

Local Properties of Phase-Separated Polymer Surfaces by Force Microscopy

Makoto MOTOMATSU, Heng-Yong NIE¹, Wataru MIZUTANI¹ and Hiroshi TOKUMOTO¹

Joint Research Center for Atom Technology (JRCAT) Angstrom Technology Partnership (ATP),
c/o National Institute for Interdisciplinary Research (NAIR), 1-1-4 Higashi, Tsukuba, Ibaraki 305
¹JRCAT, NAIR, 1-1-4 Higashi, Tsukuba, Ibaraki 305

(Received December 30, 1993; accepted for publication March 19, 1994)

Force microscopy techniques such as atomic force microscopy (AFM), friction force microscopy (FFM), and force modulation microscopy (FMM) were applied to polymer blend and copolymer surfaces to observe phase-separated structures and distinguish the individual components. We observed a continuous phase-separated structure of polystyrene (PS)/polyethyleneoxide (PEO) polymer blend, a micro-phase-separated structure of styrene (S)/butadiene (B) S-B-S-B block copolymer, and islands-sea phase-separated structures of PS/poly-methylmethacrylate (PMMA) polymer blend and diblock copolymer with AFM. FFM and FMM were applied to PS/PMMA polymer blend and diblock copolymer, and FFM differentiated PS from PMMA.

KEYWORDS: morphology, phase separation, atomic force microscopy, force microscopy, copolymer, polymer blend, PS, PMMA

1. Introduction

Since polymers are generally insoluble with other polymers, polymer blends and multiblock copolymers show phase separation, unless there are attractive interactions between them, such as hydrogen bonds. The phase-separated polymers have been studied mainly with bulk materials. Recently, surfaces or interfaces of polymers have been growing in importance from the standpoint of surfactants, adhesives, or polymer blends (alloys). To observe the phase separations of polymers in real space, optical microscopy (OM) and transmission electron microscopy (TEM) have been widely used. However, these methods have problems. In OM, the spatial resolution is limited; TEM requires complicated sample preparations such as slicing the specimen with a microtome and selectively dissolving a dye containing a heavy atom in one of the polymers to enhance the contrast. In addition, sample damage by the electron beam is also an issue. Moreover, it is very difficult in both methods to observe only the surfaces which determine important chemical and mechanical properties such as reactivities and textures.

In contrast, atomic force microscopy (AFM) can resolve nanometer-scale morphology with simple sample preparation. In addition, AFM-related force microscopies such as friction force microscopy (FFM),¹⁾ force modulation microscopy (FMM),²⁾ and ultrasonic force microscopy (UFM)³⁾ are capable of differentiating polymer species on the surfaces. By using them, we observed phase-separated polymer surfaces and measured physical properties of different types of polymers, and compared the results with those obtained by TEM.

2. Experimental

Four types of specimens were prepared as follows. Polystyrene (PS) and polyethyleneoxide (PEO) were blended in benzene solution with 1:1 wt. ratio, styrene(S)-butadiene(B) S-B-S-B block copolymer was dissolved into toluene solution, PS and poly-methylmethacrylate (PMMA) were blended in toluene solution with 1:1 wt. ratio, and PS/PMMA diblock copolymer was also dissolved into toluene solution.

The concentrations were set at 2 wt% for all. These solutions were spin-coated on glass substrates at 2000 rpm, then dried under vacuum at 170°C for 3 h to form 200-300-nm-thick films. Here we estimated weight-average molecular weight M_w and number-average molecular weight M_n as follows: for PS $M_w=19600$, $M_w/M_n=1.01$; for PMMA $M_w=12000$, $M_w/M_n=1.1$; for PS/PMMA diblock copolymer $M_w(\text{PS})=28500$, $M_w(\text{copolymer})=58500$, $M_w/M_n=1.06$. AFM measurements were carried out using a Seiko Instruments SPA-300 unit in air.

3. Results

We observed PS/PEO polymer blend and S-B-S-B block copolymer. A typical continuous phase-separated structure was observed for PS/PEO polymer blend film, as shown in Fig. 1. It is normally observed for the insoluble polymers when their ratio is close to 1:1. As shown in Fig. 2, small dots of S-B-S-B block copolymer of approximately 20 nm in diameter were observed, corresponding to the spherical PS dots which Kämpf *et al.*⁴⁾ observed with S-B-S block copolymer using TEM.

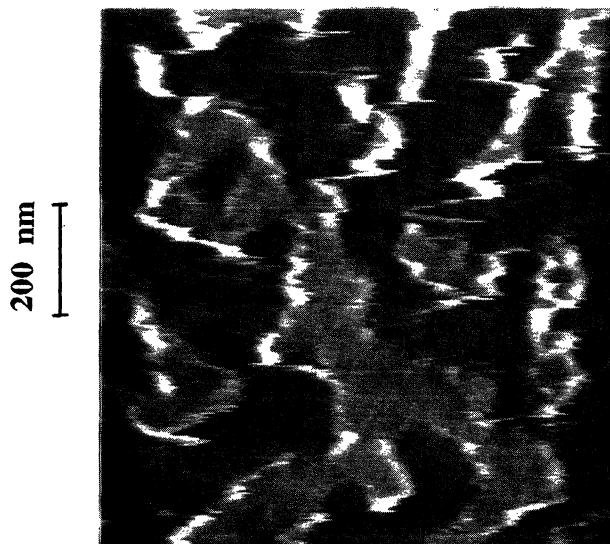


Fig. 1. AFM image of PS/PEO (1/1) polymer blend.

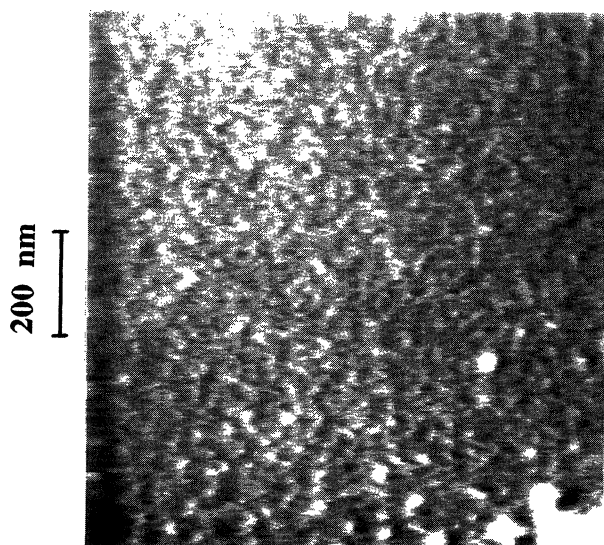


Fig. 2. AFM image of S-B-S-B block copolymer.

The phase-separated patterns depend on such factors as the polymer species, thermal treatment. We observed islands-sea phase-separated structures of PS/PMMA polymer blend film and PS/PMMA diblock copolymer, which are completely different patterns from those observed in PS/PEO film. Figure 3(a) is an AFM image of the PS/PMMA diblock copolymer surface, showing depressions 500–2000 nm in diameter and 10–20 nm in depth. Maaloum *et al.*⁵⁾ reported a similar phase-separated PS/PMMA diblock copolymer surface with AFM and found that the patterns depend on the thermal treatment condition. An FFM map (Fig. 3(b)) and a friction force loop along the line (Fig. 3(c)) show that the depressed parts have larger friction forces by 1.6 nN. Figure 4 is an FFM map of the copolymer which shows the distribution of the stiffness⁶⁾ of the films. FMM is a compliance measurement using the modulating method. There are no significant differences between the two phases, except for the topographic effect or edge effect. From the FMM measurement, it was very difficult to determine which phase corresponds to PS or PMMA.

Figure 5(a) is an AFM image of PS/PMMA polymer blend film, showing hillocks of 500–2000 nm in diameter and 50–70 nm in height. It should be noted that each PS or PMMA homopolymer film prepared in the same manner exhibited flat surfaces without any hillocks or depressions. An FFM map (Fig. 5(b)), and a friction force loop along the line (Fig. 5(c)) show that the hillocks have smaller friction forces by 1.6 nN.

4. Discussion

The differences in the topography and the friction force on the surfaces of PS/PMMA polymer blend and diblock copolymer films are discussed based on the physical properties of PS and PMMA bulk polymers.⁷⁾ Bulk properties of PS and PMMA differ slightly, as shown in Table I. For example, the difference in Young's modulus between PS and PMMA is only 10%. Therefore, the FMM measurement (Fig. 4) shows the

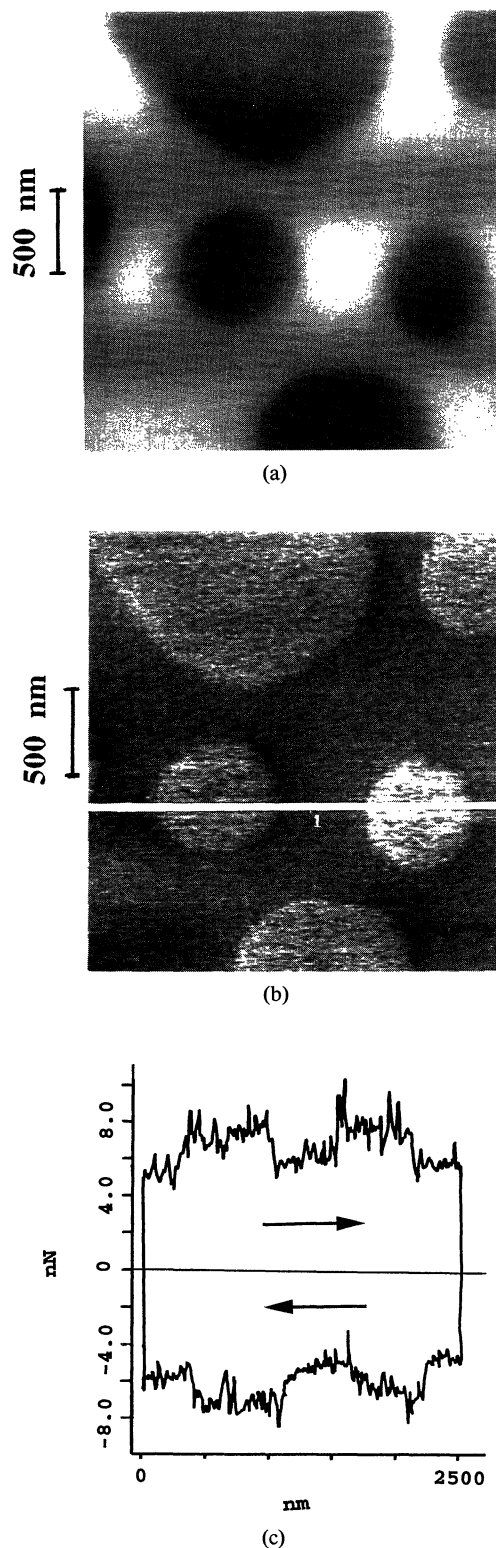


Fig. 3. PS/PMMA diblock copolymer with AFM and FFM: (a) topography, (b) friction force map, and (c) force loop. Scanning was from the left to the right and from the right to the left along the line marked in (b). Peak positions are slightly shifted between the two scans due to the hysteresis of the PZT.

difficulty of detecting a topography-related difference in hardness by the compliance measurement using the modulation method for PS/PMMA samples. For another reason, under the surface pattern made by one component, there can be an other component in the

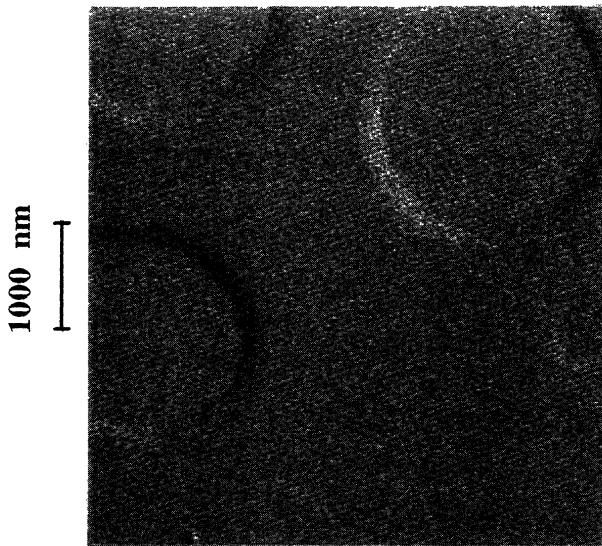


Fig. 4. Stiffness map of PS/PMMA diblock copolymer with FMM.

film; thus the hardness does not reflect that of the surface component.

Surface phase separation occurs due to the difference in the surface tension, and the polymers with higher surface tension should form a higher topography. The difference of the surface tension value (Table II)⁸⁾ between these polymers is very small. However, the molecular weights are significantly different from those in ref. 8. According to Le Grand and Gaines,⁹⁾ molecular weight must be taken into account to evaluate the surface tension. We use the following equation^{8,9)} which fits the surface tension data γ within an accuracy of 0.1 dyne/cm,

$$\gamma = \gamma_\infty - k_e / M_w^{2/3}, \quad (1)$$

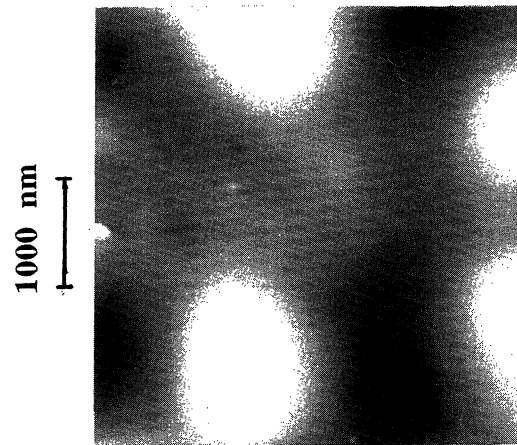
where k_e is an empirical constant and γ_∞ is the surface tension at infinite molecular weight. According to eq. (1), the surface tension increases with the molecular weight. γ of our PS ($M_w=19600$) is calculated at 29.5 using $k_e=372.7$ and $\gamma_\infty=29.97$ at 176°C.⁹⁾ The calculation of γ for PMMA is difficult since no k_e is reported.

Table I. Physical properties of bulk PS and bulk PMMA.

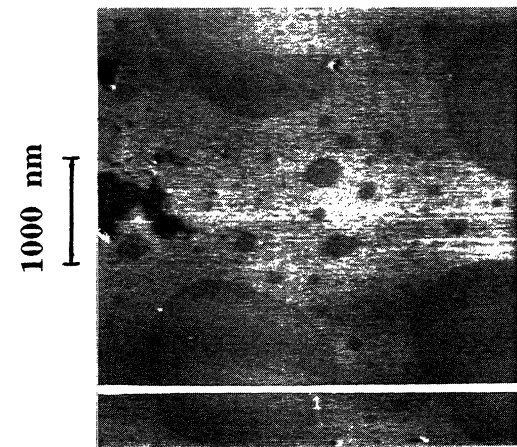
	PS	PMMA
Rockwell hardness		
M-scale	66	72
R-scale	124	125
Young's modulus (GPa)	3.4	3.7
Friction coefficient		
(metal against polymer)	0.4-0.5	0.4-0.5
(polymer against polymer)	0.4	0.25

Table II. Surface tension (dynes/cm) of bulk PS and bulk PMMA at 20°C, 140°C, and 180°C.

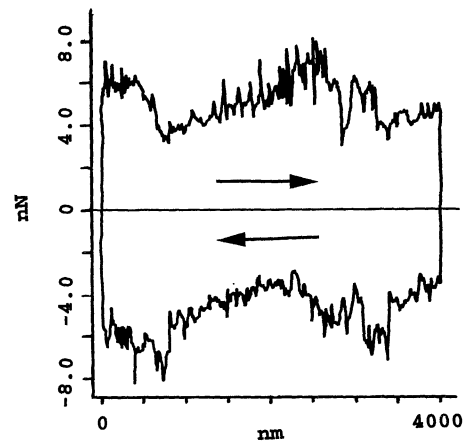
	20°C	140°C	180°C
PS (M: 44000)	40.7	32.1	29.2
PMMA (M: 3000)	41.4	32.0	28.9



(a)



(b)



(c)

Fig. 5. PS/PMMA (1/1) polymer blend with AFM and FFM: (a) topography, (b) friction force map, and (c) force loop. Scanning was from the left to the right and from the right to the left along the line marked in (b). Peak positions are slightly shifted between the two scans due to the hysteresis of the PZT.

However, we can assume $k_e=340-390$, which is common to most polymers consisting of C, H, and O.⁸⁾ From the values in Table II, the surface tension of our PMMA ($M_w=12000$) is calculated as 29.9-30.0 at 180°C. The value is larger than that of the PS by 0.4-

0.5 dynes/cm. The surface tension difference of 0.1 dyne/cm is sufficient to cause the topography difference. Therefore, we assume that the higher topography parts correspond to PMMA.

For the friction force difference in PS/PMMA samples with FFM, the coefficient of the bulk polymers depends on the opposing material (Table I). Against polymers, PS shows a larger coefficient than that of PMMA. Although the bulk friction coefficient of the polymer against the tip material is unknown, most probably, the tip picks up the material being scanned. Provided that the bulk properties and nanoscale surface properties are the same, we assume that the smaller friction force surface corresponds to that of PMMA. The results derived from surface tension and friction are consistent if we attribute higher topographic parts with smaller friction to the PMMA or PMMA component of the copolymer.

5. Conclusions

We observed phase-separated polymer surfaces with AFM, FFM, and FMM. PS/PEO polymer blend shows a typical continuous phase separation with a characteristic length of about 200 nm, while S-B-S-B block copolymer film shows a micro-phase separation with dots of 20 nm in diameter, comparable to the observation with TEM.

PS/PMMA polymer blend and copolymer films show islands-sea phase-separated structures, hillocks and depressions, respectively. Friction force changes in accordance with the topography, although the FMM does not show a clear difference in the stiffness. In our ex-

periment, the PMMA has higher surface tension and smaller friction coefficient than the PS, and higher topographic parts have smaller friction force for both PS/PMMA polymer blend film and PS/PMMA diblock copolymer film. We conclude that the smaller friction force and higher topography surface correspond to PMMA.

Acknowledgement

This work was performed under the management of a technological research association, the Angstrom Technology Partnership (ATP) in the Joint Research Center for Atom Technology (JRCAT) partly supported by New Energy and Industrial Development Organization (NEDO).

- 1) E. Meyer, R. Overney, R. Lüthi, D. Brodbeck, L. Howald, J. Frommer, H.-J. Güntherodt, O. Wolter, M. Fujihira, H. Takano and Y. Gotoh: *Thin Solid Films* **220** (1992) 132.
- 2) D. Anselmetti, Ch. Gerber, B. Michel, H.-J. Güntherodt and H. Rohrer: *Rev. Sci. Instrum.* **63** (1992) 2316.
- 3) O. Kolosov and K. Yamanaka: *Jpn. J. Appl. Phys.* **32** (1993) 1095.
- 4) G. Kämpf, H. Krömer and M. Hoffmann: *J. Macromol. Sci. Phys. B* **6** (1972) 167.
- 5) M. Maaloum, D. Ausserre, D. Chatenay and Y. Gallot: *Phys. Rev. Lett.* **70** (1993) 2577.
- 6) H. Y. Nie, T. Shimizu, W. Mizutani, M. Motomatsu and H. Tokumoto: in preparation for publication.
- 7) L. E. Nielsen: *Mechanical Properties of Polymers* (Reinhold, New York, 1967).
- 8) S. Wu: *J. Macromol. Sci.-Rev. Macromol. Chem. C* **10** (1974) 1.
- 9) D. G. Le Grand and G. L. Gaines Jr.: *J. Colloid Interface Sci.* **31** (1969) 162.