

# Crystallization-induced structure fluctuation of crystallized microdomain structure composed of strongly segregated crystalline-crystalline diblock copolymers

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## ABSTRACT

Crystallization-induced structure fluctuations in the layer thickness direction and disordering of pre-crystallized structure in crystallized microdomain structure that consist of a strongly segregated crystalline-crystalline diblock copolymer, poly(ethylene glycol)-*block*-poly(perfluorooctyl ethyl acrylate) (PEG-*b*-PFA-C<sub>8</sub>), were investigated. The structure formation process during isothermal crystallization was monitored by *in-situ* time-resolved simultaneous SAXS/WAXD measurements and thermal analysis. At early stage of isothermal crystallization, three dimensional growth of the PEG lamellar crystals within lamellar microphase-separated morphology induced the volume shrinkage of PEG phase, resulting in the reduction of PEG layer thickness, increase of PFA-C<sub>8</sub> layer thickness and disordering of pre-crystallized PFA-C<sub>8</sub> crystals. At late stage of isothermal crystallization, one dimensional growth, thickening of PEG lamellar crystals induced the increase of PEG layer thickness and reduction of PFA-C<sub>8</sub> layer thickness. The structure fluctuation in the crystallized microdomain structure depends on the crystal growth dimension.

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## 1. Introduction

Self-assembly of block copolymers derives various ordered microphase separated structures, such as spheres, cylinders, gyroids and lamellae, depending on the volume fractions of the components and the chain architecture [1]. Crystalline block copolymers provide the hierarchically ordered structure including microphase separated structure and crystalline structure, which is called crystallized microdomain structure [2–7]. The crystallized microdomain structure provides unique physical properties and functionalities. In the case of crystalline-amorphous block copolymers, the elastic modulus of the block copolymer increases if

the crystalline block crystallized within spherical microdomains [8]. The block copolymer films remain transparent after crystallization because the spherical microdomain size is order of tens of nanometers, which is much smaller than wavelength of visible light. Control of the degree of crystallinity and the orientation of the crystals in the microdomains provides the gas permeability reduction and elasticity to the block copolymer films [9]. Crystalline-crystalline block copolymers also provide the hierarchically ordered structure including microphase separated structure and double crystalline structure. Crystalline-crystalline biodegradable block copolymers have been applied to biomaterials because the biocompatibility and physical properties can be manipulated by combining different crystalline polymers or adjusting the ratio of the constituting blocks [6,7]. The donor-acceptor conjugated block copolymers have been investigated for the application to photovoltaic cells, and it is getting understood that the light absorption, charge separation and charge transport depend on the morphology, size and orientation of ordered microdomains and crystalline structure [10,11].

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Morphology of the crystalline block copolymers depends on the crystallization process. The microphase separated morphology in the melt is destroyed through crystallization if the crystallization driving force is stronger than the microphase separation driving force (Break-out crystallization), and the crystallized lamellar morphology is obtained [12,13]. On the other hands, the microphase separated morphology in the melt is retained during crystallization if the crystallization driving force is weaker than the microphase separation driving force (Confined crystallization), and crystallized microdomain structure consisting of microphase separated structure and crystalline structure is obtained [2–7]. Confined crystallization has been observed in crystalline-glassy amorphous (order-disorder transition temperature ( $T_{ODT}$ ) > glass transition temperature ( $T_g$ ) of amorphous block > crystallization temperature ( $T_c$ ) of crystalline block) [3,4], and intermediate segregated crystalline-rubbery amorphous (intermediate  $\chi N$  values,  $T_{ODT} > T_c > T_g$ , confined crystallization depends on the thermal treatment employed during the crystallization process) [14,15], and strongly segregated crystalline-rubbery amorphous (high  $\chi N$  values,  $T_{ODT} > T_c > T_g$ ) [7,14,15], and strongly segregated crystalline-crystalline (high  $\chi N$  values) [2,5–7] block copolymers. In case of the confined crystallization, crystallization induces deformation of the ordered microdomain structure to some extent due to the volume change, leading to the deterioration of physical properties and functionalities. However, the crystallization-induced structure disordering and conditioning during the isothermal crystallization in the crystallized microdomain structure of crystalline-crystalline block copolymers has not been understood yet.

This paper is a report of the structure formation process of crystallized microdomain structure during the isothermal crystallization from the melt state. We propose a crystalline-crystalline diblock copolymer, which consists of poly(ethylene glycol) (PEG) and poly(perfluorooctylethyl acrylate) (PFA- $C_8$ ) (PEG- $b$ -PFA- $C_8$ ) [16]. The PFA- $C_8$  consists of rigid perfluorooctylethyl ( $R_f$ ) side chains to build bilayer lamellar structure of the  $R_f$  groups with hexagonal packing [17,18]. The stacked layered structure could be defined as Sm-F or Sm-I phase. These phases are just the boundary between mesophase and crystal phase in the phase classification. Actually, the mesophase did not present clear fluidity in the equilibrium state, even though the structure was characteristic to the high ordered smectic phase. On the view point of the mobility of the main-chain and  $R_f$  groups, the mesophase may be deal with as a disordered crystal. That is, PEG block is subjected to similar restricted field to that formed by the other crystalline polymer. For the simplicity, we expediently called the high ordered phase “crystal phase”. The block copolymer is composed of hydrophilic PEG and fluorinated PFA- $C_8$ , and has large  $\chi$  parameter to give clear interface of the microdomains [19,20]. The microphase separated morphology in the melt is retained during crystallization due to the strong segregation. The large electron density contrast is also beneficial to obtain the clear scattering peaks in SAXS to give insights for the detailed structure fluctuation. Because the diffraction peaks of PEG and PFA- $C_8$  crystals are separated, the crystal growth is individually estimated by WAXD. The PEG- $b$ -PFA- $C_8$  is a suitable model system to investigate the structure formation process of the crystallized microdomain structure. The structure formation process in the isothermal crystallization was precisely investigated by *in-situ* time-resolved simultaneous SAXS/WAXD measurement and thermal analysis.

## 2. Experimental section

### 2.1. Materials

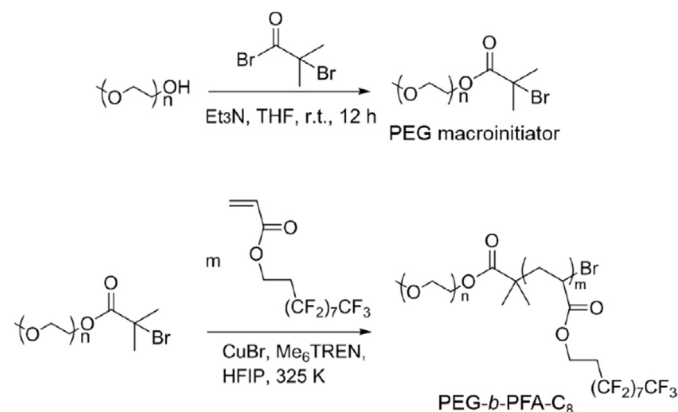
Poly(ethylene glycol) monomethyl ether (Aldrich, St. Louis, MO)

with number-average molecular weight ( $M_n$ ) of 20,000 and polydispersity index ( $M_w/M_n$ ) of 1.1 was dried by azeotropic distillation with anhydrous toluene before use. Copper(I) bromide (CuBr, Wako Pure Chemicals, Osaka, Japan, 99.9%) was washed successively with acetic acid and ethanol, and dried under vacuum. Triethylamine ( $Et_3N$ , Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, >99.0%) was distilled under reduced pressure before use. 2-Perfluorooctyl ethyl acrylate (FA- $C_8$ ) was provided by Daikin Industry Ltd., and was purified by repeating distillation under reduced pressure to remove contaminants such as 2-perfluorodecylethyl acrylate. 2-Bromo-2-methylpropionyl bromide (Aldrich, St. Louis, MO, 98%), tris[2-(dimethylamino)ethyl]amine ( $Me_6TREN$ , Alfa Aesar, 99%), tetrahydrofuran (Wako Pure Chemical Industries, Osaka, Japan, 97.0%), methanol (Wako Pure Chemical Industries, Osaka, Japan, 99.5%), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, Central Glass Co., Ltd., Yamaguchi, Japan, 99.9%), AK-225 (Asahi Grass Co., Tokyo, Japan), which is a mixture of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,1,2,3-pentafluoro-propane, were used as received.

### 2.2. Synthesis of PEG- $b$ -PFA- $C_8$

All procedures for the polymerization and purification of FA- $C_8$  monomer were carried out under a fume hood because the bioaccumulation of the degraded products of poly(fluoroalkyl acrylate)s with long  $R_f$  groups ( $C \geq 8$ ) have a potential risk of environmental load and health hazard [21,22].

The PEG- $b$ -PFA- $C_8$  were synthesized by two-step procedure (Scheme 1). The bromo-terminated PEG macroinitiator was prepared by a previously reported method [23]. PEG macroinitiator (0.0665 mmol), FA- $C_8$  (10.1 mmol), and HFIP (13.3 mL) were charged in a glass tube, and the solution was degassed by freeze-pump-thaw cycles. CuBr (0.0627 mmol) was introduced into another glass tube and then degassed by several cycles of vacuum pumping and flushing with argon.  $Me_6TREN$  (0.0952 mmol)/HFIP solution (0.14 M) was degassed by freeze-pump-thaw cycles, and then was added to the glass tube with CuBr. The copper catalyst solution was degassed by freeze-pump-thaw cycles, and was injected to the PEG macroinitiator/FA- $C_8$ /HFIP solution. The resulting mixture was degassed by freeze-pump-thaw cycles, and then the tube was sealed under reduced pressure. The polymerization was carried out by stirring in a bio-shaker at 325 K, 190 rpm for 3 h. The reaction mixture was poured into a large amount of methanol to obtain the diblock copolymer and remove the copper catalyst and unreacted bromo-terminated PEG macroinitiator.



**Scheme 1.** Synthesis of PEG- $b$ -PFA- $C_8$  by atom transfer radical polymerization of FA- $C_8$  with a PEG macroinitiator.

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