

DILUTE SOLUTION PROPERTIES OF BISPHENOL A POLYCARBONATE: EXCLUDED VOLUME TREATMENTS*

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The volume effects of bisphenol A polycarbonate in dilute solutions show a serious departure from Flory's theory. However, the variation of the swelling factor α with molecular weight conforms to the treatments of Kurata *et al.* and Fixman. Molecular weights below 20,000 do not seem to apply to any of the theories, probably indicating the limit of the excluded volume treatments.

Effects of excluded volume arising from interactions of nonbounded segments of polymer chains in dilute solutions is expressed in terms of the swelling factor α . The swelling factor α is a function of a single variable z defined by

$$z = B(\bar{s}_0^2/M)^{-3/2} M^{1/2} \quad (1)$$

where B represents the polymer-solvent interaction parameter, (\bar{s}_0^2) is the mean square radius of gyration in the unperturbed state and M , the molecular weight. The hydrodynamic treatment of Flory¹ is

$$\alpha^5 - \alpha^3 = Cz \quad (2)$$

C being a numerical constant. The ratio $(\alpha^5 - \alpha^3)/M^{1/2}$ instead of being a constant increases with increasing molecular weight.² Sitaramaiah³ also obtained a similar deviation for polycarbonate solutions.

A number of statistical theories of excluded volume effects have been proposed by several authors.⁴⁻⁶ These treatments are known as the third power law equations because of the term α^3 . Kurata *et al.*'s⁴ relationship is

$$\alpha^3 - \alpha = (4/3) g(\alpha) z \quad (3)$$

$$\text{where } g(\alpha) = [1 + (1/3\alpha^2)]^{-3/2} \quad (4)$$

Fixman⁵ has expressed the relationship in a simpler form,

$$\alpha^3 - 1 = 2z \quad (5)$$

Ptitsyn⁶ has recently proposed the following equation,

$$(4.68 \alpha^2 - 3.68)^{3/2} = 1 + 9.36z \quad (6)$$

These equations are in good agreement with experimental data^{7,8} and with Monte Carlo

calculations^{9,10} as well. Sitaramaiah³ also found that the behaviour of polycarbonate solutions fits in excellently with the treatment of Kurata *et al.*⁴

Experimental

Determinations of viscosities and osmotic pressures at 25°C for polycarbonate fractions in different solvents have already been described.^{11,12} Molecular weights below 25,000 have been determined by vapour pressure osmometry at 37°C in chloroform.¹³

Results

Values of the swelling factor α have been calculated from the relationships^{14,14a} between the intrinsic viscosity $[\eta]$ and molecular weight M ,

$$[\eta] = K M^{1/2} \alpha^3 \quad (7)$$

$$[\eta] = K M^{1/2} + 0.51 \cdot B \Phi M \quad (8)$$

$$\text{where } K = \Phi (6 \bar{s}_0^2 / M)^{3/2} \quad (9)$$

Φ is the so-called universal constant and α_η is the swelling factor determined from viscometric studies. K values for different polycarbonate-solvent systems have been determined graphically¹⁵ using equation 8. Values of α_η thus obtained are given in Table 1. Number average molecular weights \bar{M}_n are used in these calculations.

Figure 1 gives the plots of different theories for polycarbonate solutions in chloroform at 25°C. These plots have been drawn assuming the condition¹⁴ of equality between α and α_η .

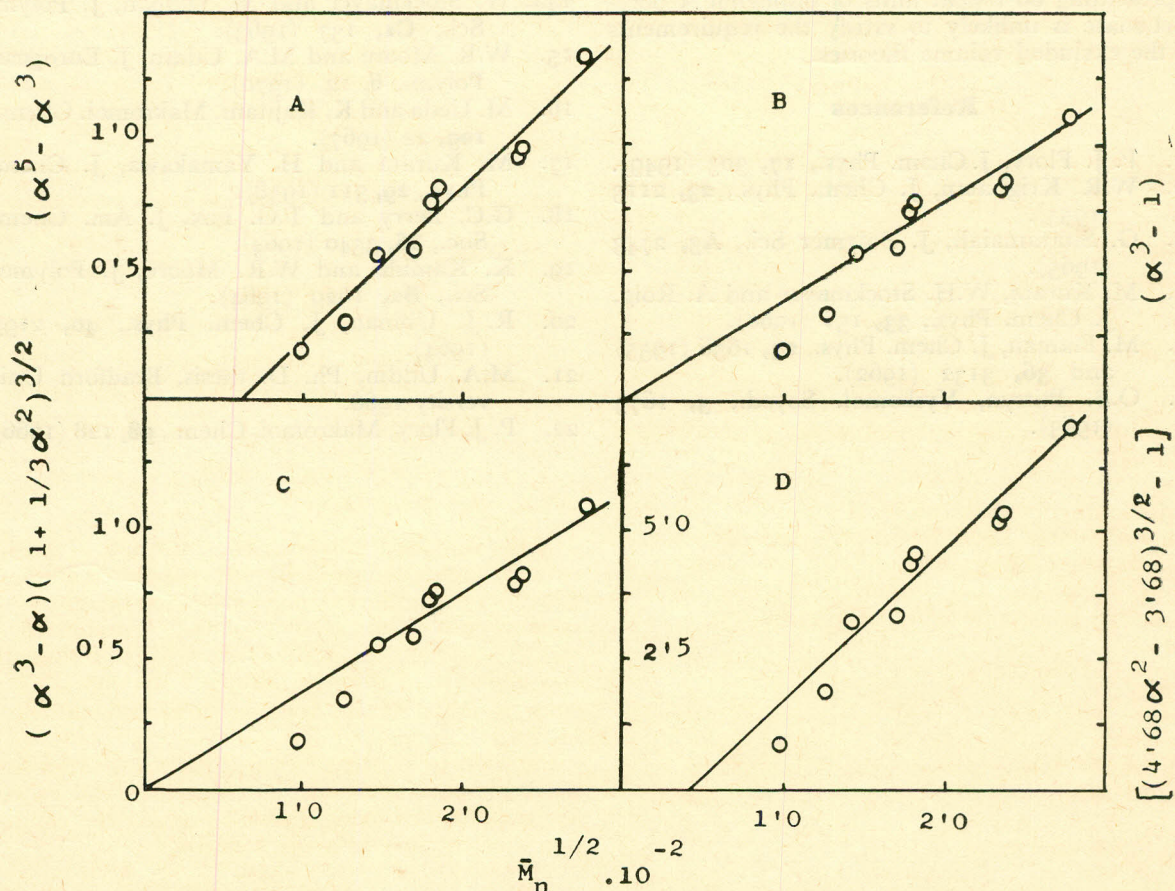
Discussion

Figure 1 shows that Flory's relationship does not hold for polycarbonate solutions. The plot of $(\alpha^5 - \alpha^3)$ against $\bar{M}_n^{1/2}$ makes an intercept on the abscissa as reported by Sitaramaiah.³ The plot of Ptitsyn's equation also gives a similar intercept and the modification suggested by Ueda and Kajitani¹⁶ does not indicate any improvement.

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TABLE I.—VALUES OF α_η IN DIFFERENT SOLVENTS AT 25°C.

Fraction	$M_n \cdot 10^{-4}$	α_η values					
		Chloroform	Methylene chloride	Ethylene chloride	Dioxan	Tetrahydrofuran	Cyclohexanone
1	7.69	1.28	1.29	1.18	1.25	1.19	1.14
2	5.63	1.23	—	—	1.22	1.17	1.12
3	5.48	1.23	1.24	1.13	—	—	—
4	3.28	1.21	—	1.14	—	—	1.13
5	3.16	1.20	1.20	—	1.18	1.14	—
6	2.85	1.16	1.16	1.11	1.14	1.12	1.11
7	2.14	1.16	1.16	1.10	1.15	1.12	1.12
8	1.62	1.10	1.09	1.04	1.10	1.09	1.04
9	0.95	1.06	—	—	1.08	1.13	1.05

Fig. 1.—Plot of the theories of (A) Flory, (B) Fixman, (C) Kurata *et al.* and (D) Ptitsyn for bisphenol A polycarbonate solutions in chloroform at 25°C.

The relationships of Kurata *et al.*⁴ and Fixman⁵ give better fit for polycarbonate. Consideration of the difference between α and α_η arising from the non-Gaussian characteristics of polymer chains given by¹⁷

$$\alpha_\eta^3 = \alpha^{2.43} \quad (10)$$

does not appreciably improve any of these relationships. Agreements in other solvents are also of the same order.

Berry and Fox¹⁸ have expressed doubt about the applicability of the excluded volume treatments for $M < 10^5$. This limitation may probably include the effect of appreciable draining. Calculations based on the method of Kamide and Moore¹⁹ and Ullman²⁰ do not suggest such effects for polycarbonate.²¹ However, equations 3 and 5 appear to hold for polycarbonate solutions for $M < 10^5$. Two points in the plots of Kurata *et al.* and Fixman for $\bar{M}_n < 20,000$ falling much below the straight lines probably indicate the breakdown of these treatments. This is in agreement with the conclusion²² that the excluded volume treatments fail to apply for chain length below 100–400 units for vinyl polymers. Similar limitations may also be expected for polycarbonate and a molecular weight of 20,000 representing 80 repeat units of bisphenol A polycarbonate is unlikely to satisfy the requirements of the excluded volume theories.

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