European Polymer Journal 49 (2013) 3392–3401

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Synthesis and characterization of fluorinated liquid-crystalline elastomers containing chiral liquid-crystalline crosslinking units

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ARTICLE INFO

Article history:
Received 2 March 2013
Received in revised form 7 July 2013
Accepted 9 July 2013
Available online 26 July 2013

Keywords:
Liquid-crystalline polymers (LCPs)
Polysiloxanes
Chiral
Fluorinated polymers

ABSTRACT

Fluorinated chiral liquid-crystalline elastomers (LCEs) were graft copolymerized by a one-step hydrosilylation reaction with polymethylhydrogenosiloxane, a fluorinated LC monomer 4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoyloxy)phenyl 4-(undec-10-enoyloxy)benzoate (**PPUB**) and a chiral crosslinking LC monomer (3*R*,3a*R*,6*S*,6a*R*)-6-(undec-10-enoyloxy)hexahydrofuro[3,2-*b*]furan-3-yl 4′-(4-(allyloxy)benzoyloxy)biphenyl-4-carboxylate (**UHAB**). The chemical structure, liquid-crystalline behavior and polarization property were characterized by use of various experimental techniques. The effective crosslink density of the LCEs was characterized by swelling experiments. The thermal analysis results showed that the temperatures at which 5% weight loss occurred were greater than 250 °C for all the LCEs, and the residue weight nearby 600 °C increase with increasing chiral crosslinking components in the polymer systems. All the samples showed chiral smectic C mesophase when they were heated. The glass transition temperature and mesophase-isotropic phase transition temperature of fluorinated elastomers increased slightly with increase of chiral crosslinking mesogens in the polymer systems, but the enthalpy changes of mesophase-isotropic phase transition decreased slightly. In XRD curves, all the samples exhibited strong sharp reflections at small angles suggesting smectic layered packing arrangement. These fluorinated chiral LCEs showed 0.1–0.2 μC/cm^2 of spontaneous polarization with increasing chiral crosslinking component.

1. Introduction

Liquid crystalline elastomers (LCEs) have generated significant research interest because they combine the rubber elasticity of lightly cross-linked polymer chains with the orientational order of liquid crystals. These uncommon materials have been developed as promising functional materials due to their remarkable properties such as interesting mechanical, electrical, and optical properties [1–4].

The polymer network structure of LCEs is usually produced by the introduction of crosslinking segment into LC polymer systems. Through chemical design, various functional groups and mesogens can be introduced into the polymer networks for different application considerations [5–8], and different crosslinkings can result in materials with distinct properties [9]. At the present time nematic, cholesteric, and smectic phases have been identified in LCE systems. On the one hand, the LCE materials can show unique macroscopic features, such as huge thermomechanical response and soft elasticity, which make LCEs very promising for shape-memory applications [10–13]. On the other hand, the large deformations allowed by rubber elasticity can be coupled with the electrooptical properties of liquid crystals in the LCE materials. Networks containing chiral side groups were shown to exhibit piezoelectric and nonlinear optical activity in the cholesteric and chiral smectic C (S_C^*) phases [14].

Introduction of chiral functional groups to LCEs has become one of the most important and complex topics in

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http://dx.doi.org/10.1016/j.eurpolymj.2013.07.020

liquid crystal research. Chiral LC polymers may exhibit a marvelous variety of mesophases, including blue phases, cholesteric phase, and S_C^* phase. Chiral smectic C liquid crystal is one of the most fantastic LC phases since it can form helical structure. S_C^* elastomers have attracted interest in both industrial and scientific fields due to their additional properties such as ferroelectricity, piezoelectricity and pyroelectricity [15–17]. In synthetic categories, networks with S_C^* structures have been made by the photocrosslinking of S_C^* main-chain or side-chain liquid-crystal polymers. They can also be made through the thermally or chemically induced crosslinking of S_C^* or cholesteric mixtures consisting of nematic and chiral monomers.

Fluoropolymers display a unique combination of properties, including thermal stability, chemical inertness, self-extinguishing, and peculiar surface and electric properties, and are commonly used in high-end applications, such as aerospace and microelectronics. Thus fluoropolymers have generated significant research interest due to these attractive properties. Most research approaches have been focusing on the copolymerization of fluorinated monomers with functional co-monomers to form functional fluorocopolymers [18–21]. The innovative development of new types of highly fluorinated functional polymers with easy processability has become very attractive. In this study, we prepared fluorinated S_C^* LCEs in a one-step reaction, in which both the fluorinated liquid crystalline monomer and chiral mesogenic crosslinking agent are linked to the polymer backbone, as shown in Fig. 1.

2. Experimental

2.1. Materials and methods

Poly(methylhydrogeno)siloxane (**PMHS**, $M_n \approx 2300$) was obtained from ALDRICH without any further purification. 4′-Hydroxybiphenyl-4-carboxylic acid, bromopropene, 4-hydroxybenzoic acid, hexachloroplatinic acid hydrate, *p*-benzenediol, perfluorooctanoyl chloride, isosorbide and undec-10-enoic acid were purchased from Beijing HWRK Chemical Co. and used without any further purification. Pyridine, thionyl chloride, toluene, ethanol, chloroform, tetrahydrofuran (THF) and methanol were purchased from Shenyang Chemical Co.

FTIR spectra of the samples were performed on Perkin-Elmer instruments Spectrum One Spectrometer (PerkinElmer, Foster City, CA) by the KBr method. ^{1}H NMR (300 MHz) spectra were obtained with a Varian WH-90PFT NMR Spectrometer (Varian Associates, Palo Alto, CA) with tetramethylsilane (TMS) as an internal standard. The element analyses (EA) were carried out by using an Elementar Vario EL III (Elementar, Germany). Thermal behaviors were determined by using a NETZSCH TGA 209C thermogravimetric analyzer and a NETZSCH instruments DSC 204 (Netzsch, Wittelsbacherstr, Germany) at heating and cooling rates of 10 °C min^{-1} under nitrogen atmosphere. A Leica DMRX polarized optical microscope (POM, Leica, Wetzlar, Germany) equipped with a Linkam THMSE-600 hot stage (Linkam, Surrey, England) was used to observe the thermal transitions and to analyze the anisotropic textures. X-ray measurements of the samples were performed using Cu Kα (λ = 1.542 Å) radiation monochromatized with a Rigaku DMAX-3A X-ray diffractometer (Rigaku, Japan). Measurement of optical rotation (α) was carried out with a PerkinElmer instrument Model 341 Polarimeter at room temperatures using sodium light source (λ = 589 nm). The spontaneous polarization of the S_C^* samples were measured using a TD-88A ferroelectric material parameter test instruments (Nanjing NDWH Electron Co. Ltd., China).

2.2. Synthesis of fluorinated liquid crystalline monomers

The synthesis routes of fluorinated liquid crystalline monomer 4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoyloxy)phenyl 4-(undec-10-enoyloxy)benzoate (**PPUB**) is shown in Fig. 2. The intermediates 4-(chlorocarbonyl)phenyl undec-10-enoate (***1***) used in this work was synthesized according to previous reported procedure [22]. *p*-Benzenediol (55.0 g, 0.5 mol) and 8 mL pyridine were dissolved in 450 mL dry THF. To the solution, it was added dropwise with 80 mL THF solution of compound ***1*** (32.3 g, 0.1 mol). The reaction mixture was stirred at 65 °C for 32 h. The solvent was distilled out partly under reduced pressure. After cooling to room temperature, the residue was poured into 600 mL cold water. The precipitates were isolated by filtration, washed by hot water and dried in a vaccum oven. Recrystallization in alcohol resulted in white crystals of 4-hydroxyphenyl 4-(undec-10-enoyloxy)benzoate (***2***). Yield: 67%. m.p.: 94 °C. IR (KBr, cm^{-1}): 3408 (—OH), 3051, 2938, 2870 (CH_3, —CH_2—, —CH— and Ar—H), 1755–1720 (C=O in different ester linkage), 1608, 1499 (Ar), 1293, 1255, 1167 (C—O). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.27–1.59 [m, 12H, $CH_2{=}CHCH_2(C\underline{H}_2)_6CH_2COO{-}$]; 2.21–2.36 [m, 4H, $CH_2{=}CHC\underline{H}_2(CH_2)_6C\underline{H}_2COO{-}$]; 4.91–5.15 (m, 2H, $C\underline{H}_2{=}CH{-}$); 5.94–6.18 (m, 1H, $CH_2{=}C\underline{H}{-}$); 7.16–8.13 (m, 8H, Ar—$\underline{H}$).

Perfluorooctanoyl chloride (43.2 g, 0.1 mol) was dissolved in 255 mL THF to obtain a solution. It was added dropwise with 250 mL dry THF solution containing compound ***2*** (39.6 g, 0.1 mol) and 15 mL pyridine. The reaction mixture was stirred at 65 °C for 24 h. Some solvent was distilled under reduced pressure. After cooling to room temperature, the mixture was poured into 1000 mL cold water and acidified with 6 N sulfuric acid. The precipitates were recrystallized in alcohol, isolated by filtration, and dried in a vaccum oven to obtain white crystals of fluorinated liquid-crystalline monomer **PPUB**. Yield: 61%. IR (KBr, cm^{-1}): 3057, 2955, 2873 (—CH_2— and —CH—), 1752, 1720 (C=O in different linkage), 1172 (C—O—C), 1149 (C—F). Anal. Calcd for $C_{32}H_{27}F_{15}O_6$: C, 48.50%; H, 3.43%. Found: C, 48.42%; H, 3.46%. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.24–1.56 [m, 10H, $CH_2{=}CHCH_2(C\underline{H}_2)_5\ CH_2CH_2COO{-}$]; 1.72–1.86 [m, 2H, $CH_2{=}CHCH_2(CH_2)_5C\underline{H}_2CH_2COO{-}$]; 2.01–2.12 [m, 2H, $CH_2{=}CHC\underline{H}_2(CH_2)_5CH_2CH_2COO{-}$]; 2.32–2.42 [m, 2H, $CH_2{=}CHCH_2(CH_2)_5CH_2C\underline{H}_2COO{-}$]; 4.92–5.13 (m, 2H, $C\underline{H}_2{=}CH{-}$); 5.83–5.98 (m, 1H, $CH_2{=}C\underline{H}{-}$); 7.24–7.43 (m, 6H, ortho to O, Ar—$\underline{H}$); 8.12 (d, *J* = 8.1 Hz, 2H, ortho to carbonyl, Ar—$\underline{H}$).

2.3. Synthesis of chiral liquid crystalline crosslinking agent

The synthesis routes of chiral liquid-crystalline crosslinking agent (3*R*,3a*R*,6*S*,6a*R*)-6-(undec-10-enoyloxy)