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Process and kinetics of order–order transition from bcc-sphere to hex-cylinder in polystyrene-*block*-polyisoprene-*block*-polystyrene: Time-resolved SAXS and TEM studies

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Abstract

We have studied the process and kinetics of the order–order phase transition (OOT) from spheres in a body-centered-cubic lattice (bcc-sphere) to hexagonally packed cylindrical microdomains (hex-cylinder) for a polystyrene-*block*-polyisoprene-*block*-polystyrene triblock copolymer, induced by abrupt temperature drops. In this study, time-resolved small-angle X-ray scattering (SAXS) measurements are conducted to investigate the OOT processes *in situ* and at *real time*. Transmission electron microscopy observations for specimens rapidly frozen below the glass transition temperature at particular times in the OOT processes are also conducted to visualize the transient structures developed during the OOT. We elucidated the following pieces of evidence. (I) The OOT proceeds via the nucleation and growth process as follows: After quenching the specimen, the system stays at a bcc-sphere state in the incubation period, t_i. After this period, (II) anisotropic grains of hex-cylinder are nucleated at the vicinity of grain boundaries of bcc sphere. (III) The growth of the grains appears to be faster along the cylindrical axis than along the direction perpendicular to it, on the contrary to the growth of hex-cylinder from the disordered phase. The OOT involves deformation of spherical domains toward a [111] direction of a bcc lattice, followed by coalescence and connection of them to cylindrical microdomains. (IV) The rate of OOT as observed by time-resolved SAXS was found to depend on quench depth, $\Delta T\ (\equiv T_{\mathrm{OOT}}-T_{\mathrm{cyl}})=4$–$10$ K, or thermodynamic driving force for the OOT, $\varepsilon\ (\equiv \Delta T/T_{\mathrm{OOT}})=0.0087$–$0.0217$, where T_{OOT} is the OOT temperature between hex-cylinder and bcc-sphere: The larger ΔT or ε is, the shorter t_i is and the faster the transformation rate, R_T, is after the incubation time. (V) Consequently, the time change of a characteristic parameter as observed by SAXS at various ΔTs fall on to a master curve when real time is reduced with t_i, revealing that the following two intriguing conclusions: (i) t_i and R_T^{-1} have the same temperature dependence, and hence the system has only single time scale, and (ii) the transformation after the incubation period starts only when the characteristic parameter reaches a temperature independent critical value.

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1. Introduction

Recently, block copolymers have been recognized as advanced nano-materials, because they could self-assemble into various patterns with nano-periodicity and can be used as templates for nano-fabrications toward advanced practical applications. A better control of the structures may require information on the process and kinetics of the phase transitions for the block copolymers, such as the order–disorder transition (ODT) and the order–order transition (OOT). In this work, we focus on kinetics and process of the thermally induced OOT from equilibrium bcc-sphere phase (spherical microdomains in body-centered cubic symmetry) to equilibrium hex-cylinder phase (cylindrical microdomains in hexagonal symmetry).

To our surprise, there are no reports on time-resolved small-angle X-ray scattering (SAXS) and small-angle neutron scattering studies about process and kinetics of the OOT from bcc-sphere to hex-cylinder, except for a very short report at a given quench depth, $\Delta T\ (\equiv T_{\mathrm{OOT}}-T_{\mathrm{cyl}})=11$ K, by Kim and his coworkers [1], although the process

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and mechanism have been actively studied by static methods [2–7] as will be detailed below. Here, T_{OOT} and T_{cyl} are, respectively, defined the OOT temperature and a measuring temperature below T_{OOT} where hex-cylinder exists at equilibrium. In this work, we aim to: (i) systematically study *in situ* and at *real time* kinetics of the OOT process as a function of ΔT by means of time-resolved SAXS; (ii) elucidate morphological changes with time during the OOT process. The latter study involves transmission electron microscopy (TEM) on the specimen quenched at particular times set during the OOT process, guided by time-changes in characteristic scattering parameters as analyzed from the time-resolved SAXS experiments.

The equilibrium phase behavior of block copolymers, especially AB-type diblock copolymers composed of A- and B-block chains, is well understood both theoretically [8,9] and experimentally [10,11]. In the weak segregation regime, the microdomain structure of the diblock copolymers depends not only on the volume fraction of constituent block chains, f, [12–14] but also on the product, χN, [8,12, 15–17] where χ is the Flory–Huggins segmental interaction parameter, and N is the total degree of polymerization, so that the diblock copolymers exhibit the OOT when χN is changed.

The thermally induced OOT was predicted by Leiber [15] for the first time about a quarter of a century ago. Since then, the theoretical studies were promoted further [16]. However, the OOT was not confirmed experimentally for some time after the Leibler's theoretical prediction. In 1993, Hashimoto and his coworkers experimentally found for the first time the thermoreversible OOT between hex-cylinder and bcc-sphere [3]. Since then, the studies about the OOT were advanced not only theoretically [8,9,18–25] but also experimentally. Especially, the OOT between hex-cylinder and bcc-sphere were most studied, [2,4–7,26–28] and as a consequence, the OOT process was elucidated as follows: In the OOT process from hex-cylinder to bcc-sphere, the cylinders are burst into a series of spheres with the cylindrical axes being transformed to the [111] direction of bcc-sphere as schematically shown in Fig. 1(a); On the other hand, in the OOT from bcc-sphere to hex-cylinder, spheres along the [111] direction of a bcc lattice are deformed and interconnected to cylinders, as also shown in Fig. 1(a) [4,7,26,28]. Here, Fig. 1(b) and (c) represent the illustrations of hex-cylinder viewed from the direction of cylindrical axes and bcc-sphere viewed from the [111] direction in a bcc lattice, respectively.

The reason why the OOT process and kinetics have been hardly explored *in situ* and at *real time* seems to be because the OOT, especially from hex-cylinder to bcc-sphere, occurs relatively fast, as estimated by calculation of the energy barrier between the two phases by Matsen [25]. This makes it difficult to follow the process *in situ* and at *real time*. By several theoretical approaches, kinetic pathways of the OOT have been evaluated, and the transient or metastable structures in the pathways have been presented [18–25]. However, unfortunately, they are not fully explored experimentally yet. In 1997, Sakamoto et al. reported the SAXS profiles and the linear dynamic mechanical response as a function of temperature for an asymmetric polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymer having its f lies near the borderline between hex-cylinder and bcc-sphere [2]. They elucidated that the OOT from hex-cylinder to bcc-sphere took place on heating process at ca. 183 °C for the SIS sample. Successively, in 1998, Kim et al. reported the OOT kinetics from bcc-sphere to hex-cylinder in the same triblock copolymer as Sakamoto et al. employed by using synchrotron small-angle X-ray scattering (SAXS) [1]. They presented the time evolutions of SAXS intensity profile, $I(q)$, magnitude of the scattering vector (q) at the first-order peak, q_{m}, the peak intensity, $I_{\mathrm{m}}=I(q=q_{\mathrm{m}})$, and the square of the half-width at half maximum, σ_q^2, in the OOT process for only a single quench depth of 11 K. Here, q is defined by $q=(4\pi/\lambda)\sin(\theta/2)$ with λ and θ being the wavelength of the incident X-ray and the scattering angle, respectively. We think that more systematic time-resolved investigations as a function of ΔT are needed for a better understanding of the OOT process and kinetics of the triblock copolymer.

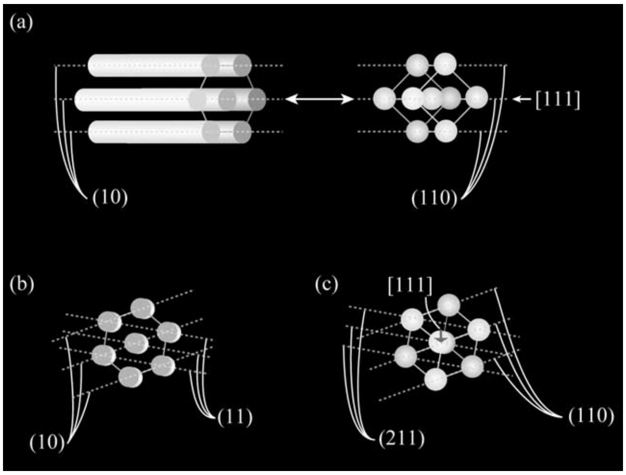

Fig. 1. (a) Schematic illustration showing the spatial arrangement of the microdomain structures before and after the OOT between hex-cylinder and bcc-sphere. The dotted lines indicate not only the directions of both cylindrical axes and the [111] direction in a bcc lattice but also the symmetry planes perpendicular to the plane of the paper. (b) Schematic illustration of hex-cylinder viewed from the direction of cylindrical axes. (c) Schematic illustration of bcc-sphere viewed from the [111] direction in a bcc lattice. Both in (b) and (c), the dotted lines represent the symmetry planes perpendicular to the plane of the paper.

Therefore, we conducted the time-resolved SAXS and TEM experiments as described earlier. The TEM observations will help us to visualize transient structures developed during the OOT. The reciprocal-space observation by SAXS and the real-space observation by TEM are complementary, and they reinforce themselves each other.

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