Structure and Photoisomerization of the Z-Type Langmuir−Blodgett Films of a New Series of Azo-Containing Chiral Copolymers[†]

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Three copolymers, A1, A2, and A3, poly{2-hydroxyethyl methacrylate}$_{1−x}$-*co*-{6-[4-((((((*S*)-2-methylbutyl)-oxy)carbonyl)phenyl)azo)phenoxy]hexyl methacrylate}$_x$ with x = 0.25, 0.50, and 0.75, respectively, were successfully deposited as Z-type Langmuir−Blodgett (LB) films. The isobar curves and the compression−expansion isotherms of the three copolymers on water show that the polymer monolayers have good quality. Polarized UV−vis and IR spectroscopic measurements reveal that the LB films of A1, A2, and A3 on substrates are organized with the long axis of azobenzene moiety preferentially along the film normal, and the LB films of A1 have additional in-plane orientation. The LB films of A1, A2, and A3 are all capable of trans-to-cis and cis-to-trans photoisomerizations. Photoinduced liquid crystal alignment alteration from the homeotropic mode to planar mode is achieved with the Z-type films of A1. It is concluded that the LB films of A1 have the right occupied molecular area for photoinduced liquid crystal alignment regulation.

Introduction

There is recently a growing trend in controlling liquid crystal (LC) alignments using the photoisomerization of azobenzene derivatives.[1] Azobenzene-containing materials are capable of reversible molecular geometric shape change between the rodlike and bent forms, upon irradiated by visible or ultraviolet light. Using azobenzene derivatives as the modification layers in the LC cell, optical information can be written and erased out by changing the electric vector of the linearly polarized light incident on the LC cell. The LC systems modified with such photosensitive materials have potential applications in the fields of photomemory, optical storage, and light drive display. Modification of LC systems with self-assembled films on silica,[2] Langmuir−Blodgett (LB) films,[3] and casting films[4] of azobenzene derivatives has been reported.

Mobius and Ringsdorf[5] et al. reported investigations on the structural changes of the LB films of an azobenzene-containing polymer induced by ultraviolet or visible illumination. Their results show that the azo-containing polymer is successfully deposited as Y-type films which have layered structure and in-plane orientation. We synthesized a series of polymers (Figure 1) very similar to Ringsdorf's and tried to characterize the structure of
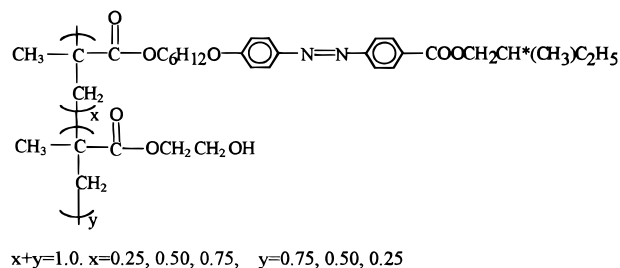

x+y=1.0. x=0.25, 0.50, 0.75,　y=0.75, 0.50, 0.25

Figure 1. Structure of the copolymers: A1, x = 0.25; A2, x = 0.50; A3, x = 0.75.

the LB films of these polymers, to study the photoisomerization of the LB films, and finally, to investigate the photoinduced LC alignment control by these films. Our studies show that the polymers form Z-type films, and photoisomerization of these films can induce reversible planar and homeotropic alignment of LC cell. The results imply that the Z-type films can be used in optical storage devices as photosensitive modification layers.

Experiment

The copolymers used are poly{2-hydroxyethyl methacrylate}$_{1−x}$-*co*-{6-[4-((((((*S*)-2-methylbutyl)oxy)carbonyl)phenyl)azo)phenoxy]-hexyl methacrylate}$_x$, as shown in Figure 1.

The copolymer with x = 0.25 is denoted by A1, the copolymer with x = 0.50 is denoted by A2, the copolymer with x = 0.75 is denoted by A3. Synthesis of the copolymers was published.[6] Chiefly, the azo-containing monomer was prepared from 4-hydroxy-4′-((((*S*)-2-methylbutyl)oxy)carbonyl)azobenzene by etherification with excess 1,6-dibromohexane and reaction of the resulting 4-(6-bromohexyloxy)-4′-((((*S*)-2-methylbutyl)oxy)carbonyl)azobenzene with potassium methacrylate. The polymerization was carried out in degased toluene with AIBN as initiator. The completeness of polymerization was determined by the disappearance of the methyl and vinyl proton signals of the methacrylic group at 1.94−1.96 ppm and 5.50−6.10 ppm in the ^{1}H NMR spectrum and of the vinyl absorption at 1600−1640 cm^{-1} in the IR spectrum.

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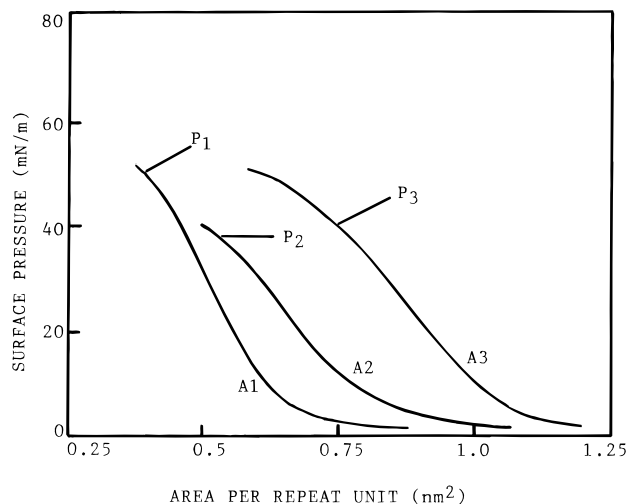
(6) Tian, Y. Q.; Ren, Y. Z.; Sun, R. P.; Zhao, Y. Y.; Tang, X. Y.; Huang, X. M.; Xi, S. Q. *Liq. Cryst.* **1997**, *22*, 177.

Figure 2. Surface pressure−area isotherms of the three copolymers A1, A2, and A3 on water at 20.0 °C.

Film preparation was carried out on KSV5000 LB film balance (Finland). The subphase was deionized and double distilled water, with pH = 6.0 and surface tension 72.8mN/m, kept at 20 ± 0.5 °C. The $\pi-A$ isotherms of the polymers were measured after the surface tension of the subphase had been zeroed. The substrate was hydrophilic CaF_2, quartz, and ITO glasses, which had been fluxed with 2-propanol. The deposition speed was 5 mm/min.

Polarized UV−vis spectra were obtained with Hitachi Model 650-0155 polarizers and a Shimadzu UV-3100 spectrophotometer (Japan). Polarized infrared spectra were obtained with BIO-RAD FTS-7 spectrophotometer and a wire-grid polarizer (Perkin-Elmer).

The photochromism experiment was done by irradiating the LB films on CaF_2 with the light from a low-pressure 80 W Hg lamp. Two sharp cut-off filters: 360 nm filter and 450 nm filter were used for the trans-to-cis and cis-to-trans isomerization, respectively. The irradiated LB films were carefully kept in the dark and taken to the detection with spectrophotometer immediately. The delay between the irradiation and detection was less than 15 s.

Liquid crystal cell was constructed with nematic E70 and glass rod spacers of 10 or 40 μm diameter. The spacers were sandwiched by two quartz plates covered with different layers of Z-type LB films and sealed with an epoxy resin adhesive. The cell was set between two crossed polarizers and exposed alternatively to 360 and 450 nm light. The pretilt angle at different state was determined by an LCD parameter tester (homemade) with a precision of ±0.2°.

Results and Discussions

1. Conformation, Stability, and Reversibility of the Polymer Monolayer on Water. Pressure−area isotherms on water of three copolymers containing azo percentage 25%, 50%, and 75% were shown in Figure 2. It is seen that on each isotherm there is a steep region where surface pressure increases fastest with compression. The collapse point is considered to be the turning point after this fastest increase. As indicated in Figure 2, the collapse points on the isotherms of A1, A2, and A3 are respectively P_1 (50 mN/m, 0.38 nm²), P_2 (38 mN/m, 0.52 nm²), and P_3 (40 mN/m, 0.75 nm²). Conformations of the polymer monolayers of A1, A2, and A3 at the collapse pressure can be analyzed as follows. For the polymer A1, the area occupied by one azo side chain at P_1 is simply 0.38 nm², since each repeat unit of A1 contains one azo side chain and three hydroxyethyl groups. For the polymer A2, each azo side chain occupies an area 0.52 nm²/2 = 0.26 nm² at P_2, since each repeat unit of A2 contains two azo side chains and two hydroxyethyl groups. For the polymer A3, the area occupied by one azo side chain at P_3
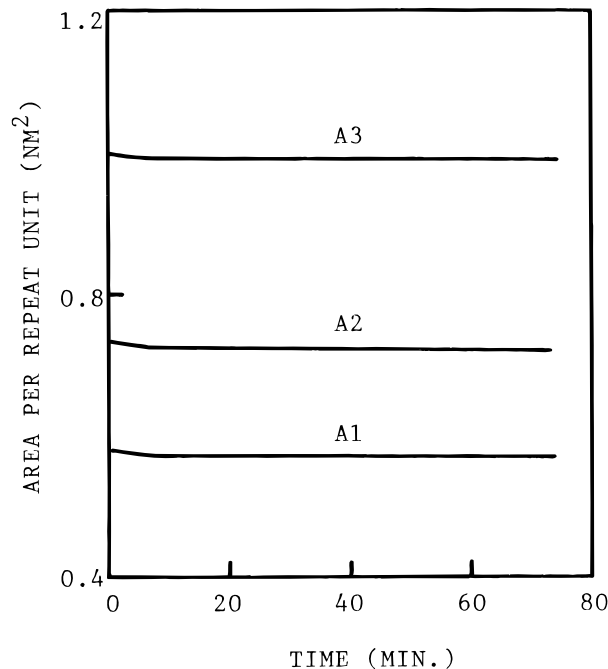

Figure 3. Isotherms of surface area versus time during maintainence at a certain pressure and at 20.0 °C: A1, stabilized at 20 mN/m; A2, stabilized at 18 mN/m; A3, stabilized at 18 mN/m.

is 0.75 nm²/3 = 0.25 nm², since each repeat unit of A3 contains three azo side chains and one hydroxyethyl group. As is well-known, the tightest packing of azobenzene derivatives produces the smallest cross-sectional area of 0.25 nm².[7] It can be imagined that the azo side chains of A2 and A3 are the most tightly packed at the collapse pressure, with the azo side chains standing upward on water; while the azo side chains of A1 are not packed so tightly, allowing some free space to exist in the monolayer.

It is intriguing to discuss the free space available between azo side chains at deposition pressures. For applications in photoinduced LC alignment regulation, the azo-containing polymers at the air/water interface need to be transferred onto solid substrates at certain deposition pressures. The deposition pressures for A2 and A3 are empirically chosen to be 18 mN/m. The deposition pressure for A1 may be higher, i.e., 20 mN/m, since the collapse pressure of A1 is higher than A2 and A3. It is calculated from the $\pi-A$ isotherms (Figure 2) that the azo side chain of A1 occupied an area of 0.55 nm², that of A2 has an area of 0.35 nm², and that of A3 has an area of 0.4 nm². Again, the azo side chain of A1 has the largest area, and this is favorable for alignment regulation[2] of LC cells by azobenzene molecular films. Aoki[2] mentions that when the occupied area of azo moiety exceeds 0.5 nm², there is much free space available for the LC molecules to stick to the azo layer so that the azo moiety may interact readily with the LC molecules. This is why we choose the LB films of A1 for photoinduced alignment regulation of LC molecules, rather than the LB films of A2 and A3 (see below).

The quality of the polymer monolayers on water of A1, A2, and A3 is good. The stability of the monolayers is checked by holding the surface pressure at a certain value (we prefer the deposition pressure) and recording the area loss. The polymer monolayer on water is very stable, as is seen from Figure 3. For all three polymers the area loss per repeat unit over about 80 min of stabilization is less than 0.02 nm². This indicates that the azo side chains
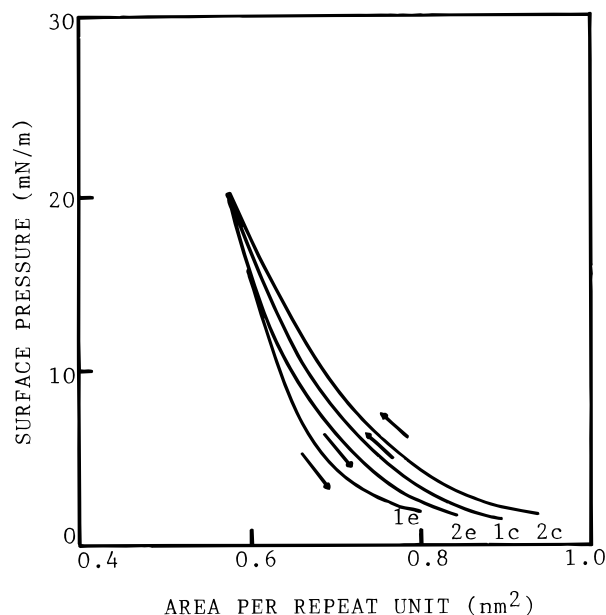
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Figure 4. Compression−expansion isotherms of the polymer A1 on water at 20 °C with target pressure 20 mN/m: (1c) compression of the first loop; (1e) expansion of the first loop; (2c) compression of the second loop; (2e) expansion of the second loop. The compression and expansion speeds are both 10 mm/min.

Table 1. Apparent Transfer Ratios (TR) of A1 during Y-Type and Z-Type Deposition onto Hydrophilic CaF₂ at 20 mN/m with Upstroke Speed 5 mm/min and Downstroke Speed 30 mm/min

Z-type				Y-type			
layer	TR	layer	TR	layer	TR	layer	TR
1	0.88	2	0.87	1 up	0.85	2 down	0.44
3	0.86	4	0.89	3 up	0.88	4 down	0.56
5	0.85	6	0.89	5 up	0.88	6 down	0.41
7	0.85	8	0.83	7 up	0.95	8 down	0.61
9	0.88	10	0.86	9 up	0.95	10 down	0.32
11	0.87	12	0.87	11 up	0.88	12 down	0.41
13	0.85	14	0.80	13 up	0.94	14 down	0.55
15	0.86	16	0.82	15 up	0.88	16 down	0.59
17	0.81	18	0.80	17 up	0.89	18 down	0.55

are packed uniformly on water due to compression. Scratches and defects in the monolayers are scarce.

Gaines[8] has given some remarks on the quality of polymer monolayers on water. He used hysteresis loops of compression−expansion isotherms of surface pressure−area to test the quality of polymeric monolayers. Hysteresis loops can be examined in terms of the coincidence of target points among different loops and the changes between the compression and expansion isotherms of one loop. Figure 4 shows the hysteresis loops of A1 on water. The second loop meets the first loop exactly at the same target point (20.0 mN/m, 0.56 nm²). Whether in the first loop or in the second loop, the expansion isotherm is basically the same as the compression isotherm, and no significant hysteresis is observed. This means that no irreversible rearrangements occur in the polymer monolayer as a result of compression. The polymer main chain should be remote and well extended at the air/water interface. Moreover, hysteresis studies of the polymer monolayers of A2 and A3 also give the above conclusions.

The deposition behavior of A1 monolayer from water onto CaF₂ is summarized in Table 1. Other substrates such as ITO-coated glass and quartz were also used and give the same results as CaF₂. Besides, the deposition
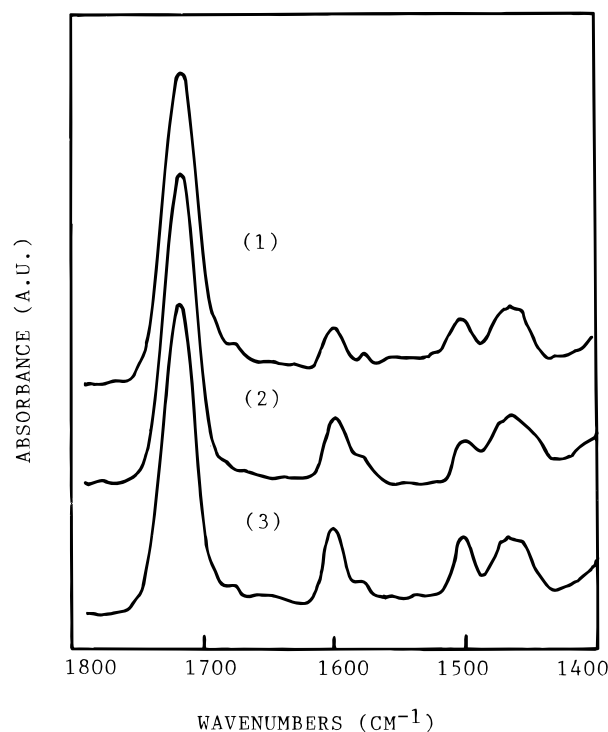
(8) Gaines, G. L., Jr. *Langmuir* **1991**, *7*, 834.

Figure 5. Polarized infrared spectra of 100-layer Z-type films of A1 deposited at 20 mN/m at 20.0 °C onto both sides of CaF₂ slide: (1) $A_\perp(i=0°)$; (2) $A_\parallel(i=0°)$; (3) $A_\parallel(i=45°)$.

behavior of A2 and A3 is the same as A1 and will not be listed in Table 1. It is concluded from Table 1 that Z-type transfer of A1 (transfer on the upstrokes only) is successful, while Y-type transfer fails. During Y-type transfer of A1, the transfer ratios on the upstrokes are always satisfactory, while those on the downstrokes are always bad. Sufficient dry and various dipping speeds were tried to optimize the transfer ratios in downstrokes, and Table 1 lists the optimal values. In addition, the Z-type transfer ratios remain in the range of 0.8−0.9 up to 100 layers.

Ringsdorf[5] et al. report studies on the LB films of a similar azo copolymer, which gives good Y-type depositions. The only difference is that their polymer has an ether linkage between the chiral group and the phenylazo group and our polymer has an ester linkage between the chiral group and the phenylazo group (see Figure 1). The reason may be that the ester linkage is more hydrophilic than the ether linkage. Sagiv[9] et al. considered that some hydrophilic group located at an appropriate position along the hydrophobic chain of an LB material may give rise to successful Z-type depositions. Other examples of Z-type forming materials are polymers, as reported by Mumby,[10] Stroeve,[11] and Ren.[12]

2. Orientation of the Azobenzene in the LB Films. Orientation of the azobenzene in the Z-type films of all the three polymers is examined using polarized infrared and UV−vis spectroscopy.[13] Figure 5 shows the polarized IR spectra of A1 multilayers at different incidence angles, with resolution 4 cm⁻¹ and 64 scans. Only the region 1800−1400 cm⁻¹ is given, since the spectra at other regions

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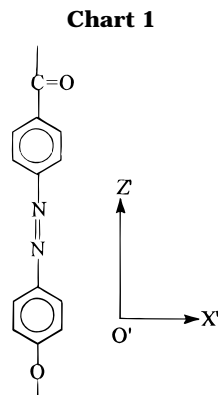
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Chart 1

are highly overlapped and no information can be drawn therefrom. The band at 1717 cm^{-1} is due to carbonyl stretching of the three esters of A1. Although the carbonyl stretching is polarized along the C=O double bond, this band cannot be a dichroism since the LB process should have introduced no arrangements into the three ester groups this band represents. The band at 1600 cm^{-1} is due to ring breathing mode of benzenes. The two benzenes of the polymer are para-substituted, and the polymer has a C_{2v} symmetry. The 1600 cm^{-1} band is originally a$_1$ mode, but slightly mixed with b$_1$ mode, and is expressed as (a$_1$ + b$_1$) mode.[14] It is polarized mainly along the Z' direction, and a little along the X' direction of benzene ring (Chart 1). The band at 1581 cm^{-1} is due to b$_1$ ring deformation mode of para-substituted benzenes and is polarized along the X' direction. Because this band is so weak, it is safe not to draw orientation information therefrom. In the following discussions, we do not mention this band. The band at 1500 cm^{-1} is due to a$_1$ ring deformation mode of para-substituted benzenes and is polarized along the Z' direction. The overlapped bands around 1460 cm^{-1} are mainly due to CH$_2$ deformation mode of the many CH$_2$ at various positions of the polymer.

Direct comparison of the two spectra $A_\perp(i = 0°)$ and $A_\parallel(i = 0°)$ in Figure 5 shows that the azobenzene of A1 has "in-plane" orientation. When light irradiates along the normal to film, $A_\perp(i = 0°)$ and $A_\parallel(i = 0°)$ are obtained with the electric vector of light perpendicular and parallel to the dipping direction, respectively. With the 1717 cm^{-1} band as a standard, it is seen that the two 1600 cm^{-1} bands are stronger in $A_\parallel(i = 0°)$ than in $A_\perp(i = 0°)$. Thus the X' direction of benzene ring is aligned preferentially parallel to the dipping direction in the Z-type films. Uznanski[15] et al. mention that the two benzene rings of azobenzene are not coplanar, but twisted at some angle in the opposite direction with respect to the azo linkage (see Figure 6). The above preferred alignment should be an average orientation over the two benzenes.

Direct comparison of the two spectra $A_\parallel(i = 0°)$ and $A_\parallel(i = 45°)$ in Figure 5 shows that the azobenzene of A1 stands up in the LB films. $A_\parallel(i = 45°)$ is obtained for tilted irradiation, and the electric vector of light has an angle of 45° with respect to the film plane and its projection into the film plane is parallel to the dipping direction. With the 1717 cm^{-1} band as a standard, direct comparison shows that the 1600 cm^{-1} band and 1500 cm^{-1} band are stronger in $A_\parallel(i = 45°)$ than in $A_\parallel(i = 0°)$. Therefore the Z' direction of the two benzene rings is aligned preferentially along the normal to the film of A1.

Polarized UV–vis spectra $A_\perp(i = 0°)$ and $A_\parallel(i = 0°)$ in Figure 7 also show that the azobenzene of A1 has "in-

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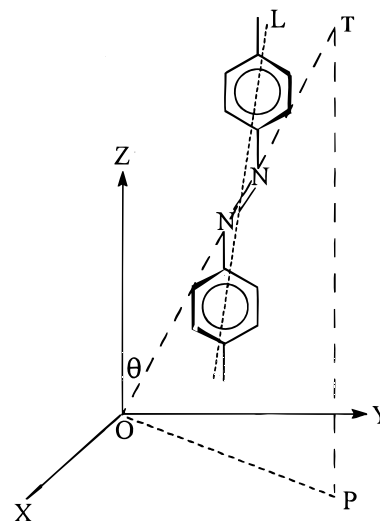

Figure 6. Orientation of the azobenzene unit of A1 in the Z-type LB films. XOY is the film plane. OX is the dipping direction. L is the long axis of azobenzene. OT is the direction of the transition moment of the band at 360 nm.
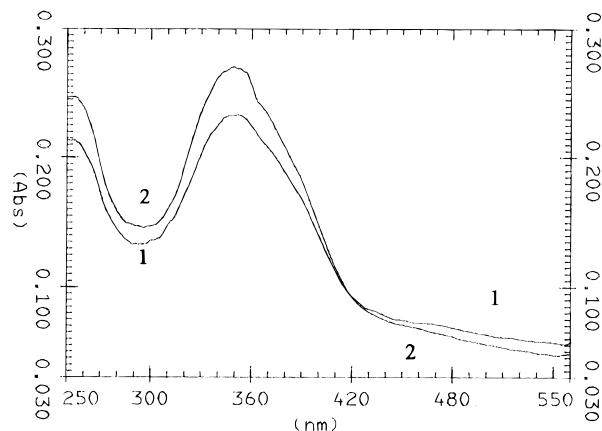

Figure 7. Polarized UV–vis spectra of 18-layer Z-type films of A1 deposited at 20 mN/m at 20.0 °C onto both sides of the CaF$_2$ slide: (1) $A_\parallel(i=0°)$; (2) $A_\perp(i=0°)$.

plane" orientation. The band around 360 nm is known as the $\pi-\pi^*$ transition of *trans*-azobenzene,[15] polarized about 17° with respect to the long molecular axis of azobenzene. As shown in Figure 6, OT is the 360 nm transition moment and L is the long molecular axis of azobenzene. Here we are concerned with the projection of OT in the film plane, i.e., OP. From Figure 7 OP is determined to be preferentially perpendicular to the dipping direction. It is noteworthy that this "in-plane" orientation of the azo chromophore has nothing to do with that derived from polarized IR measurements, since we do not know the orientation of the 360 nm transition moment relative to the two benzene planes.

For the Z-type films of A2 and A3 the two spectra $A_\perp(i = 0°)$ and $A_\parallel(i = 0°)$ are virtually the same both in the infrared region and in the UV–vis region, and these films have no in-plane orientation. The two spectra $A_\parallel(i = 0°)$ and $A_\parallel(i = 45°)$ of the Z-type films of A2 and A3 are different. A detailed analysis shows that the azobenzene stands upward in these films.

3. Photoisomerization of the Z-Type Films of A1. The photoisomerization of all the three copolymers in chloroform solution were studied. Their spectra are the same as those reported in ref 16 and will not be shown here. For example, the copolymer A3 of concentration 2.6

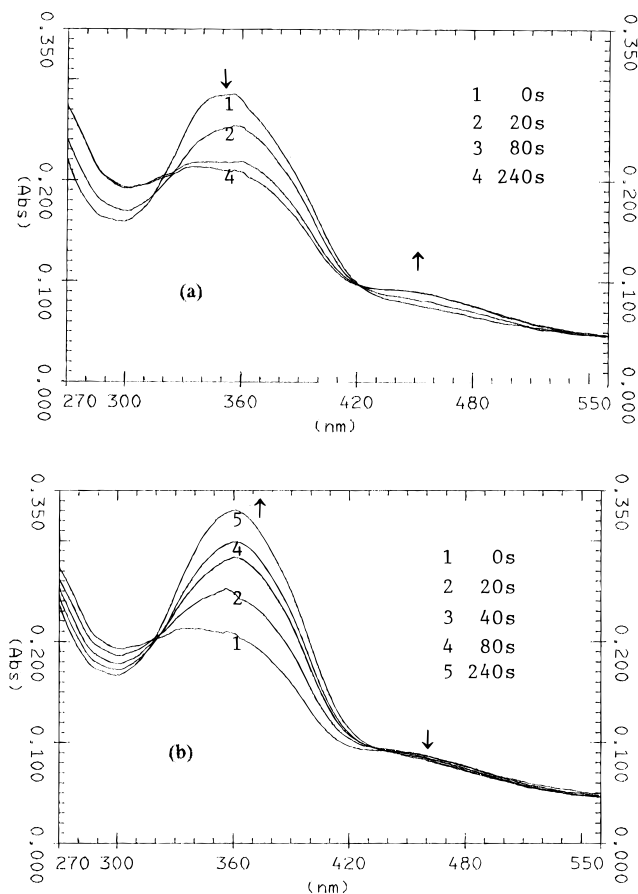(16) Niemann, M.; Ritter, H. *Macromol. Chem.* **1993**, *194*, 1169.

Figure 8. Ordinary (unpolarized) spectral changes upon irradiation of 18-layer Z-type films of A1 deposited at 20 mN/m at 20.0 °C onto both sides of a CaF$_2$ slide: (a) irradiation at 360 nm; (b) irradiation at 450 nm. The spectra were recorded with unpolarized, normally incident light.

$\times$ 10^{-5} in chloroform (quartz cell, length 1.0 cm) has an original absorbance of $X_1 = 2.66$ at 360 nm. After irradiation with 360 nm for 7 min, this absorbance decreases to $X_2 = 0.50$. Subsequent irradiation with 450 nm light for 7 min causes the absorbance at 360 nm reincrease to $X_3 = 2.48$. It is seen that X_3/X_1 is 93%, i.e., the azobenzene isomers do not recover 100%.

Parts a and b of Figure 8 show the spectral changes during photoisomerization of Z-type LB films of A1 with 360 nm light and 450 nm light, respectively. The spectral changes were recorded with unpolarized detecting light incident along the film normal. It is seen that the LB films have good photoisomerization behavior. The Z-type films of A2 and A3 also have similar photoisomerization behavior, only that it takes longer irradiation for these films to be isomerized from trans to cis. This is apparently due to the smaller free space available in the LB films of A3 and A2, as discussed above. Furthermore, there is some difference between the isomerization behavior of the LB films of the polymers and their corresponding solutions. For example, the X_3/X_1 of 18-layer Z-type films of A1 is 0.28/0.24 = 116%, considerably more than 100%; the X_3/X_1 of 18-layer Z-type films of A3 is 0.40/0.29 = 137%, also considerably more than 100%. (The value of the absorbance is read from the spectra after baseline correction.)

However, these isomerization phenomena are not observed when the spectra are recorded as $A_{\parallel}(i = 45°)$, i.e., the electric vector of the detecting light has a component

along the film normal. The X_3/X_1 of 22-layer Z-type films of A1 is 0.485/0.475 = 102%. Therefore the unreasonable recovery observed using unpolarized detecting light is merely due to orientation change of the azobenzene unit after a cycle of photochemical trans-to-cis and cis-to-trans isomerization. After this cycle of isomerization the long axis of azobenzene lies more in the film plane.

4. Photoinduced Liquid Crystal Alignment Regulation. The LC alignment control using the photoisomerization of the copolymers gives similar results as reported by Kawanishi[17] et al. Homeotropic alignment of the LC cell modified with Z-type films of A1, A2, and A3 on quartz is induced almost immediately after the cell construction. Pictures of this alignment have been taken with a conoscopic microscope (not shown). The pretilt angle for this homeotropic alignment is 89.8°. The homeotropic alignment of the cell modified with Z-type films of A1 turns to inhomogeneous planar alignment with multidomain textures after 10 min of unpolarized UV irradiation (360 nm, 80 W mercury lamp), and turns to homogeneous planar alignment after polarized UV irradiation. The pretilt angle for this planar alignment is 0.5°. Both the inhomogeneous and homogeneous planar alignment are not stable. After exposure under white or visible light for 5 min, they disappear and homogeneous homeotropic alignment results. In addition, the cells modified with Z-type films of A2 and A3 do not undergo a satisfactory homeotropic to planar change, whether using unpolarized or polarized UV irradiation. This may be due to the incomplete trans-to-cis photoisomerization of the Z-type films of A2 and A3. Aoki[2] et al. mention that the alignment change from homeotropic to planar mode starts at a critical point determined by the absolute number of the remaining trans isomers after the ultraviolet irradiation. The X_2/X_1 of the Z-type films of A1 is 66%, the X_2/X_1 of the Z-type films of A3 is 79%.

Summary

Three copolymers A1, A2, and A3 containing 25%, 50%, and 75% azobenzene units, respectively, were synthesized and successfully deposited as Z-type LB films. The monolayers of these polymers on water were examined through $\pi-A$ isotherms, isobar curves, and compression–expansion isotherms and show good stability and reversibility. The Z-type films of A1, A2, and A3 on CaF$_2$ were characterized through polarized UV–vis and IR spectroscopy. Photoisomerization of these Z-type films was studied with both ordinary and polarized detecting light and subsequently applied to control liquid crystal alignment. It is found that the Z-type films of only A1 has an in-plane orientation and has the right occupied molecular area for photoisomerization and photoinduced LC alignment regulation. In addition, the long axis of the azobenzene in the Z-type films of A1, A2, and A3 is orientated preferentially along the film normal, and this upward orientation relaxes during the trans-to-cis isomerization with ultraviolet light.

(17) Kawanishi, Y.; Tamaki, T.; Sakuragi, M.; Seki, T.; Suzuki, Y.; Ichimura, K. *Langmuir* **1992,** *8*, 2601.