

Strong Orientation Correlation and Optical Anisotropy in Blend of Cellulose Ester and Poly(ethylene 2,6-naphthalate) Oligomer

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ABSTRACT: Molecular orientation of two aromatic additives in cellulose acetate propionate (CAP) matrix was investigated from orientation birefringence data and an intermolecular orientation correlation represented by nematic interaction (NI) was evaluated. Poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) oligomers with low molecular weight (ca. 400 g mol⁻¹) were used as the additives. The NI strengths of CAP-PET and CAP-PEN were determined to be 0.28 ± 0.05 and 0.96 ± 0.15, respectively. In particular, compared with other polymer/polymer and polymer/small additive blends, the NI value in CAP/PEN blend is much stronger and represents the perfect orientation correlation. The strong orientation correlation is possibly due to the rigid naphthalate structure in PEN. Contrary, a relation between birefringence and orientation function for CAP in bulk and blend showed the same trend, suggesting that the orientation behavior of CAP determines the orientation birefringence. As two ester groups in CAP are responsible for birefringence, the alignment of the ester groups is affected by only the main chain orientation. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40570.

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INTRODUCTION

Birefringence is one of the most important properties for optical devices. When a polymer film is stretched beyond a glass transition temperature (T_g), an orientation birefringence, Δn , is induced as well as a stress, σ , due to the chain orientation.¹ Δn is represented by the difference between two refractive indices, $n_{//}$ and n_{\perp} , in the directions parallel and perpendicular to the stretching direction, respectively.

$$\Delta n = n_{//} - n_{\perp} \quad (1)$$

For most amorphous polymers, σ is proportional to Δn since both properties are associated with the orientation of the chain segment.

$$\Delta n = C\sigma \quad (2)$$

where C is the stress-optical coefficient, which reflects the polarizability anisotropy for a repeating unit of polymers. Equation (2) is called the stress-optical rule (SOR). Furthermore, Kuhn and Grun² introduced Δn by using the model of the statistical segment approach represented as,

$$\Delta n = \frac{2\pi}{9} \frac{(n+2)^2}{n} \frac{\rho N_A}{M_{\text{seg}}} \Delta\alpha \left[\frac{3\langle \cos^2\theta \rangle - 1}{2} \right] \quad (3)$$

where n , ρ , and N_A are refractive index, density and Avogadro's number. M_{seg} and $\Delta\alpha$ are molecular weight and polarizability anisotropy of chain segment for the oriented polymers, and θ is the average angle between the segment and stretching direction. Therefore, as predicted by eq. (3), Δn can be improved by increasing the polarizability anisotropy of the polymers, such as polystyrene (PS) and polycarbonate (PC) exhibiting high values of Δn .

Cellulose derivatives are polymers that are expected to meet the growing future demand for biomass-based polymers.³⁻¹² Particularly, cellulose esters have been studied so far for their application in optical films due to their other properties such as heat resistance and transparency.^{8,12-16} Retardation films with extraordinary wavelength dispersion, where birefringence increases with wavelength, have been focused on for their use in optical devices such as stereo [three-dimensional (3D)] and organic electro-luminescence (OEL) displays.^{14,17} For this reason, some

cellulose esters such as cellulose acetate propionate (CAP), which shows the extraordinary dispersion, are appropriate materials for the retardation films.¹⁴ However, contrary to PS and PC, the level of Δn does not satisfy the demand of the present retardation films, in which Δn at 400 nm should be higher than 5×10^{-3} for 50 μm thickness. Therefore, Δn of cellulose esters has to be improved by using some processing methods as described below.

In order to produce optical films with high performances, various techniques such as blending with other polymers^{18,19} or small molecules,^{20–23} copolymerization,^{24–26} and lamination²⁷ of sheets have been studied. Among these techniques, the addition of small molecules is relatively easier due to better miscibility with matrix polymer. Tagaya et al.²⁰ reported that a small amount of aromatic additives with large electric polarizability compensates the birefringence of poly(methyl methacrylate) (PMMA). Abd Manaf et al.²³ also found that tricresyl phosphate (TCP) improves the birefringence of cellulose esters.

In the previous article,²⁸ we investigated molecular orientation of aromatic esters, which have various alkyl groups, dissolved in stretched CAP films, by using a nematic interaction (NI) theory which discusses intermolecular orientation correlation. The result showed that the shorter alkyl chain in additives exhibited high molecular orientation, meaning that the intermolecular NI is improved. However, the enhancement of birefringence by these additives did not satisfy the present requirement for retardation film. We think that the reason of the small improvement is due to weak intermolecular NI between CAP and the additives although the strength was not quantitatively evaluated. In order to enhance the birefringence more, the absolute value of the NI should be evaluated and compared with that of other polymer blends. Additionally, since the tensile stress also affects the orientation birefringence according to the SOR, the stress effect on the NI strength during stretching should be investigated.

In this study, the intermolecular NI strength in blends of CAP and two low-mass compounds is compared with the some literature data for other synthetic polymer blends. Based on the obtained results, the effect of tensile stress on the additive orientation is also discussed. Furthermore, the relation between chain orientation and birefringence of CAP in blends is investigated.

EXPERIMENTAL

Materials

CAP (Figure 1) used in this study was produced by Eastman Chemical Company. The weight-average and number-average molecular weights (M_w and M_n) of CAP were 1.9×10^5 and 7.9×10^4 , respectively, determined by a gel-permeation chromatography (GPC, HLC-8020 Tosoh, Japan) with TSK-GEL[®] GMHXL using standard PS samples. Degrees of substitution for acetyl and propionyl groups per a pyranose unit of CAP were 0.19 and 2.58, respectively.

Aromatic compounds used as additives, such as poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) oligomers (PEN, Figure 1), were synthesized from ethylene glycol and

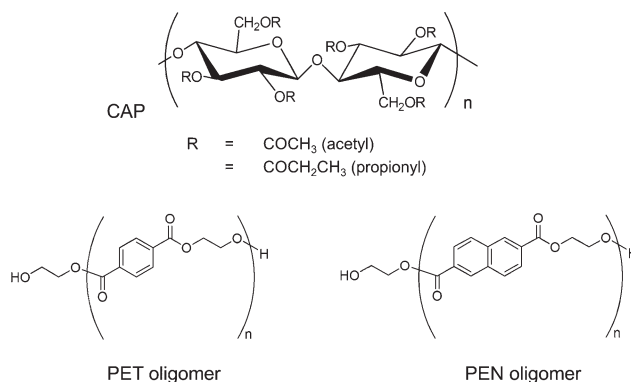


Figure 1. Chemical structures of cellulose acetate propionate (CAP) and poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) oligomers.

dimethyl terephthalate (DMTPh) or dimethyl naphthalene 2,6-dicarboxylate (DMNDC) as following reactions. EG with an excess molar quantity was mixed with DMTPh (or DMNDC) in a flask. After adding tetraisopropyl titanate as a catalyst for the esterification reaction into the flask, the mixture was stirred at 200°C for half a day under a nitrogen atmosphere. Finally, by removing the residual EG at 200°C *in vacuo*, PET or PEN oligomer was obtained. The number-average molecular weight and the distribution of polymerization in the additive oligomers are summarized in Table I. The molecular weights were determined from average-hydroxyl number in the terminal group, which was estimated by using potassium hydroxide.

Sample Preparation

CAP and the additive oligomer with various compositions were mixed in a molten state by a 60 cc batch-type internal mixer (Labo-plastmil, Toyoseiki, Japan) at 200°C for 6 min. The blade rotation speed was 30 rpm. The additive concentration was 0–20 phr (1 phr is 1 g per 100 g of CAP), and the composition is denoted as CAP/PET 100/10 in this article. The mixing condition was chosen from the following reasons. (1) Torque level becomes too high beyond 30 rpm. (2) Torque level reached almost a constant value at 6 min. (3) Long residence time leads to thermal degradation.

In order to prevent hydrolysis degradation and transesterification, CAP was dried *in vacuo* at 80°C for 2 h before the melt mixing. The moisture content in dried CAP was estimated to be 0.6 wt % by a Karl Fisher moisture meter (Mitsubishi Chemical Analytec, Japan) while those in PET and PEN without drying were to be 0.5 and 1.0 wt %, respectively. It was concluded that the moisture content did not generate the chemical reactions as mentioned above because GPC data in Figure 2 shows that the molecular weight and its distribution of CAP, PET, and PEN seem to be almost similar before/after melt-mixing as described later.

After being kept in vacuum oven at room temperature for 1 day, the blend samples were compressed to make sheets with a thickness of 200–300 μm at 200°C for 5 min under 10 MPa by a compression-molding machine (Table-type-test press SA-303-I-S, Tester Sangyo, Japan). As the glass transition temperature T_g of CAP is 145°C and melting points of both two additives are

Table I. Molecular Weight and Melting Point of PET and PEN Oligomers

Additive	M_n^a	Fraction of polymerization degree ^b			T_m (°C)
		$n = 1$	$n = 2$	$n \geq 3$	
PET	418	0.30	0.29	0.41	84
PEN	390	0.56	0.29	0.15	85

^aDetermined from the average hydroxyl number in additives, which is estimated with potassium hydroxide.

^bDetermined from GPC data.

almost 85°C determined by using a differential scanning calorimeter (DSC-822e, Mettler Toledo, Swiss), CAP and CAP/additive blends were molded at 200°C, in order to eliminate the molecular orientation generated by the melt-compression. The compressed sheets were subsequently cooled down to 25°C for 5 min. The deviation of thickness in each film sample was $\pm 5 \mu\text{m}$.

In some polymer blends, the melt-mixing possibly generates hydrolysis, which reduces the molecular weight of CAP, and trans-esterification, which grafts PET and PEN to the chain of CAP. However, the GPC data in Figure 2 show the molecular weight and its distribution of CAP, PET, and PEN in the blends did not change from pure materials. The molecular weight data of CAP, which were determined by using standard PS samples (Tosoh, Japan), were listed in Table II. These results can confirm that any chemical reactions such as hydrolysis and trans-esterification did not take place during the melt-mixing.

Measurements

Dynamic mechanical analysis (DMA) for the sample films was performed to measure tensile storage and loss moduli, E' and E'' , respectively, at 10 Hz as a function of temperature by using a tensile oscillatory rheometer (DVE-E4000, UBM, Japan) from 25 to 180°C with a heating rate of 2°C min⁻¹.

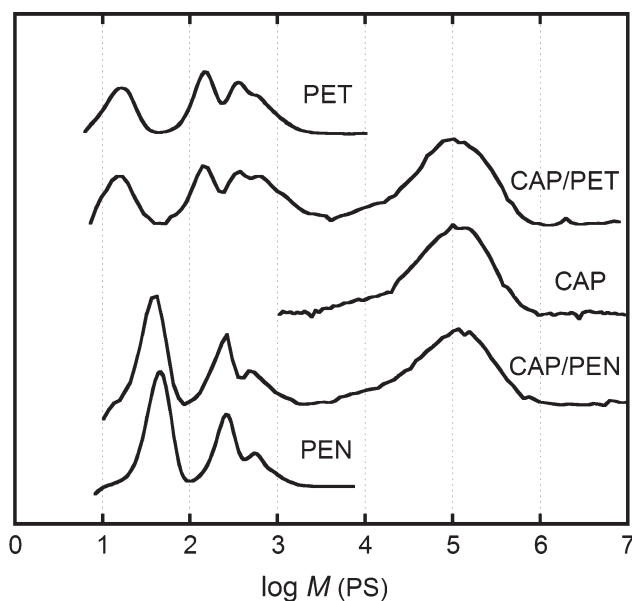


Figure 2. Molecular weight distributions for CAP, PET, and PEN in bulk and blend after melt-mixing. The molecular weight was calculated from the elution time of GPC by using polystyrene standard samples.

For a hot-stretching test, specimen films were cut into $10 \times 20 \text{ mm}^2$. The films were stretched from an initial length of 10 mm with a stretching speed of 0.5 mm s^{-1} (a strain rate = 0.05 s^{-1}) by using a tensile drawing machine (DVE-3, UBM, Japan). The stretching temperature was determined from the DMA data, where the tensile modulus was 10 MPa at 10 Hz as described later. The films were immediately quenched by cold air blowing after stretching to avoid relaxation of molecular orientation. The stretched samples were kept in a humidic chamber (IG420, Yamato, Japan) at 25°C and 50%RH for 1 day in order to ignore the moisture effect on the optical properties as previously reported.²⁹

The birefringence of the drawn films was measured by an optical birefringence analyzer (KOBRA-WPR, Oji Scientific Instruments, Japan) as a function of wavelength. The details of the optical system are explained in our previous article.¹⁴

RESULTS AND DISCUSSION

Dynamic Mechanical Analysis for CAP and CAP Blends

Figure 3 shows temperature dependence of storage modulus E' and loss tangent $\tan \delta$ ($= E''/E'$) at 10 Hz for CAP and CAP blends with 9.1 wt % (10 phr) of additives. By mixing additives with CAP, α peak of $\tan \delta$, which reflects the glass transition of matrix polymer, becomes broader and shifts to a lower temperature, suggesting that the additives act as a plasticizer for CAP. Furthermore, the blends exhibit no extra peak as compared with pure CAP, indicating that the additives are well dissolved in CAP. On the other hand, β relaxation at 70°C, which was assigned to be hindered rotation of the substituted ester group of CAP, was observed as a shoulder of $\tan \delta$.^{30,31} As the addition of PET and PEN enhance rotational motion reflecting the β relaxation of CAP, the peak at 70°C in the blends became stronger than that in bulk. As seen in Figure 4, DSC data of CAP/PET and CAP/PEN blends show no extra peak and transition at 70°C compared to CAP. The result suggests that PET and PEN exhibit cooperatively glass transition with CAP matrix, so that single T_g was observed in DMA data of the blends.

Table II. Weight- and Number-Average Molecular Weights, M_w and M_n , of CAP in Bulk and Blends

	M_w (10^5)	M_n (10^5)
CAP	1.9	7.9
CAP/PET 10 phr	1.6	7.7
CAP/PEN 10 phr	1.8	6.3

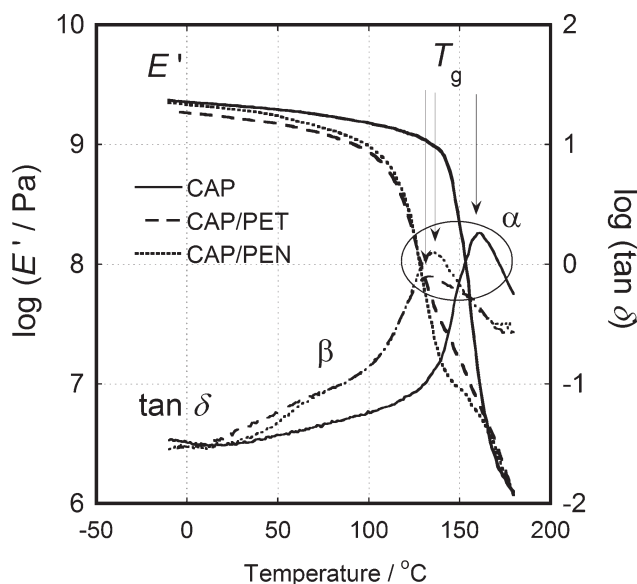


Figure 3. Temperature dependence of tensile storage modulus E' and $\tan \delta$ ($= E''/E'$) for bulk CAP, and CAP/additive blends with the weight fraction of 100/10 wt/wt. The oscillatory frequency is 10 Hz and heating rate is 2°C min^{-1} .

Especially, CAP/PEN blend with 100/20 wt/wt became opaque. Furthermore, as shown in Figure 4, the CAP/PEN blend exhibits two glass transition temperatures (T_g s) while the bulk CAP and other blends with lower concentration of additives show single T_g in the temperature range of this study. This result suggests that two phases having different compositions exist in CAP/PEN 100/20 blend. Unlike CAP/PEN 100/20 blend, CAP/PET 100/20 film was clear although the DSC curve shows two T_g s in Figure 4. We think that the result is because the size of separated minor phase in the CAP/PET blend is too small to scatter the visible lights.

Composition dependence of T_g determined from $\tan \delta$ is shown in Table III. CAP/PET and CAP/PEN show the same trend for

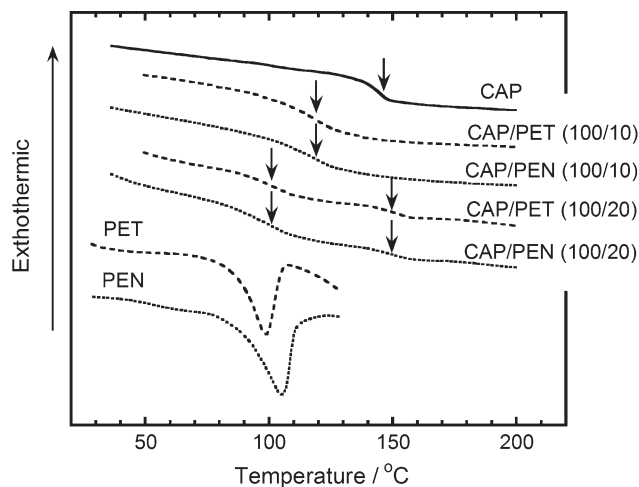


Figure 4. DSC curves of bulk CAP and CAP/additive blends in first heating scan with a rate of $10^\circ\text{C min}^{-1}$. The blend compositions are shown in the figure.

Table III. Glass Transition Temperature T_g and Drawing Temperature T_{draw} for CAP, CAP/PET, and CAP/PEN Blends

Content of additive (phr)	T_g ($\tan \delta$)		T_{draw}	
	CAP/PET	CAP/PEN	CAP/PET	CAP/PEN
0	161		163	
5	149	148	154	154
10	133	136	156	150
15	123	125	148	148
20	115	119	146	146

T_g is determined from a peak of $\tan \delta$.

T_g , inferring that PET and PEN comparably plasticize CAP. This may be because both chemical structures and the molecular weights are similar.

Stress–Strain Curves for CAP and CAP/Additive Blends

As mentioned in the introduction, the orientation birefringence of polymers is generated by chain orientation. Therefore, a following relation is obtained.

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

$$\Delta n^0 = \frac{2\pi}{9} \frac{(n+2)^2}{n} \frac{\rho N_A}{M_{\text{seg}}} \Delta \alpha \quad (5)$$

where Δn^0 is an intrinsic birefringence where the anisotropic molecule perfectly orients to the stretching direction, and F is the Hermans orientation function corresponding to the bracket in the right hand in eq. (3), [$3\langle \cos^2 \theta \rangle - 1/2$]. Therefore, in order to investigate the effect of additives on the orientation birefringence for CAP, the chain orientation of CAP in stretched films should be controlled. Prior to the stretching test of the sample films, stretching temperatures were determined from DMA data according to the previous article,²⁸ and listed in Table III. The difference between T_g and T_{draw} becomes larger with the additive concentration, suggesting that the distribution of the relaxation time for CAP chain is broadened by the additives compared with that in the bulk.

Figure 5 shows stress–strain curves of the CAP and CAP blends films. The stress for the three films reached the same level, indicating that the orientation birefringence of CAP component is similar even in the blends by assuming the SOR represented in eq. (2). Therefore, the difference in orientation birefringence between CAP and the blend is originated from the additive orientation as examined in previous articles.^{28,32}

Orientation Birefringence in Stretched Films of CAP/Additive Blends

Figure 6 shows orientation birefringence Δn and its wavelength dependence for CAP and CAP/additive films with the engineering strain of 1.0 with a strain rate of 0.05 s^{-1} . Positive birefringences that increase with the increase in additive content were observed for both CAP/PET and CAP/PEN systems except for both blends with a composition of 100/20. As shown in Figure 3, CAP/PET and CAP/PEN 100/20 blends do not show strain-hardening behavior compared to other samples, indicating that the degree of orientation for CAP is lower than that in others

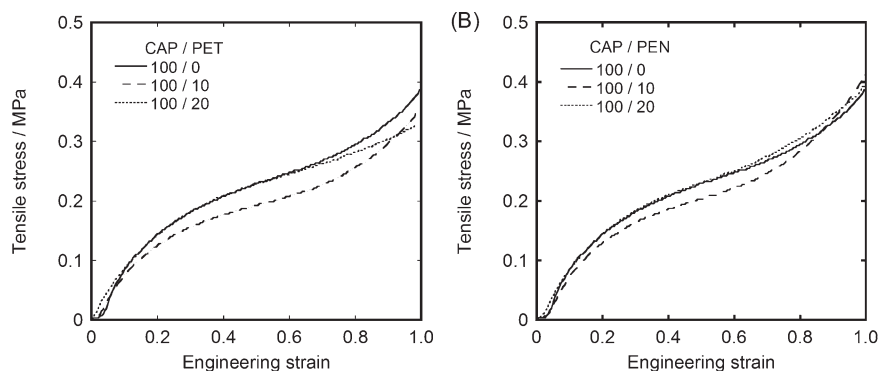


Figure 5. Stress–strain curves with the initial draw rate of 0.05 s^{-1} for CAP and CAP/additive blends. The drawing temperatures were shown in Table II.

because the strain hardening enhances the orientation of chain between entanglement couplings.³³ The phase separation for the blends, as suggested from DSC data, should also originate the stress–strain behavior since the phase boundary can reduce the stress. For these reasons, CAP/additive blends with 100/20 show smaller orientation birefringence than those with 100/15 in Figure 6.

CAP shows positive birefringence having extraordinary wavelength dispersion: birefringence increases with wavelength, λ . According to Yamaguchi et al.,¹⁴ the extraordinary dispersion originated from the contributions of two ester groups bound perpendicular to the main chain of CAP. Compared with the result of CAP, the wavelength dependence for the blend films gradually changes to ordinary dispersion: Δn decreases with λ . This result indicates that PET and PEN additives contribute to the birefringence because general polymers such as PS, PC, and PMMA, and small molecules show the ordinary dispersion. Therefore, the change in the wavelength dispersion in Figure 6 reflects the birefringence of the additives (PET and PEN).

Now, the effect of PET and PEN on birefringence is compared with that in the other polymer blends. In previous works, we reported that aromatic additives such as TCP,²³ dioctyl phthalate (DOP),³⁴ and various kinds of ester compounds²⁸ enhance the birefringence of CAP. The increment by the additives was just 5×10^{-4} at the same experimental conditions with this study. Tagaya et al. compensated the negative birefringence of PMMA by aromatic compounds, which show the positive birefringence.²⁰ The change in birefringence by the aromatic additives is less than 5×10^{-4} even at 7 wt % of the stilbene,

which shows the highest intrinsic birefringence in their article. Contrary, in this study, we found that, especially, PEN enhanced the birefringence with 20×10^{-4} , which is much larger than the increment in the other systems described above. This difference is attributed to two factors, the intrinsic birefringence Δn^0 and the orientation function F_i of the additives as represented in eq. (6). The former is determined by the polarizability anisotropy of its chemical structure and the latter is related to the orientation coupling with the matrix CAP. In order to examine the effect of the additives on birefringence, total birefringence in the blends is separated into two components.

Separation of Birefringence into Two Components

The SOR is not allowed to separate the birefringence into components for CAP blends.²⁸ Therefore, in order to evaluate the contributions of PET and PEN to Δn of the blends, the information of their wavelength dispersion, $\Delta n(\lambda)/\Delta n(\lambda_0)$, is necessary as represented in a following equation.

$$\begin{aligned} \Delta n_{\text{blend}}(\lambda) &= \Delta n_{\text{CAP}}(\lambda) + \Delta n_{\text{add}}(\lambda) \\ &= \Delta n_{\text{CAP}}^0(\lambda) \phi_{\text{CAP}} F_{\text{CAP}} + \Delta n_{\text{add}}^0(\lambda) \phi_{\text{add}} F_{\text{add}} \end{aligned} \quad (6)$$

Here, ϕ is the volume fraction. The detail of the derivation for eq. (6) is described in Appendix. The birefringence data of PET and PEN with high molecular weights were reported.^{35,36} However, Δn of PET and PEN oligomers used in this study had the different wavelength dispersion from the reported data because the end-group more dominantly affects the birefringence

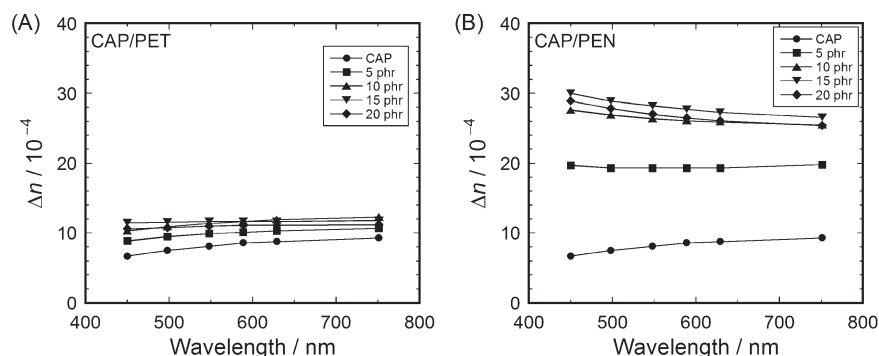


Figure 6. Wavelength dispersion of orientation birefringence Δn for CAP and CAP/additive blends at various compositions with a draw rate of 2.0.

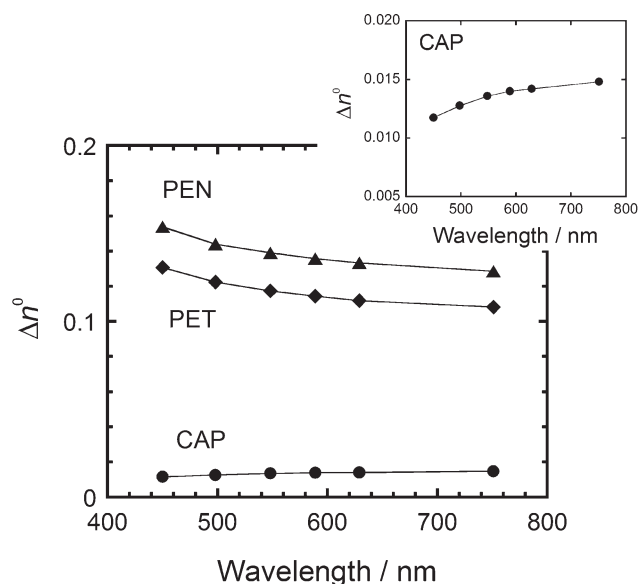


Figure 7. Wavelength dispersion of intrinsic birefringence Δn^0 for CAP, and PET and PEN oligomers. The wavelength dispersion was determined from experimental data while the absolute values were obtained from the literature¹¹ for CAP, and simulated result for PET and PEN.

parameters than the polymers. Hence, the wavelength dispersions of PET and PEN were determined as follows.

Now, the SOR in eq. (2) is assumingly applicable for CAP in the blend with the smallest amount of additives (~ 5 wt %) at the small draw ratio. First, Δn of the blend at CAP/additive (100/5 wt/wt) was separated to determine the wavelength dispersion, $\Delta n(\lambda) / \Delta n(\lambda_0)$. The intrinsic birefringence for each component, Δn^0 , was obtained by multiplying $\Delta n(\lambda) / \Delta n(\lambda_0)$ with Δn^0 at a certain wavelength λ . The value of Δn^0_{CAP} at 629 nm was 0.0142 as reported by Maeda and Inoue.¹¹ On the other hand, Δn^0_{add} at high frequencies was estimated to be 0.114 and 0.136 for PET and PEN, respectively, by using a molecular dynamics (MD) simulation and bond polarizability parameters as the following procedure. PET and PEN oligomers with $n = 1$ in Figure 1 were used as model structures to calculate Δn^0_{add} . The MD simulation was performed at 450 K and 0.1 MPa with PCFF force field³⁷ in Materials Studio 5.5 software (Accelrys) until the density of a cubic periodic structure containing 128 molecules became constant. Temperature and pressure were

controlled by Andersen³⁸ and Berendsen³⁹ methods, respectively. The polarizability anisotropy of each molecule was calculated from the bond polarizability parameters reported by Bunn.⁴⁰ The intrinsic birefringence, Δn^0_{add} , was estimated from the average polarizability anisotropies of 128 molecules for PET and PEN.

The wavelength dispersions of Δn^0_{CAP} and Δn^0_{add} are shown in Figure 7. CAP exhibits the extraordinary wavelength dispersion.¹⁴ In contrast, PET and PEN oligomers show ordinary dispersion similarly to PET and PEN with high molecular weights.³⁶ By applying eq. (9), Δn of the blends were separated into CAP and additive components, Δn_{CAP} and Δn_{add} , respectively.

Orientation Birefringence of CAP in Blend

The concentration dependence of Δn_{CAP} is shown in Figure 8(A). The wavelength for Δn_{CAP} is 629 nm due to the following reason. The intrinsic birefringence for CAP was determined at 633 nm.¹¹ As seen in Figure 7, the intrinsic birefringence for PET and PEN becomes constant at higher wavelengths than 600 nm. To evaluate the molecular orientation of all components, Δn was monitored at 629 nm close to 633 nm.

In CAP/PET and CAP/PEN blends, Δn_{CAP} decreases with increasing the additive concentration while Δn_{add} increases. According to the NI theory,²² Δn_{CAP} and Δn_{add} are affected by NI parameters between CAP-CAP and CAP-additive, $\epsilon_{\text{CAP,CAP}}$ and $\epsilon_{\text{CAP,add}}$, respectively, as follows:

$$\begin{aligned} \Delta n_{\text{blend}} &= \Delta n_{\text{CAP}} + \Delta n_{\text{add}} \\ &= \left[\frac{\phi_{\text{CAP}} \Delta n^0_{\text{CAP}} (1 - \epsilon_{\text{CAP,CAP}})}{1 - \phi_{\text{CAP}} \epsilon_{\text{CAP,CAP}}} + \frac{\phi_{\text{CAP}} \phi_{\text{add}} \epsilon_{\text{CAP,add}} \Delta n^0_{\text{add}}}{1 - \phi_{\text{CAP}} \epsilon_{\text{CAP,CAP}}} \right] F_{\text{CAP}} \end{aligned} \quad (7)$$

Even if the intramolecular NI for CAP does not work ($\epsilon_{\text{CAP,CAP}} = 0$), Δn_{CAP} decreases with the additive concentration as shown by the dotted line in Figure 8(A). However, the obtained value of Δn_{CAP} is smaller than that with $\epsilon_{\text{CAP,CAP}} = 0$, implying that $\epsilon_{\text{CAP,CAP}}$ is larger than zero. By using eq. (7), $\epsilon_{\text{CAP,CAP}}$ was estimated from the experimental data in Figure 8 to be 0.70 ± 0.15 . For some polymers such as polyisoprene, polybutadiene, and PS, the intramolecular NI $\epsilon_{\text{poly-poly}}$ was reported to be almost 0.3.^{41,42} Therefore, the NI strength in CAP is larger than that in the general polymers. We think that the larger value of $\epsilon_{\text{CAP,CAP}}$ is originated by the orientation of

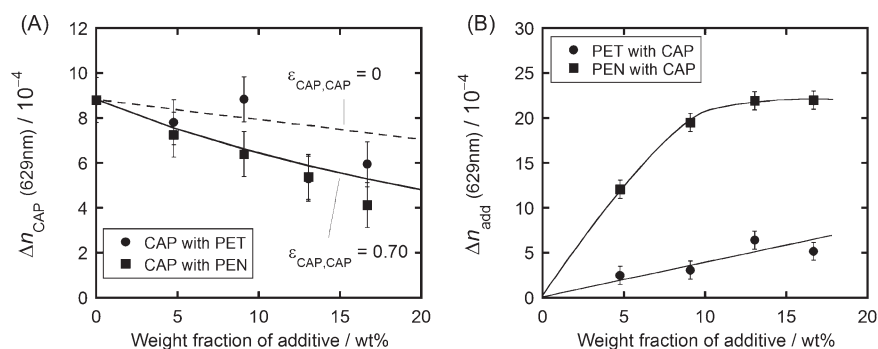


Figure 8. Concentration dependence of component birefringence, (A) Δn_{CAP} and (B) Δn_{add} , at 629 nm for CAP and the additives, respectively. The dotted and solid lines in figure (A) are calculated result with $\epsilon_{\text{CAP,CAP}} = 0$ and 0.70, respectively. The Δn_{CAP} data in CAP/PET blend was previously reported.²⁸

substituted ester groups in CAP, because, according to Yamaguchi et al.,¹⁴ Δn_{CAP} is determined by the orientation of acetyl and propionyl groups. Furthermore, the orientation correlation between polymer chains will be also associated with the ester species. However, the further discussion for the contribution of the ester groups cannot be carried out in this article.

Orientation Correlation of Additives with CAP Matrix

For PET and PEN oligomers, Δn_{PET} and Δn_{PEN} increased with their content as shown in Figure 8(B). The NI theory derives the relation for Δn_{add} as follows²²:

$$\Delta n_{\text{add}} = \Delta n_{\text{add}}^0 \phi_{\text{add}} F_{\text{add}} = \Delta n_{\text{add}}^0 \phi_{\text{add}} \left[\frac{\phi_{\text{CAP}} \varepsilon_{\text{CAP,add}}}{1 - \phi_{\text{CAP}} \varepsilon_{\text{CAP,CAP}}} \right] F_{\text{CAP}} \quad (8)$$

The orientation of CAP segment, F_{CAP} is written from eqs (2) and (4) as,

$$F_{\text{CAP}} = \frac{C_{\text{CAP}}}{\Delta n_{\text{CAP}}^0} \sigma = [1.76 \times 10^{-7} \text{ Pa}^{-1}] \sigma \quad (9)$$

The proportionality, $C_{\text{CAP}}/\Delta n_{\text{CAP}}^0$ is independent of the intramolecular NI between CAP chains because the orientation correlation enhances only birefringence.³³ By applying eqs (8) and (9) to Δn_{add} , the intermolecular NI between CAP and additive molecule, $\varepsilon_{\text{CAP,add}}$, was evaluated. For the calculation, $\varepsilon_{\text{CAP,CAP}}$ was 0.70 ± 0.15 , and the volume fraction, ϕ , was regarded as the weight fraction because the densities of CAP, PET, and PEN are not so different (1.22 , 1.19 , and 1.20 g cm^{-3} , respectively). The average values of $\varepsilon_{\text{CAP,add}}$ were estimated to be 0.28 ± 0.05 and 0.96 ± 0.15 for CAP-PET and CAP-PEN, respectively. Since the intrinsic birefringences, Δn^0 , in eq. (8) for PET and PEN are almost similar, the large value of the NI in CAP/PEN will originate the strong birefringence of PEN in the blends, which is represented in Figure 9.

The values of intermolecular NI between polymer chains were reported to be around 0.3 – 0.4 .^{41–43} Contrary, in PS/rod-like molecule mixtures, the intermolecular NI strength was less than 0.1 .²² Compared with these results, the intermolecular NI strength in CAP/PEN blend is relatively large, suggesting that

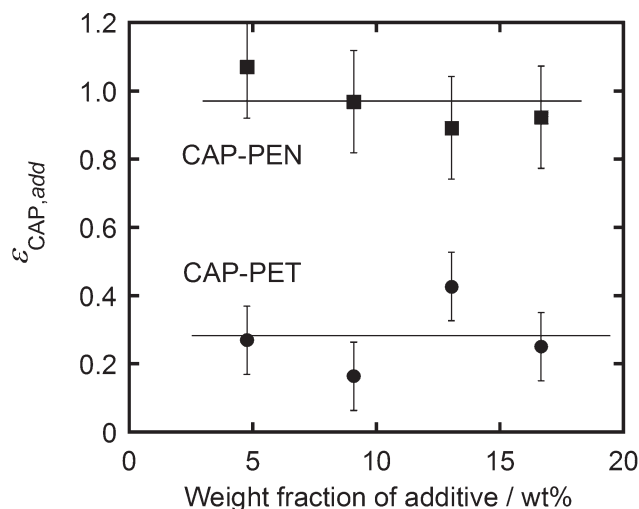


Figure 9. Nematic interaction parameters between CAP and PET or PEN, $\varepsilon_{\text{CAP,add}}$ in CAP/PET and CAP/PEN blends.

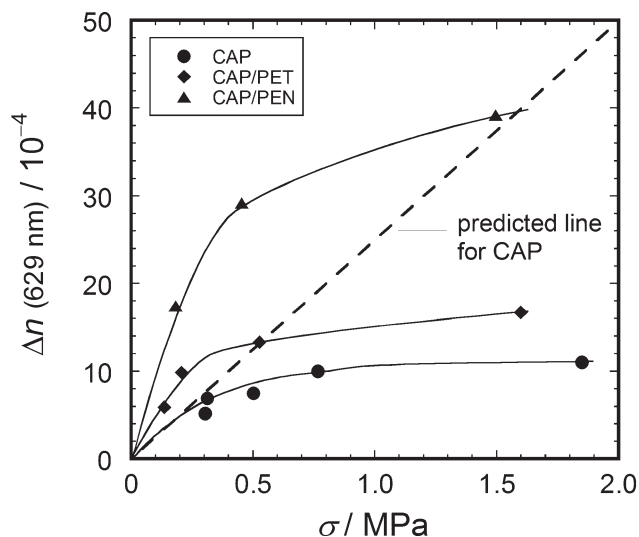


Figure 10. Relation between σ and Δn for CAP and CAP/additive blend films. The composition of CAP/additive blend is 100/10 wt/wt. The dotted line is predicted value by using the stress-optical coefficient for CAP $C = 2.5 \times 10^{-9} \text{ Pa}^{-1}$ which was reported by Maeda and Inoue.¹¹

the rigidity of PEN molecule strongly enhances the intermolecular orientation correlation with the matrix polymer since the naphthalate group is relatively rigid than the others such as the phthalate group in PET. Additionally, the side chain structure in CAP also affects the orientation coupling with the additives. However, the effect of ester groups in the matrix polymer on the intermolecular NI is not clear. It is necessary to investigate the effect of ester groups on the NI strength between cellulose ester and additive molecules in a future study.

Orientation Birefringence of CAP and CAP Blend Films During Stretching

In order to evaluate the orientation behavior of PET and PEN in the blend films during the hot-stretching, orientation birefringence, Δn , of CAP and CAP/additive blends (100/10 wt/wt) was measured against the tensile stress σ as shown in Figure 10.

Since the stress–strain curves are not completely the same in the bulk and blends, Δn is plotted against σ in Figure 10 to discuss the effect of PET and PEN in the blends. The dotted line was the estimated result by assuming the SOR with the stress-optical coefficient ($C = 2.5 \times 10^{-9} \text{ Pa}^{-1}$) which was taken to be from the literature.¹¹ The SOR is not applicable even for bulk CAP except at smaller tensile stress ($<0.3 \text{ MPa}$ in this experiment) as already discussed in previous article.¹⁴ The initial slope, C , of the blends is larger than that of the bulk because of the parallel orientation of PET and PEN to the chain direction of CAP originated by intermolecular NI. In the figure, CAP/PEN shows higher Δn than CAP/PET due to the higher orientation of PEN than PET, corresponding to the discussion of the result in Figure 6.

Additive Orientation in CAP Matrix During Stretching

First, Δn for CAP/PET and CAP/PEN blends in Figure 10 was separated into two components with the same procedure to obtain data in Figure 8. Figure 11(A) compares the orientation birefringences of CAP, PET, and PEN components, Δn_{CAP}

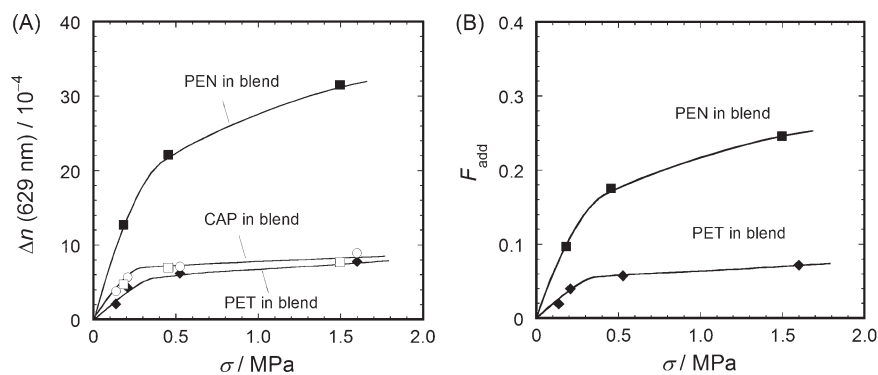


Figure 11. (A) Relation between stress, σ , and component birefringences, Δn_{CAP} and Δn_{add} , for CAP and additives, respectively. (B) Relation between σ and orientation functions of additives, F_{add} , in stretched CAP films.

Δn_{PET} and Δn_{PEN} , at various stresses. Although the stress dependence became weaker with the stress, both Δn_{PET} and Δn_{PEN} seem to be associated with Δn_{CAP} indicating that the orientational coupling represented by intermolecular NI is independent of the draw ratio, that is, the tensile stress. The orientation functions of the additives, F_{PET} and F_{PEN} , calculated by eq. (8), are shown in Figure 11(B). The result demonstrates that the additive molecules orient along the chain direction of matrix CAP in the beginning of stretching, and F reaches to a limiting value with increasing stress. In other words, the orientation of additives along to the matrix chain does not relax during the stretching at large stresses in this experimental range. The ratio of F is approximately 3 which is similar to 3.5 ($=\epsilon_{CAP,PET}/\epsilon_{CAP,PET}$) calculated in the previous section, suggesting that the NI parameters is applicable even to the drawn films with larger draw ratio (>3) in the range of this experiment.

Orientation of CAP Chain in Bulk and Blend During Stretching

Figure 12(A) shows Δn_{CAP} of CAP in bulk and blends at various stresses during the stretching. The values of Δn_{CAP} in both blends are similar although a small difference between them for the concentration dependence is observed in Figure 8(A). Furthermore, Figure 12(A) demonstrates that CAP in blends exhibits smaller Δn_{CAP} than in the bulk state, suggesting that the intramolecular NI between CAP chains works because Δn_{CAP}

is independent of tensile stress σ without the intra-NI; $\epsilon_{CAP,CAP} = 0$ in the following equation.

$$\Delta n_{CAP} = \frac{\phi_{CAP} \Delta n_{CAP}^0}{1 - \phi_{CAP} \epsilon_{CAP,CAP}} F_{CAP} \quad (10)$$

$$\sigma = \sigma_{CAP} \propto \phi_{CAP} F_{CAP}$$

From Figure 12 (A), $\epsilon_{CAP,CAP}$ is estimated to be 0.70 ± 0.15 by using eq. (10). Although this value greatly agrees with the result from Figure 8 (A), the value of $\epsilon_{CAP,CAP}$ is too large compared with general polymers to discuss quantitatively the orientational correlation of CAP chains. It is necessary to describe that the large strength between the chain segments is apparently obtained because the birefringence is induced by the orientation of two ester groups.

According to Buchanan et al., a rotational motion of the side-chain in the bulk CAP is observed at -40°C in the dynamic mechanical data, suggesting that the orientation relaxation of the ester groups can immediately take place during the hot stretching above T_g .³¹ However, since the ester groups are directly bound to the pyranose ring in the chain backbone, the relaxation of the ester groups during the stretching is not perfectly allowed. Therefore, we think that the orientation behavior of the ester groups is indirectly associated with the chain orientation of CAP as discussed later.

Further discussion on the orientation behavior of matrix CAP in the blends is allowed based on the obtained results. Equation (8) gives a following relation for F_{CAP}

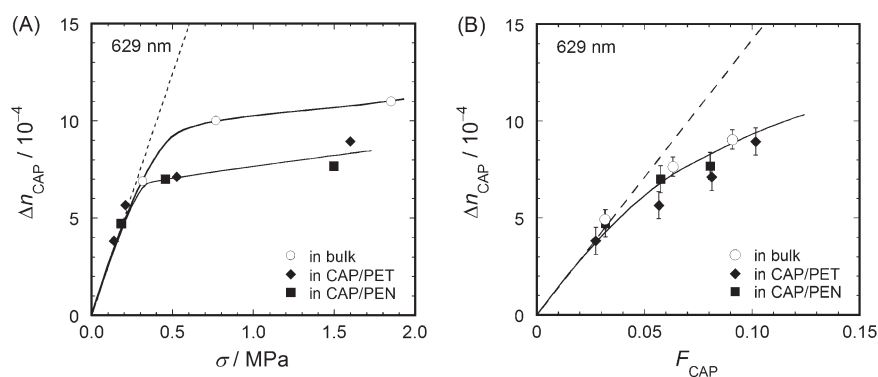


Figure 12. (A) Comparison of orientation function of CAP, F_{CAP} , in bulk and blends at various tensile stresses. (B) Relation between F_{CAP} and Δn_{CAP} at 629 nm in bulk and blend. The dotted line represents the predicted values by assuming the SOR with the intrinsic birefringence, Δn_{CAP}^0 of 0.0142.

$$F_{\text{CAP}} = \left[\frac{1 - \phi_{\text{CAP}} \varepsilon_{\text{CAP,CAP}}}{\phi_{\text{CAP}} \varepsilon_{\text{CAP,add}}} \right] F_{\text{add}} \quad (11)$$

Figure 12(B) shows F_{CAP} calculated from the factors, $\varepsilon_{\text{CAP,CAP}}$ and $\varepsilon_{\text{CAP,add}}$. The value of F_{CAP} in bulk, which was reported by using a Fourier-transform infrared (FTIR) dichroism method,¹⁴ is also plotted with an opened circle. The dotted line is predicted results by assuming the SOR with the reported value.¹¹ The SOR theory is based on that the orientation of main-chain of polymers originates both stress and birefringence when the polymeric materials are deformed. The results at higher F_{CAP} (<0.05) in Figure 12(B) do not agree with the predicted line, meaning that the SOR is not applicable to CAP in both bulk and blend. According to Yamaguchi et al., the acetyl and propionyl groups in CAP are responsible for the orientation birefringence as given by the following equation.¹⁴

$$\Delta n_{\text{CAP}} = \Delta n_{\text{ac}}^0 F_{\text{ac}} + \Delta n_{\text{pr}}^0 F_{\text{pr}} \quad (12)$$

The intrinsic birefringences for acetyl and propionyl groups, Δn_{ac}^0 and Δn_{pr}^0 , are negative and positive, respectively. The orientation function, F_i , is not necessarily agreement with the main-chain orientation, F_{CAP} , because the ester groups are connected to the pyranose ring, which is a fundamental unit of the chain backbone.

In Figure 12(B), at the low range of F_{CAP} (<0.05), Δn_{CAP} is proportional to F_{CAP} , meaning that the ester groups orient cooperatively with the main chain. Contrary, at the high range of F_{CAP} (≥ 0.05), Δn_{CAP} is smaller than the predicted line, indicating that the ester orientation becomes weaker than the chain orientation. The result suggests that, at larger draw ratios, that is, at higher F_{CAP} , the acetyl orientation becomes stronger than the propionyl orientation because the negative contribution from Δn_{ac} becomes larger than the positive one from Δn_{pr} . However, the origin of the difference between F_{ac} and F_{pr} cannot be discussed further in this article. The comparison of the results for CAP and CAP/additive blends implies that PET and PEN additives do not affect the orientation cooperativity between the main-chain and ester groups because Δn_{CAP} in bulk and blend seems to be a single function of F_{CAP} . This means that only the main-chain orientation F_{CAP} determines F_{ac} and F_{pr} , supporting the evaluation method for component birefringence in CAP/additive blends because the ratio of the side-chain orientation, $F_{\text{ac}}/F_{\text{pr}}$, affects the absolute value of birefringence and its wavelength dispersion.

CONCLUSIONS

The orientation birefringence, Δn , for homogeneous blends of CAP and additives was examined, in order to investigate molecular orientations in the stretched films by considering intra- and intermolecular NI reflecting an orientation correlation. PET and PEN oligomers were used as the additives. Component birefringences for CAP and the additive, Δn_{CAP} and Δn_{add} , were determined from the total birefringence of the blends, according to the procedure previously reported.

From the result of blends at various compositions, the blends exhibit lower Δn_{CAP} than the bulk CAP, indicating that the

intramolecular NI works between the CAP chains. On the other hand, Δn_{PET} and Δn_{PEN} in blends increase with increasing PET or PEN concentration. The theoretical analysis concerning the orientational correlation evaluates the NI strengths between CAP-PET and CAP-PEN to be 0.28 ± 0.05 and 0.96 ± 0.15 , respectively. This difference in the NI might be reflected by the chemical structure and molecular rigidity of the additives. Especially, the NI value in CAP/PEN blend shows much stronger than that in other polymer/polymer and polymer/low mass additive blends.

The orientation behaviors of PET and PEN in blend film during drawing were examined from the component birefringence, Δn_{PET} and Δn_{PEN} . The result demonstrated that the orientation functions of PET and PEN, F_{PET} and F_{PEN} , gradually increase with stretching. Additionally, the comparison of the component birefringences at various stresses during stretching revealed that the additive molecules orient parallel to the CAP chain at the beginning of stretching. This suggests that the NI strength between CAP and additive is constant during stretching.

The intramolecular NI strength for the orientation function of CAP, F_{CAP} , was estimated from F_{PET} and F_{PEN} based on the NI theory with $\varepsilon_{\text{CAP,add}}$, which is independent of the tensile stress. The relation between Δn_{CAP} and F_{CAP} in blend was almost similar to that in bulk, meaning that the chain orientation of CAP determines the birefringence even in blends although the stress-optical rule is not applicable. The result indicates that the orientation of ester groups bound to a pyranose ring in CAP is affected by only the main-chain orientation.

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APPENDIX

The refractive index, n , shows the wavelength dependence due to the existence of a resonance wavelength in the ultraviolet region. Since Δn is a difference of n along to two directions, it is also dependent on the wavelength, λ , as represented by the Sellmeier type relation.⁴⁴

$$\Delta n(\lambda) = A + \frac{B}{\lambda^2 - \lambda_{\text{ab}}^2} \quad (A1)$$

where λ_{ab} is an absorption wavelength, and A and B are the Sellmeier coefficients. Since the Hermans orientation function, F_i , is independent of λ , the following relation is considered,

$$\frac{\Delta n(\lambda)}{\Delta n(\lambda_0)} = \frac{\Delta n^0(\lambda)}{\Delta n^0(\lambda_0)} = \text{const.} \quad (A2)$$

where λ_0 is the reference wavelength. Equation (A2) indicates that wavelength dependence of orientation birefringence is determined by the chemical structure of a repeating unit for the polymer. For CAP/additive blends, two component

birefringences, Δn_{CAP} and Δn_{add} , are functions of λ as represented in eq. (6).

$$\begin{aligned}\Delta n_{\text{blend}}(\lambda) &= \Delta n_{\text{CAP}}(\lambda) + \Delta n_{\text{add}}(\lambda) \\ &= \Delta n_{\text{CAP}}^0(\lambda) \phi_{\text{CAP}} F_{\text{CAP}} + \Delta n_{\text{add}}^0(\lambda) \phi_{\text{add}} F_{\text{add}}\end{aligned}\quad (6)$$

The orientation function of CAP, F_{CAP} , in this equation does not represent the chain orientation of CAP because the SOR is not applicable as reported by Yamaguchi et al.¹⁴ As mentioned above, since the wavelength dependence of birefringence is determined by the chemical structure, the component birefringence can be estimated from Δn_{blend} by solving the system of two eq. (6) with two wavelengths, λ_1 and λ_2 . By using this method, the orientation functions, F_{CAP} and F_{add} , can also be determined.

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