Chapter 1

Background

1.1 Introduction

Liquid crystals (LCs) have historically attracted scientific and technological interest due to their unique optical properties. Biologists were puzzled by a birefringent fluid well before 1888, the date commonly cited as the year liquid crystals were discovered. In that year, Austrian botanist Friedrich Reinitzer recorded the phase-transition temperatures of cholesteryl benzoate, which turns a milky white at 145.5 ^{o}C and transparent at 178.5 ^{o}C, and he considered the possibility that a phase intermediate between that of the isotropic liquid and crystalline solid could exist [1]. The subsequent 50 years of liquid crystal science saw slow but steady advances in understanding the molecular structure, surface interactions, and electric field response of liquid crystals, but it was not until the early 1970s that the successful commercialization of a pocket calculator with a display device that utilized liquid crystals sparked an intense interest in the field [2]. The discovery of the dynamic scattering mode and the twisted-nematic mode in displays was crucial to the commercial implementation of liquid crystals, which otherwise might have languished as a scientific curiosity with no practical utility. To this day, the term “liquid crystal” is widely associated with the acronym LCD (liquid crystal display), and the second most well known application of liquid crystals among the general public may be the mood ring, which takes advantage of the colorful textures that chiral nematic liquid crystals reflect.

In the last twenty years, however, as the interest in liquid crystals has blossomed, so has their incorporation in a wide variety of materials. The unique properties of liquid crystals affords them potential utility in a wide range of applications that extends beyond displays. Indeed, potential uses of liquid crystals recently cited in the scientific literature include artificial muscles [3, 4], acoustic polarizers [5, 6], tunable lasers [7], and optical data storage [8]. It is conceivable that in another twenty years, liquid crystals will come to dominate an entirely different market unrelated to displays.

The applications listed stem from a particular class of material known as a liquid crystal elastomer. Elastomers are more commonly known as rubbers, and their ability to sustain large deformations while retaining a memory of their initial configuration enables a wide range of functionality. When combined with liquid crystals, the result is a highly responsive material that can react to electric or magnetic fields, heat, or light by changing shape, color, and even size. Furthermore, they have a reliable memory of where they began, and will return to their initial state on removal of the external influence. These novel properties arise from the combination of LC order, polymer elasticity, and topological constraints or translational order of a crosslinked rubber.

The first liquid crystal elastomer was prepared in 1981 [9], and later the method was improved so that *aligned* liquid crystal elastomers could be produced [10]. The advantage of the method is its simplicity, and it gives liquid crystal scientists access to liquid crystal elastomers which can be made quickly and easily. Studies on these materials have led to a molecular model which can successfully explain most of the phenomena exhibited by these unique rubbers, in particular their ability to change shape and rotate the molecular orientational order in response to a variety of external stimuli [11]. The story of liquid crystal-polymer materials is by no means complete, however. The elastomers produced by Finkelmann and coworkers [9, 10] represent the first successful attempt at fabricating rubbery liquid crystal networks, and this initial success has inspired the search for new ways to combine liquid crystals and polymers [12]. Much remains to be done to improve the materials first produced over twenty years ago. In particular, the field lacks materials with a well-defined structure, which can give both improved material properties and also facilitate comparisons to theory, many predictions of which remain to be tested [11, 6, 13]. Additionally, novel ways of combining polymers and liquid crystals can enable new applications, and several examples from the past five years demonstrate this [14, 3, 15, 16, 17].

In this thesis, we present two novel materials that incorporate liquid crystal order and a polymer network. One is made by the self-assembly of block copolymers and the other by covalently crosslinking end-functionalized telechelic polymers. Both have unique structures, and we seek to understand how this affects their material properties. We begin this chapter with a brief review of scientific topics relevant to this work. We begin by defining the nematic liquid crystal phase and describing the elastic and viscous forces present. Next, we discuss different types of polymer-liquid crystal materials that have been studied, including liquid crystal elastomers. Finally, we discuss the theory of nematic rubber elasticity and its predictions for "soft" deformations in liquid crystal elastomers. After this overview of the field, we lay out the main objectives of this thesis.

1.2 Liquid crystals

1.2.1 The nematic mesophase

A useful definition of LCs is given by deGennes and Prost [18]: LCs have liquid-like order in at least one dimension, and they possess a degree of anisotropy in their mechanical, optical, and/or structural properties characteristic of some degree of order. Various types of molecules satisfy this definition. For example, amphiphilic molecules, such as surfactants in solution with a selective solvent, can form associated structures in which molecules are ordered in layers. Also, long, rigid molecules such as polypeptides, DNA, or viruses will display LC phases when highly concentrated in solution, due to steric interactions between highly anisotropic molecules. These types of LC phases that occur in solution, and whose phase behavior is strongly concentration dependent, are known as lyotropic LCs [18]. On the other hand, small organic molecules that exhibit LC ordering in the pure state are known as thermotropic LCs. This is because temperature, as opposed to concentration (as in lyotropic LCs), determines the phase of the thermotropic LC. Ordering in thermotropic LCs arises both from steric effects and from intermolecular Van der Waals forces [1]. LC molecules and phases are oftentimes referred to as mesogens and mesophases, respectively.

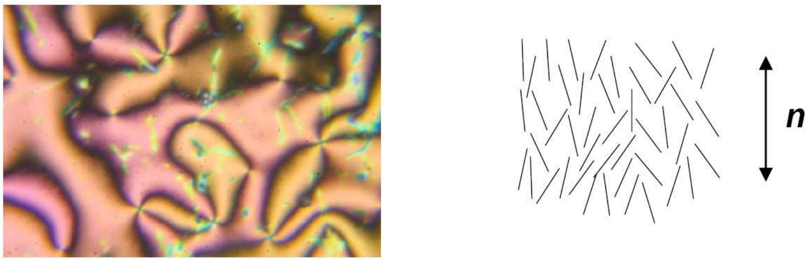

Figure 1.1: Nematic texture under polarized optical microscopy (left), and schematic of the nematic mesophase (right). The nematic phase has uniaxial symmetry, as indicated by the double-headed arrow.

The simplest LC phase is called the nematic phase. The term nematic comes from the Greek word for “threads” [18] and refers to the thread-like defects observed in nematics (Fig. 1.1). Molecules in the nematic mesophase have a preferred direction of orientational order, known as the director n, but they have no positional long-range order. The molecule 4-cyano-4′-n-pentylbiphenyl (5CB) is a thermotropic LC (Fig. 1.2). 5CB is crystalline below 20 ^{o}C, but displays the nematic mesophase from 20 ^{o}C up to 35 ^{o}C, above which temperature 5CB behaves like a conventional fluid. The transition temperature from the nematic to the isotropic phase is known as the T_{NI}. In this study, we are primarily concerned with thermotropic, nematic LCs.

The degree of order in a nematic LC is typically quantified by the order parameter S (Eq. 1.1), where θ is the angle between the director and the local molecular orientation. For a perfectly ordered nematic, S has a value of 1, while for an isotropic sample S has a value of 0. The order parameter is a useful way to quantify the degree of order in a liquid crystal, and it affects the anisotropy of material properties such as birefringence or dielectric anisotropy. Values of S typically vary between 0.3 and 0.8.

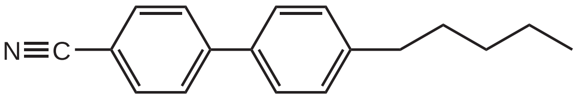

Figure 1.2: Chemical structure of 5CB. 5CB has a rod-like structure with a length of $\sim$ 20 $\AA$ and a width of $\sim$ 5 $\AA$.

$$S = \left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle \tag{1.1}$$

1.2.2 Liquid crystal elasticity

The lowest free energy state for a nematic is one in which all the mesogens are uniformly aligned with the director. In reality, thermal fluctuations prevent realization of this low energy state, and the molecules fluctuate around the preferred direction. Furthermore, uniform alignment may be incompatible with boundary conditions or external fields. Understanding the energy of these deviations from uniform alignment is important if we want to predict the equilibrium structure of nematics.

The situation is greatly simplified if we use a continuum approximation, which is justified by the much larger length scale ($\sim\ 1\,\mu m$) over which the director deviates, relative to the molecular size ($\sim\ 20\,\AA$). In this case, there are three basic types of deformation: splay, twist, and bend (Fig. 1.3), with associated elastic constants K_1, K_2, and K_3, respectively [18]. Each of these deformations has an associated elastic constant, which is in general temperature dependent. The LC elastic free energy density F_d is also known as the Frank elastic energy density (Eq. 1.2). The three elastic constants typically are of the same order of magnitude, typically 10^{-11} N – 10^{-12} N [19].

$$F_d = K_1(\nabla \cdot n)^2 + K_2(n \cdot \nabla \times n)^2 + K_3(n \times \nabla \times n) \tag{1.2}$$

1.2.3 Dynamic properties of the nematic director

In a uniform nematic monodomain, mesogens fluctuate about their equilibrium position due to thermal energy fluctuations. We can describe the amplitude and time scale for these thermal fluctuations by taking into account the Frank elastic and viscous forces for a fluctuation. Since orientational deformations over smaller length scales have a larger associated Frank penalty, the amplitude of the director fluctuations increases with increasing length scale. Similarly, the lifetime of an orientational fluctuation is larger for longer-wavelength distortions. These fluctuations are "overdamped" because

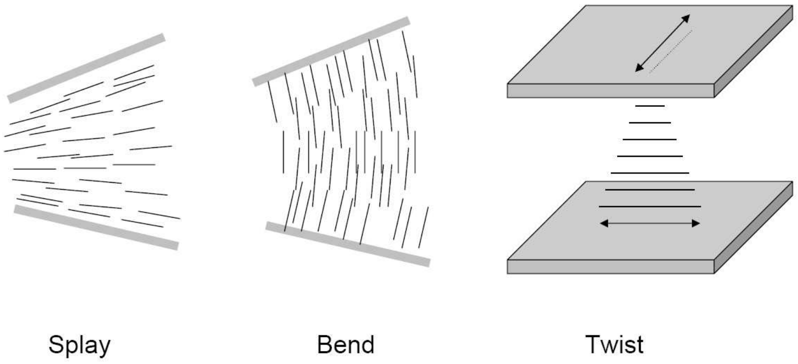

Figure 1.3: Splay, bend, and twist distortions of a nematic liquid crystal (Adapted from de Gennes and Prost, *The Physics of Liquid Crystals*, 1993, Oxford University Press, Inc., Oxford)

the rotational inertia of the molecules is small compared to the dissipation associated with rotational motion.

A quantitative treatment shows that there are two normal director modes for orientational fluctuations. These modes are a combination of splay-bend and twist-bend, and the relaxation rates associated with each will be different due to the different associated viscosities and elastic constants.

$$\begin{aligned} \langle|\delta n_1(\mathbf{q})|^2\rangle &= \frac{k_BT}{K_1q_\perp^2+K_3q_{||}^2} \\ \langle|\delta n_2(\mathbf{q})|^2\rangle &= \frac{k_BT}{K_2q_\perp^2+K_3q_{||}^2} \end{aligned} \tag{1.3}$$

The amplitudes of the orientational fluctuations are determined by a ratio of thermal and elastic forces (Eq. 1.3), in which $\mathbf{q}$ is the wavevector for the distortion (inversely related to the length scale), k_B is the Boltzmann constant, and T is the temperature. The wavevector $\mathbf{q}$ has two components, $q_\perp$ and $q_{||}$, which are the components perpendicular to and parallel to the preferred direction, respectively. For pure LCs, orientational fluctuations decay exponentially with time, $\delta n_\alpha(\mathbf{q},t) \sim \exp[-\Gamma_\alpha(\mathbf{q})t]$, where Γ is the relaxation rate. These relaxation rates are determined by a ratio of elastic and viscous forces (Eq. 1.4).

$$
\begin{aligned}
\Gamma_1(\mathbf{q}) &= \frac{K_1 q_\perp^2 + K_3 q_\parallel^2}{\eta_1(\mathbf{1})} \\
\Gamma_2(\mathbf{q}) &= \frac{K_2 q_\perp^2 + K_3 q_\parallel^2}{\eta_2(\mathbf{1})} \qquad (1.4)
\end{aligned}
$$

The amplitude and lifetime of a fluctuation depends on its orientation relative to the nematic director, and different orientations will have different degrees of contribution from splay, twist, and bend, and different associated viscosities. Experimentally, these three contributions can be decoupled by measuring the time-correlation of the scattered-light intensity at a particular angle and sample orientation[20] (see Chapter 4 for experimental details). This is a useful way to measure the elastic constants and viscosity coefficients for LCs.

1.3 Liquid crystalline elastomers and gels

1.3.1 LC polymers: anisotropic chains

LC polymers (LCPs) consist of mesogenic groups incorporated in a polymer chain. They can be incorporated into the backbone of a polymer chain, in which case the polymer is called a main-chain LCP, or the mesogens can be linked to the backbone by a flexible spacer, resulting in a side-group liquid crystal polymer (SGLCP) (Fig. 1.4). As shown in Fig. 1.4, LCPs typically have an anisotropic backbone conformation. This anisotropy arises from the liquid coupling between the liquid crystal ordering of the mesogens and the polymer backbone conformation [21]. The degree of anisotropy is dependent on the LC order parameter, which in turn is temperature dependent [22] and can also be modulated by UV light [23]. This ability to control the polymer conformation with temperature changes and UV is the basis for a variety of potential applications [24].

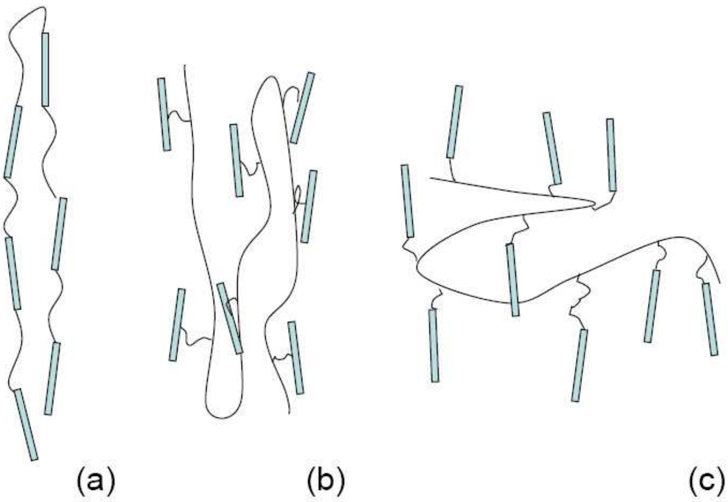

Figure 1.4: Schematic of (a) main-chain LCP, (b) side-on SGLCP, and (c) end-on SGLCP. (Adapted from Warner and Terentjev, *Liquid Crystal Elastomers*, 2003, Oxford University Press, Inc., Oxford.) As shown, main-chain LCPs and side-on SGLCPs typically have a prolate backbone conformation, while end-on SGLCPs typically have an oblate backbone conformation.

1.3.2 LC elastomers

Liquid crystal elastomers are composed of rubbery LCPs crosslinked into a network [11]. The anisotropic chain conformation of the network strands results in novel elastic properties not present in isotropic elastomers. In particular, nematic elastomers can exhibit a soft resistance to strains [25], and their macroscopic shape can change anisotropically in response to temperature [10].

The most popular method for preparing LC elastomers involves functionalization and crosslinking of a polysiloxane polymer (Fig. 1.5). This was first devised by Finkelmann et al. [9], and later work allowed the method to be used to form aligned LC elastomers [10].

1.3.3 LC gels

The term LC gels is loosely applied to materials that combine small molecule LCs with macromolecules [26, 27, 28, 12]. LC gels typically have faster dynamics and a lower threshold for response compared with LC elastomers. Therefore, LC gels are oftentimes studied for their potential use in displays. Also, LC gels can show shape changes in response to temperature and external fields, similar to LC elastomers.

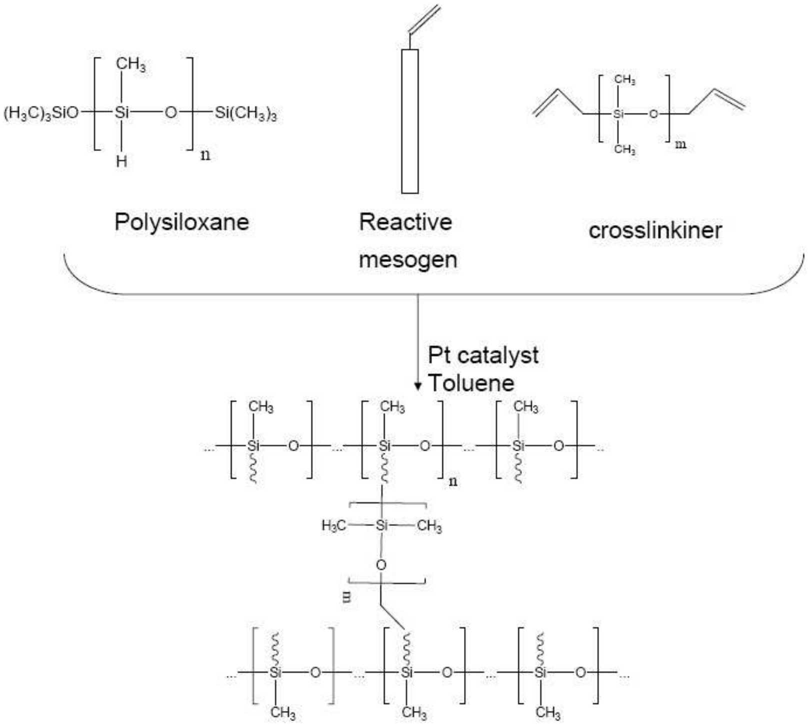

Figure 1.5: Schematic representation of a popular method [9] for preparing nematic LC elastomers

One type of LC gel is made by polymerizing mesogenic acrylates dissolved in an LC solvent [29]. In contrast to LC elastomers, the polymer backbone does not have to be rubbery, since the resulting network is swollen with solvent. The first LC gel of this type was produced in 1986 [26], but these types of LC gels drew little attention until more recently [30, 29]. Recent investigations have observed low-threshold electric field-induced shape changes [31], and temperature induced deswelling followed by reswelling when heating through the nematic-to-isotropic transition temperature [32].

Polymer-stabilized liquid crystals (PSLCs) are made by polymerizing exclusively mesogenic diacrylates (as opposed to monoacrylates) dissolved in an LC solvent [27, 33]. In contrast to LC gels made from monoacrylate monomers, PSLCs have a heterogenous structure that consists of a macroscopically phase separated polymer matrix encompassing the LC solvent [34]. The overall polymer concentration is dilute, typically 5 wt %, and therefore PSLCs retain the fast electro-optic response of small molecule LCs. The response can be faster, in fact, than small molecule LCs, since the polymer matrix provides a driving force throughout the volume of the material for the LC director to return to its original orientation upon removal of the field [27]. Different types of LC order have been incorporated into PSLCs, and they are of interest for electro-optic devices.

Another polymer-LC composite related to PSLCs, and also studied for its electro-optical properties, is known as a polymer-dispersed liquid crystal (PDLC). In contrast to PSLCs, PDLCs have a high polymer content, typically 90-95 wt % [35]. The structure of PDLCs consists of LC droplets dispersed in a continuous polymer matrix. Like PSLCs, PDLCs have a fast and reversible electro-optic response.

LC gels can also be made by mixing small-molecule gelators with a liquid crystal solvent [36, 28]. The gelators physically associate into a network of fibrous aggregates. The gels are thermoreversible, exhibit a fast electro-optic response, and gel at a low content ~ 1 wt % of added gelator.

1.3.4 Block copolymer self-assembly for LC elastomers and gels

Block copolymer self-assembly has recently been investigated for producing LC elastomers and gels. LC gels can be produced by the association of triblock polystyrene-SGLCP-polystyrene copolymers in a small molecule nematic LC [14], and this is the topic of Chapter 2. Nematic elastomers can also be made by block copolymer self assembly [3, 37, 15]. The advantages of these materials are that the macromolecular structure is produced in a controlled way, and therefore the resulting materials have a regular structure. Furthermore, self-assembly gives access to unique morphologies, such as a lamellar arrangement of blocks [3] and a thermally reversible structure [14, 3, 15].

1.4 The molecular theory of nematic rubber elasticity

The molecular theory of nematic rubber elasticity formulated by Warner and Terentjev [11] is an extension of classical rubber elasticity. In this “neo-classical” theory of nematic rubber elasticity, the chains in the network are assumed to be phantom, Gaussian, spontaneously anisotropic chains, and this neo-classical theory can successfully explain the spontaneous distortions, mechanical instabilities, and director-strain coupling [11]. Recent efforts have been made to include non-classical effects in nematic rubbers such as excluded volume interactions [13], entanglements [38], and deviations from the Guassian limit [39]. Here, we will focus exclusively on the neo-classical theory of nematic rubber elasticity, which we utilize in Chapter 3 to explain a spontaneous texture transition in LC gels. (The material reviewed here is covered extensively in Warner and Terentjev, *Liquid Crystal Elastomers*, 2003, Oxford University Press, Inc., Oxford.)

In contrast to classical elastomers, LC elastomers have an end-to-end distance that depends on the local orientation of the nematic director. This is because the chains in an LC network are anisotropic, as explained in Section 1.3.1. The anisotropy in the polymer chains can be expressed in terms of a step length tensor $l_{ij} = l_{\perp}\delta_{ij} + (l_{\|} - l_{\perp})n_i n_j$, in which $l_{\perp}$ and $l_{\|}$ are the effective lengths of steps parallel and perpendicular to the director $\mathbf{n}$ for a freely jointed chain. These step lengths are directly related to the mean square end-to-end distance, $\langle R_i R_j \rangle = \frac{1}{3} l_{ij} L$, where L is the arc length of the polymer chain. A more useful expression relates the ratio of the step lengths to the ratio of the radii of gyration of the chain, $\frac{l_{\|}}{l_{\perp}} = (\frac{R_{\|}}{R_{\perp}})^2$. The probability for an anisotropic strand having an end-to-end vector $\underline{\mathbf{R}}$, in terms of the step length tensor and the polymer arc length L, is given in Eq. 1.5.

$$p(\mathbf{R}) \sim \exp\left(-\frac{3}{2L}\mathbf{R}\cdot\underline{\underline{\mathbf{l}}}^{-1}\cdot\mathbf{R}\right) \tag{1.5}$$

Before computing the free energy expression for a crosslinked rubber, we need to distinguish between the conditions during crosslinking, described by step length tensor $\underline{\underline{\mathbf{l}}}_o$, and the conditions under which a strain is imposed which have an associated step length tensor $\underline{\underline{\mathbf{l}}}$. The resulting free energy expression is found by taking an average over all end-to-end vectors in the initial and final states (Eq. 1.6). Network deformations are accounted for by the deformation gradient tensor $\underline{\underline{\lambda}}$, which relates a separation vector on the undeformed body $\underline{\mathbf{R}}_o$ to that on the body under an imposed strain $\underline{\mathbf{R}}$, by the relationship $\underline{\mathbf{R}} = \underline{\underline{\lambda}}\cdot\underline{\mathbf{R}}_o$. The free energy expression (Eq. 1.6) is the basis for nematic rubber elasticity.

$$F \;=\; \frac{1}{2}\mu\left(Tr[\underline{\underline{l_o}}\cdot\underline{\underline{\lambda}}^T\cdot\underline{\underline{l}}^{-1}\cdot\underline{\underline{\lambda}}]\right) \tag{1.6}$$

1.4.1 Soft elasticity

Soft elasticity refers to a phenomenon in the framework of the neoclassical theory of rubber elasticity (Eq. 1.6) in which a nematic rubber can undergo a non-trivial deformation at no cost to the free energy. This is presented schematically in Fig. 1.6. Under some imposed strains, the network chains can rotate the distribution of chains at constant average shape of the network chains, and therefore the strain is perfectly "soft."

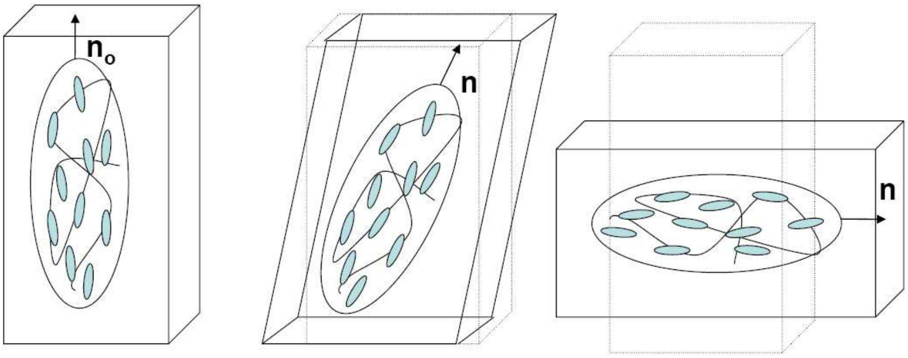

Figure 1.6: Schematic representation of a soft elastic distortion in a nematic elastomer. The box represents the macroscopic elastomer shape, and the LC chain depicts rotating nematic director which accomodates the shape change.

All soft deformations can be expressed in terms of the initial and final step length tensors, and an arbitrary rotation $\underline{\underline{\mathbf{W}}}_\alpha$ (Eq. 1.7) [40]. However, this does not give a practical method for computing optimal deformations. Most methods use Eq. 1.6 as a starting point [11], but it is also possible to begin by finding the displacements in the sample and computing the resulting deformation gradient tensor $\underline{\underline{\lambda}}$, as demonstrated in Chapter 3.

$$\underline{\underline{\lambda}} = \underline{\underline{l}}^{(1/2)} \cdot \underline{\underline{W}}_\alpha \cdot \underline{\underline{l}}_o^{(-1/2)} \tag{1.7}$$

1.4.2 Semi-softness

Several requirements must be met for softness to be possible in an elastomer. The network must be ideal, and all strands must be identical. Furthermore, the network must have an isotropic reference state. An elastomer that does not satisfy all these requirements cannot undergo strictly "soft" deformations, but it can nevertheless achieve nearly "soft" behavior, or "semi-softness." Experimentally, "semi-softness" has been observed as a small resistance to deformation before a "soft" plateau in the modulus [41]. Semi-softness that arises from polydispersity in the network or compositional fluctuations can be accounted for by including an additional term, weighted by the semi-softness parameter α, in the free energy expression (Eq. 1.8) [11].

$$
\begin{aligned}
F \quad = \quad & \frac{1}{2}\mu\left(Tr[\underline{\underline{l_o}} \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{l}}^{-1} \cdot \underline{\underline{\lambda}}]\right) + \\
& \frac{1}{2}\mu\alpha\left(Tr[(\underline{\underline{\delta}} - \underline{n_o}\ \underline{n_o}) \cdot \underline{\underline{\lambda}}^T \cdot \underline{n}\ \underline{n} \cdot \underline{\underline{\lambda}}]\right) \qquad (1.8)
\end{aligned}
$$

1.5 Objectives

Experimental research is limited by the materials available. This work aims to further the understanding of LC-polymer materials by producing novel LC gels and investigating their equilibrium and dynamic properties. A major aim is to prepare LC networks which have a regular structure, and we achieve this using self-assembly and end-linking of telechelic polymers. In Chapter 2, we present our approach for preparing liquid crystal gels self-assembled from a triblock copolymer, and we demonstrate the gels' favorable electro-optical properties, as well as the various methods for alignment. In the subsequent three chapters, we seek to understand the structure of the gel and the manifestation of rubber elasticity in the gels' macroscopic properties. In Chapter 3, we detail investigations into a spontaneous texture transition that appears in a uniformly aligned gel subject to small changes in temperature. While stripes have been observed in previous LC elastomers, the response discussed in this chapter is unique for its sensitivity to small changes in temperature and appearance in a gel confined between substrates. We formulate a description based on the neo-classical molecular theory of nematic rubber elasticity that accounts for the observed texture transition. The dynamics of orientational fluctuations in liquid crystal gels are expected to be modified due to the presence of a polymer network, and our gels provide a unique opportunity to study the director dynamics in monodomains (Chapter 4). We find that the gels show long-time relaxation modes due to a coupling between the polymer network and the nematic director, and we present a qualitative picture that describes the observed anisotropy and time scale of the response. Chapter 5 presents the results of rheometry and neutron scattering experiments to investigate the structure of the physical gels. The studies show that the LC order of the host solvent imparts unique properties to the micellar gels. The micelles and intermicellar network inherit the anisotropy of the host solvent, and dramatic structural and rheological changes occur across the T_{NI} due to a changing solvent selectivity. In addition to our studies of physical LC gels, we pursued model covalent networks. Ring-opening metathesis polymerization (ROMP) allowed the preparation of end-functionalized LC polymers which could be crosslinked via “click” chemistry (Chapter 6). These networks hold promise for elucidating structure-property relationships in LC elastomers.

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