Pulp Production and Processing: From Papermaking to High-Tech Products

Editor

Valentin I. Popa

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12 Optical Properties of Cellulose Esters and Applications to Optical Functional Films

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12.1 Optical Properties of Polymeric Materials

The refractive index is one of the most important optical properties for transparent materials, which is defined as the ratio of the optical velocity in vacuum to that in a medium. Therefore, the value is always larger than 1 and decides the refractive angle as expressed by the well-known Snell's law. Materials with a high refractive index are preferably employed as lenses, whereas clothes made of fibres with a low refractive index provide a 'deep' colour, due to the low level of reflection. Since cellulose esters have a relatively low refractive index, which is similar to that observed in silk, some of them are employed for specific clothes that require a 'deep' black effect.

Cellulose esters are also employed for optical displays such as a liquid crystal display. In this application, various types of polymer films are required to construct a display, such as antiglare film, retardation film, protective film, brightness enhancement film and diffusion film. In particular, polarisation is an extremely important property for retardation and protective films.

This property is expressed by birefringence Δn. In the case of oriented polymer films, the birefringence can be controlled by varying the stretching ratio. Consequently, it is always used for a retardation film that gives a specific retardation ($\Gamma = d \Delta n$; d is the film thickness). Another important optical film used in displays is the protective film, which is used to protect a polariser from moisture. Therefore, it has to be free from birefringence so that the polarised light will not be disturbed.

In the case of retardation films used in a colour display, retardation not only at a specific wavelength, but also in the broad range of visible light has to be controlled. For example, the absolute value of birefringence must show an increase with increasing the wavelength for wavelength-phase difference plates, such as a quarter-wave plate and a half-wave plate. This property is known as 'extraordinary wavelength dispersion' of birefringence. These days, a multiband quarter-wave plate, one of the retardation

films that gives a retardation of a quarter of a wavelength, is required because it is used for advanced display devices, i.e., as glasses for a 3D-display and antifilms for an electroluminescent display. Conventional polymers however, show ordinary dispersion, in which the orientation birefringence increases with the wavelength. This behaviour can be expressed by the following equation which was proposed based on the Sellmeier relation, **Equation 12.1**:

$$n(\lambda)^2 = 1 + \sum_i \frac{A_i}{\lambda^2 - B_i} \tag{12.1}$$

where λ and $n(\lambda)$ are the wavelength of light and the average refractive index, respectively. A and B are the Sellmeier coefficients.

Based on the Kuhn and Grün model proposed for the stress-optical behaviour of crosslinked rubbers, the orientation birefringence $\Delta n(\lambda)$ of an oriented polymer is expressed as follows [1–6]:

$$\Delta n(\lambda) = \frac{2\pi}{9} \frac{(n(\lambda)^2 + 2)^2}{n(\lambda)} N \, \Delta\alpha(\lambda) \left(\frac{3\langle\cos^2\theta\rangle - 1}{2} \right) \tag{12.2}$$

where N, $\Delta\alpha(\lambda)$ and θ are the number of chains in a unit volume, the polarisability anisotropy and the angle that a segment makes with the stretch axis, respectively. The last bracketed term $(3\langle\cos^2\theta\rangle - 1)/2$ is identically equal to the Hermans orientation function [3, 7], whereas the other part in the right hand side of the term is called intrinsic birefringence, which is independent of the molecular weight and determined by the chemical structure of the monomer unit. Consequently, **Equation 12.2** can be written as:

$$\Delta n(\lambda) = \Delta n^0(\lambda) F \tag{12.3}$$

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

Considering that stress in the rubbery state is originated from the entropy loss by chain orientation, the following stress-optical rule is derived:

$$\Delta n(\lambda) = C\sigma \tag{12.4}$$

$$C = \frac{2\pi}{45k_B T} \frac{(n(\lambda)^2 + 2)^2}{n(\lambda)} \Delta\alpha(\lambda) \tag{12.5}$$

where σ is the stress, C is the stress-optical coefficient and k_B is the Boltzmann constant.

Regarding the wavelength dispersion, the following simple relation is derived:

$$\frac{\Delta n(\lambda)}{\Delta n(\lambda_0)} = \frac{\Delta n^0(\lambda)}{\Delta n^0(\lambda_0)} = const. \tag{12.6}$$

where λ_0 is the arbitrary standard wavelength.

According to **Equation 12.6**, the wavelength dispersion of birefringence, i.e., normalised birefringence $\Delta n(\lambda)/\Delta n(\lambda_0)$, is a constant and determined by the chemical structure.

Both **Equation 12.1** and **Equation 12.6** demonstrate that it is extremely difficult to obtain a polymeric film exhibiting extraordinary wavelength dispersion of the orientation birefringence. For example, the orientation birefringence of stretched films of polycarbonate (PC) is shown in **Figure 12.1**. As seen in the figure, the absolute values of the birefringence decrease with the wavelength. The wavelength dispersion of the birefringence is therefore, contrary to that of an ideal wavelength phase different plate. Furthermore, the wavelength dispersion of birefringence is also independent of the draw ratio as demonstrated in **Figure 12.1**, in which both curves of the normalised orientation birefringence fall on one line.

However, some stretched films of cellulose esters are known to show extraordinary wavelength dispersion. In this chapter, the wavelength dispersion of orientation birefringence for cellulose esters is discussed in detail, after a brief introduction on the concept of controlling the optical anisotropy. Finally, an advanced method to obtain the extraordinary dispersion of the orientation birefringence is proposed.
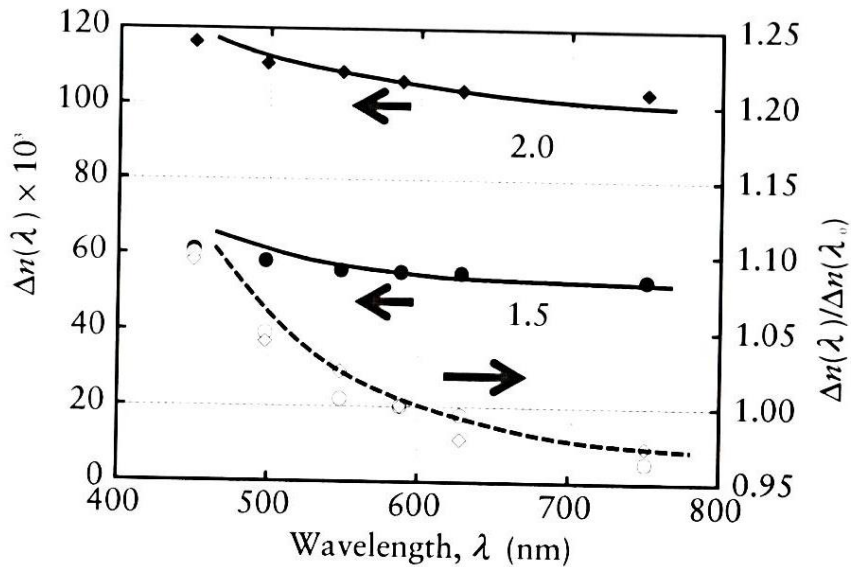
Figure 12.1 Wavelength dependence of (closed symbols) orientation birefringence and (open symbols) normalised orientation birefringence for stretched PC films at draw ratios of (circles) 1.5 and (diamonds) 2.0

12.2 Wavelength Dispersion of Orientation Birefringence

An ideal wavelength phase difference plate shows a consistent retardation value, e.g., quarter wavelength ($\lambda/4$), over a wide range of visible light. As retardation is given by the product of birefringence and thickness, a retardation film must show an increase in birefringence with increasing wavelength. Industrially, the so-called extraordinary dispersion of the orientation birefringence is achieved by piling together two or more polymer films of different wavelength dispersion, with their fast axes set to be perpendicular to each other, as illustrated in **Figure 12.2**. By rotating one of the films at 90°, its fast direction is converted into the slow one ($B_{\parallel} \rightarrow B_{\perp}$) and the combination of the birefringence from these films yields extraordinary wavelength dispersion of orientation birefringence. However, as two or more films are stuck together to produce the required retardation, the adhesion process requires intense care regarding the direction of the optical axes and is rather costly. Thus, having a single material that shows extraordinary dispersion of orientation birefringence is desired as the cost production and thickness can be reduced.

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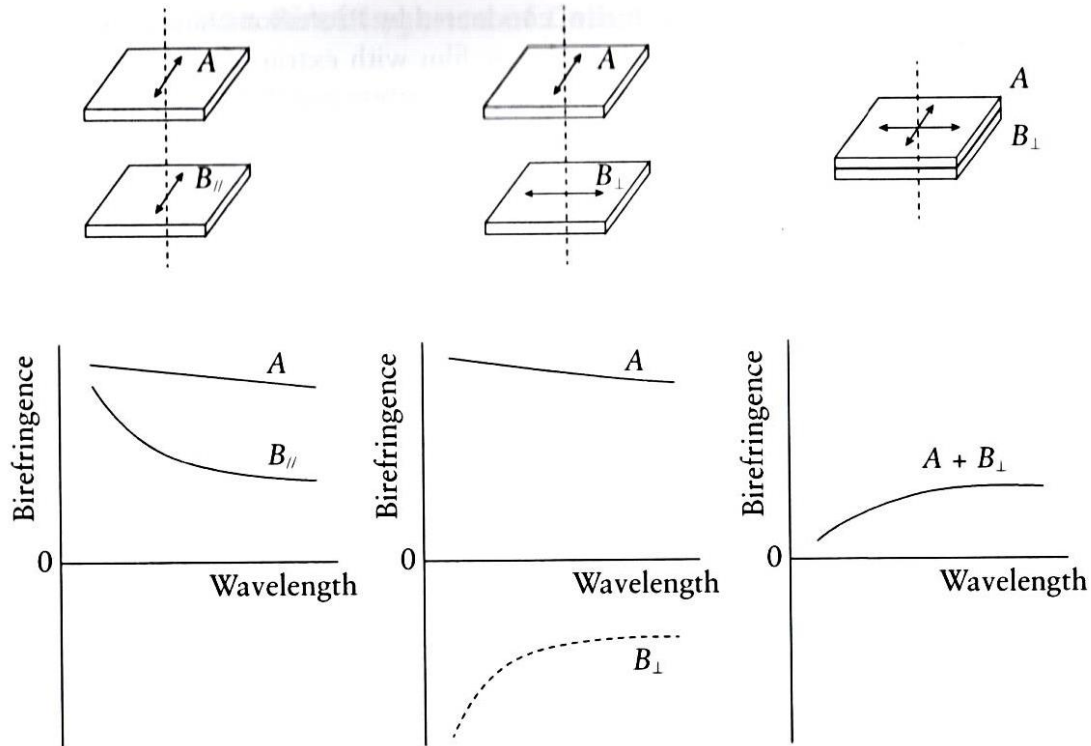
Figure 12.2 Combination of two films having different wavelength dispersion to produce an extraordinary wavelength dispersion of orientation birefringence

The polymer blend method has been employed as a means of controlling birefringence in polymers. Uchiyama and Yatabe [8, 9] have successfully produced polymer films with extraordinary wavelength dispersion of orientation birefringence by using a miscible blend 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 birefringence with weak wavelength dependence. Although both polymers show ordinary wavelength dispersion, blends of certain composition exhibit extraordinary wavelength dispersion due to the summation of the contributions from both polymers as follows:

$$\Delta n = \Delta n_F + \sum_i \phi_i \Delta n_i \tag{12.7}$$

where i refers to the i-th component, ϕ_i is the volume fraction and Δn_F is the birefringence arising from structural or deformation effects.

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Additional research carried out in Japan, conducted by Professor Ougizawa and co-workers [10], obtained a transparent polymer film with extraordinary wavelength dispersion from a miscible blend comprising of polynorbornene (NB) and poly(styrene-*co*-maleic anhydride) (SMA) at appropriate blend ratios. As predicted from the chemical structure, NB has a positive birefringence with weak wavelength dispersion, while SMA has a negative birefringence with strong wavelength dispersion.

A specific copolymer also shows extraordinary wavelength dispersion, which was first demonstrated by Uchiyama and Yatabe [11], when employing two monomers such as 2,2-*bis*(4-hydroxyphenyl)propane (BPA) and 9,9-*bis*(4-hydroxy-3-methylphenyl) fluorine (BMPF). Similar to the blend method, one monomer (BPA) has a positive birefringence with weak wavelength dispersion, while the other (BMPF) has a negative birefringence with a strong dispersion for the copolymer.

In principle, the extraordinary wavelength dispersion of birefringence produced by the blend and copolymerisation techniques is achieved by using a similar concept to that of the piling method (**Figure 12.2**) as illustrated in **Figure 12.3** below.
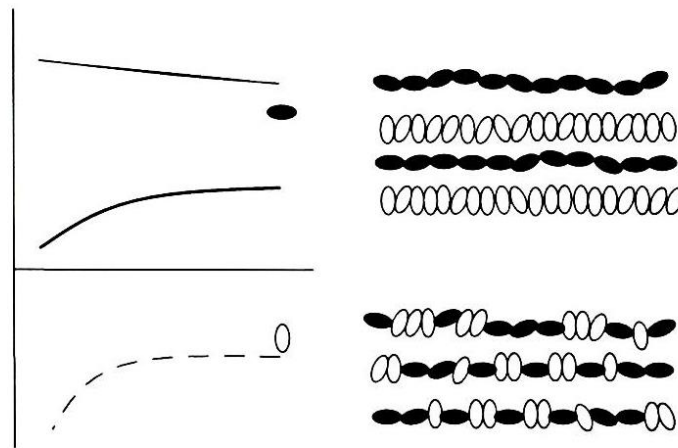

Figure 12.3 Illustration of the miscible blend and random copolymerisation methods to produce extraordinary wavelength dispersion of orientation birefringence. Reproduced with permission from M. Yamaguchi, M.E.A. Manaf, K. Songsurang and S. Nobukawa, *Cellulose*, 2012, **19**, 3, 601. ©2012, Springer [12]

Addition of needle-shaped solid particles demonstrating strong optical anisotropy also modifies the orientation birefringence and its wavelength dispersion, as reported by Koike and co-workers [13].

12.3 Orientation Birefringence of Cellulose Esters

Interestingly, some cellulose esters have been known to show extraordinary wavelength dispersion of orientation birefringence. The wavelength dispersions of orientation birefringence for various types of films of cellulose esters stretched at a draw ratio of 2.0 are shown in **Figure 12.4** [14]. The numerals in the cellulose acetate butyrate (CAB) samples represent the weight fraction (wt%) of the butyryl group. All samples were uniaxially stretched at a temperature where the storage modulus at 10 Hz was 10 MPa, in order to provide the same stress level for all samples having different glass transition temperatures. Except for cellulose triacetate (CTA), all CAB, cellulose acetate propionate (CAP) and cellulose diacetate (CDA) samples employed in this experiment exhibited a positive birefringence with extraordinary wavelength dispersion. Among them, CDA showed the largest value of orientation birefringence indicating the significant contribution of the hydroxyl group to positive birefringence. CTA shows negative birefringence with ordinary dispersion, in agreement with the result by El-Diasty and co-workers [15]. The result demonstrates that the acetyl group provides negative birefringence.
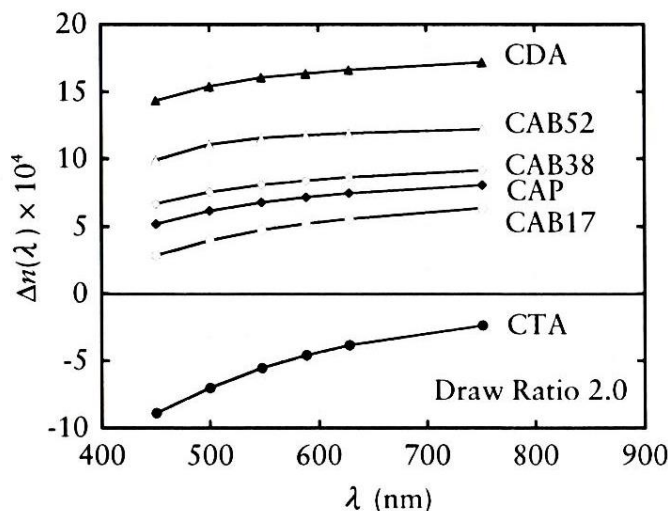
Figure 12.4 Wavelength dependence of orientation birefringence for stretched films of various cellulose esters. The numerals in the CAB label represent the weight concentration of the butyryl group. The degree of substitution of the propionyl group in CAP is 2.58, and those of the butyryl group are 0.73, 1.74 and 2.64 for CAB17, CAB38 and CAB52, respectively. Reproduced with permission from M. Yamaguchi, K. Okada, M.E.A. Manaf, Y. Shiroyama, T. Iwasaki and K. Okamoto, *Macromolecules*, 2009, 42, 22, 9034. ©2009, ACS Publications [14]

The contribution of the hydroxyl and acetyl groups in CDA were calculated from the experimental results of CTA and CDA using the same relation as **Equation 12.6**, assuming: (i) orientation relaxation is ignored; (ii) contribution of the main chains is ignored; (iii) contribution of the crystalline part of CTA is ignored; and (iv) both hydroxyl and acetyl groups have the same orientation function in CTA and CDA at a constant draw ratio. As seen in **Figure 12.5**, the considerable contribution of the hydroxyl group is confirmed, although the molar content in CDA is lower than that of the acetyl group.
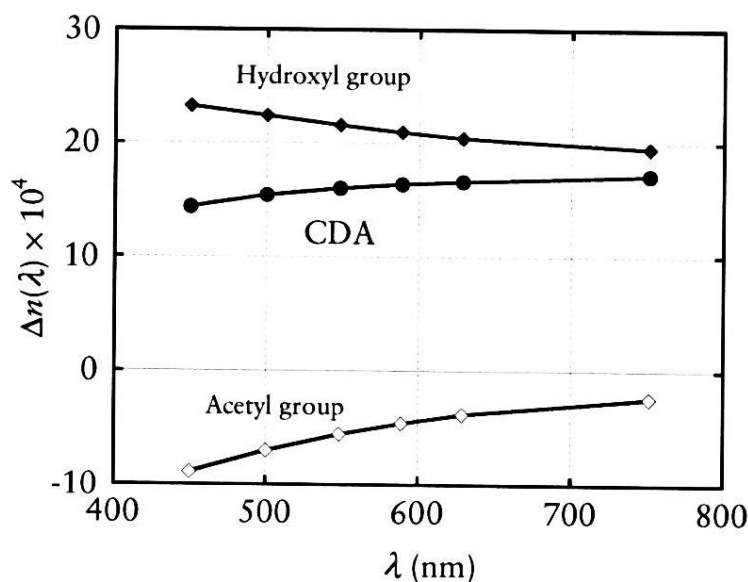
Figure 12.5 Contribution of (closed diamonds) hydroxyl and (open diamonds) acetyl groups to the orientation birefringence of (closed circles) CDA at a draw ratio of 2.0. The birefringence values of both groups are derived from the experimental results of CTA and CDA. Reproduced with permission from M. Yamaguchi, K. Okada, M.E.A. Manaf, Y. Shiroyama, T. Iwasaki and K. Okamoto, *Macromolecules*, 2009, **42**, 22, 9034. ©2009, ACS Publications [14]

Furthermore, it was found that the positive birefringence increases upon increasing the butyryl content, as evidenced in **Figure 12.6** (plotted against the degree of substitution of butyryl or propionyl, S_b) [16]. The figure indicates that CAB with an S_b of 0.35 of the butyryl group content shows no birefringence. Moreover, the figure shows that the butyryl group has a stronger impact on the birefringence than the

propionyl group, since the data of CAP is displaced downward from the solid line. As mentioned in **Figure 12.5** however, the hydroxyl group significantly affects the orientation birefringence. Therefore, the concentration of the hydroxyl group should always be considered in addition to the butyryl or propionyl content.
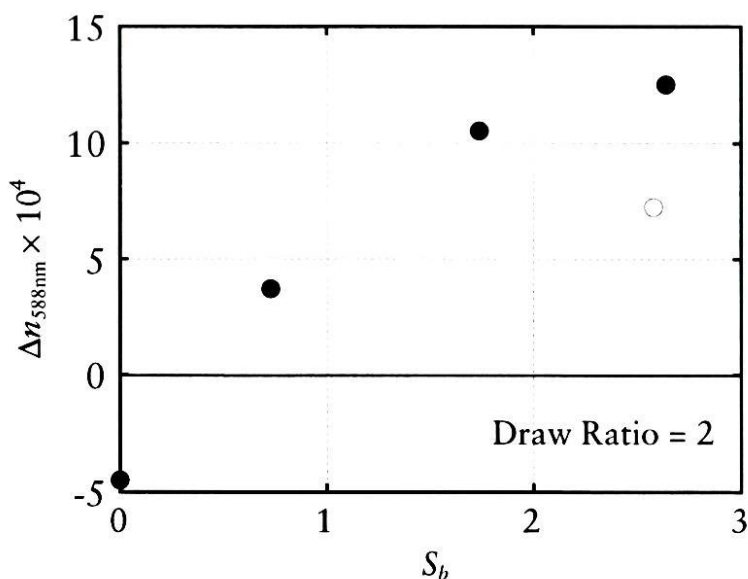
Figure 12.6 Orientation birefringence at a draw ratio of 2 plotted against the degree of substitution of the butyryl group, S_b, for CAB (closed symbols). The open symbol denotes the data for CAP plotted against the degree of substitution of the propionyl group. Reproduced with permission from M. Yamaguchi, M.E.A. Manaf, K. Songsurang and S. Nobukawa, *Cellulose*, 2012, **19**, 3, 601. ©2012, Springer [12]

The effect of the species of ester groups on the wavelength dispersion is evaluated from the normalised orientation birefringence as shown in **Figure 12.7**. Data for CAB38, which is located between those for CAB17 and CAB52, is omitted in the figure for a better view of the results. It is obvious that the acetyl group shows the strongest wavelength dependence. As shown in the figure, the slope of the normalised orientation birefringence of CAP is larger than that of CAB52, although both contain a similar level of the degree of substitution of ester groups. This suggests that the propionyl group provides a stronger wavelength dependence of the birefringence than the butyryl group. Furthermore, the wavelength dependence of the normalised

orientation function becomes weaker as the butyryl content is increased. This is reasonable due to the weak wavelength dependence of the butyryl group.
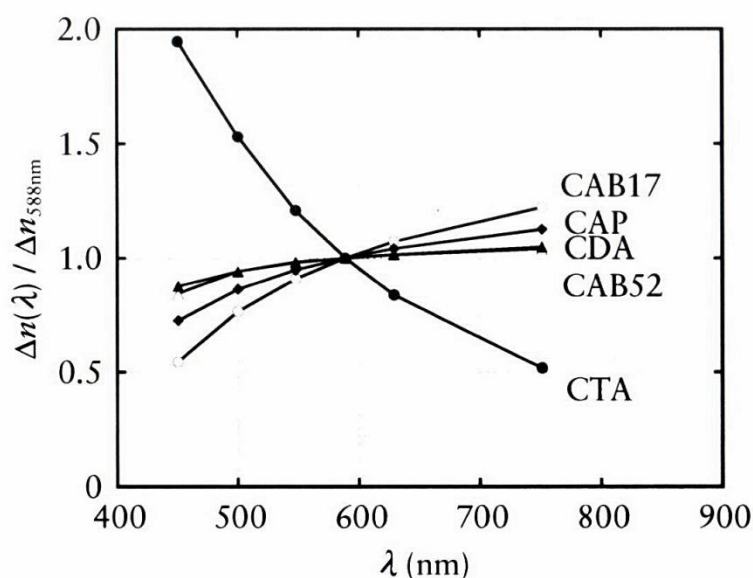
Figure 12.7 Wavelength dependence of orientation birefringence for stretched films of various cellulose esters. The numerals in the CAB label represent the weight concentration of the butyryl group. The degree of substitution of the propionyl group in CAP is 2.58, and those of the butyryl group are 0.73 and 2.64 for CAB17 and CAB52, respectively. Reproduced with permission from M. Yamaguchi, K. Okada, M.E.A. Manaf, Y. Shiroyama, T. Iwasaki and K. Okamoto, *Macromolecules*, 2009, **42**, 22, 9034. ©2009, ACS Publications [14]

Regarding the wavelength dependence of the ester groups, the following relation is expected:

$$-\frac{d(\Delta n(\lambda))}{d\lambda}\bigg|_{Acetyl} > \frac{d(\Delta n(\lambda))}{d\lambda}\bigg|_{Propionyl} > \frac{d(\Delta n(\lambda))}{d\lambda}\bigg|_{Butyryl} \tag{12.8}$$

The orientation function F of the pyranose ring in the CAP film was evaluated by the infrared dichroic ratio D ($= A_{//}/A$) of the absorption band at 880 cm^{-1}, whose electric

vector is perpendicular to the main chain. It was found not to be proportional to $-(D-1)/(D+2)$, as seen in **Figure 12.8** [14]. As $(D-1)/(D+2)$ is proportional to the Hermans 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 the main chains, but rather by the species and the concentration of the hydroxyl and ester groups. Consequently, the orientation birefringence of CAP is mainly determined by the following relation:

$$\Delta n(\lambda) = \Delta n_A^0(\lambda)F_A + \Delta n_P^0(\lambda)F_P + \Delta n_{OH}^0(\lambda)F_{OH} \tag{12.9}$$

where $\Delta n_A^0(\lambda)$, $\Delta n_P^0(\lambda)$ and $\Delta n_{OH}^0(\lambda)$ are the intrinsic birefringences, and F_A, F_P and F_{OH} are the orientation functions of the acetyl, propionyl and hydroxyl groups, respectively. The contribution of the hydroxyl group is of course neglected, when esterification is completed for all hydroxyl groups in the initial cellulose.
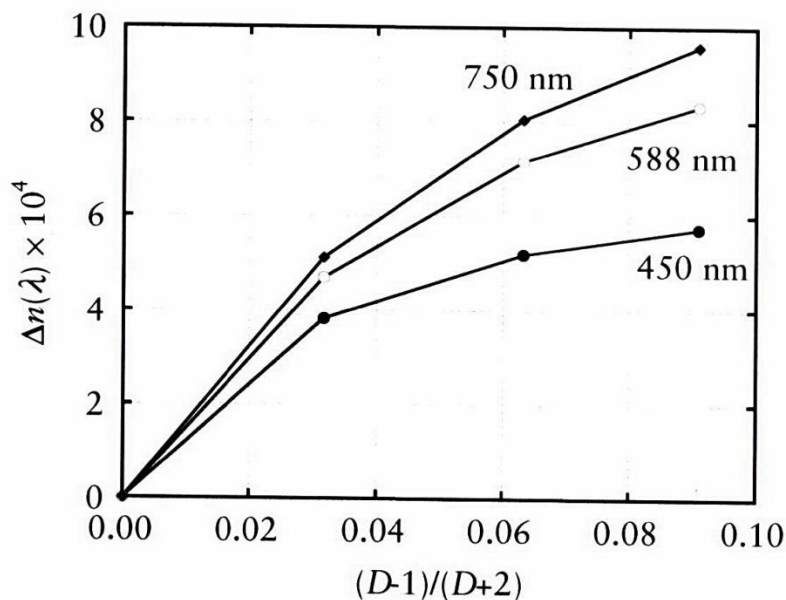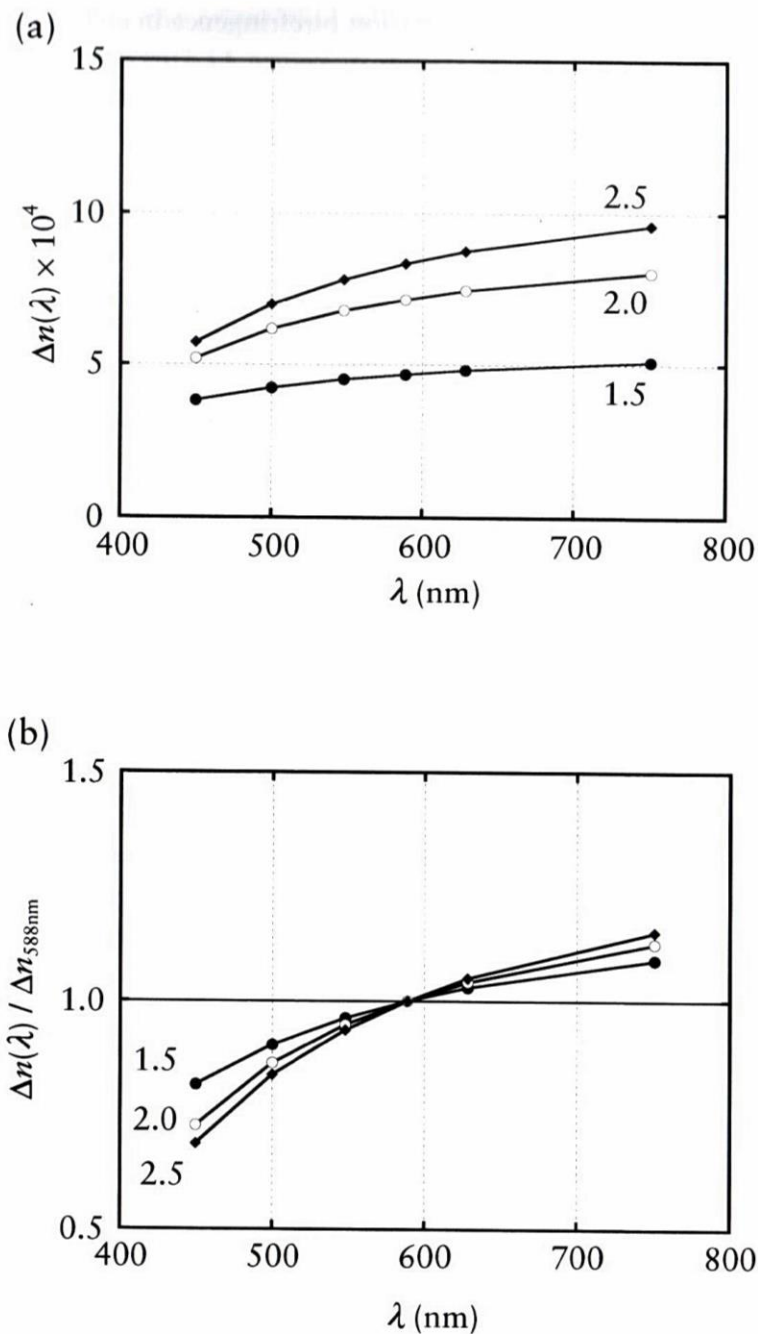

Figure 12.8 Relation between $(D-1)/(D+2)$ and orientation birefringence at various wavelengths. Reproduced with permission from M. Yamaguchi, K. Okada, M.E.A. Manaf, Y. Shiroyama, T. Iwasaki and K. Okamoto, *Macromolecules*, 2009, **42**, 22, 9034. ©2009, ACS Publications [14]

As mentioned previously, the fact that CTA shows negative orientation birefringence with ordinary dispersion suggests that the acetyl group provides negative orientation birefringence. On the contrary, the propionyl and butyryl groups, as well as the hydroxyl group, provide positive birefringence with weak wavelength dispersion. Therefore, it can be concluded that the extraordinary wavelength dispersion, as observed in some cellulose esters, is attributed to the combination of negative and positive birefringences having different wavelength dependence. Furthermore, it is indicated that the flexible and bulky methylene parts of the ester groups with longer alkyl chains, such as propionyl and butyryl, lead to the parallel orientation of the polarisability anisotropy along the flow direction, whereas those of the acetyl group orient perpendicular to the flow direction.

The formation of the extraordinary wavelength dispersion of orientation birefringence in cellulose esters such as CAP is illustrated in **Figure 12.9** [14]. In the figure, the polarisability anisotropy of the ester groups, i.e., acetyl and propionyl are represented by ellipsoids. As depicted in the figure, the addition of both components, denoted by a bold line, gives the extraordinary dispersion with a positive orientation birefringence, when the wavelength dependence of the propionyl group is weaker than that of the acetyl group. This is similar to the formation of the extraordinary wavelength dispersion of birefringence as observed in the miscible blend as well as random copolymerisation methods. In the case of CDA, the dark circles represent the hydroxyl groups.
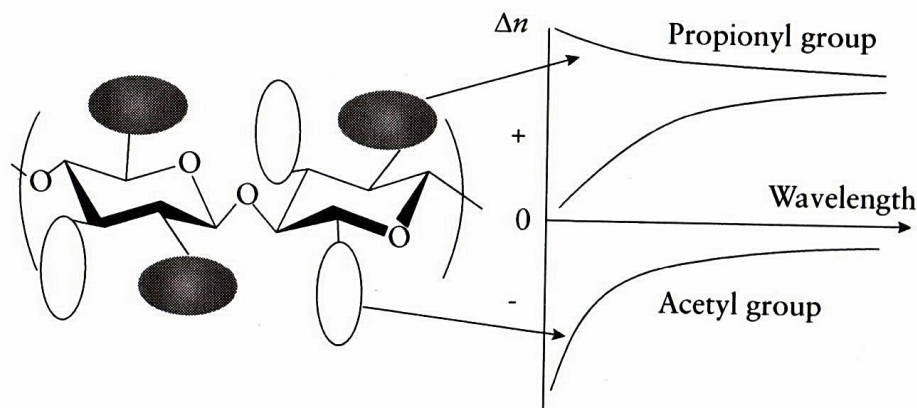
Figure 12.9 Illustration of CAP molecules and the contribution of each ester group to the orientation birefringence. Reproduced with permission from M. Yamaguchi, K. Okada, M.E.A. Manaf, Y. Shiroyama, T. Iwasaki and K. Okamoto, *Macromolecules*, 2009, **42**, 22, 9034. ©2009, ACS Publications [14]

(a)

(b)

Figure 12.10 Wavelength dependence of (a) orientation birefringence and (b) normalised orientation birefringence of stretched CAP at various draw ratios: (closed circles) 1.5, (open circles) 2.0 and (closed diamonds) 2.5. Reproduced with permission from M. Yamaguchi, K. Okada, M.E.A. Manaf, Y. Shiroyama, T. Iwasaki and K. Okamoto, *Macromolecules*, 2009, 42, 22, 9034. ©2009, ACS Publications [14]

The wavelength dispersion of the orientation birefringence in cellulose esters is also dependent upon the draw ratio as shown in **Figure 12.10** [14]. It is obvious that the extraordinary dispersion becomes pronounced upon increasing the draw ratio, which is not observed in a conventional polymer as discussed earlier (**Figure 12.1**). Considering that the acetyl group shows a strong wavelength dispersion, the result indicates that the contribution of the acetyl group, i.e., $F_A/(F_A+F_P)$, increases with the draw ratio. From an industrial point of view, the phenomenon indicates that the wavelength dispersion can be controlled by stretching conditions such as the degree of stretching (draw ratio), stretching temperature and stretching speed, which is extremely important information for the actual application.

12.4 Advanced Methods to Control Orientation Anisotropy

It has been revealed that the orientation birefringence of a polymer film is modified by the addition of a low-mass compound exhibiting strong optical anisotropy. Upon stretching, low-mass compounds, which are dissolved in a polymer matrix, are forced to orient in the same direction as the polymer chains by intermolecular orientation correlation called 'nematic interaction' [17, 18]. This intermolecular interaction was originally used to explain the orientation relaxation of a short chain in a polymer melt with a broad molecular weight distribution. It has since been clarified that the nematic interaction is expected to occur in a polymer blend system as long as the system is miscible. Quantitative studies on the nematic interaction in miscible polymer blends have been carried out by Urakawa and co-workers [19–22] based on the orientation coupling theory [23]. This technique uses miscible blends which can be employed to modify the wavelength dispersion of orientation birefringence. Yamaguchi and co-workers studied the effect of a small addition of poly(lactic acid) (PLA) on the orientation birefringence of CAP. They found that PLA is miscible with CAP on a molecular scale when the amount of PLA is less than 3 wt% [24]. Moreover, the orientation birefringence of CAP is greatly enhanced even upon a small addition of PLA as shown in **Figure 12.11**. Considering that the relaxation times are 0.045 s for PLA and approximately 1,000 s for CAP at the stretching temperature, the high level of orientation of PLA chains without relaxation is attained by the cooperative alignment (nematic interaction) with CAP chains. The study indicates that a retardation film having a high level of birefringence, leading to a thin film, can be designed by polymer blends composed of only biomass-based materials. Furthermore, the blends with more than 3 wt% of PLA exhibit large haze values, indicating the existence of phase-separated morphology, as previously reported by Tatsushima and co-workers [25]. As a result, the blends lose transparency and show a 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 when compared with CAP, as illustrated in **Figure 12.12**. As demonstrated for this method, attention has to be focused on the miscibility. Yamaguchi and Masuzawa found that CAP is miscible with poly(vinyl acetate) (PVAc) which has a negative orientation birefringence [26]. Although they only showed that the birefringence at a specific wavelength decreases with the PVAc content, the wavelength dispersion must be modified. They also revealed that poly(epichlorohydrin), having a negative birefringence, is miscible with CAP [27]
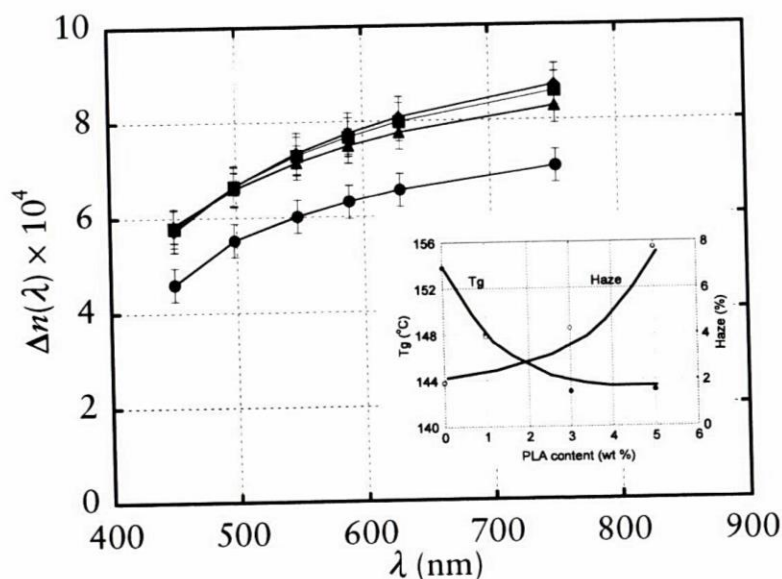
Figure 12.11 Wavelength dependence of orientation birefringence for CAP and CAP/PLA blends stretched at a draw ratio of 2.0: (circles) PLA, (diamonds) 1 wt% of PLA, (triangles) 3 wt% of PLA and (squares) 5 wt% of PLA. The relation between PLA content with regard to the Tg and haze value of the blend are shown in the subfigure. Reproduced with permission from M. Yamaguchi, S. Lee, M.E.A. Manaf, M. Tsuji and T. Yokohara, *European Polymers Journal*, 2010, **46**, 12, 2269. ©2010, Elsevier [24]

Besides polymeric materials, plasticisers such as diethyl phthalate (DEP) and tricresyl phosphate (TCP) are effective in modifying the orientation birefringence of cellulose esters [28–30]. This phenomenon is also attributed to nematic interaction. The degree of modification depends on the intrinsic birefringence of the plasticiser, as well as the nematic interaction coefficient between the plasticiser and the host polymer. Such a

phenomenon is also observed in a solution-cast film [29]. Moreover, some low-mass compounds contribute negative orientation birefringence, when the optical slow axis is perpendicular to the long axis of the low-mass compound [30]. Using a low-mass compound such as a plasticiser is of great benefit, because there are numerous miscible systems due to the large mixing entropy. Because both TCP and DEP contribute to positive orientation birefringence, their incorporation into CTA, which has a negative birefringence with ordinary dispersion, results in the blends having extraordinary wavelength dispersion. **Figure 12.13** shows the orientation birefringence of pure CTA and CTA with 5 and 10 wt% of TCP. CTA with 10 wt% of TCP shows extraordinary wavelength dispersion, in which the orientation birefringence shows almost an ideal dispersion (indicated by the straight dotted line) as required for a multiband quarter-wave plate [31]. Since the molecular shape of TCP is disc-like, more effective rod-shaped low-mass compounds with strong optical anisotropy will be found in the near future. Preliminary experimental results have been reported by our research group [32].
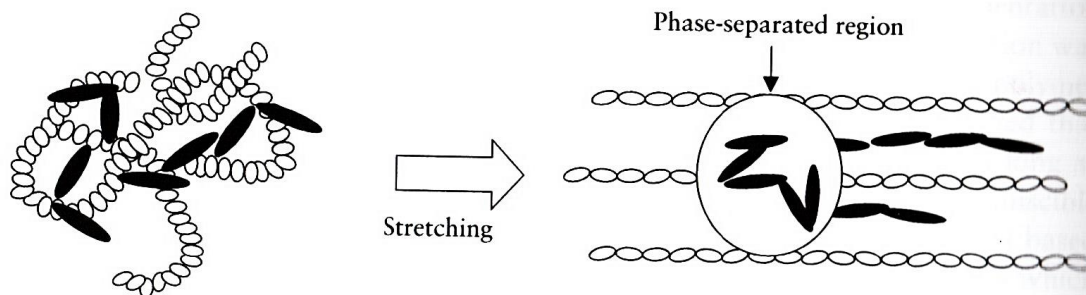

Figure 12.12 Phenomenon of the relaxation of PLA in the phase-separated region for the CAP/PLA blends with above 3 wt% of PLA, illustrated using polarisability anisotropy of (open ellipsoids) CAP and (closed ellipsoids) PLA

Although the orientation of the main chain does not directly affect the orientation birefringence of cellulose esters, it has an impact on the orientation of the ester groups as well as the hydroxyl group. Furthermore, the orientation of the main chain strongly affects the nematic interaction with low-mass compounds. Therefore, the main chain orientation, which is proportional to the stress, should be considered even for cellulose esters. For a better understanding, the effect of stress relaxation on the orientation birefringence was studied by holding the stretched sample in a hot chamber at various residence times [31]. We found that the orientation birefringence decreases monotonically with increasing holding time after stretching. Furthermore, there is

no further decrease in the orientation birefringence above a 30 min holding time. The results suggest that the TCP molecules relax the orientation when left at a high temperature without being quenched. In order to further confirm the contribution of TCP, the stretched sample of the CTA/TCP (95/5) blend was immersed in methanol for 24 h to remove TCP, and the orientation birefringence was measured. There was no considerable change in the dimension of the sample after 24 h of immersion, suggesting there is almost no alteration in the degree of stretching upon immersion in methanol. Furthermore, it was confirmed by IR spectral analysis that TCP was completely removed. Orientation birefringence of the CTA/TCP (95/5) before and after the methanol immersion is shown in **Figure 12.14** [31]. After the immersion, 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. This result suggests that the positive birefringence in the CTA/TCP blend is strongly attributed to the orientation of TCP.
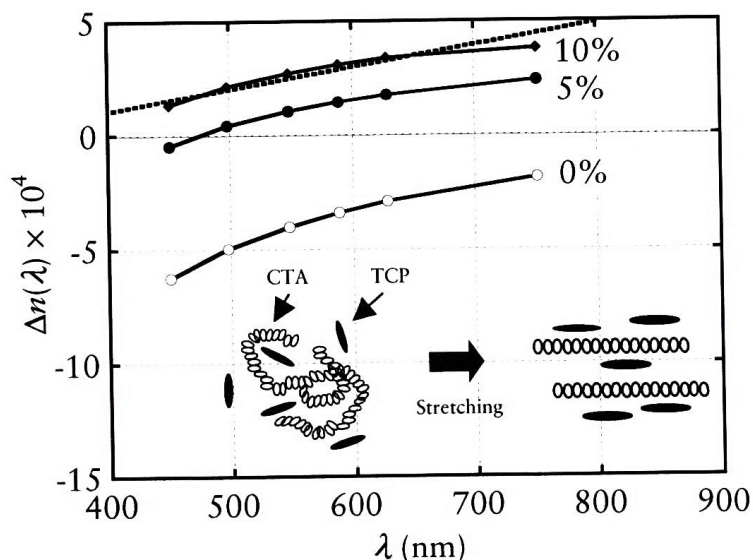
Figure 12.13 Wavelength dependence of orientation birefringence for (open circles) CTA, (closed circles) CTA/TCP (95/5) and (closed diamonds) CTA/TCP (90/10), stretched at a draw ratio of 1.5. In the figure, the straight dotted line represents the ideal wavelength dispersion for a multiband quarter-wave plate with a thickness of 400 μm. The polarisability ellipsoids of the CTA/TCP blends are shown below the curves. Reproduced with permission from M.E.A. Manaf, M. Tsuji, Y. Shiroyama and M. Yamaguchi, *Macromolecules*, 2011, **44**, 10, 3942. ©2011, ACS Publications [29]
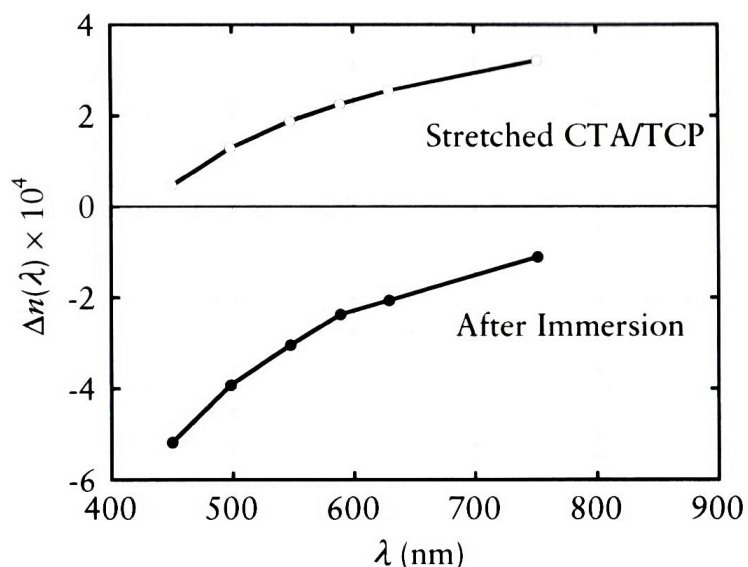
Figure 12.14 Wavelength dependence of orientation birefringence for CTA/TCP (95/5) (open circles) prior to immersion and (closed circles) after the extraction of TCP. Reproduced with permission from M.E.A. Manaf, M. Tsuji, Y. Shiroyama and M. Yamaguchi, *Macromolecules*, 2011, **44**, 10, 3942. ©2011, ACS Publications [29]

12.5 Conclusions

Cellulose esters, which have been used as photographic film and polariser protective film due to their high transparency and excellent heat resistance, have a huge potential as a high-performance optical film. Some cellulose esters such as CAP and CAB show extraordinary dispersion of orientation birefringence, i.e., the magnitude of birefringence increases with the wavelength, a property essential for retardation films such as quarter-wave plate. Although this property can be provided by various techniques – through the piling of two films, blending of two polymers of opposite birefringence or by random copolymerisation, these techniques involve an adhesion or combination of two different types of polymers. In the case of cellulose esters, the orientation birefringence is mainly determined by the type and amount of substitution groups, so it is possible to tailor the retardation/birefringence by manipulating the degree of substitution of the ester groups with intense focus on the hydroxyl group. We found that certain ester groups such as propionyl and butyryl as well as the hydroxyl group contribute to positive birefringence, while the acetyl group contributes to negative birefringence. Furthermore, addition of a suitable plasticiser is also effective

in modifying the orientation birefringence of cellulose esters, provided the blend is miscible.

Acknowledgements

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