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## Liquid Crystals

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Online publication date: 06 August 2010

**To cite this Article** Tian, Yanqing , Ren, Yanzhi , Sun, Ruipen , Zhao, Yingying , Tang, Xinyi , Huang, Ximin and Xi, Shiquan(1997) 'Synthesis of a series of chiral copolymers with azo groups and investigations of reversible liquid crystalline alignment induced by the LB films of these materials', Liquid Crystals, 22: 2, 177 — 183

**To link to this Article: DOI:** 10.1080/026782997209540

**URL:** http://dx.doi.org/10.1080/026782997209540

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LIQUID CRYSTALS, 1997, VOL. 22, NO. 2, 177–183

# Synthesis of a series of chiral copolymers with azo groups and investigations of reversible liquid crystalline alignment induced by the LB films of these materials

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(*Received 12 June 1996; in final form 15 September 1996; accepted 1 October 1996*)

A series of liquid crystalline copolymers, poly{2-hydroxyethyl methacrylate}-co-{6-[4-(*S*-2-methyl-l-butyloxycarbonylphenylazo)phenoxy]hexyl methacrylate} with an azobenzene moiety as photoreactive mesogenic unit, was prepared and investigated by using DSC, polarized optical microscopy and X-ray diffraction. The results show that these polymers exhibit smectic phases. Z-type Langmuir–Blodgett films of these copolymers were successfully deposited onto calcium fluoride and quartz. Reversible homeotropic and planar liquid crystal alignments were induced by using the photochromism of the LB films of one of the copolymers containing 20·6 mol% of the azo unit.

## 1. Introduction

Particular interest in the preparation and investigation of azo-dye containing liquid crystalline polymers has increased recently because of their potential application in optical storage devices due to both the reversibility of the isomerization and the large steric volume change between the two isomeric states [1–4]. Also, functional groups such as azo which is capable of the photoisomerization and chiral groups which can cause ferroelectric properties can be introduced into polymers easily by the method of copolymerization. Previously, some side chain liquid crystalline copolymers with chiral groups and azo groups have been prepared and investigated [5–8] and if the chiral polymers with azo groups exhibit N* or $S_C^*$ phases, the change of pitches for the N* phase and the spontaneous polarization (*P*s) for the $S_C^*$ phase occurring with UV/VIS irradiation can be investigated. Moreover, liquid crystals can be regulated by using photosensitive materials such as azobenzene, stilbene and spiropyran, because these materials possess a common feature—a photosensitively reversible molecular geometric shape change between the rod-like and bent forms induced by changing the wavenumber or the polarization direction of the incident light [9–11]. Optical information can be easily written and erased by simply changing the electric vector of the incident linearly polarized light; therefore liquid crystal systems composed of photosensitive materials have potential significance in the application fields of photo-memory, optical storage and electro-optic display devices. The modification of liquid crystalline molecules by means of linearly polarized light when using Langmuir–Blodgett (LB) mono-/multi-layers or cast films of these photosensitive materials has been recently investigated [9–12]. The reversible control of planar alignment and homeotropic alignment of a nematic liquid crystal (NLC) by azobenzene-containing ultrathin films has been demonstrated through such a ‘command surface’.

The aim of this work is two fold: one is to prepare a new series of copolymers as shown in figure 1 with an azobenzene moiety as photoreactive mesogenic unit and to investigate their liquid crystalline behaviour; the other

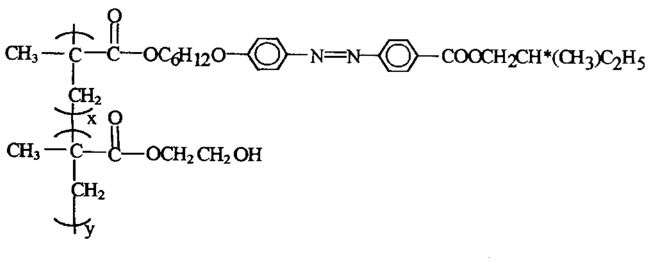
x+y=1.0. x=0.25, 0.50, 0.75, y=0.75, 0.50, 0.25

Figure 1. The structure of the copolymers.

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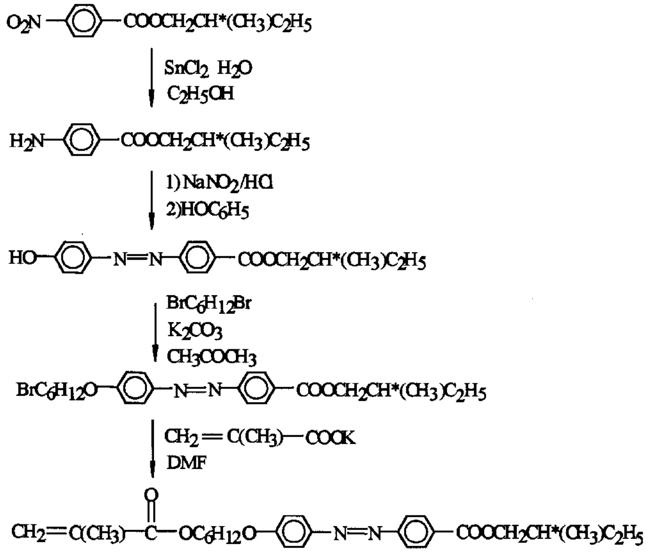
aim is to align nematic liquid crystals by using LB mono-/multi-layers of the amphiphilic copolymers, poly{6-[4-(*S*-2-methyl-l-butyloxycarbonylphenylazo)-phenoxy]hexyl methacrylate}-co-{2-hydroxyethyl methacrylate}, containing the azo unit. The results show that mono-/multi-layers of the copolymers containing 20% of azo unit can reversibly control the planar alignment and homeotropic alignment of NLC. The results show that the pretilt angles of the planar and homeotropic alignments are 0·5 and 89·8 degrees, respectively; this implies that the LB/LC/LB system sandwiched with 6-layers Z-type LB films of the copolymers containing 20 mol % of azo unit can provide absolute photochemical induction and modulation of liquid crystal alignment. The results imply that this system can be used in optical storage devices, and further experiments are in progress.

## 2. Experimental

### 2.1. *Solvents and materials*

The solvents and other materials were commercial products which were purified by distillation or recrystallization before use. The *S*-(-)-2-methyl-l-butanol (Aldrich 99%) was used without further purification.



### 2.2. *Monomer synthesis*

#### 2.2.1. *4-(S-2-Methylbutyloxycarbonyl) nitrobenzene*

This compound was prepared by the reaction of 4-nitrobenzoyl chloride and *S*-2-methylbutanol according to a general procedure and purified by column chromatography using $CH_2Cl_2$ as eluent. A yellow oil was obtained. Yield: 80%. IR 1729 cm$^{-1}$ (CO ester), 1530 cm$^{-1}$ ($NO_2$). $[\alpha]_D^{19} = +6{\cdot}1$ ($c = 1{\cdot}06$, $CHCl_3$). $C_{12}H_{15}NO_4$ (Mol: 237·2). Calcd: C 60·75, H 6·40, N 5·91%. Found: C 60·66, H 6·30, N 5·74%.

#### 2.2.2. *4-(S-2-Methylbutyloxycarbonyl)aminobenzene*

The compound was prepared by the reduction of 4-(*S*-2-methylbutyloxycarbonyl)nitrobenzene with $SnCl_2{\cdot}2H_2O$ in ethanol and purified by column chromatography using $CH_2Cl_2$ as eluent. A white solid was obtained. Yield: 65%, m.p. 42–44°C (43·3–45°C [13]). IR 1693 cm$^{-1}$ (CO–) 1637 cm$^{-1}$ ($NH_2$). $[\alpha]_D^{16} = +6{\cdot}4$ ($c = 2{\cdot}64$, $CHCl_3$).

#### 2.2.3. *4-Hydroxy-4′-(S-2-methylbutyloxycarbonyl)-azobenzene*

The azo compound was synthesized by the standard method of reference [13] and purified by column chromatography using cyclohexane:ethyl acetate (4:1) as eluent. This gave the product as an orange solid. Yield: 70%, m.p. 113–115°C (114·5–116°C) [13]. IR: 1719 cm$^{-1}$ (CO–). $[\alpha]_D^{16} = +6{\cdot}80$ ($c = 1{\cdot}32$, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm): 0·954(t, 3 H, $-CH_2\underline{CH}_3$). 0·991(t, 3 H, $CH\underline{CH}_3$). 1·309–1·905 (m, 5 H, CH and $CH_2$), 4·15–4·20 (m, 2 H, $OCH_2$), 4·23–4·26 (m, 1 H, OH), 6·98(d, 2 H, aromatic), 7·91–7·93(dd, 4 H, aromatic), 8·18(d, 2 H, aromatic).

#### 2.2.4. *4-(6-Bromohexyloxy)-4′-(S-2-methylbutyloxycarbonyl)azobenzene*

60 ml of 1,6-dibromohexane, 18 g of potassium carbonate and 0·7 g of potassium iodide were heated to 65°C with stirring in 150 ml of acetone; a solution of 18·7 g (0·06 mol) of 4-hydroxy-4-(*S*-2-methylbutyloxycarbonyl) azobenzene in 150 ml of acetone was added dropwise during 2 h. The mixture was stirred and heated under reflux for 20 h. The inorganic salt was filtered off and washed with acetone; the acetone solution was evaporated to about 120 ml, and then 160 ml of ethanol was added. The precipitate was separated after cooling in an ice-box and recrystallized from ethanol. An orange solid was obtained. Yield: 19 g (66·6%), Cr 60°C $S_A$ 66°C I. IR 1724 cm$^{-1}$ (CO–). $[\alpha]_D^{16} = +3{\cdot}55$ ($c = 1{\cdot}49$, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHZ): 0·96 ppm (t, 3 H, $-CH_2\underline{CH}_3$), 1·03 ppm (t, 3 H, $CH\underline{CH}_3$), 1·31–1·93 ppm (m, 13 H, CH and $CH_2$), 3·44 ppm (t, 2 H, $-CH_2Br$), 4·06 ppm (t, 2 H, $O\underline{CH}_2CH_2$), 4·18–4·26 ppm (m, 2 H, $O\underline{CH}_2CH$), 7·01 ppm (d, 2 H, aromatic), 7·91 and 7·94 ppm (dd.4 H, aromatic), 8·17 ppm (d, 2 H, aromatic). $C_{24}H_{31}BrN_2O_3$ (Mol: 475·5). Calcd: C 60·62, H 6·57, N 5·89%. Found: C 60·74, H 6·43, N 5·70%.

#### 2.2.5. *4-[6-(Methacryloyloxy)hexyloxy]-4′-(S-2-methyl-1-butyloxycarbonyl)azobenzene*

6·0 g (0·013 mol) of 4-(6-bromohexyloxy)-4′-(S-2-methylbutyloxycarbonyl)azobenzene, 4·0 g (0·032 mol) of potassium methacrylate and 40 ml of dry DMF were stirred at 60–65°C for 4 h. The mixture was poured into ice-water, the precipitate was filtered and dried in air, and then recrystallized three times from ethanol. Yield: 5·5 g (90%), m.p. 71–72°C. IR: 1726 and 1709 cm$^{-1}$ (CO–, ester), 1632 cm$^{-1}$ ($CH_2=C(CH_3)$). $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm): 0·97 (t, 3 H, $CH_2\underline{CH}_3$), 1·03 (t, 3 H, $CH\underline{CH}_3$), 1·35–1·90 (m, 13 H, CH and $CH_2$), 1·95 (s, 3 H, $=C(CH_3)$), 4·05 and 4·17 (t, 4 H, $\underline{OC}H_2CH_2$), 4·18–4·24 (m, 2 H, $O\underline{CH_2}CH$), 5·55 and 6·10 (ss, 2 H, $CH_2=$), 7·01 (d, 2 H, aromatic), 7·91 and 7·94 (dd, 4 H, aromatic), 8·17 (d, 2 H, aromatic). $C_{28}H_{36}N_2O_5$ (Mol: 482·59). Calc: C 69·98, H 7·55, N 5·83%. Found: C 70·09, H 7·59, N 5·94%.

### 2.3. *Polymer synthesis*

All the homo- and co-polymers were synthesized by free radical polymerization according to the following procedure: 500 mg of monomer or monomer mixture and 2 mol % of AIBN (based on the monomer) as initiator were placed in a Schlenk tube and dissolved in 5–7 ml of freshly distilled toluene. The solution was degassed by passing nitrogen for 1 h and then polymerized at 70°C for 24 h. The homopolymers and copolymers were precipitated in ethanol, redissolved in $CHCl_3$ and reprecipitated with ethanol. The purified polymers were dried in vacuo at 60–65°C for 36 h. The compositions of these polymers were determined by UV spectroscopy. The properties of the resulting polymers are listed in the table (see below).

### 2.4. *Characterization of the monomers and polymers*

FTIR spectra for all of the molecular compounds and polymers were obtained using a Nicolet 5DX-FTIR spectrometer. Elemental analyses were obtained using a Perkin-Elmer 240C microanalyser. $^1$H NMR spectra were recorded with a Unity 400 NMR instrument operating at 400 MHz in $CDCl_3$.

The mesomorphic properties of the polymers were studied by DSC, polarizing optical microscopy and X-ray diffraction. DSC was carried out with a Perkin-Elmer DSC-7 instrument with a heating/cooling rate of 10°C min$^{-1}$; the maximum in a DSC enthalpy peak was taken as the phase transition temperature. The textures of the mesophases were probed by polarizing optical microscopy with a Zeiss Jena optical microscope. X-ray diffraction was carried out with a Philips PW-1700 system with a monochromatic CuK$\alpha$($\lambda$=0·15418 nm) X-ray beam and using quenched films.

Solutions of the polymers in $CHCl_3$ and the LB films were irradiated by using an 80 W Hg lamp for the photoisomerization. The UV/VIS spectra were recorded with a Shimadzu UV 3100 spectrophotometer.

Table 1. Results from the characterization of the polymers poly{2-hydroxyethyl methacrylate}-co-{6-[4-(*S*-2-methyl-1-butyloxycarbonylphenylazo)phenoxy]hexyl methacrylate}.

| Azo-content/mol % | | | |
|---|---|---|---|
| Feed | Determined | Yield/% | Liquid crystal transitions/K |
| 25 | 20·6 | 54 | g320$S_A$342·5I |
| 50 | 45·8 | 62 | g316$S_A$342·0I |
| 75 | 68·2 | 61 | g310$S_A$349·8I |
| 100 | 100 | 75 | g322$S_C^*$335·1$S_A$372·1I |

The azo content was determined from UV/VIS absorption.

### 2.5. *LB films preparation*

The LB films of the copolymers were deposited using a KSV5000 (Finland) system. The copolymers were dissolved in $CHCl_3$ and spread on the subphase of deionized and doubly distilled water at 20 ± 0·5°C. The substrates were $CaF_2$, quartz or ITO glass. Z-type LB films were deposited at 20 mN m$^{-1}$ or 18 mN m$^{-1}$ with a speed of 5 mm min$^{-1}$. The transfer ratios were around 100% and very stable.

### 2.6. *Cell construction*

The nematic liquid crystal E70 (from Merck Ltd) was mixed with glass beads of 10 or 40 μm diameter and sandwiched between two quartz plates covered with 6 layers of Z-type LB film and sealed with an epoxy resin adhesive.

### 2.7. *Alignment change determination*

The cell was set between two crossed polarizers and exposed alternately to UV (360 nm) and visible (450 nm) light from an 80 W mercury lamp filtered through a coloured glass filter. The pretilt angles at different stages were determined by a liquid crystal display parameter tester, using the rotating crystal method with a precision of ±0·2° (Changchun Institute of Physics, PRC).

## 3. Results and discussion

### 3.1. *Characterization of the polymers*

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.

The polymer composition was determined by UV spectroscopy. An acceptable yield and agreement between initial comonomer ratio and copolymer composition was obtained (see the table) in all cases.

### 3.2. *Liquid crystalline behaviour*

All of the polymers containing 20·6, 45·8, 68·2 and 100 mol % of azo group exhibited mesophase behaviour. The phase transition temperatures recorded by DSC are given in the table in detail. Using polarizing optical microscopy no typical texture could be observed, and X-ray diffraction was used to identify the mesophases using quenched films after annealing at 70°C for 24 h. Figure 2 shows the X-ray diffractograms. For the copolymer containing 20·6 mol % of azo groups, the first diffraction peak is at $d=6{\cdot}448$ nm (see figure 2 (*a*)), while the monomer length in an all *trans*-form is only $L=3{\cdot}23$ nm, giving $d/L\approx 2$. This result implies that this polymer has a bilayer arrangement $\mathrm{S_{A2}}$ in its liquid crystalline state. The copolymer containing 45·8 mol % of azo group has two diffraction peaks in the low angle region: one is at $d=4{\cdot}29$ nm, and the other is at $d=3{\cdot}27$ nm (see figure 2 (*b*)). This implies that the polymer has an interdigitated smectic phase ($\mathrm{S_{A_d}}$, $1<d/L<2$) together with a monolayer smectic ($\mathrm{S_{A_1}}$, $d/L\approx 1$) phase. Only a few papers have reported the phenomenon of coexisting $\mathrm{S_{A_1}}$ and $\mathrm{S_{A_d}}$ phases such as [14, 15]. On the contrary, the copolymer containing 68·3 mol % of azo unit has only a first diffraction peak at $2\theta=2{\cdot}78°$, $d=3{\cdot}18$ nm; this $d$ value is very close to the monomer length, so this copolymer exhibits a monolayer smectic A phase. The X-ray diffraction studies also showed that the homopolymer with 100 mol % of azo group is also monolayer. The possible structures of the different smectic mesophases of these copolymers are sketched in figure 3. Many papers have reported the existence of $\mathrm{S_{A_1}}$, $\mathrm{S_{A_d}}$ and $\mathrm{S_{A_2}}$ phases, for copolymers. We believe that the different phase structures for the three copolymers under discussion here may be caused by the different amounts of poly(2-hydroxyethyl methacrylate) contained in these copolymers. Because many hydroxy groups exist in these copolymers, intra- and inter-molecular hydrogen bonding effects cannot be ignored. For the copolymer containing 20·6 mol % of azo groups, many inter-molecular hydrogen bonds between hydroxy groups may be formed and cause the polymer to form a bilayer smectic ($\mathrm{S_{A_2}}$). For the copolymer with 50 mol % of azo group (i.e., only 50 mol % of hydroxy group), the inter-molecular hydrogen bonding together with the tendency of the side chains to overlap dominates, and as a result, this polymer adopts the $\mathrm{S_{A_d}}\mathrm{S_{A_1}}$ arrangements. For the copolymer with 31·8 mol % of hydroxy group, the $\mathrm{S_{A_1}}$ style is adopted ($d/L\approx 1$), and two possible arrangements for this are shown in figure 3. Of course further experiments must be performed in order to determine how the hydrogen bonds actually affect the liquid crystalline arrangement.

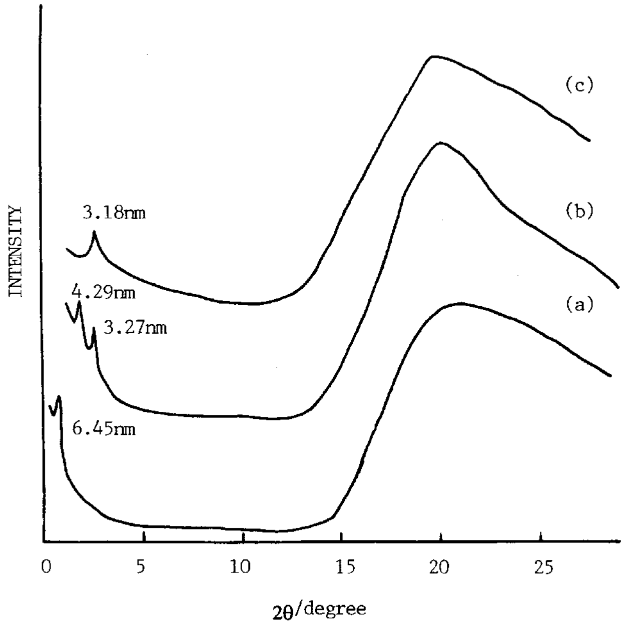


Figure 2. X-ray diffractograms of the copolymers obtained from quenched films containing 20·6 mol % (*a*), 45·8 mol % (*b*), and 68·2 mol % (*c*) of azo unit.

### 3.3. *Reversible liquid crystalline alignment induced by the LB films*

Pressure–area isotherms of the three copolymers on water are shown in figure 4. It is seen that the pressure–area isotherms of the copolymers have good linear segments and give collapse pressures at about 45, 35 and 35 mN m$^{-1}$ for the copolymers containing 20·6, 45·8 and 68·2 mol % of azo unit, respectively. The deposition pressures for these polymers were empirically chosen to be 20, 18 and 18 mN m$^{-1}$, respectively. Transfers of the three polymers were successful on the upstroke with stable ratios of about 100% and unsuccessful on the downstroke with ratios of about 50%. Thus, Z-type LB films were prepared for the experiment.

The photoisomerization of all three copolymers in chloroform solution was studied. Their spectral changes were very similar, as previously reported [16], and will not be shown individually here. For example, the copolymer with 68·2 mol % azo unit in chloroform has an original absorbance of $X_1=2{\cdot}665$ at 360 nm. After irradiation at 366 nm for 7 min, this absorbance decreases to $X_2=0{\cdot}500$. Subsequent irradiation with 450 nm light for 7 min causes this absorbance to increase to $X_3=2{\cdot}487$. It is seen that $X_3/X_1$ is 0·933.

The photoisomerization of the 20 layer Z-type LB films with 20·6 mol % of azo unit is shown in figures 5 (*a*) and 5 (*b*) after irradiation at 366 and 450 nm, respectively. The results show that the LB films undergo good photoisomerization. The LB films composed of 45·8 and 68·2 mol % of azo unit also behave analogously.

However, the tendency of the optical density at 360 nm to become weaker after UV irradiation becomes less and less for the copolymers with 45·8 and 68·2 mol % of azo unit. Furthermore, there is some difference in behaviour between the LB films and the corresponding polymer

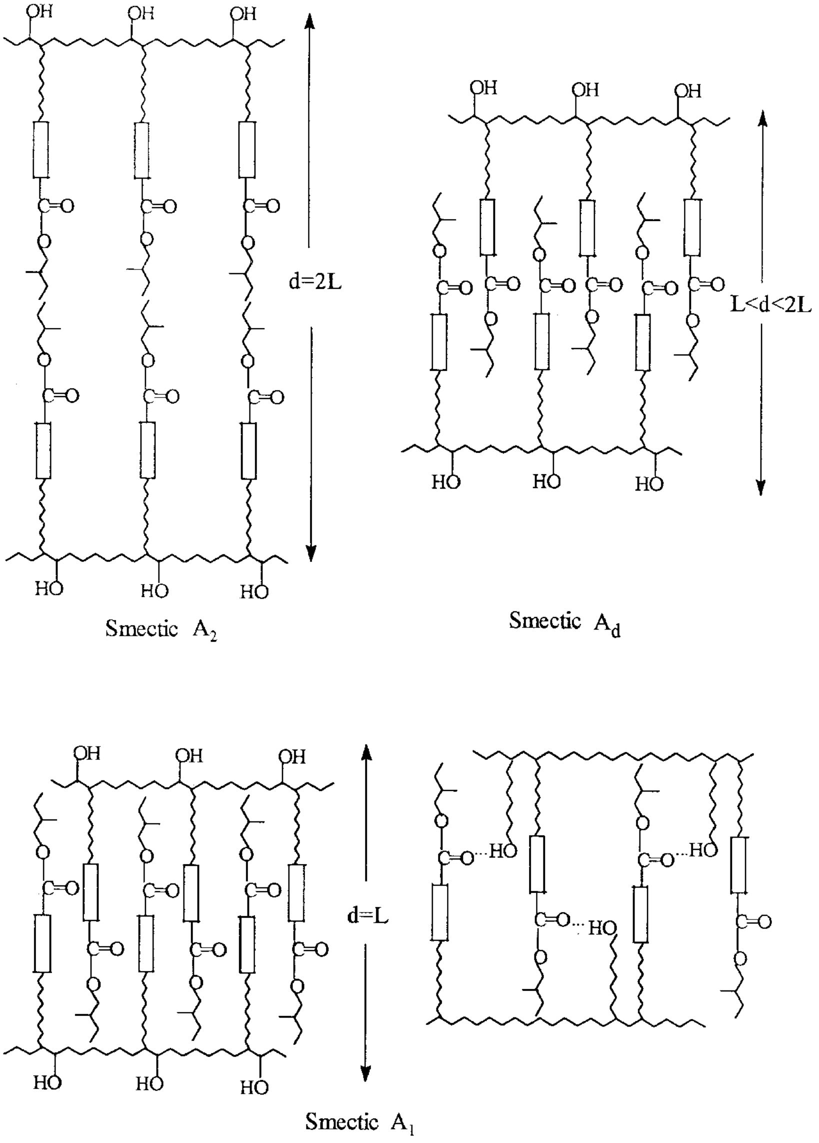


Figure 3. The possible arrangements in the $S_{A1}$, $S_{Ad}$ and $S_{A2}$ mesophases.

solutions. For the chloroform solution, the optical density ($X_3$) of the absorbance at 350–360 nm after being irradiated at 366 nm and then at 450 nm is back to 85–93% of the original value ($X_1$). However, for the LB films, the optical density ($X_3$) at 350–360 nm after irradiation at 366 nm and then at 450 nm is now 120–130% of the original value ($X_1$). An example is shown in figure 5. This difference may be caused by the difference between the rigidity of the LB films and the mobility in the solutions.

The liquid crystal cells were constructed by sandwiching the nematic material E70 (Merck Ltd) between two quartz glasses carrying separate layers of Z-type LB films. The cell thickness was adjusted with tiny glass beads of 10 or 40 μm, added to the nematic LC. The homeotropic alignment formed was extinct between crossed polarizers and showed no variation of transmission with rotation. The results show that a one layer LB films is enough to control the LC alignment, but more layers give better orientation of NLC. We found that six layers were best for orientation of the NLC, and 6 layer LB films were therefore chosen. The pretilt angle for the homeotropic alignment was 89·8° for the cell constructed with 6 layer LB films having 20·6 mol % azo unit. After unpolarized UV exposure (366 nm) using an 80 W high pressure Hg lamp for 10 min, the cell with LB films of copolymer containing 20·6 mol % azo unit had an inhomogeneous multi-domain texture suggesting low orientational order of the planar alignment [17]. However, the cells with LB films of copolymers containing 45·8 and 68·2 mol % of azo unit did not give the planar alignment even after long UV exposure, this

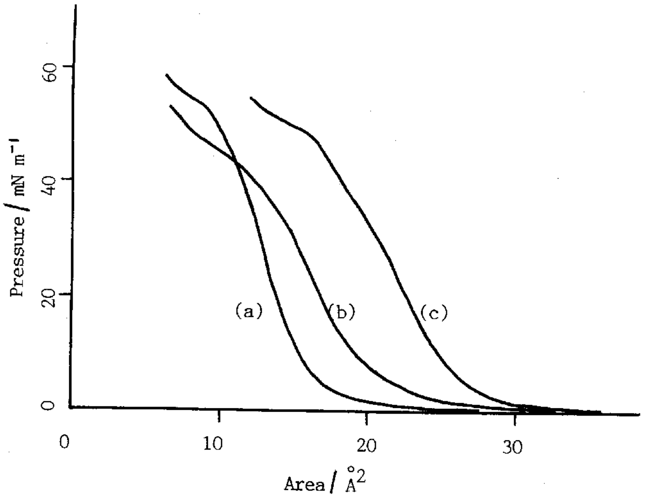
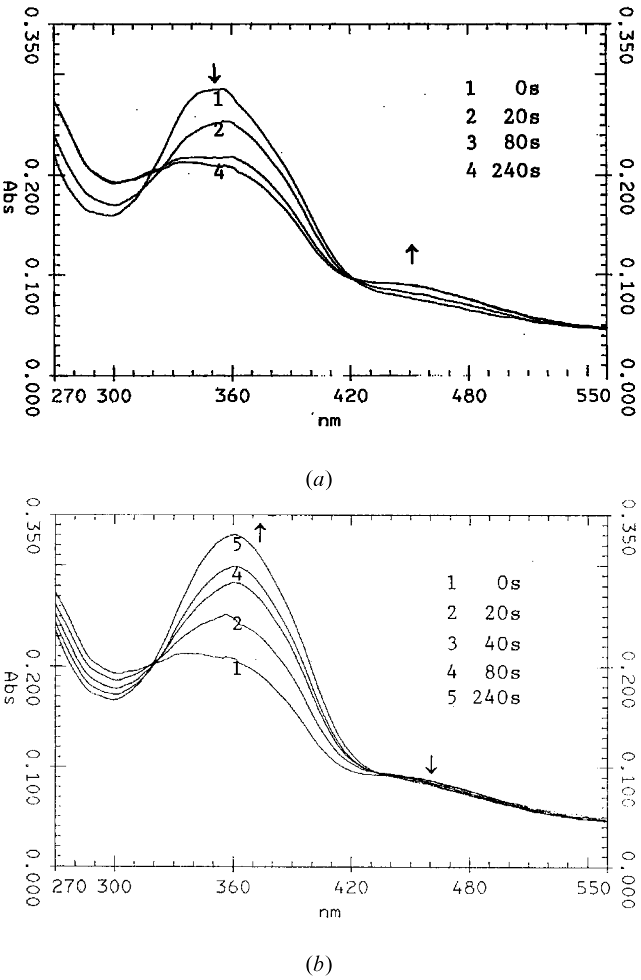


Figure 4. The π–A curves of copolymers with 20·6 mol% (*a*), 45·8 mol% (*b*), and 68·2 mol% (*c*) of azo unit on water at 20·0°C.

implying that the cells with lower amounts (such as 20·6 mol%) of azo unit can control the homeotropic and planar liquid crystal alignment, whereas cells with higher amounts of azo unit (such as 45·8 and 68·2 mol%) in the copolymers can only induce homeotropic arrangement. Finally, when we applied linearly polarized UV light, a homogeneous planar alignment which showed a white–dark change using polarizing optical microscopy was obtained within 10 min. As the azimuthal orientation $\phi$ of the sample is varied from 0° to 90°, the brightness increases, becomes brightest at 45° and then again becomes dark at 90°. On successive rotations, the cell becomes bright at 135° and 315°. Similarly, one observes dark positions at 180° and 270°. The pretilt angle for the planar alignment is 0·5°. However, both the inhomogeneous planar and the homogeneous planar alignments are not very stable. Even on exposure to white or visible light, within 5 min, the planar alignment disappears, and the homogeneous homeotropic alignment results. This may be caused by the instability of the *cis*-isomer of the azo group.

## 4. Summary

In summary, in this paper we have described the investigation of liquid crystal copolymers and studied the liquid crystal alignment induced by these copolymers containing the azo group. The copolymer composed of 20·6 mol% azo unit can regulate the homeotropic and planar alignment of a liquid crystal, and it is possible that the liquid crystal system can be used in the field of optical storage. Further experiments are in progress.



(*a*)

(*b*)

Figure 5. The UV/VIS spectral changes upon irradiation of 20 layer Z-type LB films with 20·6 mol% of azo unit: (*a*) irradiation at 366 nm, (*b*) irradiation at 450 nm. The arrows indicate the increase or decrease of optical density.

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