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Ionic liquid crystals derived from the protonation of poly(propylene imine) dendrimers with a cholesterol-based carboxylic acid

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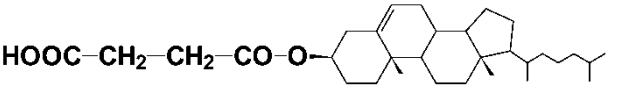
The liquid crystalline character of salts resulting from the interaction of poly(propylene imine) dendrimers with 3-cholesteryloxycarbonylpropanoic acid has been studied. The supramolecular structure and consequently the observed liquid crystalline phases are dictated by the degree of protonation of primary amino groups as compared with that of tertiary ones, determined by FTIR spectroscopy in the bulk and by NMR spectroscopy in solution. Glass transition temperatures of the materials are about 38°C. At higher temperatures they are transformed to smectic C* phases while a second-order smectic C phase to smectic A phase transition is observed between 90 and 110°C depending on dendrimer generation. At about 150°C the onset of degradation is observed. The influence of the ionic dendrimeric scaffold on the thermotropic properties is discussed.

1. Introduction

The thermotropic liquid crystalline behaviour of ionic amphiphiles [1] has been extensively investigated in recent years. Thus the liquid crystalline phases of a diversity of amphiphilic salts including protonated amines [2], aliphatic quaternary ammonium salts [3], carboxylates [4], sulphonates [5], pyridinium [6] and quaternary phosphonium salts [7] were investigated. The same amphiphilic molecules self-assemble in water forming micelles, vesicles or a diversity of lyotropic liquid crystal phases. For this reason they are characterized as amphotropic [8, 9]. Thermotropic liquid crystalline behaviour is also exhibited by dipolar amphiphilic compounds [10] which, as expected, are found to be affected by the nature of their polar and lipophilic segments. The driving force behind the formation of amphiphilic liquid crystals is the segregation of the lipophilic and hydrophilic segments giving rise to the formation of organized structures.

In view of the liquid crystalline character exhibited by dendrimers functionalized [11] at their external groups with appropriate moieties, and with the aim of extending and broadening the spectrum of ionic moieties participating in the formation of ionic-type liquid crystals, we investigate here the potential mesomorphic behaviour of ionic salts based on dendrimeric and cholesterol acid derivatives. The molecular structure of these salts bearing dendrimeric and cholesterol moieties is significantly different from the conventional structure of amphiphilic salts and this is primarily the incentive that prompted their investigation. In the present study, the salts were formed from the protonation of diaminobutane poly(propylene imine) dendrimers with 3-cholesteryloxycarbonylpropanoic acid (structure shown below). The liquid crystalline behaviour was studied with polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and by X-ray diffraction (XRD) studies.



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2. Experimental

2.1. *Materials and synthesis*

Amine-terminated diaminobutane poly(propylene imine) dendrimers of various generations, DAB-4 to DAB-64, were purchased from DSM Fine Chemicals Company and used as received. Succinic anhydride was purchased from Merck UK and recrystallized from

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chloroform before use. Cholesterol, purchased from Merck, was recrystallized twice from ethanol.

3-Cholesteryloxycarbonylpropanoic acid was prepared by a method analogous to that reported in the literature [12]. Thus, to 0.004 mol of cholesterol dissolved in dry acetone, 20% molar excess of succinic anhydride and triethylamine were added. The reaction mixture was heated at reflux for about 24 h. The solvent was distilled off and the remaining material recrystallized twice from glacial acetic acid; yield 69%. The melting point and infrared peaks agree with those reported in the literature: m.p. 178.1°C (onset temperature determined by DSC, second heating run), lit 177–179°C; FTIR 1731 cm^{-1} (ester carbonyl), 1710 cm^{-1} (acid carbonyl). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.5$–2.05 (m, cholesterol skeleton), 2.35 (d, H_4), 2.65 (t, $C\underline{H}_2CH_2COOH$), 2.70 (t, $CH_2C\underline{H}_2COOH$), 4.5 (m, $\underline{H}_{3a}$), 5.4 (d, $\underline{H}_{6a}$). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 177.35$ (HOO$\underline{C}$), 171.49 ($\underline{C}OO$), 139.9 (C_5), 122.8 (C_6), 74.51 (C_3), 56.8 (C_{14}), 55.9 (C_{17}), 50.3 (C_9), 42.3 (C_{13}), 39.7 (C_{16}), 39.5 (C_{24}), 38.8 (C_4), 37.0 (C_1), 36.5 (C_{10}), 36.2 (C_{22}), 35.8 (C_{20}), 31.8 (C_7, C_8), 29.2 ($CH_2\underline{C}H_2COOH$), 28.9 ($\underline{C}H_2CH_2COOH$) 28.2 (C_{12}), 28.0 (C_{25}), 27.7 (C_2), 24.6 (C_{15}), 23.8 (C_{23}), 22.8 (C_{27}), 22.6 (C_{26}), 21.0 (C_{11}), 19.3 (C_{19}), 18.7 (C_{21}), 11.8 (C_{18}). Elemental analysis for $C_{31}H_{50}O_4$: calc. C 76.50, H 10.35; found C 76.22, H 10.38%.

The preparation of the dendrimeric salts was performed in dichloromethane by reacting poly(propylene imine) dendrimers of the first to fifth generation DAB_n, $n = 1$–5, (1 mmol) with equimolar quantities of 3-cholesteryloxycarbonylpropanoic acid (CA) with respect to the primary amino groups. The solution was stirred for half an hour and the solvent was slowly removed under reduced pressure. The materials obtained, DAB-CA_n, were exhaustively dried under vacuum and their structure was established by FTIR and NMR (see later).

2.2. *Characterization*

Liquid crystal textures were observed using a Leitz–Wetzlar polarizing microscope equipped with a Linkam hot stage. Thermotropic polymorphism was investigated by DSC employing a DSC-10 calorimeter (TA instruments) at heating/cooling rates of 10°C min^{-1}. Thermal stability was assessed by thermogravimetry employing a TGA 2050 analyser (TA instruments) at a heating rate of 10°C min^{-1}. Liquid crystalline phases were investigated by XRD using Cu $K_{\alpha 1}$ radiation from a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA) and an R-AXIS IV image plate. Powder samples were sealed in Lindemann capillaries and heated employing an Instec hot stage. FTIR studies were performed using a Nicolet Magna 550 spectrometer. The structure of the dendrimeric salts was established by ^1H and ^{13}C NMR (500 and 62.9 MHz respectively, in $CDCl_3$ at 25°C).

3. Results and discussion

3.1. *Spectroscopic studies*

The formation of the dendrimeric-cholesteric acid salts was confirmed by the complete protonation of the cholesteric acid derivative as indicated by FTIR spectroscopy. Thus, the broad OH stretching band centred at 3000 cm^{-1} as well as the carbonyl stretching absorption band at 1710 cm^{-1} is not present in the spectra of the DAB-CA_n compounds. The latter band is replaced by two new bands at 1560 and at 1402 cm^{-1} corresponding to the asymmetric and symmetric stretching modes of the COO^- group.

Due to the possibility of multiple protonation for dendrimers, the actual protonated sites should be determined. Specifically, poly(propylene imine) dendrimers bear primary amino groups at their external surface and tertiary amino groups in the core and branches. The primary amino groups are more basic than the tertiary ones, although the differences in pK values are small especially for the tertiary amino groups located in the core [13]. The protonation sequence of these dendrimers in water, studied in detail by pontentiometric titration [13] and ^{15}N NMR [14], clearly suggests that, even at low proton concentrations, the outermost primary amino groups and the tertiary amino groups of the odd shells are protonated simultaneously. In the present case FTIR spectroscopy in the bulk phase was used in the first place for providing qualitative insights on the degree of protonation of dendrimeric nitrogens.

In the spectra of the salts, the NH_2 asymmetric and symmetric bands of the parent dendrimer at 3352 and 3295 cm^{-1} were not completely suppressed; unexpected if complete protonation of the surface amino group had occurred. Instead they appeared less intense and broader. Additionally the characteristic NH_3^+ absorption bands at 2650 and 2180 cm^{-1}, as well as the deformation band at 1644 cm^{-1}, were rather weak in intensity as compared, for example, with the spectrum of a fully protonated dendrimer (figure 1). Furthermore, the bending NH_2 band of the non-protonated dendrimer was still present at 1574 cm^{-1}. Of interest is the symmetric stretching band of the CH_2 groups attached to the tertiary nitrogen band located at 2802 cm^{-1}. The position of this band, which normally should be detected at *c.* 2850 cm^{-1}, is due to interactions between the lone pair of the nitrogen and the CH bond which lies in a *trans*-position to it [15, 16]. This effect does not

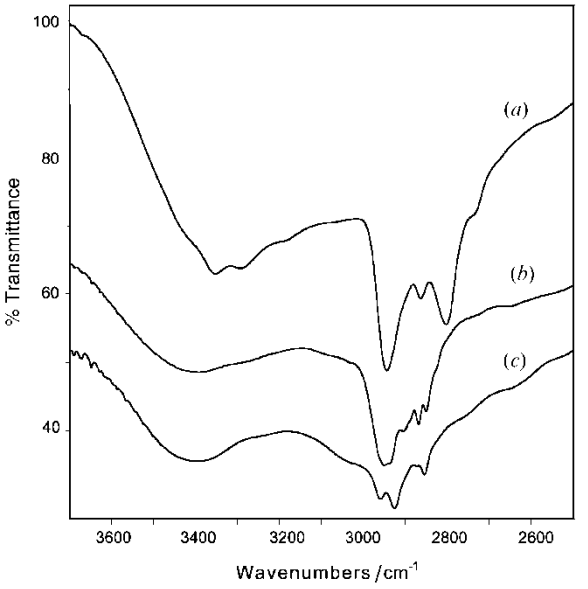

Figure 1. FTIR spectra of (*a*) the parent fourth generation dendrimer DAB_4, (*b*) the cholesteric acid ionic derivative $DAB\text{-}CA_4$, (*c*) the fully protonated DAB_4 dendrimer obtained after addition of 62 equivalents of hydrochloric acid.

occur when the lone pair is delocalized or donated into a vacant orbital. Indeed this band is completely suppressed in the spectrum of a fully protonated dendrimer. In the spectra of the salts under study this band is barely observed. This band as well as that at 2500 cm^{-1} attributed to the NH^+ groups clearly suggest that protonation of the tertiary amino group is taking place.

The structure of the protonated complexes was also quantitatively investigated in $CDCl_3$ solution by ^1H and ^{13}C NMR (500 MHz and 62.9 MHz, respectively). COSY and HSQC 2D-NMR experiments were employed for the unequivocal assignment of the peaks. A broad peak centred at approximately 5.0 ppm was observed, corresponding to the protons of protonated tertiary and primary amino groups. The α-CH_2 protons relative to the protonated primary and tertiary amino groups appear at 3.0 and 2.75 ppm, respectively, while the β-CH_2 protons relative to the same groups appear at 1.85 ppm. Additionally, a peak at 1.70 ppm was observed corresponding to the ($NH^+CH_2C\underline{H}_2C\underline{H}_2CH_2NH^+$) methylene groups. The peaks of α-CH_2 and β-CH_2 protons relative to COOH that appeared at 2.73 and 2.63 ppm, respectively, in the spectrum of cholesteryl acid, are now shifted to 2.55 and 2.45 ppm, respectively, due to the ionization of the carboxylic group. However, peaks attributed to methylene protons related to the non-protonated tertiary and primary amino groups also appeared in the spectrum of the salts. It should be noted that these peaks, observed at 2.55 ppm ($NCH_2CH_2C\underline{H}_2NH_2$), 2.45 ppm ($NC\underline{H}_2$), 1.55 ppm ($NCH_2C\underline{H}_2CH_2NH_2$ and $NCH_2C\underline{H}_2CH_2N$) and 1.10 ppm ($NCH_2C\underline{H}_2C\underline{H}_2CH_2N$), co-exist with the peaks of the cholesteric derivative as established by 2D-NMR experiments.

Integrating the peaks of α-CH_2 relative to protonated primary amino groups at 3 ppm and of α-CH_2 protons relative to the non-protonated tertiary amino groups at 2.45 ppm, an approximate estimate of their ratio could be obtained, which was found to depend on the dendrimer generation. Thus, the number of protonated tertiary amino groups compared with that of protonated primary amino groups is lower for the first and second generation dendrimeric salts. For the higher generation dendrimers, the number of protonated tertiary amino groups becomes progressively higher as the dendrimer generation proceeds from third to fifth. Specifically, for the first and second generation derivatives approximately 75% of the primary amino groups are protonated while for the fourth and fifth generation the number of protonated tertiary amino groups is almost equal to that of protonated primary amines (table 1). This result is rather unexpected since, as already mentioned, the primary amino groups are slightly more basic and they are also greater in number than the tertiary ones in every generation (for example, the number of primary amino groups is 32 for the fourth

Table 1. Number of total (protonated and non-protonated) primary and tertiary amino groups of the $DAB\text{-}CA_n$ compounds[a] and the ratio of protonated to total primary amino groups as determined by NMR.

Compound	Number of primary amino groups	Number of tertiary amino groups	Ratio of protonated to total primary amino groups
$DAB\text{-}CA_4$	4	2	0.75
$DAB\text{-}CA_8$	8	6	0.70
$DAB\text{-}CA_{16}$	16	14	0.61
$DAB\text{-}CA_{32}$	32	30	0.49
$DAB\text{-}CA_{64}$	64	62	0.48

[a]*n* represents the number of the primary amino groups as well as the number of protonated cholesteric acid moieties

generation dendrimer and the number of tertiary amino groups is 30, table 1). A possible explanation is that the cholesteric moiety preferably resides in the interior of the dendrimeric moiety as a result of the encapsulating properties of high generation dendrimers [17].

Analogous results were obtained by ^{13}C NMR; the α-carbons of the methylene groups relative to the protonated and non-protonated tertiary amino groups appear as two broad peaks centred at 50.5 and 52.5 ppm, respectively. Also the α- and β-carbons relative to protonated primary amino groups appear at 38.2 and 28.0 ppm, respectively; while the same carbons relative to non-protonated groups appear at 39.5 and 31.8 ppm, respectively. Additionally, two peaks at 25.5 and 24.0 ppm were observed attributed to the central carbons of the non-protonated and protonated dendrimeric core, respectively. Also, the α- and β-carbons relative to COO^- appear at 32.5 and 31.2 ppm, respectively. Although it could be argued that the ionization in solution could be different from that in the bulk phase, the NMR results agree with those observed by FTIR and definitely show that the ionization of tertiary amino groups is more pronounced for high generation than for low generation dendrimers.

3.2. *Thermal and optical studies*

The dendrimeric salts were anisotropic glasses at room temperature showing birefringence under the polarizing microscope. Their glass transition temperatures, measured by DSC during the second heating run, range from 36 to 38°C. At higher temperatures they become birefringent fluids, suggesting the presence of liquid crystalline organization. Additionally a second-order transition is observed by DSC between 90 and 110°C which is hardly detectable by POM (figure 2). This transition corresponds to an SmC*–SmA transition, as established by X-ray experiments (see later). The transition temperatures are slightly higher for the first and second generation derivatives and decrease with increasing dendrimer generation (table 2). No other phase transitions can be detected either by POM or DSC up to about 150°C where the onset of degradation is observed before isotropization. On cooling below about 35°C the compounds are transformed into birefringent glasses.

The thermal stability of the dendrimeric salts under nitrogen was also studied by thermogravimetry. Decomposition starts at temperatures above 150°C (weight loss less than 0.1%). They are therefore less stable than cholesterol-functionalized poly(propylene imine) dendrimers [18] in which the cholesterol moiety was covalently attached to the dendrimeric surface, apparently due to their ionic character.

Figure 2. Optical texture of DAB-CA_4 observed under the polarizing microscope at 110°C.

3.3. *X-ray diffraction studies*

In direct contrast to the cholesterol covalently functionalized poly(propylene imine) dendrimers [18] the currently investigated ionic dendrimeric derivatives do not exhibit crystalline structures at room temperature. This indicates that the cholesteric moieties are not in close proximity to each other which would result in their lateral organization and therefore crystallization within the layers. They must therefore be surrounded, at least partially, by the dendrimeric branches. This is in agreement with the conclusions drawn already from the FTIR and NMR spectroscopic data.

The X-ray patterns at temperatures below the T_g reveal the existence of lamellar organization within the salts. Specifically they contain two sharp small angle reflections and two broad peaks in the wide angle region centred at 5.5 and 4.5 Å, suggesting the disordered state of the cholesteric moieties and aliphatic segments, respectively. They are therefore in a smectic glass phase.

At temperatures above the glass transition, the X-ray patterns remain qualitatively the same, indicating that the lamellar ordering persists. The lamellar spacing, however, slightly but unquestionably increases with temperature suggesting the presence of an SmC* phase (figure 3). At temperatures just above the second-order transition, the thickness of the layers increases as a result of a smectic C

Table 2. Transition temperatures (°C) of the DAB-CA_n compounds detected by DSC.

Generation	T_g	SmC*→SmA
1	37	102
2	38	108
3	36	93
4	38	91
5	38	88

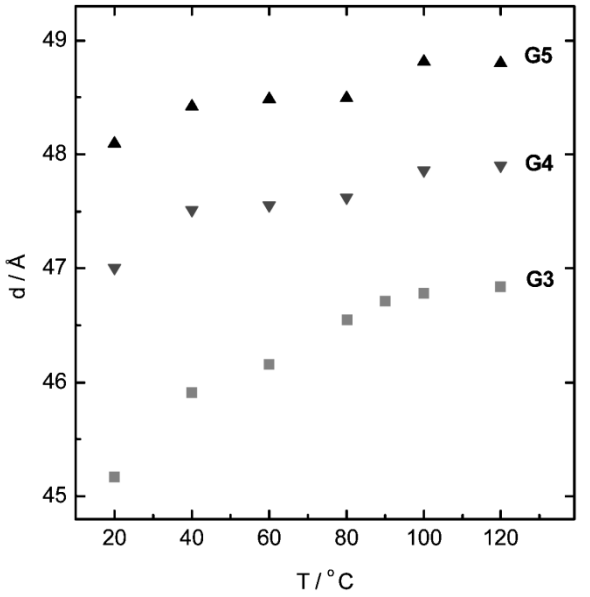

Figure 3. Temperature dependence of the lamellar spacings of cholesteric acid ionic derivatives.

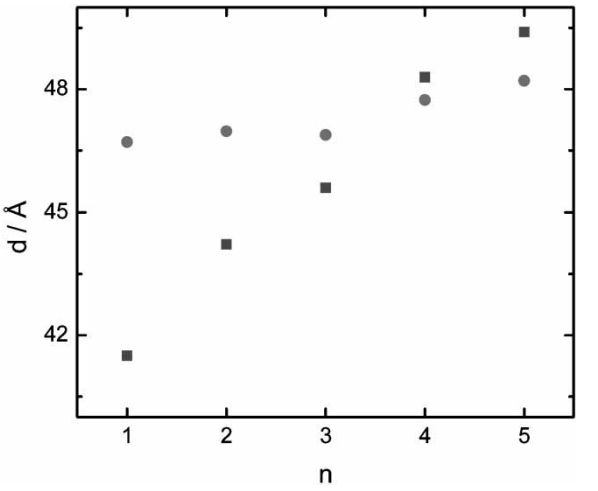

Figure 4. Lamellar spacings as a function of dendrimer generation of ionic (●) and covalently (■) functionalized cholesteric derivatives.

to smectic A transition. At lower temperatures, therefore, the cholesteric moieties are aligned in the same direction and tilted with respect to the layer normal. At temperatures above the SmC*–SmA transition the *d*-spacings remain constant suggesting either that the cholesterol units are orthogonal to the smectic layers or that not all moieties are tilted in the same direction [19]. Assuming that the moieties are orthogonal to the smectic layers the tilt angles determined are about 10° at temperatures just above the T_g, approaching zero at temperatures near the SmC*–SmA transition. The presence of a tilted phase is rather unusual for such derivatives since smectic C phases are only reported in steroidal systems with aromatic ester and carbonate substituents [20], or in cholesteric acid derivatives hydrogen-bonded to rod-like mesogenic pyridine derivatives [21]. It is therefore evident that the presence of the cholesteric moiety in the dendrimeric ionic scaffold plays a crucial role in the formation of the tilted phase, either by freezing the rotation of the cholesterol moiety or by changing the strength of the dipole–dipole interaction that determines whether or not a smectic C phase is observed [19].

At this point it is interesting to compare the lamellar spacings in the SmA phase of the dendrimeric salts with those of the covalently cholesterol-functionalized dendrimeric derivatives (figure 4). For the low generation ionic compounds the thicknesses of the lamellae are higher than those of the covalently functionalized cholesteric derivatives. This can be the result of the ionic character of the dendrimeric scaffold which expands due to the presence of the positive charges [22]. Upon increasing the dendrimer generation, on the other hand, the thicknesses of the layers are lower than those of the covalently functionalized dendrimeric derivatives. This is probably because the cholesterol units are penetrating inside the dendrimeric branches. The opposite is true for the low generation dendrimers, in which encapsulation of cholesterol units is not favoured since these molecules are structurally similar to low molar mass compounds. It can be inferred that significant cholesterol encapsulation starts at the third generation dendrimeric derivative (DAB-CA_3) which, as a result, has a *d*-spacing slightly lower than that of DAB-CA_2.

4. Concluding remarks

The degree of multi-protonation of the primary amino groups as compared with that of the tertiary amino groups for these dendrimeric-cholesterol based salts is crucial in determining their supramolecular structure. In turn, due to these structural features, smectic C* phases are obtained at low temperatures, and are transformed to smectic A phases at higher temperatures.

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