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Spatial Anisotropy in Poly(vinylcinnamate) Films

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A null ellipsometry technique is applied to the study of spatial structural properties of poly(vinylcinnamate) (PVCN) and poly(vinyl *E*-4-fluorocinnamate) (PVCN-F) films before and after irradiation with actinic UV light. Based on the results, three-dimensional (3D) orientational configurations of cinnamoyl fragments are estimated. The orientation of cinnamoyl groups in original PVCN films is spatially isotropic, while in PVCN-F films a slight preference for the out-of-plane alignment is detected. Both uniaxial and biaxial structures were induced by polarized UV light depending on material and irradiation conditions. In the irradiated films the refractive index reaches its minimum along the direction of polarization of the actinic UV light ***E*** and maximum in the directions perpendicular to ***E***. This indicates effective crosslinking of cinnamate groups along the direction of light polarization and preferential orientation of the remaining cinnamate fragments in the directions perpendicular to ***E***. Under certain irradiation conditions for PVCN-F and under all irradiation conditions for PVCN the remaining cinnamoyl fragments are distributed randomly in the plane perpendicular to ***E***. The result is a negative A-plate with the optic axis along the polarization direction. The polymer films irradiated with nonpolarized light have refractive properties typical of uniaxial plates with positive birefringence (positive C and O plates). The optic axis of these films is determined by the direction of light propagation and corresponds to preferential orientation of the cinnamoyl fragments. The obtained films may be used for compensation of liquid crystal displays and improvement of their optical characteristics.

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KEYWORDS: photoinduced anisotropy, photoalignment, poly(vinylcinnamate), retardation film, ellipsometry

1. Introduction

Photoinduced optical anisotropy (POA) is defined by the birefringence and optical dichroism that occur in photosensitive films under irradiation with polarized light. It has been observed in several classes of photosensitive polymers.[1–5)] Polymers containing cinnamate groups are among the most broadly studied. The distinctive features of cinnamate-containing polymers are their high sensitivity to UV light and the high thermal stability of the induced anisotropy. These features are closely connected to the photochemistry of cinnamate compounds. The main photochemical reaction initiated by UV light in cinnamates is $(2+2)$ photocycloaddition that produces covalent bonding of two neighboring cinnamate units. The obtained cross-linked products are stable to thermal and light factors. In addition, *trans-cis*-isomerization of cinnamoyl fragments can be more or less effective and depends on molecular constitution and irradiation conditions.[6–9)] Both photodimerization and *trans-cis*-isomerisation generated by polarized light induce the orientational ordering of cinnamoyl units through the angular hole-burning mechanism.[10)] Irradiation with polarized UV light induces angular photodepletion of the reactive cinnamoyl groups that is most efficient in the direction of light polarization ***E***. This is effectively translated into preferential orientation of the remaining cinnamoyl units perpendicular to the ***E*** direction. For the sake of simplicity, in the vast majority of studies the latter process is considered to be two-dimensional (2D), i.e., only the changes in the film plane are taken into account. The orientation of cinnamate fragments is assumed to be uniaxial with the optic axis in the plane of the film.[11–13)] The evaluation of the in-plane orientational order requires quite simple experiments involving measurements of in-plane birefringence and absorption dichroism. However, the 2D photoordering model does not describe this process adequately. Indeed, the real photoordering process takes place in the three-dimensional (3D) space and in general the induced orientational structures are effectively biaxial.

The description of the 3D orientational structures requires more complicated experimental methods. These methods can be divided in two groups: measurements of absorption coefficients[14,15)] and refractive indices.[10,16–18)] There is a significant challenge in the application of known absorption methods to the case of cinnamate polymers because the polymer films possess low absorption dichroism. In contrast, methods grounded on measurements of refractive indices are much more attractive. Recently we suggested null ellipsometry as an effective tool for the study of 3D orientational configurations. The great potential of this method was demonstrated for films of azobenzene-containing polymers[18,19)] and thin liquid crystalline layers.[20)] The 3D orientational structures of nonirradiated films as well as films irradiated under various irradiation conditions were investigated.

In the present work we apply null ellipsometry to study 3D orientational configurations of the cinnamate-containing polymers. The well-known representative of this polymer series, poly(vinylcinnamate) (PVCN), is chosen for this purpose. This polymer originally developed as photoresist,[21)] was later applied for photoalignment of liquid crystals (LCs).[22,23)] The peculiarities of the in-plane ordering in PVCN films have been comprehensively studied.[2,8,9,11–13,23–25)] Our new results supplement earlier studies and describe both in-plane and out-of-plane ordering in PVCN layers. Based on these results we suggest the potential application of PVCN films as retardation films for LC displays.

2. Experimental

2.1 Samples

We used poly(vinylcinnamate) with $M_w = 200{,}000$ purchased from Aldrich and poly(vinyl *E*-4-fluorocinnamate) with $M_w = 30{,}000$ synthesized in the Institute of Bioorganic Chemistry and Petrochemistry, NASci. of Ukraine. Poly(vinyl *E*-4-fluorocinnamate) was readily prepared from 4-fluorocinnamoyl chloride obtained by heating of 4-fluorocinnamic acid in excess of thionyl chloride. The 4-fluorocinnamic acid was obtained by a Knoevenagel reaction between 4-fluorobenzaldehyde and malonic acid in pyridine. The distillation of 4-fluorocinnamoilchloride is a very important step in the synthesis of high-quality product.

Polymers were dissolved in dichloroethane at a concentration of 30 g/l. Films were obtained by casting the filtered solution on the glass substrates using the spin coating technique. The films were subsequently dried at 90°C for over 1 h. The thickness of the films was measured using a profilometer from Tencor Instruments and was about several microns.

To induce anisotropy in the films we used the UV light from a Xe lamp supplied by Oriel Corp. The maximal irradiation density of nonpolarized light used in our experiments was $40\,\mathrm{mW/cm^2}$ in the wavelength range of 326–400 nm. To irradiate the samples with polarized light, we used a dichroic UV polarizer supplied by Oriel Corp. The intensity of polarized light in the sample position was about $15\,\mathrm{mW/cm^2}$. The light polarization direction corresponded to the x axis of the film (Fig. 1). The sample was mounted on a rotating stage in order to control the incidence angle of the actinic light.

2.2 Method and experimental setup

To measure the light-induced birefringence in polymer films we used a transmission ellipsometry technique with a polarizer, quarter-wave compensation plate and rotating analyzer in fixed positions (Fig. 1).[18] The quarter-wave plate converts the elliptically polarized light passing through the sample into linearly polarized light. The rotation angle of the polarization plane of the light after it passes through phase plate can be determined by rotation of the analyzer to a position of minimum light transmission at an angle φ. At the normal incidence of the testing light, the angle φ is related to in-plane retardation $(n_y - n_x)d$ as follows: $(n_y - n_x)d = \lambda\varphi/180$ (x, y, and z are principal axes (Fig. 1), d and λ are film thickness and light wavelength, respectively). The method used for in-plane birefringence measurements is known as the Senarmont technique. It can be extended for oblique light incidence. In the latter case, the angle φ depends on the in-plane retardation $(n_y - n_x)d$, the out-of-plane retardation $(n_z - n_x)d$ and the absolute value of one of the refractive indices of the biaxial film, for example, n_x. The angle φ can be calculated as a function of light incidence angles θ of the testing beam assuming a particular optic axis distribution. The calculations were carried out using Berreman's 4×4 matrix method.[26] The experimental curves $\varphi(\theta)$ were fitted to the theoretical one. The absolute value of the refractive index was measured by means of an Abbe refractometer and used in the fitting process.

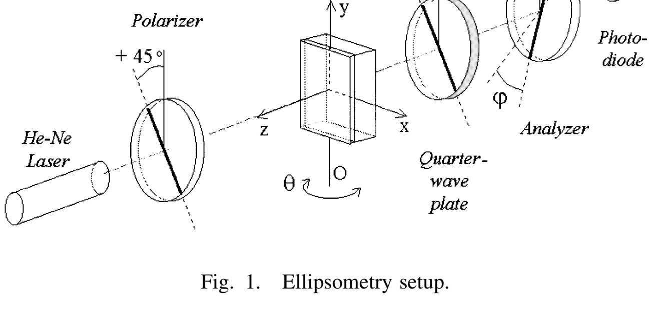

Fig. 1. Ellipsometry setup.

The measurement setup included a low-power He–Ne laser ($\lambda = 632.8\,\mathrm{nm}$), two calcite Glan-Thompson polarizers mounted on rotational stages from Oriel Corp., a Babinet-Soleil compensator adjusted to produce the retardation of a quarter wave for the light wavelength of $\lambda = 632.8\,\mathrm{nm}$ and a sample holder mounted on the rotational stage by Oriel Co. The light intensity was measured with a photodiode connected to a Keithley multimeter. The setup was automatically controlled by a personal computer. The rotation accuracy was better than 0.2°. A detailed description of the applied method can be found elsewhere.[18]

3. Results and Discussion

The average refractive index of PVCN and PVCN-F polymers measured with the Abbe refractometer was about 1.58. This value was used in all subsequent fitting procedures. The φ versus θ curves for the nonirradiated films of nonfluorinated (PVCN) and fluorinated (PVCN-F) poly(vinylcynnamate) are presented in Fig. 2 (curves 1 and 2). There is no difference in the experimental data obtained for vertical and horizontal positions of the sample axis x, indicating that the samples are isotropic in the x–y plane. The modeling of $\varphi(\theta)$ curves for the PVCN-F film gives the following relationship between the three principal dielectric indices: $n_x = n_y < n_z$. If one assumes that the higher polarizability and, hence, a higher refractive index occurs in the direction of preferential orientation of the cinnamoyl

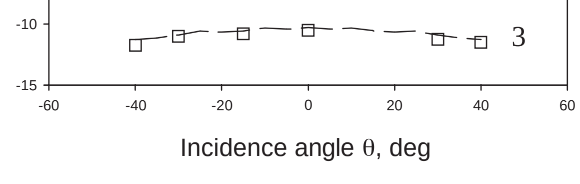

Fig. 2. Measured (symbols) and modeled (lines) φ versus θ curves. 1,1′-nonirradiated PVCN film; 2,2′-nonirradiated PVCN-F film; 3,3′-polarized light irradiated PVCN film ($15\,\mathrm{mW/cm^2}$, 30 min). Curves 1, 2, 3 and 1′, 2′, 3′ correspond to horizontal and vertical positions of the sample axis x, respectively. Modeling results: curves 1 and 1′—$n_x = n_y = n_z$ (isotropic film); curves 2 and 2′—$n_x = n_y < n_z$ (positive C-plate, $(n_z - n_x)d = 8\,\mathrm{nm}$); curves 3 and 3′—$n_x < n_y = n_z$, (negative A-plate, $n_y - n_x = 26\,\mathrm{nm}$).

units, the relationship indicates a preferential out-of-plane alignment of the groups and their random distribution in the film plane. Contrary to this case, the relationship between the three principal indices for the nonfluorinated PVCN film suggests that they feature a spatially isotropic distribution of cinnamate units: $n_x = n_y = n_z$. We must note that in our previous studies[17,18,26] we did not notice the isotropic spatial distribution of functional groups in the polymers that had side groups with high polarizability. The observation stands true for all previously studied azopolymer homologues that show either liquid crystalline or amorphous phases. Comparing the mesogenic properties of azobenzene fragments and the nonmesogenic properties of cinnamate units, one may conclude that the structure and properties of photosensitive fragments plays a decisive role in the ordering of photosensitive polymers in nonirradiated films.

The preferential homeotropic alignment of cinnamate units observed in the case of PVCN-F films may be caused by fluor substituents. The fluorinated units possess hydrophobic properties and prefer the out-of-plane alignment. Evidently, the fluor atoms play the same role in the phase formation of PVCN films as the alkyl chains in the previously studied azopolymers.[18,19,27]

The typical phase shifts versus light incidence angle detected in the films of nonfluorinated poly(vinylcinnamates) are shown in Fig. 2 (curves 3 and 3′). Figure 3 shows the measured values of in-plane $(n_y - n_x)d$ and out-of-plane $(n_z - n_x)d$ optical retardation versus irradiation dose for both types of polymers. The modeling of phase shift curves for PVCN-F film gives the following correlation between the indices: $n_x < n_y \leq n_z$. This relationship indicates that the induced orientational structure is biaxial in general. The biaxiality is especially clear for high exposures whereas the beginning stage of irradiation is characterized by uniaxial ordering. In contrast, the films of nonfluorinated PVCN retain the same correlation between indices $n_x < n_y = n_z$ throughout the entire irradiation process. The curves in both cases have a maximum at intermediate intensities. The induced birefringence decreases gradually at high illumination levels. The data obtained by us are in good agreement with in-plane birefringence $(n_y - n_x)d$ versus light intensity data presented by other authors.[9,13,23] According to ref. 23, the saturation and the subsequent decrease in induced birefringence may be caused by the exhaustion of the number of reactive cinnamate fragments in the direction of light polarization ***E*** and their gradual depletion in the directions that are not parallel to ***E***. The maximum value of the birefringence is about 0.005.

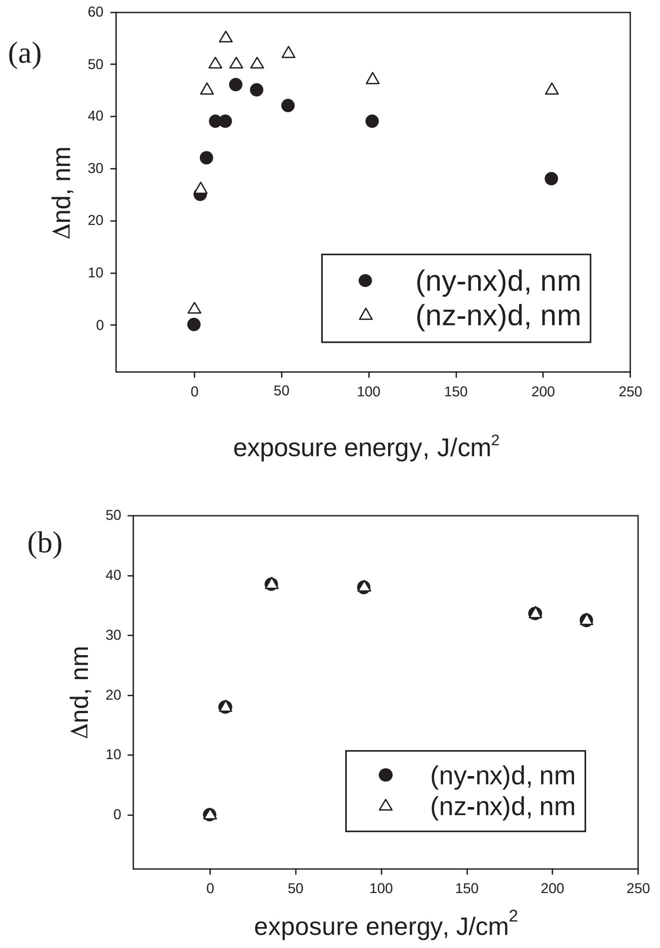

Fig. 3. Birefringence kinetics in PVCN-F (a) and PVCN (b) films.

The irradiated films of nonfluorinated PVCN have a quite unusual structure that was not considered prior to application of the POA method. Indeed, the correlation $n_x < n_y = n_z$ indicates that the induced optic axis lies in the x direction, i.e., in the polarization direction of the actinic light, and the films possess negative birefringence. Such films are usually referred to as negative A-plates. The negative A-plates in combination with other compensation films are often used in liquid crystal displays (LCDs) for compensation of the residual positive birefringence of the LC layer that compromises the optical performance of LCDs. For example, in ref. 28 a negative A-plate prepared from lyotropic discotic LC was employed to achieve viewing cone enhancements of TN LCDs. By substituting lyotropic film in TN LCD with PVCN one we obtained a quite similar viewing angle improvement.

The relationship between indices $n_x < n_y = n_z$ indicates a preferential alignment of cinnamoyl fragments in the irradiated films. It is reasonable to assume that the directions corresponding to the highest refractive index also correspond to preferable orientation of highly conjugated cinnamoyl units. The photodimerization of cinnamoyl fragments is associated with the braking down of the nonsaturated C=C bonds and their substitution with saturated ones. As a result of photoinduced processes, π-conjugation of the cinnamoyl fragments decreases substantially. The latter process decreases the polarizability of the photomodified fragments and, as a consequence, the optical refractive index. The refractive index should be maximally reduced for light polarized in the direction of maximal transformation of cinnamoyl fragments. This assumption is in full agreement with our results. The other consequence of the photoinduced transformations is the accumulation of nonmodified cinnamoyl groups in the directions perpendicular to light polarization ***E***. The latter effect was also observed earlier in ref. 8, 9 and 23 by using UV spectroscopy methods. Taking into account these facts one can conclude that the films featuring $n_x < n_y = n_z$ have cinnamoyl fragments aligned in the plane that is perpendicular to the vector ***E*** and their distribution in this plane is degenerated [Fig. 4(a)].

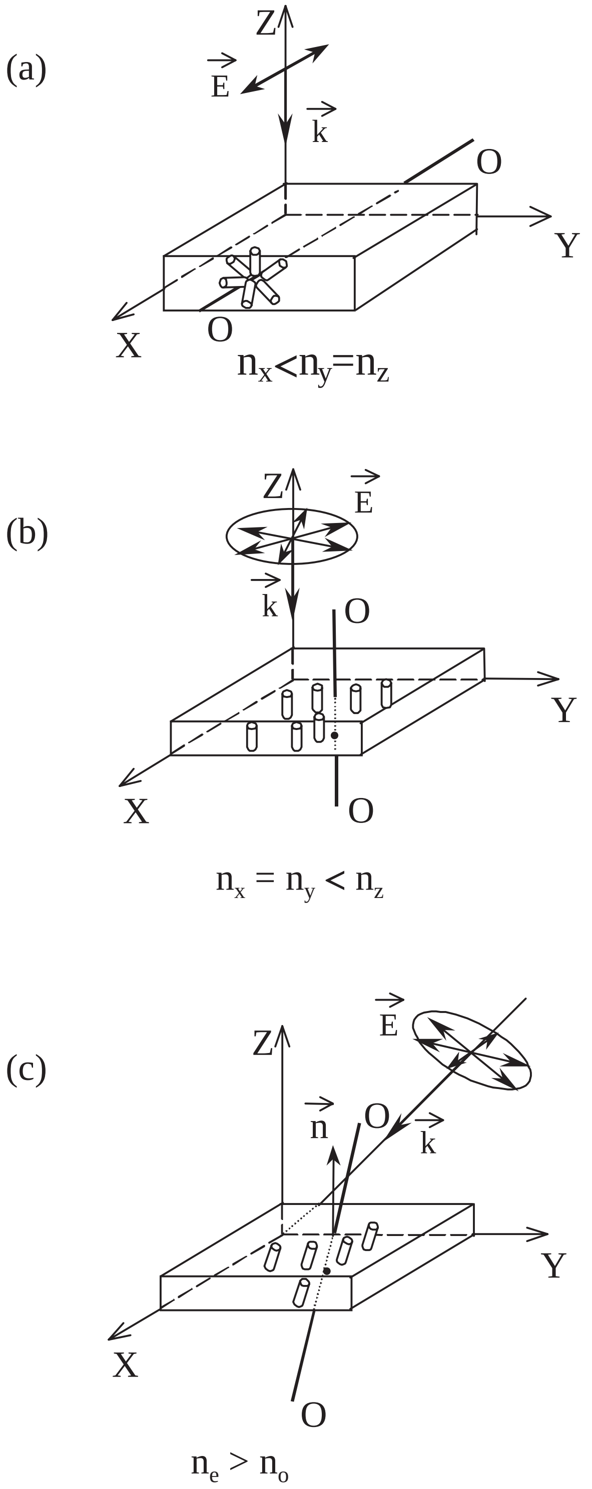

Fig. 4. Photoinduced structures for various irradiation conditions.

Such distribution of functional groups with high polarizability under UV light irradiation conditions was obtained for the first time. As mentioned above, it may occur because of non-mesogenic properties of cinnamate fragments.

One further point that requires explanation is the difference between the structures induced in PVCN-F and PVCN films [see Figs. 3(a) and 3(b)]. The biaxiality observed in the case of PVCN-F may be a result of small initial out-of-plane alignment of the cinnamoyl groups in nonirradiated PVCN-F films. We believe that the preference for homeotropic alignment in PVCN-F eliminates the degeneration in the y–z plane and, hence, induces the formation of biaxial structures.

Contrary to the previous case, the nonirradiated films of nonfluorinated PVCN feature the degenerated (isotropic) distribution of cinnamoyl fragments with no preference for homeotropic alignment. When the degenerating factor is absent, the irradiated films of nonfluorinated PVCN form uniaxial structures. We believe that the initial isotropic spatial orientation of the functional groups is a factor playing a principal role in the formation of negative A-plates under conditions of polarized UV irradiation.

Figures 5 and 6 show typical φ versus θ curves for PVCN and PVCN-F films irradiated with nonpolarized light at the

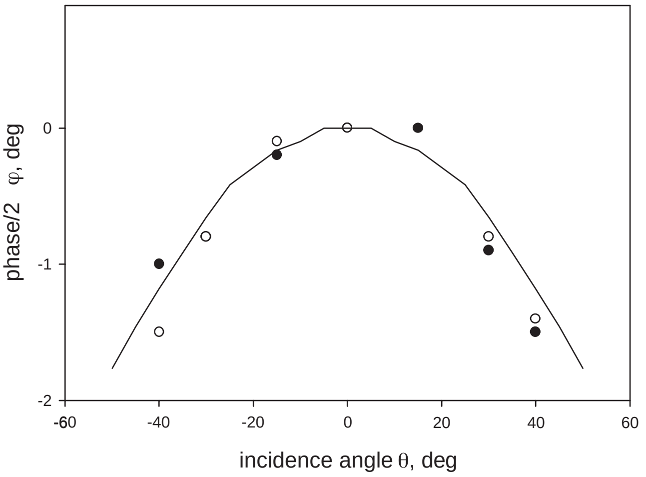

Fig. 5. Measured (symbols) and modeled (lines) φ versus θ curves for the PVCN-F film irradiated with nonpolarized light (20 mW/cm^2, 10 min) at normal incidence. Curves 1 and 1′ correspond to horizontal and vertical positions of the sample axis x, respectively. Modeling results: $n_x = n_y < n_z$, $n_z - n_x = 25$ nm (positive C plate).

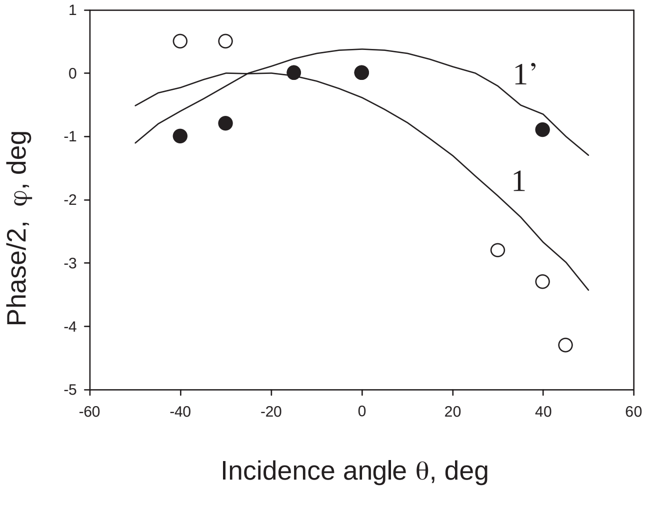

Fig. 6. Measured (symbols) and modeled (lines) φ versus θ curves for the PVCN film irradiated with nonpolarized light (20 mW/cm^2, 5 min) at the incidence angle of 45°. Curves 1 and 1′ correspond to horizontal and vertical position of the sample axis x, respectively. Modeling results: positive uniaxial film with the optic axis inclined at 20° and $n_e - n_o = 20$ nm (positive O plate).

light incidences of 0° and 45°, respectively. We obtained the following relationship between the indices: $n_x = n_y < n_z$, in the case of normal incidence of nonpolarized light. This corresponds to a positive uniaxial film with the optic axis directed along the film normal and the orientation of the cinnamate fragments along the same direction [Fig. 4(b)]. This type of film is sometimes referred to as a positive C-plate. The maximum value of induced birefringence $n_e - n_o \sim 0.005$ was obtained after lengthy UV light exposure.

The orientational configuration obtained at oblique incidence of nonpolarized light may also be described in the context of the uniaxial model. In the latter case the optic axis is tilted at an angle about 20° to the film normal. Correspondingly, the cinnamoyl units are oriented obliquely to the film surface [Fig. 4(c)]. The maximum value of n_e-n_o with this geometry is of the same order of magnitude as that for the normal incidence of the actinic light. The inclination angle of this structure can be controlled by variation of the incidence angle of the actinic light. The described films are usually referred to as positive O-plates.

4. Conclusions

We have shown that modified null ellipsometry is an effective method for the study of light-induced structures in poly(vinylcinnamates). We observed both uniaxial and biaxial structures induced by polarized light in different types of cinnamates and under various irradiation conditions. The refractive index reaches its minimum along the direction of polarization of actinic UV light, indicating the effective crosslinking of cinnamate groups. This results in a negative A-plate with the optic axis along the direction of UV light polarization. We have shown that the necessary condition for the formation of the uniaxial structure is an isotropic spatial orientation of cinnamate fragments in the original polymer film.

The structures induced in poly(vinylcinnamates) with nonpolarized UV light can also be described in the context of the uniaxial model. In this case, the cinnamate fragments accumulate along the direction of light propagation, causing positive birefringence of the photomodified films. In the case of the normal light incidence the optic axis is induced along the film normal (C plate), whereas with oblique light incidence it is inclined (O plate).

The obtained results a new application of cinnamate films. For instance, negative A-plates fabricated by irradiation of cinnamate films with UV light may be applied to the compensation of liquid crystal displays and improvement of their viewing angle performance. Since anisotropic cinnamate films also demonstrate LC aligning properties, the single films can serve simultaneously as alignment layers and optical retarders in LCDs.

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