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Liquid crystalline textures and polymer morphologies resulting from electropolymerisation in liquid crystal phases.

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A small fraction of an acrylate liquid crystalline monomer ( $\leq$ 5%) is mixed into nematic and smectic liquid crystalline phases, and polymerised through the application of a voltage (electropolymerisation). Polarising optical microscopy reveals that the textures during polymerisation are templated through stabilisation via the forming polymer. During polymerisation in the nematic phase, the director can be observed to gradually reorient into the field-on state. Scanning electron microscopy reveals rope-like and corrugated structures of a distinctive periodicity (500-750nm). Quite different polymer structures are formed by electropolymerisation in the smectic phase, such as micron-scale worm-like objects that agglomerate reversibly as the temperature changes

### 1. Introduction

A variety of polymer-liquid crystal composite systems have been created by effecting the polymerisation of a monomer component mixed into a liquid crystalline phase. In a polymer dispersed liquid crystal, this results in drops of liquid crystal encased in a polymer matrix.<sup>1</sup> A polymer stabilised liquid crystal uses a much lower fraction of monomer, which forms a polymer network, templating the liquid crystal director field in which it was formed. This can be imaged by electron microscopy of the polymer,<sup>2, 3</sup> and a resultant memory of the director structure during polymerisation is evident in the system's electro-optic properties.<sup>4-7</sup> A variety of polymer morphologies result from a competition between kinetics and thermodynamics: as the polymer molecules grow they tend to phase separate from the liquid crystal, but before the polymer can aggregate it is trapped in place by cross-linking.8

Polymerisation inside a liquid crystal can proceed by the same wide range of mechanisms as any other polymerisation. However, the most commonly used is free-radical polymerisation of acrylates initiated by UV light illumination<sup>2</sup>, <sup>6, 7, 9</sup> or via a thermally active initiator.<sup>10</sup> One possibility that has been much less extensively investigated is electrochemically initiated polymerisation. Acrylate monomers in solution generally undergo polymerisation at the cathode, producing a film of polymer grafted to the electrode. An ionic compound, such as a salt or acid, increases the conductivity of the solution, and the initiating free radical is produced by reduction at the cathode from either the monomer itself or one of the other species present.<sup>11-14</sup> Electrochemical polymerisation therefore differs from other methods in that it occurs at the electrode surfaces rather than throughout the bulk. Electrochemical polymerisations have been performed in liquid crystals before in order to produce conducting polymer films with a controlled morphology. For instance, such films have been formed in a smectic phase so that the alignment of the polymer chains can be controlled by a magnetic field during the reaction.<sup>15</sup> Here, the Smectic A LC medium was prepared from smectogenic mixtures 4-cyano-4'-n-hexylbiphenyl (6CB) and 4-cyano-4'-nof octyloxybiphenyl (8OCB) and a series of thiophene monomers were added to allow the electrochemical process. The mechanism has also been used for a chiral nematic liquid crystal, so that a

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polymer film is formed that exhibits chiral properties.<sup>16, 17</sup> The LC medium was prepared from nematic liquid crystals (6CB) by addition of a chiral compound, cholesteryl oleyl carbonate. To allow the electrochemical process tetrabutyl-ammonium perchlorate (TBAP) and mostly thiophene like monomers were added to afford the electrolyte solutions.<sup>16</sup> In the other approach, the electrochemical polymerisations in asymmetric reaction fields were performed using the N\*-LCs for the production of helical poly(3,4-ethylenedioxythiophene) films. The N\*-LC solutions were prepared by adding chiral dopant, bis-EDOT (2,2',3,3'tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxine), and TBAP into 4cyano-4'-n-pentylbiphenyl (5CB). The films were synthesized in the N\*-LC solutions. The dedoping process was performed by applying 4V to the H-PEDOT films in an acetonitrile (MeCN) solution of TBAP for five minutes at room temperature.<sup>17</sup> Then, in these reports, the films were obtained by the removal of the liquid crystal component after polymerisation, while the behaviour of the composite mixture was not investigated. Electrochemically polymerised composites with liquid crystals could therefore display different structures and properties to those previously reported. In this work, we will apply a new technology based on liquid crystals, which considers the use of electric field to promote in situ polymerisation and thus getting highly ordered systems where guest molecules can introduce new properties into the matrix which is formed.<sup>18</sup> Then, the polymer is produced without the use of polymerisation initiators as photo - or radical initiators and without the use of solvents.

#### 2 Experimental

#### 2.1 Materials

Three commercially produced liquid crystalline mixtures were used in this work. (i) ZLI1132 (Merck) has a positive dielectric anisotropy and is nematic at room temperature, having a clearing point of 69°C. (ii) ZLI2806 (Merck) has a negative dielectric anisotropy and is also nematic at room temperature with a clearing point at 75°C. (iii) FELIX M4581-050 (Clariant) is a ferroelectric liquid crystal (SmC\*) at room temperature and has a phase sequence on cooling of iso 76°C N\* 72°C SmA\* 66°C SmC\* < -20°C cryst.

The liquid crystalline monomer used in the present investigations is depicted in Figure 1, and is abbreviated as A6OA12. It is one of a family of compounds which has also been investigated for their ability to form light-sensitive liquid crystalline polymers,<sup>19</sup>. At room temperature A6OA12 is a yellow crystalline powder and has a phase sequence on cooling of iso 94.6°C N 94.4°C SmA 87.0°C SmC 61.9°C cryst.

#### 2.2 Experimental procedures

The monomer A6OA12 was added to the liquid crystal and both were dissolved in a small amount ( $\sim 0.1$ ml) of toluene. The mixtures involving the ZLI materials were placed in a vacuum chamber, where they were left for 20 minutes in order to remove the toluene and expel dissolved gas, especially oxygen,



which could interfere with the polymerisation. The mixture was then transferred into a cell, filled by capillary action, at 80°C. No indication of thermal polymerization was observed. Once filled, the cell was cooled or heated slowly at 1K/min to the relevant temperature under investigation. Alternatively, some samples involving ZLI1132 were filled at 80°C in a glove box flushed with argon, also after being left in a vacuum for 20 minutes. Whilst in the glove box, the edges of the cells were sealed with Norland Optical Adhesive 61, a UV curable glue. The glue was then cured outside the glove box by exposing it to low-intensity near-UV light for 1 hour. This procedure had no influence on the liquid crystal - monomer mixture which was explicitly checked by subjecting mixtures to UV light and observation with a Leica DMPL polarizing microscope. Mixtures made with the ZLI materials were polymerised at 60°C in the nematic phase, or at 85°C, in the isotropic phase, while mixtures with FELIX M4581-050 were polymerised at 68°C in the smectic-A\* phase or at 45°C in the smectic-C\* phase.

The cells used were mainly commercially available (AWAT, Poland) with planar and homeotropic alignment and thickness 5µm. A homemade thicker cell with planar alignment was also employed. For the latter the alignment layers were applied to indium-tin-oxide (ITO) coated glass of roughly 1cm<sup>2</sup> by spin coating four drops of a solution of 1% polyvinyl acetate in water for one minute at 3000 rpm. The glass was then baked at 100°C for 20 minutes and firmly drawn across a velvet cloth to provide the alignment in the desired direction. Two strips of 23µm thick polystyrene film were placed on either side of one substrate, and another was then held on top of this with a bulldog clip. The edges of the glass next to the strips of film were coated with Norland Optical Adhesive 61 and the cell was glued together by exposing it to low-intensity near-UV light for 1 hour. Samples were observed using polarising optical microscopy in transmission with a Leica DMLP microscope using x10 and x20 objective lenses. The morphology of the polymer network was investigated using an FEI Sirion scanning electron microscope (SEM) operated at 20kV. The liquid crystal cell was prepared for imaging using similar methods to previous work.<sup>3, 8</sup> Firstly, it was left in about 20ml of hexane for at least 36 hours to dissolve the liquid crystal, leaving only the polymer network. The cell was then split open and both substrates were sputtered with a thin layer of gold a few nanometres thick.

Electrical measurements on the ferroelectric phase used a TTI TG1010 signal generator and a Tektronix 3014B oscilloscope. The ferroelectric polarisation of the SmC\* phase was measured by using the well-established triangular wave method, first employed by Miyasato et al,<sup>20</sup> using an input triangular wave

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signal of amplitude of 10V and a frequency chosen to maximise the output while not saturating the current amplifier at 5V. The response times for ferroelectric switching were measured by applying a square wave of amplitude 10V and frequency 67Hz to the cell and recording the signal from a photodiode attached to the microscope. The smectic tilt angle was measured by rotating the cell to the position giving the lowest photodiode signal while it was under a DC voltage of +10V and then -10V; the tilt angle was half the angle between these positions.

### **3** Results and discussion

# 3.1 Nematic and isotropic phase polymerisations in mixtures of the ZLI materials

ZLI1132 suffered dielectric breakdown at a variable electric field of 7-10MVm<sup>-1</sup> at 60°C, corresponding to 35-50V on a  $5\mu$ m cell. The polymerisation was therefore stimulated with a DC voltage of 30V, i.e. an electric field of 6MVm<sup>-1</sup>. The application of an AC voltage had little effect on the sample, even when the frequency was as low as 0.01Hz.

For ZLI1132, the most noticeable effect of applying a DC electric field was that the alignment of the liquid crystal, when the field was removed gradually, converged towards the fieldon, homeotropic state. This process could be seen by periodically removing the voltage during polymerisation and observing the state that the nematic relaxed into over a few minutes. Figure 2 shows a series of photographs taken by polarising optical microscopy (POM) at half-hour intervals of voltage exposure. The red and yellow colours seen after 30-120min of exposure, though not the grey and streaky texture seen close to the end of the process, could also be observed by exposing the cell to low voltages before the polymerisation. This indicates that the zero-field equilibrium director was gradually tilting from the planar to the homeotropic state during the polymerisation process. The actual time required for this process was found to be dependent mainly on monomer concentration. For a mixture with 5% by weight monomer, the reorientation took 3-6 hours. For a mixture of 2.5% by weight monomer the final structure was the same as for larger monomer concentrations, but took up to 12 hours to be

achieved. It was found that the process is dependent on the monomer concentration, thus the concentration of the monomer at the surface of the electrode. A denser polymer which implies a faster reorientation from planar to homeotropic is expected to be observed for higher monomer concentrations. Thus, decreasing the monomer concentration increases the reorientation time, which is in accordance with polymers formed by other polymerization processes.

It was expected that the samples filled in a glove box would polymerise faster, as oxygen tends to suppress radical polymerisations, but no significant difference could be detected. Applying 30V across a 5 $\mu$ m cell of neat ZLI1132 for several hours did not affect the alignment. In the 23 $\mu$ m cell, the director realignment occurred much faster, in about 40 minutes, which is attributed to weaker planar anchoring conditions. After 20 min, it was also observed that the image appeared the same as the microscope was focussed at different locations through the thickness of the cell, indicating that the director structure did not change across the thickness.

For a positive dielectric material one would expect the capacitance of the cell to increase as the director tilts toward the homeotropic orientation. Measurements of the capacitive relative permittivity (i.e. the permittivity implied by the formula for a standard parallel plate capacitor of a homogeneous material), made by comparing the capacitance of the empty cell to that of the filled cell, are shown in Figure 3. These were consistent with the capacitive permittivity perpendicular to the director and changing toward the larger parallel permittivity as measured in a homeotropic cell.

The effect of polymerisation in the isotropic phase on the liquid crystal alignment was additionally tested. In this case the polymerisation was carried out at  $85^{\circ}$ C. The texture under polarising microscopy was then observed after cooling at 1K/min to 60°C. It appeared that the final texture (after 8 hours) was neither fully planar nor homeotropic, but of a white or light grey colour similar to that shortly before 150 min of voltage exposure in the sample shown in Figure 2. This is consistent with the interpretation that the homeotropic state generated after polymerisation in the nematic phase is due to the influence of the nematic director during polymerisation.



Figure 2. Polarising optical microscopy photographs of a 5% by weight mixture of A6OA12 in a 5 $\mu$ m AWAT cell with planar alignment, with no applied voltage as the picture was taken but after the cell had been exposed to a DC voltage of 30V for a time given by the label in the corner of the photos. The alignment direction is 45° to the polarisers and the horizontal.



Figure 3. The capacitive relative permittivity of the cell as a function of time exposed to voltage. The three series show three different cells, all filled in air with a mixture of 5% by weight A6OA12 in ZLI1132 and all exposed to 30V in 5µm cells. The texture appeared dark under polarising optical microscopy at the end of the experiment in all three cases over most of the electrode, though not necessarily at the edges. The dotted line shows the permittivity parallel to the director as measured at 60°C for the same mixture in a cell with homeotropic alignment.



Further, a mixture of 5% by weight monomer with the negative dielectric ZLI2806 was filled into a  $5\mu$ m AWAT cell with homeotropic alignment. In this case the applied voltage forced a degenerate planar alignment. For this system, however, no

noticeable effect was observed on the field-off state for any voltage below the breakdown voltage over several hours. Five samples, polymerised in the nematic phase, were prepared for imaging by scanning electron microscopy:

1. from a mixture of 5% by weight monomer in ZLI1132, which was polymerised for six hours at 60°C so that it was aligned homeotropically,

2. from a mixture of 5% by weight monomer in ZLI1132 polymerised at 60°C for two and a half hours so that it was not completely homeotropic,

3. from a mixture of 2.5% by weight monomer in ZLI1132 left for 12 hours until the director was oriented homeotropically,

4. a 5% by weight monomer sample polymerised in the isotropic phase of ZLI1132 at  $85^{\circ}$ C for eight hours, and finally

5. a sample from the 5% by weight mixture of monomer in ZLI2806, left at 30V in a 5 $\mu$ m planar cell for six hours.

In addition, a control sample was imaged from a cell which had been held at 30V for 12 hours at 60°C while it contained the neat ZLI1132 liquid crystal only. No structures could be imaged for the latter control sample, indicating a smooth substrate, while all the imaged structures of other cells must be due to a polymer formed under the above outlined conditions. It should be noted that for the process of electropolymerization a current is required. This was indeed measured, albeit low, in the order of microamperes and smaller, and respective investigations will be published elsewhere. Also, no structures were obtained from the samples which used the negative dielectric ZLI2806 mixture, corroborating the previous results when using a cell with homeotropic alignment, indicating that little polymerisation occurred.

For the samples polymerised in the nematic phase, one could observe a corrugated or rope-like structure, as shown in Figure 4. The exact appearance of these varied across the sample, but no systematic differences between the three samples polymerised in the nematic phase of ZLI1132 could be determined. The polymer structures were found on both the anode and the cathode, and there were no obvious systematic differences between these either. The periodicity of the structures was consistent, between 500-750nm. Because the length scale (width of the strands) is of the same magnitude as those structures observed via other polymerisation mechanisms in liquid crystals<sup>9</sup>, it is anticipated that it originates from the polymer growth kinetics.

All cells employed in this investigation contained spacers, which were  $5\mu$ m wide polystyrene rods used to keep the two



Figure 6. Polarising optical microscopy photographs of the texture of the 5% mixture of A6OA12 monomer in FELIX M4581-050 after polymerisation at 100V at 45°C. At the top of the pictures is the area between the ITO electrodes, and at the bottom is the unpolymerised area outside the electrodes. Pictures were

taken at (a) 45°C in the smectic-C\* phase, (b) at 71°C in the chiral nematic phase and (c) at 80°C in the isotropic phase.





Figure 7. Electro-optic measurements of ferroelectric samples. The reduced temperature is with respect to the SmA\*-SmC\* transition temperature. (a) Polarisation measurements. (b) Tilt angle of the director from the smectic layer normal as measured by rotating the cell between the dark states at +10V and -10V. (c) Response time to a square wave of 10V amplitude. This was defined as twice the time from 50% brightness to 10%. The conventional definition is 90%-10%, but this one removes the ambiguity resulting from brightness peaks which appear during the response. Each point is an average of two values measured at different points on the sample, and the larger errors in the samples with longer response time are due to a larger spread, presumably due to the more complicated texture.

glass substrates at constant distance. For all the samples made from mixtures with ZLI1132, distinct structures were seen which had formed around the spacers, as shown in Figure 4(d)and appearing to emanate out from the spacers. For the samples polymerised in the isotropic phase, these structures around the spacers were the only feature observed. This could either be related to the phase in which polymerisation occurred or alternatively to temperature. Funt and Bhadani<sup>11</sup> found that higher temperatures could decrease the molecular weight of the polymer, which may have led to the polymer being dissolved more easily by the hexane treatment. It thus appeared that the spacers had acted as nucleation points for the polymer growth, which is a reasonable assumption and is presumably either due to the surface energy of the spacers, or the electric field gradients around them. The precise appearance of the polymer structures varied slightly, and for the sample polymerised in the isotropic phase they are more localised around the spacers. As before, no differences were observed between the structures formed on the cathode and those on the anode.

#### 3.2 Smectic-A phase polymerisation in FELIX M4581-050

Mixtures of 5% by weight A6OA12 in FELIX were kept at 68°C in the smectic-A\* phase under a voltage of 50V for 16 hours, or at 45°C in the smectic-C\* phase under a voltage of 100V also for 16 hours. Both voltages were chosen to be slightly below the breakdown voltage at that temperature. The unpolymerised monomer had little effect on the temperature of the chiral nematic to smectic-A\* transition, but the transition to the smectic-C\* phase was decreased from 66°C to 60°C. This then rose again to 61-62°C after polymerisation was completed. The results obtained by polymerisation in the smectic-A\* phase were somewhat variable, perhaps for the same reasons that the polymerisation rate varied in the nematic samples, as discussed above. Figure 5(a) shows the SmA\* texture before any electric field application. On occasions after electric field application, phenomena such as depicted in Figure 5(b)-(d) were observed. Figure 5(b) and Figure 5(c) exhibit small streaks appearing as the sample is heated a few degrees into the nematic phase at zero field, which disappear as it is cooled again. The banded smectic-A\* texture is maintained into the nematic phase, which

was observed for all samples polymerised in the smectic-A\* phase, indicating the stabilisation of the texture of the low temperature phase where the polymer was formed. The streaks reappear in the smectic-C\* phase, becoming more prominent as the sample is reduced in temperature (Figure 5(d)). This can be attributed to the change of the smectic layer spacing as the tilt angle increases with decreasing temperature below the SmA\*-SmC\* transition (similar to chevrons formation in a nonpolymerized sample). The application of the large voltage (100V) at 45°C in the smectic-C\* phase created a fine array of zigzag defects in the texture. As can be seen in Figure 6, after polymerisation this texture of defects remained as the mixture was heated into the nematic and isotropic phases. In general it should be noted that both the application of a voltage as well as the surface morphology can affect the optical textures and electro-optic properties individually. In our case the polymer is formed by the application of an electric field. The reason to do so is to obtain a well oriented polymer. This will change the surface properties. Application of an electric field alone will not change the surface morphology at all, which is established during the cell production process. for example through rubbing the substrates. Once the polymer is formed, the orientation of the polymer chains (strands) are capable to change the new surface which is experienced by the liquid crystal.

The ferroelectric polarisation,  $P_s$ , was not affected significantly by polymerisations at either temperature (Figure 7(a)). The director tilt angle  $\Theta$ , was also not affected significantly in the smectic-A\* phase due to polymer formation, but apparently decreased somewhat after polymerisation in the smectic-C\* phase (see Figure 7(b). This decrease of tilt angle is presumably due to the very uneven defect texture stabilised by the polymerisation. The response time of ferroelectric switching tended to increase as the texture of the SmC\* phase became more complex while polymerisation takes place at both temperatures (Figure 7(c)).

For polymerisation in the smectic-A\* phase the polymer morphology (Figure 8(a)), was quite different to that observed for nematic samples. The unidirectional polymer strands are directed along the director and have a length of approximately  $100-200\mu m$ , at a thickness in the order of  $1-2\mu m$ .

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Figure 8. SEM images of the polymer network resulting from a 5% by weight mixture of A6OA12 monomer in FELIX M4581-050. (a) Image from the cathode and showing the boundary of the electrode (i.e. of the layer of conductive indium tin oxide). (b) Image from the anode, at higher magnification.

These dimensions are comparable to those obtained by UV polymerisation.<sup>21</sup> The faint streaks, most visible in the higher magnification image of Figure 8(b), are perpendicular to the surface alignment, i.e. parallel to the smectic layers. The larger polymer strands point in a direction consistent with the liquid crystal director (the tilt angle was observed to be about 30° at room temperature). They are equivalent to the streaks observed in polarising optical microscopy (Figure 5(d)). As observed with all the other substrates, there was no noticeable difference between the anode and the cathode surfaces.

### 4. Conclusions

From the SEM investigations, it is evident that polymerisation is occurring. The structures observed in the nematic phase of ZLI1132 in particular, with their periodic corrugations and patterns surrounding the spacer beads, are unlike any of those observed in a photoinitiated polymer network. Especially the structures formed around the spacers bear a resemblance to the flower-like structures observed in an electrochemical polymerisation on glassy carbon.<sup>22</sup> The morphology of the polymer is sensitive to the environment of polymerisation, as evidenced by the different results obtained from compounds in the smectic-A\* and the nematic phases, polymerised at comparable temperatures and at equal monomer concentration. However, both polymer structures template the texture which was present during the polymerisation process. The realignment of ZLI1132 from planar to homeotropic was demonstrated to be solely due to the polymer formed at the substrate, not due to the electric field. This was evidenced by the fact that a control cell without monomer did not show any signs by SEM of a polymer being formed.

It is expected that the polymer growth should start at the cathode. It is therefore surprising that none of the SEM images show a clear distinction between the anode and cathode surface topology. One reason could be the use of higher voltages for liquid crystal matrices than typically employed for the electrochemical polymerisation of acrylates,<sup>11, 14</sup> allowing growth to occur on both surfaces. At this point it is not certain which molecular species is in fact acting as the polymerisation initiator. It must also be clearly stated that our simple system has no added polymerization initiator and therefore the only electroactive species is the liquid crystalline methacrylic monomer A6OA12.<sup>18</sup> The lack of polymerisation in ZLI2806 could indicate that it may be connected to a component of the liquid crystalline mixtures, rather than the monomer compound, possibly an ionic impurity. One would expect that if a small concentration of some ionic compound were added as an initiator, the reaction would proceed at lower voltages and form a film solely at the cathode as is more usual. The reaction could possibly then be also more predictable.

The present investigations indicate that the polymerisation mainly takes place at the electrodes of the substrates, possibly slightly extending into the bulk for larger monomer concentrations, as no inhomogeneities were observed, even for thicker cells. The SEM images do not appear similar to those observed from other polymerisation mechanisms. A reason could be the ability to reorient the polymer strands by electric field application. This possibility is indicated by the low density, hardly crosslinked networks. In any case, the textures of the liquid crystal matrix are stabilised, presumably by the polymer close to the substrates, which can act as an additional alignment layer. These features indicate that the electropolymerisation in liquid crystals will be a rich new area of investigation.

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