Molecular weight and polydispersity measurements of polystyrene by quasielastic light scattering

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The molecular weight and polydispersity of a polydisperse polystyrene sample was measured by quasielastic light scattering. The molecular weight distribution of the polymer was represented by the Schultz distribution. The weight average molecular weight and polydispersity of distribution was adjusted until the quasielastic light scattering spectra calculated for the distribution agreed with the measured spectra. The calculation was repeated using the logarithmic normal distribution for the polymer. The calculated value of the weight average molecular weight is accurate and insensitive to the assumed molecular distribution function. However, the calculated values of the polydispersity are only of fair accuracy. Thus quasielastic light scattering gives values of the weight average molecular weight at least as accurate as elastic light scattering and gives a crude estimate of the polydispersity of the polymer.

INTRODUCTION

Quasielastic light scattering (QELS) has become a standard method of measuring diffusion coefficients of macromolecules in solution[1,2]. Tagami *et al.*[3] and Dubin *et al.*[4], have suggested measuring the molecular weight averages of macromolecules by QELS.

In principle, the size or molecular weight distribution of a polydisperse system can be obtained by deconvolution of the autocorrelation functions of the scattered light. In practice, it has been realized[5] that the deconvolution would require data that are more precise and over a wider range than is available.

A second approach, due to Koppel[6], uses the formalism of cumulant generating functions and has been applied to the analysis of latex particles[7,8] and polystyrene[9]. However, the problem with this approach is that cumulants of all orders are needed to completely specify the distribution[10], and this is impractical. Also, the concentration dependence of the diffusion coefficient and the angular dependence of the particle scattering function, $P(\theta)$, cannot be easily included.

A third approach, used in this paper, is to calculate the QELS spectrum or autocorrelation function with a parameterized distribution function and determine the parameters of the distribution function by comparison with experimental data. While there has been theoretical investigation[3,11–14], for variously shaped particles and distribution functions, experimental investigations have so far been limited to ensembles with a bimodal distribution[15,16] and to comparison of apparent diffusional coefficients[17].

In this paper, a study of molecular weight and polydispersity of NBS PS–706 polystyrene at the theta temperature will be described. Precision correlation data were obtained by using a newly constructed full-photon counting instrument[18]. Correlation functions were numerically computed with parameterized Schultz and log-normal molecular weight distributions using the proper particle scattering function $P(\theta)$ and concentration dependent diffusion constant D. These correlation functions were fit to the experimental measurements to determine the parameters in the distribution functions. The concentration dependence of D was obtained from measurements on four monodisperse polystyrene samples with molecular weights from 1.1×10^4 to 4.1×10^6 g/mole. In this paper, we will first review the background theories of QELS and describe the experimental and computational procedures. Then the concentration dependence of the diffusion constant determined using monodisperse polystyrenes and the molecular weight and polydispersity results for the polydisperse polystyrene PS–706, will be presented.

Background theory

For a polydisperse polymer solution, the electric field autocorrelation function of the scattered light is[8]

$$g^{(1)}(\tau) = \frac{\Sigma_i M_i f(M_i) P(q,M_i) \exp(-q^2 D_i \tau)}{\Sigma_i M_i f(M_i) P(q,M_i)} \tag{1}$$

where $f(M_i)$ is the weight fraction of species i with molecular weight M_i, diffusion constant D_i and particle scattering function $P(q,M_i)$ at scattering wave vector q with $|q| = (4\pi/\lambda)\sin(\theta/2)$; λ is the wavelength of light in the scattering medium and θ is the scattering angle. Equation 1 reduces to

$$g^{(1)}(\tau) = \exp(-q^2 D\tau) \tag{2}$$

for a monodisperse polymer.

The Schultz and the logarithmic normal distributions are used for $f(M)$. The Schultz distribution of molecular weight M is given[19] in terms of the parameters y and z by

$$f(M) = y^{(z+1)} M^z \times \exp(-My)/\Gamma(z+1) \tag{3}$$

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where Γ is the gamma function and the parameters y and z are given in terms of the molecular weight averages by

$$z = 1/(M_w/M_n - 1) \quad . \tag{4}$$

$$y = (z + 1)/M_w \tag{5}$$

where M_n and M_w are number averaged and weight averaged molecular weight.

We substitute

$$M = w/y \tag{6}$$

in equation 3, substitute equation 3 in equation 1 and replace summation by integration to give

$$g^{(1)}(\tau) = \frac{\int_0^\infty w^{z+1} P(q,M) \exp(-q^2 D\tau) \exp(-w) dw}{\int_0^\infty w^{z+1} P(q,M) \exp(-w) dw} \tag{7}$$

On the other hand, the logarithmic normal distribution is given[19] in terms of the parameters B and s by

$$f(M) = \frac{\exp[-(\ln M - B)^2/2s^2}{(2\pi)^{1/2} sM} \tag{8}$$

where B and s are given by

$$B = \frac{1}{2} \ln(M_w M_n) \tag{9}$$

$$s^2 = \ln(M_w/M_n) \tag{10}$$

We substitute

$$v = (\ln M - B)/2^{1/2}s \tag{11}$$

in equation 8 and substitute equation 8 in equation 1 to give

$$g^{(1)}(\tau) = \frac{\int_{-\infty}^{+\infty} \exp(2^{1/2}sv) P(q,M) \exp(-q^2 D\tau) \exp(-v^2) dv}{\int_{-\infty}^{+\infty} \exp(2^{1/2}sv) P(q,M) \exp(-v^2) dv} \tag{12}$$

In order to evaluate $g^{(1)}(\tau)$ by either equation 7 or 12, expressions for the particle scattering function, P, the diffusion constant, D, of the polymer solution are required. Since the experiment was performed at the theta temperature, the Debye function[20,21]

$$P(q,M) = 2[X - 1 + \exp(-X)]/X^2 \tag{13}$$

with

$$X = q^2 R_G^2$$

and

$$R_G^2 = 9 \times 10^{-18} M$$

was used for the particle scattering function. Where the radius of gyration R_G is in cm and molecular weight M in g/mole.

The diffusion constant D can be expanded in the polymer concentration as[20]

$$D = D_0(1 + k_D c + \ldots) \tag{14}$$

At the theta temperature, equation 14 can be expressed as[22]

$$D = A(M^{-1/2} - k_c c) \tag{15}$$

In the homodyne configuration, which was used for this study, the experimental intensity autocorrelation function is obtained as

$$C(j) = \frac{\Sigma_i n(i) n(i+j)/N}{(\Sigma_i n(i)/N)^2} \tag{16}$$

where $n(i)$ and $n(i+j)$ are the number of photon counts for a period $\Delta\tau$ centered at times i and $i+j$, respectively, and N is the total number of averages. In this full-photon counting method, equation 16 does not contain errors due to clipping the photon counts. The relationship between the intensity correlation function and the field correlation function has been shown to be[1]

$$C(\tau) = 1 + \beta [g^{(1)}(\tau)]^2 \tag{17}$$

where β is related to the efficiency of the homodyne experiment and is treated as an adjustable parameter that is determined from the measurements.

For a monodisperse polymer sample, we may substitute equation 2 in equation 17 to give

$$C(\tau) - 1 = \beta \exp(-2q^2 D\tau) \tag{18}$$

We should point out that equation (1) is only strictly applicable to a system of noninteracting particles. In a polymer solution, the particle scattering function of a molecule may be dependent on the concentration of the solution due to conformational changes in the molecule caused by interaction with other molecules. In addition, the scattered light from the individual molecules will interfere. However. at the theta temperature, the conformations and therefore the particle scattering functions of the molecules do not depend on concentration. Also, the interference of the scattered light from the individual molecules is negligible for concentrations up to 7 mg/ml used in this investigation, as has been shown by conventional light scattering experiments. Therefore, equation 1 is a good approximation for the conditions of these experiments.

On the other hand, the diffusion coefficient, D, of a polymer molecule at the theta condition, given by equation 15, is dependent on concentration even for the low concentrations, 7 mg/ml, used in this investigation. This has been predicted by theory[20] and demonstrated by experiments[23]

Table 1

Sample	M_w	M_w/M_n	$k_c' \times 10^2$ $cm^3 g^{1.5}$ $mole^{0.5}$	$A \times 10^4$ $cm^2 sec^{-1}$ $g^{0.5}$ $mole^{-0.5}$
PC–4b	1.1×10^5	1.06	6.12	1.38
PS–705	1.79×10^5	1.07	5.99	1.37
PC–13a	6.7×10^5	1.15	5.60	1.44
F–4	4.1×10^6	1.1	5.26	1.36
Ave.			5.74	1.38
PS–706		2.1		

However, even though the diffusion coefficient $D_0 = AM^{-1/2}$ at zero concentration depends on the molecular weight, the change of the diffusion coefficient with concentration, $D - D_0 = -Ak_c c$ by equation 15, is independent of the molecular weight of the polymer. Therefore,equation 15 will later be applied to individual polymer species of the polydisperse polymer sample using the total concentration of all polymer species for the concentration, c.

EXPERIMENTAL

Quasielastic light scattering

All experiments were carried out on a full-photon counting spectrometer[18]. A 4880Å line from an Ar-ion laser was used for this experiment. A cylindrical scattering cell was used and mounted at the center of a thermostatted, refractive index matched bath-goniometer. Scattered light at any desired scattering angle was collected through a periscope arrangement and detected by a thermo-electrically cooled ITT FW–130 photo-multiplier. The photon pulses were amplified, discriminated, and counted for desired intervals; then the counted number was transferred into a minicomputer through direct memory access. The full-photon counting (non-clipped) correlation function and the accidental counts were computed and averaged in real time. The results were transferred into a Univac 1108 computer for further analysis.

The temperature was controlled at 35.0 ± 0.2°C throughout the experiment.

Sample preparation

Four monodisperse polystyrene samples and one polydisperse sample were used in this study. They are listed in *Table 1*, together with their molecular weights, and M_w/M_n ratios. The molecular weights and M_w/M_n ratios of PC–13a and PC–4b were supplied by Pressure Chemical Co. The F–4 sample was kindly supplied by Professor Fetters from Akron University. The PS–705 and PS–706 samples are NBS Standard Reference Materials. Solutions of the polymers in ACS grade cyclohexane were used. The solutions were kept at 40°C, stirred gently overnight, and then filtered through a 0.45 μm millipore filter into the scattering cells. However, filtration of the solution was found to degrade the very high molecular weight F–4 sample since its molecular weight obtained from measurement of its diffusion constant after filtration was about 10% less than the reported value of 4.1×10^6. Therefore, the samples of F–4 were prepared by filtering cyclohexane into volumetric bottles containing the polymer. The bottles were then kept at 40°C for one day with occasional gentle shaking. The molecular weights determined from diffusion constant measurements with these solutions agreed with the reported value.

Computational method

The measured correlation functions of the monodisperse polystyrenes at each solution concentration were fitted to equation 2 by a nonlinear regression program to obtain the diffusion constant D. However, for the polydisperse sample, a more complicated fitting procedure was required. The correlation function of the polydisperse sample with a Schultz molecular weight distribution is given by equation 7. Suppose that the molecular weight averages M_w and M_n of the sample are known, then the parameters z and y may be calculated by equations 4 and 5 and the integrals in equation 7 numerically evaluated to give the correlation function. The integrals were evaluated by Laguere[24] integration using five terms.

In order to perform the integrations, the integrands must be evaluated for given values of w. However, the value of P and D in the integrands depend on the molecular weight and therefore, also on w. Therefore, for each value of w the corresponding molecular weight M was computed by equation 6 and then values of P and D were calculated by equations 13 and 15, respectively.

In our case, the values of M_w and M_n were not known, but are to be determined iteratively from the measured correlation function $C(\tau)$. Therefore, we assumed a series of values of M_w and M_n. For each set of values of M_w and M_n, the theoretical autocorrelation function $g^{(1)}(\tau)$ is computed by equation 4, 5 and 7. Then the value of β is determined by a least-squares fit to equation 17. The standard deviation of this fit will be small if the assumed values of M_w and M_n are close to their true values. Therefore, the values of M_w and M_n that gave the smallest standard deviation were chosen as the solutions.

The analysis was also performed using the logarithmic normal distribution for the molecular weight distribution of the polydisperse polystyrene. The method of calculation is similar to that given above except that Hermite[24] integration was used to evaluate the integrals in equation 12.

RESULTS AND DISCUSSION

The analysis for the polydisperse polystyrene requires accurate values of A and k_c' to calculate the diffusion constant by equation 15. However, the available literature values of k_c', ranging from 0.0336 to 0.0552 $cm^3\ g^{-1.5}\ mole^{0.5}$, are not sufficiently accurate.

Therefore, the concentration dependence of the diffusion coefficient was determined from measurements on four monodisperse polystyrene samples. The autocorrelation functions of each sample were measured for at least four concentrations at four or more angles at each concentration. A typical set of correlation data, $(C(\tau) - 1)$, for SRM 705 at 2.65 mg/ml and a scattering angle of 30° is shown in *Figure 1*. The fit of the correlation data to equation 18 is shown by the solid line with $q^2D = 2.68 \times 10^3\ sec^{-1}$. Values of q^2D determined for each concentration at different angles were then fit to q^2 to obtain the corresponding diffusion constant D. Two typical sets of data from polystyrenes PS–705 and F–4 at concentrations of 2.65 and 0.975 mg/ml, respectively, are displayed in *Figure 2*. These values of the diffusion coefficient at each concentration were then fitted to a linear dependence of the concentration c according to equation 15 to obtain A and k_c'. *Figure 3* shows the diffusion coefficients for all four samples and the least square fitted lines of D *versus* c.

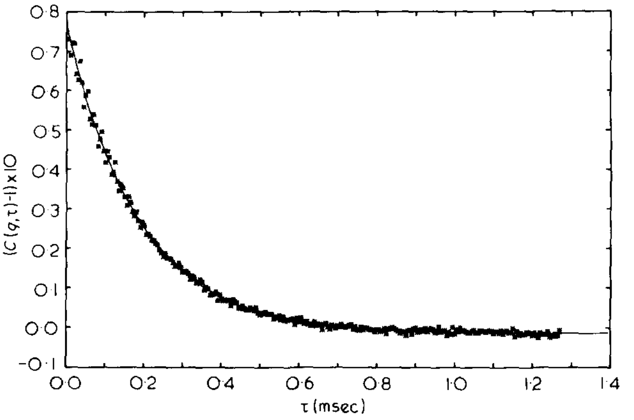

Figure 1 The intensity autocorrelation function $C(\tau)$ minus 1 *versus* time for polystyrene sample PS–705 at a concentration of 2.65 mg/ml and a scattering angle of 30°. The fit of the experimental values to equation 18 is shown by the solid line with q^2D = 2.68 x 10^3 $\sec^{-1}$

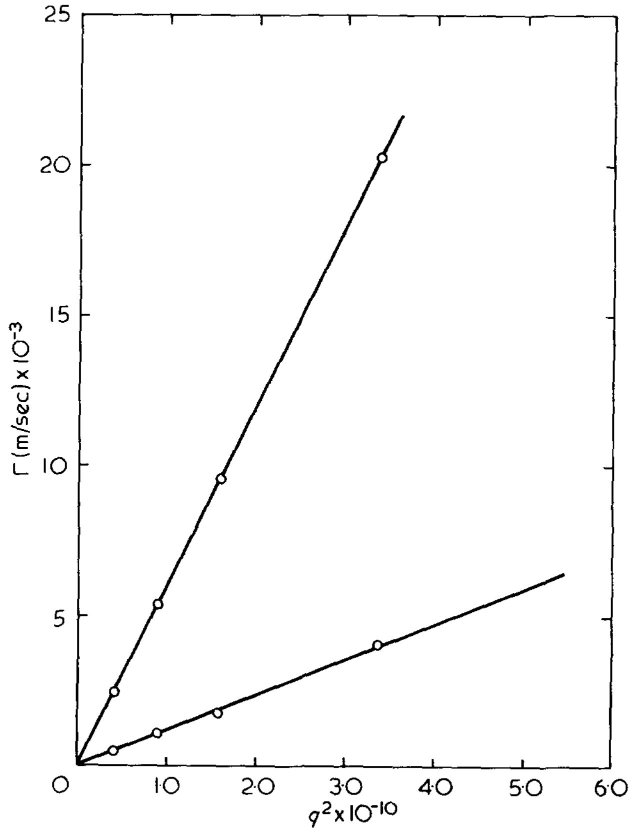

Figure 2 Values of q^2D *versus* q^2 for polystyrene samples (A) PS–705 and (B) F–4 at concentrations of 2.65 and 0.975 mg/ml, respectively. Their diffusion coefficients, D, are given by the slopes of the lines (A) = (3.021 ± 0.009) x 10^{-7} cm^2/s; (B) = (0.599 ± 0.009) x 10^{-7} $\mathrm{cm}^2/\mathrm{sec}$

The intercept of D at zero concentration is given by equation 15 as

$$D_0 = AM^{-1/2} \tag{19}$$

Equation 19 was verified by plotting in *Figure 4* the logarithm of D_0 for each sample against the logarithm of the molecular weight of the sample. A straight line of slope – 1/2 is obtained as predicted by equation 19.

Values of A and k_c' were computed for each sample from the intercept, D_0, and slope of the lines in *Figure 3*, using equation 15. They are tabulated in *Table 1*. The average values of A and k_c' obtained are 1.38 ± 0.04 x 10^{-4} $\mathrm{cm}^2\ \mathrm{sec}^{-1}\ \mathrm{g}^{0.5}\ \mathrm{mole}^{-0.5}$ and 5.74 ± 0.39 x 10^{-2} $\mathrm{cm}^3\ \mathrm{g}^{-1.5}\ \mathrm{mole}^{0.5}$, respectively. The values are used with equation 15 in the analysis of the polydisperse polystyrene sample. A small correction for partial specific volume has been neglected in the calculation of k_c'. The intensity autocorrelation functions $C(\tau)$ *versus* time τ of the polydisperse polymer PS–706 were measured for 11 conditions of solution concentration and scattering angles, with the concentrations ranged from 1.25

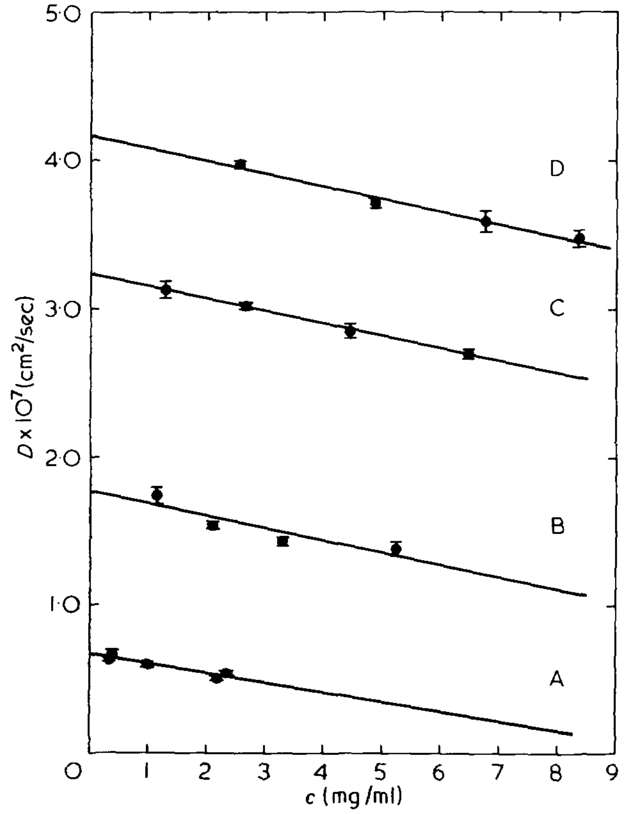

Figure 3 The diffusion coefficients, D, of the four monodisperse polystyrene samples A, F–4; B, PC–13a; C, PS–705; D, PC–46, *versus* solution concentration. The fitted lines to the data are also shown

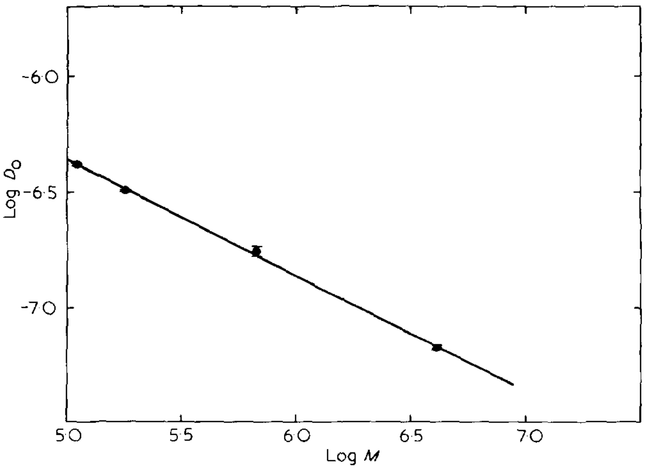

Figure 4 The logarithm of the diffusion coefficients, D_0, at zero solution concentration for the polystyrene samples in cyclohexane at 35.0 ± 0.2°C *versus* the logarithm of their molecular weights. The values fit a straight line of slope – 1/2 according to equation 19. D_0 = (1.38 ± 0.04) x 10^{-4} $M^{-1/2}$

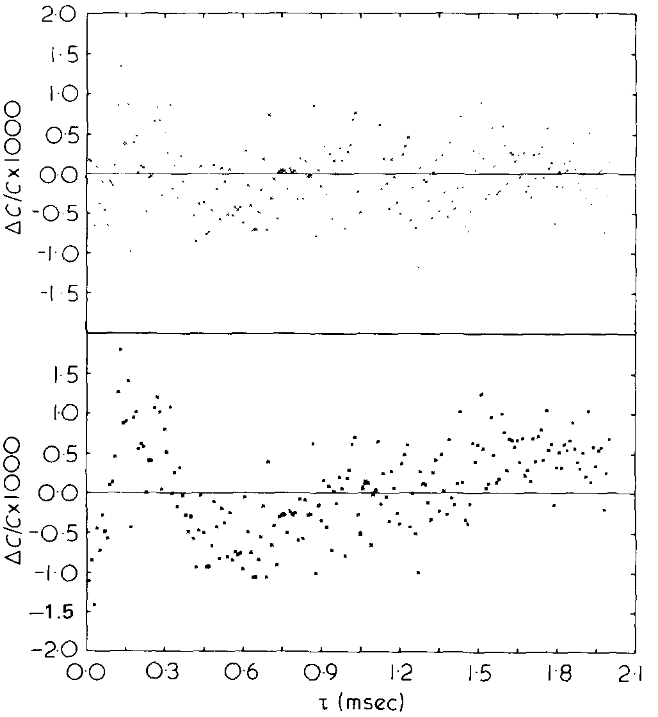

Figure 5 The relative deviation of the fit of the data to equation 17. The Schultz molecular weight distribution was used for the upper set of data and a monodisperse sample was used for the lower set of data

to 6.92 mg/ml and the scattering angles ranged from 15 to 60°. For each of these conditions, the field autocorrelation functions $g^{(1)}(\tau)$ were calculated as described in the preceding section for assumed values of the weight average molecular weight, M_w, and the polydispersity ratio, M_w/M_n, of the sample.

Then the intensity and field autocorrelation functions were fitted by least squares to equation 17 to determine the value of β. An example of the deviation obtained from such a fit is shown by the upper plot in *Figure 5*. In this case, the concentration $c = 2.85$ mg/ml, the scattering angle was 30°, the assumed values for the molecular weight and polydispersity ratio were 2.5×10^5 and 2.0 respectively, and the Schultz molecular weight distribution was used. The deviations are seen to be random with respect to time.

A test to justify the use of a molecular weight distribution was made. The above data were also fitted to equation 18 which applies for the case of a monodisperse polymer and therefore neglects the molecular weight distribution of the polymer sample. The deviations from this fit are shown in the lower half of *Figure 5* and are seen to be nonrandom with respect to τ. Therefore, the data cannot be adequately fitted without use of the molecular weight distribution of the polymer sample.

For each set of assumed values of M_w and M_w/M_n, the intensity and field autocorrelation functions were fitted by least squares to equation 17 and the standard deviations were averaged for all 11 sets of data. This average standard deviation, σ, measures how well the assumed values of M_w and M_w/M_n fit the data. This was repeated for assumed values of M_w ranging from 2.5×10^5 to 2.95×10^5 in steps of 0.05 $\times 10^5$ and for values of M_w/M_n ranging from 1.1 to 2.3 in steps of 0.1. The standard deviations, σ, are shown as a contour graph in *Figure 6*. The minimum standard deviation of 7.2×10^{-4} occurs for $M_w = 2.68 \times 10^5$ and $M_w/M_n = 1.7$. These values can be compared with values on the National Bureau of Standards certificate for PS–705 of $M_w = 2.58 \times 10^5$ by light scattering, $M_w = 2.88 \times 10^5$ by ultracentrifugation, and $M_w/M_n = 2.1$ from a fractionation study. The value of M_w is thus in excellent agreement with the certificate value, but the polydispersity M_w/M_n, is only in fair agreement.

The preceding analysis assumed the Schultz molecular weight distribution for the thermally polymerized PS–706 polystyrene. In order to evaluate the effect of this assumption, the data were reanalysed using the log-normal molecular weight distribution. The minimum standard deviation of 7.3×10^{-4} was obtained, which is only slightly higher than the minimum standard deviation of 7.2×10^{-4} obtained previously, but is located at $M_w = 2.75 \times 10^5$ and $M_w/M_n = 1.4$.

The contour graph is similar in shape to the prevous one shown in *Figure 6*. In both graphs, the standard deviation of the fit increases rapidly if M_w is varied from the value corresponding to the minimum standard deviation, while the standard deviation increases much more slowly if M_w/M_n is varied from the value corresponding to the minimum standard deviation. Thus the fit of the data is insensitive to the assumed value of M_w/M_n and the value of M_w/M_n determined by the fit is very dependent on the assumed molecular weight distribution function and the error of the experimental data. On the other hand, the value of M_w is insensitive to the assumed distribution function so can be accurately determined from the fit to the data.

CONCLUSIONS

The weight averaged molecular weight, M_w, measured by quasielastic light scattering is seen to be accurate and insensitive to the molecular weight distribution function that is assumed. However, the measured value of the polydispersity is only of fair accuracy and is very sensitive to the distribu-

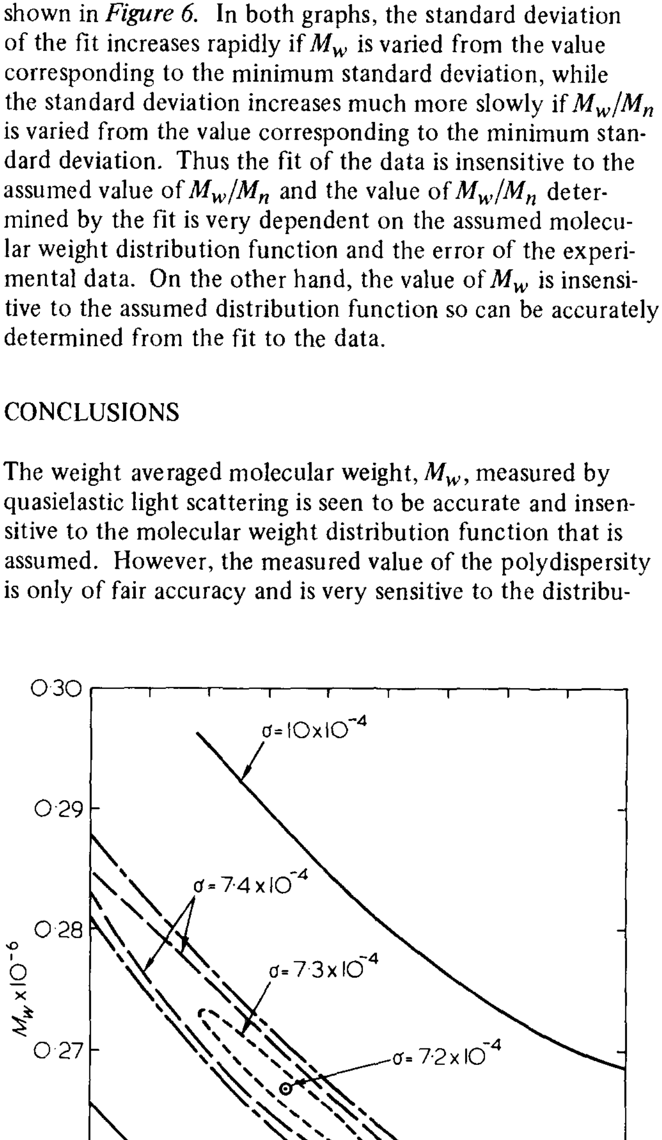

Figure 6 The standard deviations of the fit of the data for the polydisperse polymer PS–706 to equation 17 for assumed values of the weight average molecular weight and polydispersity of the polymer

tion function used in the analysis. Quasielastic light scattering therefore gives values of the weight average molecular weight at least as accurate as elastic light scattering and also gives a crude estimate of polydispersity of the polymer. It has the additional advantages that the experimental measurements are faster and it is not as sensitive to dust particles in the polymer solution. Also it does not depend on secondary standards such as the differential refractive index increments (dn/dc) and the Rayleigh ratio of benzene as does conventional light scattering.

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