

Preparation and Characterization of Novel Polyimide with Chiral Side Chain for Twist Nematic Liquid Crystal Display

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ABSTRACT: The synthesis of novel polyimide (PI) films containing chirals in side chain was investigated for utilizing in twist nematic (TN) liquid crystal display (LCD). The polyimide with amine side groups (PI4 a.m.) was prepared by two steps copolymerization of 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA), 4,4'-oxydianiline (ODA), and 3,3'-diaminobezidine (4 a.m.) in *N*-methyl-2-pyrrolidinone (NMP). In the first step, the oligomer of 6FDA and ODA with mole ratio 4 : 3 was synthesized. In the second step, the oligomer was reacted with 4 a.m. by gradually dropping the oligomer into 4 a.m. solution with the mole ratio 4 : 5. By reacting chiral compounds, mandelic acid, menthyl chloroformate, and menthyl glyoxylate hydrate using condensation reaction with amine groups along polyimide molecules, the novel polyimides can be

synthesized. Their chemical structures were confirmed by fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$). The coated glass slides pairs were coated with PI4 a.m. and with each Polyimide/chiral. The liquid crystals (LCs) were inserted between two coated glass slides at above the nematic temperature under the polarized light microscope to observe the alignment of LCs. The results showed the alignment of LCs in some certain direction under Polyimide/chiral pair, regardless of the type of the chiral molecule. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3265–3277, 2011

Key words: chiral; polyimide; liquid crystal; alignment; twist nematic

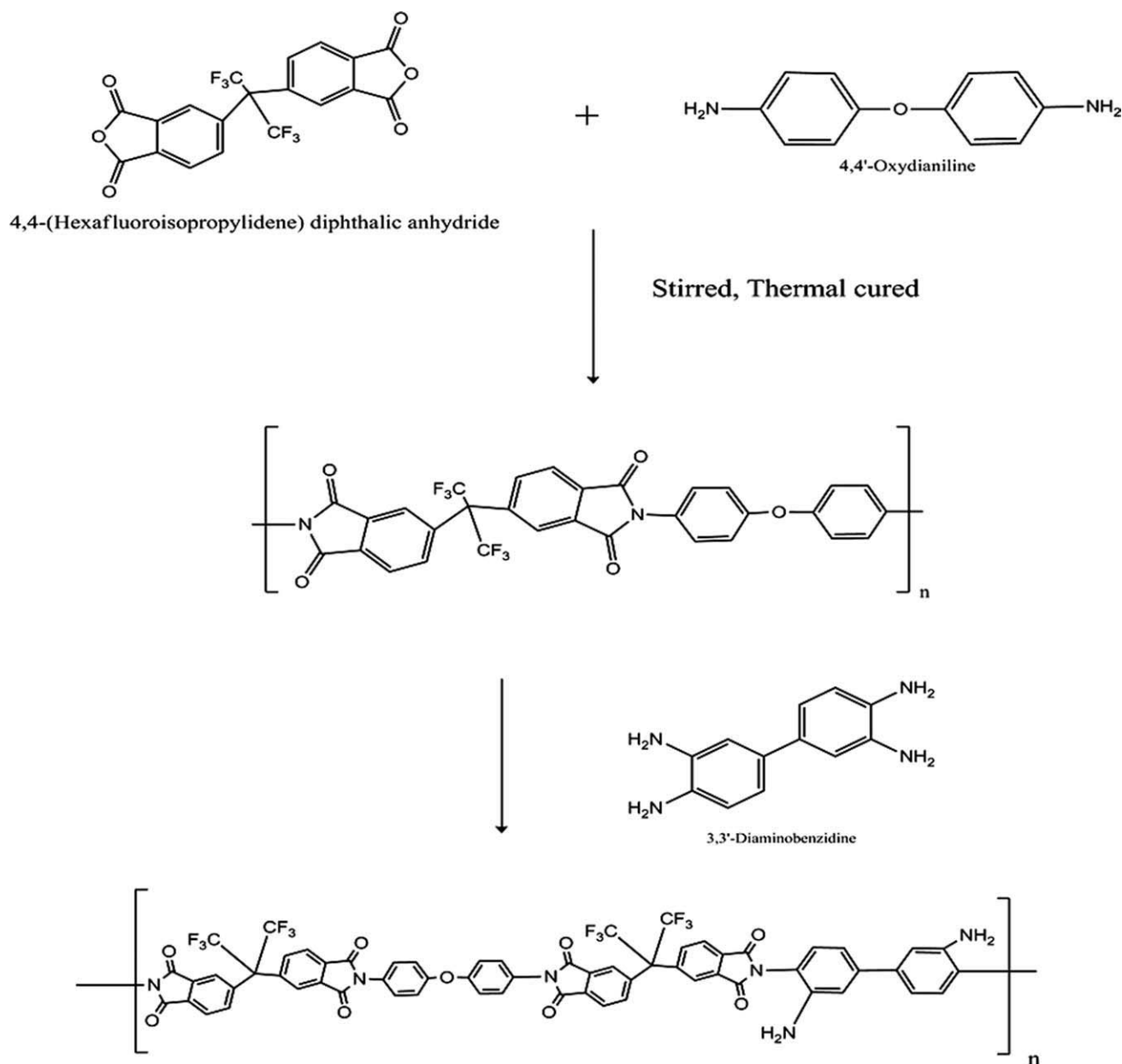
INTRODUCTION

Liquid crystal displays (LCDs) have become one of the fastest growing information display devices in recent years. They are widely used in notebook computers, PC monitors, TVs, and other devices. In conventional LCDs for notebook computers and desktop monitors, twisted-nematic (TN) LCDs are widely used. The uniform alignment of liquid crystal (LC) is one of the essential processes for LCD fabrication.¹ The most conventional process for LC alignment employs a mechanically rubbed polyimide (PI) surface. LCs were aligned due to the induced anisotropy on the substrate surface. This surface is usually a polymer such as polyimide, coated on a glass substrate.^{2–7} Because of excellent mechanical performance, high-temperature durability, low moisture absorption, good radiation, and corrosion resistance

as well as good adhesion to inorganic materials, polyimides (PIs) were widely used as liquid crystal (LC) alignment layer in LCDs. The rubbing alignment method has suitable characteristics such as uniform alignment and a high pretilt angle. Although the rubbing technique has the advantages of simplicity and a short processing time, it has serious drawbacks associated with the mechanical rubbing, such as the creation of dust particles, generation of electrostatic charge, and nonuniformity of the surface treatment over a large-area substrate. Thus, the development of mechanical-contact-free alignment methods that can replace the conventional rubbing technique is strongly desired.^{4–6} A number of alternative alignment techniques have been reported.^{7–9} Generally rubbed PI films are used in LCDs to induce tilted homogeneous alignment of LC molecules.¹⁰ This average angle formed by the axis of the LC director and the PI surface is called a pretilt angle (Θ_p), which affects the electro-optic properties of LCD devices. If PI with a low pretilt angle ($\Theta_p \leq 1^\circ$) is used in 90° TN-LCDs, the LC alignment is known to inevitably segregate into two twisted domains with reverse twisting, i.e., right-twisted and left-twisted nematic domains, and the boundary of which emerges as twist disclination lines. Twisted domains can be regarded as a kind of chiral domains

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Scheme 1 The synthesis procedure of polyimides.

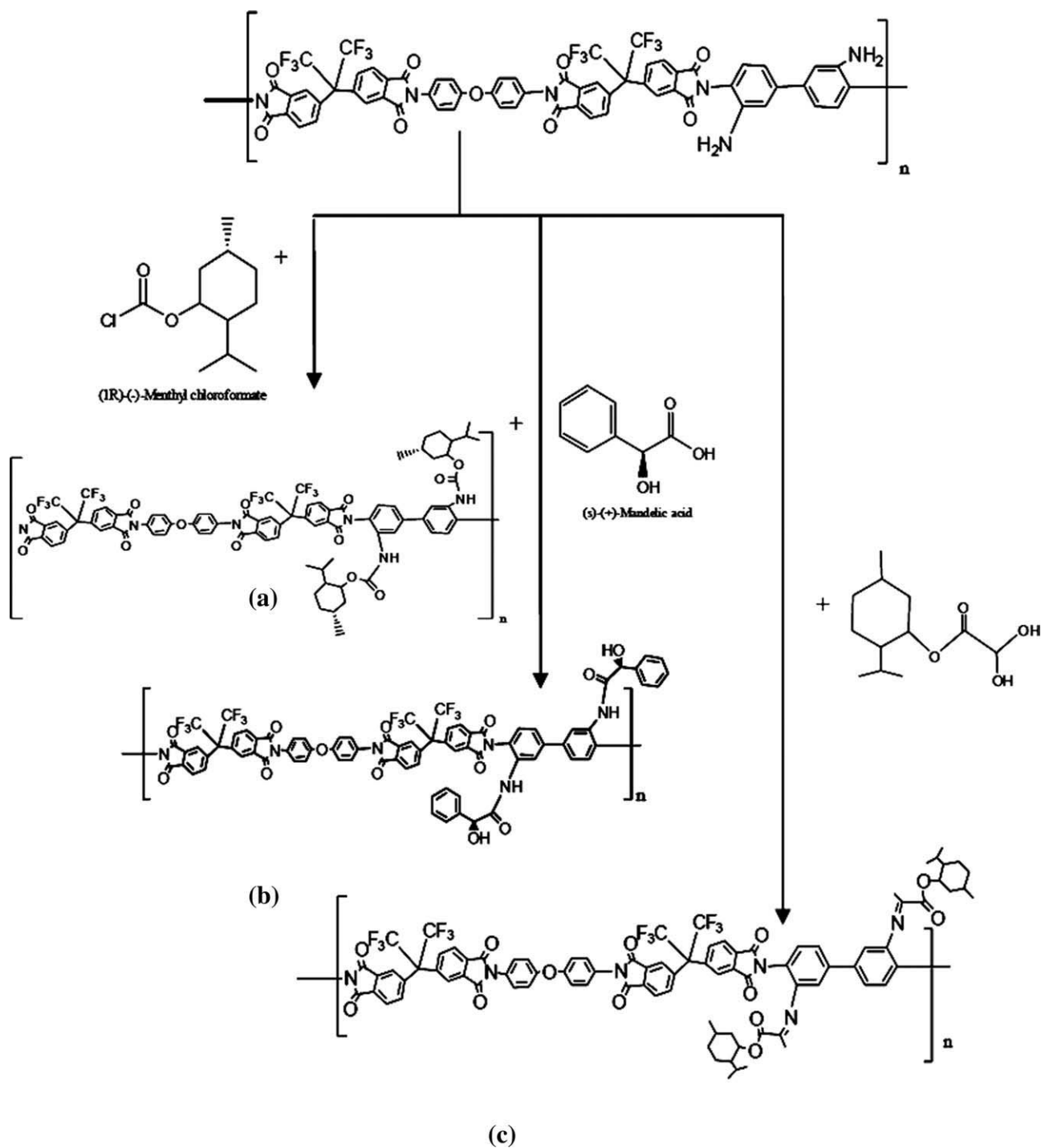
in which the molecular arrangement is twisted by extrinsic TN alignment treatment.^{11,12} To avoid this degeneracy and the twist disclinations and to realize defect-free LCD panels, the introduction of the pretilt angle of several degrees ($\Theta_p \geq 5^\circ$) and/or chiral dopant is required.¹³

Therefore, in this research, we report the synthesis of novel chiral polyimide films as shown in Scheme 1 and 2. Also, we studied LC alignment on chiral polyimide surface. We fabricated tested cell on three different surfaces: (1) slide coated with PI4AM/mandelic acid amide, (2) PI4AM/menthyl chloroformate amide, and (3) PI4AM/menthyl glyoxylate hydrate and evaluated the effect of the chiral PI films on LC alignment.

EXPERIMENTAL

Materials

(S)-(+)-mandelic acid, (1R)-(-)-menthyl chloroformate, and (1R)-(-)-menthyl glyoxylate hydrate were purchased from Alfa Aesar. *N*-hydroxysuccinic anhydride and dicyclohexylcarbodiimide, used as condensing agents, were purchased from Aldrich. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA), 4,4'-Oxydianiline (ODA), and 3,3'-diaminobenzidine (4 a.m.) were purchased from Aldrich. *N*-methyl-2-pyrrolidinone (NMP) purchased from Merck. All other chemicals were purchased from Aldrich and used as received.



Scheme 2 The possible chemical structures of (a) PI4 a.m./menthyl chloroformate amide (b) PI4 a.m./mandelic acid amide (c) PI4 a.m./menthyl glyoxylate hydrate.

Preparation of polyimide films

Polyimide oligomer was synthesized by two steps polymerization of 6FDA, ODA with 3 equiv. mol diamine and 4 equiv. mol dianhydride at 15% solid content in NMP. Then the polyimide oligomer film was redissolved in NMP and dropped into the solution of 3,3'-diaminobenzidine (4AM) by the mole

ratio 4 : 5 to obtain polyimide containing amine functional groups (PI4AM).

The processes can be explained as follow: The diamine (4,4'-ODA; 0.676 g, 0.00337 mol) was completely dissolved in NMP (17.84 mL) with stirring to obtain the ODA solution (15% w/v). After stirring, the dianhydride (6 FDA; 2 g, 0.0045 mol) was added into ODA solution. The mixture was

stirred continuously for 1 h to form the poly(amic acid) (PAA) solution. The PAA solution was then cast onto clean, dry plate glass, and subjected to thermal imidization for 1 h each at 100, 150, and 250°C to produce PI oligomer films.

The PI4AM film was prepared by the methods as follows: The core (PI oligomer film; 1 g, 0.000444 mol) was dissolved in NMP (7.459 mL) with stirring. The core solution was added by drop wise into the 4 a.m. (0.119 g, 0.000555 mol) solution. The mixture was stirred continuously for 1 h to form the PAA solution. The PAA solution was then cast onto clean, dry plate glass and subjected to thermal imidization for 1 h each at 100, 150, and 250°C to produce PI4AM films which containing amine functional groups side chain. The synthesis procedure of polyimide is shown in Scheme 1.

Reaction of amine group in polyimide with mandelic acid

PI4AM film (1 g, $-\text{NH}_2$ 0.267 mmol) was dissolved in NMP (30 mL) at 150°C for 24 h. Mandelic acid (0.184 g, 0.534 mmol), *N*-hydroxysuccinic anhydride (0.319 g, 1.36 mmol), and dicyclohexylcarbodiimide (0.566 g, 1.36 mmol) were added to a 100-mL three-necked flask with stirrer bar. The mixture was stirred at room temperature for 24 h. The solvent was removed under the reduced pressure. The residue was dissolved in ethyl acetate and washed successively with 5% sodium carbonate, water, 1N HCL, water, and brine, respectively, and dried over MgSO_4 . The solution was then filtered using glass wool and celite to remove unreacted products, and the remains were casted on glass substrate. The cast films were thermally treated at 5°C/min heated rate and the holding time was 0.5 h for 200 and 300°C each to remove reaction water in a temperature controlled oven. After the thermal treatment, the films were removed from the glass substrate by immersing into water and dried at 100°C for 24 h. PI4AM films containing amine functional groups were obtained as transparent, flexible, dark brown to yellow colored. The obtained PI4AM/mandelic acid films were redissolved in NMP at 120°C for 3 h. The solution was spin coat on slide and cured at 180°C for 1 h.

Reaction of amine group in polyimide with menthyl chloroformate

PI4AM film (1 g, $-\text{NH}_2$ 0.267 mmol) was dissolved in NMP (30 mL) at 150°C for 24 h. The PI4AM solution was added to a 100-mL three-necked flask with stirrer bar. Menthyl chloroformate (0.534 mmol, 0.24 mL) was then added to the flask, followed by triethylamine (0.267 mmol, 0.08 mL). The mixture was stirred under Ar at room temperature for 24 h. The

TABLE I
Viscosities and molecular weights of the PI and PI4AM

Sample	Intrinsic viscosities ^a	Measured M_v	Calculated M_v
PI	0.987	49,483	52,395
PI4AM	1.443	78,939	89,232

^a Measured at 40°C in the solvent NMP

solution was then filtered using glass wool and celite to remove unreacted products and the remains were then cast onto clean, dry plate glass, and subjected to thermal imidization for 1 h each at 100, 150, and 250°C. After the thermal treatment, the films were removed from the glass substrate by immersing into water and dried at 100°C for 24 h. The obtained PI4AM/menthyl chloroformate films were redissolved in NMP at 120°C for 3 h. The solution was spin coat on slide and cured at 180°C for 1 h.

Reaction of amine group in polyimide with menthyl glyoxylate hydrate

PI4 a.m. film (1 g, $-\text{NH}_2$ 0.267 mmol) was dissolved in NMP (30 mL) at 150°C for 24 h. The PI4AM solution was added to a 100-mL three-necked flask with stirrer bar. Menthyl glyoxylate hydrate (0.125 g, 0.534 mmol), was then added to the flask. The solution was stirred at 40–50°C for 1 day. The solution was then filtered using glass wool and celite to remove unreacted products and the remains were then cast onto clean, dry plate glass, and subjected to thermal imidization for 1 h each at 100, 150, and 250°C. After the thermal treatment, the films were removed from the glass substrate by immersing into water and dried at 100°C for 24 h. The obtained PI4AM/menthyl glyoxylate hydrate films were redissolved in NMP at 120°C for 3 h. The solution was then spin coat on slide and cured at 180°C for 1 h.

Analytical methods

Fourier transform infrared

Infrared survey spectra were recorded with Nicolet 6700 Fourier transform infrared (FTIR) spectrometer. The scanning ranged from 400 to 4000 cm^{-1} with scanning 64 times.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) thermograms were performed using a SDT Analyzer Model Q600 from TA Instruments, USA. The samples of 10–20 mg and a temperature range of 50–600°C at a heating rate of 10°C/min were applied. The carrier gas was N_2 UHP.

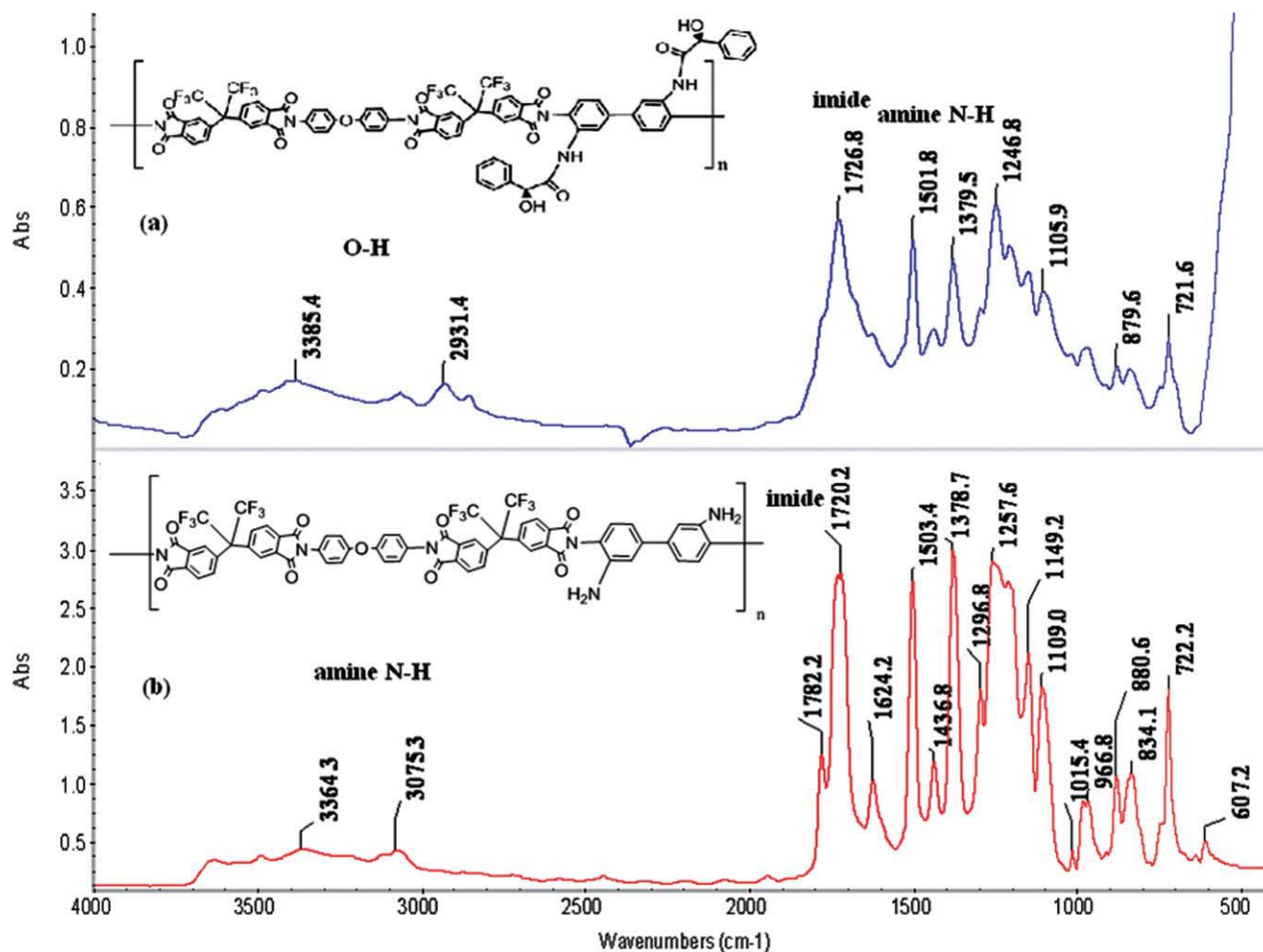


Figure 1 FTIR spectra of (a) PI4 a.m./mandelic acid amide (b) PI4 a.m. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Nuclear Magnetic Resonance Spectroscopy

The $^1\text{H-NMR}$ spectra were recorded with Bruker 400 UltraShield $^1\text{H-NMR}$ spectrometer. The scanning numbers are 128 times. The samples were dissolved in DMSO *d*₆ and ran under high temperature at 120°C.

Optical microscope

The textures of polyimide and polyimide/chiral films were characterized using optical microscope. The sample films were investigated range from 0.67X–4.5X and zoom ratio at 6.7 : 1.

RESULTS AND DISCUSSION

Polyimides oligomers were synthesized by two steps polymerization of 6FDA, ODA by mole ratio of 4 : 3. The unbalance of molar ratio was used to obtain low molecular weight polyimide with degree of polymerization of 7 for easier dissolution than high molecular

weight polyimide. Moreover, the end group will be the anhydride because the amount of dianhydride was exceeded the amount of diamine. This anhydride functionality will be further reacted with 4AM in the next step. The Polyimide oligomer was heated and imidized as the film form, so the reverse reaction was prohibited. In the second step, then the polyimide oligomer film was redissolved in NMP and gradually dropped into the solution of 3,3'-diaminobenzidine (4AM) to obtain polyimide containing amine functional groups. The 4AM as the majority will react in both end of oligomer before bonding into large molecule. Because the mole ratio of 4AM to oligomer is 5 : 4 with degree of polymerization of 9, the functional amine is excess and left in the resulted polyimide (PI4AM). The 4AM has four arms of amine, but approximately less than two arms were reacted with anhydride of the polyimide oligomer, so there are statistically more than two groups of amine left in the molecules at the junction of 4AM.

The molecular weights of the PI and PI4AM can be estimated by the solution viscosities of these

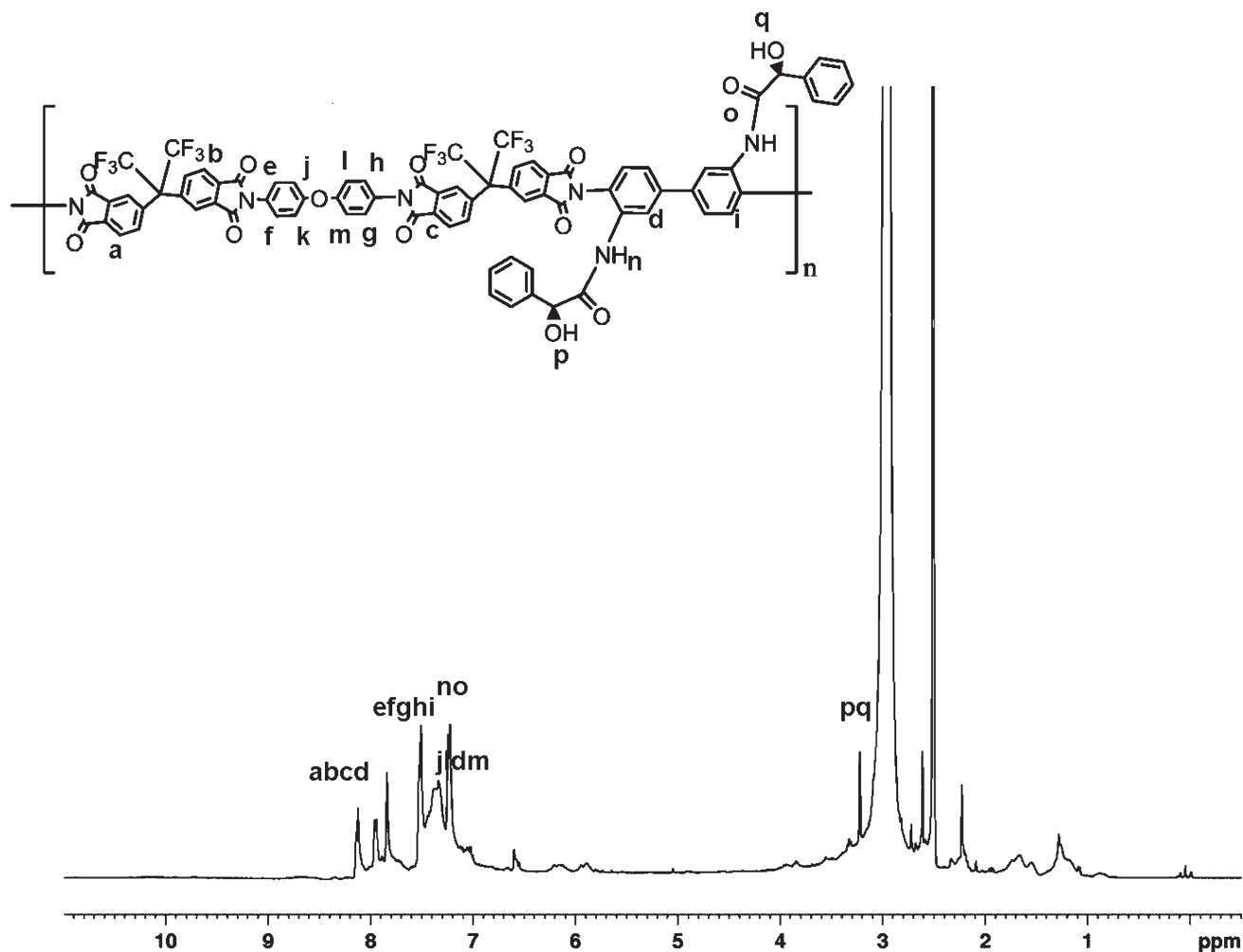


Figure 2 ^1H -NMR spectra of PI4 a.m./mandelic acid amide.

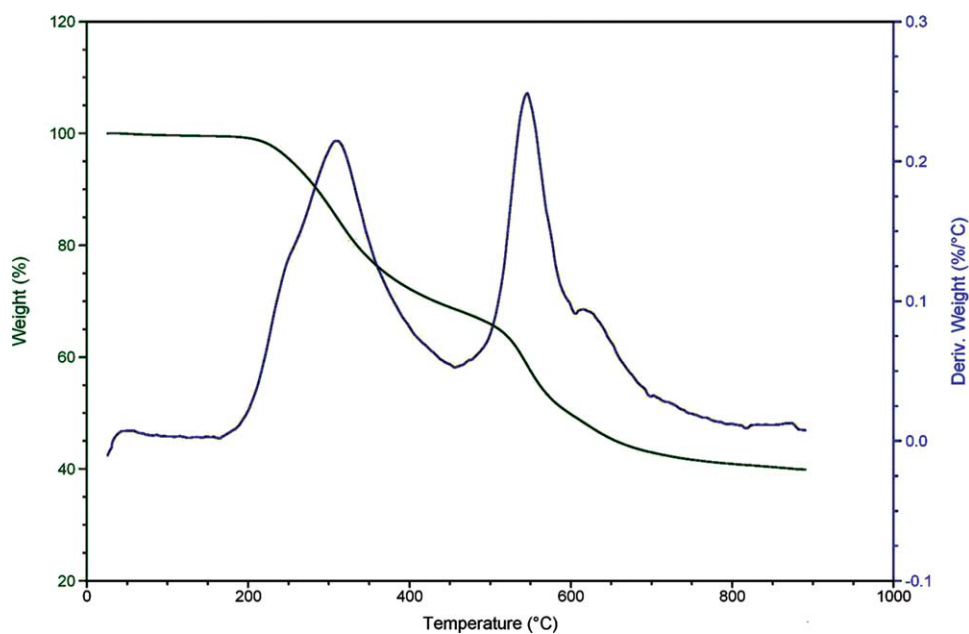


Figure 3 TGA result of PI4 a.m./mandelic acid amide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

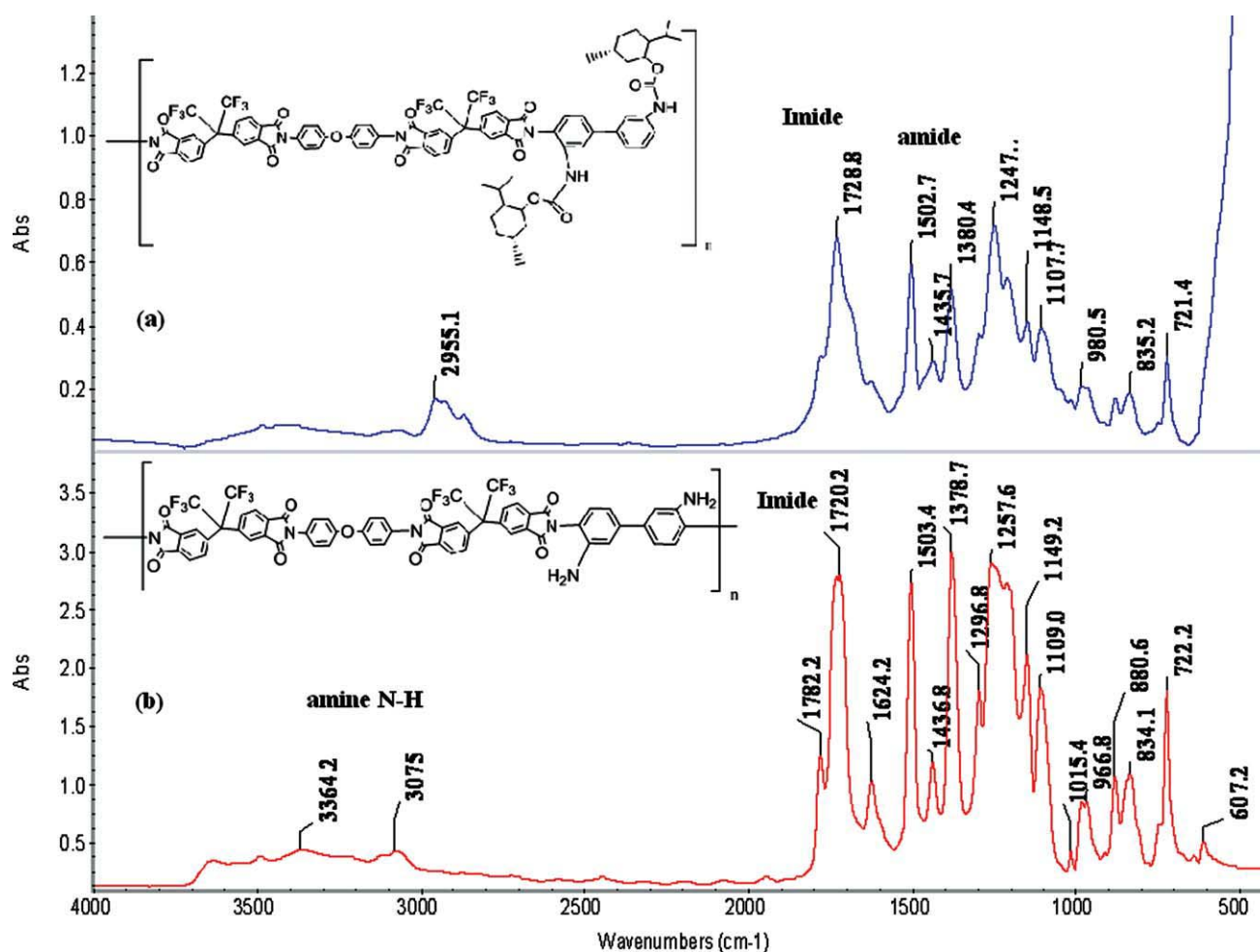


Figure 4 FTIR spectra of (a) PI4 a.m./menthylchloroformate (b) PI4 a.m. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers, measured in only the solvent NMP at 40°C. The values of the intrinsic viscosity and viscosity-average molecular weight (M_v) of the PI and PI4AM as calculated from standard Polystyrene viscosity were summarized in Table I. The molecular weights of the PI4AM were larger than PI because the PI4AM comprised about four groups of PI in the molecule. Moreover, in comparison with the stoichiometrically calculated molecular weight, the calculated molecular weights were slightly higher than the solution measured values, but still have the same trend.

The chiral compounds, mandelic acid and menthyl chloroformate, are connected to the main chain polyimide as side-chains by condensation reaction of excess amine groups in the main chain polyimide and chiral compounds. The chemical structures were confirmed by FTIR. Structural identification was performed by $^1\text{H-NMR}$. The thermal properties were shown by TGA and the alignment experiment with optical microscope showed the benefit of the novel polyimide. The details of the results can be explained as followed.

Reaction of amine group in polyimide with mandelic acid

Polyimides were synthesized by two steps polymerization of 6FDA and ODA. Then the polyimide film was reacted with 4AM to obtain polyimide containing amine functional groups known as PI4AM. Afterwards, PI4AM/mandelic acid amide was successfully synthesized by condensation reaction.

Figure 1 shows the FTIR spectra of PI4AM/mandelic acid amide and PI4AM. Functional groups after condensation of PI4AM to form PI4AM/mandelic acid amide were confirmed at the peak of 1501 and 1726 cm^{-1} resulting from bending vibration of amide $-\text{NH}$ groups and symmetric of imide ring $\text{C}=\text{O}$ respectively. The imide and amide bond confirmed the complete imidization and condensation. The amine $-\text{NH}_2$ broad peaks at 2500–3500 cm^{-1} were disappeared after condensation of PI4AM to form amide with mandelic acid, while the bands of $-\text{OH}$ group were instate presented.

Figure 2 shows $^1\text{H-NMR}$ spectrum of PI4AM/mandelic acid amide. The chemical structures were

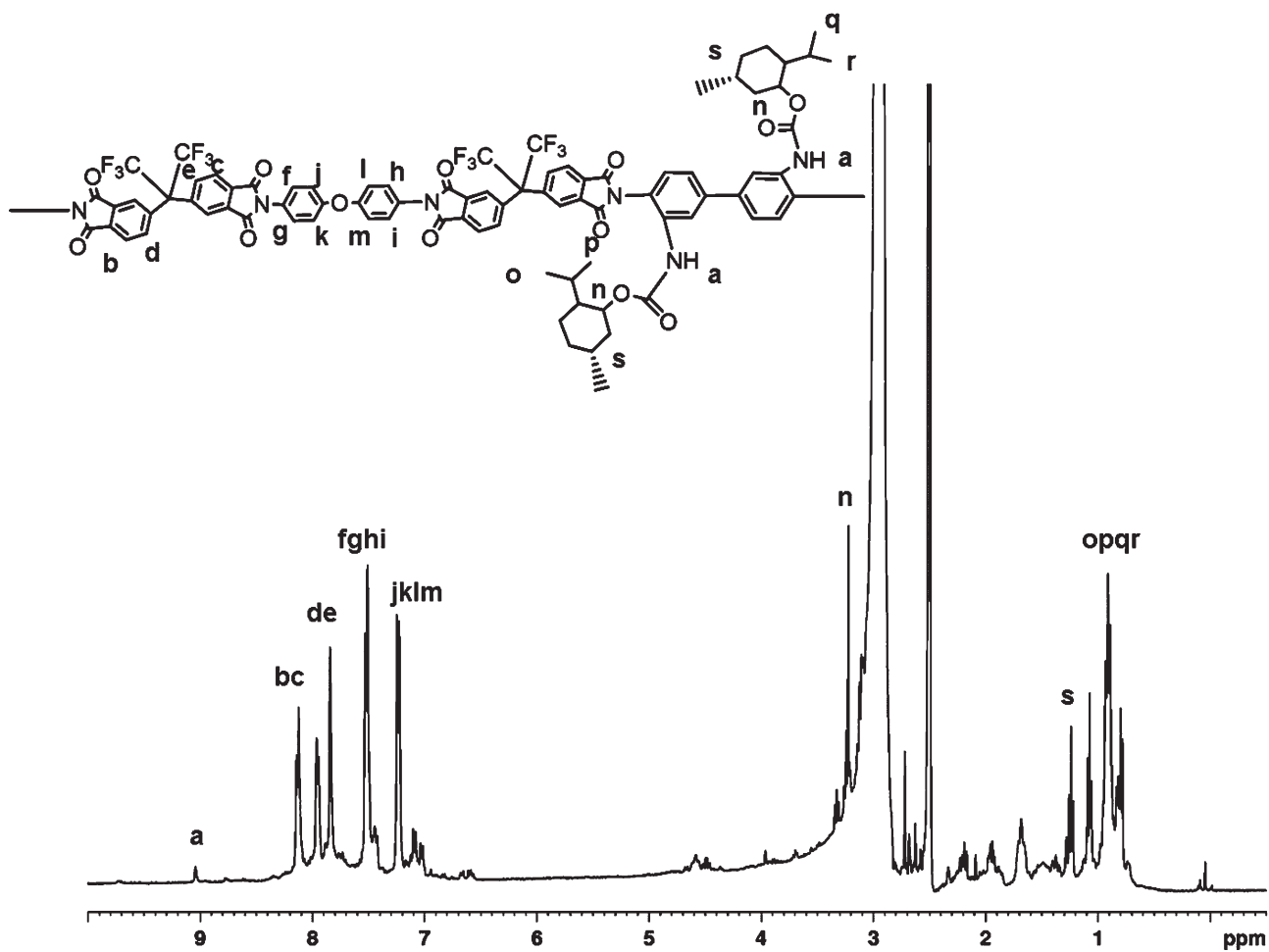


Figure 5 $^1\text{H-NMR}$ spectra of PI4 a.m./methyl chloroformate.

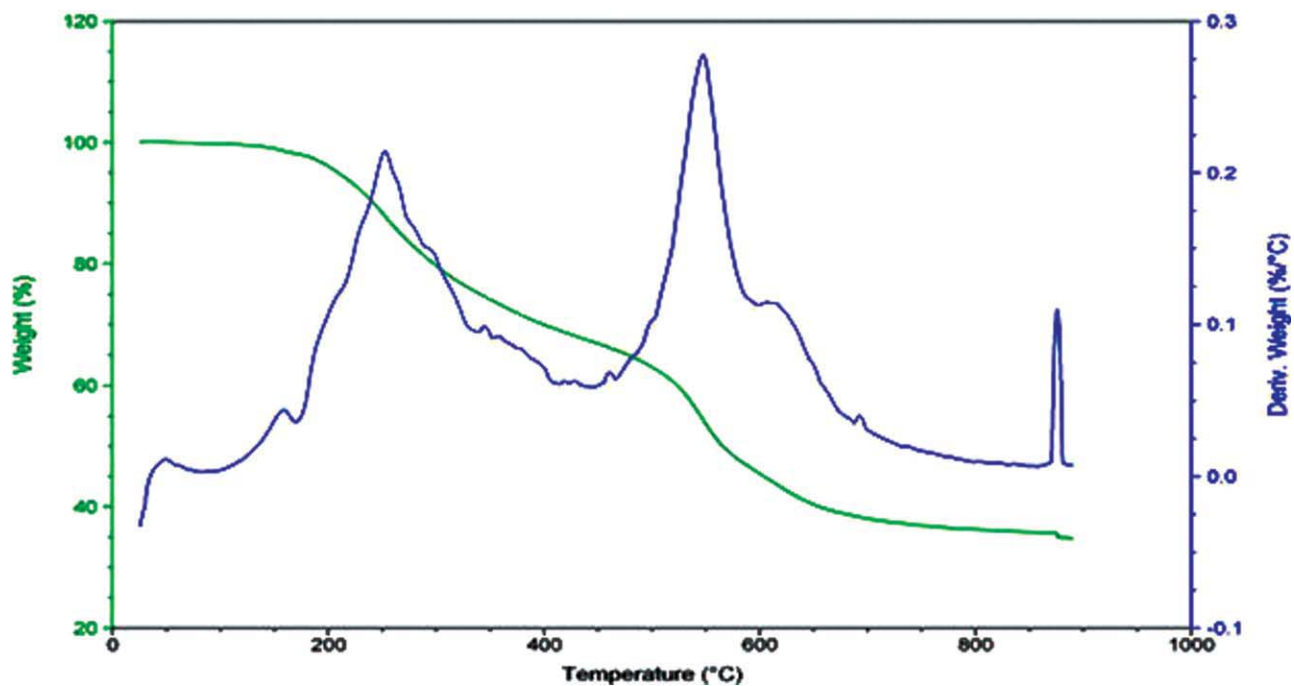


Figure 6 TGA result of PI4 a.m./methyl chloroformate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

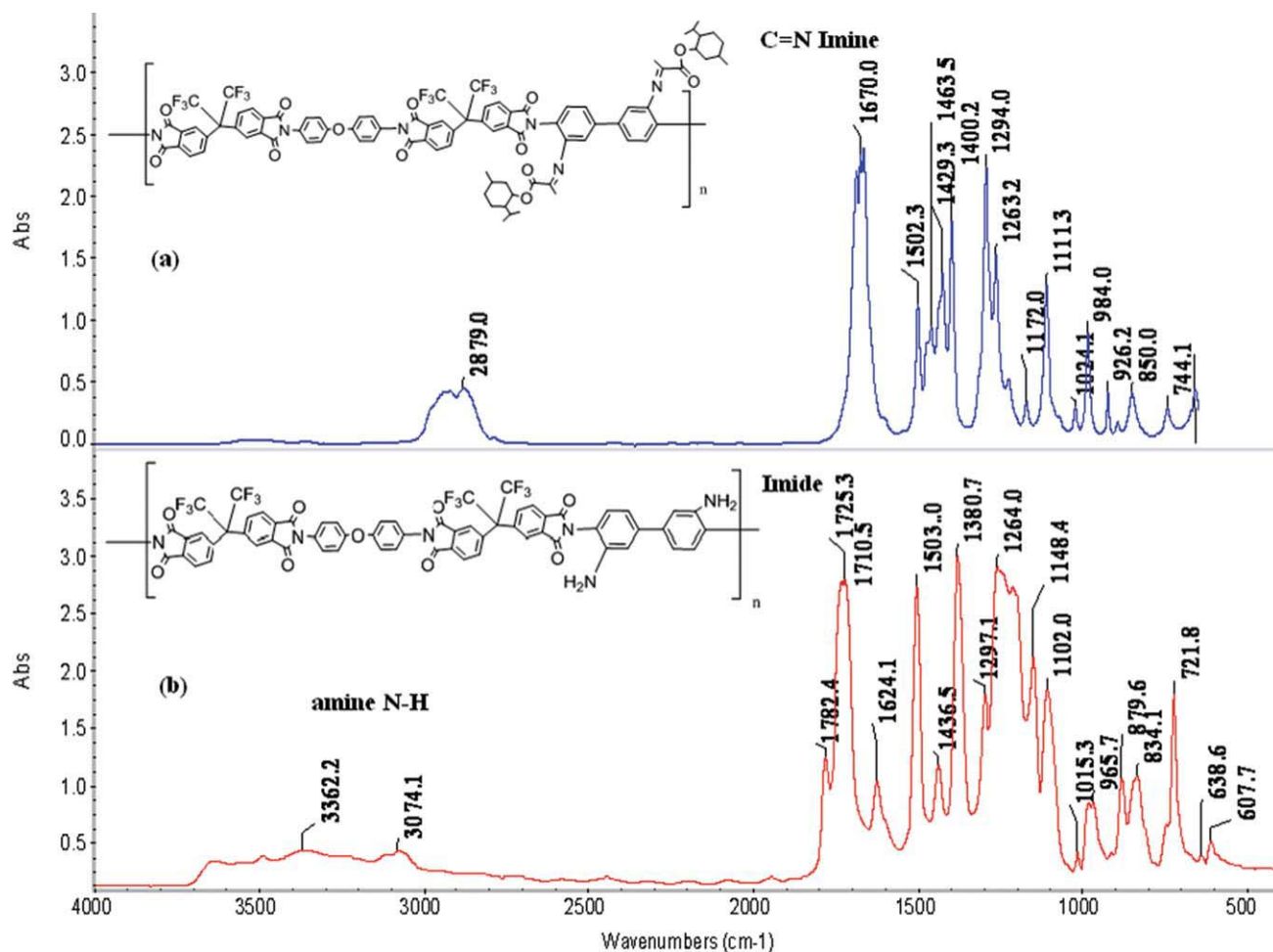


Figure 7 FTIR spectra of (a) PI4 a.m./menthyl glyoxylate hydrate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

confirmed by $^1\text{H-NMR}$ analysis. The peak appearing at 7.24 ppm confirmed the presence of NH proton resulting from attachment directly of proton to nitrogen to form amide. This amide confirmed the incorporation of PI4AM and menthyl chloroformate. The peaks presented at 6.99, 7.25, 7.83, and 8.02 ppm resulting from phenyl rings-H proton and the peak appearing at 3.65 ppm resulted from O-H proton.

The thermal properties of PI4AM/mandelic acid amide were investigated by TGA under nitrogen atmosphere at $10^\circ\text{C}/\text{min}$ heating rate. In Figure 3, the initial decomposition temperature ($T_d5\%$) of PI4AM/menthyl chloroformate is 254°C . The initial decomposition temperature ($T_d10\%$) at 280°C and char yield is 40.90%.

Reaction of amine group in polyimide with menthyl chloroformate

Polyimides were synthesized by two steps polymerization of 6FDA and ODA. Then the polyimide film was reacted with 4AM to obtain polyimide containing amine functional groups known as PI4AM.

Afterwards, PI4AM/menthyl chloroformate was successfully synthesized by condensation reaction.

Figure 4 shows the FTIR spectra of PI4AM/menthyl chloroformate and PI4AM. Functional groups after condensation of PI4AM to form PI4AM/menthyl chloroformate were confirmed at the peaks of 1502, 1720, and 1782 cm^{-1} resulting from bending vibration of amide $-\text{NH}$ groups, asymmetric and symmetric of imide ring $\text{C}=\text{O}$, respectively. The imide bond confirmed the complete imidization. The amine $-\text{NH}_2$ broad peaks at $2500\text{--}3500\text{ cm}^{-1}$ are disappeared after condensation of PI4AM to form amide with menthyl chloroformate. This disappearance confirmed the condensation reaction.

Figure 5 shows $^1\text{H-NMR}$ spectrum of PI4AM/menthyl chloroformate. The chemical structures were confirmed by $^1\text{H-NMR}$ analysis. The peaks appearing at 9.15 ppm confirmed the presence of NH proton resulting from attachment directly of proton to nitrogen to form amide. This amide confirmed the incorporation of PI4AM and menthyl chloroformate. The sharp peaks presented at 6.99, 7.25, 7.83, and 8.02 ppm resulting from phenyl rings-H proton and

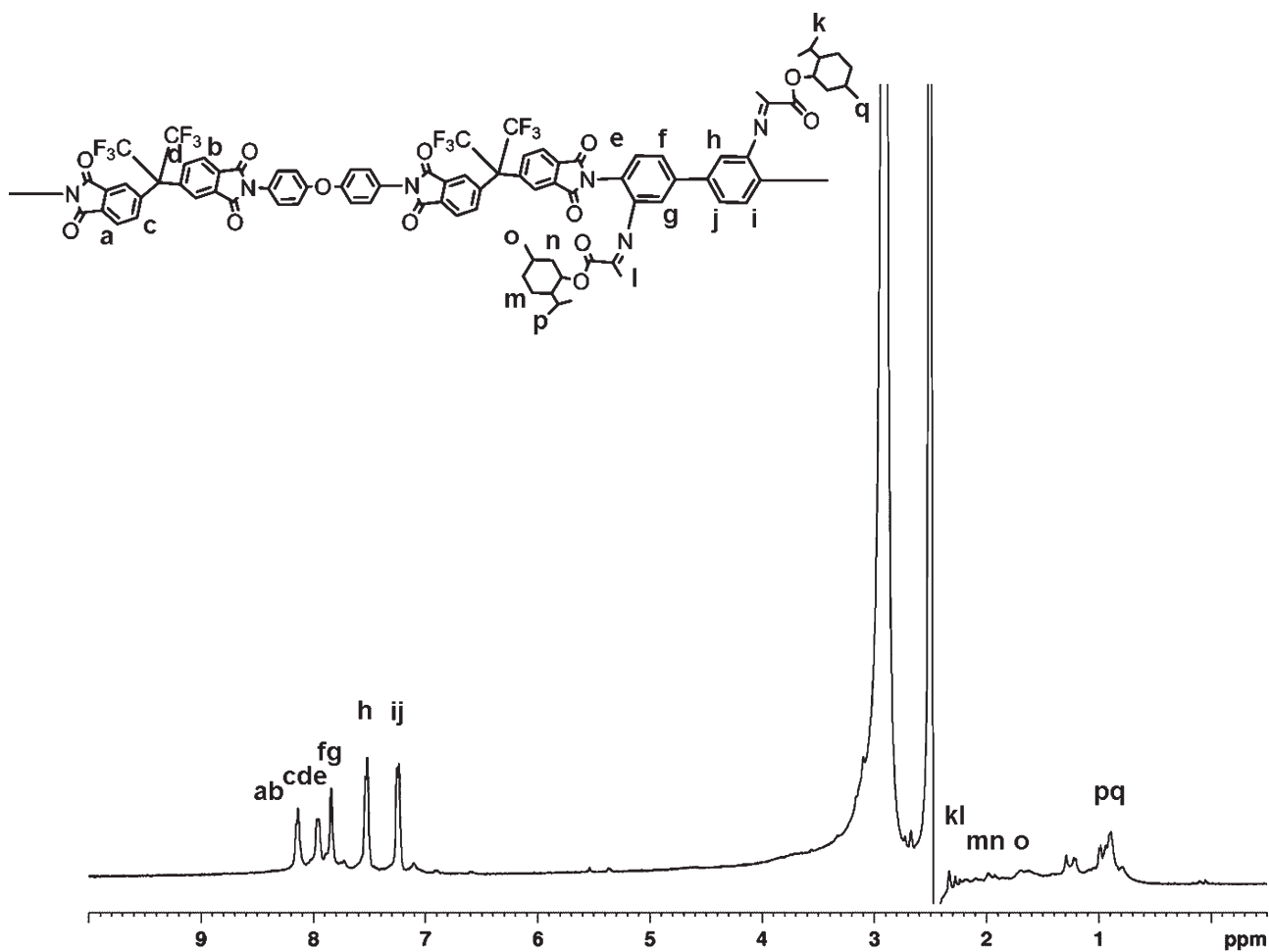


Figure 8 ¹H-NMR spectra of PI4 a.m./menthyl glyoxylate hydrate.

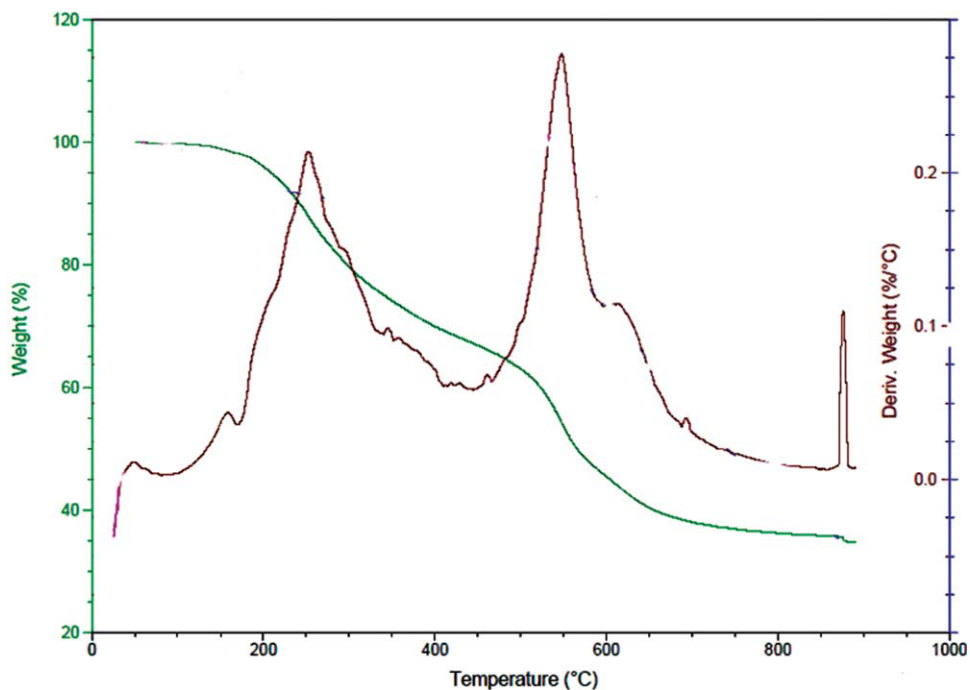


Figure 9 TGA result of PI4 a.m./menthyl glyoxylate hydrate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

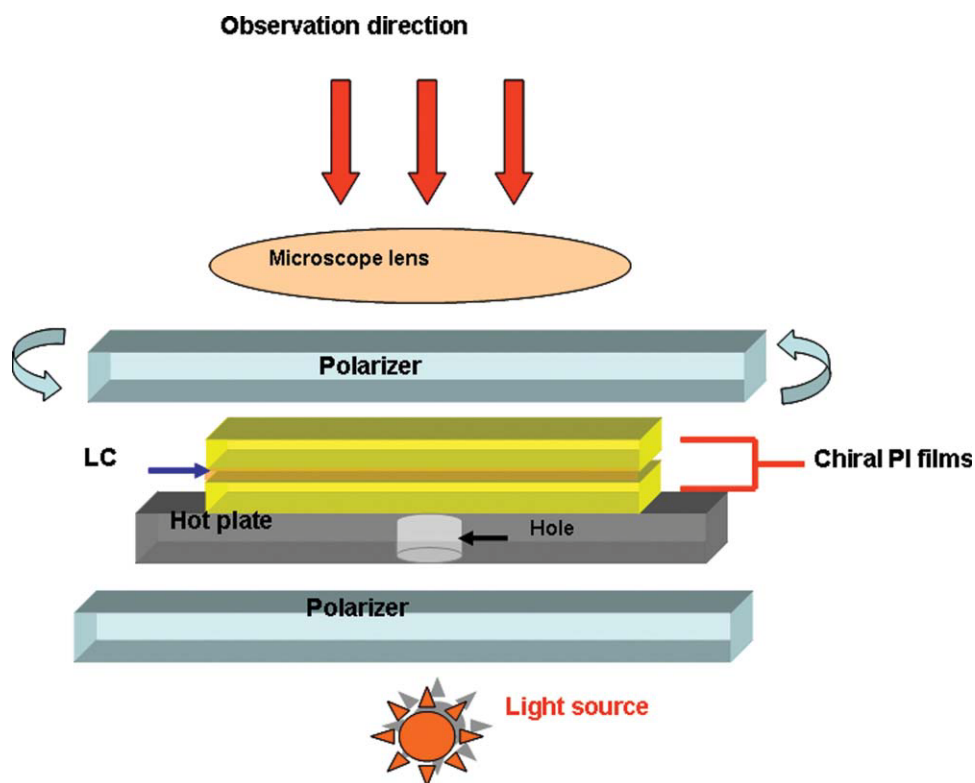


Figure 10 A schematic of experimental set up for polarizing optical microphotographs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the peak appearing at 0.91 and 0.96 ppm resulted from C—H proton.

The thermal properties of PI4AM/menthyl chloroformate were investigated by TGA under nitrogen atmosphere at 10°C/min heating rate. In Figure 6, the initial decomposition temperature ($T_d5\%$) of PI4AM/menthyl chloroformate is 209°C. The initial decomposition temperature ($T_d10\%$) at 242°C and char yield is 36.27%.

Reaction of amine group in polyimide with menthyl glyoxylate hydrate

Polyimides were synthesized by two steps polymerization of 6FDA and ODA. Then the polyimide film was reacted with 4AM to obtain polyimide containing amine functional groups known as PI4AM. Afterwards, PI4AM/menthyl glyoxylate hydrate was successfully synthesized.

The IR spectra of the imines exhibit an intense absorption at 1670 cm^{-1} that corresponds to C=N stretching and at 2879 cm^{-1} that corresponds to C—H stretching. The amine $-\text{NH}_2$ broad peaks at 2500–3500 cm^{-1} are disappeared after condensation of PI4AM to form imine with menthyl glyoxylate hydrate as shown in Figure 7. This imine confirmed the incorporation of PI4AM and menthyl glyoxylate hydrate.

The chemical structures were confirmed by ^1H -NMR analysis (see Fig. 8). The sharp peaks presented at 7.29, 7.33, 7.60, 7.70, 7.77, 7.87, 7.83, and 8.20 ppm resulting from phenyl rings-H proton. The signals at 1.68, 1.76, and 1.82 in NMR spectra belong to protons of cyclohexane rings and the peak appearing at 0.95, 0.98, 1.76, and 1.82 ppm resulted from C—H proton. The peak appearing at 2.31 ppm resulting from C-H proton which near C=N. Because of menthyl glyoxylate hydrate, reactant was completely washed away before ^1H -NMR analysis, therefore, this peak proved that the incorporation of PI4AM and menthyl glyoxylate hydrate that remained in chiral polyimide molecules.

Figure 9 shows the thermal properties of PI4AM/menthyl glyoxylate hydrate were investigated by TGA under nitrogen atmosphere at 10°C/min heating rate. The initial decomposition temperature ($T_d5\%$) of PI4AM/menthyl glyoxylate hydrate is 228°C. The initial decomposition temperature ($T_d10\%$) is at 250°C. The char yield at 800°C is 33%.

The polarizing optical microphotographs of the cells consisting of chiral PI films

To observe the effects of alignment of liquid crystal molecules under the polarizing light, four different surfaces cells were made from PI and chiral PI films. Four pairs of two quartz slides spin coated with

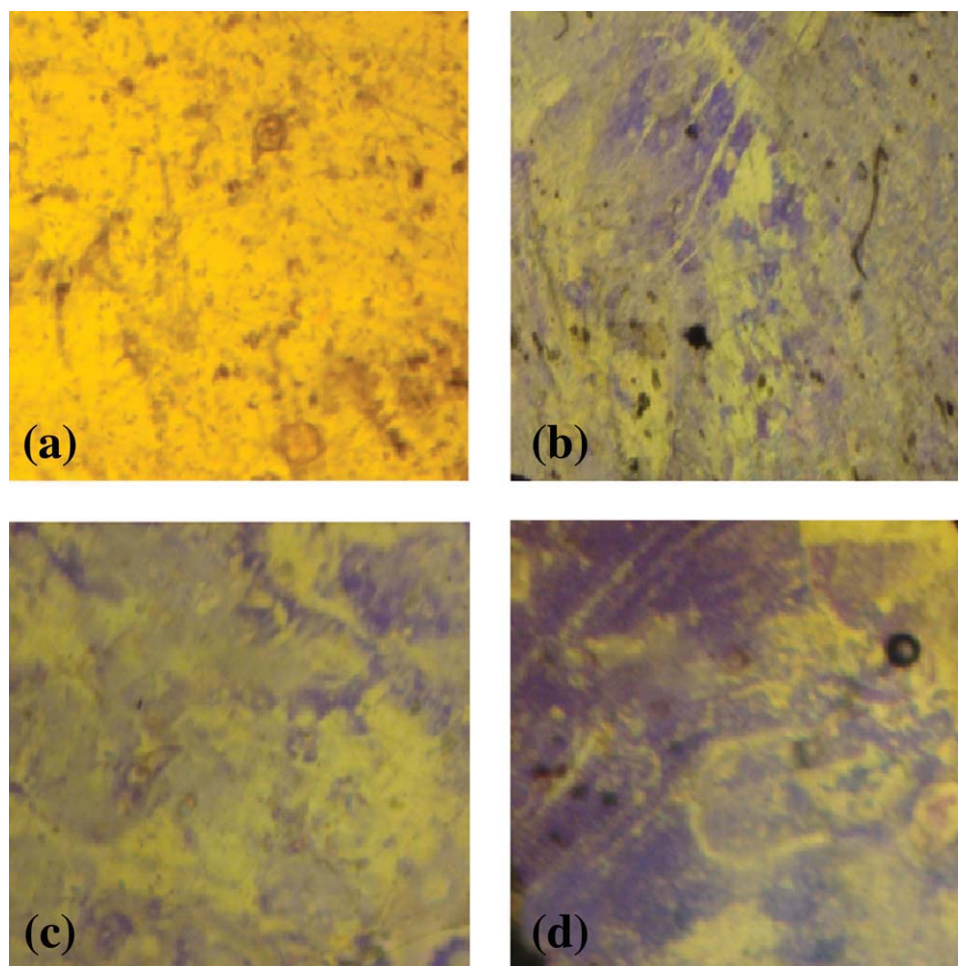


Figure 11 Polarizing optical microphotographs of PI and chiral PI sandwiches were (a) slide coated with PI4 a.m., (b) slide coated with PI4 a.m./mandelic acid amide, (c) PI4 a.m./menthyl chloroformate amide, and (d) PI4 a.m./menthyl glyoxylate hydrate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

each pair of PI or chiral PI were cured at 180°C for 1 h. These four pairs of quartz slides will have four different surfaces: (1) slide coated with PI4AM, (2) slide coated with PI4AM/mandelic acid amide, (3) slide coated with PI4AM/menthyl chloroformate amide, and (4) slide coated with PI4AM/menthyl glyoxylate hydrate. The cell comprises the pair of coated slide with the gap in between the surface of PI coated sandwich with glass slide as outside (Fig. 10). The LCs were inserted into the gap at 60°C which was slightly higher than the nematic temperature, so the LCs was in the nematic state. The cell was put under the polarized light and the light pass through the polarized filter before entering the cell and finally pass through another polarized filter before entering the microscope (see Fig. 10).

The picture of the polarizing optical microphotographs of the cells obtained when rotated the polarized filter can be seen as in Figure 11. From Figure 11(a), the PI4AM sandwich did not show any variation in light after turning the polarized light because the liquid crystal is not aligned in any direction.

Because of the unaligned liquid crystal scatter the light in various directions (isotropic scattering), so when the polarized filter rotate, there are no scatter light from the cell changed according to the changing in the polarized light. Contradict to the chiral polyimide cells, which show responses according to the changes in direction of polarized light because the molecule of liquid crystal is aligned in some certain direction. If the molecules are aligned in certain direction, the changes in polarized light will alter the changes in scatter light. In other word, there are some certain direction of polarized light that will give the maximum intensity in some direction and the minimum intensity in cross direction according to the changed in direction of polarized light.

The molecule of liquid crystal in the chiral polyimide are aligned in certain direction, so there are the maximum purple light scattered in certain direction of polarized light as can be seen in Figure 11(b–d). On the perpendicular direction of polarized light, the minimum scatter light from chiral cells was observed. Moreover, regardless of the chiral

chemical, the LCs were similarly aligned in certain direction and have the same phenomenon. This can be concluded that only the chiral characteristic of the side chain of polyimide was enough to get the alignment of LCs regardless of the type of the chiral molecules. However, in the pictures, they showed uneven morphology because of the uneven roughness of these spin coated samples. The uneven roughness of the spin-coated sample resulted in many domain inside the vision of microscope, but the main morphology were still the same. In other words, most of the morphology will scatter the maximum purple light color in some certain direction of polarized light regardless of the uneven roughness of the samples.

CONCLUSIONS

We succeeded in synthesis of novel PI films containing chirals in side chain by reacting chiral compounds: mandelic acid, menthyl chloroformate, and menthyl glyoxylate hydrate with amine side group of the polyimide. A uniform alignment was validated by polarizing optical microscopy. The molecule of liquid crystal in the chiral polyimide are aligned in certain direction, so there are the maximum purple light scattered in certain direction of polarized light. Finally, regardless of the type of the chiral molecule, the chiral side chain polyimide can align the LCs in certain direction. There are unnecessary for special chiral to make the phenomenon. We noted that this technique merits applying LCD

manufacturing to reproducible alignment of LCs in flat panel displays.

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