Synthesis and characterization of soluble polyimides for vertical alignment of liquid crystal

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A series of polyimides (PIs) with different side chain content, were copolymerized from 4-dodecyloxy-biphenyl-3', 5'- diaminobenzoate (DBPDA), 3,3'-dimethyl-4,4'-methylene-dianiline (DMMDA) and 4,4'-oxydi(phthalic anhydride) (ODPA) *via* one-step method. The PIs possessed excellent solubility in polar aprotic solvents. Thermal decomposition temperatures in nitrogen occurred above 350 °C. The resultant PI films induced excellent uniform vertical alignment of liquid crystal. Even after the rubbing process, the pretilt angles of liquid crystal were still above 89°.

Keywords: polyimides; solubility; copolymerization; vertical alignment; liquid crystal

Introduction

Generally, polyimide (PI) films are used as alignment layers in the displays. Due to their rigid chain characteristics, traditional aromatic PIs are normally insoluble and intractable in their fully imidized form, which leads to processing difficulties. Thus, PI processing is generally carried out with poly(amic acid) intermediate and then converted to PI via rigorous thermal treatment (250–300°C) [1], which is fatal to the polymer substrate used in the flexible display. Soluble PI abstracts considerable research interest. Much effort has been made on synthesis of soluble PI without deterioration of their own excellent properties, such as the introduction of bulky groups [2], flexible linkages [3], asymmetric units [4] into the backbone or copolymerization to improve solubility of PIs [5]. Synthesis of soluble PIs which can be used as LC alignments has been attempted[6]. However, the pretilt angle induced by these PIs is usually very low, which can only satisfy some common parallel aligned mode. It is well known that traditional liquid crystal displays (LCDs), which adopt the parallel alignment layer to achieve uniform alignment of liquid crystal (LC), have shown some defects, such as narrow viewing angle, low contrast ratio and slow response time [7]. The vertical aligned mode can improve these defects greatly and give LCDs good display quality; therefore the research of the vertical alignment layer has become a chief topic in the field of the LC alignment layer. Many workers have reported on vertical alignment of LCs caused by PI films [8]. However, to our best knowledge, the vertical alignment induced by soluble PIs has rarely been reported.

In this paper, the synthesis of soluble PIs were attempted from 4-dodecyloxy-biphenyl-3', 5'-diaminobenzoate (DBPDA), 3,3'-dimethyl-4,4'-methylenedianiline (DMMDA) and 4,4'-oxydi(phthalic anhydride) (ODPA) by one-step method. Then the properties of the PIs, such as solubility and thermal stability were investigated. Meanwhile, alignment ability and pretilt angle of LC induced by the PIs were also studied.

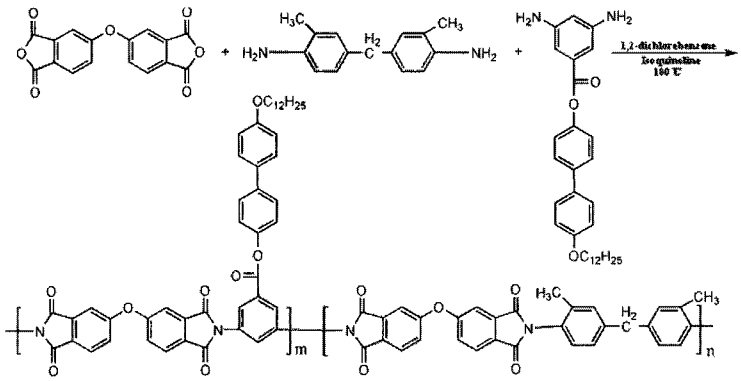
Expermental

Measurements

Thermogravimetric analysis (TGA) was performed under nitrogen on a DuPont TGA 2100 Thermogravimetric analyzer. The sample was heated using a 15 °C/min. The pretilt angles of LCs were measured by crystal rotation method using a pretilt angle tester from Changchun Inst of Optics, Polarizing microscope from Shanghai Millimeter Precision Instrument Co. Ltd. (Shanghai China) was used to evaluate the alignment behavior of LC.

Synthesis of PIs

PIs were prepared from DMMDA, DBPDA and ODPA *via* one-step method. As illustrated in Scheme 1, Molar ratios of DBPDA to DMMDA were controlled to 0: 10 (PI_0), 2: 8 (PI_2), 3:7 (PI_3), 5:5 (PI_5), 7: 3 (PI_7), and 10: 0 (PI_{10}).



Scheme 1. Synthetic scheme of PIs

Preparation of films and assembling of cells

All the PI solutions (5 wt% in NMP) were spin-coated on glass substrates, followed by drying at 100°C for 2 h to remove the solvent. Then the PI films coated on the substrates were rubbed with the constant strength, using a rubbing machine with a roller covered with a nylon cloth.

Two pieces of the rubbing substrates were assembled together in the anti-parallel direction. The cell gap was set to be 40 μm by glass spheres. LC, E7 was injected into the cell gap at the isotropic state.

RESULT AND DISCUSSIONS

Solubility

The solubility of the polymer is listed in Table 1. It can be found that, the homo-PIs, such as PI_0 and PI_{10} were partly soluble or insoluble in the polar solvents, however, the co-PIs (PI_2, PI_3, PI_5) showed

Table 1. Solubility of PIs

PIs	NMP	DMSO	DMF	DMAc	m-cresol	TCM	THF
PI_0	+-	+-	+-	+-	+-	++	+
PI_2	++	++	++	++	++	++	++
PI_3	++	++	++	++	++	++	++
PI_5	++	++	++	++	++	++	++
PI_7	+-	+-	+-	+-	++	++	+
PI_{10}	-	-	-	-	-	++	+

(++) soluble at room temperature, (+) soluble upon heating, (+-) partial soluble upon heating, (-) insoluble

good solubility. They could be dissolved easily not only in strong polar aprotic solvents, such as NMP,

DMF, DMAc, DMSO, m-cresol, but also in commonly used low-boiling-point solvents, such as TCM and THF.

Thermal stability

Thermal stability of PIs was investigated by TGA in nitrogen and their thermograms are reproduced in Figure 1. As seen in Figure 1, the PIs (PI_2-PI_5) began to degrade around 350°C, meaning that they were excellent in performance as a high-temperature polymer. It can be also found that with an increase in the content of the DBPDA, the T_d, T_5 and T_{10} of the PIs decreased, and PI_5 exhibited the lowest thermal stability. Because the long side groups were susceptible to thermal degradation, the increase in content of DBPDA cause the increase in content of long side groups, which might decrease thermal stability.

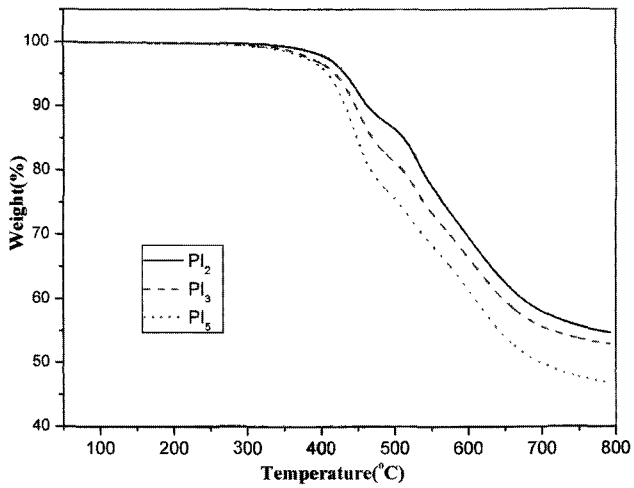


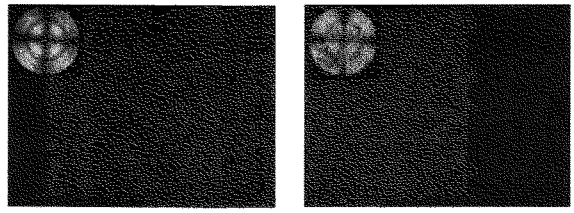
Figure 1. TGA thermograms of the PIs.

Alignment ability and pretilt angle of liquid crystal

As shown in Table 2, the PIs induced pretilt angle of 90° before rubbing process and uniform alignment of LCs. But after rubbing process, PIs with different composition of DBPDA could induce different pretilt angles of LC, because only sufficient side chains on polymer surface can produce the vertically aligned LC molecular layer. Conoscope observation of the cells was used with polarized optical microscope. As shown in Figure 2, dark crossed brush was seen clearly and not moved with the LC cell rotating before and after rubbing. The result further prove the vertical alignment was induced by PI_2. The same result could be obtained by PI_3 and PI_5.

Table 2. Pretilt angle of liquid crystals

PIs	Pretilt angle(θ_p)	
	Before rubbing	After rubbing
PI_2	90°	88.8°
PI_3	90°	89.2°
PI_5	90°	90°



(a) (b)

Figure 2. Polarized optical microscopic images of vertical LC. All of the pictures were captured under crossed polarizers. The conoscopic images are shown in the corner of the picture. (a) before rubbing, (b) after rubbing. Alignment film is PI_2.

Conslusions

DBPDA was used as a functional diamine which has a non-polar long alkyl side group connected with a biphenyl structures. A series of the PIs were synthesized using the one-step polymerization method from ODPA, DMMDA and DBPDA. Most of the PIs could be dissolved in polar aprotic solvents and low-boiling-point solvents. The PIs (PI_2-PI_5) showed good thermal properties. Without rubbing, PI_2 – PI_5 showed the vertical alignment. When the rubbing was performed, PI_3 and PI_5 showed more strong vertical alignment than the P_2.

Acknowledgments

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