



PBT-*b*-PEO-*b*-PBT triblock copolymers: Synthesis, characterization and double-crystalline properties



Jiaying Chen^a, Weichun Huang^a, Qiaozhen Xu^a, Yingfeng Tu^{a,*}, Xiulin Zhu^{a,*}, Erqiang Chen^{b,**}

^a Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

^b Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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ABSTRACT

We demonstrated here a facile method to synthesize novel double crystalline poly(butylene terephthalate)-*block*-poly(ethylene oxide)-*block*-poly(butylene terephthalate) (PBT-*b*-PEO-*b*-PBT) triblock copolymers by solution ring-opening polymerization (ROP) of cyclic oligo(butylene terephthalate)s (COBTs) using poly(ethylene glycol) (PEG) as macroinitiator and titanium isopropoxide as catalyst. The structure of copolymers was well characterized by ¹H NMR and GPC. TGA results revealed that the decomposition temperature of PEO in triblock copolymers increased about 30 °C to the same as PBT copolymers, after being end-capped with PBT polymers. These triblock copolymers showed double crystalline properties from PBT and PEO blocks, observed from DSC and WAXD measurements. The melting and crystallization peak temperatures corresponding to PBT blocks increased with PBT content. The crystallization of PBT blocks showed the strong confinement effects on PEO blocks due to covalent linking of PBT blocks with PEO blocks, where the melting and crystallization temperatures and crystallinity corresponding to PEO blocks decreased significantly with increment of PBT content. The confinement effect was also observed by SAXS experiments, where the long distance order between lamella crystals decreases with increasing PBT length. For the triblock copolymer with highest PBT content (PBT₅₄-*b*-PEO₂₂₇-*b*-PBT₅₄), this effect shows a 30 °C depression on PEO crystals' melting temperature and 77% on enthalpy, respectively, compared to corresponding PEO homopolymer. The crystal morphology was observed by POM, and amorphous-like spherulites were observed during PBT crystallization.

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1. Introduction

Double crystalline (crystalline–crystalline) block copolymers are block copolymers that two of the blocks can be crystallized, and have attracted great interests in recent years, since the ultimate phase and crystal morphology are determined not only by phase separation but also the crystallization of both blocks [1–15]. When the melting temperature of one block is far above the other, and the crystallization temperature is between the melting temperature of the two blocks, the first block with higher melting temperature will crystallize without any confinements if the two blocks are miscible

or weakly segregated in the molten state. Due to the chemical linkage between the block segments, confinement effect can be observed when the second block crystallized in the amorphous region confined by the crystals of first blocks [1–5].

For ABA triblock copolymer systems, when the two A blocks at chain end crystallized first, the confinement effect on the middle B block should be more significant compared to AB type block copolymers since the two dangling chain ends of B block are chemically linked on the crystal's surface in ABA copolymers. However, due to the problem in the synthesis of double crystalline triblock copolymers with large crystallization temperature difference and well-defined structure, previous reports on the confinement effect are mainly focused on poly(L-lactide) (PLLA) or poly(ethylene oxide) (PEO) based triblock copolymers since they can be synthesized by ring-opening polymerization (ROP), yet no significant confinement effect is observed [16–21]. For example, Russell et al. reported the synthesis of PLLA-*b*-PEO-*b*-PLLA triblock

* Corresponding authors. Tel./fax: +86 512 65882130.

** Corresponding author. Tel./fax: +86 10 62753370.

E-mail addresses: tuyingfeng@suda.edu.cn (Y. Tu), xlzhu@suda.edu.cn (X. Zhu), eqchen@pku.edu.cn (E. Chen).

copolymers, and found a melting point depression of about 6 °C for each block copolymers compared to corresponding homopolymers [20].

To study the confinement effect on other block copolymer systems, one needs to develop a facile method to synthesize other double crystalline copolymers. Recently, Brunelle et al. reported the synthesis of traditional aromatic polyesters by melt ROP of their corresponding cyclic oligoesters [22–32]. Compared to condensation polymerization, ROP of cyclic aromatic oligoesters offers the advantages of no small molecular byproduct, rapid polymerization rate, and atmospheric pressure reaction conditions [22–39]. However, the application of ROP of cyclic aromatic oligoesters to synthesize structural well-defined block copolymers has not been reported. We believe this ROP method should be applicable to synthesize aromatic polyester-based double crystalline triblock copolymers using dihydroxy-terminated polyether as macroinitiator. On the other hand, since poly(ether–aromatic ester) block copolymers are important industrial copolymers with many applications [40–45], our synthetic method can also be used to synthesize block copolymers with potential applications.

In the current work, a facile route towards the synthesis of poly(ether–ester) triblock copolymers was developed via ROP of COBTs using titanium isopropoxide as catalyst. In order to avoid the transesterification reactions which takes place at the high melting polymerization temperature (~280 °C) [28], a solution polymerization system was selected at much lower polymerization temperature (146 °C) and with 1,1,2,2-tetrachloroethane as solvent. PBT-*b*-PEO-*b*-PBT triblock copolymers with different PBT length but same PEO length were synthesized using PEG as macroinitiator. The structure of the triblock copolymers is well characterized by ¹H NMR, gel permeation chromatography (GPC) and thermogravimetric analysis (TGA). The crystallization behaviours of these double crystalline block copolymers were studied by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS) and polarized optical microscopy (POM). As we expected, significant confinement effect on PEO blocks after PBT crystallized was observed.

2. Experimental section

2.1. Materials

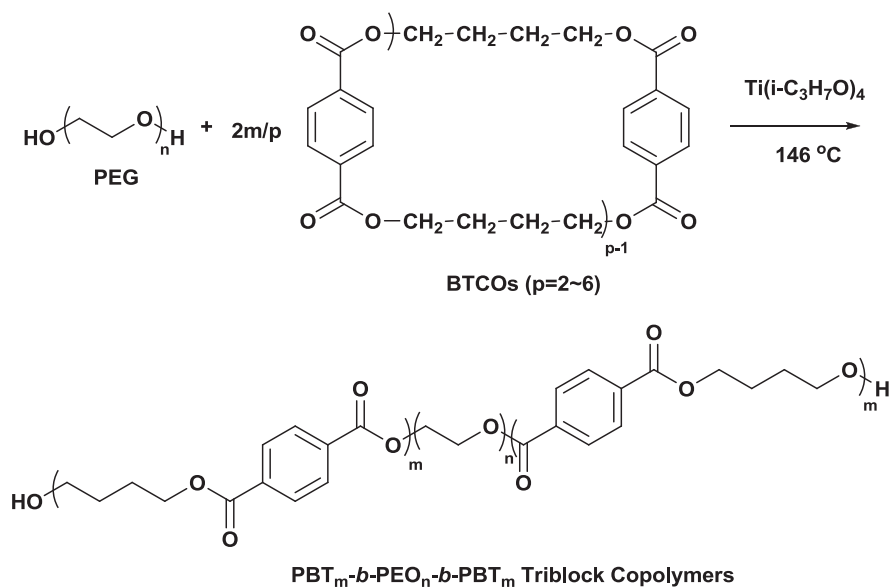
Poly(ethylene glycol) (PEG) with dihydroxyl end groups and number-average molecular weights of 10,000 g/mol was purchased from Alfa Aesar. Cyclic oligo(butylene terephthalate)s (COBTs) were purchased from Star-better (Beijing) Chemical Materials Co., Ltd. Titanium isopropoxide (Aldrich, 99%) and all the other chemicals were used as received.

2.2. Polymerization

Three PBT-*b*-PEO-*b*-PBT triblock copolymers (P1, P2 and P3) with different PBT block length were synthesized according to Scheme 1, by changing the feeding ratio of PEG/COBTs (P1: $W_{\text{PEG}}/W_{\text{COBTs}} = 2/1$, P2: $W_{\text{PEG}}/W_{\text{COBTs}} = 1/1$, P3: $W_{\text{PEG}}/W_{\text{COBTs}} = 1/2$), with PEG ($M_n = 10,000$ g/mol, PDI = 1.03) used as macroinitiator and COBTs as monomer. A typical experimental procedure for the copolymer synthesis is described as follows: in a two-necked 250 ml flask purged with nitrogen, predetermined amount of COBTs, PEG and 1,1,2,2-tetrachloroethane (solid content 15.7 wt%) were charged. The mixture was heated to slightly reflux and titanium isopropoxide (500 μL) was added, after which the solution was kept at the temperature for 4 h under vigorous stirring. The solution was precipitated in petroleum ether, the solid was filtered and extracted by ethyl acetate for 24 h to remove the unreacted PEG and COBTs. The solid was dried under vacuum for 24 h and then stored in a desiccator.

2.3. Characterization

¹H NMR spectra of the copolymers were recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using CF₃COOD/CDCl₃ (1:10 in volume) as the solvent and tetramethylsilane (TMS) as the internal reference at room temperature. GPC experiments were performed on a modular system comprising a Waters 1515 pump, 717 plus autosampler, and 2414 refractive index detector



P1: $m=17$, $n=227$; P2: $m=32$, $n=227$; P3: $m=54$, $n=227$

Scheme 1. Synthetic route of PBT-*b*-PEO-*b*-PBT triblock copolymers via ring-opening polymerization of COBTs with PEG as macroinitiator.

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