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SMALL ANGLE NEUTRON SCATTERING STUDY ON STAR DI-BLOCK COPOLYMERS

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Determining structural properties, phase transitions and stability of polymer mixtures is very important to produce new materials with desired and interesting properties. Small Angle Neutron Scattering Technique (SANS) has been one of the most powerful and intensely used methods for the characterization of polymers for last decades. In this study, we use a model based on Gaussian Random Phase Approximation (RPA) to describe Star Di-block Copolymers (SDC) mixtures with homo-polymers. We could able to predict the miscibility and phase transitions of the various mixtures along with their structure factors, producing a thermodynamic picture of the system. Also the results suggest that scattering intensity will be dictated by the structure factor of the core or shell parts of star polymer only, which depends on the homo-polymer type of the mixture.

Keywords: Neutron Scattering, RPA, Star Polymers

INTRODUCTION

A polymer, also known as a 'macromolecule', contains a large number of repeating structural units called monomers which are linked together to form long chains. If all the monomers are of the same type, these are homo-polymers. If they have two or more types of monomers, these are copolymers [1]. Star polymers are branched polymers with several arms attached to a common center. If the arms are of di-block copolymer, i.e., having two different polymers connected at their ends, we then obtain star di-block copolymer (SDC). The structure and thermodynamic properties of star polymers and its mixtures have been focus of a vast literature, just to name a few [2-5]. Due to the their rheological and thermodynamic properties, Star polymers, blends containing star polymers or star polymer solutions may provide new materials with desired and useful physical and chemical properties [6]. A typical polymer may include hundreds of thousands of monomers. Unfortunately, we need to enhance our understanding and ability to design polymers since they can possess amazingly complex micro structures due to huge number of internal degrees of freedom and self-organization process.

The coherent small angle neutron scattering technique (SANS) has played a crucial role in the study of structure, properties and phase situations of polymeric materials. In these experiments mono-energetic neutron beam of wavelength λ is elastically scattered by a sample and the resulting scattering pattern is analyzed to probe the sample (Fig. 1). This pattern is obtained as a function of modulus of scattering vector, $q = (4\pi/\lambda) \sin\theta/2$ where θ is the scattering angle. The wavelength of neutrons that is used in the experiments is on the order of 0.2-1.0 nm and, hence is very suitable for our purposes. When combined with deuterium labeling, this technique becomes an excellent tool for investigating polymers. By exchanging of hydrogen and deuterium, which makes no differences chemically but causes

scattering contrast, it becomes possible to highlight single molecules or parts of them among others and to clarify complex micro structures [7-9].

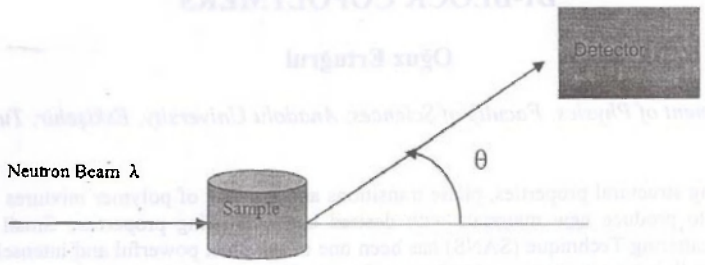

Figure 1. A schematic representation of a SANS experiment: λ is the wavelength of the neutron beam and θ is the scattering angle. [9]

The data collected by this method are in q space and need to be analyzed with varying mathematical operations to obtain the information in real space. Very often the solution is not unique and some modeling approach has to be carried out to extract the conformational information. Multi-component Random Phase approximation (RPA) method has been widely used to predict structure and thermodynamic properties of polymeric materials.

THEORY

In the SANS experiments, the measured absolute intensity I(q) can be expressed by

$$I(q) = D^{T} S(q) D \qquad (1)$$

where D (and D^{T}) is a column vector (and its transpose) describing the contrast, i.e., contains the coherent scattering length contrast factors and S(q) is the structure factor matrix that contains all the information about sample. In this study, we first define the structure factors of the components of the star di-block copolymer in order to analyze the behavior of the SDC in solutions or its mixture with homo-polymers.

Star Di-block Copolymers

For an SDC with f identical arms, we need to obtain structure factors for each component. If we consider A-B di-block copolymer arms, i.e., having two different polymers A and B connected at their ends, we then write the structure factor for A-type polymer S_{AA} as

$$S''_{AA}(q) = \phi_A f N_A P_{AA} \qquad (2)$$

where ϕ_A is volume fraction of component A, the f is the number of arms, N_A is the number of reference volume units of component A. P_{AA} can be given as follows:

$$P_{AA}(q) = \frac{1}{f}(P_{a_1a_1} + (f-1)P_{a_1a_2}) \tag{3}$$

$$P_{a_1a_1} = \frac{1}{N_A}(1 + \frac{2x_A}{1-x_A}(1 - \frac{1}{N_A}\frac{(1-x_A^{N_A})}{1-x_A})) \tag{4}$$

$$P_{a_1a_2} = \frac{x_A}{N_A^2}\frac{(1-x_A^{N_A})^2}{(1-x_A)^2} \tag{5}$$

$$x_A = e^{-\frac{q^2a^2}{6}} \tag{6}$$

and a is the statistical segment length of component A.

Note that for $a \rightarrow \infty$ and $N_A \rightarrow 0$ while keeping a^2N_A as constant, the structure factor in Eq. (2) reduces to that of given in Benoit's study [10].

We can similarly obtain the structure factor for B-type polymer S^0_{BB} as follows:

$$S^0_{BB}(q) = \phi_B f N_B P_{BB} \tag{7}$$

$$P_{BB}(q) = \frac{1}{f}(P_{b_1b_1} + (f-1)x_A^{2N_A}P_{b_1b_2}) \tag{8}$$

Here definitions of parameters in Eqs. (2-3) are given in a similar way as above.

For the non-interacting single arm, i.e., A-B di-block copolymer, the structure factor S^0_{AB} can be given as follows:

$$S^0_{AB}(q) = \sqrt{\phi_A\phi_B N_A f N_B f}\; P_{AB} \tag{9}$$

$$P_{AB}(q) = \frac{1}{f}(1 + (f-1)x_A^{N_A})\; P_{a_1b_1} \tag{10}$$

$$P_{a_1b_1} = \frac{\sqrt{x_A x_B}}{\sqrt{N_A N_B}}\frac{[1-(x_A)^{N_A}][1-(x_B)^{N_B}]}{(1-x_A)(1-x_B)} \tag{11}$$

Finally we now could state total scattering law, structure factor for the interacting SDC polymer melts by using the (incompressible) random phase approximation (RPA) [11], as

$$S_{AA}(q) = \frac{S^0_{AA}(q)\ S^0_{BB}(q) - S^0_{AB}(q)S^0_{BA}(q)}{S^0_{AA}(q) + S^0_{BB}(q) + 2S^0_{AB}(q) - 2\chi(S^0_{AA}(q)\ S^0_{BB}(q) - S^0_{AB}(q)S^0_{BA}(q))} \quad (12)$$

where χ is the Flory-Higgins interaction parameter between the different components that governs the phase behavior of the system.

In the SANS experiments, the measured absolute intensity I(q) is proportional to S_{AA} given in Eq. (12). Flory-Higgins interaction parameter χ can be obtained by fitting the data and hence the phase behavior can be predicted. Some structural parameters characterizing the system as defined above can be extracted for some limiting cases as well.

Star Di-block Copolymer Mixtures with Homo-polymers

We investigate the structure factor matrix of the SDC mixed with a homo-polymer. All of the arms of the SDC are again assumed identical and consist of A-B di-block copolymer. The SDC is mixed with a different homo-polymer C. For this multi-components system we have three distinct components. However, because of incompressibility, our mixture can be regarded as having two components. One component is eliminated since background component is not connected to any other components as well. (Here we may choose background component as the homo-polymer C.). Therefore all of our matrices will be (2x2) matrices.

Using the random phase approximation (RPA), the structure factor matrix [12, 11] is in the form of

$$S(q) = \begin{bmatrix} S_{AA}(q) & S_{AB}(q) \\ S_{BA}(q) & S_{BB}(q) \end{bmatrix} \quad (13)$$

and is given by

$$S^{-1} = (S^0)^{-1} + v \quad (14)$$

where $S^0(q)$ is the bare system structure factor that describes the structure factor matrix in the absence of interactions and v(q) is the excluded volume matrix that describes the interactions between all of the different components. The bare system structure factor matrix $S^0(q)$ and the excluded volume matrix v(q) are given respectively by

$$S^0 = \begin{bmatrix} S^0_{AA} & S^0_{AB} \\ S^0_{BA} & S^0_{BB} \end{bmatrix} \quad (15)$$

$$v = \frac{1}{S^0_{CC}} E\,E^T + \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} \quad (16)$$

where E (and E^T) is a column matrix (and its transpose) and each element of E is equal to 1,

$$m_{ij} = \chi_{ij} - \chi_{ic} - \chi_{jc} \tag{17}$$

The Flory-Higgins interaction parameters χ_{ij} between different components i and j can be expressed more explicitly as

$$\chi_{ij} = w_{ij} - (w_{ii} + w_{jj})/2 \tag{18}$$

where w_{ij} is the interaction potential between i and j. Keeping in mind that we have only two different components, i =A and j =B, elements of matrix m can be simplified as

$$m_{AA} = \chi_{AA} - \chi_{AC} - \chi_{AC} = -2\,\chi_{AC} \tag{19}$$

$$m_{BB} = \chi_{BB} - \chi_{BC} - \chi_{BC} = -2\,\chi_{BC} \tag{20}$$

$$m_{AB} = \chi_{AB} - \chi_{AC} - \chi_{BC} = m_{BA} \text{ (due to symmetry)} \tag{21}$$

Now we have the complete set of equations and can look at two different cases: case i; when C=A, i.e., homo-polymer is the same kind as the inner arms of the SDC and case ii; when C=B, i.e., homo-polymer is the same kind as the outer arms of the SDC.

For case i, i.e., when C=A, we obtain the following equations:

$$v = \frac{1}{S^0_{CC}} E\,E^T + \begin{bmatrix} 0 & 0 \\ 0 & -2\chi_{BA} \end{bmatrix} \tag{22}$$

$$S^{-1} = (S^0)^{-1} + \begin{bmatrix} \frac{1}{S^0_{CC}} & \frac{1}{S^0_{CC}} \\ \frac{1}{S^0_{CC}} & \frac{1}{S^0_{CC}} - 2\chi_{BA} \end{bmatrix} \tag{23}$$

In this case, the measured absolute intensity I(q) in the SANS experiment from Eq. (1) will be obtained as

$$I(q) = \begin{bmatrix} (a-c) \\ (b-c) \end{bmatrix}^T \begin{bmatrix} S_{AA} & S_{BA} \\ S_{BA} & S_{BB} \end{bmatrix} \begin{bmatrix} (a-c) \\ (b-c) \end{bmatrix} \tag{24}$$

$$I(q) = (a-c)^2 S_{AA} + 2\,(a-c)(b-c)\,S_{BA} + (b-c)^2 S_{BB} \tag{25}$$

where a, b and c are the scattering length densities for polymer A, B and C, respectively. As a result we end up

$$I(q) = (b-a)^2 S_{BB} \tag{26}$$

Here S_{BB} is

$$S_{BB} = \frac{S^0_{BB}S^0_{CC} + \Delta^0}{S^0_{CC} + S^0_{AA} + S^0_{BB} + 2S^0_{AB} - 2\chi\left[S^0_{BB}S^0_{CC} + \Delta^0\right]} \tag{27}$$

where $\Delta^0 = S^0_{BB}S^0_{AA} - \left(S^0_{AB}\right)^2$

This result indicates that intensity I(q) will only be determined by interacting polymer B for this case.

Whereas for the case ii, i.e., when C=B, we obtain the following equations:

$$v = \frac{1}{S^0_{CC}} E E^T + \begin{bmatrix} -2\chi_{AB} & 0 \\ 0 & 0 \end{bmatrix} \tag{28}$$

$$S^{-1} = (S^0)^{-1} + \begin{bmatrix} \frac{1}{S^0_{CC}} - 2\chi_{AB} & \frac{1}{S^0_{CC}} \\ \frac{1}{S^0_{CC}} & \frac{1}{S^0_{CC}} \end{bmatrix} \tag{29}$$

$$I(q) = (a-b)^2 S_{AA} \tag{30}$$

As seen this time, the interacting polymer A dictates the scattering intensity.

Note that S_{AA} in Eq. (30) is given by

$$S_{AA} = \frac{S^0_{AA}S^0_{CC} + \Delta^0}{S^0_{CC} + S^0_{AA} + S^0_{BB} + 2S^0_{AB} - 2\chi\left[S^0_{BB}S^0_{CC} + \Delta^0\right]} \tag{31}$$

and when there is no homo-polymer C (which means N_C=0 or ϕ_C=0), Eq. (31) reproduces the Eq. (12), as expected, since this special case corresponds to the SDC only.

As results, we obtained the structure form factors, scattering intensities, for the SDC and SDC-mixture for some special cases as seen in Eqs. (12, 26, and 31). This would enable us to obtain the crucial parameters (the Flory-Higgins interaction parameter χ, statistical segment length a and segment units N). How ever, for example, the Flory-Higgins interaction parameter χ cannot be calculated from theory. These parameters can be extracted from experiments by fitting the data. Therefore the thermodynamic properties of the multi-component mixture could be characterized. The effect of various parameters (ϕ, f, or χ) on the

phase behavior of the mixture can also be analyzed by numerical methods which will be the subject of another work.

CONCLUSION

In this work we investigated the absolute intensity I(q) of SANS for star polymers and its mixtures. On the basis of RPA, we found that the scattering intensity will be dictated by the structure factor of the core or shell parts of star polymer only, depending on the homopolymer type of the mixture. The simplified results will help us to analyze SANS data for the prediction of the thermodynamic picture of the system. Since Flory-Higgins interaction parameters χ govern the phase situation of the mixture, the determination of the Flory-Higgins interaction parameters χ by fitting SANS data gives us information about miscibility of the mixture.

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