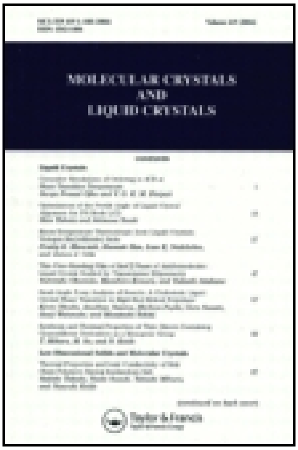

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Effect of curing temperature on pretilt angles of polyimide alignment layer

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EFFECT OF CURING TEMPERATURE ON PRETILT ANGLES OF POLYIMIDE ALIGNMENT LAYER

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Poly(amic acid ester) and poly(amic ester) of polyimide precursors were prepared from the corresponding poly(amic acid) with controlling esterification ratio of the pendent carboxylic group. These three different precursors were examined for the generation of pretilt angle after curing at various temperatures. All three alignment layers generated maximum tilt angle when they were cured at the temperature approximately 20°C below the maximum imidization temperature. The results indicated that the proper stiffness of main chain and residual functional group in the alignment layer were important for the generation of high pretilt angle.

Keywords: alignment layer; different precursors; imidization temperature; pretilt angle

INTRODUCTION

Rubbing polymer surfaces into one direction causes aligning the polymer chains on the surface. When liquid crystal (LC) molecules are placed on the rubbed surface, unidirectional alignment of LC molecules with a certain inclined angle (pretilt angle) is achieved. The generation of pretilt angle is important to prevent the reverse tilt disclination, which appears as defect, and pretilt angle of higher than 2° is needed for fabrication of defect free TFT-LCDs [1]. Since rubbing is simply a mechanical shearing process and the generation of pretilt angle is related to the molecular interactions between the polymers and LC molecules, T_g and molecular structure of polymers are important factors of the alignment layer for the LCD.

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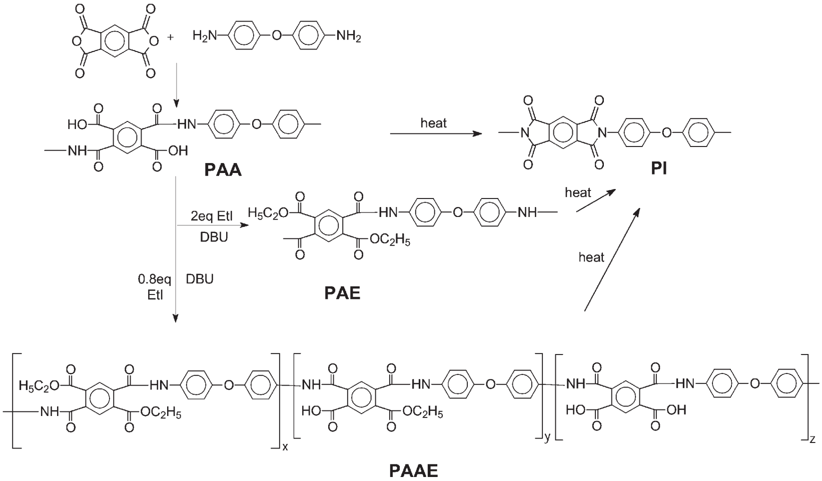
Polyimides (PIs) are commercially employed for the alignment layer because it produced a stable and reproducible alignment and tilt angle after rubbing with a cloth roller.

The alignment and generation of pretilt angle are understood by the electronic and steric interaction between the liquid crystal molecules and the molecules at surface together with the effect of microgrooves created by rubbing [2–5]. The surface molecules of PI alignment layer were oriented along the rubbing direction even though the rubbing was carried out under remarkably small loads and at the temperature more than hundred degrees below the T_g of PI. Toney *et al.* reported that molecular orientation occurred only at the near-surface region and they suggested that T_g and the yield stress of the near-surface region be relatively lower than those of bulk region [6]. We also observed that the surface morphology and orientation were changed at much lower temperature than the bulk T_g of PI [7].

It has been reported that pretilt angle increased with the increase of curing temperature thus molecular structure and imidization degree that related to the thermo-mechanical properties affected pretilt angles [8]. Recently Paek reported that the increase of pretilt angles with the increase of imidization degree only hold for the main-chain poly(amic acids) (PAAs) not for the alkylated poly(amic acids) [9]. Since PI was prepared by curing PAAs and T_g of the resulting PIs increased as the imidization degree increased, understanding curing effect on alignment layer is important.

In the course of synthesis of different PI precursors, we found that the carboxylic acid group in PAA could be readily alkylated to produce the cor-



SCHEME 1 Preparation of PAA, PAE, and PAAE.

responding ester group by reacting PAA with 1,8-diazabicyclo-[5,4,0]-7-undecene (DBU) and ethyl iodide. (Scheme 1) By controlling the added amount of DBU and ethyl iodide, we could prepare poly(amic ester) (PAE), a full ester of PAA, and poly(amic acid-*co*-amic ester) (PAAE), a half ester of PAA. Although these precursors had different curing properties, they should yield the same molecular structure of PI after curing. In this work, we examined the dependence of the pretilt angle on the curing conditions of the different precursors to gain more insight of the relationship between curing temperature and the generation of pretilt angle after rubbing.

EXPERIMENTAL

PAA solution was prepared by reacting stoichiometric amounts of pyromellitc dianhydride and 4,4′-oxydianiline in N-methylpyrrolidone (NMP) for 6 h at room temperature under nitrogen atmosphere. After the addition of calculated amounts (2 eq. for PAE and 0.8 eq. for PAAE) of DBU, the viscous solution was stirred for 30 min. Equimoalr amounts of ethyl iodide to the DBU was then added and the solution was stirred for 24 h at room temperature (scheme 1). After precipitating and drying, the dried PAAE and PAE were dissolved into NMP and viscosity of the solution was adjusted to give approximate100 nm thick coatings on to ITO-glass at 2000 rpm. After drying spin-coated plates in vacuum oven at 50°C for 6 h, the plate was heated for 0.5 h each at 80°C, 100°C, 130°C, 150°C, 180°C, 200°C, 250°C, 300°C, and 350°C under a flow of nitrogen with heating rate 5°C/min. Thermal behavior of precursors was examined using differential scanning calorimeter (Perkin Elmer DSC-7).

The heat-treated spin-coated plates were rubbed using a machine equipped with nylon roller (FSA-90-011, Wande Inc. Co. Ltd.) and the sandwich-type cells with a LC layer thickness of $70 \pm 0.5\,\mu\text{m}$ were assembled as opposite glass plate had antiparallel rubbing direction. The pretilt angles of LC cells were measured by the crystal rotation method and average value was reported [10–11]. The used LC was BL001 (Merck Co. Ltd.).

RESULTS AND DISCUSSION

The carboxylic group in PAA was almost quantitatively alkylated when alkyl iodide was reacted with PAA in NMP solution using DBU as a base. (Scheme 1) All three precursors, PAA, PAE and PAAE produced PI with the same chemical structure after thermal curing but their curing behaviors were different so that it was possible to compare the effect of curing

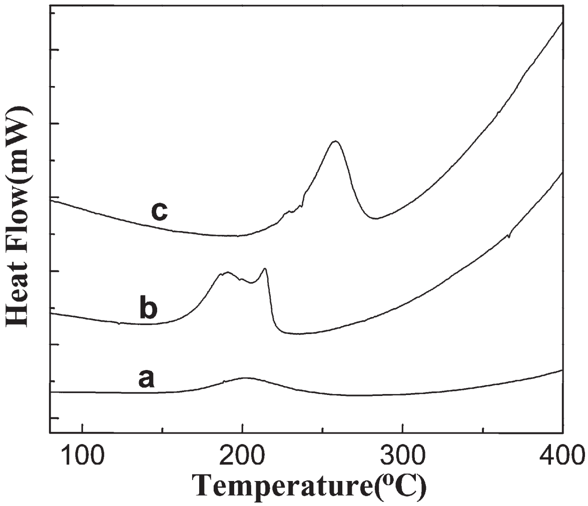


FIGURE 1 DSC diagram of a) PAA, b) PAAE, and c) PAE.

temperature on the LC alignment between alignment layers with similar structures. Figure 1 shows DSC thermograms of these precursors. The endothermic peaks in Figure 1 corresponded to the maximum imidization temperature, which did not show up in the second scan. The observed maximum imidization temperature (T_{maxI}) was 201°C and 258°C for PAA and PAE, respectively. These endothermic peaks were related to the evaporation of water and ethanol, which were generated from the intramolecular cyclization of amide acid and amide ester units in the precursors. The T_{maxI} of PAE was about 57°C higher than that of PAA due to the lower reactivity of amide nitrogen with ester group than that with carboxylic acid group. PAAE showed two T_{maxI} at 187°C and 215°C as imidization of acid moiety occurred first and imidization of ester moiety occurred afterward. The reason why T_{maxI} of PAAE was observed at lower temperature than PAA and PAE is not clear. We speculated that if alkylation reaction produced y segment enriched PAAE (Scheme 1) then the molecular structure of PAAE might be more adaptable for the imidization.

Next the pretilt angle was measured with each precursor coatings at various temperatures and the results are plotted in Figure 2. The pretilt angle increased as the increase of curing temperature and then decreased after it reached maximum. Although all the polymer membrane in the present experiment produced good quality alignment of LC regardless of the curing temperature, which was the pre-requirement of measuring pretilt angle, the pretilt angle started to decrease after curing at near and

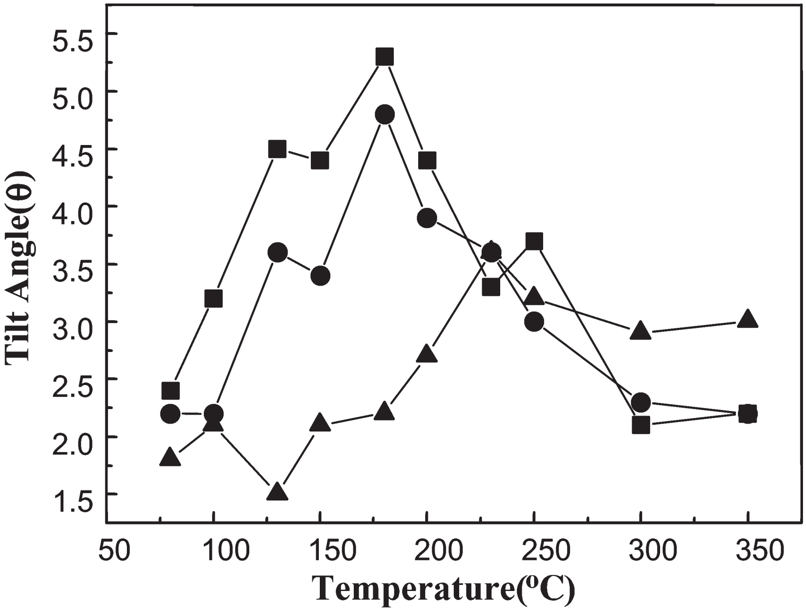


FIGURE 2 Dependence of pretilt angle on curing temperature (–■–; PAA, –●–; PAAE, –▲–PAE).

higher than T_{maxI}. The observed maximum pretilt angles were 5.3° for PAA at 180°C, 4.8° for PAAE at 180°C, and 3.6° for PAE at 230°C. It is interesting to note that the maximum pretilt angles were generated just approximately 25 to 30°C below the T_{maxI} of each precursors. This result implied that there were certain curing temperature ranges to generate high pretilt angle.

The curing temperature of polyimides was directly related to the degree of imidization, which in turn affected T_g and stiffness of polyimides. It is believed that the imidization degrees of PAA and PAAE cured at the temperature where they showed the highest pretilt angle were less than 70% because the imidization degree of PAAs cured at T_{maxI} for 30 min was about 80% from the FT-IR study.

The above results implied that it was necessary to have rigid segments and soft segments in the polymer chain for the generation high pretilt angle by rubbing method. As the imidization proceeded, more rigid imide units would be produced in the polymer chain and consequently higher pretilt angle was obtained after rubbing. The decrease of pretilt angle after reaching the maximum could be explained by the fact that polyimide chain might become too rigid to generate high pretilt angle by rubbing. The molecules in the polymer surface were still oriented into the rubbing direction after curing at near and above T_{maxI} but not enough deformation could occur for the generation of high pretilt angle.

Another factor of importance is the residual functional group. Effect of surface polarity of polyimide with polar and nonpolar side groups was reported by Lee *et al.* [12]. According to their study, polyimide backbone and nonpolar side chain were reorganized by rubbing such that polar functional group oriented outward of the surface and non-polar group fold inward (partially hidden underneath the surface). Thus, the surface became more polar after rubbing with polar nylon cloth. This kind of reorientation is probably caused by the electronic attraction between polar cloth and polar functional groups. Since polar functional groups such as carboxylic acid and ester were abundant in PAA and PAAE when the precursors were cured below T_{maxI}, the polymer surface should become more polar after rubbing. It was apparent that carboxylic acid group was more effective to generate high pretilt angle than ethyl ester group as the maximum pretilt angles of PAA were measured higher than that of PAAE and PAA.

CONCLUSION

We investigated a qualitative relationship between pretilt angle and curing temperature. The observation of maximum pretilt angle during the curing process is new finding and can be understood as both the residual polar group and proper stiffness are important. For this main-chain type polyimide, proper thermo-mechanical stability and orientation stability of polymer membrane were obtained approximately 20°C below the T_{maxI} and the residual functional groups such as acid, ester and amide acted as the side chain functional group.

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