

DETERMINATION OF CRITERIA OF POLYMER POLYDISPERSITY BASED ON THE FREE DIFFUSION MEASUREMENTS WITH A POLARIZATION INTERFEROMETER

B. PORSCH and M. KUBÍN

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6*

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The procedure of evaluation of the experimental data obtained with a polarization interferometer and yielding, for a polydisperse polymer, three different average values of the diffusion coefficient, has been extended to include the calculation of another, fourth in order, average value of this coefficient. Deviation graphs for the polarization interferometer have been defined, and conditions for the optimum use of the suggested procedure have been determined. Sucrose, biphenyl and a standard polystyrene fraction were used as monodisperse compounds to check up the method. Criteria of polydispersity of unfractionated samples of polyisobutylene and two different polystyrenes were determined.

Measurements of the free diffusion of polymers in dilute solutions can yield — besides parameters characterizing the hydrodynamic behaviour of the polymer-solvent system — also some useful information about the polydispersity of the polymer. A number of interferometers¹⁻⁴ have been used for this purpose; a polarization interferometer suggested by Bryngdahl⁵⁻⁸ was found to be very suitable.

The apparatus allows to compare two beams separated by a small distance b (the distance is a constant of the apparatus and depends only on the choice of the optical elements), passing through the diffusion cell at two points where the instantaneous refractive index has values n_1 and n_2 ; the corresponding interferometric conditions are given by^{5,6}

$$\frac{n_2 - n_1}{b} = \left(\frac{\Delta n}{\Delta x} \right)_{\Delta x=b} = j \frac{\lambda}{2bl} = a_j \approx \frac{dn}{dx}; \quad (I)$$

here, λ is the wavelength of the light used, l is the thickness of the cell, and j is a natural number. With respect to the bell-shaped gradient curve it follows from Eq. (I) that one pair of interference fringes (maximum or minimum) is formed for each j at a point where dn/dx is j times the constant of the apparatus $\lambda/2bl$. The substitution of a derivative for the difference quotient $(\Delta n/\Delta x)_{\Delta x=b}$ is permissible after a certain time since the beginning of the experiment, when the deviations between $(\Delta n/\Delta x)_{\Delta x=b}$ and dn/dx can be neglected^{5,9}.

In the present paper, an earlier procedure⁸ has been extended which enabled three different average values of the diffusion coefficient D to be determined from the data obtained with Bryngdahl's interferometer. For this apparatus, fringe deviation

graphs have been defined which can be used as a basis for a fourth average value of D ; conditions for the optimum treatment of the experimental data have also been described. Sucrose, biphenyl and a standard monodisperse polystyrene were used to check up the method; the ratios of different average values of the diffusion coefficient were used as criteria of polydispersity for polyisobutylene and two different polystyrene samples.

THEORETICAL

For the free diffusion of a polydisperse polymer, the refractive index gradient is given by¹⁰

$$\frac{dn}{dx} = \frac{\Delta n_0}{2\sqrt{(\pi t)}} \int_0^{\infty} f(D) D^{-1/2} \exp(-x^2/4Dt) dD; \quad (2)$$

here, Δn_0 is the initial difference between the refractive indices of the two solutions, D is the diffusion coefficient, x is the coordinate in the cell, t is time and $f(D)$ is the distribution function of the diffusion coefficients, so defined that the product $f(D) dD$ gives the weight fraction of the polymer having the diffusion coefficient between D and $D + dD$. If $\exp(-x^2/4Dt)$ is expanded into a series, we obtain from (2)

$$\frac{dn}{dx} = \frac{\Delta n_0}{2\sqrt{(\pi t)}} \mu_{-\frac{1}{2}} \left[1 - \frac{\vartheta^2 \mu_{-\frac{3}{2}}}{\mu_{-\frac{1}{2}}} + \frac{\vartheta^4 \mu_{-\frac{5}{2}}}{2 \mu_{-\frac{1}{2}}} - \frac{\vartheta^6 \mu_{-\frac{7}{2}}}{6 \mu_{-\frac{1}{2}}} + \dots \right], \quad (3)$$

where $\vartheta^2 = x^2/4t$. The individual moments μ_r of the distribution $f(D)$ are defined by

$$\mu_r = \int_0^{\infty} D^r f(D) dD. \quad (3a)$$

In our previous papers^{7,9} the above equation was used to derive the approximate relationship

$$\ln(t/t_0) = \tau = \ln [(\Delta n_0)^2/4\pi a_j^2 t_0 D_1] - (\eta/8D_2); \quad (4)$$

t_0 is the chosen time unit. From the slope and intercept of the linear part of the dependence described by (4) between the experimentally available quantities τ and η , two average values of the diffusion coefficient, D_1 and D_2 , can be determined. The variable η is given by the expression

$$\eta = (2x)^2/t, \quad (4a)$$

where $(2x)$ is the distance between the two fringes of a given pair at a given t . By

comparing the definitions of ϑ and η there follows a relationship $\vartheta^2 = \eta/16$ between these experimentally available quantities.

We shall further use Eq. (3) as a basis for a more general treatment of experimental data obtained with the polarization interferometer, which will allow to check up the limits of validity of approximations employed in the derivation of Eq. (4). At the same time, this procedure will serve as a basis for defining the fringe deviation graphs.

Let us define a series of average diffusion coefficients^{1,2} as follows: $D_1 = (\mu_{-1/2})^{-2}$, $D_2 = \mu_{-1/2}/\mu_{-3/2}$, $D_3 = \mu_{-3/2}/\mu_{-5/2} \dots$ etc. (the definition of further average values is evident). The fractions of moments in brackets in Eq. (3) can be expressed in terms of these average diffusion coefficients. On rearrangement, we obtain

$$\frac{dn}{dx} = \frac{\Delta n_0}{2\sqrt{(\pi D_1 t)}} \left[1 - \frac{\vartheta^2}{D_2} + \frac{\vartheta^4}{2D_2 D_3} - \frac{\vartheta^6}{6D_2 D_3 D_4} + \dots + \frac{(-1)^i \vartheta^{2i}}{i! \prod_{j=2}^i D_j} + \dots \right]. \quad (5)$$

Equation (5) can be further rearranged, if we rewrite the fractions $(1/D_2 \dots D_i)$ according to

$$\frac{1}{D_2 \dots D_i} = \frac{1}{D_2^{i-1}} + \frac{D_2^{i-2} - (D_3 \dots D_i)}{D_2^{i-1}(D_3 \dots D_i)}, \quad (5a)$$

so that the result will be

$$\begin{aligned} \frac{dn}{dx} = \frac{\Delta n_0}{2\sqrt{(\pi D_1 t)}} & \left[\left(1 - \frac{\vartheta^2}{D_2} + \frac{\vartheta^4}{2D_2^2} - \frac{\vartheta^6}{6D_2^3} + \dots \right) + \right. \\ & \left. + \left(\frac{\vartheta^4}{2} \frac{D_2 - D_3}{D_2^2 D_3} - \frac{\vartheta^6}{6} \frac{D_2^2 - D_3 D_4}{D_2^3 D_3 D_4} + \dots \right) \right]. \quad (6) \end{aligned}$$

However, the first expression in brackets in Eq. (6) represents the series expansion of the function $\exp(-\vartheta^2/D_2)$; it can be seen, therefore, that Eq. (4) can be obtained from the exact relationship (6) after raising to the second power, taking logarithms and substituting $\vartheta^2 = \eta/16$, if the second term in brackets is neglected. This term describes the curvature of the experimental relationship $\tau = f(\eta)$, which is due to the polydispersity of the sample. To determine D_1 and D_2 from (6), we must find a condition which will allow us to choose such a region of the η -values in which the deviations from the straight line (4) are negligible within limits of accuracy of the apparatus. This is satisfied by the requirement that the deviations should be smaller than one per cent, which can be written as the inequality

$$\exp\left(-\frac{\vartheta^2}{D_2}\right) \cong 10^2 \left[\frac{\vartheta^4}{2} \frac{D_2 - D_3}{D_2^2 D_3} - \frac{\vartheta^6}{6} \frac{D_2^2 - D_3 D_4}{D_2^3 D_3 D_4} + \frac{\vartheta^8}{24} \frac{D_2^3 - D_3 D_4 D_5}{D_2^4 D_3 D_4 D_5} - \dots \right]. \quad (7)$$

From Eq. (6), another average diffusion coefficient D_3 can also be determined. Similarly to other authors^{3,11,12}, we can define for the polarization interferometer the fringe deviation graphs, which express the deviations of the observed gradient curve $(dn/dx)_{\text{exp}}$ from an ideal course $(dn/dx)_{\text{id}}$, corresponding to a monodisperse compound having the same Δn_0 and the same diffusion coefficient D_1 . In our case it is of more advantage to define the deviation with respect to a hypothetical compound which has the same Δn_0 , D_1 and D_2 as the diffusing polymer, and for which it also holds $D_2 = D_3 = \dots = D_1$.

Substituting $\vartheta = x/2 \sqrt{t}$ we obtain from Eq. (6) for the deviation Ω

$$\Omega = \left(\frac{dn}{d\vartheta}\right)_{\text{id}} - \left(\frac{dn}{d\vartheta}\right)_{\text{exp}} = -\frac{\Delta n_0}{\sqrt{(\pi D_1)}} \left(\frac{\vartheta^4}{2} \frac{D_2 - D_3}{D_2^2 D_3} - \frac{\vartheta^6}{6} \frac{D_2^2 - D_3 D_4}{D_2^3 D_3 D_4} + \dots \right) \quad (8)$$

At the same time, we have arrived from the values dn/dx to the generalized gradient curve^{8,10} $dn/d\vartheta$. It is easy to demonstrate that for the maximum ordinate H_m of this generalized curve it holds $H_m = \Delta n_0 / (\pi D_1)^{1/2}$; on substitution into Eq. (8) we obtain the result

$$\Omega = -H_m \left[\frac{\vartheta^4}{2} \frac{D_2 - D_3}{D_2^2 D_3} - \frac{\vartheta^6}{6} \frac{D_2^2 - D_3 D_4}{D_2^3 D_3 D_4} + \dots \right] \quad (9)$$

Since Δn_0 , D_1 (and thus also H_m) and D_2 can be determined by a procedure described earlier⁸, it is possible to calculate $(dn/d\vartheta)_{\text{id}} = [\Delta n_0 / \sqrt{(\pi D_1)}] \exp(-\vartheta^2/D_2)$. The quantity $(dn/d\vartheta)_{\text{exp}}$ is experimentally available^{8,10}; the diffusion coefficient D_3 can then be determined from the initial slope of the graph $\Omega = f(\vartheta^4)$.

EXPERIMENTAL

Biphenyl, polyisobutylene (reprecipitated Oppanol B-15), polystyrene BASF III D and the solvents benzene, heptane and toluene were the same as in our previous paper⁸. The unfractionated polystyrene Z ($M_w = 145\,000$) was prepared by radical polymerization. The monodisperse polystyrene (Pressure Chemical Co.) had $M_w = 160\,000$, $M_w/M_n < 1.08$. Sucrose was of pharmaceutical purity (Spofa, Prague). The apparatus, diffusion cell, thermostat, preparation of samples and measuring procedure have been described earlier^{8,9,13}. All measurements were carried out at 25°C; short-time temperature oscillations in the cell⁹ were of the order of 10^{-4} °C.

RESULTS AND DISCUSSION

In order to determine, with the required accuracy, the region of η for which Eq. (4) is valid, the inequality (7) has to be solved. To obtain a solution of this inequality with an adequate accuracy, it suffices to consider the first three terms in the brackets; moreover, a simplifying assumption $D_1/D_2 = D_2/D_3 = D_3/D_4$ was also used. To which extent this assumption is justified can be seen from Fig. 1 which represents

the dependences between the individual ratios D_i/D_{i+1} and the polydispersity index M_w/M_n calculated under the assumption that the shape of the molecular weight distribution is described either by the Schulz-Zimm¹⁴⁻¹⁶ or by the generalized logarithmic-normal^{16,17} function. It can easily be shown that in the latter case the simple relationship $D_2/D_3 = D_3/D_4 = \dots = D_i/D_{i+1}$ is valid. The Figure shows that the assumption $D_1/D_2 \approx D_i/D_{i+1}$ is well fulfilled for the Schulz-Zimm distribution. Although the values D_i/D_{i+1} obtained for the generalized logarithmic-normal distribution are larger than D_1/D_2 , the differences still lie within limits of a sufficient approximation, especially if we bear in mind that the right-hand side of the inequality (7) will participate only by one per cent in the calculations of D_1 and D_2 . Fig. 2 shows the resulting dependences between D_1/D_2 and the ratio (η_c/D_2) (it holds again $\eta = 169^2$) obtained by solving inequality (7) under the given assumptions for 1% and 2% deviation. The graph determines unambiguously the maximum admissible value η_c of the experimentally available quantity η in dependence on the diffusion coefficient D_2 and the width of molecular weight distribution characterized in our case by the ratio D_1/D_2 . This general analysis also shows that an analogous condition given in our paper⁷ is too strict for the values of D_1/D_2 commonly encountered.

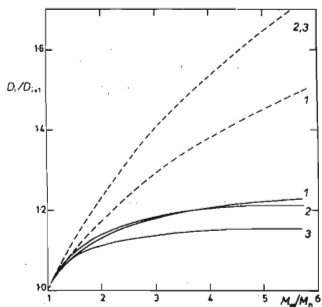


FIG. 1

Dependence between D_i/D_{i+1} and the Index of Polydispersity M_w/M_n for the Selected Molecular Weight Distribution Functions ----- Generalized logarithmic-normal distribution, ——— Schulz-Zimm distribution; 1 D_1/D_2 , 2 D_2/D_3 , 3 D_3/D_4 ; the value $\alpha = 0.556$ from equation $D = K \cdot M^{-\alpha}$ was used in the calculation.

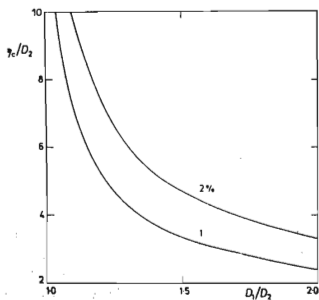


FIG. 2

Dependence of η_c/D_2 on D_1/D_2 for 1% and 2% Deviation from the Linear Course of the Graph $\tau = f(\eta)$

The experimental results are summarized in Table I. The procedure of calculation of Δn_0 , D_1 and $D_0 = [\int_0^\infty D^{1/2} f(D) dD]^2$ has been described previously⁸. The graph in Fig. 2 was used for the calculation of D_2 ; this graph allows to determine the region of η in which the dependence $\tau = f(\eta)$ is linear, independently of the data scatter, thus making the best use of the largest possible number of experimental points so as to achieve the maximum accuracy of the calculated values of D_1 and D_2 . The procedure is as follows: first, a reasonable value of D_1/D_2 is chosen; D_2 is determined approximately⁷, and the maximum admissible η_c is found from Fig. 2. D_2 is then calculated from the linear part of the dependence $\tau = f(\eta)$ thus limited, and Δn_0 , D_1 and D_0 are calculated from the generalized curve. For the ratio D_1/D_2 determined by this procedure, the corresponding η_c is again found, compared with the preceding value, and the calculation is repeated if necessary (Fig. 3).

The values of D_3 were determined from the initial slope of the deviation graphs according to Eq. (9). A direct comparison of the individual systems under investigation is enabled by Fig. 4: the plot of the reduced quantity Ω/H_m against the reduced variable η^4/D_2^2 is only slightly affected by numerical values of H_m and D_2 (Eq. (9)). These reduced deviation graphs of biphenyl and sucrose are a direct measure of the experimental error; therefore, the values of D_3 have not been calculated here. The

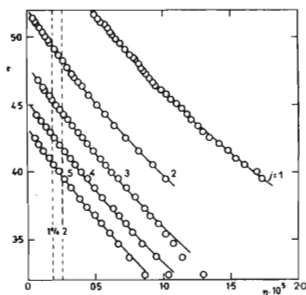


FIG. 3

Curves $\tau = f(\eta)$ for Five Pairs of the Interference Fringes

For the individual curves, orders of the interference fringes (j) are given; the region of 1% and 2% deviation from a straight line dependence determined according to Fig. 2 is indicated by the dashed lines.

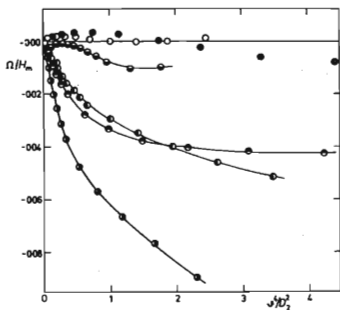


FIG. 4

Reduced Deviation Graphs of the Individual Systems

○ Biphenyl, ● sucrose, ⊙ monodisperse polystyrene, ⊙ unfractionated polystyrene Z, ⊙ unfractionated polystyrene D, ⊙ polyisobutylene.

curve for a standard polystyrene fraction in Fig. 4, from which the ratio $D_2/D_3 \approx 1.01$ can be found, indicates the sensitivity of the deviation graphs to small changes in the polydispersity indices. At the same time, it is possible to compare both samples of polydisperse polystyrenes with polyisobutylene. It seems that the molecular weight distribution of polyisobutylene is of a different type than that of both polystyrenes, which exhibit much lower D_2/D_3 values at identical or even higher D_1/D_2 (Table I).

It can be seen from Table I that the largest scatter of experimental values is found with D_0 . This can be understood if we bear in mind that in the calculation of D_0 the lower part ("tail") of the generalized gradient curve plays a considerable role, and that this "tail" has to be determined partly by approximation⁸. On the other hand, to calculate D_3 , neither the points for small experimental times, which are most seriously affected by the uncertainty in the determination¹³ of the zero-time correction (they correspond to the above-mentioned "tail") nor the knowledge

TABLE I

Average Diffusion Coefficients (D_i) of Biphenyl in Benzene, Sucrose in Water, Monodisperse Polystyrene (M) in Toluene, Polyisobutylene in Heptane and Two Unfractionated Polystyrenes (D and Z) in Toluene at 25°C

c_2^0 Initial concentration of solution.

Compound	c_2^0 g/dl	D_0	D_1	D_2	D_3	D_1/D_2	D_2/D_3	D_0/D_1
		$10^{-7} \text{ cm}^2/\text{s}$						
Biphenyl	0.098	156.0	155.0	156.0	—	0.993	~1	1.006
	0.100	154.0	155.0	155.3	—	0.998	~1	0.993
	0.103	153.5	154.8	154.5	—	1.002	~1	0.992
Sucrose	0.100	54.5	53.0	52.4	—	1.01	~1	1.03
	0.092	52.0	51.4	52.2	—	0.99	~1	1.01
	0.055	53.7	52.7	51.6	—	1.02	~1	1.02
Polystyrene M	0.079	4.01	3.94	3.92	3.88	1.00	1.01	1.02
Polyisobutylene	0.295 ^a	9.12	7.81	6.73	6.06	1.16	1.11	1.17
	0.106	8.86	7.50	6.14	5.34	1.22	1.15	1.18
	0.055	8.59	7.26	5.87	4.73	1.24	1.24	1.18
	0.053	8.15	7.20	5.99	4.87	1.20	1.23	1.13
Polystyrene Z	0.044	(13.1)	(8.20)	5.93	4.94	—	1.20	—
	0.078	5.68	4.60	3.91	3.62	1.18	1.08	1.23
	0.119	5.32	4.47	3.71	3.47	1.18	1.07	1.18
Polystyrene D	0.084	5.12	4.54	3.93	3.60	1.16	1.09	1.13
	0.079	5.76	4.13	3.17	2.91	1.30	1.09	1.39
	0.119	4.65	3.78	2.95	2.61	1.28	1.13	1.23

^a Concentration of the upper layer c_1^0 was 0.236 g/dl.

of Δn_0 is needed. It is sufficient to know the maximum ordinate of the generalized curve and the points in its vicinity which can always be determined with good accuracy. This finding is documented by an experiment with polyisobutylene (see Table I), where the initial concentration $\Delta c_0 = 0.044$ g/dl was already too low for an accurate determination of D_0 and D_1 ; however, it was still possible here to determine the diffusion coefficient D_3 which is in satisfactory agreement with D_3 measured at higher Δc_0 . Let us also mention that in the case of ratios D_2/D_3 corresponding to higher concentrations measured (0.295 and 0.106 g/dl), the concentration dependence is somewhat more pronounced than in the case of D_1/D_2 (or D_1 and D_2 alone). For these reasons, and also with respect to the fact that for the determination of D_0 it is necessary to assume a certain shape⁸ of distribution of diffusion coefficients $f(D)$, D_3 appears to be more advantageous also for the three-parameter distribution function, suggested¹⁶ for an approximate determination of the distribution of diffusion coefficients based on the free diffusion measurements.

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