Neutron reflectivity studies of composite nanoparticle – copolymer thin films

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Abstract

Neutron reflection was used for the investigation of a new class of copolymers – composite materials, consisting of symmetric polystyrene–polybuthylmethacrylate (PS–PBMA) diblock copolymer with incorporated nanoparticles γ-Fe_2O_3 of a few nanometers in diameter. The presence of the nanoparticles induces an elastic distortion of the copolymer matrix. From the experiments we obtained information about the lamellar order of the polymer matrix, the distribution of the nanoparticles in the film and the distortion of the interfaces caused by the nanoparticles. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Block copolymers are increasingly used in biomedical and microelectronics applications as compatibilizing agents (polymeric alloys), surfactants and adhesives. Thus a fundamental understanding of the behavior of copolymers at the surface and interface is essential. In thin films, the lamellar microdomains are found to orient parallel to the free surface. This orientation in combination with the sensitivity of the neutron specular reflection (NSR) gives details on the morphology of the copolymers [1].

With the experiments described below we started NSR investigation of the new class of copolymers – composite materials, consisting of copolymers with incorporated nanoparticles of a few nanometers in diameter. The key point is that the copolymer matrix is able to order the nanoparticles in a macroscopic crystal of several hundred Ångstroms. By changing the copolymer characteristic one can vary the structure of the film (from lamellar

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to cubic). Changing in addition the nanoparticle size and material, one can influence the macroscopic properties (optical, magnetic, etc.) over a wide range.

The presence of the nanoparticles induces an elastic distortion of the copolymer matrix, leading in the worse case to particle exclusion and in the best to self-organization of the particles. Once the mixing is achieved, it is important to understand the interaction between the particles, the correlation between the adjacent layers, the influence of the particle presence on the medium properties.

We investigated thin films of composite materials, consisting of symmetric, diblock copolymers of polystyrene (PS) and polybutylmethacrylate (PBMA) with γ-Fe_2O_3 nanoparticles [2,3]. NSR experiments were performed on the spectrometers D17 (ILL, Grenoble) [4] and SPN (JINR, Dubna) [5].

2. Sample preparation and NSR experiment

Diblock copolymers A–B, dissolved in toluene, cast and spin coated onto a silicon substrate (5 cm in diameter and 1 mm thick) and having been annealed under vacuum at 150°C, within 3 days the microphase separated into a lamellar morphology. The lamellae are parallel to the film surface, and their thickness is given by $nL/2$, where n is integer even and L is the lamellar period (A–B–B–A).

PBMA segregates to the air/surface interface due to a lower surface energy compared to the one of PS.

The first sample was a symmetric polystyrene–polybutylmethacrylate PS–PBMA diblock copolymer film with the molecular weight of the copolymer Mw = 82 K. The reflectivity profile obtained for a thin PS–PBMA film is shown in Fig. 1. From the data analysis we deduced that the multilayer structure is composed of three lamellar periods L (PS–PBMA–PBMA–PS) with the total bi-layer thickness of 29 nm. A SiO_2 layer with a thickness of about 5 nm was determined on the Si substrate. PBMA segregates to the air/surface and substrate interfaces as predicted. The interfacial profile between the microdomains is the subject of further analysis. We measured the reflectivity from PS–PBMA thin film and showed that the lamellar structure for this type of copolymer can be detected without prior deuteration of the copolymers. To get a better intensity in the Bragg peak one should increase the number of the lamellar periods L.

The next NSR experiments were made with films of symmetric d-PS–PBMA (where "d" stands for a deuterated copolymer) diblock copolymer with the molecular weight Mw = 170 K. Nanoparticles made of γ-Fe_2O_3 with the average diameter of 4 nm were incorporated in the deuterated PS-domains.

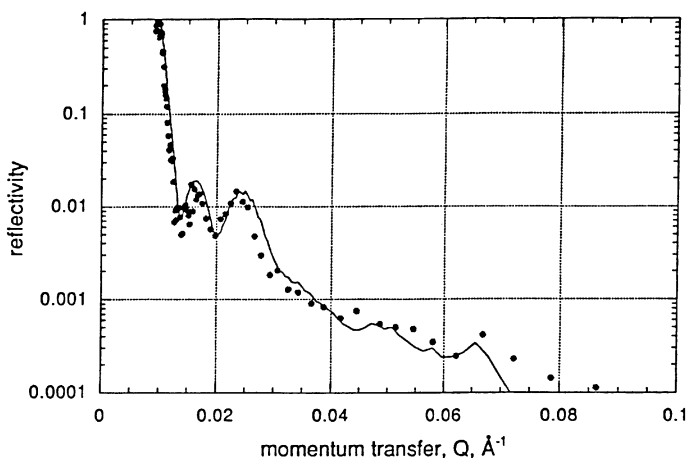The reflectivity profile obtained for a thin PS–PBMA film is shown in Fig. 2a. The measured

Fig. 1. Experimental reflectivity profile for the symmetric PS–PBMA not deuterated film with molecular weight Mw = 82 K. The solid line is the calculated reflectivity for 3 lamellar periods L = 29 nm each.
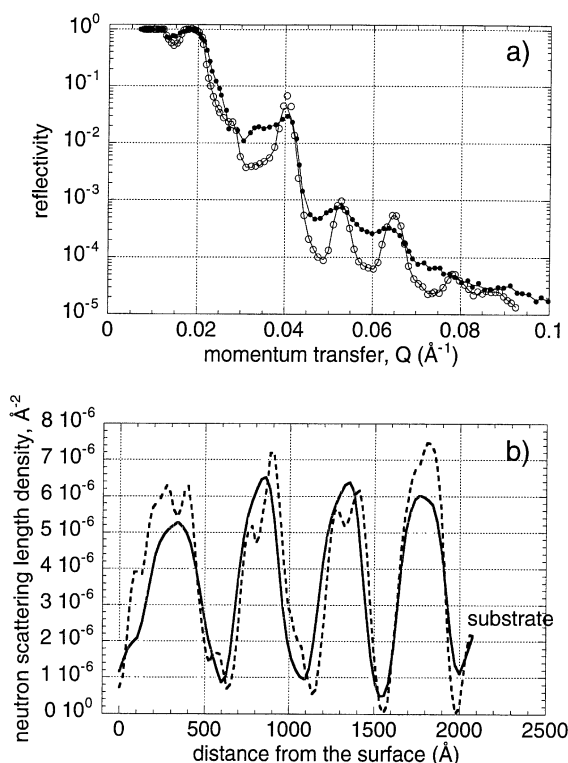
Fig. 2. (a) Experimental reflectivities for d-PS-PBMA films with Mw = 170 K. The open cirrcles corespond to a pure copolymer film, the filled circles show the reflectivity from the same copolymer film but with 4 nm nanoparticles incorporated in the PS lamellae. The solid lines show the best fit to the experimental data. (b) Neutron scattering length density (NSLD) profile from the fit to the experimental reflectivities from Fig. 2a. The solid line corresponds to the pure d-PS–PBMA film, the dashed line shows the NSLD profile for the sample with nanoparticles.

data are shown by open circles, whereas the solid line represents the calculated reflectivity. Due to the orientation of the lamellae parallel to the film surface, seven orders of Bragg reflections were measured. From the data analysis we deduced that the multilayer structure is composed of 4 lamellar periods L (PS–PBMA–PBMA–PS) with 11.5 nm PBMA and 13.5 nm d-PS microdomains. PBMA segregates to the air/surface and substrate interfaces.

For the second sample we used nanoparticles of (γ-Fe_2O_3) single monodomains of 4 nm diameter

which were incorporated in the d-PS domains prior to the film preparation with the volume fraction of 2%. The reflectivity profile from [PS–d-(γ-Fe_2O_3)]–PBMA sample is shown in Fig. 2 with the filled circles. The presence of the Bragg peaks proves that the sample with incorporated nanoparticles keeps the multilayer structure with the same bilayer thickness as for the pure copolymer sample. The reduced contrast of the Bragg peaks is caused by the distortions in the lamellae. The fit to the data is shown by the solid line. The neutron scattering length density profiles obtained after the fit to the data for pure copolymer film and for the film with incorporated nanoparticles are shown in Fig. 2b with solid and dashed lines, respectively. The nanoparticles used for the sample preparation were polydispersed ($\sigma = 0.4$) with a diameter of about 4 nm. From the fit to the data we determined that the smaller nanoparticles (4 nm) are concentrated close to PS–PBMA interfaces and the bigger ones (6 nm) at the center of the lamellae (see Fig. 2b).

3. Conclusions

Neutron reflection was used for the study of a new class of copolymers – composite materials. The composite films were made of symmetric polystyrene–polybutylmethacrylate (d-PS–PBMA) diblock copolymer with incorporated nanoparticles γ-Fe_2O_3 of a few nanometers in diameter. It has been shown that the high-resolution neutron reflectivity allows a detailed study of the nanoparticles distribution within the lamellae.

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