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Description	



<b>Control of Three-Dimensional Refractive Indices</b>
of Uniaxially-Stretched Cellulose Triacetate
with Low-Molecular-Weight Compounds
$\mathbf{V}_{\mathbf{r}}$
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#### 29 Abstract

A method to control the 3D refractive indices and wavelength dispersion of birefringence of 30 polymer films by uniaxial stretching with addition of various low-molecular-weight 31 compounds (LMCs) with strong polarizability anisotropy is developed. Biomass-derived 32 cellulose triacetate (CTA) films containing a small amount of crystallites at the stretching 33 temperature are found to show planar deformation to some degree only by uniaxial stretching. 34 Although molecular orientation evaluated from the in-plane and out-of-plane birefringences 35 of pure CTA seems consistent with uniaxial deformation, LMC addition pronounces the 36 deviation of the refractive index from uniaxial symmetry. Rod-shaped molecules are found to 37 greatly enhance both in-plane and out-of-plane birefringences because of their marked 38 orientation in the stretching direction. Conversely, the out-of-plane birefringence increases 39 more than the in-plane one upon addition of disk-shaped molecules, because the LMC 40 molecules tend to be embedded in the film plane. Consequently, 3D refractive indices of 41 42 CTA can be controlled only by uniaxial stretching, not biaxial one, with an aid of an 43 anisotropic LMC.

## 44 Keywords: Birefringence; Cellulose triacetate; Blend; Orientation

45

## 46 **1. Introduction**

Cellulose triacetate (CTA) is a biomass-derived material that has found application in 47 films produced by solution casting because of its severe thermal degradation beyond its 48 melting point [1-3]. The common optical film applications of CTA include as a photographic 49 50 film base and polarizer protection film because of the attractive properties of these films such as high transparency and excellent heat resistance [1,3,4]. CTA films are currently widely 51 employed in liquid crystal displays, and show promise for use in advanced systems such as 52 3D and electroluminescent displays. To be used in polarizer protective and retardation films, 53 it is important to control the birefringence of CTA. For example, polarizer protective films 54 need to be free from birefringence, and thus advanced methods to erase birefringence have 55 been proposed recently [5-7]. For retardation films, specific retardation, *i.e.*, the product of 56 birefringence and thickness, is required. 57

58 It is well known that the orientation birefringence of polymers is determined by the chain orientation and polarizability anisotropy of the repeating unit. For example, a polymer 59 showing positive birefringence has a larger molecular polarizability, and thus refractive index, 60 in the main chain direction than those in the perpendicular directions. The magnitude of 61 birefringence is further controlled by the chain orientation in the stretched film. In general, 62 refractive indices in the in-plane directions  $(n_x \text{ and } n_y)$  can be controlled by uniaxial 63 stretching. However, the refractive index in the film-thickness direction  $(n_z)$  should be 64 modulated in addition to  $n_x$  and  $n_y$  to obtain optical displays with a wide viewing angle. 65 Therefore, an advanced method should be used to control the refractive index  $n_7$  and to 66 satisfy the relationship between the refractive index in each direction. 67

To date, the most conventional method to obtain the 3D control of refractive indices isbiaxial stretching, as exemplified by van Horn and Winter [8], which has the drawback of

being expensive. Therefore, much attention has been focused on a new alternative method.
The Cakmak research group recently reported the thickness distribution of optical anisotropy
in solution-cast films in detail, indicating that the refractive index in the film thickness
direction can be controlled by solvent evaporation rate [9-11].

As well as 3D control, the wavelength dispersion of birefringence also has to be precisely modulated for high-performance retardation films. For example, a specific retardation, *e.g.*, a quarter or half of the wavelength, should be provided in the whole visible light region for multi-band wave plates. Because most conventional polymers show ordinary wavelength dispersion of orientation birefringence as expressed by the Sellmeier relation (equation 1), various techniques have been proposed to obtain films showing extraordinary dispersion [12-16].

81 
$$\Delta n(\lambda) = A + \frac{B}{\lambda^2 - \lambda_{ab}^2}, \qquad (1)$$

where  $\lambda_{ab}$  is the wavelength of a vibrational absorption peak in the ultraviolet region, and *A* and *B* are the Sellmeier coefficients. We previously found that transparent films of cellulose acetate propionate show positive in-plane birefringence that increases with wavelength; *i.e.*, extraordinary wavelength dispersion [15-17].

86 Several methods have been already proposed to control the birefringence in polymeric 87 materials, such as copolymerization with appropriate monomers [18], doping with anisotropic 88 crystals [19] and blending with another polymer [14-16] or a low-molecular-weight 89 compound (LMC) [17,20]. In the polymer blend method, miscible polymer pairs showing 90 different signs of intrinsic birefringence with different wavelength dispersion are mixed on a 91 molecular scale to minimize light scattering.

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CTA films prepared by solution casting show uniform thickness, high transparency, 92 and adequate mechanical properties. The sign of out-of-plane birefringence in a solution-cast 93 CTA film is opposite to that of the in-plane orientation birefringence in a hot-stretched one. 94 Moreover, the wavelength dispersion of the out-of-plane birefringence is extraordinary for a 95 solution-cast film. Our previous study also revealed that the out-of-plane birefringence and its 96 wavelength dispersion of a solution-cast film can be modified by the addition of an LMC that 97 is miscible with CTA, such as tricresyl phosphate (TCP) [21]. This is attributed to the 98 molecular orientation of TCP induced by the nematic interaction, *i.e.*, intermolecular 99 orientation correlation, between CTA and TCP. 100

101 In this study, both the 3D refractive indices and wavelength dispersion of birefringence of films are controlled by uniaxial stretching, in which the anisotropy in the 102 shrinkage between lateral and thickness directions is used. It is well known that the lateral 103 104 shrinkage of a polymer film extruded from T-die, known as "neck-in", is small for a polymer melt showing marked strain-hardening in elongational viscosity [22-25]. In other words, the 105 transversal orientation in the film plane occurs to some degree, although it is not so obvious 106 compared with equi-biaxial elongation for a polymer melt with marked strain-hardening. 107 Therefore, long-chain branched polymers, *e.g.*, low-density polyethylene produced by radical 108 109 polymerization, are preferably used in industry to reduce the neck-in level during T-die film processing. Moreover, various methods to enhance strain-hardening have also been proposed 110 [26-29]. Yamane et al. showed marked strain-hardening in elongational viscosity for 111 poly(lactic acid) (PLA) having a small amount of stereocomplex crystals whose melting point 112 is higher than that of a conventional PLA [27]. Because CTA also contains a small amount of 113 crystallites [1,3], which act as branch points, at the stretching temperature, it is expected to 114 115 show strain-hardening; *i.e.*, transversal orientation besides the orientation to the stretching

direction, only by uniaxial stretching. The transversal refractive index caused by the 116 transversal orientation of CTA chains is magnified by LMCs because of their nematic 117 interaction with CTA. In this work, two types of LMCs are used from the viewpoint of 118 molecular shape: TCP and triphenyl phosphate (TPP) as disk-shaped molecules and 4-cyano-119 4'-pentylbiphenyl (5CB) as a rod-shaped one. Finally, the mechanism of this phenomenon is 120 discussed based on molecular orientation. Since the control of 3D refractive indices and their 121 wavelength dispersion are strongly required to produce advanced displays, the phenomenon 122 described in this paper will be seriously considered for the industrial application. 123

124

#### 125 **2. Experimental**

The polymeric material used in this study was commercially available CTA produced by Acros Organics. The degree of substitution of CTA was 2.96, and its weight-average molecular weight  $M_w$  was  $3.50 \times 10^5$  Dalton, which was evaluated using a gel permeation chromatograph (Tosoh, HLC-8020) with TSK-GEL® GMHXL as a polystyrene standard. TCP and TPP purchased from Daihachi Chemical Industry were employed as disk-shaped LMCs. 5CB from Wako Pure Chemical Industries was used as a rod-shaped LMC. Their chemical structure is shown in Figure 1.

133

#### [Fig.1]

134 CTA films were prepared by solution casting. CTA with/without an LMC (5 wt%) 135 was dissolved in a mixture of dichloromethane ( $CH_2Cl_2$ ) and methanol ( $CH_3OH$ ) with a 136 weight ratio of 9 to 1, and stirred for 24 h at room temperature before casting. All samples 137 were perfectly dissolved into the mixed solvent. The resulting solution containing 4 wt% 138 CTA was poured into a flat-bottomed glass petri dish with a diameter of 80 mm and height of 139 15 mm at room temperature to allow the solvent to evaporate at a uniform rate. The thickness140 of the films was 100 μm.

Uniaxially oriented films were prepared by hot stretching using a tensile machine with a temperature controller (UBM, DVE-3 S1000) at a draw ratio of 1.5. The stretching temperature was determined from dynamic mechanical analysis (DMA) data with a tensile storage modulus of 10 MPa at 10 Hz. The initial distance between the clamps was 10 mm, and the width of the sample was 5 mm. Because the stretching rate was 0.5 mm s<sup>-1</sup>, the initial strain rate was  $0.05 \text{ s}^{-1}$ . The samples were quenched immediately after stretching under a flow of cold air to prevent relaxation of the molecular orientation.

The temperature dependence of oscillatory tensile moduli in the solid state was measured at 10 Hz from 0 to 250 °C at a heating rate of 2 °C min<sup>-1</sup> by DMA (UBM, E-4000) using rectangular samples that were 5 mm wide and 20 mm long.

The optical properties of the film samples were measured at room temperature by an 151 optical birefringence analyzer (Oji Scientific Instruments, KOBRA-WPR). The retardation in 152 the thickness direction (out-of-plane retardation)  $R_{th}$  was determined by retardation 153 measurements at oblique incidence angles of  $0^{\circ}$  and  $40^{\circ}$  as a function of wavelength by 154 changing color filters. The corresponding birefringence was calculated using the film 155 thickness measured by a digital micrometer. Prior to measurements, the samples were placed 156 in a chamber (Yamato, IG420) with temperature and humidity controlled at 25 °C and 50% 157 RH, respectively, for 1 day, to control the moisture content in the films. The in-plane 158 retardation  $(R_{in})$  and  $R_{th}$  are respectively defined as follows: 159

160  $R_{in} = \Delta n_{in} \times d = (n_x - n_y) \times d$ (2)

161 
$$R_{th} = \Delta n_{th} \times d = \left(\frac{n_x + n_y}{2} - n_z\right) \times d$$
(3)

where *d* is film thickness, *x* is the stretching direction, *y* is the direction perpendicular to the stretching direction in the film plane, and *z* is the thickness direction. The refractive indices in the three principal axes,  $n_x$ ,  $n_y$  and  $n_z$ , were determined from  $\Delta n_{in}$  and  $\Delta n_{th}$ , assuming the average refractive index  $\overline{n}$  is constant irrespective of the stretching procedure. The average refractive index  $\overline{n}$  was measured by an Abbe refractometer.

Wide-angle X-ray diffraction (WAXD) patterns were measured using a graphitemonochromatized Cu Kα radiation beam (Rigaku, R-AXIS IIc). The sample film was
mounted to direct the X-ray beam in the normal direction of the film.

Attenuated total reflection (ATR) was measured using an infrared absorption
spectrometer (Perkin Elmer, Spectrum 100) to study the molecular orientation in the films.
KRS-5 was used as an ATR crystal.

Thermal analysis was conducted with a differential scanning calorimeter (Mettler-Toledo, DSC822) under a nitrogen atmosphere. Samples (~10 mg) were heated from room temperature to 320 °C at a heating rate of 20 °C min<sup>-1</sup>.

176

#### 177 **3. Results and Discussion**

178 **3.1.** Characteristics of Solution-Cast Films

179 The temperature dependence of oscillatory tensile moduli such as storage modulus E'180 and loss tangent *tan*  $\delta$  for CTA and its blends was measured at 10 Hz to determine the 181 temperature at hot stretching. Figure 2 reveals that the glass transition temperature  $T_g$ , which

is defined as the peak temperature of tan  $\delta$  in this study, is located around at 209 °C for pure 182 CTA. For the blends,  $T_g$  decreases to 180, 179 and 183 °C upon addition of 5 wt% TCP, TPP 183 and 5CB, respectively. The relaxation peaks ascribed to  $T_g$  are broad for the blends, which is 184 typical for plasticized polymers. The dynamic mechanical properties of CTA/TCP and 185 CTA/TPP are similar, while CTA/5CB shows a slightly higher  $T_g$  with a broader peak than 186 the other blends. Furthermore, E' shows a plateau beyond the glass-to-rubber transition, 187 which is much higher than the rubbery plateau modulus for a typical polymer [30]. This is 188 attributed to the presence of CTA crystallites. DSC measurements indicate that the melting 189 point  $T_m$  of CTA is around 303 °C, which is higher than the stretching temperature. Therefore, 190 the crystallites act as crosslinking or branching points during hot stretching. 191

192

## [Fig.2]

The wavelength dispersion of the out-of-plane birefringence of the solution-cast films 193 is shown in Figure 3. CTA shows positive birefringence  $(n_z < n_x, n_y)$  that increases with 194 wavelength; *i.e.*, extraordinary wavelength dispersion. Because the birefringence of CTA is 195 mostly determined by the orientation of acetyl groups, the positive out-of-plane birefringence 196 is attributed to the in-plane alignment of acetyl groups induced by solution casting, as 197 reported in our previous paper [21]. The addition of LMCs greatly enhances the out-of-plane 198 birefringence of CTA. The enhancement is caused by the orientation of LMC molecules in 199 the film plane accompanied with CTA chains. In other words, the long axis of 5CB and the 200 disk plane of TCP and TPP orient in the film plane. 201

202

[Fig.3]

203

204

**3.2. Optical Anisotropy of Stretched Films** 

Figure 4 shows the wavelength dispersion of the in-plane and out-of-plane 206 birefringences of the CTA films stretched at a draw ratio of 1.5. The stretching temperatures 207 at which the tensile storage modulus is 10 MPa at a frequency of 10 Hz of pure CTA, and 208 209 CTA/TCP, CTA/TPP and CTA/5CB blends, were 214, 185, 184 and 188 °C, respectively. Figure 4a reveals that CTA shows negative in-plane birefringence that decreases with 210 increasing wavelength, *i.e.*, ordinary wavelength dispersion, similar to most conventional 211 polymers [7,17,18,20]. The negative orientation birefringence of the CTA film indicates that 212 the direction of the polarizability anisotropy associated with the acetyl groups is 213 perpendicular to the main chain, which aligns in the stretching direction. Consequently, the 214 refractive index in the oriented direction is lower than that in the perpendicular direction, *i.e.*, 215 negative orientation birefringence, as reported previously [7,15-17,21,31]. After hot 216 217 stretching, both the in-plane and out-of-plane birefringences of CTA become negative (Figure 4b). This is reasonable because the acetyl groups are oriented perpendicular to the stretching 218 219 axis.

220

### [Fig.4]

In contrast, the blends show anomalous behavior. The addition of 5CB markedly 221 increases both in-plane and out-of-plane birefringences and changes their sign from negative 222 to positive. The results obtained for stretched CTA/5CB correspond to the trends of the 223 solution-cast film in Figure 3. This is presumably caused by the large polarizability 224 anisotropy of 5CB with positive birefringence. The experimental results indicate that the 5CB 225 molecules are forced to orient in the stretching direction accompanying the alignment of the 226 227 polymer chains because of their nematic interaction [32-34]. It is known that a nematic interaction occurs in a miscible system when an LMC molecule is of appropriate size to move 228

cooperatively with chain segments of a host polymer [35-38]. Besides the large polarizability
anisotropy, the strong nematic interaction between CTA and 5CB will also be responsible for
the pronounced orientation birefringence of this blend film. Upon addition of disk-shaped
LMCs, the sign of in-plane and out-of-plane birefringences changes from negative to positive
with extraordinary wavelength dispersion. Moreover, the enhancement of out-of-plane
birefringence is larger than that of in-plane birefringence.

The relationship between in-plane and out-of-plane birefringences of general polymers after uniaxial stretching can be given by the following equation assuming uniaxial symmetry deformation; *i.e.*,  $n_y = n_z$  in equation (3).

$$\Delta n_{th} = \frac{\Delta n_{in}}{2} \tag{4}$$

The birefringences of CTA seem to follow equation (4), as shown in Figure 4. 239 However, the difference in the out-of-plane birefringence between CTA and the blends with 240 LMCs is similar to that in the in-plane birefringence. In particular, the marked enhancement 241 of the out-of-plane birefringence induced by the disk-shaped LMCs compared with that of the 242 in-plane birefringence should be noted. These results are quite different from equation (4), 243 even considering the nematic interactions in the blend films. To clarify the mechanism of the 244 marked out-of-plane birefringence of the blend films, the interaction between CTA and the 245 LMCs was also evaluated by ATR measurements focusing on the C-O-C stretching vibration 246 in the pyranose ring (1029  $\text{cm}^{-1}$ ) and C=O stretching vibration in the carbonyl group (1735 247 cm<sup>-1</sup>) (data not shown). None of the LMCs affect the position or intensity of the peaks from 248 the pyranose ring and carbonyl group of CTA, indicating that there is no specific interaction 249 such as chemical or electrostatic interactions between CTA and these LMCs. 250

To clarify the orientation of CTA chains in the blends, the drawn samples were immersed in methanol for 24 h to remove the LMCs following the method developed by Manaf *et al.* [16]. The orientation birefringence of the films was then measured again after drying at room temperature under vacuum.

255

# [Fig.5]

After immersion in methanol for 24 h, there were no considerable changes in the dimensions of the samples, suggesting that the degree of stretching is hardly affected by methanol immersion. FT-IR spectra confirmed that all LMCs in the blend films were dissolved in the methanol during immersion.

The wavelength dispersion of the in-plane and out-of-plane birefringences of the 260 stretched films after methanol immersion is presented in Figure 5. The birefringences of the 261 262 blends decrease and approach to those of pure CTA following methanol immersion. This result demonstrates that the molecular orientation of CTA chains is not affected by LMC 263 addition. This is reasonable because stretching of all films was performed at the same stress 264 level as mentioned later. Furthermore, it is found from 2D-WAXD patterns that the intensity 265 on the equator for (500) plane in the crystalline form of CTA-I is not affected by LMC 266 addition, supporting the result in Figure 4. 267

The normalized refractive indices, *i.e.*,  $n_i/\overline{n}$ , along the three principal axes were calculated from both in-plane and out-of-plane birefringences and are depicted in Figure 6.

In the case of pure CTA, the normalized refractive indices in the y and z directions, *i.e.*,  $n_y/\overline{n}$  and  $n_z/\overline{n}$ , are almost the same. However,  $n_y$  is slightly larger than  $n_z$ , suggesting that the CTA film shows transversal stretching to some degree. In other words, the transversal shrinkage in the film plane is smaller than the shrinkage in the thickness direction. Consequently, the molecules are slightly oriented to the *y*-direction besides their marked orientation in the *x*-direction. This is reasonable because CTA will show pronounced strainhardening during hot stretching because of the presence of crystallites [1,3]. As a result, planar elongational deformation, which is a kind of biaxial deformation, occurs rather than purely uniaxial deformation, especially in the center part of the film. This is observed in Tdie film processing for a polymer with long-chain branches [22-25].

280

# [Fig.6]

The stress-strain curves measured during hot stretching are shown in Figure 7. Both 281 strain and stress are true values, assuming that the Poisson ratio is 0.5. The true stress 282 increases monotonically with true strain. Because the final stress level is almost the same for 283 all films, the degree of the orientation of CTA chains is the same, as discussed above (see 284 Figure 5). Instead of quantitative evaluation of the strain-hardening, the width of the stretched 285 films was measured. This information directly relates to the level of neck-in; that is, lateral 286 reduction of the films. It is found that the width of the stretched films is almost the same as 287 that of the initial unstretched films (reduction of just 5% compared with the initial film) at a 288 draw ratio of 1.5. This result demonstrates that planar deformation occurs during uniaxial 289 stretching in these experiments. 290

291

#### [Fig.6]

The refractive index anisotropy caused by planar deformation is magnified by LMC addition. In the case of rod-shaped molecules such as 5CB, however, the principal axis of the molecules is basically oriented in the *x*-direction. Therefore, the transversal (*y*-axis) orientation is not pronounced so much ( $n_x >> n_y >> n_z$ ), because the long axis of 5CB has to change its direction to show the transversal orientation. On the contrary, disk-shaped molecules tend to embed themselves in the film plane even for the low level of transversal orientation of the polymer chains, because the transversal orientation does not disturb the *x*axis orientation of the disk-shaped LMC molecules. As a result, the blends show a larger refractive index in the *y*-direction than that in the *z*-direction ( $n_y \gg n_z$ ). Furthermore, the contribution of CTA chains ( $n_y > n_x$ ) to the orientation birefringence is not negligible, so  $n_y$  is larger than  $n_x$ .

- 303 Consequently, it can be concluded that the order of the refractive indices of the films 304 is as follows:
- 305 CTA,
- $306 n_y \ge n_z > n_x (5)$
- 307 CTA with disk-shaped LMC,
- $308 n_y > n_x > n_z (6)$
- 309 CTA with rod-shaped LMC,
- $310 n_x >> n_y >> n_z. (7)$

These experimental results demonstrates that the 3D control of refractive indices can be achieved using an appropriate LMC only by uniaxial stretching, which has not been reported to the best of our knowledge. The shape of LMC molecules is an important factor influencing the refractive index ellipsoid of a stretched film. Furthermore, the crystallinity of the film and stretching conditions will also affect the refractive index ellipsoid because they determine the lateral orientation in the film plane. Finally, it is indicated that this technique will be available for most polymer materials showing marked strain-hardening behavior in

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elongational viscosity, in which polymers having a low degree of crystallinity with high  $T_m$ , such as poly(vinyl chloride) and poly(ethylene terephthalate) are included. Moreover, various methods have been proposed recently to provide the strain-hardening.<sup>26-29</sup> Therefore, advanced optical films will be prepared by uniaxial stretching in near future.

322

## 323 **4.** Conclusion

324 Uniaxial hot stretching of CTA, which contains a small amount of crystallites at the stretching temperature, causes transversal stretching in the film plane to some degree besides 325 elongation in the stretching direction. This is directly confirmed by the change in dimensions 326 of the film after hot stretching. Consequently, the orientation in the transversal direction is 327 more pronounced than that in the thickness direction, leading to large out-of-plane 328 birefringence compared with that for pure uniaxial deformation. The orientation birefringence 329 caused by non-uniaxial deformation is greatly magnified by LMC addition, and can be 330 controlled by the shape of the LMC molecules. In the case of disk-shaped molecules, both  $n_x$ 331 and  $n_y$  are enhanced. Conversely,  $n_x$  is strongly enhanced with a slight increase in  $n_y$  by the 332 addition of rod-shaped molecules. These experimental results suggest the great possibility of 333 3D control of refractive indices by adjusting the amount of crystallites in the matrix polymer 334 and/or the shape of LMCs. Because an expensive biaxial stretching machine is not required at 335 this technique, the industrial application will be considered seriously. 336

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# 440 **Figure Captions**

- 441 **Figure 1.** Chemical structure of LMC samples used in this study.
- 442 **Figure 2.** Temperature dependence of tensile storage modulus *E*' and loss tangent *tan*  $\delta$  of 443 CTA (circles), CTA/TCP (95/5) (diamonds), CTA/TPP (95/5) (triangles) and 444 CTA/5CB (95/5) (squares) at 10 Hz.
- 445 **Figure 3.** Wavelength dispersion of the out-of-plane birefringence  $\Delta n_{th}(\lambda)$  of solution-cast 446 films of CTA (circles), CTA/TCP (95/5) (diamonds), CTA/TPP (95/5) 447 (triangles) and CTA/5CB (95/5) (squares).
- 448 **Figure 4.** Wavelength dispersion of (a) in-plane birefringence  $\Delta n_{in}(\lambda)$  and (b) out-of-449 plane birefringence  $\Delta n_{th}(\lambda)$  of stretched films of CTA (circles), CTA/TCP 450 (95/5) (diamonds), CTA/TPP (95/5) (triangles) and CTA/5CB (95/5) (squares). 451 The draw ratio was 1.5.
- 452 **Figure 5.** Wavelength dispersion of (a) in-plane birefringence  $\Delta n_{in}(\lambda)$  and (b) out-of-453 plane birefringence  $\Delta n_{th}(\lambda)$  of stretched films of CTA (circles), CTA/TCP 454 (95/5) (diamonds) and CTA/TPP (95/5) (triangles) after immersion in methanol. 455 The draw ratio was 1.5.
- 456 Figure 6. Wavelength dispersion of normalized refractive indices along the three principal
  457 axes of CTA, CTA/TCP, CTA/TPP and CTA/5CB films.
- 458 **Figure 7.** True stress ( $\sigma_T$ ) true strain ( $\varepsilon_T$ ) curves of films of CTA (circles), CTA/TCP 459 (95/5) (diamonds), CTA/TPP (95/5) (triangles) and CTA/5CB (95/5) (squares).









5CB



Songsurang et al., Figure 2









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Songsurang et al., Figure 7



- *x*: stretching direction
- y: transversal direction
- z: thickness direction