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Modification of Poly(vinyl cinnamate) Photo-alignment Layers Using Polymerizable Mesogens

Eung Jin Kim*, Jin Woo Lee and O Ok Park†

Center for Advanced Functional Polymers, Department of Chemical Engineering,
Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea
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Abstract–Polymerizable mesogens were blended with poly(vinyl cinnamate) (PVCi) in order to improve the alignment properties of liquid crystals (LC) on the layer surface. Two types of cyanobiphenyl monomers, which have short (n=0) and long (n=11) spacers, were prepared, respectively. Polarized UV exposure at the elevated temperature increased the inclusion of the monomers into the network of the photo-products. Compositional studies showed that the short-spacer monomer improved homogeneous LC alignment and thermal stability, whereas the long-spacer monomer contributed to generate homeotropic LC alignment.

Key words: Photo-alignment, Poly(vinyl cinnamate), PVCi, Mesogens, Alignment Layer

INTRODUCTION

Uniform alignment of liquid crystals has been a prerequisite subject of liquid crystal displays (LCDs), and the progress in highly informative LCD has accompanied many advanced techniques to align LC molecules. Photo-alignment, which can generate local angular variation of LC alignment, was one of the promising processes to make complex hybrid liquid crystal displays with a high degree of spatial resolution [Schadt et al., 1992]. The technique generally utilizes photo-polymers in which the anisotropic photoreaction can be induced by the polarized UV exposure. In the photo-polymers various light-sensitive functional groups, such as cinnamoyl groups or azo dyes, are included into the polymers by copolymerization or by blending techniques [Schadt et al., 1995; Iimura et al., 1993].

Poly(vinyl cinnamate) has been widely investigated not only as a basic study of the photo-alignment, but also as a starting material for device applications. The photo-polymer, however, has some limitations such as the low-order parameter of LC alignment, poor thermal stability of the layer, and difficulties in generating the pretilt angle. Therefore various photo-polymers have been tried to overcome the weakness raised by the photo-alignment processes [Song et al., 1996].

In previous reports, mesogenic monomers were introduced to the interface of polymer and liquid crystals, and it was possible to increase the anisotropic interaction between them [Shannon et al., 1994; Kim and Park, 1995]. In this report, the mesogenic monomers were polymerized into the network of PVCi by the photoreaction with the cinnamate groups in order to improve the alignment properties of the layer (Fig. 1). Two kinds of cyanobiphenyl monomers were utilized; one has a very short spacer (n=0, MCBA0) and the other has a long one (n=11, MCBA11). Two distinctively different lengths of the spacers showed unique characteristics in aligning LC molecules, and the same mesogenic core of the monomer could increase the interaction with LC at the interface (Fig. 1).

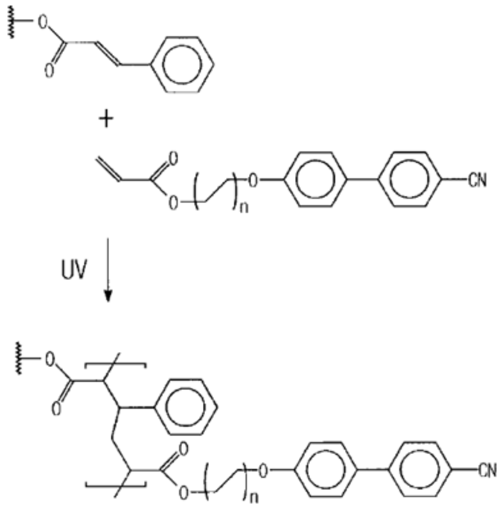

Fig. 1. Inclusion of the mesogenic monomers into the network of PVCi photo-products (The structures of the PVCi network and the homopolymer are omitted).

EXPERIMENTAL

Two cyanobiphenyl acrylate monomers, MCBA0 and MCBA11, were prepared by the same procedures as the previous reports [Kim and Park, 1995; Shibaev et al., 1982]. They were crystalline powders at room temperature. MCBA0 showed the nematic phase between 103 °C and 126 °C, and became an isotropic state over the temperature. MCBA11 did not show any mesophase and melted at 92 °C.

The polymerizable mesogens and PVCi were dissolved into

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†To whom correspondence should be addressed.
E-mail: oopark@sorak.kaist.ac.kr
*Present address: Flat Display Lab., Technology Division, Samsung Display Devices Co. LTD., 575 Shin-Dong, Paldal-Gu, Suwon 442-390, Korea

cyclohexanon by 2 wt% and then spin-coated onto ITO glasses and quartz plates with 3,000 rpm for 30 sec. For FT-IR measurement, thicker samples were cast on silicone wafers. They were dried for 24 hours in vacuum at 65 °C to ensure the removal of any remaining solvent.

Polarized UV light was exposed on the spin-coated films with a high-pressure Mercury lamp (500 W). A filter was inserted between the lamp and the polarizer to regulate the wavelength of the light around 300 nm. The samples were illuminated for 10 minutes with 2.4 J/cm^2 of exposure energy at 110 °C.

Photo-induced orientation of the film was monitored by retardation measurement [Kwon and Park, 1992; Yoon et al., 1990] before LC cell fabrication, and the film thickness was measured by Alpha-Step (TENCOR Instrument). The surface morphologies were observed by microscopy and by SEM. Parallel E7 (E. Merck) cells were fabricated to observe the aligned texture with the size of 1.2 cm×1.5 cm. The cell gap was kept by 8 µm spacers, and the true gap size was calculated by the interference spectrum. E7 was injected into the cell at 65 °C by the capillary action, and then cooled slowly to room temperature.

RESULTS AND DISCUSSION

1. Characterization of the Modified PVCi Films

The blends of PVCi-MCBA11 showed phase-separated layers over the whole composition after spin-coating on the ITO glasses as shown in Fig. 2. PVCi formed a continuous layer but the monomer showed aggregation owing to their inability to form films. The monomer domains gave surface roughness as the content was increased. Such domains were reduced definitely by the polarized UV exposure at the elevated temperature as shown in Fig. 3.

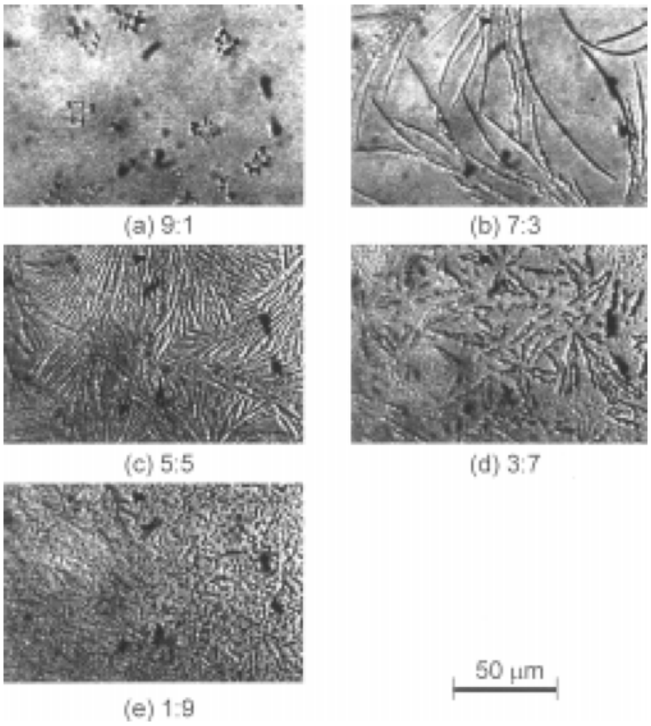


Fig. 2. Microscopic images of PVCi-MCBA11 (x : y) blend films after spin-coating.

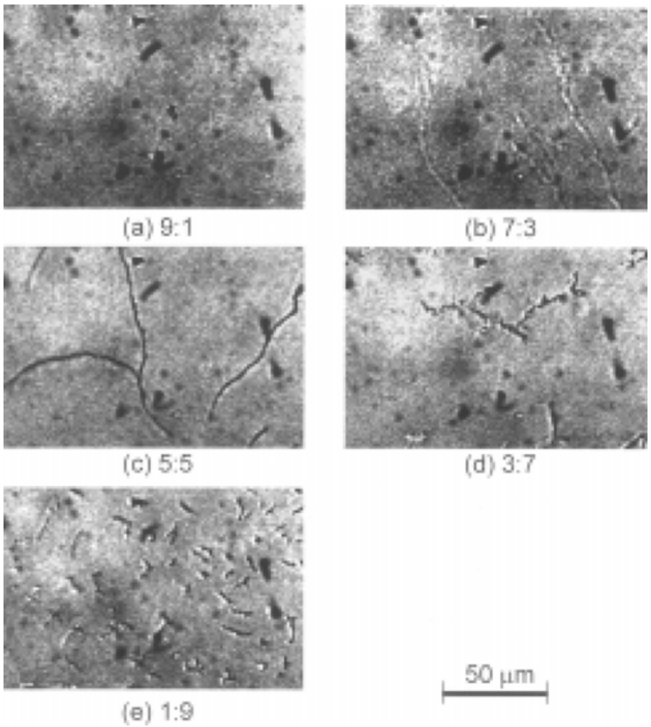


Fig. 3. Microscopic images of PVCi-MCBA11 (x : y) blend films with UV exposure at 110 °C.

In the high monomer concentration, the domains still remain after the exposure.

PVCi showed better miscibility with MCBA0 than with MCBA 11. In the PVCi-MCBA0 blends, submicron domains appeared from the composition of 50 : 50 wt% under SEM observations. After the polarized UV exposure the monomer domains disappeared as in the previous case. The phase-separated structure was hardly observed under 70 wt% content of MCBA0.

FT-IR studies showed that MCBA0 was polymerized into the PVCi networks by UV exposure at the elevated temperature. The peak of C=C at 900 cm^{-1} was reduced after the exposure compared with the reference peak of –CN at 2,333 cm^{-1} (Fig. 4). The mesogenic acrylate monomers can be polymerized either with cinnamoyl radicals or with the main chain radicals. It is possible to consider such reaction, as in Fig. 1, based on the stereoisomer analysis of the PVCi photo-products. Among the PVCi photo-pro-

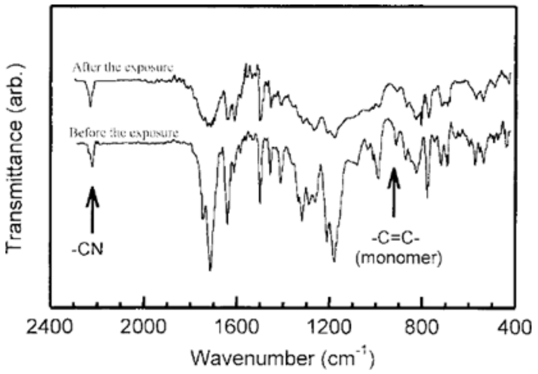


Fig. 4. FT-IR spectra of PVCi-MCBA11 (7 : 3); (upper : after UV exposure at 110 °C, lower : before UV exposure).

ducts, the main chain type products rated higher than 30% by the radical reaction, which is different from the [2+2] cycloaddition between two cinnamate groups [Egerton et al., 1981; Kim et al., 1998; Nakamura and Kikuchi, 1967]. By the reaction of the acrylate monomers and the main chain type radicals, the mesogenic monomers can be included into the photo-products. As observed in the morphological changes after UV exposure, it is possible to regard that the inclusion of the monomers into the PVCi network resulted in the removal of their initial domains.

Linearly polarized UV exposure induced anisotropic reaction as shown in the birefringence measurements. The anisotropy generated was perpendicular to the polarization of the UV light so that the induced birefringence was negative. The induced retardation (δ) by the polarized UV exposure showed similar level over all the blend composition, except two high MCBA0 contents (Fig. 5(a)]. Because the film thickness (d) decreased with the monomer content, the birefringence (Δn) of the exposed film increased as in Fig. 5(b);

$$\Delta n=\frac{\lambda\,\delta}{2\pi d} \tag{1}$$

where λ is the wavelength of He-Ne laser. It was also known that the anisotropy improvement wholly came from the monomer because of the monotonic increase of the birefringence with the composition.

2. Effects of the Modified PVCi's on the LC Orientation

As intended in the blends of PVCi with mesogenic monomers, LC alignment was improved in the parallel cells with the PVCi-MCBA0 layers compared with the PVCi layer. Small addition of MCBA0 resulted in homogeneous and defect-free LC domains, when the monomer content was within 30 wt% (Fig. 6). Such a domain is noticed by the black part of the cells which means parallel orientation of LC directors with one of the polarized axes. Over 50 wt% of MCBA0, LC alignment became worse and many defects appeared. In this range, the isolated domains still remained after UV exposure. If the exposure energy was increased to reduce the domains in the film, the LC orientation was improved even on the layers of the high MCBA0 content.

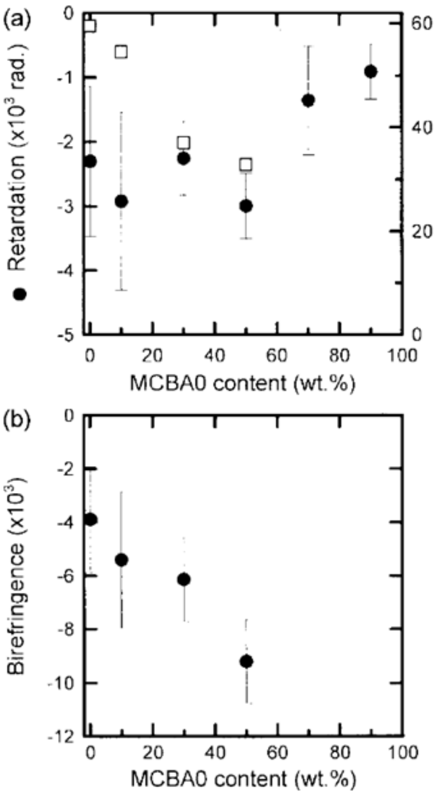


Fig. 5. (a) Induced retardation and thickness of PVCi-MCBA0 (x : y) films, and (b) the birefringence as the function of MCBA0 concentration.

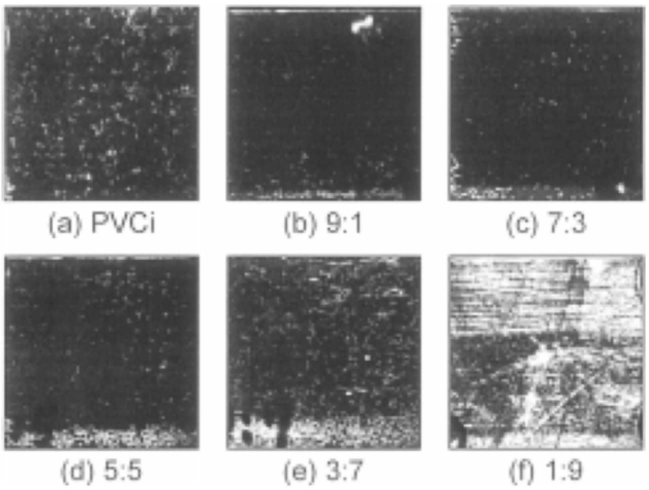
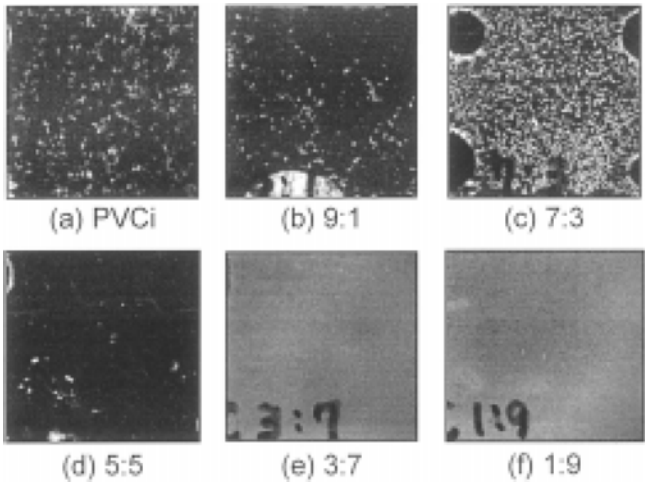


Fig. 6. Images of E7 parallel cells using PVCi-MCBA0 (x : y) films exposed to polarized UV at 110 °C (Director axis was matched to one of the crossed polarizer axis, 1 cm× 1 cm).

In the photo-reaction of PVCi and the monomer, the partial generation of the mesogenic homopolymer might not lower the alignment properties of the blend films, because its anisotropy is quite high in nature. The isolated domains of such homopolymers or the unreacted monomer could deteriorate the LC alignment in the case of high monomer contents.

The improved alignment by the small addition of MCBA0 was also kept stable at the elevated temperature. After annealing at 90 °C and slow cooling to room temperature, LC orientation was quite disturbed and many defects appeared in the cell with PVCi layer. However, in the cells with 10 or 30 wt% of MCBA0, the layers of PVCi-MCBA0 still preserved the LC alignment up to 120 °C. Such an improved thermal property can be explained by the rigid nature of the side chain liquid crystalline polymer (SCLCP) which has the same monomer [Percec and Pugh, 1989]. In the short spacer SCLCP, the rigid mesogenic groups were directly attached to the polymeric backbone without a flexible spacer, so that the rigid ordering of the mesogens was transferred to the backbone. It also induced a high glass transition temperature of the SCLCP (T_g=150 °C). Similar behavior can be expected in the blend systems of PVCi and MCBA0, which improved the thermal stability of the LC orientation.

The cells with the layers of PVCi-MCBA11 also showed fewer defects within 10 wt% monomer content, but the alignment became worse as MCBA11 content was increased (Fig. 7). An interesting case was 50 wt% of MCBA11, which showed a perfect



(a) PVCi (b) 9:1 (c) 7:3

(d) 5:5 (e) 3:7 (f) 1:9

Fig. 7. Images of E7 parallel cells using PVCi-MCBA11 (x : y) films exposed to polarized UV at 110 °C (Director axis was matched to one of the crossed polarizer axis, 1 cm×1 cm).

homeotropic alignment. In that case the LC directors were normal to the polymer layer so that the intensity did not change by rotating the sample under the crossed polarizers. Homeotropic alignment is often observed in the cells in which the alignment polymer has long alkyl side groups [Uchida and Seki, 1992]. The long nature of the spacer in MCBA11 induced the homeotropic alignment when the monomer was included in the photo-curing of the PVCi. In the higher composition of MCBA11 more than 70 wt%, the exposed film could not orient the liquid crystals because of many irregular domains which prevented uniform alignment of LC molecules. Also, the inclusion of the monomer MCBA11 into the photo-product lowered T_g and made the network flexible, which was the opposite case of MCBA0. LC injection at 65 °C could erase the photo-induced anisotropy in the soft film.

3. Effects of the Modified PVCi's on the Surface Anchoring Energy

The microscopic observation of the parallel LC cells directly showed the change of the azimuthal anchoring energy which was calculated by the width of the Neel wall (Fig. 8) [Kim et al., 1998]. The anchoring energy in PVCi-MCBA0 cells was increased with the monomer contents lower than 50 wt% and then decreased by adding MCBA0 with higher concentration. The level of the anchoring energy was similar to that of PVCi layer over the entire composition. It may indicate that PVCi offered the basic LC alignment, and the monomer cooperated with PVCi for the alignment by increasing the anisotropic interaction with LC at the interface. In the low concentration of MCBA0, the monomer was included into the polymer networks and the isolated domains were minimized, so that both the LC alignment and the anchoring energy could be improved. In the case of monomer MCBA11, the anchoring energy was lowered by the monomer addition because of softening of the film.

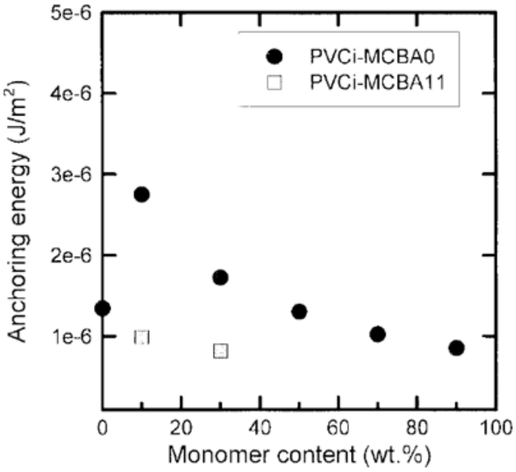


Fig. 8. Surface anchoring energy as the function of the monomer content.

CONCLUSIONS

As described in the previous literature, both the anisotropic Van der Waals force and the morphological effect are important factors in controlling the orientation of LC molecules [Tony et al., 1995]. In this study the addition of the mesogenic groups was aimed at increasing the physico-chemical interactions between the photo-polymer surface and LC molecules. Mesogenic monomers were successfully included into the PVCi network by anisotropic photo-reaction, so that it improved not only the LC alignment property but also the thermal property.

The short-spacer monomer MCBA0 cooperated for the anisotropy generation of the exposed layers and improved the thermal stability within 30 wt% content. MCBA11 monomer, which has a long spacer, softened the blend layers but contributed to generate the homeotropic LC alignment around 50 wt%. Therefore, the composition of the blend layers should be carefully chosen in order to control the alignment properties of the photo-polymer.

The blending technique may allow an easy modification of the photo-polymer by combining the mesogenic monomers which have unique roles in LC alignment.

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