



Soluble polyimide as liquid crystal perpendicular alignment layer

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ABSTRACT

Three polyimides (PIs) were prepared from a diamine containing biphenyl ester group as a side chain and a corresponding dianhydride chosen from 1,2,3,4-cyclobutanetetracarboxylic dianhydride (PI-1), 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (PI-2) or pyromellitic dianhydride (PI-3). Chemical structures of the resulting PIs were confirmed by Fourier transform infrared spectroscopy (FT-IR) and ¹H NMR spectroscopy. While PI-3 was insoluble in any of organic solvents after the imidization process, PI-1 and PI-2 showed good solubility in polar aprotic solvents. Especially, PI-2 exhibited remarkable solubility even in chloroform and tetrahydrofuran. Liquid crystal (LC) alignment layers were prepared from these PIs by conventional rubbing processes, and subjected to fabricate LC cells for the characterization of alignment properties. In all cases, a uniform alignment was observed as confirmed by angle dependence polarizing microscopic technique. LC alignment directors of these polymer films were found to be perpendicular to the rubbing direction due to the perpendicularly attached biphenyl moiety to the main chain. LC pretilt angle and electro-optical properties of these LC cells were also investigated.

Introduction

Polyimides (PIs) have attracted considerable attention in the past several decades because of their excellent properties and wide application areas such

as in microelectronics, space and aviation vehicles, packaging and coating. Due to their advantageous properties, such as excellent mechanical performance, moderate optical transparency, low moisture absorption, dimensional stability, heat resistance, good radiation and chemical corrosion resistance as

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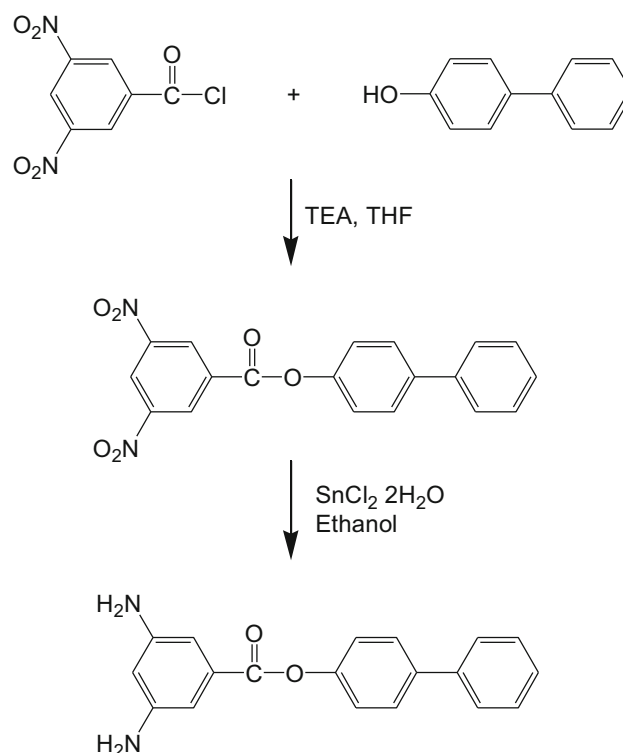
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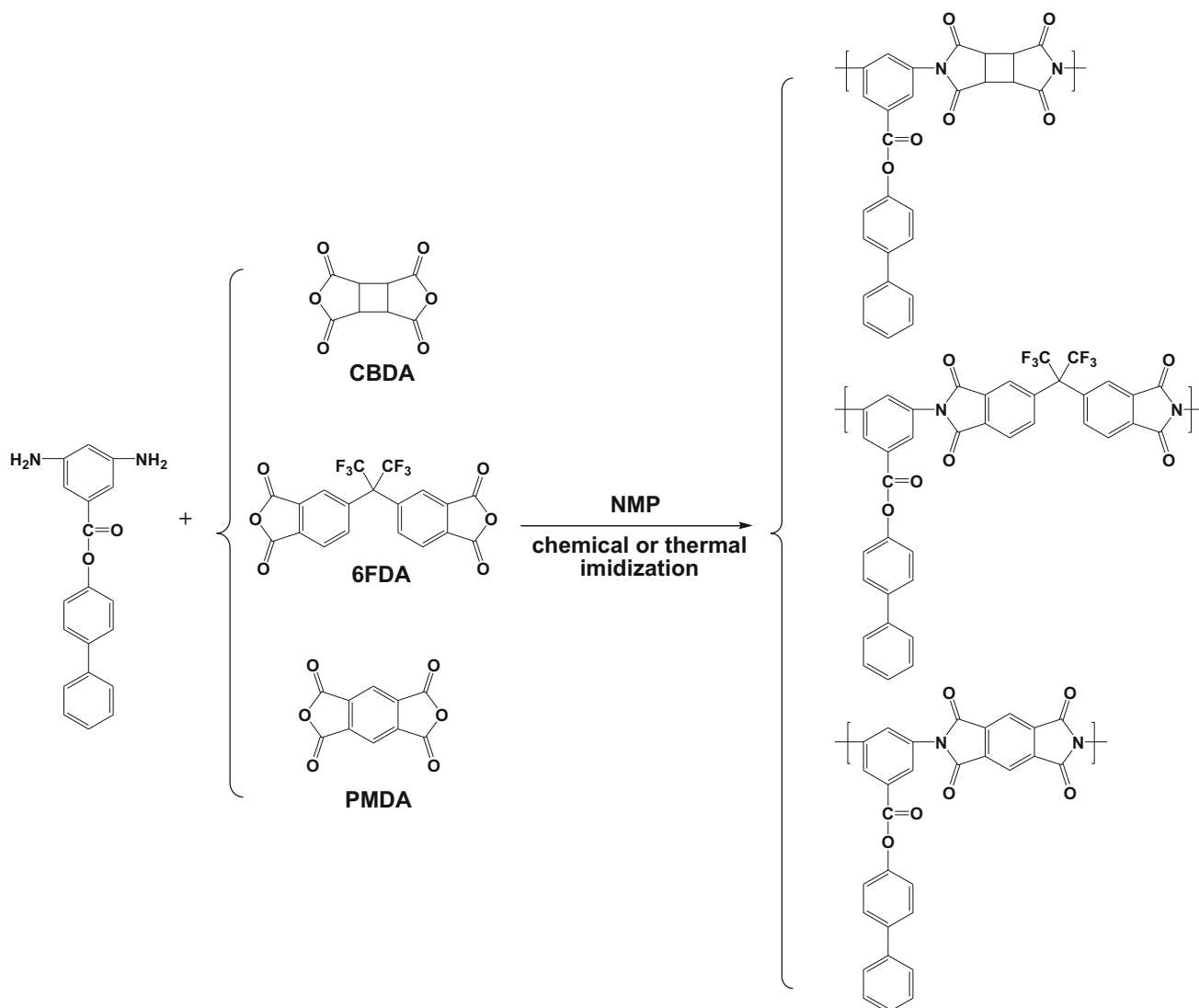
well as good adhesion to inorganic materials, PIs are widely used as an alignment layer for liquid crystals (LCs) [1–5]. Alignment layer is one of the important functional films in liquid crystal display (LCD). The function of alignment layer is to force LC molecules to possess a predetermined mono-domain orientation. LC alignment is not only a scientific interest but also an important technological issue because the orientation of LC molecules is crucial for optimizing the operation of LCD [6–8]. In addition, the alignment layers become more important due to the recent developments in polymerizable liquid crystalline molecules, which are also known as reactive mesogens. To develop various optical films by using reactive mesogens, their alignment in a specific direction is a key issue [9–11]. To induce the LC alignment, mechanical rubbing of a polymer thin film is the most widely used technique. Even though there are some other methods such as photo-alignment and ion-beam irradiation [12–14], mechanical rubbing method has been considered as a simple and convenient method, making it more popular for the preparation of alignment layers in commercial production of LCDs [15]. In most cases, rubbing of PI films has been found to create microgrooves on the film surface as well as to orient polymer main chains along the rubbing direction [16]. It was believed the unidirectional microgrooves and the oriented polymer main chains cooperatively align LC molecules along the rubbing direction owing to their anisotropic interactions with the LC molecules [17]. On the other hand, some of the polymer films have been found to align LC director perpendicular to the rubbing direction. Such examples can be found in polyimides containing fluorenyl groups [18], polystyrene derivatives containing coumarin side groups [19], and brush-type polyimides with phenyloxy bristle units [20]. It would be particularly useful if we could have both materials of parallel alignment layer and perpendicular alignment layer, especially for fabricating a film-patterned retarder (FPR) which is necessary to realize 3D TV. After printing two alternating strips of both materials on a plastic film substrate, a single rubbing process would be enough for the preparation of parallel and perpendicular alignment layers, simultaneously. For such an application, solubility of the polymeric material is also an important issue for printing patterned alignment layers on a plastic substrate. Traditional aromatic PIs are, however, normally insoluble, and the processing

is generally carried out with poly(amic acid) (PAA) intermediate which is subsequently converted to PI via rigorous thermal treatment (at higher than 250 °C). Therefore, it is advantageous to develop soluble PI alignment materials that can be processed at lower temperature on a plastic substrate.

In this paper, we report the syntheses and properties of three polyimides which can align liquid crystal molecules perpendicular to the rubbing direction. Firstly, as shown in Scheme 1, we synthesized biphenyl-4-yl 3,5-diaminobenzoate (BPBDA), which contains biphenyl ester group as a side chain. Three different polyimides (PIs) were prepared from BPBDA and three dianhydrides, 1,2,3,4-cyclobutanetetracarboxylic dianhydride (PI-1), 4,4'-(hexafluoroisopropylidene) dipthalic anhydride (PI-2) or pyromellitic dianhydride (PI-3) as illustrated in Scheme 2. Alignment characteristics of these polymeric materials such as the direction of LC director to the rubbing direction, and the pretilt angle in addition to the electro-optical properties of LC cells fabricated with these alignment layers were investigated. Two of the resulting polyimides was soluble in organic solvents, rendering its processing at low temperature.



Scheme 1 Synthetic scheme of BPBDA.



Scheme 2 Synthetic scheme of polyimides.

Materials and methods

Materials

4-Phenylphenol, 3,5-dinitrobenzoyl chloride, triethylamine, tin (II) chloride dehydrate, 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA), 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and pyromellitic dianhydride (PMDA) were purchased from Aldrich and used as received. Tetrahydrofuran (THF), ethanol, acetic anhydride, pyridine and N-methyl-2-pyrrolidone (NMP) were purchased from SHOWA and purified by distillation after stirring with CaH_2 overnight.

Measurements

^1H NMR spectra were recorded on a Bruker Avance Series DRX-600 NMR spectrometer with tetramethylsilane (TMS) as an internal standard in CDCl_3 or DMSO-d_6 . Fourier transform infrared (FT-IR) spectra were obtained from KBr pellets with a Nicolet NEXUS-470 FT-IR spectrometer. Thermogravimetric analyses (TGA) were carried out on a TGA 2050 (TA Instruments) under nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ up to $800\text{ }^\circ\text{C}$. Differential scanning calorimetry (DSC) was conducted on a DSC 2010 (TA Instruments) at a heating/cooling rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Nikon LV100POL polarized optical microscope (POM) was used to observe LC alignment. The angle dependence (polar

diagram) of the polarized absorbance of LC cells containing black dichroic dye was experimentally determined using an optical setup equipped with a He–Ne laser (632.8 nm wavelength), a polarizer, a rotational sample stage, and a photodiode detector. Pretilt angle was measured by an optic system, PAMS-100 T (SESIM Photonics Technology, Korea). The electro-optical performances such as residual direct current (RDC) and voltage holding ratio (VHR) of the cell fabricated from these PIs were also tested. RDC was evaluated by measuring capacitance–voltage hysteresis using Agilent Precision LCR Meter, 4284A. 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 each step of 0.1 V interval. Amplitudes of the RDC at positive and negative cycles are defined as the voltage difference between rise and fall at half of the maximum capacitance. VHR was measured with a SESIM VHR-200, where 5 V was applied to the cell with a frequency of 60 Hz.

Synthesis of biphenyl-4-yl 3,5-diaminobenzoate (BPBDA)

A flask equipped with a magnetic stirrer was charged with a solution of 4-phenylphenol (1.7021 g, 0.01 mol) and triethylamine (1.53 ml, 0.011 mol) in 20 mL of dry THF. 3,5-Dinitrobenzoyl chloride (2.3056 g, 0.01 mol) dissolved in 10 mL of dry THF was added dropwise to the stirred solution at 0 °C. The mixture was stirred at ambient temperature for 12 h and subsequently poured into a large amount of water. The light yellow solid precipitate was filtered off, washed with dilute aq. NaOH and then with water, and dried under a vacuum to yield biphenyl-4-yl 3,5-dinitrobenzoate. A purified sample was obtained by recrystallization from THF (mp. 227 °C; yield 92%). ¹H NMR (CDCl₃), δ (ppm): 9.36–9.32 (m, 3H, aromatic ortho to NO₂); 7.71–7.33 (m, 9H, aromatic of biphenyl).

The reduction of dinitro-compound was conducted as follows: biphenyl-4-yl 3,5-dinitrobenzoate (3.6407 g, 0.01 mol) and tin (II) chloride dehydrate (11.28 g, 0.05 mol) was added to a one-neck flask containing ethanol (200 ml). The mixture was stirred at 80 °C for 6 h, and, after cooled to room temperature, poured into 0.25 M of aqueous sodium bicarbonate with stirring for 3 h. The light yellow solid precipitate was filtered off, washed with water and dried in vacuum overnight. Then, the solid was

dissolved in chloroform, and the solution was filtered to remove insoluble solid. BPBDA was obtained after evaporating the filtrate and dried in a vacuum oven (mp 172 °C; yield 86%). ¹H NMR (CDCl₃), δ (ppm): 7.64–7.24 (m, 9H, aromatic of biphenyl); 6.95 (s, 2H, aromatic ortho to NH₂); 6.25 (s, 1H, aromatic between NH₂), 3.74 (br, 4H, NH₂).

Syntheses of polyimides

Three polyimides containing biphenyl ester in the side chain were synthesized from BPBDA and a corresponding dianhydride chosen from CBDA, 6FDA and PMDA. The resulting polyimides are abbreviated as PI-1 (BPBDA-CBDA), PI-2 (BPBDA-6FDA) and PI-3 (BPBDA-PMDA), respectively. General procedure for the PI syntheses was illustrated as follows: 2.0 mmol of dianhydride was added to a stirred solution of 2.0 mmol of diamine in 10 mL of NMP in a 50-mL two-necked flask equipped with a nitrogen inlet and outlet. The mixture was stirred at room temperature under a gentle flow of dry nitrogen until the solution became clear, and then reacted at 0 °C for 24 h to give a viscous solution of poly(amic acid) (PAA) in NMP. The PAA was subsequently converted into PI by either a thermal or a chemical imidization process. Chemical imidization was carried out by adding 3 mL of acetic anhydride/pyridine mixture (2:1 v/v) into the PAA solution with subsequent stirring for 1 h at room temperature and at 120 °C for 8 h to yield a PI solution. After cooling, the viscous solution was poured slowly into a 1:1 (v/v) mixture of deionized water and methanol to give a fibrous precipitate, which was collected by filtration, washed thoroughly with methanol, and finally dried in a vacuum oven at 80 °C overnight. The conversion was nearly quantitative. For thermal imidization, above PAA solution was cast onto a glass plate, which was dried in an oven at 80 °C for 30 min, and heated at 150 °C for 2 h and at 250 °C for 1 h, stepwisely, in a furnace under N₂ atmosphere. Polyimide film was peeled off from the glass plate after cooling to room temperature to give a free-standing film.

Fabrication of LC cells

Polyimide or PAA solution (5 wt%) in NMP was spin-coated on a clean glass substrate at 600 rpm for 20 s and subsequently at 3000 rpm for 60 s. In case of soluble polyimides (PI-1 and PI-2), the film was

stored in an oven at 80 °C overnight to remove the solvent. When PAA was used (PI-3), the film was pre-baked in an oven at 80 °C for 10 min, and then imidized on a hot plate at 230 °C for 1 h. The resulting films were rubbed with a rubbing machine (RMS-50-M, Namil Optical Components Co.) using a conventional rubbing technique [21]. Then, antiparallel LC cells were constructed by assembling two glass plates antiparallel to the rubbing direction with each other. Cell gap was maintained to 10 μm using a cell gap tape. The fabricated LC cells were filled with a nematic LC (MJ951160, Merck Co., $n_e = 1.5646$, $n_o = 1.4766$, and $\Delta\epsilon = 7.4$, where n_e , n_o , and $\Delta\epsilon$ represent extraordinary refractive indexes, ordinary refractive indexes, and dielectric anisotropy, respectively) by capillary action and then sealed with epoxy resin.

Fabrication of FPR

To demonstrate a possible application of the above PIs which can align liquid crystal molecules perpendicular to the rubbing direction, we prepared a FPR by using a simple fabrication method as follows: On a cleaned glass substrate, 5 wt% PAA solution of PI-1 in NMP was spin coated at 600 rpm for 20 s and subsequently at 3000 rpm for 60 s. The film was pre-baked in an oven at 80 °C for 10 min, and then imidized on a hot plate at 230 °C for 1 h. Then, a strip pattern of conventional PI alignment layer (SE-6514, Chisso) was bar coated on the above PI-1 layer, and cured stepwisely at 80 °C for 5 min and at 230 °C for 60 min. The strip patterned alignment layers were subjected to the conventional rubbing process in the direction parallel to the strip pattern. Reactive mesogen (RMS03-013, Merck) was spin coated at 400 rpm for 23 s and subsequently at 3000 rpm for 70 s, which was then cured by UV irradiation for 1 min with an intensity of 25mW/cm².

Results and discussion

Synthesis and characterization

To introduce a biphenyl ester group perpendicular to the polymer main chain, biphenyl-4-yl 3,5-diaminobenzoate (BPBDA) was prepared via two step synthesis as shown in Scheme 1. The reduction of biphenyl-4-yl 3,5-dinitrobenzoate was performed in

the presence of tin (II) chloride dehydrate, which provided a high yield. The diamine was reacted with CBDA, 6FDA or PMDA in NMP at 0 °C for 24 h to obtain poly(amic acid) (PAA). Firstly, chemical imidization of PAA was attempted by using acetic anhydride and pyridine mixture. In the case of CBDA-BPBDA and 6FDA-BPBDA, highly viscous PI solution was obtained after 9 h, which gave PI-1 and PI-2 as a fibrous powder. On the other hand, the chemical imidization of PMDA-BPBDA was failed because the reaction mixture became a gel after adding acetic anhydride and pyridine, probably due to the low solubility of PI-3. Thermal imidization was successful to give a free-standing film in all case. The inherent viscosities (η_{inh}) of PI-1 were measured to be 0.86 dL g⁻¹ at 30 °C in N,N-dimethylacetamide (DMAc). Chemical structure of PI-1 and PI-2 was confirmed by ¹H NMR as depicted in Fig. 1. Peaks at 7.96 and 8.44 ppm correspond to the aromatic protons in BPBDA in the polymer main chain. Peaks ranging from 7.8 to 7.36 ppm are attributed to the aromatic protons of BPBDA in the side chain. Peak at 3.82 ppm is the proton in CBDA unit. There appeared no resonance signals in the range of 9–12 ppm, which supports complete transformation of poly(amic acid) to PI. All the three PIs were also characterized by FT-IR spectroscopy as shown in Fig. 2. All spectra showed no trace of amine or acid, which indicates poly(amic acid)s were fully imidized. Absorption bands at 1780 cm⁻¹ (C = O asymmetric stretch), 1725 cm⁻¹ (C = O symmetric stretch), 1340 cm⁻¹ (C-N stretch), 720 cm⁻¹ (C=O bend) are corresponding to the characteristic imide bands.

Table 1 displays the solubility of PIs in various organic solvents. PI-1 and PI-2 exhibited good solubility in aprotic polar solvents such as dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), DMAc and NMP. PI-2 was even soluble in chloroform and THF. In contrast, PI-3 was insoluble in any organic solvents. This can be ascribed to the structural difference between CBDA, 6FDA and PMDA. Compared to PI-3, both PI-1 and PI-2 have a backbone structure of reduced intermolecular interaction due to the CBDA and 6FDA unit, respectively, resulting in an enhanced solubility. In the UV/Vis spectra shown in Fig. 2, PI-3 exhibited a strong absorption centered at 320 nm which corresponds to the charge-transfer complex between the electron-accepting PMDA units and electron-donating BPBDA units [22]. On the other hand, no such absorption was

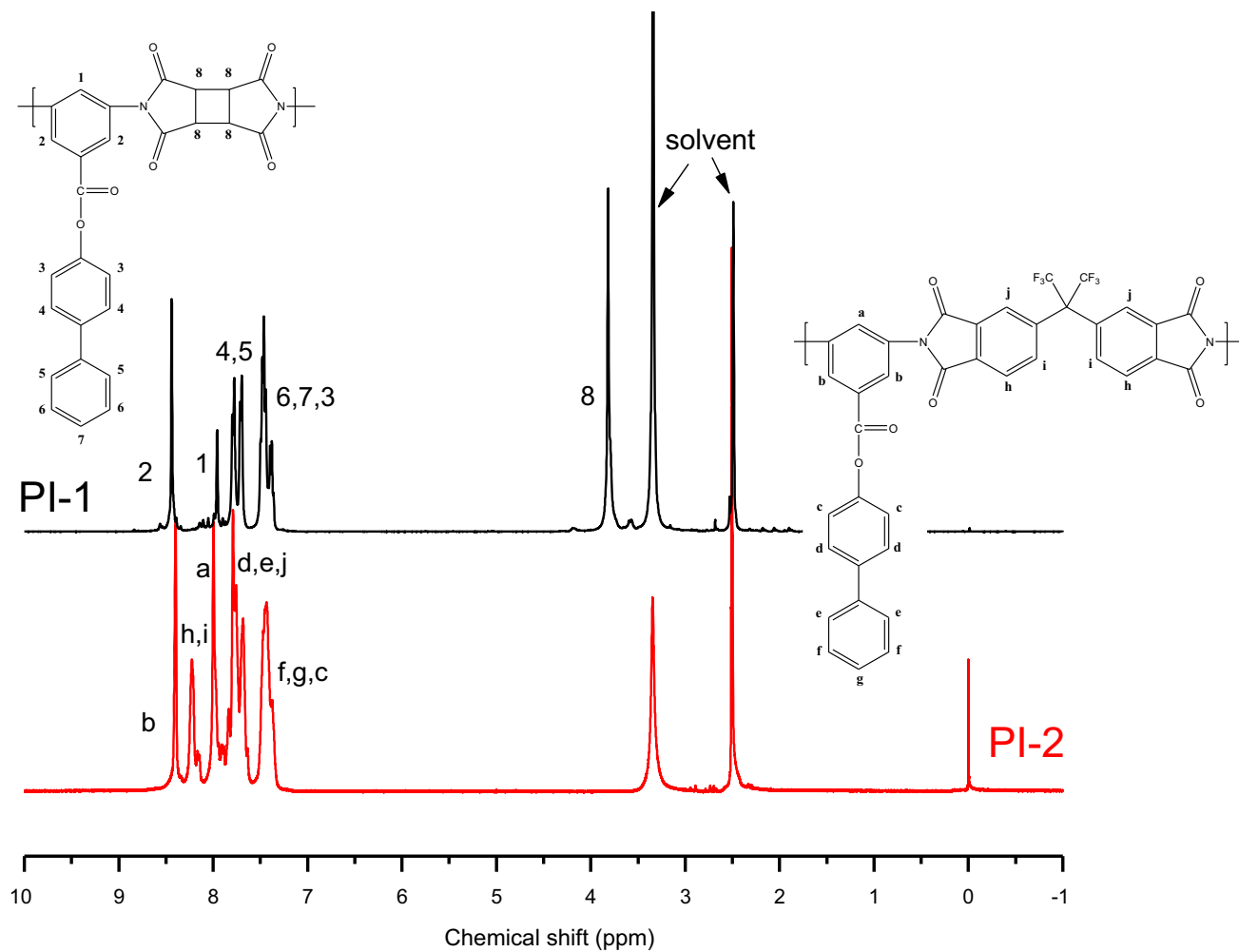


Figure 1 ^1H NMR spectra of PI-1 and PI-2.

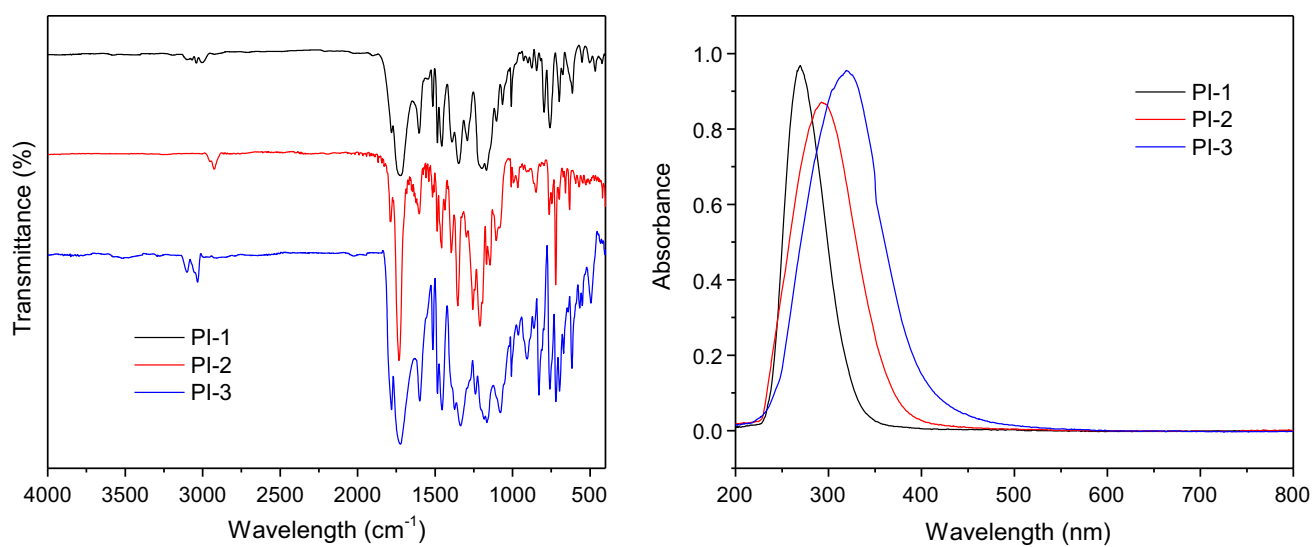


Figure 2 FT-IR and UV/Vis spectra of polyimides.

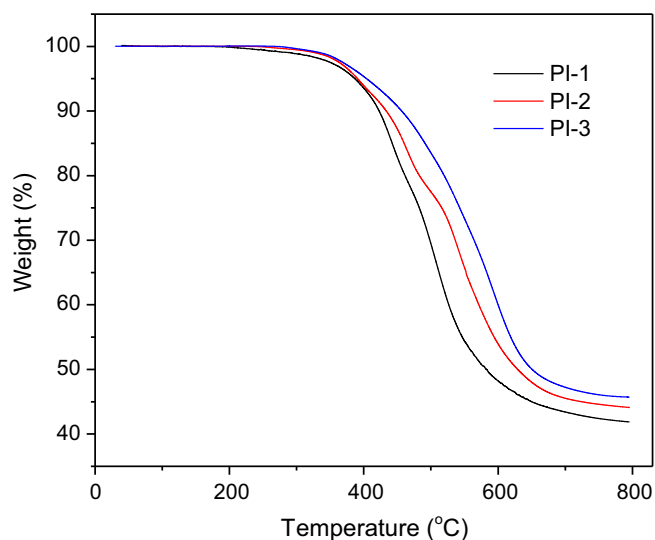
Table 1 Solubility of polyimides

Sample	DMSO	NMP	DMAc	DMF	m-cresol	Xylene	Methanol	Chloroform	THF
PI-1	+	+	+	+	–	–	–	–	–
PI-2	+	+	+	+	–	–	–	+	+
PI-3	–	–	–	–	–	–	–	–	–

+ : soluble; – : insoluble

found in the case of PI-1 and PI-2, supporting the above discussion.

Thermal stability of polyimides was studied by TGA under nitrogen atmosphere as displayed in Fig. 3. The results of initial decomposition temperature (T_d), temperature at 5% weight loss (T_5), temperature at 30% weight loss (T_{30}), heat resistant index (T_{HRI}), and residual weight at 800 °C (R_w) are summarized in Table 2. As shown in Fig. 3 and Table 2, all the polyimides exhibited good thermal stabilities up to 290 °C with R_w values in the range 42–46%. The heat resistant index of polyimides was calculated according to reference [23, 24] and the values increased from PI-1 to PI-3, which were 222.4 °C, 234.5 °C, 245.7 °C, respectively. PI-3 shows better thermal stability than PI-1 and PI-2, which should attribute to the stable and planar backbone of fully aromatic PI-3 as well as higher intermolecular interaction. Glass transition temperatures (T_g) of the polyimides were investigated by using differential scanning calorimetry (DSC) as displayed also in Fig. 3. PI-2 showed a T_g at 210 °C, while PI-1 and PI-3 exhibited no distinct glass transition up to 300 °C.

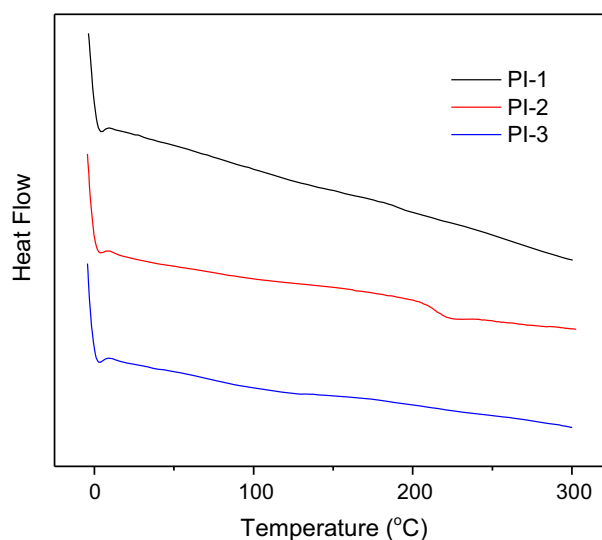
**Table 2** Thermal properties of polyimides

Sample	T_d (°C)	T_5 (°C)	T_{30} (°C)	T_{HRI} (°C)	R_w (%)
PI-1	293	386	499	222.4	42
PI-2	329	391	537	234.5	44
PI-3	340	406	565	245.7	46

$$T_{HRI} = 0.49 \times [T_5 + 0.6 \times (T_{30} - T_5)] \quad [23, 24]$$

Alignment ability and pretilt angle of liquid crystal

In Fig. 4, POM images of antiparallel LC cells fabricated from the rubbed alignment layers of PI-1, PI-2 and PI-3, respectively. In all cases, the rubbed PI layers showed uniform and defect-free LC alignments with marginal difference in optical retardation probably arising from different pretilt angles of PI's and slightly different cell gaps. Darkest and brightest images were observed, respectively, when the rubbing direction was parallel and $\pm 45^\circ$ to polarizer or analyzer. This result indicates that LC molecules in the cell possess a homogenous planar alignment, and all the PI films have strong ability to induce LC

**Figure 3** TGA and DSC curves of polyimides.

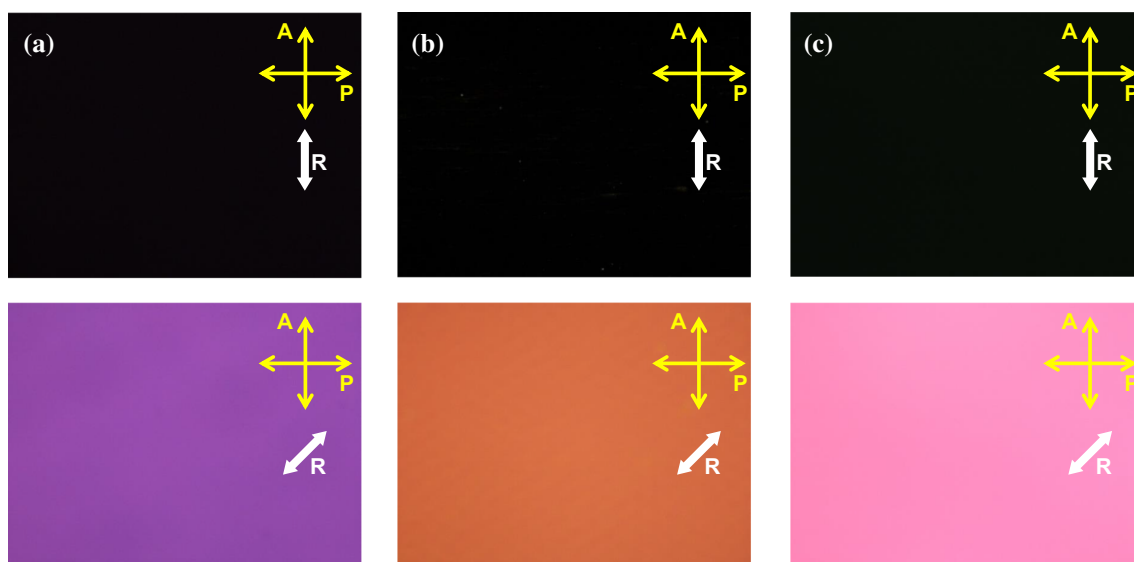


Figure 4 Polarized optical microscopic images of antiparallel LC cells fabricated from **a** PI-1, **b** PI-2 and **c** PI-3. Rubbing direction is parallel (top) and $+45^\circ$ (bottom) to analyzer, respectively.

alignment. The homogeneity of LC alignment was further investigated by measuring an angle-dependent polarized light intensity of dichroic LC cells containing small amount of black dichroic dye in the LC mixture as illustrated in Fig. 5. All of the cells exhibited a maximum absorbance along the direction of $90^\circ \leftrightarrow 270^\circ$ with respect to the rubbing direction, which clearly indicates that in all cases, LC molecules on the rubbed film surfaces are homogeneously aligned with the director perpendicular to the rubbing direction. Although it requires a further investigation, we speculate the mechanism of this perpendicular alignment as follows. In general, if the flexible lateral chains were used, they also would undergo reorientation along the main chain by the rubbing process, generating a surface anisotropy along the rubbing direction. On the other hand, the PI structures in this work were designed to have a high

density of rigid aromatic biphenyl esters directly connected to the main chain perpendicularly. Therefore, when the main chain of PI at the surface layer is oriented along the rubbing direction, the direction of rigid biphenyl groups should be perpendicular to the rubbing direction due to both the direct attachment and the steric hindrance caused by high density of the side chains. The stronger anchoring interaction between the LC molecules and BPBDA units compared to that between the LC and the PI main chain results in the perpendicular alignment of LC to the rubbing direction.

Pretilt angle of LC molecules in the cell was measured by PAMS-100 T from SESIM Photonics Technology. The LC cells with the synthesized PI alignment layers showed very small pretilt angles from 0° to 0.01° , which could contribute to higher contrast ratio in a VA-mode LCD or FPR. It is

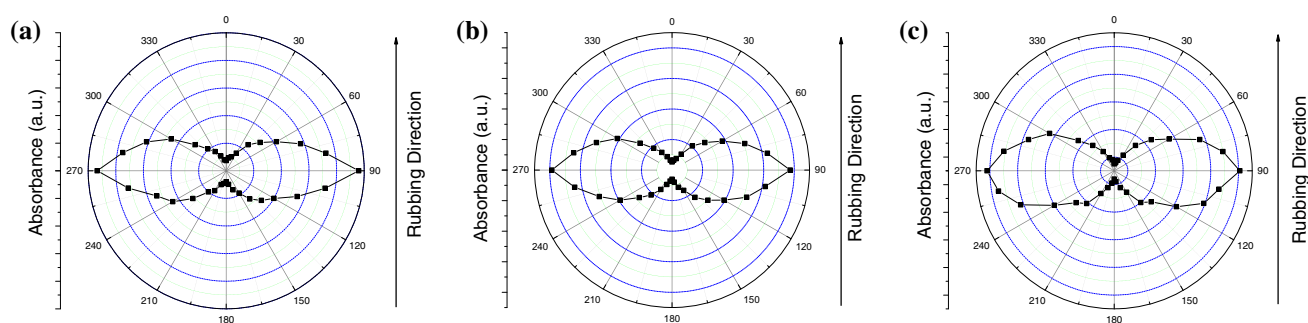


Figure 5 Angle-dependent polar absorption diagrams of antiparallel LC cells fabricated from **a** PI-1, **b** PI-2 and **c** PI-3.

speculated that the biphenyl units in polymer side chain could be oriented perpendicular to the rubbing direction, and the molecular interaction between biphenyl units and LC molecules is high enough to align the LC molecules relatively planar to the substrate regardless of the backbone structure [16, 25]. The uniform and homogeneous LC alignment throughout the cell is essential to achieve optimal electro-optical performance of LCD.

Electro-optical performance

To evaluate electro-optical performances of LC cells fabricated from rubbed PI films on ITO glass substrates, residual direct current (R-DC) and voltage holding ratio (VHR) were measured, and the results were compared with those of the cell fabricated from rubbed commercial PI film (SE-6514, Nissan Fine Chemical, Japan) as summarized in Table 3. For R-DC measurements, we prepared experimental cells under the condition of electronically controlled birefringence (ECB) mode. The antiparallel cells were constructed with a cell gap of 20 μm and were injected LC (MJ951160, Merck) having a positive dielectric anisotropy ($\Delta\epsilon$) of 7.4 and optical birefringence (Δn) of 0.088. From the average width of hysteresis in C-V curves, the R-DC was estimated to be 0.045, 0.022, 0.012, and 0.204 V for PI-1, PI-2, PI-3 and SE-6514 cells, respectively. R-DC is mainly attributed to ionic impurities of LC materials, and the alignment layer materials as well as the fabrication process of LC cell. Considering that the same LC materials and the same fabrication process were used, it is noteworthy that all of the synthesized PIs show lower R-DC value. VHR is also an important performance parameter in active matrix LCDs. It is defined as the ratio of transient voltage to applied voltage in pulse driving. A high value of VHR is required for high-quality images. In this work, VHR measurements were carried out with adjusting a peak-to-peak voltage to 10 V and a bias voltage to 5 V. VHRs of PI-1, PI-2, PI-3 and SE-6514 cells were measured to be 97.7,

97.9, 97.8 and 98.6%, respectively. All of the PI cells show slightly lower VHR values than the commercial SE-6514. By the same instrument, polar anchoring energies were also estimated to be 6.87×10^{-4} , 6.06×10^{-4} , 5.45×10^{-4} and 7.04×10^{-4} J/m² for PI-1, PI-2, PI-3 and SE-6514, respectively (Table 3). These anchoring energies are comparable to those found for the rubbing type PIs currently used in the LCD industry. With decent electro-optic properties such as R-DC, VHR and polar anchoring energy values, the synthesized PIs are considered to be promising as an alignment layer, providing a perpendicular alignment of LC director to the rubbing direction.

In Fig. 6, we demonstrated a possible application of these alignment layers for the simple preparation of FPR. Firstly, PI-1 was spin coated on a glass substrate and dried. On this layer, a strip pattern of conventional PI alignment layer (SE-6514) was bar coated, which was thermal cured subsequently. After one conventional rubbing process was applied in the direction parallel to the strip pattern, reactive mesogen (RMS03-013C, Merck) was spin coated and subsequently UV cured. As shown in Fig. 6 (right), POM images with $\lambda/4$ film clearly revealed reactive mesogens on either side of alignment layer aligned perpendicular to each other.

Conclusions

Three polyimides containing biphenyl ester units in the side chain were synthesized for application as a liquid crystal alignment layer. Polymer structures were confirmed by FT-IR and ¹H NMR. All of the rubbed polymer films uniformly aligned LC molecules with the director perpendicular to the rubbing direction. Antiparallel cells fabricated from the rubbed polymer films exhibited high VHR and low R-DC values. The uniform and thermally stable films with the alignment perpendicular to the rubbing direction presented a great potential as an alignment layer in

Table 3 Electro-optical properties of ECB cells fabricated from polyimides

Sample	R-DC (V)	VHR (%)	Polar anchoring energy ($\times 10^{-4}$ J/m ²)
PI-1	0.045	97.7	6.87
PI-2	0.022	97.9	6.06
PI-3	0.012	97.8	5.45
SE-6514	0.204	98.6	7.04

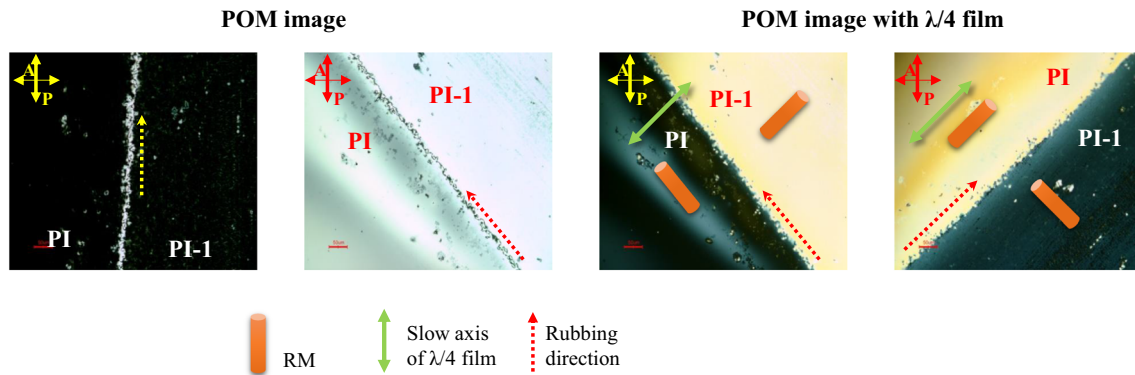


Figure 6 POM images (left) and POM images with $\lambda/4$ film (right) of fabricated FPR.

fabricating advanced LC devices or flexible optical films.

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