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A "side-on" liquid crystalline polymer with the cholesterol moiety

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Summary

Starting from cholesterol a new type of liquid crystalline side-chain polymer is synthesized whose cholesterol moiety is attached laterally to the polymer backbone. Phase structure and phase transformation temperatures were determined, proving that the polymer forms a cholesteric phase and, according to previous results at "side-on" liquid crystalline polymers, no smectic phases exist.

1. Introduction

A vast number of cholesterol derivatives is known showing liquid crystal (l.c.) phases above the melting point. In all these substances the steroid ring system forms the rigid rod-like part of the mesogenic moiety, in which the hydroxy group of cholesterol has been subject to chemical variation by forming esters, ethers or carbonates (Lit. 1-6). Smectic or cholesteric phases exist, depending on the chemical constitution of the substituents at the hydroxy group. The l.c.-phase behaviour of all these compounds has been intensively investigated (Lit. 7-8). The introduction of polymerizable groups at the cholesteryl moiety via the hydroxy group has also been studied (Lit. 4). While the monomeric compounds often exhibit a cholesteric phase, for the corresponding homopolymers nearly exclusively smectic phases are observed.

In contrast to the rich chemical variation at the hydroxy group no attempt has been made to form cholesterol l.c.-derivatives using the reactivity of the C_5-C_6 double bond. Responsible therefore may be the problem of forming isomers in common addition reactions, since the substituents may be oriented axially (α) or equatorially (β) to the planar steroid ring system. On the other hand for laterally substituted cholesterol monomers it can be assumed that the corresponding polymers exhibit a cholesteric phase as recently described for laterally substituted non-chiral mesogens. For these monomers and polymers exclusively nematic phases have been observed (Lit. 10).

In this paper will be presented an easy accessable synthesis path to 6-alkenyl substituted cholesteryl derivatives. The phase behaviour of a reactive monomer and a polysiloxane homopolymer will be described.

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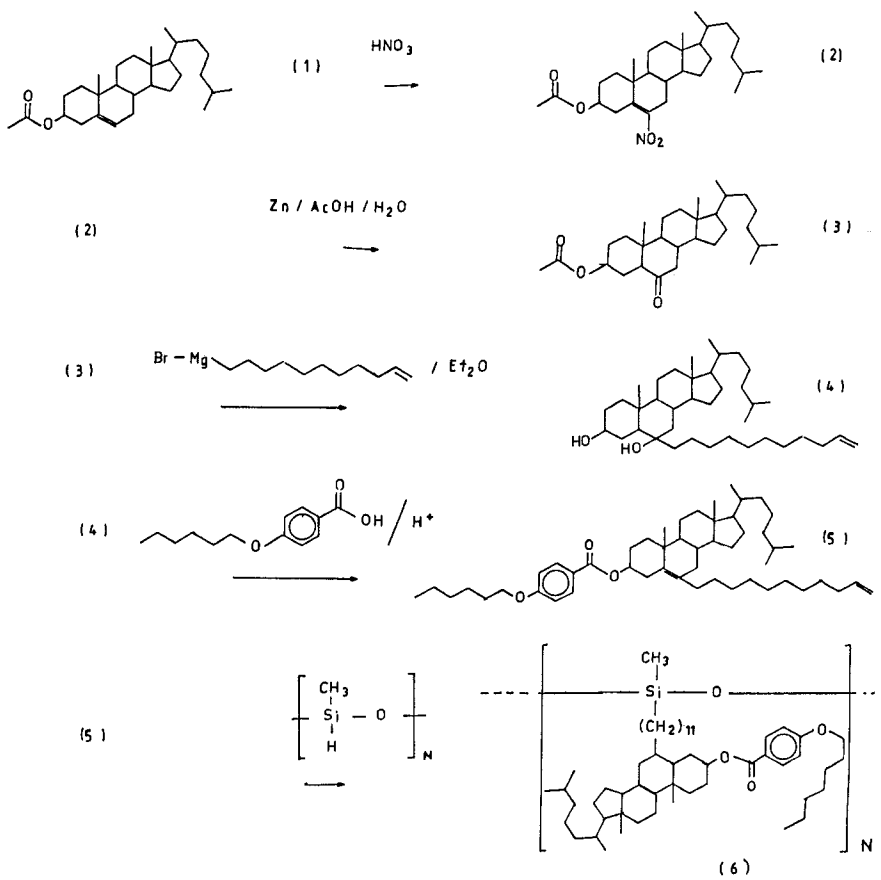
2. Synthesis

In the introduction we mentioned the problem of α/β-isomerism, which occurs when the sp^2-hybridized carbon atom C_6 of cholesterol is transformed to sp^3. This can be avoided, if in the product C_6 is also sp^2 hybridized. Our synthesis route to realize this concept is shown in the following scheme:



Scheme: Synthesis of monomer and polymer

In the first step cholesteryl acetate (1) was nitrated at the C-C double bond with HNO_3, yielding (2). Then the nitro group was converted to an oxo group by zinc-dust destillation with acetic acid in the presence of water. Thereafter the ketone (3) was transformed to the diol (4) in a Grignard-reaction. This product was esterified with 4-hexyloxybenzoic acid

under acidic conditions. In this reaction the hydroxy group at C_3 was esterified while the hydroxy group at C_5 was eliminated forming the cholesteric derivative (5) with sp^2 hybridized C_6.

The monomer (5) was added via a polymeranalogous reaction to a poly(methyl hydrogen)siloxane ($\bar{r}$=95) in the presence of a platin catalyst.

Phase behaviour

The l.c.-phase behaviour of monomer and polymer was investigated by DSC, polarization microscopy and additionally X-ray measurements for the polymer.
The monomer (5) shows a cholesteric to isotropic tranformation at 313 K. The cholesteric pitch p was determined by measurements of the selective reflexion wavelength and the average refractive index $\bar{n}$. In a range of 280 K to 312 K p varies between 888 nm and 974 nm.

DSC-measurements of the polymer show a glass transition at 308 K with a change in the heat capacity Δ cp of 0.2 J/g^{-1}. This Δcp value is of the same order as observed in isotropic or nematic polymers and suggests that no ordered layered structure exist in the polymer. At 320 K the polymer shows a first order phase transformation to the isotropic state with a phase transformation enthalpy Δ H=0.7 $J \cdot g^{-1}$. This value is typical for cholesteric phases. Polarization microscopy gave no further informations about the phase structure since the high viscosity of the polymer did not allow the formation of a specific texture. To prove the cholesteric structure suggested by DSC-data an additional X-ray measurement was performed. Actually only a broad halo without small angle reflexions is observed, which has to be expected for nematic or cholesteric systems.

Conclusion

The presented synthesis applies the concept of l.c.-side chain polymers with laterally attached mesogenic moieties to cholesterol derivatives. In contrast to polymers containing cholesterol derivated monomers with end-on fixed spacer, the new synthesis allows to obtain cholesterol derivated homopolymers exhibiting a cholesteric phase. The new polymer confirms the results on previously investigated "side-on" l.c.-side chain polymers, which indicate that the lateral substitution of mesogenic monomers strongly reduces the ability of forming smectic polymers.

Experimental

3-Acetyl-6-nitrocholesterol (2) was prepared as in lit. 9).

3-Acetyl-6-oxocholestan (3) was prepared as in lit. 9).

3,6-Dihydroxy-6-undecenylcholestan (4) was prepared by a Grignard-reaction under nitrogene atmosphere.

The Grignard-reagent was prepared from 19.8 g (80 mmol), 1-bromoundec(10)en and 1.75 g (72 mmol) Mg-turnings in 50 ml anhydrous diethylether. 5.3 g (12 mmol) (3) dissolved in 50 ml diethylether were added. The solution was stirred to 6 hours. Excess Grignard reagent then was decomposed by methanol. The precipitated salts were dissolved with 10 % aqueous hydrochloric acid. The etheral layer was washed twice with water and evaporated. The residue was recrystallized twice from CH_2Cl_2, furnishing 3.4 g (51 % yield) of white crystals with mp. 140°C.
IR: (KBr) (cm^{-1}): 3500, 2930, 1640, 1460, 1380, 1250, 790.

^{1}H-NMR: ($CDCl_3$, =ppm): 5.7 (m,1H) 4.8 (t,2H) 3,5 (s,1H) 2.1-0.7 (m,63H).

Anal. calculated: C: 82.05 % H: 11.93 %
found: C: 82.3 % H: 11.90 %

4-Hexyloxybenzoyl-6-undec(10)enylcholestanol (5) was prepared by azeotropic esterification of (4) with 4-Hexyloxybenzoic acid.
10 g (45 mmol) 4-Hexyloxybenzoic acid and 2.5 g (45 mmol) (4) were dissolved in 100 ml anhydrous $CHCl_3$. 0.29 g (0.15 mmol) 4-toluenesulfonicacidmonohydrate were added. The solution was refluxed 5 days over a water seperator filled with molecular sieves (Ø 4 Å).
Thereafter the solution was evaporated and the residue dissolved in CH_2Cl_2. When cooling to -5°C most of the non-converted 4-hexyloxybenzoic acid precipitated. The remaining solution was washed twice with saturated $NaHCO_3$ solution and dried over Na_2SO_4. The solution was concentrated and the product separated by flash chromatography yielding 1.9 g (57 % yield) of an opaque melt.
IR: (film) (cm^{-1}): 2940, 1700, 1630, 1600, 1500, 1240, 1150, 1100.

^{1}H-NMR: ($CDCl_3$, δ =ppm): 7.4 (q,4H), 5.7 (n,1H), 4.9 (t,3H), 4.0 (t,2H), 2.1-0.6 (m,72H).

Anal. calculated: C: 82.42 % H: 11.12 %
found: C: 82.52 % H: 11.15 %

MS: (chemical induction) molecule peak at 742 m/e

The polymer (6) was synthezised by polymeranalogous conversion of (5) with poly(methylhydrogen)siloxane (n = 95) in presence of a platin catalyst (SLM 86003, Wacker Chemie). Monomer and polymer were dissolved equimolar in absolute toluene, degassed with nitrogene, and the catalyst added. The solution was held 3 days at 50°C. The polymer was purified by four-time precipitation into methanol.

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