FROM SYNTHESIS TO PIEZOELECTRIC STUDIES OF CENTRAL-RING-SUBSTITUTED BENT-CORE LIQUID CRYSTALS AND THEIR COMPOSITES

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CHAPTER 1

Introduction

Liquid crystal phases are the phases of matter that exist between the isotropic liquid and well-ordered crystalline solid phases[1]. These are phases that have more order than the isotropic fluid, but less order than the crystal phase and therefore can exhibit properties of each phase at the same time. Molecules in the solid state are frozen in place - something defined as positional order. They are also restricted in the ways in which they orient themselves with one another. This is defined as orientational order. Both positional and orientation order are properties inherent to crystalline solids. Upon raising the temperature and melting the solid into the liquid phase, both types of order are lost. The molecules are positioned and oriented randomly through space and over time. (This phase is more specifically called the isotropic liquid phase, or simply isotropic phase). In contrast, when a material melts from the solid to a liquid crystal phase, some of the positional order may be lost, yet some of the orientational order remains. The material may now be able to flow as a liquid and take the shape of its container and also maintain some properties of the crystal dependent on orientational order, such as anisotropies in the speed of sound and the index of refraction. The discovery of liquid crystal phases is typically attributed to Austrian botanist Friedrich Reinitzer in 1888[2]. After observing the materials exhibit both liquid and crystalline properties, his collaborator, German physicist Otto Lehmann, coined the term flüssiger Kristall, German for liquid crystal[3], [4].
The liquid crystal phases are typically found in molecules with some kind of shape anisotropy, such as rod or cigar-shaped molecules. Other shapes can also show liquid crystal phases (e.g., disc or brick-like molecules), however, the example of rod-like molecules will be used in the following explanation as they are the most common and widely studied.

Beginning with the least ordered, the nematic phase is typically seen at temperatures just below the isotropic phase. This phase is defined by the molecules possessing only orientational order, i.e., the molecules tend to align along a particular axis while their positions are random (see Figure 1.1). The axis of orientation is called the director, typically labeled \( \hat{n} \). Note that, even though unit vector notation is used, the director is a non-polar axis in which \( \hat{n} \) is equivalent to \( -\hat{n} \). It is this phase that appears in the vast majority of liquid crystal devices, including display applications.

Upon further cooling, one may find the smectic liquid crystal phases. These phases are characterized by the layering of molecules - a situation which adds positional order in one direction. As seen in Figure 1.1, there are two basic variations of the smectic phase: those where the director is perpendicular to the plane of the layers (normal to the layers) and those where the director is at some angle with respect to the layer normal. The former is called the smectic A (SmA) phase and the latter is called the smectic C (SmC) phase. (In this nomenclature, the letters A and C are purely historical and only represent the chronological order in which the phases were classified.) Additionally, the SmC phase can have two sub-variations. The layers may be tilted all in the same direction (called synclinic) or they may alternate directions from layer to layer (called
anticlinic). The distinction is notated with a subscript - SmC$_s$ or SmC$_a$, respectively. In these smectic phases, the molecules are still free to diffuse in the plane of the layer, i.e., they are fluids in the two dimensions of the plane of the layer with a degree of positional order holding them into the layers in the third direction.

A collection of molecules exhibiting various liquid crystal phases is shown in Figure 1.2.

<table>
<thead>
<tr>
<th>Isotropic</th>
<th>Nematic</th>
<th>Smectic A</th>
<th>Anticlinic</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Isotropic" /></td>
<td><img src="image" alt="Nematic" /></td>
<td><img src="image" alt="Smectic A" /></td>
<td><img src="image" alt="Anticlinic" /></td>
</tr>
</tbody>
</table>

*Figure 1.1: Cartoon representations of the isotropic liquid, nematic, and smectic phases.*
Figure 1.2: A collection of molecules exhibiting liquid crystal phases with the corresponding nicknames used in this dissertation. They show the following liquid crystal phases: MBBA: N; 5CB: N; 8CB: N, SmA; 6OO8: N, SmC; 3RBC-S: SmA; ClPbis10BB: N.

This has not been an exhaustive list of the liquid crystal phases. Various shapes and properties of molecules can lead to more complicated and interesting phases. However, in the scope of this dissertation, all phases studied here belong to one of these phases or can be described as a derivative of one of these. The focus will be on molecules with a bent shape, like bananas or boomerangs, also called bent-core liquid
crystals (BCLCs) (see 3RBC-S and ClPbis10BB in Figure 1.2). Variations of these liquid crystal phases found in bent-core molecules will be discussed later in this chapter (Section 1.1).

Liquid crystal phases from bent-shaped molecules were first discovered by Vorländer in 1929[5]. Unfortunately, little research was done on these materials for nearly 60 years when there was a renewed interest in ferroelectric phases of liquid crystal molecules. Previously, ferroelectric liquid crystal phases were known to only exist when made from chiral molecules[6]. With the potential to have a large and fast electro-optic response[7], the drive to eliminate the high cost of producing chiral molecules led to research on ferroelectric phases from achiral molecules. Tredgold's prediction[8] of ferroelectricity in smectic liquid crystal phases of achiral bent-core molecules led to the first experimental confirmations[9–11] of such a phenomenon - thus sparking the current wave of research on bent-core liquid crystals (BCLCs). The following sections in this chapter will describe some of the various properties and research areas of BCLCs.

1.1 Phase Behavior Based on Molecular Shape

Due to the molecular shape, bent-core molecules prefer to pack in layers to most efficiently fill the space. This leads to the smectic-like phases being the most common phases of bent-core liquid crystals - and there are many variations. Symmetry arguments arising from the kink in the molecule allow for types of smectic phases that are not seen with typical rod-like (calamitic) liquid crystal molecules. In order to discuss these phases, in addition to the standard liquid crystal director, \( \hat{n} \), we will define unit vectors \( \hat{p} \), pointing along the direction of the kink, and \( \hat{m} \), normal to the molecular plane and
perpendicular to $\hat{p}$ (see Figure 1.3). When the molecules aggregate into smectic layers, we can define the unit vector normal to the layer plane called $\hat{k}$. Additionally, symmetry allows there to be a dipole moment along the kink direction, $\hat{p}$. (In fact, it is difficult to make a bent-core molecule that does not have a at least some dipole moment component in that direction.)

![Figure 1.3: Schematic structure of the ferroelectric SmAP_F and anti-ferroelectric SmAP_A.](image)

*Figure 1.3: Schematic structure of the ferroelectric SmAP_F and anti-ferroelectric SmAP_A.*

For clarity, the molecules lay in the xz-plane (the plane of the page). The net layer polarization, $\bar{P}$, also lies in this plane.

Just as with standard rod-like molecules, there can be a smectic A phase (SmA) where the director $\hat{n}$ is parallel to the layer normal $\hat{k}$. However, one must now consider the direction of the kink, $\hat{p}$, as the degeneracy of rotation around $\hat{n}$ has been broken. Due to steric/entropic interactions, the molecules of a given layer prefer to have $\hat{p}$ all pointing in the same direction. This leads to a macroscopic layer polarization in which
one can observe two manifestations (Figure 1.3): a ferroelectric smectic A phase (SmAP$_F$) in which all the layers have $\hat{p}$ in the same direction, or an anti-ferroelectric smectic A phase (SmAP$_A$) where $\hat{p}$ alternates in opposite directions from layer to layer. (The letter P for "polar" is used in the labels of these phases).

Let me digress for a moment to discuss more about polarization and ferroelectricity. Polarization is defined as the dipole moment density in a material. It has SI units of C·m/m$^3$ (usually simplified to C/m$^2$). A material that has a spontaneous non-zero polarization and is electrically switchable is called ferroelectric. Ferroelectric materials can have the direction of polarization defined by applying an external field and exhibit a hysteresis loop in an alternating electric field[12]. In bent-core liquid crystals, polarization values can be more than $10^{-3}$ C/m$^2$.[12] Due to dipole-dipole interactions, this is sometimes sufficient to cause the polarization to arrange itself in an alternating (antiparallel) fashion from layer to layer. This arrangement is called anti-ferroelectric. In anti-ferroelectric materials the opposing polarizations cancel one another and therefore they have no net spontaneous polarization, however, they will exhibit ferroelectric switching under applied electric fields.

Now consider the smectic C phase (SmC). In SmC phases of rod-like molecules, the molecular director points at some non-zero angle, $\theta$, with respect to the layer normal, $\hat{k}$. Layers can be arranged in a synclinic, SmC$_s$ (all layers tilting in the same direction), or an anticlinic, SmC$_a$ (layers alternate the direction of tilt) pattern. In BCLCs, one must define two tilt angles in order to fully describe the orientation of molecules within the
layer. We will define \( \theta \) as the angle between \( \hat{n} \) and \( \hat{k} \), and \( \alpha \) as the angle by which \( \hat{p} \) rotates out of the plane of the layer around the director axis, \( \hat{n} \) (see Figure 1.4).

![Figure 1.4](image)

**Figure 1.4**: Graphical explanation of the two defined tilt angles. \( \theta \) is defined as the angle the director, \( \hat{n} \), makes with the layer normal. \( \alpha \) is defined as the angle by which \( \hat{p} \) rotates out of the plane of the layer about \( \hat{n} \). A coordinate system is shown to assist in the explanation. In this system, \( \hat{n} \) can be restricted to the \( yz \)-plane without any loss of generality. In that case, \( \alpha \) can alternatively be defined as the angle between \( \hat{p} \) and the \( x \)-axis.

First let us consider the case where \( \hat{p} \) remains in the plane of the layer (\( \theta \neq 0, \alpha = 0 \)). Four distinct arrangements now exist. As with SmC phases of rod-like molecules, there is a synclinic and an anticlinic arrangement. And, as with the SmAP phases of bent-cores, there can be a ferroelectric and an anti-ferroelectric phase. The combinations of tilt and polar orientations give rise to the SmC\( _s \)P\( _F \), SmC\( _s \)P\( _A \), SmC\( _a \)P\( _F \), and SmC\( _a \)P\( _A \) phases[13]. Figure 1.5 contains the schematic structure of these phases. Notice that an individual SmCP layer has only \( C_2 \) symmetry (two-fold rotation axis around \( \hat{p} \)). This is the same symmetry as found in SmC* materials made of chiral rod-like
molecules. Likewise, each SmCP layer has a particular physical chirality or handedness even though the molecules are achiral[13] (this is called *layer chirality*). In the case of SmC$_s$P$_A$ and SmC$_a$P$_F$, the layers alternate right- and left-handed, making the entire domain racemic. On the other hand, SmC$_s$P$_F$ and SmC$_a$P$_A$ have layers of similar chirality, making the domain overall chiral, with equal probability of being all right- or left-handed. More about chirality will be discussed in Section 1.2.

Now we consider the situation in which $\hat{m}$ remains in the plane of the layer but $\hat{p}$ is free to tilt out of the layer ($\theta \neq 0$, $\alpha = 90^\circ$). Just as above, there are four variations. The letter "T" for "tipping"[14] is used in this case to distinguish it from the SmCP cases. The four phases are then written as SmT$_s$P$_F$, SmT$_s$P$_A$, SmT$_a$P$_F$, and SmT$_a$P$_A$ phases (Figure 1.5).

![Schematic of single tilted structures](image)

*Figure 1.5: Schematic of single tilted structures. The crossbar denotes that that end of the molecules is tilting out of the plane of the page.*
Now consider both $\theta$ and $\alpha$ at arbitrary angles not 0° or 90°. This is the most general tilted smectic phase possible [15], sometimes annotated as SmC$_G$ (the "G" is for "general"). Combining the various arrangements for each parameter (tilt, tip, and polarity) one find eight distinct phases: SmC$_s$T$_s$P$_F$, SmC$_s$T$_s$P$_A$, SmC$_a$T$_s$P$_F$, SmC$_a$T$_s$P$_A$, SmC$_a$T$_d$P$_F$, SmC$_a$T$_d$P$_A$, SmC$_a$T$_a$P$_F$, and SmC$_a$T$_a$P$_A$ (see Figure 1.6).

![Figure 1.6: Schematics of the double tilted smectic phases.](image)

The nematic phase can also be observed in certain BCLCs. In order to observe the nematic phase, the molecule must have some steric or electrostatic inclusion in the core that hinders the layer packing. This inclusion can frustrate the smectic order and force the molecules into the more fluid nematic phase. Bent-core nematics will be discussed in more detail in Section 1.3.

### 1.2 Chirality

Chirality, in its simplest definition, means a lack of mirror symmetry. In other words, an object that is chiral cannot be superimposed onto a mirror image of itself. To
members of the liquid crystal community, the most familiar manifestation of this asymmetry is molecular chirality. Of the various ways a molecule can be chiral, the most common is that it contains a carbon atom bonded in a tetrahedral arrangement to four different groups. This creates a molecule that cannot be superimposed on its mirror image, no matter what rotations or translations are applied to it. Figure 1.7 shows an example of a right and left molecule of a generic amino acid. If two of the four groups are the same (for example, both hydrogen atoms) then the mirror image can be superimposed onto the original by a rotation and the molecule is considered achiral.

Figure 1.7: Example of molecular chirality in amino acids with images of hands to show the right- and left-handedness of the molecules. The hands themselves also represent chiral objects on a larger scale.

In general, one can form the same liquid crystal phases from chiral molecules as one finds from achiral molecules; however, there are distinctions. The molecular
chirality attempts to manifest itself as a rotation of the director through space. For example, in a nematic phase of chiral molecules one will observe the director rotate around a helical axis through space with the axis oriented perpendicular to the local director (Figure 1.8). This phase is called the "chiral nematic" or "cholesteric" phase, often abbreviated as N* (the * is used to denote that the phase is chiral). The name "cholesteric" originates from the first liquid crystal molecules being ester derivatives of cholesterol. The distance over which the director rotates by a full 360° is defined as the pitch, p. Additionally, one can have more complicated chiral smectic phases. The twist grain boundary phase, or TGBA* phase, a strongly chiral form the SmA* phase, is a phase in which the competition between smectic layering and director rotation force the smectic layers to break periodically at a twist grain boundary. The chiral smectic C (SmC*) phase is able to keep the director rotation through space without disrupting the smectic layering by rotating the direction of tilt from layer to layer (Figure 1.8).

The rotation of the director through space has notable effects on light in and near the visible spectrum. First, the optical axis of linearly polarized light will rotate as it passes through chiral materials. This is known as optical activity. In isotropic fluids of chiral molecules, the amount of rotation is roughly 1° of rotation per centimeter traveled. In chiral liquid crystal phases, the effect is amplified by the helical structure and can be as large as 100° per micrometer! [16] Additionally, the periodic nature of the helix causes total reflection of one handedness of circularly polarized light within a certain wavelength range. The results of both optical activity and selective total reflection are
widely used in applications today, such as electronic signage, e-readers, thermometers, and jewelry.

![Figure 1.8: Cartoons of A) cholesteric phase showing the director rotation through space, and B) the director configuration in the chiral smectic C (SmC*) phase. The pitch is defined as the distance over which the director rotates by 360°.](image)

One must also consider the fact that molecular chirality does not lead to a helical rotation of the director around just one axis, but that it urges rotation of the director in all three dimensions. However, one quickly realizes that this sort of director deformation cannot fill space completely and keep the constant helical pitch demanded by chiral liquid crystal phases. Yet, under certain conditions, it is energetically favorable[17] to form a 3-D lattice of "double-twist" cylinders that exhibit rotation of the director in three
dimensions (see Figure 1.9). These phases are called "blue phases" or BPs due to the bluish color observed in the first observed samples[12]. This 3-D rotation of the director is achieved at the expense of the limited diameter of the cylinder (approximately one quarter of the pitch) and of defects (disclination lines) that appear where the cylinders meet[17]. Three types of blue phases have been observed; BPI having a body-centered cubic structure, BPII having a simple cubic structure, and BPIII having an amorphous structure (short-range cubic).

Figure 1.9: Schematic of double twist cylinder showing continuous rotation of the director from one cylinder to another.

One finds that the natural pitch of phases composed of a single type of chiral molecule is rarely in the range for the desired application. As such, most chiral liquid
crystal phases are made up of mixtures of different types of molecules in order to better control the pitch and phase behavior for the given application. An achiral liquid crystal host doped with a few percent of a chiral molecule will exhibit the chiral liquid crystal phases and is the most common type of mixture used in applications today.

It can be argued on symmetry alone[6] that phases with C$_2$ symmetry (such as SmC*) allow for the existence of a permanent polarization along the symmetry axis and thus can be ferroelectric. It was for this reason that the first evidence of ferroelectricity in liquid crystals was sought after and found in SmC* materials[6]. The individual layers of a SmCP or SmCTP phase also have this same C$_2$ symmetry, have layer chirality, and allow for ferroelectricity. This layer chirality can be described by a chiral order parameter of the form[18]:

$$\chi = \langle \left[ 2 \left( \hat{k} \times \hat{n} \cdot \hat{p} \right) \right] \hat{k} \cdot \hat{n} \rangle = \sin 2\theta \cos \alpha$$  \hspace{1cm} (1.1)

where $\chi$ is the chiral order parameter and the other arguments are as previously defined in Section 1.1 (see Figure 1.4). One can see that the achiral SmAP ($\theta = 0^\circ$) and SmTP ($\alpha = 90^\circ$) phases have a chiral order parameter $\chi = 0$, while the maximum value $\chi = 1$ is achieved in the SmCP phase with $\theta = 45^\circ$. Right-handed layers will have positive values of $\chi$, while left-handed layers have negative values.

It is also interesting to note the relationship between chirality, polarization, and tilt of the molecular plane in these bent-core smectic systems. If two of the three are present, then the third must also be present[13], [19], [20].
1.3 **Bent-core Nematics**

The nematic phase of bent-core liquid crystals (BCNs) is historically much less common, with observations being published after the turn of the millennium[21–25]. In order to prevent the molecules from packing into smectic layers, some kind of steric or entropic inclusion should be present on the molecules, i.e., a bump in the molecular shape. These inclusions are usually in the form of a chemical functional group such as a halogen, methyl, or cyano group. A collection of bent-core molecules that form nematic phases is shown in Figure 1.10.

The most remarkable distinction between the nematic phases of rod-like molecules and those of bent-core molecules is the evidence for smectic-like clusters existing in the nematic phases of the latter[26–31]. Figure 1.11 shows a cartoon representation of the clusters. The concept of clusters in the nematic phase has been around for some time[32]. Smectic-like clusters have been found in rod-like molecules[33], however, they are only associated with pre-transitional effects and are only seen very near to the nematic-smectic transition[28]. In BCNs, the clusters have been shown to exist through the entire nematic range, and in some cases even persist well into the isotropic phase.[34]

First proposed in 2002 by Stojadinovic et al.[26] and then Dominici et al.[35–37], the short range ordering can be attributed to the translational frustration caused by the
Figure 1.10: Representative bent-core molecules that form nematic phases.
Figure 1.11: Cartoon of the proposed smectic-like clusters in the nematic phase.

bent shape of the molecules. Various studies have been done, including $^2\text{H}$ NMR[31], [35], viscosity measurements[38–40], magnetic field-induced phase transitions[41], [42], and dynamic light scattering[26], [30], [43]. The results show remarkable differences between the BCNs and the nematic phases of rod-like molecules, particularly the restricted molecular motions in the dynamics of the systems. For example, viscosity measurements have found values two orders of magnitude higher than in typical calamitic nematics[38], [40], indicating a hindrance of the molecular motion in the bent-core systems. Furthermore, Bailey et al.[39] found the best fit to the shear rate dependence of their viscosity data were from equations normally used to describe the viscosity of particle suspensions. The fit results indicated a system of soft, deformable nanoparticles of radius ~10 - 20 nm. As this was a system of a pure bent-core compound with no added nanoparticles, it was concluded that the molecules themselves were aggregating into
clusters of similar radius. Clusters of this size would correspond to roughly a few smectic layers comprised of only a few hundred molecules. Studies of the temperature dependence of the viscosity showed only a minor relationship, even as the material was heated above the clearing point, indicating that the clusters persist into the isotropic phase. $^2$H NMR studies have also shown that the clusters can persist into the isotropic phase[31], [35]. Together, these point to a hindered molecular dynamic process in the phases of these bent-core materials that is not present in rod-like molecules - further evidence of the existence of smectic clusters.

Small Angle X-Ray Studies (SAXS) have also been performed on BCNs and also show evidence of smectic clusters in the nematic and isotropic phases[34], [44–46]. The robustness of the clusters was even proven by Hong et al.[47] via SAXS measurements that showed that the clusters can expel rod-like molecules in systems of mixtures of the two. More will be discussed about SAXS in Sections 2.1 and CHAPTER 4. Recently, Zhang et al.[27] used cryogenic transmission electron microscopy (Cryo-TEM) to show the first direct images of smectic layers in a nematic phase.

1.4 Piezoelectricity

Piezoelectricity is the linear coupling between mechanical stress and electric polarization of a material. More specifically, the direct piezoelectric effect is the property of certain materials in which an electric polarization is induced in a material when a stress is applied in certain directions. Conversely, the converse piezoelectric effect occurs when a material undergoes a stress as a result of induced polarization caused by an external electric field. The word "piezoelectricity" is derived from the
Greek word *piezein* (πιέζειν) meaning to press tight or squeeze[12], [48]. The distinction between the direct and converse effects is mostly historical.

Piezoelectricity can be written mathematically in terms of polarization and stress as:

\[ P_i = \sum_{jk} d_{ijk} T_{jk} \]  

(1.2)

where \( P_i \) is the induced polarization in the material, \( T_{jk} \) is the stress tensor, and \( d_{ijk} \) is the piezoelectric charge constant tensor. The indices \( i, j, k \) represent the coordinate indices (i.e., \( x, y, z \)). Alternatively, the relationship can be written in an equivalent form:

\[ S_{jk} = \sum_i d_{ijk} E_i \]  

(1.3)

where \( S_{jk} \) is the strain tensor and \( E_i \) is the externally applied electric field. This form is more convenient when considering the converse effect.

It is important to note that the given equations apply when the piezoelectric material is modeled as a current source, i.e., the material is part of a closed circuit in which external charges can flow and accumulate on the surface. It is possible, instead, to model the piezoelectric material as a voltage source in an open circuit. In this case, a different piezoelectric constant is used, \( g_{ijk} \), which is called the piezoelectric voltage constant. Corresponding equations are as follows:

\[ E_i = -\sum_{jk} g_{ijk} T_{jk} \]  

(1.4)

\[ S_{jk} = \sum_i g_{ijk} P_i \]  

(1.5)

The relationship between \( d_{ijk} \) and \( g_{ijk} \) is:
\begin{equation}
    d_{ijk} = \varepsilon g_{ijk} = \varepsilon_r \varepsilon_0 g_{ijk}
\end{equation}

where \(\varepsilon\) is the electric permittivity of the material, \(\varepsilon_r\) is the relative permittivity (sometimes called the dielectric constant), and \(\varepsilon_0\) is the permittivity of free space.

At this point we can make some simplifications to the notation. Due to the symmetry of the stress and strain tensors, each one having only six independent terms, they are often each written as a single six-element vector. The most common mapping of the indices are: \(11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3, 23 = 32 \rightarrow 4, 13 = 31 \rightarrow 5, \) and \(12 = 21 \rightarrow 6\) (called Voight notation). \(d_{ijk}\) and \(g_{ijk}\) can then be transformed to \(3 \times 6\) matrices in which the indices \(j\) and \(k\) have been combined using the above notation into one index \(j\), written as \(d_{ij}\) and \(g_{ij}\).

Additionally, in our work, we are only considering forces of compression in the vertical direction (i.e., the \(z\) or \(3\) direction using the above notation) and are only measuring the electric response also in the vertical direction (see Figure 1.12), therefore, we are only concerned with the piezoelectric constants \(d_{33}\) and \(g_{33}\).

Piezoelectricity was first discovered by Pierre and Jacques Curie in 1880 when they noticed positive and negative charges on crystals compressed in particular directions[49], [50]. Although theoretically predicted by René Just Haiiy and Antoine César Becquerel, their experiments were inconclusive, leaving the Curie brothers as the first to observe the phenomenon. Inspired by this, only one year later, Gabriel Lippmann theoretically predicted the existence of the converse piezoelectric effect[51] followed immediately by the experimental confirmation of theory by the Curie brothers. The first
Figure 1.12: Graphical explanation of the orientation of force and the measured electric response.

practical application of piezoelectricity appeared in 1918, proposed by Langevin, in which he used the direct and converse piezoelectric effect to produce and detect underwater sound waves, thus opening the field of hydroacoustics, ultrasonics, and sonar[52]. Shortly after, Cady, demonstrated that the frequency of an electrical oscillating circuit can be stabilized with the addition of a resonating quartz crystal. First used as a frequency standard by the National Bureau of Standards, they later proved invaluable to the development of radio communication[12]. Further developments came in the 1940s with the discovery of ferroelectric materials exhibiting much larger piezoelectric responses[12]. So far, the piezoelectric effect has been found in a wide variety of materials including ceramics, polymers, biological materials (such as bone and tendon), and liquid crystals[12], [53]. The most common piezoelectric materials produced commercially today are ceramics of lead zirconate titanate (Pb[Zr$_x$Ti$_{1-x}$]O$_3$, 0 ≤
x ≤ 1), abbreviated PZT. The best known example of a piezoelectric polymer is polyvinylidene fluoride (PVDF).

In order for a material to be piezoelectric it needs to be non-centrosymmetric (i.e., lack inversion symmetry). It is, in fact, a material's symmetry that determines whether or not it is piezoelectric. As liquid crystals are also materials of reduced symmetry, they cannot be left out of the discussion. Table 1.1 shows some of the liquid crystal phases and their non-zero piezoelectric constants. The lack of inversion symmetry may be caused by molecular chirality or by particular molecular shapes and packing (such as in SmCP).

![Table 1.1: Select liquid crystal phases and their non-zero piezoelectric constants.](image)

Measuring the piezoelectricity of liquid crystals raises an interesting dilemma - they are liquids (at least in some directions) and as such, they flow when pushed. The equations previously shown will lose some physical meaning when given a static stress resulting in the constant flow of material. However, if the applied stress is periodic in nature (the net flow is zero) these equations can be used, with the amplitude of vibration...
as input to the strain. Additionally, one may freeze the fluid into a glassy state or incorporate it into a polymer. In these cases it is possible to measure the piezoelectric response of the fluid as the symmetry of the fluid can be maintained in a more solid form. More discussion of the experimental procedures will be discussed in Section 2.3. Results of the measurements will be discussed in CHAPTER 6.

1.5 Outline and Goals

In this work, we will present the results of various experiments on central ring substituted bent-core liquid crystals. CHAPTER 2 describes the experimental techniques developed and used in studying these materials. Following that, CHAPTER 3 presents the synthetic procedure used to create one of these bent-core mesogens. This molecule, along with several other bent-core molecules studied, has a nematic phase in which smectic-like clusters have been shown to exist. Part of this work, particularly CHAPTER 4, aims to characterize these clusters using small angle X-ray scattering measurements. We attempt to better understand the differences in cluster behavior based on the phase sequence of the material. Further, some bent-core materials exhibit an unusual phase called the X phase. This relatively unstudied phase is known to be optically isotropic as well as ferroelectric. X-ray studies of this phase can be found in CHAPTER 4, while CHAPTER 5 will focus entirely on other methods of characterizing the X phase. Because of the polar order and ferroelectricity of some of these bent-core liquid crystal phases, they can also exhibit piezoelectricity. In CHAPTER 6 we will present the results of piezoelectric studies of bent-core molecules, both as pure materials and when part of a polymer composite. Finally, in CHAPTER 7 we will summarize our results.
CHAPTER 2

Experimental Techniques

2.1 Small Angle X-Ray Scattering

Small angle X-ray scattering (SAXS) is a powerful tool used to probe the structure of materials on the nanoscale level. Since liquid crystals have features in the range of a few nanometers, SAXS is especially suited for studying the structure of the liquid crystal phases. SAXS is best explained in terms of Bragg diffraction, in which strong reflections of light (constructive interference) can occur at certain angles of incidence off a periodic structure depending on the wavelength of light and the spacing within the structure. The Bragg condition is met when beams of light scattered off adjacent layers of the periodic structure are in phase with each other, i.e., interfere constructively. The conditions under which these reflections occur is given by Bragg's Law:

\[ n\lambda = 2d \sin \theta \]  

(2.1)

in which \( \theta \) (the Bragg angle) is the angle of incidence upon the plane normal to the direction of periodicity, \( d \) is the periodicity of the spacing, \( \lambda \) is the wavelength of light, and \( n \) is an integer value representing the order of the reflection.[54] Figure 2.1 shows a graphical explanation of this geometry. If the Bragg condition is not met, the reflections will not occur. It is these reflections that are the subject of SAXS measurements.
We will now only consider the scattering that satisfies the Bragg condition and gives strong reflections. Instead of speaking in terms of incident angles, it is often common in SAXS studies to speak in terms of the scattering wavevector, $\bar{q}$. The scattering wavevector is defined as $\bar{q} = \bar{k}_{r} - \bar{k}_{i}$, where $\bar{k}_{r}$ and $\bar{k}_{i}$ are the wavevectors of the reflected (scattered) and incident light, respectively. Figure 2.2 shows a graphical explanation of the scattering wavevector. In the regime of small angles, elastic scattering dominates, ensuring that the magnitudes of the incident and reflected wavevectors are equal (i.e., they have the same wavelength), $|\bar{k}_{i}| = |\bar{k}_{r}| = 2\pi / \lambda$. By combining this with Equation 2.1 (Bragg’s Law), we can determine that, at the Bragg condition, the angle between $\bar{k}_{i}$ and $\bar{k}_{r}$ is $2\theta$, and the magnitude of the scattering wavevector of the reflected beam is found to be $q = 2\pi n / d$. By knowing the wavelength of light and measuring $q$ or $2\theta$, one can determine the periodicity of the structure being probed.
Figure 2.2: Graphical explanation of the scattering wavevector at the Bragg condition.

We must further consider that a bulk sample of material may contain many domains with various orientations in three dimensions. This is the case with a powder sample. Assuming a fixed incident beam, only domains with orientations that satisfy the Bragg condition will contribute to the final scattering pattern. Extending the schematic in Figure 2.2 to multiple domains randomly oriented in three dimensions (a powder sample), one would find the scattered light makes a cone around the incident beam with angle $2\theta$. Projecting this light onto a screen or camera would produce a ring pattern. See Figure 2.3 for a schematic of a typical powder diffraction pattern.
Scattering images can become more complicated by introducing aligned samples, samples with periodicity in multiple directions, anisotropic molecules, and various phases such as liquid crystal phases. Consider the isotropic liquid phase. There is no long range positional or orientational order, however, there is short range correlation between molecules. This short range order will still produce a scattering peak corresponding to the distance between molecules, appearing as a diffuse ring in the scattering pattern. If the molecules are anisotropic (as is the case for liquid crystal molecules), then there will be two rings, one corresponding to the short axis of the molecule and one corresponding to the long axis. Figure 2.4 shows the scattering pattern for the isotropic phase as well as other liquid crystal phases. In aligned liquid crystal phases the rings will collapse into spots as there is no longer random distribution of orientations in three dimensions. In the nematic phase, one finds a pair of diffuse spots corresponding to the long axis oriented along the director, and a second pair of spots farther out corresponding to the short axis.
and perpendicular to the director (see Figure 2.4B). In the smectic phases, there is now long range order along the smectic layers causing the inner spots (corresponding to the direction of the smectic layers) to become typical Bragg-like sharp peaks. In the smectic C phase the inner spots separate into four peaks because of the degeneracy of the layer tilt. The angle that those spots make with the horizontal (director) axis is the tilt angle of the molecules in smectic layers (shown as $\theta$ in Figure 2.4D).

Figure 2.4: Schematic of 2-D SAXS patterns for the A) isotropic, B) nematic, C) smectic A, and D) smectic C phases. For the liquid crystal phases, the director is assumed to be along the horizontal direction.

As an estimation, if we desire a scattering angle of 1° (for the first order reflection) and are probing a feature that is 30 Å (typical of liquid crystals), we can
calculate that we should use a wavelength of ~1 Å. This corresponds to a photon energy of ~12 keV, a value easily achieved using a synchrotron light source.

SAXS measurements were taken at the X6B beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The X6B beamline uses photons from a bending magnet source approximately 20.8 m upstream of the sample position (Figure 2.5). The specific setup of this beamline allows for photon energies ranging from 6.5 keV to 19 keV. For all of the SAXS experiments in this dissertation, unless otherwise noted, the beamline was configured for a photon energy of 16 keV (\(\lambda = 0.7749\) Å) with a collimated beam size of 0.2 mm × 0.3 mm (horizontal × vertical). The entire flight path of the beam was evacuated except for a few small gaps separating the user accessible flight path from the detector and the high vacuum upstream flight path. At these boundaries, the vacuum was maintained by and the beam passed through either beryllium windows or Kapton® windows. Evacuation of the flight path was necessary to eliminate scattering and absorption of the beam by the air.

![Beamline Schematic](image)

*Figure 2.5: Beamline Schematic. The equipment was set up to have a collimated beam size of 0.2 mm × 0.3 mm (horizontal × vertical) at the sample.*
When studying samples of pure liquid crystal, the material was placed inside a cylindrical fused quartz capillary with outer diameter of ~1 mm and wall thickness of 0.01 mm (purchased from Charles Supper Co.). The capillaries were placed in one of a series of custom-built aluminum cassettes designed to fit into a standard heat stage (Instec model HCS402) that allowed temperature control with 0.1°C precision. The cassettes were designed to also hold neodymium iron boron (NdFeB) magnets to allow application of an aligning magnetic field. The field was measured to be 1.5 T across a 2.5 mm gap. Figure 2.6 shows an image of the typical cassette used to hold the capillaries.

Our original method called for cutting and sealing the capillaries to a length of roughly 1 cm using a propane torch. This allowed the capillary to fit inside the cassette and not interfere with the heat stage. As the capillaries are extremely fragile, many were broken in the cutting process. The sealing process was required to keep the material protected from the vacuum of the x-ray flight path. Any air bubbles trapped inside the material would expand rapidly when the material melted in the vacuum, sometimes shattering the entire capillary. In an attempt to solve this problem, a custom accessory piece to the heat stage was built. Designed to replace the original spacers that maintained the gap between the front and back heating plates, this new spacer had a port in line with the capillary slot in the cassette, allowing the capillaries to be inserted from outside the heat stage. This provided us with several advantages. First, it saved time when changing samples, as disassembly of the heat stage and removal of the cassette was not required. Also, it eliminated the need to cut the capillaries to fit inside the heat stage. By using the
capillaries at their full length (~80 mm), the risk of damaging the capillary was much lower. In the event of an air bubble explosion, the air was free to escape out the top of the capillary with little risk of damage to the capillary and leaving any sample material splattered on the inner wall of the capillary. This method proved much more efficient.

Figure 2.6: Photograph of cassette and heat stage, viewed along the path of the beam (X-rays traveling into the page). The red dotted line represents the approximate position of the capillary as it sits in the space and cassette. The X-ray beam passes through the small hole situated between the magnets near the bottom of the capillary.
The heat stage itself was mounted to the inside of a removable flange of a custom-built vacuum chamber which was connected to the flight path via vacuum bellows on each side. The vacuum chamber was mounted on vertical and horizontal motion stages to enable centering of the sample in the beam's path. Vertical positioning was done by manually adjusting the stage. Horizontal position adjustment and temperature control of the heat stage was controlled remotely via computer located outside of the safety hutch.

Two-dimensional SAXS images were recorded on a Princeton Instruments 2084 × 2084 pixel array CCD detector. Analysis of the scattering images was performed with the assistance of the Datasqueeze software. Before analyzing the samples, the software was calibrated using scattering images of silver behenate (AgBe). AgBe is the silver salt of the fatty acid behenic acid (Figure 2.7) and commonly used as a calibration standard in X-ray diffraction studies. The well known scattering peaks from AgBe allow the software to find the relationship between pixel number and the magnitude of the scattering wavevector, $q$ (see Figure 2.2). A 2-D scattering image of AgBe is shown in (Figure 2.7). For AgBe, the first order peak corresponds to a spacing of 58.380 Å, giving a $q$-value of 0.1076 Å$^{-1}$. Similarly, by providing the software with the d-spacings associated with the first, second, and third order peaks, it can construct the values in $q$-space associated with each pixel in the image.

After loading any image file into Datasqueeze and before any analysis, it is necessary to "dezing" the image. "Zingers" are random saturated pixels usually caused by cosmic rays impacting on the CCD array. Datasqueeze has the capability to locate
these zingers and remove them by replacing them with an average of the surrounding data. Once the image has been dezinged, it can be used for analysis or calibration.

Figure 2.7: Top: 2-D X-ray scattering image of AgBe showing multiple orders of reflections. Bottom: Molecular structure of AgBe.

2.2 Polarizing Optical Microscopy

Polarizing optical microscopy (POM) has been an invaluable tool for the liquid crystal scientist since the discovery of liquid crystals. It was through this method that the first liquid crystal phases were observed over 120 years ago and it is safe to say that it still remains a fundamental and necessary tool for every liquid crystal laboratory around the world.

The experimental setup is nearly identical to any standard optical microscope, except for simple addition of two linear polarizers in the path of the light, one placed just before the sample and the other placed just after the sample, usually oriented 90° to one
another. This allows the user to observe optical effects that are not seen otherwise. In the case of liquid crystals, the optical effect typically observed is birefringence.

In non-birefringent materials, the linearly polarized light passes through the material unaffected and is subsequently blocked by the second polarizer (typically called the \textit{analyzer}) that is positioned perpendicular to the incoming light polarization. Birefringent materials alter the polarization state of the light depending on the orientation of the material with respect to the incoming polarization. This means that there may be a component of the polarization that is not blocked by the analyzer, allowing the light to pass through to the user. The intensity of the transmitted collimated light through crossed polarizers can be described by the following equation[12]:

\[ I = I_0 \sin^2 2\phi \sin^2 \left( \frac{\pi \Delta nd}{\lambda} \right) \]  

(2.2)

where \( d \) is the thickness of the material, \( \lambda \) is the wavelength of light, \( \Delta n \) is the birefringence of the material, \( \phi \) is the angle the optical axis of the material makes with the incoming polarization direction. One can see that the transmitted intensity is maximum when the optical axis is at \( \phi = 45^\circ \) to the polarizer direction and when \( \pi \Delta nd/\lambda = \pi/2 \). Concerning the latter condition, for a given sample of fixed thickness and birefringence, some wavelengths of light will be blocked while others will be transmitted, sometimes leading to brilliant colors that can be quite beautiful.

There are limitations to equation 2.2. \( \Delta n \) is actually an effective birefringence \((\Delta n_{\text{eff}})\) based on the projection of the optical axis onto the plane perpendicular to the propagation of light. For example, if the optic axis is oriented parallel to the direction of
light, then the light sees no effective birefringence ($\Delta n_{eff} = 0$). Additionally, the equation only applies to uniaxial materials, and only if the material is uniform throughout the sample. In the case of liquid crystals, it is not always trivial to produce a thin film with uniform alignment throughout. Various domains and defects may easily form depending on the sample. If the non-uniformities are much shorter than the wavelength of light, then the light cannot resolve the individual features and the resulting output will be dependent on some average of the properties throughout that sample. For example, a SmC* material with a pitch much shorter than the wavelength of light will appear as a SmA material as the rotation of the director is averaged out over a wavelength. If, in another sample, the optical axis averages out in all directions over a wavelength of light, then the material may even appear optically isotropic (an example of this will be discussed in CHAPTER 5). If the non-uniformities are on a length scale roughly equal to or larger than the wavelength of light, then the light can resolve the features and the output will act accordingly, revealing information about the non-uniformities to the observer.

One must not assume that having non-uniformities in the sample is always a bad thing. It is, in fact, this phenomenon that proves most useful to the liquid crystal scientist. The various liquid crystal phases have characteristic defects and non-uniformities often unique to that phase. To the well-trained eye, these "textures" can identify the phase under observation.

In the course of this work, the POM images were observed using an Olympus BX60 polarizing optical microscope. The samples were placed in a computer-controlled
Instec Hot Stage to regulate the temperature. The images were captured using a Hitachi CCD camera under transmitted light between crossed polarizers. Unless otherwise noted, the images of pure LC samples (i.e., not a polymer composite) were taken in standard test cells with 5µm gap and planar alignment oriented at 45° to the polarizer (see Section 2.4 for preparation of the test cells).

### 2.3 Piezoelectric Measurements

Measurements of piezoelectricity were performed using a homemade setup in which a small sinusoidal force is applied to a sample and the resulting voltage and current measured from electrodes on the sample. A schematic of the setup can be seen in Figure 2.8. The samples are sandwiched between an aluminum heating block and an aluminum foot (a square of ~1 in²) that presses on the sample with a small sinusoidal force. The force is provided by a simple audio speaker and is transmitted through an aluminum rod connected to the speaker at one end and with the aluminum foot on the other end. The rod is roughly 1 ft in length, chosen to increase the distance between the speaker and the sample measurement circuit in order to reduce any induced signal caused by the speaker. The rod passes into a thermally insulating polytetrafluoroethylene (PTFE) box that surrounds the heating block and contains the foot. Small holes in the insulating box allow wires to pass through for sample measurement and temperature control. The heating chamber is mounted on a three-axis positioner, allowing centering of the sample under the speaker and, more importantly, allowing the vertical motion to bring the sample in contact with the foot. The heating block is controlled by an Omega Engineering CNi16 temperature controller with an Acopian YO30MX250 power supply.
Figure 2.8: Schematic of electromechanical experimental setup (exploded view).

The foot is not rigidly attached to the aluminum rod. Instead, when the sample is raised into position, the foot makes solid contact with the rod through a steel ball, allowing the foot to pivot so that it lays flat against the sample. The stack (sample, foot,
ball, rod) is held together by a small static force by raising the heating block such that all parts are in contact and pushing on the speaker. The stack is raised such that the speaker membrane is pushed about 0.05" past its equilibrium position. This static force is necessary so that all parts remain in solid, continuous contact with each other when the speaker is activated and supplying a sinusoidal force. The speaker should never be able to pull the rod off of the steel ball.

Attached to the foot is an accelerometer (Brüel & Kjær type 4375) that can be used to estimate the actual displacement of the foot while force is being applied to the sample. This displacement can be used to calculate the resulting strain of the sample.

The speaker is a 5¼", 4 Ω paper cone speaker and is powered by a stereo "boom box" (Sony MHC-RG20). The stereo driver is designed to power an 8 Ω speaker, so a 4 Ω resistor was added in series with the speaker. The volume setting on the stereo was set to near one half of the maximum volume, and remained in that position for all experiments. This volume was chosen to avoid any distortion of the signal that might occur at high volumes.

At the center of the measurement system is the lock-in amplifier (EG&G Instruments, model 7265). It serves two main functions. It measures the RMS current or voltage from the sample (or accelerometer) as the force is being applied. It also provides the sinusoidal signal to the stereo via the oscillator output on the lock-in to one of the line level inputs on the stereo. The lock-in's internal oscillator provides the sinusoidal reference signal used by the lock-in to perform the measurements. The oscillator output
RMS voltage can be set between 0 V and 5 V, however, in these experiments, the voltage is limited to under 0.5 V as these are typical "line-level" voltages in audio electronics.

The applied force can be written as:

\[ F(t) = F_0 \sin(\omega t) \]  

(2.3)

where \( F \) is the force on the sample at any given time, \( F_0 \) is the amplitude of the oscillating force, and \( \omega \) is the angular frequency. Recalling the geometry of the measurements and the fact that we’re only concerned with quantities in the vertical direction (see Figure 1.12), we can make some simplifications. Because we operate in the regime of very small strains and only consider compression in one direction, the relationship between stress and strain simply follows Hooke's Law:

\[ T = YS \]  

(2.4)

where \( Y \) is the Young's Modulus, and we will drop the indices on the stress and strain as everything will be in the vertical (\( z \) or 3) direction. Additionally, the stress can be rewritten as \( T = F/A \), where \( A \) is the area over which the force is applied. The strain can also be rewritten as \( S = s/L \), where \( s \) is the displacement of the top surface of the sample and \( L \) is the equilibrium thickness of the sample.

Equations 1.2 and 1.4 can now be written in more experimentally useful terms as:

\[ I = d_{33} \frac{dF}{dt} = d_{33} \omega F \]  

(2.5)

\[ V = g_{33} L \frac{F}{A} \]  

(2.6)

where \( I \) is the current generated by the material (measured in a closed circuit) and \( V \) is the voltage across the material (measured as an open circuit).
In order to know the force that is applied by the speaker, a commercially available PZT disk (Steiner & Martins, Inc. model SMD25T07F3000WL) was used as a calibration sample. The published values of the piezoelectric constants for this material are $d_{33} = 320 \times 10^{-12} \text{ C/N}$ and $g_{33} = 25 \times 10^{-3} \text{ m}^2/\text{C}$. Since the lock-in amplifier gives voltage and current as RMS values, the force is also considered as RMS values.

Knowing the force on the sample and measuring the voltage and current from the piezoelectric sample, one can use equations 2.5 and 2.6 calculate the piezoelectric constants $d_{33}$ and $g_{33}$. If one knows both $d_{33}$ and $g_{33}$, then one can use equation 1.6 to calculate the relative dielectric constant of the material.

The accelerometer was used to calculate the displacement using the following equation:

$$V_{\text{accel}} = b o^2 s$$  \hspace{1cm} (2.7)

where $V_{\text{accel}}$ is the RMS voltage measured from the accelerometer by the lock-in amplifier, $b$ is the voltage conversion constant for the accelerometer, and $s$ is the RMS displacement of the top surface of the sample (measured as the displacement of the bottom of the aluminum foot). For this accelerometer, $b = 0.608 \text{ mV/ms}^2$.

By knowing the force and the displacement, one can calculate the Young's Modulus of the material using equation 2.4.

### 2.4 Cell preparation

A liquid crystal "cell" is one of the most basic elements of measuring the properties of liquid crystal and it is the basis for the majority of applications and products that use liquid crystals. The cell, in its most simple form, is a thin layer of liquid crystal
material sandwiched between two transparent substrates. The thickness of the liquid crystal layer (called the "cell gap") varies depending on the application and properties to be studied, but is usually in the range of 2 to 50 μm. The substrates are usually glass, but can be made from plastic or any other transparent material. Various layers or coatings are usually applied to the surface of the substrates, such as alignment layers to impose boundary conditions on the director or electrically conductive coatings to allow application of electric fields to the liquid crystal. The cells can be used in various experiments, such as observing the textures of phases using POM, measuring dielectric constants, polarization, switching times, and voltages. In this section, we will focus on the preparation of the substrates and assembly of the cells that were used in this research.

The process takes place in a cleanroom to prevent any airborne particulate contamination which could cause non-uniformities in the substrate coatings or the cell gap. We start with commercially purchased glass that has been coated with a layer of indium tin oxide (ITO) approximately 23 nm thick. ITO is an optically transparent, electrically conducting oxide in wide use as a glass coating for various applications. The glass arrives as 14" × 14" sheets 1.2 mm thick. These glass sheets are then cut into smaller 7" × 7" pieces using a computer controlled glass scriber. The glass is then placed in an ultrasonic bath of warm deionized water and mild detergent. After about 10 minutes of cleaning, the glass is removed and rinsed extensively with clean deionized water to remove any detergent that remains. The water is then rinsed off using isopropyl alcohol and the glass immediately placed in a drying oven at 80°C. The alcohol rinse
prevents water spots from forming during the drying process. The glass is allowed to dry in the oven for approximately 15 minutes.

Next, the glass undergoes a UV/ozone cleaning process. The UV/ozone process is a dry chemical process designed to clean any remaining organic residue from the surface. The process works as follows. The glass is placed in a chamber near a UV light source producing light in two wavelengths of importance: 185 nm and 254 nm. Light at 185 nm is absorbed by O₂ in the air and converted into O₃ (ozone). Light at 254 nm is absorbed by O₃ and broken down into O₂ again. In both processes, an intermediate of atomic oxygen (O) is formed, a highly reactive oxidizing agent. The 254 nm light also serves to excite any organic matter that exists on the surface making it more reactive with the atomic oxygen. As ozone is constantly being created and destroyed, there is a constant supply of atomic oxygen. Any organic material is quickly broken down into volatile compounds such as water or carbon dioxide. Assuming the substrates have been properly precleaned (as above) the UV/ozone cleaning process usually takes only a few minutes (in our case we clean for 5 minutes).

After the UV/ozone cleaning, we begin the photolithography process. This is a wet chemical process that is used to pattern the ITO layer into desired electrodes for cells. In this case, each piece of 7" × 7" glass will be patterned with electrodes for 80 cells. First, a layer of photoresist (Microposit S1818) is deposited on the glass using a spin coater (500 rpm for 7 seconds then 1500 rpm for 30 seconds). The glass is then immediately placed on a hot plate at 95°C to allow any remaining solvent to dry, leaving a uniform photoresist layer on the glass. The glass is then exposed to UV light in the
areas where the ITO will be etched away. This is accomplished using a mask with the pattern of the electrodes printed in black, UV blocking ink on a transparent sheet. Figure 2.9 shows the pattern used for the majority of cells in these experiments.

![Figure 2.9: Photo-mask showing pattern etched into ITO (black areas represent areas of ITO in the finished product). Left: The mask. Four of these patterns fit onto one 7" × 7" glass. Right: The unit cell. The gray dotted line represents the boundary of one single glass piece as it would be in the finished product. The smaller features of the pattern are for alignment purposes during assembly and have no function in the finished product.](image)

After exposure to the UV light, the photoresist layer is developed. The UV light has been exposed to and chemically altered the areas where the photoresist is to be removed. The glass is placed in the developer solution (active ingredient: tetramethylammonium hydroxide) for 45 seconds and agitated during this time. This
dissolves the photoresist that has been exposed to UV light and leaves behind the photoresist in the pattern of the desired electrodes. The glass is then placed in a bath of clean deionized water to stop the development process. At this point, a quality control check is often done. One of the glass pieces is blown dry with nitrogen gas then placed under a microscope. The pattern of photoresist is checked for accuracy and to ensure that it is still intact and has not peeled off the surface. If the glass passes the quality check, the glass will be placed in an acid etch bath. The acid bath is a solution of hydrochloric and nitric acids that attacks the ITO layer and removes it from the surface of the glass. The photoresist is much more resistant to the acid and therefore protects the ITO beneath it. The process must be carefully timed depending on the strength of the acid solution. Once the acid has removed the ITO in the exposed areas, it will continue to eat away the ITO under the photoresist, destroying the pattern entirely. The etching time is determined beforehand using a piece of scrap glass in which one etches various spots on the glass for increasing lengths of time. Then, the spots are checked for conductivity. The minimum time required to etch a non-conductive spot is used as the etch time for the glass substrates. This ensures that the acid has removed the ITO in the exposed areas yet has not had time to significantly etch under the photoresist. In our work, this time was typically between 2 and 10 minutes. After this time, the glass is placed in a bath of clean deionized water to stop the etching process. Again, another quality control check may be done, checking the conductivity of the etched areas as well as examining the glass under the microscope to ensure the photoresist layer is still intact.
The remaining photoresist can now be removed. The glass is placed in a solution of potassium hydroxide (KOH) for approximately 10 minutes, stripping the remaining unexposed photoresist, followed by another bath of clean deionized water. At this point, the photolithography process is complete and a final inspection of the process is done.

The 7" × 7" glass is now cut into quarters of 3.5" × 3.5", again using the computer controlled glass scriber, each piece now containing electrodes for 20 cells. The glass is cleaned again as described above, using both the ultrasonic bath and the UV/ozone processes. It is now ready to receive the alignment layer that will be in contact with the liquid crystal material.

Using the spin coater again, a solution of polyimide is spun into a thin layer on the clean glass. The polyimide layer will determine how the liquid crystal director will orient itself with the surface of the substrate. For planar alignment, we use polyimide SE-2170 (from Nissan Chemical). For homeotropic alignment, we use SE-1211 (also from Nissan Chemical). After the spin coating, the glass is immediately placed on a hot plate at ~80°C to cure (soft bake) for around 1 min. This is followed by a curing (hard bake) process in an oven for 30 minutes at 200°C for SE-2170 or 180°C for SE-1211.

The homeotropic alignment layer is now complete, however, the planar alignment polyimide must still be rubbed. The rubbing process determines the direction that the liquid crystal director will point along the surface. To do this, an aluminum block covered with a clean velvet cloth is placed on the surface of the glass and dragged across in the direction of desired alignment. For each piece of glass, this process is repeated 10 times, to ensure sufficient alignment.
The glass substrate is now complete, and ready for assembly into cells. Recall, each 3.5" square piece of glass contains electrodes for 20 cells. Two pieces of glass with like alignment layers will be sandwiched together to make 20 cells in one batch. The glass is separated into two sets: the glass that will receive the spacers, and the glass that will receive the glue. The spacers are what determine and maintain the desired cell gap. In our work, 5 μm glass sphere spacers are used most commonly, however, various other sizes and construction (e.g., glass fibers, polymer spheres) can be used. To apply the spacers to the substrate, a nebulizer powered by compressed air is used. A small amount of the spacers are placed into a nebulizer and, inside a containment box with the substrates, a small burst of compressed air will eject a fine dust of spacers from the nebulizer that fall and land on the substrates.

At the same time, the other set of glass substrates is receiving the glue that will hold the cells together. A computer controlled xy-dispenser dispenses through a needle and syringe two thin lines of glue on either side of each of the 20 cells on the glass. The glue used is NOA68 (Norland Products). Once the glue is placed on the array of cells, it is ready to be mated to its corresponding glass with the spacers. The mask is designed such that ITO is patterned with alignment markings in order to ensure two electrodes are placed directly over top of one another in an offset pattern as seen in Figure 2.10. After firmly pressing the substrates together, they are placed in a UV curing light box (long wavelength UV light) for 7 min.

Each sandwich of glass now contains 20 individual cells, however, they are still one solid piece. The glass sandwich is returned to the computer controlled glass scribe
where each side is scribed with the pattern of the individual cells. The cells are then carefully broken out individually by hand, yielding the finished product. One piece of 14" × 14" ITO-coated glass is now 160 liquid crystal test cells.

Figure 2.10: Schematic of a cell in final stage of assembly as seen from the top and from a perspective view. The black areas represent areas of ITO on the inward-facing surfaces of the glass. The result is a 5 mm × 5 mm active area in the center of the cell where electric fields can be applied.

2.5 Polymer Sample Preparation

Preparations of the polymer composites were done by Andrea Charif of the Department of Polymer Science at the University of Akron (Akron, Ohio).

Commercially available linear poly(styrene-b-isobutylene-b-styrene) block copolymer (SIBS) was chosen as the host polymer for these experiments and used as received from Kaneka Corporation (as SIBSTAR 073T, 31 wt% PS, $M_n = 66,700$ g/mol; $M_w/M_n = 1.24$) (PS = polystyrene, PIB = polyisobutylene). This type of block copolymer is a known biocompatible polymer: it is used in clinical practice as the polymeric coating on the drug-eluting Taxus® coronary stent under the “Translute” trade name[55]. Figure
2.11 shows the block structure and appearance of SIBS. It is a flexible rubbery material but can be processed as plastic; it belongs to the family of thermoplastic elastomers.

![Block Structure of SIBS](image)

**Figure 2.11: Structure of linear poly(styrene-b-isobutylene-b-styrene) block copolymer (SIBS)**

The BCLC 4-chlororesorcinol bis [4-(4-n-decacyloxybenzoyloxy) benzoate] (M1118 in Figure 1.10) was synthesized by Dr. Katalin Fodor-Csorba's group in Budapest following the method of Pelzl et al[56] and used as received.

Mixtures were made of various concentrations of BCLC in SIBS (0%, 10%, 20%, 50%). Composite films were prepared by solution casting 7 wt% solutions of the BCLC/polymer mixture in tetrachloroethylene (Aldrich, ACS reagent, used as received). The solution was stirred at 40°C until homogeneous after which it was poured into open Teflon dishes approximately 1 cm deep and 2.5 cm in diameter. The solution was allowed to dry at room temperature overnight. Additional vacuum drying was carried out for 24 h at room temperature. After the solvent had evaporated the films were removed and cut
into smaller pieces. The samples were then compression molded in a temperature controlled Carver® hydraulic press (Figure 2.12).

![Compression molding device and sample images of various concentrations of the liquid crystal. Right: Hydraulic press. Left: Mold. The mold consists of three stainless steel plates - top, middle and bottom. The middle plate (1 mm thick) has a 2 cm × 2 cm square cut into it as the mold cavity. The top and bottom plates are solid to hold the sample inside the cavity created by the middle plate. The sample is shown in the mold.](image)

The mold containing the material was placed in the hydraulic press and heated to 150 °C for 20 min at a pressure of 200 psi. The pressure was then increased to approximately 700 psi (~50 atm) and kept at constant pressure and constant temperature. After 2 min the system was cooled at room temperature while maintaining the high pressure. The sample was removed when the temperature reached 70°C and then
quenched to room temperature to freeze the liquid crystal into the ferroelectric X phase (see CHAPTER 5). Stainless steel molds were used to produce samples of 2 cm × 2 cm lateral dimensions and 1 mm thickness (Figure 2.12). Figure 2.13 shows images of samples of select compositions. The opaque nature of the obtained films is evidence of the formation of a two phased system in which the liquid crystal segregates from the polymer matrix into micron-sized domains with difference in refractive index with respect to the pure polymer.

Figure 2.13: Photographs of compression molded samples of various concentrations.

From left to right: 0%, 10%, 20%, and 50% M1118 in SIBS.
CHAPTER 3

Chemical Synthesis

3.1 Introduction

This chapter describes the synthetic procedure followed to produce the crosslinker 1,4-di(10-undecenyloxy)benzene and the bent-core molecule 4,6-dichloro-1-[4′-(8-octene-1-yloxy)-1,1′-biphenyl-4-carboxylate]-3-[4′-(8-octyloxy)-1,1′-biphenyl-4-carboxylate] phenylene (NP002 in Figure 1.10). The motivation to create these compounds was to make a liquid crystalline elastomer from a bent-core molecule similar to that reported by Verduzco et al.[57] Bent-core liquid crystal elastomers, while being a relatively new class of materials, have shown many interesting properties, most notably a large flexoelectric effect.[58–61]

In order to attach the bent-core mesogen to a polymer backbone, the end of one of the aliphatic tails was provided with a terminal olefin group, which when reacted with the polymer backbone could yield a side-chain liquid crystalline polymer. The crosslinker had similar structural features, except with a terminal olefin group at each end of the molecule. Because the liquid crystal molecule and the crosslinker each contain the same functional unit, they could be attached to the polymer backbone in the same reaction.

Figure 3.1 shows the synthetic scheme used to create the crosslinker (1,4-di(10-undecenyloxy)benzene). It is essentially a Williamson ether synthesis involving nucleophilic attack by an alkoxide ion on an alkyl halide.[62]
Figure 3.1: Scheme for synthesis of crosslinker 1,4-di(10-undecenyloxy)benzene

Figure 3.2 shows the synthetic scheme followed to produce the bent-core liquid crystal NP002 (4,6-dichloro-1-[4’-(8-octene-1-yloxy)-1,1'-biphenyl-4 carboxylate]-3-[4’-(8-octyloxy)-1,1'-biphenyl-4-carboxylate] phenylene). The bent-core liquid crystalline molecule 13 is prepared by the sequential O-acylation of 4,6-dichlororesorcinol (11) by acid chlorides 10 and 8, using the tertiary amine, triethylamine, as a catalyst. Acid chlorides 10 and 8 were prepared from the corresponding carboxylic acids 9 and 7, respectively. Compound 9 was commercially available, and compound 7 was prepared in a Williamson ether synthesis[62], using commercially available 4 and 5, followed by hydrolysis of the protecting ester group in 6 to give the free carboxylic acid.
Figure 3.2: Scheme for synthesis of bent-core liquid crystal NP002
3.2 Experimental

The starting materials, hydroquinone (1) (ReagentPlus®, 99%), 11-bromo-1-undecene (2), ethyl 4'-hydroxybiphenyl-4-carboxylate (4), 8-bromo-1-octene (5), 4,6-dichlororesorcinol (II), triethylamine, dimethyl formamide (DMF), oxalyl chloride were purchased from Sigma-Aldrich and used as received unless otherwise noted. Solvents 1-butanol (ACS grade), chloroform (ACS grade), 2-butanone were purchased from Sigma-Aldrich and used as received. Diethyl ether (EMD OmniSolv®), tetrahydrofuran (THF) (EMD DriSolv®), and ethyl acetate (EMD HPLC grade) were purchased from VWR and used without further purification. Methanol (HPLC grade) and ethanol (200 proof anhydrous HPLC grade) were purchased from Pharmco-AAPER and used as received. Dichloromethane (EMD HPLC grade, purchased from VWR) was dried over calcium hydrde and distilled prior to use. All other reagents were purchased commercially from Sigma-Aldrich and used without further purification unless otherwise noted.

Thin layer chromatography (TLC) was used to monitor and analyze the reactions. TLC plates (10 cm × 20 cm) were purchased from Analtech (Silica Gel GHLF 250 μm). Spots were visualized under short-wave ultraviolet light.

Solution $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy was carried out using a Varian 200 MHz spectrometer. Samples were prepared in 5 mm o.d. NMR tubes in which ~20 mg of the measured compound is dissolved in ~1 mL of solvent. Solvents used were chloroform-$d$ (CDCl$_3$) (with 0.03% v/v tetramethylsilane as reference standard) and dimethyl sulfoxide (d$_6$-DMSO).
Melting points were initially determined using a Fisher-Johns melting point apparatus.

3.3 Synthesis

3.3.1 1,4-di(10-undecyloxy)benzene (3)

Synthesis of the crosslinker 1,4-di(10-undecyloxy)benzene (3) was performed by a modification of the procedure presented by Ali et al. [63]. At room temperature, hydroquinone (I) (3.31 g, 30.1 mmol) was dissolved in 1-butanol (30 mL) inside a two-neck 100 mL round-bottom flask, equipped with a reflux condenser with attached drying tube. While stirring, dry sodium hydroxide (1.24 g, 31.0 mmol) was added followed by the addition of 11-bromo-1-undecene (2) (7.1 g, 30.1 mmol). The reaction mixture was heated to 100°C and left to stir under reflux for approximately 1.25 h. Another portion of 11-bromo-1-undecene (6.95 g, 29.8 mmol) was then added to the flask followed by another portion of sodium hydroxide (1.21 g, 30.3 mmol). The mixture was left to stir at 100°C for a further 3 h. At this time the heating bath was turned off and the mixture was allowed to cool to room temperature. Stirring was continued overnight. The reaction mixture had become nearly solid and the contents of the round-bottom flask were transferred to a 500 mL separating funnel utilizing diethyl ether (150 mL) and a stirring rod to break up the solid. The mixture was washed five times with 2% w/w aqueous solution of sodium hydroxide (20 mL each) followed by four washings with deionized water (25 mL each). The organic layer was dried over anhydrous magnesium sulfate (~5 g) overnight. The drying agent was filtered off and the resulting solution concentrated in
vacuo and crystallized from methanol to yield 9.34 g of white flakes; mp. 59-60°C (lit. 60-61 °C); 76% yield. $^1$H NMR (CDCl$_3$): $\delta$ 1.20-1.55 (24H, m), 1.68-1.82 (4H, m), 1.99-2.09 (4H, m), 3.89 (4H, t), 4.90-5.04 (4H, m), 5.71-5.92 (2H, m), 6.81 (4H, s). $^{13}$C NMR (CDCl$_3$): $\delta$ 26.05, 28.93, 29.11, 29.44, 29.51, 33.79, 68.69, 114.10, 115.43, 139.22, 153.24.

3.3.2 4’-(8-octen-1-yloxy)1,1’-biphenyl-4-carbonyl chloride (8)

*Ethyl 4’-(8-octen-1-yloxy)1,1’-biphenyl-4-carboxylate (6)*

Synthesis of (6) was performed by a modification of the procedure presented by Mann et al.[64] Ethyl 4’-hydroxy-4-biphenyl carboxylate (4) (1.56 g, 6.4 mmol), 8-bromo-1-octene (5) (1.26 g, 6.6 mmol), potassium carbonate (4.06 g, 29.4 mmol), potassium iodide (26 mg, 0.16 mmol), and 2-butanol (20 mL) were added to a 100 mL single-neck round-bottom flask equipped with a reflux condenser and drying tube. The mixture was heated to 85°C and stirred vigorously under reflux for approximately 24 h. The reaction was monitored by TLC using 20% v/v ethyl acetate in n-hexanes. (Note: ~3 mL of 2-butanol was added roughly 12 h into the reaction to replace some of the evaporated solvent.) The mixture was filtered through a sintered glass filter to remove the potassium salts. A few mL of 2-butanol was used to wash the salts in the filter funnel. The resulting solution was collected into a single-neck 100 mL round-bottom flask and evaporated to dryness. $^1$H NMR (CDCl$_3$): $\delta$ 1.37-1.46 (9H, m), 1.78-1.86 (2H, m), 2.06-2.09 (2H, m), 3.97-4.04 (2H, m), 4.34-4.46 (2H, m), 4.92-5.05 (2H, m), 5.76-5.89 (1H, m), 6.96-7.02 (2H, m), 7.54-7.65 (4H, m), 8.06-8.12 (2H, m). $^{13}$C NMR
(CDCl3): δ 14.39, 25.92, 28.85, 29.21, 33.72, 60.89, 68.10, 114.32, 114.94, 126.40, 128.33, 128.56, 130.08, 132.26, 139.02, 145.19, 159.41, 166.62.

4’-(8-octen-1-yloxy)1,1’-biphenyl-4-carboxylic acid (7)

The synthesis of (7) was performed by a modification of the procedures presented by Mann et al.[64] and Xu et al.[65] Ethanol (20 mL) was added directly to the reaction flask containing the ethyl 4’-(8-octen-1-yloxy)1,1’-biphenyl-4-carboxylate (6) (approximately 2.26 g 6.4 mmol). A 9.1% w/w solution of sodium hydroxide (2.01 g, 50 mmol) in water (20 mL) was added and the mixture stirred vigorously under reflux at 90°C overnight. The mixture was allowed to cool during which it solidified into a white material with consistency similar to custard. The precipitate was filtered off using a Buchner funnel. The suction of the filter was left to run for about an hour to allow the material to more effectively dry in air. To ensure that all of the sodium salt had been converted to the desired free carboxylic acid, the material was added to a 100 mL single-neck round-bottom flask with glacial acetic acid (15 mL) and ethanol (15 mL). The mixture was stirred vigorously under reflux at 120°C for 2 h. The mixture was removed from the heat/stirring and allowed to cool overnight at room temperature. Again, a soft custard-like solid formed. The material was filtered in a Buchner funnel and the resulting solid was washed with deionized water (500 mL). The product was placed into a drying dish to air-dry for 2 h. The dish was then placed into a vacuum desiccator under high vacuum for roughly 3 days. The final product (7) was obtained by recrystallization from acetic acid/ethanol (60 mL/60 mL) and dried again under vacuum in the desiccator overnight to afford a white powder (1.77 g, 5.46 mmol, 85% yield); mp. 173-175; 1H
NMR ($d_6$-DMSO): δ 1.40 (6H, s), 1.76-2.06 (4H, m), 3.97-4.02 (2H, m), 4.89-5.03 (2H, m), 5.27-5.88 (1H, m), 6.94-7.00 (2H, m), 7.54-7.64 (4H, m), 8.03-8.08 (2H, m); $^{13}$C NMR ($d_6$-DMSO): δ 24.71, 27.64, 28.02, 32.52, 66.871, 113.34, 113.88, 125.11, 127.12, 127.98, 129.15, 130.85, 137.80, 143.63, 158.23, 167.00.

$4'$-(8-octen-1-yloxy)-1,1'-biphenyl-4-carbonyl chloride (8)

$4'$-(8-octen-1-yloxy)-1,1'-biphenyl-4-carboxylic acid (0.811 g, 2.5 mmol) was dissolved in a minimal amount of dry dichloromethane (10 mL) in a 100 mL three-neck round-bottom flask. The flask was equipped with a dry nitrogen gas supply line, a reflux condenser with drying tube, and a dropping funnel. The reaction was conducted under a nitrogen atmosphere. A catalytic amount of DMF (3 drops) were added to the solution. The flask was cooled in an ice bath to near 0°C. While stirring, oxalyl chloride (1 mL) was added drop-wise through the dropping funnel over a period of about 5 min. The solution was allowed to warm to room temperature over 30 min. The reaction mixture was warmed to 40°C and stirred for another 20 min. At this time the cooling water to the condenser was turned off to allow solvent from the reaction mixture to evaporate. The solvent was allowed to evaporate for 25 min, after which the resulting product was placed under high vacuum for 1 h to remove any residual solvent and DMF. The resulting acid chloride 8 was yellowish white in appearance and was utilized in the synthesis of 12 without purification.
3.3.3 4'-n-octylxybiphenyl-4-carbonyl chloride (10)

The acid chloride 4'-n-octyloxybiphenyl-4-carbonyl chloride (10) was prepared from 4'-n-octyloxybiphenyl-4-carboxylic acid (9) (1.00 g, 3.1 mmol) in the same manner as the synthesis of 4'-(8-octen-1-yloxy)1,1'-biphenyl-4-carbonyl chloride (8).

3.3.4 4,6-Dichloro-1-hydroxy-3-[4'-(8-octyloxy)-1,1'-biphenyl-4-carboxylate]-phenylene (12)

The synthesis of 4,6-dichloro-1-hydroxy-3-[4'-(8-octyloxy)-1,1'-biphenyl-4-carboxylate]-phenylene (12) was performed by a modification of the procedure presented by Verduzco et al.[57] Commercial 4,6-dichlororesorcinol (11) was purified by dissolving most of the solid in chloroform (50 mL) and removing the residual dark insoluble solid by filtration. A small amount of chloroform was used to wash this dark impurity. The solution was evaporated to dryness and then placed under high vacuum for several hours. The purified dichlororesorcinol (6.12 g, 34.2 mmol) was dissolved in dry THF (20 mL) in a 100 mL three-neck round-bottom flask followed by the addition of freshly prepared 4'-n-octyloxybiphenyl-4-carbonyl chloride (10) (approximately 1.09 g, 3.1 mmol) and triethylamine (4 mL). The reaction vessel was equipped with a dry nitrogen gas supply and a reflux condenser with drying tube. The mixture was heated to 60°C and left to stir for 24 h under nitrogen. After allowing the mixture to cool to room temperature, the solution was mixed with 1 N HCl (10 mL) and added to a separating funnel. The aqueous layer was drained and 30 mL of ethyl acetate was added to the organic layer. The organic solution was washed five times with a 10 wt% aqueous solution of KOH (20 mL, 10 mL, 15 mL, 15 mL, 10 mL) followed by three more
washings of 1 N HCl (10 mL each). The mixture was washed a final time with a saturated aqueous solution of sodium bicarbonate (10 mL). MgSO₄ was added as a drying agent to the organic layer and the mixture allowed to sit overnight. The MgSO₄ was filtered off and the filtrate evaporated to dryness. The crude product was recrystallized from ethanol to afford 1.24 g of compound (I2) (83% yield). mp. 113-117°C; ¹H NMR (CDCl₃): δ 0.88-0.94 (3H, m) 1.30-1.48 (10H, m), 1.76-1.87 (2H, m), 4.00-4.06 (2H, m), 5.76 (1H, s), 7.00-7.04 (3H, m), 7.47-7.74 (5H, m), 8.24-8.28 (2H, m); ¹³C NMR (CDCl₃): δ 14.08, 22.64, 26.03, 29.22, 29.34, 31.79, 68.17, 111.90, 115.01, 117.80, 118.76, 126.30, 126.67, 128.38, 129.43, 130.96, 131.79, 146.49, 146.81, 150.90, 159.65, 164.02.

3.3.5 4,6-Dichloro-1-[4'-(8-octene-1-yloxy)-1,1'-biphenyl-4 carboxylate]-3-[4'-(8-octyloxy)-1,1'-biphenyl-4-carboxylate] phenylene (I3) ("NP002")

The synthesis of I3 was performed by a modification of the procedure presented by Verduzco et al.[57] Under anhydrous conditions, 4,6-dichloro-1-hydroxy-3-[4'-(8-octyloxy)-1,1'-biphenyl-4-carboxylate]-phenylene (I2) (1.24 g, 2.5 mmol) was dissolved in dry THF (20 mL) and added to a 100 mL three-neck round-bottom flask containing 4'-(8-octen-1-yloxy)1,1'-biphenyl-4-carbonyl chloride (8) (approximately 0.9 g, 2.5 mmol). The reaction vessel was equipped with a dry nitrogen gas supply line and a reflux condenser with drying tube. Triethylamine (2 mL) was then added to the flask. The mixture was heated at reflux under nitrogen and stirred overnight. After cooling to room temperature, the mixture was added to 1 N HCl (10 mL) in a separating funnel. The aqueous layer was drained and ethyl acetate (10 mL) was added to the organic layer. The
mixture was washed twice more with 1 N HCl (5 mL) followed by a final wash with a saturated aqueous solution of sodium bicarbonate (8 mL). The desiccant MgSO₄ was added and the mixture allowed to stand overnight. The MgSO₄ was filtered off and the filtrate was evaporated to dryness. The resulting product was placed under high vacuum for 1 h. The crude product was recrystallized from absolute ethanol to yield white crystals of I3 (1.252 g, 1.57 mmol, 63% yield). mp. 88-89°C; ¹H NMR (CDCl₃): δ 0.82-0.96 (3H, m), 1.21-1.43 (16H, m), 1.78-1.82 (4H, m), 2.01-2.11 (2H, m), 3.99-4.05 (4H, m), 4.93-5.05, (2H, m), 5.76-5.90 (1H, m), 6.98-7.03 (4H, m), 7.40-7.73 (10H, m), 8.24-8.28 (4H, m); ¹³C NMR (CDCl₃): δ 14.08, 22.64, 25.89, 26.04, 28.83, 29.24, 29.35, 31.81, 33.68, 68.12, 68.18, 114.32, 115.04, 119.56, 125.03, 126.24, 126.74, 128.41, 130.73, 131.00, 131.84, 138.98, 146.21, 146.59, 159.71, 163.69.
CHAPTER 4

Small Angle X-Ray Scattering Results

Two of the common parameters one can extract from a feature on a 2-D scattering image are the periodicity, \( d \) (sometimes called \( d \)-spacing), and the correlation length, \( \xi \), of the structure causing the scattering. \( d \) is the characteristic periodicity of the structure. In many of our measurements of liquid crystal materials, \( d \) can be attributed to the smectic layer spacing. Recall that \( d = 2\pi n / q \), where \( n \) is the order of the scattering peak and \( q \) is the magnitude of the scattering wavevector. In this dissertation, we will only deal with the first order peaks \( (n = 1) \) unless otherwise noted. The correlation length is calculated using \( \xi = 2/\Delta q \), where \( \Delta q \) is the full width at half maximum (FWHM) of the scattering peak. It is calculated from the Ornstein–Zernike model\[66\], which describes the scattering profile with a Lorentzian line-shape:

\[
I(q) = \frac{I_0}{1 + \xi^2 (q^2 - q_0^2)}
\]  

(4.1)

where \( I(q) \) is the scattered intensity, \( q_0 \) is the location of the peak scattering, and \( I_0 \) is the intensity at the peak. Equation 4.1 is derived from the Fourier transform of the density-density correlation function \( G(r) \propto \exp(-r\xi/r) \). \( \xi \) is a parameter measuring the exponential decrease in the correlation of molecular positions over a distance \( r \).[67]

In a well ordered system, such as a crystal phase, the correlation length can easily be many hundreds of molecular lengths (several thousand Ångströms in systems of liquid crystal molecules). In contrast, disordered phases like the isotropic phase may have a
correlation length on the order of one molecular length. We can also use $\xi$ as a way to estimate the size of the smectic clusters inside the nematic phases of certain bent-core liquid crystals.

In this chapter, we will show the results of SAXS measurements on a selection of bent-core materials. We will discuss various physical properties of the smectic clusters found in the nematic phases, such as size and tilt angle. We will also show the SAXS data for BCLC/polymer composites, discussing the findings in terms of the structure of the X phase and impact on the piezoelectricity of the materials. The SAXS measurements were performed as described in Section 2.1.

### 4.1 Three-Ring Bent-Core

Two of the bent-core molecules studied, 3RBC-S (Figure 1.2) and 3RBC-N (Figure 1.10), are rather unusual when compared to most bent-core liquid crystal molecules - they only have three aromatic rings in their core. 3RBC-S exhibits only a smectic mesophase while 3RBC-N exhibits only a nematic mesophase. They are also important as their SAXS results have been confirmed by cryogenic transmission electron microscopy (cryo-TEM)[27].

In 3RBC-S, we observe a direct isotropic to smectic transition; the two sharp, intense SAXS peaks below the transition indicate a smectic A mesophase. POM measurements also confirmed the SmA structure. Figure 4.1 shows the SAXS results from 3RBC-S. The periodicity of the SmA layers is 3.7 nm, and barely changes with temperature until crystallization. This periodicity was confirmed by cryo-TEM, which also measured a layer spacing of 3.7 nm. Figure 4.2 shows a cryo-TEM image taken of
3RBC-S showing the smectic layering. This sample was quenched from the smectic phase (at 87°C).

Figure 4.1: SAXS results 3RBC-S. Plot of $q$ and $\Delta q$ vs. Temperature in cooling from isotropic, as well as select 2-D scattering images.
Figure 4.2: A typical cryo-TEM image of 3RBC-S quenched from 87°C. (a) A 350 nm x 500 nm area of the sample. Dark domains correspond to thick areas, and the periodic stripe texture corresponds to a less than 100 nm thick area with smectic layers in a “bookshelf” geometry (perpendicular to the substrate). (b) Enlarged image of the 70 nm x 70 nm area enclosed by the rectangle in (a), illustrating the details of the layer structure. Dark stripes correspond to the aromatic cores and lighter areas to the alkyl tails.

The two-dimensional SAXS pattern for 3RBC-N reveals the typical diffuse ring pattern in the isotropic phase. Below the transition to the nematic phase, the ring condenses to two broad arcs centered at \( q = 0.19 \text{ Å}^{-1} \), and elongated in the direction normal to the magnetic field used to align the nematic director. The peak position in \( q \)-space corresponds to short-range smectic A-type layering with layer spacing of \( d = 3.31 \text{ nm} \). This is in excellent agreement with the cryo-TEM results, where a periodicity between 3.1 and 3.5 nm was observed. At lower temperatures, the arcs take on a peanut shape and each arc splits into two broad peaks, showing the onset of layer tilt (smectic-C-
like short-range order). This shows that the wide range of layer directions evident in the TEM image (Figure 4.4d) is indeed due to layer tilt with respect to the molecular orientation, as proposed above. On the right axes of Figure 4.3 we see that the full width at half maximum ($\Delta q$) decreases with temperature from $\Delta q = 0.17 \, \text{Å}^{-1}$ in the isotropic phase to $\Delta q = 0.04 \, \text{Å}^{-1}$ just above the crystallization temperature. This indicates that on average the width of the smectic domains increases from roughly two to eight molecular lengths, again in agreement with the cryo-TEM results in Figure 4.4.

Figure 4.3: SAXS results 3RBC-N. Plot of $q$ and $\Delta q$ vs. Temperature in cooling from isotropic, as well as select 2-D scattering images.
Figure 4.4: Cryo-TEM images of 3RBC-N showing the presence of smectic clusters in the nematic phase. Images are taken after quenching from 90°C (a); 80°C (b); 70°C (c); and 65°C (d). Striped domains are smectic clusters of molecules, which are oriented in different directions even in overlapping spots at different depths in the sample.

4.2 NP002

The SAXS data of NP002 (structure shown in Figure 1.10) shows evidence of smectic clusters in the nematic phase. Figure 4.5 shows a selection of 2-D scattering images at various temperatures. At the higher temperatures in the nematic range, the scattering images show two broad peaks centered at the 3 o'clock and 9 o'clock positions. Moving to lower temperatures in the nematic range, the peaks split into four distinct spots. The angle at which the peak is off the horizontal axis is the same as the tilt angle.
of the molecules with respect to the smectic layers. However, one must be careful in this case, as the peaks are broad and can overlap in such a way as to create an apparent maximum at much lower tilt angles, e.g., in the higher temperature nematic range where the peaks appear directly on the horizontal axis (no tilt angle). In order to quantify these peaks and find the tilt angles we have plotted the intensity profile along various lines in $q$-space to find the $q_x$ (horizontal) and $q_y$ (vertical) coordinates of the peaks. This allows us to use a mathematical fit to determine where the actual peaks are in the vertical ($q_y$) position.

Figure 4.5: 2-D SAXS images of NP002.
Figure 4.6 shows the locations of the various slices in $q$-space over which the intensity profiles were plotted. The horizontal and vertical slices allowed us to determine the $q_x$ and $q_y$ positions, respectively, of the scattering peaks (we arbitrarily chose the lower left peak to analyze). The $q_x$ location of the peak was determined simply by finding the location of the maximum intensity along the horizontal slice (Profile A). The vertical slice (Profile B) was more difficult to analyze as the splitting of the peaks was not so pronounced.

![Figure 4.6: Location of intensity profiles. The slices were chosen to find the position of the lower left peak. Profile A was used to find the horizontal ($q_x$) coordinate. Profile B was used to find the vertical ($q_y$) coordinate and its position was chosen using the peak position from Profile A. Profile C was taken as a radial profile at 35° from the horizontal corresponding to the approximate peak position in the low temperature nematic range. To find the $q_y$ location of the peaks, the profile was fit using two Gaussian curves of the form:](image)
\[ I(q_y) = I_0 \left[ \exp \left( -\frac{q_y + q_{y0}^2}{2\sigma^2} \right) + \exp \left( -\frac{q_y - q_{y0}^2}{2\sigma^2} \right) \right] + h \] (4.2)

where \( I \) is the scattering intensity, \( I_0 \) is the amplitude of the scattering intensity at the peak, \( q_{y0} \) is the location of the peak along the vertical slice, \( \sigma \) is the standard deviation of the single Gaussian curve, and \( h \) is the constant background scattering intensity. This form was chosen based on previous work[33], [68] that showed that scattering profiles of smectic clusters in the nematic phases of bent-core molecules followed a Gaussian distribution. Note that the fit also takes into account the symmetry of the peaks; they must essentially be mirror images across the horizontal axis. Figure 4.7 shows an example of the scattering data along Profile B with the double Gaussian fit.

![SAXS Data](image)

**Figure 4.7:** Scattering intensity along vertical profile (Profile B) with the double Gaussian fit shown. Also shown are the two individual Gaussian curves that are the components of the double Gaussian fit. This data was taken at 107°C.
The $q$-value of the peak position in this case gives us the vertical coordinate ($q_y$) of the scattering peak and, combined with the $q_x$ position from the horizontal slice, allows us to calculate the location of the peak.

Figure 4.8 shows the plot of $q$ vs. temperature. Two data sets are plotted. One set uses the above method of finding the $q_x$ and $q_y$ (fitted) coordinates of the peak to find the magnitude of $q$. The other set takes the $q$-value of the peak directly from the Profile C data (35° slice). Both sets show that the $q$-value and, therefore, the layer spacing of the smectic clusters remains mostly unaffected by changes in temperature.

![Plot of q vs. temperature for NP002. The red square data are calculated from the $q_x$ and $q_y$ components obtained from the horizontal and vertical slices, respectively (Profiles A & B). The blue circle data are obtained directly from the $q$-value of the peak along the 35° slice (Profile C).](image)

Figure 4.9 shows the plot of tilt angle vs. temperature for NP002 as calculated from the positions of the Gaussian peaks. As temperature is decreased, the tilt angle becomes larger. The plot also shows the parameter $\Delta \theta$, which is calculated from the
standard deviation, \( \sigma \), of the Gaussian fits (eqn. 4.2); \( \Delta \theta \) is difference between the tilt angle at \( q_y = q_{y0} + \sigma \) and the peak tilt angle \( \theta \). It is a measure of the fluctuations in the tilt angle of the clusters. As temperature is decreased through the nematic range, the fluctuations in the tilt angle of the smectic clusters decrease. This is to be expected as there is less thermal energy in the system to cause fluctuations. However, the increase in tilt angle with decreasing temperature requires a bit more explanation when put in context with the trend of \( q \)-value vs. temperature (Figure 4.8). The constant \( q \)-value over the nematic range indicates that the layer spacing is relatively constant over that temperature range. That suggests that as the molecules tilt more the layers are forced apart to prevent the layer spacing from decreasing. Two possible mechanisms may cause this. One, as the temperature is decreased and the molecules tilt more, there may be less interdigitation between molecules of neighboring layers. Second, as the temperature is decreased, the flexible tails may become more ordered and more straight, elongating the molecule.
Figure 4.9: Plot of tilt angle ($\theta$) of the smectic clusters vs. temperature in NP002. The parameter $\Delta \theta$ is related to the standard deviation of the Gaussian fit of the vertical slice.

As seen in Figure 4.5, there is a significant amount of scattering emanating from the center of the images. This background scattering decreases as one moves farther from the center, creating a varying background signal. In order to estimate the significance of this, two variations of the double Gaussian fit (eqn. 4.2) were used: one in which the background value, $h$, was a fit parameter and one where the background value was fixed at a value by manually finding the scattering intensity at a location far away from the central beam and any of the scattering peaks. The fitted background value represents a high estimate due to the range of fitting being closer to the central scattering
feature. The manual background value is a low estimate. The actual data lies between these two values. Figure 4.10 shows the plots of scattering intensity for the vertical slice with both fits at 84°C. The difference in calculated tilt angle between the manual background and fitted background ranged from ~1° to ~5° with the largest difference occurring in the middle of the nematic range.

![Graph showing scattering intensity profile (Profile B) and fits for NP002 at 84°C](image)

**Figure 4.10:** Vertical scattering intensity profile (Profile B) and fits for NP002 at 84°C.

*In the fitted background curve (blue curve), the background value \( h \) was set as a fit parameter and allowed to vary. In the manual background curve (red curve), \( h \) was fixed at a value determined by manually examining the 2-D scattering image and finding the intensity at a location far away from the center beam or one of the scattering peaks.*
4.3 CN12

CN12 is another bent-core molecule that has a nematic phase (see Figure 1.10 for molecular structure). It has also been found to show evidence of smectic-like clusters in the nematic phase. Its phase sequence in cooling is: Iso 111°C N 103°C SmC 70°C SmX. One significant difference between CN12 and NP002 is that CN12 has a SmC phase below the nematic phase. This means that pre-transitional SmC fluctuations cannot be ignored and may be enhancing the more persistent type of smectic clusters attributed to the bent-core nematic. One way to distinguish the two types of phenomena is to compare the line-shape of the diffraction peak. Pre-transitional order parameter fluctuations would yield a diffraction peak with a Lorentzian shape[33], [68]. On the other hand, more persistent features, such as the smectic clusters found in BCNs, yield a Gaussian line-shape.[68] By fitting the diffraction peaks with the various functions, one can determine the nature of the structures causing the scattering.

Figure 4.11 shows 2-D SAXS images of CN12 taken in the various phases. The four-lobe pattern in the nematic phase indicates that there are tilted smectic-like clusters. The pattern at 84°C is consistent with a SmC phase as the diffraction pattern shows for bright spots on a ring. Moving below 70°C, the single ring of the SmC phase changes to multiple rings indicating a more complex layered structure denoted as SmX (indicating that it is a kind of smectic phase but was not identified more precisely in these experiments).
Beginning with the isotropic phase, Figure 4.12 shows a plot of scattering intensity vs. $q$ at 112°C. Due to the asymmetry of the curve, we chose to use a two-peak fit: with one curve to be the main peak and one peak to be a smaller and broader peak centered at a slightly higher $q$-value. Both peaks were fit using either a Gaussian or a Lorentzian profile. The best fit was given when the main (left) peak was modeled as a Gaussian and the right broader peak was modeled as a Lorentzian profile. However, all combinations of Gaussian and Lorentzian fits gave very good results with all $R^2$ values $> 0.995$. Therefore, it is difficult to make any conclusions on the nature of the scattering based on the line-shape.
Figure 4.11: 2-D SAXS images of CN12 in the isotropic phase (112°C), nematic phase (106°C), SmC phase (84°C), and SmX phase (60°C).

Figure 4.12: Scattering intensity vs. $q$ in the isotropic phase of CN12 (at 112°C). The SAXS data (blue circles) was modeled using a two-peak curve in which the peaks were either Gaussian ($G$) or Lorentzian ($L$). The continuous lines represent the various combinations of Gaussian and Lorentzian fits for each the left and right peak. The red dotted lines represent the individual components of the ($G+L$) curve in which the left peak was a Gaussian and the right as a Lorentzian curve.

The various fit profiles yielded a little more information in the nematic phase. A method similar to that used in studying the nematic phase of NP002 was used. Three
different profiles of intensity vs. $q$ were used to determine the locations of the scattering peaks. Figure 4.13 shows the locations of the profiles. First, Profile A was used to determine the horizontal ($q_x$) component of the scattering peak. Then Profile B was used to determine the vertical ($q_y$) component. Finally, using the $q_x$ and $q_y$ to calculate the tilt angle, Profile C was taken to determine the values of $q$ and $\Delta q$ used in determining the layer spacing ($d$) and correlation length ($\xi$).

![Image of intensity profiles](image)

**Figure 4.13:** Location of intensity profiles. The slices were chosen to find the position of the lower left peak. Profile A was used to find the horizontal ($q_x$) coordinate. Profile B was used to find the vertical ($q_y$) coordinate and its position was chosen using the peak position from Profile A. Profile C was taken as a radial profile at the angle determined by the $q_x$ and $q_y$ values of the peak.

Figure 4.14 shows the scattering intensity vs. $q$ for CN12 at 106°C along Profiles A, B, and C. Upon initial fitting of the vertical profile, it became apparent that neither a Gaussian nor a Lorentzian fit were accurately describing the data which seemed to fall
somewhere in between the two functions. For this reason, we chose to fit the data using the pseudo-Voight profile - a linear combination of a Lorentzian and Gaussian profiles, taking the form:

$$I(q) = I_0 \left[ \eta \frac{\gamma^2}{(q-q_0)^2 + \gamma^2} + 1 - \eta \exp\left(\frac{-q-q_0}{2\sigma^2}\right) \right] + h \quad (4.3)$$

where $I$ is the scattering intensity, $I_0$ is the amplitude of the scattering intensity at the peak, $q_0$ is the location of the peak, $\sigma$ and $\gamma$ are parameters determining the widths of the individual Gaussian or Lorentzian curves, respectively, $\eta$ is the scaling factor determining how Lorentz-like or Gauss-like the distribution is (also known as the Lorentz Fraction), and $h$ is the constant background scattering intensity. Further, the parameters $\sigma$ and $\gamma$ can be coupled as they are dependent on the width of the peak and not independent from each other. We can relate them to the FWHM ($c$) of the peak by:

$$\gamma = \frac{c}{2} \quad (4.4)$$

$$\sigma = \frac{c}{2\sqrt{2\ln 2}} \quad (4.5)$$

and substitute to yield the form of the pseudo-Voight function used:

$$I(q) = I_0 \left[ \eta \frac{c^2}{4(q-q_0)^2 + c^2} + 1 - \eta \exp\left(-4\ln 2 \frac{q-q_0}{c^2}\right) \right] + h \quad (4.6)$$

This is the form of the equation used to fit the single peaks in Profiles A and C of Figure 4.14. As with the NP002, the vertical profile (Profile B) required a split peak mirrored across $q_y=0$. In this case we used a double pseudo-Voight function of the form:
\[
I(q) = I_0 \left[ \eta \left( \frac{c^2}{4(q-q_0)^2+c^2} + \frac{c^2}{4(q+q_0)^2+c^2} \right) + 1 - \eta \left( \exp \left( -4 \ln 2 \frac{q-q_0}{c^2} \right) + \exp \left( -4 \ln 2 \frac{q+q_0}{c^2} \right) \right) \right] + h \quad (4.7)
\]

Figure 4.14: Scattering intensity vs. \( q \) for the three profiles: A, B, and C. The blue circles represent the SAXS data while the red solid lines are the pseudo-Voight fits.

The values of the Lorentz Fraction, \( \eta \), are shown in Table 4.1. Surprisingly, the fits for Profiles A and C are very Lorentzian, while the fits for the vertical Profile B are roughly an equal mix of Lorentzian and Gaussian. Profiles A and C are radial profiles, containing only information about fluctuations along \( q \) and no information about
fluctuations along $\chi$ (the polar angle) or tilt angle. Profile B, on the other hand, contains mostly information about the angle of the scattering (fluctuations in $\chi$ and the tilt angle). The fact that the radial profiles are Lorentzian in nature may suggest that those variations arise from the pre-transitional order parameter fluctuations. The vertical profile (Profile B), showing more Gaussian behavior than Profiles A and C, may have fluctuations of a different nature.

Table 4.1: Lorentz Fractions ($\eta$) for fits in the nematic phase of CN12.

<table>
<thead>
<tr>
<th></th>
<th>Profile A</th>
<th>Profile B</th>
<th>Profile C</th>
</tr>
</thead>
<tbody>
<tr>
<td>108°C</td>
<td>0.99</td>
<td>0.46</td>
<td>0.93</td>
</tr>
<tr>
<td>106°C</td>
<td>0.97</td>
<td>0.45</td>
<td>0.94</td>
</tr>
<tr>
<td>104°C</td>
<td>0.96</td>
<td>0.50</td>
<td>0.89</td>
</tr>
</tbody>
</table>

The $q$ dependence on temperature is plotted in Figure 4.15. The FWHMs ($\Delta q$) are also plotted. In the isotropic phase, the correlation lengths calculated from the FWHMs are on the order of one molecular length, while in the nematic phase it jumps to several (~5) molecular lengths, indicating that there is some order on the nano-scale, likely due to the grouping of bent-core molecules into smectic-like clusters. In the smectic phases, the correlation length jumps to ~1000 Å. This is consistent with the well ordered layered structure of a smectic phase. The scattering peaks in these phases are extremely sharp, and likely are limited by the resolution of our instruments, allowing for the correlation length to be even longer than we can measure.

The tilt angle as a function of temperature is plotted in Figure 4.16. In general, the tilt angle increases with decreasing temperature which is in agreement with previous
measurements of CN12[28]. However, previous results had also classified the phase between 103°C and 70°C not as a SmC phase, but as a phase consisting of elongated smectic-like clusters. Our results show that this phase is clearly a SmC phase.

Figure 4.15: $q$ and $\Delta q$ vs. Temperature for CN12.
Additionally, we can compare the distributions of the clusters in CN12 to those of NP002. The scattering profiles of NP002 were fit well by Gaussian distributions. The profiles in CN12 more closely resembled Lorentzian distributions. It has been shown before[68] that the pre-transitional smectic fluctuations in a nematic near to a smectic transition exhibit a Lorentzian-type distribution, at least in rod-like molecules. As NP002 does not have a smectic phase, it makes sense that it does not exhibit this type of pre-transitional behavior. CN12, on the other hand, does have a smectic phase. Its clusters exist over the entire nematic range (just as in NP002), however, the clusters seem to share at least some properties (the Lorentzian distribution) with the pre-transitional fluctuations found in materials that have a smectic phase. This indicates that the phase sequence has an effect on the properties of the smectic clusters in the nematic phase.
4.4 CI|b|s10BB with Chiral Dopant

The molecule CI|b|s10BB (see Figure 1.2 for structure) was chosen as the host in an attempt to create a blue phase from a bent-core liquid crystal. It is a relatively well studied bent-core molecule, known to have a nematic phase that shows the presence of smectic clusters[69]. It was doped with 1.9 wt% of BDH1282, a commercially available (Merck) chiral dopant. A stable blue phase, in this case BPIII[70], was observed in cooling from roughly 73°C to 54°C with isotropic phase above and smectic below. Figure 4.17 shows scattering profiles (intensity vs. \( q \)) for various temperatures as well as a typical 2-D SAXS image of the BPIII phase. Even in the magnetic field of the apparatus, there is no noticeable alignment. The results are very similar to those of the isotropic phase. This makes sense as the blue phases should appear isotropic on these length scales.
Figure 4.17: Scattering profiles and 2-D SAXS images of ClPbis10BB/BDH1281 mixture. The plot shows Intensity vs. q for the isotropic phase (75°C), BPIII (68°C and 60°C) and the smectic phase (53°C, data is plotted on the right axis).

The broad peaks indicate a very short correlation length of ~6 nm. Figure 4.18 shows a plot of q vs. temperature for both the mixture and the pure ClPbis10BB. The pure material shows a temporary decrease in the q-value at the isotropic-nematic transition. This possibly indicates that the clusters temporarily become more SmA-like at the transition and then return to SmC-like upon cooling. In the blue phase mixture, the q-values are overall smaller than in the pure material. This change in the layer spacing in the clusters suggests that the chiral dopant is present in the clusters and is not expelled, or that the tilt angle of the clusters decreases. Another important result is that the clusters are present even in the blue phase. This supports the previous conclusion that the clusters are important for stabilizing the BPIII phase instead of the BPI or BPII phases.
Figure 4.18: $q$ vs. temperature for ClPbis10BB/BDH1281 mixture and pure ClPbis10BB.

4.5 M1118 - SIBS Composite

Typical scattering images of the various concentrations of M1118 in SIBS are shown in Figure 4.19. The top row (Figure 4.19a-d) shows the 2-D scattering profile of the pure SIBS. The spot at the 11 o'clock position (more clearly seen in the inset in Figure 4.19a) indicates that there is some alignment with periodicity of 114 Å. This alignment may be a result of the compression molding process. The periodicity most likely is caused by the nanoscale phase segregation between the polystyrene and polyisobutylene blocks of the polymer. Previous SAXS and TEM studies of a similar
Figure 4.19: 2-D scattering profiles of M1118/SIBS composite material at different thermal conditions. Top row: Pure SIBS; 2nd row: 10% M1118; 3rd row: 20% M1118; Bottom row: 50% M1118. RT refers to room temperature prior to heating (i.e., the first column images are taken prior to the heating cycle). The remaining pictures were taken in cooling after heating the samples to 95°C.
SIBS material[71] showed the polystyrene (PS) end blocks segregated into cylinders (~25-30 nm dia.) in a hexagonal arrangement with a periodicity of 38 nm surrounded by a field of flexible polyisobutylene (PIB) chains (see Figure 4.20). This likely means that the 114 Å peak in Figure 4.19a is actually the third order peak corresponding to a periodicity of around ~342 Å (34.2 nm). Further SAXS studies will be necessary to confirm this. The pure SIBS shows negligible change as a function of temperature (see Figure 4.19a-d).

![Figure 4.20: Schematic of SIBS nanoscale segregation. The PS end blocks segregate into cylinders with the PIB chains filling the rest of the space (not shown).](image)

The second row of Figure 4.19 (images e - h) shows the 2-D scattering profiles of the 10% M1118 in SIBS composite material at various temperatures. Figure 4.19e shows the sample at room temperature obtained after compression molding and prior to any heating cycle. Similar to the pure SIBS, there is a scattering peak from the polymer with a periodicity of 108 Å with some alignment at the 10 o'clock position. Again, this is the third order peak corresponding to a periodicity of ~324 Å (32.4 nm). Importantly the
shape of the diffused peak becomes elongated along the periodicity, indicating anisotropic chain distribution and alignment. The aspect ratio of about 1.25 indicates that flexible chains are more likely pointing perpendicular to the periodicity. This, and the slightly decreased periodicity, is due to a stretching normal to the periodicity induced, by the liquid crystal.

Also in the 10% sample, there are two main rings from the liquid crystal at $q_1 = 0.1646 \, \text{Å}^{-1}$ and $q_2 = 0.1918 \, \text{Å}^{-1}$ with FWHM of $\Delta q_1 = 0.0066 \, \text{Å}^{-1}$ and $\Delta q_2 = 0.0266 \, \text{Å}^{-1}$ corresponding to periodicities of $d_1 = 38.2 \, \text{Å}$ and $d_2 = 32.8 \, \text{Å}$ and correlation lengths of $\zeta_1 = 303 \, \text{Å}$ and $\zeta_2 = 75 \, \text{Å}$. It can be seen that the more diffuse outer ring shows some alignment in the same direction as the polymer. Taking into account that the length of the BLC molecule is 45 Å, the shorter periodicity corresponds to about 45º tilt of the layers, where the longer one indicates about 35º tilt. In heating, the scattering image doesn't change significantly until reaching the transition to the isotropic phase at 91ºC. Figure 4.19f shows the SAXS profile at 95ºC. The scattering from the liquid crystal disappears while the scattering from the polymer remains unchanged. On cooling, in the nematic phase there is no noticeable scattering from the liquid crystal compared to that of the polymer. Upon transition to the X phase (Figure 4.19g), there is a relatively broad peak at $q = 0.1863 \, \text{Å}^{-1}$ corresponding to a spacing of $d = 33.7 \, \text{Å}$ with a correlation length of $\zeta = 110 \, \text{Å}$. This is in good agreement with previous studies[56], [72], [73] on this and similar homologs of the liquid crystal which indicate that the X phase has a tilted smectic structure with short correlation length. The fact that this correlation length is larger than that found prior to heating indicates separation of the BLC at high temperature from the
nano-confined domains into micrometer scale regions (also see Sections 6.2 and 5.2 for more discussion on microscale separation in this sample). Upon further cooling at a slow rate, the X phase transitions to a crystal phase at 53ºC. In this state we see two rings (Figure 4.19h) with similar periodicities to the quenched state prior to this heating cycle. However, there are important differences: there is no noticeable alignment in the liquid crystal, and the outer ring has a considerably larger correlation length ($\xi = 290$ Å) than prior to this heating cycle. Also, we can conclude that the outer diffuse ring appearing prior to heating (Figure 4.19e) is actually the X phase "frozen" in perhaps a glassy state at room temperature. As will be discussed in Section 6.2, we believe that this frozen-in X phase along with alignment (i.e., a net polarization) is responsible for giving this material its piezoelectric properties.

The third and fourth rows of Figure 4.19 show the SAXS images of the 20% and 50% composites, respectively. In general, they follow the same trend as the 10% material, with a few notable differences. The scattering from M1118 is stronger, as expected, in the higher concentration samples. The SAXS patterns at 20% M1118 concentration (Figure 4.19i-l) still show some alignment of the polymer chains, but the aspect ratio is only 1.13, indicating worse alignment than in the 10% composite. Although some alignment of the periodically packed PS units is still visible, no alignment of the liquid crystal peaks can be seen. The SAXS patterns of 50% composite (Figure 4.19m-p) do not show any alignment neither in the polymer, nor M1118. The SAXS pattern at room temperature before heating indicates a crystalline structure (Figure 4.19m). The isotropic fluid range shows some short-range correlations in the 50% sample
(Figure 4.19n), which are due to the smectic clusters observed in pure M1118[34]. Although the short correlated ring is still present in the X-phase range (Figure 4.19o), now crystalline peaks are also present. This is in agreement with the POM studies (Sections 5.1, 5.2 and Figure 5.6) that found the crystal phase can (and will) nucleate and grow from the X phase.

Scattering intensity of the room temperature samples is plotted as a function of $q$ in Figure 4.21. Again, one can see that the reflection peaks associated with the liquid crystal are stronger in the higher concentrations of liquid crystal.

![Figure 4.21: X-ray scattering intensity profiles of various samples with different concentrations of liquid crystal, all at room temperature prior to heating.](image-url)
CHAPTER 5
The Structure of the X-Phase

Some bent-core molecules have been known to transition to an optically isotropic state below the nematic phase[56]. This phase was first observed by Pelzl et al. and has been dubbed the \textit{X phase}[56], [72] or \textit{isotropic mesophase} (I_M) by Liao et al.[73] Their measurements indicated that it is a short correlated smectic phase[73], unfortunately, there is not yet a conclusive description of the physical arrangement of the molecules in this phase. As seen in CHAPTER 4, our SAXS measurements support that theory. It is also known to be ferroelectric[73]. One of the aims of this chapter is to investigate the properties of the X phase in order to better understand its structure. Here we will show experimental results of optical isotropy measurements as well as ferroelectric switching measurements in order to characterize this phase.

5.1 M1118 and M1120

Figure 5.1 shows the transmitted light intensity vs. temperature for a 5 μm thick cell of M1118 through crossed polarizers. This plot shows transitions in agreement with independent DSC measurements.[74] Additionally, it was verified in POM images of the same sample that the phase between 91°C and 65°C is nematic and the phase between 65°C and 53°C is an optically isotropic phase (X phase). Representative POM textures at select temperatures in cooling at 1°C/min are seen in Figure 5.2. The X phase has been seen in this material and in its homolog series of molecules with alkyl tails varying in
length from nine to twelve carbons[72] (M1118 has ten carbons). This phase can exist at room temperature if quenched quickly from the X phase (Figure 5.6d). In this case the crystallization is halted and the majority (>90% of the sample) remains in the optically isotropic state. This is shown in Figure 5.6d where both the crystalline and X phases exist at room temperature.

![Figure 5.1: Plot of transmitted light intensity vs. temperature for M1118 in cooling](taken through crossed polarizers).
Figure 5.2: Polarizing optical microscopy images of pure M1118. All images are taken in cooling from the isotropic at 95°C. Image (d) was taken at room temperature (RT) after quenching the sample from 60°C in the X phase. Image (d) was chosen to show both crystal and X phase existing together, however, greater than 90% of the total sample was the optically isotropic phase X. The polarizer, analyzer, and scale bar are the same for all images as shown in image (a).

Measurements to prove the optical isotropy of the X phase in M1120 was done by measuring the transmitted light intensity through crossed polarizers while varying the angle of incidence of the light with respect to the sample normal. In this case, the sample was contained in a standard glass test cell (see Section 2.4 for preparation of cells) with planar alignment layers and a cell gap of 5 μm. The sample was cooled from isotropic into the X phase at approximately 20°C/min and then quenched to room temperature to "freeze" the sample in the X phase. Figure 5.3 shows the results of the experiment. A sample of 5CB in a similar cell with homeotropic alignment was measured as a comparison. The sample of M1120 was measured a second time in a poled stated. The poling was achieved by applying 100 VDC to the cell (20 V/μm) while cooling the cell
from isotropic then quenching from the X phase to room temperature (in the identical
manor as described above). At room temperature the field was removed.

![Graph showing transmitted intensity vs. angle of incidence of laser light through crossed polarizers in samples of M1120 and 5CB.]

**Figure 5.3:** Transmitted intensity vs. angle of incidence of laser light through crossed polarizers in samples of M1120 and 5CB. Angle of incidence is measured in degrees from normal. The M1120 sample was measured in the X phase quenched to room temperature in both an unpoled state and then again in a poled state. 5CB was measured at room temperature in the nematic phase with homeotropic alignment. The fitted curve was found using Equation 5.2.

As expected, the 5CB in homeotropic alignment showed negligible transmission at normal incidence, and transmission increased as the angle of incidence moved away
from normal. Both samples of M1120 showed negligible transmission at all angles of incidence. The samples were rotated in the plane of the cell and the measurements repeated to ensure that the direction of the alignment layers had no effect on the measurements; similar results were measured. The results of these measurements showed that the X phase is optically isotropic, or at least the birefringence is smaller than our experiment can measure. We can estimate an upper limit of the birefringence based upon the data and instrumental error and by fitting the data with the expected values of the transmitted intensity. The expected transmitted intensity, $I$, can be found using[12]:

$$I \sim I_0 \sin^2 \left( \frac{\pi \cdot \Delta n \cdot d}{\lambda} \right)$$

(5.1)

where $I$ is the transmitted light intensity, $I_0$ is the incoming polarized light intensity, $\Delta n$ is the birefringence, $d$ is the thickness of the sample, and $\lambda$ is the wavelength of light. However, both the effective birefringence and the apparent thickness of the sample change when changing the angle of incidence. We can rewrite the above expression after correcting for these variations as:

$$I \sim I_0 \sin^2 \left( \frac{\pi}{\lambda} \cdot \frac{\sqrt{n_o^2 n_e^2}}{n_o^2 \sin^2 \theta' + n_e^2 \cos^2 \theta'} \cdot \frac{d}{\cos \theta'} \right)$$

(5.2)

where $n_e$ is the extraordinary index of refraction, $n_o$ is the ordinary index of refraction, and $\theta'$ is the angle of incidence inside the after accounting for Snell's Law, $\sin \theta = n_s \sin \varphi$, where $\theta$ is the angle of incidence upon the cell. The fit attained for 5CB in Figure 5.3 was found using $\lambda = 633$ nm, $d = 5 \mu$m, and literature values[75] of $n_o = 1.53$ and $n_e = 1.71$. The fit yielded an incident intensity $I_0 = 550$ mV. In order to
estimate the smallest measureable birefringence (the upper estimate for the birefringence of M1120), we used the same fit equation as above, however, adjusted the value of birefringence such that transmitted intensity was on the same order as the instrumental error. We have estimated that the instrumental error is roughly ±2 mV, which, at small values of birefringence, would correspond to an error in birefringence of less than 0.01. It is also this value that we can use as a conservative estimate of the smallest measurable birefringence, meaning that we can say the birefringence of M1120 is less than 0.01.

For the homolog with the twelve carbon tail (4-CBDB in Figure 1.10), it was also shown that the X phase is ferroelectric[73]. Figure 5.4 shows the ferroelectric switching current under an applied triangular waveform at various temperatures. Our measurements of ferroelectric switching currents on M1120 at 73°C yielded a polarization of ~290 nC/cm² at 42 Hz with an applied field of 32 V/μm. While this value is in the same order of magnitude as reported in 4-CBDB, it is still slightly smaller. This is likely due to the fact that we were unable to apply as high of a field and we used a higher frequency, not allowing the polarization time to saturate. As the temperature is lowered through the X phase, the switching peak becomes smaller, possibly due to the increasing viscosity of the material resisting the realignment of the molecules; by 60°C, there is no noticeable peak.
Figure 5.4: Time dependence of the ferroelectric switching current in M1120 at various temperatures. The applied voltage was at 42 Hz with an amplitude of 32 V/μm.

More possible evidence for ferroelectricity can be found by observing the cell with the naked eye. As mentioned previously, one can quench the X phase to room temperature and freeze in that phase. The cell then appears as if it has an isotropic fluid inside of it. However, over time (several hours to days), the cell becomes slightly cloudy and some small birefringent domains can be detected. In the poled sample, this cloudiness is significantly reduced. Figure 5.5 shows images of a cell containing M1120 that has been poled under a field of 100V / 5 μm (20 V/μm). The images were taken approximately 3 months after the sample was poled and left to sit. The photograph (left of Figure 5.5) shows the relative transparency of the poled area to the naked eye. The
POM image (right of Figure 5.5) shows that the unpoled area contains many birefringent domains, each on the scale of a few microns. In the poled area, the birefringent areas are significantly fewer and weaker, indicating that the poling process does have some effect on the structure of the material. Changing the angle the sample makes with the polarizers yields little change in the image, suggesting that the domains are likely randomly oriented within the plane of the cell.

![Unpoled area and Poled area](image)

*Figure 5.5: Photograph (left) and POM micrograph (right) of M1120 in a standard test cell. The poled area (electrode area) of the cell is clearly visible as the transparent square in the center of the cell (left) and as the dark area of the bottom left portion of the POM image (right). These images were taken approximately 3 months after the sample was poled in the X phase and quenched to room temperature.*

One possible model for the X phase is the so-called "dark conglomerate" (DC) phase[19], [76–85]. SAXS measurements of the X phase materials (see Section 4.5) show a single scattering peak, suggesting a layered structure and showing no evidence of
any other order. This is consistent with a smectic phase. However, the correlation length is short, and there is no alignment in the scattering image even when forming from an aligned nematic, suggesting small (~35 nm), randomly oriented domains of the smectic-like phase. This closely resembles the DC phase in some aspects. The DC phase is an optically isotropic smectic phase, however, the correlation length is much longer than that of the X phase and is more consistent with the correlation lengths of known smectic phases. Additionally, the DC phase exhibits chirality due to it being a type of SmCP phase. Domains of opposite chirality can be observed in the DC phase by slightly uncrossing the polarizers in POM. Chiral domains have been seen in the X phase [72], however, we were unable to reproduce those same results in our experiments. Further, the DC phase, upon application of an electric field, can switch to the birefringent B2 phase. No such switching was observed in our X phase materials, even with more than ten times the applied field [83]. Another difference between the X phase and the DC phase is that the DC phase is always seen just below the isotropic phase while the X phase usually appears below a nematic and sometimes even a smectic phase. Despite the similarities between the X phase and the DC phase, the differences are great enough such that we cannot say that they are the same.

A previously proposed model [73] is simply that the X phase is made up of randomly oriented SmCₐPᵥ domains of size smaller than the wavelength of light. This would satisfy the conditions of optical isotropy and the SAXS data. However, in the poled samples, there is a clear change in the appearance of the material indicating that the poling must do something. In all likelihood, the poling aligns the material to some
degree, removing the randomness in at least one direction while leaving the sample still optically isotropic. Another possibility is that the geometry of the phase makes it such that it is nearly optically isotropic. Previous work[86] has shown that it is possible that with a uniform SmCₐP phase with tilt angle of 45° and molecular opening angle of ~109.5° that the birefringence can be zero in three principle directions. Unfortunately, the opening angle of this series of bent-core molecules was measured to be ~138°[72], at least in the nematic phase. But, applying this model to a situation of randomly oriented domains that are then poled, we can see that a poled sample would likely create a ferroelectric phase with the polarization (kink direction) along the field. In the SmCP, this means that the layers would be standing parallel to the field (bookshelf alignment in our cells), and they would maintain their random orientation in the plane perpendicular to the poling direction. In this case, regardless of the tilt angle, light incident along the poling direction would see no birefringence because each domain is at a random orientation, averaging the birefringence to zero. For light incident perpendicular to the poling direction, an average of the short and long axes' indices of refraction would be seen (effectively making the material uniaxial again). If this average is near the value for the index along the intermediate axis (the kink direction) then the material would appear isotropic from any direction perpendicular to the poling direction, and consequently, from any direction. It would appear optically isotropic. While, this model does describe the phase, it is still far from the definite answer. Skeptically, we would consider that the X phase has been seen in several series of molecules. Is it likely that the principle refractive indices for each of these different molecules will fall exactly such that the phase appears
isotropic? Certainly further experimentation is required to determine the validity of this proposed model.

5.2 M1118 Elastomer

POM images of 5 μm thin slices of the 10% M1118 in SIBS composite are shown in Figure 5.6. The composite was prepared as described in Section 2.5. The samples were sliced using a microtome method and were imaged on a standard glass microscope slide also between crossed polarizers. In the 10% composite material, the POM texture observations agree with the phase transitions as seen in the DSC.[74] The material is in a nematic phase between 89°C and 65°C. Between 65°C and 53°C we find the optically isotropic X phase similar to the pure liquid crystal. If quenched from this phase to room temperature rapidly, as it was done during the sample preparation, the texture remains isotropic indicating that the X phase has been frozen into a glassy state (Figure 5.6d).

In the POM images in Figure 5.6, one can clearly see that there are micron-sized birefringent domains that exist in the X phase and at room temperature. This is in agreement with the appearance of the material to the naked eye (Figure 2.13). The birefringent domains appearing in the X phase and below are likely to be the crystal phase. The X phase (and most of the nematic phase) exists only in cooling and is metastable; the crystal phase can easily nucleate and consume the X phase. It is likely the case that the crystal phase has nucleated in some of these domains during the cooling process. Regardless, the POM images prove that the X phase can be frozen in at room temperature yielding a polymeric material with ferroelectric domains.
Figure 5.6: Polarizing optical microscopy images of the 10\% composite LC in SIBS. All images are taken in cooling from the isotropic at 95°C. Image (d) was taken at room temperature (RT) after quenching the sample from 60°C in the X phase. The polarizer, analyzer, and scale bar are the same for all images as shown in image (a). The yellow dashed line represents the edge of the sample; there is no sample in the bottom right portion of the images.
CHAPTER 6

Piezoelectric Studies

6.1 Pure Bent-core (M1120)

An attempt was made to measure the direct piezoelectric effect in the pure bent-core liquid crystal M1120. The material was filled into a standard test cell with the glue removed. The sample was measured at room temperature after being quenched from the X phase. First, the piezoelectric measurement was done on a poled sample. Then the sample was warmed to 75°C, the top of the X phase in an attempt to partially unpole the sample and the measurement taken again. A third measurement was taken after the sample was heated to isotropic, cooled to the X phase, and quenched to room temperature to produce a completely unpoled sample. The results are shown in Figure 6.1.

The results of all three measurements $d_{33}$ are in the range of ~0.5 pC/N. To estimate if the results are real, we can estimate the $d_{33}$ for a material with polarization, $P$, using the following mathematics. Begin with a simplification of Eqn 1.2

$$d_{33} = \frac{\Delta P}{\Delta T} \quad (6.1)$$

and using definitions of polarization and Hook's Law again,

$$P = \frac{\mu}{V} \quad (6.2)$$

$$\Delta T = Y \frac{\Delta L}{L} \quad (6.3)$$
where $\mu$ is the dipole moment of the material, $V$ is the volume, $\Delta L$ is the change in thickness caused by the applied force. We can rewrite $\Delta P$ as

$$\Delta P = \frac{\partial P}{\partial \mu} \Delta \mu + \frac{\partial P}{\partial V} \Delta V = \frac{1}{V} \Delta \mu - \frac{\mu}{V^2} \Delta V$$

(6.4)

and substituting to get

$$\Delta P = P \frac{\Delta \mu}{\mu} - P \frac{\Delta V}{V} = P \left( \frac{\Delta \mu}{\mu} - \frac{\Delta L}{L} \right)$$

(6.5)

Figure 6.1: $d_{33}$ vs. frequency of pure M1120 as a 10 um thick film in a standard test cell with the glue removed. The material was measured twice at room temperature after quenching from the X phase in a poled and unpoled state. Another measurement was taken on the poled sample after heating to 75°C to partially unpole the sample.
We can make the substitution $\Delta V/V = \Delta L/L$ because we assume that only the thickness of the sample is changing. Substituting $\Delta P$ and $\Delta T$ into eqn. 6.1, we get the final form

$$d_{33} = \frac{P}{Y} \left( \frac{\Delta \mu/\mu}{\Delta L/L} - 1 \right).$$

(6.6)

As shown in CHAPTER 5, the polarization of the pure bent-core was measured to be around 290 nC/cm$^2$. An upper estimate for the Young's modulus could be the layer compression modulus for a smectic which is around 1 MPa.[15] Assuming that the polarization does not rotate under the compression, we can estimate that the $d_{33}$ should be around 3 nC/N. This is three orders of magnitude larger than measured. The measurements also showed no difference in measurements for various poling states. Several reasons could be to blame. It is likely that mobile charges have screened out the DC field during the poling process and that all samples are effectively unpoled. Another mathematical possibility is that the $(\Delta \mu/\mu)/(\Delta L/L)$ term is changing because the dipoles are rotating with the compression. However, this is unlikely because the effects of the poling should be visible in this case, and they are not. It is also possible that the design of the experiment is flawed, particularly in using a standard test cell that was not intended to have a varying thickness. An improved method for measuring the piezoelectric response of the pure X phase is required.

6.2 Polymer Composite

A sample of 10% M1118 BLC in SIBS polymer composite was prepared as described in Section 2.5. The sample used in the following measurements had a thickness of 1 mm and lateral dimensions of 1 cm $\times$ 1 cm. Converse piezoelectric
measurements by Charif et al.[74] showed that the static $d_{33}$ is around 1 nC/N and the Young’s modulus is ~0.1 MPa. Using eqn. 6.6, the $d_{33}$ should be around 5 nC/N for a fully poled material. This indicates that the polymer composite is roughly 20% poled by the compression molding process.

Direct piezoelectric measurements of the composite were performed as described in Section 2.3. The composite material was measured at room temperature following the compression molding process in which the M1118 was quenched from the ferroelectric X phase (see CHAPTER 5). Because the X phase was determined to be ferroelectric, it follows that it must also be piezoelectric, and likely composite materials containing it will be piezoelectric. Figure 6.2 shows the measured piezoelectric charge constant, $d_{33}$, for the sample.

The measured piezoelectric effect strongly varies with frequency. At frequencies approaching zero (< 2 Hz) the value of $d_{33}$ rises to over 1.5 nC/N. This is comparable with previous measurements using the converse effect under DC voltages[74] in which a $d_{33}$ of ~1 nC/N was measured. As the frequency is increased, the piezoelectric response decreases significantly, hovering around $d_{33} \approx 3$ pC/N until slightly rising again around 1 kHz.
This frequency dependence of the piezoelectric response can possibly be explained based on the frequency dependence of other properties of the material, such as Young's modulus and the ability of the molecular dipoles to reorient under strain. Again, referring to eqn. 6.6, we notice that $d_{33}$ is inversely proportional to the Young's modulus. The Young's modulus is known in many materials to have a frequency dependence. In polymers such as polyisobutylene, the Young's modulus typically increases as frequency increases[87–89]. At the higher frequencies, the material is effectively stiffer and thus
has a lowered piezoelectric response. Additionally, the other components of eqn. 6.6 likely have a frequency dependence. For example, reorientation of the dipoles appears as the $\Delta \mu/\mu$ term and is compared to the strain ($\Delta L/L$). Both values would change with frequency and will have an effect on $d_{33}$. It has been shown that the direct piezoelectric response in some ferroelectric ceramics decreases with increasing frequency.[90] We cannot say for sure that the effects are the same in this polymer composite, however, it does suggest that a frequency dependence likely. Further studies are needed to determine the exact nature of the frequency dependence of this material.
CHAPTER 7

Summary

In this work, we have presented the results of various experiments on central ring substituted bent-core liquid crystals. We have synthesized a bent-core molecule that exhibits a nematic phase and is functionalized for future use in a liquid crystalline elastomer. Various experimental techniques were used to characterize properties such as smectic-like clusters in the nematic phases and piezoelectricity of polymer composites.

In CHAPTER 2, we have described the various experimental techniques used in studying the bent-core liquid crystals. We have improved the setup that is used to perform the small angle X-ray scattering measurements at Brookhaven National Laboratory. This improvement allows faster changing of samples as well as lowers the chances of losing the sample due to breakage. We have also designed and implemented an experimental setup to measure the direct piezoelectric effect. The setup is capable of varying parameters such as the frequency and amplitude of the applied force and the temperature of the sample. Also in that chapter, we describe the basics of polarizing optical microscopy and the preparation of the liquid crystal test cells that are used in POM and other experiments. We finish that chapter with the preparation of the bent-core liquid crystal polymer composite that we have used in our piezoelectric measurements.

CHAPTER 3 provides the details of the synthetic procedure used to create a bent-core liquid crystal and a crosslinker. The bent-core molecule was functionalized on one end to attach to the polymer in a side-chain configuration. The crosslinker was
functionalized on both ends with the same functional group as is on the liquid crystal. This will allow the polymer, liquid crystal, and crosslinker to be reacted at the same time creating a bent-core liquid crystalline elastomer.

In CHAPTER 4, we provided the detailed results and analysis of the SAXS measurements. The SAXS measurements were useful in analyzing the behavior of the smectic-like clusters that exist in the nematic phase of many bent-core molecules. The clusters have been shown to exist over a wide range of temperatures. We showed that the SAXS measurements agree with previous Cryo-TEM experiments on the three-ring bent-core compounds. We also compared the cluster behavior in two different materials - one with a smectic phase below the nematic (CN12) and one without (NP002). We have found that, as expected, the smectic clusters show more pre-transitional behavior in the material with a smectic phase. Further studies of these clusters is needed, as understanding these clusters can possibly shed light on the behavior of materials on the nanoscale. For example, we can ask if this system represents a kind of coexistence of the nematic and smectic phases, and on which length scales can two-phase coexistence be defined. Additionally, the clusters, just like the smectic phases of bent-core molecules, likely exhibit polar order. This could be the origin of the piezoelectric and flexoelectric responses found in some bent-core nematics. In CHAPTER 4 we also presented the SAXS results of the polymer composite made with a bent-core liquid crystal in the X phase. The X phase was shown to have a layered (smectic-like) structure with a short correlation length.
CHAPTER 5 continued the discussion of the X phase. We have shown that it is also optically isotropic and ferroelectric. From one point of view, the study of the X phase is warranted purely by scientific curiosity. While the exact smectic-like structure of the phase remains a mystery, we have added knowledge to help better understand that structure. On the other hand, there are potential applications for a ferroelectric and optically isotropic material. As shown with the polymer composites, the X phase can exist at room temperature and yield an elastomer imbued with the properties of the X phase.

Ferroelectric materials should also be piezoelectric by symmetry, and in CHAPTER 6 we showed piezoelectric measurements of materials containing the X-phase. The results of piezoelectric effect of the pure bent-core were of limited success, possibly due to the lack of poling caused by ionic screening. To avoid the ionic screening we have also tested the piezoelectric effect on a composite material where the bent-core liquid crystals in X-phase was confined in a polymer. The material showed a piezoelectric response that was in agreement with previous converse piezoelectric measurements under static (DC) fields. It was shown to be comparable to commercially available piezoelectric ceramics. However, under oscillating forces of more than a few hertz, the piezoelectric response dropped off significantly likely due to stiffening of the polymer under oscillating strain with increasing frequency.
REFERENCES


