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Photoinduced anisotropy and photoalignment of nematic liquid crystals by a novel polymer liquid crystal with a coumarin-containing side group

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A new type of photo-crosslinkable methacrylate polymer liquid crystal (PLC) with a coumarin-containing mesogenic side group was synthesized and applied as the photoalignment layer for low molecular mass nematic liquid crystals. Linearly polarized ultraviolet light was directed onto a thin film of PLC under various exposure conditions. When a film was irradiated at room temperature, a small negative optical anisotropy was generated due to angular-selective photo-crosslinking In contrast, when the film was exposed near the clearing temperature of the PLC, the induced anisotropy was positive due to thermally enhanced photoinduced reorientation of the side groups. The aggregation of the mesogenic groups was also observed when the irradiation was carried out in the liquid crystalline temperature range of the PLC. The LC alignment on the photoreacted film was greatly dependent on these irradiation conditions. It was made clear that the LC alignment was regulated by the interaction among the LC, the photo-crosslinked side groups and the remaining mesogenic side groups, and that the aggregated mesogenic groups inhibited the LC alignment.

1. Introduction

Linearly polarized ultraviolet (LP-UV) light induces an optical anisotropy in photo-crosslinkable polymer films because of angular-selective photoreaction, and the resultant films are applied as the alignment layer for liquid crystals (LCs) [1–5]. Typical materials are based on cinnamate derivatives such as poly(vinyl cinnamate) (PVCi). PVCi is a well known negative-type photoresist, and a negative optical anisotropy is induced by the LP-UV light irradiation [1, 6]. The LC aligns on the photoreacted PVCi films in a direction perpendicular to the electric vector (**E**) of the incident LP-UV light [1, 3–10]. The LC alignment behaviour on the photoreacted PVCi film is influenced by two kinds of angular selective photoreaction, viz. a [2+ 2] photocycloaddition reaction and *trans-cis*-photoisomerization [10–12]. Several kinds of cinnamate-containing polymers used for the LC alignment layer have been reported [10, 11, 13–18]. We have also studied polymethacrylates with a cinnamoyloxyalkoxybiphenyl side group (p*m*B*n*Ci in figure 1) for the LC alignment layer [19–22]. In this case, the 'whole' photo-crosslinked side mesogenic group controls the

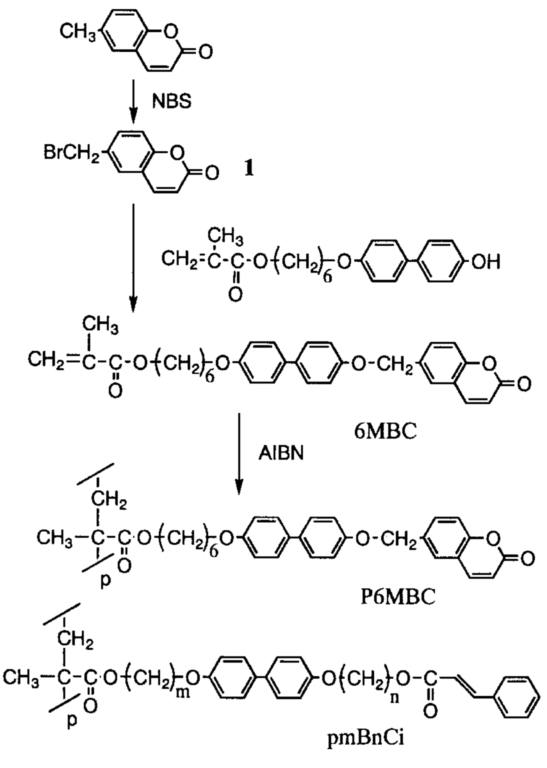

Figure 1. Chemical structures and synthetic route to the polymer liquid crystal.

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parallel LC alignment [20, 21] although it was difficult to clarify the effect of the photoisomerization of the cinnamoyl group on the LC alignment, because the spectrum of the cinnamoyl group overlaps with that of the biphenyl group.

Coumarin derivatives also undergo angular-selective photoreaction and polymer films with coumarin side groups have been applied as the LC alignment layer [2, 22–25]. Since the coumarin exhibits no photoisomerization, the LC alignment on a coumarin-containing polymer film can be brought about only by the [2+ 2] photocycloaddition reaction [23]. Shadt *et al.* reported that the LC aligns in a direction parallel to **E** of the incident LP-UV light on a polymer film comprising coumarin side groups [2]. Ichimura *et al.* made systematic studies on the effect of the spacer length using methacrylates with coumarin side groups and investigated the reversion of the LC alignment direction [23, 24]. With respect to the photochemistry of coumarin derivatives, it is known that they can produce four regioisomeric photodimers, viz. *syn*- and *anti*- head-to-head (H-H) dimers, and *syn*- and *anti*- head-to-tail (H-T) dimers [26–29]. The type of photodimer depends on the nature and the position of the substituents in the solid state. Therefore, it is important to study the influence of the type of photodimer on the LC photoalignment behaviour using coumarin-containing photopolymers.

In this work, we synthesized a novel methacrylate polymer liquid crystal (PLC: P6MBC) with a coumarin moiety at the end of the mesogenic group as illustrated in figure 1. This polymer comprises a biphenyl side group connected to a coumarin group instead of a cinnamate group as in p*m*B*n*Ci, resulting in elimination of the influence of photoisomerization. The photoreaction of a thin film was carried out by using LP-UV light under various conditions. We report here that the photoinduced optical anisotropy of the film and the LC alignment behaviour on the resultant films were greatly dependent on the irradiation conditions, the type of photodimer and the orientation of the mesogenic side groups.

2. Experimental

2.1. *Materials*

4-(6-Methacryloyloxyhexyloxy)-4′-hydroxybiphenyl was synthesized by or previously reported method [30]. Other materials were used as received from Tokyo Kasei Chemicals. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from ethanol and stored at 0°C. Monomers and the polymer were synthesized according to the reaction scheme in figure 1, and the chemical structures of the synthesized monomers and polymer were confirmed by ^{1}H NMR and FTIR spectroscopy.

2.2. *Characterization, photoreaction and LC alignment*

All analytical equipment was the same as previously reported [18–21]. Photoreaction was carried out with radiation supplied by a 250 W Xe-Hg UV lamp after passing through Glan–Taylor polarizing prisms with a cut-off filter under 290 nm. The light intensity was 12 mW cm^{-2} at 365 nm. The LC alignment behaviour was evaluated by dichroic absorption measurements utilizing the guest–host effect of a dye-doped nematic LC (ZLI 4792: Merck, T_i = 92°C) as previously described [19, 20].

3. Results and discussion

3.1. *Photoreaction and photoinduced optical anisotropy of the P6MBC film*

P6MBC exhibited a glass transition at 61°C and showed a liquid crystalline phase between 145°C and 222°C. Polymer films were irradiated by using LP-UV light at various temperatures. After exposure, all films became insoluble in organic solvents due to the [2+ 2] photo-crosslinking reaction of the coumarin group. Photoreaction and photoinduced optical anisotropy ($\Delta A = A_\parallel - A_\perp$) of the film were examined by obtaining a polarization UV absorption spectrum: $A_\parallel$ is the absorption parallel to **E** of the incident LP-UV light, and $A_\perp$ is that perpendicular to **E**. Figures 2–4 show the changes

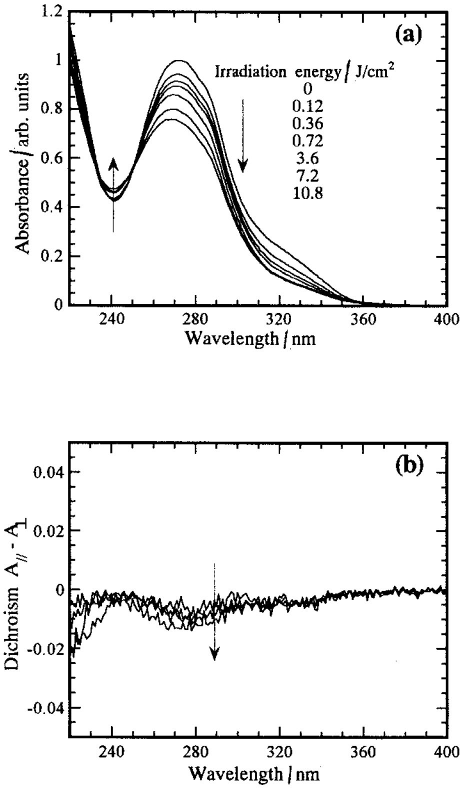

Figure 2. Change in absorbance (*a*) and induced dichroism (*b*) of P6MBC film irradiated at room temperature.

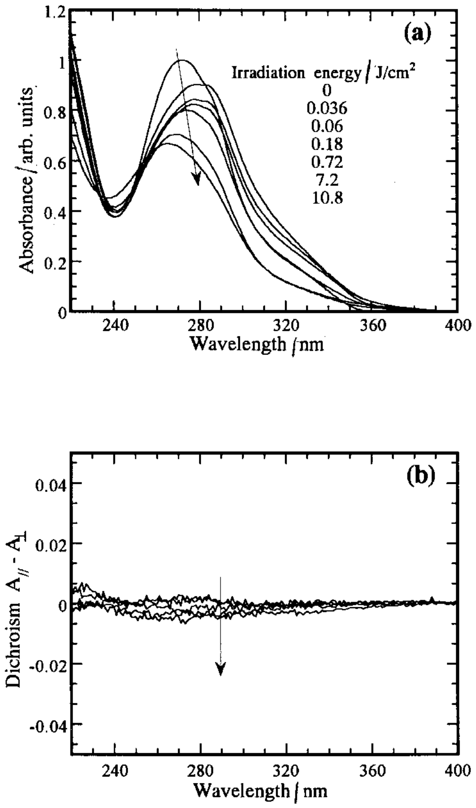

Figure 3. Change in absorbance (*a*) and induced dichroism (*b*) of P6MBC film irradiated at 180°C.

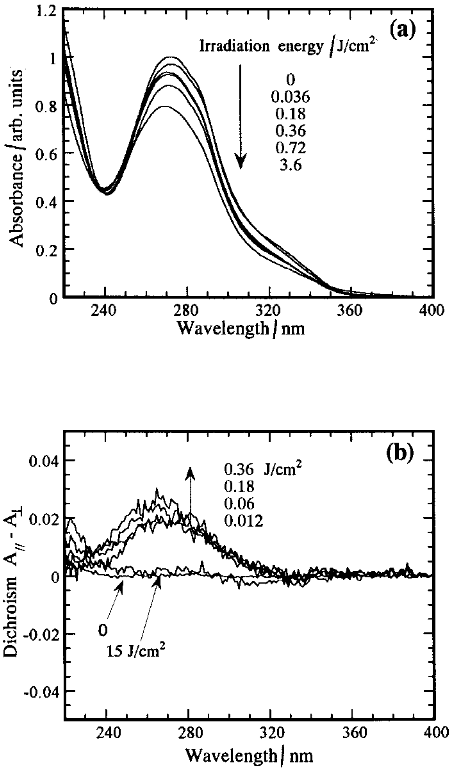

Figure 4. Change in absorbance (*a*) and induced dichroism (*b*) of P6MBC film irradiated at 220°C.

in the absorption spectra and the induced ΔA when films were irradiated at room temperature, 180°C and 220°C, respectively. When a film was irradiated at room temperature (figure 2), the absorption decreased and shifted to shorter wavelength with increasing doses of irradiation due to the photo-crosslinking of the coumarin group, and a small negative dichroism was observed because of the angular-selective photoreaction of the coumarin group. However, when the irradiation energy was 3.6 $\mathrm{J\,cm^{-2}}$ or more, the absorbance around 320 nm was not decreased, while the absorbance around 270 nm still decreased, suggesting a side photoreaction of the biphenyl group besides the photocylcoaddition reaction [20]. In contrast, when a film was irradiated at 180°C (LC temperature range), the shape of the spectrum was changed and the induced dichroism was very small as shown in figure 3. The absorption maximum shifted from 273 to 285 nm, and the absorbance around 330 nm increased after the irradiation using the range 0.0036–0.18 $\mathrm{J\,cm^{-2}}$. The shape of the spectrum became similar to that in figure 2 (*a*) when the irradiation energy was 3.6 $\mathrm{J\,cm^{-2}}$ or more. In addition, a strong decrease in the absorption and a red shift of the absorption maximum were observed even though the film was annealed at 180°C without UV light exposure (see below). The red shift and the decrease in the absorption will be a consequence of a head-to-tail (HT) aggregation or an out-of-plane alignment of the mesogenic side groups [31, 32]. The detailed orientational behaviour of the mesogenic side groups at elevated temperature is discussed later.

When the film was irradiated at 220°C (near T_i), the change in the UV spectrum was similar to that for a film irradiated at room temperature. However, the induced dichroism was positive at the beginning of the photoirradiation and decreased when the exposure energy was 3.6 $\mathrm{J\,cm^{-2}}$ or more, as shown in figure 4 (*b*). The positive dichroism is due to a thermally enhanced photoinduced orientation of the mesogenic groups in a direction parallel to **E**, since the direction of the photo-crosslinked mesogenic group is parallel to **E**. This phenomenon is similar to that observed for polymer liquid crystal films of p*m*B*n*Ci derivatives when they are irradiated by LP-UV light around T_i [20, 33, 34].

3.2. *FTIR study*

To investigate the type of photoproduct from the coumarin group, FTIR spectroscopy measurements were carried out. Figure 5 shows the change in FTIR spectrum after UV light irradiation of 0.72 $\mathrm{J\,cm^{-2}}$ at various

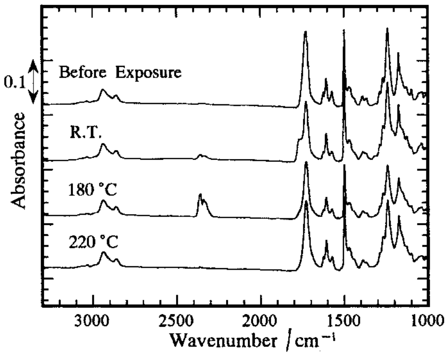

Figure 5. FTIR spectra of P6MBC film before and after irradiation of 3 J cm^{-2} exposure dose at various temperatures.

temperatures. The peak at 1730 cm^{-1} before exposure is assigned to the C=O stretching of both coumarin and ester units of polymethacrylate chains, and the peak at 1574 cm^{-1} is the *cis*-C=C stretching of the coumarin group. After exposure, the intensity of the *cis*-C=C stretching band was decreased in all cases due to the dimerization of the coumarin group.

It is reported that the difference in the isomerism of cyclobutane adducts can be distinguished by a spectral shift of the C=O stretching band of a coumarin group [28, 29]. According to the literature, the shift to higher wave numbers is attributed to the formation of an H-H dimer, while that to lower wave numbers is due to the formation of an H-T dimer [29]. For P6MBC, a new band at 1775 cm^{-1} appeared when the film was irradiated at room temperature, and the absorption of the C=O stretching band became broad when the film was irradiated at 180 or 220°C. These results suggest that the H-H dimer was the main adduct when the film was irradiated at room temperature, while the H-T dimer was the main adduct when irradiated at 180°C or 220°C. The shift to lower wave numbers might be small and it will be overlapped by the ν(C=O) of the polymethacrylate chains.

3.3. *Behaviour of the mesogenic groups at elevated temperature*

Since the UV absorption spectrum was changed after annealing in the LC temperature range of P6MBC as described in the above section, the orientational behaviour of the mesogenic groups was investigated by polarization UV spectroscopy and FTIR spectroscopy.

Figure 6 shows UV absorption spectra of films before and after annealing at 180°C for 10 min, and also the absorption spectrum of the annealed film measured at various angles (θ_m) of the incident p-polarized probe light to obtain information about the three-dimensional orientation of the mesogenic groups. For normal incidence of the probe light ($\theta_m = 0°$), the absorption decreased and a red shift of the spectrum was seen after annealing. In addition, a small shoulder-like absorption band around 285 nm, as seen before exposure, was enhanced after annealing. The same absorption band was enhanced in figure 3(*a*) when the irradiation dose was 0.18 J cm^{-2} or less. This band is a consequence of mesogenic groups arranged in the head-to-tail geometry of J-aggregates [31, 32]. Furthermore, figure 6 shows that the red shift is weakened with increasing θ_m, accompanied by an increase in the absorbances, indicating that larger amounts of J-aggregate are present in a plane parallel to the substrate and that the orientation of the mesogenic group is out-of-plane.

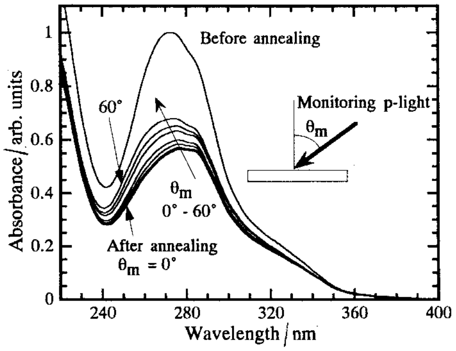

Figure 6. Absorption spectra of P6MBC film before and after annealing at 180°C for 10 min followed by quenching and measuring the spectrum at various incident angles of p-polarized monitoring light.

Figure 7 shows FTIR spectra before and after annealing at 180°C. This indicates that ν(C=C) and ω(C=C) for the side groups are decreased, while the CH vibration around 2850–2950 cm^{-1} for the methylene spacer is increased after annealing. This result also supports the out-of-plane alignment of the mesogenic groups. Similar results were obtained for the film annealed at 150°C and 200°C (LC temperature range), but neither the red shift

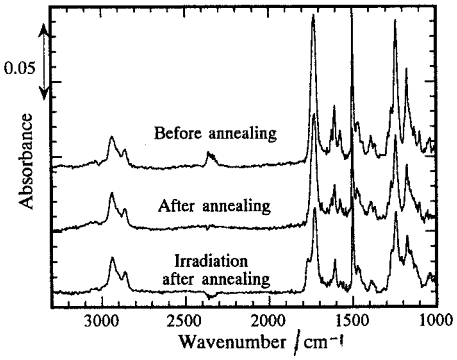

Figure 7. FTIR spectra of P6MBC film before and after annealing at 180°C for 10 min followed by quenching, and after irradiation of the annealed film using a 3 J cm^{-2} exposure dose.

nor the out-of-plane alignment was observed for the film annealed in the isotropic temperature range at 240°C. It should be noted that the decrease in the absorption was not strong when the film was irradiated at 180°C with 0.0036 or 0.06 J cm^{-2}, as shown in figure 3 (*a*). The annealing was carried out during the UV illumination. This suggests that UV exposure suppressed the out-of-plane alignment of the mesogenic groups even though the film was heated in the LC temperature range.

3.4. *Photoreaction of annealed film*

The change in the FTIR spectrum of the annealed film after exposure is also shown in figure 7. The shift of the C=O stretch to a higher wave number at 1775 cm^{-1} is clearly seen and this new band is a consequence of the H-H dimer. In the case of the annealed film, there should be a large amount of J-aggregate as described above, and the aggregated mesogenic groups will form H-T dimers. To investigate a source of the resulting H-H dimer, UV light was irradiated obliquely to the annealed film, and a relationship between the photoreacted regio-isomers and the orientational direction of the mesogenic groups was clarified by FTIR. Figure 8 plots the ratio of the absorption intensities at 1775/1730 cm^{-1} as a function of the incident angle of the UV irradiation. This shows that larger amounts of H-H dimer were obtained when the angle of the incident UV was large. This means that the mesogenic groups lying in a direction perpendicular to the substrate plane preferentially form H-H dimer.

3.5. *Alignment of LC on photoreacted P6MBC film*

Figure 9 summarizes the LC alignment behaviour on P6MBC film irradiated under various conditions. When the film was irradiated at room temperature, the LC aligned parallel to **E** and the direction was changed to perpendicular to **E** with increasing exposure dose. The reversion occurred when the exposure dose was 0.36 J cm^{-2}, where the degree of photoreaction of the coumarin groups was about 30%. The reversion of the LC alignment direction was observed for other types of polymethacrylates with coumarin side groups as studied by Ichimura *et al.* [23, 24]. They concluded that perpendicular LC alignment was brought about by the remaining coumarin groups in a direction perpendicular to **E**. Here, the perpendicular LC alignment will be due to the remaining mesogenic side groups, as is the case with Ichimura's polymer [23].

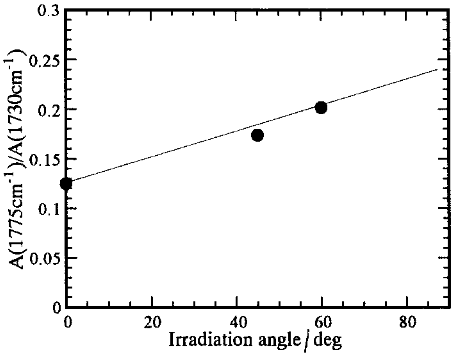

Figure 8. Ratio of the FTIR absorption intensities at 1775/1730 cm^{-1} as a function of the irradiation angle.

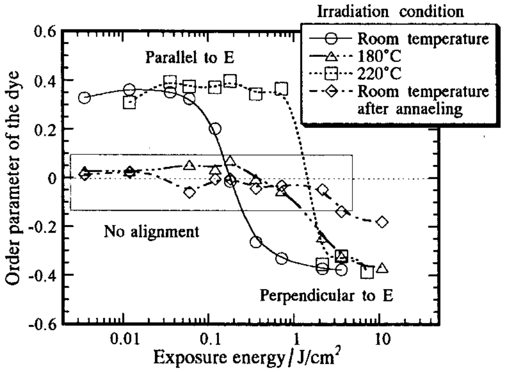

Figure 9. Order parameter and alignment direction of the parallel LC cell as a function of the irradiation dose.

On the other hand, parallel LC alignment could not be obtained when using a film irradiated at 180°C. The loss of the LC alignment ability may be ascribed to the aggregates of mesogenic groups formed in the LC temperature range. However, the LC aligned in a direction perpendicular to **E** when the irradiation energy was 4.8 J cm^{-2} or more. For this energy dose, the side-photoreaction should occur and the aggregation of the mesogenic groups becomes broken. Therefore, the interaction between the remaining mesogenic groups lying in a direction perpendicular to **E** and the LC will be increased, resulting in a perpendicular LC alignment. In addition, the LC did not align on the annealed films. The associated mesogenic groups may prevent the LC alignment although H-H dimer could be formed.

In contrast, homogeneous LC alignment could be obtained when the film was irradiated near T_i for P6MBC (220°C), and it took longer exposure doses to reverse the alignment direction from parallel to perpendicular to **E**. For the photoreaction at 220°C, the main photoreacted product is H-T dimer and the photoinduced thermal orientation of the mesogenic groups occurs as shown in figure 4. In this case, the azimuthal anchoring energy in a direction parallel to **E** should be larger than that for the film irradiated at room temperature, since both photoreacted mesogenic groups and the mesogenic groups are aligned parallel to **E**. Therefore, longer exposure doses are needed to obtain perpendicular LC alignment.

4. Conclusions

It was found that H-H cycloadducts of the mesogenic side groups were formed for P6MBC film and the film showed negative dichroism when it was irradiated at room temperature. This H-H dimer can control the LC alignment in a direction parallel to **E**, and reversion of the LC alignment direction occurred because of the increased interaction between the LC and remaining mesogenic groups in a direction perpendicular to **E**.

On the other hand, the film exhibited a positive dichroism and H-T cycloadducts were produced when the film was irradiated near the clearing temperature of P6MBC. The positive dichroism was generated by the photoinduced thermal orientation of the mesogenic groups in a direction parallel to **E**, and the LC aligned in this direction. This leads to the conclusion that both H-T dimer and oriented mesogenic groups can control the parallel LC alignment. Reversion of the LC alignment was also observed when the dichroism became smaller, and the required energy dose for the reversion was larger than that for the film irradiated at room temperature. In this case, the reversion is due to the photodegradation of the mesogenic groups in a direction parallel to **E**, resulting in an increased interaction between the LC and the remaining mesogenic groups in a direction perpendicular to **E**.

In addition, aggregation of the mesogenic groups was observed when the film was irradiated in the LC temperature range of the polymer, or was annealed before exposure. The type of cycloadduct was different in these two cases, and the parallel LC alignment was not achieved for both, suggesting that the aggregated mesogenic groups could not regulate the LC alignment.

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