Title	Material design of retardation films with extraordinary wavelength dispersion of orientation birefringence: A review
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Citation	Cellulose, 19(3): 601-613
Issue Date	2012-02-03
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/10726
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Description	

Material design of retardation films
with extraordinary wavelength dispersion
of orientation birefringence – A review

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Abstract

Orientation birefringence and its wavelength dispersion for various types of cellulose esters are reviewed. Cellulose esters such as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) show positive orientation birefringence with extraordinary wavelength dispersion, which is determined mainly by the ester groups rather than the main chains. The acetyl group provides negative orientation birefringence with strong ordinary wavelength dispersion, whereas the propionyl and butyryl groups give positive orientation birefringence with weak wavelength dispersion. Although all groups show ordinary wavelength dispersion, the summation of their orientation birefringences gives extraordinary dispersion. Moreover, the wavelength dispersion is dependent on the stretching ratio due to the difference in the orientation relaxation of each group. On the contrary, cellulose triacetate (CTA) shows negative birefringence with ordinary wavelength dispersion because it has no positive contribution. However, doping a plasticizer having positive orientation birefringence changes the orientation birefringence of CTA from negative to positive, and the wavelength dispersion from ordinary to extraordinary. This is attributed to the cooperative orientation of plasticizer molecules to the stretching direction with CTA chains, known as nematic interaction upon a hot drawing process.

Keywords: Cellulose ester; Optical Film; Orientation Birefringence;
Wavelength dispersion; Nematic Interaction

Introduction

One of the most important applications of cellulose esters is optical films such as protective film and retardation film (Edgar et al. 2004; Sata et al. 2004; Gleisser 2004; Kamide 2005; Yamaguchi et al. 2010; Yamaguchi 2010). Cellulose triacetate (CTA) films prepared by the solution-casting method are widely used for this application. Besides CTA, various cellulose esters such as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) become candidates for the optical films these days because their films can be prepared by melt-extrusion, leading to good cost-performance. For the optical application, control of retardation, i.e., product of birefringence and film thickness, is the most important aspect in material design, and thus various methods have been proposed.

In the application as polarizer protective films, the films cover a polarizing film to protect the polarizer from mechanical damage, moisture, and oxidation. In order to keep the polarizing condition of the light after passing through the polarizer, the films have to be free from birefringence. In general, however, it is difficult to obtain the birefringence-free films by extrusion method because molecules tend to orient to the flow direction by applied shear stress at the die exit. Because of the chain orientation, the occurrence of birefringence $\Delta n = n_{\parallel} - n_{\perp}$, where $n_{\parallel}$ and $n_{\perp}$ are refractive indices for light polarized in the directions parallel and perpendicular to the stretching direction, cannot be avoided, which is called "orientation birefringence". The orientation birefringence Δn of polymer materials, however, can be reduced by doping another material, because Δn is expressed by a simple addition of the birefringence from each component in a system as discussed by Stein et al. (1963), as follows;

$$\Delta n = \Delta n_F + \sum_i \phi_i \Delta n_i \qquad (1)$$

where i refers i-th component, ϕ_i is the volume fraction, and Δn_F is the birefringence arising from form or deformation effects, which is negligible for cellulose esters because of small level of the spatial fluctuation of refractive index. Therefore, when one component erases the birefringence of the others, the film is free from orientation birefringence. Hahn and Wendorff (1985) firstly revealed that a miscible binary blend composed of polymers having opposite sign of intrinsic birefringence shows no birefringence at a specific blend ratio irrespective of the molecular orientation, employing poly(methyl methacrylate) PMMA and poly(vinylidene fluoride) PVDF. Later, Saito and Inoue (1987) demonstrated 10 miscible polymer pairs having no birefringence. For cellulose esters, Yamaguchi and Masuzawa (2007) found that poly(vinyl acetate) PVAc is miscible with CAP and shows the opposite sign of intrinsic birefringence. Consequently, their blend at a specific ratio does not show orientation birefringence even after stretching. PMMA and poly(epichlorohydrin) also reduce the orientation birefringence of CAP by the same mechanism (Yamaguchi and Masuzawa 2008; Yamaguchi 2010). Ohno and Nishio (2006, 2007) found that poly(*N*-vinylpyrrolidone-*co*-methyl methacrylate) is miscible with cellulose acetate (CA), although it depends on the composition of the copolymer and degree of substitution of CA. Furthermore, the miscible copolymers reduce the orientation birefringence of CA. Iwata et al. (1996, 1997) and Tagaya et al. (2006) have developed a random copolymerization method, in which one monomer has opposite polarizability anisotropy to the other, and obtained the "zero-birefringence" polymer. Unohara et al. (2011) also proposed that the degree of orientation birefringence for cellulose diacetate-*graft*-poly(lactic acid) can be controlled by the composition of the monomers. Moreover, Tagaya et al. (2001) established another method to prepare the "zero-birefringence" polymer by addition of rod-like molecules having opposite polarizability anisotropy to that of a host polymer in order to compensate for the orientation birefringence, which is called "anisotropic molecule dopant method". Their research group also proposed that addition of rod-like crystals having strong optical anisotropy is effective to control the birefringence (Tagaya et al. 2003; Ohkita et al. 2004; Koike et al. 2006). Nakayama et al. (2006) prepared a zero-birefringence film using CTA, in which not only in-plane but also out-of-plane birefringence, i.e., retardation in the thickness direction, was controlled. Zhou et al. (2010) reported that cyclic block copolymer films prepared by melt-extrusion show significantly low level of retardation both in-plane and out-of-plane.

A retardation film is defined as a film to provide a specific optical retardation. One of the most available applications is to compensate the birefringence arising from polarizers and/or liquid crystal cell, thus it is also known as a compensation film. For the purpose, a retardation film is placed on the liquid crystal cell and/or polarizers to widen the viewing angle. In general, the retardation of such types of films is controlled to be around 5-10 nm (Scharf, 2007). Furthermore, quarter- and half-wave plates are famous examples of a retardation film, which are used to change the anisotropic condition of the incident light. Recently, a quarter-wave plate is often employed with a polarizing film to generate a circular-polarizing light for electro-luminescent panels and touch panels to prevent the reflection of ambient light. Moreover, a quarter-wave plate is used for 3D glasses. For the applications, not only birefringence at a specific wavelength but the wavelength dependence of birefringence is significantly important. The required retardation of a quarter-wave plate is, of course, a quarter of wavelength of the visible light, e.g., 147 nm for green (Fraunhofer D spectral line). Because the thickness of the film is approximately 80 μm, the birefringence required for this application is around 1.8 x 10^{-3} at 589 nm. Furthermore, a film having higher birefringence is being developed recently to reduce the film thickness and thus to improve the cost-performance.

In this review paper, the wavelength dependence of orientation birefringence, so-called wavelength dispersion, is discussed especially for cellulose esters. Although some of the cellulose esters are currently employed for retardation films because of various attractive properties, only a few papers have been published on the wavelength dispersion of the orientation birefringence to the best of our knowledge. However, for industrial applications, it is crucial to understand the wavelength dispersion as well.

Wavelength Dispersion of Orientation Birefringence for Conventional Polymers

The wavelength dispersion of orientation birefringence must be controlled precisely for color display. Based on the Kuhn and Grün model proposed for the stress-optical behavior of cross-linked rubbers, the orientation birefringence $\Delta n(\lambda)$ of an oriented polymer is expressed as follows (Kuhn and Grün 1942; Treloar 1958; Read 1975; Jenkins and White 1981; Harding 1986; Marks and Erman 1988)

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

where λ, $n(\lambda)$, N, $\Delta\alpha(\lambda)$, and θ are the wavelength of light, the average refractive index, the number of chains in a unit volume, the polarizability anisotropy, and the angle that a segment makes with the stretch axis, respectively. The last bracketed term $\left(3\langle\cos^2\theta\rangle-1\right)/2$ is identically equal to the Hermans orientation function (Hermans and

Platzek 1939; Read 1975), whereas the other part in the right term is called intrinsic birefringence determined by chemical structure. Consequently, eq. 2 can be written by;

$$\Delta n(\lambda) = \Delta n^0(\lambda) F \tag{3}$$

where $\Delta n^0(\lambda)$ is the intrinsic birefringence and F is the orientation function.

Since the orientation function is independent of the wavelength, the following simple relation is derived,

$$\frac{\Delta n(\lambda)}{\Delta n(\lambda_0)} = \frac{\Delta n^0(\lambda)}{\Delta n^0(\lambda_0)} = const. \tag{4}$$

where λ_0 is the arbitrary standard wavelength.

According to eq. 4, the wavelength dispersion of birefringence, i.e., normalized birefringence $\Delta n(\lambda)/\Delta n(\lambda_0)$, is a constant and determined by the chemical structure of a polymer. Because the film thickness does not affect the wavelength dispersion, the normalized retardation equals to the normalized birefringence. When a material shows absorption of electro-magnetic wave, the absorption coefficient has to be considered as well as the refractive index. Further, the refractive index shows a maximum at the wavelength where the absorption coefficient is a half of the maximum. As well known, a polymer shows absorption in the ultraviolet region. Therefore, $\Delta n(\lambda)/\Delta n(\lambda_0)$ of most polymeric materials decreases with increasing wavelength in the visible light, which is called “ordinary dispersion”.

Figure 1 exemplifies the measurement method of the wavelength dispersion of orientation birefringence (Yamaguchi et al. 2009a). By rotating the plate of color filters, the wavelength of the incident light is changed. Since the wavelength dispersion of refractive index for a conventional polymer is expressed by the following simple relations such as Sellmeier equation (eq. 5) and Cauchy equation (eq. 6) (Jenkins and White 1981; Harding 1986), the orientation birefringence at various wavelengths can be predicted.

$$n^2 = 1 + \sum_i \frac{A_i}{\lambda^2 - B_i} \tag{5}$$

$$n = A' + \frac{B'}{\lambda^2} + \frac{C'}{\lambda^4} + \frac{D'}{\lambda^6} \tag{6}$$

where A and B are the Sellmeier coefficients and A', B', C' and D' are the constants for Cauchy equation.

[Figure 1]

If the orientation birefringence has to be measured simultaneously with the stress-strain curve, the tensile testing machine has to be set in the optical line as shown in Figure 2 (Yamaguchi 2010). The apparatus in Figure 2 can also be employed to evaluate the photoelastic birefringence in the glassy state.

[Figure 2]

Figure 3 shows the wavelength dispersion of orientation birefringence of stretched PMMA films at various draw ratios. Since the sign of the intrinsic birefringence of PMMA is negative, the orientation birefringence decreases with the draw ratio. The wavelength dispersion of the orientation birefringence, however, can be expressed by a single curve within the experimental error as shown in Figure 3(b). This is reasonable because the normalized orientation birefringence is decided only by the chemical structure as demonstrated by eq. 4.

[Figure 3(a)][Figure 3(b)]

Figure 4 shows the retardation of stretched films of polycarbonate PC and PMMA. As seen in the figure, the absolute values of the birefringence decrease with the wavelength. Although the retardation of both films is close to a quarter-wave at 400 nm, i.e., 100 nm, the values at 800 nm are significantly smaller than a quarter of the wavelength (200 nm as a quarter of 800 nm). The wavelength dispersion of the birefringence is, therefore, contrary to that of an ideal quarter-wave plate.

[Figure 4]

Material Design of Retardation Films with Extraordinary Wavelength Dispersion

The industrial interest in the retardation film is to reduce the thickness and to adjust the retardation in the wide range of visible light. At present, the extraordinary dispersion of the orientation birefringence is attained by piling two or more polymer films having different wavelength dispersions, in which the fast direction of one film is set to be perpendicular to the fast direction of the other, as illustrated in Figure 5. When both films show positive orientation birefringence, therefore, one film has to be rotated 90 degrees to convert the fast direction to the slow one as indicated in the figure ($B_{//} \rightarrow B_{\perp}$). Although this technique is employed currently, it leads to poor cost-performance due to the complicated assembling process and results in a thick display.

[Figure 5]

Meanwhile, Uchiyama and Yatabe (2003a,b) proposed a new method using a miscible polymer blend system. They successfully controlled the wavelength dispersion using a binary blend composed of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and atactic polystyrene (PS). In the blend system, PS shows negative birefringence with strong wavelength dependence, whereas PPO exhibits a positive one with weak wavelength dependence. Although both polymers show ordinary wavelength dispersion, the blends at certain blend compositions show extraordinary wavelength dispersion as the summation of the contributions from both polymers (eq. 1). Another study on the polymer blend technique was performed by Kuboyama et al. (2007). They managed to control the wavelength dispersion of a miscible blend comprising of polynorbornene (NB) and poly(styrene-*co*-maleic anhydride) (SMA) by adjusting the blend composition and stretching conditions. In the blend system, NB has positive birefringence with weak wavelength dispersion, while SMA has negative birefringence with strong wavelength dispersion. They found that the blend shows positive birefringence with extraordinary wavelength dispersion when the content of NB is more than 40 wt%.

A similar method was proposed by employing a copolymer of two monomers such as 2,2-bis(4-hydroxyphenyl)propane (BPA) and 9,9-bis(4-hydroxy-3-methylphenyl) fluorine (BMPF) (Uchiyama and Yatabe 2003c). Similar to the blend method, one monomer (BPA) has positive birefringence with weak wavelength dispersion while the other (BMPF) has negative with strong dispersion.

The concept used in the material design for the blend and copolymerization techniques is similar to that of the piling method (Fig. 5) as illustrated in Figure 6.

[Figure 6]

Wavelength Dispersion of Cellulose esters

Some cellulose esters exhibit extraordinary wavelength dispersion of orientation birefringence. Figure 7 shows the wavelength dispersion of orientation birefringence for stretched films at a draw ratio of 2.0 employing various types of cellulose esters (Yamaguchi et al. 2009a). The numerals in the CAB samples represent the weight fraction (%) of the butyryl group. In this experiment, uniaxial stretching was performed at a temperature where the storage modulus at 10 Hz is 0.1 MPa in order to provide a same stress level for all samples having different glass transition temperature. Apparently, CTA shows negative birefringence with ordinary dispersion, as reported by El-Diasty et al. (2007). Except for CTA, however, all CAB and CAP samples exhibit positive birefringence with extraordinary wavelength dispersion. Figure 8 shows the orientation birefringence at 588 nm as a function of draw ratio for the samples. As seen in the figure, the birefringence increases with the draw ratio although the slope becomes small owing to the relaxation of chain orientation. Furthermore, the magnitude increases with the butyryl content, which can be confirmed clearly in Figure 9 (plotted against the degree of substitution of butyryl or propionyl, S_b) (Yamaguchi 2010). The figure indicates that CAB having 0.35 of S_b of the butyryl group content shows no birefringence. Moreover, the butyryl group has stronger impact on the birefringence than the propionyl one, since the data of CAP is displaced downward from the solid line.

[Figure 7][Figure 8][Figure 9]

We have evaluated the orientation function F of the pyranose-ring in the CAP film by infra-red dichroic ratio D ($= A_{//}/A_{\perp}$) and found that the orientation birefringence is not proportional to $(D - 1)/(D + 2)$, as seen in Figure 10 (Yamaguchi et al. 2009a). Because $(D - 1)/(D + 2)$ is proportional to the orientation function, the result suggests that the stress-optical rule is not applicable to CAP. In other words, the orientation birefringence of CAP is determined not by the orientation of main chains, but rather by the species and the amount of the ester groups. Consequently, the orientation birefringence of CAP is determined by the following relation;

$$\Delta n(\lambda) = \Delta n_A{}^0(\lambda) F_A + \Delta n_P{}^0(\lambda) F_P \qquad (7)$$

where $\Delta n_A{}^0(\lambda)$ and $\Delta n_P{}^0(\lambda)$ are the intrinsic birefringences, and F_A and F_P are the orientation functions of the acetyl and propionyl groups, respectively.

[Figure 10]

The extraordinary dispersion is ascribed to the contribution of both negative and positive birefringences with different wavelength dependence. Considering that CTA shows negative orientation birefringence with ordinary dispersion, the acetyl group provides negative orientation birefringence. On the contrary, the propionyl and butyryl groups provide positive birefringence with weak wavelength dispersion with an intense fashion on the butyryl group. This result suggests that the flexible and bulky methylene part in ester groups would lead to the parallel orientation of the polarizability anisotropy along the flow direction, whereas that of the acetyl group orients perpendicular to the flow direction.

Combination of negative birefringence with strong wavelength dispersion originating from the acetyl group and positive birefringence with weak wavelength dispersion from the propionyl and butyryl groups enables some cellulose esters such as CAP and CAB having appropriate ester groups to exhibit extraordinary wavelength dispersion of orientation birefringence. This situation is illustrated in Figure 11 (Yamaguchi et al. 2009a). In the figure, the polarizability anisotropy of ester groups is represented by ellipsoids. As depicted in the figure, the addition of both components, denoted by a bold line, gives the extraordinary dispersion with positive orientation birefringence, when the wavelength dependence of the propionyl group is weaker than that of the acetyl group. This is similar to the miscible blends showing extraordinary dispersion, such as PPO/PS and NB/SMA, and the copolymer of BPF and BMPF.

[Figure 11]

Figure 8 also indicates that the wavelength dispersion of the orientation birefringence is dependent upon the draw ratio. In Figure 12, the data are re-plotted as a function of the wavelength (Yamaguchi et al. 2009a). It is confirmed that the extraordinary dispersion becomes pronounced with increasing draw ratio, which cannot be observed in a conventional polymer as shown in Figure 3(b). Considering that the acetyl group shows the strong wavelength dispersion, the experimental result indicates that the contribution of the acetyl group, i.e., $F_A / (F_A+F_P)$, increases with the draw ratio. On the contrary, the propionyl group contributes greatly to the orientation birefringence at the beginning of stretching, suggesting that the orientation of the propionyl group occurs even at low stress. From the industrial point of view, the phenomenon indicates that the wavelength dispersion can be controlled by the stretching conditions such as degree of stretching (draw ratio), stretching temperature, and stretching speed, which is considerably important information for actual application. On the other hand, it is difficult to obtain a film with large retardation using CAP and CAB because negative contribution increases with increasing draw ratio.

[Figure 12]

Control of Orientation Birefringence by Nematic Interaction

Orientation birefringence can be controlled by doping a low-mass compound into a polymeric material. Low-mass compounds that are dissolved into a polymer matrix are forced to orient in the same direction as the polymer chains by intermolecular orientation correlation which is called nematic interaction (Merrill et al. 1989; Doi and Watanabe 1991). Originally, the nematic interaction was used to explain the orientation relaxation of a short chain in a polymer melt with broad molecular weight distribution. Urakawa et al. (2006, 2010) and Nobukawa et al. (2010, 2011) have quantitatively discussed the nematic interaction in miscible systems by developing orientation coupling theory suggested by Zawada et al. (1994) when a low-mass-compound having an appropriate size moves cooperatively with chain segments of a matrix polymer.

Yamaguchi et al. studied binary blends of CAP and poly(lactic acid) PLA and found that 1-3 wt% of PLA is miscible with CAP on a molecular scale (Yamaguchi et al. 2010). Moreover, they revealed that the orientation birefringence of CAP is greatly enhanced by a small addition of PLA as shown in Figure 13. At the stretching temperature, the relaxation time of PLA is only 0.045 s, whereas that of CAP is longer than 1000 s. The high level of orientation of PLA chains without relaxation is attained by the cooperative alignment with CAP chains as illustrated in Figure 14. Consequently, a retardation film having high level of birefringence, leading to a thin film, can be designed by polymer blends composed of only biomass-based materials. When the amount of PLA is more than 3 wt%, however, phase separation occurs as previously reported by Tatsushima et al. (2005). As a result, the blends lose transparency and show similar level of orientation birefringence to the blend with 1 wt% of PLA. This is reasonable because PLA chains in the dispersed phase have no nematic interaction with CAP chains, thus the orientation will relax immediately as compared to CAP.

[Figure 13][Figure 14]

Not only polymeric materials but plasticizers such as diethyl phthalate DEP and tricresyl phosphate TCP can enhance the orientation function of CAP. This phenomenon is also attributed to the nematic interaction. Figure 15 shows the orientation birefringence at various draw ratios for pure CAP and CAP with 10 wt% of the plasticizers (Yamaguchi et al. 2009b). Considering that plasticizers are always required for cellulose esters to improve the processability and adjust the vapor transmittance property, the phenomenon cannot be ignored.

[Figure 15]

Addition of aromatic plasticizers will provide ordinary wavelength dispersion because they have absorption in the ultraviolet region. Furthermore, both TCP and DEP show positive orientation birefringence. Therefore, their incorporation into CTA, having negative birefringence with ordinary dispersion, gives extraordinary wavelength dispersion. Figure 15 shows the orientation birefringence of pure CTA and CTA with 5 and 10 wt% of TCP. Apparently, CTA with 10 wt% of TCP shows extraordinary wavelength dispersion, whose orientation birefringence shows almost ideal dispersion of a multi-band quarter-wave plate (Mohd Edeerozey et al. 2011a).

[Figure 16]

In order to prove the contribution of TCP to the orientation birefringence, the effect of stress relaxation was evaluated by holding the stretched sample in a hot chamber for various residence times. As seen in Figure 17, the orientation birefringence decreases monotonically with increasing holding time after stretching, which is mainly attributed to the orientation relaxation of TCP molecules.

[Figure 17]

Moreover, the stretched sample of CTA/TCP (95/5) blend was immersed in methanol for 24 hours to remove TCP, and the orientation birefringence was measured. There is no considerable change in the dimension of the sample after 24 hours of immersion, suggesting that there is almost no alteration in degree of stretching upon the methanol immersion. Furthermore, it is confirmed by IR spectra analysis that TCP has been completely removed. Orientation birefringence of CTA/TCP (95/5) is shown in Figure 18 (Mohd Edeerozey et al. 2011a). After the immersion process, the orientation birefringence of the CTA/TCP blend decreases and approaches that of pure CTA. Therefore, the removal of TCP is reflected in the change of the orientation birefringence from positive to negative values. The result suggests that the positive birefringence in the CTA/TCP blend is strongly attributed to the orientation of TCP.

[Figure 18]

As well known, cellulose esters absorb water molecules, which have strong polarizability anisotropy. However, nematic interaction is not expected to take place when water molecules diffuse into a stretched cellulose ester films. This is reasonable because there is no movement of the matrix polymer chains to drag the water molecules. Nevertheless, absorbing the moisture is found to cause the orientation birefringence to decrease as shown in Figure 19 (Mohd Edeerozey et al. 2011b). This would be attributed to the intermolecular interaction between water molecules and the ester group in the cellulose esters, which was confirmed by IR spectra. Moreover, the degree of the reduction seems to be dependent upon the content of hydroxyl group in cellulose esters as shown in Figure 20 (Mohd Edeerozey et al. 2011b).

[Figure 19][Figure 20]

Conclusion

Material design of retardation films showing extraordinary wavelength dispersion of orientation birefringence is introduced in this paper. This will be a key technology in the field of high-performance optical films to improve the contrast of LCD. Moreover, the property is also required for electro-luminescence panels, touch panels, 3D glasses, and optical pick-up lens. Up to now, various techniques to provide the extraordinary dispersion have been proposed, such as piling films, blending with another polymer or a low-mass compound, and copolymerization with appropriate monomers. Although this property could be provided to any polymeric materials, CAP and CAB have a great benefit at the material design of multi-band retardation films such as quarter-wave plate, because they show extraordinary dispersion, even without any other component. This unique optical property of CAP and CAB is attributed to the large polarizability anisotropy of ester groups having different signs of birefringence.

Acknowledgement

The authors would like to express their gratitude to Taihei Chemicals Limited for their valuable advice and the kind supply of the samples employed in this study. Furthermore, the authors gratefully acknowledge financial supports from Japan Science and Technology Agency (Regional Research and Development Resources Utilization Program). The authors also would like to express their gratitude to Mr. Kenji Masuzawa, Mr. Takuya Iwasaki, Ms. Kyoko Okada, Mr. Yasuhiko Shiroyama, Ms. Manami Tsuji, and Ms. SoYoung Lee for their efforts to accomplish this work.

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Figure Captions

Figure 1 Schematic diagram of the retardation measurement; *L* halogen lamp, CF color filters, *P* polarizer, *S* sample film, *A* analyzer, *D* detector, *PC* computer. (Yamaguchi et al. 2009a)

Figure 2 (top) Schematic diagrams of simultaneous measurements of stress and birefringence during tensile deformation: *L* laser, *P* polarizer, *S* sample film, *A* analyzer, *D* detector, and *PC* computer.
(bottom) Picture of the machine. (Yamaguchi 2010)

Figure 3 (a) Wavelength dependence of orientation birefringence and (b) Normalized orientation birefringence for stretched PMMA films at various draw ratios: (circles) 1.5, (diamonds) 2.0 and (triangles) 2.5.

Figure 4 Wavelength dependence of retardation for stretched films; (circles) PC and (diamonds) PMMA. The thin lines represent the ideal dispersion for quarter-wave plates.

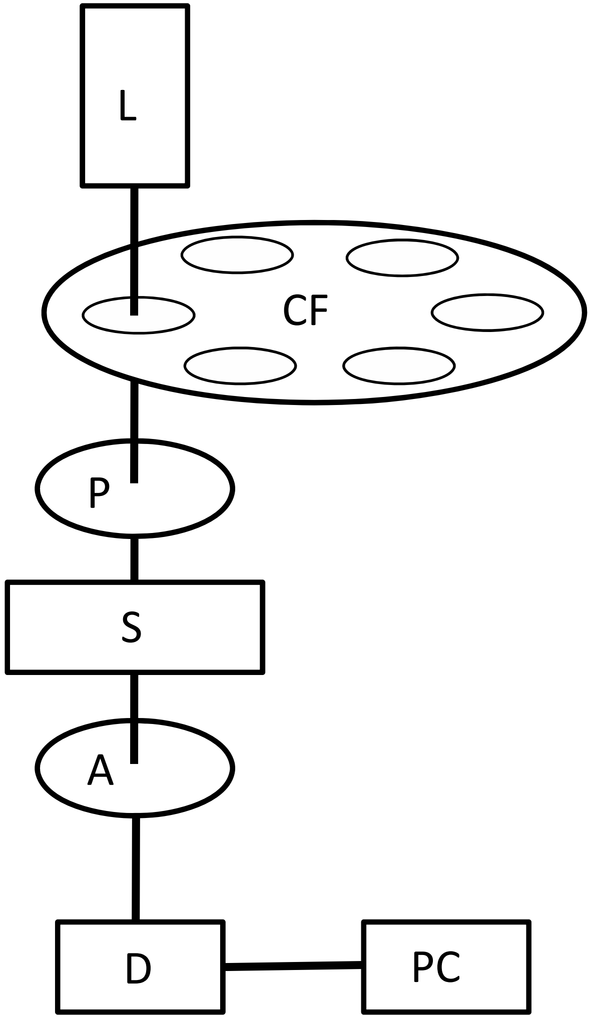
Figure 5 Illustration of the piling method to show extraordinary wavelength dispersion of orientation birefringence.

Figure 6 Illustration of the miscible blend method and the random copolymerization method to show extraordinary wavelength dispersion of orientation birefringence.

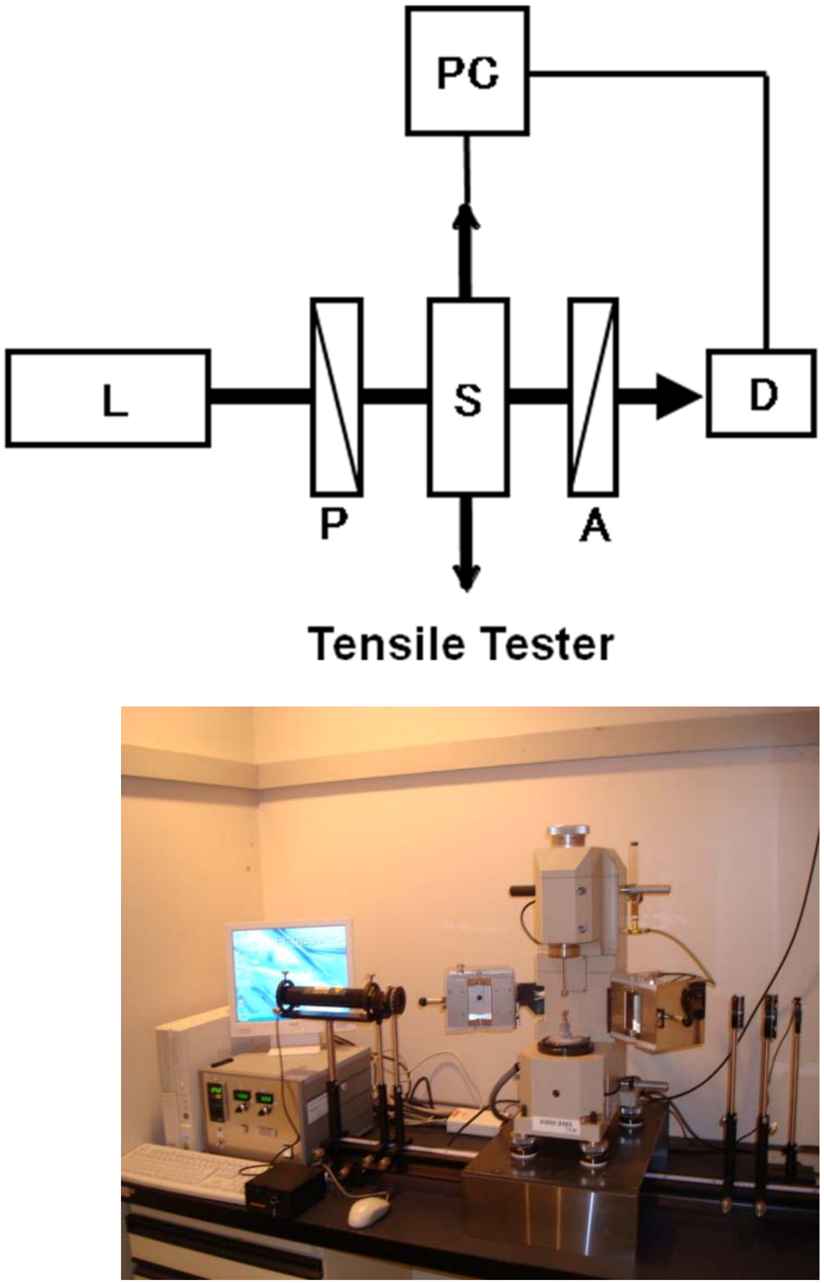
Figure 7 Wavelength dependence of orientation birefringence for stretched films of various cellulose esters such as CTA, CAP, and CAB. The numerals in the CAB samples represent the weight concentration of the butyryl group. The degree of substitution of propionyl group in CAP is 2.58, and those of butyryl group are 0.73, 1.74, and 2.64 for CAB17, CAB38, and CAB52, respectively. (Yamaguchi et al. 2009a)

Figure 8	Orientation birefringence as a function of draw ratio for various cellulose esters. The stretching was performed at the temperature where the storage modulus is 10 MPa at 10 Hz. (Yamaguchi et al. 2009b)
Figure 9	Orientation birefringence at a draw ratio of 2 plotted against the degree of substitution of butyryl group S_b for CAB (closed symbols). The open symbol denotes the data for CAP plotted against the degree of substitution of propionyl group.
Figure 10	Relation between $(D\text{-}1)/(D\text{+}2)$ and orientation birefringence for stretched CAP films at various wavelengths. (Yamaguchi et al. 2009a)
Figure 11	Illustration of CAP molecules and the contribution of orientation birefringence from each ester group. (Yamaguchi et al. 2009a)
Figure 12	Wavelength dependence of (a) orientation birefringence and (b) normalized orientation birefringence for stretched CAP at various draw ratios: (closed circles) 1.5, (open circles) 2.0, and (closed triangles) 2.5. (Yamaguchi et al. 2009)
Figure 13	Wavelength dependence of orientation birefringence for CAP and CAP/PLA blends: (circles) PLA, (diamonds) 1 wt% of PLA, (triangles) 3 wt% of PLA and (squares) 5 wt%. (Yamaguchi et al. 2010)
Figure 14	Illustration of orientation birefringence for CAP (open circles) with PLA (closed circles).
Figure 15	Orientation birefringence as a function of draw ratio for CAP and CAP with 10 wt% of plasticizers such as (circles) TCP and (diamonds) DEP. (Yamaguchi et al. 2010)
Figure 16	Wavelength dependence of orientation birefringence for (open circles) CTA, (closed circles) CTA/TCP (95/5), and (closed diamonds) CTA/TCP(90/10). (Mohd Edeerozey et al. 2011a)

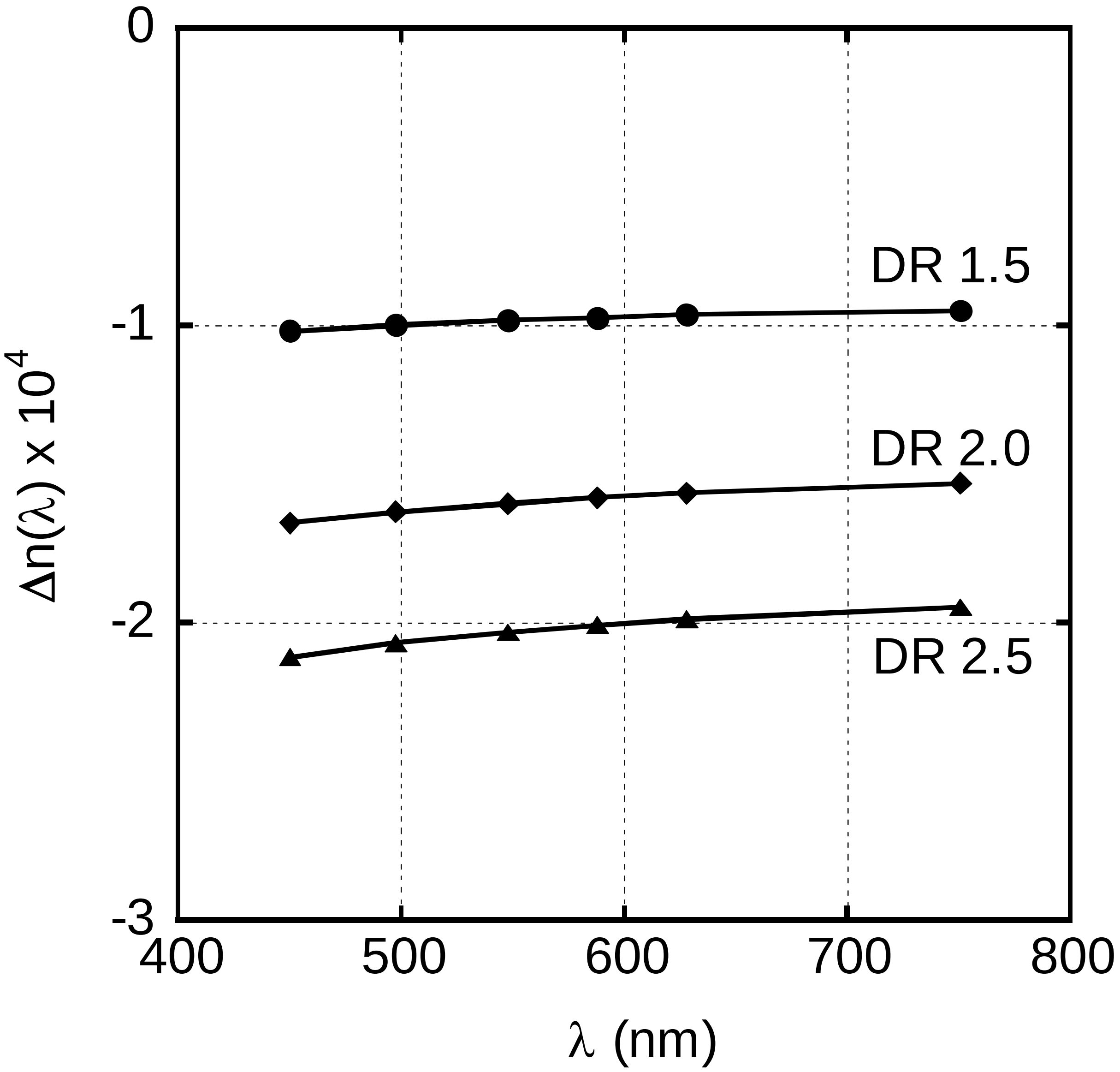
Figure 17	Wavelength dependence of orientation birefringence for CTA/TCP (95/5) having various holding times after stretching. (Mohd Edeerozey et al. 2011a)
Figure 18	Wavelength dependence of orientation birefringence for CTA/TCP (95/5) (circles) prior to immersion and (diamonds) after extraction of TCP. (Mohd Edeerozey et al. 2011a)
Figure 19	Wavelength dependence of orientation birefringence for CAP at various humidity conditions. (Mohd Edeerozey et al. 2011b)
Figure 20	Relation between moisture content in cellulose esters and orientation birefringence at 588 nm: (open circles) CTA, (closed circles) cellulose diacetate CDA, and (open diamonds) CAP. (Mohd Edeerozey et al. 2011b)



Yamaguchi et al., Figure 1



Yamaguchi et al., Figure 2



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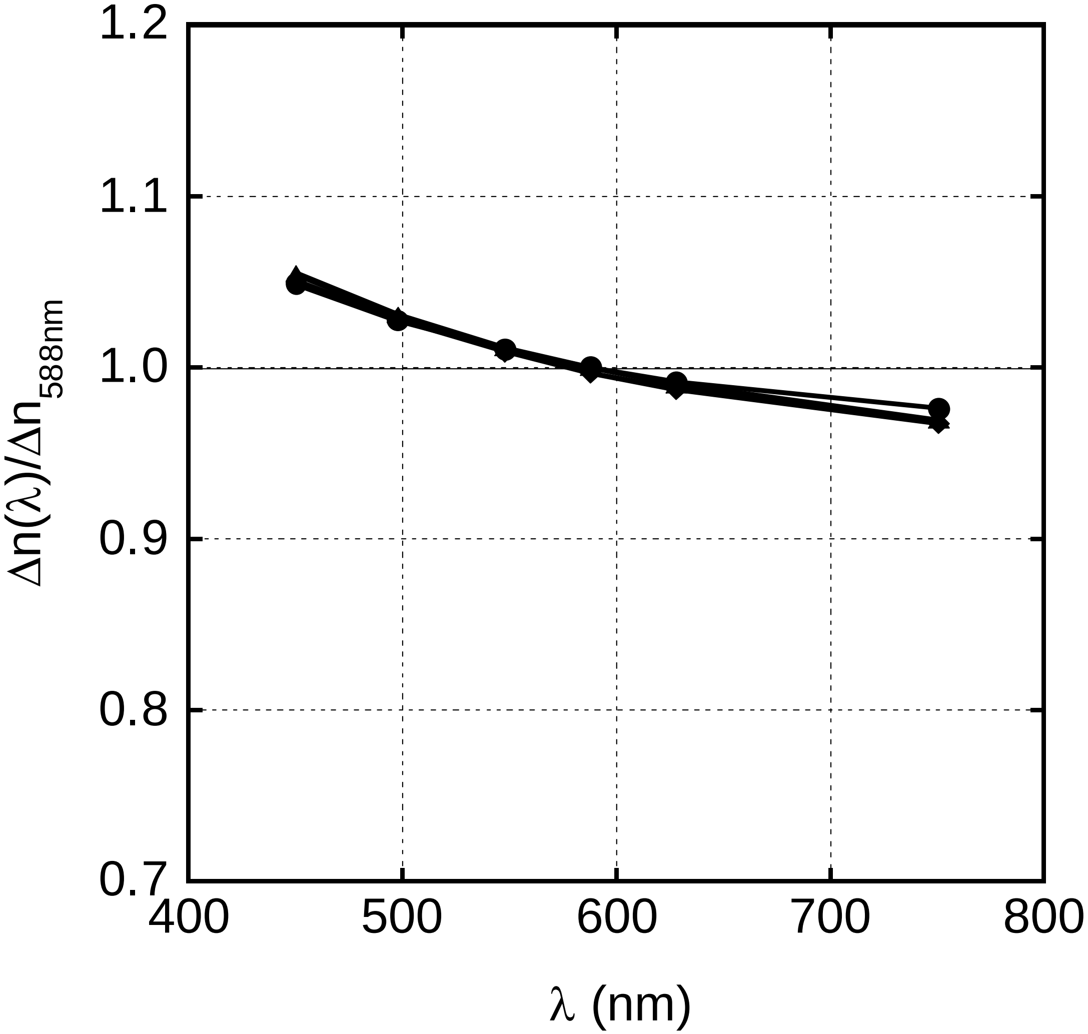
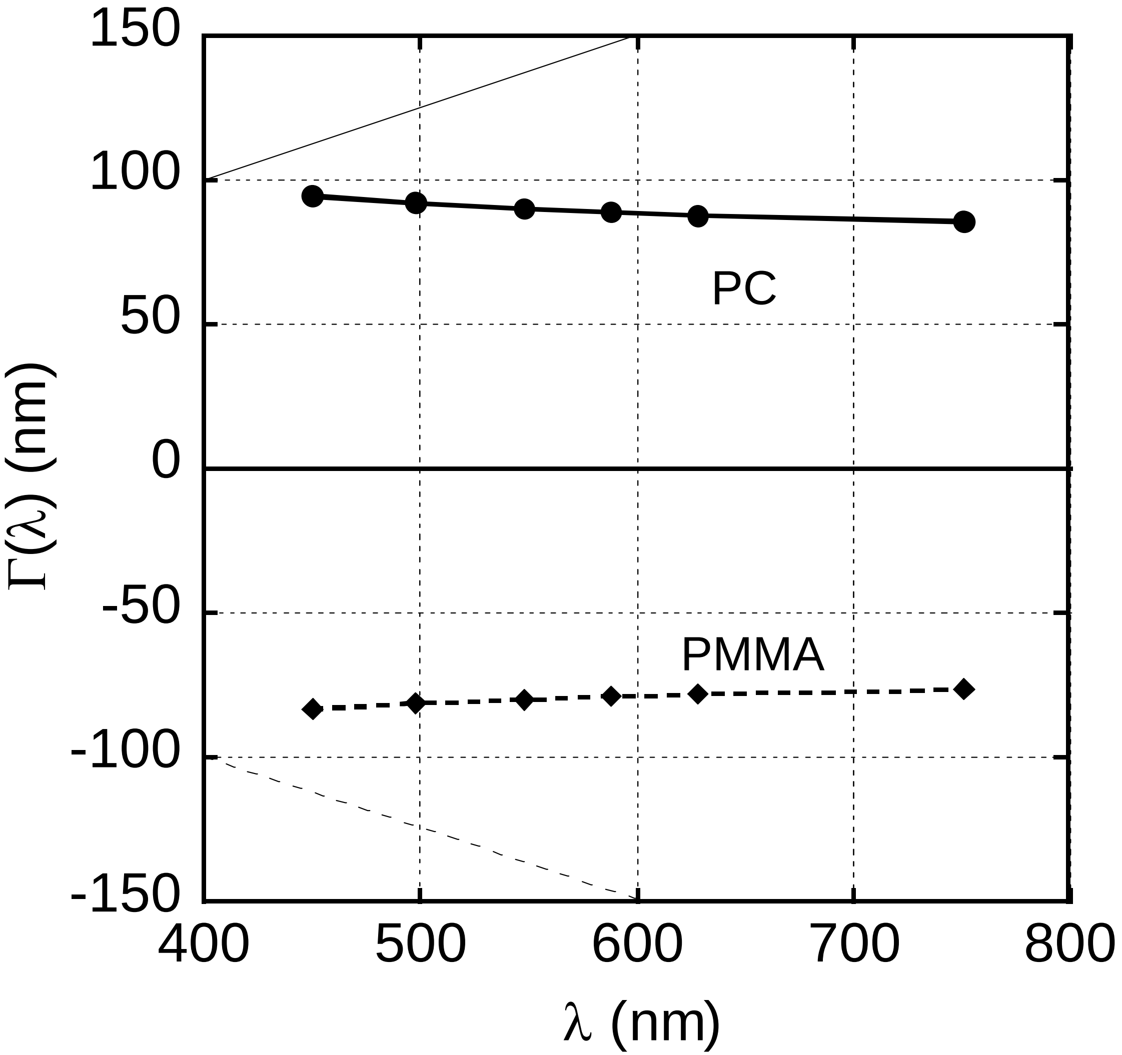
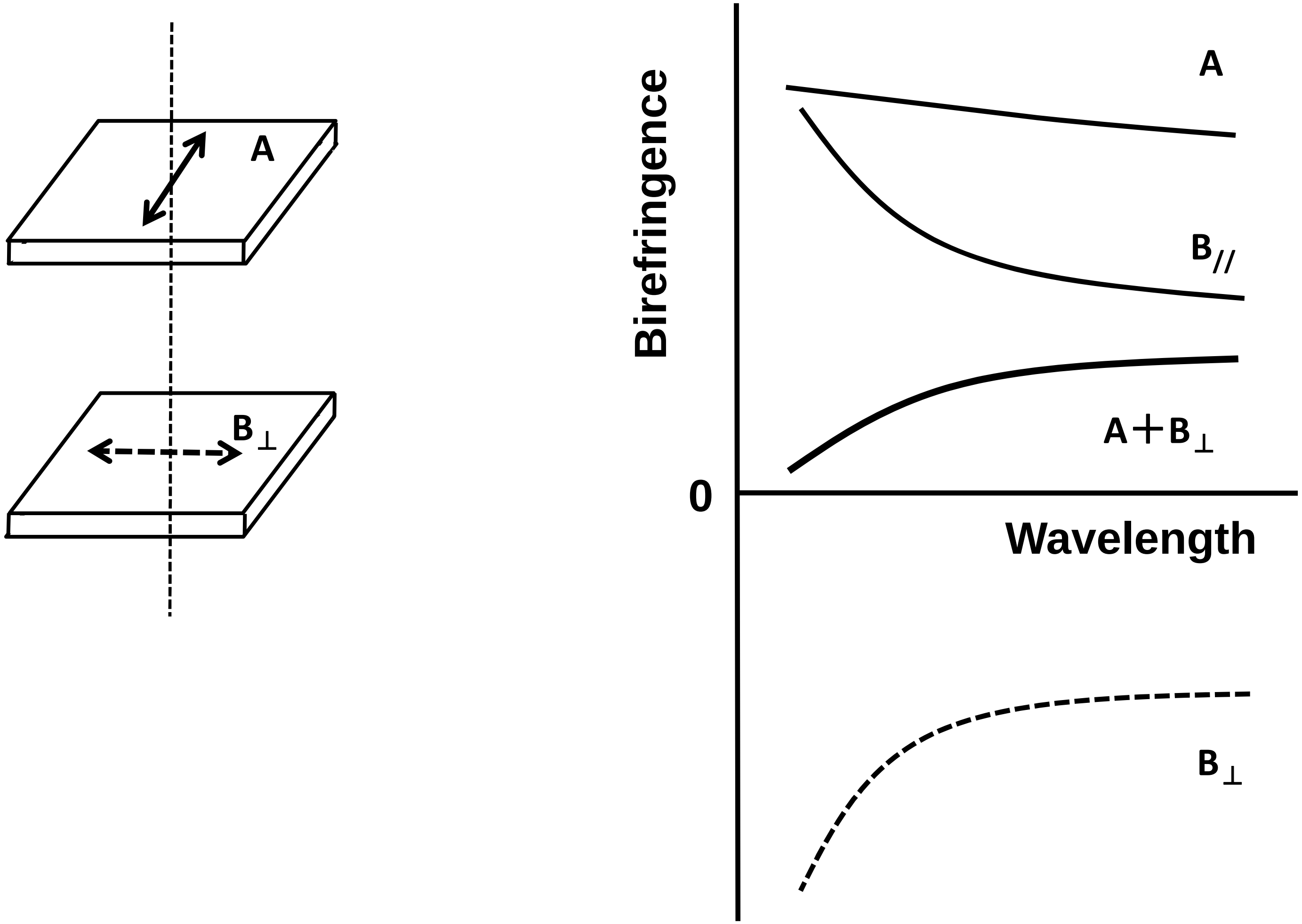


Yamaguchi et al., Figure 3(b)



Yamaguchi et al., Figure 4



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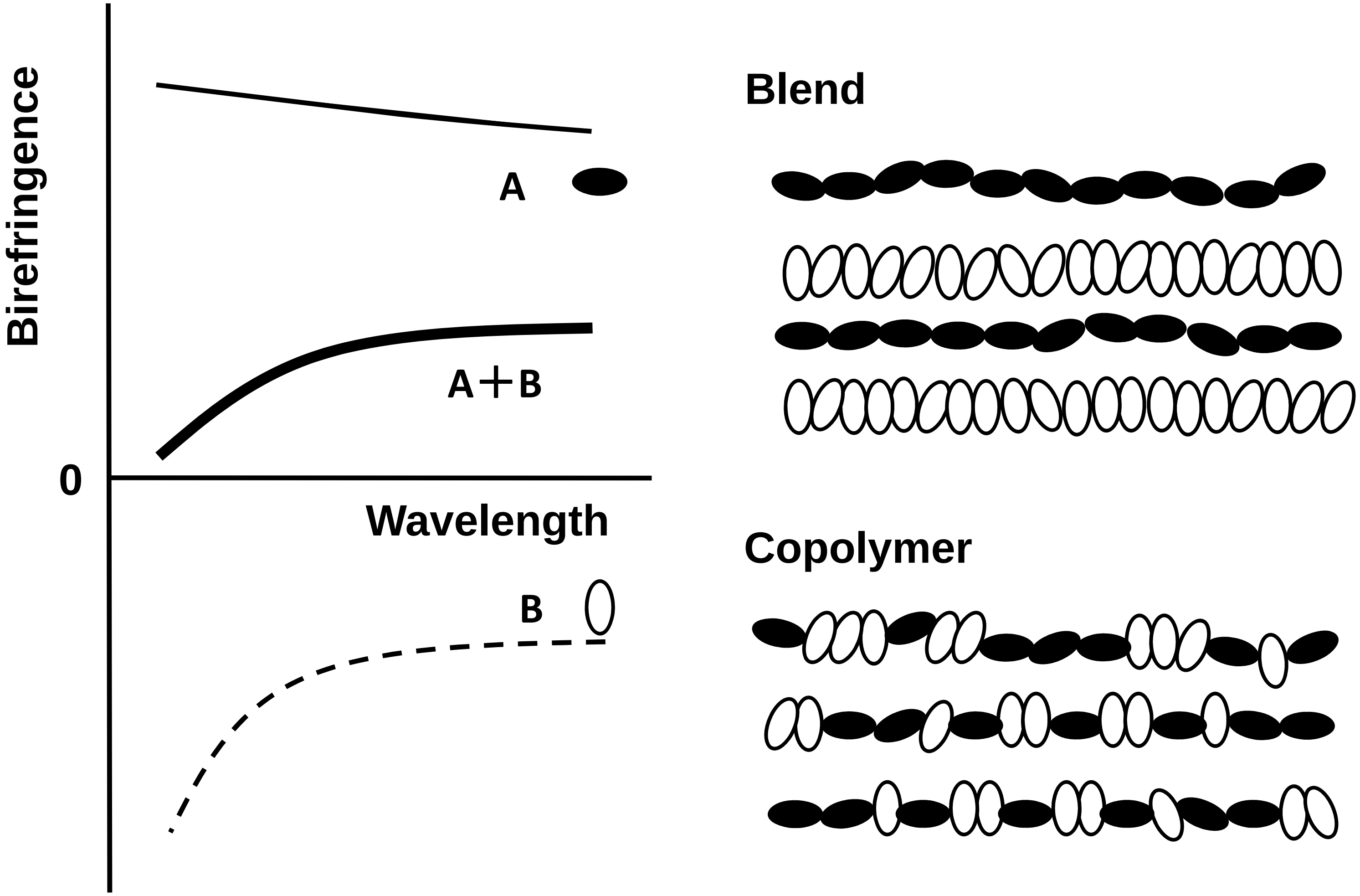

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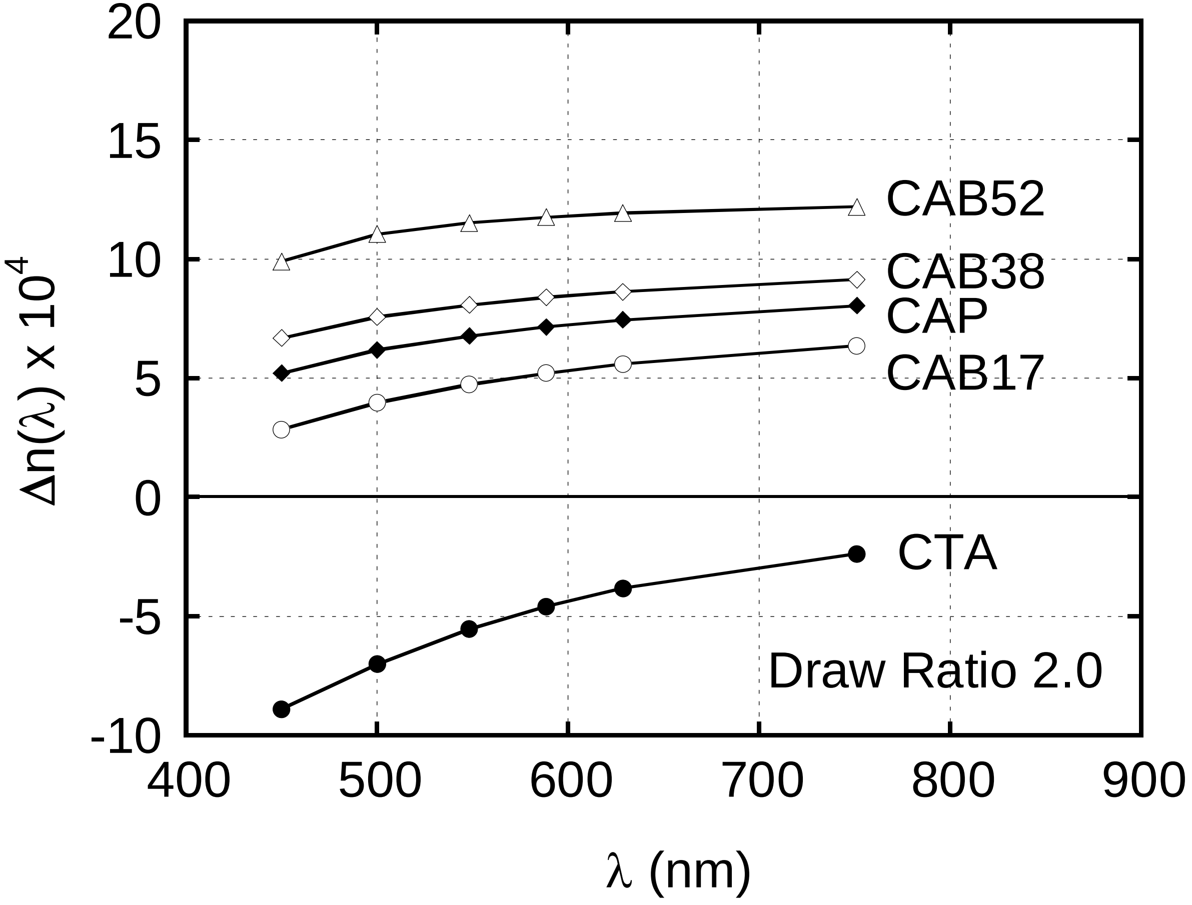
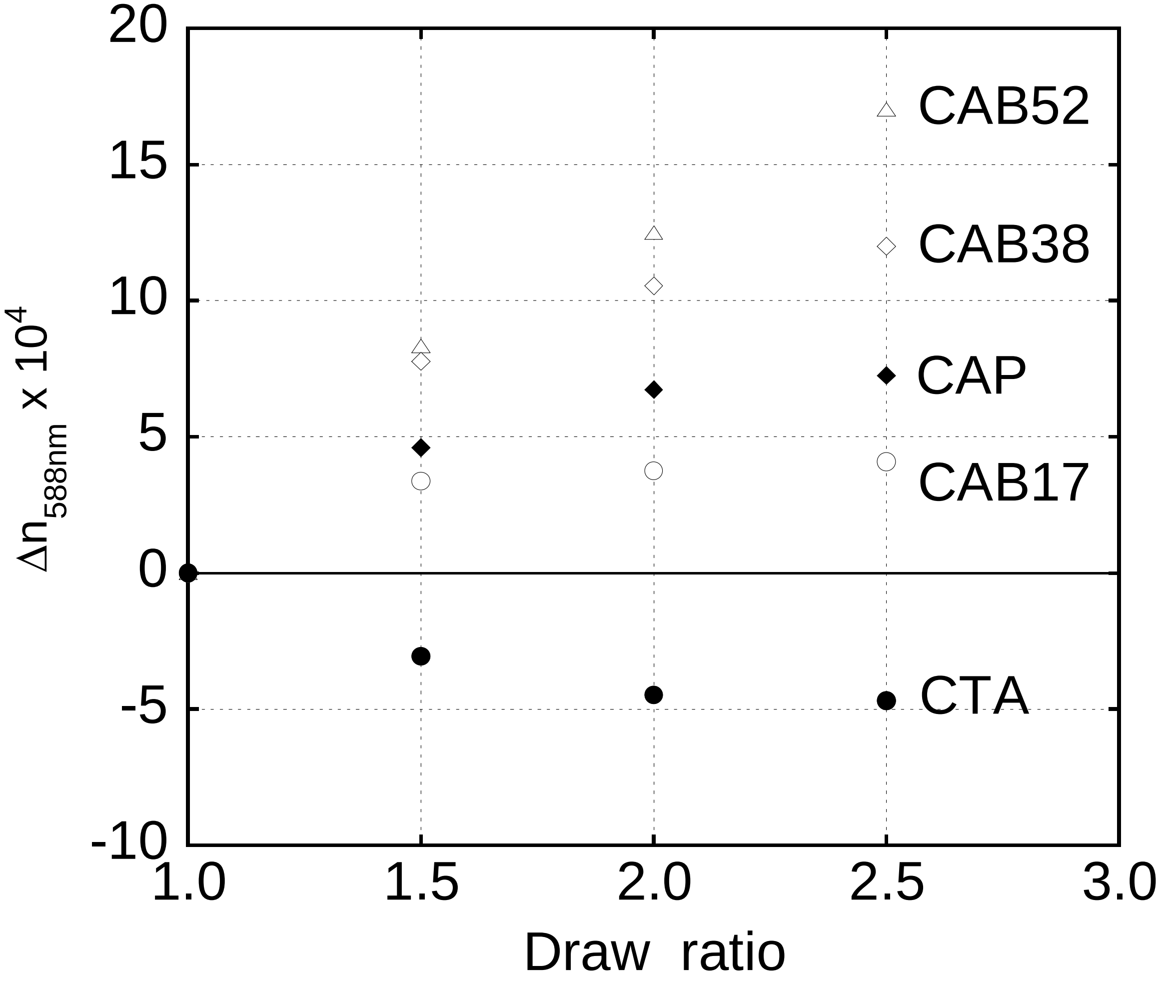


Yamaguchi et al., Figure 7



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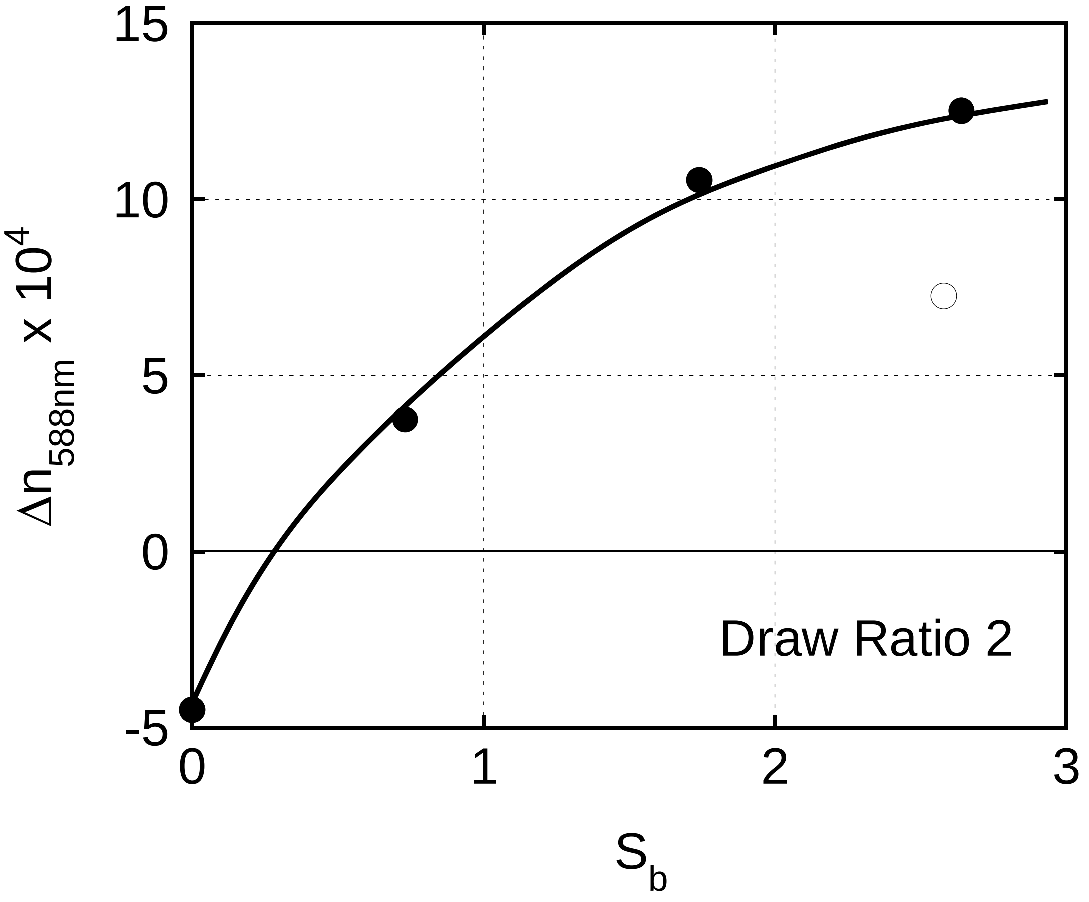

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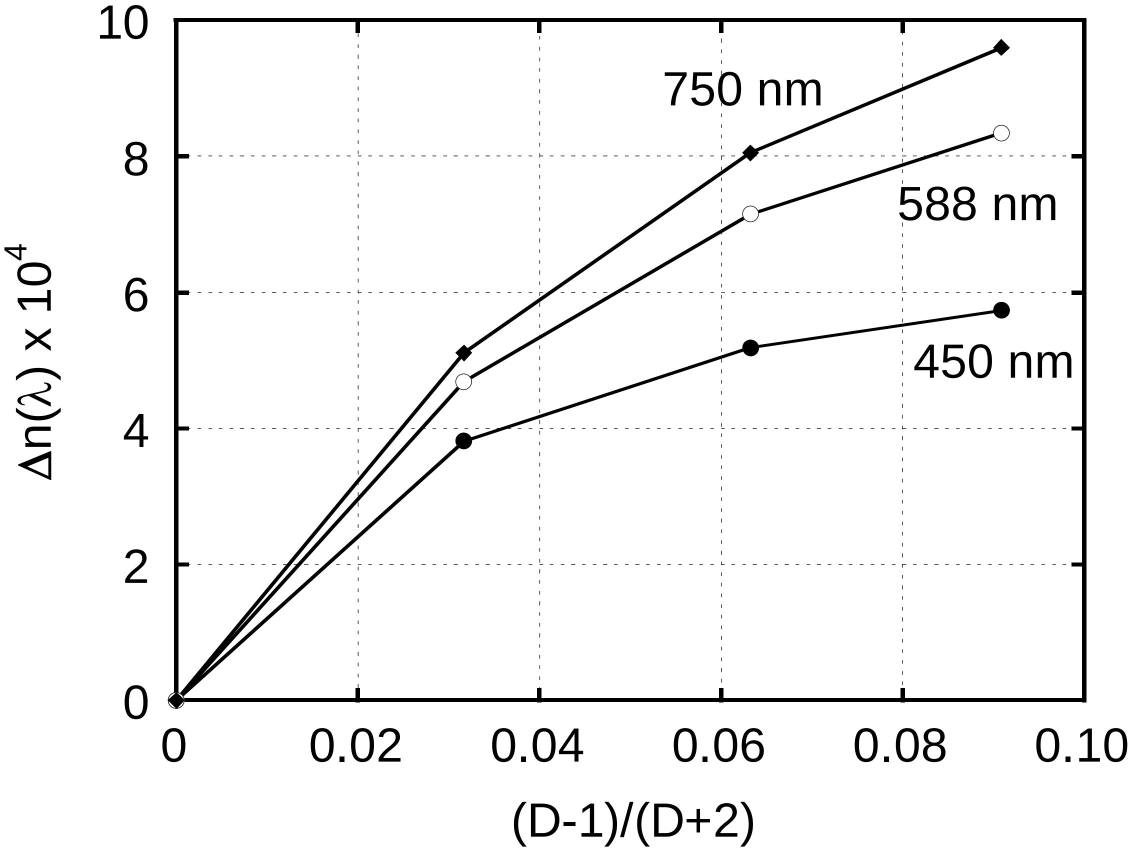
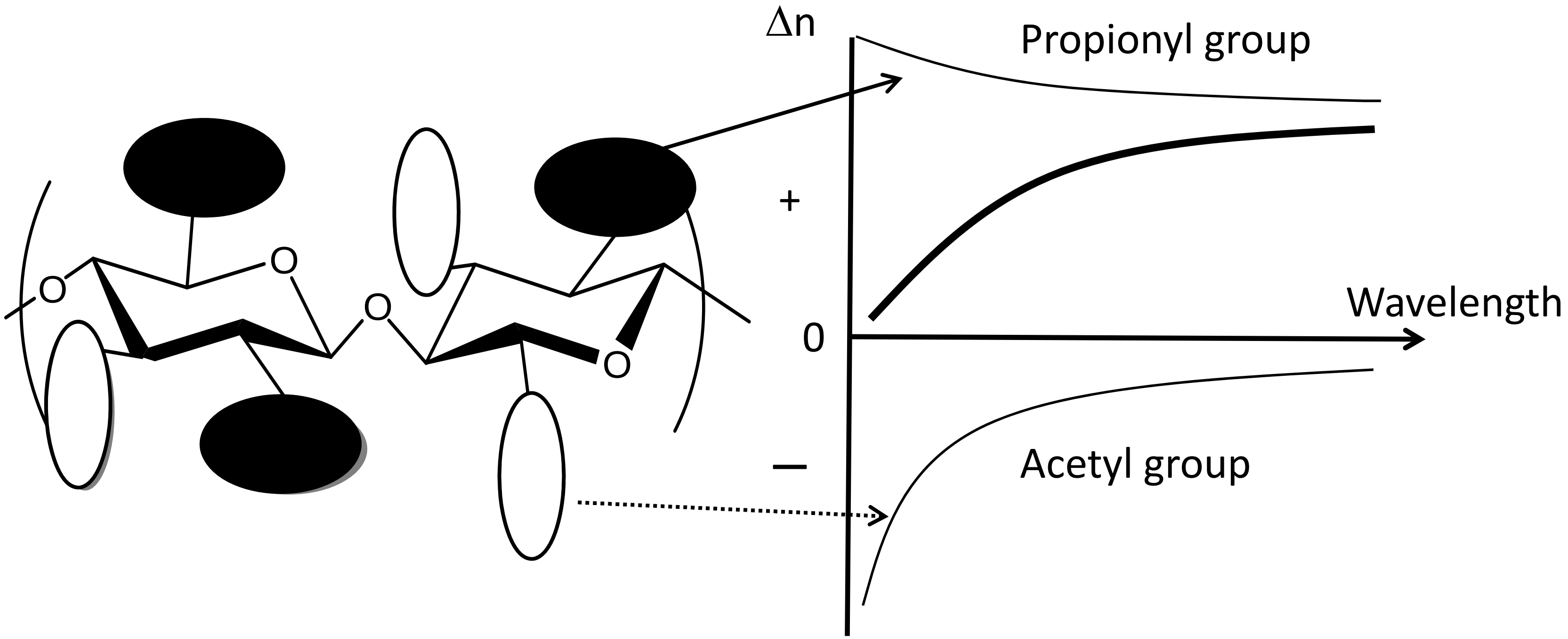


Yamaguchi et al., Figure 10



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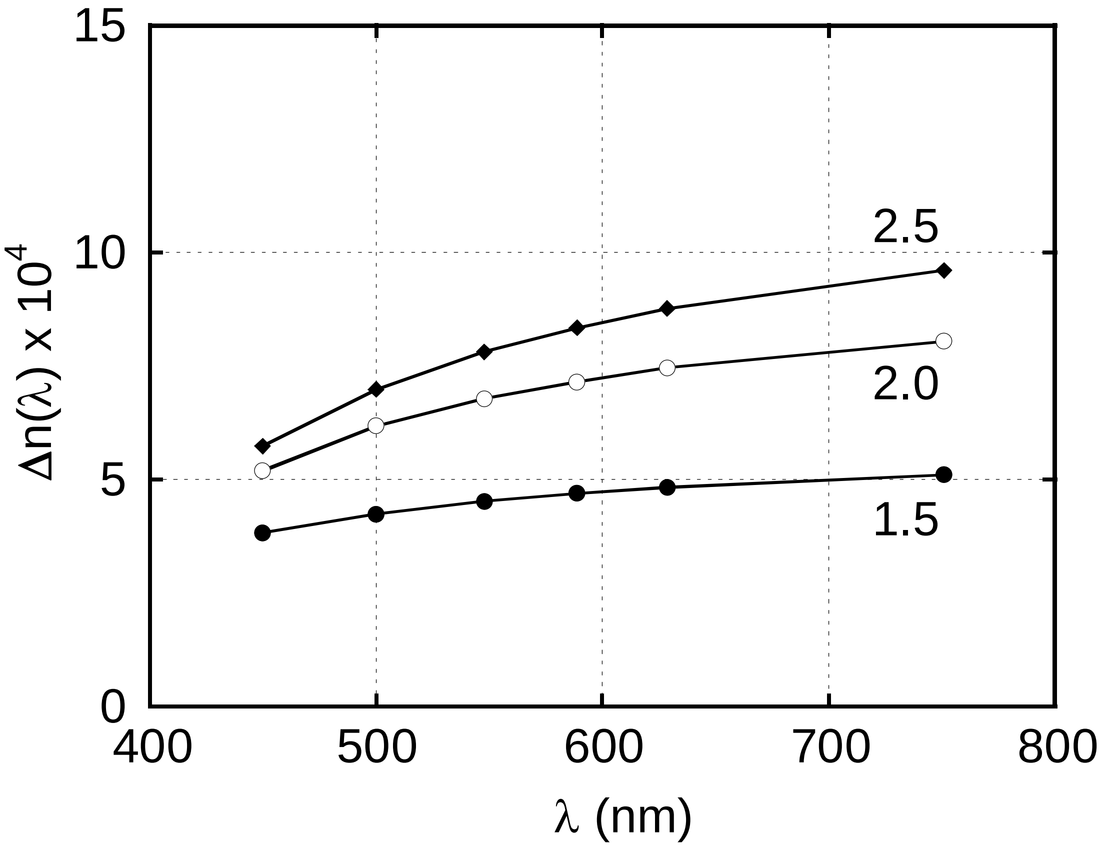

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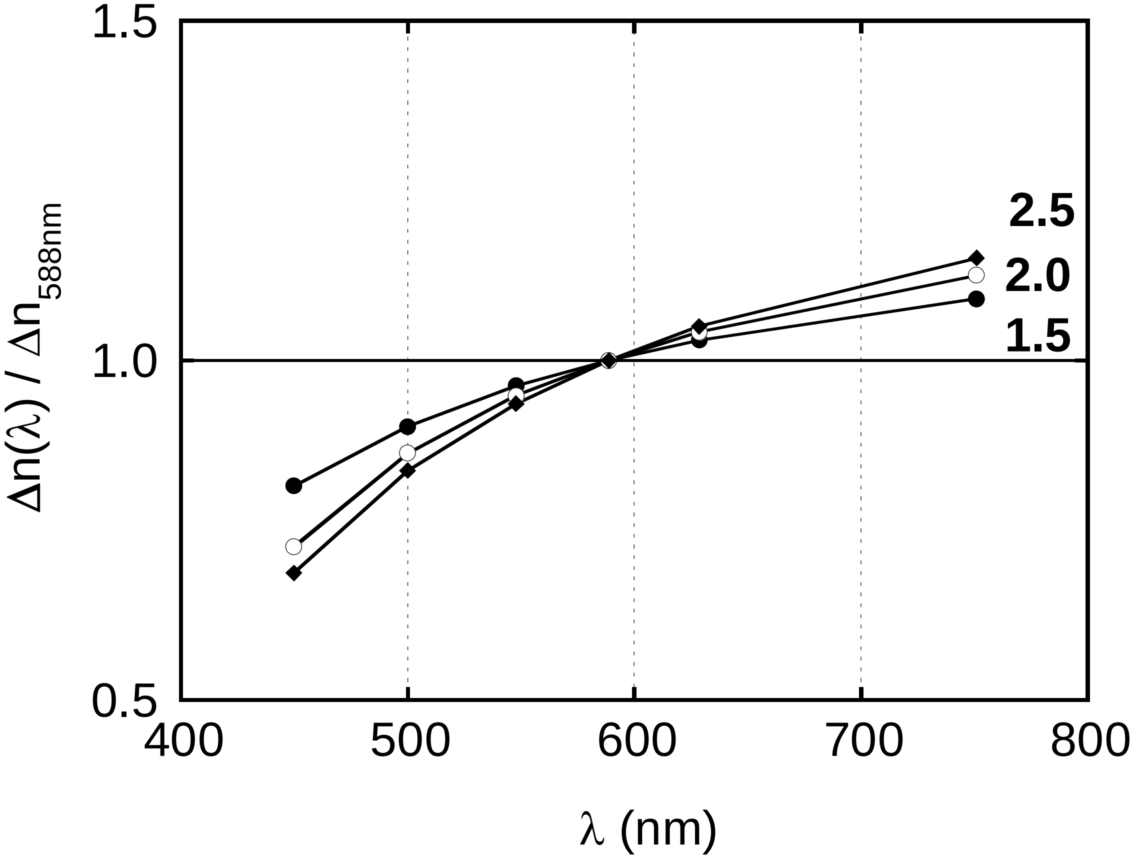

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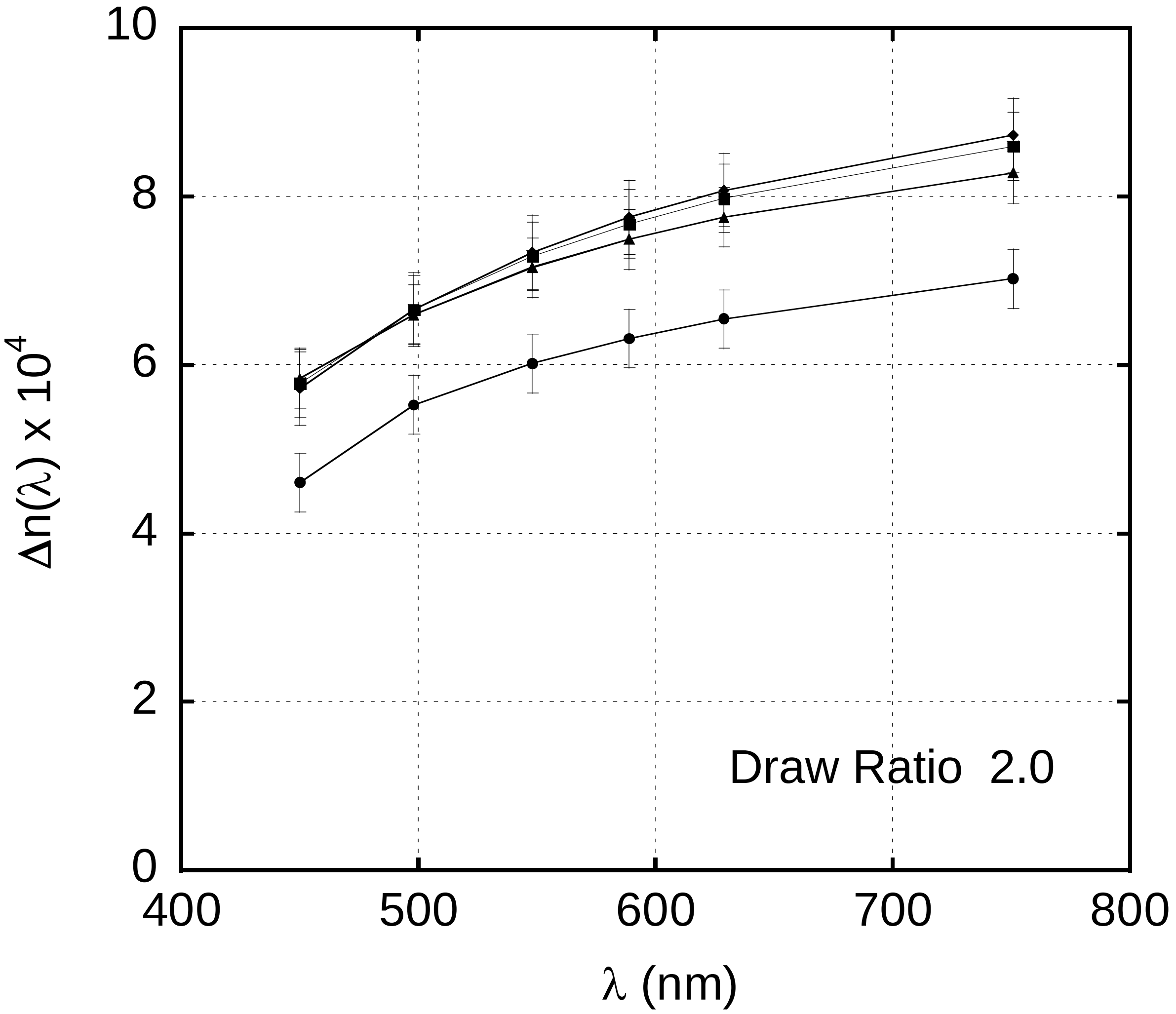

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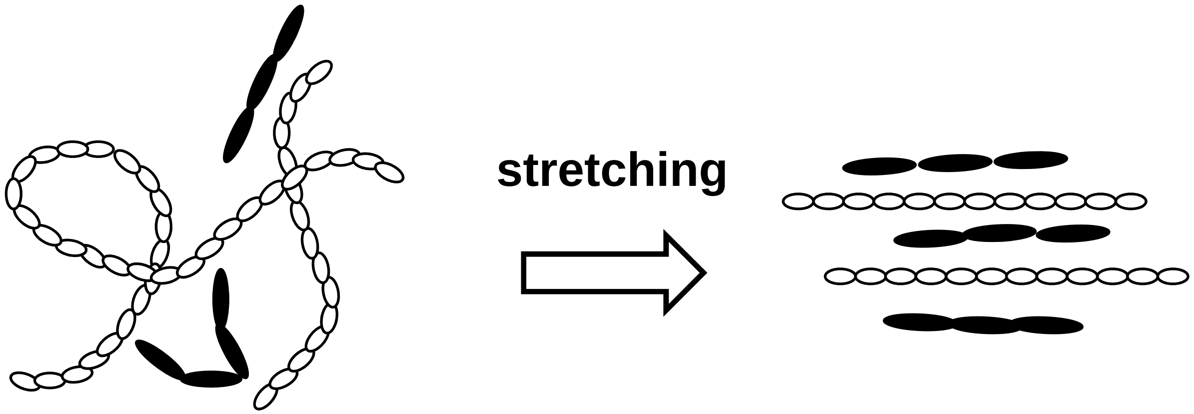
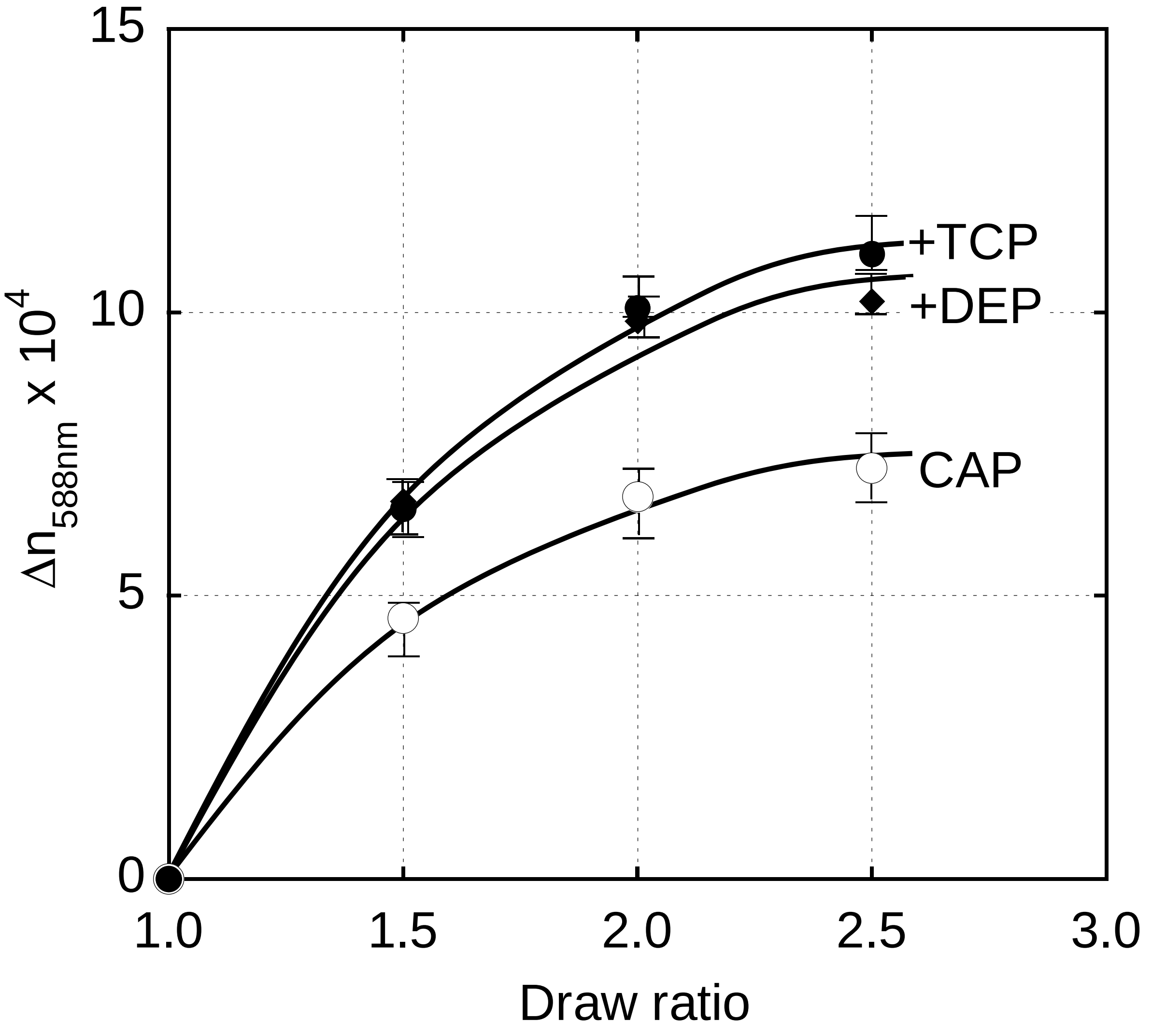


Yamaguchi et al., Figure 14



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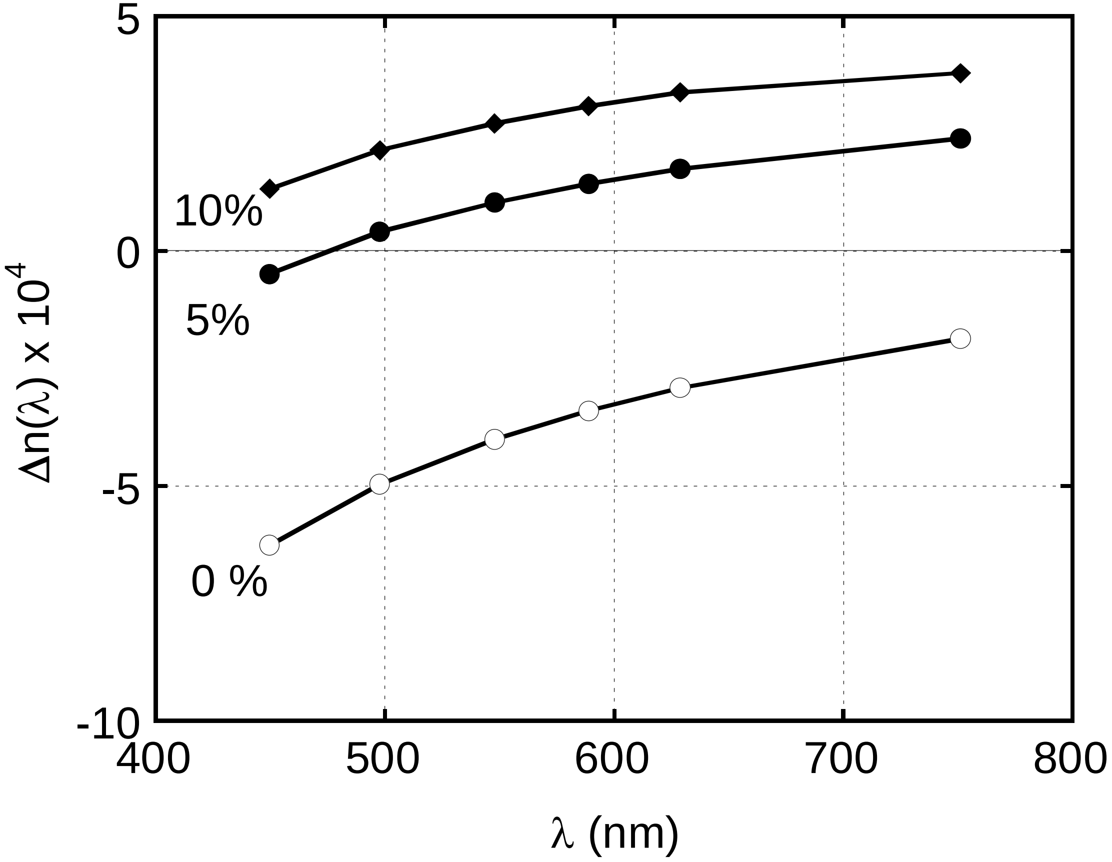

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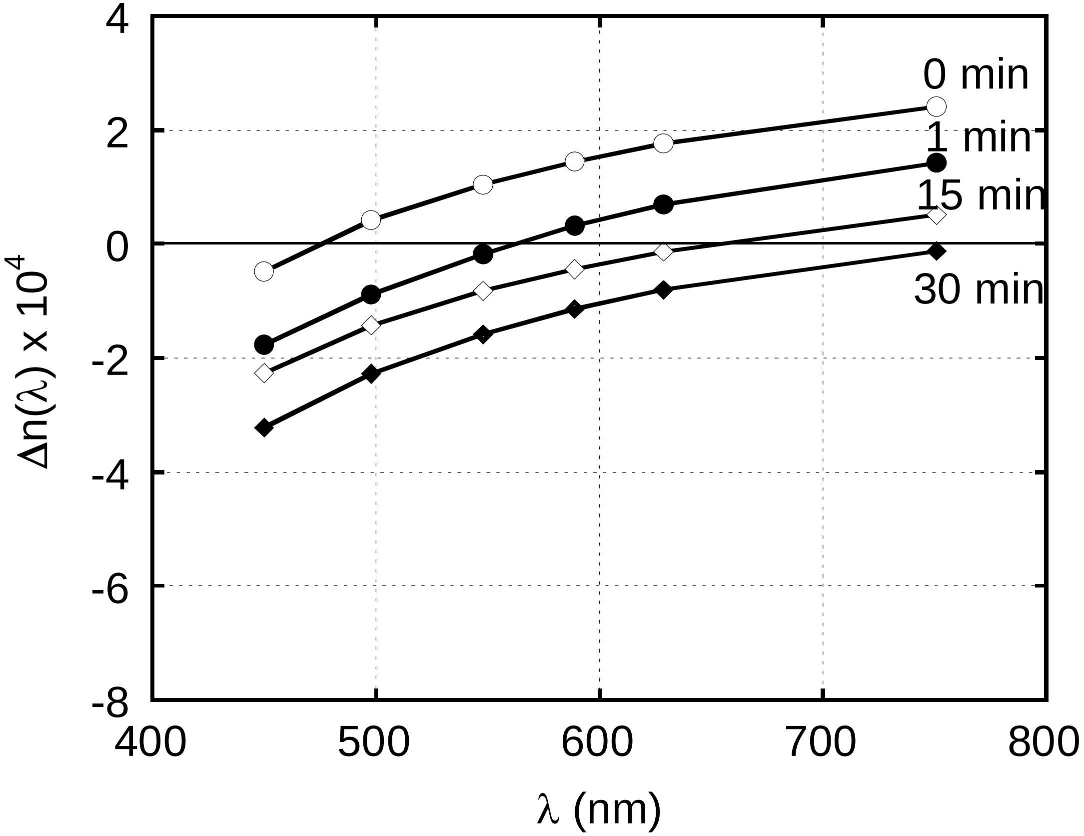
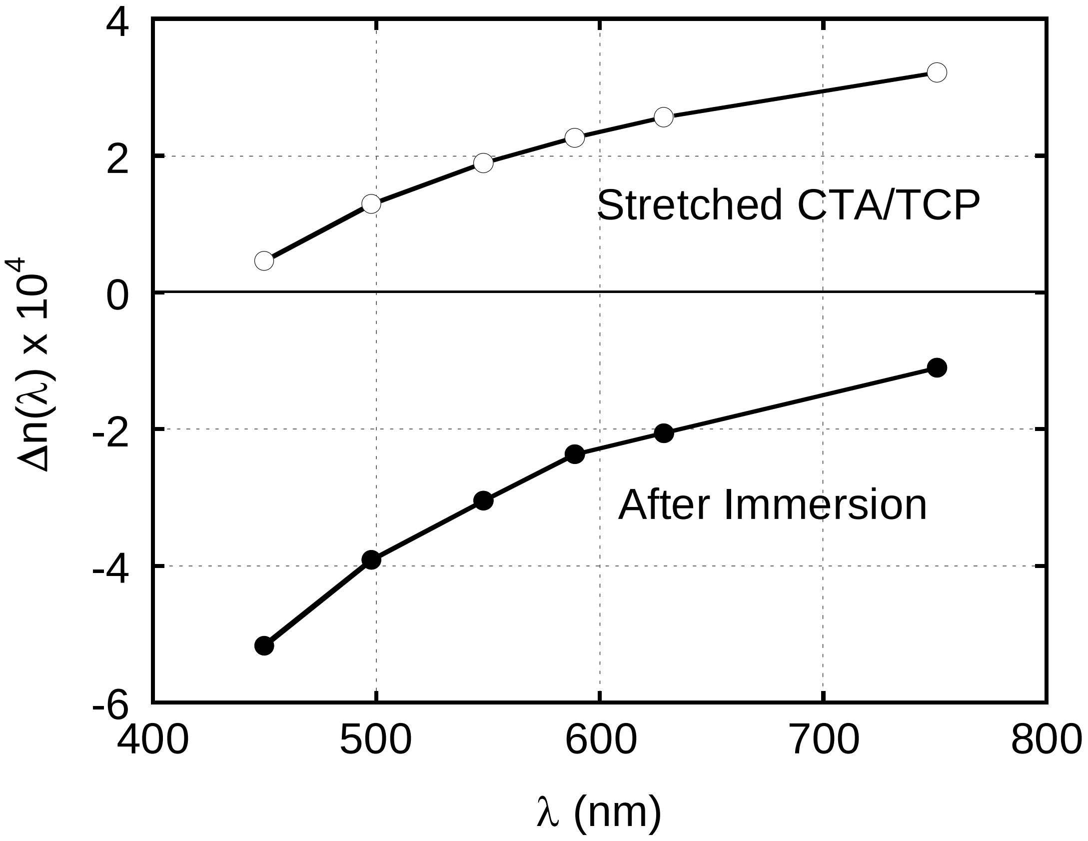


Yamaguchi et al., Figure 17



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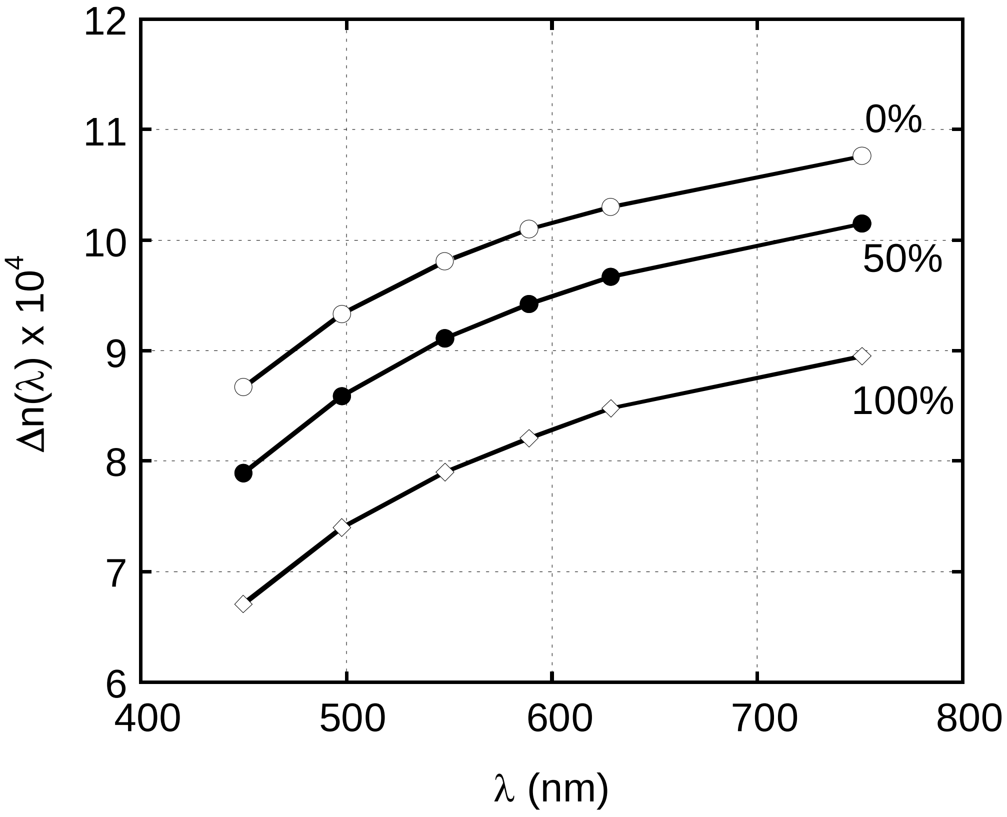

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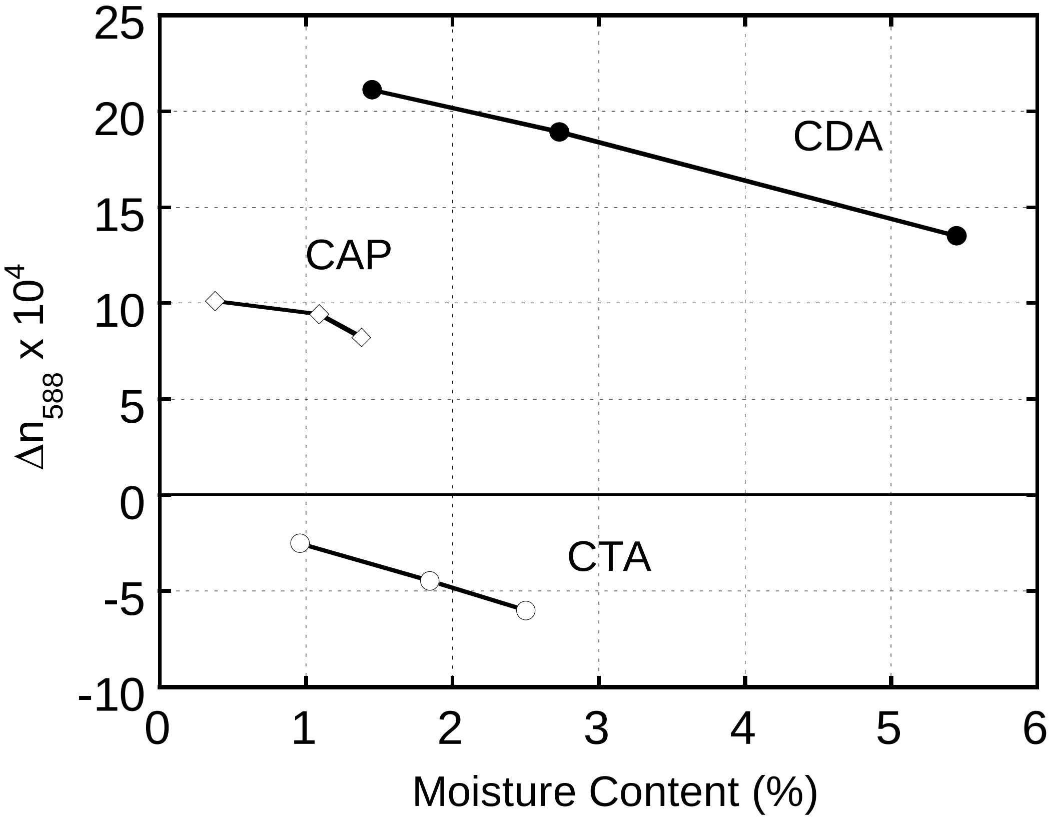

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