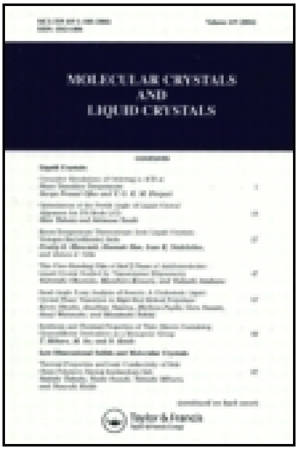

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

A Rodlike Polymer with Various Side Chain Lengths and its Ability to Align Liquid-Crystals

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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 (2001): A Rodlike Polymer with Various Side Chain Lengths and its Ability to Align Liquid-Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 368:1, 559-564

To link to this article: http://dx.doi.org/10.1080/10587250108029988

Mol. Cryst. and Liq. Cryst., 2001, Vol. 368, pp. 559-564
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Printed in the USA

A Rodlike Polymer with Various Side Chain Lengths and its Ability to Align Liquid-Crystals

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A rodlike polymer with various side chain lengths was prepared in a good quality of films. The polymer 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 cells, the ability of polymers to align LCs was evaluated, and compared to that of semi-rigid polymer containing the same type of side chains as the rodlike polymer had.

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

INTRODUCTION

Soluble, flexible polyimides are widely used in the liquid-crystal display (LCD) industry as an orientation layer material to align liquid-crystal (LC) molecules. For the LCD application, the surface of polyimide films always is mechanically rubbed with a cloth[1],[2]. The rubbed film surface has been found to induce LC alignment along the rubbing direction. However, 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 and evaluated as an LC orientation layer material. And the performance of these polymers was compared to that of semi-rigid poly(4,4'-oxydiphenylene pyromellitimide)s having the same type of side chains.

EXPERIMENTAL

A series of poly(*p*-phenylene pyromellitamic acid)s with side chains were synthesized in *N*-methyl-2-pyrrolidone (NMP) by condensation of *p*-phenylene diamine (PDA) with 3,6-bis[4-(*n*-alkyloxy)phenyloxy]pyromellitic dianhydrides (Cm-PMDAs)[3]: Cm-PMDA-PDA PAAs. In the same synthetic manner, another series of poly(4,4'-oxydiphenylene pyromellitamic acid)s were made in NMP from 4,4'-oxydiphenylene diamine (ODA) with Cm-PMDAs: Cm-PMDA-ODA PAAs. These precursor polymers had an intrinsic viscosity [η] of 0.46 - 0.68 dL/g. These PAA 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 polyimide (PI) films in a good quality (see Figure 1).

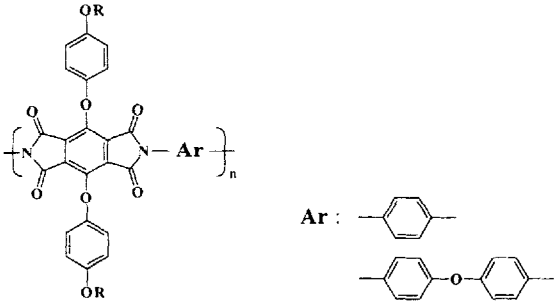

FIGURE 1 Chemical structures of rodlike and semi-rigid polyimides containing side chains: Cm-PMDA-PDA PIs and Cm-PMDA-ODA PIs. Here, R is methyl, *n*-butyl, *n*-octyl and *n*-dodecyl.

Their thermal stabilities were determined by thermogravimetry. PI films adhered on substrates were rubbed with varying rubbing density[1],[2]. The rubbed films were assembled together in the anti-parallel rubbing direction, followed by filling with 4'-*n*-pentyl-4-cyanobiphenyl (5CB) containing 1.0 wt-% Disperse Blue 1. The LC cells were characterized by crystal rotation method and plane polariscopy[1],[2].

RESULTS AND DISCUSSION

All the PI films were thermally stable up to 400°C or higher. Above this temperature, they exhibited a two-step of weight loss behavior due to the degradation of side chains and polymer backbone.

The polymer films were rubbed with various rubbing densities, and used for assembling LC cells. Their polar diagrams were mreasured. Some of the measured polar diagrams are illustrated in Figure 2. The LCs on the surface of C4-PMDA-PDA PI film were homogeneously aligned along a direction perpendicular to the rubbing direction [see Figure 2-(a)], while they were homeotropically aligned on the surface of C12-PMDA-PDA PI film [see Figure 2-(b)]. On the other hand, the C8-PMDA-PDA PI film aligned LCs homogeneously or homeotropically, depending on the rubbing strengths: rubb-

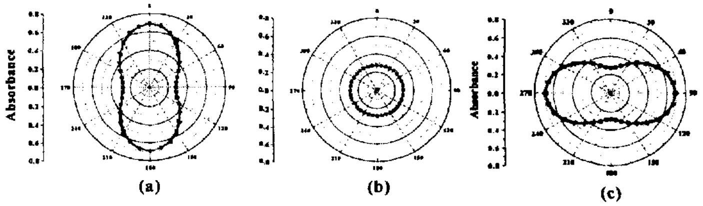

FIGURE 2 Polar diagrams measured for LC cells fabricated with PI films: (a), C4-PMDA-PDA PI; (b), C12-PMDA-PDA PI; (c), C1-PMDA-ODA PI.

ing with a low rubbing density of <100 causes a homogeneous LC alignment, whereas rubbing with a high rubbing density of >100 generates a homeotropic LC alignment. However, when LCs were homogeneously aligned on this polymer film, their alignment director stays along the rubbing direction. Overall, the LC alignment on the Cm-PMDA-PDA PI film is highly dependent on the side chain length as well as the rubbing strength. These LC alignment characteristics in the Cm-PMDA-PDA PIs are quite different from those of other polymers reported previously in the literature.

In comparison, the LC alignment on the Cm-PMDA-ODA PI film, in which its polymer chains are semi-rigid rather than fully rigid, showed to be less sensitive to the side chain length as well as the rubbing strength. A representative polar diagram measured for LC cells fabricated with the polymers is shown in Figure 2-(c). On the polar diagram, the director of LCs was stayed along the rubbing direction, regardless of the variations of side chain and rubbing strength.

In addition, the pretilt angle (α) of LCs in the cell was measured. Here, the α in a positive value is defined by an angle between the LC molecule and the film plane in the rubbing direction. On the other hand, that in a negative

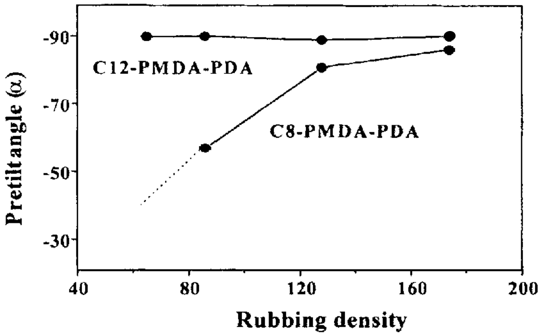

FIGURE 3 Pretilt angle variations of LC molecules on the Cm-PMDA-PDA PI films rubbed with various rubbing densities.

value is defined by an angle between the LC molecule and the film plane in the anti-rubbing direction. For the C8-PMDA-PDA and C12-PMDA-PDA PI films, LCs were aligned with α = -25 ~ -90°, depending on the side chain length and rubbing strength (see Figure 3). For the C4- PMDA-PDA PI, α was tried to measure but could not be measured because of the measurement limit of crystal rotation technique. Thus, it is expected to be α = -25 ~ -55° for LCs on this polymer film. The negative sign of pretilt in LCs on the polymer film is quite different from the positive sign of pretilt of LCs on polymer films reported so far in the literature. This may be associated to uncommon surface morphology in the film which is generated by rubbing process. That is, the surface morphology in the Cm-PMDA-PDA PI films is generated in a different way, compared to ordinary orientation layer polymers reported in the literature.

However, for LCs on the Cm-PMDA-ODA PI film a negative pretilt behavior, as well as a positive pretilt behavior was observed. As shown in Figure 4, α = 3 ~ -45° was achieved, depending on the side chain length and rubbing strength.

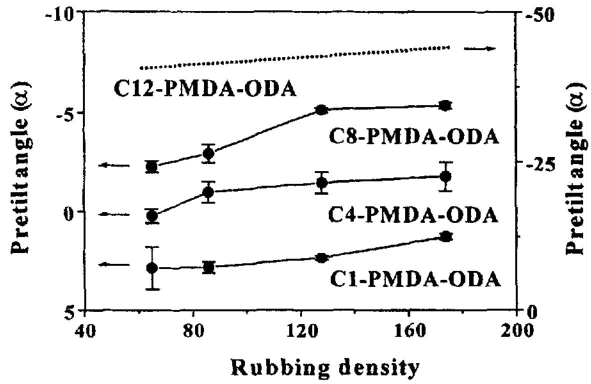

FIGURE 4 Pretilt angle variations of LC molecules on the Cm-PMDA-ODA PI films rubbed with various rubbing densities.

CONCLUSIONS

Fully rodlike Cm-PMDA-PDA PI, as an orientation layer, was demonstrated to have a strong ability to align LCs in a new way, which is never reported before. On the rubbed film surface LCs were aligned homogeneously or homeotropically, depending on the side chain length and rubbing strength. And, LCs were always pretilted negatively, regardless of the side chain length and rubbing strength. This suggests that through rubbing process of the fully rodlike polymer, side chains on the rubbed surface are oriented with a tilt angle with respect to the anti-rubbing direction rather than the rubbing direction. This unusual, unique orientation behavior might be due to the rodlike polymer backbone characteristic coupled with side chains. In comparison, semi-rigid Cm-PMDA-ODA PI, which is relatively flexible, induced homogeneous LC alignment on the rubbed surface, regardless of the side chains. However, this polymer also aligned LCs with a negative pretilt angle, depending on the side chain length and the rubbing strength, as observed for the Cm-PMDA-PDA PI films. In conclusion, these new rodlike and semi-rigid polymers 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 by the Korea Science & Engineering (Contract No. 1999-2-304-005-3).

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