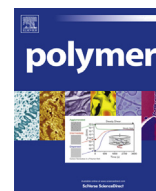




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## Extraordinary wavelength dispersion of birefringence in cellulose triacetate film with anisotropic nanopores

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### ABSTRACT

We examined birefringence in a stretched film of cellulose triacetate (CTA) after extraction of an immiscible component. The CTA film plasticized by di(2-ethylhexyl) adipate (DOA), which was added as the immiscible additive, exhibited negative birefringence to the same degree as the pure CTA film. Following removal of DOA from the film by immersion into methanol, the birefringence of the blend film changed dramatically from negative to positive. Moreover, the wavelength dependence also changed from ordinary to extraordinary, in which the absolute value of birefringence increases with wavelength. Scanning electron microscope (SEM) images revealed nanoscale ellipsoidal pores in the film after the extraction, suggesting that DOA was segregated and formed ellipsoidal domains in the CTA matrix during annealing and stretching. According to an optical theory for the nanoporous structure, we found that the form birefringence contributes to control of the optical properties of the CTA film. This phenomenon could be utilized in the design of high-performance optical films, such as quarter waveplate, because sign and wavelength dispersion of birefringence can be controlled even for a single component film.

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### 1. Introduction

Cellulose esters for use in optical films have been studied because they have favorable optical properties including transparency, thermostability, chemical resistance, and dimensional stability [1–6]. In particular, birefringence ( $\Delta n$ ), which is defined as the difference between two refractive indices, is one of the most important properties of optical films such as retardation and protection films [6–8]. Modern high-performance display devices, e.g., three-dimensional (3D) and organic electro luminescence (EL) displays, require a quarter waveplate with well-controlled  $\Delta n$  and wavelength dispersion [6,7].

For a quarter waveplate, the proportionality relationship between  $\Delta n$  and wavelength is important. To improve the optical properties of films, copolymerization [7,9], blending with other polymers or with additives [10–16], and lamination [17] have to be used because the wavelength dispersion is determined only

by the chemical structure of the polymers. However, these methods exhibit some problems; copolymerization reduces thermo-resistance, and polymer blending with low compatibility decreases film transparency. With lamination, the thermal expansion mismatch between polymer sheets restricts the useful temperature range.

The birefringence of polymeric materials has three components given by:

$$\Delta n = \Delta n_O + \Delta n_G + \Delta n_F \quad (1)$$

Here,  $\Delta n_O$ ,  $\Delta n_G$ , and  $\Delta n_F$  are orientation, glassy and form birefringence, respectively. The first term pertains to the chain orientation and the second is related to the distortion of chemical structure due to an applied force. The third term is associated with anisotropic nanostructures such as ellipsoidal structures. Based on an anisotropic dielectric theory [18] for the form birefringence, Ibn-Elhaj and Schadt [19] improved the birefringence of polymer thin films by the anisotropic nano-corrugated surface pattern. Therefore, the nano-porous structure possibly modifies birefringence of the polymeric films.

Moreover, many studies investigated porous structures in polymeric films for the application for separation membranes and

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separators in lithium ion second cells [20–22]. In general, porous films are prepared by using a thermo-induced phase separation (TIPS) of the matrix polymers and small amount of immiscible components, which are removed by immersing the films into selective solvents. We think that the porous structure by the TIPS technique contributes to the optical anisotropy, i.e., the form birefringence in cellulose ester films.

Because  $\Delta n_C$  in equation (1) is negligibly small compared to other terms for the hot-stretched polymer films, the birefringence property of stretched cellulose ester films can be modified by incorporation of an anisotropic nano-structure. In this study, the optical birefringence and its wavelength dispersion of cellulose triacetate (CTA, Fig. 1), used as a model polymer, was improved with anisotropic nano-pores.

In order to design nano-porous structure such as sea-island structures in CTA films, the phase separation technique can be utilized. Since CTA is a crystalline polymer that is insoluble in most solvents, such as methanol, removal of low-mass molecules (LMs) from the sea-island structure can be accomplished using the immersion method. Based on this idea, di(2-ethylhexyl) adipate (DOA, Fig. 1) was used as the immiscible LM and the pores were formed from sea-island structures resulting from phase separation of the CTA/DOA blend. In order to investigate the form birefringence, effects of chain orientation, crystallinity, and moisture content on birefringence of CTA film were also discussed.

## 2. Experimental

### 2.1. Samples

The CTA used in this study was produced by the Daicel Corporation (Japan). The degree of acetylation per pyranose unit of CTA was 2.96, as determined by  $^1\text{H}$  NMR spectroscopy. The weight-average and number-average molecular weights ( $M_w$  and  $M_n$ ) of CTA were  $3.5 \times 10^5$  and  $1.3 \times 10^5$ , respectively, as determined by gel permeation chromatography (GPC, HLC-8020 Tosoh, Japan) with TSK-GEL<sup>®</sup> GMHXL compared with polystyrene standards. DOA was used as a plasticizer to prepare the domains. DOA is commercially available and was supplied by Daihachi Chemical Industry (Japan).

CTA and CTA/DOA films were prepared using a solution-casting method; melt processing is not applicable because thermal degradation takes place near the melting point of CTA (around 300 °C). CTA and DOA in a ratio of 10/1 wt/wt were dissolved in a binary solvent of dichloromethane/methanol (9/1 vol/vol) and a 3 wt% solution was prepared. The solvent was evaporated at room temperature (RT) for 1 day at ordinary pressure and dried *in vacuo* for 1 day without controlling humidity. Since DOA is not volatile, the composition of the blend film was controlled by the ratio of components. The film thickness was 100–150  $\mu\text{m}$ .

### 2.2. Measurements

Dynamic mechanical analysis (DMA) of the sample films was performed to measure storage and loss moduli ( $E'$  and  $E''$ , respectively) at 10 Hz as a function of temperature using a tensile oscillatory rheometer (DVE-E4000, UBM, Japan) from 0 to 250 °C at a heating rate of 2 °C  $\text{min}^{-1}$ . The glass transition temperature ( $T_g$ ) was estimated from a peak of  $E''$  in the DMA data and is shown in Table 1.

A hot-stretching test for the films was carried out with a strain rate of 0.05  $\text{s}^{-1}$  using a tensile drawing machine (DVE-3, UBM, Japan). To avoid the thermal history effect, the films were annealed for 10 min before stretching. The drawing temperatures ( $T_{\text{draw}}$ ) were adjusted to obtain the same stress levels for CTA and CTA/DOA films, as shown in Table 1. The films were immediately quenched by cold air blowing after stretching to avoid relaxation of molecular orientation.

The orientation birefringence ( $\Delta n$ ) of the films was measured as a function of wavelength using an optical birefringence analyzer (KOBRA-WPR, Oji Scientific Instruments, Japan). The details of the optical system have been described previously [23]. Refractive indices at various wavelengths of CTA and DOA were measured by using an Abbe refractometer (DR-M2, Atago, Japan).

To remove DOA, the stretched and unstretched films were immersed in methanol for at least 8 h and dried *in vacuo* for 1 day at RT. The complete removal of DOA from the film was confirmed by the  $^1\text{H}$  NMR spectra before/after immersion using an AVANCE III NMR 400 (Bruker Corporation, Germany). The obtained films were kept in a humidity chamber (IG420, Yamato, Japan) at 25 °C and 50% relative humidity (RH) for 1 day to avoid the effects of uncontrolled moisture on the optical properties, as previously reported [24]. The moisture content of the films was determined using a Karl Fisher moisture meter (Mitsubishi Chemical Analytec Co., Ltd, Japan).

The morphology of the films was examined using a scanning electron microscope (SEM) (S4100, Hitachi Ltd, Japan) with an acceleration voltage of 20 kV. Prior to the observation, the surfaces of the films were coated with Pt–Pd in an ion-sputter machine (E1010, Hitachi Ltd., Japan). In order to examine the sea-island structure in CTA/DOA films, a light scattering (LS) measurement was carried out at room temperature by using a LS analyzer (DYNA-3000, Otsuka Electronics Co., Ltd., Japan). The correlation length, which reflects the morphology of CTA/DOA films, was estimated from the LS data.

The wide-angle X-ray diffraction (WAXD) pattern was measured at RT using a powder X-ray diffractometer (RINT-2500, Rigaku, Japan) by refractive mode to evaluate the crystallinity of CTA in the films. The experiments were carried out using CuK $\alpha$  radiation at 40 kV and 30 mA at a scanning rate of 1°  $\text{min}^{-1}$  over 2 h (Bragg angle range from 5 to 60°).

## 3. Results and discussion

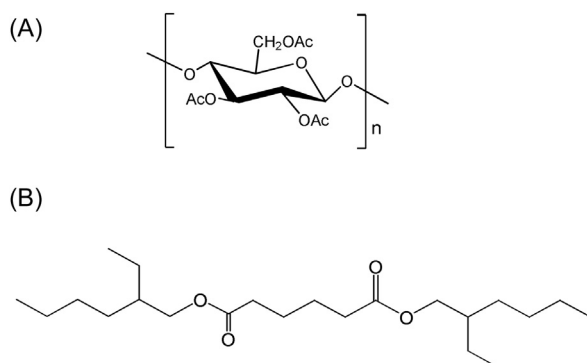
### 3.1. Plasticization effect of DOA on dynamic mechanical property of CTA

Dynamic mechanical properties of polymeric materials represent miscibility or immiscibility of the blends. Furthermore, the

**Table 1**

Glass transition and drawing temperatures ( $T_g$  and  $T_{\text{draw}}$ ) for CTA and CTA/DOA films.

	$T_g/^\circ\text{C}$	$T_{\text{draw}}/^\circ\text{C}$
CTA	188	213
CTA/DOA	183	205



**Fig. 1.** Chemical structures of CTA and DOA.

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