Synthesis and characterization of side-chain cholesterol derivatives based on double bond

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ABSTRACT

After steps of esterification, epoxidation and ring-opening, a series of novel monomers of 5-hydroxyl-6-methacryloyloxy-3-alkylate, C_nCOOCh (n = 1, 2, 3, 4, 5) were synthesized. After that, the corresponding polymers (P_nCOOCh, n = 1, 2, 3, 4, 5) were obtained by free radical polymerization. The molecular structure, composition and thermal behaviors of monomers and polymers were confirmed by ^1H NMR, FTIR, single crystal diffractometer, GPC, DSC and TGA. The results indicate that although their molecular weights are not high, all the polymers have high glass transition (T_g) and degradation temperature. In addition, T_g gradually decreases with increasing of alkyl chain lengths, and the degradation temperature increases with the increase of carbon number.

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1. Introduction

Cholesterol is a kind of cyclopentane phenanthrene derivatives (Scheme 1), belonging to the family of steroid compound. Seen from the structural formula, there are two functional groups in cholesterol skeleton, hydroxyl on C3 position and double bond on C5—C6 position. In the past years, side chain [1–5] and liquid crystal [6–12] polymers based on cholesterol have been documented, mainly because of their particular optical properties, such as selective reflection and transmission of light, thermochromism and circular dichroism [13]. The research work mentioned above were all done based on hydroxyl of the cholesterol, because C3—OH has good reactivity than the double bond. However, besides C3—OH, C5=C6 can be used to fabricate novel cholesterol derivatives having unique functions, which will be interesting and attractive. In our previous research work [14,15], a series of new type of monomers and corresponding polymers modified on C6 position have been reported, the difference is that the hydroxyl groups was protected by etherification method with different length. In this paper, the hydroxyl group was protected by esterification method with different alkyl length.

Since Zhou et al. [16] firstly proposed the concept of mesogen-jacketed liquid crystalline polymers (MJLCPs), in which the mesogenic groups are laterally attached to the polymer backbones without or with only short linkages. Then considerable attentions

have been paid on the synthesis and characterization of MJLCPs [17–21]. As known to all [6], cholesterol is a good mesogen unit with fairly rigidity. We want to know if these kinds of monomers and their corresponding polymers synthesized based on double bond of cholesterol will have the properties like MJLCPs. Wang et al. [15] in our group have synthesized novel cholesterol derivatives starting from the double-bond of cholesterol. All the polymers display apparent glass transition (T_g) and excellent degradation temperature though no liquid crystalline properties have been found. In their work, C3—OH was firstly protected by etherification, however, to our knowledge; the ether bond is not rigid enough to induce the generation of liquid crystalline. So, in this paper, we reported our new molecular design of novel cholesterol derivatives. C3—OH of cholesterol was firstly protected by esterification, and then C5=C6 was modified by oxidizing and ring-opening reaction to synthesize novel polymerizable monomers and corresponding polymers.

2. Experimental

2.1. Materials

Cholesterol, acetic anhydride, propionic acid, butyric acid, pentanoic acid, hexanoic acid, dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), pyridine, 3-chloroperoxybenzoic acid (m-CPBA), α-methacrylic acid, hydroquinone, etc., all were purchased from GuangHua Chemical Co. of China, and used as received. Tetrahydrofuran (THF, analytical reagent; GuangHua

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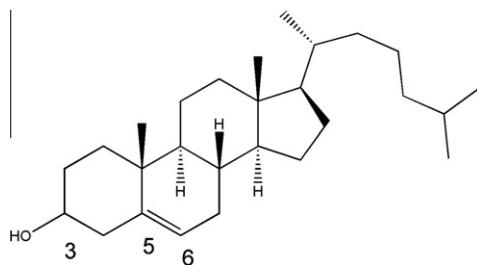
Scheme 1. The chemical structure of cholesterol.

Chemical Reagents) was refluxed over sodium and distilled before use. Benzoyl peroxide (BPO) was purified by recrystallization twice from ethanol. Chlorobenzene was washed with H_2SO_4, $NaHCO_3$, distilled water and then distilled from anhydrous magnesium sulfate. Other solvents were used directly without any purification.

2.2. Instruments

FTIR spectra were measured on a FT-IR (Nicolet) spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a BrukerARMx-400 operating at 400 MHz in deuterated chloroform. Differential scanning calorimetry (DSC) was carried out on a Thermal analysis (TA) DSC-Q30 with a liquid nitrogen cooling system. The rates of heating and cooling rates were 10 °C/min. Thermogravimetric analysis (TGA) was performed from 30 to 500 °C at a heating rate of 10 °C/min on a TA TGA-DSC Q600 thermogravimetric analyser under nitrogen atmosphere. The crystal structure was obtained on CAD4SDP-44 M/H four-circle single crystal diffractometer made by Enraf–Nonius Company of Holland. The gel permeation chromatography (GPC) was conducted with a Breeze Waters system equipped with a Water 515 HPLC pump using polystyrenes as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 ml/min at 40 °C.
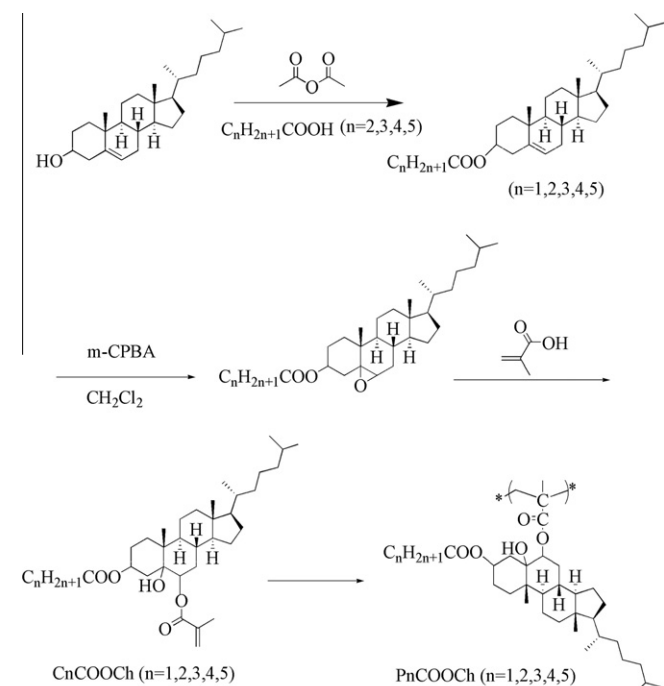
Scheme 2. The synthetic route of monomers and corresponding polymers.

2.3. Synthesis process

The final cholesteryl derivatives were synthesized starting from cholesterol. The detailed synthetic route is shown in Scheme 2.

2.3.1. Synthesis of cholesteryl acetate

Cholesterol (30 g, 0.08 mol), acetic anhydride (15 ml), DCC (8 g, 0.04 mol), and a few drops of pyridine were added to fleshly distilled THF (100 ml) and the reaction mixture was refluxed for 72 h under N_2 atmosphere. Then the white precipitate was removed by filtration and the filtrate was evaporated, the crude product was recrystallized twice from ethanol. Yield: 90.2%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ = 5.37 (s, 1H, 6-H), 4.62 (m, 1H, 3-H), 2.26 (m, 2H, —CH$_2$—), 2.01 (m, 3H, —CH$_3$), 0.67–1.96 (m, 41H). IR (KBr pellet, cm^{-1}): ν = 2942.9–2867.2 (stretching of —CH$_3$ and —CH$_2$—), 1735.7 (stretching of —C=O), 1667.6 (stretching of —C=C), 1244.7, 1032.0 (stretching of C—O—C).

2.3.2. Cholesteryl propionate

Cholesterol (5 g, 0.01 mol), DCC (2.67 g, 0.01 mol), DMAP (0.12 g, 1 mmol), propionic acid (1.9 g, 0.02 mol), and dried THF (100 ml) were mixed in a 250 ml round-bottom flask and stirred for 36 h at room temperature. The floating solid was filtrated off and the solvent was concentrated. After that, the concentrated mixture was poured into 500 ml distilled water with fierce stirring. After twice washing, the white sediment was collected and recrystallized from ethanol. Yield: 91.3%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ = 5.37 (s, 1H, 6-H), 4.61 (m, 1H, 3-H), 2.25 (m, 2H, —CH$_2$—), 0.67–1.94 (m, 46H). IR (KBr pellet, cm^{-1}): ν = 2943.8–2866.6 (stretching of —CH$_3$ and —CH$_2$—), 1737.7 (stretching of —C=O), 1664.7 (stretching of —C=C), 1243.5, 1031.2 (stretching of C—O—C).

Cholesteryl butyrate: Yield: 91.7%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ = 5.38 (s, 1H, 6-H), 4.63 (m, 1H, 3-H), 2.28 (m, 2H, —CH$_2$—), 0.67–1.93 (m, 48H). IR (KBr pellet, cm^{-1}): ν = 2945.9–2867.3 (stretching of —CH$_3$ and —CH$_2$—), 1736.9 (stretching of —C=O), 1666.8 (stretching of —C=C), 1243.5, 1032.2 (stretching of C—O—C).

Cholesteryl valerate: Yield: 92.5%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ = 5.37 (s, 1H, 6-H), 4.60 (m, 1H, 3-H), 2.25 (m, 2H, —CH$_2$—), 0.67–1.86 (m, 50H). IR (KBr pellet, cm^{-1}): ν = 2943.7–2866.8 (stretching of —CH$_3$ and —CH$_2$—), 1735.9 (stretching of —C=O), 1667.2 (stretching of —C=C), 1244.9, 1031.9 (stretching of C—O—C).

Cholesteryl caproate: Yield: 93.4%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ = 5.36 (s, 1H, 6-H), 4.61 (m, 1H, 3-H), 2.22 (m, 2H, —CH$_2$—), 0.67–1.88 (m, 52H). IR (KBr pellet, cm^{-1}): ν = 2941.8–2868.9 (stretching of —CH$_3$ and —CH$_2$—), 1736.1 (stretching of —C=O), 1668.1 (stretching of —C=C), 1246.7, 1032.5 (stretching of C—O—C).

2.3.3. Synthesis of 5,6-epoxy-cholesteryl acetate

5,6-Epoxy-cholesteryl acetate was prepared according to the method reported elsewhere [22]. Cholesteryl acetate (8.57 g, 0.02 mol), m-CPBA (4.14 g, 0.024 mol), CH$_2$Cl$_2$ (60 ml) were added to a 150 ml round-bottom flask with flap loosely capped, and then stirred for 24 h at room temperature. After removing the white precipitate, the filtrate was washed by saturated sodium bicarbonate and sodium chloride solution several times, sequentially, and purified from methanol at last. Yield: 89.2%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ = 5.02 (s, 1H, 6-H), 4.85 (m, 1H, 3-H), 2.18 (m, 2H, —CH$_2$—), 2.03 (m, 3H, —CH$_3$), 0.67–1.96 (m, 41H). IR (KBr pellet, cm^{-1}): ν = 2952.4–2868.8 (stretching of —CH$_3$ and —CH$_2$—), 1732.7 (stretching of —C=O), 1240.9, 1039.4 (stretching of C—O—C).

5,6-Epoxy-cholesteryl propionate: Yield: 91.6%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ = 5.01 (s, 1H, 6-H), 4.84 (m, 1H, 3-H),

2.20 (m, 2H, —CH₂—), 0.67–1.94 (m, 46H). IR (KBr pellet, cm⁻¹): ν = 2945.5–2851.6 (stretching of —CH₃ and —CH₂—), 1732.2 (stretching of —C=O), 1208.4, 1084.0 (stretching of C—O—C).

5,6-Epoxy-cholesteryl butyrate: Yield: 89.3%. ¹H NMR (400 MHz, CDCl₃, ppm) δ = 5.03 (s, 1H, 6-H), 4.86 (m, 1H, 3-H), 2.21 (m, 2H, —CH₂—), 0.68–1.92 (m, 48H). IR (KBr pellet, cm⁻¹): ν = 2947.5–2869.6 (stretching of —CH₃ and —CH₂—), 1732.3 (stretching of —C=O), 1191.8, 1010.5 (stretching of C—O—C).

5,6-Epoxy-cholesteryl valerate: Yield: 86.5%. ¹H NMR (400 MHz, CDCl₃, ppm) δ = 5.02 (s, 1H, 6-H), 4.84 (m, 1H, 3-H), 2.19 (m, 2H, —CH₂—), 0.66–1.87 (m, 50H). IR (KBr pellet, cm⁻¹): ν = 2957.4–2868.5 (stretching of —CH₃ and —CH₂—), 1737.5 (stretching of —C=O), 1186.8, 1029.1 (stretching of C—O—C).

5,6-Epoxy-cholesteryl caproate: Yield: 92.5%. ¹H NMR (400 MHz, CDCl₃, ppm) δ = 5.04 (s, 1H, 6-H), 4.86 (m, 1H, 3-H), 2.21 (m, 2H, —CH₂—), 0.67–1.89 (m, 52H). IR (KBr pellet, cm⁻¹): ν = 2951.8–2868.3 (stretching of —CH₃ and —CH₂—), 1738.2 (stretching of —C=O), 1174.8, 1028.2 (stretching of C—O—C).

2.3.4. Synthesis of 5-hydroxyl-6-methacrylate-cholesteryl acetate (C₁COOCh)

5,6-Epoxy-cholesteryl acetate (3 g, 6.7 mmol) and 1 mg hydroquinone were dissolved in 15 ml α-methacrylic acid without any catalyst. The reaction was allowed to proceed at 80 °C for 48 h under nitrogen atmosphere. The mixture was dissolved in acetic ether and then washed by saturated sodium bicarbonate and sodium chloride solution several times, sequentially. The organic layer was dried by magnesium sulfate anhydrous for a night, and the crude product was obtained after evaporation of solvent under reduced pressure. And then it was purified by silica gel column chromatography with mineral ether and acetic ether (8:1). Yield: 58.8%. ¹H NMR (400 MHz, CDCl₃, ppm) δ = 5.62, 6.13 (s, 2H, =CH₂), 5.31 (m, 1H, 6-H), 4.78 (s, 1H, 3-H), 2.22 (m, 2H, —CH₂—), 2.01 (m, 3H, —CH₃), 0.67–1.98 (m, 45H). IR (KBr pellet, cm⁻¹): ν = 3474.9 (stretching of —OH), 3101.7 (stretching of —C=CH₂), 2941.9–2869.5 (stretching of —CH₃ and —CH₂—), 1737.0, 1696.2 (stretching of —C=O), 1636.1 (stretching of —C=C), 1241.7, 1025.2 (stretching of C—O—C).

5-Hydroxyl-6-methacrylate-cholesteryl propionate (C₂COOCh): Yield: 62.2%. ¹H NMR (400 MHz, CDCl₃, ppm) δ = 5.60, 6.11 (s, 2H, =CH₂), 5.19 (m, 1H, 6-H), 4.74 (s, 1H, 3-H), 2.26 (m, 2H, —CH₂—), 0.68–2.05 (m, 50H). IR (KBr pellet, cm⁻¹): ν = 3478.2 (stretching of —OH), 2945.9–2869.1 (stretching of —CH₃ and —CH₂—), 1737.1, 1701.3 (stretching of —C=O), 1636.0 (stretching of —C=C), 1188.4, 1013.3 (stretching of C—O—C).

5-Hydroxyl-6-methacrylate-cholesteryl butyrate (C₃COOCh): Yield: 56.7%. ¹H NMR (400 MHz, CDCl₃, ppm) δ = 5.60, 6.12 (s, 2H, =CH₂), 5.17 (m, 1H, 6-H), 4.74 (s, 1H, 3-H), 2.25 (m, 2H, —CH₂—), 0.66–2.07 (m, 52H). IR (KBr pellet, cm⁻¹): ν = 3486.8 (stretching of —OH), 2943.1–2869.2 (stretching of —CH₃ and —CH₂—), 1731.9, 1701.3 (stretching of —C=O), 1636.1 (stretching of —C=C), 1282.4, 1011.7 (stretching of C—O—C).

5-Hydroxyl-6-methacrylate-cholesteryl valerate (C₄COOCh): Yield: 58.5%. ¹H NMR (400 MHz, CDCl₃, ppm) δ = 5.60, 6.11 (s, 2H, =CH₂), 5.15 (m, 1H, 6-H), 4.73 (s, 1H, 3-H), 2.25 (m, 2H, —CH₂—), 0.66–2.06 (m, 54H). IR (KBr pellet, cm⁻¹): ν = 3474.9 (stretching of —OH), 3101.7 (stretching of —C=CH₂), 2941.9–2869.5 (stretching of —CH₃ and —CH₂—), 1737.0 (stretching of —C=O), 1636.1 (stretching of —C=C), 1241.7, 1025.2 (stretching of C—O—C).

5-Hydroxyl-6-methacrylate-cholesteryl caproate (C₅COOCh): Yield: 62.1%. ¹H NMR (400 MHz, CDCl₃, ppm) δ = 5.59, 6.11 (s, 2H, =CH₂), 5.16 (m, 1H, 6-H), 4.73 (s, 1H, 3-H), 2.24 (m, 2H, —CH₂—), 0.66–2.08 (m, 56H). IR (KBr pellet, cm⁻¹): ν = 3476.6 (stretching of —OH), 2951.7–2868.5 (stretching of —CH₃ and —CH—), 1717.9, 1702.4 (stretching of —C=O), 1637.4 (stretching of —C=C), 1159.5, 1017.6 (stretching of C—O—C).

2.4. Synthesis of polymers

All the free radical polymerization occurred in chlorobenzene with BPO as initiator. A representative polymerization was as follows: typically, 0.3 g CₙCOOCh and 2 mg BPO were placed in a reaction tube with a magnetic stir bar, and then, 1.5 g chlorobenzene was added. After that, the reaction mixture was purged with nitrogen and subjected to four freeze–thaw cycles and sealed under vacuum. The tube was placed into an oil bath at 90 °C for 48 h. The tube was broken and the mixture was precipitated into methanol. White precipitates were filtered and dissolved in THF again. After another process of precipitation, white solids were collected and dried under vacuum at 60 °C for 24 h.

3. Results and discussion

3.1. Synthesis and characterization of monomers

In our previous work [14], the hydroxyl group on C3 position was firstly protected by etherification method, in this paper, the hydroxyl group was firstly esterified by acetic anhydride or fatty acid with different chain length. For the synthesis of cholesteryl acetate, many methods such as esterified by acylchloride [23,24], DCC–DMAP [25], acetic anhydride [26], etc. can be adopted. The method by anhydride was adopted in this experiment due to its less pollution and relatively mild reaction conditions. The other cholesteryl esters were synthesized by directly esterification with different fatty acids under DCC–DMAP catalyst.

After the esterification on C3 position, the double bond between C5, C6 position was oxidated and with an epoxy-ring-opening reaction with methacrylic acid to obtain a series of new monomers, just as the method we reported [14].

The structures of all the monomers were confirmed by ¹H NMR and FTIR. Take C₂COOCh as an example, the characteristic absorption peak of CH₂=CH— was found at about 1636 cm⁻¹ in FTIR spectra. The ¹H NMR spectrum of monomer C₂COOCh (Fig. 1) showed the representative resonances of the vinyl group at 6.11 and 5.60 ppm, indicating that ring-opening occurred between epoxide and α-methacrylic acid. The spectrum also showed the characteristic resonances of —COOCH— (c and d) on C6 and C3 position at 5.19 and 4.74 ppm, respectively. All of the above results verified that the terminal double bond was connected to the cholesterol side-chain as a pendant group, and the polymerizable monomers were successfully obtained.

In our previous work [15], we have proved that the polymerizable group is connected on C6 position by single crystal. Again, a single crystal of monomer C₁COOCh was cultivated from its acetic ether solution, and clear pictures were obtained through four-circle single crystal diffractometer shown in Fig. 2. The picture of monomer C₁COOCh shows that C3 connects with CH₃COO— (up), C5 with —OH (down) and C6 with CH₂=C (CH₃) COO— (up). The detailed single crystal data are listed in Table 1.

3.2. Synthesis and characterization of polymers

The free radical polymerizations of monomers were carried out in chlorobenzene at 90 °C using BPO as the initiator. The polymerization results are summarized in Table 1. All the monomers can be polymerized to give the corresponding polymers, but the molecular weights are not high, corresponding to 8–12 repeat units. This may be due to the fact that the large lateral structure exhibits steric hindrance, decreasing the accessibility of the double bond for polymerization. The polymers obtained are white solids that have good solubility in many common organic solvents, such as THF, chloroform, dichloromethane, toluene, dimethylsulfoxide (DMSO)
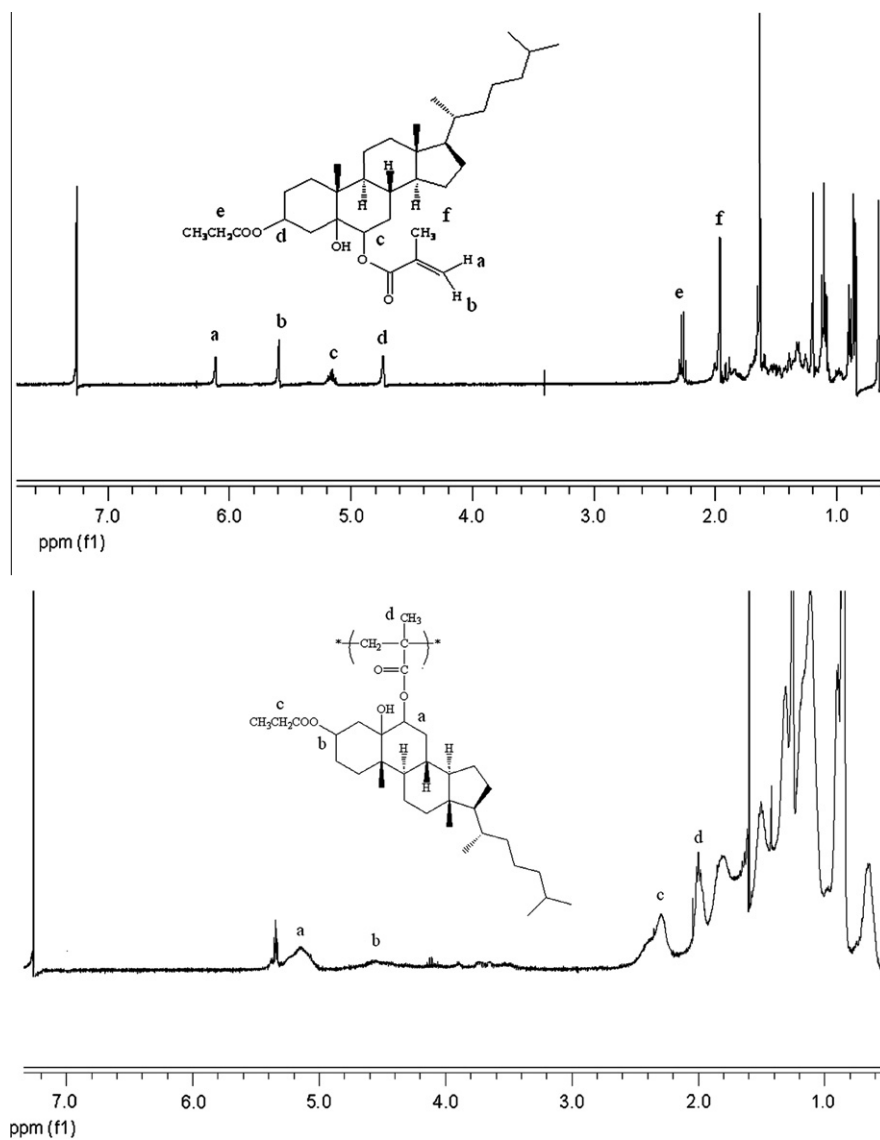
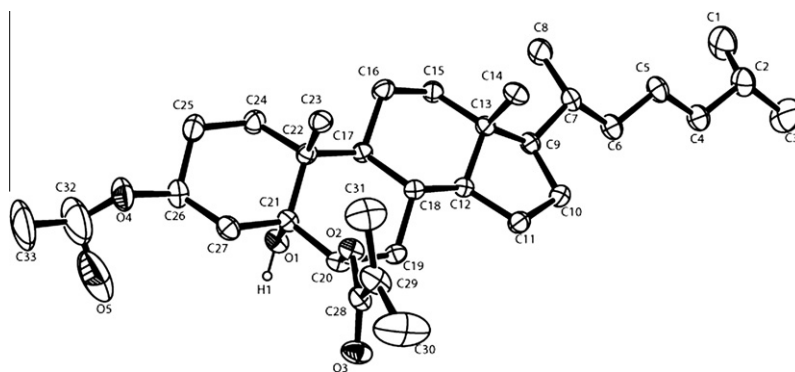Fig. 1. ^{1}H NMR spectra of monomer C$_2$COOCh and polymer P$_2$COOCh.

Fig. 2. The crystal structure of C$_1$COOCh.

and ethyl acetate. The chemical structures of C$_n$COOCh and P$_n$COOCh were confirmed by a combination of analytical techniques, for example, infrared (IR), ^{1}H NMR (Fig. 1). The characteristic peaks at 5.8–6.4 ppm of vinyl groups in the ^{1}H NMR spectrum of monomer disappeared after being polymerized and those of the —CH—CH$_2$—, polymer backbone were observed instead, indicating

the formation of the polymers. The results of polymerization are summarized in Table 2. The sharp characteristic signals of C$_n$COOCh became broad after polymerization due to the limited mobility of protons.

Fig. 3 presents DSC thermograms of the polymers on the second heating, and the phase transition temperatures are summarized in

Table 1
Crystal data for monomer C₁COOCh.

Parameter	C₁COOCh
Crystal size (mm³)	$0.36 \times 0.28 \times 0.19$
Formula	$C_{33}H_{54}O_5$
Temperature (K)	296.0
Formula weight	530.76
Crystal system	Monoclinic
Space group	C_2
a, b, c (Å)	31.9922, 9.9421, 10.3358
α, β, γ (°)	90.00, 93.758(3), 90.00
Volume (Å³)	3280.4(2)
Z	4
ρ_{calc} (mg, mm³)	1.075
$F(000)$	1168
Reflections collected	7423
Final R indices (all data)	$R_1 = 0.0756$, $wR_2 = 0.1692$

Table 2
Polymerization, GPC, DSC and TGA results of polymers.

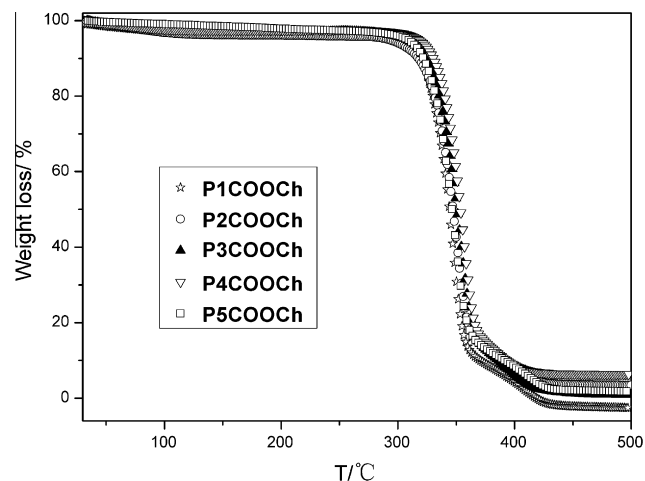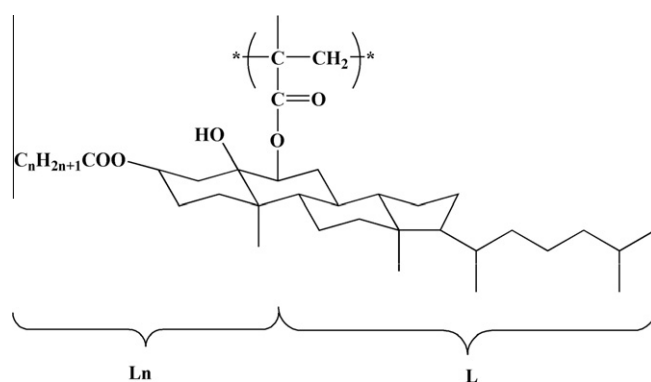| Polymers	Yield[a] (%)	M_n[b]	M_w[b]	D[b]	T_g (°C)	T_{d1}[c] (°C)	T_{d2}[d] (°C)
P₁COOCh	61	5880	8420	1.43	222.5	329.4	347.3
P₂COOCh	57	3850	5180	1.35	180.1	330.5	349.9
P₃COOCh	54	3380	4660	1.38	178.6	333.3	353.6
P₄COOCh	49	3320	4460	1.34	175.6	337.4	356.1
P₅COOCh	42	3200	4380	1.37	173.3	342.7	360.2

[a] Yield was calculated after twice molecular weight fractionation through dissolution–precipitation.
[b] Obtained from a Waters 2410 GPC instrument, linear PS as standards.
[c,d] The temperature at which starting weight loss and maximum weight loss of the sample was reached from TGA under nitrogen atmosphere at 10 °C/min.

Fig. 3. DSC thermograms of the polymers.

Fig. 4. TGA thermograms of the polymers.

Scheme 3. The structure diagram of the corresponding polymers.

Table 3
The length of L_n with different carbon number through molecular modeling.

Polymers	Length of L_n (Å)
P₁COOCh	5.252
P₂COOCh	5.959
P₃COOCh	7.094
P₄COOCh	8.034
P₅COOCh	9.249

Table 2. For all the polymers, glass transitions can be observed clearly. The temperature of glass transition (T_g) of polymers decreased slightly from 222.5 to 173.3 °C with increase of carbon number (n) in alkyl chains on C3 position from 1 to 5. Because the alkyl chains are flexible, more carbon numbers offer more flexibility for polymer domains. That is to say, the existence of flexible side group is helpful for the movement of polymer chain. Because C₁COOCh has relatively smaller steric hindrance, after polymerizing, higher molecular weight with a higher T_g was obtained. There are not other thermal transitions displayed in the DSC thermograms, which tell us that all the polymers are amorphous rather than crystalline. Even under POM, we cannot observe any liquid crystal phase transition, which indicated that all the polymers did not behave liquid crystal properties due to the damage of dou-

ble bond on cholesterol. In cholesterol esters, double bond offers rigidity to the mesogen units, however, the ring-opening reaction destroyed the rigidity, and then no mesogen units exist to be free orientation. Compared to polymers with etherification on C3—OH [15], polymers with esterification have a higher T_g, which shows us that ester bond has indeed more rigidity than ether bond.

Fig. 4 shows TGA thermograms of the polymers, and the TGA data is listed in Table 2. It exhibited that the initial weight loss temperatures were greater than 329 °C for all the polymers, indicating that they behave excellent thermal stability. In addition, as the length of side chain at C3 position increases gradually, the degradation temperature presents an increasing trend. Because with the increase of carbon number, the symmetry of the side chain increases and the steric hindrance also increases. The linkage point is gradually moving to the middle of the side chain, more steric hindrance provides more thermal stabilities of polymers. The final decomposition temperature can reach higher than 400 °C,

indicating that the polymers have good thermal properties and can be potentially used as heat-resisting materials.

In order to better understand the alkyl length influence on T_g and thermal properties, simply molecular modeling was used to describe the molecular structure. We suppose that all the alkyl chains connected on C3 position are straight line arrangement. The side chain was divided into two parts from C6 position, as shown in Scheme 3, the length of left part L_n is changeable with the alkyl length changes, and the length of right part L is fixed. Here L is 13.237 Å, while the length of the other side is L_n (n = 1–5) presenting in Table 3. Seen from the structure diagram of molecule and Table 3, the distance from C6 to the terminal group of alkyl chain becomes increasingly large with the increase of carbon number. And the result implies that the side chain gets much better symmetry. The improvement of side chain symmetry provides more regular arrangement and high stereo-tacticity in polymers.

4. Conclusion

A series of novel cholesteryl monomers with different ester chain length on C3 position and their corresponding polymers were prepared. The polymerizable groups are connected in the lateral part of cholesterol skeleton. After polymerization, the structures of all the monomers and polymers were characterized by ^{1}H NMR, FTIR. And all the polymers were characterized by GPC, DSC, POM, and TGA. Though all the polymers were not observed having liquid crystal properties, high temperature of T_g and degradation temperature was detected. In addition, the T_g of the polymers decreases, while the degradation temperature increases with increase of the chain length. On one hand, the side chain is flexible, and it is helpful for chain movement. Longer side chain offer more flexibility to the molecular chain, so the T_g decreases. On the other hand, the symmetry of the side chain is helpful for improving the steric hindrance and then the degradation temperature increases. The maximum weight loss temperature is higher than 350 °C. And these kinds of polymers can be used as heat-resisting materials due to the thermal stabilities.

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