Small angle neutron scattering of partially segregated polymer blends

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Small angle neutron scattering (SANS) has been used extensively to investigate the conformation of macromolecules. However, the scattered intensity has been found to be extremely sensitive to the segregation of the isotopic labelled species. The segregation has resulted in enormous increases in both the radius of gyration and the molecular weight. A theoretical treatment based on the Zernicke–Prins equation with a modified pair correlation function has been developed in this work; the size and the degree of segregation can be calculated from the scattering data using the equations obtained herein.

Keywords Long chain conformations; macromolecules; neutron scattering; radius of gyration; segregations; small angle scattering

Small angle neutron scattering (SANS) has been extensively used to elucidate the conformation of polymer molecules in solutions and in blends. Deuterated macromolecules are commonly mixed with the hydrogenerated macromolecules to obtain scattering contrast. One of the well studied polymer systems is polyethylene (PEH) blended with the deuterated species (PED) which is used as the labelled chain[1−3]. Segregation of the two species has frequently been observed in this blend system and is a consequence of the difference between the melting points of these two species. The segregation has resulted in enormous increases in the radius of gyration R'_g and the apparent molecular weight M'_w as observed by different investigators[1−2]. In some cases, the apparent molecular weight from SANS can be several orders of magnitude larger than that of each of the constituent polymers. A theoretical treatment[13] based on a paraclustering model has been proposed to account for these differences. The validity of such a model has already been questioned by others[4]. As will be shown later, the increase in both M_w and R_g from SANS measurements can easily be accounted for quantitatively providing the centres of mass of the labelled chains are not randomly distributed throughout the specimen. Whether the labelled chains interconnect themselves to form a supernetwork or not will be considered here. Formation of such a supernetwork is the essential part of the paraclustering model.

One can approach this problem from the viewpoint implied by the well-known Zernicke–Prins[5] equation,

$$I(h) = I_0(h)\bar{N}\left(\overline{f_n^2(h)} - \frac{\bar{N}}{V}\overline{f_n(h)}^2 \int_v \left(1 - P_c(r_{k,j};v')\right) \frac{\sin hr}{hr}4\pi r^2 \mathrm{d}r\right)$$

(1)

where $I_0(h)$ is the scattering constant and is proportional to $(b_D - b_H)^2$, where b_D and b_H are the scattering lengths per protonated and deuterated monomers, respectively, $\bar{N}$ is the total number of labelled molecules within the scattering volume V, $f_n(h)$ is the form factor of an individual macromolecule of n monomers for both H and D species, h is the scattering vector equal to $(4\pi/\lambda)\sin\theta$, and $P_c(r_{j,k};v')$ is the pair correlation function of the centres of mass of the PED molecules j and k. The subscript c of the pair correlation function denotes clustering of the PED molecules. The symbol v' within the parenthesis of the correlation function $P_c(r_{j,k};v')$ denotes the local specific volume of the PED species within the clusters, and v is the macroscopic average specific volume defined as $V/\bar{N}$. The relation between $P_c(r_{j,k};v')$ and the unclustered one $P(r_{j,k};v)$ holds the key to the present problem and will be addressed in the following sections.

One simple model of segregation is where the centres of mass of the labelled chains are only allowed to exist within a portion (φ) of the total volume; the rest of the volume being free of the labelled chains. The local concentration of the labelled chain within the clusters is therefore $N/\varphi V$ and zero outside the clusters. It is further assumed that the distribution of the centres of mass of the labelled chains within the clusters is random. Without further specifying the size and the shape distribution of these clusters, one can always define another correlation function $\gamma_c(r)$[5] for these clusters regarding these clusters as a homogeneous phase and the space outside these clusters as the other phase. The physical meaning of the function $\gamma_c(r)$ can be understood readily from the following relation between the probability function $Z(r)$ and $\gamma_c(r)$ in such a hypothetical two phase system. The function $Z(r)$ is defined as a conditional probability for a point to be located in a cluster provided another point of a distance r away is also in a cluster. These two points do not have to be in the same clusters. It has been shown[5] that:

$$Z(r) = \varphi + (1-\varphi)\gamma_c(r). \tag{2}$$

The pair correlation function $P_c\left(r_{j,k};\dfrac{V}{N}\right)$ of the clustered system is defined as a probability of finding a centre of mass of a labelled chain located within volume dv_k at a distance $r_{j,k}$ away from point j of volume dv_j which is occupied by the centre of mass of another labelled chain. The above event can be decomposed to the following two independent events: within a volume V containing N/φ labelled chains, both ends of $r_{j,k}$ are occupied by the centres of mass of the labelled chains; concurrently, both ends of $r_{j,k}$ are situated within these clusters. Therefore, the function $P_c\left(r_{j,k};\dfrac{V}{N}\right)$ equals the product of the probability function of these two independent events mentioned above.

$$P_c\left(r_{j,k};\frac{V}{N}\right) = P\left(r_{j,k};\frac{\varphi V}{N}\right)\left(1 + \frac{1-\varphi}{\varphi}\gamma_c(r)\right). \tag{3}$$

It is noteworthy that the function $Z(r)$ is normalized by the factor φ in the above equation. This normalization is a direct consequence of the definition of the pair correlation function $P(r)$.

The term $P(r_{j,k};\varphi V/N)$ denotes a pair correlation function in an unclustered system; however, the average specific volume occupied by each labelled chain is $\varphi V/N$ instead of V/N. As recognized before[6], the pair correlation function (unclustered) does not depend on the labelled chain concentration in the case of isotopic labelling provided the molecular weights of the H and D species are the same. Consequently equation (3) can be written as:

$$P_c\left(r_{j,k};\frac{V}{N}\right) = P\left(r_{j,k};\frac{V}{N}\right)\left(1 + \frac{1-\varphi}{\varphi}\gamma_c(r)\right) \tag{3a}$$

By substituting equation (3a) into equation (1), one has

$$I(h) = I_0(h)\bar{N}\left(\overline{f_n^2(h)} - \frac{\bar{N}}{V}\overline{f_n(h)}^2 \int_v \left(1 - P\left(r_{j,k};\frac{V}{N}\right)\right)\right.$$
$$\frac{\sin hr}{hr}4\pi r^2 dr + \frac{\bar{N}}{V}\overline{f_n(h)}^2 \int_v \left(\frac{1-\varphi}{\varphi}P\left(r_{j,k};\frac{V}{N}\right)\gamma_c(r)\right)$$
$$\left.\frac{\sin hr}{hr}4\pi r^2 dr\right) \tag{4}$$

The first two terms of equation (4) represent exactly the scattering intensity caused by N labelled chains randomly distributed in volume V. The additional contribution to the scattering intensity due to clustering or segregation is represented by the third term embracing $\gamma_c(r)$, the correlation function of the clusters treated as a two-phase system.

Following the work of Debye *et al.*[7], the function $\gamma_c(r)$ for a system with randomly distributed clusters of irregular shape and size can be represented by

$$\gamma_c(r) = e^{-r/a} \tag{5}$$

where a is the so called correlation length. The average linear dimension or the chord length l_c of the clusters is related to a through the well-known Porod relation[8]

$$l_c = \frac{a}{1-\varphi} \tag{6}$$

From the same reasoning, the average opening size between the clusters is simply a/φ where φ is the volume fraction occupied by clusters as defined above.

The pair correlation function $P(r_{j,k};V/N)$ of a randomly distributed case arises mainly from the excluded volume effect among the centres of mass of the macromolecules. The long chain molecules are known to be highly interpenetrated in a bulk system. Nevertheless the centres of mass of molecules are not likely to overlap each other. The linear dimension l of this excluded volume is expected to be much smaller than the radius of gyration R_g of individual molecule, consequently, the contribution of intermolecular scattering to the total scattering intensity is insignificant for the isotopic labelling cases[9]. One can approximate the pair correlation function by the following formula

$$P\left(r_{j,k};\frac{V}{N}\right) = 1 - e^{-r/l} \tag{7}$$

to demonstrate the idea that for two or more centres of mass of long chain molecules gathered within a small volume l^3 is not favourable. The exact functional form of $P(r_{j,k};V/N)$ is not essential to the forthcoming derivation since the contribution to the scattering intensity arising from it will be neglected in the simplifications used later on.

By substituting equations (5) and (7) into the third term of equation (4), the additional scattering caused by segregation can be expressed as

$$\frac{\bar{N}^2}{V}\overline{f_n(h)}^2\left(\frac{1-\varphi}{\varphi}\right)\int_v P\left(r_{j,k};\frac{V}{N}\right)\gamma_c(r)\frac{\sin hr}{hr}4\pi r^2 dr$$

$$= \frac{\bar{N}^2}{V}\overline{f_n(h)}^2\left(\frac{1-\varphi}{\varphi}\right)\int_v (e^{-r/a} - e^{-r/l'})\frac{\sin hr}{hr}4\pi r^2 dr \tag{8}$$

where $l' \equiv al/(a+l)$ and is a quantity even smaller than l.

From certain experimental data[1], it is clear that the additional contribution to scattering intensity due to segregation manifests itself mainly in the vicinity of $hR_g \leqslant 1$. At a higher h region, the segregation has little effect on the scattering intensity and the scattering is believed to arise largely from intramolecular correlation. Within such a low angular region, the approximation scheme similar to that used in deriving the Guinier equation is a reasonable one when applied to both $\overline{f_n^2(h)}$ and $\overline{f_n(h)}^2$, and to the integral of equation (8) as follows.

In the Guinier region, i.e., $hR_g \leqslant 1$, both $\overline{f_n^2(h)}$ and $\overline{f_n(h)}^2$ for an isotropic specimen can be expressed as

$$\overline{f_n^2(h)} \simeq \overline{f_n(h)}^2 \simeq n^2\left(1 - \frac{R_g^2 h^2}{3}\right). \tag{9}$$

By substituting equations (8) and (9) into equation (4) and carrying out the integration one obtains

$$I(h) \simeq I_0(h)\bar{N}\,n^2\left(1 - \frac{R_g^2 h^2}{3}\right)$$

$$\left(1 - \frac{\bar{N}}{V}\left\{\frac{kl^3}{(1+h^2l^2)^2} - \frac{1-\varphi}{\varphi}\left[\frac{ka^3}{(1+h^2a^2)^2} + \frac{kl'^3}{(1+h^2l'^2)^2}\right]\right\}\right)$$

$$(10)$$

where k is a constant equal to 8π. The term containing l in the above equation represents the contribution to scattering intensity from intermolecular origin. Such a contribution has been found to be negligible[9] in the case of isotopic blends, consequently, this term will be neglected hereafter. Since l' is even smaller than l as is evident from the definition of l', the term containing l' will also be neglected. All these simplifications result in

$$I(h) \simeq I_0(h)\bar{N}\,n^2\left(1 - \frac{R_g^2 h^2}{3}\right)\left(1 + \frac{\bar{N}}{V}\frac{1-\varphi}{\varphi}\frac{ka^3}{(1+h^2a^2)^2}\right).$$

$$(10a)$$

In the small angle region where $ha \leqslant 1$, the above equation can be approximated further by neglecting all the terms with order higher than $h^2 a^2$:

$$\frac{I(h)}{I_0(h)} \simeq \bar{N}n^2\left(1 + \frac{k\bar{N}(1-\varphi)}{V\varphi}a^3\right.$$

$$\left. - h^2\left(\frac{R_g^2}{3} + \frac{k\bar{N}}{V}\frac{1-\varphi}{\varphi}\frac{R_g^2 a^3}{3} + \frac{2k\bar{N}}{V}\frac{1-\varphi}{\varphi}a^5\right)\right)$$

$$(11)$$

The average number, Y, of labelled chains per cluster with an average linear dimension of l_c can be expressed as

$$Y = \frac{l_c^3 \bar{N}}{\varphi V} = \frac{a^3 \bar{N}}{v\varphi(1-\varphi)^3}.$$

$$(12)$$

The relation between a, φ and l_c is given in equation (6) above. Equation (11) can then be rewritten in terms of Y, the correlation length a, and the fraction φ of volume occupied by the labelled chains. This equation is

$$\frac{I(h)}{I_0(h)} \simeq \bar{N}\,n^2(1 + k(1-\varphi)^4 Y)\left(1 - h^2\left(\frac{R_g^2}{3} + \frac{2k(1-\varphi)^4 Ya^2}{1+k(1-\varphi)^4 Y}\right)\right)$$

$$(13)$$

Consequently, the apparent molecular weight M'_w and the corresponding radius of gyration R'_g are larger than the corresponding quantities of the individual labelled chain by the following factors:

$$\frac{M'_w}{M_w} = 1 + k(1-\varphi)^4 Y$$

$$(14)$$

$$\frac{R_g'^2}{R_g^2} = 1 + \frac{6k(1-\varphi)^4 Ya^2}{(1+k(1-\varphi)^4 Y R_g^2}$$

$$(15)$$

Since there are two equations (equations (6) and (12)) relating these four unknowns Y, φ, a, l_c, all of them can be determined unambiguously from the experimentally measured quantities M'_w and R'_g. The increase of the apparent molecular weight M'_w by labelled chain segregation is not equal to Y, the number of molecules per cluster. Instead the value of φ as well as Y determines the magnitude of M'_w/M_w as shown by equation (14).

Strictly speaking, equations (14) and (15) hold true only for the angular region of $ha \leqslant 1$ and $hR_g \leqslant 1$. These criteria need to be verified after both the values of a and R_g have been obtained from the experimental results. The experiment needs to be repeated if an inappropriate h region was covered in the previous experiment.

The validity of both equations (14) and (15) will be tested at the extreme cases of $\varphi = 1$ and $\varphi = 0$ as follows.

As φ approaches unity, the apparent molecular weight M'_w approaches M_w, the molecular weight of individual labelled chain (equation (14)). The above result is desirable since the condition $\varphi = 1$ dictates that the labelled chains are randomly distributed throughout the whole sample. As to the other extreme case of $\varphi = 0$, all the labelling chains cluster into a small volume. The apparent molecular weight will approach infinity as evident from equations (12) and (14). The increase of the apparent radius of gyration due to clustering is expressed by equation (15); as φ approaches unity the value of R'_g goes to R_g.

The physical meaning of Y expressed in equation (12) merits further discussion. For the case that all the labelled chains segregate into isolated clusters, the meaning of Y is straightforward and it stands for the average number of labelled chains per cluster. However, if the labelled chains segregate within an interconnected domain as proposed by Sadler and Keller for PEH/PED blends[3], the value of Y stands for the average number of the labelled chains occupied by a volume equal to l_c^3 where l_c is about the width (although greater) of the interlinking branches of the labelled chain-rich domain.

In a recent SANS study of PED/PEH blends with 5% wt. labelled chains, the measured values of M'_w and R'_g go through a maximum with increasing annealing temperature. Such puzzling results can be rationalized easily within the theoretical framework presented in this paper. The value of φ for specimens annealed in the temperature range from $100°$ to $110°C$ has been found to be near 0.9 indicating that only 10% of the volume has been depleted of PED molecules. At higher annealing temperatures (up to $126°C$), the value of φ reaches 0.6 and the corresponding value of l_c, Y etc. were also smaller than those of the annealed at relatively lower temperature. A more complete account of the effect of annealing and deformation on the cluster size will be covered in a forthcoming paper.

In summary, the increase of the values of apparent M'_w and R'_g from SANS measurements in isotopic labelling polymer blends can be easily explained using the Zernicke–Prins equation. As long as the centres of mass of the labelled chains are not randomly distributed within the specimen, an enormous increase in both M'_w and R'_g will be observed. The ratio M'_w/M_w is related, but not equal, to the number of labelled chains per cluster (equation (14)). The accompanying increase of the radius of gyration R'_g does not reflect the change of the average size of the cluster in a straightforward manner (equation (15)).

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