On the unperturbed dimensions of bisphenol A polycarbonate

Nobuhiko Maeda and Takashi Norisuye*
Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560, Japan
(Received 10 November 1992; revised 9 December 1992)

Intrinsic viscosities $[\eta]$ of bisphenol A polycarbonate in dichloromethane, tetrahydrofuran and a mixture of 1,1,2,2-tetrachloroethane and toluene (78.5 wt% toluene), all at 25°C, have been determined for 13 fractions ranging in weight-average molecular weight M_w from 2.3×10^3 to 2×10^5. To estimate $(\langle S^2 \rangle_0/M)_\infty$ (the ratio of the unperturbed mean-square radius of gyration to the molecular weight M at infinite M) of the polymer, the $[\eta]$ data were analysed on the basis of the theory of Yoshizaki *et al.* for unperturbed touched-bead, worm-like chains but, in actuality, with the Bushin–Bohdanecký method applied. It is shown that the slope of a plot of $(M_w^2/[\eta])^{1/3}$ *versus* $M_w^{1/2}$ at low M_w, where excluded-volume effects on $[\eta]$ are negligible, gives $(\langle S^2 \rangle_0/M)_\infty$ directly to a good approximation. The estimated $(\langle S^2 \rangle_0/M)_\infty$ values for the polycarbonate in the three solvents are all $(2.2 \pm 0.2) \times 10^{-3}$ nm^2, and are in good agreement with the literature data from small-angle neutron scattering in the bulk state. Excluded-volume effects on $[\eta]$ in the tetrachloroethane–toluene mixture are significant only for M_w above 10^5, while those in dichloromethane and tetrahydrofuran are appreciable for M_w above 5×10^3 to around 10^4, or above 5–10 in terms of the Kuhn segment number.

(Keywords: polycarbonate; unperturbed dimensions; intrinsic viscosity)

INTRODUCTION

Experimental determination of the unperturbed dimensions of poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene), usually referred to as bisphenol A polycarbonate (PC), leaves much to be desired. The value of $(\langle S^2 \rangle_0/M)_\infty$ determined by Berry *et al.*[1] from light scattering in a theta solvent, butyl benzyl ether at 170°C, is about 50% smaller than those[2,3] from small-angle neutron scattering (SANS) in the bulk state. Here, $\langle S^2 \rangle_0$ and M denote the unperturbed mean-square radius of gyration and the molecular weight, respectively, and the subscript ∞ signifies the asymptotic limit of high M. Berry *et al.*[1] showed the $(\langle S^2 \rangle_0/M)_\infty$ value in butyl benzyl ether to be consistent with their viscosity data in another theta solvent for PC, a dioxane–cyclohexane mixture (63.9 wt% dioxane) at 25°C, but they remarked that measurements in these theta solvents presented considerable difficulties due to polymer degradation and aggregation (see ref. 1 for the preparation of solutions). Because of such difficulties in characterizing PC in a poor solvent, Tsuji *et al.*[4] used tetrahydrofuran (THF), a good solvent, and analysed sedimentation coefficient data for low-molecular-weight samples on the basis of the Yamakawa–Fujii theory[5] for unperturbed worm-like cylinders to estimate the worm-like chain parameters, i.e. the persistence length and the molar mass per unit contour length. The $(\langle S^2 \rangle_0/M)_\infty$ value calculated with those parameters comes close to the SANS values mentioned above. Although this value may not be free from excluded-volume effects in THF, the discrepancy between it and the value of Berry *et al.* in the theta solvent is too large. Recent conformation calculations[6–9] predict $(\langle S^2 \rangle_0/M)_\infty$ values that are intermediate between these experimental values.

The present study was undertaken to estimate $(\langle S^2 \rangle_0/M)_\infty$ of PC from viscosity measurements on samples of relatively low molecular weight in dichloromethane (DCM), THF and a mixture of 1,1,2,2-tetrachloroethane (TCE) and toluene (TOL), all at 25°C. TOL is a non-solvent for PC, while the others are good solvents. We expected that addition of an appropriate amount of TOL to TCE solutions of PC should extend the molecular weight range in which excluded-volume effects on intrinsic viscosity $[\eta]$ can practically be ignored (see the Experimental section for the composition of TOL studied). In the work reported below, we present $[\eta]$ data for the three solvents and analyse them using the recent theory of Yoshizaki *et al.*[10] for touched-bead, helical, worm-like chains but confining ourselves to the Kratky–Porod worm-like chain[11], a special case of the helical, worm-like chain model[12,13].

EXPERIMENTAL

Samples

Six PC samples with viscosity-average molecular weights M_v of 1×10^4 to 1.6×10^5 (in DCM at 25°C), chosen from our stock, were divided into 74 parts by repeating fractional precipitation with DCM as the solvent and heptane as the precipitant. The procedures were essentially the same as those reported by Tsuji *et al.*[4]. Nine appropriate middle fractions, designated M-1 to M-9, were chosen for the present work. In addition, four low-molecular-weight fractions, M-10 to M-13, were studied. They were prepared in the following way.

---

* To whom correspondence should be addressed

0032-3861/93/163475-06

A PC sample with an M_v of 3.4×10^4 was depolymerized in DCM by addition of a small quantity of methanol containing about 0.6 wt% sodium hydroxide. After being continuously shaken for about 4 min, the solution was neutralized with trifluoroacetic acid. The polymer was recovered by reprecipitation into methanol, washed with methanol a few times, and dried *in vacuo*. Its M_v was 4×10^3. The polymer obtained in this way was divided into 17 parts by repeated fractional precipitation with the above-mentioned solvent–precipitant system.

All the fractions M-1 to M-13 were stored in nitrogen-filled bottles at −20°C after being dried *in vacuo*. They were dried again overnight before the preparation of solutions.

Molecular weight determination

Weight-average molecular weights M_w for the fractions of higher molecular weight (M-1 to M-4) were determined by light scattering in THF at 25°C. Scattering intensities were measured on a Fica 50 light-scattering photometer in an angular range from 30 to 150° with vertically polarized incident light of 436 nm wavelength. The Rayleigh ratio of pure benzene[14] at 25°C and 436 nm was taken to be $46.5 \times 10^{-6}\,\mathrm{cm}^{-1}$. Its depolarization ratio was determined by the method of Rubingh and Yu[15] to be 0.394. Test solutions were made optically clean by filtration through Millipore filters (type FG or FH), followed by centrifugation at $2.5 \times 10^4\,g$ for 2 h. Other experimental procedures were essentially the same as those employed by Tsuji *et al.*[4]. The intensity data obtained were analysed by Berry's square-root plot[16] to evaluate A_2 (the second virial coefficient) and $\langle S^2 \rangle_z$ (the z-average mean-square radius of gyration) as well as M_w. Optical anisotropy effects on these quantities were negligible for the four fractions studied.

The specific refractive index increment for PC in THF at 25°C was $0.193\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ at 436 nm and $0.185\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ at 546 nm when determined for a fraction with an M_v of 7.0×10^3 using a modified Schulz–Cantow differential refractometer. These values agreed closely with those reported by previous workers[4,17]. Measurements on other fractions with M_v values of 2.7×10^3 and 1.6×10^5 gave essentially the same specific refractive index increments.

Values of M_w for the fractions of lower molecular weight (M-4 to M-13) were determined by sedimentation equilibrium in a Beckman Spinco Model E ultracentrifuge with THF at 25°C as the solvent. A Kel-F 12 mm double-sector cell was used. The length of the solution column was adjusted to about 1.5 mm and the rotor speed was chosen to be 1.1×10^4 to $3.0 \times 10^4\,\mathrm{rev\,min}^{-1}$. For the partial specific volume $\bar{v}$ of PC in THF at 25°C, the previously determined value[4] of $0.774\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ was used.

Ratios of M_z (the z-average molecular weight) to M_w were also evaluated from sedimentation equilibrium data by the method[18] described elsewhere. However, those for some fractions, for which the equilibrium polymer concentration at the cell bottom was about twice that at the meniscus, could not be determined with reasonable accuracy.

Viscometry

To choose an appropriate weight fraction w_T of TOL in TCE–TOL mixtures for viscometry, the dependence of $(\ln \eta_r)/c$ on w_T at 25°C was determined for two fractions with M_v values of 1.3×10^4 and 1.5×10^5. Here, η_r and c denote the relative viscosity and the polymer mass concentration, respectively. Densities of TCE–TOL mixtures at 25°C were measured as a function of w_T and their values at desired w_T were obtained by graphical interpolation. Very dilute solutions with η_r below 0.3, prepared by adding TOL to TCE solutions of PC, were stable and their viscosities could be measured without difficulty over the range of w_T from 0 to 0.785.

As expected, $(\ln \eta_r)/c$ for either fraction decreased monotonically with increasing w_T, and at a w_T value of 0.67 it came close to the 'unperturbed $[\eta]$ value' calculated from the theory of Yoshizaki *et al.*[10] using the worm-like chain parameters reported by Tsuji *et al.*[4] for THF solutions. Light-scattering measurements showed, however, that A_2 for fraction M-1 at a w_T value of 0.67 is still of the order of $10^{-4}\,\mathrm{mol\,g}^{-2}\,\mathrm{cm}^3$ at 25–40°C, and hence that a mixture with a much higher TOL composition is desirable for use in viscometry. Nonetheless, evidence was obtained for the tendency of aggregation at c above $0.8 \times 10^{-2}\,\mathrm{g\,cm}^{-3}$, and the aggregation became pronounced as time elapsed; we did not try to heat the solutions above 40°C, because Berry *et al.*[1] encountered pronounced degradation of PC in heated solutions. Further, newly prepared solutions with w_T at 0.83 became turbid only half a day after preparation. At this stage, we deemed it almost impossible to obtain A_2 at large w_T by light-scattering measurements requiring high polymer concentrations, and decided to use the mixture with w_T at 0.785 (the highest TOL composition in the above-mentioned viscometry) without knowledge of A_2.

Intrinsic viscosities at 25°C of all fractions in DCM, THF and the TCE–TOL mixture with w_T at 0.785 were determined using Ubbelohde-type viscometers having flow times of 170–220 s for the solvents. The highest polymer concentration in the mixed solvent was adjusted so that η_r was about equal to or less than 0.3. In evaluating η_r, a density correction was made using a $\bar{v}$ of $0.774\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ in THF. The Huggins constant k' was estimated on the assumption that $\bar{v}$ does not depend on c.

RESULTS

Molecular weight and radius of gyration

Figure 1 illustrates the Zimm plot in the square-root form for PC fraction M-1 in THF at 25°C, where K is the optical constant and R_θ is the reduced scattering intensity at scattering angle θ. The values of M_w, A_2 and $\langle S^2 \rangle_z$ obtained from light-scattering measurements are presented in *Table 1*, along with those of M_w, A_2 and M_z/M_w from sedimentation equilibrium. The M_w values for fraction M-4 from the two methods are in good agreement. Another point to be made here is that the five fractions M-4, M-5, M-8, M-12 and M-13 are narrow in molecular weight distribution, as indicated by M_z/M_w.

Figure 2 shows that the present data for $\langle S^2 \rangle_z$ in THF are consistent with those of Tsuji *et al.*[4]. The solid straight line approximately fitting the plotted points has a slope of 1.1, which indicates that the PC chain is perturbed by excluded-volume effects in the M_w range examined (see the Discussion section for the interpretation of the indicated dashed line).

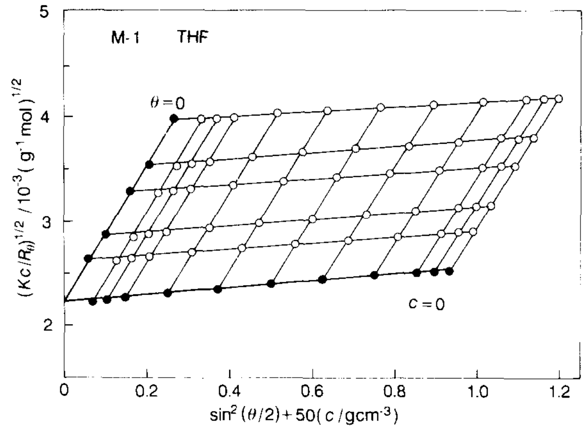

Figure 1 Zimm plot in the square-root form for PC fraction M-1 in THF at 25°C

Table 1 Results from light-scattering and sedimentation equilibrium measurements on PC fractions in THF at 25°C

Fraction	$10^{-4}M_w$	10^4A_2 (mol g^{-2} cm^3)	$\langle S^2\rangle_z$[b] (nm^2)	M_z/M_w
M-1	20.1[a]	7.31	554	
M-2	13.3[a]	7.64	330	
M-3	7.47[a]	8.71	188	
M-4	5.43[a]	9.21	130	
	5.41	11		1.06
M-5	2.77	10		1.11
M-6	1.73	10		
M-7	1.31	14		
M-8	0.980	13		1.01
M-9	0.648	24		
M-10	0.568	19		
M-11	0.342	18		
M-12	0.339	26		1.08
M-13	0.231	47		1.12

[a] From light scattering

[b] The uncertainty arising from graphical determination is about ±4% for fractions M-1 and M-2 and about ±10% for M-3 and M-4

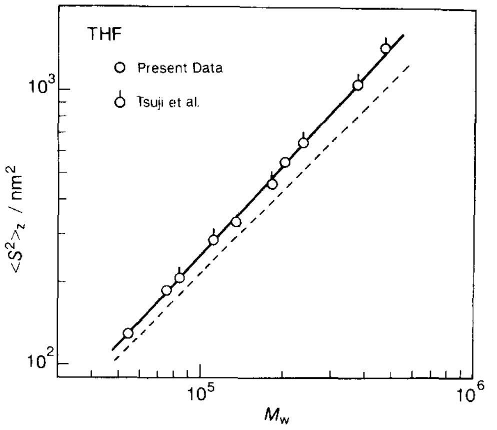

Figure 2 Molecular weight dependence of $\langle S^2\rangle_z$ for PC in THF at 25°C. The dashed line represents the unperturbed $\langle S^2\rangle$ values for the worm-like chain with a persistence length of 1.59 nm and a molar mass per unit contour length of 241 nm^{-1}

Intrinsic viscosity

Table 2 summarizes results from viscosity measurements on all PC fractions in DCM, THF and the TCE–TOL mixture with w_T at 0.785. In *Figure 3*, the values of $[\eta]$ in the three solvents are plotted double-logarithmically against M_w. The following remarks may be in order. (1) The curves fitting the plotted points for the respective solvents bend down at low molecular weights, but for M_w greater than 2×10^4 they are essentially linear. For example, the slope of the curve for the TCE–TOL mixture is about 0.73 at low M_w and decreases to 0.62. Such a gradual decrease in slope is similar to that usually observed for weakly stiff chains. (2) The curve for DCM, in which $[\eta]$ is the largest at high M_w, intersects that for THF at M_w around 10^4 and merges with that for the TCE–TOL mixture at M_w around 5×10^3. This viscosity behaviour suggests that the unperturbed dimensions of PC in THF should be somewhat larger than those in the other solvents.

DISCUSSION

Data analysis

Consider a touched-bead, worm-like chain consisting of N beads of diameter d and denote its persistence length by q. The contour length L of the chain is equal to Nd. According to the theory of Yoshizaki *et al.*[10], the dimensionless quantity $[\eta]M/(2q)^3$ of the touched-bead chain is a function of $L/2q$ (the reduced contour length) and $d/2q$. We have found that for a fixed $d/2q$ between 0.1 and 0.4 (i.e. for a weakly stiff or flexible chain), $L^3/[\eta]M$

Table 2 Results from viscosity measurements on PC fractions in DCM, THF and a TCE–TOL mixture (78.5 wt% TOL) at 25°C

	DCM		THF		TCE–TOL	
Fraction	$[\eta]$ (cm^3 g^{-1})	k'	$[\eta]$ (cm^3 g^{-1})	k'	$[\eta]$ (cm^3 g^{-1})	k'
M-1	224	0.38	205	0.42	169	0.46
M-2	168	0.42	160	0.43	135	0.46
M-3	112	0.40	104	0.44	90.3	0.47
M-4	92.2	0.43	86.2	0.45	75.5	0.49
M-5	57.6	0.42	54.5	0.44	48.8	0.54
M-6	41.2	0.45	40.2	0.42	36.6	0.47
M-7	34.3	0.43	34.1	0.43	30.8	0.48
M-8	28.1	0.44	28.3	0.43	25.8	0.48
M-9	19.5	0.44	20.2	0.44	18.7	0.46
M-10	17.6	0.50	18.7	0.44	17.3	0.49
M-11	12.2	0.47	13.3	0.44	12.2	0.48
M-12	12.2	0.50	13.3	0.47	12.1	0.54
M-13	8.7	0.58	9.7	0.48	9.0	0.55

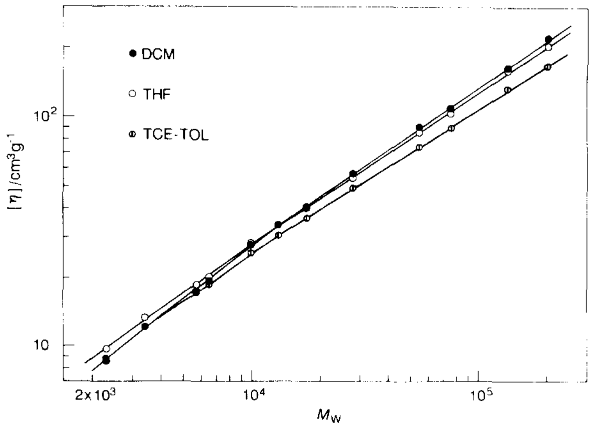

Figure 3 Molecular weight dependence of $[\eta]$ at 25°C for PC in DCM, THF and the mixture of TCE–TOL with w_T at 0.785

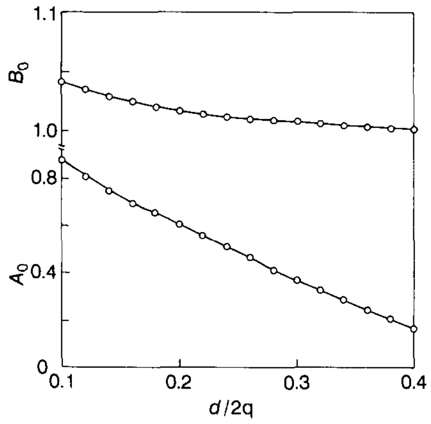

Figure 4 A_0 and B_0 from equations (2) and (3) as functions of the reduced diameter $d/2q$

varies linearly with $(L/2q)^{1/2}$ over a range of practical interest, and that in such a range of $(L/2q)^{1/2}$ the expression of Yoshizaki *et al.* can be replaced to a good approximation by

$$(M^2/[\eta])^{1/3} = A + BM^{1/2} \tag{1}$$

where

$$A = A_0 \Phi_\infty^{-1/3} M_L \tag{2}$$

and

$$B = B_0 \Phi_\infty^{-1/3} (6\langle S^2 \rangle_0 / M)_\infty^{-1/2} \tag{3}$$

with

$$(\langle S^2 \rangle_0 / M)_\infty = q/3M_L \tag{4}$$

In these equations, A_0 and B_0 are functions of $d/2q$, Φ_∞ is the Flory viscosity factor in the coil limit ($2.87 \times 10^{23}\,\mathrm{mol}^{-1}$), and M_L is the shift factor (or the molar mass per unit contour length) defined by

$$M_L = M/L \tag{5}$$

The values of A_0 and B_0 are presented in *Figure 4*. It can be seen that B_0 is very close to unity in the range of $d/2q$ examined. In this $d/2q$ range, equation (1) with equations (2) and (3) is applicable for $L/2q$ larger than 2–3, but $L/2q$ must be smaller than 200 for a $d/2q$ of 0.1 and 600 for a $d/2q$ of 0.25; for a $d/2q$ of 0.4, virtually no upper limit exists in $L/2q$.

Equation (1) has the same form as that found by Bushin *et al.*[19] and Bohdanecký[20] as an approximation to the Yamakawa–Fujii equation[21] for long, stiff, worm-like cylinders, and is an extension of the Bushin–Bohdanecký approximation to relatively short, flexible, worm-like chains. An advantage of this approximation is that since B_0 is around 1, the slope of a plot of $(M^2/[\eta])^{1/3}$ *versus* $M^{1/2}$ gives $(\langle S^2 \rangle_0/M)_\infty$ directly to a good approximation if excluded-volume effects on $[\eta]$ are negligible in the molecular weight range considered. For a good solvent system, the plot may bend down owing to excluded-volume effects, but if there is a low M region in which volume effects are negligible, its slope in such an M region should still give an approximate value of $(\langle S^2 \rangle_0/M)_\infty$.

Figure 5 shows the plots of $(M_w^2/[\eta])^{1/3}$ *versus* $M_w^{1/2}$ constructed from the present data in DCM, THF and the TCE–TOL mixture with w_T at 0.785. The plotted points for the mixed solvent (*Figure 5c*) fall on a straight line over a wide range of M_w from 3×10^3 to 1×10^5. The downward deviations of the points for the two fractions of highest molecular weight may be ascribed to excluded-volume effects. On the contrary, the linearity of the plot for either DCM or THF (*Figures 5a* and *5b*) is limited to a region of low M_w owing to pronounced excluded-volume effects. The approximate values of $(\langle S^2 \rangle_0/M)_\infty$ evaluated from the slopes of the indicated straight lines with a B_0 value of 1 may be corrected for B_0 if $d/2q$, or more generally a set of worm-like chain parameters q, M_L and d, is estimated for each solvent. Since the intercept A and slope B of each straight line in *Figure 5* give two relations among q, M_L and d, we need one more relation for determining the three unknowns. To this end, we use the relation

$$\bar{v} = \pi N_A d^2 / 6M_L \tag{6}$$

which assumes that $\bar{v}$ is equal to the volume occupied by 1 g of touched-bead, worm-like chains (N_A is the Avogadro constant).

The worm-like chain parameters obtained with $\bar{v} = 0.774\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ for the three solvents are as follows: $q = 1.59\,\mathrm{nm}$, $M_L = 241\,\mathrm{nm}^{-1}$ and $d = 0.77\,\mathrm{nm}$ in THF and $q = 1.61\,\mathrm{nm}$, $M_L = 259\,\mathrm{nm}^{-1}$ and $d = 0.79\,\mathrm{nm}$ in the TCE–TOL mixture and in DCM (we note that the set of parameters in the last solvent is not very accurate because of the narrow linear region in the $(M_w^2/[\eta])^{1/3}$ *versus* $M_w^{1/2}$ plot). The q and d values obtained yield 1.01 for B_0 in the three solvents (see *Figure 4*). The parameter set in THF is not very different from that ($q = 1.8\,\mathrm{nm}$, $M_L = 260\,\mathrm{nm}^{-1}$, and a cylinder diameter of 0.66 nm) estimated by Tsuji *et al.*[4] from sedimentation coefficients

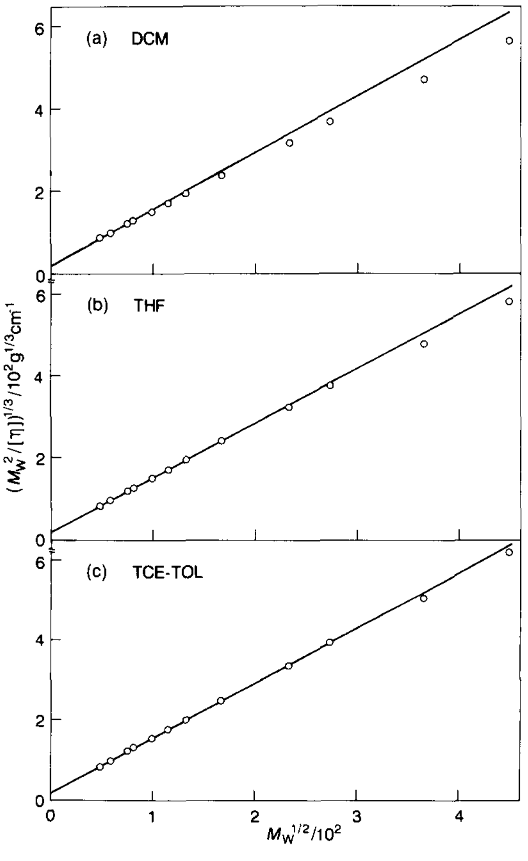

Figure 5 Plots of $(M_w^2/[\eta])^{1/3}$ *versus* $M_w^{1/2}$ for PC fractions in (a) DCM, (b) THF and (c) the TCE–TOL mixture with w_T at 0.785

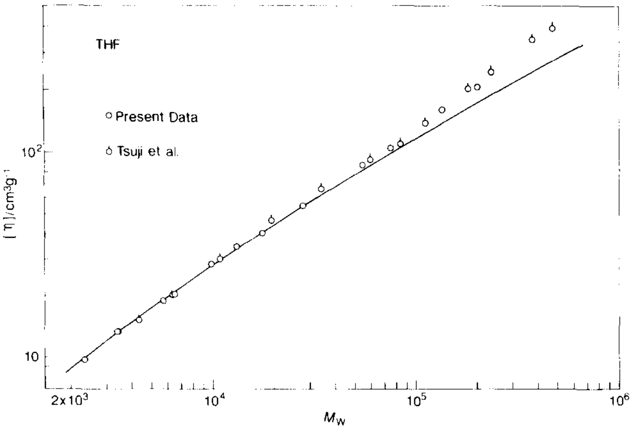

Figure 6 Excluded-volume effects on $[\eta]$ for PC fractions in THF, indicated as upward deviations of data points from the theoretical curve for the unperturbed, touched-bead, worm-like chain with $q = 1.59$ nm, $M_L = 241\ \mathrm{nm^{-1}}$ and $d = 0.77$ nm. The curve is calculated from the theory of Yoshizaki *et al.*[10]

on the basis of the worm-like cylinder model[5]. Another point to note is that the M_L values of 240–260 $\mathrm{nm^{-1}}$ in the three solvents are close to that of 244 $\mathrm{nm^{-1}}$ calculated from crystallographic data[22]. Before discussing the unperturbed dimensions, we will examine the excluded-volume effects by comparing the $[\eta]$ data with the values computed from the theory of Yoshizaki *et al.*[10] using the above parameter values.

Figure 6 shows that the two sets of $[\eta]$ data for THF from the present work and from Tsuji *et al.*[4] fall on the theoretical curve up to an M_w of 5×10^3 to around 10^4 and then deviate upwards from it. It was found that the data for DCM also begin to deviate from the theoretical curve for DCM at an M_w of around 5×10^3 (not shown here). The molecular weight of 5×10^3 to around 10^4 for the onset of the volume effect in the two good solvents corresponds to a reduced contour length of 5–10, which is much smaller than our previous estimate (about 50)[23] based on the q and M_L values of Tsuji *et al.* for PC in THF but comparable to the recently reported values for other flexible chains[24–26] modelled by either the worm-like chain or the helical worm-like chain. Note that the reduced contour length of the helical worm-like chain is defined as the ratio of L to the stiffness parameter λ^{-1}, and that λ^{-1} is equal to $2q$ in the worm-like chain limit[12,13]. In *Figure 2*, the data points for $\langle S^2\rangle_z$ in THF appear above the dashed line which represents the $\langle S^2\rangle_0$ values calculated from the Benoit–Doty expression[27] for the worm-like chain with $q = 1.59$ nm and $M_L = 241\ \mathrm{nm^{-1}}$. This finding is consistent with what we have seen for $[\eta]$ in *Figure 6*.

On the other hand, the circles in *Figure 7* representing the measured $[\eta]$ in the TCE–TOL mixture with w_T at 0.785 are fitted accurately by the theoretical curve when M_w is below 10^5, indicating that excluded-volume effects in this solvent are significant only for the two fractions of highest molecular weight. To confirm this, additional viscosity measurements were attempted at larger w_T. It was found that solutions with w_T at 0.862 and with η_r smaller than 0.15–0.2 were stable enough to allow measurements with moderate accuracy (Huggins constants were comparable to or only slightly larger than those for w_T at 0.785 in *Table 1*), whereas those with w_T above 0.87 were too unstable to do so, especially for fractions of lower molecular weight, or even became turbid immediately after the addition of TOL. The results obtained for several fractions with w_T at 0.862 are shown by crosses in *Figure 7*. We see that when w_T is increased from 0.785 to 0.862 the $[\eta]$ values for the two fractions of highest molecular weight come close to the theoretical line, while those for the others remain almost unchanged. This confirms that the PC chain with M_w below 10^5 in the TCE–TOL mixture with w_T at 0.785 is essentially unperturbed by the excluded-volume effect.

Unperturbed dimensions

In *Table 3* the values of $(\langle S^2\rangle_0/M)_\infty$ obtained from the above analysis of the viscosity data are compared with the literature data[1–4]. Our values in the three solvents are close to those of Gawrisch *et al.*[2] and Ballard *et al.*[3] from SANS in the bulk state and not very different from that of Tsuji *et al.*[4] from sedimentation coefficients in THF, though the data analysis by the last group underestimates excluded-volume effects. The $(\langle S^2\rangle_0/M)_\infty$ of Berry *et al.*[1], determined directly by light scattering in a theta solvent, is too small compared to these values.

The present viscosity method for estimating $(\langle S^2\rangle_0/M)_\infty$, i.e. the Bushin–Bohdanecký plot[19,20], requires no precise worm-like chain parameters, but it builds on the accuracy of the current polymer hydrodynamics, especially the Φ_∞ value of $2.87\times10^{23}\ \mathrm{mol^{-1}}$ (see equation (3)). Typical experimental values[28,29] of Φ_∞ for flexible polymers in theta solvents range from 2.3×10^{23} to $2.8\times10^{23}\ \mathrm{mol^{-1}}$, being appreciably or slightly smaller than $2.87\times10^{23}\ \mathrm{mol^{-1}}$. If Φ_∞ for PC is taken as $2.5\times10^{23}\ \mathrm{mol^{-1}}$ regardless of the kind of solvent, our $(\langle S^2\rangle_0/M)_\infty$ values become larger by 10%. On the other hand, if short PC chains are similar to stiff chains in viscosity behaviour, the use of $2.87\times10^{23}\ \mathrm{mol^{-1}}$ for Φ_∞ may introduce no significant error. The reason is that the $[\eta]$ theory of Yamakawa and co-workers[10,21,30] for worm-like chains (based on the cylinder or touched-bead model) gives essentially the same q and M_L values as those evaluated from $\langle S^2\rangle$ for typical stiff polymers such as poly(hexyl isocyanate)[31] and DNA[32]. In view of such uncertainty arising from the theoretical Φ_∞, it seems reasonable to conclude that the $(\langle S^2\rangle_0/M)_\infty$ value of PC in dilute solution at room temperature is $(2.2\pm0.2)\times10^{-3}\ \mathrm{nm^2}$ (distinction between the values for THF and those for the other solvents is irrelevant). Since this value is still in good agreement with

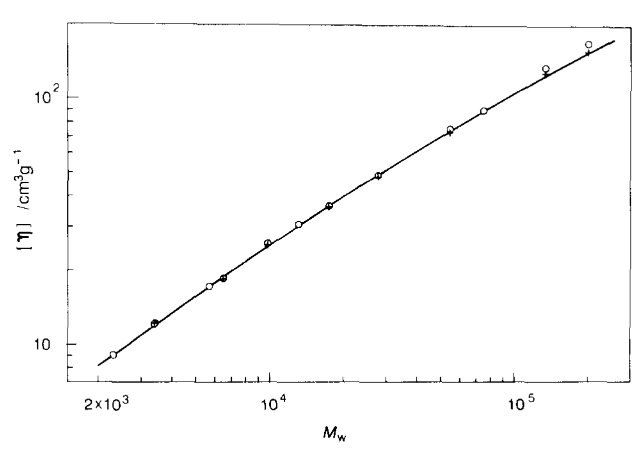

Figure 7 Comparison between the measured and calculated $[\eta]$ values: (○) TCE–TOL mixture with w_T at 0.785; (+) TCE–TOL mixture with w_T at 0.862; (——) unperturbed values calculated from the theory of Yoshizaki *et al.*[10] with $q = 1.61$ nm, $M_L = 259\ \mathrm{nm^{-1}}$ and $d = 0.79$ nm

Table 3 Unperturbed dimensions of PC

Authors	Solvent	$10^3(\langle S^2\rangle_0/M)_\infty$ (nm^2)	Method
Maeda and Norisuye	TCE–TOL (78.5 wt% TOL)	2.07	Viscosity
	THF	2.20	Viscosity
	DCM	2.07[a]	Viscosity
Berry *et al.*[1]	Butyl benzyl ether	1.44	Light scattering
Tsuji *et al.*[4]	THF	2.3	Sedimentation
Gawrisch *et al.*[2]	Bulk	2.14	SANS
Ballard *et al.*[3]	Bulk	2.09	SANS
Williams and Flory[33]		1.45	Calculation
Yoon and Flory[6]		1.8	Calculation
Sundararajan[7]		1.87	Calculation
Laskowski *et al.*[8]		1.8	Calculation
Hutnik *et al.*[9]		1.72	Calculation

[a] Not very accurate

those from SANS, we may further conclude that PC has essentially the same, unperturbed dimensions in solution and in the bulk state, as is the case for typical amorphous polymers.

Table 3 also presents theoretical values[6–9,33] of $(\langle S^2\rangle_0/M)_\infty$ from conformation calculations. Williams and Flory's early calculation[33] lent support to Berry's experimental value but was modified later by Yoon and Flory[6] and also by others[7–9], as indicated in the table. The modified unperturbed dimensions are much larger than Williams and Flory's value. However, they are still appreciably or somewhat smaller than the experimental value of $(2.2\pm0.2)\times10^{-3}$ nm^2 in both solution and the bulk state. Further theoretical elaboration is needed to reach a closer agreement.

REFERENCES

1 Berry, G. C., Nomura, H. and Mayhan, K. G. *J. Polym. Sci. (A-2)* 1967, **5**, 1
2 Gawrisch, W., Brereton, M. G. and Fischer, E. W. *Polym. Bull.* 1981, **4**, 687
3 Ballard, D. G. H., Burgess, A. N., Cheshire, P., Janke, E. W. and Nevin, A. *Polymer* 1981, **22**, 1353
4 Tsuji, T., Norisuye, T. and Fujita, H. *Polym. J.* 1975, **7**, 558
5 Yamakawa, H. and Fujii, M. *Macromolecules* 1973, **6**, 407
6 Yoon, D. Y. and Flory, P. J. *Polym. Bull.* 1981, **4**, 693
7 Sundararajan, B. C. *Macromolecules* 1987, **20**, 1534
8 Laskowski, B. C., Yoon, D. Y., McLean, D. and Jaffe, R. L. *Macromolecules* 1988, **21**, 1629
9 Hutnik, M., Argon, A. S. and Suter, U. W. *Macromolecules* 1991, **24**, 5956
10 Yoshizaki, T., Nitta, I. and Yamakawa, H. *Macromolecules* 1988, **21**, 165
11 Kratky, O. and Porod, G. *Recl Trav. Chim. Pays-Bas* 1949, **68**, 1106
12 Yamakawa, H. and Fujii, M. *J. Chem. Phys.* 1976, **64**, 5222
13 Yamakawa, H. *Annu. Rev. Phys. Chem.* 1984, **35**, 23
14 Deželić, Gj. and Vavra, J. *Croat. Chem. Acta* 1966, **68**, 1106
15 Rubingh, D. N. and Yu, H. *Macromolecules* 1976, **9**, 681
16 Berry, G. C. *J. Chem. Phys.* 1966, **44**, 4550
17 Schulz, G. V. and Horbach, A. *Makromol. Chem.* 1959, **29**, 93
18 Norisuye, T., Yanaki, T. and Fujita, H. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 547
19 Bushin, S. V., Tsvetkov, V. N., Lysenko, E. B. and Emel'yanov, V. N. *Vysokomol. Soedin., Ser. A* 1981, **23**, 2494
20 Bohdanecký, M. *Macromolecules* 1983, **16**, 1483
21 Yamakawa, H. and Fujii, M. *Macromolecules* 1974, **7**, 128
22 Bonart, R. *Makromol. Chem.* 1966, **92**, 149
23 Norisuye, T. and Fujita, H. *Polym. J.* 1982, **14**, 143
24 Einaga, Y., Koyama, H., Konishi, T. and Yamakawa, H. *Macromolecules* 1989, **22**, 3419
25 Kitagawa, T., Sadanobu, J. and Norisuye, T. *Macromolecules* 1991, **23**, 602
26 Fujii, Y., Tamai, Y., Konishi, T. and Yamakawa, H. *Macromolecules* 1991, **24**, 1608
27 Benoit, H. and Doty, P. *J. Phys. Chem.* 1953, **57**, 958
28 Miyaki, Y., Einaga, Y., Fujita, H. and Fukuda, M. *Macromolecules* 1980, **13**, 588
29 Konishi, T., Yoshizaki, T. and Yamakawa, H. *Macromolecules* 1991, **24**, 5614
30 Yamakawa, H. and Yoshizaki, T. *Macromolecules* 1980, **13**, 633
31 Murakami, H., Norisuye, T. and Fujita, H. *Macromolecules* 1980, **13**, 345
32 Godfrey, J. E. and Eisenberg, H. *Biophys. Chem.* 1976, **5**, 301
33 Williams, A. D. and Flory, P. J. *J. Polym. Sci. (A-2)* 1968, **6**, 1945