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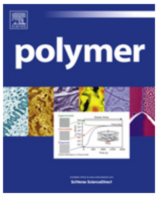

Poly(n-butyl methacrylate) end-capped polyrotaxanes *via* ATRP initiated with α-cyclodextrin and Pluronic 17R4 based inclusion complexes

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ABSTRACT

A series of polyrotaxane (PR)-based triblock copolymers comprising a PR middle block and poly(n-butyl methacrylate) (PBMA) flanked blocks were prepared *via* bulk ATRP of n-butyl methacrylate initiated with polypseudorotaxanes self-assembled from α-cyclodextrins (α-CDs) with 2-bromoisobutyryl terminated Pluronic 17R4 at 35 °C. Their structure was verified by ^{1}H NMR, FTIR, GPC, WXRD and TGA analyses. The dethreading of entrapped α-CDs during the polymerization process was effectively impeded through an elaborated choice of Pluronic 17R4, a PPG–PEG–PPG triblock copolymer, in which α-CDs site-selectively include with the middle PEG block and are inhibited by the flanked PPG blocks. The degree of polymerization of attached PBMA blocks appeared to be tunable to some extent. The polydispersity index of the resulting PR-based triblock copolymers is in a low range of 1.28–1.50. As an attempt toward the materialization of these unique supramolecular polymers, a selected sample was dissolved in methylene dichloride and electrospun into micro-sized particles. Nevertheless, they can be not only casted into tough films but also melt extruded into sticks.

1. Introduction

The concept of rotaxane structure, which consists of a macrocyclic molecule interlocked with a linear axis, was first proposed in 1961 [1] and the first polyrotaxane (PR), which contains multiple cyclic molecules entrapped on a linear axis, was reported in 1967 [2]. However, it was not until 1990s when Harada et al. reported the polypseudorotaxanes (PPRs) made from the self-assembly of α-cyclodextrins (α-CDs) with poly(ethylene glycol) (PEG) [3] that great process has been made in the fabrication of a large variety of PRs with sophisticated structures and functionalities [4–9]. The PR-based triblock copolymers are generally constructed from PPRs by end-capping with polymer blocks *via* atom transfer radical polymerization (ATRP) of vinyl monomers [10–13]. An introduction of ATRP as an end-capping technique in the preparation of PRs offers many advantages over the traditional coupling methods, for instants, it can be carried out in water at room temperature to impede the substantial dethreading of entrapped CDs [12,13], and a vast number of vinyl monomers can be polymerized into the lengthily tunable polymer blocks. Importantly, attaching polymer blocks give birth to a series of novel PR-based triblock copolymers with the distinct characters from those PRs end-stopped by bulky molecules, such as micellization in aqueous solution as carriers for the drug controlled release [14,15], dual thermo- and solvent-responsiveness [16–19], distal PR-based polymeric brushes [20] and nano-reinforcements for polymer matrices [21].

Several PR-based triblock copolymers had been reported in literature. However, almost all of them were end-capped by polymer blocks *via in situ* ATRP of hydrophilic vinyl monomers, such as 2-(dimethylamino)ethyl methacrylate (DMA) [11], 2-hydroxypropyl methacrylate (HPMA) [12], 2-hydroxyethyl methacrylate (HEMA) [13] and N-isopropylacrylamide (NIPAAm) [16–19]. However, those products are generally lack of the sufficient mechanical strength to be subjected to melt extrusion, electrospinning, casting and so forth. Evidently using ATRP of hydrophobic vinyl monomers to end-cap PPRs would provide a variety of intriguing PR-based triblock copolymers because as many hydrophobic vinyl monomers as hydrophilic ones could be polymerized *via* ATRP [22]. It offers a unique opportunity to materialize the CD-based PR species, which were unachievable previously due to their robust hydrogen bond nature [4–6].

To materialize CD-based PR species, Ito et al. had made a great contribution during the past decade in the preparation of topological slide-ring gels [23–30]. The slide-ring gels were made from CD-based PRs, in which entrapped CDs were covalently bonded in a unique manner of figure- of-eight cross-links. It was shown that

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these cross-links can pass along the polymer chains freely to equalize the tension of the threaded polymer chains just like pulleys so that the nano-scale heterogeneity in the structure and stress are automatically equalized in the gel materials. For the PR-based triblock copolymers, however, they not only own a mechanically interlocked structure, but also possess the intrinsic properties of the block copolymers, such as melt extrusion, electrospinning and casting. Until now, there is only one study dealing with using ATRP of hydrophobic methyl methacrylate (MMA) monomer to prepare PR-based triblock copolymers [21]. As the process proceeded in *N*,*N*-dimethylformamide (DMF) at 50 °C, it led to a large amount of CDs to slip off the polymeric chain and resulted in a bimodal molecular weight distribution.

Poly(*n*-butyl methacrylate) (PBMA), a transparent polymeric elastomer at room temperature undergoing a grass transition at around 20 °C, has been extensively investigated due to its sound flexibility and processability [31–34]. Moreover, PBMA can be synthesized *via* ATRP at ambient temperature [35], implying that it is suitable to end-cap PPRs because the dethreading of CDs becomes critical at high temperature. Therefore, incorporating PBMA into PRs would create a series of unique triblock copolymers in which two flanked PBMA blocks play as the soft or elastic segments and a middle PR block acts as the rigid or hard segments. Herein the PR-based triblock copolymers end-capped by hydrophobic PBMA were prepared *via* bulk ATRP of BMA initiated by PPRs self-assembled from α-CDs with 2-bromoisobutyryl terminated Pluronic 17R4 at 35 °C in this study. At first an inclusion complex (IC) formed from α-CD with 2-bromoiso- butyryl terminated PEG was chosen as initiator to initiate ATRP of BMA either in DMF or in bulk. However, few α-CDs were found to be entrapped on the PEG chain after the process, possibly due to fact that BMA competes with the guest polymer for α-CDs leading to the severe dethreading of α-CDs [4]. Alternatively, a reverse Pluronic named Pluronic 17R4 (PPG_{14}–PEG_{24}–PPG_{14}) was used because α-CDs can site-selectively include with the middle PEG block to be inhibited by the flanked PPG blocks in ATRP of BMA [36–39]. As the end-capping process proceeded in bulk rather than in DMF or DMSO, the dethreading of α-CDs induced by solvents was greatly depressed. Furthermore, the reaction temperature set at 35 °C not only reduced the dethreading of α-CDs caused by higher temperature, but also guaranteed the reaction to proceed as quickly as possible.

2. Experimental

2.1. Materials

Pluronic 17R4 (Sigma, USA) was dried at 80 °C under vacuum. Its molecular weight is ca. 2700 and the content of PEG is 40 wt%. α-CD (WAKO, Japan) was used as received without further purification. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA) and 2-bromoiso- butyryl bromide were purchased from Sigma, USA. *n*-Butyl methacrylate (BMA) (Acros, Belgium) was washed with NaOH aqueous solution, dried with CaH_2 and distilled at reduced pressure. Triethylamine (TEA) (VAS Chemical Reagents Company, Tianjin, China) was refluxed with p-toluenesulfonylchloride and distilled under vacuum. Tetrahydrofuran (THF) was refluxed with Na and distilled before use. All other solvents and reagents were of analytical grade.

2.2. Synthesis of 2-bromoisobutyryl terminated Pluronic 17R4 macroinitiator (BrB–17R4–BBr)

Pluronic 17R4 was converted to the corresponding ATRP macroinitiator by the end-capping reaction with an excess amount of 2-bromoisobutyryl bromide in dry THF as follows: In a 100 ml three-neck round-bottom flask, Pluronic 17R4 (5.36 g, 2.0 mmol) was dissolved in dry THF (40 ml). After 10 min stirring in ice bath under nitrogen, TEA (0.61 g, 6.0 mmol) was added, to which 15 ml dry THF containing 2-bromoisobutyryl bromide (1.38 g, 6.0 mmol) was added dropwise under nitrogen. The reaction continued for 2 h at 0 °C and for another 24 h at room temperature under stirring. Finally, the mixture was centrifugated to remove the precipitated salt and the residual solvent was removed by rotary evaporation. The purified product was dried under vacuum, yield 90.4%. ^{1}H NMR analysis was used to calculate the degree of esterification (>98%). ^{1}H NMR (DMSO–d_6, 400 MHz): δ: 1.03–1.04 (*d*, 74H, $-CC(CH_3)O-$), 1.86 (*s*, 12H, $-C(CH_3)_2Br$), 3.41–3.51 (*m*, 180H, $-CH_2CH_2O-$ and $-CH_2CH(C)O-$) ppm.

2.3. Preparation of PPR comprising α-CDs and BrB–17R4–BBr

Pluronic 17R4 is soluble in water at room temperature. However, upon converting into a macroinitiator, BrB–17R4–BBr becomes insoluble in water at room temperature. Therefore, the self-assembly of α-CDs with BrB–17R4–BBr proceeded at 5 °C according to literature [38] as follows: BrB–17R4–BBr (0.596 g, 0.2 mmol) was added to 12 ml of α-CD (1.167 g, 1.2 mmol) aqueous solution in a centrifuge tube, followed by vigorous stirring for 24 h to produce PPR precipitates. The feed molar ratio of α-CD to BrB–17R4–BBr was kept at 6:1 in this paper. The precipitated PPR was collected by centrifugation and lyophilized. Yield, ca. 0.289 g. For the convenience of expression, the resulting PPR was designated as R-PPR6, where R stands for Pluronic 17R4 containing macroinitiator and 6 is the feed molar ratio of α-CD to BrB–17R4–BBr. ^{1}H NMR (DMSO–d_6, 400 MHz): δ: 1.04–1.05 (*d*, 74H, $-CC(CH_3)O-$), 1.88 (*s*, 12H, $-C(CH_3)_2Br$), 3.41–3.51 (*m*, 180H, $-CH_2CH_2O-$ and $-CH_2CH(C)O-$), 4.48 (*s*, 6 *n*H, –O(6)H of α-CD), 4.80–4.81(*d*, *n*6H, C(1)H of α-CD), 5.49 (*s*, 12 *n*H, –O(2)H and –O(3)H of α-CD) ppm.

2.4. Synthesis of PR-based triblock copolymer via ATRP of BMA in bulk

The procedure for preparation of R6CD400B was given below as a typical example. In a sealable Pyrex reactor containing R-PPR6 (0.221 g, ca. 2.52×10^{-5} mol), BMA (1.43 g, 10.1 mmol) was added before PMDETA (10.5 mg, 6.07×10^{-5} mol) was added. The mixture was stirred for 10 min before quenched in liquid nitrogen and Cu(I)Br (7.2 mg, 5.04×10^{-5} mol) was added, followed by degassing three times using a nitrogen purge. The reactor was sealed under vacuum and the reaction started and maintained at 35 °C for 12 h. The polymerization stopped after breaking the Pyrex reactor. The crude product was dissolved in 20 ml dry chloroform and washed with water by vigorous stirring and ultrasonication, centrifugated to remove the catalysts and water. The purification process repeated three times. Finally, the product was precipitated from chloroform with anhydrous methanol and dried under vacuum. Yields and compositions are presented in Table 1. ^{1}H NMR (DMSO–d_6/$CDCl_3$ (1:1 in volume), 400 MHz): δ: 0.75 (*s*, 3 *m*H, $-CH_3$ of *n*-butyl), 0.89 (*s*, 3 *m*H, $-CC(CH_3)C-$ of BMA), 1.03–1.04 (*d*, 74H, $-CC(CH_3)O-$), 3.86 (*s*, 2 *m*H, $-OCH_2C-$ of *n*-butyl), 3.32–3.35 (*m*, 12 *n*H, C(2)H and C(4)H of α-CD), 3.62–3.69(*m*, 18 *n*H, C(5)H, C(6)H, and C(3)H of α-CD), 4.81 (*s*, 6 *n*H, C(1)H of α-CD) ppm.

For the convenience of expression, the obtained PR-based triblock copolymer were designated as RnCDmB, where R means BrB–17R4–BBr, *n* stands for the feed molar ratio of α-CD to BrB–17R4–BBr and *m* stands for that of BMA to BrB–17R4–BBr. CD and B represent α-CD and BMA, respectively. As the entrapped α-CDs may slip to the PPO segments, the whole PPRs formed from α-CD and Pluronic 17R4 were considered as a middle segment in the resulting PR-based triblock copolymers.