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Imprinting the Quasi Bookshelf Texture of a Ferroelectric Liquid Crystal into Nano-scaled Polymer Fibrils

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ABSTRACT
Polymer-stabilized ferroelectric liquid crystals (PSFLCs) are made by photopolymerizing 3% reactive mesogenic monomer on a quasi bookshelf texture of a ferroelectric liquid crystal (FLC). We observe the formation of nano-scaled polymer fibrils templated by the two dimensionally ordered host. The polymer fibrils capture the orientation of the host with thin polymer fibrils interweaving the smectic layers. The SEM study highlights the difference in morphology of the polymer fibrils depending on polymerization conditions; that is, polymerizing with or without the presence of an electric field. The polymer networks suppress the cone of rotation of FLC and thus, facilitate the switching and shorten the response time of the PSFLCs. We observed the threshold-less switching behavior in PSFLCs from samples polymerized with and without the field.

INTRODUCTION
Polymer stabilized liquid crystals (PSLCs) have rapidly developed into a unique class of electro-optical materials and play an important role in display\textsuperscript{1,2} and photonic\textsuperscript{3,4} technologies. The polymer network morphology of PSLCs, unique among these applications, plays a critical role in the performance of each device.\textsuperscript{5,6} The polymer network is typically formed via a controllable photopolymerization process using a wide variety of optical pattern forming states of liquid crystal hosts. The resultant polymer networks not only mimic the phase and structures of liquid crystals but also, under applied external field, control the reorientation of liquid crystal molecules in the surrounding area of polymer network. The polymer morphology itself is of considerable interest in the study of polymerization-induced phase separation in orientationally-ordered media. Despite reports on polymer stabilized ferroelectric liquid crystals\textsuperscript{7-10} the specific morphology of the polymer network and its precise connection to the electro-optical properties of ferroelectric liquid crystal (FLC) system remain open issues. In this paper, we report the study of polymer networks formed in a FLC and the influences of network morphology on electro-optical properties of the composite system.

EXPERIMENTAL DETAILS
The CS1024 FLC obtained from Chisso Japan was used as the host (96.85wt%). A mesogenic monomer 1,4'-{bis[4-(6-acryloyloxy)hexoxy]benzoate}-2-methyl-benzene (BBMB6) (3wt%) was used to form polymer networks in CS1024. A small amount of photo initiator Irgacure 369 (0.15wt%) was added to the mixtures of monomer/liquid crystal. The mixtures of FLC/monomer/photoinitiator were loaded into commercial LC cells (with 4 μm
spacing between anti-parallel rubbed polyimide alignment layers and ITO electrode area of 0.9x0.9 mm² by capillary action. The FLC mixtures were photopolymerized by UV illumination (the light source has a wavelength of 365 nm and 0.4 mW/cm²) at room temperature with (4V/µm 34 Hz triangle wave) or without an applied field. The sample to be polymerized under the electric field, was first heated to isotropic and then cooled to the desired polymerization temperature under the applied field. Polarizing microscopy study indicated that the transition temperatures of FLCs decrease with the addition of reactive monomers. The spontaneous polarization measurements on pure FLC, FLC/monomer mixture, and polymer-stabilized samples were carried out using the triangular wave method. The samples were placed in a Mettler FP 5 hot stage for temperature control within 0.1 degree Celsius and electric field applied by HP33120A function generator in combination with a HP6824A power amplifier. The polarization reversal current data were measured across a 30-Ohm resistor and detected with a HP54600 digital oscilloscope and recorded with a PC. For each temperature, multiple measurements were taken to reduce statistical errors. The quality of alignment was evaluated with a Nikon polarizing microscope.

We prepared PSFLC samples with a LC diacrylate monomer BBMB6 and studied their electro-optical properties including spontaneous polarization and switching characteristics using cells with a 4µm cell gap. The temperature dependence of spontaneous polarization of the PSFLC sample (CS1024/BBMB6 polymerized with the triangular wave, 8V/µm, 34 Hz, at 25°C) was studied under the applied field of 8V/µm. Figure 1a shows the maximum spontaneous polarization (Ps) value of 35 nC/cm² at 25°C. There is a slight decrease in Ps value compared with that of the pure CS1024 because of a smaller tilt angle caused by the formation of polymer network.

Figure 1b shows the field dependence of spontaneous polarization of the PSFLC samples prepared from CS1024/BBMB6. As shown in 1b, we observed a slight decrease in Ps value of PSFLC compared with the pure FLC because of the smaller tilt angle as a result of the formation of polymer network. A faster switching time was observed (Figure 1c, 80µs at 8V/µm, 34 Hz, triangular wave) for the PSFLC sample compared with that of the neat CS1024. Figures 2a and 2b show the PSFLC switched between the bright and dark state under the applied electric field of square wave, 8V/µm, 1 Hz. The PSFLC displays a stripe texture observed from a polarizing optical microscopy study. A distinct optical contrast was observed between the two different optical states. The SEM study highlights the difference in morphology of the polymer fibrils depending on polymerization conditions; that is, polymerizing with or without the presence of electric field. The cells of PSFLCs were immersed in hexane and dichloromethane at a mixture ratio of 8:2 to extract the liquid crystal. The cells were kept in solvent for several days and fresh solvent was used each day. After the FLC was removed, the cells were opened carefully. The SEM images highlight the difference in polymer morphology for the PSFLC samples from CS1024 polymerized with or without the presence of electric field. Nano-scaled thin and uniaxially aligned polymer fibrils with lateral brushes are observed for the CS1024 sample polymerized without the presence of electric field (Figure 2c). The fibrous networks formed without the application of electric field are tilted with respect to the rubbing direction (up-down arrow direction), indicating that the polymer network formed parallel to the smectic layers. In the case of CS1024 polymerized with the presence of electric field, we observed thicker polymer fibrils (Fig. 2d). The polymer fibrils from the sample polymerized with applied electric field possess a pattern of crossed stripes. The crossed polymer fibrils separate with
Figure 1. The plots of spontaneous polarization as a function of temperature (a), spontaneous polarization as a function of applied field (b), and switching time vs. the applied electric field (c) of a PSFLC sample.

interval close to the period of 10 micron. In both samples slimmer polymer fibrils interweave between the smectic layers.

The V-shaped switching behavior was observed for the PSFLC at applied field of 8V/µm, 34 Hz, triangular wave (Fig. 3). In comparison with PSFLC prepared with a mesogenic-like polymer network, the PSFLC prepared with a mesogenic monomer provides a better contrast and steepness of the T-V curve due to a better alignment of FLC before and after polymerization.}\textsuperscript{11}
Figure 2. The quasi-bookshelf texture of a PSFLC sample is switched from the bright state (a) to the dark state (b); the SEM images of polymer fibrils of (c) a PSFLC sample polymerized without the presence of electric field and (d) a PSFLC sample polymerized with the presence of electric field (the double arrows represent the polyimide rubbing direction).

Figure 3. The V-shaped switching of a PSFLC sample at applied field of 8V/µm, 34 Hz, triangular wave.

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SUMMARY

We demonstrated the formation of morphologically and optically anisotropic polymer fibrils using the quasi bookshelf optical texture of FLC as a template. The polymer fibrils formed between and interweaving among the smectic layers act as additional surfaces for controlling the reorientation of FLC molecules. Improvements in electro-optical properties including the increase in spontaneous polarization value as a function of temperature and applied field and fast switching at a lower applied field due to better FLC alignment of a PSFLC are achieved with a mesogenic monomer. The templated polymer fibrils suppress the symmetric rotation of FLC under applied field and resulted in V-shaped switching. The PSFLC represents significant advances in producing FLC display with gray-scale capability.

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11. unpublished results.