Influence of Aligned Fine Polymer Fibers on Thermal Phase Transition of Liquid Crystal

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This paper describes the thermal phase transition behavior of a liquid crystal (LC) material anchored by molecular-aligned small polymer fibers. The polymers were formed by the photopolymerization of liquid crystalline mono-functional acrylate monomers in a nematic-phase LC/monomer solution film with a thickness of 2μ m. The polymer fibers, which were obtained from a 20wt% concentration monomer, were highly oriented parallel to the rubbing direction of polyimide alignment layers coated onto the substrates. The composite film was heated to the isotropic phase and was then cooled down. The spatial distribution of the isotropic to nematic phase transition of the LC in the composite film was observed using a polarizing microscope. It was found that the phase-transition temperatures of the LC material near to the polymer fibers were higher than those of the LC areas with poor polymer dispersion. This means that polymer fiber surfaces with a molecular skeleton of aligned side chains enhance the alignment order of the LC material. On the other hand, from the results of a separate experiment based on the polymerization of an isotropic-phase LC/monomer solution, it was confirmed that isotropic polymer surfaces without molecular alignment could reduce the isotropic to nematic phase-transition temperature.
  Key words: liquid crystal, phase transition behavior, polymer fiber, polymer molecular alignment, composite film

1. INTRODUCTION

  Liquid crystal (LC) alignment, which is generally controlled by temperature, can create various electrooptic effects for display applications. The alignment order of the LC is not only decided by a molecular-size ordered self-assembly phenomenon in the bulk LC, but also by the interface with the LC material. For example, the thermal phase transition of the LC is changed by an aligned polymer surface such as rubbed alignment layers on a substrate.[1] Aligned polymers can also be formed with a multi-functional monomer in the LC by a polymerization-induced phase separation process, [2] and the use of a main-chain type aligned polymer increases the isotropic to nematic phase transition temperature of LC materials dispersed between the polymers.[3]
  On the other hand, we have tried to form a highly-aligned polymer [4] using a liquid crystalline mono-functional monomer dissolved in LC. The polymerization makes it possible to fix the highly-aligned monomers as side chains without crosslinking. This is because crosslinking generally creates main-chain branch and alignment disorder of molecular networks. It has been found that the anchoring effects of polymer fibers formed from the aligned mono-functional monomer can stabilize fragile LC alignment, like the smectic layers of ferroelectric LC [6] and can spatially modulate the threshold voltage [7] for LC alignment changes.
  In this paper, we studied the thermal phase transition behavior of LC anchored by molecular-aligned polymer fibers. We clarify that side-chain-aligned polymer fibers formed with a mono-functional monomer can raise the isotropic to nematic phase transition temperature.

2. PREPARATION

  In this study, the experimental samples were composed of a composite film of LC and polymer materials sandwiched between glass substrates, as shown in Fig. 1. The small polymer fiber networks, which were formed in the LC layer in the gap between the substrates, were aligned in a specific direction. Anisotropic polymer morphology incorporating surface-molecular alignment can efficiently anchor the LC molecules.
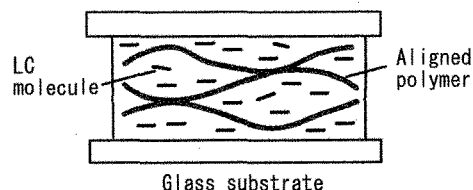

Fig. 1 Schematic diagram of the LC/polymer composite film with molecular alignment.

  The anisotropic polymers [8,9] were obtained by using a photopolymerization-induced phase separation method [10] of aligned mono-functional monomers in an LC/monomer solution film. Namely, a 2- μ m-thick composite film of the LC and the polymer networks was formed from an aligned nematic-phase homogeneous solution of ultraviolet (UV) light-curable liquid crystalline mono-functional acrylate monomer [11] (UCL-001 from Dainippon Ink Chem.) and an LC material (CS-1030 from Chisso). The LC that was used has a thermal phase sequence consisting of crystal phase -

-5°C - chiral smectic C phase - 70°C - smectic A phase - 74°C - nematic phase - 88°C - isotropic phase, and the liquid crystalline monomer shows a nematic to isotropic phase temperature of 46°C. The LC/monomer solution was inserted into the gap between two glass substrates, onto which rubbed polyimide alignment layers (AL-1254 from JSR) were coated in advance. The cell contained 2-μ m-diameter spacer particles to generate the substrate gap, i.e. the thickness of the composite film. The rubbing directions of the two alignment layers were anti-parallel.

Here, the thermal phase sequence of a solution containing 20wt% monomer exhibits a phase transition from the nematic to the isotropic phase at 78°C. When a solution that was heated to 70°C in the nematic phase was irradiated through one side of the substrate with UV light with a center wavelength of 365 nm, the aligned monomer was polymerized. During this process, the monomer molecules almost kept their alignment [4] and were fixed by the formed main chains to become the side chain parts of the formed polymer. As the mono-functional monomers are aligned and fixed as mesogenic cores in parallel to the LC molecules in the nematic phase solution, the main chains must be formed approximately in perpendicular to the side chain direction and the LC alignment direction.

The polymer components then separated from the LC material due to the increase in the degree of polymerization, and the polymer adopted a morphology consisting of aligned fiber networks. Although the detailed fiber formation mechanism has not been clarified until now, we consider that strong thermal movement of the LC molecules in the rubbing direction disturbs the polymer aggregation normal to the rubbing direction, [4] as shown in Fig. 2. This is because the polymer molecular alignment order increases with increasing temperature of the nematic-pahse solution during polymerization.
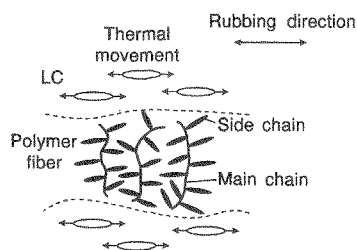

Fig.2 Formation model of the aligned polymer fibers in the LC material.
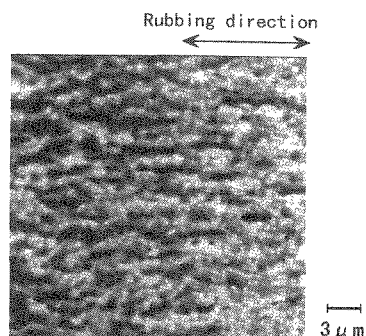

Fig.3 Microscopic photograph of the formed polymer fiber networks.

The polymer fibers obtained from 20wt% concentration monomers were highly oriented parallel to the rubbing direction of the alignment layers coated onto the substrates. A typical polymer morphology that was formed with the phase separation under a UV light intensity of 30 mW/cm^2 is shown in Fig. 3. A bright polymer image containing aligned submicron-diameter fibers can be observed by confocal laser microscopy (VK8510 from Keyence). So far, we have also confirmed the alignment of side chains containing the tolane skeletons by Raman spectral polarization microscopy [5] of polymer fibers. Namely, the polymer fibers have the tolane skeletons in parallel to the fiber direction.

3. PHASE TRANSITION BEHAVIOR
3. 1 Anisotropic polymer system

A composite film formed under a UV light intensity of 1 mW/cm^2 was first heated to the isotropic phase of the LC component in a temperature-controlled bath (WT-STC200 from Toyo) attached to a polarizing microscope (Optiphoto 2-POL from Nikon). Here, the size of the formed polymer fiber was determined in advance to be large with weak UV irradiation during phase separation so that the LC material between the polymer fibers could be observed clearly. Fig. 4 (a) shows the optical anisotropy of the polymer fibers, which was observed using a polarizing microscope with crossed polarizers. The incident polarization direction is oblique from the polymer fiber (i.e. rubbing) direction. Polymers that exhibit birefringence are seen as bright areas, while isotropic-phase LC component is not recognized in the figure. The birefringence of the polymer fibers indicates that the polymer is aligned in parallel to the rubbing direction.

Subsequently, the solution was gradually cooled down in a rate of 0.6 °C/min., as shown in Figs. 4 (b), (c) and (d). The spatial distribution of the isotropic to nematic phase transition of the LC in the composite film was observed using the microscope. The nematic phase areas are seen as bright areas because a nematic phase LC with its director alignment parallel to the polymer fiber direction causes light leakage due to LC birefringence under crossed polarizers. Here, the light-transmission axes of the polarizers were oblique (45°) from the LC alignment. The observed LC birefringence was much larger than those of the polymers. In Fig. 4 (c), the LC areas along the polymer fibers undergo a phase transition. It was found that the phase-transition temperature of the LC material near the polymer fibers is higher than those LC areas remote from the polymers. This experimental result indicates that polymer surfaces with a molecular skeleton of aligned side chains can enhance the alignment order of the LC material that we used.

For this sample, it should also be noted that island-like LC areas remote from the polymer fibers underwent an isotropic to nematic phase transition at high temperatures. This phase transition behavior is caused by the rubbed alignment layers [1] that we used on the substrates. We considered that the highly aligned polymer fibers and the polyimide alignment layers could promote the ordered alignment of the LC in a composite film containing large polymer fibers.

Next we formed a composite film of finer polymer fibers by using intense UV irradiation at 20 mW/cm^2. A similar operation was performed for the heated composite film sample, and the results are shown in Fig. 5. The birefringence of the aggregated fine polymer fibers is confirmed by the bright areas in Fig. 5 (a). When the composite film was cooled, the isotropic-phase areas without phase transition showed as the dark areas in Fig. 5 (c), and these correspond to the poor polymer density areas in Fig. 5 (a). The phase transition temperatures of the regions of LC with poor polymer density are lower than those with polymer fiber aggregation. In the case of fine aligned polymer networks, only the polymer fibers influence the phase transition behavior of the dispersed LC, and the polyimide alignment layers on the substrates do not vary the thermal behavior of the LC. It was found that the thermal LC behavior in LC/polymer composite films is controlled by surface molecular alignment and dispersed polymer morphology. From the experimental results of Figs. 4 and 5, it was confirmed that aligned polymer surfaces promote the LC alignment, as shown in the alignment model of Fig. 6.
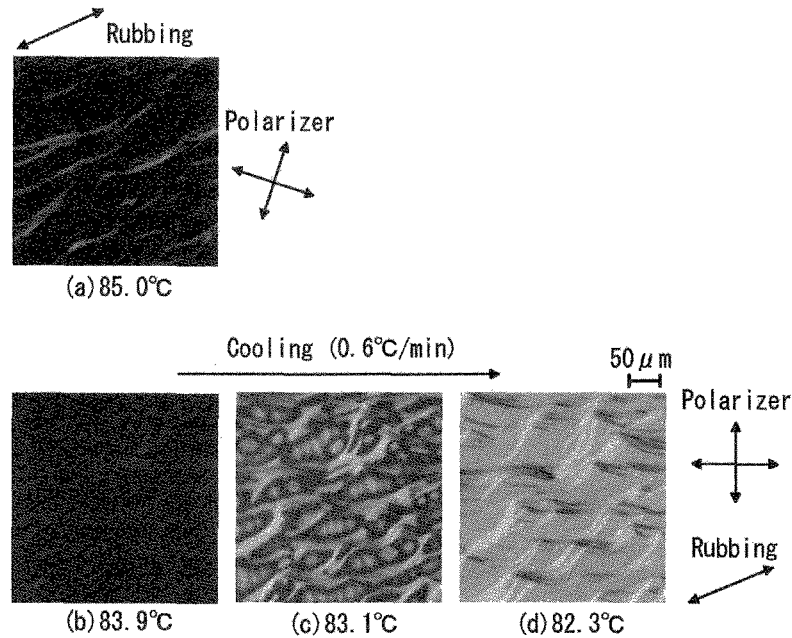

Fig.4 Polarizing microscope images of the composite film of the LC and the large polymer fibers at different temperatures.
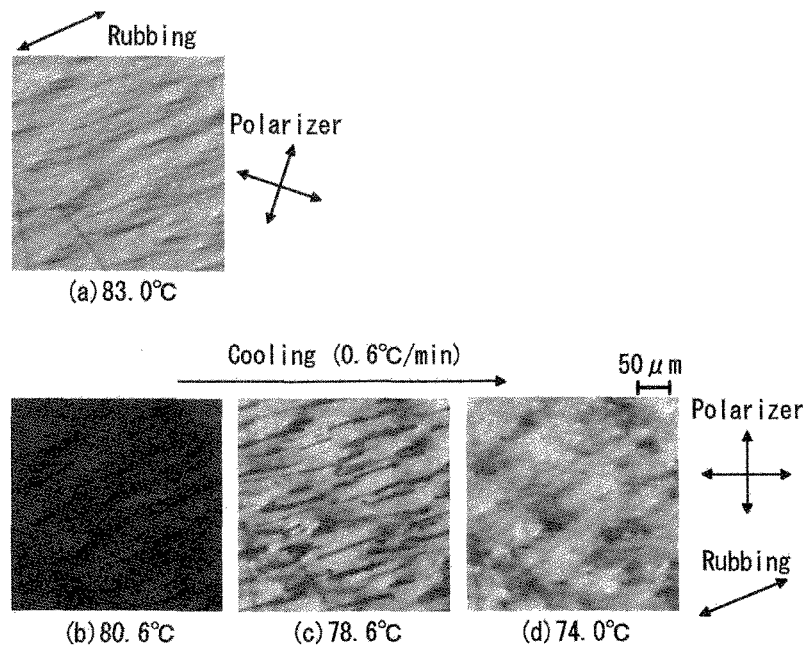

Fig.5 Polarizing microscope images of the composite film of the LC and the fine polymer fibers at different temperatures.

3. 2 Isotropic polymer system

We also fabricated a composite film containing isotropic polymers as a reference sample in order to confirm that aligned polymers promote LC alignment. In this experiment, a polymer-dispersed LC cell with LC microdroplets was prepared using photopolymerization-induced phase separation without any monomer alignment. A cyano-terphenyl nematic LC [12] (BL-008 from Merck) was used as the LC material because its large optical anisotropy makes it easy to recognize the isotropic to nematic phase transition phenomenon in a composite film. The LC has a nematic to isotropic phase transition temperature of 97.8 °C. Polythiol/polyene prepolymer [13] (NOA-65 from Norland Products) containing a benzophenone photo-initiator was utilized as a UV light-curable monomer material. A solution with 50wt% concentration of monomer does not exhibit an LC phase at any temperature.

An isotropic-phase solution was heated to 50°C while sandwiched by glass substrates and UV light was then used to illuminate the solution. The LC component separated from the solution and LC microdroplets formed due to the aggregation of the LC component. The LC droplets were finally stabilized in the solid polymer matrix. [14]

The composite film that was formed was examined using polarizing microscopy based on the method used in Figs. 4 and 5. The experimental results are shown in Fig. 7. When the composite film was cooled, nematic-phase LC areas (seen as bright regions) start to grow from the center of the LC droplets. This result shows that the isotropic polymer walls surrounding the LC droplets reduce the isotropic to nematic phase-transition temperature. This experiment confirmed that isotropic polymer surfaces without molecular alignment disturbed the LC alignment in the thermal phase transition process.
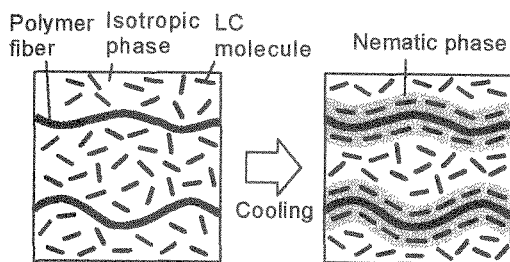
4. CONCLUSIONS

We studied the thermal phase transition behavior of LC material anchored by molecular-aligned polymer fibers that were formed by photopolymerization-induced phase separation with monofunctional monomer alignment. It was confirmed that side-chain-aligned polymer fibers could raise the isotropic to nematic phase transition of the LC material.

It is considered that finer and denser polymer structures, such as nanopolymers that exhibit molecular alignment, are greatly capable of controlling the temperature behavior of LC material. The LC operating temperature range may be enlarged considerably based on this effect.

5. REFERENCES

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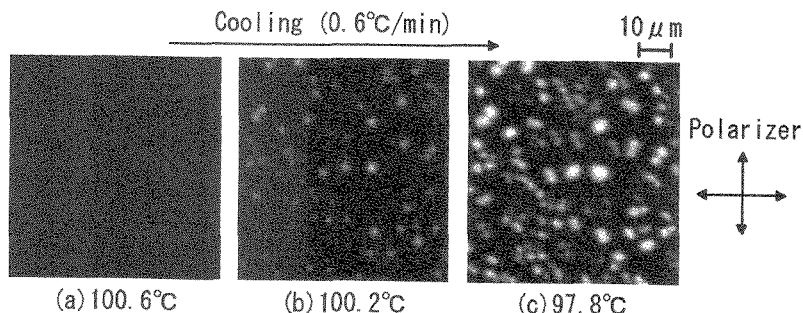Fig.6 LC alignment change model around the aligned polymer fibers.

Fig.7 Polarizing microscope images of the composite film of the LC microdroplets and the isotropic polymer matrix at different temperatures.