European Polymer Journal, 1970, Vol. 6, pp. 97–105. Pergamon Press. Printed in England.

ESTIMATION OF POLYMER POLYDISPERSITY BY DIFFUSION MEASUREMENTS AT LOW CONCENTRATION*

M. KUBÍN and B. PORSCH

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6—Petriny, Czechoslovakia

Abstract—A method is described for calculating, from measurement of free diffusion by means of the wave front shearing interferometer, three different average diffusion coefficients which can characterize the polydispersity of a sample. The method was tested by measurements on a monodisperse sample, viz. biphenyl. The criteria of polydispersity were determined for two non-fractionated polymers, polyisobutylene and polystyrene. A comparison of calculated and measured number and weight average mol. wts. illustrates the scope of the method.

INTRODUCTION

SINCE Gralén's original proposal,(1) several attempts(2–4) have been made to estimate the polydispersity of polymers from measurements of free diffusion in dilute solutions, but the low accuracy of experiments has hindered a wider use of this technique. More recently, however, an interesting modification of Jamin's interferometer was proposed by Daune *et al.*,(5–7) enabling at least two different averages of diffusion coefficient to be determined, which in turn can serve for characterization of polymer polydispersity. Cussler(8) determined the same averages from the data of Gouy's interferometer, and Sundelöf(9) studied the possibility of calculating by a convolution procedure the distribution of diffusion coefficients from data obtained with the Rayleigh interferometer.

In 1957, Bryngdahl(10, 11) constructed the wave front shearing interferometer, which has since proved to be a precise and sensitive tool for studying free diffusion in the region of very low initial concentration differences.(12–14) In the present paper a new method of handling the experimental data obtained by measuring free diffusion of polydisperse samples with this apparatus is described. This procedure enables us to determine with satisfactory precision three different, well-defined averages of diffusion coefficient. The possibilities of the method are illustrated with experimental data on free diffusion measurements on monodisperse and polydisperse samples.

THEORETICAL

The diffusion cell is placed in a beam of parallel light; two rays, separated in the cell by a small distance b (given by the choice of optical elements), are compared by means of the Savart double plate(10, 11) and allowed to interfere. If we denote by n_1 and n_2 the values of refractive index at the corresponding points inside the cell, the condition for interference of the two beams is(10)

$$(n_1 - n_2)l = \Delta n\, l = j\lambda/2, \tag{1}$$

where l is the thickness of the cell, λ is the wave length of the monochromatic light

---

* Paper presented at the Third Prague Microsymposium on Distribution Analysis and Fractionation of Polymers, 23–26 September 1968.

employed and j, a natural number, determines the order of the interference fringe. Dividing Eqn. (1) by the product bl, we obtain

$$\frac{\Delta n}{b} = \left(\frac{\Delta n}{\Delta x}\right)_{\Delta x = b} \simeq \frac{\mathrm{d}n}{\mathrm{d}x} = j\frac{\lambda}{2bl} = a_j. \tag{2}$$

From Eqn. (2) it follows that the j-th fringe is formed at the point where the refractive index gradient ($\mathrm{d}n/\mathrm{d}x$) has a given value, determined by the parameter of the instrument $a_j = j(\lambda/2bl)$. Due to the bell-shaped gradient curve in free diffusion, pairs of fringes are always formed; the distance ($2x$) between the two fringes of a given pair is measured on a photograph, taken at a time t.

For free diffusion of a polydisperse polymer, the refractive index gradient is given by the equation(15)

$$\frac{\mathrm{d}n}{\mathrm{d}x} = \frac{\Delta n_0}{2\sqrt{(\pi t)}} \int_0^\infty \frac{f(D)}{\sqrt{D}} \exp\left(-\frac{x^2}{4Dt}\right)\mathrm{d}D \tag{3}$$

where Δn_0 is the initial difference in refractive index between the two solutions, and $f(D)$, the distribution of diffusion coefficients, characterizes the polydispersity of the sample and is defined in such a way that the product $f(D)\mathrm{d}D$ designates the weight fraction of the polymer with diffusion coefficient lying between D and $D + \mathrm{d}D$.

In a previous communication,(14) a procedure based on Eqn. (3) was derived for the evaluation of experimental data for polydisperse samples; it was shown that from the slope and intercept of the linear dependence (valid for sufficiently high values of t) between the two variables $\tau = \ln(t)$ and $\eta = (2x)^2/t$,

$$\tau = \ln\left[\frac{(\Delta n_0)^2}{4a_j^2 D_1}\right] - \frac{\eta}{8D_2}, \tag{4}$$

two average diffusion coefficients D_1 and D_2 can be determined. (For evaluation of D_1, the quantity Δn_0 had to be known from an independent measurement.) These quantities are defined by the following expressions:

$$D_1 = \left\{\int_0^\infty D^{-1/2} f(D)\mathrm{d}D\right\}^{-2}, \tag{5}$$

$$D_2 = \frac{\int_0^\infty D^{-1/2} f(D)\mathrm{d}D}{\int_0^\infty D^{-3/2} f(D)\mathrm{d}D}. \tag{6}$$

The average D_1 is identical with the diffusion coefficient D_A, determined by the "height–area" method. By applying the Hölder inequality to the definition of D_1 and D_2, it can be shown that the relation $D_1 \geq D_2$ must hold; the sign of equality is valid for monodisperse samples.

There exists another possibility for obtaining a set of average diffusion coefficients for a polydisperse sample together with the initial refractive index difference Δn_0 from free diffusion measurements. It is well known(9, 16) that the introduction of a new variable

$$\vartheta = x/2\sqrt{t} \tag{7}$$

leads for free diffusion to time-independent diagrams, which enable us to collect all information from different exposures on one master curve. Thus, the time-independent (generalized) gradient curve is the functional relation between the derivative $(\mathrm{d}n/\mathrm{d}\vartheta)$ and ϑ. For diffusion coefficient independent of concentration (or at sufficiently low initial concentration difference), the generalized gradient curve is symmetrical about the origin and only positive values of ϑ need to be considered. The semi-moments μ_r' of the generalized gradient curve can then be defined as

$$\mu_r' = \int\limits_0^\infty \vartheta^r \frac{\mathrm{d}n}{\mathrm{d}\vartheta}\,\mathrm{d}\vartheta. \tag{8}$$

If we introduce ϑ into Eqn. (3), insert the resulting expression for $(\mathrm{d}n/\mathrm{d}\vartheta)$ into Eqn. (8) and perform the integration over ϑ, we obtain the formula

$$\mu_r' = \frac{\Delta n_0}{2\sqrt{\pi}}\,\Gamma\left(\frac{r+1}{2}\right)\int\limits_0^\infty D^{r/2} f(D)\,\mathrm{d}D \tag{9}$$

which enables us to calculate from the experimentally available quantities μ_r' a set of diffusion averages based on the integrals occurring on the right-hand side of Eqn. (9).

For the wave front shearing interferometer the construction of the generalized gradient curve is very simple:(15) The following equation,

$$\frac{\mathrm{d}n}{\mathrm{d}\vartheta} = 2\sqrt{t}\,\frac{\mathrm{d}n}{\mathrm{d}x} = 2a_j\sqrt{t}, \tag{10}$$

which follows from Eqn. (2) and from the fact that the refractive index gradient is equal to the constant a_j, shows that it is only necessary to plot $\sqrt{t}$, multiplied for the j-th pair by $2a_j$, against ϑ. The experimental determination of b, necessary for the calculation of a_j, has been described elsewhere.(13)

To ensure that all points from the individual fringe pairs fall on the same line, the Savart double plate must be very exactly adjusted to be perpendicular to the incident beam. However, it is possible to calculate a correction for imperfect adjustment of the double plate directly from the experimental data. The maladjusted Savart plate introduces an additional optical path difference γ to the two emerging wave fronts,(11) so that the parameter a_j is now given by

$$a_j = \frac{j\dfrac{\lambda}{2} + \gamma}{bl}\,. \tag{11}$$

To determine the correction factor γ, we note that the diffusion average D_1, occurring in the intercept of the straight line (4), must be the same for all fringe pairs. Hence, putting

$$A_j = \frac{(\Delta n_0)^2}{4a_j^2 D_1}$$

determined from the intercept of the j-th pair, we have for two successive pairs

$$\frac{a_{j+1}}{a_j} = \sqrt{\left(\frac{A_j}{A_{j+1}}\right)} \tag{12}$$

and

$$\gamma = \frac{\lambda}{2}\left[\frac{1}{\sqrt{\left(\frac{A_j}{A_{j+1}}\right)} - 1} - j\right]. \tag{13}$$

Comparison of Figs. 1 (a and b) illustrates the effect of applying the correction γ.

Due to the fact that the early exposures (with $t < 4\,\Delta t$ approximately, where Δt is the zero time correction) must be disregarded, because the shape of the gradient curve is for low values of t influenced by the unavoidable imperfection of the initially formed boundary, the outermost part (corresponding to the earliest exposures) of the generalized gradient curve is never defined.

This can be obviated in the following way. Let us assume that the distribution $f(D)$ can be approximated by the function

$$f(D) = \frac{q^{p-1}}{\Gamma(p-1)} D^{-p} \exp\left[-\frac{q}{D}\right], \tag{14}$$

where q and p are two adjustable parameters. It is then possible to derive an explicit expression for $(\mathrm{d}n/\mathrm{d}\vartheta)$ as a function of ϑ by inserting from (14) into the equation

$$\frac{\mathrm{d}n}{\mathrm{d}\vartheta} = \frac{\Delta n_0}{\sqrt{\pi}} \int_0^\infty \exp\left\{-\frac{\vartheta^2}{D}\right\} \frac{f(D)}{\sqrt{D}}\,\mathrm{d}D, \tag{15}$$

which is in effect Eqn. (3) rewritten in terms of ϑ. The result then reads

$$\frac{\mathrm{d}n}{\mathrm{d}\vartheta} = \frac{\Delta n_0}{\sqrt{\pi}} q^{p-1} \frac{\Gamma\left(p - \frac{1}{2}\right)}{\Gamma(p-1)} \frac{1}{(\vartheta^2 + q)^{p-1/2}}. \tag{16}$$

This expression can serve for approximating the "tail" of the generalized gradient curve for the calculation of its moments, if the two parameters p and q are first adjusted in such a way that the function (16) approaches the experimental points as closely as possible. The full curve in Fig. 1b was calculated in this way. The uncertainty introduced into the calculated μ_r' by this approximation is obviously the lower, the smaller is the area under the approximate "tail" in comparison with the area under the experimental points (i.e., the higher is the initial concentration difference between the two solutions in the diffusion cell), and the lower is r. This condition limits to a certain

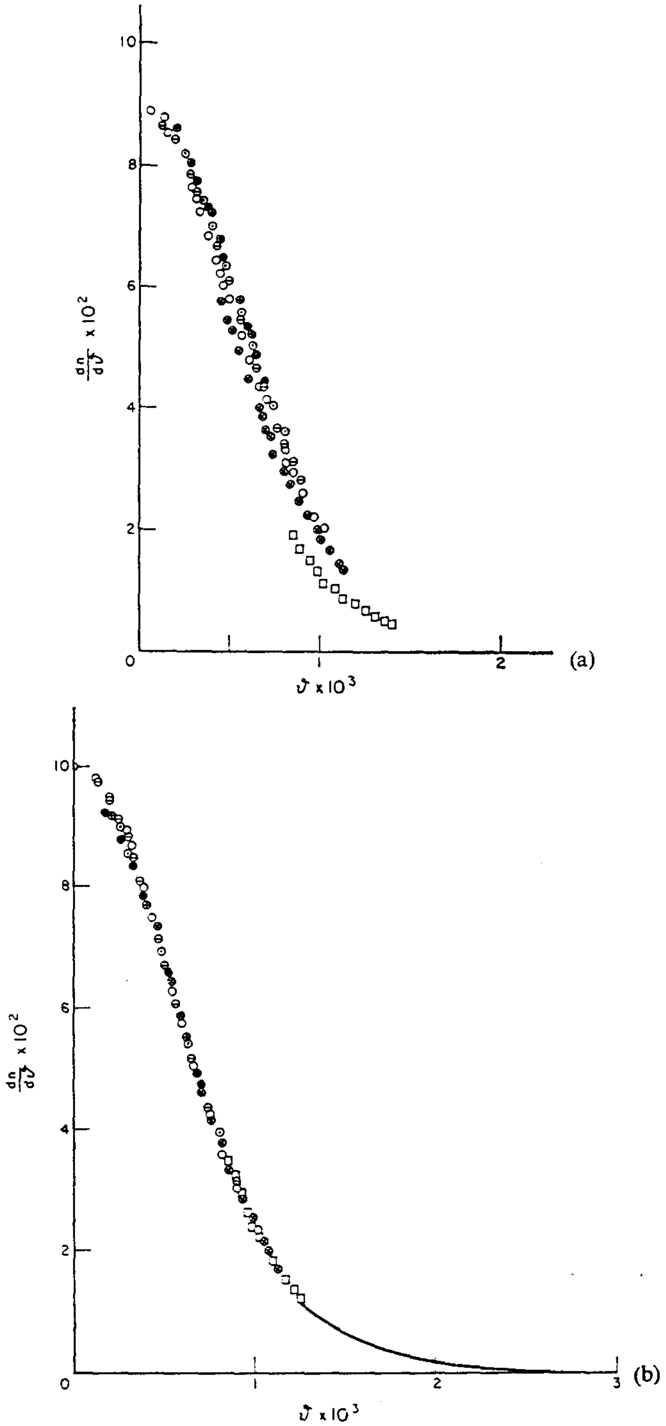

FIG. 1. Generalized gradient curve calculated from seven fringe pairs for diffusion of a non-fractionated polyisobutylene in *n*-heptane (experiment PIB 11) at 25°: (a) without correction for imperfect adjustment of Savart double plate (b) with correction γ calculated from fringe pairs 3 and 4. (Different points originate from different fringe pairs.)

extent the possibility of the instrument to measure diffusion at extremely low concentration differences, which would otherwise be feasible if only D_2 were required. However, in view of the disturbing effect of the concentration dependence of D, it is necessary to keep the initial concentration difference as low as possible, and we therefore limit ourselves to the calculation of the first element from the set of average diffusion coefficients, defined on the basis of formula (9). This quantity, D_0, can be determined from the zeroth and first moments of the generalized gradient curve by means of the expression

$$D_0 = \left[\int_0^\infty D^{1/2} f(D) \mathrm{d}D\right]^2 = \pi\,(\mu_1'/\mu_0')^2, \tag{17}$$

as obviously

$$\mu_0' = \Delta n_0/2. \tag{18}$$

The validity of $D_0 \geq D_1$ can be again proved by applying the Hölder inequality to the definition of the two averages.

EXPERIMENTAL

Apparatus

The design of our instrument, the diffusion cell and the measuring procedure were described earlier.(13) The interference patterns were registered photographically by means of an automatic camera of our own construction, controlled by a programmed timing device; 45–55 exposures were taken during each experiment. ORWO Spectral Platten, type WO 1 Gelb Rapid or WO 3 Gelb Extrahart were employed, developed in ORWO MH-28 developer, diluted in the ratio 1:4.

Materials

Zone-refined biphenyl was the same as in our previous work.(13)

Polyisobutylene was a commercial sample Oppanol B-15, reprecipitated (twice) by acetone from a benzene solution in order to remove the low-mol. wt. additives.

Polystyrene (Polystyrol III D, BASF) was used as obtained.

n-heptane (A.R., ex VEB Berlin-Chemie, Adlershof, b.p. 98·5°), benzene and toluene (both A.R., ex Lachema Brno) were distilled before use.

RESULTS AND DISCUSSION

To verify experimentally the derived expressions and to check the possibilities of the method, the diffusion in three systems has been followed: biphenyl (representing a monodisperse solute) in benzene and two non-fractionated polymers with wide mol. wt. distribution, viz., polyisobutylene in *n*-heptane and polystyrene in toluene. The results are summarized in Table 1. The average diffusion coefficient D_2 was determined from the slope of the straight part of the plot τ vs. η (Eqn. 4); the quantity D_1 was calculated from the corresponding intercept, with Δn_0 given by Eqn. (18). D_0 was determined from the first moment of the generalized gradient curve according to Eqn. (17). A digital computer NE 803 was programmed to handle the calculations.

The two criteria of polydispersity (D_1/D_2 and D_0/D_1) listed in the last two columns of the Table, should be higher than or equal to unity as required by the definition of the three quantities involved. The diffusion coefficients D_0, D_1 and D_2 for the pure substance biphenyl indeed coincide. (The published values of D for this system(9, 17) are $1 \cdot 55_8 \times 10^{-5}$ and $1 \cdot 55_0 \times 10^{-5}$ cm^2 sec^{-1}, respectively.) The small deviations of the two ratios D_1/D_2 and D_0/D_1 from the theoretical value of unity indicate the

TABLE 1. VALUES OF THREE AVERAGE DIFFUSION COEFFICIENTS DETERMINED AT 25° BY POLARIZATION INTERFEROMETER FOR BIPHENYL IN BENZENE (BIPH), POLYISOBUTENE IN *n*-HEPTANE (PIB) AND POLYSTYRENE IN TOLUENE (PS)

Code	c_2*	$D_0 \times 10^7$	$D_1 \times 10^7$	$D_2 \times 10^7$	D_1/D_2	D_0/D_1
	[g dl^{-1}]		[cm^2 sec^{-1}]			
BIPh-1	0·100	155·0	154·4	156·1	0·989	1·004
BIPh-2	0·101	157·0	156·4	157·2	0·995	1·004
BIPh-3	0·050	157·9	157·7	156·2	1·009	1·001
BIPh-4	0·51	156·1	157·1	156·5	1·004	0·994
PIB-5†	0·295	9·12	7·81	6·73	1·16	1·17
PIB-11	0·106	8·86	7·50	6·14	1·22	1·18
PIB-7	0·055	8·59	7·26	5·87	1·24	1·18
PIB-12	0·053	8·15	7·20	5·99	1·20	1·13
PIB-F‡	0·0654	11·6	11·3	10·8	1·05	1·03
PS-1	0·079	5·76	4·13	3·17	1·30	1·39
PS-2	0·119	4·65	3·78	2·95	1·28	1·23

* Initial concentration of the measured solution (lower layer).

† Concentration c_1 of the upper layer was 0·236 g/dl.

‡ A rough fraction, amounting to 25 per cent of the whole polymer, approximately.

TABLE 2. COMPARISON OF WEIGHT AND NUMBER AVERAGE MOL. WTS., CALCULATED FROM DIFFUSION COEFFICIENTS BY MEANS OF EQNS. (19) AND (20), WITH EXPERIMENTAL VALUES

	$\bar{M}_n \times 10^{-3}$			$\bar{M}_w \times 10^{-3}$			$\bar{M}_w/\bar{M}_n$		
	Calc.	Osmometry	GPC	Calc.	Light scattering	GPC	Calc.	Osmometry light scattering	GPC
Polystyrene	49	74	63	227	295	289	4·6	4·0	4·6
Polyisobutylene	68	71	—	173	145	—	2·5	2·0	—

experimental error. The consistency within a single experiment is very good, the deviations being less than 0·5 per cent in most cases; the variation between experiments amounts to approximately 1 per cent.

Non-fractionated polyisobutylene was measured at different concentrations as indicated; in all cases except PIB-5 (the highest concentration), the upper layer was pure *n*-heptane. The diffusion coefficients for PIB-5 are higher than the others, indicating a slight concentration dependence. The figures in the last two columns again indicate the scatter of the results, which is somewhat higher in this region of much lower diffusion coefficients.

Four fractions, amounting to approximately 25 per cent of the whole polymer, were separated by fractional precipitation in the system benzene–methanol; the diffusion of the last one was measured. The resulting decrease in the criteria D_1/D_2 and D_0/D_1 is in accord with the expected narrower distribution of the fraction as compared with the parent polymer.

The results of experiment PS-1 are included in the Table, although the initial concentration difference was too low here (in view of the unfavourable refractive index increment for polystyrene in toluene); the diffusion coefficient D_0 is accordingly not reliable and the calculation of mol. wt. averages for polystyrene, described below, was based on the results of experiment PS-2.

Instead of characterizing the polydispersity by means of the two diffusion criteria, it is possible to go over to the more usual ratio $\bar{M}_w/\bar{M}_n$. In a previous paper(18) a new exponential function was proposed which proved to be a versatile model for approximating the distribution curves of polymers, and a graphical method was elaborated for determining its three parameters from the experimentally found average diffusion coefficients D_0, D_1 and D_2. If used to approximate the distribution function $f(D)$, it has the form

$$f(D) = \frac{|s| t^{(u+1)/s}}{\Gamma\left(\frac{u+1}{s}\right)} \cdot D^u \exp\left[-tD^s\right]. \tag{19}$$

If the coefficients K_D and α in the well-known equation

$$D = K_D M^{-\alpha} \tag{20}$$

are known, the distribution (19) can be transformed into the mol. wt. distribution $g(M)$ using the relation $g(M) = -f(D)\,(\mathrm{d}D/\mathrm{d}M)$. It is easy to show that $g(M)$ will be of the same form as (19) (only the numerical values of the three parameters s, u and t being different); from $g(M)$ the number and weight average mol. wts. $\bar{M}_n$ and $\bar{M}_w$ can be calculated and compared with experimental values. We applied this procedure to our diffusion data, using the published values K_D and α for polystyrene(19) and polyisobutylene.(14) (Note a misprint in Ref. 19: K_D should read $2{\cdot}37 \times 10^{-5}$.) The average mol. wts. calculated in this way are compared in Table 2 with experimental values, obtained from osmometry and light scattering (and, for polystyrene, also with values calculated from results of gel permeation chromatography).

In view of the various approximations involved, the agreement can be considered as fair and it will encourage our further work in this direction.

Acknowledgements—The number average mol. wts. were kindly supplied by Dr. Böhmer (Polymer Institute, Slovak Academy of Sciences), the light scattering measurements were performed by Dr. Tuzar and the GPC data are due to Dr. Spacek (both from the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences). All this help is gratefully acknowledged.

REFERENCES

(1) N. Gralén, *Kolloid Z.* **95**, 188 (1941).
(2) T. Svedberg, *J. phys. Colloid Chem.* **51**, 3 (1947).
(3) G. Meyerhoff, *Makromolek. Chem.* **12**, 45 (1954).
(4) I. Sakurada and M. Hosono, *Bull. Inst. chem. Res. Kyoto Univ.* **41**, 179 (1963).
(5) M. Daune, L. Freund and G. Scheibling, *J. Chim. phys.* **54**, 924 (1957).
(6) M. Daune and L. Freund, *J. Polym. Sci.* **23**, 115 (1957).
(7) A. Cifferi and M. Daune, *J. Polym. Sci.* **27**, 581 (1958).
(8) E. L. Cussler, Jr., *J. phys. Chem.* **69**, 1144 (1965).
(9) L.-O. Sundelöf, *Ark. Kemi,* **25**, 1 (1965).
(10) O. Bryngdahl, *Acta chem. scand.* **11**, 1017 (1957).
(11) O. Bryngdahl, *Ark. Fys.* **21**, 289 (1962).
(12) W. J. Thomas and E. McK. Nicholl, *Appl. Optics* **4**, 823 (1965).
(13) B. Porsch and M. Kubín, *Colln Czech. chem. Commun. Engl. Edn,* **33**, 1028 (1968).
(14) B. Porsch and M. Kubín, *J. Polym. Sci.* **C16**, 515 (1967).
(15) O. Bryngdahl and S. Ljunggren, *Acta chem. scand.* **16**, 2162 (1962).
(16) A. Boltzmann, *Annln. Phys.* **53**, 959 (1894).
(17) C. L. Sandquist and P. A. Lyons, *J. Am. chem. Soc.* **76**, 4641 (1954).
(18) M. Kubín, *Colln Czech. chem. Commun. Engl. Edn,* **32**, 1505 (1967).
(19) R. N. Mukherjea and P. Rempp, *J. Chim. phys.* **56**, 94 (1959).