Synthesis and mesomorphism of new aliphatic polycarbonates containing side cholesteryl groups

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ABSTRACT

New cholesterol side-functionalised polycarbonate polymers were synthesised by the ring-opening homo- and copolymerisation reaction of the cyclic monomer cholesteryl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate and L,L-lactide using Sn(Oct)\textsubscript{2} as a catalyst. The chemical structures and average molecular weights of the cyclic monomer, homopolymer and block copolymers obtained in this study were characterised using FT-IR, \textsuperscript{1}H NMR and gel permeation chromatographic measurement. The mesomorphism and mesophase structure were investigated with polarising optical microscopy, differential scanning calorimetry and X-ray diffraction measurement. As a result, the homopolymer and block copolymers showed an enantiotropic smectic A (SmA) phase. With the concentration of the lactide segment increasing, the glass transition temperature and isotropic temperature of the corresponding block copolymer all decreased. In addition, XRD suggested that the homopolymer and two block copolymers showed the SmA double-layer packing of side chains.

1. Introduction

As known, liquid crystal (LC) materials have been widely used in the field of electro-optical display devices because their flexible ordered structures can lead to systems displaying switchable optical modulation.[1–5] In fact, LC compounds are also useful in biorelated fields because their self-organising structures through non-covalent specific interactions are compatible with those in living systems.[6,7] Moreover, LC compounds can produce response...
through the self-assembling ability under external stimuli, such as temperature, pressure and electromagnetic fields.

In recent years, aliphatic polycarbonates have been found to be promising biomaterials because of their good biodegradability and biocompatibility.[8–10] Until now, many modification approaches have been used to obtain the desirable properties. Among them, the incorporation of the bioactive or self-assembly functional compounds to the polymer chain has currently become one of the most important modification strategies.[11–19]

Cholesterol has high thermodynamic affinity towards cell membrane and ability to change the fluidity and permeability of the membrane as an important structural component in mammalian cells.[20] In addition, a bioactive role for cholesterol has also been confirmed in the central nervous system, where its production by glial cells promotes improved synapsogenesis by surrounding neurons.[21] Due to its universal effect, cholesterol can play important roles in the functions of biological system and LC soft matter and become an interesting component with bioactive, regardless of cell type and receptor map on the membrane. The first LC compound, discovered over a century ago, was a cholesterol derivative. So far, many LC compounds based on cholesterol have been reported to investigate optical-electric properties, thermochromism and circular dichroism.[22–27] In addition, as a natural biodegradable LC polymer materials. In recent years, LC polymers based on cholesterol have attracted considerable attention in the biomaterials fields.[15–18,28–34] Stupp and co-workers synthesised cholesterol end functionalised oligo(l-lactic acid).[15] Afterwards, Cheng [16] and Yang et al. [17] also reported cholesteryl end-capped aliphatic polycarbonates and dicholesteryl end functionalised triblock poly(ε-caprolactone), respectively, as biodegradable polymers. Among the above research reports, the functionalised cholesteryl units were located in the terminal groups of macromolecular main chain. However, to the best of our knowledge, little research on the biodegradable aliphatic polycarbonate containing side cholesteryl groups as biomimetic units is reported. Therefore, it is necessary to synthesise new biodegradable side chain LC polycarbonate derived from cholesterol, and to study their structure–property relationships and further explore the potential applications in drug delivery and tissue engineering templates.

In this work, we reported a new active cyclic carbonate monomer based on cholesterol, and the corresponding side chain LC homopolymer and block copolymers with aliphatic polycarbonate backbone. Herein, we only discuss the synthesis, structure, average molecular weights, mesomorphism and mesophase structure of the obtained target products with FT-IR, 1H NMR, polarising optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD).

2. Experimental method

2.1. Materials

All chemicals were obtained from the indicated sources and used as-received. Benzyl chloride was purchased from Shanghai Chemical Plant (Shanghai, China); 2,2-dimethylolpropionic acid from Jinan Wandoxin Chemical Industry Co., Ltd. (Jinan, China); and ethyl chloroformate from Jiangshu Xinyi Huili Fine Chemical Co., Ltd. (Xinyi, China). Cholesterol was purchased from Xiayi Beier Biological Products Co., Ltd. (Xiayi, China). Stannous octoate [Sn(Oct)2] was purchased from Sigma-Aldrich. D,L-Lactide (DLLA) was purchased from Jining Daigang Biological Engineering Co., Ltd. (Jinan, China). Tetrahydrofuran (THF) was dried over potassium hydroxide and then distilled over sodium-potassium alloy in argon atmosphere. All other solvents and reagents used were purified by standard methods.

2.2. Characterisation

FT-IR spectra were measured as a KBr disc at the ambient on a PerkinElmer spectrum One (B) spectrometer (PerkinElmer, Foster City, CA). 1H NMR spectra were measured using a Bruker ARX 600 (Bruker, Germany) high-resolution NMR spectrometer, and chemical shifts were reported in ppm with tetramethylsilane (TMS) as an internal standard. The special optical rotations were characterised on a PerkinElmer 341 polarimeter. The average molecular weights of the polymers were obtained with gel permeation chromatography (GPC) measurements at room temperature on a Waters 1515 instrument calibrated with a polystyrene standard, and using THF as an eluent. The optical textures were observed with a Leica DMRX POM (Leica, Germany) equipped with a Linkam THMSE-600 (Linkam, United Kingdom) cool and hot stage. The phase behaviour was determined with a Netzsch DSC 204 (Netzsch, Hanau, Germany) equipped with a cooling system at a heating and cooling rates of 10°C/min in a nitrogen atmosphere. The mesophase structure was identified using a Bruker D8
Advance (Bruker, Germany) X-ray diffraction (XRD) measurement with a nickel-filtered Cu-Kα radiation.

2.3. Monomer synthesis

The synthetic route of the cyclic carboxylate monomer is outlined in Scheme 1. Benzyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (1) and benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (2) were prepared according to the method reported by Hu and co-workers.[19]

2.3.1. 5-methyl-2-oxo-1,3-dioxane-5-carboxylic acid (3)

The compound 2 (7.5 g, 30 mmol), 10% Pd/C (75 mg), and ethyl acetate (100 mL) were added to a 250 mL three-neck flask with a magnetic stir bar under an argon atmosphere. The reaction mixture was stirred for 24 h at room temperature under a hydrogen system. The Pd/C was filtered off with centrifugal method, the filtrate was evaporated to dryness. After the crude product was recrystallised with ethyl acetate, the white powder was obtained. Yield: 81%; mp: 170°C; IR (KBr, cm⁻¹): 2650, 2561 (–COOH); 1750, 1704 (C = O); 1205, 1165 (C–O–C). ¹H NMR (δ, ppm from TMS in CDCl₃): 4.75 (d, 2H, J = 10.8 Hz, –CH₂O–), 4.25 (d, 2H, J = 7.2 Hz, –CH₂O–); 2.45–0.69 (m, 46H, rest of the protons from cholesterol and CH₃, in the cyclic monomer).

2.3.2. Cholesteryl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (M₅C)

In a 500 mL three-neck flask with a magnetic stir bar, the compound 3 (3.2 g, 20 mmol), N,N’-dicyclohexylcarbodiimide (DCC) (1.04 g, 5 mmol), and 4-dimethylaminopyridine (DMAP) (0.24 g, 2 mmol) were dissolved in anhydrous dichloromethane (200 mL). After stirring for 1 h, cholesterol (7.72 g, 20 mmol) solution containing 20 mL of dichloromethane, was added dropwise to the above-mentioned mixture. The reaction mixture was stirred for 36 h at room temperature. After 10 mL of distilled water was added into the resulting mixture and allowed to stir for 0.5 h, a solid, N,N’-dicyclohexyl urea, was precipitated by high-speed centrifugation and filtered off. The organic layer was dried with anhydrous MgSO₄, and removal of solvent under reduced pressure resulted in crude product as a slightly yellow solid. The crude product was further purified by column chromatography using silica as the packing material and a gradient of petroleum ether/ethyl acetate (3:1) mixtures as the eluent, and a white solid was obtained. Yield: 42%; mp: 153°C. IR (KBr, cm⁻¹): 2967, 2842 (–CH₂–, –CH₃); 1745, 1731 (C = O). ¹H NMR (δ, ppm from TMS in CDCl₃): 5.40 (d, 1H, J = 4.2 Hz, –CH = C in cholesterol); 4.72 (m, 1H, –COOC(CH₃)< in cholesterol); 4.67 (d, 2H, J = 7.2 Hz, –CH₂O–), 4.21 (d, 2H, J = 7.2 Hz, –CH₂O–); 2.45–0.69 (m, 46H, rest of the protons from cholesterol and CH₃, in the cyclic monomer).

2.4. Polymers synthesis

The synthetic route of the homopolymer and copolymers is outlined in Scheme 2. These polymers were prepared through ring-opening polymerisation reaction using Sn(Oct)₂ as a catalyst.

2.4.1. Homopolymerisation

The monomer M₅C (5.29 g, 0.01 mol) and Sn(Oct)₂ toluene solution (80 μL, 0.25 mol/L) were added to a glass polymerisation flask, which was degassed in a vacuum by several vacuum-purge cycles, and then sealed under an argon atmosphere. After the mixture was reacted for 24 h at 160°C in an oil bath, the crude polymer was dissolved in THF and re-precipitated in methanol. The homopolymer HP was dried in a vacuum at room temperature until a constant sample mass was obtained as white powder. IR (KBr, cm⁻¹): 2966, 2843 (–CH₃, –CH₂–); 1748 (C = O); 1250 (C–O–C). ¹H NMR (CDCl₃, TMS, δ, ppm): 5.39 (–CH = C in cholesterol);
4.65, 4.42, 3.70 (–CH₂O–); 4.22 (–COOC₃H in cholesterol); 2.42–0.67 (rest of the protons from cholesterol and CH₃, in the cyclic monomer).

2.4.2. Copolymerisation

The block copolymers CP-1 and CP-2 were synthesised by a procedure similar to that for HP, using the monomers M₁C and DLLA. Their polymerisation feed is shown in Table 1. The synthesised copolymers were identified using FT-IR and ¹H NMR. The structure characterisation of CP-1 is given below as an example.

IR (KBr, cm⁻¹): 2950, 2847 (–CH₃, –CH₂–); 1756 (C = O); 1262 (C–O–C). ¹H NMR (CDCl₃, TMS, δ, ppm): 5.37 (–CH = C in cholesterol); 5.02 (–CH=C in lactide); 4.66, 4.45, 3.71 (–CH₂O–); 4.27 (–COOCH < in cholesterol); 2.45–0.68 (rest of the protons from cholesterol and CH₃, in the cyclic monomer).

3. Results and discussion

3.1. Synthesis and characterisation

The compound 3 with side carboxyl groups was obtained by hydrogenolysis reaction to result in the deprotection of side benzyl groups for the compound 2 using Pd/C catalyst under a hydrogen system. The new cyclic carboxylate monomer were synthesised by the esterification of intermediate compound 3 with carboxyl group and the commercially available cholesterol using DCC as the condensation agent and DMAP as the catalytic system in dry dichloromethane. The crude product was purified by silica gel column chromatography to result in a white powder as the target monomer M₃C. The corresponding synthetic route is shown in Scheme 1. The chemical structure was confirmed by FT-IR and ¹H NMR. FT-IR spectra of M₃C showed typical stretching vibration bands at 1745 cm⁻¹ attributed to ester C = O in cyclic carboxylate, and 1731 cm⁻¹ assigned to ester C = O in cholesteryl carboxylate. ¹H NMR spectra of M₃C showed characteristic double-signal peaks at 5.40 ppm assigned to the cholesteryl olefinic proton, multiplet signals at 4.72 ppm assigned to the methenyl proton for –COOCH< group in cholesterol, and double peaks at 4.67 and 4.21 ppm attributed to the methylene protons in cyclic carboxylate. Figure S1 shows ¹H NMR spectra of M₃C.

Until now, it is a most efficient method and crucial strategy to synthesise aliphatic polycarbonate polymers by the ring-opening polymerisation reaction. The homopolymerisation and copolymerisation were carried out in polymerisation flask equipped with a sealing cap using Sn(Oct)₂ as a catalyst and the optimum reaction conditions were identified to be 24 h at 160° C, and the molar ratio of the monomer to Sn(Oct)₂ was 500:1. The synthesised polymers are soluble in

| Polymer | M₃C (mol) | DLLA (mol) | [M]/[I] a | DP b | Yield (%) | Mₙ c (kDa) | M_p/Mₙ | PDI |
|---------|----------|------------|-----------|------|-----------|------------|---------|-----|
| HP      | 0.01     | –          | 500       | 11   | 92        | 6.35       | 1.53    |     |
| CP-1    | 0.009    | 0.001      | 500       | 13   | 93        | 8.62       | 1.43    |     |
| CP-2    | 0.008    | 0.002      | 500       | 15   | 90        | 9.78       | 1.48    |     |

a Molar ratio of monomer to catalyst; bDP, average degrees of polymerisation; cMₙ values determined by GPC in THF using PS standards, g/mol; PDI is M_p/Mₙ, polydispersity index.
common organic solvents such as THF, toluene, chloroform and so on. The chemical structures of the homopolymer HP, and copolymers CP-1 and CP-2, shown in Scheme 2, were also confirmed by \(^1\)H NMR spectrometry. Figures S2 and S3 show \(^1\)H NMR spectra of HP and CP-1. After polymerisation, the resonance peaks of the polymers are rather broad owing to slower motion of the protons, indicating the successful polymerisation. In addition, a new signal at 3.70 ppm appeared for HP because of the ring-opening of the cyclic carbonate monomer. The average molecular weight \((M_n)\) and the polydispersity index (PDI) of the polymers, summarised in Table 1, were determined by GPC. Moreover, results of GPC analysis indicate that no monomer exists in the polymer samples.

The specific optical rotation of the chiral monomer and polymers was evaluated at 25°C in THF, and the obtained results are summarised in Table 2. Theoretically, specific rotation shows the effect of the net vector of the polar bonds of the chiral molecules on polarised light. The specific rotation of cholesterol is \(-31.5^\circ\) (ether). Accordingly, the specific rotation of the chiral monomer and polymers derived from cholesterol revealed negative values. As can be seen in Table 2, the monomer \(M_{LC}\) showed lower specific rotation absolute value. The results suggest that the existence of cyclic carbonate segment influenced the molecular polarity leading to the decrease of the specific rotation absolute value. In addition, the specific rotation absolute value of the homopolymer HP was less than that of the corresponding monomer, which indicated that the molecular weight also could affect molecular polarity. Compared to the homopolymer, the specific rotation absolute values of the copolymers decreased because the optically inactive lactide segments were introduced to the polymer backbone. This of course affected the amount of optically active sites.

### 3.2. POM analysis

POM is one of the essential tools for the optical texture characterisation of newly synthesised mesogenic materials, and on the other hand can provide a determination of both phase transition temperatures and mesophase type. According to POM observation results, \(M_{LC}\) did not reveal mesophase texture on heating and cooling cycles because of bulky steric hindrance and rigidity. However, the corresponding homopolymer HP showed an enantiotropic mesophase and batonnet texture of a smectic A (SmA) phase, which was also confirmed by XRD analyses. The optical texture of HP at 127°C is shown in Figure 1(a). For the block copolymers, the incorporation of the lactide chain segment to the polycarbonate main chain did not change the mesophase type, but affected the phase transition temperatures. With increasing temperature, the typical fan-shaped texture appeared, and the birefringence disappeared at 125°C for CP-1 and 98°C for CP-2. The optical texture of CP-1 at 85°C is shown in Figure 1(b).

### 3.3. DSC analysis

The thermal properties and the phases of the monomer and polymers obtained in the study are summarised in Table 2. The phase sequence, phase transition

![Figure 1](image-url)
temperatures and enthalpy changes were obtained during the first cooling and second heating scans from DSC. The DSC curves of the monomer MLC, shown in Figure 2, only revealed an endothermic peak on heating and an exothermic peak during cooling process; this indicated that MLC was a non-mesogenic compound, which is consistent with POM results. Figure 3 shows DSC curves of HP. The homopolymer showed a glass transition at 49.9°C and an LC to isotropic phase transition at 133.9°C during heating process. In addition, an isotropic-to-mesophase transition appeared at 115.7°C during cooling process. The mesophase was also confirmed by POM and XRD. The DSC curves of the two copolymers, shown in Figure 4, all showed a glass transition at low temperature and an LC to isotropic phase transition at high temperature. As can be seen in Table 2, the glass transition temperature \( T_g \) and the isotropic temperature \( T_i \) of the copolymers were less than those of the homopolymer. Moreover, with the concentration of the lactide segment increasing, the \( T_g \) and \( T_i \) of the corresponding copolymer all decreased. This indicated that the lactide segment played a dilution role similar to the plasticisation effect in the copolymer. In general, the molecular weights of the LC polymers can affect the thermal properties in the region.[35] The phase transition temperatures increased with increasing molecular weights, but the transitional properties of the final properties did not lie in the regime in which they would show a marked molecular weight dependence. Moreover, the thermal properties were also affected by the flexible lactide segment similar to the plasticisation effect.

### 3.4. XRD analysis

As known, XRD is a powerful analytical tool to recognise the mesophase orientation and sequence distribution of LC polymers. To further identify mesophase structure, the temperature-dependent XRD measurement was carried out. Figure 5 shows the XRD pattern of HP at 80°C.
and 115°C. The XRD pattern of HP revealed two sharp reflections at a small-angle region and a diffuse peak at a wide-angle region. In general, the sharp peak corresponding to the periodic distance is characteristic of a smectic phase in which the molecules are stacked into layer with short range, liquid-like positional order within the layers, and the broad peak corresponds to the average lateral distance between the neighbouring mesogenic side chain. To confirm the presence of the SmA phase, the temperature-dependent $d$-spacing of the smectic layers, shown in Figure 5, were obtained in the mesophase range. On cooling from 115°C to 80°C, the $d$-spacing was constant. The calculated $d$-spacing of corresponding first-order and second-order reflections was 39.8 and 20.4 Å, respectively. This gives strong evidence for the formation of an SmA phase. Moreover, a batonnet texture, shown in Figure 1(a), was clearly observed with POM, which is a characteristic texture of an SmA phase. According to the molecular modelling calculation in the extended conformation using ChemBio3D-Ultra, employing MM2 minimal energy, the estimated all-trans molecular length $L$ of the most extended conformation for HP is about 20.0 Å. A $d/L$ ratio of 1.99 ($d = 2L$) was calculated, suggesting double layers. Schematic representation of the molecular arrangement of the pendant LC groups and SmA arrangements model for HP are shown in Figure 6, which is consistent with the results reported by Imrie and co-workers.[36] Similar to HP, the XRD patterns of the copolymers CP-1 and CP-2 also showed two sharp reflections and a diffuse peak, moreover, their corresponding $d$-spacing hardly changed, which indicated that the incorporation of the lactide segment to the polymer chain did not change the mesophase type and molecular arrangements. As an example, the XRD pattern of CP-1 at 100°C is shown in Figure 7.

4. Conclusions

The synthesis of a new cyclic carbonate monomer based on cholesterol and the corresponding polymers is presented. The cyclic chiral monomer only showed a melt transition and did not reveal mesophase texture. The homopolymer and block copolymers all showed enantiotropic mesomorphism and exhibited batonnet or fan-shaped texture of an SmA phase on heating and cooling cycles. The incorporation of the lactide chain segment to the polycarbonate chain did not change the mesophase type, but obviously affected the phase transition temperatures. With the

Figure 6. (colour online) Schematic representation of the molecular arrangement of the pendant LC groups for HP.

Figure 7. XRD pattern of CP-1 at mesophase.
concentration of the lactide segment increasing, the $T_g$ and $T_i$ of the corresponding copolymer all decreased. XRD result showed that the molecular arrangement model of the polymers displayed the SmA double-layer structure.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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