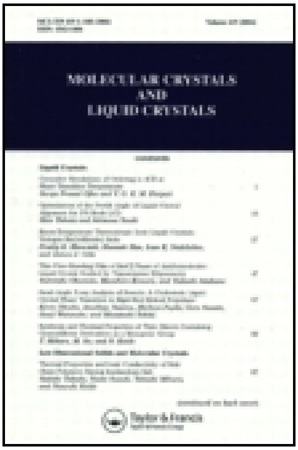

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Surface Properties of Rubbed Polyimide for Alignment of Liquid Crystal

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Surface Properties of Rubbed Polyimide for Alignment of Liquid Crystal

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The surface tensions with the structural changes in the alignment layer surface due to rubbing was compared with the curing temperature and the rubbing strength. At low curing temperature, the polar component of surface tensions had a high contribution, but at high curing temperature, the dispersion component was greater than the polar components. These indicated that the surface cured at high temperature were less polar than those at low temperature, while, rubbing resulted in the larger polar component and induced the ordering of polar groups on the surface in the X-ray measurement. Then, the ordering of polar groups in the rubbed surface could be conjectured to play an important role in the alignment of liquid crystals from the fact that the layer with a high dispersion component also aligned liquid crystals along the rubbing direction.

Keywords: Liquid crystals, Surface tensions, Alignment films, X-ray diffraction, Polar component.

1. INTRODUCTION

Liquid crystals were aligned by the interfacial interaction between liquid crystals and the rubbed surface. The interfacial interaction force was propagated into the bulk by elastic forces[1] and then liquid crystals were aligned in the cell with a preferential orientation. The interfacial interaction could be classified into two groups; one was the elastic forces due to the topological effects of microgrooves generated by rubbing[2] and the other was the physicochemical interactions originated from the interfacial energy between liquid crystals and the surface[3], in which the surface was suggested to have undergone the following changes: a reorientation of polymer chains by local melting due to rubbing[4] and a surface memory effect due to the plastic deformation[5]. It was not clearly whether the alignment of liquid crystal was mainly induced from the physicochemical interaction or the geometrical deformation.

For reorienting polymer chains, much heat was required to locally melt them down, but it might not be sufficiently generated on the surface by rubbing only. However, the heat generated by rubbing could to some degree contribute to increase the temperature of the surface and then enhanced the change of the surface structure. Even if the

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alignment layers were not rubbed, the functional groups and concentrations of the surface group would be rearranged[6] and at an elevated temperature, they were rearranged within a short period[7]. Such a structural rearrangement was represented by a difference of the surface tension before and after rubbing treatment[8]. Many people suggested that the interface orientation could be determined in terms of the surface energies[1, 3, 8, 9, 10 11].

In this work, the alignment of liquid crystals on the polyimide layer was investigated by the comparison of the surface tensions and the structural change of the layer surface before and after rubbing. The conditions of the layer formation, i.e., the imidization temperature, were also investigated before rubbing the layer, and after rubbing, the surface tensions and the spreading of liquid crystal.

EXPERIMENTAL

Polyamic acid, the precursor of PMDA/ODA (poly 4,4-oxydiphenylene pyromellitimide) polyimide, was spin-coated on the ITO glass. After vacuum-drying at 100°C for 1hr, the coated films were cured at temperatures of 150, 200, 250, 300, and 350°C for 1hr. The film at 350°C was completely imidized[12]. The thickness of the film cured was about 120 nm. The cured films at 350°C were rubbed by slightly contacting with a rubbing cloth of velvet (Yoshikawa Co.) at various rotating speeds (rpm) of the cylinder. Each rotating speed was denoted to be the rubbing strength (L) of 50, 100,150, 200, and 250, respectively[13].

The degree of imidization of curved films was determined by an IR spectra normalized against the internal aromatic absorbance band, which was usually independent of film thickness[12]. The degree of imidization was quantified by the absorbance of each cured film using an FR-IR spectrometer. All FT-IR spectra were recorded at a resolution of 4-cm^{-1} with a DTGS detector of a Bomem spectrometer at room temperature. 70 scannings were performed in order to lower the ratio of signal to noise (S/N).

Water/Ethanol mixtures[8] were used to measure the contact angles of cured films at specified temperatures using a goniometer-microscope. A polar and dispersion component of surface tensions were determined from contact angles of curved films by using eqn. (1)[14] and the least-squares method.

$$1+\cos\theta = 2[(\gamma_S^d\gamma_L^d)^{1/2}+(\gamma_S^p\gamma_L^p)^{1/2}]/\gamma_L \qquad (1)$$

Where γ was the surface tension and θ was the contact angle of a droplet of liquid on the treated surface. The subscripts S and L refer to a polymer and a liquid, respectively. The superscripts d and p refer to the dispersion component and the polar component.

RESULTS AND DISCUSSIONS

Imidization vs Surface Tension

Figure 1 showed the degree of imidization of the coated films at the specified temperatures. The characteristic bands of polyimide were as follows; 720 cm^{-1} for the

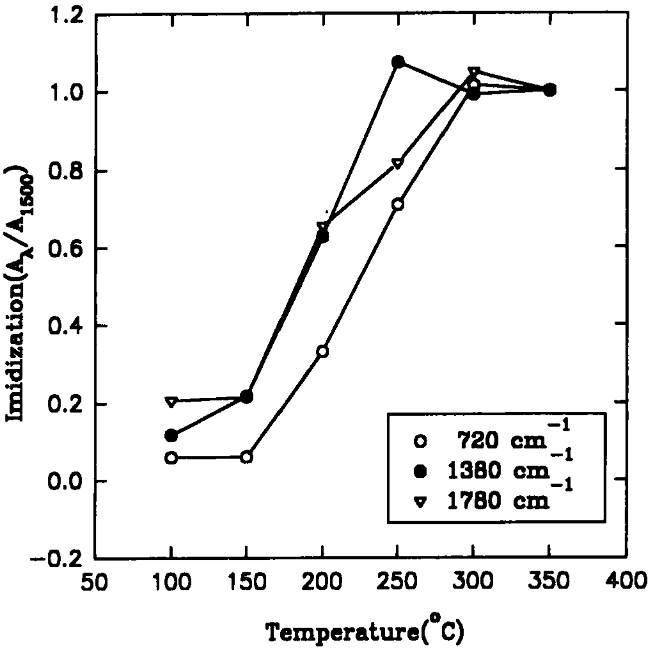


FIGURE 1 The imidization of PMDA/ODA with a curing temperature for 1 hr.

bending vibration of imide bond, 1380 cm^{-1} for the —C—N— stretching vibration, and 1780 cm^{-1} for the symmetric vibration of the carbonyl group[12]. At a temperature lower than 200°C, polyamic acid was hardly imidized, but the imidization started to proceed at 200°C and almost completed over 250°C. The imidization did not conspicuously proceed above 250°C, therefore it was reasonable that the complete imidization was achieved at 350°C.

In Figure 2, the surface tensions of cured films were plotted to the specified temperatures. The total surface tensions did not vary much within the range of temperature tested. The dispersion component increased up to 200°C and slowly above that temperature. The dispersion components similarly behaved along the imidization with curing temperature, but the polar component decreased in reverse. As a result, a polarity (γ^p/γ^t) was gradually reduced with temperature. Figure 2 also showed that as polyamic acid was imidized, the dominant contribution of total surface tension was shifted from the polar to the dispersion component. It can be explained that because the polar component of the surface tension was directly related to atomic percentage of the polar groups[3], more polar groups such as oxygen and nitrogen in polyamic acid exposed on the surface with a low degree of the imidization lower temperature gradually were situated in the bulk with an increase of temperature.

At 200°C of the intermediate degree of imidization, higher dispersion components of the surface tensions seemed to originate from a formation of anhydride by the reaction of Figure 3[15]. It can be measured by following the anhydride carbonyl absorbance near 1860 cm^{-1} in the FT-IR spectrum[12] and was shown to be most activated at the

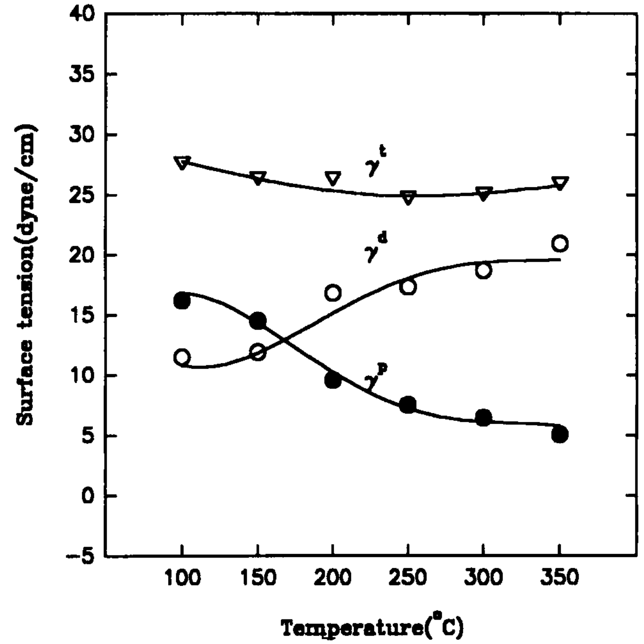


FIGURE 2 The dependence of the surface tension of the curing temperature.

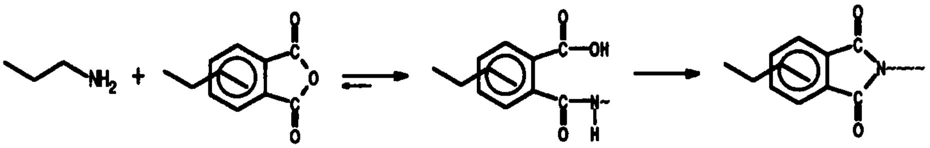
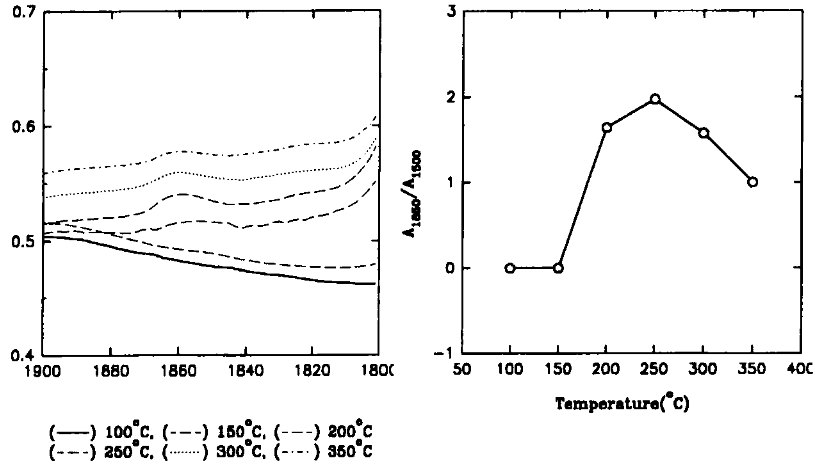


FIGURE 3 The imidization reaction of polyamic acid to polyimide and the formation of anhydride and amine.

temperature of 200°C in Figure 4. The anhydride was formed with amines by chain-scissions. In a vacuum or air, the groups of polymer contributing to the dispersion component of surface tension tended to expose onto the surface[16] but the polar groups of polymer could be reoriented toward the bulk[6]. Therefore, it was speculated that the formation of anhydride shortened main chains and then polar groups could be easily mobilized and reoriented toward the bulk. Consequently, at 200°C, the dispersion groups of polymers richly accumulated on the surface and therefore the dispersion components of surface tensions resulted in a large value. The dispersion component above 250°C remained unchanged by the subsequent formation of the imide group and the prevention of the formation of anhydride[15].

Wetting of Liquid Crystal on the Cured Surface

When liquid crystal E7 (Merck Co.) was dropped on the cured film surfaces, the contact angles between the surfaces were measured and plotted in Figure 5. The contact angles



(a) (b)

FIGURE 4 The quantitative comparison of the anhydride formation during the imidization of PMDA/ODA (a) Characteristic FT-IR absorbance of anhydride (1850 cm^{-1}) with temperature (b) Ratio of absorbance of anhydride to 1500 cm^{-1}.

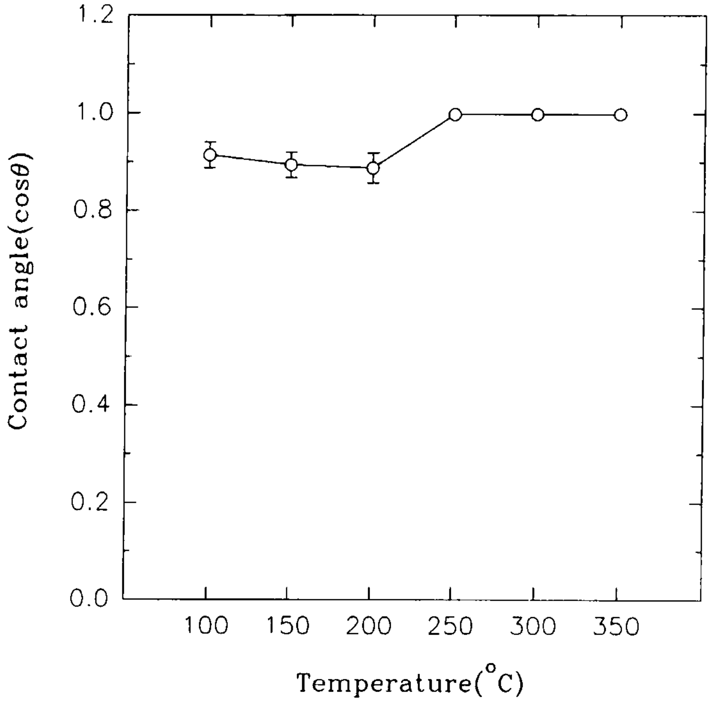


FIGURE 5 The contact angles of liquid crystal E7 at a different curing temperature.

did not change until 200°C, but decreased above 250°C. Liquid crystals had large contact angles with the films of high polar components, in which the degrees of imidization were low, while, liquid crystals were well spread on films of high dispersion components, in which the degrees of imidization were high. In this case, therefore, the dispersion component seemed to play a dominant role for the in-plane spreading of liquid crystals on the surface.

However, a film surface imidized at 200°C had a large contact angle of liquid crystals in spite of high dispersion components in Figure 5. The degree of imidization at 200°C was about 60% and the residue still remained as polyamic acid, some anhydrides and amines, as shown in Figure 3. Then, the polar groups of the residue would anchor the polar part of the liquid crystal on the surface and would inhibit the spreading.

Rubbing vs Surface Tension

Figure 6 shows the surface tensions of the rubbed surfaces under various conditions of rubbing strength. The dispersion components decreased as the rubbing strength increased but the polar component inversely increases, while the total surface tension remained unchanged. Thus, the polarity increased with the rubbing strength. This indicated that the polar groups were positioned from the bulk to the surface, and then oriented on the surface due to rubbing. Such surface restructuring could be measured by X-ray diffraction.

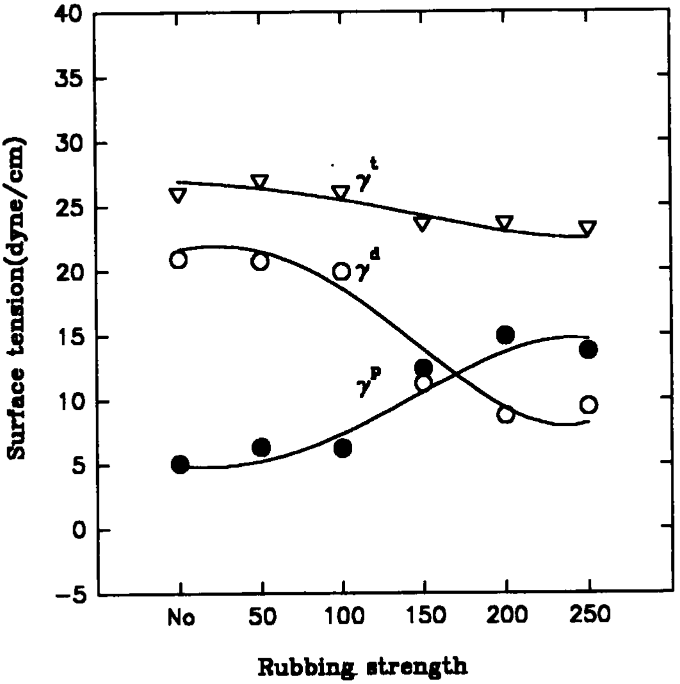
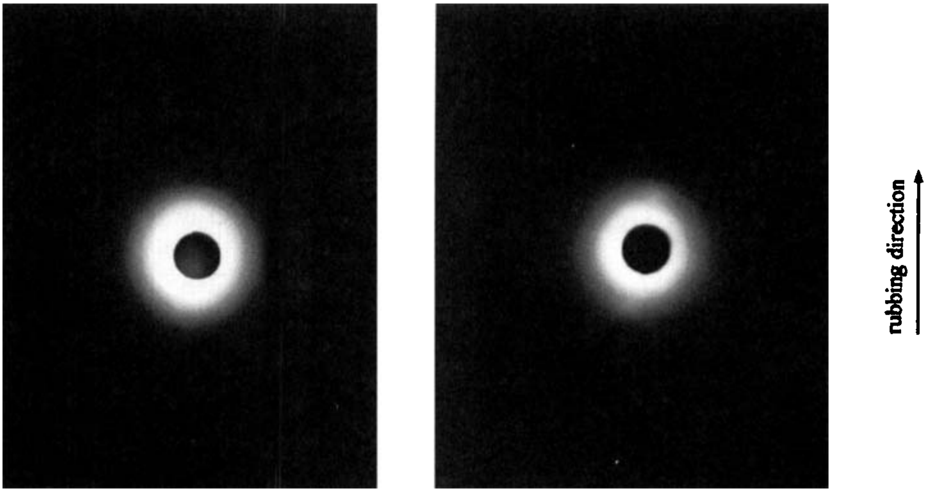


FIGURE 6 The dependence of the surface tension on the rubbing strength.

Because the surface tension depended on molecular packing (density) and was proportional to the fourth power of the density[17], the slight decrease of the surface tension with the rubbing strength could be attributed to the decreased surface density. And this decreased surface density resulted in an enhanced surface mobility. While the enhanced surface mobility was consequence of the decreased surface density, and hence increased free volume, the atomic level mobility did propagate for some distance into the bulk[17]. Therefore, surface restructuring had taken place into the depth direction from the surface due to rubbing. Such surface restructuring had taken place into the depth direction from the surface due to rubbing. such surface restructuring could be represented by the ordering of the intermolecular periodicity in Figure 7. These photographs were taken by the irradiation of an X-ray beam to the edge direction of the multiple film, (a) without and (b) with rubbing. Multiple film ($L = 150$) was made by the over-piling of rubbed film.

The ordering of the surface functional groups could take place not only in the dispersive groups but also in the polar groups. So, the ordering of the surface groups could be regarded to contribute to the alignment of liquid crystals due to rubbing, while the high polar component in Figure 6 indicated that rubbing induced the polar groups more easily to be exposed and ordered on the rubbed surface than the dispersive groups did. On the surface with a high dispersion component of $L = 100$ in Figure 6, rubbing also might have induced the ordering of the polar groups onthe surface, even though its degree was small and then the contribution to the surface tension was low.



(a) (b)

FIGURE 7 The X-ray photograph taken by the irradiation of an X-ray beam to the edge of multiple film (a) unrubbed film (b) rubbed film.

When the pretilt angle was measured with the rubbing strength[19], the pretilt angle on the surface of $L = 100$ was small as shown in Figure 8. In Figure 8, the cell of $L = 50$, owing to its partially poor alignment, was omitted in the comparison of the pretilt angles with the rubbing strength. The pretilt angle gradually increased and had the maximum value at $L = 200$ and then decreased at the high rubbing strength of $L = 250$. The surface with a high polar component gave a high pertilt angle of liquid crystals, which might be closely related to its large contact angle in Figure 5. Likewise, a low pretilt angle on the surface with a high dispersion component might be related to the spreading of liquid crystals in Figure 5.

Therefore, the magnitude of the polar component and the ordering of polar groups could be considered to be responsible for the alignment of liquid crystals. However, the latter seemed to play a dominant role in the alignment of liquid crystals from the fact that liquid crystals could be aligned even at the surface with a high dispersion component of $L = 100$ in Figure 6. On the other hand, it was reported that the dipole moment of liquid molecules contacting with a solid surface had a strong adsorption affinity influenced by the polar groups on the solid polymer surface[20]. So, the ordered polar groups favored the polar groups of liquid crystal materials, the interaction between ordered polar groups of the rubbed surface and the polar groups of liquid crystal molecules caused them to anchor at the surface and stabilized the well-aligned state of liquid crystals with a pretilt angle.

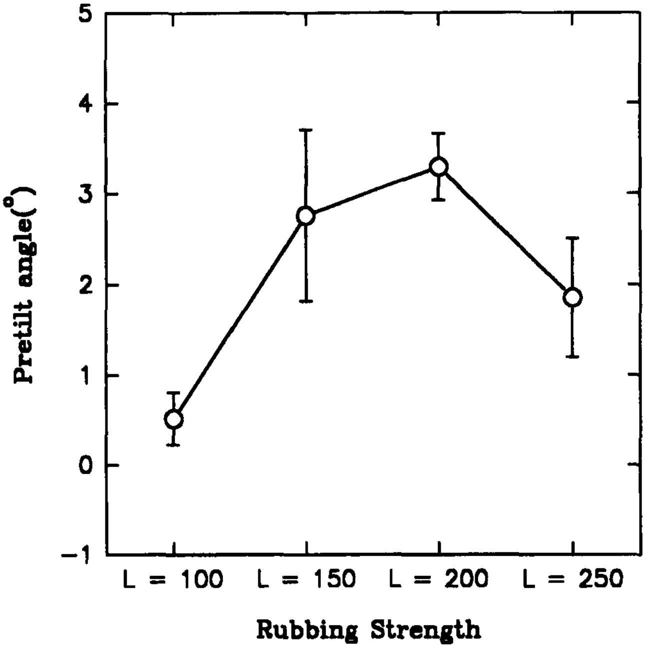


FIGURE 8 The pretilt angle variations of liquid crystal cell (E7) with the rubbing strength by the crystal rotation method.

CONCLUSIONS

The major contribution to the surface tensions shifted from the polar component to the dispersion component as the degree of imidization increases. This shift causes the spreading of liquid crystals to be enhanced on the surface. On the other hand, the spreading of liquid crystals was suppressed on a surface of a high polar component. Rubbing resulted in the enhanced mobility of the surface groups due to the decreased surface density. consequently, it induced the polar groups more easily to be exposed and ordered on the rubbed surface. Then, liquid crystals were aligned with a larger pretilt angle on the ordered surface of much more polar groups than on dispersive groups.

Acknowledgements

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