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Synthesis of novel multi-arm star azobenzene side-chain liquid crystalline copolymers with a hyperbranched core

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Abstract

A series of novel multi-arm star side-chain liquid crystalline (LC) copolymers with hyperbranched core moieties were synthesized by atom transfer radical polymerization (ATRP) using a multi-functional hyperbranched polyether as the initiator and chlorobenzene as the solvent. The multi-functional hyperbranched polyether initiator was prepared from poly(3-ethyl-3-(hydroxymethyl)oxetane) (PEHO) and 2-bromo-2-methylpropionyl bromide. The azobenzene side-chain liquid crystalline arms were designed to have an LC conformation of poly[6-(4-methoxy-4′-oxy-azobenzene)hexyl methacrylate] with different molecular weights. Their characterization was performed with ^{1}H NMR, size exclusion chromatograph (SEC), differential scanning calorimetry (DSC) and thermal polarized optical microscopy (POM). The multi-arm star side-chain liquid crystalline copolymers exhibited a smectic and a nematic phase, and the phase transition temperatures from the smectic to the nematic phase and from the nematic to isotropic phase increased with increasing the molecular weight of the multi-arm star side-chain liquid crystalline copolymers from 1.78×10^4 to 9.07×10^4.

Keywords: Liquid crystalline polymer; Atom transfer radical polymerization; Hyperbranched polymer; Copolymer

1. Introduction

Over the past decade, star-shaped polymers have generated a great deal of interest within the scientific community due to their particular bulk and solution properties [1,2]. In general, star polymer can be prepared by two basic synthetic approaches, which are known as arm-first technique and core-first technique. The arm-first technique involves the synthesis of preformed arms, usually through different living polymerizations to prepare linear living polymer chains, followed by reaction with a multi-function linking agent [3,4] or some cross-linked agents [e.g., divinylbenzene] to form star-shaped polymer [5–12]. The core-first technique involves the use of a multi-functional initiator such as the functional hyperbranched polymer and dendrimer [13–21]. The number of arms in the star-shaped polymer prepared by the core-first technique can be determined by the number of initiating sites on the multi-functional initiator.

Side-chain liquid crystalline polymers (LCPs), which represent a combination of liquid crystalline behavior and polymeric properties, have been the subject of intensive research during the last decade. Many linear side-chain liquid crystalline block copolymers have been synthesized by different living polymerizations [22], such as controlled/living radical polymerizations includes nitroxide-mediated radical polymerization [23–26], reversible addition–fragmentation chain transfer (RAFT) [27] and atom transfer radical polymerization (ATRP) [28–34]. For example, Tian and co-workers [31] have prepared amphiphilic side-chain liquid crystalline diblock

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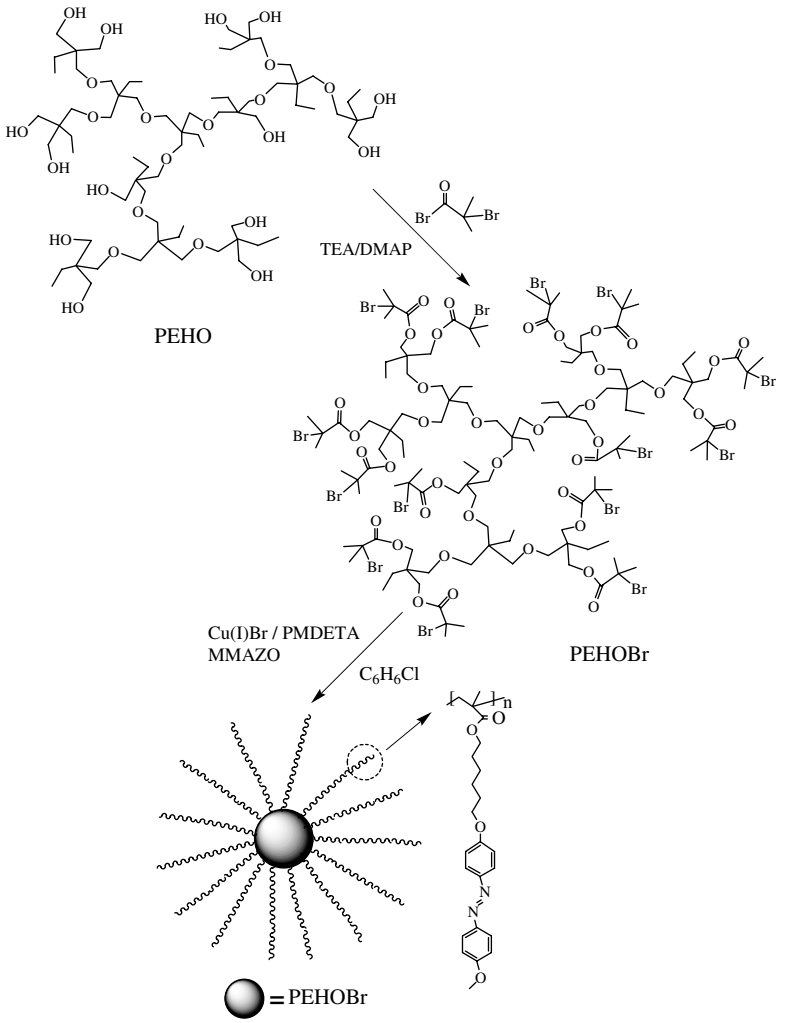

Scheme 1.

copolymers with azobenzene moieties by atom transfer radical polymerization (ATRP). We have also synthesized amphiphilic side-chain liquid crystalline block copolymers with *p*-methoxyazobenzene moieties by ATRP [32,33]. Kasko et al. [29] reported three-arm star side-chain liquid crystalline polymer with cyanobiphenyl moieties by ATRP. The side-chain liquid crystalline polymers containing azobenzene have potential applications in the fields of information storage, optical memory, waveguide switch, and so forth [35]. On the other hand, the cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane to form hyperbranched polyethers has gained increased interest in recent years [36–39]. The hyperbranched polyether architectures are greatly affected by reaction conditions [38,39]. In this work, we reported the synthesis of series novel multi-arm star side-chain liquid crystalline copolymers with *p*-methoxyazobenzene moieties using multi-functional macroinitiators by ATRP. The multi-functional macroinitiator was synthesized from poly(3-ethyl-3-(hydroxymethyl)oxetane), esterified with 2-bromo-2-methylpropionyl bromide. It was used for the atom transfer radical polymerization of 6-(4-methoxy-4′-oxy-azobenzene)hexyl methacrylate (MMAZO) in the presence of Cu(I)Br and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) in chlorobenzene. The multi-arm star copolymers are designated P_n ($n = 1$–11). The synthetic process is presented in Scheme 1.

2. Experimental section

2.1. Materials

N,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%), 2-bromo-2-methylpropionyl bro-

mide (Acros, 98%), 4-(dimethylamino)-pyridine (DMAP) (Acros, 99%) were used without further purification. Cu(I)Br (Shanghai Chemical Reagents Co., A.R.grade, 99%) was purified by stirring over 24 h in acetic acid. After filtration, it was washed with absolute ethyl alcohol and ether and then dried in vacuo. Chlorobenzene (C_6H_6Cl) (Shanghai Chemical Reagents Co., A.R.grade, 99%) and Triethylamine (TEA) (Shanghai Chemical Reagents Co., A.R.grade) were purified as described [33]. Tetrahydrofuran (THF) (Shanghai Chemical Reagents Co., A.R.grade) was refluxed with CaH_2 and distilled. All other chemicals were used as received. The poly(3-ethyl-3-(hydroxymethyl)oxetane) (PEHO) [M_n(DMF) = 8.60×10^3, $M_w/M_n = 1.20$, ^{1}H NMR (DMSO-d_6, δ/ppm): 4.15 (br, –CH_2O**H**), 3.30–3.00 (br, m, –C**H**$_2$OH, –C**H**$_2$O–), 1.25 (br, –C**H**$_2$$CH_3$), 0.8 (br, –$CH_2$C**H**$_3$). ^{13}C NMR (DMSO-$d_6$, δ/ppm): 71.5 (t, –**C**H_2O–), 61.8 (s, –**C**H_2OH), 43.3 (s, **C**(CH_2–)$_4$), 23.4 (t, –**C**$H_2$$CH_3$), 7.45 (s, CH_2 **C**H_3)] was prepared as reported in the literature [38] from 3-ethyl-3-(hydroxymethyl)oxetane. The azobenzene monomer, 6-(4-methyl-4′-oxy-azobenzene) hexyl methacrylate (MMAZO) was prepared using the procedure described by Craig and Imrie [40].

2.2. Characterization

NMR spectra were obtained on a 400 Varian NMR instrument using $CDCl_3$ or DMSO-d_6 as solvent, tetramethyl silane as the internal standard. Molecular weights M_n and polydispersity M_w/M_n were measured on a size exclusion chromatograph (PE series 200, 100 μL injection column, 10 μm PL gel 750 mm mixed-B columns) equipped with RI detector using DMF as an eluent at 40 °C. The column system was calibrated by a set of mono-dispersed standard polystyrenes. A Perkin–Elmer Pyris-1 differential scanning calorimeter was used to determine the thermal transitions which were read as the maximum or minimum of the endothermic or exothermic peaks, respectively. Glass transition temperatures (T_g) were read as the middle of the change in heat capacity. Pure indium was used as a reference material to calibrate both the temperature scale and the melting enthalpy before the sample was tested. Samples with a typical mass of 5.0 ± 0.1 mg were encapsulated in sealed aluminum pans and were heated at 10 °C/min heating rate from −20 to 160 °C under nitrogen for the first scan, immediately cooled at 10 °C/min cooling rate to −20 °C and then heated at 10 °C/min heating rate from −20 to 160 °C for the second scan. A Leica DMLP microscope equipped with a Leitz 350 hot stage was used to observe the thermal transitions and to analyze the anisotropic textures. Fourier Transform Infrared (FT-IR) spectra were recorded on a Perkin–Elmer Spectrum one spectrometer.

2.3. Synthesis of multi-functional macroinitiator (PEHOBr)

The synthesis of multi-functional macroinitiator was achieved using poly(3-ethyl-3-(hydroxymethyl)oxetane) (PEHO) and 2-bromo-2-methylpropionyl bromide in dry THF solvent in the presence of TEA and DMAP. In a typical experiment, PEHO (6.00 g, 51.7 mmol hydroxyl-groups) was dissolved in 50 mL dry THF. Then, TEA (6.00 g, 59.0 mmol) and DMAP (0.73 g, 5.9 mmol) were added. The solution was transferred into a 150 mL three-neck round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet and a magnetic stirrer. The flask was then cooled in a water/ice bath. 2-bromo-2-methylpropionyl bromide (15.00 g, 65.2 mmol) in 20 mL THF was added dropwise to the solution while stirring. After adding completely, the temperature was allowed to rise to room temperature subsequently. The reaction was continued under stirring for 24 h. After removing precipitate by filtering, the solution was washed twice with water, once with 5% $NaHCO_3$ solution, and again with water before being dried with anhydrous Na_2SO_4 and precipitated in cold (0 °C) methanol. The residue was filtered and dried in vacuo yielding a colorless sticky solid. The yield was 35.6%.

^{1}H NMR ($CDCl_3$, δ/ppm): 4.11–4.07 (br, m, –C**H**$_2$-OOC–), 3.34–3.22 (br, m, –C**H**$_2$O–), 1.92 (s, –C(C**H**$_3$)$_2$-Br), 1.61–1.36 (br, m, –C**H**$_2$–), 0.92–0.79 (br, m, –C**H**$_3$). IR (KBr, ν/cm^{-1}): 1730 (C=O). SEC (DMF): $M_n = 1.07 \times 10^4$, $M_w/M_n = 1.25$.

2.4. Synthesis of multi-arm star copolymer

The multi-arm star copolymers were synthesized in the presence of the multi-functional macroinitiator, PEHOBr, in chlorobenzene with Cu(I)Br as catalyst and PMDETA as ligand. Typically, an oven-dried Schlenk tube was charged with PEHOBr multi-functional macroinitiator (0.039 g, 0.15 mmol *tert* Br-group), MMAZO (0.350 g, 1.14 mmol), Cu(I)Br (1.43 mg, 0.01 mmol), chlorobenzene (3.000 g) and a magnetic stirrer, and the tube was sealed with a rubber septum and degassed three cycles by pulling a vacuum and back-filling with argon gas. Then, PMDETA (1.73 mg, 0.01 mmol) was added via a syringe. The reaction was carried out at 90 °C for 12 h, and then cooled to room temperature. The sample was further diluted with THF, removed copper salts through a plugged column of neutral aluminum oxide and precipitated in a large volume of petroleum ether. The sample was purified by reprecipitating three times from THF to petroleum ether and dried in a vacuum oven overnight at 50 °C. The conversion of polymerization was determined gravimetrically.

3. Results and discussion

3.1. Synthesis

The multi-functional macroinitiator (PEHOBr) was synthesized by reacting the poly(3-ethyl-3-(hydroxymethyl)oxetane) (PEHO) and 2-bromo-2-methylpropionyl bromide (Scheme 1), and carried out at 0 °C in the presence of TEA and DMAP in THF as solvent. Its characterization was investigated with ^{1}H NMR and FT-IR. The characteristic absorption peak of the ester group at 1730 cm^{-1}, which is not present in the poly(3-ethyl-3-(hydroxymethyl)oxetane), is observed on the FT-IR spectrum of the multi-functional macroinitiator because of the esterification. Also, as can be seen in the new signals at 4.11–4.07 ppm from (–C**H**$_2$OOC–) and 1.92 ppm from [–C(C**H**$_3$)$_2$Br], which are not present in the poly(3-ethyl-3-(hydroxymethyl)oxetane) (Fig. 1(B)), appear for the multi-functional macroinitiator (Fig. 1(A)) in $CDCl_3$ after esterification. Therefore, the multi-functional macroinitiator was successfully synthesized.

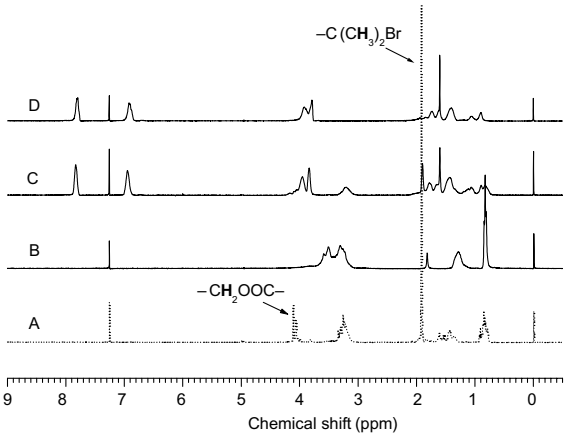

Fig. 1. ^{1}H NMR spectra ($CDCl_3$): (A) PEHOBr, (B) PEHO, (C) P_4, (D) P_{11}.

It is known that the tertiary bromoester-groups are effective initiator for ATRP of methylacrylate deriva-

Table 1
Characterization and thermal transitions data of the multi-arm star copolymers

Polym.	Yield (%)	wt[a] (%)	M_n[b] ($\times10^{-4}$)	M_w/M_n	Phase transitions temp. (°C) and enthalpy changes (J/g)[c]	
					Second heating	First cooling
PEHO			0.86	1.20	g35	g34
PEHOBr			1.07	1.25	g−4	g0
P_1	56	25	1.78	1.45	g49	g46
P_2	57	20	1.97	1.42	g48 S65(0.6) N105(0.3)I	g45
P_3	62	15	2.01	1.43	g53 S68(0.3) N106(0.3)I	g50
P_4	67	10	2.29	1.46	g50 S85(0.5) N106(0.3)I	g55 N91(−0.5)I
P_5	70	5	2.63	1.49	g56 S84(0.4) N105(1.0)I	g55 N102(−1.0)I
P_6	86	2.5	3.28	1.50	g66 S79(0.8) N119(1.9)I	S75(−3.4) N118(−2.8)I
P_7	87	2	4.31	1.57	g72 S86(1.2) N128(1.5)I	S81(−3.1) N126(−2.7)I
P_8	85	1.5	5.64	1.63	g74 S92(2.1) N134(3.0)I	S87(−3.0) N132(−2.9)I
P_9	83	1	7.73	1.55	g76 S93(2.4) N135(3.3)I	S89(−3.1) N134(−3.0)I
P_{10}	88	0.5	9.07	1.68	g77 S94(2.5) N137(3.7)I	S90(−3.1) N135(−2.7)I
P_{11}[d]	85	0	2.24	1.21	g75 S91(4.1) N132(3.3)I	S88(−4.4) N130(−3.2)I

[a] wt% = $[W_{PEHOBr}/(W_{PEHOBr} + W_{MMAZO})] \times 100\%$, where W_{PEHOBr} and W_{MMAZO} are the weights of the multi-functional macroinitiator and monomer (MMAZO).

[b] M_n, number-average molecular weight determined by SEC.

[c] S = smectic phase, N = nematic phase, g = glassy phase, I = isotropic.

[d] Homopolymer was synthesized by ATRP using ethyl 2-bromo-2-methylpropionate as initiator, PMDETA as ligand and Cu(I)Br as catalyst in chlorobenzene solvent. Polymerization time is 10 h, Polymerization temperature is 100 °C.

tives [41]. The multi-functional macroinitiator was used to initiate the monomer MMAZO in chlorobenzene solution for the multi-arm star copolymer by ATRP. In order to obtain different degrees of polymerization, the ratio of monomer-to-initiator was varied (Table 1). From Fig. 1, we can observe the characteristic resonance originating from phenyl moieties at both 7.80 and 6.91 ppm and that from PEHO segment at 3.30–3.22 ppm in P_4 (Fig. 1(C)). Fig. 2 depicts SEC curves of some multi-arm star copolymers. From SEC analysis, the multi-arm star copolymers possessed a narrow unimodal peak, and the molecular weight of multi-arm star copolymers increased. Also, the polydispersity of multi-arm star copolymer was around 1.60 and narrower. So far, the multi-functional macroinitiator can initiate MMAZO to produce a multi-arm star copolymer in chlorobenzene solvent by ATRP. According to the literatures reported, the resulting multi-arm star side-chain liquid crystalline block copolymers with *p*-methoxyazobenzene moieties are the first multi-arm star azobenzene liquid crystalline copolymer synthesized by ATRP.

3.2. Thermotropic phase behavior

Homopolymer based on the monomer MMAZO is a thermotropic liquid crystalline polymer that can exhibit a smectic phase and a nematic phase transition [33], and the phase transition temperatures of the smectic phase to the nematic phase transition and the nematic phase transition to the isotropic are designated as T_{S-N} and T_{N-I} correspondingly. Table 1 summarizes the equilibrium thermotropic behavior of the multi-arm star copolymers, which is originated from the first cooling scans and on subsequent second heating scans. Fig. 3 presents the second heating and the first cooling DSC curves of the multi-arm star copolymers. To investigate the liquid crystal properties of the multi-arm star copolymers, the different weight ratio of multi-functional macroinitiator-to-monomer was varied to control the degree of polymerization of each arm. From Fig. 3 and Table 1, the multi-arm star copolymer (P_1) did not exhibit liquid crystal properties when the multi-functional macroinitiator/monomer weight ratio was 25%. It was possible that the molecular weight of the liquid crystalline polymer arms was lower or the hyperbranched polyether core was compatible with the liquid crystalline polymer arms. With increasing the molecular weight from 1.97×10^4 to 9.07×10^4 and decreasing the multi-functional macroinitiator/monomer weight ratio from 25% to 0.5%, T_{S-N} changed 65 to 94 °C, T_{N-I} increased from 105 to 137 °C, and T_g changed from 48 to 77 °C, and the liquid crystalline phase transition temperatures (T_{S-N}, T_{N-I}) of the multi-arm star copolymers were greatly improved, and the multi-arm star copolymers mainly exhibited properties of the liquid crystalline polymer arms. This change trend was similar to linear side-chain liquid crystalline block copolymers [31–33].

The polarized optical microscopy (POM) can identify the mesophases. We can observe the thermal transitions

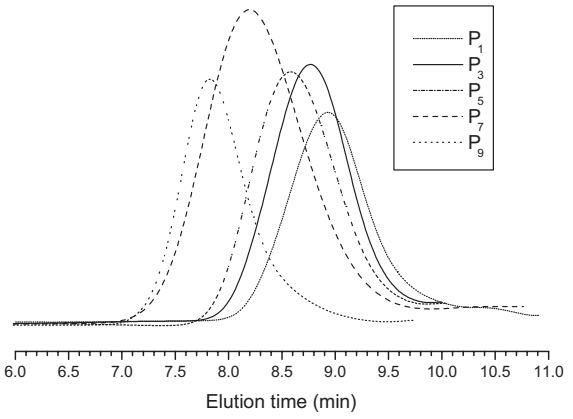

Fig. 2. SEC traces of some multi-arm star copolymers.

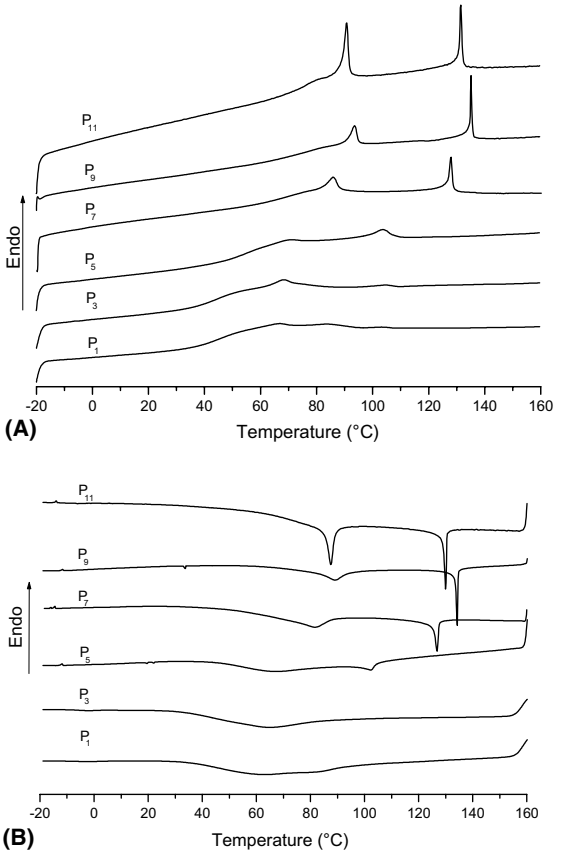

Fig. 3. DSC curves of some multi-arm star copolymers by ATRP: (A) the second heating curves; (B) the first cooling curves.

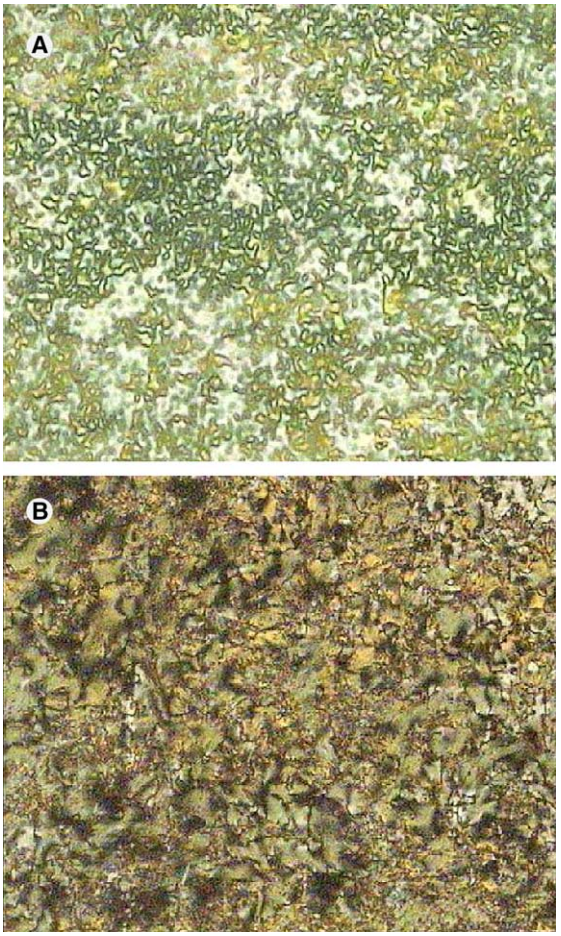

Fig. 4. Representative polarized optical micrograph of the texture of P_7: (A) 116 °C; (B) 81 °C (magnification: 200×).

of the multi-arm star copolymers and analyze their anisotropic textures by polarized optical microscopy. For example, the anisotropic textures cannot observe during the heating and cooling procedures of the sample P_1. For P_7, sample was heated to isotropic phase and subsequently cooled to 124 °C, a representative schlieren nematic texture (Fig. 4(A)) was observed. Further cooling into the smectic phase yielded a typical focal-conic fan texture (Fig. 4(B)). Fig. 4 shows a representative polarized optical micrograph.

4. Conclusions

Novel multi-arm star azobenzene side-chain liquid crystalline copolymers with different molecular weight were synthesized successfully by ATRP using hyperbranched polyether multi-functional macroinitiator in the presence of Cu(I)Br and PMDETA as catalyst system in chlorobenzene solvent. The change trend of the liquid crystal properties, which were stabilized greatly with increasing the molecular weight of the liquid crystalline polymer arms in the multi-arm star azobenzene side-chain liquid crystalline copolymers, was similar to linear azobenzene side-chain liquid crystalline block copolymers.

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