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Preparation of novel polyimides containing aryl ester side chains end-capped with alkoxy groups and studies on their surface properties

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A novel diamine containing aryl ester side chains end-capped with alkoxy groups was synthesised and characterised by Fourier transform infrared spectrometry and ^{1}H-nuclear magnetic resonance. Based on the diamine, a series of copolyimide alignment films were prepared by a one-step process. The effects of side chain content of polyimides on surface energy, surface element components and surface morphology were studied by contact angle measurement, attenuated total reflection Fourier transform infrared spectrometry, x-ray photoelectron spectroscopy and atomic force microscopy. These investigations show that the surface energy decreases linearly with the increase of side chain content in a certain range and then levels off. Side chains with alkyl groups can transfer to the surface spontaneously, which makes the content of side chain on the surface notably higher than that in the matrix. However, when side chain content reaches 60 mol%, further transference stops. The enrichment of side chains on the surface of alignment films could be considered as the reason for the increase of the pretilt angle.

Keywords: polyimide; side chain; alignment films; surface energy

1. Introduction

Polyimides (PI) have been widely used to form alignment films for liquid crystal (LC) display because of their excellent heat resistance, low dielectric constant and other good performance factors [1]. As alignment films, PI interact with LC molecules after rubbing, and force them to orient with a pretilt angle. The reason for this phenomenon was first considered to be the result of interaction between the LC molecules and the microgrooves that were engendered by rubbing. Chiou *et al.*'s experiment, in which they made microgrooves on the PI surface by a soft embossing method enabling the PI to align LCs, supports this hypothesis [2]. However, further experiments show that LC molecules can be aligned homogeneously on film without rubbing, for example, using UV or ion beam-treated PI, or even a PI film without any treatment [3, 4]. Ishihara *et al.* discovered a phenomena in which LCs were perpendicular to the rub direction with zero pretilt angle [5]. Lee *et al.* found that hypo-microcosmic nanometer grooves on the surface of polystyrene (PS) were created by the benzene ring in the side chains of PS. The interaction of benzene rings both with PS and LCs resulted in the alignment of LCs perpendicular to the rub direction [6, 7]. This shows that the dominant factor that aligns LCs is not the microgroove, but the component and molecular arrangement of the PI surface.

Incorporation of alkyl side chains is a very effective way of improving pretilt angles of LCs [8, 9]. Usually the introduction of alkyl side chains is found to decrease PI surface energy [10], but no study has provided an explicit reason. Here we prepared copolyimides by a one-step method based on a novel diamine containing aryl ester side chains end-capped with alkoxy groups, 4-[(4′-butoxyphenoxy)carbony1]phenyl-3′,5′-diaminobenzoate (BCDA). Copolyimides with different alkyl side chain contents were characterised with regard to surface properties and surface element components. The relationship between side chain content and surface properties was discussed and established by mathematical methods. The results indicate that in PI films, side chains with alkyl groups can transfer to the surface spontaneously, and thus their content on the surface is higher than that in the matrix, which may provide some indication of the molecular design of alignment films. It also suggests that further understanding of the reason for the improvement of the pretilt angle can be gained by introducing alkyl side chains into PI.

2. Experiment

2.1 *Materials*

3,5-Dinitrobenzoic acid (99%, Shanghai Wulian Chemical Corp., Shanghai, China) was recrystallised from ethanol. 5% palladium on activated carbon (Pd/C, Acros Organics, New Jersey) was used as received. 4,4′-diaminodiphenyl ether (ODA, Shanghai Institute of Synthetic Resins, China) was purified by recrystallisation from ethanol. 4,

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4′-oxydiphthalic anhydride (ODPA, Acros Organics, New Jersey) was dried for 5 h at 180°C prior to use. *N*-Methyl-2-pyrrolidinone (NMP, Pu Yang MYJ Technology, China) was distilled under reduced pressure after drying by P_2O_5. Other reagents were used as received.

2.2 *Monomer synthesis*

The synthesis procedure of BCDA is shown in Scheme 1.

2.2.1 *4-Acetoxybenzoic acid (1)*

4-Acetoxybenzoic acid **(1)** was prepared according to Yang *et al.* [11].

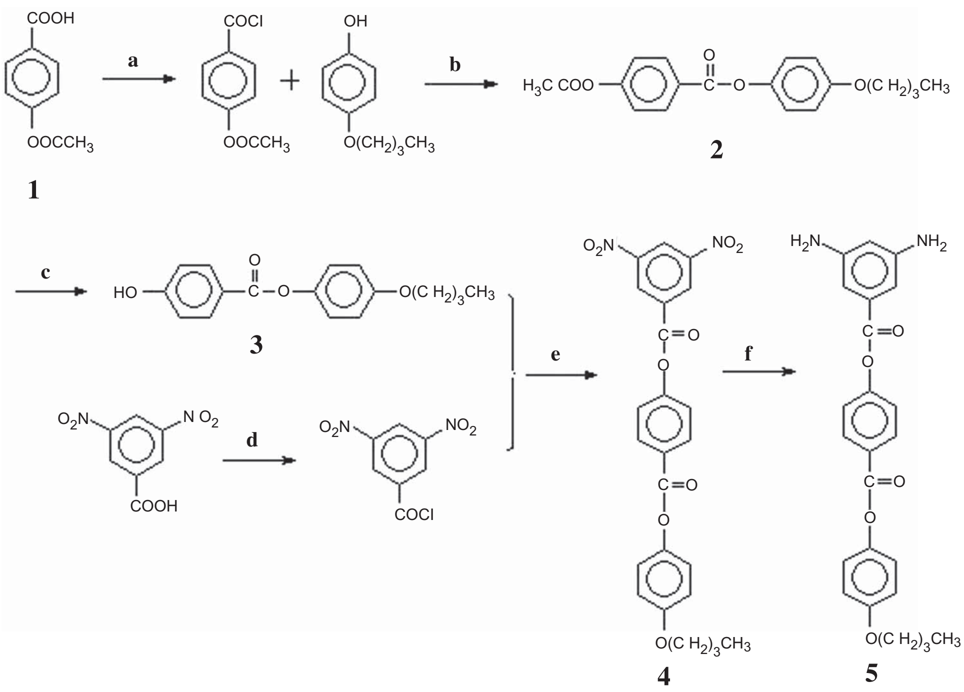
2.2.2 *4-Butoxyphenyl-4 acetoxybenzoate (2)*

1 (16.1 g, 0.09 mol) and thionyl chloride (0.54 mo1) were mixed and stirred for 5 h at reflux. The excess thionyl chloride was removed by distillation in a vacuum. The obtained acyl chloride was subsequently dissolved in 30 ml tetrahydrofuran (THF) (solution I). 4-Butoxyphenol (0.18 mo1) and pyridine (0.81 mo1) were dissolved in 90 mL THF (solution II). Solution II was dropped into solution I with ice cooling. The mixture was stirred for 12 h to yield **2**. **2** was recrystallised from the mixture of ethanol and petroleum ether of 1:2 v/v (mp.81.1–81.8°C, yield 87.2%).

FTIR (KBr, cm^{-1}): 2958.44, 2871.24 (fatty group υ_{CH}), 1761.20, 1733.31 ($\upsilon_{c=o}$), 1270.06, 1246.42 and 1190.98 ($\upsilon_{c\text{-}o\text{-}c}$). ^{1}H-NMR ($CDCl_3$, δ ppm): 0.96 (t, 3H, J = 14.8, CH_3 on butyl group), 1.47 (m, 2H, J = 20.4, CH_2 between methylene and methyl), 1.74 (m, 2H, J = 15.2, CH_2 between two methylenes), 2.33 (s, 3H, CH_3COO-), 3.95 (t, 2H, J = 13.2, -CH_2O-), 6.91 (m, 2H, J = 8.8, aromatic H *ortho* to butoxy), 7.09 (m, 2H, J = 9.2, aromatic H *meta* to butoxy), 7.22 (m, 2H, J = 6.8, aromatic H *ortho* to acetoxy), 8.21 (m, 2H, J = 8.8, aromatic H *meta* to acetoxy), ^{1}H-NMR ($CDCl_3$, δ ppm): 0.96 (t, 3H, J = 14.8, CH_3 on butyl group), 1.47 (m, 2H, J = 20.4, CH_2 between methylene and methyl), 1.74 (m, 2H, J = 15.2, CH_2 between two methylenes), 2.33 (s, 3H, CH_3COO-), 3.95 (t, 2H, J = 13.2, -CH_2O-), 6.91 (m, 2H, J = 8.8, aromatic H *ortho* to butoxy), 7.09(m, 2H, J = 9.2, aromatic H *meta* to butoxy), 7.22 (m, 2H, J = 6.8, aromatic H *ortho* to acetoxy), 8.21 (m, 2H, J = 8.8, aromatic H *meta* to acetoxy).

2.2.3 *4-Butoxyphenyl-4′-hydroxybenzoate (3)*

2 (5.0 g, 0.015 mol), and diluted ammonia (50 ml 25 wt% ammonia in 55 ml H_2O) were added into a flask



Scheme 1. Preparation route of 4-((4′-butoxyphenoxy)carbonyl)phenyl-3″,5″-diaminobenzoate (BCDA). Reagents and conditions: (a) thionyl chloride (6 equiv), reflux, 5 h; (b) THF, pyridine (6 equiv), ice cooling, 12 h; (c) diluted ammonia, 51°C, 8 h; (d) thionyl chloride (6 equiv), reflux, 5 h; (e) THF, pyridine (6 equiv), ice cooling, 12 h; (f) ethanol, H_2, Pb/C, 80°C, 2.0 MPa, 5 h.

and stirred for 8 h at 51°C. After cooling to room temperature, HCl aqueous solution (2 mol L^{-1}) was used to adjust the pH to 1.0 with stirring for 2.5 h. The precipitate was filtered, washed with water and recrystallised from toluene to obtain a grey acicular crystal **3** (mp. 154.2–155.1°C, yield 80.6%).

FTIR (KBr, cm^{-1}): 3375.23 (υ_{OH}), 2957.47, 2917.68 and 2871.22 (fatty group υ_{CH}), 1699.70 ($\upsilon_{c=o}$), 1275.38, 1241.23 and 1193.42 ($\upsilon_{c\text{-}o\text{-}c}$). The IR spectrum showed only one ester bond. ^{1}H-NMR (CDCl$_3$, δ ppm): 0.96 (t, 3H, $J = 14.4$), 1.45 (m, 2H, $J = 22.4$), 1.73 (m, 2H, $J = 14.8$), 3.94 (t, 2H, J=12.8), 6.25 (s, 1H, -OH), 6.87 (m, 2H, $J = 8.4$, aromatic H *ortho* to hydroxyl group), 6.91 (m, 2H, $J = 8.8$, aromatic H *ortho* to butoxy), 7.08 (m, 2H, $J = 8.8$), 8.08 (m, 2H, $J = 8.4$, aromatic H *meta* to hydroxyl group).

2.2.4 *4-[(4′-Butoxyphenoxy) carbonyl]phenyl-3″,5″-dinitrobenzoate (**4**)*

3 (1.0 g, 0.0035 mol) was dissolved in 25 ml THF and 5 ml pyridine (solution III) in a flask. 3,5-Dinitrobenzoic acid (0.0039 mo1) was acyl chloridised. The obtained acyl chloride 7 was subsequently dissolved in 20 ml dried THF and added into solution III dropwise with stirring for another 12 h. The precipitate was filtered, washed with water and recrystallised from the mixture of ethanol and 1,2-dichloroethane (1:1 v/v) to obtain **4**. (mp. 147.2–148.3°C, yield 74.5%).

FTIR (KBr, cm^{-1}): 2957.01, 2921.97 and 2853.28 (fatty group υ_{CH}), 1746.98, 1729.16 ($\upsilon_{c=o}$), 1544.51, 1346.19 (υ_{NO2}), 1267.02, 1244.54 and 1193.42 ($\upsilon_{c\text{-}o\text{-}c}$). ^{1}H-NMR (CDCl$_3$, δ ppm): 0.97 (t, 3H, $J = 14.4$, CH$_3$ of butyl group), 1.46 (m, 2H, $J = 22.4$,), 1.75 (m, 2H, $J = 14.8$), 3.96 (t, 2H, $J = 12.8$), 6.93 (m, 2H, $J = 12.4$), 7.11 (m, 2H, $J = 8.8$), 7.42 (m, 2H, J = 8.8, aromatic H *ortho* to 3″,5″-dinitrobenzoxy), 8.32 (m, 2H, $J = 8.0$, aromatic H *meta* to 3″,5″-dinitrobenzoxy), 9.32 (m, 3H, $J = 10.8$, aromatic H *ortho* to nitro group).

2.2.5 *4-((4′-Butoxyphenoxy)carbony1)phenyl-3″,5″-diaminobenzoate (**5**)*

4 (3.5 g), 5% palladium on activated carbon (5 wt%) and ethanol (100 ml) were added into a small-scale hydrogenation autoclave equipped with a magnetic stirrer. The autoclave was placed into an 80°C water bath, flushed three times with hydrogen, and then pressurised to 1.2 MPa. After being agitated for 2 h, the solution was filtered. The filter cake was placed into 50 ml THF and filtered again to remove Pd/C. The filtrate was poured into deionised water and the precipitate was collected and dried under a vacuum at 40°C to produce a white compound which was then recrystallised by 1,2-dichloroethane to form a yellow crystal **5** (BCDA). The m.p. is 153.2–153.6°C. Yield: 98.9%.

FTIR (KBr, cm^{-1}): 3433.36, 3420.90 (υ_{NH2}), 2956.73, 2869.57 (fatty group υ_{CH}), 1726.54 ($\upsilon_{c=o}$), 1273.22, 1245.92 and 1189.06($\upsilon_{c\text{-}o\text{-}c}$). ^{1}H-NMR (CDCl$_3$, δ ppm): 0.95 (t, 3H, $J = 14.6$), 1.45 (m, 2H, $J = 22.2$), 1.75 (m, 2H, $J = 14.6$), 3.77 (s, 4H, 2NH$_2$), 3.94 (t, 2H, $J = 12.8$,), 6.27 (s, 1H, aromatic H *ortho* to 2NH$_2$), 6.91 (m, 4H, $J = 8.8$, aromatic H *ortho* to butoxy and *meta* to NH$_2$), 7.10 (m, 2H, $J = 9.0$), 7.26 (m, 2H, $J = 14.0$, aromatic H *ortho* to 3″,5″-diaminobenzoxy), 8.24 (m, 2H, $J = 8.6$, aromatic H *meta* to 3″,5″-diaminobenzoxy).

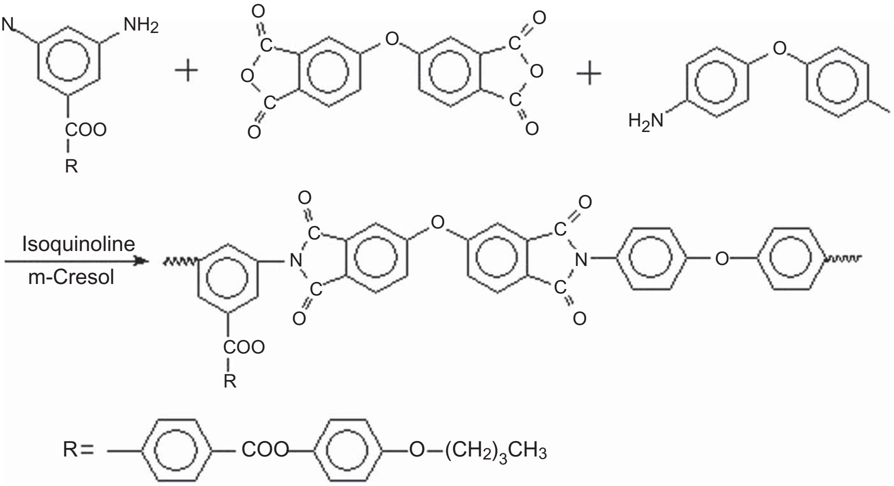
2.3 *Preparation of polyimides and films*

The polyimides were copolymerised from BCDA with different ratios of ODA and ODPA. The polymerisation procedure is shown in Scheme 2. BCDA and ODA (total molar amount 0.001 mol) were dissolved in *m*-cresol in a 25 ml three-necked round-bottom flask equipped with a mechanical stirrer and a nitrogen inlet, and then ODPA (0.00102 mol) was added into the solution. The reaction mixture was stirred at 180°C for 6 h with nitrogen flow to give a yellow polyimide solution. The solid contents of the solutions were 10 wt%. Molar contents of BCDA were controlled to 100%, 60%, 50%, 40% and 20%. The PIs were named as PI-BCDA 1.0, PI-BCDA 0.6, PI-BCDA 0.5, PI-BCDA 0.4 and PI-BCDA 0.2, respectively.

Polyimide solutions were cast on glass and cured at 100°C and 200°C each for 1 h to give touch films.

2.4 *LC cell fabrication and pretilt angle measurement*

PI films prepared on the ITO-coated glass were subsequently rubbed with a roller covered with commercial rubbing cloth, and the rubbing strength L was calculated as follows: $L = lN(2\pi rn/60\upsilon - 1)$, where L (mm) is the total length of the rubbing cloth that touches a certain point of the film; l (0.3 mm) is the contact length of the rubbing roller circumference; N is the cumulative number of rubbings; υ (17.2 mm s^{-1}) is the velocity of the substrate stage; and n (700 rpm) and r (22.5 mm) are the rubbing roller rotational speed and the radius, respectively. LC cells were fabricated from two pieces of rubbed PI films assembled in an antiparallel rubbing direction with 43 μm (cell gap) thick spacers and filled with 4-pentyl-4′-cyanobiphenyl (5CB) by the capillary method. The pretilt angles for the fabricated LC cells were measured by a crystal rotation method with a PAT-20 measurement device (Chanchun Liancheng Instrument Co., Ltd.).



Scheme 2. Preparation of copolyimides with side chain content.

3. Characterisation

Fourier infra-red spectrum tests (FTIR) were carried out using Nicolet 560 FTIR equipment. A ZeSe pellet was used as the reflection plate in attenuation total reflection FTIR (ATR-FTIR), and the incidence angle was 45°. Nuclear magnetic resonance (NMR) spectrum tests were carried out on Bruker-ACE 2000 MHz, and the test frequency was 400 MHz. Surface energies of PI film (γ_c) were tested on Drop Sharp Analysis 100 Krüse auto visual contact angle test equipment. X-ray photoelectron spectrum (XPS) was obtained using XSAM800 XPS equipment. For measuring pretilt angles, 5 wt% polyimide solutions were spin-coated on 25 mm × 25 mm ITO-coated glass at 500 rpm for 5 s and 1500 rpm for 10 s, respectively, followed by thermal cure at 100°C and 200°C for 1 h each. Surface morphology of PI films was examined by atomic force microscopy (AFM). Tapping mode was used to obtain both height and phase images on a Digital Instrument NanoScope III with Multimode scanning probe setup (Multimode SPM). Thermogravimetric analysis (TGA) was performed on a Netzsch 209 TG instrument; samples were tested under N_2 (99.99%) at a heating rate of 10°C min^{-1}.

4. Results and discussion

4.1 Monomer and polymer

The diamine **5** was synthesised through six steps. The key step was the selective hydrolysation of ester bonds to prepare compound **3**. According to the method of Yang *et al.* [11], compound **3** would not be obtained before the concentration of ammonia, the temperature and time are adjusted. The optimal condition of selective hydrolysation is: the ratio of ammonia (25 wt%)/water is 9/10 (v/v); reaction temperature and time are 51°C and 8 h, respectively. By this method, the yield of **3** was enhanced up to 80.6%. Moreover, the different side chain contents of polyimides achieved by the one-step method had 0.2–0.4 dL g^{-1} inherent viscosity, and all the polyimide films are tough enough for the preparation of alignment films.

4.2 Pretilt angles

The pretilt angles of PI-BCDA0.0, PI-BCDA0.1, PI-BCDA0.2, PI-BCDA 0.4 and PI-BCDA 0.5 alignment films are 1.3°, 3.5°, 4.6°, 7.7° and 13.2°, respectively, as shown in Table 1. Namely, the higher the side chain content, the greater the pretilt angle obtained. At the same time, when the side chain content increases, the surface energy of the alignment films decreases (see below).

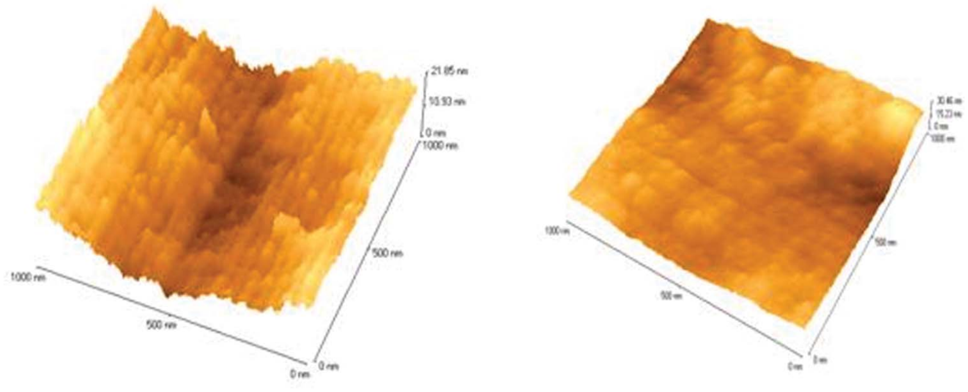
4.3 Atomic force microscopy

Figure 1(a) and 1(b) are AFM images of the surface morphology of non-rubbed PI films and PI films annealed at 270°C for 1 h, respectively. The surface of the non-rubbed PI films shows a profile with a relief height of about 3 nm and lots of microgrooves. Lee *et al.* obtained a similar result of non-rubbed

Table 1. Relationship between pretilt angle and side chain content.

PI-BCDA X[a]	0	10	20	40	50
Pretilt angle	1.3°	3.5°	4.6°	7.7°	13.2°

Note: X[a]: percentage of BCDA in diamine.



(a) (b)

Figure 1. AFM image of PI-BCDA0.5: (a) non-rubbed; (b) annealed (colour version online).

polystyrene films because of the phenyl alignment on the surface [6]. Generally, microgrooves are obtained on the surface of alignment films by rubbing: how could microgrooves be formed on the surface of the non-rubbed PI-BCDA0.5 films? In order to answer this question, TGA experiments were carried out. The TGA results indicate that the alkoxy group of the side chain is decomposed gradually at 270°C. At the same time, the surface profile of PI films annealed at 270°C became smoother, as shown in Figure 1(b). These results indicate that the microgrooves on the surface of non-rubbed PI films are related to the alignment of alkoxy groups on the surface, and the difference of polarity between alkoxy groups and the matrix may result in phase separation which forms microgrooves.

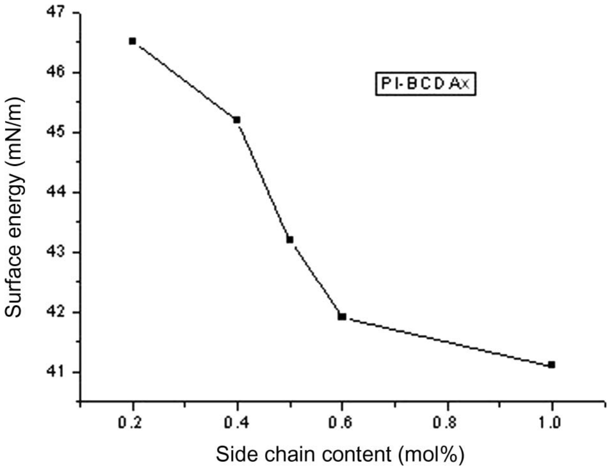


Figure 2. Relationship between side chain content and γ_c.

4.4 Surface energies of polyimides

Incorporation of lower polarity alkyl side chains is a very effective way to improve the pretilt angle of LCs, which usually results in the decrease of surface energy of PI alignment films. AFM results indicate that the alkoxy group side chains aggregate on the surface of PI alignment films, and that the aggregation includes two aspects. One is the stoichiometric increase of BCDA with side chains, and the other is the transfer of side chains from the matrix to the surface of the film because of the difference of polarity between alkoxy groups and the matrix. The latter, however, is usually ignored, and the two aspects have not been analysed in detail. Surface energy (γ_c) is an important property for polyimide alignment layers. The introduction of alkyl side chains could considerably influence the γ_c of polyimide surface. The relationship between the side chain content and γ_c is shown in Figure 2. γ_c decreases monotonically with the increase of side chain content, while it levels off when the side chain content exceeds 60%.

According to the research of Rastogi and Pierre [12], the γ_c of random copolymer of ethylene oxide and propylene oxide is equal to the sum of each separate segment's γ_c. In this paper, there is no control on the chemical structure sequence of polyimides during polymerisation, so the polyimides are random copolymers, which would satisfy Rastogi and Pierre's condition. Based on the experimental data of the surface energy (γ_c), a linear simulation was conducted and is shown in Figure 3. The dashed line was deduced from the following linear equation:

$$\begin{aligned} \gamma_c &= 49.17457 - 11.73429x_1 \\ R^2 &= 0.94431 \end{aligned} \tag{1}$$

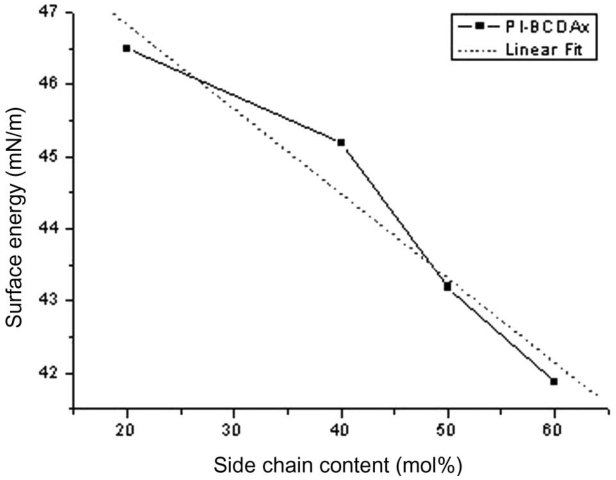


Figure 3. γ_c of PI-BCDAx linearly simulation curve. Note: (solid line: actual line; dashed line: simulation line).

where x_1 is the percentage of PI (BCDA-ODPA) repeat structure group, and R^2 is the linear relationship ratio of the four points in the Figure 3. (It is up to 0.94431, which indicates that the linear simulation equation is effective and practicable.)

Supposing γ_{c1} and γ_{c2} were the surface energies of PI (BCDA-ODPA) and PI (ODA-ODPA) segments respectively, and x_1 and x_2 were the percentage of corresponding repeat structure groups, then:

$$\gamma_c = \gamma_{c1}x_1 + \gamma_{c2}x_2 \tag{2}$$

$$\gamma_c = \gamma_{c1}x_1 + \gamma_{c2}(1 - x_1) \tag{3}$$

after transposition,

$$\gamma_c = (\gamma_{c1} - \gamma_{c2})x_1 + \gamma_{c2}. \tag{4}$$

Substitute (1) into (4):

$$(\gamma_{c1} - \gamma_{c2}x_1) + \gamma_{c2} = -11.73429x_1 + 49.17457,$$
$$\text{then}, \gamma_{c1} = 37.44028, \gamma_{c2} = 49.17457.$$

Additionally, according to Wu's Equation [13], the $\gamma_{c.PE}$ of polyethylene is about 36.0 mN m^{-1}, and the $\gamma_{c.PI}$ of polyimide with no side chain is about 47.0 mN m^{-1}. If the influence of the relationship ratio R^2 was considered, it could be deduced that $\gamma_{c1} = \gamma_{c.PE}$ and $\gamma_{c2} = \gamma_{c.PI}$. According to the discussion above, it was clear that surface energies of PI films consisted of two parts, that is, the energy of non-polar alkyl side chains (γ_{c1}, $\gamma_{c.PE}$) and highly polar polyimide main chains (γ_{c2}, $\gamma_{c.PI}$).

4.5 Surface composition of alignment films

The decrease of polyimide surface energy originates from the compositional change of the surface, which is also affected by the side chain content. Increasing the non-polar composition usually lowers the surface energy. When the number of PI (BCDA-ODPA) segments increases, the surface side chain content increases. However, the increase of surface side chain content may be caused by two reasons: first, the adding of BCDA monomers with side chains; and second, the transference of side chains from the matrix to the surface derived by the polarity difference between alkyl side chains and PI main chains. However, it is difficult to differentiate these by surface energy test alone. Thus, ATR-FTIR and XPS were utilised to further characterise the polyimide surface. Furthermore, a mathematical method was also used. The ATR-FTIR results of PI-BCDA 0.2, PI-BCDA 0.4 and PI-BCDA 0.5 are shown in Figure 4.

Figure 4 shows that the absorption strength of C–H (2849–2958 cm^{-1}) of alkyl side chains increases with the increasing of PI (BCDA-ODPA) segment number, while the absorption at 1780 cm^{-1} ascribed to the imide cycle decreases notably. The ratios of the absorption area of C–H ($A_{C\text{-}H}$) to that of C=O ($A_{C=O}$) as interior standard at 1780 cm^{-1} are 5.5, 30.52 and 37.21 for PI-BCDA 0.2, PI-BCDA 0.4 and PI-BCDA 0.5, respectively. Generally, the experimental absorption area ratios should be consistent with the ratio of the amount of BCDA added during polymerisation, $A_{C\text{-}H0.4}/A_{C\text{-}H0.2}=0.4/0.2=2.0$, $A_{C\text{-}H0.5}/A_{C\text{-}H0.2}=0.5/0.2=2.5$, and $A_{C\text{-}H0.5}/A_{C\text{-}H0.4}=0.5/0.4=1.25$. However, the experimental results show that the corresponding ratios of the absorption area are 5.5, 6.77, and 1.22, respectively. This indicates that when the ratio of BCDA/ODA is less than 0.5, more side chains transfer toward the surface, while when the ratio of BCDA/ODA exceeds 0.5, the transference of side chain levels off or even stops. In this case, the experimental absorption area ratio can be considered as consistent with the ratio of BCDA added during polymerisation.

In order to further accurately determine the surface composition, an XPS experiment was employed. The XPS results of PI-BCDA 0.2, PI-BCDA 0.4 and PI-BCDA 0.5 are shown in Figures 5, 6 and 7, respectively, and the contents of elements C, O, N on the alignment film surface are listed in Table 2.

Since element N only exists in the main chain and the content of element C is higher in alkyl side chains than in the main chain, by comparing the ratio of the two elements we could deduce the distribution of the main chain and side chain on the surface of alignment films. In Table 2, with the increase of the side chain content, the percentage of N and O decreases, while

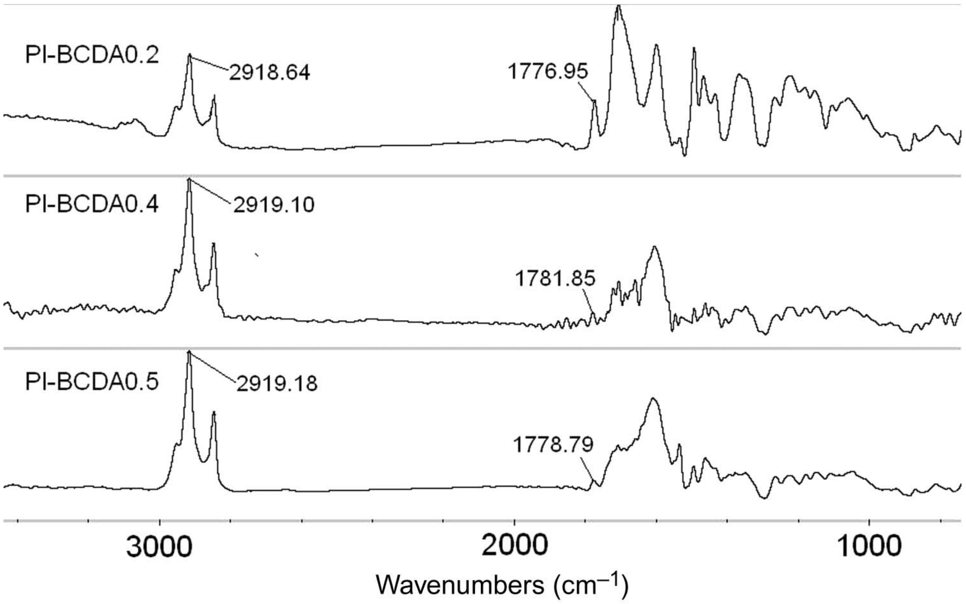


Figure 4. ATR-FTIR of PI-BCDA 0.2, PI-BCDA 0.4 and PI-BCDA 0.5.

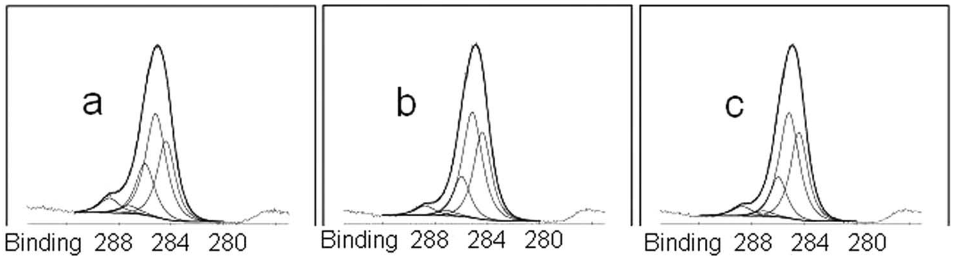


Figure 5. C element in PI-BCDA*x* detected by XPS (a: PI-BCDA 0.2; b: PI-BCDA 0.4; c: PI-BCDA 0.5).

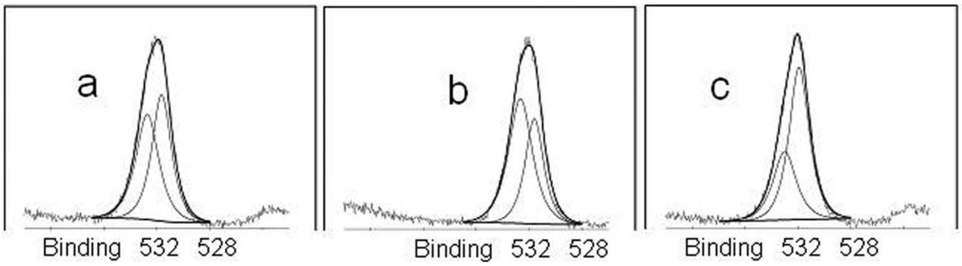


Figure 6. O element in PI-BCDA*x* detected by XPS (a: PI-BCDA 0.2; b: PI-BCDA 0.4; c: PI-BCDA 0.5).

both theoretical and experimental values of the percentage of C increases. However, the experimental values of the percentage of element N existing only in the main chains of PI-BCDA 0.2, PI-BCDA 0.4 and PI-BCDA 0.5 are 3.6%, 1.8%, and 1.3%, which are obviously lower than the corresponding theoretical values 5.1%, 4.7%, and 4.5%. If this phenomenon resulted only from the content difference of added monomers, then the changes of the surface component should be consistent with the theoretical value. Thus, the XPS results indicate that the increase of side chain content on the surface is not only caused by increasing

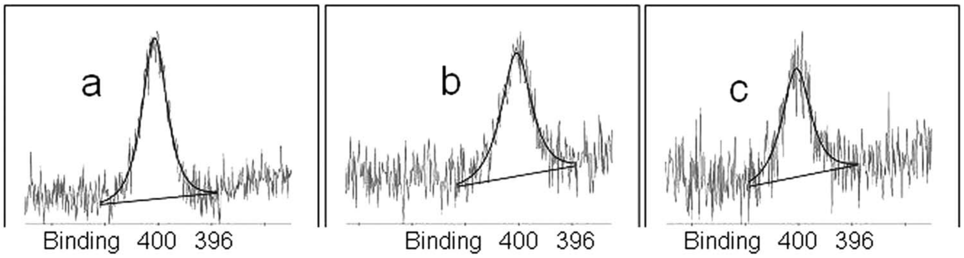


Figure 7. N element in PI-BCDAx detected by XPS (a: PI-BCDA 0.2; b: PI-BCDA 0.4; c: PI-BCDA 0.5).

Table 2. The contents of element C, O, N on the alignment film surface.

	Theoretical (calculated) value			Experimental value		
Composition	C%	O%	N%	C%	O%	N%
PI-BCDA 0.2	80.1	14.8	5.1	81.9	14.5	3.6
PI-BCDA 0.4	82.1	13.2	4.7	86.4	11.8	1.8
PI-BCDA 0.5	83.0	12.5	4.5	87.4	11.3	1.3

monomer content. Namely, more side chains with alkyl groups have transferred from the matrix to the surface, which also agrees with the results of ATR-FTIR and surface energy characterisation. It is hoped that this study may provide some insight into the reason for the pretilt angle increase caused by the introduction of alkyl groups into PI alignment films.

5. Conclusion

A novel diamine containing aryl ester side chains end-capped with alkoxy groups was synthesised successfully and was characterised by FTIR and ^{1}H-NMR. Based on the diamine, a series of copolyimide alignment films were prepared by a one-step process. The results of surface energy investigations, ATR-FTIR and XPS indicate that side chains with alkyl groups could transfer to the surface spontaneously, making the content of the side chain on the surface notably higher than that in the matrix; this is the reason for the increase of the pretilt angle of PI alignment films.

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