



# Polystyrene-*block*-polyethylene-*block*-polystyrene triblock copolymers: Synthesis and crystallization-driven self-assembly behavior



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## ABSTRACT

In this work, we reported the synthesis of a series of novel semicrystalline ABA triblock copolymers with polyethylene midblock and polystyrene endblocks *via* the combination of ring-opening metathesis polymerization (ROMP), hydrogenation and reversible addition-fragmentation chain transfer (RAFT) polymerization. First, an  $\alpha,\omega$ -dihydroxyl-terminated polycyclooctadiene (PCOD) was synthesized *via* the ROMP of cyclooctadiene by the use of the Grubbs second generation catalyst and with *cis*-2-butene-1,4-diol as the chain transfer agent. The  $\alpha,\omega$ -dihydroxyl-terminated PCOD was then hydrogenated into an  $\alpha,\omega$ -dihydroxyl-terminated polyethylene (PE); the latter was allowed to react with 2-methyl-2-[(dodecylsulfanylthiocarbonyl) sulfanyl]propanoic acid to afford a macromolecular chain transfer agent (*i.e.*, Macro-CTA) for the RAFT polymerization of styrene. By controlling the lengths of PS endblocks, a series of polystyrene-*block*-polyethylene-*block*-polystyrene (PS-*b*-PE-*b*-PS) triblock copolymers were obtained. The successful synthesis of the ABA triblock copolymers were demonstrated by means of nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). The results of differential scanning calorimetry (DSC) and atomic force microscopy (AFM) indicate that the PS-*b*-PE-*b*-PS triblock copolymers were microphase-separated in bulks and their morphologies were quite dependent on the mass ratios of PE to PS blocks. Transmission electron microscopy (TEM), atomic force microscopy (AFM) and dynamic light scattering (DLS) showed that the triblock copolymers displayed crystallization-driven self-assembly (CDSA) behavior in selective solvent (*viz.* 1,4-dioxane). Depending on the lengths of PS blocks, the CDSA behavior of all the triblock copolymers generated spherical and cylindrical micelles. It was found that the quantity of the cylindrical micelles increased with decreasing the lengths of PS blocks.

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## 1. Introduction

Block copolymers are a class of polymeric assemblies containing two or more subchains which are linked through covalent bonds. Depending on the miscibility of the component subchains, block copolymers can be homogenous or microphase-separated. The formation of microphase-separated morphologies results from thermodynamic immiscibility of subchains [1–7]. The block copolymers with microphase-separated morphologies have found a variety of applications ranging from thermoplastic elastomers, high-impact thermoplastics to pressure-sensitive adhesives. In

addition, the microphase-separated patterns of block copolymers in bulks can also be applied in some advanced technologies such as information storage and photonic crystals. Analogous to low molecular surfactants, amphiphilic block copolymers in solvents selective for one block are self-assembled into micellar nanoobjects, in which the insoluble block forms the cores whereas the soluble constitutes the coronas [8]. Such a micellization behavior has been well studied for many years both from theoretical and from experimental aspects; the approaches to control the morphologies of micellar nanoobjects are well established. The micellar systems of block copolymers can be applied in the aspects of viscosity modification of fluid, cosmetics, lubrication of surfaces, drug delivery and solubilization of insoluble substance [7,9].

The block copolymers containing crystalline subchains are

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highly of interest. In this class of block copolymers, the crystallization of component subchain could be in a confined fashion, depending on its melting and crystallization temperatures, the glass transition temperatures ( $T_g$ 's) of other noncrystalline blocks and the microphase-separated morphologies of the block copolymers [9–12]. In addition, the crystallization of component subchain has a profound impact on self-assembly behavior of block copolymers in selective solvent; a so-called crystallization-driven self-assembly (CDSA) phenomenon would be displayed. The crystallization of insoluble blocks in the process of self-assembly can exert additional variables to affect the morphologies of micelles. Vilgis and Lin et al. [13,14] first rationalized the effect of crystallization on equilibrium parameters of micellization by the use of scaling laws; these theoretical works predicted that spherical, cylindrical, lamellar and platelet micelles can be formed with the CDSA behavior. Recently, these micelles with a variety of morphologies have been reported to form in selective solvents with the block copolymers containing some common crystalline subchains [15] such as poly (ethylene oxide) (PEO) [16–19], poly ( $\epsilon$ -caprolactone) (PCL) [20–24], polylactide [25] and poly (ferrocenyldimethylsilane) (PFS) [26–35].

The block copolymers containing polyethylene (PE) have attracted considerable interest in the past years. For instance, Richter et al. investigated the self-assembly behavior of poly (ethylene-*alt*-propylene)-*block*-polyethylene [P (E-*alt*-P)-*b*-PE] diblock copolymer in decane, a solvent selective for poly (ethylene-*alt*-propylene) block [36]. It was found that the self-assembly of the diblock copolymer was coupled with the crystallization of PE, affording the micrometer-sized platelets with thicknesses of several nanometers. Schmalz et al. [37] reported the formation of worm-like micelles from a polystyrene-*block*-polyethylene-*block*-poly (methyl methacrylate) triblock terpolymer in toluene and tetrahydrofuran solutions. More recently, Yin and Hillmyer et al. [38] reported a comparative investigation of the self-assembly behavior in water of two diblock copolymers containing poly (*N,N*-dimethylacrylamide), other blocks of which were polyethylene (PE) and poly (ethylene-*alt*-propylene) [P (E-*alt*-P)-*b*-PE], respectively. Both of the diblock copolymers had similar composition and overall molecular weights. It was found that disk-like micelles were formed with the diblock containing the crystalline insoluble subchain (*viz.* PE) whereas the spherical micelles were obtained for that containing noncrystalline insoluble block [*i.e.*, P (E-*alt*-P)]. The same investigators [39] found that by varying the composition of poly (*N,N*-dimethylacrylamide)-*block*-polyethylene diblock copolymers, the micellar structures were formed with oblate ellipsoidal, cylindrical, and bilayer morphologies. In all these previous block copolymers, the PE blocks were obtained *via* the hydrogenation of polybutadienes that were synthesized *via* anionic polymerization of 1,3-butadiene. It is known that anionic polymerization of 1,3-butadiene would render 1,2- and 1,4-addition structures, the ratios of which are quite dependent on the polarity of the solvents used [40]. The hydrogenation of 1,4-addition product affords the polymers with the main chain of polyethylene whereas that of 1,2-addition product renders the polymers with the main chain of poly (1-butene) (or poly (ethyl ethylene)). Therefore, the hydrogenated polybutadienes were actually the random copolymers of ethylene with a small amount of 1-butene (or ethyl ethylene). It is such a small number of copolymerization units that would cause a significant depression in melting point and crystallinity of so-called PE chains. It is desirable to obtain the block copolymers, PE block of which had high structural regularity and crystallinity. Hillmyer and Grubbs et al. [41] recently reported the ring-opening metathesis polymerization (ROMP) of cyclooctadiene (COD) by the use of ruthenium-based metathesis catalyst. The ROMP of COD

yielded  $\alpha,\omega$ -difunctional polycyclooctadiene (PCOD), which can be exactly taken as a polybutadiene of 1,4-addition. Therefore, the hydrogenation of  $\alpha,\omega$ -difunctional PCODs will definitely afford an  $\alpha,\omega$ -difunctional PE homopolymers. Such  $\alpha,\omega$ -difunctional PE homopolymers can be used as macromolecular initiators or chain transfer agents to synthesize ABA triblock copolymers with PE midblocks *via* living and controlled radical polymerizations. The ABA triblock copolymers containing PE midblocks can be taken as ideal models to investigate crystallization-driven self-assembly behavior in selective solvents. To the best of our knowledge, there has been no previous report yet.

In this work, we explored to synthesize polystyrene-*block*-polyethylene-*block*-polystyrene (PS-*b*-PE-*b*-PS) triblock copolymers *via* the combination of ROMP and reversible addition-fragmentation chain transfer (RAFT) polymerization. In this first step, an  $\alpha,\omega$ -dihydroxy-terminated polycyclooctadiene (PCOD) was synthesized *via* the ROMP of cyclooctadiene with a sufficiently high molecular weight. Thereafter, the  $\alpha,\omega$ -dihydroxy-terminated PCOD was hydrogenated into an  $\alpha,\omega$ -dihydroxy-terminated polyethylene. The latter was then functionalized into a macromolecular chain transfer agent (denoted Macro-CTA) for the RAFT polymerization of styrene to obtain the PS-*b*-PE-*b*-PS triblock copolymers. To the best of our knowledge, the studies on CDSA behavior of PS-*b*-PE-*b*-PS triblock copolymers have not been reported yet. The goal of this work is to investigate the effect of architecture of ABA triblock copolymer with the insoluble and crystalline midblock on CDSA behavior. The CDSA behavior of the triblock copolymers in 1,4-dioxane was investigated by means of AFM and transmission electron microscopy (TEM).

## 2. Experimental

### 2.1. Materials

1,5-Cyclooctadiene (COD) (99%) and *cis*-2-butene-1,4-diol (>95%) were purchased from TCI Co., Shanghai, China. Before use, COD was distilled over calcium hydride ( $\text{CaH}_2$ ) and *cis*-2-butene-1,4-diol was distilled under reduced pressure. Styrene (S) was purchased from Shanghai Reagent Co., China; before use, the inhibitor was removed by passing the monomer through a neutral alumina column. The Grubbs second generation catalyst (97%) was purchased from Aldrich Co., USA and used as received. 2-Methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid was synthesized by following the method of literature reported by McCormick et al. [42]. All other reagents and solvents used in this work were purchased from Shanghai Reagent Co., China. Before use, toluene, *o*-xylene and tetrahydrofuran were refluxed over sodium and then distilled.

### 2.2. Synthesis of $\alpha,\omega$ -dihydroxy-terminated polycyclooctadiene and polyethylene

To a flame-dried flask, 25 mL of anhydrous chloroform was charged. The solvent was purged with argon for 30 min and then *cis*-2-butene-1,4-diol (0.100 g, 0.68 mmol) and the Grubbs second generation catalyst (4.4 mg, 5.2 mmol) dissolved in 2.0 mL of chloroform were added with vigorous stirring. The flask was immersed in a thermostated bath at 40 °C and then 1.0 mL of COD (8.600 g, 79.6 mmol) was dropwise added. The polymerization was carried out at 40 °C for 10 h and then the reacted mixture was dropwise added to 200 mL of methanol to obtain the precipitates. After dried *in vacuo* at 30 °C for 24 h, the product (8.300 g) (*i.e.*,  $\alpha,\omega$ -dihydroxy-terminated PCOD) was obtained with the monomer conversion of about 95%. FTIR ( $\text{cm}^{-1}$ , KBr window): 3432 ( $\nu_{\text{OH}}$ , R-OH), 3006 ( $\nu_{\text{CH}}$ , H-C=C-H), 1646 ( $\nu_{\text{C=C}}$ , H-C=C-H), 957 ( $\gamma_{\text{CH}}$ ,  $-\text{CH}_2-$ );

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