Data fitting in photon correlation spectroscopy studies of dilute polymer solutions

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Two methods of processing data from photon correlation studies of polydisperse polymer samples in dilute theta solution have been compared using computer generated correlation functions. Force-fitting a single exponential to the data gives a value for the diffusion coefficient D only slightly less than D_z, the z-average value returned by the cumulants method. Both methods are shown to give the same concentration dependence for D.

Keywords Spectroscopy; photon correlation spectroscopy; polymer solutions; dilute solutions; theta solution; diffusion coefficient

In studies of the diffusion of polymers in dilute solution by photon-correlation spectroscopy[1], two procedures are commonly used in analysing the data to obtain the diffusion coefficient D: these are the method of cumulants and force-fitting a single exponential to the data. In this communication, the two methods are compared by applying them to data that has been computer-generated to simulate results from polydisperse samples. It will be shown that, although the methods give different averages of D, they both correctly determine the concentration dependence of D for a polydisperse sample in dilute theta solution.

The normalized intensity autocorrelation function $g^{(2)}(\tau)$ of the light scattered from a dilute polymer solution is related to the first-order (optical) correlation function $g^{(1)}(\tau)$ through the Siegert relation:

$$g^{(2)}(\tau)=1+\beta|g^{(1)}(\tau)|^2 \qquad (1)$$

where β is a factor less than unity which depends on the optical arrangement. For a perfectly monodisperse sample of small molecular size,

$$|g^{(1)}(\tau)|=\exp(-\Gamma\tau)$$

where $\Gamma=DK^2$ and K is the scattering vector ($=(2\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength of the light in the solution and θ the scattering angle). The radius of gyration R_g has to be sufficiently small so that $x=K^2R_g^2<0.1$, otherwise intramolecular motion will distort $g^{(1)}(\tau)$ in a complicated way[2]. Except for the highest molecular weights ($M>10^7$) or the broadest distributions with substantial tails in this region, the condition can be met by carrying out the experiment at sufficiently low angle.

Even for narrow fractions, $|g^{(1)}(\tau)|$ should be represented by a distribution of exponentials:

$$|g^{(1)}(\tau)|=\int G(\Gamma)\exp(-\Gamma\tau)\mathrm{d}\Gamma. \qquad (2)$$

$G(\Gamma)$ is a distribution function which depends on the distribution of molecular weights $f(M)$ and some function of the polarizability of the molecule $\mu(M)$ as well as the Debye scattering factor $P(x)[=(2/x^2)(e^{-x}-1+x)]$; the latter can be written as $P(K,M)$ since $R_g=R_g(M)$.

The linear concentration dependence of D in dilute solution can be written as $D=D_0(1+k_Dc)$, where D_0 is the value of D at infinite dilution and c is the concentration. In a previous communication[3] it was established that the appropriate value for the coefficient k_D for a polydisperse sample in a theta solution was the weight-averaged value, $\bar{k}_D^\theta$, and that this single coefficient determines the concentration behaviour of all molecular-weight species in the polydisperse solution. As a result, $G(\Gamma)$ scales linearly with c:

$$G(\Gamma,c)=G_0(\Gamma_0)/(1+\bar{k}_D^\theta c) \qquad (3)$$

where $\Gamma=\Gamma_0(1+\bar{k}_D^\theta c)$. Here, $G(\Gamma,c)$ expresses explicitly the concentration dependence, and $G_0(\Gamma_0)$ is the distribution function at infinite dilution. The non-theta case is more complex because the second virial coefficient A_2 is non zero; it will not be considered in this communication

Fitting procedures

In the cumulants method of data analysis[4], the logarithm of $|g^{(1)}(\tau)|$ is fitted to a second-order polynomial in τ: $\ln|g^{(1)}(\tau)|=a_0+a_1\tau+a_2\tau^2$. The procedure is carried out for a sequence of runs at decreasing values of $\tau_{\max}$, the delay time of the last channel. Thus shorter spans of trace are fitted, and the limiting value of a_1 as τ approaches zero yields the z-average value of D: $a_1=-D_zK^2$ as $\tau\to0$. The limiting values of a_1 and a_2 together give a measure of the polydispersity of the sample. For the theta case,

$$\bar{M}_w/\bar{M}_n-1=8a_2/a_1^2 \qquad (4)$$

A detailed discussion of the method has recently been given by Selser[5].

The experimentally determined correlation function $C(\tau)$ of the scattered intensity is normalized to obtain $g^{(2)}(\tau)$ by dividing each point by a far point, ideally $C(\infty)$, or by a normalization constant obtained from the monitor channels of the correlator. In either case, unavoidable statistical fluctuations and chance events in the detection system will introduce error into the divisor, with a resulting error in all the derived points of $g^{(2)}(\tau)$. In

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practice, these points would be better represented by the expression $g^{(2)}(\tau)=1+\beta|g^{(1)}(\tau)|^2+\delta$, where δ is a small 'misnormalization' term ($\ll\beta$) which will vary from run to run on the same sample.

In the above fitting procedure, it is not possible to allow for this additional term, and its neglect will introduce a systematic error in all the points of $|g^{(1)}(\tau)|$; this will particularly influence the value obtained for a_2. Thus, while it is unlikely that any appreciable error will occur in the value obtained for D_z from a_1, any conclusions drawn about polydispersity from a_2 may be misleading, especially, if a_2 varies from run to run.

An alternative method of data fitting automatically accommodates the uncertainty in the baseline by force-fitting a single exponential function plus a constant to the normalized experimental data. The function $1+\alpha\exp(-B\tau)+\varepsilon$ is fitted with α, B and ε as adjustable parameters. The value $\bar{D}$ obtained from B ($=2\bar{D}K^2$) represents some average value of D for the distribution, and the parameter $\varepsilon(\ll\alpha)$ incorporates the fluctuating misnormalization term δ. This procedure gives reproducible values for B from run to run[6] provided the same length of trace is fitted; $\tau_{\max}$ is usually set to equal four decay times ($4/B$) in order to avoid too long a tail or too little curvature.

Although $\bar{D}$ is not a simple and recognizable average of the molecular weight distribution, this usually presents no problems since well-defined average values for D are rarely required. Rather, one is interested in the way in which $\bar{D}$ varies under changing conditions, such as concentration, and under theta conditions the variation of any average value of D with concentration will give $\bar{k}_D^\theta$.

It remains to be shown that, for the theta case, the single-exponential force-fit procedure does indeed return a value of $\bar{D}$ which is the same average of the molecular weight distribution whatever the concentration, provided that the length of trace fitted always spans the same number of decay times ($1/B$). This can be seen by expressing $|g^{(1)}(\tau)|$ (equation (2)) in terms of $G_0(\Gamma_0)$. Writing $1+\bar{k}_D^\theta c$ as γ for short, we have $G(\Gamma,c)=G_0(\Gamma_0)/\gamma$ (equation (3)) and $\Gamma=\gamma\Gamma_0$. Since γ is a constant for a particular solution, independent of Γ, $\mathrm{d}\Gamma/\mathrm{d}\Gamma_0=\gamma$ and thus equation (2) becomes

$$
\begin{aligned}
|g^{(1)}(\tau)| &= \int G_0(\Gamma_0)\exp(-\Gamma\tau)\mathrm{d}\Gamma_0 \\
&= \int G_0(\Gamma_0)\exp(-\Gamma_0\gamma\tau)\mathrm{d}\Gamma_0.
\end{aligned}
$$

The value of the integral evaluated at a particular value of $\gamma\tau$ is seen to be independent of c, and so the shape of the correlation function is the same at all concentrations when plotted against $\gamma\tau$. By setting the sample time T_s between data points on the correlator to be proportional to $1/\gamma$, the shape of the finite span of the correlation function that is fitted will be the same at all concentrations. This is what is done in adjusting T_s to make the trace span a definite number of force-fit decay times.

Data generation and fitting

Data for the 48 points of the simulated correlation functions were constructed for two different molecular weight distributions $f(M)$, a log-normal distribution and a uniform distribution (i.e. $f(M)$ constant over a range of M, and zero outside this range). For each distribution, three different polydispersity ratios were considered with $\bar{M}_w/\bar{M}_n=1.06$, 1.12 and 1.18, and the two fitting procedures were applied to the data for a wide range of spans to see the effect of varying the length of trace.

Since the amplitude of the light scattered by a molecule is proportional to M, $G(\Gamma)$ is proportional to M^2 as well as $f(M)$. Thus

$$G(\Gamma)\mathrm{d}\Gamma\propto f(M)M^2(\mathrm{d}M/\mathrm{d}\Gamma)\mathrm{d}\Gamma$$

which, for the theta case where $\Gamma\propto M^{-1/2}$, becomes

$$G(\Gamma)\mathrm{d}\Gamma\propto f'(\Gamma)\Gamma^{-7}\mathrm{d}\Gamma$$

since $(\mathrm{d}M/\mathrm{d}\Gamma)\propto\Gamma^{-3}$; $f'(\Gamma)$ is the function $f(M)$ transformed into Γ space. Equation (2) can then be written as

$$|g^{(1)}(\tau)|=\int_0^\infty f'(\Gamma)\Gamma^{-7}\exp(-\Gamma\tau)\mathrm{d}\Gamma\Big/\int_0^\infty f'(\Gamma)\Gamma^{-7}\mathrm{d}\Gamma$$

The integrals were performed on a DEC-system 10 computer using standard NAG algorithms and evaluated at 48 delay times to simulate data from a 48 channel correlator ($\tau_{\max}=48\ T_s$).

Log-normal distribution

$$f(M)=\frac{1}{\sqrt{2\pi}\sigma}\frac{1}{M}\exp\left[-\left(\ln\frac{M}{m}\right)^2/2\sigma^2\right]$$

where m is the median. $\bar{M}_n=me^{\sigma^2/2}$ and $\bar{M}_w=me^{3\sigma^2/2}$ so $\bar{M}_w/\bar{M}_n=e^{\sigma^2}$. A straightforward substitution of M by Γ^{-2} gives $f'(\Gamma)$, which will of course be unnormalized. The value of Γ for m (Γ_m) is arbitrarily set at unity without loss of generality since it is the product of $\Gamma\tau$ that determines the value of the exponential in the integral for $|g^{(1)}(\tau)|$. [Thus, in the calculation, the length of the trace can be varied by an appropriate choice of $\tau_{\max}$.] In fact, for each polydispersity, data sets were calculated for ten different trace lengths with values of $\Gamma_m\tau_{\max}$ between 0.4 and 4.0 in steps of 0.4.

In the cumulants method of data fitting, no attempt was made to simulate uncertainty in the baseline of $g^{(2)}(\tau)$ as would occur in practice. The value obtained for $\bar{\Gamma}(=a_1)$ scarcely changed with span length fitted; it increased by only 5 parts in 10^3 as $\Gamma_m\tau_{\max}$ varied from 4 to 0.4 for the highest polydispersity considered. In an actual experiment, statistical fluctuations would introduce uncertainties greater than this, so at these levels of polydispersity it is not necessary to take a series of runs of decreasing $\tau_{\max}$. The values obtained for $\bar{\Gamma}$ did indeed equal $\bar{\Gamma}_z$, which for this distribution is $\Gamma_m e^{-7\sigma^2/8}$.

Estimates of the polydispersity obtained from equation (3) gave values which increased slightly as the length of trace fitted (i.e. $\tau_{\max}$) was reduced, and the values extrapolated to $\tau_{\max}=0$ gave good estimates for the polydispersity. For example, in the case of polydispersity $\bar{M}_w/\bar{M}_n=1.18$, the values calculated for $\bar{M}_w/\bar{M}_n$ at $\Gamma_m\tau_{\max}=4$ and 0.4 were 1.139 and 1.165 respectively. Indeed the extrapolated estimates of $\bar{M}_w/\bar{M}_n-1$ were only 2%, 3% and 6% below their actual values for the polydispersities 1.06, 1.12 and 1.18 respectively.

The single exponential force-fit procedure was applied directly to $g^{(2)}(\tau)$ as calculated from equation (1) with β equal to 0.25, typical of experimental values. The change in $\bar{\Gamma}(=B/2)$ with varying time span $\tau_{\max}$ was more marked than in the previous procedure, but even so it was not great. As $\Gamma_m\tau_{\max}$ varied from 4 to 0.4, $\bar{\Gamma}$ increased for the three polydispersities $\bar{M}_w/\bar{M}_n=1.06$, 1.12 and 1.18 by only 1%, 2% and 3% respectively. Thus the requirement always to fit to a certain fixed number of decay times ($1/B$) in order to obtain the same distribution average for comparison purposes can be relaxed without introducing much error. For example, a variation of 10% in $\tau_{\max}$ will change $\bar{\Gamma}$ by only a fraction of a per cent.

The value of $\bar{\Gamma}$ for $\bar{\Gamma}\tau_{\max}=2$ was slightly lower than $\bar{\Gamma}_z$, the value given by the cumulants method. The variation with polydispersity is shown in *Table 1*, normalized against $\bar{\Gamma}_z$. Also shown are the calculated changes in Γ_n and Γ_w, the values of Γ for $M=\bar{M}_n$ and $\bar{M}_w$, since these molecular weights are often known and used to characterize samples. (Note that Γ_n and Γ_w are not the number- and weight-average values for Γ, but $\bar{\Gamma}_z$ is the z-average value.)

Uniform distribution

$$f(M)=1/(2\Delta m) \quad \text{for } m-\Delta m \leqslant M \leqslant m+\Delta m$$
$$=0 \quad \text{otherwise}$$

This distribution was chosen because of its simple mathematical form and as a contrast to the more smoothly changing log-normal distribution. In this case $\bar{M}_n=m$ and $\bar{M}_w=m+\Delta m^2/3m$ so $\bar{M}_w/\bar{M}_n=1+(\Delta m^2/3m^2)$. Γ_n, the value of Γ at $M=\bar{M}_n$, was arbitrarily set at unity and values of the span $\Gamma_n\tau_{\max}$ ranged from 4 to 0.4.

In the cumulants method, the variation of $\bar{\Gamma}$ over the range of fitted spans was greater than in the case of the log-normal distribution. For the three polydispersities, $\bar{M}_w/\bar{M}_n=1.06$, 1.12 and 1.18, $\bar{\Gamma}$ increased by 0.25%, 0.62% and 0.93% respectively as $\Gamma_n\tau_{\max}$ decreased from 4 to 0.4. However, the extrapolated value of $\bar{\Gamma}$ at $\Gamma_n\tau_{\max}=0$ was again $\bar{\Gamma}_z$. The polydispersity estimates calculated from equation (2) gave values of $\bar{M}_w/\bar{M}_n-1$ which were 10%, 19% and 29% too low for the three polydispersities $\bar{M}_w/\bar{M}_n=1.06$, 1.12 and 1.18. The discrepancy is ten times greater than for the previous smoother distribution, and is most likely due to the sharp cut-off of the distribution.

The values of $\bar{\Gamma}$ from the single exponential force-fit procedure were again only slightly lower than the values of $\bar{\Gamma}_z$. Inspection of *Table 2* will reveal that the difference is never more than one per cent.

Table 1 Log-normal distribution

$\bar{M}_w/\bar{M}_n$	$\bar{\Gamma}/\bar{\Gamma}_z$	$\Gamma_n/\bar{\Gamma}_z$	$\Gamma_w/\bar{\Gamma}_z$
1.06	0.9967	1.0371	1.0073
1.12	0.9934	1.0734	1.0143
1.18	0.9904	1.1090	1.0209

Table 2 Uniform distribution

$\bar{M}_w/\bar{M}_n$	$\bar{\Gamma}/\bar{\Gamma}_z$	$\Gamma_n/\bar{\Gamma}_z$	$\Gamma_w/\bar{\Gamma}_z$
1.06	0.9968	1.0365	1.0068
1.12	0.9943	1.0711	1.0121
1.18	0.9923	1.1038	1.0161

Estimating polydispersity from the force-fit procedure

Although the single exponential force-fit procedure does not provide an easy analytic means of estimating the polydispersity, it is possible to obtain an indication of this from a plot of the residuals between the fitted curve and the data points, which take the characteristic form shown in *Figure 1*. The relative amplitude of the variations, say as measured by the height of the central flat maximum, increases with polydispersity and the present study enables a calibration to be made. The height, relative to the amplitude of the exponential, is given in *Figure 2* for both distributions and the three polydispersities.

It is clear from these figures that data of high signal-to-noise ratio is required to obtain such an estimate, particularly for low polydisperse samples, otherwise the characteristic shape will be lost in the noise.

A further note of caution is necessary, however, since a similar residual plot will be obtained if there is heterodyning or if there are internal motion effects, but these would also give misleading estimates in the cumulants method.

Conclusion

It has been shown that both methods of data fitting will give the correct value for k_D^θ, and both can give an estimate of the sample polydispersity. The choice of procedure may be determined by experimental considerations; in particular, uncertainty in the baseline of the correlation function may favour the use of the single-exponential force-fitting method in order to obtain reproducible values for D. Alternatively, the cumulants method may be easier to carry out with limited computing facility.

The non-theta case is more complicated since $G(\Gamma,c)$ does not simply scale with c as in the theta case. $G(\Gamma,c)$ is

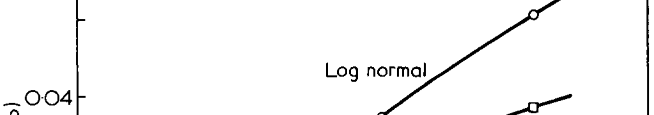

Figure 1 Characteristic pattern at residuals in force fitting a single exponential to the data

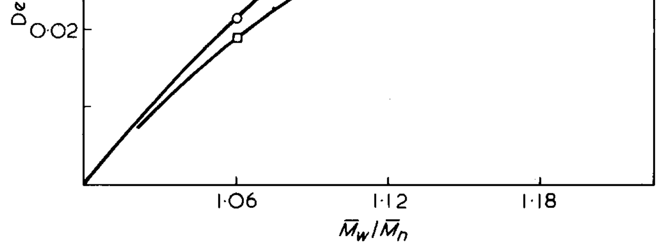

Figure 2 Variation of the height of the central maximum at the residuals with polydispersity, expressed as a percentage of the exponential amplitude

not just compressed or expanded along the Γ axis with changing c, but changes its shape. Thus the particular average of the distribution function which is determined by either of the two methods ($\bar{\Gamma}_z$ or $\bar{\Gamma}$) will change with concentration. Clearly this case requires further study.

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Polymerization of hexachlorocyclotriphosphazene by sulphur and selenium

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The thermal bulk polymerization of hexachlorocyclotriphosphazine is described. The possibility of obtaining soluble polymer using sulphur and selenium as catalysts was investigated. It was found that the catalytic activity of selenium was much lower than that of sulphur. Monomeric sulphur may be acting as a chlorine-attractive agent for hexachlorocyclotriphosphazine.

Keywords Polymerization; bulk thermal; catalysis; sulphur; selenium; hexachlorocyclotriphosphazine

Introduction

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ polymerizes rapidly without gel formation, in glass or stainless steel reactors at 220°–290°C using catalysts[1] such as $AlCl_3$, $Et_3Al_2Cl_3$, Et_3Al, Et_2AlOEt, Br_3B, Al, B, Cr, Ni, Mg, Cu, Mn, Co or Fe. The polymerization of $(NPCl_2)_3$ in different solvents was reported by Retuert[2]. The present work describes the thermal bulk polymerization of $(NPCl_2)_3$ and the possibility of obtaining soluble polymer using sulphur and selenium as catalysts.

Experimental

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ was prepared by reaction of phosphorus pentachloride with ammonium chloride in tetrachloroethane[3]. (M.pt. of pure trimer, 112°C.)

A mixture of hexachlorocyclotriphosphazene (2.5 g) and small amount of sylphur or selenium was placed in a pyrex tube (200 × 40 mm) which was then evacuated to 10 mm for 1 h, sealed and heated in an oven just below 300°C. When the polymerization was complete the product was treated with benzene and the polymer precipitated by addition of n-heptane using the method of Allcock[4]. Unreacted trimer was recovered by vacuum distillation. As the precipitated polydichlorophosphazene was unstable in water, chlorine in the polymer was substituted with a nucleophilic reagent by refluxing in benzene for 24 h. After the water was added to remove aniline hydrochloride formed during the reaction, the benzene solution was dried over anhydrous sodium sulphate.

The M_n and M_w of polydianilinophosphazene were determined by gel permeation chromatography using THF as the solvent.

Results and Discussion

The relation between yields of linear and crosslinked polymer or oligomer and reaction time at 250°C when 100 mg of sulphur was added is shown in *Figure 1*.

It is found that the maximum yield of linear polydianilinophosphazene occurs with a reaction time of 15 h, the recovered product is mostly hexachlorocyclotriphosphazene and crosslinked polymer is formed after 23 h. Yield of linear polydianilinophosphazene is shown in *Figure 2* when the amount of sulphur is changed and the reaction temperature and time are kept constant.

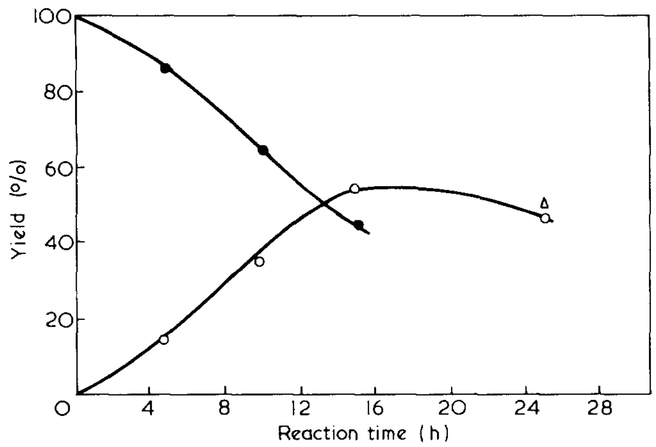

Figure 1 Relation between reaction time and oligomer (●), linear (○) or crosslinked polymer (△) using sulphur at 250°C. Linear polymer: $[NP(HNC_6H_5)_2]_n$

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