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Liquid Crystals

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Polymer networks formed in liquid crystals

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Monomers with reactive double bonds were mixed with liquid crystals and polymerized under UV irradiation. The polymer networks formed are anisotropic and consist of fibrils. The orientation of the polymer networks depend on the orientation of the liquid crystals during polymerization. Optical and scanning electron microscopy (SEM) were used to study the polymer networks.

1. Introduction

In liquid crystal displays the liquid crystals are usually sandwiched between two parallel glass plates. At zero field, the orientation of the liquid crystals is controlled by alignment layers in the inner surface of the plates; however, sometimes the surface effect is not strong enough for the display to operate properly. Recently it has been demonstrated that polymer networks could be used to stabilize certain liquid crystal states and modify the properties of liquid crystals [1-4]. When a monomer is polymerized in a liquid crystalline environment, the polymer network formed is fibre-like and anisotropic because of the aligning effect and the anisotropic diffusion properties of the liquid crystal. The orientational order and the direction of the polymer network depend on the order and direction of the liquid crystal. During polymerization the configuration of the liquid crystal can be controlled by the surface alignment layer, external electric field and/or temperature. Consequently the configuration of the polymer network can be controlled by those parameters [5]. After polymerization, the polymer network in turn affects the orientation of the liquid crystal [3, 4, 6].

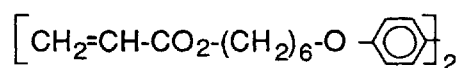
In this paper we report a study of polymer networks formed in different liquid crystal environments. Monomers were photopolymerized in nematic and cholesteric liquid crystal phases. After polymerization the sample cells were immersed in an organic solvent. The liquid crystal dissolved in the solvent while the polymer network was left on the substrates. Then the polymer network was studied by scanning electron microscopy (SEM), which showed clearly that the polymer networks were oriented along the same direction as the liquid crystal during the polymerization.

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2. Sample preparation

In our experiments the monomers used were laboratory synthesized bifunctional monomers whose structures are shown in figure 1. The monomers have a rigid core and two flexible hydrocarbon tails. At each end of the hydrocarbon tail there is a reactive double bond which could be polymerized under UV irradiation. The nematic liquid crystal used was either ZLI4389 or E48 and the chiral dopant used to make cholesterics was R1011 (all from E. Merck). The photo-initiator was benzoin-methylether (BME from Polyscience). The liquid crystal, monomer and photo-initiator were mixed and filled into sample cells by capillary action in a vacuum chamber. The cells were then irradiated by UV light from a mercury lamp. The irradiation time was usually from half to a few hours because of the low concentration of the monomer. The polymerization took place at room temperature except when otherwise specified. In some cases an external

Monomer 1



Monomer 2

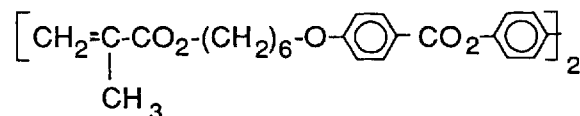


Figure 1. Chemical structure of monomers.

electric field was applied during the polymerization. The frequency of the field was 500 Hz.

The cells were immersed in hexane to remove the liquid crystal. After the liquid crystal was dissolved in the solvent, we split the cells with great care in order not to disrupt the structure of the polymer network. Although the removal of the liquid crystal was slow and took a few days, hexane was effective in removing the liquid crystal without deforming the polymer network. The solvent with dissolved liquid crystal was allowed to evaporate in a vacuum chamber. The networks were coated with palladium and investigated by SEM.

3. Results and discussion

3.1. Nematics/monomer

We began the studies by investigating the alignment effect on the polymer network formed in a nematic phase. The cell glass plates were coated with polyimide and buffed for homogeneous alignment of the liquid crystal. The buffing directions of the top and bottom plates were anti-parallel. The cell gap was controlled by 15 μm glass fibre. The mixture was 97.0 per cent of ZLI4389, 2.7 per cent of the monomer **1** and 0.3 per cent of BME. Before polymerization the cell was examined under an optical microscope with crossed polarizers, and it was observed that the liquid crystal was aligned very well along the buffing direction. When the rubbing direction was parallel or perpendicular to the polarizer, the cell had a uniformly black texture. When the rubbing direction made a 45° angle with the polarizer, the cell had a uniformly bright texture. The cell was then irradiated with UV light to polymerize the monomer.

After polymerization the cell was again examined by optical microscopy and its optical properties remained the same. The cell was immersed in hexane. After the liquid crystal was removed, we took the top and bottom glass plates apart. The SEM picture in figure 2 shows that the polymer network consists of fibrils and is anisotropic. The fibrils of the polymer network are parallel to the rubbing direction. The polymer network appears much more dense than 2.7 per cent (the concentration of the monomer). The discrepancy is due to the fact that the polymer network collapsed in the direction perpendicular to the surface of the substrate. The retraction in the direction parallel to the surface but perpendicular to the fibrils was observed and may play an important role. The retraction along the fibrils is comparatively much smaller. It should be emphasized that the actual size of the fibrils may be smaller than that shown in the picture because of residual liquid crystal around the polymer network and the metal coating in the SEM study. This anisotropic structure of the liquid crystal-free polymer network also can be observed by optical microscopy. An optical microscope picture is

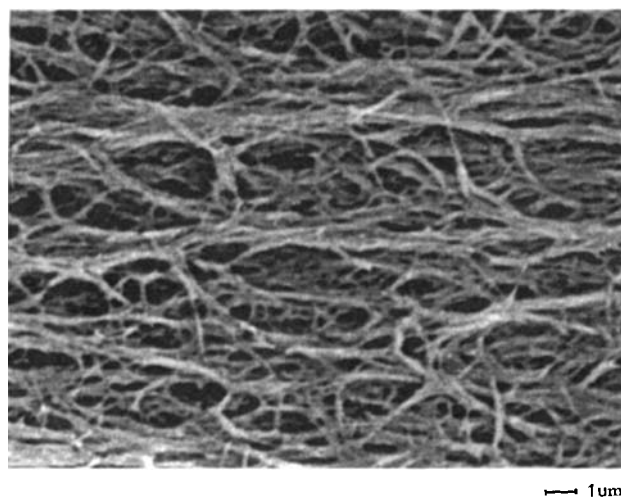


Figure 2. Top view SEM picture of the polymer network formed in the nematic liquid crystal in the homogeneous state.

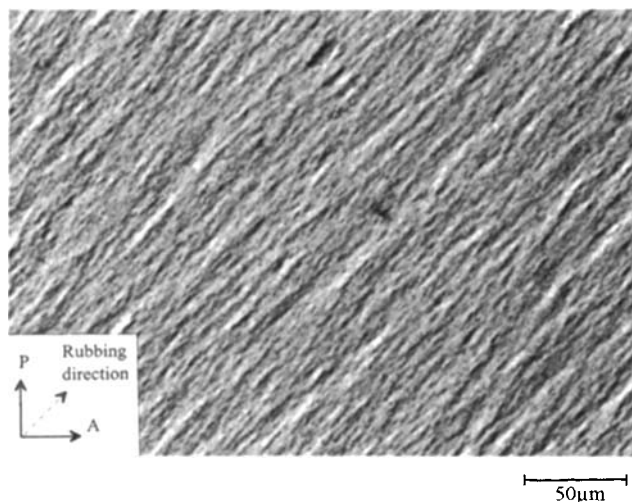
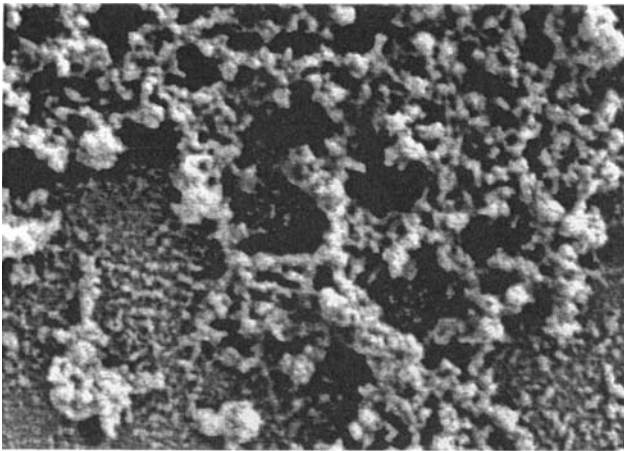


Figure 3. Optical microscope picture of the polymer network formed in the nematic liquid crystal in the homogeneous state. The averaged direction of the network makes a 45° angle with crossed polarizer and analyser.

shown in figure 3 where the polymer network makes a 45° angle with the crossed polarizers.

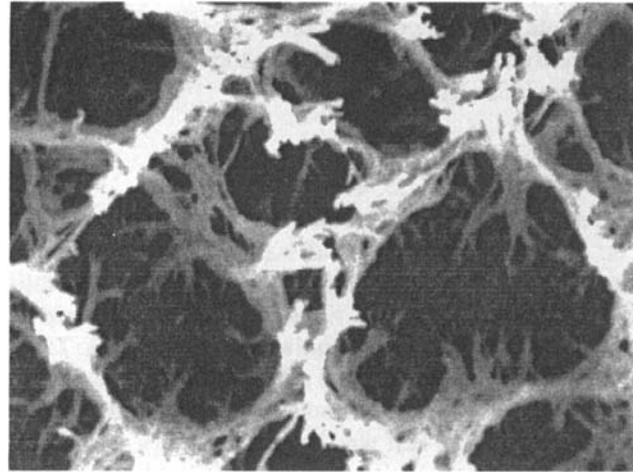
We also had a nematic/monomer cell irradiated by UV light in the isotropic phase of the liquid crystal. Now the environment of the polymerization is isotropic; therefore the polymer formed does not show any anisotropic properties. The SEM picture in figure 4 shows that the polymer looks more or less like globules.

The homeotropic state of a nematic liquid crystal can be achieved either by use of a surface alignment layer or by applying an external electric field. We made a 15 μm thick cell without any special surface treatment for alignment



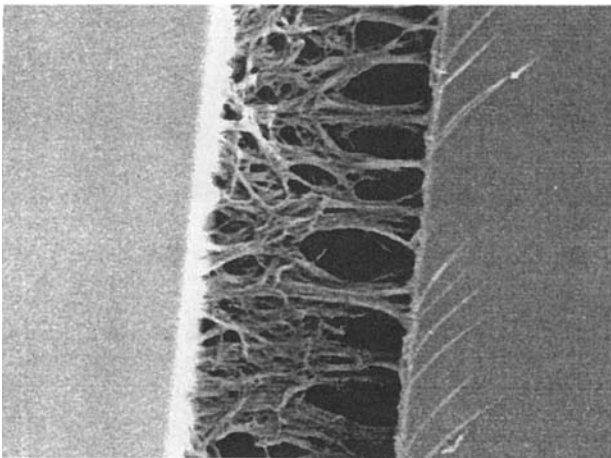
→ 1µm

Figure 4. SEM picture of the polymer network formed in the nematic liquid crystal in the isotropic phase.



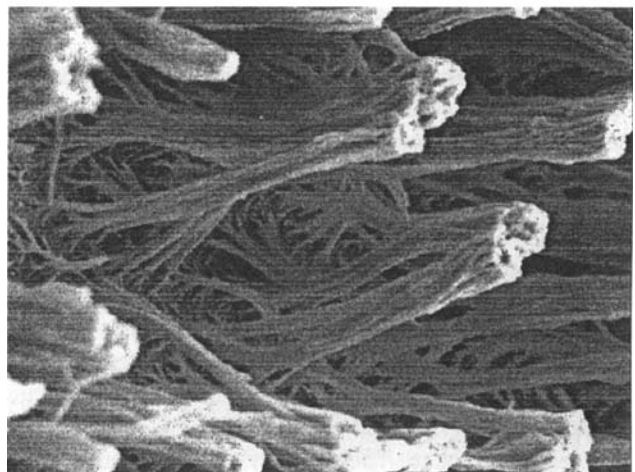
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Figure 6. Top view SEM picture of the polymer network formed in the nematic liquid crystal in the homeotropic state with the homeotropic alignment layer.



→ 10µm

Figure 5. Edge-on view SEM picture of the polymer network formed in the nematic liquid crystal in the homeotropic state with the homeotropic alignment layer.



→ 1µm

Figure 7. SEM picture of the polymer network formed in the nematic liquid crystal in the homeotropic state under an applied electric field. The normal of the substrate was tilted a few degrees away from the incident electron beam.

except cleaning. The cell was irradiated by UV light with the material in the homeotropic state in the presence of an a.c. voltage of 20 V. The polymer network formed was perpendicular to the cell surfaces. The SEM picture shown in figure 5 is an edge-on view with the polymer network attached to both glass substrates. This picture shows clearly that the polymer network is fibre-like and perpendicular to the substrates. The SEM picture shown in figure 6 is a top view. The polymer network looks like a honeycomb. As we mentioned, the polymer network is fibre-like. The honeycomb was formed by the retraction of the fibrils in the direction parallel to the substrate during solvent evaporation. We studied the effect of the applied

field in the polymerization. We made a second cell with an a.c. voltage of 100 V during the polymerization. The SEM picture of the polymer network shown in figure 7 was taken with the sample tilted such that the incident electron beam made an angle of 45° with the normal of the substrate. One end of the polymer network is attached to the substrate like tree roots while the other end is a sharp fracture formed when the cell was split. The orientational order of the network looks higher than that formed in lower electric field. We also made a cell with an homeotropic

alignment layer of octadecyltrichlorosilane. SEM showed that the polymer network formed in this cell is quite similar to the polymer network formed in the homeotropic state in the presence of an electric field.

3.2. Cholesteric/monomer

We made a cholesteric liquid crystal/monomer sample. The cholesteric liquid crystal was a mixture of nematic liquid crystal E48 and chiral agent R1011 in the ratio 99.5:0.5. The cholesteric liquid crystal then was mixed with monomer **2** and photoinitiator in the ratio 93:7:0.7. The cell gap was 15 μm . The substrates were coated with polyimide and rubbed for homogeneous alignment of the liquid crystal. The cell was irradiated by UV light in the planar state where the material had a helical structure with the helical axis perpendicular to the substrate. During the polymerization the liquid crystal director was parallel to the substrate and therefore the polymer network formed was also parallel to the substrate. The top view SEM picture is shown in figure 8. Because of the helical structure, the fibrils are twisted in contrast to that in figure 2 where the fibrils are unidirectionally aligned.

We made another sample with cholesteric liquid crystal where the concentration of the chiral agent R1011 was 2.2 per cent, the monomer concentration 4.5 per cent and the photo-initiator concentration 0.5 per cent. In the polymerization process an a.c. electric field was applied such that the liquid crystal was in the homeotropic state. The polymer network formed was perpendicular to the substrates. The SEM picture shown in figure 9 was obtained with the normal of the substrate tilted 45° away from the incident direction of the electron beam. The picture shows that the polymer network is perpendicular to the substrate. The large void in the middle was formed when we took the two glass plates apart. The polymer in that region stuck on the other glass plate.

The lateral size and density of the fibrils of the polymer network are sensitive to the UV intensity during the polymerization. We made a mixture with the following components: 91.8 per cent of E48, 0.5 per cent of R1001, 7 per cent of monomer **2** and 0.7 per cent of BME. We filled the mixture into three 15 μm cells with buffed polyimide as the homogeneous alignment layer. The cells were irradiated with three different UV intensities: 0.04, 0.4 and 4 mW cm^{-2} . The SEM pictures of the polymer networks formed under the different UV intensities are shown in figure 10 (a), (b) and (c), respectively. When the UV intensity was low, there were fewer free radicals produced from the decomposition of the photoinitiator during polymerization. The free radicals did not only initiate the chain reaction but also terminated the chain reaction. With fewer free radicals, the polymer chain can

grow longer and larger. The polymer networks formed by the biacrylate have very high molecular weights. The fibrils were very long (a few microns) and the effect of UV intensity on the longitudinal size of the fibrils is not easily observed. The lateral size (submicrons) of the fibrils is, however, affected significantly by the UV intensity. Under lower UV intensity, laterally larger fibrils are formed and the distance between neighbouring fibrils was larger.

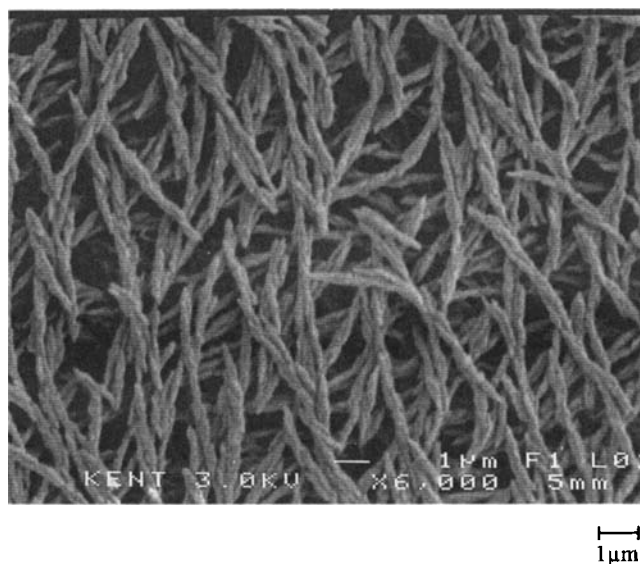


Figure 8. Top view SEM picture of the polymer network formed in the cholesteric liquid crystal in the planar state.

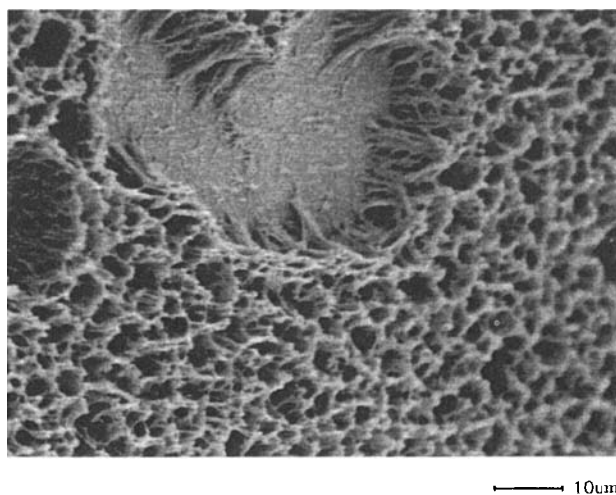
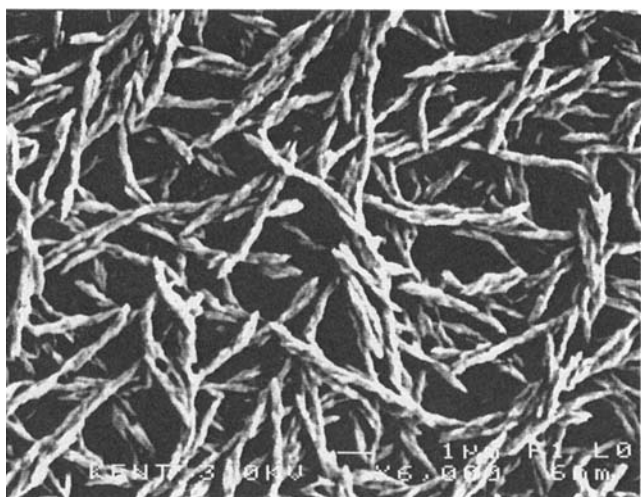
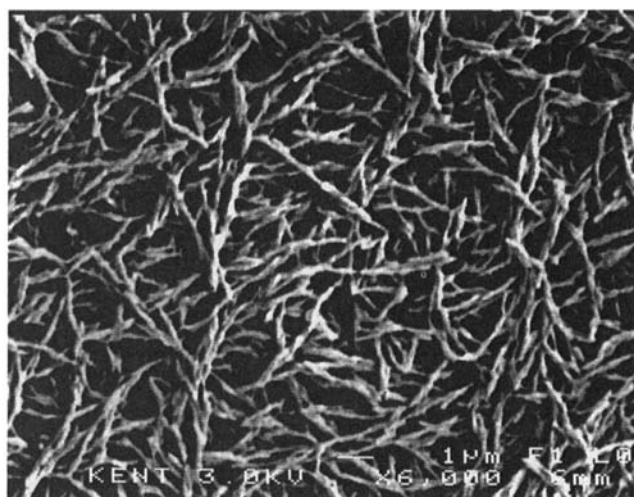


Figure 9. SEM picture of the polymer network formed in the cholesteric liquid crystal in the homeotropic state under an applied electric field. The normal of the substrate was tilted a few degrees away from the incident electron beam.



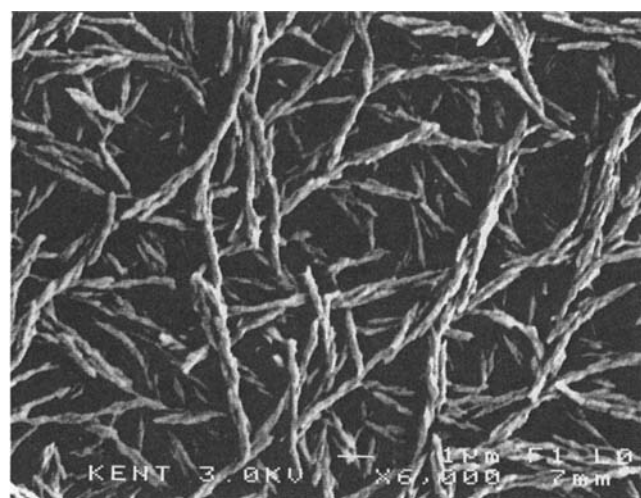
1µm

(a)



1µm

(c)



1µm

(b)

Figure 10. Top view SEM pictures of the polymer networks formed in the cholesteric liquid crystal in the planar state. The UV intensities used for the polymerization were (a) 0.04 mW cm^{-2} , (b) 0.4 mW cm^{-2} and (c) 4.0 mW cm^{-2} , respectively.

When the polymer network is used to align bulk liquid crystal, it is more effective than a surface alignment layer. We have used the network to stabilize cholesteric textures and made haze-free light valves [3]. We have also used the polymer network to control the hysteresis in the cholesteric–nematic transition [6]. Our study is preliminary in the area of polymer modified and stabilized liquid crystals. Further study is under way to have a better understanding of the interaction between liquid crystal and polymer networks.

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4. Conclusions

It has been demonstrated that the structure of polymer networks formed in a liquid crystal environment can be controlled by the configuration of the liquid crystal. UV intensity for polymerization has a profound effect on the structure of the polymer network. Polymer networks with laterally larger and stronger fibrils are formed at low UV intensity. After polymerization the polymer network, in turn, strongly affects the properties of the liquid crystal.

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