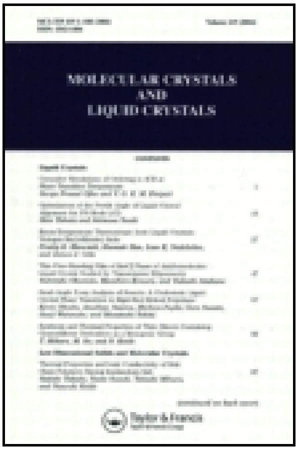

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Characterizations of Photo-Alignable Multi-Functioning Polyimide Material

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Characterizations of Photo-Alignable Multi-Functioning Polyimide Material

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For a potential application in thin-film-transistor liquid crystal display (TFT-LCD) manufacturing as a multi-functioning layer working as an overcoat layer and LC alignment layer simultaneously, a novel chloromethylated polyimide was synthesized. The electrical performances of liquid crystal (LC) cells with chloromethylated polyimide alignment layers were investigated. The polymer layer acted as a multifunctional layer that does role of planarization layer and photo-alignment layer with high photosensitivity and excellent thermal stability, simultaneously. The capacitance-voltage characteristics of LC cells fabricated from the photo-aligned layers were measured. The LC cells with rubbed and photo-aligned layer showed higher residual DC values and corresponding lower voltage holding ratios compared to the commercial alignment layer, probably due to the photo-induced ionic charges on the alignment layer. Mechanical rubbing of the extensively purified polymer layer did not generate much difference in residual DC when compared to commercial polyimides.

Keywords: alignment layer; chloromethylated polyimide; multi-functioning layer; overcoat layer; photo-alignment

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INTRODUCTION

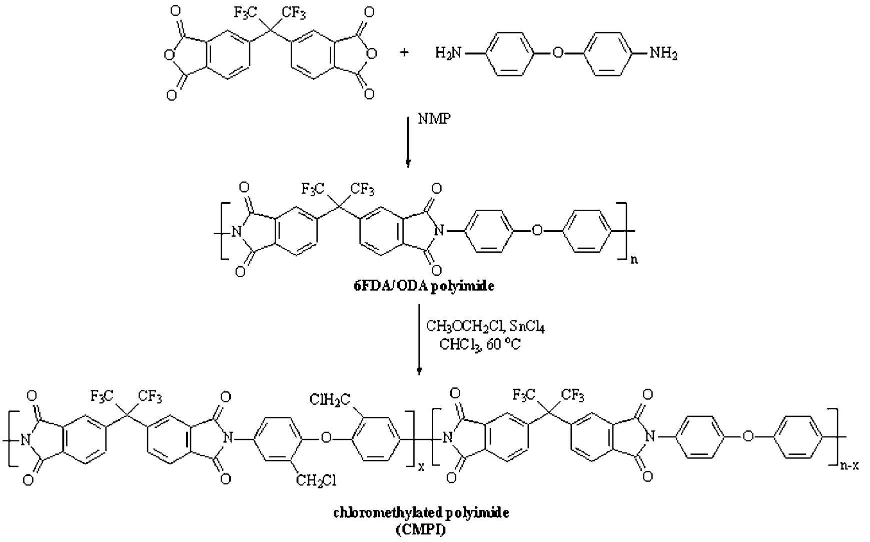
In the recent technologies concerned with high image quality and large size thin film transistor liquid crystal displays (TFT-LCDs), a variety of switching modes such as in-plane-switching (IPS) and fringe-field switching (FFS) has been introduced [1–3]. The main characteristic of both modes is that the electrodes exist only on one substrate, generally bottom or so called TFT substrate. On the other substrate, color filter substrate, only polymeric thin layers are required which includes black matrix, red-green-blue (RGB) color filters, a planarization layer known as an overcoat (OC) layer, and an alignment layer. Among these, overcoat layer not only protects the color filter layer, but provides a planar surface between the non-smooth color filter patterns and alignment (AL) layer [4]. To fabricate a TFT-LCD with high performance, a spin-coatable overcoat layer with high optical transmittance, high thermal stability, and good adhesion to color filter is required. On top of the OC layer, an AL layer, generally made of polyimide (PI), is coated to align the liquid crystal (LC) in a specific direction. It is more desirable if the polyimide could possess an aligning ability of LC by means of photo-irradiation. Currently, only a rubbing of PI surface with a fabric pelt, which definitely is not suitable for a large area display, is possible to induce an aligning of LC in the commercial production of TFT-LCD panels.

These two layers, namely an OC layer and an AL layer, can be combined by one polymeric layer, if there is an available material that possesses the required properties of both layers. Recently, we have introduced a new concept of multi-functioning polymeric layer, where one polymeric layer can act as an OC layer as well as an AL layer, simultaneously [5]. According to this, a soluble and transparent polyimide can be used as a multi-functioning layer, in which an aligning of LC was accomplished by a conventional rubbing method. As an extension of this work, we now report the synthesis of a novel photo-alignable multi-functioning polyimide (MPI), and its material characteristics and electro-optical performances.

EXPERIMENTAL

Synthesis

Synthesis of chloromethylated polyimide (CMPI). The synthetic scheme of CMPI was shown in Scheme 1. Chloromethylated polyimide (CMPI) was synthesized via chloromethylation of fluorinated polyimide prepared from 4,4-diaminodiphenylether (ODA) and



SCHEME 1 Schematic representation of chloromethylated polyimide synthesis.

4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) in the presence of chloromethyl methyl ether and tin(IV) chloride as a catalyst according to the literature [6]. Polymer having two chloromethyl units per one repeating unit was used for this work.

Physical Properties

The adhesion test of CMPI films on a glass substrate was performed following the ASTM D3359-B. The transparency of CMPI was examined by measuring the light transmittance of 1.1 μm thick film at 400 nm. Planarizability was tested for 1 μm thick films on a color filter substrate by examining the surface roughness with surface profiling instrument (alpha-step) as described in the text book [7].

Photo-Alignment

CMPI solution (1.0 wt.%) in cyclohexanone was spin-coated on a glass substrate, and the film was baked at 180°C for 1 h to remove the solvent. The thickness of CMPI film was controlled at ca. 70 nm. Photo aligning of the polymer film was performed according to our previous report [8]. Linearly polarized UV light (LPUVL) of ranging 230–320 nm with an intensity of ca. 5 mW/cm^2 was irradiated on the

CMPI film. The incident angle of light was 45° and the irradiation was conducted in air. LC cells (cell gap = 50 μm) were assembled with two irradiated CMPI-films so that the incident polarization direction of LPUVL was anti-parallel. A nematic LC, MJ00443 (Merck) containing with 1 wt.% black dichroic dye, was injected into the cell at room temperature. The cell was annealed at 77°C (5°C higher than T_c of LC) for 10 min, and cooled down slowly to remove the flow effect.

Electro-Optical Performances

Preparation of electrically controlled birefringence (ECB) cells for testing the electro-optical performances such as residual direct current (R-DC) and voltage holding ratio (VHR) was conducted as described in the literature [9,10]. The R-DC was evaluated by measuring capacitance-voltage hysteresis using a LCR-meter (4284A Precision LCR meter, Agilent). The DC voltage was swept from 0 to +10 V, and then changed from +10 V to −10 V, and finally from −10 V to 0 V, with an each step of 0.1 V. Amplitudes of the R-DC at positive and negative cycles, are defined as the voltage difference between rise and fall at half of the maximum capacitance. To measure the VHR, the 5 V was applied to the cell with a frequency of 60 Hz.

RESULTS AND DISCUSSION

CMPI was soluble in most of organic solvents including chloroform, THF, and cyclohexanone as well as in polar aprotic solvents such as NMP and DMSO. The glass transition temperature of CMPI measured by differential scanning calorimetry (DSC) was in the range of 258 ~ 262°C. The thermogravimetric analysis (TGA) of CMPI showed 2-step thermal decompositions, which are corresponding to the decomposition of side functional groups at near 285°C, and the decomposition of the main chain at above 480°C, respectively. CMPI films with thickness of about 1000 Å was prepared on a glass substrate, and the adhesion of sample was compared before and after the thermal treatment at 230°C for 30 min. CMPI showed adhesion grade of 3B, which was increased to 5B after thermal treatment showing a perfect adhesion. CMPI was optically clear, and showed transmittance higher than 96.9% at 400 nm wavelength for 1 μm thick film. Interestingly, even after heat treatment at 230°C for 240 min in air, the transmittance decreased less than 1.5% (transmittance = 95.5%). Depending on the solid content (SC) of CMPI solution, the degree of planarization (DOP) on a color-filter substrate varied from 0.2 to 0.48 (at SC of 5 and 15%, respectively).

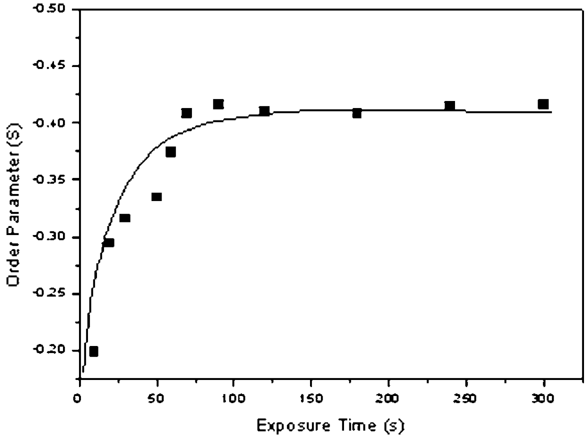


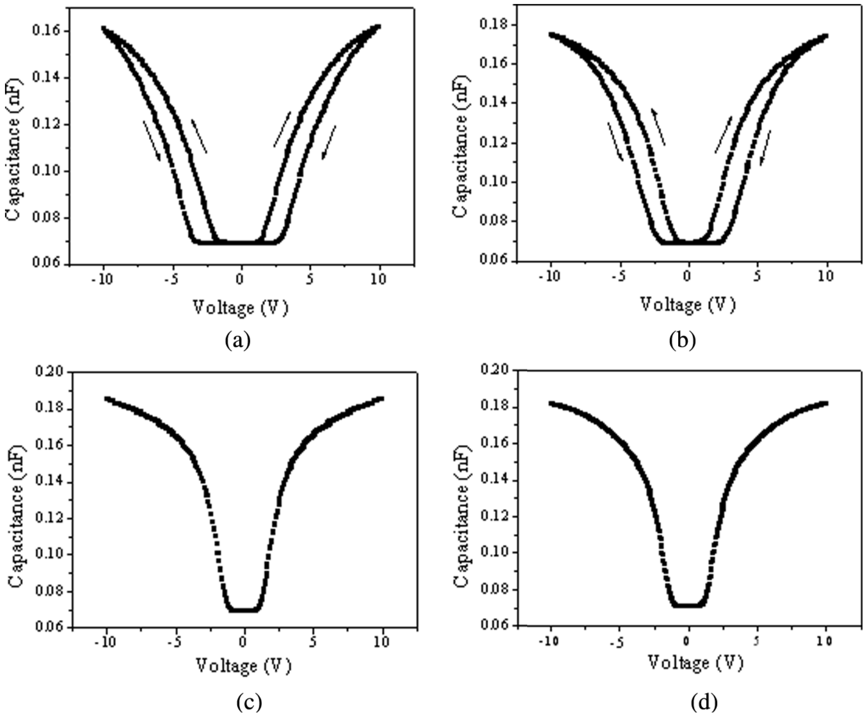
FIGURE 1 The relationship between the exposure time and the order parameter of LC cells fabricated by CMPI films with LPUVL irradiation.

The relationship between the exposure time and the order parameter of LC cells fabricated by CMPI films with LPUVL irradiation was also examined, and the result was shown in Figure 1. The LCs were aligned homogeneously with no defect on the CMPI-coated substrates when the LPUVL was irradiated for 50 s or longer. Order parameters of LC cells initially increased logarithmically with irradiation time, and approached a constant value when irradiation time was over 70 s. Compared to this, no alignment behavior was observed for 6FDA-ODA PI under the same condition even after an extended exposure time of up to 30 min.

R-DC, and VHR of LC cells fabricated from photo-aligned CMPI film on glass substrates were measured to evaluate electro-optical performances, and the results were compared with those from rubbed commercial AL layer and rubbed CMPI layer. In order to evaluate the characteristics of residual DC, we prepared experimental cells under the condition of ECB mode. By using a photo-aligned CMPI film, anti-parallel cells (abbreviated as P-CMPI) were constructed with a cell gap range of $3.8 \sim 4.0\,\mu m$, and were injected super-fluorinated LC mixtures (MJ951160) with positive dielectric anisotropy of 7.4 and birefringence of 0.088. For comparison, a commercial homogenous alignment material (AL16139, JSR) was coated on a glass substrate, and pre-baked at 100°C for 10 minutes and at 200°C for 2 hours. After a rubbing process, an anti-parallel cell (R-COMM) was prepared. Another anti-parallel cell (R-CMPI) was prepared by using a rubbed CMPI layer in the same way.

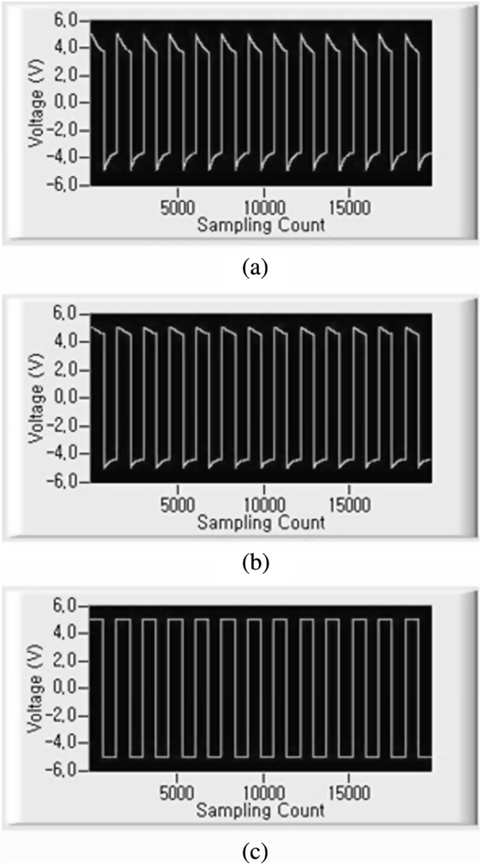
Figure 2 (a-c) shows the C-V curves of the P-CMPI, R-CMPI, and R-COMM cells. From the average width of hysterisis in C-V curves, the R-DC was estimated to be 1.463, 1.449, and 0.015 V, respectively for P-CMPI, R-CMPI, and R-COMM. Cells prepared from CMPI either rubbed or photo aligned showed larger R-DC values compared to R-COMM. This can be attributed to two main reasons, the ionic impurities produced by photo decomposition during the irradiation process, and the chemical impurities remained in CMPI after the purification by reprecipitation. When we extensively purified CMPI by reprecipitating chloroform solution into methanol/water mixture for several times, R-DC value of R-CMPI significantly improved as low as 0.075 as shown in Figure 2(d). Measurements for purified P-CMPI samples are now in progress, the result of which will be published elsewhere.

Figure 3 shows the measured VHRs of P-CMPI, R-CMPI and R-COMM, respectively. This measurement was carried out by adjusting peak-to-peak voltage as 10 V with a bias voltage of 5 V in both cells.



(a) (b) (c) (d)

FIGURE 2 Voltage-dependent capacitance (R-DC) curves of (a) P-CMPI, (b) R-CMPI, (c) R-COMM and (d) purified R-CMPI respectively.



(a)

(b)

(c)

FIGURE 3 Measured voltage holding ratios (VHRs) of P-CMPI, R-CMPI and R-COMM, respectively.

VHRs of P-CMPI, R-CMPI and R-COMM were measured to be 86.7, 96.9 and 99.4%, respectively. While R-CMPI and R-COMM showed similar values of VHR in tolerable range, VHR characteristics of P-CMPI was comparatively inferior. It was confirmed from our previous research that the photo alignment of CMPI is induced by a photo decomposition mechanism, generating ionic species such as amine and anhydride as a result [11]. It seems to be attributed to the photo-oxidative cleavage of imide ring in conjunction with chloromethyl side groups. The photo decomposed ionic species in the CMPI alignment film may contribute to the high R-DC and poor VHR characteristics of the photoaligned LC cell. In Table 1, were summarized

TABLE 1 Comparison of Electro-Optical Data for P-CMPI, R-CMPI and R-COMM

Sample	R-DC (V)	VHR (%)
P-CMPI	1.463	86.7
R-CMPI	1.449 (0.075)*	96.9
R-COMM	0.015	99.4

*R-DC value in parenthesis was measured after repetitive purification processes.

the results of electro-optic measurements of R-DC, and VHR for P-CMPI, R-CMPI and R-COMM, respectively. Further investigations on the photo decomposed species and their effects on the electro-optical performances of LC cell are now in progress.

CONCLUSIONS

We synthesized soluble transparent polyimide via chloromethylation of conventional polyimide, and demonstrated that the resulting polymer can be used as a multi-functioning polymeric layer working as an over-coat and alignment layer for TFT-LCD manufacture, simultaneously. The soluble polyimide showed excellent transparency, good adhesion, high thermal stability, and satisfactory planarization behavior as well as an aligning capability of LC either by conventional rubbing or photo aligning technique. The photosensitivity of the material was high providing a homogeneous and high quality alignment with comparably small exposure dose. Photo-aligned cell, however, showed inferior electrical characteristics in residual-DC and voltage holding ratio measurements compared to rubbed cells. It can be ascribed to the ionic species in the film either produced from photo decomposition or remaining after the synthesis. Further investigation with respect to the origin of deterioration should be necessary in the future to improve the electrical properties. Nevertheless, this polymeric material is promising in order to reduce process steps and cost especially in the IPS and FFS devices.

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