

Surface Segregation in Miscible Polymer Mixtures of Block Copolymer / Homopolymers

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In a miscible blend of two polymers with equivalent degree of polymerization, the lower surface energy component is enriched at the surface to minimize the total free energy of the system. However, it is impossible to strictly control a chain arrangement along the direction normal to the surface. In this study, we evaluated surface segregation phenomena in mixtures of poly(4-trimethylsilylstyrene)(T), polyisoprene(I), and their block copolymer (TI), whose blends are miscible at room temperature,¹ and compare to what extent of segregation of T homopolymer and that of T block of TI in T/TI/I blend films.

Normal T (hT), its partially deuterated one (dT), normal I(hI), poly(4-trimethylsilylstyrene-block-isoprene) (hTI) and poly(deuterated 4-trimethylsilylstyrene-block-isoprene) (dTII) were used in this study. Weight average molecular weights, M_w , for hT, dT, hI, hTI and dTI are 34k, 43k, 24k, 85k and 65k, respectively. Surface free energy of T, being evaluated to be 31.9 mJ/m² based on contact angle measurements, is lower than that of I of 37.4 mJ/m². dT/hTI/hI and hT/dTI/hI blend films were prepared by spin-coating method from toluene solutions onto silicon wafers. Since the volume fractions of T, TI and I were 1:1:1, the ratio of T to I in the whole film is 1:1. Neutron reflectivity (NR) measurements were carried out using MINE-2 reflectometer. Incident neutrons have the wavelength of 0.88 nm and the resolution of 5.1 %. The reflectivity was calculated on the basis of the scattering length density profile along the depth direction by using Parratt 32.

Fig.1(a) shows neutron reflectivity profiles for dT/hTI/hI and hT/dTI/hI blend films. Experimental data sets were repre-

sented by circles and squares. Solid lines denote the calculated neutron reflectivities based on the scattering length density, (b/V), profiles shown in the parts (b) and (c) of Fig. 1. The (b/V) values for dT, hT and hI were taken to be 3.63×10^{-4} , 0.57×10^{-4} and $0.27 \times 10^{-4} \text{ nm}^{-2}$, respectively, using the scattering lengths per monomeric units and the bulk densities of these polymers. Since the calculated curves were in good agreement with the experimental data, it can be conceived that the model (b/V) profiles well represent the composition profiles in the blend films normal to the surface. For the dT/hTI/hI blend film, the (b/V) value at the surface is higher than that of the internal bulk region, as shown in Fig.1(b). This means that dT homopolymer is enriched at the surface. On the other hand, for the hT/dTI/hI blend film, dTI was not segregated at the surface. These results indicate that surface segregation power of T component of TI is much lower than that of T homopolymer.

Reference [1] M. Harada, T. Suzuki, M. Ohya, D. Kawaguchi, A. Takano, Y. Matsushita, *Macromolecules*, 38, 1868-1873 (2005).

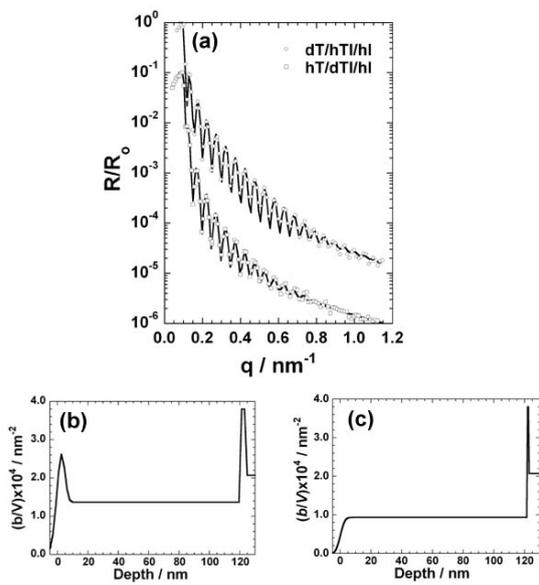


Fig. 1. (a) Neutron reflectivity profiles for $dT/hTI/hI$ and $hT/dTI/hI$ blend films. Solid lines denote the calculated reflectivities based on scattering length density, (b/V) profiles for (b) $dT/hTI/hI$ and (c) $hT/dTI/hI$ blend films.