

AND LIQUID CRYSTALS	
LETTERS SECTION	
CONTENTS	
Leiber V. A. BELYAROV and V. P. ORLOV: Sorbar Guidol Electromagnetic Wares in Cholontric Films	
H. R. REAND and R. PLEINER: Dislocitie Properties Near the A.C ^a Transition in Structic Liquid Crystals	
C. HEPPEE, A. RANFT and B. SABASCHUS: Bond and Splay Elastic Constants of Some Discotic Nonadic Compounds	0

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Contraction of side-on nematic liquid crystalline elastomers micropillars: Influence of molecular parameters

Renbo Wei & Xiufu Hua

To cite this article: Renbo Wei & Xiufu Hua (2017) Contraction of side-on nematic liquid crystalline elastomers micropillars: Influence of molecular parameters, Molecular Crystals and Liquid Crystals, 643:1, 83-96, DOI: 10.1080/15421406.2016.1262710

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1262710



Published online: 23 Feb 2017.



🕼 Submit your article to this journal 🗗





View related articles 🗹



🌔 🛛 View Crossmark data 🗹

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=gmcl20



Contraction of side-on nematic liquid crystalline elastomers micropillars: Influence of molecular parameters

Renbo Wei^{a,b} and Xiufu Hua^{b,c}

^aResearch Branch of Advanced Functional Materials, School of Microelectronics and Solid-State Electronics, High Temperature Resistant Polymer and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu, China; ^bDepartment of Chemical Engineering, Key Laboratory of Advanced Materials (MOE), Tsinghua University, Beijing, China; ^cDepartment of Scientific Research and Development, Tsinghua University, Beijing, China

ABSTRACT

We investigated the structure-property relationship of nematic liquid crystalline elastomer (LCE) actuators obtained from a series of nematic side-on monomers. The liquid crystalline acrylate monomers were designed and synthesized with different tail lengths. Combining a soft lithography technique with photo-polymerization/photo-crosslinking of aligned nematic liquid crystalline monomers and crosslinkers, nematic LCE micropillars were obtained, based on the new monomers. Through microscopic observation, influence of some structural parameters on the thermo-mechanical behavior of the micropillars was investigated. The thermo-mechanical behavior of the LCEs showed a close correlation with to the tail length of the monomer and the spacer length of the crosslinker.

KEYWORDS

Actuator; liquid crystalline elastomer; molecular parameters; nematic; side-on

1. Introduction

As a unique type of the smart polymeric materials, liquid crystalline elastomers (LCEs) have recently attracted considerable attention from the material research community owing to their interesting properties and potential applications [1–16]. The combination of the anisotropic orientation of liquid crystals with the rubbery elasticity of polymer networks, give these materials specific properties, such as stimuli-induced reversible, anisotropic shape changes. Their applications as artificial muscles [17], actuators [18], micro-pump and micro-valves for microfluidic devices [19–21], and opto-mechanical shutters [22], have been intensively investigated.

Up to now, there are mainly two kinds of LCEs, namely nematic [23] and smectic LCE [24], according to the LC phases exhibit in the systems. Nematic LCEs are the simplest and most widely investigated one in which the mesogen are uniformly spatial orientated. In the nematic LCEs, the average macromolecular conformation is coupled with the orientational nematic mesogens [25]. In the nematic phase, the polymeric main-chains elongate when their mesogens are oriented; while in the isotropic phase, they recover a random coil conformation,

CONTACT Renbo Wei S weirb10@uestc.edu.cn; Xiufu Hua k hua_xiufu@163.com Research Branch of Advanced Functional Materials, School of Microelectronics and Solid-State Electronics, High Temperature Resistant Polymer and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu 610054, China. Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl. © 2017 Taylor & Francis Group, LLC driven by entropy [25]. A change in the average molecular shape is thus introduced, from elongated to coiled at the nematic-isotropic phase transition, which could be translated at a macroscopical level in a shape change of the elastomer sample. Taking advantage of the sensitivity of liquid crystals to various physical stimuli, thermo-responsive [26, 27], photo-responsive [28–30], magnetic-responsive [31], and electro-responsive [32–34] LCE materials have been developed.

On the other hand, the molecular structure of the constituent molecules in liquid crystals is a fundamental factor in determining the mesophase properties, both in low molecular weight and liquid crystalline polymers (LCPs) [35-39]. LCPs can be classified according to their chemical structures, into two main families, main-chain LCPs, and side-chain LCPs [40-43]. Side-chain LCPs can be divided into two kinds, "end-on" and "side-on" LCPs, depending on whether the mesogenic groups are attached terminally or laterally to the polymer backbone via a flexible spacer [23, 40-42]. In "end-on" LCPs, in which the mesogenic groups are linked to the backbone through one of their end groups, smectic phases are usually favored [44]. In contrast, the nematic phase is favored in "side-on" LCPs, in which the mesogens are laterally attached to the polymer backbone [45-48]. In addition to the mesogen-attaching mode, the mesomorphic properties of LCPs and LCEs are also closely related to mesogenic units [49] and linking groups [50]. In our previous study [35], the correlation of thermo-mechanical behavior of the LCEs with the crosslinking density and length of the flexible spacer linking the mesogenic core to the backbone were quantitatively investigated. The tail length of the monomer and the spacer length of the crosslinker are another two key factors that need to be studied. The tail length of the monomer plays an important role to influence the transition temperature of the monomer [51]. The spacer length of the crosslinker determines the coupling strength between different polymer chains [52, 53].

Another critically important issue in the domain of nematic LCEs is to obtain monodomain (called "liquid single crystal elastomer" by Finkelmann [54]) nematic elastomers with uniaxial alignment. "Liquid single crystal elastomer" samples have been fabricated by methods such as drawing fibers from a polymer melt [5], stretching pre-crosslinked films [1, 55], crosslinking in liquid crystalline cells [29, 40], aligning with electric or magnetic fields [26, 27], and others [4, 56–58]. We have demonstrated previously that by using a magnetic field in the suitable geometry, we could get thin glassy polymer film covered by a regular structure like array of pillars and gratings [59–61].

In this study, influence of tail length of the monomer and the spacer length of the crosslinker on the properties of the side-on LCEs is 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 tail length are selected. Monomers with tail of methoxyl, oxyethyl, butoxy, hexyloxy, and octoxy groups (4-AD ω B) are synthesized and characterized by ¹H NMR, ¹³C NMR, COSY, FT-IR, POM, and DSC. The monomers are mixed with crosslinking agents with different spacer lengths in different ratios and a photo initiator, and then LCE pillars are prepared with the mixture by the soft-lithographic technique. The effects of the tail length of the monomers and spacer length of the crosslinkers on thermomechanical properties of LCE micropillars are studied by microscopically characterizing. The correlation of thermomechanical behavior of the micro-structured LCEs with tail length of the monomer and spacer length is quantitatively revealed by the study.

2. Experimental section

2.1 Materials

2,5-Dihydroxybenzoic acid (99%), anisic acid (98%), and 4-*n*-butyloxybenzoic acid (98%) were purchased from Alfa Aesar. 4-Ethoxybenzoic acid (99%) and 1,4-butanediol acrylate (99%) were purchased from J&K Chemical. 4-Hexyloxybenzoic acid (98%), 4-*n*-octyloxybenzoic acid (98%) and 1,5-pentanediol diacrylate (97%) were purchased from TCI. 1,6-Hexanediol diacrylate (98%) was purchased from Adamas-beta. 2-Benzyl-2-(dimethylamino)-4'-morpholinobutyro-phenone (97%) was purchased from Sigma Aldrich. All other reagents were commercially available products and used as received without further purification. Tetrahydrofuran (THF) was purified by distillation with sodium and benzophenone. Deionized water (resistivity >18 M Ω cm) was obtained from a Milli-Q water purification system. AIBN was recrystallized from anhydrous methanol before use.

2.2 Synthesis

2.2.1 4-Chloro-1-butanol acrylate

4-Chloro-1-butanol (4.3 g, 40 mmol) and triethylamine (10.1 g, 100 mmol) were dissolved in DCM (80 mL) in an ice bath. Acryloyl chloride (5 mL, 55 mmol) in 40 mL DCM was added dropwise into the solution with stirring. After acryloyl chloride was added, the reaction was carried out overnight. Triethylamine salt was filtered and the filtrate was washed water (100 mL), 5% HCl solution (100 mL) and water (100 mL) and dried over MgSO₄. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with DCM as eluting solvent to yield white powder (95%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 6.36, 6.08, 5.81 (3m, 3H, CH₂=CH), 4.16 (t, 2H, -CH₂-COO), 3.54 (t, 2H, -CH₂-Br), 1.82 (m, 4H, -CH₂-CH₂-CH₂-). ¹³C NMR (75 MHz, *d*₆-DMSO) δ (ppm): 166.0, 131.9, 128.9, 63.9, 45.5, 29.3, 26.2.

2.2.2 4'-Acryloyloxybutyl 2,5-dihydroxybenzoate

Solid KHCO₃ (3.0 g, 30 mmol) was added to a stirred mixture of 4-chloro-1-butanol acrylate (3.2 g, 20 mmol) and 2,5-dihydroxybenzoic acid (3.8 g, 25 mmol) in DMF (100 mL). The mixture was heated to 50°C and stirred for 24 h. The reaction mixture was cooled down to room temperature, diluted with water (100 mL), and extracted twice with 50 mL DCM. The organic phases were washed twice with water (50 mL) and dried over MgSO₄. After evaporation of the solvents, the residue was subjected to column chromatography on silica gel with DCM as eluting solvent to yield white powder (90%). ¹H NMR (600 MHz, d_6 -DMSO) δ (ppm): 9.99 (b, 1H, OH), 9.20 (b, 1H, OH), 7.13 (d, 1H, ArH), 6.98 (m, 1H, ArH), 6.82 (d, 1H, ArH), 6.34, 6.19, 5.94 (3m, 3H, CH₂=CH), 4.34, 4.19 (2t, 4H, -CH₂-O), 1.79 (m, 4H, -CH₂-). ¹³C NMR (150 MHz, d_6 -DMSO) δ (ppm): 25.3, 33.8, 64.2, 65.2, 113.0, 114.6, 118.7, 124.4, 128.7, 132.2, 150.1, 153.9, 166.0 and 169.5.

2.2.3 4''-Acryloyloxybutyl 2,5-di(4'-butyloxybenzoyloxy) benzoate (4-ADBB)

A solution of 4'-acryloyloxybutyl 2,5-dihydroxybenzoate (2.8 g, 10 mmol), 4-*n*-butyloxybenzoic acid (4.1 g, 21 mmol), *N*,*N*-dicyclohexylcarbodiimide (6.2 g, 30 mmol), and pyrrolidinopyridine (0.48 g, 3 mmol) in 100 mL of dichloromethane was stirred at room temperature for 24 h. The *N*,*N*-dicyclohexyl urea was filtered and the filtrate was washed with water (150 mL), 5% acetic acid solution (150 mL), and water (150 mL), and

dried over Na₂SO₄. After evaporation of the solvents, the residue was subjected to column chromatography on silica gel with DCM as eluting solvent to yield white powder (70%). ¹H NMR (300 MHz, d_6 -DMSO) δ (ppm): 8.09 (m, 4H, ArH), 7.84 (d, 1H, ArH), 7.66 (m, 1H, ArH), 7.49 (d, 1H, ArH), 7.12 (m, 4H, ArH), 6.25, 6.13, 5.91 (3m, 3H, CH₂=CH), 4.11 (m, 6H, -CH₂-O), 3.95 (t, 2H, -CH₂-O), 1.72 (m, 4H, -CH₂-), 1.48 (m, 8H, -CH₂-), 0.95 (t, 6H, -CH₃). ¹³C NMR (75 MHz, d_6 -DMSO) δ (ppm): 15.3, 20.3, 26.2, 32.2, 65.2, 66.5, 69.4, 116.4, 122.3, 126.1, 126.8, 129.5, 130.0, 132.9, 133.9, 148.8, 149.4, 164.9, 165.2, 165.9 and 166.4. IR (KBr, cm⁻¹): 3075 (-C=C-H, s), 2958, 2934, 2872 (C-H, s), 1732 (C=O, s), 1634 (C=C, s), 1608, 1581, 1512 (Benz. ring, s), 1475, 1389 (C-H, m), 1252, 1182, 1166, 1073 (C-O-C, s). Elemental analysis: calcd.: C 68.3%, H 6.3%; found: C 68.2%, H 6.3%.

2.2.4 4''-Acryloyloxybutyl 2,5-di(4'-methyloxybenzoyloxy) benzoate (4-ADMB)

4-ADMB was similarly prepared as mentioned for the 4-ADBB synthesis. ¹H NMR (600 MHz, d_6 -DMSO) δ (ppm): 8.11 (m, 4H, ArH), 7.84 (d, 1H, ArH), 7.65 (m, 1H, ArH), 7.49 (d, 1H, ArH), 7.14 (m, 4H, ArH), 6.28, 6.13, 5.91 (3m, 3H, CH₂=CH), 4.15 (t, 2H, -CH₂-O), 3.95 (t, 2H, -CH₂-O), 3.89 (s, 6H, CH₃-O), 1.55 (m, 2H, -CH₂-), 1.49 (m, 2H, -CH₂-). ¹³C NMR (150 MHz, d_6 -DMSO) δ (ppm): 25.0, 25.1, 56.2, 64.1, 65.3, 114.8, 114.9, 121.1, 121.4, 125.0, 126.0, 128.4, 128.8, 131.9, 132.7, 147.9, 148.6, 164.1, 164.4, 164.8 and 165.9. IR (KBr, cm⁻¹): 3082 (-C=C-H, s), 2955, 2932, 2847 (C-H, s), 1743 (C=O, s), 1636 (C=C, s), 1608, 1579, 1513 (Benz. ring, s), 1384 (C-H, m), 1257, 1180, 1164, 1073 (C-O-C, s). Elemental analysis: calcd.: C 65.7%, H 5.1%; found: C 65.7%, H 5.0%.

2.2.5 4''-Acryloyloxybutyl 2,5-di(4'-ethyloxybenzoyloxy) benzoate (4-ADEB)

4-ADEB was similarly prepared as mentioned for the 4-ADBB synthesis. ¹H NMR (600 MHz, d_6 -DMSO) δ (ppm): 8.10 (m, 4H, ArH), 7.84 (d, 1H, ArH), 7.64 (m, 1H, ArH), 7.48 (d, 1H, ArH), 7.12 (m, 4H, ArH), 6.29, 6.13, 5.90 (3m, 3H, CH₂=CH), 4.17 (m, 6H, -CH₂-O), 3.95 (t, 2H, -CH₂-O), 1.55 (m, 2H, -CH₂-), 1.49 (m, 2H, -CH₂-), 1.36 (t, 6H, -CH₃). ¹³C NMR (150 MHz, d_6 -DMSO) δ (ppm): 15.0, 19.1, 25.1, 56.6, 64.3, 65.3, 115.1, 115.2, 121.2, 125.0, 126.4, 128.4, 128.8, 131.9, 132.8, 148.1, 148.6, 163.6, 164.0, 164.8 and 165.9. IR (KBr, cm⁻¹): 3077 (-C=C-H, s), 2956, 2932, 2849 (C-H, s), 1731 (C=O, s), 1638 (C=C, s), 1606, 1581, 1508 (Benz. ring, s), 1492, 1393 (C-H, m), 1253, 1181, 1160, 1067 (C-O-C, s). Elemental analysis: calcd.: C 66.7%, H 5.6%; found: C 67.0%, H 5.4%.

2.2.6 4"-Acryloyloxybutyl 2,5-di(4'-hexyloxybenzoyloxy) benzoate (4-ADHB)

4-ADHB was similarly prepared as mentioned for the 4-ADBB synthesis. ¹H NMR (600 MHz, d_6 -DMSO) δ (ppm): 8.09 (m, 4H, ArH), 7.84 (d, 1H, ArH), 7.64 (m, 1H, ArH), 7.47 (d, 1H, ArH), 7.11 (m, 4H, ArH), 6.26, 6.13, 5.90 (3m, 3H, CH₂=CH), 4.14 (t, 2H, -CH₂-O), 4.09 (m, 4H, -CH₂-O), 3.95 (t, 2H, -CH₂-O), 1.74 (m, 4H, -CH₂-), 1.54 (m, 2H, -CH₂-), 1.49 (m, 2H, -CH₂-), 1.46 (m, 4H, -CH₂-), 1.31 (m, 8H, -CH₂-), 0.88 (t, 6H, -CH₃). ¹³C NMR (150 MHz, d_6 -DMSO) δ (ppm): 22.6, 25.1, 25.2, 25.6, 29.0, 31.5, 64.1, 65.3, 68.5, 68.6, 115.1, 115.2, 120.8, 121.2, 124.9, 125.0, 126.0, 128.3, 128.8, 131.8, 132.6, 132.7, 148.0, 148.6, 163.9, 164.1, 164.6 and 165.9. IR (KBr, cm⁻¹): 3082 (-C=C-H, s), 2956, 2931, 2858 (C-H, s), 1736 (C=O, s), 1638 (C=C, s), 1606, 1581, 1512 (Benz. ring, s), 1491, 1393 (C-H, m), 1250, 1181, 1159, 1061 (C-O-C, s). Elemental analysis: calcd.: C 69.8%, H 7.0%; found: C 69.4%, H 6.9%.

2.2.7 4''-Acryloyloxybutyl 2,5-di(4'-octyloxybenzoyloxy) benzoate (4-ADOB)

4-ADOB was similarly prepared as mentioned for the 4-ADBB synthesis. ¹H NMR (600 MHz, d_6 -DMSO) δ (ppm): 8.08 (m, 4H, ArH), 7.82 (d, 1H, ArH), 7.60 (m, 1H, ArH), 7.43 (d, 1H,

ArH), 7.09 (m, 4H, ArH), 6.26, 6.10, 5.88 (3m, 3H, CH₂=CH), 4.14 (t, 2H, $-CH_2-O$), 4.08 (t, 4H, $-CH_2-O$), 3.96 (t, 2H, $-CH_2-O$), 1.74 (m, 4H, $-CH_2-$), 1.54 (m, 2H, $-CH_2-$), 1.49 (m, 2H, $-CH_2-$), 1.43 (m, 4H, $-CH_2-$), 1.29 (m, 16H, $-CH_2-$), 0.87 (t, 6H, $-CH_3$). ¹³C NMR (150 MHz, *d*₆-DMSO) δ (ppm): 14.5, 22.6, 25.1, 25.2, 26.0, 29.0, 29.2, 29.3, 31.8, 64.1, 65.4, 68.5, 68.6, 115.1, 115.2, 120.8, 121.2, 125.0, 126.1, 128.3, 128.8, 131.8, 132.7, 132.8, 132.9, 148.0, 148.5, 163.9, 164.1, 164.6 and 165.9. IR (KBr, cm⁻¹): 3081 (-C=C-H, s), 2955, 2926, 2862 (C–H, s), 1738 (C=O, s), 1638 (C=C, s), 1603, 1580, 1511 (Benz. ring, s), 1492, 1398 (C–H, m), 1254, 1184, 1077 (C–O–C, s). Elemental analysis: calcd.: C 71.0%, H 7.5%; found: C 70.9%, H 7.6%.

2.2.8 Polymerization of the monomers in solution

To test the polymerization ability, the monomers were also polymerized in solutions. The polymerization of 4-ADBB was given as an example for the procedure, the other monomers were similarly polymerized. 0.144 g 4-ADBB (0.2 mmol), 0.6 mg AIBN (2%) and 2 mL 1,4-dioxanewere were added to a Schlenk flask. After degassing by three freeze-pump-thaw cycles, the flask was immersed in an oil bath preheated to 60°C. The polymerization was carried out at the temperature for 20 h. After the reaction, the mixture was diluted with THF and poured into an excess amount of petroleum ether. The precipitate was collected by filtration, washed with petroleum ether and then dried in a vacuum oven for 24 h. GPC: $M_n = 7.6 \times 10^3$, $M_w/M_n = 1.48$, ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.16–7.93 (m), 7.88–7.71 (m), 7.45–7.30 (m), 7.23–7.10 (m), 7.00–6.75 (m), 4.22–3.67 (m), 1.84–1.60 (m), 1.58–1.29 (m), 1.04–0.81 (m). FT-IR (KBr, cm⁻¹): 2959, 2939, 2873, 1732, 1606, 1579, 1511, 1489, 1250, 1162, and 1060.

2.2.9 Preparation of PDMS molds

PDMS molds which is suitable for the preparation of LCE micropillars with diameter of 20 μ m and length of about 70 μ m was similarly prepared according to previous report [60].

2.2.10 Fabrication of LCE micropillars

The LCE micropillars were fabricated by the previously reported method [60].

2.3 Characterization

¹H and ¹³C NMR and COSY 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 CDCl₃. FT-IR spectra were collected on a Nicolet 560-IR spectrometer: the samples were mixed with KBr 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 mm 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.



Scheme 1. Synthetic route of the monomers.

3. Results and discussion

3.1 Synthesis and characterization

The monomers were synthesized through three-step reactions as shown in Scheme 1. 4-Chloro-1-butanol acrylate was first obtained from the esterification between the 4-chloro-1-butanol and acryloyl chloride. Then, 4'-acryloyloxybutyl 2,5-dihydroxybenzoate was obtained by reaction between 4-chloro-1-butanol acrylate and 2,5-dihydroxybenzoic acid. Finally, the monomers were obtained by the esterification between 4'-acryloyloxybutyl 2,5-dihydroxybenzoate and the 4-*n*-alkoxybenzoic acids under standard conditions (dicyclohexylcarbodiimide and pyrrolidinopyridine). This newly developed procedure is simple and straightforward compared with the previously reported scheme [23, 62], and more convenient than our previous procedure [35] as the high yield of the first reaction. The last step in this procedure also ensures us to obtain monomers with different lengths (n = 1, 2, 4, 6, 8) of the tail on the mesogen. The analytical results, obtained from ¹H NMR, ¹³C NMR, and FT-IR, were given in the experimental section. In addition, the COSY spectrum of 4-ADOB with resonance signal assignments is shown in Fig. 1 as a typical example. All of these results confirm that the series of the nematic side-on acrylate monomers are successfully synthesized.

The mesomorphic properties of the monomers were characterized by DSC and POM. Figure 2 shows the DSC curves of the monomers on the first heating (Fig. 2A) and first cooling (Fig. 2B) scans. 4-ADOB melts at 63°C (peak value) and shows a small endothermic transition at 80°C (peak value), which corresponds to the clearing point ($T_{\rm NI}$) of the monomer on heating. On the cooling scan, an exothermic transition around 79°C (peak value) is observed for 4-ADOB, while no crystallization peak can be detected. The other monomers show higher melting point as the tail length decreases (Fig. 2). For 4-ADMB and 4-ADHB, no clearing points is detected by DSC, and for 4-ADEB, both of melting and clearing point is not detected. POM observations show that 4-ADMB and 4-ADHB enter nematic phases when heated. Figure 3 shows some representative images of the textures of the monomers observed by POM.



Figure 1. COSY spectrum of 4-ADOB.



Figure 2. DSC curves of the monomers: (A) the first heating scan, from bottom to top: 4-ADMB, 4-ADEB, 4-ADBB, and 4-ADOB.



Figure 3. POM images of the monomers. (A) 4-ADBB at 87°C; (B) 4-ADMB at 71°C; (C) 4-ADHB at 50°C; (D) 4-ADOB at 60°C.

In order to compare with the properties of the LCEs, the monomers were also polymerized by radical polymerization in solution. The characterization of the corresponding side-on liquid crystalline polymers gives further information on the physical properties of the samples, particular of their mesomorphic properties. The obtained polymers have average molecular weights (M_n) around 1.0 × 10⁴ and polydispersity index (PDI) below 2.5 (Table 1). The phase transition temperatures obtained DSC are also given in there.

3.2 Fabrication of LCE micropillars

Using the nematic acrylate monomers synthesized above, LCEs were prepared under the form of thin films covered with micropillars. The method was described in the experimental section and also in the previous reports [26, 27] in detail. In the process, monomers and crosslinking agents in different ratios were mixed with 5% (mol%) of the photoinitiator, 2-benzyl-2-(dimethylamino)-4-morpholinobutyrophenone. After heating the mixture to the isotropic phase, a piece of the PDMS mold was gently pressed down on the melted sample, which fills

Polymers	M _n	PDI	T _g (°C)	T _{NI} (DSC,°C)
P4ADMB	1.2×10^{4}	1.97	63	142
P4ADEB	7.7×10^{3}	2.02	64	*
P4ADBB	7.6×10^{3}	1.48	36	99
P4ADHB	1.2×10^{4}	2.20	13	_
P4ADOB	9.9×10^{3}	1.39	24	90

Table 1. The GPC and DSC data of the polymers.

*No transition temperature was observed.



Figure 4. Typical optical micrographs and SEM images of the LCE micropillars: (A) and (B) optical microscopic graphs; (C) POM image; (D) SEM image.

the inner column-shaped structures of the mold. When the sample was cooled down to enter the nematic phase with the magnetic field alignment, it was irradiated by the UV light with the argon gas protection for the polymerization and crosslinking. A thin glassy polymer film covered by a regular array of pillars was obtained after cooling to room temperature and peeling off the PDMS mold. Separate micropillars were obtained from the pillar array by carefully cutting them off from the substrate with a razor blade.

Figure 4 shows the optical microscope and SEM images of the micropillar array and separate pillars made from 4-ADBB. In Fig. 4(A), the optical microscope image shows regular alignment of the micropillars in the array on a large scale, indicating that micro-structures with uniform sizes can be obtained with a high efficiency by this method. Figure 4(B) shows the optical microscope image of the separate pillars suspended in silicon oil. The average length of the micropillars was measured to be around 65 μ m. Figure 4(C) is a typical POM image of the separate micropillars placed between the crossed polarizers and observed at the room temperature. The bright images due to the birefringence evidence the mesogenic alignment in the micropillars. Similar optical anisotropy is observed for the micropillars obtained from the other monomers. Figure 4(D) shows the SEM image of the pillars. The pillar sizes were also measured from the SEM images by carefully cutting off the pillars before the sputtering treatment. The lengths of the micropillars are also estimated to be about 65 μ m.

3.3 Effect of the spacer length of crosslinker

The effect of the spacer length of crosslinkers on the thermo-mechanical behavior of the LCEs was studied by using the micropillars. The result obtained for 4-ADBB is presented below to elucidate the effect. In the experiment, 4-ADBB and 5 mol% photoinitiator were mixed with



Figure 5. The optical micrographs of a single LCE pillar at different temperatures: (A) room temperature; (B) 130°C; (C) room temperature again.

20 mol% of crosslinking agents of 1,4-butanediol acrylate, 1,5-pentanediol diacrylate and 1,6hexanediol diacrylate, respectively. The regular arrays of LCE micropillars on glass substrates and separate micropillars were obtained from these samples by the method mentioned above. The shape changes of these individual micropillars, suspended in silicon oil to prevent them from sticking on the microscope glass slides, were studied as a function of the temperature by POM equipped with the hot stage. Figure 5 shows typical optical micrographs of a single LCE micropillar obtained from 4-ADBB with 20 mol% of the crosslinking agent 1,6-hexanediol diacrylate at room temperature (Fig. 5(A) and Fig. 5(C)) and 130°C (Fig. 5(B)). By heating to a temperature above the nematic-to-isotropic phase transition temperature of the LCE, a significant contraction of the micropillar in the longitudinal direction is observed. While cooling back to room temperature, the micropillar recovers its original shape. As the micropillars prepared by this method are uniform, the thermo-mechanical deformation in the same scale is also observed for other pillars in the array. It can be estimated from the micrographs that the micropillar contracts up to 76% of the original length in the longitudinal direction.

To better understand the thermomechanical properties of the LCEs, the contraction and relaxation were measured as a function of the temperature with a slow temperature variation (with the heating and cooling rates + or -1° C per minute) from 90°C to 130°C and back. Figure 6 shows the deformation of the micropillars with the temperature, where the pillars were made from 4-ADBB and with 20 mol% of different crosslinker agents. The deformation in the figure is given as the length ratio between the contracted pillar and the original one.



Figure 6. The length change of the LCE pillars obtained from 4-ADBB with different crosslinkers. ■: 1,4-butanediol acrylate; •: 1,5-pentanediol diacrylate; ▲: 1,6-hexanediol diacrylate.



Figure 7. The reversible switch between contraction and extension of the LCE pillars obtained from 4-ADBB with different crosslinkers. ■: 1,4-butanediol acrylate; •: 1,5-pentanediol diacrylate; ▲: 1,6-hexanediol diacrylate.

All of the LCE micropillars show significant contraction. Among the LCE micropillars showing the thermo-mechanical responses, all of the pillars show almost the same contraction as the crosslinking density is the same. The measured contractions are 26%, 20%, and 24% (the contraction is defined as $(L_0-L_T)/L_0$) for micropillars crosslinked by 1,4-butanediol acrylate, 1,5-pentanediol diacrylate, and 1,6-hexanediol diacrylate, respectively. The temperature for the LCE micropillars to reach the maximum contraction increases with the increasing of the spacer length of the crosslinker. The LCE micropillar crosslinked by 1,4-butanediol acrylate shows the lowest transition temperature among them. This observation is the same result as that of the effect of the spacer length of the monomer we have observed before [35]. As the spacer length of 1,4-butanediol acrylate is much shorter, the stronger coupling between the mesogens and backbone exists. As a result, the polymeric chains between the crosslinks will be distorted more significantly with respect to the equilibrium conformation. This departure from the equilibrium can be treated as an internal tension, which will trigger the relaxation to occur at a lower temperature to maximize the entropy.

The thermo-mechanical deformation behavior was further investigated through repeated contraction-extension variations by cycling up to ten times. The good reversibility and robustness shown in Fig. 7 verify the elasticity of the materials.

3.4 Effect of the tail length of monomer

The result obtained from 4-ADBB as the representative shows that LCE micropillars with reversible thermo-mechanical deformation and different temperatures at which the LCE micropillars reach the maximum contraction can be obtained by introducing a proper crosslinker. By similar method, LCE micropillars were prepared from the other synthesized acrylate monomers to study the effect of the tail length on the properties of the LCEs. In the experimental section, acrylate monomers with flexible tail groups of methoxyl (4-ADMB), oxyethyl (4-ADEB), butoxy (4-ADBB), hexyloxy (4-ADHB), and octoxy (4-ADOB) were synthesized and polymerized into corresponding linear polymers (P4ADMB, P4ADEB, P4ADBB, P4ADBB, P4ADBB). Only 4-ADMB, 4-ADBB, and 4-ADOB were used to fabricate the LCE micropillars as no liquid crystalline property was observed for 4-ADEB,



Figure 8. The length change of the LCE pillars obtained from different monomers with crosslinker 1,6-hexanediol diacrylate. ■: 4-ADMB; •: 4-ADBB; ▲: 4-ADOB.

P4ADEB, and P4ADHB both from the DSC and POM results (Table 1). In all experiments reported below, the crosslinking agent was fixed to be 1,6-hexanediol diacrylate and the concentration of it was controlled to be 20 mol%. Similarly results were observed on samples with the other crosslinking agents.

Figure 8 shows the contraction and relaxation of the micropillars made from 4-ADMB, 4-ADBB, and 4-ADOB with the temperature variation. The deformation in the figure is given as the length ratio of the contracted pillar to the original one. The micropillars show almost the same contraction, which are 22%, 24%, and 22% made from 4-ADMB, 4-ADBB, and 4-ADOB, respectively, indicating that the tail length has little affection on the contraction of the LCE micropillars. Another remarkable point that can be seen from Fig. 8 is that the transition temperature of the LCEs is closely related to the tail length of the monomers. For the LCE micropillars made from 4-ADMB, the transition temperature is around 136°C. The transition temperature decreased obviously with the increment of the tail length of the monomer,



Figure 9. The reversible switch between contraction and extension of the LCE pillars obtained from different monomers with different crosslinker of 1,6-hexanediol diacrylate. ■: 4-ADMB; • : 4-ADBB; ▲: 4-ADOB.

and decreased to 92°C for the LCE micropillars made from 4-ADOB. On one hand, the $T_{\rm NI}$ of the linear polymers and the LCEs decreased with the increment of the tail length of the monomer; on the other hand, monomer with longer tail length has a bigger conformation, which strengthens the correlation between the mesogens and backbone. Hence, the polymeric chains will be distorted more significantly with respect to the equilibrium conformation. This departure from the equilibrium can be treated as an internal tension, which will trigger the relaxation to occur at a lower temperature to maximize the entropy [35].

Similar to the result given in Fig. 7, a good reversibility and robustness can also be observed for the LCEs with the different tail lengths. Figure 9 shows the repeated contraction-extension variations by cycling up to 10 times, which verifies the good elasticity of the materials.

4. Conclusions

In order to investigate the structure-property relationship, we synthesized a series of side-on liquid crystalline acrylate monomers with different tail lengths (4-AD ω B). The monomers were characterized by ¹H NMR, ¹³C NMR, COSY, FT-IR, POM, and DSC. LCE micropillars were made from these newly synthesized monomers by the soft lithography and photopolymerization/photocrosslinking with different crosslinkers. The effect of the spacer lengths of the crosslinkers and the tail lengths of the monomers on the thermomechanical deformation of the LCE micropillars were systematically studied. The contraction of the LCE micropillars showed little relationship with these two molecular parameters, while the transition temperature of the LCEs is closely related to both of them. The transition temperature of the LCEs decreases with the decrement of the spacer length of the crosslinker and the increment of the tail length of the monomer.

Acknowledgment

The financial support from National Natural Science Foundation of China (Project No. 51603029) is gratefully acknowledged.

References

- [1] Ji, Y., Huang, Y. Y., Rungsawang, R., & Terentjev, E. M. (2010). Adv. Mater., 22, 3436.
- [2] Warner, M. et al. (2003). Liquid Crystal Elastomers, Oxford University Press: Oxford, UK.
- [3] van Oosten, C. L., Bastiaansen Cees, W. M., & Broer, D. J. (2009). Nat. Mater., 8, 677.
- [4] Ohm, C., Serra, C., & Zentel, R. (2009). Adv. Mater., 21, 48592.
- [5] Yoshino, T., Kondo, M., & Ikeda, T. (2010). Adv. Mater., 22, 1361.
- [6] Yamada, M., Kondo, M., & Ikeda, T. (2008). Angew. Chem. Int. Ed., 47, 4986.
- [7] Yang, H., Liu, J. J., & Zhang, X. Q. (2015). Chem. Commun., 51, 12126.
- [8] Liu, X. Y., Wei, R. B., & Keller, P. (2015). Adv. Funct. Mater., 25, 3022.
- [9] Michal, B. T., McKenzie, B. M., & Rowan, S. J. Macromolecules, 48, 3239.
- [10] Li, Y. Z., Pruitt, C., & Kessler, M. R. (2015). Macromolecules, 48, 2864.
- [11] Garcia-Amoros, J., & Velasco, D. (2015). Macromol. Rapid Commun., 36, 755.
- [12] Zeng, H., Wasylczyk, P., & Wiersma, D. S. (2015). Appl. Phys. Lett., 106, 111902.
- [13] Ware, T. H., & White, T. J. (2015). Polym. Chem., 6, 4835.
- [14] Yan, M., Tang, J. H., & Chen, E. Q. (2015). J. Meter. Chem. C, 3, 8526.
- [15] Yakacki, C. M., Saed, M., & Bowman, C. N. (2015). RSC Adv., 5, 18997.
- [16] Taylor, H. W., Michael, E. M., & Timothy, J. W. (2015). Science, 347, 982.
- [17] Ohm, C., Brehmer, M., & Zentel, R. (2012). Adv. Polym. Sci., 250, 49.
- [18] Torras, N., & Crompvoets, F. M. H. (2014). Sensor Actuat. A Phys., 208, 104.

- [19] Chen, M. L., Huang, H. T., & Yu, Y. L. (2011). Appl. Phys. A Mater., 102, 667.
- [20] Chen, M. L., Xing, X., & Cheng, F. (2010). Appl. Phys. A Mater., 100, 39.
- [21] Fleischmann1, E. K., Liang, H. L., & Zentel, R. (2012). Nat. Commun. 3, 1178.
- [22] Serak, S., Tabiryan, N., & Bunning, T. J. (2010). Soft Matter, 6, 779.
- [23] Thomsen, D. L., Keller, P., & Ratna, B. R. (2001). Macromolecules, 34, 5868.
- [24] Lehmann, W., Skupin, H., & Kremer, F. (2001). Nature, 410, 447.
- [25] Cotton, J. P., & Hardouin, F. (1997). Prog. Polym. Sci., 22, 795.
- [26] Buguin, A., Li, M. H., & Keller, P. (2006). J. Am. Chem. Soc., 128, 1088.
- [27] Yang, H., Buguin, A., & Keller, P. (2009). J. Am. Chem. Soc., 131, 15000.
- [28] Finkelmann, H., Nishikawa, E., & Warner, M. (2001). Phys. Rev. Lett., 87, 015501.
- [29] Yu, Y. L., Nakano, M., & Ikeda, T. (2003). Nature, 425, 145.
- [30] Lv, J. A., Wang, W. R., & Yu, Y. L. (2014). Macromol.Rapid Commun., 35, 1266.
- [31] Riou, O., Lonetti, B., & Mauzac, M. (2015). Angew. Chem. Int. Ed., 54, 10811.
- [32] Courty, S., Mine, J., & Terentjev, E. M. (2003). Euro. Phys. Lett., 64, 654.
- [33] Huang, C., Zhang, Q. M., & Jákli, A. (2003). Adv. Funct. Mater., 13, 525.
- [34] Urayama, K., Honda, S., & Takigawa, T. (2005). Macromolecules, 38, 3574.
- [35] Wei, R. B., Zhou, L. Y., & Keller, P. (2013). Polymer, 54, 5321.
- [36] Vinayakumara, D. R., Kumar, M., & Kumar, S. (2015). RSC Adv., 5, 26596.
- [37] Han, J., Wang, Z. Z., & Zhu, L. R. (2015). RSC Adv., 5, 47579.
- [38] Luo, Y. B., Chen, S., & Zhang, H. L. (2015). RSC Adv., 5, 54920.
- [39] Samui, A. B., Pandeya, S., & Mishra, S. P. (2015). RSC Adv., 5, 68351.
- [40] Ikeda, T., Nakano, M., & Kanazawa, A. (2003). Adv. Mater., 15, 201.
- [41] Ogawa, H., & Finkelmann, H. (2004). Macromol. Chem. Phys., 205, 593.
- [42] Beyer, P., Braun, L., & Zentel, R. (2007). Macromol. Chem. Phys., 208, 2439.
- [43] Bispo, M., Guillon, D., & Finkelmann, H. (2008). *Macromolecules*, 41, 3098.
- [44] Finkelmann, H., & Rehage, G. (1984). Adv. Polym. Sci., 60/61, 99.
- [45] Gray, G. W., Hill, J. S., & Lacey, D. (1991). Mol. Cryst. Liq. Cryst., 197, 43.
- [46] Mu, J., Okamoto, H., & Feng, X. S. (2001). Colloid Surf. A, 181, 303.
- [47] Lecommandoux, S., Achard, M. F., & Hardouin, F. (1998). Liq. Cryst., 25, 85.
- [48] Achard, M. F., Lecommandoux, S., & Hardouin, F. (1995). Liq. Cryst., 19, 581.
- [49] Ober, C. K., Jin, J., & Lenz, R. W. (1984). Adv. Polym. Sci., 59, 103.
- [50] Chen, X. F., Shen, Z. H., & Zhou, Q. F. (2010). Chem. Soc. Rev., 39, 3071.
- [51] He, X. Z., Zhang, B. Y., & Lin, J. R. (2005). J. Appl. Polym. Sci., 96, 1204.
- [52] Zhang, B. Y., He, X. Z., & Zhou, Q. H. (2007). J. Appl. Polym. Sci., 107, 1479.
- [53] Hu, J. S., Yang, L. Q., & Song, Z. W. (2010). Liq. Cryst., 37, 1385.
- [54] Küpfer, J., & Finkelmann, H. (1991). Macromol. Rapid. Commun., 12, 717.
- [55] Finkelmann, H., Kim, S. T., & Taheri, B. (2001). Adv. Mater., 13, 1069.
- [56] Ohm, C., Brehmer, M., & Zentel, R. (2010). Adv. Mater., 22, 3366.
- [57] Ohm, C., Kapernaum, N., & Zentel, R. (2011). J. Am. Chem. Soc., 133, 5305.
- [58] Ohm, C., Haberkorn, N., & Zentel, R. (2011). Small, 7, 194.
- [59] Wei, R. B., He, Y. N., & Keller, P. (2013). Macromol. Rapid. Commun., 34, 330.
- [60] Wei, R. B., He, Y. N., & Keller, P. (2014). Macromol. Rapid. Commun., 35, 1571.
- [61] Wei, R. B., Zhang, H. X., & Keller, P. (2014). Liq. Cryst., 41, 1821.
- [62] Keller, P., Thomse, D. L., & Li, M. H. (2002). Macromolecules, 35, 581.