

# Synthesis of a Side Chain Liquid Crystalline Polycarbonate with a Chiral Backbone

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**ABSTRACT:** We report the experimental demonstration of a novel and environmentally benign supercritical carbon dioxide (ScCO<sub>2</sub>) technique that yields an optically active, side chain liquid crystalline polycarbonate in a single-step reaction. The obtained polymer is worthwhile, since it is highly stereoregular and can find applications in an enlarged mesomorphic temperature range compared to its acrylic analogues. The synthesized materials were characterized by IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR, while the thermal properties were measured by DSC. Polarized optical micrograph and wide angle X-ray diffraction were used for the mesogenic property characterization of the copolymer. The transfer chirality from the backbone to the mesophase is demonstrated on the optical microscopy textures. Being consistent with the <sup>13</sup>C-NMR, X-ray implies an ordered polymeric

structure. The DSC analysis of the copolymer indicates that the  $T_i$  (the clearing point temperature) value does not change dramatically, whereas a pronounced decrease in  $T_g$  (the glass transition temperature) value is observed from that of its acrylic analogues. Hence, the obtained polymer exhibits another practical benefit by widening the mesomorphic temperature range. This study is the insightful combination of material processing and chemical design that elucidates the advantages of ScCO<sub>2</sub> application, in terms of liquid crystallinity and the tacticity of the obtained polymer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1915–1921, 2006

**Key words:** supercritical carbon dioxide (ScCO<sub>2</sub>); polycarbonates; chiral; liquid-crystalline polymers (LCP); cholesteric

## INTRODUCTION

Recently, side-chain liquid crystalline polymers (SCLCPs) have been receiving increasing attention, both from a scientific and a commercial point of view.<sup>1</sup> Among these polymers, optically active SCLCPs have attracted much attention because of the wide range of their potential applications, in particular, in the fields of optics and electro-optics.<sup>2</sup> Many applications of liquid crystals (LCs) require chiral and optically active materials (e.g., doping nematics with such materials to give better response in displays<sup>3,4</sup>), and ferroelectric properties of smectic LCs are only observed with chiral mesogenic molecules.<sup>5,6</sup> Chirality can be introduced in SCLCPs at various levels. Although such a center in the backbone appears particularly interesting in most polymers, in the literature, they are located in the terminal position of the pendant mesogenic units. The introduction of chirality in the polymer backbone may give information about the magnitude of decoupling between the mesogenic units and the arrangement of polymer backbone through the spacer group.<sup>7</sup>

As the literature reveals, the use of CO<sub>2</sub>, on the other hand, has permeated almost all parts of the chemical industry, and that careful application of CO<sub>2</sub> technology can result in products that are cleaner, less expensive, and of purity.<sup>8</sup> Prominent among the current efforts, which aim the chemical utilization of carbon dioxide, is the copolymerization of epoxides and CO<sub>2</sub> to yield polycarbonates. In comparison to the alternative route involving the use of highly toxic phosgene, polycarbonate synthesis in ScCO<sub>2</sub> media presents a single-step reaction and an environmentally benign approach.<sup>9,10</sup>

Thus, in the present study, a desire to combine these three valuable aspects (liquid crystallinity, chirality, supercritical carbon dioxide application) has mainly motivated us to synthesize a side chain liquid crystalline polycarbonate with a chiral backbone. The results of this study are not only of interest for the synthesis of an optically active SCLCP, which potentially provides a short optoelectronic response time,<sup>4</sup> but also, the synthesis method offers a single-step reaction, which does not cause an environmental damage compared to the alternative routes.

## EXPERIMENTAL

All the materials were supplied from Aldrich Co. and were used as received. Characterizations of the cata-

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lyst monomer and polymer were performed using ATR method by Fourier transform infrared spectroscopy (FTIR) recorded on Equinox 55/S Fourier transform (Bruker).  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  were recorded on Unity Inova 500 MHz nuclear magnetic resonance (Varian AG, Switzerland). DSC thermal analyses were run at  $\text{N}_2/\text{N}_2$  atmosphere with a heating rate of  $10^\circ\text{C}/\text{min}$ , using Netzsch Phoenix differential scanning calorimeter 204 (Selb, Germany). The number-average molecular weights ( $M_n$ ) and polydispersity index ( $M_w/M_n$ ) were measured using gel permeation chromatography on a Agilent Model 1100 instrument containing a pump, a refractive index detector, and four Waters Styragel columns HR 5E, HR 4E, HR 3, HR 2; and THF was used as eluent at a flow rate of  $0.3\text{ mL}/\text{min}$  at  $30^\circ\text{C}$ . Data analysis was performed with PL Caliber software. The system was calibrated with narrow polystyrene standards (Polymer Laboratories). The optic microscope images were obtained by the Nikon Eclipse MD600 microscope. The controlled heating was maintained by a Mettler Toledo FP90 central processor and FP82 HT-Hot-stage. Samples were gradually heated at  $2^\circ\text{C}/\text{min}$  in a temperature range of  $40\text{--}120^\circ\text{C}$ . The XRD pattern was recorded on an X-ray powder diffractometer (Bruker AXS-D8, Karlsruhe, Germany). The measurement was performed in the  $2\theta$  range of  $1^\circ\text{--}25^\circ$  at 40 kV and 40 mA, using Cu  $K\alpha$  radiation. In the measurement, the step size was  $0.03^\circ$  and data collection period was 2 s in each step.

The sample for the XRD experiment was prepared by rapid quenching of the polymer, annealed at its liquid crystalline state.<sup>11</sup> The experimental procedure for the sample preparation is given later: A film of the polymer cast on a single crystal silicon wafer was heated in a furnace to its isotropic state, at which the sample annealed for 10 min. Subsequently, the sample was cooled to its liquid crystalline state and annealed there for 10 min, the silicon wafer was thrown into a liquid nitrogen Dewar flask. The wafer was taken out from the flask and warmed to room temperature.

Polymerizations held in  $\text{ScCO}_2$  were performed by P-50 High Pressure Pump Contrivance (Thar) in a 100 mL, high-pressure, stainless steel vessel. Heating was achieved with a heating band, and temperature was controlled by a thermocouple adapted to the vessel.

### Synthesis of the catalyst

The catalyst is prepared as in Ref.<sup>12</sup> by treating zinc oxide with phthalic anhydride in the presence of alcohol.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.1 (t,  $\text{CH}_3$ ), 4.24 (m,  $-\text{C}(\text{O})-\text{OCH}_2$ ), 7.48 and 7.55 (d, 2a-CH $\rightarrow$ ), 7.93 ppm (s, 2a-CH $\rightarrow$ ).  $^{13}\text{C-NMR}$ :  $\delta$  13.760, 62.005, 127.698, 130.147, 130.269, 130.662, 133.427, 133.980, 169.695, 175.634. IR (ATR) 1725, 1611, 1591, 1551, 1443, 1406, 1287, 1128, 1081, 1040, 878, 844, 749, and  $707\text{ cm}^{-1}$ .

### Synthesis of the monomer (mesogenic epoxide)

To a solution of 4-cyano-4'-hydroxybiphenyl (6.6 mmol) in anhydrous DMF (5 mL) was added CsF (19.9 mmol). The reaction mixture was stirred for 3 h, and (S)-glycidyl-3-nitrobenzenesulfonate (nosylate) (6.6 mmol, 98.8%) was added. The reaction mixture was stirred at  $25^\circ\text{C}$  overnight, under an inert atmosphere. After water was added, the solution was extracted with EtOAc. The organic phase was dried ( $\text{MgSO}_4$ ) and evaporated. The residue was purified by column chromatography on silica gel (1:1, hexane/EtOAc) to give (S)-monomer with a 95% yield.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.77 (dd, 1H), 2.92 (t, 1H), 3.36 (m, 1H), 3.98 (dd, 1H), 4.28 (dd, 1H), 7.09 (dd, 2a-CH $\rightarrow$ ), 7.51 (dd, 2a-CH $\rightarrow$ ), 7.66 (m, 4a-CH $\rightarrow$ ).  $^{13}\text{C-NMR}$ : 44.611, 50.055, 68.833, 110.190, 115.103, 115.202, 119.028, 127.050, 127.126, 128.385, 128.419, 128.533, 132.031, 132.554, 145.046, 159.039. IR (ATR) 2222, 1601, 1524, 1491, 1448, 1289, 1261, 1181, 1115, 1033, 1000, 971, 912, 857, 833, 817, 752, 679,  $661\text{ cm}^{-1}$ .

### Synthesis of the copolymer

To obtain the copolymer in a 100 mL stainless steel reactor, 2.4 g catalyst (40% of the monomer by weight percentage) and 6 g of mesogenic epoxide are added, and a small amount of dichloromethane is used as cosolvent. The reaction mixture is pressurized by carbon dioxide up to 4500 psi and stirred magnetically at  $90^\circ\text{C}$ . After a definite time, the volatile fractions are removed from the reaction mixture at RT under reduced pressure, and the residue was obtained.<sup>12</sup>

$^1\text{H-NMR}$  (DMSO):  $\delta$  4.06 (m, 2H), 4.23 (m, 2H), 4.98 (d, 1H), 7.01 (dd, 2a-CH $\rightarrow$ ), 7.71 (dd, 2a-CH $\rightarrow$ ), 7.87 (m, 4a-CH $\rightarrow$ ).  $^{13}\text{C-NMR}$ : 159.045, 156.710, 145.072, 132.572, 132.550, 132.050, 131.676, 129.267, 128.407, 127.145, 119.050, 116.067, 115.213, 110.186, 72.652, 70.493, 69.238, 68.307, 66.880, 63.539. IR (ATR): 2874, 2222, 1747, 1602, 1522, 1494, 1454, 1400, 1246, 1180, 1115, 1036, 915, 820, 734,  $701\text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

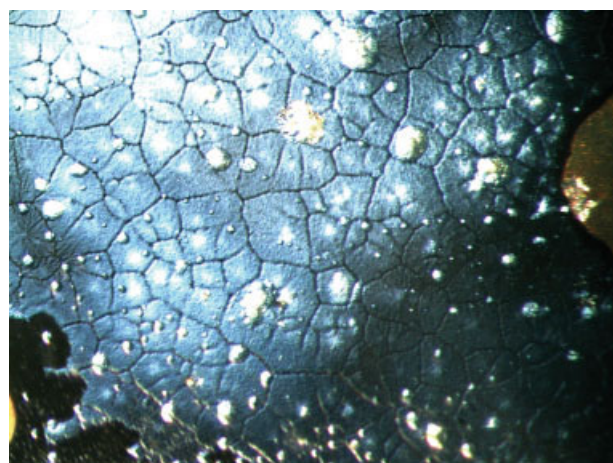
In the present study, a polycarbonate backbone was synthesized via the direct copolymerization of  $\text{CO}_2$  and mesogenic epoxide. To prepare this aliphatic polycarbonate, we used a catalyst that is prepared by reacting zinc oxide with a phthalic anhydride in the presence of an alcohol.<sup>12</sup>

The mesogenic epoxide was prepared by a nucleophilic reaction between 4-cyano-4'-hydroxybiphenyl and glycidyl nosylate. To ensure the enantiopurity of the mesogenic epoxide, a completely controlled reaction by cesium fluoride (CsF), providing convenient excess to enantiopure materials, is used.<sup>13</sup> We adapt the earlier protocol and synthesize the enantiopure

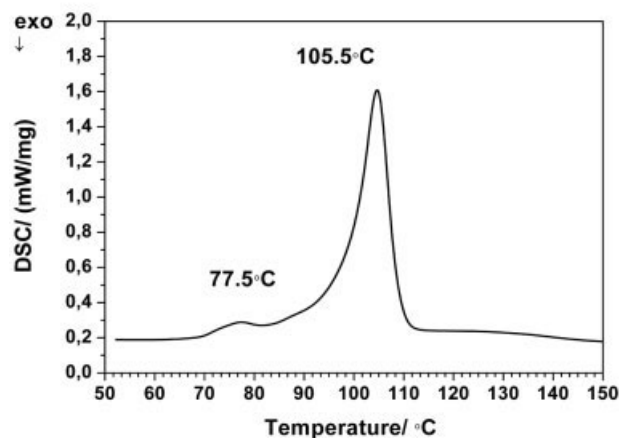
mesogenic epoxide, that is precursor for the synthesis of optically active SCLC polycarbonate in  $\text{ScCO}_2$ . The reactions of oxiranes with nucleophiles are constituted basically by two types of transformations: ring opening and nucleophilic substitution. The substitution leads to the retention of the chiral center, while the chirality sense is reversed upon ring opening. Since a decrease in enantiomeric purity is caused by the competition of ring opening with the nucleophilic attack, glycidyl nosylate, displaying an enhanced leaving character, is employed to force the reaction in favor of nucleophilic substitution.

The spectrum data obtained for the monomer illustrate that the reaction mechanism prefers the nucleophilic substitution reaction instead of the ring opening transformation. In the FTIR spectra, the three-membered ring compounds of epoxides usually give three bands, and for our monomer, the following values are observed: a medium intensity symmetric stretching vibration at  $1261\text{ cm}^{-1}$ , an asymmetric vibration at  $857\text{ cm}^{-1}$ , and a strong absorption at  $833\text{ cm}^{-1}$ . The strong absorption at  $2222\text{ cm}^{-1}$  is indicative of the CN bond stretching. The stretch which is to the downfield of  $3000\text{ cm}^{-1}$  and the absorptions occurring in pairs at  $1601$  and  $1490\text{ cm}^{-1}$  on the other hand are indicative of the aromatic rings. In the  $^1\text{H-NMR}$ , the disappearance of the nosylate's aromatic hydrogen peaks and the hydroxyl peak of the 4-cyano-4'-hydroxybiphenyl is a clear evidence of the success in the nucleophilic reaction. In agreement with the analytical data obtained from IR and  $^1\text{H-NMR}$  spectra,  $^{13}\text{C-NMR}$  spectrum provides another evidence for the successive nucleophilic reaction, giving epoxy ring peaks at specifically  $50.0$  and  $44.6\text{ ppm}$ , and a peak corresponding to the spacer ethylene unit at  $68.8\text{ ppm}$ .

Having two different planar structures (the biphenyl unit and the epoxy ring) around an oxygen atom, the synthesized mesogenic epoxide offers a chiral center from the methine carbon of the epoxide. As revealed in the literature, mesogenic molecules with short spacer units tend to present a nematic LC mesophase, whereas the ones with longer spacer units present a smectic LC mesophase.<sup>7</sup> Hence, having only one spacer unit and a chiral center, the monomer should give a chiral nematic (cholesteric) texture. The LC phase of the synthesized monomer is observed clearly under the optical microscope, as shown in Figure 1(a). In the second heating cycle, the so-called oily-streaks texture, which is the most commonly observed appearance of cholesteric phases, is obtained for the monomer at about  $79^\circ\text{C}$ . On the other hand, the DSC thermogram of the monomer in Figure 1(b) shows a small shoulder at about  $77.5^\circ\text{C}$  and a clearing point at  $105.5^\circ\text{C}$ , which is consistent with the monomer phase transition at  $105.9^\circ\text{C}$ , as reported by Taton et al.<sup>7</sup> Attributable to the optic microscope textures, the DSC data illustrate that the crystalline–cholesteric



(a)



(b)

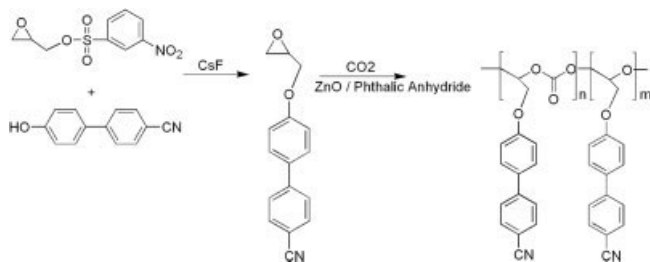
**Figure 1** (a) The cholesteric transition of the monomer is obtained in the second heating cycle at  $79^\circ\text{C}$  (original magnification calibration  $10 \times 20$ ). (b) The DSC thermogram of the monomer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

transition involves a very small change in enthalpy, whereas the transition from the ordered cholesteric mesophase to the disordered isotropic state results in a larger change in enthalpy at  $105.5^\circ\text{C}$ .

As illustrated in Scheme 1, polymerization of epoxides in supercritical carbon dioxide ( $\text{ScCO}_2$ ) media results in block copolymers consisting of both etheric and carbonate units. Such structures have been obtained in literature by employing different kind of catalyst systems.<sup>9,14</sup> The  $m:n$  ratio of the copolymer has been determined as  $1:10$  by comparing the methine hydrogen of the ether and the carbonate groups in  $^1\text{H-NMR}$ .

By using this highly enantiopure monomer and the synthesized achiral catalyst, we obtain an isotactic polymer. As proposed in the literature, optically active polymers can be synthesized by using either optically active monomers or optically active catalysts.<sup>15</sup> Spe-

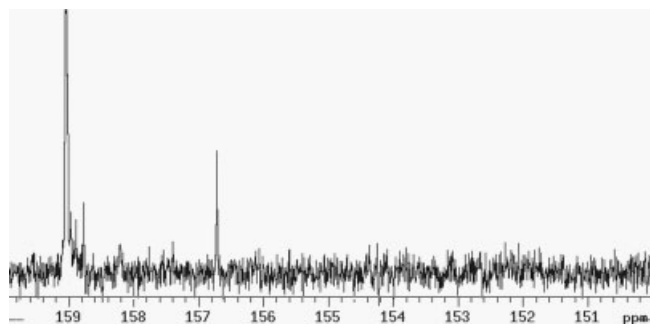




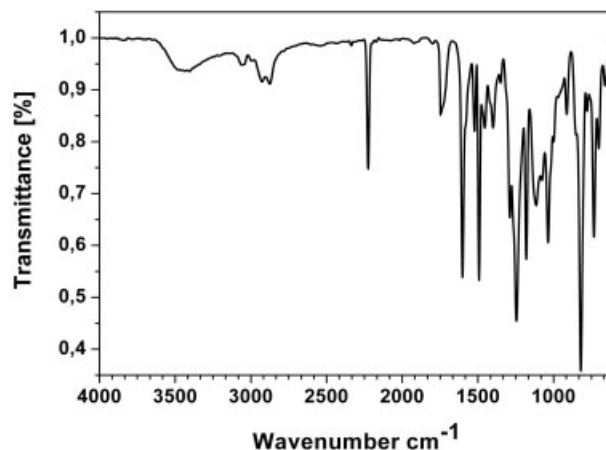
**Scheme 1** The representation of the reactions. For monomer synthesis, the mixture was stirred at room temperature (RT), under inert conditions in anhydrous DMF. The copolymerization is done under the conditions of  $90 \pm 3^\circ\text{C}$  for 24 h in  $\text{ScCO}_2$ , with a small amount of dichloromethane as cosolvent. The reaction mixture is pressurized by  $\text{CO}_2$  up to 4500 psi.

cifically, in the copolymerization with  $\text{CO}_2$ , racemization does not take place,<sup>16</sup> and the polymerization does not proceed via the enantiomorphic site control.<sup>17</sup> So, being aware of these advantages of polymerization in  $\text{ScCO}_2$  media, by using achiral catalysts, chiral epoxides should give chiral polymers. Owing to the fact that the monomer we used is highly enantiopure and also the ring opening of the epoxide results always from the backside attack,<sup>18</sup> this special stereoregularity can be rationalized as isotactic. The isotacticity of copolymer is illustrated by a single carbonyl resonance at 156.7 ppm in Figure 2, representing a single chiral environment.<sup>19</sup>

The other characterizations are also in agreement with the synthesis of the copolymer. In the FTIR spectrum, the most characteristic change, going from monomer to polymer, is the appearance of a sharp peak at  $1747\text{ cm}^{-1}$ , originating from the  $\text{C}=\text{O}$  stretching of the carbonate group in the polymer (Fig. 3). Also, the other characteristic stretching vibration of the carbonate group, depending on the  $\text{C}-\text{O}-\text{C}$  bond vibrations, is observed at  $1246\text{ cm}^{-1}$ . The strong absorption at  $2222\text{ cm}^{-1}$  is due to the cyano bond stretching in the spacer unit. In the  $^1\text{H-NMR}$  spectrum, the shift to lower fields is observed for the epoxy protons.



**Figure 2** The expanded portion of the  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) spectrum of the copolymer in the range of 160 and 150 ppm.



**Figure 3** The FTIR spectrum of the synthesized copolymer.

The methylene and the methine protons are shifted to 4.23 and 4.98 ppm, respectively. This downfield shift of the protons in the backbone is caused by the strong deshielding effect of the carbonate group in comparison with the monomeric epoxy group. Additionally, the methylene units in the spacer groups give a broad band at 4.06 ppm. In the table given later, different polymerization conditions and their corresponding polymerization conversions are given. The polymerization conversions are calculated by comparing the unreacted nosylate's methylene peak and the biphenyl methylene peak in  $^1\text{H-NMR}$ . Using more catalyst tends to increase the polymer conversion, whereas short reaction times yield a low polymerization conversion. On the other hand, longer reaction times tend to decrease the weight of the synthesized polymer.<sup>20</sup> This decrease in the molecular weight is due to the relatively slow initiation and rapid propagation reaction, while the cyclic carbonate is formed in a simultaneous side reaction and by depolymerization of the already formed polymers. For this reason, the optimum reaction conditions to be used with the mesogenic epoxide appear to be a temperature of  $90^\circ\text{C}$ , a pressure of 4500 psi, and a reaction time of 24 h.

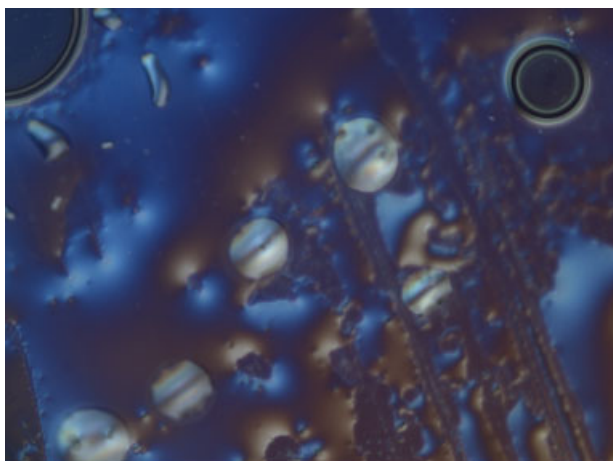
The LC phase of the bulk polymer was unambiguously defined by textural observation by optical microscope. On cooling from the isotropic melt, the cholesteric phase transitions are observed at  $83.7^\circ\text{C}$  and  $85.9^\circ\text{C}$ . The droplets are characteristics of nematic mesophase, since they occur nowhere else.<sup>11</sup> For a chiral nematic (cholesteric) mesophase, different colors in the droplet correspond to different twist states of the cholesteric liquid crystalline polymer. Such cholesteric droplets, representing different colors, are observed at  $83.7^\circ\text{C}$  in Figure 4(a). Therefore, the coexistence of a cholesteric structure was verified by textural observation.

Since the coupling is strong between the mesogenic unit and the polymer backbone (due to the short

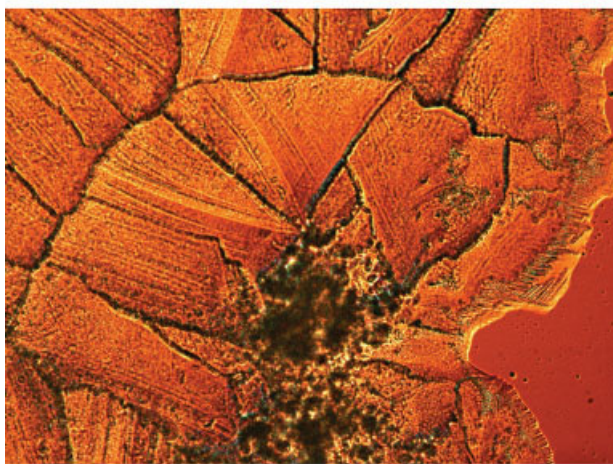
**TABLE I**  
**Polymerization Conditions and Conversion**

Polymer	Polymerization conditions	Molar feed ratio $N_{\text{cat}}/N_{\text{mon}}$	Polymerization conversion (%)	$M_n$ value	Polydispersity
P-1	$T = 90^\circ\text{C}$ , $P = 4000$ psi, $t = 20$ h	1/5	36	$5.3 \times 10^4$	1.17
P-2	$T = 90^\circ\text{C}$ , $P = 4500$ psi, $t = 20$ h	2/5	50	–	–
P-3	$T = 90^\circ\text{C}$ , $P = 4500$ psi, $t = 24$ h	2/5	61.5	$2.1 \times 10^5$	1.26

spacer length), a transfer of chirality from the backbone to the mesophase is expected. However, in the analogues with a longer spacer group, the effect of the chiral centers of the polymer backbone is not detected.<sup>7</sup> The optic microscope textures confirm this chirality transfer and, consequently, we observe a chiral nematic texture for the copolymer.



(a)



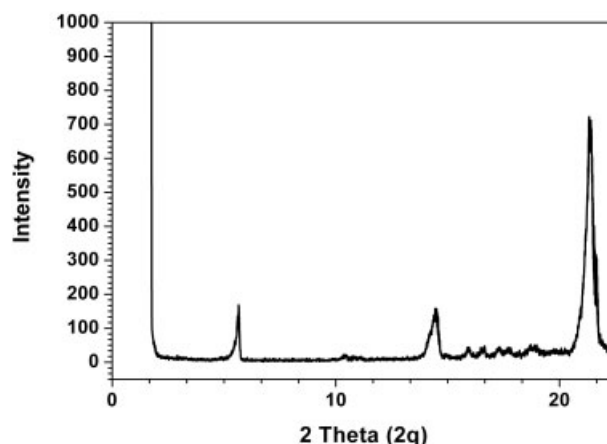
(b)

**Figure 4** The cholesteric textures of the bulk polymer observed by polarized light microscopy in the second cooling cycle (a) at  $83.7^\circ\text{C}$  (the original magnification calibration  $10 \times 20$ ) (b) at  $85.9^\circ\text{C}$  (the original magnification calibration  $10 \times 50$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

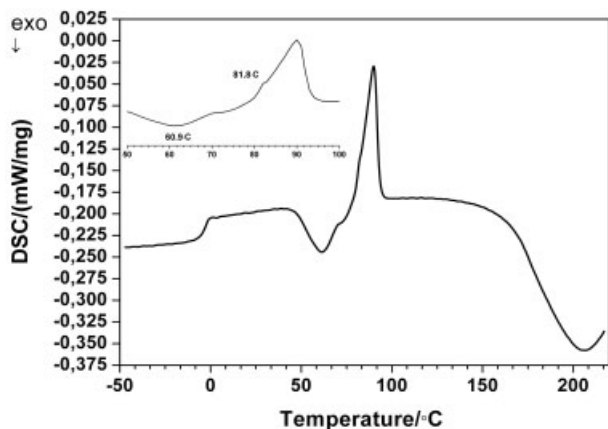
To gain more information on the mesomorphic structure of the copolymer, we carried out X-ray diffraction. The polymer sample for the X-ray diffraction experiment was prepared by freezing the molecular arrangements in the liquid crystalline state by liquid nitrogen, as previously reported in the literature.<sup>11</sup>

No reflections were observed at low angles, indicating that there is no layer ordering within the mesophase, which takes the polymeric mesophase out of smectic classification. The copolymer shows an X-ray diffraction pattern consisting of two mid-angle reflections and one high-angle reflection (Fig. 5). The two mid-angle reflections at about  $2\theta = 5.6^\circ$  and  $2\theta = 14.53^\circ$  are characteristic peaks of the copolymer, which are observed in the crystalline form as well, and correspond to the average intermolecular distance about  $15.73 \text{ \AA}$  and  $6.119 \text{ \AA}$ , respectively. The peak at high angle region, which is centered at about  $2\theta = 21.36^\circ$ , gives the average distance of the shorter preferred spacing of  $4.15 \text{ \AA}$ . The appearance of a broad or sharp peak furnishes a qualitative indication of the degree of order. Explicitly, the sharp peak at high angle region implies an ordered side chain structure between the main chains.

The phase assignment was conducted by optical polarizing microscopic observation and X-ray diffraction measurement. The results correlate with each other, and the coexistence of a cholesteric structure was verified.



**Figure 5** The X-ray measurement for the copolymer at room temperature.



**Figure 6** The DSC thermogram of the copolymer in the second heating cycle with a heating rate of 10°C/min.

Moreover, from the DSC thermogram mentioned earlier, a glass transition ( $T_g$ ) curve at  $-3.3^\circ\text{C}$  and a decomposition peak at  $203.4^\circ\text{C}$  are observed. It is meaningful to state that depending on the side groups and the catalyst utilized, different  $T_g$  values have been reported in the literature for such kind of copolymers, ranging from  $-19^\circ\text{C}$  to  $145^\circ\text{C}$ .<sup>21</sup> The exothermic peak at  $60.9^\circ\text{C}$ , on the other hand, represents the crystallization of the polymer ( $k \rightarrow k'$  transition) (Fig. 6). As the temperature increases, the crystal packing transforms to a better ordered sub-phase, thus releasing heat to the surrounding.<sup>22</sup> The big endothermic peak at  $90.1^\circ\text{C}$  actually involves two transitions: a crystal-to-cholesteric transition and a cholesteric-to-isotropic transition. Polarized optical microscopy observation is in agreement with these transitions as well. If the DSC thermogram of the copolymer is expanded, a small shoulder on the peak at  $90.1^\circ\text{C}$  is observed, which represents the two overlapping peaks. Same overlapping peaks are observed for the copolymers having different  $m:n$  ratio in Table I. As it is shown in Table II, for the obtained polymer, the  $T_i$  value does not change dramatically, whereas a pronounced decrease in  $T_g$  value is observed from that of its acrylic analogues.<sup>23</sup> Hence, the present study exhibits another practical benefit in terms of liquid crystallinity by widening the mesomorphic temperature range ( $\Delta T = T_i - T_g$ ).

**TABLE II**  
Comparison of the  $T_g$  and  $T_i$  Values  
of Analogue Polymers

Reactants	Spacer unit	$T_g$ ( $^\circ\text{C}$ )	$T_i$ ( $^\circ\text{C}$ )
Our polymer	$N = 1$	$-3.3$	$90.1$
Acryloyl chloride and 4-cyano-4'-hydroxybiphenyl <sup>23</sup>	$N = 3$	$68$	$97$
Acryloyl chloride and 4-cyano-4'-hydroxybiphenyl <sup>23</sup>	$N = 6$	$45.5$	$124$

## CONCLUSIONS

By using an environmentally benign approach, the synthesis of a mesogenic epoxide and its copolymerization with  $\text{CO}_2$  has yielded an optically active SCLCP in a single-step reaction. The presence of a chiral center in the main chain is beneficial, since it provides information about the magnitude of decoupling between the mesogenic unit and the backbone. As demonstrated with the chiral nematic (cholesteric) phase transition on the optical microscopy textures, a transfer of chirality from the macromolecular backbone to the mesophase becomes feasible. Being consistent with the  $^{13}\text{C}$ -NMR spectrum, the appearance of a sharp peak at high angle regions in the X-ray diffraction pattern implies an ordered side chain structure between the main chains. Additionally, the carbonate group in the backbone can provide enough flexibility to the mesogenic unit to introduce liquid crystallinity, and the ether moieties in the backbone further enhance flexibility. Therefore, a SCLCP with a flexible backbone was prepared for the possibility of obtaining better electro-optical properties than those of their nonflexible analogues. It is now possible to synthesize different spacer-length LCPs in  $\text{ScCO}_2$  media, which are precursors for a great variety of different liquid crystalline applications. Finally, our copolymer presents an extended mesomorphic temperature range compared to those of its acrylic analogues. This can be a good basis in the material design for preparing the practical materials suitable for device applications. Attributable to the flexible backbone, polymers that are synthesized in  $\text{ScCO}_2$  media may lead to different thermal applications. We describe the advantages of polymerization in  $\text{ScCO}_2$  media, in terms of liquid crystallinity and the stereoregularity of the obtained polymer. Starting from the fact that copolymerization mechanism in  $\text{ScCO}_2$  media does not alter the arrangement of the enantiopure monomer, one can easily obtain a highly stereoregular polymer by a purposeful design of a chiral monomer or catalyst.

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