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Synthesis of well-defined easily crosslinkable azobenzene side-chain liquid crystalline polymers via reversible addition–fragmentation chain transfer polymerization and photomechanical properties of their post-crosslinked fibers

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ABSTRACT

The synthesis of a series of well-defined easily crosslinkable azobenzene (azo) side-chain liquid crystalline polyacrylates (including both homopolymers with an *N*-hydroxy-succinimide carboxylate-substituted azo mesogen and copolymers with both the above crosslinkable azo mesogen and a non-crosslinkable azo mesogen) via reversible addition–fragmentation chain transfer (RAFT) polymerization and photomechanical properties of their post-crosslinked fibers are described. The RAFT polymerizations of the azo monomers proved to be living and well-controlled, as revealed by their linear kinetic plots as well as the linear increase of the molecular weights of the azo polymers with monomer conversions and their low molar-mass dispersities ($D \leq 1.17$). All the obtained azo polymers exhibited high thermal stability and relatively low glass transition temperatures, but only the azo homopolymers with longer flexible spacers and azo copolymers showed liquid crystallinity. In addition, the crosslinked azo polymer fibers with easily controlled diameters and high alignment order were obtained by the first fabrication of the uncrosslinked azo polymer fibers by the simple melt spinning method and their subsequent crosslinking with a difunctional primary amine under mild conditions. The contents of the crosslinkable azo mesogen in the polymers had significant influence on the photomechanical properties of their post-crosslinked fibers, and those with appropriate crosslinking densities could exhibit fast and reversible photoinduced bending and unbending behaviors and excellent photodeformation fatigue resistance even at close to room temperature.

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1. Introduction

Recent years have witnessed considerable interest in the azobenzene (azo)-containing liquid crystalline elastomers (LCEs) because of their combined intriguing properties of anisotropic liquid crystals, flexible polymer

elastomers, and photoresponsive materials as well as their great potential applications in photomechanical devices [1–12]. Such photo-driven actuating systems can convert light energy into mechanical power directly through a clean, non-contact, and remote control strategy. It has been well established that the azo LCEs will experience a reduction in the alignment order upon their irradiation with UV light because of the *trans* to *cis* photoisomerization of the azo moieties, where the rod-like *trans*-azo isomer stabilizes the liquid crystalline alignment and the bent *cis*-azo

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isomer lowers the liquid crystalline order parameter. In particular, the changes of the alignment order can only be generated on the surfaces of the azo LCEs upon their exposure to UV light due to the large extinction coefficient of the azo polymers, thus leading to an uneven distribution of the anisotropic deformation along the LCE films or fibers and their bending behaviors [13,14].

Recently, Ikeda and coworkers reported very interesting three-dimensional photomobility of the crosslinked azo liquid crystalline polymer fibers [14]. Such azo LCE fibers were prepared by two-step reactions [15], which involved the first synthesis of a side-chain liquid crystalline polymer with a hydroxyl-substituted azo mesogen by the traditional free radical polymerization and the rather quick pulling of its mixture with a crosslinking agent (i.e., 4,4'-methylenebis(phenyl isocyanate)) with the tip of a toothpick at an appropriate temperature. Upon irradiation with UV light, the above-obtained azo LCE fibers showed obvious photoinduced bending behaviors, and the bending direction could be controlled by changing the direction of the UV irradiation toward the fibers, which makes them highly promising in artificial muscles and light-driven actuators. However, the photomobility of such azo LCE fibers occurred only when they were heated above 90 °C due to their high glass transition temperatures (T_g). In addition, the fiber-drawing process took place simultaneously with the fast crosslinking reaction, which makes it a challenging task to obtain azo LCE fibers with well-controlled properties such as desired diameters and alignment order. Therefore, the development of a versatile strategy for obtaining azo LCE fibers with easily controlled properties (i.e., diameters and alignment order) and excellent photodeformation behaviors at close to room temperature is highly desirable.

In this paper, we describe a new, facile, and highly efficient approach to achieve azo LCE fibers with easily controlled diameters and high alignment order as well as good photomechanical properties even at close to room temperature. A series of well-defined easily crosslinkable side-chain liquid crystalline polyacrylate-type homopolymers with an *N*-hydroxysuccinimide carboxylate-substituted azo mesogen and copolymers with both the above crosslinkable azo mesogen and a non-crosslinkable hexyl carboxylate-substituted azo mesogen were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization [16–18] for this purpose (Scheme 1). It is well known that RAFT polymerization could provide well-defined polymers with predetermined molecular weights and low molar-mass dispersities (\bar{D}) [16–18], and polymers with low \bar{D} are necessary for the fabrication of polymer fibers with better mechanical properties [19]. The kinetics of the RAFT polymerizations as well as the chemical structures, thermal and phase transition properties, and photoresponsivity of the resulting azo polymers were studied and characterized in detail. In addition, the azo LCE fibers with easily controlled diameters and high alignment order were directly prepared by the first fabrication of the uncrosslinked azo polymer fibers by the simple melt spinning method [20] and their subsequent post-crosslinking in a solution of a difunctional primary amine under mild conditions, which proved to be capable of

showing fast and reversible photoinduced bending and unbending behaviors and high photodeformation fatigue resistance at close to room temperature. Furthermore, the effect of the contents of the crosslinkable azo mesogen in the azo polymers on the photomechanical properties of their post-crosslinked fibers was also investigated.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF, Tianjin Jiangtian Chemicals, China, 99%) was refluxed over sodium and then distilled. *N,N*-dimethylformamide (DMF, Tianjin Jiangtian Chemicals, 99.5%) was dried with anhydrous magnesium sulfate (MgSO_4) and then distilled under vacuum. Anisole (Tianjin Fuchen Chemical Reagent Factory, 99%) was dried with anhydrous sodium sulfate (Na_2SO_4) and then distilled under vacuum. Triethylamine (TEA, Tianjin Jiangtian Chemicals, 99%) was dried with anhydrous Na_2SO_4 and then distilled. Azobisisobutyronitrile (AIBN, Chemical Plant of Nankai University, Analytical grade (AR)) was recrystallized from ethanol prior to use. Cumyl dithiobenzoate (CDB) was prepared following a literature procedure [21]. Acryloyl chloride was prepared by the reaction between acrylic acid (Tianjin Damao Chemical Reagent Factory, 99.5%) and benzoyl chloride (Tianjin Jiangtian Chemicals, 98%). 4-((4-Hydroxy)phenylazo)benzoic acid, 4-((4-(ω -hydroxyalkyloxy)phenylazo)benzoic acid (HAzoA-*m* (*m* = 2, 6, 10)), and 4-((4-(ω -acryloyloxyalkyloxy)phenylazo)benzoic acid (AAzoA-*m* (*m* = 2, 6, 10)) were synthesized according to our previously reported procedure (Scheme 1) [22]. The synthesis of the acrylate-type azo monomers including *N*-hydroxysuccinimide 4-((4-(ω -acryloyloxyalkyloxy)phenylazo)benzoate (AAzoS-*m* (*m* = 2, 6, 10), Scheme 1) and hexyl 4-((4-(ω -acryloyloxydecyloxy)phenylazo)benzoate (AAzoH-10, Scheme 1) is described in Supplementary Information. *N,N'*-dicyclohexylcarbodiimide (DCC, Tianjin Jiangtian Chemicals, AR), 4-(dimethylamino)pyridine (DMAP, Merck, AR), *n*-hexanol (Tianjin Bodi Chemicals, 99%), 1,6-hexanediamine (Tianjin Jiangtian Chemicals, 98%), and all the other reagents were commercially available and used without further purification.

2.2. Synthesis of the azo side-chain homopolymers (PAAzoS-*m* (*m* = 2, 6, 10) and PAAzoH-10) via RAFT polymerization (Scheme 1)

The typical RAFT polymerization procedure for AAzoS-10 is presented as follows: AAzoS-10 (0.329 g, 0.6 mmol) and anisole (3 mL) were added into a one-neck round-bottom flask (10 mL) and a clear solution was obtained after the ultrasonic treatment. AIBN (2.61 mg, 0.016 mmol) and CDB (4.41 mg, 0.016 mmol) were then added into the above solution, and the reaction mixture was bubbled with argon for 20 min, sealed, and then immersed into a thermostated oil bath at 70 °C in the dark. After 24 h of polymerization with stirring, the reaction mixture was cooled down to room temperature and was then added dropwise into methanol (20 mL). The precipitate was

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