Chinese Journal of Polymer Science Vol. 32, No. 12, (2014), 1610–1619

Chinese Journal of Polymer Science
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Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2014

Effects of Side Chains with Similar Lengths and Different Structures of Polyimides on Liquid Crystal Alignment Behavior*

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Abstract Polyimides (PI) with different side chains in structure were synthesized by copolycondensation of pyromelliticmdianhydride (PMDA) with 3,5-diamino-(4′-methane acid hexyl ester) phenyl-benzamide (C6-PDA), (4-butoxy-biphenol)-3′, 5′-diaminobenzoate (C4-BBDA) and 3, 5-diamino-benzoic acid decyl ester (C10-DA) named PI-PDA, PI-C4, PI-DA, respectively. The lengths of side chains of PI-PDA and PI-DA are as similar as that of PI-C4. Through the pretilt angle tests it is demonstrated that neither the structure of side chains nor the rubbing process could make an obvious difference on vertical alignment property when the lengths of the side chains are similar, standing at around 1.6 nm. The measurement of surface energy of PI surfaces further proved this result. The result of the X-ray photo-electron spectroscope measurement indicated that the side chains of PIs stretched out from the polymer bulk phase and accumulated on the surface.

Keywords: Polyimides; Homeotropic alignment; Liquid crystal.

INTRODUCTION

It is well known that the quality of initial alignment for liquid crystals (LCs) in liquid crystal display (LCD) plays an important role in contrast ratio, response time and threshold voltage[1]. The average inclination angle of the LC molecules away from the surface of alignment layer is called "pretilt angle", which determines the optical and electrical performance of industrial LCD devices in a significant way, and the alignment layer is the most common instrument to induce initial arrangement of LCs uniformly. Aromatic polyimides (PIs) are widely used as LC alignment layer materials because of their excellent properties such as their outstanding thermal properties, mechanical properties and electrical properties[2].

Traditional LCDs, which adopt the parallel alignment layer to achieve uniform alignment of LCs, have shown some defects, such as narrow viewing angle, low contrast ratio and slow response time[3]. In order to overcome these unexpected shortcomings, vertical alignment approaches of LCs have recently been introduced and then gained great attention from both academic and industrial fields. Many workers have reported the vertical alignment of LCs on PI films[4–11].

Generally speaking, the functionalization of side chains of diamine utilized to synthesize the PI is the most efficient way to induce the vertical alignment. Recently, more and more efforts have been exerted in understanding the relationship between the functional diamines and the pretilt angles[12–15]. Chae *et al.*[16] found that when the lengths of the alkyl chains increased from six carbon atoms to ten carbon atoms, the pretilt angles

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* This work was financially supported by the National Natural Science Foundation of China (Nos. 50973067 and 51173115), and the Ministry of Education (the Foundation for Ph.D. training, Grant No. 20110181110030) of China.

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Received March 5, 2014; Revised April 22, 2014; Accepted April 28, 2014
doi: 10.1007/s10118-014-1550-6

also increased from 25° to 55°. Lee *et al.*[17] discovered that side chains with rigid and flexible units can perform a stable LC vertical orientation. Liu *et al.*[1] synthesized a series of diamines with a side chain containing a rigid biphenyl unit and a non-polar alkyl side end group and obtained a vertical alignment with its pretilt angles larger than 89°. Xia *et al.*[18] synthesized a diamine with an imide ring and flexible alkyl chains on its side chains and proved that when the content of functional diamine was higher than 20%, the pretilt angle induced by the PIs could still be larger than 89° even after rubbing for five consecutive times. In spite of all these efforts, however, the relationship between pretilt angle and the structure of PI side chain has not yet been completely understood. In our previous report[1], the effect of side chains with different lengths and similar structure on pretilt angles has been studied. But the effect of side chains with similar lengths and different structure on pretilt angles has not been carefully investigated yet.

In this study, we used three PIs with different side chains in structure which were comparable in length to induce LCs aligning vertically. The preparation of PI-C4 with side chains containing a biphenyl group had been achieved in previous report[10]. PI- PDA based on 3,5-diamino-(4′-methane acid hexyl ester)phenyl-benzamide (C6-PDA) had side chain attaching a phenyl group and terminated by alkyl chain was synthesized, then PI-DA based on 3, 5-diamino-benzoic acid decyl ester had a full alkyl side chain was prepared. Then the alignment ability of LC induced by the three PIs was studied, as well as three PIs' aggregation structure and thermal property.

EXPERIMENTAL

Materials

3, 5-dinitrobenzoyl chloride (DNBC) was purchased from Zhuorui Chemical Industry (Shanghai, China). *N*-Decyl alcohol and *n*-hexanol were purchased from Chengdu Kelong Chemical Reagent Factory (Sichuan, China), pyromellitic dianhydride (PMDA) was purified by recrystallization from acetic anhydride. *N*-Methyl-2-pyrrolodone (NMP) was purchased from Bodi Chemical Reagents Co. Ltd. (Tianjin, China), and then purified by vacuum-distillation over calcium hydride. A nematic LC, E7 (n_0 = 1.521, Δn = 0.22, T_{n-1} = 60 °C) was purchased from Shijiazhuang Crown Display Material Co. Ltd. (Hebei, China).

Measurements

Fourier transform infrared spectroscopy (FTIR) was recorded on a Nicolet 560 Fourier transform spectrophotometer. Nuclear magnetic resonance (^{1}H-NMR) spectra was obtained from a 400 MHz Unity INVOA 400 spectrophotometer using $CDCl_3$ as a solvent. The pretilt angles of LCs were measured by crystal rotation method using a pretilt angle tester from the Changchun Institute of Optics, Fine Mechanics and Physics (Changchun, China), and at least five different points on the cells were selected for measurements. Surface energy was measured by drop sharp analysis with 100 Kruse Anto visual contact angle test equipment. Thermal gravimetric analysis (TGA) was taken from a DuPont TGA 2100 at a heating rate of 15 $K\cdot min^{-1}$ under nitrogen flow. Wide-angle X-ray diffraction measurements (WAXD) were implemented by using a Philips X'Pert PRO MPD (Philips, Netherlands). The X-ray photo-electron spectroscope (XPS) measurements of the samples were performed at room temperature with an XSAM800 Kratos instrument system employing monochromatic Mg Kα X-ray radiation. The rubbing process was operated with a rubbing machine from TianLi Co. Ltd. (Chengdu, China). The mass spectra was obtained from a GCMS-QP2010 Plus (SHIMADZU, Japan). The elemental analysis was performed by a Euro EA 3000 (LEEMAN LABS INC., USA). DSC testing was performed on a PerkinElmer (Waltham, MA, USA) DSC7 differential scanning calorimeter at a scanning rate of 20 $K\cdot min^{-1}$ under flowing nitrogen (30 $cm^3\cdot min^{-1}$). Polarizing microscopy images were obtained from polarized optical microscope (Shanghai Millimeter Precision Instrument Co. Ltd., China) under room temperature with the magnification of 40 times. The lengths of the diamines were calculated by materials studio 6.0.

Monomer Preparation

Synthesis of 3, 5-diamino-(4′-methane acid hexyl ester) phenyl-benzamide

Synthesis of 4-nitrobenzoic hexyl ester (1a): To a 250 mL three necked bottle with an agitator, n-hexanol and excess triethylamine (TEA) were added to tetrahydrofuran (THF), with influx of nitrogen gas, 4-dinitrobenzoyl chloride dissolved in THF was slowly added drop by drop to the reactor. After the reaction, the mixture was filtered, the solution was precipitated in excess sodium carbonate solution, and THF was removed by distilling under reduced pressure. Then the liquid product was extracted by ethyl acetate, the solvent was removed by distilling under reduced pressure. The crude product obtained from distilling can be used in the next step directly without further purification. Yield: 46.2%. ^{1}H-NMR ($CDCl_3$, δ): 0.9(t, 3H, CH_3), 1.32(sextet, 2H, CH_2), 1.23(quintet, 4H, CH_2), 1.79(quintet, 2H, CH_2), 4.39(t, 3H, CH_2), 8.21(d, 2H, aromatic C—H), 8.31(d, 2H, aromatic C—H).

Synthesis of 4-aminobenzoic hexyl ester (1b): 4-Nitrobenzoic hexyl ester was dissolved in ethanol, which was then placed in hydrogen atmosphere along with 5% Pd/C (catalyst for hydrogenation). The reduction reaction was carried out at 80 °C for 3 h. After filtering of the reaction mixture, the solvent was removed by distilling under reduced pressure. The liquid product was dried under reduced pressure at 30 °C. The crude product can be used in the next step directly without further purification. Yield: 68.4%. ^{1}H-NMR ($CDCl_3$, δ): 0.9(t, 3H, CH_3), 1.3(sextet, 2H, CH_2), 1.41(quintet, 4H, CH_2), 1.75(quintet, 2H, CH_2), 4.29(t, 3H, CH_2), 7.88(d, 2H, aromatic C—H), 6.63(d, 2H, aromatic C—H), 4.0(s, 2H, NH_2).

Synthesis of 3, 5-dinitrogen-(4′-methane acid hexyl ester) phenyl-benzamide (1c): To a 250 mL three necked bottle with an agitator, 4-aminobenzoic hexyl ester and excess TEA were added to THF, with influx of nitrogen gas, DNBC dissolved in THF was slowly added drop by drop to the reactor. After the reaction, the mixture was filtered, the solution was precipitated in excess sodium carbonate solution, then filtered and washed by hydrochloric solution for more than three times, after which the yellow product was dried under reduced pressure at 60 °C. The crude product can be used in the next step directly without further purification. Yield: 51.3%. ^{1}H-NMR ($CDCl_3$, δ): 0.9(t, 3H, CH_3), 1.43(sextet, 2H, CH_2), 1.32(quintet, 4H, CH_2), 1.78(quintet, 2H, CH_2), 4.38(t, 3H, CH_2), 8.13(d, 2H, aromatic C—H), 7.79(d, 2H, aromatic C—H), 8.22(s, 1H, NH), 9.17(s, 2H, new aromatic C—H), 9.26(s, 1H, new aromatic C—H).

Synthesis of 3, 5-diamino-(4′-methane acid hexyl ester) phenyl-benzamide (1d): 3, 5-dinitrogen-(4′-methane acid hexyl ester) phenyl-benzamide was dissolved in ethanol, which was then placed in hydrogen atmosphere along with 5% Pd/C (catalyst for hydrogenation). The reduction reaction was carried out at 80 °C for 3 h. After filtering of the reaction mixture, the solvent was removed by distilling under reduced pressure. The crude product was recrystallized from ethanol. Yield: 76.1%. ^{1}H-NMR ($CDCl_3$, δ): 0.87(t, 3H, CH_3), 1.40(sextet, 2H, CH_2), 1.30(quintet, 4H, CH_2), 1.69(quintet, 2H, CH_2), 4.25(t, 3H, CH_2), 7.93(d, 4H, aromatic C—H), 6.30(s, 2H, new aromatic C—H), 6.01(s, 1H, new aromatic C—H), 5.0(s, 4H, NH_2). Elemental analysis for $C_{20}H_{25}N_3O_3$ (%): Calcd.: C, 67.52; H, 7.03; N, 11.82; Found: C, 68.37; H, 7.16; N, 11.74. ESI-MS: calc. $M^+ = 355.19$, obsvd. $(M+H)^+ = 355.95$.

Synthesis of 3, 5-diamino-benzoic acid decyl ester

Synthesis of 3, 5-dinitrogen- benzoic acid decyl ester (2a): To a 250 mL three necked bottle with an agitator, *n*-decyl alcohol and excess TEA were added to THF, while influxing nitrogen gas, DNBC dissolved in THF was slowly added drop by drop to the reactor. After the reaction, the mixture was filtered, the solution was precipitated in excess sodium carbonate solution, then filtered and washed by hydrochloric solution for more than three times, after which the yellow product 3, 5-dinitrogen-benzoic acid decyl ester was dried under reduced pressure at 60 °C. The crude product can be used in the next step directly without further purification. Yield: 39.8%. ^{1}H-NMR ($CDCl_3$, δ): 0.95(t, 3H, CH_3), 1.36(sextet, 2H, CH_2), 1.43(quintet, 12H, CH_2), 1.75(quintet, 2H, CH_2), 4.42(t, 2H, CH_2), 9.27(d, 2H, aromatic C—H), 9.33(s, 1H, aromatic C—H).

Synthesis of 3, 5-diamino- benzoic acid decyl ester (2b): 3,5-Dinitrogen-benzoic acid decyl ester was dissolved in ethanol, which was then placed in hydrogenator along with 5% Pd/C (catalyst for hydrogenation).

The reduction reaction was carried out at 80 °C for 3 h. After filtering of the reaction mixture, the solvent was removed by distilling under reduced pressure. The crude product was recrystallized from ethanol. Yield: 69.7%. ^{1}H-NMR ($CDCl_3$, δ): 0.93(t, 3H, CH_3), 1.33(sextet, 2H, CH_2), 1.40(quintet, 12H, CH_2), 1.70(quintet, 2H, CH_2), 4.32(t, 2H, CH_2), 6.78(d, 2H, aromatic C—H), 6.17(s, 1H, aromatic C—H), 4.05(s, 4H, NH_2). Elemental analysis for $C_{17}H_{28}N_2O_2$ (%): Calcd.: C, 69.76; H, 9.57; N, 9.57; Found: C, 70.71; H, 9.70; N, 10.25. ESI-MS: calc. $M^+ = 292.22$, obsvd. $(M+H)^+ = 293.00$

Polymer Preparation and Film Preparation

To a 50 mL reactor equipped with an agitator, the synthesized diamine (1 mmol) was dissolved in NMP, and PMDA (0.218 g, 1 mmol) were added into the reactor. The solid content of the mixture solution is 15 wt%. After being stirred at room temperature for 24 h, the mixture was spin-coated on the glass substrates washed by isopropyl alcohol. They were prebaked at 80 °C for 30 min and baked at 250 °C for 2 h to be imidized under nitrogen. The PI films thus obtained were rubbed by means of rayon velvet fabric. The rubbing strength is defined as

$$\mathrm{RS} = NM(2nr\pi/60v-1)$$

where N is the number of times the substrates are rubbed, M (mm) is the depth of deformation of the rayon fabric due to contact with the film surface, v ($\mathrm{mm\cdot s^{-1}}$) is the velocity of the substrate stage, and n ($\mathrm{r\cdot min^{-1}}$) and r (mm) are the rolling speed and radius of the roller, respectively.

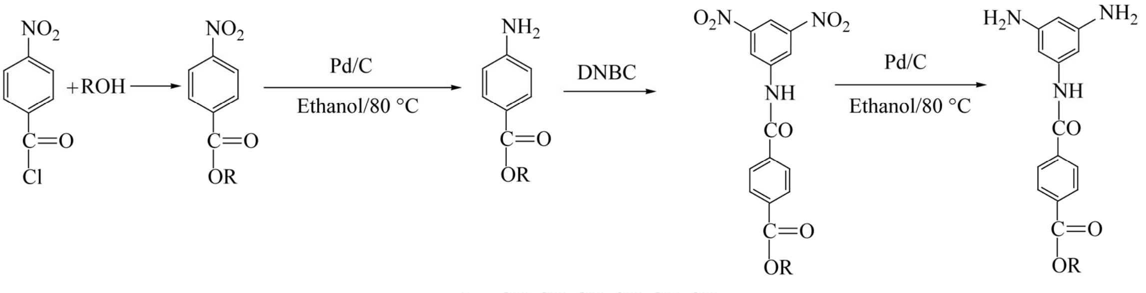
LC Cell Preparation

LC cells for the pretilt angle measurement were assembled by bonding two pieces of the substrates using a 40 nm spacer. The substrates were arranged such that they had antiparallel rubbing direction. 7E was injected between a cell gap by a capillary method at room temperature, which was followed by sealing the injection hole with photo-curable epoxy resin.

RESULTS AND DISCUSSION

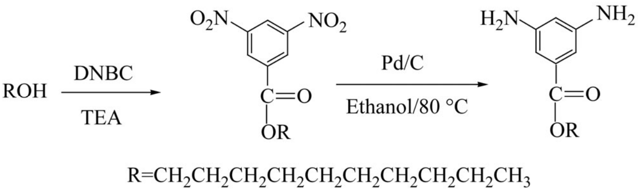
Monomer Synthesis

The (4-butoxy-biphenol)-3′,5′-diaminobenzoate (C4-BBDA) was synthesized according to the previous work as mentioned above[10]. The methods to synthesize functional diamines 3, 5-diamino-(4′-methane acid hexyl ester) phenyl-benzamide (C6-PDA) and 3, 5-diamino-benzoic acid decyl ester (C10-DA) are shown in Schemes 1 and 2, respectively.



$R = CH_2CH_2CH_2CH_2CH_2CH_3$

Scheme 1 The synthetic route to the functional diamine C6-PDA



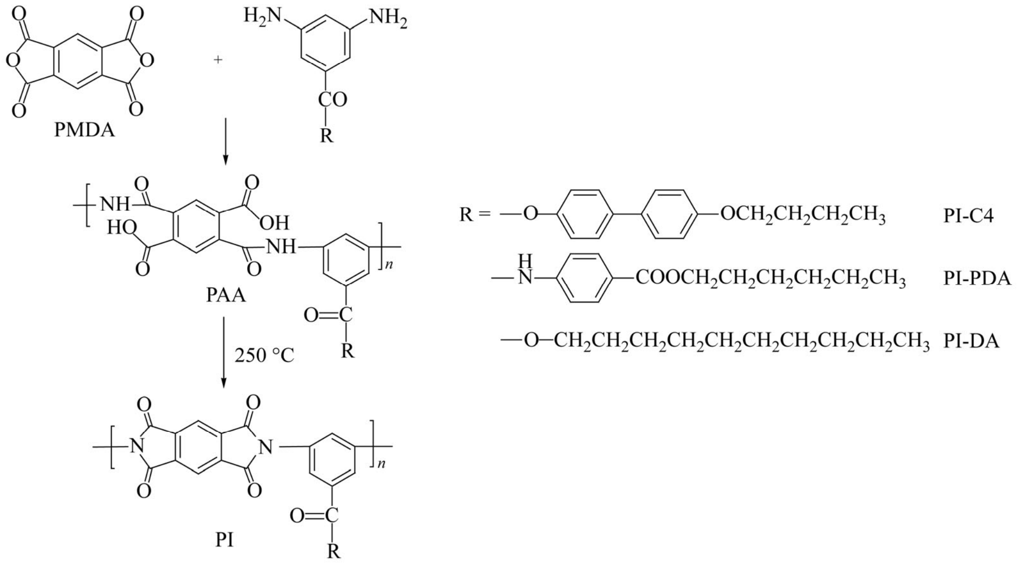
Scheme 2 The synthetic route to the functional diamine C10-DA

First, 4-nitrobenzoic hexyl ester (1a) was synthesized by coupling *n*-hexanol with 4-dinitrobenzoyl chloride in the presence of THF and TEA. Secondly, the nitro group was reduced by hydrogen. Then 3, 5-dinitrogen-(4′-methane acid hexyl ester) phenyl-benzamide (1c) was obtained by the reaction of reduction product (1b) and DNBC. Finally the ultimate product was achieved by the reduction of (1c). The reduction reaction, which was carried out by hydrogen in a high-pressure reaction kettle in order to acquire a high yield, was essential among these steps.

4-Dinitrobenzoyl chloride was deliberately selected as it is very reactive. The reaction must be processed at around 0 °C in order to avoid side reactions. In this step, TEA was utilized as a catalyst as well as acid scavenger due to the fact that the hydrogen chloride generated in the reaction may have a negative effect to the alcohol. The synthesis of C10-DA experienced almost the same procedure as C6-PDA, including the acylation reaction and the reduction reaction.

Polymer Synthesis

The method used to synthesize the PIs was described in Scheme 3. The three different PIs were prepared from C6-PDA, C4-BBDA and C10-DA, and commercially available pyromellitic dianhydride (PMDA) *via* a two-step procedure. The polymerization was carried out by reacting stoichiometric amounts of the diamines with the dianhydrides at a concentration of 15% solids in NMP. The ring-opening polymerization at room temperature for 24 h produced PAAs, which was then followed by sequential heating till 250 °C to obtain the PIs. The chemical structures of all three PIs have been confirmed by IR. As an example, the FTIR spectrum of PI-PDA is shown in Fig. 1. There are absorption bands that are typical of N—H stretching at 3369 cm^{-1}, as well as aliphatic C—H



Scheme 3 The synthetic route to the three PIs

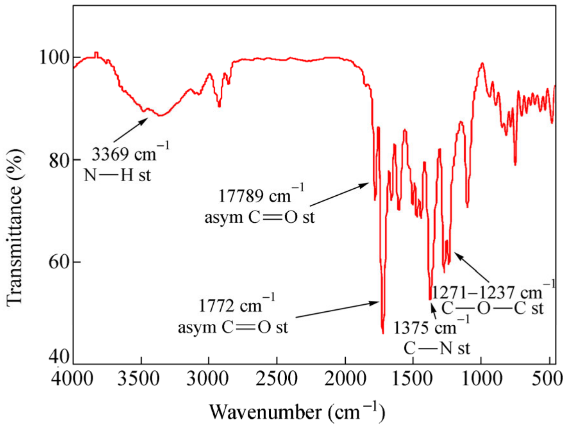


Fig. 1 FTIR spectrum of PI-PDA

stretching at 2929–2865 cm^{-1}. Strong bands at 1778 cm^{-1} and 1722 cm^{-1} indicate that there are symmetrical and unsymmetrical vibrations of the two imide carbonyl groups. Absorption bands are observed at 1375 cm^{-1} and 1271–1237 cm^{-1} due to the vibrations of C—N and C—O—C, respectively. Thus, the copolymer has been successfully obtained.

Aggregation Structure

Figure 2 shows the side chain lengths of the diamines ranging from 1.5079 nm to 1.6835 nm, which are extremely similar to each other.

Wide-angle X-ray diffraction measurements were carried out for PI films, and the results are shown in Fig. 3. Broad diffraction peaks are observed in three curves representing three different PIs with different structures. Copolymerization could break up the structural regularity of the PIs. In the meantime, the steric effect caused from a high density of side chains increased the intermolecular distance and free volume. These two factors made it almost impossible for PIs to crystallize. Hence, the three PIs with different structures all have amorphous morphologies.

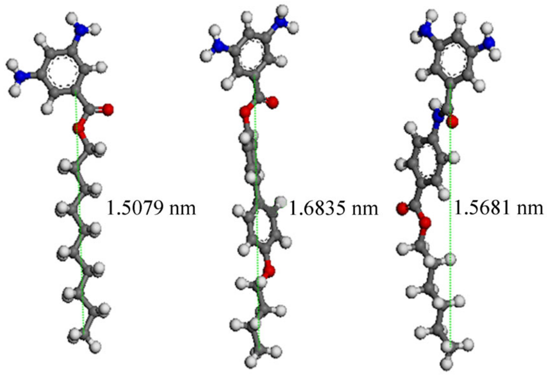


Fig. 2 Side chain lengths of diamines

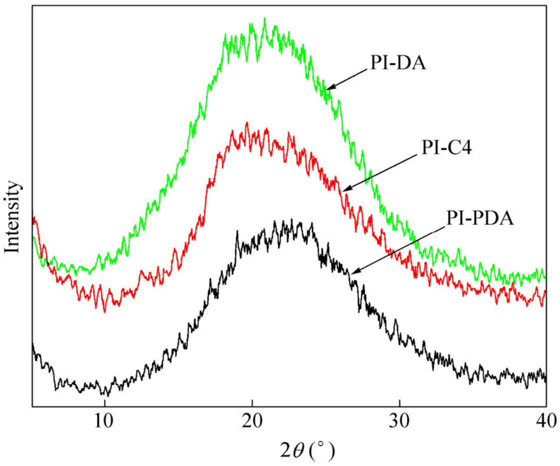


Fig. 3 WAXD diffraction patterns of synthesized polyimides

Thermal Properties

The glass-transition temperatures of the three different PIs were obtained from DSC testing and the results were summarized in Table 1. DSC curves in Fig. 4 revealed that all PIs cannot crystallize which was in accordance with the results gained from WAXD. The value of T_g for the three different PIs were quite close, ranging from

214 °C to 231 °C, as they have the same backbone structure and the similar lengths of side chains. The tiny differences may be caused by the difference in the flexibility of side chains since the flexible side chains with smaller steric hindrance lead to a tighter chain packing, which requires a higher temperature for segments to mobilize. So PI-C4 has the lowest T_g while PI-DA had the highest T_g. Thermal stability of PI films were studied by TGA under nitrogen atmosphere at a heating rate of 15 K/min. From Fig. 5, it is known that all the PIs began to degrade at temperatures higher than 338 °C, which indicated that all these three PIs were excellent in thermal stability. The TGA curves show that the polymer decomposition has a two-step weight loss behavior. The first step was the degradation of side chains while the second step was the weight loss of polymer backbones. The decomposition temperatures of PIs elevate with the increase in rigidness of side chains. 5% weight loss of each PIs was around the temperature of 400 °C for PI-C4, 380 °C for PI-PDA and 369 °C for PI-DA, respectively. The decomposition temperature at 10% weight loss was 439 °C for PI-C4, 401 °C for PI-PDA, 386 °C for PI-DA, as is shown in Table 1. Therefore, though the three PIs have different structures, their thermal abilities are all of sufficient quality to satisfy the usage requirements.

Table 1. Thermal properties of the PIs synthesized in the present work

Sample^a	T_g^{b} (°C)	T_d^{c} (°C)	T_5^{c} (°C)	T_{10}^{c} (°C)	R_{800}^{c} (wt%)
PI-C4	214	344	400	439	47.2
PI-PDA	221	342	380	401	44.5
PI-DA	231	338	369	386	33.2

[a] The measured samples were obtained by a thermal imidization method;

[b] T_g is the glass-transition temperature obtained from DSC;

[c] T_d is the decomposition onset temperature; T_5 and T_{10} are the temperatures required for weight loss of 5% and 10%, respectively. R_{800} is the residual weight (%) at 800 °C in nitrogen.

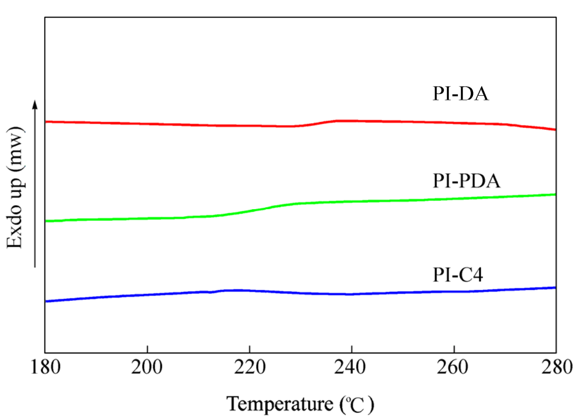


Fig. 4 DSC curves of PIs

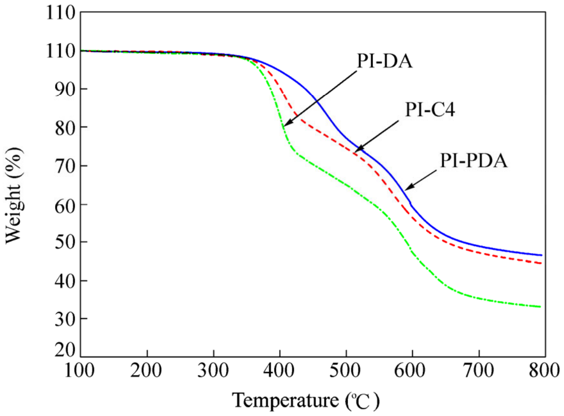


Fig. 5 TGA curves of PIs

Alignment Properties of PI Films

Effect of chemical structure of side chains on pretilt angles

Pretilt angle could be affected by a quantity of factors such as electronic interaction and anchoring energy, *etc*. In this research, pretilt angles of three LC cells made of three different types of PIs were obtained by means of a pretilt angle tester in order to investigate the effect of chemical structure of side chains on pretilt angles, and the results are shown in Table 2.

Table 2. Surface free energy on PI surfaces and pretilt angles of LC cells before and after rubbing

Sample	Before rubbing		After rubbing	
	Pretilt angle (°)	Surface energy (mN·m^{-1})	Pretilt angle (°)	Surface energy (mN·m^{-1})
PI-C4	90	46.34	90	46.71
PI-PDA	89.8	44.79	89.8	45.83
PI-DA	89.3	42.39	89.2	43.02

The Table 2 indicates that no matter whether the PI films had been rubbed or not, three different types of PI films' pretile angles were all higher than 89°, which means that the vertical alignment had been successfully induced. This result proved that most of the side chains didn't fall down after rubbing. Hence, rubbing doesn't have an obvious influence on the inducing of vertical alignment in this condition. Despite the similarities mentioned above, PI-C4 had the largest pretilt angle. Then the values of angles were followed by PI-PDA and PI-DA. The slight differences can be attributed to the difference between three side chains' rigidity. PI-C4's side chains have a structure of biphenyl which is the most rigid structure among the three types of side chains. Thus it can induce vertical alignment with the pretilt angles standing at 90°. PI-PDA has the second largest pretilt angle as its side chains have a phenyl ring and an amide bond which can contribute to its rigidity. As for PI-DA, the long flexible chains which have the smallest rigidity, lead to a minimum pretilt angle reaching 89.4° before rubbing and 89.3° after rubbing, respectively. Thus, we can see that although the three PIs have totally different side chain structures, they can all induce the vertical alignment before and after rubbing.

The contact angles of deionized water and methylene iodide on the surfaces of the PI films were measured, and the calculated surface free energies are listed in Table 2. All three types of films' surface energies experienced a very slight upward trend which coincides with the variation of pretilt angles before and after rubbing. It is the usual accepted sense that surface free energy has a close relationship with the pretilt angles of LCs[19]. Therefore, the little changes on surface energy further prove that the rubbing process can hardly influence LCs' vertical alignment. This result illustrates that the three different side chains with different structures could still orient out of the film plane and cover the polar groups in the backbone after rubbing, otherwise there would be a dramatic increase on surface energies.

Uniformity of LC vertical alignment

To investigate the uniformity of LC vertical alignment on the different PI films, conoscope observation of the LC cells was used with polarized optical microscope (POM). When the optic axis of LCs is uniformly perpendicular to the substrate, the incident light will not break up into normal and abnormal light, neither the direction of pathway changes. In this condition, the unchanged dark will be observed from POM during rotating the LC cells placed between two crossed polarizes. As is shown in Fig. 6, dark crossed brushes are clearly seen and not move with the LC cell rotating. The result proved that even though three PIs have entirely differently side chains, the vertical alignment were all induced uniformly.

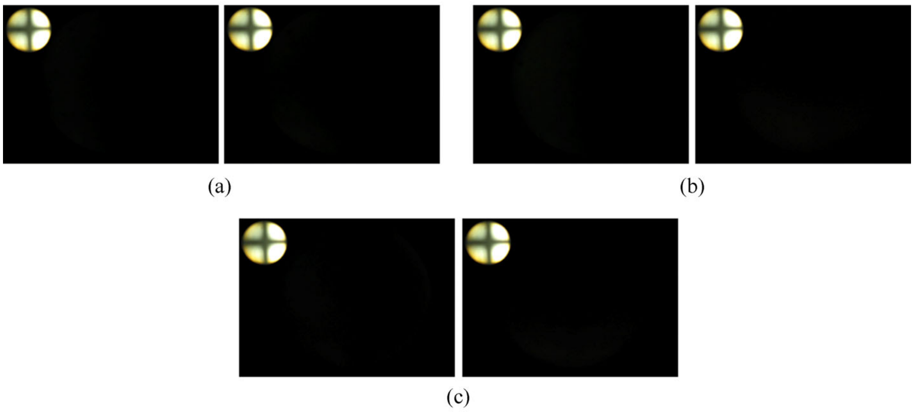

(a) (b) (c)

Fig. 6 POM images and conoscopic images before and after rotating by 45° of LC cells: (a) PI-C4, (b) PI-PDA and (c) PI-DA

Surface Elements of PIs

Three different PI films were characterized by XPS in order to obtain the information about surface elements and the arrangment of side chains. The results of XPS are shown in Table 3.

Table 3. Content of elements of PIs

Type of PI films	Atomic Percentage (%)					
	284.77 eV C—C or C=C		285.91 eV C—O or C—N		288.87 eV C=O	
	Theoretic value	Test value	Theoretic value	Test value	Theoretic value	Test value
PI-C4	68.9	60.9	20.5	25.3	10.6	13.8
PI-PDA	69.8	56.3	18.6	25.0	11.6	18.7
PI-DA	66.7	62.1	20.5	22.7	12.8	15.2

Figure 7 shows the XPS spectra of C_{1s} for three different polyimides. The component peak at 284.77 eV is attributed to carbon atom bonds, including C—C and C=C. The peaks at 285.91 eV and 288.87 eV are due to the carbon atom singly bonded to oxygen atom or nitrogen atom, C—O or C—N, and carbon oxygen double bond, C=O, respectively. It can be seen from the Table 3 that in spite of some slight differences, the test values of three PIs with different structures and their theoretic values are in good agreement. The theoretic values are calculated based on the hypothesis that all the side chains align vertically against the plane and cover the total area of the plane surface. Thus, this match of two sorts of data indicated that most of the side chains stretched out from the polymer bulk phase and accumulated on the surface, which was similar as what the hypothesis described. As a result of the accumulating, vertical alignment could be induced through the interactions between liquid crystal molecules and the side chains. Hence, despite the differences on side chain structures, all three PIs show the same arrangement behavior of side chains.

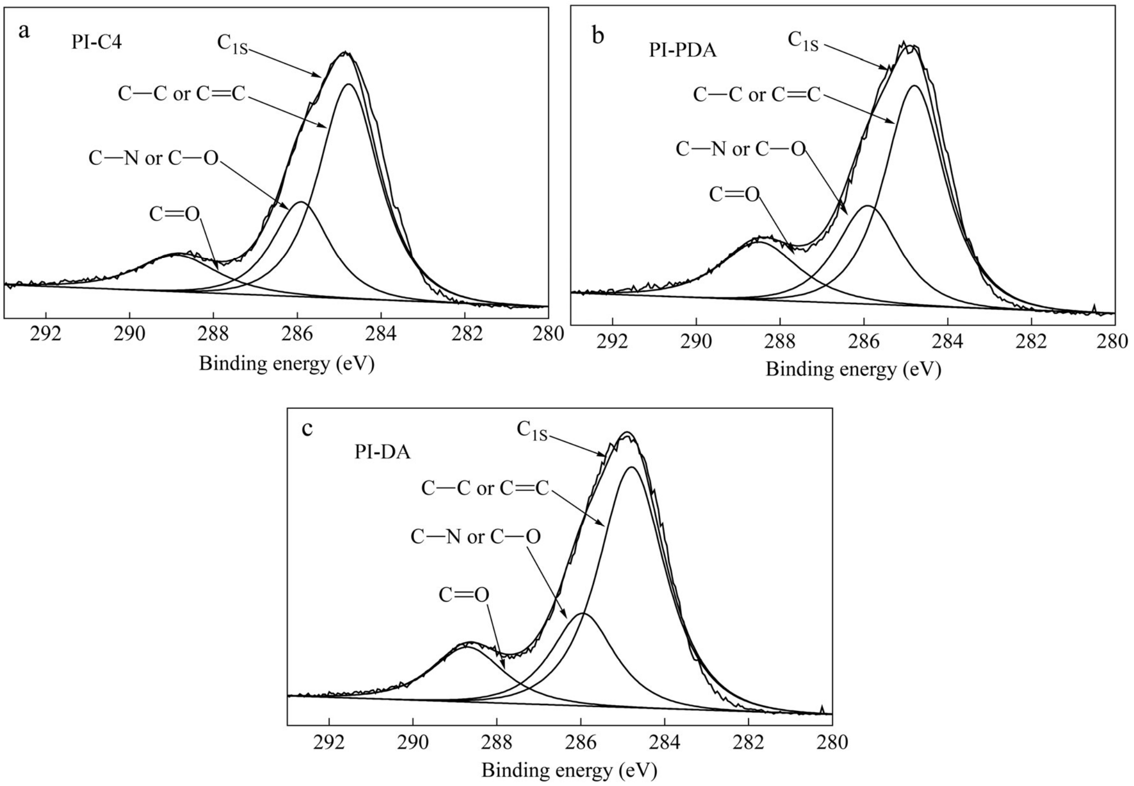


Fig. 7 XPS spectra of three kinds of PI (incident angle 10°)

CONCLUSIONS

Three types of PIs with different structures and very similar lengths were successfully synthesized. All these three PIs are amorphous and excellent in thermal stability, the decomposition temperature of PIs elevates with the rigidness rise of side chains. The homeotropic alignment could be induced by three PIs with each of their pretilt angles higher than 89° though their side chain structures were different. The pretilt angles and the surface energies hardly changed before and after rubbing process for all three types of PIs, which indicated that neither the structure of side chains nor the rubbing process could make a difference on vertical alignment property when the length of the side chain were similar, standing at around 1.6 nm. The arrangement of side chains which stretch out from the polymer bulk phase and accumulate on the surface are almost the same for three PIs despite the differences on their side chain structures. Therefore, it can be seen that different side chain structures can hardly influence the alignment behaviors of PIs as long as the side chain lengths are very similar.

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