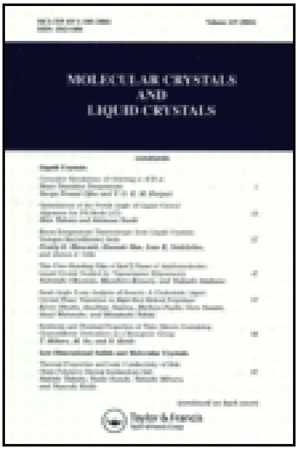

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Photoalignment Mechanism of Liquid Crystals on Poly(vinyl cinnamate) Surfaces

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Surface hydrogenation reaction was performed in order to clarify the mechanism of photoalignment using poly(vinyl cinnamate) (PVCi). The reaction makes it possible to remove any surface ordering of the cinnamate side groups, which may happen during the photoalignment process while the generated photoproducts are still intact. After considering LC alignment and the azimuthal anchoring energy of the hydrogenated PVCi/E7 cells, it was confirmed that the alignment of liquid crystal molecules is mainly induced by the photoproducts.

Keywords: Photoalignment; poly(vinyl cinnamate); mechanism; liquid crystal; hydrogenation

1. INTRODUCTION

Recently, several approaches have been made to obtain a uniform alignment of liquid crystal (LC) molecules via various photoprocesses [1-6]. Such efforts are effective not only for overcoming major drawbacks of the

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mechanical rubbing treatment but also for photopatterning of LC alignment with varying azimuthal directors. The latter makes it possible to reveal multi-domain LCD which improves the viewing angle characteristics of TN-LCD [7].

Since the first attempt of linear photopolymerization (LPP) with poly(vinyl methyl methoxy cinnamate), many photopolymers or photo-techniques have been suggested to improve the properties of LCD, such as the pretilt angle, thermal stability, and so on [4–6]. Along with those improvements, it has been explained that the major controlling force of LC alignment is the dispersion interaction between the photopolymer and LC molecules.

However, there still exists a controversy in which the component of the polymer interacts with LC molecules anisotropically. In the case of poly(vinyl cinnamate) (PVCi) two distinctively different explanations were suggested: first, the photoproducts would show directional preference to the normal direction of UV polarization [1–3, 6]; second, the side groups still remaining after anisotropic depletion could be responsible for the alignment of LC molecules [5, 8]. The side groups whose axes are normal to UV polarization would be hardly affected by the polarized UV irradiation so that they would induce LC alignment to the axis direction. Another mechanism considers the E/Z transformation of the residual cinnamate side groups [9], but it may be included in the role of the side groups in this step. Anyhow, it is important to clarify which moiety induces the alignment of LC for further improvement of the photoalignment technique.

In our approach, efforts have been made to remove only one anisotropic contribution out of the two possibilities. The reason is that the generation of the photoproducts as well as the depletion of the side groups simultaneously forms the anisotropic distribution during the photoalignment process using linearly polarized light. We found that the surface hydrogenation of the cinnamate side groups is appropriate because it removes rigidity of the side groups by changing the lateral double bonds into single bonds while the photoproducts are still intact. In this paper, it is reported that the alignment of LC molecules is still preserved after such modification. It means that the photoproduct is the main component which induces LC alignment.

The hydrogenation of the surface cinnamate groups can be done with the action of the Rhodium catalyst [10]. At first, hydrogen molecules are activated by the Rhodium(I) catalyst, and π bonds of the side groups are coordinated to the Rhodium(III) center, which is located right above the C=C plane. There follows the addition of new hydrogen atoms (Fig. 1).

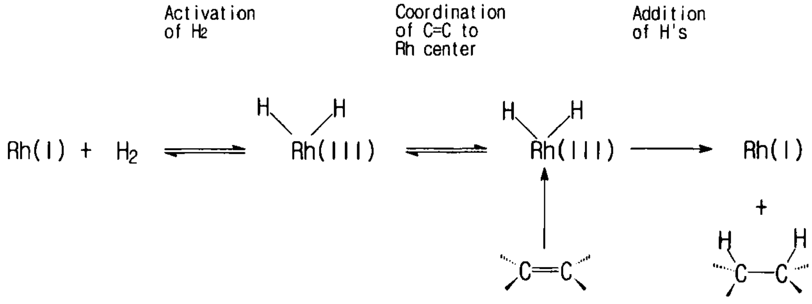


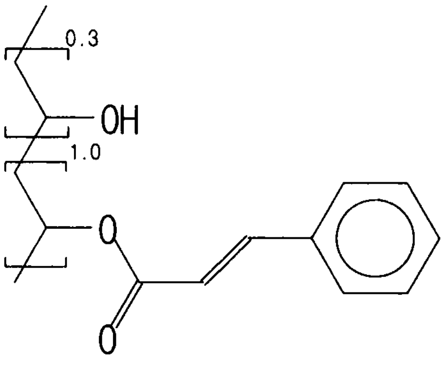
FIGURE 1 Hydrogenation of surface cinnamate groups by the Rhodium catalyst.

2. EXPERIMENTAL

PVCi (Aldrich Co.) of the following structure was spin-coated to glass substrates and quartz plates at 3000 rpm for 25 sec using a 2 wt% solution of 2,6 thinner (Nissan Chem. Co.), and then was baked at 150°C for one hour to ensure the removal of any solvent. The thickness of the layers was measured by an Alpha-Step 250 (TENCOR Instrument).

We selected $RhH(CO)(PPh_3)_3$ (Wako Co.) and methanol as the catalyst and the solvent, respectively, in order to prevent any physical/chemical change of the layers, except the hydrogenation, by the catalytic solution.

For a mild reaction condition to observe the transient behavior of hydrogenation, 0.6 nmol $RhH(CO)(PPh_3)_3$ solution was prepared in methanol per unit area (cm^2) of PVCi layer. Hydrogen gas pressure in the



STRUCTURE 1

autoclave was kept to 70–75 kg/cm^2 at 50°C for 24 hours. An increased amount of catalyst shortened the reaction time. The condition and confirmation of the hydrogenation reaction by spectroscopies will be found in detail elsewhere [12].

We put three types of PVCi layers in the autoclave: (A) virgin PVCi layers, (B) rubbed PVCi layers, and (C) PVCi layers photoaligned with 36 mJ/cm^2 of the exposure energy. Photoalignment was carried out with 0.22 mW/cm^2 of linearly polarized UV light at 256 nm for 20 minutes.

After the hydrogenation reaction the layers were rinsed with fresh methanol and dried for two hours at 50°C. Parallel E7 cells were fabricated to observe the aligned texture with the size of 1.2 cm x 1.5 cm. The cell gap was kept by 8 μm spacers, and the true gap size was calculated by the interference spectrum.

3. RESULTS AND DISCUSSION

3.1. Orientational Distribution of the Side Groups and the Photoproducts After the Photoalignment

In this section, the usual phenomena are discussed in order to adopt an appropriate experimental approach clarifying the main component because

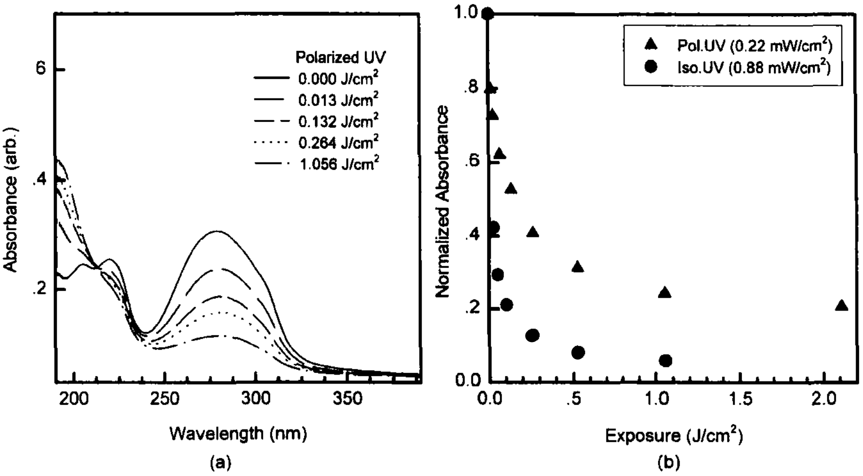
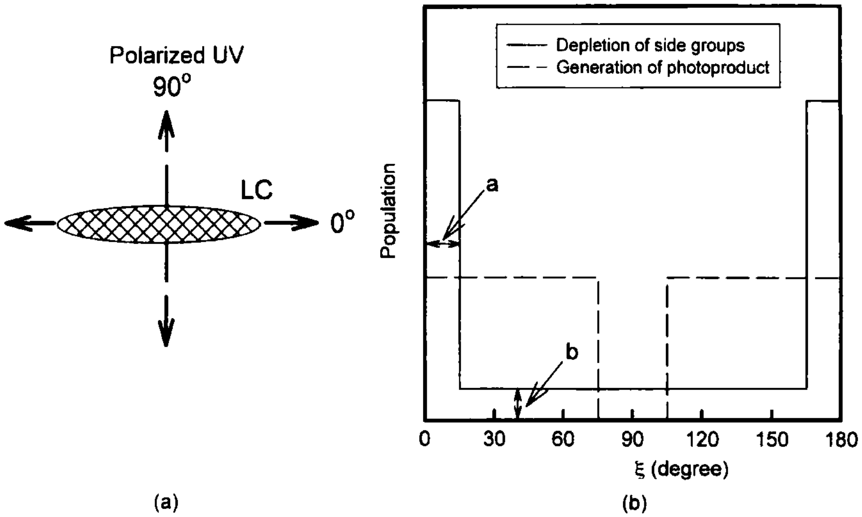


FIGURE 2 (a) UV spectra of irradiated PVCi with polarized UV (0.22 mW/cm^2 at 256 nm) and (b) the normalized absorbance at 280 nm as a function of polarized and isotropic UV exposure.

the photoproducts and the side groups are involved simultaneously: both the generation of the photoproducts and the depletion of the cinnamate side groups happen anisotropically during the photoreaction process. We start by assuming that, in order to open room for any possibilities, both the photoproducts and the side groups induce the orientation of the LC.

When a decrease of the C=C group (280 nm) was observed during the photoreaction with UV spectroscopy (Fig. 2), two major results were obtained; (1) the photoreaction proceeded up to 95% after irradiation of isotropic UV; (2) 75% of the conversion was reached after irradiation of linearly polarized UV.

Based on these facts, a simple orientational distribution on each of the two moieties may be drawn after irradiation of polarized UV in the direction of 90 degrees (Fig. 3). In the distribution of the residual side groups after the depletion, the value of *b* should be very small because it is related to the isotropic conversion (95%). The depletion angle would be wide because the conversion rate was still high (75%) after the polarized irradiation. Hence, the value of *a* should be small, and the distribution of side groups should show angular preference around 0 degree. Such an anisotropic distribution may play a role in aligning LC molecules to the perpendicular direction as others have expected [5, 8].



(a) (b)

FIGURE 3 (a) Orientation direction of LC molecules after photoalignment and (b) angular distribution of the side groups and the photoproducts.

A broad distribution of a photoproduct is also predicted in the same manner, which must make LC molecules be aligned in the direction of 0 degree. The distribution was drawn by assuming that a single product would be generated from two side groups by irradiation, which satisfies the following populational transformation:

$$D_{\mathrm{gen}}(\xi) = \frac{1}{2}\left[1 - D_{\mathrm{dep}}\left(\xi + \frac{\pi}{2}\right)\right] \tag{1}$$

The alignment of LC molecules perpendicular to UV polarization may be explained by the interaction of the laterally configured phenyl groups either in β-truxinate or in the main chain type product, which have a high population rate of the photoproducts [11]. Such phenyl groups that are attached to the cyclobutane rings or to the main chain are configured to the perpendicular direction of UV polarization in the solid state reaction. It is interesting to note that the main chain type product has a similar structure to polystyrene which shows negative birefringence when the layer is stretched or buffed.

If the order parameters are calculated from their normalized distributions by the following equation;

$$S = \frac{1}{2}\int D(\xi)(3\cos^2\xi - 1)\sin\xi\, d\xi \tag{2}$$

the value of the parameters falls between 0.1 and 0.2 by 0.264 J/cm^2 of the usual polarized exposure (Fig. 4). It means that, without any preferential change in two distributions, it will be difficult to distinguish which moiety has the anisotropic interaction with LC molecules. In previous reports, which suggested the anisotropic depletion model [5, 8], they were not successful in explaining the mechanism. They just questioned the role of photoproducts having diverse isomers and considered the origin of the alignment from the aspect of the side groups only. As long as there exist two anisotropic distributions the mechanism can be described in the same manner if the depletion replaces the generation using the populational transformation, or vice versa.

Therefore, hydrogenation becomes an appropriate experimental approach for the identification of the mechanism because it removes only one candidate preferentially while the other is not changed. The next section describes such a role clearly.

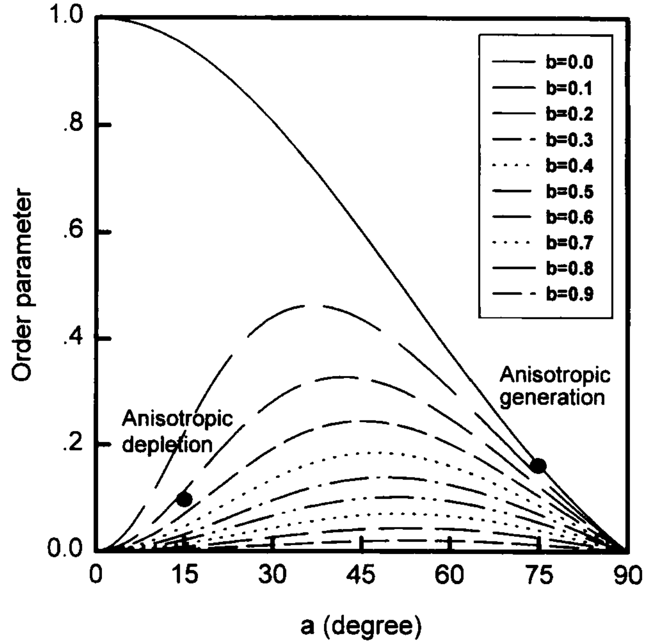


FIGURE 4 Order parameter of simple square-type distribution.

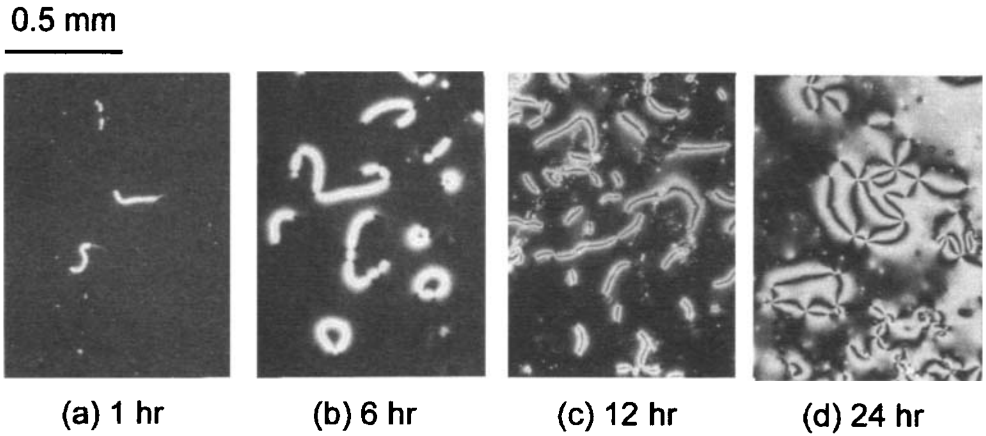
3.2. Removal of Anisotropic Ordering in the Side Group

The surface hydrogenation reaction changes the double bonds in the cinnamate side groups into single bonds. Therefore, it is expected that: (1) it prevents any formation of the photoproducts in the surface region after hydrogenation and (2) the hydrogenated flexible side chains will lose alignability.

The latter is predicted by the thermal property of 30% hydrogenated PVCi whose Tg is 61°C [12]. The glass transition temperature of the fully hydrogenated PVCi is predicted by 30°C based on the Fox equation. Such a drastic depression of Tg wholly comes from the flexible nature of the hydrogenated side chain. Injection of LC at 65°C would make the hydrogenated portion move thermally and randomly.

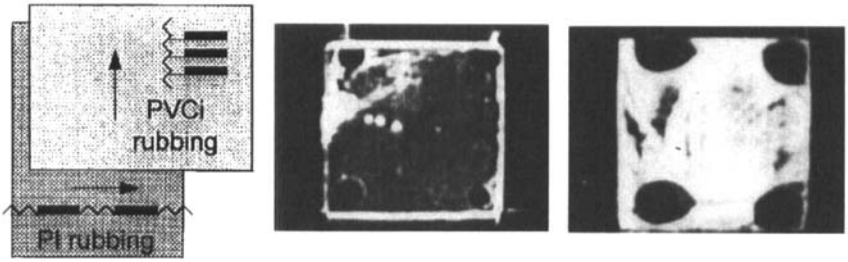
As phenomenologically aimed, photoalignment of sample (A) with E7 does occur less and less when hydrogenation proceeds (Fig. 5). The reaction had also been confirmed by ^{1}H-NMR and UV spectroscopy [12].

Figure 6 shows another aspect of hydrogenated PVCi. The texture of the hybrid cell changed from parallel to twisted alignment after the hydrogena-



(a) 1 hr (b) 6 hr (c) 12 hr (d) 24 hr

FIGURE 5 Photoaligned textures of pre-hydrogenated PVCi/E7 parallel cells under crossed polarizers according to the hydrogenation time. (See Color Plate V).



(a) Hybrid cell (b) Before hydrogenation (c) After 24hr hydrogenation

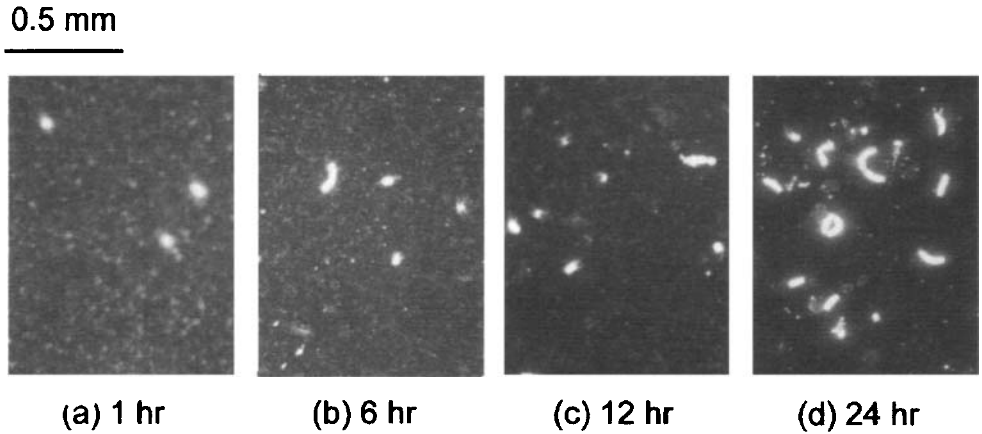
FIGURE 6 Removal of the ordering of the PVCi side groups by surface hydrogenation.

tion. When the PVCi layer was rubbed uniaxially with clothes, LC molecules oriented to the normal direction. It is considered that the polymer chain would be stretched to the rubbing direction and cinnamate side groups be configured to the normal direction. Therefore, a rubbed PVCi layer shows negative retardation as a polystyrene layer does. Iimura *et al.* [5] measured the negative retardation and reported disappearing retardation by irradiating isotropic UV. After the hydrogenation reaction, the direction of LC alignment changed to the rubbing direction because there remained the orientation of the polymer backbone only. This phenomenon also suggests that the hydrogenated cinnamate side groups lost the ordering ability because of the flexible nature of the chains.

It is interesting to refer here the conformation of the alkyl chains attached to the stiff main chain liquid crystalline polymer [13, 14]. Structural investigation according to the length of the alkyl groups found that the side chains of less than eight carbons do not render a layered structure of the polymer, which means that they are in a laterally disordered state with a rotational degree of freedom. The hydrogenated cinnamate side group should also be in the disordered state because it has three rotational centers and a bulky phenyl group at the end.

Based on the above observations, it is confirmed that hydrogenation will remove plausible ordering of the PVCi side groups which may arise from the depletion of the cinnamate groups during the photoalignment process.

However, the samples which had been photoaligned in advance (sample C) still preserved LC alignment, even though hydrogenation proceeded (Fig. 7). The results from UV spectroscopy tell us that the side groups were almost hydrogenated throughout the whole layer after the reaction (Fig. 8).



(a) 1 hr (b) 6 hr (c) 12 hr (d) 24 hr

FIGURE 7 Photoaligned textures of post-hydrogenated PVCi/E7 parallel cells under crossed polarizers according to the hydrogenation time. (See Color Plate VI).

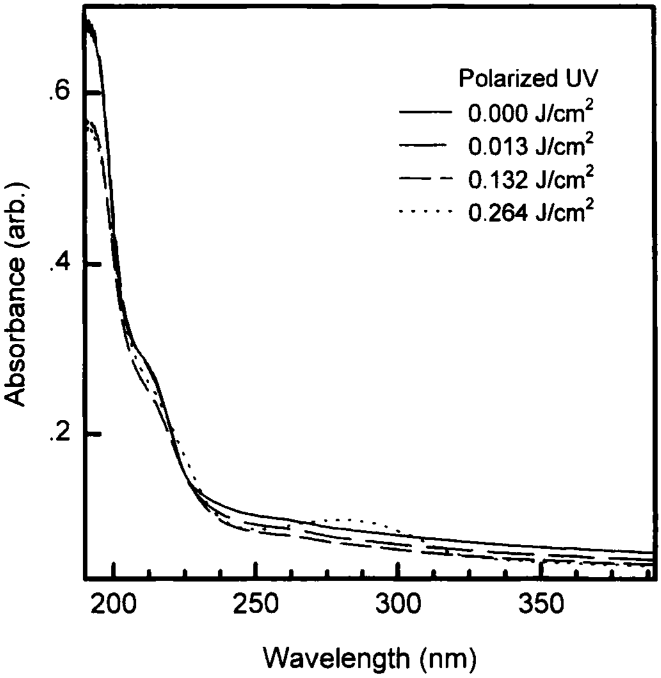


FIGURE 8 UV spectra of post-hydrogenated PVCi layers with various exposure energies.

In that condition the flexible side groups in the surface region are not expected to show any ordering because they would be disturbed by the addition of new hydrogen atoms at the reaction time and by the injection of LC at 65°C. Therefore, it is concluded that LC alignment originates from the photoproducts anisotropically generated by linearly polarized UV.

3.3. Azimuthal Surface-anchoring Energy

Also, the Neel walls formed in samples (A) and (C) were clearly compared with each other (Fig. 9). The width is reversely related to the surface-anchoring energy [5].

While the pre-hydrogenated PVCi (sample A) shows a decrease of the anchoring energy with the hydrogenation time, the post-hydrogenated PVCi (sample C) shows little change (Fig. 10). Because PVCi photoalignment is related to the photoproducts, the surface-anchoring energy of LC on the post-hydrogenated PVCi is hardly affected by hydrogenation.

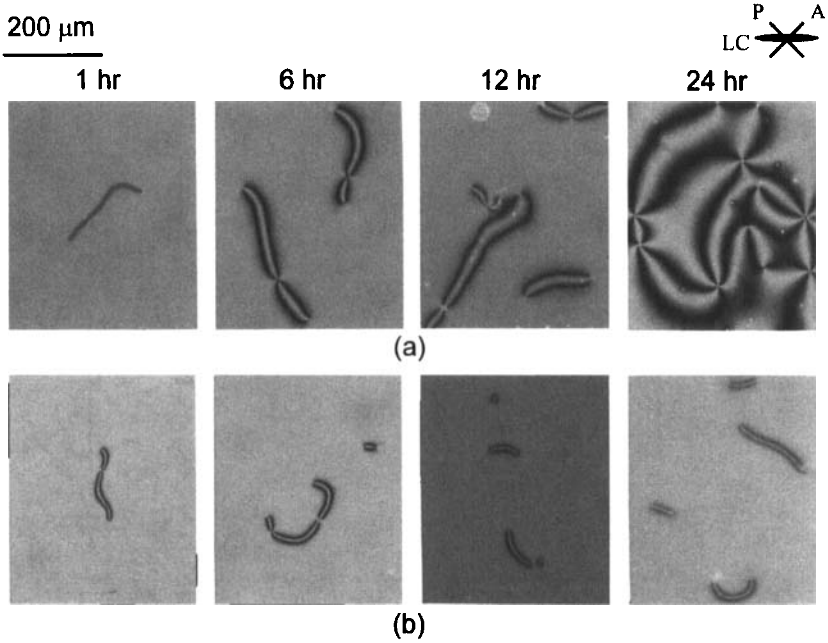


FIGURE 9 Microscopic textures of Neel walls in (a) pre-hydrogenated PVCi/E7 parallel cells and (b) post-hydrogenated PVCi/E7 parallel cells according to the hydrogenation time. (See Color Plate VII).

In the hydrogenation of the photoaligned PVCi with different exposure energies, LC alignment was still retained in every sample (Fig. 11). If the role of the side groups was important, the alignment should be lost in the weakly irradiated sample after hydrogenation, where all the side groups were changed to flexible ones. A small reduction in the anchoring energy of the photoaligned samples indicates that the contribution of the side groups remaining after the depletion is rather low in the photoalignment. Those phenomena clearly support the view that LC alignment is controlled by the photoproducts.

These present data do not allow any further conclusion in selecting a specific isomer as the contributing photoproduct. They only dispose the plausible explanation with the remaining side groups. Changing the distribution of the photoproducts may be an approach to recognize the contributing isomer because the isolation of the photoproducts is very difficult. However, rather than a molecular moiety, a specific functional group such as the lateral phenyl group may be the origin of PVCi photoalignment, which needs more investigation in the future.

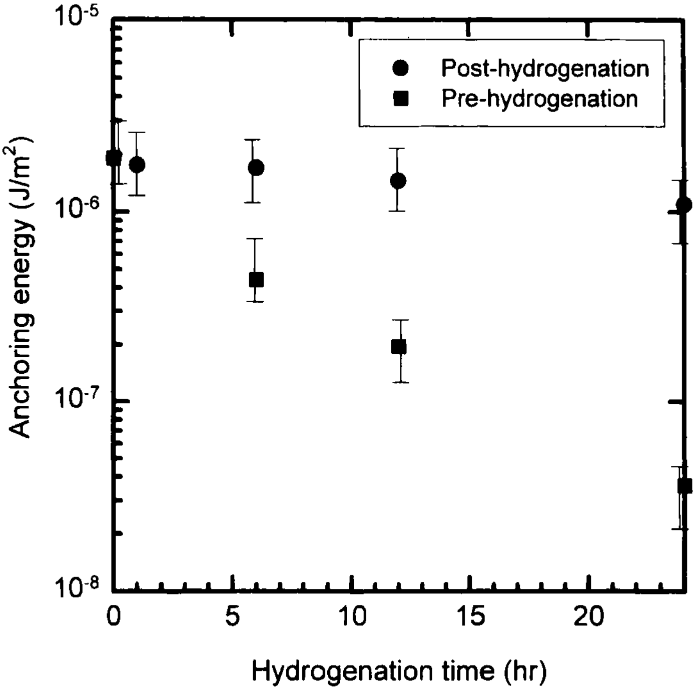


FIGURE 10 Azimuthal surface-anchoring energy according to the hydrogenation time.

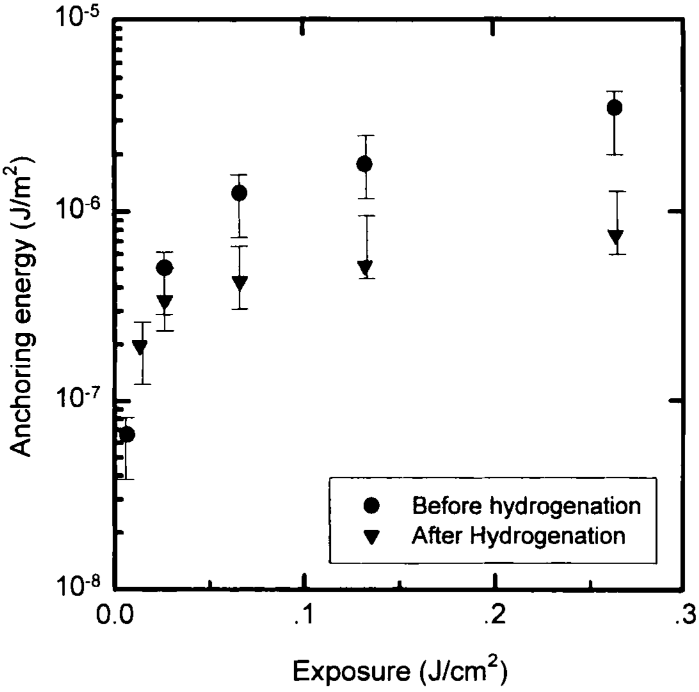


FIGURE 11 Azimuthal surface-anchoring energy according to the exposure energy.

4. CONCLUSION

With the surface hydrogenation reaction, it was possible to remove the ordering of the cinnamate side groups, while the anisotropically generated photoproducts were still intact. Photoalignment of LC molecules on the PVCi layer was always preserved even though hydrogenation was performed. It identifies that the alignment of LC molecules is mainly induced by the photoproducts.

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