Polyimides with Alkyl-branch and Fluorinated Side Chains for Liquid Crystal Alignment

Yang Zhenghua   Zhang Chunhua

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences; Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation; Changchun 130022

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INTRODUCTION

The alignment of liquid crystal molecules is one of the most important technologies in liquid crystal device fabrication.[1-3] It is generally a simpler matter to produce either homogeneous or homeotropic alignment. For example, rubbed polyimides have been widely used for homogeneous alignment. Particularly, precise control of the pretilt angle, defined as the angle made between the long axis of the liquid crystal molecules and the plane of the surface, is strongly required with super-twisted nematic liquid crystal displays (STN-LCDs). It is very important to realize chemical structure effect on the pretilt angle in order to reveal the mechanism for the generation of the pretilt bias. There are several well-known relationships between the pretilt angle and the chemical structure of the alignment layer. Chemical structures of some polymers which induce relatively high pretilt angles have reported.[4-5] For example, alkyl-branch polyimides and fluorinated side chains lead to higher pretilt angles. But the number of polyimides for which the relationship between chemical structures and pretilt angles has been studied is quite limited.

In this paper, we discuss the relationship between the polyimides with side chains and fluorinated side chains and pretilt angles.

EXPERIMENTAL

Polyamic acids were synthesized by the reaction between 4,4'-(p-phenylenedioxy)diphthalic dianhydride(PDDA) and appropriate diamines with side chains or fluorinated side chains. These polyamic acids were coated onto glass plates with indium tin oxide (ITO). Polyimide films having a thickness of about 500 Å were obtained by heat treatments of polyamic acids on the solid plates at 250℃ for 30 minutes. Film thickness was controlled by rotation speed of spinning coating. The rubbing process was carried out under the following conditions: cylinder rotation speed, 750 rpm; cylinder diameter, ϕ50 mm; moving speed of solid plate, 240 mm/min. Two solid plate were set in the opposite direction to obtain a uniformly pretilted liquid crystal orientation. The gap between two plates was controlled to about 25 μm. The liquid crystal used in these experiments was PN—001 (from Japan, n_o=1.533 n_e=1.787 Δn=0.254). Pretilt angles were measured by the crystal rotation method.

RESULTS AND DISCUSSION

1. Alkyl-branched polyimides

Alkyl-branch structure fetched in the polyimides main chain is one of most effective method to improve the pretilt angles. A series of polyimides having methyl or methoxy groups have been synthesized. Figure 1 shows the procedure for synthesis of polyimides based on 4,4'-(p-phenylenedioxy) diphthalic dianhydride. Table 1 shows the polyimide structure and the pretilt angles. We can see from Table 1, the pretilt angles of PI 1-3 and PI

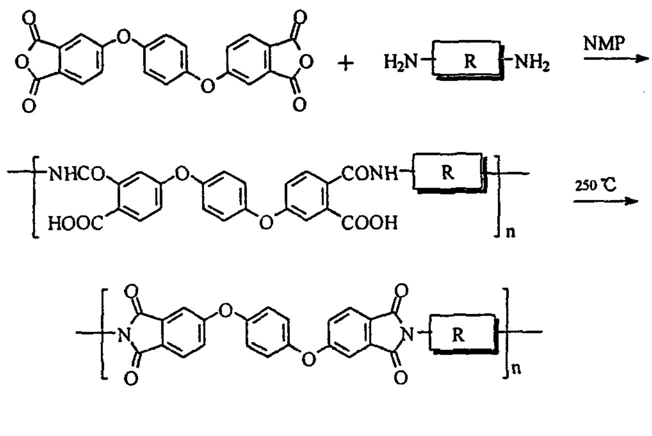
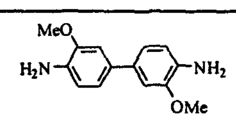
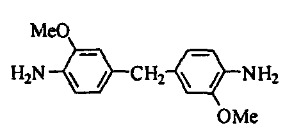
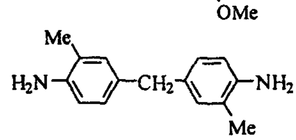
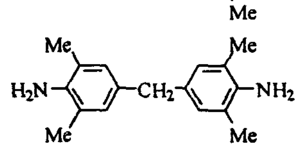


Figure 1 Procedure for synthesis of PDDA polyimides

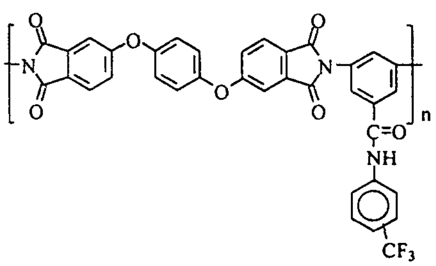
Table 1 Alkyl-branch polyimides and its pretilt angles

samples	diamines	dianhydrides	pretilt angles(°)
PI 1-1		**PDDA**	**1.5**
PI 1-2		**PDDA**	**2.0**
PI 1-3		**PDDA**	**3.5**
PI 1-4		**PDDA**	**4.0**

1-4 which have methyl branch is 4°; the pretilt angles of PI 1-1 and PI 1-2 which have methoxy branch is 2°. These results may be attributed to steric interactions between liquid crystal molecules and aligned branched alkyl chains. The rigidity of C-C bond is superior to the C-O bond, and the steric interactions of methyl groups is more effective than methoxy groups.

2. Polyimides with fluorinated side chains

Fluorinated side chains branched to polyimides can induce high pretilt angles. Two kinds of polyimides containing CF_3 branch have been synthesized. Figure 2 shows the structure and the pretilt angles. The pretilt angles of PI 2-1 is 15°, two times than PI 2-2. The only difference of two polyimides in chemical structure is the position of CF_3 group. When the CF_3 group is in the *p* position, the interaction between F atom and liquid crystal molecules is more effective, because the *p* position in steric chemistry is more available to contact with liquid crystal molecules. The essential mechanism needs to be study further.



PI 2-1 **CF_3=*p* position** **pretilt angle=15°**

PI 2-2 **CF_3=*m* position** **pretilt angle=7°**

Figure 2 the structure and the pretilt angle of fluorinated polyimides

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