(10) It is essential to have an accurate value of the dissolution temperature $T_d°$ or the melting point T_m in making plots of $\ln G + E_D^*/RT$ vs $1/T(\Delta T)$ since otherwise distortions (missed transition or a spurious transition) can result. This is especially true of the I → II transition. In crystallization from the melt at low undercoolings, E_D^* may be identified with Q_D^*, the activation energy of reptation.[8,9] When the undercooling range is large, one uses $E_D^*/RT \rightarrow U^*/R(T - T_\infty)$. In constructing Table I we have omitted reports of transitions where we had reason to suspect significant errors in T_m or $T_d°$.

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(25) In the cases of *cis*-poly(isoprene) and poly(ethylene oxide) the growth rate data suggest a reversion to regime II behavior at temperatures above regime I. This possibility was anticipated prior to its observation: the defects that define L may anneal away or have a short lifetime at high T_x. See: Hoffman, J. D. *Polymer* **1985**, *26*, 1763. If the defects should be especially labile, regime I might not occur at all.

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Photochemical Alignment Regulation of a Nematic Liquid Crystal by Langmuir–Blodgett Layers of Azobenzene Polymers as "Command Surfaces"[1]

The nature of substrate surface plays an essential role in liquid-crystal (LC) alignment.[2] Recent investigations in our group have revealed that parallel ⇌ homeotropic reversible alignment mode changes of a nematic liquid crystal are induced by the cis ⇌ trans photochromic reaction of azobenzene (Az) layers attached on the cell substrates.[3,4] This phenomenon involves alignment changes of ca. 10^4 liquid-crystal molecules commanded by only a couple of Az units on the surface, and in this sense we proposed to refer to these photochromic surfaces as "command surfaces".[3] In this communication we demonstrate that (i) alignment changes are induced by Langmuir–Blodgett (LB) mono- and multilayers of amphiphilic polymers containing Az units, (ii) these molecularly controlled Az layers favorably give detailed information on the conditions for the LC response, and (iii) understanding the present phenomenon demands the knowledge of orienting mechanisms on a molecular level at the LC/photochromic layer interface.

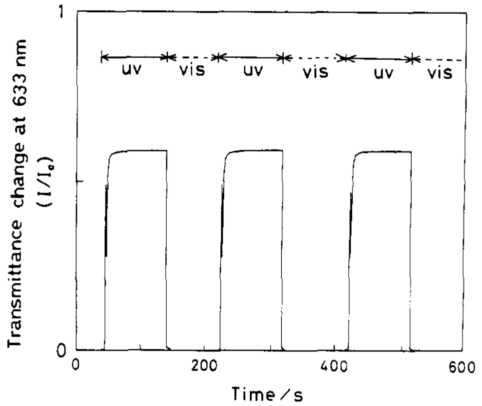
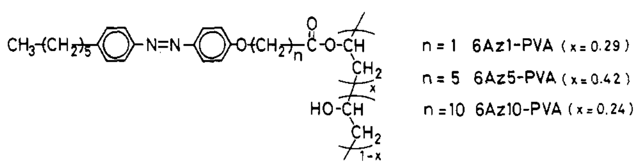


Figure 1. Reversible transmittance change of He–Ne laser light (633 nm) through a LC cell constructed with two glass plates covered with the 6Az10-PVA LB monolayer and polarizers upon alternate exposure of UV and visible light. I and I_0 indicate the laser beam intensities passed through two crossed polarizers with an LC cell and two parallel polarizers without an LC cell, respectively. UV (366 nm) and visible (436 nm) light irradiations were performed using a 500-W super-high-pressure mercury lamp and appropriate combinations of Corning glass filters.

LB mono- and multilayers on glass substrates were prepared from poly(vinyl alcohol) having Az side chains (6Az*n*-PVA).[5] These polymer-type amphiphiles were required to obtain photoreactive Az–LB films.[6] Az–LB films composed of simple amphiphiles such as carboxylic acid derivatives were not applicable for the present purpose because of their poor photoreactivity.[7] 6Az*n*-PVA was spread from a 1 × 10^{-3} mol dm^{-3} chloroform solution on a Langmuir trough (Lauda film balance) filled with doubly distilled water at 21 ± 0.5 °C. 6Az*n*-PVA in chloroform was previously converted to the cis form (≅90%) upon UV light irradiation before spreading on the subphase, and the monolayers were deposited onto glass plates at good transfer ratios (>0.9). This *cis*-Az deposition was adopted throughout the experiments because the films obtained in this procedure gave the higher cis conversion than *trans*-Az deposited ones.[6] Film preparations were achieved under safe light. A nematic liquid crystal 1 (DON 103, C-17-N-73-I, Dainippon Ink & Chemicals Inc.) mixed with 8-μm glass spacer was sandwiched between two glass substrates modified with the LB films. Alignment changes of the liquid crystal was observed with the transmitting He–Ne laser light (633 nm) through the cell set between two crossed polarizers as previously described.[3,4]



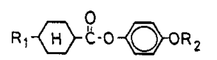

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Figure 1 shows the transmittance changes of 633-nm light through the monolayered 6Az10-PVA/liquid-crystal

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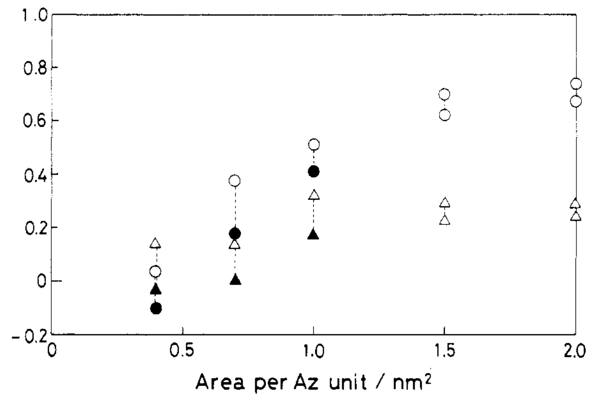

Figure 2. Contact angle of water as a function of two-dimensional Az density on substrates. The contact angle of a droplet was measured after 1 min after placing. The 6Az10-PVA monolayer was deposited onto unmodified (circles) and ethyl-silylated (triangles) glass surfaces. Of the paired points, the upper and the lower correspond to the data for *cis*- and *trans*-Az surfaces, respectively. Open and closed symbols indicate LC alignment of parallel and homeotropic monolayers, respectively.

cell upon alternate exposure to UV (365 nm) and visible (436 nm) lights at room temperature. These changes are evidently induced by the photoisomerization of the surface Az unit. *trans*-Az gave the homeotropic LC alignment and no polarized 633-nm light passed through the cell, and as the Az isomerized to the cis form on UV irradiation, parallel alignment was induced resulting in a bright LC cell. The reverse occurred upon visible light. This proves that only Az monolayer is sufficient to control the LC alignment. Distance between the polymer backbone and Az unit was an important factor for the response. Monolayered 6Az*n*-PVA with longer methylene spacers (n = 5, 10) gave photoresponsive LC cells, whereas, for the polymer with $n = 1$, no responding behavior was observed. LC cells constructed with buildup multilayers of 6Az10-PVA LB films (3-9 layers deposited in Y-mode) also indicated almost identical transmittance changes and response times, suggesting that the surface layer in contact with LC molecules induces the LC alignment change. The occupying area of Az unit (A_{oc}) of 6Az10-PVA on the substrate surface was changed from 0.4 to 2.0 nm² by controlling the monolayer area on the water subphase. In this experiment, clean (unmodified) and ethyl-silylated[8] glass surfaces were used to evaluate the influence of the surface energy. Figure 2 indicates the relationship between A_{oc} and wettability for water (θ: contact angle of a droplet) and the LC alignment under the given conditions. For both series of the glass surface, increasing the Az density reduced the hydrophilicity of the surface and, for identical samples, conversion of Az from the trans to the cis form enhanced the wettability. When A_{oc} was 0.4 nm², the two sets of glass surfaces gave almost the same wetting property, and as A_{oc} increased, more hydrophilic surfaces were obtained for the unmodified glasses than the ethyl-silylated ones. These results are suggestive of good covering of the amphiphilic polymer at the high Az density and greater exposure of the substrate surface at lower density. LC responses were observed when A_{oc} was less than 1 nm², irrespective of the magnitude of the wettability, implying that the occurrence of LC response is primarily determined by A_{oc} and that arguments with macroscopic thermodynamic parameters[2,9] are less significant in the present system.[10] Our results support the proposal of Hiltrop and Stegemeyer[11] on the orientation of LCs on solid substrates coated with amphiphilic monolayers that the alignment strongly depends on the parameters, such as molecular structures of both the amphiphilic molecules and the LC molecules and packing density of the amphiphilic monolayer.

Our current efforts are being focused on the dependence of the chemical structure of Az derivatives on the LC response behaviors since subtle differences in the interaction mode between the photochromic layer molecules and LC molecules may lead to significant changes in LC alignment behaviors.

Registry No. DON 103, 115288-48-7; 6Az10-PVA, 121886-84-8; 6Az5-PVA, 121886-83-7; 6Az1-PVA, 120112-81-4.

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Ribbon-Shaped Structures via Repetitive Diels-Alder Reaction. A Polycatafusene

We are involved in the synthesis of ribbon (ladder) polymers, which can be considered as part of the graphite lattice.[1,2] Recently, we have proposed a route into this intriguing class of polymers that is based on repetitive Diels-Alder (DA) reactions of the bifunctional diene 1 and the bifunctional dienophile 2.[3] In the first step, this route

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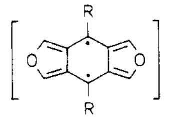
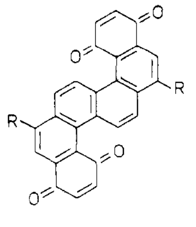


a; R = $(CH_2)_5CH_3$
b; R = $(CH_2)_{11}CH_3$



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