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

Mol. Cryst. and Liq. Cryst., 2000, Vol. 349, pp. 279-282
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Liquid-Crystal Alignment on the Rubbed Film Surface of Semi-Flexible Copolyimides Containing *n*-Alkyl Side Groups

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Semi-flexible copolyimides with various alkyl chain lengths (BTDA-ODA/CnMPD PIs) were newly synthesized in *N*-methyl-2-pyrrolidone from benzophenonetetracarboxylic dianhydride, 4,4′-oxydiphenylene diamine, and 3,5-diaminobenzoyl *n*-alkanoates. The films were rubbed with varying rubbing densities, and on the rubbed surface the alignment behavior of a nematic liquid-crystal (LC) was examined. LCs were always aligned along the rubbing direction either homogeneously or homeotropically, depending on the side chain length as well as the rubbing density. The results inform that flexible *n*-alkyl side groups in the copolyimide play a critical role to align LCs on the surface, and their role is strongly dependent on its length. In addition, thermal, optical, and dielectric properties were investigated.

Keywords: semi-flexible copolyimide with side chains; rubbing process; liquid-crystal alignment; pretilt angle

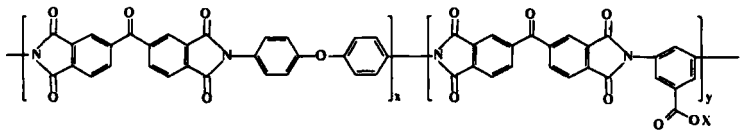
INTRODUCTION

Rubbing process is widely used in the liquid-crystal display (LCD) industry for fabricating orientation layers to control the alignment of liquid-crystal (LC) molecules. However, the alignment mechanism of LCs on the rubbed surface has not been fully understood yet. Further, the LCD industry is still seeking

a new orientation layer material having high performance for developing advanced LCDs. In this study, a series of semi-flexible copolyimides with *n*-alkyl side chains were synthesized in thin films. The films were rubbed and employed to examine the alignment behavior of LCs on the surface. In addition, thermal, optical and dielectric properties were measured.

EXPERIMENTAL

A series of copoly(amic acid) precursors containing various alkyl chains were synthesized in *N*-methyl-2-pyrrolidone from the polycondensation of benzophenonetetracarboxylic dianhydride (BTDA) with a mixture of 4,4'-oxydiphenylene diamine (ODA) and 3,5-diaminobenzoyl *n*-alkanoate (CnMPD)[1] (1:1, molar ratio). The precursor solutions were cast, dried at 80°C for 1 h, and thermally imidized at 300°C for 1 h at under nitrogen atmosphere, giving ca. 200 nm or 4.0-6.0 μm thick copolyimide films (see Figure 1) in accordance to the desires. The PI films adhered on substrates were rubbed, and assembled together in the anti-parallel rubbing direction by using 50 μm polyester film spacers, followed by filling with 4-*n*-pentyl-4'-cyanobiphenyl containing 1.0 wt-% Disperse Blue 1. Polar diagram was constructed from the absorbencies of a linearly polarized He-Ne laser beam measured as a function of rotational angle. And, pretilt angle (α) of the LCs was measured using a crystal rotation apparatus[2]. In addition, refractive



X= CH_3 : BTDA-ODA/C1MPD
$(CH_2)_5CH_3$: BTDA-ODA/C6MPD
$(CH_2)_{11}CH_3$: BTDA-ODA/C12MPD
$(CH_2)_{17}CH_3$: BTDA-ODA/C18MPD

FIGURE 1 Chemical structures of semi-flexible copolyimides containing *n*-alkyl side chains: x = y = 0.5.

refractive indices and thermal properties were measured according methods described elsewhere[2-4].

RESULTS AND DISCUSSION

On the rubbed copolyimide film, the pretilting behaviors of LCs was sensitive to the side chain length. As shown in Figure 2, the pretilt angle (α) of LCs varied over 6-80°, depending on the side chain length as well as the rubbing density. The copolyimide with alkyl chains of $\leq$ 12 carbons induced a homogeneous LC alignment with α < ca. 55°. Here, for the copolyimide with alkyl chains of 12 carbons the α is expected to be in the range of 25-55° because it could not be measured due to a limit of measurement tool. The LC director was parallel to the rubbing direction. On the other hand, the copolyimide with alkyl chains of 18 carbons caused a nearly homeotropic LC alignment with α = 78-83°. From these results it is concluded that the alkyl side chain and its length in the copolyimide play a critical role in controlling the alignment of LCs on the rubbed surface. In addition, the thermal stability of the LC alignment was investigated by changing annealing temperature. For all the copolyimides, the α apparently was not changed with annealing below 120-160°C, but degraded with annealing above 120-150°C.

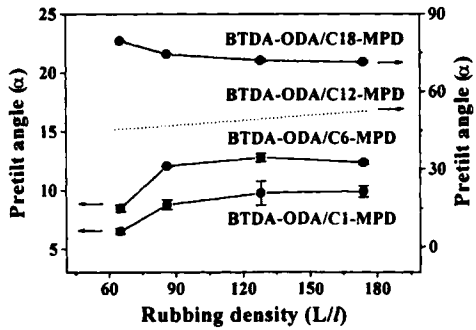


FIGURE 2 The pretilt angles of LC molecules on the BTDA-ODA/Cn-MPD PI films rubbed with various rubbing density.

The copolyimide films were thermally stable up to ca. 350°C. Above 325°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 1.643-1.681, the out-of-plane birefringence in the range of 0.005-0.016, and the dielectric constant in the range of 2.699-2.826: the longer side chain length in the polymer gave the smaller refractive index, birefringence, and dielectric constant. These results might be attributed to the free-volume gains in the film which are caused by the incorporated side chains into the polymer backbone.

CONCLUSIONS

A series of new copolyimides with various alkyl side chains were synthesized, giving a good quality of thin films. The polymers are thermally stable up to ca. 350°C in spite of containing flexible alkyl side chains, and further have a relatively low dielectric constant with a very low anisotropy. The copolymers exhibited an excellent rubbing processability. Nematic LCs on the film surface was pretilted with 6-83°, depending upon the side chain length as well as the rubbing density. That is, the alignment of LCs is controlled well on the film surface by changing the side chain length as well as the rubbing density. Conclusively, the new BTDA-ODA/CnMPD PIs are a good candidate material for LCD applications as orientation layers to control LC alignment.

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), by the KOSEF (Contract No. 95-0300-13-01-3), and by the Ministry of Industry & Energy and the Ministry of Science & Technology (G7 Project Program).

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