

# Division of Multidisciplinary Chemistry – Polymer Materials Science –

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## Scope of Research

The structure and molecular motion of polymer substances are studied using mainly scattering methods such as neutron, X-ray and light with intension of solving fundamentally important problems in polymer science. The main projects are the mechanism of structural development in crystalline polymers from glassy or molten state to spherulites, the dynamics in disordered polymer materials including low-energy excitation, glass transition and local segmental motions; formation processes and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions.

### KEYWORDS

Polymer Physics  
Polymer Properties  
Scattering  
Neutron Scattering  
Synchrotron X-ray Scattering

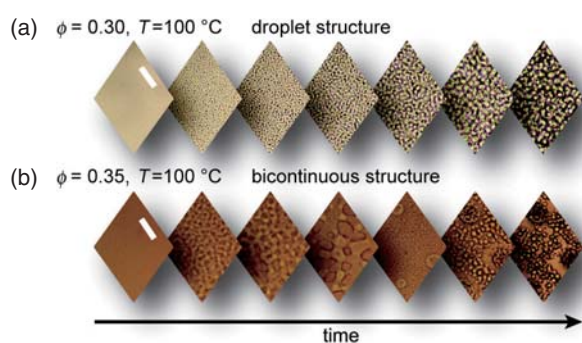


## Selected Publications

Kanaya, T.; Inoue, R.; Saito, M.; Seto, M.; Yoda, Y., Relaxation Transition in Glass-forming Polybutadiene as Revealed by Nuclear Resonance X-ray Scattering, *J. Chem. Phys.*, **140**, [144906-1]-[144906-5] (2014).  
Tanaka, K.; Nishida K.; Gabrys, B. J.; Lawrence, M. J.; Kanaya T., Critical Dissolution Ionic Strength of Aqueous Solution of Chitosan Hydrochloride Salt, *Sen'i Gakkaishi (J. Soc. Fiber Sci. Technol., Jpn.)*, **70**, 225-231 (2014).  
Inoue, R.; Kanaya, T.; Hu, Y.; Masuda, T.; Nishida, K.; Yamamuro, O., Relationship between the Local Dynamics and Gas Permeability of Polyacetylenes Containing Polymethylated Indan/tetrahydronaphthalene Moieties, *Polymer*, **55**, 182-186 (2014).  
Hara, A.; Inoue, R.; Takahashi, N.; Nishida, K.; Kanaya, T., Trajectory of Critical Point in Polymerization-Induced Phase Separation of Epoxy/Oligoethylene Glycol Solutions, *Macromolecules*, **47**, 4453-4459 (2014).  
Wernecke, J.; Okuda, H.; Ogawa, H.; Siewer, F.; Krumrey, M., Depth-Dependent Structural Changes in PS-b-P2VP Thin Films Induced by Annealing, *Macromolecules*, **47**, 5719-5727 (2014).

## Trajectory of Critical Point in Polymerization-induced Phase Separation of Epoxy/oligoethylene Glycol Solutions

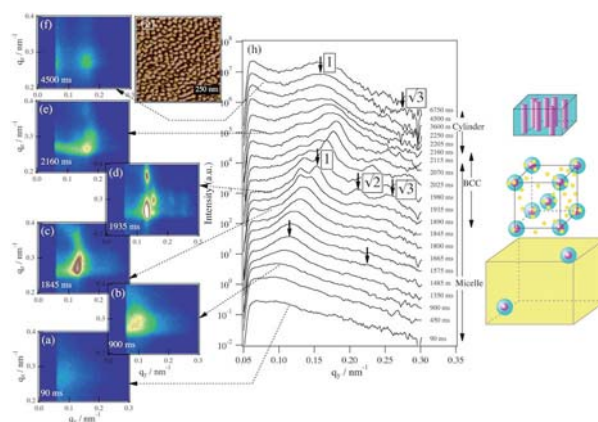
In this work, we have studied kinetics of polymerization-induced phase separation of epoxy solution in oligoethylene glycol using light scattering (LS) and optical microscope (OM). It was found that special double droplet morphology was observed only in a very narrow range of epoxy fraction ( $\phi \sim 0.35$ ), which depended on the reaction temperature. In the narrow range the phase separation rate was very fast and the bicontinuous structure which was typical in spinodal decomposition-type phase separation was observed only in the very early stage (see Figure 1), suggesting that the solutions in the narrow fraction range entered directly the spinodal decomposition region without crossing the bimodal region. It is therefore considered that the temperature dependent narrow fraction range corresponds to the trajectory of the critical point of the phase separation curve in the fraction-temperature diagram.



**Figure 1.** Time evolutions of OM images for  $\phi = 0.30$  (a) and  $0.35$  (b) after the phase separation starts at  $T_r = 100$  °C.

## Spin-coating Process of PS-*b*-P2VP through the *in-situ* Fast GISAXS Measurements

Block copolymer thin films has been recently noticed considerable attention because the self-assembly of the periodic nanoscale has potential in highly density data storage, solar cells and nanostructured membranes. In order to optimize the physical properties by controlling the long-range order and the orientation of the microdomains, various processes have been accordingly utilized in recent years. It is well known that the structure of microdomains as well as the physical properties of thin films is decisively affected by the interactions from the surface and interface. Besides the interactions, the solvent selectivity, film thickness and the solvent evaporation rate also affect the structural development of the microdomains. In this work, ordering transition mechanism of nanostructures in spin-coated poly(styrene-*b*-2vinylpyridine) (PS-*b*-P2VP) films has been investigated. In contrast to the lamellar structure observed in the bulk as a thermodynamically stable structure, a cylindrical structure forms in both PS-*b*-P2VP thin films. From the *in-situ* grazing small angle X-ray scattering (GISAXS) measurements on thin film fabricated by spin-coating, the oriented cylindrical structure along perpendicular to the film surface formed: after the successive transitions from micelles in solution to the BCC lattice of micelles, oriented cylindrical structures are observed in thin film (Figure 2). In this transition, undergoing vitrification of PS and P2VP prohibited further this transition from the cylinder to lamellar structure. The cylinder perpendicularly aligned on the substrate grown in thin films fabricated by spin-coating is found to be a new non-equilibrium structure caused by the rapid solvent evaporation and the convection effect that solvent could efficiently evaporate from inside the thin films.



**Figure 2.** Time-resolved two dimensional GISAXS images (a) - (f) at the incident angle of  $0.14^\circ$ , the surface AFM image (g) and time-resolved in-plane profiles at  $q_z = 0.298$  nm<sup>-1</sup> (h) of PS-*b*-P2VP during spin-coating.