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Alignment of liquid crystal molecules on oriented (E-CE)C/PAA films

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A film of ethyl-cyanoethyl cellulose/polyacrylic acid, (E-CE)C/PAA, using an alignment layer of liquid crystal (5CB), was prepared by shearing and then photo-polymerization of an (E-CE)C/AA solution. The orientation of the (E-CE)C chains in the sheared film and the alignment of the 5CB molecules on the films were investigated by polarizing optical microscopy and FTIR. It was found that the (E-CE)C/PAA oriented film showed perfect alignment ability for the 5CB molecules. The director of the 5CB molecules on the oriented film does not lie along the orientation direction of the (E-CE)C main chains, but inclines to that of the (E-CE)C main chains. The direction of the 5CB molecular orientation on the (E-CE)C/PAA oriented film is influenced by the degree of orientation of the (E-CE)C chains in the oriented film.

1. Introduction

Alignment layers in liquid crystal (LC) display devices are usually produced by mechanically rubbing polyimide films. For scientific and technical purposes, many studies have been carried out to understand the mechanism of the alignment of liquid crystal molecules on the surface of the rubbed film; several mechanisms have been proposed, including microgrooves on the surface formed during rubbing, and an anisotropic molecular force between the oriented polymer chains and LC molecules. The anisotropic molecular force mechanism has emerged as the most likely [1–3]. However, the rubbing process may introduce dust and static electricity, which give rise to serious problems for the LC display manufacturing process.

To overcome the disadvantages of the rubbing method, a number of rubbing-free approaches have been reported [4–11]. Recently, a novel method, the flow-induced orientation of LC polymers (LCPs) such as hydroxylpropylcellulose [12] and ethylcellulose [13] in solution has been presented, firstly by Mori *et al.* [12]. In this method, the oriented LCP films are solidified by vaporizing the solvent in a desiccator; low molar mass LC molecules may then be homogeneously aligned on the oriented LCP films. This method can overcome the disadvantages of the rubbing method, but the time of the solidification of the oriented films is excessive and it is difficult to control the orientation of the LCP chains. Photopolymerization of monomer solvent in the solution is a good choice for freezing-in the orientation of the LCPs in solution and preparing LCP oriented films [14, 15].

Ethyl-cyanoethylcellulose, (E-CE)C, a cellulose derivative with two different ether groups, dissolves in many organic solvents to form liquid crystalline solutions. In acrylic acid (AA), (E-CE)C can form liquid crystalline solutions when the concentration is above a critical value, and the liquid crystalline structure can be frozen-in by photopolymerization of the AA [14, 15]. The oriented (E-CE)C/PAA film may be a good candidate for an LC alignment film.

In this study, (E-CE)C was used as a liquid crystalline polymer, and AA as a solvent to prepare the alignment film. The effects of relaxation of the oriented polymer chains in the sheared solution film on the alignment of a low molar mass liquid crystal (5CB) were studied. The variation of the director of 5CB molecules with variation of the orientation of the (E-CE)C/PAA film is also discussed.

2. Experimental

The polymer (E-CE)C was obtained by the reaction of ethyl cellulose with acrylonitrile. The degree of substitution for ethyl was about 2.1, and for cyanoethyl was

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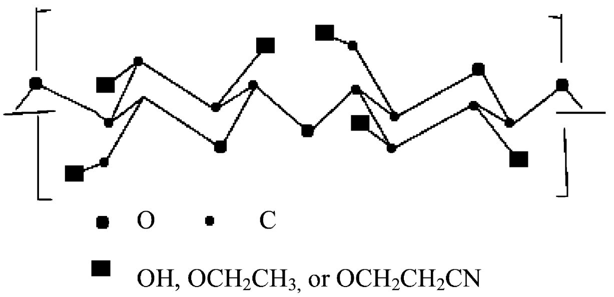

Figure 1. Molecular structure of (E-CE)C.

about 0.33, as determined by elemental analysis (CHN-O-RAPID, Heraeus, Germany). The molecular structure of the (E-CE)C is shown in figure 1. The AA was a chemically pure reagent and distilled in vacuum before use. The (E-CE)C/AA solutions were prepared by weighing the desired amount of (E-CE)C and AA into a vial, with 3% (with respect to the solvent AA) benzoin ether as a photoinitiator. The mixtures were stored in darkness for more than two weeks at room temperature, forming homogeneous solutions.

The (E-CE)C/AA solution was coated onto the surface of a clean glass substrate at room temperature and sheared by moving a glass bar at a speed of 8–10 mm s^{-1}. The thickness of the solution films, controlled by a PET spacer, was about 15 μm. The sheared solution film, relaxed for a desired time, was inserted in a chamber and irradiated with a 250 W high intensity mercury arc lamp until polymerization of the AA was complete. The (E-CE)C/PAA oriented film was obtained and used as the alignment layer.

4-Cyano-4′-*n*-pentylbiphenyl (5CB, supplied by Qinghua Liquid Crystal Company, China), a nematic liquid crystal, was dropped from a capillary onto the oriented film to form a droplet with a diameter of about 2 mm. The sample was observed under a polarizing optic microscope (POM, Olympus BH-2) with or without a hot stage (STC200C, USA). A digital camera (Nikon, COOLPIX 4500, Japan) was used to record the optical images.

The orientation of the (E-CE)C chains in the (E-CE)C/PAA oriented films was estimated from IR dichroic spectra of the oriented films, which were recorded by a FTIR spectrometer (Brucker EQUINOX55). POM was used to observe the banded texture of the oriented films and the disclination lines of 5CB on the oriented film.

3. Results and discussion

3.1. *The orientation of (E-CE)C in (E-CE)C/PAA films*

Liquid crystalline polymer under shear may be oriented along the shearing direction. On the cessation of shearing, the oriented polymer chains begin to relax to form a banded texture. The banded texture may disappear and form a multidomain structure with increasing relaxation time if the oriented solution film is not solidified. Figure 2 shows the relaxation of 40% (E-CE)C/AA oriented solution films for different relaxation times. The banded texture is clearly observed by POM after relaxing for 30 s, figure 2 (*a*). If the sample is rotated, brightness and darkness of the visual field can be observed under crossed polarizers. The intensity of the light is strongest when the angle between the shearing direction and the polar direction of the polarizer is 45°, and is weakest when the angle is 0° or 90°. This implies that the molecular chains in the oriented film are oriented along the shearing direction. With further increase of the relaxation time, the banded texture becomes obscure and gradually disappears, figures 2 (*b*, *c*). When the relaxation time is greater than 30 min, no brightness or darkness of the visual field can be observed, even if the sample is rotated; this suggests that the orientation of the (E-CE)C chains in the films has disappeared. For 50% (E-CE)C/AA solution, the banded texture changes with increasing the relaxation time, but the variation of light intensity with rotation of the sample is still observed even after a relaxation time of 60 min, because the relaxation of the (E-CE)C chains in the oriented solution film is slowed by the high viscosity of the concentrated solution. For 25%

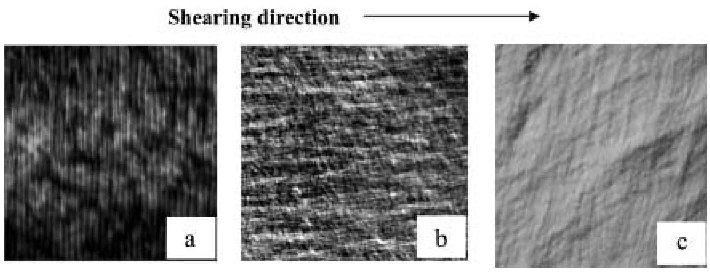

Figure 2. POM micrographs of sheared films from 40% (E-CE)C/AA solution. The relaxation time is (*a*) 30 s, (*b*) 4 min, (*c*) 8 min.

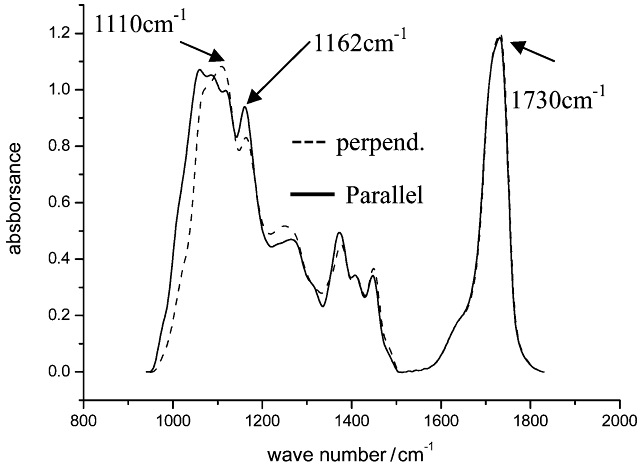

Figure 3. FTIR spectra of oriented films from 50% (E-CE)C/AA solution relaxing for 30 s after shearing, for two orthogonal polarization directions of the incident light.

(E-CE)C/AA, which is an isotropic solution, the whole visual field is dark and no characteristic structure is observed under crossed polarizers.

The time of shearing during the preparation of oriented films may influence their quality. In our experiments, high quality films were obtained after five applications of unidirectional shearing. On increasing the time of shearing, the surface of the film became rough, especially with 50% (E-CE)C/AA solution, which is disadvantageous to the alignment of 5CB.

Figure 3 shows the FTIR dichroic spectra of a 50% (E-CE)C/PAA oriented films. The orientation degree of the (E-CE)C chains in the oriented films is estimated from the dichroic ratio of the absorbance $A(1162)$, denoting the absorbance at 1162 cm^{-1}, for the antisymmertric stretching of the bridging C–O–C grouping in (E-CE)C, which is believed to be parallel to its main chain [16]. The absorbance is normalized to minimize experimental errors by dividing the absorbance $A(1162)$ by the absorbance $A(1730)$ of the carbonyl (C=O) in PAA as a reference vibration. The dichroic ratio is given by $R_{\|}/R_{\perp}$, where $R_{\|}$ and $R_{\perp}$ denote the absorbance ratios $A_{\|}(1162)/A_{\|}(1730)$ and $A_{\perp}(1162)/A_{\perp}(1730)$, respectively, and $A_{\|}$, $A_{\perp}$ denote the absorbance obtained with a probe ray polarized parallel and perpendicular to the shearing direction, respectively.

Table 1 shows the influence of the relaxation time of the oriented films on the ratio $R_{\|}/R_{\perp}$. It is found that the ratio $R_{\|}/R_{\perp}$ is greater than 1 after shearing, which suggests that the (E-CE)C chains in the oriented films are oriented along the shearing direction. It is interesting that the 25% (E-CE)C/AA solution is isotropic, but the (E-CE)C chains are still oriented after shearing, and the $R_{\|}/R_{\perp}$ ratio is 1.15. This ratio decreases with increased relaxation time. On relaxing for 30 min, for the 40% (E-CE)C/AA solution, and 15 min for the 25% (E-CE)C/AA solution, the dichroic ratio becomes equal to 1. The dichroic ratio of the 50% (E-CE)C/AA solution is still greater than 1 after relaxing for 60 min. These results suggest that the degree of orientation of (E-CE)C decreases with increasing relaxation time. The orientation disappears totally after relaxing for 30 min in the 40% solution, and for 15 min in the 25% solution. However, the orientation in the 50% solution is still retained after relaxing for 60 min.

Table 1. The influence of relaxation time on the $R_{\|}(1162)/R_{\perp}(1162)$ ratio.

Relaxation time/min	Solution concentration		
	25%	40%	50%
0.5	1.15	1.48	2.00
4	1.09	1.13	1.20
8	1.04	1.05	1.15
15	1.00	1.04	1.12
30		1.00	1.08
60			1.06

3.2. *Alignment of 5CB on (E-CE)C/PAA films*

Yamaguchi and Sato [17] have proposed a model for the director distribution and disclination line in a nematic LC (NLC) droplet for homogeneous surface alignment. If the NLC molecules uniformly align parallel to the alignment surface, the NLC director changes gradually from parallel alignment at the alignment surface to perpendicular alignment at the air interface, figure 4 (*a*). Then a straight disclination line appears at the centre of a droplet, figure 4 (*b*). The director of low molar mass LC molecules on alignment layers can thus be ascertained easily with this model.

Figure 5 shows the process of disclination line formation. A curve across the droplet can be observed under crossed polarizers after the 5CB is dropped on the

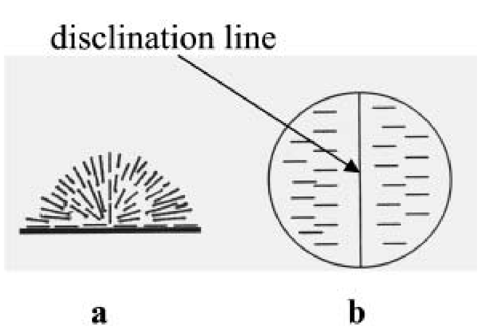

Figure 4. Model of director distribution (*a*) and disclination line (*b*) in an NLC droplet for homogeneous surface alignment.

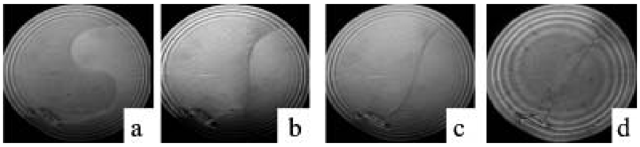

Figure 5. The formation process of a disclination line in a 5CB droplet after (*a*) 5 s, (*b*) 77 s, (*c*) 129 s, (*d*) 6 min. The alignment film prepared from 50% (E-CE)C solution was relaxed for 30 s.

oriented film surface, figure 5 (*a*). The curve moves towards the centre to form a straight disclination line over several minutes, figures 5(*b–d*), while the ends of the line at the edge of the droplet remain stationary. It is suggested that the 5CB molecules are homogeneously aligned on the oriented film and the direction of the disclination line is determined at the start of its formation.

The alignment of the 5CB molecules on the oriented film is influenced by the concentration of the (E-CE)C/AA solution and the relaxation time of the oriented (E-CE)C/AA solution films. Figures 6, 7 and 8 show micrographs of the 5CB droplets on the (E-CE)C/PAA oriented films prepared from solutions with concentration of 25%, 40% and 50%, respectively. From these figures the straight disclination line is clearly observed in the droplet. It is suggested that the 5CB orientation is parallel to the alignment surface at the film surface, according to the model. But the lines are not perpendicular to the shearing direction. That is, the director of the 5CB molecules inclines to the orientation direction of the (E-CE)C chains in the oriented film. The phenomenon of the inclination is related to the structure of the (E-CE)C chain. According to the proposed mechanism, the LC alignment on the oriented film is induced by the interaction between LC molecules

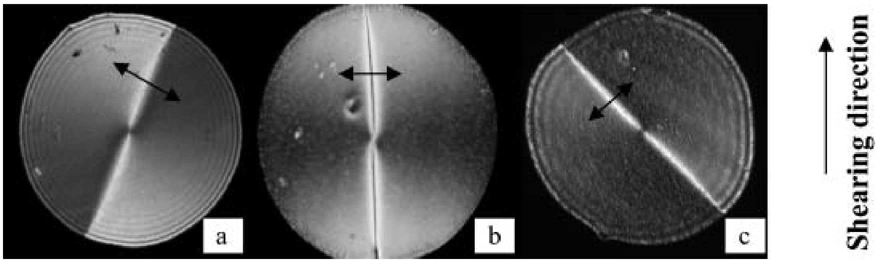

Figure 6. Disclination lines on oriented films formed from 25% (E-CE)C/AA solution after relaxing for different times: (*a*) 30 s, (*b*) 2 min, (*c*) 8 min. The double-headed arrows perpendicular to the disclination line show the 5CB alignment direction on the films.

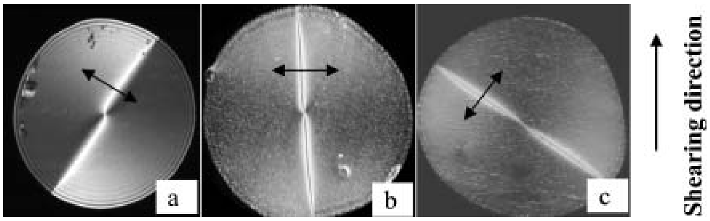

Figure 7. Disclination lines on oriented films formed from 40% (E-CE)C/AA solution after relaxing for different times: (*a*) 30 s, (*b*) 4 min, (*c*) 10 min. The double-headed arrows perpendicular to the disclination line show the 5CB alignment direction on the films.

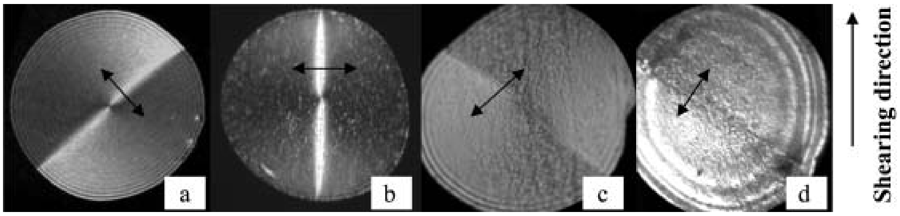

Figure 8. Disclination lines on oriented films formed from 50% (E-CE)C/AA solution after relaxing for different times: (*a*) 30 s, (*b*) 5 min, (*c*) 10 min, (*d*) 60 min. The double-headed arrows perpendicular to the disclination line show the 5CB alignment direction on the films.

and oriented polymer chains [1–3, 18, 19]. Thus the oxygen atom (O) and the cyano group (C≡N) in the (E-CE)C chains may play an important role in the alignment of the 5CB molecules because of the strong interaction of the p-electrons of the oxygen atom and π-electrons of the C≡N group in the (E-CE)C chains with the π-electrons of the biphenyl in the 5CB molecules. This interactive force may not be strongest along the main chains, but inclines to the main chains because the side groups with the oxygen atoms and the C≡N groups are perpendicular to the main chains [16]. Therefore, the 5CB director on the oriented film is inclined to the direction of the (E-CE)C main chains. This phenomenon has also been observed on the oriented film surface of other cellulose derivatives [12, 13] and polystyrene [17, 18]. On an oriented polystyrene film obtained by the rubbing method, the orientation of low molar mass LC molecules is perpendicular to the polystyrene main chains because of the phenyls perpendicular to the main chain [17, 18].

It can also be seen from figures 6, 7 and 8 that the direction of the disclination line varies with the relaxation time of the sheared solution film. With a relaxation time of 30 s, the disclination line inclines clockwise against the shearing direction. But the angle between the line and the shearing direction is about 20°, 30°, and 45° when the oriented film is prepared from the 25%, 40%, and 50% (E-CE)C/AA solutions, respectively. This difference results from differences in the degree of orientation of the polymer chain in the film surfaces. It is worth noting that for the isotropic 25% solution the polymer chains can also be oriented after shearing (table 1) and the film can also be used as the alignment layer to align 5CB.

With relaxation times of 2, 4 and 5 min for the 25%, 40%, and 50% solutions, respectively, the disclination lines are almost parallel to the shearing direction. And with further increase of the relaxation time, the disclination line inclines counterclockwise against the shearing direction. When the relaxation time is greater than 15 min for the 25% solution and 30 min for the 40% solution, the disclination line can hardly be observed because the orientation of the (E-CE)C chains in the oriented films disappears (table 1). The straight disclination line on the oriented film formed from 50% solution can still be observed after relaxing for 60 min, figure 8(*d*). The angle between the direction of the line and the shearing direction is 60°–75°, which is consistent with Mori's results [12]. It is suggested that the homogeneous alignment of 5CB on the sheared film is dependent on the orientation of polymer chains in the film. If the orientation of the (E-CE)C chains in the oriented film is retained, the oxygen atoms and the C≡N groups distribute uniformly. The atoms and the groups, whose distance is less than the correlation length of the 5CB molecule, act as pinning centres, sufficient to align the LCs fully [2, 20]. During relaxation of the sheared films, the relative location and distance between pinning centres are changed, which results in the variation of the ordered distribution of the polar groups and the atoms in the (E-CE)C chains. Therefore, 5CB molecular alignment is changed. As a result, the 5CB director is varied with invariance of the director of the (E-CE)C chains. If the orientation of the (E-CE)C chains in the oriented film disappears, the polar atoms (oxygen) and the groups (C≡N) are distributed non-uniformly in the films. So the films cannot align the 5CB molecules.

In order to investigate the homogeneity of alignment of the ordered film, 20 droplets of 5CB were dropped on the ordered film. It was found that the disclination lines in the droplets on the ordered film after relaxing for 30 s are almost parallel. With increasing relaxation time of the ordered film, the disclination lines in the droplets become non-parallel, and the angles between the lines become bigger. As an example, the angle between the disclination lines in the 5CB droplets on the ordered film from 50% (E-CE)C/AA solution is about 15° after relaxing for 60 min. It is suggested that the alignment property of the ordered film is better if the relaxation time is shorter.

The alignment of the 5CB molecules is influenced by temperature. If the droplet is heated from room temperature to the clearing point of 5CB (34.8°C) at a rate of 0.1°C min^{-1}, the disclination line disappears suddenly and dark brushes appear at the centre of the droplet, figure 9 (*a*); these amalgamate into a large dark cross in the centre of the droplets, figure 9 (*b*). Subsequently, the whole visual field becomes bright under crossed polarizers. When the temperature decreases from 36°C to room temperature at a rate of 0.1°C min^{-1}, a reversible process is observed. When the temperature is lower than 34.6°C, the disclination line appears again, figure 9 (*c*); the direction of the line is the same as that before heating, figure 5(*d*). After several

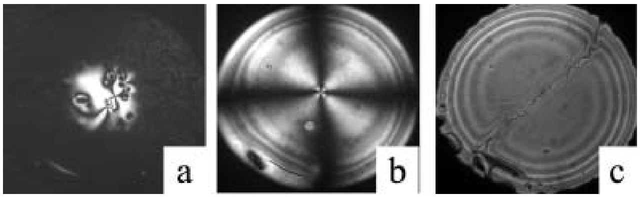

Figure 9. The variation of 5CB alignment on the oriented film with temperature: (*a*, *b*) 34.8°C; (*c*) 34.6°C. The alignment film prepared from 50% (E-CE)C solution was relaxed for 30 s.

recycles of heating and cooling, the alignment ability of the oriented film for the 5CB molecules is unchanged. When the temperature is above T_g of PAA (about 100°C), the alignment ability of the oriented film is almost lost, because the motion of PAA chain segments results in a change in the orientation of the (E-CE)C chains in the film. The orientation of the 5CB on the ordered film remains unchanged for several months under ambient conditions (exposure to air and light), which reflects the stability of the ordered film. Therefore, the alignment property of the ordered film is very stable when the temperature is lower than 100°C.

4. Conclusion

The (E-CE)C chains in (E-CE)C/AA solution are oriented by shearing and the sheared film of (E-CE)C/AA solution can be solidified by photopolymerization of the AA. The (E-CE)C/PAA oriented film can be used as an alignment layer which shows perfect alignment ability toward 5CB molecules. The alignment of 5CB molecules depends on the orientation of the (E-CE)C chains in the oriented film. If this orientation disappears entirely, it cannot align the 5CB molecules. If the orientation of the (E-CE)C chains is retained to some degree, the 5CB molecules can be oriented. The orientation direction of the 5CB molecules on the oriented film is changed with variation of the degree of orientation of the (E-CE)C chains in the film. Variation of the 5CB director is considered to result from the variation of ordered distribution of the cyano groups and oxygen atoms in the (E-CE)C chains during relaxation of the sheared films.

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