

Synthesis, photochemical properties, and self-assembly of diblock copolymer bearing azobenzene moieties



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ABSTRACT

This study describes the synthesis of an azobenzene-containing diblock copolymer, poly(StO₅₀-*b*-Azo₇), by using the macro-chain transfer agent StO macro-CTA, and employing sequential reverse addition-fragmentation transfer (RAFT) polymerization. We studied the effects of azobenzene (azo) unit on *E/Z* photoisomerization, the phase transition temperature, and self-assembly behavior of diblock copolymer, and evaluated the characteristic time involved in the decay process of the photoisomerization kinetics of diblock copolymer. Diblock copolymer poly(StO₅₀-*b*-Azo₇) exhibited moderate thermal stability, with thermal decomposition temperature of 5% weight loss at approximately 340.9 °C, suggesting that the enhancement of the thermal stability was attributed to the incorporation of azo segments into block copolymer. The diblock copolymer showed lower *E-Z* photoisomerization rates ($T_1 = 68.0$ s) compared with azo monomer ($T_1 = 10.95$ s). Gradually adding water to the tetrahydrofuran (THF) solution of poly(StO₅₀-*b*-Azo₇) produced spherical micelles. Spherical aggregates of poly(StO₅₀-*b*-Azo₇) were obtained (mean diameter = approximately 181.4 nm) by diluting the polymer disperse in a mixture of THF/H₂O (water content = 10 vol%), and are shown in TEM images of the diblock copolymer. The results of this study contribute to research on the development of photoresponsive polymer materials.

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1. Introduction

Applying block polymers containing azobenzene (azo) chromophores as photosensitive materials has gained considerable academic and industrial attention in the past decade because such polymers exhibit favorable properties such as the photo induced orientation of the azo chromophores, liquid crystallize anisotropy, photomechanical bending, and surface-relief grating formations [1–4]. Ultraviolet (UV) light induced changes in configuration of polymer chains, resulting in *E-Z* isomerization or disorganization of chromophore fragments such as azo and stilbene, can be applied to provide a motor function for contractions in photoresponsive materials [5,6].

The self-assembly of block copolymers into various microphase-segregated nanostructures, such as spheres, cylinders, gyroids, and lamellae, has been widely researched as a novel approach to chemical synthesis, nanofabrication, and other applications in materials science [7–10]. Previous studies have prepared amphiphilic block copolymers

by using techniques such as anionic living polymerization [11,12], atom transfer radical polymerization (ATRP) [13–18], and reversible addition-fragmentation chain transfer (RAFT) [19–22]. Living free radical polymerization techniques, such as nitroxide-mediated polymerization [23,24], ATRP [25–28], RAFT [29,30], and single-electron transfer living radical polymerization [31–33] have been widely used to generate complex macromolecular architectures with well-defined end groups of narrow polydispersity. These techniques facilitate additional control in designing advanced core-shell microspheres and functional particles. RAFT polymerization is a powerful tool for controlling the manipulation of macromolecular architectures, because it can polymerize various monomers. Furthermore, it exhibits tolerance toward a wide range of functional groups and facilitates the preparation of block copolymers exhibiting narrow polydispersity indices (PDIs) [34]. In addition, no impurity or residual reagent (e.g., ATRP metal ions, dipyriddy ligands) need be removed from the polymerization product, and the reaction temperature is relatively low (typically between 60 °C and 70 °C). The availability of RAFT components has led to an increase in reports on the synthesis of block copolymers composed of azo polymer and other segments. Recently, Zhao et al. [35] employed the RAFT technique to prepare novel side-chain liquid crystalline (LC) diblock copolymers (PAzoMA-*b*-PBiPMA) by using 2-(2-cyanopropyl) dithiobenzoate as the RAFT agent. The results of that study verified that the photo induced orientation of

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azo mesogens in PAzoMA could propagate through the interface into microphase-segregated PBiPMA domains, thereby aligning the orientation of biphenyl mesogens in PBiPMA. Zhu et al. [36] employed the RAFT technique to synthesize polystyrene with a terminal functionalized with an azo structure, and achieved enhanced fluorescence emission after UV irradiation. Ikeda and his coworkers [8] synthesized an azo-based LC diblock copolymer (PEO-*b*-PM11AzCN), demonstrating that the supramolecular-ordered nanostructures that can hierarchically assemble in block copolymer films are widely used as templates or scaffolds to prepare nanomaterials according to supramolecular cooperative motions.

In our previous report [37], we examined the effects of terminal groups and spacer length of low molecular weight azo chromophore structures on photoreactivity and mesomorphic properties. We found that M6 with six methylene segments as spacer and with electron-donating (methoxy) terminal group showed a steady state for *Z*-*E* isomerization in darkness after 54 h. We investigated the temperature dependence of selective light reflection of cholesteric LCs. We also used the conventional radical polymerization method to synthesize photoisomerizable LC polymers (CP3–CP5) containing cinnamoyl groups by using 2,2'-azoisobutyronitrile (AIBN) as the initiator, and performed *E*-*Z* photo stationary states within 10–20 m of UV irradiation ($\lambda_{\text{irr}} = 300$ nm). However, these LC polymers showed extremely little self-assembled aggregates in aqueous solution [38]. Based on the original investigations above, in this study, we employed a two-step RAFT polymerization technique to synthesize a macro-chain transfer agent, StO macro-CTA, and a novel azo block copolymer, poly(StO₅₀-*b*-Azo₇). The azo structures rendered the diblock copolymer photoactive, facilitating our investigation of the effects of azo on *E*/*Z* photoisomerization, as well as the self-assembly behavior of diblock copolymer at various THF/H₂O concentrations. We observed that poly(StO₅₀-*b*-Azo₇) and Azo monomer exhibited the steady state during *Z*-*E* isomerization in darkness after 13.0 h and 52.0 h, respectively, implying that Azo monomer used a rotation mechanism with high potential energy profile to achieve a slower rate of *Z*-*E* isomerization in darkness than poly(StO₅₀-*b*-Azo₇) did [39–41]. Meanwhile, poly(StO₅₀-*b*-Azo₇) exhibited a high photo induced response and rapid microphase separation, indicating the practical potential of these copolymers for use in photosensitive materials. Also remarkably, poly(StO₅₀-*b*-Azo₇) containing azo chromophores have been demonstrated to integrate the photoresponsive properties of azo polymers with the self-assembling characteristics of block copolymers through the use of RAFT techniques.

2. Experimental

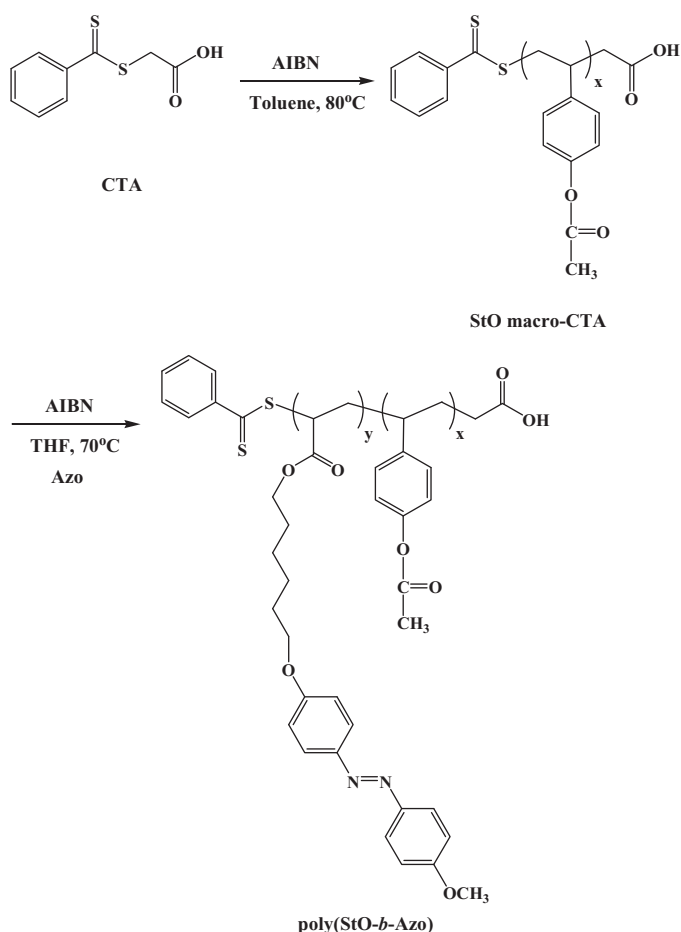
2.1. Materials

Synthetic routes for the target StO macro-CTAs and diblock copolymer are shown in Scheme 1. 4-Acetoxy styrene (StO) was stirred over CaH₂ overnight and distilled under reduced pressure prior to use. AIBN was recrystallized from methanol twice. All organic solvents and reagents were purchased from Acros, Alfa, and Aldrich Chemical Co. and used without further purification. Toluene and THF were dried with appropriate drying agents, calcium hydride or sodium, then distilled under reduced pressure and stored over 4 Å molecular sieves before use. 6-(4-Methoxy-azobenzene-4'-oxy) hexyl acrylate (Azo) was synthesized following the processes reported in the literature [39] and our previous reports [37,42].

2.2. Synthesis of polymers (Scheme 1)

2.2.1. Synthesis of macromolecular chain transfer agents (StO macro-CTAs)

A Schlenk tube was charged with StO (2.0 g, 12.3 mmol), thiobenzoylmercaptoacetic acid (CTA) (0.0261 g, 0.123 mmol), AIBN



Scheme 1. Synthetic routes of StO macro-CTA and diblock copolymer.

(0.0202 g, 0.123 mmol), toluene (20.0 mL) and a magnetic stirrer. The composition monomer/CTA/AIBN was used as 100/1/1 in molar ratio. The mixture was purged with dry nitrogen and subjected to three freeze–pump–thaw cycles to remove any dissolved oxygen. Then the tube was sealed under vacuum and immersed in an oil bath at 80 °C. The polymerization times are in the range of 4–48 h. The reaction was stopped and the tube was quickly cooled down to the room temperature with cold water. The mixture was poured into excess cold methanol. The product was purified by reprecipitating twice from chloroform to cold methanol and dried in vacuum at room temperature overnight. Monomer conversion was determined using ¹H NMR, and polystyrene-equivalent molecular weights of all polymers were determined using GPC. For kinetic studies, the same procedure was adopted as described above except aliquots were taken at predetermined intervals and the conversion and molecular weights were determined by ¹H NMR analyses.

2.2.2. Synthesis of diblock copolymer (poly(StO₅₀-*b*-Azo₇))

The typical experiment was as follows: Azo (1.0 g, 2.6 mmol), StO macro-CTA (100 mg), AIBN (10.0 mg, 0.061 mmol) and 10 mL anhydrous THF were added in a Schlenk tube. After degassing with three freeze–pump–thaw cycles, the tube was sealed under vacuum and immersed into an oil bath at 70 °C for 48 h. The mixture was diluted with THF and then dropped into diethyl ether. The product was purified by reprecipitating twice from THF to cold diethyl ether and dried in a vacuum oven at room temperature overnight. Yield: 41.6%. G 96.5 °C S_A 135.6 °C I (heating). $\lambda_{\text{max}} = 358$ nm. ¹H NMR: (acetone-*d*₆, δ in ppm): 6.38–7.10 (br, aromatic, Ar-H), 3.86–4.03 (br, 4H, -OCH₂-), 3.81–3.85 (br, 3H, OCH₃), 2.30 (s, 2H, -CH₂COOH),

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