

Division of Multidisciplinary Chemistry – Polymer Materials Science –

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Scope of Research

The structure and molecular motion of polymer substances are studied, mainly using scattering methods such as X-ray, neutron, and light with intent to solve fundamentally important problems in polymer science. The main projects are studied on 1) the morphologies and the dynamics of self-assembling processes in block copolymers, 2) the hierarchical structures in crystalline polymer and rubber-filler systems, 3) the viscoelastic effects in glassy materials, 4) formation processes and ordering structures in polymer thin films.

KEYWORDS

Polymer Physics
Self Assembly
Hierarchical Structure

Polymer Properties
Softmatter



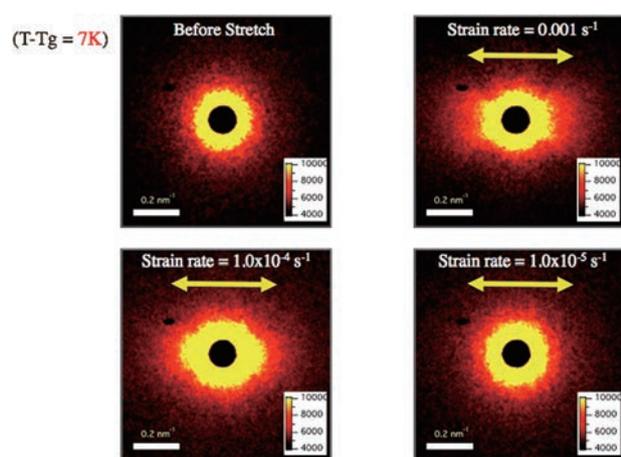
Selected Publications

Kishimoto, M.; Mita, K.; Jang, J.; Takahashi, N.; Ogawa, H.; Nishida, K.; Kanaya, T.; Takenaka, M., A Study on the Isothermal Crystallization of Poly(3-methylbutene-1), *Polym. J.*, **51**, 173-182 (2019).
Hattori, G.; Takenaka, M.; Sawamoto, M.; Terashima, T., Nanostructured Materials via the Pendant Self-Assembly of Amphiphilic Crystalline Random Copolymers, *J. Am. Chem. Soc.*, **27**, 8376-8379 (2018).
Ogawa, H.; Takenaka, M.; Miyazaki, T.; Kanaya, T., Order-order Transition Processes of Thin-Film Symmetric and Asymmetric PS-*b*-P2VP during Spin Coating, *Macromolecules*, **51**, 10040-10051 (2018).

Strain-Induced Enhancement of Density Fluctuations in Glassy Polymers

Polymer glass cannot deform isothermally because, by definition, micro-Brownian motion will be limited in the glass state. However, plastic flow in polymer glass can easily occur under conditions of stress. Here we aim at clarifying the universality of the enhancement in other glassy polymers such as polycarbonate (PC) and polystyrene (PS).

Figure 1 shows two-dimensional (2D) SAXS patterns of PC sample before stretching. The scattering pattern before stretching was isotropic. We stretched PC to the strain $\varepsilon = 0.12$ at temperature $T = 412\text{K}$ with strain rates $\dot{\varepsilon} = 1.00 \times 10^{-3}$ to $1.00 \times 10^{-5} \text{ s}^{-1}$. At 1.00×10^{-3} and $1.00 \times 10^{-4} \text{ s}^{-1}$, the scattering patterns become anisotropic, thereby exhibiting the so-called abnormal butterfly pattern. On the other hand, at $1.00 \times 10^{-5} \text{ s}^{-1}$, the enhancement of the scattering patterns along the stretch direction is not observed. These results suggest that the density fluctuations are not enhanced by the stretch at $1.00 \times 10^{-5} \text{ s}^{-1}$ and that the critical strain rate $\dot{\varepsilon}_c$ of the strain-induced enhancement of density fluctuations exists between 1.00×10^{-4} and $1.00 \times 10^{-5} \text{ s}^{-1}$ at 412K . We also found the strain-induced enhancement of density fluctuations occurs in PS. $\dot{\varepsilon}_c$ increases with temperature. A similar tendency can be observed in PMMA and PS. These results indicate that the strain-induced enhancement of density fluctuations is a universal feature in glassy polymers.



Density fluctuations are induced at higher strain rate.

Figure 1. 2D-SAXS images of stretched PC at 412K and $\varepsilon = 0.12$.

Order-order Transition Processes of Thin-film Symmetric and Asymmetric PS-*b*-P2VP during Spin Coating

Order-order transitions during spin-coating processes in symmetric and asymmetric poly(styrene-block-2-vinylpyridine) (PS-*b*-P2VP) were investigated by using grazing incidence small-angle X-ray scattering (GISAXS). When the composition was symmetric (e.g., the copolymer P2VP volume fraction, f_{P2VP} , was 0.50), we found that loose-packed nano-cylindrical structures formed after the transition from micelles to a body-centered cubic (BCC) lattice structure during evaporation. After the BCC (110) plane aligned perpendicular to the substrate, microdomains coalesced into a cylindrical structure. This coalescence was caused by the convection effect of the solvent, and vitrification of PS and P2VP further prohibited transitions from the cylindrical structure, although generally, the equilibrium morphology in the bulk state is lamellae. For an asymmetric composition with $f_{\text{P2VP}} = 0.70$, lamellar structures formed perpendicular to the substrate. During evaporation, the micelles transformed to hexagonal close-packed (HCP) structures, and then BCC structures appeared. The microdomains of the BCC structures merged parallel and perpendicular to the film surface before evaporation was complete, and hence, the lamellar structures were formed. Furthermore, well-packed hexagonal-packed nano-cylindrical structures with long-range order perpendicular to the substrate were formed in the PS-*b*-P2VP thin film with an $f_{\text{P2VP}} = 0.30$ and corresponded to the equilibrium morphology in the bulk state. During evaporation, the micelle structures directly transitioned to nano-cylindrical structures. The micelles grew perpendicular to the film surface before evaporation was complete.

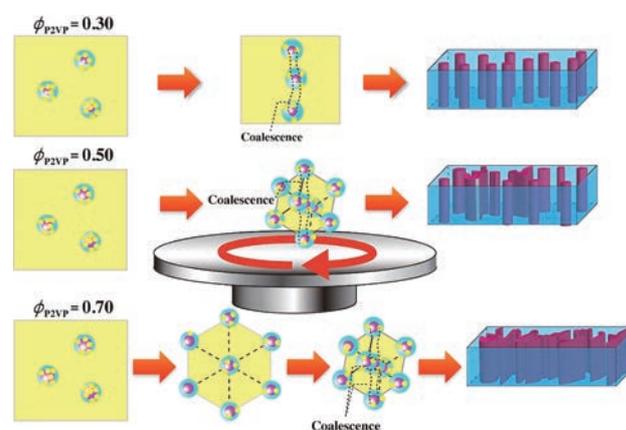


Figure 2. Cross-sectional views of the transition processes in toluene solvent during spin-coating of PS-*b*-P2VP block copolymer at $f_{\text{P2VP}} = 0.30, 0.50$ and 0.70 , respectively.