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Effect of Alkyl Side Chain of Soluble Polyimide Orienting Layer on Liquid Crystal Alignment

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The surface properties of soluble polyimide with alkyl side chain as alignment layer were studied by contact angle, pretilt angle and thermal property(Tg) measurements. The contact angle before rubbing was higher than after rubbing and lower glass transition temperature (Tg) were obtained for polyimides with longer alkyl side chain. The pretilt angle was affected by alkyl side chain length and glass transition temperature of polyimide.

Keywords: polyimide; pretilt angle; alkyl side chain length; glass transition temperature

INTRODUCTION

The study of interfacial properties between the liquid crystal molecules and the surface of alignment layer is essential for the understanding of liquid crystal alignment mechanism. Two mechanisms of liquid crystal alignment by rubbed polymer surface have been proposed. One is based on microgrooves¹ and the other concept is that dipole interaction between LC molecules and oriented polymer molecules². The pretilt angle generation in nematic liquid crystal on various alignment layers by unidirectional rubbing has been demonstrated and discussed by many researchers. Polyimide with alkylene in main chain³ and alkyl branched polyimide⁴⁻⁷ were studied to examine the effect of structure on the pretilt angle. The even-odd effect of alkyl chain was observed and relatively high pretilt angles by some of alkyl branched polymer have been reported.

In this paper, we will present the synthesis of soluble polyimides with various alkyl side chain and discuss the relationship between thermal property of polyimide on alkyl chain length and pretilt angle. 206 C. LEE *et al*.

FIGURE 1 Structure of the prepared polyimide $(R: H, -(CH_2)_mCH_3; m = 0 \sim 5)$

EXPERIMENTAL

For the preparation of soluble alicyclic polyimide (4-(2,5-dioxotetra hydrofuran-3-yl)-tetralin-1,2-dicarboxylic anhydride(DOTDA)) was added to a solution 3,5-diaminobenzoic acid(DABA) in NMP and the reaction mixture was stirred at room temperature for 24h. Xylene was added to this polymer solution and then refluxed azeotropically for 5h. After precipitated in methanol, alkylation was performed with 1,8-diazabicyclo-[5,4,0]-7-undecene(DBU) and alkyliodide. Synthesis of soluble aromatic polyimide(mPDA/DDDM/PMDA/6FDA) was carried out in the similar manner.

The polyimide solution dissolved in NMP was spin-coated onto clean ITO-glass at 2000rpm for 15s. The thickness of aligning layer was approximately 0.1 μ m. After drying at 80 °C for 6h, the plate was annealed at 180 °C for 0.5h. Heat-treated substrates were rubbed using a machine equipped with nylon roller. The LC cells were assembled with rubbing direction of the opposing glass plates aligned in antiparallel manner. The cell gap was 70 \pm 0.5 μ m. The pretilt angle of LC cells was measured by the crystal rotation method. Contact angle measurements were made using a RAME'-HART Inc. (Model 100-00 115). The used LCs were BL001 (Merck Co. Ltd.).

RESULTS AND DISCUSSION

The pretilt angle, thermal property(Tg) and water contact angles are shown in Table 1. Contact angle before rubbing was higher than contact angle after rubbing. These results indicated that alignment surface became more polar by rubbing. Thus, polar groups of an alignment layer were reoriented outward plane of the surface by rubbing with nylon roller, while nonpolar groups such as alkyl side chain folded inward.

However we did not find a clear relationship between the pretilt angles and contact angles. The glass transition temperature(Tg) of polyimide decreased with the increase

				_			
R	Н	m=0	m=1	m=2	m=3	m=4	m=5
contact angle before rubbing	70	67	67	69	72	73	78
contact angle after rubbing	53	54	56	57	61	62	66
$Tg(\mathbb{C})$	360	258	254	249	219	219	187
Tilt angle	2.5	1.9	3.2	0.9	_	-	_

TABLE 1. Measured contact angle, pretilt angle and glass transition temperature of soluble alicyclic polyimide (DOTDA/DABA) with a various alkyl side chain

of alkyl side chain. When the number of carbons in side chain become more than 4, the glass transition temperature(Tg) of alignment polymer decreases significantly. In this case we were unable to measure the pretilt angle. Since the LC cell had to be heated at the isotropic temperature of the LC to fill the cell, thermal stability of surface of alignment layer is very important.

Although the thermal behavior of bulk polymer and polymer surface is different, the thermal behavior of polymer surface may depend on thermal properties of bulk polymer. For comparison, temperature dependence of pretilt angles of soluble aromatic PI(mPDA/ DDDM/ PMDA/ 6FDA) with higher Tg (334 °C) was investigated.

Fig.2 shows a variance of pretilt angle of LC cell assembled after annealing at each temperature. When the annealing temperature became more than 120 °C, the pretilt angle dropped to near to zero. Fig.3 shows pretilt angles change of assembled LC cell at

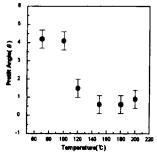


FIGURE 2 Change of pretilt angle of LC cell assembled after annealing

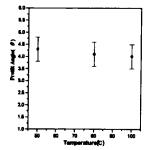


FIGURE 3 Change of pretilt angle of assembled LC cell.

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each temperature. We were unable to measure the pretilt angle for sample annealed more than 120 $^{\circ}$ C. With polarized microscopy, the LC cell was shown to have disclination and the alignment of LC was destroyed. Since polyimide with ethyl side chain (m=1 in Table 1; Tg=254 $^{\circ}$ C) decreased its pretilt angle to near zero at 60 $^{\circ}$ C, the higher Tg may provide stable pretilt amgle. The surface orientation of alignment layer was affected by thermal stability.

CONCLUSION

The alignment layer polyimide with alkyl side chain became polar by rubbing. We did not find a clear relationship between the pretilt angles and contact angles. The pretilt angle was affected by alkyl side chain length and glass transition temperature(Tg) of alignment polyimide. When the number of carbons in side chain was more than 4, the Tg decreased significantly. Surface orientation was destroyed at certain temperature which can be related to the Tg of polyimides.

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