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Description	

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3 **Optical Anisotropy in Solution-Cast Film**  
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25 **Abstract**

26 The out-of-plane birefringence and its wavelength dispersion are studied employing solution-  
27 cast films of cellulose triacetate (CTA). In solution-cast process, CTA molecules are induced  
28 to align in the film plane. Although refractive index is the lowest in the oriented direction for  
29 the CTA films stretched more than 110%, refractive index is found to be the lowest in the  
30 normal direction for the unstretched cast film. ATR measurements reveal that in-plane  
31 alignment of the acetyl group which provides strong polarizability anisotropy is responsible  
32 for the phenomenon. Furthermore, the out-of-plane birefringence is found to increase with  
33 increasing wavelength, *i.e.*, extraordinary wavelength dispersion, whereas a stretched CTA  
34 film shows ordinary wavelength dispersion. The level of the out-of-plane birefringence in  
35 cast films depends on the preparation conditions, which is predictable considering the  
36 evaporation rate. Moreover, it is demonstrated for the first time that the out-of-plane  
37 birefringence and its wavelength dispersion can be modified by addition of a certain  
38 plasticizer such as tricresyl phosphate (TCP). During the evaporation, TCP molecules orient  
39 in the film plane accompanying the orientation of CTA chains by intermolecular orientation  
40 correlation, called nematic interaction. This technique will widen the scope of material design  
41 of retardation films because there are numerous liquid compounds having strong  
42 polarizability anisotropy.

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45 **Keywords:** Cellulose Triacetate; Out-of-Plane Birefringence; Solution-Cast

46

## 47 Introduction

48 With the rapid growth of optical devices these days, there is a continuing trend to develop a  
49 potential material for optical films with improved functions and good cost-performance. In  
50 particular, cellulose triacetate (CTA), one of the biomass-derived materials, has been studied  
51 intensively because of their attractive properties such as high transparency and excellent heat  
52 resistant (Edgar et al. 2004; Sata et al. 2004; Yamaguchi 2010; Yamaguchi et al. 2012). At  
53 present, CTA films are widely employed in liquid crystal display (LCD) and potentially used  
54 for advanced systems such as 3D display and electro-luminescent display in near future. In  
55 LCD application, CTA films are used as a polarizer protective film and a retardation  
56 (compensation) film. In order to be used in such applications, birefringence control is  
57 extremely important. In the case of polarizer protective films, for example, the films have to  
58 be free from birefringence, and thus, various methods to erase the birefringence have been  
59 proposed recently (Tagaya et al. 2001; Tagaya et al. 2003; Tagaya et al. 2006; Yamaguchi  
60 2010; Yamaguchi et al. 2012). For retardation films, specific retardation, *i.e.*, the product of  
61 birefringence and thickness, should be provided. In industries, CTA films are produced by a  
62 solution-cast method because melt processing is not applicable due to the severe thermal  
63 degradation beyond the melting point (Edgar et al. 2004; Sata et al. 2004; Yamaguchi 2010).  
64 Therefore, the information on the molecular orientation and the birefringence of a solution-  
65 cast film is significantly important.

66 For optical anisotropic films, three refractive indices,  $n_x$ ,  $n_y$  and  $n_z$ , along three  
67 principal axes have to be taken into consideration. The  $x$ -axis is the direction showing the  
68 maximum refractive index within the film plane in general, the  $y$ -axis is the direction  
69 perpendicular to the  $x$ -axis within the film plane, and the  $z$ -axis is the thickness direction and  
70 is normal to the  $x$ - $y$  plane.

71 It is well known that a solution-cast method provides films without molecular  
 72 orientation in the film plane, *i.e.*,  $n_x = n_y$ . This is the reason why a solution-cast film is  
 73 preferably employed for a protective film rather than a melt-extruded one. However, the other  
 74 component of birefringence, namely out-of-plane birefringence, is generally not zero.  
 75 Therefore, it has to be precisely controlled to provide a high quality display.

76 In this study, the in-plane birefringence ( $\Delta n_{in}$ ) and out-of-plane birefringence ( $\Delta n_{th}$ )  
 77 are defined by the following equations.

$$78 \quad \Delta n_{in} = n_x - n_y \quad (1)$$

$$79 \quad \Delta n_{th} = \frac{n_x + n_y}{2} - n_z \quad (2)$$

80 Based on the Kuhn and Grün model, the orientation birefringence  $\Delta n(\lambda)$  of an oriented  
 81 polymer is expressed in the following relation (Kuhn and Grün 1942; Treloar 1975; Read  
 82 1975; Harding 1986; Marks and Erman 1988).

$$83 \quad \Delta n(\lambda) = \frac{2\pi}{9} \frac{(\bar{n}(\lambda)^2 + 2)^2}{\bar{n}(\lambda)} N \Delta\alpha(\lambda) \left( \frac{3\langle \cos^2 \theta \rangle - 1}{2} \right) \quad (3)$$

84 where  $\lambda$ ,  $\bar{n}(\lambda)$ ,  $N$ ,  $\Delta\alpha(\lambda)$ , and  $\theta$  are the wavelength of light, the average refractive index, the  
 85 number of chains in a unit volume, the polarizability anisotropy, and the angle that a segment  
 86 makes with the stretch axis, respectively. The bracketed term  $(3\langle \cos^2 \theta \rangle - 1)/2$  is identically  
 87 equal to the Hermans orientation function (Hermans and Platzek 1939), which is commonly  
 88 denoted as  $F$ . Therefore, eq. 3 can also be written in the following form for a homogeneous  
 89 material.

$$\Delta n(\lambda) = \Delta n^0(\lambda)F \quad (4)$$

91 where  $\Delta n^0(\lambda)$  is the intrinsic birefringence.

92 In the case of a crystalline polymer such as CTA, the contributions from both  
 93 crystalline and amorphous phases have to be considered even if it has no form birefringence  
 94 (Stein et al. 1963), as shown in the following equation.

$$\Delta n(\lambda) = \phi_c \Delta n_c^0(\lambda)F_c + (1 - \phi_c) \Delta n_a^0(\lambda)F_a \quad (5)$$

96 where  $\phi_c$  is the volume fraction of the crystalline phase (degree of crystallinity) and  $c$  and  $a$   
 97 represent crystalline and amorphous regions, respectively.

98 For solution-cast films, the molecular orientation is caused by the stress induced by  
 99 solvent removal. The alignment of polymer molecules during a solution-cast process has been  
 100 investigated by several researchers (Sosnowski and Weber 1972; Croll 1979; Prest and Luca  
 101 1979; Prest and Luca 1980; Cohen and Reich 1981; Machell et al. 1990; Greener and Chen  
 102 2005; Lei et al. 2001). According to these studies, polymer molecules generally tend to align  
 103 in a film plane. Consequently, the in-plane refractive indices ( $n_x$  and  $n_y$ ) are higher than the  
 104 out-of-plane refractive index ( $n_z$ ) when a material shows positive orientation birefringence.  
 105 Furthermore, it is known to be difficult to control the out-of-plane birefringence which can  
 106 affect the performance of the displays.

107 Sosnowski and Weber (1972) reported that the optical anisotropy in a solution-cast  
 108 film of polystyrene is given by the result of the stress developed in a coated film during  
 109 drying process, which makes polymer chains align in the film plane. Prest and Luca (1979)  
 110 also demonstrated similar results using polystyrene, polycarbonate and poly(2,6-  
 111 dimethylphenyleneoxide). They showed that the sign of birefringence depends upon the

112 orientation of the dominating polarizable group relative to the chain backbone. Furthermore,  
113 the out-of-plane birefringence was found to be pronounced for a thin film. Prest and Luca  
114 (1979, 1980), Cohen and Reich (1981), and Machell et al. (1990) studied the effect of  
115 polymer formulations with various casting conditions such as coating thickness, drying  
116 temperature and polymer concentration on birefringence values. They found that the out-of-  
117 plane birefringence is determined by the competition between the normal stress induced by  
118 the drying process and the Brownian motion leading to random conformation by entropic  
119 force. Therefore, it is necessary to predict the stress applied by evaporation accurately to  
120 evaluate the out-of-plane birefringence. The growth of stress in solution-cast films was  
121 studied in detail by several researchers. Croll (1979) developed a simple elastic model to  
122 predict the stress, which was later modified by Lei et al. (2001). Greener and Chen (2005)  
123 calculated the out-of-plane birefringence by using the model. They found that the out-of-  
124 plane birefringence occurs when the solvent concentration is beyond a critical value. At this  
125 stage, the compression stress applied in the normal direction to the film plane starts to build  
126 up and induces molecular orientation in the film by overcoming the entropic force.

127         Since the intrinsic birefringence in eqs. 3 and 4 is a function of wavelength, the  
128 orientation birefringence is dependent upon the wavelength. Therefore, birefringence control  
129 is required in a wide range of visible light. In particular, the extraordinary wavelength  
130 dispersion has been desired recently because of the industrial importance for high  
131 performance retardation films. The property can provide a specific retardation, *e.g.*, quarter or  
132 half of the wavelength, in the whole visible light. However, the wavelength dispersion of  
133 most polymers is represented by the following relation called the Sellmeier equation (Kuhn  
134 and Grün 1942).

$$\Delta n(\lambda) = A' + \frac{B'}{\lambda^2 - \lambda_{ab}^2} \quad (6)$$

136 where  $\lambda_{ab}$  is the wavelength of a vibrational absorption peak in ultraviolet region and  $A'$   
137 and  $B'$  are the Sellmeier coefficients. The equation indicates that the absolute value of  
138 birefringence decreases with increasing the wavelength, *i.e.*, ordinary wavelength dispersion.

139 At present, various techniques are proposed to obtain films showing extraordinary  
140 wavelength dispersion. One of the conventional methods is by piling two or more polymer  
141 films having different wavelength dispersions, in which the fast axis of one film is set to be  
142 parallel to the slow axis of the other films (Yamaguchi et al. 2009a; Mohd Edeerozey et al.  
143 2011a; Yamaguchi et al. 2012). Although this technique is currently employed in industry to  
144 fabricate retardation films, it leads to poor cost-performance due to the complicated  
145 processing operation and results in a thick display. Therefore, it is more favorable to use a  
146 single film with extraordinary wavelength dispersion of birefringence. Blending with another  
147 polymer (Uchiyama and Yatabe 2003a; Uchiyama and Yatabe 2003b; Kuboyama et al. 2007)  
148 or a low-mass compound (Yamaguchi 2009a; Mohd Edeerozey et al. 2011a),  
149 copolymerization with appropriate monomers (Uchiyama and Yatabe 2003c), and addition of  
150 nonspherical materials having polarizability anisotropy (Koike et al. 2006) are promising  
151 techniques to provide the extraordinary dispersion.

152 In our preceding paper (Yamaguchi et al., 2009b), it was demonstrated that cellulose  
153 acetate propionate (CAP) and cellulose acetate butyrate (CAB) having appropriate  
154 substitution of each ester group show extraordinary wavelength dispersion. Moreover, the  
155 sign of orientation birefringence of CTA is negative, whereas that of CAP and CAB is  
156 positive. It was also shown in the paper that the orientation of main chains is not important to  
157 decide the orientation birefringence. Based on these experimental results, it was deduced (but



158 not proved directly) that the contribution of both acetyl and propionyl/butyryl groups plays an  
159 important role in the birefringence, although the contribution of the hydroxyl group was  
160 ignored. Because of this complicated origin of the orientation birefringence of cellulose  
161 esters, the effect of biaxial mode, such as stretching in one direction with a constant width,  
162 has not been clarified yet at the best of our knowledge. Furthermore, the photoelastic  
163 birefringence in the glassy state was also investigated and found to be positive even for CTA.  
164 The opposite sign of the stress-optical coefficient between rubbery and glassy states for CTA  
165 suggests that the origin of the birefringence is completely different between these states, as  
166 the same manner with the stress generation. In the case of the rubbery state, the orientation of  
167 chain segments decides the birefringence, in which Rouse motion is completely allowed, as  
168 assumed in the classical theory of rubber elasticity (Doi and Edwards 1986). On the other  
169 hand, the deviation from the location at the lowest potential energy function for atoms in a  
170 chain, accompanying bond stretching and/or distortion of bond angle, is responsible for the  
171 generation of both stress and birefringence in the glassy state. Therefore, CTA shows positive  
172 photoelastic birefringence even after stretching in the glassy state. Moreover, the effect of  
173 plasticizer addition is mentioned in this study. Although the species of plasticizers are known  
174 to affect the orientation birefringence, the detailed mechanism has not been clarified.

175 In the following paper (Yamaguchi et al. 2009a), the effect of the hydroxyl group on  
176 the orientation birefringence was examined using cellulose diacetate (CDA). It was found  
177 that the hydroxyl group provides positive orientation birefringence to a great extent. The  
178 result indicates that the hydroxyl group in CAP and CAB plays an important role in the  
179 orientation birefringence, although it was not mentioned in the original paper (Yamaguchi et  
180 al. 2009b). Moreover, nematic interaction between CTA chains and plasticizer molecules was

181 indicated during stretching in the rubbery state, which can be applicable to control the  
182 wavelength dispersion.

183 In this study, it is found that the sign of the out-of-plane birefringence in a solution-  
184 cast CTA film is opposite to the in-plane orientation birefringence in a hot-stretched one.  
185 Moreover, the out-of-plane birefringence in a cast film is found to show extraordinary  
186 dispersion. The mechanism of this peculiar phenomenon is discussed in detail. Finally, the  
187 effect of nematic interaction in a solution-cast film is also discussed using CTA films  
188 containing a specific plasticizer with large polarizability anisotropy, which will be an  
189 advanced technique to control the out-of-plane birefringence.

190

## 191 **Experimental**

192 Cellulose triacetate (CTA) was obtained from Acros Organic. The degree of  
193 substitution is 2.96, and the molecular weight  $M_w$  is  $3.50 \times 10^5$  which was evaluated using a  
194 gel permeation chromatograph (Tosoh, HLC-8020) with TSK-GEL<sup>®</sup> GMHXL as polystyrene  
195 standard. The plasticizer used in this study was tricresyl phosphate (TCP) produced by  
196 Daihachi Chemical Industry. The CTA films were prepared using a solution-cast method.  
197 Both CTA and CTA/TCP (95/5 in weight) were dissolved into dichloromethane ( $\text{CH}_2\text{Cl}_2$ )  
198 and methanol ( $\text{CH}_3\text{OH}$ ) in 9 to 1 weight ratio and stirred for 24 hrs at room temperature  
199 before casting. In order to study the effect of solvent, chloroform ( $\text{CHCl}_3$ ) was also employed  
200 instead of dichloromethane in the same ratio. The solution containing 4 wt% of CTA was  
201 poured into a glass petri dish (80 mm dia x 15 mm H) with a flat bottom at room temperature  
202 to allow the solvent to evaporate. The thickness of the films obtained was from 50 to 300  $\mu\text{m}$ ,  
203 which was controlled by varying the amount of the CTA solution.

204 During the drying process, evaporation rate was measured by weight loss using an  
205 electronic balance (Mettler Toledo, AB204-S). Moreover, the effect of the evaporation rate  
206 was investigated by preparing cast films dried with various conditions. A solution dried by  
207 exposing directly to the open atmosphere was used as a standard condition for evaporation  
208 process. To prepare films with (i) slow and (ii) very slow evaporation conditions, petri dishes  
209 containing the solution were covered with an aluminium foil having large and small holes,  
210 respectively. The weight loss by evaporation  $V_e$  was calculated by the following equation.

$$211 \quad V_e (\%) = \frac{G_0 - G(t)}{G_0} \times 100 \quad (7)$$

212 where  $G_0$  is the initial weight of CTA solution;  $G(t)$  is the weight of CTA solution after  $t$   
213 minutes at room temperature.

214 The temperature dependence of oscillatory tensile moduli in the solid state was  
215 measured from 0 to 250 °C by a dynamic mechanical analyzer (UBM, E-4000) using  
216 rectangular specimens with 5 mm in width and 20 mm in length. The frequency and heating  
217 rate used were 10 Hz and 2 °C/min, respectively.

218 Uniaxial oriented films were also prepared by hot-stretching using a tensile machine  
219 with a temperature controller (UBM, DVE-3 S1000) at various draw ratios employing  
220 rectangular specimens with 10 mm in width. The sample was free from the width direction,  
221 *i.e.*, simple extension without width constraint. The initial distance between the clamps was  
222 10 mm, and one of the clamps moved at a stretching rate of 0.5 mm/s. The stretching was  
223 performed at the temperature where the tensile storage modulus is 10 MPa at 10 Hz, *i.e.*,  
224 217 °C. After stretching, the drawn sample was quenched immediately by cold air blowing to  
225 avoid relaxation of the molecular orientation. Then the sample was removed from the  
226 machine to measure the birefringence.

227 The optical properties of CTA films were measured at room temperature by a  
 228 polarized optical microscope (Leica, DMLP) and an optical birefringence analyzer (Oji  
 229 Scientific Instruments, KOBRA-WPR). The retardation in the thickness direction (out-of-  
 230 plane birefringence)  $R_{th}$  was determined by retardation measurements at an oblique incidence  
 231 angle of  $40^\circ$  as a function of wavelength by changing color filters. The corresponding  
 232 birefringence was calculated using the film thickness measured by a digital micrometer. Prior  
 233 to the measurement, the CTA films were placed in a temperature-and-humidity control  
 234 chamber (Yamato, IG420) at  $25^\circ\text{C}$  and 50% RH for one day, because the moisture in the film  
 235 affects the orientation birefringence (Mohd Edeerozey et al. 2011b). Since a small amount of  
 236 the water which has strong interaction with acetyl or hydroxyl group cannot be eliminated  
 237 even under a vacuum condition, this treatment is appropriate to obtain the reproducible data.  
 238 Although all samples should be fully dried up in a hot vacuum oven prior to this treatment,  
 239 we avoided it because the thermal history to remove the moisture and solvent will affect the  
 240 crystalline state of CTA. Furthermore, we confirmed that the exposure to vacuum condition  
 241 at room temperature for one day does not affect any properties such as dynamic mechanical  
 242 properties and birefringence, suggesting that the sample does not contain the solvent.

243 The in-plane retardation ( $R_{in}$ ) and out-of-plane retardation ( $R_{th}$ ) are respectively  
 244 defined as the following relations.

$$245 \quad R_{in} = \Delta n_{in} \times d = (n_x - n_y) \times d \quad (8)$$

$$246 \quad R_{th} = \Delta n_{th} \times d = \left( \frac{n_x + n_y}{2} - n_z \right) \times d \quad (9)$$

247 where  $d$  is the film thickness.

248 The refractive indices in three principal axis, such as  $n_x$ ,  $n_y$  and  $n_z$ , are determined by  
249  $\Delta n_{in}$  and  $\Delta n_{th}$ , assuming the average refractive index  $\bar{n}$  is a constant irrespective of  
250 stretching. The average refractive index  $\bar{n}$  was measured by an Abbe refractometer.

251 Attenuated total reflection (ATR) measurements using an infrared absorption  
252 spectrometer (Perkin Elmer, Spectrum 100) were performed to study the molecular  
253 orientation in CTA films. The KRS-5 was employed as an ATR crystal.

254 Thermal analysis was conducted by a differential scanning calorimeter (DSC)  
255 (Mettler, DSC820) under a nitrogen atmosphere. The samples were heated from room  
256 temperature to 320 °C at a heating rate of 20 °C/min. The amount of samples in an aluminum  
257 pan was about 10 mg in weight.

258 Wide-angle X-ray diffraction (WAXD) measurements were performed at room  
259 temperature using a powder X-ray diffractometer (Rigaku, RINT2500) by reflective mode.  
260 Samples were mounted directly into the diffractometer. The experiments were carried out  
261 using CuK $\alpha$  radiation operating at 40 kV and 30 mA at a scanning rate of 1°/min over  $2\theta$   
262 (Bragg angle) range from 5° to 55°.

263

## 264 **Results and Discussion**

### 265 **Effect of film thickness**

266 The molecular orientation in the film occurs when the relaxation time of the solution  
267 becomes longer than the characteristic time for the biaxial deformation applied by the  
268 compressional stress due to the solvent evaporation, which was quantitatively calculated by

269 Croll (1979). Therefore, the evaporation rate has to be considered to discuss the birefringence  
270 in a solution-cast film.

271 Figure 1 (a) shows the growth curves of the weight loss (in percent) for the CTA  
272 solutions to obtain films with various thicknesses. Since all films are prepared using the same  
273 petri dish, the thickness is adjusted by the initial volume of the solution. As seen in the figure,  
274 the values reach to 96% eventually, suggesting that the solvent is almost fully evaporated at  
275 this process. Expectedly, it takes a longer time to prepare a thicker film. This is reasonable  
276 because the surface area of the solution is the same irrespective of the film thickness.

277 In Figure 1 (b), the weight loss (in gram) is plotted against the exposure time. The  
278 weight loss is proportional to the exposure time at first, and the slope is constant for all  
279 samples. Then, the slope becomes low in the final stage, as CTA retards the solvent  
280 evaporation. Considering that the initial slope is the same for all samples, the exposed area of  
281 the solution determines the evaporation rate. The result suggests that evaporation occurs  
282 homogeneously without creating a solid film on the top of the solution. Moreover, the figures  
283 indicate that the stress applied by the reduction of the solution increases with decreasing  
284 thickness of the final film because of the rapid drying process. The distribution of molecular  
285 orientation, *i.e.*, birefringence, in the thickness direction in the film is confirmed by the  
286 polarized optical microscope. Thin films of  $x$ - $z$  plane cut out from the cast films by an  
287 ultramicrotome are observed under crossed polars by inserting a full wave plate. It is found  
288 that a homogeneous birefringence color is detected in the whole area of the specimen,  
289 demonstrating that molecular orientation is uniform in the thickness direction. This result  
290 indicates that compression deformation takes place uniformly by the solvent evaporation.

291 [Figure 1]

292 The wavelength dispersion of the out-of-plane birefringence in cast films is shown in  
293 Figure 2. It is found that the solution-cast films of CTA show positive birefringence ( $n_z < n_x,$   
294  $n_y$ ) that increases with increasing wavelength, *i.e.*, extraordinary wavelength dispersion. This  
295 is an anomalous phenomenon for a conventional polymer film. The in-plane birefringence is,  
296 on the other hand, negligible for all films. Generally, the orientation birefringence of CTA is  
297 determined by the contribution of acetyl and hydroxyl groups considering the previous  
298 researches at the best of our knowledge (El-Diasty et al. 2007; Yamaguchi et al. 2009a;  
299 Yamaguchi et al. 2009b). Since the direction of polarizability anisotropy associated with the  
300 acetyl group is perpendicular to the main chain, the refractive index in the oriented direction  
301 is the lowest, *i.e.*, negative orientation birefringence. Moreover, it is known that the absolute  
302 value of birefringence decreases with increasing the wavelength, *i.e.*, ordinary wavelength  
303 dispersion, for CTA, as similar to most conventional polymers (Uchiyama and Yatabe 2003c;  
304 Yamaguchi et al. 2009b; Yamaguchi et al. 2010; Yamaguchi et al. 2012). However, the  
305 contribution of the hydroxyl group cannot be ignored, which provides positive and ordinary  
306 wavelength dispersion (Yamaguchi et al. 2009a).

307 [Figure 2]

308 Figure 2 also demonstrates that the birefringence decreases with increasing film  
309 thickness, indicating that the refractive index in the in-plane direction decreases with  
310 increasing the film thickness. The decrease in the molecular orientation for a thick film is  
311 reasonable, because of the slow rate of solvent removal. Since the solvent can be entrapped in  
312 a thick film for a long time as shown in Figure 1, the molecules are less oriented in the film  
313 plane. Similar results have been reported by another research group, Greener et al. (2005).  
314 According to them, a thin film shows a high value of birefringence because the stress builds  
315 up faster in the drying process than the stress relaxation.

316 In order to clarify the effect of film thickness on the birefringence, ATR  
317 measurements are performed focusing on the C-O-C stretching vibration in the pyranose ring  
318 ( $1029\text{ cm}^{-1}$ ) and C=O stretching vibration in the carbonyl group ( $1735\text{ cm}^{-1}$ ). It should be  
319 noted that the same spectra were obtained for both surfaces (air and glass sides), indicating  
320 that the skin layer is not well-developed on the free surface (or the contribution of the skin  
321 layer on the birefringence can be ignored). As seen in Figure 3, the absorbances of the  
322 pyranose ring and the carbonyl group decrease with increasing the film thickness.  
323 Considering that the penetration depth of IR beam into the sample is approximately  $2.2\text{ }\mu\text{m}$  at  
324  $1029\text{ cm}^{-1}$  and  $1.2\text{ }\mu\text{m}$  at  $1735\text{ cm}^{-1}$ , the film thickness itself does not affect the absorbance.  
325 The results indicate that the pyranose ring and the carbonyl group are aligned in the film  
326 plane, which is pronounced in a thin, *i.e.*, rapid evaporation film. The in-plane orientation of  
327 the carbonyl group will be responsible for the positive out-of-plane birefringence. In the case  
328 of a hot-stretched film of CTA, the carbonyl group orients perpendicular to the stretching  
329 direction. Consequently, the refractive index in the perpendicular direction is always higher  
330 than that in the stretching direction, leading to negative orientation birefringence. On the  
331 contrary, the carbonyl group preferably exists in a film plane for a solution-cast film, which is  
332 attributed to the in-plane orientation of the pyranose ring. As a result, the refractive index in  
333 the film plane is larger than that in the thickness direction, although the backbone chains of  
334 CTA are also in the film plane.

335 [Figure 3]

336 According to our previous paper (Yamaguchi et al. 2009a), the extraordinary  
337 wavelength dispersion for CDA was considered to be attributed to the contributions of the  
338 polarizability anisotropy of both hydroxyl and acetyl groups, in which the hydroxyl group in  
339 CDA provides positive birefringence with weak wavelength dispersion and the acetyl group



340 gives negative one with strong wavelength dispersion. Moreover, the magnitude of the  
341 birefringence from the hydroxyl group was estimated to be three times as large as that from  
342 the acetyl one (Yamaguchi et al. 2009a). In this study, CTA cast films also show  
343 extraordinary wavelength dispersion. However, this cannot be explained by the simple  
344 summation of both acetyl and hydroxyl groups because of the large amount of the acetyl  
345 group. The difference in the wavelength dispersion of refractive indices among three  
346 principal directions should be considered to explain the extraordinary dispersion. When  $n_z$   
347 shows marked decrease with the wavelength as compared with  $n_x$  and  $n_y$ , extraordinary  
348 wavelength dispersion is expected.

349 It is also interesting to note that water molecules absorbed in CTA contribute to  
350 negative orientation birefringence slightly, at which the magnitude of the birefringence  
351 change is almost independent of the wavelength (Mohd Edeerozey et al. 2011b).

352 In the case of CTA, the crystallization state has to be considered, because it is well  
353 known that CTA is a crystalline polymer (Watanabe et al. 1968; Takahashi et al. 1979; Cao et  
354 al. 2000; Sata 2004; Cerqueira et al. 2006). Irrespective of the crystallinity, CTA films always  
355 exhibit high level of transparency. This is attributed to the reduced light scattering originated  
356 from the polarizability difference of crystalline aggregates, because the correlation distance is  
357 shorter than the wavelength of visible light as discussed previously (Norris and Stein 1958;  
358 Tenma and Yamaguchi 2004). The heat of fusion of the perfect CTA crystal has been  
359 discussed for a long time after the pioneering work by Takahashi et al. (1979). The value was  
360 recently reported to be 58.8 J/g by Cerqueira et al. (2006).

361 As shown in Table 1, it is found that the degree of crystallization is almost constant  
362 irrespective of the film thickness. The degree of the crystallization is calculated to be 17 – 23  
363 wt% based on the literature data (Cerqueira et al. 2006). Furthermore, WAXD measurements

364 are also carried out and shown in Figure 4. The top pattern in the figure will be discussed  
365 later. It is found from the bottom pattern in Figure 4 that a broad peak is detected around 7-8  
366 degree with amorphous background, which is a similar diffraction pattern to that reported by  
367 Cao et al. (2000). The result indicates that the orientation birefringence has to be discussed  
368 using eq. 5. However, we avoid the discussion on the contribution of crystalline phase, at  
369 least for cast films, because it is difficult to obtain the information on the intrinsic  
370 birefringence as well as the orientation function of both amorphous and crystalline phases  
371 separately.

372 [Table 1][Figure 4]

373 It can be concluded from Figures 1-3, the achievable anisotropy is found to be a  
374 function of the evaporation rate. Therefore, further study is performed focusing the effect of  
375 evaporation rate.

376

### 377 **Effect of evaporation rate**

378 The evaporation rate is controlled by covering the petri dishes with an aluminium foil.  
379 The growth curves of the weight loss are shown in Figure 5. In the figure, the “standard”  
380 represents the cast film obtained by drying uncovered petri dishes, the same drying method to  
381 the samples in Figure 1. The “slow” and “very slow” denote the cast films obtained with an  
382 aluminium foil having large and small holes, respectively. The thickness of all films is  
383 approximately 100  $\mu\text{m}$ . As seen in the figure, the evaporation rate can be controlled by this  
384 technique. The initial slope of the standard is three times larger than that of the very slow.

385 [Figure 5]

386 The wavelength dispersion of the out-of-plane birefringence of the samples is shown  
387 in Figure 6. All films show positive birefringence with extraordinary wavelength dispersion  
388 irrespective of the evaporation rate. However, the magnitude of the birefringence increases  
389 with increasing the evaporation rate. Therefore, a similar situation with a thick film occurs for  
390 the film evaporated slowly. The decrease in the birefringence for a film obtained by the  
391 prolonged evaporation process suggests that stress, *i.e.*, molecular orientation, is relaxed. It is  
392 reasonable because the polymer chains are able to move randomly during the cast process.

393 [Figure 6]

394 The effect of the evaporation rate on the crystallization of CTA is also studied by  
395 DSC. As shown in Table 1, however, the heat of fusion, and thus, the degree of  
396 crystallization is not changed at this experimental condition.

397

### 398 **Effect of solvent type**

399 The species of solvents affects the evaporation rate and thus the out-of-plane  
400 birefringence, as shown in Figures 7 and 8, respectively. As seen in Figure 7, the evaporation  
401 rate of the mixed solvent of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$  is faster than that of  $\text{CHCl}_3$  and  $\text{CH}_3\text{OH}$ ,  
402 because the vapor pressure of  $\text{CH}_2\text{Cl}_2$  is higher than that of  $\text{CHCl}_3$  at room temperature.  
403 Moreover, it is identified that the whole curve of the  $\text{CHCl}_3/\text{CH}_3\text{OH}$  solution is almost the  
404 same as that of the  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  solution with an aluminium foil having small holes  
405 (“slow” in Figure 5). The result demonstrates that the retardant effect of the evaporation by  
406 CTA is almost the same for both solvents. This would be attributed to similar molecular  
407 interaction with CTA for both solvents.

408 [Figure 7] [Figure 8]



431 best of our knowledge, however, the nematic interaction in solution-cast films has not been  
432 studied yet.

433 Figure 10 shows the out-of-plane birefringence of a CTA film containing 5 wt% of  
434 TCP with the data of pure CTA. As seen in the figure, addition of TCP greatly enhances the  
435 out-of-plane birefringence of CTA. Since the evaporation rate is not affected by the addition  
436 of TCP (but not presented here), the enhancement is attained by the orientation of TCP  
437 molecules in the film plane accompanied with CTA chains. Also in this experiment, the  
438 degree of crystallization remains unchanged as shown in Table 1.

439 [Figure 10]

440 In order to confirm the contribution of TCP to the birefringence, the CTA/TCP film is  
441 immersed in methanol for 24 hrs to remove TCP. Then, the out-of-plane birefringence is  
442 measured again after drying at room temperature under a vacuum condition. Prior to the  
443 measurement, it is ensured that the methanol immersion does not affect the birefringence of  
444 pure CTA. The removal of TCP is confirmed by FT-IR spectra, and the sample is kept in the  
445 temperature-and-humidity controller for 24 hrs before being measured for birefringence. The  
446 FT-IR spectrum for CTA/TCP shows a strong absorption peak around  $780\text{ cm}^{-1}$ , which is not  
447 detected in CTA but appears in TCP spectrum. This peak is attributed to the vibration of C-H  
448 bond in meta-disubstituted benzene of TCP (Mohd Edeerozey et al. 2011a). Therefore, the  
449 lack of this peak suggests that TCP has been completely removed out. After methanol  
450 immersion, the birefringence of CTA/TCP decreases approaching to that of pure CTA, as  
451 illustrated in Figure 11. The result demonstrates that TCP molecules oriented by nematic  
452 interaction enhance the out-of-plane birefringence. In other words, the out-of-plane  
453 birefringence can be controlled by not only evaporation rate but also additives.

454 As mentioned in the introduction, the competition of molecular motion and  
455 deformation applied by the solvent evaporation determines the molecular orientation in a  
456 solution-cast film. In other words, CTA chains orient in the film plane by applied uniaxial  
457 compression deformation due to the solvent evaporation. At the same time, TCP molecules  
458 orient cooperatively with the CTA chains. Therefore, the orientation relaxation of TCP  
459 molecules will be affected strongly by the existence of a solvent, although the relaxation time  
460 is reduced for both CTA and TCP. The experimental results indicate that the nematic  
461 interaction, *i.e.*, orientation of TCP molecules, occurs only at the final stage of evaporation.  
462 Therefore, a solvent that retards the evaporation rate at the final stage to obtain smooth  
463 surface will have a strong influence on the orientation of additives.

464 [Figure 11]

465

### 466 **Effect of hot-stretching**

467 The hot-stretching is performed at 217 °C, at which the tensile storage modulus at 10  
468 Hz was 10 MPa, *i.e.*, rubbery state. The stress-strain curve is shown in Figure 12, which is a  
469 typical one for a viscoelastic body in the rubbery region.

470 [Figure 12]

471 The refractive indices at 588 nm along three principle axes for films with various  
472 draw ratios are illustrated in Figure 13. In this experiment, the hot-stretching was performed  
473 in the  $x$  direction.

474 As mentioned, the unstretched film is randomly oriented in the film plane, *i.e.*,  $n_x =$   
475  $n_y$ , but the principle refractive index in the thickness direction  $n_z$  is lower than  $n_x$  and  $n_y$ ,

476 which results in the positive out-of-plane birefringence. On the contrary, a hot-drawn film  
477 shows negative in-plane birefringence.

478 [Figure 13]

479 The wavelength dispersion of in-plane and out-of-plane birefringences for the  
480 stretched films is shown in Figure 14. As seen in the figure, the order in the refractive indices  
481 changes with the draw ratio. When the draw ratio is around 1.035,  $n_z$  is almost the same as  
482  $(n_x+n_y)/2$  at 588 nm. Beyond this draw ratio, the out-of-birefringence of the unstretched  
483 sample shows extraordinary wavelength dispersion, whereas in-plane and out-of-plane  
484 birefringences for the stretched films exhibit ordinary wavelength dispersion. Moreover, the  
485 out-of-birefringence of the stretched films is almost independent of the applied strain level,  
486 when the draw ratio is larger than 1.1.

487 The negative in-plane birefringence in CTA suggests that the direction of the  
488 polarizability anisotropy associated with the acetyl group is perpendicular to the main chain.  
489 This result corresponds with the previous reports (El-Diasty et al. 2007; Yamaguchi et al.  
490 2009a; Mohd Edeerozey et al. 2011ab).

491 Because the hot-stretching is carried out beyond the glass transition temperature, the  
492 degree of crystallinity has to be considered more seriously. The top pattern in Figure 4 shows  
493 the WAXD profile of a stretched film at a draw ratio of 1.5. As seen in the figure, several  
494 distinct peaks are clearly detected, which are attributed to the thermal history beyond the  
495 glass transition temperature with the flow induced crystallization during stretching.  
496 Therefore, the contribution of crystalline phase cannot be ignored especially after hot-  
497 stretching. It was found that the extraordinary wavelength dispersion of CAP becomes  
498 pronounced with increasing the draw ratio (Yamaguchi et al. 2009a). The result indicates that

499 the acetyl group plays a more important role in the total birefringence with increasing the  
500 draw ratio. A similar situation is expected also for CTA, because the acetyl group is in the  
501 crystalline structure with the strong polarizability anisotropy in the direction perpendicular to  
502 the chain axis (Sikorski et al. 2004). In other words, the wavelength dispersion and the  
503 magnitude of birefringence for CTA, including solution-cast films, can be modified by  
504 controlling the crystalline state.

505 [Figure 14]

506

## 507 **Conclusion**

508 The orientation birefringence of CTA films produced by a solution-cast method is  
509 studied. Prior to stretching, the CTA film shows positive out-of-plane birefringence with  
510 extraordinary wavelength dispersion, whereas the stretched film shows negative in-plane  
511 birefringence. The positive birefringence is attributed to the in-plane orientation of the acetyl  
512 group in CTA, which is confirmed by ATR. Furthermore, it is found that a thin film shows  
513 marked birefringence, which is originated from the molecular orientation in the film plane  
514 due to the stress applied by the solvent evaporation. Similarly, prompt evaporation enhances  
515 the birefringence irrespective of the species of solvents. Moreover, the out-of-plane  
516 birefringence of CTA is found to increase with the addition of TCP. This is attributed to the  
517 molecular orientation of TCP by the nematic interaction, *i.e.*, intermolecular orientation  
518 correlation, between CTA and TCP.

519



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- 629

630 **Table Caption**

631 Table 1 Thermal Properties of Solution-Cast Films Obtained by Various Conditions

632

633 **Figure Captions**

634 Figure 1 (a) Growth curves of the weight loss (%) for CTA solutions to obtain films with  
635 various thicknesses; 50  $\mu\text{m}$  (circles), 100  $\mu\text{m}$  (diamonds), 200  $\mu\text{m}$  (triangles)  
636 and 300  $\mu\text{m}$  (squares).

637 Figure 1 (b) Growth curves of the weight loss (g) for CTA solutions to obtain films with  
638 various thicknesses; 50  $\mu\text{m}$  (circles), 100  $\mu\text{m}$  (diamonds), 200  $\mu\text{m}$  (triangles)  
639 and 300  $\mu\text{m}$  (squares).

640 Figure 2 Wavelength dispersion of out-of-plane birefringence for cast films with various  
641 thicknesses; 50  $\mu\text{m}$  (circles), 100  $\mu\text{m}$  (diamonds), 200  $\mu\text{m}$  (triangles) and 300  
642  $\mu\text{m}$  (squares).

643 Figure 3 Relation between film thickness and absorbances of pyranose ring ( $A_{1029}$ )  
644 (circles) and carbonyl group ( $A_{1735}$ ) (diamonds) for cast films obtained from  
645  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  at the standard condition.

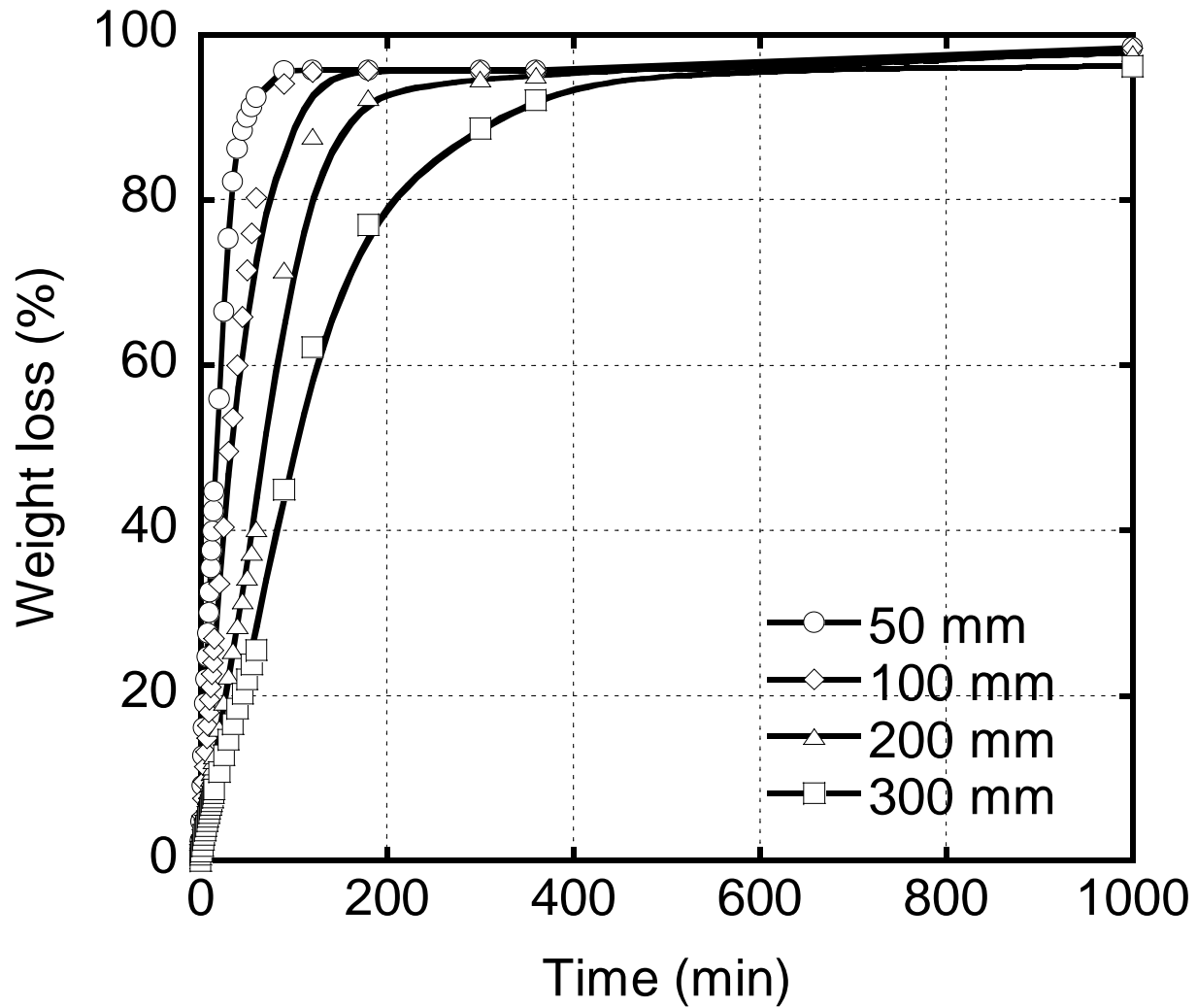
646 Figure 4 Wide-angle X-ray diffraction patterns for (bottom) a cast film with a thickness  
647 of 100  $\mu\text{m}$  obtained from  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  at a standard condition, and (top) a  
648 film stretched at a draw ratio of 1.5.

649 Figure 5 Growth curves of the weight loss (%) for CTA solutions at various evaporation  
650 rates; standard (circles), slow (diamonds) and very slow (triangles).

- 651 Figure 6 Wavelength dispersion of out-of-plane birefringence for films obtained at  
652 various evaporation rates; standard (circles), slow (diamonds) and very slow  
653 (triangles).
- 654 Figure 7 Growth curves of the weight loss (%) for CTA solutions using  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$   
655 (circles) and  $\text{CHCl}_3/\text{CH}_3\text{OH}$  (diamonds) as solvents.
- 656 Figure 8 Wavelength dispersion of out-of-plane birefringence for the cast films obtained  
657 from  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (circles) and  $\text{CHCl}_3/\text{CH}_3\text{OH}$  (diamonds) at the standard  
658 condition. The thickness of the films was 100  $\mu\text{m}$ .
- 659 Figure 9 Out-of-plane birefringence at 588 nm for the cast films plotted against the initial  
660 slope of the weight loss (g);  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (standard) (circle),  
661  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (slow) (diamond),  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (very slow) (triangle) and  
662  $\text{CHCl}_3/\text{CH}_3\text{OH}$  (standard) (square).
- 663 Figure 10 Wavelength dispersion of out-of-plane birefringence for CTA (circles) and  
664 CTA/TCP (diamonds). The cast films with a thickness of 100  $\mu\text{m}$  were  
665 prepared by  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  at the standard condition.
- 666 Figure 11 Wavelength dispersion of out-of-plane birefringence for CTA/TCP before  
667 (closed diamonds) and after immersion in methanol (open diamonds). The  
668 original cast film with a thickness of 100  $\mu\text{m}$  was prepared by  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$   
669 at the standard condition.
- 670 Figure 12 Stress ( $\sigma$ ) – strain ( $\varepsilon$ ) curve at 217 °C for CTA. The cast film with a thickness of  
671 100  $\mu\text{m}$  was prepared by  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  at the standard condition.

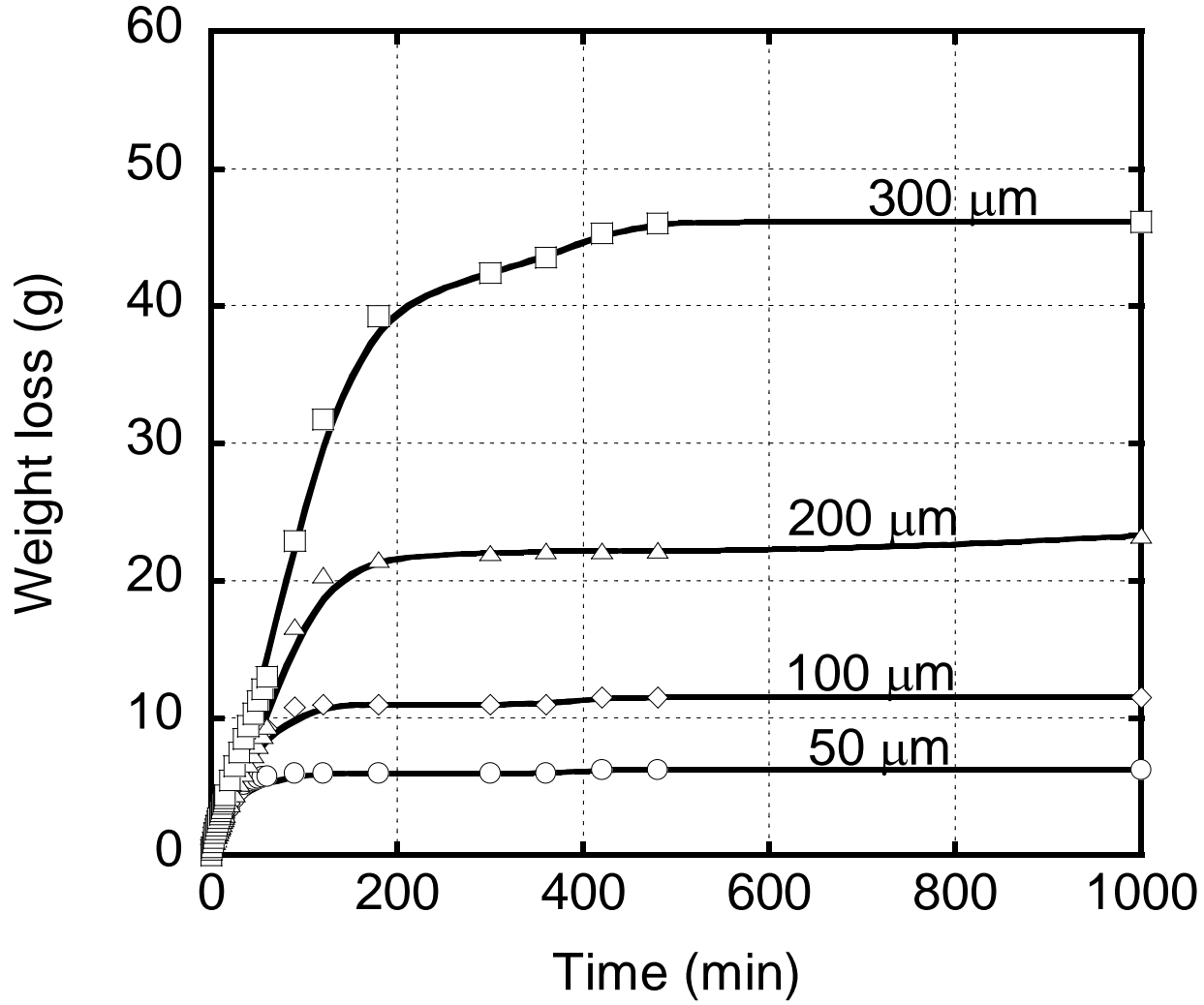
672 Figure 13 Refractive indices along three principle axes;  $n_x$  (circles),  $n_y$  (triangles) and  $n_z$   
673 (diamonds) for CTA films stretched at various draw ratios. The original cast  
674 films with a thickness of 100  $\mu\text{m}$  were prepared by  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  at the  
675 standard condition.

676 Figure 14 Wavelength dispersion of (a) in-plane birefringence and (b) out-of-plane  
677 birefringence for a cast film (circles) and stretched films with draw ratios of 1.1  
678 (diamonds), 1.3 (triangles), and 1.5 (squares). The cast films with a thickness of  
679 100  $\mu\text{m}$  were prepared by  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  at the standard condition.

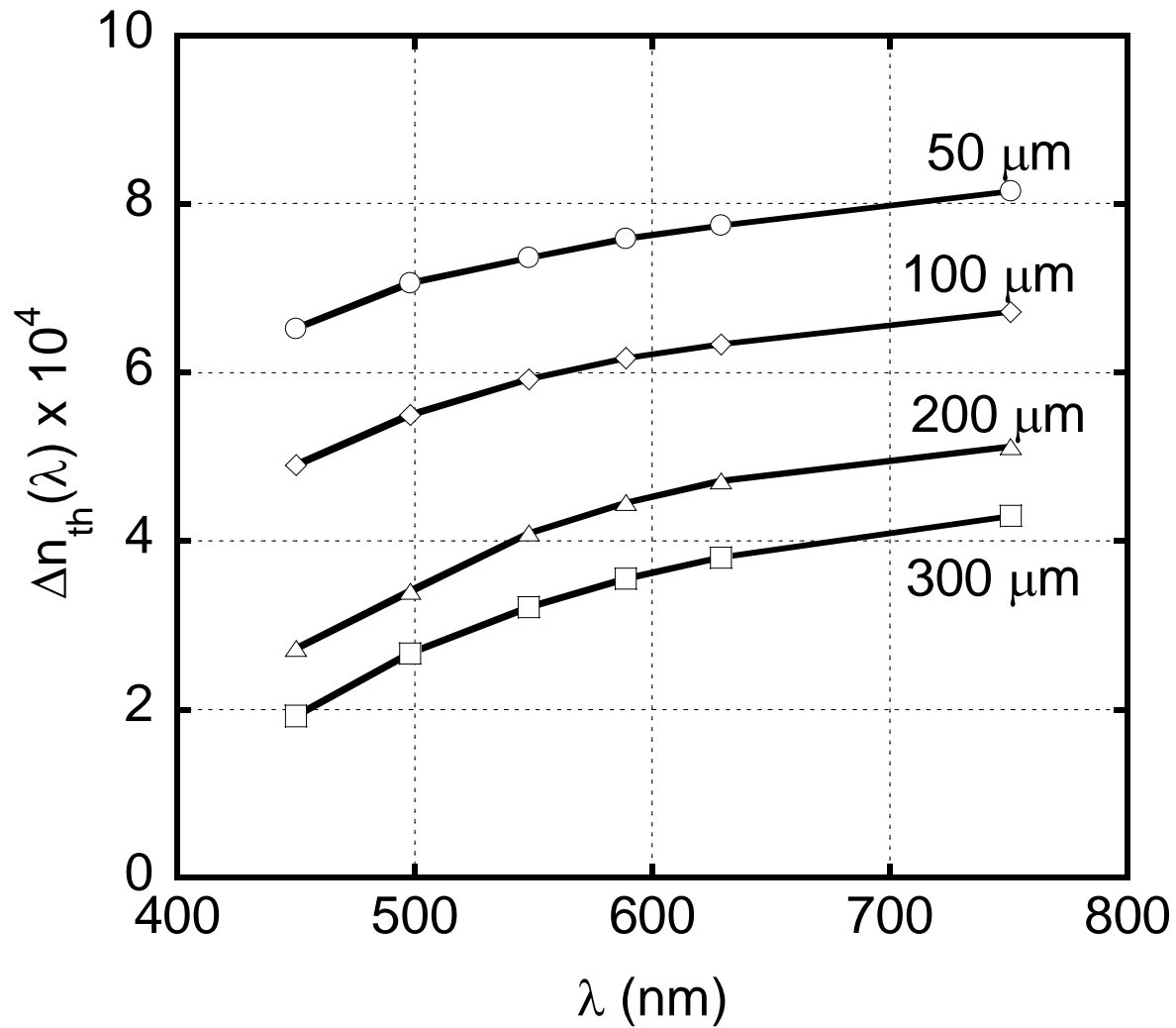


Songsurang et al., Figure 1 (a)

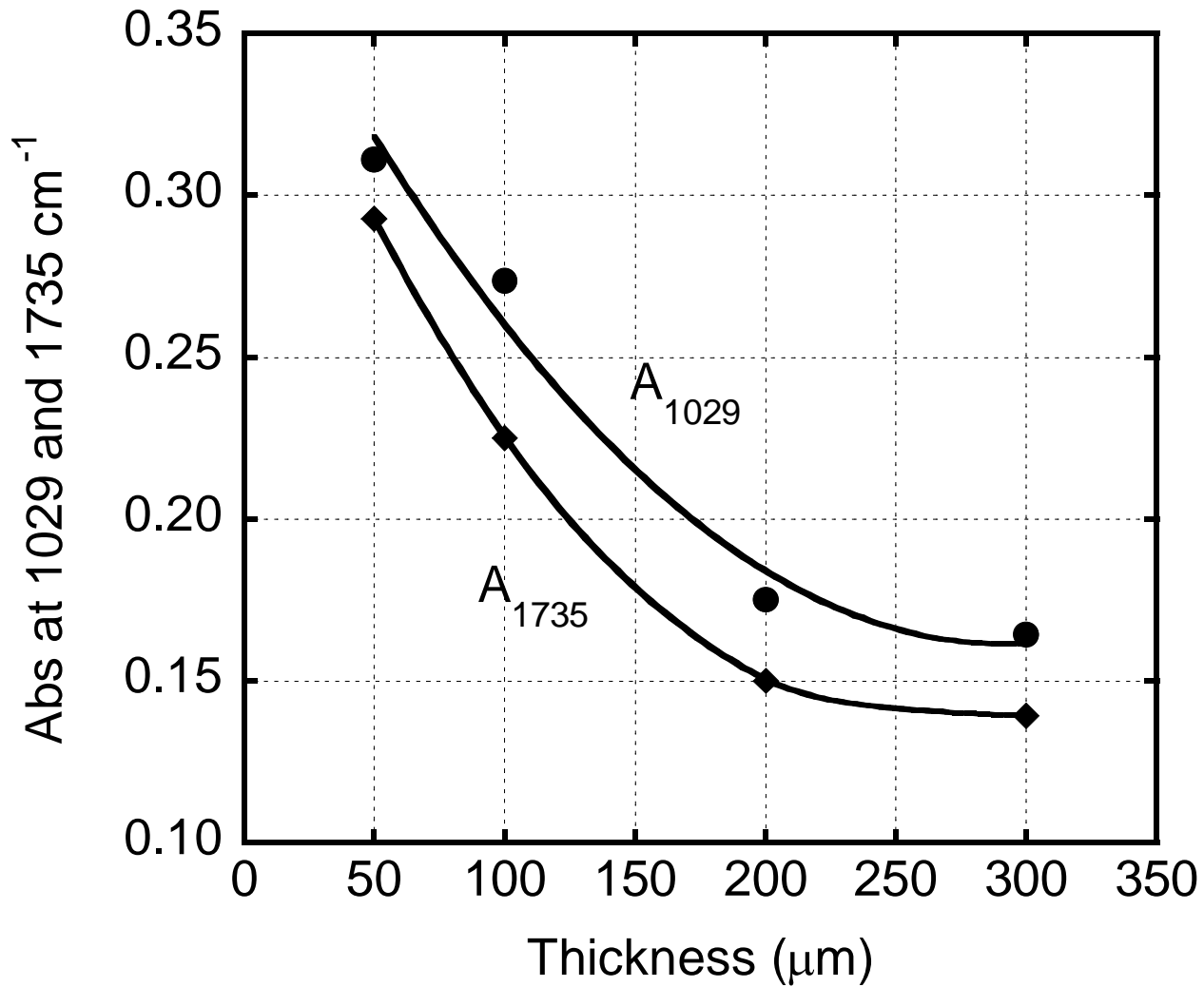




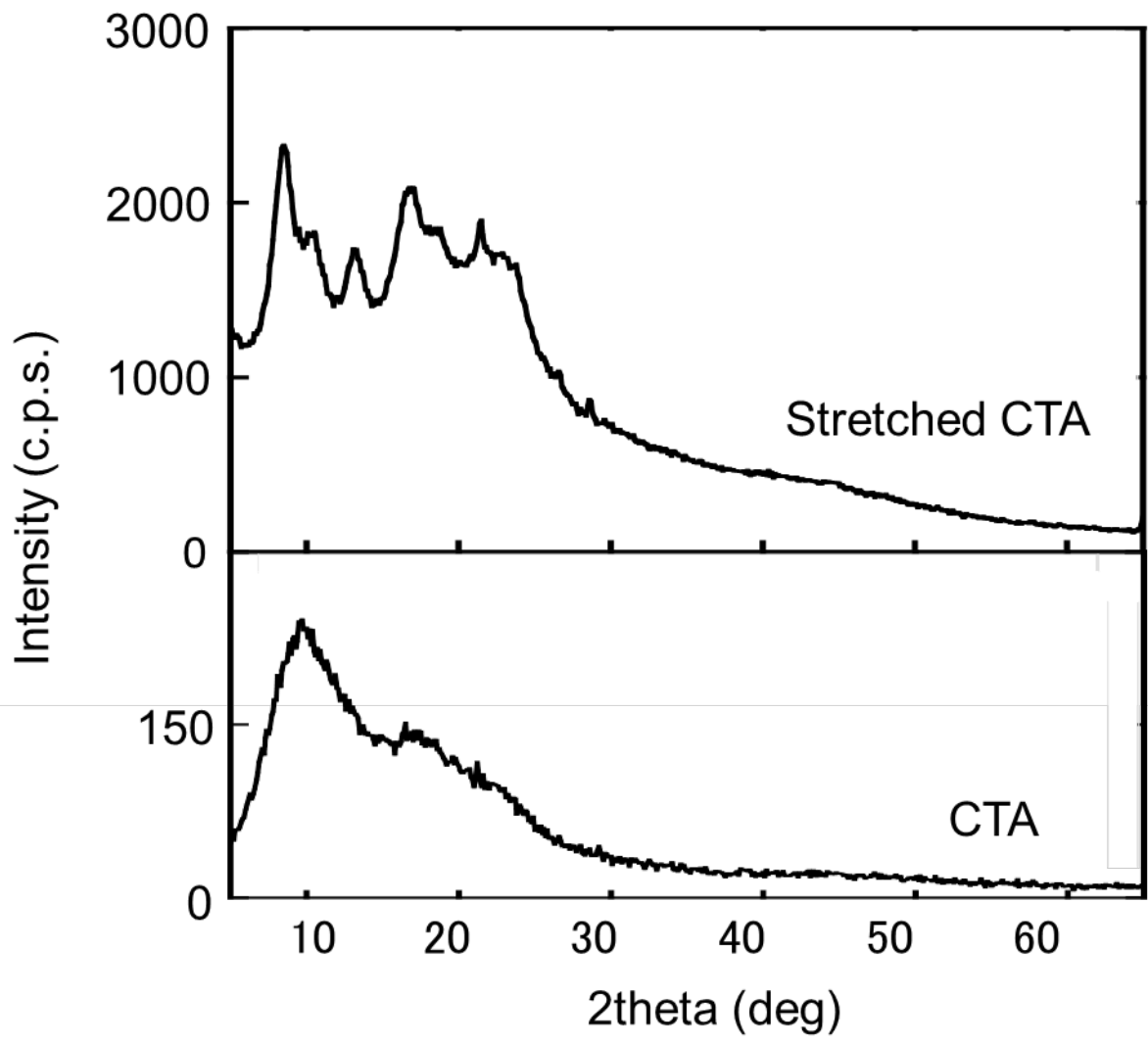
Songsurang et al., Figure 1 (b)



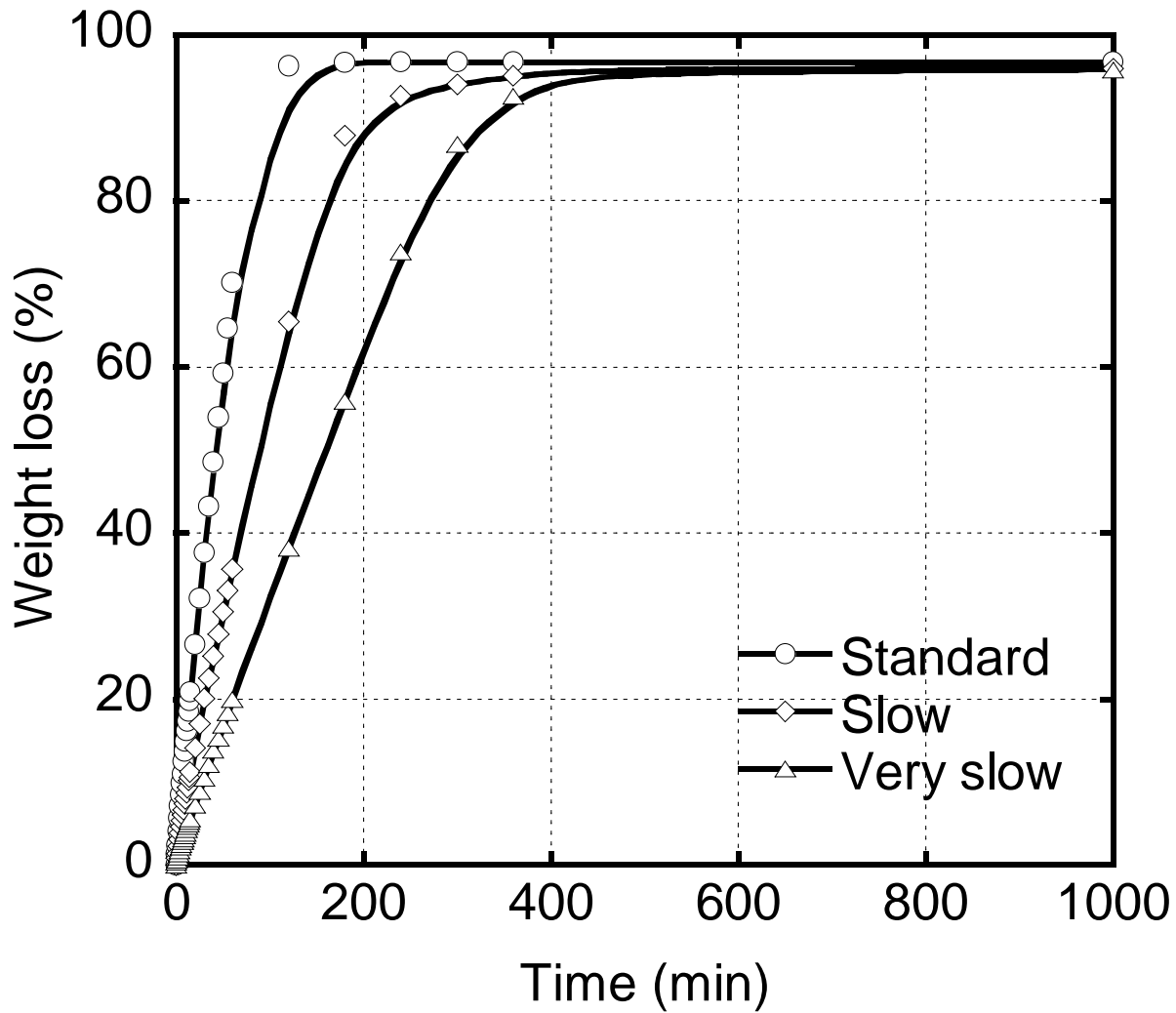
Songsurang et al., Figure 2



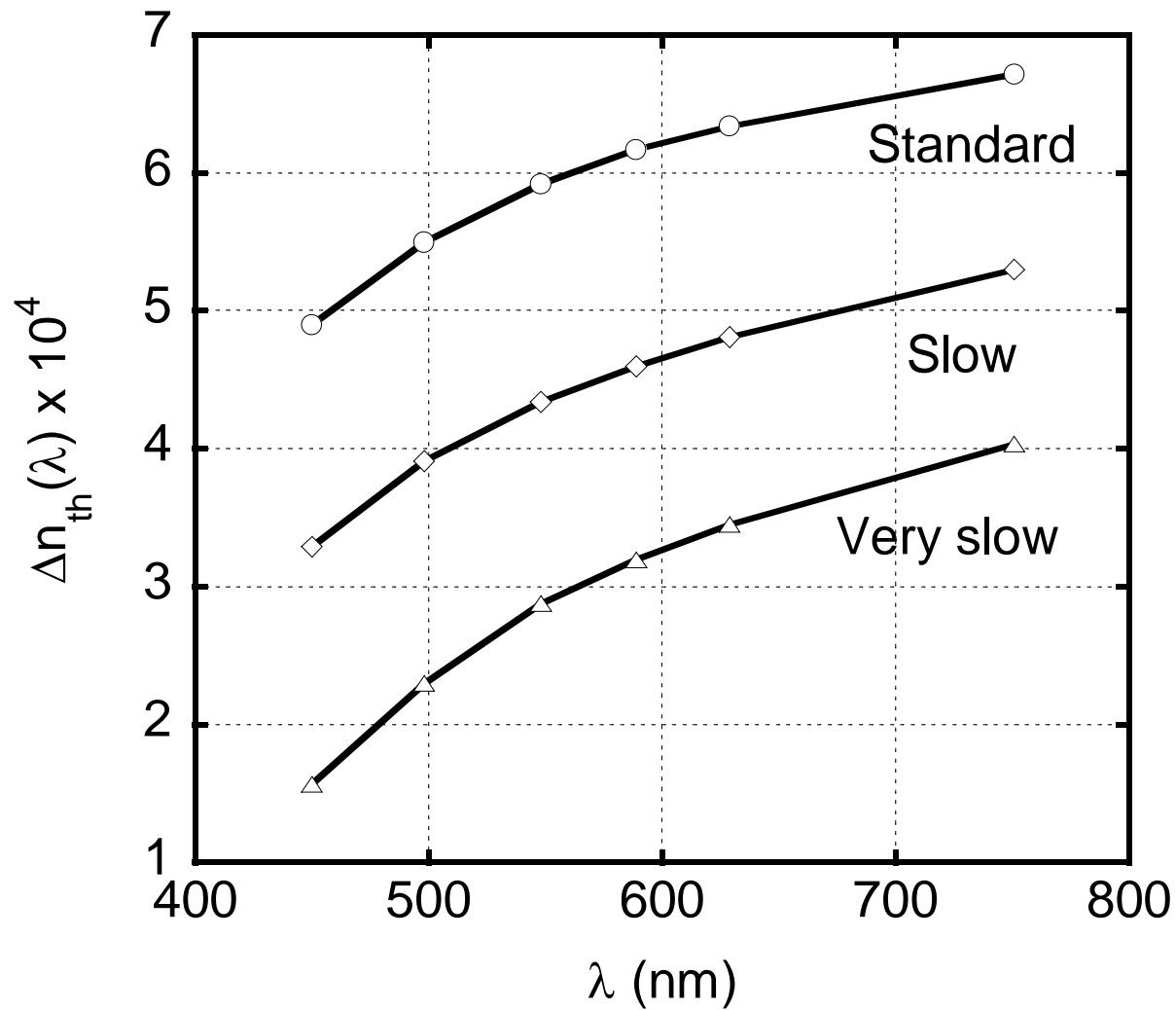
Songsurang et al., Figure 3



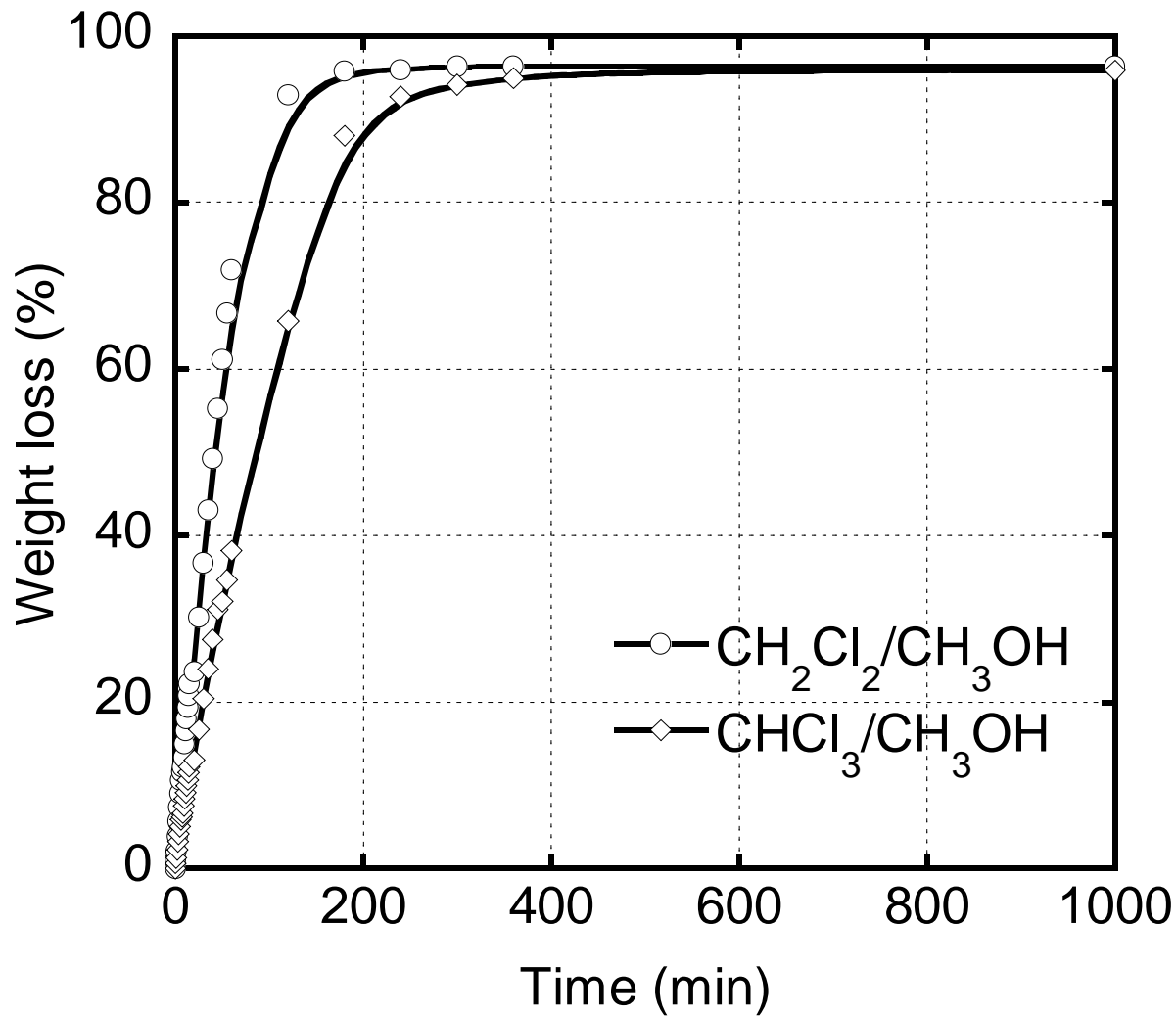
Songsurang et al., Figure 4



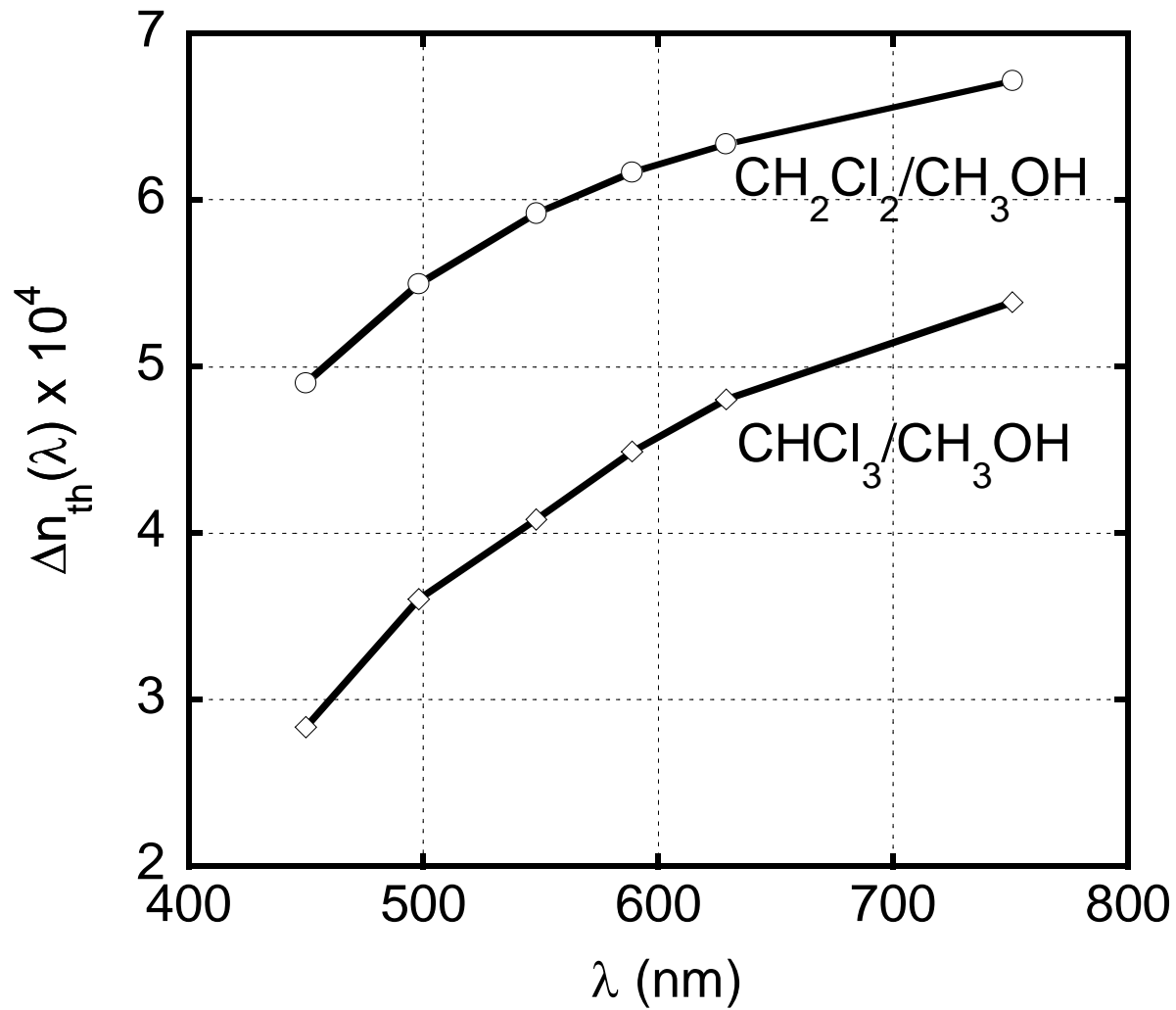
Songsurang et al., Figure 5



Songsurang et al., Figure 6

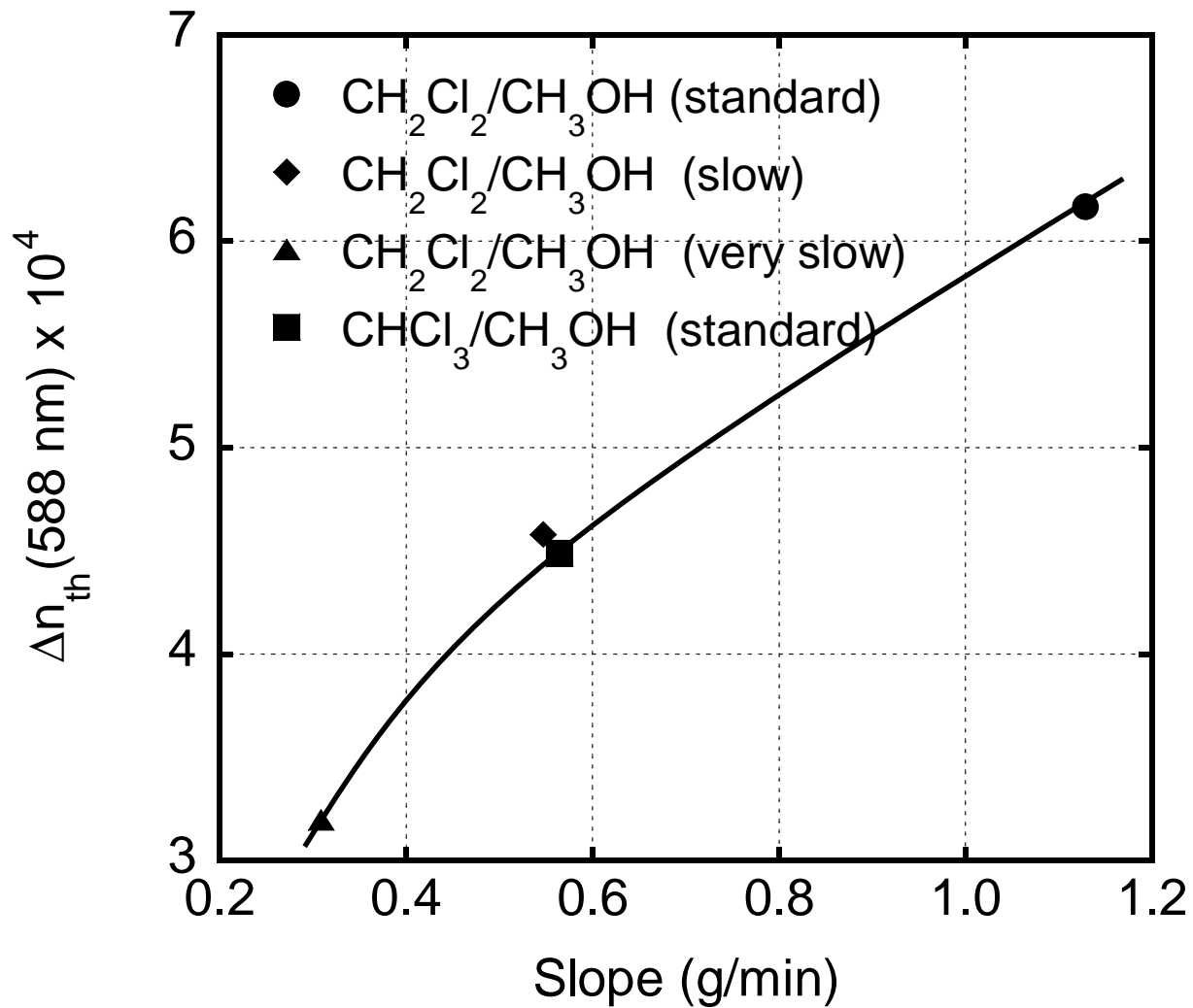


Songsurang et al., Figure 7

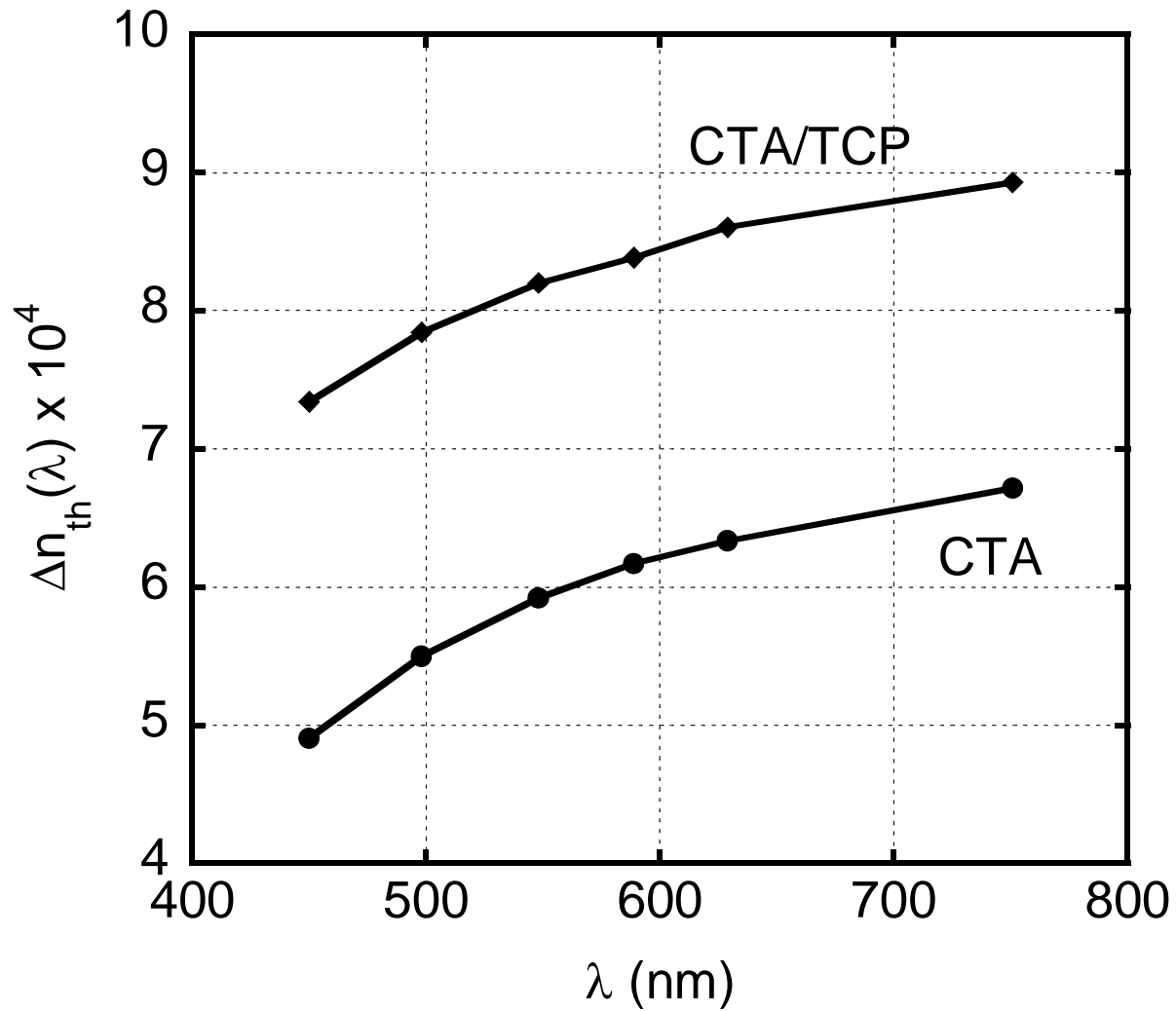


Songsurang et al., Figure 8

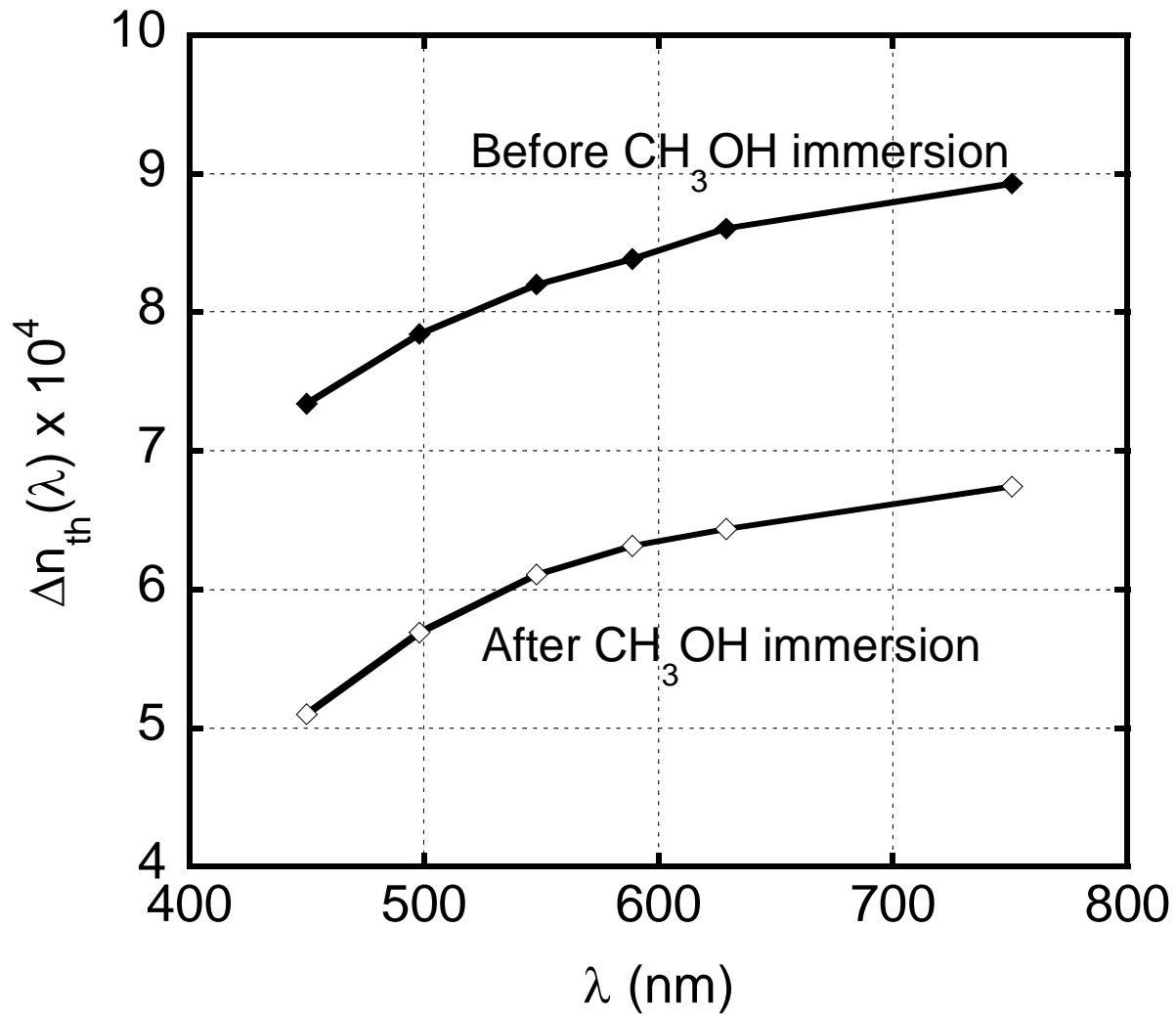




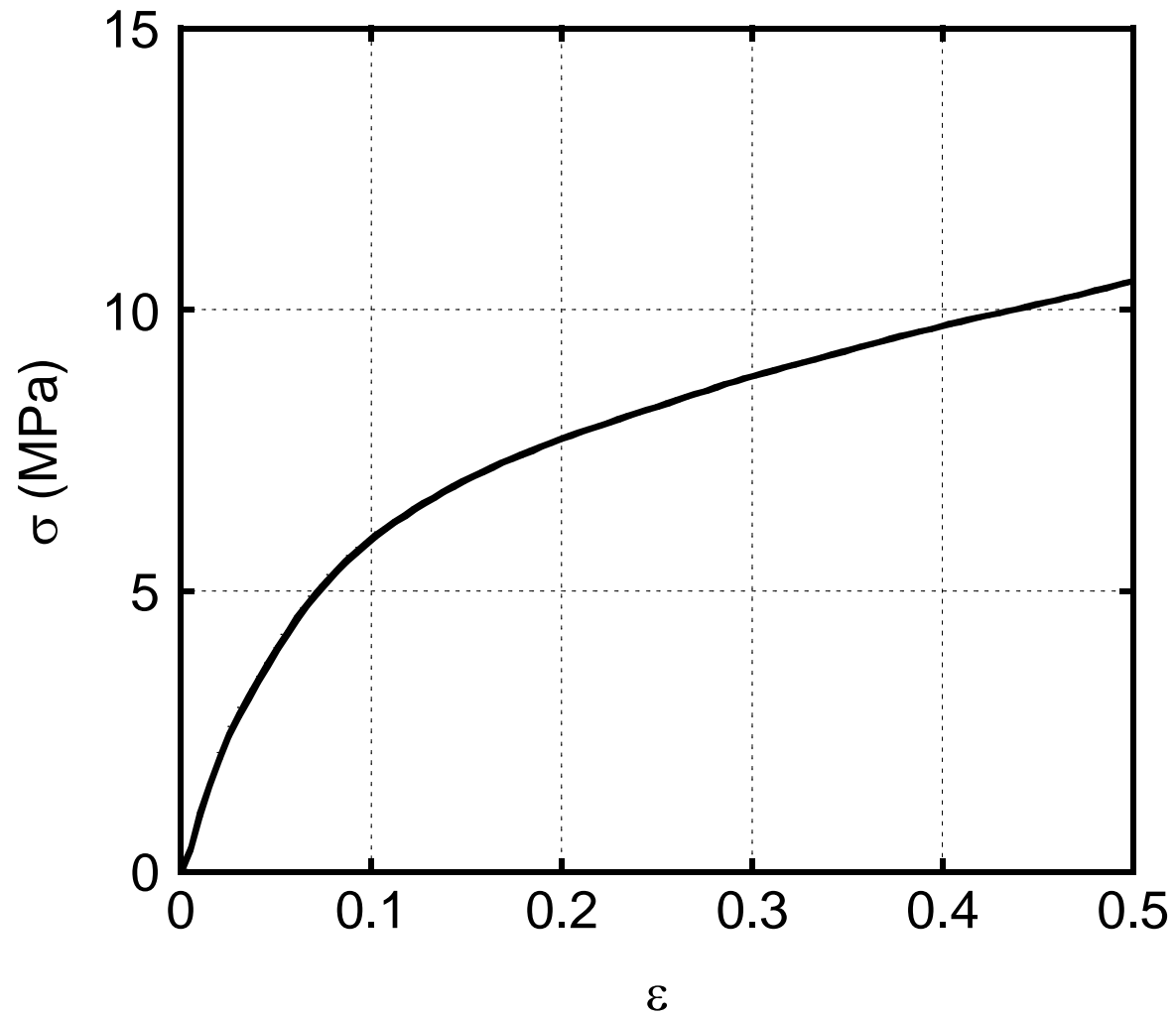
Songsurang et al., Figure 9



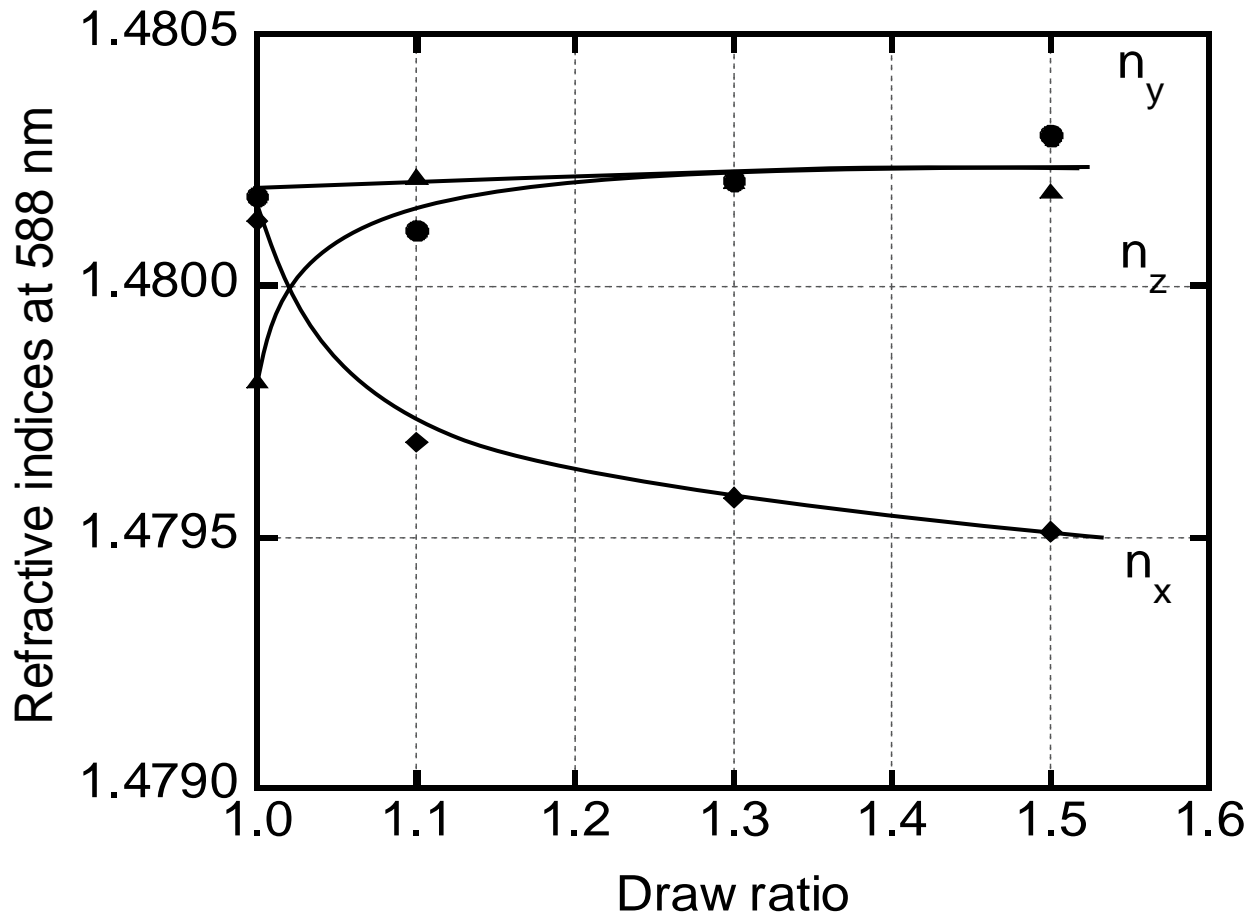
Songsurang et al., Figure 10



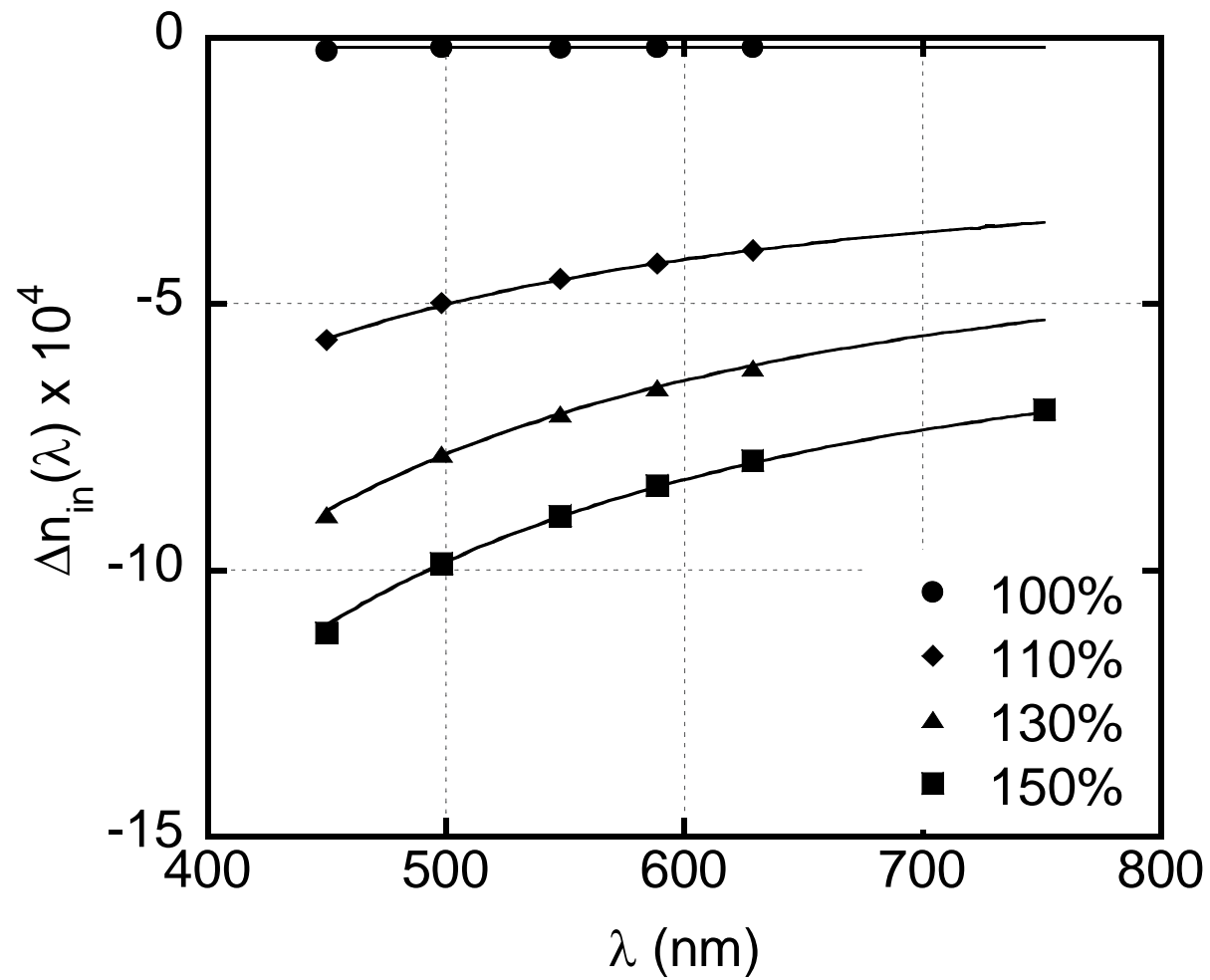
Songsurang et al., Figure 11



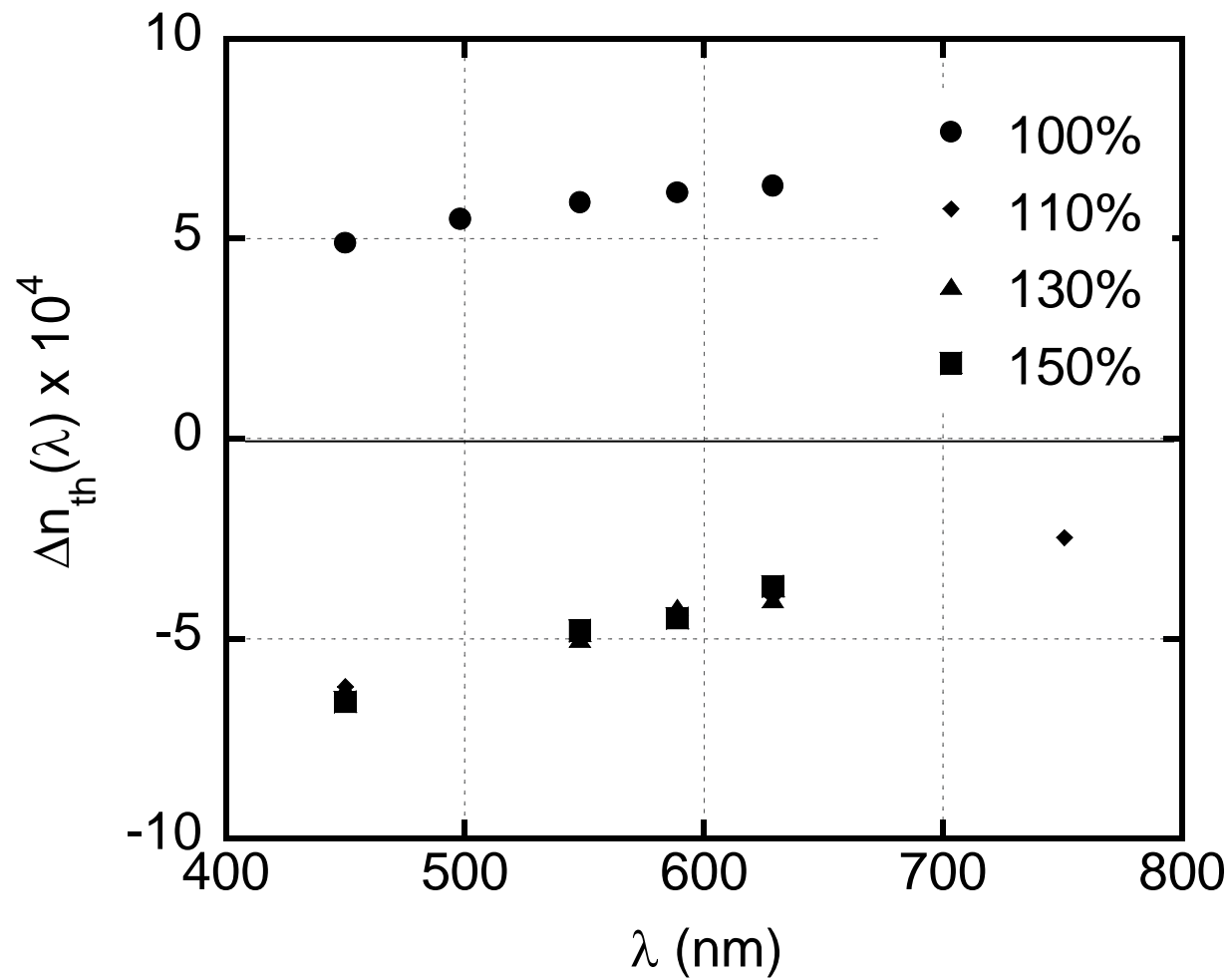
Songsurang et al., Figure 12



Songsurang et al., Figure 13



Songsurang et al., Figure 14a



Songsurang et al., Figure 14b

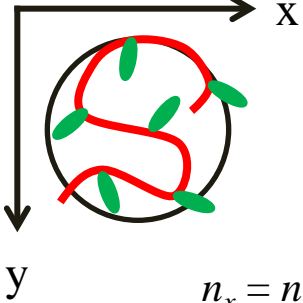
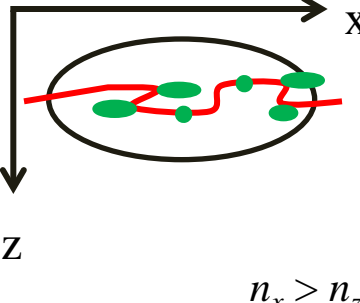
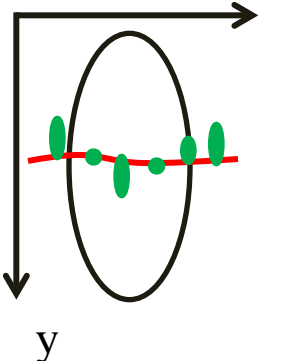
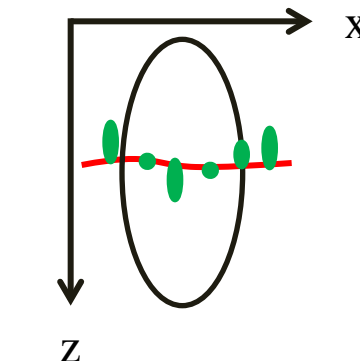
**Table 1. Thermal Properties of Solution-Cast Films Obtained by Various Conditions**

Conditions				Heat of Fusion (J/g)
Thickness	Evaporation Rate	Solvent	TCP	
50 $\mu\text{m}$	Standard	$\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	Not included	13.8
100 $\mu\text{m}$	Standard	$\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	Not included	12.7
200 $\mu\text{m}$	Standard	$\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	Not included	11.5
300 $\mu\text{m}$	Standard	$\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	Not included	10.9
100 $\mu\text{m}$	Slow	$\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	Not included	12.1
100 $\mu\text{m}$	Very slow	$\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	Not included	11.3
100 $\mu\text{m}$	Standard	$\text{CHCl}_3/\text{CH}_3\text{OH}$	Not included	12.1
100 $\mu\text{m}$	Standard	$\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	Included	10.2



# Illustrations

## Orientation of CTA molecules and refractive index ellipsoids of acetyl group

Film	Top-View	Side-View	Orientation of acetyl group & birefringence
<ul style="list-style-type: none"><li>As Cast</li></ul> <p>Polymer chains exist in the <math>x</math>-<math>y</math> plane.</p>	 <p><math>n_x = n_y</math></p>	 <p><math>n_x &gt; n_z</math></p>	<p>perpendicular to the <math>z</math> direction.</p> <p>↓</p> <p>positive <math>\Delta n_{th}</math></p>
<ul style="list-style-type: none"><li>After Stretching</li></ul> <p>Polymer chains are oriented in the <math>x</math> direction.</p>	 <p><math>n_y &gt; n_x</math></p>	 <p><math>n_z &gt; n_x</math></p>	<p>perpendicular to the <math>x</math> direction.</p> <p>↓</p> <p>negative <math>\Delta n_{in}</math></p>