Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: S. W. Lee, S. I. Kim, Y. H. Park, M. Ree, K. H. Lee & J. C. Jung (2000): Fully Rodlike Polyimides Containing Flexible Side Chains with Various Lengths and Their Ability to Align Liquid-Crystals on the Rubbed Surface, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 271-274

To link to this article: http://dx.doi.org/10.1080/10587250008024917

Mol. Cryst. and Liq. Cryst., 2000, Vol. 349, pp. 271-274
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Fully Rodlike Polyimides Containing Flexible Side Chains with Various Lengths and Their Ability to Align Liquid-Crystals on the Rubbed Surface

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Rodlike poly(*p*-phenylene pyromellitimide)s with various side chains (Cm-PMDA-PDA PIs) were newly prepared in a good quality of films. The polyimide films were rubbed, and used in constructing liquid-crystal (LC) cells which were filled with a nematic LC containing a dichroic dye. For the LC cell, both pretilt angle and alignment director of LCs were dependent strongly on the side chain length as well as the rubbing density. On the polymer film, both homogeneous and homeotropic LC alignments were achievable by either changing the side chain length or varying rubbing density. Unlike polymers reported previously as a LC alignment layer material, the Cm-PMDA-PDA PI induced LCs to pretilt with a negative angle rather than a positive angle: this is a unique property characteristic of the Cm-PMDA-PDA PIs. In addition, film properties were measured.

Keywords: rodlike polyimide with side chains; rubbing process; liquid-crystal; homogeneous alignment; homeotropic alignment; negative pretilt angle

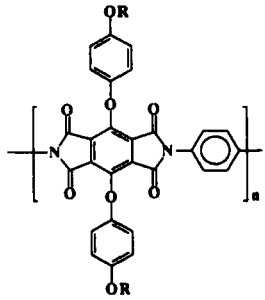
INTRODUCTION

Soluble, flexible polyimides are widely used in the liquid-crystal display (LCD) industry as an orientation layer of liquid-crystal (LC) molecules. For the LCD application, the surface of polyimide films always is mechanically rubbed with a cloth. The rubbed film surface is found to induce the alignment of LCs along

the rubbing direction. For this LC alignment phenomenon, several mechanisms have been proposed[1,2]. However, the alignment mechanism of LCs on the rubbed surface has not been fully understood yet. And, new high performance polymers for the orientation layer are still needed to improve the functional performance and reliability of LCDs. In this study, a series of rodlike poly(*p*-phenylene pyromellitimide)s with side chains were prepared in a good quality of films. For these polymer films treated by rubbing process, we investigated the aligning and pretilting behaviors of LCs on the surface. In addition, thermal, optical and dielectric properties were measured.

EXPERIMENTAL

A series of poly(*p*-phenylene pyromellitamic acid) precursors with side chains were synthesized in *N*-methyl-2-pyrrolidone (NMP) by condensation of 3,6-bis[4-(*n*-alkyloxy)phenyloxy]pyromellitic dianhydrides (Cm-PMDA)[3] with *p*-phenylene diamine (PDA): intrinsic viscosity was 0.46 - 0.68 dL/g. The precursor solutions were cast on glass substrates, dried at 80°C for 1 h, and thermally imidized at 300°C for 1 h under a nitrogen atmosphere, producing 6.0-7.0 μm thick polyimide films (see Figure 1). The PI films adhered on substrates were rubbed with varying rubbing density (L/*l*)[1,2]. The rubbed films were assembled together in the anti-parallel rubbing direction by using 50 μm



R= $(CH_2)_3CH_3$: C4-PMDA-PDA
R= $(CH_2)_7CH_3$: C8-PMDA-PDA
R= $(CH_2)_{11}CH_3$: C12-PMDA-PDA

FIGURE 1 Chemical structures of fully rodlike polyimides containing side chains.

thick polyester film spacers, followed by filling with 4-*n*-pentyl-4'-cyanobiphenyl containing 1.0 wt-% Disperse Blue 1. The LC alignment was examined by measuring the absorbencies of a linearly polarized He-Ne laser beam (632.8 nm) as a function of rotational angle, allowing the construction of polar diagrams. And, pretilt angle (α) of the LCs was measured using a crystal rotation apparatus[1,2]. Refractive indices and thermal properties were measured by a prism coupling technique[4,5] and a thermogravimetry[1,2], respectively.

RESULTS AND DISCUSSION

The PI films were thermally stable up to 425°C. Above 425°C, they exhibited a two-step of weight loss behavior due to the degradation of side chains and polymer backbone. Depending on the side chain length, the bulk refractive index was in the range of 1.596-1.638, the out-of-plane birefringence in the range of 0.005-0.026, and the dielectric constant in the range of 2.547-2.683: the longer side chain length in the polymer gave the smaller refractive index, birefringence, and dielectric constant. These results might be attributed to free-volume gains in the film which are caused by the incorporated side chains.

On the rubbed Cm-PMDA-PDA PI films, the pretilting behavior of LCs was quite different from those reported so far in the literature. The LCs were pretilted with a negative angle rather than a positive angle: that is, the pretilt angle was in the range -25 ~ -90°, depending on the side chain length well as the rubbing density as shown in Figure 2. Here, it is noted that for the C4-PMDA-PDA PI, the pretilt angle of LCs could not be measured because of the measurement limit of crystal rotation technique but expected to be in the range of -25 ~ -55°. These results indicate that either homogeneous or homeotropic LC alignment is achievable by changing the side chain length as well as the rubbing density. This was evident in the polar diagram. For the homogeneous alignment, the LC director was also influenced by the side chain length: the C4-PMDA-PDA PI film caused the LC director to be perpendicular to the rubbing direction while the C8-PMDA-PDA PI film induced the LC director to be parallel to the rubbing direction.

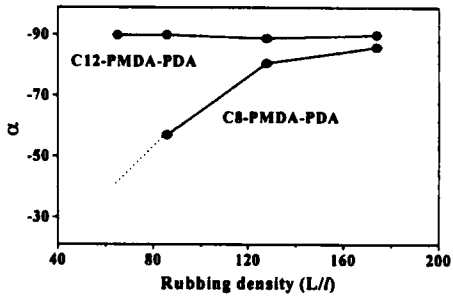


FIGURE 2 Pretilt angle variations of LC molecules on the Cm-PMDA-PDA PI films rubbed with various rubbing densities.

CONCLUSIONS

Rodlike Cm-PMDA-PDA polyimides with various side chain lengths were investigated as an orientation layer of LCs. Due to the rodlike polymer backbone characteristic coupled with side chains the polymer films have revealed their own unique properties in aligning LCs on the rubbed surface, which are quite different from the ordinary orientation layers reported previously. In conclusion, the polyimides are suitable for applications in the fabrication of microelectronic devices including LCDs.

Acknowledgements
This study was supported in part by the Ministry of Education (New Materials Research Fund in 1998 and Basic Science Research Institute Program, BSRI-98-3438) and by the Ministry of Industry & Energy and the Ministry of Science & Technology (G7 Project Program).

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