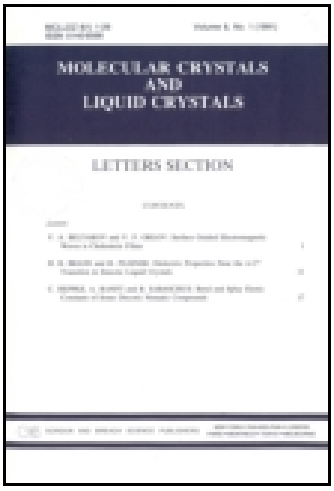

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Photo-Alignment Using Benzophenone Sensitized Photodecomposition of the Polyimide

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Photo-Alignment Using Benzophenone Sensitized Photodecomposition of the Polyimide

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For more aggressive photo-decomposition of polyimide, the photoreactions employing triplet mechanism and the double fragmentation reactions were carried out. The polyimide was synthesized with cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA) and 4, 4′-diaminobenzophenone (DABP) by condensation reaction. The benzophenone is well known triplet photo sensitizer, which was mixed with the equal mole ratio of the CBDA, The imidization reaction was confirmed by imide peak formation in FT-IR spectra. The orientation of polymer chains was confirmed by polar dichroic ratio of the liquid crystal cells. The benzophenone chromospheres shortened the UV irradiation time for the photodecomposition and induced the orientation of the polyimide chains.

Keywords Polyimide; photo-decomposition; liquid crystal display; photo alignment

1. Introduction

A liquid crystal display (LCD) is composed of several components such as the liquid crystal, the color filters and the liquid crystal alignment layers. The liquid crystal alignment layers have an important role to align liquid crystal molecules which regulated the transmission of light. The rubbing method has been the most popular mass production process to align liquid crystals in LCD. The rubbing methods cause scratches, damages and static electricity on the substrate. The cost effective ultra-hi-definition TV requires fast and dust free alignment processes. There has been increasing interest in contactless align methods in the past decade although the methods generally have low anchoring energy for the liquid crystals than rubbing method [1]. There have been many papers on the photo-induced alignment by irradiating UV. The UV-alignment methods are very useful the widening wide viewing angle of large scale LCD TV [2]. The photo-alignment methods incurred the deformation of polymer chains near the polymer surface which selectively reacted with the polarized light. Photo-reactions that can be used for the photo-alignment are decomposition, isomerization and dimerization. The dimerization requires severe structural arrangement before the photoreaction, which is unflavored by entropy. Photo-decomposition and photo-isomerization reactions are entropically favored unimolecular reactions. Many isomerization reactions are reversible, which deteriorated the long term picture quality. Ultimately, we incorporated the 4, 4′-diaminobenzophenone (CBDA-DABP) as the triplet sensitizer to cyclobutane-1, 2, 3,

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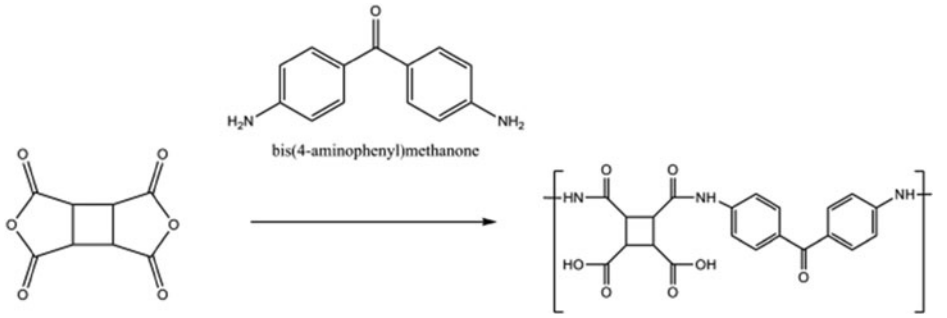


Figure 1. Synthetic scheme of polymerization with cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA) and 4, 4′-diaminobenzophenone(DABP).

4-tetracarboxylic dianhydride. In this work, we reported the synthesis of new polyimide and photochemical behavior of polyimide films used for LCD.

2. Experimental

2.1. Polymer Synthesis

Synthesis scheme of polyamic acid was shown in Fig. 1. The polyamic acid was prepared from 1g of CBDA (0.0051 mol), and 1.08 g of DABP (0.0051 mol). A mole ratio of CBDA and DABP was 1:1. 1.08 g of DABP was dissolved in 13.3 ml of NMP (solid contains of 15 wt%) with nitrogen-purged, and then mixture put in flask and 1 g of CBDA was added slowly to solution. The reaction mixture was stirred at 0∼10°C for 24 hr in ice bath [3]. CBDA and 4, 4′-diaminobenzophenone (DABP), were commercially available Sigma Aldrich and used as obtained. N-methyl-2-pyrrolidone (NMP) was reagent grade and was purified before use.

2.2. Fabrication of Liquid Crystal Cell

LC cells were prepared to evaluate the alignment properties of liquid crystals in between alignment layers. Coating solution was the polyamic acid (1.5 g), NMP (2.1 g), γ-butyrolactone (1.2 g), and 2-butoxyethanol (2.25 g) [4]. The ratio was 1: 1.4: 0.8: 1.5 by weight. To improve interactions between polyamic acid and surface of substrate, and to reduce viscosity of polyimde, γ-butyrolactone and 2-butoxyethanol were added to coating solution [5]. The polyimide solutions were coated onto indium tin oxide (ITO) substrate using spin coater at 2500 rpm for 60 sec. The coated-films were pre-baked at 90°C for 10 min to vaporize solvent and then hard-baked at 230°C for 60 min in vacuum oven (model 280A) [6]. During the hard-bake process, polyamic acid became polyimide. Fig. 2 shows imidization reaction.

To align liquid crystal on polyimide film, the polyimide films were irradiated linearly polarized UV light (LPUV) at 254 nm wavelength using low pressure Hg-lamp. Polyimide have orientation by dissolve the molecular structure of polyimide in a fixed direction. Place two substrates with opposite coated layer horizontal and vertical direction and glue substrates using 4.5 μm spacer and UV hardening agent. A nematic liquid crystal (E7,

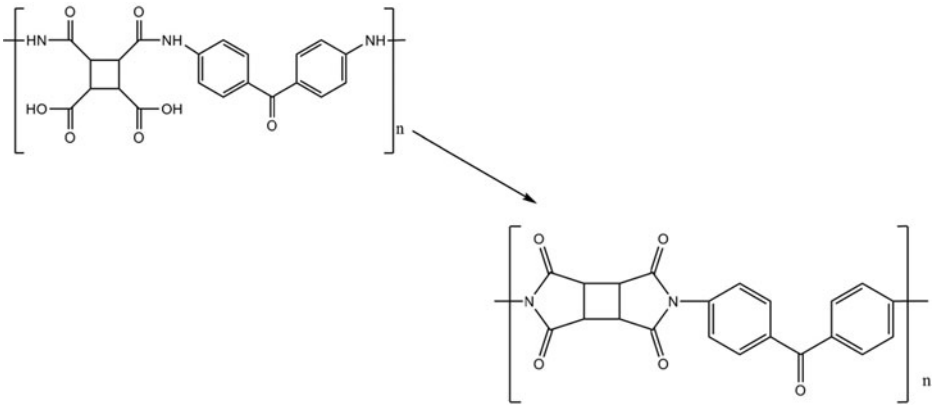


Figure 2. The imidization reaction of cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA) and 4, 4′-diaminobenzophenone (DABP).

Merck) containing dichroic dye (disperse blue) was optically evaluated alignment properties. A dichroic dye which has a peak at 655 nm was used to confirm [7] from UV-visible spectrometer (Agilent 8453). A liquid crystal mixture was injected between a cell gaps by capillary method at 50°. A nematic range of liquid crystal (E7) is −10°C∼60.5°C [8].

2.3. Measurements

The measurement of synthesized polyamic acid was carried out with Fourier transform infrared spectroscopy (FT-IR, F-510/520 Series). A small amount (about of 0.1∼0.2% of the KBr amount) of CBDA and DABP which are powder were mixed with KBr [9]. To measure properties of liquid crystal cell, the polar diagrams were made by UV-visible spectrometer [10]. From these measurements of alignment properties of polyimide, the dichroic ratio(R) is calculated from the Maier–Saupe theory [11].

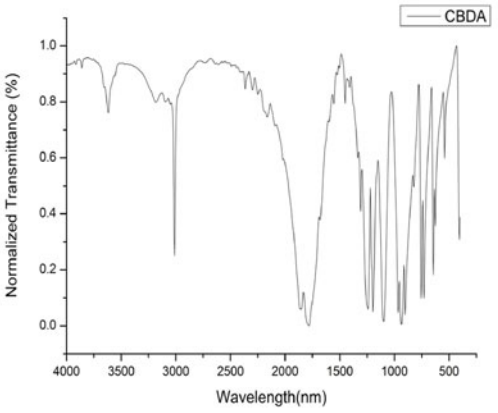
$$R = A_{par}/A_{perp}$$

A_{par} and A_{perp} are the absorbance at a given wavelength, measured respectively parallel and perpendicular to the drawing direction. A_{par} and A_{perp} were obtained from UV-visible spectrometer with the intensity of 1.8 mW/cm^2. [12]. We irradiated polarized UV on each alignment layer for 2, 4, 6, 8, 10, 12, 14, 16 min and compared polyimide containing benzophenone moiety with the reference polyimide without triplet sensitizer. The reference polyimide (CBDA-DDM) was synthesized with CBDA and DDM.

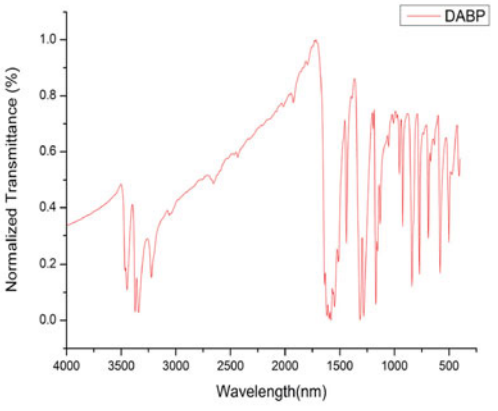
3. Results and Discussion

As can be seen in Fig. 3, the spectrum of the CBDA shows characteristic peaks of anhydride at 1786 cm^{-1} and 1725 cm^{-1} for the symmetric and asymmetric vibration bands of the C=O. The spectrum of the DABP showed broad amine peaks at 3300∼3500 cm^{-1}. Aromatic C=C Bending at 1558 cm^{-1} and C−N stretching band at 1360∼1366 cm^{-1} are characteristic DABP bands. Polymerization of CBDA and DABP was followed by disappearance of amine peaks and followed by appearance of pronounced amide peak at 1690 cm^{-1}.

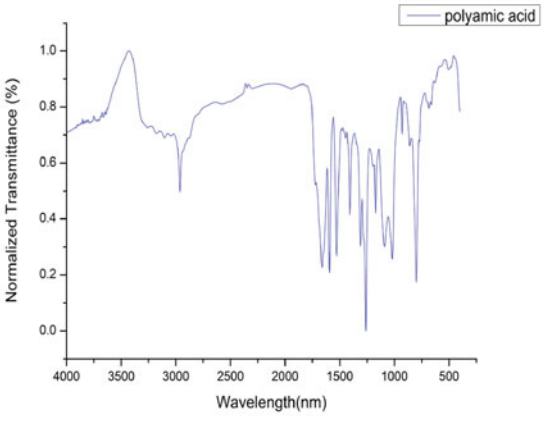
Fig. 4 showed polar-diagram of LC cell containing photo-alignment layers (a) without irradiation and (b) after irradiation for 10 min. The straight lines of circle in the polar



(a)



(b)



(c)

Figure 3. IR-spectra of (a) cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA) (b)Diaminobenzophenone(DABP) (c) Polyamic acid synthesized with CBDA and diaminobenzophenone (KBr pellet).

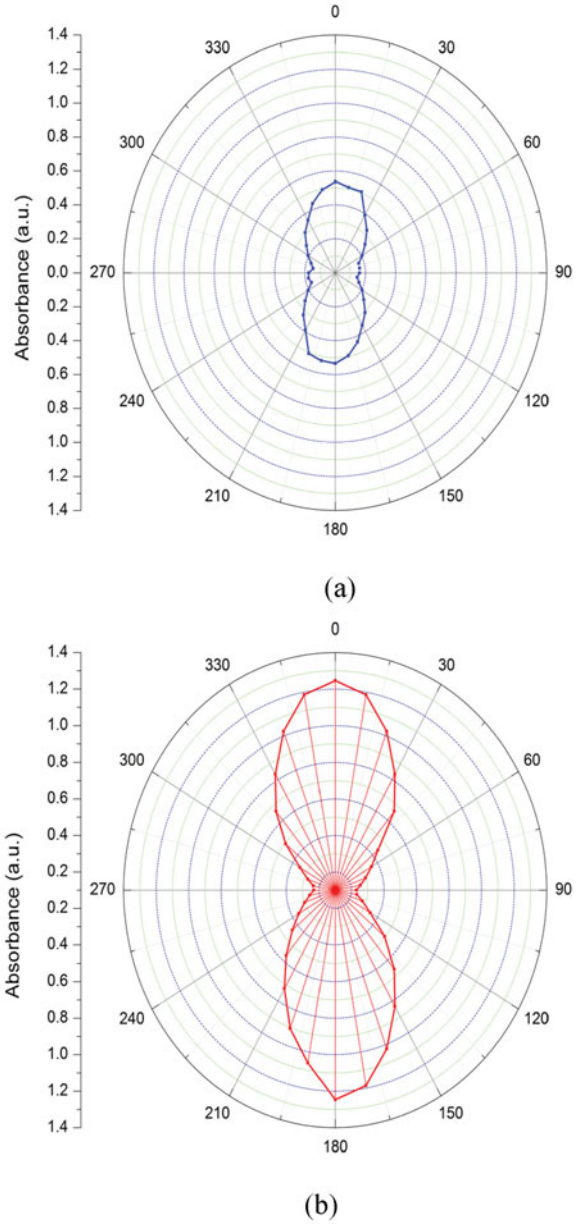


Figure 4. Polar-diagram of LC cell containing CBDA - DABP (a) without irradiation (b) after irradiation for 10 min.

diagram are the polarization angle (degrees 0°∼360°) and each circle means absorbance change. Dichroic ration change was dramatic for the alignment layer contains bezophenone moiety. The smaller absorbance change and round shape of polar diagram of Fig. 4 (a) indicate random orientation. The small orientation to the angle 0° resulted from the capillary injection of LC. Fig. 4 (b) are the absorbance change of LC cells containing CBDA-DABP as alignment layer. Irradiation for 10 min of the LC cells had absorbance of

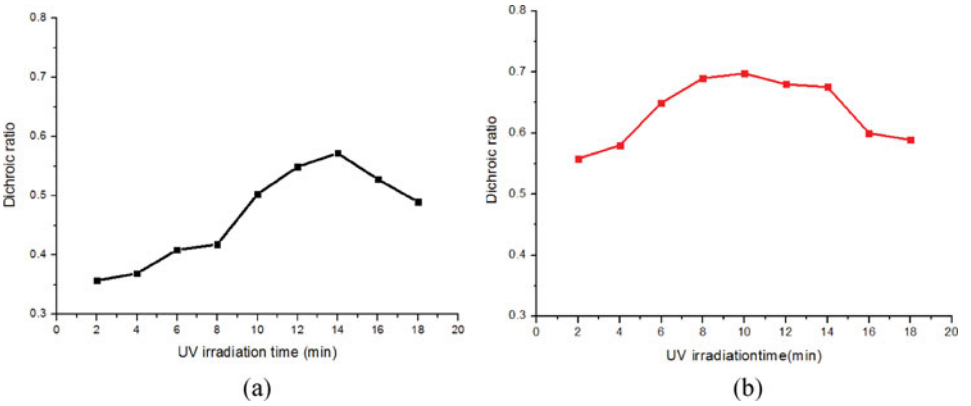


Figure 5. Dichroic ratio of LC cells using (a) CBDA-DDM and (b) CBDA-DABP as an alignment layer polymer.

1.27961 at 0° and 0.0843 at 90°, whereas absorbance values of (a) CBDA-DABP without irradiation are 0.53789 at 0° and 0.0903 at 90°. Random orientation of LC cannot make high contrast images. Because LC molecules in between polyimide alignment layers without UV irradiation are randomly oriented, and the LC orientation can be controlled by LPUV [13].

As can be seen in Fig. 5, highest dichroic ratio was 0.5710 after 14 min photo irradiation of CBDA-DDM, which compared with 0.7246 for the LC cells containing CBDA-DABP after irradiation for 10 min. The dichroic ratio was 1.27 times higher for the LC cells containing CBDA-DABP, which had benzophenone moiety as triplet sensitizer. Highest dichroic ratio attained with short irradiation time for the LC cells containing CBDA-DABP. It means that benzophenone triplet sensitizer incorporated in CBDA-DABP is more sensitive to the LPUV [14, 15]. The benzophenone triple sensitizer made longer excited lifetime for polyimide. Therefore, there was more chance of photo-alignment reaction. The orientation of LC was parallel to the polarization axis, which was usually perpendicular for most studies with direct irradiation of chromospheres [16–20]. The energy transfer between benzophenone and the imide is under investigation. The curves of the dichroic ratio in Fig. 5 means orientation in polyimide films disappears after some time, because polyimide decomposition was extended after critical time.

4. Conclusions

A new polyamic acid was synthesized from CBDA and DABP. Synthesis of polyamic acid (CBDA-DABP) is measured by FT-IR. Polymerization of CBDA and DABP was followed by disappearance of amine peaks and followed by appearance of pronounced amide peak at 1690cm^{-1}. Orientation of liquid crystal was verified by polar diagram. Irradiation for 10 min of the LC cell had absorbance of 1.27961 at 0° and 0.0843 at 90°, whereas absorbance values of CBDA-DABP without irradiation are 0.53789 at 0° and 0.0903 at 90°. Also, compared with reference polyimide, new polyimide (CBDA-DABP) reduced time to align liquid crystal. It means that benzophenone triplet sensitizer incorporated in CBDA-DABP is more sensitive to the LPUV. It was demonstrated by this study new polyimide (CBDA-DABP) could be sufficiently applicable to a LCD.

Acknowledgment

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