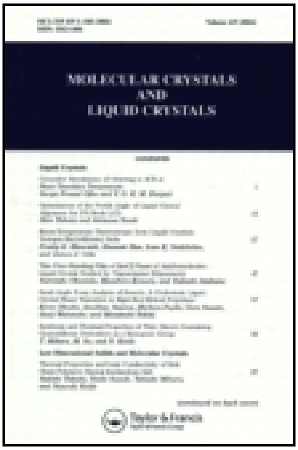

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Azimuthal Anchoring Energy and Pretilt angle of Photo-aligned Nematic Liquid Crystals on a Polyimide and Poly(vinyl cinnamate) Blend Alignment Layer

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Azimuthal Anchoring Energy and Pretilt angle of Photo-aligned Nematic Liquid Crystals on a Polyimide and Poly(vinyl cinnamate) Blend Alignment Layer

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The azimuthal anchoring energy and pretilt angle of a nematic liquid crystal (E7) which was aligned on a thin layer of polyimide (PI) and poly(vinyl cinnamate) (PVCi) blend by the irradiation of polarized UV on the surface, were studied. Within a PVCi content of 10~100 wt%, the azimuthal anchoring energy remains unchanged with the decrease of the PVCi content in the blend, which is attributed to the preferential occupation of the surface by cinnamate chromophore. The blend alignment layer revealed a significantly enhanced thermal stability of azimuthal anchoring in comparison with the pure PVCi based alignment layer on account of the stiffening of the layer by the incorporated PI, which caused low thermal relaxation of the structural anisotropy developed from PVCi in the blend. The addition of PI into PVCi was also found to be effective for improving the thermal stability of the pretilt angle.

Keywords: Photo-induced liquid crystal alignment; Polyimide; Poly(vinyl cinnamate); Blend; Thermal stability; Azimuthal anchoring energy; Pretilt angle

INTRODUCTION

In recent years, the control of molecular orientation of liquid crystal (LC) on a thin layer of photo-reactive polymer has attracted considerable attention in the field of liquid crystal displays[1,2] due to its potential application to the rubbing-free production of LC alignment layers. It has been reported that the LC photo-alignment is

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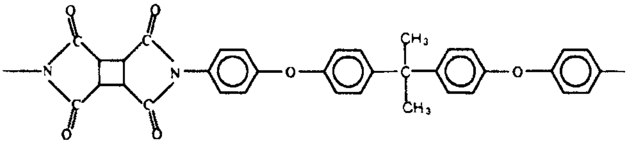
performed with the use of the alignment films having cis-trans chain conformational transition[3,4], photo-crosslinking[5~8]. and photo-dissociation of polymers[9,10].

A thin film of poly(vinyl cinnamate) (PVCi), one of the representative photo-crosslinkable photoresists, provides a photo-active surface for achieving the photo-control of in-plane alignment of LC with polarized UV irradiation[5]. Despite its capability to align LC, PVCi suffers from its low thermal stability in practical applications: LC alignment is significantly disrupted upon the prolonged exposure to temperatures approaching 100°C.[6]

Recently, we have improved the thermal stability of LC alignment on PVCi layers by incorporating thermally stable polyimide (PI) into the PVCi by means of blending.[11,12] The PI derived from cyclobutane dianhydride and 2,2-bis(4-aminophenoxyphenyl)propane (CBDA-BAPP) could be used as an effective component for blending with PVCi due to its good miscibility with PVCi. The structure of CBDA-BAPP polyimide is shown below.



CBDA-BAPP Polyimide

For the blend alignment layer, the uniform LC alignment was maintained even after the annealing of the corresponding LC cell at 170°C for 10 min[11,12], which demonstrated that the blending of the thermally stable polymer with PVCi can be a simple and effective way to overcome the drawback of PVCi.

The present article reports on the azimuthal anchoring energy and pretilt angle of a nematic liquid crystal (E7, Merck), which are of critical importance in electro-optic operation of LCD on the PI/PVCi blend alignment layers. The effect of the blend ratio on the azimuthal anchoring energy and pretilt angle is discussed. The thermal stabilities of the azimuthal anchoring and pretilt angle of the E7 nematic liquid crystal for the PI/PVCi blend alignment layers are also evaluated.

EXPERIMENTAL

Material

PVCi, the weight-averaged molecular weight of which is 200,000, was purchased from Aldrich and used as received. PVCi is actually the copolymer of vinyl cinnamate and vinyl alcohol. The relative fraction of the vinyl cinnamate unit in the copolymer determined from the ^{1}H NMR spectrum of the PVCi was 76 mol%. The nematic liqud crystal, E7, was purchased from Merck. The synthesis of CBDA-BAPP polyamic acid, the precursor of CBDA-BAPP polyimide, is described elsewhere.[11,12]

Film preparation

The 1 wt% NMP solution of the mixture of CBDA-BAPP polyamic acid and PVCi was spin-coated onto a glass substrate at 1800 rpm and the cast was prebaked at 60°C for 1 hr. The thermal imidization of the cast was then conducted at 200°C for 1 hr.

After the thermal imidization of polyamic acid in the blend alignment layer, the photo-reaction of PVCi was carried out by irradiating polarized UV on the blend alignment layer. The polarized UV light (250~340nm) was obtained by passing the light from a 300W high-mercury arc (Oriel) through a UV linear dichroic polarizer (27320, Oriel) and a UV filter (51650, Oriel) for the irradiation on polymer thin films. The intensity of the irradiated UV measured by a UV detector (UIT-150, Ushio) was 5mW/cm^2.

For brevity, the blend will be designated in this paper as PI*n*, where *n* indicates the wt% of polyimide in the blend.

Liquid crystal alignment

The homogeneously aligned LC cell was constructed by sandwiching the nematic LC (E7) between a pair of glass substrates covered with a thin film of the blend, and sealed with an epoxy resin adhesive. The thickness of the LC layer was adjusted by spherical spacers of 8μm diameter for the azimuthal anchoring energy measurement and by a thin film of 50μm thickness for the pretilt angle measurement. The E7 liquid crystal was injected into the cell via capillary action in the isotropic phase, and the cell was gradually cooled to room temperature.

Azimuthal anchoring energy and pretilt angle measurement

The azimuthal anchoring energy of LC on the blend alignment layer was determined by measuring the width of a disclination wall called the Neel wall.[7,13] The width of the Neel wall, *w*, is defined as the distance between two black brushes where the director is rotated from 45° to 135° with respect to the director in a uniformly aligned region. The azimuthal anchoring energy (E_φ) is then calculated using the following formula.

$$E_\varphi = 2dK_1/w^2 \tag{1}$$

Here K_1 and d represent the elastic constant for splay deformation and the thickness of the LC layer respectively.

The pretilt angle of nematic LC on the blend substrate was measured by means of the crystal rotation method as described elsewhere.[14,15]. From the transmittance as a function of the incident angle of He-Ne a laser beam as a probing light passed through a cell set between two crossed polarizers, and the value for pretilt angle was determined.

RESULTS AND DISCUSSION

Effect of blend ratio on azimuthal anchoring energy of the nematic LC aligned on the blend alignment layers

Figure 1 shows the plot of the azimuthal anchoring energy of the nematic LC on the blend alignment layers as a function of the PVCi content in the PI/PVCi blend. The polarized UV (irradiation energy : 1.5 J/cm^2) was irradiated on the alignment layer at normal incidence. The azimuthal anchoring energy for pure PVCi was about 4×10^{-6} J/m^2 which is the same as the previously reported one determined from a twisted angle of LC in the TN cell by Bryan-Brown and his coworkers[8]. It is about three times higher than that for pure PI owing to the higher photo-reactivity of PVCi. From Fig. 1, the azimuthal anchoring energy is found to be independent of the blend ratio in the range of PVCi content from 10 to 100 wt%. However, below 10 wt% of the PVCi content, the value for the azimuthal anchoring energy of the LC on the blend layers approached that for the pure PI-based alignment layer as the PVCi content decreased. It is quite interesting that, above 10 wt% of the PVCi content, the azimuthal anchoring energy of the LC was not reduced with the decrease of PVCi content. The consideration of the surface structure can provide a feasible explanation for this behavior. Since liquid crystal alignment is governed by the outermost part of the alignment layer, it can be profoundly affected by the orientation of surface functional group. Providing that the surface is preferentially occupied by the cinnamate chromophore above 10 wt% of the PVCi content, the weak dependency of the azimuthal anchoring energy of the LC on the blend ratio would be feasible.

In order to obtain information on the surface structure of the PI/PVCi blend layer, the water contact-angle was measured by varying the blend ratio and the results are shown in Fig. 2. Interestingly, the blend ratio dependence of the water

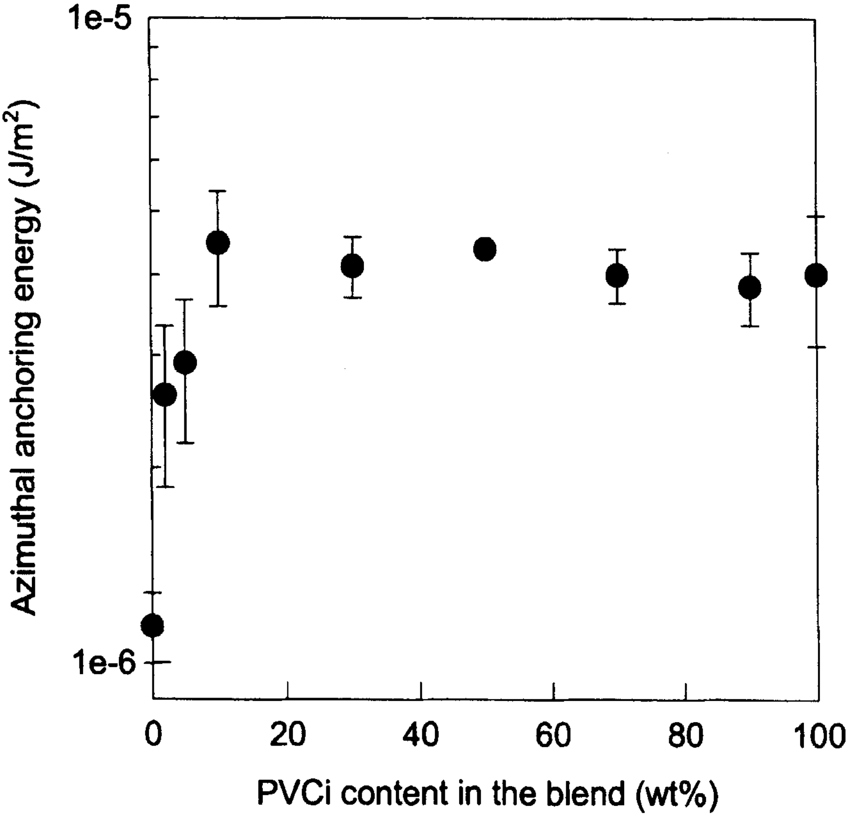


FIGURE 1 Plot of azimuthal anchoring energy of E7 nematic liquid crystal on the PI/PVCi blend layer exposed to polarized UV of 1.5J/cm^2 at normal incidence as a function of the PVCi content in the blend

contact-angle resembled that of the azimuthal anchoring energy. Above 10 wt% of the PVCi content, the water contact-angle was nearly unchanged by the blend ratio as in the case of the azimuthal anchoring energy. The value for the water contact-angle approached that for pure PI with a decrease of PVCi content below 10 wt% of the PVCi content. The above behavior indicates that the surface of the blend alignment layer is close to that of pure PVCi when the PVCi content in the blend exceeds 10 wt%. It is owing to the lower surface energy of PVCi compared to PI as listed in Table. 1. In spite of the larger dispersion part of the surface energy for PVCi compared to PI, the total surface energy of PVCi was lower than PI due to its much smaller polar surface energy. To minimize the surface energy of the blend layer, the cinnamate groups would orient toward the surface and determine the properties associated with interaction between the LC and the alignment layer such as the azimuthal anchoring energy.

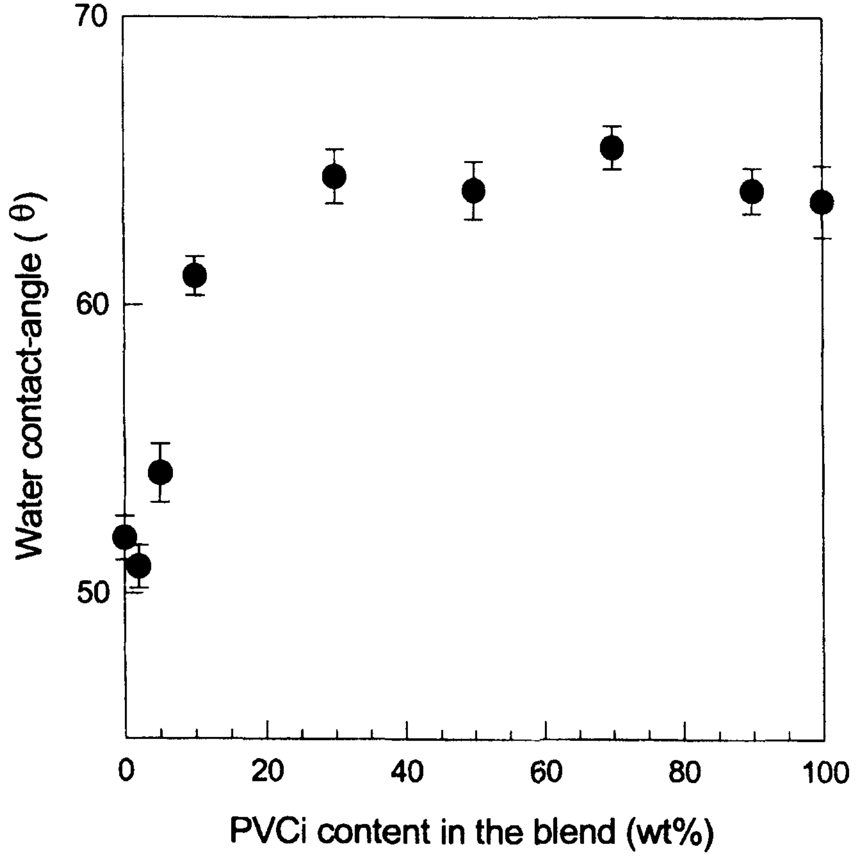


FIGURE 2 Plot of water contact-angle on PI/PVCi blend layer without exposure to polarized UV as a function of the PVCi content in the blend

TABLE I Surface energy of PI, PVCi and PMMA used in this work

	γ^d(dyne/cm)	γ^p(dyne/cm)	γ(dyne/cm)
CBDA-BAPP PI[a]	12.9	35.5	48.4
PVCi[a]	22.6	19.3	41.9
PMMA[b]	29.6	11.5	41.1

a. determined from contact-angles of water and ethylene glycol.
b. reference 16

The correlation between the azimuthal anchoring energy and the water contact-angle for the miscible blend of poly(methyl methacrylate) (PMMA) and

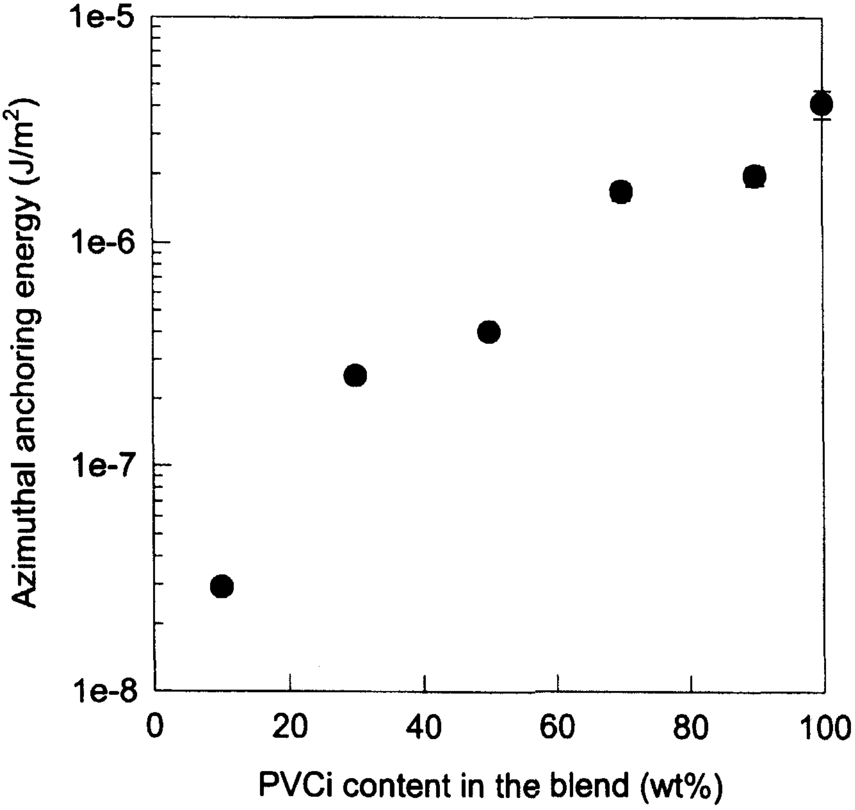


FIGURE 3 Plot of azimuthal anchoring energy of E7 nematic liquid crystal on PMMA/PVCi blend layer exposed to polarized UV of 1.5J/cm^2 at normal incidence as a function of the PVCi content in the blend

PVCi could support the above explanation of the importance of the surface structure of LC alignment. PMMA does not have the capability to align liquid crystal on its surface exposed to polarized UV. Figures 3 and 4 represent the dependence of the azimuthal anchoring energy and water contact-angle on the blend ratio for the PMMA/PVCi blend respectively. The azimuthal anchoring energy steadily decreased with increasing the PMMA content in the blend, which could be well correlated with the water contact-angle behavior: the gradual decrease of the water contact-angle with the PVCi content. Since the surface energy of PMMA is comparable to that of PVCi as shown in Table. 1, the surface concentration of the cinnamate group will decrease with the increase of the PMMA content, resulting in the decrease of the azimuthal anchoring energy with the PMMA content. The comparison of the azimuthal anchoring energy for the PI/PVCi blend and PMMA/PVCi blend provides the merit of PI as a blending component for PVCi to improve thermal stability without scarifying the azimuthal anchoring energy.

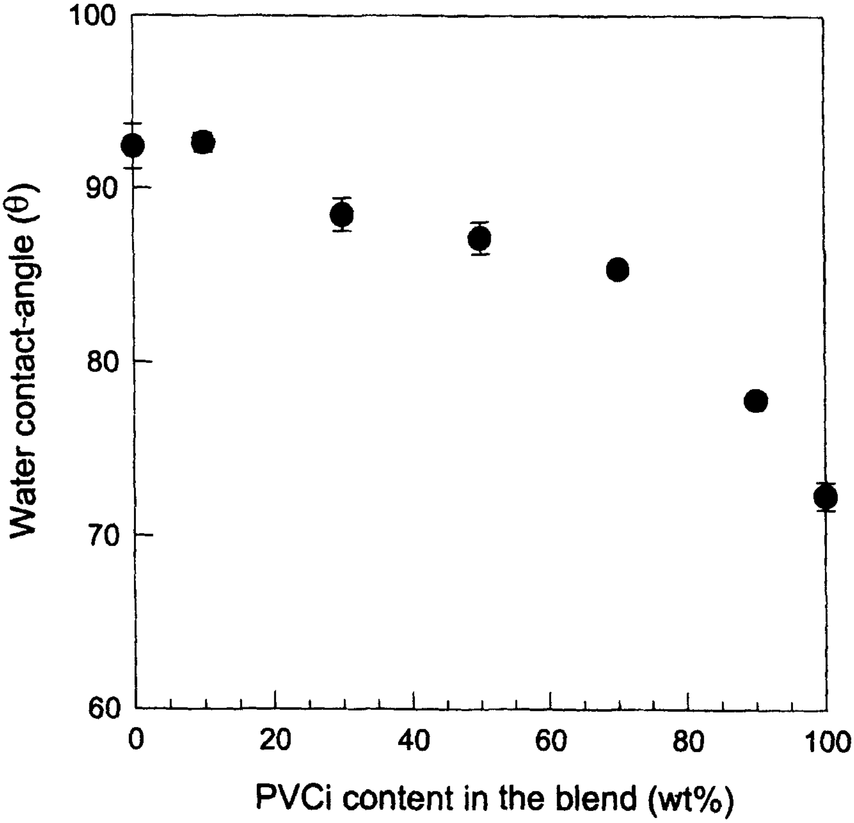


FIGURE 4 Plot of water contact-angle on PMMA/PVCi blend layer without exposure to polarized UV as a function of the PVCi content in the blend

Effect of annealing temperature on the azimuthal anchoring energy of nematic LC aligned on the blend alignment layers

In order to obtain information on the thermal stability of LC alignment, the anchoring energy of the LC was measured after the annealing of LC alignment layer or LC cell at various temperatures ranging from 100 to 200°C. Figure 5 shows the change of the azimuthal anchoring energy of the LC with the annealing temperature of the LC alignment layer for PVCi, PI50 and PI90. The thermal imi-

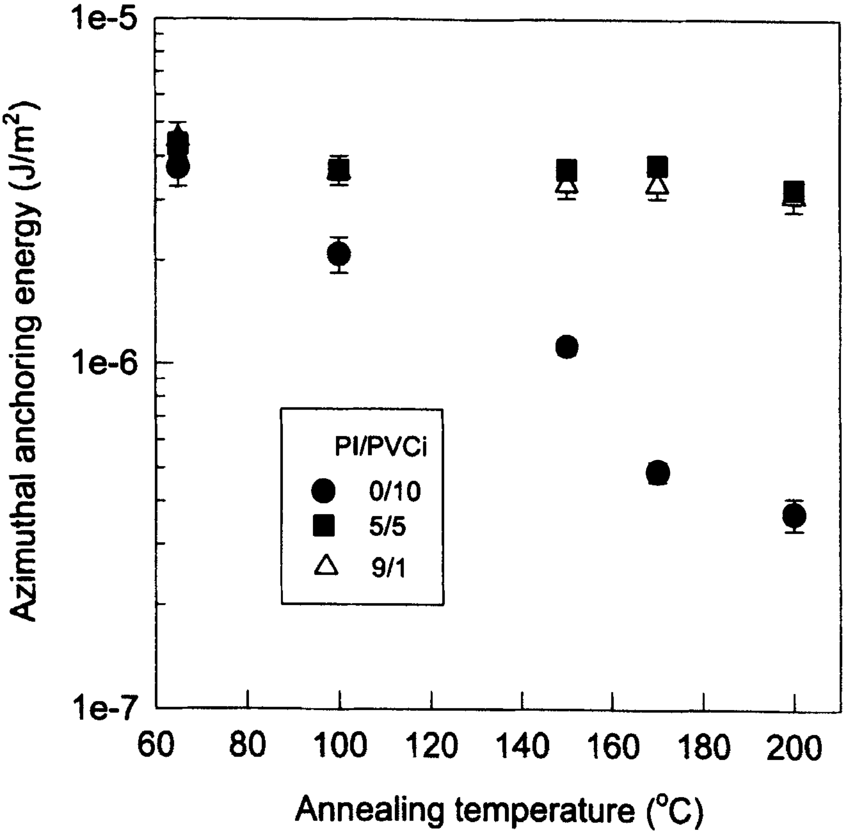


FIGURE 5 Change of azimuthal anchoring energy of E7 nematic liquid crystal on PVCi, PI50, and PI90 alignment layers by the annealing at various temperatures for 10 min

dization temperature and the energy of the irradiated polarized UV for the specimen were 200°C and 1.5 J/cm^2 respectively. PVCi showed a gradual decrease of the azimuthal anchoring energy with the annealing temperature, while, the azimuthal anchoring energies for PI50 and PI90 were not changed even after heating at 180°C for 10 min.

The azimuthal anchoring energy of a LC is generally considered to be dependent on the structural anisotropy of the surface of the substrate.[5,7] Li and coworkers[12] previously reported that the azimuthal anchoring energy increases exponentially with increasing the optical anisotropy of the PVCi film. The higher thermal stability of the azimuthal anchoring means that the structural anisotropy developed from PVCi is well preserved during the annealing as schematically

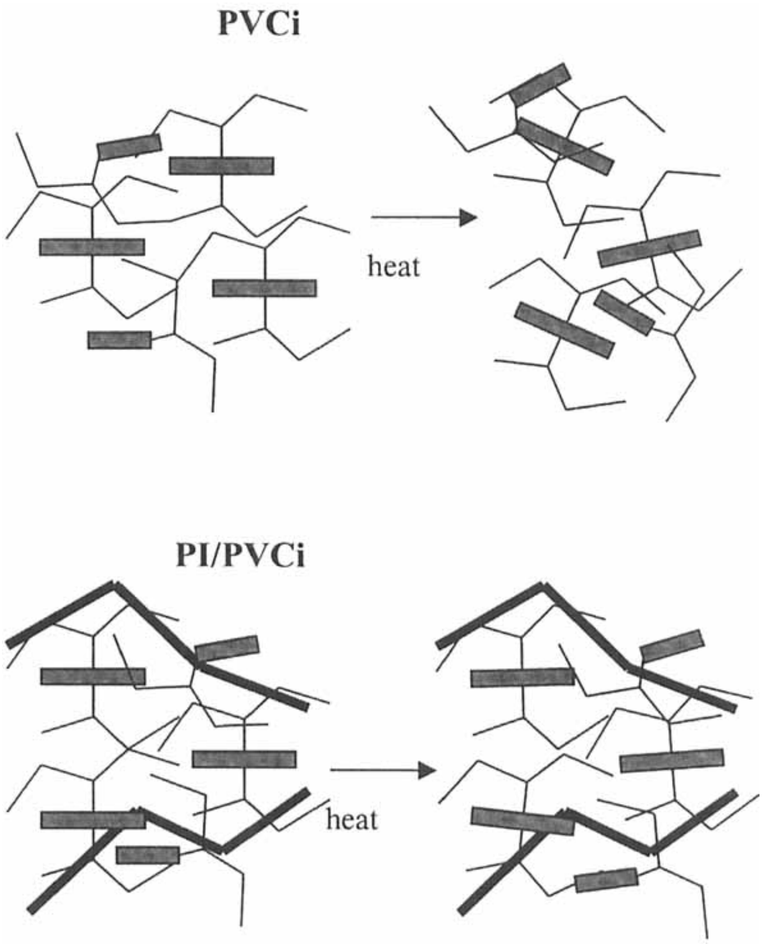


FIGURE 6 Schematic illustration of thermal relaxation of the structural anisotropy for the PVCi and PI/PVCi blend alignment layers during the heating at enhanced temperature

illustrated in Fig. 6. For pure PVCi, the thermal motion of the main chain may randomize the anisotropic distribution of the dimer or the unreacted cinnamate group. However, in the case of the blend alignment layer, the thermal relaxation of the PVCi chain would be prohibited by the rigid PI chain.

Figure 7-(a) and (b) show the polarized UV spectra for the PVCi and PI50 alignment layers exposed to polarized UV of 3J/cm^2 respectively. The generation of dichroism in the cinnamate absorption at 278 nm by the exposure to polarized UV is apparent for both PVCi and PI50. When the polarization direction of the

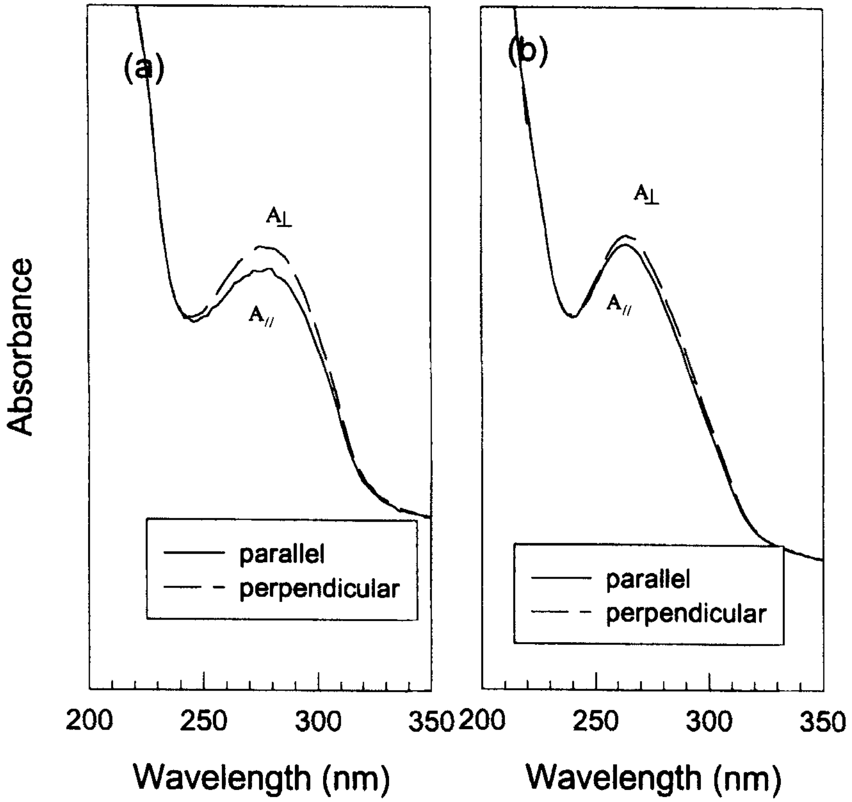


FIGURE 7 Polarized UV spectra for a) PVCi and b) PI50 alignment layers exposed to polarized UV of 3J/cm^2 at normal incidence

probing UV radiation was identical to that of the polarization direction of actinic UV, the smaller cinnamate absorption resulted. It is due to the higher degree of photo-reaction of the cinnamate groups aligned along the polarization direction of actinic UV.[5] For the quantitative comparison of the structural anisotropy, the dichroic ratio (DR) of the alignment layer, defined as $DR=(A_{\perp}-A_{//})/(A_{\perp}+A_{//})$, was determined. Here $A_{\perp}$ and $A_{//}$ are absorbances at 278nm of the cinnamates with a probing light of electric vectors perpendicular to and parallel to an electric vector of actinic polarized light respectively. The observed DR value was 0.04 for PVCi and 0.019 for PI50. The positive DR value is indicative of the higher depletion of the cinnamate group in the polarization direction of actinic UV. The reason for the smaller DR value for PI50 compared with PVCi is that, for PI50, the absorbance at 278nm contains the contribution from PI that weakly contributes the DR value. After heating at 50°C for 10 min, the dichroism for the cinnamate absorption nearly disappeared for PVCi, whereas, the significant dichroism was preserved for PI50 as shown in Fig. 8. The value for DR after heating was 0.0084 and 0.015 for PVCi and PI50 respectively. It is clear that the incorporated PI stiffens the layer and thus maintains the anisotropy developed in the surface-concentrated PVCi under the annealing at enhanced temperature.

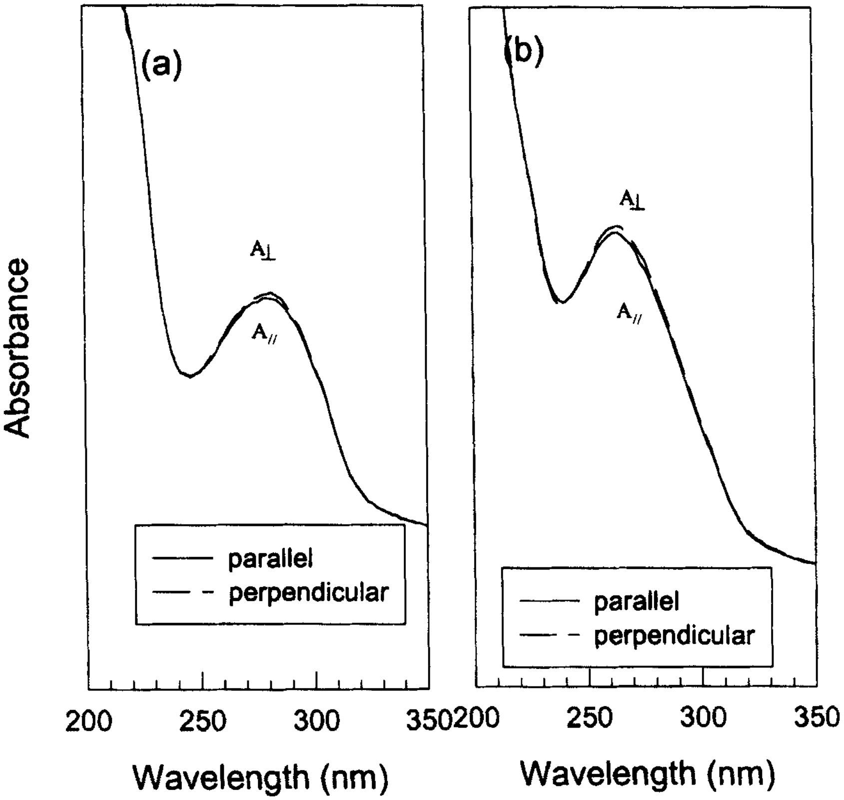


FIGURE 8 Polarized UV spectra after the annealing at 150°C for 10 min for a) PVCi and b) PI50 alignment layers exposed to poalrized UV of 3 J/cm^2 at normal incidence

The azimuthal anchoring energy after the annealing of the LC cell was also investigated as a function of the annealing temperature for the pure PVCi and PI/PVCi blend alignment layers. The results are presented in Fig. 9. The LC cell prepared with the blend alignment layer of higher PI content showed better thermal stability of azimuthal anchoring. It implies that, even in contact with liquid crystal, the thermal relaxation of the structural anisotropy could be reduced by

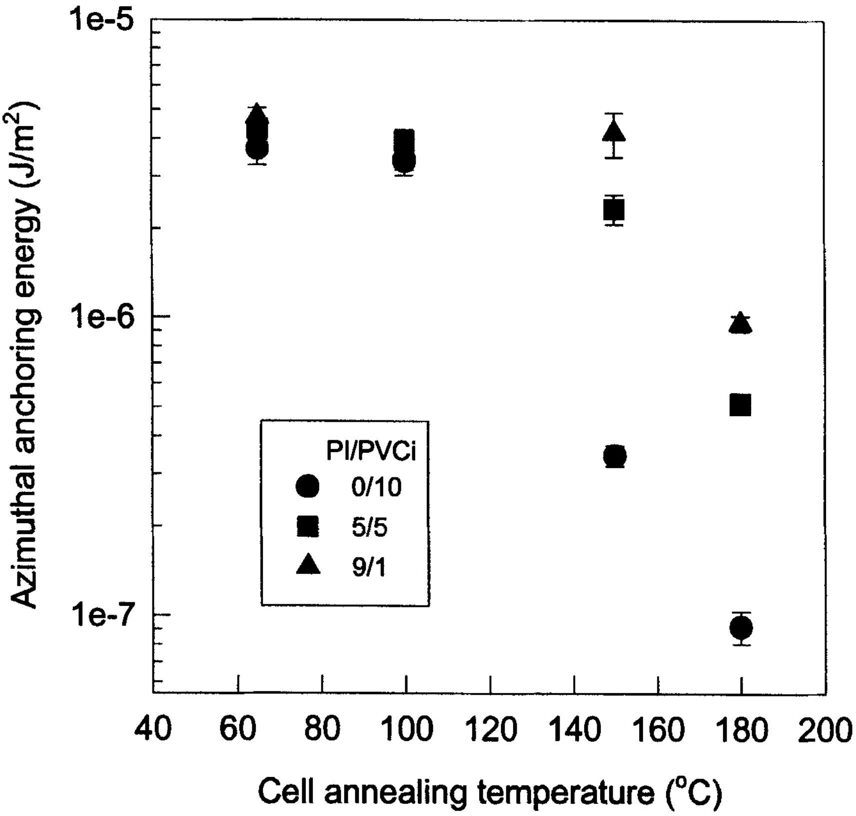


FIGURE 9 Change of azimuthal anchoring energy of E7 nematic liquid crystal on PVCi, PI50, and PI90 alignment layers by the annealing of the LC cells at various temperatures for 10 min

the incorporated PI. In addition, the comparison of Figs. 5 and 9 shows that the cell annealing leads to a larger decrease of the azimuthal anchoring energy compared to the simple alignment layer annealing. The thermal decomposition of the LC or the reaction between the LC and the alignment layer would be responsible for this behavior.

Effect of blend ratio and annealing temperature on the pretilt angle of nematic LC aligned on the blend alignment layers

There are two important factors to be considered in utilizing the PI/PVCi blend for practical device applications such as an LC alignment layer: one is an ability to align LC unidirectionally, and the other is a function to generate the pretilt

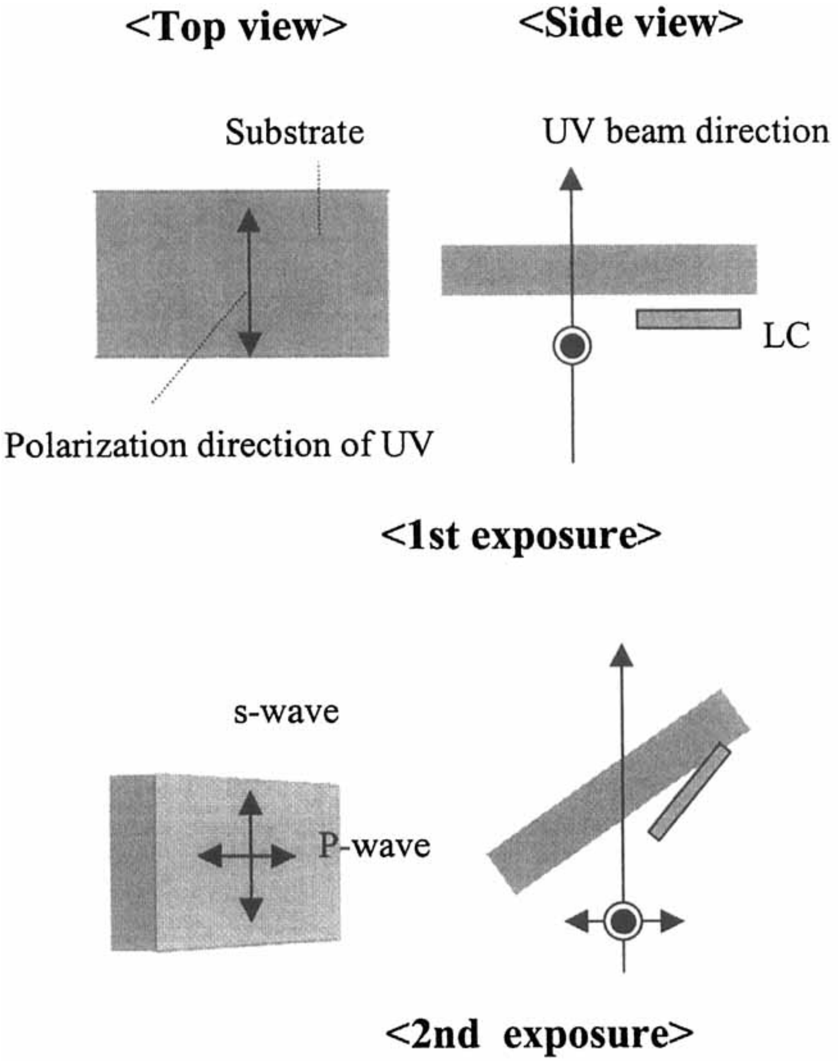


FIGURE 10 Schematic illustration of the modified double exposure for the generation of the pretilt angle

angle for avoiding the appearance of reverse tilt disclinations. The unidirectional alignment of LC on the blend alignment layers can be easily achieved by the exposure of the layer to linearly polarized UV at normal incidence as demonstrated before. However, in this case, the generation of pretilt angle is nearly impossible.[7] Recently, it has been reported that the double exposure method, which consists of the first exposure of linearly polarized UV and the second exposure of p-polarized UV at oblique incidence, is effective to generate a certain pretilt angle.[7] For pure PVCi, the pretilt angle ranging from 0~0.3° was achieved by means of the double-exposure depending on the incidence angle of the second exposure.[7]

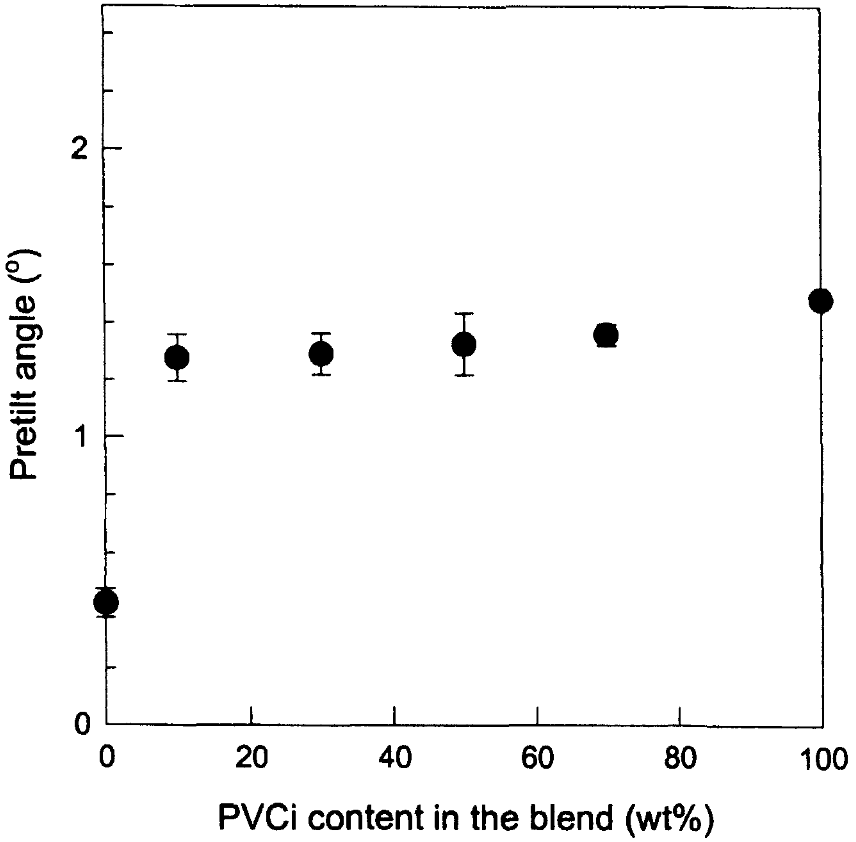


FIGURE 11 Plot of the pretilt angle generated by the modified double exposure as a function of PVCi content. (First exposure : 3J/cm^2 at normal incidence, 1.2J/cm^2 of unpolarized UV at 45°)

In our work, the double-exposure method was modified so that the unpolarized UV was used in the second exposure instead of p-polarized UV as described in Fig. 10. Since the electric vector of p-polarized UV for the second exposure and that of the linearly polarized UV for the first exposure are perpendicular to each other, the second exposure can reduce the degree of unidirectional LC alignment in some cases. Therefore, the unpolarized UV, in which s-polarized component preserves the unidirectional alignment induced during the first exposure and p-polarized component provides a certain pretilt angle, was employed as an actinic UV for the second exposure.

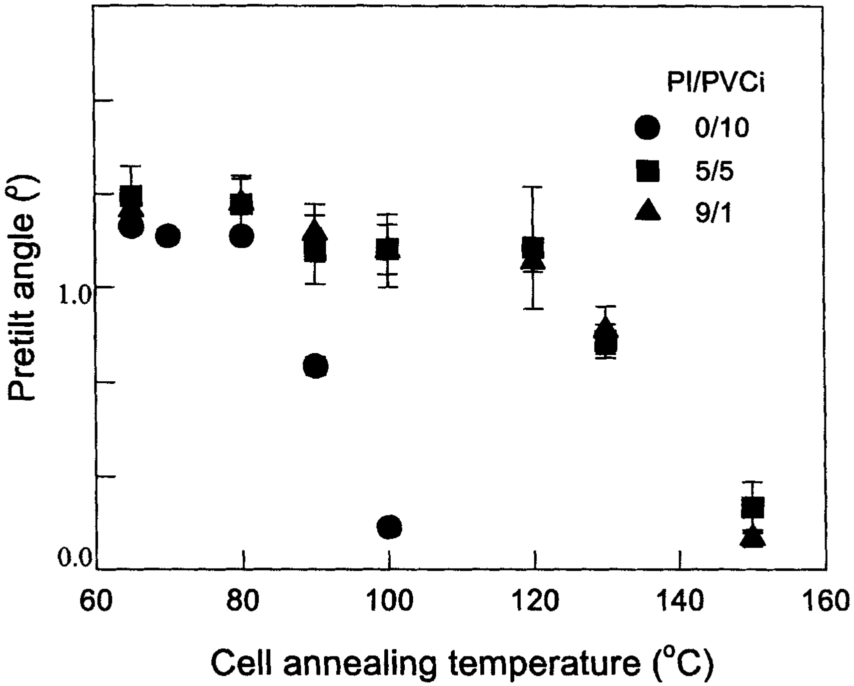


FIGURE 12 Change of the pretilt angle with annealing of the LC cell prepared with PVCi, PI50, and PI90 at various temperatures

By using the modified double-exposure method, we succeeded in creating the pretilt angle more than 1° for the PVCi and PI/PVCi blend alignment layers. Figure 11shows the plot of the pretilt angle of E7 as a function of the blend ratio of the PI/PVCi blend alignment layer. The polarized UV of 3J/cm^2 was irradiated at normal incidence as a first exposure, and the irradiation of unpolarized UV (1.2J/cm^2) at 45° was followed as a second exposure. The measured pretilt angle was not dependent on the blend ratio and comparable to that for pure PVCi. It reconfirms that the LC alignment on PI/PVCi is determined by the surface of the alignment layer where the cinnmate group is concentrated.

To investigate the thermal stability of the pretilt angle, the LC cells were annealed at various temperatures for 0min and then subjected to the pretilt angle measurements. The changes of the pretilt angle with annealing temperature for PVCi, PI50, and PI90 were shown in Fig. 12. For pure PVCi, the pretilt angle was found to be stable under the annealing at 80°C, but it rapidly approached 0° above 80°C. By contrast, the LC cells with PI50 and PI90 showed a significantly enhanced thermal stability of the pretilt angle: for both PI50 and PI90, the initial pretilt angle remained unchanged up to 120°C.

Acknowledgements

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