Dynamic Interplay between Phase Separation and Crystallization in a Poly(ε-Caprolactone)/Poly(ethylene glycol) Oligomer Blend

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We have investigated the crystallization effect on the phase separation of a poly(ε -caprolactone) and poly(ethylene glycol) oligomer (PCL/PEGo) blending system using simultaneous small-angle light scattering and differential scanning calorimetry (SALS/DSC) as well as simultaneous small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), and DSC (SAXS/WAXS/DSC) at NSRRC BL17B3. When the PCL/PEGo system, of a weight ratio of 7/3, is quenched from a melt state (160 °C) to temperatures below the spinodal point and the melting temperature of PCL (63 °C), the structural evolution observed exhibits characteristics of (Ⅰ) early stage of spinodal decomposition SD, (Ⅱ) transient pinning, (Ⅲ) crystallization-induced depinning, and (Ⅳ) diffusion-limited crystallization as described on Figure 1. The time dependent scattering data of SALS, SAXS and WAXS, covering a wide range of length scale, clearly show that the crystallization of PCL intervenes significantly in the ongoing viscoelastic phase separation of the system, only after the early stage of SD. The effect of preordering before crystallization revives the structural evolution pinned by the viscoelastic phase separation. The growth of SAXS intensity during the preordering period conforms to the Cahn-Hilliard theory. In the late stage of the phase separation, the PCL-rich matrix, of spherulite crystalline domains developed due to the faster crystallization kinetics, traps the isolated PEGo-rich domains of a slower viscoelastic separation.

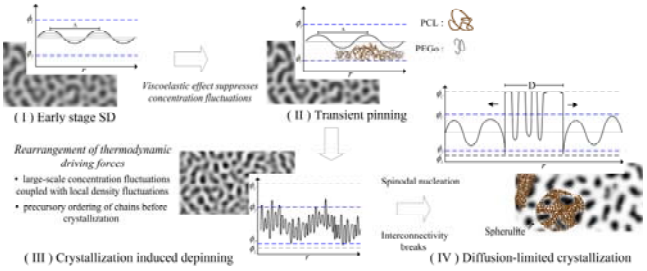

Figure 1. Cartoons for the morphologies and the corresponding concentration(ϕ)/density fluctuations in the four stages, Ⅰ, Ⅱ, Ⅲ, and Ⅳ, of the structural evolution of the PCL/PEGo (7/3) blend, with Λ for the wavelength of concentration fluctuations of the liquid-liquid phase separation and D for the size of PCL spherulites. The dark zones are for PEGo domains, whereas the relatively bright zones represent the PCL-rich domains of a higher viscoelasticity