Imaging of Dynamic Viscoelastic Properties of a Phase-Separated Polymer Surface by Forced Oscillation Atomic Force Microscopy

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Introduction. Recently, surface molecular motion of polymeric solids has been paid great attention due to its importance in practical application such as permselective membrane, biomaterials, and adhesives. Since molecular chains at the surface of polymeric solids have a larger degree of freedom than those in the bulk, the state of thermal molecular motion of molecular chains at the surface is expected to be different from that in the bulk.[1]

The atomic force microscope (AFM) has become a widely used instrument for the observation of surface topography.[2] AFM profiles the topography of the sample by scanning a probe over the sample surface with a constant force between the surface and probe tip. It has been revealed that AFM can be used for the measurement of static mechanical properties by measuring the response of the sample to an increased or decreased load by the tip.[3] If the sample was deformed sinusoidally, the dynamic viscoelastic behavior at the outermost surface can be evaluated by measuring the cantilever deflection under such a condition.[4] Also, the scanning over the surface in the $X-Y$ direction provides the image of dynamic viscoelastic functions with a nanometer-scale resolution. The purpose of this paper is to present the applicability of two-dimensional imaging of dynamic viscoelastic functions of the phase-separated polymeric surface by utilizing forced oscillation AFM.

Principle and Experimental Setup. When the tip is in a repulsive force region of the force curve, the surface of the specimen might be deformed by the indentation of the tip. The modulation of the vertical sample position leads to the modulation of the force between the tip and sample. This force modulation results in an indentation of the tip against the sample depending on its viscoelastic properties. The phase difference between the modulation signal of the sample position and the modulated response of the tip corresponds to the mechanical loss tangent, $\tan\delta$, of the surface region. Figure 1 shows the experimental setup for the two-dimensional imaging of dynamic viscoelastic functions by utilizing a forced oscillation AFM. The AFM equipment used in this study is SFA300 (Seiko Instruments Industry Co.) with an SPI3700 controller. The sample is mounted on an XYZ piezoscanner with a 1- or 20-μm scan range which has a resonance frequency of 9–15 kHz. A commercially available silicon nitride cantilever with integrated tips (Olympus Co., Ltd., Japan) was used. The cantilever has a spring constant of 0.022 N m^{-1}. The deflection of the cantilever is measured by a position-sensitive four-segment photodiode (PSD) and fed into the feedback loop that controls the height of the sample. The sample position in the z-direction was modulated sinusoidally by applying the sinusoidal voltage generated by the frequency generator (OSC). The modulation frequency was 5 kHz which was below the resonance frequency of the piezoscanner. The z-sensitivity of the piezoscanner is 2.4 nm V^{-1} for the 1-μm scanner and 4.46 nm V^{-1} for the 20-μm scanner. The modulated force was detected by the deflection of the cantilever. The deflection signal obtained through PSD was filtered by a band-pass filter (BPF) in order to reduce the high- and low-frequency noises and fed into a two-phase lock-in amplifier. The reference signal used was the sinusoidal signal from OSC which corresponded to the dynamic strain signal. The output in-phase and out-phase signals were fed into the SPI3700 and displayed simultaneously under a scanning frequency of 1 Hz. The in-phase and out-phase signals correspond to the real and imaginary parts of the dynamic modulus. The measurement of dynamic viscoelasticity was carried out at 293 K in air under a repulsive force of 0.021 nN. Quantitative measurement of the modulus has not been achieved yet because of difficulty in the evaluation of the exact contact area and net applied strain amplitude. Further effort is under way in order to measure dynamic viscoelasticity quantitatively.

The samples used in this study were an immobilized octadecyltrichlorosilane (OTS; $CH_3(CH_2)_{17}SiCl_3$)/[2-(perfluorooctyl)ethyl]trichlorosilane (FOETS; $CF_3(CF_2)_7CH_2CH_2SiCl_3$) mixed monolayer films[5,6] and also polystyrene (PS)/poly(vinyl methyl ether) (PVME) ultrathin blend films.[7,8] The OTS/FOETS mixed monolayer was prepared by the upward drawing technique. The mixture solution of OTS/FOETS (50/50, mol/mol) was spread on the water surface. OTS and FOETS were hydrolyzed on the water surface, and the hydroxyl groups of silanes were polymerized to form a Si–O–Si linkage. Then, the monolayer was transferred onto a silicone wafer and was covalently bonded to Si–OH groups of the silicon wafer surface. The details of the preparation method of OTS/FOETS mixed monolayers will be published elsewhere.[6] The PS/PVME (50/50, w/w) ultrathin blend film was dip-coated on SiO-coated substratum from a 0.1 wt % toluene solution. The film thickness was ca. 25 nm. It was revealed that the PS/PVME ultrathin blend film showed phase-separated PVME domains with a diameter of ca. 200 nm. The details for the preparation of the ultrathin blend film will be reported elsewhere.[7,8]

Results and Discussion. It was revealed that the immobilized organosilane monolayer was stable compared with the monolayer of conventional amphiphilic molecules because of the presence of covalent bond formation between the substrate and monolayer.[6] Then, the organosilane monolayer is suitable for the surface viscoelastic measurement, since mechanical stability is required for the surface viscoelastic measurement. The cyclic compressive strain must be applied in the repulsive force region for surface viscoelastic measurement. In the case of the mechanically unstable stearic acid monolayer, the monolayer was completely swept out during first scanning and the image of viscoelasticity could not be obtained. Figure 2a shows the AFM image for the OTS/FOETS (50/50, mol/mol) mixed monolayer. The OTS/FOETS mixed monolayer was in a phase-separated state, and circular flat-topped OTS domains of ca. 1-μm diameter were surrounded by a flat FOETS

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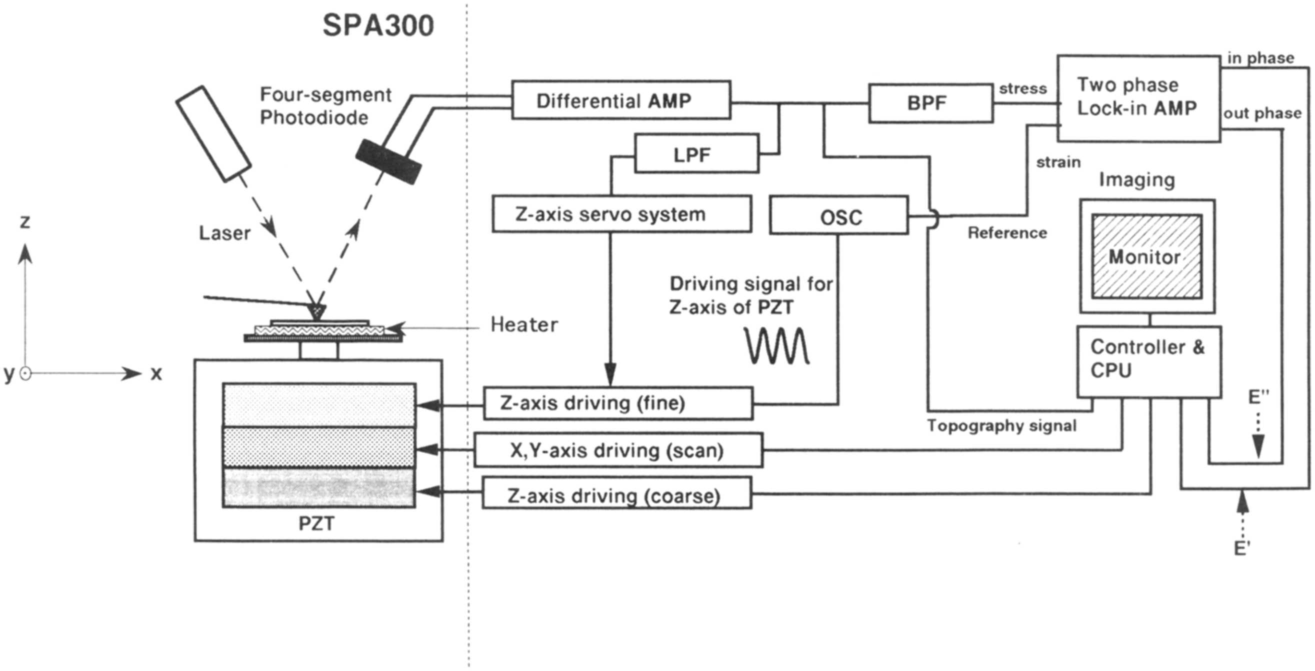
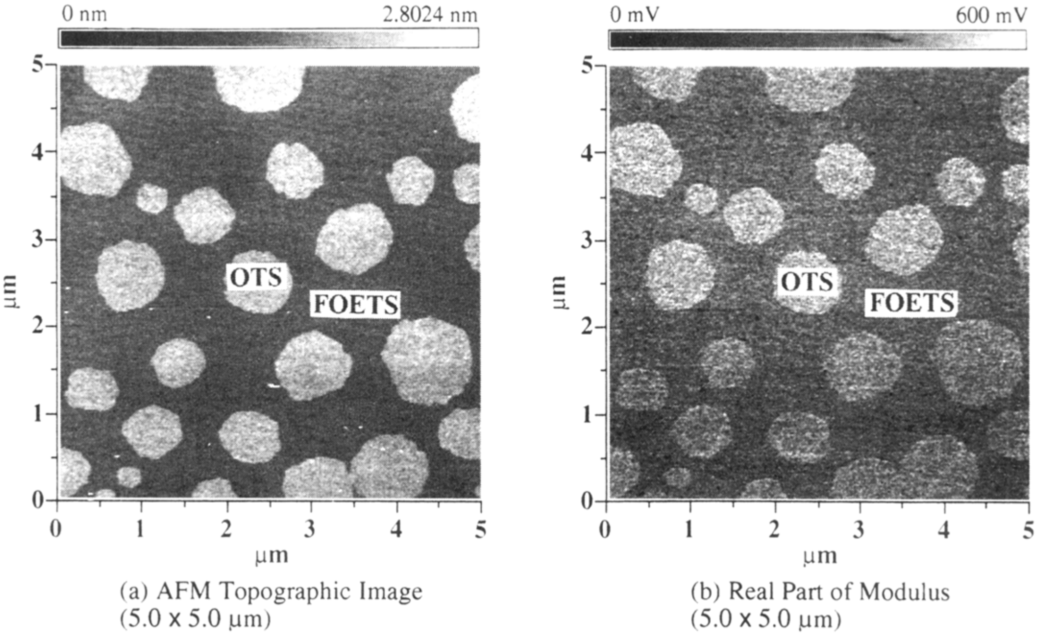


Figure 1. Schematics of imaging of dynamic viscoelasticity by utilizing forced oscillation atomic force microscopy.



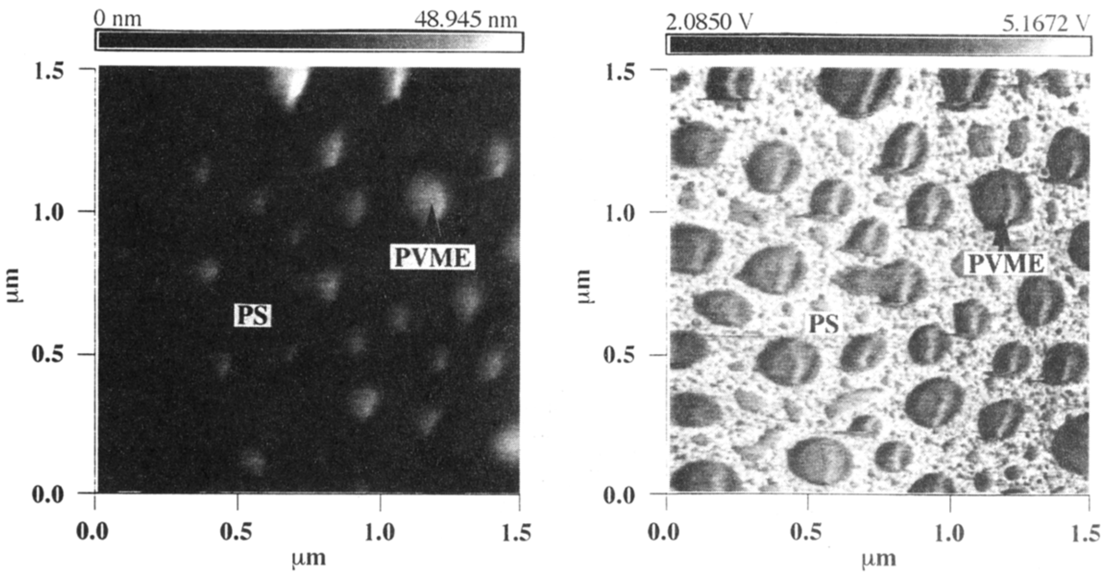
(a) AFM Topographic Image
(5.0 x 5.0 μm)

(b) Real Part of Modulus
(5.0 x 5.0 μm)

Figure 2. AFM topographic image (a) and image of the real part of the modulus (b) of the immobilized OTS/FOETS (50/50, mol/mol) mixed monolayer at 293 K with a modulation frequency of 5 kHz and a dynamic *z*-axis modulation of 0.89 nm.

matrix. The difference in height between OTS and FOETS was ca. 1.3 nm, which corresponded to the difference in molecular length of these molecules.[6] The OTS formed circular domains even if the molar percent of OTS was 75%. An electron diffraction (ED) pattern revealed that the OTS monolayer was in a crystalline state, while the FOETS monolayer was in an amorphous state at 293 K. The ED study indicates that crystallization of OTS molecules is an important origin for phase separation. Figure 2b shows the image of the real part of the dynamic modulus for the OTS/FOETS (50/50) monolayer. The dynamic modulation along the *z*-axis was 0.89 nm. The bright part corresponds to the higher modulus region. Since the OTS region is in a crystalline state at 293 K, it is reasonable that the OTS has a higher modulus than that of the amorphous FOETS region.

The PS/PVME ultrathin blend film prepared from a toluene solution showed a phase-separated structure when the thickness of the film was less than twice as large as the radius of gyration of the components. The presence of the PS and PVME phases on the surface was confirmed by the X-ray photoelectron spectroscopic measurements of the blend film surface. Figure 3a shows the AFM image of a PS/PVME (50/50, w/w) ultrathin blend film. The PS/PVME ultrathin blend film was in a phase-separated state, and circular droplet-like PVME domains of ca. 200-nm diameter and 10–25-nm height were present on the flat PS. The details of the formation mechanism of the phase-separated structure will be published elsewhere.[7] Since the bulk glass transition temperature of PS is higher than 293 K, whereas that of PVME is less than 293 K, it is expected that the glassy PS and the rubbery PVME



(a) AFM Topographic Image
(5.0 x 5.0 µm)

(b) Real Part of Modulus
(5.0 x 5.0 µm)

Figure 3. AFM topographic image (a) and image of the real part of the modulus (b) for the PS/PVME (50/50, w/w) ultrathin blend film at 293 K with a modulation frequency of 5 kHz and a dynamic *z*-axis modulation of 1.2 nm.

phases can be distinguished apparently on the basis of the surface dynamic viscoelastic measurement. Figure 3b shows the two-dimensional image of the real part of the modulus for the PS/PVME ultrathin blend film at 293 K under a modulation frequency of 5 kHz and a dynamic *z*-axis modulation of 1.2 nm. Since parts a and b of Figure 3 were imaged simultaneously, it seems reasonable to conclude that the PS matrix and the PVME droplet domains showed bright and dark regions, respectively. The magnitude of mechanical tan δ for PVME calculated from the magnitudes of the real and imaginary parts of the modulus was ca. 0.25, whereas that of PS was ca. 0.1. The magnitude of tan δ for PVME is quite reasonable because PVME is in a rubbery state at room temperature. The magnitude of tan δ for bulk PS was ca. 0.01 at 11 Hz. The magnitude of tan δ for the PS surface at 293 K is larger than that for bulk. These results indicate that PS chains at the PS–air interface should have a larger molecular mobility compared with that in the bulk, due to their larger free volume fraction induced from the asymmetric environment of the PS at the PS–air interface. A similar increase in the molecular mobility at the surface region has been observed for the PS–poly(methyl methacrylate) diblock copolymer.[9]

It can be concluded from the results mentioned above that the two-dimensional mapping of dynamic viscoelastic functions for the polymeric solid surface was successfully obtained by forced oscillation AFM. The two-dimensional resolution of the viscoelastic image is less than 100 nm, which is better than that of any other two-dimensional spectroscopic methods, such as secondary ion mass spectroscopy (SIMS) and Auger electron spectroscopy (AES). This method can be carried out in an air or water environment without any pretreatment. More quantitative analysis of surface dynamic viscoelasticity will be published in the future.

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