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α–Hydrazono–β–keto Esters as Command Molecules[1)]

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The nematic director alignment in the liquid crystal cell was reversibly regulated by geometrical isomerization of α–hydrazono–β–keto ester derivatives directly linked on the substrate surface. The reversible change in the shape of the photochromic molecules may be responsible for regulating the alignment of the nematic liquid crystals.

The alignment of nematic liquid crystals (LCs) can be regulated between the homeotropic and parallel modes by geometrical photoisomerization of monolayered azobenzenes bound on substrate plates.[2)] Such photoactive surfaces regulating the LC alignment have been proposed to call command surfaces since a single azobenzene molecular unit can control the alignment alteration of ca. 10^4 LC molecules during the process of *trans*/*cis* photoisomerization.[2)] The working mechanism for the photocontrol of LC alignment has been proposed as follows. The *trans*–isomer units with a rod–like molecular shape can make surrounding LC molecules almost vertical with respect to the substrate surface. Upon exposure to uv light, the drastic deformation of the molecular shape of azobenzene unit takes place to induce the reorientation of LC molecules surrounding the command units. The bent form of the *cis*–isomer may be favorable for the parallel alignment of the nearest neighbor LC molecules. The successive reorientation occurs through the cell to result in the parallel alignment of the whole LC molecules lying over the irradiated area. This interpretation has been supported by the fact that a stilbene attached on glass plates acts as a command molecule.[3)] This paper aimed at verifying the assumption that the photoinduced shape change between rod–like and V–shaped molecules covering substrate surfaces provides the command power for the LC alignment by employing an α–hydrazono–β–keto ester (HKE) residue as a command molecule, taking notice of its reversible molecular shape alteration which markedly resembles that of azobenzenes and stilbenes.[4)]

Our studies on the command surfaces comprising the azobenzene monolayer re–

vealed that a head group at the chromophore plays an important role in the LC alignment alteration.[5] So, we introduced a hexyl or methoxy residue as a head substituent into the phenyl ring of hydrazono group of HKE whereas a triethoxysilyl group was linked to an alkyl ester residue to attach the photochromic unit to silica surfaces. As seen in Fig. 1, the introduction of substituents in this way makes the molecular shape changes quite similar to that of azobenzenes substituted at *p*–positions.

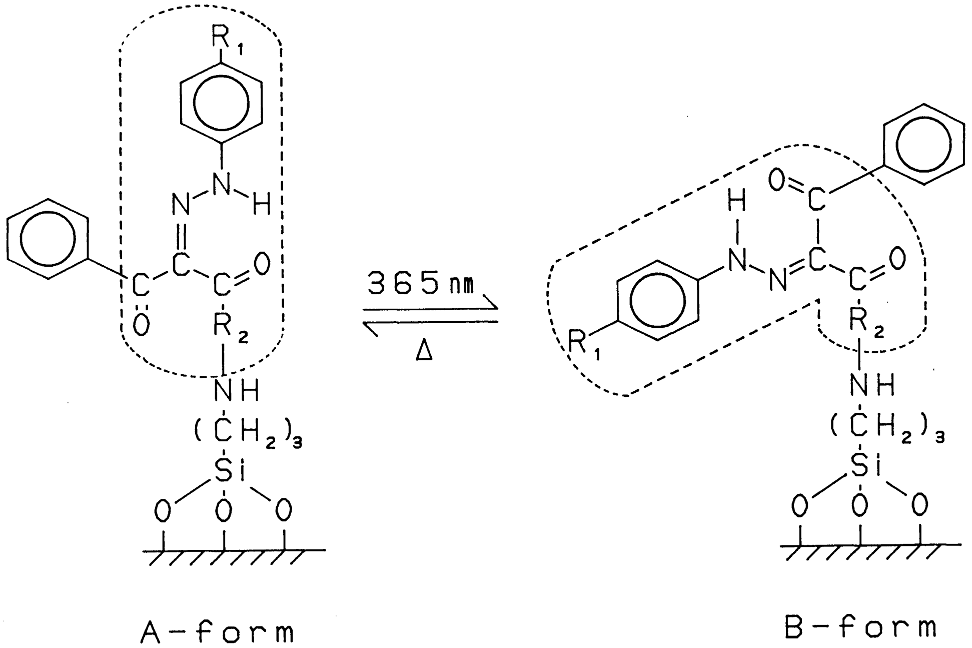
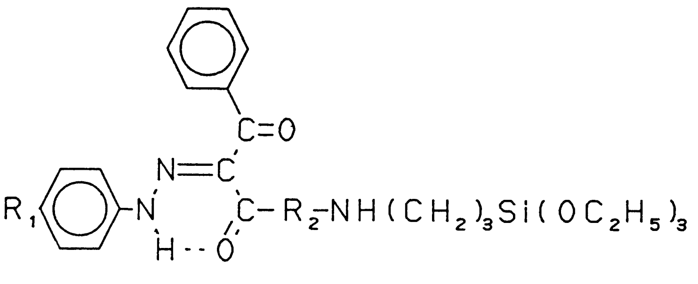


Fig. 1. Schematic illustration of geometrical isomerization of α–hydrazono–β–keto ester (HKE) derivatives linked on the substrate surface

1a; $R_1=C_6H_{13}$, $R_2=$ –
1b; $R_1=C_6H_{13}$, $R_2=OCH_2CO$
1c; $R_1=C_6H_{13}$, $R_2=O(CH_2)_5CO$
1d; $R_1=OCH_3$, $R_2=OCH_2CO$



Chemical formula

We synthesized one α–hydrazono–β–keto acid and three HKEs with carboxylic acids, which were condensed with 3–aminopropyltriethoxysilane to afford silylating reagents (**1a**, **b**, **c**, and **d**). They have a different length of alkane chain as a spacer on account of the fact that the spacer length attaching azobenzene moiety onto silica surface affects the command efficiency.[5] Quartz plates were treated with ethanolic solutions of the silylating reagents in a conventional way.[1]

Although the quantity of absorbance change was considerably small, the photoisomerization from the A–form (λ_{max} = 370 – 390 nm) to the B–form (λ_{max} = 400 – 420 nm) was confirmed for plates modified with **1b**, **1c**, and **1d**. No spectral change was observed for a plate modified with **1a**, reflecting changes in the spacer length and/or a hydrogen bonding acceptor from the ester carbonyl to the amide carbonyl. In marked contrast to the solution photochromism,[4] the HKE units attached on quartz surface exhibited no reverse isomerization from the B–form to the A–form upon exposure to visible light. Moreover, the B–form was so stable that no thermal isomerization took place till the plates were heated above 100 °C. The anomalous photoresponse implies that the B–form is extraordinarily stabilized in the monolayer bound on silica surface. This may be due to the formation of hydrogen bond(s) between the B–form molecules and silanol group(s), though not evidenced.

LC cells were fabricated by sandwiching a cyclohexanecarboxylate–type nematic LC (DON–103; K–17–N–73–I, Rodic Co.) suspending rod glass spacers with the diameter of 8 μm between two surface–modified quartz plates. The initial LC alignment of all the cells examined was homeotropic. The cells allowed no transmittance and looked

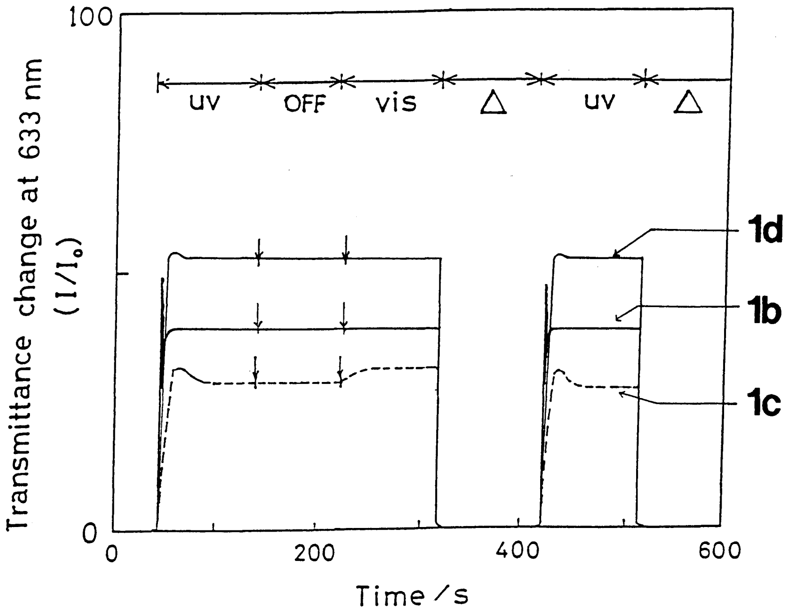


Fig. 2. The photoirradiating and heating responses of nematic liquid crystal cells consisting of substrates chemically modified with α–hydrazono–β–keto ester derivatives (**1b**, **1c**, and **1d**). Monitored by the transmittance of a linearly polarized He–Ne beam through a crossed polarizer.

dark when placed between a couple of crossed polarizers. UV exposure made the cells bright, except an LC cell fabricated with plates modified with **1a**. The inactiveness of this kind of cells is obviously ascribable to the absence of the photochromic reaction of α–arylhydrazono–β–benzoyl acetamide moiety. Figure 2 shows the transmittance change of a linearly polarized He–Ne laser beam passed through the LC cells fabricated with plates modified with **1b**, **1c**, and **1d**, respectively, and a crossed polarizer. The increase in the transmittance of the monitoring He–Ne beam upon uv irradiation reflects that the LC molecules are transformed into the parallel alignment. The transmittance of the uv–exposed cells was not altered on prolonged storage at room temperature, indicating that photoimages stored in the cells are markedly stable. Furthermore, no observable change in the transmittance of the monitoring He–Ne beam was induced upon exposure to visible light, either, because the B–form was very stabilized. The recovery of the initial homeotropic alignment was achieved only by heating the cell up to 65–70 °C. Thus, the repetitive response of the cells can be done by applying a combination of uv light and thermal energy. This behavior of the cell is in quite contrast to that of cells consisting of plates modified with the azobenzene monolayer. The latter demonstrated the reversible response upon alternate exposure to uv and visible lights which were effective for the photoisomerization.[1)]

In conclusion, HKE molecules are able to regulate the reorientation of LC molecules, supporting strongly that the molecular shape change due to the geometrical isomerization is one of the requirements for command molecules. We stress here that the HKE photochromism displaying a relatively slight spectral change is dramatically amplified with aid of the command surface function to visualize to the naked eyes.

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