

AN ESTIMATION OF THE POLYDISPERSITY OF TECHNICAL POLYSTYRENE FROM FREE DIFFUSION MEASUREMENTS BY MEANS OF A POLARIZATION INTERFEROMETER

B. PORSCH and M. KUBÍN

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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The possibility to estimate the polydispersity of industrial polymer samples from the diffusion data obtained by means of a polarization interferometer was checked experimentally. The method is more sensitive in the region of lower molecular weights and clearly indicates the presence of as little as a few per cent of low-molecular weight additives.

A successful determination of polymer polydispersity from free diffusion measurements requires sufficiently accurate experimental data. This condition is fulfilled by a number of interferometers used for this purpose¹⁻⁴. In addition, the polarization interferometer suggested by Bryngdahl⁵⁻⁶ allows measurements in very dilute polymer solutions, so that even in thermodynamically good solvents the effect of the concentration dependence can be neglected in most cases, and the amount of rather difficult experimental work can consequently be reduced. Recently⁷⁻⁹, we suggested for this interferometer a procedure for the evaluation of experimental data enabling four different average values of the diffusion coefficient to be determined for a polydisperse sample; they are defined by

$$D_0 = \left[\int_0^{\infty} D^{1/2} f(D) dD \right]^2, \quad (1a) \quad D_1 = \left[\int_0^{\infty} D^{-1/2} f(D) dD \right]^{-2}, \quad (1b)$$

$$D_2 = \frac{\int_0^{\infty} D^{-1/2} f(D) dD}{\int_0^{\infty} D^{-3/2} f(D) dD}, \quad (1c) \quad D_3 = \frac{\int_0^{\infty} D^{-3/2} f(D) dD}{\int_0^{\infty} D^{-5/2} f(D) dD}. \quad (1d)$$

Here, the weight distribution function of the diffusion coefficient $f(D)$ is defined so that the product $f(D) dD$ gives the weight fraction of a polymer with the diffusion coefficient between D and $D + dD$. The fractions D_i/D_{i+1} can be used as a measure of polydispersity, similarly to the ratios M_w/M_n and/or M_z/M_w .

In this work we attempted to use D_0 , D_1 , D_2 , and D_3 to estimate the polydispersity of technical (industrial) polymer samples. The first sample studied was a polystyrene with a very broad molecular weight distribution; it has been shown previously¹⁰ that the determination of the polydispersity index M_w/M_n by usual methods is very difficult for this polymer. This sample was chosen intentionally, in order to verify the possibilities offered by diffusimetry under extremely difficult conditions. The molecular weight distribution of the other technical polystyrene chosen was investigated in detail¹¹ in a project launched by the International Union of Pure and Applied Chemistry. Compared to the former sample its characterization should be an easier task; however, here too a considerable scatter of the M_w/M_n values was recorded¹¹. We also investigated the effects of a different thermodynamic quality of the solvent and of reprecipitation of the original sample.

EXPERIMENTAL

Polystyrene I (BASF III-D) has been produced^{10,12} for more than 30 years by a two-step thermal bulk polymerization at two temperatures up to a conversion of about 99.5%; it was used without any additional treatment. The reprecipitated reference sample was obtained by twice precipitating a 2% benzene solution of polystyrene I with a fivefold volume of methanol. Polystyrene II (Monsanto Chemicals - Lustrex) was distributed¹¹ under the scheme of a comparative study of the possibilities of characterization of commercial polymers, organized by the International Union of Pure and Applied Chemistry; it was also used without any additional treatment.

Toluene and cyclohexane, reagent grade (Lachema, Brno, Czechoslovakia) were distilled on a column (150 cm, Berl saddles).

The apparatus used, the stainless steel diffusion cell, the thermostat, the preparation of solutions, the experimental procedure and data evaluation have been described elsewhere^{7-9,13,14}.

The experiments in toluene were measured at 25°C, in cyclohexane at 35°C (θ — solvent).

RESULTS AND DISCUSSION

Experimental results are summarized in Table I; in this work diffusion against pure solvent was always measured. The initial concentration differences varied from 0.063 to 0.129 g/dl, so that the concentration dependence of D can be neglected¹⁵, and it may be assumed that the diffusion coefficient measured at a concentration \bar{c}^0 is equal to the quantity D^0 corresponding to infinite dilution. The mean values calculated from the experimentally determined averages D_i were used to calculate the respective polydispersity indices D_i/D_{i+1} given in Table II.

The comparison of D_i/D_{i+1} (Table II) shows that the distribution of the diffusion coefficients of polystyrene I (PS I) is considerably broader than that of polystyrene II (PS II). The greatest differences appear for the indices D_0/D_1 and the smallest for D_2/D_3 . The reprecipitation of PS I which removed part of the low-molecular fractions (the reprecipitated sample is denoted by PS I/P) leads to a decrease in the D_0/D_1 and D_1/D_2 indices and a small increase in the D_2/D_3 index. It may be inferred that

the distributions of the PS I and PS II samples differ particularly in the lower molecular weight region. The reason why different values of these indices have been found in toluene and cyclohexane, respectively, is a difference in the molecular weight dependence of the diffusion coefficient in the two solvents; this dependence is of the general form

$$D^{\circ} = K_D M^{-\alpha}; \quad (2)$$

Cantow¹⁶ found for polystyrene in cyclohexane at 35°C $K_D = 1.21 \cdot 10^{-4}$, $\alpha = 0.49$; new data published by King and coworkers¹⁷ are described by Eq. (2) with the parameters $K_D = (1.3 \pm 0.2) \cdot 10^{-4}$, $\alpha = 0.497 \pm 0.006$. For the diffusion of polystyrene in toluene at 25°C Mukherjea and Remp¹⁸ found $K_D = 2.37 \cdot 10^{-4}$, $\alpha = 0.54$; the values corresponding to our own measurements¹⁹ are $K_D = 2.69 \cdot 10^{-4}$, $\alpha = 0.546$.

If K_D and α are known, one may calculate from the distribution of the diffusion coefficients $f(D)$ the molecular weight distribution $g(M)$ according to

TABLE I

Diffusion Coefficients ($10^{-7} \text{ cm}^2 \text{ s}^{-1}$) of Technical Polystyrene Samples (PS) in Toluene and Cyclohexane

Polymer	Solvent	\bar{c}^a	D_0	D_1	D_2	D_3
PS I	toluene	0.0493	5.07	3.85	3.03	2.78
		0.0646	4.42	3.76	3.11	2.89
		0.0623	4.87	3.83	3.12	2.86
		0.0623	5.00	3.81	3.09	2.91
		0.0498	4.28	3.75	3.13	2.86
		0.0521	4.76	3.76	3.02	2.78
		0.0521	4.98	3.77	3.01	2.75
PS I	cyclohexane	0.0392	4.12	3.48	2.98	2.78
		0.0392	3.84	3.49	3.09	2.90
PS I/P ^b	toluene	0.0492	4.66	3.88	3.29	3.06
		0.0642	4.65	3.93	3.25	2.93
		0.0642	4.61	3.82	3.17	2.86
PS II	toluene	0.0507	4.17	3.58	3.15	2.96
		0.0507	4.00	3.61	3.22	3.08
PS II	cyclohexane	0.0511	3.78	3.42	3.15	2.98
		0.0318	3.73	3.50	3.22	3.06

^a The measurements were always performed against pure solvent and \bar{c}° (g dl^{-1}) is therefore half the actual concentration of the measured solution. ^b Twice reprecipitated sample.

$$g(M) = -f(D)(dD/dM). \quad (3)$$

The probably simplest route consists in describing the form of $f(D)$ by means of one of the empirical multiparameter distribution functions. The three-parameter distribution²⁰

$$f(D) = \frac{|s| t^{(u+1)/s}}{\Gamma\left(\frac{u+1}{s}\right)} \cdot D^u \exp(-tD^s) \quad (4)$$

contains all commonly used two-parameter distributions as special or limiting cases. A nomogram²⁰ based on the experimental values of D_0/D_1 and D_1/D_2 was constructed in order to determine the parameters u , s , t of the above equation. It follows from the properties of function (4) that it should always hold either $u > 0$ and $s > 0$, or $u < 0$ and $s < 0$. This is reflected in the respective nomograms²⁰ used for determining these parameters from the indices D_0/D_1 and D_1/D_2 in such a way that for each D_1/D_2 there exists a maximum value of D_0/D_1 which actually determines the limit of applicability of (4) for an adequate representation of the experimental data. By combining Eqs (2)–(4) one may proceed from $f(D)$ to the molecular weight distribution $g(M)$ which formally has the same form as Eq. (4), with only the numerical values of its parameters changed. It is easy to derive the expressions

$$s^* = -\alpha s, \quad u^* = -[\alpha(u+1) + 1], \quad t^* = t(K_D)^s, \quad (5a, b, c)$$

TABLE II

Polydispersity Indices D_1/D_{1+1} from Measurements in Toluene and Cyclohexane and Calculated M_w , M_n , M_w/M_n Values of Technical Polystyrene (PS) Samples

Polymer	Solvent	D_0/D_1	D_1/D_2	D_2/D_3	M_w , · 10 ⁻⁴	M_n , · 10 ⁻⁴	M_w/M_n^a	M_w/M_n^b
PS I	toluene	1.26 ^c	1.24	1.08	23.1	1.87	12.3	14.4
	cyclohexane	1.14	1.14	1.07	20.0	3.26	6.1	4.9
PS I/P ^d	toluene	1.20	1.20	1.10	21.1	3.27	6.4	7.0
PS II	toluene	1.13	1.13	1.05	22.2	7.44	3.0	3.1
	cyclohexane	1.08 ₇	1.08 ₈	1.05	18.3	7.24	2.5	2.4

^a Calculated with $K_D = 2.69 \cdot 10^{-4}$, $\alpha = 0.54_6$ for toluene¹⁹ or $K_D = 1.21 \cdot 10^{-4}$, $\alpha = 0.49$ for cyclohexane¹⁶. ^b Calculated with $K_D = 2.37 \cdot 10^{-4}$, $\alpha = 0.54$ for toluene¹⁸ or $K_D = 1.3 \cdot 10^{-4}$, $\alpha = 0.497$ for cyclohexane¹⁷. ^c M_n and M_w calculated with the corrected $D_0/D_1 = 1.24$ — see the text for explanation. ^d Twice reprecipitated sample.

where u , s , and t are parameters of Eq. (4) determined from the experimental ratios D_i/D_{i+1} , while the corresponding values with an asterisk are parameters characterizing the molecular weight distribution $g(M)$. For $g(M)$ too it must hold simultaneously either $u^* > 0$ and $s^* > 0$, or $u^* < 0$ and $s^* < 0$. From the known parameters s^* , u^* , t^* one can calculate²¹ M_n , M_w and their ratio which is commonly used for the characterization of the polymer polydispersity. Here it is assumed implicitly that both the shape of the distribution of the diffusion coefficients $f(D)$ and the molecular weight distribution $g(M)$ can be adequately described by Eq. (4). This assumption is probably not fulfilled for the sample PS I: Meyerhoff¹⁰ studied extensively the possibilities of determining the molecular weight and polydispersity index of this technical polymer and found $M_w = 3.8 \cdot 10^5$ from the fractionation data and $M_{SD} = 3 \cdot 10^5$ by combining sedimentation velocity and free diffusion measurements. The osmotically determined M_n values varied within a range of 45000 to 125000 (i.e. $M_w/M_n = 3-8.4$) according to the membrane used. The ebulliometrically obtained M_n was 4500; owing to the presence of approximately 0.5% of volatile components in the sample he estimated M_n to be 6000 (i.e. $M_w/M_n \sim 63$), and stated that the determination of a correct M_n was extremely difficult. He saw the obvious cause of difficulties in the presence of low-molecular weight components (oligomers + monomer) in the sample. Indeed, the results of fractionation¹⁰ indicated that the molecular weight distribution of this sample had no maximum.

Our attempt to calculate the number and weight average molecular weights for PS I by means of empirical distribution (4) with the parameters read from a nomogram²⁰ using experimental values of D_0/D_1 and D_1/D_2 measured in toluene has also revealed that expression (4) cannot be used for PS I. The parameter u read off from the nomogram lay at the limit of applicability of the nomogram, and the quantities u^* and s^* calculated from (5) differed by their signs, $u^* = -0.023$, $s^* = +1.29$. (It should be noted that for $u^* = 0$ and $s^* = 1.29$ we would obtain $M_w = 2.2 \cdot 10^5$, $M_n = 0$; consequently, in this range of u^* , s^* the average M_n is very sensitive and the weight average rather insensitive to changes in the ratio D_0/D_1). To make the application of the above-mentioned procedure for the determination of M_n and M_w still possible, we intentionally adjusted the experimental D_0/D_1 (cf. Table II) to become $D_0/D_1 = 1.24$ (with respect to the scatter of D_0 in Table I, this change is not quite unjustified); in this way, the parameters were changed to $u^* = 0.08$, $s^* = 1.09$. The averages M_w ; M_n and their ratio calculated from these values by using the data for K_D and α in ref.¹⁹ are then given in columns 6-8, Table II. The same calculations were performed for K_D and α taken from a paper by Mukherjea and Rempp¹⁸ (last column in Table II). The comparison of the indices M_w/M_n thus calculated illustrates the effect of the experimental error in the parameters of Eq. (2) on the results obtained by such procedure. It should also be borne in mind that in the calculations^{9,14} of D_0 both the effect of uncertainty in the determination of the zero-time correction Δt_c (which is at any rate only an average value for a polydisperse

sample) and the approximative calculation of the lower part of a generalized gradient curve⁸ (needed for the calculation of D_0 and D_1) play the predominant part. Moreover, the correction Δt_c and the lower part of the generalized curve are both determined from experimental points which correspond rather to its middle part where the presence of oligomers is relatively less important. On the other hand, the low-molecular weight fractions affect to the greatest extent the lower part of the generalized gradient curve, so that the procedure used partly suppresses their effect.

The ratios D_0/D_1 and D_1/D_2 measured for PS I in cyclohexane yielded $s^* = 1.81$ and $u^* = 0.127$; both values had the same sign, but the low value of $|u^*|$ again indicates that we are close to the limit of applicability of expression (4). There is another reason why the presence of a large amount of oligomers in PS I can cause complications in the calculation of M_n and M_w by using the procedure suggested above: in the low-molecular weight region both the refractive index increment²² and the exponent¹⁸ α in Eq. (2) depend on molecular weight. It cannot be expected that these changes will be the same for different solvents; one is therefore not surprised to find differences between M_w and M_n if the measurements of PS I are carried out in toluene and cyclohexane (Table II). M_w and M_n in cyclohexane were again calculated with the parameters K_D and α according to ref.¹⁶ and also (the last column in Table II) with the values taken from ref.¹⁷.

The ratios D_2/D_3 (Table II) of all samples investigated here are always considerably lower than the other two diffusion criteria of polydispersity. It is known that the

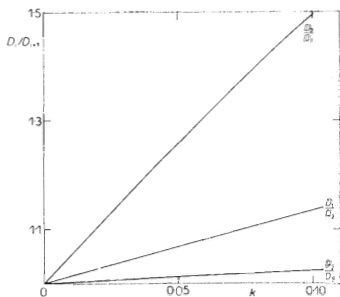


FIG. 1

Dependence of the Polydispersity Indices D_i/D_{i+1} on the Amount of the Low-Molecular Weight Admixture A in the Monodisperse Polymer B

Averages calculated for $D_A/D_B = \delta = 20$; k is the ratio of relative concentrations of the two components ($k = C_A/C_B$).

average M_n is much more sensitive towards the presence of low-molecular weight components in the sample than the weight average M_w ; a similar behaviour can be expected also for the average diffusion coefficients defined by Eq. (1). With respect to the inequality^{8,15} $D_0 \geq D_1 \geq D_2 \geq D_3$, and also because the diffusion coefficient always decreases with increasing molecular weight, one may expect that the average D_0 will be the most sensitive to the presence of oligomers. To elucidate the effect of low-molecular weight admixtures on the behaviour of the individual ratios D_i/D_{i+1} we shall generalize a procedure used by Champagne and coworkers²³ for the analysis of diffusion in three-component mixtures.

Let us consider the diffusion of two compounds A and B with different diffusion coefficients D_A, D_B in a given solvent. Relative concentrations expressed by means of refractive indices are C_A, C_B ($C_A + C_B = 1$); in agreement with ref.²³ we define $k = C_A/C_B$, choose $D_A/D_B = \delta = 20$, and restrict ourselves to the region $C_A \ll C_B$ ($0 \leq k \leq 0.1$), that is, a small amount of a low-molecular weight admixture A is present. (As α is usually close to 0.5, the chosen $\delta = 20$ corresponds to approximately $M_A/M_B = 400$; thus, if the molecular weight of the component B is $2 \cdot 10^5$, the component A is a pentamer).

The relationship

$$\frac{D_1}{D_2} = (k + 1)^2 \frac{1 + k\delta^{-3/2}}{(1 + k\delta^{-1/2})^3} \quad (6)$$

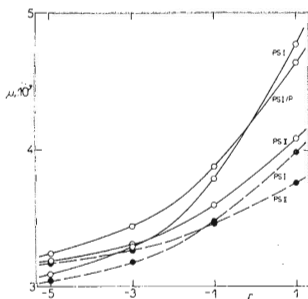


FIG. 2

Graphic Interpolation of $\mu_r = [\int_0^\infty D^{r/2} f(D) dD]^{2/r}$ for $r = 2$ and -4
Solvent: \circ toluene; \bullet cyclohexane.

was derived²³ for the ratio of the average diffusion coefficients D_1/D_2 . Similarly, from definitions of D_i we can derive the expressions

$$\frac{D_0}{D_1} = \frac{1}{(k+1)^4} (1 + k\delta^{1/2})^2 \cdot (1 + k\delta^{-1/2})^2 \quad (7)$$

and

$$\frac{D_2}{D_3} = \frac{(1 + k\delta^{-1/2})(1 + k\delta^{-5/2})}{(1 + k\delta^{-3/2})^2} \quad (8)$$

The dependence of these criteria on $k = C_A/C_B$ is shown in Fig. 1. One can see that the presence of oligomers is most strongly reflected in the ratio D_0/D_1 , less strongly in D_1/D_2 , and that D_2/D_3 is only very little affected. For instance, for 5% of the "pentamer" ($k = 0.05$) we obtain $D_0/D_1 \sim 1.26$, $D_1/D_2 \sim 1.07$, and $D_2/D_3 \sim 1.01$. Thus, the above calculation explains qualitatively the relationship between D_2/D_3 and D_1/D_2 (a similar behaviour of the two indices has also been observed by Mukherjea and Rempp¹⁸ for polystyrene) and confirms the high sensitivity of this method to the presence of small amounts of low-molecular weight fractions. The indices D_0/D_1 and D_1/D_2 indicate the presence of even very small quantities of oligomers which cannot be detected *e.g.* in the determination of the distribution of sedimentation coefficient, and which must therefore be neglected. If the distribution of the sedimentation coefficient and the average M_{sD} are measured by combining sedimentation with diffusion, the suggested procedure provides us with very useful supplementary information. Similarly, it is possible to supplement the data obtained by GPC, where the low-molecular weight admixtures can be hidden in the uncertainty of baseline position. Let it be noted in this connection that the lower absolute M_w values of PS I (Table II) compared with the data of Meyerhoff¹⁰ may be due to this higher sensitivity to low-molecular weight fractions.

Reprecipitation changes the distribution of the sample PS I in such a way that the distribution can adequately be described by (4) without any problems. The values of M_n and M_w calculated for PS I/P by using the three-parameter function (4) from the diffusion measurements in toluene (Table II) suggest that double precipitation removes a part of the oligomeric fractions, even though according to the index M_w/M_n also this sample has still a very broad molecular weight distribution.

M_w/M_n of PS II is roughly half that of polystyrene I. The low values of D_2/D_3 compared with D_1/D_2 again indicate the presence of oligomers; but their relative participation is obviously lower. This is favourably reflected both in the agreement between the absolute values of M_w , M_n and M_w/M_n (Table II) with the literature¹¹ and in the good agreement found for the two solvents used. Strazielle and Benoît¹¹, critically evaluating the results obtained in a number of laboratories, give M_n 70000,

M_w 230000, and M_w/M_n 3.4 as the most likely values; the average indices M_w/M_n from a number of GPC, light scattering, osmometric, and fractionation measurements were 3.89, 3.22, and 3.06. Also the agreement between average molecular weights calculated with various pairs of constants in Eq. (2) (the last two columns in Table II) for PS II is very good in the two solvents, which again indicates a lower content of oligomers.

A more general procedure for the determination of the distribution of the diffusion coefficient than the empirical distribution function (4) is the expansion into a series of generalized Laguerre polynomials. A successful calculation of $f(D)$ requires a sufficient number of moments of the type $\int_0^\infty D^{r/2} f(D) dD$; the moments for $r = 1, -1, -3, -5$ can be determined experimentally (cf. Eq. (1a - c)), while graphic interpolation gives the intermediate values for $r = -2, -4$. A suitable plot is that in Fig. 2: we plot the values of $[\int_0^\infty D^{r/2} f(D) dD]^{2/r}$ (all having the dimensions of D) against r . However, it was found that not even these seven moments were sufficient, because the respective expansion converges too slowly. Nevertheless, Fig. 2 allows a qualitative comparison of the samples. It can be seen that the greatest differences appear in the low-molecular weight region. The comparison of curves for PS I and PS I/P shows the effect of reprecipitation (decrease in the low-molecular weight fractions). One may assume that the character of the distribution of the diffusion coefficients of PS I after reprecipitation is similar to PS II, though much broader (cf. D_i/D_{i+1}). Moreover, this again demonstrates the sensitivity of the method to minor changes in the content of low-molecular weight fractions which frequently affect technological properties of the polymer.

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