New Liquid Crystal Photoalignment Materials Based on Photosensitive Polyimides Having Long Alkoxy Cinnamate Chains

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Abstract:
A series of new photosensitive polyimides having long alkoxy cinnamate chains were synthesized for liquid crystal (LC) photoalignment material. The polymer after irradiating linearly polarized UV light induced homogeneous and stable LC alignment. The chemical structure of the polymeric material was characterized and their photochemical LC alignment behavior was evaluated.

1. Introduction

The surface alignment of liquid crystals is a crucial element of the performance in LCD technology. Though the rubbing method is still the current technique for the mass production of liquid crystal displays, there are several drawbacks such as the electrostatic charging, dust and mechanical damage generated by rubbing, which lowers the production yield of LCDs. In resent years a series of novel techniques have been developed for replacing the traditional rubbing method, among them, LC alignment produced by using Polaized UV exposure is the most promising non-rubbing technique.[1] According to the photochemical reaction responsible for photoalignment, three classes of materials can be categorized, including azobenzene-containing polymer. photo-reactive polymers with photocrosslinkable groups, and photodegradable polyimide and polyester derivatives.

We have synthesized new photosensitive polyimides based on functionalization of chloromethylated polyimide (CMPI).[2,3] The poly(imide methylene cinnamate) (PIMC) is one of the resulting polymer, which shows excellent photosensitivity and thermal stability making it a promising photo-alignment material.[4] As an extension of previous work, we synthesized the poly(imide methylene *p*-alkoxycinnamate)s with various alkyl chain length and investigated their properties as photoalignment material.

2. Experimental

Materials

N-Methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), pyridine, and chloroform were dried via refluxing over CaH_2 and distilled prior to use. N,N-Dimethyl formamide (DMF) was dried via refluxing over $MgSO_4$, and distilled before use. 4,4'-Diaminodiphenylether (ODA, TCI) was sublimed at 220 ^oC under reduce pressure. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, Aldrich), tetra-*n*-butylammonium bromide

(TBAB, Aldrich), potassium carbonate, chloromethyl methyl ether (TCI), tin(IV) chloride (99%, Aldrich), *p*-alkoxybenzaldehyde, malonic acid, and piperidine (99%, Aldrich) were used as purchased without further purification.

p-Alkoxycinnamic acids used in this work were obtained by Knovenagel reaction according to literature.

Synthesis of 6FDA-ODA polyimide

ODA (2.00 g, 10.0 mmol) was dissolved in NMP (70ml), then 6FDA (4.44g, 10.0mmol) was added to the solution. After the reaction mixture was stirred at room temperature for 24 h under nitrogen, acetic anhydride (5 mL) and pyridine (5 mL) were added and stirred at 60 °C for 12 h the for imidization. Then, the solution was poured into water, and the white fibrous precipitate was collected and dried in a vacuum oven.
^{1}H-NMR (DMSO-d_6, d *ppm*): 7.24 (d, 4H), 7.50 (d, 4H), 7.75 (s, 2H), 7.96(d, 2H), 8.19 (d, 2H); FT-IR (film, cm^{-1}): 1785, 1727 (imide C=O), 1374 (imide C-N).

Chloromethylation of 6FOD-PI (CMPI)

6FOD-PI (9.00 g) was dissolved in 220 mL chloroform. The solution was heated to 60 °C, and proper chloromethyl methyl ether and tin (IV) chloride were slowly added under a nitrogen atmosphere. The final mixture was poured into methanol. The precipitate was collected and dried in a vacuum oven. The reprecipitation was preceded for several times using the same method. The degree of chloromethylation can be controlled by the amount of reagent and the reaction time.
^{1}H-NMR (DMSO-d_6, d *ppm*): 4.78 –5.01 (m), 7.05–7.18 (m), 7.24 (d), 7.50 (m), 7.70 (s), 7.75 (s), 7.96 (d), 8.19 (d); FT-IR (film, cm^{-1}): 1785, 1727 (imide C=O), 1374 (imide C-N), 790.7 (C-Cl).

Cinnamate esterification of CMPI (PIMCO-*n*)

The degree of substitution for CMPI samples used in this work was ca. 150 ± 10 % (vs. repeating unit).

CMPI (1.00 g) dissolve in DMF (35ml), 1 equiv. (to -CH_2Cl) of p-alkoxycinnamic acids, K_2CO_3 and TBAB were added. The reaction mixture was stirred for 24 h at 40 °C under nitrogen atmosphere. The solution was poured into water, reprecipitation from THF into methanol and dried in a vacuum oven. PIMCO-n will be used for abbreviation of poly(imide methylene p-alkoxycinnamate)'s, where n denotes for the number of carbons in the alkoxy side chain.
^{1}H-NMR (DMSO-d_6, d *ppm*): 5.35–5.38 (m), 6.61 (d), 7.05–7.18 (m), 7.24(d), 7.35 (s), 7.50 (m), 7.65 (d), 7.70 (s), 7.75 (s), 7.96 (d), 8.19 (d); IR (film, cm^{-1}): 1785, 1727 (imide C=O), 1635, 768 (-CH=CH-), 1374 (imide C-N).

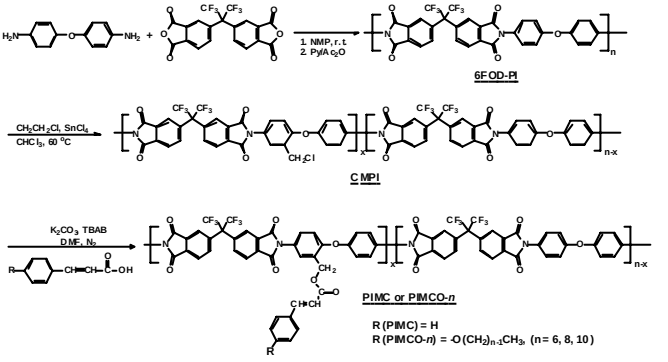

Fig. 1. Schematic diagram of syntheses for PIMC and PIMCO-n

Characterization

^{1}H-NMR spectra were recorded on JEOL 400 (400 MHz) instrument. DMSO-d_6 or $CDCl_3$ was used as a solvent for sample preparation. Tetramethylsilane (TMS) was used as a reference for peak assignments. Fourier transform infrared (FT-IR) spectra were obtained by Jasco 300E FT-IR spectrometer. The liquid crystalline behavior was investigated by using an optical polarizing microscope. The pretilt angle of the nematic LC was measured by the crystal rotation method.

3. Results and Discussion

Synthesis and characterization of CMPI and PIMCO-*n*

The structures of compounds were characterized by ^{1}H-NMR and FT-IR spectroscopy. The spectral dates were in accordance with the expected molecular formulas.

In NMR spectra of 6FOD-PI, the peaks at 8.20-7.92 and 7.30-7.47 ppm corresponding to protons of 6FDA and ODA, respectively. After chloromethylation, the new peak appears at 4.85-4.91 ppm where represents the chloromethyl group. When esterification processed with the CMPI by alkoxy cinnamate completely, the chloromethyl peak disappears, new peak moved to 5.37 ppm. Another new peaks at 6.61 and 7.7 ppm corresponding to vinyl protons, and at 7.35 and 7.50 ppm corresponding to aromatic protons of cinnamoyl group appeared. Protons of oxymethylene unit, and other protons of alkyl group were observed at 3.93 and 0.85-1.75 ppm, respectively.

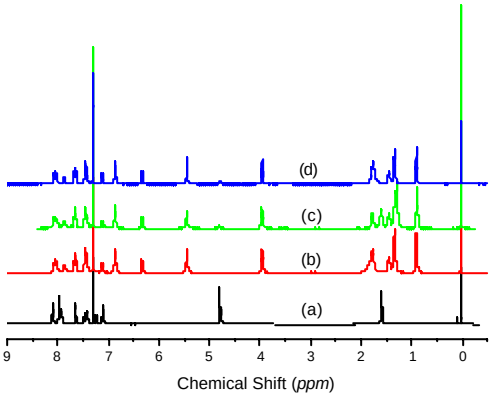

Fig. 2. 1H-NMR spectra (in DMSO-d6) of (a) CMPI, (b) PIMCO-6, (c) PIMCO-8, and (d) PIMCO-10.

In FT-IR spectra, stretching vibrational peaks of C=O, characteristic of polyimides, were found at 1785 and 1727 cm^{-1}. A peak corresponding to C-N stretching vibration was observed at 1374 cm^{-1}. After the esterification, as shown in Fig. 3, the peak at 790.7 cm^{-1}, corresponding to CH_2-Cl stretching disappeared, and new peaks at 1635.3 and 767.5 cm^{-1} were observed corresponding to -CH=CH- stretching, and =C-H out-of-plane bending, respectively.

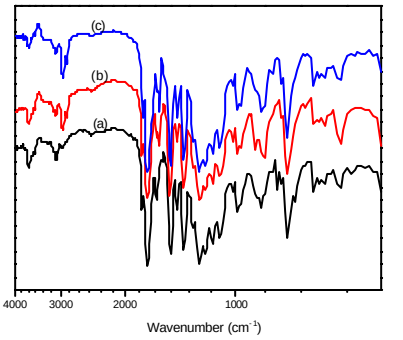

Fig. 3. FT-IR spectra of (a) PIMC, (b) PIMCO-6 and (c) PIMCO-8

Photoalignment of LC on PIMCO-*n*/PIMC Films

LC cells were prepared by using PIMC or PIMCO-*n* alignment layers to investigate their properties as photoalignment material.

In Fig. 4, cross-polarized optical microscopic images of LC cell prepared from photo-irradiated PIMCO-*8* were displayed and indicate that the liquid crystal alignments are uniform. It was obvious that PIMCO-*n*'s have a potential to be used as photo-alignment material in TFT-LCD fabrication.

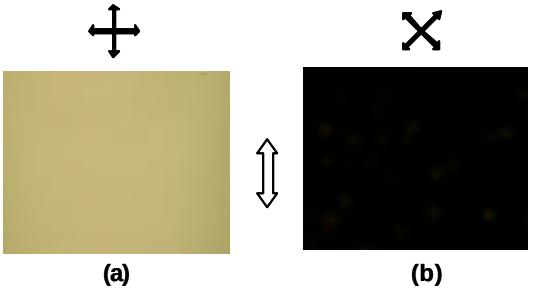

Fig. 4. Optical microscopic images of LC cell prepared from PIMCO-*6* thin film. White arrow indicates the direction of polarized light used for photo-aligning, and black arrows indicate the optic axis direction of polarizer.

Pretilt angles of LC of photoalignment films based on PIMCO-*n*

The polymer films based on PIMCO-*n*, after irradiation of polarized UV light with 45° incident angle and 40 mW/cm^2 irradiation energy, homogeneously aligned liquid crystals without defect within 15 seconds, which proved its high photosensitivity. The pretilt angle was expected to exhibit homeotropic alignment characteristics by polyimides with long alkoxy cinnamate chain, but the resulting pretilt angle is very low which shows in Fig. 5. It is supposed that the high surface energy of polyimide main chain impact the pretilt angle, the further work is on the process.

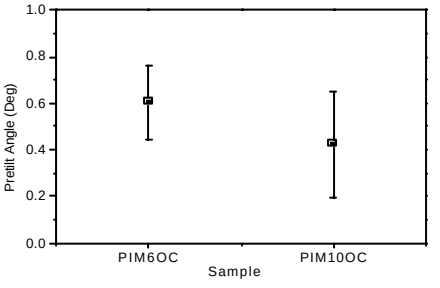

Fig. 5. Pretilt angles of LC cells based on PIMCO-*6*, *10* films.

Pretilt angles of LC of rubbing films based on the mixture of PIMCO-*n* and PIMC films

We have ever proved the rubbing alignment cells based on the different ratio of the two polyimides PIMC and PIMCO-*10* mixture can make good homogenous alignment, the LC cells can be kept good stability at room temperature for more than 6 months. The ratios have different effort on pretilt angle, and some ratio can greatly improve the pretilt angle, which showed in Table 1.

Sample PIMC: PIMCO-*10*	100%: 0%	80%: 20%	60%: 40%	40%: 60%	0%: 100%
Pretilt angle (deg)	0.40	11.16	4.25	10.27	3.65
Cell gap (㎛)	59.29	60.50	65.22	61.70	72.24

Table 1. Pretilt angles of LC cells based on PIMC and PIMCO-*10* mixture by rubbing method.

4. Summary

We have developed a series of new photo-crosslinkable side-chain polyimides (PIMCO-*n*/PIMC) for photoalignment of liquid crystals. The films exhibit good photosensitivity by the alkoxy cinnamate side chain and their excellent thermal stability were assuranced by the polyimide main chain. Its low pretilt angles are proper for the in-plane switching TFT-LCD.

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