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Liquid crystal photo-alignment layers made from aromatic bismaleimides

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We propose a new type of liquid crystal photo-alignment layer made from aromatic bismaleimides. Aromatic bismaleimides are expected to react anisotropically by irradiation of polarized ultraviolet (UV) light. In the fabrication process of the new photo-alignment layers the curing process is much shorter than that needed for conventional polymeric types of photo-alignment layers. We have proved that the use of aromatic bismaleimides enables liquid crystal molecules to be aligned homogeneously by irradiation of polarized UV light. In particular *N,N'*-*p*-phenylenebismaleimide shows good photo-alignment characteristics and high UV sensitivity. In studying the relationship between molecular structures of aromatic bismaleimides and photo-alignment properties, we find that aromatic bismaleimides that have a linear molecular structure and resonance structure produce good photo-alignment layers.

1. Introduction

Liquid crystal alignment techniques using polarized ultraviolet (UV) light, have the potential to replace conventional rubbing methods, and thus have attracted the attention of many researchers [1–3]. All the photo-alignment layers reported so far have been polymeric in nature. In layers of this type, polymeric materials are coated onto glass substrates and irradiated by polarized UV light. Two steps are needed to fabricate these layers, a polymerization step and a photo-alignment step, both of which have slow reaction rates. Furthermore, the curing process for polyimide alignment layers is excessively long [1, 3]. To overcome these disadvantages, we propose a new type of photo-alignment layer made from aromatic bismaleimides; the main advantage of layers of this type is that they do not require a long curing process.

In this paper, we report that the use of aromatic bismaleimides enables liquid crystal molecules to be homogeneously aligned by irradiation with polarized UV light. We also report on the relationship between the molecular structures of aromatic bismaleimides and their photo-alignment properties.

2. Experimental

Several types of aromatic bismaleimides were used as the photo-alignment layer in our experiments. Commercial grade *N,N'*-*p*-phenylenebismaleimide, *N,N'*-*m*-phenylene-

bismaleimide and *N,N'*-*o*-phenylenebismaleimide were used without further purification. Aromatic bismaleimides BMI-20, BMI-50 and BMI-80, produced by K-I Chemical Industry Co. Ltd., were also used without further purification.

Aromatic bismaleimide solutions of 0.8 wt % concentration in NMP (*N*-methyl-2-pyrrolidone)/toluene, 8/2, solvent were poured onto glass substrates coated with ITO (indium tin oxide) and were spin-coated at 2.0 krpm. The glass substrates were then heated to 100°C for several minutes to remove the solvent. A SPOTCURE UIS25102 (USIO Electronics Co. Ltd.) UV lamp with deep UV mirrors was used as the UV light source. The UV light was changed to polarized light of 2.6 mW cm⁻² strength through a grand-laser prism. The light strengths were measured using a UV light power meter with a 254 nm detector. The UV dose ranged from 0.1 to 2.0 J cm⁻² (irradiation time ranged from 0.6 to 12.8 min). The polarized UV light irradiated the aromatic bismaleimide layer in an N₂ atmosphere.

The parallel alignment empty cells of 5 μm thickness were made using substrates with an aromatic bismaleimide layer. Nematic liquid crystal (E7, Merck Ltd.) was inserted into the empty cells on a 90°C hotplate under atmosphere pressure. In the experiments to the measure dichroic ratio, 0.5 wt % of a dichroic dye was dissolved in the liquid crystal.

Alignment conditions of the liquid crystal cells were observed using a polarized microscope. To evaluate the

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alignment uniformity quantitatively, we used the extinction transmittance T_{ext} and order parameter S . T_{ext} is defined as:

$$T_{\text{ext}}(\%) \equiv \frac{\text{minimum transmittance by rotating LC cell under crossed polarizers}}{\text{transmittance under parallel nicol state (no cell)}} \times 100.$$

In our experiments, cells with no alignment, such as schlieren-texture cells, result in a T_{ext} of about 30%. T_{ext} becomes smaller as the alignment uniformity increases. The order parameter S was calculated from the absorbance A and dichroic ratio $D(=A_{\parallel}/A_{\perp})$ using

$$S \equiv \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} = \frac{D - 1}{D + 2}$$

where A_{\parallel} is the absorbance in the parallel direction of the dye axis and A_{\perp} is the absorbance in the perpendicular direction of the dye axis. S becomes 0 for no alignment and increase as the molecular alignment increases.

UV absorption spectra of the bismaleimide layers were measured with a UV-365 (Simadu Co. Ltd.) UV spectrometer. *N,N'*-*p*-phenylenebismaleimide solution (0.8 wt %) was spin-coated at 0.5 krpm on 1 mm thick quartz substrates, which were then heated to 100°C for several minutes to remove the solvent. The UV absorption curves were measured for various UV doses. IR absorption spectra of the bismaleimide layers were measured with an IR-7000 (JEOL) FTIR spectrometer. *N,N'*-*p*-phenylenebismaleimide solution (0.8 wt %) was spin-coated at 1.0 krpm onto 0.5 mm thick Si wafers, after which the wafers were heated to 100°C for several minutes to remove the solvent. The FTIR absorption curves were measured before and after UV irradiation.

3. Results and discussion

In our first experiment, we used *N,N'*-*p*-phenylenebismaleimide as the photo-alignment layer; its molecular structure is shown in figure 1. Since *N,N'*-*p*-phenylene-

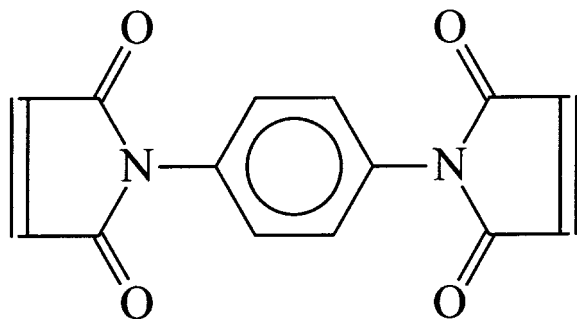


Figure 1. Molecular structure of *N,N'*-*p*-phenylenebismaleimide.

bismaleimide has both a linear molecular shape with a resonant structure and thus a high dichroic ratio, and maleimide groups of high reactivity at both ends, it was expected that its use would provide good liquid crystal alignment layers after irradiation with polarized UV light.

Polarized microphotographs of liquid crystal cells fabricated using *N,N'*-*p*-phenylenebismaleimide are shown in figure 2. The photographs are of three different cells irradiated with different UV doses. It can be seen that the alignment state improved as the UV dose was increased.

Figure 3 shows the relationship between T_{ext} of the photo-alignment liquid crystal cells and UV dose. T_{ext} decreases as the UV dose increases becoming almost saturated at 0.5 J cm⁻². This dependence of T_{ext} on the UV dose is consistent with the microscope observations, which showed that a good alignment state was obtained at 0.5 J cm⁻² UV light irradiation (figure 1).

To evaluate the alignment uniformity, we also used the order parameter S . The experimental results using dichroic dyes showed that the alignment direction of the liquid crystal molecules was perpendicular to the direction of the polarized plane of UV light. Then A_{\parallel} is the dichroic ratio perpendicular to the plane of polarization of the UV light. Figure 4 shows the relationship between S for the photo-alignment liquid crystal cells and UV dose. S is seen to increase as the UV dose increases, becoming almost saturated at 0.5 J cm⁻². The UV dose is nearly equal to the UV dose for T_{ext} saturation in figure 3. The values of S for a liquid crystal cell with a polyimide alignment layer was 0.73, and thus, the alignment uniformity of phenylene bismaleimide cells is almost the same as that of rubbing alignment cells. The good alignment state obtained at 0.5 J cm⁻² UV dose shown in figures 3 and 4 demonstrates that *N,N'*-*p*-phenylenebismaleimide layers have very high sensitivity to polarized UV light.

To obtain more information about the reaction of *N,N'*-*p*-phenylenebismaleimide, we measured the changes in the UV absorption spectra with UV irradiation. Figure 5 shows changes in the UV absorption spectra of *N,N'*-*p*-phenylenebismaleimide with increased UV irradiation; the UV doses range from 0 to 5.0 J cm⁻². The arrows show the direction of change of the UV absorption curve. It can be seen that *N,N'*-*p*-phenylenebismaleimide has broad absorption peaks at 224 and 193 nm. These peaks become smaller with increased UV irradiation, indicating that the phenylenebismaleimide has reacted. When UV absorption spectra of *N,N'*-*p*-phenylenebismaleimide was measured using acetonitrile as solvent, a 305 nm absorption peak was observed. This peak can apparently be attributed to the resonance structure of *N,N'*-*p*-phenylenebismaleimide. However, no

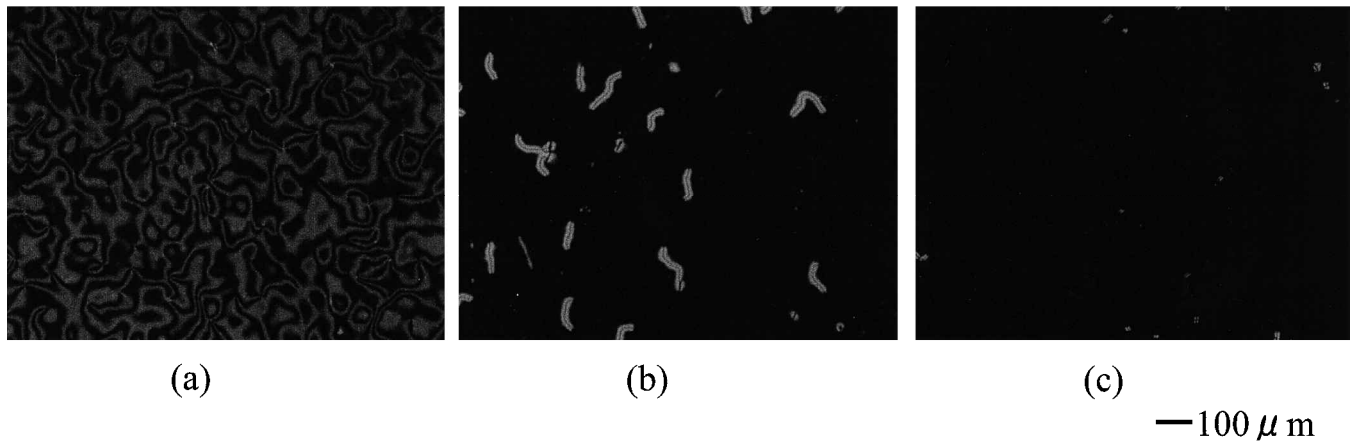


Figure 2. Polarized microphotographs (under crossed polarizers) of liquid crystal cells fabricated using N,N' -*p*-phenylenebismaleimide as the alignment layer. UV dose: (a) 0.1, (b) 0.2, (c) 0.5 J cm^{-2} .

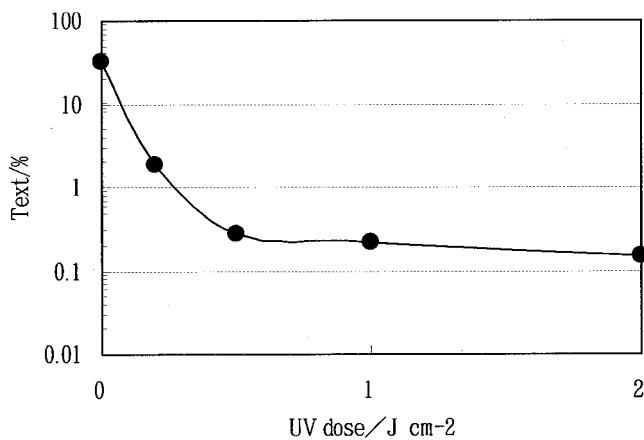


Figure 3. Dependence of extinction transmittance on UV dose. Alignment layer is N,N' -*p*-phenylenebismaleimide.

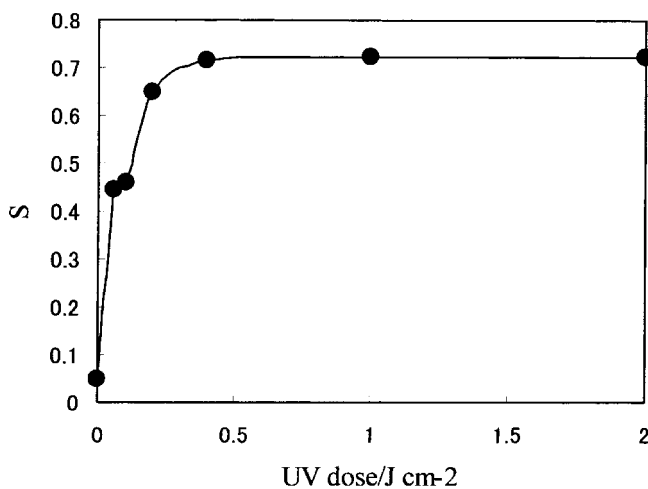


Figure 4. Dependence of order parameter S on UV dose. Alignment layer is N,N' -*p*-phenylenebismaleimide.

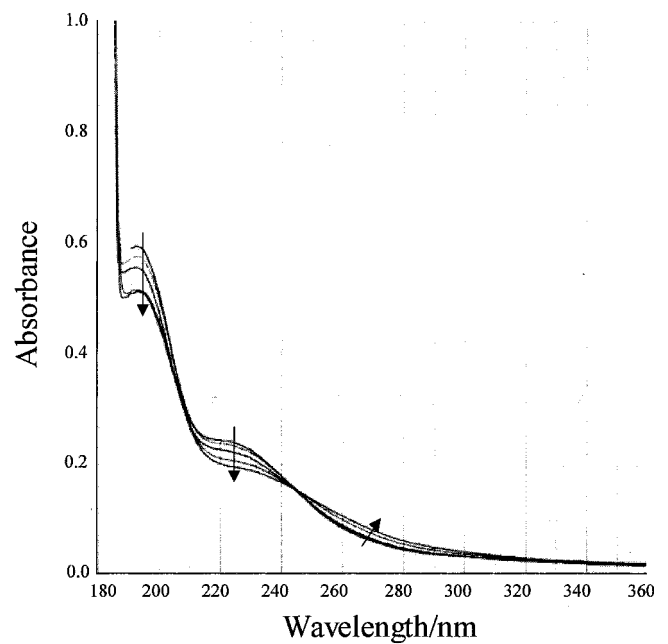
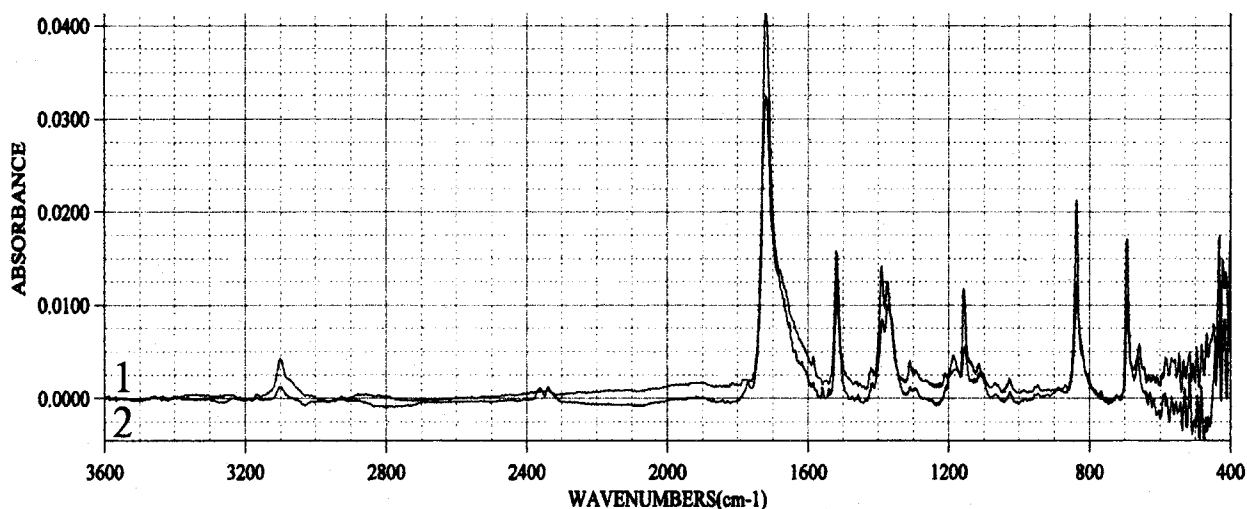


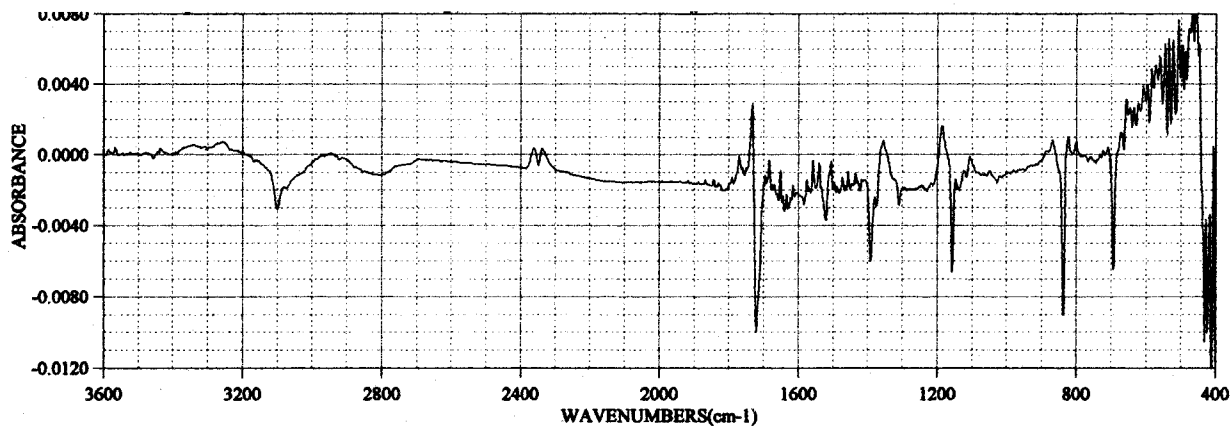
Figure 5. The change in the UV absorption curve of a N,N' -*p*-phenylenebismaleimide layer with increased UV irradiation. Arrows indicate the changing direction of the absorption curve with increased UV irradiation. UV doses of 0, 0.2, 0.7, 2.0 and 5.0 J cm^{-2} were used.

305 nm peak could be detected from the absorption curves of N,N' -*p*-phenylenebismaleimide thin solid layers.

To obtain information about the reaction of the functional groups in N,N' -*p*-phenylenebismaleimide, which could not be obtained from UV absorption spectra, we measured its IR absorption spectra. Non-polarized UV light at a dose of 2.0 J cm^{-2} was used to irradiate N,N' -*p*-phenylenebismaleimide layer on a Si wafer. Figure 6(a) shows the IR spectra of N,N' -*p*-phenylenebismaleimide



(a)



(b)

Figure 6. Changes in IR absorption spectra of a N,N' -*p*-phenylenebismaleimide layer on UV irradiation. (a) Before UV irradiation (1) and after UV irradiation (2) at dose = 2.0 J cm^{-2} ; (b) the difference spectrum, (2-1).

before and after UV irradiation; figure 6(b) is the difference of these spectra. The band appearing at 3100 cm^{-1} is due to $=\text{C}-\text{H}$ stretching vibration in the maleimide group [4, 5]. Figure 6(a) and (b) show that this $=\text{C}-\text{H}$ stretching band almost disappeared with UV irradiation. The bands appearing at 1150 cm^{-1} and at around 1380 cm^{-1} are due to the asymmetric stretching vibration of $\text{C}-\text{N}-\text{C}$ bonds which are conjugated with a $\text{C}=\text{C}$ double bond [4, 5]. Figure 6(b) shows that the positions of these bands are shifted and become broader with UV irradiation. These results indicate that the $\text{C}=\text{C}$ double bond in the maleimide group reacted on irradiation with UV light.

To clarify the influence of molecular structure on photo-alignment properties, we have also studied the isomers

N,N' -*o*-phenylenebismaleimide and N,N' -*m*-phenylenebismaleimide. The extinction transmittance, T_{exp} , of these isomer were $p = 0.16$, $m = 0.28$, $o = 1.27$, with a 1.0 J cm^{-2} UV irradiation dose. These alignment data are consistent with polarizing optical microscopy results. In these observations, the alignment situation when using the *m*-isomer was nearly equal to that when using the *p*-isomer; on the other hand, when using the *o*-isomer, many alignment defects were observed. This result indicates that a linear molecular structure such as that seen in N,N' -*p*-phenylenebismaleimide is preferable for good photo-alignment of liquid crystal molecules but is not absolutely required for photo-alignment characteristics.

In another experiment, we examined three other kinds of aromatic bismaleimides to clarify the influence of

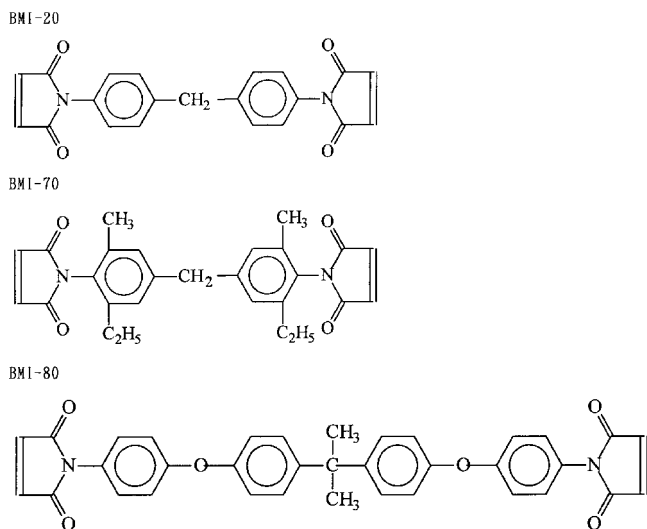


Figure 7. Molecular structures of other aromatic bismaleimides.

molecule structure on photo-alignment properties. The structures of these aromatic bismaleimides are shown in figure 7; none have a resonance structure between the two terminal maleimide groups. Despite being irradiated with polarized UV light at a dose of 2.0 J cm^{-2} , liquid crystal cells fabricated using each of these aromatic maleimides showed only a schlieren texture and no photo-alignment state. This indicates that the photo-alignment properties of aromatic bismaleimides depend on the molecular structure and suggests that a resonance structure is required for obtaining photo-alignment characteristics.

4. Conclusions

We have studied the photo-alignment properties of layers made from aromatic bismaleimides, and have found

that some types of aromatic bismaleimide can align liquid crystal molecules homogeneously after polarized UV light irradiation. In particular, *N,N'*-*p*-phenylenebismaleimide shows good photo-alignment characteristics and high UV sensitivity; alignment occurs at a dose of less than 0.5 J cm^{-2} .

The photo-alignment properties of aromatic bismaleimides are dependent on the molecular structure. Two isomers of *N,N'*-*p*-phenylenebismaleimide, viz. *N,N'*-*m*-phenylenebismaleimide and *N,N'*-*o*-phenylenebismaleimide, both show photo-alignment characteristics, but their UV sensitivity is $p > m \gg o$. Other aromatic bismaleimides, which do not have a resonance structure between the two terminal maleimide groups, showed no photo-alignment characteristics. These results suggest that linear aromatic bismaleimides are preferable for obtaining good photo-alignment properties and that a resonance structure of the molecule is required.

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