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Liquid Crystal Alignment on a New Bifunctional Photoreactive Side-Chain Copolymer

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A layer of a new bifunctional photoreactive side-chain copolymer (SCCP) is used for aligning liquid crystal (LC) molecules. The SCCP consists of a photo-crosslinking group as well as photo-isomerizing group. For producing uniform alignment of a nematic LC, a linearly polarized ultraviolet (LPUV) light is exposed to the SCCP film. The quality and the stability of the LC alignment upon the LPUV exposure are studied.

Keywords: liquid crystal alignment; photo-crosslinking; photo-isomerizing; bifunctional copolymer

INTRODUCTION

The control of the liquid crystal (LC) alignment by a polarized light has attracted much attention from both fundamental and practical points of view. A photo-induced method of aligning LC molecules has several advantages over a conventional rubbing technique such as non-contact and no contaminants involved. It has been reported that some polyimides (PIs) exhibit an irreversible anisotropic chemical reaction induced by a linearly polarized ultraviolet (LPUV) light which causes the change in the alignment of LC molecules¹⁻³. Moreover, the nematic LC orientation on a dichroic dye-doped polyimide layer can be controlled by a linearly polarized laser beam⁴, and the optical regulation of the alignment of nematic

LCs can be achieved on a substrate attached with photo-isomerizable chromophores^{5,6}.

In this paper, we report on the physical mechanism for the LC alignment on a layer of a new bifunctional photoreactive side-chain copolymer (SCCP) by a LPUV laser light. In addition to the photo-isomerization, the photo-crosslinking effect on the stability of the LC alignment acquired during the LPUV exposure is studied.

EXPERIMENTAL

The chemical structure of the SCCP which has a liquid crystalline state is shown in Fig. 1. The side-chain groups, from left to right in the structure, are a photo-crosslinking group, a nematic LC mesogenic group, and a photo-isomerizing group. The composition of the SCCP we studied is $X : Y : Z = 1 : 8 : 2.5$. For understanding the photo-crosslinking effect on the alignment stability, another SCCP with only photo-isomerizable group, $X : Y : Z = 0 : 3 : 1$, was also examined in the dynamics of the light-induced optical anisotropy. In order to prepare an alignment layer, the SCCP solution of 5 % by weight in tetrahydrofuran was spin-coated on a glass substrate at room temperature. The LC used was ZLI-2293 of E. Merck which has the nematic phase at room temperature. One substrate of the LC cell has the SCCP layer to control the LC alignment, and the other has a rubbed PI layer to promote the homogeneous alignment. The cell thickness was maintained as 125 μm using film spacers.

We first examine the photo-induced optical anisotropy of the SCCP layer itself which was exposed to a linearly polarized light of a He-Cd laser (325 nm in wavelength and about 27 mW/cm² in intensity) used as a pump beam. The optical anisotropy in the SCCP layer was measured with a probe beam of a He-Ne laser (632.8 nm in wavelength) under crossed polarizers. One of the crossed polarizers was arranged to make an angle of 45° with respect to the polarization direction of the pump beam. Next, the LC alignment in the cell with one SCCP surface and one rubbed PI surface

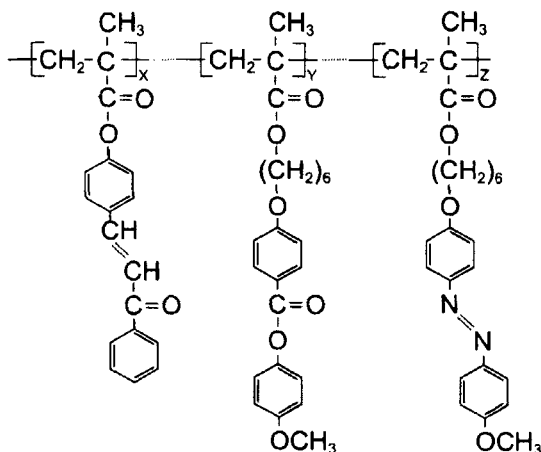


FIGURE 1 The chemical structure of the photoreactive SCCP.

was determined from microscopic measurements when the polarization of the pump beam was rotated with respect to the rubbing axis.

RESULTS AND DISCUSSION

The bifunctional SCCP used in our study exhibits two absorption peaks at about 320 nm and 360 nm, which are associated with the photocrosslinking and photo-isomerizing, azobenzene, side-chain groups, respectively. It is well known that photoreactive moieties, for example, azochromophors, can control the nematic LC director upon the exposure of a linearly polarized light. This originates from the collective reorientation of azo-dye molecules through the trans-cis-trans photo-isomerization.

Similar molecular reorientation of the SCCP would be expected when exposed to the LPUV light whose wavelength corresponds to the absorption peak at 360 nm. In our case, however, the SCCP was found to undergo a photochemically-induced nematic-isotropic phase transition (PNIT).⁷

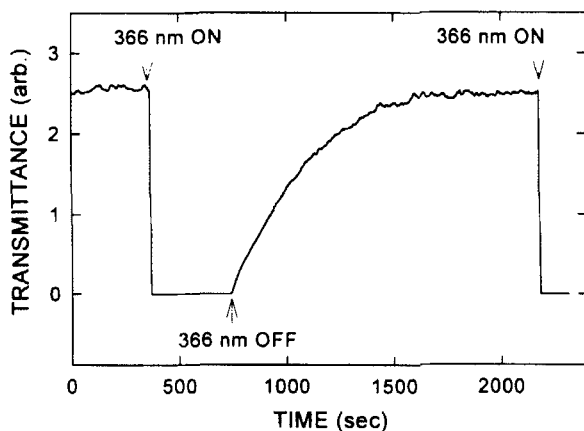


FIGURE 2 The change in the transmittance caused by a photochemical nematic-isotropic phase transition upon the LPUV exposure of 366 nm.

This is clearly seen from Fig. 2 which shows the change in the transmittance through the SCCP layer upon the exposure of the LPUV light of 366 nm. The LPUV light was generated from a Hg lamp in conjunction with a band-pass filter and a polarizer. Before exposing the SCCP layer to the LPUV light, there exists an optical anisotropy due to the intrinsic liquid crystallinity of the SCCP acquired during film formation. Upon the LPUV exposure from the Hg lamp, the anisotropy disappears since the SCCP experiences PNIT. When the LPUV was turned off, the optical anisotropy was gradually recovered and reached an equilibrium value. In fact, the stable LC alignment on a photoreactive polymer layer should be achieved by means of photo-crosslinking in addition to photo-induced orientational ordering. The PNIT behavior tends to disrupt the LC molecular orientation.

We now examine the photo-crosslinking behavior of the SCCP at the absorption peak of 320 nm. In contrast to the exposure case of 366 nm, no PNIT occurs upon the LPUV exposure of 325 nm from a He-Cd laser

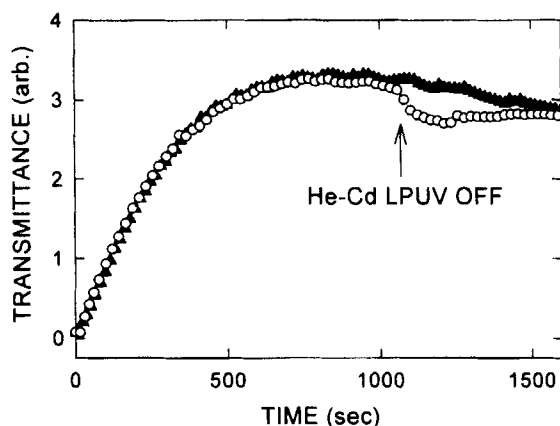


FIGURE 3 The change in the transmittance associated with the photo-induced optical anisotropy by the LPUV exposure of 325 nm. Filled triangles and open circles represent the data obtained with a successive LPUV exposure and a finite LPUV exposure, respectively.

used as a pump beam. In Fig. 3, the change in the transmittance of a probe beam (He-Ne laser) through the SCCP is shown as a function of the LPUV exposure time. Filled triangles and open circles represent the data obtained with a successive LPUV exposure and a finite LPUV exposure, respectively. As expected, the transmittance increases monotonically with the exposure time until the photo-induced optical anisotropy becomes to saturate. One interesting point is that the transmittance reaches a maximum at about 800 sec and tends to slightly decrease with further increasing the exposure time. This is related to the photo-crosslinking effect which reduces the free volume for the SCCP and thus disrupts the degree of molecular ordering. Note that the photo-isomerizing effect, giving PNIT, is negligible at 325 nm. In the case of a finite LPUV exposure for 1050 sec, the transmittance shows no rapid decay and remains finite because of the photo-crosslinking effect.

We now describe how the photo-crosslinking group affects the stabil-

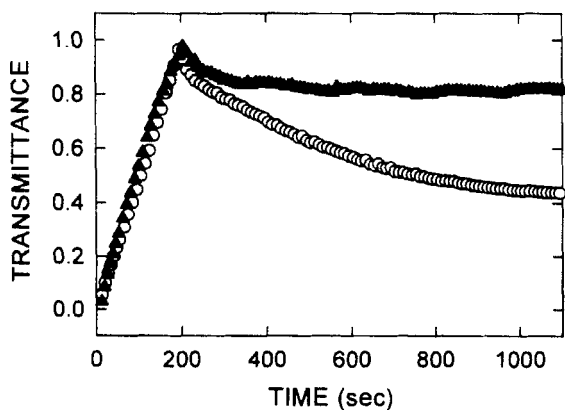


FIGURE 4 The effect of the side-chain photo-crosslinking group on the stability of the induced optical anisotropy. Filled triangles and open circles represent two different SCCP's with and without the photo-crosslinking group, respectively.

ity of the optical anisotropy in the SCCP layer acquired upon the LPUV exposure. The SCCP without the photo-crosslinking group was used for studying the relaxation behavior of the induced optical anisotropy. In Fig. 4, filled triangles and open circles represent the data obtained from two different SCCP's with and without the photo-crosslinking group, respectively. Clearly, the transmittance (filled triangles) through the SCCP with the photo-crosslinking group stays fairly constant, showing better stability after the LPUV exposure for 200 sec. As shown in Fig. 4, the attachment of the photo-crosslinking group to the SCCP would be critical for stabilizing the LC alignment.

Based on the results in Fig. 3, the LPUV exposure time for a stable LC alignment was determined to be about 10 minutes. The LC cell was made with two glass substrates, one of which has the SCCP layer exposed to the LPUV and the other has a rubbed PI layer. The cell has three different regions where the polarization direction of the LPUV is (a) par-

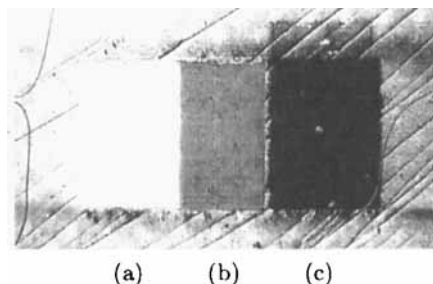


FIGURE 5 The aligned textures of a nematic LC, ZLI-2293, under crossed polarizers. The LC cell was made with two glass substrates, one of which has a rubbed PI surface and the other has a SCCP layer exposed to the LPUV light. The polarization direction of the LPUV is (a) parallel, (b) twisted by 45° , and (c) perpendicular to the rubbing axis.

allel, (b) twisted by 45° , and (c) perpendicular to the rubbing axis. A nematic LC, ZLI-2293, was filled into the cell, and the aligned textures were observed with an optical polarizing microscope. The aligned textures in the three regions are shown in Fig. 5. The rubbing axis lies in the direction from the top to the bottom. One of crossed polarizers in the microscope coincides with the rubbing axis. It is noted that the LC director on the SCCP layer is perpendicular to the polarization direction of the LPUV. This is consistent with the previous results for the alignment characteristics of nematic LCs on other polymer systems containing only azo-chromophores^[4-6]. The cases of (a) and (b) correspond to the 90° and 45° twisted-nematic structure.

CONCLUDING REMARKS

We have demonstrated that the stable LC alignment can be obtained on a new bifunctional photoreactive SCCP layer upon the LPUV exposure. The collective reorientation of the LC molecules is mainly achieved by the photo-isomerizing group while the alignment stability is governed by using

the photo-crosslinking group. The SCCP we studied undergoes the PNIT upon the LPUV exposure at the wavelength which coincides with the absorption peak of the photo-isomerizing group. A basic understanding of the physical mechanism for the LC alignment on other bifunctional SCCP systems, at a molecular level, remains to be carried out.

Acknowledgements

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