Manufacture of Photopatterned Coatable Polarizer Using Lyotropic Chromonic Liquid Crystal Based on Perylene

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Abstract

We report the syntheses bis-(N,N-diethylaminoethyl) perylene-3,4,9,10-tetracarboxylic diimide (PDI) of lyotropic chromonic liquid crystal and it dissolves in photocurable ionic monomer solution. PDI-acrylic acid solution was observed whether liquid crystal phase appeared in each concentration. Thin film polarizer was prepared by simultaneously coating and aligning the solution of PDI-acrylic acid (in the chromonic nematic phase) onto glass substrates using a mechanical shearing force and was cured by irradiation of UV light. Also Photopatterned polarizer is manufactured by same process.

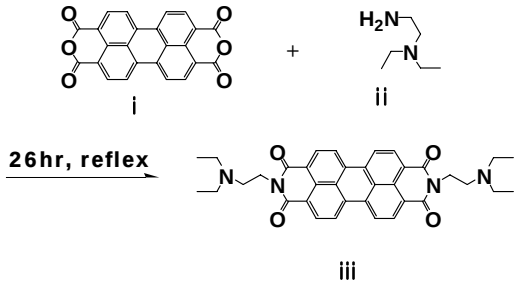
1. Introduction

Lyotropic chromonic liquid crystals (LCLCs) are fundamentally different from conventional amphiphilic system. Due to their disc-like molecular shape, chromonic molecules stack face to face forming columnar aggregates. It is generally believed that π-π interaction of the aromatic cores is the main mechanism of molecular face-to-face stacking.[1-2] Because of the polyaromatic molecular core, many LCLC materials absorb light in the visible and near-infrared range. This absorption is anisotropic, it was suggested the aligned LCLC molecules can be used as a coatable thin film polarizer.[3] Usually, the aligning of columnar aggregates was achieved by shear-coating an aqueous lyotropic LCLC solution. However, the existing water-based process has many drawbacks such as the tricky process control especially related with humidity, destruction of ordered state of dye molecules, crack of coated thin-film and poor mechanical stability.

In this research, we demonstrate the novel fabrication of thin film polarizer utilizing a photocurable organic-based lyotropic LCLC solution. By using an organic solution instead of water-based solution, this new method provided various advantages such as excellent coating characteristics and improved mechanical/chemical stability.

2. Experimental

Bis-(N,N-diethylaminoethyl)perylene-3,4,9,10-tetracarboxylic diimide (PDI) was synthesized by a modification to the literature procedure as reported previously and characterized by ^{1}H NMR, FT-IR and UV-vis spectroscopy.[4]



i ; 3,4,9,10-perylenetetracarboxylic dianhydride,

ii ; N, N-diethylethylenediamine,

iii ;bis-(N,Ndiethylaminoethyl)perylene-3,4,9,10-tetrarcarboxylic diimide(PDI),

Scheme . Synthesis of bis-(N,N-diethylaminoethyl) perylene-3,4,9,10-tetracarboxylic diimide (PDI)

PDI has liquid crystal phase generally after acid treated in water. We dissolved PDI with ionic monomer and prepared PDI-acrylic acid solution by different concentration, where the liquid crystal phases were confirmed by polarized microscope (POM) image.

Our technique is a sequence of the following steps. First, we prepare PDI-acrylic acid solution over 25wt% and add small quantity of photo initiator and cross-linker. Second, the solution was coated by shear force on substrate. Finally, the shear-aligned columnar aggregates of chromonic molecules in the lyotropic state was cured by irradiation of UV light to obtain thin film polarizer.

Photopatterned polarizer can be manufactured by preceding process. Thin film polarizer was coated by PDI-acrylic acid of 25 wt% (crosslinker of 25wt% in acrylic acid) from shear force on glass substrate. Before the UV curing, photomask was put down on coated substrate. For removal of uncured part, curing film was developed by chloroform during 30min.

3. Results and discussion

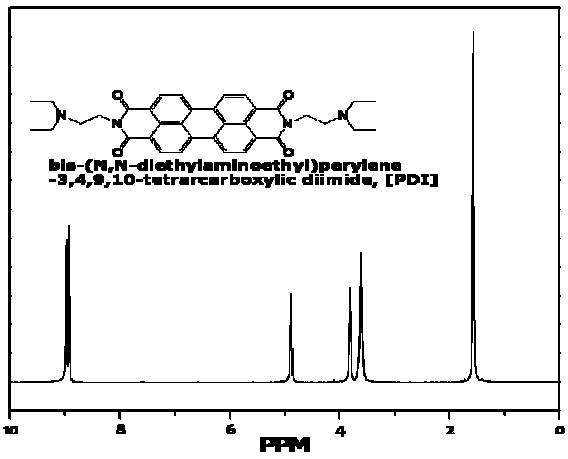


Fig. 1 ^{1}H-NMR spectrum of PDI, CF_3COOD as solvent

The synthetic PDI was determined by ^{1}H NMR, IR and UV measurement. Figure 1 shows the NMR spectrum of PDI[5]: NMR (CF_3COOD) δ ppm: 8.94(4H), 8.75(4H), 4.83(4H), 3.76(4H), 3.58(8H), 1.54(12H).

Figure 2 is the IR spectrum of PDI and PTCDA, which was measured by KBr pellet method: 2971, 2811, 1697, 1652, 1590, 1515, 1444, 1353, 1291, 1245, 1166, 1098, 851, 803, 746 cm^{-1} (PDI). PDI of strong peak at 1353cm^{-1} proves that the C-N imide bond exists and C-O bond of PTCDA decreases.

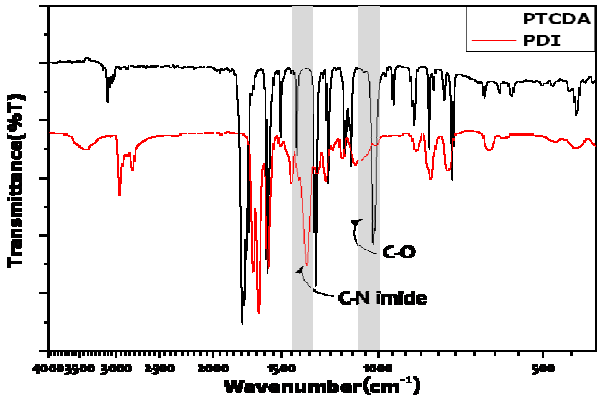


Fig. 2 IR spectrum of I and PTCDA(perylene-3,4,9,10-tetracarboxylic dianhydride)

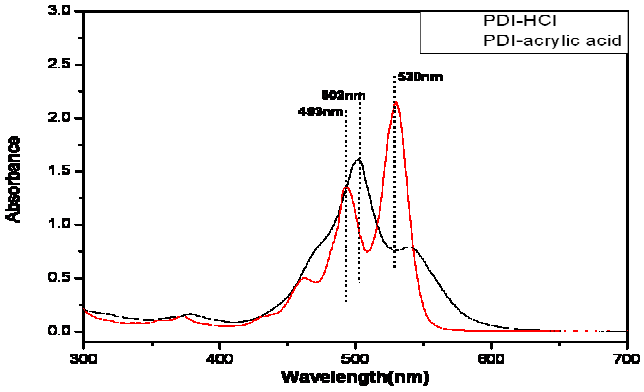


Fig. 3 UV spectrum of PDI, HCl aqueous solution and acrylic acid as solvent

UV spectrum of PDI was studied in HCl-aqueous and acrylic acid solution, which was shown in figure 3. There is a strong peak at 502nm in HCl aqueous and two strong peaks at 493, 530nm in acrylic acid.

We prepared PDI-acrylic acid solution of 5-30wt% concentration and observed liquid crystal phases (chromonic nematic phase) by POM.

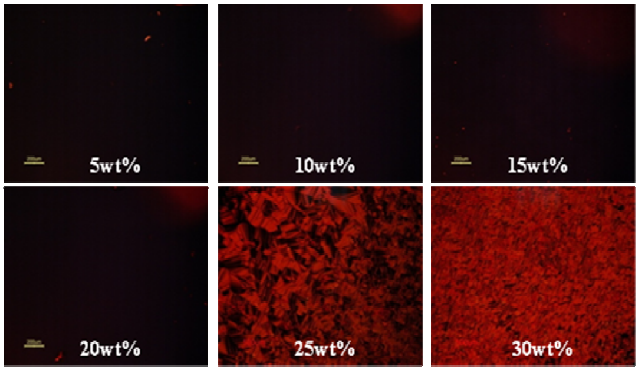


Fig. 4 Concentrations of PDI-acrylic acid solution

Figure 4 show liquid crystal phase by each concentrations. Observation of LC phase was impossible to PDI-acrylic acid solution of 5-20wt%. On the other hand, PDI-acrylic acid solution to 25-30wt% showed nematic liquid crystal phases.

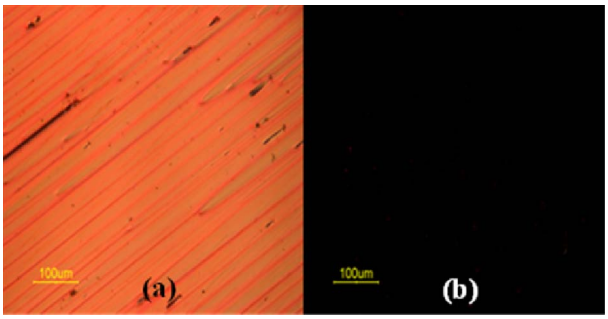


Fig. 5 Cross- polarized optical microscope images of the thin film prepared from photocurable PDI-acrylic acid solution by shear-coating (cured): (a) 45˚ , and (b) 0˚ or 90˚ to the shearing direction.

Figure 5 shows cross-POM image of the thin film polarizer. When the corss-polarized light was 45˚ to the shearing direction, the film displayed a bright image (Figure 5a), while dark image was observed when the corss-polarized light was 0° or 90° to the shearing direction (Figure 5b). [6]

Figure 6(a) was exhibited when manufactured photo-patterned polarizer was observed by POM. When polarization axis of incident light is parallel or perpendicular of shear direction, we are showed definitely pattern of film. Because uncured part was removed by chloroform, we were able to confirm difference of thickness of film from α-step result and knew that thickness of film is about 1μm.

4. Summary

We have shown that a liquid-crystalline phase exists in PDI-acrylic acid solution. PDI-acrylic acid solution showed liquid crystal phase when the concentration of PDI is over 20wt%. The shear-aligned columnar phase of chromonic molecules in the lyotropic state was cured by irradiation of UV light to obtain thin film polarizer. Manufacture of thin film photopatterned is possible due to UV curing step and thickness of the thin film is approximately 1μm. New process can coat substrate polarizer film on various substrates.

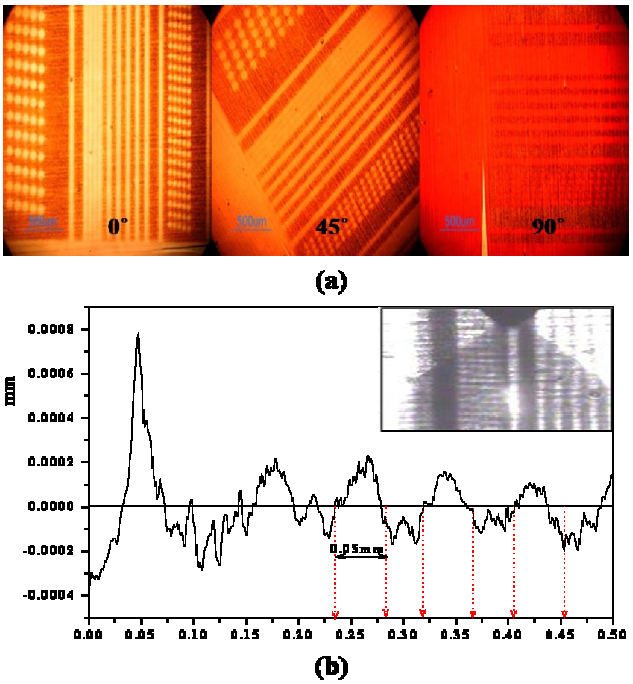


Fig. 6 POM image of photo-patterned polarizer and α-step result.

Acknowledgement

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