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The Generation of Biaxial Optical Anisotropies in Polyimide Films by an Uniaxial Stretch Method

Jinn-Shing KING*, Wha-Tzong WHANG, Wen-Chin LEE[1] and Li-Ming CHANG[1]

Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, R.O.C.
[1]*Materials Research Laboratories, Industrial Technology Research Institute,*
Building 77, No. 195, Section 4, Chung Hsing Road, Chutung, Hsinchu 310, Taiwan, R.O.C.

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A new biaxial-retardation film prepared from the uniaxial-stretched polyimide (PI) film was developed for compensating the viewing angle of liquid-crystal displays. A new aliphatic PI showing high transparence and low glass-transition temperature was firstly prepared for the biaxial-retardation film purpose. Both retardations in x–y and x–z planes of PI films were highly increased after stretching them uniaxially at 260 °C. Good uniformity of birefringence in well-stretched PI films was observed visually with two crossed polarizers. The birefringence variations of $nx - ny$ (difference of refractive indexes between x- and y-axes) and $nx - nz$ during the stretching process were highly affected by PI structure. [DOI: 10.1143/JJAP.45.L501]

KEYWORDS: liquid crystal display, viewing angle, biaxial retardation film, stretch, polyimide

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 Harris and coworkers since 1996.[3,4] In this case, birefringence of PI 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-plate and a 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 PI film. Because of their high glass transition temperatures ($T_g > 300$ °C), traditional PI films are rarely considered in generating biaxial retardation through stretching. In this study, two low-T_g PIs were synthesized and their films were successfully stretched at 260 °C. The PIs are different in the used dianhydrides of aromatic and aliphatic structures. We compare these two uniaxial-stretched PI films in terms of their biaxial retardation properties. The stretched PI films show both high in-plane and out-plane birefringence over 0.015 in 40% elongation. Uniform in-plane retardation was observed between two crossed polarizers. Two outstanding features of these biaxial retardation films deserve special mention: (1) It reduces cost by eliminating an A-plate and the combining process. Also, since the commercial PI films are already produced by a biaxial stretch during imidization process, additional equipment to produce the uniaxial stretch may be not needed. (2) It is a thin and freestanding film. Thus, the thickness of wide-viewing-angle polarizer could be reduced for a better polarizer design. Both features are particularly attractive for LCD polarizer makers.

The structures of dianhydride and diamine monomers are shown in Fig. 1. The precursors of PIs (polyamic acid: PAA) were prepared by polycondensation reaction with one dianhydride and the BAPP diamine. The PI films were then fabricated by curing the PAA films in N_2 oven by step heating to 300 °C. The resulting 20-micron films of D2192-BAPP (D-B) and 6FDA-BAPP (6F-B) 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 thermal mechanical analysis (TMA) method. To stretch PI 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. The stretched samples of PI films are showed in Fig. 2 with polarizers. To study the compensating property to the light leakage from the crossed polarizers, we put four stretched samples into one set of crossed polarizers, where the stretch direction of each sample was kept at 45 deg to each polarization of polarizer. Figure 2 shows the pictures of five PI films observed from three view angles of 45, 0, and −45 deg. When the view

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*E-mail address: AlexKing@itri.org.tw

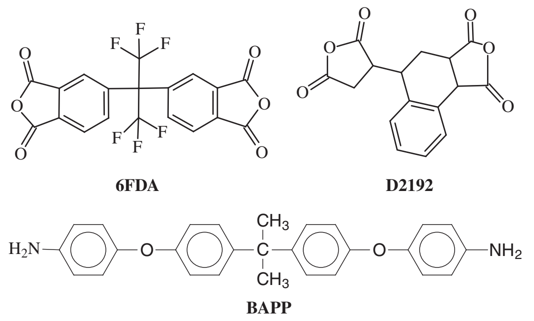

Fig. 1. Chemical structures of the 6FDA, D2192 and BAPP monomers used for biaxial retardation film studies. [D2192-, 3,4-Dicarboxy-1,2,3,4-tetrahydro-1-naphthalenesuccinic acid dianhydride; 6FDA-, Hexafluoroisopropylidene diphthalic anhydride; BAPP-, 4,4′-(4,4′-Isopropylidenediphenyl-1,1′-diyldioxy) dianiline].

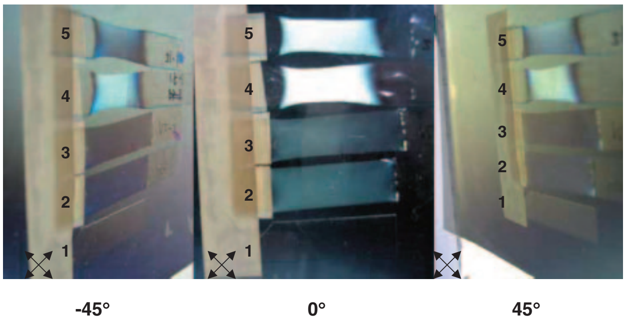

Fig. 2. The photos of light leakage in three viewing angle from stretched PI films that were sandwiched in two crossed polarizers. The arrows in the pictures correspond to the polarization direction of an analyzer and a polarizer.

angle was shifted to ±45 deg, the light leakage was observed visually. Sample 1 is the non-stretched D-B film which shows no influence on the light change in three view angles. Samples 2 to 5 are stretched D-B films of different stretching conditions. As expected, the stretched D-B films could reduce the light leakage at view angle of ±45 deg, and exhibited a visually observed compensating property of an A-plate. No color shift was observed, and the birefringence was very uniform. The brightest light was observed in sample 4 that exhibits largest *R*0 (retardation in *x*–*y* plane, A-plate) in three view angles. Sample 4 necked under a strong stretching condition and thus showed higher retardation than others.

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 setup has been described elsewhere in detail.[9,10] The two in-plane refractive indices (RIs), 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 RI normal to the film plane (n*z*) was obtained. Due to the necking problem in some samples with high preload force, three points of each sample were measured at 632.8 nm wavelength. A wafer was used as a substrate to carry the samples which were pressed against the prism uniformly.

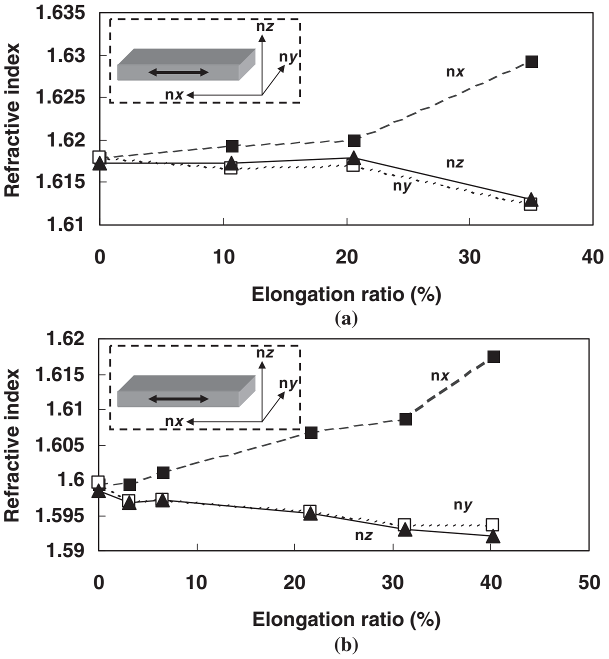

Fig. 3. Refractive indexes of each axis, n*x*, n*y*, and n*z*, in D-B films (a) and in 6F-B films (b) at different elongation ratios. The arrow in the illustration corresponds to the stretch direction applied on the PI films.

For accurate measurements, the thickness of PI films should not be larger than 20 µm. The n*x*, n*y*, and n*z* of the stretched PI films with controlled elongation ratios were showed in Fig. 3.

Figure 3 shows the variations of n*x*, n*y*, and n*z* induced from the elongation change of D-B films and 6F-B films. To analyze the correlation between the birefringence variations and elongation degrees of PI films, we took stretched D-B films for the example. Birefringence (n*x* − n*y*) of the stretched D-B film was calculated from the measured RI and shown in Fig. 4. The preload force is the key factor to control the stretch condition. Figure 4(a) shows the correlation between preload force and the birefringence of stretched samples. The preload force was varied from 0.01 to 0.3 N while the birefringence (in average) induced increased from 0.0004 to 0.0176. The non-uniformity of birefringence induced by necking phenomenon was observed in the sample with high preload force of 0.3. Usually, point 2 was close to the neck position of sample, which is near the pulling side. The stretch ratio of D-B film reached a limit (limited by chamber size of DMA 2980) when preload force exceeded 0.2 N at 260 °C. The excessive preload force of 0.3 N generated a necking area in the PI film. Consequently a higher birefringence near point 2 was induced, which increased the average value of birefringence of this sample in Fig. 4(b). In conclusion, adjustment of the stretching force is important for generating uniform birefringence in PI films.

In order to evaluate the biaxial retardations of PI samples, we can calculate the retardation through multiplying Δn by thickness measured by SPA-4000. We can also measure the retardations of *R*0 and *R*th (retardation in *x*–*z* plane, C-plate) of PI samples by an instrument (RETS-3200RF) made by Otsuka Electronics. The retardation data from the prism coupler method were compared with data from the direct

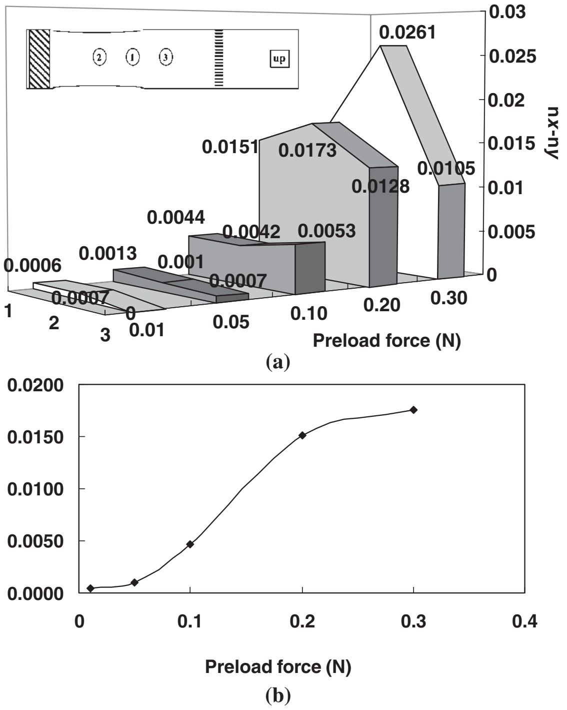

Fig. 4. The birefringence of stretched D-B films at different preload forces. (a) shows the birefringence data that correspond to their measuring sites in each sample. (b) shows the correlation between the preload force and average birefringence of each stretched D-B film.

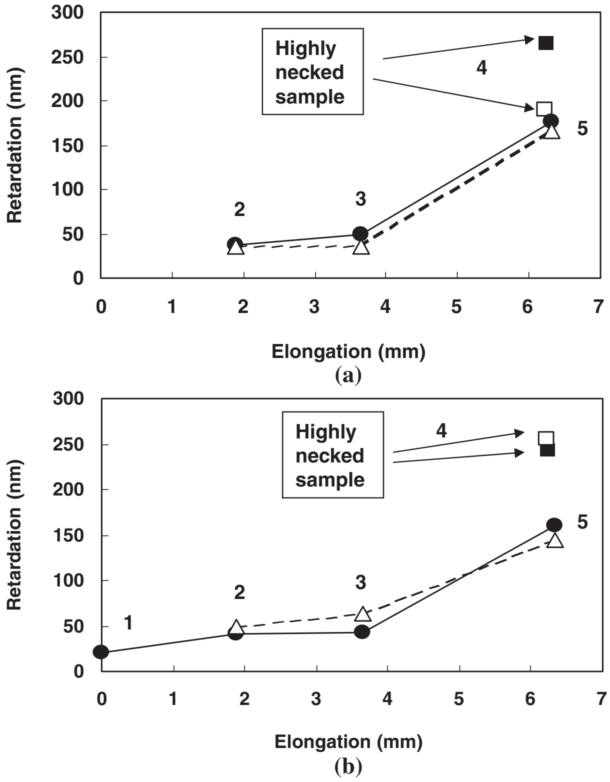

Fig. 5. The retardations, *R*0 (a) and *R*th (b), of the stretched D-B films which were evaluated by a prism coupling method and a direct retardation measurement. The marked numbers are the sample IDs. (● and ■: by prism coupling method; □ and △: by direct retardation measurement.) All data are the average value of three points on a sample including both methods.

retardation measurement. Figure 5 shows the compared results. The data points in Fig. 5 belong to five D-B films with different elongations mentioned in Fig. 2. Both methods gave obvious *R*0 and *R*th in each stretched PI films, which demonstrates the generation of biaxial retardation. The *R*0 and *R*th retardations evaluated by these two different methods are quite matched except for the highly necked sample 4 in *R*0 comparison. The retardation of sample 4 calculated from Δn and thickness is 266.87 which is higher than the value of 189.13 measured from RETS-3200RF instrument. This result reminds us that, while samples of 4 and 5 may have the same elongation ratio, the degrees of necking phenomenon by different preload forces can be different. Moreover, the prism coupler method can sense local deviation of birefringence better than direct retardation measurement. It may be due to the smaller beam size of Hi–Ni laser used in SPA-4000. In conclusion, the biaxial retardation of uniaxial-stretched PI films was confirmed by both methods of RI measurement and direct retardation measurement.

In the final part of this study, we discuss the effect of PI structure on the induced birefringence with a stretch. Figure 3(a) shows the variations of nx, ny, and nz, which were induced by the elongation change of D-B films. Because of the soft and bended structure of aliphatic dianhydride and BAPP diamine, the out-of-plane birefringence (TE − TM or nx − nz) is very low, down to 0.0007. With an increase in elongation ratio, the in-plane birefringence (nx − ny) increased sharply after a slow rise at beginning. It is interesting to note that the out-of-plane birefringence also increased significantly with the increase of elongation ratio. The fact that nz and ny have the same trend of RI variation is not surprising as this had been reported in earlier publications.[11)] But we found the degrees of RI variation in y and z axles are almost the same, which may be attributed to the initial soft and bended structure of D-B. The rearrangement of polymer chains during stretch period showed the same influence on in-plane (nx − ny) and out-of-plane (nx − nz) anisotropies of D-B films.

The RI variation of 6F-B films in Fig. 3(b) shows more gradual change with the increase of elongation ratio, when compared with that of D-B films. At the same elongation ratio (= 0.2), 6F-B film exhibits more than three times larger birefringence than D-B film does. Although the 6F-B has a fully aromatic structure, the bended structure and soft linkage group give the 6F-B film low out-of-plane (TE − TM or nx − nz) birefringence (= 0.0012). However, the larger dipole moment of 6F-B polymer chains induces higher degree of chain–chain interaction[11)] during the stretch process. Hence 6F-B films exhibit larger birefringence at the same elongation ratio when compared with D-B films. Due to the significant effect of PI structure on the induced birefringence of stretched PI films, we can easily modify the compensation performance of the biaxial-retardation PI films through designing the PI structure and controlling elongation condition. Nevertheless, we need to trade-off among many properties, such as transparence vs high dipole structures.

Further studies on the effect of PI structure are being conducted with suitable simulation methods[12)] to clarify the influence of molecular polarizability on the induced birefringence. We think the dipole–dipole interaction could be a major force in chain–chain interaction. Besides, calculating the intrinsic birefringence of PI structure may give us more information to uncover the mystery of stretching-induced birefringence.

In summary, we have developed a new biaxial retardation film for compensating the viewing angle of LCD. The stretch of PI films was successfully performed at 260 °C with our low-T_g PIs. The D-B film that shows high transparence to visible light is very suitable for many optical film applications, such as retardation films. The prism coupler method has been used to measure the nx, ny, and nz of the stretched PI films and shown higher sensitivity to birefringence variation than the direct retardation measurement. The advantages of PI biaxial-retardation films are that both the high thickness and high cost problems of the wide-viewing-angle polarizer in the high competitive LCD industry may be overcome simultaneously. Methods for analyzing the correlation between PI structure and induced birefringence with a stretch are under further investigation.

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