

# Synthesis and Characterization of a Novel Liquid Crystalline Star-Shaped Polymer Based on $\alpha$ -CD Core via ATRP

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**ABSTRACT:** Well-defined side-chain liquid crystalline star-shaped polymers were synthesized with a combination of the “core-first” method and atom transfer radical polymerization (ATRP). Firstly, the functionalized macroinitiator based on the  $\alpha$ -Cyclodextrins ( $\alpha$ -CD) bearing functional bromide groups was synthesized, confirmed by <sup>1</sup>H-NMR, MALDI-TOF, and FTIR analysis. Secondly, the side-chain liquid crystalline arms poly[6-(4-methoxy-4-oxy-azobenzene) hexyl methacrylate] (PMMAzo) were prepared by ATRP. The characterization of the star polymers were performed with <sup>1</sup>H-NMR, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermal

polarized optical microscopy (POM). It was found that the liquid crystalline behavior of the star polymer  $\alpha$ -CD-PMMAzo<sub>n</sub> was similar to that of the linear homopolymer. The phase-transition temperatures from the smectic to nematic phase and from the nematic to isotropic phase increased as the molecular weight increased for most of these samples. All star-shaped polymers show photoresponsive isomerization under the irradiation with Ultraviolet light. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2120–2126, 2009

**Key words:**  $\alpha$ -CD; liquid crystalline polymer; atom transfer radical polymerization; star-shaped polymer

## INTRODUCTION

Recently, many works based on the synthesis of star-shaped polymers have been reported. More and more attentions have been attracted toward star-shaped homopolymers<sup>1–6</sup> or block copolymers<sup>7</sup> due to their branched structures and unique rheological properties, which are different from those of their linear polymeric counterparts. For example, star-shaped polymers have lower melting points and solution viscosities and superior mechanical properties. Furthermore, they are more processable. Therefore, they can be used as rheology modifiers or pressure-sensitive adhesives.<sup>8</sup> The synthesis of star-shaped polymers with controllable structures could basically be divided into two different approaches. One is the so-called

“arm first” strategy in which linear living polymer was synthesized initially, followed by coupling reaction with a multifunctional coupling agent. The other is the so-called “core first” method in which a multifunctional initiator was used to form multiarm star polymers,<sup>1,2</sup> this method is advantageous, since no need to remove the linear arms from the product but in the arm-first method it is necessary, furthermore, it was easy to control the structure of star-shaped polymer.<sup>9,10</sup> Over the past years, the core-first approach with radical initiator had attracted greater attention, many polymers have been synthesized by living anionic and living cationic polymerizations,<sup>11–14</sup> ATRP,<sup>1</sup> RAFT,<sup>15,16</sup> and others.<sup>2</sup> All of these, ATRP method have been greatly used for synthesizing of the well-defined star-shaped polymers.<sup>17–20</sup>

Cyclodextrins (CDs) are a series of cyclic molecules consisting of 6–8 d(+)-glucose units with very regular structure, which means each CD molecule contains 18–24 hydroxyl groups. Theoretically, they are excellent star-shaped polymer initiators after being decorated with multifunctional groups. In the past decades, as the prices of the cyclodextrins were brought down greatly, the theoretical macroinitiator has become realistic. The first example of star-shaped polymer synthesized by ATRP from  $\beta$ -CD core was reported

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by Haddleton and coworkers,<sup>21</sup> 21-arm methyl methacrylate (MMA) and styrene star polymers were synthesized. Furthermore, the macroinitiator based on  $\beta$ -cyclodextrin bearing functional bromide groups was synthesized by Karaky and coworkers,<sup>22</sup> then, the polymerization of the tert-butyl acrylate monomer was optimized to avoid a star–star coupling reaction and allowed the synthesis of a well-defined organosoluble star polymer. Another report was that the functionalized macroinitiators based on the  $\alpha$ -CD bearing functional bromide and iodide groups were synthesized,<sup>23</sup> after that, polystyrene star polymers were obtained utilizing iron-mediated ATRP.

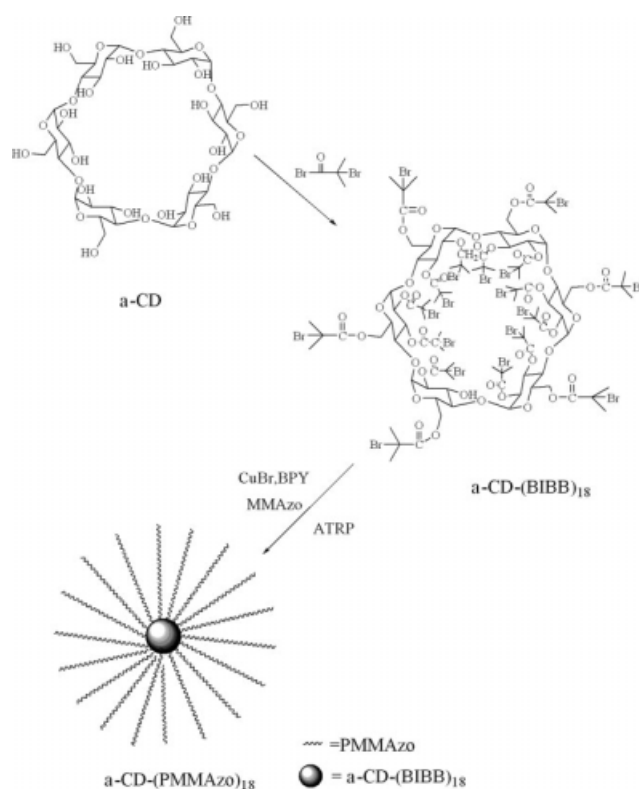
In recent years, liquid crystal homopolymers and block copolymers have been widely studied because of their potential applications such as switchable windows, displays, color projectors, and other electric–optical systems.<sup>24–28</sup> The azobenzene-containing side-chain liquid crystal polymers are distinguished for their properties as materials in a range of advanced electro-optical technologies,<sup>29</sup> because it is well known that azobenzene chromophores exhibit photoinduced reversible trans-cis isomerization, which can significantly influence the bulk and solvent properties of azobenzene-containing side-chain liquid crystal polymer.<sup>30</sup> The interests of the scientists are not only on the performance of the linear liquid–crystal polymer, but also on the behavior of the star-shaped polymer. As it was reported, three-arm star side-chain liquid crystalline polymer with cyanobiphenyl moieties was synthesized by Kasko et al.<sup>31</sup> Moreover, the azobenzene-containing polymethacrylate was firstly grafted from poly(3-ethyl-3-(hydroxymethyl)oxetane) (PEHO) by ATRP.<sup>32</sup> Our purpose was synthesis of a novel liquid crystal star-shaped polymer representing a combination of the cheap and easy-decorated  $\alpha$ -CD and liquid crystalline behavior of PMMAzo. So far, as we known, the star-shaped polymers based on  $\alpha$ -CD core, side-chain liquid crystal polymers arms have rarely been reported.

In our work, the detailed process was described as Scheme 1, starting from the synthesis of a new CD derivative bearing functional bromide groups macroinitiator, afterward, the macroinitiator was used to initiate MMAzo by ATRP, which possessed excellent information memory property. Finally, the liquid crystalline behavior and other performances of  $\alpha$ -CD-PMMAzo<sub>n</sub> were investigated.

## EXPERIMENTAL

### Materials

$\alpha$ -Cyclodextrin ( $\alpha$ -CD, analytical grade) was purchased from Tianjin Chemical Third Factory (Tianjin, China), and recrystallized twice from aqueous solution before use. Tetrahydrofuran (THF) (Shantou,



**Scheme 1** The general synthesis route of  $\alpha$ -CD-PMMAzo<sub>n</sub>

China) was distilled from a purple sodium ketyl solution. CuBr (Shanghai Chemical Reagents, Shanghai, China; A.R. grade, 99%) was stirred in glacial acetic acid, filtered, and washed three times with acetone. The solid was dried under vacuum at room temperature overnight. 2-Bromoisobutyryl bromide (BIBB) (98%, Alfa, Karlsruhe, Germany) was freshly distilled at room temperature under vacuum. The azobenzene monomer, 6-(4-methoxy-4-oxy-azobenzene) hexyl methacrylate (MMAzo) was prepared using the procedure described by Stewart D and Imrie CT.<sup>33</sup> Spartein (98%, Acros, Geel, Belgium). All other chemicals were purified according to conventional methods or used as received.

### Synthesis of the macroinitiator $\alpha$ -CD-BIBB<sub>m</sub>

The reports about decoration of cyclodextrin with the viewpoint of organic synthesis are limited.<sup>34,35</sup> The Macroinitiator  $\alpha$ -CD-BIBB<sub>m</sub> was synthesized according to the literature<sup>22</sup> as Scheme 1 showed. A 100-mL round-bottom three-necked flask with a magnetic stirring bar was charged with  $\alpha$ -CD (1.73 g,  $1.7 \times 10^{-3}$  mol) and kept under nitrogen before the addition of 30 mL of pyridine. After the complete dissolution of  $\alpha$ -CD, the reaction medium was cooled to 0°C under stirring. A solution of BIBB (11.3 g,  $49.13 \times 10^{-3}$  mol) in 10 mL of chloroform (CHCl<sub>3</sub>) was slowly added within 2 h in the ice bath. After the addition

completed, the ice bath was removed, and the reaction mixture was further stirred at room temperature for 3 days. Then, the organic layers were washed for several times with iced water to remove the salt, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The reaction mixture was poured into diethyl ether, and the precipitate was collected by filtration. The obtained solid was dissolved in THF and precipitated from petrol ether three times and collected by filtration. The precipitate was dried under vacuum at 50°C to give of  $\alpha$ -CD-BIBB<sub>m</sub> as white powder. Mass: 3.87 g, Yield: 76%.

### General procedure for synthesis of star polymer by ATRP

A Schlenk flask with a magnetic stirrer and a rubber septum was charged with  $\alpha$ -CD-BIBB<sub>m</sub>: MMAzo: CuBr: Spartein = 1/18:  $n$  : 1 : 2 ( $n$  stand for the degree of polymerization), after being dissolved by THF, they were deoxygenated with bubbling nitrogen for 30 min before addition into the flask. The flask was degassed by three freeze-pump-thaw cycles after 10 min of stirring and then immersed in an oil bath thermostated at 80°C for 14 h under magnetic stirring. After that, the tube was placed in an ice bath to stop the reaction. The reaction mixture was dissolved in THF, passed through a short column of alumina to remove the catalyst, precipitated in methanol, and dried under vacuum at room temperature until a constant weight was obtained. The star-shaped polymers were designated P<sub>n</sub> ( $n$  = 1–4).

### Measurements

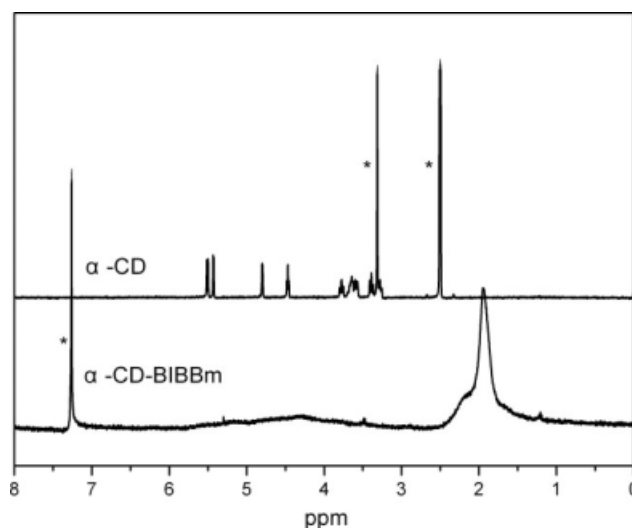
<sup>1</sup>H-NMR spectras were obtained at 25°C on a Bruker AV400 NMR spectrometer (400 MHz) using CDCl<sub>3</sub> as solvent. Polarized optical microscope observation was performed on a Leica DMLP microscope equipped with a Mettler FP82 hot stage, and the starting and ending temperatures were 40°C and 160°C, respectively. FTIR spectra were recorded on a Perkin-Elementer Spectrum one FTIR spectrophotometer, 64 scans were signal-averaged with a resolution of 2 cm<sup>-1</sup> at room temperature. Samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks. Thermograms were obtained using a Seiko DSC-6200 instrument with a heating rate of 10°C min<sup>-1</sup> under nitrogen atmosphere from 40°C to 150°C. Molecular weights and molecular weight distributions were measured with a Waters 1515 gel permeation chromatograph equipped with three Styragel columns (103, 104, and 105 Å) using THF as an eluent (1.0 mL min<sup>-1</sup>) at 35°C. The column system was calibrated by a set of monodisperse polystyrene standards. Ultraviolet-visible (UV-vis) spectra were measured using a PE

Lambda 20 spectrophotometer. UV irradiation was carried out with a 300W high-pressure mercury lamp coupled with UV filters (<360 nm). MALDI-TOF mass spectrometry was performed using a Bruker Daltonics Biflex III spectrometer equipped with a 337 nm nitrogen laser, a delay extraction, and reflector. The MALDI mass spectra represent averages over 100 laser shots. This instrument operated at an accelerating potential of 20 kV. The polymer solutions (10 g L<sup>-1</sup>) were prepared in THF. The matrix solution (DHB) was dissolved in THF. The polymer solution (2  $\mu$ L) was mixed with 20  $\mu$ L of the matrix solution, and 2  $\mu$ L of a sodium iodide solution (10 g L<sup>-1</sup> in methanol) was added to favor ionization by cation attachment. The final solution (1  $\mu$ L) was deposited onto the sample target and allowed to dry in air at room temperature.

## RESULTS AND DISCUSSION

### Synthesis and characterization of the macroinitiator

The first part of this study was to synthesize a multifunctional initiator based on  $\alpha$ -CD by reacting the  $\alpha$ -CD with BIBB (Scheme 1), and carried out at 0°C under nitrogen in the presence of pyridine and CHCl<sub>3</sub> as solvent. Firstly, its characterization was investigated with <sup>1</sup>H-NMR. A new chemical shift at 2.0 ppm could be observed, which would be attributed to the methylene protons of bromoisobutyryl group. As can be seen from the Figure 1 that the chemical shift area for the methylene and methine protons of  $\alpha$ -CD became wider, a series of wide peaks had replaced the original acuity peaks because of the different degree of bromoesterification by



**Figure 1** <sup>1</sup>H-NMR spectra of  $\alpha$ -CD and  $\alpha$ -CD-BIBB<sub>m</sub> (asterisk is solvent or water).

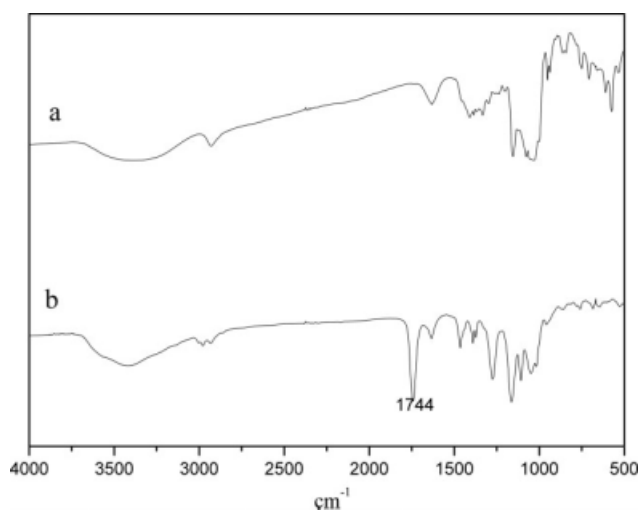


Figure 2 FTIR spectra of (a)  $\alpha$ -CD; (b)  $\alpha$ -CD-BIBB<sub>m</sub>.

BIBB. According to the literature mentioned,<sup>36</sup> by comparing the integral area for the signal of the methyl group of BIBB around  $\delta = 2.0$  ppm to the integral area of methylene and methine protons of  $\alpha$ -CD at 3.0–5.0 ppm, the degree of bromoesterification of  $\alpha$ -CD could be determined to be 80%, which means the number of initiated arms is around 14.

To investigate the exact arm number of the  $\alpha$ -CD-BIBB<sub>m</sub> further, we introduced MALDI-TOF-MS to determine the absolute molecular weight of  $\alpha$ -CD and  $\alpha$ -CD-BIBB<sub>m</sub>. The absolute molecular weight of  $\alpha$ -CD-BIBB<sub>m</sub> is 2909, so it was easy to come to a conclusion that the exact arm number of the  $\alpha$ -CD-BIBB<sub>m</sub> was 13, which was very close to the result of the NMR determined value 14.

The introduction of the 2-bromoisobutyryloxy groups onto  $\alpha$ -CD was further confirmed by FTIR. The characteristic absorption peak of the ester group at 1744  $\text{cm}^{-1}$ , which was not present in the spectrum of  $\alpha$ -CD [Fig. 2(a)], but was observed in the FTIR spectrum of the macroinitiator [Fig. 2(b)] because of the esterification of  $\alpha$ -CD. Nevertheless, the broad

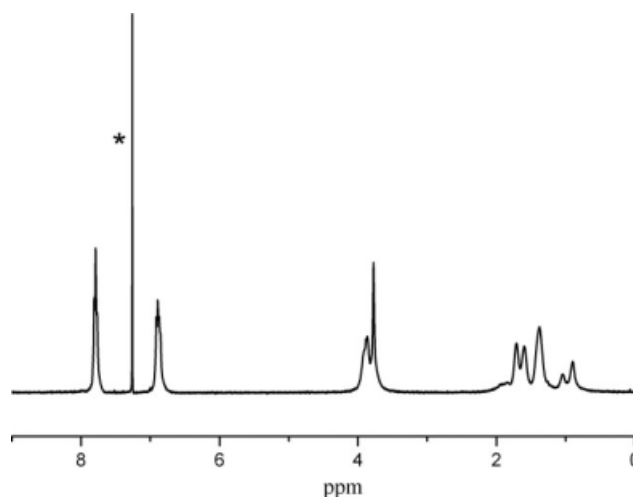


Figure 3  $^1\text{H-NMR}$  spectra of  $\alpha$ -CD-PMMAzo<sub>n</sub> in  $\text{CDCl}_3$ .

peaks of  $-\text{OH}$  was not disappeared because of the incomplete bromination of  $\alpha$ -CD.

#### Synthesis and characterization of the star-shaped polymer

The  $^1\text{H-NMR}$  spectra of the  $\alpha$ -CD-PMMAzo<sub>n</sub> ( $[\text{M}_0]/[\text{I}_0] = 80$ ) is stated in Figure 3, almost the same as the PMMAzo homopolymer. The chemical shift of the  $\alpha$ -CD is invisible because of its relative neglectable molecular weight compared to that of PMMAzo grafted onto the arms of  $\alpha$ -CD, which coincide with other report.<sup>32</sup>

The molecular weights and polydispersities of the star polymers are summarized in Table I. The GPC curves of the star polymers are shown in Figure 4. Four single peaks are obtained. The GPC curves indicate that the molecular weights turn larger after increasing the ratio of the monomer to the macroinitiator, and showing no bimodality and containing no residual macroinitiator. The polydispersity is around 1.5, which is quite an optimistic result compared with other star-shaped polymers.

TABLE I  
Characterization and Thermal Transition Data of the Star Polymer

Sample <sup>a</sup>	$[\text{M}]_0/[\text{I}]_0^b$	Yield <sup>c</sup> (%)	$M_{n,\text{th}}^d (\times 10^{-4})$	$M_{n,\text{GPC}}^e (\times 10^{-4})$	$M_w/M_n^e$	Phase transition temperature ( $^{\circ}\text{C}$ ) <sup>f</sup>
P <sub>1</sub>	20 : 1	55	5.95	4.58	1.47	S91N126I
P <sub>2</sub>	40 : 1	37	7.91	5.43	1.62	S86N127I
P <sub>3</sub>	60 : 1	32	10.18	6.48	1.36	S91N132I
P <sub>4</sub>	80 : 1	30	12.65	7.67	1.54	S92N133I

<sup>a</sup> For star polymers, polymerization time is 14 h, and polymerization temperature is 80 $^{\circ}\text{C}$ .

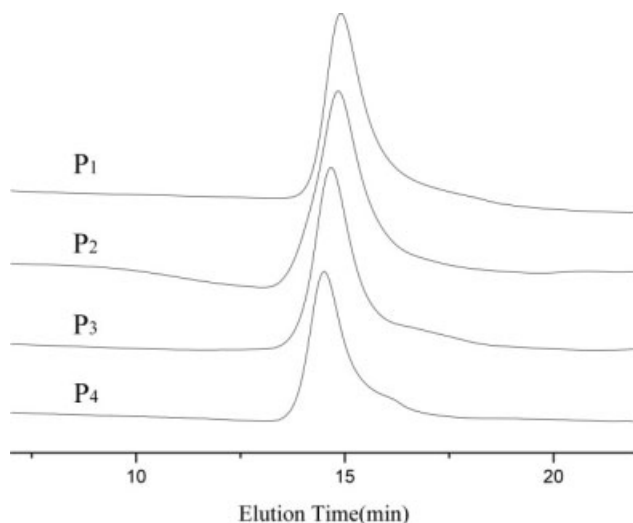
<sup>b</sup>  $[\text{M}]_0$  and  $[\text{I}]_0$  stand for the initial concentration of the monomer and the initiator, respectively.

<sup>c</sup> Yield was calculated according to eq. (2).

<sup>d</sup>  $M_{n,\text{th}}$  stand for the theoretical molecular weight.

<sup>e</sup>  $M_{n,\text{GPC}}$  stand for the molecular weight measured by GPC.

<sup>f</sup> Date for the second heating process; S, smectic phase; N, nematic phase; and I, isotropic phase.



**Figure 4** GPC curves of the polymer P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, and P<sub>4</sub>.

The conversion was determined gravimetrically and calculated according to eq. (1):

$$\text{Conv.(\%)} = (W_p - W_i)/W_m \times 100\% \quad (1)$$

where  $W_p$ ,  $W_i$ , and  $W_m$  are the weight of the polymer produced, the initial weights of the initiator, and the weight of monomer, respectively. On account of the  $W_i$  being too little relative to  $W_p$ , and  $W_m$ , we can consider the  $W_i$  as zero in this system, so the eq. (1) can be reduced to eq. (2):

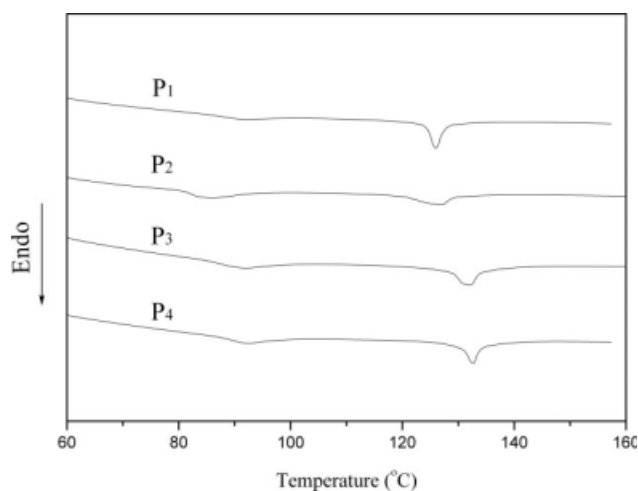
$$\text{Conv.(\%)} = W_p/W_m \times 100\% \quad (2)$$

Based on the conversion of monomer and the molar ratio of monomer  $\{[M]_0\}$  to initiator  $\{[I]_0\}$ ,  $M_{n,\text{th}}$  of each serial of polymer can be calculated according to eq. (3):

$$M_{n,\text{th}} = \text{Conv.} \times \{[M]_0/[I]_0\} \times M \times N + M_i \quad (3)$$

where  $M_i$ ,  $M$ , and  $N$  are the number-average molecular weight of the initiator macroinitiator  $\alpha$ -CD-BIBB<sub>m</sub>, the molar weight of the monomer MMAZO, and the number of initiated arms on CD, respectively. Here, we use  $N$  as 13 to obtain the  $M_{n,\text{th}}$ . The calculated  $M_{n,\text{th}}$  of the polymers is expressed in Table I.

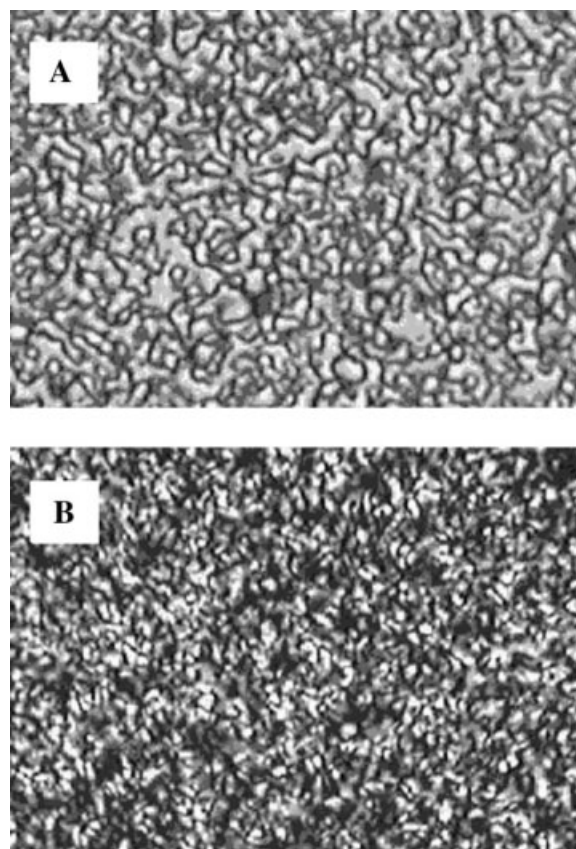
It can be observed from the table that the GPC determined molecular weights of the star-shaped polymer are smaller than the theoretical molecular weight especially when the molecular weight is higher. This may be due to two reasons. One is the difference in solvent property between the star-shaped polymer and the standard polystyrene; the other is that the star-shaped polymers usually have smaller hydrodynamic volume comparing with the linear polymers of the same molecular weight.<sup>37,38</sup> When the molecular weight is higher, this tendency becomes more obvious.



**Figure 5** DSC curves of the second heating process of the star polymers.

### Thermotropic phase behavior

Figure 5 shows the second DSC heating curves of the star-shaped polymers P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, and P<sub>4</sub>. As reported in the literature,<sup>39</sup> linear polymer PMMAzo was a thermotropic liquid crystalline polymer that could exhibit a smectic phase and a nematic phase transition. The liquid crystal behavior of the star



**Figure 6** Representative polarized optical micrograph of the texture of P<sub>3</sub> (A) 125°C and (B) 80°C.

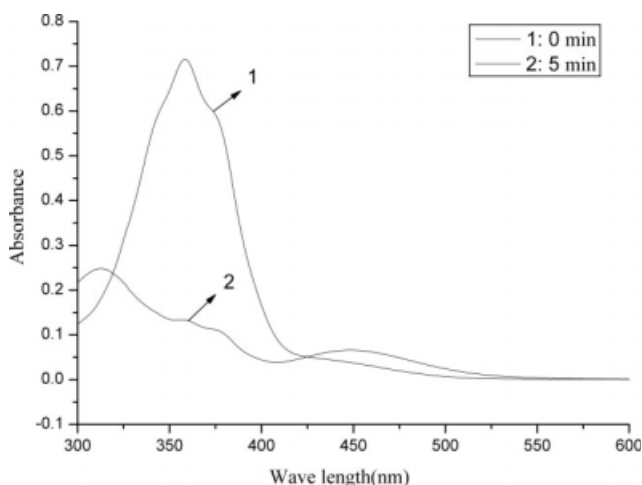
polymer  $\alpha$ -CD-PMMAzo<sub>n</sub> was similar to that of linear homopolymer. For most of the samples, the phase-transition temperatures from the smectic to nematic phase and from the nematic to isotropic phase increase as the molecular weight increases.

The anisotropic textures of the polymers could be observed and analyzed by POM. For the star-shaped polymer P<sub>3</sub>, it was heated to isotropic phase and subsequently cooled to below 132°C, representative schlieren nematic textures [Fig. 6(A)] was observed at 125°C. Further cooling into 80°C yielded a representative smectic texture [Fig. 6(B)].

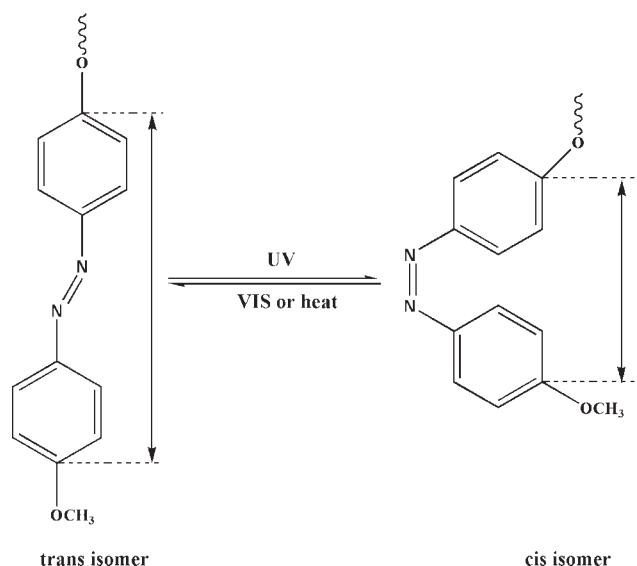
### Photoresponsive behavior

The photoisomerization of the star-shaped polymers in THF solution was studied by UV-vis absorption spectra under irradiation with ultraviolet light. These star-shaped polymers were readily soluble in THF at room temperature. The UV-vis spectra of P<sub>1</sub> in THF solution before and after UV exposure for 5 min are given in Figure 7. Upon irradiation with 360-nm light, the intensity of the  $\pi$ - $\pi^*$  transition band at 358 nm decreases, whereas the intensity of the  $n$ - $\pi^*$  transition at 445 nm increases. After UV exposure for 5 min, the curves seem no different from curve 2, which indicates that the isomerization is completed in 5 min. The star-shaped polymer P<sub>2</sub>-P<sub>4</sub> exhibit similar photoresponsive behavior.

This phenomenon corresponds to the conformation change of the azobenzene moieties of the star-shaped polymers. The azobenzene moieties show a large change in the molecular length, in which the distance between 4- and 4'-carbons reduces from trans to cis isomer upon UV irradiation,<sup>40</sup> and the length rovers after the cis to trans isomerization occurred thermally or/and photochemically due to the *trans* form corresponds to an energy lower than *cis* form by about



**Figure 7** UV-vis spectra of  $\alpha$ -CD-PMMAzo<sub>n</sub> in THF upon irradiation with 360 nm UV light at room temperature.



**Figure 8** Conformational changes of azobenzene moieties in star-shaped polymers.

48 kJ mol<sup>-1</sup>.<sup>41</sup> Thus, with increasing irradiation time, the distance between 4- and 4'-carbons in azobenzene is gradually decreased (Fig. 8).

### CONCLUSIONS

A series of novel star polymers based on the  $\alpha$ -CD as the core, the side chain liquid crystal polymers PMMAzo as the arms with different molecular weight were synthesized by ATRP using the “core first” method. <sup>1</sup>H-NMR and MALDI-TOF spectra confirmed the structure and the average arms of the macroinitiator. Meanwhile, the liquid crystal behavior of the polymer was investigated. Every star-shaped polymer showed photoresponsive isomerization under the irradiation with ultraviolet light. To the best of our knowledge, it is the first liquid crystalline star-shaped polymer based on the  $\alpha$ -CD as the core, and the side-chain liquid crystal polymers PMMAzo as the arms. The applications of such kind of star-shaped polymer as a new kind of electric-optical and information memory property material are still under our research.

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