Theory of correlations in partly labelled homopolymer melts

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Small-angle neutron scattering by a polymer melt with partly tagged chains is considered. When several types of chain (differently labelled) are present in the system a new long-range correlation effect which modifies the scattering spectrum is predicted. This effect will arise because of the chemical polydispersity of the sample. A general formalism is developed to calculate the scattering intensity and is applied to special cases: diblock and triblock chains. It is shown that even a small chemical polydispersity leads to important long-range fluctuations and modifies the scattering spectrum substantially.

INTRODUCTION

Small-angle neutron scattering (SANS) which is extensively employed in the field of polymer physics, is particularly suited to the study of long-range correlations in homopolymer melts[1-4]. There are 3 reasons for this:

(i) Deuteration enables selective tagging of specific monomers along polymer chains; this labelling is efficient since deuterium and hydrogen have different coherent scattering amplitudes for cold neutrons;

(ii) the effective repulsion between deuterated and hydrogeneous monomers is weak; even for high molecular masses, the segregation effects are negligible for both a mixture of deuterated and hydrogeneous chains[5] and a melt of partly deuterated chains[5,6];

(iii) the neutron wavelengths available make it possible to observe scattering due to long-range fluctuations of deuterated monomer densities.

Experimental efforts have focused on SANS studies of mixtures of completely deuterated and hydrogenated chains[1-3]. Detailed studies of molten polystyrene show that the polymer chains in a homopolymer melt are essentially ideal and that their scattering function is of the Debye type up to scattering wavevectors $q \simeq 0.1$ A^{-1} (ref 2), confirming theoretical predictions[7].

De Gennes has predicted a 'correlation hole' effect[8,5] for partly labelled chains. Experimental studies of these systems are in progress[4,9]. De Gennes considered a homopolymer melt with *all* chains partly tagged, each having the same sequence of tags[8,5]. In this case, in a macroscopic volume*, the concentration of the deuterated monomers ρ_D is proportional to the overall monomer density ρ: $\rho_d = f\rho$, where f denotes the fraction of deuterated monomers in each chain, $f = N_D/N$. The overall monomer density fluctuations are weak since the bulk compressibility modulus of molten polymers is low. Therefore, the neutron scattering intensity I, at a scattering wave vector $q = 0$, is expected to be small. At higher q ($qR < 1$) the intensity substantially increases, since locally $\rho_D(\tau)$ may be different from f and the deuterated monomer concentration fluctuations more important than those of the overall density. For large wavevectors $q > 1/R$ the scattering intensity decreases since it is essentially due to independent scatterers (tagged portions of the chains) whose form factor decreases as q increases. Hence, we expect a bump at the intermediate range of scattering vectors (see *Figures 2* and *3* for diblock and triblock chains, respectively), which reflects the correlation hole effect in τ-space. A detailed discussion of the spatial correlations in the system of identical chains is given in refs 5 and 10. De Gennes[8,5] developed a self-consistent theory, the random phase approximation (*RPA*), which permits calculation of the scattering spectrum $I(q)$. This method has been applied to systems with various sequences of labelled monomers along the chains[4,11].

The conclusion that for scattering vectors $q \simeq 0$ there is practically no scattering intensity is only valid when all the chains have the same composition and tags sequence. This is never the case since the chemical sequence of the partly labelled chain always shows statistical deviations from the average structure — chemical polydispersity. We expect that at small q vectors the correlation hole effect will be masked by another effect of completely different nature, namely, the effect of mixing different chains. In a system with various labelled chains it is possible to have in the macroscopic volume a fluctuation of the concentration of a particular type of chain and consequently of the deuterated monomer concentration even though the overall monomer density remains constant. The aim of the present paper is to study the influence of the 'mixing' effect due to chemical disorder on the neutron scattering spectra of partly labelled chains. We will show that even for small chemical polydispersities the mixing effect in diblock and triblock chains is of a crucial importance. It dominates the correlation hole effect at low-**q** vector range and plays an important role in the intermediate range.

We will also discuss a pedagogical example of a mixture of partly deuterated and completely deuterated chains which illustrates the qualitative features of the mixing effect.

It is worthwhile to remark that our results supplement the earlier indications that the chemical disorder plays an

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* A volume much bigger than R^3; R denotes the radius of gyration of chains in a θ solvent. $R = Na^2$.

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important role in copolymer solutions[12,13] and in copolymer melts[6].

RANDOM PHASE APPROXIMATION FOR A MIXTURE OF PARTLY LABELLED CHAINS

We will consider general case of homopolymer melt with partly labelled chains. We suppose that several ($p>1$) types of chains are present; each type of chain is characterized by the polymerization index N_k and the sequence of tagged molecules described by a set $\{\mu_i\}$ where $\mu_i=1$ if the ith monomer of the chain is deuterated and $\mu_i=0$ if it is protonated ($i=1, \ldots, N_k$) (e.g. a diblock chain of length N and composition f has μ_1, μ_2, μ_{fN} equal to 1 and $\mu_{fN+1}, \ldots, \mu_N$ equal to 0).

The neutron scattering intensity is related to the Fourier transform of the density correlation functions

$$I(q)=\tilde{S}_{\mathrm{HH}}(q)a_{\mathrm{H}}^2+2\tilde{S}_{\mathrm{HD}}(q)a_{\mathrm{H}}a_{\mathrm{D}}+\tilde{S}_{\mathrm{DD}}(q)a_{\mathrm{D}}^2 \qquad (1)$$

where $a_{\mathrm{H}}(a_{\mathrm{D}})$ denotes the coherent scattering amplitude of a protonated (deuterated) monomer. $\tilde{S}_{\mathrm{DD}}(q)$, $\tilde{S}_{\mathrm{HD}}(q)$ and $\tilde{S}_{\mathrm{HH}}(q)$ are the Fourier transforms of the respective monomer density correlation functions:

$$\begin{aligned}\tilde{S}_{\mathrm{DH}}(\vec{r})&=\langle\rho_{\mathrm{D}}(\vec{\tau})\rho_{\mathrm{H}}(0)\rangle-\langle\rho_{\mathrm{D}}\rangle\langle\rho_{\mathrm{H}}\rangle\\&=\langle\delta\rho_{\mathrm{D}}(\vec{\tau})\delta\rho_{\mathrm{H}}(0)\rangle\end{aligned} \qquad (2)$$

We will neglect the effects of the bulk compressibility (they are much weaker than those due to the correlation hole), i.e. we assume that at any point $\delta_{\mathrm{H}}(\vec{\tau})+\rho_{\mathrm{D}}(\vec{\tau})=\rho=$ constant. Then, from the definition of correlation functions

$$\tilde{S}_{\mathrm{DD}}(q)=\tilde{S}_{\mathrm{HH}}(q)=-\tilde{S}_{\mathrm{HD}}(q)=-\tilde{S}_{\mathrm{DH}}(q)=\tilde{S} \qquad (3)$$

and

$$I(q)=\tilde{S}(q)(a_{\mathrm{D}}-a_{\mathrm{H}})^2 \qquad (4)$$

To calculate the scattering intensity of the system it is thus sufficient to determine the correlation function $\tilde{S}$.

Let us suppose, quite formally, that weak external potentials V_{H} and V_{D} act on unlabelled and labelled monomers, so that the energy of interaction reads:

$$\int[V_{\mathrm{D}}(\vec{\tau})\delta\rho_{\mathrm{D}}(\vec{\tau})+V_{\mathrm{H}}(\vec{\tau})\delta\rho_{\mathrm{H}}(\vec{\tau})]\mathrm{d}^3r$$

The average change of the monomer density at point $\vec{\tau}$ due to the action of these external potentials may be given in terms of response functions of the system[8,5,6]. The response functions are directly related to the correlation functions (for detailed discussion and derivation of these relations see ref 6).

For Fourier transforms of the change in average monomer density we obtain:

$$\begin{aligned}\Delta\rho_{\mathrm{D}}(q)&=-\frac{1}{kT}[\tilde{S}_{\mathrm{DD}}(q)V_{\mathrm{D}}(q)+\tilde{S}_{\mathrm{DH}}(q)V_{\mathrm{H}}(q)]\\\Delta\rho_{\mathrm{H}}(q)&=-\frac{1}{kT}[\tilde{S}_{\mathrm{HD}}(q)V_{\mathrm{D}}(q)+\tilde{S}_{\mathrm{HH}}(q)V_{\mathrm{H}}(q)]\end{aligned} \qquad (5)$$

with an incompressibility condition:

$$\Delta\rho_{\mathrm{D}}+\Delta\rho_{\mathrm{H}}=0 \qquad (6)$$

and where k denotes the Boltzmann constant, T the absolute temperature.

The basic point of the *RPA* method is that in polymer melts chains are nearly ideal. The interactions between monomers impose a constant overall monomer density. Therefore, it seems reasonable to describe the system as if it were composed of ideal independent chains whose monomers are subject to external potentials V_{D} and V_{H} and to a self-consistent potential V expressing monomer interactions and ensuring the incompressibility. The response of the system may be written as[6]:

$$\begin{aligned}\Delta\rho_{\mathrm{D}}&=-\frac{1}{kT}S_{\mathrm{DD}}(V_{\mathrm{D}}+V)+S_{\mathrm{DH}}(V_{\mathrm{H}}+V)]\\\Delta\rho_{\mathrm{H}}&=-\frac{1}{kT}[S_{\mathrm{HD}}(V_{\mathrm{D}}+V)+S_{\mathrm{HH}}(V_{\mathrm{H}}+V)]\end{aligned} \qquad (7)$$

From equations (7) and (6) we obtain V. Inserting V into (7) then gives $\Delta\rho_{\mathrm{D}}$ in terms of V_{D} and V_{H}. The correlation function $\tilde{S}$:

$$\tilde{S}=(S_{\mathrm{DD}}S_{\mathrm{HH}}-S_{\mathrm{HD}}^2)/(S_{\mathrm{HH}}+2S_{\mathrm{HD}}+S_{\mathrm{DD}}) \qquad (8)$$

is expressed entirely in terms of the monomer density correlation of ideal, independent chains. This is the essential result of the *RPA* method for partly labelled homopolymer melt. The functions S_{DD}, S_{HD} and S_{HH} are easy to calculate for any mixture of chains with an arbitrary sequence of tagged monomers. The concentration of deuterated monomers may be written as:

$$\rho_{\mathrm{D}}(\vec{\tau})=\sum_{k=1}^{P}\sum_{i=1}^{N_k}\mu_i\rho_i(\vec{\tau})$$

where $\rho_i(\tau)=1$ when an ith monomer of the kth type of chain lies at point τ. It should be noted that $\langle\rho_i\rangle=\varphi_k/N_k$, where φ_k is the concentration of chains of type k ($\Sigma_{k=1}^{P}\varphi_k=1$). Thus, for *independent* chains we find:

$$\begin{aligned}S_{\mathrm{DD}}(\vec{\tau})&=\langle\rho_{\mathrm{D}}(0)\rho_{\mathrm{D}}(\vec{\tau})\rangle-\langle\rho_{\mathrm{D}}\rangle^2\\&={}^{P}\textstyle\sum^{k=1}\displaystyle\sum_{l=1}^{P}\sum_{i=1}^{N_k}\sum_{j=1}^{N_l}\mu_i\mu_j[\langle\rho_i\rho_j\rangle-\langle\rho_i\rangle\langle\rho_j\rangle]\\&=\sum_{k=1}^{P}\sum_{i=1}^{N_k}\sum_{j=1}^{N_k}\mu_i\mu_j[\langle\rho_i\rho_j\rangle-\langle\rho_i\rangle\langle\rho_j\rangle]\end{aligned} \qquad (9)$$

There are two possibilities of having $\rho_i(0)\rho_j(\tau)=1$: Either there is an ith monomer of a chain of type k at point 0 and a jth monomer of the same chain at point τ, or there is an ith monomer at 0, jth at τ but they belong to different chains (of the kth type). Thus:

$$\langle\rho_i(0)\rho_j(\tau)\rangle=\frac{\varphi_k}{N_k}P_{ij}^{(k)}(0,\tau)+\varphi_k^2/N_k^2 \qquad (10)$$

where $P_{ij}^{(k)}(0,\tau)$ denotes the probability that the chain of the kth type has the ith monomer at 0 and the jth at point τ. From equations (9) and (10) we obtain;

$$S_{DD}(q)=\sum_{k=1}^{P}\frac{\varphi_k}{N_k}\sum_{i,j=1}^{N_k}\mu_i\mu_jP_{ij}(q) \qquad (11)$$

and similarly:

$$S_{HH}(q)=\sum_{k=1}^{P}\frac{\varphi_k}{N_k}\sum_{i,j=1}^{N_k}(1-\mu_i)(1-\mu_j)P_{ij}(q) \qquad (12)$$

$$S_{HD}(q)=\sum_{k=1}^{P}\frac{\varphi_k}{N_k}\sum_{i,j=1}^{N_k}(1-\mu_i)\mu_jP_{ij}(q) \qquad (13)$$

We observe that

$$\sum_{i,j=1}^{N_k}\mu_i\mu_jP_{ij}/N_k$$

for example, is the deuterated monomer concentration correlation function of a homopolymer melt composed entirely of chains of the kth type. Thus, the correlation functions S_{DD}, S_{HH}, S_{HD} are equal to the average over all types of chains of the respective correlation functions. It is important to note that:

$$S=S_{HH}+S_{DD}+2S_{HD}=\sum_{k=1}^{P}\frac{\varphi_k}{N_k}\sum_{i,j=1}^{P}P_{ij} \qquad (14)$$

is the correlation function of overall monomer density in a mixture of independent chains. Till now no assumptions about the nature of the chains have been made. For a melt of linear polymers the chains are essentially ideal, so we put:

$$P_{ij}(q)=\exp(-y|i-j|) \qquad (15)$$

where $y=q^2a^2/6$*.

We conclude that the *RPA* method permits the neutron scattering intensity of a mixture of partly labelled homopolymers with different types of chains to be found in terms of monomer density functions and may be easily calculated for given composition of the mixture with the help of equations (11)–(14).

EXAMPLE: MIXTURE OF DIBLOCK AND ENTIRELY LABELLED CHAINS

In studying the effects of chemical polydispersity we must make some assumptions about the distribution of lengths of the tagged sequences in the chains. This complicates the description of physical effects. Before tackling the problem of chemical polydispersity we will consider a simple example, namely, a homopolymer melt composed of only two types of chains: (1) completely deuterated chains with N monomers; (2) the partly deuterated diblock chains with composition $=N_D/N$ (N_D the length of deuterated sequence). This example, intuitively simple, illustrates the respective roles of the 'mixing' and correlation hole effects.

If we denote by φ the concentration of partly tagged chains we find from equations (11)–(15) the following expression for the correlation functions S_{DD}, S_{DH}, S_{HH} and S:

$$S_{DD}(q)=\varphi Ng(f)+(1-\varphi)Ng(1)$$

$$S_{HH}(q)=\varphi Ng(1-f)$$

$$S_{HD}(q)=\tfrac{1}{2}\varphi N[g(1)-g(1-f)-g(f)]$$

$$S(q)=Ng(1) \qquad (16)$$

where $g(f)$ denotes the Debye function:

$$g(f)=2[fNy+\exp(-fNy)-1]/N^2y^2 \qquad (17)$$

To obtain equation (16) it has been supposed that both N_D and N–N_D are so large that the summation over monomers in equations (11)–(14) may be replaced by an integral[6,11]. The presence of completely labelled chains affects only the q dependence of the S_{DD} function. Other functions S_{DH} and S_{HH} are changed only by a factor φ. Therefore, the scattering intensity is determined by the correlation function $\tilde{S}$ equal to (see equations 8 and 16):

$$\tilde{S}=\varphi^2\tilde{S}_1+\varphi(1-\varphi)Ng(1-f) \qquad (18)$$

where $\tilde{S}_1$ is the correlation function which will be observed in the homopolymer melt with all chains partly marked, i.e. with $\varphi=1$:

$$\tilde{S}_1=N\{g(f)g(1-f)-\tfrac{1}{4}[g(1)-g(f)-g(1-f)]^2\}/g(1) \qquad (19)$$

The first term in equation (18) reflects both the direct correlations between monomers of the same chain and the correlation hole effect. The second term is entirely due to the 'mixing' effect. Actually, this term vanishes for homogeneous systems, i.e. both for $\varphi=0$ and $\varphi=1$ as might be expected. For a mixture of labelled and partly labelled chains (i.e. $\varphi=0.1$) this term takes a maximum value $\varphi(1-\varphi)f^2N$ for $q=0$. We observe that even for small values of φ the scattering due to fluctuation in deuterated monomer concentration is large compared with bulk density correlations. The 'correlation hole' term $\varphi^2\tilde{S}_1$ vanishes at $q=0$ as discussed in detail above. We therefore conclude that in the system considered there is a strong forward scattering and for small q vectors the 'mixing' effect dominates.

In *Figure 1* we show the dependence of neutron scattering intensity on $x=\sqrt{Ny}=qR$ ($R=$the radius of gyration of a chain in a θ solvent) for the simple symmetrical case $f=1/2$ and for different fractions of the diblock chains φ. For $\varphi=1$ the scattering function $\tilde{S}=\tilde{S}_1$; this is the case considered by de Gennes[5] with all chains partly labelled. $\tilde{S}$ has a bump due to the 'correlation hole' effect. As we decrease φ (i.e. increase the fraction of completely labelled chains) the 'mixing' effect plays an important role. First of all it gives a strong forward scattering, e.g. for $\varphi=0.7$ even the value of $S(0)$ is bigger than the maximum scattering reached for $\varphi=1$ at $qR\simeq 2$. Secondly the maximum of the peak moves toward $q=0$ and becomes less pronounced. It may be proved that for $\varphi\leqslant 0.5$ (most of chains are completely marked) $\tilde{S}$ becomes a monotonously decreasing function of q. For $\varphi=0.5$ $\tilde{S}(0)$ attains a maximum value. Decreasing φ further ($\varphi<0.5$) diminishes the scattering intensity and for $\varphi=0$ there is no scattering (only scattering due to bulk compressibility remains) since there is no contrast. In the asymptotic region $qR\gg 2$ we obtain:

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* The formalism permits us to consider other types of molecules, e.g. shaped molecules (see Appendix).

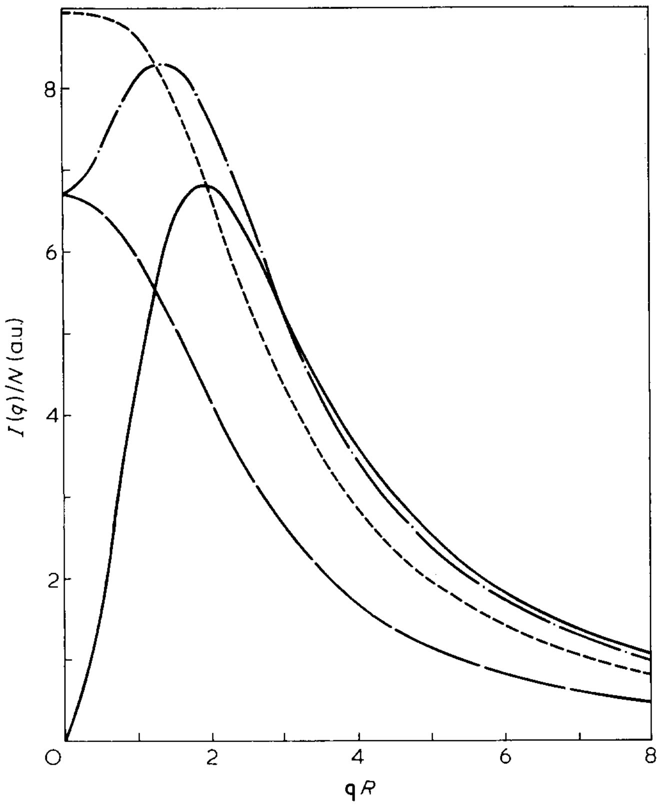

Figure 1 Neutron scattering intensity as a function of qR for mixtures of symmetrical diblock chains (f = 1/2) and completely labelled chains with different fractions of diblock chains. ——, 1; — — — — — —, 0.25; — · — · —, 0.75; · · · · · ·, 0.5

$$\tilde{S}(q) \simeq \frac{12}{q^2a^2}\varphi(1-f)$$

This might be expected: $\tilde{S}$ is due to the independent scatterers — the tagged portion of the chains. With changes in φ and f the value of the scattering changes but not the q-dependence (for Gaussian chains).

It is interesting to remark that $f=0$ corresponds to the mixture of labelled and unlabelled chains. In this case:

$$\tilde{S}(q) = \varphi(1-\varphi)Ng(1)$$

In the Appendix we present a simple physical approach which permits us to find the scattering intensity for the symmetrical case $f=1/2$.

EFFECT OF CHEMICAL POLYDISPERSITY ON SCATTERING FUNCTIONS OF DIBLOCK AND TRIBLOCK CHAINS

The example considered in the preceeding section is an oversimplified case of the chemical disorder. However, it gives a qualitative picture of the effects which may be encountered in practice since any partly labelled chain system is in fact a mixture of different types of chains as the result of the chemical polydispersity. Here we will examine the scattering functions of two types of systems on which neutron experiments are focused, namely melts of diblock and triblock chains.

Triblock chains

We consider a polymer melt with partly deuterated chains. The average (model) chain has a sequence of $\overline{Nf_1}$ deuterated monomers, then $\overline{Nf_2}$ hydrogenated monomers and at the end $\overline{Nf_3}$ deuterated monomers. Each chain is supposed to be a triblock chain but its Nf_1, Nf_2 and Nf_3 may be different from the average. The bar over the quantity denotes the average value over the distribution of different sequence lengths. From equations (11)–(15) we obtain the following formula:

$$S_{DD} = \overline{N[g(f_1)+g(f_2)+g(f_3)+g(1)-g(1-f_1)-g(1-f_3)]}$$

$$S_{HH} = \overline{Ng(f_2)}$$

$$S_{HD} = \tfrac{1}{2}(S - S_{11} - S_{22})$$

$$S = \overline{Ng(1)} \tag{20}$$

where

$$\overline{Ng(f)} = 2\overline{\left(fy + \frac{1}{N}e^{-fNy} - \frac{1}{N}\right)} \tag{21}$$

We have assumed that $\varphi(N, f_1, f_2)$, the fraction of chains with the length N and composition f_1 and f_2 ($f_3 = 1 - f_1 - f_2$) is equal to the probability that a chain has the polymerization index N and composition f_1 and f_2. The scattering function $\tilde{S}(q)$ of the melt is given by equation (8) with S_{DD}, S_{DM} and S_{HH} given by equation (20).

It should be noticed that without chemical polydispersity the scattering intensity of chains with deuterated ends should be equal to that with the central part deuterated (if N, f_1, f_2 and f_3 are the same for both cases).

Diblock chains

We suppose that chains have two sequences. The average number of deuterated monomers is $\overline{Nf}$. We obtain the formula for S_{DD}, S_{DH}, S_{HH} from equation (20) by putting f_3 equal to 0 and $f_1 = f$:

$$S_{DD} = \overline{Ng(f)}, \qquad S_{HH} = \overline{Ng(1-f)} \tag{22}$$

Unfortunately, in general, the average value $\overline{Ng(f)}$ (equation 21) cannot be expressed in terms of simple measurable averages such as $\overline{Nf}$, $\overline{Nf^2}$ or $\overline{N^3f^3}$. The detailed form of the scattering function will depend on the probability distribution $\varphi(N, f_1, f_2)$ (on $\varphi(f, N)$) and consequently on the way the polymer molecules are synthesized. However, it will be possible to give some model-independent predictions for low scattering vector range (below). Here we will study a simple model of molecular mass distribution which is usually supposed to describe adequately a product of a copolymerization reaction[12]. Partly labelled polymers studied in neutron experiments are prepared by anionic polymerization. It will be supposed that the distribution of molecular masses of each sequence (block) is independent of the mass of other sequences. We will assume a model distribution of molecular mass — the Schultz–Zimm distribution[14,15].

$$\varphi(n) = v^{k+1}n^k\exp(-vn)/\Gamma(k+1) \tag{23}$$

where $\varphi(n)$ denotes the probability that the chain (in our case a sequence) has n monomers, v and k are constants and $\Gamma(x)$ denotes the Γ function (when k is an integer $\Gamma(k+1) = k!$). This distribution function is a two parameter

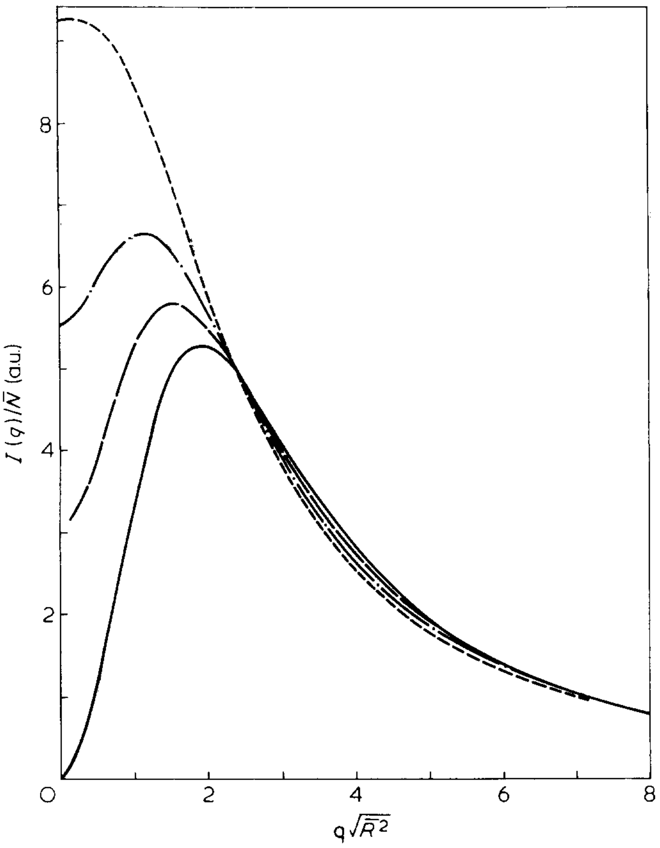

Figure 2 Neutron scattering intensity of symmetrical diblock partly deuterated chains as a function of $q\sqrt{\overline{R^2}}$ for different chemical polydispersities: ———, 1; — — — — — —, 1.25; — · — · —, 1.5; · · · · · · , 2

distribution frequently used to describe a product of polymerization reactions. These parameters may be related to the average molecular mass $\bar{n}$ and the coefficient $\lambda = \overline{n^2}/\bar{n}^2$ characterizing the polydispersity:

$$k=\frac{2-\lambda}{\lambda-1}; \qquad v=1/(\lambda-1)\bar{n} \tag{24}$$

The above assumptions may be summarized by writing for triblock copolymers

$$\varphi(N_1, N_2, N_3)=\varphi_1(N_1)\varphi_2(N_2)\varphi_3(N_3) \tag{25}$$

N_1, N_2 and N_3 denote the length of respective blocks and φ_1, φ_2 and φ_3 are the distributions of type (23) characterized by the respective parameters $\overline{N_i}$ and $\overline{\varphi_i}$ (related to k_i and v_i by (24), $i=1, 2, 3$). Similarly for diblock copolymers we may write:

$$\varphi(N_1, N_2)=\varphi_1(N_1)\varphi_2(N_2) \tag{26}$$

Under these assumptions the average value $\overline{Ng(f)}$ required to calculate the scattering function $\tilde{S}$ is easy to find, e.g. for triblock chains:

$$Ng(f_1)=\int_0^\infty \mathrm{d}N_1 \int_0^\infty \mathrm{d}N_2 \int_0^\infty \mathrm{d}N_3 \varphi_1(N_1)\varphi_2(N_2)\cdot$$

$$\varphi_3(N_3)\cdot 2\left[f_1 y+\frac{l}{N}\mathrm{e}^{-fN_1y}-\frac{1}{N}\right]\Big/y^2 \tag{27}$$

We will not give the results for the general case of arbitrary compositions of chains here. We will limit our discussion to the case when the average length and the polydispersity of each sequence are the same, i.e. $\varphi_1(n)=\varphi_2(n)=\varphi_3(n)$ for triblock chains and $\varphi_1(n)=\varphi_2(n)$ for diblock chains. In this case we get the following formula for the averages appearing in equations (20) and (22).

Triblock chains.

$$\overline{Ng(f_1)}=\overline{Ng(f_2)}=\overline{Ng(f_3)}$$

$$=2N\left\{\frac{1}{3}x+\frac{3}{4-\lambda}\left[(1+\frac{x}{3}(\lambda-1)\Big)^{-A}F(A, 1; 3A; z)-1\right]\right\}\Big/x^2$$

$$\overline{Ng(1-f_1)}=\overline{Ng(\mathrm{f}-f_3)}$$

$$=2N\left\{\frac{2}{3}x+\frac{3}{4-\lambda}\left(1+\frac{x}{3}(\lambda-1)\right)^{-2A}F(2A, 1; 3A; z)-1\Big]\right\}\Big/x^2$$

$$\overline{Ng(1)}=2N\left\{x+\frac{3}{4-\lambda}\left[\left(1+\frac{x}{3}(-1)\right)^{-B}-1\right]\right\}\Big/x^2 \tag{28}$$

where $x=q^2\overline{R^2}$; $\bar{R}$ denotes the average radius of gyration of the chain in solvent, i.e. $R^2=\bar{N}a^2/6$; λ describes the polydispersity of each sequence $\lambda=\overline{N^2f^2}/(\overline{Nf})^2$

$$A=1/(\lambda-1); \qquad B=\frac{4-\lambda}{\lambda-1}; \qquad z=\frac{x(\lambda-1)}{x(\lambda-1)+3} \tag{29}$$

$F(\alpha, \beta; \gamma; z)$ denotes the hypergeometric function[16].

Diblock chains.

$$\overline{Ng(f)}=\overline{Ng(1-f)}$$

$$=2\bar{N}\left\{\frac{1}{2}x+\frac{2}{3-\lambda}\left[\Big(1+\frac{x}{2}(\lambda-1)^{-A}F(A, 1; 2A; z_1)-1\right]\right\}\Big/x^2$$

$$\overline{Ng(1)}=2\bar{N}\left\{x+\frac{2}{3-\lambda}\left[\left(1+\frac{x}{2}(-1)\right)^{-B_1}-1\right]\right\}\Big/x^2 \tag{30}$$

where

$$B_1=\frac{3-\lambda}{\lambda-1}; \qquad z_1=\frac{x(\lambda-1)}{x(\lambda-1)+2} \tag{31}$$

To sum up: we may calculate the scattering spectra of triblock and diblock symmetrical chains making use of equations (8), (20), (28), (29) and (8), (23), (30) and (31), respectively.

DISCUSSION AND CONCLUSIONS

We have plotted the intensity of the neutron scattering by diblock and triblock polymer melts as a function of $q\bar{R}$ for different values of polydispersity parameter λ. *Figures 2* and *3*. Even small chemical polydispersity affects strongly the neutron scattering spectra (*Figure 4*). As may be

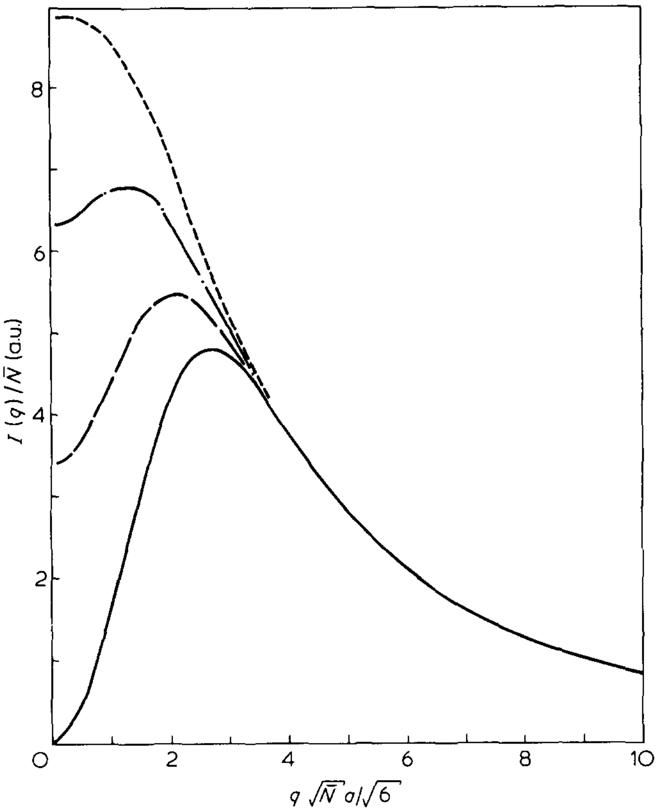

Figure 3 Neutron scattering intensity of symmetrical diblock partly deuterated chains as a function of $\sqrt{qR}$ for different chemical polydispersities. ——, 1; – – – – – –, 1.25; —·—·—, 1.50; · · · · · ·, 1.75

expected, the effect due to mixing of chains with different sequences of deuterated monomers is most pronounced in the low q region: it leads to strong forward scattering. Moreover, the mixing effect moves the peak in scattering intensity toward $q=0$ and makes the peak larger and less pronounced. In the case of diblock chains for $\lambda=2$, the peak completely disappears. This is a general, model independent result for symmetrical chains. For $q\bar{R}\ll 1$ for diblock chains, we obtain:

$$\tilde{S}(q)\simeq\overline{Nf^2}-\frac{\overline{Nf^2}}{N}-\frac{1}{3}y\left\{\overline{N^2f^3}\left(1-2\frac{\overline{Nf}}{N}-\right.\right.$$

$$\left.\left.3\frac{\overline{Nf}}{N}(\overline{N^2f}-\overline{N^2f^2})+\frac{\overline{Nf^2}}{N^2}\overline{N^2}\right\}\right. \tag{32}$$

In the symmetrical case $\overline{Nf}=\frac{1}{2}\bar{N}$ so that:

$$\tilde{S}(q)\simeq\overline{Nf^2}-\tfrac{1}{4}\bar{N}+\tfrac{1}{12}\bar{N}x\left(1-\frac{\lambda}{2}\right) \tag{33}$$

where $x=q^2\bar{R}^2=q^2\bar{N}y^2$. We see that for $\lambda=2$ the term proportional to q^2 vanishes and $\tilde{S}$ takes a maximum for $q=0$ (*Figure 2*).

It is interesting to observe that if it were possible to obtain a partly labelled polymer melt in which all chains would have the same composition but different lengths (i.e. for which $\overline{Nf}=\bar{N}f$) the scattering intensity would vanish for $q=0$. This is a natural conclusion. In such a system the mixing effect is absent since in any macroscopic volume the concentration of deuterated monomers is equal to fp just as in the case of a system with all chains identical.

In the asymptotic region $qR\gg 1$ the scattering intensity for diblock polymers is given by

$$\tilde{S}(q)\simeq\frac{12\bar{f}\cdot(1-f)}{q^2a^2}\qquad q\bar{R}\gg 1$$

We observe that it is independent of the polydispersity λ for the symmetrical case for which:

$$\tilde{S}(q)\simeq\frac{3}{q^2a^2}\qquad q\bar{R}\gg 1$$

Similarly for symmetrical triblock molecules we find:

$$S(q)\simeq\frac{4}{q^2a^2}\qquad q\bar{R}\gg 1$$

independent of the polydispersity.

In conclusion we may say that the long-range correlations observed in SANS experiments on partly labelled homopolymer melts are due to two effects: the correlation hole effect and the mixing effect resulting from chemical polydispersity. The mixing effect dominates in the low scattering vector range and leads to strong forward scattering. Its magnitude depends on the distribution of molecular masses of polymer chains. The bump in the neutron scattering is due to the existence of the correlation hole. Its form depends, however, on the chemical polydispersity. The experimental results[4] agree qualitatively with these conclusions. The bump calculated with $\lambda=1$ is narrower than the experimental. In order to

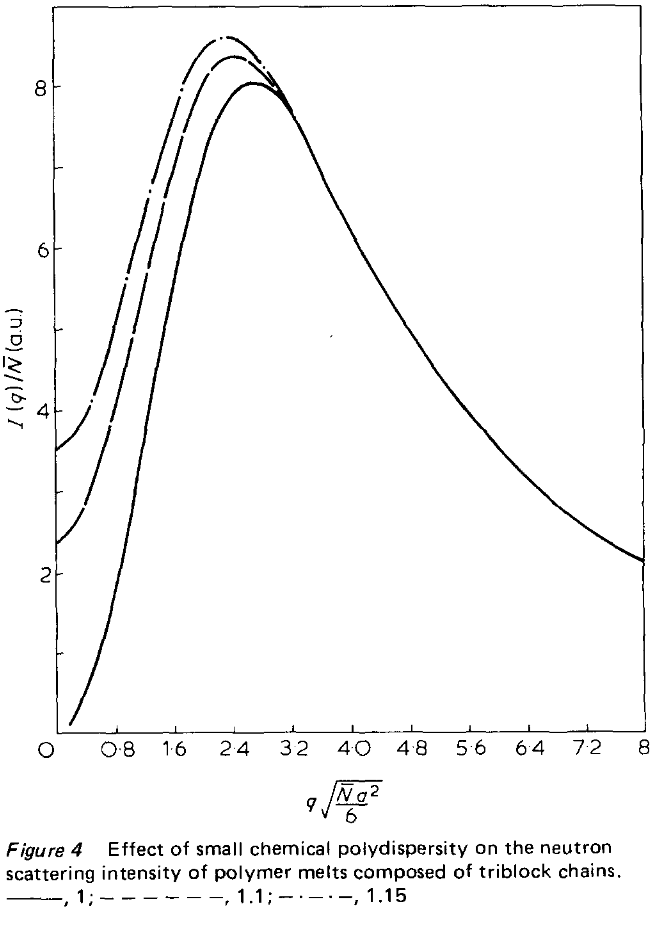

Figure 4 Effect of small chemical polydispersity on the neutron scattering intensity of polymer melts composed of triblock chains. ——, 1; – – – – – –, 1.1; —·—·—, 1.15

make quantitative comparisons the g.p.c. analysis of deuterated part of chain and then of final product of reaction should be made. This analysis would permit us to obtain the distribution function and to calculate the average value of $\overline{Ng(f)}$ (see equation 27). For $\bar{R}$ we take the value of radius of gyration of chains measured in a θ solvent; the experimental data on scattering intensity may then be fitted without adjustable parameters: the *RPA* method of describing the correlations in polymer melts may be tested.

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APPENDIX

Mixture of symmetric diblock and completely labelled chains: a simple physical approach

The approach presented here applies when the chemical polydispersity can be neglected and the system contains symmetrical diblock chains (i.e. $f=1/2$). It gives some interesting physical intuitions.

Consider first, the system composed of entirely labelled chains (i.e. $\varphi=0$). For this system:

$$\tilde{S}(\tau)=\sum_{i=1}^{N}\sum_{j=1}^{N}[\langle\rho_i(0)\rho_j(\tau)\rangle-$$

$$\langle\rho_i(0)\rangle\langle\rho_j(\tau)\rangle]=0 \qquad \text{(A-1)}$$

since ρ has no fluctuations (apart those due to small bulk elastic modulus). There are two possible ways of having $\rho_i(0)\rho_j(\tau)=1$: either both monomers belong to the same chain or they belong to different chains. Thus quite generally

$$\tilde{S}(\tau)=\sum_{i,j}[P_{ij}(\tau)+Q_{ij}(\tau)] \qquad \text{(A-2)}$$

where P_{ij} and Q_{ij} denote intrachain and interchain contributions, respectively. This means that:

$$Q(\tau)=\sum_{i,j}Q_{ij}(\tau)=-\sum_{i,j}P_{ij}(\tau)$$

When there are only partly labelled chains (i.e. $\varphi=1$):

$$\tilde{S}(\tau)=\sum_{i,j}\mu_i\mu_jP_{ij}+\sum_{i,j}\mu_i\mu_jQ_{ij} \qquad \text{(A-3)}$$

The essential trick of the method is to use the symmetry of the chains. For diblock symmetrically labelled chains, with $f=1/2$, μ_i may be replaced by $1-\mu_i$ without changing the scattering spectrum. This means that for interchain scattering contributions $Q_{ij}=Q_{i,N}=Q_{N-i,j}$ and consequently:

$$\sum_{i,j}\mu_i\mu_j\mathrm{Q}_{ij}=\sum_{i,j}(1-\mu_i)(1-\mu_j)Q_{ij}$$

$$=\sum_{i,j}(1-\mu_i)\mu_jQ_{ij}=\tfrac{1}{4}Q \qquad \text{(A-4)}$$

Thus, for this case ($\varphi=1$) we find a general result:

$$\tilde{S}=\sum_{i,j}\mu_i\mu_jP_{ij}-\tfrac{1}{4}\sum_{i,j}P_{ij} \qquad \text{(A-5)}$$

As in a flexible homopolymer mixture the chains are Gaussian and P_{ij} is given by equation (15), yielding the well-known result for the scattering intensity, $I(q)=\tilde{S}(q)(a_{\mathrm{D}}-a_{\mathrm{H}})^2$:

$$\tilde{S}(q)=Ng(\tfrac{1}{2})-\tfrac{1}{4}Ng(1) \qquad \text{(A-6)}$$

Now, when φ is arbitrary we can write

$$\tilde{S}(\tau)=\varphi\sum_{i,j}\mu_i\mu_jP_{ij}+(1-\varphi)\sum_{i,j}P_{ij}$$

$$+\varphi^2\sum_{i,j}\mu_i\mu_jQ_{ij}+(1-\varphi)^2\sum_{i,j}Q_{ij}$$

$$+2\varphi(1-\varphi)\sum_{i,j}\mu_iQ_{ij} \qquad \text{(A-7)}$$

with the last term expressing the correlations between labelled and partly labelled chains. From equation (A-7), we obtain:

$$\tilde{S}(q)=\varphi Ng(\tfrac{1}{2})-\tfrac{1}{4}\varphi^2Ng(1) \qquad \text{(A-8)}$$

This result agrees with that obtained above (we should put $f=1/2$ in general equation (18)).

It should be noted that this method applies also to the case of all partly labelled symmetrical chains ($f=\frac{1}{2}$) but with different polymerization indices (the case discussed above).

Similar reasoning may be applied to the case of a melt of star-shaped molecules of n-arms with one arm labelled. When we suppose that all arms contain $N/2$ monomers and that the star-shaped molecule may be treated as a set of Gaussian-independent chains, we obtain:

$$\tilde{S}(q)=\frac{2(n-1)}{n}[Ng(\tfrac{1}{2})-\tfrac{1}{4}Ng(1)] \qquad \text{(A-9)}$$