

ELECTROCHROMETIC STUDIES ON POLAR MULTILAYERS OF LIQUID CRYSTALLINE POLYMERS

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ABSTRACT

Electrochrometic measurements were carried on the Z-type Langmuir-Blodgett films of two liquid crystalline polymers: mono-{6-[4-(phenylazo) naphthyloxy] hexyl} (1a) and mono-{6-[4-(anthraquinone-1-azo) naphthyloxy] hexyl} (2a) ester of polymaleic acid. It was found that for both polymers, poling fields parallel and antiparallel to dipole moments of the polymer side chains induce red and blue shift in absorption bands, respectively. For polymer 1a blue shift is accompanied by absorbance increase, while red shift by absorbance decrease; but for polymer 2a only decrease in absorbance is observed. A simple model was proposed to analyze the results.

INTRODUCTION

Langmuir-Blodgett (LB) technique deserves the reputation for fabricating ultrathin ordered organic films. This technique conventionally makes use of amphiphilic molecules, which usually have great static electric dipole moments. In Z-type and X-type LB films dipole moments statistically point toward one direction and build up polar films. As a result of

Received December 5, 1993

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constructive summation of dipoles, nonlinear optical effects can be expected for such films^[1].

There is another technique called poling that can also induce a certain order, and makes use of molecules of charge-transfer variety which also have great dipole moments. In a poling process the molecules are first heated to near glass transition temperature to reduce viscosity and then rearranged by a critical external electric field^[2,3].

Thus comes the idea of combining the two techniques: to pole polar LB films. In the light of two recent papers which claims that external forces can be applied to induce large scale ordering^[4] and that LB films are well ordered and can be melted without destroying their initial order and structure^[5], this combination is expected to produce an order better than original LB films.

Moreover, poling polar films may produce some interesting spectral changes. While the traditional poling of amorphous molecules predicts only red shift and absorbance decrease, poling polar films may give both red and blue shifts in wavelength, both decrease and increase in absorbance because the dipoles in polar films are not at random orientation. In fact, the well-known absorbance decrease comes from electro-optics of liquid crystals about randomly oriented molecules. The mechanism herein is simply that an applied voltage will always cause a more vertical alignment of randomly oriented molecules and a decrease in absorption intensity under irradiation along the film normal, because the transition dipole has been rotated away from the direction of the electric vector of the exciting light.

EXPERIMENTAL

Two liquid crystalline polymers were used in the experiment: (Fig. 1) mono- $\{6-[4-(\text{phenylazo}) \text{ naphthyloxy}] \text{ hexyl}\}$ ester of polymaleic acid (1a) and mono- $\{6-[4-(\text{anthraquinone-1-azo}) \text{ naphthyloxy}] \text{ hexyl}\}$ ester of polymaleic acid (2a). Synthesis of 1a and 2a was reported in Ref. [6]. A detailed characterization of the Z-type LB films of 2a was reported in Ref. [7]. This paper presents only a brief description of film preparation and characterization of 1a. The polymer 1a, dissolved in chloroform, was spread to deionized and double distilled water of $\text{pH} = 5.5$ at $20 \pm 0.5^\circ\text{C}$, and transferred at surface pressure 18 mN/m on upstrokes only. The Z-type films of 1a were then taken to polarized infrared measurements of normal incidence and tilted incidence, comprising Vandevyver's $A_{\parallel} (i = 0)$ and $A_{\parallel} (i = \pi/3)$ ^[8].

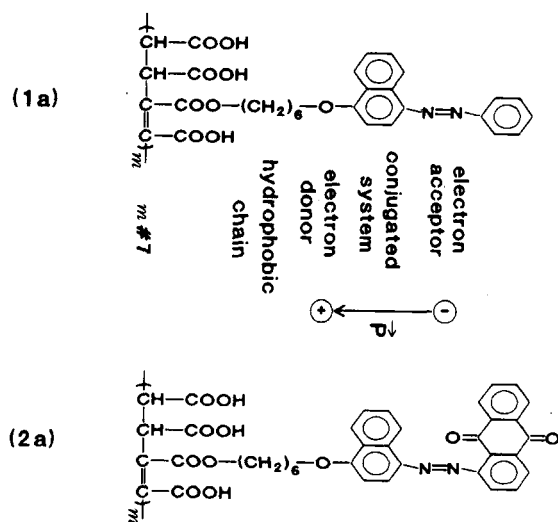


Fig. 1 Structure of the polymers (1a) and (2a)

In the electrochrometic experiment two samples of 16-layer Z-type films of 1a and 14-layer Z-type films of 2a were used. The multilayer was first deposited on indium tin oxide (ITO) coated glass or quartz, and then taken to vacuum evaporation of about 10nm thick gold or aluminium, which is highly conductive and semitransparent. (Although aluminium electrode was used in poling 1a films, it was not recommended because their oxidation in air may lead to an increase in threshold voltage). External potentials were applied across the bottom ITO electrode and top metal electrode. As shown in Fig. 2, the electric field was perpendicular to film plane. This poling setup exactly followed a design proposed by Canon Research Center^[9].

The poling setup was put into the sample cell of Shimadzu UV-365 spectrophotometer (Japan), where it was normally irradiated, heated and poled. Variation in absorbance and resistance after poling was measured versus heating temperature. Unfortunately, there seems to be no defined relationship between the temperature and poling voltage, resistance change or absorbance change. Indeed poling efficacy was indifferent to the exact temperature in a wide range around 60—80°C. For simplicity, the poling temperature T_p was chosen to be 70°C. Since the glass transition temperatures T_g of the two polymers are around 90°C, it is noteworthy that T_p is twenty degrees below T_g . In addition, the multilayer was observed

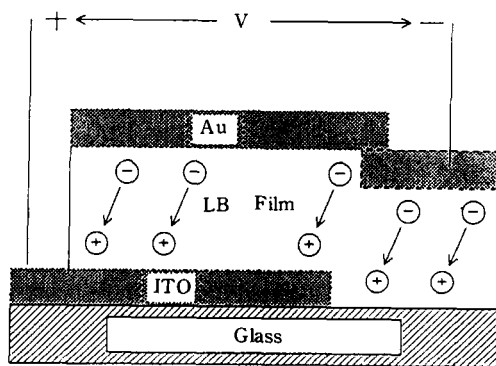


Fig. 2 Cross-sectional schematic representation of poling geometry

under a microscope before and after poling to ensure that catastrophic break down events have not occurred.

RESULTS AND DISCUSSION

1. Orientation of static dipole moments in the multilayer

As shown in Fig. 1, polymer 2a is of the charge-transfer variety and the side chains can have great static dipole moments. The ether oxygen acts as an electron donor and is somewhat positively charged; the anthraquinone as an acceptor and is negatively charged. The dipole moment, by definition, directs from anthraquinone to oxygen. Because in the Z-type films the polymer main chains lie parallel to film plane while side chains preferentially stand upward^[7], the dipole moment should point downward, i. e., toward film support. (see Fig. 2) Noting that the donor and acceptor are distantly separated, the dipole magnitude may be very large. It is estimated to be approximately 10 Debyes^[10].

The following discussion shows that the dipole moment of 1a in Z-type films also directs toward film support.

The two peaks in Fig. 3 are empirically assigned to CH₂ antisymmetrical and symmetrical stretching at 2918 cm⁻¹ and 2851 cm⁻¹, respectively. Their transition moments are at right angles with each other as well as with the hydrocarbon chain. That $A_{\parallel}$ ($i = \pi/3$) is conceivably less than $A_{\parallel}$ ($i = 0$) at these bands indicates that the hydrocarbon chain should stand up on film support. Through a conventional method, the angle between this chain and

the film normal is calculated to be 29° ^[8].

In Fig. 4 the peaks of interest are: $1726, 1597, 1451$ and 1382 cm^{-1} . The 1726 cm^{-1} band is assigned to $\text{C}=\text{O}$ stretching of carboxylic acids and can be regarded as no dichroism at all. The 1597 and 1382 cm^{-1} bands are due to ring breathing of naphthalenes, both polarized along the short axis of naphthalene^[11]. In spectrum $A_{\parallel}$ ($i = \pi/3$) the two small peaks 1467 and 1451 cm^{-1} may be due to CH_2 scissoring and ring breathing of mono-substituted benzenes, respectively^[12].

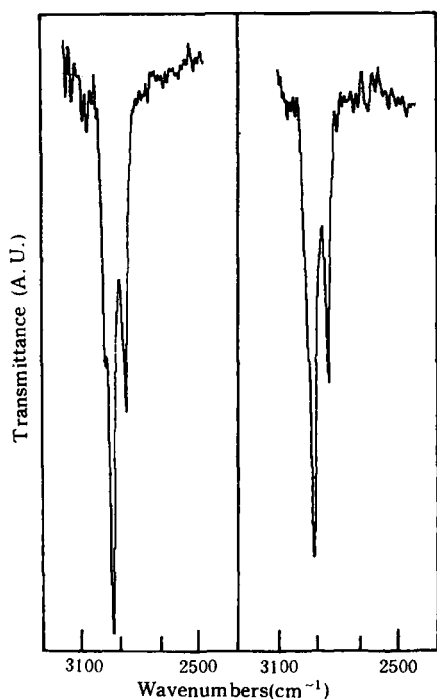


Fig. 3 Polarized infrared transmission spectra of 1a films in the range of $2500\text{--}3100\text{ cm}^{-1}$; the right spectrum is $A_{\parallel}$ ($i = \pi/3$); the left one is $A_{\parallel}$ ($i = 0$)

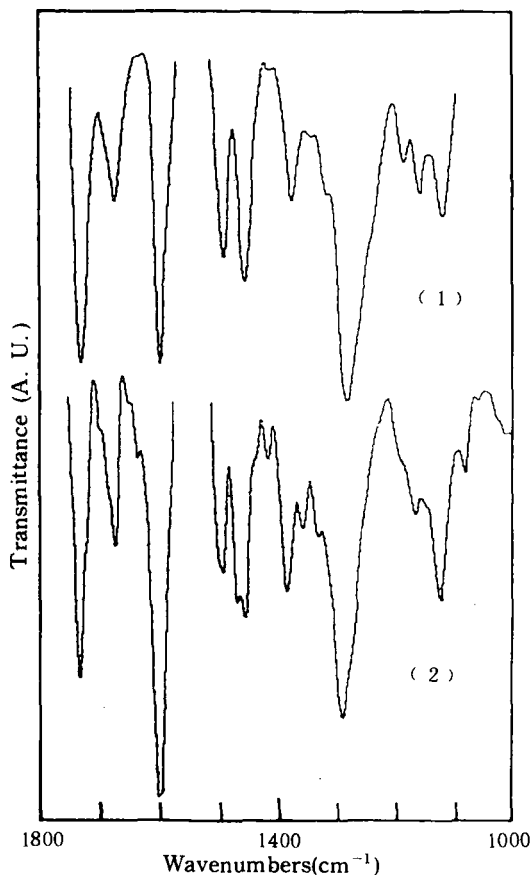


Fig. 4 Polarized infrared transmission spectra of 1a films in the range of $1000\text{--}1800\text{ cm}^{-1}$; (1) $A_{\parallel}$ ($i = 0$); (2) $A_{\parallel}$ ($i = \pi/3$)

Choosing the 1726 cm^{-1} band as a standard, direct comparison of the two spectra $A_{\parallel}$ ($i = \pi/3$) and $A_{\parallel}$ ($i = 0$) makes it clear that the absorption intensities at $1597, 1451$ and 1382 cm^{-1} increases relatively. Therefore the transition moments at these bands direct preferentially to film normal. From

the above assignment, the short axis of naphthalene must point upward. So far as the transition moment at 1451 cm^{-1} is inferred to direct along the axis through the 1 and 4 positions of the mono-substituted benzene, this axis should also point upward.

Since this axis, the short axis of naphthalene and the hydrocarbon chain actually comprise what might be called the direction of the azo side chain, it can be concluded that azo side chains direct upward on film support. Thus the static dipole moment of polymer 1a (Fig. 1) in the Z-type multilayer should direct toward film support.

2. Threshold voltages

The threshold voltages for the Z-type multilayer of 1a (2a) heated at 70°C were -14V (-8.5V) and $+11\text{V}$ ($+6\text{V}$) when the applied field directed downward and upward respectively. It is noticed that at any threshold voltage the electric resistance of the multilayer system increased over one order. For example, at -8.5V (6V) the resistance of 2a films increased from $2.6\text{K}\Omega$ ($3.2\text{K}\Omega$) to $77\text{K}\Omega$ ($85\text{K}\Omega$).

This asymmetry in poling voltage and resistance with respect to field direction can be easily understood so long as the polarity of Z-type films is considered. Nevertheless, there is no easy way to explain the remarkable increase in resistance (over one order).

In fact, a potential up to 10 volt does correspond to an electric field that is strong enough to overcome thermal motion and break weak intermolecular bonds and thereby reorient the polymers. The following estimation shows that the alignment energy significantly exceeds thermal energy E_T and is comparable with interlayer bonding energy, which turns out to be interlayer hydrogen bonding energy E_H in 2a films. On the one hand, a potential of -8.5V across the 2a film of thickness $14 \times 2.3\text{nm} = 32.2\text{nm}$ corresponds to field strength 2.6MV/cm . (Layer thickness has been calculated from X-ray diffraction patterns.) With respect to local field correction $E_{\text{local}}/E_{\text{applied}} \approx 2$, E_{local} is about 5MV/cm ^[3]. The electrostatic alignment energy of a dipole moment $\mu = 10\text{D}$ under such an electric field is equal to 1.7×10^{-20} Jolt. On the other hand, E_T is approximately $K_B T$, approximately 5×10^{-21} Jolt at $T = 350$ Kelvin, and E_H is typically ten thousand Jolts per mole, approximately 1.7×10^{-20} Jolt for each bonding.

Page et al. have developed a mature theory that estimates poling fields and explains spectral changes induced by corona poling of amorphous

materials^[9]. In their theory the threshold field of an azo dye is evaluated to be 2MV/cm—2.4MV/cm, not far from our 2.6MV/cm; also, red shift of wavelengths and absorbance decrease are quantitatively explained.

3. *Two basic principles on light absorption*

In our experiment both red and blue shift of wavelengths, increase and decrease of absorbance were observed. To get a good understanding of the spectral changes during poling the polar sample, we may begin from two basic principles on light absorption. The first is about band absorbance. It simply states that the probability that a molecule of dipole moment P absorbs a photon of electric vector E and hops from ground state to excited state is proportional to $(\phi_g|\mu|\phi_e)^2 \cos^2 \alpha$, where μ is the magnitude of P , α in the range $[0, \pi/2]$ is the angle between P and E ^[6]. Principally, both the dipole magnitude and direction may be changed by poling, thus an absorbance change is due to the variation both in μ and in α .

Another principle states that the maximum wavelength of a band depends on the angle between the optical absorption transition moment and electric vector of light that excites the molecule^[3]. Within the scope of this paper, the transition moment is parallel to static dipole moment, hence the maximum wavelength depends on α . (Recall that α has been defined as the angle between the light electric vector and static dipole moment). The band is red shifted when α becomes larger and blue shifted when α becomes smaller.

4. *Spectral changes induced by poling*

Fig. 5 and Fig. 6 show the electrochromic behavior of 1a films and 2a films, respectively. It is notable in Fig. 5 that a red shift relative to the new film is accompanied by an absorbance decrease, while a blue shift is accompanied by an absorbance increase. However, this relation is not reflected in Fig. 6, where only absorbance decrease is observed. In the following discussion the "normal" phenomenon of 1a films is attributed to mere rotation of dipole direction by electric field, while the "abnormal" phenomenon of 2a films is explained in terms of both the rotation of dipole direction and the variation in dipole magnitude.

In Fig. 5 curve 1 is the absorption spectrum of new 1a film. The 350nm band is assigned to $\pi-\pi^*$ transition of trans azo isomers whose transition moment is roughly along the long axes of azo moieties^[7]; the 440nm band is assigned to $n-\pi^*$ transition of cis azo isomers, whose transition moment

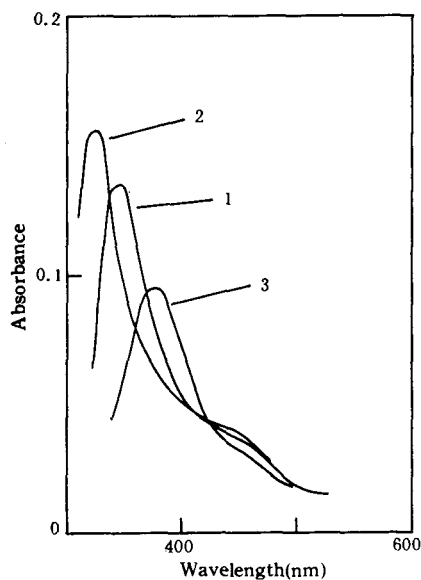


Fig. 5 Absorbance change of 16-layer Z-type films of 1a due to an external field (1) new film; (2) after poling by +11V; (3) after poling by -14V

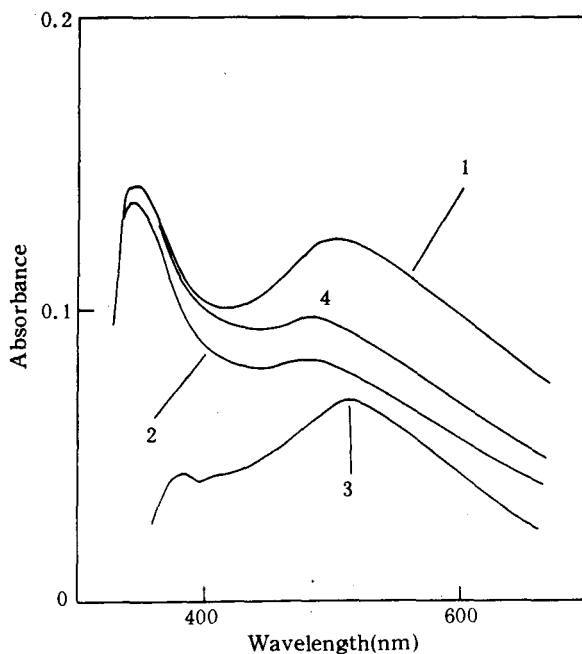


Fig. 6 Absorbance change of 16-layer Z-type films of 2a due to an external field (1) new film; (2) after poling by +6V; (3) after poling by -8.5V; (4) after cutting off +6V

direction is difficult to determine. We are only interested in the 350nm band because its transition moment is along the same direction as the static dipole moment, i. e., along the azo side chains.

According to the above two principles, provided the dipole magnitude μ in the formulas $(\phi_g | \mu | \phi_e)^2 \cos^2 \alpha$ does not change under electric field, red and blue shift should be accompanied by absorbance decrease and increase, respectively; this is exactly what is observed in poling 1a films with -14V and +11V. In fact, a downward E_{pole} exerts a force that rotates dipole moments to its direction, causing α_- larger than α_0 , as shown in the top scheme of Fig. 7. The increased angle α then results in a decrease in absorption intensity and red shift. Alternatively, an upward E_{pole} rotates dipole moments in such a way that α_+ becomes smaller than α_0 , giving an increase in absorption intensity and blue shift.

Similarly, the electrochromism of 2a films poled by -8.5V can be explained. In Fig. 6 the 500nm band is due to charge-transfer transitions, whose transition moment is also along the azo side chains. Comparing curve

3 to curve 1, there are red shift and absorbance decrease at this band, which can be ascribed to the increase in angle α . Here again, the explanation is based on the assumption that the downward field only rotates the dipole direction of 2a molecule, but not change its magnitude. However, in order to understand the strange behavior of curve 2 where blue shift is accompanied by band decrease, the hypothesis that the dipole magnitude of 2a has been reduced by a field antiparallel to it must be incorporated. The reasoning runs as follows. The blue shift should reflect a decrease in α , which would in turn give an increase in absorbance if μ in the formula $(\phi_g | \mu | \phi_e)^2 \cos^2 \alpha$ did not change; because the band absorbance has actually decreased μ must have become smaller. In Fig. 7 the smaller circle, that is, smaller charge illustrates that μ_+ of 2a is less than μ_0 .

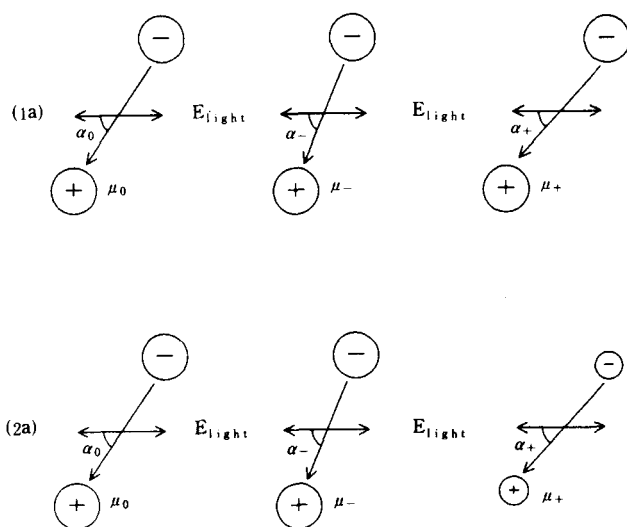


Fig. 7 Schematic illustration of the dipole moment orientation in 1a and 2a films relative to the electric vector of exciting light

(1a) 0, new film; +, poled by +11V; -, poled by -14V;

(2a) 0, new film; +, poled by +6V; -, poled by -8.5V

Physically, it is imaginable that an antiparallel E_{pole} can exert a force that moves the electron cloud around anthraquinone toward substrates through the conjugated bridge (Fig. 1), and thus the dipole magnitude decreases. On the other hand, it seems that a parallel field would move the positive charge of 2a dipole moment downward and negative charge upward. Since the distance between the negative site (anthraquinone) and positive site

(oxygen) cannot be lengthened, the dipole magnitude does not change, i. e., μ_- should be equal to μ_0 .

It is also imaginable that if the external forces disappear, the electron cloud would return to anthraquinones and the reduced dipole moment would recover. In fact, on cutting off the applied +6V, curve 2 in Fig. 6 switches to curve 4 immediately (within one second). It is seen that at the 500nm band absorbance increases but wavelength does not recover. Therefore the dipole magnitude has increased with the cut-off of electric fields, while its direction has not responded promptly.

This relaxation behavior is consistent with the physical intuition that electrons move faster than molecules. While recovery of the original dipole magnitude relies on the motion of electron cloud, relaxation of the dipole direction, hence azo side chains, consists in the motion of molecules.

It should be mentioned that it takes several weeks for all the other poled spectra in Fig. 5 and Fig. 6 to recover. That cut-off of applied potentials does not lead to any immediate change in these spectra is the evidence that their relaxation involves slow reorientation of the polymer side chains.

In summary, this paper reports the electrochrometic behavior of the LB films of two polymers. The interesting spectral changes such as red and blue shifts, absorbance decrease and increase suggest that both the magnitude and direction of static dipole moments are open to change during poling. In addition, a physical picture about the poling process is given.

Further research concerning quantitative description of the poling process and relaxation behavior is in progress.

Keywords:

LB films; LCP; Electrochrometric

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