

Novel triblock copolymers synthesized via radical telomerization of *N*-isopropylacrylamide in the presence of polypseudorotaxanes made from thiolated PEG and α -CDs

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Abstract

A protocol for the preparation of novel triblock copolymers comprising a polyrotaxane center block and outer blocks of poly(*N*-isopropylacrylamide) (PNIPAAm) as bulky stoppers was developed, in which *N*-isopropylacrylamide was allowed to telomerize in the presence of polypseudorotaxanes made from the self-assembly of thiol end-capped PEG with a varying amount of α -CDs under UV irradiation in aqueous solution. The molecular structure of the resulting copolymers was characterized in detail by ^1H NMR, FTIR, XRD, TG and DSC analyses. It was demonstrated that the PNIPAAm blocks are successfully attached to the two terminals of the polypseudorotaxanes and each block having the minimum 7 NIPAAm units seems long and bulky enough to efficiently impede the dethreading of α -CDs from the PEG axle to give rise to the triblock polyrotaxane-containing copolymers.

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1. Introduction

Polyrotaxanes and polypseudorotaxanes are topological molecules composed of macrocycles threaded onto linear polymer backbones without covalent bonds linking these two species. Their unique molecular architecture related to cyclodextrins (CDs) has drawn extensive interests since the first account reported in the 1990s [1], because of their prospective applications as stimuli-responding systems [2–4], polyrotaxane networks [5,6], biosensors [7,8], tissue engineering scaffolds and carriers for drug controlled release [9,10]. As is well known, the end-capping is a common measure to hold back the dethreading of CDs from polymer axles during the process of polyrotaxane preparation and application. A number of methods have been tried for the rapid and efficient end-capping manipulation [1,11–13]. Recently, a method which

involves an initial conversion of a hydroxyl terminated PEG into a ditosylated PEG, threading it into the cavity of a commercially available unprotected cyclodextrin, and then displacement of the tosyl end groups with bulky blocking groups has been disclosed [14]. An effective and convenient method for the end-capping of polypseudorotaxanes using cyclodextrins not only as macrocyclic molecules but also as stoppers has also been reported [15]. Alternatively, we have recently prepared and identified a series of supramolecular structured hydrogel networks based on photocurable polypseudorotaxanes using cross-linking junctions as topological stoppers [16–18].

As well documented, poly(*N*-isopropylacrylamide) (PNIPAAm) is a class of stimuli-sensitive polymers showing a lower critical solution temperature (LCST) around 32 °C in water [19]. Below this temperature, the polymer molecular chains start to unfold, while above that, they collapse. So a phase-transition process occurs within a specific temperature range. Meanwhile, thiols are long known as very important multifunctional reagents in the fields of organic and polymer

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synthetic chemistry [20,21]. In particular, the radical telomerization involving thiol compounds and alkene monomers has been widely used to prepare a great variety of block copolymers or crosslinked networks [22–24]. Our interest, however, lies in taking advantage of this unique radical telomerization technique to attach the temperature-sensitive PNIPAAm block to each terminal of polypseudorotaxanes made from the self-assembly of thiolated PEG with a varying range of α -CDs to synthesize a kind of novel triblock copolymers, PNIPAAm-*b*-polyrotaxane-*b*-PNIPAAm, where polyrotaxane as a center block and outer blocks of PNIPAAm as bulky stoppers to prevent the dethreading of α -CDs from the polymeric axle. Here, it is not necessary to protect α -CDs due to their hydroxyl groups incapable of reacting with vinyl monomers under the reaction conditions. To our best knowledge, polymer blocks have not yet been reportedly used as stoppers in the preparation of polyrotaxanes. On the other hand, incorporating different lengths of stimuli-responsive polymer blocks into polypseudorotaxanes not only yields a kind of novel polyrotaxanes but also endows the triblock copolymers the new properties.

2. Experimental section

2.1. Materials

N-Isopropylacrylamide (NIPAAm) (Acros, Belgium) was purified by recrystallization from *n*-hexane. α -CD (Sigma, USA) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Fluka, Switzerland) were used as received. PEG (PEG 4k, $M_n = 4000$) was imported from Japan and distributed domestically. *p*-Toluenesulfonic acid and thioglycolic acid were supplied by VAS Chemical Reagents Company, Tianjin, China. Thioglycolic acid was distilled under reduced pressure before using. All other solvents and reagents were of analytical grade.

2.2. Preparation of thiolated PEG

PEG 4k was chain-end thiolated by esterification reaction using thioglycolic acid in the presence of *p*-toluenesulfonic acid as a catalyst. Briefly, 10 mg *p*-toluenesulfonic acid, 10 g of PEG 4k, and 1.38 g thioglycolic acid were added to 100 ml of toluene preheated to 120 °C. The reaction was allowed to proceed for 10 h under nitrogen atmosphere and driven forward by the continuous removal of water produced. The thiolated polymer was purified by precipitation in anhydrous ether (200 ml) at 5 °C. This sequence was repeated three times using dichloromethane as a solvent. The product was then dried under vacuum at room temperature for 2 days with a yield of 92%. FTIR/cm⁻¹: 2866 (CH₂, CH₃), 1736 (C=O), 1109 (C–O); ¹H NMR (CDCl₃)/ppm: δ 4.298 (s, 4H, –CH₂–O–C(=O)–), 3.645–3.819 (m, 360H, –OCH₂–CH₂–O–), 3.298 (s, 4H, –O–C(=O)–CH₂–), 2.010–2.050 (t, 2H, –SH). The GPC result showed a unimodal peak with a polydispersity index of 1.02.

2.3. Preparation of polypseudorotaxane

A saturated aqueous solution containing a predetermined amount of α -CDs was added to a certain volume of 20 wt% PEG-thiolated polymer solution in water at room temperature. The resulting mixture was sonicated for 10 min and then allowed to stand for gelation. Gelation took place rapidly to yield a physical hydrogel because of the supramolecular self-assembly between α -CDs and the thiolated PEG 4k. The gel was washed with a small amount of distilled water and then directly freeze-dried to give rise to a polypseudorotaxane.

2.4. Synthesis of triblock polyrotaxane-containing copolymer

Firstly, a physical gel was formed upon mixing a certain volume of 20 wt% thiolated PEG 4k aqueous solution with a predetermined amount of α -CDs in water. Secondly, a calculated volume of 20 wt% NIPAAm aqueous solution together with an appropriate amount of photo initiator solution of 2,2-dimethoxy-2-phenyl acetophenone (DMPA) in *N*-vinylpyrrolidone (10 mg/ml) was directly added to the resultant physical gel, vigorously stirred, and then exposed to 365 nm UV lamp of 20 W (Institute of Electric-Light Resources, Beijing, China) for 30 min. After centrifugation, the precipitate was collected by filtration, washed with deionized water, and freeze-dried at –50 °C to give white powder. The powder product was further purified by the following sequence: 0.5 g crude freeze-dried product was dissolved in 20 ml DMSO and allowed to stand for 12 h at 60 °C. Afterwards, the solution was dropped into 200 ml of acetone to give rise to white precipitate again. The precipitate formed was collected by filtration and washed with 50 ml of cold water three times to yield the target triblock copolymer.

For the sake of expression, the triblock polyrotaxane-containing copolymers were designated as *m*-*x*CD-*m*, where *m* stands for the feeding molar ratio of the monomer NIPAAm to –SH in the thiolated PEG, and *x* for that of α -CDs added to the thiolated PEG. For comparative purposes, PNIPAAm and the corresponding triblock copolymers without α -CDs were prepared in acetone, precipitated in cooled hexane and dried under vacuum at 30 °C until constant weight. These triblock polymers without α -CDs were named as *m*-0CD-*m*, where *m* bears the same meaning as the foregoing.

2.5. Measurements

¹H NMR (400 MHz) spectra was recorded as solutions using a Bruker ARX 400 NMR instrument at room temperature with DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as internal standard. FTIR spectra were measured using Shimadzu IR Prestige-21 FTIR spectrometer at room temperature in the range between 4000 and 500 cm⁻¹, with a resolution of 2 cm⁻¹ and 20 scans. Powder samples were prepared by dispersing the samples in KBr and compressing the mixture to form disks.

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