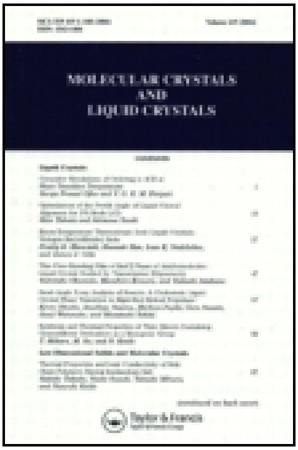

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Preparation of photo-crosslinked films of new Chalcone-based side chain type liquid crystalline polymers and its application to alignment film

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PREPARATION OF PHOTO-CROSSLINKED FILMS OF NEW CHALCONE-BASED SIDE CHAIN TYPE LIQUID CRYSTALLINE POLYMERS AND ITS APPLICATION TO ALIGNMENT FILM

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We synthesized two kinds of side chain type polymers containing chalconyl moieties to investigate the alignment's capability of photo-crosslinked polymer films. One is methacrylate type polymer having the chalconyl moiety in the side chain, and the other is imide type polymer. A smectic phase was exhibited for the methacrylate type polymers, while no mesophases were observed for the imide type polymer. These polymer films were irradiated with linearly polarized UV (LPUV) light (350 nm) under different conditions. The liquid crystalline (LC) cell was fabricated from the polymer film irradiated with LPUV light to examine the alignment properties of low molecular liquid crystal on the film. A mixture of a low molecular liquid crystal and a dichroic dye was filled in the LC cells. Alignment behavior of the low molecular liquid crystal was discussed by the dichroic ratio of the dichroic dye in the LC cell.

Keywords: chalcone; photo-dimerization; polyimide; side-chain liquid crystalline polymer; smectic phase

INTRODUCTION

The alignment of LC molecules plays an important role for liquid crystalline display (LCD)s. The rubbing process has been mainly employed for the uniaxial orientation of the LC molecules. However, the rubbing process has many disadvantages for LCDs such as generation of electrostatic charge and dust. Therefore, many methods of alignment technique for LC molecules are focused on rubbing free methods. Photo-alignment procedure is recognized as one of rubbing free methods and is investigated

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as one of candidates that overcome the generation of electrostatic charge and dust for the rubbing process [1,2].

Photo-alignment procedure is based on photochemical reactions such as photo-isomerization [3–5], photo-dimerization (photo-crosslinking) [2,6–12] and photodecomposition. Generally photo-dimerization of photosensitive groups in the polymer was employed to obtain a stable alignment of low molecular weight LC molecules. It would be desirable that photodimerization occurs by the exposure of relatively longer wavelength of the UV light to avoid partial degradation of polymer films by the irradiation of the UV light [13]. It is well known that the photoreaction of chalconyl moieties takes place by irradiation with relatively longer wavelength of the UV light. Photosensitive polymers containing chalcone derivatives have been studied for the photo-alignment film [13–19].

We thought that the alignment behavior of the LC molecules would be easily improved by the liquid crystalline polymer surface where mesogenic groups having similar chemical structure to that of the LC molecules existed. In this study, we investigated the photoreaction of the chalcone-based polymer films, as shown in Figure 1. The extent of the photoreaction for the chalconyl group in the polymers was examined by UV-vis spectroscopy measurements. The LC cell was fabricated from the polymer film irradiated with the LPUV light. A mixture of low molecular liquid crystal and the dichroic dye was filled in the LC cell. The alignment direction of the LC molecules was discussed by the dichroic ratio of the dichroic dye in the LC cell.

EXPERIMENTAL

Materials

Details of synthesis of polymers 1 and 2 were described in other literature [20]. Polymer 3 was prepared according to Scheme 1.

Characterization

UV-vis spectroscopy measurements were carried out with a HITACHI U-3410 spectrophotometer.

Linearly Polarized UV Light Irradiation

The polymer film was made by spin-coating on a quartz substrate from a chloroform solution. The polymer film was irradiated with a 500 W super high-pressure mercury lamp with a glan laser prism and a cut filter (350 nm). The LPUV light intensity was 1.89 mW/cm^2 at 365 nm. The

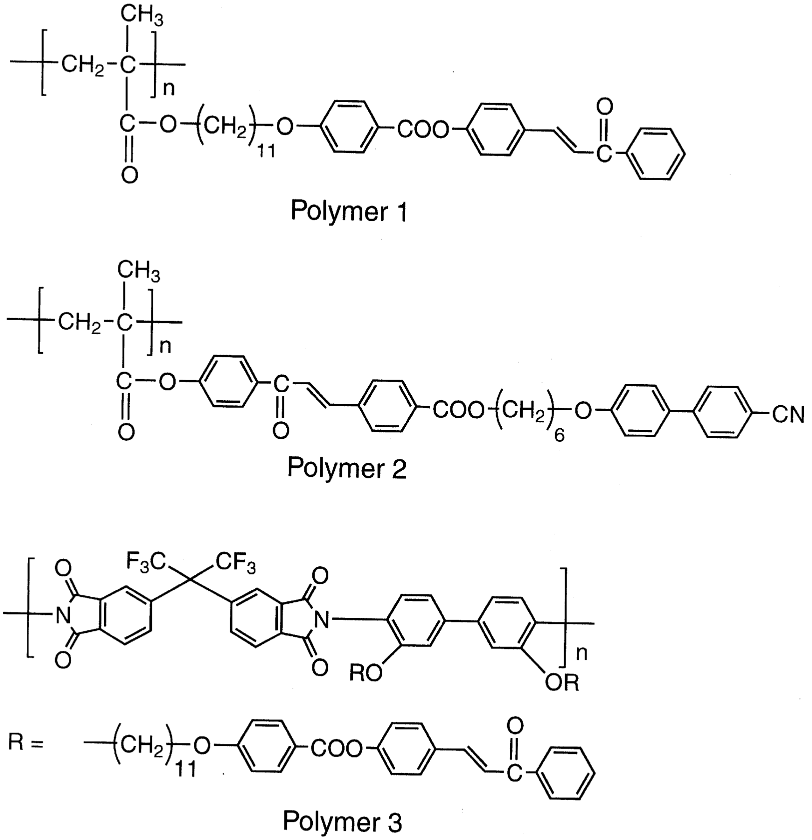
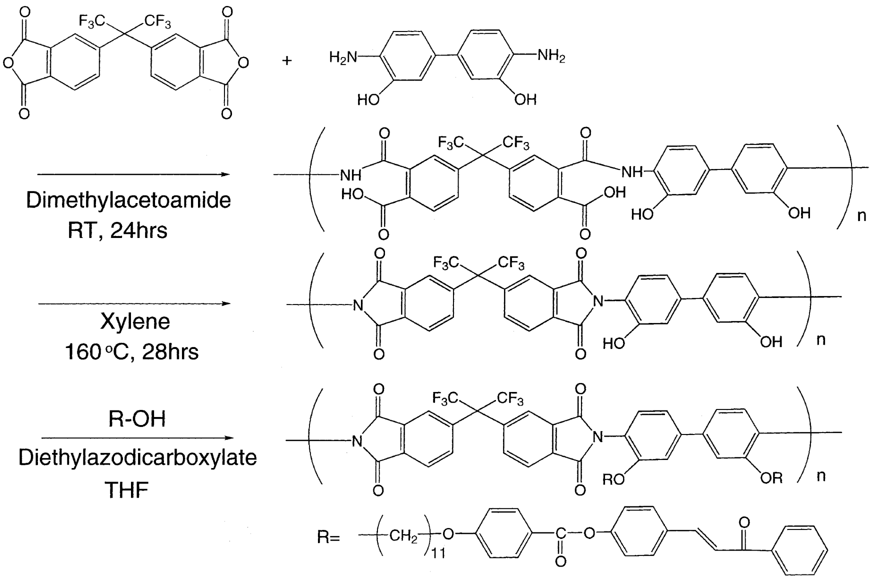


FIGURE 1 Chemical structures of polymer containing chalcone moiety.

polymer 1 and 2 films were irradiated with the LPUV light under different conditions as follows: (1) irradiation at room temperature after spin-coating, (2) irradiation at room temperature after annealing the spin-coated film in a LC state, (3) irradiation in a LC state, (4) irradiation in an isotropic phase. On the other hand, the polymer 3 film was irradiated under the two conditions as follows: (1) irradiation at room temperature after spin-coating, (2) irradiation above glass transition temperature.

Alignment Behavior of LC Molecules

A sandwich type LC cell was fabricated in an antiparallel fashion of the polymer films irradiated with the LPUV light. A mixture of the low molecular weight liquid crystal (MBBA; p-methoxybenzylidene-p-n-butylaniline or



SCHEME 1 Synthesis of polymer 3.

5CB; 4-cyano-4′-n-pentylbiphenyl) with the dichroic dye (M137) was injected in the LC cell. The thickness of the LC cell was 10 μm. Alignment behavior of the LC molecules was investigated based on the dichroic ratio (DR) of the absorbance at 640 nm for the dichroic dye, which were obtained by polarized UV-vis spectroscopy measurements. The DR was defined as follow:

$$\text{Dichroic ratio (DR)} = \frac{A_{para} - A_{per}}{A_{para} + A_{per}}$$

A_{para} and A_{per} indicate the absorbance parallel and perpendicular to the incident electric vector of the exposed LPUV light, respectively.

RESULTS AND DISCUSSION

Thermal Properties of Polymers

We synthesized two kinds of polymers containing chalconyl moieties, one is a methacrylate polymer having the chalconyl moiety in the side chain, and the other is a polyimide as shown in Figure 1. One of methacrylate type polymers have the chalconyl moiety directly connected to the benzoate component (polymer 1), and the other is a polymer with a spacer group introduced between the cyanobiphenyl and the chalconyl moiety (polymer 2). The polyimide (polymer 3) was synthesized by polymer reaction as shown in Scheme 1.

Synthesis of methacrylate type monomers and polymers were described in other literature [20]. The number-average molecular weight of the polymer 1 was 27,300 and the dispersion of the polymer 1 was 3.7, while that of the polymer 2 was 3,300 and the dispersion was 1.2. The number-average molecular weight of the polymer 3 was 14,000 and the dispersion was 1.6.

Thermal properties of the polymers were summarized in Table 1. Details of the thermal behavior of polymers 1 and 2 were described in other literature [20,21]. Only a baseline shift was observed in the DSC curves of polymer 3. The baseline shift was attributed to glass transition temperature. Birefringence was not observed for the polymer 3. Therefore we concluded that no mesophases were exhibited for polymer 3.

Photoreaction of Polymer Films

These polymer films were irradiated with LPUV light at different conditions. UV-vis spectra of polymer 3 film exposed to the LPUV light at 180°C were shown in Figure 2. A peak around 320 nm in the spectra decreased with irradiation time, while a peak around 265 nm increased with irradiation time.

The same tendency of the changes in the UV-vis spectra was observed for the polymer 1 and 2 films [21]. The peak around 320 nm was assigned to the mesogenic group containing the chalcone derivative with the trans conformation, while the peak around 265 nm was attributed to the dimer structure formed by the photo-dimerization [14]. The peak around 265 nm was also observed in the UV-vis spectrum of polyimide backbone in polymer 3. However the peak around 265 nm in the UV spectrum of the polyimide backbone did not change with LPUV light irradiation. Therefore the change in the absorbance of the peak around 265 nm was attributed to the formation of the dimer structure of the chalcone derivative.

TABLE 1 Thermal Properties of Polymers

Polymers	Phase transition temperatures/°C
Polymer 1	$\mathrm{g} \underset{31}{\overset{34}{\rightleftarrows}} \mathrm{Sm} \underset{188}{\overset{196}{\rightleftarrows}} \mathrm{I}$
Polymer 2	$\mathrm{g} \underset{78}{\overset{87}{\rightleftarrows}} \mathrm{Sm} \underset{162}{\overset{165}{\rightleftarrows}} \mathrm{I}$
Polymer 3	$\mathrm{g} \underset{83}{\overset{87}{\rightleftarrows}} \mathrm{I}$

g; glassy, Sm; smectic phase, I; isotropic phase.

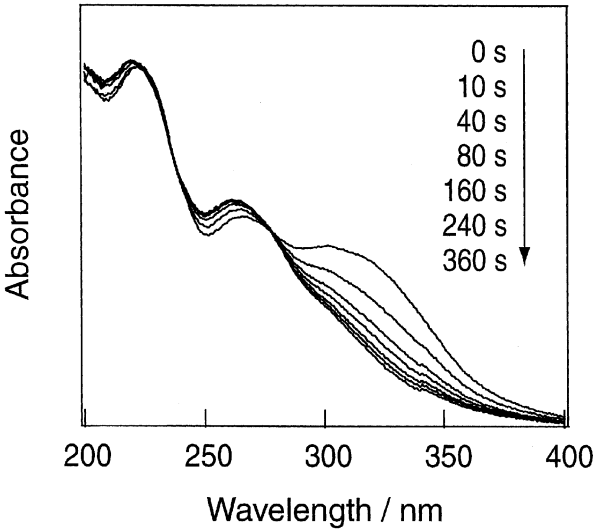


FIGURE 2 UV-vis spectra of polymer 3 film irradiated with LPUV light at 180°C.

The photo-dimerization and photo-isomerization are known as a possible photoreaction of the photo-reactive molecules like the chalconyl or the cinnamoyl groups. We investigated the photoreaction of the chalconyl groups by FT-IR measurements. We confirmed that a main photoreaction of the chalconyl groups in our polymer films was attributed to the photo-dimerization on the basis of a decrease in the peak ($984\,\mathrm{cm}^{-1}$) assigned to the olefin C-H out-of-plane bending for the trans chalconyl groups and a shift to the higher wave number for the peak ($1666\,\mathrm{cm}^{-1}$) assigned to the ketone group [13].

The extent of the photo-dimerization was estimated by the decrease in the absorption peak around 320 nm. The extent of the photo-dimerization in the LC state of the polymer 1 and 2 was larger than that in the other states (as described in experimental section, spin-coated film (1) and annealed film (2)). Furthermore, the photo-dimerization of the polymer films in the LC state was faster than that of the polymer films in other states as shown in Figure 3. These results indicated that the extent of photo-dimerization would be dependent upon the orientation and thermal motion of the chalcone moiety.

In the annealed film, the orientation of the chalcone moiety would be similar to that in the LC state, because LCPs can lock-in the mesogenic orientational order below the glass transition temperature. If only the orientation of the chalcone moiety were important for the extent of the photo-dimerization, the extent of the photo-dimerization in the annealed

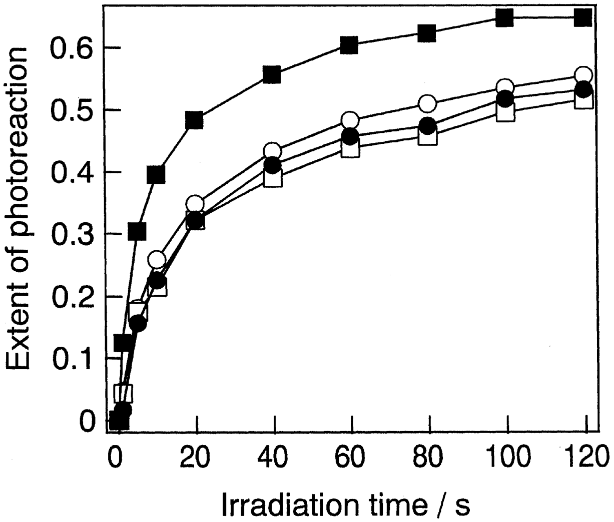


FIGURE 3 Extent of photoreaction for the polymer 1 film irradiated with LPUV light at 220°C (filled circles), at 170°C (filled squares). Open squares and circles indicate the extent of photoreaction for the polymer 1 film irradiated after annealing and spin-coating, respectively.

film should be larger as well as that in the LC state. However the extent of the photo-dimerization in the annealed film was not so large compared to that in another states. The result indicated that its thermal motion of the chalcone moiety in the LC state would play an important role in the larger extent of photo-dimerization.

Thermal motion of the chalcone moiety in the LC state would occur when the polymer film was heated above its glass transition temperature. Therefore the photo-dimerization temperature would be one of the important factors in determining the extent of the photo-dimerization. In this study, we employed the reduced temperature (0.86) for the photo-dimerization temperature in the LC state of polymers 1 and 2; however an appropriate temperature condition for the photo-dimerization of the chalcone moiety would be present.

Alignment Behavior of Low Molar Mass LC on Irradiated Polymer Films

We calculated the DR of the dichroic dye according to the equation as shown in experimental section and investigated the alignment behavior of the LC molecules based on the DR value [21]. The positive DR value indicated that the LC molecules were aligned parallel to the electric vector of the incident LPUV light, while the negative DR value displayed that these LC molecules were aligned perpendicular to the electric vector of the LPUV light.

The relationship between LPUV light irradiation time of the polymer 1 films exploited for the LC cells and the DR values of the LC cells (5CB) were summarized in Figure 4. In the LC cell fabricated from the polymer 1 films irradiated with LPUV light in the LC state, the DR values were positive when the irradiation time was 80 or 120 s. The absolute value was larger than that of the DR value of the LC cells fabricated from the polymer 1 films irradiated in other conditions. These results indicated that the LC molecules were easily aligned parallel to the electric vector of the incident LPUV light in the LC cells fabricated from the polymer 1 films irradiated in the LC state. The uniaxial alignment behavior of the LC molecules was achieved using the polymer 1 films where the photo-induced anisotropy was generated by the orientation of both non-reacted side chains and dimerized moieties in the same direction [21]. The anisotropy due to the orientation of both non-reacted side chains and dimerized moieties was induced in the parallel direction to the electric vector of the incident LPUV light. We considered that the photo-induced anisotropy on the surface of

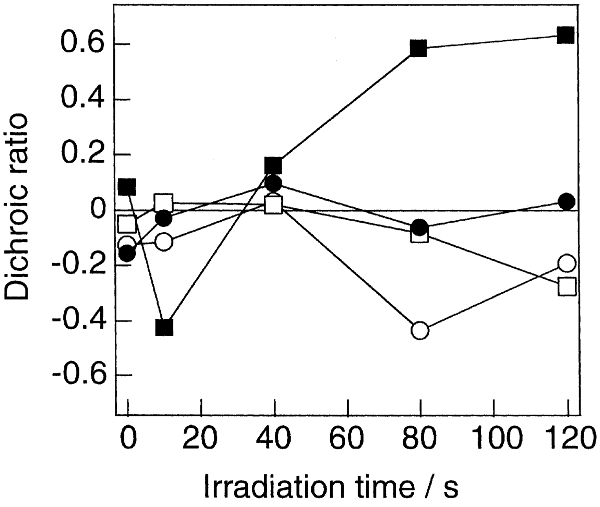


FIGURE 4 Dichroic ratios of the dichroic dye in the LC cell (5CB): the LC cells fabricated from the polymer 1 films irradiated with LPUV light in the isotropic phase (220°C; filled circles), in the LC state (170°C; filled squares), after annealing (open squares) and after spin-coating (open circles).

the polymer film would determine the alignment direction of LC molecules on the surface of the polymer film.

Positive or negative DR values were detected for the LC cell fabricated from the polymer 1 films irradiated in the isotropic state. Furthermore the absolute value of the DR value was very small even if the irradiation time increased. This result showed the homeotropic alignment of the LC molecules in the LC cells. This alignment behavior was confirmed by conoscopic observation of the optical microscopy measurement. In the case of the LC cell fabricated from the polymer 1 film irradiated after spin-coating or after annealing, the LC molecules were aligned perpendicular to the electric vector of the incident LPUV light. However the absolute DR values were very small.

Figure 5 displayed the DR values of the LC cells fabricated from the polymer 2 film irradiated with LPUV light. In the case of the LC cell fabricated from the polymer 2 film irradiated with LPUV light at room temperature (after spin-coating or after annealing), the DR values were negative and small. This result indicated that the LC molecules tended to be aligned perpendicular to the electric vector of the incident LPUV light; however uniaxial alignment of the LC molecules was not obtained. In the case of the LC cells fabricated from the polymer 2 film irradiated in the

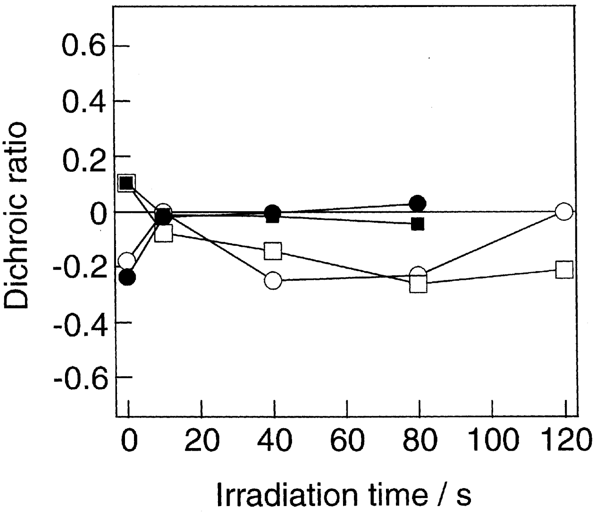


FIGURE 5 Dichroic ratios of the dichroic dye in the LC cell (5CB): the LC cells fabricated from the polymer 2 films irradiated with LPUV light in the isotropic phase (185°C; filled circles), in the LC state (150°C; filled squares), after annealing (open squares) and after spin-coating (open circles).

LC or isotropic state, the DR values were almost zero. The homeotropic alignment of the LC molecules was detected by the conoscopic observation of polarized optical microscopy measurements.

Figures 6 and 7 showed the DR values of the LC cells fabricated from the polymer 3 film irradiated with LPUV light. The irradiation temperatures were determined based upon glass transition temperature of the polymer 3. The LC cells fabricated from the irradiated polymer 3 films tended to show positive DR values. In the case of the LC cells fabricated from polymer 3 film irradiated at 130 or 180°C, the DR values increased with the irradiation time (up to 80 s for MBBA or 160 s for 5CB). While for the LC cells fabricated from the polymer 3 film irradiated after spin-coating (at room temperature), the DR values increased slowly with the irradiation time. These results indicated that the LC molecules were aligned parallel to the electric vector of the LPUV light. The change in the DR values with the irradiation time was dependent upon the irradiation temperatures. The irradiation above glass transition temperature would play an important role to obtain parallel alignment behavior of LC molecules.

We examined that the DR values of the polymer 3 film to investigate the photo-induced anisotropy of the irradiated polymer 3 film. The DR values of the peak around 265 nm for the polymer 3 film were positive. This result indicated that the dimerized moieties were aligned parallel to the electric

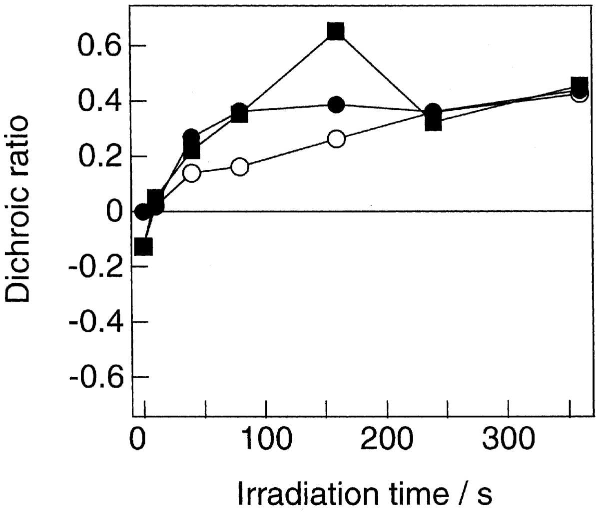


FIGURE 6 Dichroic ratios of the dichroic dye in the LC cell (MBBA): the LC cells fabricated from the polymer 3 films irradiated with LPUV light at 180°C (filled circles), at 130°C (filled squares) and after spin-coating (open circles).

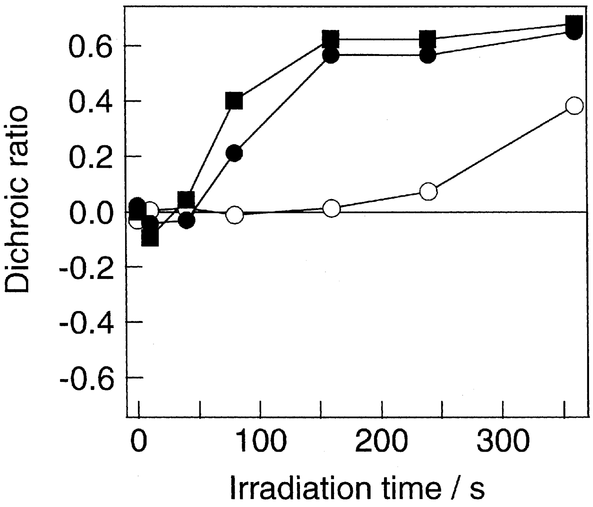


FIGURE 7 Dichroic ratios of the dichroic dye in the LC cell (5CB): the LC cells fabricated from the polymer 3 films irradiated with LPUV light at 180°C (filled circles), at 130°C (filled squares) and after spin-coating (open circles).

vector of the incident LPUV light. On the other hand, non-reacted side chains for the polymer 3 film were aligned to the perpendicular to the electric vector due to the negative DR values for the peak around 320 nm.

The parallel alignment behavior of LC molecules of 5CB or MBBA in the LC cell would be originated from the photo-induced anisotropy on the surface of the irradiated polymer film, although the interaction between the photo-induced anisotropy and LC molecules is not clarified at the present time. The photo-induced anisotropy on the surface of the irradiated methacrylate polymer 1 film occurred from the orientation of both the dimerized moieties and non-reacted side chains. However the photo-induced anisotropy of the polymer 3 film would be mainly based upon the generation of the dimerized moieties of chalcone derivatives, and LC molecules would be aligned along the photo-induced anisotropy based upon the generation of the dimerized moieties on the surface of the polymer 3 films. We did not clarify the reason why LC molecules were aligned along the photo-induced anisotropy based upon the generation of the dimerized moieties for the polymer 3 films, although the alignment behavior of LC molecules in the LC cell using methacrylate polymer 1 film was dependent upon the photo-induced anisotropy originated from both the dimerized moieties and non-reacted side chains. We would anticipate that the large positive DR values for the LC cells would be obtained due to the photo-induced anisotropy originated from the alignment of both the dimerized moieties and non-reacted side chains if we will exploit liquid crystalline polyimide for the alignment film of the LC cells, because large positive DR values were obtained for the LC cells fabricated from the LC methacrylate polymers irradiated in the LC state compared to the isotropic state.

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