Liquid Crystals Derived from Hydrogen-Bonded Supramolecular Complexes of Pyridinylated Hyperbranched Polyglycerol and Cholesterol-Based Carboxylic Acids

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ABSTRACT: A hyperbranched polyether polyol was reacted with isonicotinoyl chloride hydrochloride for the introduction of the pyridinyl moiety at the external surface. This pyridinylated hyperbranched polymer was subsequently interacted with cholesterol-based carboxylic acids for the formation of the corresponding hydrogen-bonded supramolecular complexes. The materials obtained exhibited smectic A liquid crystalline phases over a broad thermal range from room temperature up to above 170 °C. Within this smectic layer the cholesterol moieties are located above and below the hyperbranched scaffold. Increasing the spacer length, located between the carboxylic group and the cholesterol moiety, the temperature range of the liquid crystalline phases of the complexes is lowered.

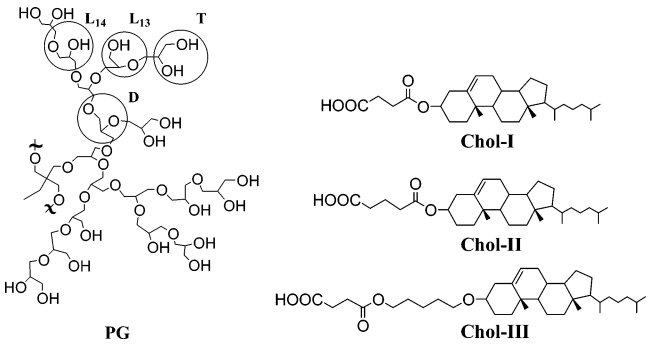
Introduction

The introduction of mesogenic groups at the external surface of dendrimers[1] has been established as a strategy for the preparation of liquid crystals.[2] In most cases the mesogenic groups have been primarily attached covalently at the surface groups of dendrimers. The same strategy has been employed for the preparation of hyperbranched liquid crystalline polymers.[3] On the other hand, noncovalent synthesis for the preparation of supramolecular complexes based on dendrimers exhibiting liquid crystalline character has received limited attention.[4]

Extensive work has been conducted during the past decade for preparing liquid crystals derived from hydrogen-bonding interactions between a diversity of complementary molecules.[5] In a recent paper we have reported the synthesis and characterization of hydrogen-bonded dendrimeric liquid crystals.[6] However, to our knowledge at least, analogous hydrogen-bonded supramolecular complexes based on hyperbranched polymers have not yet been reported, and this is one of the reasons for undertaking this investigation. For preparing this type of hydrogen-bonded complexes a two-stage strategy can be followed: Initially, at the external groups of hyperbranched polymers recognizable moieties are attached, which interact, at a second stage, through hydrogen bonding with mesogenic molecules bearing complementary moieties. The resulting hydrogen-bonded materials can potentially exhibit liquid crystalline character.

In the present study pyridinyl moieties were introduced at the external surface of a polyglycerol (hyperbranched polyether polyol, M_n = 5000, PG) through esterification of its hydroxy groups with isonicotinoyl chloride hydrochloride. Pyridinyl groups were subsequently interacted, through hydrogen bonding with succinic acid monocholesteryl ester, Chol-I, pentanedioic acid monocholesteryl ester, Chol-II, or succinic acid mono(5-cholesteryloxypentyl) ester, Chol-III (Scheme 1). In this manner, cholesteryl moieties were noncovalently attached at the external surface of the hyperbranched polymer, and the role of the spacers in modifying the liquid crystalline character of these supramolecular complexes was investigated. Hydrogen-bonding formation was established by FT-IR spectroscopy while the liquid crystalline character of the hydrogen-bonded complexes was identified with polarized optical microscopy and differential scanning calorimetry and established by X-ray diffraction.

Scheme 1



Experimental Section

Materials. Hyperbranched polyether polyol (polyglycerol M_n = 5000, M_w/M_n = 1.5, PG) bearing 68 hydroxy groups according to the technical data sheet, was purchased from Hyperpolymers GmbH, Germany. The polyglycerol backbone consists[7] of linear (L), dendritic (D), and terminal (T) units (Scheme 1). L_{13} and L_{14} describe the two different glycerol-like units, in which either a primary/secondary or primary/primary ether linkage is formed, respectively. Isonicotinoyl chloride hydrochloride [4-(chlorocarbonyl)pyridinium chloride], *p*-toluenesulfonyl chloride, and DMAP were obtained from Aldrich. Glutaric anhydride, succinic anhydride, cholesterol, and 1,5-pentanediol were purchased from Lancaster.

Synthesis of Cholesterol-Based Carboxylic Acids. Succinic acid monocholesteryl ester, Chol-I, was prepared by a method previously described.[8] Mp = 178.1 °C.

Pentanedioic acid monocholesteryl ester, Chol-II, was prepared by an analogous method. Specifically, to a stirred suspension of cholesterol (5.17 mmol, 1 equiv) in 20 mL of acetone, glutaric anhydride (9.31 mmol, 1.8 equiv) and triethylamine (1.8 equiv) were added, and the mixture was refluxed for 3 days under an inert atmosphere. The completion

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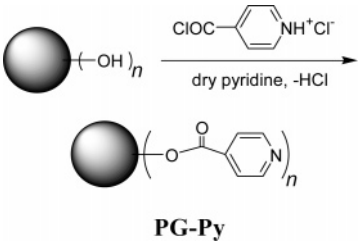
of the reaction was confirmed by TLC analysis. The solvent was removed, and the product was redissolved in dichloromethane (20 mL). The resulting solution was washed sequentially with aqueous 0.5 N HCl, saturated NH_4Cl, and water. The organic phase was dried over anhydrous magnesium sulfate, and the solvent was evaporated. The residue was recrystallized twice from ethanol, giving a solid material (yield 71%); mp 131−133 °C. The NMR signals were in line with those reported in the literature for analogous compounds.[9] ^{1}H NMR (300 MHz, CDCl3): δ = 5.30 (d, H_{6a}), 4.54 (m, H_{3a}), 2.37 (t, HOOCCH_2), 2.30 (t, CH_2COO), 2.24 (d, H_4), 2.00−1.85 (m, HOOCCH$_2$CH_2), 2.05−0.50 (m, cholesterol skeleton). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 178.8 (HOO*C*), 172.3 (*C*OO), 139.6 (C_5), 122.7 (C_6), 74.1 (C_3), 56.7 (C_{14}), 56.1 (C_{17}), 50.0 (C_9), 42.3 (C_{13}), 39.7 (C_{16}), 39.5 (C_{24}), 38.1 (C_4), 36.9 (C_1), 36.6 (C_{10}), 36.2 (C_{22}), 35.8 (C_{20}), 33.5 (HOOC*C*H$_2$), 32.9 (*C*H$_2$COO), 31.9 (C_7), 31.8 (C_8), 28.2 (C_{12}), 28.0 (C_{25}), 27.8 (C_2), 24.3 (C_{15}), 23.8 (C_{23}), 22.8 (C_{27}), 22.6 (C_{26}), 21.0 (C_{11}), 19.9 (*C*H$_2$CH$_2$COO), 19.3 (C_{19}), 18.7 (C_{21}), 11.8 (C_{18}). LRMS: [M + Na$^+$] 523, [M + 2Na$^+$] 545. Anal. Calcd for $C_{32}H_{52}O_4 \cdot {}^1/_2H_2O$: C, 75.40; H, 10.48. Found: C, 75.47; H, 10.50.

Succinic acid mono(5-cholesteryloxypentyl) ester, Chol-III, was prepared in three steps following a method analogous to the one reported by Ringsdorf et al.[10] A solution of cholesterol (2.58 mmol, 1 equiv) in 40 mL of dichloromethane was treated with *p*-toluenesulfonyl chloride (3.62 mmol, 1.4 equiv), DMAP (0.26 mmol, 0.1 equiv), and triethylamine (1.1 mL, 3 equiv) at room temperature for 2 days under an inert atmosphere. The reaction mixture was washed with 5% aqueous $NaHCO_3$ and water, and subsequently, the organic layer was dried over anhydrous $MgSO_4$. Finally, the solvent was removed, and the solid was subjected to column chromatography (silica gel, petroleum ether/ethyl acetate 9:1) to give the 3β-*p*-toluenesulfonyloxycholest-5-ene (yield 72%); mp 130−132 °C. The NMR signals were identical to those reported in the literature.[11] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, 2H, aryl-H), 7.26 (d, 2H, aryl-H), 5.22 (broad s, H_{6a}), 4.25 (m, H_{3a}), 2.40 (s, 3H, p-CH_3), 2.44−0.50 (m, cholesterol skeleton).^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 144.4 (p-C), 138.8 (C_5), 134.6 (i-C), 129.7 (o−C), 127.6 (m−C), 123.5 (C_6), 82.4 (C_3), 56.6 (C_{14}), 56.1 (C_{17}), 49.9 (C_9), 42.2 (C_{13}), 39.6 (C_{16}), 39.5 (C_{24}), 38.8 (C_1), 36.8 (C_{10}), 36.3 (C_4), 36.1 (C_{22}), 35.7 (C_{20}), 31.8 (C_7), 31.7 (C_8), 28.6 (C_{12}), 28.2 (C_{25}), 28.0 (C_2), 24.2 (C_{15}), 23.8 (C_{23}), 22.8 (C_{27}), 22.5 (C_{26}), 21.6 (p-CH_3), 21.0 (C_{11}), 19.1 (C_{19}), 18.7 (C_{21}), 11.8 (C_{18}). LRMS: [M$^+$] 540.

Subsequently, to a suspension of 3β-*p*-toluenesulfonyloxycholest-5-ene (2.77 mmol, 1 equiv) in 25 mL of anhydrous dioxane, 1,5-pentanediol (27.7 mmol, 10 equiv) was added, and the mixture was stirred under reflux for 2 days under a dry nitrogen atmosphere.[12] The solvent was removed under vacuum, and the residue was dissolved in $CHCl_3$ (20 mL) and washed sequentially with water, saturated $NaHCO_3$, water, and brine. The organic phase was dried over anhydrous $MgSO_4$. The extract was concentrated and subjected to column chromatography (silica gel, using petroleum ether/ethyl acetate 9:1 to 1:1), giving cholest-5-en-3β-oxy-pentan-5-ol as a colorless product (yield 61%); mp 101−103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.29 (d, $H_{6\alpha}$), 3.62 (t, HOCH_2CH$_2$), 3.42 (t, CH$_2$CH_2O), 3.08 (m, $H_{3\alpha}$), 2.42−0.50 (m, HOCH$_2$CH_2CH_2CH_2-CH$_2$O, cholesterol skeleton).^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 141.0 (C_5), 121.4 (C_6), 79.0 (C_3), 67.9 (CH$_2$*C*H$_2$O), 62.7 (HO*C*H$_2$CH$_2$), 56.7 (C_{14}), 56.1 (C_{17}), 50.1 (C_9), 42.3 (C_{13}), 39.7 (C_{16}), 39.5 (C_{24}), 39.1 (C_4), 37.2 (C_1), 36.8 (C_{10}), 36.1 (C_{22}), 35.7 (C_{20}), 32.4 (HOCH$_2$*C*H$_2$), 31.9 (C_7), 31.8 (C_8), 29.7 (*C*H$_2$CH$_2$O), 28.4 (C_2), 28.2 (C_{12}), 28.0 (C_{25}), 24.2 (C_{15}), 23.8 (C_{23}), 22.8 (C_{27}), 22.5 (C_{26}), 22.4 (*C*H$_2$CH$_2$CH$_2$O), 21.0 (C_{11}), 19.3 (C_{19}), 18.7 (C_{21}), 11.8 (C_{18}). LRMS: [M$^+$] 472.

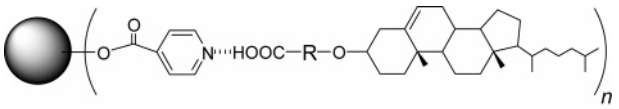
Finally, to a stirred solution of cholest-5-en-3β-oxy-pentan-5-ol (0.63 mmol, 1 equiv) in 12 mL of dichloromethane, succinic anhydride (1.01 mmol, 1.6 equiv) and triethylamine (1.7 equiv) were added. The solution was stirred under an inert atmosphere for 4 days. The solution was then diluted in 30 mL of dichloromethane and extracted sequentially with aqueous 0.5 N HCl, saturated NH_4Cl, and water. The organic phase was dried over anhydrous magnesium sulfate, and the solvent was

Scheme 2



PG-Py

Scheme 3



PGPy-Chol-N, N=I, II, III

distilled off, yielding succinic acid mono(5-cholesteryloxypentyl) ester, Chol-III (yield 51%); mp 109−111°C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.31 (d, $H_{6\alpha}$), 4.11 (t, COOCH_2CH$_2$), 3.48 (t, CH$_2$CH_2O), 3.15 (m, $H_{3\alpha}$), 2.65 (t, HOOCCH_2), 2.59 (t, HOOCCH$_2$CH_2COO), 2.39−2.10 (m, H_4), 2.09−0.5 (m, COOCH$_2$CH_2CH_2CH_2CH$_2$O, cholesterol skeleton). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 177.2 (HOO*C*), 172.2 (*C*OO), 141.0 (C_5), 121.5 (C_6), 79.2 (C_3), 67.7 (CH$_2$*C*H$_2$O), 64.8 (COO*C*H$_2$CH$_2$), 56.7 (C_{14}), 56.1 (C_{17}), 50.2 (C_9), 42.3 (C_{13}), 39.8 (C_{16}), 39.5 (C_{24}), 39.1 (C_4), 37.2 (C_1), 36.9 (C_{10}), 36.2 (C_{22}), 35.8 (C_{20}), 31.9 (C_7), 31.8 (C_8), 29.6 (*C*H$_2$CH$_2$O), 29.1, 29.0 (COOCH$_2$*C*H$_2$CH$_2$, HOOC*C*H$_2$), 28.3 (HOOCCH$_2$*C*H$_2$COO), 28.2 (C_{25}), 24.3 (C_{15}), 23.8 (C_{23}), 22.8 (C_{27}), 22.6 (C_{26}), 22.5 (*C*H$_2$CH$_2$CH$_2$O), 21.0 (C_{11}), 19.4 (C_{19}), 18.7 (C_{21}), 11.8 (C_{18}). LRMS: [M + Na$^+$] 595, [M + 2Na$^+$] 617. Anal. Calcd for $C_{36}H_{60}O_5 \cdot {}^4/_3H_2O$: C, 72.44; H, 10.58. Found: C, 72.35; H, 10.51.

Synthesis of Pyrinidylated Polyglycerol Hyperbranced Polymer (PGPy). Isonicotinoyl chloride hydrochloride (2.0 g, 11.2 mmol) was dissolved in dry pyridine, and to this solution 0.5 g (0.1 mmol, 6.8 mmol with respect to hydroxy groups) of PG was added (Scheme 2). The reaction mixture was allowed to react for 4 days at room temperature. Following condensation of the reaction mixture, the precipitated salt was removed by filtration. Subsequently, the solvent of the filtrate was distilled off, and the remaining material was dissolved in dry dimethylformamide and reprecipitated with water. The so-obtained solid material was dried over phosphorus pentoxide in a vacuum at about 45 ° C. The extent of pyridinylation was estimated by inverse gated (IG) ^{13}C NMR.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.71 (broad s, 2H, C*H*N), 7.71 (broad s, 2H, CC*H*), 5.58−4.08 (broad m, CH_2OOC, C*H*OOC next to the esterified hydroxy groups), 4.03−3.03 (broad m, CH_2, C*H* protons of the polyglycerol). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 164.2 (OCO), 150.5 (2 *C*HN), 136.7 (*C*), 122.3 (2 C*C*H), 77.9 (D), 76.4 (L_{14}, T), 72.7 (L_{14}, T), 72.2−67.5 (2D, 2T, L_{14}, L_{13}), 67.4−66.4 (T) 65.1−63.3, 59.7 (T, L_{13}).

Formation of Hydrogen-Bonded Complexes by the Interaction of PGPy with Cholesterol-Based Acid Derivatives. To 1 mmol of pyridinylated PG, dissolved in dry DMF, 50 mmol of a cholesterol-based acid derivative (Chol-I, Chol-II, or Chol-III) was added. This ratio corresponds to the number of all the primary and secondary terminal as well as of the primary L_{13} groups (see below). The solvent was distilled off under reduced pressure, and the remaining material was extensively dried under vacuum. Subsequently, these materials were heated at temperatures above the melting points of the corresponding acids and slowly cooled, affording the PGPy−Chol-*N* complexes (Scheme 3), where *N* denotes the number of the corresponding acid derivative.

Characterization. The thermal stability of the hyperbranched complexes was studied by thermogravimetry employing a TGA-2050 instrument (TA Instruments) with heating rates of 5 °C min^{-1}. Liquid crystal textures were observed using a Leitz-Wetzlar polarizing microscope equipped with a Linkam hot stage. Thermotropic polymorphism was investi-

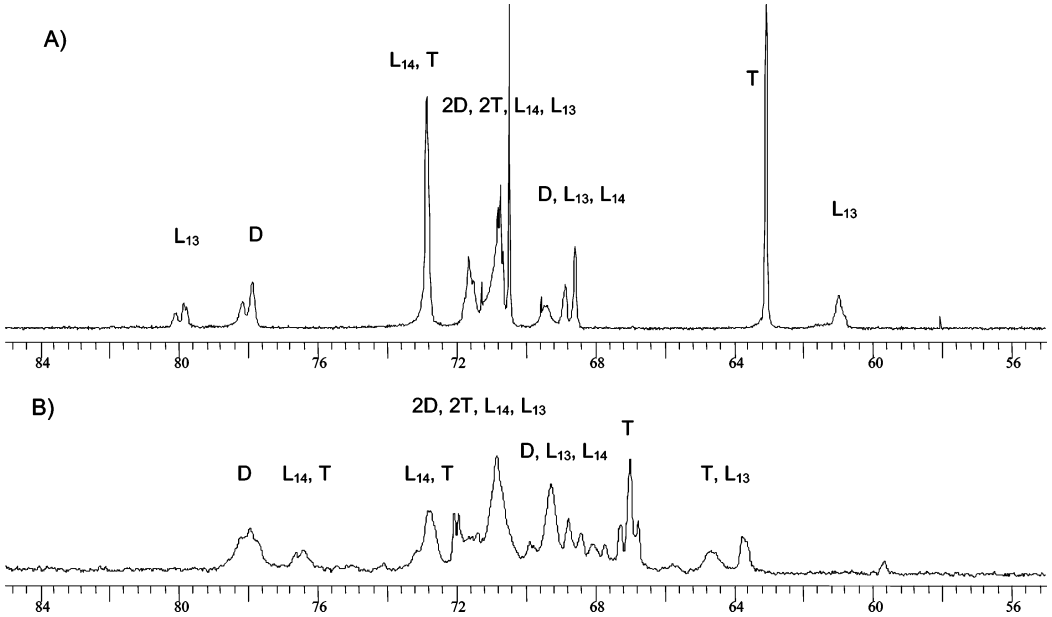


Figure 1. ^{13}C NMR spectra (DMSO-d_6) of the polyglycerol, PG (A), and the pyridinylated polyglycerol, PGPy (B). Carbons in the terminal, dendritic, linear 1,3, and linear 1,4 units are indicated by T, D, L_{13}, and L_{14}, respectively.

gated by differential scanning calorimetry employing a DSC-10 calorimeter (TA Instruments) operating under nitrogen at heating and cooling rates of 10 °C min^{-1}. The thermal behavior was registered during the second heating run, i.e., after first heating the samples above the melting temperature of the corresponding hydrogen-bonded complexes. Liquid crystalline phases of the complexes were also investigated by X-ray diffraction, using Cu Kα 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. FT-IR studies were performed using a Nicolet Magna spectrometer at a resolution of 4 cm^{-1}.

Results and Discussion

From inverse gated ^{13}C NMR experiments conducted in PG itself, in which the prerequisites for the reliable integration of the signals are fulfilled,[7a,b] the percentage of the four different structural units of polyglycerol was estimated. As already mentioned, the polyglycerol backbone consists of linear (L), dendritic (D), and terminal (T) units, while L_{13} and L_{14} describe the two different glycerol-like units (Scheme 1). In accordance with calculations previously reported for this type of hyperbranched polyglycerols,[7b] it was found that in the polymer used the T units comprise the 34% and the D units the 27%, while the linear units comprise 39% in total (11% L_{13} and 28% L_{14}). Regarding the hydroxy groups, it was found that the primary and secondary terminal hydroxy groups (T) comprise the 64% of the total hydroxy groups of the polymer, while the primary L_{13} and the secondary L_{14} hydroxy groups the 10.5% and 25.5%, respectively.

Pyridinylation of PG was conveniently achieved by esterification employing isonicotinoyl chloride hydrochloride under mild experimental conditions. The resulting pyridinylated polyglycerol, PGPy, was obtained in the form of a thick paste not showing any mesomorphism. Ester bond formation was confirmed by the appearance in the ^1H NMR spectra of characteristic signals between 4.08 and 5.58 ppm, corresponding to the α-methylene and methine protons of PG adjacent to the ester bond and of two broad signals at 7.71 and 8.71 ppm attributed to the two different aromatic protons of the pyridinyl moiety. It was found that almost all the primary hydroxy groups of the polymer (T and L_{13}) were pyridinylated, while the secondary (T and L_{14}) hydroxy groups were also pyridinylated but to a lesser extent. This was established by the disappearance of the signals due to the α- and β-methylene and methine carbons relative to the two different primary hydroxy groups at 61.0 (L_{13}), 63.1 (T), 70.5 (T), and 79.6−80.3 ppm (L_{13}) in the ^{13}C NMR spectra, which have been assigned according to previous reports,[7b,c] along with the partial disappearance of the respective signals relative to the two different secondary hydroxy groups at 68.6 (L_{14}), 70.5 (T), 71.6 (T), and 72.8 ppm (L_{14}) (Figure 1). The ester bond formation was also confirmed by the concurrent appearance of the signals at 63.7, 64.7, 66.7, 67.0, 67.2, 71.9, 72.0, and 76.4 ppm attributed to the α-methylene and methine carbons relative to the ester groups. In addition, the carbonyl carbon appeared at 164.2 ppm, while the aromatic carbons of the pyridinyl group appeared at 122.3, 136.7, and 150.5 ppm.

Inverse gated (IG) ^{13}C NMR experiments of PGPy were conducted in order to estimate the percentage of the esterification. By calculating the integral ratio of the total area corresponding to all polymer's carbons to the pyridinyl aromatic carbons, it was found that ~85% of the total hydroxy groups have been esterified. As discussed above, all the primary T and L_{13} hydroxy groups (42.5% of the total) as well as the majority of the secondary groups were functionalized. It is reasonable to assume that the most of the secondary T groups (32% of the total) were also substituted in preference to the less accessible secondary L_{14} hydroxy groups. It has to be mentioned that complete functionalization was not achieved due to steric hindrance, and similar results have been reported in the case of cyanobiphenyl functionalized hyperbranched polyether polyols.[3a,b] Taking into account the fact that each hyperbranched polymer is bearing 68 hydroxy groups (according to the technical data sheet), which was also confirmed with the IG ^{13}C NMR experiments, the average number of the esterified hydroxy groups is approximately 58.

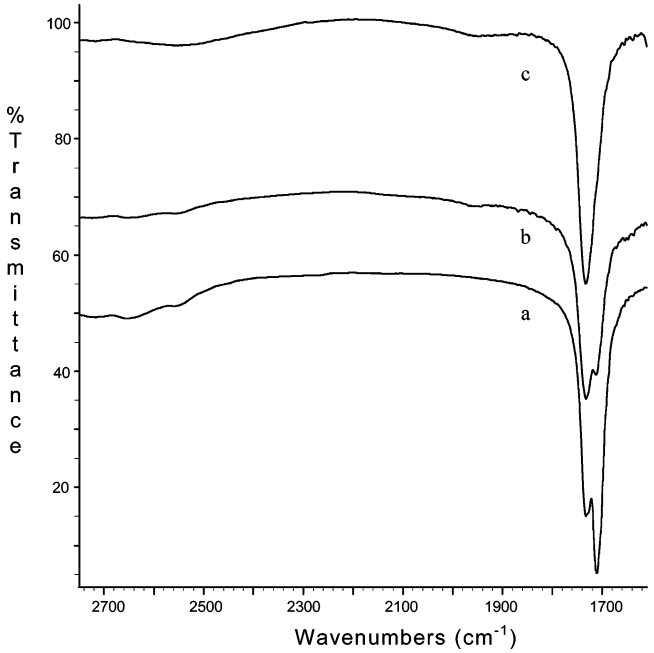


Figure 2. Infrared spectra of (a) succinic acid monocholesteryl ester, Chol-I, (b) mixture of PGPy with Chol-I resulting after evaporation of their DMF solution, and (c) of the hydrogen-bonded complex PGPy−Chol-I obtained after heating the previous sample at 180 °C, i.e., above the melting temperatures of the cholesteric acid derivative.

As mentioned in the Experimental Section, hydrogen-bonded complexes were obtained by the interaction of the cholesterol acid derivatives and the pyridinylated hyperbranched polymer PGPy at a 50:1 molar ratio to secure hydrogen bond formation between the acid and the more accessible T and L_{13} pyridine moieties. In this connection, it should be noted that variations in the degree of functionalization with mesogenic moieties in liquid crystalline derivatives of hyperbranched polyether polyols had no effect on the type of mesophase observed.[3a,b] The complexes were formed by slow evaporation of their DMF solution under vacuum and subsequent heating the samples above the melting temperature of the corresponding acids. The formation of hydrogen-bonded complexes was established by infrared spectroscopy. At room temperature, the infrared spectra of the obtained mixtures do not result from a superposition of the spectra of the pure components. Specifically, the carbonyl band of the carboxylic acids, centered between 1708 and 1710 cm^{-1} for the different cholesterol-based acid derivatives (Figure 2a), shifted to higher wavelengths upon hydrogen bond formation. Thus, in the spectra of the complexes (Figure 2c) only one band is present centered at 1732 cm^{-1} which results from the superposition of the ester carbonyl band of the acids at 1737 cm^{-1} and that of the PGPy at 1732 cm^{-1}. A second derivative analysis of this band clearly reveals the presence of four bands located at 1719, 1726, 1732, and 1737 cm^{-1} for all the PGPy−Chol complexes. The presence of the two new bands at 1719 and 1726 cm^{-1} suggests the formation of hydrogen bonds with a double minimum-energy potential.[13] Additionally, in the spectra of the pure acids that are present in the dimeric form, the bands at about 2650 and 2560 cm^{-1} which are attributed to OH Fermi resonances are replaced in the spectra of PGPy−Chol complexes by new bands at 2550 and 1960 cm^{-1} as a result of intermolecular hydrogen bonding between the nitrogen of the pyridine ring and the hydroxy group of the carboxylic acid.[14] On the other hand, it has to be noted that simple evaporation of their DMF solution, which is usually employed for the formation of similar low-molecular-weight complexes,[5,13] is not sufficient to obtain complete complex formation (Figure 2b).

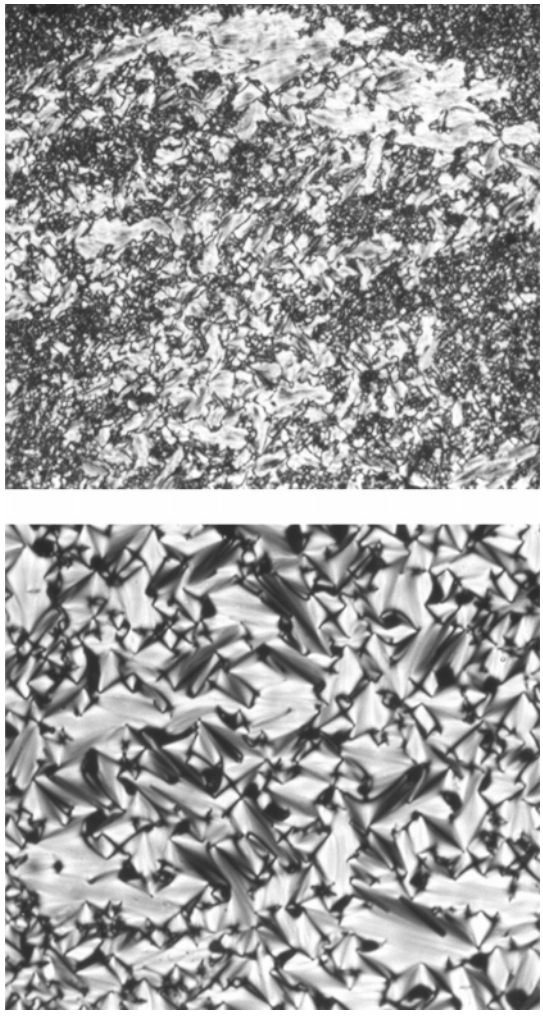


Figure 3. Optical textures of PGPy−Chol-I (top) and PGPy−Chol-II (bottom) in the smectic A phase observed by polarizing microscopy.

Table 1. Thermal Transitions of Hydrogen-Bonded PGPy Complexes with Cholesterol-Based Carboxylic Acids

complex	T_g/°C	T_k/°C (ΔH/J g^{-1})	T_s/°C (ΔH/J g^{-1})	T_i/°C (ΔH/J g^{-1})
PGPy−Chol-I		155.1 (14.6)	167.9 (2.2)	177.8 (1.35)
PGPy−Chol-II	10.5			152.5 (1.9)
PGPy−Chol-III	−8.5			117.0 (2.5)

The thermotropic liquid crystal polymorphism of the complexes was investigated by polarizing optical microscopy and differential scanning calorimetry. The PGPy−Chol-I complex exhibited a crystalline−crystalline transition at about 160 °C, and it was then transformed to a birefringent fluid at temperatures above ca. 170 °C, becoming isotropic at temperatures above 180 °C. On cooling well-developed fan-shaped textures were observed (Figure 3, top), suggesting the presence of a smectic A phase. On further lowering the temperature, crystal formation was shown, however, with a significant hysteresis of about 50 °C. This polymorphic behavior was confirmed by DSC (Table 1). On the other hand, the PGPy−Chol-II and PGPy−Chol-III complexes, having a longer spacer between the

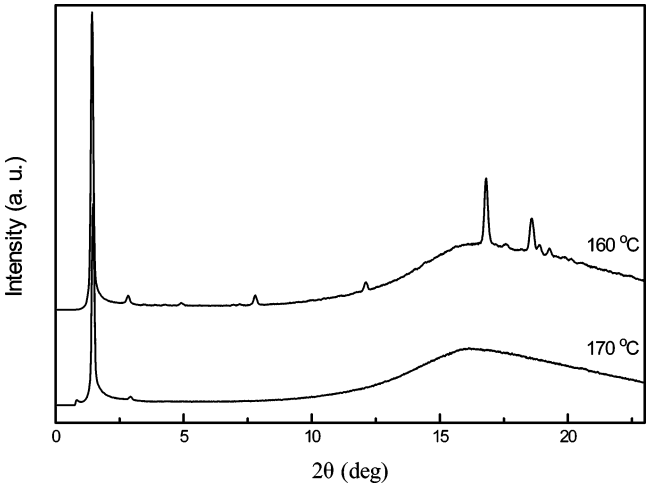


Figure 4. X-ray diffraction patterns of PGPy−Chol-I in the crystalline smectic and smectic A phase.

cholesterol moiety and the carboxylic acid group, exhibit liquid crystalline phases at room temperature becoming isotropic at significantly lower temperatures, i.e, at about 150 and 115 °C for PGPy−Chol-II and PGPy−Chol-III, respectively. On cooling from the isotropic phase, they also produce well-developed fan-shaped textures (Figure 3, bottom). The DSC results were in line with the polarizing optical microscopy observations, while they additionally established the presence of a glassy phase at temperatures below 10.5 °C for PGPy−Chol-II and −8.5 °C for PGPy−Chol-III (Table 1). It is interesting to note that even an additional methylene group in the spacer of PGPy−Chol-II significantly changes its thermal behavior compared to PGPy−Chol-I. This can be attributed to the odd−even effect commonly encountered in liquid crystalline compounds.

Thermogravimetric experiments showed that the hydrogen-bonded complexes are all thermally stable up to their isotropization temperatures. Significant weight losses were registered about 20 °C above their smectic to isotropic transition. They are therefore more thermally stable than the analogous poly(ethylene imine) dendrimeric hydrogen-bonded complexes.[6]

X-ray experiments confirmed the polymorphism observed by polarizing optical microscopy and DSC. The X-ray diffractograms of PGPy−Chol-I at room temperatures contained a number of sharp Bragg reflections in the small- and wide-angle region, revealing the presence of a well-developed three-dimensional lattice. The reflections are different from those registered for Chol-I, clearly confirming the formation of a pyridine−acid complex. Additionally, a broad peak present at the wide-angle region centered at ∼4.5 Å suggests that although the cholesterol moieties are organized in a three-dimensional structure, the hyperbranched polymeric scaffold is, as expected, in a disordered conformation.

On heating above the first transition, the X-ray diffractograms (Figure 4) give evidence for the evolution of a three-dimensional molecular ordering with a lamellar structure. They contain more than two equidistant sharp reflections in the small-angle region with a lamellar period of 62.4 Å at 160 °C and a broad peak together with a number of sharp reflections in the wide-angle region as a result of interlayer correlations, suggesting the presence of a crystalline smectic phase. On further heating above the second thermal transition, in the smectic A phase, the diffraction pattern contains two

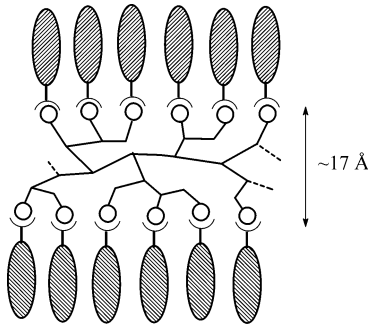


Figure 5. Schematic representation of the proposed molecular structure of the hydrogen-bonded complexes in the smectic A phase. For simplicity, only a portion of the dendritic branches is shown as straight lines, while pyridine and cholesteryl moieties are shown as circles and ellipses, respectively.

small-angle equidistant sharp reflections related to a smectic layering with a lamellar thickness of 60.5 Å at 170 °C and a diffuse halo in the wide-angle region, consisting of two partially overlapping broad peaks centered at 5.5 and 4.5 Å representing respectively the mean lateral distance of cholesterol moieties and of the branches of the dendritic scaffold that are in a disordered state. On further heating above the clearing temperature, the diffraction pattern confirms the presence of an isotropic melt. On cooling, even with very slow rates, the smectic A phase can be observed even below 120 °C. On the other hand, fast cooling (>20 °C min^{-1}) preserves the smectic A phase down to room temperature. In this case, the crystalline smectic phase is formed during the subsequent heating run at temperatures above 140 °C. It is therefore evident that the presence of the dendritic part imposes kinetic constraints to the formation of the thermodynamically stable crystalline phases.

The X-ray patterns of PGPy−Chol-II and PGPy−Chol-III complexes confirm the presence of smectic A phases even at room temperature. They contain three sharp equidistant small-angle peaks corresponding to smectic layer distances of 64.3 and 70.7 Å, respectively, and a halo at the wide-angle region indicating that the pyridinyl−cholesteric acid groups are arranged in a disordered fashion. The lamellar spacings decrease with increasing temperature due to the lateral expansion of the cholesterol and the hyperbranched repeating units, which is a further proof that no smectic C phases are formed. From the density of the two complexes[15] (1.07 and 1.06 g cm^{-1} for PGPy−Chol-II and PGPy−Chol-III, respectively) and the experimental lamellar spacings, we can deduce the cross-sectional area of each complex in the layers. The calculated cross-sectional area is in both cases remarkably the same (880 and 872 $Å^2$ for PGPy−Chol-II and PGPy−Chol-III, respectively). Since the cross-sectional area of the cholesterol moiety[16] is 36.6 $Å^2$, it is evident that the area occupied by each dendritic complex can accommodate ∼24 cholesterol, corresponding, within experimental error, to half of the cholesteric acid molecules in each complex. Moreover, by the known cross-sectional area of the complexes and the density of PGPy[15] (1.22 g cm^{-1}), the thickness of the dendritic part, ∼17 Å, can be deduced. It is therefore safe to assume that the hyperbranched moiety has the same dimensions in both cases adopting a rather flat conformation, which is required for the packing of the cholesterol groups in separate sublayers above and below the hyperbranched part of the complexes (Figure 5). It can be argued that the anchoring sites of the cholesteryl acid derivatives are not all located at the

external region of the hyperbranched molecule. However, because of the flexible nature of the polyether hyperbranched scaffold, the pyridyl moieties segregate to satisfy the strong tendency of the mesogenic cholesteric groups to assemble in a lamellar organization.

Conclusions

The interaction of pyridinylated polyglycerol hyperbranced polymer with cholesterol-based acids leads to the formation of supramolecular hydrogen-bonded complexes exhibiting smectic A liquid crystalline phases. When a short spacer is introduced between the carboxylic group and the cholesterol moiety, the resulting complex is a crystalline material at room temperature, exhibiting mesomorphism only at high temperatures. On the other hand, the increase of the spacer length affords materials that are mesomorphic even at room temperature.

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References and Notes

(1) (a) Dvornic, P. R.; Tomalia, A. *Macromol. Symp.* **1994**, *88*, 123−148. (b) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875−909. (c) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681−1712. (d) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665−1688. (e) Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864−883. (f) Vögtle, F.; Schalley, C. A. *Dendrimers, Topics in Current Chemistry*; Springer: Berlin, 2001. (g) Tully, D. C.; Fréchet, J. M. J. *Chem. Commun.* **2001** 1229−1239. (h) Fréchet, J. M.; Tomalia, D. A. *Dendrimers and Other Dendritic Polymers*; Wiley Interscience: New York, 2002.

(2) (a) Cameron, J. H.; Facher, A.; Lattermann, G.; Diele, S. *Adv. Mater.* **1997**, *9*, 398−403. (b) Richardson, R. M.; Ponomarenko, S. A.; Boiko, N. I.; Shibaev, V. P. *Liq. Cryst.* **1999**, *26*, 101−108. (c) Baars, M. W. P. L.; Söntjens, S. H. M.; Fischer, H. M.; Peerlings, H. W. I.; Meijer, E. W. *Chem.—Eur. J.* **1998**, *4*, 2456−2466. (d) Yonetake, K.; Masuko, T.; Morishita, T.; Suzuki, K.; Ueda, M.; Nagahata, R. *Macromolecules* **1999**, *32*, 6578−6586. (e) Bauer, S.; Fischer, H.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1589−1592. (f) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855−9866. (g) Yeardley, D. J. P.; Ungar, G.; Percec, V.; Holerca, M. N.; Johansson, G. *J. Am. Chem. Soc.* **2000**, *122*, 1684−1689. (h) Tsiourvas, D.; Stathopoulou, K.; Sideratou, Z.; Paleos, C. M. *Macromolecules* **2002**, *35*, 1746−1750. (i) Guillon, D.; Deschenaux, R. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 515−525. (j) Tsiourvas, D.; Felekis, T.; Sideratou, Z.; Paleos, C. M. *Macromolecules* **2002**, *35*, 6466−6469.

(3) (a) Sunder, A.; Quincy, M.-F.; Mülhaupt, R.; Frey, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2928−2930. (b) Quincy, M.-F.; Kautz, H.; Frey, H. *Polym. Mater. Sci. Eng.* **2001**, *84*, 647−648. (c) Zhang, X.; Chen, Y.; Gong, A.; Chen, C.; Xi, F. *Liq. Cryst.* **1998**, *25*, 767−769.

(4) Zimmerman, S. C.; Lawless, L. J. *Top. Curr. Chem.* **2001**, *217*, 95−120. (b) Percec, V.; Ahn, C.-H.; Bera, T. K.; Ungar, G.; Yeardley, D. J. P. *Chem.—Eur. J.* **1999**, *5*, 1070−1083. (c) Precup-Blage, F. S.; Schenning, A. P. H. J.; Meijer, E. W. *Macromolecules* **2003**, *36*, 565−572.

(5) (a) Paleos, C. M.; Tsiourvas, D. *Angew. Chem., Int. Ed.* **1995**, *34*, 1696−1711. (b) Paleos, C. M.; Tsiourvas, D. *Liq. Cryst.* **2001**, *28*, 1127−1161. (c) Kato, T. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; pp 969−979. (d) Tschierske, C. *Prog. Polym. Sci.* **1996**, *21*, 775−852. (e) Paleos, C. M.; Tsiourvas, D. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 257−267.

(6) Felekis, T.; Tsiourvas, D.; Tziveleka, L.; Paleos, C. M. *Liq Cryst.* **2004**, *32*, 39−43.

(7) (a) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30−35. (b) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 4240−4246. (c) Sunder, A.; Türk, H.; Haag, R.; Frey, H. *Macromolecules* **2000**, *33*, 7682−7692.

(8) Tsiourvas, D.; Felekis, T.; Sideratou, Z.; Paleos, C. M. *Liq Cryst.* **2004**, *31*, 739−744.

(9) Wilson, W. K.; Sumpter, R. M.; Warren, J. J.; Rogers, P. S.; Ruan, B.; Schroepfer, G. J., Jr. *J. Lipid Res.* **1996**, *37*, 1529−1555.

(10) Decker, G.; Ringsdorf, H. *Liq. Cryst.* **1993**, *13*, 57−69.

(11) Buchanan, H. J.; Cox, P. J.; Doidge-Harrison, S. M. S. V.; Howie, R. A.; Jaspars, M.; Wardell, J. L. *J. Chem. Soc., Perkin Trans.* **1997**, *1*, 3657−3664.

(12) Krishnan-Ghosh, Y.; Gopalan, R. S.; Kulkarni, G. U.; Bhattacharya, S. *J. Mol. Struct.* **2001**, *560*, 345−355.

(13) (a) Tian, Y.; Su, F.; Zhao, Y.; Luo, X.; Tang, X.; Zhao, X.; Zhou, E. *Liq. Cryst* **1995**, *19*, 743−748. (b) Sideratou, Z.; Tsiourvas, D.; Paleos, C. M.; Skoulios, A. *Liq Cryst.* **1997**, *22*, 51−60. (c) Kato, T.; Fujishima, A.; Fréchet, J. M. J. *Chem. Lett.* **1990**, 919−922. (d) Lee, J. Y.; Painter, M. M. *Macromolecules* **1988**, *21*, 954−960.

(14) (a) Odinokov, S. E.; Mashkovsky, A. A.; Glazunov, V. P.; Iogansen, A. V.; Rassadin, B. V. *Spectrochim. Acta A* **1976**, *32*, 1355−1363. (b) Johnson, S. L.; Rumon, K. A. *J. Phys. Chem.* **1965**, *69*, 74−86.

(15) The density of the compounds was measured at 23 °C by determining the weight of a 1 mL volume-calibrated pycnometer filled with spectroscopic grade acetonitrile in which about 0.2 g of polymer sample was immersed.

(16) Craven, B. M.; DeTitta, G. T. *J. Chem. Soc., Perkin Trans. 2* **1976**, 814−822.

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