



Control of three-dimensional refractive indices of uniaxially-stretched cellulose triacetate with low-molecular-weight compounds

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ARTICLE INFO

Article history:

Received 22 May 2014

Received in revised form 15 July 2014

Accepted 19 July 2014

Available online 30 July 2014

Keywords:

Birefringence

Cellulose triacetate

Blend

Orientation

ABSTRACT

A method to control the 3D refractive indices and wavelength dispersion of birefringence of polymer films by uniaxial stretching with addition of various low-molecular-weight compounds (LMCs) with strong polarizability anisotropy is developed. Biomass-derived cellulose triacetate (CTA) films containing a small amount of crystallites at the stretching temperature are found to show planar deformation to some degree only by uniaxial stretching. Although molecular orientation evaluated from the in-plane and out-of-plane birefringences of pure CTA seems consistent with uniaxial deformation, LMC addition pronounces the deviation of the refractive index from uniaxial symmetry. Rod-shaped molecules are found to greatly enhance both in-plane and out-of-plane birefringences because of their marked orientation in the stretching direction. Conversely, the out-of-plane birefringence increases more than the in-plane one upon addition of disk-shaped molecules, because the LMC molecules tend to be embedded in the film plane. Consequently, 3D refractive indices of CTA can be controlled only by uniaxial stretching, not biaxial one, with an aid of an anisotropic LMC.

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1. Introduction

Cellulose triacetate (CTA) is a biomass-derived material that has found application in films produced by solution casting because of its severe thermal degradation beyond its melting point [1–3]. The common optical film applications of CTA include as a photographic film base and polarizer protection film because of the attractive properties of these films such as high transparency and excellent heat resistance [1,3,4]. CTA films are currently widely employed in liquid crystal displays, and show promise for use in advanced systems such as 3D and electroluminescent displays. To be used in polarizer protective and retardation

films, it is important to control the birefringence of CTA. For example, polarizer protective films need to be free from birefringence, and thus advanced methods to erase birefringence have been proposed recently [5–7]. For retardation films, specific retardation, *i.e.*, the product of birefringence and thickness, is required.

It is well known that the orientation birefringence of polymers is determined by the chain orientation and polarizability anisotropy of the repeating unit. For example, a polymer showing positive birefringence has a larger molecular polarizability, and thus refractive index, in the main chain direction than those in the perpendicular directions. The magnitude of birefringence is further controlled by the chain orientation in the stretched film. In general, refractive indices in the in-plane directions (n_x and n_y) can be controlled by uniaxial stretching. However, the

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refractive index in the film-thickness direction (n_z) should be modulated in addition to n_x and n_y to obtain optical displays with a wide viewing angle. Therefore, an advanced method should be used to control the refractive index n_z and to satisfy the relationship between the refractive index in each direction.

To date, the most conventional method to obtain the 3D control of refractive indices is biaxial stretching, as exemplified by van Horn and Winter [8], which has the drawback of being expensive. Therefore, much attention has been focused on a new alternative method. The Cakmak research group recently reported the thickness distribution of optical anisotropy in solution-cast films in detail, indicating that the refractive index in the film thickness direction can be controlled by solvent evaporation rate [9–11].

As well as 3D control, the wavelength dispersion of birefringence also has to be precisely modulated for high-performance retardation films. For example, a specific retardation, *e.g.*, a quarter or half of the wavelength, should be provided in the whole visible light region for multi-band wave plates. Because most conventional polymers show ordinary wavelength dispersion of orientation birefringence as expressed by the Sellmeier relation (Eq. (1)), various techniques have been proposed to obtain films showing extraordinary dispersion [12–16].

$$\Delta n(\lambda) = A + \frac{B}{\lambda^2 - \lambda_{ab}^2}, \quad (1)$$

where λ_{ab} is the wavelength of a vibrational absorption peak in the ultraviolet region, and A and B are the Sellmeier coefficients. We previously found that transparent films of cellulose acetate propionate show positive in-plane birefringence that increases with wavelength; *i.e.*, extraordinary wavelength dispersion [15–17].

Several methods have been already proposed to control the birefringence in polymeric materials, such as copolymerization with appropriate monomers [18], doping with anisotropic crystals [19] and blending with another polymer [14–16] or a low-molecular-weight compound (LMC) [17,20]. In the polymer blend method, miscible polymer pairs showing different signs of intrinsic birefringence with different wavelength dispersion are mixed on a molecular scale to minimize light scattering.

CTA films prepared by solution casting show uniform thickness, high transparency, and adequate mechanical properties. The sign of out-of-plane birefringence in a solution-cast CTA film is opposite to that of the in-plane orientation birefringence in a hot-stretched one. Moreover, the wavelength dispersion of the out-of-plane birefringence is extraordinary for a solution-cast film. Our previous study also revealed that the out-of-plane birefringence and its wavelength dispersion of a solution-cast film can be modified by the addition of an LMC that is miscible with CTA, such as tricresyl phosphate (TCP) [21]. This is attributed to the molecular orientation of TCP induced by the nematic interaction, *i.e.*, intermolecular orientation correlation, between CTA and TCP.

In this study, both the 3D refractive indices and wavelength dispersion of birefringence of films are controlled by uniaxial stretching, in which the anisotropy in the

shrinkage between lateral and thickness directions is used. It is well known that the lateral shrinkage of a polymer film extruded from T-die, known as “neck-in”, is small for a polymer melt showing marked strain-hardening in elongational viscosity [22–25]. In other words, the transversal orientation in the film plane occurs to some degree, although it is not so obvious compared with equi-biaxial elongation for a polymer melt. Therefore, long-chain branched polymers with marked strain-hardening, *e.g.*, low-density polyethylene produced by radical polymerization, are preferably used in industry to reduce the neck-in level during T-die film processing. Moreover, various methods to enhance strain-hardening have also been proposed [26–29]. Yamane et al. showed marked strain-hardening in elongational viscosity for poly(lactic acid) (PLA) having a small amount of stereocomplex crystals whose melting point is higher than that of a conventional PLA [27]. Because CTA also contains a small amount of crystallites [1,3], which act as branch points, at the stretching temperature, it is expected to show strain-hardening; *i.e.*, transversal orientation besides the orientation to the stretching direction, only by uniaxial stretching. The transversal refractive index caused by the transversal orientation of CTA chains is magnified by LMCs because of their nematic interaction with CTA. In this work, two types of LMCs are used from the viewpoint of molecular shape: TCP and triphenyl phosphate (TPP) as disk-shaped molecules and 4-cyano-4'-pentylbiphenyl (5CB) as a rod-shaped one. Finally, the mechanism of this phenomenon is discussed based on molecular orientation. Since the control of 3D refractive indices and their wavelength dispersion are strongly required to produce advanced displays, the phenomenon described in this paper will be seriously considered for the industrial application.

2. Experimental

The polymeric material used in this study was commercially available CTA produced by Acros Organics. The degree of substitution of CTA was 2.96, and its weight-average molecular weight M_w was 3.50×10^5 Dalton, which was evaluated using a gel permeation chromatograph (Tosoh, HLC-8020) with TSK-GEL[®] GMHXL as a polystyrene standard. TCP and TPP purchased from Daihachi Chemical Industry were employed as disk-shaped LMCs. 5CB from Wako Pure Chemical Industries was used as a rod-shaped LMC. Their chemical structure is shown in Fig. 1.

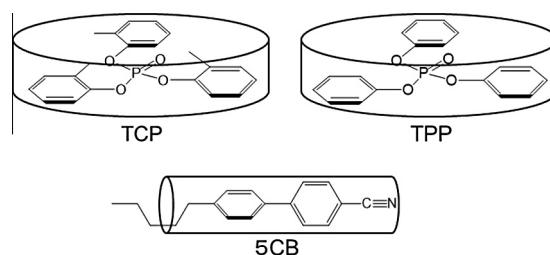


Fig. 1. Chemical structure of LMC samples used in this study.

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