

Structural and Thermodynamic Studies on Polymer and Organic Microcrystals
Confined by Interface and Surface

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1 Introduction

Organic and polymeric materials are widely used in the various fields from the electronics such as organic EL to the automobiles, because of those light weight and flexibility, which induce easy designed to fix with other materials and the purpose of products. Polymeric materials are normally used as the complex systems with other polymers, organic and inorganic materials as blends and composites. For the complex material systems, the interface between materials and the air surface have the important role against the structure and the physical properties of system, especially with the decrease of materials. Generally the air surface induces the molecular motion and the interface influences the molecular mobility depending on the interaction between molecules in separated materials.

In this thesis, the effect of surface and interface on the morphology and the phase transitions of polymer thin film and the organic nano-crystals. The thesis consisted of 7 chapters, including the introduction (Chapter 1) and the conclusion (Chapter 7). The other chapters described the establish of evaluation methods for thin films (Chapter 2), the phase transition and morphology of polymer thin film (Chapter 3), the phase transition of nano-crystal of primary alcohols (Chapter 4), the structural and morphological analysis of alcohol nano-crystals (Chapter 5) and the application of confined space consisted of surface and interface (Chapter 6).

2 Establishment of the method to evaluate thin films (Chapter 2)

The methods to evaluate the phase transition and the morphology of thin sample or very small amount of samples were established. The sensitivity of DSC (Differential Scanning Calorimeter) was improved by the multiple thermocouples system. The stability of baseline was improved by optimizing the thermal flow path and by the barrier for noise reduction. The target sample of the high sensitive DSC realizes to measure sample with micro-gram mass. The phase transition detected by the high sensitive DSC can be discussed with the structure in nanometer or micrometer scale observed by SPM (Scanning Probe Microscope). The SPM's trace ability against the sample surface was improved by adapting new scanning method, SIS mode. Addition to the feedback control system of the tapping mode, the new

control system to evaluate the actual sample surface, the cantilever was escaped from the sample surface to normal direction after the observation and was moved to the next sampling position then approached to the sample surface to evaluate the interaction. The control system realized to observe molecular image of sample surface.

3 Phase transitions and crystal structures of polymer thin film (Chapter 3)

The effect of thickness of poly(ethyleneoxide) thin film on the phase transition and the structure was revealed. The morphology and thickness of crystalline lamella differed between the solution grown crystal (SGC) and the crystal cooled from the molten state (SCC). Stacked crystalline lamellas, the edge-on and flat-on types of crystals were observed in SGC. On the other hand all crystals of SCC were flat-on type and the thickness of crystalline lamella was uniform. The crystal structure caused the difference of the melting peaks in DSC heating curves of SGC and SCC. The melting temperature shifted lower temperature side according to the thickness of crystalline lamella or small Gibbs energy. The melting temperature depression is explained by Thomson-Gibbs equation for bulk polymers. The thicknesses of the crystalline lamellas calculated by melting temperature depression were corresponded to the thicknesses measured by SPM. These results suggested that the amorphous layers existed in the air surface and the substrate interface. Moreover the substrate interface prevented the crystallization as the thickness of the thin film become thinner. It was suggested that the nucleation occurred however the crystal growth was prevented by the morphology observation by SPM and analyzing the crystallization dynamics by DSC.

4 Phase transition of low molecular organic compound thin film (Chapter 4)

The phase transition and structure of solution grown crystal, SGC and slow cooled crystal from the molten state, SCC of *n*-alkyl alcohol thin film were investigated to evaluate the influences of air surface and substrate interface to the phase transition; the solid-state transition, the melting and the crystallization, and the morphology. The crystal c-axis aligned normal to the substrate surface for both SGC and SCC.

It is suggested that the metastable α -phase existed at the surface of SGC of even number of alkyl carbon samples (C18, C16) and the metastable α -phase melted at lower temperature than bulk sample. The solid-state of SCC with even number of carbon observed clearly because the influence of the surface to the solid-state was larger than that to the melting. Both even and odd number of carbon samples classified 3 groups by the film thickness dependence of the melting and solid-state transition temperature depression, and the crystal morphologies (the flat polygonal plate, the flat round shape and the granular).

Though the melting point depression of polymer thin film was explained by Thomson-Gibbs equation, the melting temperature depression of *n*-alkyl alcohol was too small to explain by the effect of surface. The extensive Thomson-Gibbs equation, considered the melting point depression by the air surface and the repression of the melting point depression at the substrate interface, was proposed for *n*-alkyl alcohol nano-crystals.

On cooling process, the substrate interface prevented the crystallization and the crystallizing exothermic peak scarcely observed with thinner the thickness. The crystals with even number of carbon didn't transfer to low temperature stable phase due to the surface and the low temperature stable phase (γ phase) and high temperature stable phase (α phase) coexisted. It is necessary to consider the influences of both the active molecular motion in the surface and the repressing the molecular diffusion in the interface for *n*-alkyl alcohol nano-crystals.

5 Structural analysis of low molecular organic compound (Chapter 5)

The effects of the interface and surface to the crystal morphologies of *n*-alkyl alcohol nano-crystals were revealed by SPM observation. The SCC formed the flat plate and polygonal shaped crystals looked like the single crystal, due to the influence of the interface as the sample mass was smaller. The ratio of the interface and the surface become larger significantly with sample mass decrease, and the phase transition and the morphology were influenced. The critical thicknesses influenced by the substrate interface were 60 layers in unit of the bimolecular lamella for both even and odd number of carbon samples. The metastable α -phase at the surface was expected by observing the phase transition of even carbon number samples. The surface molecules were active, the surface of crystals was difficult to observe molecular image by SPM observation. The damaged surface layer of crystal by thermally and mechanically repeated by the rearrangement of molecules, these phenomena also indicated the active molecules in the surface layer.

After stripping the active surface layer by the SPM cantilever, the molecular images of more stable crystal plane was obtained. Molecular image of methyl end group of alkyl alcohol was observed clearly.

6 Application of confined space consisted of surface and interface (Chapter 6)

It is expected that the materials whose function is expressed at high efficiency by using the high energy phase on surface as the reaction field are developed.

The gold nano particles were generated by using micro phase separation of the amphiphilic block copolymer as nano reactor. The gold doped into the cylinders selectively was reduced and the gold

particles were formed at near the surface.

As other application, the supported ability of Prussian blue was improved by using high energy area of wool surface as reaction field. The Prussian blue nano particles were compounded into the cuticle layer.

7 Conclusions

The evaluation method for thin film by high sensitive DSC and SPM was established and it was applied to the polymer thin film and organic compound nano-crystals. The effects of the air surface and the substrate interface to the phase transitions and the morphology were revealed. The surface enhanced the molecular motion and the interface disturbed the molecular diffusion. The obtained results are concerned to understand the molecular dynamics and the various properties of thin film and composites. These are expected to contribute to develop the minimized material