



# Microphase separation and crystallization behaviors of bi-phased triblock terpolymers with a competitively dissolved middle block



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## ABSTRACT

A series of poly( $\epsilon$ -caprolactone)-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene (PCL-*b*-PnBA-*b*-PS) triblock terpolymers with fixed PCL and PnBA block lengths but different PS block lengths were prepared. In all of these triblock terpolymers the PnBA block can be competitively dissolved in both the PCL and PS phases to form bi-phase structures in the melt, as revealed by atomic force microscopy (AFM). Due to the “competitive dissolution effect” of the PnBA middle block, the microphase separation and crystallization behaviors of these triblock terpolymers are different from those of common diblock copolymers to some extent. As revealed by the Flory-Huggins parameters, more PnBA segments tend to dissolve in the PS phase. Therefore, the volume fraction of the PS-rich phase ( $f_{PS-rich}$ ) is evidently larger than the calculated volume fraction of the PS block ( $f_{PS}$ ), and the phase boundaries between two different structures shift to lower  $f_{PS}$ . There also exists a thick interphase layer between the PS-rich and PCL-rich phases due to competitive dissolution of the PnBA block. However, confined crystallization can only occur at a larger  $f_{PS-rich}$ , though the measured glass transition temperature ( $T_g$ ) is high for the PS block. This can be attributed to a high fraction of the soft zone surrounding the PCL-rich phase and the lower volume fraction of the hard zone.

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## 1. Introduction

The microphase separation and crystallization behaviors in diblock copolymers, triblock terpolymers and star-like block copolymers have been widely studied in past decades [1]. In traditional amorphous AB diblock copolymers different ordered structures including body-centered cubic spheres (BCC), hexagonally packed cylinders (HEX), gyroid (GYR), lamellae (LAM) and hexagonally perforated lamellae (HPL) can be formed, depending on the segregation strength  $\chi_{AB}N$  and the volume fraction  $f$  [2]. The microphase separation behavior of diblock copolymer has been well understood through theoretical description and experimental study. Meanwhile microphase separation of ABC triblock terpolymers also attracts many researchers because of their potential applications in sacrificial templates [3–7], polymer electrolytes [8,9], nanolithography [10,11]. As for the ABC triblock terpolymers, six parameters affect the final morphology, including the total polymerization degree  $N$ , three Flory-Huggins interaction parameters

( $\chi_{AB}$ ,  $\chi_{BC}$ ,  $\chi_{AC}$ ) and the volume fractions  $f_A$ ,  $f_B$  [12–16]. The microphase separation behavior of triblock terpolymers can be classified into three types according to the relative magnitude of the three Flory-Huggins interaction parameters: type I frustration system ( $\chi_{AB} < \chi_{AC} < \chi_{BC}$ ), type II frustration system ( $\chi_{AC} < \chi_{AB} < \chi_{BC}$ ) and non-frustration system ( $\chi_{AB} < \chi_{BC} < \chi_{AC}$ ) [12]. In type II frustration system the A block and C block are more compatible but not directly linked by chemical bond, which may cause many striking morphologies [17]. In experimental aspect, the microphase-separated morphology of many triblock terpolymers has been widely studied, and some interesting morphologies including  $O^{70}$ ,  $Q^{230}$ ,  $Q^{214}$ , knitting-pattern and helical superstructure have been found [18–30].

However, in most triblock terpolymers the differences in  $\chi$  among different blocks are not large enough to result in tri-phase separation and the bi-phase structures are usually observed [31–35]. There are two situations in the bi-phase separated systems. The first is that the most incompatible blocks are located at the head and tail of one block, respectively ( $\chi_{AB}$ ,  $\chi_{BC} < \chi_{AC}$ ), so that the middle block is dissolved in both phases formed by the two most incompatible blocks. In such a system, the dissolution of the

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middle B block in two phases depends on its compatibility between the A and C blocks, thus we call it “competitive dissolution”. Moreover, the “competitive dissolution” of the middle B may change the volume fractions of microdomains and thus the microphase separation behavior. The second is that the most incompatible A, B two blocks are linked directly and the third C block is at the head or tail of polymer chain ( $\chi_{AC}, \chi_{BC} < \chi_{AB}$ ). If  $\chi_{BC} < \chi_{AC} < \chi_{AB}$ , the tail block C prefers to stay nearby the B domains from the viewpoint of enthalpy and entropy. However, if  $\chi_{AC} < \chi_{BC} < \chi_{AB}$ , the enthalpy and entropy work contradictorily, which may induce defects in the bi-phase structures. In the bi-phased triblock terpolymers, the  $\chi_{AC}$  and  $\chi_{BC}$  may also change with temperature, which would cause transition from  $\chi_{BC} < \chi_{AC} < \chi_{AB}$  to  $\chi_{AC} < \chi_{BC} < \chi_{AB}$  or vice versa. Consequently, there exist some differences between the microphase separation behaviors of bi-phased triblock terpolymers and common diblock copolymers. So far, little attention has been paid to the former, although it may represent the most case of triblock terpolymers.

When a crystalline block is present in an AB diblock copolymer, break-out crystallization, confined crystallization and templated crystallization could happen, depending on the volume fraction ( $f$ ), the glass transition temperature ( $T_g$ ) of the amorphous block, the crystallization temperature ( $T_c$ ) of the crystalline block, the order to disorder transition temperature ( $T_{ODT}$ ) and the Flory-Huggins interaction parameter at crystallization temperature ( $\chi_c$ ) [36–41]. When the crystalline block is the majority in diblock copolymers, break-out crystallization usually occurs [40]. As the crystalline block is the minor component and  $T_{ODT} > T_g > T_c$ , crystallization is usually confined in the pre-formed microdomains due to the vitrification effect of the amorphous block [37,41]. If  $T_{ODT} > T_c > T_g$ , either break-out crystallization, confined crystallization or templated crystallization can take place [38]. When the relative segregation strength ( $\chi_c/\chi_{ODT}$ ), which is the ratio of the  $\chi$  at  $T_c$  to the  $\chi$  at  $T_{ODT}$ , is large enough, confined crystallization occurs; otherwise break-out crystallization prevails. Templated crystallization could be observed when the segregation strength and the crystallization force are comparable. Crystallization behavior in triblock terpolymers and even pentablock terpolymers has also attracted lots of attentions [42–51]. Abetz et al. studied the morphologies of polybutadiene-*b*-polystyrene-*b*-poly(ethylene oxide) (PB-*b*-PS-*b*-PEO) and its corresponding hydrogenated triblock terpolymers, polyethylene-*b*-polystyrene-*b*-poly(ethylene oxide) (PE-*b*-PS-*b*-PEO) [43,44]. After hydrogenation, the former PEO dominated morphologies were altered due to crystallization of the PE block. Balsamo and Müller et al. extensively studied the morphologies of polystyrene-*b*-polybutadiene-*b*-poly( $\epsilon$ -caprolactone) (PS-*b*-PB-*b*-PCL) with a tri-phase structure [46–49]. When the PCL block is the minority, the original microphase structure changed from circular cylinders to cylindrical polygons [46], or from layer by layer lamellae to cylinder in lamellas, after PCL crystallization [48]. When the PCL block is the majority, ellipsoidal core-shell cylinders were observed in PCL matrix [49]. We notice that the triblock terpolymers in all above works have a tri-phase structure. By contrast, crystallization behavior of bi-phased triblock terpolymers is rarely reported. Based on results of diblock copolymer, the crystallization behavior of block copolymers is mainly dependent on the volume fraction and competition between crystallization and microphase separation. In the triblock terpolymers with a bi-phase structure, the dissolved block may have two opposite effects on the crystalline block. On the one hand, it will enhance the volume fraction of the crystalline block and thus higher possibility for break-out crystallization. On the other hand, it will dilute the crystalline block and reduce the crystallizability, leading to inclination of confined crystallization. Moreover, the previous microphase separation mode in the melt (no matter  $\chi_{AC}, \chi_{BC} < \chi_{AB}$  or not) will also

influence the following crystallization. As a result, the crystallization behavior in the triblock terpolymers with a bi-phase structure may be different to some extent from that of diblock copolymers, and it needs further study.

Herein we focused on the microphase and crystallization behaviors of triblock terpolymers exhibiting a bi-phase structure with  $\chi_{AB}, \chi_{BC} < \chi_{AC}$ , thus a series of poly( $\epsilon$ -caprolactone)-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene (PCL-*b*-PnBA-*b*-PS) triblock terpolymers were prepared. In such a system, the  $\chi_{AC}$  is the biggest and we intentionally made the middle PnBA block a little shorter so that it could be competitively dissolved into both the PCL and PS phases to form PCL- and PS-rich phases. The bi-phase structure in PCL-*b*-PnBA-*b*-PS triblock terpolymers was confirmed by atomic force microscopy (AFM). The microphase separation and crystallization behaviors were then discussed and compared with common diblock copolymers.

## 2. Experimental

### 2.1. Materials

The PCL-*b*-PnBA-*b*-PS triblock terpolymers were prepared by ring-opening polymerization of  $\epsilon$ -caprolactone, followed by sequential atom transfer radical polymerization of *n*-butyl acrylate and styrene. The synthetic route is shown in Scheme S1 of supplementary material. The initiator was synthesized according to other papers [52,53]. Halogen exchange reaction happened before styrene polymerization. The details of polymerization procedures and characterizations of the products were provided in supplementary material. The GPC result in Fig. S5 shows that all samples have relatively narrow polydispersity (PDI < 1.17). Structural information of the PCL-*b*-PnBA-*b*-PS triblock terpolymers is listed in Table 1. For convenience, C shorts for PCL, B for PnBA, S for PS, and the superscripts stand for the polymerization degrees of corresponding blocks. All the samples used in the present work have the same PCL and PnBA block lengths but different PS lengths.

### 2.2. Characterizations

Molecular weights and polydispersity (PDI) were characterized by gel permeation chromatography (GPC) using a Waters system calibrated with standard polystyrenes. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min <sup>1</sup>H NMR spectra were recorded on a Bruker DMX-400 instrument using CDCl<sub>3</sub> as solvent. Polarized optical microscopy (POM) observations were carried out on an Olympus microscope (BX51) equipped with a hot stage.

Temperature-variable small-angle X-ray scattering (SAXS) experiments were performed at BL16B1 beamline in Shanghai Synchrotron Radiation Facility (SSRF), China. The wavelengths of X-ray at SSRF are 1.24 Å. The sample-to-detector distance was set as 2000 mm. Two-dimensional (2D) SAXS patterns were recorded by

**Table 1**  
Structural information of PCL-*b*-PnBA-*b*-PS triblock terpolymers.

Sample	$M_n^a$ (10 <sup>3</sup> g/mol)	$f_{PCL}^b$ (%)	$f_{PnBA}^b$ (%)	$f_{PS}^b$ (%)	PDI <sup>c</sup>
C <sub>170</sub> B <sub>95</sub> S <sub>115</sub>	43.5	44	28	28	1.11
C <sub>170</sub> B <sub>95</sub> S <sub>190</sub>	51.3	37	24	39	1.13
C <sub>170</sub> B <sub>95</sub> S <sub>229</sub>	55.4	34	22	44	1.11
C <sub>170</sub> B <sub>95</sub> S <sub>304</sub>	63.2	30	20	50	1.14
C <sub>170</sub> B <sub>95</sub> S <sub>409</sub>	74.1	25	17	58	1.16

<sup>a</sup> Determined by <sup>1</sup>H NMR.

<sup>b</sup> The densities of 1.081 g/cm<sup>3</sup>, 1.041 g/cm<sup>3</sup> and 1.05 g/cm<sup>3</sup> for amorphous PCL, PnBA and PS, respectively, were used for calculation [54,55].

<sup>c</sup> Determined from GPC.

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