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폴리(비닐 신나메이트)와 올리고머 신나메이트 블렌드를 기반으로 한 그루브 패턴 표면의 광배향막

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Photoinduced Alignment Based on the Blend of Poly(vinyl cinnamate) and Oligomeric Cinnamate via Linear Polarized UV Irradiation onto Groove Patterned Surface

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초록: 액정표시소자의 광배향막으로 적용하기 위하여 올리고머 신나메이트와 폴리(비닐 신나메이트) (PVCi)의 블렌드를 이용하여 그루브 패턴을 형성하고 광배향 특성을 관찰하였다. UV-vis 스펙트럼 분광계를 이용하여 자외선 조사 시간에 따른 광반응 속도를 평가한 결과 올리고머 신나메이트는 폴리(비닐 신나메이트)에 비해 빠른 반응속도를 나타내었다. 폴리(비닐 신나메이트)를 주성분으로 하여 올리고머 신나메이트를 블렌드한 경우 반응속도가 약간 향상되는 특성을 확인하였다. 올리고머 신나메이트는 높은 결정성으로 인해 표면 그루브 패턴을 단독으로 형성할 수 없었지만 폴리(비닐 신나메이트)와의 블렌드를 통하여 그루브 패턴을 형성할 수 있었으며 그루브 패턴에서도 polar plot에 의해 분자 배향성을 나타냄을 확인하였다. 올리고머 신나메이트와 고분자계 신나메이트의 블렌드를 통하여 반응속도의 향상과 박막 구조의 패턴을 형성하기에 적합함의 확인을 통해 새로운 광배향막 재료로 적용 가능함을 알 수 있었다.

Abstract: Photo-alignment property of groove patterned surface prepared from blend of poly(vinyl cinnamate) (PVCi) and oligomeric dicinnamate was investigated for the application for alignment layer of liquid crystal display. The study of the photoreaction kinetics using UV-vis spectrum with the irradiation time showed that the reaction rate of oligomeric cinnamate was enhanced compared to that of PVCi. Blend where PVCi was main component showed a slight improvement on the photoreaction rate. It was unable to obtain groove patterned surface only using oligomeric cinnamate itself owing to the high crystalline character. However, blending of PVCi made it possible to obtain clear surface pattern. Molecular orientation could be confirmed from the polar plot data. It can be suggested that blend of oligomeric cinnamate and polymeric cinnamate is promising material for the photoalignment layer.

Keywords: cinnamate, photo-alignment, oligomer, linear polarized UV.

Introduction

UV curing technology has been widely used in the various industrial fields owing to its intrinsic advantage such as ability of low temperature processing.[1] Nowadays, utilization of UV curable material in the electronic display is attracting much interest.

Liquid crystal alignment layer is one of the major components in the liquid crystal display (LCD) and rubbing process has been widely adopted for the fabrication. Photo-alignment method, which use linear polarized UV irradiation for the molecular orientation can replace rubbing process to form

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alignment layer.[2] It is advantageous in the view point of removing problems of rubbing process which are accumulation of electrostatic charge, dust contamination, and uneven rubbing strength on the large area display.

Among the method to prepare photo-alignment layer, photo-reaction of monoolefinic chromophore through [2+2] photo-cycloaddition mechanism is well known and poly(vinyl cinnamate) (PVCi) is representative photopolymer.[3] Many of previous work focused on the design of the new polymers with cinnamate moiety and investigated photo-aligning property.[4-8]

In our previous work, we have reported polymer blends for alignment layer and proposed that concept of blend system is potential approach of combining the merits of each system.[9,10] However, until now there are few reports of photo-alignment layer using the blend of polymeric and oligomeric cinnamates.

In this report, we prepared photoreactive blends based on polymeric and oligomeric cinnamates and applied on the groove patterned surface for the photo-alignment. Synthesis and characterization of oligomeric cinnamates, preparation of the groove pattern using blend via soft lithography, and photoalignment property of the system are investigated.

Experimental

Materials. 1,4-Butanediol, 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol were purchased from Sigma Aldrich and used as received. Cinnamoyl chloride was purchased from Tokyo Kasei Inc. triethylamine (TEA) was purchased from Fluka. Reaction solvent tetrahydrofuran (THF) was purchased from Junsei. Chem. and used after distillation under sodium ribbon. PDMS precursor (SylgardTM 184) which is used for the preparation of stamp for the groove pattern formation was from Dow Corning. Other chemicals were of reagent grade and were used as received.

Synthesis of Oligomeric Cinnamates. 1,4-Butanediyl dicinnamoyl ether (2Ci-BD), 1,6-hexanediyl dicinnamoyl ether (2Ci-HD), 1,8-octanediyl dicinnamoyl ether (2Ci-OD), and 1,10-decanediyl dicinnamoyl ether (2Ci-DD) were synthesized by the reaction of 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol, with cinnamoyl chloride, respectively. Diols and TEA dissolved in distilled THF were placed in the round bottom flask equipped with dropping funnel where the temperature was set to 33 ℃. Flask was N_2 purged for 30 min prior to introduction of reactant. Thrice amount (based on mole) of cinnamoyl chloride, completely dissolved in distilled THF compared to alkyl diol, was introduced in the reaction flask through dropping funnel for 15 min. Reaction temperature was

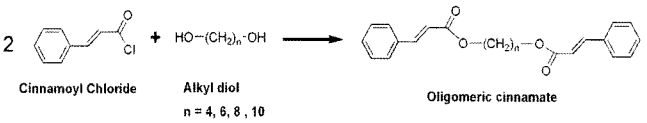

Figure 1. Synthetic scheme of oligomeric cinnamate.

maintained at 40 ℃ through the reaction and the reaction was proceeded for 24 h under magnetic stirring. N_2 was purged at a rate of 10 cc/min during the reaction. The resulting product was obtained by removing byproduct TEA · HCl powder by centrifugation followed by the precipitation in the distilled water. Trace of impurity and unreacted reactant were removed by the washing the product with methanol for 5 times. Finally, product was vacuum dried for 24 h to obtain white powder. The reaction scheme is summarized in Figure 1.

Characterization of Oligomeric Cinnamates. The structure of synthesized oligomeric cinnamates with different alkyl chain length were characterized by ^{1}H-NMR spectra ($CDCl_3$ as solvent) using a Bruker 500 MHz spectrometer with tetramethylsilane as internal standard at room temperature. Conversion of the product was obtained through the calculation of integrated peak area. All products showed over 95% conversion. Number of washing procedure was related with obtaining high purity samples. DSC measurements were carried out under nitrogen atmosphere (50 mL/min) at a heating rate of 10 ℃/min using TA Q20 DSC thermal analyzer in the temperature range of -80~200 ℃. UV-vis spectra of cinnamated oligomers with the different UV exposure times were collected using UV-vis spectrometer (Optizen 2120UV plus, Mecasys). Oligomeric dicinnamates are dissolved in cyclohexanone to prepare 1 wt% solution. Drops of the solution were spread onto the quartz plate and dried for 10 min at room temperature before UV-vis spectrometer measurement.

2Ci-BD ; ^{1}H-NMR ($CDCl_3$), δ : 1.73 (m, 4H, $-OCH_2-\underline{CH_2CH_2}CH_2O-$), 4.27 (t, 4H, $-O\underline{CH_2}CH_2CH_2\underline{CH_2}O-$), 6.42 (d, 1H, $-CH=\underline{CH}-COO-$), 7.67 (d, 1H, $-\underline{CH}=CH-COO-$), 7.36-7.56(m, 5H, phenyl proton). 2Ci-HD; ^{1}H-NMR ($CDCl_3$), δ : 1.34 (m, 4H, $-OCH_2CH_2\underline{CH_2CH_2}CH_2CH_2O-$), 1.72 (m, 4H, $-OCH_2\underline{CH_2}CH_2CH_2\underline{CH_2}CH_2O-$), 4.20 (t, 4H, $-O\underline{CH_2}CH_2CH_2CH_2CH_2\underline{CH_2}O-$), 6.42 (d, 1H, $-CH=\underline{CH}-COO-$), 7.66 (d, 1H, $-\underline{CH}=CH-COO-$), 7.35-7.55(m, 5H, phenyl proton). 2Ci-OD ; ^{1}H-NMR ($CDCl_3$), δ : 1.37 (m, 4H, $-OCH_2CH_2\underline{CH_2CH_2CH_2CH_2}CH_2CH_2O-$), 1.70 (m, 4H, $-OCH_2\underline{CH_2}CH_2CH_2CH_2CH_2\underline{CH_2}CH_2O-$), 4.20 (t, 4H, $-O\underline{CH_2}CH_2CH_2CH_2CH_2CH_2-CH_2\underline{CH_2}O-$) 6.42 (d, 1H, $-CH=\underline{CH}-COO-$), 7.66 (d, 1H, $-\underline{CH}=CH-COO-$), 7.35-7.56(m, 5H, phenyl proton). 2Ci-DD ; ^{1}H-NMR ($CDCl_3$), δ : 1.31 (m,

4H, $-OCH_2CH_2CH_2\underline{CH_2CH_2CH_2CH_2}CH_2-CH_2CH_2O-$), 1.38 (m, 4H, $-OCH_2CH_2\underline{CH_2}CH_2CH_2CH_2-CH_2\underline{CH_2}CH_2CH_2O-$), 1.71 (m, 4H, $-OCH_2\underline{CH_2}CH_2CH_2-CH_2CH_2CH_2CH_2\underline{CH_2}CH_2O-$), 4.19 (t, 4H, $-O\underline{CH_2}CH_2CH_2-CH_2CH_2CH_2CH_2CH_2\underline{CH_2}O-$), 6.42 (d, 1H, $-CH=\underline{CH}-COO-$), 7.66 (d, 1H, $-\underline{CH}=CH-COO-$), 7.36–7.56 (m, 5H, phenyl proton). FT-IR (KBr) : 1710 cm^{-1} (C=O); 1634 cm^{-1} (C=C);

Preparation of Photo-alignment Layer. 20 wt% THF solutions of PVCi with oligomeric cinnamates (90:10 based on weight) are spin coated onto the glass plate at 550 rpm. Groove type micropattern was generated by the PDMS stamp through solvent-assisted micromolding (SAMIM). PDMS stamp for SAMIM process were fabricated by replication from patterned master. Detailed process for the preparation of patterned master is presented in the previous work.[11] Linearly polarized UV light (500 W high pressure mercury lamp with a UV linear dichroic polarizer (27320, Oriel) and a UV filter (59800, Oriel)) was irradiated onto the coated glass plate. The intensity of the irradiated UV light measured using a UV detector (UTT-150, Ushio) was 4 mW/cm^2. In-plane orientation of the liquid crystal (E7) was observed by polarized microscope. LCD cells were fabricated by sandwiching two glass plates with photo-alignment layer. Cell gap was 10 μm. E7 as liquid crystal and methyl blue as probing dye were used. E7/methyl blue solution was filled into the cell followed by baking at 65 ℃ for 10 min. 653 nm peak of methyl blue was utilized to obtain polar plots of LCD cells.

Result and Discussion

Synthesis and Characterization of Oligomeric Cinnamates. Oligomeric cinnamates were synthesized through the reaction between acryloyl chloride group of cinnamoyl chloride and hydroxyl group of alkyl diol. Chemical structures were determined by ^1H-NMR spectra and the representative image of 2Ci-DD is illustrated in Figure 2. From the spectra, presence of methylene proton peaks at 6.30 and 7.40 ppm and a phenyl proton peak at 7.15–7.40 ppm in the product confirms the incorporation of cinnamate group. Degree of substitution was defined as cinnamate groups substituted for hydroxyl groups of alkyl diol and calculated based on the integral of peak intensity from NMR spectrum. The reaction was also checked by the FT-IR measurement of the synthesized oligomeric dicinnamates and the image of oligomeric cinnamates is illustrated in Figure 3. C=O stretching vibration was observed at 1710 cm^{-1} and C=C stretching vibration at 1634 cm^{-1}.

Thermal properties of the oligomeric cinnamates are shown in Figure 4. DSC spectra showed sharp melting endotherm for the prepared oligomeric cinnamates. Considering the melting temperatures of cinnamoyl chloride being 35~37 ℃, oligomeric cinnamates showed higher melting temperature. Melting temperature was lowered with the increase of the alkyl chain. However, 2Ci-DD which was originated from 1,10-decanediol didn't follow

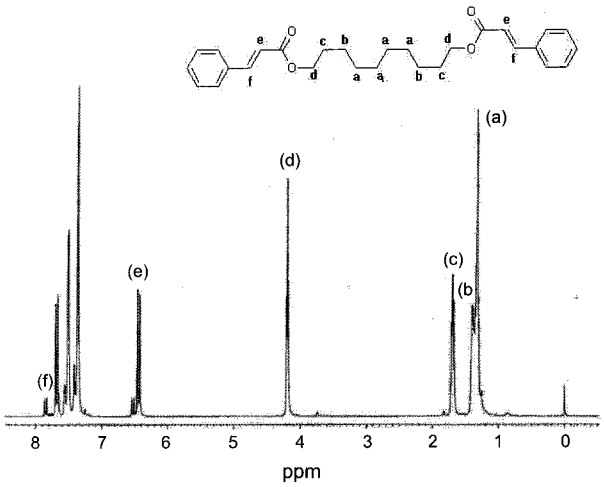

Figure 2. ^1H-NMR spectrum of 2Ci-DD.

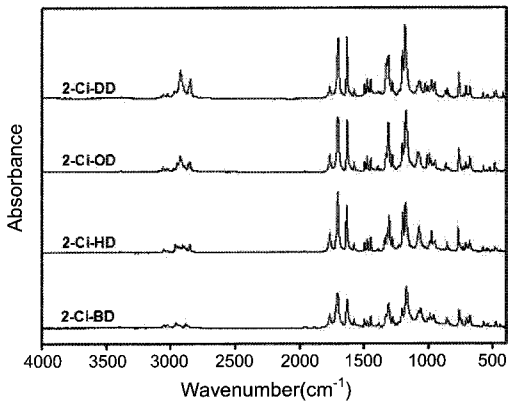

Figure 3. FT-IR spectrum of oligomeric cinnamates.

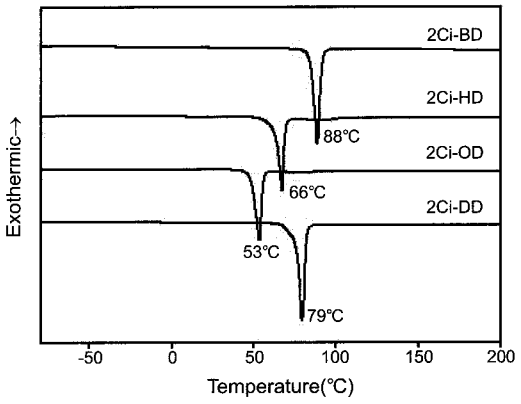

Figure 4. DSC thermograms of oligomeric cinnamates.

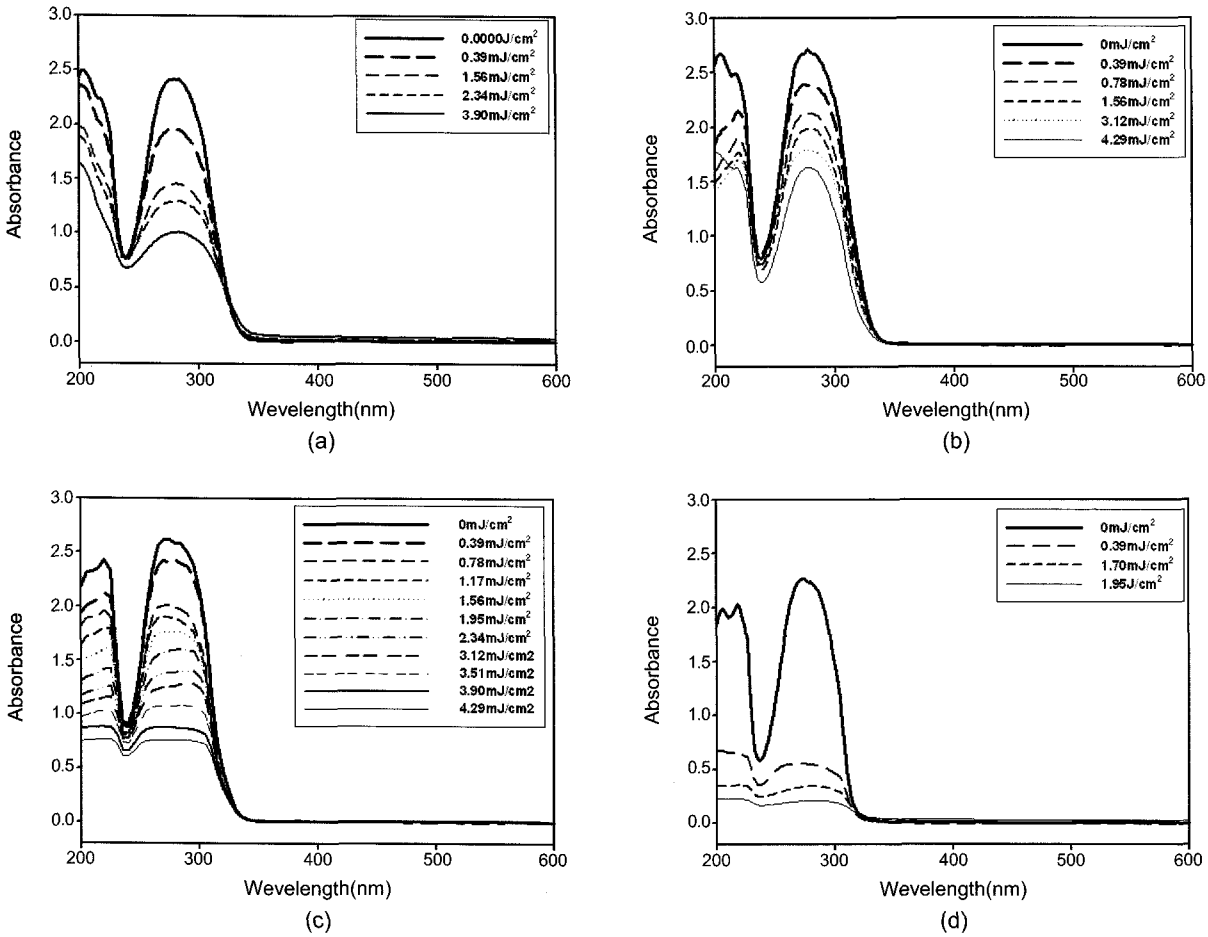

Figure 5. UV absorption of (a) 2Ci-BD; (b) 2Ci-HD; (c) 2Ci- OD; (d) 2Ci-DD with the UV irradiation.

the trend.

This implies that crystallization of the oligomer was facilitated by the increase of the flexibility during BD to OD. However, for the DD case, it is supposed that the ease of the packing of alkyl chains influence on the crystallization behavior of the 2Ci-DD.[12]

The UV-induced [2+2] cycloaddition reaction of oligomeric cinnamates was investigated with the irradiation time (Figure 5). Characteristic peak of cinnamate was observed around 280 nm which is originated from cinnamoyl groups and the peak intensity decreased with the irradiation. This is owing to the [2+2] cyclization of olefinic π electrons in the cinnamate group. Interestingly, from the result of UV irradiation onto 2Ci-OD and 2Ci-DD, very small peak was remained with the UV irradiation. This is not generally observed for the cinnamates moiety in polymers. It can be postulated that oligomeric chains with flexible alkyl chain result in higher reactivity. Additionally, close packing induced by the alkyl chains accelerates the reaction to form cyclobutane between intermolecular cinnamoyl reactions. Among the oligomeric cinnamates, 2Ci-DD needed smallest energy

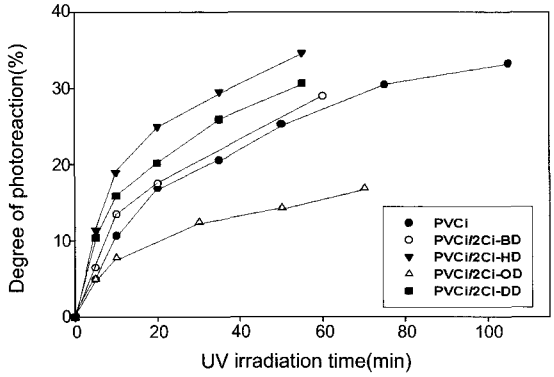

Figure 6. Degree of photoreaction with the UV irradiation time.

of UV irradiation for the almost complete photoreaction.

Groove Surface Pattern Formation by SAMIM. Blends of PVCi and oligomeric cinnamates were prepared for the preparation of photo-alignment layer with groove patterns. Since the thick coatings of oligomeric cinnamates can't be applied onto the glass plate owing to high crystallinity, blended PVCi provides thick coating property for the groove pattern. Blend ratio (PVCi : oligomeric cinnamate=90 : 10)

was determined by the clear solution formation of PVCi and oligomeric cinnamate in the solution. It is expected that the selection of oligomeric cinnamates will influence of the photo-reaction rate and this was measured by the decrease of the characteristic peak in the UV-vis spectra with the irradiation time for the blend samples. As shown in Figure 6, reaction rate of blended samples is slightly enhanced except for 2Ci-OD compared to that of pristine PVCi. In spite of considerable high reaction rate of 2Ci-DD samples, there was a small difference of the rate enhancement with the oligomeric species. From the result, it could be mentioned that blending of low molecular weight cinnamates can improve photo-reaction rate of polymeric cinnamates.

Previous results show that grating groove on the surface can also provide alignment by the minimization of elastic strain when the LC director orients to parallel to the groove and the structure of the groove effect on alignment property.[13,14]

Surface groove pattern was formed on the coated glass plate via solvent-assisted micromolding (SAMIM). Actually, solvent for the coated polymer which should not swell the PDMS mold is used for SAMIM procedure. We first used acetone as a solvent to wet PDMS and conformal contact over coated films on the glass plate was performed. However,

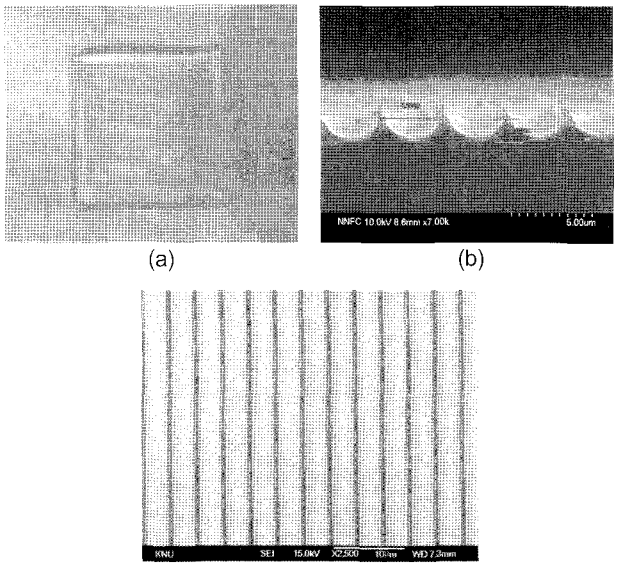

Figure 7. Image of PDMS stamp (a); SEM image of the stamp surface (b); SEM image of replicated groove pattern surface on glass plate (c).

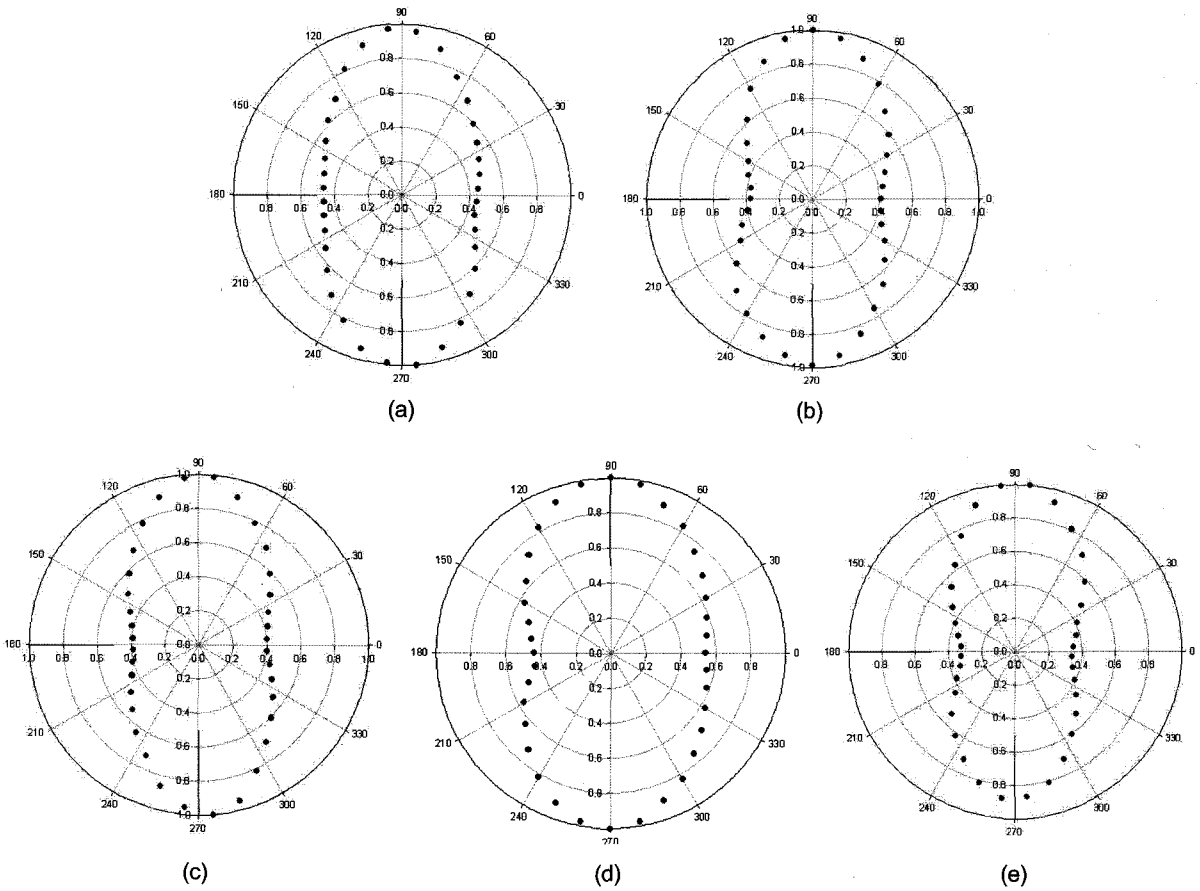

Figure 8. Polar plot of (a) PVCi; (b) PVCi/2Ci-BD blend; (c) PVCi/2Ci-HD blend; (d) PVCi/2Ci-OD blend; (e) PVCi/ 2Ci- DD blend.

acetone was not a good candidate solvent for our samples and we tried methanol instead and we could successfully obtain micron-sized groove surface pattern. The image of PDMS stamp and the surface groove pattern by SAMIM is illustrated in Figure 7.

LC Alignment Property of Blend Cinnamates. The alignment direction of the nematic LC on the groove patterned surface was determined from the anisotropic absorption of a small amount of dichroic dye dissolved in LC.[7] Linear polarized UV perpendicular to the groove pattern was irradiated to form alignment layer prior to cell assembly. The results of polar plot were illustrated in the Figure 8.

As shown in the Figure 8, all the samples are aligned perpendicular (90°-270° line) to the UV irradiation direction. The result shows that blend samples are well aligned on the groove patterned surface.

Conclusions

New photo-aligning material based on the blend of oligomeric and polymeric cinnamates have been prepared. Addition of oligomeric cinnamates influenced on the reaction rate of PVCi with the species used. Groove patterned surface could be fabricated under the assistance of SAMIM method which could not be obtained when the high crystalline oligomeric cinnamate was applied only. The result of polar plot shows the molecular orientation is well generated on the groove patterned surface.

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