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Effect of backbone on the biaxial retardation of polyimide films in uniaxial stretch

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Abstract

A biaxial-retardation film prepared from the uniaxial-stretched polyimide (PI) film was developed for compensating the viewing angle of liquid-crystal displays. Good uniformity of in-plane birefringence in well-stretched PI films was observed visually with two crossed polarizers. The prism coupling method was used to measure the n_x, n_y, n_z, and thickness of the stretched PI films. The birefringence variations of $n_x - n_y$ (difference of refractive indices between *x*- and *y*-axes) and $n_x - n_z$ during the stretching process were highly affected by PI structure. The polarizability tensors and intrinsic birefringences of the PI repeat units were estimated by Gaussian 98W. It was found that the stretch-induced birefringence is more related to the average polarizability per volume at the low elongation period.

Keywords: Optical materials; Polyimide; Computer modelling and simulation; Birefringence

1. Introduction

Polymer films with large anisotropic optical properties are not favored in communication media application such as polymer waveguides [1,2]. On the other hand, large birefringent polymer films have important application in optical films for liquid crystal display (LCD) [3–6]. Therefore, methods are needed to adjust the optical anisotropies between minimum and maximum values for optimization in different applications. The stretch or draw method is now a common used way in industry to induce the birefringence of optical films.

Optical anisotropies of polymer films are mostly related to the chemical structures and fabrication processes. Some polymers with rigid structure show high birefringence after casting film on substrates. Aromatic polyimides (PIs) were found to be used as uniaxial negative birefringent compensators (negative C plate) for twisted nematic (TN) LCDs by Dr. Harris since 1996 [3,4]. In this case, birefringence of polyimide films could be adjusted by varying chemical structures through the copolymerization. However, negative C plate can only compensate the light leakage from the LC layer. Light leakage from the crossed polarizer, in the off-axis, is a serious problem in high-quality LCDs that require a wide-angle view and high contrast ratio in all azimuthal directions. A conventional method to compensate both the light leakage from the LC layer and crossed polarizer is using a combination of an A- and C-plate [5,6]. Another alternative is to use biaxial retardation films [7]. The A-plate or biaxial retardation film is usually fabricated through stretching or drawing polymer films [8]. Due to the low birefringence, the commercial compensation films need high thickness (>80 μm). Moreover, two sheets are usually required to have enough compensating performance.

To simultaneously overcome the high thickness and high cost problems of the wide-viewing-angle polarizer in the high competitive LCD industry, we suggested a biaxial retardation film of high retardation value by uniaxially stretching a thin polyimide film in an earlier publication [9]. We found that the birefringence generated by a uniaxial stretch was greatly affected by the structure of PI backbone. However, detailed mechanisms governing how the PI structure affects the induced birefringence have not been fully understood. Recently, new studies on intrinsic birefringence for the PIs having various aromatic structures were reported [10–12]. We think the intrinsic birefringence may play a key role in the structural effects on the stretched-induced birefringence. Moreover, little is known about the influence of main

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chain structure on the induced birefringence when the elongation is low.

This paper described the results of the studies on stretch-induced birefringence using different main chain structures while keeping the same stretch conditions. We have prepared two low-T_g polyimides based on 4,4′-(4,4′-isopropylidenediphenyl-1,1′-diyldioxy) dianiline (BAPP) which has soft and bended structure. Two dianhydrides of aromatic and aliphatic structures were used to modify the main chain structures of PIs. The PI films were obtained and successfully stretched at 260 °C. Their applications as LCD retardation films were evaluated, and the correlation between PI structures and stretch-induced birefringence was discussed.

2. Experimental

2.1. Materials

In our experiments, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) was purchased from Aldrich. 3,4-Dicarboxy-1,2,3,4-tetrahydro-1-naphthalenesuccinic acid dianhydride (D2192) was obtained from TCI. 4,4′-(4,4′-Isopropylidenediphenyl-1,1′-diyldioxy) dianiline (BAPP) was obtained from Chriskev. 6FDA was purified by sublimation under reduced pressure before use. D2192 and BAPP were used as received. *N*-Methyl-2-pyrrolidone (NMP) was dried via the benzene azeotrope. As the precursors of PI, poly(amic acid) (PAA) solutions were prepared by the polycondensation reaction of one dianhydride and the BAPP diamine in NMP. The respective dianhydride was added to the BAPP solution and mechanically stirred at 25 °C for 48 h under N_2 purge. The inherent viscosities of the obtained PAA solutions were measured using Ubbelohde viscometers at a concentration of 0.5 g dl^{-1} at 25 °C. The measured PAA viscosities of D2192-BAPP (D-B) and 6FDA-BAPP (6F-B) were 0.67 and 0.63 dl g^{-1}, respectively. PAA films were prepared by soft baking of PAA solutions on poly(ethylene terephthate) (PET) films at 70 °C for 1 h. The PAA films were removed from the PET films, fixed between two steel frames, and then step heated to 300 °C in N_2 oven. The resulting 20 micron-films of D2192-BAPP and 6FDA-BAPP were colorless and slightly yellow, respectively. The D-B film and 6F-B film exhibited glass transitions at 250 and 254 °C, respectively under the TMA (Thermal mechanical analysis, Q400 by TA Instrument) method.

2.2. Stretch of PI films

To stretch the polyimide film, we used the dynamic mechanical analyzer (DMA 2980 by TA Instrument). Stress relaxation method set-up in the software of DMA 2980 was used to perform the stretch process. The five controlled factors were preload force (N), strain (%), isothermal temperature (°C), soak time (min), and relaxation time (min). Preload force is a key factor to control the extending ratio when other factors are suitable. The isothermal temperature and soak time were set to be 260 °C and 5 min, respectively, according to a series of pretests with several D-B films.

2.3. Measurement of optical property

A UV–vis spectrometer (Lambda 900 by Perkin-Elmer) with an integrating sphere (PELA-1020 by Labsphere Inc.) was used to evaluate the Haze and transparency of the prepared PI films. The measurement of Haze followed the ASTM 1003-92 standard method.

To analyze the birefringence change in stretched PI films, the prism coupling method (SPA-4000 by SAIRON Technology) was used to measure the n_x, n_y, n_z, and thickness of the stretched PI films. The principle and instrumental set-up has been described elsewhere in detail [13,14]. The two in-plane refractive indices (RI), n_x and n_y, and the film thickness were obtained from two measurements with s-light in parallel and perpendicular to the sample stretch direction. From corresponding measurements using p-light, the refractive index normal to the film plane (n_z) was obtained. Due to the necking problem in some samples under high preload force, three points of each sample were measured at a wavelength of 632.8 nm. A wafer was used as a substrate to carry the samples which were pressed against the prism uniformly. For accurate measurements, the thickness of PI films should not be larger than 20 μm.

2.4. Calculation of polarizability tensor

The Gaussian 98W program package (version 5.4) was used for Hartree–Fock (HF) and the density functional theory (DFT) calculations for PI repeat units of D2192-BAPP and 6FDA-BAPP. The B3LYP hybrid functional was employed in the DFT calculations. The semi-empirical method (AM1) of Hartree–Fock theory (HyperChem Pro 6, version 6.03) was used to optimize the structures of PI repeat units. The STO-3G and 6-31G of B3LYP were used to calculate the molecular polarizability and volume of the optimized PI structures.

3. Results and discussion

3.1. Stretch conditions of PI films

The stretch of PI films was performed by DMA 2980. The preload force was designed to be a key factor for controlling the extending ratio. For this purpose, we did some pretests for seeking the suitable stretch conditions with the D-B films. The test results are summarized as follows. First, under long relaxation times, all stretched samples would extend to maximum elongation (limited by the chamber size of DMA 2980) even at the smallest preload force. Thus, we set a short relaxation time of 0.01, in order to examine the effect of the preload force. Second, as the high strain exacerbates the necking problem of stretched samples the strain factor was limited to no more than 0.05, usually 0.01.

The stretched samples of PI films are shown in Fig. 1. With the open-chamber system of our DMA 2980, even nitrogen purge could not prevent yellowing (due to oxidation) of most D-B films during the stretching period at 260 °C, which is higher than the T_g of the PI film (see the three samples on the right in Fig. 1). However, the stretched D-B films under large preload force (such as over 0.2 N) and without nitrogen purge were colorless. Perhaps the large preload force required a shorter time to reach maximum elongation at the over-T_g temperature and did not allow enough time for the film to yellow (see the two samples on the left in Fig. 1). The necking phenomenon of D-B films after stretching under large preload forces was significant because we did not have proper clamping apparatus. However, such necking phenomenon should not occur at biaxial-stretch production lines in industry.

3.2. Optical properties of haze and transparency

The calculated Hazes of D-B film and 6F-B film are smaller than 0.1 and 0.16, respectively, at the scanned wavelength from 780 to 380 nm. Fig. 2 shows the visible spectrum of PI films that measured with the same integrating sphere. Both PI films showed high transparency close to 89% at 550 nm. The 6F-B film showed lower transparency than D-B film at wavelength lower than 480 nm. The D-B film showed excellent colorless quality as compared with other PI films without fluorine atoms [15].