Phase Transition Behavior of Organic Thin Film Observed High Sensitive DSC
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Introduction
With decreasing the size of material, the structure and the molecular mobility of materials are influenced by the material-gas interface (surface) and the material-substrate interface (interface) due to the decrease of surface/volume ratio. The glass transition of polymer-gas surface is lower than that of bulk polymer, and the molecular mobility of polymer-solid substrate interface is expected to be lower than that in bulk polymer due to the attractive interaction between polymer and substrate surface. In this study, the phase transitions of organic thin films with thickness less than 1 μm were investigated as a function of thickness.

Experiment
Sample
• Poly(ethylene oxide) PEO : CH₃(OCH₂CH₂)ₘCH₃
  m = 114, 272, and 454, mono-dispersed
Preparations
• Toluene solution of PEO, 0.1 to 1.0 wt%
• Solvent casting, 5 to 10 μl on aluminum open pan

Experiments
• DSC : X-DSC7000 (SII NanoTechnology)
  Temperature : 290 → 350 → 350 K
  Scanning Rate : 5 K/min
• AFM : E-sweep (SII NanoTechnology)
  Dynamic force mode
  Cantilever
  Spring constant : 40 N/m
  Resonance frequency : 310 kHz

Results

DSC heating curves of PEO272
1st heating
2nd heating
1st heating
2nd heating

Fig.1 DSC curves of 1st heating for PEO272
Fig.2 DSC curves of 2nd heating for PEO272

Melting temperature of Micro phase
PEO114
PEO272
PEO454

Fig.3 Relations between melting temperature and the thickness in 1st Heating
Fig.4 Relations between melting temperature and the thickness in 2nd Heating

Surface structure (AFM topography and line profile of PEO272)

Cast film
1st heating
Cooled film
2nd heating

Fig.5 DSC curves of cooling for PEO272

Crystallization process of Micro phase
Nucleation process

Crystal growth process

Conclusion
• Melting temperature decreased with decreasing thickness. In the thin film with 1 μm thickness, two types of crystal existed.
• Crystallization process delayed by the interaction between PEO and the substrate surface.
• The effect of molecular weight on the retardation of nucleation process was observed.