Cholesteric Solid Films Formed by Spin-Coating Solutions of Dicholesteryl Esters

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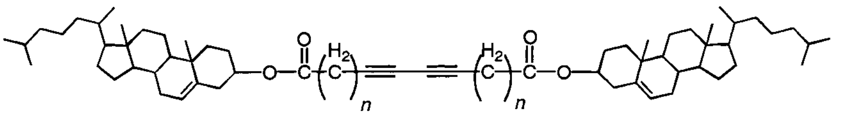
A main topic in supramolecular chemistry is the establishment of well-defined, organized, solid molecular assemblies with more than a single molecular layer.[1] The lyotropic liquid crystalline property of various compounds has been utilized for such self-assembly with formation of solid films[2] or fibers.[3] Upon removal of solvent, lyotropic polymers in solution turn into solids with retention of liquid crystalline molecular ordering. Liquid crystals with low molecular weight, on the other hand, tend to form crystals upon evaporation of solvent if the melting point of the compound is above room temperature. This is because low molecular weight compounds crystallize faster than polymers with high molecular weight and broad molecular weight distribution. Here we report that several dicholesteryl esters of diacetylene dicarboxylic acids with molecular weights higher than 1000 show surface-directed self-assembly, and form an optically reflecting solid film on spin-coating from solutions. It is verified that the reflection of the light is based on a stable helical molecular ordering in the solid film.

Dicholesteryl esters containing a diacetylene unit (DC-*n*; *n* = 2–8, 10) have a relatively high molecular weight, among the highest known for low molecular weight cholesteryl esters.



DC-*n* (*n* = 2 - 8, 10)

The diyne unit is introduced as a connector to form the symmetric molecular structure with a long hydrocarbon chain. These compounds form white crystals upon recrystallization from hexane/CH_2Cl_2 or upon removal of solvent from a solution in CH_2Cl_2. Except for DC-3, each crystal shows a clear melting point above 105 °C, no *meso* phases on heating, and a thermotropic cholesteric phase above 80 °C on cooling. All the DC-*n* esters show high solubility in, for example, benzene, halogenated solvents, and tetrahydrofuran.

If a 15 wt% solution in CH_2Cl_2 is spin-coated at 7000 rpm on to a glass plate at 22–23 °C, DC-8 forms a red solid film (Figure 1, right-hand side). The color is temperature-independent below 75 °C and changes into white above this temperature. Colored solid films are obtained from DC-6, DC-7, DC-8, and DC-10, but not from DC-2, DC-3, DC-4, and DC-5; the latter just forms white crystals. Some compounds containing diyne units are known to polymerize topochemically in the crystalline state to provide colored conjugated polymers.[4] However, all of the DC-*n* esters are chemically quite stable even under UV light, and the color disappeared when the solid film obtained after spin-coating was redissolved in solvent. Therefore the color observed after spin-coating is not due to polymerization of the diyne unit.

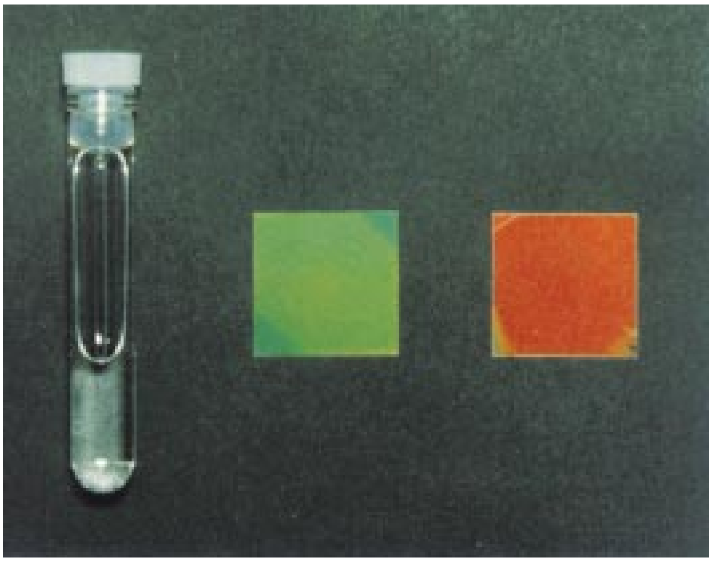


Figure 1. A photograph (taken at room temperature) of irridescent green and red solid films on glass plates obtained by spin-coating solutions of DC-8 in CH_2Cl_2 at 38–40 and 22–23 °C, respectively. A sample of the transparent, colorless solution of DC-8 is shown for comparison. The size and the thickness of the glass plates are 18 × 18 mm and 0.15 mm, respectively. The thickness of the colored solid films is around 1.8 μm.

The red film obtained with DC-8 shows a reflection band with a peak at 618 nm (width at half-height 80 nm; Figure 2), a large optical rotation dispersion in the positive sense (1.0 deg m^{-1} at maximum), and a large circular dichroism (0.9 deg m^{-1}) centered at the reflection band (Figure 3). The reflectance increases from 1 to 22% with increasing film thickness; the film thickness could be con-

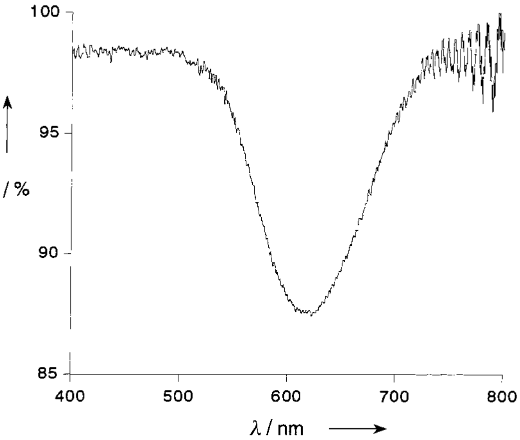


Figure 2. Transmission spectrum of the red solid film shown in Figure 1. A negative peak in the measurement of transmission is not due to absorption of the film but reflection, which is verified by the coincidence of the positions of peaks in separate measurements of reflection and circular dichroism spectra.

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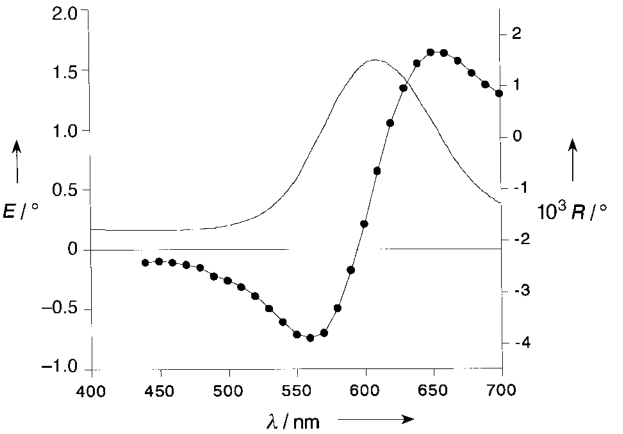

Figure 3. Optical rotation dispersion (•–•–) and circular dichroism spectrum (——) of the red solid film shown in Figure 1.

trolled between 0.5 and 2.0 μm by changing the initial concentration of the solution and the spin speed on coating. These optical features of the solid films are explained by alignment of the molecules into helices, the axes of which are perpendicular to the surface, like for molecules in a known cholesteric liquid crystalline phase.[5] The X-ray diffraction pattern of the film shows just one broad band in the wide-angle region, which is typical for cholesteric liquid crystals. We concluded that a cholesteric molecular ordering was formed and fixed during spin-coating. Although similar solid films with helical ordering have already been obtained by slow evaporation of solvent from a solution of lyotropic poly(γ-methyl glutamate)[2b, 6] or poly(γ-benzyl L-glutamate),[2a, 6] no examples for nonpolymeric compounds have been reported.

Changing the temperature of the substrate allows control of the fixed color. The two samples of DC-8 with different colors in Figure 1 were obtained by tuning the temperature. Figure 4 shows the relationship between the temperature of the substrate during coating and the wavelength of the reflection band for the colored solid films obtained (coating by the bar-coater method, see the Experimental Section). The peak shifts toward longer wavelengths (530 to 832 nm) as the substrate is cooled from 40 to 2 °C, that is, in a temperature region substantially lower than that of the thermotropic cholesteric phase of the compound. If the temperature of the substrate is set above 40 °C, DC-8 does not form the colored solid films; instead, just white crystals appear. The color also depends on the structure of the dicholesteryl compounds and the solvents used (Table 1).

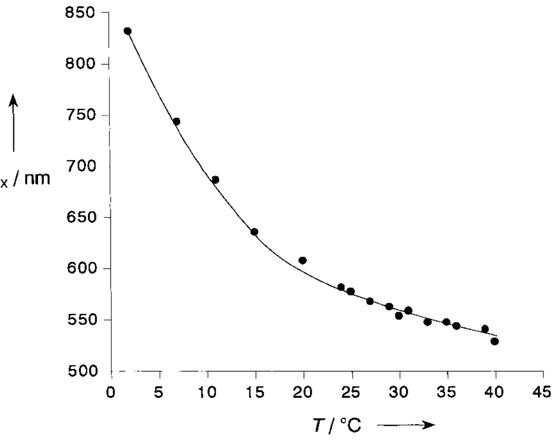

Figure 4. Relationship between the surface temperatures of the substrate and the wavelength of the transmission band for the colored solid films obtained from DC-8. The temperature was controlled and measured with a hot stage (Iuchi Thermo Plate TP-80).

Table 1. Wavelength of the peak observed in transmission spectra of colored solid films formed from DC-8 dissolved in various solvents at 25 °C.

Solvent	λ_{max} [nm]
dichloromethane	585
1,2-dichloroethane	660
chloroform	692
tetrahydrofuran	636
benzene	597

If the spinning speed is under 2000 rpm and the concentration of the solution in CH_2Cl_2 is higher than 15 wt%, or if the spinning speed is 7000 rpm and the concentration of the solution in CH_2Cl_2 is higher than 30 wt%, DC-8 forms white crystals rather than the colored film. It is impossible to obtain colored films thicker than 3 μm. This means that the molecular alignment in a helical mode is surface-directed. On a flat surface the helical axes are uniformly arranged perpendicular to the surface—the effect of the surface extends only about 3 μm. This length is far shorter than the thickness with which a uniform Grandjean texture is attainable for thermotropic cholesteric liquid crystals between a pair of glass plates. This is the reason why evaporation of a solution containing a large amount of DC-*n* in CH_2Cl_2 just resulted in white crystals.

To explain how solid films with a cholesteric molecular ordering are formed, it is reasonable to assume that dicholesteryl esters that are known to be thermotropic liquid crystals with a cholesteric phase above 80 °C show a cholesteric phase at room temperature in the presence of solvents. If the solution shows a cholesteric phase in a certain concentration range at room temperature, the mixture should change from an isotropic solution into a colored cholesteric state above a critical concentration on drying. Then the ordering of molecules can be frozen in the solid upon further drying, keeping the spatially periodic structure.

To see if the assumption is valid or not, we investigated mixtures of DC-8 and 1,2-dichloroethane in different ratios with differential scanning calorimetory (Figure 5). Pure DC-8 shows two exotherm peaks, between which a cholesteric phase is observed. Upon addition of 1,2-dichloroethane, both transitions shift toward lower temperature, and the temperature region in which the mixture shows a cholesteric phase narrows. At 81 wt% DC-8 two peaks merge into one exotherm at 47 °C. At this concentration the mixture is an isotropic solution (above 47 °C) or a crystal with a separated solvent (below 47 °C). The merged transition shifts to lower temperature as the concentration is lowered. These results indicate that mixtures of DC-8 and 1,2-dichloroethane in different ratios do not show a liquid crystalline phase at 47 °C or lower; at this temperature, coating from the solution

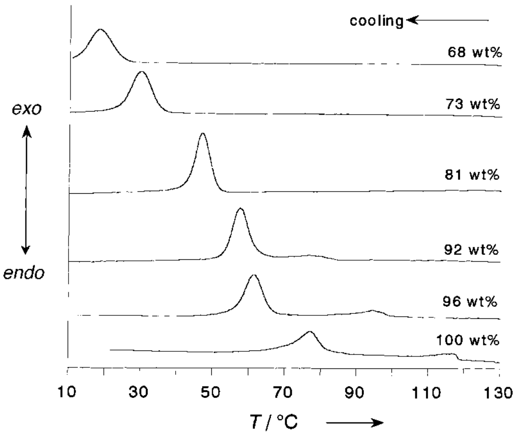

Figure 5. Differential scanning calorimetory thermograms for mixtures of DC-8 and 1,2-dichloroethane in different ratios (cooling rate 2 °C min^{-1}). The concentration of DC-8 is noted above each line.

afforded a cholesteric solid film. Although it is not clear how the solid film is constructed, it is likely that a nonequilibrated change in the concentration of the DC-8 solution on coating shifts the temperature region for the cholesteric phase to lower than that for the static thermotropic phase.

Experimental Section

Dicholesteryl esters DC-*n* ($n = 2-8, 10$) were synthesized by condensation of cholesterol and the corresponding diacids or by oxidizative coupling of the corresponding acetylene derivatives as reported.[7] MIKASA 1H-DX was used for spin-coating. The surface temperature of the substrate was controlled and monitored by a drier and an infrared thermometer (TASCO THI-400S), respectively. For bar coating, a wire bar (Tester Sangyo Co., Ltd.; no. 12) was used on a temperature-controlled stage (Iuchi THERMO PLATE TP-80).

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Al_{30}: A Giant Aluminum Polycation

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Aluminum hydrolysis plays a key role in strategic fields like catalysis, the Bayer process for aluminum production, geochemistry, soil science, water treatment, and material sciences. However, elucidation of all hydrolyzed aluminum species in solution has not yet been achieved.[1–8] Beyond the monomers $[Al(H_2O)_6]^{3+}$ and $[Al(OH)_4]^-$, only the Keggin polycation $[Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]^{7+}$ (ε-Al_{13}) has been identified by X-ray diffraction (XRD)[9–10] and characterized in solution by ^{27}Al NMR. Several other species with hitherto unidentified ^{27}Al NMR signals at $\delta = 4$, 64.5, 70, and 76 were observed, along with broad signals in the 5 – 12 ppm range. Despite the numerous aforementioned studies, no new assignment has been established. In this in situ ^{27}Al NMR study, thermal treatment of a ε-Al_{13} solution evolves the new polycation $[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$ (Al_{30}). The $\delta = 70$ and 7 – 12 NMR signals are now definitely assigned to this species. The Al_{30} precipitated as a sulfate and its established structure consists of two δ-Al_{13} Keggin units linked by four AlO_6 octahedra. Although polyanions reach considerably larger sizes,[11] Al_{30} is unique by its size. It is the biggest polycation ever characterized, and the δ-Al_{13} units have never before been observed, neither in polycation nor polyanion chemistry.

Polycations are usually based on Keggin structures and described in polyoxometalate chemistry.[12–15] Keggin ions isomerize under five forms, α, β, γ, δ, and ε, shown in Figure 1 a.

Tungstate and molybdate polyanions usually exhibit α- and β-Keggin structures (with or without cation vacancies) and can lead to pseudo-Keggin dimers by condensation.[12–15] Dimerisation has never been observed for aluminum polycations, but two polycationic Al_{13} Keggin isomers are known: α-Al_{13} in the mineral zunyite[16] and ε-Al_{13}.[9, 10, 17] The ε-Al_{13} polycation is obtained from hydrolysis of an aqueous $AlCl_3$ solution by NaOH at 95 °C with a hydrolysis ratio $m_h = [OH]/[Al]$ between 1.5 and 2.5. It has a central AlO_4 tetrahedron (narrow ^{27}Al NMR signal at $\delta = 63$), surrounded by twelve corner- and edge-sharing AlO_6 octahedra (very broad NMR signal around $\delta = 12$). The 1:12 Al^{IV}:Al^{VI} ratio between peaks at $\delta = 63$ and 12 confirms the polycation structure. The α-Al_{13} cation in zunyite[16, 18] (synthesized from aluminum hydroxide and silica under hydrothermal treatment at 300 °C) has

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