Neutron Scattering from a Solution of a Polymer in a Polymer. The Effect of Long-Range Heterogeneities

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ABSTRACT: Solid polyethylene and polydeuterioethylene melt at different temperatures. Consequently, a mixture of these two species in the melt or in solution crystallize at different rates leading to sample heterogeneities arising from isotopic segregation. This phenomenon can be expected to occur for other crystalline polymers. The determination of polymer size and shape by small-angle neutron scattering is normally performed by isotopic labeling, substituting deuterium in place of hydrogen. The phenomenon of isotopic segregation has a profound influence on the analysis of experiments. An analysis appropriate to partially segregated systems is proposed using a simple model of an isotopically segregated sample. An important consequence of the analysis is that the excess scattering arising from the labeled solute cannot be separated from the background unless the heterogeneities in isotopic composition are properly accounted for.

The measurement of molecular size and shape of a polymer molecule in bulk can be and has been carried out by small-angle neutron scattering (SANS). The neutrons "see" isotopically labeled molecules against an unlabeled background by dissolving deuterated polymer molecules in a matrix of protonated polymer of the same speices or vice versa. The most thorough studies have been performed on amorphous bulk polymers,[2,3] investigations of crystalline polymers have been troublesome, and reliable results are difficult to come by.[4,5]

There are several reasons why crystalline polymers need special attention. First of all, an important linear dimension of crystalline polymers is the interlamella distance, a number of the order of 100–200 Å. This is the same size range as the molecular sizes of the polymer molecules; thus, forward scattering from the background overlaps the scattering from the tagged molecules. As a consequence, special attention must be paid to the proper subtraction of the background.

Second, crystalline polymers contain microvoids which scatter strongly in the forward direction. This has been demonstrated for polyethylene[6,7] to vary from sample to sample, and should be anticipated to a greater or lesser degree in other crystalline polymers.

The third factor is isotopic segregation in the sample arising from different crystallization rates of the deuterated and protonated species.[6,7] This is a serious difficulty in polyethylene,[8] and similar problems are anticipated for other crystalline polymers. It is essential that any analysis of scattering from crystalline polymers take this into account.

In what is to follow, we derive the neutron scattering equations for a crystalline polymer which contains long-range inhomogeneities in concentration. In addition, a procedure is described for analysis of experiments on heterogeneous systems which cannot be analyzed by conventional techniques.

Fluctuations in Density and Concentration

It is correct and convenient to calculate SANS envelopes by assuming that all atomic nuclei in a monomer unit are concentrated at a single point. We make this assumption and denote the scattering lengths of the labeled and unlabeled monomers as a_D and a_H, respectively. Concentration will be expressed as volume fraction, c_D for the tagged material and c_H for the matrix. The mean scattering length is

$$\bar{a} = a_H\bar{c}_H + a_D\bar{c}_D \tag{1}$$

$\bar{c}_H$ and $\bar{c}_D$ are the mean values of c_H and c_D.

In the calculation, the scattering length is represented as a continuous function of position. Thus

$$a(\mathbf{r}_i) = (\rho(\mathbf{r}_i)/\bar{\rho})(a_Hc_H + a_Dc_D) \tag{2}$$

$\rho(\mathbf{r}_i)$ is the density of monomer units at $\mathbf{r}_i$, $\bar{\rho}$ is the average of $\rho(\mathbf{r}_i)$. The fluctuations in a, ρ, and c_D are expressed as follows:

$$a(\mathbf{r}_i) = \bar{a} + \delta a(\mathbf{r}_i) \tag{3a}$$

$$\rho(\mathbf{r}_i) = \bar{\rho} + \delta\rho(\mathbf{r}_i) \tag{3b}$$

$$c_D(\mathbf{r}_i) = \bar{c}_D + \delta c_D(\mathbf{r}_i) \tag{3c}$$

$$c_H(\mathbf{r}_i) = \bar{c}_H - \delta c_D(\mathbf{r}_i) \tag{3d}$$

The fluctuations in concentration are dependent, as shown in eq 3c and 3d.

The scattering from the sample arises from the fluctuations in scattering length. These fluctuations may be expressed in terms of fluctuations in density and in concentrations.

$$\delta a(\mathbf{r}_i) = (\bar{a}/\bar{\rho})\delta\rho(\mathbf{r}_i) + (a_D - a_H)\delta c_D(\mathbf{r}_i) \tag{4}$$

If the common assumption that density fluctuations and concentration fluctuations are independent is made, the scattering law is decomposed into two independent terms, one described by a density correlation function and another by a concentration correlation function. These are defined by

$$\gamma_\rho(\mathbf{r}) = \langle\delta\rho(\mathbf{r}_i)\delta\rho(\mathbf{r}_i + \mathbf{r})\rangle/\langle(\delta\rho)^2\rangle \tag{5a}$$

$$\gamma_c(\mathbf{r}) = \langle\delta c_D(\mathbf{r}_i)\delta c_D(\mathbf{r}_i + \mathbf{r})\rangle/\langle(\delta c_D)^2\rangle \tag{5b}$$

The angle brackets designate an ensemble average.

The correlation functions $\gamma_\rho(\mathbf{r})$ and $\gamma_c(\mathbf{r})$ measure the distance over which the memory of a density fluctuation or concentration fluctuation exists. They are both normalized to unity at $\mathbf{r} = 0$, and approach zero at large $\mathbf{r}$.

In a two-component system, the correlation function is simply related to the probabilities that two points separated by a vector $\mathbf{r}$ are in the same or different material.[9]

Let $p_{12}(\mathbf{r})$ be the probability that the vector $\mathbf{r}$ ends in material 2, given that the origin is in material 1. The subscripts 1 and 2 may be either H or D. These probabilities become

$$p_{DD}(\mathbf{r}) = \bar{c}_D + \bar{c}_H\gamma_c(\mathbf{r}) \tag{6a}$$

$$p_{DH}(\mathbf{r}) = \bar{c}_H - \bar{c}_H\gamma_c(\mathbf{r}) \tag{6b}$$

$$p_{HH}(\mathbf{r}) = \bar{c}_H + \bar{c}_D\gamma_c(\mathbf{r}) \tag{6c}$$

$$p_{HD}(\mathbf{r}) = \bar{c}_D - \bar{c}_D\gamma_c(\mathbf{r}) \tag{6d}$$

The Scattering Law for a Homogeneous Material. The intensity of coherent neutron scattering is obtained by sum-

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ming over all pairs of elements in the sample. Thus

$$I(\mathbf{q}) = \bar{\rho}^2 \int\int a(\mathbf{r}_i)a(\mathbf{r}_j) \exp[i\mathbf{q}\cdot\mathbf{r}_{ij}]\,\mathrm{d}\mathbf{r}_i\,\mathrm{d}\mathbf{r}_j \tag{7a}$$

In discrete notation eq 7a takes the form

$$I(\mathbf{q}) = \sum_{\mathrm{m,p}} \sum_{i,j} a_i(\mathrm{m})a_j(\mathrm{p}) \exp[i\mathbf{q}\cdot\mathbf{r}_{ij}] \tag{7b}$$

The sample occupies a volume V and is composed of N_{D} tagged molecules containing n_{D} monomer units each. The untagged molecules are N_{H} in number, each with n_{H} monomer units. $a_i(\mathrm{m})$ is the fluctuation of the scattering length of monomer i on molecule m. $\mathbf{q}$ is the wave vector, equal to $(2\pi/\lambda)(\mathbf{k} - \mathbf{k}_0)$, where $\mathbf{k}$ and $\mathbf{k}_0$ are unit vectors in the directions of scattered and incident neutron beams and λ is the neutron wavelength. The magnitude of $\mathbf{q}$ equals $(4\pi/\lambda)\sin(\theta/2)$ where θ is the angle between $\mathbf{k}_0$ and $\mathbf{k}$. $\mathbf{r}_{ij}$ is the vector connecting monomer i to monomer j.

Equation 7a can be integrated over volume keeping $\mathbf{r}_{ij}$ constant. Setting $\mathbf{r}_{ij} = \mathbf{r}$ and $\mathbf{r}_j = \mathbf{r}_i + \mathbf{r}$, we find

$$I(\mathbf{q}) = \bar{\rho}^2 V \int \langle a(\mathbf{r}_i)a(\mathbf{r}_i + \mathbf{r})\rangle \exp[i\mathbf{q}\cdot\mathbf{r}]\,\mathrm{d}\mathbf{r} \tag{8}$$

The average $\langle a(\mathbf{r}_i)a(\mathbf{r}_i + \mathbf{r})\rangle$ is expandable in terms of density and concentration variables using eq 3a and 4. The correlation functions $\gamma_\rho(\mathbf{r})$ and $\gamma_{\mathrm{c}}(\mathbf{r})$ have been invoked as convenient representations of the ensemble averages of spatially correlated fluctuations in density and in concentration. Carrying out the arithmetic details, one finds

$$I(\mathbf{q}) = I_\rho(\mathbf{q}) + I_{\mathrm{c}}(\mathbf{q}) \tag{9a}$$

$$I_\rho(\mathbf{q}) = \bar{a}^2\langle(\delta\rho)^2\rangle V \int \gamma_\rho(\mathbf{r}) \exp[i\mathbf{q}\cdot\mathbf{r}]\,\mathrm{d}\mathbf{r} \tag{9b}$$

$$I_{\mathrm{c}}(\mathbf{q}) = (a_{\mathrm{H}} - a_{\mathrm{D}})^2\langle(\delta c_{\mathrm{p}})^2\rangle V\bar{\rho}^2 \int \gamma_{\mathrm{c}}(\mathbf{r}) \exp[i\mathbf{q}\cdot\mathbf{r}]\,\mathrm{d}\mathbf{r} \tag{9c}$$

$I_{\mathrm{c}}(\mathbf{q})$ may be divided into two parts, that which arises from distances between monomer units within a polymer molecule and the rest which originated from intermolecular pairs of monomer units. Thus

$$I_{\mathrm{c}}(\mathbf{q}) = \underset{\text{(intramolecular)}}{I_1(\mathbf{q})} + \underset{\text{(intermolecular)}}{I_2(\mathbf{q})} \tag{10}$$

$I_2(\mathbf{q})$ is of the order of c_{D}^2 and tends to vanish if the molecules are randomly arranged. $I_1(\mathbf{q})$, which contains all the information on shape and size of a polymer molecule, is preferably spelled out in the discrete notation used in eq 7b. $I_1(\mathbf{q})$ takes the form

$$I_1(\mathbf{q}) = \sum_{\mathrm{m}} \sum_{i,j} (a_{\mathrm{H}} - a_{\mathrm{D}})^2\langle\delta c_D(i)\delta c_D(j)\rangle \exp[i\mathbf{q}\cdot\mathbf{r}_{ij}] \tag{11}$$

If i is on a deuterated molecule, $\delta c_{\mathrm{D}}(i) = 1 - \bar{c}_{\mathrm{D}} = \bar{c}_{\mathrm{H}}$, and $\delta c_{\mathrm{D}}(i) = -\bar{c}_{\mathrm{D}}$ if i is on a protonated molecule. Therefore

$$\delta c_{\mathrm{D}}(i)\delta c_{\mathrm{D}}(j) = \bar{c}_{\mathrm{H}}^2$$

on a deuterated molecule and equals $\bar{c}_{\mathrm{D}}^2$ on a protonated molecule. Thus defining

$$S_{\mathrm{D}}(\mathbf{q}) = \left\langle \sum_{i,j} \exp[i\mathbf{q}\cdot\mathbf{r}_{ij}] \right\rangle \tag{12a}$$

for a D molecule

$$S_{\mathrm{H}}(\mathbf{q}) = \left\langle \sum_{i,j} \exp[i\mathbf{q}\cdot\mathbf{r}_{ij}] \right\rangle \tag{12b}$$

for an H molecule we find

$$I_1(\mathbf{q}) = N(a_{\mathrm{D}} - a_{\mathrm{H}})^2\bar{c}_{\mathrm{H}}\bar{c}_{\mathrm{D}}[\bar{c}_{\mathrm{H}}S_{\mathrm{D}}(\mathbf{q}) + \bar{c}_{\mathrm{D}}S_{\mathrm{H}}(\mathbf{q})] \tag{13}$$

$S_{\mathrm{D}}(\mathbf{q})$ and $S_{\mathrm{H}}(\mathbf{q})$ are the molecular scattering functions for D and H molecules. $S_{\mathrm{D}}(0)$ and $S_{\mathrm{H}}(0)$ equal n_{D}^2 and n_{H}^2, respectively. $N = N_{\mathrm{H}} + N_{\mathrm{D}}$, the total number of polymer molecules in the sample.

A polymer which contains only H monomer units would scatter according to the equation

$$I_\rho(\mathbf{q}) = a_{\mathrm{H}}^2 S_{\mathrm{D}}(\mathbf{q}) \tag{14a}$$

$$S_{\mathrm{D}}(\mathbf{q}) = \langle(\delta\rho)^2\rangle V \int \gamma_\rho(\mathbf{r}) \exp[i\mathbf{q}\cdot\mathbf{r}]\,\mathrm{d}\mathbf{r} \tag{14b}$$

The scattering of the D polymer dissolved in a protonated matrix is

$$I(\mathbf{q}) = I_\rho(\mathbf{q}) + I_1(\mathbf{q}) + I_2(\mathbf{q}) \tag{15a}$$

$$I_\rho(\mathbf{q}) = (a_{\mathrm{H}}\bar{c}_{\mathrm{H}} + a_{\mathrm{D}}\bar{c}_D)^2 S_D(\mathbf{q}) \tag{15b}$$

$I_1(\mathbf{q})$ is given in eq 13. $I_2(\mathbf{q})$, which sums over intermolecular pairs, is not important for our purpose.

The Scattering Law for Heterogeneous Polymer. Equations 13, 15a, and 15b express the scattering intensity of a solution of one polymer in another. These relationships are simple extensions of well-known results on polymers dissolved in low molecular weight solvents. We are especially interested in the problem of sample heterogeneity brought about by isotopic segregation in the process of polymer crystallization from the melt or from solution. The scattering laws are modified depending on the distribution of the isotopic species.

We choose a model in which the sample is composed of subsamples each of different isotopic composition. Within a subsample, the isotopic content is uniform. The subsamples are sufficiently large that interference between the waves emanating from different subsamples may be safely neglected.

This model is based on a reasonable view of the crystallization process. As a polymer crystal is being formed, the concentration of isotopic species which precipitates may differ from the concentration in the contiguous melt or solution, but it is, nevertheless, determined by that concentration. As crystallization proceeds, the concentration in the melt (solution) changes by selective depletion. Therefore, one should expect a local uniformity which changes only as the concentration of the yet uncrystallized material changes.

We consider the sample as composed of ν subsamples. The ith subsample has a mean concentration $\bar{c}_{\mathrm{D}}(i)$.

The mean concentration of the overall sample is $\mathbf{c}_{\mathrm{D}}$. A similar definition holds for $\bar{c}_{\mathrm{H}}(i)$ and $\mathbf{c}_{\mathrm{H}}$. Then

$$\bar{c}_{\mathrm{D}}(i) = \mathbf{c}_{\mathrm{D}} + \delta_i \tag{16a}$$

$$\sum_{i=1}^{\nu} V_i\delta_i = 0 \tag{16b}$$

$$\bar{\delta}^2 = \frac{1}{V}\sum_{i=1}^{\nu} V_i\delta_i^2 \tag{16c}$$

$$\bar{\delta}^3 = \frac{1}{V}\sum_{i=1}^{\nu} V_i\delta_i^3 \tag{16d}$$

The summation is carried out over all i subsamples. V_i is the volume of the ith subsample and δ_i is the fluctuation of $\bar{c}_{\mathrm{D}}(i)$ from the overall mean.

The scattering law, taking isotopic segregation into account, is found by substitution of eq 16a through 16d in eq 13 and 15b. $\gamma_\rho(\mathbf{r})$ and $\gamma_{\mathrm{c}}(\mathbf{r})$ are presumed to be insensitive to isotopic segregation.

The results are

$$I_\rho(\mathbf{q}) = [(a_{\mathrm{H}}\mathbf{c}_{\mathrm{H}} + a_{\mathrm{D}}\mathbf{c}_{\mathrm{D}})^2 + \bar{\delta}^2(a_{\mathrm{H}} - a_{\mathrm{D}})^2]S_{\mathrm{D}}(\mathbf{q}) \tag{17a}$$

$$S_{\mathrm{D}}(\mathbf{q}) = \langle(\delta\rho)^2\rangle V \int \gamma_\rho(\mathbf{r}) \exp[i\mathbf{q}\cdot\mathbf{r}]\,\mathrm{d}\mathbf{r} \tag{17b}$$

$$\begin{aligned} I_1(\mathbf{q}) = N(a_{\mathrm{D}} - a_{\mathrm{H}})^2[&\mathbf{c}_{\mathrm{H}}\mathbf{c}_{\mathrm{D}}(\mathbf{c}_{\mathrm{H}}S_{\mathrm{D}}(\mathbf{q}) + \mathbf{c}_{\mathrm{D}}S_{\mathrm{H}}(\mathbf{q})) \\ &- \bar{\delta}^2\{(3\mathbf{c}_{\mathrm{H}} - 1)S_{\mathrm{D}}(\mathbf{q}) + (3\mathbf{c}_{\mathrm{D}} - 1)S_{\mathrm{H}}(\mathbf{q})\} \\ &+ \bar{\delta}^3\{S_{\mathrm{D}}(\mathbf{q}) - S_{\mathrm{H}}(\mathbf{q})\}] \end{aligned} \tag{17c}$$

Equation 17c simplifies if the molecular weights of the tagged and untagged polymer are the same. The result is

$$I_1(\mathbf{q}) = N(a_D - a_H)^2(\mathbf{c}_D\mathbf{c}_H - \bar{\delta}^2)S_D(\mathbf{q}) \qquad (18)$$

Discussion

The determination of molecular size and shape of a polymer from a small-angle neutron-scattering experiment depends on a proper subtraction of background scattering. If this is done and one retains only linear terms in c_D and terms up to powers of $\mathbf{q}^2$ in $S_D(\mathbf{q})$, one finds from eq 14

$$I_1(\mathbf{q}) = \{(a_D - a_H)^2 N_A VMc/M_0^2\}[1 - \mathbf{q}^2 R_g^2/3 + O(\mathbf{q}^4)] \qquad (19)$$

N_A is Avogadro's number, M_0 is the molecular weight of the labeled monomer, M is the molecular weight of the polymer molecule, c is concentration of the labeled monomer in the sample expressed in g/mL, and R_g is the radius of gyration of the polymer molecule.

The problem in data analysis arises in the proper separation of the background scattering. If the data are analyzed by assuming that the scattering from the matrix is given by eq 15b, while, in fact, eq 17a applies, one finds the apparent scattering from single-labeled molecules is given by

$$I_1^{\mathrm{app}}(\mathbf{q}) = I_1(\mathbf{q}) + \bar{\delta}^2(a_D - a_H)^2 S_D(\mathbf{q}) \qquad (20)$$

The importance of the final term can be estimated by expanding $I_1(\mathbf{q})$ and $S_D(\mathbf{q})$ up to powers of $\mathbf{q}^2$. Equation 20 becomes

$$I_1^{\mathrm{app}}(\mathbf{q}) = (a_D - a_H)^2 N_a V \left[\frac{Mc}{M_0^2(\mathrm{D})}\left(1 - \frac{\mathbf{q}^2 R_g^2}{3}\right) + \frac{\bar{\delta}^2\langle(\delta\rho)^2\rangle 8\pi\alpha^3 N_a}{M_0^2(\mathrm{H})}(1 - 2\alpha^2\mathbf{q}2)\right] \qquad (21)$$

M_0(D) and M_0(H) are molecular weights of CD_2 and CH_2, respectively, $\langle(\delta\rho)^2\rangle$ is the mean square fluctuation density expressed in g/mL, and M is the molecular weight of the labeled polymer. It has been assumed for the purpose of making an easy estimate that $\gamma_\rho(\mathbf{r}) = e^{-\mathbf{r}/\alpha}$ where α is a mean characteristic length of density fluctuations. If we assume $M = 10^5$, $c = 0.01$ g/mL, $\bar{\delta}^2 = 10^{-4}$, and $\alpha = 150$ Å, eq 21 becomes[10]

$$I_1^{\mathrm{app}}(\mathbf{q}) = (a_D - a_H)^2 N_A V \times \left[3.91\left(1 - \frac{\mathbf{q}^2 R_g^2}{3}\right) + 0.391\,(1 - 2\alpha^2\mathbf{q}^2)\right] \qquad (22)$$

For the specific example we have used here, it is clear that the apparent **M** would be 10% too large. The radius of gyration of bulk polyethylene should be between 100 and 150 Å. The apparent radius of gyration from ref 22 would then be 40–50% too large. These effects, particularly for larger δ^2, are easily large enough to account for the discrepancies reported in ref 6, and no model of clustered, deuterated molecules has been involved.

The difficulty is that $\bar{\delta}^2$ is generally unknown. Fortunately, in many cases, the molecular weight of the labeled polymer is known, and one can use this knowledge to estimate $\bar{\delta}^2$. A possible procedure is as follows.

$$I_1(\mathbf{q}) = I_1^{\mathrm{app}}(\mathbf{q}) - aI_0(\mathbf{q}) = (a_D - a_H)^2 VN_A Mc/M_0^2(\mathrm{D}))(1 - b\mathbf{q}^2 + \rho\mathbf{q}^4) \qquad (23)$$

Use the known value of molecular weight and an absolute calibration of the neutron-scattering spectrometer to obtain the leading coefficient on the right-hand side of eq 22. Obtain a, b, and c by a linear least-squares fit of experimental data collected in the low **q** regions. Use these values to calculate $I_1(\mathbf{q})$, which, thus obtained, is to be used for subsequent calculations of the molecular size.

This method has been applied to small-angle neutron scattering of polydueterioethylene in a polyethylene matrix.[11] The corrections are substantial. With this system, we have found that the correction procedure is necessary only in the low-angle region. The shapes of scattering curves are insensitive to this correction at higher **q** because of the rapid decrease of matrix scattering with increasing **q** in our experiments.

Conclusions

1. Formal equations for small-angle neutron scattering of a polymer dissolved in a polymer matrix have been worked.
2. These equations have been applied to a system which is heterogeneous in composition owing to partial isotopic segregation. It has been shown that the principal difficulty with interpretation of data originates in the subtraction of the term in matrix scattering.
3. A procedure is recommended for obtaining the molecular scattering of a polymer solute in a material which is heterogeneous in concentration.

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