This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

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

Preparation of vertical alignment layers by blending polyimide precursors with and without side chains

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

To cite this Article Lai, Hua , Liu, Xiangyang , Qin, Lin , Li, Ming and Gu, Yi(2009) 'Preparation of vertical alignment layers by blending polyimide precursors with and without side chains', Liquid Crystals, 36: 2, 173 — 178

To link to this Article: DOI: 10.1080/02678290902752140

URL: http://dx.doi.org/10.1080/02678290902752140

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Liquid Crystals,
Vol. 36, No. 2, February 2009, 173–178

Preparation of vertical alignment layers by blending polyimide precursors with and without side chains

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

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

(Received 25 December 2008; final form 15 January 2009)

A series of polyimides (PIs) were prepared from the precursors, blends of a poly(amic acid) and a side-chain poly(amic acid), based on a diamine 4′-(*tert*-butyldimethylsiloxy)biphenyl-4-yl 3,5-diaminobenzoate (DPA). The blended polyimide (bl-PI) films were relatively tough. The surface properties of the bl-PI films were characterised by surface energy measurement, X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance infrared spectroscopy (ATR-IR). The results showed that the non-polar side chains were highly enriched on the surface and 90° pretilt angles of liquid crystal molecules were generated regardless of side chain content. For comparison, the copolyimides (co-PI) with different DPA contents were synthesised. It was found that the enrichment of the side chain on the surface increased with increasing DPA content and the pretilt angles of liquid crystal molecules rose from 3° to above 20° when DPA content increased from 10% to 30%. For the polyimides based on a diamine without a non-polar end group, 4′-biphenyl-4-yl 3,5-diaminobenzoate (DABBE), both bl-PIs and co-PIs could only generate the same low pretilt angles. In conclusion, by blending poly(amic acids) based on DPA, tough vertical alignment layers could be prepared.

Keywords: polyimide; blend; alignment layers; pretilt angle; side chain

1. Introduction

In today's liquid crystal displays (LCDs), one of their indispensable parts are the so-called alignment layers, which are coated on indium tin oxide (ITO)-coated glass to control the alignment of liquid crystal molecules (LCM) (*1*). Usually, the alignment layers are polyimide (PI) films. Besides the property of aligning, PI films need to induce LCM to certain pretilt angles for different display modes. For supertwisted nematic (STN) LCD, pretilt angles ranging from 5° to 20° are needed, particularly for vertical aligned nematic (VAN) LCD, where pretilt angles of 90° are a must (*2*). In order to raise the pretilt angles, side chains, mostly long and bulky, are incorporated into the PIs, which results in low molecular weight, and thus bad mechanical strength, of the resultant films. Li *et al.* (*3*) prepared homopolyimide precursors poly(amic acid)s based on a diamines pendent with a long alkyl group and an alicyclic dianhydride, exhibiting inherent viscosities lower than 0.22 dL g^{-1}, a level that could not afford strong polyimide films. Kim *et al.* (*4*) reported the same results in which the intrinsic viscosities of the side-chain poly(amic acid)s were about 0.25 dL g^{-1}. Copolymerisation of side-chain diamines with common diamines can raise the strength of polyimide films. Lee *et al.* (*5*) used 4,4′-Diaminodiphenylmethane (DDM) and a diamine with side chains at a ratio of 9:1 to obtain copoly(amic acid)s that showed an inherent viscosity higher than 0.75 dL g^{-1}. However, the decrease of side chain content may also induce pretilt angles to decrease. Lai *et al.* (*6*) found that copolyimides (co-PI) based on a diamine containing the *tert*-butyldimethylsiloxy group could not obtain a pretilt angle of 90° until the side chain content was higher than 70%. Liu *et al.* (*7*) also reported that pretilt angles decreased sharply from 90° to 3° when the side chain content decreased to 20%.

A blending method was proposed to solve the aforementioned dilemma, in which mixtures of polyimides with and without side chains (blended polyimides (bl-Pis)) could possess the integration of mechanical strength and vertical alignment ability. The mixtures were derived from precursor blends of the poly(amic acid) based on 4′-(*tert*-butyldimethylsiloxy)biphenyl-4-yl 3,5-diaminobenzoate (DPA) and 3,3′,4,4′-biphenyl dianhydride (BPDA) and the poly(amic acid) based on *m*-phenylenediamine (*m*-PDA) and BPDA with a different composition by thermal imidisation. The effect of the calculated side chain content on the properties of polyimide films and the pretilt angles was investigated. The results obtained were compared with that of the corresponding co-PI based on DPA, *m*-PDA and BPDA. For a comparison of the dependence of pretilt angles on the structure of side chains, bl-PIs and co-PIs based on a

---

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

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290902752140
http://www.informaworld.com

diamine without a non-plar end group, 4′-biphenyl-4-yl 3,5-diaminobenzoate (DABBE), were prepared and tested. The reason for the different results was discussed.

2. Experiments

2.1 Materials

DPA and DABBE were synthesised in our lab as reported in literatures (*6*, *8*, *9*). *m*-PDA was purified by sublimation. BPDA (Acros Organics, New Jersey) was dried for 5 hrs at 180°C prior to use. *N*-Methyl-2-pyrrolidinone (NMP) (Pu Yang MYJ Technology, China) was distilled under reduced pressure after being dried by P_2O_5. The ITO-coated glass was obtained from CSG Holding Co., Ltd, China. The 4-pentyl-4′-cyanobiphenyl (5CB, $n_o = 1.53$, $n_e = 1.74$, $Td = 24°C$, $Ti = 34°C$) was supplied by Beijing Tsinghua Yawang Liquid Crystal Materials Co. Ltd., China.

2.2 Measurements

Inherent viscosities were measured at 0.5 g dL^{-1} concentration in NMP at 25°C using an Ubbelohde viscometer. The contact angles of the deionised water and the methylene iodide on the surface of the PI films were measured by a Krüss DSA100 goniometer system (Krüss GmbH, Germany). Each sample was tested three times and the mean contact angles were obtained. A Young's harmonic mean equation was applied to predict the surface energies from the contact angles. Attenuated total reflectance infrared spectroscopy (ATR-IR) spectra were recorded on a Nicolet 560 Fourier transform spectrometer (Thermo Nicolet Corporation, USA). The internal reflection element was a crystalline ZeSe plate with an aperture angle of 45° yielding 32 internal reflections. X-Ray photoelectron spectroscopy (XPS) measurements were made with a Kratos ASAM800 spectrometer (Kratos Analytical Limited, UK) using AlK_α (1486.6 eV) monochromatised radiation. High-resolution spectra were acquired with a pass energy of 10 eV and a take-off angle of 20°.

2.3 Preparation of bl-PIs and co-PIs

2.3.1 Blending process

Homopoly(amic acid) solutions were condensed using DPA, *m*-PDA with BPDA, respectively. The polymerisation procedure is given below, as illustrated in Figure 1(a). In a 25 ml three-necked round-bottom flask, equipped with a mechanical stirrer and a nitrogen-inlet, 0.001 mol diamine were dissolved in NMP and then BPDA (0.3001 g, 0.0012 mol) was added into the solution with a solid content of 10wt%. The reaction mixture was stirred at 0°C for 12 hrs with a

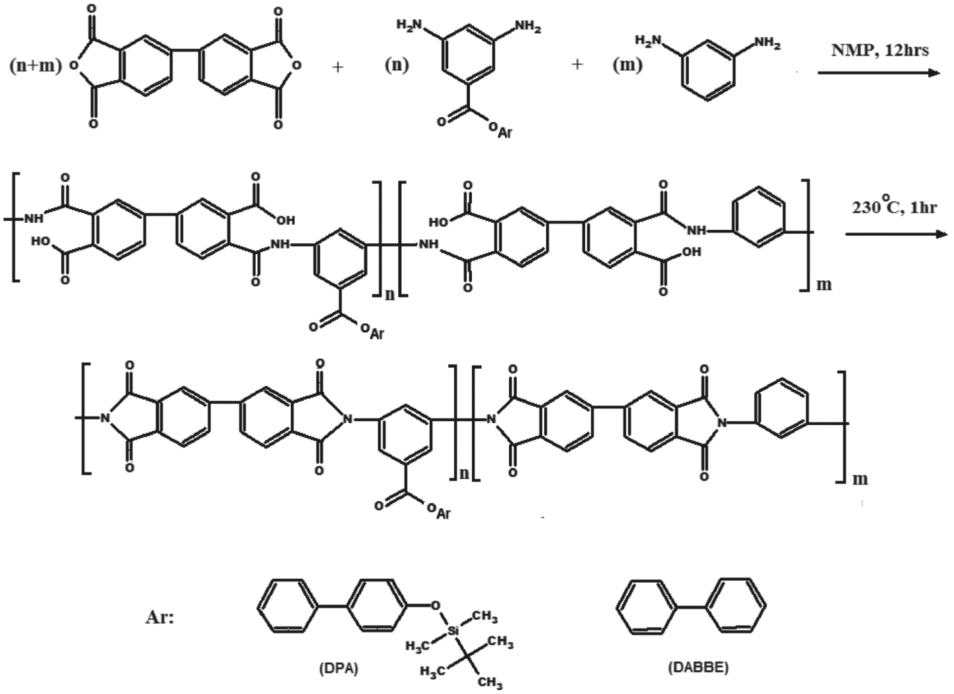


Figure 1. Synthetic route of polyimides (a) homopolymers ($n = 0$ for polyimide based on *m*-PDA; $m = 0$ for polyimide based on DPA or DABBE); (b) copolymers $n{:}m$ = 1:9, 2:8, 3:7.

nitrogen flow to give a yellow poly(amic acid) solution. The poly(amic acid) solutions based on DPA, and that based on *m*-PDA, were mixed, with ratios of 1:9, 2:8 and 3:7, to get blended poly(amic acid) solutions. The PIs from the corresponding poly(amic acid)s were named as co-PI-DPA10, co-PI-DPA20 and co-PI-DPA30, respectively. We did not study the polyimides with DPA content higher than 30% because of the non-flat surface caused by phase separation, and those with DPA content lower than 10%, although the vertical alignment of liquid crystals could still be achieved when DPA content was 5%.

2.3.2 *Copolymerisation process*

Copoly(amic acid) solutions were condensed using DPA, *m*-PDA and BPDA together. The copolymerisation procedure was similar to the homopolymerisation mentioned above. The molar content of the DPA was controlled to 10%, 20%, 10% and 30%, as shown in Figure 1(b). The PIs from the corresponding poly(amic acid)s were named as co-PI-DPA10, co-PI-DPA20 and co-PI-DPA30, respectively.

The preparation of bl-PIs and co-PIs based on DABBE are similar to that of bl-PIs and co-PIs based on DPA. The corresponding polyimides were named as bl-PI-DABBE10, bl-PI-DABBE20 and bl-PI-DABBE30 and co-PI-DABBE10, co-PI-DABBE20 and co-PI-DABBE30, respectively.

2.4 LC cell fabrication and pretilt angle measurement

Poly(amic acid) solutions (10wt%) were spin-coated on 25×25 mm^2 ITO-coated glasses at 500 rpm for 5 s and 1500 rpm for 10 s, respectively, followed by thermal imidisation under 230°C for 1 hr. The prepared PI films were subsequently rubbed with a rubbing strength of 57.0 mm, using the same method described in (*6*). 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, China). Large pretilt angles, near 90°, were confirmed by conoscopy using a Leica DM LB polarised light microscope (Leica Microsystems, Germany).

3. Results and discussion

3.1 The strength of polyimide films

The introduction of bulky side chains into diamines DPA and DABBE resulted in tremendously lowered reactivity with dianhydrides. The inherent viscosities of homopoly(amic acid)s, based on DPA and DABBE with BPDA, were 0.25 and 0.34 dL g^{-1}, respectively, which showed the polyimides obtained by thermal imidisation had a very low molecular weight and hardly afforded any non-cracked films. The poly(amic acid) based on *m*-PDA and BPDA, revealing an inherent viscosity of 1.2 dL g^{-1}, could be used to prepare strong polyimide films while the pretilt angles were no bigger than 3°. For copoly(amic acid)s, the inherent viscosities decreased when the ratios of DPA to *m*-PDA rose. Results showed that the inherent viscosities were 0.91, 0.71 and 0.68 dL g^{-1} when the content of the DPA was 10%, 20% and 30%, respectively, and although non-cracked films were obtained, the apparent strength rapidly decreased when the content of DPA increased. The blended poly(amic acid)s showed inherent viscosities near 1.2 dL g^{-1} and all obtained tough films. With the same content of DPA, films made by blending were apparently stronger than those made by copolymerisation. Thus, by using the blending method, films with relatively high mechanical strength could be obtained in the presence of the low reactivity composition of side-chain diamines, which would give rise to high pretilt angles, or 90° pretilt angles.

3.2 The surface construction of polyimide films

What a surface is constructed by is the most important issue for alignment layers, as the alignment and pretilt angles of LCM are determined by the surface. By using the surface energy measurement, XPS and ATR-IR, the surfaces of the polyimide films were characterised. In Figure 2, we give the results of the surface energies measurement. For bl-Pis-based DPA, each film exhibited almost the same surface energies, lying in the range 37.78–37.79 nM m^{-1}, which means, from the point of view of enrichment of the *tert*-butyldimethylsiloxy group on surface deserved lower surface energies, that the surface construction of bl-PI films was independent of the calculated side chain content. The data from XPS also proved the conclusion in which the Si content on the surface of bl-PI-DPA10, bl-PI-DPA20 and bl-PI-DPA30 was 2.91%, 2.12% and 2.13%, respectively. For homopolyimides based on DPA and BPDA, the surface energy and Si content on the surface were 34.43 nM m^{-1} (*6*) and 3.11%. Thus, a presumption could be made that the surface construction of bl-PI films is similar to that of the homopolyimide based on DPA and BPDA.

For co-PI based on DPA, the surface energies decreased from 46.06 nM m^{-1} to 41.44 nM m^{-1} when the calculated side chain content increased from 10% to 30%, showing the enrichment of side chains

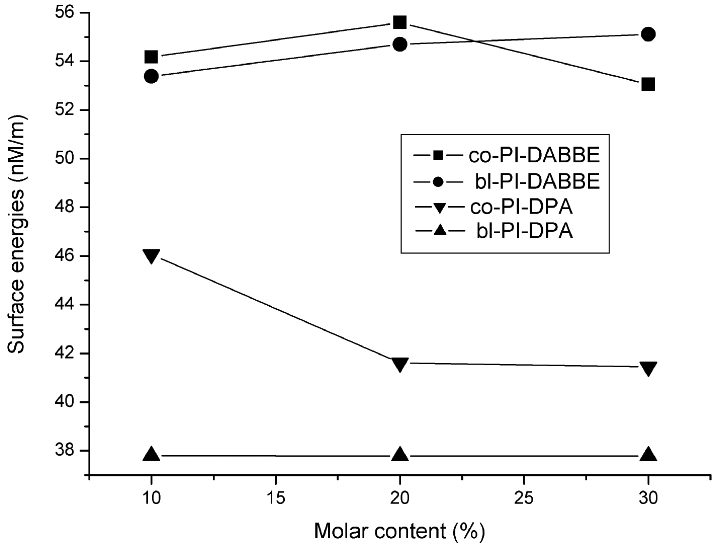


Figure 2. Surface energies of PI films.

enhanced with the calculated side chain content increasing, while it was still lower than that for the bl-PIs. From the ATR-IR shown in Figure 3, the absorption at 2850–2960 cm^{-1}, assigned to –CH$_3$ on the *tert*-butyldimethylsiloxy group of bl-Pis, was slightly stronger than that of co-PIs for the same side chain content, indicating that the enrichment of side chains on the surface of bl-PI films was higher than that of side chains on the surface of co-PI films. This result was consistent with the surface energies measurement. However, the difference between the absorption of bl-PIs and that of co-PIs was not remarkable because ATR-IR is not fully surface-sensitive with a testing depth of more than 2 μm.

The higher enrichment of bl-PIs compared with co-PIs was attributed to the following reasons. Firstly, for the bl-PIs, the homopolyimide based on DPA was easy to separate and enrich on the surface, during the

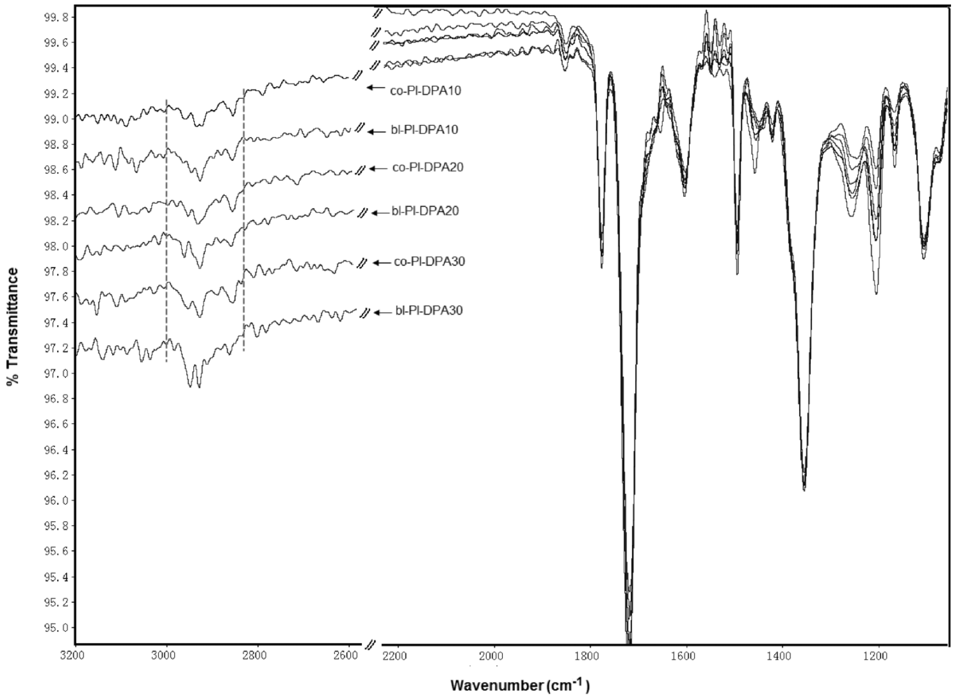


Figure 3. ATR-IR of co-PI-DPAs and bl-PI-DPAs.

imidisation process, from the homopolyimide based on *m*-PDA, because the former contained many highly non-polar *tert*-butyldimethylsiloxy groups and had a low weight molecule of precursor. The separation and enrichment made the surface of bl-PIs just like that of homopolyimides based on DPA, with almost the same surface energies and Si content on the surface without being affected by the calculated side chain content. Secondly, for the co-PIs, the separation and enrichment of side chains onto the surface were somehow difficult because the non-polar *tert*-butyldimethylsiloxy groups, sparsely distributed on the macromolecule, and the co-PIs had fairly high molecular weight, thus lowering the mobility of the side chains. The increasing of the calculated side chain content not only incorporated more non-polar *tert*-butyldimethylsiloxy groups, but also reduced molecular weight, which resulted in lower surface energies.

For the bl-PIs and co-PIs based on DABBE, the surface energies of the film with different calculated side chain content were almost the same, ranging from 53.05 to 55.59 nM m^{-1}, as shown in Figure 2. The reason was that in the absence of non-polar *tert*-butyldimethylsiloxy groups, no separation and enrichment could take place, in other words, the construction of films was not influenced by blending or copolymerisation.

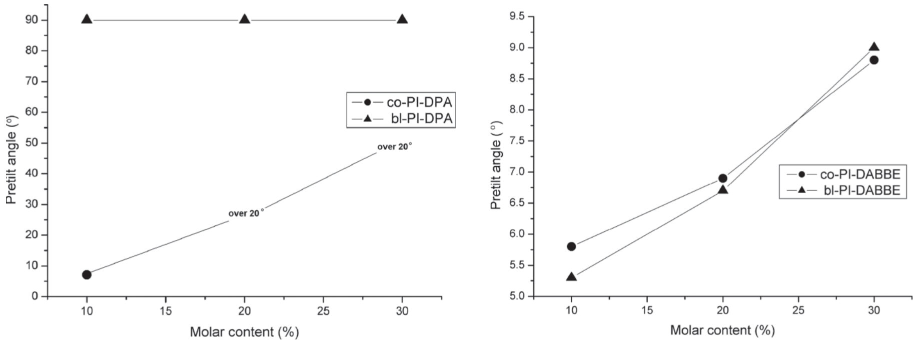
3.3 *Pretilt angles of LCM on bl-PIs and co-PIs*

The pretilt angles of LCM on the bl-PI films based on DPA were found to be 90°, without being affected by the calculated side chain content, as shown in Figure 4(a). The conoscopic image seen in Figure 5 shows a black cross, which confirmed the vertical alignment of LCM. The interpretation of the vertical alignment was that the surface construction of the bl-PI films was almost the same as that of the homopolyimide based on the DPA, which we already proved to be of vertical aligning ability in (*6*). On these surfaces, the side chains (mainly the biphenyl groups) were perpendicular to the surface, which led to the vertical alignment of LCM through the exclusive interaction between the biphenyl groups both on the side chains and the LCM.

For co-PIs based on DPA, the pretilt angles monotonically increased from 7.3° to 20° with the side chain content rising from 10% to 30%. The results were also explained in the literature (*6*), attributed to the pretilt angles being determined by the side chains' geometric structure, which may tend to an orientation more and more perpendicular to the surface when the side chains content increases. Vertical alignment of the LCM could not be obtained due to the enrichment of the side chains on the surface being insufficient to make the side chains (mainly the biphenyl groups) perpendicular to the surface.

For the bl-PIs and co-PIs based on DABBE and not containing non-polar *tert*-butyldimethylsiloxy groups, the pretilt angles were enhanced with increased side chain content, but were still very small (seen in Figure 4(b)). With the same side chain content, the pretilt angles were almost the same for the bl-PIs and co-PIs based on DABBE. In Section 3.2, we considered that a similar surface construction was obtained for both blending and copolymerisation. Therefore, it is easy to understand the similarity of pretilting ability for the bl-PIs and co-PIs based on DABBE.

The discussion made above indicated that the presence of the non-polar *tert*-butyldimethylsiloxy groups was indispensable in order to raise pretilt angles by propelling the enrichment of side chains onto the surface. One conclusion also reached was that the vertical alignment layers of polyimides with relative mechanical strength could be obtained by blending, which might provide a potential, alternative way for fabricating alignment layers for multi-domain vertical alignment (MVA) LCD.



(a) (b)

Figure 4. The dependence of pretilt angles of liquid crystal molecules on the molar content of polyimides: (a) PI-DPA; (b) PI-DABBE.

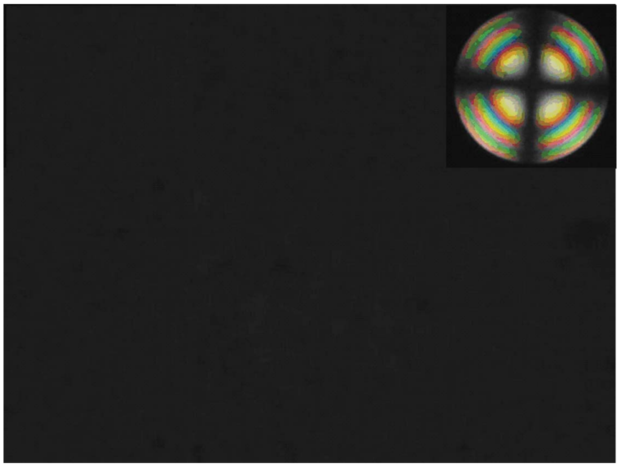


Figure 5. An optical micrograph with a conoscopic image of cells assembled with bl-PI-DPAs taken between crossed polarisers.

4. Conclusion

Polyimides were prepared from blends of the precursors, a poly(amic acid) based on *m*-PDA and a side-chain poly(amic acid) based on DPA. The bl-PI films exhibited surface construction similar to that of the homopolyimide film based on DPA with almost the same surface energies and Si content on the surface regardless of the calculated side chain content. These films generated a 90° pretilt angle for LCM. The result was attributed to the non-polar side chains being highly enriched on the film surface. The co-PI based on DPA displayed lower enrichment of side chains compared with the corresponding bl-PIs and consequently lower pretilt angles. For the polyimides based on DABBE, a diamine without non-plar end groups, both bl-PIs and co-PIs could only generate the same low pretilt angles. In conclusion, by blending poly(amic acids) based on DPA, tough vertical alignment layers could be prepared.

Acknowledgements

We are grateful for financial support from the National Natural Science Foundation of China (No. 50433010 and 50773044) and the Doctoral Fund of the 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; pp 36–40.
(2) Lee, Y.J.; Kim, Y.W.; Ha, J.D.; Oh, J.M.; Yi, M.H. *Polym. Adv. Technol.* **2007**, *18*, 226–234.
(3) 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.
(4) Kim, S.I.; Ree, M.; Shin, T.J.; Jung, J.C. *J Polym Sci, Part A: Polym. Chem.* **1999**, *37*, 2909–2921.
(5) Lee, Y.J.; Choi, J.G.; Song, I.; Oh, J.M.; Yi, M.H. *Polymer* **2006**, *47*, 1555–1562.
(6) Lai, H.; Qin, L.; Liu, X.Y.; Gu, Y. *Euro. Polym. J.* **2008**, *44*, 3724–3731.
(7) Liu, Z.J.; Yu, F.F.; Zhang, Q.; Zeng, Y.; Wang, Y.H. *Euro. Polym. J.* **2008**, *44*, 2718–2727.
(8) Fan, H.J.; Gu, Y.; Xie, M.L. *J Polym Sci, Part A: Polym. Chem.* **2003**, *41*, 554–559.
(9) Liu, X.Y.; Xu, W.; Ye, G.D.; Gu, Y. *Polym. Eng. Sci.* **2006**, *46*, 123–128.