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Polymer 46 (2005) 7266–7272
polymer
www.elsevier.com/locate/polymer

Effect of side chain structure on the liquid crystalline properties of polymers bearing cholesterol, dihydrocholesterol and bile acid pendant groups

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Received 27 March 2005; received in revised form 25 May 2005; accepted 13 June 2005
Available online 11 July 2005

Abstract

Four methacrylate derivatives of steroid molecules, namely cholic acid methyl ester, lithocholic acid methyl ester, cholesterol and dihydrocholesterol, were synthesized. A 10-carbon spacer separates the rigid core and the polymerizable methacrylate group. These monomers and their corresponding polymers were characterized for their liquid crystalline properties by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. It was found that only the compounds bearing the planar cholesterol-based moieties, and not those bearing the esterified bile acid groups, possess liquid crystalline phases. A detailed X-ray study showed that the dihydrocholesterol polymer possesses the same two mesophases as the cholesterol polymer, but with reduced thermal stability.

Keywords: Bile acids; Cholesterol; Dihydrocholesterol

1. Introduction

Cholesterol and bile acids are all biological molecules belonging to the family of steroid compounds. Cholic acid and lithocholic acid are commonly occurring bile acids biosynthesized from cholesterol in the liver of mammals. The transformation from cholesterol to bile acids results in two major structural changes. The first is the hydrogenation of the double bond on cholesterol and the second is a conformational flip of ring A from the 5α- to the 5β-position, with the simultaneous addition of one or more hydroxyl groups to the steroid skeleton. In addition, C24 is converted from a saturated alkyl group to a carboxylic acid group.

Liquid crystalline (LC) molecules [1–3] and side chain polymers [4–9] based on the cholesterol moiety have previously been documented. Since the structure of lithocholic acid and cholic acid is similar to that of cholesterol, it is of interest to investigate whether or not they may also act as mesogenic groups. Polymers from the methacrylamide and methacrylate derivatives of bile acids have been made and their properties investigated [10–14], since some may be useful in applications such as drug delivery, asymmetric synthesis, molecular recognition and artificial receptors [15–18]. We have previously synthesized esterified bile acid-containing monomers and corresponding polymers with two and six carbon spacers but did not observe any LC properties [19]. This may be attributed to one or a combination of the following factors: (a) the spacer being too short to allow sufficient decoupling of the rigid group from the polymerizable group or the polymer chain, (b) the presence of a bend in the bile acid units, possibly coupled with that of the ester end group separated from the bile acid group by an alkyl moiety, and (c) the lack of double bond in the bile acid units (present in cholesterol) that may be needed to enhance rigidity.

To help clarify these questions, we have selected for comparison the two bile acid-based compounds mentioned above and two cholesterol-based compounds, all with a long spacer of 10 methylene units. Of the latter, one is the same cholesterol compound as reported in the literature [7–9,20], to which we will compare our results and add some additional data. The other is the dihydrocholesterol compound, which has a saturated steroid skeleton and will

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doi:10.1016/j.polymer.2005.06.037

thus help address factor (c) above. Furthermore, to our knowledge this polymer has never been investigated previously, except for a brief study by differential scanning calorimetry and polarizing optical microscopy of a polysiloxane-based example with a very short spacer (three methylenes), for which an unidentified smectic phase was reported [21]. It will be shown that the bile acid compounds have no liquid crystalline character, whereas the dihydrocholesterol compounds show similar mesomorphic behavior to the cholesterol compounds, with at least one of the polymer mesophases appearing to possess two simultaneous packing structures [7,9].

2. Experimental

2.1. Materials

Cholic acid, lithocholic acid, methacrylic acid and 11-bromoundecanoic acid were purchased from Aldrich and used as received. Cholesterol and dihydrocholesterol were purchased from Sigma and used as received. 2,2′-Azoisobutyronitrile (AIBN) was purchased from Eastman Kodak (Rochester, USA) and recrystallized from ethanol before use.

2.2. Instruments

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AMX 300 in deuterated chloroform. Elemental analyses were carried out on an EA 1108 CHN Fisson Instrument. The molecular weights of polymers, relative to polystyrene standards, were determined by size exclusion chromatography (SEC) using a Waters 410 system. A 2% (w/v) polymer solution in tetrahydrofuran (THF) was injected into the column using THF as the eluent. Differential scanning calorimetry was performed with a TA Instruments DSC 2910, using heating and cooling rates of 10 °C/min under a flow of helium; 5–10 mg samples were sealed in standard DSC aluminium pans, and were heated and cooled twice. An Axioskop 2 Plus (Zeiss) polarizing optical microscope, equipped with a 25X Leica objective and a THMS 600 (Linkam) heating stage, was used to observe birefringence. The X-ray diffraction measurements were conducted on a Bruker diffractometer (Siemens Kristalloflex 760 generator), operated at 40 kV and 40 mA, equipped with sealed tube Cu K_α (1.542 Å) radiation collimated by a graphite monochromator and a 0.3 mm pinhole; the diffraction pattern was captured by an AXS two-dimensional wire-grid detector (HI-STAR). Powder samples were placed in 1.0 mm diameter Lindemann capillaries (Charles Supper). Extended molecular lengths were estimated using Hyperchem 6.01 (Hypercube), and include van der Waals radii at the extremities of the molecules.

2.3. Monomer synthesis

The synthetic route for the preparation of the monomers containing cholic acid, lithocholic acid, cholesterol and dihydrocholesterol are shown in Fig. 1.

2.3.1. Methyl 3α-(11-bromoundecanoyloxy)-7α, 12α-dihydroxy-5β-cholan-24-oate (*1*)

A solution of cholic acid methyl ester (4.22 g, 10 mmol), prepared from cholic acid according to a procedure published previously [13], and 11-bromoundecanoic acid (2.65 g, 10 mmol) in 30 mL benzene and methanol (v/v = 1:1) was heated to 80–85 °C for 10 h and catalyzed by 1 mL concentrated HCl. After removing the solvent, the mixture was dissolved into 50 mL chloroform and washed with water (30 mL × 3). The organic layer was dried over anhydrous sodium sulphate overnight and filtered. The solvent was evaporated and the product was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 7:3). The product, a clear soft solid, was dried in vacuum at 50 °C for 24 h. The yield obtained was 35%. ^{1}H NMR ($CDCl_3$): $\delta = 3.66$ (s, OCH_3), 3.86 (s, 7-CH), 3.99 (s, 12-CH), 4.58 (m, 3-CH), 3.40 (m, $BrCH_2$), 2.20 (m, CH_2COO). $(C_{36}H_{61}O_6Br)_n$ $(669)_n$ Calcd C 64.57, H 9.11. Found C 64.45, H 9.51.

2.3.2. Methyl 3α-(11-methyacryloyloxy-undecanoyloxy)-7α, 12α-dihydroxy-5β-cholan-24-oate (*2*)

Compound **2** was prepared by a method similar to the one described in the literature [22]. Potassium methacrylate was prepared by reacting $KHCO_3$ (10 g, 0.1 mol) with methacrylic acid (0.5 mol) in a flask in 500 mL methanol. The solid was dissolved in the solvent after stirring for 2 h at room temperature. The solution was filtered and the solvent was removed by rotary evaporation. A white solid was obtained after washing with hexane (30 mL × 3) and drying in vacuum at room temperature. Then 1 g of **1** (1.5 mmol), potassium methacrylate (0.24 g, 2.2 mmol) and hydroquinone (6 mg, 0.375 mmol) were dissolved in 50 mL DMF in a flask equipped with a condenser. The mixture was heated to 120 °C for 12 h. After removing the solvent under vacuum, the mixture was dissolved in chloroform and filtered to remove the salt. The product was purified by column chromatography (eluent: hexane/ethyl acetate 7:3). Finally, a clear liquid product was obtained, with a yield of 53%. ^{1}H NMR ($CDCl_3$): $\delta = 3.66$ (s, OCH_3), 3.86 (s, 7-CH), 3.99 (s, 12-CH), 4.13 (m, $COOCH_2$), 4.58 (m, 3-CH), 6.10 and 5.50 (s, CH_2=). $(C_{40}H_{66}O_8)_n$ $(674)_n$ Calcd C 71.20, H 9.97. Found C 71.13, H 10.03.

Compounds **3–8** were prepared similarly to compounds **1** and **2**.

2.3.3. Methyl 3α-(11-bromoundecanoyloxy)-5β-lithocholan-24-oate (*3*)

Yield 41%, white solid. ^{1}H NMR ($CDCl_3$): $\delta = 2.30$ (m, CH_2COO), 3.40 (m, $BrCH_2$), 3.65 (s, OCH_3), 4.70 (m,

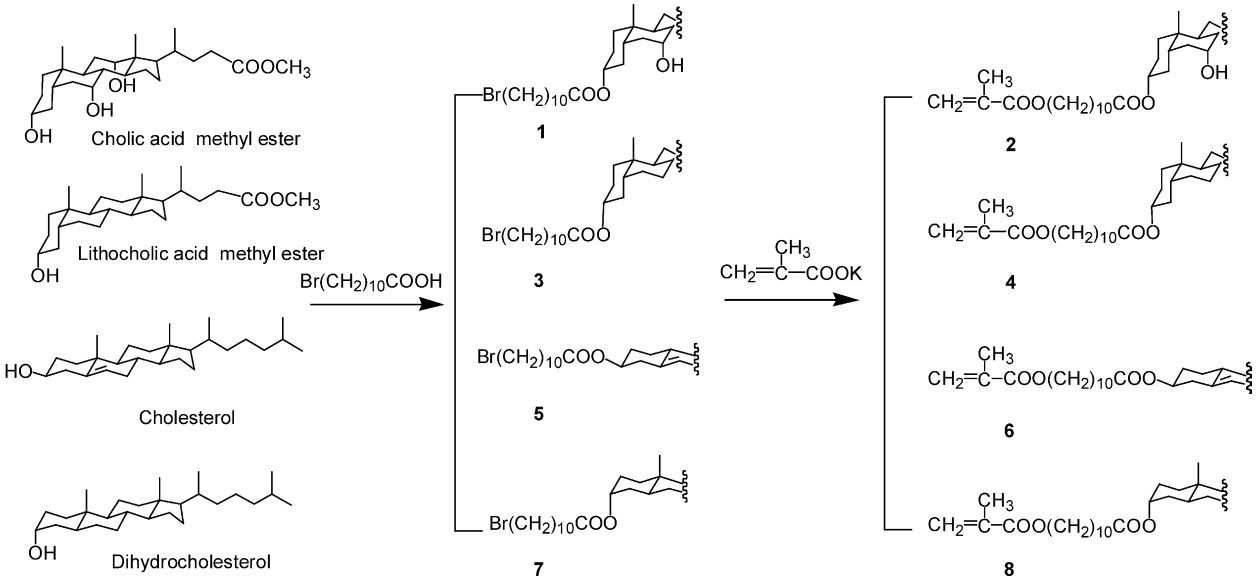

Fig. 1. The synthesis of methacrylic monomers containing the steroid moieties.

3-CH). $(C_{36}H_{61}O_4Br)_n$ $(637)_n$ Calcd C 67.80, H 9.58. Found C 67.20, H 9.65.

*2.3.4. Methyl 3α-(11-methacryloyloxy-undecanoyloxy)-5β-lithocholan-24-oate (**4**)*

Yield 24.5%, colorless liquid. ^{1}H NMR ($CDCl_3$): δ= 2.30 (m, CH_2COO), 3.66 (s, OCH_3), 4.14 (m, $COOCH_2$), 4.70 (m, 3-CH), 6.10 and 5.50 (s, CH_2=). $(C_{40}H_{66}O_6)_n$ $(642)_n$ Calcd C 74.70, H 10.28. Found C 74.38, H 10.08.

*2.3.5. Cholesteryl 11-bromoundecanoate (**5**)*

Yield 45%, white solid.^{1}H NMR ($CDCl_3$): δ=2.30 (m, CH_2COO), 3.40 (m, $BrCH_2$), 3.65 (s, OCH_3), 4.70 (m, 3-CH), 5.38 (s, 6-CH). $(C_{38}H_{65}O_2Br)_n$ $(649)_n$ Calcd C 70.21, H 10.01. Found C 69.89, H 9.86.

*2.3.6. Cholesteryl 11-methacryloyloxyundecanoate (**6**)*

Yield 32%, white solid.^{1}H NMR ($CDCl_3$): δ=2.30 (m, CH_2COO), 4.13 (m, $COOCH_2$), 4.60 (m, 3-CH), 5.38 (s, 6-CH), 6.09 and 5.54 (s, CH_2=). $(C_{42}H_{70}O_4)_n$ $(654)_n$ Calcd C 77.06, H 10.70. Found C 76.96, H 11.07.

*2.3.7. Dihydrocholesteryl 11-bromoundecanoate (**7**)*

Yield 47.2%, white solid. ^{1}H NMR ($CDCl_3$): δ=2.30 (m, CH_2COO), 3.40 (m, $BrCH_2$), 4.69 (m, 3-CH). $(C_{38}H_{67}O_2Br)_n$ $(635)_n$ Calcd C 71.81, H 10.55. Found C 71.68, H 11.90.

*2.3.8. Dihydrocholesteryl 11-methacryloyloxyundecanoate (**8**)*

Yield 60%, white solid. ^{1}H NMR ($CDCl_3$): δ=2.30 (m, CH_2COO), 4.10 (m, $COOCH_2$), 4.69 (m, 3-CH), 6.09 and 5.54 (s, CH_2=). $(C_{42}H_{72}O_4)_n$ $(656)_n$ Calcd C 78.75, H 11.25. Found C 78.61, H 11.54.

2.4. Preparation of polymers

All polymers were prepared by the following procedure. About 0.6–0.8 mmol of the monomer was dissolved in 10 mL of dry THF, and 3 mol% of AIBN was added. The mixture was degassed with a slow stream of nitrogen for 30 min. The temperature was then raised to 60 °C and maintained for 48 h. Methanol (100 mL) was added to precipitate the polymer, and the product was collected after centrifugation. The yields were typically 70–90%. The polymers were dried in vacuum at 40 °C for 48 h.

3. Results and discussion

The monomers containing cholic acid methyl ester (**2**), lithocholic acid methyl ester (**4**), cholesterol (**6**) and dihydrocholesterol (**8**), all with a 10-carbon spacer at position 3, were synthesized by the same method. Cholesterol, dihydrocholesterol and lithocholic acid each have a single hydroxyl group, located at position 3, whereas cholic acid has three hydroxyl groups. Cholic acid and lithocholic acid also have a carboxylic acid group, which was protected by a methyl ester group before esterification by 11-bromoundecanoic acid. Although there are three hydroxyl groups in cholic acid, the reactivity of the OH group at position 3 is much higher than those at positions 7 and 12 [11], and esterification occurred preferably at this position, as evidenced clearly by the change of the chemical shift of the CH group at position 3 (from ~3.5 to ~4.6 ppm for the proton). The yields of this step were less than 50% because of side reactions during esterification.

The second step was based on a previously described method [20] with some modifications. The ^{1}H NMR spectra of compounds **1**–**8** are shown in Fig. 2. After attachment of

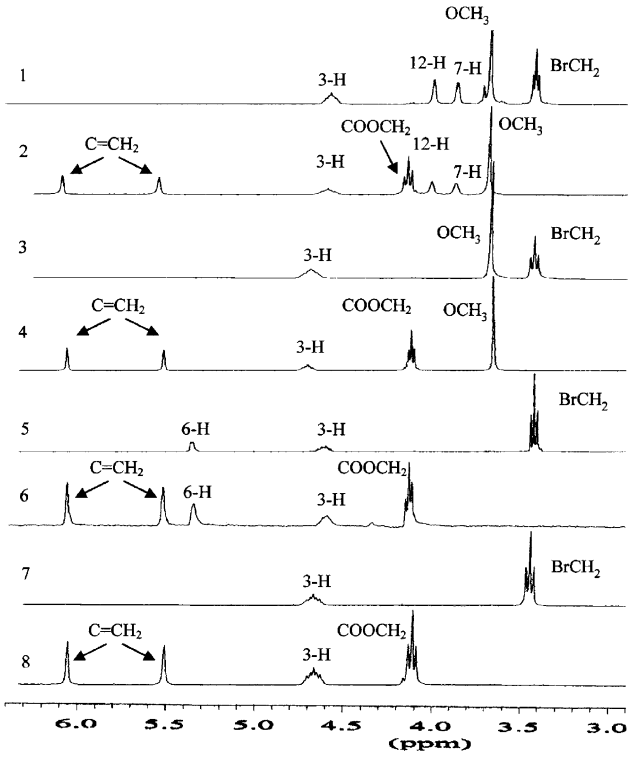

Fig. 2. ^{1}H NMR spectra of the intermediates and the monomers.

the methacryloyl groups, proton signals of the double bond appeared at 6.10 and 5.54 ppm, and the signal of the methylene group previously bearing bromine shifted from 3.40 to 4.13 ppm. After polymerization, the ^{1}H signals of the double bond of the monomer precursors disappeared in the NMR spectra. Even after optimization of the reaction conditions, the molar masses of the polymers remained relatively low (Table 1). The relatively narrow polydispersity indices (Table 1) can be attributed to fractionation having occurred during the precipitation procedure used to purify the polymers.

The DSC cooling thermograms of the monomers (compounds **2**, **4**, **6** and **8**) are shown in Fig. 3. Only the cholesterol and dihydrocholesterol derivatives show well-defined thermal transitions. Previous literature work reported that the cholesterol monomer melts at 55 °C [8] or 59 °C [20], and possesses a monotropic [20] or enantiotropic [8] smectic A phase followed by an enantiotropic chiral nematic phase between about 58 and 63 °C [8,20]. We observed a melting peak on first heating at 31 °C (as reported also by Minezaki et al. [23]), followed by

Table 1
Molecular weights of the polymers synthesized

Polymer	M_n	M_w
P1 (cholic acid)	7100	8700
P2 (lithocholic acid)	8900	11,500
P3 (cholesterol)	16,500	17,300
P4 (dihydrocholesterol)	10,400	12,600

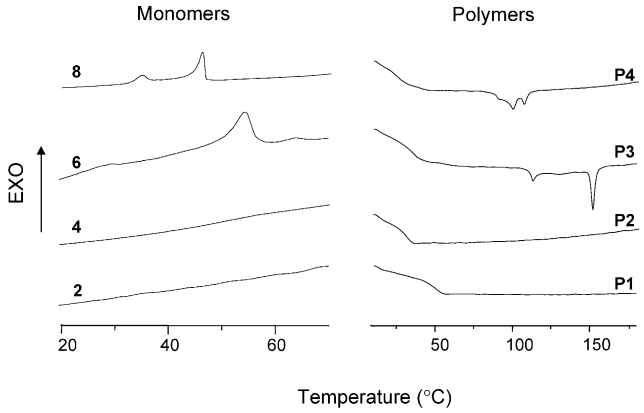

Fig. 3. DSC thermograms of the monomers and polymers. Shown are the cooling thermograms after the first heating (cooling rate: 10 °C/min).

low-enthalpy peaks at 53, 58 and 65 °C; on cooling, low enthalpy peaks appeared at 64 and 55 °C with no crystallization, as in Refs. [8,20]. The monomer was isotropic above 64 °C. For the dihydrocholesterol monomer, we observed a melting peak on first heating at 43 °C, followed by a weak peak at 48 °C (on second heating, melting after recrystallization occurred at 33 °C, followed by peaks at 36 and 47 °C); on cooling, peaks appeared at 45 and 33 °C with no crystallization. The monomer was isotropic above the highest temperature transition. Polarizing optical microscopy observations indicated that the liquid crystalline phases are smectic A and chiral nematic, the same sequence as observed in the cholesterol monomer. In contrast, the DSC thermograms of the cholic methyl ester and lithocholic methyl ester monomers were featureless and neither of those monomers showed any birefringence between crossed polarizers. It was noted, however, that lithocholic ester monomer partially crystallized after long refrigeration, giving a melting point of 37 °C.

The DSC cooling thermograms of the polymers (**P1**, **P2**, **P3** and **P4**) are also shown in Fig. 3. The cholesterol polymer gives a low-intensity peak at 115 °C (110 °C on cooling), and a sharp peak at 154 °C (147 °C on cooling), in excellent agreement with literature values for this polymer despite the higher molecular weights of the latter [7,9]. The birefringence observed also concords with the literature reports [7,9]. The dihydrocholesterol polymer shows two closely spaced peaks with maxima at 101 and 108 °C on second heating (about 5 °C higher on first heating) and at 104 and 96 °C on cooling [24]. It is isotropic above about 110 °C. Below this temperature, the birefringence observed is similar to that of the cholesterol polymer. The bile acid-containing polymers, like the corresponding monomers, show no birefringence between crossed polarizers at and above ambient temperature, and no phase transitions other than a glass transition were apparent in their DSC thermograms [24]. They are thus concluded to be isotropic. Glass transition temperatures for all of the polymers are near ambient temperature. The variation of the molar masses of

the same polymer within the range of the samples did not result in notable differences in the results.

X-ray diffractograms of the cholesterol and dihydrocholesterol monomers and polymers at temperatures above the melting point and after cooling from the isotropic phase are given in Figs. 4–7. Both the monomers and polymers show a broad halo in the wide-angle region, indicating the absence of crystallinity and reflecting the average lateral distance between the monomers and side chains, respectively (5.2–5.5 Å from the lowest to the highest temperatures investigated).

In the small-angle region, the diffractograms of the monomers (Figs. 4 and 5) in their lower temperature mesophase are characterized by a single, sharp peak giving a Bragg spacing of 34–35 Å, which is the same as the molecular lengths calculated for the monomers in their most extended conformations. In the higher temperature mesophase, the single peak is of very low intensity and gives a slightly smaller spacing of 33 Å. These diffractograms are consistent with the mesophases being smectic A and chiral nematic, respectively, as indicated by polarizing optical microscopy. The X-ray data indicate that the smectic A phase is single-layer.

The small-angle pattern observed for the cholesterol polymer (Fig. 6) in the lower temperature mesophase is the same as that reported in the literature for this polymer [7,9]. The dihydrocholesterol polymer (Fig. 7) also gives this pattern in the mesophase below the double transition. The pattern consists of three non-equidistant reflections that correspond to spacings of 53–58, 32–33 and 21 Å. The exact spacings tend to decrease with increasing temperature in this phase, especially that corresponding to the first reflection. This was documented for the first two reflections for the cholesterol polymer in Ref. [9b], where it was also shown that the first reflection gives a lower spacing by 3–4 Å after cooling from the melt, and is thus dependent on thermal

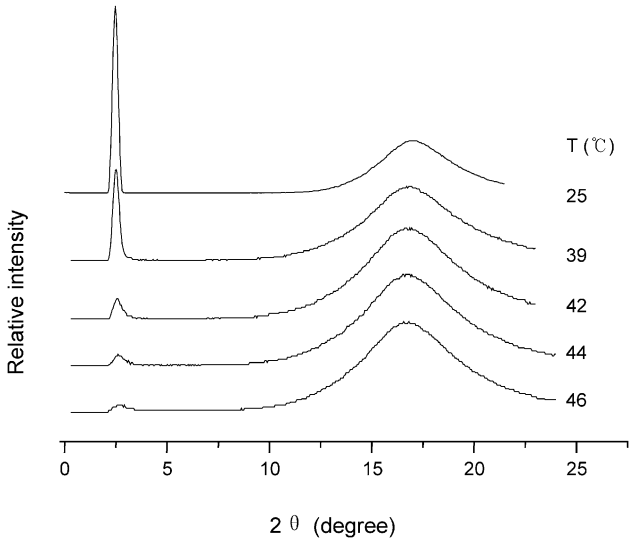

Fig. 5. X-ray diffractograms of the dihydrocholesterol monomer (**8**), taken at the nominal temperatures indicated during cooling.

history. Our data corroborate these observations for the cholesterol polymer and indicate the same trend in the dihydrocholesterol polymer.

Since the three reflections are not equidistant, they cannot correspond to first-, second-, and third-order reflections of a lamellar phase, although polarizing optical microscopy textures suggest a smectic A phase [7]. Instead, they have been rationalized, for the cholesterol polymer, as arising from two different co-existing lamellar packing structures (noting that oriented samples indicate perpendicular orientation of the mesogenic groups relative to the lamellar planes) [7,9]. The first reflection, which corresponds to a Bragg spacing that is somewhat less than twice the calculated molecular length, is attributed to a partially interdigitated bilayer structure (SmA_d) of antiparallel side

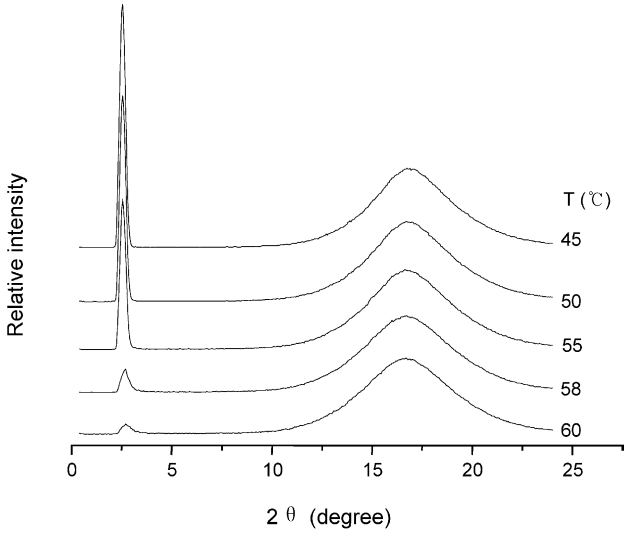

Fig. 4. X-ray diffractograms of the cholesterol monomer (**6**), taken at the nominal temperatures indicated during cooling.

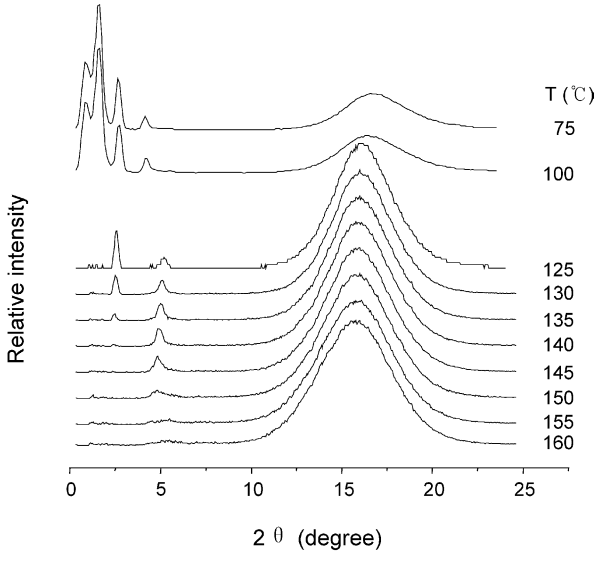

Fig. 6. X-ray diffractograms of the cholesterol polymer (**P3**), taken at the nominal temperatures indicated during heating.

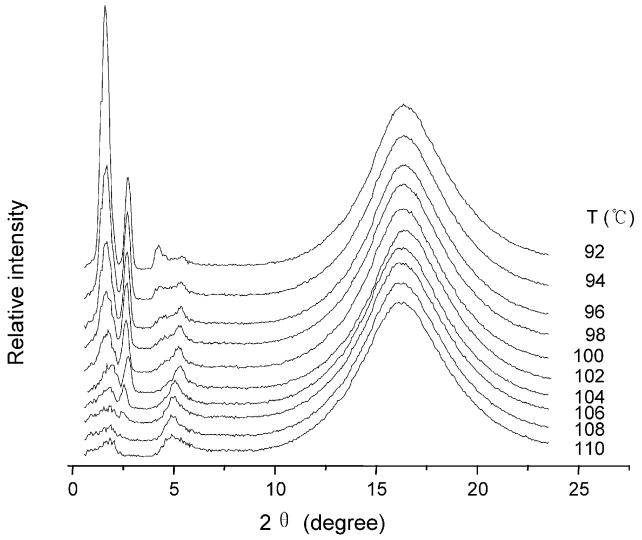

Fig. 7. X-ray diffractograms of the dihydrocholesterol polymer (**P4**), taken at the nominal temperatures indicated during cooling.

chains with overlapping alkyl tails. The second reflection, which gives a Bragg spacing that is comparable to one calculated molecular length, was attributed to a single-layer structure (SmA_1) composed of antiparallel side chains that are completely interdigitated. The third reflection is associated with the partial bilayer structure, and is attributed to the subplane composed of the cholesterol moieties and the overlapping alkyl chains. This structure was observed for spacer lengths of 9–11 methylene groups, whereas shorter spacers (1–7 methylenes) give rise to a non-interdigitated bilayer structure only and longer spacers (14 and 15 methylenes) to the completely interdigitated antiparallel monolayer structure only [7,9]. In the light of this interpretation, our results indicate that the dihydrocholesterol polymer gives rise to the same two coexisting lamellar structures.

The relative proportions of the two phases can be qualitatively estimated from the intensities of the reflections involved. In the case of our two polymers, the three reflections are of sharply decreasing intensity, in contrast to the literature for the cholesterol polymer where the first peak is reported to be similar in intensity to or weaker than the second peak [7,9]. This suggests that our polymers are characterized by a greater proportion of the partial bilayer structure than those in the literature. It was suggested that bilayer packing may more easily form nearer the ends of the polymer chains, where there is greater mobility [9b]. If true, the lower molecular weights of our polymers compared to those investigated in the literature [7,9] may account for the greater proportion of bilayer structure in our case.

Yamaguchi and Asada [9b] observed that the reflections corresponding to 55 and 33 Å disappear at the lower and upper transition temperatures, respectively, with no increase in intensity of the 33-Å reflection at the lower transition (they did not investigate the reflection corresponding to 21 Å). They concluded that the partial bilayer structure becomes isotropic at the lower transition and the single layer structure becomes isotropic at the higher transition, implying that the single-layer structure coexists with the isotropic phase in the temperature region between the two transitions [9b]. On the other hand, Freidzon et al. observed circular dichroism for this polymer, indicating a cholesteric component to the structure [7a]. They proposed that, at the transition between the two mesophases, a twisting of the single-layer smectic layers along an axis parallel to the layers occurs [7b]. This resembles a twist-grain boundary (TGB) phase [25].

Our more complete observations indicate rather complex behavior in this phase. For the cholesterol polymer (Fig. 6), the two reflections corresponding to 55 and 21 Å disappear at the lower-temperature transition (consistent with both being associated with the bilayer structure), and, especially, a new reflection appears near 5°, corresponding to a Bragg spacing of 17 Å. The single-layer reflection of the lower-temperature mesophase remains present, but with a much lower intensity; significantly, it decreases progressively in intensity and then disappears well before the transition to the isotropic phase [26]. In contrast, the new 17-Å reflection remains approximately constant in intensity throughout this mesophase. Both of these reflections tend to decrease slightly in angle (increase in spacing) with increasing temperature, as observed also for the 33-Å reflection in Ref. [18] and which is opposite to the tendency observed in the lower-temperature mesophase. The fact that their spacings are in 1:2 ratio (for example, 33.6 and 16.9 Å at 125 °C and 34.2 and 17.2 Å at 130 °C) suggests that they are first- and second-order reflections of the single-layer phase. However, this seems to be belied by the evolution in intensity. Furthermore, the appearance of the 17-Å reflection at the lower-temperature transition and its relative narrowness suggests that the bilayer structure does not become isotopic at this transition.

Our data for the dihydrocholesterol polymer (Fig. 7) completely parallel the observations for the cholesterol polymer, but over a narrow temperature range. As the double transition region is crossed [27], the first and third reflections (associated with the bilayer structure) decrease rapidly in intensity and the second reflection (associated with the single-layer structure) more slowly, consistent with the former disappearing during the lower transition and the latter somewhat later. The second reflection also shows a small increase in the associated Bragg spacing with increasing temperature in the range. Simultaneously with the disappearance of the third reflection of the lower-temperature mesophase, a new low-intensity peak clearly grows in at a somewhat higher angle (5.4° in the 92 °C diffractogram), and it moves to smaller angles with increasing temperature. In the 98–106 °C diffractograms, the reciprocal spacings associated with the two reflections (near 2.5 and 5°) are in a 1:2 ratio. However, the first disappears before the second, as indicated in particular by

the 106 and 108 °C diffractograms. The latter then seems to evolve into the broader band at 5° in the 110 °C diffractogram, which is presumably at or just above the transition to the isotropic phase. Thus, again, the X-ray data suggest that the bilayer structure evolves into a phase that is not isotropic at the lower-temperature transition. It is possible that the mesophase above this transition in both the cholesterol and dihydrocholesterol polymers is also characterized by two packing structures, at least in the temperature range up to the disappearance of the reflection near 2.5°, and may involve a TGB phase. However, further study is needed to clarify this (as well as the possible existence of a third DSC transition as noted in Refs. [26, 27]).

4. Conclusion

The dihydrocholesterol polymer is liquid crystalline, and shows thermal and structural behavior that is similar to that of the cholesterol polymer. In both, the structural characteristics are unusual, in that at least the lower temperature mesophase appears to be characterized by two co-existing smectic A packing structures, one of which appears responsible for the transition into the higher temperature mesophase, which, in turn, also appears complex. The saturation of the cholesterol double bond, giving dihydrocholesterol, only reduces the thermal stability of the mesophases. In contrast, the two bile acid polymers, where the rigid side chain moiety has a bent structure and is also terminated by an ester group with an intervening short alkyl sequence, both of which are typically unfavorable to liquid crystallinity, are simply amorphous polymers.

Acknowledgements

Financial support from NSERC of Canada, FQRNT of Quebec, and the Canada Research Chair program is gratefully acknowledged. The authors thank Dr Yubao Zhang for his technical assistance in the X-ray experiments and Dr Mohamed Benouazzane for his help with the polarizing optical microscopy. We also acknowledge our membership in the FQRNT-supported multi-university Centre for Self-Assembled Chemical Structures (CSACS).

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[24] We also synthesized a sample of this polymer with lower molecular weight (M_n = 2900, M_w = 4100) and found essentially the same liquid crystalline behavior except that the transitions occur at lower temperatures; i.e. there is a double transition about 3 °C apart at 77 °C on heating and 72 °C on cooling. Since the bile acid polymers have molecular weights significantly higher than this dihydrocholesterol polymer which is liquid crystalline, we conclude that the lack of mesophase formation in the bile acid polymers is not a consequence of their degrees of polymerization being insufficiently high. This conclusion is supported by the fact that no mesophase formation is observed in the corresponding monomers either.
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[26] Possibly, the very shallow hump that appears about mid-way between the two transitions in the DSC corresponds to this phenomenon.
[27] The shoulder on the low-temperature side of the double transition may reflect a third transition, in parallel with the possibly three transitions for the cholesterol polymer, as noted in Ref. [26].