

# Synthesis of novel aromatic polyimides containing bulky side chain for vertical alignment liquid crystals

Ying Han Wang\*(汪映寒), Jian Wang(王 剑)

*State Key Laboratory of Polymer Materials Engineering of China; College of Polymer Science and Engineering, Sichuan University; Chengdu 610065, China*  
(四川大学 国家聚合物材料工程重点实验室)

## Abstract

In this study, a novel 4-(4-octyloxybenzoyloxy)biphenyl-3',5'-diaminobenzoate and polyimides based on it were synthesized. The polyimide with mesogenic unit side chain exhibited excellent vertical alignment for nematic liquid crystal(LC). The pretilt angles of LCs above 89° were kept after the rubbing process with 220mm rubbing strength. The polyimide films as the alignment layer were baked at 120°C for 12hr, the vertical alignment of LCs was still uniform and stable. Meanwhile, the UV-vis spectra of the novel polyimide films showed the high transparency in a visible wave length.

*Keywords:* Polyimide; Liquid crystal; Vertical alignment

The alignment of a nematic liquid crystal (LC), consisting of an assembly of rodlike molecules, on rubbed polymer surfaces underlies the manufacture of today's flat panel displays. Due to excellent mechanical performance, 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 as LC alignment layer in liquid crystal displays (LCDs). Recently, a vertical alignment method has been used to improved alignment of the liquid crystals (LCs) with negative dielectric anisotropy for a faster response time and a higher contrast ratio compared to a twisted nematic liquid crystal displays. Some workers have reported on vertical alignment of LCs caused by PI films [1-5]. Lee et al. reported on a PI containing a dianhydride with an aromatic side chain, which induced a pretilt angle of 70°~80° after a rubbing process[5]. Further, Wang, Kim and coworkers reported the effect of a long alkyl side group on the pretilt angle, which showed that non-polar long alkyl side chains increased the pretilt angle to 86°[6-8]. Lee and Yi et al. reported that a PI with side chain containing rigid alicyclic rings and long alkyl end group gave a pretilt angle of 86° after the rubbing process and discussed the effect of the side chain structure on the pretilt angles [4]. However, the pretilt angle did not meet the requirement for the multi-domain vertical alignment mode, which requested a pretilt angle above 89° after a rubbing process [4]. Recently, Y. J. Lee et al. synthesized a novel polyimide inducing a pretilt angle above 89° [9], but the side chain with very long alkyl may deteriorate thermal stability and uniformity for the liquid crystal alignment layers, and the thermal stability and uniformity of the vertical alignment were not mentioned in their paper.

In this study, a novel aromatic polyimide containing bulky LC side chain was successfully synthesized. The synthetic route for the novel diamine, vertical alignment properties for LCs, thermal stability and the preliminary study on their properties were described in this paper.

## Experimental

Synthesis of monomers 4-octyloxybenzoic acid **1**: Methyl *p*-hydroxybenzoate ( 3.8g, 0.025mol) in dry THF(15 mL) was slowly added to a mixture of 70% NaH (0.9g,0.026mol) in THF (15 mL) at 0°C. After evolution of hydrogen ceased, dry DMF (10 mL) followed by the bromooctane (5.8g, 0.03

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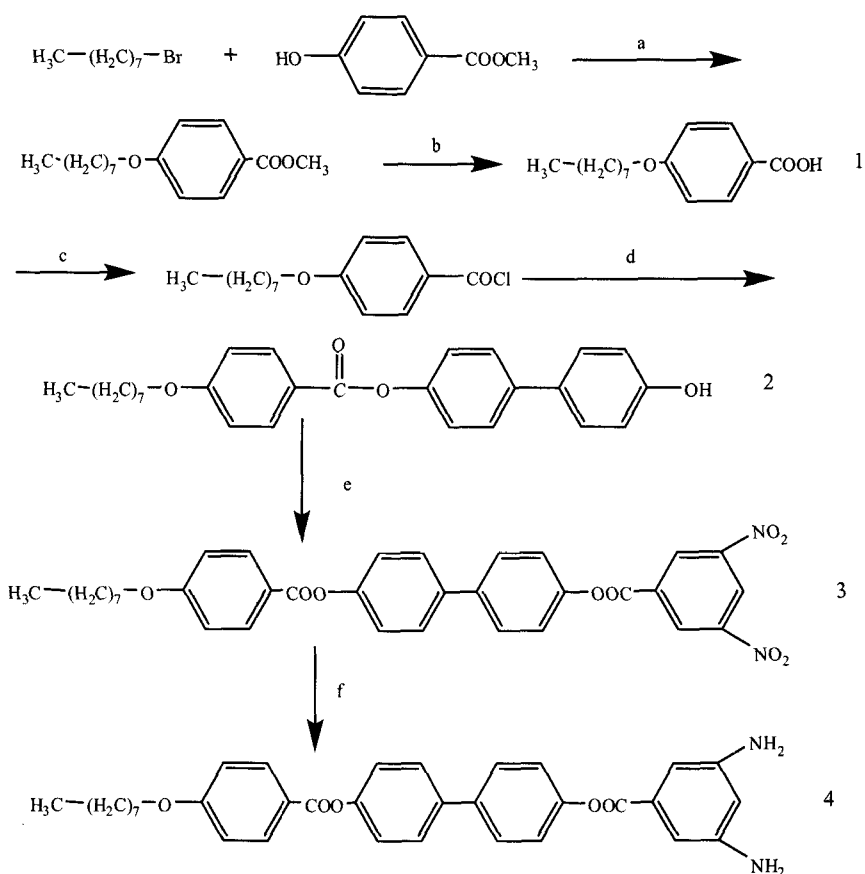
\* Corresponding author  
E-mail: wangyinghan@vip.sina.com

mol) in THF(10 mL) was added. The mixture was refluxed for 5hr at 60°C. After cooling to room temperature, 50 mL of water was added. The water layer was extracted twice with diethyl ether, and then incorporated diethyl ether solution into organic layer. The THF and diethyl ether was removed by vacuo. The remaining liquid was dissolved in 60mL of ethanol and NaOH (1.6g, 0.04mol) was added. After being refluxed for 2hr, the crude product was precipitated in dilute hydrochloric acid and was further recrystallized from ethanol to give 5.2 g of white crystals, Yield: 83%. FTIR (KBr,  $\text{cm}^{-1}$ ): 3434(-OH), 2927, 2850(-CH<sub>3</sub>, -CH<sub>2</sub>-), 1689(C=O), 1606, 1512 (Ar-), <sup>1</sup>H-NMR(CDCl<sub>3</sub>,  $\delta$ ppm): 0.87-0.90(t, 3H, -CH<sub>3</sub>), 1.25-1.36(m, 8H,-(CH<sub>2</sub>)<sub>4</sub>-), 1.43-1.50(quint, 2H, -O-C-C-CH<sub>2</sub>-), 1.77-1.84(quint, 2H, -O-C-CH<sub>2</sub>-), 4.00-4.04(t, 2H, -O-CH<sub>2</sub>-), 6.91-8.07(m, 4H, aromatic).

Synthesis of 4-(4-octyloxybenzoyloxy)-4'-hydroxybiphenyl **2**: **1**(1.5 g, 0.006 mol) was reacted at 60°C with 6 mL of thionyl chloride for 6 hr, and then the excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride. The acid chloride was dissolved in 5 mL of tetrahydrofuran(THF) and then added dropwise to a solution of 4,4-dihydroxybiphenyl(0.024 mol, 4.4 g) in 25 mL of THF and 2.0 mL of pyridine under quick stirring. The reaction mixture was stirred for 48 hr at room temperature. After the removal of the excess solvent, the rest was poured into 2% sodium hydroxide solution. The precipitate was filtered and washed with dilute hydrochloric acid, water, and ethanol successively. The 1.9g of white crystals was obtained by recrystallization from a mixture of benzene and chloroform of 4:1 v/v. yield: 76%. FTIR(KBr,  $\text{cm}^{-1}$ ):3452(-OH), 2924, 2854(-CH<sub>3</sub>,-CH<sub>2</sub>-), 1728(C=O), 1608, 1497 (Ar-), 1261(C-O-C) <sup>1</sup>H-NMR(CDCl<sub>3</sub>, $\delta$ ppm): 0.90-0.93 (t,3H,-CH<sub>3</sub>), 1.27-1.38 (m,8H,-(CH<sub>2</sub>)<sub>4</sub>-), 1.46-1.54 (quint, 2H, -O-C-C-CH<sub>2</sub>-), 1.81-1.88 (quint, 2H, -O-C-CH<sub>2</sub>-), 4.05-4.08(t, 2H, -O-CH<sub>2</sub>-), 5.0(br s, 1H, -OH), 6.88-8.20(m, 12H, aromatic H).

Synthesis of 4-(4-octyloxybenzoyloxy)biphenyl-3',5'-dinitrobenzoate **3**: 3,5-dinitrobenzoyl chloride (1.1g, 0.0046mol)was dissolved in 10mL THF, and then added dropwise to a solution of compound **2**(1g, 0.0023 mol) in 15 mL of THF and 0.7 mL of pyridine in ice-bath condition. The reaction mixture was stirred for 48hr at room temperature and then poured into 0.5% sodium hydroxide solution. The precipitated crude solid was recrystallized from 1,2-dichloroethane to yield 0.85g (61%) of white crystals. <sup>1</sup>H-NMR(CDCl<sub>3</sub>,  $\delta$ ppm): 0.90-0.93(t,3H,CH<sub>3</sub>-), 1.25-1.56[m, 10H, CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>-], 1.81 (m, 2H, CH<sub>2</sub>-C-O-), 4.05(t, 2H, -CH<sub>2</sub>-O-), 7.0-8.2(m, 12H, aromatic H of phenyl and biphenyl), 9.32-9.36(m, 3H, aromatic H ortho to nitro group).

Synthesis of 4-(4-octyloxybenzoyloxy)biphenyl-3',5'-diaminobenzoate **4**: **3**(0.001mol, 0.6g) was charged in a hydrogenation reaction chamber and a catalytic amount of Pd/C(5%) in 20 mL of THF were added. The hydrogen was introduced under 1MPa pressure. The reaction mixture was stirred for 24hr under high pressure at 75°C. The solution was then filtered to remove Pd/C. After the removal of the excess solvent, the rest was purified by column chromatography with Silica gel, using a 1/1 (v/v) petroleum ether /ethyl acetate mixture as the eluant, furnished **4** (0.22 g, 40%) (fourth band). FTIR (KBr,  $\text{cm}^{-1}$ ):3447.3364(-NH<sub>2</sub>), 2924, 2853(-CH<sub>3</sub>,-CH<sub>2</sub>-), 1727(C=O), 1606, 1493 (Ar-), 1259(C-O-C), <sup>1</sup>H-NMR(CDCl<sub>3</sub>,  $\delta$ ppm): 0.90-0.93(t, 3H, CH<sub>3</sub>-), 1.28-1.569 [m, 10H, CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>-], 1.81-1.88 (m, 2H, CH<sub>2</sub>-C-O-), 4.06-4.09(t, 2H, -CH<sub>2</sub>-O-), 6.29 (s, 1H, aromatic H between NH<sub>2</sub>), 6.98(s, 2H, aromatic H between NH<sub>2</sub> and C=O), 7.0-8.2(m, 12H, aromatic H of phenyl and biphenyl).



Scheme 1. Synthetic route to monomers. (a) NaH, DMF, THF; 60°C (b) NaOH; (c) SOCl<sub>2</sub>; (d) 4,4'-dihydroxybiphenyl, Py, THF; (e) 3,5-dinitrobenzoyl chloride, Py, THF; (f) H<sub>2</sub>, 5%Pd/c, 75

Polymerization: A small bottle with a magnetic stirrer was placed a solution of diamine 4 in the quantitative NMP, then pyromellitic dianhydride(PMDA) was added into the solution. After the mixture was stirred for 1 hr at room temperature, the 4, 4'-methylenedianiline(MDA) was added into the small bottle, and the solid content was fixed on at 25 wt%. The agitation was lasted for 2-48hr at ambient temperature to form poly(amic acid)s. The poly(amic acid)s precursors were thermally imidized at 230°C for 2hr. The molar ratios of diamine 4 and MDA are 1:3, 1:5, 1:7, 1:9, named P1-1, PI-2, PI-3,PI-4, respectively.

## Results and discussion

The diamine 4 was synthesized through 5 steps, and the key step was preparation of the monoester compound 2. According to selecting proper solvent of recrystallization, diester could be successfully removed and pure monoester could be obtained.

Due to the steric hindrance of the bulky side chain and the electric withdrawing group(C=O) in bulky side chain, reactivity of the diamine 4 was very low. In order to solve the issue, the polymerization reactions were carried out by 25wt% reactant concentration in NMP, and the inherent viscosity of ploy(amic acid)s were efficiently increased. The inherent viscosities of the ploy(amic acid)s and polymerization condition of the PIs were shown in Table 1.

Table 1 The inherent viscosity and polymerization condition of the polyimides

Polyimide	$\eta_{inh}$ (dL/g) <sup>a</sup>	Solid (wt%)	Reaction time(h)
PI-1	0.22	25%	48
PI-2	0.32	25%	40
PI-3	0.38	25%	36
PI-4	0.48	25%	2.5

<sup>a</sup> 0.5 g/dL in concentrated NMP at 30°C.

FTIR spectroscopy show the characteristic imide I, II bands at 1777, 1727 and 1373cm<sup>-1</sup> and C-H stretching vibrations of aliphatic groups in 2854-2926cm<sup>-1</sup>. XRD show that the polyimide was amorphous.

Liquid crystal molecules (5CB) exhibited uniform homeotropic alignment on most of the polyimide films, and the pretilt angles of LCs were above 89°. But PI-4 could not induce LCs vertical alignment on substrate, and 5CBs show homoogeneous alignment on LC cells. The LC cells using the PI-1,2,3 films as the alignment layer were baked at 120°C for 12h, the vertical alignment of LCs was still uniform and stable, and the pretilt angles closely to 90° were still kept. The vertical alignment possess a excellent rubbing stability, and the high pretilt angle above 89° were kept even increasing rubbing strength(RS) to 220mm. That implies the novel aromatic polyimide containing bulky side chain possesses strong and stable vertical alignment ability for LCs.

The UV-vis spectra of the novel polyimide films show the high transparency in a visible wave length which is extremely desirable when PIs are applied to optical devices such as color LCDs.

The further studies on the properties and the application for LCD on these PIs are in progress now and these results will be published later.

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