Polydispersity corrections to small-angle scattering data from polymers in the melt and in dilute solution

A. T. Boothroyd*
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK
(Received 8 June 1987; revised 15 November 1987; accepted 12 January 1988)

Small-angle neutron scattering from polydisperse molten polymers is considered. It is shown that if the sample consists of a blend of protonated and deuterated molecules, in which both components have the same molecular mass distribution, then the scattered intensity is just a linear combination of the single-chain scattering functions for each degree of polymerization. With this result, a moments approach giving the corrections to small-angle scattering data for polydisperse samples in terms of the sample mass averages, M_n, M_w, M_z etc. is presented. The method has the advantage that the exact nature of the molecular mass distribution need not be known, and that the formulae are not restricted to asymptotic regions of the spectrum. The procedure is illustrated for Gaussian linear and star-branched polymers, and applied to some synthetic and real data. Validity of the derived formulae is restricted to samples with small degree of polydispersity, typically $M_w/M_n < 1.3$. In addition, several exact results relevant to polydisperse star molecules are derived.

(Keywords: polydispersity; small-angle scattering; neutron scattering; scattering function; molten polymers; Gaussian macromolecules; star polymers)

INTRODUCTION

From the small-angle part of the elastic scattering spectrum of a system of non-interacting particles a measure of the size of the scatterers can be obtained in the form of their z-average, mean square radius of gyration, $\langle S^2\rangle_z$†. Much more information is available, though, if the spectrum is continued to larger values of the wavevector transfer, $\mathbf{Q}$, where correlations between units within *the interior* of the scatterer are probed. A direct test can be applied to a theoretical description for the molecular conformation by comparing the experimental scattering data with the static structure factor (scattering function), $S(\mathbf{Q})$.

In a recent neutron scattering study of molten star-branched polymers[1] the objective was to test the validity of the Gaussian model for such molecules and to extract the mean square radius of gyration on the basis of this model. It became of interest to calculate what effect the small variation in the molecular mass of the molecules had upon the full $S(\mathbf{Q})$ calculated for a monodisperse sample, and to produce formulae for fitting to the entire Q range of the experimental data.

Two problems arose. First, how do the scattering functions for the individual molecules of different masses combine in the blend of protonated and deuterated polymer used for the neutron scattering experiment? Second, the only knowledge available of the polydispersity was contained in the first three molecular mass averages, M_n, M_w and M_z, estimated from size exclusion chromatography. The shape of the distribution was unknown.

This paper discusses these two problems. In the first part it is shown that, provided the molecular mass distributions of the labelled and unlabelled components are the same, the scattering function for the blend is just the mean of the mass-dependent scattering functions. Then, an approximate formula for the scattering function of a polydisperse system is derived by a moments method, in which the molecular mass distribution enters only through the mass averages M_n, M_w, M_z, etc. By means of example, the formula is then applied to the case of Gaussian linear and star-branched polymers and the limitations of the treatment are discussed. Finally, the results for Gaussian stars are used to analyse some experimental data, and various features of the results are interpreted with the help of a numerical example.

SCATTERING FROM MOLTEN BLENDS

The sample is taken to be comprised of a blend of protonated and deuterated versions of the same polymer. The macroscopic, coherent sample cross-section measured in a small-angle neutron scattering experiment can be written in terms of the fluctuations in scattering length density[2]. In an incompressible melt the scattering arises from the difference between the scattering lengths of the protonated and deuterated chains. If d and h are the respective scattering lengths for a deuterated and protonated monomer, and $\delta\phi_d(\mathbf{Q},N)$ is the fluctuation in

---

* Present address: Department of Physics, University of Warwick, Coventry CV4 7AL, UK

† It should be noted that two averaging processes have taken place in $\langle S^2\rangle_z$. The term 'mean square' refers to the average of S^2 over all possible configurations of the molecule, and is indicated in this paper by angular brackets. For polydisperse samples a quantity may also be averaged over the mass distribution. This will be denoted by a bar, e.g. $\overline{N^2}$, unless the average is weighted by some power of N when an alphabetic subscript will be used in the conventional way. Thus, the notation $\bar{Y}$ is equivalent to Y_n. The notation $\langle S^2(N)\rangle$ will be employed to indicate the mean square radios of gyration of a monodisperse sample with degree of polymerization N.

0032-3861/88/091555-07$03.00

deuterated monomer density in Q-space for a chain of N monomers, then the cross-section may be written:

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}=(d-h)^2\frac{1}{V}\langle\sum_N \delta\phi_{\mathrm{d}}(\mathbf{Q},N)\sum_{N'}\delta\phi_{\mathrm{d}}(-\mathbf{Q},N')\rangle$$

$$=(d-h)^2\frac{1}{V}\left\{\sum_N f_N X_N S_N+\sum_N\sum_{N'} f_N f_{N'} X_N X_{N'} S_{NN'}\right\} \qquad (1)$$

where X_N is the number of chains which have degree of polymerization N, f_N is the fraction of these which are deuterated, and S_N and $S_{NN'}$ are the intra- and inter-chain pair correlation functions, given by:

$$S_N=\sum_{\substack{i\\ \text{same chain}}}^{N}\sum_{j}^{N}\langle\exp\{i\mathbf{Q}\cdot(\mathbf{R}_i-\mathbf{R}_j)\}\rangle \qquad (2)$$

$$S_{NN'}=\sum_{\substack{i\\ \text{different chains}}}^{N}\sum_{j}^{N'}\langle\exp\{i\mathbf{Q}\cdot(\mathbf{R}_i-\mathbf{R}_j)\}\rangle \qquad (3)$$

In terms of S_N and $S_{NN'}$ the incompressibility condition is:

$$\sum_N X_N S_N+\sum_N\sum_{N'} X_N X_{N'} S_{NN'}=0 \qquad (4)$$

If it is assumed that the labelled and unlabelled samples have the *same* molecular mass distribution, i.e. $f_N=f_{N'}=f$, then it follows from equations (1) and (4) that:

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}=(d-h)^2 f(1-f)\frac{1}{V}\sum_N X_N S_N \qquad (5)$$

Hence, it is proved that with these conditions the total scattering function is just a linear combination of the single-chain structure factors. This result may also be deduced from a calculation by means of the random phase approximation^3, but the present derivation is much simpler and does not have recourse to the assumption of ideal chains required by the RPA. For instance, equation (5) is as equally valid for oriented as for unperturbed chains.

MOMENTS METHOD

It will be convenient in this paper to convert sums over numbers of monomers into integrals, and to express the polydispersity in terms of the differential number distribution, $x(N)$. The various mass averages in common use arise from $x(N)$ according to:

$$M_{\mathrm{n}}=m\bar{N}$$

$$M_{\mathrm{w}}=\frac{m^2}{M_{\mathrm{n}}}\overline{N^2} \qquad (6)$$

$$M_{\mathrm{z}}=\frac{m^3\overline{N^3}}{M_{\mathrm{w}}M_{\mathrm{n}}}$$

where m is the mass of one monomer. The mean scattering function, from equation (5), is expressed as:

$$S(\mathbf{Q})=\int_0^\infty S(\mathbf{Q},N)x(N)\mathrm{d}N \qquad (7)$$

For all that follows the scattering system will be taken to be isotropic, so that $\mathbf{Q}$ can be replaced by Q. It is also convenient to define a constant A such that:

$$\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q)=\frac{m^2}{M_{\mathrm{n}}}S(Q) \qquad (8)$$

With this definition all bulk sample properties and parameters dependent upon the nature of the radiation source are contained in A and are decoupled from the molecular mass constants.

The method proceeds by expanding $S(Q,N)$ in a Taylor series about a fixed degree of polymerization N_0:

$$S(Q,N)=S(Q,N_0)+\sum_{k=1}^{\infty}\frac{(\Delta N)^k}{k!}S^{(k)}(Q,N_0) \qquad (9)$$

where

$$\Delta N=N-N_0$$

Inserting this series into the integral in equation (7) yields:

$$S(Q)=S(Q,N_0)+\sum_{k=1}^{\infty}\frac{\overline{\Delta N^k}}{k!}S^{(k)}(Q,N_0) \qquad (10)$$

The averages can be written as moments of $x(N)$ or, by means of equations (6), in terms of mass averages. For a narrow number distribution only the first few terms need be retained. The sample cross section, from equation (8), is:

$$\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\simeq\frac{m^2}{M_{\mathrm{n}}}S(Q,N_0)+m(1-M_0/M_{\mathrm{n}})S'(Q,N_0)$$

$$+\frac{1}{2!}(M_{\mathrm{w}}-2M_0+M_0^2/M_{\mathrm{n}})S''(Q,N_0)$$

$$+\frac{1}{3!}\frac{1}{m}(M_{\mathrm{z}}M_{\mathrm{w}}-3M_{\mathrm{w}}M_0+3M_0^2-M_0^3/M_{\mathrm{n}})S'''(Q,N_0) \qquad (11)$$

The form of $S(Q,N)$ calculated from the proposed model is now used to evaluate as many derivatives as there are mass averages known. In the applications discussed in this work it will be assumed that only M_{n}, M_{w} and M_{z} are known, and so formulae will be derived from equation (11).

APPLICATION OF FORMULA

Gaussian, linear polymers

In the Gaussian model of a polymer chain the separation of two units i and j is assumed to follow a Gaussian distribution of variance:

$$\langle r_{ij}^2\rangle=6K|i-j| \qquad (12)$$

For linear polymers of N monomers this results in the Debye scattering function^4:

$$S(Q,N)=\frac{2N^2}{u^2}(\mathrm{e}^{-u}+u-1) \qquad (13)$$

where

$$u = Q^2 KN = Q^2 \langle S^2(N) \rangle$$

Evaluating the derivatives at $N = N_0$, and inserting into equation (11) gives:

$$\begin{aligned}\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega} \simeq{}& \frac{2M_0^2}{M_n}\frac{1}{u_0^2}(\mathrm{e}^{-u_0} + u_0 - 1) \\ &+ 2M_0(1 - M_0/M_n)\frac{1}{u_0}(1 - \mathrm{e}^{-u_0}) \\ &+ (M_w - 2M_0 + M_0^2/M_n)\mathrm{e}^{-u_0} \\ &- \tfrac{1}{3}(M_z M_w/M_0 - 3M_w + 3M_0 - M_0^2/M_n)u_0 \mathrm{e}^{-u_0}\end{aligned} \qquad (14)$$

In the limit $u_0 \ll 1$ equation (14) becomes:

$$\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega} \simeq M_w(1 - \tfrac{1}{3}Q^2 \langle S^2 \rangle_z) \qquad (15)$$

This is the correct universal form for small Q, since for linear polymers

$$\langle S^2 \rangle_z = \langle S^2(M_z) \rangle = KM_z/m \qquad (16)$$

It should be noted that it requires three derivative terms in the Taylor expansion, equation (11), to obtain this result.

For $u_0 \gg 1$ the correct limiting form:

$$\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega} \simeq \frac{2m}{KQ^2}\left(1 - \frac{1}{Q^2 \langle S^2 \rangle_n}\right) \qquad (17)$$

is also obtained, but only one derivative term is needed for this result.

Up to this point there has been no discussion about what value to choose for M_0. Some guidance in its choice is provided by the limiting forms of the polydisperse scattering function, equations (15) and (17). As Q becomes very large the dependence of $\mathrm{d}\Sigma/\mathrm{d}\Omega$ upon the mass of the sample diminishes and eventually the scattering functions of all Gaussian polymers coincide, regardless of their mass. Hence, the Debye function with $M = M_w$ coincides with the polydisperse function both at $Q = 0$ [equation (15)] and as Q tends to infinity. The general choice $M_0 = M_w$ seems appropriate, therefore, since $S(Q, N_0)$ then represents that Debye function which fits the polydisperse curve at the extremes. This choice is also useful because M_w is often the most accurately known of the mass averages, and because the scattering function simplifies slightly:

$$\begin{aligned}\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega} \simeq{}& \frac{M_w^2}{M_n}\frac{1}{u_w^2}[(\tfrac{1}{3}u_w^3 + u_w^2 + 2u_w + 2)\mathrm{e}^{-u_w} - 2] \\ &+ \frac{M_w}{u_w}[2 - (u_w + 2)\mathrm{e}^{-u_w}] - \frac{M_z}{3}u_w \mathrm{e}^{-u_w}\end{aligned} \qquad (18)$$

Gaussian, star-branched polymers: variable arm lengths

A star-branched polymer is constructed by linking f linear chains at a single point: the star point. The ith arm has n_i units, so the total number of units in the star is:

$$N = \sum_{i=1}^{f} n_i \qquad (19)$$

It will be assumed that the linear chains which became the arms can all be described by one number distribution $x(n_i)$. The molecular mass averages of the arms will be denoted by M_n^a, M_w^a, M_z^a etc., whilst those of the star as a whole will be M_n^s, M_w^s, M_z^s.

The Gaussian model for a star supposes that equation (12) for the mean square separation of two units is valid regardless of whether i and j lie on the same or on different arms. The scattering function for such a star is[5]:

$$S(Q,\{n_i\}) = \frac{2}{Q^4 K^2}\left[\sum_{j=1}^{f}[y_j - (1 - \mathrm{e}^{-y_j})] + \sum_{j=1}^{f}\sum_{k=j+1}^{f}(1 - \mathrm{e}^{-y_j})(1 - \mathrm{e}^{-y_k})\right] \qquad (20)$$

where

$$y_j = Q^2 K n_j$$

In this equation the first sum corresponds to intra-arm correlations whilst the double sum arises from inter-arm correlations. If all arms are identical, then equation (20) reduces to the Benoit equation for a uniform star:

$$S(Q,N) = \frac{2N^2}{fy^2}\left[\mathrm{e}^{-y} + y - 1 + \frac{(f-1)}{2}(1 - \mathrm{e}^{y})^2\right] \qquad (21)$$

where

$$y = Q^2 KN/f$$

If the Benoit equation together with its derivatives is simply inserted into the moments expansion, equation (11), then this sort of polydispersity corresponds to an ensemble of molecules in which all the stars are self-similar, i.e. of various sizes but the same shape. In practice this situation may occur if monodisperse arms are grafted onto a finite-size, polydisperse centre, or in forming a star-branched block copolymer, but in such cases it is unlikely that the centre will have the same scattering length density/refractive index as the arms, or even that Gaussian statistics will still be valid.

A better description of the polydispersity of star-branched polymers is one in which the arms are of independently varying lengths and attached at a point. The probability distribution function for the number of units in the whole chain is then an f-fold convolution of that for an arm. For this distribution it is no longer true that the mass averages for the star (M_n^s, M_w^s, M_z^s etc.) are obtained from those of an arm (M_n^a, M_w^a, M_z^a) by simply multiplying by f, The correct relationships are given in the appendix.

Before proceeding on to the approximate scattering function in terms of these mass averages it will be useful, for comparative purposes, to calculate the scattering function for the special case of a star whose arms have the Schulz distribution, a form ubiquitous in polymer science[6]:

$$x(N)=\frac{y^z N^{z-1}}{\Gamma(z)}\mathrm{e}^{-yN} \qquad (22)$$

where y and z are related to the mass averages by:

$$y=m(M_\mathrm{w}-M_\mathrm{n})^{-1} \qquad (23a)$$

$$z=(M_\mathrm{w}/M_\mathrm{n}-1)^{-1} \qquad (23b)$$

and $\Gamma(z)$ is the gamma function. Benoit's equation for a star with arms $\{n_i\}$, equation (20), needs to be averaged over the probability distribution for $\{n_i\}$:

$$S(Q)=\int S(Q,\{n_i\})x(\{n_i\})\mathrm{d}\{n_i\} \qquad (24)$$

Since the arm lengths are assumed to be independent $x(\{n_i\})$ can be taken as a product of the number distribution functions of the arms, which are Schulz distributions in this example. The result is:

$$\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}=\frac{2M^\mathrm{s}_\mathrm{n}}{f^2u}\{f\{1-u^{-1}[1-(1+u/z)^{-z}]\}$$
$$+\tfrac{1}{2}f(f-1)u^{-1}[1-(1+u/z)^{-z}]^2\} \qquad (25)$$

where

$$z=(M^\mathrm{a}_\mathrm{w}/M^\mathrm{a}_\mathrm{n}-1)^{-1}=[f(M^\mathrm{s}_\mathrm{w}/M^\mathrm{s}_\mathrm{n}-1)]^{-1}$$

and

$$u=\frac{Q^2KM^\mathrm{s}_\mathrm{n}}{fm}$$

Equation (25), like Benoit's equation, comprises two terms, the first of which corresponds to intra-arm correlations, and the second term is the contribution from inter-arm correlations. For small Q, such that $u/z\ll 1$, equation (25) takes the approximate form:

$$\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\simeq M^\mathrm{s}_\mathrm{w}\left[1-\tfrac{1}{3}Q^2\frac{K(M^\mathrm{s}_\mathrm{n})^2}{mM^\mathrm{s}_\mathrm{w}}\left(\frac{3f-2}{f^2}+\frac{M^\mathrm{s}_\mathrm{z}M^\mathrm{s}_\mathrm{w}}{(M^\mathrm{s}_\mathrm{n})^2}-1\right)\right] \qquad (26)$$

which is of the correct limiting form if the coefficient of $\tfrac{1}{3}Q^2$ is identified with $\langle S^2\rangle_z$:

$$\langle S^2\rangle_z=\frac{K(M^\mathrm{s}_\mathrm{n})^2}{mM^\mathrm{s}_\mathrm{w}}\left(\frac{3f-2}{f^2}+\frac{M^\mathrm{s}_\mathrm{z}M^\mathrm{s}_\mathrm{w}}{(M^\mathrm{s}_\mathrm{n})^2}-1\right) \qquad (27)$$

Equation (27) reduces to the mean square radius of gyration of a monodisperse star if $M^\mathrm{s}_\mathrm{n}=M^\mathrm{s}_\mathrm{w}=M^\mathrm{s}_\mathrm{z}$:

$$\langle S^2(M)\rangle=\frac{KM}{m}\left(\frac{3f-2}{f^2}\right) \qquad (28)$$

Hence, for stars $\langle S^2\rangle_z\neq\langle S^2(M_z)\rangle$, in contrast to equation (16) for linear molecules, so it is not possible to convert one mass-average, mean square radius of gyration to another by simply multiplying by the ratio of the two mass averages.

The scattering function and $\langle S^2\rangle_z$, equations (25) and (27), both agree with the treatment by Burchard with cascade theory[7] of a most probable distribution, which is a special case of a Schulz distribution in which $M^\mathrm{a}_\mathrm{w}/M^\mathrm{a}_\mathrm{n}=2$.

The moments expansion method will now be applied to the same problem. Expanding arbitrary arm lengths, $\{n_i\}$, about a particular value of n_0 gives

$$S(Q,\{n_i\})=S(Q,\{n_0\})+\sum_{i=1}^{f}(n_i-n_0)\frac{\partial S}{\partial n_i}(Q,\{n_0\})$$
$$+\frac{1}{2!}\sum_{i=1}^{f}\sum_{j=1}^{f}(n_i-n_0)(n_j-n_0)\frac{\partial^2 S}{\partial n_i\partial n_j}(Q,\{n_0\})$$
$$+\frac{1}{3!}\sum_{i=1}^{f}\sum_{j=1}^{f}\sum_{k=1}^{f}(n_i-n_0)(n_j-n_0)(n_k-n_0)\frac{\partial^3 S}{\partial n_i\partial n_j\partial n_k}(Q,\{n_0\})$$
$$+\ldots \qquad (29)$$

$S(Q)$ is the Fourier transform of a *pair* distribution function so, for any branched polymer, will be constructed from terms containing no more than two arm lengths [c.f. equation (20)]. Thus, all third and higher derivatives in which three or more of the arm suffices are different must be zero. After the derivatives have been evaluated and substituted into equation (29) the answer may be expressed either in terms of the arm molecular masses or those of the star as a whole. The latter is written down here, but it is easy to convert to the other form by means of the relationships in the appendix:

$$\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\simeq\frac{2}{f}\frac{(M^\mathrm{s}_0)^2}{M^\mathrm{s}_\mathrm{n}}\frac{1}{y_0^2}\left[\mathrm{e}^{-y_0}+y_0-1+\frac{(f-1)}{2}(1-\mathrm{e}^{-y_0})^2\right]$$
$$+\frac{2}{f}M^\mathrm{s}_0(1-M^\mathrm{s}_0/M^\mathrm{s}_\mathrm{n})\frac{1}{y_0}[1-\mathrm{e}^{-y_0}+(f-1)\mathrm{e}^{-y_0}(1-\mathrm{e}^{-y_0})]$$
$$+[fM^\mathrm{s}_\mathrm{w}-(f-1)M^\mathrm{s}_\mathrm{n}-2M^\mathrm{s}_0+(M^\mathrm{s}_0)^2/M^\mathrm{s}_\mathrm{n}]\frac{\mathrm{e}^{-y_0}}{f}$$
$$[1-(f-1)(1-\mathrm{e}^{-y_0})]+\frac{(f-1)}{f}\frac{(M^\mathrm{s}_\mathrm{n}-M^\mathrm{s}_0)^2}{M^\mathrm{s}_\mathrm{n}}\mathrm{e}^{-2y_0}$$
$$-[f^2M^\mathrm{s}_\mathrm{z}M^\mathrm{s}_\mathrm{w}/M^\mathrm{s}_0-3f(f-1)M^\mathrm{s}_\mathrm{w}M^\mathrm{s}_\mathrm{n}/M^\mathrm{s}_0+(f-1)(2f-1)(M^\mathrm{s}_\mathrm{n})^2/$$
$$-3f(M^\mathrm{s}_\mathrm{w}-M^\mathrm{s}_\mathrm{n})+3(M^\mathrm{s}_0-M^\mathrm{s}_\mathrm{n})-(M^\mathrm{s}_0)^2/M^\mathrm{s}_\mathrm{n}]\frac{y_0\mathrm{e}^{-y_0}}{3f}$$
$$[1-(f-1)(1-\mathrm{e}^{-y_0})]+\frac{(f-1)}{f}(1-M^\mathrm{s}_\mathrm{n}/M^\mathrm{s}_0)$$
$$[fM^\mathrm{s}_\mathrm{w}-(f-1)M^\mathrm{s}_\mathrm{n}-2M^\mathrm{s}_0+(M^\mathrm{s}_0)^2/M^\mathrm{s}_\mathrm{n}]y_0\mathrm{e}^{-2y_0} \qquad (30)$$

where

$$y_0=Q^2Kn_0=Q^2KN_0/f$$

The small Q form of this function is identical with the general formula, equation (26), as expected.

As in the case of linear polymers discussed earlier, the best value for the mass M^s_0, about which the expansion is made, is the one which makes the scattering function for a monodisperse star, equation (21), of mass M^s_0 most nearly fit the polydisperse scattering function over the Q range of the data. Once again, the functions for monodispersity and polydispersity coincide in the limits of small and large Q. At large Q the asymptotic form is:

$$\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\simeq\frac{2m}{Q^2K}\left[1+\frac{f(f-3)}{2Q^2K}\frac{m}{M_{\mathrm{n}}^{\mathrm{s}}}\right] \tag{31}$$

so equation (21) with $M_0^{\mathrm{s}}=M_{\mathrm{w}}^{\mathrm{s}}$ coincides both at $Q=0$ and at large Q with the polydisperse scattering function, suggesting this as a good choice for the mass to expand about if data is taken over a wide range of Q.

Gaussian, star-branched polymers: variable number of arms

For high functionality branched polymers (large f) the origin of the polydispersity is liable to change. Rather than arising from the polydispersity of the linear branches, it is more likely that the variation in the number of branches will contribute most to the overall spread in molecular mass. The scattering function for a sample containing star-branched polymers in which there is a distribution of functionalities, but each arm is the same length, can be calculated exactly in terms of the mass averages.

The fraction of molecules having functionality f is x_f, and the number of scattering units along each arm is n. This time the scattering function is:

$$S(Q)=\sum_{f=1}^{\infty}S(Q,nf)x_f \tag{32}$$

where $S(Q,nf)$ is the Benoit formula for a monodisperse star of mass mnf, equation (21). Inspection of equation (21) reveals that the f dependence in $S(Q,nf)$ takes the form of terms linear and quadratic in f, so that the result of the sum in equation (32) contains only the mass averages $M_{\mathrm{n}}^{\mathrm{s}}$ and $M_{\mathrm{w}}^{\mathrm{s}}$. The cross-section is:

$$\begin{aligned}\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}=\frac{2mn}{y^2}&[\mathrm{e}^{-y}+y-1+\tfrac{1}{2}(M_{\mathrm{n}}^{\mathrm{s}}/nm-1)(1-\mathrm{e}^{-y})^2]\\&+1/y^2\,(M_{\mathrm{w}}^{\mathrm{s}}-M_{\mathrm{n}}^{\mathrm{s}})(1-\mathrm{e}^{-y})^2\end{aligned} \tag{33}$$

where

$$y=Q^2Kn$$

Unlike the moments expansion formulae, equation (33) is *exact*, and applies to any degree of polydispersity. The small Q form is:

$$\frac{1}{A}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\simeq M_{\mathrm{w}}^{\mathrm{s}}[1-\tfrac{1}{3}Q^2Kn(3-2mn/M_{\mathrm{w}}^{\mathrm{s}})] \tag{34}$$

so that the z-average, mean square radius of gyration of the sample is:

$$\langle S^2\rangle_z=Kn(3-2nm/M_{\mathrm{w}}^{\mathrm{s}}) \tag{35}$$

The cross-section, equation (33), agrees with a special case derived by Casassa and Berry[8] in which the number of arms attached to the centre followed a binomial distribution. Their model is valid if the probability of an arm being attached to a unit of the centre is independent of the number of arms already attached, which is a good assumption for a comb molecule, but not for a star.

LIMITATIONS OF FORMULAE

To illustrate the accuracy of the moments expansion the scattering curves were calculated for a linear polymer sample with two specific number distributions: a Schulz, and a rectangular distribution. M_{w} and $\langle S^2(M_{\mathrm{w}})\rangle$ were chosen to be the same for both distributions, and a set of curves was generated with different $M_{\mathrm{w}}/M_{\mathrm{n}}$. Each curve was compared with the third order moments expansion formula, equation (18), and with the Debye function.

Figure 1 plots the worst percentage deviation of the moments expansion and the Debye function from the curves for the two number distributions when the functions are made to coincide at $Q=0$ and at large Q. The worst deviations from the moments formula are seen to be much less than from the Debye function, and the results are of similar magnitude for both types of polydispersity. Assuming that the two examples here are representative of most realistic number distributions, and that scattering experiments typically have Poisson noise of one or two per cent, it seems reasonable to apply the moments expansion formula to samples with $M_{\mathrm{w}}/M_{\mathrm{n}}$ up to about 1.3. The error is then no more than the statistical noise on the data (and considerably better for most of the Q range).

EXAMPLES

(i) To illustrate the polydispersity effect in molten blends of protonated and deuterated polymers, some experimental neutron scattering data are presented for three-arm polyethylene stars. The protonated and deuterated components had the same molecular mass distribution because they were both obtained by saturating a common parent polybutadiene. The spectra were taken on the small-angle facility at NBS, Gaithersburg, with good statistics, and fitted to both the Benoit equation and to the moments expansion formula over the whole Q-range of the data. Details of the data analysis and fitting procedure are given elsewhere[1], but

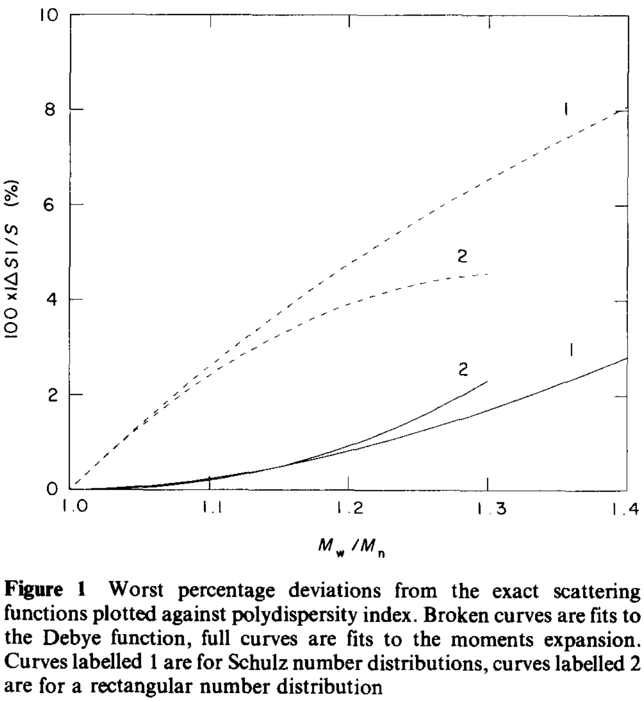

Figure 1 Worst percentage deviations from the exact scattering functions plotted against polydispersity index. Broken curves are fits to the Debye function, full curves are fits to the moments expansion. Curves labelled 1 are for Schulz number distributions, curves labelled 2 are for a rectangular number distribution

the corrected spectra are displayed in *Figure 2* and the results of the fits are listed in *Table 1*. The values of M_z^s/M_w^s are known only approximately, but variation of ±1% produces only a small change in the results, and does not affect the general trends.

Two features of the results are of note. First, the value of $\langle S^2\rangle$ from the Benoit equation fit is initially larger than $\langle S^2(M_w)\rangle$, but becomes smaller as the molecular mass increases. Second, the value of χ^2 (the sum of the weighted square-deviations, per data point) is, in each case, smaller for the fit to the moments expansion formula than to the Benoit equation.

(ii) To help interpret the radius of gyration behaviour observed in the data fitting above, and to further illustrate the effects of a small polydispersity, a numerical experiment was performed. Some test data were generated for a four-arm star whose arms had a Schulz number distribution with $M_w^a/M_n^a=1.2$, i.e. $M_w^s/M_n^s=1.05$. The sample was chosen to have $M_w^s=50\,000$ and $K/m=0.05$, so that $\langle S^2(M_w^s)\rangle^{1/2}=39.53$ Å. The data are generated as 100 points in the range $0.0 \leqslant Q \leqslant 0.2$ Å^{-1} and fitted in the very small and very large Q limits to the Benoit formula and also to the equivalent moments expansion, equation (30), expanded about M_w.

The curve is displayed in *Figure 3* and the results of the fits are listed in *Table 2*. Clearly, the moments expansion formula, which is exact in the limits of small and large Q, is able to give results consistently close to the correct value of $\langle S^2(M_w^s)\rangle^{1/2}$. The Benoit equation, on the other hand, produces a radius of gyration which decreases as the interval in Q shifts to larger Q. This is a consequence of equations (26) and (31), which show, respectively, that in the small Q limit it is $\langle S^2\rangle_z^{1/2}$ and in the large Q limit, $\langle S^2(M_n^s)\rangle^{1/2}$, which are characteristic of the scattering function. The expected values at these extremes, $\langle S^2\rangle_z^{1/2}=42.06$ Å [from equation (27)] and $\langle S^2(M_n^s)\rangle^{1/2}=37.65$ Å [from equation (28)], have been inserted into *Table 2* for comparison.

The systematic change in the radius of gyration over different regions of the scattering curve is in the same sense as that observed in the experimental data. Whilst the possibility that the polymers may not be Gaussian cannot be ruled out entirely, the trends in radius of

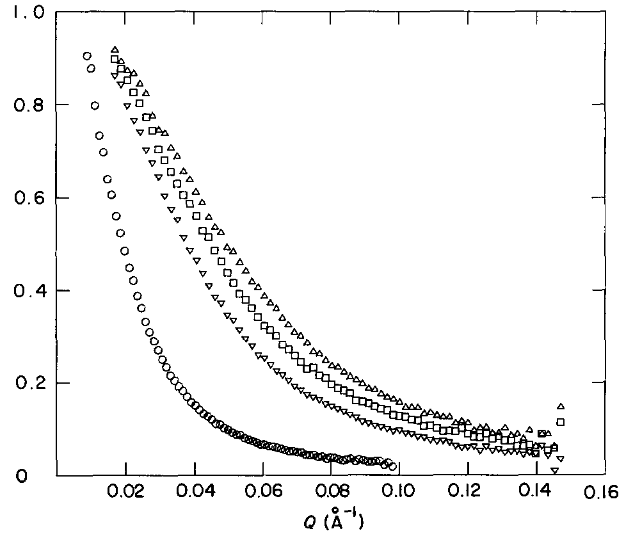

Figure 2 Neutron scattering spectra of the four three-arm star polymers used in example (i), normalized to unity at $Q=0$. The molecular masses are: 5700 (△); 7000 (□); 9200 (▽); 41 000 (○)

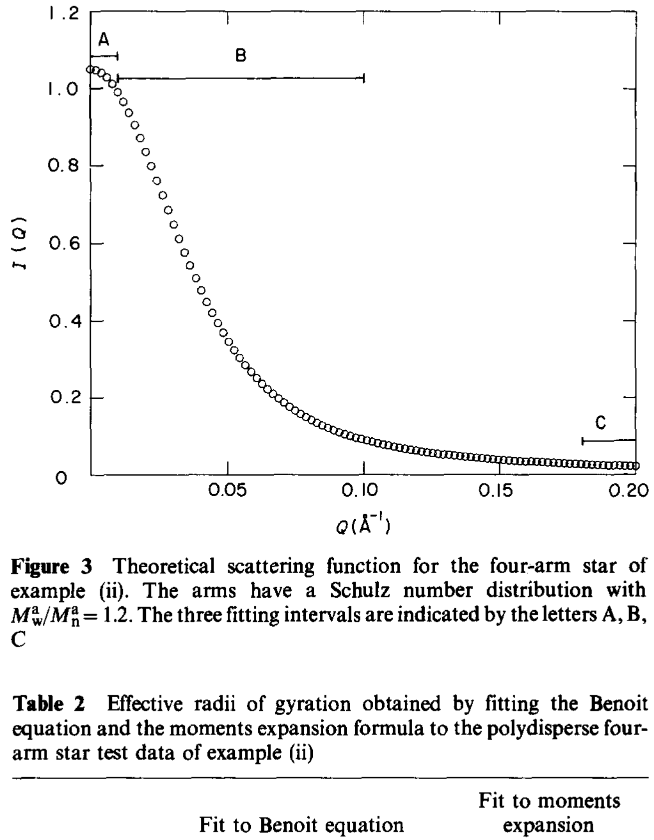

Figure 3 Theoretical scattering function for the four-arm star of example (ii). The arms have a Schulz number distribution with $M_w^a/M_n^a=1.2$. The three fitting intervals are indicated by the letters A, B, C

Table 2 Effective radii of gyration obtained by fitting the Benoit equation and the moments expansion formula to the polydisperse four-arm star test data of example (ii)

Q range of fit (Å^{-1})	Fit to Benoit equation		Fit to moments expansion	
	$\langle S^2\rangle^{1/2}$ (Å)	$I(Q=0)$	$\langle S^2\rangle^{1/2}$ (Å)	$I(Q=0)$
lim ΔQ as $Q\rightarrow 0$	42.06	1.050	39.53	1.050
A 0.00→0.01	41.98	1.050	39.52	1.050
B 0.01→0.10	40.24	1.035	39.63	1.052
C 0.18→0.20	38.68	1.005	39.63	1.056
lim ΔQ as $Q\rightarrow\infty$	37.65	1.000	39.53	1.050

Table 1 Neutron scattering data for four samples of molten three-arm star polymers. The spectra were converted to absolute intensity and fitted to the Benoit equation and to the moments expansion formula

			Fit to Benoit equation			Fit to moments expansion		
$\frac{M_w^s}{10^3}$	$\frac{M_w^s}{M_n^s}$	$\frac{M_z^s}{M_w^s}$	$\langle S^2\rangle^{1/2}$ (Å)	$\frac{d\Sigma}{d\Omega}(0)$ (cm^{-1})	χ^2	$\langle S^2\rangle^{1/2}$ (Å)	$\frac{d\Sigma}{d\Omega}(0)$ (cm^{-1})	χ^2
5.7	1.03	1.03	31.4	1.57	0.835	31.1	1.59	0.787
7.0	1.05	1.05	34.8	1.50	0.689	34.6	1.53	0.677
9.2	1.02	1.02	40.7	2.58	1.23	40.7	2.61	1.06
41.0	1.05	1.04	79.9	13.0	0.738	80.9	13.6	0.702

gyration combined with the smaller χ^2 for the moments expansion fit suggest that it is the effects of polydispersity which are being observed.

DISCUSSION

The aim of the work described in this paper was to reexamine the problem of polydispersity from a different starting point, namely one in which the only knowledge of the molecular mass distribution is contained within the first few mass averages. This has been achieved by writing the scattering function as a series expansion in the moments of the molecular mass distribution, and the main results presented here are the approximate formulae for Gaussian linear and star polymers, equations (14) and (30).

A prerequisite for the moments method is that the scattering functions for different masses combine linearly. This has been shown to be the case for blends of molten polymers providing the mass distributions of the labelled and unlabelled components are the same. Scattering from very dilute solutions also satisfies the linear combination condition.

The formulae are intended to be used in conjunction with a theoretical calculation of $S(Q,N)$. Polydispersity is introduced through the moments expansion of $S(Q,N)$, and a direct fit to the experimental data then provides a test of the proposed model. The form of the moments expansion is computationally simple; it contains no integrals, and is differentiable for use in standard fitting routines.

The approximate formulae are necessarily restricted to cases where the molecular mass distribution is relatively narrow, typically $M_w/M_n < 1.3$. However, the experimental data presented here shows that polydispersity may still be evident even with a very monodisperse sample. Furthermore, it is only with such well-characterized samples that detailed experiments can be performed to test our understanding of chain conformation, and it is for application in these sorts of studies that the work is intended. Synthetic chemists are now able to produce samples of such quality, and to achieve the most accurate experimental results there will be an increasing demand for careful data analysis to correct for any non-idealities.

ACKNOWLEDGEMENTS

The author would like to acknowledge the comments and suggestions of Dr R. C. Ball and Dr G. L. Squires of the Cavendish Laboratory during the preparation of this paper.

REFERENCES

1 Horton, J. C., Squires, G. L., Boothroyd, A. T., Fetters, L. J., Rennie, A. R., Glinka, C. J. and Robinson, R. A. *Macromolecules* to be published

2 Squires, G. L., 'Introduction to the Theory of Thermal Neutron Scattering', Cambridge University Press, 1978, Chapter 4

3 Boué, F., Nierlich, M. and Leibler, L. *Polymer* 1982, **23**, 29

4 Debye, P. *J. Phys. Colloid Chem.* 1947, **51**, 18

5 Benoit, H. *J. Polym. Sci.* 1953, **11**, 507

6 Berry, G. C. in 'Encyclopedia of Materials Science and Engineering' (Ed. M. B. Bever) Pergamon, 1986, Vol. 15, pp. 3759–3767

7 Burchard, W. *Macromolecules* 1977, **10**, 919

8 Casassa, E. F. and Berry, G. C. *J. Polym. Sci.* (*A-2*) 1966, **4**, 881

APPENDIX

Relationships between the mass averages for a star and its arms

The correct relationships can be derived by recalling a property of the moments of convoluted distributions. If

$$Y(y) = X_1(x_1)^* X_2(x_2)^* \ldots {}^* X_f(x_f)$$

then the rth moment of Y is:

$$\overline{y^r} = \int \mathrm{d}y\, y^r \int \mathrm{d}x_1 \ldots \int \mathrm{d}x_f X_1(x_1) \ldots X_f(x_f) \delta\left(Y - \sum_{i=1}^{f} x_i\right)$$

$$= \int \mathrm{d}x_1 \ldots \int \mathrm{d}x_f \left(\sum_{i=1}^{f} x_i\right)^r X_1(x_1) \ldots X_f(x_f)$$

$$= \sum_{i=1}^{f} \overline{x_i^r} + \sum_{i>}^{f} \sum_{j}^{f} \left(\sum_{\alpha=1}^{r-1} \frac{r!}{\alpha!(r-\alpha)!} \overline{x_i^\alpha}\ \overline{x_j^{r-\alpha}} \right)$$

$$+ \sum_{i>}^{f} \sum_{j>}^{f} \sum_{k}^{f} \left(\sum_{\alpha=1}^{r-2} \sum_{\beta=1}^{r-\alpha-1} \frac{r!}{\alpha!\beta!(r-\alpha-\beta)!} \overline{x_i^\alpha}\ \overline{x_j^\beta}\ \overline{x_k^{r-\alpha-\beta}} \right) + \ldots$$

Putting $X_i(x_i)$ equal to the number distribution for each arm, the first three moments of the star are:

$$\bar{N} = f\bar{n}$$

$$\overline{N^2} = f\overline{n^2} + f(f-1)\bar{n}^2$$

$$\overline{N^3} = f\overline{n^3} + 3f(f-1)\overline{n^2}\bar{n} + f(f-1)(f-2)\bar{n}^3$$

From these, the molecular mass averages of the star in terms of the arms are then:

$$M_n^s = f M_n^a$$

$$M_w^s = M_w^a + (f-1)M_n^a \qquad \text{(A1)}$$

$$M_z^s = \frac{M_z^a M_w^a + 3(f-1)M_w^a M_n^a + (f-1)(f-2)(M_n^a)^2}{M_w^a + (f-1)M_n^a}$$

Inverting these,

$$M_n^a = M_n^s / f$$

$$M_w^a = M_n^s[(M_w^s/M_n^s - 1) + 1/f] \qquad \text{(A2)}$$

$$M_z^a = \frac{f^2 M_z^s M_w^s / M_n^s - 3f(f-1)M_w^s + (f-1)(2f-1)M_n^s}{f[f(M_w^s/M_n^s - 1) + 1]}$$