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Photo-alignment of low-molecular mass nematic liquid crystals on photoreactive polyimide and polymethacrylate film by irradiation of a linearly polarized UV light

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Summary

Photocrosslinkable polyimide and polymethacrylate comprising chalcone moieties in the side chain were synthesized for fabricating the alignment layer of liquid crystals. Chalcone group was introduced into the side chain unit of the polymer backbone. We observed a photodimerization behavior either in solution or in film by irradiation of a UVlight. Linearly polarized UV irradiation on the chalcone-polymer films induced optical anisotropy of the polymer film and the resultant film can be used for alignment layers for low molecular weight nematic liquid crystals.

Introduction

Conventional rubbing technique in practical application has been widely used for the liquid crystal alignment. But, it has several problems such as dust and static charge due to the mechanical contact of rubbing cloth, causing mechanical damage of active display layer. Moreover, the general method to achieve high performance for liquid crystal device (LCD) requires surface anchoring conditions that cannot be induced by a traditional mechanical rubbing method. Therefore, the photo-alignment technique for LC display has received much attention in recent years because of its clean and photo-patternable system to widen the viewing angle.[1-7] Many kinds of photoreactive polymers that can undergo anisotropic isomerization or photocrosslinking reactions have been reported for the photo-alignment of LC.[3-9] Nematic liquid crystal (NLC) can be aligned homogeneously on the photoreactive polymer film which is usually exposed to a linearly polarized light (LPL).[10-13]

For example, anisotropic [2+2] cycloaddition of the polyvinylcinnamate (PVCi) film can induce irreversible low molecular weight-liquid crystal (LMW-LC) alignment. [14] The polymers containing chalcone group in the side chain were also frequently studied for application to LC photo-alignment layer.[15] The induction mechanism of optical anisotropy in the film is identical with that in the polyvinylcinnamate. Because of poor solubility arising from the rigid-rod nature of chalcone backbone polymers, most research works involved only polymers that contain the chalcone unit in the side chain.[16-18]

In this work, we synthesized a new photoreactive soluble polyimide and polymethacrylate. Chalcone group was also introduced into the side chain unit of the new photoreactive polymers, which is highly sensitive to the LPL photochemically. The capability of photocrosslinking of new compounds was demonstrated using UV-Vis absorption spectroscopic analysis. The optical anisotropy of the film induced by irradiation of a LP-UV light is also investigated by using the polarized UV absorption spectroscopy. Photocrosslinking was performed to elaborate the rigid matrix after UV exposure and angular selective photochemical reaction performed to induce high optical anisotropy. We also investigated the azimuthal orientation of LC molecules and the direction of LC alignment determined by monitoring the dichroism of a dichroic dye (1,4-Bis-methylamino-anthraquinone; Disperse blue 14) dissolved in nematic liquid crystals.

Experimental

Figure 1 shows the structures of the photoreactive polymers such as soluble polyimide and polymethacrylate used in this study. The synthetic procedure of all compounds for this study was well described in our previous report.[19]

UV-Vis absorption spectroscopy: Absorption spectra were obtained using a Hewlett Packard UV-Vis 8453 spectrophotometer (PDA type, λ=190-1100 nm). The polymers were dissolved in THF and cast onto quartz plate followed by drying in vacuo at 50ºC for 6 hr.

For the polarized absorption spectroscopic study to investigate the order parameter during UV illumination, we equipped Glan-Taylor polarizer in front of the probe beam coming from the spectrophotometer. For the spectroscopic study under UV irradiation, we employed a linearly polarized He-Cd laser (Liconix 3675NX, λ=325 nm, I=210mW/cm^2) in this experiment. The intensity of the pump beam was measured to be 26 mW/cm^2 by using a 13PEM001 (MELLES GRIOT) detector and power meter.

Photoirradiation: In order to make thin polymer films for LC alignment layer, 0.5 wt% solutions of the chalcone-polymers were prepared with tetrachloroethane, filtered using 0.2 μm PTFE membrane filter (Acrodisc) and were spin-coated on quartz plate and borosilicate glass.

Light from high pressure Hg lamp (Nanotek Co. 1kW) was passed through IR filter and broad bandpass filter (λ=300-380 nm) to isolate the certain wavelength range of the light. A UV linear polarizer (27320 UV linear dichroic polarizer, Oriel Co.) was used for linearly polarized light irradiation.

***Determination of LC Photoalignment*:** A LC cell was assembled by sandwiching nematic liquid crystals between two glass plates spin-coated with chalcone-polymer. Photoirradiation of chalcone-polymer film was performed before LC cell fabrication. The NLC (4’-Pentyl-biphenyl-4-carbonitrile; 5CB, Merck Co.) was filled into a cell in its isotropic state by a capillary action. In order to eliminate the capillary effect, the cell was heated to 42ºC above T_{NI} (38ºC) and filled into the cell. The extent of the LC photo-alignment was determined by measuring the transmitted light intensity of a linearly polarized light from He-Ne laser (λ=632.8

nm, I=1 mW/cm^2) through the LC cell as a function of the cell rotation angle under crossed polarizers. The direction of LC alignment was determined by monitoring polarized absorbance of a dichroic dye (Disperse blue 14) dissolved in 5CB rotating the sample under single polarizer.

Results and discussion

Synthesis and characterization: Synthesized polymer structures were simply illustrated in **Figure 1**. The photoreactive polyimide and polymethacrylate contain unsaturated carbonyl moieties as photosensitive groups in the side chain. 4-Hydroxy chalcone and 4-(2-hydroxyethoxy)chalcone were synthesized following the conventional method, which gave a good yield (~70%).[16,17] In the polymethacrylate (CPMA), we firstly synthesized the methacrylate monomer using methacryloyl chloride and 4-hydroxychalcone. The methacrylate monomers were polymerized under a radical initiator of 2,2'-Azobisisobutyronitrile (AIBN, 1 mole %). The soluble polyimde (CPI) was synthesized by condensation of specific dianhydride and diamine bearing two trifluoromethyl groups, respectively. In this case, the diamine has two hydroxy groups substituted to the benzene ring. In order to reduce the geometrical hindrance and increase the degree of substitution, we reacted the chalcone with ethylene spacer such as 4-(2-hydroxyethoxy)chalcone to the precursor polyimide by way of Mitsunobu etherification. The substitution was successfully performed and the degree of substitution was found to be 80% determined by NMR spectroscopic technique. The intrinsic viscosities of CPMA and CPI were determined to be 0.07 and 0.20 in tetrahydrofuran at 25°C, respectively. Those polymers are well soluble even in acetone, chloroform, methylene chloride, tetrahydrofuran etc. The glass transition temperatures, T_g of CPMA and CPI are 103 and 158°C, respectively.

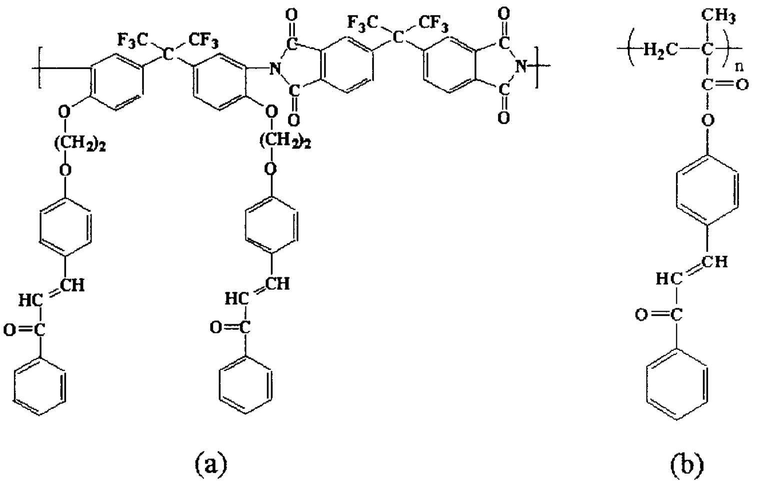


Figure 1. Synthesized polymer structures for this study. (a) Chalcone-polyimide (CPI), (b) Chalcone-polymethacrylate (CPMA).

Polarized UV-Vis absorption spectroscopy under irradiation of a linearly polarized light: We recorded the absorption spectrum every 0.5 second during irradiation of a linearly polarized He-Cd laser (I=210 mW/cm^2). We can observe the change in UV absorption spectrum and dichroism. $A_{\parallel}$ denotes the parallel absorption and $A_{\perp}$ perpendicular absorption with respect to the electric field of the incident LP-UV pump light. In these two polymers, the parallel absorbance at λ_{max} was observed to be smaller than the perpendicular absorbance in the whole range of the irradiation time period. Using the two traces of the absorbance, we could analyze the optical anisotropy of the thin film in terms of the difference of the absorbance and the dichroism.

In Figure 2, the difference of the absorbance ($\Delta A = A_{\parallel} - A_{\perp}$) of the polyimide and the polymethacrylate at λ_{max} reached to the minimum after 23 and 10 sec exposure, respectively. Then the difference value increased gradually under further UV irradiation. For longer period of UV exposure, the anisotropy of the film decreased slowly due to the formation of a higher extent of cyclobutane in any directions that is far away of polarization direction of UV light. The induction rate of optical anisotropy in the polyimide was found to be smaller than in the polymethacrylate in the initial stage of the LP-UV irradiation. In addition, the dichroism was also smaller than that of the polymethacrylate. This is attributable to the chain rigidity of the polymer backbone as well as the density of the chalcone group in the unit volume. Assuming that the dichroism of the polyimide was observed to be smaller under the same exposure dose, the effect of optical anisotropy in the film will be compared to investigate the LC alignment behavior on the film surface.

Photocontrol of LC alignment: There are many reports that dealt with the LC alignment using the photoreactive side chain polymer containing cinnamate and chalcone group.[3-9, 14] The orientational direction of LC molecules caused by linearly polarized light irradiation of polymers with photoreactive side chains including azobenzenes, cinnamates, and benzylidenephthalimidines is perpendicular to the electric field vector of actinic polarized light. Thin films of chalcone-polymers on a substrate plate were exposed to LP-UV light (λ=300-360 nm) followed by the fabrication of LC cell using the above two plates coated with chalcone-polymer. In this case, we used a high pressure mercury lamp (1 KW) equipped with a IR filter and a linear UV polarizer for induction of the optical anisotropy of the film.

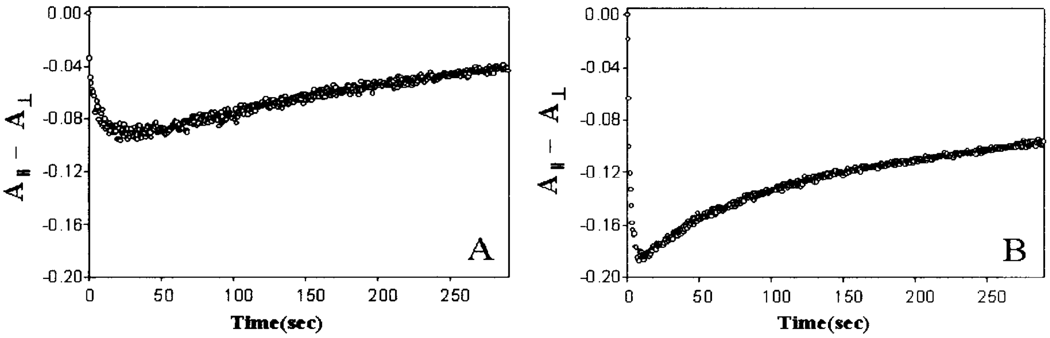


Figure 2. Exposure time dependence of dichroism of the two polymer films. A: Polyimide (CPI), B: Polymethacrylate (CPMA).

Photoinduced azimuthal LC alignment was investigated by measuring transmitted intensity of a polarized He-Ne laser beam as a probe light passed through a LC cell as a function of the rotational angle of the cell. Irradiation with a linearly polarized UV light resulted in the control of azimuthal orientation of LC for chalcone-polymer as revealed by the regular appearance of periodicity in transmitted light intensity at 90° difference. As shown in Figure 3, the azimuthal orientation of LC layers was generated under a linearly polarized UV light whose minimum exposure dose is about 0.5-1 J/cm^2 for the generation of homogeneous alignment by chalcone-polymer film. As the exposure energy increased, the homogeneous LC alignment was more clearly observed, as is usual. In the case of CPMA alignment layer, the transmitted intensity was observed relatively much higher. This can be explained by the fact that the higher optical anisotropy in film could be achieved as can be seen in Figure 2. This implies that more LC molecules were forced to orient homogeneously by the reoriented molecules on the surface of CPMA.

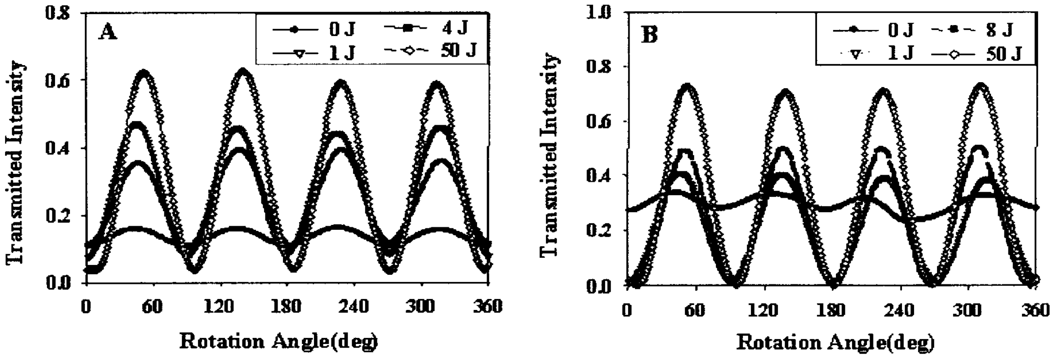


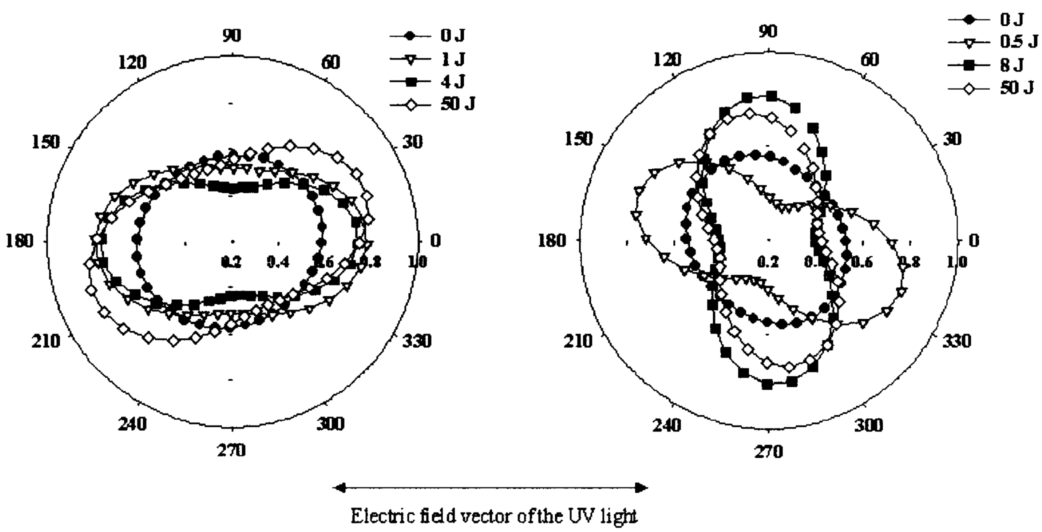
Figure 3. Angular dependence of transmitted light intensity of a linearly polarized He-Ne laser beam passed through the LC cell with the change of the power of the LP-UV light. A: CPI, B: CPMA.

The dichroism of the polymer film increased in the initial stage of irradiation and then decreased for prolonged irradiation. However, the transmitted intensity through the LC cell does not follow that tendency. This means that the degree of homogeneous LC alignment is not directly related to the dichroism, that is, optical anisotropy. There should be an optimized level of anisotropy that can control a limited number of LC molecules. Therefore, although the dichroism of the polymer film goes higher than a limited value, the anisotropy of the LC cell cannot be affected much.

Direction of LC alignment: The direction of LC alignment was determined by measuring the dichroic property from cooperative alignment of a dichroic dye (Disperse blue 14, 0.2wt%) dissolved in 5CB.

Figure 4 illustrated the circular diagram of absorbance of the dichroic dye (Disperse blue 14) dissolved in 5CB (0.2wt%) in an LC cell. The arrow indicates the electric field vector of the LP-UV light. The direction of LC insertion was identical to the above electric field direction. On this alignment layer of CPI, the aligning direction of LC molecules was observed to be parallel to the electric field vector of the LP-UV light. On the contrary, the alignment layer of CPMA induced the perpendicular alignment of LC molecules to the electric field direction of LPL-UV.

As far as the photo-alignment mechanism is concerned, The parallel alignment was proposed to result from photoproducts of the cinnamates attached to polymer chain while perpendicular alignment is determined by E/Z photoisomerization of the cinnamates in the side chain of the polymer.[20] It was also suggested that the induction of optical anisotropy by photochemical reactions consists of two processes.[21] They include the angular-selective photochemical transformation of molecules with a transition dipole moment in parallel with the electric field vector of excitation light and the reorientation of the photoisomerizable groups, leading to the preferential displacement of molecules oriented perpendicularly to the electric field vector of the excitation light. It can be performed in the side chain polymer containing the chalcone group as a side chain unit.



(a) (b)

Figure 4. Circular diagrams of absorbance of the 0.2 wt% dichroic dye (Disperse blue 14) dissolved in 5CB with the change of the intensity of the LP-UV light. The electric field vector of the LP-UV light is shown by the arrow. (a) CPI, (b) CPMA.

However, the polyimide showed parallel alignment and the polymethacrylate, perpendicular alignment of LC molecules in this study. (See Figure 4) We can suggest that the direction of LC alignment is also strongly related to the geometry of the position of the chalcone unit and the physical properties of the polymers.

The chalcone moiety itself is rigid rod-shaped when it was tethered to the polymer backbone as a side chain pendent group. It seems that molecular reorientation of chalcone group in the polyimide induced by linearly polarized light can hardly take place due to the high T_g of the matrix. When the side chain undergoes E/Z transformation and reorientation, the main chain motion also was accompanied with the side chain motion. The chalcone group was relatively restricted to be E/Z photoisomerized and it follows that the LC photo-alignment is determined by optical anisotropy generated by angular-selective photochemical reaction that results in the consumption of the chalcone group and the formation of dimerized photoproducts. Resulting from the photodimerized products, the strong anisotropic van der Waals interaction between the cyclized photoproduct and liquid crystal molecules results in parallel alignment of liquid crystal molecules. Additionally, the aromatic ring character in the main chain of CPI also interacts with the LC molecules for alignment. In the case of the polymethacrylate (CPMA), we could observe very similar behaviors that were reported in the literature.[14-18] It could indicate that the molecular reorientation process followed by E/Z transformation was easily induced due to low T_g of the polymer.

Although the anisotropy of the alignment layer was thoroughly studied by polarized infrared spectroscopy, it can be assumed that the parallel orientation of LC molecules is governed by the anisotropically photodimerized products of chalcone moieties and the rigid main chain unit in CPI. It is also assumed that the existence of chalcone unit as a side chain unit plays an important role in determining the mode of photoalignment, although further studies are necessary to measure the order parameter of the LP-UV exposed film of chalcone-polymer.

In Figure 5, we could see the dependence of the order parameter of LC molecules on the exposure energy in the fabricated LC cell. In the cell with the alignment layer of CPI, under moderate intensity of UV light, the LC molecules were observed to be parallel to the electric field vector of the actinic light. After prolonged irradiation, the order parameter decreased slightly. It can explained that in the low power of UV light, the LC molecules were governed by the photodimerized product and over long term exposure, the molecular reorientation of the chalcone group was performed in a small extent. But, the polymethacrylate showed clear existent behavior of perpendicular alignment of the LC molecules over a whole range of the UV power.

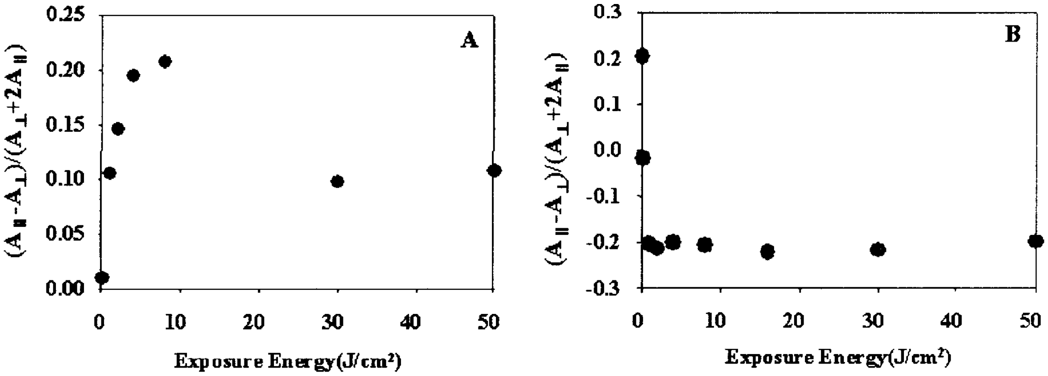


Figure 5. Exposure energy dependence of the order parameter of the LC cell. A: CPI, B: CPMA.

CONCLUSION

We synthesized the photo-crosslinkable polyimide (CPI) and the polymethacrylate (CPMA) comprising chalcone group. Cyclobutane structures were formed under UV irradiation in two compounds between the side chains that were confirmed by spectroscopic analysis. We clarified anisotropic LP-UV photoreaction of the polyimide and the polymethacrylate compound.

Homogeneous alignment by irradiation of chalcone-polymer film with LP-UV light was induced when the irradiation was carried out before cell assembly. The orientational direction of LC molecules on the polyimide alignment layer was parallel to the electric field vector of the excitation light. It was determined by cyclized photoproducts from angular-selective photodimerization in the side chains. The alignment direction on the polymethacrylate alignment layer was observed opposite, that is, perpendicular alignment to the electric field direction of actinic UV light.

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