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Relationship between the Alignment of Liquid Crystal and Macroscopic Properties of Pyrolyzed Polyimide Langmuir-Blodgett Films

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The aligning properties of liquid crystal on pyrolyzed polyimide Langmuir-Blodgett (PPI LB) films were studied together with the conductivity and the morphology of PPI LB films. The aligning direction of the liquid-crystal was parallel to the dipping direction of the LB films.

Recently, we have reported that the pyrolyzed polyimide Langmuir-Blodgett (PPI LB) films exhibit a high conductivity which is stable over months.[1,2] Several studies have been reported on the aligning properties of liquid crystals (LCs) on polyimide LB films which are the precursor of PPI LB films.[3-6] It is suggested that the aligning properties of the LC on the polyimide LB films are related to the molecular alignment of polyimide. We have found that the aligning effect of the LB films is maintained after the pyrolysis of the LB films at 1000 °C.[7] In this paper, we will report the relationship between the LC aligning properties and the macroscopic properties of the PPI LB films such as conductivity and morphology to elucidate the mechanism of the aligning effects of the LB films on the LC.

The biphenyl-type polyamic acid (U-WANIS-A, Ube Kosan Ltd.) was used as a precursor of the polyimide LB films. A nematic LC of Merck E-7 was used for the studies on aligning properties of the PPI LB films. An anthraquinone dye (D5, BDH Ltd.) was used as a dichroic dye.[8] For the determination of the aligning direction, two quartz plates on which 15-layered LB films were formed were made to face with their dipping directions parallel to each other. The assembled cell was filled with the LC containing the dichroic dye. The content of the dye was 1 wt%. A twisted nematic (TN) LC cell was prepared using the PPI LB films on quartz plates with their dipping directions perpendicular to each other. The cell was filled with the LC without the dichroic dye. The contrast of the cell was measured as described previously.[7] The conductivity of the PPI LB films was determined by a dc 4-probe method. The thickness of 75-layered films was measured by the stylus method.[2] The image of the surface of PPI LB films was taken by field-emission scanning electron microscopy (FE-SEM) operating in the secondary electron emission mode at low accelerating voltage.[9]

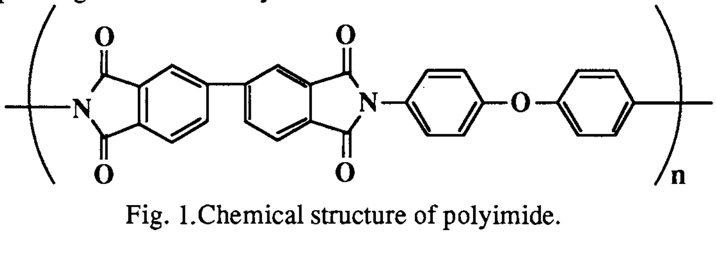


Fig. 1.Chemical structure of polyimide.

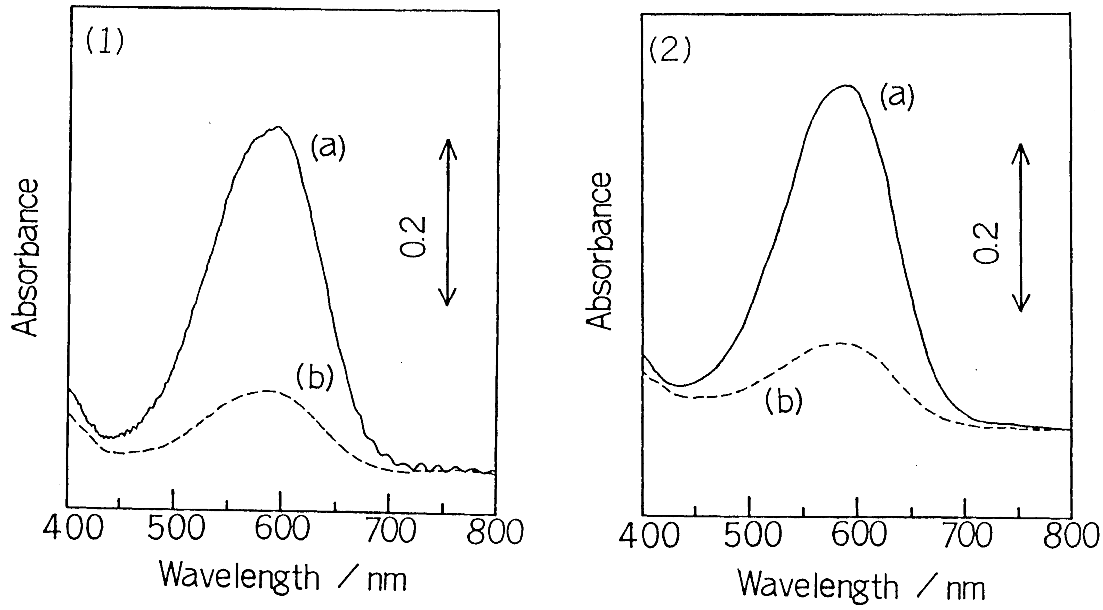


Fig. 2. Polarized absorption spectra of anthraquinone in the LC cell with the polyimide LB films (1) and the PPILB films (2); (a): parallel to the dipping direction, (b): perpendicular to the dipping direction.

Figure 2 shows the polarized absorption spectra of the LC cell with the dichroic dye using the polyimide LB films and the PPI LB films by varying the polarizing angle. In both cases, the absorbance obtained with the polarization of monitoring light parallel to the dipping direction is larger than that with the perpendicular polarization. This indicates that the LC aligning properties of the polyimide LB films parallel to the dipping direction were preserved even after the pyrolysis. The dichroic ratio D ($D=A_{//} / A_{\perp}$, at 594 nm) of the LC cells with the polyimide LB films and the PPI LB films was 4.48 and 4.11, respectively.

Figure 3 shows the relationship between the layer number and the conductivity of the PPI LB films. The conductivity was below the limit of detection for 1- and 3-layered samples and was constant at about 100 S/cm for the samples of more than 11 layers. In the case of Kapton-type PPI LB films, the conductivity increased gradually until 51 layers. We assume that , at small layer numbers, conduction channels are formed incompletely and that is the reason of small conductivities. These results suggest that the biphenyl-type PPI LB films in this study gave a constant structure in terms of the developement of conduction channels at smaller layer numbers compared with the Kapton-type PPI LB films.

Figure 4 shows the relationship between the layer number and the contrast (the ratio of transmittance at the angle between the analyzer and the polarizer 90° to that at 0°) of the twisted nematic (TN) LC cells using the PPI LB films. The contrast of the cell was very low without LB films, indicating that the alignment of the LC is almost random. The contrast of the LC on the PPI LB films increased with an increase in layer number and became constant at about 100 for the samples of more than 15 layers. This relationship is similar to that of conductivity as is seen in Fig. 3.

The morphology of the LB films was studied in order to examine further the difference in the structure of the film with the variation of the layer number. Figure 5 shows the FE-SEM pictures of the surface of 5- and 15-layered PPI LB films. The 5-layered PPI LB film has a network structure with an uneven surface probably due to the volume loss during the pyrolysis. It is interesting that this network has an anisotropic structure with

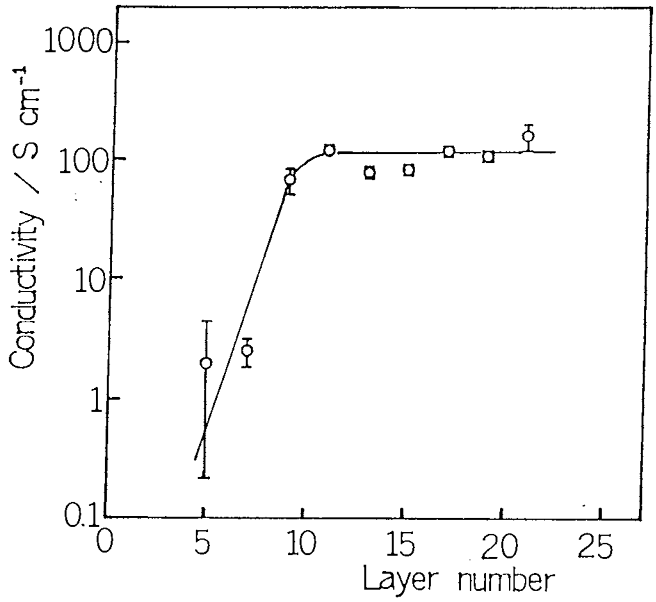


Fig. 3. Relationship between the layer number and the conductivity of the PPI LB films.

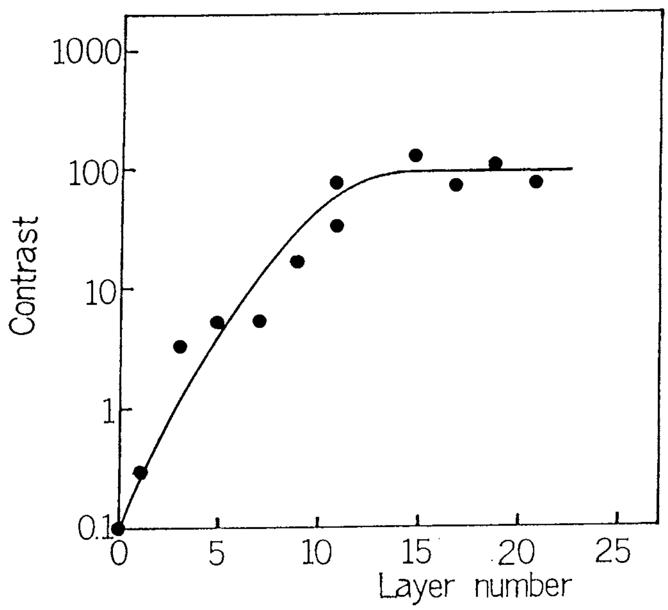
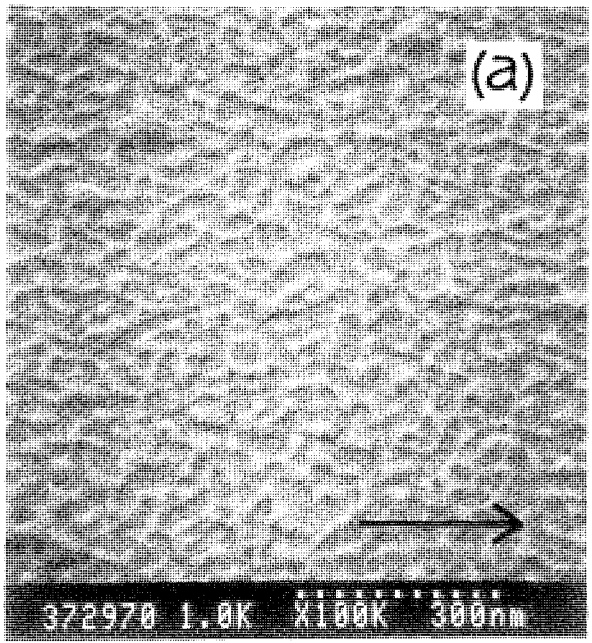


Fig. 4. Relationship between the layer number and the contrast of TN LC cells using PPI LB films.

the aspect ratio of 1.4 determined from $L_{//} / L_{\perp}$ according to Smith and Lobb,[10] where $L_{//}$ and $L_{\perp}$ are the average network widths of the PPI LB films parallel and perpendicular to the dipping direction, respectively. This tendency is similar to that of polyimide LB films[3,7] whose anisotropic structure is caused by the flow orientation during the dipping process,[11] suggesting that the polymer alignment of the polyimide remains in the elements of the network structure. On the other hand, the 15-layered sample shows a flat surface throughout the film.

At present, the following explanation can be offered for the conductivity and the alignment properties of the PPI LB films. The increase in the conductivity with an increase in layer number should arise from the



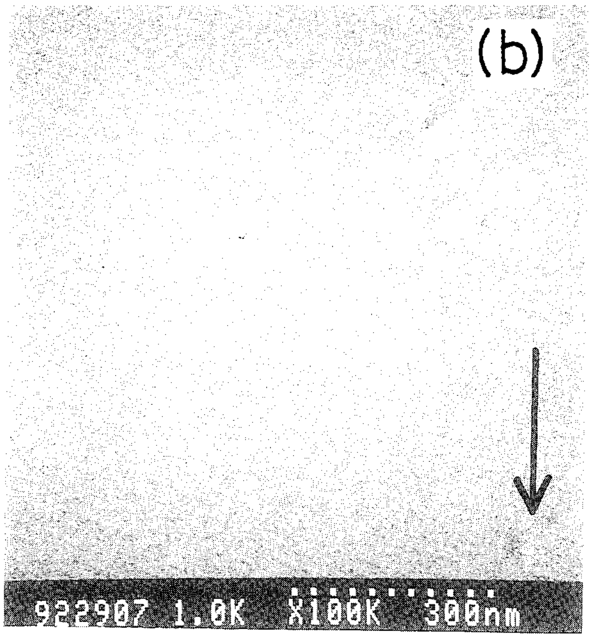


Fig. 5. FE-SEM image of 5-layered (a) and 15-layered PPI LB films (b). The dipping direction is indicated by an arrow.

development of conduction channels in the PPI LB films. The poorer alignment properties in case of the LC cell with smaller layer numbers is probably due to the defects and disorders of the film which decreased with an increase in layer number. Both of the conductivity and alignment properties of the LB films became constant at the layer number over 11-15, where the morphology of the PPI LB films became flat and smooth. The flat and smooth surface of the LB films more than 15 layers suggests that the alignment of the LC on the LB films is determined by the structure at the molecular level rather than the morphological anisotropy observed in the samples of smaller layer number. In this case, the alignment direction of the LC should be related to the direction in which the polymer aligns. The measurements polarized IR spectra and atomic force microscopy.are now in progress.

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