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Thermal phase transition behaviour of liquid crystals in submicron pores formed with stretched polymer fibrils

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This paper discusses thermal phase transitions in a nematic liquid crystal material, filling a highly strained porous polyolefin film. Ruptured and aligned polymer fibrils, whose minimum diameter reaches several tens of nm, formed polymer networks in the porous film. From observations of temperature-controlled composite films using a polarizing microscope, it was noted that the isotropic-to-nematic phase transition temperatures of submicron liquid crystal domains, located in or near molecularly aligned streak-like polymer areas, were significantly higher than those located at some distance from these areas. It was assumed that the highly aligned polymer chains in the fine fibrils promote the nematic phase of the liquid crystal. The stretched porous polymer, exhibiting spatial ordering on a submicron scale, is thus suitable for the control of thermal phase transitions in a liquid crystal.

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1. Introduction

Nano- to submicrometer scaled polymer structures are intrinsically capable of changing various properties of organic materials with which they are in intimate contact in a large area, in the case of nano-composite systems. Some organic materials, such as elongated liquid crystal (LC) molecules, comprising a special molecular skeleton containing both rigid and flexible parts, exhibit self-assembly of molecular alignment in a particular temperature range, in spite of their violent thermal molecular movement.

It is interesting to study the interaction between fine polymer structures and LC alignment in a composite system. The alignment of nematic LC directors on polymer surfaces is controlled by molecular interactions between the fixed long polymer chains and the rod-like LC molecules. To orient the LC alignment in an arbitrary direction, the control of alignment direction and ordering parameters of the polymer molecular chains are both important. The spatial distribution of alignments in the polymer surface should also be considered, as the macroscopic LC alignment is determined by the balance of the elastic forces between adjacent small LC domains with disparate alignment directions.

Conventionally, a rubbing process on polymer film surfaces such as polyimide and polyvinylalcohol has been used for LC alignment control in flat panel display applications. In this case, the polymer film is brushed with rayon fibres mounted on a spinning roller, roughly aligning the main or side polymer chains in the microgrooves thus formed [1]. On the other hand, it has been reported that aligned polymer networks [2, 3], which are in advance formed by photopolymerization of monomers in an LC solution, can stabilize surrounding LC alignment. The influence of polymer network surfaces on LC alignment order has also been discussed [4].

We have offered an alternative method of orienting polymer chains using a stretched porous polyolefin polymer having a simple main chain molecular structure, while various isotropic porous films [5, 6] have been examined with a view to filling with LC to control LC molecular alignment. In the submicron-ordered pores of our anisotropic porous film, it is thought that the molecular alignment and morphology of the polymers decide LC alignment [7]. However, the detailed structure of the polymer networks and their influence on LC properties have as yet not been clarified.

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In this paper, we report that the stretched porous polymer is composed of several tens of nm scaled, aligned fibrils and anchoring by the porous polymer modifies the thermal phase transition behavior of submicron nematic LC domains filling the pores.

2. The stretching process

The alignment in the porous polymer films was obtained mechanically by heating. As the polyolefin used (with polyethylene as a major component) has a simple molecular structure of main chains without side chains, it is easily deformed and extended by heating. Initially, an isotropic porous polyolefin film (thickness 15 μm, porosity 45%), of the type utilized as a membrane pore filter, was gradually stretched, keeping its temperature at about 100°C [8]. This is much higher than the glass transition point of the polymer.

As the volume and porosity of the film increase, the polymer main chains become aligned in the direction of stretching, as shown in figure 1. This is because the mechanical force with heating is able to unravel the random coil structure of the main molecular chains with strong thermal movement in the polymer bulk of the film. The extent to which the spatial distribution in molecular alignment will be modified in the film depends on its original inhomogeneous polymer-dispersion structure. For example, small polymer areas which contain no loose parts may first be highly stretched when stretching a porous film.

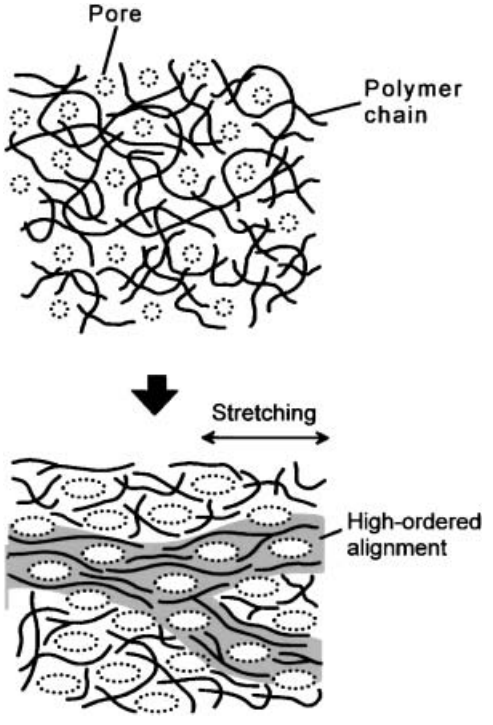
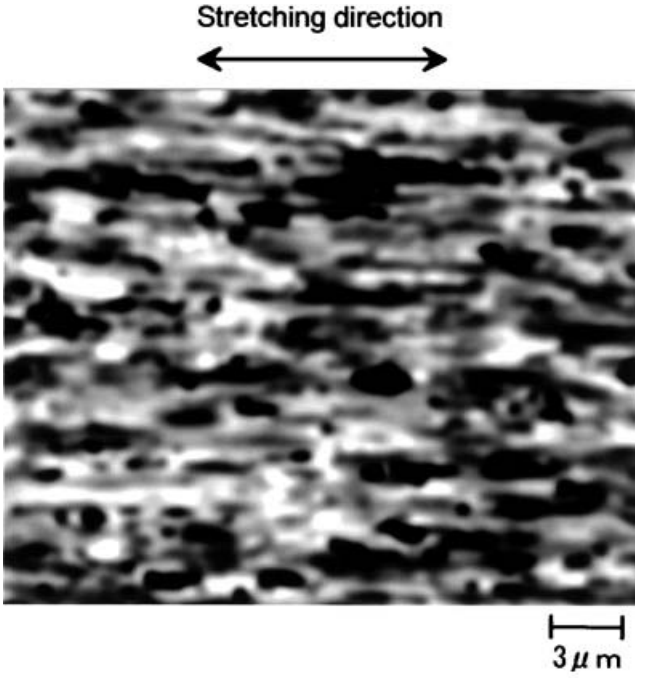


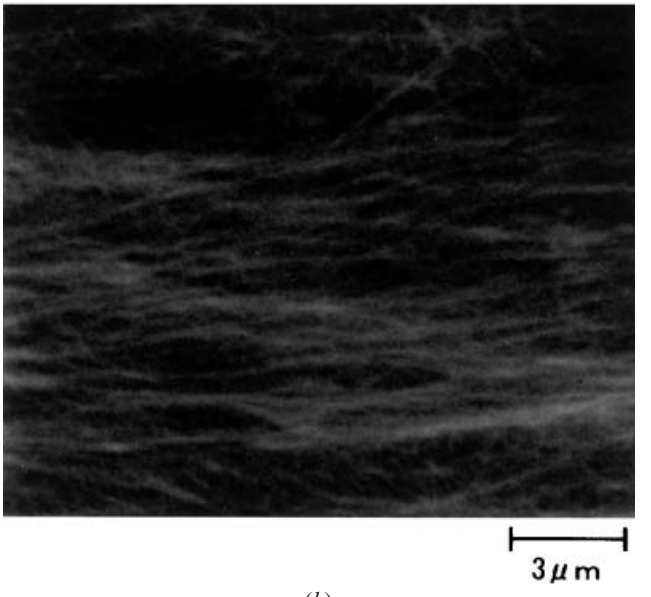
Figure 1. Mechanism of polymer molecular main chain alignment in a stretched porous polymer film.

3. Polymer observation

The globally deformed polymer morphology is shown in figure 2 (*a*). The three-dimensional images of the polymer were observed with a confocal laser



(*a*)



(*b*)

Figure 2. Microscopy photographs of the stretched porous polymer film. Observations using (*a*) a confocal laser microscope, and (*b*) a scanning electron microscope.

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microscope (Keyence VK8510) with large focal depth, where two-dimensional image layers, obtained by optically scanning at the focal point of the laser light illumination, are superimposed for various focal depths. As the extension ratio was increased, the pore shape was extended in the direction of stretching. When the extension ratio had increased to 4.5, the porous film thickness decreased from 15 to 7 μm. The figure shows that the polymer film retained submicron pore networks.

To examine the polymer structure in more detail, the polymer surface structure was observed using an environmental scanning electron microscope (Philips XL-70) to obtain higher resolution. Figure 2 (*b*) shows an experimental result, where the polymer morphology was observed directly on a sample with metal coating. With this type of observation, only the polymer surface can be seen, in contrast to figure 2 (*a*). Fine polymer fibrils, with minimum diameter reaching several tens of nm, can be identified as being highly aligned in the direction of stretching. The fibrils are generated by exfoliating the polymer by a high degree of mechanical stretching.

It has been confirmed that the macroscopic polymer networks seen in figure 2 (*a*) are composed of an aggregation of smaller aligned fibrils. These aligned fine fibrils must influence the behaviour of LC molecules of several nm length.

4. Phase transition

The interaction between the polymer and LC was examined by observing the thermal behaviour of LC filling the porous film. The stretched porous polymer, thickness 10 μm, was filled with a nematic LC mixture (JB-1017 from Chisso). The LC cell, with a gap of 10 μm, was assembled by sandwiching the composite film between transparent electrodes, ITO-coated on glass substrates. Conventional alignment layers, such as rubbed polyimide, were not used in this LC cell.

After heating the assembled cell to 100°C, it was gradually cooled at a rate of $0.6^{\circ}\mathrm{C\,min^{-1}}$ in a temperature-controlled bath, and the LC phase change in the cell was observed using a polarizing microscope with crossed polarizers. Figure 3 shows microscopy photographs of the composite film at different temperatures, where the polarization direction of incident light is at an angle of 45° to the stretched direction of the polymer. At the high temperature shown in figure 3 (*a*), the LC material is in the isotropic phase and not recognizable. The streak-shaped bright areas in the figure are a result of light leakage due to birefringence of the stretched porous polymer material. This leads the polymer chains to align locally parallel to the direction of stretching, and the porous film has its optical axis in the same direction.

In the stretched film, the streak-like elongated polymer areas are particularly stretched due to a local concentration of tensile stress, resulting from the original inhomogeneous pore structure, as shown in the lower frame of figure 1. It should be noted that the streak-like polymer areas with a high order of molecular alignment are ten to a hundred times larger than the fibril and pore size observed in the porous film shown in figure 2. We also confirmed that most polymer regions in stretched systems, except for the streak-like areas, have weak birefringence with low-ordered molecular alignment.

The subsequent cooling process induced an isotropic to nematic phase transition in the LC, with a transition temperature of around 80°C. In the cooler state shown in figure 3 (*b*), the LC material in the pores undergoes the phase transition, observed as bright spots in the figure. This is because the nematic phase LC material, with its director alignment parallel to the stretching

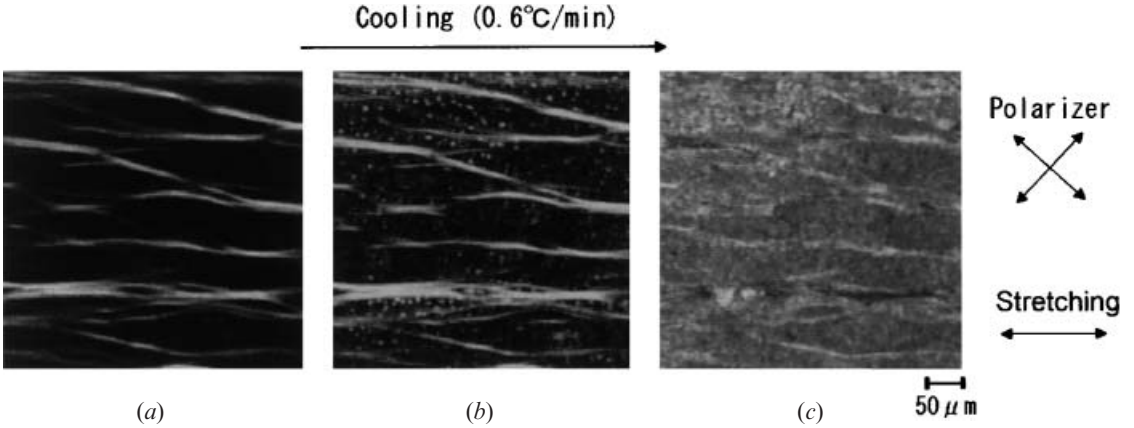

Figure 3. Polarizing microscopy photographs of the LC/polymer composite film controlled at various temperatures: (*a*) 80.7°C, (*b*) 80.1°C, (*c*) 77.0°C.

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direction, causes light leakage due to birefringence under the crossed polarizers. In the figure, many small LC domains, confined close to the polymer pore surface, see figure 2 (*a*), individually undergo the phase transition, but their transition temperatures are higher in or near the streaked polymer areas than in those domains remote from these areas.

We consider that the fine fibril surfaces of the highly aligned polymer chains in the streak-like polymer areas promote the order parameter and the nematic phase in the LC material. Finally, the cell was further cooled and all isotropic LC domains in the pores then returned to the nematic phase, figure 3 (*c*).

Such local LC thermal behaviour observed in the stretched porous film has an analogy to a wetting phase transition in alignment [9], as confirmed with a rubbed alignment layer. On the other hand, it has been theoretically indicated that anisotropic polymer networks heighten the order parameter of surrounding LC [4]. A wetting phase transition phenomenon has also been recognized in molecular-aligned polymer networks obtained from the photopolymerization-induced phase separation of an anisotropic LC/monomer solution [10, 11]. When using a stretched porous polymer, the LC phase transition temperature in the polymer structures can be known precisely. This is because no LC impurity (remaining monomer and photoinitiator) or no LC composition change during the phase separation process are induced.

Utilizing such LC alignment effects in porous polymers, we can create electro-optic devices such as planar alignment [7] and twisted alignment [12] LC cells. For example, rotation in the polarization of the incident light has already been achieved using a twisted alignment cell, in which two porous films are laminated, having orthogonal directions of stretching. The cell does not use the conventional polyimide alignment layers that require the rubbing process (generating microdust and electricity) and which also need high temperature baking, unsuitable for light-weight and anti-shock plastic substrates.

5. Conclusions

In conclusion, we have studied the stretched porous polymer morphology and thermal LC phase transition behaviour in a porous polymer film. The polymer structure, incorporating the molecularly aligned surfaces, selectively raised the isotropic to nematic phase transition temperature of the LC material.

The fine fibrils in the stretched porous polymer facilitate the creation of submicron LC domains where thermal phase transitions are spatially controlled. This LC alignment control method based on porous polymer films will also generate functional electro-optic devices.

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