

Chain and Microphase-separated Structures of Ultrathin Polyurethane Films

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Abstract. Measurements are presented how chain and microphase-separated structures of ultrathin polyurethane (PU) films are controlled by the thickness. The film thickness is varied by a solution concentration for spin coating. The systems are PUs prepared from commercial raw materials. Fourier-transform infrared spectroscopic measurement revealed that the degree of hydrogen bonding among hard segment chains decreased and increased with decreasing film thickness for strong and weak microphase separation systems, respectively. The microphase-separated structure, which is formed from hard segment domains and a surrounding soft segment matrix, were observed by atomic force microscopy. The size of hard segment domains decreased with decreasing film thickness, and possibility of specific orientation of the hard segment chains was exhibited for both systems. These results are due to decreasing space for the formation of the microphase-separated structure.

1. Introduction

Block copolymers are quite attractive materials to create microelectronic devices, data storage system, membranes, etc, because they form a highly ordered fine structure spontaneously.[1,2] Since different block sequence is chemically connected each other, each component can form not large domains but a nanometer sized structure. Thus, the size of the microphase-separated structure is controllable by change in the each block length. The structure itself as well as the size of microphase-separated domains can also be controlled by the ratio of block sequence, incorporation of another component (triblock copolymer) and so on. To employ a block copolymer for an application mentioned above, the films should be thin enough. Due to surface and interfacial effects, the thickness of the film can cause a different morphology than the equilibrium bulk morphology to have the lowest free energy, resulting in a changing morphology as the film thickness changes.[3]

Polyurethane (PU) can be classified into a multi-block polymer, which possesses strong polar groups in the molecular chains.[4] It is well-known that the PUs consist of the hard and soft segments, and exhibit a microphase-separated structure. In terms of thin film preparation, it is expected that the strong polar groups will help to form a stable film even at a molecular level and strongly affect the microstructure of the polymer films. Also, the multiblock structure will

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restrict the segregation of lower surface free energy components at the film surface, resulting in the formation of the lateral phase separation. Furthermore, the strong polar groups of urethane groups are expected to show a new property, for example, ferroelectric devices.

In this paper, we investigated the effect of film thickness on the chain and microphase-separated structures of ultrathin PU films.

2. Experiments

2.1. Sample preparation

Polyurethanes were synthesized from poly(oxytetramethylene) glycol ($M_n=2000$), 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butandiol (BD) by a prepolymer method. This PU is strongly microphase-separated. The hard segment contents were 34 and 45 wt%. One more PU with strong microphase separation were synthesized from poly(oxypropylene) glycol (PPG: $M_n=2000$), MDI and a chain extender with a controlled chain length (OU5). Another PU with weak microphase separation was synthesized from PPG, 2,4-tolyrene diisocyanate (TDI) and BD by a prepolymer method. The hard segment content was 25 wt%. Thin PU films were prepared by spin coating. The concentration of a tetrahydrofuran solution was changed to control the film thickness. Detailed descriptions of the experimental procedure are described in earlier publication from this research group.[5]

2.2. Chain and microphase-separated structures

Fourier-transform infrared (FT-IR) spectra were collected using a Biorad FTS-3000 equipped with a mercury-cadmium-telluride detector to investigate the molecular orientation of the hard segment chains in the PU films. For the transmission FT-IR measurement, a double side polished silicon wafer was employed. p-Polarized infrared beam was used and incident angles were 10 and 74°.

A microphase-separated structure of the PU films was observed using a Seiko Instrument atomic force microscopy (AFM). Since the PU includes the rubbery soft segments at room temperature, we took an intermittent mode for the observation. Both topography and phase images were collected simultaneously. To avoid the destruction of the sample surface, the images were acquired under ambient condition using light to moderate tapping, $r=0.90-0.80$, where $r=(\text{set point amplitude}/\text{free amplitude of oscillation})$. Cantilevers employed were SI-DF-20 with spring constant of 14 N m^{-1} and resonance frequency of 130 kHz.

3. Results and discussion

Figure 1 shows the FT-IR spectra for the thin PU films with the thick and thin PTMG-MDI-BD PU films

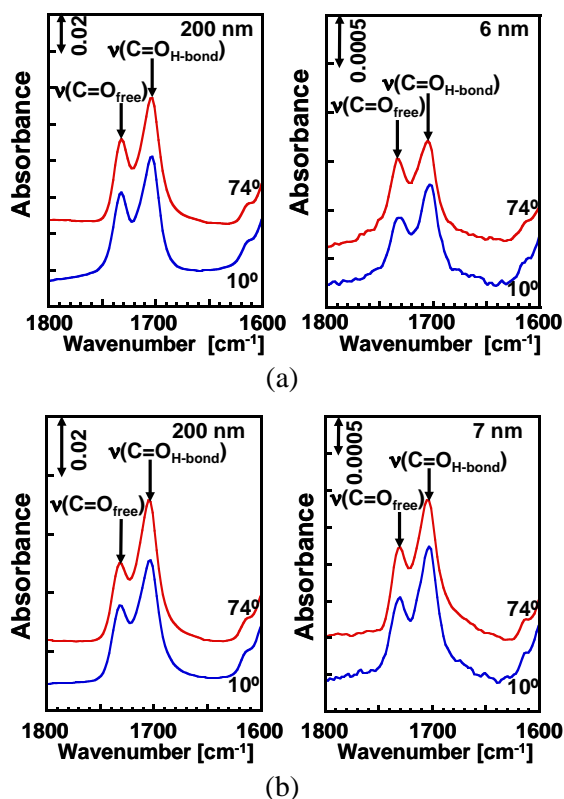


Figure 1. The FT-IR spectra for the thin PU films with (a) 34 and (b) 45 wt% of hard segment contents at incident angles of 10 and 74°.

with hard segment contents of (a) 34 and (b) 45 wt% measured at incident angles of 10 and 74°. In the spectra shown here, one can see two peaks at 1704 and 1730 cm^{-1} . These peaks can be assigned to the hydrogen bonded carbonyl stretching band ($\nu(\text{C}=\text{O}_{\text{H-bond}})$) and free one ($\nu(\text{C}=\text{O}_{\text{free}})$), respectively. The intensity ratio of $\nu(\text{C}=\text{O}_{\text{free}})$ peak, to $\nu(\text{C}=\text{O}_{\text{H-bond}})$ one ($I\nu(\text{C}=\text{O}_{\text{free}})/I\nu(\text{C}=\text{O}_{\text{H-bond}})$) of the PTMG-MDI-BD-45 film are smaller than for the PTMG-MDI-BD-34 one. This is because microphase separation was progressed as the hard segment content increases. Figure 2 (a) shows thickness dependence of $I\nu(\text{C}=\text{O}_{\text{free}})/I\nu(\text{C}=\text{O}_{\text{H-bond}})$ for the PTMG-MDI-BD films with hard segment contents (HSCs) of 20, 34 and 45 wt%. $I\nu(\text{C}=\text{O}_{\text{free}})/I\nu(\text{C}=\text{O}_{\text{H-bond}})$ for the PTMG-MDI-BD-34 and -45 films increased with decreasing film thickness at around 10 nm thickness. This roughly indicates the chain structure below 10 nm thickness is quite different from that of thicker films. Discussion on a chain structure in detail will be given later. On the other hand, the magnitude of $I\nu(\text{C}=\text{O}_{\text{free}})/I\nu(\text{C}=\text{O}_{\text{H-bond}})$ for the PTMG-MDI-BD-20 film exhibited the quite large magnitude at the thicker region, indicating that the hard segment chains are dispersed into a soft segment phase. This is due simply to a phase mixing trend of the sample. And the magnitude of $I\nu(\text{C}=\text{O}_{\text{free}})/I\nu(\text{C}=\text{O}_{\text{H-bond}})$ decreased with decreasing film thickness. In other words, decreasing film thickness causes a microphase-separated trend. As the variety of $I\nu(\text{C}=\text{O}_{\text{free}})/I\nu(\text{C}=\text{O}_{\text{H-bond}})$ with the film thickness exhibited opposite trend depending on the degree of microphase separation, another two samples, which are strongly microphase-separated and microphase-mixing systems, were investigated.

Figure 2 (b) shows the thickness dependence of $I\nu(\text{C}=\text{O}_{\text{free}})/I\nu(\text{C}=\text{O}_{\text{H-bond}})$ for the PPG-MDI-OU5 film with a HSC of 25 wt% and PPG-TDI-BD one with a HSC of 40 wt%. For the PPG-MDI-OU5 film, which is a microphase-separated system, trend was the same with that for the PTMG-MDI-BD-34 and -45 films. On the other hand, for the PPG-TDI-BD film, which is a microphase mixing system, the trend was the same with the PTMG-MDI-BD-20 film. Furthermore, the peak position of $\nu(\text{C}=\text{O}_{\text{H-bond}})$ for the PPG-MDI-OU5-25 film was shifted to lower wavenumber region with decreasing film thickness.(not shown) Therefore, it seems reasonable to consider that strong constrain is induced in the ultrathin state, as the hard segment chains with strong aggregation force possess a preferable domain size in bulk.

Measurement at different incident angle in FT-IR measurement gives us important information on molecular orientation. For instance, one can estimate the direction of $\nu(\text{C}=\text{O})$ in the film. It is well-known that the MDI-BD-based hard segment chains crystallize in the triclinic structure and form a plane formed with a zigzag chain.[6] The results that the magnitude of $I\nu(\text{C}=\text{O}_{\text{free}})/I\nu(\text{C}=\text{O}_{\text{H-bond}})$ measured at 74° is smaller than at 10° imply that a plane formed with a zigzag chain, in which the hard segment chains form this in the crystal, orient to the surface normal. This is the case for the PPG-MDI-OU5-25 films. However, PTMG-MDI-

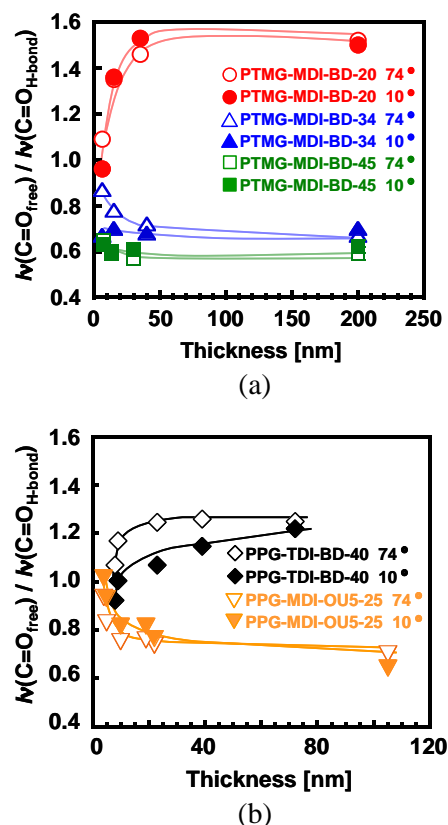


Figure 2. Thickness dependence of intensity ratio of $\nu(\text{C}=\text{O}_{\text{free}})$ peak, to $\nu(\text{C}=\text{O}_{\text{H-bond}})$ one for (a) the PTMG-MDI-BD films with hard segment contents (HSCs) of 20, 34 and 45 wt% and (b) the PPG-MDI-OU5 film with a HSC of 25 wt% and PPG-TDI-BD film with a HSC of 40 wt%.

BD 34 and -45 did showed opposite trend. Currently, we do not have concrete interpretation for this result. We will discuss this elsewhere.

Figure 3 shows the AFM phase images of the PTMG-MDI-BD-34 films with various film thicknesses and the PPG-TDI-BD-40 one. No characteristic feature was detected for the PPG-TDI-BD-40 film. The brighter part corresponds to the larger phase lag region. It is quite hard to interpret the phase images because these images are formed by some factors, for example, surface elasticity, adhesion force and so on. Concerning the occupied area, it seems reasonable to consider that the darker domains and a brighter matrix correspond to the hard and soft segments, respectively. As one can see the size of the microphase-separated structure seems to be different depending on the film thickness, that is, the size of domains decreased with decreasing film thickness. For the PTMG-MDI-BD-34 films, the size of microphase-separated domains was depressed at the thickness of 20 or 6 nm. The interdomain spacings of the PTMG-MDI-BD-34 films were estimated to be 27 and 21 nm for 200 and 6 nm thicknesses, respectively, by fast Fourier transform (FFT) images. Same things happened for the PTMG-MDI-BD-45 films. Furthermore, grazing incident small-angle scattering measurement gave consistent results.[5] Therefore, we can reasonable to conclude that the microphase-separated structure can be formed even on the condition that the thickness is much smaller than the interdomain spacing for bulk, and the interdomain spacing decreases at the ultrathin state.

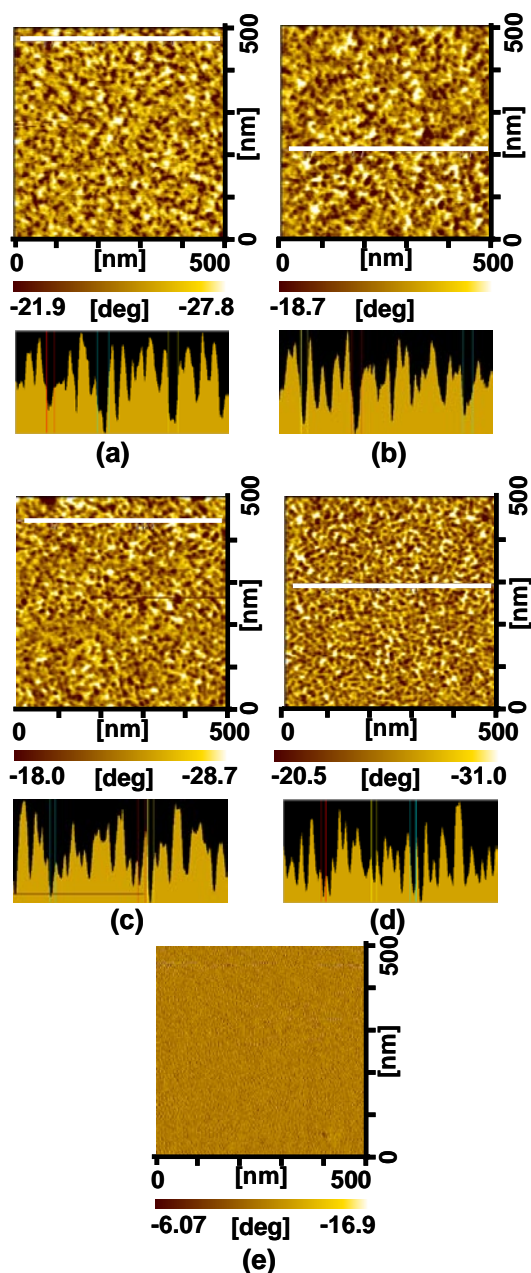


Figure 3. AFM phase images and profiles of the PTMG-MDI-BD-34 films with various film thicknesses. (a) 200, (b) 35, (c) 14 and (d) 6 nm. (e) AFM phase image of the PPG-TDI-BD 40 film.

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