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

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Zhen Sun[a]; Ailin Qin[a]; Zihua Chen[a]; Yinghan Wang[a]
[a] State Key Laboratory of Polymer Materials Engineering of China, College of Polymer Science and Engineering, Sichuan University, Chengdu, Sichuan, People's Republic of China

To cite this Article Sun, Zhen , Qin, Ailin , Chen, Zihua and Wang, Yinghan(2010) 'Large pretilt angle induced by an anhydride-terminal hyperbranched polyimide liquid crystal alignment layer', Liquid Crystals, 37: 3, 345 — 348
To link to this Article: DOI: 10.1080/02678290903564437
URL: http://dx.doi.org/10.1080/02678290903564437

Liquid Crystals,
Vol. 37, No. 3, March 2010, 345–348

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Zhen Sun, Ailin Qin, Zihua Chen and Yinghan Wang*

State Key Laboratory of Polymer Materials Engineering of China, College of Polymer Science and Engineering, Sichuan University, Chengdu, Sichuan 610065, People's Republic of China

(Received 20 November 2009; final version received 16 December 2009)

Through the polycondensation of a four-functional amine with pyromellitic dianhydride, a hyperbranched polyimide (HPI) was synthesised in this study. The HPI was used for liquid crystal alignment layers. Wide angle X-ray diffraction measurement showed that the HPI film was amorphous. The morphology of the surface layer of film was determined by atomic force microscopy. It is novel that a larger pretilt angle, above 8°, has been achieved with the rubbed HPI alignment layers. This result was different from that in a previous report, in which only a 2.8° pretilt angle was induced by a HPI alignment film.

Keywords: polyimide; hyperbranched polyimide; pretilt angle; alignment layer

1. Introduction

The alignment method is one of the most important techniques for the manufacture of liquid crystal displays (LCDs). In order to understand how the alignment layer orients liquid crystal (LC) molecules, a great deal of effort has been made. Unfortunately, so far the detailed alignment mechanism of the LC molecules has not been understood clearly.

There are two major models for the mechanism of LC alignment: surface microgrooves [1, 2] and intermolecular interaction [3–5] between LCs and polymer chains on the surface of the alignment layers. Recently, the intermolecular interactions between LC molecules and polymer segments have received more attention [6–9].

Polyimide (PI) films are widely used as LC alignment layers in LCDs for their advantageous properties, such as excellent optical transparency, adhesion, heat resistance, etc. The applications of traditional PIs (linear PIs) are restricted due to their difficulty in manufacture. Hyperbranched polymers have received more and more attention due to their unique physical and chemical properties compared with linear polymers, such as good solubility and low solution viscosity [10, 11]. Therefore, the hyperbranched polyimides (HPIs) are useful as they can overcome the disadvantage during manufacture of linear PIs. In previous work of our group, Zhang et al. [12] reported on a HPI used for the alignment layer, but the pretilt angle was only 2.8°. The alignment layer with a low pretilt angle was only used in low-quality twisted nematic (TN) LCDs.

In this study, a new HPI was synthesised. The structure of HPI film was also studied with wide angle X-ray diffraction (WAXD). The alignment behaviour of LC molecules on the surface of the HPI was focused. In order to understand the mechanism of the LC molecular alignment, the surface of the HPI layer was investigated by atomic force microscopy (AFM). It is novel that a larger pretilt angle, above 8°, has been achieved with the rubbed HPI alignment layers. This result was different from that in the previous report, in which only a 2.8° pretilt angle was induced by a HPI alignment film [12].

2. Experimental details

The four-functional amine, 2, 2'-bis (3, 5-diamindo-4-hydroxyphenyl)-propane (b), was synthesised by two steps according to the previously reported procedure (Scheme 1) [13, 14]. The dinitro precursor 2, 2'-bis (4-hydroxy-3, 5-dinitrophenyl)-propane (a) was prepared from bisphenol-A reaction with HNO_3 in a round-bottomed flask. The reaction was stirred for 30 min at 0°C, 2 h at 30°C, and 2 h at 50°C. The yield was about 81%. The four-functional amine (b) was reduced from (a) with hydrazine hydroxide and Pd/C in alcohol at 75°C. The reaction was finished and the four-functional amine was obtained 5 h later. The yield of the monomer (b) was about 90%. The structure of (a) and (b) were confirmed by ^{1}H-nuclear magnetic resonance (NMR). (a) ^{1}H NMR ($CDCl_3$, δ): δ 1.158 (s, 6H, CH_3), 8.084 (s, 4H, aromatic C-H), 11.386 (s, 2H, OH). (b) ^{1}H NMR (DMSO, δ): δ 1.366 (s, 6H, CH_3), 4.215 (s, 8H, NH_2), 5.830 (s, 4H, aromatic C-H), 7.187 (s, 2H, OH).

In a thoroughly dried 100 ml three-neck round-bottomed flask equipped with a nitrogen inlet and magnetic stirrer, 0.5886 g (2.7 mmol) pyromellitic dianhydride (PMDA) was dissolved in 15 ml *N*-methylpyrrolidone (NMP) under N_2 flow. Then, 0.2592 g (0.9 mmol) of (b) in 10 ml of NMP was dropped to

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

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290903564437
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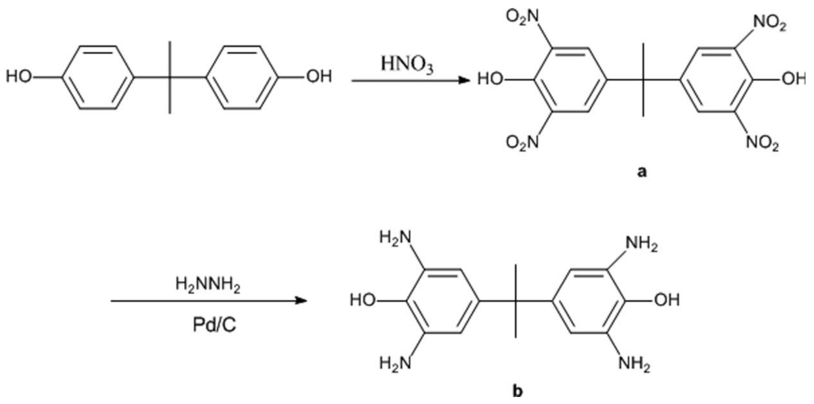
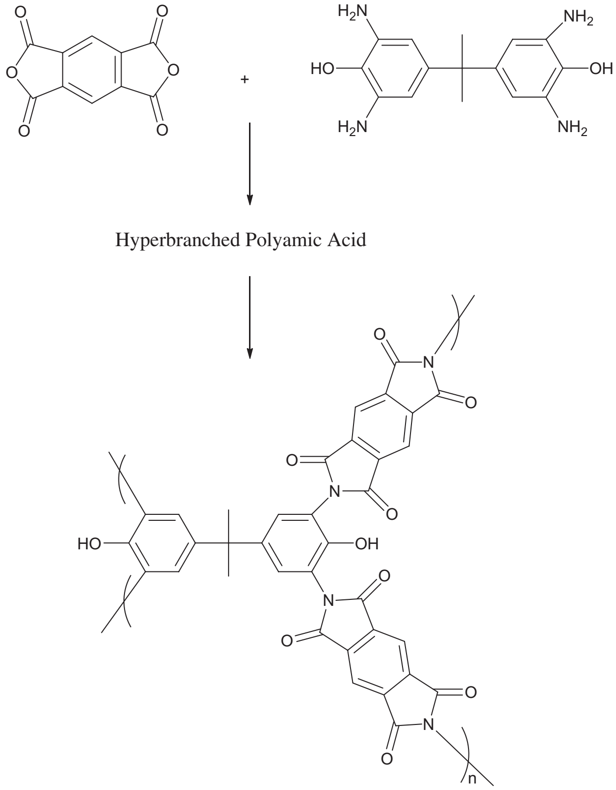


Scheme 1. Synthesis of the four-functional amine (b).



Scheme 2. Synthesis of the HPI.

the three-neck round-bottomed flask through a syringe over 2 h under magnetic stirring at room temperature. The reaction was further conducted for 24 h. The hyperbranched poly(amic acid) (HPAA) solution was attained (Scheme 2). The HPAA was then imidised and this was confirmed by Fourier transform infrared (FTIR) spectroscopy. IR: 3340 cm^{-1} (s, OH), 1851 cm^{-1}, 1789 cm^{-1}, 1723 cm^{-1} (C=O), 1358 (C-N). The bands at 1640 cm^{-1} of the C=O on the CO–NH and 1540 cm^{-1} of C–N on the C–NH have completely disappeared. All of these demonstrated that imidisation was complete.

The HPAA solution was spin-coated on indium tin oxide (ITO)-coated glass substrates treated with isopropyl alcohol. They were prebaked at 80°C for 30 min and baked at 250°C for 2 h to be completely imidised under nitrogen. The films were rubbed twice on the rubbing machine. LC cells were assembled with two pieces of the rubbed substrates in an anti-parallel rubbing direction by using 40 μm thick spacers. The LC cells were filled with E7 (a mixture of LCs with CN groups) by capillarity. In order to remove the flow-induced memory that may be caused by the LC injection process, the LC cells were heated to 60°C for 10 min. The pretilt angles of the LCs were investigated by the crystal rotation method using a pretilt angle tester (Changchun Inst of Optics).

3. Result and discussion

The alignment of E7 molecules in the LC cells observed by optical microscopy is uniform and homogeneous. The intensity of the transmission light in the LC cells changes periodically (bright and dark alternate) with a period of 90° while the LC cells were rotated between crossed polarisers, as shown in Figure 1. The pretilt angle of the LCs was above 8°, which was measured by the crystal rotation method.

The structures of the HPI and the surface morphology of the alignment layers are the key factors influencing LC alignment. The surface morphology was determined by the substrate, the imidisation process, the chemical structure of the HPI and the rubbing process. The rubbing technique is an important method for LC alignment. Hyperbranched polymers have low entanglement density and good mobility. Accordingly, not only does the rubbing process bring on microgrooves by the shear force, but it also results

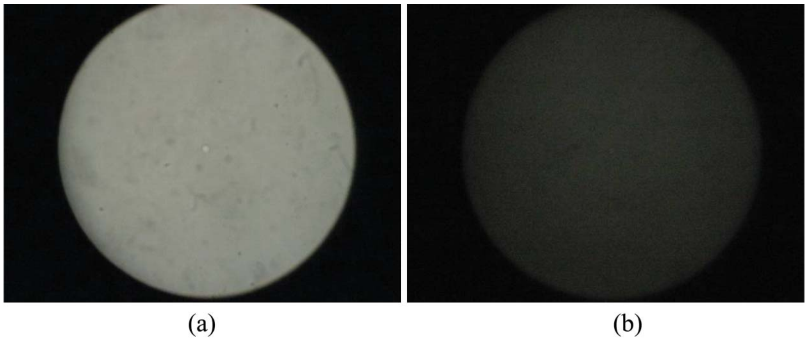


Figure 1. Polarised photographs of the LC cell with the HPI films. (a) Bright state of the LC cell. (b) Dark state of the LC cell. The intensity of the transmission light in the LC cells changes periodically (bright and dark alternate) with a period of 90° while the LC cells are rotated between crossed polarisers.

in the orientation of HPI chain segments on the surface by interaction among functional groups on the rayon velvet fabric and HPI segment [15]. The conformation became more non-planar and asymmetric after rubbing.

Therefore, the surface morphology of HPI films over an area of $2.0 \times 2.0\ \mu m^2$ was examined by the AFM technique (Explorer SPM, Vecco Instruments), as shown in Figure 2. In this image we can see many microgrooves, which are produced by the rubbing process aligned parallel to the rubbing direction. The average width of microgrooves is around 90 nm. The dimension of the microgrooves generated in the rubbing process is much larger than that of the LC molecules. The interaction between the LC molecules and the microgrooves is quite weak. Meanwhile, the sizes of the chemical repeat unit of the polymer chain are comparable to those of LC molecules. The interaction between the LC molecules and the polymer chain segments is stronger. Accordingly, microgrooves are not the dominant factor for the LC molecule alignment in comparison with the segments of the polymer [16, 17]. However, all of this does not mean that the physical topography of the surface has no effect on the LC molecule alignment.

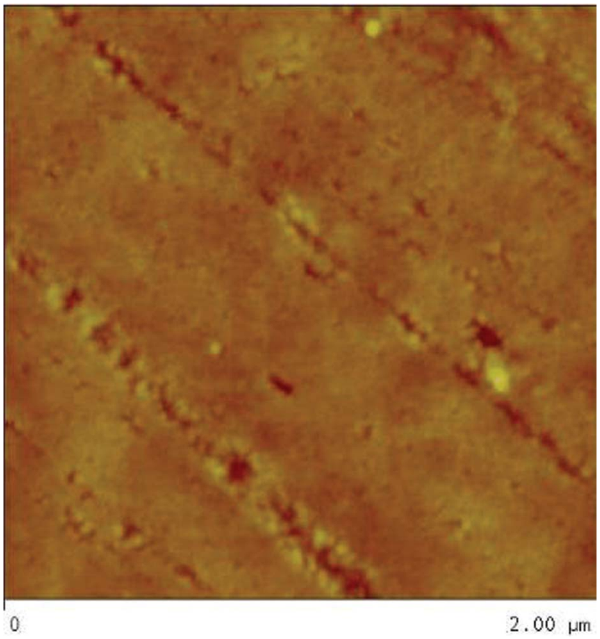


Figure 2. Surface AFM images of scratches on the HPI.

The WAXD measurement was used to investigate the morphology of the HPI thin film by Philips X'Pert PRO MPD (Philips, Netherlands). There is no sharp peak, except a low-wide peak ($2\theta \approx 15°$–$30°$) shown in Figure 3. The amorphous scattering gives rise to a broad band, indicating that the film is completely amorphous. In amorphous polymers there is no long-range order, but the broad-band region indicates that there is a short-range order consisting of segments of polymer. Therefore, the orientation of the LC molecules is independent of the long-range order of the polymer chains in the alignment layer, and might be controlled by the short-range order of some effective parts (hydroxy groups, carbonyl C=O bonds, π systems, and so on).

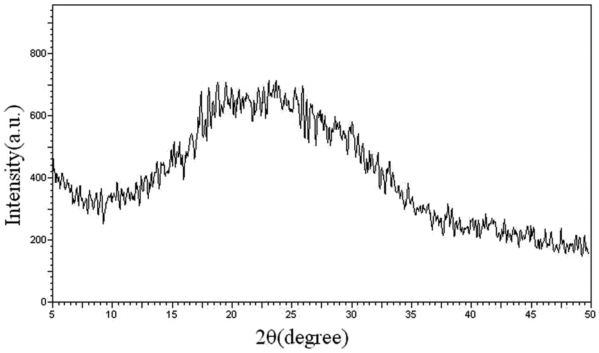


Figure 3. WAXD spectra of the HPI film.

A LC molecule has an aromatic mesogen, a polar cyano group and an aliphatic tail. Hence, the dipolar interaction of the polar groups (carbonyl C=O bonds) on imide rings with the cyano terminal of LC molecules is so strong that it can successfully orient LC molecules. The aliphatic parts of the LC molecules interact with the CH_3-C-CH_3 in the HPI chains by Van Der Waals (VDW) force just as a physical supporting point. The system of the LC molecules and the polymer segments is stable. The LC molecules are repulsed away from alignment layer [16], and the large pretilt angle has been achieved.

The interactions between the short-range order of some effective parts and the LC molecules drive LCs to orient and the physical supporting point may affect the tilt angle of the LC molecules. The pretilt angle increases with the tilt angle of the LC molecules. Consequently, the chemical and physical interactions between LC molecules and the alignment layer may jointly determine the alignment of the LCs.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 50973067). Funding was received from the State Key Laboratory of Polymer Materials Engineering of China (Sichuan University) and the project was sponsored by the Scientific Research Foundation for Returned Overseas Chinese Scholars, State Education Ministry, and Science (No. 20071108-18-12).

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