

EVALUATION OF POLYDISPERSITY INDEX M_w/M_n BY QUASIELASTIC LIGHT SCATTERING

Petr ŠTĚPÁNEK, Zdeněk TUZAR and Čestmír KOŇÁK

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

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The response of quasielastic light scattering to the polydispersity of scattering objects has been investigated. A new method of the polydispersity index determination has been suggested, suitable for the range $1.02 \leq M_w/M_n \leq 2.0$ and consisting in the measurement of the dependence of the apparent decay time on the correlator sampling time. The polydispersity index can be determined by comparing these dependences with the theoretical ones obtained using correlation curves simulated for various values of the polydispersity index, assuming lognormal and Schulz-Zimm distributions of molecular weights. The test measurements on polystyrene standards having molecular weights in the range $9 \cdot 10^3 - 20.6 \cdot 10^6$ give polydispersity index values M_w/M_n that are in a good agreement with those given by the manufacturer. The polydispersity index for polystyrene having the molecular weight $M_w = 20.6 \cdot 10^6$ thus determined was $M_w/M_n \doteq 1.35$.

Much effort has been devoted in polymer science to the characterization of the polydispersity of molecular weights M . Polydispersity may be described either by the molecular weight distribution curve or, in the case of simple distributions, by using moments of the distribution curve, most often by means of the ratio of the weight and number average molecular weight, M_w/M_n . To determine this ratio called the polydispersity index two different methods are usually needed (*e.g.*, integral light scattering and osmometry), the sensitivity, and in some cases also the suitability of which depend on the molecular weight of the sample.

Methods of the analysis of quasielastic light scattering (QELS) by which the polydispersity index can be determined are mostly based on the method of cumulants^{1,2}, or they are derived from it³⁻⁶, *i.e.* they are based on the fitting of the logarithm of the correlation curve by a polynomial. The cumulant method is very sensitive to the correct determination of the baseline value. An error in the baseline value is very strongly projected into the value of the first cumulant, and thus also into the polydispersity values. Different procedures used for the baseline determination have been discussed by Oliver⁷.

Procedures in which the simulated correlation functions are directly compared with experimental data are used to a lesser extent. Thus, *e.g.*, in ref.⁸ the theoretical

autocorrelation function is simulated by means of a suitable two-parameter distribution so as to fit experimental data as well as possible. It has been demonstrated that such procedure allows M_w to be determined with sufficient accuracy, but that the polydispersity index determination is subjected to a considerable error. In ref.⁹ similar data are obtained by fitting autocorrelation functions extrapolated to zero scattering angle and zero concentration.

In this study we suggest a new simple method of determination of the polydispersity index M_w/M_n , based only on the measurement of quasielastic light scattering. The procedure is independent of molecular weight and in the case of a precise measurement very low values of the polydispersity index can be determined. The method is based on the variation of the apparent decay time τ_c as determined from the correlation function of a polydisperse sample with the extent of time interval used ($\Delta T, \tau_{\max}$); here, $\tau_{\max} = m \Delta T$ and ΔT is the sampling time and m is the number of correlator channels. This dependence has been calculated theoretically by using simulated correlation curves corresponding to various polydispersity indices for a given distribution. It has been tested on solutions of polystyrene standards with polydispersity indices indicated by the manufacturer, mostly on the basis of measurements of integral light scattering, osmometry, and GPC.

THEORETICAL

Basic Relations

For monodisperse particles in a dilute solution or dispersion the homodyne autocorrelation function $G(\tau)$ measured by photon correlation spectroscopy is a simple exponential. For an arbitrary sampling time, ΔT , we have (τ being the delay time)

$$G(\tau) = B + A|g^{(1)}(\tau)|^2, \quad (1)$$

where A and B are constants, and

$$g^{(1)}(\tau) = \exp(-\tau/\tau'_c) \quad (2)$$

is the electric field autocorrelation function of scattered light with the decay time, τ'_c .

For a polydisperse sample the function $g^{(1)}(\tau)$ is given by⁵

$$g^{(1)}(\tau) = \frac{\int Mf(M) P(K, M) \exp(-D(M, K, c) K^2 \tau) dM}{\int Mf(M) P(K, M) dM}, \quad (3)$$

where $f(M)$ is the number distribution function of particles having the molecular weight M , diffusion coefficient $D(M, K, c)$ and particle scattering function $P(K, M)$;

$K = (4\pi/\lambda) \sin(\theta/2)$ is the scattering vector, λ is the wavelength of light in the medium and θ is the scattering angle. For the limiting case of zero scattering angle and zero concentration, relation (3) is simplified to

$$g^{(1)}(\tau) = \int Mf(M) \exp(-D_0(M) K^2\tau) dM \Big/ \int Mf(M) dM, \quad (4)$$

where $D_0(M)$ is the diffusion coefficient value in the limit of zero concentration for which a general power law¹⁰

$$D_0(M) = aM^{-\nu} \quad (5)$$

is valid; here, the exponent ν describes the compactness of the particle and is equal to the inverse fractal dimension¹¹ of the object, $\nu = 1/D_f$. In the first approximation, $\nu = 1/3$ ($D_f = 3$) for hard spheres, $\nu = 1/2$ ($D_f = 2$) for an unperturbed polymer coil, and $\nu = 3/5$ ($D_f \approx 1.67$) for a swollen polymer coil; a is a constant particular for the given polymer-solvent system.

Thus, to calculate the function $g^{(1)}(\tau)$ using relation (4), one needs to know the dependence of the diffusion coefficient on molecular weight, as well as the corresponding molecular weight distribution, $f(M)$. In polymer science, the lognormal and Schulz-Zimm molecular weight distributions are in common use for this purpose.

The lognormal molecular weight distribution is described by means of the parameters M_0 and $\beta = (2 \ln(M_w/M_n))^{1/2}$ using the following relation

$$f(M) = \frac{1}{\beta} \frac{1}{\sqrt{M}} \frac{1}{M} \exp\left(\beta^{-2} \left(\ln \frac{M}{M_0}\right)^2\right), \quad (6)$$

which provides an adequate description of asymmetrical molecular weight distributions. By means of the parameters $z = [(M_w/M_n) - 1]^{-1}$ and $y = (z + 1)/M_w$, the Schulz-Zimm molecular weight distribution can be described by the relation (Γ is the gamma function)

$$f(M) = \frac{y^{z+1}}{\Gamma(z+1)} M^z \exp(-My) \quad (7)$$

and is suitable for, e.g., a description of the molecular weight of polymers obtained by radical polymerization.

Computer Simulations

The autocorrelation function was generated on a computer by numerical integration in the form

$$G(j, \Delta T) = \left(\int_0^{M_{\max}} M f(M) \exp(-D(M) K^2 \cdot \Delta T \cdot j) dM \right)^x, \quad (8)$$

first, for the limiting case ($K \rightarrow 0$, $c \rightarrow 0$), then including complicating factors, *i.e.*, nonzero concentration, nonzero scattering angle and random noise. In relation (8), normalization terms and the constants A , B from Eq. (1) (which, as is demonstrated below, are useless) have been omitted. For a homodyne measurement, $x = 2$; by choosing $x = 1$, we obtain results corresponding to the heterodyne detection. The M_{\max} value was chosen so as to make $f(M_{\max})$ virtually zero; j is the number of the correlator channel, $j = 1, \dots, m$. The autocorrelation function was generated in 100 points, since many correlators, both commercial and home made, have the same number of channels or a number close to it¹².

For the given M_w/M_n , the correlation curves thus obtained with various sampling times ΔT were force fitted to a single exponential (by a nonlinear iterative procedure), which gave the apparent decay time, τ_c . In order to obtain undistorted information from the autocorrelation function, simulated or measured, two conditions must be met¹³: the sampling time (ΔT) must be shorter at least ten times than the decay time (τ_c), and the maximum delay time, τ_{\max} , should at least be equal to τ_c . For a correlator having m channels, these conditions are given by the inequalities

$$\tau_c/m < \Delta T < \tau_c/10. \quad (9)$$

For monodisperse particles the forced single exponential fit gives the same τ_c values, $\tau_c = \tau'_c$ for any ΔT which satisfies relation (9). If the distribution $f(M)$ has a nonzero width, the apparent τ_c determined by the force fitting of a single exponential through the correlation curve varies with ΔT (even if conditions (9) are observed); it is evident, moreover, that this variation will be the greater the larger the width of the distribution. The apparent decay time can then be represented as an increasing function of ΔT .

The representation of $\tau_c(\Delta T)$ can be made independent of molecular weight, if the normalization variables τ_c/τ_c^* and $\Delta T/\Delta T^*$ are used, where τ_c^* corresponds to τ_c at ΔT^* . The ΔT^* value can be chosen in a defined way anywhere in the interval given by inequality (9). The most advantageous from the experimental standpoint (for a correlator with 100 channels) was the choice $\Delta T^* = \tau_c/10$, which provides the greatest response to polydispersity and compensates even a major error involved in the determination of the normalization time τ_c^* by real measurement. For the given type of distribution and the given value of the exponent ν in relation (5), the normalized τ_c/τ_c^* vs $\Delta T/\Delta T^*$ plot depends only on the polydispersity index M_w/M_n . For this method it is assumed that the exponent ν does not depend on molecular weight M . A comparison between the measured and theoretical τ_c/τ_c^* vs $\Delta T/\Delta T^*$ dependences allows us to determine the polydispersity index of the sample. The

procedure is also independent of the amplitude and background of correlation curves, because the only parameter used is the apparent τ_c .

EXPERIMENTAL

The polymers used were polystyrene standards; the characteristics are given in Table I. Toluene (good solvent for polystyrene) and cyclopentane (Θ -solvent at 20.8°C), both purity grade solvents (Lachema, Czechoslovakia) were rectified and dried before use. The samples were prepared by weighing and were optically cleaned by filtration (0.22 μm teflon Millipore filter), for $M_w \leq 1.2 \cdot 10^6$, and by centrifugation (Beckman Ultracentrifuge, model L8-55, 1 hour at 15 000 rpm.) for $M_w \geq 2 \cdot 10^6$.

The measurements were carried out using a homodyne photon correlation spectrometer, with a 96-channel correlator of our own construction based on principles outlined in ref.¹⁵, and with a He-Ne laser (Spectra Physics model 125 A) or an Ar laser (Carl Zeiss Jena, model ILA 120-1). The apparatus used is described in detail in ref.¹⁶. The sample was thermostated to 26.2°C \pm 0.05°C. Exact temperature regulation was found to be very important in order to obtain repeated measurements with minimal scatter required by the method described. The scattering angle lay in the range between 9 and 90°.

TABLE I

Polystyrene standards used for the measurement. The concentration (g/ml) and the KR_G value at which the sample was measured are given, along with the polydispersity index values given by the manufacturer and determined experimentally. The values marked with asterisk are probably somewhat higher than the real ones, as they were measured at $KR_G < 0.5$. Manufacturers of the standards are denoted with the abbreviations PC (Pressure Chemicals) and TS (Toyo Soda)

$M_w \cdot 10^6$	$c \cdot 10^3$ (g/ml)	KR_G	M_w/M_n		Producer
			labelled	found	
0.009	50.0	0.037	1.06	1.03 \pm 0.01	PC
0.0204	20.0	0.060	1.06	1.04 \pm 0.03	PC
0.050	10.0	0.103	1.06	1.04 \pm 0.03	PC
0.110	5.0	0.165	1.06	1.05 \pm 0.02	PC
0.390	0.8	0.351	1.10	1.08 \pm 0.02	PC
0.670	0.6	0.484	1.15	1.20 \pm 0.04	PC
1.260	0.33	0.32	1.05	1.08 \pm 0.04	TS
2.000	0.30	0.525	1.30	1.40 \pm 0.07	PC
2.890	0.40	0.653	1.09	1.20*	TS
3.840	0.20	0.864	1.05	1.15*	TS
5.480	0.29	0.510	1.15	1.18*	TS
6.770	0.20	0.864	1.14	1.20*	TS
20.60	0.10	0.762	—	1.35*	TS

For each sample the correlation function $G(\tau)$ was measured at various sampling times (ΔT) covering the whole interval given by inequalities (9). At each sampling time the measurement was carried out ten times, and the mean value and standard deviation of the apparent decay time were determined. The greatest possible care was devoted to the determination of the normalization values τ_c^* and ΔT^* , the errors of which are projected into values of all points on the experimental curve τ_c/τ_c^* vs $\Delta T/\Delta T^*$. In view of the scatter of measurement ΔT cannot be adjusted exactly to $\tau_c^*/10$. For this reason, the measurements were always carried out at a ΔT value slightly lower and slightly higher than ΔT^* , and a relatively exact ΔT^* value was obtained by interpolation.

RESULTS AND DISCUSSION

RESULTS OF AN ANALYSIS OF SIMULATED CURVES FOR LIMITING CONDITIONS

We shall start by giving the results of an analysis of simulated correlation functions for the limiting case of measurement, *i.e.*, without including the effect of noise, finite concentration c and finite scattering angle θ . Fig. 1 shows the function τ_c/τ_c^* vs

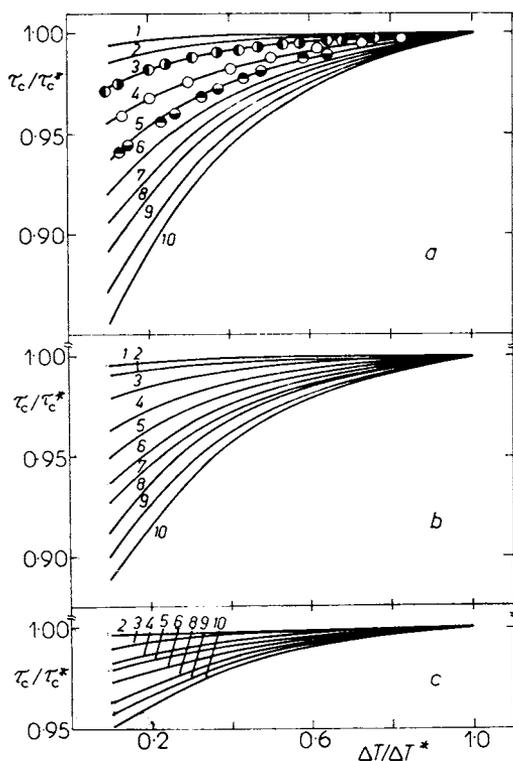


FIG. 1

The calculated function τ_c/τ_c^* vs $\Delta T/\Delta T^*$ for the given polydispersity index values M_w/M_n , (1 1.02, 2 1.05, 3 1.10, 4 1.20, 5 1.30, 6 1.40, 7 1.50, 8 1.60, 9 1.80, 10 2.00) for the case of the lognormal molar mass distribution, homodyne detection, in the limit of zero concentration and zero scattering angle ($\Delta T = \tau_c^*/10$ is the normalization point). *a* Polymer in a good solvent, $\nu = 0.577$; points \circ represent the average value obtained from simulated correlation curve for M_w/M_n 1.2 and with 1% noise. The results of simulation involving the concentration effect are described for M_w/M_n 1.1 by points \bullet ($M_w = 10^5$, $c = 5 \cdot 10^{-4}$ g/ml) and \circ ($c = 5 \cdot 10^{-3}$ g/ml), for M_w/M_n 1.3 they are described by points \bullet and \circ (the same concentrations). *b* Polymer in Θ -solvent, $\nu = 0.500$; *c* dispersion of rigid spheres, $\nu = 0.333$

$\Delta T/\Delta T^*$ at various values of polydispersity index for a situation of the highest practical importance in the polydispersity determination, *i.e.*, for a homodyne measurement assuming the lognormal distribution, for a polymer in a good solvent (Fig. 1a), for a polymer in the Θ -solvent (Fig. 1b) and for hard spheres (Fig. 1c). With respect to the ν value in relation (5), polydispersity manifests itself most strongly in the case of swollen coils (Fig. 1a), when the molecular weight distribution is most markedly transferred into the distribution of relaxation times. Thus, a good solvent should be used preferably in the experimental determination of the polydispersity of a linear polymer employing this method. A Θ -solvent (Fig. 1b) is important in the measurement of polydisperse samples having a high molecular weight, because swelling of the coil in a good solvent may impede meeting the condition of a sufficiently small measurement angle (*cf.* below).

The method becomes still more sensitive if a heterodyne detection is used (in Fig. 2); this detection, however, is less commonly applied in practice. Analogous curves for the case of polydispersity described by the Schulz-Zimm distribution are given in Fig. 3 for various types of solvents used and for the homodyne detection. It can be seen that for this type of distribution the method provides a somewhat smaller response to polydispersity than in the case of lognormal distribution. The numerical values of points used in plotting the individual curves in Figs 1–3 are available on request.

LIMITS OF APPLICABILITY

The curves in Figs 1–3 were calculated for the limiting conditions given above. Obtaining experimental data in the limit of zero scattering angle and zero concentration requires a time-consuming extrapolation to $K \rightarrow 0$ and $c \rightarrow 0$. It can be expected, however, that at sufficiently small K and c the results in Figs 1–3 could be used directly in real measurement. Let us now evaluate the individual effects for typical conditions met in the measurement of quasielastic light scattering.

Effect of Noise

The selected autocorrelation curves were generated with a Gaussian distributed random noise with standard deviation of 1% that is typical of good experimental autocorrelation functions. For each case, 10 functions were generated each time, and from them ten slightly scattered τ_c values were obtained. The average values fitted well the ideal curves. An example is given in Fig. 1a for $M_w/M_n = 1.2$.

Effect of Measurement Angle

Usually, in scattering measurements it is sufficient to satisfy the condition $KR_G < 1$, where R_G is the radius of gyration of the particle; however, due to the high sensitivity

of our method apparent in Figs 1–3, one has to verify whether such condition is really sufficient in this case. The effect of a measurement angle was tested experimentally using a polystyrene standard, $M_w = 1.2 \cdot 10^6$, having rather a narrow distribution and at the same time such molecular weight which in the usual angular range covers the necessary region of $K = 1/R_G$. Fig. 4 shows the τ_c/τ_c^* vs $\Delta T/\Delta T^*$ plot for various KR_G values; the value of $R_G = 53.2$ nm was obtained from integral light scattering. It can be seen in Fig. 4 that the condition $KR_G < 0.5$ must be satisfied, otherwise the apparent polydispersity index values are higher than the real ones. This condition must be satisfied especially for samples having high polydispersity, as in such case the high-molecular-weight part of distribution plays an important role.

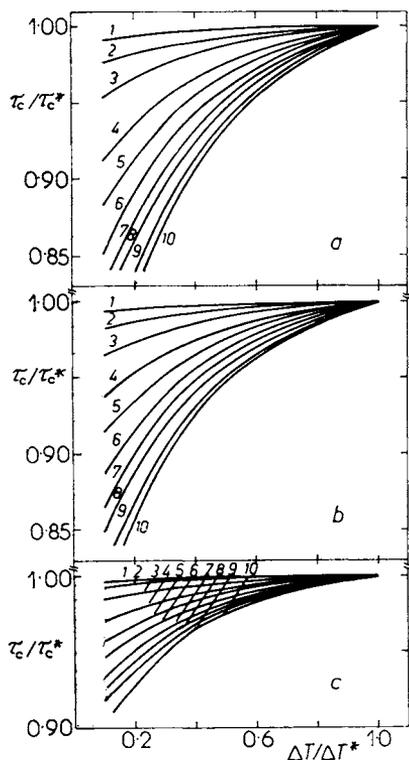


FIG. 2

The same as Fig. 1 for heterodyne detection

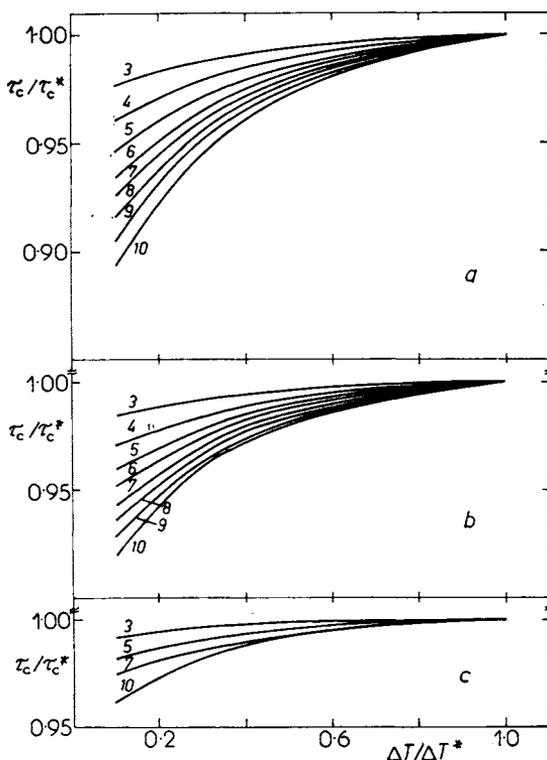


FIG. 3

The same as Fig. 1 for the Schulz-Zimm distribution of molecular weights and homodyne detection

Effect of Concentration

At finite concentration the diffusion coefficient is affected by thermodynamic and hydrodynamic interactions and it must be considered in the form of virial expansion

$$D(M) = D_0(M) \cdot (1 + k_D(M) \cdot c + \dots) \quad (10)$$

The parameter $k_D(M)$ depends rather strongly on molecular weight, which becomes obvious from its approximate expression as¹⁰

$$k_D(M) \approx 2A_2(M)M - [\eta](M) - \bar{v}_1, \quad (11)$$

where $A_2(M)$ is the second virial coefficient of osmotic pressure, $[\eta](M)$ is the intrinsic viscosity and \bar{v}_1 is the partial molar volume of polymer. The effect of concentration was tested on a case of homodyne measurement using a polymer with the lognormal distribution in a good solvent (Fig. 1a).

In the autocorrelation function (8) the expression for $D_0(M)$ was substituted by expression (10). The dependence $k_D(M) = 1.98 \cdot 10^{-3} M^{0.81}$ (for concentration in g/g) was taken from the literature¹⁴ for the system polystyrene-benzene; we assumed that it would be identical in the system polystyrene-toluene, at least as far as the molecular weight exponent is concerned. The assumed values were: molecular weight 10^5 , polydispersity M_w/M_n 1.1 or 1.3 and concentration in the range $5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ g/g. The τ_c/τ_c^* vs $\Delta T/\Delta T^*$ dependences for the highest and lowest concentrations are given in Fig. 1a. There is no perceptible difference between these

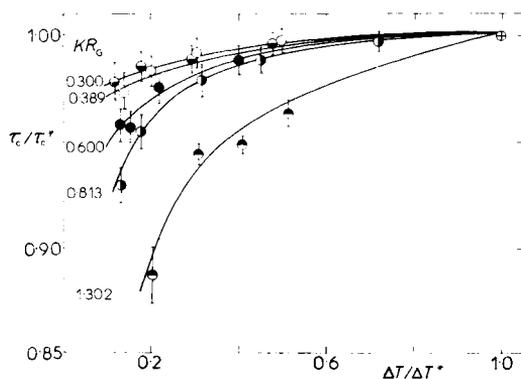


FIG. 4

Experimental dependence of τ_c/τ_c^* on $\Delta T/\Delta T^*$ for measurements at various angles using the standard $M_w = 1.2 \cdot 10^6$. The curves have been parametrized by the KR_G value

dependences and the curve for the limiting case, $c = 0$. This means that the effect of parameter k_D in relation (10) on the results of the method described here can be neglected in this concentration range for molecular weights of the order of magnitude 10^5 ; for other molecular weights the concentrations must be adjusted accordingly.

For low concentrations the independence of normalized τ_c values of c was also confirmed experimentally. For polystyrene having the molecular weight (M_w) $1.2 \cdot 10^6$, the curves τ_c/τ_c^* vs $\Delta T/\Delta T^*$ were plotted for three relatively low concentrations $c \cdot 10^3$ (g/g) 0.3, 0.5, 1.0. All three curves coincide within the limits of experimental error, corresponding to the value $M_w/M_n = 1.08 \pm 0.04$.

EXPERIMENTAL RESULTS

The polydispersity indices of the samples, M_w/M_n , were determined by comparing the experimental dependences τ_c/τ_c^* vs $\Delta T/\Delta T^*$ with the theoretical ones (Figs 1–3). Some examples of the experimental τ_c vs ΔT dependences are demonstrated in Fig. 5. A complete set of M_w/M_n data for polystyrene standards is given in Table I.

The M_w/M_n values for samples from Table I having the molecular weight higher than $3 \cdot 10^6$ are systematically higher than the reported ones, as in these cases the measurement could not be performed at a sufficiently low angle, predominantly for technical reasons. Moreover, measurements at small angles ($\theta < 10^\circ$) are difficult, especially for high molecular weights, because they lead to very long decay times, and hence also to very long measurements times. The latter can be reduced to a limited extent by using a low-viscosity Θ -solvent (e.g., cyclopentane for polystyrene standards). Furthermore, measurements at such angles may suffer from substantial errors due to uncertainty in the determination of the scattering vector given by the finite solid angle of observation. It seems that for the purposes of polydispersity

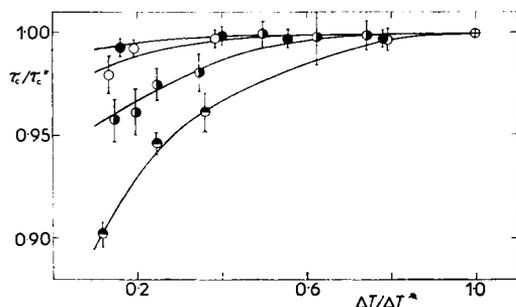


FIG. 5

Experimental dependences τ_c/τ_c^* vs $\Delta T/\Delta T^*$ for chosen polystyrene standards, M_w ● $9 \cdot 10^3$, ○ $1.1 \cdot 10^5$, ◐ $2.0 \cdot 10^6$, ● $6.7 \cdot 10^6$

index determination it would be suitable to use small angle light scattering apparatuses (such as Chromatix KMX-6) equipped with an aperture which suitably restricts the magnitude of the solid angle.

In general, it may be stated that the measured values of the polydispersity index mostly approach those given by the producer. For the Toyo Soda sample, $M_w = = 20.6 \cdot 10^6$, M_w/M_n not given, our estimated value $M_w/M_n \approx 1.35$ could not be compared with any other data.

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