

SMALL ANGLE NEUTRON SCATTERING FROM POLYMER MELTS: STRUCTURAL INVESTIGATION AND PHASE BEHAVIOUR



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The Small-Angle Neutron Scattering (SANS) techniques have been used to study the structural properties and phase behavior of polymer melts. A model based on Random Phase Approximation (RPA) is proposed to predict the experimental data. By fitting the model to data we could be able to obtain radius of gyration (a measure of size of a polymer) and phase transition for the sample.

INTRODUCTION

A polymer, also known as a 'macromolecule', consists of a large number of repeating structural units called monomers which are linked together to form long chains [1,2]. If all the monomers are of the same type, these are homopolymers. If they have two or more types of monomers, these are copolymers. Natural and synthetic polymers can be produced to obtain new materials tailored with desired mechanical, optical, electrical, and other physical properties that can be used in modern life [3]. A typical polymer may include hundreds of thousands of monomers. Unfortunately, we yet to advance our understanding and ability to design polymers since they can possess amazingly complex micro structures due to huge number of internal degrees of freedom.

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 [4]. In these experiments monoenergetic neutron beam of wavelength λ is elastically scattered by a sample and the resulting scattering pattern is analyzed to probe the sample. 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 [5], 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 [6].

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.

THEORY

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

$$I(q) = (b_1 - c b_2)^2 V_1^{-1} S(q) \quad (1)$$

where b_i is the coherent scattering length of a segment of component i , V_i is the segment volume of component i , c is the ratio V_1/V_2 and $S(q)$ is the structure factor that contains all the information about sample.

Using the random phase approximation (RPA) for homogeneous binary mixture of polymers, structure factor can be written [7, 8] as

$$\frac{1}{S^0} = \frac{1}{S_A^0} + \frac{1}{S_B^0} - 2\chi_{AB}, \quad (2)$$

$$S_i^0(q) = N_i \phi_i P_i(q) \quad i = A, B, \quad (3)$$

$$P_A = \frac{1}{N_A^2} \left\langle \sum_{i=1}^{N_A} \sum_{j=1}^{N_A} e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} \right\rangle_{\psi(\vec{r}_{ij})} \quad (4)$$

where $S_i^0(q)$ is the bare structure factor for homopolymer i , χ_{AB} is the effective Flory-Huggins interaction parameter between A and B, P_i is the partial structure factor, N is the degree of polymerization, ϕ is the volume fraction, \vec{r}_i is the position vector and the bracket indicates that average should be taken with respect to some distribution function Ψ .

We can also express the structure factor for diblock copolymers based on the RPA as the following

$$S(q) = \frac{S_A^0 S_B^0 - (S_{AB}^0)^2}{S_A^0 + S_B^0 + 2S_{AB}^0 - 2\chi_{AB} (S_A^0 S_B^0 - (S_{AB}^0)^2)}, \quad (5)$$

$$S_{AB}^0 = \sqrt{\phi_A N_A \phi_B N_B} P_{AB}, \quad (6)$$

$$P_{AB} = \frac{1}{N_A N_B} \left\langle \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} e^{i\vec{q} \cdot (\vec{r}_{A_i} - \vec{r}_{B_j})} \right\rangle_{\psi(\vec{r}_{ij})} \quad (7)$$

By adopting Gaussian distribution [9] and considering limit case, we reproduce the famous Debye forms for the aforementioned partial structure factors:

$$P(q) = \frac{2}{x^2} (x - 1 + (1 + \varepsilon x)^{-1/\varepsilon}), \quad (8)$$

$$x = q^2 R_g^2, \quad (9)$$

$$\varepsilon = M_w/M_n - 1, \quad (10)$$

where R_g is the radius of gyration, ε describes polydispersity [10], M_w and M_n are the weight average and number average molecular weights, respectively. We note that polydispersity effect becomes important especially at low q values [4, 10].

RESULTS AND DISCUSSIONS

We reexamine the SANS results obtained at representative temperatures for samples B2B5 (a binary mixture of two homopolymers) and BB10 (a diblock copolymer) that are described elsewhere [11].

The SANS data obtained from the sample B2B5 were fitted with our model by using R_g and χ as adjustable parameters. The results illustrated in Figure 1, 2 and 3 show a very good agreement with the data.

As seen from the figures, we observe that the sample mixture is phase separated macroscopically at temperature of 248 K since $I(q) \rightarrow \infty$ as $q \rightarrow 0$. Radii of gyration were also obtained from fitting as shown in Table 1.

Table 1. Radii of gyration for binary mixture

Temperature (K)	R_{gA} (Å)	R_{gB} (Å)
248	252	37
274	272	93
361	193	85

Table 2. Interaction parameter χ for diblock copolymer at various temperatures

Temperature (K)	Interaction parameter χ
266	4.3×10^{-3}
303	4.1×10^{-3}
363	3.9×10^{-3}

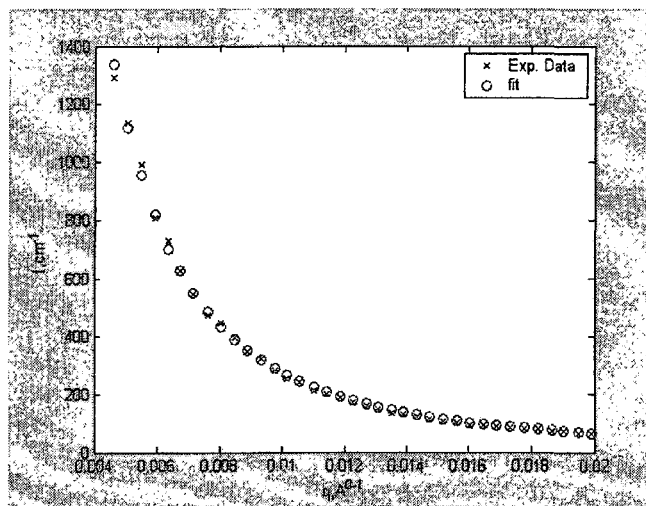


Fig. 1. SANS results for binary mixture at $T=248$ K. Crosses and circles correspond to SANS data and predicted values, respectively

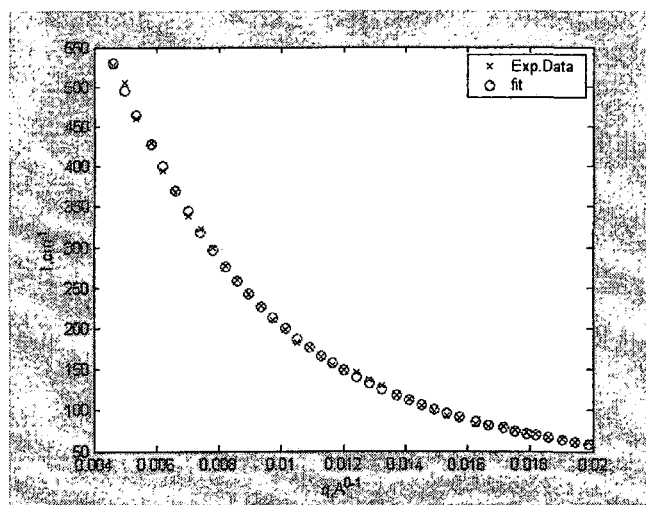


Fig. 2. SANS results for binary mixture at $T=274$ K. Crosses and circles correspond to SANS data and predicted values, respectively

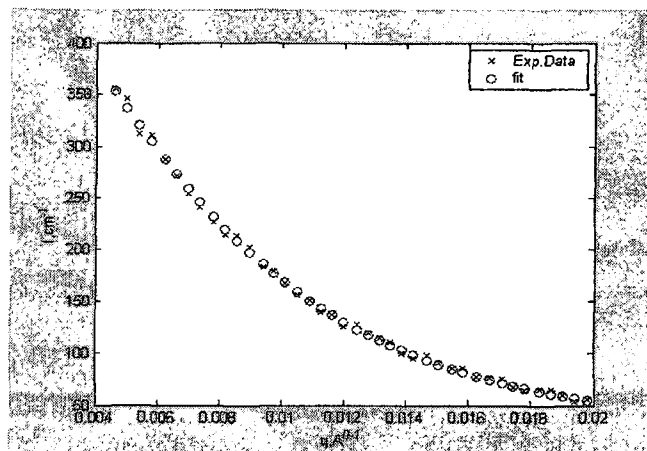


Fig. 3. SANS results for binary mixture at $T=361$ K. Crosses and circles correspond to SANS data and predicted values, respectively

The SANS results for BB10 diblock copolymer sample were also tested by our model as given in Figure 4, 5 and 6.

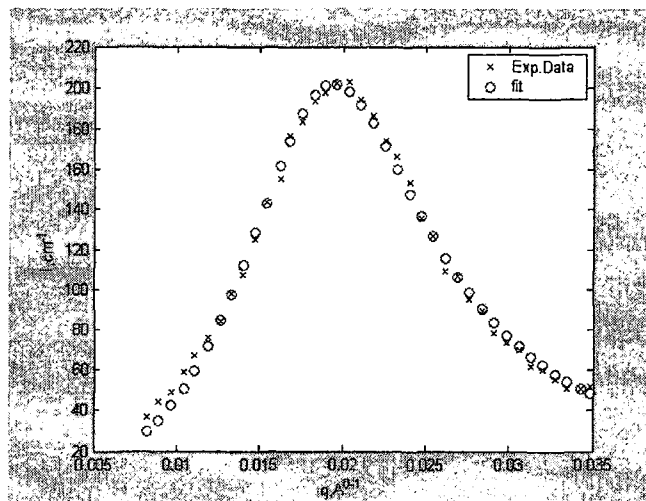


Fig. 4. SANS results for diblock copolymer at $T=363$ K. Crosses and circles correspond to SANS data and predicted values, respectively

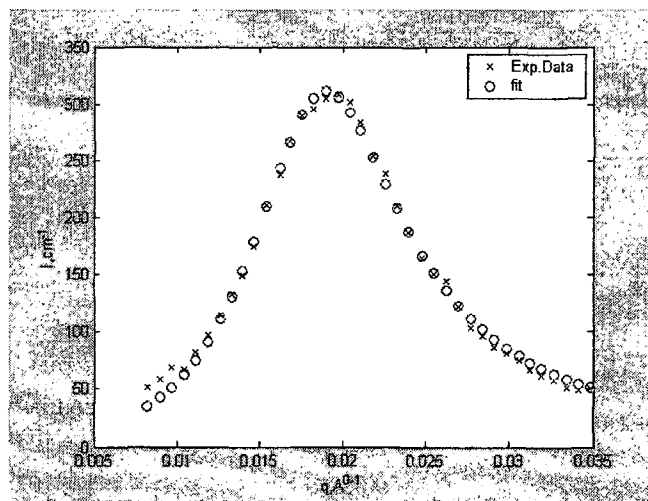


Fig. 5. SANS results for diblock copolymer at $T=303$ K. Crosses and circles correspond to SANS data and predicted values, respectively

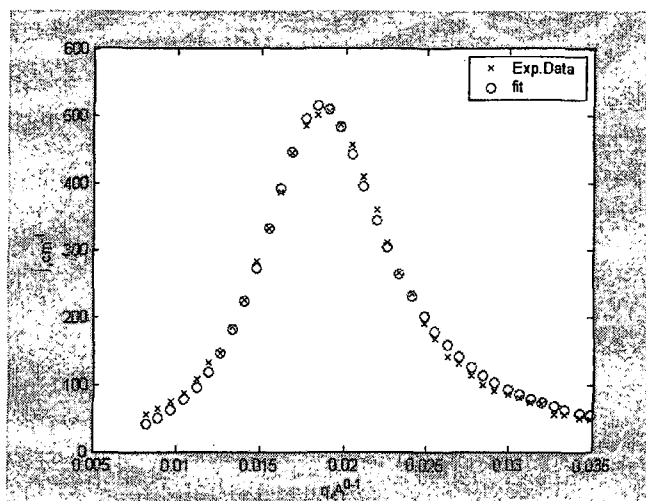


Fig. 6. SANS results for diblock copolymer at $T=266$ K. Crosses and circles correspond to SANS data and predicted values, respectively

These figures indicate perfect harmony between the data and predicted values. As seen there is a clear peak at 266 K. This implies a microphase separation since $I(q) \rightarrow \infty$ as $q \rightarrow q^*$. The microphase separation (on the length scale given by the polymer size) is caused by chemical incompatibilities between the different blocks that make up block copolymer molecules. Table 2 shows obtained values of the effective Flory-Huggins interaction parameter χ for varying temperatures. As seen from Table 2, miscibility decreases with increasing temperature.

CONCLUSIONS

Two kinds of polymer melts, binary mixture and diblock copolymer, have been reexamined. By fitting our model to the SANS data, we were able to obtain the effective Flory-Huggins interaction parameters χ for each case. For diblock copolymer, we see that χ decreases with increasing temperature, showing the temperature effect on separation. Diblock copolymer underwent microphase separation while homopolymer binary mixture phase separated macroscopically. The size of polymers changes with temperature as well. Therefore it is obvious that SANS provides a unique tool for investigating polymers [12-16].

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CATION-EXCHANGER FABRIC PREPARED BY ELECTRON BEAM-INDUCED GRAFT COPOLYMERIZATION OF BINARY MONOMER MIXTURE

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Applying the electron-beam preirradiation method in air the cation - exchanger fabric (CEF) containing sulfonic acid (R-SO₃H) groups was prepared by graft copolymerization of sodium styrenesulfonate with acrylic acid onto nonwoven polypropylene fabric. The effect of reaction conditions on the grafting yield and reaction mechanism was examined. It was found that the received CEF contains groups of strong acid (R-SO₃H) and weak acid (R-COOH) in almost equal proportion.

The ion-exchange properties of the CEF towards Cu(II) and Co(II) ions were investigated depending on the form of the CEF and a pH of the solution. It was shown that the utilization of the CEF in Na- form allows to make the best use of its ion-exchange capacity.

Electron beam irradiation; Preirradiation graft copolymerization; Polypropylene fabric; Sodium styrenesulfonate; Cation-exchanger fabric.

INTRODUCTION

The production of sorption-active natural and synthetic fibers and textile materials is of both great scientific and practical interest. The application of economical and ecologically clean radiation technologies for this purpose is now under the intent attention of researchers [1,2,3].