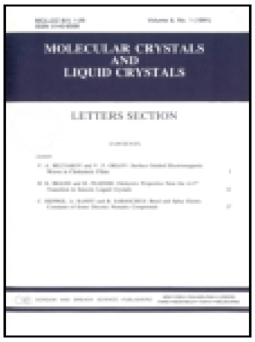

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Synthesis and Photo-Alignment Properties of Novel Polyimides with Cyclobutane-1, 2, 3, 4-Tetracarboxylic Dianhydride (CBDA)

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To improve effectiveness of photo-alignment, new polyimides containing cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA) were designed including 4, 4′-diaminobenzophenone (DABP) and carbohydrazide by amide bond. For evaluating polyimides, a mole ratio of 4, 4′-diaminobenzophenone(DABP) and carbohydrazide was controlled to 0:100, 30:70, 50:50, 70:30, 100:0. The mixed solid contains 15wt% of solvent which is n-methyl-2-pyrrolidone (NMP). The synthesized polyimide was analyzed using the Fourier transform infrared (FT-IR). We obtained polar dichroic ratios and evaluate alignment of liquid crystal. For more aggressive photo-decomposition of polyimide, the photoreactions employing triplet mechanism and the double fragmentation reactions were carried out.

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

1. Introduction

A Liquid crystal displays have been widely used for simple numeric displays to large information displays because of their low voltage and current, high contrast ratio. The liquid crystal alignment layer has, especially, an important role to align liquid crystal molecules uniformly. The rubbing method has been the most popular mass production process to align liquid crystals in Liquid Crystals Display (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 [1].

To overcome the limitations of mechanical rubbing, photo-alignment has been proposed as a ‘non-contact’ alternative. Photo-alignment methods utilize linearly polarized ultraviolet (LPUV) light to generate chemical anisotropy on photo-reactive alignment surfaces through axis selective photoreaction. The anisotropic intermolecular interactions between alignment surfaces and liquid crystals have been observed to be strong enough to orient liquid crystals on the alignment surfaces [2].

The 4, 4′-diaminobenzophenone and carbohydrazide were employed as the triplet sensitizer for the cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride. In this work, we

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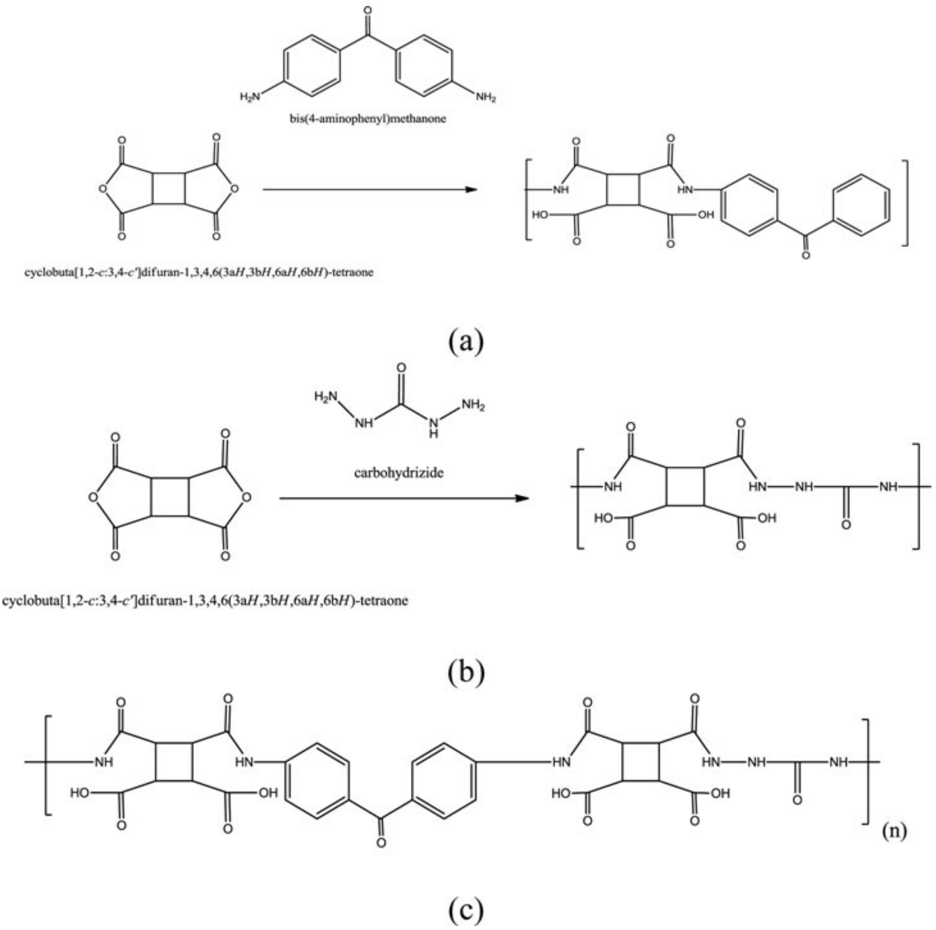


Figure 1. (a) Synthetic scheme of polymerization with cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA) and 4, 4′-diaminobenzophenone(DABP), (b) Synthetic scheme of polymerization with cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA) and carbohydrazide, (c) Synthetic scheme of polymerization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

reported the synthesis of new polyimides and photochemical behavior of polyimide films used for LCD.

2. Experimental

2.1. Polymer Synthesis

Synthesis scheme of polyamic acid was shown in Figure 1, 2, 3. Polyamic acid were prepared from cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA), 4, 4′-diaminobenzophenone(DABP) and carbohydrazide. The polyamic acid was prepared from 1g of CBDA (0.0051 mol), and 1.08 g of DABP (0.0051mol). A mole ratio of CBDA

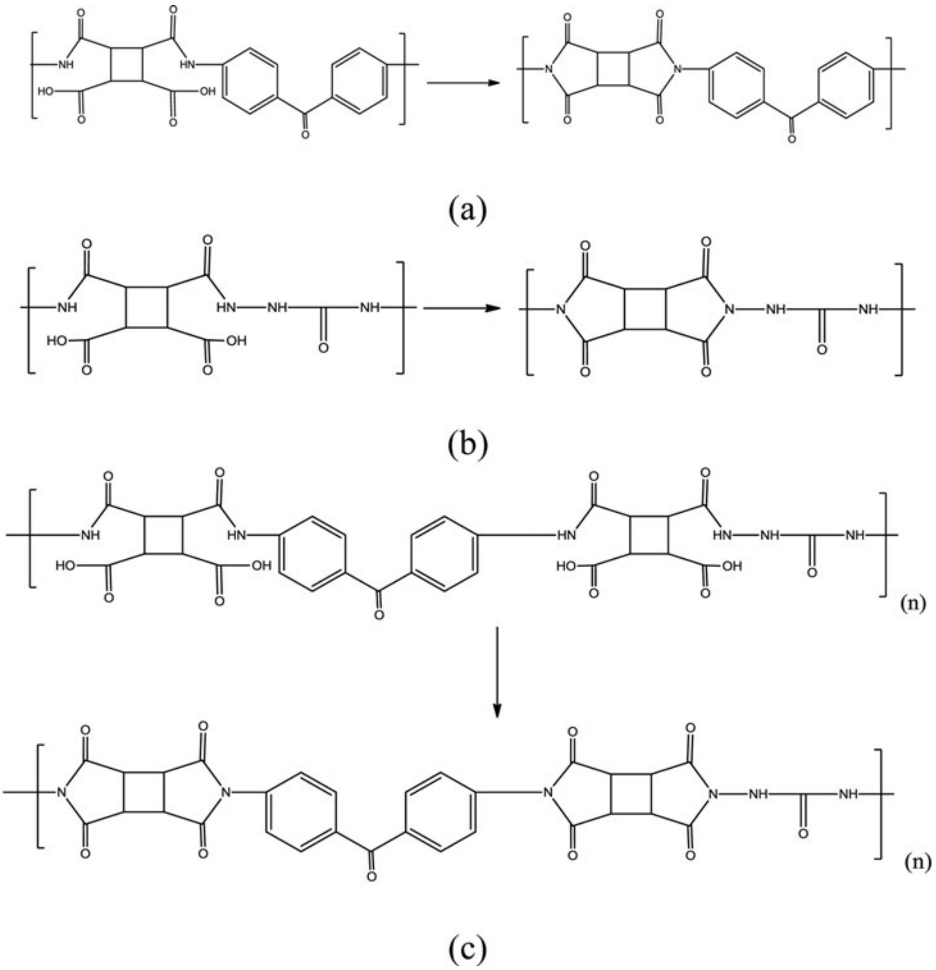
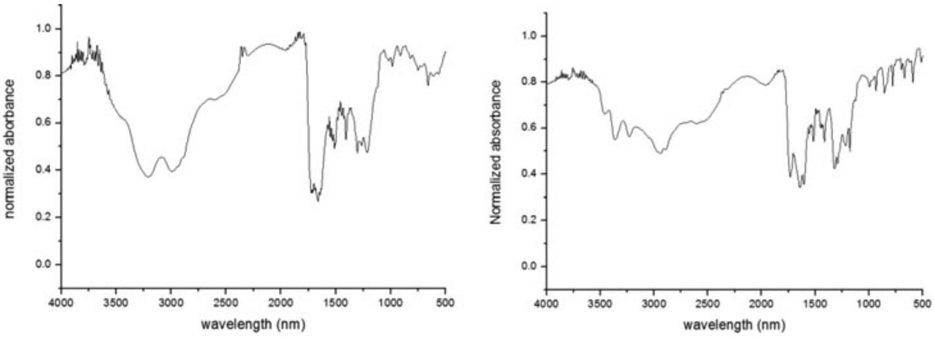


Figure 2. (a) The imidization reaction of cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA) and 4, 4′-diaminobenzophenone(DABP), (b) The imidization reaction of cyclobutane-1, 2, 3, 4-tetracarboxylic dianhydride (CBDA) and carbohydrazide, (c) The imidization reaction of cyclobutane-1, 2, 3, 4-tetracarboxylic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

and DABP was 1:1. 1.08 g of DABP was dissolved in 13.3ml 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]. Fixed CBDA and molar ratios of DABP and carbohydrazide was controlled to 0: 100, 30: 70, 50: 50, 70:30 and 100: 0 to obtain the polyamic acid.

CBDA and 4, 4′-diaminobenzophenone (DABP) and carbohydrazide were commercially available Sigma Aldrich and used as obtained. N-methyl-2-pyrrolidone (NMP) was reagent grade and was purified before use.



(a) (b)

Figure 3. IR-spectra of (a) Polyamic acid synthesized with CBDA and Carbohydrazide (KBr pellet), (b) Polyamic acid synthesized with CBDA and DABP, carbohydrazide (KBr pellet).

2.2. Fabrication of Liquid Crystal Cell

LC cells were prepared to evaluate the alignment properties of liquid crystals in between alignment layers. polyamic acid solution (solid content 15 wt%) was diluted to a concentration of 6 wt% using mixtures NMP (0.5 g), γ-butyrolactone (0.5 g), and 2-butoxyethanol (0.5 g) [4]. The ratio was 2: 1: 1: 1 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].

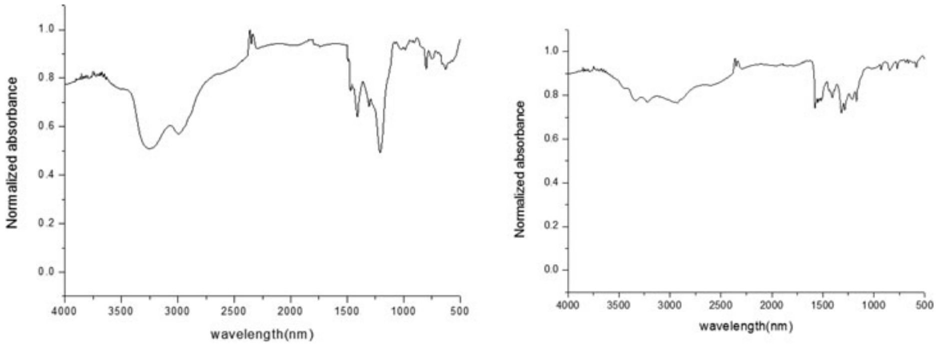
The polyimide solutions were coated onto indium tin oxide (ITO) substrate using spin coater at 2500 rpm for 30 sec. The coated-films were pre-baked at 90°C for 10 min to vaporize solvent and then hard-baked at 230°C for 30 min in vacuum oven (model 280A) [6]. During the hard-bake process, polyamic acid change to polyimide. Figure 2 shows imidization reaction.

To align liquid crystal on polyimide film, the polyimide films were irradiated linearly polarized UV light (LPUV). Place two substrates with opposite coated layer horizontal and vertical direction and glue substrates using 4.4γm spacer and UV hardening agent. A nematic liquid crystal (E7, 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°C. A nematic range of liquid crystal (E7) is -10°C $\sim$ 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 $\sim$ 0.2% of the KBr amount) of CBDA and DABP, carbohydrazide 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) (b)

Figure 4. IR-spectra of (a) after imidization synthesized with CBDA and Carbohydrazide (KBr pellet), (b) After imidization synthesized with CBDA and DABP, carbohydrazide (KBr pellet).

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 [12]. We irradiated polarized UV on each alignment layer for 5, 10, 15 min.

3. Results and Discussion

As can be seen in Fig. 3, the spectra show characteristic peaks of anhydride at 1786 cm^{-1} and 1725 cm^{-1} for the symmetric and asymmetric vibration bands of the C=O and showed broad amine peaks at 3300 ~ 3500cm^{-1}, COOH bonding at 1710cm^{-1} and CONR$_2$(amide)

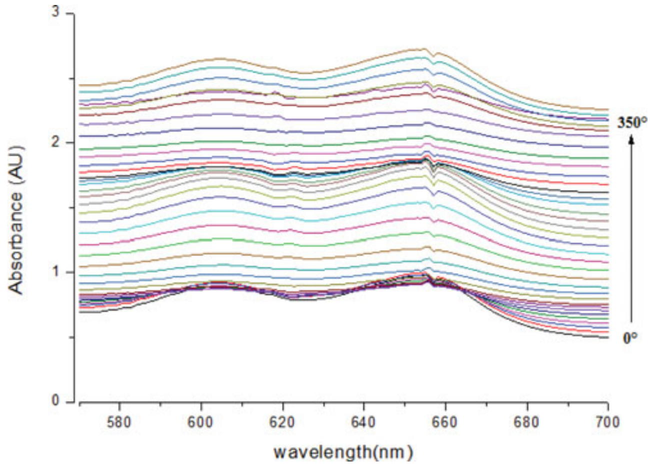


Figure 5. Showed the spectra of LC cell containing photo-alignment layers (CBDA and DABP, carbohydrazide 10:5:5) after irradiation for 10 min. The peaks of graph are the polarization angle (degrees 0°C ~ 360°C) and each line means absorbance change. The peak at 655 nm gradually increased at the intervals of 0°C to 90°C and 180°C to 270°C. The peaks intensity gradually decreased at the intervals of 90°C to 180°C and 270°C to 360°C.

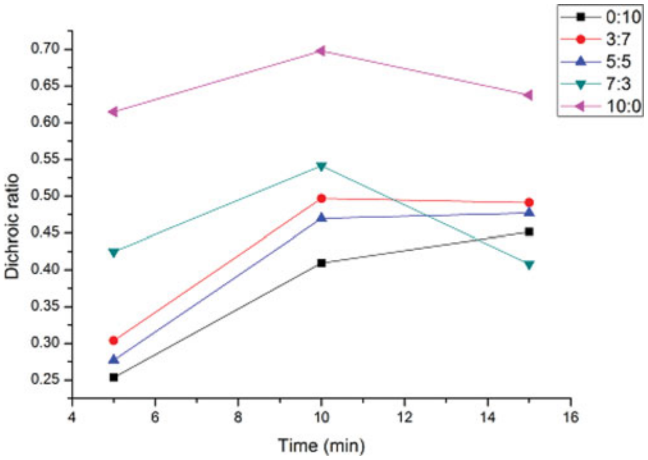


Figure 6. Dichroic ratio of LC cells using CBDA-DABP and carbohydrazide. DABP-carbohydrazide ratio (0:10, 3:7, 5:5, 7:3, 10:0).

at 1690 cm^{-1} . Aromatic C=C bonding at 1558cm^{-1} and C—N stretching band at 1360 ∼ 1366cm^{-1} show characteristic DABP bands.

As can be seen in Fig. 4, the spectra show that characteristic peaks of COOH bonding at 1710cm^{-1} and CONR$_2$(amide) at 1690 cm^{-1} disappear after imidization.

Figure 5 shows that uv-vis spectra of LC cell containing photo-alignment layers (CBDA and DABP, Carbohydrazide ratio 10:5:5) after irradiation for 10 min. The peaks of graph are the polarization angle (degrees 0°C ∼ 360°C) and each line means absorbance change. The peak at 655 nm gradually increased at the intervals of 0°C to 90°C and 180°C to 270°C. The peaks intensity gradually decreased at the intervals of 90°C to 180°C and 270°C to 360°C. As can be seen in Fig. 6, Dichroic ratio of LC cells using CBDA-DABP and carbohydrazide.DABP-carbohydrazide ratio (0:10, 3:7, 5:5, 7:3, 10:0). Highest dichroic ratio was 0.70 after 10 min photo irradiation of CBDA-DABP. All dichroic ratio data were the highest until 10 min irradiation and gradually decrease. Dichroic ratio is significantly different from the first five minutes but, PI that carbohydrazide has contained shows a tendency to difference of dichroic ratio is reduced more and more as time goes on. The dichroic ratio are highest when the LC cell does not contained carbohydrazide (10:10:0).

4. Conclusions

A new polyamic acid was synthesized from CBDA and DABP, carbohydrazide. Synthesis of polyamic acid is measured by FT-IR. Polymerization of CBDA and DABP, carbohydrazide was followed by disappearance of amine peaks and followed by appearance of pronounced amide peak at 1690cm^{-1}. CBDA-DABP contained LC cell is higher than carbohydrazide. 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. [13,14]. It was demonstrated by this study new polyimide could be sufficiently applicable to a LCD.

Acknowledgment

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