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Microdomain-Tailored Crystallization Kinetics of Block Copolymers

Hsin-Lung Chen,*,† Shu-Ching Hsiao,†
Tsang-Lang Lin,‡ Kazuhiro Yamauchi,§
Hirokazu Hasegawa,§ and Takeji Hashimoto§

Department of Chemical Engineering, National Tsing Hua University, Hsin-Chu, Taiwan 30013, R. O. C.; Department of Engineering and System Science, National Tsing Hua University, Hsin-Chu, Taiwan 30013, R. O. C.; and Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

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Self-assembly of diblock copolymers (A-*b*-B) can generate a variety of microdomain (MD) structures (lamellae, hexagonally packed cylinders, body-centered cubic (bcc) spheres, and gyroids) depending on the volume fraction of the block chains (f_A) and the segregation power denoted by χN (χ = Flory−Huggins interaction parameter, N = overall chain length).[1−3] Because the MD size is usually on the order of the radius of gyration of the block chains, these domains offer a nanoscaled template wherein the dynamics and structural changes associated with the phase transformation can be drastically different from those in the bulk homopolymers. This study centers on the kinetics of crystallization in the MDs of a diblock copolymer. The crystallization behavior of block copolymers has gained significant attention in recent years.[4] Since crystallization is an ordering process, formation of crystals within the MDs would generate a structure of "order-within-order", where the formation of the hard (crystalline) phase may be effectively templated by the long-range ordered soft phase, a process that closely mimics the biomineralization.[5] Crystallization within the MDs requires the introduction of an equilibrium degree of chain folding,[6,7] in contrast to the kinetically introduced chain folding in homopolymer crystallization. Sometimes, the initial melt morphology may be destroyed by the driving force of crystallization to form crystalline lamellae.[8−12]

Despite the inherently rich morphology in block copolymers, a full use of the MD structure to finely manipulate the kinetics and thermodynamics of crystallization remains a challenge to polymer scientists. In this report, we demonstrate that the crystallization kinetics in the nanoscaled MDs of a diblock system can be precisely tailored by its MD morphology. A symmetric diblock copolymer, poly(ethylene oxide)-*block*-poly(1,4-butadiene) (PEO-*b*-PB), with PEO and PB being the crystalline and amorphous blocks, respectively, is blended with various amount of a low molecular weight PB homopolymer. The PB homopolymer is solubilized into PB MDs to swell the PB block chains (satisfying the wet-brush criterion)[13,14] and thereby yields the blends containing lamellar, cylindrical, and spherical PEO MDs in the melt state with increasing volume fractions of PB. The crystallization kinetics of the PEO blocks within these nanoscaled domains is then studied by the differential scanning calorimetry (DSC) to explore the correlation between crystallization kinetics and MD morphology.

The symmetric PEO-*b*-PB with the polydispersity index (M_w/M_n) = 1.04 was synthesized by sequential anionic polymerization of butadiene and ethylene oxide (Polymer Source, Inc.). M_n of the PEO and PB blocks was 6000 and 5000, respectively, which prescribed the volume fraction of PB f_{PB} = 0.50. The 1,4-addition PB homopolymer with M_n = 2600 and M_w/M_n = 1.04 was also synthesized by anionic polymerization (Polymer Source Inc.). Microphase-separated PEO-*b*-PB/PB blends were prepared by solution mixing using chloroform as the cosolvent, followed by removing the solvent in vacuo at 50 °C.

The MD morphology of PEO-*b*-PB/PB blends in the melt state was probed by small-angle X-ray scattering

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† Department of Chemical Engineering, National Tsing Hua University.

‡ Department of Engineering and System Science, National Tsing Hua University.

§ Kyoto University.

* To whom correspondence should be addressed. Tel +886-3-5721714; Fax +886-3-5715408; E-mail hlchen@che.nthu.edu.tw.

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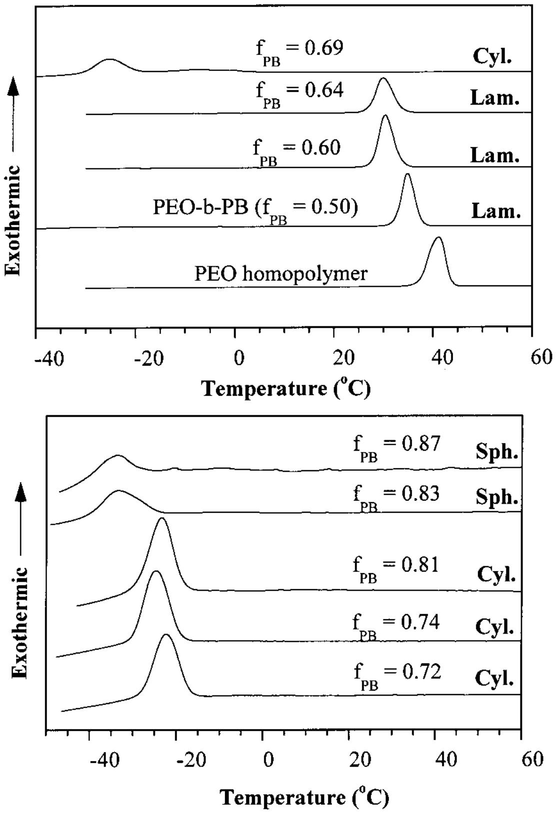


Figure 1. Crystallization exotherms of PEO-*b*-PB/PB blends. The cooling rate was 5 °C/min.

(SAXS) and transmission electron microscopy (TEM) to make sure that blending did induce morphological transformation. The observed MD structure is summarized as follows:

lamellae: 0.50 (neat PEO-*b*-PB) $\leq f_{PB} \leq$ 0.64

hexagonally packed PEO cylinders: $0.69 \leq f_{PB} \leq 0.81$

bcc packed PEO spheres: $0.83 \leq f_{PB}$

where f_{PB} denotes the overall volume fraction of PB. The average thickness of PEO lamellar MD is 7.80 nm, and the average radii of the cylindrical and spherical MDs are 7.25 and 7.40 nm, respectively.

The crystallization kinetics of PEO blocks within the three MD morphologies can be readily evaluated by the fixed cooling rate experiment in a DSC. The samples were first annealed at 80 °C (T_m of PEO < 80 °C < order−disorder transition temperature (T_{ODT}); T_{ODT} > 150 °C) for 10 min followed by cooling at −5 °C/min to record the crystallization exotherms. The results are shown in Figure 1. The peak temperature of the exotherm is defined as the "freezing (or crystallization)" temperature (T_f) where a higher T_f corresponds to a faster crystallization rate. Figure 2 plots T_f as a function of f_{PB}. T_f of the PEO blocks in neat PEO-*b*-PB is 35 °C, about 5 °C lower than that of PEO homopolymer with the same molecular weight. T_f decreases slightly (<5 °C) with increasing PB composition when the melt morphology is lamellar. However, T_f drops almost discontinuously by as much as 55 °C at f_{PB} = 0.69, where the melt morphology transforms into cylinders. T_f levels off with further addition of PB, but a depression of 9 °C is identified as the melt morphology transforms from cylinders to spheres (i.e., at f_{PB} = 0.83). Figure 2 clearly depicts three regimes of crystallization kinetics corresponding precisely to the three morphological patterns of PEO-*b*-PB/PB blends. To our knowledge, this is the first time that the parallel transition of crystallization kinetics with MD morphology has been revealed.

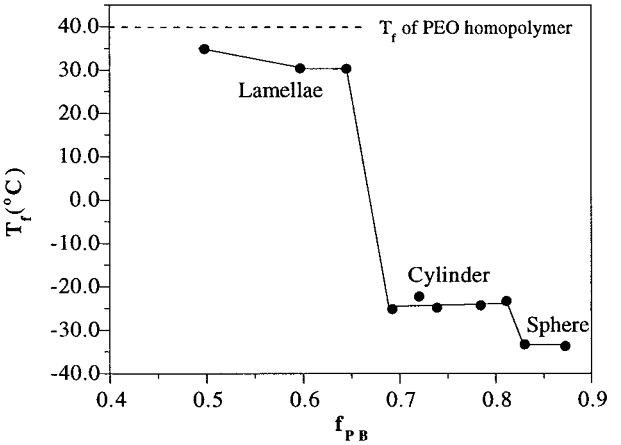


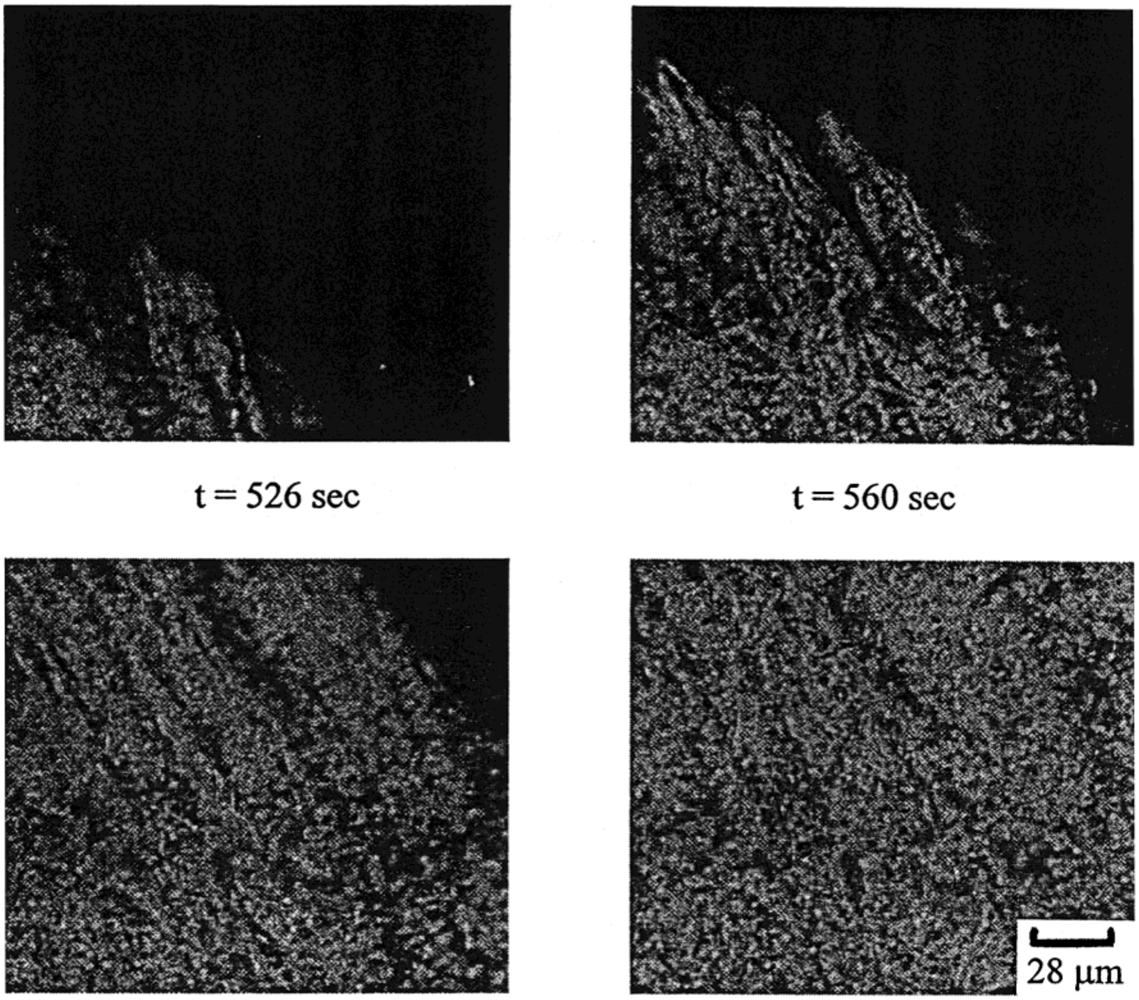
Figure 2. A plot showing the freezing temperature (T_f) of the PEO blocks as a function of f_{PB}. Three regimes of crystallization kinetics corresponding precisely to the three morphological patterns can be identified.

The distinct correlation between MD structure and crystallization kinetics can be associated with the frustration of crystal growth caused by the nanoscopically limited continuity of PEO MDs. In the homopolymer melt, crystallization starts out from homogeneous or heterogeneous nucleation, followed by the growth of numerous lamellar crystals that aggregate into a superstructural identity called "spherulite". The size of spherulites is usually in the micrometer range, so that they can be observed conveniently under polarized optical microscopy (POM). In the bulk melt of homopolymers, the concentration is always spatially continuous, so the crystal growth fronts of spherulites can advance freely until they impinge the boundaries of other spherulites.

The microphase-separated melt of block copolymers composes of grains with size on the micrometer scale, wherein the discrete MDs are arranged on the ordered lattice. The continuities of PEO concentration normal to the interface of lamellar MDs and along the radial directions of cylindrical and spherical MDs are limited to nanometer scale. Let us consider the "strict confinement model", where the crystallization is assumed to be strictly confined within the individual PEO MDs, and the cooperativity in crystallization among the MDs located in a given and any other grains is prohibited. A scenario identical to this model is taking one grain out of the microphase-separated melt followed by inducing crystallization within the PEO MDs in this grain. The growth of PEO crystals, in this case, will be frustrated when the growth front reaches the MD boundary. Because the crystal growth cannot advance toward other MDs, every PEO MD has to acquire a crystalline nucleus to initiate the crystallization within it. If we assume each MD contains one nucleus, the nucleation density (N_ρ^b) for crystallization in the microphase-separated melt can be expressed as

$$N_\rho^{b} = f_{PEO}/V_{MD}^{PEO} \qquad (1)$$

where V_{MD}^{PEO} is the average volume of a PEO MD in



t = 526 sec

t = 560 sec

t = 578 sec

t = 608 sec

Figure 3. Crystallization in the lamellar melt of neat PEO-*b*-PB observed by POM. The crystallization was conducted by cooling from 80 °C ($t = 0$) at 5 °C/min. The crystal growth spreading over the scale of hundreds of micrometers is by POM, showing that the crystal growth does propagate into the macroscopic scale.

the grain with the MD dimensions limited by the grain boundary. The nucleation density for crystallization in the homopolymer melt is inversely proportional to the average volume of a PEO spherulite ($V_{\mathrm{sph}}{}^{\mathrm{PEO}}$):

$$N_{\rho}{}^{\mathrm{h}} = 1/V_{\mathrm{sph}}{}^{\mathrm{PEO}} \tag{2}$$

Comparing eq 1 with eq 2, it can be seen that $N_{\rho}{}^{\mathrm{b}} \gg N_{\rho}{}^{\mathrm{h}}$ as long as $V_{\mathrm{sph}}{}^{\mathrm{PEO}} \gg V_{\mathrm{MD}}{}^{\mathrm{PEO}}$.[15] The enormously high nucleation density in the microphase-separated melt makes nucleation the rate-determining process for crystallization. Moreover, nucleations within the MDs must principally be homogeneous because the macroscopic impurity particles cannot be contained within the nanoscopic MDs to serve as the heterogeneous nuclei.[16,17] The exceedingly large undercooling required to induce crystallization in cylindrical and spherical morphologies is an indication of homogeneous nucleation controlled crystallization.[18]

The frequency of homogeneous nucleation is determined by the probability of successfully establishing the crystalline embryos (or clusters) with the critical dimensions through thermal fluctuation. Such a probability is directly proportional to the volume of the individual PEO MD.[18] The volume of the MD follows the order of lamellae > cylinder > sphere, so the nucleation rate (and hence the overall crystallization kinetics) undergoes a distinct transition at the morphological transformation. Although this analysis is rigorously held for strictly confined crystallization, it offers a rationale for the observed transition of crystallization kinetics with MD morphology.

A close look at Figure 2 reveals a discrepancy with the “strict confinement model”. It follows from eqs 1 and 2 that crystallization in lamellar melt should require a much higher nucleation density than that in the homopolymer.[19] In other words, we expect the crystallization rate to be $T_{\mathrm{f}}(\mathrm{lam}) \ll T_{\mathrm{f}}$ (homopolymer) instead of $T_{\mathrm{f}}(\mathrm{lam}) \approx T_{\mathrm{f}}(\mathrm{homopolymer})$ observed in Figure 2. The proximity of crystallization kinetics implies that crystallization is highly cooperative among the PEO lamellar MDs, so that the crystal growth could propagate over a macroscopic scale comparable to the spherulitic crystallization in homopolymer.

If crystal growth in lamellar melt can advance over a macroscopic scale, it should be observable under POM. Figure 3 presents the crystallization in the lamellar melt of neat PEO-*b*-PB revealed by POM. The crystal growth spreading over the scale of hundreds of micrometers can be monitored with the resolution of POM, showing that the crystal growth does continue into the macroscopic scale.

It is not unusual that crystal growth in lamellar block copolymers can advance over a macroscopic scale, as spherulites had been observed in some instances.[8,20−22] The long-range crystal growth may stem from the extensive continuity of PEO concentration across the grain boundary, where the molten PEO lamellar MDs in a grain connect with the PEO domains in the adjacent grains at the boundary through Scherk's surface.[23,24] Continuous crystal growth may proceed across the grains with such a continuity, approaching the length scale of spherulitic crystallization in homopolymers. The long-range growth, in this case, is assisted by the preexisting melt morphology, where the continuity of MD structure exists through the grain boundary via Scherk's surface.

Since T_g of PB is lower than the freezing temperatures of the PEO blocks, the long-range growth may also arise from the "cross communication" among individual PEO MDs, where the driving force of crystallization disrupts the preexisting lamellar morphology by allowing the crystal growth front in a PEO lamellar MD to propagate into another PEO MDs. The long-range crystal growth, in this case, is assisted by crystallization itself (through the crystallization driving force) regardless of the existence of the MD continuity before crystallization. The morphology of PEO-*b*-PB/PB blends after crystallization is currently studied by TEM. The preliminary result indicates that the PEO lamellar MDs become highly tortuous and interconnected after crystallization, suggesting the occurrence of "cross communication".

In conclusion, we have demonstrated the implementation of MD transformation to finely tailor the crystallization kinetics in a diblock copolymer. When concentration continuity is seriously frustrated and crystallization is largely confined within the individual MDs, homogeneous nucleation becomes the rate-determining process for crystallization. The direct proportionality between the nucleation rate and MD volume renders the basis for the parallel transition of crystallization kinetics with the MD morphology.

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