TOWARD AN ADVANCED MONOLITHIC PRECURSOR
TEMPLATED FROM HEXAGONAL LYOTROPIC LIQUID CRYSTALS

by

GUANG WANG

M. E., Guangdong Ocean University, Zhanjiang, P. R. China, 2010
B. Agr. Jilin Agricultural University, Changchun, P. R. China, 2007

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I am the author of the thesis entitled

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The organic nanofiltration (NF) membranes with pores of uniform size in the range of 1-5 nm have opened up the possibility of performing highly selective small molecules and water purification based on molecular size-exclusion of hydrated salt ions. The template method from hexagonal lyotropic liquid crystals (LLCs) presents a unique path for the fabrication of NF membranes with a uniform pore size and high surface area. The hydrophilic area within the assembly could be utilized by dissolving with polymerizable species and therefore the nanostructure could be cured after physicochemical process. The continuity of cylinders (mesochannels) can also be controlled and extended to the bulk materials after reorientation through appropriate strategies. However, the conversion from soft template to robust membrane is still a significant challenge. The two main difficulties associated with it are the phase retention during photo-polymerization from monomer to polymer phase and the reorientation of mesochannels in a facile way for high flux property.

This thesis presents a comprehensive exploration of the hexagonal system of dodecyl trimethylammonium bromide (DTAB) before and after adding different monomers, poly (ethylene glycol) diacrylate (PEGDA), 2-hydroxyethyl methacrylate (HEMA), and 1,6-Hexanediol diacrylate (HDDA), including the dimensional element calculation, phase behaviours/rheological properties as function of temperature, localization of water/monomers within the unit cell, and the reorientation of mesochannels under external fields. Small angle X-ray/neutron scattering (SAXS/SANS) were used to explore the lipid structure and its dimensions, phase behaviours, alignment and the reconstruction work. Some other instruments such as rheometer, differential scanning calorimetry (DSC), and $^1$H and $^2$H NMR were also applied to characterize the phase behaviours and conduct the reorientation experiments under magnetic field.

Firstly, the hexagonal packing systems with/without different monomers in structural dimensions ie $d$-spacing, lipid core diameters, water and head group thickness, and the surface area available to single lipid were calculated and compared. It demonstrates that the exchange of D$_2$O/H$_2$O ratios will not affect the structural dimensions and phase behaviours significantly but adding monomers will introduce some new interesting properties to the hexagonal system. There will be a rearrangement of the hexagonal system.
system where a small number of aggregates with a broader water and head group thickness but a smaller lipid core diameter are formed. Any excess monomer will not affect the structural dimensions further but will form an aqueous phase that coexists with the hexagonal system without destroying the hexagonal packing. The hexagonal systems with monomer are sensitive to temperature with a reversible phase transition temperature depending on the monomer composition observed and, a lowest complex viscosity is found due to the transition from hexagonal phase to micellar phase. A corresponding decrease in the longest relaxation time to ¼ of that in the binary system after adding monomers from rheometer is in good agreement with the changes in elemental dimension and the sensitivity of the system to temperature.

Secondly, the 2D hexagonal unit cell was reconstructed to localise the water/monomer within the template by using membrane diffractometer. An appropriate monomer ratio and their distribution within the hydrophilic region are believed to utmosely compensate for the entropy loss and enthalpy reduction during polymerization. The uniform water environment and monomer distribution (long and short chain monomers) in the hydrophilic region within the template will facilitate the fabrication of robust membranes originated from the highly cross-linked monomers.

Finally, the reorientation of the mesochannels with the long range being perpendicular to the substrate was conducted under a magnetic or an electric field. The $^2$H NMR measurement displays that the system with monomer mixture of PEGDA and HEMA cab be more easily aligned when compared to the system with only PEGDA. The in situ reorientation of the system in a static electric field conducted in SAXS/WAXS beamline in Australian Synchrotron proves that the system can be well aligned with the order parameter at 0.63. This number can be significantly improved by reducing sample aperture or sample thickness and therefore reducing the domains with diverse azimuthal angle. The reorientation of the mesochannels will remarkably increase the continuity of the nanopores and therefore form a monolith with physical robustness after polymerization.
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<th>Description</th>
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<tbody>
<tr>
<td>LLCs</td>
<td>Lyotropic liquid crystals</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small angle X-ray scattering</td>
</tr>
<tr>
<td>SANS</td>
<td>Small angle neutron scattering</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>$^1$H NMR</td>
<td>Hydrogen Nuclear magnetic resonance</td>
</tr>
<tr>
<td>$^2$H NMR</td>
<td>Deuterium Nuclear magnetic resonance</td>
</tr>
<tr>
<td>2D reconstruction</td>
<td>2 dimensional reconstruction</td>
</tr>
<tr>
<td>PEGDA</td>
<td>Poly (ethylene glycol) diacrylate</td>
</tr>
<tr>
<td>HEMA</td>
<td>2-Hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>HDDA</td>
<td>1,6-Hexanediol diacrylate</td>
</tr>
<tr>
<td>DTAB</td>
<td>Dodecyl trimethylammonium bromide</td>
</tr>
<tr>
<td>ANSTO</td>
<td>Australian Nuclear Science and Technology Organisation</td>
</tr>
<tr>
<td>AINSE</td>
<td>the Australian Institute of Nuclear Science and Engineering</td>
</tr>
<tr>
<td>HZB</td>
<td>Helmholtz-Zentrum Berlin</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulphate</td>
</tr>
<tr>
<td>CPP</td>
<td>the critical packing parameter</td>
</tr>
<tr>
<td>SLD</td>
<td>Scattering length density</td>
</tr>
<tr>
<td>PAA</td>
<td>Polyacrylic acid</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>SAS</td>
<td>Small angle scattering</td>
</tr>
<tr>
<td>$d$</td>
<td>$d$-spacing</td>
</tr>
<tr>
<td>$R$</td>
<td>the radius of lipid core</td>
</tr>
<tr>
<td>$d_w$</td>
<td>the water and head group thickness</td>
</tr>
</tbody>
</table>
\( c \) the volume fraction of surfactant
\( S \) Average surface area available to each head
FT Fourier transform
\( f_n \) Structure factors
Quokka Fixed wavelength SANS instrument in ANSTO
Bilby Time of flight SANS instrument in ANSTO
V1 Membrane diffractometer in HZB
OPAL Open Pool Australian Light water
FWHM the full width at half maximum
SDD Sample to detector distance
\( S_{CD} \) Local order parameter
PLM Polarized light microscopy
\( \eta^* \) Complex viscosity modulus
\( G' \) Storage modulus
\( G'' \) Loss modulus
\( \tau \) The longest relaxation time
MP Match point
D_{34}-DTAB Fully-deuterated DTAB
D_{25}-DTAB Tail-deuterated DTAB
ODF Orientation distribution function
CHAPTER 1 INTRODUCTION

1.1 Research objectives

The objective of this study is to prepare the NF membranes templated from hexagonal LLCs which uniquely has a uniform pore size and high surface area. The whole process consists of exploring the effect of monomers on structural dimensions and their rheological properties, reconstructing the hexagonal unit cell to localize the water/monomer within the template, optimizing the monomer composition and their distribution for a robust polymer structure, and finally reorientating the mesochannels with the long range being perpendicular to the surface of membrane for high flux property.

The NF membranes commonly used in water purification or desalination have drawn increasing attention recently. However, the pore size distribution cannot be easily controlled and the continuity and orientation of the pores through the whole films cannot be maintained. The hexagonal LLCs offers us a good template method for the fabrication of organic NF membranes with uniform and adjustable pore size in the range of 1-5 nm. The high surface area and both utilizable hydrophobic and hydrophilic areas make it not only favourable in drug delivery, biology reactor, catalysis, and optical devices, but also in separation technology (Chung & Park 2009; Lu et al. 2008; Vallooran, Negrini & Mezzenga 2013; Wei & Ma 2008). The templated nanostructure is accessible by mixing amphiphiles and water molecules at designated ratio under certain conditions, normally at ambient environment. The continuity of cylinders can also be controlled and extended to the bulk materials after reorientation through appropriate strategies. Many methods have been developed to control the orientation of cylinders. However, those methods are normally accompanied with a high-cost of synthesis or equipment or complex conditions and therefore not possible to be put into practice (Feng et al. 2015; Ma et al. 2011; Mauter, Elimelech & Osuji 2010; Shan et al. 2012; Teng et al. 2012; Vallooran, Negrini & Mezzenga 2013; Yamauchi, Nagaura & Inoue 2009). The external force especially from the electric field, as the most cost-effective tool in the normal lab and industry, has not been developed for reorientation of mesochannels, which is partially because of the phase
transition happened frequently and also due to the contact issue and dielectric breakdown concern of the electric field.

On the other hand, the researchers have demonstrated that the changes in energetics including a decrease of entropy and enthalpy reduction originated from the loss of the conformational freedom of the growing polymer chain are the main reasons to destroy the nanostructure during photo-polymerization (Forney, Baguenard & Guymon 2013). The attempts to maintain the nanostructure have been made by synthesizing the polymerizable surfactant molecules or introducing a stronger network (Forney, Baguenard & Guymon 2013; Gin et al. 2001). Recently, the surface tension during dehydration after polymerization was found to be crucial to maintaining the structure and the zero surface tension via CO$_2$ critical point drying method can successfully retain the structure (Zhang et al. 2014a). Although those methods sound attractive and did increase the retention rate to some extent, the key problem that haunting in the mind is the localization of the monomer and its optimal ratio within the hexagonal template before polymerization. The phase transition or separation problem mentioned above could be highly possible if the monomer is not evenly distributed or only concentrate on some specified area within the template. The research has proven that the trehalose, a solute, always prefers to concentrate in the middle of bilayer structure instead of the expected even distribution (Kent et al. 2014). However, the localization of the monomer within the 2D hexagonal unit cell has not been explored. The small scale changes in energetics cannot be explored by using normal tools but the reconstruction of the hexagonal unit cell through the SAXS/SANS measurement.

The ultimate objective of this study is to prepare the robust NF membranes with a uniform distribution of pore size and high continuity. The soft hexagonal LLCs mesophase formed of DTAB and water with monomer will be acted as a template in this research. The reorientation of mesochannels will be executed under magnetic field using NMR facility first and then conducted in an electric field by using the newly designed electrode in-situ with SAXS/SANS measurement. 2D reconstruction of the hexagonal unit cell will be applied to locate the water/monomer through SANS measurement after contrast variation, and the optimal composition and distribution of monomers are selected. Finally, the template with perpendicularly aligned and uniform nanopores in the range of 1-5 nm was prepared for the fabrication of robust NF membranes.
1.2 Outline of the thesis

The thesis consists of 6 more chapters listed as follows:

Chapter 2 gives a comprehensive literature review on the application of membrane technology and development of the relevant materials in separation industry, the introduction of the LLCs and its application in many areas, the template methods developed for materials fabrication, and the up-to-date progress on the preparation of NF membrane templated from hexagonal LLCs.

Chapter 3 presents the materials, chemicals, instrumentations, and experimental techniques used in the thesis, the sample preparation procedure and some characterization methods.

Chapter 4 explores the effect of different monomers on the important structural dimensions of hexagonal packing and the phase behaviour of the systems with various monomer compositions as a function of temperature. The addition of hydrophilic monomers will induce a rearrangement of the hexagonal system by diminishing the aggregate numbers with a smaller lipid core diameter and a wider water and head group thickness. $^1$H and $^2$H NMR measurements were further used to probe the hexagonal system. The rheological property of the system with and without monomers was studied to give a further explanation on the different phase behaviours and physical property.

Chapter 5 investigates the 2D reconstruction of the hexagonal unit cell templated from the binary system of DTAB and water with and without monomers by using membrane diffractometer after contrast variation. The small scale changes in scattering length density (SLD) corresponding to the contrast variation were used to localize the water/monomer within the template after Fourier reconstruction. The optimal monomer composition and distribution within the template will further enforce the mechanical property by increasing the cross-link density of polymerized work.

Chapter 6 studies the macroscopic reorientation of the mesochannels templated from the ternary hexagonal phase of $\alpha$-deuterated DTAB, water, and different monomer compositions under magnetic field of NMR spectrometer for the first time together with temperature variation. Reorientation of the system with different monomer compositions can be all realized easily but the degree of alignment varies depends on the monomer composition. The system with monomer mixture of PEGDA and HEMA
presents a higher degree of alignment and was selected to fully investigate the reorientation in an electric field with an \textit{in-situ} SAXS measurement to quantify the reorientation. In order to achieve the \textit{in-situ} SAXS experiment, an electrode was specially designed and allowed to investigate reorientation in a direction parallel to the electric field. Measurements on the sample stage of SAXS/WAXS beamline in Australian Synchrotron, SANS measurement were also conducted to confirm the reorientation results. The order parameter from the azimuthal distribution after alignment was extracted to quantify the reorientation effect.

Chapter 7 gives a summary of the highlight and achievements obtained from the research and some further strategies that could benefit the fabrication of NF membrane and its physicochemical property for the potential actual application.
CHAPTER 2 LITERATURE REVIEW

2.1 Development of membrane industry

2.1.1 Water crisis

Water scarcity is recognized as a major threat to human activity and therefore water purification technologies are drawing increasing attention worldwide. Consistent with the data in “water in crisis” edited by Gleick: the entire body of the world’s water sources is predominantly made up of oceans with only a small quantity of fresh water making up the remainder. Only 2.5% is fresh water which is what life including the human being and other lives are consuming to survive. Actually, among this limited freshwater, only 31.3% is surface and ground water which can be used by humans and the remaining 68.7% is actually found in the form of Glaciers and ice caps as shown in Figure 2.1 (Gleick 1993). Various sources typically due to inadequate sanitation, algal blooms, detergents, fertilizers, pesticides, chemicals, potentially toxic metals, salinity and high sediment loads have seriously contaminated water quality and are effectively reducing the supply of freshwater for human use (Falconer & Humpage 2005; Foley et al. 2005; Rozell & Reaven 2012).

![Figure 2.1 Distribution of water resources on the earth (Gleick 1993).](image)

As the Earth’s driest inhabited continent, Australia has been struggling to cope with the consequences of devastating chronic droughts. Although it is relatively abundant in the tropical north where few people live according to the distribution of run-off in Australia, in the more populated and temperate south, water is relatively scarce (Figure...
2.2) (Thomas 1999). In the south, the increasing climate variability by declining rainfall, rapid population growth, and the previous poor governance systems have led to the over allocation of surface and groundwater supplies. Many state governments have enacted water restrictions in many cities for several years including watering lawns, using sprinkler systems, washing vehicles, etc.

![Figure 2.2 Distribution of run-off in Australia (Falconer & Humpage 2005).](image)

In recent years, desalination has drawn more attention by scientists and governments and played an important role in some countries to some extent. However, the expenditure on desalination including infrastructure, energy, and maintenance cannot be ignored. The energy consumption of seawater desalination methods is listed in Table 2.1 from which one can see that although the energy consumption of some desalination methods has almost reached as low as 3 kWh/m³, it is still much higher than local fresh water supplies that only use 0.2 kWh/m³ or less (Dashtpour & Al-Zubaidy 2012; Goldstein & Smith 2002). An economical and environmentally sustainable method of water recycling is therefore essential. Application of membrane technology is widely used for water recycling.
Table 2.1 Energy consumption of various desalination methods (Al Gobaisi 2000; Ghalavand, Hatamipour & Rahimi 2015; Younos & Tulou 2005).

<table>
<thead>
<tr>
<th>Desalination method</th>
<th>MSF</th>
<th>MED</th>
<th>MVC</th>
<th>RO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical energy (kWh/m$^3$)</td>
<td>4-6</td>
<td>1.5-2.5</td>
<td>7-12</td>
<td>3-3.5</td>
</tr>
<tr>
<td>Thermal energy (kWh/m$^3$)</td>
<td>50-100</td>
<td>60-100</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Total equivalent electrical energy (kWh/m$^3$)</td>
<td>13.5-25.5</td>
<td>6.5-11</td>
<td>7-12</td>
<td>3-5.5</td>
</tr>
</tbody>
</table>

Note: Multi-stage Flash - MSF; Multi-Effect Distillation - MED; Mechanical Vapour Compression - MVC; Reverse Osmosis – RO.

Water recycling is divided into treatment and purification processes, by which undesirable chemicals, biological contaminants, suspended solids and gases are removed from the contaminated water. The methods used for wastewater treatment comprise physical processes such as filtration, sedimentation, and distillation; biological processes such as slow sand filters or biologically active carbon; chemical processes consist of flocculation and chlorination and the use of electromagnetic radiation like ultraviolet light (Scott & Ollis 1995; Slokar & Majcen Le Marechal 1998). No matter what kind of processes they are, membrane technology had been extensively used and played an important role in water treatment due to diverse advantages including (Logan & Elimelech 2012):

- Relatively low energy consumption
- Working at normal conditions without the addition of chemicals
- Ease of use and widespread popularity
- Environmental friendliness without any by products
- Well-understood process methods

### 2.1.2 Membrane filtration

Since the first commercial separation membrane was reported in the 1960s, many polymeric and inorganic membranes have been developed for commercial purposes including reverse osmosis, ultrafiltration, nanofiltration, microfiltration, electrodialysis, and pervaporation membranes. All these membranes have been extensively used either individually or in combination in various purification processes according
to their specific characteristics (Peters 2010). The detailed applications and classification of membrane filtration processes are shown in Figure 2.3 (Hughes 1996).

![Figure 2.3 Applications and classification of membrane filtration process (Hughes 1996).](image)

### 2.1.3 Other innovative membrane technologies

Apart from traditional membrane filtration processes, recently, innovative processes such as membrane contactors, catalytic membrane reactors, microbial fuel cell membrane and membrane bioreactors, have been extensively studied and shown strong potential applications in separation industry. Membrane contactors are typically fabricated with a hydrophobic hollow-fibre micro-porous membrane which acts as a support to allow a gaseous phase and a liquid phase contact directly and make mass transfer between the phases without dispersing one phase into the other by applying breakthrough pressure (Cartinella et al. 2006; Gabelman & Hwang 1999; Lai, Chen & Liou 2013). Microbial fuel cell membrane is a technology that uses exoelectrogenic biofilms on the anode to degrade organic matter and produce renewable energy in the form of electricity (Malaeb et al. 2013; Rubaba et al. 2013). Besides, an emerging waste-water-treatment technology by using the membrane reactors to retain biomass and purify effluent has been found to be well suited for applications such as water reuse. The membrane reactors with small sizes offer a host of technical advantages
over activated sludge systems compared to traditional activated sludge process (Daigger et al. 2005; Shannon et al. 2008; Yang, Cicek & Ilg 2006). These innovative technologies/methods make those membranes more versatile and more advantageous and therefore will be applied widely in various separation areas. However, due to the potential deficiency like membrane fouling or low effluent quality, these technologies were normally used by combining with other membrane filtration processes to improve wastewater treatment (Kimura et al. 2005; Malaeb et al. 2013).

2.1.4 Membrane materials

For wastewater treatment, the membrane materials need to have the good film-forming ability, high mechanical, chemical and thermal resistant properties, environmental friendly, as well as good permeability and selectivity. In addition, membranes should have different and specified abilities according to various requirements and application areas. Generally, membranes can be divided into organic membranes and inorganic membranes according to the raw materials. Inorganic membranes mainly include metal, alloy, ceramic, composite and glass membranes. These inorganic membranes are very popular due to the properties such as:

- High strong acid, strong base, temperature, and concentration resistant
- High flux and separation efficiency, and normally renewable
- High filtration pressure resistant
- Easy to preserve

However, organic membranes with many unique properties, such as plenty of raw materials, low cost, and high loading density have been extensively applied in practice, occupied about 85% of the whole membrane market. Especially as the development of material science, lots of complex materials synthesized or modified by inorganic materials were applied to fabricate membranes including cellulose and its derivatives, poly-sulfone, poly-acrylonitrile, Poly-vinylidene fluoride, poly (ether ether ketone), polyether sulphone, polyimide as well as silicone rubber polymers (Devrim et al. 2009; Drews et al. 2007; Guruprasad & Shashidhara 2004; Kute & Banerjee 2007; Lin et al. 2006; Mashak & Taghizadeh 2006; Patel et al. 2010; Peng et al. 2005; Wang et al. 2008; Zhang, Rong & Lu 2005). These materials all have been used in practice according to their specific characteristics like mechanical and thermal-stability, tolerance to the most solvents or the commercial availability. However, the
disadvantages of them such as poor hydrophilicity and biocompatibility still need to be further improved for extensive applications in water and protein filtration and membrane bioreactor. Besides, the novel carbon nanotube and graphene oxide membranes were also prepared for ionic and molecular sieving, which presents a new generation of ultrathin, high flux, energy-efficient membranes (Hinds et al. 2004; Mi 2014).

Except for these highly hydrophobic materials, some soft materials including the natural and man-made polymers with nanostructure have gradually attracted the attention of scientists who want to use them to fabricate novel nanomaterials for separation technology because of their inherent nontoxicity, excellent biocompatibility, and renewable properties. These polymers obtained via chemical or physical crosslinking reaction has been mainly used for tissue engineering and biomedical applications (Klouda & Mikos 2008; Lai & Baccei 1991). In some areas such as wastewater treatment, gas separation, and desalination, hydrogels show extensive application prospect. So far, many hydrogel materials such as chitosan, PEGDA, as well as some small molecules have been employed to fabricate the membranes (He, Echeverri & Kyu 2014; Mi et al. 2001; Putrie & Setyawan 2014).

2.1.5 NF membranes

The polymer membranes with morphologies at nanometer size have great potential to be applied in various areas (Chung & Park 2009; Lu et al. 2008; Vallooran, Negrini & Mezzenga 2013; Wei & Ma 2008), especially for the NF membranes that have a uniform pore size in the range of 1-5 nm and high specific surface area, opening up the possibility of performing highly selective small molecules and water purification based on molecular size-exclusion of hydrated salt ions (Fornasiero et al. 2008; Mi 2014). A more permeable separation layer with uniform pore distribution will significantly maintain or improve salt rejection while increasing the flux compared to RO. The transport of water molecules through hydrophobic double-walled carbon nanotubes has demonstrated that the fluxes are over three orders of magnitude higher than those predictions by using continuum hydrodynamic models (Hinds et al. 2004; Holt et al. 2006; Hummer, Rasaiah & Noworyta 2001). However, membranes with the necessary anisotropic transport properties due to oriented carbon nanotubes will be difficult and costly to be prepared. The high performance of membranes based on
nanometer size (1-5 nm) in diameter, however, encouraged the development of various nanostructured and nanoreactive membranes for use in water purification for diverse pollutants (Allabashi et al. 2007; Athanasekou et al. 2012; Dotzauer et al. 2006; Liu et al. 2012; Srivastava et al. 2004).

Figure 2.4 Schematic showing the trade-off between permeability and selectivity of synthetic NF membranes.

An ideal membrane for NF would require the generation of a thin film with physically continuous and vertically aligned nanopores with a narrow size distribution. However, currently developed fabrication techniques for NF membranes, such as tract etched, particle-assisted wet, and phase inversion precipitation, are all suffering from kinetically controlling pores of random size and orientation and therefore subject to a ubiquitous trade-off behaviour between permeability and selectivity as shown in Figure 2.4. Highly permeable membranes lack selectivity and vice versa. The polymer membranes presenting the highest selectivity at a given permeability always lay near or on a line called the upper bound and this behaviour (the slop), observed in all cases in both dense and porous membranes, absolutely depends on the parameters of the molecules/ions pair (Park et al. 2017). This departs considerably far from the ideal and limits their use. Therefore, for the polymer NF membranes, the ability to precisely control morphology, the size, and anisotropy over a large scale is quite challenging but essential for this application.
2.2 Lyotropic liquid crystal

The nanostructured materials that exhibit size and shape dependent properties have shown obvious potential applications in various areas. During the past twenty years, many methods from lithographic techniques to chemical syntheses have been developed to prepare nanostructured materials with controlled structure in size, shape as well as dimensionality (Trindade, O'Brien & Pickett 2001; Wang, Chen & Jiao 2009). Among these strategies, the template method from lyotropic liquid crystal was regarded as the most useful route and a number of papers reporting the mesoporous materials have been published since the template synthesis was firstly explored by Martin (Mao et al. 2014; Martin 1994; Thubsuang et al. 2014). The LLCs, as a kind of soft matters that is easily deformed and/or structurally altered by the thermal or mechanical stress of the magnitude of thermal fluctuations, is a self-assembled system after dissolving the amphiphiles into a hydrophilic medium like water. LLCs possesses different mesophases including micelle, lamellar, hexagonal, cubic, inverted cubic, and inverted hexagonal phases depending on various factors in the system as shown in Figure 2.5. These hierarchical complexes all have a constant lattice ranging from several nanometres to tens of nanometres which could be acted as the template candidate for designing novel nanomaterials.

Figure 2.5 Different types of aggregates formed by surfactants with water (Gin et al. 2001).
2.2.1 Classification and characteristics of surfactants

Amphiphilic molecules (surfactants) normally contain one or more hydrophobic organic tails and a hydrophilic head-group. They can be classified into different types according to the properties of the ion generated after dissolving into water. At the same time, some novel surfactants synthesized by scientists also present new potential applications. The basic classification and the shape of different surfactants are shown in Figure 2.6.

![Diagram showing classification of surfactants (a) and the shape of different surfactants (b).](image)

Figure 2.6 Diagram showing classification of surfactants (a) and the shape of different surfactants (b).
Cationic surfactants

The normal structure of cationic surfactants is shown in Figure 2.7. The amphiphile is a cation. The most commonly used cationic surfactants are quaternary ammonium compound whose charged group being quinquevalent nitrogen atoms. Cationic surfactants have high water solubility and are stable in the acidic and alkaline environment. Besides, they are also used to sterilize the skin, mucosa, and surgical instruments due to the excellent bactericidal effect. Cationic surfactants used for nanostructure templates include DTAB, cetyltrimethylammonium bromide (CTAB), as shown in Figure 2.8.

Figure 2.7 Diagram showing the structure of cationic surfactants.

![Diagram showing the structure of cationic surfactants](image)

Figure 2.8 Molecular structure of DTAB (top) and CTAB (bottom).

Anionic surfactants

The most active part of the anionic surfactants are the anions generated after dissolving into water. The main anionic surfactants include Carboxylate (R-COONa), Sulphate (R-OSO₃Na), Sulphonate (R-O₂Na), and Phosphate (R-OPO₃Na₂). Normally, the anionic surfactants all have excellent emulsion capability and can be used in different areas according to various properties derived from diverse structures. The commonly
used anionic surfactant to form a template is sodium dodecyl sulphate (SDS), as shown in Figure 2.9.

![Figure 2.9 Molecular structure of SDS.](image)

**Ampholytic surfactants**

The presence of both positive and negative groups in the molecular structure gives ampholytic surfactants special properties, such as cationic or anionic surfactants in a solvent with different pH value. Lecithin pattern, a natural ampholytic surfactant derived from soybean and yolk, is very sensitive to heat and can be easily hydrolyzed under acidic or alkaline conditions and in the presence of the enzymes. Another two types of ampholytic surfactants are:

- Amino acid pattern: R-NH₂⁺-CH₂CH₂COO⁻
- Betaine pattern: R-N⁺(CH₃)₂-COO⁻

**Non-ionic surfactants**

Non-ionic surfactants do not dissociate after dissolving in water. The hydrophilic part of them mainly consists of oxyethylene groups (Myrij and Brij), polybasic alcohol (Span and Tween) or acyl-amin. Normally, non-ionic surfactants can be divided into ester, ether, amine, amide and a mixed type of ester and ether (Tween).

**Special surfactants**

Fluorinated surfactants with Fluorocarbon chains acting as the hydrophobic part have extremely high surface activity. They can decrease the surface tension of water to less than 20 mN·m⁻¹. Besides, they are very stable and show antioxidant, strongly acidic and alkaline and high temperature resistant. Other special surfactants including silicon surfactants, high molecular surfactants, bio-surfactants, amino series surfactants etc. were also used in diverse areas according to their special properties.
2.2.2 Phase formation and their behaviours

The amphiphilic characters of those surfactant molecules prefer to self-assembly into aggregates after contacting with water or other hydrophilic agents, with the heads defining the interfaces of phase separated aqueous domains and the tails forming hydrophobic regions. These aggregates consist of simple individual structures such as micelles, vesicles and highly organized yet fluid condensed assemblies with one-, two-, or three- dimensional nano-scale hierarchical complexes as the increase of the percentage of surfactant in the system.

<table>
<thead>
<tr>
<th>Amphiphile “shape”</th>
<th>Amphiphile structure</th>
<th>$\rho = \frac{\nu}{a_0 l_c}$</th>
<th>Rel. H$_2$O content</th>
<th>Aggregate structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic tails</td>
<td>Conical</td>
<td>$&lt; 1/3$</td>
<td>High</td>
<td><img src="image" alt="Conical" /></td>
</tr>
<tr>
<td>Hydrophilic head</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1/3 - 1/2$</td>
<td>Medium</td>
<td><img src="image" alt="Conical" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\approx 1$</td>
<td>Medium</td>
<td><img src="image" alt="Cylindrical" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$&gt; 1$</td>
<td>Low</td>
<td><img src="image" alt="Cylindrical" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.10 Relationships between shape, ratio of surfactant and their preferred aggregates according to the Israelachvili Model (Israelachvili 1985).

The self-assembled nanostructures adopting different mesophase totally depend on the molecular shape and the lipid tail length of investigated surfactants or copolymers, their composition, and the experimental conditions (Figure 2.10) (Hyde et al. 1996; Yaghmur et al. 2009; Yaghmur, Sartori & Rappolt 2012). Normally, for a specified surfactant or a mixture of surfactants system, the assembled nanostructure has the temperature-, concentration- and pressure- dependent behaviours as shown in Figure 2.11 (Mcgrath 1995; Yaghmur et al. 2009). Phase transition between different morphologies of aggregates is realizable along by adjusting the concentration of
surfactant, temperature, and pressure, which can be detected by a number of techniques including DSC, NMR, SAXS/SANS, freeze-fracture electron microscopy as well as cryo-transmission electron microscopy.

Figure 2.11 (Left), temperature-pressure behaviour of fully hydrated tetradecane-loaded monoolein/water system and (Right), temperature-concentration dependent behaviour of LLCs formed of DTAB and water (Mcgrath 1995; Yaghmur et al. 2009).

There are two aspects that should be noted about the formation of the LLCs morphologies: the bending energy tends to assist surfactants in forming mesophase which is hindered by the mainly packing frustrations (Gruner 1985; Gruner 1989; Shearman et al. 2010). Besides, the hydrophobic effect that induces segregation into hydrophobic and hydrophilic domains dominates the self-assembly process of the surface-active materials and further forms the ordered mesophase. All of these actions are embodied in the form of curvature on the interface. Actually, the effects of the concentration and the shape of the surfactant molecules on morphologies are all derived from the changes of the curvature on the interface of the aggregates. Two values can be used to judge the curvature at any point on the interface: the mean interfacial curvature, $H$, and the Gaussian curvature, $K$ (Gruner 1989; Hyde 2001; Rappolt 2006). $H$ is defined as the average of the principal curvatures $C_1$ and $C_2$:

$$H = \frac{C_1 + C_2}{2}$$

(2.1)

While $K$ is depicted as:

$$K = C_1 \cdot C_2$$

(2.2)
Basically, the principal curvature is zero in the lamellar phase, while in the bi-continuous cubic phase, the principal curvature is nonzero and of opposite sign: $C_1 = -C_2$, and in the hexagonal phase, one principal curvature is zero and the second is nonzero (Yaghmur et al. 2012; Yaghmur, Sartori & Rappolt 2012).

On the other hand, the curvature can also be rationalized on a molecular level. The critical packing parameter (CPP, also called molecular shape factor), $\rho$, is normally used to describe the molecular geometry of surfactant and the formation of self-assembled structure, which is given by:

$$\rho = \frac{V}{a_0 l_c}$$

(2.3)

where $V$ is the hydrophobic chain volume, $a_0$ is the effective hydrophobic/hydrophilic interfacial area, and $l_c$ is the hydrophobic chain length.

The corresponding CPP to different phase morphologies are shown in Figure 2.10. Furthermore, the tendency to form inverted mesophase is dictated by increasing the mean negative curvature modulus of the interface shown in Figure 2.12. Normally, the curvature defined to be negative when the surfaces bent toward the surrounding water and tend to form inverted mesophase, otherwise it will be positive and prefer to form normal mesophase. The zero state is the flat interface without bend such as lamellar mesophase.

Figure 2.12 Schematic description for the nanostructure of LLCs depending on the mean interfacial curvature (Iglic & Kulkarni 2013). $L_\alpha$, lamellar phase; $V_2$, inverted bio-continuous cubic phase; $H_2$, inverted hexagonal phase; $I_2$, inverted discontinuous cubic phase; and $L_2$, inverted micellar solution.
2.2.3 Applications of LLCs

The inherent properties of LLCs such as nanostructure and high surface area make it favourable to actual application in many areas. The lamellar and inverted hexagonal phases so far have been extensively studied because of the prevalence of organized lipid structure in biology. The dysfunction of the semi-permeable barrier of cell membrane originated from phase transition from lipid bilayer structure to non-bilayer structure, mostly inverse hexagonal phase, as a response to the external stresses such as high temperature and dehydration was regarded as one of the apoptosis mechanism. The more detailed progress on the research of lipid bilayer and some vesicles please refer to the book named “Advances in Planar Lipid Bilayers and Liposomes” (volume 18) (Iglic & Kulkarni 2013). More complicated hexagonal and cubic phases have drawn increasing attention as they are the most promising paths in preparing nanomaterials by incorporating hydrophobic or hydrophilic reagents separately or concurrently into domains of LLCs with well-defined nanoscale geometries. The fabricated complex materials by crosslinking a mixture of two incompatible polymerizable monomers within a hexagonal LLCs template possess various new physical properties depending on the monomer composition (Clapper & Guymon 2006). Some studies with hexagonal LLCs system demonstrated various applications in the areas such as conducting materials, semiconductor, catalyst, and the drug delivery medium (Hulvat & Stupp 2004; Pecinovsky, Nicodemus & Gin 2005; Vallooran, Negrini & Mezzenga 2013; Wolosiuk, Armagan & Braun 2005). The fabrication of the NF film templated from hexagonal LLCs started from the 1990s because of the special properties including uniform pores of nano-scale and high surface area (Kresge et al. 1992).

2.3 Template method from hexagonal LLCs

The template method is divided into the hard template and soft template, as shown in Figure 2.13 (Yamauchi & Kuroda 2008). The hard template usually consists of silica (Lu & Schüth 2006; Mulvaney et al. 1997), mesoporous carbon (Dong et al. 2003; Xia & Mokaya 2005), anodic aluminium oxide (Orikasa et al. 2006), while the soft template is composed of biomolecules, block polymers, polymer gels, fibres as well as emulsions (Chall et al. 2013; Salmaoui et al. 2013). Soft template method has drawn more attention for the fabrication of nanostructured materials because it is more
versatile than the hard one (Van Bommel, Friggeri & Shinkai 2003). The inherent properties like non-toxicity and good biocompatibility make it irreplaceable in some areas including contact lenses, tissue scaffolds as well as biology. For separation industry, especially for water purification, desalination, and gas separation that are closely associated to the society and environment the organic polymer materials are more desirable. Direct templating of hexagonal LLCs has been proved to be a very versatile approach and demonstrated many advantages with highly ordered networks and narrow pore-size distributions. However, LLCs are inherently fluid, and therefore lack the robustness required for membrane application. A facile method to fabricate the NF polymer membrane by using self-assembling LLCs as template is photopolymerization by using diene reactive group compared with other methods owing to two main reasons:

1) Fast initiation rate and readily controlled through light intensity and photoinitiator concentration (Decker 2002; Odian 2004).

2) Inherent sensitive properties of LLCs phase behaviours to concentration, temperature and pressure mentioned above.

Figure 2.13 Template methods for the fabrication of mesoporous materials. Hard template (a) and soft template (b) (Yamauchi & Kuroda 2008).

However, the polymerization of the more complex non-lamellar LLCs still shows some problems on phase retention after polymerization and following a series of
processes (Clapper & Guymon 2006; Depierro, Olson & Guymon 2005; Sievens-Figueroa & Guymon 2008; Zhang et al. 2012a). Understanding potential factors that affect the phase retention and their mechanisms is the key for the following experiments.

2.3.1 Phase transition and separation

The phase transition during polymerization by driving changes in interface curvature has been reported, from which the hexagonal structure was shown to transform to the lamellar phase firstly (Thundathil, Stoffer & Friberg 1980). As the monomer phase is substituted by a polymer phase, the changes in polarity of the dispersion medium and the partitioning of each compound will occur accordingly. The decrease of entropy and the reduction in enthalpy are mainly originated from the loss of the freedom of the growing polymer chain accompanied with polymerization (Forney, Baguenard & Guymon 2013). After that, some more work on the factors that can affect the structure retention or polymerization kinetics in LLCs system has been reported by Guymon’s group (Depierro, Olson & Guymon 2005; Lester & Guymon 2002; Sievens-Figueroa & Guymon 2008). In their research, the polarity and mobility of the monomer and the photo-initiator are all important factors influencing the polymerization kinetics in those systems. Briefly, the mobile and hydrophilic initiators have shown an independent initiation rate in LLCs system of various composition and morphology. While the rate of initiation with the immobile and hydrophobic ones appears highly dependent on LLCs order and composition, the aliphatic chain length, on the other hand, also played an important role in controlling the polymerization rate. Therefore the order of the hexagonal phase decreases as the aliphatic tail increases. In addition, apart from the polymerization, the treatments of the polymerized materials including surfactant removal, and dehydration are all critical to retain the morphology with the precisely controlled nanostructure.

2.3.2 Phase retention

The disruption of the inner structure during photo-polymerization is the main obstacle for the fabrication of organic NF membranes. To resolve this problem, some considerations and actions have been taken to retain the desired phase:
1) The location of diene groups conjugated with the acyl chain carbonyl should not interfere with the biocompatibility of the interface and have less effect on curvature.

2) The entropy loss and enthalpy reduction should be compensated by using the monomers with a high number of reactive entities so that the monomer can be polymerized with lowest conversion rate.

3) The structure of the selected surfactant or surfactant mixtures or any other molecules dissolved in the system is also important to predict the preference of the packing pattern (Gruner 1985; Rappolt et al. 2003).

4) A more thermodynamically stable template with long rearrangement times should be developed.

5) Some small multifunctional monomers with high mobility that form cross-linked networks easily could be used to enforce the instant interface curvature during polymerization.

Lots of efforts have been made to conquer the phase transition/separation of hexagonal LLCs during polymerization, which can be summarized and listed as follows.

**2.3.2.1 Application of co-surfactant**

Co-surfactants play an important role in directing the formation of mesophase, stabilizing the LLCs at required mesophase and controlling the alignment process by acting as structure directing agents, charge transfer complexation agents, hydrophobic swelling agents or as stabilizers (Hara, Nagano & Seki 2010; Ma et al. 2011; Melosh et al. 2001; Vallooran, Bolisetty & Mezzenga 2011). The main mechanism is that co-surfactants will partition at the interface between the hydrophobic and hydrophilic domain and reduce the repulsive interaction of the adjacent head group, by which they can control the curvature and stabilize the current phase. For some alcohols with medium or long chains, they could diffuse into the hydrophobic domain and transfer the current phase to another phase because of the swelling effect. Based on these mechanisms, co-surfactant could also be an effective tool to make the hexagonal phase stable or realize the phase transition (Giacomelli et al. 2010; Xu et al. 2004). Additionally, the pore size of the nanochannels could be controlled by changing the mass ratio of surfactant/co-surfactant as well (Feng, Bu & Pine 2000).
2.3.2.2 Surfactant analogues

Thermodynamically driven phase separation within surfactant mesophase often prevents polymer morphology from being precisely controlled after photo-polymerization, which further induces the changes of properties that highly depend on the nanostructures (Clapper, Sievens-Figueroa & Guymon 2007; Kumaraswamy et al. 2005). Previous results demonstrated that the birefringence decreased and the fan-like optical texture was less defined after photo-polymerization (Figure 2.14). Meanwhile, the scattering intensity decreased and the position of scattering peaks changed due to the less ordered nanostructure. Research also shows that the phase separation during the polymerization is the result of a decrease of entropy originated from the loss of the conformational freedom of the growing polymer chain in the LLCs template, combined with a reduction of enthalpy due to the polymer staying solvated within the amphiphiles (Forney, Baguenard & Guymon 2013; Gin et al. 2008). Therefore, the analogues of the surfactant were synthesized by grafting the diene group into the head or tail of surfactants to improve the compatibility between the monomer and surfactants, and to counterbalance the loss of entropy during photo-polymerization, by which the retention rate of the hexagonal structure was improved after polymerization. Figure 2.15 shows the DTAB analogues. Alternatively, the synthesized surfactant molecules with a special molecular shape that prefer to form the stable hexagonal packing based on the Israelachvili Model is also a good choice to increase the retention rate (Gin et al. 2001).

![Figure 2.14 Polarized light microscope images before (a) and after (b) photo-polymerization of hexagonal LLCs of DTAB, H₂O, and PEGDA.](image-url)
2.3.2.3 Special drying process

Apart from two ways of retention of nanostructure mentioned above during the photo-polymerization process, removal of surfactant and the dehydration process are also key steps to maintain the hexagonal phase as it is necessary to remove the surfactant from the system by immersing the polymerized membrane into distilled water for a long time. The water will inevitably diffuse into the template even in polymerized system. In this case, it is generally believed that a higher cross-link density by incorporating some small multifunctional monomers or the monomers with a high number of reactive groups would significantly decrease the effect of hydration on the polymer system. On the other hand, research has shown that maintaining the low surface tension during the dehydration process was the key to retaining the original structure of materials. Critical point carbon dioxide (CO$_2$) drying method with lower or even zero surface tension proved to be an efficient way to enhance the internal filamentous structure of biofilm and porous materials including organic and inorganic materials (Dudley & Kolasinski 2009; Valentin et al. 2005; Zhang et al. 2012a). The fundamental is that the surface tension maintains constant during the whole drying process including substituting the water with liquid CO$_2$ and followed by drying the membrane at CO$_2$ critical point at which the density of the liquid and gaseous phases is identical. The reinforcement effect of the silica network penetrated into the hexagonal LLCs template after

Figure 2.15 Surfactant analogues synthesized by previous research (Forney, Baguenard & Guymon 2013).
crosslinking under UV light was shown to significantly strengthen and retain the nanostructure (Zhang et al. 2014b).

2.3.2.4 Distribution of monomers

An important issue overlooked by the researchers so far is the distribution of the monomer(s) within the LLCs hexagonal template which could also be a critical reason that can control the phase retention. The physical robustness of the polymerized materials absolutely depends on the water region thickness and the monomer distribution within it, which could be evenly or concentrated in some specified area. Undoubtedly, the thicker water channel and the evenly distributed monomer are preferable for robustness of membrane. However, any small scale shape changes within the hexagonal unit cells could not be explored by using normal characterization methods but the Fourier reconstruction from the SLD map. The SLD from SANS data that is sensitive to overall molecules included in the system could be obtained after reconstruction and the effect of the monomer(s) on the SLD map can be arrested and enlarged in a mathematic way after Fourier transform. The reconstruction work was mainly practiced by using the lipid structure to localize the trehalose and the coenzyme Q10 within the system due to their actual biological functions in biology system (Hauß et al. 2005; Kent et al. 2014). The solutes were all shown to have a preference within the lipid structure and some have a specified orientation with respect to the membrane plane (Figures 2.16 and 2.17). The reconstruction work (Ding et al. 2004; Harper et al. 2001; Turner & Gruner 1992) were generally explored by using inverted hexagonal LLCs with SAXS or SANS data. However, the reconstruction of relatively complex 2D hexagonal LLCs has not yet been reported. Additionally, the hexagonal LLCs normally presents a very stable property to temperature, for example, like DTAB whose hexagonal binary system with water is still intact at up to 100 °C, although it is called soft matter. However, the rheological behaviour of the hexagonal LLCs is less known because of its much higher viscosity than a lamellar phase. The different hexagonal packing systems with the monomer distributed within it are worthy of being explored for further structure retention and final membrane fabrication.
Figure 2.16 Diagram showing the distribution of trehalose within the lipid bilayer structure (Kent et al. 2014).

Figure 2.17 Simulation of the lipid membrane with embedded ubiquinone (dark grey) (Hauß et al. 2005).
2.4 Reorientation of mesochannels

The retention of hexagonal phase is the prerequisite for the fabrication of NF membrane with porosity. The membranes with controllable nanostructure in dimensionality such as pore size, wall thickness, but favourable orientation, are very important materials for further applications in the treatment of surface water, ground water, and industrial wastewater in which different contaminants such as toxic metals, organic and inorganic compounds, bacteria and viruses could be found. The dimensional elements of the hexagonal packing include pore size, water and head group thickness and the average area available to each head group and could be calculated by using the volume fraction of amphiphiles and water molecules from SAXS/SANS measurement (Luzzati & Husson 1962; Tate & Gruner 1989). And to some extent, the pore size could be also adjustable by using some organic molecules (Feng, Bu & Pine 2000). However, the inherent preference of isotropic distribution of the mesochannels within the template severely limits the filtration efficiency even if the nanostructure is precisely controlled during the whole process. In addition, the mechanical property will be significantly improved for a monolith after aligning the cylinders through the film. Therefore, the continuity of nanopores through the whole film by reorientating the mesochannels will be another key obstacle for the actual application.

Polymer membranes with well-defined pores in the range of 1-10 nm have the potential to selectively distinguish and transport certain molecules or ions based on their shape, size, and chemical properties. Several methods have been developed to align the hexagonal mesochannels with the long range being parallel or perpendicular to the substrate according to the actual requests. However, in contrast to the pores with long-axis parallel to the substrate, the materials with perpendicularly aligned channels in respect to the film surface are obviously more versatile for optoelectronic devices, separators with high flux, ultra-high-density recording media as well as novel controlled drug release system (Gibbons et al. 1995; Miller et al. 1999; Vallooran, Negrini & Mezzenga 2013; Wu, Kuan-Ju et al. 2007). The strategies developed to align mesochannels templated from hexagonal LLCs are comprehensively discussed as follows.
2.4.1 External field

The application of commonly used external fields including magnetic field, electrical field, and shear force, has shown powerful ability to administrate mesochannels’ orientation. Magnetically induced anisotropy alignment has been achieved during the last few years by mainly using the high magnetic field of the NMR spectrometer permanent magnet (Clawson, Holland & Alam 2006; Firouzi et al. 1997). Deuterium NMR spectroscopy can be used to characterize the aggregates structure and to quantify the degree of alignment. The overall diamagnetic susceptibility of the aggregates is the key parameter that administrates the orientation with respect to the field direction. The overall orientation of the mesochannels could be easily controlled by incorporating the molecules with large positive/negative diamagnetic susceptibility and therefore adjusting the overall diamagnetic susceptibility of the aggregates (Firouzi et al. 1997). The field strength, on the other hand, is another key parameter to decide the degree of alignment. Due to the negative diamagnetic susceptibility of the alkyl chains in many of surfactants and the low magnetic susceptibility of whole surfactant molecules the alignment normally requires very high magnetic field (>3 Tesla) (Majewski & Osuji 2010). Very recently, the transparent membranes with vertically aligned 1 nm pores have been reported after reorientation under magnetic field with the strength higher than 3 T (Figure 2.18) (Feng et al. 2014). Additionally, the research found that introducing the ferromagnetic nanoparticles into the hexagonal phase can make the nanostructures more easily aligned in a low magnetic field (Vallooran, Bolisetty & Mezzenga 2011). However, the necessary condition is that the mesophase periodicity has to be larger than the diameter of the nanoparticles. The aggregation and phase separation of nanoparticles inside the system always confine the application of the magnetic field.

The electrical field is another promising tool to align the mesochannels in films. It was initially applied for the alignment of the lamellar mesophase (Amundson et al. 1994). However, for non-lamellar mesophases, research has shown that the electric field can induce the phase transition between hexagonal and cubic phase by the interaction between the electric field and materials via different mechanisms (Giacomelli et al. 2010; Ku, Saville & Aksay 2007; Xu et al. 2004). For dielectric materials, the dipole (polarization) effect can be used to orient liquid crystals, for which normally high strength is needed (E>10^5 V/m) (Korner et al. 1996). While in a system with charges
the electrokinetic effect will be sensitive to the applied strength and therefore the required strength is less (Tsori et al. 2003). However, some inherent disadvantages like electrode contact issue and electrical breakdown concern always limit its actual application and therefore the electric field for reorienting the hexagonal LLCs has not been reported extensively.

![Figure 2.18 Prepared NF membrane templated from hexagonal LLCs and its TEM images after reorientation under strong magnetic field (Feng et al. 2014).](image)

Shear force, as another important external field to induce alignment was firstly demonstrated by Hillhouse (Hillhouse et al. 1997). Normally the mesochannels in hexagonal phase with their direction aligned along the flow direction (air flow or water flow) and the induced shear force can guide the reorientation of tubular domains according to the flow rate, flow directions as well as the ambient conditions (Hillhouse, Van Egmond & Tsapatsis 1999; Shan et al. 2012; Su, Lu & Lu 2008). Sometimes, the other external forces could be used together with the shear force to improve the reorientation effect (Figure 2.19).
Figure 2.19 Illustration of the process for vertically aligned mesochannels by using shear force (Shan et al. 2012).

Figure 2.20 Diagram showing the formation of vertically aligned nano-holes by confining the LLCs precursor into the nanoholes on PPA substrate (Yamauchi, Nagaura & Inoue 2009).
2.4.2 Confinement in a small space

It is possible to align the mesochannels when the hexagonal LLCs are formed in a small space as the structure of crystals with long axis will form along with a specified direction. Research has shown that when the CTAB was introduced into the matrices of polyacrylic acid (PAA) channels as structural directing agent the mesochannels of hexagonal aggregates were mostly parallel to the PAA channels under suitable conditions (Figure 2.20) (Yamaguchi et al. 2004; Yamauchi, Nagaura & Inoue 2009). In addition, some researchers also used this micro- or nano-space in situ with the external field or some other effects to align the mesochannels (Trau et al. 1997; Wu, Chia - Wen et al. 2007). However, this method is difficult to be applied in membrane fabrication.

2.4.3 Other methods

Apart from the ways mentioned above, some other methods were also developed to align the mesochannels in hexagonal LLCs and have shown potential value. The most commonly used method was the modification of the substrate surface. Some scientists reported the mesochannels were prepared and aligned on mica, graphite, silica, quartz glass, and polymer films which acted as substrates by using substrate-molecule interaction that definitely regulates the orientation of mesochannels (Aksay et al. 1996; Miyata & Kuroda 1999; Yang et al. 1996). Interestingly, a versatile strategy to achieve the perpendicular alignment by the $\pi$-$\pi$ interaction between the organic template molecules and 2-dimensional $\pi$ plane graphite or silicon wafer surfaces with different surface energies was reported (Hara, Nagano & Seki 2010). Meanwhile, the application of the electrochemically assisted alignment of the mesochannels in silica films was explored, in which various conducting supports and even electronic paper were explored to conduct the alignment of the mesochannels (Walcarius et al. 2007; Weng et al. 2010). In addition, a series of novel Gemini surfactants, which have a high charge density and two polar head groups were also successfully used to prepare the NF membranes with mesochannels normal to the membrane surface (Ma et al. 2011). Most recently, a simple method called stöber-solution growth approach was explored to prepare highly ordered perpendicular mesochannels transformed from uniform mesoporous nanospheres after a series of interactions between components in stöber-solution under suitable conditions (Teng et al. 2012).
2.5 Conclusions

The polymer materials with nanometer size morphologies have potential to be applied in various areas. However, the ability to precisely control morphology, the size, and anisotropy of nanostructure over a large scale is still challenging but essential for further applications. This is especially critical in fabrication of NF membranes who have exhibited exceptional separation effect in some separation technology areas. The challenge associated with the conventional fabrication techniques of NF membranes is the limitation in controlling the homogeneity of pore size and their continuity. Although the template method from hexagonal LLCs possesses thermodynamical controlled pores through the interaction between the amphiphiles and water molecules, the perpendicularly aligned pores to the transport direction over large scale is required to enhance the permeability. Furthermore, the LLCs inherent lacks the robustness of materials and therefore cannot be applied directly. Control over the phase morphology with high nanostructure retention has been confirmed to be thermodynamically unreliable. The growing polymer chains from monomer molecules will inevitably affect the polarity of the system and result in a complete loss order template. Therefore, the two main tasks for the fabrication of NF membranes by using template method from hexagonal LLCs are the structure retention during photo-polymerization and the reorientation of mesochannels in a facile way to improve the continuity and high flux property.

The extensively exploration of the thermodynamically driven phase behaviours during polymerization has been reported and the factors involved including aliphatic chain length, photo initiator, structure and monomer selected, and the ordering effect. However, the key question overlooked by them and needs to be understood is the effect of monomer (s) on hexagonal LLCs involving the appropriate concentration, localization and distribution within the template, the structure dimensional elements and the mechanical property after polymerization. The large-scale shape changes can be easily studied by using many characterization methods. However, the energetics of small-scale shape changes within hexagonal LLCs and their effect on the finalized robust membrane are not well understood.

The continuity of nanopores is the challenge associated with the conventional fabrication techniques of NF membranes. The tunable and scalable external forces such as electric and magnetic field are more promising to present an intriguing option.
compared to the developed methods or techniques as for the effectiveness and the scalability. Especially for the electric field, the electrode developed for *in-situ* SAXS and SANS measurement presents a facile and scalable strategy to conduct the reorientation of meoschannels from hexagonal LLCs in a static electric field. Further, the electric field provides an excellent compatibility with thin film geometries, and is inherently scalable from lab to practical applications.

Finally, a monolithic membrane template with vertical aligned uniform pores and polymerizable species solubilized is obtained to be cured under UV source for robust NF membranes fabrication.
CHAPTER 3 MATERIALS AND METHODOLOGY

3.1 Introduction

The organic NF membrane with a narrow pore-size distribution in the nanometer range and a high surface area has gained an increasing attention. The versatility of NF membranes in many areas like catalysis, drug delivery, and separation technology, etc. makes it favourable. However, the current technologies on the fabrication of NF membranes are still out of favour with the customers to some extent due to the limitations in controlling the homogeneity of pore size, and their continuity and orientation through films. To the actual application side, the cost-effectiveness should also be considered. The nanostructure templated from hexagonal LLCs offers us a promising method for the fabrication of organic NF membrane with a uniform pore size in the range of 1-5 nm (Figure 3.1). The continuity and the orientation of mesochannels could be controllable through the use of appropriate strategies.

Figure 3.1 Schematic showing the fabrication of NF membranes templated from hexagonal LLCs.
In this study, the hexagonal LLCs formed of DTAB and water is acted as a template. Different monomers, HDDA, PEGDA, and HEMA, were added into the binary system of DTAB and water concurrently in different ratio or separately to secure the nanostructure by using photopolymerization. The effect of monomers on the structural dimensions of hexagonal packing and its phase behaviours prior to polymerizing was explored which will be beneficial to retain and control the dimensions of the nanopores. The localization of water/monomers within the template was investigated through 2D reconstruction of the hexagonal unit cells and therefore the optimal monomer composition was decided finally which will significantly benefit the mechanical properties of the polymerized membranes. The mesochannels with high continuity were oriented under magnetic and electric fields by using NMR facility and \textit{in-situ} SAXS/SANS measurements, respectively. The electric field is more favourable owing to its accessibility in the normal lab and actual application without the use of any special conditions and facility. The organic NF membranes with a vertically aligned nanopores are accessible. In this chapter, all materials, experimental techniques and the facilities used for characterization will be presented.

3.2 Materials and sample preparation

\textbf{Surfactants}

DTAB (99%), was purchased from Sigma-Aldrich (Australia). The chemical was stored in the desiccator and used as received. The \(\alpha\)-deuterated DTAB for NMR measurement was synthesised by using National Deuteration Facility in ANSTO. The synthesis procedures of 4 steps are as follows (Figure 3.2 presents the chemical reaction equations):

(1) Synthesis of dodecanamide (Wang, Chen & Jiao 2016)

A solution of ammonium hydroxide (28-30%, 150 mL) was cooled in an ice bath, and lauroyl chloride (20 g) was added via syringe over 10 mins, forming a white emulsion. The mixture was filtered, washed with water and dried under vacuum to give a white solid (17.8 g, 98% yield).

Lauroyl chloride was purchased from Sigma-Aldrich.
$^1$H NMR (DMSO-d$_6$): 7.24 (Br, 1H), 6.67 (Br, 1H), 2.51 (m, 2H), 1.46 (m, 2H), 1.26 (Br, 16H), 0.86 (m, 3H). $^{13}$C NMR (DMSO-d$_6$): 174.8 (s), 35.6 (s), 31.8 (s), 29.6 (s), 29.5 (s × 3), 29.4 (s), 29.3 (s), 25.6 (s), 22.6 (s), 14.5 (s).

(2) Synthesis of dodecan-1-amine-d$_2$

Dodecanamide (8.75 g, 43.9 mmol) was suspended in dry THF (180 mL), in a 1000 mL 3-neck Schlenk flask under N$_2$. The suspension was cooled in an ice bath. LiAlD$_4$ (2.66 g, 65.8 mmol, 1.5 Equiv.) was cautiously added portion by portion, only adding an additional portion once any reaction had ceased. The mixture was allowed to warm to room temperature and refluxed overnight. The reaction mixture was cooled in an ice bath with a flow of nitrogen and cautiously quenched by the very slow dropwise addition of water. The reaction mixture was extracted with ethyl acetate (300 mL), with the organics dried over Na$_2$SO$_4$ and evaporated to give a clear oil that solidified upon cooling (7.0 g, 85% yield).

$^1$H NMR (CDCl$_3$): 1.50-1.38 (Br, 4H), 1.27 (Br, 16H), 0.88 (m, 3H). 2H NMR (CDCl$_3$): 2.61 (Br). $^{13}$C NMR (CDCl$_3$): 41.9 (m), 33.7 (s), 32.0 (s), 29.7 (complex), 29.6 (s), 29.5 (s), 27.0 (s), 22.8 (s), 14.2 (s).

(3) Synthesis of dodecyl trimethyl ammonium iodide-d$_2$ (Wolosiuk, Armagan & Braun 2005)

Dodecan-1-amine-d$_2$ (6.95 g, 37.4 mmol) was dissolved in anhydrous CH$_2$Cl$_2$ (60 mL), to which K$_2$CO$_3$ (12 g, 86.8 mmol, 2.3 Equiv.) was added under nitrogen. Methyl iodide (9.3 mL = 21.2 g, 150 mmol, 4 Equiv.) was added via a syringe, with a condenser fitted to the flask. After 2 h, an additional 8 equiv. of methyl iodide was added, with a catalytic amount of 18-crown-6, with the reaction mixture heated gently. Ethyl acetate (100 mL) was added and the suspension washed with aqueous sodium thiosulfate (3 × 200 mL), with the organic layer dried over Na$_2$SO$_4$ and evaporated to give a pale yellow solid (11.6 g, 87% yield).

$^1$H NMR (CDCl$_3$): 3.37 (Br, 9H), 1.71 (m, 2H), 1.32 (Br, 4H), 1.21 (Br, 14H), 0.83 (t, 3H). $^2$H NMR (CDCl$_3$): 3.52 (Br). $^{13}$C NMR (CDCl$_3$): 53.7 (s), 32.0 (s), 29.7 (s), 29.6 (s), 29.5 (s), 29.4 (s), 29.3 (s), 26.2 (s), 23.1 (s), 22.8 (s), 14.2 (s). $^{13}$C NMR (CDCl$_3$) (1H, 2H decoupled): 63.4 (s), 53.6 (s), 31.9 (s), 29.6 (s), 29.5 (s), 29.4 (s), 29.3 (s), 29.2 (s), 26.1 (s), 23.0 (s), 22.7 (s), 14.1 (s).

(4) Synthesis of dodecyl trimethyl ammonium bromide-d$_2$
(4.1) Preparation of bromide ion exchange resin

Biorad AG 1-X8 (190 g) stirred in saturated sodium bicarbonate (200 mL) for 2 h. The solution was decanted off, replaced with fresh sodium bicarbonate solution and stirred overnight. The resin was then filtered and washed with H2O (2 L) until the filtrate was pH neutral. The resin was suspended in H2O (200 mL), aqueous HBr (48%) was added via pipette until no reaction was observed. The resin was filtered and washed with H2O until the filtrate was pH neutral, and then washed with acetone (500 mL).

(4.2) Conversion of iodide to bromide

A slurry of the previously prepared resin in CH2Cl2 was loaded into a glass column (I.D. 2.5 cm). A slurry of dodecyl trimethyl ammonium iodide-d2 (9 g) in CH2Cl2 was poured onto the column and eluted slowly over 1 h. The eluate was filtered and evaporated to give a pale yellow solid. The solid was recrystallised from methanol by triturating with diethyl ether (4.7 g, 60 % yield). Particle Induced X-ray Emission (PIXE) accelerator based Ion Beam Analysis (IBA) technique was used for the analysis of the complete replacement of the iodide by the bromide anion.

\[ ^1H \text{NMR (CDCl}_3\text{): } 3.42 (\text{Br, 9H}), 1.69 (\text{m, 2H}), 1.30 (\text{Br, 4H}), 1.21 (\text{Br, 14H}), 0.84 (\text{t, 3H}). \]

\[ ^2H \text{NMR (CDCl}_3\text{): } 3.52 (\text{Br}). \]

\[ ^{13}C \text{NMR (CDCl}_3\text{): } ^{13}C \text{NMR (CDCl}_3\text{): } 53.4 (\text{s}), 31.9 (\text{s}), 29.6 (\text{s}), 29.5 (\text{s}), 29.4 (\text{s} \times 2), 29.3 (\text{s}), 26.2 (\text{s}), 23.1 (\text{s}), 22.7 (\text{s}), 14.2 (\text{s}). \]

\[ ^{13}C \text{NMR (CDCl}_3\text{) (1H, 2H decoupled): } 66.2 (\text{s}), 53.3 (\text{s}), 31.9 (\text{s}), 29.6 (\text{s}), 29.5 (\text{s}), 29.4 (\text{s}), 29.3 (\text{s}), 29.2 (\text{s}), 26.1 (\text{s}), 23.0 (\text{s}), 22.7 (\text{s}), 14.2 (\text{s}). \]

Figure 3.2 Chemical reaction equations used in the synthesis procedures of α-deuterated DTAB.
Figure 3.3 Molecular structure of main chemicals used in the research.
Monomers (cross-linker)

PEGDA (MW=575 g/mol), HEMA (97%), and HDDA (80%) were all purchased from Sigma-Aldrich company (Australia).

Initiator

2-hydroxy-2-methylpropiophenone (97%, also called Darocur®1173) was purchased from the Sigma-Aldrich company (Australia). The absorption peaks in UV/Vis locate at 245, 280, 331 nm and the boiling point is 80-81 °C. The initiator was stored in the fridge and sealed with Parafilm.

Water

The Deionised H$_2$O (16MΩ at 25 °C) (DI water) was produced in the lab using Direct-Q3 Water Purification System from Millipore. The D$_2$O was purchased from the Cambridge Isotope Laboritories, Inc. (D, 99.9%, CAS: 7789-20-0). All chemicals were stored according to the instructions and used as received. The molecular structure of all main chemicals are listed in Figure 3.3 and the crosslinking reaction of HEMA, and PEGDA and HEMA are presented in Figure 3.4, respectively.

Sample Preparation

The hexagonal LLCs template was prepared by using DTAB and water in a volume ratio of 66/34 (%). The ratio of DTAB/water is identical for all measurements except those specified. The contrast variation by changing the ratios of D$_2$O/H$_2$O (v/v) were applied in all the systems for SANS measurements. The monomers, PEGDA and HEMA, were added into the binary system separately at 22% (v/v), or concurrently with identical monomer volume percentage but various ratios between them. The higher volume percentage of PEGDA were also applied for further explorations. HDDA, however, has a lower volume percentage in the binary system, at 9.5% (v/v), due to the hydrophobic effect which will lead to the phase separation easily. All the mixtures in small vials were sealed with Parafilm and put into the water bath at 50 °C until a homogenous transparent liquid crystal sample observed (at least 12 h). Typically, the equilibrium time was longer for the binary system. The samples were left at room temperature (25 ± 2 °C) for further homogenization for at least 5 days prior to the final measurements.
Figure 3.4 Schematic representation of polymerization process under UV light. (a), free radical generation under UV light; (b), interaction between active free radical and \( \text{C} = \text{C} \) bond; polymerization of PEGDA molecules with (c) and (d) without HEMA. The quantity of the PEGDA and HEMA molecules within the crosslinking network are randomly distributed.
3.3 Small Angle Scattering Technique

Scattering occurs when an incident wave (light, X-ray, neutrons, electrons) interacts with a sample particle like an electron or nucleus and therefore the wave will be scattered isotropically as a different wave with the same energy to incident wave or less. For the scattered wave with the same energy as the incident one, the Rayleigh or Thomson scattering happened, which is called elastic scattering as well. Otherwise, the inelastic scattering will present and parts of energy from incident wave will be transformed into other forms of energy like heat, or light. Here, the small angle scattering (SAS) technique is the main tool used to characterize the structure of LLCs. We only focus on the elastic scattering because the inelastic scattering cannot produce interference phenomenon and therefore does not carry structure information. No matter what kind of the light source applied the basic theory is always identical but the only one reason what is selected distinctively among them is the actual size of the object or lattice due to the difference in wavelength of the light source. For the object with a structure in nano-size (1-100 nm), the small angle X-ray/neutron scattering (SAXS/SANS) are the optimal tools because $q$-range related wavelength of the X-ray and neutrons can cover the range. For X-ray scattering, the incident X-ray wave interacts with the electrons around the matter. While for SANS, the scattering will happen between the incident neutrons and the nucleus of the matter. The SLD is normally used to measure the scattering power of the atoms or the structure units from a material. The scattering for X-ray and neutrons, increases with the physical density and the intrinsic scattering power, arise from the electron density and the nuclear scattering lengths of the atoms and the structure units, respectively. The diffraction pattern of elastic scattering can be presented as functions of $q$-vector. The difference between the incident wave vector and the scattered wave vector can be given by:

\[ q = \frac{4\pi}{\lambda} \sin \theta \]  

(3.1)

where $\theta$ is the half of the angle between incident and scattered wave as shown in Figure 3.5. For the fixed wavelength instruments like Quokka, the $q$ value relies on $\theta$ only, while for the Time of Flight Mode (TOF) instrument such as Bilby, apart from the $\theta$, the $\lambda$ is also a key factor.
Figure 3.5 Experimental schematic of SAXS/SANS measurement in a transmission scattering geometry. $\lambda$ is the wavelength of the incident beam (X-ray or Neutrons); $\theta$ and $\phi$ represent the scattering angle and the azimuthal angle with respect to the incident beam; X, Y, Z are defined as horizontal, vertical and collinear directions to the incident beam, respectively. The azimuthal distribution depends on the anisotropy of the nanostructure.

For a given scattering from the elements in two planes with inter-planar distance at $d$, the scattering angle can be calculated

$$n\lambda = 2d_{hkl} \sin \theta$$  \hspace{1cm} (3.2)

where $n$ is the diffraction order. $d_{hkl}$ is the distance between repeated planes in the lattice.

Combining the equations (3.1) and (3.2), the relationship between the spacing of each diffraction peak and $d$-spacing could be yielded (Eq. 3.3). For an example of using the first peak of the hexagonal lipid phase, the $d$-spacing can be therefore calculated by using its peak position in $q$-vector (Eq. 3.4):

$$d_{Bragg} = \frac{2\pi}{q_{Peak}}$$  \hspace{1cm} (3.3)

$$d = \frac{d_{10}}{\cos 30^\circ} = \frac{4\pi}{q_{10}\sqrt{3}}$$  \hspace{1cm} (3.4)

In actual applications, SAXS/SANS are the most efficient and complementary techniques to characterize the nanostructure in the range of 1-10 nm.
3.3.1 Small Angle X-ray Scattering

SAXS provides direct, faster and accurate spatial information on the size, shape and 3-dimensional arrangement of nanostructure when compared to other techniques. It can be used to study the phase morphologies of LLCs and hexagonal lattice parameters before and after polymerization. This will allow us to ascertain the effect of polymerisation on the overall structure. Another unique advantage of SAXS/SANS is that we can define the degree of alignment by using the azimuthal intensity (Figure 3.5). SAXS instrumentation includes the lab-based and the synchrotron beamline camera.

The lab-sourced SAXS typically has a copper anode that produces Kα (1.54 Å) and Kβ (1.392 Å) radiation concurrently. The monochromated beam with Kα at 1.54 Å could be achieved after removing the Kβ by using the filter. However, the lab-sourced SAXS instrument applied here in ANSTO does not use nickel filter, therefore, the beam divergence is a little bit higher than the one with nickel filter. The flux from the lab-sourced instrument is limited due to the ability to dissipate heat from the anode and the exposure time varies depending on the instrument, sample thickness and the concentration of scatters within the sample. But normally the exposure time will be much longer especially for the samples with weak diffraction and/or special thickness request. Multiple images can be recorded and added together to obtain high-quality data compared to background scattering.

Compared to the lab-sourced instrument, the synchrotron SAXS has many more advantages. First of all, the energy of the X-rays from synchrotron can be tuned to comply with the special requests. Care should be taken for the sample with the X-ray sensitive groups included during synchrotron SAXS measurement since high energy/low wavelength with somewhat lower flux of X-ray will be delivered at sample position. The high flux X-rays at lower energy are more possible to initiate the in-situ reaction or damage. In this case, an energy of 17keV is ideal for minimizing radiation damage to the sample (Tyler, Law & Seddon 2015). But sometimes the longer wavelength (lower energy) will be requested to achieve a lower q-range for more information there. Secondly, instead of the anode, the Synchrotron produces X-ray by directing a beam of electrons into a storage ring and accelerates them with the speed close to that of the light. The X-rays will be emitted at a tangent to the travel route direction of the electrons. The flux with many orders of magnitude greater than that
from lab-sourced instrument makes the data collection more efficient, normally with varying between 0.1 and 120 s shoot time needed which totally depends on the scattering density of samples or actual requests. Besides, the high flux makes some \textit{in-situ} SAXS measurements possible which are severely limited with the lab-sourced instrument. Finally, the SAXS and WAXS detectors applied simultaneously and the movable sample to detector distance (SDD) make synchrotron SAXS favourable to cover much broader $q$-range. The calculation of $d$-spacing from SAXS requires the specified SDD which can be calibrated by using a well-known calibrant, silver behenate, with a characteristic $d$-spacing at 58.38 Å.

### 3.3.2 Small Angle Neutron Scattering

Compared to SAXS measurements, some special features of the neutrons make SANS complementary to SAXS and sometimes more favourable. Firstly the neutron with charge-neutral property can penetrate the electron density around atoms and interact with the nuclei directly. In addition, the deep penetration and non-destructive examination of neutrons make the measurement on very large or costly samples possible. Secondly, unlike the SAXS, the scattering power from neutron scattering is not directly related to atomic numbers; therefore, light elements like hydrogen and lithium are generally more visible, which can be specially used for distinguishing the isotope within the samples. From Figure 3.6 we can see that the scattering from X-ray strictly depends on the atomic number of elements. However, the neutron scattering is not directly relevant to that. In particular, for the samples with large populations of the light elements like hydrogen and deuterium, the contrast variation is accessible via isotopic substitution. Because the scattering of neutrons from them can be accurately calculated and easily made a comparison to theoretical prediction.

The unique feature of neutron scattering is that the SLD could be adjusted by using isotope substitution to distinguish various ingredients in the sample, which is also called contrast variation. SLD can be computed from the scattering lengths and material densities by using equation:

$$SLD = \frac{\sum_{i=1}^{N} b_i}{V_m}$$  \hspace{1cm} (3.5)

where the sum of the scattering length contributions ($b_i$) from $N$ atoms within the molecule or unit cell divide by the volume, $V_m$. 


Figure 3.6 Comparison of the scattering cross sections from SANS (Green) and SAXS (red) with respect to the atomic number. The numbers in the middle are the bond coherent scattering lengths for each atom (×10⁻¹⁴ cm⁻¹).

For a single molecule, $V_m$ is the molecular volume, and the sum includes all the atoms in the molecule. $V_m$ can be calculated from the known bulk density of the molecule ($\rho$) and the molecular weight ($M$):

$$V_m = \frac{\sum_{i=1}^{N} M_i}{\rho N_A}$$  \hspace{1cm} (3.6)

where $N_A$ is the Avogadro constant; $M_i$ is the atomic molar mass for each element.

Thus:

$$SLD = \frac{\sum_{i=1}^{N} b_i}{V_m} = \frac{\rho N_A \sum_{i=1}^{N} b_i}{\sum_{i=1}^{N} M_i}$$  \hspace{1cm} (3.7)

Note that the above sum is over every atom in the representative volume (i.e. a particular atom repeated twice should be added twice)

The effective scattering length is mainly from the interaction between a neutron and the nucleus, and also includes the contributions from various electromagnetic interactions which normally can be negligible here. For the interaction between the neutron and a nucleus, the simplified function for bound scattering length ($b$) can be expressed by (Sears 1992)

$$b = b_c + \frac{2b_i}{\sqrt{I(I+1)}} \cdot S \cdot I$$  \hspace{1cm} (3.8)

where $b_i$ and $b_c$ are the bound incoherent and coherent scattering lengths, respectively. $I$ and $S$ are the spins of nucleus and neutron, respectively.
The spin of the neutron is $\frac{1}{2}$ as mentioned above. Therefore, the bound scattering length will be all attributed to the coherent scattering length if the scatterer nucleus with the nuclear spin at zero (I=0). The total scattering cross section is given by 

$$\sigma_T = 4\pi\langle |b|^2 \rangle$$

(3.9)

And the absorption cross section can be expressed by 

$$\sigma_A = \frac{4\pi}{k} \langle b_c \rangle$$

(3.10)

where $K$ is the incident neutron wave vector. The absorption cross section is only relevant to the bound coherent scattering length for unpolarized neutron scattering. The total scattering cross section is of the form:

$$\sigma_T = \sigma_c + \sigma_i$$

(3.11)

$$\sigma_c = 4\pi|b_c|^2$$

(3.12)

$$\sigma_i = 4\pi|b_i|^2$$

(3.13)

For the system with the spatial correlation between nuclei or crystal structure with the same scattering length, the information on the structure or spatial correlation will be presented as coherent scattering. The scattering from the nuclei without any spatial correlation or structural information in all or parts of sample attributes to incoherent scattering. For the sample with different distribution from isotope, then the average over both the spin and the scattering length will be considered for the calculation of the total, incoherent and coherent scattering cross section, respectively. In actual measurement, the calculation of the scattering cross section under specified wavelength is crucially important in designing the experiment and obtaining the high-quality data.

The other care that needs to be taken is the data reduction for SANS measurement during the experiment. The calibration and correction of the intensity to an absolute scale are necessary not only for identifying the artefacts in scattering but also for comparing the scattering data from different samples with contrast variation. The reason why we have to do it during the experiment is because the scattering from materials other than the sample, like the stray neutrons and electronic noise, will always accompany with the scattering from the sample. All those problems need supplementary measurements during the scattering measurement, which includes empty beam measurement for normalization and calculating transmission, blocked
beam measurement for subtraction of electronic noise and background neutrons (dark current measurement), transmission measurement, and the detector sensitivity measurement to determine the sensitivity of each individual pixel of the detector. After that, the calibration to an absolute intensity could be realized by measuring a standard sample with a known absolute cross section at \( q=0 \) under the same experimental conditions.

### 3.3.3 SAS techniques for hexagonal LLCs

The most direct way to distinguish the hexagonal LLCs mesophase is to compare the ratio of the Bragg scattering peaks on the \( q \)-vector from SAXS/SANS measurements, which has been assigned as \( 1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}:1/\sqrt{9}:1/\sqrt{12} \) for hexagonal packing, and the Miller indices corresponding to the plane \((1,0)\), \((1,1)\), \((2,0)\), \((2,1)\), \((3,0)\), \((2,2)\) of first 6 peaks are presented in Figure 3.7. Generally, the reciprocal spacing \( q \) value of the Bragg peaks of hexagonal packing can be given

\[
q_{hk} = q_{10} \sqrt{h^2 + hk + k^2}
\]

where \((h,k)\) indicates the different planes for hexagonal packing; \( h \) and \( k \) are Miller indices.

Figure 3.7 Example of a radially averaged SAXS pattern for hexagonal mesophase formed of DTAB and water showing the Bragg reflections with corresponding planes indicated.
3.3.3.1 Calculation of structural dimensions

The hexagonal LLCs structures formed of DTAB and water are all assembled into cylinders with the hydrocarbon chains of the surfactant molecules located inside, and the hydrophilic region wrapped around the lipid cylinders with the polar head group at the water interface. The lipid cores are deemed to be cylindrical while the basis vector length, $d$, is the distance between adjacent lipid cores (centre-centre, Figure 3.8). In this case, the relationship of $d$-spacing ($d$), radius of the lipid core ($R$) and the water and head group thickness ($d_w$) (assume the water were evenly distributed within the unit cell) can be expressed as:

$$d = 2(R + \frac{d_w}{2})$$  \hspace{1cm} (3.15)

Figure 3.8 Schematic display of the hexagonal LLCs packing and its structure dimensional elements.
In addition, the parameters within the unit cell can be calculated using equations including (Forney, Baguenard & Guymon 2013; Seelig 1977):

\[
R = d \sqrt{c\sqrt{3}/2\pi}
\]  

(3.16)

where \( c \) is the volume fraction of the surfactant

For the phase with hexagonal periodicity, the interfacial area per hydrophilic head group of surfactant, \( S \), can be expressed by (Leadbetter & Norris 1979):

\[
S = 2 \frac{V_{\text{mole}}}{RN_a}
\]  

(3.17)

where \( V_{\text{mole}} \) is the molar volume of the surfactant and \( N_a \) is Avogadro’s number.

If we consider the two-dimensional hexagonal unit cell with the lattice of the length, \( l \), then the volume of the unit cell can be given by (Luzzati & Husson 1962):

\[
V_{\text{cell}} = \frac{d^2\sqrt{3}}{2} \times l = 2\sqrt{3} \left( R + \frac{d_w}{2} \right)^2 \times l
\]  

(3.18)

And the volume of the lipid core and water region are

\[
V_l = \pi l R^2
\]  

(3.19)

and

\[
V_w = l \times \left( 2\sqrt{3} \left( R + \frac{d_w}{2} \right)^2 - \pi R^2 \right)
\]  

(3.20)

Therefore, the volume per surfactant molecule occupied is

\[
V_m = \frac{V_l}{N}
\]  

(3.21)

where \( N \) is the number of surfactant molecules within the unit cell.

The total surface area of the surfactant molecules at the interface is

\[
A_s = 2\pi R l
\]  

(3.22)

And then the average area per polar group at the interface can also be expressed by:

\[
S = \frac{A_s}{N}
\]  

(3.23)

Therefore, the ratio of the volume to the area is given by:

\[
\frac{V_m}{S} = \frac{V_l}{A_s} = \frac{R}{2} = \frac{d}{2} \sqrt{c\sqrt{3}/2\pi}
\]  

(3.24)
The parameters mentioned above can be used to evaluate the structural dimensions of hexagonal LLCs phase and their changes with the various ambient condition and sample composition. The \(d\)-spacing is calculated from SAXS diffraction peaks and the volume fraction of surfactant will be used to calculate and compare the changes in structural dimensions.

Another parameter used in the calculation of the structural dimensions is the density of DTAB. We assume that the density of the constituents in the mixture is always identical to its bulk value as research has demonstrated that the density of DTAB in a water medium is slightly dependent on the concentration and the temperature. Here, the molar volume of DTAB with specified concentration is taken as \(280 \times 10^{-6} \text{ m}^3/\text{mol}\) (Pople et al. 1998; Takata et al. 2009). The molecular weight of the DTAB used as received are 308.34 g/mol. Therefore, the volume of a single DTAB molecule is 465 Å\(^3\) and the density of the DTAB is 1.10 g/cm\(^3\) accordingly.

### 3.3.3.2 \textit{In-situ} SAS measurement in an electric field

The cell was designed for SAXS/SANS measurements in directions parallel to the electric field with conducting samples (Figure 3.9). The electrode consists of a layer of conducting material and a supporting material. Quartz glasses (25.4×25.4 mm, 1 mm thickness) were acting as the supporting materials due to its high transmission for the X-rays and neutrons. The Teflon/rubber ring (Black) with a central hole was used to control the sample thickness and to make the electrodes parallel so that optimal scattering signal was obtained. The copper/aluminium was applied as conductive materials placed outside to avoid the contact with the water within the sample. The thickness of the sample can be controlled by adjusting the thickness of Teflon and rubber ring. The cell was designed to optimise the scattering signal through an adjustable thickness but also give a minimal and reproducible isotropic background signal suitable for characterising the scattering anisotropy. The cell windows must have a minimal but homogenous (for consistency of background subtraction) scattering signal. Ensuring constant dimensions (sample thickness/distance between electrodes) and orthogonality between beam and sample windows is important for both background subtraction and homogeneity of the electric field. The cell applied for \textit{in-situ} SAXS measurement and the temperature controller are shown in Figure 3.10. The
X-rays will pass through small holes on the copper plate. More information on the cell and discussion will be presented in Chapter 6.

Figure 3.9 Diagram of the cell in parallel (longitudinal section) direction with incident X-ray. Note: a, Teflon or rubber ring; b, copper/aluminium plate; c, quartz glass (1 mm thickness); and d, sample at specified thickness.

Figure 3.10 Electrode (left), the temperature controller (middle), and the electrode holder (right) designed for in-situ SAXS/SANS measurement in an electric field together with temperature variation.
3.3.3.3 Methods and instrumentation

For SAXS measurements, three different sample containers will be applied. The first one is the quartz capillary with a diameter of 1.5 or 2.0 mm, which can be well sealed by using Araldite epoxy resin. The second one is designed by Australian National University. This is a brilliant design as the sample can be easily put in and kept for a long time. The cells sealed by using windows made of Polychlorotrifluoroethylene are solvent tight and therefore has accurate sample thickness (Figure 3.11). However, the exposure time or times is limited especially when a high flux X-ray like 8 keV is selected. The last sample cell was developed by ourselves for in-situ SAXS/SANS measurements in an electric field (Figure 3.10).

![Cell from Australian National University for temperature variation. (Left), cell accessories for loading sample (right) and the holder for cell (left); (Right), compress machine and relevant moulds used for packing the cells after loading sample.](image)

The lab-sourced SAXS measurements were performed on Bruker SAXS (ANSTO, Sydney, with a 3 pinhole collimated Cu (Kα and Kβ) source and a VANTEC2000 2D detector (68 μm² resolution and 2048×2048 pixels, Figure 3.12). The SDD was 732 mm giving a q-range of 0.01-0.35 Å⁻¹ to cover the first 3 peaks as only first 3 peaks are observable by using lab-sourced SAXS instrument. The pre-prepared homogeneous sample was transferred into quartz capillaries and then mounted in an aluminium sample holders after sealed with Araldite epoxy resin. The temperature was varied from room temperature to up to 300 °C by using a controller. Background measurements from empty capillary were recorded and subtracted from the sample data. The measurements with temperature variation required will have a 10 mins
equilibration time for each temperature prior to measuring with a ramp of 5 °C. The exposure time for scattering experiment at each temperature point was 3600 s.

Figure 3.12 Lab-sourced SAXS instrument (top), the sample holder (bottom-right), and the sample chamber (bottom-left).

The synchrotron SAXS measurements were performed in Australian Synchrotron (Melbourne) (Beam time ID: M9489 and M10395). The Pilatus-1M detector was applied for data collection and the 0.6 m camera length was selected to give a q-range of 0.015-0.95 Å⁻¹ which is enough to cover all observable diffraction peaks. The energy of X-ray was controllable from 11-20 keV according to the actual requests. The exposure time was 2 s. At least 3 exposures were taken at different spots within each sample to check the sample homogeneity, to prevent X-ray initiating damage or polymerization, and to get the standard deviation of collected data. The sealed quartz
capillary or cell was mounted in the holder covered with Kapton window which provided very low-intensity uniform background scattering. Empty capillary or cell measurements were made and subtracted from the final data.

The electrode developed by ourselves together with the temperature controller with thermocouples inside was placed onto the sample stage for reorientation measurement under electric field. The temperature variation was applied in-situ with SAXS/SANS measurement in an electric field as shown in Figure 3.13 that the temperature from ambient state would be heated up quickly to transition temperature which varied depending on the monomer composition and then at least 30 mins’ equilibration was applied, followed by slowly cooling down to the ambient conditions with a ramp of 0.05 °C/min. The sample was left at room temperature longer under an electric field for full recrystallization. The azimuthal distribution of the mesochannels with respect to the incident X-ray/neutron was obtained after data reduction and the order parameter was extracted from the azimuthal distribution.

![Figure 3.13 Temperature variation for the reorientation of mesochannels in an electric field in-situ with SAXS/SANS measurement. A, room temperature; B, equilibration for 30 mins at transition temperature; C, cooling down to room temperature with the cooling rate at 0.05 °C/min; and D, more time for recrystallization.](image)

The sample for 2D reconstruction was formed of the same weight ratio of DTAB to water as mentioned in sample preparation, with and without different monomer composition including either PEGDA, or HEMA alone or with the mixture of them. The water consists of a different volume ratio of D_{2}O:H_{2}O for contrast variation including 100%, 90%, 80% and 70% of D_{2}O. The SANS measurements were performed by using V1 membrane diffractometer at the Berlin Neutron Scattering Centre of the Hahn-Meitner-Institute, Helmholtz-Zentrum Berlin (Berlin, Germany),
the neutron scattering facilities in ANSTO (Quokka and Bilby, Sydney, Australia). More detailed information on three instruments will be presented in Chapter 5.

The V1 measurements were carried out by using the aluminium tubes with 4 mm diameter as the sample holder. Then neutron beam was defined by the slit system with a neutron wavelength of $\lambda = 0.456$ nm. The area detector ($^3$He, $19 \times 19$ cm$^2$) with pixel size at 1.5×1.5 mm$^2$ was positioned 1025.7 mm from the sample and moved around the sample around an arc of constant distance (Figure 3.14). The angle for the data collection was firstly set in the range of 6-30° where more peaks were expected to be observed. However, only up to five peaks were observed with 100% D$_2$O used, which covered a $q$-range between 1-6.5 nm$^{-1}$. The final range was selected between 6-25° to cover all diffraction peaks.

![Figure 3.14 Diagram of the V1 instrument in HZB. The sample will be positioned in the middle, the detector will move around the sample around an arc with constant distance. The long white tube between the detector and sample was used to avoid electronic noise and background neutrons.](image)

For Quokka and Bilby measurements (Figure 3.15), the samples were mounted into the demountable cells made of Titanium covered by quartz windows and sealed with O-ring. The thickness was controllable by choosing the cell with a different spacer.
Quokka is a 40-m long SANS instrument and was a major driver for getting the high-performance cold source into Open Pool Australian Lightwater (OPAL) reactor. The incident neutron wavelength at $\lambda=5$ Å with the wavelength resolution at 10% ($\Delta\lambda/\lambda$, FWHM) was applied. Measurements were made at the SDD of 1.35 m and the source-to-sample distance of 20 m by using 1 mm sample thickness giving a $q$-range of 0.02-0.57 Å$^{-1}$. The counting time was 3600 s for each sample. Similarly, Bilby is a second SANS instrument in ANSTO to operate in TOF mode using a wide range of wavelength between 2-20 Å. Compared to quokka, the Bilby has the ability to achieve a high wavelength resolution up to 4% depending on the chopper setup and the actual SDD. Another distinctive feature of Bilby is that it can achieve a wide dynamic $q$-range with a single measurement, which can be realized by Quokka as well but need to be performed measurements several times with different SDD separately and added them together. The SDD of 7 m was selected for Bilby measurement to get the best wavelength resolution with $\Delta\lambda/\lambda$ of 5. Different measurement time, sample and guide aperture were adjusted to obtain the high-quality data. The data were collected by using 1 mm sample thickness at various wavelengths between 2-20 Å as a function of their time of flight from chopper system to the detector and then averaged to a unity.

Figure 3.15 Diagram of Quokka (left) and Bilby instrument (right) in ANSTO.
3.4 Nuclear Magnetic Resonance

3.4.1 Reorientation from NMR

The $^2$H NMR spectrum is dominated by the coupling between the electric quadrupole moment of the quadrupolar $^2$H nucleus and its local electric field gradient. Molecular dynamics have dramatic effects on the line shape due to the orientation dependence of this quadrupolar interaction. For a crystal sample with a short-range order, rapid anisotropic molecular motions within the anisotropic geometry of an individual aggregate will produce a time-averaged quadrupolar interaction. The corresponding $^2$H NMR line shape and the quadrupolar splitting provide the information on the mean shape and asymmetry of the aggregate, the average local order parameters of the C-$^2$H bond, and the overall distribution of the aggregate director axes (Wilchinsky 1962).

For a liquid-like hydrophobic area, the substitution of the hydrogen atom closest to the head group is the best choice to explore the quadrupolar interaction and therefore the information on the orientation of cylinders assembled by surfactants (molecular structure of $\alpha$-deuterated DTAB displayed in Figure 3.3). By contrast, a surfactant molecule with the tail or whole molecule deuterated would make the line shape more complicated due to overlapping signals. For a hexagonal packing system, the director axis of the aggregate is parallel to the cylindrical axes and the quadrupolar splitting of cylindrical aggregates in a single domain can be expressed as (Wilchinsky 1962):

$$
\Delta v_{\text{single domain}} = |2\delta_1 \cdot \frac{1}{2}(3\cos^2\theta_{DB} - 1)|
$$

(3.25)

$$
\delta_1 = \delta \cdot \frac{1}{2}(3\cos^2\theta_{PM} - 1)_M \cdot \frac{1}{2}(3\cos^2\theta_{MD} - 1)_D
$$

(3.26)

where $\delta$ and $\delta_1$ are static and time-averaged anisotropy parameters, respectively. $\theta_{PM}$ is the angle between the C-$^2$H bonds and the surfactant molecule axis. The term $\frac{1}{2}(3\cos^2\theta_{DB} - 1)$ depends on the average orientation of cylinders’ director $D$ with respect to the applied field $B$ (Lovell & Mitchell 1981; Mitchell & Windle 1988). The term $\frac{1}{2}(3\cos^2\theta_{PM} - 1)_M$ represents the local order parameter ($S_{CD}$) of the C-$^2$H bonds and generally increases with the decrease of temperature (Lovell & Mitchell 1981; Mitchell & Windle 1988; Wilchinsky 1962). The other term $\frac{1}{2}(3\cos^2\theta_{MD} - 1)_D$ represents the average orientation of the molecular axis originated from the
translational diffusion of the surfactant molecule within the aggregate. $\theta_{MD}$ is the angle between the surfactant molecule axis $M$ and $D$.

The time-averaged electric field gradient along the direction parallel to the director axis of the aggregate will be determined by combining the fast local motions of the hydrocarbon chains of surfactant molecules and the translational diffusion of the surfactant molecules within the aggregates. For a liquid crystal only with the short-range order, all the molecules will demonstrate a random orientation, which will give the “Pake doublet” powder pattern NMR line shape due to the quadrupolar splitting. Therefore, the quadrupolar splitting of the powder can be rewritten as:

$$\Delta \nu_{\text{powder}} = |\delta \cdot S_{CD} \frac{1}{2} (3 \cos^2 \theta_{MD} - 1)_D| \quad (3.27)$$

For a hexagonal phase, the average $\theta_{MD}$ is always 90°, while it will be 0° for a lamellar phase, thus,

$$\Delta \nu_{\text{powder}}^{\text{hex}} = \delta \cdot S_{CD} \cdot \frac{1}{2} \quad (3.28)$$

$$\Delta \nu_{\text{powder}}^{\text{lam}} = \delta \cdot S_{CD} \cdot 1 \quad (3.29)$$

Therefore, the quadrupolar splitting of the lamellar phase is always expected to be twice as large as that of hexagonal phase when the order parameters, $S_{CD}$, are equal. For the system with all molecules sampling all orientations isotropically like the micelle phase, the electric field gradient will be averaged to zero over time and the $^2$H NMR spectra will show a narrow isotropic peak instead of the “Pake doublet” powder pattern.

The interaction between the magnetic field and the anisotropy of the diamagnetic susceptibilities of the constituent molecules is crucial to decide the minimum free energy for reorientation ($G_{\text{reor}}$) under magnetic field. For a single molecule within the aggregate, the overall diamagnetic susceptibility can be given by $\Delta x^m = x_{\parallel}^m - x_{\perp}^m$, where $x_{\parallel}^m$ and $x_{\perp}^m$ are the parallel and perpendicular diamagnetic susceptibility of one molecule, respectively. Therefore, the free energy for reorientation derived from the interaction between magnetic field and collective diamagnetic susceptibilities of all molecules within the aggregate are calculated (Firouzi et al. 1997; Peppas & Khare 1993):

$$\Delta x^d = x_{\parallel}^d - x_{\perp}^d = \sum_i N_i \Delta x_i^m \cdot \frac{1}{2} (3 \cos^2 \theta_{M,D} - 1)_D \quad (3.30)$$
\[ G^{\text{reor}} = -\frac{1}{3} \Delta x^d B^2 \cdot \frac{1}{2} (3 \cos^2 \theta_{DB} - 1) \] (3.31)

where \( x^d \parallel \) and \( x^d \perp \) are the parallel and perpendicular diamagnetic susceptibility of collective molecules within an aggregate. \( N_i \) is the total numbers of molecule \( i \) and \( \Delta x^m_i \) is the anisotropy of the diamagnetic susceptibility of molecule \( i \).

Therefore, the minimum free energy of a single domain depends on \( \Delta x^d \), the field strength \( B \), and the angle between \( D \) and \( B \). In the hexagonal system with a constant aggregate number under a magnetic field, the reorientation energy will be minimized when the conditions meet \( \Delta x^d > 0 \) and \( D \parallel B \), or \( \Delta x^d < 0 \) and \( D \perp B \). For the binary system of DTAB and water, all molecules within aggregate have negative diamagnetic susceptibility along their molecule axis, plus the orthogonal relationship between the molecule axis and the director axis one can conclude that the collective diamagnetic susceptibility of the aggregate along the director is positive, namely \( \Delta x^d > 0 \). The reorientation energy will be minimal when the orientation of the aggregates are parallel to the magnetic field direction (\( D \parallel B \)) (Firouzi et al. 1997). However, the majority of the hexagonal mesochannels distributed isotropically with the remainder being a little bit orientated in the system in the actual state. The energy from the magnetic field must be higher than the highest reorientation energy needed for a single aggregate so that a high degree of alignment could be realized.

### 3.4.2 \(^2\)H NMR measurement

The hexagonal packing system for reorientation under magnetic field using NMR facility is formed of \( \alpha \)-deuterated DTAB and H\(_2\)O with/without different monomer compositions including either PEGDA, or HEMA alone and the mixture of them. The sample was placed into 5 mm o.d. NMR tubes at 3-4 cm in length directly for equilibration after sealed with Parafilm and the tap instead of the vials used before. The \(^2\)H NMR experiments were performed at 11.7 T on a Bruker Avance III 500 MHz spectrometer with a 5 mm static probe, using a standard solid echo pulse sequence with \( \pi/2 \) pulse lengths of 10 \( \mu \)s, a 50 \( \mu \)s echo delay, a recycle delay of 2 s, and 80 scans. The \(^2\)H NMR measurements were performed \textit{in-situ} with a varying temperature. The temperature was quickly heated up to phase transition temperature and then slowly cooled down to 20 °C with a ramp of 0.05 °C/min.
3.4.3 \(^1\)H NMR measurement

The special physical properties were originated from the high polarity and the ability to form hydrogen-bonded networks among themselves. However, when the water molecules are confined in a small geometry system, they can also interact with the surfaces through hydrophobic and hydrophobic interactions and hydrogen-bond network (Grünberg et al. 2004). This will lead to new structure or state that is not observable in bulk water phase. This phenomenon is more prominent in the phase with anisotropic property in which the \(^1\)H chemical shift of water molecules depends highly on the structural and dynamical properties of the hydrogen atoms. The \(^1\)H chemical shift from water molecules in the system may help in understanding water molecules’ state at the molecular level and therefore the distribution of monomer within the hexagonal template.

The \(^1\)H NMR experiments were performed on a Bruker 500 MHz Avance III high-resolution spectrometer with the samples packed into standard 5 mm NMR tubes. A 15 μs π/2 pulse length was used with 4 scans acquired for each spectrum and a recycle delay of 1 s. Due to the lack of deuterated solvent, no \(^2\)H lock was used. Also, due to the difficulty of packing gel-like samples into the bottom of NMR tubes, the quality of the shimming varied from sample to sample, manifesting the variation in the \(^1\)H line width and shape as well as slight shifts of the peak positions. The spectra were therefore manually aligned after the acquisition.

The hexagonal packing systems formed of DTAB and H\(_2\)O with/without monomer were prepared in NMR tubes directly according to the sample preparation procedures discussed in 3.2 to distinguish the proton environment within the template. In order to distinguish the chemical shifts from the different proton groups, PEGDA, HEMA, and DTAB molecules dissolved in D\(_2\)O were used as the references, respectively. It should be noted that the concentration of DTAB was below the critical micelle concentration.

3.5 The curing system

The fabrication of NF membrane will be performed after reorientation under electric field instantly by applying the photopolymerization under UV light with specified wavelength. The initiator selected here had a characteristic absorption peaks in UV band at 245, 280, and 311 nm, respectively. The OmniCure S2000 with 5 mm liquid
light guide with adjustable collimating adaptor was applied for photopolymerization. The relative irradiance was calibrated with OmniCure R2000 and corrected with cure site detector firstly before polymerizing (Figure 3.16). Reorientation and polymerization was performed consecutively on the samples with an initiator at 0.5% (wt) of total sample weight.

Figure 3.16 OmniCure curing system (left) and the accessories (right) for calibration and correction.

### 3.6 Other characterization methods

#### 3.6.1 Polarized light microscopy

The polarized light microscope is designed to observe and photograph samples that are visible primarily due to their optically anisotropic characteristic. The dark field is obtained from the orthogonality between the polarized light paths of two separate polarizers (one called polarized and the other called analyser depending on the position with respect to the sample stage). For the sample with the optically isotropic property, the field of view presents no difference. However, the sample with birefringence property (or doubly-refracting) will produce two individual wave components that are each polarized in mutually perpendicular planes, ordinary and extraordinary wavefronts. The velocities of which are different and vary with the propagation direction through the sample. The constructive and destructive interference between two components passing through analyser makes the field visible, depending on the angle between the incident polarized light and the sample. There will be 4 alternatively bright and dark fields if the sample was rotated 360º. When the darkest field is observed, it is called the position of extinction. Otherwise, it is called diagonal position
(45° from the position of extinction). When the lambda compensator is applied, the field of view will be colourful due to the interference colours. But the changes in colour is only dependent on the sample and its thickness.

Figure 3.17 Picture of the ELIPSE 80i microscopy together with Linkam Scientific Instruments for temperature control.

In this study, the ELIPSE 80i microscopy was applied to distinguish the hexagonal LLCs which has a typical fan-shape birefringence property combining the two polarizers (Figure 3.17). To explore the phase behaviours of the hexagonal system as a function of temperature, the sample was diluted in ethanol and then dropped onto the sliding glass. The sample was covered with glass quickly after evaporation of ethanol, followed by sealing with Araldite epoxy resin. The temperature control was realized by using TMS 94 from Linkam Scientific Instruments Ltd from room temperature to
80 °C or higher with the ramp at 1 °C/min. But the cooling down process from highest temperature to room temperature was performed naturally.

3.6.2 Rheometer

The rheological measurements were performed using a cone-and-plate geometry (d=40 mm, $\theta=2^\circ$) in a shear rheometer (TA instrument). The tests were executed in a closed environment sealed with oil to limit water evaporation during measurements. Samples were loaded onto the sample stage and the initial stress sweep tests were performed at 0.1 Hz from 0.01-1000 Pa to find the linear viscoelastic region for each sample, followed by the frequency sweep from 0.01-100 Hz at specified stress value to explore the linear region again. After that, the stress and the angular frequency used for the temperature sweep are specified at 10 Pa and 10 rad/s (1.6 s$^{-1}$ in Hz) for all measurements.

3.6.3 Differential scanning calorimeter

The thermos-analytical technique was applied by using TA Q 200+ differential scanning calorimetry (DSC) for the phase transition trace of the hexagonal system with/without monomers as a function of temperature (Figure 3.18). The sample was loaded onto the bottom of the DSC pans and covered with matching lids and crimped. The sample was dispersed in a thin layer to prevent unnecessary interruption with sample thickness. A matching empty pan and lid were crimped and used during measurement to provide a baseline. Temperature scans started from 25 to 80 °C with the ramp at 5 °C /min, followed by a cooling down process with the same ramp. Each temperature will be isothermal for 5 mins. The heat flow was collected as a function of temperature.
Figure 3.18 Picture of the DSC TA Q 200+ instrument.
CHAPTER 4 STRUCTURAL DIMENSIONS AND PHASE BEHAVIOURS

4.1 Introduction

Previous research demonstrated that the range of hexagonal LLCs mesophase of DTAB in a binary system of DTAB and water is 36-45% in volume fraction, and the structure is extremely stable to temperature (up to ~100 °C) (Mcgrath 1995). The high stability of the hexagonal structure of DTAB offers us an excellent template for the fabrication of NF membranes with uniform nanostructure in shape and size by incorporating the hydrophobic and hydrophilic reagents in separate domains with well-defined nanoscale geometries. The hexagonal LLCs cannot be used for a number of applications directly due to lack of physical robustness. The photo-polymerization after adding monomers with reactive diene groups into the template is normally preferable due to its fast initiation rate and therefore can retain the original nanostructure over a wide range of physical and chemical conditions. However, the addition of monomers will inevitably impart some new properties to the system which are not well known. The detailed information on structural dimensions of the hexagonal LLCs system and its phase behaviours under different ambient conditions after adding monomers is still missing although the obvious hexagonal structure can be surely observed at room temperature. By contrast, the inverted hexagonal phase formed of different phospholipid species and a polar solvent such as water has been shown to exhibit temperature and lipid volume dependence of the structural dimensions (Forney, Baguenard & Guymon 2013; Seelig 1977). An understanding of the changes in structural dimensions of hexagonal system and its phase behaviours will allow us to control the dimensions of the nanomaterials and maintain the nanostructure from the template (LLCs mesophase).

In this chapter, three monomers (PEGDA, HEMA, and HDDA) with different chain length and hydrophilicity were added into the binary system of DTAB and water in various volume percentage. The monomers, PEGDA and HEMA, are present in the water affinity due to the presence of the polyethylene glycol and hydroxyl groups and will locate in hydrophilic region, while the HDDA prefers to sit in the hydrophobic region due to long alkyl chain in the molecule. The detailed molecular structure of the
monomers were displayed in Figure 3.3. They all contain the acrylate groups at one or both ends that can be polymerized by radical polymerization. Variation of the monomer with different chain length will increase the crosslink density and therefore enhance the mechanical properties after conversion from the soft template to robust materials (Forney, Baguenard & Guymon 2013; Peppas & Khare 1993). The structural dimensions of the systems will be calculated before and after adding monomers and the phase behaviours with respect to temperature will be explored. Instead of the weight percentage, the system will be illustrated by using volume fraction of amphiphiles and the other constituents (water and monomer) to simplify the system for structure dimension calculation. The phases present will be characterized by using PLM, SAXS, and NMR. The rheometer and DSC measurements will be assessed to explore the changes in the inner structure corresponding to changes in dimensional elements and phase behaviours of all systems. The hexagonal structure range of DTAB and water selected from McGrath’s work will be used to explore the structural dimensions and phase behaviours of the systems with/without monomers as a function of temperature (Mcgrath 1995).

4.2 Structural dimensions

In this section, the structural dimensions of the binary hexagonal system before and after adding various monomers was explored for the fabrication of NF membranes with uniform pore size. The sample preparation procedure was described in Chapter 3. The hexagonal LLCs was identified initially by using PLM as shown in Figure 4.1 that all systems possess a high birefringence fan-like optical texture which is the typical hexagonal packing. The detailed information on the application of PLM to distinguish the hexagonal LLCs was descripted in Section 3.6.1. The difference in colour or brightness between the images could be attributed to the application of the compensator lambda and/or the different thickness of the samples. The liquid-like region was observed in the ternary system with hydrophilic monomer PEGDA (Figure 4.1B), indicating that the aqueous-rich region could coexist with the hexagonal phase in the system.
Figure 4.1 Polarized light microscopy images of (A), binary system; (B), with PEGDA (22%, v/v); (C), HDDA (9.5%, v/v); and (D), HEMA (22%, v/v). The same scale bar in A is applied to the others.

4.2.1 Monomer composition variation

The pore size of the fabricated membrane largely depends on the diameter of the lipid core in the template and the mechanical property is mainly developed from the thickness of water and head groups, monomer distribution and its crosslink density after polymerization. Therefore, the changes in structural dimensions are critical for further governing the geometry of nanostructure in the fabricated membranes and their mechanical properties. The aggregates of hexagonal packing are normally described as circular cylinders and the unit cell dimensions can be then calculated from the locations of the Bragg peaks if we assume that the symmetry of the aggregates is higher than that of the array and the paraffin and the polar region is completely segregated. The structural elements of the hexagonal LLCs system and its packing parameters are schematically displayed in Figure 3.8. The hexagonal range of the DTAB with H₂O is
36-45% in volume fraction at 20 °C as mentioned above. The data shown in Figure 4.2 demonstrate that the average area per polar head of surfactant, the $d$-spacing, and the thickness of the water and head groups decrease inconsistently as the volume fraction of DTAB rises in the binary system, while the diameter of lipid core increases slightly at the same time (Mcgrath 1995). The $d$-spacing and the water and head group thickness significantly decrease by 4.2 and 4.8 Å, respectively. The difference of 0.6 Å attributes to the slight increase of the lipid core diameter. The increase in lipid core diameter and the decrease in mean area per head group imply that the increase of the ratio of DTAB molecules (w/w) can only increase the number of hexagonal aggregates within the system rather than the average aggregation numbers. Consequently, changing the ratio of DTAB in a binary system will not affect the pore size of the system significantly but will affect the thickness in water and head group region.

Figure 4.2 Dimensions of the structural elements of the binary system of DTAB and H$_2$O as a function of volume fraction of DTAB (Mcgrath 1995). $S$, average surface area available to per head group; $d$, $d$-spacing; $D_l$, diameter of the lipid core; and $d_w$, water and head group thickness.
Figure 4.3 $^1$H NMR spectra of (A), DTAB in D$_2$O; (B), the binary system of DTAB and H$_2$O; (C), the binary system with PEGDA (22%, v/v); (D), PEGDA in D$_2$O; (E), the binary system with a monomer mixture (22%, v/v) with PEGDA: HEMA=1:4 (v/v); and (F), HEMA in D$_2$O.

The research has proven that above the limiting hydration point in the inverted hexagonal system that the liquid crystal will coexist with a bulk water phase and the crystal phase will show a constant lattice size as long as the bulk water phase is present (Tate & Gruner 1989). The aqueous-rich region could not be observed in the binary
system from PLM and SAXS measurement, because the scattering from aqueous phase without structure information will contribute to the scattering in the low-\(q\) region. The PLM also has limitation to obtain detailed information on phase composition. However, the fingerprint of the water molecules within the hexagonal packing could be observable from \(^1\)H NMR spectrum in which the water molecules in a different environment will present different \(^1\)H chemical shifts as shown in Figure 4.3. At a low concentration of DTAB molecules in D\(_2\)O, various high intensity peaks are present, assigned to the different H groups of DTAB molecules (Figure 4.3A). Additionally, a peak at 4.7 ppm is seen, attributed to H\(_2\)O or HDO molecules present in the solvent. However, when the ratio of DTAB to H\(_2\)O increases to the hexagonal packing range (Figure 4.3B), the characteristic peaks of DTAB molecules are broadened significantly due to the highly reduced dynamics, with only two peaks located at 4.4 and 4.6 ppm being observed, indicating the DTAB molecules are confined very well into a hexagonal packing system. These two peaks are attributed to the water molecules located in two different environments that are not undergoing exchange at the timescale of the NMR experiment (ms). When the PEGDA is added into the binary system a single broad peak from water molecules is found at about 4.5 ppm (Figure 4.3C). This suggests that the water molecules are all experiencing a single average environment after adding the PEGDA. Meanwhile, the peaks from PEGDA molecules are observed at around 6 ppm and 3.5 ppm, confirming the aqueous-rich phases coexisting with the hexagonal structure, but all the molecules are confined well in each phase. In addition, an obvious broad peak at 1.1 ppm contributed to the DTAB molecules in the system is observed. When a mixture of monomer (PEGDA: HEMA=1:4, v/v) was selected and added into the system instead of the PEGDA alone (Figure 4.3E), a broader water peak maintains at the same position, implying the water molecules exist in a more restricted environment when compared to the system with PEGDA alone because the width of the peak increased. The DTAB molecules are confined very well again like that in the binary hexagonal system and the peaks from the monomers are broadened significantly, indicating the monomers was confined to the hexagonal system very well. The intensity of the peak from PEGDA molecules reduces obviously due to lower percentage of the PEGDA in the monomer mixture. From the \(^1\)H NMR, it can conclude that the water environment in the binary system is different but will become homogeneous after the monomers are added. The aqueous-rich phase after adding PEGDA alone will coexist with the hexagonal system but it
will disappear after the parts of PEGDA are replaced with HEMA. The water and monomer molecules are all confined very well within the hexagonal system when the monomer mixture of PEGDA and HEMA is applied.

Figure 4.4 $^2$H NMR line shape of (A), the binary system of $\alpha$-deuterated DTAB and H$_2$O; (B), the binary system with PEGDA (22%, v/v); and (C), the binary system with a monomer mixture (22%, v/v) with PEGDA: HEMA=4:1 (v/v).

In order to further confirm the detailed information on hexagonal packing structure and its composition, the $^2$H NMR spectrum was obtained by using $\alpha$-deuterated DTAB and H$_2$O (Figure 4.4). The synthesis procedure and the molecular structure of $\alpha$-
deuterated DTAB are displayed in Figures 3.2 and 3.3 in Chapter 3. The typical hexagonal packing structure with a “Pake doublet”-style $^2$H line shape ($\Delta v=12.1$ kHz) was observed in the binary system. Unsurprisingly, a narrow peak (FWHM=4.2 Hz) in the centre of $^2$H NMR line shape was observed after adding PEGDA alone, which is attributed to isotropically mobile surfactant molecules (Figure 4.4B). The freely mobile DTAB molecules account for 1.25% in the system after the fitting of the two components in the NMR spectrum. In principle, the free DTAB molecules should be present in form of the micelle phase, but this is not observable from SAXS measurement. When the monomer composition was varied by changing the ratio of PEGDA to HEMA, the central isotropic peak disappeared again indicating that the pure hexagonal crystalline phase of DTAB without any isotropic surfactant molecules is available by adjusting the monomer composition (Figure 4.4C). All these observations are in agreement with $^1$H NMR measurements. The presence of an aqueous-rich phase with isotropically distributed DTAB molecules is at the expense of parts of hexagonal packing. But the pure hexagonal packing will restore after increasing the ratio of HEMA in monomer composition. The fittings of the NMR spectra from three different systems prove that the intensity of hexagonal structure in the system with either PEGDA or the monomer mixture of PEGDA and HEMA is almost twice as high as that in the binary system. This implies that the dimensional elements of the hexagonal structure must be changed significantly after adding monomers as the DTAB molecules are equal in three systems. It is noticed that the quadrupolar splitting of the Pake doublet decreased from 12.1 kHz in the binary system to 11.9 and 10.8 kHz in the system with PEGDA alone and with a monomer mixture of PEGDA and HEMA, respectively. The decrease of the local order parameter indicates the higher local molecular mobility of the C-$^2$H bond within the aggregates. In the molecular structure of $\alpha$-deuterated DTAB, the C-$^2$H bond is very close to the head group. Therefore, the mobility of the C-$^2$H bond could be partially regarded as the mobility of the head groups implying the less stiffness and more vulnerable curvature of hexagonal packing in the system with monomers but the changes are varying, depending on the monomer composition.
Figure 4.5 Structural dimensions of the hexagonal system of (A), d-spacing; (B), water and head group thickness; (C), diameter of the lipid core; (D), the average surface area to each head; and (E), the full width at half maximum. Note: a, the binary system of DTAB and water; b, the binary system with PEGDA (22%, v/v); c, the binary system with HDDA (9.5%, v/v).
Apart from the changes in the purity of the hexagonal phase within the system, the detailed information on the structural dimension of the hexagonal packing is worth of investigating by correlation of the monomers on the binary system. Figure 4.5 shows the structural dimensions of the binary system of DTAB before and after adding different monomers as a function of D$_2$O:H$_2$O ratio at room temperature. It is noted that varying the ratio of D$_2$O to H$_2$O does not obviously affect the structural dimensions in each system involved in the figure. However, the addition of hydrophilic monomer has been shown to significantly change the structural dimensions compared to the binary system, with $d$-spacing and the diameter of lipid core decreased by 5.67% and 16.69%, respectively, and the water and head group thickness and the average surface area per head group increased by 57.61% and 20.03%, respectively. By contrast, the addition of HDDA only slightly changes the structural dimensions including 0.72% of $d$-spacing, 4.15% of diameter of the lipid core, 28.70% of water and head group thickness, and 4.33% of the average surface per head group compared to the binary system, a trend that is identical to that in the system with PEGDA except for the $d$-spacing that rises a little bit. The ratio of the hydrophobic monomer added into the system is much less than the hydrophilic one as the phase transition originated from the swelling effect was found if more hydrophobic monomer was applied. Therefore, the effect of HDDA on the hexagonal LLCs template will not be further explored. Another parameter worthy of being noted is the width of the scattering peak which can give a rough information about the crystal structure. It is noted that the width of the Bragg peak from the system with PEGDA is almost twice as wide as that in binary system as shown in Figure 4.5E. The wider peak is mainly attributed to the smaller crystallite size and more disorder within the system which indirectly confirmed that the grain size decreased significantly after the monomers were added with respect to that in the binary system. Meanwhile, the hexagonal packing system is getting more complicated with multi-phase presented in the system. All those parameters are in good agreement that the addition of monomers makes the hexagonal packing structure less reassuring.

It has been proven that the reduction in radius of the water core in inverted hexagonal LLCs phase accounts for most of the reduction in $d$-spacing during temperature variation (Seelig 1977). An interesting phenomenon appeared after adding the hydrophilic monomer here is the reduction in $d$-spacing originated from the synergistic effect of the decrease of lipid core diameter and the increase of water and head group
thickness. In principal, the hydrocarbon chains will fill the interstitial matrix by stretching to the maximum length they can be. The variation of the lipid thickness in inverted hexagonal phase has been denied energetically by the researchers but the slightly changes is still possible due to the lateral splay from the increased gauche rotamers within the lipid area as the temperature increases (De Vries 1972; Forney, Baguenard & Guymon 2013). The diameter of lipid core from this system, however, decreased by 5.66 Å in average which is exactly equal to the increase in the water and head group thickness by 3.40 Å and the decrease of the d-spacing by 2.26 Å. Another striking difference between the calculated values here and the data from the reference are the water and head group thickness and the diameter of lipid core of the binary system of DTAB and H2O, which are about 13 Å and 27.6 Å in reference (Figure 4.2) compared to about 5.9 Å and 33.9 Å here, respectively. The other parameters are all well consistent with each other including the d-spacing, the average surface available to the hydrophilic group. Considering the equations introduced in Chapter 3, the calculation of the diameter of lipid core is only involved with the d-spacing and the volume fraction of the surfactant, since the d-spacing only depends on the scattering peak position, which is almost consistent to that in reference. Therefore, the only one reason led to the difference in calculation of the lipid and water and head group thickness could be the calculation of the volume fraction of surfactant in the system.

The hydrophilic monomers significantly changed the structural dimensions of the binary system of DTAB and H2O. Figure 4.6 demonstrates the dimensions of structural elements of the binary system with various hydrophilic monomer composition, respectively. There is no obvious change in d-spacing as the ratio of PEGDA increases in the ternary system and changing the percentage of PEGDA in monomer mixtures does not affect anything obviously. All the parameters levelled out when the long chain monomer was replaced by the one with a short chain gradually with an only subtle decrease of d-spacing and the lipid core diameter by 0.96 Å and 1.4 Å, respectively, and a slightly increase in the average surface area available to the head group by 2 Å² observed. Another noteworthy tendency from the system with increasing ratio of PEGDA is that the diameter of the lipid core decreased by 3.4 Å while the water and head group thickness and the average surface area to head group increased by 4.11 Å and 9.6 Å², respectively. But the d-spacing is invariable at the same time.
Figure 4.6 Structural dimensions of the binary system with various volume percentage of PEGDA (A and B), and with a specified volume percentage of monomer mixture (22%, v/v) at different ratio of PEGDA: HEMA (C and D) at room temperature. Note: $d$, $d$-spacing; $D_l$, the diameter of the lipid core; $d_w$, the water and head group thickness; $V_m/S$, the ratio of volume to the area per lipid molecule; $c$, the ratio of DTAB; and $S$, the average surface area available to the single lipid head.

When we compare the changes in those parameters in the system with/without PEGDA (Figure 4.5), one can deduce that the hexagonal aggregates must be rearranged into a new hexagonal system with lower aggregate numbers and broader water and head group thickness after adding hydrophilic monomers. The increase of monomer ratio to DTAB and H$_2$O will increase the water and head group thickness and decrease the lipid core diameter without affecting the $d$-spacing anymore. The hydrophilic
monomer penetrates into the space between head groups and therefore decreases the acting force between them, which is a critical factor that makes the system stable (Figure 4.7). Otherwise, it is impossible for the aggregates with identical lipid numbers to decrease the diameter and increase the average surface area concurrently. The decrease of 3.4 Å or higher is also unrealistic for the paraffin chains of surfactant due to the inner spatial reciprocity. In addition, the ratio of monomer PEGDA added into the binary system is not proportional to the increase of the water and head group thickness, implying that the excess monomer will coexist with the hexagonal system without destroying the hexagonal packing, which is in good agreement with the NMR and PLM results.

However, even though the hexagonal packing is relatively stable after adding the monomer, it is reasonably sure that the stability of the hexagonal packing of the ternary system will be much less than that in the binary system owing to the weaker interaction between hydrophilic heads of surfactant. The template with a smaller \( d \)-spacing and pore size and much wider water and head group thickness after adding monomer was obtained for the fabrication of NF membrane (Figure 4.7). However, the optimal monomer ratio and its composition still need to be further explored for the robust property.

![Figure 4.7](image)

Figure 4.7 Schematically show the evolution of structural dimensions of the hexagonal template after adding polymerizable species prior to polymerizing (Assuming that monomers/water molecules are evenly distributed within the hydrophilic region). Note: \( D_{11} > D_{12} \) and \( d_1 < d_2 \).
4.2.2 Temperature variation

The addition of monomers has significantly affected the dimensions of the hexagonal nanostructure by rearranging the hexagonal packing and introducing the monomer between the head groups. Of particular interest of the research is the dimensional elements of the binary system with/without monomer versus temperature. The binary system of DTAB and water is extremely stable to a temperature up to 100 ºC. However, the addition of monomer has changed the curvature of hexagonal packing and therefore will make the system vulnerable to ambient environments. The stability of the hexagonal packing and its behaviours are the key information for maintaining the nanostructure during polymerization. Detailed study on the changes in structural dimensions of the binary system after adding monomers and their phase behaviours versus temperature has not been reported. From Table 4.1, it can be seen that the d-spacing, lipid core diameter, and the water and head group thickness decreased by 5.3, 4.2, and 1.1 Å, respectively after heating up to specified temperature (phase transition temperature). But the surface area available to each lipid head increased by 11 Å². As it is known the LLCs is actually a dynamic equilibrium system. The fast translational diffusion of the surfactant molecules within the aggregates creates a time-averaged mesophase (Firouzi et al. 1997; Seelig 1977). The inevitable water loss owing to a long stay at high temperature (95 ºC) will lead to an increase in the relative ratio of DTAB temperately and as a consequence, the system will respond quickly by rearranging the aggregate numbers together with the decrease of the diameter of lipid core. At the same time, the water region thickness decreased by 1.1 Å. Therefore, the total decrease of the d-spacing is 5.3 Å. Although the majority of water will be back to the hexagonal system again after the annealing process, a small amount of liquid was found on the capillary wall which is also confirmed by the final structural dimensions. It is generally believed that the structural dimensions will be intact if the compositional constituents maintained the same after the annealing process. When the monomer was added into the binary system, the change in all the parameters mentioned above presented an identical trend compared to the binary system (Tables 4.2 and 4.3).
Table 4.1 Structural dimensions of the binary system of DTAB and H₂O as a function of temperature.

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<th>R (Å)</th>
<th>d (Å)</th>
<th>S (Å²)</th>
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</tbody>
</table>

Note: d, d-spacing; R, radius of the lipid core; d, water and head group thickness; S, average area available to each lipid head; and Vₘ/S, the ratio of volume to the area per lipid molecule (same to below).

Table 4.2 Dimensions of the structural elements of binary system with PEGDA (22%, v/v) as a function of temperature.

<table>
<thead>
<tr>
<th>°C</th>
<th>d (Å)</th>
<th>R (Å)</th>
<th>d (Å)</th>
<th>S (Å²)</th>
<th>Vₘ/S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>34.0</td>
<td>11.4</td>
<td>11.2</td>
<td>81.4</td>
<td>5.7</td>
</tr>
<tr>
<td>95</td>
<td>31.8</td>
<td>10.6</td>
<td>10.4</td>
<td>87.1</td>
<td>5.3</td>
</tr>
<tr>
<td>25</td>
<td>32.9</td>
<td>11.0</td>
<td>10.8</td>
<td>84.1</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 4.3 Dimensions of the structural elements of the binary system with a monomer mixture (22%, v/v) with PEGDA: HEMA=1:4 as a function of temperature.

<table>
<thead>
<tr>
<th>°C</th>
<th>d (Å)</th>
<th>R (Å)</th>
<th>d (Å)</th>
<th>S (Å²)</th>
<th>Vₘ/S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>34.2</td>
<td>13.06</td>
<td>8.07</td>
<td>71.2</td>
<td>6.5</td>
</tr>
<tr>
<td>60</td>
<td>33.2</td>
<td>12.70</td>
<td>7.85</td>
<td>73.2</td>
<td>6.3</td>
</tr>
<tr>
<td>25</td>
<td>33.7</td>
<td>12.88</td>
<td>7.96</td>
<td>72.2</td>
<td>6.4</td>
</tr>
</tbody>
</table>
Figure 4.8 1D SAXS pattern of the binary system with a monomer mixture (22%, v/v) with PEGDA: HEMA at 1:4 as a function of temperature. Insets are relevant 2D patterns. A, 25 °C before heating; B, 60 °C; and C, 25 °C after cooling.
An interesting reversible phase transition, from hexagonal phase to isotropic state, was observed from SAXS measurements with the variation of specified transition temperature point dependent on monomer composition (Figure 4.8). The 1D and 2D SAXS pattern further confirmed the phase transition of the system with the monomer mixture of PEGDA and HEMA, whose transition temperature at about 60 °C, at which a broad scattering peak was observed instead of the sharp and narrow first order scattering peak of hexagonal phase at beginning (Figure 4.8B). It is also noted that the scattering intensity of the first peak is much higher than that of the original state after the annealing process. For the system with PEGDA alone, the transition temperature is at about 90 °C, while it will change to about 45 °C when PEGDA was replaced gradually by HEMA. The direct optical evidence from PLM is given in Figures 4.9 and 4.10, from which the reversible phase transition of hexagonal structure and the renucleation during the annealing process was observed in the system with different monomers. The structural dimensions in the system with monomers after annealing process complied with the tendency in the binary system with only a slight difference being observed. The sensitivity of the system after adding monomers to temperature makes the system more versatile and the detailed information on subtle changes in smaller scale within the hexagonal packing is desired.

Figure 4.9 PLM images of the binary system with HEMA (22%, v/v) as a function of temperature.
Figure 4.10 PLM images of binary system with PEGDA (22%, v/v) as a function of temperature.

4.3 Rheological properties

It has been confirmed that the tolerance of hexagonal packing system to various solutes is limited, and the excess aqueous solute will form a bulk region and coexist with the liquid crystal phase without affecting the packing parameters. It is also noted that after adding monomers the structure is much more sensitive to temperature. As a short-range ordered crystal, the distinct changes in structural dimensions with respect to temperature must be associated with inner structural and physicochemical properties. Rheology is the general response of a material to flow and deformation under applied forces. The general viscoelastic oscillatory response of a material to the applied stress and frequency will give basic physical properties. Also examining the nanostructure of the hexagonal system is essential for gaining a better understanding of the relationship between composition, viscoelastic properties, and microstructure. It has been shown that the hexagonal phase behaves as a shear thinning fluid with a well-defined zero-shear-rate viscosity and elastic properties (Feng et al. 2015; Hoag & Gin 2000). However, the rheological behaviours of the hexagonal liquid crystals are still
The macroscopic bulk rheological behaviours of the hexagonal system with/without monomers also reflect internal microstructure and therefore is very important for further application as well as a theoretical point of view. To investigate the dynamic fingerprint of the hexagonal system after adding monomer, the oscillatory- and temperature-dependences of all systems as a function of shear force were measured, respectively. The detailed method was presented in Chapter 3, and the amplitude and frequency sweep results are shown in Figure 4.11. In order to prevent the unexpected effect from varying sample composition all the samples will be firstly applied amplitude and frequency sweep to find the linear region between storage and loss modulus, then followed by the further complex viscosity measurements. The stress and frequency specified at 10 Pa and 10 rad/s (1.6 s\(^{-1}\) in Hz) were found suit all sample compositions.

![Figure 4.11 Amplitude (A) and frequency (B) sweep for complex viscosity measurement.](image)

The complex viscosity varies with applied angular frequency, \(\omega\), which is given by \(2\pi f\), where \(f\) is the frequency (Hz). Master curves of complex viscosity modulus (\(\eta^*\)), storage (\(G'\)) and loss modulus (\(G''\)) for the binary system with/without various compositions at 25 °C are shown in Figure 4.12, respectively. During the whole frequency range from 0.1 to 100 rad/s, all systems showed a reduction in the complex viscosity as the shear rate increases, which could be ascribed to a progressive alignment of the cylinders as the shear rate increases. At low enough angular frequency,
a viscous or terminal region was observed at where $G'' > G'$. It should be mentioned that the limit of the rheometer at very low frequency originated from the mechanical inertia has been eliminated. A crossover frequency, $\omega_c$, ($G' = G''$) at very low frequency was observed in all systems and the elastic behaviour dominated in this region. Both moduli increase with the angular frequency without achieving the maximum value in the rubbery or plateau region. The longest relaxation time ($\tau$), the reciprocal of the crossover frequency ($\omega_c$), obtained here are 196.3, 52.4 and 61.6 s for the binary system with 68% DTAB, and the binary system with PEGDA and a monomer mixture of PEGDA and HEMA, respectively (Table 4.4). The another way to obtain the relaxation time is by plotting $G'/G''$ against angular frequency shown in Figure 4.13 and the relaxation time can be obtained from the slope of the straight line. The Maxwell model can be simply used to explore the rheological behaviours at specified frequency range where the value of $G'/G''$ against frequency is a linear relationship. From the Figure 4.13, it can be seen that the binary system with different ratios of DTAB at low angular frequency and the binary system with monomers at all frequency range can be fitted very well by using the Maxwell model, whose elements can be expressed as

\begin{align*}
G' &= \frac{G(\omega \tau)^2}{1+(\omega \tau)^2} \quad (4.1) \\
G'' &= \frac{\eta_0 \omega}{1+(\omega \tau)^2} \quad (4.2) \\
\eta^* &= \sqrt{\frac{G^2+G''^2}{\omega^2}} \quad (4.3)
\end{align*}

where $G$ is the characteristic modulus and twice of the modulus at the crossover frequency. $\eta^*$, the complex viscosity which can be given by $G^*\tau$.

The crossover frequency, relaxation time, characteristic modulus and complex viscosity at crossover frequency were listed in Table 4.4 for further comparison of the systems with different compositions. In addition, the zero-shear-rate viscosity, $\eta_0$ can be obtained by using $G'' = \omega \times \eta_0$ at low enough frequency region where the $G''$ is linear with increasing frequency and $G'$ is quadratic according to the Maxwell model. The $\eta_0$ values for different samples were also listed in Table 4.4 for comparison. No obvious change in crossover frequency was observed between the binary system with a different ratio of DTAB. When comparing the moduli of the different systems, it can be seen that the $\eta_0$ only decreases slightly but the longest relaxation time reduces to almost one fourth in the system with monomers with respect to the binary system.
Figure 4.12 Complex viscosity ($\eta^*$, ▲), storage modulus ($G'$, ■), and loss modulus ($G''$, ●) versus angular frequency of the binary system with (A), DTAB and H$_2$O (66/34, v/v); (B), DTAB and H$_2$O (58/42, v/v); (C), the binary system of DTAB and H$_2$O (66/34, v/v) with PEGDA (22%, v/v); and (D), the binary system of DTAB and H$_2$O (66/34, v/v) with monomer mixture (22%, v/v) with PEGDA: HEMA=1:4.

Table 4.4 Maxwell model elements from oscillatory tests of the date set in Figure 4.12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\omega$ (s$^{-1}$)</th>
<th>$\tau$ (s)</th>
<th>$G$ (Pa)</th>
<th>$\eta^*$ (Pa.s)</th>
<th>$\eta_0$ (kPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.005</td>
<td>196.3</td>
<td>8049</td>
<td>1580</td>
<td>319</td>
</tr>
<tr>
<td>C</td>
<td>0.019</td>
<td>52.4</td>
<td>3937</td>
<td>206</td>
<td>244</td>
</tr>
<tr>
<td>D</td>
<td>0.016</td>
<td>61.6</td>
<td>4294</td>
<td>264</td>
<td>277</td>
</tr>
</tbody>
</table>
Figure 4.13 Storage ($G'$) and loss modulus ($G''$) ratio as a function of the angular frequency of (□), the binary system of DTAB and H$_2$O (66/34,v/v); (☆), the binary system of DTAB and water (58/42,v/v); (○), the binary system of DTAB and H$_2$O (66/34,v/v) with PEGDA (22%, v/v); and (△), the binary system of DTAB and H$_2$O (66/34, v/v) with a monomer mixture (22%, v/v) with PEGDA: HEMA=1:4.

The much lower moduli and shorter relaxation time distinctly showed that the addition of monomer led to a significant change in size and stiffness of the cylindrical structure compared to that in the binary system. In another word, the hexagonal structure of the ternary system, unlike the stable binary system, will be much more sensitive to the ambient conditions. The system with bigger crystals and high stability normally needs more relaxation time. When we recall the changes in structural dimensions of hexagonal packing after adding monomers, it is not hard to conclude that the decrease of the lipid core diameter together with the increase of the water and head group thickness are a good response to the changes in rheological properties here with the longest relaxation time decreased to 1/4 after adding monomers. All those changes are attributed to the rearrangement of the hexagonal system by reducing the aggregate number with hydrophilic monomer penetrated into the head groups to avoid the repulsive interaction and therefore stabilizing the hexagonal structure. But this structure is much more sensitive compared to the binary system.
Figure 4.14 Complex viscosity of DTAB and water system with a different ratio of PEGDA and HEMA as a function of temperature (A, C) increasing and (B, D) decreasing; (E), complex viscosity from a binary system with a different weight ratio of DTAB. $\sigma = 10 \text{ Pa}$, $\omega = 10 \text{ rad/s}$. 
Another parameter that is directly observable in Figure 4.12 is the complex viscosity which decreases significantly during the rheological property measurement as the increase of shear rate in all systems at room temperature. From the conclusion obtained above one can deduce that the complex viscosity of the system before and after adding monomers must be significantly different with respect to ambient conditions. To further confirm this conclusion, the temperature sweeps at specified frequency and stress were performed on all samples and the results are displayed in Figure 4.14. All samples were carried out of the amplitude and frequency tests firstly to find the linear relationship between $G'$ and $G''$ at different stresses and frequencies followed by the temperature sweep. That is why the original complex viscosity of each sample is much lower than that in Figure 4.12 because a progressive alignment state will be achieved after stress and frequency sweep.

It also should be mentioned that the complex viscosity could be a little bit of artefacts as evaporation is inevitable during temperature variation, especially at the higher temperature range. As the temperature increases, there is a significant decrease of complex viscosity to almost zero in the system with PEGDA alone at 60 °C and this temperature will decrease to 40 °C when the PEGDA was replaced gradually by HEMA in the system. More interestingly, the transition is reversible when the temperature reaches room temperature at 25 °C at where the viscosity will be much higher than the original state before heating which could attribute to the evaporation of water and/or the recovery of the random state due to the thermal motion.

However, it is confirmed that the transition point of complex viscosity of binary system versus the temperature was not observable (Figure 4.14E), indicating the hexagonal packing in the binary system is stiff enough to the temperature variation, which is also confirmed by the PLM observation and SAXS investigation. The zero point of the complex viscosity in the system with monomers during temperature variation could be attributed to the phase transition to the micelle phase at where the viscosity is proven to be very low because of the lower aggregation number (Kent et al. 2014). The isotropic micelles are not possible to be observed under PLM observation, but from SAXS results a broad and low scattering intensity peak can be seen in $q$-vector. However, in order to confirm the change in complex viscosity during temperature variation is due to the break-down of hexagonal structure instead of the progressive alignment, the DSC experiment was carried out within the identical temperature range.
by using the samples without shearing process shown in Figure 4.15. DSC has been of great value in studying both the loss of crystallite order during the heating process and the reordering of such systems after cooling down. The thermal (enthalpy) transition is primarily related to the loss of the crystallinity or transition between different crystal structures.

The break-down of the hexagonal structure to micellar phase must be associated with the endothermic peak observed at specified temperature point. The DSC results from Figure 4.15 indicates that the ternary systems are not thermally stable with an isotropization point at 58 °C and 45 °C for the system with PEGDA and HEMA, respectively. And these transitions could be recovered after cooling down to the room temperature. The peaks on the curve correspond to the endothermic and exothermic behaviours happened during reversible phase transition, but it should be noted that the transition temperature is slightly different to the ones measured from rheometer and PLM results. The DSC results are dependent on the weight and thickness of the samples in the aluminium holder and delayed than the actual point. Again, the binary system of DTAB and H₂O is quite stable without any peaks or points found. All these results are consistent with the conclusion from the rheological investigation that the addition of the monomer significantly changed the size and stiffness of the binary system and made the system sensitive to the ambient conditions.
Figure 4.15 DSC profiles of the binary system of DTAB and H₂O (66/34, v/v) with (A), PEGDA (22%, v/v) and (B), monomer mixture (22%, v/v) with PEGDA: HEMA=1:4; (C), the binary system of DTAB and H₂O (66/34, v/v).
4.4 Conclusions

The structural dimensions of the hexagonal LLCs formed of DTAB and water with and without various monomer composition were calculated and the responses of all the systems to temperature variation were presented in this chapter. For the binary system, increasing the ratio of DTAB to water will increase the number of aggregates in the system and therefore decrease the $d$-spacing originated from the decrease of the water and head group thickness and the slight decrease of lipid chain length. The binary hexagonal system is extremely stable to temperature with only slight structural elements affected after annealing process up to 98 °C. The difference is largely originated from the escape of water from the hexagonal system. The situation will be changed significantly after adding monomers into the binary system. The effect of hydrophobic monomer, HDDA, on the structural dimensions is not obvious when only 9.5% (v/v) of it was applied in the binary system. The hydrophobicity significantly limits the application of HDDA as it locates in the lipid core and changes the curvature of the interface by swelling the hydrophobic area. Besides, the ultimate objective of the thesis is to fabricate the NF membranes and this makes the effect of the hydrophobic monomer on the template less important compared to the hydrophilic ones. Therefore, the effect of HDDA on the hexagonal LLCs template will not be further explored. On the contrary, the hexagonal aggregates will rearrange into a new hexagonal system with a lower aggregate number as hydrophilic monomers are introduced between head groups to stabilize the nanostructure. The most direct response to this is the significant changes in dimensional elements. The structural dimensions of the system especially the lipid core diameter and the water and head group thickness are critical parameters that will determine the pore size and the pore wall thickness of fabricated NF membranes and consequently, their mechanical property in actual application.

In addition, an aqueous rich phase was observed to coexist with the new hexagonal system after PEGDA was added alone and the hexagonal phase becomes more disordered with a small amount of DTAB molecules isotropically distributed (micelle phase) instead of the relatively pure hexagonal packing phase in the binary system. The aqueous-rich phase with DTAB molecules will join the hexagonal packing after the PEGDA partially replaced with HEMA at appropriate monomer percentage, the excess aqueous phase in hexagonal system will inevitably affect the effectiveness of
the membrane after polymerization. As a consequence, the assessment of a number of excessive monomers and how to further prevent the effect of them need to be further explored. The optimal monomer ratio and its composition will benefit the mechanical property of the fabricated membrane accordingly.

The most noteworthy results from this chapter are the effect of the monomer on structural dimensions of hexagonal packing and its phase behaviours, which has also been explored in every details with rheological investigation and DSC measurements. The decrease of the lipid core diameter after adding monomers is mainly originated from the rearrangement of the hexagonal system with a lower aggregate number and penetration of the monomer into head groups which will decrease the interaction between head groups of surfactant. As a response to the changes in structural dimensions after monomer were added, the longest relaxation time decreased to $\frac{1}{4}$ accordingly from rheological measurement compared to that in the binary system. Although the stability of the system decreased significantly which will increase the risk of retention of the nanostructure during polymerization, a delightful phase transition point at where the complex viscosity coming to zero was found after adding monomers and this transition is reversible after heating up to various transition temperature depending on the monomer composition. The orientation and continuity of the pores could be easily controlled synchronously with renucleation after the annealing process under external forces.
CHAPTER 5 LOCALIZATION OF THE WATER/MONOMER WITHIN THE TEMPLATE

5.1 Introduction

Chapter 4 demonstrated that the monomers significantly affected the hexagonal packing of the binary system by rearranging the hexagonal aggregates and therefore changing the structural dimensions. It was also confirmed that the excessive monomer/water will form a bulk aqueous phase and coexist with the hexagonal phase depending on the monomer composition, which could significantly reduce the filtration efficiency after polymerization. Although the longest relaxation time of the binary system with PEGDA and HEMA from the rheological investigation are almost identical, the phase transition temperature of the system with long chain PEGDA is almost twice as high as that with a short chain HEMA, which implies HEMA affects the hexagonal packing more easily. Another noteworthy phenomenon from the $^2$H NMR line shape is that a small fraction of isotropically distributed $\alpha$-deuterated DTAB molecules in an aqueous rich phase was found coexisting with hexagonal packing system, but no free $\alpha$-deuterated DTAB molecules were found in the system when the PEGDA was partially replaced with HEMA. Therefore, it proves that the short chain monomer like HEMA prefers to locate closer to the interface between hydrophilic and hydrophobic area and therefore influences the hexagonal packing compared to long chain molecules like PEGDA.

The short chain molecules are more sensitive to the temperature and therefore more easily affect the curvature of hexagonal packing. However, it is a tricky question to be scientifically answered and to our knowledge, the localization of monomers/water within the hexagonal packing system have not been explored very well. Previous research by using lamellar structure has revealed that the trehalose at physiological concentration, as a solute, is preferred to concentrate in the centre of the water channel instead of evenly distributed within the system (Kent et al. 2014). For inverted hexagonal phase consisted of hexagonal phase and the excess aqueous phase (above limiting hydration), the concentration of the solute between water channel in lipid phase and aqueous phase was also found significantly different (Kent et al. 2010).
On the other side, the distribution of monomers within the hexagonal system is critical for the fabrication of NF membranes and the improvement of their mechanical property. The entropy and enthalpy decrease during polymerization from the previous research could be only part of reasons for phase separation or transition and the other possible determinant reason could be originated from the physicochemical changes of the template after incorporation of monomers before polymerization. The optimal monomer composition can be defined by at where the hexagonal system is as pure as possible without any other phases co-existed, and the monomer evenly distributed within the water channel, which is a prerequisite that the system can furthest defence/compensate the thermodynamic changes during polymerization and therefore obtain the film with robust mesoporous structure. However, in actual applications, the large–scale shape transition is easily characterized by using techniques like DSC, NMR, X-ray and neutron diffractions, freeze-fracture electron microscopy as well as cryo-transmission electron microscopy. The characterization of the shape changes within nanoscale has been a challenge for a long time, especially for an existing question here: where the monomer/water sits within the hexagonal template?

As the development of the high intensity X-ray and neutron beamlines with high wavelength resolution, the reconstruction of liquid crystals like lamellar and more complex two dimensional inverted hexagonal packing has been developed by using SAXS and SANS. The localization of monomer within 1D lamellar structure has been explored through the changes in electron density map (SAXS) or SLD map (SANS). However, the study by using more complicated 2D hexagonal system is still intact although some reconstruction work for the inverted hexagonal system was presented (Ding et al. 2004; Harper et al. 2001; Pan et al. 2006). The SAXS from synchrotron has a high wavelength resolution at specified energy without flux limitation. Therefore the more scattering peaks after contrast variation will be observable, which can give us more specific information on the changes of crystal lattice constants. However, the phasing from electron density map within the unit cell is quite a challenge at the moment.

In this chapter, 2D reconstruction of the hexagonal unit cell will be achieved to localise monomers/water within the template by using membrane diffractometer. The optimal monomer composition can be defined accordingly for the robust NF membrane. Due to the relative low wavelength resolution and flux limitation property, the SANS
measurement always takes a long time and only the first three or four peaks are visible depending on the wavelength resolution, contrast of the scatter, and the intensity of neutrons. However, technically, SANS measurement could still be a good technique after dedicated design and parameters optimization for Fourier reconstruction. The SANS data used for reconstruction work were collected from V1 diffractometer (HZB, Germany), Quokka and Bilby in Australia, respectively. The more detailed information on the methods for instrumentation and reconstruction was presented in Chapter 3.

5.2 Diffraction from various instruments

X-ray and neutron diffractions are the most commonly used methods for studying lipid structures. However, some limitations and advantages in themselves will dedicate their applications for different measurements according to the actual requests. The 1D SAXS and SANS scattering curves of the hexagonal system of DTAB and water (H$_2$O or D$_2$O) are presented in Figure 5.1. The effect of H$_2$O/D$_2$O exchange is insignificant for hexagonal packing system presented in Chapter 4. Although the identical sample composition was applied the scattering curves from X-ray and neutron diffractions are different (A and B). Firstly, the intensity of the SANS is much lower than that from SAXS due to the flux limitations of neutron instrument. Secondly, the width of the SANS pattern is much broader because the collimation is not as good as X-rays and the wavelength resolution of the neutron is much lower than X-ray, with $\lambda/\Delta\lambda = 5\% - 10\%$. This breadth will be aggravating after diffraction by a variety of factors from a sample like a crystallite size and disorder. Another comparison between x-ray and neutron diffractions is that a higher angle (higher $q$) can be seen for neutron diffractions than that for X-ray diffraction due to less uncertainty in the position of the diffracting objects or nuclei. The more uncertainty around diffracting electrons leads to variable path lengths travelled by diffracted wave and therefore less coherence (Debye-Waller effect). However, this situation is not significant for the scattering in a small angle.
Figure 5.1 1D SAXS/SANS pattern of hexagonal LLCs system from (A), SAXS measurement of DTAB and H₂O and (B), measurements from V1, Bilby, and Quokka of DTAB and D₂O. The sample thickness and measurement time are respectively included in the parentheses.

When the scattering curves from V1, Bilby, and Quokka were plotted in one graph (Figure 5.1B) it can be seen that the position and width of the peaks from three instruments are almost identical to each other. But the data from V1 has a higher quality with 5 peaks observed although the background is much higher than that from Quokka and Bilby. This is originated from the much thicker sample (4 mm) applied compared to only 1mm sample thickness from Quokka and Bilby measurement. The multiple scattering and the relative higher incoherent scattering from hydrogens in the thicker sample will be added into the background. On the other side, one may see that
the incoherent scatterings from Bilby and Quokka are quite different by using the sample with same thickness which is attributed to the averaged results for all wavelength from 2-20 Å in TOF-mode from Bilby instrument who gives a wavelength dependent background, incoherent and coherent scattering, while the measurement from Quokka only used unique wavelength at 5 Å with λ/Δλ =10%. Another superiority from V1 is that the cell is made of circular tubes. The scattering of the Neutron beam will experience an identical route and give a homogenous absorption rate from the sample which will benefit the width of the scattering peaks. Otherwise, the absorption effect could not be ignored and need to be subtracted from scattering file especially when the scattering happened at higher angle.

5.3 Reconstruction of the hexagonal LLCs unit cells

The neutron diffraction has been proved to be a powerful tool to characterize the hexagonal LLCs and probe the interaction between the introduced solutes, like water and monomers, and the lipid structure. The contribution from introduced molecules to the scattering length profile of the hexagonal unit cell could be calculated and reconstructed in a manner of the SLD map after Fourier Transform (FT). This is accomplished by applying the contrast variation from isotopic substitution. The variation in the structure factors as a function of D2O/H2O ratios within the water channel enables the identification and localization of the introduced molecules. The 1H NMR study on the hexagonal system before and after adding different monomers has presented that the water environment in small scale is significantly distinct between the systems with different composition (Chapter 4). The transition from the microscopic SLD map to the quantified information between the systems with different composition is still not well understood.

5.3.1 Fourier Transform

The characteristic reconstruction of the object from SAXS/SANS measurement can be accomplished in a mathematical way compared to the optical microscopy which directly realizes the reconstruction with the help of a lens system. The SAS pattern of an object obtained from FT is related to the spatial correlation of the electron density or the SLD in scatterer. The FT is to decompose or separate an overall function in time domain into a sum of sinusoids with different frequency. Conversely, electron density
or SLD profile also can be reconstructed from SAXS/SANS pattern. The scatterer and the essence of incident wave are different between SAXS and SANS but the basic theory on reconstruction is identical. For example with the electron density reconstruction using SAXS data, the structure factors can be expressed from the intensity of Bragg peaks which is from two distinct contributions in the sample including the individual atomic structure factors \( f_n \) and the spatial correlation of all atoms in the molecule or within the unit cell. Therefore, the structure factor is a function of all the atomic coordinates within the unit cell. The Fourier transform of the electron density of all atoms within the unit cell and their spatial correlation can be expressed by (Tyler, Law & Seddon 2015):

\[
F_{hkl} = \sum_n f_n \cdot \exp 2\pi i (hx_n + ky_n + lz_n) \tag{5.1}
\]

However, the function of all atoms is generally not known. Alternatively, one can also calculate the structure factor via the smooth distribution of the electron density within the unit cell and the scattering of all volume elements. If we assume a unit cell with three-dimensional structure in infinitely periodic, the electron density can also be expressed by a three-dimensional series

\[
\rho_{xyz} = \sum_h \sum_k \sum_l C_{h'k'l'} \cdot \exp [2\pi i(h'x + k'y + l'z)] \tag{5.2}
\]

where \( C_{h'k'l'} \) are the Fourier coefficients.

For a centrosymmetric structure, it can then be given:

\[
\rho_{xyz} = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl} \cdot \exp[-2\pi i(hx + ky + lz)] \tag{5.3}
\]

For this research only focuses on a hexagonal packing phase, the equation above becomes (Harper et al. 2001):

\[
\rho_{hex}(x, y) = \rho_{avg} + \sum_{h=1}^{\infty} \sum_{k=1}^{\infty} F_{h,k} \left[ \cos(hA + kB) + \cos(hA - (h + k)B) + \cos((h + k)A - kB) \right] + \sum_{h=0}^{\infty} \sum_{k=0}^{\infty} F_{h,k}^{(h\neq0 \text{ and } k=0) \text{ or } (h=0 \text{ and } k\neq0)} \left[ \cos(hA + kB) + \cos(h + k) \frac{(A-B)^2}{2} \right] \tag{5.4}
\]

where

\[
A = \frac{2\pi(x+y\cot(\frac{\pi}{3}))}{d} \tag{5.5}
\]

\[
B = \frac{2\pi y}{d \sin(\frac{\pi}{3})} \tag{5.6}
\]
It should be noted that the intensity of scattered wave is proportional to the square of its amplitude because the reflection with equal amplitude originated from the symmetric points in reciprocal lattice contributes to the actual intensity but one of them will be out of phase. In addition, according to the Friedel’s law, the squared amplitude is centrosymmetric, but the phase is antisymmetric. The phase of the reflection is 0 or π in a centrosymmetric crystal. Therefore the phase problem of the structure factors can be assigned accordingly as positive and negative easily. The intensity is available from the amplitude of the Bragg peaks, however, the phase is lost and cannot be determined directly from a single measurement. From the variation in experimental parameter (contrast variation) in batch experiments (at least three measurements), one can assign the phase of structure factor of each peak. However, the more the Bragg peaks obtained, the harder the phasing as the number of phase combinations is 2^n, where n is the number of peaks observed. Sometimes, some supplementary methods will be considered to best match the structure factor of all peaks and the correct reconstruction of low-resolution electron density map within the unit cell of crystal by FT is available. Similar to the reconstruction from SAXS basing on the electron density file within the unit cell, the reconstruction from SANS mainly depends on the SLD file.

To assign correct phase of the structure factor of each Bragg peak, the prerequisites are to correct and normalize the intensity of them after contrast variation. Factors that need to be considered for correction of the integrated intensity of each peak include Lorentz correction, multiplicity factors, absorption effect, extinction, and polarization corrections. The absorption and extinction from the lipid system with weak scattering can be minimized by using a thin sample. And the polarization effect is not significant from the source to the detector. Therefore, the Lorentz-correction which accounts for the scattering angle dependence of the scattered intensity is applied to correct the intensity:

\[ q = \frac{4\pi \sin^2 \frac{\theta}{2}}{\lambda} \]  

(5.7)

where the angle \( \theta \) is the angle in radian (angle between incident and scattering wave), so the Lorentz correction at small angle region is

\[ \sin \theta \approx \theta = \frac{q + \lambda}{2\pi} \]  

(5.8)
The multiplicity factor denoting the number of planes with the same \( d \)-spacing contributing to each Bragg peak must be considered even though they have different orientations. The intensity has to be divided by this factor. For a hexagonal packing system, the Bragg peak with the plane \((2\ 1), (3\ 1), (3\ 2)\) and \((4\ 1)\) each has a multiplicity factor of 12 and the remaining peaks have a multiplicity of 6.

The intensity of each Bragg peak from hexagonal packing system can be normalized to the first order amplitude after Lorentz and multiplicity correction and then converted to relevant structure factor.

\[
I_{h\ k} \propto \frac{mA_h^2}{\sin \theta} \approx \frac{mA_h^2}{\theta} \tag{5.9}
\]

where \( I_{(h\ k)} \) is the scattering intensity (area under the peak) of each peak, \( \sin \theta \) is the Lorentz correction, and \( m \) is the multiplicity factor. Therefore the structure factor can be calculated by

\[
A_q = \pm \sqrt{\frac{I_{(h\ k)\sin \theta}}{m}} \tag{5.10}
\]

In general, the reconstruction of the hexagonal unit cell can be completed by using several steps.

### 5.3.2 Contrast calculation and variation

In actual application, the SLD of a molecule or part of the molecule can be calculated and matched by adjusting the ratio of \( \text{D}_2\text{O}/\text{H}_2\text{O} \) because of the opposite neutron cross section between hydrogen (negative) and deuterium (positive). And the preparation of the \( \text{D}_2\text{O} \) is more cost-effective compared with other deuterated molecules in chemistry industry. Varying the contrast of water in the hexagonal system is easily accomplished by exchanging \( \text{D}_2\text{O}/\text{H}_2\text{O} \), and the packing parameters of hexagonal system are quite independent to the ratio of \( \text{D}_2\text{O}/\text{H}_2\text{O} \). The minimum in the difference in SLD denotes the point at which the contrast of the water (\( \text{H}_2\text{O}/\text{D}_2\text{O} \)) matches that of the rest in the system, called match point (MP).
Figure 5.2 MP of PEGDA and HEMA in H$_2$O/D$_2$O system.

Table 5.1 (Estimated) Density and SLD of different ratio of D$_2$O/H$_2$O.

<table>
<thead>
<tr>
<th>Percentage of D$_2$O (v/v)</th>
<th>100</th>
<th>80</th>
<th>60</th>
<th>40</th>
<th>20</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated density (g/mL)</td>
<td>1.107</td>
<td>1.083</td>
<td>1.060</td>
<td>1.039</td>
<td>1.018</td>
<td>0.998</td>
</tr>
<tr>
<td>Estimated SLD (×10$^{-6}$ Å$^{-2}$)</td>
<td>6.38</td>
<td>4.88</td>
<td>3.43</td>
<td>2.05</td>
<td>0.72</td>
<td>-0.56</td>
</tr>
</tbody>
</table>

Table 5.2 (Estimated) Volume, density, and SLD of mainly used molecule or part of a molecule.

<table>
<thead>
<tr>
<th>Molecules or part of molecules</th>
<th>Volume (Å$^3$)</th>
<th>Density (g/cm$^3$)</th>
<th>SLD (×10$^{-6}$ Å$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTAB</td>
<td>465</td>
<td>1.1</td>
<td>-0.243</td>
</tr>
<tr>
<td>Tail of DTAB minus CH$<em>3$ (C$</em>{11}$H$_{22}$)</td>
<td>267</td>
<td>0.75</td>
<td>-0.27</td>
</tr>
<tr>
<td>Head of DTAB</td>
<td>142</td>
<td>1.63</td>
<td>0.17</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>29.9</td>
<td>1.0</td>
<td>-0.56</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>30.2</td>
<td>1.1</td>
<td>6.38</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>56</td>
<td>0.446</td>
<td>-0.82</td>
</tr>
<tr>
<td>PEGDA</td>
<td>852.8</td>
<td>1.12</td>
<td>0.9</td>
</tr>
<tr>
<td>HEMA</td>
<td>201.5</td>
<td>1.073</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Note: atomic weights of 12.01 for carbon and 1.01 for hydrogen used to calculate the molecule weight.
Figure 5.3 1D SANS pattern after contrast variation by using (A), tail-deuterated (D_{25}-DTAB) or (B), fully-deuterated DTAB (D_{34}-DTAB) with hydrogenated DTAB, D_{2}O and/or H_{2}O, respectively. Note: the MP for tail-deuterated DTAB/hydrogenated DTAB=5:95 (v/v); fully-deuterated DTAB/hydrogenated DTAB=3:97 (v/v); and D_{2}O:H_{2}O=8:92 (v/v).

The match point of each monomer could be found by increasing the ratio of D_{2}O/H_{2}O shown in Figure 5.2. The estimated density and the SLD of different D_{2}O/H_{2}O, and the volume, density and SLD of all mainly used molecules are also given in Tables 5.1.
and 5.2 for calculation of the match point. It can be seen that the match point of PEGDA and HEMA are 21%, 22%, respectively. Technically, the SLD of the monomers could be matched by using 21.5% of D$_2$O in D$_2$O/H$_2$O mixture. The contrast match makes it possible to distinguish the various ingredients and their position within the system.

Figure 5.4 Scattering curve of the binary system with 21% D$_2$O (v/v) applied in water.

Further to the calculation of the match point, the 1D SANS curves of the binary hexagonal system by using tail- or fully-deuterated DTAB with hydrogenated DTAB, D$_2$O and/or H$_2$O at their match points are displayed in Figure 5.3, respectively. When D$_2$O and deuterated DTAB are applied in the sample, the scattering is very low (red) due to the low contrast between different parts of the nanostructure. However, the first diffraction peak is still observable from the system of tail-deuterated DTAB and D$_2$O, while the system of fully-deuterated DTAB and D$_2$O is not. Because the contrast in the system of partly deuterated DTAB and D$_2$O is still pronounced. The scattering will be getting stronger when the contrast between hydrogen and deuterium is higher. The highest scattering amplitude is observed when the samples consist of deuterated DTAB and H$_2$O or hydrogenated DTAB and D$_2$O. In an ideal case, the construction elements derived from the samples with D$_2$O/H$_2$O around the MP will give the information to the utmost extent. However, it was found that the scattering from the sample with 21.5%
D$_2$O (v/v) used in water is very weak with the only first reflection peak observed (Figure 5.4). Many hydrogens in the sample will inevitably increase the incoherent background and therefore the scattering peaks are disappeared in the higher $q$-vector. In such a case, the reconstruction is not possible. Therefore, the higher ratio of D$_2$O:H$_2$O is needed for contrast and finally for reconstruction. Here, in our experiment, the different volume percentage of D$_2$O in water at 60%, 70%, 80%, and 100% was selected for contrast variation. Some systems only have three contrasts with 60%, 80% and 100% of D$_2$O.

5.3.3 Structure factors and phasing

The calculation of the structure factors is mainly from the diffraction amplitude of the lipid-water system with different contrast by changing the ratio of D$_2$O/H$_2$O. The detailed information on the calculation and correction of the structure factor was described above. The data normalized to the first order amplitude for a further Fourier reconstruction are presented in Table 5.3, from which we can get some information that the contrast variation by changing the D$_2$O/H$_2$O ratios cannot provide to demonstrate the significant effect on the diffraction amplitude in the binary system. The main reason could be attributed to the anisotropy of the sample which is impossible to be solved after transferring the sample into the tubes. However, the systems after adding monomers are sensitive to temperature and therefore could be easy to get an isotropic distribution after temperature variation. Accordingly, the effect from contrast variation will become prominent from the systems with monomers except for the one with 22% PEGDA (v/v) which presents an unreasonable data set. The maximum difference after contrast variation is actually found in the system with HEMA. Massive PEGDA molecules together with some water molecules will form a separate aqueous phase and coexist with the hexagonal phase in the system and therefore their contribution cannot be included in the hexagonal structure. Meanwhile, the excessive PEGDA molecules will weaken the effect of D$_2$O on the system as some of the water in the hexagonal system including H$_2$O and D$_2$O will be replaced by PEGDA. Therefore, the system with 8.6% PEGDA (v/v) has a better contrast from different ratio of D$_2$O/H$_2$O, while the systems with 22% (v/v) PEGDA or more do not. HEMA, on the other side, was found to better penetrate into the hexagonal phase without any aqueous-rich phase observed.
Table 5.3 Diffraction amplitudes of hexagonal systems consisted of various monomer compositions and their \(d\)-spacing with contrast variation.

<table>
<thead>
<tr>
<th>Percentage of D(_2)O (v/v)</th>
<th>Amplitudes</th>
<th>(d)-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1 0)</td>
<td>(1 1)</td>
</tr>
<tr>
<td>Binary system (B)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>1.0</td>
<td>0.23</td>
</tr>
<tr>
<td>70%</td>
<td>1.0</td>
<td>0.24</td>
</tr>
<tr>
<td>80%</td>
<td>1.0</td>
<td>0.26</td>
</tr>
<tr>
<td>100%</td>
<td>1.0</td>
<td>0.26</td>
</tr>
<tr>
<td>B+8.6% PEGDA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>1.0</td>
<td>0.18</td>
</tr>
<tr>
<td>70%</td>
<td>1.0</td>
<td>0.19</td>
</tr>
<tr>
<td>80%</td>
<td>1.0</td>
<td>0.22</td>
</tr>
<tr>
<td>100%</td>
<td>1.0</td>
<td>0.25</td>
</tr>
<tr>
<td>B+22% PEGDA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>1.0</td>
<td>0.17</td>
</tr>
<tr>
<td>70%</td>
<td>1.0</td>
<td>0.17</td>
</tr>
<tr>
<td>80%</td>
<td>1.0</td>
<td>0.17</td>
</tr>
<tr>
<td>100%</td>
<td>1.0</td>
<td>0.19</td>
</tr>
<tr>
<td>B+39% PEGDA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>1.0</td>
<td>0.15</td>
</tr>
<tr>
<td>70%</td>
<td>1.0</td>
<td>0.15</td>
</tr>
<tr>
<td>80%</td>
<td>1.0</td>
<td>0.17</td>
</tr>
<tr>
<td>100%</td>
<td>1.0</td>
<td>0.20</td>
</tr>
<tr>
<td>B+22% HEMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>1.0</td>
<td>0.088</td>
</tr>
<tr>
<td>80%</td>
<td>1.0</td>
<td>0.115</td>
</tr>
<tr>
<td>100%</td>
<td>1.0</td>
<td>0.186</td>
</tr>
<tr>
<td>B+4.4% PEGDA+17.6% HEMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>1.0</td>
<td>0.090</td>
</tr>
<tr>
<td>80%</td>
<td>1.0</td>
<td>0.132</td>
</tr>
<tr>
<td>100%</td>
<td>1.0</td>
<td>0.202</td>
</tr>
</tbody>
</table>

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In principle, for a centrosymmetric system, the diffraction amplitudes are real and the absolute value of structure factor varies linearly as a function of the ratio of D$_2$O/H$_2$O. The plots of the structure factors (absolute value) with the volume percentage of D$_2$O in water are displayed in Figure 5.5. It can be seen that the absolute value of the structure factor is not strictly proportional to the ratio of D$_2$O/H$_2$O, especially for the first order diffraction. The situation associated with this is problematic for several possible reasons:

- The ideal state of the prepared sample for the data collection and reconstruction should be an absolutely isotropic distribution which means the diffraction intensity in each ring should be identical in a circle (azimuthal intensity). However, technically, it is not possible to get the situation although the homogenization process has been manually attempted prior to measurement. And this is especially true for the binary system that is very stable to up to 100 °C. Therefore, in such a case the diffraction amplitude obtained cannot be regarded as the absolute actual amplitude it should have. However, the diffraction amplitudes of the second and third peaks are found to vary linearly with the percentage of D$_2$O and the slopes are small, which could be attributed to the less contribution from water molecules to the diffraction at higher $q$-vector.

- Subtraction of flat incoherent background becomes increasingly important in the intermediate-angle neutron scattering range varying from 1-7 nm$^{-1}$ for the structure factor calculation. The vast hydrogen atoms in not only H$_2$O but also DTAB molecules will give rise to a strong scattering component even in a system with D$_2$O only. From the diffraction patterns by using a sample with different ratio of fully deuterated and/or hydrogenated DTAB molecules, and D$_2$O and/or H$_2$O presented in Figure 5.3(B), it can be seen that the sample consists of fully-deuterated DTAB and D$_2$O presents the scattering with the lowest background, although the scattering peaks are not observable as well. However, the sample with hydrogenated DTAB and D$_2$O has the highest flat background due to the massive hydrogens in DTAB molecules. The contribution to the background from the incoherent scattering should be correctly calculated and subtracted before the coherent scattering is analysed.
However, there is no exact way to calculate the background as the bound atom cross section of \(^1\)H cannot be applied to the polymers, and is a strong function of temperature and wavelength. Meanwhile, the inelastic scattering, multiple scattering, and even the detector efficiency can also affect the measured background. On the other hand, for the sample in which there is a high concentration of deuterium, the incoherent scattering from deuterium is no longer negligible which makes the calculation of incoherent scattering from hydrogen atoms more complex.

In such a case, some useful information from other characterization techniques could be very useful to distinguish the phase of each diffraction amplitude. First of all, the hexagonal packing of the system of DTAB and water has been confirmed as a packing with a lipid columnar in the middle and the hydrophilic head located outside and interacted with water molecules. The phase of the first diffraction amplitude is then determined to be a negative value, otherwise it will present the inverted hexagonal phase. Therefore, the choices for the all possible phase assignments reduce to 4.

All the possible results of different systems with 80% D$_2$O are shown in Figure 5.6. From the SLD map reconstructed by using the structure factors from different systems, it can be seen that in the hexagonal packing system, all have a red lipid core with the water and head group region being outside in blue colour. From the calculation of the structure dimensional elements in Chapter 4, it has been confirmed that the lipid core diameter should be bigger than the water and head group thickness which excludes the assignments (−, −, −) and (−, +, −). Additionally, the \(^1\)H NMR spectrum has shown that the addition of monomer will make the original two different water environments become uniform within the template, which is contradictory to the assignments (−, +, +). Therefore, the only one choice expected to be the right assignment for the hexagonal system is (−, −, +). The 3D view of the reconstructed hexagonal unit cell is shown in Figure 5.7.
Figure 5.5 Structure factors (absolute value) from contrast variation by changing ratios of D$_2$O/H$_2$O in the binary system with/without various monomers (v/v). A, the binary system (B); B, B+8.6% PEGDA; C, B+22% PEGDA; D, B+39% PEGDA; E, B+4.4% PEGDA+17.6% HEMA; and F, B+22% HEMA. The straight line in each panel is a fit to the average amplitudes of each peak.
Figure 5.6 SLD maps of four possible phase choices with (A): ---; (B): --+; (C): +--; and (D): +++ of the systems with/without various monomers (v/v). Notes: top, left (the binary system (B); middle (B+8.6% PEGDA); right (B+22% PEGDA) and bottom, left (B+39% PEGDA); middle (B+4.4% PEGDA +17.6% HEMA); right (B+22% HEMA).
Figure 5.7 A 3D view of the reconstructed hexagonal unit cell by using the binary system with D$_2$O/H$_2$O at 8:2.

From the SLD map in Figure 5.6B, it can be seen that the water molecules prefer to concentrate on some specified regions instead of the homogeneous distribution within the template from the binary system, while the systems with HEMA applied present a more uniform monomer distribution within the water and head groups region compared to the system with PEGDA. The excessive PEGDA molecules will be excluded from the hexagonal system and therefore will not affect the hexagonal packing parameters any more. The thicker monomer wall around the lipid core with uniformly distributed monomers will significantly boost the ability to resist the thermodynamic effect during polymerization. The monomer system consisted of monomers with various chain lengths will enforce the robustness by increasing the crosslink density in the polymer network. However, in the present case, more work is needed to quantify the distribution of water/monomer within the hexagonal unit cell from the reconstructed SLD.
5.4 Conclusions

The reconstruction of the hexagonal unit cell was explored to locate water/monomer within the template in this section. The data after contrast variation from different neutron instruments including V1, Quokka, and Bilby were collected and compared. From the current data set, it can be concluded that the data set from membrane diffractometer have a higher quality compared to background and therefore were applied for the reconstruction. However, the expected linear relationship between the diffraction amplitude and the volume percentage of D\textsubscript{2}O cannot be obtained after correction which could be attributed to the anisotropic spread within the system owing to the high viscosity and the incoherent background subtraction. However, the knowledge of the system and some other techniques were used to confirm the phases of 3 diffracted orders are as -, -, +, respectively. The 2D reconstruction of the hexagonal unit cell from the systems with different monomer composition was completed and the distribution of water/monomer was visually observed from the SLD map. The systems incorporated with HEMA alone or with a little bit PEGDA together present more homogeneous water and head group region compared to the binary system and the binary system with PEGDA alone. However, more work is needed to quantify the distribution of water/monomer and compare the difference between the systems with various monomer composition. Finally, the binary system with HEMA and PEGDA will be applied for further process due to its superiorities obtained until now.
CHAPTER 6 MACROSCOPICALLY REORIENTATE THE MESOCHANNELS UNDER EXTERNAL FORCES

6.1 Introduction

The organic NF membrane with a uniform pore size in the range of 1-5 nm has opened up the possibility of performing highly selective small molecules and water purification based on molecular size-exclusion of hydrated salt ions. The hexagonal LLCs mesophase especially suits the fabrication of NF membranes due to the uniform pore size in nano-scale and their high surface area. More importantly, the continuity of mesochannels within the template could be improved if the orientation of the mesochannels can be controlled and extended to the macroscopic scale through appropriate alignment strategies. Currently, some methods have been used to perpendicularly align mesochannels with respect to the substrate by using Gemini surfactants, substrate-templating growth strategies, and stöber approach. However, those approaches normally require special substrate modification. And the complex conditions or special equipment cannot be scaled up for large volume production and practical application (Hara, Nagano & Seki 2010; Ma et al. 2011; Teng et al. 2012). Compared to those methods, applying external forces presents an intriguing option as they are tunable, scalable and capable of producing an orientation in different geometries.

However, direct alignment over large scale under external forces at room temperature normally requires much stronger force which is impractical for a commercial process. Previous research has demonstrated that the main reason that opposes the aligning torque produced by external field could be the high viscoelasticity in the system. For the binary system of DTAB and water, the complex viscosity maintained a steady perturbed state from the rheological investigation. Even the complex viscosity of the system after adding monomers reduced significantly, it is still quite steady at room temperature. However, the addition of monomers imparts the system a diverse property with respect to temperature: a lowest complex viscosity temperature point varies depending on the sample compositions could be found. More importantly, the viscosity is reversible after slowly cooling down to the room temperature which provides an excellent opportunity that the macroscopical reorientation of the
mesochannels could be easily realized by imposing the minimum free energy that a single aggregate is needed to overcome the viscosity for reorientation during the annealing process. The hexagonal structure will then regenerate under the guidance of the external forces originated from the interaction between all molecules within the assembly under the external fields (Figure 6.1). The minimum free energy between the unaligned and aligned state of the aggregates varies depending on the thermal energy in the system, the property of all molecules under the external field, and the field strength applied. According to the conclusion drawn in Chapter 4, the viscoelastic forces can be easily reduced by heating the system above its phase transition temperature depending on monomer composition. The so-called isotropic distribution here is the state that all the molecules within the system have all possible orientations over time (micelle phase).

Figure 6.1 Schematic show of the reorientation process for NF membrane fabrication (Zhang et al. 2012b).

In order to increase continuity of the nanopores and therefore the high flux property of the fabricated NF membranes, the macroscopical orientation of the mesochannels templated from viscous hexagonal LLCs system in bulk material with the long range being perpendicular to the surface of the membrane was investigated first by using NMR facility in-situ with temperature variation. A cell to accurately control the temperature and apply electric field was developed and implemented into the X-ray/neutron beam as an electrode for in-situ SAXS/SANS measurement in an electric field. The detailed sample preparation and experimental methods were described in Chapter 3.
6.2 Reorientation under magnetic field

The collective diamagnetic susceptibility of all molecules within the aggregates, and the spatial relationship between the molecule axis and the main director of the aggregates play a key role in orientating cylinders under external forces and the degree of alignment in the system (Firouzi et al. 1997). The reason why the α-deuterated DTAB was applied for the reorientation experiment is because the deuterium closest to the head group will directly give the information on the spatial location of the head group of surfactant molecules within the aggregates and therefore the hexagonal structure and their alignment. The time-averaged electric field gradient along the direction parallel to the director axis of the aggregates will be determined by combining the fast local motions of the hydrocarbon chains of surfactant molecules and the translational diffusion of the surfactant molecules within the aggregates. The detailed information on the key factors governing the spatial location between the C-2H bond, surfactant molecules, and aggregates and the applied field was described in Chapter 3. The reorientation experiment was implemented under 11.7 T magnetic field with temperature varied by using the system with/without monomers, respectively.

The 2H NMR experiment was implemented by using the hexagonal system formed of DTAB, water, and a monomer mixture of PEGDA and HEMA first with 1H decoupling on and different recycle delay time shown in Figure 6.2. The relative intensity of the central narrow peak originated from isotropically distributed DTAB molecules in an aqueous environment significantly decreased with the increase of recycling delay time until it is absolutely gone with using 2 s of delay time. In addition, the heating effect from the 1H decoupling radio frequency (RF) field also accounts for part of the relatively high intensity of the central peak confirmed by further exploration at 30 °C after turning the 1H decoupling off (Figure 6.3). Another phenomenon from the 2H NMR line shape is that the hexagonal structure has started phase transition at 30 °C, which is not observable in PLM images of sample monomer composition (Figure 4.8) in which the hexagonal structure is still intact at the same temperature. The slow heating rate could be necessary to give more detailed information on phase behaviours with respect to temperature. Finally, the 1H decoupling was turned off and the recycle delay time was selected at 2 s for all subsequent NMR measurements.
Figure 6.2 $^2$H NMR spectra of the binary system with a monomer mixture (22%, PEGDA: HEMA =1:4, v/v) using recycle delay time of (A), 0.25 s; (B),1 s; and (C), 2 s at 20 °C with $^1$H decoupling on.

Figure 6.3 $^2$H NMR spectra of the binary system with a monomer mixture (22%, v/v, PEGDA: HEMA =1:4) with $^1$H decoupling on (D) and off (E), respectively, at 30 °C with recycle delay time at 2 s.
Figure 6.4 $^{2}$H NMR spectra of $\alpha$-deuterated DTAB molecules for the ternary system of DTAB, water, and a monomer mixture (22%, v/v) with PEGDA: HEMA=1:4. (A), un-orientated, 20 °C; (B), isotropic distribution at 50 °C; (C), 40 °C during the annealing process; (D), hexagonal domains $\parallel$ Applied field, 20 °C after annealing process with the cooling rate at 0.5 °C /min; and (E), hexagonal domains $\perp$ Applied field, 20 °C after rotation of 90° respect to the spectrometer.
The reorientation of mesochannels templated from the same sample composition was followed by heating it above the phase transition temperature (50 °C) and the $^2$H NMR spectra are shown in Figure 6.4. At 20 °C (Figure 6.4A), the Pake pattern with quadrupolar splitting ($\Delta \nu$) of 10.8 kHz of the hexagonal structure system with the mesochannels isotropically distributed was obtained. The phase could be easily destroyed after heating up to 50 °C where a narrow isotropic $^2$H NMR peak appeared, indicating that the isotropic distribution of the deuterated surfactant molecule orientations dominates the system (Figure 6.4B). The sample was then slowly cooled down to 20 °C at a rate of about 0.05 °C/min. It was noted that the two broader peaks ($\Delta \nu=20.7$ kHz) firstly appeared at 40 °C during annealing process and the intensity of the quadrupolar doublet increased significantly with the central peak disappearing concurrently after further cooling to 20 °C. The two sharp peaks with high intensity and a narrow FWHM ($\approx 1$ kHz) Gaussian distribution ($\Delta \nu=22.2$ kHz) were observed finally (Figure 6.4D) implying the high ratio of hexagonal domains are oriented with the director axis on average parallel to the applied field, because the positive overall diamagnetic susceptibility ($\Delta \chi>0$) from the hexagonal aggregates will cause the domains to preferentially align parallel to the applied field (Firouzi et al. 1997).

However, there is still a small amount of the hexagonal domains being found to be in a different orientation (low intensity powder pattern with $\Delta \nu=11.1$ kHz), though no isotropically mobile surfactant molecules are observed after annealing process, indicating current monomer composition is preferable to be acted as the template for the fabrication of NF membrane. The further confirmation of the alignment was obtained after the sample was rotated by 90° with respect to the spectrometer field (Figure 6.4E), and the two narrow and sharp doublet with a narrower FWHM ($\approx 0.7$ kHz) Gaussian distribution ($\Delta \nu=11.1$ kHz) arises, indicating orthogonality between the director axis of the aggregate domain and the applied field. The illustration in Figure 6.5 shows the reorientation of the mesochannels under magnetic field from $^2$H NMR spectrums.

In addition, the increase of the quadrupolar splitting during the cooling was noticed as well which can be attributed to the temperature-dependent local order parameters ($S_{CD}$). When the sample was left for a longer time under magnetic field, the $S_{CD}$ still keeps increasing slightly (not shown). This is because the regeneration of the crystal will take some time. The increase of $S_{CD}$ with decreasing temperature corresponds to the
lower local molecular mobility of the C–2H bond. The lower mobility is associated with longer relaxation time of the aligned structure which can be maintained for a long time even after it was taken out from the applied field. The research has confirmed by using the binary system of CTAB and water that the relaxation time could be maintained at least 6 months (Firouzi et al. 1997). The detailed information on the relaxation time here is not available but the 2H NMR spectrum from the same sample after 4 hours is still intact which will allow for further process.

![Diagram](image)

Figure 6.5 Illustration showing the reorientation process under magnetic field in-situ with temperature variation. Note: the blue line is the field direction. A, original state; B, micellar phase; C, reorientation of mesochannels parallel to the field direction; and D, rotation of NMR tube by 90° respect to the spectrometer.

The identical reorientation procedure was implemented by using the sample with PEGDA (22%, v/v) alone as a solute after heating up to 90 °C (Figure 6.6). The whole process is quite similar to that shown in Figure 6.4 but the ratio of the aligned domains are much lower and a small ratio of isotropically mobile surfactant molecules was
found in the system instead of the pure hexagonal packing in the system with a monomer mixture of PEGDA and HEMA. The dependent local order parameters of the system with PEGDA are higher than those in the system with a monomer mixture, indicating that the relaxation time of the system with monomer PEGDA will be longer than the one with monomer mixture.

![Figure 6.](image)

Figure 6. $^2$H NMR spectra of $\alpha$-deuterated DTAB molecules for a ternary system of DTAB, water, and PEGDA (22%, v/v). (A), un-orientated, 20 °C; (B), isotropic distribution at 90 °C; (C), hexagonal domains\perp Applied field, 20 °C after annealing process with the cooling rate at 0.5 °C /min); and (D), hexagonal domains\perp Applied field, 20 °C after rotation of 90° respect to spectrometer field.

The alignment results from the system with different monomer compositions imply that the reorientation can be easily achieved under external magnetic field together with variation in temperature. As a contrast, the binary hexagonal system formed of DTAB and water was unable to be aligned even the temperature is up to 95 °C as shown in Figure 6.7. The much higher phase transition temperature and the lower
alignment degree of the system with PEGDA alone compared to that in the system with a monomer mixture of PEGDA and HEMA make it unfavourable for practical applications. In addition, the system with a monomer mixture also possesses a homogeneous hexagonal system without isotropic phase. Another superiority of the system with monomers of different chain length is that it can improve the cross-linking density of the polymer network and therefore enhance the mechanical strength of the polymerized system. Therefore, the following reorientation experiment was preferentially implemented by using the system with a monomer mixture (22%, v/v) with PEGDA: HEMA=1:4.

Figure 6.7 $^2$H NMR spectra of the binary system of $\alpha$-deuterated DTAB and water. (A), un-oriented, 20 °C and (B), 20 °C after the annealing process.

### 6.3 Reorientation in an electric field

Compared to the magnetic field, the electric field is a more promising tool for reorientation experiment as it can be more easily implemented in the lab and for practical applications. Although the magnetic field possesses some advantages like space-pervasive nature, the absence of electrode contact and the breakdown concerns from the dielectric constant, the access to the strong magnetic field for alignment is still far away from the practical application. On the contrary, the electric field is accessible after a thorough consideration and design. In order to explore its clear guiding principles on what type of surface interaction and factors are effective on exerting vertical alignment, an electrode used for reorientation experiment was developed for in-situ SAXS/SANS measurement.
SAXS/SANS are the most efficient techniques to characterize the nanostructure in the range of 1-10 nm. It provides direct, fast and accurate space information on the size and 3-dimensional arrangement of pores compared with other facilities. Therefore, it can be used to study the phase morphologies of LLCs and hexagonal lattice parameters. In addition, this will allow us to ascertain the effect of polymerisation on the overall structure. X-ray scattering is particularly useful for determining orientational order parameters on global average when the complete characterization of an orientation distribution function is possible. The SAXS experiments were implemented at Australian Synchrotron and in ANSTO.

6.3.1 Development of an electrode

The main focus of the cell shown in Figure 3.9 is to obtain the phase behaviours and nanostructure information in-situ with changes in an electric field from precise scattering by further limiting the background absorption and scattering or any other interference factors.

For SAXS measurement, there are two options for conductive materials, one is to use the copper plates connected with the high voltage supplier directly and acted as the conductive surface. An alternative way is to sputter a thin aluminium layer onto the thin quartz glasses (0.2 mm thickness) which act as a conductive layer. But the thickness and homogeneity of the conductive layer need to be strictly controlled to avoid reducing the transmission and to maintain the uniformity of the electric field. The comparison between the SAXS signal from the sample in the capillary (2 mm diameter) and the cell with sputtering aluminium (≈1 mm thickness) is shown in Figure 6.8. The 0.2 mm thickness quartz glass sputtered with aluminium at 1 µm±10% thickness was used as the electrode and the sample thickness was controlled at 0.5 mm. The scattering intensity from the cell is much lower than that from the capillary, which probably partially due to the different sample thickness. But the barrier of the aluminium layer on the transmission of X-ray is considerable. The much thinner aluminium layer was considered, but the control of the thickness and homogeneity is more difficult. In principle, the transmission of quartz glass to X-ray is dependent on the wavelength and there is no significant difference between quartz glass with 0.2 mm and 1 mm thickness. Considering the actual application, the 1 mm thickness quartz
glass with thin copper/aluminium plate connected with high voltage supplier and being outside was selected to act as the electrode for SAXS/SANS measurements.

A hole on electrodes is necessary for X-ray to pass through and to realize the in-situ measurement in an electric field. In principle, the fringe field effect is an inevitable problem as long as there is an edge, and the sample close to the edge will expose to the electric field with various strength and direction. However, it is still possible that the fringe field effect is negligible after calculation and simulation of the whole electrode model. In this case, the effect of the conductive layer on the transmission of X-ray can be easily addressed and the high cost of sputtering and its limitations were eliminated accordingly. The finite element analysis software was designed to predict

Figure 6.8 SAXS profiles of the hexagonal LLCs system in cell (A) and capillary (B).
how a substance reacts to the physical effects. The fringe field effect in an electrode could be simulated with specified parameters such as relative area, distance, field strength, and the holes relevant information. The holes with a diameter \(D\) at 1 and 2 mm located in the middle of both copper plates (100×100 mm) were applied because the scattering of X-ray will happen from the side face to the X-ray detector. The 2000 voltage was applied for final simulation. The effect of the fringe field effect on primitive field strength (field strength between electrodes without the holes) between electrodes with different distance is shown in Figure 6.9. It can be seen from the simulation that the red circle along the hole observed indicating the charges are more concentrating on the edge (the fringe effect) and the field strength in the black area is much lower than the other areas. The field strength along the way from the centre of the hole with \(D=1\) mm to that of the other one is extremely divergent. When 3 mm distance selected, the deviation to the primitive field strength could be up to almost 50% on both end of the road (closest to the electrodes), and the minimum deviation is located at about 1 mm away from the electrode with 1 mm diameter hole, at about 3% lower. When the distance was enlarged to 5 mm, the identical situation was obtained on both end of the road compared to 3 mm distance. However, a very broad region was obtained between where the field strength is quite close to the primitive field strength, from 0.9-3% deviation (lower), indicating that the sample at specified position between electrodes with holes can access almost the same strength respect to that between the electrodes without holes. In addition, for the electrodes with larger distance, a higher voltage will be needed to achieve the same field strength compared to the ones with smaller distance. However, the breaking voltage will be another limitation that needs to be noticed during actual application accordingly.

For SANS measurement, the high transmittance of aluminium materials to neutron beam offers us a good opportunity to execute the SANS measurement in an electric field by using the thinner aluminium sheet directly as an electrode without any holes. Also, the relatively bigger beam size of SANS than SAXS measurement will need a bigger hole and therefore will make the effects of fringe field stronger.
Figure 6.9 Simulation of the effect of a hole in the centre of electrodes on field strength.
Figure 6.10 Transmission ratio of the direct beam with sample to the direct beam without sample from Bilby with the same composition but different thickness at 2 mm (A) and 1 mm (B) versus the neutron wavelength.
Another two key parameters normally needed to be considered before implementing the SAXS/SANS measurements are sample thickness and the wavelength selected. For X-ray without flux limitation, the absorption must be kept small by controlling the thickness for obtaining high-quality SAXS data. However, the much longer time or multiple images needed for the thin sample with weak diffraction to increase the signal to noise. On the contrary, the transmission and multiple scattering will be the main problems for the thicker samples. The wavelength of X-ray selected for measurement also needs to be considered especially when the light-sensitive group is included in samples since high energy/low wavelength with somewhat lower flux will be delivered at sample position. Otherwise, the high flux X-ray will initiate the in-situ polymerization process when the sample has reactive groups. In this case, the wavelength at 20 keV was selected for measurement. For a given material, the optimum thickness can be calculated from the linear absorption coefficient ($\mu$) at specified wavelength, which is given by

$$d_{opt} = \frac{1}{\mu}$$  \hspace{1cm} (6.1)

For neutrons scattering where there is a flux limitation, the measurement under specified wavelength will normally need much longer time than that for SAXS measurement, in particularly when the experiment has limitations of the beam size and/or needs higher wavelength resolution. However, the conditions used for the measurement can be optimized according to the actual requests. The introduction of the time-of-flight mode into SANS facility makes it more flexible and versatile by choosing the sample aperture, guide aperture, and how many guides being used, respectively, and the wavelength is selectable from 2-20 Å to obtain the optimal measurement parameters. The sample thickness, similarly, is a key parameter in SANS measurement. For the sample without H$_2$O or hydrogen atoms, the low transmission and the high coherent scattering originated from the multiple scattering for the thick sample will severely affect the quality of the analysis of the curves. Conversely, the high incoherent scattering originated from hydrogen atoms will reduce the dynamic range of measurement. Similarly, for a very thin sample, it will generally take very long time to obtain high-quality scattering curve. The count rate on the detector as a function of neutron wavelength from the sample with the same composition but the different thickness was displayed in Figure 6.10. It is noted that the transmission decreases as the neutron wavelength increases and the transmission from 2 mm
thickness sample is much lower than that from 1 mm one in the selected wavelength range. The lower counts rate (data not shown) from the sample with 2 mm thickness indicates that the stronger scattering happened which can be mainly attributed to the multiple scattering and the incoherent scattering originated from the hydrogen atoms. The incoherent scattering of the sample with hydrogen atoms varies depending on the wavelength shown in Figure 6.11 that the incoherent scattering increases with the neutron wavelength increasing. Again, for a given material with defined thickness, the interaction of the neutrons with materials can be expressed by

\[ I_0 = I_T + I_{\text{non-}T} \]  \hspace{1cm} (6.2)
\[ I_{\text{non-}T} = I_S + I_A \]  \hspace{1cm} (6.3)
\[ I_S = I_{\text{Coh}} + I_{\text{Incoh}} \]  \hspace{1cm} (6.4)
\[ I_{\text{Coh}} = I_{\text{Single}} + I_{\text{Multiple}} \]  \hspace{1cm} (6.5)

The transmission and scattering intensity can be calculated, respectively, by

\[ T = \frac{I_T}{I_0} = e^{-(I_{\text{non-}T})d} \]  \hspace{1cm} (6.6)
\[ I_S \propto d e^{-(I_{\text{non-}T})d} \]  \hspace{1cm} (6.7)

Therefore, the maximum scattering intensity will happen when the transmission is at 37% for all the samples. However, when the coherent scattering dominates in the system \((I_{\text{non-}T} \approx I_{\text{Coh}})\), which means no hydrogen atoms are presented in the sample, the thickness will be too thick with the transmission only at 37%. In this case, the thickness of the sample with transmission \(\geq 90\%\) will be ideal. Conversely, if the coherent scattering is weak \((I_{\text{non-}T} \approx I_{\text{Incoh}} + I_A)\) in a system with much hydrogen atoms, the optimal thickness could locate at where the transmission is 37%, namely, \(d = 1/I_{\text{Non-}T}\).
Figure 6.11 SANS pattern of the binary sample with PEGDA (22%, v/v) from different wavelengths.

However, in actual application, it is very hard to balance the requests on optimal thickness between for SAXS/SANS measurement and for the materials fabrication. Here, the sample thickness of 0.5 mm and less was selected for the reorientation experiment to avoid the interference from the multi-domains with different azimuthal distribution after the alignment of the thick sample. Another consideration on the thickness is originated from the actual thickness needed for the fabrication of the NF membrane.

6.3.2 Reorientation under electric field

The reorientation of mesochannels under electric field was mainly completed by using the ternary system of DTAB, water and a monomer mixture of PEGDA and HEMA due to its relatively lower phase transition temperature and purer hexagonal structure. A temperature controller was designed as well for varying temperature in situ with SAXS experiment in an electric field. The temperature was heated up to 60±2 °C and
levelled out for half an hour to make sure the sample was completely transited to isotropic state, followed by an annealing process with a cooling rate at 0.05 °C/minute. The detailed information of the experiment is described in Figure 3.13 of Chapter 3. The whole process was executed automatically under the field strength of 666667V/m and the SAXS measurement was firstly implemented in the isotropic state and followed by obtaining the data every half an hour to avoid the in-situ polymerization initiated by X-ray during reorientation.

The azimuthal distribution profile of the first scattering peak obtained from SAXS patterns was obtained and shown in Figure 6.12. The isotropic distribution was easily achieved after heating up to 60 °C (Figure 6.12A) which is also proven by PLM and NMR results. The six-dot 2D SAXS pattern in Figure 6.12B indicates that the orientation of cylinders is being parallel to the incident beam and therefore perpendicular to the sample surface. However, the 2D pattern and the resulted 1D azimuthal distribution demonstrated that they are not all symmetrical in intensity, which can be attributed to the non-orthogonality relationship between the incident beam and the sample surface. More complicated distributions within the system were observed when the different sites were checked on aligned sample as shown in Figure 6.12C. It is generally believed that the divergent distribution from various hexagonal domains with slight defects is presented in the system. Similarly, when the beam size or irradiated sample area are getting bigger, more domains will be included and the azimuthal distribution tends to be more divergent and weaker but the orientation of all domains are still perpendicular to the sample surface (Figure 6.13). The 2D SANS patterns shown in Figure 6.14 exhibit the azimuthal distribution of the aligned sample under electric field by applying the different sample aperture. The distribution of aligned cylinders become more concentrated on the six distinct dots when the sample aperture decreased from 12.5 to 2.5 mm in diameter. It should be noted that even for the sample aperture at 2.5 mm, the beam size of SANS is still about 150-fold of that from SAXS measurement in Figure 6.12. The azimuthal distribution from SANS/SAXS pattern demonstrated that the reorientation of mesochannels within the whole sample area is achievable in an electric field easily. The dimensions of the hexagonal structure after reorientation is identical to that in the system before annealing process (data not shown).
Figure 6.12 Azimuthal distribution of the mesochannels within the template from SAXS measurement before (A) and after (B) temperature variation under electric field, and the situation in some other area (C). Insets are the relevant 2D patterns.
Another situation that needs to be attended is that the scattering intensity is very weak from both SAXS and SANS pattern due to the thin sample at about 0.25 mm applied. The main reason to choose the thin sample is primarily considered for the membrane fabrication after the alignment. Another consideration is due to the accessibility of the clear 2D scattering pattern indicating the orientation respect to the incident beam, which will be much more complicated in the thick sample with more multiple scattering and more domains included.

Figure 6.13 Schematic of 2D SAXS pattern of aligned hexagonal structure with a different rotation of various domains along an axes parallel to the tube axis. A, 0°; B, 5°; C, 10°; and D, 20°.
Figure 6.14 2D SANS pattern on the azimuthal distribution of cylinders from the hexagonal system of DTAB, water, PEGDA, and HEMA respect to the incident beam at 20 °C after temperature variation under electric field using different sample aperture of A, 12.5 mm; B, 7.5 mm; C, 2.5 mm; and D, 2.5 mm at different position.

6.3.3 Order parameter extraction

As previously indicated, the X-ray scattering could provide both the structural information and the orientation parameters. Actually, a number of spectroscopic methods can also be used to measure orientation in both crystalline and non-crystalline polymers including Infrared Dichroism, Polarized Raman scattering, Optical birefringence, NMR, and SANS can be applied to extract the orientation information. However, all the techniques discussed so far can give $<P_2>$ (harmonic components/coefficients, same as below) and some can give $<P_4>$ and $<P_6>$. None of them can give a complete orientation distribution function (ODF). The method to obtain the orientation information from X-ray scattering by correlating the ODF with the angle ($\alpha$), the angle between the unit axis and the director of the system was developed for the system with randomness, but the complicated calculations always
make it in a dilemma (Wilchinsky 1962). The sharp scattering peaks from the crystalline polymers are easily separable from their neighbours, and for the background to be subtracted. The resulted azimuthal profile is then directly related to the distribution of structural unit axis. A more useful method to extract the full orientation distribution without recourse to solving integral equations or inverting matrices was reported by Lovell and Mitchell and followed by a detailed explanation in the book (Lovell & Mitchell 1981; Mitchell & Windle 1988). But the uniaxial system, the units distributed symmetrically about only one axis, is essential for the reliable evaluation of scattering profile.

The angular distribution of the structural units to the director axis (Figure 6.15) can be described in a mathematical way as spherical harmonics. The first four harmonic components are abbreviated as \( P_0, P_2(\cos \alpha), P_4(\cos \alpha), P_6(\cos \alpha) \) or simplified as \( P_0, P_2, P_4, \) and \( P_6, \) respectively:

\[
P_0 = 1 \tag{6.8}
\]

\[
P_2 = (3 \cos^2 \alpha - 1) / 2 \tag{6.9}
\]

\[
P_4 = (35 \cos^4 \alpha - 30 \cos^2 \alpha + 3) / 8 \tag{6.10}
\]

\[
P_6 = (231 \cos^6 \alpha - 315 \cos^4 \alpha + 105 \cos^2 \alpha - 5) / 16 \tag{6.11}
\]

Figure 6.15 Anisotropic distribution of the structural units with respect to director axis.
The ODF $f(\alpha)$ is usually expanded in terms of Legendre polynomials with the summation of these components functions, written $<P_{2n}(\cos \alpha)>$ also called expanded coefficients, to define the orientational order parameters. The “$<$” denotes the globally averaged amplitude which is experimentally available from the intensity profile of X-ray scattering. The scattering $P(\alpha)$ from X-ray profile of a sample with a macroscopic but less than perfect orientation is resulted from the convolution of orientation distribution $D(\alpha)$ and the scattering of a single structural unit $I'(\alpha)$. They all have a cylindrical symmetry which can be expanded in series of even-order Legendre polynomials $<P_{2n}(\cos \alpha)>$, e.g. (Lovell & Mitchell 1981):

$$I_{2n}^S = (4n + 1) \int_0^\pi I^S(\alpha)P_{2n}(\cos \alpha) \sin \alpha \, d\alpha$$  \hspace{1cm} (6.12)

The formula can also be applied to $D(\alpha)$ and $I'(\alpha)$. For a uniaxial system with mirror symmetry, the convolution between them can be given by:

$$I_{2n}^S = \left(\frac{2\pi}{4n+1}\right) I_u^{2n} D_{2n}$$  \hspace{1cm} (6.13)

The relationship between them can be more conveniently expressed as

$$<P_{2n}(\cos \alpha)>_S = <P_{2n}(\cos \alpha)>_u <P_{2n}(\cos \alpha)>_D$$ \hspace{1cm} (6.14)

where

$$<P_{2n}(\cos \alpha)>_S = \int_0^\pi I^S(\alpha)P_{2n}(\cos \alpha) \sin \alpha \, d\alpha$$ \hspace{1cm} (6.15)

And then

$$<P_{2n}(\cos \alpha)>_D = \frac{<P_{2n}(\cos \alpha)>_S}{<P_{2n}(\cos \alpha)>_u}$$ \hspace{1cm} (6.16)

The Legendre polynomials can be expressed in terms of the normalized amplitudes of the spherical harmonics:

$$<P_{2n}(\cos \alpha)>_S = \frac{\int_0^\pi I^S(\alpha)P_{2n}(\cos \alpha) \sin \alpha \, d\alpha}{\int_0^\pi I^S(\alpha) \sin \alpha \, d\alpha}$$ \hspace{1cm} (6.17)

Now the calculation of the orientation distribution was only relevant to the azimuthal profile as a function of angle $\alpha$ and the scattering from the single structural unit. For a system with perfectly aligned structure, the model with a set of regularly spaced and infinitely long rods could be used to obtain the relevant coefficients. The rods will be
defined to the equatorial plane where $\alpha$ is $90^\circ$ or the meridional plane with $\alpha$ at $0^\circ$. The coefficients of the model with equatorial reflection can be obtained by

$$< P_{2n}(\cos \alpha) >_u = \frac{(2n)!}{(-1)^n 2^n (n!)^2}$$  \(6.18\)

Therefore,

$$<P_2 (\cos \alpha)>_u = -\frac{1}{2}; <P_4 (\cos \alpha)>_u = \frac{3}{8}; <P_6 (\cos \alpha)>_u = -\frac{5}{16}; <P_8 (\cos \alpha)>_u = \frac{35}{128}$$

And

$$<P_2>_D = <P_2>_S = -2 <P_2>_u = -\frac{\frac{\pi}{2} I^s(\alpha)(3 \cos^2 \alpha - 1) \sin \alpha d\alpha}{\int_0^{\frac{\pi}{2}} I^z(\alpha) \sin \alpha d\alpha}$$  \(6.19\)

However, when the meridional reflection is preferred, then

$$<P_2>_D = <P_2>_S = \frac{\frac{\pi}{2} I^z(\alpha)(3 \cos^2 \alpha - 1) \sin \alpha d\alpha}{2 \int_0^{\frac{\pi}{2}} I^z(\alpha) \sin \alpha d\alpha}$$  \(6.20\)

Thus the full description of the orientation distribution reduces to the azimuthal distribution of the intensity function at a specified value in $q$ vector from the SAXS pattern. Actually, the second order term, $<P_2 (\cos \alpha)>_D$ or $<P_2>$, is more frequently used to evaluate the experimental data. Here, from the scattering pattern in Section 6.3.2 it can be seen that the uniaxial system was realized after the alignment under the electric field and therefore complied with the requirements of the equations. The hexagonal cylinders (domains) are aligned parallel to the main director of the electric field. The SAXS/SANS provides a globally averaged orientation distribution because the area on the sample illuminated by incident X-ray is much larger with respect to the structural unit ($\mu$m vs nm). In addition, the anisotropy from the background should be removed from the azimuthal profile which denotes the probability of finding structural units whose orientation could be described by angle $\alpha$ and director. For the azimuthal profile with an arbitrary reflection, the $<P_2>$ would be zero; if all units aligned perfectly to the main director, then $<P_2>$ would be 1.
Figure 6.16 Gaussian fitting of the experimental azimuthal profile from aligned sample.

From the azimuthal profile in Figure 6.12B, the Gaussian fitting of the azimuthal profile is shown in Figure 6.16 and the detailed fitting results are listed in Table 6.1.

Table 6.1 Elements from Gaussian fitting.

<table>
<thead>
<tr>
<th></th>
<th>$y_0$</th>
<th>$A$</th>
<th>$W$ (rad)</th>
<th>$\alpha_c$ (rad)</th>
<th>FWHM (rad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>590</td>
<td>1441</td>
<td>0.015</td>
<td>0.19</td>
<td>0.018</td>
</tr>
<tr>
<td>Peak 2</td>
<td>502</td>
<td>158</td>
<td>0.013</td>
<td>1.23</td>
<td>0.016</td>
</tr>
</tbody>
</table>

The Gaussian function used for fitting is given by

$$y = y_0 + \frac{A}{\sqrt{\pi/2}} e^{-\frac{2(a-a_c)^2}{w^2}}$$

(6.21)

Therefore, the azimuthal angle is converted to the radian between $0-\pi/2$. The distribution functions as function of $\alpha$ of the peaks are given by:

$$I^\xi(\alpha)_1 = 590 + 76704e^{-\frac{(\alpha-0.19)^2}{0.000225}}$$

(6.22)

$$I^\xi(\alpha)_2 = 502 + 9698e^{-\frac{(\alpha-1.23)^2}{0.000169}}$$

(6.23)
The orientation of cylinders here is preferentially parallel to the field direction and confined to the Equatorial plane. However, the direction of the incident X-ray respect to the symmetry axis also imparts the calculation in different ways (Figure 6.17). Here, the domain director is parallel to the incident X-ray from the 2D scattering pattern, which is applied to the type A in Figure 6.17. In addition, for the hexagonal packing system, as mentioned before, the 6 azimuthal peaks should be symmetric in scattering intensity if the incident X-ray is normal to the sample surface. Therefore only the azimuthal Gaussian distribution of the first peak will be used to evaluate the orientational order parameters.

![Diagram](image)

**Figure 6.17** Relationship between incident X-ray and symmetry axis.

Therefore, the Eq. 6.22 can be expressed as

$$I^x(\alpha) = 590 + 76704e^{-\frac{(\alpha-1.38)^2}{0.000225}}$$  \hspace{1cm} (6.24)

The final orientational order parameters from the aligned system under electric field by using Eq. 6.19 and 6.24 is 0.63, which is much higher than the other aligned hexagonal systems which are normally between 0.4-0.5 or less (Pople et al. 1998; Vallooran, Bolisetty & Mezzenga 2011).

However, it is supposed to be much higher in the real aligned system compared to the calculated value. Firstly, the spatial correlation, although it is much lower in LLCs system with domain structure, is linked and interacts with the orientation correlations.
which will increase the width of the peaks. Also, the separation of the spatial and orientational correlations is the requirement for the equations mentioned above. Secondly, the scattering from the air and incoherent scattering will give a negative effect especially when the aqueous-rich phase is presented in the system, and makes the quality of local orientational order to be reduced and therefore the decrease of the global average parameter. Thirdly, all the calculations were executed by assuming the infinitely long rods which are not possible in actual application. The finite length of structure unit will give a smearing of the diffraction pattern out of the equatorial plane, which is afterward confirmed that the effect could be negligible for orientation parameter less than 0.8 (De Vries 1972; Leadbetter & Norris 1979). The hexagonal system has been aligned well for the fabrication of the monolithic polymer membrane.

6.4 Conclusions

The reorientation of mesochannels templated from the system of DTAB and water with and without monomers was investigated using NMR spectrometer (11.7 T) together with temperature variation, respectively. The mesochannels in the ternary system with varying phase transition temperature depending on the composition can be reoriented easily. But the binary system of DTAB and H\textsubscript{2}O cannot be aligned under the same conditions. The degree of the alignment in the system with a monomer mixture of PEGDA and HEMA is much higher than that with PEGDA alone. However, the small amount of extant unaligned structure are presented in both ternary systems. The system with a monomer mixture is more favourable due to its much lower phase transition temperature, the higher degree of alignment, and more pure hexagonal structure presented.

An electrode was designed and tested for measuring structural alignment with small angle X-ray/neutron scattering (SAXS/SANS) anisotropy in a static electric field. The holes were positioned in the centre of the copper plates with 1 mm and 2 mm in diameter for irradiation of X-rays. Although the field strength on the line from the centre of the 1 mm hole to that of the other one is divergent to the primitive strength, the position between electrodes at where the strength is almost the same as the primitive strength which is available but absolutely depends on the distance between the electrodes. For the electrodes with 5 mm distance, the position with 0.9% lower of the primitive strength (400,000 V/m) can be accessed to execute the reorientation.
The optimal SAXS scattering signal through an adjustable sample thickness controlled by Teflon or rubber spacer was produced with a minimal and reproducible isotropic background and suitable for characterising the scattering anisotropy. The inherent bigger beam size and the high transmission of aluminium to neutrons make the thin aluminium plates favourable to act as the conductive layer outside without the holes for SANS measurement in an electric field. The sample thickness and wavelength selected for SAXS and SANS measurement are vital in obtaining high-quality scattering curves after optimization and actual requests during measurement.

The alignment with the long range of cylinders being perpendicular to the sample surface is successfully realized in an electric field together with varying temperature. However, the sample thickness and/or the sample area included in the X-ray/neutron beam are crucial to view the alignment results as more domains with different azimuthal distribution included into the beam will make the 2D pattern of reorientation unrecognizable, even they are all aligned very well. The pore size of the hexagonal system before and after reorientation are invariant but a little bit smaller with respect to the system before temperature variation. The orientational order parameter from the azimuthal distribution function after alignment is about 0.63, indicating the majority of the cylinders are perpendicularly aligned with respect to the sample surface. The reorientation of the mesochannels templated from hexagonal LLCs in an electric field is promising for the further actual application.
CHAPTER 7 CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The template method from hexagonal LLCs formed of DTAB and H$_2$O was explored for the fabrication of NF membranes with the uniform nanopores in the range of 1-5 nm. The nanostructure templated from hexagonal LLCs with a uniform distribution and high surface area make it favourable not only in separation technology, but also in various other areas. The extensive range of pure hexagonal packing formed of DTAB and H$_2$O make it ideal to act as a template. Moreover, it presents a high stability to the temperature up to 100 °C. The soft template, however, cannot be applied directly as lack of the robustness. The nanostructure from hexagonal LLCs need to be further retained through physicochemical methods. Photo-polymerization after adding the monomers with light sensitive groups gives a preferable route to convert the soft template to robust polymer materials. However, incorporation of monomers will inevitably affect the physicochemical property of the template precursor and the final membrane product. Therefore the investigation of a new hexagonal LLCs template system with polymerizable units solubilised is desirable to be conducted for further NF membranes fabrication.

On the other hand, the continuity of nanopores through the whole membrane will severely limits the mechanical property and their actual filtration efficiency. A monolith after alignment, however, is regarded as the ideal template precursor for the NF membranes fabrication. The developed methods or techniques for reorientation of mesochannels templated from hexagonal LLCs are still out of favour as for the effectiveness and the scalability. As a consequence, a facile and scalable strategy to conduct the reorientation presents an intriguing option and needs to be developed.

In this study, the hydrophilic monomers HEMA and PEGDA (also called cross-linker) were added into the hexagonal LLCs template to prepare a monolithic template precursor for NF membranes fabrication. The physicochemical properties of the template formed of DTAB, water, and monomer (s) were extensively investigated and discussed. At last, a monolithic template was achieved after the alignment in a static electric field by using a novel electrode designed by ourselves. The strategy provides
an excellent compatibility with thin film geometries and scalability in practical applications:

1. The dimensional elements of the hexagonal unit cells were firstly calculated and compared between the systems with various monomer composition and/or the exchange of D$_2$O/H$_2$O ratios including $d$-spacing, the diameter of lipid core, water and head group thickness, and the average surface area available to each lipid head. HDDA, a hydrophobic monomer, presents a swelling effect in the lipid core region and facilitates the phase transition accordingly. Therefore, only 9.5% (v/v) of HDDA was applied to prevent from the unexpected phase transition. The effect of HDDA on structural dimensions was insignificant compared to the binary system. Besides, compared to the HDDA located in the lipid core in the hexagonal LLCs template of DTAB and water, the effect of the hydrophilic monomer on the structural dimensions is more desirable for the further fabrication of the NF membranes. Therefore, the detailed information on the effect of HDDA was not further explored. The hydrophilic monomer, PEGDA and HEMA, presented an obvious effect on the structural dimension compared to the binary system with the lipid core diameter decreased, and the water and head group thickness and the average surface area available to each head increased. The reasonable interpretation for this could be a rearrangement of the hexagonal packing system with a lower aggregate number after the monomer (s) was added. The reduction in $d$-spacing, unlike the inverted hexagonal system whose decrease in $d$-spacing is mainly from the reduction in water core diameter, is a synergistic action originated from the decrease of the lipid core and the increase of the hydrophilic region. The exchanges of D$_2$O/H$_2$O and/or PEGDA/HEMA presented little effect on the structure dimensional elements, which benefit the further exploration. Another phenomenon observed from the system with PEGDA alone is that a small amount of isotropically distributed DTAB molecules in aqueous-rich phase was observed to coexist with the hexagonal phase when the excess monomer was added. However, the free DTAB molecules would join in the pure hexagonal system without any aqueous phase again as the PEGDA was partially replaced with HEMA when the monomer percentage is moderate.
2. The stability to temperature variation and the rheological behaviours under external forces are the important parameters for hexagonal LLCs system to act as a template for the fabrication of robust NF membranes. The results demonstrated that the systems with monomer (s) solubilised, unlike the binary system that is stable up to 100 °C, have a significant decrease in stability to temperature with a reversible phase transition temperature varies depending on the monomer compositions observed. Meanwhile, the transition temperature of the system with PEGDA is almost twice as high as the one with HEMA. The phase transition from where the micelle phase with lowest complex viscosity was observed offers an opportunity for further administration of the reorientation of mesochannels under external forces. However, a robust template needed to resist the thermodynamic effect during curing process is also desirable. Therefore, the balance between flexibility and stability could be adjusted by changing the ratio of PEGDA/HEMA. The further investigation of rheological properties demonstrated that the rheological behaviours in the systems with PEGDA and/or HEMA all obeyed Maxwell model and from which the calculated longest relaxation time in the ternary systems almost decrease to ¼ of that from the binary system. This can surely confirm and interpret the significant decrease in stability in the systems with monomer (s).

3. The identical structural dimension but the extremely significant difference in phase transition temperature between the systems with PEGDA and HEMA presents an interesting phenomenon for further exploration. The localization and distribution of the different molecules within the template could be the best explanation. The 2D reconstruction of the hexagonal unit cell was achieved to locate the water/monomer (s) by using different SANS instruments such as Quokka, Bilby, and V1 diffractometer. However, the potential difficulties in preparing isotropic sample and the unpredictable incoherent scattering from hydrogens make the scattering amplitude inaccurate. The lower wavelength resolution of the Quokka and the wavelength dependent background problem of the Bilby using the time of flight mode make them unfavourable for reconstruction work in present case. The data from V1 diffractometer presented a higher quality and consequently were used to reconstruct the hexagonal unit cell. From the SLD map one can conclude that the systems with a mixture of
PEGDA and HEMA or HEMA alone present a more uniform distribution in the hydrophilic region. Therefore, the monomer(s) added into the binary system by mixing the PEGDA and HEMA will be the best choice to act as the template for the robust NF polymer membranes. The thicker monomer region (water and head group thickness) and the uniform monomer distribution within the hydrophilic region will significantly boost the resistance to the thermodynamic controlled phase separation and benefit the mechanical property of the polymerized materials. However, the accurate localization of water/monomers within the template will need some more detailed information.

4. The continuity of the pores through the whole film is another critical point that severely limits the filtration efficacy. Meanwhile, the formation of a monolithic template after reorientation will significantly boost the mechanical property during and after polymerization as well. A high degree of alignment with the long range being perpendicular to the surface could be achieved in-situ with temperature variation under the strong magnetic field. The system with the mixture of PEGDA and HEMA incorporated presents a higher degree of alignment and a high accessibility at a much lower temperature compared with the system with PEGDA only. More importantly, the relaxation of the aligned structure will take a long time at room temperature.

5. The electric field is more promising to be conducted and put into practice without any special equipment and complex conditions needed. The electrode especially compatible with thin film geometries was developed and the in-situ SAXS measurement together with temperature variation was performed by inserting an electrode on the SAXS beamline to observe the reorientation. The dielectric permittivity of the aggregates make them preferentially parallel to the field direction, and therefore perpendicular to the membrane surface. The continuity of the mesochannels could be significantly enhanced and the order parameter, \( <P_2> \), extracted from the azimuthal distribution of the first diffraction order is 0.63. This number will boost significantly if the diminishing sample thickness and/or sample aperture was selected for measurement otherwise more domains with divers azimuthal angle will be included in the calculation and therefore will diminish the final extracted value. The SANS
measurement from Bilby confirmed the perpendicularly aligned results in an electric field and the 2D pattern where the 1D azimuthal distribution reduced from is getting better gradually from the diminishing sample aperture. In addition, the order parameter is basically obtained from the SAXS measurement in which the small pores on the conducting materials of electrode are needed for X-ray to pass through. Although the strength in the middle of pores has been proved to be almost same to the area without pores from simulation by using the 5 mm thickness electrode, the fringe effect from electric field could not be ignored and this will significantly decrease the extracted order parameters. Therefore, the alignment results could be significantly increased when the electrode without holes is applied.

The hexagonal LLCs system of DTAB and water could be acted as the template for the fabrication of organic NF membranes after the hydrophilic monomers was added into the hydrophilic moiety. The appropriate monomer composition and its ratio to lipid system could be accessible to maintain the nanostructure during polymerization and increase the crosslink density of polymer net. The continuity and the mechanical property could be significantly enhanced after reorientation of mesochannels in an electric field. Finally, a monolithic template with perpendicularly aligned nanopores in a uniform pore size through the whole system was achieved for the preparation of the robust NF membranes.

7.2 Future work

In this study, the monolithic template precursor for the fabrication of high flux organic NF membranes has been successfully prepared. However, several avenues for potential future work are needed to fulfil the robust NF membranes fabrication.

1. The introduction of the silica network has been found to reinforce the hexagonal LLCs template and significantly boost the structure retention rate in combination with the CO$_2$ critical point drying method from our previous work (Zhang et al. 2012b; Zhang et al. 2014a). Researchers have been trying to control over the phase curvature chemically or physically to increase the retention rate of the nanostructure. However, an important issue overlooked by the researchers but should be given an emphasis is the composition and distribution of the monomer (s) within the hexagonal LLCs template which
could also be a critical mechanism that can control the phase retention and its filtration efficiency. It must be stressed here that any defects in the template for the fabrication of separation sieves will severely limit the actual application. Therefore, a single hexagonal LLCs phase with appropriate monomer composition and volume percentage would be necessary for further process. Meanwhile, the physical robustness of the polymerized NF membranes highly depends on the thickness of hydrophilic area where the pore wall thickness comes from after polymerization. Undoubtedly, the thicker water channel and the evenly distributed monomer(s) are preferable for the robustness of membranes. The optimal monomer composition and distribution of PEGDA and HMEA and their percentage in the system could be further explored from the reconstruction work, which will give more detailed information within the unit cell such as the numbers of the water molecules per lipid and the monomers incorporated into the system and their distribution.

2. A suitable thin yet mechanically robust film will significantly improve the permeability of NF membranes. The inherent viscoelasticity of the hexagonal LLCs makes it troublesome to prepare membrane template precursor with an exact thickness. The robustness, on the other hand, sets a lower threshold on the thickness of film. Fortunately, a reversible phase transition as a function of temperature could be realized by incorporating small molecules into the template without significantly affecting the structure. Those small molecules enable the further process of the samples in a flow regime at as low as about 45 \(^\circ\)C, depending on various systems via molecular design, thereby enable the controlling of the thickness after cooling down to room temperature. The introduction of small molecules with high number of reactive groups also helps to increase the cross-linking density and further benefit the mechanical property. Besides, the alcoholic molecules such as methanol or ethanol are also good options to disperse the samples under a flow state, after that the desired membrane thickness could be obtained by evaporating the alcoholic molecules. However, the evaporation process should be carefully maneuvered to maintain the water contents in the template.

3. The cares on the thermodynamic changes during photo-polymerization and the followed dehydration process should be taken for retention of the
nanostructure. The monomer composition could be adjusted according to the actual requirements. The effect of polymerization rate on structure retention should be taken into account. The ratio and the polarity of initiators will imparts some new thermodynamic property during polymerization.

4. Further to this, to get a monolithic membrane template for the fabrication of NF membranes and to improve the mechanical property, the facile and scalable methods for reorientation of mesochannels are essential to fabricate NF membranes templated from hexagonal LLCs as an actual practice. The most commonly used method for the reorientation is mainly from the strong magnetic field ($>3 \text{ T}$) (Tousley et al. 2014). However, a more promising method probably should be from electric field, which presents a similar reaction mechanism as electric field is easily accessible in the laboratory and the actual practice. Although it has some disadvantages, such as contact issues and breakdown concerns compared to the magnetic field, those concerns can be overcome by appropriate design. More importantly, the electric field could provide an excellent compatibility with thin film geometries, and is inherently scalable from lab to actual application.

5. As an increasing emphasis on the environmental concerns, the renewable/sustainable materials used as the structure-directing agent or the reactive monomer will gain more attention. Recent research for the NF membranes polymerized by using plant-derive fatty acid molecules templated into highly ordered columnar mesophase opened up a promising route for the sustainable development of NF membranes (Feng et al. 2017). Actually, the amphiphiles rich in living systems such as plants or animals are environment-friendly and could be considered as a good potential candidate for membrane materials.

6. Lastly, the characterization and performance tests need to be conducted by using polymerized NF membranes alone or in combination with other membrane materials acted as a support substrate. The optimal membrane thickness, a key parameter to break ubiquitous trade-off behaviour between permeability and selectivity, will be examined according to the actual filtration efficiency and the mechanical property needed.
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APPENDIX A

Characterization during synthesis of $\alpha$-deuterated DTAB

The synthesis of $\alpha$-deuterated DTAB and its characterization are presented from Figure A.1- A.13 and in Table A.1.

Figure A.1 $^1$H NMR spectrum of dodecanamide.

Figure A.2 $^{13}$C NMR spectrum of dodecanamide.
Figure A.3 $^1$H NMR spectrum of dodecan-1-amine-$d_2$.

Figure A.4 $^2$H NMR spectrum of dodecan-1-amine-$d_2$. 
Figure A.5 $^{13}$C NMR of dodecan-1-amine-$d_2$.

Figure A.6 $^1$H NMR spectrum of DTAI.
Figure A.7 $^2$H NMR spectrum of DTAI.

Figure A.8 $^{13}$C NMR spectrum of DTAI.
Figure A.9 $^{13}$C NMR spectrum of DTAI with $^1$H, $^2$H decoupled.

Figure A.10 $^1$H NMR spectrum of DTAB.
Figure A.11 $^2$H NMR spectrum of DTAB.

Figure A.12 $^{13}$C NMR spectrum of DTAB.
Figure A.13 $^{13}$C NMR spectrum of DTAB with $^1$H, $^2$H decoupled.

Table A.1 X-ray determination of bromine/iodine content before and after counter-ion conversion.

<table>
<thead>
<tr>
<th></th>
<th>Before ($\mu$g/cm$^2$)</th>
<th>After ($\mu$g/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromine</td>
<td>0.027 ± 0.008</td>
<td>33.114 ± 0.21</td>
</tr>
<tr>
<td>Iodine</td>
<td>98 ± 0.181</td>
<td>0.048 ± 0.013</td>
</tr>
</tbody>
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APPENDIX B

SANS data from Quokka and Bilby

Figure B.1 2D SANS pattern (azimuthal distribution) of the aligned nanostructure after several days since reorientation experiment in an electric field (8 h measurement).

As described before, the SANS data from Quokka (Figure B.2) and Bilby (Figure B.3) are not suitable for reconstruction in present case. The low wavelength resolution ($\lambda/\Delta\lambda$) of Quokka always broaden the diffraction peaks and make the second and third peaks vanished. The wavelength depended background and the anisotropy of the crystal in sample (Figure B.5), on the other hand, from the scattering of Bilby make it out of favour as well. The calculated contrast variation sometimes cannot match the experimental data in some system. Therefore, the data from V1 were used to reconstruct the hexagonal unit cell.
Figure B.2 1D SANS pattern from Quokka by using the binary system with contrast variation by changing the ratio of D$_2$O/H$_2$O.

Figure B.3 1D SANS pattern from Bilby by using the binary system with 8.6% PEGDA (v/v) with contrast variation by changing the ratio of D$_2$O/H$_2$O.
Figure B.4 Azimuthal distribution of the ternary hexagonal LLCs system of DTAB, D$_2$O, 22% PEGDA (v/v) under electric field without temperature variation.

The hexagonal LLCs systems are quite stable even to very high voltage like $6 \times 10^6$ V/m (Figure B.4). Therefore, temperature variation is necessary for reorientation.

Figure B.5 2D SANS pattern of the binary system with 100% D$_2$O applied from Bilby for reconstruction.
Figure B.6 2D SANS pattern of the hexagonal system with 8.6% PEGDA applied from Bilby for reconstruction by using 100, 80, and 60% of D$_2$O (From top to bottom).
LIST OF PUBLICATIONS AND PRESENTATIONS

Publications


2. **Guang Wang**, Chris J. Garvey, Weiwei Cong, Maria Forsyth, Jenny Pringle, and Lingxue Kong. Rheological Behaviours Corresponding to Phase Behaviours of Hexagonal Lyotropic Liquid Crystalline Template (In preparation)


4. Si Qin, Dan Liu, **Guang Wang**, David Portehault, Ying Chen and Weiwei Lei. High and Stable Ionic Conductivity in 2D Nanofluidic Ion Channels between Boron Nitride Layers. *Journal of the American Chemical Society* (2017), 139 (18), 6314–6320. (doi:10.1021/jacs.6b11100)

Presentations


6. **G. Wang**. “*In situ* small angle X-ray scattering measurements of liquids in an electric field” (Poster Presentation) Australian Synchrotron User Meeting in Australian Synchrotron (Melbourne, Australian) (2013)

7. **G. Wang**. “*In situ* small angle X-ray and neutron scattering measurements of self-assembled templates in an electric field” AINSE-ANBUG Neutron Scattering Symposium (Poster presentation) (Sydney, Australia) (2013).