

Microphase-separated Structure of Ultrathin Polyurethane Films

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Abstract

We firstly observed the effect of film thickness on a microphase-separated structure of polyurethane at the ultrathin states. The interdomain spacing of domains decreased with decreasing film thickness due simply to the reduction of the space for domains.

Introduction

The versatile properties of polyurethanes are generally attributed to the formation of a microphase-separated structure that arises due to incompatibility of the hard segment and hard segment sequences. Surface coating, elastomers, foams and biomaterials are given as applications of polyurethanes. These all performances are deeply related to the microphase-separated structure. In this study, we investigated the microphase-separated structure of polyurethane in the ultrathin state.

Experimental

Polyurethanes were synthesized from poly(oxytetramethylene) glycol ($M_n=2,000$), 4,4'-diphenylmethane diisocyanate and 1,4-butanediol by a prepolymer method. The hard segment content was 34 wt%. Polyurethane thin films were prepared by spin coating. The concentration of a tetrahydrofuran solution was changed to control the film thickness.

Results & Discussion

The interdomain spacing of the microphase-separated structure for a bulk polyurethane sample was ca. 25 nm by small-angle X-ray scattering. In the infrared spectra, the hydrogen bonded and free carbonyl stretching bands were observed. These two carbonyl stretching bands are closely related to the state of microphase separation. The intensity of the hydrogen bonded carbonyl stretching band was twice as large as that of the free one. Since the peak intensity ratio of these two bands did not show strong thickness dependence in the range 6 - 200 nm, it seems that the hard segment chains formed domains even at the ultrathin state. In other word, the

microphase separation exists at the ultrathin state. Figure 1 shows AFM phase images of the polyurethane films with thickness of (a) 200 and (b) 7 nm. One can observe the microphase-separated structure, which consists of hard segment domains (darker parts) and a soft segment matrix (brighter parts). The interdomain spacing exhibited constant values for thicker films, in contrast, that decreased below 10 nm thickness. The grazing incident small-angle scattering measurement also showed same trend. Therefore, we can reasonable to conclude that the microphase-separated structure can be formed on the condition that the thickness is smaller than the interdomain spacing for bulk, and the interdomain spacing decreases at the ultrathin state. This is simply related to the decreasing space of the crystallization of the hard segment domains in the ultrathin films.

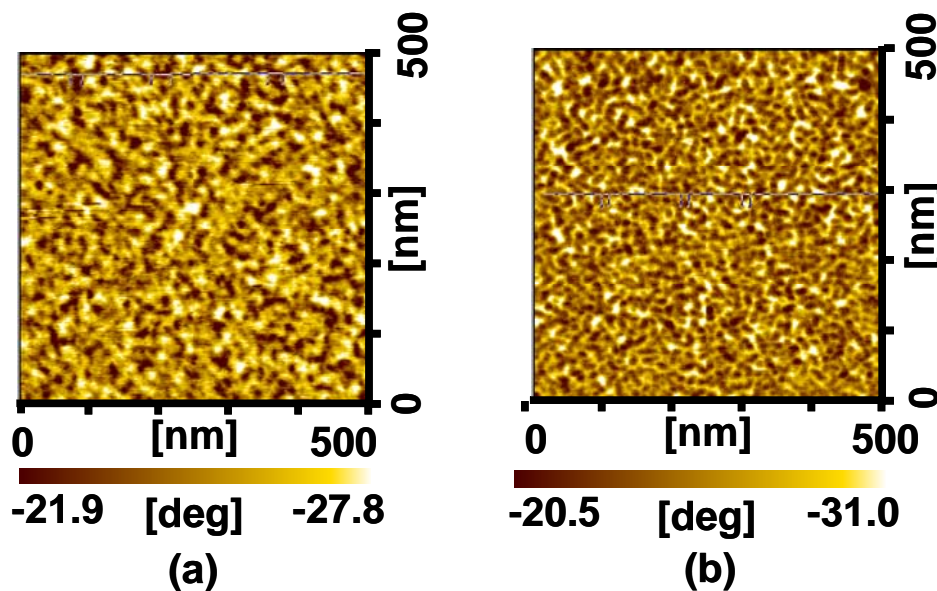


Figure 1. AFM phase images of polyurethane films with thickness of (a) 200 and (b) 6 nm.

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References

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