



**Friday,  
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**2:00 pm**

**Room 8335  
Chemistry Building**

## ***Epitaxial Order-Order Phase Transition of Diblock Copolymers***

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Block copolymers undergo order-order phase transitions which exhibit an epitaxial relationship between the morphology of two phases. In most of the previous experimental studies, X-ray or neutron scattering methods were used together with transmission electron microscopy (TEM) for the structural analysis. In so doing, macroscopic alignment of the microphase domains were often tried to elucidate the structure more clearly. We used thin film on Si wafer substrate, in which the densest plane of the minor phase orients parallel to the substrate plane near perfectly after thermal annealing without applying any external field.<sup>1</sup> Internal structure of the thin films was investigated by grazing incidence small-angle X-ray scattering (GISAXS), TEM and electron tomography (ET) along the phase transition path. GISAXS has been used efficiently to investigate the internal structure of block copolymer thin film. ET is a powerful tool allowing us to observe the 3D-structure directly. One of the extensively studied examples is the phase transition from or to double gyroid (DG) structure, which is more intriguing than the others due to the structural complexity of DG phase. By virtue of good domain orientation in thin film and the powerful methods for the structural investigation, we were able to observe the coexisting structure of DG and hexagonally oriented cylinder (HEX) phase unambiguously.<sup>2</sup> There is a general consensus that the phase transition between HEX and DG has an epitaxial relationship between  $\{121\}_{\text{DG}}$  plane and  $\{10\}_{\text{HEX}}$  plane, and between  $\langle 111 \rangle_{\text{DG}}$  direction and the HEX cylinder axis, respectively. But we found that another epitaxial transition exists between  $\langle 220 \rangle_{\text{DG}}$  direction and the HEX cylinder axis. Another epitaxial transition investigated in detail is the DG and hexagonally perforated layer (HPL) structure. As expected,  $\{003\}_{\text{HPL}}$  and  $\{121\}_{\text{DG}}$  are in epitaxial relationship. At the phase boundary  $\{220\}_{\text{DG}}$  and  $\{110\}_{\text{HPL}}$  are in contact each other. It was interesting to note that the alternate HPL layer are connected to each single gyroid at the phase boundary. The lattice dimension of DG and HPL does not match each other well. It may be a reason why  $\text{DG} \rightarrow \text{HPL}$  OOT is hardly observed. The third epitaxial transition studied is the  $\text{HPL} \leftrightarrow \text{HEX}$  transition, which is not observed in bulk. In thin film, the stability of HPL phase is enhanced and the transition is observed bypassing DG phase.<sup>3</sup> As expected,  $\{003\}_{\text{HPL}}$  and  $\{10\}_{\text{HEX}}$  are in epitaxial relation and the HEX cylinder axis is parallel to  $\langle 110 \rangle_{\text{HPL}}$ . It is interesting to note that  $\{003\}_{\text{HPL}}$  and  $\{10\}_{\text{HEX}}$  are always parallel to the film plane for the transition of  $\text{HPL} \rightarrow \text{HEX}$  while HPL layers are oriented along  $3 \times \{10\}_{\text{HEX}}$  for the transition of  $\text{HEX} \rightarrow \text{HPL}$ .