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Effect of molecular parameters on thermomechanical behavior of side-on nematic liquid crystal elastomers

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ABSTRACT

We investigated the structure–property relationship of liquid crystal elastomers (LCEs) obtained from a series of nematic side-on monomers. A new synthetic strategy was developed to obtain the acrylate monomers (*n*-ADBB), which gave us the opportunity to easily modify the spacer lengths of the monomers. Through magnetic field alignment, well-defined LCE micropillars were fabricated from the monomers by a method combining soft lithography and photopolymerization/photocrosslinking of the monomers and a crosslinker. The influence of structural parameters on the thermomechanical deformation of the microstructures was studied through microscopic observations. The study quantitatively revealed the correlation of thermomechanical behavior of the microstructured LCEs with the crosslinking density and length of the flexible spacer linking the mesogenic core to the backbone. With a proper control of the structural parameters, optimized performances such as large reversible contraction, good elasticity and mechanical robustness were demonstrated for this type of LCEs.

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1. Introduction

Liquid crystalline elastomers (LCEs) have been intensively investigated in recent years owing to their fascinating properties and potential applications [1–10]. Combining anisotropic orientation of liquid crystals (LCs) with the rubbery elasticity of polymer networks, the materials are endowed with specific properties, such as stimuli-induced reversible deformation and anisotropic shape changes. Depending on the LC phases exhibited by the systems, LCEs are divided into nematic LCE [11], smectic LCE [8], and others. The nematic LCE with uniform spatial orientation is the simplest and most widely studied type among them. In a nematic LCE, the average macromolecular shape is coupled with the orientational nematic order [1,12]. The polymer chains elongate when their mesogens orient in the nematic phase, while in the isotropic phase, they recover a random coil conformation, driven by entropy [12]. At the nematic–isotropic phase transition, a change in the average molecular shape from elongated to coiled conformations will be triggered and translated at a macroscopical level to induce a shape deformation of the elastomer sample. Making use of the sensitivity of mesophases to various physical stimuli, LCEs with thermo-responsive [13,14], photo-responsive [15,16], and electro-responsive [17–19] functions have been developed. In recent years, their applications as artificial muscles [20], micropumps and microvalves for microfluidic devices [21–23], and opto-mechanical shutters [24], have been actively explored.

Understanding structure–property relationship of the LCEs is extremely important for optimizing properties and achieving real applications. Different LCEs with the mesogenic units in the main-chain and side-chains have been synthesized and investigated [2,3,8,11,25–27]. For the LCEs with side-chain architecture, both "end-on" and "side-on" LCEs, depending on whether the mesogenic groups are attached terminally or laterally to the polymer backbone via a flexible spacer, have been developed and intensively investigated [2,3,8,11,25]. For liquid crystal polymers (LCPs) and LCEs, the end-on structure usually tends to form a smectic phase, especially for those with longer spacers [28]. On the other hand, the nematic phase is favored in "side-on" LCPs and LCEs, in which the mesogens are laterally attached to the polymer backbone [29–32]. In addition to the mesogen-attaching mode, the mesomorphic properties of LCPs and LCEs are also closely related to mesogenic units [33], linking groups [34].

There are several critically important issues need to be addressed in order to further understand the structure–property

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relationship. The spacer length and crosslinking density are two key control factors that need to be studied. The spacer length determines the coupling strength between the side-chain mesogenic units and the backbone, which plays an important role to influence the molecular shape change during the phase transition. Crosslinking density controls the topological restrain between the polymeric chains and affects the mechanical properties related to the chain conformation [35]. In order to explore the structure–property relationship, nematic LCEs with uniaxial alignment and mono-domain (named 'liquid single crystal elastomer' by Finkelmann [36]) are required. The 'liquid single crystal elastomer' samples have been obtained by methods such as stretching pre-crosslinked films [2,4,8], drawing fibers from a polymer melt [9], crosslinking in liquid crystalline cells [3,16], aligning with electric or magnetic fields [13,14], and others [6,37–40]. Among them, obtaining a regular array of pillar-like microstructures by soft-lithography and magnetic field alignment is an appealing new approach [13,14]. Although many efforts have been devoted to the LCE study, to our knowledge, a systematic study on the effects of the spacer length and crosslinking density by using the well-defined microstructures has not been reported in the literature yet.

In this study, influences of crosslinking density and spacer length on the properties of the side-on LCEs were investigated by using pillar-like microstructures obtained by the method combining soft-lithography and magnetic field alignment. In order to keep the LCEs all in the nematic phase, the side-on nematic monomers with different spacer length were selected. An improved strategy was developed to synthesize side-on LC acrylate monomers with the different spacer lengths. Monomers with different spacer lengths, which contained 2, 3, 4, 5 and 6 methylenes (*n*-ADBB, *n* representing the numbers of the methylenes), were synthesized and characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, POM and DSC. The monomers were first mixed with the crosslinking agent in different ratios and a suitable amount of the photoinitiator. Then, LCE pillars were prepared with the mixture by the soft-lithographic technique. The effects of the crosslinking density and spacer length were studied by microscopically characterizing thermomechanical properties of the LCE micropillars, which were separated from the substrates. The correlation of thermomechanical behavior of the micro-structured LCEs with the crosslinking density and length of the flexible spacer was quantitatively revealed by the study.

2. Experimental section

2.1. Materials

2,5-Dihydroxybenzoic acid (99%) and 4-n-butyloxybenzoic acid (98%) were purchased from Alfa Aesar and used as received. Crosslinking agent, 1,6-hexanediol diacrylate (98%) was purchased from Adamas-beta and used as received. Photoinitiator, 2-benzyl-2-(dimethylamino)-4′-morpholinobutyrophenone (97%), was purchased from Sigma Aldrich and used as received. Tetrahydrofuran (THF) was purified by distillation with sodium and benzophenone. Deionized water (resistivity $>$ 18 MΩ cm) was obtained from a Milli-Q water purification system. Azo-bis-isobutryonitrile (AIBN) was recrystallized from anhydrous methanol before use. All other reagents were commercially available products and used as received without further purification.

2.2. Characterization

^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM-ECA300 or JEOL JNM-ECA600 NMR spectrometer with tetramethylsilane (TMS) as the internal standard at ambient temperature in d_6-DMSO or $CDCl_3$. FT-IR spectra were collected on a Nicolet 560-IR spectrometer: the samples were mixed with KBr powder and then pressed into thin transparent disks. The molecular weights and molecular weight distributions were measured using a gel permeation chromatographic (GPC) instrument equipped with a PLgel 5 μm mixed-D column and a refractive index (RI) detector (Wyatt Optilab rEX). The measurements were carried out at 35 °C and the molecular weights were calibrated with polystyrene standards. THF was used as the eluant and the flow rate was 1.0 mL/min. Thermal analyses of the compounds were carried out using TA Instruments DSC Q2000 system with a heating rate of 10 °C/min in a nitrogen atmosphere. Polarizing optical microscopic (POM) observations were conducted on a Nikon LV 1000 POL microscope equipped with a CCD camera and a hot stage. The SEM measurements were performed on a field emission microscope (Hitachi S-4500) with the accelerating voltage of 15 kV. The samples prepared for SEM studies were observed after sputter coating treatment with Au.

2.3. 2″-Acryloyloxyethyl 2,5-di(4′-butyloxybenzoyloxy)benzoate (2-ADBB)

The monomer was synthesized through three-step reactions as shown in Scheme 1. 2′-Bromo-ethyl 2,5-dihydroxybenzoate (A_2) was first obtained from the nucleophilic substitution reaction between 2,5-dihydroxybenzoic acid and 1,2-dibromoethane. Then, 2′-acryloyloxyethyl 2,5-dihydroxybenzoate (B_2) was obtained by reaction between A_2 and acrylic acid. The synthetic details and analytic results of the intermediates are given in the Supporting information. In the final step, a solution of B_2 (2.5 g, 10 mmol), 4-n-butyloxybenzoic acid (4.1 g, 21 mmol), N,N-dicyclohexylcarbodiimide (6.2 g, 30 mmol), and 4-pyrrolidinopyridine (0.48 g, 3 mmol) in dichloromethane (100 mL) was stirred at room temperature for 24 h. The N,N-dicyclohexyl urea was filtered and the filtrate was sequentially washed with water (150 mL), 5% acetic acid solution (150 mL), and water (150 mL), and dried over $MgSO_4$. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with DCM as eluting solvent to yield white powder (70%). ^{1}H NMR (600 MHz, d_6-DMSO) δ (ppm): 8.10 (m, 4H, ArH), 7.83 (d, 1H, ArH), 7.65 (m, 1H, ArH), 7.50 (d, 1H, ArH), 7.13 (m, 4H, ArH), 6.27, 6.07, 5.88 (3m, 3H, CH_2═CH), 4.38, 4.20 (2t, 4H, −CH_2−O), 4.11 (t, 4H, −CH_2−O), 1.74, 1.46 (2m, 8H, −CH_2−), 0.96 (t, 6H, −CH_3). ^{13}C NMR (150 MHz, d_6-DMSO) δ (ppm): 14.2, 19.2, 31.1, 62.4, 63.6, 68.2, 68.3, 115.2, 115.3, 121.3, 121.5, 124.3, 124.5, 126.0, 128.4, 128.6, 131.9, 132.3, 132.6, 132.7, 148.1, 148.3, 163.7, 163.9, 164.8 and 165.8. IR (KBr, cm^{-1}): 3078 (−C═C−H, s), 2956, 2936, 2870 (C−H, s), 1731 (C═O, s), 1609, 1582, 1512 (Benz. ring, s), 1470 (C−H, δ), 1302, 1250, 1200 1166 (C−O−C, s). EA: C 68.0 (calcd 67.5), H 5.9 (calcd 5.9).

2.4. 3″-Acryloyloxypropyl 2,5-di(4′-butyloxybenzoyloxy)benzoate (3-ADBB)

3-ADBB was similarly prepared as mentioned for the 2-ADBB synthesis. The synthetic details and analytic results of the intermediates A_3 and B_3 are given in the Supporting information. ^{1}H NMR (300 MHz, d_6-DMSO) δ (ppm): 8.10 (m, 4H, ArH), 7.85 (d, 1H, ArH), 7.65 (m, 1H, ArH), 7.49 (d, 1H, ArH), 7.12 (m, 4H, ArH), 6.24, 6.10, 5.88 (3m, 3H, CH_2═CH), 4.20 (t, 2H, −CH_2−O), 4.10 (m, 6H, −CH_2−O), 1.75 (m, 6H, −CH_2−), 1.47 (m, 4H, −CH_2−), 0.95 (t, 6H, −CH_3). ^{13}C NMR (75 MHz, d_6-DMSO) δ (ppm): 14.2, 19.2, 27.8, 31.1, 61.5, 62.2, 68.3, 115.3, 120.9, 121.2, 124.8, 125.0, 126.1, 128.5, 128.7, 132.0, 132.7, 148.1, 148.7, 163.8, 164.2, 164.8 and 165.8. IR (KBr, cm^{-1}): 3077 (−C═C−H, s), 2958, 2934, 2869 (C−H, s), 1731 (C═O, s), 1634 (C═C, s), 1609, 1582, 1512 (Benz. ring, s), 1475, 1392 (C−H, δ), 1251, 1182, 1166, 1075 (C−O−C, s). EA : C 67.9 (calcd 68.0), H 6.1 (calcd 6.1).

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