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Synthesis and characterisation of new types of side chain cholesteryl polymers

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ABSTRACT

A series of cholesterol derivatives have been synthesised via the alkylation reaction of the 3-hydroxyl group with the aliphatic bromide compounds with different chain lengths, namely 3β-alkyloxy-cholesterol. The double bond between the C5 and C6 positions in these cholesterol derivatives was oxidised into epoxy, followed by an epoxy-ring-opening reaction with the treatment with acrylic acid, resulting in a series of 3β-alkyloxy-5α-hydroxy-6β-acryloyloxycholesterol, C_nOCh (n = 1, 2, 4, 6, 8, 10, 12), The acrylate group is connected to the C6 position, which is confirmed by the single crystal structure analysis. The corresponding polymers, PC_nOCh, were prepared via free radical polymerisation. The structure of monomers and the resulting polymers were characterised with nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR) and gel permeation chromatography (GPC). The thermal properties of PC_nOCh were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). To determine the secondary structure of polymers, circular dichroism (CD) spectra were performed. It was found that not all monomers produce high-molecular-weight polymers because of steric hindrance. However, all polymers have a helical structure, which can be enhanced by increasing the alkoxy chain length. In addition, increasing the alkoxy chain length decreases the glass transition temperature and increases the decomposition temperature of the polymers.

Cholesteryl derivatives and some polymers bearing cholesterol have attracted considerable interest for their unique optical properties, including selective reflection of light, thermochromism and circular dichromism [1–5]. Cholesterol has the nature of a mesogen, which usually makes polymers have liquid crystalline properties [6–11].

Almost all of those cholesteryl polymers were prepared using the hydroxyl group at C3 position of cholesterol with or without suitable flexible spacers. However, in the cholesterol skeleton, except for the hydroxyl group on C3, there still exists a double bond between C5 and C6. A suitable method can be used to functionalise the C6 position; for example, one can introduce a hydroxyl group on the C6 position, and then a suitable polymerisable group can be introduced to yield a series of new monomers and their corresponding polymers. To the best of our knowledge, there is no such reported research.

To produce the above-mentioned new derivatives starting from the C6 position, the hydroxyl group at C3 is first protected by different lengths of alkoxy groups by the etherification method, and then the double bond is epoxided. Next, acrylic acid to open it and a series of new acrylate derivatives of steroid molecules is obtained, namely 3β-alkylxoy-5α-hydroxy-6β-acryloyloxycholesterol, C_nOCh (n = 1, 2, 4, 6, 8, 10, 12).

Because the polymerisable groups are connected on the lateral side of the cholesterol structure, the steric hindrance is quite large; thus, these monomers are quite like the mesogen-jacketed monomers in which the polymerisable groups are connected to the mesogenic units at their lateral parts with or without short flexible spacers, as reported by Zhou et al. [12–15]. If the cholesteryl skeleton has enough rigidity, it can be regarded as a mesogen and the corresponding polymers may have mesogen-jacketed properties; if not, the polymers, at least, have a helical structure because of the large side groups bearing on the main chain.

1. Experimental

1.1. Materials

Cholesterol, sodium hydrogen, idomethane (MeI), bromoethane, *n*-butyl bromide, bromohexane, 1-bromooctane, 1-bromodecane, 1-bromododecane, potassium iodide, benzoyl peroxide, chlorobenzene, acrylic acid, potassium iodide, tetrahydrofuran (THF), dichloromethane and 3-chloroperoxybenzoic acid (mCPBA) were purchased from Guanghua Chemical Co. of China. THF (analytical reagent; Guanghua Chemical Reagents) was purified by refluxing over sodium and was freshly distilled before use. Benzoyl peroxide (BPO) was purified by recrystallisation from

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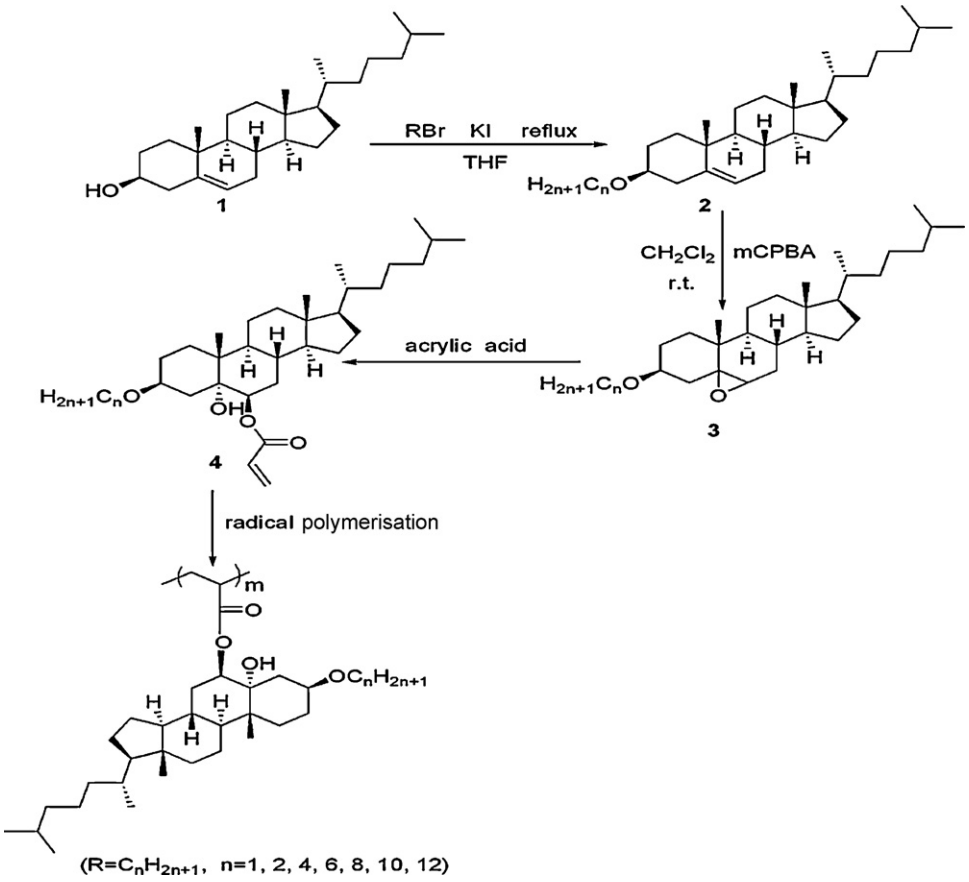

Scheme 1. Synthetic routes for monomers and polymers.

methanol and dichloromethane. Chlorobenzene was washed with H_2SO_4, $NaHCO_3$ and distilled water separately, refluxed over CaH_2 and distilled before use. Other solvents were used as received.

1.2. Measurements

Nuclear magnetic resonance (NMR) spectra were recorded at room temperature on BrukerAMx-400 operating at 400 MHz for ^1H in deuterochloroform. Elemental analyses were determined on a Carlo ERBA 1106 instrument. Differential scanning calorimetry (DSC) was carried out on a thermal analysis (TA) DSC-Q30 in nitrogen at a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was performed from 30 to 500 °C at a heating rate of 10 °C min^{-1} on a TA TGA-DSC Q600 thermogravimetric analyser under nitrogen atmosphere. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and the polydispersity (M_w/M_n) of polymers was estimated by gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump. THF was used as the eluent at a flow rate of 1.0 ml min^{-1} at 25 °C. The calibrating curve was obtained against a series of polystyrene standards. Circular dichroism (CD) spectra were recorded on JASCO J-810. The sample solution was thermostatted at the desired temperature with a Julabo F25-Me controller. The light path length of the quartz cell used was 10 mm. The concentration was 2 g l^{-1}.

1.3. Monomer synthesis

The synthetic route for the preparation of the monomers is shown in Scheme 1.

1.3.1. Cholesteryl 3β-alkyloxy

A typical synthesis method is shown as follows: 5.00 g (12.95 mmol) of cholesterol was dissolved in 40 ml of freshly distilled THF, 0.47 g (19.42 mmol) NaH and 1.33 g (14.09 mmol) of MeI were added. The reaction mixture was kept at 60 °C for 24 h; then the reaction mixture was quenched with 40 ml of distilled water and extracted with 10 ml petroleum ether. The organic layer was washed with H_2O, dried (anhydrous $MgSO_4$) and evaporated to give a residue. The product was obtained by recrystallisation from petroleum ether.

Cholesteryl 3β-methoxy: yield: 96.80%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.68 (s, 3H), 0.85–2.37 (m, 43H), 3.02–3.06 (m, 1H, C3–H), 3.35 (s, 3H, $-OCH_3$), 5.34–5.36 (t, 1H, C6–H). FTIR (KBr) ν = 2934.09 cm^{-1} (stretching of $-CH_3$), 2866.50 cm^{-1} (stretching of $-CH_2-$), 1636.94 cm^{-1} (stretching of =CH–), 1190.59 cm^{-1} (stretching of $-O-CH_3$).

Cholesteryl 3β-ethoxy: yield: 54.30%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.68 (s, 3H), 0.85–2.40 (m, 43H), 3.15–3.19 (m, 1H, C3–H), 3.50–3.55 (m, 2H, $-O-CH_2-$), 5.33–5.35 (t, 1H, C6–H). FTIR (KBr) ν = 2931.84 cm^{-1} (stretching of $-CH_3$), 2855.19 cm^{-1} (stretching of $-CH_2-$), 1658.20 cm^{-1} (stretching of =CH–), 1108.93 cm^{-1} (stretching of $-O-CH_3$).

Cholesteryl 3β-butoxy: yield: 42.80%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.68 (s, 3H), 0.87–2.40 (m, 47H), 3.09–3.16 (m, 1H, C3–H), 3.44–3.48 (m, 2H, $-O-CH_2-$), 5.33–5.35 (t, 1H, C6–H). FTIR (KBr) ν = 2931.66 cm^{-1} (stretching of $-CH_3$), 2852.66 cm^{-1} (stretching of $-CH_2-$), 1108.32 cm^{-1} (stretching of $-O-CH_3$).

Cholesteryl 3β-hexyloxy: yield: 60.20%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.67 (s, 3H), 0.85–2.41 (m, 51H), 3.00–3.20 (m, 1H, C3–H), 3.42–3.46 (m, 2H, $-O-CH_2$), 5.33–5.34 (t, 1H, C6–H). FTIR

(KBr) ν = 2934.11 cm^{-1} (stretching of $-CH_3$), 2846.05 cm^{-1} (stretching of $-CH_2-$), 1107.02 cm^{-1} (stretching of $-O-CH_3$).

Cholesteryl 3β-octyloxy: yield: 66.90%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.68 (s, 3H), 0.85–2.40 (m, 59H), 3.00–3.15 (m, 1H, C3–H), 3.42–3.46 (m, 2H, $-O-CH_2-$), 5.33–5.34 (t, 1H, C6–H). FTIR (KBr) ν = 2929.75 cm^{-1} (stretching of $-CH_3$), 2852.25 cm^{-1} (stretching of $-CH_2-$), 1106.25 cm^{-1} (stretching of $-O-CH_3$).

Cholesteryl 3β-decyloxy: yield: 64.50%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.68 (s, 3H), 0.85–2.40 (m, 63H), 3.00–3.20 (m, 1H, C3–OH), 3.42–3.46 (m, 2H, $-O-CH_2-$), 5.33–5.35 (t, 1H, C6–OH). FTIR (KBr) ν = 2931.15 cm^{-1} (stretching of $-CH_3$), 2852.12 cm^{-1} (stretching of $-CH_2-$), 1108.82 cm^{-1} (stretching of $-O-CH_3$).

Cholesteryl 3β-dodecyloxy: yield: 29.00%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.68 (s, 3H), 0.85–2.40 (m, 67H), 3.00–3.20 (m, 1H, C3–H), 3.42–3.46 (m, 2H, $-O-CH_2-$), 5.33–5.35 (t, 1H, C6–H). FTIR (KBr) ν = 2930.71 cm^{-1} (stretching of $-CH_3$), 2851.942852.12 cm^{-1} (stretching of $-CH_2-$), 1108.92 cm^{-1} (stretching of $-O-CH_3$).

1.3.2. Cholesteryl 3β-alkyloxy-5,6-epoxy

Cholesteryl 3β-alkyloxy-5,6-epoxy was synthesised by epoxiding the double bond of cholestryl 3β-alkyloxy using mCPBA as reported in the literature [12].

Cholesteryl 3β-methoxy-5α,6α-epoxy: yield: 86.2%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.60 (s, 3H), 0.84–2.40 (m, 41H), 2.88–2.90 (m, 1H, C6–H), 3.32 (s, 3H, $-OCH_3$), 3.38–3.43 (m, 1H, C3–H). FTIR (KBr) ν = 2948.25 cm^{-1} (stretching of $-CH_3$), 2866.68 cm^{-1} (stretching of $-CH_2-$), 1104.72 cm^{-1} (stretching of $-O-CH_3$).

Cholesteryl 3β-ethoxy-5α,6α-epoxy: yield 87.8%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.60 (s, 3H), 0.63–2.10 (m, 43H), 2.88–2.90 (m, 1H, C6–H), 3.48–3.51 (m, 3H, $-OCH_2-$ and C3–H). FTIR (KBr) ν = 2946.17 cm^{-1} (stretching of $-CH_3$), 2868.68 cm^{-1} (stretching of $-CH_2-$), 1112.43 cm^{-1} (stretching of $-O-CH_3$).

Cholesteryl 3β-butoxy-5α,6α-epoxy: yield: 66.1%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.61 (s, 3H), 0.85–2.10 (m, 47H), 2.88–2.90 (m, 1H, C6–H), 3.38–3.53 (m, 3H, $-OCH_2-$ and C3–H). IR (KBr) ν = 2934.42 cm^{-1} (stretching of $-CH_3$), 2867.54 cm^{-1} (stretching of $-CH_2-$), 1104.18 cm^{-1} (stretching of $-O-CH_3$).

Cholesteryl 3β-hexyloxy-5α,6α-epoxy: yield: 78.7%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.61 (s, 3H), 0.86–2.04 (m, 51H), 2.88–2.89 (m, 1H, C6–H), 3.41–3.46 (m, 3H, $-CH_2-O-$, C3–H). FTIR (KBr) ν = 2933.24 cm^{-1} (stretching of $-CH_3$), 2866.95 cm^{-1} (stretching of $-CH_2-$), 1109.42 cm^{-1} (stretching of –O–).

Cholesteryl 3β-octyloxy-5α,6α-epoxy: yield: 80.6%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.60 (s, 3H), 0.85–2.10 (m, 55H), 2.88–2.89 (m, 1H, C6–H), 3.39–3.51 (m, 3H, $-CH_2-O-$ and C3–H). FTIR (KBr) ν = 2931.34 cm^{-1} (stretching of $-CH_3$), 2867.32 cm^{-1} (stretching of $-CH_2-$), 1115.42 cm^{-1} (stretching of –O–).

Cholesteryl 3β-decyloxy-5α,6α-epoxy: yield: 82.5%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.61 (s, 3H), 0.85–2.10 (m, 59H), 2.88–2.89 (m, 1H, C6–H), 3.37–3.53 (m, 3H, $-O-CH_2-$ and C3–H). FTIR (KBr) ν = 2929.35 cm^{-1} (stretching of $-CH_3$), 2852.50 cm^{-1} (stretching of $-CH_2-$), 1466.64, 1376.14, 1113.64 cm^{-1} (stretching of –O–).

Cholesteryl 3β-dodecyloxy-5α,6α-epoxy: yield: 64.3%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.60 (s, 3H), 0.85–2.10 (m, 63H), 2.88–2.89 (m, 1H, C6–H), 3.41–3.45 (m, 3H, $-O-CH_2-$ and C3–H). FTIR (KBr) ν = 2928.32 cm^{-1} (stretching of $-CH_3$), 2852.63 cm^{-1} (stretching of $-CH_2-$), 1110.62 cm^{-1} (stretching of –O–).

1.3.3. Cholesteryl 3β-alkyloxy-5α-hydroxy-6β-acryloyloxy

A total of 1.20 mmol of epoxy compound was dissolved in 10 ml acrylic acid. After vigorous stirring at 60 °C for 48 h, the mixture was quenched with saturated $NaHCO_3$, and the resulting solution was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative column chromatography (silica gel, eluent: ethyl acetate/petroleum ether = 1:4), and cholesteryl 3β-alkyloxy-5α-hydroxy-6β-acryloyloxy was obtained.

Cholesteryl 3β-methoxy-5α-hydroxy-6β-acryloyloxy C_1OCh: yield: 63.2%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.67 (s, 3H), 0.84–1.98 (m, 42H), 3.31 (s, 3H, $-OCH_3$), 3.55–3.62 (m, 1H, C3–H), 4.79 (s, 1H, C6–H), 5.82–5.86 (m, 1H, =CH–), 6.05–6.14 (q, 1H, =CH), 6.34–6.40 (q, 1H, =CH). FTIR (KBr) ν = 3454.26 cm^{-1} (stretching of C6–OH), 2943.31 cm^{-1} (stretching of $-CH_3$), 2866.79 cm^{-1} (stretching of $-CH_2-$), 1712.51 cm^{-1} (stretching of –CO–), 1613.94 cm^{-1} (stretching of $-CH=CH_2$), 1100.36 cm^{-1} (stretching of –O–).

Cholesteryl 3β-ethoxy-5α-hydroxy-6β-acryloyloxy C_2OCh: yield: 62.8%. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.67 (s, 3H), 0.85–2.10 (m, 44H), 3.45–3.54 (m, 2H, $-OCH_2-$), 3.66–3.71 (m, 1H, C3–H), 4.78 (s, 1H, C6–H), 5.83–5.85 (d, 1H, =CH–), 6.10–6.13 (d, 1H, =CH), 6.35-6.40 (d, 1H, =CH). FTIR (KBr) ν = 3489.87 cm^{-1} (stretching of C6–OH), 2943.55 cm^{-1} (stretching of $-CH_3$), 2867.67 cm^{-1} (stretching of $-CH_2-$), 1710.53 cm^{-1} (stretching of –CO–), 1613.26 cm^{-1} (stretching of $-CH=CH_2$), 1106.60 cm^{-1} (stretching of –O–).

Cholesteryl 3β-butoxy-5α-hydroxy-6β-acryloyloxy C_4OCh: yield: 63.5%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.67 (s, 3H), 0.85–2.02 (m, 53H), 3.41–3.45 (m, 2H, $-OCH_2-$), 4.77 (s, 1H, C6–H), 5.83–5.85 (d, 1H, =CH–), 6.06–6.13 (d, 1H, =CH), 6.35–6.40 (d, 1H, =CH). FTIR (KBr) ν = 3501.77 cm^{-1} (stretching of C6–OH), 2942.97 cm^{-1} (stretching of $-CH_3$), 2868.28 cm^{-1} (stretching of $-CH_2-$), 1712.23 cm^{-1} (stretching of –CO–), 1626.01 cm^{-1} (stretching of $-CH=CH_2$), 1103.94 cm^{-1} (stretching of –O–).

Cholesteryl 3β-hexyloxy-5α-hydroxy-6β-acryloyloxy C_6OCh: yield: 55.0%. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.67 (s, 3H), 0.85–2.20 (m, 48H), 3.40–3.44 (m, 1H, C3–H and $-OCH_2-$), 4.78 (s, 1H, C6–H), 5.82–5.86 (m, 1H, =CH–), 6.05–6.14 (q, 1H, =CH), 6.34–6.40 (q, 1H, =CH). FTIR (KBr) ν = 3475.11 cm^{-1} (stretching of C6–OH), 2936.83 cm^{-1} (stretching of $-CH_3$), 2867.91 cm^{-1} (stretching of $-CH_2-$), 1706.27 cm^{-1} (stretching of –CO–), 1614.00 cm^{-1} (stretching of $-CH=CH_2$), 1102.93 cm^{-1} (stretching of –O–).

Cholesteryl 3β-octyloxy-5α-hydroxy-6β-acryloyloxy C_8OCh: yield: 69.3%. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.60 (s, 3H), 0.85–2.10 (m, 55H), 3.45–3.53 (m, 3H, C3–H and $-OCH_2-$), 4.75 (s, 1H, C6–H), 5.81–5.86 (m, 1H, =CH–), 6.05–6.12 (q, 1H, =CH), 6.31–6.40 (d, 1H, =CH). FTIR (KBr) ν = 3462.18 cm^{-1} (stretching of C6–OH), 2932.28 cm^{-1} (stretching of $-CH_3$), 2867.33 cm^{-1} (stretching of $-CH_2-$), 1711.49 cm^{-1} (stretching of –CO–), 1622.89 cm^{-1} (stretching of $-CH=CH_2$), 1115.24 cm^{-1} (stretching of –O–).

Cholesteryl 3β-decyloxy-5α-hydroxy-6β-acryloyloxy C_{10}OCh: yield: 58.13. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.61 (s, 3H), 0.85–2.10 (m, 59H), 3.37–3.53 (m, 3H, C3–H and $-OCH_2-$), 3.38–3.57 (m, 3H), 4.74 (s, 1H, C6–H), 5.84–5.86 (m, 1H, =CH–), 6.05–6.13 (q, 1H, =CH), 6.35–6.40 (d, 1H, =CH). FTIR (KBr) ν = 3456.54 cm^{-1} (stretching of C6–OH), 2928.41 cm^{-1} (stretching of $-CH_3$), 2852.74 cm^{-1} (stretching of $-CH_2-$), 1709.49 cm^{-1} (stretching of –CO–), 1624.60 cm^{-1} (stretching of $-CH=CH_2$), 1113.46 cm^{-1} (stretching of –O–).

Cholesteryl 3β-dodecyloxy-5α-hydroxy-6β-acryloyloxy C_{12}OCh: yield: 82.1%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.67 (s, 3H), 0.85–2.20 (m, 57H), 3.38–3.66 (m, 3H, C3–H and $-OCH_2-$), 4.77 (s, 1H, C6–H), 5.83–5.86 (d, 1H, =CH–), 6.06–6.13 (q, 1H, =CH), 6.36–6.40 (d, 1H, =CH). FTIR (KBr) ν = 3522.95 cm^{-1} (stretching of C6–OH), 2925.37 cm^{-1} (stretching of $-CH_3$), 2851.75 cm^{-1} (stretching of $-CH_2-$), 1712.48 cm^{-1} (stretching of –CO–), 1630.01 cm^{-1} (stretching of $-CH=CH_2$), 1105.97 cm^{-1} (stretching of –O–).

1.4. Polymer synthesis

All the corresponding polymers were prepared by free radical polymerisation in chlorobenzene. A representative procedure is as

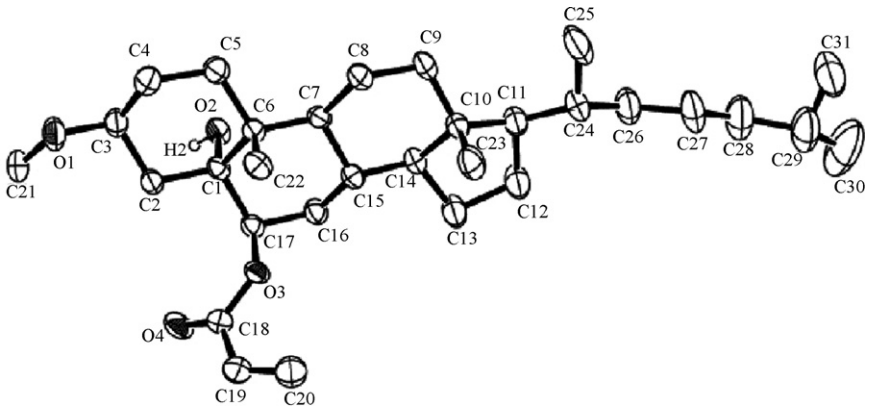

Fig. 1. The crystal structure of 3β-alkoxy-5α-hydroxy-6β-acrylatecholestane.

follows: C_1OCh (0.20 g, 0.41 mmol), BPO (5.00 mg, 0.020 mmol) and chlorobenzene (0.8 g) were added to a reaction tube. After three freeze–pump–thaw cycles, the tube was sealed under vacuum and placed in an oil bath thermostatted at 90 °C for 48 h. After being cooled to room temperature, the tube was opened and the solution was dropped into cold methanol (10 ml). White solids precipitated and were filtered and then dried under vacuum for 24 h.

2. Results and discussion

2.1. Synthesis

The cholesteryl monomers, cholesteryl 3β-alkyloxy-5α-hydroxy-6β-acryloyloxy, were prepared though a three-step synthetic route as shown in Scheme 1. The cholesterol was etherised by alkyl halides with different chain lengths. To introduce a polymerisable group on position C6, the double bond was converted to two-diol on position C5 and position C6 by oxidation using HCOOH and H_2O_2. The hydroxyl group at position C6 can be connected to a polymerisable group by esterification under DCC and DMAP as catalysts [16]. It was found that the reactivity of the hydroxyl group on C6 is quite low resulting in low yield. As a result of larger steric hindrance at the C5 position, the reactivity of the hydroxyl group on C5 is lower than that on C6.

To improve the reactivity of C5 and C6 of cholesterol, the epoxidation method was adopted and then the epoxide was opened using suitable reagents with carboxyl groups, such as acrylic acid. Cholesteryl 3β-alkyloxy-5,6-epoxy was obtained in the presence of 3-chloroperoxybenzoic acid in dry CH_2Cl_2 under nitrogen atmosphere. The target monomers were prepared by opening the epoxy ring by an excess amount of acrylic acid at 60 °C without any catalyst. ^{1}H NMR, and elemental analysis confirmed the expected structures. The synthetic route developed in the present work is quite efficient, and therefore is more convenient for exploring new cholesterol derivatives.

2.2. The space structure of C_1OCh

The double bond in the cholesterol structure provides rigidity, but little is known about the space structure without a double bond..To determine this, cholesteryl 3β-dodecyloxy-5α-hydroxy-6β-acryloyoxy was cultivated to a single crystal, and the structure was confirmed by X-ray diffraction (XRD) (seen in Fig. 1). It was found that C5–OH and C6–O–CO– are axial bonds, but the direction is opposite, and the C3–O–R is in the same direction with C6–O–CO–. The detail data is: space group: 21; unit space cell: a = 5.791 Å, b = 9.336 Å, c = 21.524 Å; density (calculated) 1.072 mg m^{-3}; absorption coefficient: 0.069 mm^{-1}; F(0 0 0) = 540; crystal size: 0.48 mm × 0.46 mm × 0.44 mm; reflection collected: 3600.

2.3. Polymerisation

The free radical polymerisations of monomers were carried out in chlorobenzene at 90 °C using BPO as the initiator. The polymeriszation results are summarised in Table 1. All the monomers can be polymerised 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 polymerisation. The polymers obtained are white solids that have good solubility in many common organic solvents, such as THF, chloroform, dichloromethane, toluene, dimethylsulphoxide (DMSO) and ethyl acetate.

The chemical structures of C_nOCh and PC$_n$OCh were confirmed by a combination of analytical techniques, for example, infrared (IR), ^{1}H NMR and elemental analysis. Fig. 2 shows the ^{1}H NMR spectra of C_1OCh and PC$_1$OCh in $CDCl_3$. The characteristic three peaks at 5.8–6.4 ppm of vinyl groups in the ^{1}H NMR spectrum of monomer disappeared after being polymerised and those of the –CH–CH$_2$–, polymer backbone were observed instead, indicating the formation of the polymers. The results of polymerisation are summarised in Table 1. The sharp characteristic signals of C_1OCh became broad after polymerisation (Fig. 2(b)) due to the limited mobility of protons.

2.4. Thermal properties

DSC results clearly show that the structure of PC$_n$OCh is amorphous rather than crystalline. As Fig. 3 shows, no crystal peak can be observed, only glass transition temperature presents at the tem-

Table 1
Polymerisation results and cholesteryl monomers.

Polymers[a]	Yield (%)	M_n[b] (×10^{-3})	M_w (×10^{-3})	PDI[b]	T_g (°C)	T_d[c] (°C)
PC$_1$OCh	90	5.19	10.00	1.93	179.7	334.5
PC$_2$OCh	84	4.71	6.83	1.11	173.3	339.5
PC$_4$OCh	79	4.69	6.74	1.44	152.2	343.6
PC$_6$OCh	63	4.32	6.87	1.59	119.2	352.1
PC$_8$OCh	84	4.05	6.27	1.55	112.2	345.2
PC$_{10}$OCh	77	4.41	6.57	1.49	101.2	353.6
PC$_{12}$OCh	80	4.85	7.15	1.48	96.7	355.8

[a] PC$_n$OCh are products obtained by polymerising the corresponding monomer C_nOCh, and n represents the number of C in alky chain.
[b] PDI: polydisperity index, expressed as M_w/M_n, where M_n is the number average weight, and M_w is weight average molecular weight.
[c] T_d: the degradation temperature.

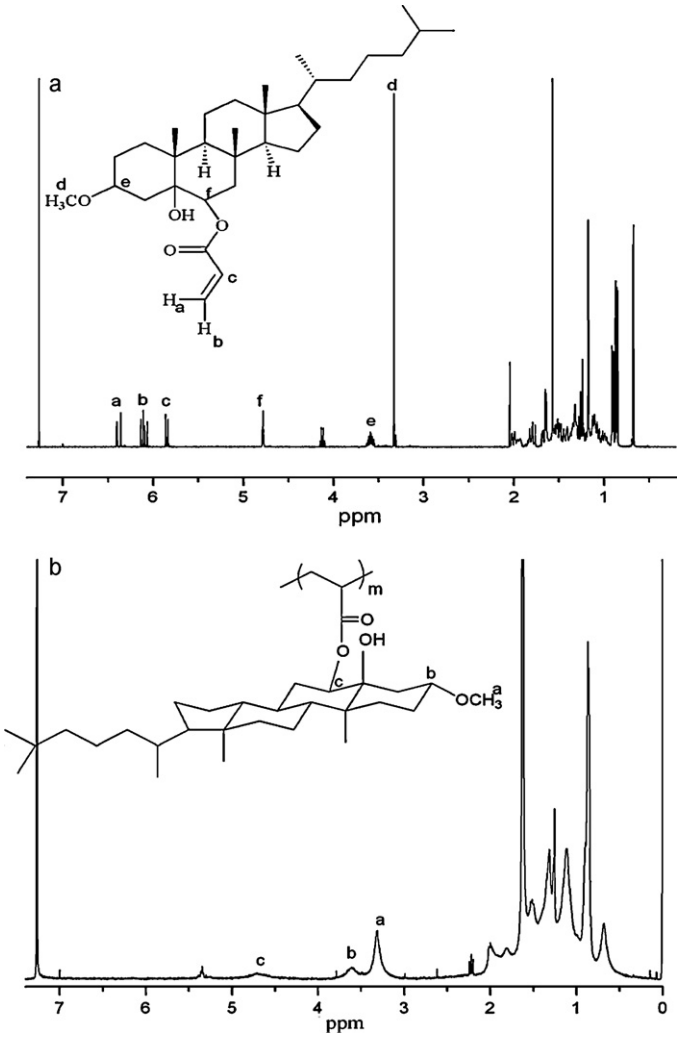

Fig. 2. ^{1}H NMR spectra of C_1OCh in $CDCl_3$ (a) and PC_1Ch in $CDCl_3$ (b), respectively.

perature region from 20 to 250 °C and the number of carbon atoms in alky chains on C3 position has an obvious effect on T_g. When the carbon number (n) increases from 1 to 12, T_g decreases from about 179.7 to 96.7 °C (Table 1). This is because the longer alky chains

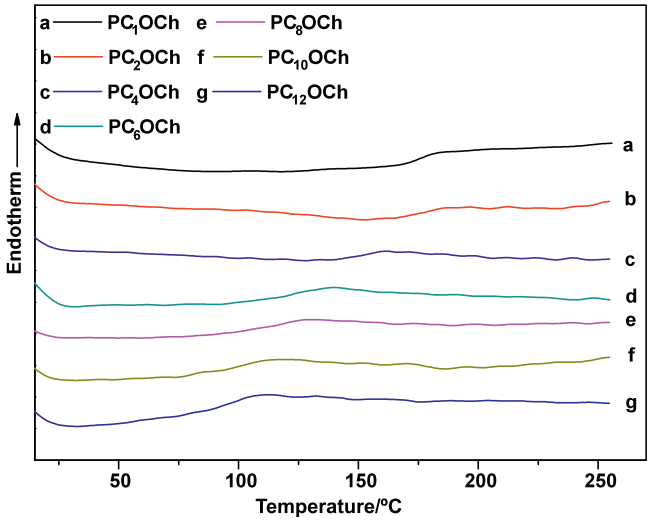

Fig. 3. DSC thermograms of PC_nOCh observed from the second scanning.

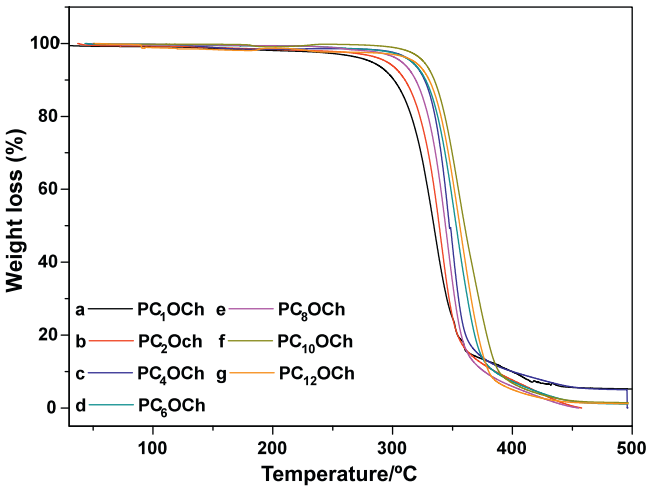

Fig. 4. TGA thermograms of PC_nOCh.

bring about more free volume, which promotes the flexibility of lateral structure, leading to the relatively low T_g.

TGA was performed to study the thermal stability property of the synthesised polymers. Fig. 4 shows that all polymers have high thermal stability, and the main mass loss occurs at a temperature region from approximately 300–400 °C, although they do not have high molecular weight. In addition, generally speaking, the degradation temperature, as listed in Table 1, increases with increasing carbon number. When the carbon number increases, the symmetry of the side group increases and the steric hindrance also increases. These characteristics are helpful to improve the thermal stability of polymers.

2.5. CD spectra

CD spectroscopy was used to characterise the chiroptical properties of monomers C_nOCh and polymers PC_nOCh. Figs. 5 and 6 show the CD spectra of C_nOCh and PC_nOCh in THF, respectively. The CD spectra of C_1OCh and C_6OCh exhibit similar negative and positive Cotton effects at 196 and 203 nm, C_2OCh and C_{10}OCh exhibit resemble positive Cotton effects at 198 nm, C_4OCh possess a strong negative Cotton effect at 202 nm and C_8OCh and C_{12}OCh represent negative and positive absorbents, respectively. From the above results, the C_3 alkyl chain has an obvious relationship with the CD spectroscopy of C_nOCh.

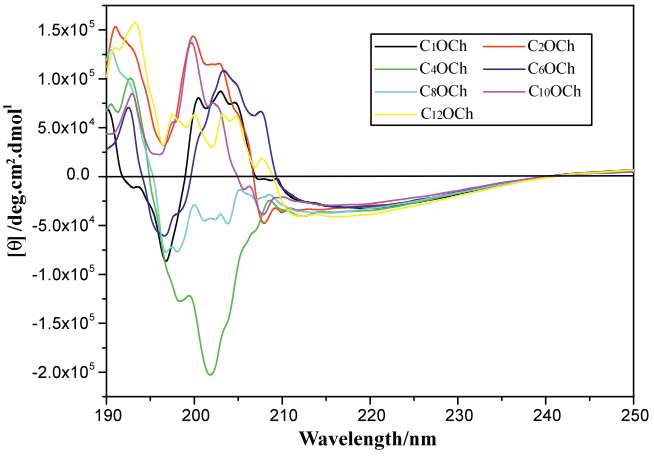

Fig. 5. Comparison of the CD spectra of model monomers C_nOCh (recorded at 20 °C in THF), [θ] = molar ellipticity with repeating unit: deg cm^2 dmol^{-1}.

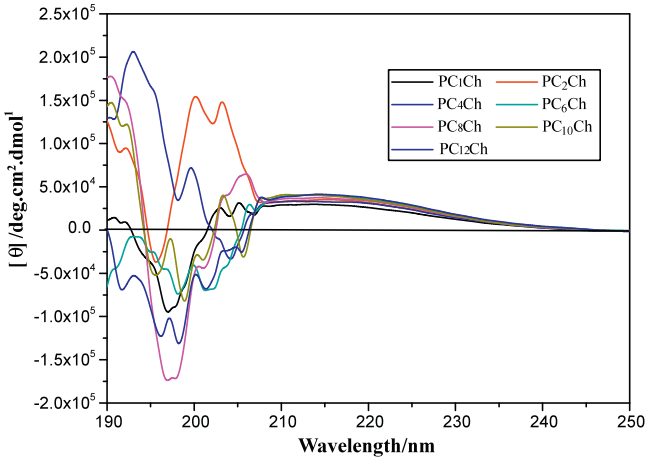

Fig. 6. Comparison of the CD spectra of model monomers PC_nOCh (recorded at 20 °C in THF), [θ] = molar ellipticity with repeating unit: deg cm^2 dmol^{-1}.

Compared to these monomers, the corresponding polymers behave differently. PC_1OCh exhibits a negative Cotton effect at 198 nm, PC_2OCh shows a negligible negative and strong positive Cotton effect at 198 nm and 202 nm and PC_4OCh has a positive Cotton effect at 193 nm. With the length of the alkyl chain, PC_6OCh–$PC_{12}OCh$ all exhibit a negative Cotton effect at 196 nm and 198 nm, which illuminate the macromolecular conformations of proteins and helical polyester by the incorporation of rigid cholesterol into the chains of polymers. Due to the asymmetrical microenvironment of helical main chain, chiral side groups show strong optical activity of n–n^* transition. Therefore, the presence of Cotton effects of PC_nOCh (n = 6–12) was consistent with a chiral secondary structure, which positioned cholesterol groups in a skewed way. For a linear polymer chain such as PC_nOCh (n = 6–12), the reasonable chiral secondary structure is a helical conformation with one prevailing screw sense.

Further, we can explain the helical confirmation of the main chain. The space hindrance on the main chain increases when the C3-alkyl of cholesterol increases and for an effective array of side groups, the side groups must adopt optimum conformation.

3. Conclusion

In this article, a series of new monomers and corresponding polymers starting from cholesterol were synthesised. All the polymers are amorphous and thermally stable. Their T_g values decrease with increasing alkyl chain lengths, and the degradation temperature increases with the length of the alkyl chain. The helical conformations of the polymers are determined through CD spectra, and this effect is pronounced when the alkyl chain lengths are longer.

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