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Sol-Gel Phase Transition of Switch-Functionalized Cholesterols as Detected by Circular Dichroism

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Cholesterol derivatives containing an azobenzene moiety coupled to C3 of a steroidal moiety showed the reversible sol-gel phase transition in certain organic solvents. Strong ICD spectra appeared in the gel phase, but the ICD disappeared in the sol phase. The sol-gel phase transition which accompanies the drastic ICD spectral change was synchronously induced by light-mediated cis-trans isomerism of the azobenzene moiety.

Induced circular dichroism (ICD) spectra observed for chiral molecules appear when chromophoric moieties are organized into a specific orientation: for example, higher-order structures in polypeptides can provide the backbone for helical structures required for the appearance of ICD spectra.[1] The similar (but mechanistically-different) ICD spectra appear in the liquid crystal and related systems.[2-6] It is known that the intensity of the ICD band is sensitively affected by the phase transition.[3-6] We recently synthesized several cholesterol derivatives bearing a chromophoric azobenzene moiety.[7] Quite accidentally, we found that some of them act as excellent gelators of organic fluids: recrystallization from butanol or cyclohexane-benzene mixed solvents results in "gels" of these solutions.[7] The gels showed a clear sol-gel phase transition.[7] It occurred to us that if these gelators take some specific orientation in the gel phase, the sol-gel phase transition may be conveniently detected by the ICD technique. In the present letter we report a novel, drastic ICD change induced by the sol-gel phase transition.

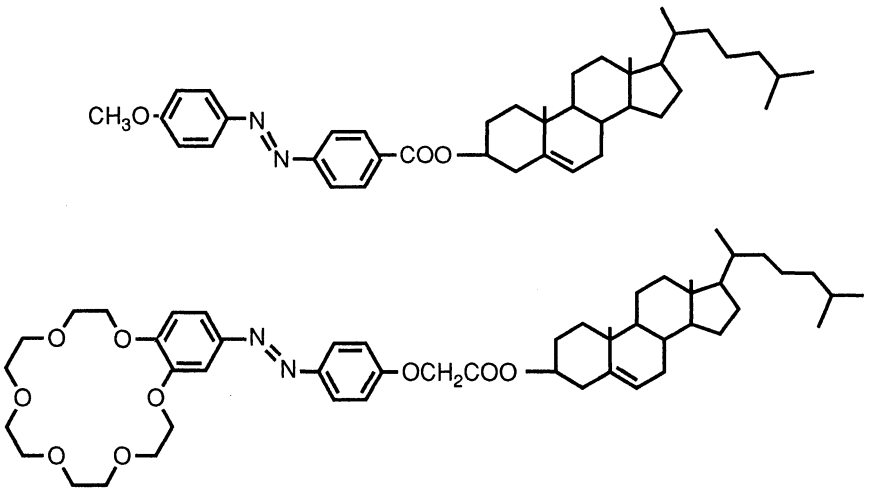
The gelator (**1** or **2**) was mixed with solvent in a septum-capped test tube and the mixture was heated until the gelator was dissolved. The solution was put into a demountable flow-through optical cell (0.20-0.05 mm) and the solution was cooled gradually to form a gel. A Jasco J-720 CD spectropolarimeter was used for the CD measurement and a Shimadzu UV-2200 spectrophotometer was used for the UV measurement. In the CD measurement, the CD spectra were not affected by the angle of the sample cell.

As shown in Fig. 2, the λ_{max} at 360 nm observed in the isotropic phase (60 °C) changed to a weak shoulder in the gel phase (22 °C) and a new absorption maximum appeared at 310 nm. In the isotropic phase the solution was totally CD-silent whereas in the gel phase an exciton coupling band appeared, which intersected the $\theta=0$ line at 310 nm (same as the λ_{max} of the absorption spectrum in the gel phase).8)

The similar absorption and CD spectral changes were observed for **2** (Fig. 3). The absorption maximum (365 nm) with a smooth Gaussian curve in the isotropic phase (60 °C) is converted to an asymmetric curve with a few shoulders in the gel phase. The CD spectra are well correlated with the absorption spectra: in the isotropic phase the solution is CD-silent whereas in the gel phase a clear exciton coupling appears which intersects the $\theta=0$ line at 365 nm (same as the λ_{max} of the absorption spectrum in the gel phase) and accompanies a few maxima at the wavelengths where the shoulders appear.

In Fig. 4, we plotted transmittance (800 nm) and maximum and minimum intensity of CD spectra for **1** against the same temperature abscissa. Transmittance sensitively decreases when the solution changes from isotropic to gel.7) It is clearly seen from Fig. 3 that two parameters change synchronously at around 40 °C. This supports the view that the appearance of the CD band is ascribed to cholesterol-dependent orientation of the azobenzene chromophore in the gel phase.

The sol-gel phase transition can be induced by light-mediated cis-trans isomerization of the azobenzene moiety.7) When the gel solution of **1** was photoirradiated by a high-pressure Hg-lamp through a Toshiba UV-D35 color filter ($330<\lambda<380$ nm), trans-to-cis photoisomerization took place and the isotropic solution resulted. As shown in Fig. 5, the CD spectrum disappears. When the isotropic solution was photoirradiated through a Toshiba Y-46 color filter ($\lambda>460$ nm), the gel solution was re-formed and the CD spectrum regenerated. The results indicate that photo-induced sol-gel phase transition occurs reversibly, which can be conveniently monitored by the CD technique.



1

2

Fig. 1.

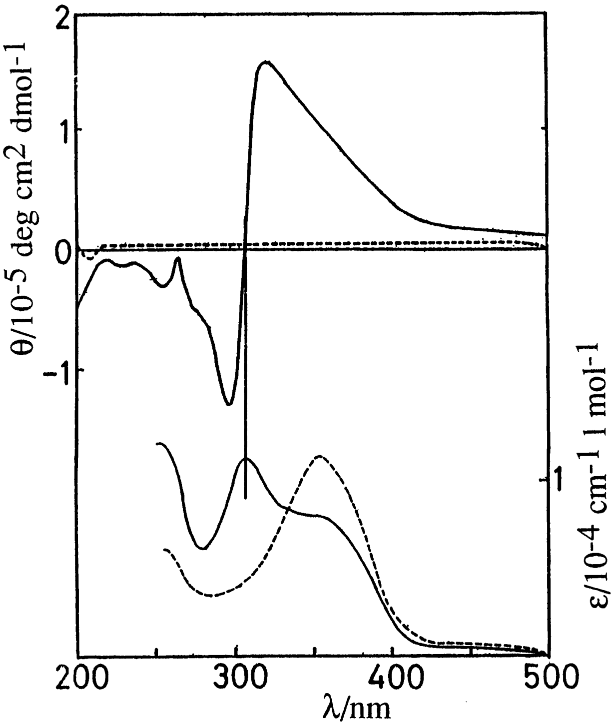


Fig. 2. CD spectra (above) and UV absorption spectra (below) for a **1**-butanol system, [**1**]= 0.2 wt%; the gel state at ca. 22 °C (———); the isotropic solution state at ca. 60 °C (------). The ε is not corrected for light scattering (also in Figs. 3 and 5).

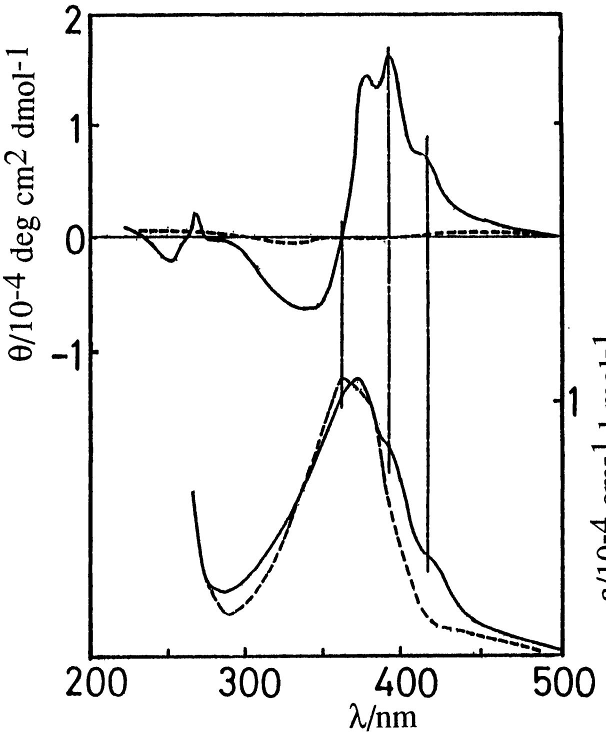
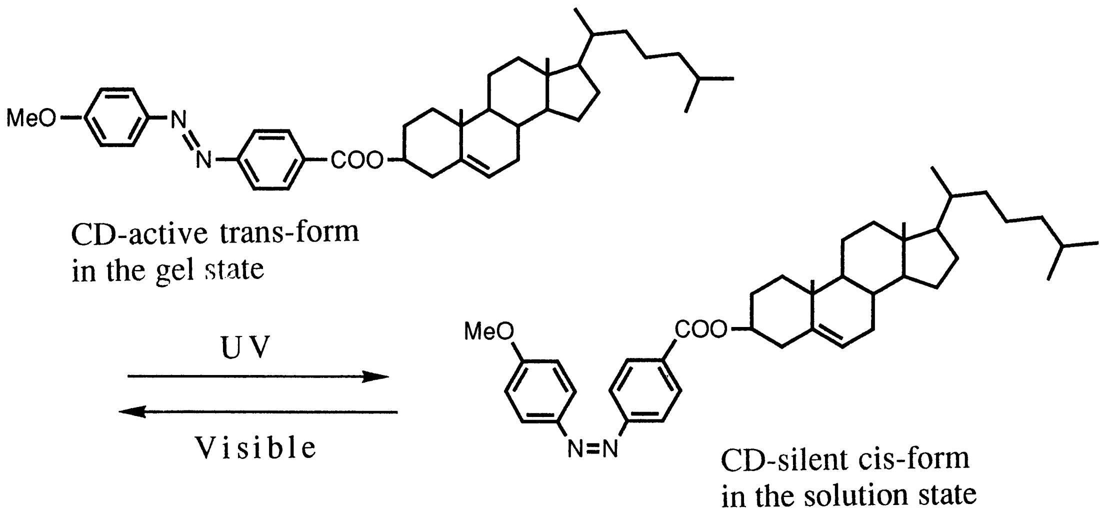


Fig. 3. CD spectra (above) and UV absorption spectra (below) for a **2**-methylcyclohexane/benzene (4:1 w:w) system, [**2**]= 4 wt%; the gel state at ca. 22 °C (———); the isotropic solution state at ca. 60 °C (------).



Scheme 1.

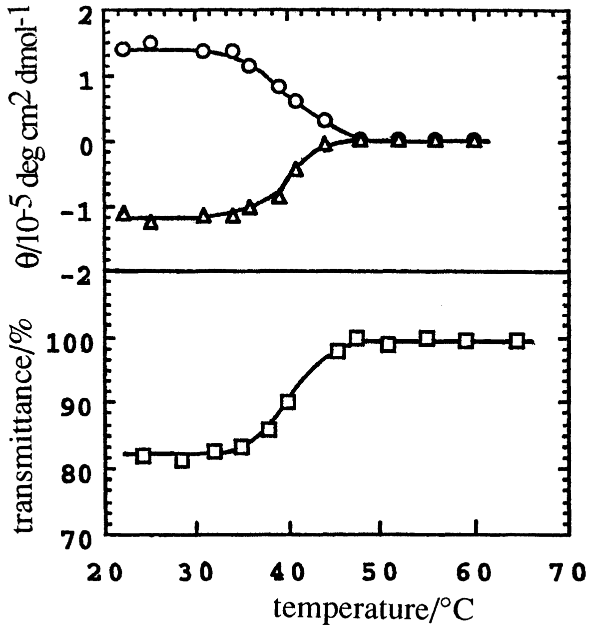


Fig. 4. (a) Temperature dependence of maximum (o) and minimun (Δ) intensity of CD spectra for a **1**-butanol system ([**1**]=0.2 wt%); (b) Temperature dependence of transmittance for a **1**-butanol system ([**1**]=0.2 wt%).

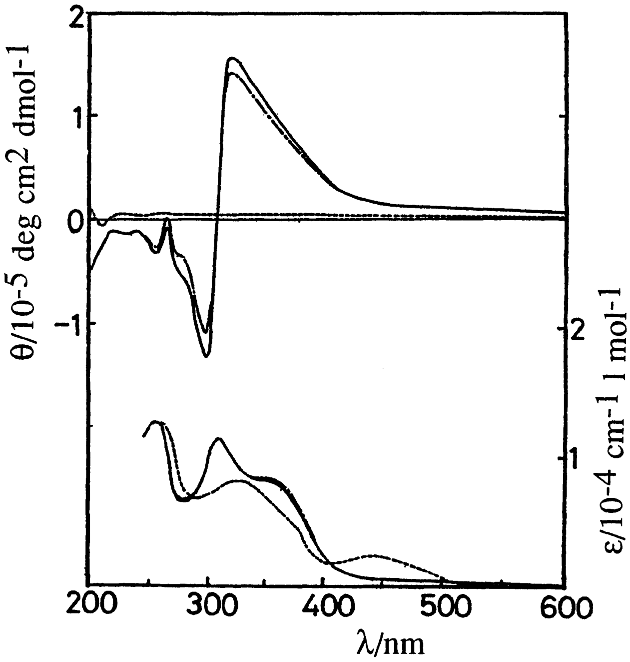


Fig. 5. Photoinduced change of CD spectra (above) and absorption spectra (below) for a **1**-butanol system at 22 °C, [**1**]=0.2 wt%; before irradiation (———); after UV irradiation (- - - - - - -); after VIS irradiation (—— - ——).

In conclusion, the present study revealed that in the gel phase cholesterols in **1** and **2** aggregate under a specific orientation, which enforces chromophoric azobenzenes to interact in an asymmetric manner. The process can be conveniently "read-out" by the CD technique. We believe that these novel properties would be useful as new chiroptical memory storage or display devices.

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8) Provided that the transition moment at 310 nm is opposite to that at 360 nm, the similar ICD band (but not the exciton coupling) could appear. At present, this possibility is not excluded.

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