Surface-assisted Photomanipulation of Orientation of a Polymer Liquid Crystal

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The alignment photocontrol of liquid crystalline polymer films was achieved by a thin film of a polymethacrylate with *p*-cyanoazobenzene side chains as a command layer, which was exposed to linearly polarized light in advance.

Our systematic studies on command surfaces have established that the alignment of nematic liquid crystals (LCs) is controlled by structural as well as orientational manipulation of photo-reactive molecules which are tethered to substrate surfaces.[1] Representative procedures to prepare command surfaces involve the chemisorption of photo-reactive molecules such as azobenzenes on surfaces through covalent bonds[2] as well as hydrogen bonds,[3] the covering of surfaces with thin films of polymers bearing photo-reactive residues[4,5] and the deposition of monolayers of photo-reactive polymers by the Langmuir-Blodgett technique.[6] This surface-assisted photochemical technique to provide uniaxially aligned nematics has been of practical significances in applying to produce LC-aligning films employed in LC display devices[7,8] and to fabricate light-driven LC devices and the other versatile optical elements.[9] Liquid crystalline materials employed so far for the photoalignment belong to nematic LCs of low molecular weights. On the other hand, photoaligned polymeric materials have been prepared by in-situ radical photopolymerization of liquid crystalline methacrylates to give highly birefringent materials having versatile applicability.[10] Because of the inhibitory effect of atmospheric oxygen the radical polymerization of liquid crystalline monomers has to be carried out in a sealed cell. We described previously that cationic photopolymerization of liquid crystalline epoxy monomers to avoid the oxygen effect, whereas the monomers were filled also in a sealed cell.[11] From practical viewpoints, it is more convenient to perform the orientational photocontrol of polymer films because of the simplicity in fabrication. Consequently, we examined the possibility to carry out the alignment control of a liquid crystalline polymer. We report here that the molecular orientation of a readily available liquid crystalline polymer is controllable by a thin film of poly(4-cyano-4'-methacryloyloxyazobenzene) (**1**). As mentioned in the preceding paper, [12] this polymer exhibits extraordinary thermal stability of photoaligned states induced by irradiation with linearly polarized light and subsequent heat treatment. To authors' knowledge, this is the first example to realize the alignment photocontrol of polymeric materials by using command surfaces.

Our first attempt to carry out the alignment control of a thin layer of a nematic LC polymer, poly{4-methoxyphenyl [4-(3-acryloyloxypropyloxy)benzoate} (**2**) (Mw = 4200, Mw/Mn = 1.63, T_{NI} = 76 °C) was made by using a silica plate, the surface of which was modified with a silylating reagent having an azobenzene (**3**).[13] Our previous work demonstrated that a silica surface chemisorbed with **3** possesses the ability to generate homogeneous alignment of low-molecular-weight nematics by irradiation with linearly polarized light. It followed that a silica glass plate modified with **3** was exposed to linearly polarized 436 nm light to induce optical anisotropy of a chemisorbed monolayer, followed by spin-coating of a 20 wt% solution of the LC polymer **2** in toluene on the plate. Since the homogeneous alignment of layers of LC polymers is obtained usually by annealing them at a temperature slightly lower than their transition temperature leading to an isotropic phase to accelerate the molecular mobility of the polymers, the plate covered with the layer of **2** was set on a stage of a polarized microscope and heated at 75.5 °C to follow changes in the LC texture. No generation of homogeneous alignment was observed even after 30 min. It is very likely that the photogenerated anisotropy of the chemisorbed molecular layer is relaxed during the spin-coating of the solution because of the action of the solvent.

Consequently, a thin film of the polymer with *p*-cyanoazobenzene side chains (Mw = 4.3 x 10^4, Mw/Mn = 3.3) was used, taking notice of the fact that the polymer displays high thermostability and enhancement at elevated temperatures in photoalignment.[12] The film of **1** (ca. 30 nm in thickness) was irradiated with linearly polarized 436 nm light at an exposure dose of 0.1 J/cm^2 and subsequently baked at 240 °C for 2 min to enhance the photodichroism of the azobenzene chromophore. It was confirmed that essentially no optical anisotropy of the film is observable by a polarized microscope due to its extreme thinness. A toluene solution of the polymer **2** was subsequently spin-coated on the photoirradiated film, leading to a layer of LC polymer of ca. 1.2 μm thickness. It should be mentioned that the polymer **1** is insoluble in toluene. The sample was heated at 75.5 °C for 30 min to be subjected to polarized microscopic observation. It was found that

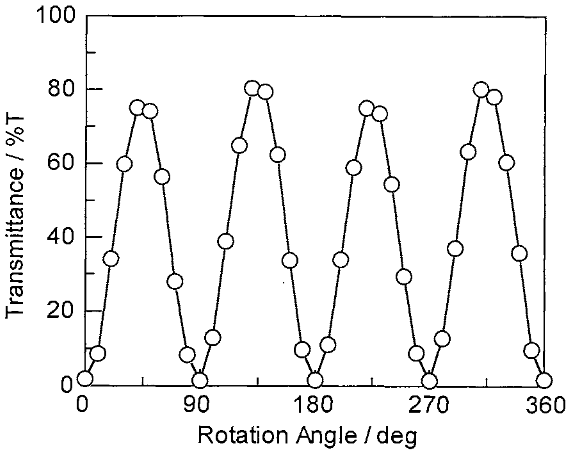

Figure 1. Angular dependence of transmittance of He-Ne laser beam through an liquid crystalline polymer film. The LC polymer was spin-coated on a photooriented azobenzene polymer layer and annealed at 75.5 °C slightly below the clearing temperature for 30 min.

homogeneous alignment is generated. Figure 1 shows the birefringence of the layer of **2**, which was monitored by transmitted light intensity of a linearly polarized He-Ne laser beam passed through the sample and a polarizer at a crossed position as a function of rotation angle of the sample.

The photoaligned state of the LC polymer layer was quite stable toward heat and light because of the fixation of the photoalignment of the azobenzene film after annealing. On the other hand, birefringent photoimages recorded in an LC polymer layer were obtainable according to the following procedure. A whole area of a thin film of the azobenzene polymer was illuminated with linearly polarized 436 nm light, followed by the second irradiation of the film through a photomask with the same light after rotating the electric vector at 45 degree. Since the reorientation of the azobenzene chromophores is readily induced for films before annealing, the molecular axis of the azobenzene upon the second photoirradiation through a photomask is determined by its electric vector so that latent photoimages are formed in the film. After the imagewise irradiation, the film was baked at 240 °C to enhance and fix the photoimages. When an LC polymer film was spin-cast on the annealed film and heated at the elevated temperature, clear photoimages with excellent optical quality exhibiting a high resolution power were observed by a polarized microscope, as shown in Figure 2. Four µm lines and spaces were resolved. The images disappeared at temperatures above T_{NI} of **2** and recovered completely by cooling down.

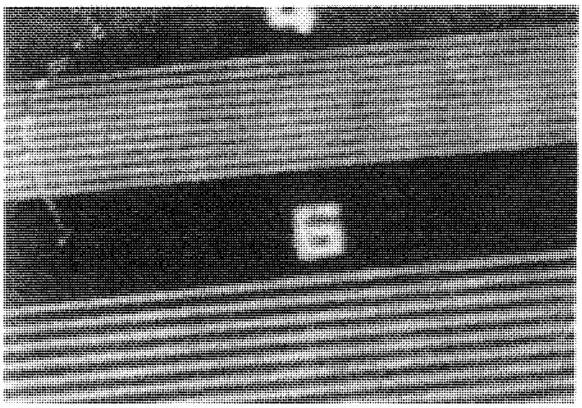

Figure 2. A polarized micrograph of a patterned LC polymer film.

In summary, a novel method to control the alignment of an LC polymer has been developed by using a thin film of the azobenzene polymer **1**. This technique opens ways to provide versatile optical elements based on the controlled molecular orientation in polymer films.

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