

Evaluation of internal dynamics in linear macromolecules

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Photon correlation spectroscopy has been used extensively as an attractive method to determine the relaxation times of the low order long range internal modes in large polymers. The extraction of this data from practical polymers is shown here to be sensitive to very small degrees of polymer polydispersity. The S-exponential sum method is used to investigate the conditions under which this measurement can be made and still yield meaningful intramolecular dynamical information.

(Keywords: internal dynamics; photon correlation spectroscopy; exponential analysis)

INTRODUCTION

The investigation of the internal dynamics of high molecular weight polymers provides valuable information to evaluate theoretical models of random coil scattering systems in the presence of hydrodynamic interactions. In the course of this study we found that the presence of polydispersity in the scattering system profoundly influences the extraction of internal mode information; this we could have predicted from the results of our earlier computer simulations^{1,2}. When dealing with high molecular weight polymers it is very difficult to obtain monodisperse scattering samples, this is mainly because it is difficult to manufacture the polymer with a narrow weight distribution and high molecular weight and so we conclude that the polydispersity problem should be considered when analysing photon correlation functions from these systems. It is possible to use lower molecular weight samples (e.g. $M_w < 2 \cdot 10^6$) which can be monodisperse but this is undesirable because we then have to observe the fluctuations at higher scattering angles in order to satisfy the condition $KR_G \geq 1-2$ for the internal motions to be detectable. Also we then have a decrease in the scattered intensity which makes the accumulation of good quality data sets very difficult.

In previous papers^{1,2} we have demonstrated that it was possible to obtain polydispersity information from the parameters of the S-exponential sum^{3,4} without having to input 'a priori' information about the type of particle size distribution or the data accuracy. Having shown with computer simulated unimodal and bimodal distribution data sets that it was possible to calculate the correct moments of the distribution with an accuracy dependent upon the data accuracy we went on to show that the same was true for real experimental data sets of the unimodal distribution types². In this paper we consider the determination of the moments of a bimodal distribution for data sets which consist of a linewidth distribution and an internal mode component.

THE DYNAMICAL REGIMES

When considering polymeric systems it is useful if we quantify the characteristic length that describes the scattering system and also the characteristic length that describes the scattering probe. We can define the following two dimensions.

(1) In dilute solutions the scattering species are well separated and so we may consider them as being independent. The only characteristic length of any importance is then some quantity which is a measure of the average polymer dimension and which is usually taken to be the radius of gyration of the scattering species. In concentrated solutions we can no longer consider the scattering species as being independent and for the particular case of a random coil macromolecule it can be considered that, since there are many contact points between the coils, the polymer solution behaves as a polymer network swollen by the solvent. The important characteristic length is then the average distance between contact points. In this pseudo-gel regime the average contact distance can be shown to be^{5,6}

$$\xi = R_G(c/c^*)^{\nu/(1-\nu)}; \quad \nu = 0.6 \quad (1)$$

where c is the solution concentration, R_G is the radius of gyration of the random coil and c^* is the critical concentration which delimits the dilute and pseudo-gel regions and is defined as the concentration at which R_G is equal to the average macromolecular separation.

$$c^* = M/(R_G^3 A) \quad (2)$$

where A is Avogadro's constant.

(2) Apart from the lengths associated with the scattering system we also have to consider the characteristic length of the scattering probe; at a given scattering angle we measure only those fluctuations which have imparted a given momentum transfer q and so the scattered light reflects properties of the scattering system on a length

scale of order q^{-1} . As we go to higher scattering angle the observed scattering vector increases and so we probe fluctuations that provide information on the local properties of the random coil.

A convenient graphical summary of the various dynamical regimes is shown in Figure 1 where we illustrate qR_G against (c/c^*) . In the study presented here we have worked at concentrations much less than the critical concentration and so we are not concerned with the pseudo-gel properties of the polymer network.

In the dilute regime we may define three separate regions depending upon the observed scattering vector.

(a) $qR_G \ll 1$. The characteristic length of the probe is very much greater than the radius of gyration of the scattering species and it is only possible to measure the motion of the centre of mass. The autocorrelation function then has the form

$$|g^{(1)}(t)| = |E(t)E(t+\tau)| \propto S(q\tau) \propto e^{-Dq^2\tau} \quad (3)$$

where $S(q,\tau)$ is the dynamic scattering factor and D is the diffusion constant of the scattering species.

(b) $qR_G = 1-2$. In this intermediate region the radius of gyration and the inverse scattering vector q^{-1} are comparable in size and so we can access both internal motion and diffusive dynamics. The autocorrelation function then has the approximate form

$$|g^{(1)}(\tau)| \propto S(q,\tau) \propto A_1 e^{-q^2 D\tau} + A_2 e^{(-q^2 D\tau + 2\tau/\tau_1)} \quad (4)$$

where τ_1 is the characteristic time of the first Rouse-Zimm mode; the exact expression depends upon the model of the scattering system used. In this intermediate region the higher internal modes are only of small amplitude and do not contribute significantly to the correlation functions. Equation (4) is only correct when all the macromolecules have the same radius of gyration and it is one of the aims of this paper to see how, in the presence of polydispersity and taking due regard of the limited and finite resolution in linewidth space, the extraction of internal mode information can be made. We will see that it is a very difficult separation problem.

(c) $qR_G \gg 1$: The length scale of the probing scattering vector is very much smaller than the radius of gyration of the macromolecule and so we can only access information about the local internal motions of the chain. At higher values of qR_G the set of internal modes cannot be

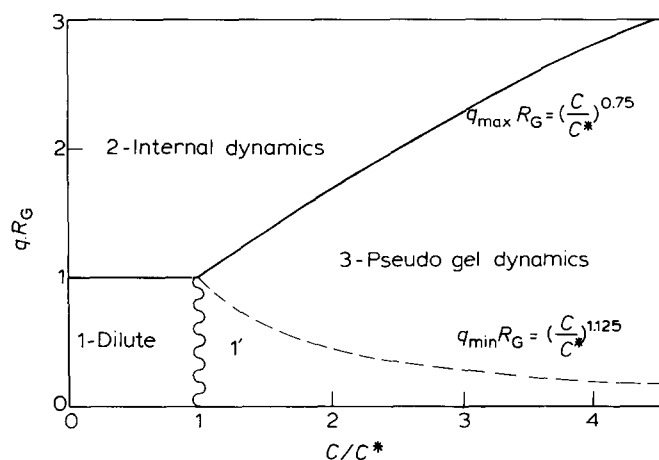


Figure 1 Dynamical regimes for size and concentration variation

individually observed and we have to consider instead a collective mode. The time dependent correlation function has been evaluated for the Rouse model in the presence of hydrodynamic interactions by de Gennes and Dubois-Violette^{7,8} where they find

$$S(\underline{q},t) = S(\underline{q}t) \cdot G(\tau^{-1}(q)t) \quad (5)$$

with

$$G(\tau^{-1}(q)t) = (\tau^{-1}(q)t)^{2/3} \int_0^\infty du \exp(-u(1+h(u))(\tau^{-1}(q)t)^{2/3}) \quad (6)$$

$$h(u) = (4/\pi) \int_0^\infty \frac{dy \cos(y^2)}{y^3} (1 - \exp(-y^3 u^{-3/2})) \quad (7)$$

$$\tau^{-1}(q) = \frac{K_b T q^3}{2^{3/2} 3 \pi \eta} \quad (8)$$

We have investigated all three dynamical regions given above.

DEFINITIONS

Some of the parameters used in this paper have been presented elsewhere^{3,4}; we paraphrase them here for completeness.

(a) For two linewidths Γ_n and Γ_{n-1} to be resolved the inequality

$$\frac{\Gamma_n}{\Gamma_{n-1}} > \exp(\pi/\omega_{\max})$$

must be satisfied, with

$$\omega_{\max} \approx \frac{-2 \ln(\text{noise level})}{\pi \sqrt{\pi}}$$

The noise level is defined as

$$\begin{aligned} \text{noise level} &\approx \frac{(\text{r.m.s. residual after fitting})}{(\text{sum of exponential amplitudes})} \\ &= |N|/|E(0)| \end{aligned}$$

(b) The linewidths obtained from the S-exponential sum algorithm and heterodyne correlation decay curve can be used directly to obtain the moments of a linewidth by use of the following definition.

$$\mu_i = \frac{\sum_{i=1}^r (\Gamma_i - \bar{\Gamma})^i}{\sum_{i=1}^r a_i}$$

where

$$\bar{\Gamma} = \frac{\sum_{i=1}^r a_i \Gamma_i}{\sum_{i=1}^r a_i}$$

The a_i are the amplitudes of the exponential decays (not the background) and Γ_i are the corresponding derived linewidths.

EXPERIMENTAL

The scattering system chosen consisted of a high molecular weight polystyrene dissolved in benzene. At a scattering angle of 30 degrees and a consequent scattering vector of $1 \times 10^7 \text{ m}^{-1}$ it is possible to observe the first Rouse-Zimm mode when the solute has a radius of gyration of about $1-2 \times 10^{-7} \text{ m}$. The polystyrene/benzene system has been the subject of extensive studies and we calculate from the results of Adam and Delsanti⁶ for R_G that to satisfy the equality $qR_G=1$ we require a molecular weight of approximately 3×10^6 . We select to use as low a scattering angle as possible in order to provide a high scattered intensity giving the best signal-to-noise ratio. To enable higher molecular weight samples to be used than the value evaluated above of $3 \times 10^6 \text{ m}$, and thus allowing internal modes to be observed at a scattering angle of 30 degrees with an incident wavelength of 488 nm, we have to either decrease the observed angle or increase the wavelength. The first alternative of decreasing the angle is not desirable because at angles less than some twenty degrees we encounter dust contamination effects which are especially severe with high molecular weight samples because we prefer to clean by centrifugation at speed of less than 6000 r.p.m. to avoid degradation. The second alternative is readily attained by tuning the argon ion laser to the 514.5 nm line or by using a 50 mW He-Ne laser.

The polystyrene samples used in this study were purchased commercially from the Pressure Chemical Company with the following characterization.

(a) *Sample I.* The weight-averaged molecular weight is $\bar{M}_w=13.4 \times 10^6$ and the polydispersity index $\bar{M}_w/\bar{M}_n < 1.5$. The polydispersity of the polystyrene samples gets rapidly worse for molecular weights greater than 15 million and so this sample was the largest molecular weight sample we used in determining the internal mode characteristic decay time.

(b) *Sample II.* The weight-averaged molecular weight $\bar{M}_w=10 \times 10^6$ and the polydispersity index $\bar{M}_w/\bar{M}_n < 1.2$.

(c) *Sample III.* The weight-averaged molecular weight $\bar{M}_w=9.5 \times 10^6$ and the polydispersity index $\bar{M}_w/\bar{M}_n < 1.1$.

Solutions were made by dissolving a known weight of the polymer into a known volume of benzene and the solutions were firmly sealed and left for at least two weeks at slightly raised temperature to ensure that the polystyrene was completely dissolved. In the preparation of the solutions we ensured that the concentration was much less than the critical concentration; the resulting solution parameters are:

(1) Sample I

concentration = $0.000456 \text{ g ml}^{-1}$
critical concentration = 0.0014 g ml^{-1}
 R_G = 252 nm

(2) Sample II

concentration = $0.000736 \text{ g ml}^{-1}$
critical concentration = $0.00174 \text{ g ml}^{-1}$
 R_G = 212 nm

(3) Sample III

concentration = 0.0001 g ml^{-1}
critical concentration = $0.00181 \text{ g ml}^{-1}$
 R_G = 206 nm

From the concentration values given above it is evident that all solutions have a concentration much less than the critical concentration and correspond to the dilute regime in *Figure 1*. To prepare a dust free sample for the spectrometer we used the method of spinning round sample cells in the centrifuge at speeds not exceeding 6000 r.p.m. for periods of two or more hours. The cell was transferred from the centrifuge to the spectrometer with great care and was allowed to temperature equilibrate for several hours.

Since the polystyrene samples are slightly polydisperse the initial investigation consisted of a continuation of the previous report^{1,2} whereby we could verify the results of the computer simulations of the bimodal polydisperse systems. This initial study is also necessary to establish which of the bimodal distributions given previously^{1,2} best represents our scattering system. From this knowledge we can predict whether the accurate determination of the first internal mode is feasible and, if so, under what conditions of parameters such as scattering angle, molecular weight, etc., we could best accomplish the determination of the first internal mode characteristic decay time.

A photon correlation spectrometer of advanced design⁹ was used for these studies, allowing heterodyne detection over the full range of scattering angles.

RESULTS

Extraction of moment information from bimodal linewidth distribution functions using experimental photon correlation data

If we initially restrict our attention to scattering angles such that we satisfy the inequality: $0 < qR_G < 2$, then the autocorrelation function will consist of one or two exponential decay components, the characteristic times of which are given by

$$\Gamma_1 = Dq^2 \quad \Gamma_2 = Dq^2 + 2/\tau_1$$

The first component is due to the diffusive motion of the centre of mass of the random coil and so is angular dependent as the square of the scattering vector. The second component consists of a diffusive part with an additional component due to the first internal mode and which is angular independent if we neglect the influence of higher order internal modes. The presence of the angular independent component is very convenient for investigating bimodal distributions because, by changing the scattering angle, we can vary the linewidth separation between the two peaks and so investigate the imposing of the resolution constraint¹⁻⁴ upon accurate linewidth information extraction. To obtain the best signal-to-noise with the three samples we need to observe the fluctuations at as low a scattering angle as possible and a consequence of this is that we need to use as high an incident wavelength as possible with the high molecular weight samples in order to avoid using scattering angles lower than 20 degrees, where spurious dust scattering problems are encountered. We initially used a helium-

neon laser but, as we will show later, at 50 mW this has insufficient laser power to obtain a good signal-to-noise ratio and so we had to compromise by using the 514.5 nm excitation line of the argon ion laser. The scattering vector for this wavelength at 298 K in benzene is $1.1 \times 10^7 \text{ m}^{-1}$ at an angle of 35 degrees.

In the first experiment undertaken polystyrene Sample I was used at 298 K. We formed 20 independent correlograms using an integration time of 30 minutes per data set and the linewidth information from the S-exponential sums found by using the S-exponential algorithm^{3,4} is shown in Figure 2. At this scattering angle we calculate that $qR_G = 2.8$ and on the basis of the free-draining polymer model we expect that the presence of the higher internal modes would complicate the analysis but in Figure 2 we can clearly identify an internal mode contribution at a linewidth of $2417 \pm 350 \text{ Hz}$. This is attributed to the first internal mode relaxation time for the following two reasons.

(a) When hydrodynamic interactions are accounted for Perico *et al.*¹⁰ has shown that the amplitude of the internal mode contribution to the spectrum is enhanced relative to the amplitude of the diffusive component.

(b) The value of qR_G is still small enough that we are not in the collective regime so that the individual modes should still be present. The relaxation time constant is a factor of four greater for the second internal mode as compared to the first internal mode, since we had sampled the data so that the diffusive component was correctly

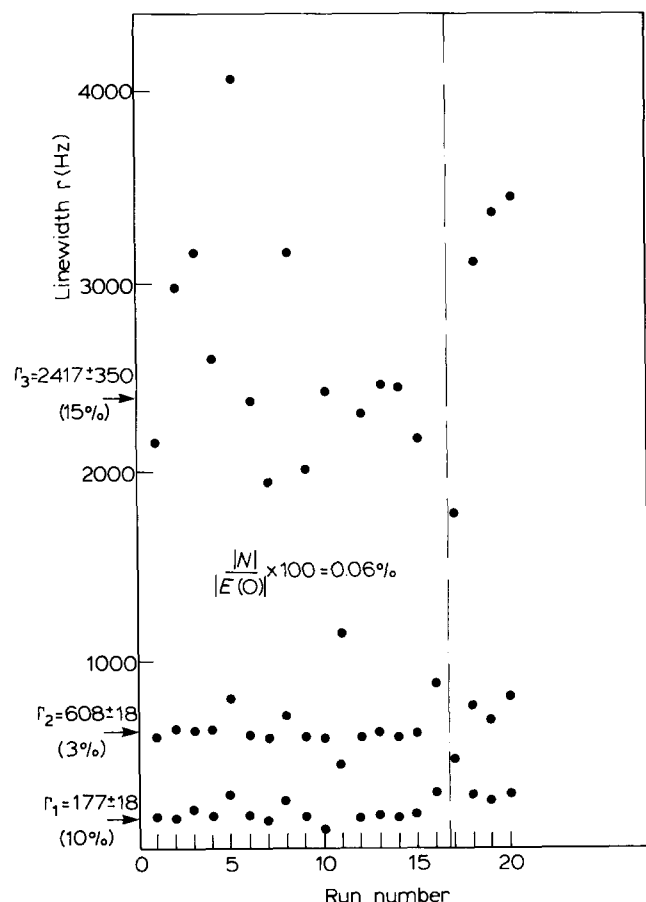


Figure 2 Photon correlation linewidths obtained from the S-exponential method for 20 separate heterodyne experiments on a sample of polystyrene of molecular weight 13×10^6 in benzene. Concentration = 0.000456 g/ml, temperature = 298K, scattering angle = 35 degrees

sampled as discussed in ref. 3, then these faster decaying components would only significantly contribute to the first few channels of the correlator and so would be very poorly defined.

From Figure 2 the other important feature to note is the presence of two plateau regions in the linewidth values of the S-exponential sums at the lower linewidth values of 608 ± 18 and $177 \pm 18 \text{ Hz}$ and this we attribute to the polydispersity of the polystyrene macromolecule. We have isolated these lower linewidth regions and (as in ref. 2) we have calculated the moments of the linewidth distribution

$$\Gamma = 505 \pm 3\% \text{ Hz} \quad \mu_2/\bar{\Gamma}^2 = 0.143 \pm 8\%$$

$$D_z = 4.18 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1} \pm 3\%$$

If we use the value for the normalized second moment in the formulae,

$$\bar{M}_w \\ \bar{M}_n \approx 1 + \frac{\mu_2}{\bar{\Gamma}^2 \alpha^2}$$

then

$$\frac{\bar{M}_w}{\bar{M}_n} \approx \frac{M_z}{M_w} \approx 1.57 \pm 10\%$$

and this is in good agreement with the characterization supplied by the manufacturer. Using the above z -averaged molecular value and the equations of Adam and Delsanti⁶ we calculate that the z -average diffusion coefficient is $D_z^{\text{cal}} = 4.14 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and so we find that the results of the polydispersity analysis and the characterization supplied by the manufacturer are in very good agreement.

If we compare the data of this section with the simulated bimodal distribution sets in ref. 2 we see that we can model the scattering system by a bimodal linewidth distribution (type III of ref. 2) and we calculate that to be able to resolve the two peaks we require a data accuracy to better than 0.4%. Using the amplitude of the correlation function at time zero and the mean residual after fitting the data set with a positive S-exponential sum we calculate that the accuracy of the real experimental data is in the region of 0.6%, and since these two resolution calculations are roughly similar we are able to resolve the bimodal nature. We also note that the error limits upon the calculated moments are of the order we expect with a broad polydisperse system and this is in agreement with previous unimodal simulations¹.

In ref. 3 we stated that if two components can be resolved then the accuracy with which a linewidth component may be obtained is dependent upon the accuracy of definition of that particular component; we can use the experimental data here to illustrate this point. We consider the largest linewidth component from Figure 2 which we have calculated as having a value

$$\Gamma = 2417 \pm 350 \text{ Hz}$$

The sampling time used in the experiment was $200 \mu\text{s}$. The corresponding u -value has been defined³ as $u = \exp(-DK^2\Delta)$ where Δ is the sample time. Thus in this case $u = 0.617$ and hence the number of decay times for this component in a fifty point data set is 23. The

amplitude of this linewidth component is approximately 1/10 of the total time dependent amplitude and so we calculate that the data accuracy for the exponential is 6%. If we refer to the results for the single exponential analysis³ we have for oversampled data of 23 decay times the mean absolute deviation of the real linewidth value from the average calculated value is approximately 1–2 times the data accuracy and so we expect that the error on the linewidth u -value ($\equiv \exp(-DK^2\Delta)$) should be

$$u_{\text{estimate}} = 0.617 \pm 0.06$$

$$\Gamma = 2417 \pm 19\% \text{ Hz}$$

We find that our calculated error estimate is very close to the experimentally found value confirming both the single exponential analysis results and our double exponential results for exponential components of different amplitude.

Having confirmed with the above results that it is possible to extract useful internal mode information from a polydisperse high molecular weight polystyrene sample we decided to increase the scattering angle so that our scattering system could be modelled by other bimodal distributions (I or II in ref. 3). We expect that at the higher scattering angle information about the first internal mode is inaccessible due to the presence of a multitude of higher internal modes. To select the scattering angle we note that the data given above has given the results

$$2/\tau_1 = 2000 \text{ Hz} \quad \bar{D}_z = 4.18 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$$

and if we select a scattering angle of 50 degrees the scattering vector has a value $1.55 \times 10^7 \text{ m}^{-1}$ ($q^2 = 2.4 \cdot 10^{14} \text{ m}^{-2}$) then we expect that the linewidth separation of the two peaks to be $|1000 \text{ Hz} (Dq^2) - 3000 \text{ Hz}|$ and so the linewidth distribution function can be modelled by the simulated data set of the bimodal distribution (type II, ref. 3) and, because of the reduced scattering intensity and hence resolving power, we expect that meaningful information about both the internal modes and the polydispersity will not be possible.

The experiment was performed with the polystyrene sample of $M_w = 13.4 \times 10^6$ dissolved in benzene at the set concentration given previously. The intensity fluctuations were observed at a scattering angle of 50 degrees and the sample temperature was 298 K. The sampling time was set at 50 μs and 32 independent correlograms were formed using an integration time of 30 min per run. The results of analysing the data sets by the S-exponential algorithm are given in Figure 3 where we plot the linewidths of the S-exponential sum for all the data sets. What is immediately apparent is that there are two plateau regions centred at approximately 2000 Hz and 900 Hz and, if we follow the previous example, these should be due to the polydispersity of the sample. There is also a large linewidth component which is very uncertain and which we attribute to the presence of internal modes. In Figure 3 we have indicated a maximum value for the linewidth components which we have used to form the moments of the 'apparent' polydispersity. For the components of the S-exponential sum whose frequency is less than this delimiting line we have calculated

$$\bar{\Gamma} = 1218 \pm 9\% \text{ Hz} \quad \bar{D}_z = 5.07 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$$

$$\mu_2/\bar{\Gamma}^2 = 0.204 \pm 20\% \quad |N|/|E(0)| \approx 0.002$$

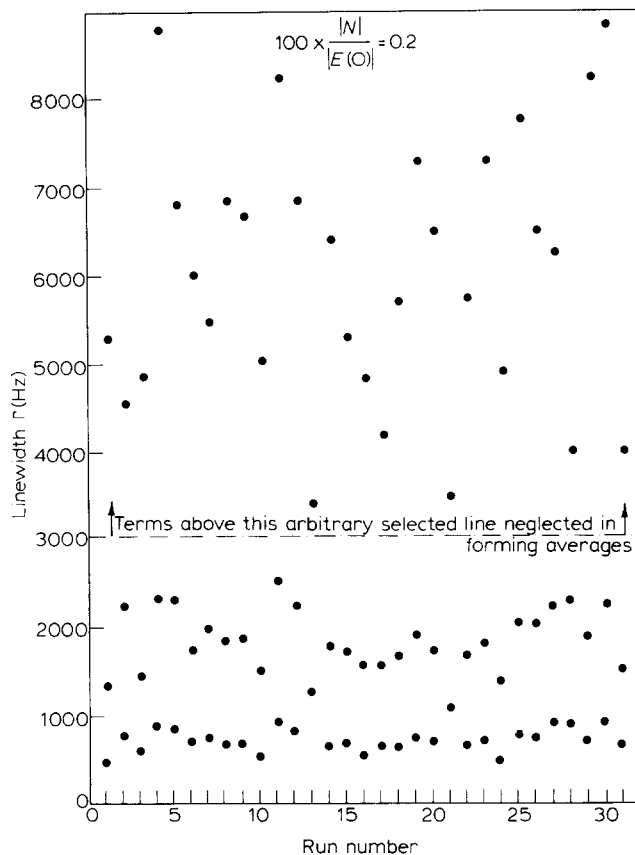


Figure 3 Linewidths for 35 separate heterodyne experiments for a sample of polystyrene of molecular weight 13×10^6 in benzene. Concentration = 0.000456 g/ml, temperature = 298 K, scattering angle = 50 degrees

If we compare these results with the results we obtained at a scattering angle of 30 degrees we find that the polystyrene sample now appears markedly more polydisperse and we attribute this to the presence of the first internal mode, at a linewidth of 3000 Hz, which cannot be resolved from the polydispersity because of the poor signal-to-noise value at the 50 degree scattering angle. This conclusion is in agreement with the results from the simulated bimodal distribution results (types I and II, ref. 3) where we have shown that we require a data accuracy in excess of 5×10^{-4} to be able to discern the bimodal distribution.

We conclude this section by mentioning that we attempted the above experiments using a 50 mW helium-neon laser but the data was orders of magnitude less accurate and we note that the polydispersity was very poorly extracted, a second high frequency linewidth component was present but it could not be accurately determined, these features we attribute to the poor resolving power obtained with the less intense He-Ne laser.

The results of this section have confirmed our resolution conditions of ref. 2 for bimodal polydisperse distributions and they have also shown that it is feasible to extract first internal mode information with data of good accuracy. The value of the first internal mode is dependent on molecular weight, typically¹¹ as

$$\tau_1 \propto M_w^{1.7}$$

and for a polydisperse scattering system the value of τ_1 is going to be a kind of weighted average. This interpre-

tation of the meaning of the measured τ_1 is difficult. To overcome this problem we have studied a very monodisperse sample of high molecular weight for which we shall now present some results.

Determination of the first Rouse-Zimm internal mode

We selected only those samples with a polydispersity index $M_w/M_n < 1.2$ and we further selected out any samples which showed a degree of polydispersity that was easily measured with our spectrometer and at the end of the search we were left with just two samples out of a starting batch of twelve. Even at this point the determination of the first internal mode relaxation time was not straightforward because one of the samples produced incorrect moment information and to explain this anomaly we performed another experiment upon a test mixture of monodisperse polystyrenes to verify our findings. These results are now presented.

Scattering sample II. The characterization of the sample gave a polydispersity index $M_w/M_n < 1.2$ and so we expect that the sample is on the limit of polydispersity detectability for our spectrometer. In ref. 2 we had not investigated the limit of a very narrow polydisperse system but in ref. 1 we have shown that if two exponentials could not be separated because the resolution limit had just been exceeded then it was still possible to obtain linewidth information but of poor quality. We have noticed that the S-exponential routine finds the best fit when the correlogram can be represented by two exponentials one of which has a large amplitude and another of small amplitude and variable linewidth which is always greater than the main component. We would then expect that for a polydisperse scattering system on the limit of resolution with internal modes present that the extraneous linewidth component due to the polydispersity would corrupt the accurate determination of the internal mode decay time. To investigate the influence of the resolution limit upon determination of the moments of a narrow polydisperse system we made up a solution (sample II) of three monodisperse samples of molecular weight

$$M_1 = 390\,000 \quad M_2 = 490\,000 \quad M_3 = 670\,000$$

and they were mixed in equal concentrations. We calculate that

$$\Gamma_3/\Gamma_1 = 1.347 \quad \Gamma_3/\Gamma_2 = 1.188 \\ I_1:I_2:I_3 = 1.0:1.107:1.46$$

and hence the moments of the distribution should be

$$\bar{\Gamma} = 2100 \quad \mu_2/\bar{\Gamma}^2 = 0.056$$

Scattering from the solution was observed at an angle of 30 degrees and the linewidth information from the S-exponential sum for a series of timed runs is shown in Figure 4. If we inspect graph (a) in Figure 4 which gives the linewidth of the S-exponential sum as a function of integration time we notice that there is an extraneous component with a linewidth greater than 4000 Hz and which does not reflect the known linewidth content of the scattering system. In the long integration time limit we find

$$\bar{\Gamma} = 1848 \text{ Hz} \quad \text{and} \quad \mu_2/\bar{\Gamma}^2 = 0.069$$

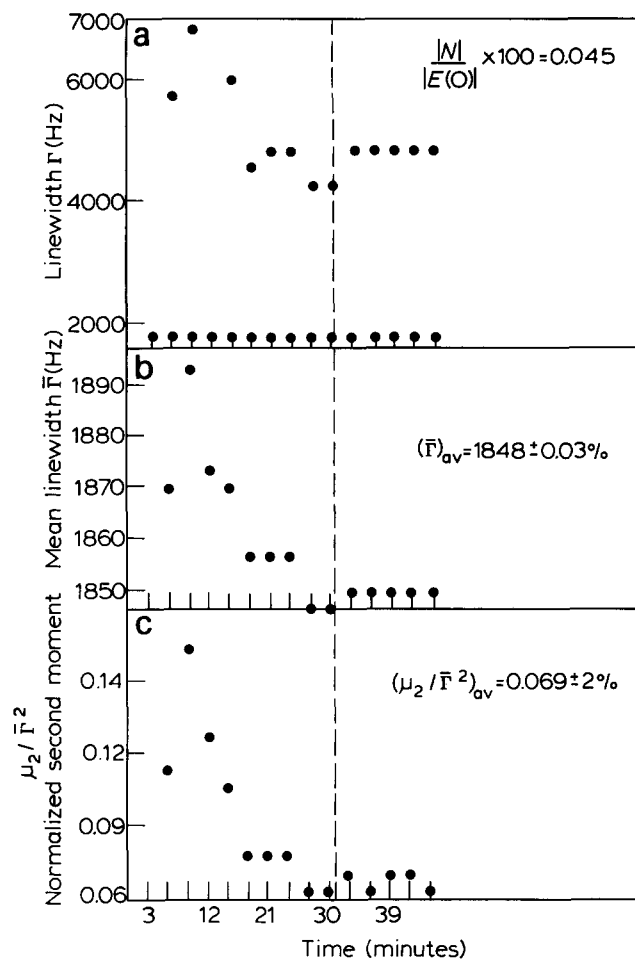


Figure 4 Scattering data from a mixture of polystyrene in benzene: $M_w^1 = 390\,000$, concentration = 0.000752 g/ml; $M_w^2 = 498\,000$, concentration = 0.000652 g/ml; $M_w^3 = 670\,000$, concentration = 0.00064 g/ml. Heterodyne detection, scattering angle = 30 degrees, sample time = 40 μ s

When we compare these with the known calculated values we see that we have poor agreement. We conclude that it is not sufficient merely to use fairly narrow fractions of polystyrene with $M_w/M_n < 1.2$ but a criterion for selecting the macromolecule, to be used to determine the first internal mode, should be that at low angle the auto-correlation function is purely single exponential so that any polydispersity which will inevitably be present cannot be detected because of lack of resolving power.

We can illustrate from sample II at an angle of 30 degrees and at a temperature of 298 K. The linewidth information obtained by analysing 20 independent data sets by the S-exponential algorithm is given in Figure 5. The integration time per run was 30 min and we had a data accuracy of 0.07% so that any spread in the linewidth values is due to the limited resolving power and not to insufficient accumulation time. In Figure 5 there is no distinct plateau regions and the spread in linewidth values is very large, this is a similar feature to that which we have previously reported for a bimodal system². From the data it is very difficult to separate the internal mode contribution and the polydispersity components.

At first sight it is rather surprising that as we increase the monodispersity of our sample that the derived linewidth information becomes less consistent but this is a direct consequence of the stringent resolving conditions which are of such paramount importance¹⁻⁴. Having

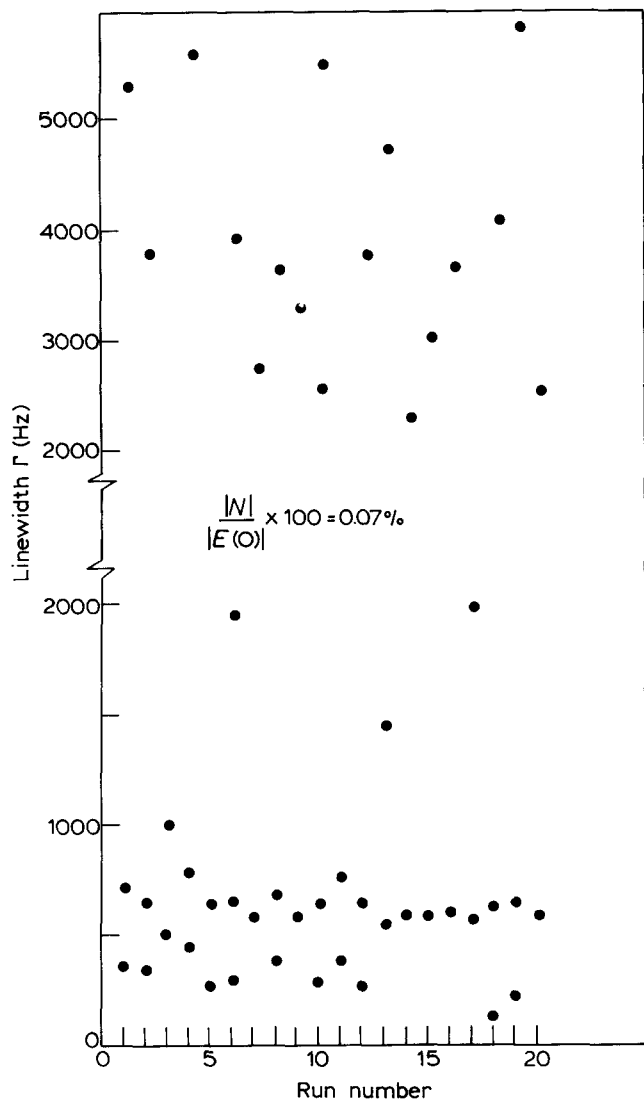


Figure 5 Linewidths for 20 separate heterodyne experiments for a sample of polystyrene in benzene, $\bar{M}_w = 10 \times 10^6$, concentration = 0.000736 g/ml, scattering angle = 30 degrees, temperature = 298K. Run time = 30 min

demonstrated this important point we shall now describe the results obtained with sample III which, as we can demonstrate, is a monodisperse high molecular weight sample.

Scattering system III. The solution was left for a period of three weeks to ensure that the polymer was completely dissolved and we then performed scattering experiments at a range of angles from 15 to 50 degrees. Shown in *Figure 6* are the linewidth values of the S-exponential sums as a function of the square of the scattering vector and the important point to note is that at a scattering angle of fifteen degrees at which $qR_G \approx 1.03$ the autocorrelation function is a single exponential with no internal motions or polydispersity detectable. Also shown in *Figure 6* is the dependence calculated from the formulae of Adam and Delsanti⁶ using the weight averaged molecular weight and it can be seen to fit our experimental points very well and this reaffirms that the sample is monodisperse. At the lower scattering angles the linewidth scales as the square of the scattering vector and we are measuring the diffusive motion of the centre of mass of the macromolecule. We expect that as the scattering angle is increased to $qR_G = 1.4-1.8$ the amplitude of the internal mode is of the

order of a fifth of the amplitude of the diffusive component and so it should be possible to detect the first internal mode. For higher values of the scattering parameter qR_G the higher internal modes become significant and any internal mode linewidth values will be difficult to interpret due to the complex analytic form of the autocorrelation function and so we have restricted our observation range of angles such that $qR_G < 1.8$. The presence of the internal mode component can be detected using an integration time of 30 minutes at a scattering vector of $q = 0.89 \cdot 10^7 \text{ m}^{-1}$ and the scattering parameter $qR_G = 1.84$, this shows that we are at the limit of the region where we can detect the first internal mode.

It is rather surprising that the autocorrelation function changes from being single exponential to double exponential over a very small angular region and to explain this feature we can consider the simulated double exponential decay curves¹. There is a factor of five between the two linewidth components and so we calculate that to be able to resolve the pair we require $\omega_{\max} = 1.95$ and data accuracy = 0.08 (8%); and as we can achieve sub 1% accuracy we can easily satisfy the resolution condition. The accuracy with which any of the components can be estimated depends upon the accuracy of that particular component and, at the value of the scattering parameter $qR_G = 1.6$, the amplitude of the diffusive component divided by the amplitude of the first internal mode component is in the ratio 7:1. We sample the decay curve so that the main component contains 3-5 decay times within the fifty point data set and so the weaker and faster decaying component is sampled with 15-25 decay times in the data set. From the residuals of the S-exponential fit we calculate that the data accuracy is of the order of 0.05% for the diffusive component and 0.7% for the internal mode component. From the results of the single deviation of the

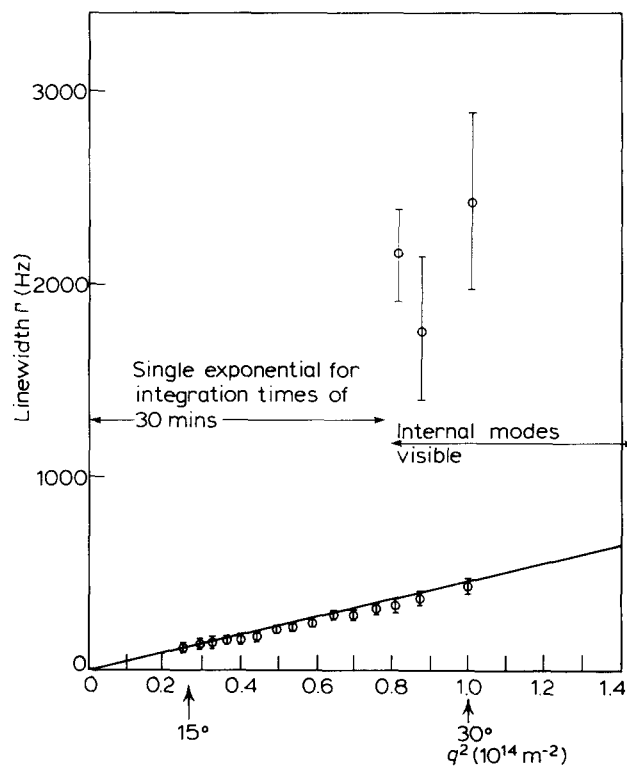


Figure 6 Scattered linewidths for polystyrene in benzene. $\bar{M}_w = 9.5 \times 10^6$, concentration = 0.0001 g/ml, temperature = 298K, heterodyne detection

calculated u -values from the true u -values as

$$u_{\text{diff}} \approx 0.92 \pm 0.005$$

which gives an error of approximately 1% for the main component. If we inspect *Figure 6* we find that our calculated and experimental error bars are of the right magnitude. For the internal mode component we have

$$u_{\text{int}} \approx 0.66 \pm 0.014$$

where we have taken into account an oversampling factor of two. We can then calculate that we should have an error of about 5–10% where experimentally we have an error of 10–15%, and again we have reasonable agreement between our simulations and our real experimental data.

DISCUSSION

We have presented experimental results taken upon dilute solutions of high molecular weight polystyrene in the good solvent benzene that verify computer simulation studies for both polydisperse and monodisperse bimodal distributions. The results show that limited instrumental resolving power makes the extraction of polydispersity information for bimodal distributions quite difficult and we find that in most scattering systems it is necessary to work at the very limit of the photon correlation spectrometer. We have not presented any data taken in the homodyne detection mode but this is due to the excellent heterodyne operation of the spectrometer used.

Having shown that the extraction of internal mode information from polydisperse samples is very difficult because of resolution and meaningful interpretation considerations we performed a whole range of trial experiments in order to locate a high molecular weight monodisperse system, using the criterion that for a system to be considered monodisperse the autocorrelation functions is single exponential at low scattering angles where $qR_G < 1$. This extensive search revealed that for a fairly monodisperse system, $M_w/M_n = 1.2$, that even the relatively small degree of polydispersity could still interfere with accurate internal mode linewidth determination and this reaffirmed the conditions imposed.

Previously reported values for the first internal mode relaxation time for high molecular weight polystyrene are available for various polymer–solvent systems with the first experimental measurements being made by King *et al.*^{12–14} and by Huang and Frederick¹⁵. These two groups used the theta solvent cyclohexane and King *et al.*

also reported results for the good solvent butan-2-one. As we have shown in this paper the presence of polydispersity has a profound influence upon the calculated S-exponential sum. The analysis technique employed by most previous groups to obtain the first internal mode was to determine a centre of mass diffusion coefficient at low angle by single exponential fitting the autocorrelation function, which because of the residual polydispersity was probably a good estimate of D_z , and then for higher scattering angles use a two exponential fit with one of the decay constants held fixed. This analysis technique undoubtedly forces the calculated first internal mode value to be averaged over polydispersity effects.

In this paper we have been primarily concerned with the influence of the linewidth resolution conditions upon the extraction of meaningful information from polydisperse polymer systems with internal dynamics. Although not systematically investigated the analysis technique has been considered whereby extrapolation of the experimentally found diffusion coefficient at low scattering angle to high scattering angle is used to reduce the fitting procedure to a four parameter non-linear least squares problem (baseline, 2 amplitudes and 1 time constant). We feel that the extrapolation error will be rather large considering the limited experimental accuracy and the routine would be prone to a large systematic error. We prefer the approach in this work which uses the guaranteed unique convergence of the S-exponential sum routine since it will not be subject to the extrapolation error.

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