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Liquid Crystals

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To cite this Article Zhang, Qin , He, Jie , Fang, Yu-Qing and Wang, Ying-Han(2008) 'Synthesis of novel hyperbranched polyimide for liquid crystal alignment', Liquid Crystals, 35: 4, 385 — 388

To link to this Article: DOI: 10.1080/02678290801932876

URL: http://dx.doi.org/10.1080/02678290801932876

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Liquid Crystals,
Vol. 35, No. 4, April 2008, 385–388

PRELIMINARY COMMUNICATION

Synthesis of novel hyperbranched polyimide for liquid crystal alignment

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(Received 4 January 2008; accepted 21 January 2008)

A novel hyperbranched polyimide (HPPI) was synthesized from a new four-functional amine and 1,2,3,4-cyclobutanetetracarboxylic dianhydride. The polyimide with hyperbranched structure exhibited excellent alignment for nematic liquid crystal (LC) compared with traditional linear polyimides. The solution viscosities of the poly(amic acids) (PAAs) and the surface morphology of PI films were investigated using an Ubbelhode-type viscometer and atomic force microscopy, respectively. The viscosities of the hyperbranched PAAs were much lower than that of the linear PAA solution at any monomer ratio (amine:dianhydride). Pretilt angles of LCs above 2.8° were achieved with HPPI.

Keywords: hyperbranched polyimide; linear polyimide; liquid crystal alignment; pretilt angle

1. Introduction

Because of excellent mechanical properties, high-temperature durability, low moisture absorption, good radiation and chemical corrosion resistance, as well as good adhesion to inorganic materials, polyimides (PIs) are widely used in liquid crystal (LC) displays. The polymers are used as LC alignment layers to induce the uniform, unidirectional alignment of LC molecules, which is critical to the optical and electrical performance of industrial LC flat-panel display devices (*1–3*). In this regard, a large number of PIs have been investigated for their alignment properties (*2, 3*). However, most previous experimental studies of LC alignment properties have been focused on linear polyimides (LPIs).

Hyperbranched polymers have received considerable attention in the past decade due to their unique physical and chemical properties compared with linear polymers, such as low solution viscosity and a large number of terminal groups. These polymers have a tree-like randomly branched topology with a branch-on-branch structure, which affords a compact, globular molecule in combination with a number of terminal groups (*4, 5*). The compact molecular structure prevents the molecular globules from penetrating one another, leading to low inter-chain entanglement. On the basis of these facts, the inherent viscosity and glass transition temperature are decreased, accordingly, so that they meet the requirements for LC alignment (*6*). Li *et al.* have prepared liquid crystalline azo-dendrimer for LC alignment and investigated the mechanism of alignment, and they proposed that LC alignment on the irradiated film was controlled by a cooperative effect of surface topography and anisotropic molecular orientation, simultaneously (*7*). At present, however, there are no other reports on LC alignment of hyperbranched polymers, in addition to the rubbing method.

In this paper, a new four-functional amine has been synthesized. A novel hyperbranched polyimide (HPPI) was prepared from this amine and 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA). The LC alignment ability was investigated by the rubbing method, and it was found that HPPI induced a larger pretilt angle of LC molecules. In order to understand the mechanism of the LC molecular alignment, the surface morphology of the rubbed PI was investigated by atomic force microscopy (AFM).

2. Experimental

For synthesis of monomer **1** (see Figure 1 A), bisphenol A (0.015 mol, 3.6 g) was dissolved in 20 ml THF, and then it was added dropwise to a solution of 3,5-dinitrobenzoyl chloride (0.045 mol, 10.35 g) in 30 ml of THF with 3.2 ml of pyridine. The reaction mixture was stirred for 48 h at room temperature and then poured into an aqueous 5% sodium hydroxide solution. The crude solid was washed repeatedly with water and sodium hydroxide solution, and light yellow solid products were obtained. ^{1}H NMR (DMSO): δ 1.735 (s, 6H, methyl), 7.343–7.408 (q, 8H, aromatic), 9.071–9.116 (t, 6H, aromatic).

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ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290801932876
http://www.informaworld.com

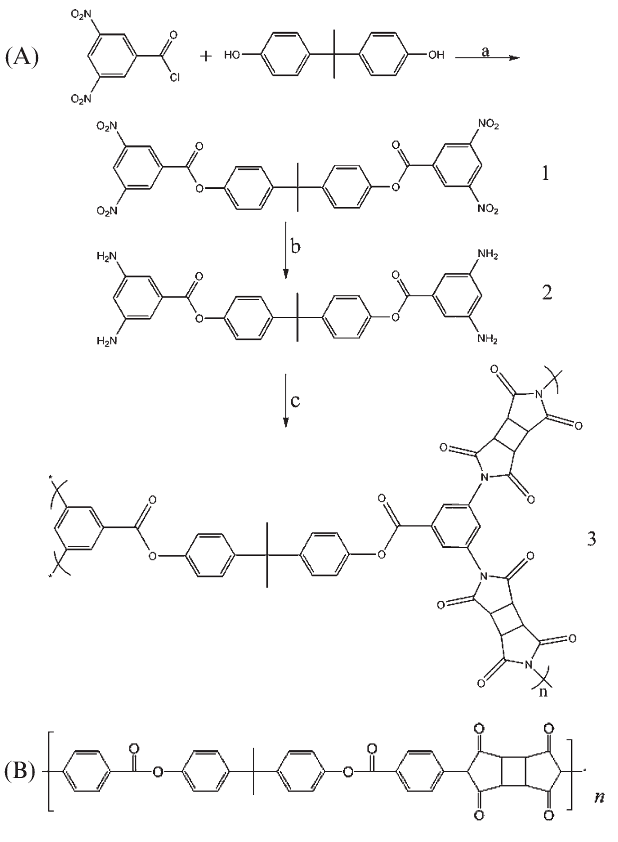

Figure 1. Synthesis and chemical structures of PIs. (A) Synthetic route of HPPI: (a) 3,5-dinitrobenzoyl chloride, Py, THF; (b) H_2, 5%Pd/C, 75°C; (c) CBDA. (B) Structure of LPI.

For synthesis of monomer **2**, **1** (0.0049 ml, 3 g) was placed in a hydrogenation reaction chamber and a catalytic amount of Pd/C (5%) in 40 ml of ethanol was added. Hydrogen was introduced under 1 MPa pressure. The reaction mixture was stirred for 24 h under high pressure at 75°C. The solution was then filtered to remove Pd/C. After removal of excess solvent, the residue was purified by column chromatography with silica gel, using a 1/1 (v/v) petroleum ether/ethyl acetate mixture as eluent, to yield **2** (1.2 g, 40%). ^{1}H NMR (DMSO): δ 1.609 (s, 6H, methyl), 5.088 (s, 8H, amido), 6.086–6.096 (t, 2H, aromatic), 6.560–6.565 (d, 4H, aromatic), 7.100–7.121 (q, 4H, aromatic), 7.296–7.318 (q, 4H, aromatic).

The typical preparation procedure of linear poly(amic acids) (LPAAs) is as follows. Into a 25 ml bottle equipped with a magnetic stirrer was placed a solution of 4 mmol diamine in 13.4 ml NMP, then 4 mmol CBDA was added slowly into the solution. The mixtures were stirred at room temperature for 24 h; the solid contents were 10 wt%. The hyperbranched poly(amic acids) (HPAAs) were prepared as follows. CBDA was dissolved in NMP in 25 ml bottle, then a solution of the amine was added dropwise through a syringe, with different monomer molar ratios of 1:3, 1:2, 1:1, 2:1 and 3:1 (amine:dianhydride), which yielded HPPI-1, HPPI-2, HPPI-3, HPPI-4 and HPPI-5, respectively. The subsequent procedure was similar to that for LPAA formation.

All of the PAA solutions were spin-coated on glass substrates, and they were pre-baked on a hot stage for 30 min at 80°C, followed by thermal imidization at 250°C for 1 h in an oven. The obtained films were rubbed with a roller covered with a rayon velvet fabric. LC cells were prepared by assembling two pieces of the films rubbed in the opposite direction, and the nematic LC (5CB) was injected into the cells in the isotropic state.

Structural identification of the PAAs was confirmed by ^{1}H NMR. For LPAA, ^{1}H NMR (DMSO: δ 1.610 (s, 6H, methyl), 3.45–3.58 (m, 4H, cyclobutane ring), 7.05–7.211 (q, 8H, aromatic), 7.790–8.121 (q, 8H, aromatic), 10.451 (s, 2H, amide), 11.250 (s, 2H, carboxyl). For HPAA-1, ^{1}H NMR (DMSO: δ 1.715 (s, 6H, methyl), 3.368–3.387 (m, 4H, cyclobutane ring), 7.199–7.362 (q, 8H, aromatic), 8.117–8.284 (t, 6H, aromatic), 10.551 (s, 2H, amide) 12.53 (s, 2H, carboxyl). For HPAA-3, ^{1}H NMR (DMSO): δ 1.697 (s, 6H, methyl), 3.664–3.684 (m, 4H, cyclobutane ring), 3.803–3.824 (t, 6H, amine), 5.530 (s, 1H, aromatic), 6.559–6.564 (d, 2H, aromatic), 7.040–7.558 (m, 11H, aromatic), 10.160 (s, 2H, amide), 12.442 (s, 2H, carboxyl).

Fourier transform infrared (FT-IR) spectroscopy of the polyimide films showed the characteristic imide I, II bands at 1777, 1727 and 1373 cm^{-1} and C–H stretching vibrations of aliphatic groups at 2854–2926 cm^{-1}. For the amino-terminated HPPI, the double bands at 3378 and 3481 cm^{-1} are assigned to the stretching absorption of N–H of the terminal amino groups. A peak at 1868 cm^{-1} (C=O stretching) indicated the existence of terminal anhydride groups for the anhydride-terminated HPPI.

Table 1. The inherent viscosity and pretilt angle of the polyimides.

Type of polyimide	η_{inh}/dl g^{-1}[a]	Pretilt angle/°	Mole ratio of monomers[b]
LPI	0.76	1.1	1:1
HPPI-1	0.40	2.8	1:3
HPPI-2[c]	–	–	1:2
HPPI-3	0.50	1.4	1:1
HPPI-4	0.47	1.5	2:1
HPPI-5	0.45	1.5	3:1

[a] Inherent viscosity of soluble PAA measured at 30°C in NMP with a concentration of 0.5 g dl^{-1}. [b] Composition of monomer is amine:dianhydride. [c] HPAA-2 became a gel.

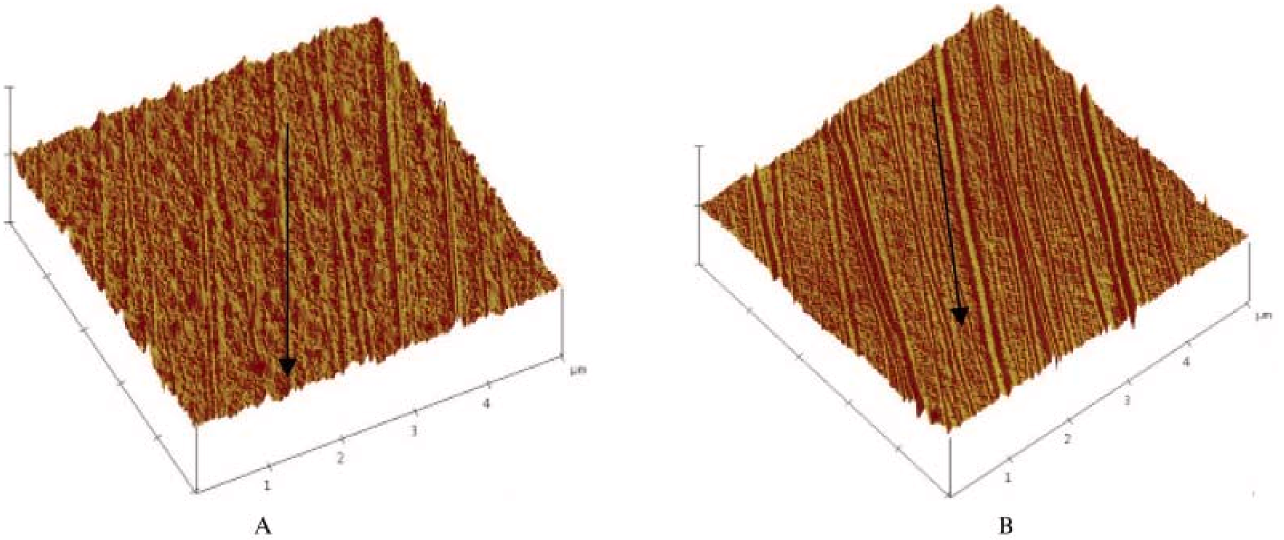

Figure 2. Surface AFM images of scratches on the PIs (the rubbing directions are indicated by black arrows): (a) HPPI-1; (b) LPI.

3. Results and discussion

Inherent viscosities of PAAs are considered to be a key parameter for the formation of thin films with good quality, and the observed viscosities are shown in Table 1. The inherent viscosities of LPAA and HPAA were in the range 0.4–0.76 dl g^{-1}, which ensured the easy formation of thin PI films. The inherent viscosity of the LPAA is larger than those of HPAAs. This is because LPAA has a higher molecular weight and higher extent of entanglement leading to a high inherent viscosity.

It was well known that LC alignment depends both on the chemical nature of the surface and on the surface topography. As shown in Table 1, the pretilt angles of LC cells fabricated with HPPIs were larger than that with LPI. The reason is that the HPPIs have markedly branched structures that interact with LC molecules, which induce the larger pretilt angle (*7–9*). On the other hand, the physical topography of the surface has significant effects on the orientation of LC alignment and groove effects are the primary factor that induce the alignment of LC molecules toward the rubbing direction (*10, 11*). Accordingly, the surface morphology of the rubbed polyimide films was investigated using atomic force microscopy (AFM), as shown in Figure 2.

The surface of the HPPI-1 film has apparent sinusoidal or zigzag packing structure. The microgroove lines, which result from the rubbing process, are aligned parallel to the rubbing direction and the root-mean-square (RMS) roughness was found to be 0.53 nm over an area of $5.0 \times 5.0\,\mu\text{m}^2$; in contrast, the microgrooves of the LPI (see Figure 1 B) film were long and deep and the RMS roughness was 1.054 nm. According to the results reported by Berreman, the anchoring energy is strongly dependent on the groove geometry (*11*). The sizes of the microgrooves of HPPIs were close to the bulk of the LC molecules; therefore, the interaction between the LC and PI was considered to be so strong that LC molecules were aligned uniformly to achieve large pretilt angle (*12*). The dimensions of the microgrooves of LPI seem too large to interact effectively with and align LC molecules. This difference in surface morphology might result from the differences in the deformation response of the different PI films to the shear force caused by the contact of fibres during the rubbing process (*13, 14*). Consequently, the pretilt angles of LC cell fabricated with HPPIs were larger than that of LPI.

Further studies on the properties and the application for LCD on the HPPI films are now in progress.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 50773045) and Science and Technology Innovation Foundation of Sichuan University (No. 2005CF09), and we thank Professor Makoto Takeishi for helpful discussions.

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