Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Effect of the skeleton structures in the side chain of polyimides on their film surface properties and pretilt angles of liquid crystal molecules

Hua Lai[a]; Ming Li[a]; Lin Qin[a]; Xiangyang Liu[a]; Yi Gu[a]
[a] State Key Laboratory of Polymer Material and Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu, Peoples Republic of China

To cite this Article Lai, Hua , Li, Ming , Qin, Lin , Liu, Xiangyang and Gu, Yi(2010) 'Effect of the skeleton structures in the side chain of polyimides on their film surface properties and pretilt angles of liquid crystal molecules', Liquid Crystals, 37: 8, 1013 — 1019

To link to this Article: DOI: 10.1080/02678291003746254

URL: http://dx.doi.org/10.1080/02678291003746254

Liquid Crystals,
Vol. 37, No. 8, August 2010, 1013–1019

Taylor & Francis
Taylor & Francis Group

Effect of the skeleton structures in the side chain of polyimides on their film surface properties and pretilt angles of liquid crystal molecules

Hua Lai, Ming Li, Lin Qin, Xiangyang Liu and Yi Gu*

State Key Laboratory of Polymer Material and Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, Peoples Republic of China

(*Received 6 February 2010; final version received 3 March 2010*)

Polyimides (**1c–4c**, **1c'–4c'**) with side chains (**1–4**) containing four different skeletons were synthesised and characterised. Results showed that a similar high side chain abundance took place on the surface of the films, which was independent of the skeleton structures, while the pretilt angles of liquid crystal molecules were considerably affected by the skeleton structures. **1c**, **1c'** and **2c**, **2c'** achieved vertical alignment while **3c**, **3c'** and **4c**, **4c'** only obtained low pretilt angles. The main reason, based on surface testing results and molecular modelling, was the different interactions between liquid crystal molecules and the skeletons in the side chains.

Keywords: liquid crystal; polyimides; pretilt angle; side chain

1. Introduction

Polyimides (PIs) are widely used as indispensable materials in many electronic products because of their excellent thermal, mechanical and dielectric properties. An example is the alignment layer in liquid crystal displays (LCDs). The alignment layers are deposited on indium tin oxide (ITO)-coated glass to control the orientation of the liquid crystal (LC) molecules, which is influenced by two factors: one is the director of the aligned LC molecules and the other is the pretilt angle, which is defined as the angle between the director and surface. The pretilt angle is correlated with some parameters of a supertwisted nematic (STN) mode LCD, and a high value is preferable for a good performance [1, 2]. However, different display modes need different pretilt angles, for example, STN mode (5–20°) [3], in-place switch mode (0°) [4], and multidomain vertical alignment mode (90°). Therefore, controlling the pretilt angle has become a topic of considerable interest in recent decades. Most research on the preparation of novel alignment layers was carried out by incorporating different kinds of side chains such as alkyl groups [5–8], fluoroalkyl groups [9, 10], and aryl groups end-capped with alkyl groups [11–15]. To the best of our knowledge, much work has been carried out on the effect of length of alkyl groups on pretilt angles, but only a few papers have discussed the skeleton structures (mostly aryl groups) of side chains [16–18], and moreover, the effect of these function groups on the pretilt angle has not been clear up until now.

Our group previously studied a new kind of PI alignment layer pendent with 4-(4''-*tert*-butyldimethylsiloxy)biphenyl group (**1**) and found the introduction of a side chain could largely enhance the pretilt angles [19]. In this study, we explored the influence of the skeletons on pretilt angles. Another three kinds of PIs, that is, 4'-((4''-(*tert*-butyldimethylsiloxy)phenoxy) carbonyl)phenyl group (**2**), 4'-(2-(4''-(*tert*-butyldimethyl- siloxy)phenyl)propan-2-yl)phenyl group (**3**) and 4'-(2-(4''-(*tert*-butyldimethyl- siloxy)phenyl)propan-2-yl)phenyl group (**4**), were synthesised. Surface energy measurements were performed by X-ray photoelectron spectroscopy (XPS) to compare the effect of skeleton structures on the surface properties of these PIs. Pretilt angles on these PI films were also tested and they were found to be significantly dependent on the skeleton structures. Molecular modelling was utilised to elucidate this result at a molecular level.

2. Experimental

2.1 *Materials*

Four diamines (**1a-4a**) in Figure 1 were synthesised by the same route as in our previous work [19]. Pyromellitic dianhydride (PMDA) (Shanghai Institute of Synthetic Resins, Shanghai, China) and 3,3',4,4'-biphenyl dianhydride (BPDA) (Acros Organics, Morris Plains, NJ, USA) was dried for 5 h at 180°C prior to use. *N*-Methyl-2-pyrrolidinone (NMP) (Puyang MYJ Technology, Puyang City, China) was distilled under reduced pressure after dry-

---

*Corresponding author. Email: guyi@scu.edu.cn

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678291003746254
http://www.informaworld.com

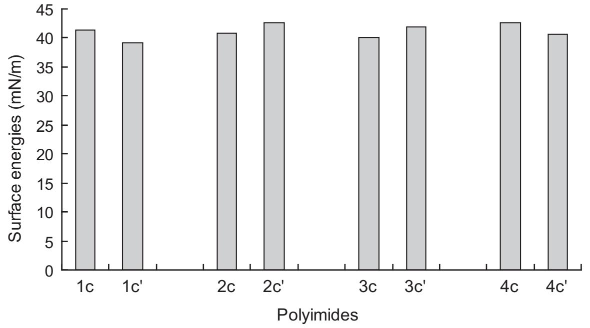


Figure 1. Surface energies of polyimides with different skeletons.

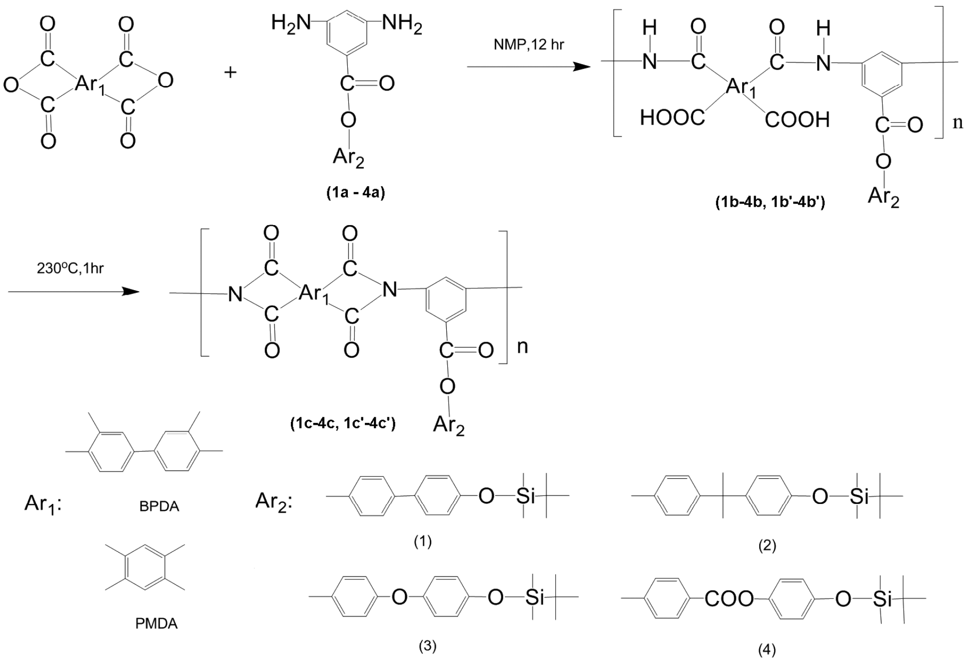
ing by phosphorus pentoxide. The ITO-coated glass was obtained from CSG Holding Co. Ltd (Shenzhen, China). 4-pentyl-4'-cyanobiphenyl (5CB, $n_o = 1.53$, $n_e = 1.74$, $T_d = 24°C$, $T_i = 34°C$) was supplied by Beijing Tsinghua Yawang Liquid Crystal Materials Co. Ltd (Beijing, China).

2.2 *General procedure for the preparation of PIs*

The precursors of the PIs, poly(amic acid) solutions, were condensed using the diamines (**1a–4a**) with PMDA or BPDA, respectively. The polymerisation procedure is illustrated in Scheme 1. In a 25 ml three-necked round-bottom flask equipped with a mechanical stirrer and a nitrogen-inlet, a diamine (0.001 mol) was dissolved in NMP and then a dianhydride (0.0012 mol) was added to the solution with a solid content of 10 wt%. The reaction mixture was stirred at 0°C for 12 h in a nitrogen flow to give a yellow poly(amic acid) solution (**1b–4b** for BPDA, **1b'–4b'** for PMDA). The respective poly(amic acid) solutions were cast on glass plates and cured under 230°C for 1 h to obtain the PI films (**1c–4c** for BPDA, **1c'–4c'** for PMDA).

2.3 *Characterisation*

Attenuated total reflection Fourier transform infrared (**ATR-FTIR**) spectroscopy was recorded on a Nicolet 560 Fourier transform spectrometer using PI films coated on calcium fluoride glass. To test surface energy, the contact angles of deionised water and methylene iodide on the surface of the PI films were measured by a Krüss DSA100 (Krüss, Hamburg, Germany) measurement device. Each sample was tested three times and mean contact angles were obtained. A Young's harmonic mean equation was applied to predict the surface energies from the contact angles. XPS measurements were made with a Kratos ASAM 800 spectrometer (Kratos Analytical Ltd, Manchester, UK) using AlK$_\alpha$ (1486.6 eV) monochromatised radiation. High resolution spectra were acquired with pass energy of 10 eV and a take-off angle of 20° or 70°, respectively. LC cell fabrication and pretilt angle measurements were made as follows. Poly(amic acid) solutions (10 wt%) were spin-coated on 25 × 25 mm ITO-coated glass at 500 rpm for 5 s and then 1500 rpm



Scheme 1. Preparation of polyimides with different side chains.

for 10 s, followed by thermal imidisation at 230°C for 1 h. The prepared PI films were subsequently rubbed with a rubbing strength of 57.0 mm. 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 (4-4')-pentyl-cyano-biphenyl (5CB) by a capillary method. The pretilt angles for the fabricated LC cells were measured by a crystal rotation method with a PAT-20 measurement device (Changchun Liancheng Instrument Co. Ltd, Changchun City, China). Large pretilt angles near 90° were confirmed by conoscopy using a Leica DM LB polarised light microscopy (Leica Microsystems, Wetzlar, Germany). Molecular mechanics and molecular dynamics simulation were performed using Materials Studio software by employing a Dreiding force field. The simulation detail can be referred to in our recent publication [20].

3. Results and discussion

3.1 Synthesis

The PIs were prepared by a conventional two-step method. The precursor poly(amic acid) solutions were found to have a low inherent viscosity of 0.25–0.30 dl g^{-1}, which resulted from the rigid and bulky side chains and *m*-phenyldiamine-typed backbones. However, when the poly(amic acid) solutions were spin-coated on to glass and imidised thermally, PI films with no crevices, even when subject to rubbing, could be obtained. The FTIR spectra of these PI films were similar, with peaks near 1780 and 1720 cm^{-1} ascribed to the stretching of carbonyl groups and at 2857–2956– cm^{-1} assigned to the stretching of C-H on $Si(CH_3)_2C(CH_3)_3$.

3.2 Surface properties

Surface energies of PI films were tested as shown in Figure 1. **1c**–**4c** possessed close surface energies, around 40.01–42.64 mN m^{-1}, which indicated that surface energies were independent of the skeleton structures. (Note: The discrepancy in surface energies for 4′-(tert-butyldimethylsiloxy)biphenyl-4-yl 3,5-diaminobenzoate (DPA) reported earlier [19], may be a result of the test conditions, such as humidity or temperature.) Furthermore, **1c'**–**4c'** exhibited nearly the same surface energies as those of **1c**–**4c**, showing that the backbones of PIs based on different dianhydrides had little effect on surface energies. Since surface energies were determined by chemical groups at the furthest surface, we considered that the PI surfaces were approximately the same, not influenced by the skeleton and backbones.

To investigate this suggestion XPS was performed on the **1c**–**4c** surface. For the four types of films, silicon content was used as the standard for side chain abundance and tested with take-off angles of 20° and 70° in order to explore the change of side chain abundance with depth. From data shown in Table 1, silicon content was found to be much higher than the theoretical value. The PI films showed similar silicon content except that **3c** had a higher silicon content of 6% due to an extra non-polar $-C(CH_3)_2-$ group. The silicon content obtained under a take-off angle of 20° was higher than that under a take-off angle of 70°. This means the side chain tends to accumulate on the surface, which resulted from the large polarity difference between the *tert*-butyldimethylsiloxy (TBDMS) groups and PI backbones.

Table 1. Theortical and measured silicon content of **1c**–**4c**.

Polymers	Silicon content (%) Take-off angle of 70°	Silicon content (%) Take-off angle of 20°	Theoretical silicon content (%)
1c	2.89	3.11	1.96
2c	2.53	2.71	1.85
3c	4.42	6.00	1.85
4c	2.53	3.18	1.92

3.3 The effect of skeleton structures on pretilt angles and molecular modelling

Pretilt angles dramatically changed with different skeleton structures, as shown in Figure 2. For non-rubbed **1c,** and **2c**, vertical alignment took place and rubbing caused a small decrease in pretilt angles. However, non-rubbed **3c** and **4c** could not align LC molecules uniformly. For rubbed **3c**, pretilt angles were found only at 2–4° and for rubbed **4c** pretilt angles were in the dark zone (around 20–70°). The type of dianhydride had no obvious effect on the pretilt angles, which suggests that the main chain structures had little effect on pretilt angle in the article.

From the surface properties mentioned above, **1c**–**4c** had close surface energies and side chain abundance on the surface. Therefore, side chain abundance could not be a convincing explication for the discrepancy in pretilt angles, that is, the TBDMS groups were not the dominant effect. Therefore, the only difference, the skeletons, could determine the pretilt angles. To confirm further our assumptions, we applied a molecular modelling method to elucidate the effect of skeleton structures on the pretilt angle of LC molecules at the molecular level, using **1c** and **3c** for comparison.

The optimised conformation of the side chains of **1c** and **3c** on the surface is shown in Figure 3. For **1c**, the side chains tended to extend outside (Figure 3(b)). For **3c**, they were positioned with $-C(CH_3)_2-$ pointing outwards (Figure 3(c)). However, the TBDMS groups in

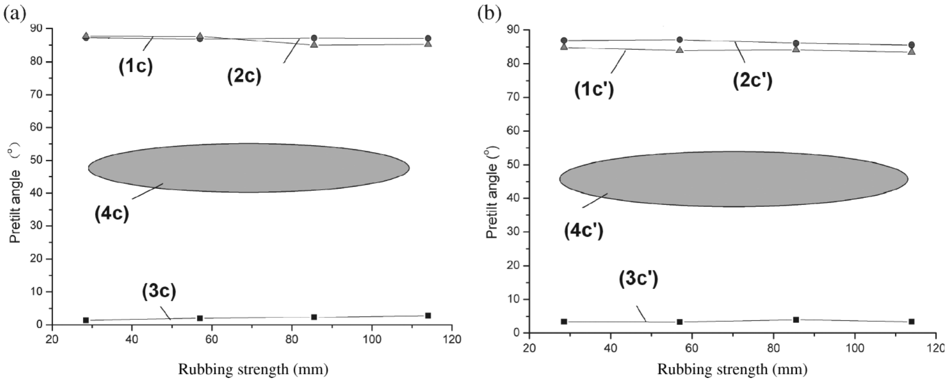


Figure 2. Dependence of pretilt angles on middle groups in the polyimides **1c**–**4c** (a) and **1c'**–**4c'** (b).

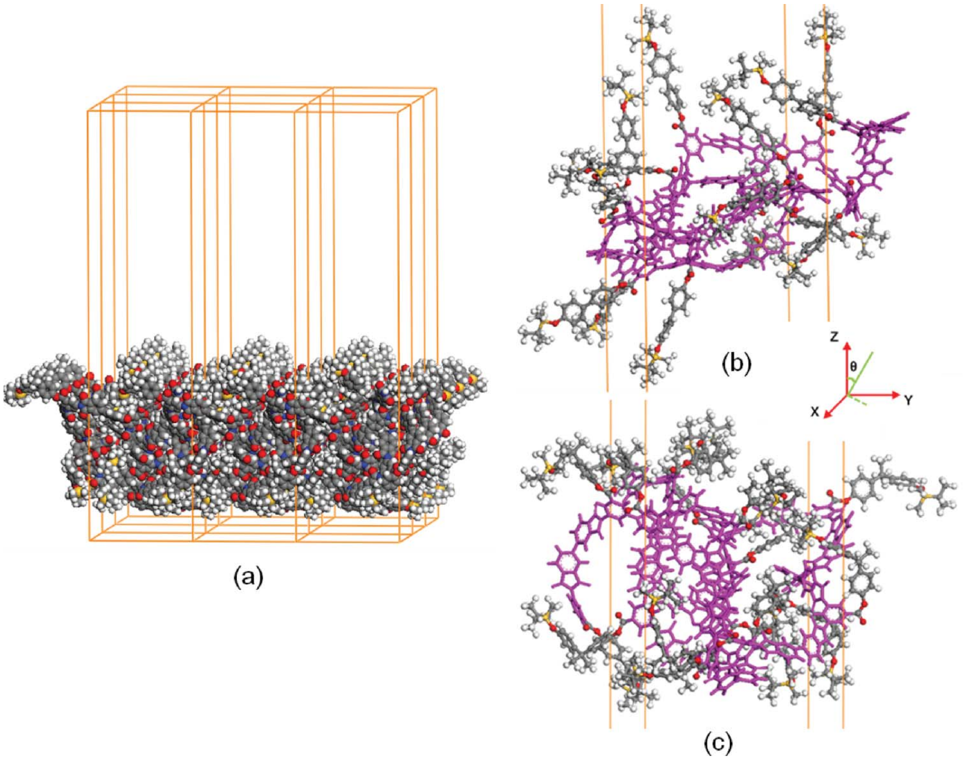


Figure 3. The initial structure before simulation (a); the optimised structures of molecular modelling for **1c** (b) and **3c** (c). (The backbone of the polyimide is presented by a pink stick model, while the side chain is represented by a ball-stick model.)

both **1c** and **3c** were enriched at the furthest surface, which was consistent with surface energies and XPS data.

The average angle between the phenyl group plane and z-axis was defined as θ (Figure 3); therefore, the average angle between the phenyl group plane of the side chain and surface (x–y plane) was $90 - \theta$. Figure 4 shows the relationship between θ and distance from the centre of mass in the z-axis. When the distance was close to -2.0 or 2.0 nm, it was considered to be 'surface area'. For **1c**, $\cos\theta$ at 'surface area' was near 1 (Figure 4(b)), which meant θ was near 0°, that is, the phenyl group in the side chain was almost vertical to the surface. For **3c**, $\cos\theta$ at 'surface area' (Figure 4(a)) was relatively lower than that for **1c**, indicating its θ was larger than 0°. Therefore, the phenyl group in the side chain was tilted towards the surface. Since **3c** contains two phenyl groups bridged with a sp^3 C, if the inner phenyl group was nearly vertical to the surface, the outside phenyl group must adopt a planar conformation, which induces an average θ higher than 0°. This explains why

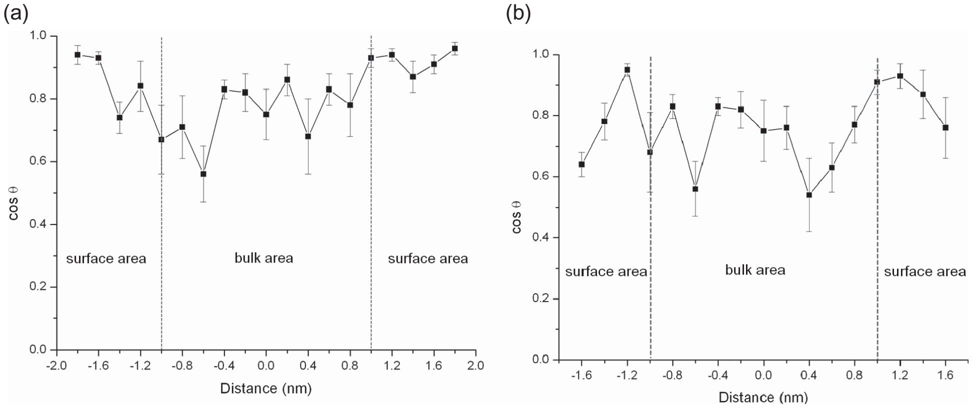


Figure 4. The relationship between the tilt angle (θ) of phenyl groups in the side chain and distance from the centre of mass in the z-axis direction for **1c** (a) and **3c** (b).

cos θ for **3c** increased from 1.0 to 1.2 nm and then decreased when the distance was more than 1.2 nm.

The tilt angle of the LC molecules to the surface was also examined by modelling the conformation of LC molecules on the previously optimised PI surfaces. The director of 5CB was defined to be the vector from C connected with the -CN group to the C connected with the alkyl group. The relationship of the probability and the angle between the vector and surface (x–y plane) is shown in Figure 5. For **1c**, tilt angles around 70–90° had the highest probability, while for **3c** a tilt angle of 0° had the highest probability. The probability for tilt angles around 70 to 90° was higher than that of –70 to –90° for **1c**, indicating the CN group on 5CB tended to point to the surface. The reason was that the CN had a strong interaction with the C=O on the main chain, which explained the spontaneous vertical alignment without rubbing [21]. On the contrary, the probability was symmetric at 0° for **3c**, indicating a CN parallel to the surface.

As many results have shown, the generation of the pretilt angle is the result of interactions, such as Van der Waals forces [22]. However, steric effects may make some interactions more favourable, especially for LC molecules. **1c**, **1c'**, **2c** and **2c'** have extended skeletons that are upstanding on the surface (Figure 6). The biphenyl core of LC molecules may match the skeleton through an inter-molecular pi-pi interaction, resulting in vertical alignment. However, **3c**, **3c'**, **4c** and **4c'** have bent skeletons with outside phenyl groups tilted from the surface. In **3c** and **3c'** particularly the outside phenyl groups were nearly planar because of the huge and non-polar spacer -C(CH_3)$_2$-. The inter-molecular pi-pi interaction between the outside phenyl group and the biphenyl core of LC molecules was less strong compared with that for **1c**. Therefore, Van der Waals force may also play an important role in the generation of a pretilt angle near 0°, apart from the interaction between the outside phenyl group and the biphenyl core of LC molecules.

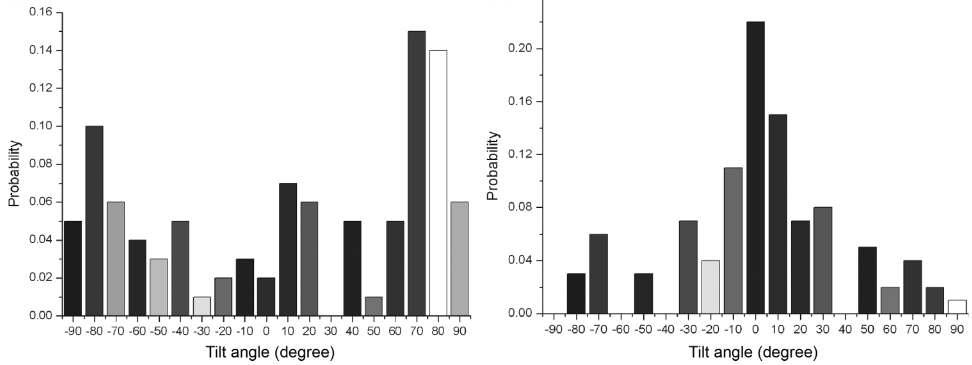


Figure 5. The probability of tilt angle of liquid crystal molecules for **1c** (a) and **3c** (b).

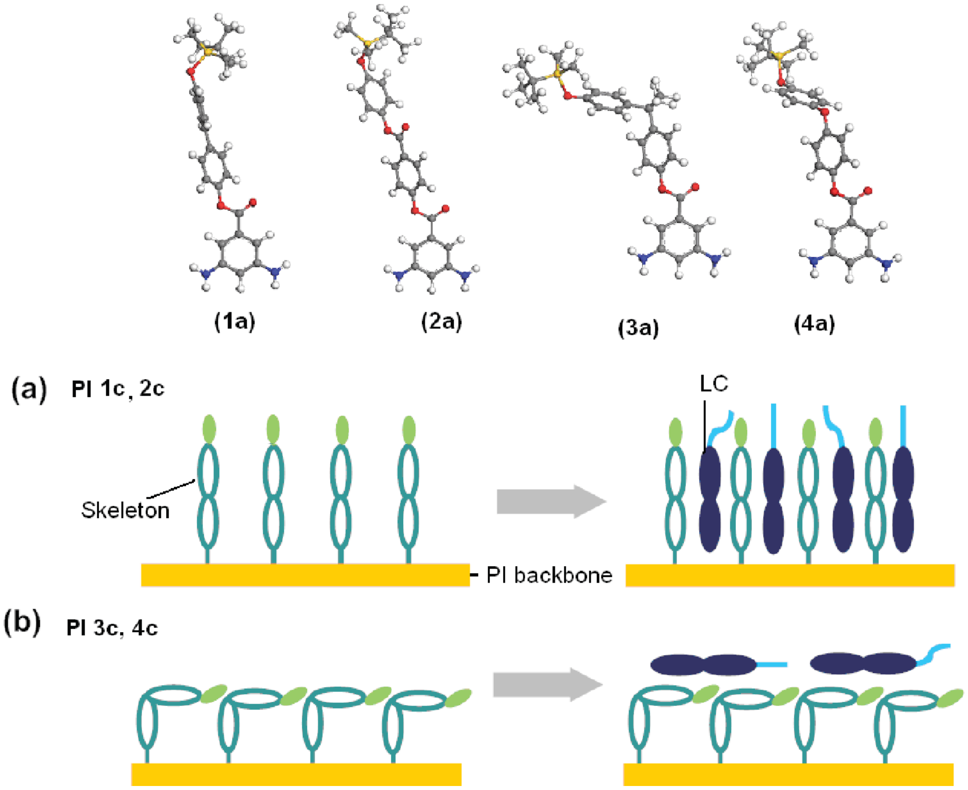


Figure 6. Schematic drawing of the alignment of liquid crystal molecules on polyimide surfaces (colour version online).

4. Conclusion

Polyimides (**1c-4c**, **1c'-4c'**) with side chains containing four different skeletons (**1–4**) were synthesised and characterised. Results from XPS measurements showed similar high side chain abundance took place on the surface of these films independent of skeleton structures. However, pretilt angles of LC molecules were considerably affected by the skeleton structures. **1c**, **1c'**, **2c** and **2c'** could achieve vertical alignment while **3c**, **3c'**, **4c** and **4c'** had low pretilt angles. Combining the surface properties and molecular modelling, it was suggested that this could be attributed to the interaction between LC molecules and the skeletons in the side chains.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 50433010 and 50773044) and the Doctoral Fund of Ministry of Education of China (No.20040610028).

References

[1] Takatoh, K.; Sakamoto, M.; Hasegawa, R.; Koden, M.; Itoh, N.; Hasegawa, M. *Alignment Technologies and Applications of Liquid Crystal Devices*; Taylor & Francis: London, 2005.
[2] Scheffer, T.; Nehring, J. *Annu. Rev. Mater. Sci.* **1992**, *27*, 555–583.
[3] Bahadur, B. *Liquid Crystals: Applications and Uses*; World Scientific: Singapore, 1990.
[4] Oh-e, M.; Yoneya, M.; Ohta, M.; Kondo, K. *Liq. Cryst.* **1997**, *22*, 391–400.
[5] Kim, D.H.; Jung, J.C. *Polym. Bull. (Heidelberg, Ger.)* **2003**, *50*, 311–318.
[6] Sarkar, A.; More, A.S.; Wadgaonkar, P.P.; Shin, G.J.; Jung, J.C. *J. Appl. Polym. Sci.* **2007**, *105*, 1793–1801.
[7] Lee, S.J.; Jung, J.C.; Lee, S.W.; Ree, M. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3130–3142.
[8] Li, L.; Yin, J.; Sui, Y.; Xu, H.J.; Fang, J.H.; Zhu, Z.K.; Wang, Z.G. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1943–1950.
[9] Liu, J.G., Li, Z.X.; Wu, J.T.; Zhou, H.W.; Wang, F.S.; Yang, S.Y. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1583–1593.
[10] Seo, D.S.; Nishikawa, M.; Kobayashi, S. *Liq. Cryst.* **1997**, *22*, 515–517.
[11] Lee, J.K.; Lee, S.J.; Jung, J.C.; Zin, W.C.; Chang, T.; Ree, M. *Polym. Adv. Technol.* **2006**, *17*, 444–452.
[12] Jung, J.C.; Lee, K.H.; Sohn, B.S.; Lee, S.W.; Ree, M. *Macromol. Symp.* **2001**, *164*, 227–238.
[13] Lee, S.B.; Shin, G.J.; Chi, J.H.; Zin, W.C.; Jung, J.C.; Hahm, S.G.; Ree, M.; Chang, T. *Polymer* **2006**, *47*, 6606–6621.

[14] Wang, D.H.; Shen, Z.H.; Guo, M.M.; Cheng, S.Z.D.; Harris, F.W. *Macromolecules (Washington, DC, US)* **2007**, *40*, 889–900.

[15] Lee, J.B.; Lee, H.K.; Park, J.C.; Kim, Y.B. *Mol. Cryst. Liq. Cryst.* **2005**, *439*, 161–172.

[16] Liu, Z.J.; Yu, F.F.; Zhang, Q.; Zeng, Y.; Wang, Y.H. *Eur. Polym. J* **2008**, *44*, 2718–2727.

[17] Lee, Y.J.; Choi, J.G.; Song, I.; Oh, J.M.; Yi, M.H. *Polymer* **2006**, *47*, 1555–1561.

[18] Lee, Y.J.; Kim, Y.W.; Ha, J.D.; Oh, J.M.; Yi, M.H. *Polym. Adv. Technol.* **2007**, *18*, 226–234.

[19] Lai, H.; Qin, L.; Liu, X.Y.; Gu, Y. *Eur. Polym. J* **2008**, *44*, 3724–3731.

[20] Li, M.; Lai, H.; Chen, B.X.; Liu, X.Y.; Gu, Y. *Liq. Cryst.* **2010**, *37*, 149–158.

[21] Makoto, Y.; Yasushi, I. *Liq. Cryst.* **1996**, *21*, 347–359.

[22] Schadt, M.; Schmitt, K.; Kozinkov, V.; Chigrinov, V. *Jpn. J. Appl. Phys.* **1992**, *31*, 2155–2164.