

Synthesis of a main-chain liquid crystalline azo-polymer via “click” chemistry

Xiaolin Kang · Jiarui Zhao · Haiyang Li · Shangjin He

Received: 25 October 2012 / Revised: 15 March 2013 / Accepted: 18 March 2013 / Published online: 16 April 2013
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Abstract A main-chain liquid crystalline azo-polymer (BPHCHA) was prepared through the copper-catalyzed “click” reaction between the alkyne group on 4,4'-bis((6-(propargyloxy)hexyl)oxy) biphenyl (BPH) and the azide group on 4-(6-azidohexyloxy)carbonyl-4'-(6'-azidohexyloxy) azobenzene (AHCHA). The “click” reaction was confirmed by FT-IR, ¹H NMR, and GPC studies. The phase transition behavior of BPH, AHCHA, and the resulting azo-polymer BPHCHA was investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). AHCHA and BPHCHA exhibited mesomorphic behavior, while BPH is a crystalline compound. A liquid crystalline phase from 39 to 69 °C for AHCHA upon heating was observed under POM. Schlieren texture was observed at 130 °C for BPHCHA on cooling from 150 °C and annealed at 130 °C for 15 min. Moreover, DSC and POM studies showed that BPHCHA exhibited monotropic mesomorphic behavior.

Keywords “Click” chemistry · Main-chain liquid crystalline azo-polymer · Differential scanning calorimetry · Polarized optical microscopy

Introduction

Liquid crystalline polymers (LCPs) offer the advantageous combination of the anisotropy of liquid crystals with the attractive bulk properties and processing possibilities of polymers. On the other hand, owing to their efficient photoisomerization and photoinduced anisotropy, polymers

with azobenzene moieties have potential utilities in holographic data storage [1, 2], optical switching devices [3, 4], diffractive optical elements [5], and other optical and photonic applications.

In the past few years, “click” reactions, as termed by Sharpless et al. [6], have gained a great deal of attention due to their high specificity, quantitative yields, and near perfect fidelity in the presence of most functional groups. The most popular “click” chemistry reaction is the Huisgen dipolar cycloaddition reaction between an azide and an alkyne, leading to 1,2,3-triazole [7–9]. The great potential of this coupling procedure for the construction of well defined (functional) polymers [10–16], bioconjugated polymers [17, 18], and polymers with complex topologies [19–24] has been quickly recognized and is the subject of intensive research.

In our previous work [25], we described the first synthesis of a side-chain liquid crystalline polymer containing the cholesteryl moiety (Ch-SCLCP) by combining the ring-opening polymerization and “click” chemistry. Recently, the preparation of side-chain liquid crystalline azo-polymers [26–28] by “click” chemistry was also reported. Tang [29] and Senthil [30] reported the synthesis of main-chain liquid crystalline polymers via “click” chemistry. However, to our knowledge, there is no report on the synthesis of main-chain liquid crystalline azo-polymer via “click” chemistry.

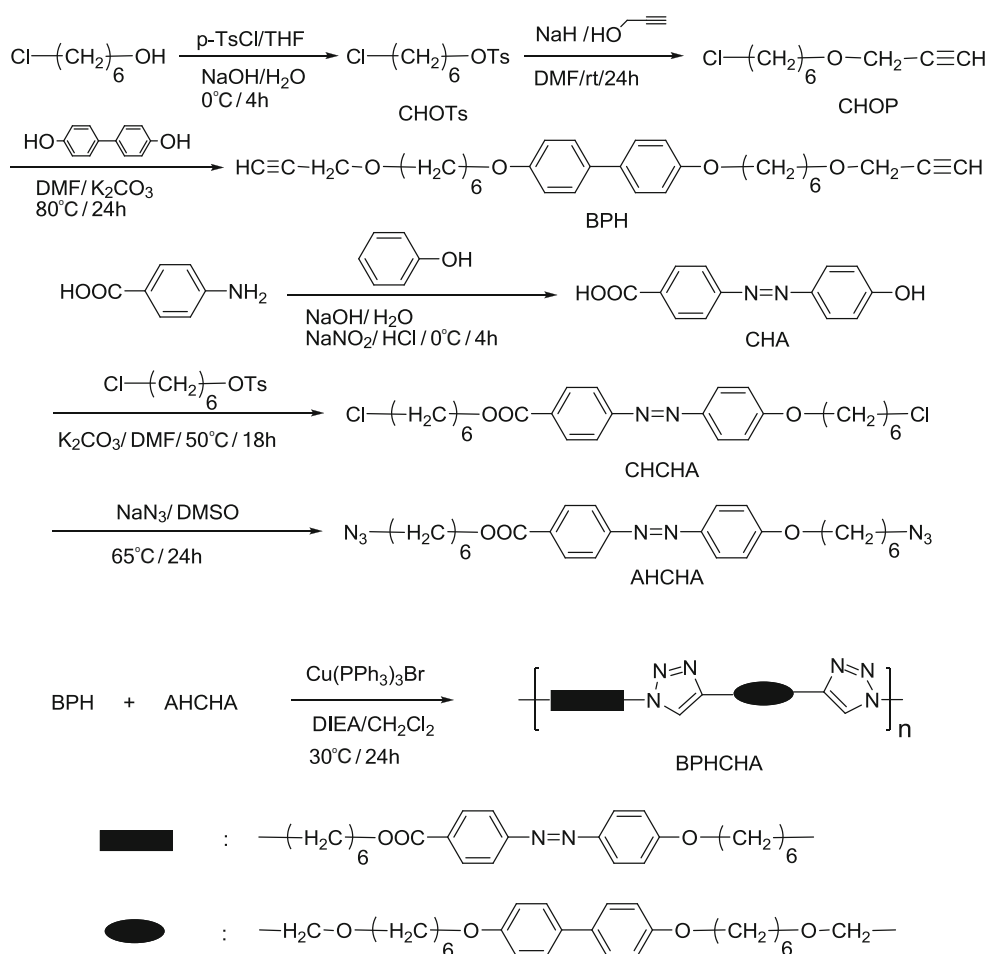
We describe herein the first synthesis of a main-chain liquid crystalline azo-polymer via “click” chemistry and the characterization of the resulting polymer.

Experimental

Caution: Because of the high explosive characteristics of compounds bearing azide group, they should be handled in very small amounts, and all reactions with these compounds

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Scheme 1 Reaction scheme for the preparation of 4,4'-bis((6-(propargyloxy)hexyl)oxy) biphenyl (BPH), 4-(6-azidohexyloxy)carbonyl-4'-(6'-azidohexyloxy)azobenzene (AHCHA), and the subsequent copper(I)-catalyzed “click” reaction



must be conducted in a well designed hood, using a safety shield or barrier to protect against possible explosion.

Materials

Propargyl alcohol (99 %) was used as received from Acros Organics. $\text{Cu}(\text{PPh}_3)_3\text{Br}$ was prepared by the reported

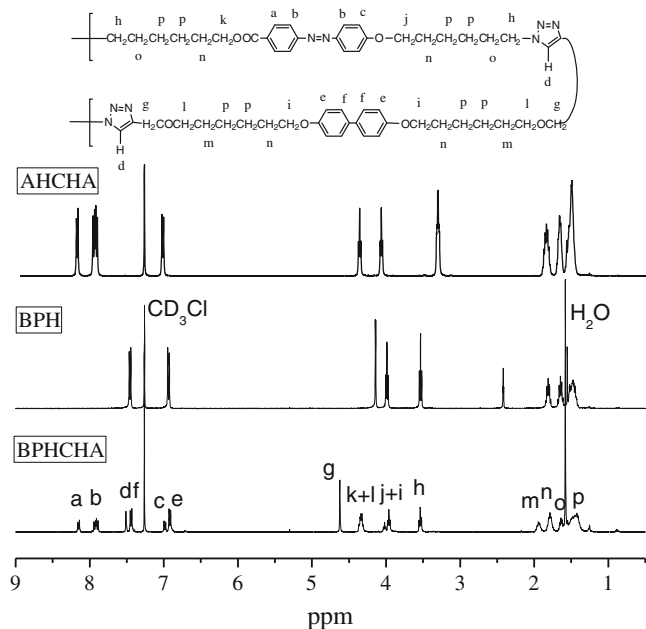


Fig. 1 ^1H NMR spectra of AHCHA, BPH, and the azo-polymer BPHCHA

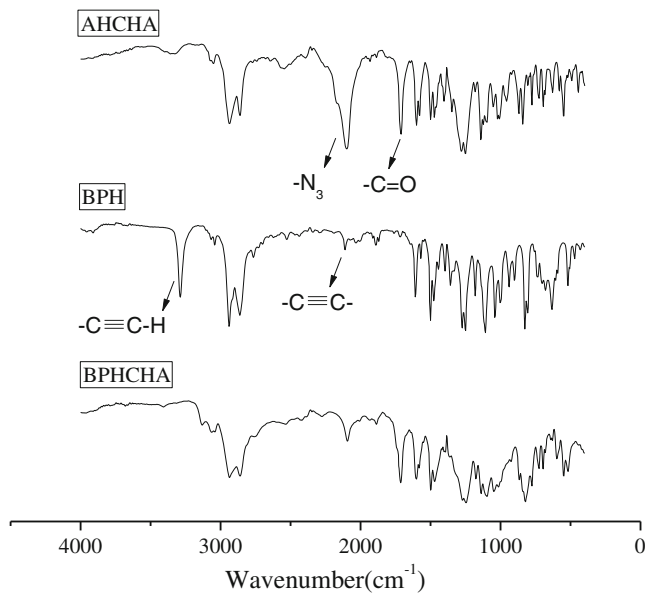


Fig. 2 FT-IR spectra of AHCHA, BPH, and the azo-polymer BPHCHA

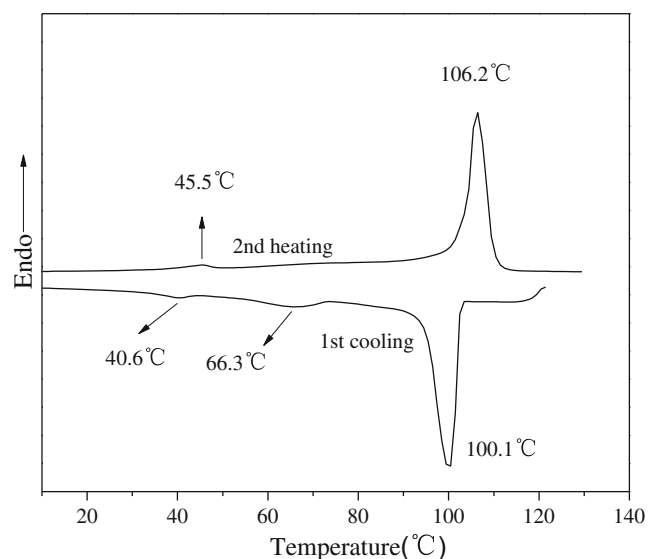


Fig. 3 DSC thermograms of BPH in the first cooling and second heating mode (10 °C/min)

procedure [31]. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and dichloromethane were purchased from Tianjin Kewei Ltd. and distilled from CaH_2 . All other chemicals were purified according to conventional methods or used as received.

Characterization

^1H NMR (400 MHz) spectra were recorded at room temperature on a Varian-400 spectrometer. CDCl_3 or $\text{DMSO}-d_6$ was used as the solvent. The chemical shifts were referenced relative to the solvent. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer. The spectral resolution was maintained at 2 cm^{-1} . Molecular weights and molecular weight distributions were measured with a Waters 1515 gel permeation chromatograph (GPC) equipped with a Waters 2410 differential refractometer as detector. Three Styragel columns (HR2, HR4, and HR6) were used in series. GPC samples were run at 40 °C with THF as the mobile phase at a flow rate of 1 mL/min, and the columns were calibrated using

narrow distribution polystyrene standards obtained from Polymer Laboratories Ltd. UK. The phase transition temperature of the polymer was determined with a NETZSCH DSC204 calorimeter under nitrogen atmosphere, at the heating and cooling rates of 10 °C/min. High purity indium and zinc were used to calibrate the calorimeter. The thermogravimetric analysis (TGA) was performed on a NETZSCH TG209 instrument, using nitrogen as purge gas, operating from 50 to 800 °C with a heating rate of 10 °C/min. Polarized optical microscopy (POM) was performed on an Olympus BX51M microscope fitted with a Linkam TH600 hot stage and a LinkamTMS94 thermal controller. To obtain micrographs, a powder sample was placed between two glass plates. The UV–Vis study of the solution of polymer in chloroform was performed on a Hitachi U-3000 spectrophotometer at room temperature.

Synthetic procedures

Synthesis of 6-chlorohexyl-4-methylbenzenesulfonate

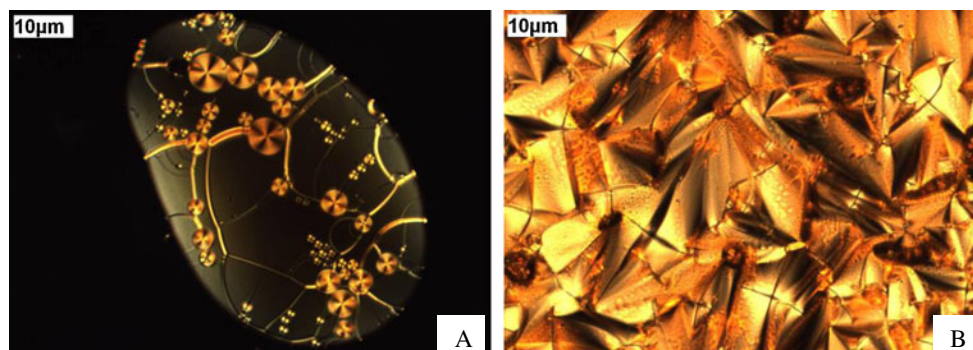
A suspension of sodium hydroxide (6.0 g, 0.15 mol) and 6-chlorohexan-1-ol (10.0 g, 73.2 mmol) in water (50 mL) was cooled with ice/water bath, and a solution of p-toluenesulfonyl chloride (15.0 g, 78.7 mmol) in THF (50 mL) was added slowly over 2 h. After being stirred for additional 2 h, the mixture was extracted twice with dichloromethane, washed with water, and dried over anhydrous MgSO_4 . After removal of MgSO_4 and solvent, 15.0 g of colorless liquid product was obtained (yield, 84.2 %).

^1H NMR ($\text{DMSO}-d_6$): 7.75–7.78 (d, 2H, ArH), 7.44–7.47 (d, 2H, ArH), 3.97–4.01 (t, 2H, O- CH_2 -), 3.53–3.57 (t, 2H, Cl- CH_2 -), 2.41 (s, 3H, Ar- CH_3), 1.52–1.64 (m, 4H, - CH_2 -), 1.18–1.30 (m, 4H, - CH_2 -).

Synthesis of 1-chloro-6-(propargyloxy)hexane

To a cold solution of propargyl alcohol (3.8 g, 67.8 mmol) in DMF (30 mL), NaH (2.4 g, 0.10 mol) was added under argon atmosphere. The mixture was stirred for 1.5 h, and then the

Fig. 4 POM images of AHCHA. **a** At 60.0 °C on the first heating scan. **b** At 30.7 °C on the first cooling scan



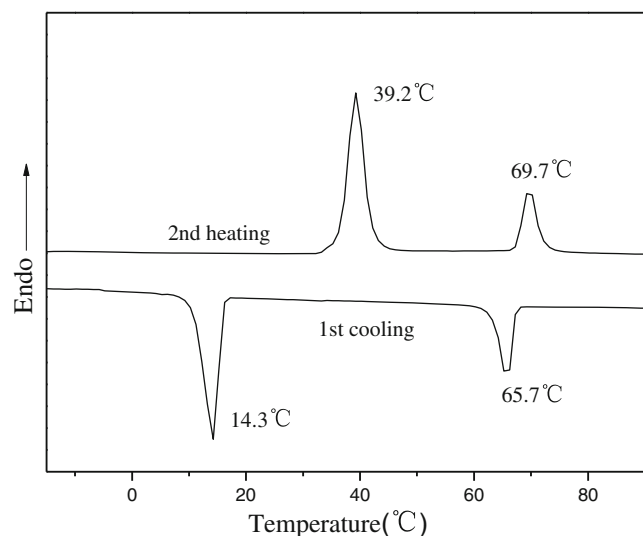


Fig. 5 DSC thermograms of AHCHA in the first cooling and second heating mode (10 °C/min)

solution of 6-chlorohexyl-4-methylbenzenesulfonate (CHOTs) (30.0 g, 0.10 mol) in DMF (20 mL) was added slowly over 3 h. The reaction mixture was stirred for additional 24 h and quenched with H₂O (300 mL). The mixture was extracted twice with dichloromethane, washed with water, and dried over Na₂SO₄. The resulting solution was concentrated under vacuum and then purified by column chromatography eluting with mixture of hexane and ethyl acetate (v/v = 20:1) to give 5.0 g of 1-chloro-6-(propargyloxy)hexane (CHOP) (yield: 42.2 %).

¹H NMR (CDCl₃): 4.12–4.13 (d, 2H, Cl-CH₂-), 3.49–3.55 (m, 4H, -CH₂-O-CH₂-), 2.43–2.44 (t, 1H, -CCH), 1.74–1.81 (m, 2H, -CH₂-), 1.57–1.62 (m, 2H, -CH₂-), 1.37–1.48 (m, 4H, -CH₂-).

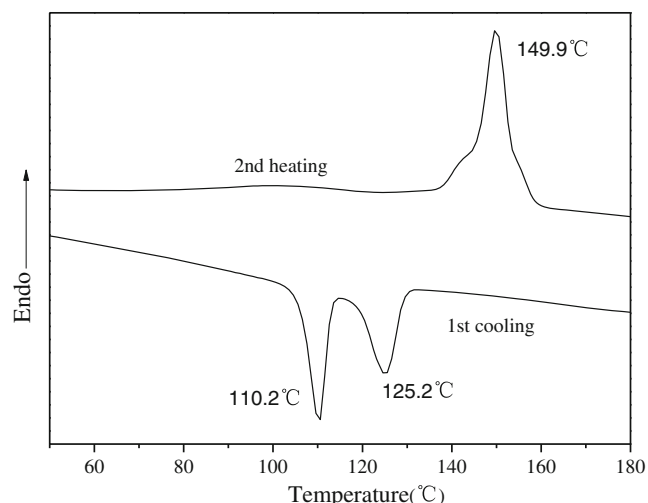


Fig. 6 DSC thermograms of BPHCHA in the first cooling and the second heating mode (10 °C/min)

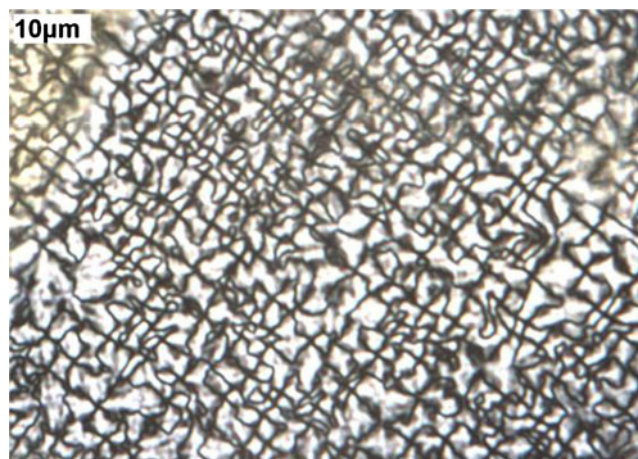


Fig. 7 POM image of BPHCHA at 130 °C on the first cooling scan

Synthesis of 4,4'-bis((6-(propargyloxy)hexyl)oxy) biphenyl

A solution of CHOP (1.17 g, 6.7 mmol), 4,4'-biphenol (0.50 g, 2.7 mmol) and anhydrous potassium carbonate (1.12 g, 8.1 mmol) in DMF (30 mL) was stirred at 80 °C for 24 h. The reaction mixture was then poured into 100 mL of water. The orange precipitate was separated and purified by twice recrystallization from ethanol, giving 0.65 g of 4,4'-bis((6-(propargyloxy)hexyl)oxy) biphenyl (BPH) (yield, 52.4 %; mp, 105 °C).

¹H NMR (CDCl₃): 7.44–7.46 (d, 4H, Ar-H), 6.92–6.94 (d, 4H, Ar-H), 4.13–4.14 (d, 4H, -O-CH₂-CCH), 3.97–4.00 (t, 4H, Ar-O-CH₂-), 3.51–3.55 (t, 4H, -O-CH₂-), 2.41–2.42 (t, 1H, -CCH), 1.77–1.84 (m, 4H, -CH₂-), 1.62–1.61 (m, 4H, -CH₂-), 1.46–1.51 (m, 8H, -CH₂-). IR (KBr, cm⁻¹): 3,287 (≡C-H); 2,109 (C≡C).

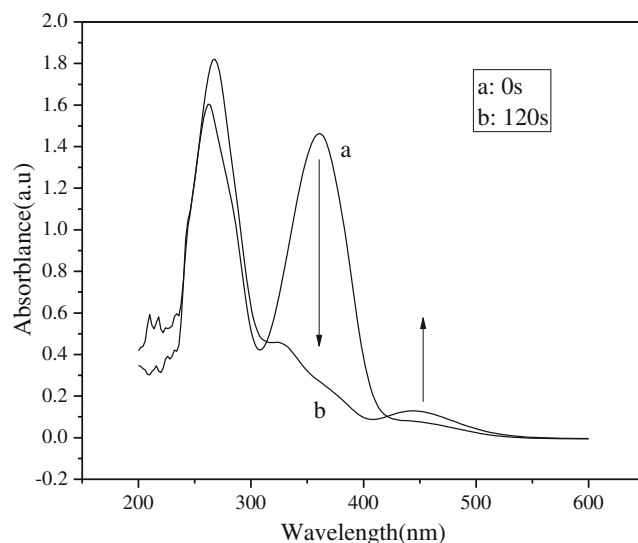


Fig. 8 UV-visible absorption spectra of the solution of BPHCHA in chloroform at room temperature **a** before UV irradiation and **b** after 120 seconds irradiation with 365 nm light

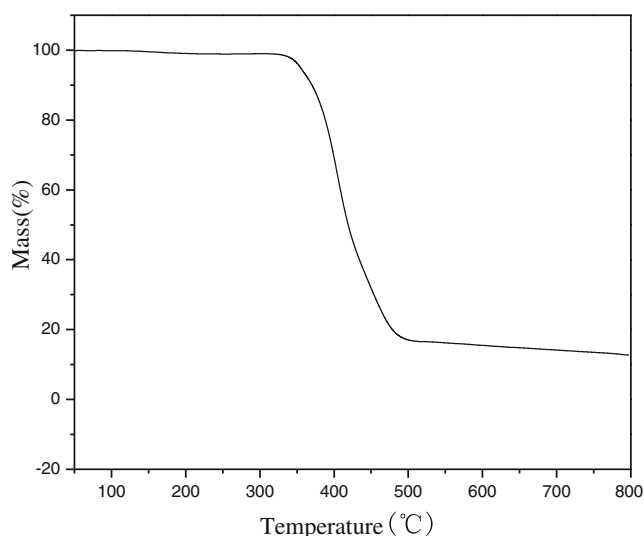


Fig. 9 Thermogravimetric curve of BPHCHA

Synthesis of 4-carboxy-4'-hydroxy-azobenzene

4-carboxy-4'-hydroxy-azobenzene (CHA) was prepared according to the previous literature [32] as follows: Cold NaNO_2 (3.8 g, 55.1 mmol) aqueous solution (30 mL water) was added to the mixture of 4-aminobenzoic acid (6.9 g, 50.3 mmol) in hydrochloric acid (15 mL, wt 36 %) at 0 °C and stirred for 20 min. Then, the solution of phenol (4.8 g, 50.6 mmol) and NaOH (7.2 g, 180.0 mmol) in water (80 mL) was added over 30 min at 0 °C. After being stirred for 2 h with ice/water bath, the pH value of the solution was adjusted to about 3 with diluted hydrochloric acid (1 M). The orange precipitate was separated and purified by twice recrystallization from saturated NaHCO_3 aqueous solution, giving 6.5 g of CHA (yield, 53 %).

$^1\text{H NMR}$ ($\text{DMSO}-d_6$): 8.00–8.02 (d, 2H, Ar-H), 7.76–7.79 (d, 2H, Ar-H), 7.70–7.72 (d, 2H, Ar-H), 6.94–6.97 (d, 2H, Ar-H).

Synthesis of 4-(6-chlorohexyloxy)carbonyl-4'-(6'-chlorohexyloxy)azobenzene

A solution of CHA (2.7 g, 11.0 mmol), CHOTs (6.4 g, 22.0 mmol) and anhydrous potassium carbonate (3.0 g, 21.7 mmol) in DMF (100 mL) was stirred at 50 °C for 18 h. Then the mixture was poured into 100 mL of water. The orange precipitate was separated and purified by twice recrystallization from ethanol to give 4.3 g of 4-(6-chlorohexyloxy)carbonyl-4'-(6'-chlorohexyloxy)azobenzene (CHCHA) (yield, 81 %; mp, 64–65 °C).

$^1\text{H NMR}$ (CDCl_3): 8.15–8.17 (d, 2H, Ar-H), 7.89–7.95 (m, 4H, Ar-H), 7.00–7.02 (d, 2H, Ar-H), 4.34–4.37 (t, 2H, $\text{ArCOO}-\text{CH}_2-$), 4.04–4.07 (t, 2H, $\text{Ar-O}-\text{CH}_2-$), 3.54–3.58 (m, 4H, $\text{Cl}-\text{CH}_2-$), 1.78–1.83 (m, 8H, $-\text{CH}_2-$), 1.50–1.59 (m, 8H, $-\text{CH}_2-$).

Synthesis of 4-(6-azidohexyloxy)carbonyl-4'-(6'-azidohexyloxy)azobenzene

A solution of CHCHA (2.0 g, 3.9 mmol) and NaN_3 (0.60 g, 9.2 mmol) in DMSO (100 mL) was stirred at 65 °C for 24 h. Then the mixture was poured into 100 mL of water. The orange precipitate was separated and purified by twice recrystallization from ethanol to give 1.6 g of 4-(6-azidohexyloxy)carbonyl-4'-(6'-azidohexyloxy)azobenzene (AHCHA) (yield, 78 %; mp, 39–40 °C).

$^1\text{H NMR}$ (CDCl_3): 8.15–8.17 (d, 2H, Ar-H), 7.89–7.95 (m, 4H, Ar-H), 7.00–7.02 (d, 2H, Ar-H), 4.34–4.37 (t, 2H, $\text{ArCOO}-\text{CH}_2-$), 4.04–4.07 (t, 2H, $\text{Ar-O}-\text{CH}_2-$), 3.27–3.31 (m, 4H, N_3-CH_2-), 1.80–1.86 (m, 4H, $-\text{CH}_2-$), 1.64–1.67 (m, 4H, $-\text{CH}_2-$), 1.49–1.52 (m, 8H, $-\text{CH}_2-$). IR (KBr, cm^{-1}): 2100 ($-\text{N}_3$), 1711 ($-\text{C}=\text{O}$).

Synthesis of azo-polymer (BPHCHA) via “click” reaction

A solution of BPH (0.10 g, 0.21 mmol), AHCHA (0.11 g, 0.22 mmol), $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (4.10 mg, 4.40×10^{-3} mmol), and *N,N*-Diisopropylethylamine (0.17 g, 1.31 mmol) in CH_2Cl_2 (5 mL) was stirred at 30 °C for 24 h under argon atmosphere. The resulting solution was precipitated into methanol, giving 0.19 g of BPHCHA with 90 % yield. GPC: $M_n=17,446$ g/mol; $M_w/M_n=1.31$.

Results and discussion

The synthetic route for the preparation of the main-chain liquid crystalline azo-polymer is shown in Scheme 1.

CHOTs was synthesized through tosylation of 6-chlorohexan-1-ol in THF/ H_2O with NaOH as the base. CHOTs reacted then with propargyl alcohol in DMF to yield CHOP. BPH was obtained by alkylation of 4,4'-biphenol under the Williamson aryl-alkyl ether synthesis using CHOP by the nucleophilic displacement reaction in DMF. The structure of BPH was confirmed by $^1\text{H NMR}$ (Fig. 1) with the $\text{C}\equiv\text{CH}$ signal at 2.4 ppm and FT-IR analysis (Fig. 2) with the alkyne C-H stretching frequency at $3,287\text{ cm}^{-1}$, $\text{C}\equiv\text{C}$ signal at $2,109\text{ cm}^{-1}$. To prepare the azobenzene-functionalized diazides, CHA was synthesized according to the reported procedure [32]. CHA reacted then with CHOTs to yield CHCHA. The expected azobenzene-functionalized diazides, namely AHCHA was prepared through azidation of CHCHA in DMSO at 65 °C for 24 h. FT-IR spectrum of AHCHA is shown in Fig. 2. The azide and carbonyl group showed absorption band at $2,100$ and $1,711\text{ cm}^{-1}$, respectively.

The “click” reaction between BPH and AHCHA was conducted in CH_2Cl_2 at 30 °C, with $(\text{PPh}_3)_3\text{CuBr}$ as the catalyst, in the presence of *N,N*-diisopropylethylamine. As evaluated with GPC, the number average molecular weight

and the molecular weight distribution of the resulting azo-polymer BPHCHA were 17,446 g/mol and 1.31, respectively. ^1H NMR spectrum of BPHCHA is shown in Fig. 1. The peaks at 7.5 and 4.6 ppm were assigned to the proton of triazole ring and its neighboring methylene protons, respectively. Moreover, the disappearance of the $\text{C}\equiv\text{CH}$ signal at 2.4 ppm was a clear indication of the “click” reaction. The “click” reaction was further confirmed by FT-IR analysis (Fig. 2) with the disappearance of the alkyne C-H stretching frequency at $3,287\text{ cm}^{-1}$, $\text{C}=\text{C}$ signal at $2,109\text{ cm}^{-1}$. It can be seen from Fig. 2, weak absorption band at $2,100\text{ cm}^{-1}$ still exhibited, which should be ascribed to the polymer chain end group, i.e., azide group, resulting from the stoichiometry excess of AHCHA in the “click” reaction.

The phase transition behavior of BPH, AHCHA, and the resulting azo-polymer BPHCHA was investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) with heating/cooling rate of $10\text{ }^\circ\text{C}/\text{min}$.

In Fig. 3, DSC thermograms of BPH of the first cooling and second heating scans are shown. Three exothermic peaks at 100.1 , 66.3 , and $40.6\text{ }^\circ\text{C}$ were observed in the thermogram of the first cooling scan. The microscopic observation suggested that these three peaks corresponded to liquid–crystal, crystal–crystal and crystal–crystal transitions, respectively. During the second heating scan, endothermic peak at $45.5\text{ }^\circ\text{C}$ should be the crystal–crystal transition, and the other at $106.2\text{ }^\circ\text{C}$ corresponds to the melting of BPH.

Figure 4 shows the POM images of AHCHA. Upon heating, the sample melted at $39\text{ }^\circ\text{C}$. Above this point, we observed a liquid crystalline texture [Fig. 4a], which was transformed into the dark-field view at $69\text{ }^\circ\text{C}$. Upon cooling, the birefringence appeared at $60\text{ }^\circ\text{C}$, and focal-conic texture [Fig. 4b] was seen in the crystals. To support this finding, AHCHA was investigated by means of DSC. Upon the first cooling (Fig. 5), exothermic peak at $65.7\text{ }^\circ\text{C}$ represented transition from isotropic phase to liquid crystalline phase, and the second exothermic peak at $14.3\text{ }^\circ\text{C}$ corresponded to the crystallization of AHCHA. In the second heating scan, two endothermic peaks at 39.2 and $69.7\text{ }^\circ\text{C}$ were associated with melting and isotropization transitions, respectively.

Figure 6 show DSC thermograms of the resulting azo-polymer BPHCHA of the first cooling and second heating scans. In the cooling scan, two exothermic transitions were exhibited at 125.2 and $110.2\text{ }^\circ\text{C}$, which should ascribed to the isotropic to liquid crystal and liquid crystal to crystal transitions, respectively. During the second heating scan, only one endothermic peak at $149.9\text{ }^\circ\text{C}$ corresponding to the melting transition showed on the DSC thermogram. The phase transitions were confirmed by the POM. Sample was heated from room temperature to $165\text{ }^\circ\text{C}$, and the isotropic melting temperature was observed to be $150\text{ }^\circ\text{C}$. When it cooled to $130\text{ }^\circ\text{C}$ and was annealed for 15 min, Schlieren texture was observed (Fig. 7). The DSC and POM studies

showed that the resulting azo-polymer BPHCHA exhibited monotropic mesomorphic behavior, which is similar to the work, reported by Macknight [33] and Chiellini [34].

The UV–Vis absorption spectra of the solution of azo-polymer BPHCHA (0.048 mg/mL) in chloroform are given in Fig. 8. Two absorption bands centered around 365 and 455 nm related, respectively, to the $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ electronic transitions of the azobenzene group. Upon irradiation with 365 nm light, azobenzene group undergoes a trans-to-cis photoisomerization process. Correspondingly, the absorption band at 365 nm decreased obviously, while the absorption band at 455 nm slightly increased.

The TGA curve of azo-polymer BPHCHA is shown in Fig. 9. The weight loss of 5.0 % was at $354.7\text{ }^\circ\text{C}$. The fairly high thermal stability for the azo-polymer BPHCHA might be attributed to the introduction of rigid groups, namely biphenyl groups and triazole rings onto the polymer chain [35].

Conclusion

Alkyne-terminated and azide-terminated compounds, BPH and AHCHA, were prepared through the copper-catalyzed “click” reaction between the alkyne groups on BHP and the azide groups on AHCHA, a main-chain liquid crystalline azo-polymer BPHCHA was obtained. The “click” reaction was confirmed by FT-IR, ^1H NMR, and GPC studies. The phase transition behavior of BPH, AHCHA, and the resulting azo-polymer BPHCHA was investigated by DSC and POM. A liquid crystalline phase from 39 to $69\text{ }^\circ\text{C}$ for AHCHA upon heating was observed under POM. Schlieren texture was observed at $130\text{ }^\circ\text{C}$ for BPHCHA on cooling from $150\text{ }^\circ\text{C}$ and annealed at $130\text{ }^\circ\text{C}$ for 15 min. DSC and POM studies showed that BPHCHA exhibited monotropic mesomorphic behavior. The UV–Vis analysis showed trans-to-cis photoisomerization of azobenzene group when the solution of azo-polymer BPHCHA in chloroform was irradiated with 365 nm light. Moreover, the azo-polymer BPHCHA exhibited fairly high thermal stability as investigated with TGA.

Acknowledgment We thank the Natural Science Foundation of Tianjin (10JCYBJC02100) for financial support.

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