Unperturbed Dimension of Polymer Molecules from Viscosity Measurements in Different Solvents

Subasini Lenka[a]; Padma L. Nayak[a]; Manoranjan Dash[a]

[a] Laboratory of Polymers and Fibers Department of Chemistry, Ravenshaw College, Cuttack, Orissa, India

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SUBASINI LENKA, PADMA L. NAYAK, and MANORANJAN DASH

Laboratory of Polymers and Fibers
Department of Chemistry
Ravenshaw College
Cuttack 753003, Orissa, India

ABSTRACT

An expression for the determination of the cross-over point concentration, C_x, of the polymer in a number of solvents has been derived, and an expression relating C_x with the unperturbed dimension of polymer molecules $(\overline{r_0}^2)^{1/2}$ has been proposed. The unperturbed dimensions for polymethyl acrylate, polyethyl acrylate, polybutyl acrylate, polyacrylonitrile, and polyvinyl pyrrolidone have been calculated.

INTRODUCTION

Polymer dimensions are quite readily obtained from measurements of intrinsic viscosity, but interpretation of such measurements requires separation of inter- and intramolecular interactions. A number of methods are available for the determination of the unperturbed dimensions of polymer molecules. The two most important methods often used are: 1) Viscosity measurements of polymer solutions at the θ-temperature [1] and 2) building up suitable expressions [2-5]

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relating the intrinsic viscosity to the molecular weight by following a mathematical extrapolation procedure.

Unfortunately, the attainment of θ-temperature or θ-solvent experimentally is often very difficult or impossible, especially if the polymer is crystalline. A θ-solvent by definition is one in which the excess chemical potential of the solution becomes zero and is characterized by the second viral coefficient, A_2, becoming zero.

In this communication we propose a new equation for the determination of unperturbed dimension of polymer molecules from a knowledge of the cross-over point concentration.

CROSS-OVER POINT CONCENTRATION

It has been illustrated by Eirich and Riseman [6] that the plot of the slope versus intercept of Huggins' [7] linear equation, $\eta_{sp}/C = [\eta] + k'[\eta]^2 C$, for a polymer in different solvents gives a straight line. It has been shown by Streeter and Boyer [8] that the existence of such a linear relationship between the slope and the intercept necessitates that the plot of η_{sp}/C versus C for a polymer in different solvents should meet at a common point, the corresponding concentration at the converge point being called "the cross-over point concentration." Therefore it was realized that the parameter derived at such a cross-over point should be independent of the solvent and is an inherent property of the polymer alone. Cleverdon and Smith [9] have shown that the η_{sp}/C value at such a cross-over point should be independent of solvent and is related to the intrinsic viscosity at the precipitation point. Similar attempts have been made by Gundiah et al. [10] though they started with Kraemer's equation [11]. Their approach is more realistic in view of the fact that the cross-over concentration in Kraemer's plot is on the positive side of the concentration axis, whereas the cross-over point concentration in Cleverdon and Smith's [9] method is on the negative side of the concentration axis. Gundiah et al. [10] have observed that the intrinsic viscosity at the cross-over point concentration is almost equal to the intrinsic viscosity at the precipitation point in a θ-solvent. However, no attempt has been made to correlate the cross-over point concentration with other inherent properties of the polymer.

CROSS-OVER POINT CONCENTRATION FROM HUGGINS' EQUATION

Huggins derived the following equation for polymer solutions by using Stokes' law:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C$$

where η_{sp} = specific viscosity

$[\eta]$ = intrinsic viscosity

C = concentration in g/dL

k' = Huggins' constant

Eirich and Riseman [6] have explained the significance of k' which, although constant for a polymer-solvent system, changes with a change of solvent, introducing the concept of back-coiling mechanism.

Now, let us consider the equation of cross-over point concentration in the Huggins' plot. If C_x is the concentration at which all the η_{sp}/C vs C curves meet when extrapolated, then at C_x,

$$(\eta_{sp}/C)_x = [\eta]_1 + k_1'[\eta]_1^2 C_x$$

$$= [\eta]_2 + k_2'[\eta]_2^2 C_x$$

$$= \ldots P_x \text{ (say)} \tag{1}$$

In general,

$$[\eta]_i + k_i'[\eta]_i^2 C_x = P_x$$

or

$$k_i'[\eta]_i^2 = p_x/C_x - [\eta]_i/C_x$$

$$= \alpha + \sigma[\eta]_i \tag{2}$$

Equation (2) is the well-known Eirich-Riseman [6] relationship. Validity of this equation has been tested by many workers, though the value of C_x has been obtained directly in only a few cases. The expression for α and σ have been given by Bhatnagar et al. [13] in introducing the theory of rate process to viscous flow. Recently, Ibrahim [14] has shown both theoretically and experimentally the approximate nature of Huggins' equation as compared to the empirical equation of Schulz and Blaschke [15], considering the parent equation

$$\eta_{sp}/C = \frac{[\eta]}{1 - k[\eta]C'}$$

obtained by the extension of Kuhn's hydrodynamic treatment. Evidently,

$$\eta_{sp}/C = [\eta] + k[\eta]^2 C + k^2[\eta]^3 C^2 + \cdots$$

$$\approx [\eta] + k'[\eta]^2 C + \cdots \qquad \text{(at low concentration)} \qquad (3$$

This is the well-known Huggins' equation. On the other hand, if one does not neglect any term, then

$$\eta_{sp}/C = [\eta] + k[\eta]\eta_{sp} \qquad (4$$

This is the Schulz-Glaschke equation.

From the derivation it is evident that Eq. (4) involves no approximation and should be regarded as an equation of choice so far as a two-parameter equation relating to viscosity and concentration is concerned.

As expected, k' differs from k, sometimes by as high as 300% [14]. Since the values of k' and k are obtained by dividing the slopes of Eqs. (1) and (4) by $[\eta]^2$ and $[\eta]$, respectively, any error in the value of $[\eta]$ will influence the values of these parameters. An equation which gives k directly, but fundamentally the same as in Eq. (4), is that proposed by Heller:

$$\frac{C}{\eta_{sp}} = \frac{1}{[\eta]} - kC \qquad (5$$

The important aspect of this equation is that it gives the value of k directly as the slope and is thus unaffected by any error in $[\eta]$ values

CROSS-OVER POINT CONCENTRATION FROM HELLER'S EQUATION

Let us consider the condition for a cross-over point concentration in Eq. (5). Proceeding as before,

$$\left(\frac{C_x}{\eta_{sp}}\right)_x = \frac{1}{[\eta]_1} - k_1 C_x = \frac{1}{[\eta]_2} - k_2 C_x = P \text{ (say)}$$

So, at the cross-over point,

$$\frac{1}{[\eta]_i} - k_i C_x = P$$

or

$$\frac{1}{[\eta]} = P + kC_x \tag{6}$$

Therefore, the condition that the plots of C/η_{sp} vs C for a polymer in different solvents should meet at a common point necessitates that plots of $1/[\eta]$ vs k for different solvents should be linear. This has been verified by many workers. The actual convergence of the C/η_{sp} vs C plot at a point is shown in Fig. 1.

SIGNIFICANCE OF CROSS-OVER POINT CONCENTRATION

In order to understand the theoretical significance of the cross-over point concentration, the approach of Bhatnagar et al. [13] has
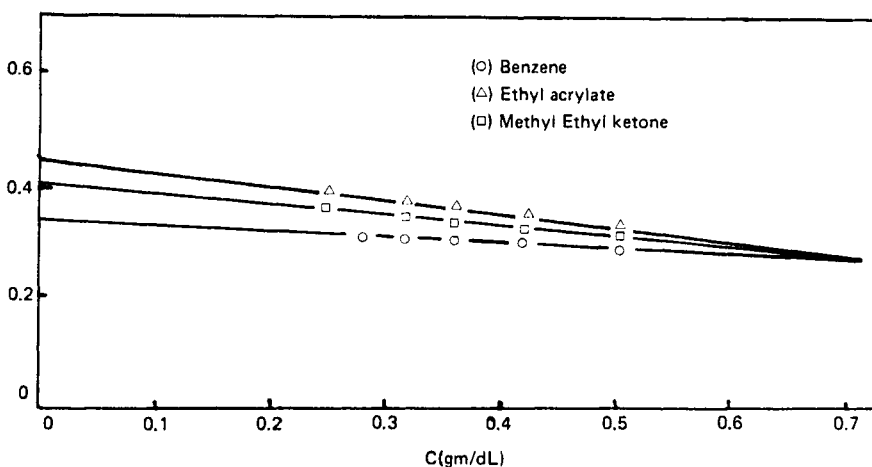

(O) Benzene
(△) Ethyl acrylate
(□) Methyl Ethyl ketone

C(gm/dL)

FIGURE 1.

been followed. They have derived an expression for the relative viscosity, η_{rel}, by considering the equivalent sphere model for polymer molecules in solutions. Without making any approximation in the expressions of fluidities as was done by Bhatnagar et al. [13], we obtain,

$$\eta_{rel} = e^{X_2} (\gamma/RT)[\, 1 - x_2 \, \{1 - w(p)F(y)\}]^{-1} \tag{7}$$

where the symbols have the same meaning as those used by Eyring [17] and Bhatnagar et al. Therefore, we can write

$$\frac{1}{\eta_{sp}} = \frac{1}{(\eta_{rel} - 1)} = \frac{1}{e^{X_2} (\gamma/RT)[\, 1 - x_2 \, \{1 - w(p)F(y)\}]^{-1} - 1}$$

$$= \frac{1 - x_2 \, \{1 - w(p)F(y)\}}{e^{X_2} (\gamma/RT) - 1 + x_2 \, \{1 - w(p)F(y)\}}$$

$$= \frac{1 - x_2 \, \{1 - w(p)F(y)\}}{x_2 \, \{1 - w(p)F(y) + (\gamma/RT)\}} \qquad \text{(considering dilute solutions)}$$

Putting the value for x_2 according to Ref. 13:

$$\frac{1}{\eta_{sp}} = \frac{1}{9.347 \times 10^{20}(\overline{r^2})^{3/2} /M \{1 - w(p)F(y) + (\gamma/RT)\}C}$$

$$- \frac{1 - w(p)F(y)}{1 - w(p)F(y) + (\gamma/RT)}$$

or

$$\frac{C}{\eta_{sp}} = \frac{1}{9.347 \times 10^{20} (\overline{r^2})^{3/2}/M \{1 - w(p)F(y) + (\gamma/RT)\}}$$

$$- \frac{1 - w(p)F(y)}{1 - w(p)F(y) + (\gamma/RT)} C$$

or

$$C/\eta_{sp} = 1/[\eta] - kC$$

where

$$[\eta] = 9.347 \times 10^{20}(\overline{r^2})^{3/2}/M\{1 - w(p)F(y) + (\gamma/RT)\}$$

an expression exactly identical with that derived by Bhatnagar et al., and

$$k = \frac{1 - w(p)F(y)}{1 - W(p)F(y) + (\gamma/RT)}$$

Now,

$$\frac{1}{[\eta]} = \frac{1}{9.347 \times 10^{20}(\overline{r^2})^{3/2}/M\{1 - w(p)F(y) + (\gamma/RT)\}}$$

$$= \frac{A}{1 - w(p)F(y) + (\gamma/RT)}$$

where

$$A = \frac{1}{9.347 \times 10^{20}(\overline{r^2})^{3/2}/M}$$

or

$$\frac{1}{[\eta]} = A\left[\frac{1 - w(p)F(y)}{1 - w(p)F(y) + (\gamma/RT)} + \frac{w(p)F(y)}{1 - w(p)F(y) + (\gamma/RT)}\right]$$

$$= Ak + B + \cdots \tag{8}$$

where

$$B = \frac{Aw(p)F(y)}{1 - w(p)F(y) + (\gamma/RT)}$$

TABLE 1. Values of $(\bar{r}_0{}^2/M)^{1/2}$ Calculated by Using Eq. (10)

Polymer	Molecular weight $\times 10^4$	$(\bar{r}_0{}^2/M)^{1/2}$ $\times 10^{11}$	$C_0 \times 10^2$ (g/mL)
Poly(methyl acrylate)	151.3	107.4	7.01
Poly(ethyl acrylate)	54	785	3.01
Poly(butyl acrylate)	227.5	623.6	2.926
Poly(acrylonitrile)	5.5	1199	2.6315
Poly(vinyl pyrolidone)	5.36	2253	4.04

Though the expression for B seems to be solvent-dependent, the numerical value of B ($B \approx 0$) is very small due to the extremely small value of $w(p)F(y)$ in dilute solution. It is quite reasonable to take B as a constant.

According to Eq. (8), a plot of the slope of $1/[\eta]$ against k should give the value of A, which is the cross-over point concentration. By comparing Eqs. (6) and (8) it will be observed that

$$C_x = \text{Cross-over point concentration} = A$$

$$= [9.347 \times 10^{20} (\bar{r}^2)^{3/2}/M]^{-1} \qquad (9)$$

If we assume that $(\bar{r}^2)^{1/2} = (r_0{}^2)^{1/2}$ becomes the unperturbed root-mean-square end-to-end distance, then

$$(\bar{r}_0{}^2)^{1/2} = 2.204 \times 10^{-8}(M/C_0)^{1/3} \qquad (10)$$

where C_0 = cross-over concentration in g/mL = $0.01C_x$

This equation is strikingly similar to Eq. (11) derived by Cornet [18] when considering a uniform segment density of polymer molecules at the critical concentration, C_{cr}:

$$(\bar{r}_0{}^2)^{1/2} = 2.84 \times 10^{-8}(M/C_{cr})^{1/3} \qquad (11)$$

The values of $(\bar{r}_0{}^2/M)^{1/2}$ calculated by using Eq. (11) for polymethyl acrylate, polyethyl acrylate, polybutyl acrylate, polyvinyl pyrrolidone, and polyacrylonitrile are described in Table 1.

DISCUSSION

In deriving Eq. (10) it has been assumed that $(\bar{r}^2)^{1/2}$ becomes $(\bar{r_0}^2)^{1/2}$ at the cross-over point concentration. The validity of such an assumption is supported by the fact that at this unique concentration the viscosity parameters are independent of the solvents. It has been shown theoretically by many workers [18-23] that the expansion factor, α, decreases with increasing concentrations of polymer solutions. Therefore, there is a possibility that at a certain concentration the expansion parameter attains a value of unity corresponding to the unperturbed dimension of polymer molecules. Maron et al. [23, 24] have shown that the total effective volume of a polymer molecule in a solution at higher concentrations is independent of the solvent used and that the molecules attain their unperturbed dimension at such concentrations. The values of C_x obtained for different polymers with the help of Eq. (6) are in the higher concentration range comparable to the values of C_{cr} obtained by Cornet [25].

Determination of unperturbed dimensions by the θ-temperature method is not popular in view of the fact that the determination of the θ-temperature in a convenient range of a polymer-solvent system is rather cumbersome. It has been shown by Cornet [25] and Burchard [26] that it is almost impossible to determine the unperturbed dimensions from experimentally determined perturbed values. In view of these facts, our expression as well as Cornet's expression for the determination of an unperturbed dimension, $(\bar{r_0}^2)^{1/2}$, appears to be quite promising.

ACKNOWLEDGMENT

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