Liquid Crystal Microdroplets from Complex Binary Liquid Mixtures

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and say, “My Lord, increase me in knowledge.”

— 20:114
I, Mehzabin Patel, confirm that the work presented in this thesis is my own. I confirm that it has been clearly indicated where information has been derived from other sources.
Abstract

Liquid crystals and binary fluid mixtures are fields of soft matter, which individually offer unique properties for applications in displays, drug delivery, sensors and optoelectronics. They are both responsive to external stimuli and may take part in self-assembly processes. When a liquid crystal becomes a component of a binary fluid mixture, one can envisage that the complex interplay presents interesting phenomena. In this work, the thermotropic liquid crystal, 4-cyano-4’-pentylbiphenyl (5CB) was combined with methanol (MeOH) to form a partially miscible liquid mixture with an upper critical solution temperature (UCST).

The research presented herein is in four parts. First, the formation of liquid crystal-rich droplets by temperature-induced phase separation was investigated. The tuning of early-stage isotropic and nematic liquid crystal-rich droplet size and number through manipulation of nucleation and growth conditions was studied by exposure to simple temperature protocols in the range of 35 °C to -5 °C. Second, the dynamics of late-stage phase separation was investigated. This isotropic liquid-liquid crystal binary system presented a unique advantage, wherein the interactions of a binary liquid reaching equilibrium could be visualised through the optical properties of the liquid crystal, enabling a comparative study of bulk and microscale phase separation. Thirdly, the effect of surfactants and particles on this binary liquid system was investigated. Block co-polymers were found to increase nucleation points, and silica nanoparticles were found to lead to porous structures. Finally, the reversibility of the binary system was exploited for the production of microparticles. Reactive mesogens were incorporated into the liquid crystal 5CB, and photopolymerisation was employed to create temperature-responsive porous microparticles, which could be tuned in its size and ability to shrink and swell. Furthermore, the binary liquid could be separated from the microparticle by heating.

The results achieved through this work offer a potential for the development of finely tuned liquid crystal droplets and microparticle production by simple temperature control, and offer novel insights into liquid-liquid phase separation, and the optical manipulation of liquid crystals.
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## Contents

Abstract ................................................................. 3
Acknowledgments ......................................................... 4
List of Abbreviations ..................................................... 8
List of Figures ............................................................ 17

### I Preface
Impact statement ......................................................... 19
Thesis Overview .......................................................... 20

### II Background

1 Introduction .............................................................. 22
   1.1 Binary Liquids ................................................... 22
      1.1.1 Spinodal Decomposition .................................... 22
      1.1.2 Nucleation .................................................. 24
   1.2 Liquid Crystals ................................................... 29
      1.2.1 Liquid Crystal Properties .................................. 29
      1.2.2 Liquid Crystal Phases ..................................... 30
      1.2.3 Nematic Order Parameter ................................... 31
      1.2.4 Nematic Elasticity ......................................... 33
      1.2.5 Birefringence ............................................... 34
      1.2.6 Liquid Crystal Droplets .................................... 36
      1.2.7 Applications of Liquid Crystal Droplets ................. 41
      1.2.8 Liquid Crystals in Binary Liquids ........................ 46

2 Materials and Methods ............................................... 50
   2.1 Materials .......................................................... 50
      2.1.1 Liquid Crystal 4-cyano-4'-pentylbiphenyl (5CB) ........ 50
      2.1.2 Liquid Crystal (RM257) .................................... 50
      2.1.3 Microfluidic Chip .......................................... 51
   2.2 Materials Characterisation ...................................... 51
      2.2.1 Optical Microscopy .......................................... 51
### Contents

2.2.1.1 Thermal Analysis of Temperature Stage ........................................... 54
2.2.1.2 Polarised Optical Microscopy (POM) ............................................... 56
2.2.1.3 Photopolymerisation Set-Up .......................................................... 59
2.2.1.4 Analysis for Droplet Characterisation ............................................. 60
2.2.2 Scanning Electron Microscopy ............................................................ 62
2.2.3 Focused Ion Beam Microscopy ............................................................ 63
2.2.4 FTIR ...................................................................................................... 63
2.2.5 Dynamic Light Scattering .................................................................... 64
2.2.6 Thermogravimetric Analysis ............................................................... 65

### III Results

3 Temperature-Induced Liquid Crystal Microdroplet Formation in a Partially Miscible Liquid Mixture

<table>
<thead>
<tr>
<th>3.1 Introduction</th>
<th>........</th>
<th>67</th>
</tr>
</thead>
</table>

3.2 Experimental

| 3.2.1 5CB Droplet Formation | ........ | 68 |

3.3 Results and Discussion

| 3.3.1 5CB/MeOH temperature quench | ........ | 69 |
| 3.3.2 5CB/MeOH cooling rate | ........ | 70 |
| 3.3.3 Nematic 5CB-rich droplets | ........ | 74 |

3.4 Conclusions ......................................................................................... 77

4 Long Term Phase Separation Dynamics in a Liquid Crystal Containing Binary Fluid Mixture

| 4.1 Introduction | ........ | 79 |

4.2 Experimental ......................................................................................... 81

4.3 Results and Discussion ........................................................................ 81

4.4 Conclusions ......................................................................................... 85

5 Surfactant and Particle Effects on Binary Liquids

| 5.1 Introduction | ........ | 87 |

5.2 Experimental ......................................................................................... 89

5.3 Results .................................................................................................. 92

| 5.3.1 Surfactant Effects | ........ | 92 |
| 5.3.2 Particle Effects | ........ | 95 |
| 5.3.2.1 Characterisation of Silica NPs | ........ | 95 |
| 5.3.2.2 Silica NP Effect on 5CB/MeOH Binary Liquid System | ........ | 97 |

5.4 Conclusion ............................................................................................ 99
## Contents

### 6 Liquid Crystal-Templated Porous Microparticles via Photopolymerisation of Temperature-Induced Droplets in a Binary Liquid Mixture

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Introduction</td>
<td>101</td>
</tr>
<tr>
<td>6.2 Experimental</td>
<td>102</td>
</tr>
<tr>
<td>6.3 Results and Discussion</td>
<td>103</td>
</tr>
<tr>
<td>6.4 Conclusions</td>
<td>110</td>
</tr>
</tbody>
</table>

### V Summary

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>V Summary</td>
<td>113</td>
</tr>
</tbody>
</table>

### 7 Conclusions

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 Conclusions</td>
<td>113</td>
</tr>
</tbody>
</table>

### 8 Future Work

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 Future Work</td>
<td>115</td>
</tr>
</tbody>
</table>

### VI Appendix

<table>
<thead>
<tr>
<th>Appendix A: Binary Liquids Confined to a Droplet</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1 Introduction</td>
<td>118</td>
</tr>
<tr>
<td>A.2 Experimental</td>
<td>118</td>
</tr>
<tr>
<td>A.3 Results</td>
<td>119</td>
</tr>
<tr>
<td>A.4 Conclusion</td>
<td>120</td>
</tr>
</tbody>
</table>

### Bibliography

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bibliography</td>
<td>120</td>
</tr>
</tbody>
</table>
List of Abbreviations

5CB 4-cyano-4'-pentylbiphenyl
CMC Critical Micelle Concentration
ATR Attenuated Total Reflection
DLS Dynamic Light Scattering
DMF Dimethylformamide
FIB Focused Ion Beam
FTIR Fourier Transform Infrared
LC Liquid Crystal
LCD Liquid Crystal Display
LCE Liquid Crystal Elastomer
LCST Lower Critical Solution Temperature
MeOH Methanol
MSD Mean Square Displacement
NA Numerical Aperture
NP Nanoparticle
OPD Optical Path Difference
PDLC Polymer Dispersed Liquid Crystal
PIPS Polymerisation-Induced Phase Separation
PVA Poly(vinyl alcohol)
POM Polarised Optical Microscopy
PSD Particle Size Distribution
RM257 2-methyl-1,4-phenylene bis4-[3-(acryloyloxy)propoxy]benzoate
PDMS Poly(dimethylsiloxane)
SEM Scanning Electron Microscopy
SIPS Solvent Induced Phase Separation
Si  Si  Silica
Si NP  Si NP  Silica Nanoparticle
TEOS  TEOS  Tetraethyl orthosilicate
TIPS  TIPS  Thermally Induced Phase Separation
WPM  WPM  Whey Protein Microgel
TGA  TGA  Thermogravimetric Analysis
UCST  UCST  Upper Critical Solution Temperature
UV  UV  Ultra Violet

**Symbols**

$C$  Composition
$d$  Thickness
$D$  Density
$F$  Elastic Free Energy
$g$  Gravitational Constant
$G$  Gibbs Free Energy
$L$  Diameter
$l_c$  Capillary Length Scale
$n$  Growth exponent
$\hat{n}$  Director
$r$  Radius
$R$  Resolution
$s$  Defect Charge
$S$  Nematic Order Parameter
$t$  Time
$T$  Temperature
$T_{NI}$  Nematic-Isotropic Transition Temperature
$T_{pst}$  Phase Separation Temperature
$\mu$  Chemical Potential
$\eta$  Universal Growth Exponent
$\Delta n$  Birefringence
$\Delta p$  Laplace Pressure
$\gamma$  Interfacial Tension
$\lambda$  Illumination Wavelength
List of Figures

1.1 Temperature composition (T-C) phase diagram for a binary fluid mixture. UCST is the upper critical solution temperature. A mixture with a composition \( C_0 \) will be a single miscible phase at all temperatures beyond the binodal line. As temperature decreases, the binodal line will be intersected, and two immiscible liquids will form. Compositions of the phase separated liquids at equilibrium (\( A \) and \( B \)) are indicated by the tie lines, which connect at \( C_1 \) and \( C_2 \).

1.2 Free energy in phase separation. Phase diagram and corresponding free energy diagrams of binary liquid mixtures with differing compositions \( C_S \) (a) and \( C_N \) (b) as they are cooled from a single phase, to \( T_x \) by spinodal decomposition (a) and nucleation (b).

1.3 Free energy diagram for classical nucleation theory (CNT).

1.4 Concentration \( c \), of diffusing species as a function of position \( x \).

1.5 Coexistence of phases. (a) Two phases separated by a flat interface. (b) A droplet embedded in a continuous phase. (c) Two droplets which will undergo Ostwald ripening.

1.6 Geometrical shapes forming LC phases. (a) Calamitic (rod shaped), (b) discotic (disc shaped) (c) bent-core (or banana) shaped mesogens.

1.7 Molecular structure and shape of 4-cyano-4’-pentylbiphenyl (5CB).

1.8 Thermotropic calamitic LC mesophases. Schematic illustration of rod-like molecules representing molecular arrangement and phase transition behaviour of thermotropic LCs.

1.9 Order parameter in LCs. (a) The coordinate system illustrates the parameters required for calculating the order parameter according to the director, \( \hat{n} \). The polar angle \( \theta \) expresses the deviation of a single molecule from \( \hat{n} \) and the azimuthal angle \( \phi \) defines the direction of deviation. (b) Plot of order parameter, \( S \), of a LC system as a function of temperature.

1.10 Schematic of deformations in a nematic LC. Aligned LC showing (a) splay, (b) twist and (c) bend deformations.
1.11 Wavefront propagation through a LC. (a) Fast and slow axis of an ellipsoid. (b) Spherical ordinary wavefront. (c) Ellipsoidal extraordinary wavefront. Figure adapted with permissions from ref\textsuperscript{1}. Copyright © 2013 WileyBlackwell. 35

1.12 Positive and negative birefringence. Scheme to show how the relative magnitude of $n_o$ and $n_e$ determine whether the LC is optically (a) positive or (b) negative. 36

1.13 Topological defects in a (a) bipolar (b) twisted bipolar (c) concentric (d) radial (e) twisted radial (f) axial LC droplet. The black dot indicates the location of the disclination and the dotted lines represent the surrounding LC molecules and their orientations. 37

1.14 Schematic representation of the morphology within LC drops. For homeotropic anchoring (top), decreasing the size of the droplet induces a transition from a radial to a uniform morphology. For planar anchoring (bottom), decreasing the drop size induces a transition from a bipolar morphology to a radial configuration. Figure adapted with permission from Ref\textsuperscript{2}. Copyright 2012 Royal Society of Chemistry. 39

1.15 Classic structure of surfactants. Its amphiphilic nature is represented with a hydrophilic head and a hydrophobic tail. A schematic diagram of a micelle (right) of oil in aqueous suspension. 40

1.16 Classic structure of Pickering emulsions. Particles assemble at interface between (a) oil-in-water (O/W) and (b) water-in-oil (W/O) droplets. (c) The three-phase contact angle ($\theta$) and the particle-oil ($\gamma_{po}$), particle-water ($\gamma_{pw}$) and oil-water ($\gamma_{ow}$) interfacial tensions for a O/W Pickering emulsion. 41

1.17 Electro-optical switching in PDLC films. (a) and (b) off and on states, respectively. (c) Transmission of PDLC cell as a function of the applied voltage. (d) The interior smart panels before (off) and after switching on. Figure reprinted with permission from ref\textsuperscript{3}. Copyright 2016 Elsevier. 43

1.18 Schematic illustration of structural transition of PBA-doped 5CB microdroplets at (a) pH = 5.7 and (b) 6.0. Enzymatic reaction of penicillin G produces penicilloate and hydrogen ion. Figure reprinted with permission from ref\textsuperscript{4}. Copyright 2017 Elsevier. 44

1.19 SARS-CoV-2 ssRNA detection using LCs. (a) Schematic illustration of the optical response of the surfactant DTAB-decorated LC (E7) film to the adsorption of the ssDNA probe. (b) Design and photograph of a LC-based detection kit for ssRNA-CoV, and test result readout by smartphone app for negative and positive test results. Figure reprinted with permission from ref\textsuperscript{5}. Copyright 2020 Elsevier. 45
1.20 Biomimetic fluid circulation in a loop driven by artificial cardiac muscles. 
   a) Schematic fluid circulation design shows the loop mainly consisting of 
   artificial cardiac muscle, two check valves, reservoir, and fluid-containing 
   tubes which link all parts together. b) Photograph of a fluid circulation 
   loop. Scale bar: 5 cm. Inset shows the artificial cardiac muscles. Scale 
   bar: 1 cm. c) Artificial cardiac muscle pumped out red fluid mimicking 
   arterial blood and pushed blue fluid mimicking venous blood back to 
   the chamber within 3 beats. Scale bar: 5 cm. Figure reprinted with 
   permission from ref[6]. Copyright 2022 Wiley.

1.21 (a) Optical image of a bimorph with a heater sandwiched between the 
   LCE-CB and Kapton film. The inset shows the schematic in exploded 
   view. (b) Optical image of the bimorph before (left image) and after (right 
   image) the heater is turned on. Figure reprinted with permission from 
   ref[7]. Copyright 2018 Wiley.

1.22 Phase diagram of a Binary Mixture of 5CB and MeOH. The phase diagram 
   is divided into four zones: isotropic (I), nematic (N), isotropic + isotropic 
   (I+I) and nematic + isotropic (N+I). Figure reprinted with permission from 
   Ref[8]. Copyright 2018 Royal Society of Chemistry.

2.1 Chemical structure of 4-cyano-4'-pentylbiphenyl (5CB).

2.2 Chemical structure of 2-methyl-1,4-phenylene bis4-[3-(acryloyloxy)propoxy]benzoate 
   (RM257).

2.3 Design and measurements of microfluidic chip chamber.

2.4 Schematic of an optical microscope. The diagram illustrates transmitted 
   bright-field microscopy and includes illustration of light rays from the light 
   source to the detector.

2.5 Schematic of the Linkam (a) PE120 and (b) LTS120 temperature con-
   trolled stage.

2.6 FLIR thermal imaging of Linkam microscope stage over time. Thermal 
   images for the Linkam stage set to (a) -5°C, (b) Schematic of points (1-5) 
   on the stage wherein temperature was measured. (c) Corresponding 
   temperature - time graph for the various measured points.

2.7 FLIR thermal imaging of Linkam microscope stage during cooling.

2.8 Polarised light microscopy. The light path depicts the polarisation of 
   light when the polariser and analyser are at 90° to each other (left). 
   A birefringent specimen is placed between the polariser and analyser, 
   which splits the polarised light into the ordinary $n_o$ and extraordinary 
   $n_e$ components, which are recombined at the analyser (right). Figure 
   adapted with permissions from Ref[9].
2.9 Michel-Levy birefringence chart. The chart is used to determine the
birefringence $\Delta n$, using the thickness, $d$ and path difference which shows
three orders of the interference colour spectrum. Figure adapted with
permission from Ref[10] available under Creative Commons Attribution-
Share Alike 2.0 Generic license. .............................................. 57

2.10 (a) Uniaxial interference figure showing isochromes, isogyres and melatope.
(b) Uniaxial figure under crossed polarised light showing first order grey
interference colours. Uniaxial figure after insertion of a $\lambda$ plate, showing
(c) optically positive and (d) negative character. .................................. 58

2.11 Schematic of the optical microscope set-up. Illustration of the Zeiss
AxioScope.A1 with motorised Prior stage. For clarity, the light path is
highlighted. Transmitted light served for sample analysis. High intensity
light from a Prior Lumen 200 metal halide lamp served for photopoly-
merisation via the reflection port and a suitable filter combination. Figure
adapted with permission from Ref. [9] ............................................. 59

2.12 Schematic illustration of the photopolymerisation set-up. A halide lamp
serves as a light source. A 365 ± 2.0 nm bandpass filter blocks all other
wavelengths. A dichroic longpass pass filter is placed at 45° angle, to
transmit light to the sample. The transmitted light source provides light to
the sample and camera. ............................................................... 60

2.13 A representation of the steps taken by the computational script. (a)
Edge detection performed by a Sobel transform that returns the gra-
dient of an image. (b) Droplets identified after separation from the
background through a watershed transform. (c) Processed image af-
fter re-segmentation of adjoining droplets, and filtering of partial droplets
touching the edges of an image. .................................................. 61

2.14 Sample images of the second watershed treatment to segment droplets
in contact with one another. (a,b,c) Droplets identified as a single fea-
ture (yellow) distinguished from the background (purple) after the initial
watershed segmentation and CCL step. (d,e,f) Droplets re-segmented
from one another after a watershed treatment. A new label was assigned
(green) to the segmented droplets to distinguish them from the initial
droplet label (yellow) and the background (purple). .......................... 62

3.1 Reversible droplet formation. a-e: Nucleation and early-stage growth of
isotropic droplets over the initial 0.2 seconds at 22.5°C. f-j: Disappear-
ance of mature droplets over 7 seconds upon heating to 35°C. Scale bar:
1 µm. ................................................................................. 70
3.2 Droplet diameter vs. quench depth. a-c: Microscopic images of isotropic 5CB-rich droplets in MeOH-rich continuous phase 20 seconds after nucleation at quench depths of (a) $\Delta T = 0.5^\circ C$, (b) $\Delta T = 2.5^\circ C$ and (c) $\Delta T = 7.5^\circ C$. In all cases, the mixture was cooled from 35$^\circ C$ at a cooling rate of 20$^\circ C$ min$^{-1}$. The scale bar represents 10$\mu m$. (d) Overview of droplet mean diameter and standard deviation for respective quench depths over time.

3.3 Effect of Quench Depth on Number of Isotropic 5CB-rich Droplets. (a) The number of droplets over time is presented for a quench depth of $\Delta T = 7.5^\circ C$, $\Delta T = 2.5^\circ C$ and $\Delta T = 0.5^\circ C$, respectively, at a cooling rate of 20$^\circ C$ min$^{-1}$. Original data points and data smoothed by adjacent averaging (20 points).

3.4 Dispersity and Trajectory of Isotropic Droplets According to Quench Depth. (a-c) Diameter histogram of isotropic 5CB-rich droplets over time at quench depths of (a) $\Delta T = 0.5^\circ C$, (b) $\Delta T = 2.5^\circ C$, (c) $\Delta T = 7.5^\circ C$. (d-f) Trajectory of droplets along the x and y axis over the course of 60 seconds at quench depths of (d) $\Delta T = 0.5^\circ C$, (e) $\Delta T = 2.5^\circ C$, (f) $\Delta T = 7.5^\circ C$. (g-i) Mean square displacement (MSD) of droplets at quench depths of (g) $\Delta T = 0.5^\circ C$, (h) $\Delta T = 2.5^\circ C$, (i) $\Delta T = 7.5^\circ C$ over time. The colour code represents the time at which a new droplet entered the frame.

3.5 Droplet number vs. cooling rate. a-d: Microscopic images of isotropic 5CB-rich droplets in MeOH-rich continuous phase 5 seconds after nucleation at cooling rates of (a) 20$^\circ C$ min$^{-1}$, (b) 10$^\circ C$ min$^{-1}$, (c) 5$^\circ C$ min$^{-1}$ and (d) 1$^\circ C$ min$^{-1}$ for a quench depth of $\Delta T = 7.5^\circ C$. The scale bar represents 10$\mu m$. (e) Overview of number of droplets for respective cooling rates over time.

3.6 Dispersity and trajectory of isotropic droplets according to cooling rate. (a-b) Polydispersity of 5CB-rich droplets over time with cooling rates of (a) 1$^\circ C$ min$^{-1}$, (b) 20$^\circ C$ min$^{-1}$. (c-d) Trajectory of droplets along the x and y axis over the course of 60 seconds at cooling rates of (c) 1$^\circ C$ min$^{-1}$, (d) 20$^\circ C$ min$^{-1}$. (e-f) Mean Square Displacement of droplets at cooling rates of (e) 1$^\circ C$ min$^{-1}$, (f) 20$^\circ C$ min$^{-1}$ over time. Quench depth: $\Delta T = 7.5^\circ C$. 
3.7 Formation of nematic droplets. Image sequence for a temperature quench of \( \Delta T = 27.5 \, ^\circ\text{C} \). (a-c) Bright-field images of (a) isotropic droplets just above the transition temperature, (b) undergoing isotropic-nematic phase transition, (c) nematic droplets. (d) Corresponding nematic droplets imaged under cross-polarised light. Each image snapshot is taken 1 second apart. The scale bar represents 10 \( \mu \text{m} \). (e) Overview of droplet mean diameter (with standard deviation) and temperature over time (cooling rate: 20 \( ^\circ\text{C} \, \text{min}^{-1} \)). 

4.1 Nematic droplet size progression over time. (a/b) Bright-field (top) and cross-polarised (bottom) images of 5CB-rich droplets (a) after isotropic to nematic transition at -5 \( ^\circ\text{C} \) and (b) after 120 minutes at -5 \( ^\circ\text{C} \). Scale bar: 10 \( \mu \text{m} \). (c) Change in diameter of 41 droplet in the frame of an image between time of isotropic-nematic transition point (a) and 120 minutes later (b). Note that the data points coloured in purple relate to droplets that had undergone coalescence.

4.2 Birefringence measurements. Evolution of 5CB-rich droplets under (a) Brightfield (b) crossed polarised light over time. (left-right) (c) Colours of the Michel-Levy chart representing decreasing birefringence. The scale bar represents 10 \( \mu \text{m} \).

5.1 Route to bijel fabrication. Single fluid phase of ethylene carbonate (EC) and xylene is quenched to the spinodal demixing region forming a bicontinuous network with EC-rich and xylene-rich phases stabilised by fumed silica at the interface, here shown by confocal microscopy. Adapted from Ref.[11] with permission from the Royal Society of Chemistry.

5.2 Schematic of the formation of a cellular network. The image shows the evolution and eventual remixing of nitromethane-rich droplets in an ethylene glycol-rich continuous phase, contained by silica particles at the interface. Adapted from Ref.[12] with permission from the Royal Society of Chemistry.

5.3 Molecular structure of the block copolymer poly(isobutylene)-b-poly(ethyleneoxide), PIB\( \text{39}-\text{block}-\text{PEO}_{36} \).

5.4 Chemical reaction scheme for silica NP production.

5.5 Schematic illustration of fluorescence microscopy set-up. A metal halide lamp serves as a light source. Excitation and emission filters are placed in the light path to block unwanted wavelengths. The transmitted light source provides light to the sample and the camera.

5.6 Macroscopic effect of block-copolymer PIB-b-PEO on 5CB/MeOH mixture upon cooling from 35 \( ^\circ\text{C} \) to 15 \( ^\circ\text{C} \). (a) 5CB/MeOH mixture only. (b) 1 \% PIB-b-PEO in MeOH/5CB mixture.
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.7</td>
<td>Effect of block-copolymer PIB-PEO on isotropic 5CB-rich droplets. (a) Overview of droplet mean diameter and standard deviation and (b) overview of number of droplets of a mixture of 5CB and MeOH with and without PIB-PEO. Cooling rate: 5 °C min⁻¹. Quench Depth: ΔΤ = 7.5 °C.</td>
</tr>
<tr>
<td>5.8</td>
<td>Determination of CMC of PIB-PEO in MeOH by DLS. Correlation functions and scattered intensity of PIB-PEO at various concentrations.</td>
</tr>
<tr>
<td>5.9</td>
<td>SEM images of silica nanoparticles. Scale: 100 nm.</td>
</tr>
<tr>
<td>5.10</td>
<td>Size distribution by intensity for silica NPs obtained from DLS at 20 °C.</td>
</tr>
<tr>
<td>5.11</td>
<td>Thermogravimetric analysis (TGA) of silica-APTES NPs, and silica-APTES-NHS fluorescein NPs.</td>
</tr>
<tr>
<td>5.12</td>
<td>Nematic droplets with silica NPs at the surface. (a) Brightfield image, (b) cross polarised image, and (c) fluorescence image of 5CB-rich droplets surrounded by silica NPs at their surface and in the MeOH. Scale: 10 μm.</td>
</tr>
<tr>
<td>5.13</td>
<td>Silica NP organisation around 5CB-rich droplet before and after heating. Isotropic 5CB-rich droplets at -5 °C after nematic-isotropic transition under (a) brightfield (b) fluorescence microscopy. Single phase 5CB/MeOH at 35 °C with silica NPs retaining previous droplet configuration under (c) brightfield (d) fluorescence microscopy.</td>
</tr>
<tr>
<td>6.1</td>
<td>Schematic Illustration of the Microparticle Formation Process. (a) A homogeneous mixture of 70vol% MeOH + 30vol% 5CB/RM257 is prepared at 35 °C, i.e. above the upper critical solution temperature. (b) Isotropic LC enriched droplets are nucleated at 23 °C, which (c) continue to grow during further cooling. (d) Cooling below 0 °C triggers isotropic-to-nematic phase transition of the 5CB/RM257 mesogens. (e) Subsequent exposure to UV light (365 nm) polymerises the photoreactive RM257 mesogens, providing a porous structural matrix that is suitable for extraction and no longer temperature-sensitive.</td>
</tr>
<tr>
<td>6.2</td>
<td>Photopolymerisation of 5CB/RM257-rich droplets. (a) Effect of UV light (365 nm) exposure time at 90 mW cm⁻² on diameter of droplets upon heating after photopolymerisation. (b-d) LC-rich droplets and templated microparticles after UV light exposure for 300 seconds. The same field of view of images shown under brightfield (top) and crossed-polarised light (bottom). (b) 5CB/RM257-rich droplets cooled to -5 °C. (c) 5CB/RM257-rich droplets at -5 °C after photopolymerisation. (d) RM257 polymer particles after heating to 35 °C.</td>
</tr>
<tr>
<td>6.3</td>
<td>Birefringence of LC-templated microparticles. (a) Colours of the Michel-Levy chart decreasing from third-order (left) to first-order (right) interference colours. (b) Evolution of a LC particle with increasing temperature after photopolymerisation between crossed polarisers and (c) between crossed polarisers with a λ plate inserted. Scale: 10 μm.</td>
</tr>
</tbody>
</table>
6.4 Birefringence measurements. Birefringence values of polymerised particles as a function of temperature from -5 to 35°C. . . . . . . . . . . . . . . 106

6.5 Microparticle shrinking and swelling after photopolymerisation. Particles exposed to UV light (365 nm) for (A) 1 minute and (B) 5 seconds. (A/B)i. 5CB/RM257-rich droplets at -5°C, immediately after UV exposure. (A/B)ii. LC templated microparticles after heating to 35°C. (A/B)iii. Swollen microparticles after cooling to -5°C, surrounded by newly nucleated droplets of 5CB. Images under Brightfield light (A and B. Top) and between crossed polarised light (A and B. Bottom). Scale: 10 µm. . . . 107

6.6 Swelling and shrinking of microparticles. Diameter of microparticles as a function of temperature over two cooling and heating sequences. Colour notation indicated different length of UV exposure for photopolymerisation (5 seconds, 30 seconds and 5 minutes). . . . . . . . . . . . . . . . . . . 108

6.7 FTIR analysis of 5CB, 5CB/RM257 after photopolymerisation, and after washing by centrifugation and redispersion in acetone. The adsorption near 2250 cm\(^{-1}\) relates to the C–N bond in 5CB. The adsorption at 1750 cm\(^{-1}\) is characteristic of the C=O bond in RM257. . . . . . . . . . . . . . 109

6.8 Microparticle Extraction. 1. Single and 2. Fused polymeric microparticle templated from radial droplets in a binary liquid (a) under Brightfield light, (b) Crossed polarisers, (c) FIB microscopy figures. Scale: 1 µm. . . . . . 110

A.1 Binary Liquid Mixture of 5CB/MeOH Confined to a Droplet. (left) Schematic of 5CB/MeOH droplet immersed in silicone oil. (right) Phase diagram of binary mixture of 5CB/MeOH (adapted with permission from the Royal Society of Chemistry)\(^8\), showing isotropic to nematic phase transition of droplets of 5CB/MeOH mixtures immersed in silicone oil. Images show droplets of 5CB/MeOH mixtures at their transition temperature under crossed polarised light. Scale bar: 10 µm. . . . . . . . . . . . . . . . . . 120
I

Preface
Impact Statement

Liquid-in-liquid droplets are typically generated by the partitioning of immiscible fluids, e.g. by mechanical shearing with macroscopic homogenisers or microfluidic flow focusing. After their discovery over a century ago, liquid crystal droplets have continued to find promise in varied applications from optoelectronics to drug delivery. However, common approaches suffer from complex synthetic protocols and poor scalability. An alternative route to liquid crystal droplets is by temperature control in a partially miscible liquid mixture, which is in principle scalable in the bulk and offers implementation in circular processes. Isotropic or nematic droplets can be produced through temperature-induced phase separation, which enables to tune droplet size and number via control over nucleation and growth conditions.

The dynamics of late-stage phase separation is of interest for a fundamental understanding. By incorporating a liquid crystal in a binary liquid, molecular phenomena can be visualised through their optical properties. This allows us to develop an understanding of phase separation on the microscale in comparison to the bulk, and factors which affect the contour of a bulk phase diagram can be identified in this way.

Furthermore, the effect of common stabilisers, such as surfactants and particles, on the route to phase separation have been established. Block co-polymers have been found to create micelles in methanol, which is generally not seen in alcohols, and silica nano-particles have been found to create porous arrangements in the continuous phase.

Finally, the possibility of this system to be utilised for the production of polymeric microparticles was investigated using reactive mesogens. This enables the generation of not only well-defined droplets by temperature-induced phase separation, but the conversion of these droplets into permanent microparticles via photopolymerisation. Herein, the liquid crystal droplets served as a template for microparticle production. Liquid crystal-templated polymeric microparticles offer complex internal architectures and unique optical properties. The resulting microparticles are porous and have the ability to shrink and swell by temperature control. The advantage of such a process is that the template can then be extracted by temperature control. Such use of a reversible materials templating approach for an irreversible polymer product has relevance in optical displays, drug delivery, chemical separation, emulsion stabilisation and catalysis.
Thesis Overview

The aim of this thesis was to study droplet formation in a binary liquid mixture containing an isotropic liquid and a liquid crystal.

Chapter 1 presents the relevant theoretical framework for liquid crystals and binary liquids. Fundamentals of the phase behaviour of binary liquids are examined. Thereafter, liquid crystals as a state of matter are introduced, including fundamental characteristics, such as phases, order parameter, transitions and optical properties. The concept of confining liquid crystals in droplets is then discussed in its historical context and alongside the unique characteristics that emerge from such arrangement. Building on this background, the combination of binary liquids and liquid crystals is proposed and recent examples reviewed. Chapter 2 provides a detailed description of the material preparation and characterisation techniques used in this work.

The results are thereafter presented in 4 parts: Chapter 3 focuses on droplet formation and effects of various experimental factors. The properties of isotropic and nematic droplets, and temperature-controlled methods to tune the liquid crystal properties are investigated. Chapter 4 is devoted to late-stage phase separation. In this chapter, the effect of binary liquid phase separation on the liquid crystal droplets and their optical properties is studied, including the effect of confinement in a binary liquid.

Chapter 5 investigates methods for arresting phase separation and their effects using surfactants and particles in binary liquid mixtures. Chapter 6 presents a concept of utilising this droplet formation process for the production of microparticles. Reactive liquid crystals are incorporated into the system and subsequently photopolymerised. Microparticle products, and their swelling and shrinking capabilities are then investigated, as well as extraction of the binary liquid mixture. Finally, Chapter 6 provides conclusive remarks of this doctoral research as well as an outlook, including suggestions for future experiments.
II
Background
Chapter 1

Introduction

Liquid crystals and binary fluid mixtures are fields of soft matter research, which individually have unique properties and a plethora of applications. In this chapter, theoretical background is provided on both liquid crystals and binary fluid mixtures in their own right. This serves as a foundation for the subsequent discussion on the implications of incorporating liquid crystals in binary fluid mixtures.

1.1 Binary Liquids

Binary liquid mixtures are composed of two types of liquid components, $A$ and $B$. Some binary liquids exhibit a miscibility gap for certain compositions and temperatures ranges. A $(T - C)$ binary liquid phase diagram shows the different phases that form at all volume compositions ($C$) of two different liquids and over a range of temperatures ($T$). This is described in Figure 1.1. For a mixture with an upper critical solution temperature (UCST), the system is single phase above the temperature threshold. Other binary liquid mixtures become immiscible with increasing temperature and therefore have a lower critical solution temperature (LCST). In the miscible region, the Gibbs free energy function ($\Delta G$) has a simple single minimum, but when the miscible binary liquid mixture reaches the binodal line, the homogeneous phase becomes thermodynamically unstable. The system can lower its free energy by separating into two phases. Cooling below the binodal line in the Temperature ($T$) - Composition ($C$) phase diagram induces a more energetically favourable phase separated system. In his classical treatment of phase transformations, Gibbs distinguished two types of transformations: spinodal decomposition and nucleation.\textsuperscript{13,15}

1.1.1 Spinodal Decomposition

Spinodal decomposition is described as being small in degree, and large in extent,\textsuperscript{15} as exemplified by a small composition fluctuation over a large area. At the phase separation temperature $T_x$, the Gibbs free energy $G$, can be plotted as a concave function of
1.1 Binary Liquids

Figure 1.1: Temperature composition ($T$-$C$) phase diagram for a binary fluid mixture. UCST is the upper critical solution temperature. A mixture with a composition $C_0$ will be a single miscible phase at all temperatures beyond the binodal line. As temperature decreases, the binodal line will be intersected, and two immiscible liquids will form. Compositions of the phase separated liquids at equilibrium ($A$ and $B$) are indicated by the tie lines, which connect at $C_1$ and $C_2$.

Composition $C$, for the phase separation. Regions of negative curvature ($\frac{\delta^2 G}{\delta C^2})_{T,P} < 0$ lie within the inflection points of the curve ($\frac{\delta^2 G}{\delta C^2})_{T,P} = 0$, as shown in Figure 1.2. When a binary fluid with composition $C_S$, is moved into this region of negative curvature, i.e. the spinodal region of a phase diagram by cooling from the single phase region above UCST, to a lower temperature $T_X$, the composition will initially be the same everywhere, and its free energy $G_0$ will be higher than equilibrium on the free energy curve, as shown in Figure 1.2a. For compositions within the spinodal, there is no thermodynamic barrier to the growth of the new phases. The system will become unstable due to small spontaneous fluctuations in composition, which result in $A$-rich and $B$-rich regions, thereby reducing the total free energy. Uphill diffusion, which is characterised by the occurrence of diffusion up against a concentration gradient, takes place until the equilibrium compositions, $C_1$ and $C_2$ are reached. Equilibrium compositions are those corresponding to the free energy minima. Phase separation by spinodal decomposition creates bicontinuous patterns, which have a characteristic length scale that grows in time. These bicontinuous domains grow in order to reduce the interfacial energy in the system. Phase separation proceeds by diffusion at first and thereafter the interfaces become sharper as the compositions approach equilibrium. Eventually, gravity will overcome the two phases, which have different densities, and the
bicontinuous morphology will no longer remain.

Figure 1.2: Free energy in phase separation. Phase diagram and corresponding free energy diagrams of binary liquid mixtures with differing compositions \( C_S \) (a) and \( C_N \) (b) as they are cooled from a single phase, to \( T_x \) by spinodal decomposition (a) and nucleation (b).

### 1.1.2 Nucleation

Nucleation is described as being large in degree, and small in extent.\(^{16}\) In Figure 1.1, the points on the phase diagram enclosed between the binodal curve and the spinodal curve define the metastable region, where phase separation proceeds by nucleation. When a binary fluid with composition \( C_N \) is moved into the nucleation region of a phase diagram by cooling from the single phase region above UCST, to a lower temperature \( T_X \), the initial system free energy, \( G_0 \) is still higher than equilibrium, \( G_{eq} \) as shown in Figure 1.2. The compositions falling within the nucleation curve are associated with a positive curvature, \( (\delta^2 G / \delta C^2)_{T,P} > 0 \) on the free energy curve.

Here, small composition fluctuations lead to an increase in free energy, therefore phase separation does not proceed by spinodal decomposition, and a free energy barrier must be overcome in order to form nuclei of a critical size, beyond which the nuclei grow spontaneously. Nucleation can proceed homogeneously or heterogeneously. Homogeneous nucleation is uniform throughout the material, and there is equal probability
of nucleation occurring at any place in the material, whereas heterogeneous nucleation occurs at specific locations, such as local defects, interfaces and impurities. In contrast to heterogeneous nucleation, homogeneous nucleation also requires a large driving force, i.e. large undercooling. Heterogeneous nucleation is far more common than homogeneous nucleation, which requires experimentally complex conditions.

There are a number of theories and approaches for explaining nucleation, the classical nucleation theory (CNT) is the most popular example, and describes the kinetics of homogeneous nucleation. The free energetic cost of forming a critical nucleus, $\Delta G_{\text{nuc}}$ (referred to as the nucleation barrier), is explained by the free energy diagram in Figure 1.3. The growth of a nucleus results in a positive contribution to the free energy because of the newly formed interfacial energy contribution, i.e. the surface free energy, $\Delta G_s$. However, there is also a negative contribution to the free energy because additional volume of the favoured phase is formed, i.e. the bulk free energy, $\Delta G_v$. The total free energy, $\Delta G$ of a nucleus/droplet is defined as the sum of the surface free energy $\Delta G_s$, and the bulk free energy $\Delta G_v$.

To reduce the interfacial area of the nucleating phase, they adopt a spherical shape during nucleation. For a spherical droplet of radius $r$, the surface energy $\gamma$, and the free energy of the bulk $\Delta G_v$, give the total free energy $\Delta G$:

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v. \tag{1.1}$$

The bulk free energy itself $\Delta G_v$ is the difference in free energy per unit of volume between the nucleating phase and the phase nucleation is occurring in.\[16,18–21\]
1.1 Binary Liquids

The growth of the nucleus or droplet typically obeys a universal growth law, which follows the growth of a characteristic length ($L$), and is usually defined by the diameter of the nuclei:

$$L(t) \sim t^n,$$  \hspace{1cm} (1.2)

with $t$ as the time after a temperature quench to induce phase transition or separation and $n$ as the universal growth exponent.\textsuperscript{22} For material systems with conserved order parameters (systems which are assumed to consist of two different species), such as the phase separation of binary blends, a growth exponent of $\frac{1}{3}$ is predicted.\textsuperscript{23,24} For material systems with non-conserved order parameters (systems which are assumed to be described by the state variable with many different states)\textsuperscript{25}, such as liquid crystals, the growth exponent is expected to depend on the temperature quench depth, varying from $\frac{1}{2}$ to 1.\textsuperscript{22,26,27} The growth of the nucleus has been widely investigated in material systems pertaining to isotropic fluids.\textsuperscript{28–33} In addition, studies have been performed on binary mixtures of two liquid crystals with distinct transition temperatures,\textsuperscript{34} isotropic liquids with the liquid crystal as the continuous phase,\textsuperscript{35,36} and droplets of liquid crystals in a polymer matrix (PDLC).\textsuperscript{37,38}

Equation 1.2 describes the growth law when droplets nucleate heterogeneously. After nucleation, the nuclei continue to grow further and composition of the continuous phase moves towards that of the other equilibrium phase. The successive stages of growth have been explained as diffusion, an intermediate regime and a coarsening by reduction of interface (by Ostwald ripening or Brownian collisions induced coalescence).\textsuperscript{31}

![Figure 1.4: Concentration $c$, of diffusing species as a function of position $x$.](image)
Diffusion is driven by differences in chemical potentials of the molecular species. The chemical potential \( \mu \) is the Gibbs free energy per mole of the substance and is a measure of the ability of a substance to cause a chemical reaction due to its internal chemical energy or external energy. It describes the tendency to change the number of a systems’ component molecules and therefore, a higher chemical potential will be driven to reduce the number of molecules of a certain type. Each species has its own chemical potential, and a binary liquid is characterised by a set of chemical potentials, which describe the tendency of one type of molecule to move in or out of a local region. Therefore, gradients of chemical potential, which stem from differences in concentration during phase separation, drive diffusive fluxes. Fick’s 2\(^{\text{nd}}\) law of diffusion describes the rate of accumulation/depletion of concentration within the volume as proportional to the local curvature of the concentration gradient:

\[
\frac{\delta C}{\delta t} = \chi \frac{\delta^2 C}{\delta x^2},
\]

where the concentration \( C \) accumulation/depletion rate is proportional to the diffusivity \( \chi \) and the 2\(^{\text{nd}}\) derivative (or curvature) of the concentration, as shown in Figure 1.4. Driven by diffusion, two nuclei/droplets meet and coalesce. The driving force of coalescence is to separate a dispersion into two uniform phases, which have minimal contact with each other. This stage of droplet evolution corresponds to a growth law of \( L(t) \sim t^{1/2} \).

Diffusion and coalescence will proceed until an intermediate regime of slower growth is subsequently achieved. Afterwards, phase separation is driven by Ostwald ripening. Consider two systems in which the chemical potential \( \mu \), is constant in space. The first is a single droplet in a continuous phase with a chemical potential \( \mu_r \), the second is two phases separated by a flat interface with a chemical potential \( \mu_\infty \), as described in Figure 1.5a and b. The difference in chemical potentials of the flat interface \( \mu_\infty \), and the surface with finite radius of curvature \( \mu_r \), is given by

\[
\mu_r - \mu_\infty = V \frac{2\gamma}{r},
\]

where \( V \) is the molar volume, \( \gamma \) is the surface tension and \( r \) is the droplet radius. The difference between these two systems is that for a flat interface the pressure is homogeneous across the interface, whereas for a droplet, there is a difference in pressure across the interface. The pressure contained in the droplet will be higher than the outside, and the difference between the two is known as Laplace pressure (\( \Delta p \)):

\[
\Delta p = \frac{2\gamma}{r}.
\]

The Laplace pressure (\( \Delta p \)) governs how a system containing multiple droplets develops. Chemical potential is governed by composition and pressure, and in two droplets of differing sizes, as shown in Figure 1.5c, the chemical potential \( \mu \) in the smaller droplet...
is bigger than \( \mu \) in the larger droplet as they have different Laplace pressures.\(^{39}\) Thus, bigger droplets grow at the expense of the smaller ones by a phenomenon known as Ostwald ripening.\(^{43,44}\) The Laplace pressure governs the ripening of a system to reach either system a or b, shown in Figure 1.5a and b. This process leads to a reduction of the total interface and a growth law of \( L(t) \sim t^{\frac{1}{3}} \).\(^{45}\)

![Figure 1.5: Coexistence of phases. (a) Two phases separated by a flat interface. (b) A droplet embedded in a continuous phase. (c) Two droplets which will undergo Ostwald ripening.](image)

Domain sizes continue to grow till they reach the capillary length scale \( l_c \). This is the point where the Laplace pressure (\( \Delta p \)) balances out the pressure due to gravity (hydrostatic pressure, \( P = \Delta pgh \)). Therefore, the capillary length scale \( l_c \) is:

\[
l_c = \left( \frac{\gamma}{gD} \right)^{\frac{1}{2}},
\]

(1.6)

where \( \gamma \) is the surface tension, \( g \) is the gravitational constant, and \( D \) is the density difference between the two phases. Thereafter, gravity becomes important and fluid flow can develop. This flow commences when domains of the more dense phase overcomes the interfacial tension which keeps them suspended.\(^46\) The system may stay in a meta-stable condition rather than reaching equilibrium due to the presence of a distinct thermodynamic barrier and positive surface tension. At equilibrium, \( \mu \) is constant at both sides of the interface and there is no longer a diffusive flux across the phase boundary.

Beyond phase separation, the temperature to which a binary fluid mixture is cooled determines the composition in each phase according to the Lever rule. The Lever rule is a formula used to determine the relative amounts of each phase (\( A \) and \( B \)) of a binary liquid. In the example shown in Figure 1.1, a binary fluid mixture is cooled to a target temperature, \( (T_x) \), with composition, \( C_0 \), the horizontal line that segments through this point is terminated at points \( A \) and \( B \). These tie lines indicate the composition of the two phases. The relative amounts in each liquid is inversely proportional to the length of \( C_1 \) and \( C_0 \), and \( C_0 \) and \( C_2 \):

\[
\frac{A}{B} = \frac{C_2 - C_0}{C_0 - C_1},
\]

(1.7)
where \( A \) is rich in the minority liquid and \( B \) is rich in the majority liquid. Each phase separated component contains the above calculated amount of the other component at equilibrium.

### 1.2 Liquid Crystals

Liquid crystals were discovered in 1888 by Friedrich Reinitzer and Otto Lehmann, who observed double melting behaviour while studying cholesteryl benzoate found in carrots. They concluded this was a new state of matter that exhibited characteristics of both liquid and crystalline phases, which they referred to as a liquid crystal (LC)\(^{47,48}\). In 1922, Friedel and Grandjean coined the modern terminology for LCs - smectic, nematic, cholesteric\(^{49}\) and in 1958, the Frank-Oseen-Zocher Theory drew attention to their disclinations or defects\(^{50}\). By 1962, the work of Gray became instrumental in laying the foundation of the LC display industry\(^{51}\). In the following decades, research into LCs has evolved beyond the realm of display technologies into fields such as chemical and biological sensors, lasers, drug delivery, and non-linear optics, as well in the advancement of fundamental science\(^{52-54}\).

#### 1.2.1 Liquid Crystal Properties

LCs are fluid in nature, with some degree of anisotropy, resulting from the packing of non-spherical building blocks, known as mesogens\(^{55}\). This means they flow like a liquid, but retain crystalline properties, such as orientational and positional order. LCs are classified into two main categories: lyotropic and thermotropic. In lyotropic LCs, the phase is a function of the concentration and temperature, certain compositions of which trigger the formation of amphiphilic molecules and supermolecular structures such as spherical or rod-like micelles and bilayers\(^{52,56}\). Their physio-chemical properties provide an interesting interface with biology and equally, have been found relevant in cosmetic, soap, food and detergent production\(^{57}\).

![Figure 1.6: Geometrical shapes forming LC phases. (a) Calamitic (rod shaped), (b) discotic (disc shaped) (c) bent-core (or banana) shaped mesogens.](image_url)
Thermotropic LCs are the most extensively explored LC because of their optical properties, their ability to interact with electric fields, they are easy to handle, and there are many different types. Their various mesophases are controlled by molecular structure and temperature, and there are three classical types, discotic, calamitic and bent-core (or banana) shaped mesogens, as shown in Figure 1.6. Discotic mesogens contain a disk-like rigid core, where one molecular axis is much shorter than the other two, and usually organise in to columns. Calamitic mesogens contain a rod-like rigid core, where one molecular axis is longer than the other two, and can often organise in to layers. Bent-core shaped mesogens incorporate a bent rigid core. Both lyotropic and thermotropic LCs typically consist of organic molecules.

One single type of LC molecule may exhibit many different types of ordering, called mesophases. In particular, the thermotropic alkylcyanobiphenyls (CBs) are an important class of mesogens initially developed by Gray et al. As is typical for many nematogens, these molecular structures consist of a central aromatic core, with a cyano group and a hydrocarbon chain as terminal groups, respectively. They exhibit solid and liquid phases, and one or more intermediate LC phases. CBs are widely used due to their well-established and scalable synthesis and outstanding properties near room temperature, such as their high chemical stability and strong birefringence. They possess a pronounced sensitivity to applied electric fields, which were successfully employed in the first LC displays. The first and most common member of the CB family is 4-cyano-4'-pentylbiphenyl (5CB), as shown in Figure 1.7. Extending the hydrocarbon chain gives the homologous nCB series: 4-cyano-4'-hexylbiphenyl (6CB), 4-cyano-4'-heptylbiphenyl (7CB) and 4-cyano-4'-octylbiphenyl (8CB), going up to 12CB. When n<7, the LCs display a nematic phase, and when n>7, the LC exhibit nematic and smectic A ordering (which are described in the following chapter).

Figure 1.7: Molecular structure and shape of 4-cyano-4'-pentylbiphenyl (5CB)

1.2.2 Liquid Crystal Phases

Figure 1.8 presents a schematic of frequently observed phases of calamitic thermotropic LCs, which are detailed in this section. Most thermotropic LCs exhibit an isotropic phase (Figure 1.8a). Here, the LC has been sufficiently heated until there is an absence of long range order, thus, the LC displays the properties of a conventional liquid. Thermotropic phases are temperature-dependent. As the temperature of an isotropic LC reduces, it undergoes an isotropic-nematic phase transition. In the nematic phase (Figure 1.8b),
the mesogens have long range orientational order, but no positional order, i.e. the long axes of the molecules in a structure are parallel, but the molecules are able to move freely in three directions and rotate about the long axis. The axis along which the mesogens generally align is known as the director (abbreviated, $\hat{n}$). The temperature at which the phase transition from the isotropic to a nematic phase occurs is specific to the LC and referred to as the nematic-isotropic transition temperature or clearing point ($T_{NI}$). In the smectic phases, the molecules are organised into layers with positional order and orientational order. The smectic A phase (Figure 1.8c) has orientational order and comprises of molecules ordered in to layers, which move freely relative to each other and with the layer normal parallel to the surface. Within a layer, the molecules have no translational order: they can move freely in two directions, and rotate about the long axis. Closely related is the smectic C phase (Figure 1.8d), where the director lies at angle to the layer normal resulting in a tilted alignment. The smectic B phase is more ordered than smectic A and C, and exhibits local organisation of the mesogens in the layer, while remaining mutually parallel and normal to the plane of the layer, thus, forming a hexagonal arrays within the layer. Many subtypes of smectic phases have been identified over the years which can also be formed by chiral molecules, generating chiral smectic phases. In the cholesteric phase (Figure 1.8e), the molecules organise into layers with no positional ordering within layers, but the director axis periodically varies. The molecules are parallel, move freely in two directions, and form an angle with the direction of the molecular axes in the preceding layer, thereby arranging into a helical structure. Finally, the crystal phase (Figure 1.8f) is the highest ordered state, in which the molecules exhibit long-range positional and orientational order. Each molecule has a fixed position and orientation in the three-dimensional crystal lattice, and there is no freedom to move or rotate.

Discotic LCs, often referred to as columnar phases, also enable the formation of additional mesophases, which fall into three categories: discotic nematic, discotic chiral nematic, and columnar. The discotic nematic is similar in structure to the calamitic nematic, with the mesogens demonstrating orientational order, but here, the short axis of the molecules align with $\hat{n}$. The same applies in the discotic chiral nematic phases. Columnar phases are the discotic equivalent of the calamitic smectic phase, and have positional order due to the columnar stacking of mesogens. A number of columnar phases exist, and more complicated discotic phases are also described which are analogous to the smectic phases. A large number of thermotropic LCs have been identified over the years. The following chapters will focus primarily on the nematic phase.

### 1.2.3 Nematic Order Parameter

The director, $\hat{n}$, indicates the general direction along which molecules align. There is no physical polarity along the director axis, therefore $+n$ and $-n$ are indistinguishable.
Figure 1.8: Thermotropic calamitic LC mesophases. Schematic illustration of rod-like molecules representing molecular arrangement and phase transition behaviour of thermotropic LCs.

The long range orientational order of LCs is quantified by a nematic order parameter, which describes the statistical distribution of molecules among their orientation along \( \hat{n} \), and is given as follows:

\[
S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle,
\]

where \( \theta \) is the deviation between the long axis of a single mesogen and average direction of the whole ensemble, as shown in Figure 1.9a. The brackets denote an average over all of the molecules in the sample thus integrating over the angles \( \theta \) and \( \phi \), defined in Figure 1.9a.

For an isotropic LC, the average of the cosine terms is zero, and therefore \( S = 0 \). For complete orientational order, \( S = 1 \). In an isotropic-nematic phase transition, \( S \) jumps from zero to a \( > 0 \) value, typically around \( S = 0.4 \). The order parameter of a LC can range between \( S = 0.3-0.9 \), with values decreasing as a function of temperature. This is illustrated for a nematic LC in Figure 1.9b. The order parameter of 5CB is 0 at 35 °C, and increases to 0.6 at 30 °C. The value for nematic order parameter \( S \) can be determined experimentally from diamagnetic measurements, dichroism and nuclear magnetic resonance spectra.

The isotropic to nematic phase transition is of first order. Water to ice is a common example of a first order phase transition. A first order phase transition is typically associated with a discontinuity in the entropy \( \Delta S \), a latent heat \( L = T \Delta S \), where an
amount of energy is absorbed or released during phase transformation), sudden volume change, and a change in order parameter. A liquid with disordered molecules become suddenly ordered at the phase transition and therefore, a first order phase transition is associated with a discontinuous jump in the order parameter. In a second order phase transition, the entropy is continuous at phase transition. For example, the continuous increase of the magnetisation in a ferromagnetic-paramagnetic phase transition.

For an isotropic-nematic phase transition, the heat of transition is only 1 kJ mol\(^{-1}\) as only orientational order is lost at \(T_{NI}\). This leads to an abrupt increase in other thermodynamic properties such as the specific heat, thermal expansion and isothermal compressibility near \(T_{NI}\). The entropy and volume change of this transition is much lower than that of the solid-nematic transition.

### 1.2.4 Nematic Elasticity

Nematic LCs possess a tendency for long-range linear orientation, therefore spatial deformations or distortions that incur mesogen orientation away from the director \(\hat{n}\), result in free energy penalties. These deformations occur when constraints are imposed on the LC by surface orientation or spatial confinement, or by external fields, such as magnetic, electric, etc. \cite{79} Frank\cite{50} and Oseen\cite{80} showed that this orientational elasticity could be described in terms of three basic deformations: splay, twist, and bend, which are illustrated in Figure 1.10. The contribution for each deformation to the full elastic free energy, \(F\), of a bulk nematic is given as a sum of the three terms:

\[
F = \frac{1}{2} [K_{11}(\nabla \cdot \hat{n})^2 + (K_{22}(\hat{n} \cdot \nabla \times \hat{n})^2) + (K_{33}(\hat{n} \times \nabla \times \hat{n})^2)]
\] (1.9)
1.2 Liquid Crystals

$K_{11}$ (splay), $K_{22}$ (twist), and $K_{33}$ (bend) are the Franks constants for the respective distortion and indicate the resistance of a nematic mixture to these elastic deformations. Each deformation is described by the appropriate combination of the vector operators on $\hat{n}$, i.e. divergence $(\nabla \cdot \hat{n})$ and curl $(\nabla \times \hat{n})$ squared. Typically, $K_{11}$ and $K_{22}$ have a somewhat similar value, whereas $K_{33}$ is about two or three times larger.

![Figure 1.10: Schematic of deformations in a nematic LC. Aligned LC showing (a) splay, (b) twist and (c) bend deformations.](image)

A solid or fluid surface in contact with the nematic LC provides a boundary condition. The presence of this surface induces a perturbation of the nematic order over a thickness near the surface. At such a phase boundary, the LC has a preferential molecular orientation at the interface that minimizes the surface free energy. Two principle surface conditions can be distinguished, homeotropic and planar anchoring. Anchoring refers to the preferred director orientation. In homeotropic alignment LCs are aligned perpendicular to the surface and with a planar alignment, the director $\hat{n}$ is parallel to the surface. The shape of the surface which the LC connects with, and the preferred anchoring at the interface can affect both the elastic free energy and interfacial free energy term. Different types of surface can be manipulated to obtain a preferred anchoring for a particular LC. For example, 5CB aligns homeotropically on surfaces with low surface tensions, such as poly(dimethylsiloxane) (PDMS) coated surfaces, and displays planar anchoring on high surface tension surfaces, such as silica and poly(vinyl alcohol) (PVA) coated surfaces.

1.2.5 Birefringence

For LC phases, the refractive index $n_{\parallel}$ parallel to the director, $\hat{n}$, differs from the refractive index $n_{\perp}$ perpendicular to $\hat{n}$. In addition, nematic LCs are uniaxial. This means that they have one optic axis, and the optical properties of the LC are rotationally symmetrical about this axis. These factors, along with the long-range orientational order of a uniaxial nematic LC translate to its optically anisometric nature. The magnitude of optical anistotropy is known as the birefringence, $\Delta n$, and is defined as:
\[ \Delta n = n_\parallel - n_\perp. \] (1.10)

The magnitude and wavelength dependence of the birefringence \( \Delta n \), of LCs is of fundamental interest and is a key parameter in LC applications. For example, birefringence is responsible for the appearance of interference colours in liquid crystal displays (LCDs). Light passing through a LC will experience \( n_\perp \) as the ordinary refractive index \( n_o \), and \( n_\parallel \) as the extraordinary refractive index \( n_e \). For a system with two refractive index values \( n_o \) and \( n_e \), the optical path difference (OPD) can be determined from the equation:

\[ \text{(OPD)} = (n_o - n_e) \times d, \] (1.11)

where \( d \) is the thickness in nanometers of the sample. OPD is also referred to as the relative retardation, as the velocity of the slower ray will be retarded with respect to the faster ray. This retardation value can be quantitatively determined with equation 1.11.

Figure 1.11: Wavefront propagation through a LC. (a) Fast and slow axis of an ellipsoid. (b) Spherical ordinary wavefront. (c) Ellipsoidal extraordinary wavefront. Figure adapted with permissions from ref [1]. Copyright © 2013 WileyBlackwell.

The ordinary wave in a LC observes the laws of normal refraction, shown in the circular section of the indicatrix in Figure 1.11a. It is therefore described as generating a spherical wavefront as illustrated in Figure 1.11b. These waves propagate through an isotropic LC at constant velocity because the refractive index experienced by the waves is uniform in all directions. The extraordinary wave travels along a different path, and can be described as the surface of an ellipsoid as their refractive index varies as a function of direction, as shown in Figure 1.11c.

When the wavefront is travelling in a direction parallel to the long axis of the ellipsoid in the indicatrix shown in Figure 1.11a, it will reach its greatest velocity and is therefore known as the fast axis. Correspondingly, the wavefront will have the slowest velocity when travelling perpendicular to the long axis, and is therefore known as the slow axis. Wavefronts travelling between the long and short axis will experience a gradient of
1.2 Liquid Crystals

When the extraordinary refractive index \( n_e \) is greater than the ordinary refractive index \( n_o \), birefringence can be classified as positive, and when the refractive index \( n_o \) is greater than \( n_e \), this is termed negatively birefringent, i.e \( \Delta n \) is less than zero. This is illustrated in Figure 1.12.

**Figure 1.12:** Positive and negative birefringence. Scheme to show how the relative magnitude of \( n_o \) and \( n_e \) determine whether the LC is optically (a) positive or (b) negative.

In general, the birefringence \( \Delta n \) of a LC decreases as the wavelength of the incident light decreases, or as the temperature increases. The internal order of a LC phase reduces as the LC nears its nematic-isotropic transition temperature, and upon reaching the isotropic phase, \( n_o = n_e \).

### 1.2.6 Liquid Crystal Droplets

LCs are extremely susceptible to external fields and interfacial boundary conditions. Consequently various methods have been proposed to control the orientation of LC molecules, such as electric field, magnetic field, light, surface treatment and topographic confinement.\(^{86–92}\) Topographic confinement has emerged as one of the most effective tools to control the order and orientation of LC phase. The curved confinement of LCs triggers the generation of new structures with an intriguing combination of control over the composition and microscopic structure, including well-defined mesogen orientations, enhanced interfacial area, a rich phase space, tunable optical properties and stimuli response.\(^{93–100}\) Significant phenomenology is also offered, where surface anchoring of the LC molecules can allow manipulation of their topological defects or dislocations.\(^{101}\)

LC droplets have therefore attracted considerable interest particularly in the last few decades with the invention of polymer-dispersed liquid crystals (PDLCs) for optoelectronic devices. They have also had applications in switchable scattering devices, and in chemical and biological sensing.\(^{53,54,102–105}\)

When LC molecules are confined to spherical droplets, they experience competition between interfacial tension and elastic deformations because of their rod-like shape.
and phase, which then determine the internal configurations and thus the optical properties of the droplet. Boundary conditions impose topological constraints on the director \( \hat{n} \), resulting in disclinations or defects. These are topological singularities of molecular arrangement in LCs, which occur when the director \( \hat{n} \), makes a \( \pi \) rotation along a fictitious closed loop taken inside the LC. The droplet then adopts a specific configuration that will minimise the free energy.

LC droplets can adopt a range of director configurations and defect types, examples of which are shown in Figure 1.13. The configuration depends critically on the boundary conditions imposed. If the boundary conditions are parallel, i.e. \( \hat{n} \) is along the surface, the droplet will adopt bipolar, twisted bipolar or concentric configurations, as shown in Figure 1.13a, b and c, respectively. If the boundary conditions are homeotropic, i.e. \( \hat{n} \) is normal to the surface, the droplet will adopt a radial, twisted radial or axial configuration, as shown in Figure 1.13d, e and f, respectively. For planar anchoring the bipolar configuration (1.13a) is most typically observed. The same elastic deformations discussed in the previous sections are present in nematic droplets. For example, in a bipolar droplet both splay and bend deformations are present, and in a radial droplet, only splay exists. A variant of the bipolar and radial structure comes in the form of the twisted bipolar and radial structure, as shown in Figure 1.13b and e, respectively.

![Figure 1.13: Topological defects in a (a) bipolar (b) twisted bipolar (c) concentric (d) radial (e) twisted radial (f) axial LC droplet. The black dot indicates the location of the disclination and the dotted lines represent the surrounding LC molecules and their orientations.](image)

Each droplet shown in Figure 1.13 displays black dot point defects. Figure 1.13a illustrates a bipolar droplet with two diametrically opposite surface point defects, while Figure 1.13d depicts a single point defect in the centre of the droplet. Point defects are isolated points in which the molecular orientation is undefined and discontinuous, and are classified by an integer topological charge, \( s \). The strength of the defect, \( s \), is
defined by the rotation of the director, $\hat{n}$, on a closed path around the defect. $s$ indicates how many multiples of $2\pi$ the director rotates. Since $+n$ and $-n$ are indistinguishable, half-integer values of $s$ are allowed. The number indicates the strength of that particular disclination, and the sign tells us which disclinations are capable of cancelling each other out if they come into contact. Bipolar droplets have two $s = +1$ located at a distance of one diameter on the droplet surface, whereas radial droplets have a topological charge $s = +1$ located at the centre of the drop.

LC droplets dispersed in an isotropic fluid, and their related topological defects, have been extensively studied, particularly since the development of PDLCs. Several methods have been explored for the formation of stable and uniform LC droplets. Many of the widely studied LCs are not soluble in water and typically considered as the oil phase in oil-in-water type emulsions. Therefore, LC droplets dispersed in an aqueous medium are commonly studied. Droplets in regular emulsions vary in size and polydispersity depending on the emulsification method. The mechanism of emulsification requires energy to disperse droplets in a liquid by shear forces, and the amount of energy is dependent on the size of the droplet. Mechanical methods such as vortex, sonication, and homogenisation with optional fractionation or dispersion polymerisation have been used for LC droplet formation. All of these methods are quick to perform but lead to polydisperse droplets. In addition, LCs have been emulsified in glycerol, encapsulated in polymeric capsules, produced through microfluidics, and dispersion polymerisation. Microfluidics has been a widely applied route for uniform LC droplet formation in recent years. This method provides excellent size control and can generate droplets with diameters between 10-100 $\mu$m. However, microfluidic droplet generation typically produces relatively small numbers of droplets and is limited by the material and channel of the device. Furthermore, templating techniques that rely upon the sacrificial use of silica spheres and encapsulation by polyelectrolyte multilayers have also been employed.

The configuration of a LC droplet depends on its size, the presence of certain analytes, surfactants, particles or polymers at their interface, as well as the existence of external fields or shear flow. In return, these experimental factors can be used to manipulate the director field and trigger a switch of the orientation and, thus, its optical properties. Therefore, consideration must be given when selecting the route to LC droplet formation.

**Size Effect**

When a material is confined to a droplet, the surface area to volume ratio increases, and interfacial interactions become more important. In contrast, for LCs, bulk properties retain an important role even as the size of the droplet decreases. Studies have shown that LC droplets exhibit a bipolar configuration when there is planar anchoring, and decreasing the droplet size induces a transition from bipolar to a radial configuration, as
shown in Figure 1.14. In this transition, the curvature penalizes the surface energy and the bulk free energy. For homeotropic anchoring, decreasing the size of the LC droplet induces a transition from a radial configuration to a uniform morphology. Here, the bulk free energy decreases, and the surface free energy increases. Experiments showed that the influence of the topological constraints imposed by the interface vanishes upon reaching a critical radius (800 nm), and the director configuration is then determined solely by the bulk elasticity of the LC.

Surfactant Effect

Surfactants (or amphiphiles) are molecules containing a polar ‘head’ group which is water-soluble, and a non-polar ‘tail’ which is oil soluble, as described in Figure 1.15. The ‘head’ group may have no charge (non-ionic), a negative charge (anionic), a positive charge (cationic), or both positive and negative groups (zwitterionic). They are commonly used in detergents, emulsifiers and wetting agents to lower the interfacial tension between two liquids. When the surfactant concentration is high, surfactants aggregate and form micelles, where the hydrophobic tail form the core and the hydrophilic heads are in contact with the surrounding liquid, as shown in Figure 1.15-right. The point at which micelles are formed is called the critical micelle concentration (CMC).
The configuration of a LC droplet in water is sensitive to the types and concentrations of surfactants present in the aqueous phase. Brake et al. found that bolaamphiphile surfactants (amphiphilic molecules with hydrophilic groups at both ends of a long hydrophobic hydrocarbon chain), such as ((11-hydroxyundecyl) trimethylammonium bromide (HTAB), dodecyl-1,12-bis(trimethylammonium bromide) (DBTAB), and 11-(ferrocenylundecyl) trimethylammonium bromide (FTMA)) caused planar anchoring of 5CB mesogens. On the other hand, alkyltrimethylammonium halides (C\textsubscript{n}TABs, n > 8), sodium dodecyl sulfate (SDS), and N,N-dimethylferrocenylalkylammonium bromides (FC\textsubscript{n}ABs, n > 12) triggered homeotropic orientation of 5CB mesogens. In this study, the orientation of the LC was found to be governed by aliphatic chain length and the areal density of the adsorbed surfactant. Sharma et al. used anionic sulphate-based and cationic trimethylammonium-based surfactants and reported that the chain length and head group of a surfactant were key factors for stabilising and controlling the alignment of LC.

**Particle Effect**

There are two areas of interest when studying particle effect on LC droplets. The first involves individual nanoparticles for self-assembly at the LC droplet interface. In these studies, it was found that particles aggregate at the poles of bipolar droplets and assemble into robust, quantized arrangements that can be mapped onto hexagonal lattices. The second involves using nanoparticles (NPs) to decorate a droplet via the Pickering stabilisation mechanism. Pickering emulsions utilise solid particles as stabilisers, which accumulate at the interface between two immiscible liquids to lower the interfacial energy, stabilise and prevent droplets from coalescence. Water-in-oil (W/O) or oil-in-water (O/W) emulsions may form, as shown in Figure 1.16. This is mainly determined by the wettability of the particles, as described by the Young equation and

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**Figure 1.15:** Classic structure of surfactants. Its amphiphilic nature is represented with a hydrophilic head and a hydrophobic tail. A schematic diagram of a micelle (right) of oil in aqueous suspension.
three-phase contact angle, $\theta$:

$$\cos \theta = \frac{\gamma_{\text{po}} - \gamma_{\text{pw}}}{\gamma_{\text{ow}}} \quad (1.12)$$

Stable Pickering emulsions are formed when the contact angle is close to $90^\circ$. Particles with moderately hydrophilic surfaces tend to form O/W emulsions (due to $\theta < 90^\circ$), whereas slightly hydrophobic particles form W/O emulsions (where $\theta > 90^\circ$). The stability of Pickering emulsions is also dependent on the particle size, shape and concentration.\(^{140}\) They are typically based on either inorganic or organic particles such as silica ($\text{SiO}_2$), magnesium hydroxide, clay, hydroxyapatite and others. These types of emulsions find use in a variety of applications, such as food manufacturing, cosmetics, agrochemicals and therapeutic delivery.\(^{140}\)

![Figure 1.16: Classic structure of Pickering emulsions. Particles assemble at interface between (a) oil-in-water (O/W) and (b) water-in-oil (W/O) droplets. (c) The three-phase contact angle ($\theta$) and the particle-oil ($\gamma_{\text{po}}$), particle-water ($\gamma_{\text{pw}}$) and oil-water ($\gamma_{\text{ow}}$) interfacial tensions for a O/W Pickering emulsion.](image)

Pickering stabilisation of LC droplets is not very well studied. However, recently biocompatible soft materials, such as a whey protein microgel (WPM) have been used to facilitate the analysis of surfactant-induced configurational transition of LC droplets in water. The WPM particles were able to irreversibly adsorb at the LC–water interface and maintain stability over time.\(^{141}\) Similar findings were reported for ethyl cellulose (EC) nanoparticles which were also found to irreversibly adsorb to the LC-water interface, resulting in close hexagonal packing.\(^{142}\) In related research, modified silica NPs have also been used to mediate either planar or homeotropic LC anchoring.\(^{143}\)

### 1.2.7 Applications of Liquid Crystal Droplets

LCs are most well-known for their long history of being used as stimuli-responsive materials in a range of technologies,\(^{52,81,144-146}\) in particular, liquid crystal displays (LCDs).\(^{38,102,147-153}\) LCDs have been used for the fabrication of smart (switchable) windows and flat-panel display.\(^{38,154,157}\)

LC microdroplets embedded in a polymer matrix have attracted considerable interest
in optoelectronic applications, such as variable transmittance windows and reflective mode displays. Polymer-dispersed liquid crystals (PDLCs) are composed of a LC and a polymer, and can be prepared in one of the following three ways: polymerisation-induced phase separation (PIPS) is a process where a monomer is mixed with a LC, polymerisation is subsequently induced, and the phase separation of LC droplets incurs as a result. In solvent-induced phase separation (SIPS), or more accurately, non-solvent induced phase separation (NIPS), the LC and polymer are first dissolved in a solvent, which is then evaporated at a controlled rate, to trigger phase separation of the LC and polymer.

Finally, there is thermally-induced phase separation (TIPS), where the polymer has a melting temperature below its decomposition temperature. A homogeneous mixture of polymer and LC is thermally quenched at a specific rate, which induces phase separation, and leads to the formation of LC droplets as the polymer hardens. The phase separation of LC and polymer proceeds by nucleation and growth with both liquids in their isotropic state forming LC-rich and LC-depleted regions. When the LC concentration exceeds its critical value within the LC-rich domains, a nematic phase develops, provided that the temperature is below the clearing point of the LC. The size, shape, and distribution of LC domains are dictated by thermodynamic phase equilibria and also depend on phase separation kinetics and anisotropic ordering of LC.

Figure 1.17 illustrates how an electro-optical electroconducting cell containing LC droplets in a polymer matrix are used in switchable windows. Figure 1.17a and b depicts the cell before and after switching on an electric field and Figure 1.17c shows the transmittance of the cell as a function of applied voltage. In the cells, the proper selection of refractive indices of the polymer matrix (np) and the mixture of LCs (no) causes the initially non-transparent mixture to become optically transparent under application of an electric field. Figure 1.17d shows the PDLC device used in smart switchable interior panels.

Solution-dispersed LC droplets are a promising platform for chemo- & biosensing. LC sensors are based on changes in the orientation of LC molecules induced by specific bonding events of molecules. A disturbance in LC orientation induces a transition of the colour and brightness of the LCs viewed under a polarised optical microscope. The change in colour indicates the presence of target molecules, and the change in colour or brightness indicates the concentration of the target molecules.

Recent studies of LC-based sensors have demonstrated the ability to report a range of physical stimuli, including mechanical shear, temperature, electric and magnetic fields, and light. The response of the LC is also used to indicate the presence of an analyte. Recently, LCs have been found to respond to targeted chemical and biological species and thus show great potential in the field of biosensors.

There are two main forms of LC biosensors, those in which LCs interact with
chemically-modified solid interfaces; and those that incorporate a LC/aqueous interface, such as LC thin films and droplets.\textsuperscript{164-167} There are various intermolecular interactions involved in biomolecular detections, such as the enzymatic reactions, immunoreactions, and noncovalent interactions.\textsuperscript{144} LCs have been demonstrated for the successful detection of surfactants, lipids, heavy metals, glucose, enzymes, volatile organic compounds, DNAs and proteins, bacteria/mammalian cells, antigens and antimicrobial peptides (AMPs).\textsuperscript{4,105,144,150,154-170} In addition, detection have been successfully demonstrated for a range of analytes, such as bacteria and viruses ($10^4$ pfu mL$^{-1}$),\textsuperscript{171} endotoxin (pM),\textsuperscript{113} protein immunoassays (pM),\textsuperscript{159} and lithocholic acid (µM).\textsuperscript{172} Other applications include the use of LC microdroplets as self-reporting and self-regulating containment for controlled cargo release,\textsuperscript{173} tunable optical microresonators,\textsuperscript{174,177} microlasers,\textsuperscript{178,179} optical switches,\textsuperscript{180,181} light responsive 3D superstructures,\textsuperscript{182} microswimmers,\textsuperscript{183,185} as well as for materials templating.\textsuperscript{119}

For example, Wang et al. developed a new LC microdroplet-based pH sensor and explored its application for the detection of enzymatic reactions in penicillinase.\textsuperscript{4} 5CB microdroplets doped with 4-pentyl-biphenyl-4-carboxylic acid (PBA) displayed phase transitions from bipolar to radial as the pH values increased from 5.7 to 6.0, as described in Figure \ref{fig:1.18}. Since penicillinase hydrolyses penicillin G into hydrogen ion (H$^+$) and penilloate (see Figure \ref{fig:1.18}c), the pH of the aqueous solution is expected to decrease.
as well. As a result, the pH-sensitive 5CB microdroplet was able to detect the H+ released from such an enzymatic reaction.

![Figure 1.18: Schematic illustration of structural transition of PBA-doped 5CB microdroplets at (a) pH = 5.7 and (b) 6.0. Enzymatic reaction of penicillin G produces penicilloate and hydrogen ion. Figure reprinted with permission from ref[4]. Copyright 2017 Elsevier.](image)

A recent and prevalent example is the development of a LC sensor for the ultrasensitive and selective detection of femtomolar concentrations of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2). This was done by triggering ordering transitions in LC (E7) films decorated with cationic surfactant dodecyltrimethylammonium bromide (DTAB) and 15-mer single-stranded deoxyribonucleic acid (ssDNA) probe, as illustrated in Figure 1.19. Based on this sensor, a LC diagnostic kit and a smartphone-based application were developed to enable automatic detection of SARS-CoV-2 at home, holding important social value under the recent global pandemic.

Elastomeric materials made with LCs (LCEs), have been used as mechanical actuators that undergo a change in shape in response to a predefined stimulus (change of temperature, pH variations, ion concentration, electric field, etc). Here, polymerisation of mono and bifunctional acrylate monomers results in the formation of a polymer network, which retains the original alignment of the unpolymerised matrix. This couples the molecular order of the mesogenic precursors into an elastic material. De Gennes identified that as a consequence of this coupling, reversible shape changes (actuation) and highly nonlinear, anisotropic stress-strain responses were possible. Furthermore, different stimuli-responsive artificial muscles can be prepared with LCEs, including thermo-responsive, photo-responsive, electro-responsive muscle-like materials. Wang et al. recently developed a strategy to spatially arrange LCE fibers to construct artificial cardiac muscles for bioinspired deformations and functions. The LCE fibers were obtained by a two-step crosslinking method, and spatially arranged in biological
1.2 Liquid Crystals

Figure 1.19: SARS-CoV-2 ssRNA detection using LCs. (a) Schematic illustration of the optical response of the surfactant DTAB-decorated LC (E7) film to the adsorption of the ssDNA probe. (b) Design and photograph of a LC-based detection kit for ssRNACoV, and test result readout by smartphone app for negative and positive test results. Figure reprinted with permission from ref \(^5\). Copyright 2020 Elsevier.

architectures as cardiac muscle fibers. This demonstrated deformations based on the actuation of LCE fibers in 3D architecture, resulting in reliable and consistent pumping to mimic the blood circulatory system, as demonstrated in Figure 1.20.

Furthermore, LCE-based actuating structures have been implemented in soft robotics. \(^7\) Wang et al. fabricated an adaptive soft robot, constructed with actuators of open-mesh shaped thin deformable resistive heaters and thermal responsive artificial muscles of a bilayer structure composed of carbon black doped LCEs (LCE-CB) nanocomposite and Kapton tape (polyamide, PI) to mimic the locomotion of an inchworm. \(^7\) Figure 1.21 shows the bimorph construct. Upon electrical stimulation, the thermally induced mechanical mismatch between the LCE-CB and Kapton film drives the bending deformation at slightly above the transition temperature; 80°C. Figure 1.21b presents the optical images of the bimorph before and after electrical stimulation.
1.2 Liquid Crystals

1.2.8 Liquid Crystals in Binary Liquids

When a LC is a part of a binary liquid mixture, we can expect the co-occurrence of macroscopic phase separations and LC ordering. In these systems, the orientational and translational order of the LC, as well as the concentration of the LC in the binary liquid, are closely related to the phase separation. LCs in a binary mixture have been studied both experimentally and theoretically, in particular with polymers and nanoparticles. Early work studied the effect of non-nematogenic doping on the isotropic to nematic phase transition temperature. Humphries and Luckhurst reported that the temperature at which the transition from the nematic to the isotropic LC phase occurs, increases with anisotropy in the intermolecular potential. The transition temperature will decrease if a solute is added to the LC which, on average, reduces the anisotropic interactions.

The most well-known and most researched LCs in a binary liquid are polymer-dispersed liquid crystals (PDLCs). There has also been research on binary systems consisting of an isotropic fluid and a LC as the continuous phase. Loudet et al. reported that such a system containing a mixture of silicone oil and the LC E7 (a mixture of cyano-biphenyl and terphenyl molecules) does not fully separate into two phases, but self organise into highly ordered arrays of monodisperse colloidal droplet chains. This

Figure 1.20: Biomimetic fluid circulation in a loop driven by artificial cardiac muscles. a) Schematic fluid circulation design shows the loop mainly consisting of artificial cardiac muscle, two check valves, reservoir, and fluid-containing tubes which link all parts together. b) Photograph of a fluid circulation loop. Scale bar: 5 cm. Inset shows the artificial cardiac muscles. Scale bar: 1 cm. c) Artificial cardiac muscle pumped out red fluid mimicking arterial blood and pushed blue fluid mimicking venous blood back to the chamber within 3 beats. Scale bar: 5 cm. Figure reprinted with permission from ref[6]. Copyright 2022 Wiley.
was explained as being due to the long and short-range forces of the LC continuous phase in which the isotropic droplets were embedded, that affect the separation and the structures formed. Furthermore, the addition of additives could alter the structures of the phase separation by stabilising domains, which are unstable in the absence of surfactants until they reach a well-defined size, or allow the formation of twisted structures.

There are also binary systems of LC mixtures. In a mixture of two LCs, two isotropic-nematic transitions may be observed. Brochard et al. described phase diagrams with complex shapes, including isotropic - nematic and isotropic - isotropic - nematic - nematic phase coexistence both with maximum and minimum temperature azeotropes for generic mixtures.

Much less studied are binary liquid systems consisting of a non-polymeric isotropic continuous phase and LC dispersed phase. A typical phase diagram of an isotropic liquid - LC mixture contains a coexistence (binodal) line, and an isotropic-nematic phase transition line. Araki and Tanaka reported how in a certain region of the phase diagram, both compositional change (phase separation) and orientational ordering (nematic ordering) take place simultaneously. Reyes et al. investigated binary mixtures of 5CB and ethanol, and reported a broad miscibility gap that lead to phase separation between two distinct phases via spinodal decomposition or nucleation and growth. Dependent on the concentration of 5CB and the temperature of the mixture, the LC-rich phase could be isotropic or nematic at the binodal line, or a phase transition was possible as the temperature was lowered.

Recently, a study be Serrano et al. reported on the macroscopic phase behaviour of...
a binary mixture composed of 5CB and methanol (MeOH).\textsuperscript{8} The corresponding phase diagram is shown in Figure 1.22 for reference, detailing experimental results which were confirmed by differential scanning calorimetry (DSC). Four different arrangements were found as a function of temperature and volume fraction, namely monophasic isotropic (I), monophasic nematic (N), biphasic isotropic-isotropic (I+I) and biphasic isotropic-nematic (N+I). This system displayed a Temperature $T$ - Composition $C$ phase diagram with an UCST of 25 $^\circ$C. The phase behaviour was subsequently implemented in thermoresponsive microfluidic architectures.\textsuperscript{208}

The differences in this study and its corresponding phase diagram (Figure 1.22), with the studies mentioned above, may have a number of explanations. First, the phase diagram in Figure 1.22 is presented with volume % of methanol and 5CB instead of moles. Further, the scope of the study by Serrano \textit{et al.} focused on the experimental results for phase separation of 5CB and methanol, which were confirmed by DSC. This study did not investigate the spinodal line of phase separation, however, the line of nematic onset was investigated. Here, the differences may lie in the fact that in the study by Serrano \textit{et al.}, where there is less than 12% methanol, there is no phase separation, as the methanol remains diluted in the 5CB, and the entire system becomes nematic. When there is more than 12% methanol in the system, isotropic 5CB and methanol will phase separate, and the 5CB will transition from isotropic to nematic at $-1^\circ$C, regardless of the increasing amounts of methanol. This may be due to the phase separation-phase transition gap. At 0$^\circ$C on the phase diagram, the system has phase separated, and the 5CB-rich region gets richer as the temperature is lowered, and thus isotropic-nematic transition takes place.
Figure 1.22: Phase diagram of a Binary Mixture of 5CB and MeOH. The phase diagram is divided into four zones: isotropic (I), nematic (N), isotropic + isotropic (I+I) and nematic + isotropic (N+I). Figure reprinted with permission from Ref[8]. Copyright 2018 Royal Society of Chemistry.
Chapter 2

Materials and Methods

This chapter is an introduction to the key experimental and characterisation techniques employed to develop and analyse materials and their properties in this doctoral work.

2.1 Materials

2.1.1 Liquid Crystal 4-cyano-4’-pentylbiphenyl (5CB)

4-cyano-4’-pentylbiphenyl (5CB) belongs to the alkycyanobiphenyl family (CB) family developed by Gray et al. The molecular structure of 5CB is presented in Figure 2.1. 5CB is widely studied because of its isotropic–nematic phase transition near room temperature. At 22.5 °C, 5CB undergoes a crystal-nematic transition and the nematic-isotropic phase transition occurs at 35 °C. The 5CB used in this work was sourced from Synthon Chemicals (99.5% (GC)) and used without further purification.

![Chemical structure of 4-cyano-4’-pentylbiphenyl (5CB)](image)

Figure 2.1: Chemical structure of 4-cyano-4’-pentylbiphenyl (5CB)

2.1.2 Liquid Crystal (RM257)

2-methyl-1,4-phenylene bis4-[3-(acyloyloxy)propoxy]benzoate (RM257), shown in Figure 2.2, is a reactive crosslinker with acrylate groups at each end of the mesogen, which react to form a polymer. RM257 is a solid at room temperature, and transitions to the nematic phase at 67 °C and to an isotropic liquid at 127 °C. The RM257 used in this work was obtained from Apollo Scientific, and used without further purification.
2.1.3 Microfluidic Chip

For extraction and analysis of droplets, a microfluidic glass chip fabricated by Dr Alexander Iles (Lab on a Chip, University of Hull) was used. A schematic of the microchip is given in Figure 2.3, showing a 35 x 5 x 0.03 mm chamber. The microchip was fabricated from two layers of Schott B270 glass 3 mm base and 1 mm top layer. These precoated glass wafers were exposed to UV with a mask to create the pattern for etching. The glass was etched with buffered HF solution to create the chamber. Then, a Datron 7 CNC milling machine served to create the access holes and this was thermally bonded to the etched bottom layer. The top layer featured 1.5mm diameter inlet and outlet holes. PTFE tubing was glued on each end and used to insert liquid into the channel using a glass syringe.

2.2 Materials Characterisation

2.2.1 Optical Microscopy

Optical microscopy for LC analysis provides not only images of micrometer-scale features via a multitude of phase contrast methods, but also alludes to their mesogen alignment and birefringence properties, i.e. providing reliable information about phe-
nomena on the molecular scale. Therefore optical microscopy has served for many decades as the primary method of LC analysis.

Microscopes use visible light and a series of lenses designed to produce magnified visual or digital images of objects that are too small to be seen with the naked eye. They work in a similar manner to a simple magnifying glass but instead of a single lens, rely on a relay lens system. An optical microscope can use either transmitted or reflected light, the main difference being the illumination configuration. Reflected light is used for fluorescence and imaging specimens that are opaque as light can be directed onto the surface and returned to the microscope objective by reflection. Transmitted light relates to the specimen being illuminated from the opposite side. This work focuses on transmitted light.

Figure 2.4: Schematic of an optical microscope. The diagram illustrates transmitted bright-field microscopy and includes illustration of light rays from the light source to the detector.

Brightfield illumination is the primary technique used in the following experiments, and requires an attenuation of the transmitted light when passing through the specimen. The term brightfield refers to the mounting position of the light source. This helps to observe specimens because it makes the object appear against a bright background. The contrast is generated by the absorption of part of the transmitted light in dense areas of the specimen. Other contrast enhancing techniques, which are readily employed in
2.2 Materials Characterisation

transmitted light microscopy include differential interference contrast (DIC), polarised light, phase contrast and darkfield microscopy.

A schematic of the optical train is presented in Figure [2.4]. Light is produced by a light source, travels through a circular field diaphragm, from which the condenser gathers wavefronts and concentrates them into a cone of light that illuminates a small area of the specimen located on the stage with uniform intensity.\textsuperscript{210} In addition, the condenser provides a means of regulating contrast.\textsuperscript{211} The transmitted light is captured by the objective, which produces the base magnification and relays a real image of the object to the eyepiece. The eyepiece, located closest to the eye or sensor projects and magnifies this image and yields a virtual image of the object. The objective and condenser can contain multiple lenses to prevent chromatic and spherical aberrations and improve image flatness.\textsuperscript{210}

The magnification and resolution of specimen depends heavily on the objectives. Magnifications are available ranging from 2X to 200X, and are denoted by an X next to the numeric value. The resolution achieved by the optical microscope is a measure of clarity, and is known as the Abbe diffraction limit. It is described as the minimum visible distance between two specimen points:

\[ d_0 = \frac{\lambda}{2n \sin(\theta)}, \]  

(2.1)

where \(d_0\) is the resolution or separation distance, \(\lambda\) is the illumination wavelength, \(n\) is the imaging medium refractive index, and \(\theta\) is equal to one-half of the objective angular aperture.\textsuperscript{212} Resolution is directly proportional to the illumination wavelength, and also depends on the refractive index of the imaging medium and the objective angular aperture, which is the semi-angle of the cone of light falling on the lens.\textsuperscript{212} As mentioned above, resolution is defined by the separation distance. The resolving power is the efficiency with which the microscope or technique can reveal two points as separate. The resolving power can be expressed by the following equation, and is termed the numerical aperture (\(NA\)) of the objective:

\[ NA = n \cdot \sin\theta, \]  

(2.2)

Furthermore, the resolution depends on the \(NA\) of the objective and the condenser. The relationship between numerical aperture \(NA\), wavelength of light used \(\lambda\), and resolution \(d_0\) can be expressed as:

\[ d_0 = \frac{1.22\lambda}{NA_{(obj)} + NA_{(cond)}}, \]  

(2.3)

where \(NA_{(obj)}\) and \(NA_{(cond)}\) is the NA of the objective and condenser respectively.\textsuperscript{212}

In this work, a Zeiss Axio Scope.A1 with a Prior H101F XY motorised stage was used. Digital capture through an optical microscope allows the ability to enhance features and extract information. Two types of cameras were used for image acquisition: Photron
Fastcam MC1 high-speed camera and a Lumenera Infinity 3-3UR camera. For this work, time-resolved digital image acquisition was carried out using a Photron Fastcam MC1 high-speed camera taking 50 frames per second (fps) at a resolution of 576 x 576 pixels, and a Lumenera Infinity 3-3UR camera was used, taking 1 fps with a resolution of 1936 x 1456 pixels.

For temperature-sensitive specimen, the optical microscopy stage was configured to hold a Linkam temperature controlled stage including the LTS120 and the PE120, shown in Figure 2.5. Specimen temperature could be controlled from 0.1°C min⁻¹ to 30°C min⁻¹ in the range of −30°C to 120°C using a water circulation pump. The stage had gas valves to enable nitrogen gas purging of the specimen environment. The Linkam temperature controlled stage had a sample area of 35 x 35 mm and an aperture of 5 mm in diameter. A T96 Peltier LinkPad controller was used to control the temperature, with an available temperature range of -25 to 120°C and an adjustable heating/cooling rate of 0.01 to 20°C min⁻¹.

![Figure 2.5: Schematic of the Linkam (a) PE120 and (b) LTS120 temperature controlled stage](image)

### 2.2.1.1 Thermal Analysis of Temperature Stage

The Linkam temperature-controlled microscope stage(s) was fitted with a 5 mm opening in the centre of the Peltier heated area to facilitate transmission microscopy. In addition, the heat source was fitted on one side of the stage, thus the left side was heated before the right side. For experiments where long term temperature accuracy was required, excluding thermal gradients or fluctuations was necessary. Therefore, a forward looking infrared (FLIR) camera was used to create an infrared image of the stage. FLIRs are thermal cameras which make pictures from heat instead of visible light. In addition, they detect small differences in heat and display them as different colours. Different materials absorb and radiate thermal energy at different rates, and FLIRs detect these subtle temperature differences and translate them into image detail.
Figure 2.6: FLIR thermal imaging of Linkam microscope stage over time. Thermal images for the Linkam stage set to (a) -5°C, (b) Schematic of points (1-5) on the stage wherein temperature was measured. (c) Corresponding temperature - time graph for the various measured points.

An FLIR camera was focused on the Linkam temperature stage, and the temperature of the stage was reduced to −5°C and thermal imaging of the stage was processed over time. Simultaneously, experiments were carried out in order to ensure that thermal fluctuations or gradients of the temperature stage did not impact results. The software FLIR research studio was used to analyse the results. Figure 2.6a depicts an image taken with the camera −5°C. Figure 2.6b presents a scheme for the points at which temperature was measured over time and Figure 2.6c presents this data in a graph. The graph confirms the general fluctuation over time was below 1°C, and did not surpass the nematic-isotropic transition temperature, nor did time effect the temperature of the stage. It was also observed that there was a temperature gradient from left to right on the stage, corresponding to the placement of the heat source. However, this gradient was small (0.5°C) and did not affect the order of the droplets.

Figure 2.7: FLIR thermal imaging of Linkam microscope stage during cooling.

Furthermore, during heating and cooling, there was a gradient of temperature from the edges to the centre of the stage. This was due to the 5 mm opening in the centre of the stage. Figure 2.7 shows two thermal images of the Linkam stage at different points
during cooling showing that there is a lag in the temperature at the centre of the stage in comparison to the edges during cooling. The difference in temperature between the stage and the opening did not exceed $1^\circ \text{C}$ at any point during cooling.

2.2.1.2 Polarised Optical Microscopy (POM)

Polarised Optical Microscopy (POM) is a contrast enhancing technique, which can be employed in order to examine the alignment and birefringence properties of LCs. Light from a light source of a microscope vibrates in more than one plane, i.e. in a variety of directions. When a polariser is placed before the condenser, the light waves travel in a unidirectional fashion, i.e. in a single plane. When another polariser, or analyser, is added after the objective at $90^\circ$, the polarised light is blocked, i.e. there is extinction and no light can pass through, as shown in Figure 2.8 (left).

Figure 2.8: Polarised light microscopy. The light path depicts the polarisation of light when the polariser and analyser are at $90^\circ$ to each other (left). A birefringent specimen is placed between the polariser and analyser, which splits the polarised light into the ordinary $n_o$ and extraordinary $n_e$ components, which are recombined at the analyser (right). Figure adapted with permissions from Ref 9.

Birefringence is the double defraction of light in a molecularly ordered material, such as a LC, due to orientation-dependent differences in refractive index. Birefringence causes one ray (ordinary, $n_o$) to be retarded relative to the other (extraordinary, $n_e$) as they experience different speeds while travelling through the medium. This is described in detail in Chapter 1.2.5. The recombination of the two rays at the analyser can produce interference colours. A schematic of POM when interacting with a birefringent material is shown in Figure 2.8 (right).

Optical anisotropy can be studied in the POM with the addition of retardation plates (fixed optical path difference) or compensation plates (variable optical path difference). Retardation plates are composed of birefringent material, such as quartz, mica, or gypsum minerals, have a precise thickness and the optical axis is contained in the plane of the plate. They are designed to introduce a fixed amount of retardation between the
2.2 Materials Characterisation

$n_o$ and $n_c$ rays passing through the LC. The most common retarders introduce phase retardations of $\lambda$, $\lambda/2$, and $\lambda/4$, i.e. wavelength ranges of 530 - 570 nm, 260 - 280 nm and 137 - 150 nm, respectively. A wavefront passing through a $\lambda$ retardation plate remains linearly polarised and retains the same vibration plane.

The birefringence of LCs can be determined quantitatively when observed under crossed polarised light in an optical microscope. Quantitative analysis of the interference colours can be accomplished by consulting a Michel-Levy chart, an example of which is shown in Figure 2.9. The Michel-Levy chart can be used when two of the three variables - birefringence, thickness and path difference are known. The colours visualised under microscope can be correlated with the thickness and birefringence of the LC.

![Michel-Levy Birefringence Chart](image)

Figure 2.9: Michel-Levy birefringence chart. The chart is used to determine the birefringence $\Delta n$, using the thickness, $d$ and path difference which shows three orders of the interference colour spectrum. Figure adapted with permission from Ref[10] available under Creative Commons Attribution-Share Alike 2.0 Generic license.

The x-axis marks the orders of retardation in multiples of 550 nm. The black area at the beginning (left-side) of the chart is known as zero-order black. The area between 0 and 550 nm displays first order interference colours, and the magenta colour seen at 550 nm is known as first-order red. The following set of colours in the 550 - 1100 nm region are termed second order colours, and so on. The chart in Figure 2.9 presents three orders of interference colours, but many Michel-Levy charts are available with up to sixth order interference colours.\[213\]

When a $\lambda$ plate is placed above the objective and below the analyser in the optical path, its slow axis is oriented 45° with respect to the crossed polarisers. A relative retardation at green wavelengths of 550 nm is introduced, and the green light is extinguished by crossed polarisers, resulting in the background to appear magenta red - the complimentary colour of green. A $\lambda$ plate is often referred to as a first order red plate because it produces the interference color similar to the first order magenta colour.
appearing in the Michel-Levy chart. The images obtained from insertion of a $\lambda$ plate into the optical microscope can be used to determine the fast and slow direction of the birefringent specimen, and the optic sign of uniaxial crystals.

Figure 2.10: (a) Uniaxial interference figure showing isochromes, isogyres and melatope. (b) Uniaxial figure under crossed polarised light showing first order grey interference colours. Uniaxial figure after insertion of a $\lambda$ plate, showing (c) optically positive and (d) negative character.

Under cross-polarised light, a LC droplet with a radial defect will contain dark bands that form a black cross called isogyres. The isogyre cross marks the areas where there is extinction. Depending on the thickness and birefringence of the LC, bands of colour that form concentric circles may also be present. These bands of colour are called isochromes. The isochromes represent the emergence of rays from the LC of the same retardation, i.e., the same birefringence colours. At the intersection point of the isogyres is the melatope, where light that has travelled along the optic axis exits in the field of view. The isogyre cross splits the LC droplet into 4 sectors, as shown in Figure 2.10a. If the LC is optically positive, upon insertion of the $\lambda$ plate into the light path, the NE and SW quadrants of the interference figure will display addition by one order (550 nm). For example, a LC exhibiting 1st order grey (Figure 2.10b) colours will now produce 2nd order blue colours (Figure 2.10c). The NW and SE quadrants will turn 1st order yellow, because subtraction by one order (550 nm) will have occurred in these quadrants. For an optically negative LC, the opposite is the case, i.e. the NE and SW quadrants of the interference figure turn 1st order yellow, due to the subtraction by one order (550 nm) that occurred in these quadrants (Figure 2.10d). The NW and SE quadrants will turn 2nd order blue, as addition will have occurred in these quadrants. The Michel-Levy chart (Figure 2.9) can be useful for visually determining the addition or subtraction of the LC quadrants, and thus, their optic sign.

In the birefringence experiments reported herein, a polariser and analyser were
used to study the qualitative birefringence of LCs, and a $\lambda$ plate and the Michel-Levy chart (Figure 2.9) was used for quantitative analysis of birefringence.

### 2.2.1.3 Photopolymerisation Set-Up

![Figure 2.11: Schematic of the optical microscope set-up. Illustration of the Zeiss AxioScope.A1 with motorised Prior stage. For clarity, the light path is highlighted. Transmitted light served for sample analysis. High intensity light from a Prior Lumen 200 metal halide lamp served for photopolymerisation via the reflection port and a suitable filter combination. Figure adapted with permission from Ref.9](image)

Photopolymerisation is a technique that uses light of a specific spectral range (often visible or ultraviolet (UV)) to initiate and propagate a polymerisation reaction forming a linear or crosslinked polymer structure. In microscopy, optical filters can be used to selectively transmit a selected range of the optical spectrum. Excitation filters are placed in the light path of the optical microscope, and pass only wavelengths within a set excitation range. Emission filters are placed within the imaging path of the optical microscope to pass only wavelengths within a set emission range. Dichroic filters are mirrors which are placed in between the excitation filter and the emission filter and reflect the light coming through the excitation filter and passes the light coming from the sample.
2.2 Materials Characterisation

Figure 2.11 illustrates the photopolymerisation set-up used in Chapter 6. A Zeiss Axio Scope.A1 with a Prior H101F XY motorised stage was configured to hold another light source. A Prior Lumen 200 metal halide lamp was placed in the reflected light source position, i.e. in the optical path between the objective and the camera. A hard coated OD 4.0 10nm bandpass filter (purchased from Edmund Optics) was used to selectively pass photons of 365 ± 2.0 nm wavelength. A 450 nm dichroic longpass filter (purchased from Edmund Optics) was placed at a 45° angle of incidence to reflect the light that passed through the bandpass filter to the sample, while allowing the (lower energy) light for imaging, originating from the halogen light source in transmission configuration, to pass through, as shown in Figure 2.12. Thus, the sample could be exposed to a specific wavelength range for photopolymerisation by the turning of a dial, while allowing simultaneous viewing of the process with transmitted light.

Figure 2.12: Schematic illustration of the photopolymerisation set-up. A halide lamp serves as a light source. A 365 ± 2.0 nm bandpass filter blocks all other wavelengths. A dichroic longpass pass filter is placed at 45° angle, to transmit light to the sample. The transmitted light source provides light to the sample and camera.

2.2.1.4 Analysis for Droplet Characterisation

After image acquisition, quantitative droplet investigation was carried out by digital image analysis in Python, following a custom-built code. Please note this section was extracted from Ref.217 by M. Patel et al. The associated Python code was written by collaborator Dr Anand N Pallipurath Radhakrishnan.

Droplet images were recorded on an optical microscope (Zeiss, Axio Scope A1) connected to a digital camera at 50 frames per second for short term analysis (Photron
2.2 Materials Characterisation

Figure 2.13: A representation of the steps taken by the computational script. (a) Edge detection performed by a Sobel transform that returns the gradient of an image. (b) Droplets identified after separation from the background through a watershed transform. (c) Processed image after re-segmentation of adjoining droplets, and filtering of partial droplets touching the edges of an image.

Fastcam MC1) and 1 frame per second for long term analysis (Lumenera Infinity 3-3UR). The diameter and the number of droplets were measured from the recorded images using a routine developed on Python 3.5 along with NumPy, SciPy, Matplotlib, and scikit-image modules. The script operated as follows. All images in a corresponding folder were opened and converted to a gray-scale format. The droplets in the images were subsequently separated from the background via a watershed algorithm, where a Sobel filter was used to identify the edges of the droplets (Figure 2.13a). The Sobel transform detected the edges of features based on the pixel gradients in the image, thereby preserving the size of the droplets. This resulted in a binary image. A binary fill hole step was then performed to ensure that all the pixels inside the droplets were also considered. A connected component labelling (CCL) step was subsequently carried out to distinguish between the droplets in an image, where each droplet was assigned a unique label (Figure 2.13b). The first watershed step did not separate droplets in contact with one another, and hence were identified as a single droplet. To address this issue, a second round of watershed algorithm was implemented, where a conditional filter chose features with $< 95\%$ circularity and a pixel area > around $\frac{2}{3}$ of the average area of all droplets in a given image. The watershed algorithm was performed on one feature at a time in the binarised format, and the newly re-segmented droplets were issued unique labels (Figure 2.14). The new labels were over-written on the initially labelled image. Droplets touching the borders of the images were then removed to avoid analysing droplets that were only partially included in the field of view of the camera, as shown in Figure 2.13c. The equivalent circular diameter and the number of droplets in each frame were then calculated, stored in an array and later exported in the CSV file format. Pixel areas were converted to actual $\mu m^2$ based on the magnification used in the optical microscopy. Particle Size Distributions (PSDs) of the droplets in each frame were also calculated. This automated analysis protocol provided results for the number of droplets, the average diameter as well as standard deviation as a function of time.
Figure 2.14: Sample images of the second watershed treatment to segment droplets in contact with one another. (a,b,c) Droplets identified as a single feature (yellow) distinguished from the background (purple) after the initial watershed segmentation and CCL step. (d,e,f) Droplets re-segmented from one another after a watershed treatment. A new label was assigned (green) to the segmented droplets to distinguish them from the initial droplet label (yellow) and the background (purple).

Calculation of trajectories and mean square displacement (MSD) of droplets was carried out using Fiji,\textsuperscript{223} ImageJ,\textsuperscript{224} Droplets were tracked using a Particle Detector and Tracker plugin: MOSAIC,\textsuperscript{225} which outputs the x and y coordinates of each trajectory for further calculation. The mean square displacement (MSD) is given by the Einstein formula:\textsuperscript{226}

$$MSD = \left\langle \frac{1}{N} \sum_{i=1}^{N} |r_d - r_d(\tau_0)|^2 \right\rangle_{\tau_0},$$ \hspace{1cm} (2.4)

Where \(N\) is sample size and \(r_d\) are the coordinates and dimensions.

## 2.2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a surface imaging technique which uses electrons for imaging in a similar way that light microscopes use visible light. The wavelength (\(\lambda\)) of electrons are much smaller than that of light, and are calculated using the de Broglie wavelength equation:

$$\lambda = \frac{h}{mv},$$ \hspace{1cm} (2.5)

where \(h\) is the Planck constant, \(m\) is the mass, and \(v\) is the velocity. Momentum is given to electrons by accelerating it through a potential difference, giving it a kinetic energy. Thus, increasing the accelerating voltage of the SEM will decrease the electron wavelength, and produce a higher resolution. SEM has a greater depth of field, and a higher resolution 1000 times greater than that of an optical microscope.
The SEM operates by generating an electron beam from an electron gun, and accelerating it through a series of lenses and apertures, which act to focus it on to the surface of a sample. The electron beam ranges in energy from several hundred eV to over 30 keV and focuses onto a 5 nm-in-diameter spot. The electron beams scan the sample in a zig-zag type pattern (raster scanning) across the x-y plane, and interacts with atoms on the sample surface. A number of electromagnetic interactions occur resulting in the emission of secondary electrons and backscattered electrons that are characteristic of the sample. These signals are collected by detectors. The detector signal is synchronised with known locations of the electron beam on the sample, and the signal is used to develop the corresponding image pixel. Since SEM uses electrons to produce an image, most SEMs require that the samples be electrically conductive. In order to view non-conductive samples, the sample is usually coated with a thin layer of a conductive material using a sputter coater.

SEM images were obtained using a JEOL JSM 6701F scanning electron microscope operating an accelerating voltage of 10.0 kV. The instrumental resolution was about 23 nm as determined with gold particles sputtered onto a carbon substrate. The SEM sample chambers operated at low pressure (less than $3 \times 10^{-4}$ Pa), hence, the samples were dried before sample preparation. Samples were prepared using conductive carbon adhesive tabs which were added to aluminium stubs and coated in gold using an Agar manual sputter coater with a current of 30 mA for 15 seconds.

### 2.2.3 Focused Ion Beam Microscopy

The working principle of a focused ion beam microscope (FIB) resembles that of SEM, however, while a SEM uses a focused electron beam to image the sample, a FIB setup relies on a focused beam of ions, instead. One example is a helium ion microscope, which employs a focused beam of helium ions across a surface to generate an image from the resulting secondary electron emissions. Helium ions can be focused into a smaller probe size and provide a smaller interaction volume at the sample surface compared to electrons, therefore the helium ion microscope generates higher resolution images with better contrast. In consequence, a resolution of $<0.3$ nm may be obtained at an acceleration voltage of 25-30 kV with beam currents between 1 fA and 25 pA.

In this work, a helium ion microscope (Orion Nanofab, Carl Zeiss) at an acceleration voltage of 25 kV was used for the physical characterisation of LC microparticles. Samples were prepared by coating with a thin layer of gold as described for SEM.

### 2.2.4 FTIR

Fourier transform infrared spectroscopy (FTIR) is a technique used to obtain the infrared spectrum of absorption, emission, and photoconductivity of solids, liquids, and
gases. The infrared absorption bands may serve to identify molecular components and structures.

The infrared beams pass through a Michelson interferometer which modulates the wavelength from a broadband infrared source. The beam then passes through the sample gas cell before it hits the detector. The detector measures the intensity of transmitted or reflected light as a function of wavelength. The raw data 'interferogram' is recorded consisting of the detector signal as a function of time. An absorbance spectrum is obtained from a Fourier transform.\textsuperscript{229,230} The FTIR spectra are usually presented as plots of intensity versus wavenumber (in cm\textsuperscript{-1}), which is the reciprocal of the wavelength. The intensity can be plotted as the percentage of light transmittance or absorbance at each wavenumber.

In this work, IR spectra were measured in the 4000 to 1500 cm\textsuperscript{-1} wavenumber region using an FTIR spectrometer VERTEX 70/70v (Bruker Corporation, Germany) coupled with platinum diamond attenuated total reflectance (ATR). Samples were placed on the ATR crystal, and then the spectrum was recorded. The spectrum of air was used as a background before each sample analysis. Background and sample spectra were taken at room temperature (22\textdegree C) at a spectral resolution of 0.4 cm\textsuperscript{-1}. 100 scans were performed for each measurement.

### 2.2.5 Dynamic Light Scattering

Dynamic light scattering (DLS) is a tool for studying the diffusion behaviour of spherical particles in solution.\textsuperscript{231} DLS provides information about particle size (hydrodynamic diameter, $d_H$) and size distribution (polydispersity index, PDI) by measuring the speed at which particles are diffusing due to Brownian motion to serve for size determination of the suspended particle ensembles. This is done by directing a single frequency laser to the sample and measuring the rate at which the intensity of the scattered light fluctuates. The intensity is then used to generate a correlation function. The correlation function $G(\tau)$ describes how long a particle ensemble is located at the same spot within the sample. If particles remain at the same position for a certain period, the correlation function is linear. If there is an exponential decay, the particle is moving. Furthermore, the correlation function $G(\tau)$ is used to determine the translational diffusion coefficient. This is done by comparing the intensity of the scattered light at a time $t$, with the intensity of the same intensity trace shifted by the delay time $\tau$.\textsuperscript{232}

Large particles exhibit a slower Brownian motion in comparison to smaller ones. The relation between the speed of the particles and the particle size is given by the Stokes-Einstein equation (2.6). The speed of the particles is given by the translational diffusion coefficient, $D_c$.

$$D_c = \frac{k_B T}{6\pi \eta R_H},$$

(2.6)
Where $D_c$ is the diffusion coefficient, $K_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\eta$ is the solvent viscosity, and $R_H$ is the hydrodynamic radius. $R_H$ is the hypothetical measurement of a hard sphere that diffuses with the same speed through the solvent. A requirement for the Stokes-Einstein equation is that the movement of the particles must be solely based on Brownian motion. Thus, sedimentation would lead to inaccurate results.

Analysis of particles or micelles was carried out by dynamic light scattering (DLS) (Beckman Coulter DelsaMax Pro) at 20°C. 10 measurements were taken for each sample. All particles were 1 mg/mL dispersions in MeOH placed in disposable plastic cuvettes for measurement.

### 2.2.6 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) provides information about the physical and chemical phenomena of a sample, such as chemisorptions, thermal decomposition, phase transitions, absorption and desorption. In TGA, the mass of a sample is measured as it is heated or cooled over time in a given environment. The plot of weight change against temperature is called the thermogravimetric curve or thermogram. The first derivative curve is also usually plotted on the thermogram. The peak of the first derivative indicates the point of greatest rate of change on the weight loss curve. This is also known as the inflection point.

Thermogravimetric analysis (TGA) was performed on a Discovery TGA (Perkin Elmer Pyris1) operated using TA Instruments Trios (version 3.81) software. The thermograms of the samples were recorded under air with a heating rate of 20°C min$^{-1}$ with all samples heated to 500°C.
III
Results
Chapter 3

Temperature-Induced Liquid Crystal Microdroplet Formation in a Partially Miscible Liquid Mixture


Liquid-in-liquid droplets are typically generated by the emulsification of immiscible fluids by shearing or microfluidics. In contrast, partially miscible liquids with a critical solution temperature display a temperature-dependent mixing behaviour. In this work, we demonstrate how cooling an isotropic liquid-liquid crystal mixture from a miscible to an immiscible state allows the controlled formation of microdroplets. This temperature-induced approach offers a scalable and reversible alternative to droplet formation with relevance in diagnostics, optoelectronics, materials templating and extraction processes.

3.1 Introduction

The nucleation and growth of microscopic droplets is of profound and widespread relevance in colloidal and interfacial science and technology. The intrinsic, spontaneous formation and growth of a nucleus upon cooling of binary systems has been studied from a theoretical perspective of the phase ordering process. Much work has been done to understand systems showing condensation, crystallisation, phase separation of binary alloys, and more recently LC mixtures.

In recent studies of nucleation in a binary liquid mixture, Mauri et al. observed how phase separation is a convection-driven process, induced by a body force which is proportional to the chemical potential gradients. Later, the same group found that
phase separation followed the diffuse interface model, where convection and diffusion were coupled via a nonequilibrium capillary force. This driving force induces a material flux which is much more pronounced than that due to pure molecular diffusion alone.\cite{17} Further, Tanaka demonstrated that droplet motion is hydrodynamically driven by a Marangoni force due to an interfacial tension gradient produced in each droplet as a consequence of composition correlation among droplets.\cite{241}

When a LC is entered as one or both component(s) of a binary liquid mixture, interesting phenomena are observed with technological relevance. Conventionally, LC droplets are generated by the partitioning with another immiscible fluid (see Chapter 1.2.6 for further details). The formation of LC microdroplets in an isotropic non-polymeric continuous phase by temperature-induced phase separation has to the best of our knowledge, not been investigated to-date. A study be Serrano et al. recently reported on the macroscopic phase behaviour of a binary mixture composed of 5CB and MeOH.\cite{8} The corresponding phase diagram is shown in Figure 1.22 for reference.

This chapter focuses on how a binary mixture composed of 5CB and MeOH enables the temperature-induced formation of LC microdroplets. We investigate the droplet evolution to resolve nucleation and growth processes and identify critical parameters that govern the number and size distribution of LC droplets. Finally, we quench the liquid mixture below the isotropic-to-nematic transition temperature and study the feasibility of this approach for the generation of temperature-stable and well-defined nematic droplets.

### 3.2 Experimental

#### 3.2.1 5CB Droplet Formation

**Reagents** 5CB (see Chapter 2.1.1). MeOH (HPLC grade) was purchased from Sigma Aldrich. All compounds were used without further purification.

**Sample preparation** 5CB and MeOH with a volume ratio of 30:70 were mixed in a sealed glass cuvette, which was enclosed by a Peltier-regulated sample compartment that allowed control over both temperature and stirring (Quantum Northwest, Qpod 2e). Unless stated otherwise, a 30:70 volume ratio of 5CB:MeOH was used for all experiments. Samples were heated to 35 °C in the cuvette.

For microscopic analysis, 10 µl of the homogeneous 5CB:MeOH mixture was deposited between a glass slide and cover slip and sealed with varnish (purchased from Rimmel: containing 15-40 % ethyl acetate, 15-40 % butyl acetate, 5-15 % nitrocellulose, 1-10 % isopropylalcohol) to prevent MeOH evaporation. This made an 18 × 18 mm² sealed sample compartment of 30 µm thickness. The sealed slide was analysed under an optical microscope. A binary liquid mixture of 30 vol % 5CB, 70 vol % MeOH was used for all experiments, unless stated otherwise.
Sample analysis: The slide was placed under an upright microscope (Zeiss, Axio Scope A1) that was operated in transmission and primarily in brightfield mode. Fine temperature control was achieved by an enclosed Peltier-driven sample stage (Linkam, PE120). For low temperature experiments, a Linkam LTS120 was used and nitrogen was introduced into the chamber to prevent condensation. In-situ droplet formation and short-term growth were recorded by time-resolved digital image acquisition using a Photron Fastcam MC1 high-speed camera taking 50 frames per second (fps) at a resolution of 512 x 512 pixels. For nematic droplet analysis, a Lumenera Infinity 3-3UR camera was used, taking 1 fps with a resolution of 1936 x 1456 pixels. See Chapter 2.2.1 for a detailed description of the microscope set-up and underlying working principles. For temperature quench and cooling rate experiments, the cell was heated to 35 °C and then cooled at a defined cooling rate ranging from 1 °C min⁻¹ to 20 °C min⁻¹ to a target temperature below $T_{ps}$. Note that for the purpose of this study, $T_{ps}$ is referred to as the phase separation temperature on the binodal line for a particular composition. The quench depth $\Delta T$ relates to $|T_{target} - T_{ps}|$. With a 30:70 vol % mixture of 5CB:MeOH, the $T_{ps}$ was 22.5 °C. Quantitative droplet investigation was carried out by a computational image analysis code developed in Python, as described in Chapter 2.2.1.4. The automated analysis protocol enabled the extraction of kinetic information. Droplets from the high-speed images were identified, distinguished, and the number of droplets, the average diameter as well as standard deviation computed as a function of time. Calculation of trajectories, displacement and mean square displacement (MSD) of droplets was carried out using Fiji. Droplets were tracked using the particle detector and tracker plugin MOSAIC, which provided the x and y coordinates of each trajectory for further calculation.

3.3 Results and discussion

The recently reported phase diagram by Serrano et al. demonstrated how a binary mixture of 5CB and MeOH displays four different arrangements as a function of temperature and volume fraction. As mentioned in Chapter 1.1, a spinodal curve divides the region inside the phase coexistence curve of a phase diagram into an unstable region, in which phase separation is driven by spinodal decomposition, and a metastable region where phase separation is triggered through a nucleation and growth process. For an off-critical mixture as used herein, demixing typically occurs via nucleation and growth. A characteristic example for the nucleation and growth process observed under high speed imaging is shown in Figure 3.1(a-e). Samples were heated to 35 °C, a temperature well above their UCST, to ensure a monophasic solution. When cooled from 35 °C at a rate of 1 °C min⁻¹, droplets began to nucleate at 22.5 °C and grow. The nucleation of these droplets occurred over 0.2 seconds. If adjacent droplets met, they coalesced. These droplets were allowed to grow and mature. Upon reheating of the
3.3 Results and discussion

Figure 3.1: Reversible droplet formation. a-e: Nucleation and early-stage growth of isotropic droplets over the initial 0.2 seconds at 22.5 °C. f-j: Disappearance of mature droplets over 7 seconds upon heating to 35 °C. Scale bar: 1 µm.

Sample up to 35 °C at 1 °C min⁻¹, the droplets disappeared and the mixture became monophasic, as shown in the sequence of images in Figure 3.1(f-j). The temperature where microdroplets formed was in general agreement with the macroscopic critical solution temperature for a mixture of 30 vol % 5CB and 70 vol % MeOH recently reported by Serrano et al.

3.3.1 5CB/MeOH temperature quench

Droplet growth upon demixing for off-critical mixtures of binary fluids was generally described in three phases. Nucleation occurred when a concentration partitioning reached a critical size (phase I, timescale: µs). Nucleation occurred instantaneously, i.e. phase separation of 5CB occurred where all droplets nucleated in a single instant, after which no new occurrences of nucleation occurred, even as the temperature of the system decreased. After this, the droplet grew spontaneously by diffusion (phase II, timescale: ms). Thereafter or simultaneously, the droplets underwent further growth by coalescence and Ostwald ripening (phase III, timescale: s-min).

Figure 3.2(a-c) displays microscopic images of 5CB-rich droplets in the MeOH-rich continuous phase 20 seconds after nucleation with quench depths (ΔT) of (a) ΔT = 0.5 °C, (b) ΔT = 2.5 °C and (c) ΔT = 7.5 °C, respectively. Figure 3.2(d) depicts a time-resolved evolution of the mean droplet size for different quench depths. While a shallow quench depth of ΔT = 0.5 °C led to a droplet diameter of around 4.7 ± 1.2 µm at 60 seconds, a quench depth of ΔT = 2.5 °C resulted in droplets of 7.6 ± 2.2 µm in size, increasing ΔT = 7.5 °C caused a further increase in droplet diameter...
3.3 Results and discussion

Figure 3.2: Droplet diameter vs. quench depth. a-c: Microscopic images of isotropic 5CB-rich droplets in MeOH-rich continuous phase 20 seconds after nucleation at quench depths of (a) $\Delta T = 0.5^\circ C$, (b) $\Delta T = 2.5^\circ C$ and (c) $\Delta T = 7.5^\circ C$. In all cases, the mixture was cooled from 35 $^\circ C$ at a cooling rate of 20 $^\circ C$ min$^{-1}$. The scale bar represents 10 $\mu m$. (d) Overview of droplet mean diameter and standard deviation for respective quench depths over time.

...to 10.4 $\pm$ 2.2 $\mu m$ within the observed time span as shown in Figure 3.2d. Following equation [1.2], increasing the quench depth ($\Delta T$) from 0.5 $^\circ C$ to 2.5 $^\circ C$ and 7.5 $^\circ C$ led to an increasing growth exponent of 0.19, 0.32 and 0.35 respectively, in the first stages of droplet growth. The dependence of the growth exponent on quench depth is in agreement with previous studies. However, this was primarily discussed for phase transitions of liquid crystal mixtures, where the growth exponent increased from 0.5 to 1, rather than phase separations. For phase transitions, the dependence of the growth exponent on quench depth was related to a larger difference in free energy between the isotropic and the ordered state.

Notably, the dependence of the mean droplet size once reaching a steady state after temperature quench $\Delta T$ is in line with a study by Luo and coworkers for supersaturation-induced emulsions, who found that the droplet volume was linearly proportional to the applied quench depth. In our work, the observed droplet diameter of 4.7 $\pm$ 1.2 $\mu m$ ($\Delta T = 0.5^\circ C$), 7.6 $\pm$ 2.2 $\mu m$ ($\Delta T = 2.5^\circ C$) and 10.4 $\pm$ 2.2 $\mu m$ ($\Delta T = 7.5^\circ C$) also followed closely a $L \propto \Delta T^{1/3}$ relationship.

Analysis of the number of droplets as a function of time provided further insights, as shown in Figure 3.3. For a quench depth of $\Delta T = 0.5^\circ C$, the number of droplets...
increased over 20 seconds and then settled slightly below the maximum level. In contrast, at $\Delta T = 7.5^\circ C$ droplets appeared within the first seconds and then reduced in count significantly over time. Previous research focused on the effect of quench depth on the critical nucleus size, with an understanding that with increasing quench depth, the free energy barrier to nucleation is reduced to values similar to the energy of thermal fluctuations at the spinodal. In this context, the critical nucleus size was found to decrease with an increasing quench depth which is in line with our observations.

The dispersity of droplets was further investigated by analysis of larger sample sizes, using images acquired at frame rates of 1 image per second. The droplet population is presented in a histogram in Figure 3.4(a-c) over the course of the initial 60 seconds. Notably, the evolution of both droplet size and size distribution was found to depend strongly on the quench depth ($\Delta T$). For (a) $\Delta T = 0.5^\circ C$, the droplets remained relatively stable, with some larger droplets that formed at the expense of smaller ones. In contrast, for (c) $\Delta T = 7.5^\circ C$, the droplet population became multimodal after 30s, with an overall profound size increase and broadening of the detected droplet diameters.

Droplet motion was analysed through individual trajectories along the x and y axis, as presented in Figure 3.4(d-f). Each droplet was followed throughout its residence in the field of view. The colour coding in the legend illustrates the time $t_0$ when the droplet first entered the frame, i.e. for $t_0 = 0$ seconds the droplets formed within the field of view, while for $t_0 \geq 0$ seconds the droplets formed elsewhere, then moved inside the field of view.
view and were tracked thereafter. For a quench depth (d) $\Delta T = 0.5^\circ \text{C}$, the motion was essentially random around the starting position, with few droplets exhibiting directional motion away from the starting point.

Figure 3.4: Dispersity and Trajectory of Isotropic Droplets According to Quench Depth. (a-c) Diameter histogram of isotropic 5CB-rich droplets over time at quench depths of (a) $\Delta T = 0.5^\circ \text{C}$, (b) $\Delta T = 2.5^\circ \text{C}$, (c) $\Delta T = 7.5^\circ \text{C}$. (d-f) Trajectory of droplets along the x and y axis over the course of 60 seconds at quench depths of (d) $\Delta T = 0.5^\circ \text{C}$, (e) $\Delta T = 2.5^\circ \text{C}$, (f) $\Delta T = 7.5^\circ \text{C}$. (g-i) Mean square displacement (MSD) of droplets at quench depths of (g) $\Delta T = 0.5^\circ \text{C}$, (h) $\Delta T = 2.5^\circ \text{C}$, (i) $\Delta T = 7.5^\circ \text{C}$ over time. The colour code represents the time at which a new droplet entered the frame.
As the quench depth increased to (e) $\Delta T = 2.5^\circ C$, there were more instances of directional motion with some random fluctuation around the starting position. At a quench depth of (f) $\Delta T = 7.5^\circ C$, droplet movement appeared primarily directional and along the same axis. Hence, in addition to diffusion and coalescence led by Brownian motion, we identified a directional motion of the droplets, which became more pronounced with increasing quench depth. The corresponding mean square displacement (MSD) is shown in Figure 3.4(g-i) as a function of time lag, $\tau$, with $\tau = t - t_0$. If the droplet trajectories were solely led by diffusion, a linear correlation between the quench depth and the MSD would be expected. However, the curvature of the graphs, particularly at large quench depths, suggests an external force. In comparison to the steep increase in MSD for $t_0 < 10$ seconds, a shallow incline was observed for droplets that moved later into the field of view, suggesting that the directional droplet motion was a direct consequence of the applied cooling and faded thereafter. A likely cause of directional droplet motion in immiscible fluid mixtures is related to Marangoni-driven flow, where a temperature gradient across the droplet interface leads to non-uniformity in surface tension. This was demonstrated in detail by Cho et al.\textsuperscript{[248]} in our experimental set up, droplets were formed in a liquid cell that was cooled on a microscopy temperature stage with circular cut-out. As a consequence, cooling resulted in a temperature gradient from edge to centre of the cell, as discussed in Chapter 2.2.1.1 and demonstrated in Figure 2.7. We found the droplets to be driven from the hot to the cold region, i.e. from perimeter to centre. As the quench depth ($\Delta T$) was increased, a larger temperature gradient was observed along the plate for a longer period of time, thus increasing directional droplet motion.

Our findings emphasise the factors that influence droplet growth by coalescence, namely the interdroplet distance and the droplet motion, both of which are affected by the temperature quench. Eventually, with increased spacing and reduced mobility, the droplets reached a steady state, after which events of further coalescence and Ostwald ripening were observed occasionally.

### 3.3.2 5CB/MeOH cooling rate

We further investigated the effect of cooling rate on droplet formation and growth, as shown in Figure 3.5. In all experiments, a homogeneous mixture of 5CB and MeOH was cooled from $35^\circ C$ to $15^\circ C$, with a quench depth of $\Delta T = 7.5^\circ C$ below $T_{ps}$ at cooling rates varying between $20^\circ C$ min$^{-1}$ and $1^\circ C$ min$^{-1}$. For all cooling rates, a representative snapshot of LC droplets taken 5 seconds after nucleation, is shown in Figure 3.5(a-d). Results from the computational analysis of droplets are presented in Figure 3.5e.

Cooling rates of $\geq 20^\circ C$ min$^{-1}$ led to greatly increased initial numbers of droplets, which rapidly decayed over the first 20 seconds. In contrast, slower cooling rates resulted in a lower initial number of droplets which remained more constant over time. The
development of the number of droplets with time may be directly related to the droplet density. Faster cooling rates ($\geq 10 \degree \text{C min}^{-1}$) led to a higher droplet density and thus smaller interdroplet distances, which in turn implied a higher probability for coalescence. We note that at a cooling rate of $1 \degree \text{C min}^{-1}$, the number of nucleated droplets was ten times less in comparison to a cooling rate of $20 \degree \text{C min}^{-1}$. The rate of cooling and related droplet density had a direct impact on the observed growth mode; at high cooling rates, droplet growth was dominated by coalescence. In contrast, at lower cooling rates and enhanced interdroplet distances, nucleation growth proceeded without coalescence.

As a result, the cooling rate affected the polydispersity for droplet diameter: slow cooling rates of $1 \degree \text{C min}^{-1}$ resulted in a smaller average diameter and standard deviation compared to fast cooling rates of $20 \degree \text{C min}^{-1}$. To quantify the droplet movement, we analysed the individual droplet trajectories as detailed in Figure 3.6. While we observed directional motion at both $1 \degree \text{C min}^{-1}$ and $20 \degree \text{C min}^{-1}$, the gradient of the MSD was cooling rate-dependent. As pointed out above, faster cooling rates and thus higher droplet densities implied a higher probability for coalescence. Thus, the increased MSD may be a direct consequence of coalescence-induced coalescence cascade processes and related hydrodynamic flow.\[\text{247-249}\] As the quench depth remained the same for the cooling rate experiments, in the long-term, the volume fraction of droplets were eventually the same irrespective of their growth mode.
3.3 Results and discussion

Figure 3.6: Dispersity and trajectory of isotropic droplets according to cooling rate. (a-b) Polydispersity of 5CB-rich droplets over time with cooling rates of (a) $1 \degree C \text{ min}^{-1}$, (b) $20 \degree C \text{ min}^{-1}$. (c-d) Trajectory of droplets along the x and y axis over the course of 60 seconds at cooling rates of (c) $1 \degree C \text{ min}^{-1}$, (d) $20 \degree C \text{ min}^{-1}$. (e-f) Mean Square Displacement of droplets at cooling rates of (e) $1 \degree C \text{ min}^{-1}$, (f) $20 \degree C \text{ min}^{-1}$ over time. Quench depth: $\Delta T = 7.5 \degree C$. 

Quench depth: $\Delta T = 7.5 \degree C$. 
3.3 Results and discussion

3.3.3 Nematic 5CB-rich droplets

5CB is a thermotropic LC and a transition from the isotropic to the nematic phase is expected upon cooling. In the nematic phase, the LC exhibits a long-range orientational order without positional order. Volume confinement leads to an elastic distortion of the mesogen director field, typically resulting in topological defects, such as point defects with radial, bipolar or preradial configuration. The type of mesogen arrangement in LC droplets is highly sensitive to their size, boundary conditions and/or external fields.

![Image](attachment:image.png)

Figure 3.7: Formation of nematic droplets. Image sequence for a temperature quench of $\Delta T = 27.5^\circ$C. (a-c) Bright-field images of (a) isotropic droplets just above the transition temperature, (b) undergoing isotropic-nematic phase transition, (c) nematic droplets. (d) Corresponding nematic droplets imaged under cross-polarised light. Each image snapshot is taken 1 second apart. The scale bar represents 10 $\mu$m. (e) Overview of droplet mean diameter (with standard deviation) and temperature over time (cooling rate: 20 $^\circ$C min$^{-1}$).

In the previous sections, the droplets remained in the isotropic phase. According to the phase diagram by Serrano et al., (see Figure 1.22) the phase transition of MeOH-enriched 5CB from the isotropic to the nematic state is expected at -0.5 $^\circ$C. The controlled formation of nematic droplets was therefore the subject of the following study. A homogeneous mixture of 5CB and MeOH was cooled from 35 $^\circ$C to -5 $^\circ$C, corresponding to a quench depth of $\Delta T = 27.5^\circ$C. Below the $T_{ps}$, the droplets nucleated and grew by diffusion and coalescence. Upon reaching the isotropic-nematic phase transition line, the droplets became nematic. Figure 3.7a-c shows bright-field images of droplets taken 2 seconds apart, revealing the isotropic-nematic transition and the position of defects in the droplet. Figure 3.7d presents polarised light micrographs of nematic 5CB-rich droplets in the MeOH-rich continuous phase that exhibit a radial configuration with homeotropic anchoring of the LC. As shown in Figure 3.7e, the diameter
of the droplets increased rapidly when cooling through the isotropic temperature range. Upon reaching the nematic phase, the droplet growth by coalescence slowed down considerably. The growth exponent $n = 0.36$ was similar to the previously discussed isotropic quench ($n = 0.35$, $\Delta T = 7.5 ^\circ C$).

Historically, nematic LC droplets have been prepared either through phase separation of a polymer - LC mixture (PDLC)\textsuperscript{37} or conventional bulk mechanical shearing through homogenisation. While these offer scalable solutions, their preparation is often plagued by a lack of size control.\textsuperscript{111,111–117} Alternative methods such as microfluidic processing and polyelectrolyte multilayer templating offer access to well defined LC droplets, yet the former is limited to larger diameter and the latter involves a relatively elaborate preparative protocol.\textsuperscript{96,121,123,125,126} In comparison, the herein proposed route of nematic LC droplet formation distinguishes itself through the ease of fabrication, control and tunability of the achieved droplet populations, and reversibility of formation.

### 3.4 Conclusions

In conclusion, we report on the controlled formation of LC microdroplets by a temperature-induced phase separation process, and the identification of crucial parameters that govern this phenomenon. Cooling from $35 ^\circ C$ to below the phase separation temperature of $22.5 ^\circ C$ initiated LC droplet nucleation. The growth patterns were found primarily dependent on the quench depth and the cooling rate of droplets. The temperature quench depth played a crucial role for the observed motion, affecting droplet size and dispersity. The cooling rate had a strong influence on the number of droplet nuclei. Upon cooling to $-5 ^\circ C$ into the nematic regime, droplets adopted a radial configuration. Thus, phase segregation of liquid mixtures with a critical point of miscibility may offer control over nucleation and size evolution of droplets with ease of fabrication and reversibility of the process. Such transient LC droplets with well-defined size and mesogen arrangement provide in our view, a multitude of opportunities for materials templating and sensing applications.
Chapter 4

Long Term Phase Separation Dynamics in a Liquid Crystal Containing Binary Fluid Mixture


The dynamics of long term phase separation in binary liquid mixtures have been the subject of numerous investigations. In this chapter, we study a binary liquid where the minority phase is confined to a LC-rich droplet by investigating the evolution of the nematic droplets in size, defect and mesogen alignment over time. The interactions of a binary liquid reaching equilibrium can be visualised through the internal configurations of the LC-rich droplet. Furthermore, we elucidate the differences in thermodynamics of phase separation in bulk systems vs phase separation in microscale and droplet systems.

4.1 Introduction

The effect of nonmesogenic species, in particular polymers, on the phase transitions of LCs is of interest for understanding mesogenic order and tuning viscoelastic properties. Generally, the transition temperature decreases if a solute is added to the LC, thus reducing the anisotropic interactions. Thoen et al. found solutes such as biphenyl and cyclohexane caused a linear decrease in the nematic-isotropic and the nematic-smectic-A transition temperature with increasing mole fraction. The nematic-isotropic transition was described as a first-order transition with latent heat that was independent of mole fraction of the solute. Studies using hexane as a solute, however, found that the isotropic to nematic phase transition shifted toward lower tem-
4.1 Introduction

It was deduced that the addition of a solvent diluted the LC, resulting in an impurity mechanism, which introduced a concentration fluctuation and softened the viscoelastic properties of the mixture with respect to that of a pure LC. Furthermore, simulation work by Jana et al. deduced that the addition of an impurity, such as hexane, to a LC increased the entropy of a LC/hexane system by inducing random orientation of the LC molecules, therefore phase transitions were entropy-driven.

Serrano et al. and Fornerod et al. investigated a binary liquid mixture of an isotropic liquid, MeOH, with a LC, 5CB. The dilution using MeOH allowed to finely tune (i.e. reduce) the isotropic-to-nematic transition temperature of 5CB. MeOH was miscible with 5CB below 10 vol %, but reduced the isotropic-nematic phase transition temperature from 35°C to 7.8 ± 0.4°C with 10% MeOH. Above 10%, there was initially an isotropic-isotropic liquid phase separation, and thereafter an isotropic-nematic phase transition of the LC component with decreasing temperature. This was also demonstrated by Reyes et al. using ethanol as the non-nematogenic component.

The dynamics of liquid-liquid phase separation has been the subject of numerous investigations in food science, polymer physics and most recently, cell biology. The biological significance of liquid-liquid phase separation is evidenced by membraneless structures found in cells. Proteins are driven into another phase with different physiochemical properties by multivalent macromolecular interactions. This induces the formation of membraneless organelles which are spherical bodies that rapidly form and dissolve, and exhibit dynamic internal organisation. For example, liquid-phase compartments in the nucleus and the cytoplasm remain separated from each other through phase separation. Moreover, biomolecular condensates formed by phase separation have been found to regulate key cellular processes involved in cancer cell pathology, and the dysregulation of liquid-liquid phase separation is increasingly implicated as a driver of oncogenic activity. Furthermore, the dynamics in the late stage of the phase separation has received considerable attention. After the initial processes of nucleation and coarsening, domain growth of the new phases proceeds through a sequence of physically distinct hydrodynamic, viscous or inertial effects which ultimately lead to thermodynamic equilibrium. Generally, Ostwald ripening dominates in driving the system to equilibrium until domain sizes reach the capillary length, after which fluid flow develops, as discussed in Chapter 1.1.2.

Chapter 3 showed that cooling of an off-critical mixture of a binary fluid composed of 5CB and MeOH led to nucleation and growth of LC droplets which could be isotropic or nematic according to their temperature. We reported the tuning of the size and number of droplets by temperature quench and cooling rate. When phase separation is led by nucleation, and the minority phase is a nematic LC droplet, new perspectives are offered through the ability to study the physical properties of the droplet evolving towards equilibrium through the internal configurations of a LC. We demonstrate this
experimentally, using polarised optical microscopy, and explain the interactions leading towards the equilibrium of a phase-separating binary liquid. Furthermore, we elucidate the differences in thermodynamics of phase separation in bulk systems vs phase separation in droplet systems. We rely on computer simulations and thermodynamic considerations to rationalise our results and elucidate the role of droplet size on the phase behaviour.

### 4.2 Experimental

**Reagents** 5CB (see Chapter 2.1.1). MeOH (HPLC grade) was purchased from Sigma Aldrich. All compounds were used without further purification.

**Sample preparation** Sample preparation was identical to that described in Chapter 3.2.1.

**Sample analysis:** The slide was placed under an upright microscope (Zeiss, Axio Scope A1) that was operated in transmission and primarily in brightfield mode. Fine temperature control was achieved by an enclosed Peltier-driven sample stage (Linkam LTS120), and nitrogen was introduced into the chamber to prevent condensation. Droplet growth was recorded with a Lumenera Infinity 3-3UR camera, taking 1 fps with a resolution of 1936 x 1456 pixels. See Chapter 2.2.1 for a detailed description of the microscope set-up and underlying working principles. The cell was heated to 35 °C and then cooled at 20 °C min⁻¹ to -5 °C. Droplet diameter analysis was undertaken using Fiji. Volume calculations of spherical droplets was deduced from the obtained 2D diameter. Analysis of birefringence was carried out with polarised optical microscopy (POM) and the Michel-Levy chart, as described in Chapter 2.2.1.2.

### 4.3 Results and Discussion

Isotropic 5CB-rich droplets were formed from a binary liquid mixture of 5CB and MeOH by cooling, as discussed in Chapter 3. At -1 °C, the 5CB-rich droplets adopted a nematic radial configuration, with a single point defect at the centre of the droplet as described in Figure 4.1a. Prior to the isotropic-nematic transition of 5CB-rich droplets in the MeOH-rich continuous phase, the phase separation of isotropic 5CB droplets was dominated by coalescence while cooling. After adopting nematic order, 5CB-rich droplets rarely coalesced, even those in close proximity, or touching. According to Terentjev, the enhanced stability of nematic emulsions over their isotropic counterpart is due to the elastic energy of the nematic curvature. They explained that the energy barrier for coalescence was determined by the elastic constant and the surface tension of the LC droplet, and while the isotropic LC droplets had no bulk elasticity, the nematic structures were topologically stabilised by their defects. Similarly, in our experiments, phase
separation of nematic droplets proceeded primarily by Ostwald Ripening. Figure 4.1(a and b) demonstrate how the morphology of the 5CB:MeOH mixture evolved from many smaller droplets ($13.7 \pm 4.9 \mu m$) immediately after isotropic to nematic transition (Figure 4.1a), to fewer droplets with a larger size distribution ($19.5 \pm 6.5 \mu m$), 120 minutes later (Figure 4.1b).

As time $t$ evolved, smaller droplets disappeared into the majority phase and diffused through the matrix, depositing onto the larger droplets by Ostwald ripening. Ostwald ripening occurred in order to reduce the total interfacial area of a system via diffusional mass transfer from regions of high interfacial curvature to regions of low interfacial curvature,\textsuperscript{270} in order for the system to reach thermodynamic equilibrium.\textsuperscript{270} In an off-critical partially miscible liquid mixture, as the total interfacial area of the system reduces and larger droplets grow, the amount of each component dissolved in the other is expected to reach a stable or metastable state where the phases are at or close to equilibrium. This amount is determined by the Lever rule (see Equation \textsuperscript{1.7}\textsuperscript{237,271}).

In order to understand the effect of Ostwald Ripening in this system, shrinking and growing droplets were studied, and the change in diameter and volume of droplets was analysed. Figure 4.1c highlights the diameter change of each droplet in an image frame (with a green cross) from the isotropic - nematic transition point at time $t = 1.2$ minutes to the nematic - isotropic transition after 120 minutes. The purple crosses represent droplets whose diameter change was largely due to coalescence. In the frame of the image, the sample size was 41 droplets. The graph shows a linear plot for droplets
with a diameter $\leq 13\,\mu m$ which shrunk completely into the MeOH-rich phase. The remaining droplets with a diameter above $13\,\mu m$ underwent a change in diameter of up to $\pm 5\,\mu m$. Overall, there was a total increase in volume by $15\%$. In general, during Ostwald ripening the total number of droplets is expected to decrease, while the average diameter of droplets increases and volume remains the same. In this system, the apparent increase in volume may be attributed to the small sample size or an increasing volume of MeOH entering the droplet in order to reach equilibrium.

In addition to a change in size, the micrographs in Figure 4.1(a to b) display a visible change in the appearance of the droplets over time, as the point defects were no longer observed in Figure 4.1b. This was further investigated under both brightfield and cross-polarised light, presented in Figure 4.2(a and b), which shows the evolution of a single 5CB-rich droplet in the MeOH-rich continuous phase at a constant temperature of -5°C over time. The first droplet image, Figure 4.2(a/b-left), was taken after the isotropic-nematic transition and the following images (going right) were captured at different intervals (labelled in the figure) until the final image, which was acquired once the nematic-isotropic transition took place at 118-120 minutes. In the first 114 minutes, the radial defect in the centre of the LC moved to the surface of the droplet, giving the droplet an escaped-radial configuration. After the defect reached the surface of the droplet, the nematic order in the droplet decreased by the formation of an isotropic shell on the edges while the centre remained nematic. In the following 2 minutes, this nematic sphere shrunk and eventually disappeared completely leaving an entirely isotropic 5CB-rich droplet. The way in which the nematic to isotropic transition transpired inside a droplet is in contrast to research on a 5CB droplet immersed in silicone oil, where the nematic phase would disappear at many random locations inside the droplet before the droplet transitioned to the isotropic phase.\cite{272, 273} The radial to escaped-radial movement of a defect has been observed in previous studies during a topological transformation.
often induced by an electric field, where a radial droplet transforms from a radial to bipolar configuration.\textsuperscript{87}

The change in nematic order was further observed through their decreasing retardation over time. Analysing the colours of the droplets with a Michel-Levy chart, depicted in Figure \textsuperscript{4.2c}, provides evidence of the decreasing birefringence over time, with the polarisation going from second to first order colours. Within each droplet, the order of interference colours seen in the isochromes decreased towards the melatope. This may be due to the defect at the core, which is not birefringent and reduces the birefringence around it.

We can extract temperature-dependent compositional information for a binary mixture from the phase diagram via the Lever rule\textsuperscript{237,271,274} (Equation \textsuperscript{1.7}) for computing the mixture composition at equilibrium. Thus, in a 70:30 MeOH:5CB mixture, the majority phase is expected to be composed of 76.6 vol % MeOH, and 23.4 vol % 5CB at equilibrium. Accordingly, the minority phase was expected to contain 88.5 vol % 5CB, and 11.5 % MeOH at equilibrium. When the minority phase of a binary liquid is a nematic LC droplet, changes in their internal configuration result in changes in the optical properties of the droplet. Thus, the changing internal configuration of the LC droplet may be explained by the shift towards equilibrium of the binary mixture due to the uptake of MeOH in the 5CB-rich droplet. This uptake of MeOH may have caused a deformation of the director due to the changing elastic energy of the LC, as explained by Sigdel and Denolf\textsuperscript{255,256}.

It is worthy to note, all observations (defect movement, phase transitions) mentioned above took place at the same time and in the same way for all droplets in the field of view, regardless of size of the droplet.

In a binary liquid mixture with partial miscibility, there is a diffuse interface barrier between the phases, which is defined by interfacial tension, and increases with temperature.\textsuperscript{16,208} Here, the diffuse interface barrier between the LC 5CB-rich phase and MeOH-rich phase allowed exchange of individual molecules between the two components, and therefore the amount of MeOH in the 5CB-rich phase increased in order to eventually reach the equilibrium state. At equilibrium, there is no chemical potential difference across the phase boundary, and thus no net diffusive flux.\textsuperscript{260}

This 5CB-MeOH diffusive flux was investigated through the progression of the defect structure within a single two-component droplet with computer simulation in collaboration with Dr Martin Bates (University of York) using an anisotropic soft-core model.\textsuperscript{275} In this work, Dr Bates found that MeOH near the surface of a LC droplet could escape into the continuous phase, while solvent close to the centre of the droplet would phase separate within the droplet and segregate near the radial defect point. In both experiment and simulation, the size of the nematic region was constant, and the defect formation and motion in the simulations was similar to that in the experiment. The observed behaviour deviated when the defect reached the surface. It was speculated that the existence of
disorder at the interface was responsible for the subsequent shrinkage of the nematic region. Since the defect represents a region of disorder, the composition within the defect region is likely to be different to that of the bulk majority and minority phases. This imperfection at the surface may allow MeOH from the surrounding environment to enter the nematic region, causing the region around the defect to transform to the isotropic phase, with the droplet size remaining constant but the nematic region shrinking.

Furthermore, we also compared our observations to bulk phase separation. A regular phase diagram will account for bulk phase separation and isotropic-nematic phase transition in the bulk phase. In a bulk system at -5°C, the LC phase will remain in the nematic phase indefinitely. However, the results found in micro-scale phase separation exhibited a deviation from the bulk phase diagram where, the initially nematic LC droplets underwent a phase transition to the isotropic phase at -5°C. A thermodynamic explanation was given by Dr Seishi Shimizu (University of York) who elucidated that the relative stability of 5CB in the nematic phase decreased in droplet form in comparison to the bulk, while the relative stability of MeOH in the nematic phase increased. Thus, the nematic phase was becoming less stable in smaller droplets over time by the destabilisation of 5CB and stabilisation of MeOH.

In a separate experiment, after the nematic-isotropic transition of the 5CB-rich droplet, the temperature of the system was decreased further from -5°C to -10°C. With this cooling, the droplets transitioned back to the nematic phase. Thus, a change in temperature caused a shift in the equilibrium conditions. In consequence, the system worked again towards reaching equilibrium. Finally, we note that an FLIR camera was used to take thermal images of the Linkam temperature stage as the temperature was cooled to -5°C, and held here during the phase separation experiment, and while the nematic-isotropic transition took place (as discussed in Chapter 2.2.1.1). Temperature fluctuations were very small and did not reach the nematic-isotropic phase transition temperature, therefore possible inaccuracies in the temperature stage were not responsible for the observed phenomena of phase transition.

**4.4 Conclusions**

We have shown how a phase diagram for a binary liquid mixture can deviate from the bulk behaviour for small droplets when interfacial tension is introduced. In a binary liquid mixture containing a LC-rich droplet phase at -5°C, the internal configuration changed over time resulting in observable differences in the optical properties of the droplet. Droplets transformed from a nematic radial to a escaped-radial configuration and finally a nematic-isotropic transition took place after 120 minutes. In comparison, the bulk system remained nematic at -5°C indefinitely. This deviation from the bulk system was a result of the interfacial tension of the droplet. The phase transitions and equilibrium conditions from a bulk phase diagram shifted to lower temperatures for
microscale phase separation. The experimental evidence was further supported both through simulations and thermodynamic calculations in collaboration with Dr Martin Bates and Dr Seishi Shimizi (University of York). The nematic-isotropic transition of the 5CB-rich droplet also suggests that the droplets nucleate with more 5CB than the equilibrium composition of the 5CB-rich phase and this is why they start out being nematic, temporarily. Furthermore, lowering the temperature of the system introduced an isotropic - nematic transition of the droplets once again, reinforcing the explanation that MeOH uptake is responsible for the nematic-isotropic droplet phase transition.
Chapter 5

Surfactant and Particle Effects on Binary Liquids

Arrested phase separation is an intriguing route for the production of metastable materials with potentially useful and interesting properties. The previous chapters demonstrated the formation of LC-rich droplets, and their eventual phase separation. In this chapter, we investigate strategies to stabilise droplets and prevent coalescence by studying the effect of conventional liquid stabilisers and particles on an isotropic liquid-liquid crystal system.

5.1 Introduction

Conventionally, emulsification of two immiscible fluids is achieved by the presence of surfactants, colloids or polymers. As discussed in Chapter [1.2.6], LCs form emulsions by the self assembly of surfactants or lipids in aqueous or non-aqueous media. The ordering of such particles at the LC interface become coupled to the orientational order of the LC, leading to a change in the optical appearance of the LC. Recent studies have shown that the orientational ordering in LCs can be triggered by lipids, surfactants, proteins and viruses. This behaviour allows LC-based reporting, wherein events at the nanoscale can be observed with conventional optical microscopy.

Particles have also been used to stabilise the interface between immiscible fluids by forming a shell. This is discussed in Chapter [1.2.6]. Clegg et al. combined components of binary liquids with pickering emulsions to create a new class of soft solids known as bicontinuous interfacial jammed emulsion gels or ‘bijels’. This was achieved by utilising phase separation of a binary liquid via spinodal decomposition to form a bicontinuous arrangement. The domains were then pinned by jamming a monolayer of colloidal particles that were trapped at the interface, as shown in Figure 5.1.

Prior to this work, Meeker et al. used 5CB with 5 vol% of poly(methyl methacrylate) (PMMA) particles to form a particle network by applying a temperature quench
5.1 Introduction

Figure 5.1: Route to bijel fabrication. Single fluid phase of ethylene carbonate (EC) and xylene is quenched to the spinodal demixing region forming a bicontinuous network with EC-rich and xylene-rich phases stabilised by fumed silica at the interface, here shown by confocal microscopy. Adapted from Ref. 11 with permission from the Royal Society of Chemistry.

from isotropic to nematic. When phase transition began, nuclei of the nematic phase appeared and began to confine the PMMA particles in the residual isotropic phase, as a PMMA particle in the nematic phase would cause a high elastic energy penalty. This created a soft solid with a significant storage modulus. 291,292

Figure 5.2: Schematic of the formation of a cellular network. The image shows the evolution and eventual remixing of nitromethane-rich droplets in an ethylene glycol-rich continuous phase, contained by silica particles at the interface. Adapted from Ref. 12 with permission from the Royal Society of Chemistry

The formation of networks via nucleation and growth instead of spinodal decomposition, are less researched. Clegg et al. created emulsions via nucleation and growth following an off-critical quench of a binary mixture of oil and alcohol containing silica particles. 12,293 Nitromethane-rich droplets in an ethylene glycol-rich continuous phase formed and silica particles arranged onto the liquid interface and became trapped be-
between the droplets. This emulsion had long-term stability due to the silica particles at the interface and also a surplus population in the continuous phase. Upon heating, the droplets expanded due to coalescence and the particles became arranged in the space between the droplets. A disappearance of the continuous phase can also be achieved via evaporation of one of the phases; this is illustrated in Figure 5.2.

In the following experiments, surfactants and silica particles were used in the 5CB/MeOH partially miscible liquid system, with motivation to study their effect on bulk phase separation and microscale LC droplets and achieve stabilisation.

5.2 Experimental

Reagents 5CB as described in Chapter 2.1.1. MeOH (HPLC grade) was purchased from Sigma Aldrich. The block copolymer poly(isobutylene)-b-poly(ethyleneoxide), PIB$_{39}$-block-PEO$_{36}$ was synthesized by BASF as described elsewhere with a $M_n$ of 4.85 kg/mol and a polydispersity of 1.26. The molecular structure for this block copolymer is shown in Figure 5.3.

![Molecular structure of the block copolymer poly(isobutylene)-b-poly(ethyleneoxide), PIB$_{39}$-block-PEO$_{36}$](image)

Figure 5.3: Molecular structure of the block copolymer poly(isobutylene)-b-poly(ethyleneoxide), PIB$_{39}$-block-PEO$_{36}$.

Tween 60 (nonionic detergent), Tween 80, sodium dodecylbenzenesulfonate (technical grade), sodium dodecyl sulfate (92.5-100.5% based on total alkyl sulfate content basis), dioctyl sulfosuccinate sodium salt ($\geq 97\%$), dodecylethlyldimethylammonium bromide ($\geq 98\%$), hexadecyltrimethylammonium bromide (BioXtra, $\geq 99\%$), Pluronic F127 (BioReagent), Pluronic F108, were purchased from Sigma Aldrich.

For silica NP synthesis: Tetraethyl orthosilicate (TEOS, 99%), aqueous ammonia hydroxide (28-30%), (3-Aminopropyl)triethoxysilane (APTES, 99%), Anhydrous dimethylformamide (DMF, 99.8%) and triethylamine (TEA, $\geq 90\%$) were obtained from Merck. Ultra-pure water was obtained from a Millipore filtration system, operated at 18.2 MOhm. Ethanol (HPLC grade) was purchased from Fischer Chemical. All compounds were used without further purification.
Surfactant sample preparation The above mentioned surfactants were mixed at 0.1-2% in MeOH by vortex, till the mixture was clear. 5CB and MeOH (containing surfactant) with a volume ratio of 30:70 were mixed in a sealed glass cuvette, which was enclosed by a Peltier-regulated sample compartment that allowed control over both temperature and stirring (Quantum Northwest, Qpod 2e).

Silica nanoparticle sample preparation Silica nanoparticles (NPs) were prepared according to previously published procedures, and a scheme is provided in Figure 5.4. Briefly, 10 mL ethanol, 0.25 mL ammonium hydroxide (30 w/v %), and 1.4 mL millipore water were mixed in a round-bottom flask at room temperature for 10 minutes. 4.4 mL of TEOS was added to the mixture and heated to 75°C. The flask was stirred for 1 hour which yielded a colloidal solution of silicon dioxide (SiO$_2$) NPs. The particles were separated by centrifugation (Thermo Scientific Multifuge X1R) for 20 minutes at 13500 rpm, and resuspended in ethanol by vortex and placing in an ultrasonic bath (Ultrasonic Cleaner USC - THD). The particles were purified by centrifugation and resuspension three times.

![Chemical reaction scheme for silica NP production.](image)

Figure 5.4: Chemical reaction scheme for silica NP production.

APTES functionalisation: 100 mg of silica NPs were dispersed into a 2:1 by volume mixture of ethanol:water. With stirring, APTES (up to 1 mol% with respect to the amount of silica NPs) was added and stirred overnight in a sealed flask at RT. The NPs were then washed with ethanol 3 times using centrifugation and redispersion by vortex and sonication.

NHS-fluorescein functionalisation: 50 mg aminated silica NPs in ethanol were centrifuged and redispersed in anhydrous DMF three times. The aminated silica NPs (50 mg) were dispersed in anhydrous dimethylformamide (DMF, 15 mL) in a flask which
Figure 5.5: Schematic illustration of fluorescence microscopy set-up. A metal halide lamp serves as a light source. Excitation and emission filters are placed in the light path to block unwanted wavelengths. The transmitted light source provides light to the sample and the camera.

was covered in black foil to prevent light, and stirred vigorously at room temperature for 24 hours with NHS-fluorescein (using 2x molar excess with respect to the loading of the amine groups on the nanoparticles) and TEA (75 \( \mu \)L). The Si-APTES-NHS fluorescein NPs were then washed three times with MeOH using centrifugation and redispersed into MeOH (10 mL) by vortex at 0.1-2 % NPs. The NPs in MeOH (30 %) was mixed with 5CB (70 %) in a sealed glass cuvette, which was enclosed by a Peltier-regulated sample compartment that allowed control over both temperature and stirring (Quantum Northwest, Qpod 2e).

**Sample analysis:** Sample analysis was identical to that described in Chapter 3.2.1. Fluorescence filter sets were integrated into the microscope to track fluorescent particles, as illustrated in Figure 5.5

Macroscopic analysis of the phase was carried out as previously reported. In short, a digital microscope (Dino-Lite) was mounted to the optical port of the temperature controlled cuvette compartment. The amount of time to reach full phase separation was defined as time from when the cloud point is visible, to when a clear solution is visible. Results were obtained by analysis of videos that were obtained for all samples.

Scanning electron microscopy (SEM) images were taken on a Jeol 6701F SEM. Silica NP samples for SEM were prepared by depositing and drying a drop of silica powder dispersed in MeOH onto a glass plate, and sputter coating with a layer of gold. Diameters were measured using ImageJ and average values were calculated by counting a minimum of 50 particles.

Thermogravimetric analysis (TGA) was performed automatically on a Discovery TGA.
5.3 Results

5.3.1 Surfactant Effects

To investigate the effect of surfactants on the phase separation behaviour of a binary mixture of 5CB and MeOH macroscopically, a number of surfactants in varying concentrations were dissolved in the MeOH phase (70%) before mixing with 5CB (30%) in a cuvette. The mixture was subsequently cooled from 35°C to 15°C (quench depth: $\Delta T = 7.5^\circ$C). Upon cooling, the mixture went from a clear, miscible mixture, to a cloudy mixture. As phase separation took place, the 5CB and MeOH separated, with the opaque 5CB settling beneath the MeOH. Macroscopic phase separation was observed as the time taken for the mixture to turn from a cloudy solution, to a clearly phase separated MeOH above 5CB.

Table 5.1: Library of surfactants at various vol %, employed to study the delay of overall time for macroscopic phase separation upon cooling of the binary liquid mixture to 15°C.

<table>
<thead>
<tr>
<th>Category</th>
<th>Surfactant</th>
<th>Mw</th>
<th>CAS No.</th>
<th>0.1 wt%</th>
<th>1.0 wt%</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>No surfactant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>Non-ionic</td>
<td>Span 20</td>
<td>346</td>
<td>1338-39-2</td>
<td>12</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tween 60</td>
<td>1309</td>
<td>9005-67-8</td>
<td>7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tween 80</td>
<td>1310</td>
<td>9005-65-6</td>
<td>9</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Anionic</td>
<td>(SDBS)</td>
<td>348</td>
<td>25155-30-0</td>
<td>4</td>
<td>6</td>
<td>5%: 6</td>
</tr>
<tr>
<td></td>
<td>(SDS)</td>
<td>288</td>
<td>151-21-3</td>
<td>3</td>
<td>5</td>
<td>5%: 12</td>
</tr>
<tr>
<td></td>
<td>(AOT)</td>
<td>445</td>
<td>577-11-7</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cationic</td>
<td>(DDAB)</td>
<td>322</td>
<td>68207-00-1</td>
<td>11</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CTAB)</td>
<td>364</td>
<td>57-09-0</td>
<td>10</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Block copolymer</td>
<td>(PIB-b-PEO)</td>
<td>6122</td>
<td>9003-11-6</td>
<td>8</td>
<td>38</td>
<td>2%: 42</td>
</tr>
<tr>
<td></td>
<td>Pluronic F127</td>
<td>12500</td>
<td>9003-11-6</td>
<td>5</td>
<td>16</td>
<td>5%: 5</td>
</tr>
<tr>
<td></td>
<td>Pluronic F108</td>
<td>14600</td>
<td>9003-11-6</td>
<td>16</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>
Common surfactants previously used to stabilise 5CB in water were tested in varying concentrations along with other non-ionic, ionic, block copolymer and blends of surfactants, including Span 20, Tween 60, Tween 80, Sodium dodecylbenzene sulfonate (SDBS), Sodium dodecyl sulfate (SDS), Dioctyl sulfosuccinate sodium salt (AOT), Dodecylethylidimethylammonium bromide (DDAB), Hexadecyltrimethylammonium bromide (CTAB), poly(isobutylene)-b-poly (ethyleneoxide) (PIB-b-PEO), Pluronic F127 and Pluronic F108. Table 5.1 shows the time taken for macroscopic phase separation with 0.1 wt% and 1 wt% of surfactant compared to phase separation without surfactant. Non-ionic and ionic surfactants did not cause any significant delay in phase separation in the cuvette, and proceeded to phase separate in the same time as 5CB/MeOH without any surfactant. These surfactants were designed for water systems, and therefore would not have the same effect in MeOH which can weaken the hydrophobic bond. However, block copolymer surfactants were found to have a hindering effect on phase separation. Among the surfactants investigated, 1.0 vol% of the block copolymer poly(isobutylene)-block-poly(ethylene oxide) (PIB-b-PEO) exhibited the most pronounced effect on macroscopic phase separation. Here, phase separation time was over 4 times longer than without any surfactant. Figure 5.6 illustrates macroscopic phase separation without (Figure 5.6a) and with (Figure 5.6b) Block-Copolymer PIB-b-PEO. It is evident that the presence of PIB-b-PEO resulted in a more cloudy mixture. This observation was explained upon analysis of microscopic phase separation.

The effect of 1 % PIB-b-PEO was investigated by optical microscopy. Results are presented in Figure 5.7. It was found that more than 5 times the number of droplets nucleated compared to a mixture without PIB-b-PEO, as shown in Figure 5.7a. Figure 5.7b shows the mean droplet size increased at a slower rate and was 6 µm compared to 11 µm without surfactant at 60 seconds. Thus, the macroscopic retardation of phase separation, and the more cloudy appearance, may be attributed to the nucleation of a
larger number of droplets, with a smaller mean droplet size and slower rate of droplet growth.

Figure 5.7: Effect of block-copolymer PIB-b-PEO on isotropic 5CB-rich droplets. (a) Overview of droplet mean diameter and standard deviation and (b) Overview of number of droplets of a mixture of 5CB and MeOH with and without PIB-b-PEO. Cooling rate: 5 °C min⁻¹, Quench Depth: ΔT = 7.5 °C.

In contrast, Gupta et al.³⁰⁰ reported that the presence of surfactants did not influence the separation time of partially miscible liquids. In fact, our findings are similar to this at lower concentrations, the only exception being the effect of higher concentration. Surface-active agents are known to lower the interfacial tension between the two largely immiscible liquids, however, in the PIB-b-PEO system described above, the surfactant is in a micellar form. This was determined by dynamic light scattering (DLS) to measure the critical micelle concentration (CMC) as described by Hoda et al.³⁰¹ the results for which are displayed in Figure 5.8.

Experimental correlation function data for concentrations below 1 x 10⁻⁶ mol⁻¹ of PIB-b-PEO showed poor signal to noise ratios, and therefore low intercepts of 1.0. In this case, size distribution information could not be obtained. Above concentrations of 1 x 10⁻⁶ min⁻¹ of PIB-b-PEO, the intensity of scattered light increased and the intercepts of correlation functions become much higher; with 1.4 to 1.5, and size distributions could be obtained. This was related to the presence of micelles, thus the CMC value was found to be below 1x10⁻⁶ mol L⁻¹ in MeOH at 20 °C, with a hydrodynamic diameter of 66 ± 3 nm. This diameter did not change at higher concentrations. Figure 5.8 also presents intensity as a function of a log-10 concentration of PIB-b-PEO. Below the CMC, scattering intensities are close to zero and constant. Once the CMC is reached, the intensity increases with concentration, as described by the exponential increase in the log-10 concentration of PIB-b-PEO.

A concentration of 3 x 10⁻³ mol L⁻¹ of PIB-b-PEO was used for this system and therefore well above the CMC. When the same experiment was repeated with a PIB-b-PEO concentration below the CMC, there was no effect on phase separation time or
nucleation number. The presence of surfactant micelles of block copolymer PIB-b-PEO therefore explain the nucleation of a larger number of droplets. The micelles can act as nucleation points in which droplet growth occurs, or they may solubilise the molecules of the material and affect the relative supersaturation, which effects both nucleation and growth.  

It is interesting to note that the block copolymer PIB-b-PEO forms micelles in MeOH, evidenced by DLS and the increased number of nucleation points. Most amphiphiles dissolve at a molecular scale in methanol or other alcohols, as the hydrophobic bond is weakened, therefore self-assembly to form micelles was unexpected. The CMC has been found to decrease sharply as the hydrocarbon chain length of the alcohols becomes larger. Furthermore, studies have shown that the addition of alcohols to micelles in water, in fact, decrease the tendency to form micelles.  

Finally, when cooling the droplet into the nematic region, phase transition occurred with the droplets adopting a radial configuration. In contrast to previous research, the incorporation of any of the mentioned surfactants to the 5CB/MeOH mixture had no influence on the orientational order of the LC droplets.

### 5.3.2 Particle Effects

#### 5.3.2.1 Characterisation of Silica NPs

Silica NPs were prepared as discussed in the Experimental section of this chapter. SEM images of silica NPs are presented in Figure 5.9. Diameter of NPs were measured using ImageJ, and the average calculated particle size by this mode of characterisation was $46 \pm 10$ nm.
Data from DLS of silica NPs dispersed in ethanol is presented in Figure 5.10 and presents an average hydrodynamic diameter of 124 nm and a polydispersity index of 0.23. Particle size measurements by DLS are generally expected to be larger than SEM as DLS measures the hydrodynamic radius and weights the size distribution differently. Furthermore, larger particles are typically overrepresented due to their enhanced scattering cross-section.

The silica NPs were then subject to thermogravimetric analysis (TGA), Figure 5.11 shows the thermogram of the modified silica NPs with APTES and NHS fluorescein heated from room temperature to 600 °C. For both APTES-modified silica NPs and NHS-modified silica NPs, distinct steps in the mass loss can be observed from the derivative curve. The peaks seen before 100 °C are attributed to the release of water from the polycondensation of the hydroxyl groups on the surface of the NP. For the silica-APTES thermogram, the second peak at 500-600 °C corresponds to the decomposition
of the APTES functional groups chemically anchored to the silica surface. For the silica-NHS thermogram, we see two further peaks at 400 and 550 °C. The peak at 400 °C corresponds to the melting point of NHS fluroscein (420 °C) and would therefore be due to the excess NHS fluroscein or other organic residue combusting. The peak at 550 °C would be as a result of the NHS-functional groups grafted to the silica. The TGA demonstrates mass loss at the expected regions, however due to the mass quantity present we cannot accurately calculate grafting density.

![Graph showing TGA of silica-APTES NPs and silica-APTES-NHS fluoroscein NPs](image)

Figure 5.11: Thermogravimetric analysis (TGA) of silica-APTES NPs, and silica-APTES-NHS fluoroscein NPs

### 5.3.2.2 Silica NP Effect on 5CB/MeOH Binary Liquid System

Varying percentage suspensions (0.1-2%) of silica NPs in MeOH were made as discussed in the Experimental Section. A homogeneous mixture of 5CB/(MeOH + silica NPs) in a sealed compartment was cooled from above the UCST to below $T_{ps}$ and into the nematic region at -5 °C. Droplets formed by nucleation and growth, and droplet behaviour was observed by optical microscopy, and fluorescence microscopy was carried out with the use of fluorescence filter sets integrated into the microscope as described in Figure 5.5.

For suspensions of silica NPs in MeOH above 1 %, aggregation of particles was observed, therefore 0.1 % and 1 % suspensions were used. Under fluorescence microscopy, it was observed that particles surrounded the 5CB-rich droplets soon after nucleation but did not prevent coalescence. Their growth rate did not differ from a 5CB/MeOH mixture without any NPs. The silica NPs were seen to flow in the MeOH-rich phase around the 5CB-rich droplets until a steady stage was reached and flow had decreased. Droplets in the nematic phase were unaffected by silica NPs and their configuration remained nematic. The defect progression proceeded in the same manner as discussed in Chapter 4 and nematic-isotropic transition occurred over time.
5.3 Results

Figure 5.12: Nematic droplets with silica NPs at the surface. (a) Brightfield image, (b) cross polarised image, and (c) fluorescence image of 5CB-rich droplets surrounded by silica NPs at their surface and in the MeOH. Scale: 10 µm.

After observing the long term effects of silica NPs on 5CB-rich droplets, the mixture was heated above the UCST. The droplets became miscible in the MeOH and disappeared from view. However, the silica NPs had become dominated by gravity and had arranged at the bottom of the slide in a porous arrangement, which was no longer affected by heating or flow of 5CB/MeOH, as illustrated in Figure 5.13.

Figure 5.13: Silica NP organisation around 5CB-rich droplet before and after heating. Isotropic 5CB-rich droplets at -5 °C after nematic-isotropic transition under (a) brightfield (b) fluorescence microscopy. Single phase 5CB/MeOH at 35 °C with silica NPs retaining previous droplet configuration under (c) brightfield (d) fluorescence microscopy.
5.4 Conclusion

The effect of surfactants on a 5CB/MeOH binary liquid mixture was investigated. It was found that block copolymer PIB-\textit{b}-PEO had the most pronounced effect on phase separation. The presence of PIB-\textit{b}-PEO resulted in a higher droplet number, and a smaller droplet diameter during growth of the droplet. This was reasoned to be due to the presence of micelles. For block copolymer concentrations below the CMC, there was no effect on phase separation. While PIB-\textit{b}-PEO was able to delay phase separation, it did not stabilise the LC crystal droplets in the long term.

The effect of silica NPs on a 5CB/MeOH binary liquid mixture was also investigated. It was found the silica NPs were able to arrange at the droplet surface but did not prevent coalescence, phase transition or Ostwald ripening. However, upon heating of mixture to form an isotropic single phase of 5CB and MeOH, the silica NPs remained in their previous arrangement with a porous structure observed. This approach provides a novel concept for the templating of inorganic material by phase separation with a recoverable structure directing agent.
Chapter 6

Liquid Crystal-Templated Porous Microparticles via Photopolymerisation of Temperature-Induced Droplets in a Binary Liquid Mixture


Porous polymeric microspheres are an emerging class of materials, offering stimuli-responsive cargo uptake and release. In this chapter, we describe a new approach to fabricate porous anisotropic microspheres based on temperature-induced droplet formation and light-induced polymerisation. We study the microparticles and their swelling and shrinking capabilities, and the reversibility of this templating process. The use of a reversible materials templating approach to obtain porous microparticles provides new insights into binary liquid manipulation and potential for microparticle production.


6.1 Introduction

Micrometre-sized polymeric particles have attracted interest in technologies and applications such as optical displays, drug delivery, chemical separation, emulsion stabilisation and catalysis. Material platforms based on LCs offer complex internal architectures and unique optical properties. As an example, difunctional mesogenic monomers have been used to form LCE droplets/shells, which possess the ability to undergo changes in shape in response to external stimuli. Several studies have demonstrated their promising applications as actuators, for example their unique suitability as artificial muscles, and their potential as micropumps. Furthermore, the long-range order and fluidic properties of LCs confined in a droplet serve as a template for polymerisation reactions which result in anisotropic polymeric particles with distinct shapes and configurations. Such LC droplets usually contain a mixture of reactive (polymerisable) and non-reactive (non-polymerisable) thermotropic mesogens with tunable configurations. The reactive mesogens are photopolymerised, and the non-reactive mesogens are extracted, leaving micrometre-sized anisotropic polymeric particles with distinct shapes and complex internal structures. Nanoporosity of the microparticles can be tuned, and “patchy particles” have been developed where colloids are positioned at the defects of the LC droplet.

There are several approaches for the formation, control and stabilisation of LC microdroplets as mentioned in Chapter 1.2.6. These methods are often influenced by the presence of surfactants, polymers or colloids. In Chapter 3, we established a route to LC microdroplets based on temperature-induced formation in a binary liquid mixture of 5CB and MeOH. Droplet formation by nucleation in a binary liquid mixture undergoes a series of stages of growth from nucleation to growth by diffusion, coalescence and Ostwald ripening. Arresting the phase separation process at one of these stages would open a new avenue for the temperature-controlled formation of stable particles. There are also some notable examples of binary fluid systems forming networks and structures. Clegg et al. utilised this method with colloidal particles in a partially miscible mixture to form cellular networks. Colloidal particles have also been used to arrest the demixing of a partially miscible liquid by spinodal decomposition to form bicontinuous interfacially jammed emulsion gels (bijels). Chapter 5 addresses alternative routes taken in the course of this research to prevent phase separation, and their consequences.

The formation of anisotropic LC microparticles by temperature-induced droplet formation and light-induced polymerisation is an interesting concept. Firstly, it utilises the natural demixing of a binary liquid by temperature control to form droplets. Secondly, it employs photopolymerisation of the reactive mesogens, and extraction of non-reactive mesogens by heating, thereby exploiting a reversible templating process to create a microparticle product, which has the ability to undergo shape change by swelling and shrinking in response to external stimuli. Previous research has investigated the formation of non-anisotropic polymer capsules using double emulsions or multiple
emulsions. In a similar manner, phase separation was induced, followed by photopolymerisation.

In this chapter, we incorporate the reactive mesogen 2-methyl-1,4-phenylene bis4-[3-(acryloyloxy)propoxy]benzoate (RM257) in the binary system mentioned above for the production of LC microparticles. We study the cooling-induced formation of 5CB/RM257-enriched droplets in methanol, photopolymerise them in their nematic phase and further investigate the polymeric microparticles. We used optical cross-polarised microscopy to quantify phase and shape of the particles, and focused ion beam microscopy (FIB) imaging to form a descriptive analysis of the microparticle texture.

6.2 Experimental

Reagents

5CB and RM257 as described in Chapter 2.1.1 and 2.1.2. MeOH (HPLC grade) was purchased from Sigma Aldrich. Dichloromethane (99 %, puriss) (DCM), MeOH (HPLC grade), Acetone (99.8 % Chromasolv) and 1-hydroxycyclohexyl phenyl ketone were purchased from Sigma Aldrich. All compounds were used without further purification.

Sample preparation

5CB and RM257 (20 wt %) were placed in a glass vial and mixed by vortex and heated till the mixture was clear. DCM was added to the vial on a hot plate and stirred at 60 °C overnight. The mixture was then placed in a vacuum oven at 30 °C for 1 hour. Photoinitiator 1-hydroxycyclohexyl phenyl ketone (1 wt %) was added and mixed at room temperature for 3 hours. In the following chapter, the 80 / 20 wt % / wt % mixture of 5CB and RM257 will be referred to as 5CB/RM257. Multicomponent LCs are commonly used to tailor material properties, such as the clearing point. In the following experiments, 5CB and RM257 mixtures are treated as a single component, until polymerisation. Samples of (30 %) 5CB/RM257 and (70 %) MeOH were mixed in a glass cuvette, which was enclosed by a Peltier-regulated sample compartment that allowed control over both temperature and stirring (Quantum Northwest, Qpod 2e). Samples were heated to 35 °C in the cuvette.

Sample analysis:

5CB-rich microdroplets were studied by optical microscopy in a 18 x 18 mm² sealed sample compartment of 30 µm thickness. The slide was placed under an upright microscope (Zeiss, Axio Scope A1) that was operated in transmission and primarily in brightfield mode. Crossed polarisers were used to observe anisotropic behaviour. A λ waveplate (550 nm) was used to introduce a fixed amount of retardation between the ordinary (n_o) and extraordinary (n_e) rays passing through the LC, and quantify the birefringence using the Michel-Levy chart. A temperature controlled sample stage (Linkam, LTS120) was used for all experiments. Nitrogen was introduced into the chamber to prevent condensation at low temperatures. For droplet analysis, a Lumenera Infinity 3-3UR camera was used, with a resolution of 1936 x 1456 pixels. The sample stage was pre-heated to 35 °C, and then cooled at 20 °C min⁻¹ to −5 °C. Note that in
6.3 Results and Discussion

the following study, $T_{ps}$ is referred to as the phase separation temperature on the binodal line for a particular temperature and composition.

Photopolymerisation of the LCs was performed using a Prior Lumen 200 UV lamp that delivered 90 mW cm$^{-2}$ through illumination from the top-side of the optical microscope objective using a 365 nm excitation filter, while allowing simultaneous viewing of the process with transmitted light, as shown in Figure 2.12. The LC droplets were exposed to UV light for a period of 5 seconds to 5 minutes.

For extraction and analysis of droplets, a microfluidic glass chip (as described in Chapter 2.1.3) was used. A glass syringe was used to take samples from the heated cuvette and insert the homogeneous 5CB/RM257 and MeOH mixture into the channel via the PTFE tubing. Droplet formation and exposure to UV light was conducted as described above. Extraction of the polymer was carried out by flushing the chamber with acetone. The particles were washed twice by centrifugation and redispersed into acetone. 5CB removal was confirmed using an FTIR spectrometer VERTEX 70/70v, (Bruker Corporation, Germany) coupled with platinum diamond ATR. Image analysis of the particles was done by optical microscopy and a FIB helium ion microscope (Orion Nanofab, Carl Zeiss) at an acceleration voltage of 25 kV.

Quantitative droplet investigation was carried out by computational image analysis as described in Chapter 2.2.1.4, and using Fiji ImageJ. Droplets from the images were distinguished, and the number of droplets, the average diameter and standard deviation computed as a function of time.

6.3 Results and Discussion

5CB/RM257-rich droplets were formed by cooling a mixture 5CB/RM257 with MeOH under an optical microscope from 35 °C to -5 °C at 20 °C min$^{-1}$ as illustrated in Figure 6.1a-d. Imaging began at 35 °C, and upon reaching $T_{ps}$, enriched droplets of isotropic 5CB/RM257 formed by nucleation and subsequently grew as they continued cooling. The droplets underwent an isotropic-to-nematic transition at 0 °C and formed nematic micrometer-sized radial droplets as shown in Figure 6.1d.

We note that as a consequence of the presence of RM257, the observed phase separation temperature and isotropic-nematic transition occurred at 1-2 °C higher than that described by the binary phase diagram of pure 5CB and MeOH. A full phase diagram for 5CB/RM257 and MeOH has not been mapped, and this change in phase separation/transition was only for the observed volume ratio in comparison to the 5CB/MeOH binary system. In the absence of RM257, 5CB-enriched droplets were also found to form radial droplets in methanol. In comparison, previous studies show that 5CB-rich droplets dispersed in water generated bipolar configurations and for 20 wt/wt % RM257/5CB mixtures, axial configurations were made. These differences in LC configuration have been ascribed to its influence on either the elastic constants...
Figure 6.1: Schematic Illustration of the Microparticle Formation Process. (a) A homogeneous mixture of 70 vol% MeOH + 30 vol% 5CB/RM257 is prepared at 35 °C, i.e. above the upper critical solution temperature. (b) Isotropic LC enriched droplets are nucleated at 23 °C, which (c) continue to grow during further cooling. (d) Cooling below 0 °C triggers isotropic-to-nematic phase transition of the 5CB/RM257 mesogens. (e) Subsequent exposure to UV light (365 nm) polymerises the photoreactive RM257 mesogens, providing a porous structural matrix that is suitable for extraction and no longer temperature-sensitive.

and/or surface anchoring of the nematic mixture, which will differ in a partially miscible liquid mixture. A mixture of non-reactive mesogens as the majority component, and reactive mesogens as the minority component may be used for materials templating. A photoinitiator is also added to the mixture, therefore, when 5CB/RM257-rich droplets were exposed to UV light (365 nm), the RM257 mesogens formed a permanently cross-linked polymer network swollen with non-reactive 5CB mesogens. The alignment of the 5CB acted as the template for the RM257. Previous research has demonstrated that the anisotropic internal ordering of the droplet is governed by the 5CB component, and polymerisation occurs with minimal perturbation to the original alignment of the non-polymerised matrix. The optimal length of exposure time to UV light was determined by measuring the shrinkage of the particles upon heating above \( T_{ps} \). Exposure for 300 seconds resulted in no measurable changes to particle diameter before and after heating, as shown in Figure 6.2a. When droplets were exposed for less than 300 seconds, there was a reduction in particle diameter upon heating, suggesting that the RM257 had not fully polymerised. We note that photopolymerisation of the LC droplets remained birefringent even when shrinkage occurred. With a 300 second exposure time, both the configuration and size were preserved. Figure 6.2(b-d) shows 5CB/RM257-rich droplets at -5 degree before (b) and after (c) photopolymerisation, and upon heating from -5 °C to 35 °C (d). In the absence of reactive monomer RM257, 5CB-rich droplets in MeOH would follow a fully reversible process, whereby 5CB-rich droplets would undergo a nematic-isotropic transition upon heating to -1 °C and the droplets would disappear back into MeOH upon further heating above \( T_{ps} \). With the addition of the reactive monomer
6.3 Results and Discussion

Figure 6.2: Photopolymerisation of 5CB/RM257-rich droplets. (a) Effect of UV light (365 nm) exposure time at 90 mW cm\(^{-2}\) on diameter of droplets upon heating after photopolymerisation. (b-d) LC-rich droplets and templated microparticles after UV light exposure for 300 seconds. The same field of view of images shown under brightfield (top) and crossed-polarised light (bottom). (b) 5CB/RM257-rich droplets cooled to -5 °C. (c) 5CB/RM257-rich droplets at -5 °C after photopolymerisation. (d) RM257 polymer particles after heating to 35 °C.

RM257 and after exposure to UV light, polymerised particles remained intact upon heating above \(T_{ps}\), as shown in Figure 6.2d.

Figure 6.3: Birefringence of LC-templated microparticles. (a) Colours of the Michel-Levy chart decreasing from third-order (left) to first-order (right) interference colours. (b) Evolution of a LC particle with increasing temperature after photopolymerisation between crossed polarisers and (c) between crossed polarisers with a \(\lambda\) plate inserted. Scale: 10 \(\mu m\).

The birefringence (\(\Delta n\)) of 5CB/RM257-rich droplets before and after photopolymerisation was investigated using polarised optical microscopy (POM). Figure 6.3a displays the interference colours of the Michel-Levy chart, with the order of interference colours decreasing from left to right. Figure 6.3b and c) show the evolution of a single 5CB/RM257 droplet between cross-polarisers and with a first order retardation \(\lambda\) plate inserted into the optical train, respectively. After cooling the 5CB/RM257 : MeOH
mixture to $-5^\circ$C, the nematic droplet displayed third order interference on the edges of the droplet with the order of interference colours seen in the isochromes decreasing towards the melatope, as shown in Figure 6.3b(i). After photopolymerisation at $-5^\circ$C, the birefringence had reduced slightly (Figure 6.3b(ii)) and began to display second order interference colours as the droplets were heated (Figure 6.3b(iii)). At $35^\circ$C, first order interference colours could be observed (Figure 6.3b(viii)).

When a $\lambda$ plate was inserted, a relative retardation of exactly one wavelength (550 nm) was introduced between the ordinary ($n_o$) and extraordinary ($n_e$) wavefronts, and a magenta colour was observed, as shown in Figure 6.3c. At $35^\circ$C after UV exposure, the optical path difference increased for the north-east and south-west quadrants of the particle, as the colour shifted to higher order interference. In the north-west and south-east quadrants, the optical path difference decreased as the colour shifted to lower first order interference. Therefore, the particles showed a radial configuration with positive uniaxial birefringence.

![Figure 6.4: Birefringence measurements. Birefringence values of polymerised particles as a function of temperature from -5 to 35°C.](image)

Quantitative evaluation of birefringence as a function of temperature was performed using the Michel-Levy chart and the diameter of the particle, which were assumed to be spherical and thus of equal diameter. The results displayed in Figure 6.4 indicate a decrease in birefringence ($\Delta n$) with increasing temperature. The decrease in birefringence relates to the decreasing order parameter of the non-reactive LC. With RM257 arrested in a photopolymerised network, changes in the birefringence are likely related to the 5CB mesogens, either as a consequence of a reduction in their nematic director field or due to mesogen diffusion out of the microparticle. Over 50% of the birefringence reduction occurred between -5 and 5°C. A small increase in nematic-isotropic transition temperature of 5CB was to be expected here as the polymer network confined the nematic phase of the 5CB, thus increasing its stability. Between 5°C and 35°C, the
birefringence continued to decrease, albeit at a slower rate. This may be due to trapped 5CB molecules among the polymer, which were able to retain their order well above the isotropic-nematic transition temperature, or due to 5CB molecules escaping the polymer and becoming homogeneous with MeOH at high temperatures, suggesting that the particle was porous.

Figure 6.5: Microparticle shrinking and swelling after photopolymerisation. Particles exposed to UV light (365 nm) for (A) 1 minute and (B) 5 seconds. (A/B)i. 5CB/RM257-rich droplets at -5°C, immediately after UV exposure. (A/B)ii. LC templated microparticles after heating to 35°C. (A/B)iii Swollen microparticles after cooling to -5°C, surrounded by newly nucleated droplets of 5CB. Images under Brightfield light (A and B. Top) and between crossed polarised light (A and B. Bottom). Scale: 10 µm.

The hypothesis that the particles were porous was further supported in subsequent cooling and heating cycles, and shown in Figure 6.5. Upon cooling to -5°C, new 5CB-rich droplets nucleated outside of the particles and isotropic-nematic transition of these
droplets occurred at -1 °C, indicating that a substantial amount of 5CB mesogens had left the particles during the previous heating cycle. Furthermore, 5CB-rich droplets also nucleated inside the microparticle, which became swollen upon cooling to -5 °C in comparison to 35 °C. Between crossed-polarisers, nematic order of the new droplets could be seen. However, the clear radial configuration of the microparticles could no longer be observed due to the birefringence of the new nematic 5CB-rich droplets appearing in the pores of the particles, shown in Figure 6.5A(iii) and B(iii)). These factors are all consistent with the reasoning that the polymer particle was porous, as it was found to shrink and swell with heating and cooling, likely as a consequence of outgoing and incoming flux of 5CB mesogens. This behaviour was observed for all UV exposure times, as shown in Figure 6.6. In particular, particles with low exposure times had the most shrinkage of droplets upon heating, and would swell by up to 50% when cooled to -5 °C. Particles with high exposure times shrunk or swelled to a much lesser degree. This swelling and shrinking action is shown for two consecutive rounds in Figure 6.6, but could be repeated over many more cycles. A comparison of the effect of UV exposure time on shrinking and swelling of particles is shown in Figure 6.5.

![Figure 6.6: Swelling and shrinking of microparticles. Diameter of microparticles as a function of temperature over two cooling and heating sequences. Colour notation indicated different length of UV exposure for photopolymerisation (5 seconds, 30 seconds and 5 minutes).](image)

Finally, the particles were extracted by performing photopolymerisation of droplets in a microfluidic glass chip with a single chamber of diameter = 5 mm, length = 35 mm and depth = 0.03 mm, as shown in Figure 2.3. A homogeneous mixture of 5CB/RM27:MeOH above \(T_{ps}\) was syringed into the microchip and placed on the temperature stage. Cooling and photopolymerisation were performed in the same manner as described previously, and the particles were extracted by flushing the chamber with acetone. The 5CB was removed from the particles by washing with acetone and centrifugation. 5CB
removal was confirmed by FTIR analysis after each wash, see Figure 6.7, and the particles were analysed by optical microscopy and FIB microscopy. Figure 6.8 presents polymer microparticles from the binary liquid mixture. Under optical microscope with crossed polarisers, they were still birefringent (Figure 6.8(A/B ii)), and had a diameter range of 1-10 µm. FIB microscopy images presented in Figure 6.8(A/B iii) show the particles had a wrinkled surface with 200 nm particles attached to surface. The wrinkled surface indicates some degree of shrinkage of the particle after extraction of 5CB, and the presence of smaller particles on the surface is in line with secondary nucleation and photopolymerisation of RM257 from the continuous phase. Particles close to or touching each other at the time of UV exposure, fused together at their point of contact during photopolymerisation, while still maintaining their individual radial configurations as shown in Figure 6.8B.

![FTIR spectrum](image)

Figure 6.7: FTIR analysis of 5CB, 5CB/RM257 after photopolymerisation, and after washing by centrifugation and redispersion in acetone. The adsorption near 2250 cm\(^{-1}\) relates to the C–N bond in 5CB. The adsorption at 1750 cm\(^{-1}\) is characteristic of the C=O bond in RM257.

A notable observation was the presence of a crater or a tear on the surface of each particle. This exposed an inner surface that appeared to be more porous than the outer surface, which was smooth. A similar observation has been described by Young Park et al., who explained this as a competition between polymerisation and phase separation in the droplet. Upon exposure to UV light, the monomer RM257 undergoes polymerisation, and phase separation between 5CB and RM257 occurs, which directs concentration of RM257 in polymer-rich regions and 5CB in polymer-depleted (5CB-
Figure 6.8: Microparticle Extraction. 1. Single and 2. Fused polymeric microparticle templated from radial droplets in a binary liquid (a) under Brightfield light, (b) Crossed polarisers, (c) FIB microscopy figures. Scale: 1 μm.

Rich) regions. As the droplets were irradiated by UV light from above, there was one hemisphere of the droplet which was more exposed than the other, giving the particle an asymmetric shape. This phenomenon was explained by Kamal et al in the context of polymerisation-induced phase separation. Another explanation is that phase separation of 5CB and RM257 arising from UV irradiation might give rise to concentric (multiple) shell structures, therefore there is an outer shell and inner particle. Recent work by Geng et al. produced shells with a similar appearance, wherein each shell contained a single hole. From this research, we may explain that the newly formed polymer shell may attempt to enclose 5CB, and when unsuccessful, the shell would bulge and eventually break upon heating the mixture or during solvent removal. However, the particles in the above experiments appeared to be porous even without the presence of the hole. This is because after polymerisation, the 5CB was able to leave and re-enter the particles by heating and cooling. The hole was only observed after solvent removal.

6.4 Conclusions

We report the synthesis of polymeric porous microparticles from phase separation of binary liquid mixtures. Nematic 5CB/RM257-rich droplets with radial configurations were
formed by cooling, and polymerised by exposure to UV light (365 nm). Heating after polymerisation led to a reduction of the mesogen director field component and eventual escape of 5CB mesogens from the polymerised microparticle as they reached $T_{ps}$ and became miscible with MeOH. Particles were found to shrink and swell with heating and cooling due to their porous nature, as 5CB was able to enter and leave particles according to temperature change. The microparticles maintained the optical properties of nematic 5CB, retaining its radial configuration and had a different morphology on the outer surface compared to the inner surface of the particle, creating an asymmetric particle shape. The generation of porous microparticles from bulk via temperature manipulation of binary liquid mixtures provides an interesting concept for production processes. Furthermore, their anisotropic nature and ability to adapt their shape to temperature stimuli offers new opportunities for applications such as microswimmers and in actuators and microelectromechanical systems.
V

Summary
Chapter 7

Conclusions

The aim of this thesis was to investigate and exploit the possibilities that arose when a binary liquid mixture consisted of a non-polymeric isotropic continuous phase, and a LC dispersed phase. Fundamental to this research was the use of optical microscopy for the analysis of droplet size, dispersity, number of droplets and determination of optical anisotropy of LC droplets and microparticles. The optical microscope could also be configured for photopolymerisation and for fluorescence imaging.

To begin this work, we studied temperature-controlled droplet formation by nucleation of LC droplets in an isotropic medium (MeOH). LC-rich droplets could be formed by reversible heating and cooling cycles, therefore the manipulation of droplet properties was investigated. The depth of the temperature quench was found to determine droplet size, while cooling rate affected number of nucleating droplets. Isotropic 5CB-rich droplets nucleated and grew, and could be quenched further into the nematic phase. The effect of quench depth and cooling rate on trajectory and MSD of the droplets gave insight into the growth modes of this new avenue for droplet production of binary liquid mixtures (Chapter 3).

The optical properties of nematic LC-rich droplets gave insight into late-stage phase separation of 5CB and MeOH. The stability of the nematic phase was compared to the isotropic phase, and thereafter the factors governing phase separation were determined. Ostwald ripening was found as the dominant growth mode at this stage. Microscopic droplet phase separation was found to deviate from bulk phase separation due to the presence of interfacial forces, and required a lower transition temperature in comparison to the bulk. A thermodynamic explanation was given with emphasis on the effect of droplet size on the phase transition temperature. The binary system reaching equilibrium could be viewed from a new perspective due to the optical footprint of the LC, enabling detailed studies of the underlying phenomena (Chapter 4). Alternative factors which affect the contour of the bulk phase diagram were identified, such as confinement and interfacial tension.

Factors which have the capability to affect or hinder the route to phase separation were considered using surfactants and nanoparticles (Chapter 5). It was found that
block co-polymer surfactant PIB-\(b\)-PEO was found to create micelles in MeOH, thereby increasing nucleation points for 5CB-rich droplets, and affecting the growth time and rate of droplets. When silica nanoparticles were added into the continuous phase of the binary liquid, they left a porous-style structure even after the mixture was heated till no droplets remained.

Finally, the binary system was investigated for its potential in microparticle production. A reactive mesogen was incorporated with 5CB, and the nematic droplets with a radial configuration were exposed to UV light. Porous microparticles were formed, and 5CB could be extracted by heating. The microparticles retained the nematic order and could shrink and swell according to temperature, offering new opportunities and insights for applications such as actuators (Chapter 6).
Chapter 8

Future Work

Further to the aforementioned findings, this thesis creates a case for a number of subsequent studies. Chapter 3 presents a method for the controlled formation of LC droplets. One factor that was found to have an influence on the number of nucleation points as well as the mode and speed of growth were the surface properties of the glass slides used in experiments. For consistent results, slides were prepared in the same way throughout this study. However, it was noted that variation in the wetting properties (ranging from hydrophilic to hydrophobic) of the slides were found to effect results. Therefore, the effect of the surface on the heterogenous nucleation of LC droplets would be an interesting insight into nucleation and phase separation.

Chapter 4 discusses late-stage phase separation and the nematic-isotropic transition of 5CB-rich droplets. One key question was how much MeOH must be contained in the droplet to induce nematic-isotropic transition. To answer this question, an initial experiment was proposed, in which a mixture of 5CB and MeOH in varying concentrations would be injected into a medium that was immiscible with both 5CB and MeOH. Appendix A provides some initial data on this experiment, indicating that a binary liquid mixture confined to a droplet deviated from the phase diagram in the opposite manner to that described in Chapter 4. However, a complete study was not feasible in the timescale of this thesis. Research into this would provide valuable contributions for understanding aqueous two-phase systems (ATPs) and cell extraction.

In Chapter 5 it was found that PIB-b-PEO created micelles in MeOH. Micelles in alcohol are extremely uncommon, and this phenomenon deserves further investigation into how and why PIB-b-PEO was able to create micelles.

The findings in Chapter 6 are highly encouraging. However, the possibilities of microparticle production was limited by the experimental set-up. Larger-scale polymer production would be possible outside the confinement of an optical microscope. Furthermore, these investigations focus solely on radial or preradial configurations. Bipolar or axial configurations were not found to be tunable by temperature or size control. However, alternative configurations could provide new types of particles.

This research focuses on LC droplet formation with a specific concentration. Alter-
native 5CB/MeOH concentrations were studied but a 70 % MeOH with 30 % 5CB was settled upon for consistency of experiments. An interesting system to study would be containing a 5CB continuous phase with MeOH droplets. If polymerised, this would open up possibilities for the procurement of porous cellular networks.
VI
Appendices
Appendix A

Binary Liquids Confined to a Droplet

In this chapter, we investigate the isotropic-nematic transition temperature when a binary liquid system is confined to a droplet. The transitions in confinement are compared to the bulk phase diagram.

A.1 Introduction

Two-phase system droplets have been studied primarily in the field of aqueous two-phase systems (ATPs) for biological and medical applications such as cell encapsulation, bioreactors, fabrication of biomaterials, and delivery of biomolecules. In these systems, two incompatible polymer solutions are mixed in water and phase separated above a critical concentration. When confined to a droplet, they adopt a water-in-water-in-oil form with core-shell structure.

The encapsulation of a binary liquid mixture wherein one component is a LC provides insight into the effect of impurities on the configuration of a LC droplet in comparison to the effect on the bulk. Furthermore, the effect of interfacial energy on the phase transitions can be investigated.

A.2 Experimental

Reagents 5CB as described in Chapter. Silicone oil: viscosity 20 cSt (25 °C) and MeOH (HPLC grade) was purchased from Sigma Aldrich. All compounds were used without further purification.

Sample preparation Differing ratios of 5CB:MeOH were placed in a sealed glass cuvette, which was enclosed by a Peltier-regulated sample compartment that allowed control over both temperature and stirring (Quantum Northwest, Qpod 2e). Samples were heated to 35 °C in the cuvette. 10 µl of silicone oil was deposited on a glass slide on a temperature controlled stage under the microscope and heated to 35 °C. Drops of the 5CB/MeOH mixture were injected into the silicone oil via a syringe.
Sample analysis: The slide was placed under an upright microscope (Zeiss, Axio Scope A1) that was operated in transmission and primarily in brightfield mode. A temperature controlled sample stage (Linkam, PE120) was used for all experiments. For droplet analysis, a Lumenera Infinity 3-3UR camera was used, with a resolution of 1936 x 1456 pixels. The sample stage was pre-heated to 35 °C, and then cooled at 20 °C min$^{-1}$ to target temperatures. Calculation of droplet size was carried out using Fiji.

A.3 Results

In this experiment, mixtures of 5CB/MeOH at different vol % (5CB / MeOH, 90 / 10, 80 / 20, 70 / 30, 60 / 40 and 50 / 50) were made up and droplets of the mixtures were immersed in silicone oil by injection, which was immiscible with both components, (see Figure A.1). Numerical values for the concentration at which a mixture of 5CB/MeOH contained in a droplet transitioned from isotropic to nematic were obtained and the results presented in Figure A.1. The results show that the isotropic-nematic transition temperature is generally higher in droplet form than in the bulk, particularly outside of binodal line. As the 5CB/MeOH amounts become more equal, the transition temperature is closer to that of the bulk. However it was noted that when phase separation was expected before phase transition, i.e, within the binodal curve, particularly beyond 50/50 5CB/MeOH, transition temperature was more complicated as phase separation had already occurred inside the droplet before phase transition. After isotropic-nematic phase transition, there was no defect movement, or loss of nematic order over time, as observed in Chapter 3. This is because there is not a diffuse interface between the droplet and the silicone oil.

When a LC is confined, there is a latent heat reduction compared to that in bulk. A calorimetric study of LC 8CB confined to controlled pore glass by Kutnjak et al. observed that decreasing pore size resulted in a progressive disappearance of the latent heat. However, the CPG matrices had much smaller characteristic void diameters ranging from 400 to 20 nm. Wittebrood et al. used light scattering to report that the latent heat of confined LCs is reduced to half of the measured bulk value. As explained by Chen et al., the surface tension and curvature elasticity effects become more important and lead to some reduction in the nematic growth. The opposite is observed here in that for the same 5CB/MeOH mixture confined to a droplet on the micrometre scale, the isotropic-nematic temperature increases compared to that of the bulk.
Figure A.1: Binary Liquid Mixture of 5CB/MeOH Confined to a Droplet. (left) Schematic of 5CB/MeOH droplet immersed in silicone oil. (right) Phase diagram of binary mixture of 5CB/MeOH (adapted with permission from the Royal Society of Chemistry) showing isotropic to nematic phase transition of droplets of 5CB/MeOH mixtures immersed in silicone oil. Images show droplets of 5CB/MeOH mixtures at their transition temperature under crossed polarised light. Scale bar: 10 µm.

A.4 Conclusion

When an entire binary liquid system was confined to a spherical volume and experienced phase transition, the phase diagram was unable to account for the thermodynamics which came into account. It was found that spherical confinement of a binary liquid mixture will increase the phase transition temperatures in comparison to the bulk.
Bibliography


