Temperature and solvent effects on the unperturbed chain dimensions of bisphenol-A polycarbonate

Gandavarapu Ventakaramana Reddy* and Miloslav Bohdanecký†
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia

and Danuta Staszewska and Lech Huppenthal
Institute of Chemistry, Copernicus University, Toruń, Poland

The temperature dependence (from 25 to 80°C) of the intrinsic viscosity of bisphenol-A polycarbonate fractions ($0.6 \leqslant M \times 10^{-4} \leqslant 30$) was determined in dioxan and tetrachloroethane. The temperature quotient of the unperturbed mean-square end-to-end distance, $(\mathrm{d}\ln\langle R^2\rangle_0/M)_\infty\, \mathrm{d}T$, was estimated and found to be slightly negative. A weak solvent effect on the value of $(\langle R^2\rangle_0/M)_\infty$ was established. The results are compared with theoretical predictions and with reported data.

INTRODUCTION

The ratio of the unperturbed mean-square end-to-end distance (in the random coil limit) to the molecular weight, $(\langle R^2\rangle_0/M)_\infty$, and the temperature quotient, $Q \equiv \mathrm{d}\ln(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T$, are quantities which provide complementary information on the conformation of polymer chains[1]. In a previous paper[2], a method of estimating Q for stiff-chain polymers from the temperature quotient of intrinsic viscosity, $\mathrm{d}\ln[\eta]/\mathrm{d}T$, has been described. The method is based on the theory of hydrodynamic properties of the continuous wormlike cylinder model[3], and on the assumption that the contribution of the excluded volume to $\mathrm{d}\ln[\eta]/\mathrm{d}T$ may be neglected. This assumption is reasonable with cellulose derivatives but cannot be accepted with bisphenol-A polycarbonates (PC) because the excluded-volume effect is negligible only at molecular weights lower than the 'critical' value, $M_c \simeq 4 \times 10^4$ (ref. 4).

The procedure of determining the quotient Q was therefore modified and used to estimate Q from the values of $\mathrm{d}\ln[\eta]/\mathrm{d}T$ of PC fractions in dioxan and tetrachloroethane. The results are presented and discussed in this paper.

EXPERIMENTAL

Polymers and fractionation. A commercial product 'Bistan AN', produced by Izochem, Bydgoszcz (Poland), was fractionated by successive precipitation of solutions in chloroform with n-hexane[5] (S-fractions, *Table 1*). Fractions A and B were obtained similarly with the dichloromethane–methanol system from a laboratory sample prepared by transesterification[6] of diphenyl carbonate with bisphenol-A.

Viscosity-average molecular weights, M_η, were computed from the intrinsic viscosities, $[\eta]$, (in $\mathrm{dl\,g}^{-1}$) measured in chloroform or dichloromethane (at 25°C), respectively, according to the equations[4]

$$[\eta] = 3.01 \times 10^{-4} M_\eta^{0.74}$$

$$[\eta] = 2.99 \times 10^{-4} M_\eta^{0.74}$$

The M_η values of fractions A1 and A2 were estimated from $[\eta]$ (in $\mathrm{dl\,g}^{-1}$) in tetrachloroethane according to a calibration based on data in *Table 1*.

The intrinsic viscosities were determined in the standard way. The Heller method[7] was used for extrapolating data to zero polymer concentration. The $[\eta]$ values were corrected for the change with temperature of the solvent density. Corrections for the kinetic energy loss and the shear stress dependence were negligible.

RESULTS AND DISCUSSION

The PC fractions are characterized by the M_η values which is sufficient for the scope of the present study. The plots of $\ln[\eta]$ vs. T are linear from 25 to 80°C. The values of $\mathrm{d}\ln[\eta]/\mathrm{d}T$ (*Table 1*) are negative and slightly dependent on molecular weight.

Estimation of the quotient Q

In general, the temperature effect on the intrinsic viscosity of stiff-chain polymers can be expressed by the following equations[2]

$$\mathrm{d}\ln[\eta]/\mathrm{d}T = \mathrm{d}\ln[\eta]_0/\mathrm{d}T + \mathrm{d}\ln \alpha_\eta^3/\mathrm{d}T \qquad (1)$$

$$\mathrm{d}\ln[\eta]_0/\mathrm{d}T = -3\mathrm{d}\ln B_\eta/\mathrm{d}T +$$
$$3(\mathrm{d}\ln B_\eta/\mathrm{d}T - \mathrm{d}\ln A_\eta/\mathrm{d}T)[1 + (B_\eta/A_\eta)M^{1/2}]^{-1} \qquad (2)$$

Table 1 Experimental data on polycarbonate fractions

Fraction	$M_\eta \times 10^{-4\,a}$	$[\eta]$ (dl g^{-1}) at 25°C			$-(\mathrm{d}\ln[\eta]/\mathrm{d}T) \times 10^3$ (deg^{-1})	
		Chloroform	Tetrachloroethane	Dioxan	Tetrachloroethane	Dioxan
A 1	30.5^b	–	3.79	–	2.3	–
A 2	21^b	–	2.84	–	2.8	–
B 1	11.0	1.55	1.68	1.48	2.2	2.8
A 4	10.6^c	1.57^d	1.69	–	2.1	–
B 2	9.8	1.45	–	1.38	–	2.3
B 3	7.6	1.22	–	1.31	–	2.5
B 4	6.3	1.06	1.09	1.00	2.4	2.2
A 7	5.0^c	0.90^d	1.10	–	2.8	–
S 1	3.6	0.73	0.78	0.71	2.6	1.7
S 2	3.4	0.71	–	0.67	–	1.8
S 5	1.9	0.47	–	0.47	–	3.5
S 6	1.2	0.32	0.37	–	4.0	–
S 7	0.9	0.27	–	0.29	–	3.2
S 8	0.7	0.21	0.22	0.21	–	–

^{a} Unless stated otherwise, M_η was calculated from $[\eta]$ in chloroform
^{b,c} M_η estimated from $[\eta]$ in tetrachloroethane and dichloromethane, respectively
^{d} $[\eta]$ in dichloromethane at 25°C

$$\mathrm{d}\ln\alpha_\eta^3/\mathrm{d}T \simeq (C_\eta/\alpha_\eta^3)(\mathrm{d}z/\mathrm{d}T) \tag{3}$$

where

$$\alpha_\eta^3 = [\eta]/[\eta]_0 \tag{4}$$

$$\mathrm{d}z/\mathrm{d}T = (\mathrm{d}k/\mathrm{d}T)\,M^{1/2} \tag{5}$$

$$k = (3/2\pi)^{3/2}(\langle R^2 \rangle_0/M)_\infty^{-3/2}B \tag{6}$$

$$A_\eta = A_0 M_L \phi_{0,\infty}^{-1/3} \tag{7}$$

$$B_\eta = \phi_{0,\infty}^{-1/3}(\langle R^2 \rangle_0/M)_\infty^{-1/2} \tag{8}$$

$$(\langle R^2 \rangle_0/M)_\infty = \lambda^{-1}/M_L \tag{9}$$

$$\mathrm{d}\ln B_\eta/\mathrm{d}T = -\tfrac{1}{2}Q \tag{10}$$

Here, $[\eta]_0$ and $[\eta]$ are the intrinsic viscosities corresponding, respectively, to unperturbed and perturbed chains at the same temperature, α_η^3 is the viscosity expansion factor, z is the well-known excluded-volume parameter, B is the polymer–solvent interaction parameter, $\phi_{0,\infty}$ is the viscosity function in the limit of non-draining random coil[1], and C_η is a numerical factor which is zero at very low molecular weights[2,8]. The symbols λ^{-1}, M_L and d stand for the characteristics of the wormlike cylinder model, i.e. the Kuhn statistical segment length, the shift factor and the diameter, respectively. A_0 is a function of $d_r = d/\lambda^{-1}$ (ref. 8).

If the molecular weights are much lower than M_c and/or the quotient $\mathrm{d}z/\mathrm{d}T$ is zero, the term $\mathrm{d}\ln\alpha_\eta^3/\mathrm{d}T$ in equation (1) may be neglected, and equation (1) simplifies to equation (2). The parameter Q can be estimated[2] from the slope of the plot of $(M^2/[\eta])^{1/3}\,\mathrm{d}\ln[\eta]/\mathrm{d}T$ vs. $(M^2/[\eta])^{1/3}$. This method becomes unreliable if a minority of data correspond to $M \ll M_c$, and the quotient $\mathrm{d}z/\mathrm{d}T$ is non-zero and unknown.

By combining equations (1), (2), (3) and (5) we obtain

$$[1 + (B_\eta/A_\eta)M^{1/2}]\mathrm{d}\ln[\eta]/\mathrm{d}T$$
$$= 3\mathrm{d}\ln A_\eta/\mathrm{d}T - 3[(B_\eta/A_\eta)\mathrm{d}\ln B_\eta/\mathrm{d}T - (C_\eta/\alpha_\eta^3)(\mathrm{d}k/\mathrm{d}T)]M^{1/2}$$
$$- (B_\eta/A_\eta)(C_\eta/\alpha_\eta^3)(\mathrm{d}k/\mathrm{d}T)M \tag{11}$$
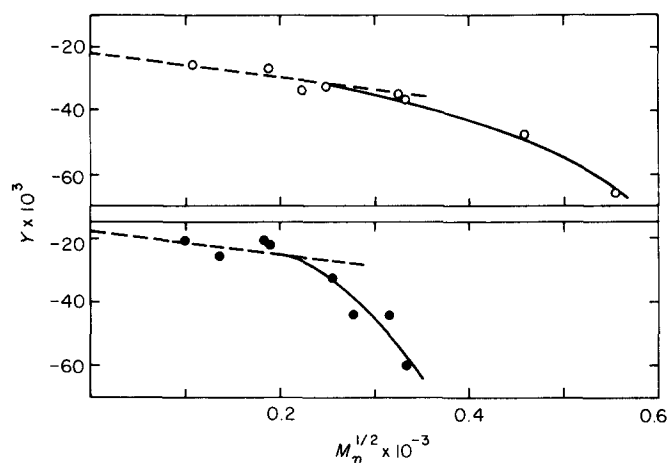
Figure 1 Plot of the intrinsic viscosity data according to equation (11). $Y \equiv [1 + (B_\eta/A_\eta)M^{1/2}]\mathrm{d}\ln[\eta]/\mathrm{d}T$ (cf. eq. (11)). Solvents: dioxan, ●; tetrachloroethane, ○. Values of $\mathrm{d}\ln[\eta]/\mathrm{d}T$ from *Table 1*

Unless $\mathrm{d}k/\mathrm{d}T = 0$, the plot of the left-hand side (LHS) vs. $M^{1/2}$ should be non-linear and the quotient Q can be estimated from the initial slope, s_i, only:

$$Q = (2/3)(A_\eta/B_\eta)s_i \tag{12}$$

The precision of estimation depends on the amount and accuracy of data in the low-molecular-weight region.

As shown by *Figure 1*, the plots according to equation (11) of the data for PC in dioxan and tetrachloroethane are non-linear. The curvature is small with the latter system and pronounced with the former where an abrupt change is observed at molecular weights close to M_c.

The trend of the plots at high molecular weights indicates that $\mathrm{d}k/\mathrm{d}T$ is negative with both solvents. This means that B decreases with increasing temperature. The absolute value, $|\mathrm{d}B/\mathrm{d}T|$, is higher with dioxan.

The initial slope of the plot for tetrachloroethane corresponds to $Q = -0.6 \times 10^{-3}$ deg^{-1} (*Figure 1*). With dioxan, the LHS values seem to be independent of molecular weight at $M < 4 \times 10^4$, which would indicate Q to be zero. The dependence can be fitted with the same slope as with tetrachloroethane (*Figure 1*). Thus, it may
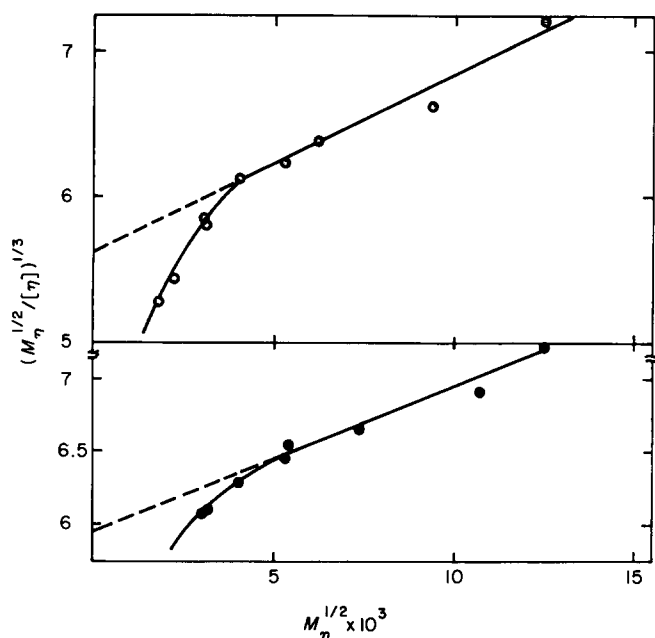
Figure 2 Plot of the intrinsic viscosity data according to equation (14b). Symbols as in *Figure 1*. Data from *Table 1*

be concluded that the Q value for PC is slightly negative, probably between zero and $-0.6 \times 10^{-3}\,\mathrm{deg}^{-1}$.

A larger negative value of Q was estimated by Sitaramaiah[9] from the temperature dependence of intrinsic viscosity. Unfortunately, the assumption underlying the evaluation (namely, that the PC molecules are non-draining random coils with strong excluded-volume effect) is at variance with the finding[4] that the wormlike chain with a weak excluded-volume effect is a more adequate model.

Estimation of the A_η, B_η and M_c values

The parameters A_η and B_η come from the equation

$$[\eta]_0 = [\phi_{0,\infty}(\langle R^2 \rangle_0/M)^{3/2}_\infty M^{1/2}][1 + (A_\eta/B_\eta)M^{-1/2}]^{-3} \quad (13)$$

which fits the results of theoretical calculations[3,8,10]. Rearranging equation (13) leads to two equivalent equations

$$(M^2/[\eta]_0)^{1/3} = A_\eta + B_\eta M^{1/2} \quad (14a)$$

$$(M^{1/2}/[\eta]_0)^{1/3} = B_\eta + A_\eta M^{-1/2} \quad (14b)$$

suitable for the estimation of A_η and B_η.

Corresponding plots for systems without excluded-volume effect are linear[8,10]. In good solvent systems, short chains (at $M \ll M_c$) remain essentially unperturbed and their intrinsic viscosity $[\eta]$ is equal to $[\eta]_0$, whereas at $M > M_c$ the chains are expanded and $[\eta] > [\eta]_0$. Consequently, the plots are linear at $M \ll M_c$ only and slope downwards above M_c^8.

The transition is particularly clear on the $(M^{1/2}/[\eta])^{1/3}$ vs. $M^{-1/2}$ dependences if the low-molecular-weight region is well covered by data. The plot for PC (*Figure 2*) is linear at high values and non-linear at low values of $M^{-1/2}$. The crossover at $M_c \times 10^{-4} \simeq 4-5$ is in agreement with values found from sedimentation coefficients[4]. The following values have been obtained for

the parameters of equation (13): $A_\eta = 100$ and $B_\eta = 6.0$ for tetrachloroethane, and $A_\eta = 120$ and $B_\eta = 5.7$ for dioxan.

Solvent effect on $(\langle R^2 \rangle_0/M)_\infty$

The $[\eta]$ values in dioxan and tetrachloroethane (*Table 1*) display a small but systematic dependence on the solvent. The same is found with other solvents as reported by Tsuji *et al.*[4] At high molecular weights, this effect might be due to differences in the polymer–solvent interaction parameters but in the low-molecular-weight region it has to be assigned to differences in $(\langle R^2 \rangle_0/M)_\infty$ and/or in other characteristics of the chain.

A sensitive, though qualitative, method to detect the solvent effect on $(\langle R^2 \rangle_0/M)_\infty$ consists of plotting Δ vs. $M^{1/2}$, where Δ is calculated from the intrinsic viscosities, $[\eta]_1$ and $[\eta]_2$, in two solvents according to the equation

$$\Delta = (M^2/[\eta]_1)^{1/3} - (M^2/[\eta]_2)^{1/3} \quad (15)$$

We have from equation (14a) that the initial slope of this plot is

$$\Delta B_\eta = B_{\eta,1} - B_{\eta,2} \quad (16)$$

Dependences of Δ vs. $M^{1/2}$ for PC (with chloroform as solvent 2) are presented in *Figure 3*. The initial slopes (at $M^{1/2} < M_c^{1/2}$) are positive with tetrahydrofuran, dichloromethane, and dioxan and negative with
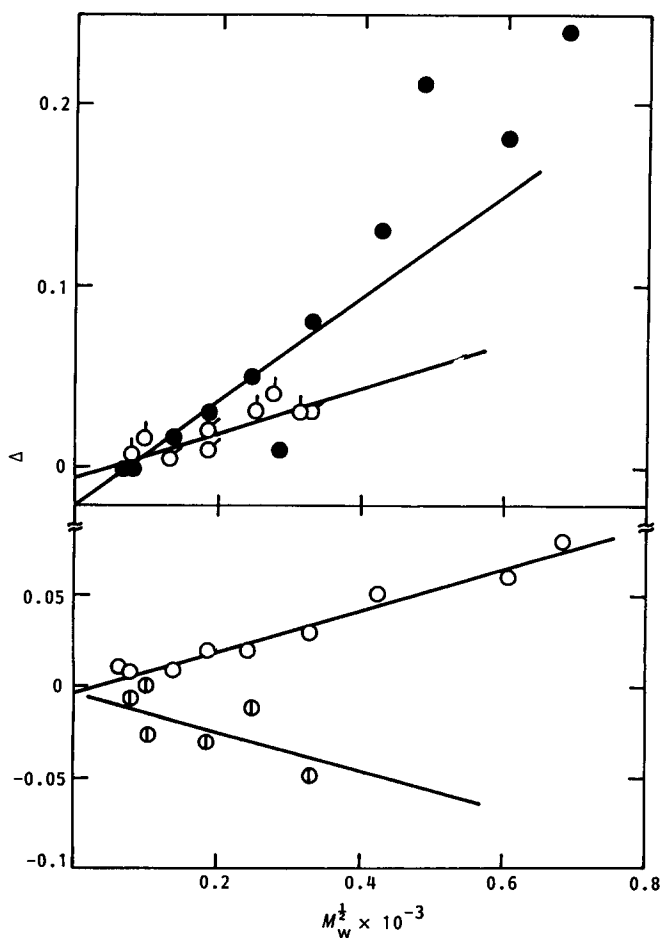

Figure 3 Plot of the intrinsic viscosity data according to equation (15). Solvents: tetrahydrofuran, ●[4]; dichloromethane, ○[4]; dioxan, ○; tetrachloroethane, ⊕ (*Table 1*)

tetrachloroethane. They show that $(\langle R^2 \rangle_0 / M)_\infty$ increases in the series of solvents: tetrahydrofuran < dioxan ⩽ dichloromethane < chloroform < tetrachloroethane, and seem to correlate with the number of chlorine atoms in the solvent molecule. The difference between the first and the last solvent is estimated to be less than 10%.

Conformational parameters of PC chains

The detailed conformational analysis by Sundara-rajan[11] shows that PC segments can assume flat-helical, extended-helical and non-helical conformations. All of them are of nearly equal energy and, therefore, occur with the same probability. Consequently, the predicted values of $(\langle R^2 \rangle_0 / M)_\infty$ and Q are low: 1.12×10^{-16} cm^2 and 0.098×10^{-3} deg^{-1}, respectively.

By recalculating, according to equation (9), the data reported for 25°C by Tsuji et al.[4] ($\lambda^{-1} = 36 \times 10^{-8}$ cm, $M_L = 26 \times 10^8$ cm^{-1}), we obtain $(\langle R^2 \rangle_0 / M)_\infty = 1.38 \times 10^{-16}$ cm^2. Nearly the same value was found by neutron scattering[12,13]. The value is higher than the predicted one by about 20%. On the other hand, a very low value, 0.85×10^{-16} cm^2, was obtained by Berry et al.[14] from the intrinsic viscosity data in a solvent–non-solvent mixture at 25°C.

An explanation for this difference is difficult. The low value reported in reference 14 is close to that calculated by Sundararajan[11] for a chain with flat-type helices, and one can speculate about a conformational change brought about by the mixed solvent. Note, however, that the effect on $(\langle R^2 \rangle_0 / M)_\infty$ observed with single solvents is less than 10%.

An alternative explanation (also speculative) might be that the mixed solvent used by Berry et al.[14] was a very poor one so that the molecules were more coiled than in the unperturbed state. The low solvent power would be indicated by a negative slope of the plot of $[\eta]/M^{1/2}$ vs.

$M^{1/2}$. The composition of the mixed solvent was adjusted so that the $[\eta]/M^{1/2}$ values were equal to those in n-butyl benzyl ether at $\theta = 170°C$ and independent of molecular weight. Unfortunately, true solutions (free from aggregations) could not be prepared at $M < 46 \times 10^4$ so that meaningful values of $[\eta]/M^{1/2}$ could be obtained for high molecular weights only ($46 \gtrsim M \times 10^{-4} \gtrsim 74$). The range of molecular weights was narrow so that a negative trend of the plot of $[\eta]/M^{1/2}$ vs. $M^{1/2}$ might escape observation.

The temperature quotient of the unperturbed chain dimensions estimated in this paper is slightly negative, and its value is not far from the predicted one. It shows that $(\langle R^2 \rangle_0 / M)_\infty$ decreases only very slowly in the range from 25 to 80°C. However, a more rapid decrease in $(\langle R^2 \rangle_0 / M)_\infty$ above 100°C is indicated[14] by the low value found in n-butyl benzyl ether at 170°C.

REFERENCES

1 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley Interscience, New York, 1969
2 Reddy, G. V. and Bohdanecký, M. *Macromolecules* 1987, **20**, 1393
3 Yamakawa, H. and Fujii, M. *Macromolecules* 1974, **7**, 128
4 Tsuji, T., Norisuye, T. and Fujita, H. *Polym. J.* 1975, **7**, 558
5 Brzeziński, J. and Wajnryb, M. *Tworzywa-Guma-Lakiery (Warsaw)* 1960, **5**, 326
6 Luňák, S. and Bohdanecký, M. *Collect. Czech. Chem. Commun.* 1956, **30**, 2756
7 Heller, W. *J. Colloid Chem.* 1954, **9**, 547
8 Bohdanecký, M. *Macromolecules* 1983, **16**, 1483
9 Sitaramaiah, G. *J. Polym. Sci. A* 1965, **3**, 2743
10 Bushin, S. V., Tsvetkov, V. N., Lysenko, E. B. and Emelyanov, V. N. *Vysokomol. Soed.* 1981, **A23**, 2494
11 Sundararajan, P. R. *Macromolecules* 1987, **20**, 1534
12 Gawrisch, W., Brereton, M. G. and Fischer, E. W. *Polym. Bull. (Berlin)* 1981, **4**, 687
13 Yoon, D. Y. and Flory, P. J. *Polym. Bull. (Berlin)* 1981, **4**, 693
14 Berry, G. C., Nomura, H. and Mayhan, K. G. *J. Polym. Sci.* 1967, **A-2**, **5**, 1