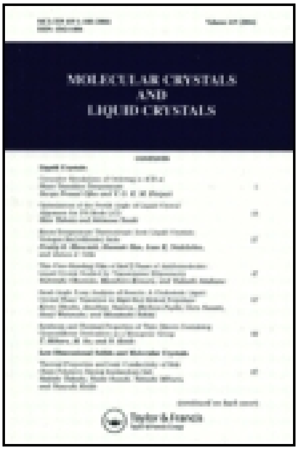

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Liquid Crystal Aligning Capabilities on a Novel Photo-Crosslinkable Polyitaconimide Containing Three Kinds of Substituents

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In this paper, we synthesized a new photo-crosslinkable polyitaconimide containing cinnamoyl moiety by radical polymerization. Also, the nematic liquid crystal (NLC) alignment capabilities on these photopolymer surfaces were studied. Good LC alignment with UV exposure on the polyitaconimide surfaces can be obtained. A homogenous alignment using UV exposure on the polyitaconimide with 1-carbon chain cinnamoyl group and 4-carbon chain cinnamoyl group can be obtained. However, a homeotropic alignment using UV exposure was observed on polyitaconimide with 6-carbon chain cinnamoyl. The LC aligning ability on the polyitaconimide depends on the side chain length of photopolymer.

Keywords: nematic liquid crystal (NLC) alignment; photopolymer; polyitaconimide; UV exposure

INTRODUCTION

Liquid crystal displays (LCDs) require uniform alignment and stable pretilt angles on a substrate layer. Surface alignment of LCs on the

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treated substrate surfaces is very important in both LC basic research and application [1]. Rubbed polyimide (PI) layers have been widely used to align LC molecules. The effects of unidirectional rubbing on the various alignment layers have been discussed [2,3]. The rubbing treatment method presents a number of obstacles, such as the generation of electrostatic charges and the creation of contaminating particles.

In our previous paper, we reported the generation of electro-static charges produced on various PI layers during rubbing [4]. Thus, rubbing-free techniques for LC alignment are required in LCD technology. The photoalignment method for LC alignment is one of the most promising rubbing-free methods. Many researchers have proposed the photoalignment of the LCs in which a poly (vinyl) cinnamate and other photopolymer layers are utilized [5–10]. But, the thermal characteristics of acrylate material in the backbone structure of photopolymers have not been satisfactory for good LC alignment capabilities.

In this work, we report on the synthesis of a new photo-crosslinkable N-[4-(Cinnamoyloxy hexoxy carbonyl) phenyl] itaconimide containing cinnamoyl moiety and the LC alignment capabilities on the photopolymer layer.

EXPERIMENTAL

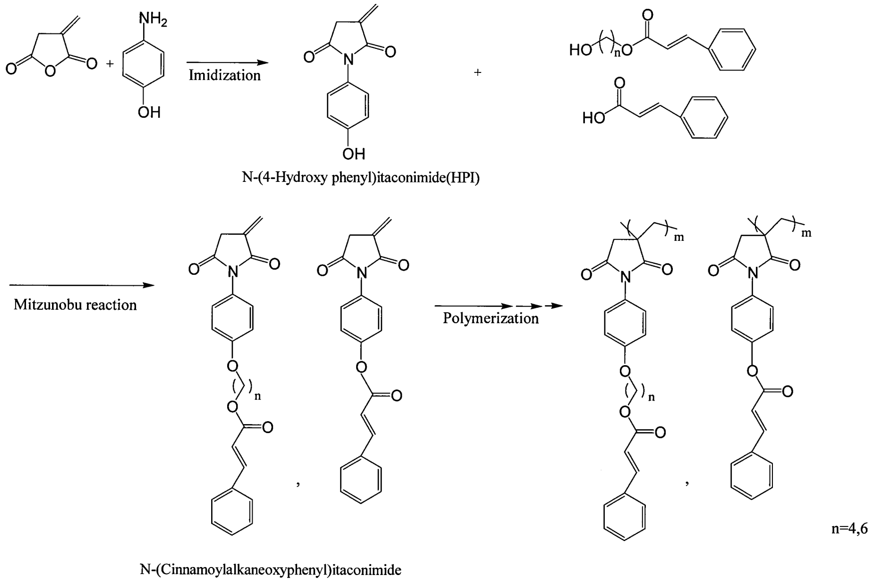
Materials

Commercial reagents (Aldrich, USA) such as itaconic anhydride, 4-aminophenol, formaldehyde and cinnamoyl chloride were used without further purification. Commercial reagents (Aldrich) such as acryloyl chloride were used after distillation. 2,2′-Azobisisobutyronitrile (AIBN) of reagent grade was recrystallized from methanol. All other reagents were used without purification.

Synthesis

N-(4-hydroxyphenyl) itaconic acid [11]

A flask was charged with itaconic anhydride (0.11 mol) dissolved in acetone (100 ml). 4-Aminophenol (0.1 mol) was added in portions over 30 min at ambient temperature, and the solution turned into a yellow slurry. The mixture was allowed to react at ambient temperature for 1.5 h, and the slurry was isolated by filtration. The precipitate was washed with acetone, and then dried at 50°C in vacuum oven. N-(4-Hydroxyphenyl) itaconic acid was obtained as a pale purple powder in a high yield of 90%.



SCHEME 1 The synthetic route of polymers, PI-O(PCPI), PI-C4(PCBI), and PI-C6(PCHPI).

N-(4-Hydroxy phenyl) itaconimide (HPI) [11]

A flask was charged with N-(4-Hydroxyphenyl) itaconic acid (0.2 mol), 4-toluenesulfonic acid (0.016 mol), DMF (21 ml), hydroquinone (2 g) and toluene (300 ml). The mixture was refluxed for 6 h until the stoichiometric amount of water from the cyclodehydration reaction was completely segregated and the slurry then turned into a clear yellow solution. The toluene was evaporated, and the residue of black liquid was poured into a large amount of water. The precipitate was collected by filtration, washed with dilute sodium bicarbonate solution (5%), then with water. After recrystallizing from a mixed solvent of water-isopropyl alcohol (1:1 v/v), pale yellow crystalline needles were obtained in a yield of 60%.

Hydroxybutyl Cinnamate

A mixture of 1,4-butanediol (0.05 mol) and THF (100 ml) in the presence of triethylamine (0.06 mol) was placed in a 500 ml flask. To the mixture was added cinnamoyl chloride (0.06 mol) in THF (100 ml) over 30 min with stirring at 0 ~ 5°C. Then, the solution was stirred for an additional 3 h at the same temperature. The precipitated triethylamine hydrochloride salt was removed from the mixture by filtering. Evaporation of the filtered solution resulted in a solid crude product. The crude product was recrystallized in ethanol.

Hydroxyhexyl Cinnamate

Hydroxyhexyl cinnamate was prepared by the same procedures as hydroxybutyl cinnamate, except using 1,6-hexanediol in place of 1,4-butanediol.

N-[4-(Cinnamoylphenyl)itaconimide(CPI) [12]

To a solution of HPI (10 mmol) and triphenylphosphine (10.7 mmol) in dry DMF was added dropwise a solution of diethyl azocarboxylate (DEAD, 10.7 mmol) and cinnamic acid (11 mmol) in dry DMF, and the mixture was stirred at room temperature for 30 h. The solvent was evaporated and crude product was purified by column chromatography.

N-[4-(Cinnamoylbutaneoxyphenyl)itaconimide(CBPI)

N-[4-(Cinnamoylbutaneoxyphenyl)itaconimide was prepared by the same procedures as a CPI, except using hydroxybutyl cinnamate in place of cinnamic acid.

N-[4-(Cinnamoylhexaneoxyphenyl)itaconimide(CHPI)

N-[4-(Cinnamoylhexaneoxyphenyl)itaconimide was prepared by the same procedures as a CPI, except using hydroxyhexyl cinnamate in place of cinnamic acid.

Polymerization of CPI, CBPI, CHPI

Polymerization was carried out at 65°C for 48 h in dimethylformamide (DMF) using AIBN as an initiator in a sealed tube. After polymerization, the polymer solution was poured into a large amount of methanol. The precipitated polymer was filtered and dried under vacuum (yield 40%). The resulting polymers were symbolized as PI-O(PCPI), PI-C4(PBPI), and PI-C6(PCHPI) (Scheme 1).

Cell Fabrication

The polymers were coated on indium-tin-oxide (ITO) coated glass substrates by spin-coating, and were cured at 130°C for 1 h. The thickness of the monomer layer was 500 Å. The linearly polarized UV (Mercury lamp of 500 W) exposure system is shown in Figure 1. The UV energy density used was 15.5 mW/cm^2. The pretilt angle of the NLC was measured by a crystal rotation method.

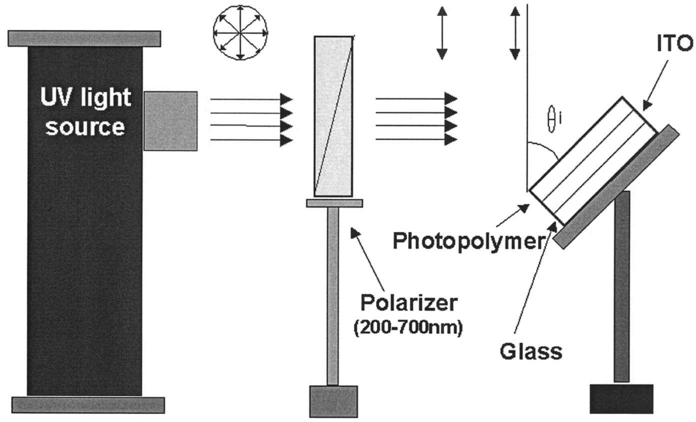
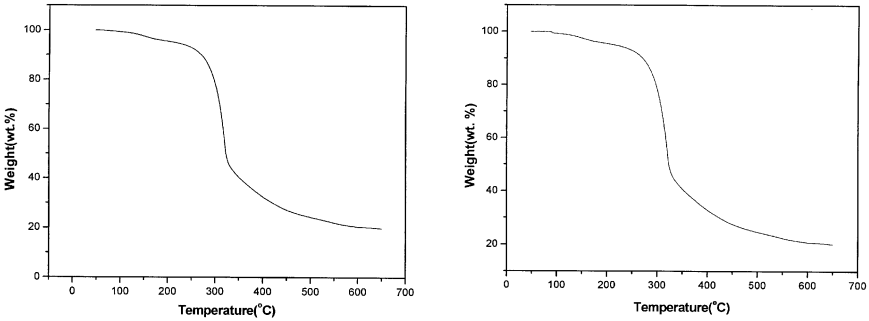
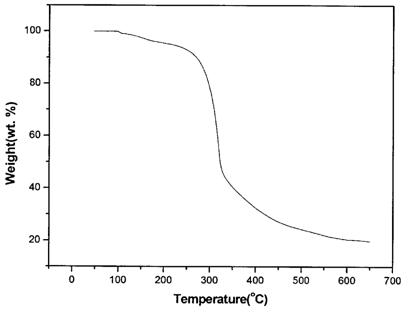


FIGURE 1 Schematic diagram of the UV exposure system.



(a) PI-C0 **(b) PI-C4**



(c) PI-C6

FIGURE 2 TGA characteristics of the photopolymer-based itaconimide.

RESULTS AND DISCUSSION

The resulting polymers were synthesized as in Scheme 1. Figure 2 exhibits the thermogravimetric analysis (TGA) characteristics of the photopolymer-based itaconimide. The TGA measurements revealed that the synthesized photopolymers have satisfactory thermal stabilities up to 350°C.

Figure 3 shows the UV absorption spectra on the three kinds of photopolymer-based itaconimide. The UV absorption was observed at $300 \sim 400\,\text{nm}$. It is considered that the UV absorption is attributable to the $[2+2]$ cycloaddition reaction by a broken C=C bond. Also, the UV absorption band shifts to the longer wavelength as the alkyl chain length increases.

Micrographs of the aligned LC cell with polarized UV exposure on the three kinds of polyitaconimide surfaces (in crossed Nicols) are shown in Figure 4; in (a) and (b), LC alignment defects were observed for UV exposure on the PI-C0 and PI-C4 layers. However, it is shown that uniform LC alignment was observed for the PI-C6. Therefore good LC alignment can be obtained on the polyitaconimide with 6-carbon chain cinnamoyl group; LC alignment thus strongly depends on the alkyl chain length of the photopolymer for polyitaconimide materials.

Figure 5 shows transmittance versus incident angle in NLC with UV exposure on the photopolymer layer-based polyitaconimide (PI-C6).

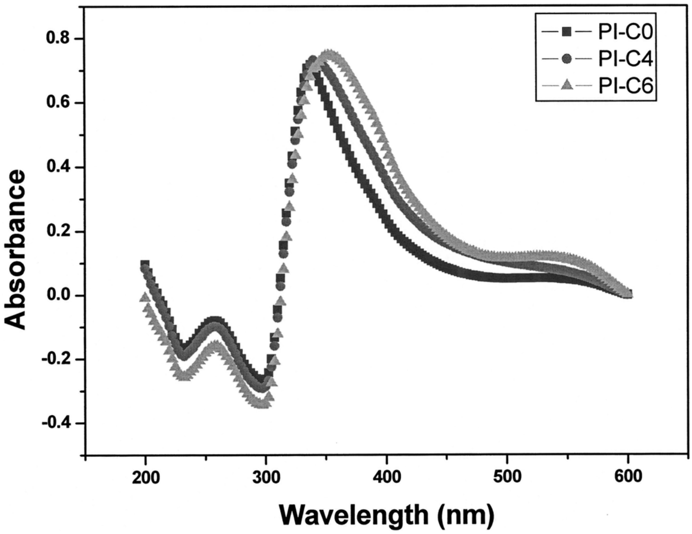
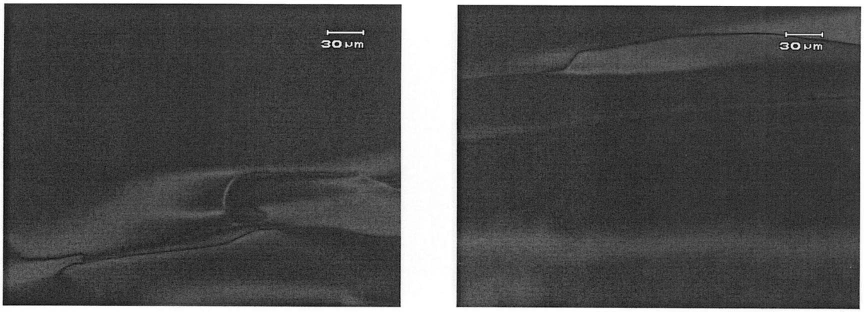
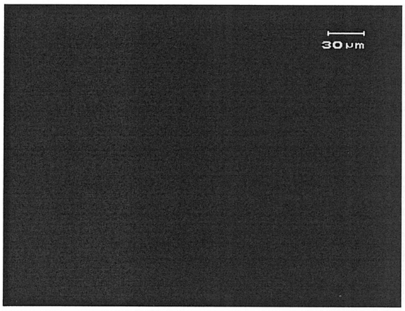


FIGURE 3 UV absorption spectra of the photopolymer-based itaconimide.

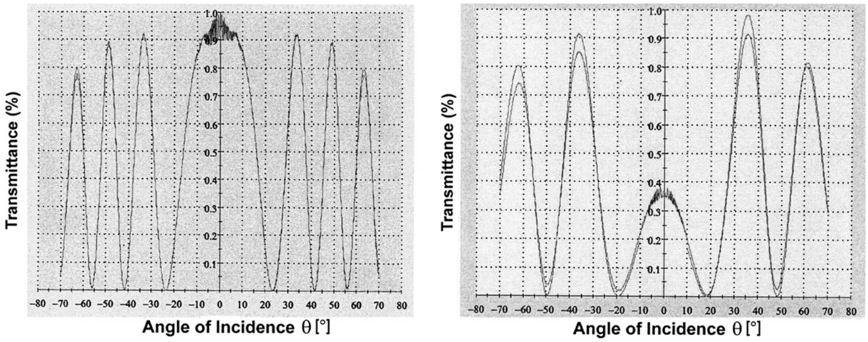


(a) PI-C0 **(b) PI-C4**



(c) PI-C6

FIGURE 4 Micrographs of photoaligned cells on the photopolymer layer-based polyitaconimide (in crossed Nicols):(a) PI-C0 (b) PI-C4, (c) PI-C6.



(a) Homoetropic alignment **(b) Homogenous alignment**

FIGURE 5 Transmittance versus incident angle in an NLC UV exposure on the polyitaconimide surface.

In Figure 5(a), the homeotropic alignment using UV exposure within 1 min on the PI-C6 layer was obtained, and the LC pretilt angle below 90° was obtained at the all-incident angle on the polyitaconimide surface. However, the homogenous alignment was obtained using UV exposure for 5 min on the PI-C6 layers as shown in Figure 5(b); the LC pretilt angle below 1° was obtained at the all-incident angle on the photopolymer surface. Therefore, LC alignment can be changed from about 89° to 1° with increasing UV exposure time. It is considered that the LC aligning ability on the polyitaconimide depends on the UV exposure time on the photopolymer surface.

CONCLUSION

In conclusion, a new photoalignment material consisting of a polyitaconimide using photodimerization by the cinnmate group was synthesized. Also, the NLC alignment capabilities on these photopolymer surfaces were studied. Good LC alignment with UV exposure on the polyitaconimide with 6-carbon chain cinnamoyl group surface can be obtained. Also, LC alignment can be changed from homeotropic to homogeneous with increasing UV exposure time. It is considered that the LC aligning ability on the polyitaconimide depends on the side chain length and the UV exposure time on the photopolymer surface.

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