



Polyether based side-chain liquid crystalline polymers: Anionic polymerization and phase structures



Yu Liu, Wei Wei, Huiming Xiong*

Department of Polymer Science, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

ARTICLE INFO

Article history:

Received 18 July 2013

Received in revised form

16 September 2013

Accepted 30 September 2013

Available online 4 October 2013

Keywords:

Side-chain liquid crystalline polyether

Anionic polymerization

Antiphase

ABSTRACT

Side-chain liquid crystalline (SCLC) polyethers with different spacers are successfully synthesized via anionic polymerization for the first time. The molecular weights of the polymers can range up to ~ 53 kg/mol with $M_w/M_n < 1.1$. The precise chemical structures including end groups have been characterized by employing Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) and the polymerization condition free of side reactions is further discussed. The phase behavior and structures of the polyethers have been investigated by combining various techniques including differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS) and polarized light microscopy (PLM). Two phase transformations are generally observed for each type of SCLC polyethers. Based on 2-dimensional (2D) X-ray patterns of oriented fiber and mechanically sheared samples, the low ordered liquid crystalline phase at high temperature is identified as a SmA phase for both SCLC polyethers. It is found that the polyether with a longer spacer exhibits a complex phase which is a mixture of a HexB phase and a frustrated HexB phase in analogy to smectic antiphase, whereas no such effect occurs for the polymer with a shorter spacer. Only HexB phase is observed for the low temperature phase of this polymer. The difference in phase structures is also revealed in the texture changes of PLM.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Over the last thirty years, substantial amount of SCLC polymers have been designed and synthesized, which have triggered significant development in fundamental science and applications [1–4]. SCLC polymers bearing inherent skeletal flexibility usually encompass polyolefins, polyacrylates, polysiloxanes and polyethers. Among them, polyether is particularly attractive due to its important characteristics such as high chemical stability as well as good elastic and adhesive properties [3,4]. In addition, polyether is known to be a typical type-A polymer with dipole moments accumulating along the chain contour [5,6]. However, synthesis of well-defined SCLC polyether with low polydispersity, controlled chain length and end functionality remains a great challenge.

Three approaches are commonly adopted to synthesize SCLC polyether through polymerization of epoxy monomers bearing mesogenic groups, including cationic polymerization [7–11], ionic coordinative polymerization [8,9,12], and anionic ring-opening polymerization [12–16]. For example, two types of polyethers

were synthesized by using cationic ring-opening polymerization, which were found to be either a mixture of cyclic oligomers and linear polymer with a yield of 85%, or a linear polymer with a low yield ($\sim 40\%$) [11]. Ionic coordinative polymerization has been also explored in the catalyst system of $AlEt_3/H_2O/acetylaceton$ [12], where the polymers were generated with a low yield and insoluble in common solvents. Soluble polymers have been made in other chelated catalyst systems, with a low yield and high polydispersity [8,9]. Low polydispersity of liquid crystalline polymers was achieved by using anionic ring-opening polymerization [15], however, the molecular weights cannot be larger than 6 kg/mol and conversion of monomer is less than 50%. A high yield of polyether could be produced, but the molecular weight is low and of a broad distribution [16]. Generally, anionic ring-opening polymerization of epoxy monomers produced liquid crystalline polymers of low molecular weight and/or of large polydispersity. After all these essentially important attempts, further systematical investigation of polymerization condition, possible side reaction and chemical structure including end groups turns out to be worthwhile.

In this paper, we report the first successful synthesis of series of well-defined SCLC polyethers by anionic polymerization. We demonstrate that all the synthesized polymers generally show

* Corresponding author. Tel.: +86 21 34202544.

E-mail addresses: hmxiong@sjtu.edu.cn, hmxiong@yahoo.com (H. Xiong).

controllable molecular weights in the range of 6–53 kg/mol with a narrow distribution of $M_w/M_n < 1.1$. The chemical structures have been well-characterized by MALDI-TOF experiment and the end groups have been clearly identified. It is shown that side reactions can be efficiently avoided under the current reaction conditions. Phase behavior and structure–property relationship of these SCLC polyethers have been further investigated by using DSC, SAXS, WAXD and PLM. It is found that increase of the spacer length of the polymer results in a more complex phase structure.

2. Experimental

2.1. Materials

Toluene was stirred over 24 h with sodium and distilled into a high-vacuum flask which was flame dried three times and contained sodium metal, and thawed repeatedly three times. 4-(4-pentyl-cyclohexyl) phenol (97%, Shanghai Boyle Chemical Co., Ltd), 1,4-Dibromobutane (98+%, TCI), glycidol (97%, J&K Chemical), potassium tert-butoxide (1M in THF, Acros Organics) were all used as received. All other reagents were of analytical grade and used as received. All solvents were purified by distillation.

2.2. Synthesis of monomers

2.2.1. Synthesis of 1-(4-bromo-butoxy)-4-(4-pentyl-cyclohexyl) benzene

1,4-Dibromobutane (39.2 mL, 0.324 mol), KOH (9.1 g, 0.162 mol), K_2CO_3 (22.44 g, 0.162 mol), CH_3OH (60 mL), acetone (100 mL) were added into a three-necked flask with a fitted stirring bar. 4-(4-pentyl-cyclohexyl)-phenol (20 g, 0.081 mol) was dissolved in 100 mL CH_3OH and 220 mL acetone, then added dropwise. The reaction mixture was stirred at 65 °C for 48 h. The solid was filtered, the resulting solution was then concentrated under reduced pressure to afford a turbid mixture. Then the entire mixture was recrystallized with 200 mL ethanol to get a white crystal (21.6 g, 70.1%). 1H NMR (400 MHz, $CDCl_3$, ppm) δ : 7.12–7.10 (d, 2H, C_6H_4), 6.82–6.80 (d, 2H, C_6H_4), 3.98–3.95 (t, 2H, CH_2O), 3.50–3.47 (t, 2H, CH_2Br), 2.43–2.36 (m, 1H, Ar- C_6H_{10}), 2.09–1.84 (m, 8H, C_6H_{10} , CH_2CH_2), 1.45–1.18 (m, 11H, C_6H_{10} , $CH_2-CH_2-CH_2$), 1.08–0.97 (q, 2H, CH_2), 0.90–0.87 (t, 3H, CH_3).

2.2.2. Synthesis of 2-{4-[4-(4-pentyl-cyclohexyl)-phenoxy]-butoxymethyl}oxirane

1-(4-Bromo-butoxy)-4-(4-pentyl-cyclohexyl)benzene (16 g, 0.042 mol), glycidol (5.8 mL, 0.084 mol), NaOH (powder, 2.52 g, 0.063 mol), DMF (500 mL) was stirred at 30 °C for 72 h. Water and ethyl acetate were added to extract the mixture into a separatory funnel. The water was removed and extracted with ethyl acetate and the organic layer was collected in an Erlenmeyer flask. Anhydrous magnesium sulfate powder was added, the solution was filtered, and then concentrated *via* a rotary evaporator to yield a turbid mixture. The mixture was purified by chromatography (SiO_2 , ethyl acetate/hexane (1:40)) to give a white crystal (8.1 g, 52%). 1H NMR (400 MHz, $CDCl_3$, ppm) δ : 7.12–7.10 (d, 2H, C_6H_4), 6.82–6.80 (d, 2H, C_6H_4), 3.97–3.94 (t, 2H, CH_2O), 3.74–3.70, 3.41–3.37 (q, 2H, OCH_2), 3.61–3.50 (m, 2H, OCH_2), 3.16–3.12 (m, 1H, OCH), 2.81–2.78, 2.62–2.60 (q, 2H, OCH_2), 2.43–2.36 (m, 1H, Ar- C_6H_{10}), 1.86–1.71 (m, 8H, C_6H_{10} , OCH_2CH_2), 1.45–1.18 (m, 11H, C_6H_{10} , $CH_2-CH_2-CH_2$), 1.08–0.97 (q, 2H, CH_2), 0.90–0.87 (t, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ : 14.4 (CH_3), 23.0 (CH_3CH_2), 26.0 ($C_6H_4OCH_2CH_2CH_2CH_2O$), 26.4 ($C_6H_4OCH_2CH_2CH_2CH_2O$), 27.0 ($CH_3CH_2CH_2$), 32.5 (CH_2CH_2CH), 33.8 ($CH-CH_2CH_2-CH$), 34.8 ($CH_3CH_2CH_2$), 37.5–37.6 (CH_2CH_2CH), 44 ($CH-Ph$), 44.9 (CH_2O), 50.9 (OCH_2CH), 67.8 ($C_6H_4OCH_2CH_2CH_2CH_2O$), 71.3

($C_6H_4OCH_2CH_2CH_2CH_2O$), 71.6 (OCH_2CH), 114.6 ($CHCHC$), 127.9 ($CCHCH$), 140.9 ($CCHCH$), 156.8 ($COCH_2$). ESI-MS for $C_{24}H_{38}O_3$ (relative ratio): (m/z) ($[M-Na]^+$ 374).

2.2.3. Synthesis of 2-[[4-(4-pentyl-cyclohexyl)phenoxy]methyl]oxirane

In a 500 mL flask, the 4-(4-pentyl-cyclohexyl)phenol (20 g, 0.081 mol), t -BuOH (200 mL), epoxy chloropropane (35.8 mL, 0.325 mol, Aldrich) and t -BuOK powder (10.3 g, 0.085 mol) were introduced and stirred at 65 °C for 3 days. The mixture was filtered. The solvents were removed by rotary evaporator, and the product was isolated by column chromatography on silica gel with hexane-ethyl acetate (40:1) as eluent, yielding a white solid (19.5 g, 80% yield). 1H NMR (400 MHz, $CDCl_3$, ppm) δ : 7.10–7.14 (d, 2H, C_6H_4), 6.82–6.88 (d, 2H, C_6H_4), 4.13–4.20 (q, 1H, OCH_2), 3.92–3.99 (q, 1H, OCH_2), 3.30–3.36 (q, 1H, OCH), 1.77–1.93 (d, 4H, Ar- C_6H_{10}), 1.15–1.47 (m, 11H, C_6H_{10} , $CH_2-CH_2-CH_2$), 0.96–1.10 (q, CH_2), 0.83–0.94 (t, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ : 14.4 (CH_3), 23.0 (CH_3CH_2), 27.0 ($CH_3CH_2CH_2$), 32.5 (CH_2CH_2CH), 33.8 ($CH-CH_2CH_2-CH$), 34.8 ($CH_3CH_2CH_2$), 37.5–37.6 (CH_2CH_2CH), 44.0 ($CH-Ph$), 44.9 (CH_2O), 50.4 (OCH_2CH), 69.1 (OCH_2CH), 114.6 ($CHCHC$), 127.9 ($CCHCH$), 140.9 ($CCHCH$), 156.8 ($COCH_2$). ESI-MS for $C_{20}H_{30}O_2$ (relative ratio): (m/z) ($[M-Na]^+$ 324).

2.2.4. Anionic ring-opening polymerization

EOBC1 ($M_w = 12,600$ g/mol) is taken as an example. A high-vacuum flask containing a stir bar was placed on the high vacuum line and flame dried. The monomers (1.0 g, 2.67 mmol) were added into the flask, and dried at 40 °C for 2 h. 18-crown-6 (27 mg, 100 μ mol) and potassium tert-butoxide (1 M in THF, 100 μ L, 100 mmol) were added under the nitrogen atmosphere and THF was then removed. Toluene was vacuum distilled into the flask. The weight ratio of monomer to solvent varied from 1:1 to 1:3, and the mole ratio of initiator to 18-crown-6 was 1:1. The reaction was cooled and maintained at 0 °C for 7 d. EOBC2, EOBC3 and EOBCV were synthesized following the same procedure.

2.3. Characterization

Gel permeation chromatography with a multi-angle laser light scattering detector (Wyatt Dawn EOS) plus a differential refractometer detector (Waters Model 2414) has been used to determine the molecular weight of the polymers and their polydispersity. The MALDI-TOF was utilized to characterize the exact mass of the polymer including the end groups, which was conducted on a Bruker Ultraflex III TOF/TOF (Bruker Daltonics, Inc., Billerica, MA), equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. The instrument was calibrated externally with a poly(methyl methacrylate) standard prior to each measurement. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was served as matrix. Sodium trifluoroacetate (NaTFA) served as cationization salt. ESI-MS measurements were performed on a Shimadzu LCMS-2020 single quadrupole liquid chromatograph mass spectrometer (LC/MS). The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, 1H NMR; 100 MHz, ^{13}C NMR) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent and the internal standard tetramethylsilane.

The thermal behaviors were investigated on a TA Q2000 with a liquid nitrogen cooler. The heating process always preceded the cooling process, and the cooling and heating rates were always kept identical. The peak temperatures were used as the transition temperatures.

Liquid crystal textures were examined using PLM (Leica 2000) coupled with Mettler hot stage (FP 82 HT with a FP-90 central

Download English Version:

<https://daneshyari.com/en/article/5181363>

Download Persian Version:

<https://daneshyari.com/article/5181363>

[Daneshyari.com](https://daneshyari.com)