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Photoresponsive diblock copolymers bearing strong push–pull azo chromophores and mesogenic biphenyl groups

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ABSTRACT

A series of diblock copolymers bearing strong push–pull azo chromophores and mesogenic biphenyl groups in the respective blocks was synthesized by reversible addition fragmentation chain transfer polymerization through two successive polymerization steps. All the diblock copolymers with different ratios of the block lengths exhibited photoinduced birefringence behavior similar to a corresponding azo homopolymer. After switching off the irradiation light, the birefringence relaxation of the diblock copolymers was found to be much smaller compared with that of the azo homopolymer, which is a very attractive advantage for photo-storage applications. On the other hand, the surface-relief-grating formation observable for azo homopolymer could not be detected for the diblock copolymers. The results indicate that the photoresponsive properties of the azo polymer block are closely related with the phase-separated structure of the diblock copolymers and can be further optimized to meet the requirement for specific applications.

1. Introduction

Polymers containing azobenzene and its derivatives (azo polymers for short) are well-known for their photoresponsive properties [1–3]. The responsive variations induced by light irradiation include phase transition [4], chromophore orientation [5], surface-relief-grating (SRG) formation [6,7], photo-mechanical thin film contraction and bending [8–10], and photoinduced colloidal deformation [11,12] among many others. These unique properties of azo polymers have been intensively investigated in recent years for many potential applications [2,3]. Azo polymers with different molecular architectures, such as side-chain polymers, main-chain polymers, dendritic polymers and block copolymers, have been prepared to understand the structure–property relationship and optimize useful properties [2,3,13–16]. Among them, the azo block copolymers are attracting most recent attention for their unique architecture and properties [16]. The hierarchical structures of block copolymers from molecule to condensed phase play a critical role to affect the photoresponsive properties. Depending on composition, block lengths and functional groups, azo block copolymers can form different phases and aggregation states that control the photoresponsive and other properties [16–18]. Synthesizing azo block copolymers with novel molecular architectures and aggregated structures is necessary to understand the structure–property relationship of this new type of materials. The photoresponsive properties of azo block copolymers are of particular interest for device applications.

The block copolymers containing strong push–pull azo chromophores possess the photoresponsive properties related to the unique feature of the functional groups. According to the spectroscopic features and isomerization behavior, the strong push–pull azo chromophores can be classified as the pseudo-stilbene type [19]. Typical photoresponsive properties, such as photoinduced orientation [2,3,5], SRG formation [6,7], photoinduced colloidal deformation [11,12], and optical nonlinearity [20,21] can be observed for the polymers containing strong push–pull azo chromophores. The photoinduced orientation and SRG formation have been intensively studied as promising properties for applications in optical data-storage, holography and others [1–3]. The preferential orientation of the azo chromophores in a direction perpendicular to the light polarization is caused by repeated *trans–cis–trans* isomerization cycles due to light irradiation [2,3]. The chromophore orientation can also cause correlative alignments of adjacent groups or segments in the azo polymers, especially liquid crystalline (LC) azo polymers. The SRG formation is attributed to the mass-transport of the azo polymers driven by an interfering light field [2,3]. However, because of the less linear shape and strong dipole–dipole interaction, the polymers functionalized with the strong

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push–pull azo chromophores usually do not form an LC phase [2]. This is different with polymers containing mesogenic azobenzene groups, which is a typical type of side-chain liquid crystalline polymers reported in previous articles [17,18,22–25].

By covalently linking a block bearing push–pull azo chromophores with a block containing mesogenic units, various LC/isotropic (I) block copolymers can be developed. The LC blocks of the copolymers tend to form the ordered sub-phase owing to the anisotropic alignment of the mesogens. As isotropic azo blocks are highly immiscible in the LC phase, the systems will strongly segregate to form a microphase-separated morphology. The LC order and phase-separated confinement which exist in such systems can result in a rich variety of morphologies and nanostructures [26–30]. This molecular design strategy is expected to introduce unique photoresponsive properties related to the strong push–pull azo chromophores into a variety of nanostructures formed from the block copolymers. Recently, we have synthesized a series of LC/I diblock copolymer bearing cholesteryl and strong push–pull azo chromophores on the side-chains of the respective blocks [31]. The diblock copolymers with different ratios of the two blocks exhibit different hierarchical structures, the azobenzene-containing blocks are confined in different microphase-separated structures. The biphenyl group is a typical mesogenic unit that has been widely used to construct LC polymers. However, to our knowledge, the block copolymers composed of both push–pull azo chromophores and biphenyl groups in respective blocks have not yet been reported in the literature.

In this study, a series of diblock copolymers composed of a block bearing pseudo-stilbene type azo chromophores and the other block containing side-chain biphenyl mesogens were synthesized. The diblock copolymers (PBiPMA$_{50}$-*b*-PAzoCN$_x$), poly(6-(4-(4′-cyanophenyl)phenoxy)hexyl methacrylate)-*block*-poly(6-(*N*-methyl-*N*-(4-(4′-cyanophenylazo)phenyl)amino)hexyl methacrylate), were synthesized by RAFT polymerization (Scheme 1). For the synthesis, a macromolecular chain transfer agent (PBiPMA$_{50}$-CTA) was prepared and a series of the block copolymers with different lengths of the azo blocks was prepared by using the different feed ratios of the azo monomers to PBiPMA$_{50}$-CTA in the second step of the RAFT polymerization. The phase behavior, LC mesophases and photoresponsive properties of the diblock copolymers were studied and compared with the homopolymers corresponding to the two blocks.

2. Experimental part

2.1. Block copolymer synthesis

2.1.1. Materials

Anisole was distilled from sodium prior to use and the other solvents were flash distilled before use. AIBN was recrystallized from anhydrous methanol before use. The starting chain transfer agent 2-(2-cyanopropyl) dithiobenzoate (CPDB) and the monomers, 6-(4-(4′-cyanophenyl)phenoxy)-hexyl methacrylate (BiPMA) and 6-(*N*-methyl-*N*-(4-(4′-cyanophenylazo)phenyl)amino)hexyl methacrylate (AzoCN) were synthesized according to literature method [32–34]. All other reagents and chemicals were purchased from commercial sources and used as received without further purification.

2.1.2. PBiPMA-CTA

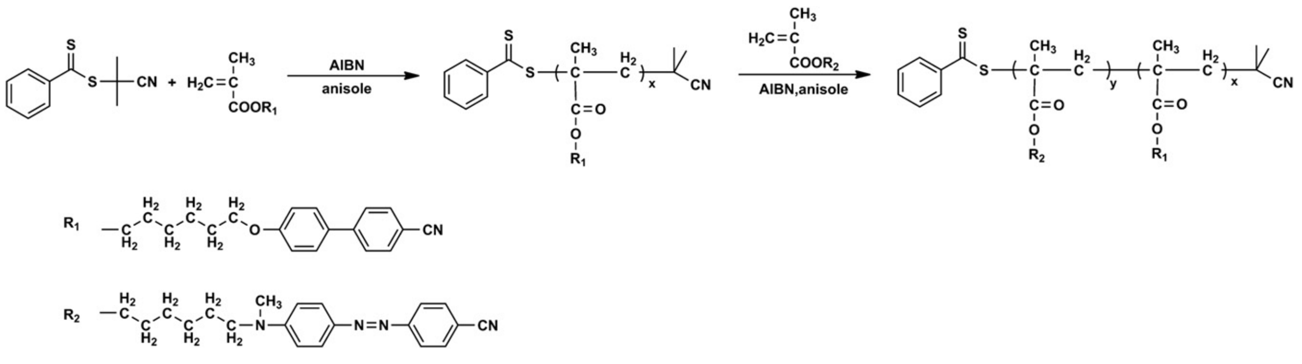
The macromolecular chain transfer agent was obtained by RAFT polymerization of the BiPMA using CPDB as the starting chain transfer agent. BiPMA (1.817 g, 5 mmol), AIBN (3.3 mg, 0.02 mmol) and CPDB (22.1 mg, 0.1 mmol) were added into a 50 mL Schlenk flask, followed by the addition of anisole (3 mL). The mixture was degassed by three freeze–pump–thaw cycles and sealed under vacuum. The flask was then placed in an oil bath set at 75 °C for 5 h and then the reaction was halted by cooling the flask with ice water. A small amount of the solution from the flask was collected for ^{1}H NMR measurement. The conversion of the monomers was calculated by Eq. (1) on the basis of the integration of the peak at 6.10 ppm ($I_{6.10}$) representing a vinyl proton from the methacrylate group of the remnant monomer and that of the peak at 6.88 ppm ($I_{6.88}$) corresponding to the two protons of the phenyl group at the ortho-position to the ether group.

$$\text{conv}\,(\%) = (1 - 2 \times I_{6.10}/I_{6.88}) \times 100\% \qquad (1)$$

The conversion estimated by this method was approximately 100%. The reaction solution was diluted with THF and precipitated into hexane to obtain the crude product. The crude product was then purified by dissolving in THF and precipitating with hexane again. The purification procedure was repeated for three times and the polymer was dried in a vacuum oven at 50 °C for 24 h. M_n (GPC) = 16,500, M_w/M_n (GPC) = 1.15. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 7.81–7.42 (overlap), 7.10–6.79 (m), 4.38–3.51 (m), 2.20–0.45 (broad). FT-IR (KBr cm^{-1}): 2939, 2860, 2224, 1724, 1603, 1522, 1495, 1396, 1250, 1180, 1059.

2.1.3. PAzoCN

The azo homopolymer was prepared for comparison with the diblock polymers. It was synthesized by using a similar procedure as the PBiPMA-CTA synthesis. AzoCN (2.02 g, 5 mmol), AIBN (1.6 mg, 0.01 mmol), and CPDB (11.1 mg, 0.05 mmol) were added into a 50 mL Schlenk flask, followed by the addition of anisole (2.5 mL). The mixture was degassed by three freeze–pump–thaw cycles and sealed under vacuum. The flask was then placed in an oil bath set at 75 °C for 72 h, and then the reaction was halted by cooling the flask with ice water. The reaction solution was diluted



Scheme 1. Synthetic route for the diblock azo copolymers.