

LETTERS

Phase-Separation Structure of a Monolayer of Binary Polymer Blend Studied by Fluorescence Scanning Near-Field Optical Microscopy

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A phase-separated monolayer of a binary mixture of pyrene-labeled poly(isobutyl methacrylate) (PiBMA-Py) and perylene-labeled poly(octadecyl methacrylate) (PODMA-Pe) was investigated by the fluorescence scanning near-field optical microscope (SNOM), which provided optical images of samples with a high resolution beyond the diffraction limit, by using evanescent field from an aperture smaller than the wavelength of light. Each phase of the PiBMA-Py/PODMA-Pe was selectively imaged as a bright area by choosing the excitation wavelength (325- or 442-nm line of a He–Cd laser). The fluorescence SNOM enabled mapping of the excitation energy transfer efficiency on the monolayer plane. The energy transfer measurement revealed that the phase separation of the PiBMA-Py/PODMA-Pe blend at the air/water interface was almost completed by annealing for 60 min at 40 °C and the phase boundary had a width of a few hundred nanometers.

Introduction

Recently, polymer monolayers, which are prepared at the air/water interface, have attracted much attention because the sequential deposition of them by the Langmuir–Blodgett (LB) technique allows one to fabricate highly controlled molecular assemblies. Mobility and conformation of a polymer chain in a monolayer is thought to be extremely constrained, considering that the polymer chain is confined into a two-dimensional plane from a random-coil conformation in a three-dimensional space.^{1–4} Thus, it is expected that the properties of polymer monolayers are different from those of polymers in bulk.

Our research project is concerned with “polymer science in two dimensions”, and we have so far investigated the properties of polymer monolayers by various optical techniques, such as Brewster angle microscopy^{5,6} and fluorescence spectroscopy.^{7,8}

However, the lateral resolution is not sufficient to observe microscopic structures due to the diffraction limit ($\lambda/2$) of conventional optical methods. Scanning near-field optical microscopy (SNOM), which has been developed recently,^{9,10} allows one to obtain a fluorescence micrograph with a high resolution beyond the diffraction limit by monitoring fluorescence from dye molecules excited by evanescent field of light from an aperture at the end of the raster-scanning optical fiber probe, whose diameter is smaller than the wavelength of light. Several studies have revealed that SNOM is a versatile tool for studying both the morphology and the spectroscopic properties of an organic thin film simultaneously.^{11–15}

In the current study, we concern with a two-dimensionally phase-separated polymer blend. The phase separation of polymer blends in three-dimensional space has been extensively studied by many workers.^{16–18} However, little is known about that of polymers restricted in a two-dimensional plane.^{19,20} We investigated a binary polymer blend, which consists of poly(isobutyl methacrylate) (PiBMA) and poly(octadecyl methacrylate) (POD-

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TABLE 1: Characterizations of PiBMA-Py and PODMA-Pe

	M_n	M_w/M_n	$f/\%$
PiBMA-Py	39 600	2.05	2.9
PODMA-Pe	11 900	2.08	2.0

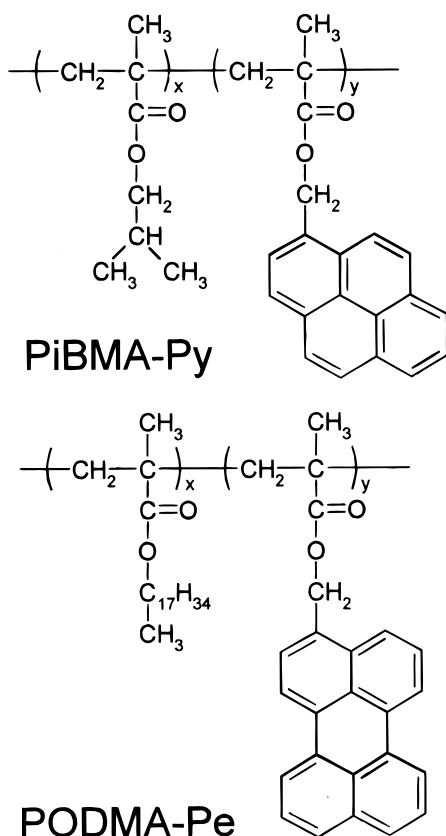


Figure 1. Chemical structures of PiBMA-Py and PODMA-Pe.

MA), by a fluorescence SNOM with a resolution of ca. 100 nm using UV and visible lasers as the light source. The excitation energy transfer method from pyrene to perylene was applied to investigate the mixing of these polymers at the phase interface.

Experimental Section

Materials. Pyrene-labeled poly(isobutyl methacrylate) (PiBMA-Py) was synthesized by the radical copolymerization of isobutyl methacrylate and 1-pyrenylmethyl methacrylate. The molecular weight was determined by GPC calibrated with polystyrene standards. The fraction of pyrene moiety introduced into the polymer chain, f , was estimated from UV-vis absorption (U3500, Hitachi) and ¹H NMR (JNM-EX400, JEOL) measurements. Perylene-labeled poly(octadecyl methacrylate) (PODMA-Pe) was synthesized from octadecyl methacrylate and 3-perylenylmethyl methacrylate and characterized similarly to PiBMA-Py. The chemical structures and the characterizations of the polymers are shown in Figure 1 and Table 1, respectively.

Phase-separated monolayers of the PiBMA-Py/PODMA-Pe blend were prepared by the following procedure. A mixed solution of PiBMA-Py and PODMA-Pe (50:50) was spread dropwise onto a subphase of purified water (Barnstead NANO Pure II) at 20 °C. The temperature of the subphase was raised to 40 °C and kept constant for 60 min. After cooling to 20 °C, the phase-separated monolayer was compressed and transferred onto a clean cover glass.

SNOM Measurements. Fluorescence SNOM images were recorded on a commercially available instrument (SP-301,

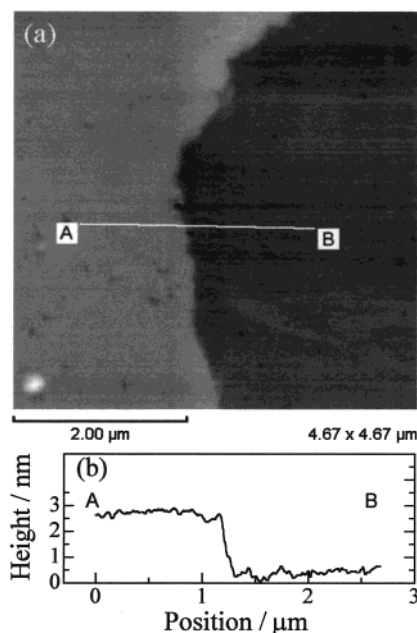


Figure 2. AFM image of a phase-separated monolayer (a) and the height profile along the line indicated in the AFM image (b).

Unisoku). The 325- and 442-nm lines of a He-Cd laser (IK5351R-D, Kimmon Electric) were used as the excitation light. The distance between the probe and a sample surface was regulated to be several nanometers by a shear force feed-back system. The fluorescence from the sample was collected by a high NA objective and detected with a photomultiplier (R2949, Hamamatsu Photonics). SNOM probes used in this study were made from an optical fiber with a pure silica core by etching in a buffered hydrogen fluoride solution following a heating-and-pulling process (P-2000, Sutter Instrument).^{21,22} The lateral resolution of our system is typically 50–100 nm. Measurements were performed at room temperature, and no image processing was applied. In our SNOM system, the vertical resolution of a topographic image, which is typically 1 nm, is rather worse than a commercially available AFM. Therefore AFM measurements were also carried out in contact mode (SPM-9500J, Shimadzu). The spring constant of the cantilever (OMCL-TR400PSA-3, Olympus) was 0.09 N m⁻¹.

Results and Discussion

A contact mode AFM image is shown in Figure 2. The bright and dark areas correspond to PODMA and PiBMA domains, respectively. The height difference between these areas was 2 nm, which was in good agreement with the thickness difference between PODMA²³ and PiBMA^{24,25} monolayers reported in the literature. This indicates that the polymer blend spread on water surface was able to be transferred onto a solid substrate as a monolayer.

Figure 3 shows the fluorescence SNOM images of a phase-separated monolayer deposited at a surface pressure of 5 mN m⁻¹. A perylene fluorescence image is shown in Figure 3a, which was recorded by collecting the fluorescence from perylene excited at 442 nm. The bright area indicates PODMA-Pe rich phase because perylene was introduced into only the PODMA chain. Figure 3b shows a pyrene fluorescence SNOM image obtained by illumination with a 325-nm evanescent field and collection of the monomer fluorescence (360–410 nm) from pyrene. PiBMA-Py rich phase could be visualized as a bright area in the image of pyrene fluorescence. The PiBMA and PODMA domains in a two-dimensional phase-separated poly-

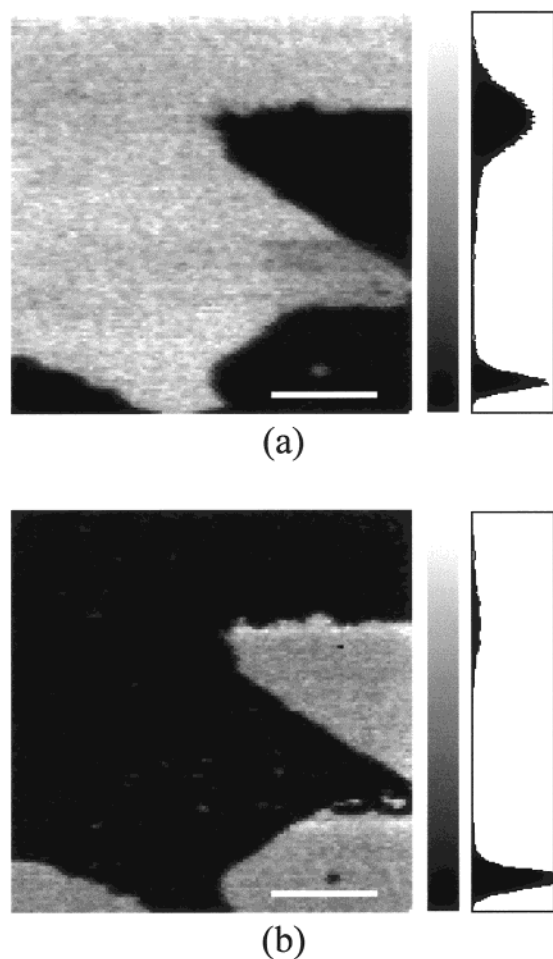


Figure 3. Fluorescence SNOM images of a phase-separated polymer monolayer. The scanning area was $15 \times 15 \mu\text{m}^2$. The scale bar in each image indicates $4 \mu\text{m}$. (a) Perylene fluorescence SNOM image. The excitation wavelength was 442 nm and the fluorescence from perylene was collected through a filter, Y-47 (Hoya). (b) Pyrene fluorescence SNOM image. The excitation wavelength was 325 nm. A filter, UV-D33S (Toshiba), was put in front of the detector to collect only the fluorescence from pyrene. The fluorescence intensity histogram for each image is shown in the right-hand side, which is the plot of the number of data points against the observed fluorescence intensity.

mer blend were able to be selectively imaged by choosing appropriate excitation wavelengths. These two fluorescence SNOM images have complementary features, that is, the bright areas in the pyrene fluorescence image (Figure 3b) exactly coincide with the regions which were darkly measured in the perylene fluorescence image (Figure 3a). This indicates that the phase-separated monolayer was able to be transferred on the solid substrate without any defect.

The energy-transfer method was combined with the fluorescence SNOM measurement in order to investigate the phase-separation structure in more detail. The excitation energy transfers from a donor (pyrene) to an acceptor (perylene) when they are close to each other. The energy transfer efficiency is very sensitive to the alteration of distance between the donor and the acceptor, and the Förster radius of a pyrene–perylene pair, at which the energy transfer efficiency is 50%, is known to be 3.3 nm.²⁶ Therefore, when pyrene is selectively excited and the perylene emission is recorded with raster-scanning the probe, the bright areas in the image obtained indicate the region where PiBMA-Py and PODMA-Pe are mixed at the molecular level.

The energy transfer image is shown in Figure 4, which was

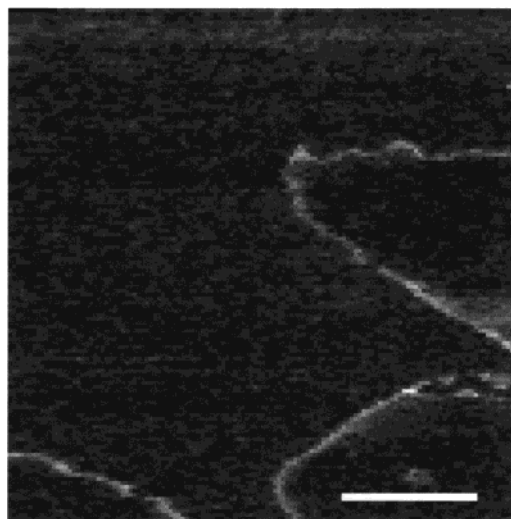


Figure 4. Energy transfer image of a phase-separated monolayer. The scanning area was the same as that of Figure 3. The scale bar in the image indicates $4 \mu\text{m}$. The excitation wavelength was 325 nm. An optical filter, Y-44 (Hoya), was used to block the fluorescence from pyrene and collect only that from perylene. The bright areas in this image indicate the regions where PODMA-Pe and PiBMA-Py were mixed at the molecular level.

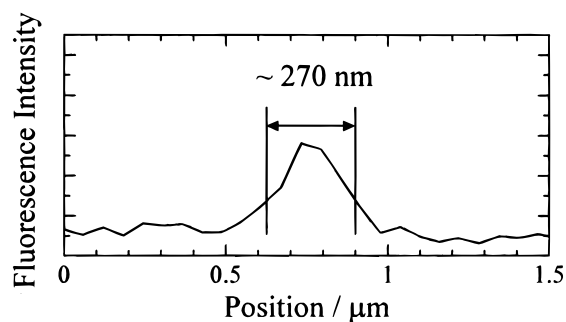


Figure 5. Typical fluorescence intensity profile of the phase interface. The interface width was ca. 270 nm.

obtained by scanning the same area as that in Figure 3 and collecting the fluorescence from perylene ($\lambda > 440 \text{ nm}$) with 325-nm illumination. In this image, only the phase boundary was recorded as a bright area. This indicates that PiBMA and PODMA are mixed at the interface. A fluorescence intensity profile at the interface is shown in Figure 5. The typical value of the interface width was 200–400 nm, which was defined as the fwhm of a fluorescence intensity profile across the phase boundary. Considering that the lateral resolution of SNOM used in this study was about 100 nm, the real width could be estimated to be 100–300 nm. The interface thickness in the bulk state was estimated to be several nanometers from Broseta's theory²⁷ by using calculated χ parameter.^{28,29} The interface width between PiBMA and PODMA domains observed in quasi two dimensions was considerably large compared to the value calculated in the three-dimensional state. Although the morphology of the boundary was influenced by the physical factors, such as shear flow and stress, during the compression process after the annealing, the interfacial width was independent of the surface pressure at deposition (data are not shown). This result suggests that the wide line of the phase boundary is determined by the miscibility between PiBMA and PODMA on the surface, rather than the effect of the compression on the water surface.

The fluorescence intensity in the energy transfer image stayed almost at the background level when measured inside of each

domain. Little PiBMA existed in the PODMA rich domain, namely $\varphi_{\text{PiBMA}} \sim 0$ and $\varphi_{\text{PODMA}} \sim 1$, where φ_A is the composition of the polymer A. The fluorescence intensity histogram for each SNOM image in Figure 3 has two clearly distinct levels, that is, the fluorescence intensity level was almost constant within each domain. These results indicate that the polymer composition, φ_{PiBMA} and φ_{PODMA} , in each phase reached the equilibrium values and almost completely phase-separated within 60 min during annealing at 40 °C.

Conclusion

The phase separation structure of a binary polymer blend restricted in a two-dimensional plane was investigated by using a fluorescence SNOM. PiBMA-Py and PODMA-Pe domains were selectively imaged by UV and visible lasers, respectively. The topographic image drawn by the excitation energy transfer efficiency revealed that the phase separation of the PiBMA/PODMA blend at the air/water interface was almost completed within 60 min at 40 °C and the phase boundary width was a few hundred nanometers.

The fluorescence method, such as the energy transfer method, in combination with SNOM is expected to be a powerful tool for investigating the morphology and properties of polymers in a two-dimensional plane.

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