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Author(s)	Songsurang, Kultida; Shimada, Hikaru; Nobukawa, Shogo; Yamaguchi, Masayuki
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Description	

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4 **Control of Three-Dimensional Refractive Indices**  
5 **of Uniaxially-Stretched Cellulose Triacetate**  
6 **with Low-Molecular-Weight Compounds**

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10 **Kultida Songsurang<sup>1,2</sup>, Hikaru Shimada<sup>1</sup>, Shogo Nobukawa<sup>1</sup>,**  
11 **Masayuki Yamaguchi<sup>1\*</sup>**

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15 **<sup>1</sup>School of Materials Science, Japan Advanced Institute of Science and Technology,**  
16 **1-1 Asahidai, Nomi, Ishikawa, 923-1292, Japan**

17 **<sup>2</sup>Program in Petrochemistry, Faculty of Science, Chulalongkorn University,**  
18 **254 Phayathai Road, Pathumwan, Bangkok, 10330, Thailand**

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23 **\*Corresponding Author**  
24 **M. Yamaguchi**  
25 **Phone +81-761-51-1621**  
26 **Fax +81-761-51-1621**  
27 **e-mail m\_yama@jaist.ac.jp**

29 **Abstract**

30 A method to control the 3D refractive indices and wavelength dispersion of birefringence of  
31 polymer films by uniaxial stretching with addition of various low-molecular-weight  
32 compounds (LMCs) with strong polarizability anisotropy is developed. Biomass-derived  
33 cellulose triacetate (CTA) films containing a small amount of crystallites at the stretching  
34 temperature are found to show planar deformation to some degree only by uniaxial stretching.  
35 Although molecular orientation evaluated from the in-plane and out-of-plane birefringences  
36 of pure CTA seems consistent with uniaxial deformation, LMC addition pronounces the  
37 deviation of the refractive index from uniaxial symmetry. Rod-shaped molecules are found to  
38 greatly enhance both in-plane and out-of-plane birefringences because of their marked  
39 orientation in the stretching direction. Conversely, the out-of-plane birefringence increases  
40 more than the in-plane one upon addition of disk-shaped molecules, because the LMC  
41 molecules tend to be embedded in the film plane. Consequently, 3D refractive indices of  
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

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

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

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

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

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

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

82 where  $\lambda_{ab}$  is the wavelength of a vibrational absorption peak in the ultraviolet region, and  $A$   
83 and  $B$  are the Sellmeier coefficients. We previously found that transparent films of cellulose  
84 acetate propionate show positive in-plane birefringence that increases with wavelength; *i.e.*,  
85 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.

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

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

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

124

## 125 **2. Experimental**

126 The polymeric material used in this study was commercially available CTA produced  
127 by Acros Organics. The degree of substitution of CTA was 2.96, and its weight-average  
128 molecular weight  $M_w$  was  $3.50 \times 10^5$  Dalton, which was evaluated using a gel permeation  
129 chromatograph (Tosoh, HLC-8020) with TSK-GEL® GMHXL as a polystyrene standard.  
130 TCP and TPP purchased from Daihachi Chemical Industry were employed as disk-shaped  
131 LMCs. 5CB from Wako Pure Chemical Industries was used as a rod-shaped LMC. Their  
132 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 ( $\text{CH}_2\text{Cl}_2$ ) and methanol ( $\text{CH}_3\text{OH}$ ) 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 thickness  
 140 of the films was 100  $\mu\text{m}$ .

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

148 The temperature dependence of oscillatory tensile moduli in the solid state was  
 149 measured at 10 Hz from 0 to 250  $^{\circ}\text{C}$  at a heating rate of  $2 \text{ }^{\circ}\text{C min}^{-1}$  by DMA (UBM, E-4000)  
 150 using rectangular samples that were 5 mm wide and 20 mm long.

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

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



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

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

167 Wide-angle X-ray diffraction (WAXD) patterns were measured using a graphite-  
 168 monochromatized Cu K $\alpha$  radiation beam (Rigaku, R-Axis IIC). The sample film was  
 169 mounted to direct the X-ray beam in the normal direction of the film.

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

173 Thermal analysis was conducted with a differential scanning calorimeter (Mettler-  
 174 Toledo, DSC822) under a nitrogen atmosphere. Samples (~10 mg) were heated from room  
 175 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

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

192 [Fig.2]

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

202 [Fig.3]

203

204

### 205 3.2. Optical Anisotropy of Stretched Films

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

220 [Fig.4]

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

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

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

$$238 \quad \Delta n_{th} = \frac{\Delta n_{in}}{2} \quad (4)$$

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

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

255 [Fig.5]

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

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

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

270 In the case of pure CTA, the normalized refractive indices in the  $y$  and  $z$  directions,  
271 *i.e.*,  $n_y/\bar{n}$  and  $n_z/\bar{n}$ , are almost the same. However,  $n_y$  is slightly larger than  $n_z$ , suggesting  
272 that the CTA film shows transversal stretching to some degree. In other words, the transversal  
273 shrinkage in the film plane is smaller than the shrinkage in the thickness direction.

274 Consequently, the molecules are slightly oriented to the  $y$ -direction besides their marked  
275 orientation in the  $x$ -direction. This is reasonable because CTA will show pronounced strain-  
276 hardening during hot stretching because of the presence of crystallites [1,3]. As a result,  
277 planar elongational deformation, which is a kind of biaxial deformation, occurs rather than  
278 purely uniaxial deformation, especially in the center part of the film. This is observed in T-  
279 die film processing for a polymer with long-chain branches [22-25].

280 [Fig.6]

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

291 [Fig.6]

292 The refractive index anisotropy caused by planar deformation is magnified by LMC  
293 addition. In the case of rod-shaped molecules such as 5CB, however, the principal axis of the  
294 molecules is basically oriented in the  $x$ -direction. Therefore, the transversal ( $y$ -axis)  
295 orientation is not pronounced so much ( $n_x \gg n_y \gg n_z$ ), because the long axis of 5CB has to  
296 change its direction to show the transversal orientation. On the contrary, disk-shaped

297 molecules tend to embed themselves in the film plane even for the low level of transversal  
 298 orientation of the polymer chains, because the transversal orientation does not disturb the  $x$ -  
 299 axis orientation of the disk-shaped LMC molecules. As a result, the blends show a larger  
 300 refractive index in the  $y$ -direction than that in the  $z$ -direction ( $n_y \gg n_z$ ). Furthermore, the  
 301 contribution of CTA chains ( $n_y > n_x$ ) to the orientation birefringence is not negligible, so  $n_y$  is  
 302 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,

$$306 \quad n_y \geq n_z > n_x \quad (5)$$

307 CTA with disk-shaped LMC,

$$308 \quad n_y > n_x > n_z \quad (6)$$

309 CTA with rod-shaped LMC,

$$310 \quad n_x \gg n_y \gg n_z. \quad (7)$$

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

318 elongational viscosity, in which polymers having a low degree of crystallinity with high  $T_m$ ,  
319 such as poly(vinyl chloride) and poly(ethylene terephthalate) are included. Moreover, various  
320 methods have been proposed recently to provide the strain-hardening.<sup>26-29</sup> Therefore,  
321 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  
325 stretching temperature, causes transversal stretching in the film plane to some degree besides  
326 elongation in the stretching direction. This is directly confirmed by the change in dimensions  
327 of the film after hot stretching. Consequently, the orientation in the transversal direction is  
328 more pronounced than that in the thickness direction, leading to large out-of-plane  
329 birefringence compared with that for pure uniaxial deformation. The orientation birefringence  
330 caused by non-uniaxial deformation is greatly magnified by LMC addition, and can be  
331 controlled by the shape of the LMC molecules. In the case of disk-shaped molecules, both  $n_x$   
332 and  $n_y$  are enhanced. Conversely,  $n_x$  is strongly enhanced with a slight increase in  $n_y$  by the  
333 addition of rod-shaped molecules. These experimental results suggest the great possibility of  
334 3D control of refractive indices by adjusting the amount of crystallites in the matrix polymer  
335 and/or the shape of LMCs. Because an expensive biaxial stretching machine is not required at  
336 this technique, the industrial application will be considered seriously.

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339



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344

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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.

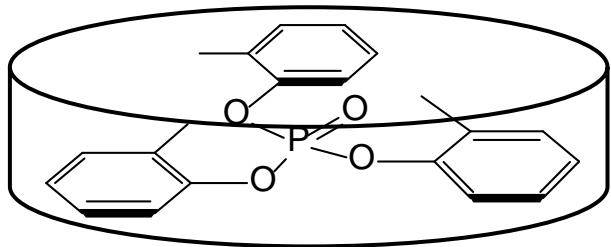
445 **Figure 3.** Wavelength dispersion of the out-of-plane birefringence  $\Delta n_{th}(\lambda)$  of solution-cast  
446 films of CTA (circles), CTA/TCP (95/5) (diamonds), CTA/TPP (95/5)  
447 (triangles) and CTA/5CB (95/5) (squares).

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.

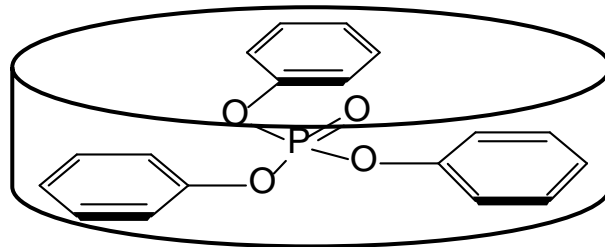
452 **Figure 5.** Wavelength dispersion of (a) in-plane birefringence  $\Delta n_{in}(\lambda)$  and (b) out-of-  
453 plane birefringence  $\Delta n_{th}(\lambda)$  of stretched films of CTA (circles), CTA/TCP  
454 (95/5) (diamonds) and CTA/TPP (95/5) (triangles) after immersion in methanol.  
455 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.

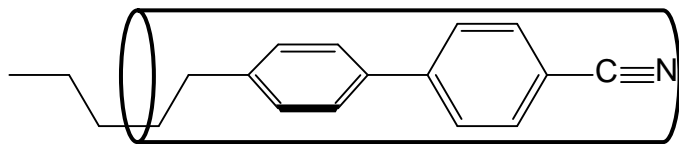
458 **Figure 7.** True stress ( $\sigma_T$ ) – true strain ( $\varepsilon_T$ ) curves of films of CTA (circles), CTA/TCP  
459 (95/5) (diamonds), CTA/TPP (95/5) (triangles) and CTA/5CB (95/5) (squares).



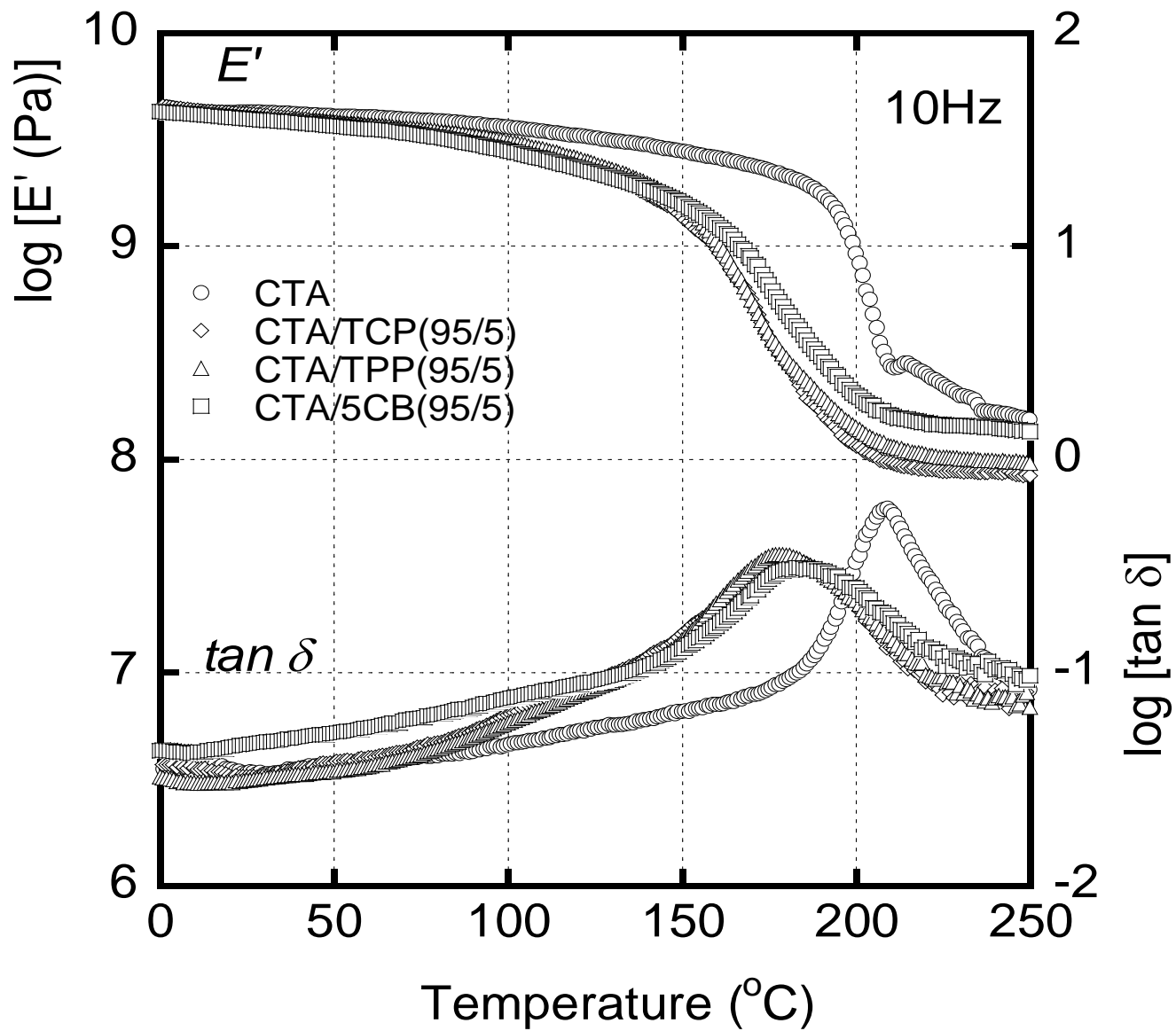
TCP



TPP

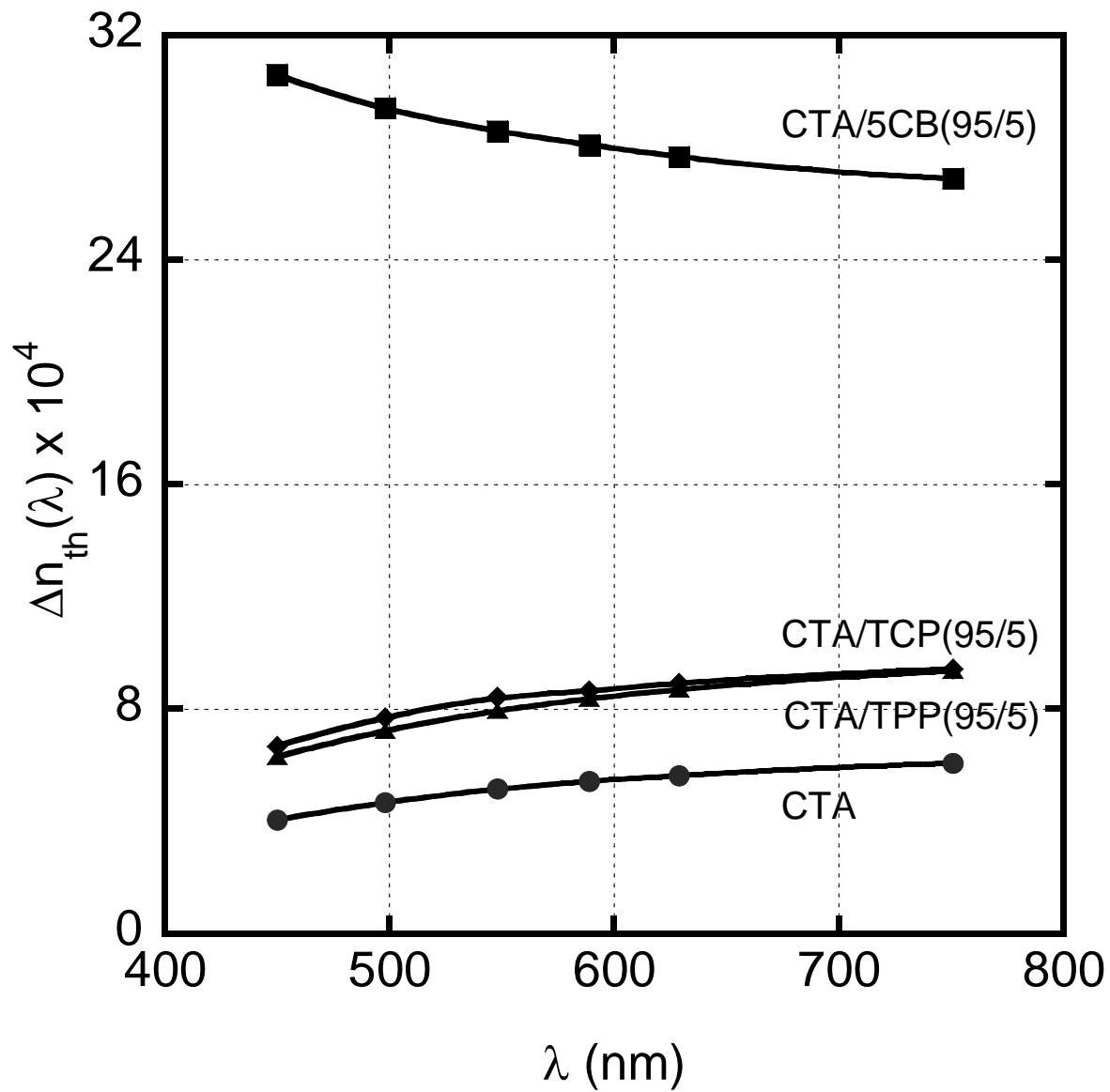


5CB

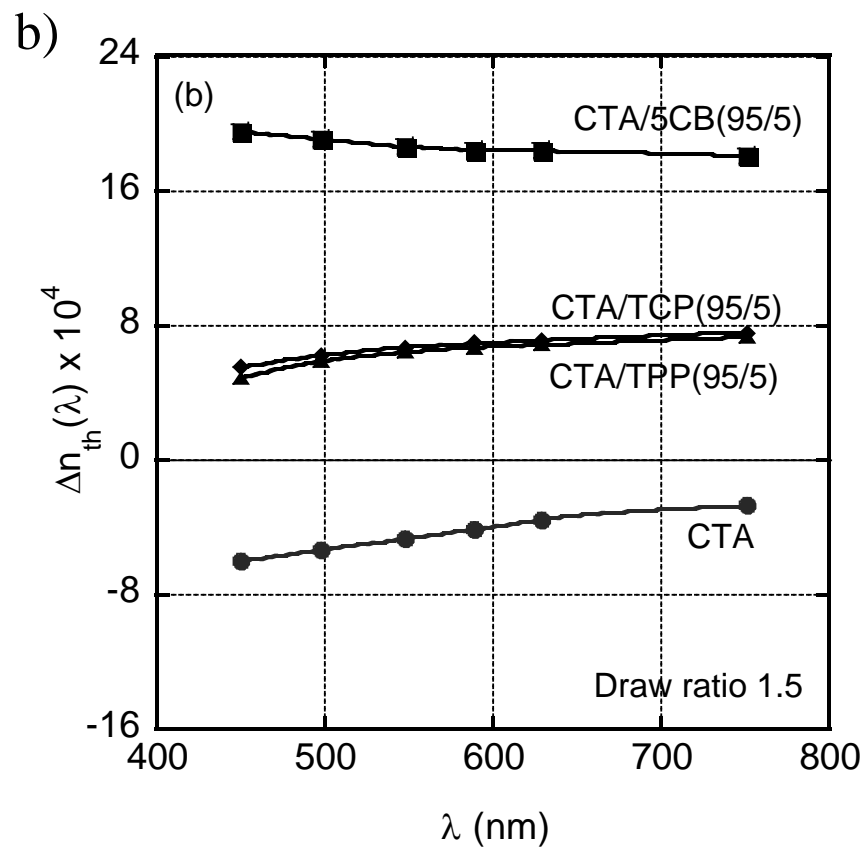
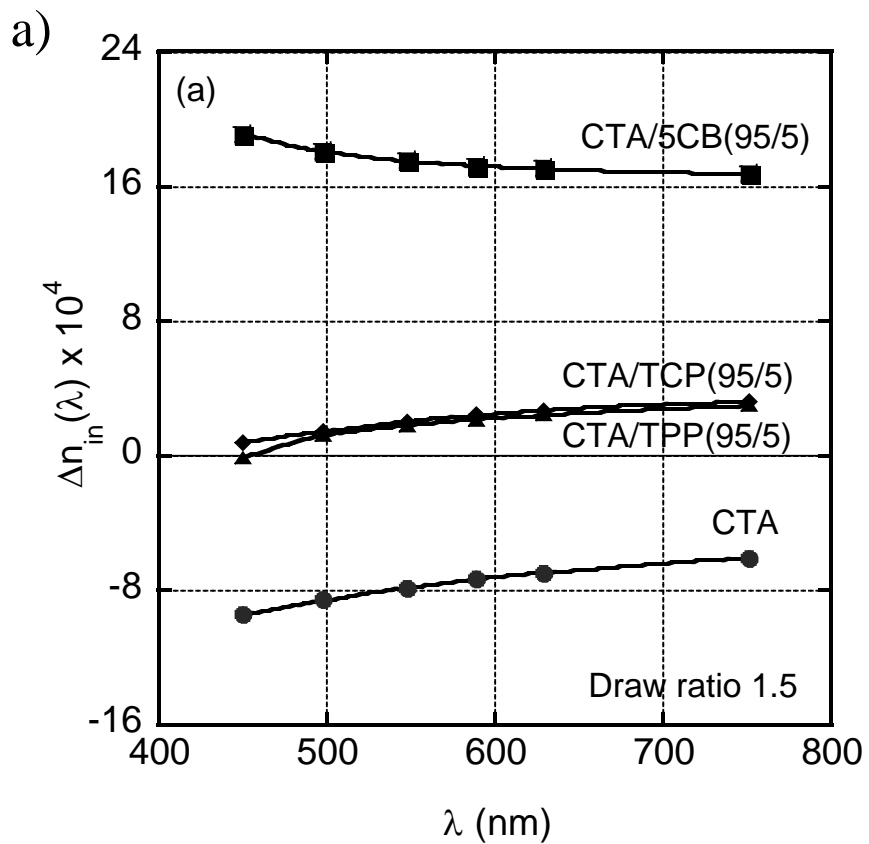


Songsurang et al., Figure 2

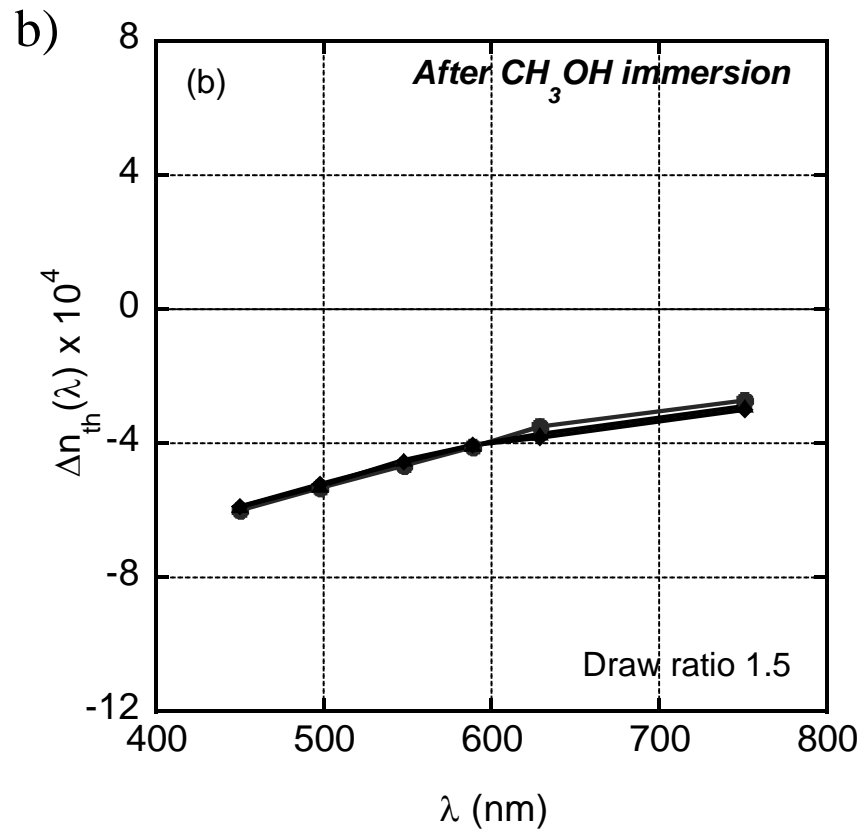
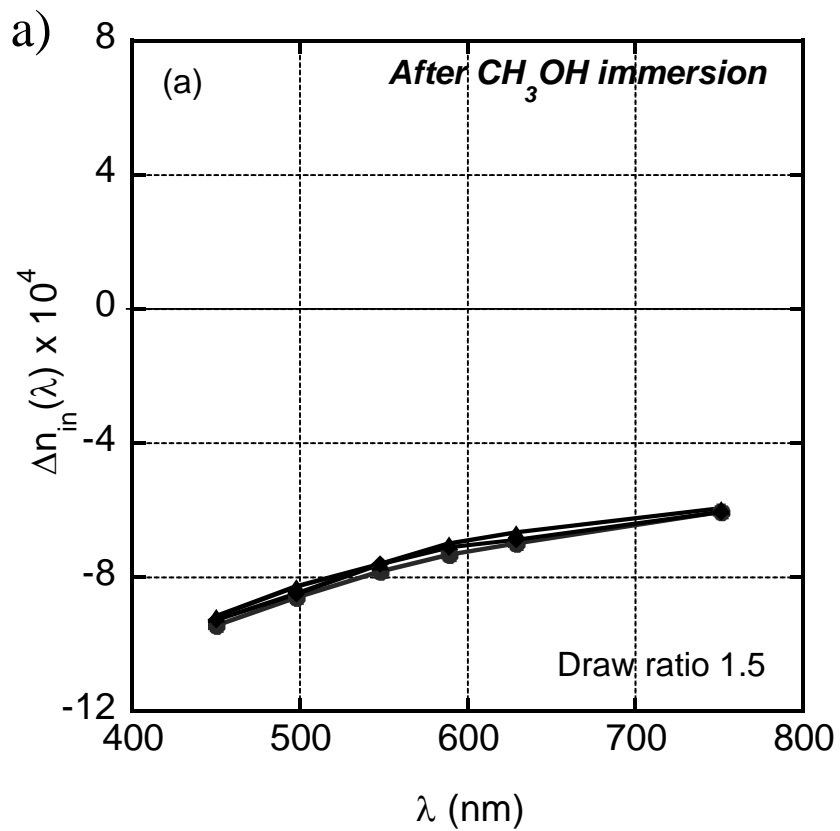




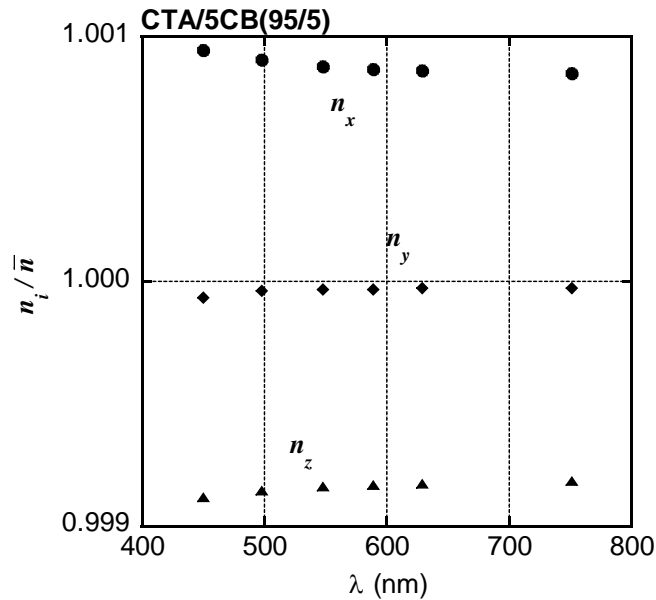
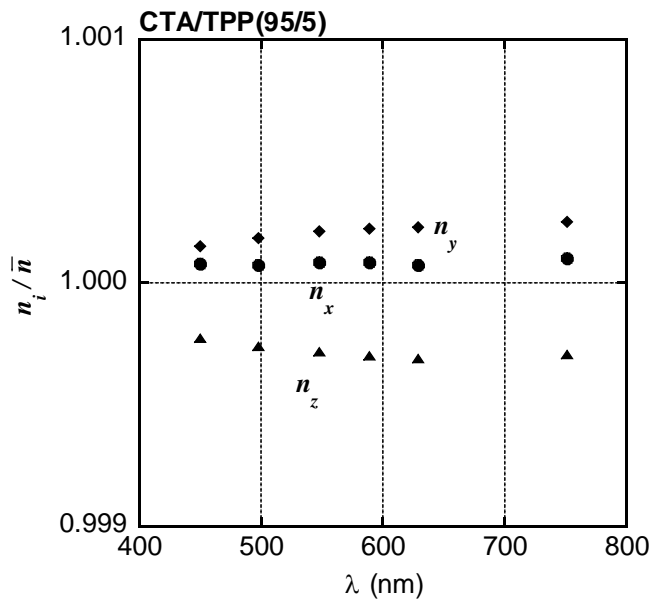
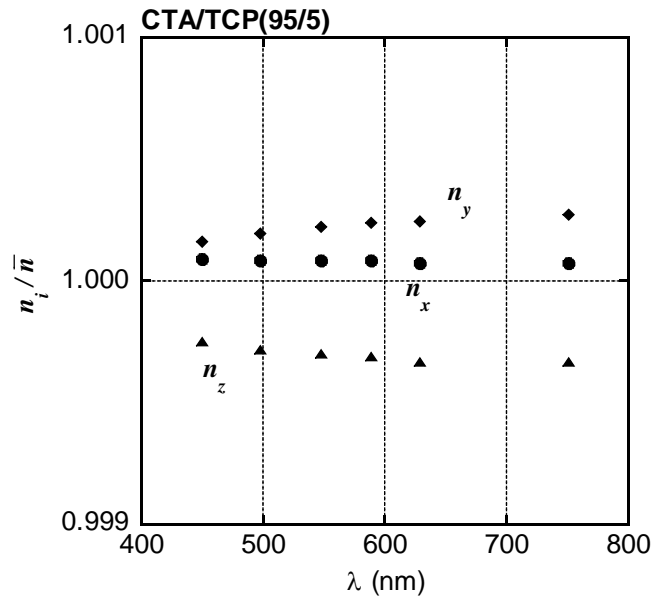
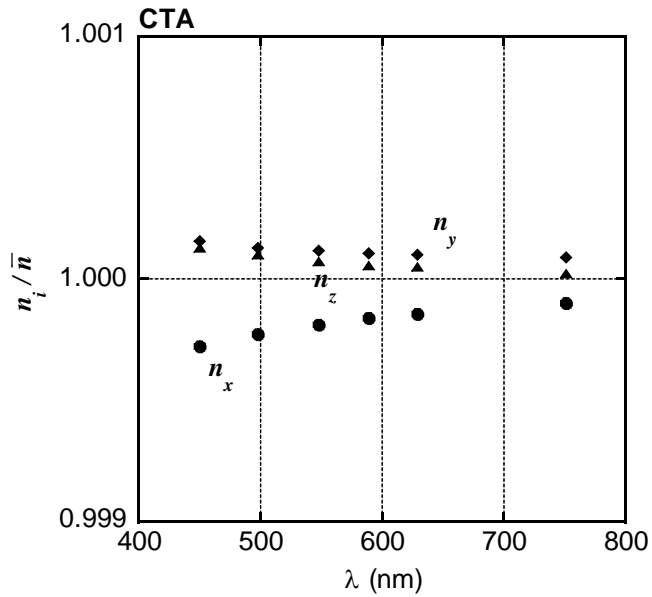
Songsurang et al., Figure 3



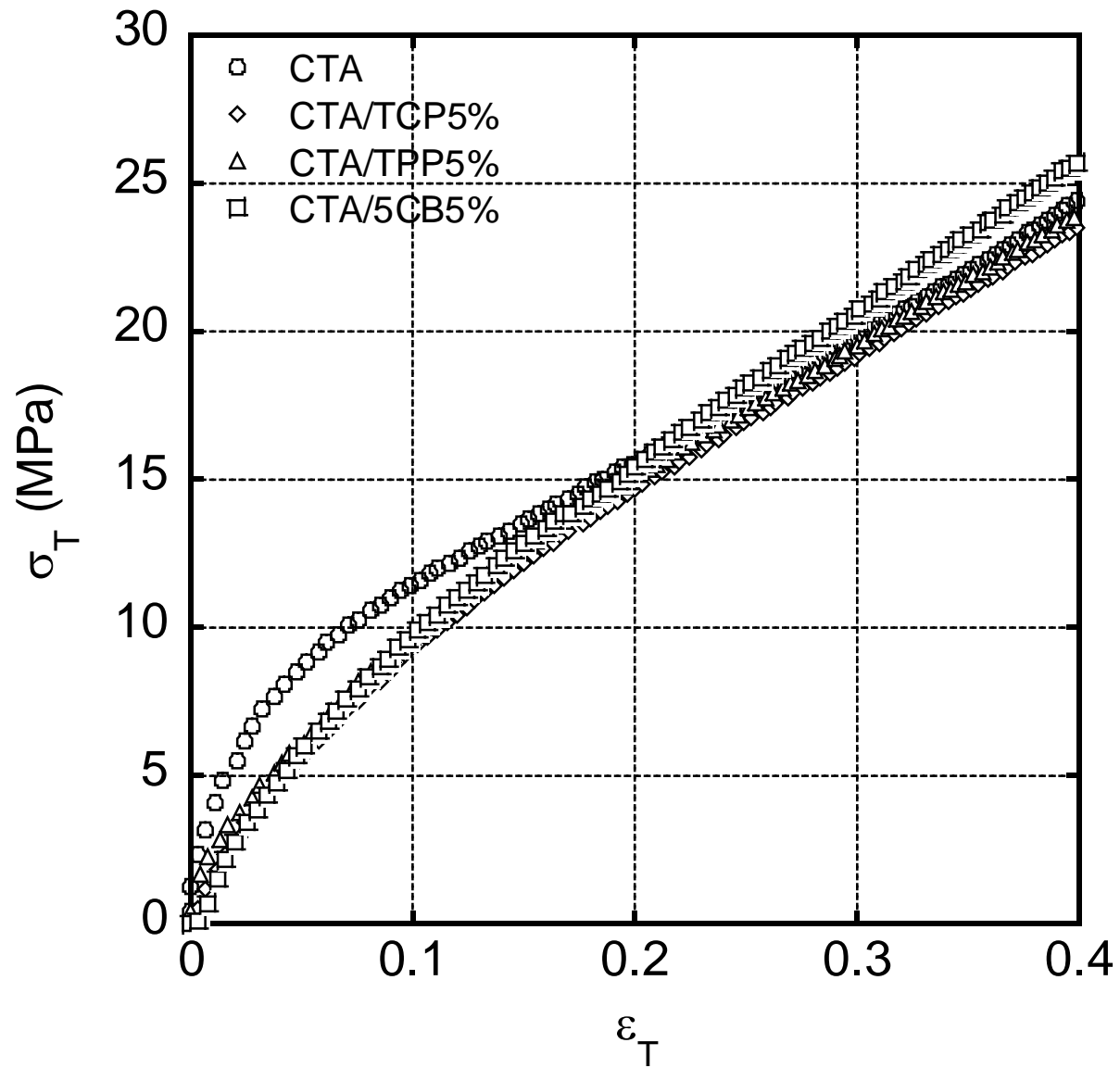
Songsurang et al., Figure 4



Songsurang et al., Figure 5

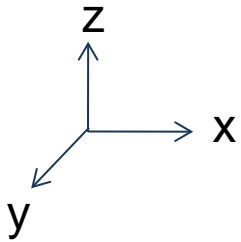
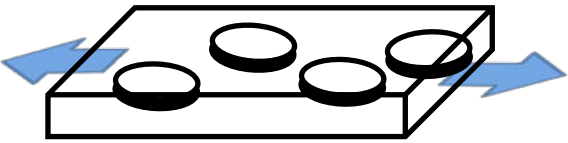


Songsurang et al., Figure 6

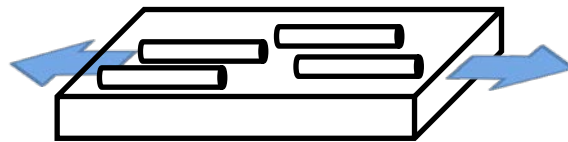


Songsurang et al., Figure 7

## Disk-shaped LMC



## Rod-shaped LMC



	Top-View	Side-View	Effect of LMC addition		
			$n_x$	$n_y$	$n_z$
Disk-shaped LMC			++	++	a little
Rod-shaped LMC			+++	+	a little

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