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Synthesis of a Novel Miktoarm Star Azobenzene Side-Chain Liquid Crystalline Copolymers by Atom Transfer Radical Polymerization

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Summary

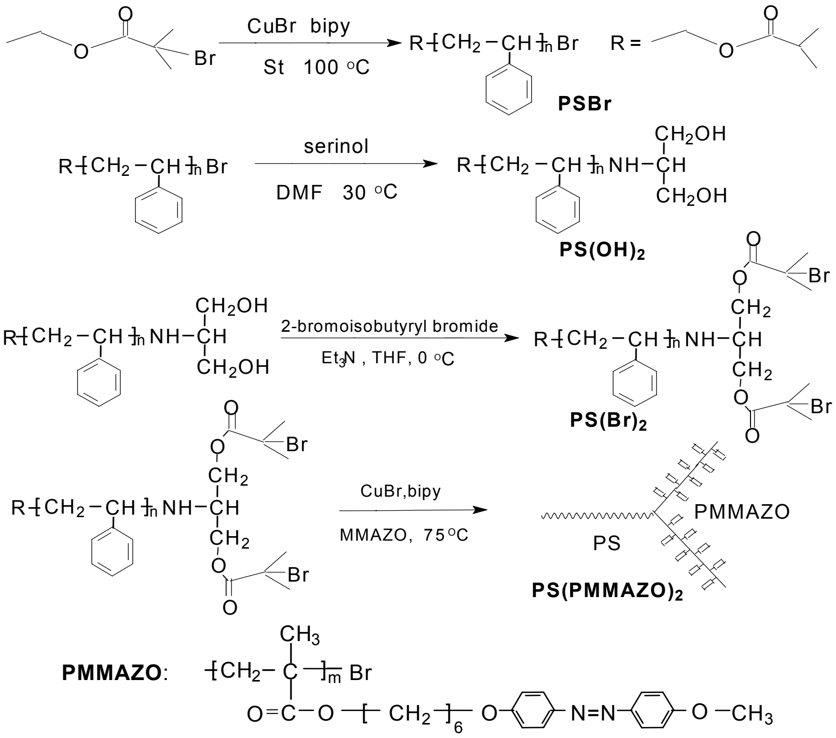
A series of miktoarm star novel azobenzene side-chain liquid crystalline (LC) copolymers were synthesized by combination of atom transfer radical polymerization (ATRP) and chemical modification of the termini of ATRP-derived polymers. These miktoarm star copolymers carrying one polystyrene (PS) arm and two poly [6-(4-methoxy-4′-oxy-azobenzene) hexylmethacrylate] (PMMAZO) arms were characterized by ^{1}H NMR and GPC. The liquid crystailline behavior of these copolymers was studied by DSC and POM. It was found that the miktoarm star copolymers have the similar LC properties to PMMAZO homopolymer, and their thermal stability of the mesophases is increased, while the phase transition enthalpies are reduced.

Introduction

The side-chain liquid crystalline polymers containing azobenzene have potential applications in the fields of information storage, optical memory, waveguide switch, and so forth [1-4]. So they have been the subjects of intensive research during the last decade. In recent years, attention on synthesis of the block copolymers with azobenzene moieties has been increasing [5-9]. Ober and co-workers developed a LC azobenzene block copolymer by linking azobenzene mesogenic groups to the isoprene block of a styrene-isoprene diblock copolymer prepared by using living anionic polymerization [5]. The group of Finkelmann reported the synthesis of azobenzene diblock and triblock copolymers through anionic polymerization [6]. Tian et al. [7] employed ATRP technique [8] to prepare an amphiphilic diblock polymer composed of a hydrophilic poly (ethylene glycol) and an azobenzene LC block. Recently, Zhao et al. synthesized a new azobenzene LC-coil diblock copolymer [10] and our group obtained an azobenzene LC-coil triblock copolymer [11].

Given the considerable interest generated by block copolymers that display a variety of microphase separation induced microdomain structures, more systematic studies on LC azobenzene block copolymers are obviously worth being conducted, in addition to the possible new morphologies in LC-coil diblock copolymers [5], the microstructures may affect the LC behavior of LC azobenzene block copolymers [10-12]. It is also conceivable that the photoisomerization of azobenzene may be used to influence the morphology or even the nanostructures that can self-assemble in block copolymers.

During these years, nonlinear block copolymers have been put under investigation in an attempt to study the influence of the macromolecular architecture on the structure-property relationships. Miktoarm star copolymers are a novel type of nonlinear block copolymers constituted of a central core bearing various kinds of pure arms of different nature. Compared with linear block copolymers, miktoarm star copolymers exhibit dramatic differences in morphology [13-18] and properties [19-22], etc. The synthesis and properties of miktoarm star polymers were reviewed by Hadjichristidis [23-25]. Recently, much interest has been directed to the research on miktoarm stars [26-29]. However, as far as we know, the study of LC azobenzene miktoarm star copolymer has not been reported by far. So we synthesized a series novel miktoarm star side chain LC copolymers comprising a PS arm and two PMMAZO ones. Our interest in miktoarm star copolymer is to design LC-coil miktoarm star copolymer with the LC part consisting of PMMAZO. We believe that the unique molecular design of LC-coil miktoarm star copolymers will have unique morphology, LC behavior and self-assembly behaviors. We expect that the studies will provide new insight into the azobenzene LC and make their block copolymers more attractive from a processing point of view.



Scheme 1. Synthetic route of precursor $PS(Br)_2$ and miktoarm star $PS(PMMAZO)_2$

As shown in Scheme 1, the synthesis of $PS(PMMAZO)_2$ we did involved three steps. The first step involved the preparation of ω-bromopolystyrene (PS) chains by ATRP using ethyl 2-bromoisobutyrate as initiator. Styrene was polymerized in bulk at 100 °C in the presence of Cu(I)Br and 2,2′-bipyridine (bipy) as catalytic system. Then, the bromo end groups of the resulting PS chains were derivatized into twice as many bromoisobutyrates in order to obtain *ω, ω′*-bis (bromo)-PS chains. The last step consisted of growing two PMMAZO blocks by ATRP.

Experimental

Materials

CuBr (Adrich, 99.9%), 2.2′-dipyridine (dipy) (Acros, 99%), ethyl 2-bromoisobutyrate (EBB)(Aldrich, 98%) , 2-Amino-1,3-propanediol (serinol) (Aldrich, 98%), 2-bromoisobutyryl bromide (Aldrich, 98%), N,N-dimethylformamide (DMF) (Shanghai Chemical Reagents Co. , A.R. grade) were used without further purification. Styrene (Shanghai Chemical Reagents Co. , A.R. grade) was stirred overnight over CaH_2 and distilled prior to use. Chlorobenzene (C_6H_5Cl) (Shanghai Chemical Reagents Co., A.R. grade) was purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with water, once with 5% sodium carbonate solution, and again with water before being dried with anhydrous calcium chloride and distilled. Triethylamine (TEA) (Shanghai Chemical Reagents Co., A.R. grade) was refluxed with KOH and distilled. Tetrahydrofuran (THF) (Shanghai Chemical Reagents Co., AR. grade) was dried by distillation from CaH_2 under N_2. All other reagents were used as received. The azobenzene monomer, 6-(4-methyloxy -4′-oxy-azobenzene) hexyl methacrylate (MMAZO) was prepared using the procedure described by Craig and Imrie [2].

Measurements

The M_n and molecular weight distribution (M_w/M_n) were measured on a WATER 1515 gel permeation chromatography (GPC) instrument with a set of HT3, HT4 and HT5, μ-styragel columns with THF as an eluent (1.0 ml/min) at 35℃. Calibration was made with polystyrene standards(PSt). The ^1H NMR spectra were recorded at 25℃ on a INOVA-400 NMR spectrometer with chloroform-d as a solvent and with tetramethylsilane (TMS) as an internal reference. Thermograms were obtained using a Perkin Elmer DSC-7 instrument. Polarized optical microscope (POM) observation was performed on a Leitz Laborlux 12POL microscope with a Leitz 350 hot stage.

Synthesis of the Homopolymer (PMMAZO)

In a dry glass tube, 4.68 mg of dipy (0.03 mmol), 1.43 mg of CuBr (0.01 mmol), 100 mg of MMAZO (0.25 mmol), 1.95 mg of EBB (0.01 mmol) and 0.4 ml of Chlorobenzene were charged, and immediately the mixture was frozen with liquid nitrogen and a vacuum was applied. After several freeze-thaw cycles, the tube was sealed under vacuum and placed in an oil bath preheated at 75℃. the reaction lasted for 15 h. The sample was diluted in THF and passed through a column with activated Al_2O_3 to remove the catalyst. Afterward, the polymer was recipitated in methanol and dried in a vacuum oven overnight at room temperature. ($M_{n,GPC}=1.3\times10^4$ g/mol and $M_w/M_n=1.18$). The conversion of polymerization was determined by gravimetrically.

Synthesis of ω*-Bromo-PS Precursor [PS(Br)]*

In a typical experiment, a dry polymerization tube was charged with 14.3mg (0.1 mmol) of CuBr, 46.9 mg (0.3mmol) of dipy, 19.5 mg (0.1mmol) of EBB, and 1.04g (10 mmol) of styrene, and then the system was degassed three times and the tube sealed off as before. The reaction was carried out at 100℃ for 6h, then cooled to room temperature. Then the sample was purified as above ($M_{n,GPC}$=0.7×10^4 g/mol and M_w/M_n=1.16) (yield: 65%).

Synthesis of ω,ω'*-Bis(hydroxy)-PS [PS(OH)$_2$]*

In a 50 ml oven-dried round-bottom flask flame, the PS(Br) (2.8g, 0.4 mmol, $M_{n,GPC}$=0.7×10^4 g/mol, M_w/M_n=1.16) was dissolved in DMF (6ml), and 1.3g (14 mmol) of serinol was added. After stirring for 72 h at 30℃, the polymer was precipitated in methanol, filtered, and dried at 35℃ under vacuum for 24 h (yield: 85%).

Synthesis of ω,ω'*-Bis(bromo)-PS [PS(Br)$_2$]*

PS(OH)$_2$ (1g, $M_{n,GPC}$=0.7×10^4 g/mol, M_w/M_n=1.16), was dissolved in dry THF (15ml) along with triethylamine (0.5 ml). A THF solution of 2-bromoisobutyryl bromide (0.50 ml, 2.4×10^{-3} mol in 2 ml of THF) was added dropwise at 0℃, over a period of 10 min. After stirring for 24h at room temperature, the polymer was precipitated twice in methanol followed by drying at 35℃ under vacuum for 24h (yield: 88%).

Synthesis of PS(PMMAZO)$_2$ Miktoarm Star Copolymers

Miktoarm star copolymers PS(PMMAZO)$_2$ were synthesized by solution polymerization in chlorobenzene. Thus in a typical solution polymerization, a polymerization tube was charged with 0.07 g of PS macro-initiator PS(Br)$_2$ (0.01 mmol), 0.5 of MMAZO (1.24 mmol), 2.86 mg of CuBr (0.02 mmol), 28.1 mg of dipy (0.06 mmol), and 2.14 g of chlorobenzene, then the system was degassed three times and the tube sealed off as before. The reaction was carried out at 75 ℃ for 15 h. The samples were precipitated from methanol and then dried in a vacuum at 50℃ for 24 h.

Results and Discussion

PS(Br)$_2$ macroinitiator (a) was synthesized [GPC results: $M_{n,GPC}$ = 0.7 × 10^4 g/mol, M_w/M_n = 1.16] similaring to literature [30], and then the PS(Br)$_2$ macroinitiator was used to initiate mononer MMAZO in chlorobenzene solution for formation of a series of PS(PMMAZO)$_2$ miktoarm star azobenzene side-chain LC copolymers as shown in scheme 1. The characterization data and thermal transitions data of the monopolymers and the miktoarm star copolymers were summarized in table 1. The results listed in table 1 show that the Mn values of the miktoarm star copolymers determined by ^{1}H NMR were larger than the counterparts based on GPC. This may be due to the difference in solvent property between the copolymer and standard polystyrene. Another reason is that star polymers usually have smaller molecular weight comparing with linear polymers. Then a profile proof of the star polymer formation was provided.

Table 1. Characterization data and thermal transitions data of the monopolymers and the miktoarm star copolymers

Polym. No	Yield (%)	wt[a] (%)	$M^{b}_{n,NMR}$ ($\times 10^{-4}$)	$M_{n,GPC}$ ($\times 10^{-4}$)	M_w/M_n	Phase transitions temp. and enthalpy changes (J/g)[c]
a		100		0.7	1.16	g87
S_1	92.1	22.3	3.25	2.98	1.27	
S_2	87.1	20.2	5.63	4.90	1.29	S83(2.0)N131(1.7)I
S_3	94.4	17.4	6.44	5.07	1.35	S84(2.5)N132(1.9)I
S_4	95.5	16.7	6.95	5.35	1.32	
S_5	95.3	10.9	8.86	7.09	1.28	S82(3.7)N131(2.3)I
S_6	92.7	9.2	11.2	9.14	1.39	S84(3.4)N133(2.7)I
P	90.0	0		1.29	1.18	S83(4.5)N129(2.8)I

[a] wt%=[$W_{PS(Br)2}$ / ($W_{PS(Br)2}$+ W_{MMAZO})] × 100%, where $W_{PS(Br)2}$ and W_{MMAZO} are the weights of the macroinitiator and monomer (MMAZO).

[b] M_n, number-average molecular weight calculated based on proton NMR data.

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

Figure 1 shows the GPC curves of macroinitiator $PS(Br)_2$ and its related $PS(PMMAZO)_2$ molecular weight. An increase in molecular weight confirmed the growth of the PMMAZO blocks from the $PS(Br)_2$ precursor and the efficiency of the crossover reaction. Moreover, the low polydispersity values (<1.4) indicated a controlled growth of the PMMAZO arms. A small shoulder in the low molar mass region attributable to unreacted precursor could, however, reflects the presence of a little unfunctionalization PS chains.

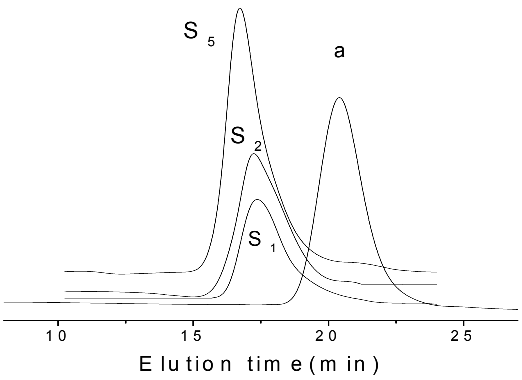


Fig. 1. GPC traces of macro-initiator (a) ($M_{n,GPC}$ = 0.7 × 10^4 g/mol and M_w/M_n = 1.16) and it's related miktoarm star copolymers with various number average molecular weight

Figure 2 shows the results of ^{1}H NMR spectra. As can be seen in the new signals at 3.9-4.1 ppm from [–$CH_2OCOC(CH_3)Br$](peak b) and 3.2-3.5 ppm from [–CHNHCH-] (peak b′), which are not present in PS(Br) [Fig. 2 (A)], appear for the $PS(Br)_2$ gemini macroinitiator [Fig.2(B)]. Therefore, the gemini macroinitiator was successfully synthesized. Also, as shown in Fig.2 (C), the signals at 7.2-6.3 (a), 2.1-1.3 ppm (d) are ascribed to the repeated PS unit. Characteristic resonance of benzene ring signals (peak h) at both 7.8 and 6.9 ppm, -OCH_3 protons signals (peak f) at 3.89 ppm and -OCH_2-Ph protons signals (g) at 1.91 ppm in PMMAZO units are all present in the ^{1}H NMR spectra of S_2. These data illustrate the presence of both St and MMAZO segments in the miktoarm star copolymer chain. Furthermore, the evolution of a signal at 0.84-1.25 ppm (peak e) is indicative of –CH_3 protons of PMMAZO block. Then another proof of the formation of the $PS(PMMAZO)_2$ miktoarm star copolymer was provided. The $M_{n,NMR}$ of the $PS(PMMAZO)_2$ can be calculated according to Eq. (1), where 2 defines the arm values of the PMMAZO and the values 7000, 340, 195, 91, 36.5 are the molar masses of $PS(Br)_2$ macroinitiator, MMAZO, EBB, serinol, HBr, respectively:

$$M_{n},_{NMR} = 7000 + 2\times[(I_h/2I_b+1) \times 340 + 195 + 91 - 3\times 81] \qquad (1)$$

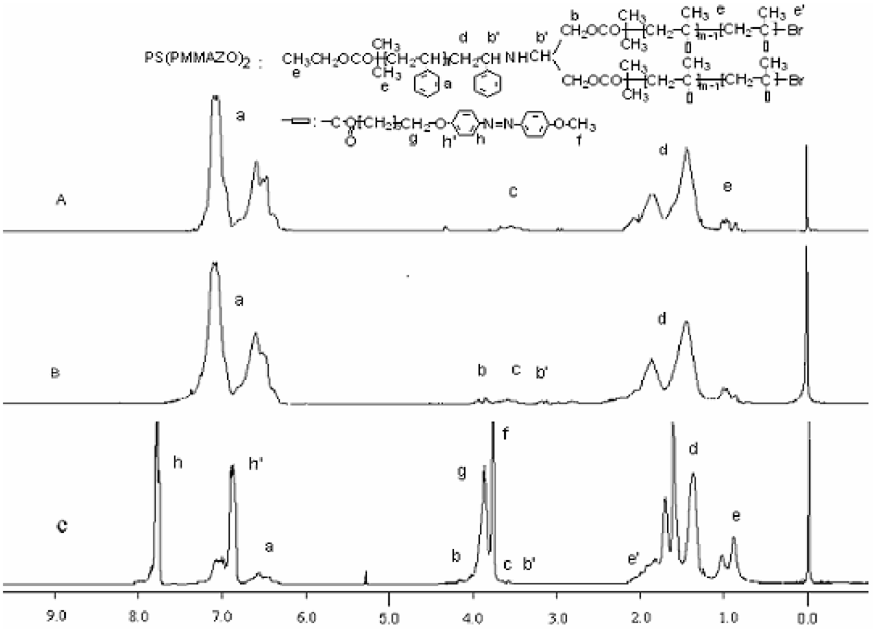


Fig. 2. ^{1}H NMR spectra: (A) PS(Br), (B) $PS(Br)_2$, (C) Miktoarm star copolymer S_2

Figure 3 compares the second DSC heating curves of the copolymers with that of the homopolymers,i.e., the PS macroinitiator and PMMAZO (P). On one hand, like the LC azobenzene homopolymer, the azobenzene arms of all copolymers display a smectic-nematic and a nematic-isotropic phase transition endotherm. On the other hand, all copolymers have higher nematic-isotropic phase transition temperatures ($T_{N–I}$) than the homopolymer P, even though their azobenzene polymer arms have a similar molecular weights to the azobenzene homopolymer (Table 1). Such an increase in thermal stability of the mesophases should be caused by the microdomain structure of the miktoarm star copolymers and the effect of mixing with the PS arms. At the same time, the phase transition enthalpies are reduced, and the apparently quite low smectic-nematic phase transition enthalpy in the copolymers may be indicative of a reduced smectic order within the microdomains.

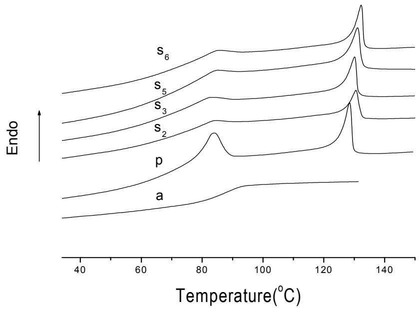


Fig. 3. DSC heating curves of some star copolymers and homopolymers

The POM can identify the mesophases. We can observe the thermal transitions of the miktoarm star copolymers and analyze their anisotropic textures by POM. For example, sample S_6 was heated to isotropic phase and subsequently cooled to 133 ℃, a representative schlieren nematic texture (Fig. 4) was observed. While further being cooled to 84 ℃, the sample didn't yield a typical focalconic fan texture, which is consistent with the DSC measurements showing no prominent transition peaks for the sample cooled from the isotropic phase. These results imply that the microdomain structure in the miktoarm star copolymer may render the arrangement of the mesogenic groups more difficult to develop. This phenomenon has not yet been reported elsewhere to our knowledge, and detailed investigations are still underway.

It will have good prospects to investigate the self-assemble behaviors and LC properties of the miktoarm star liquid crystalline copolymer and some applications. We expect that these studies may provide new insight into the polymer formation process.

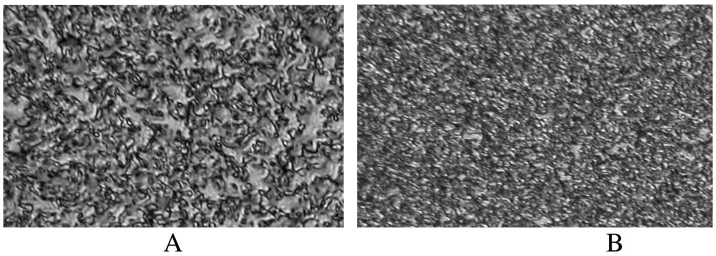

A B

Fig. 4. Representative polarized optical micrograph of the texture of S_6
(A) 133 °C; (B) 82 °C (magnification: 400×)

Conclusion

A series of novel side group liquid crystal-coil (SGLC-coil) miktoarm star copolymers with narrow molecular weight distributions was synthesized successfully by ATRP.

Their characterization was investigated using gel permeation chromatograph (GPC), proton nuclear magnetic resonance (^{1}H NMR), differential scanning calorimetry (DSC) and polarized optical microscope (POM). It was observed that all the miktoarm star copolymers showed similar LC properties to PMMAZO homopolymer. The phase transition temperatures of T_N-T_I improved and the copolymers thermal stability of the mesophases increased, while the phase transition enthalpies reduced.

Acknowledgements

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