_w with $M_L = 240$ nm^{-1}, while those of λ^{-1} have each been chosen so as to give the best fit to the data points. For both samples the agreement between theory and experiment is satisfactory. Since the chosen λ^{-1} values are in good agreement with the value 3.0 nm from $<S^2>_z^{1/2}$, we may conclude that within the k range studied, the $<S^2>_z^{1/2}$ and $P(\theta)$ data are consistently explained in terms of the KP model.

Flory viscosity factor

The values of the Flory viscosity factor $\Phi[= [\eta]M_w/(6<S^2>_z)^{3/2}]$ calculated from the present $<S^2>_z$ data and Maeda and Norisuye's data[3] for M_w, $<S^2>_z$ and $[\eta]$ are shown by circles in *Figure 5*, in which the circles with pip show the Φ data of Tsuji *et al.*[4]. The solid line represents the theoretical values for the perturbed KP chain with $\lambda^{-1} = 3.0$ nm, $M_L = 240$ nm^{-1}, $d_b = 0.77$ nm and $B = 0.22$ nm, computed from equations (1)–(6) for $<S^2>$ and the QTP expression[18] for $[\eta]$ (with the Barrett function[19] for the viscosity expansion factor):

$$[\eta] = [\eta]_0(1 + 3.8\tilde{z} + 1.9\tilde{z}^2)^{0.3} \tag{8}$$

wherein $[\eta]_0$ is given by the theory of Yoshizaki *et al.*[5] for the unperturbed KP touched-bead chain as a function of M, M_L, λ^{-1} and d_b. The d_b value of 0.77 nm has been taken from Ref. [3]; the other parameters are the same as those used in fitting the $<S^2>_z^{1/2}$ data (*Figure 3*). Except for the two data points at $M_w = 1.81 \times 10^5$ and 3.72×10^5, the agreement between theory and experiment is good, indicating that the theories adopted are capable of consistently explaining $<S^2>_z$ and $[\eta]$ for PC in THF. In fact, we have found that equation (8) with the above parameter set accurately describes the molecular weight dependence of $[\eta]$ over the entire range of M_w studied by Maeda and Norisuye.

The dashed line in *Figure 5* represents the theoretical values of Φ_0 (i.e. Φ in the unperturbed state). Interestingly, it has a shallow minimum around $M = 9 \times 10^3$ and rises gradually toward the coil limiting value $\Phi_{0,\infty}$ of 2.87×10^{23} mol^{-1} (the Kirkwood–Riseman value[20]) with increasing M. The appearance of such a minimum is a reflection of stiffness effects on $<S^2>_0$ and $[\eta]_0$, and indeed, experimental Φ for poly(hexyl isocyanate)[13], a typical stiff chain, in hexane exhibits a clear minimum around $M_w = 10^5$. For PC, the experimental Φ values stay almost constant in a broad range of molecular weight from 5×10^3 to 4.7×10^5 owing to the significant excluded-volume effects on $<S^2>_z$ and $[\eta]$ for M_w above 10^4. Another point to note is that the theoretical Φ_0 is still 2.68×10^{23} mol^{-1} even at the highest molecular weight studied, being appreciably smaller than the above-mentioned $\Phi_{0,\infty}$ value. Importantly, it is within the range of experimental $\Phi_{0,\infty}$ between 2.34×10^{23} and 2.79×10^{23} mol^{-1} for typical flexible polymers[21,22] in the theta state.

CONCLUSIONS

The previous and present data of $<S^2>_z$, $P(\theta)$ (for $k < 2$ nm) and $[\eta]$ for bisphenol A polycarbonate in THF are consistently explained by the current theories based on the worm-like chain model. In particular, the viscosity theory of Yoshizaki *et al.*[5] for unperturbed worm-like chains combined with the Barrett function[19] for the viscosity expansion factor in the quasi-two-parameter scheme allows an almost quantitative description of $[\eta]$ or Flory's viscosity factor over a broad range of molecular weight from 2.3×10^3 to 4.7×10^5. Without volume effect, the polycarbonate chain is characterized by λ^{-1} (Kuhn's segment length) = 3.0 nm and M_L (the molar mass per unit contour length) = 240 nm^{-1}. This parameter set gives the unperturbed dimensions ($<S^2>_0/M$ at infinite molecular weight) a value of 2.1×10^{-3} nm^2, which is in excellent agreement with the polydispersity-corrected literature values[23,24] in the bulk state.

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