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# Liquid Crystal Alignment Properties on Crosslinkable Polymer Films with Plasma Surface Modification

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*The plasma surface modification is carried out on a polymer film, and the surface is subsequently rubbed. The side chains of the polymer are crosslinked in the plasma process. Liquid crystal molecules uniformly align perpendicular to the rubbing direction on the unmodified surface and parallel on the modified surface. The dichroism of the polarized UV absorption to the rubbing direction is positive in the modified film as compared to the negative dichroism in the unmodified film. The sign of the dichroism is reasonable to explain easy axes of modified and unmodified film surface.*

**Keywords:** alignment patterning; crosslinkable polymer; easy axis; plasma surface modification; rubbing treatment

## INTRODUCTION

The alignment phenomenon of liquid crystal (LC) molecules on a solid surface and the technique of the alignment control have been an attractive subject in terms of physical research and LC device applications. Mechanical rubbing on the polymer surface with a cloth is used to align the LC molecules in most practical LC devices. On the other hand, some types of photo alignment techniques are also studied actively [1–4]. Recently, we have reported double treatments of UV irradiation and rubbing to change alignment properties of LC on the polymer surface. We successfully demonstrated to increase an azimuthal anchoring energy by irradiating a rubbed polyvinyl cinnamate

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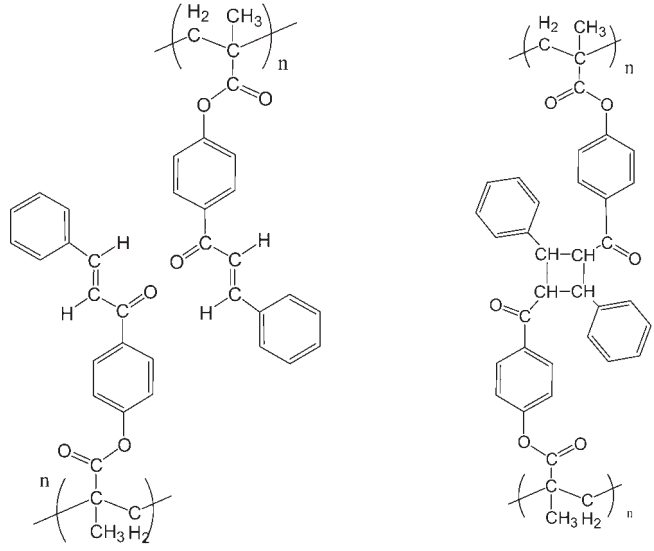
surface with unpolarized UV light. The variation of the anchoring energy can be applied to the control of the twist angle in the twisted nematic LC cell [5,6]. We also reported another photo-reactive polymer which yields two orthogonal easy axes by the unidirectional rubbing treatment and unpolarized UV irradiation [7].

On the other hand, the plasma surface modification technique has a great potential to chemically and physically change the polymer surface and to add a new function. Therefore, plasma-modified surfaces for the LC alignment have also been reported [8,9]. In this study, we apply the plasma surface modification technique to the crosslinkable polymer. The liquid crystal alignment properties on the modified surfaces are compared with the unmodified surface. The alignment mechanism of the polymer surface is also discussed.

## EXPERIMENTAL

The polymer used in this study is SAMBO AR-G developed by Sambo Chemical Industry Co. Ltd. Figure 1(a) shows the chemical structures of AR-G. When the AR-G is irradiated with UV light, a pair of



**(a)** **(b)**

**FIGURE 1** Chemical structures of (a) AR-G and (b) the crosslinked side chain.

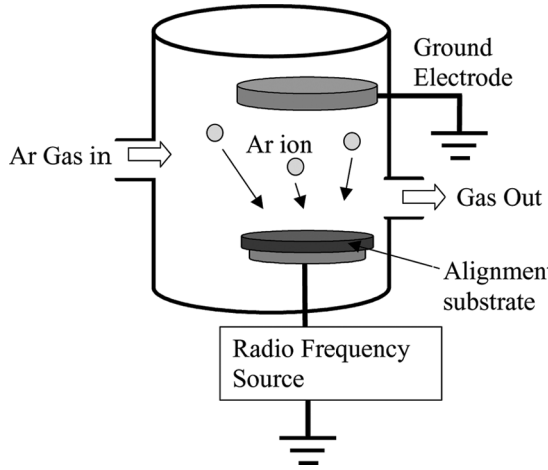



**FIGURE 2** Schematic diagram of plasma surface modification process.

chalconyl units is crosslinked by 2 + 2 cycloaddition reaction [10,11], as illustrated in Figure 1(b). A 4 wt% solution of AR-G was prepared using cyclohexanone as a solvent. The solution was spin-coated on an ITO-coated glass or a quartz glass substrate and was baked at 100°C for 10 min. The thickness of the AR-G film was about 100 nm. The nematic LC of 4′-pentyl-4-cyanobiphenyl (5CB) is used to investigate alignment properties. To elucidate the LC alignment mechanism, we measured the optical anisotropy of the rubbed AR-G film using a Glan-Tylor prism and the UV-visible spectrometer (Shimadzu Multispec-1500).

Figure 2 shows a schematic diagram of plasma surface modification process. In the plasma surface modification, a glow discharge plasma is created by evacuating a vessel, and then refilling it with a low pressure Ar gas. The gas is energized using the technique of radio-frequency energy. The AR-G film surface in contact with the gas plasma is bombarded by Ar ions. The energy is transferred from the plasma to the AR-G film to result in the surface modification. In this study, the electric radio-frequency power is 30 W and the Ar gas pressure is 30 Pa.

## RESULTS AND DISCUSSION

Figure 3 show absorption spectra of AR-G film. Before UV irradiation, a maximum absorption peak at 307 nm constituting the

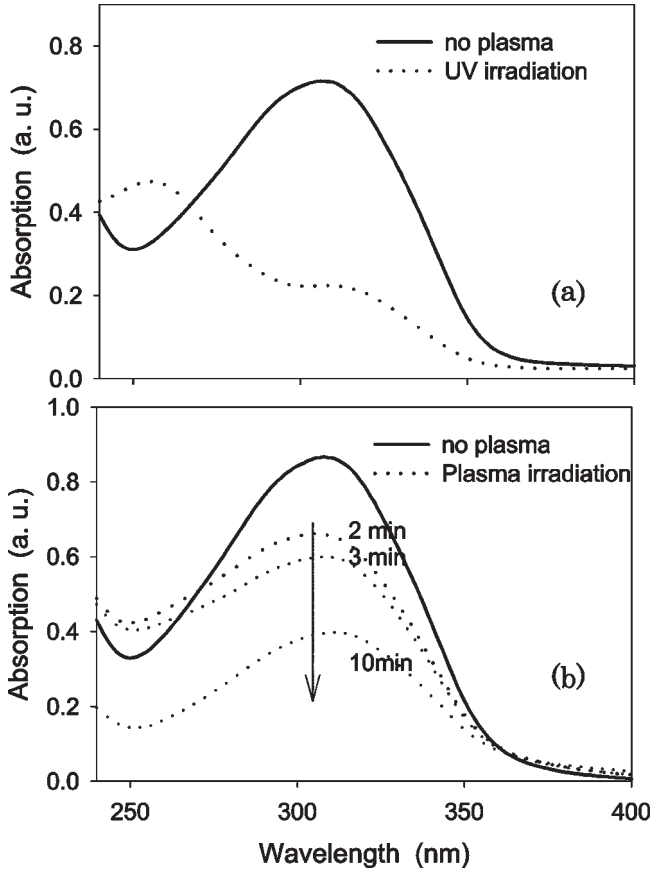



**FIGURE 3** Absorption spectra of (a) photo-crosslinked AR-G film and (b) plasma crosslinked AR-G films.

chalconyl unit is observed. When this film was irradiated with the UV light of 10 mW/cm$^2$ for 3 min, the absorption considerably decreased around 307 nm, while it increased around 250 nm, as shown in Figure 3(a). Such a change is known to be responsible to the crosslinking reaction [8]. The absorption at 300 nm decreases and that at 250 nm increases by the plasma irradiation as well as by the UV irradiation, as shown in Figure 3(b). Therefore, the crosslinking reaction may carry out by the plasma modification. The decrease of the peak level around 310 nm by the plasma modification is less than that by the UV irradiation, since the crosslinking reaction takes place only near the surface by the plasma modification.

The decomposition of double bonds is simultaneously caused and film thickness becomes thinner (see 10 min curve by the overdose of the plasma irradiation). In addition, the chemical structure after the UV irradiation may be different from that after plasma irradiation and it needs to be additionally studied.

Next the LC alignment properties are observed on the AR-G film surface irradiated with the plasma for 5 min through the stainless steel plate mask, as shown in Figure 4(a). The AR-G surface is then uniformly rubbed using the conventional rubbing machine and the rubbed PI surface is assembled as a counter substrate. The rubbing direction of the PI surface is parallel to that of the AR-G substrate, as shown in Figure 4(b). The LC in the isotropic phase is injected into the empty cell to prevent the flow induced LC alignment. When the cell is cooled to the nematic phase, the twisted nematic (TN) orientation is obtained on the unmodified (uncrosslinked) surface. On the other hand, the LC homogeneously aligns on the plasma modified surface. Then we can see the image in the alignment patterned LC cell between parallel polarizers, as shown in Figure 4(c). If two substrates are assembled with their rubbing direction perpendicular to each other, the black and white image reverses, since the TN and homogeneous orientation is obtained on the modified and unmodified surfaces, respectively. These results show that the easy axis on



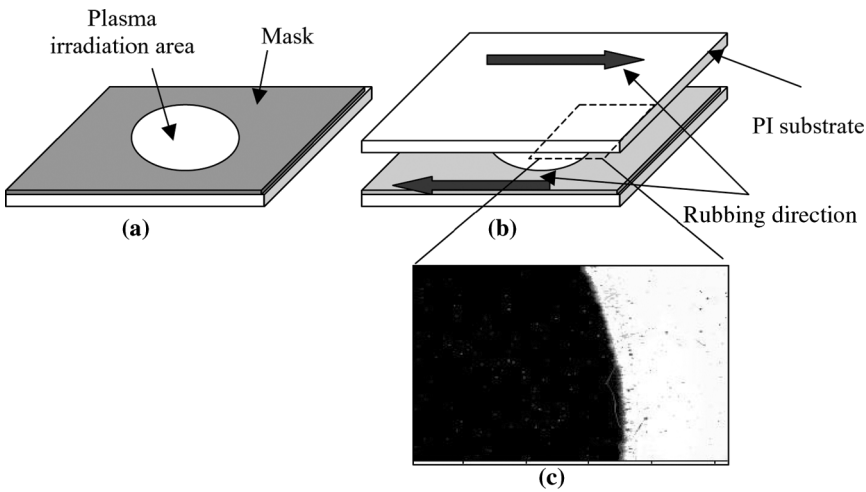



**FIGURE 4** Schematic diagrams of (a) the mask plate and (b) the LC cell assembling, and (c) the photograph of the LC cell between crossed polarizers.

the unmodified surface is perpendicular to the rubbing direction, on the other hand, is parallel on the modified surfaces. In addition, if the AR-G surface is rubbed and subsequently modified, the easy axis is still perpendicular to the rubbing direction.

In Figure 5(a), polarized absorption spectra of the rubbed AR-G film are shown before and after the plasma modification. The polarized absorption perpendicular to the rubbing direction is larger than that parallel to the rubbing direction around the peak wavelength in the unmodified film. When the film surface is irradiated with the plasma, the peak level around 307 nm decreases, and the polarized absorption perpendicular to the rubbing direction is still slightly larger than that parallel to the rubbing direction. On the other hand, the polarized absorption perpendicular to the rubbing direction is smaller than that

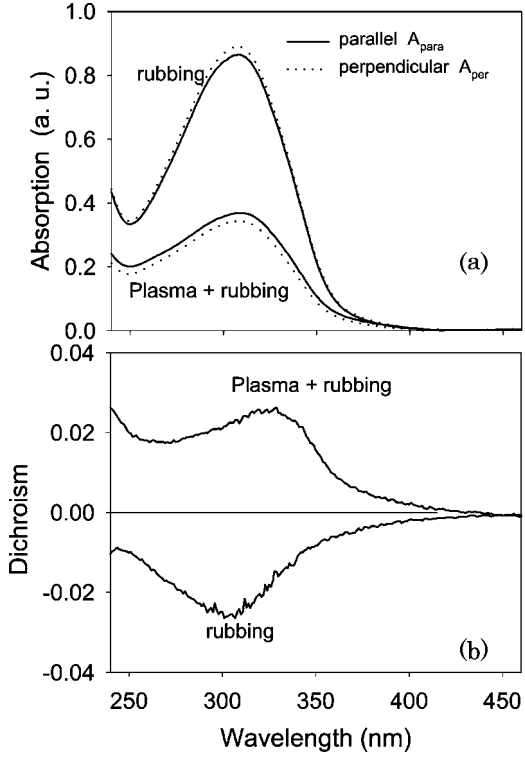



**FIGURE 5** (a) Polarized absorption spectra of the rubbed AR-G film measured before and after plasma modification and (b) dichroic absorption spectra ($A_{para}$–$A_{per}$) of rubbed films.

parallel to the rubbing direction if the AR-G surface is modified and subsequently rubbed.

We subtracted the absorptions measured parallel to the rubbing direction ($A_{para}$) from those perpendicular to the rubbing direction ($A_{per}$), and results are shown in Figure 5(b). Positive and negative signs of the dichroism are reasonable to the LC alignment direction parallel and perpendicular to the rubbing direction, respectively. The negative UV dichroism indicates that uncrosslinked side chains align perpendicular to the rubbing direction since the main chains are arranged in order parallel to the rubbing direction by the rubbing treatment. On the other hand, when the modified AR-G surface is rubbed, a positive UV dichroism is obtained, which clearly shows that

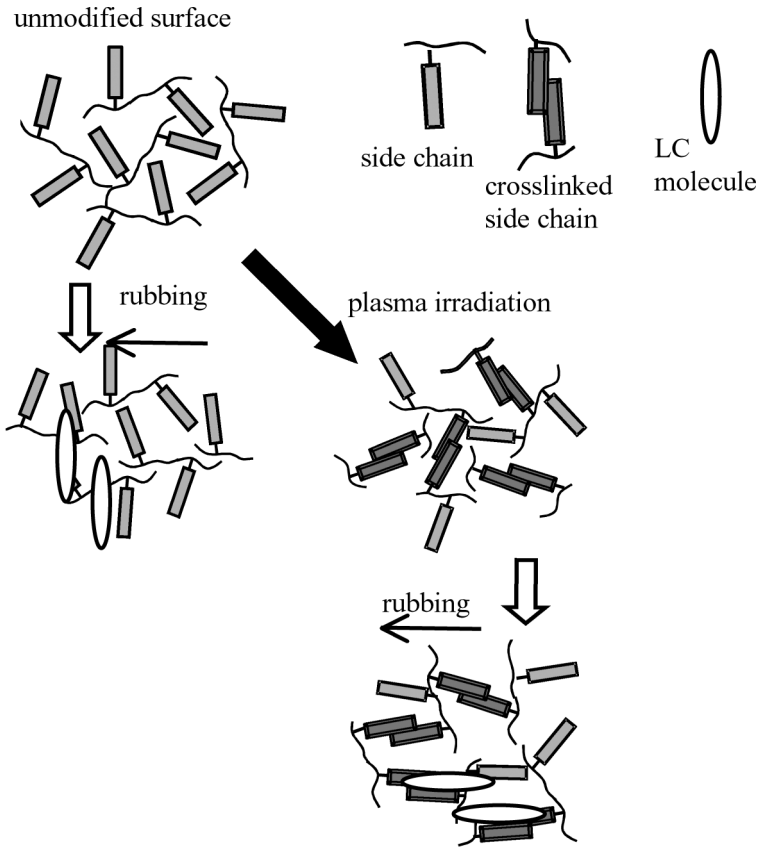



**FIGURE 6** Schematic models of polymer alignment by the rubbing and plasma irradiation processes and LC direction.

the crosslinked side chains is aligned parallel to the rubbing direction. From these results, a schematic model of the alignment mechanism is shown in Figure 6. LC molecules align parallel to the uncrosslinked and/or crosslinked side chains. Therefore, we can obtain two orthogonal easy axes by the unidirectional rubbing on the modified and unmodified surface.

## SUMMARY

We apply the plasma surface modification technique to change the LC alignment properties on the rubbed polymer film. The crosslinking reaction occurs by irradiating with the Ar plasma. LC aligns parallel to the rubbing direction on the plasma modified surface, and perpendicular on the unmodified surface. Therefore, the patterned alignment surface can easily be made by partly modifying the surface and unidirectionally rubbing on the whole surface.

Processing parameters, such as gas types, plasma treatment power, irradiation time and operating gas pressure can be varied in the plasma process. This wide range of parameters offers greater control than that offered by other modification process using UV light, ion beam and electron beam. Therefore, the wide variety of parameters in the plasma surface modification process provides us the potential to add other LC alignment functions, improve alignment properties and enhance the alignment performance.

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