INFLUENCE OF ARCHITECTURAL IMPERFECTIONS ON THE DYNAMIC MECHANICAL RESPONSE OF MAIN-CHAIN SMECTIC ELASTOMERS

A Dissertation in
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by
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Abstract

Main-chain liquid crystalline polymers that form low-temperature smectic mesophases are synthesized by linking terephthalic, bis-(4-allyloxyphenyl) ester (PPT) mesogens with 1,1,3,3,5,5 hexamethyltrisiloxane (F3) spacers via Pt-catalyzed hydrosilylation. Significant differences in thermal behavior and mesomorphic ordering are found between the polymer having unsubstituted PPT mesogens (F3-PPT-H) and the polymer having methyl substituents on the terminal rings of the mesogens (F3-PPT-CH₃). Combined evidence from polarized light optical microscopy, differential scanning calorimetry, and X-ray diffraction reveals $S_{CA}$ ordering in both polymers. To our knowledge, the $S_{CA}$ phase has been reported for the first time in the siloxane containing main-chain liquid crystalline polymers.

Smectic elastomers are synthesized by non-linear polymerization of PPT-H or PPT-CH₃ mesogens with F3 spacers and a tetrafunctional crosslinker, tetrakis(dimethylsiloxy)silane ($A₄$). The influence of structural imperfections on mechanical damping in polydomain smectic main-chain liquid crystalline elastomers (MCLCE) subjected to small strain oscillatory shear is examined. The mechanical loss factor $\tan \delta = G''(\omega)/G'(\omega)$ exhibits a strong maximum ($\tan \delta \approx 1.0$) near the smectic-isotropic (clearing) transition. "Optimal" elastomers that exhibit minimal equilibrium swelling in a good solvent are compared to highly swelling "imperfect elastomers" that contain higher concentrations of structural imperfections such as pendant chains. For the imperfect elastomers, $\tan \delta$ is markedly enhanced in the isotropic state due to relaxation of pendant chains and other imperfections. However, within the smectic state, the
magnitude of tan δ and its temperature dependence are similar for optimal and imperfect elastomers at ω = 1 Hz. The prominent loss peak near the clearing transition arises from segment-level relaxations that are insensitive to the details of chain connectivity. Smectic MCLCE can be tailored for applications as vibration-damping materials by manipulating the clearing transition temperature through the backbone structure or by deliberate introduction of structural imperfections such as pendant chains.

The stress-strain behavior of polydomain smectic main-chain liquid crystalline elastomers (MCLCE) subjected to uniaxial deformation is examined. The stress-strain curves of the MCLCE exhibit three regions. In region I, at low strain, excluded amorphous material and crosslink junctions in between smectic domains deform with minimal disordering of smectic domains. In Region II, characterized by a “plateau” stress, deformation of microdomains takes place by hairpin unfolding, followed by reformation of smectic domains in a globally oriented “monodomain” state. In Region III, at higher strain, hairpins are depleted except for “trapped” hairpins, and as elastic chains can not elongate further, deformation of the “monodomain” takes place by layer buckling.
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Chapter 1

Introduction

1.1 Liquid Crystals

Liquid crystals are a state of matter having ordering intermediate between three dimensional anisotropic ordered crystals and unordered isotropic liquids.\(^1\text{-}^6\) Partially ordered, anisotropic fluid phases are also known as mesomorphic states or mesophases ("mesos" meaning "intermediate," and "morphe" meaning "form"). Liquid crystals are either \textit{thermotropic}, where liquid crystalline ordering is obtained by change in temperature, or \textit{lyotropic}, where liquid crystalline ordering is obtained by change in the concentration of a solution.\(^1\text{-}^6\) Liquid crystalline compounds almost always contain rigid chemical units called mesogens, which typically exhibit large axial ratio (length to diameter ratio of molecule) and anisotropy in polarizability along the longitudinal axis compared to the transverse axis. These characteristics encourage spontaneous alignment of mesogens, stabilizing the liquid crystalline phase(s).

Nematic ("nema", \(\nu\epsilon\mu\alpha\), meaning thread) liquid crystals possess one dimensional orientational order (molecules lying parallel to each other) but lack positional order (molecules are not lying in layers). Nematic liquid crystals can gain translational entropy by adopting parallel orientational ordering.\(^3\) Polarizability creates greater van der Waals attraction between neighboring rods when they are parallel, further encouraging the molecules to align.\(^7,^8\)
Smectic (Greek word meaning “soap”) liquid crystals have two dimensional, orientational and positional order (molecules lying in layers with a preferred alignment direction but no positional ordering within layers). Smectic liquid crystals are generally formed as nanoscale phase separation occurs due to the tendency of mesogens to reside preferentially with neighboring mesogens, forming an alternating spacer-mesogen-spacer-mesogen arrangement. Depending upon the details of the arrangement of mesogens within layers, several types of smectic phases are possible:

Smectic A (SA)

Uniaxial smectic A (SA) is the least ordered phase of all smectics, in which molecules are arranged in parallel in layers (Figure 1.1). Within layers, molecules are randomly positioned.

Figure 1.1  Schematic representation of rod-like mesogens in smectic A phase.
Smectic B ($S_B$)

Smectic B ($S_B$) phases occur in three different structures: optically uniaxial hexagonal $S_B$, optically biaxial monoclinic $S_B$, and twisted monoclinic $S_B$. In $S_B$ phases, the mesogens are arranged in a hexagonally closed packed array.$^{9-11}$

![Schematic representation of smectic B phase.](image)

**Figure 1.2** Schematic representation of smectic B phase.

Smectic C ($S_C$)

The optically uniaxial smectic C ($S_C$) phase is closely related to the $S_A$ phase in which mesogens are arranged in layers, but the molecular long axes are tilted with respect to the layer planes and the molecular centers are packed within layer in random way.$^{9-11}$
Smectic D ($S_D$)

The smectic D ($S_D$) phase has a body-centered cubic lattice structure with Ia3d and Im3m space group.\textsuperscript{9-13}

Smectic E ($S_E$)

In the smectic E ($S_E$) phase, molecules are packed in an orthorhombic array within the layers with a herring-bone packing as shown below.\textsuperscript{9-11}

---

**Figure 1.3** Schematic representation of smectic C phase.

**Figure 1.4** Schematic representation of smectic E phase.\textsuperscript{9}
Smectic F ($S_F$)

In the smectic F ($S_F$) phase, the mesogens are arranged hexagonally with their long axes tilted with respect to the layer planes.$^{9-11}$

![Schematic representation of smectic F phase.](image)

**Figure 1.5** Schematic representation of smectic F phase.

Smectic G ($S_G$)

In the C-centered monoclinic smectic G ($S_G$) phase, the mesogens are arranged with their long axes tilted with respect to the normal to the layer planes with a hexagonal close packing arrangement within layers.$^{9-11}$

Smectic H ($S_H$)

In the monoclinic smectic H ($S_H$) phase, the mesogens have their long axes tilted with respect to the layer normal planes. This structure is equivalent to that of the $S_E$ phase with molecules tilted towards side b.$^{9-11}$
Smectic I ($S_I$)

The tilted biaxial smectic I ($S_I$) phase is an analog of $S_B$, in which molecules in the hexagonal lattice are tilted towards the apex of the hexagon $^{9-11}$ as shown in Figure 1.7.

Figures 1.6-1.7 illustrations show idealized structures, where, mesogens exhibit perfect orientational order with respect to layer normal. In real smectic LCs, some degree of orientational disorder is expected as shown in Figure 1.3. Thus, $S_A$, $S_B$, and $S_E$ are normal (orthogonal) phases while $S_C$, $S_F$, $S_H$ are tilted phases.
Biaxial Phases

Biaxial Nematic

In conventional nematic liquid crystals, there is only one optic axis, along which the refractive index of the molecules is isotropic. However in biaxial nematic phase, there is long-range orientational (but not positional) order about all three orthogonal axes, making optical behavior in two directions isotropic.\(^1\) Thus in biaxial nematic LC phase, molecules not only have orientational order, but also there is a rotational correlation about all three axes.

Smectic Ab (Biaxial Smectic A)

The smectic Ab phase (or “banana” phase) is formed by bent core molecules.\(^{14-17}\) The smectic Ab phase has also been infrequently observed in side chain liquid crystalline polymers having bent core mesogens.\(^{18,19}\)

![Schematic representation of smectic Ab phase.](Image)

**Figure 1.8**  Schematic representation of smectic Ab phase.
Smectic C\(_A\)

The smectic C\(_A\) phase is a second biaxial smectic phase proposed by Watanabe and Hayashi\(^{20-30}\) in which mesogens are tilted with respect to the layer normals, with tilt direction alternating between neighboring layers.

![Schematic representation of smectic C\(_A\) phase.](image)

**Figure 1.9** Schematic representation of smectic C\(_A\) phase.

Cholesteric Liquid Crystals

The cholesteric phase is equivalent to the nematic phase, with director twisted about an axis normal to the molecular orientation, following the helical pitch. Cholesteric phases are formed from chiral mesogens. The length of the cholesteric helix pitch is the distance which the molecular director rotates by 2\(\pi\) along the helix axis. Cholesteric phases exhibit characteristic iridescent colors and oily streaks in the polarized light.\(^9,31\)
**Chiral smectic phase (S\textsubscript{c}*)**

The chiral smectic C (S\textsubscript{c}*) phase is a twisted smectic phase formed from chiral mesogens. In this phase, layers of tilted mesogens are twisted incrementally with respect to their adjacent layers.\textsuperscript{9-11}

![Schematic representation of chiral smectic C phase.\textsuperscript{9}]

**Figure 1.10**  Schematic representation of chiral smectic C phase.\textsuperscript{9}

### 1.2 Liquid Crystalline Polymers

Liquid crystalline polymers (LCP) are semi-flexible macromolecules that exhibit partially ordered phases (mesophases), liquid-like states characterized by spontaneous segmental-level ordering. As shown in Figure 1.11, LCP are broadly classified as either the side-chain type, which have rigid, rod-like units (mesogens) attached to the polymer backbone as pendant groups (side chain liquid crystal polymers, SCLCPs),\textsuperscript{32} and main-chain types, which have mesogens directly embedded in the polymer backbone (MCLCPs).\textsuperscript{32,33} In SCLCPs, mesogens can be attached to the flexible backbone by end-on or side-on geometry as shown in Figure 1.11. Small angle neutron scattering (SANS) experiments on mixtures of protonated and partially deuterated nematic side-chain LCPs
have revealed oblate chain backbone conformation.\textsuperscript{34} On the other hand, the nematic phase formed upon heating from the smectic phase, possesses prolate backbone conformation.\textsuperscript{35} Due to segment-level ordering of mesogens, MCLCPs find applications in high tensile strength materials\textsuperscript{36} and moldings used in microelectronics.\textsuperscript{37}

**Figure 1.11** Main-chain liquid crystalline polymer\textsuperscript{38}

**Figure 1.12** Side-chain liquid crystalline polymers\textsuperscript{38}
1.3 Liquid Crystalline Networks

Liquid crystalline networks are crosslinked polymers in which mesogens are incorporated in the polymer backbone (main chain) or attached as pendant groups to the sides of polymer backbone (side chain). Polymer networks are categorized as thermosets or elastomers depending upon crosslink density. Thermosets have fewer polymer segments between crosslink junctions compared to loosely crosslinked elastomers, which have long chains between junctions.

Liquid Crystalline Elastomers (LCEs)

LCEs differ from LCTs in their lower crosslink density, and are distinguished by lower glass transition temperatures ($T_g$). The first reported LCEs were of the side chain type, synthesized by Finkelmann. LCEs exhibiting ferroelectric properties can be potentially used in bistable display devices and those exhibiting chiral nematic or smectic C* phases can be used as soft piezoelectric substances. Polydomain LCEs having local ordering within randomly oriented microdomains (often on the 1-10 µm length scale) are synthesized without application of any external electric, magnetic or mechanical field. Application of a mechanical field during crosslinking results in global
orientation of domains, producing a macroscopically ordered elastomer, known as *liquid single crystal elastomer (LSCE)* or *monodomain LCE*. LSCE can be synthesized in two distinct crosslinking steps according to procedures introduced by Finkelmann et al.\textsuperscript{45,46} A loosely crosslinked polydomain LCE is synthesized in the first step, then deformed uniaxially above a threshold stress $\sigma_{th}$, followed by a second crosslinking step to induce a permanent network anisotropy.\textsuperscript{45,46} Monodomain LCE can undergo macroscopic shape changes upon passing above the LC-to-amorphous isotropization temperature,\textsuperscript{46-49} under mechanical stress,\textsuperscript{47,50-56} or by photoisomerization of the mesogens.\textsuperscript{57,58} Monodomain LCE\textsuperscript{59-83} prepared from chiral ferroelectric precursors have been extensively studied by Zentel and others for their remarkable electromechanical properties, which suggest applications in soft actuation.\textsuperscript{49,53,84,85} Possible applications of monodomain LCEs are as wave-guides, polarizers, optical filters, alignment and compensation films for LCD displays, molecular switching and piezoelectric or pyroelectric sensors.\textsuperscript{86}

**LCEs for “Artificial Muscle”**

Various attempts have been made to develop artificial muscles from materials like dielectric elastomers,\textsuperscript{87} ferroelectric polymers,\textsuperscript{88} conducting polymers,\textsuperscript{89} carbon nanotubes,\textsuperscript{90} shape-memory alloys,\textsuperscript{91} piezoelectrics\textsuperscript{92} and hydrogels.\textsuperscript{93} The possible use of LCEs as artificial muscle was proposed by de Gennes\textsuperscript{94,95} due to strong coupling between the orientational order of the liquid crystalline system and the rubber elasticity of the polymer network. However, to function as an artificial muscle, a LCE must change its macroscopic shape in response to an applied stimulus. Smectic C main-chain monodomain LCEs show a two way shape-memory soft actuation effect.\textsuperscript{96} When a
monodomain LCE is heated below its clearing temperature, the network chains adopt ellipsoidal conformations resulting in spontaneous elongation; on the other hand, LCEs exhibit contraction above the clearing temperature due to the transition from ellipsoidal conformation to random coils. However in polydomain LCEs, as ellipsoidal domains are randomly oriented, the change in conformation at the molecular level is non additive, so polydomain LCE show no macroscopic shape change upon heating / cooling past $T_i$. Finkelmann et al.\textsuperscript{97} added photoisomerizable links in monodomain nematic liquid crystalline elastomers, which underwent a \textit{trans}- to \textit{cis}- transformation when UV-irradiated. As actuators, LCEs have advantages such as large thermally induced strain (45%) and moderate (2 - 4%) strain in electric fields. However, their use in actuator applications is hindered by high mechanical damping, slow response time, and the need to apply tremendous electric fields (1-25 MV/m)\textsuperscript{98} to achieve meaningful deformations.

\textbf{LCEs for “Vibration Damping”}

Vibrations are mechanical oscillations about an equilibrium point. Vibration damping materials including elastomers, are designed to dissipate mechanical energy as heat and thereby suppress unwanted sound waves. Viscoelastic polymers are often applied as vibration damping materials in automotive parts, aerospace components, computer hardware, and household goods to alleviate sound and vibrations caused by acoustical/structural resonance. At temperatures slightly above the dynamic glass transition, many polymers can efficiently convert mechanical energy (vibrations) into thermal energy. At glass transition temperature $T_g$, polymer chains acquire sufficient thermal energy for coordinated motion, giving rise to critical fluctuations. When the
frequency of the wave (vibration) matches with natural relaxation frequency of the polymer chain segments, maximal mechanical damping is found.\textsuperscript{99} Several polymers such as asphaltics, polyurethanes, poly (vinyl acetate) and copolymers, acrylics, natural rubber, styrene butadiene rubber (SBR), and silicone rubbers are used as damping materials, depending on the temperature and frequency range required. Polymers are applied to vibrating substrates in extension consisting of two layers (polymeric damping layer and substrate) or in a “sandwich” consisting of three layers (polymer between constrained vibrating substrate).\textsuperscript{99} Typical commercial damping elastomers have values of the mechanical loss tangent $\tan \delta (\equiv G''(\omega)/G'(\omega))$ in the range of 0.1 to 0.5 at the temperature of operation. Damping elastomers based upon thermotropic polyurethanes (TPUs), which are alternating block copolymers of polyester or polyether diols (soft segments) and diisocyanate and diol chain extender (hard segments) are studied most often. TPUs are a high-volume family of commercial thermoplastic elastomers with easily varied chemical structure and excellent processability. Yoon et al.\textsuperscript{100} have changed the $T_g$ of a polyurethane and thus its damping properties by systematically varying the content of chain extender, obtaining high $\tan \delta$ on the order of 0.7 to 0.9 at 1 Hz over a narrow temperature range of $\sim$20 °C.\textsuperscript{100} Interpenetrating polymer networks (IPNs) have also been studied as damping materials, as they exhibit high damping over broad temperature ranges in excess of 100 °C, compared to homopolymers and copolymers which exhibit a narrower damping temperature range ($\sim$ 20 – 30 °C).\textsuperscript{101} LCE of the polydomain type have potential application in vibration isolation or impact absorption due to their anomalous viscoelastic response, which is characterized by a broad spectrum of relaxation times and high mechanical damping.\textsuperscript{102}
1.4 Mechanical Properties at Small Strain Oscillatory Deformation

Dynamic mechanical analysis (DMA) is used to characterize damping in crosslinked or rubber-like viscoelastic materials. In DMA, a flat slab of the material is deformed cyclically by applying strain in a sinusoidal fashion.

\[ \sigma = \sigma_0 \sin \omega t \]  \hspace{1cm} (1.1)

\(\omega\) is angular frequency given as \(\omega = 2\pi f\), where \(f\) is frequency.

In-phase (\(\sigma'\)) and out-of phase (\(\sigma''\)) components of the stress are given as

\[ \sigma' = \sigma_0 \cos \delta \]  \hspace{1cm} (1.2)

\[ \sigma'' = \sigma_0 \sin \delta \]  \hspace{1cm} (1.3)

For Hookean solid, the strain produced is in phase with the applied stress, while for viscoelastic materials the strain lags behind the stress by a phase angle \(\delta\).

\[ \epsilon = \epsilon_0 \sin \omega t \]  \hspace{1cm} (1.4)

Experiments may be done either in shear or in uniaxial tension. For uniaxial tension the storage modulus (\(E'\)) and the loss modulus (\(E''\)) are given as
\[ E' = \sigma' / \varepsilon_0 = \frac{\sigma_0}{\varepsilon_0} \cos \delta \]  \hspace{1cm} (1.5)  

\[ E'' = \sigma'' / \varepsilon_0 = \frac{\sigma_0}{\varepsilon_0} \sin \delta \]  \hspace{1cm} (1.6)  

Where \( E^* \) is complex modulus given as  

\[ E^* = E' + iE'' \]  \hspace{1cm} (1.7)  

The loss factor (\( \tan \delta \)) is the ratio of the loss modulus to the storage modulus.  

\[ \tan \delta = \frac{E''}{E'} \]  \hspace{1cm} (1.8)  

For shear deformation,  

\[ G^* = G' + iG'' \]  \hspace{1cm} (1.9)  

and  

\[ \tan \delta = \frac{G''}{G'} \]  \hspace{1cm} (1.10)
E’’ is the equivalent energy lost during the interaction of the polymer with the sound waves resulting in heating of the polymer. Damping materials convert vibrational energy into heat, given by

$$H = \pi E'' \varepsilon_0^2$$  \hspace{1cm} (1.11)

Where, H is energy gained per unit volume per cycle, and $\varepsilon_0$ is the strain amplitude. A material will have a high damping capability if E’’ will be high at given temperature and frequency. However, practical experience has indicated that a high value of tan $\delta$ is desirable for constrained damping applications, in contrast to extensional damping applications, where maximizing E’’ or G’’ is preferential. The underlying physical reasons for this difference relate to the geometry of the damping system, which exceeds the scope of this dissertation. However, we will bear in mind that materials exhibiting high values of tan $\delta$ are desirable as vibration damping coatings in constrained geometries.

The rheological properties of isotropic polymers can be characterized over a wide frequency range (as machines can only cover limited frequency range) at a given temperature by applying the principle of time temperature superposition (TTS), which is also known as frequency temperature superposition or the method of reduced variables. According to the TTS principle, data at one temperature can be superimposed upon data at another temperature by shifting curves horizontally (frequency shift) and/or vertically (modulus shift). The data obtained over short ranges of temperature and frequencies are shifted horizontally to overlap with other data sets to obtain a “master curve”. Data need
to be shifted vertically if a viscoelastic material undergoes thermal expansion, contraction, density change or hydrological effects. TTS relies upon the assumption that the relaxation time spectrum is independent of temperature and therefore fails for materials that undergo changes in ordering (e.g. crystallization) over the temperature range of interest.

The frequency shift factor $a_T$, is given by the Williams-Landel-Ferry (WLF) equation, as

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + T - T_0}$$

(1.12)

where $C_1$ and $C_2$ are constants, and $T_0$ is a reference temperature, often taken to be $T_g$. $C_1$ and $C_2$ depend upon free volume and expansion coefficient relationships and values of 17.44 and 51.6 respectively, have been found to be hold for a wide range of amorphous polymers. TTS fails for crystalline and semicrystalline polymers due to changes in polymer backbone conformation taking place in the vicinity of phase transition. In the case of LCEs, TTS is expected to fail near phase transitions as positional and/or orientational ordering is lost with increasing temperature.

Polydomain LCE have received attention for their exceptional ability to dissipate mechanical energy over a broad range of frequencies and temperatures. Mechanical loss in many polydomain LCE far exceeds that of conventional elastomers, suggesting applications as vibration-damping soft materials. However higher mechanical loss is unfavorable for artificial muscle applications, where high loss modulus generates large amounts of heat, lowering the efficiency of the actuator. Recently, Clark et al.
demonstrated tan δ above 1.5 over wide temperature range in polydomain, nematic, side-chain, liquid crystalline acrylate elastomers. The high values of tan δ noted were attributed in part to the dynamic soft elasticity of nematic elastomers, where internal orientational degrees of freedom permit local director re-orientations with little elastic energy cost, essentially reducing the storage modulus. However, the ideas of soft elasticity are less applicable to smectic LCE. Mechanical damping in smectic LCE is thought to be suppressed by the restricting effects of smectic layers, leading to the assertion that the nematic phase is more attractive for design of vibration damping materials. However smectic LCE also exhibit high values of tan δ near their clearing transition temperatures. The physical origins of mechanical damping in smectic LCE at low deformations is a key issue motivating this thesis.

Urayama et al. have demonstrated that defective network topology alone can greatly enhance mechanical loss in elastomers without the presence of an anisotropic (LC) phase. Urayama's group studied (amorphous, non-LC) polydimethylsiloxane (PDMS) networks with variable fractions of long dangling (pendant) chains. By simply increasing the fraction of dangling chains, they were able to observe value of tan δ > 0.5, in a system with extremely flexible chains and a complete absence of liquid crystallinity or molecular-level ordering. Therefore, it is conceivable that a large variation in the mechanical loss could be observed with certain LCE purely depending upon the concentration of topological defects such as dangling chains and loops, without evoking the concept of "soft elasticity" or domain rotations.

Smectic MCLCE can be tailored for applications as vibration-damping materials by manipulating the clearing transition temperature through the backbone structure or by
deliberate introduction of structural imperfections such as pendant chains.\textsuperscript{110} However, previous studies of LCE mechanical properties have often overlooked the influence of loops and dangling chains, probably because of the lack of a synthetic protocol by which the degree of structural perfection in the network could be controlled. One of the objectives of this thesis is therefore to examine the influence of structural imperfections on mechanical damping in the polydomain, smectic, MCLCE, as the concept of soft elasticity does not apply very well to them.\textsuperscript{111}

### 1.5 Deformation of Liquid Crystalline Elastomers at High Strains

Conventional (non-liquid crystalline) elastomers exhibit typical “S”-shaped stress-strain curves as shown in Figure 1.14. When an elastomer is stretched \textit{affinely}, macroscopic deformation of the whole sample occurs in the same proportion as microscopic deformation of all network strands. At larger deformations, the finite extensibility of elongated chains produces a steeper increase in the retractive force causing large increase in the stress. As an elastomer is uniaxially elongated, the conformational entropy of the elastic chains decreases, increasing the elastic free energy, resulting in resistance to deformation; thus stress increases monotonically with applied strain.
Thus isotropic amorphous elastomers exhibit large-strain, nonlinear elastic behavior, resulting in “S” shaped form of nominal stress versus strain curve. However, LCEs undergo stress-induced macroscopic re-orientation, exhibiting a plateau in the nominal stress versus strain curve, unlike a conventional elastomer (Figure 1.15).

In the case of polydomain LCE, beyond a threshold stress ($\sigma_c$), ellipsoidal domains become oriented uniformly in the direction of applied deformation, causing a polydomain to monodomain (P-M) transition. A spontaneous elongation occurs at nearly constant stress with minimal increase in free energy. In nematic LCE, this phenomenon of macroscopic elongation of LCEs with the minimal or zero penalty of elastic free energy is described in terms of “soft elasticity”\textsuperscript{112,113} Once domain re-orientation is complete, stress increases steeply with increasing strain due to the finite extensibility of

\textbf{Figure 1.14} Stress-strain curve for an ordinary isotropic elastomer in the vicinity of room temperature.
chains, as in conventional elastomers. The nature (shape, width and slope) of the plateau depends on temperature, strain rate, the time scale of the experiments, and domain size. The width of the plateau shows an inverse relation to temperature, decreasing as temperature increases.\textsuperscript{114} The plateau vanishes above the clearing temperature as polymer network chains adopt random coil (spherical) conformations, and the network behaves as a conventional elastomer. The stress plateau and range of strains decreases with increase in temperature or decrease in strain rate.\textsuperscript{115} Clarke et al. have observed decreasing threshold stress with longer experimental time scale in polyacrylate, polydomain, side-chain, nematic liquid crystalline elastomers.\textsuperscript{116} In the case of monodomain samples, ellipsoidal domains rotate in the direction of stress when stretched in the transverse direction, such that the director points along the axis of uniaxial direction (stretching direction).\textsuperscript{46,52,117} Such a liquid single crystal elastomer (LSCE) exhibits a unique stripe domain structure.\textsuperscript{52} Polydomain-monodomain transition is also observed in the smectic main-chain LCEs deformed in uniaxial tension as shown in Figure 1.15.\textsuperscript{118}
Figure 1.15  Nominal stress-versus-nominal strain curve of smectic main-chain LCE. (Ortiz et al. Macromolecules, 1998, 31, 8531-8539).118

The mechanism for the P-M transition in smectic MCLCE is less easily explained, as domain rotations are discouraged due to the constraints of layering. The mesogens in the backbone of the main chain smectic liquid crystalline polymers and elastomers align with the local ordering due to interactions with neighboring chains. The chain axis lies essentially perpendicular to the smectic layer normals in most main-chain LCP. Very short chains may fit into the layered structure by assuming an extended-chain configuration, whereas longer chains can increase their entropy by forming hairpin folds or bends, at which the backbone reverses its direction as shown in Figure 1.16, to recover entropy reduced due to elongated backbone conformation.111
Adams et al.\textsuperscript{111} have demonstrated mathematically that main-chain LCEs (of either nematic or smectic type), when deformed by uniaxial elongation, exhibit a plateau stress due to hairpin unfolding. The number density of folds depends upon the molecular weight of the polymer chains between crosslinks. The probability of forming hairpin folds increases with increasing molecular weight between crosslinks ($M_c$), therefore exhibiting a wider plateau as $M_c$ increases. Thus a domain rotation (soft elasticity) is not the only reason for a plateau in MCLCEs. Adams et al. studied soft elastic modes\textsuperscript{119} and nonlinear elasticity of $S_A$ and $S_C$ elastomers and concluded that domain rotations are penalized in smectics due to layering. Therefore, soft elasticity is not really applicable to $S_A$ elastomers and is applicable to $S_C$ elastomers only in a very limited sense.\textsuperscript{119,120} Thus hairpins provide a more logical explanation for the plateau, although Ortiz et al.\textsuperscript{121} reported the observation of domain elongation and rotation of local director orientation, using polarized optical microscopy. Thus can the plateau be explained entirely by rotations, or are hairpins playing the dominant role in the P-M transition? One of the
goals of the present work is to understand the origin of the plateau in smectic main-chain LCEs, at a molecular level.

1.6 Scope of Dissertation

In support of our overall goals, the first step in our investigation was to synthesize main-chain liquid crystalline polymers and elastomers having stable smectic phase(s) over a broad temperature range, which have controlled crosslink density and concentration of architectural defects. The synthetic methodology we developed for monomers and polymers is described in Chapter 2. Our work produced the first report of the S_{CA} phase in main-chain polysiloxanes. In Chapter 3, we describe experimental methods followed in this study to characterize the thermal behavior, phase behavior, microstructure and physical properties of all linear polymers synthesized, using differential scanning calorimetry, optical microscopy, and X-ray diffraction. We introduce new thermal methods to obtain useful optical texture from main-chain polymers. Chapter 4 describes synthesis of “optimal” and “imperfect” main chain liquid crystalline elastomers, which have different concentration of architectural defects, and characterization of their properties at low strains by dynamic mechanical analysis. The investigation represents the first attempt to control the concentration of architectural defects in any LCE system. Chapter 5 examines stress-strain behavior at high strains in order to probe orientation phenomena occurring during uniaxial stretching. We present the first systematic study of the influence of crosslinking on the yield stress in the stress-
strain behavior of smectic MCLCE, advancing current understanding of how hairpins influence mechanical properties at large strains.
References


Chapter 2

Synthesis of New Main-Chain Liquid Crystalline Polysiloxanes with Low-Temperature Smectic Mesophases

2.1 Introduction and Background

In side-chain liquid crystalline polymers (SCLCP), mesogens are attached to the polymer backbone as pendant groups by flexible spacers. The mesogens can be aligned globally by applying an electric or magnetic filed. This change in orientation of LC side groups causes change in the conformation of the polymer backbone inducing stresses and strains to perform mechanical work. Due to ease of synthesis, side-chain liquid crystalline polymers (SCLCP) and side-chain liquid crystalline elastomers find applications as functional materials.\textsuperscript{1,2} However, main-chain liquid crystal polymers (MCLCP) and main-chain liquid crystalline elastomers (MCLCE) have a stronger coupling between mesogen orientation and backbone conformation than those of the side-chain type, and therefore exhibit stronger deviations from ordinary rubber elasticity. Main-chain liquid crystalline elastomers have received less attention than SCLCE due to their challenging synthesis and due to their generally higher transition temperatures (glass transition temperature and clearing temperature).

The primary objective of synthesis in this work is to obtain main-chain liquid crystalline polymers and elastomers that have room-temperature LC phases and a wide temperature range of mesophase stability (difference between clearing temperature $T_i$ and
glass transition temperature $T_g$). In addition, the synthetic methodology must permit systematic control over crosslink density and architectural perfection.

The glass transition temperature of a polymer depends upon the flexibility of the polymer backbone, the size and flexibility of chain substituents, tacticity, intermolecular interactions, and degree of crystallinity. The glass transition temperature in LCPs can be increased by introducing kinked units and increasing rigidity by incorporating stiff linking units. On the other hand the clearing temperature ($T_c$) of LCPs depends upon the length of the flexible spacers between the mesogenic groups, the size and polarity of substituents on the mesogens, the location of substituents on the mesogens, and the odd-even effect of methylene units in the flexible spacers. As the length of flexible methylene spacers increases, the clearing temperature decreases in a zig-zag manner. An even number of methylene spacers lead to an all-trans conformation without introducing kinks in the polymer backbone, stabilizing the LC phase and increasing the clearing temperature. Transition temperatures are reduced by frustrated chain packing, using substituents on mesogens, and by choice of ultra-flexible siloxane spacers. Because we desired LCE with $T_g$ below room temperature, our efforts aimed exclusively at design of main-chain polysiloxanes.

Previous studies of polysiloxane MCLCP and MCLCE examined mesogens of the 1,4-bis(benzoyl)hydroquinone (BHQ) type (Figure 2.1), 1-biphenyl-2-phenyl butane type, or others. On the other hand, no reports have examined polysiloxane MCLCP or MCLCE based upon the $p$-phenyleneterephthalate (PPT) type of mesogen (Figure 2.2), which have been used to prepare main-chain LC polyesters with alkyl spacers and densely crosslinked thermosets. PPT mesogens differ from the BHQ type
in the reversal of the ester bridges, which one might expect to stiffen the polymer backbone and thereby raise the temperature range of mesophase stability. However, comparing model compounds or polyesters having BHQ or PPT type mesogens, the PPT compounds often exhibit similar clearing temperatures.\textsuperscript{13,15} Thus, polysiloxanes with PPT mesogens should also exhibit low-temperature mesophases, but no study of their synthesis and properties has appeared prior to the present work.

\textbf{Figure 2.1} 1,4-bis(benzoyl)hydroquinone (BHQ) type of mesogen.

\textbf{Figure 2.2} \textit{p}-phenylene terephthalate (PPT) type of mesogen.

\textbf{Molecular Engineering of LCPs}

Generally, the structures of main-chain liquid crystalline polymers containing calamitic (rod shaped) mesogens include \textit{p}-orientated cyclic units (rigid core), linking groups, and modifying units. Mesogens are frequently constructed from a rigid core, connecting linkages, and terminal aromatic rings. Most mesogens contain three or four aromatic rings, which impart rigidity and increase polarizability. This unit has a larger
length to thickness ratio (stiffness), linear orientation, and high polarizability along the main chain - characteristics needed to form liquid crystalline phases.

**Selection of Mesogens**

In the present study, 1, 4-phenylene terephthalate is used as a rigid core to form chemically stable mesogens with terminal aromatic units. The mesogens prepared in this fashion are hereafter referred to as $p$-phenylene terephthalate or PPT compounds. The PPT type of mesogen was previously used by Barclay et al. to prepare linear LCP having long alkyl spacers.

In our work, ester groups are used as linking groups between two phenylene rings, which serves as separation between the phenylene rings, reducing the hindrance for free rotation of the rings and allowing crankshaft movements in the molecule. The ester connectors maintain rigidity and linearity of molecules while offering limited rotational freedom about the chain axis.

![Diagram of ester link between two phenyl groups](image)

**Figure 2.3** The geometry of an ester link between two phenyl groups. The length dimensions are in Å.
Conformational energy calculations\textsuperscript{3,15} indicate that due to steric repulsion, the two terminal phenylene rings tend to take a \textit{trans} conformation relative to the \(-\text{CO-O-}\) bond. The central phenylene ring takes approximately a coplanar configuration with the COO plane. The terminal rings, on the other hand, deviate from coplanarity with the COO plane by an angle of about 67°, due to the steric interactions between the hydrogen at the \textit{ortho} position on this ring and the oxygen of the carbonyl. The electron-rich phenyl group slightly shifts its bonding electrons to the carboxyl group by resonance; the ester linkage unit owns some double bond character, making rotation about the single bond joining the oxygen atom to the carbonyl group (C=O) difficult. Each ester link gives the neighboring phenylene unit a sideways displacement of 1.34 Å making the preferred conformation of the PPT unit \textquotedblleft S\textquotedblright{} shaped.\textsuperscript{15}

The transesterification reaction which takes place between phenyl esters of diacids and aryl diols at higher temperature in the presence of acid or base as a catalyst is extremely unlikely in this synthesis, as all the reactions are carried out at room temperature. The mesogen shown in the Figure 2.4 undergoes Claisen rearrangement at higher temperature \((T > 230 \, ^\circ\text{C})\) as shown in Figure 2.4. However, this problem is not posed in this study as polymerization reactions are carried out at 80 °C or less throughout this thesis. If such a re-arrangement occurred, a strong phenol absorption in the FT-IR spectrum would be observed in the range 3200-3400 cm\(^{-1}\), but no such evidence was found at any time in this study.
It is not practical to synthesize liquid crystalline polymers by simple linking together of rigid structures into rod-like molecules, as such LCPs are difficult to process due to their extremely high melting and clearing temperatures. The clearing temperature of LCPs can be reduced by introducing ortho or meta substituted phenylene units (kinks) in mesogenic unit, inserting lateral bulky substituents on the mesogens, copolymerizing different monomers to form LC copolymers, and/or by copolymerizing with two different flexible spacers. Using alkyl spacers having 6 to 12 backbone carbons Sacripante et al.\textsuperscript{4} found relatively high glass transition temperatures ($\geq 65 \, ^\circ\text{C}$) and clearing temperatures. However, we required $T_g$ below room temperature, which motivated us to use oligosiloxane connectors as spacer groups. The results of this chapter show that these semiflexible chains have a stable smectic mesophase near room temperature as intended.
Flexible spacer groups are used to connect mesogens in the main chain for two reasons: 1) to increase backbone flexibility and thus to lower $T_g$ and 2) to allow mesogens more freedom to align with each other.

Poly(dimethylsiloxane) (PDMS) is known to have the lowest $T_g$ (~ -125°C) of any polymer backbone due to two main reasons: 1) The Si-O skeletal bond is unusually long (1.63 Å) as compared to 1.42 Å for a typical C-O bond or 1.54 Å for a typical C-C bond and 2) The Si-O-Si bond angle of ~143° is much more open than the usual tetrahedral bonding occurring at ~110°. When small groups are attached to the silicon atom, chains dynamically change their spatial arrangements by rotations around the long skeletal bonds, giving more conformational degrees of freedom due to reduced steric hindrance. PDMS is thermally stable and it is soluble in common organic solvents including toluene, tetrahydrofuran, and n-alkanes.

In order to reduce clearing transition temperatures and reduce $T_g$ below room temperature, linear siloxanes with 3 and 4 silicon atoms are used as shown in the figure below. Apart from being flexible, siloxanes are thermally and chemically stable, and many can crystallize at -30 °C or below. However when copolymerized with mesogens, siloxanes form ordered mesophases at much higher temperature.

$$\text{H} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{H}$$

$\text{CH}_3 - \text{CH}_3 - \text{CH}_3 - \text{CH}_3 - \text{CH}_3 - \text{CH}_3$

1,1,3,3,5,5 hexamethyltrisiloxane (F₃)
1,1,3,3,5,5,7,7-octamethyltetrasiloxane (F₄).

**Ring Substitution (Lateral Substituents)**

Transition temperatures and phase behavior of LCPs can be further modified by affecting chain packing, which is achieved by adding lateral substituents to the cyclic units. Various lateral substituents used in this study are:

- **H** unsubstituted
- **CH₃** methyl
- **COCH₃** acetyl
- **OCH₃** methoxy
- **C(CH₃)₃** t-butyl
- **Cl** chloro

For mesogens with three phenyl units, lateral substituents can be placed on either the central phenyl ring or the terminal phenyl rings. In this work, substituents are attached systematically to the terminal phenyl rings. –CH₃ and -Cl substituents form mesogens that are mixtures of structural isomers, whereas the other substituents are placed exclusively at the 2- position.
Various mesogenic structures have been incorporated into main-chain siloxanes by previous researchers\textsuperscript{5-7} by attachment of terminal allyloxy groups, a strategy we adopt in this study.
Terephthalic acid bis-(4-allyloxyphenyl) ester

Terephthalic acid bis-(4-allyloxy-x-methylphenyl) ester (mixed isomers, x=2 or 3)

**Figure 2.5** Various mesogenic structures used in main-chain siloxanes.

bis(allyloxy) terminated PPT mesogens satisfy the characteristics such as 1) anisotropy in the shape (large length to width ratio), 2) anisotropy in the polarizability and 3) rigid units can lie parallel to form liquid crystalline phases.

**Hydrosilylation**

Linear MCLCP and MCLCE are prepared from bis(allyloxy) terminated PPT mesogens using hydrosilylation reactions. Hydrosilylation is one of the most common and important methods for silicon-carbon bond formation, which involves the addition of a Si-H bond across a π bond (C=C or C≡C bond). The reaction can be initiated 1) by transition metal catalyst such as Pt, Rh, Co, Ni or 2) radically by a free-radical initiator such as azobis(isobutyronitrile) (AIBN) or peroxide (di-t-butyl peroxide, benzoyl...
peroxide etc). The abstraction of H radical (H·) from R₃SiH is favored thermodynamically by about 20 kcal/mol (84 kJ/mol) over the abstraction by a carbon radical as shown in scheme I. The silyl radical then adds across the double bond in an anti-Markovnikov fashion (silicon bonds to the least substituted carbon), generating a carbon radical which may abstract hydrogen from R₃SiH.¹⁸ The efficiency and rate of hydrosilylation depend on the type and properties of the catalyst, olefin, and hydrosilane. Karstedt’s catalyst (Pt⁰ complexed by divinylsiloxane species, Pt₂(H₂C=CHSiMe₂CH=CH₂)₅, Pt (dvs)) has been used in this work to catalyze the hydrosilylation reaction.

The mechanism proposed by Chalk and Harrod in 1965, involves following the sequence of steps shown in scheme below.¹⁹ Hydrido-silyl complex (I) formed by oxidative addition of a hydrosilane undergoes hydrometallation to give the alkyl-silyl species (II). Reductive elimination of the alkyl and silyl ligands from II or β-silylalkyl-hydrido intermediate (III) forms the hydrosilylation product. Intermediate III is formed by silylmetallation when Rh(I) or Co(III) catalyst are used as a precursor.
Sellinger et al.\textsuperscript{20} have studied platinum catalyzed coupling reactions of allyloxy mesogens similar to mesogens synthesized in this study, with hydridosiloxanes using Karstedt’s catalyst. They have observed that primary product (85 \%) formed was the hydrosilylation product, formed by terminal addition of the silyl group to allyloxy unit as shown in Figure 2.6:
Figure 2.6  Hydrosilylation of allyloxy mesogens using Karstedt’s catalyst.\textsuperscript{20}

Three side reaction products arises from 1) oxidative silylation reactions (Figure 2.7); 2) oxysilylation reactions (Figure 2.8); and 3) from Pt catalyzed isomerization of the allyoxy group to a vinyloxy group (Figure 2.9). These products formed were less than 5% of total and were identified by $^1$H-NMR studies, mass spectral fragmentation pattern, and by size exclusion chromatography.

Figure 2.7  Oxidative silylation reaction.\textsuperscript{20}
Hydrosilylation can be catalyzed by either Pt\(^0\) or Pt\(^{II}\) catalysts. Both methods were explored in this thesis, and higher molar mass polymers were obtained with the Pt\(^0\) catalyst.

**Fractionation\(^{21}\)**

Because hydrosilylation reactions are polycondensations that produce broad molar mass distribution (expected \(M_w/M_n = 2.0\)), fractionation techniques were employed to obtain “clean” samples with well-defined \(M_w\). The various techniques of fractionation used in polymer science are precipitation fractionation, extraction fractionation, and partition fractionation. In precipitation fractionation, high molar mass polymer is precipitated selectively from solution either by gradual addition of non-solvent, or by decreasing temperature. In this method, high molecular weight polymer chains precipitate...
out first followed by lower molecular weight chains. In the extraction fractionation, polymer is gradually dissolved in the solvent/ non-solvent mixture, either by addition of a good solvent or by increasing temperature. In this method, low molecular weight polymer chains dissolve first followed by higher molecular weight chains. The partition fractionation is achieved by combination of immiscible or partially miscible solvents containing the polymer of interest.

In this work precipitation fractionation is used to obtain polymer fractions of narrow molecular weight distribution.

The dissolution of polymer in a solvent is driven by a difference in chemical potential between the pure polymer and the polymer solution of the two species, requiring small or negative value of enthalpy of mixing. According to the Gibbs-Helmholtz equation,

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \]

(2.1)

When, \( \Delta G_{\text{mix}} < 0 \), the free energy of mixing is favorable. \( \Delta S_{\text{mix}} (> 0) \) is much smaller for mixing of a (polymer + solvent) system than for mixing of two low molar mass compounds due to the large size of polymer molecules and the connectivity of the repeat units. The enthalpy of mixing (\( \Delta H_{\text{mix}} \)) is given by the following equation:

\[ \Delta H_{\text{mix}} \propto (\delta_s - \delta_p)^2 \]

where, \( \delta_s = (\Delta E_s / V_s)^{0.5} \) and \( \delta_p = (\Delta E_p / V_p)^{0.5} \)

(2.2)
\( \delta_S \) and \( \delta_P \) are Hansen solubility parameters; \( \Delta E_S \) and \( \Delta E_P \) are the internal heats of evaporation; and \( V_S \) and \( V_P \) are the molar volumes of solvent (S) and polymer (P), respectively. Solubility parameter (\( \delta_S \)) of the mixture of solvent A (\( \delta_A \)) and non-solvent B (\( \delta_B \)) having volume fractions \( \phi_A \) and \( \phi_B \), respectively, is given by the principle of additivity according to the following equation:

\[
\delta_S = \phi_A \delta_A + \phi_B \delta_B
\]  

(2.3)

The solvent and non-solvent are selected to be completely miscible with each other. Thus according to above equations, as the volume fraction of the non-solvent is increased incrementally, the solubility parameter increases, increasing the enthalpy of mixing. The resulting increase in \( \Delta G_{\text{mix}} \) causes partial precipitation of the polymer as a polymer-rich phase with volume fraction \( \phi_P \ll (1-\phi_P) \).\textsuperscript{21,22} The interaction parameter (\( \chi \)) represents solvent power; \( \chi \) is generally greater than 0.5 for non-solvents and below 0.5 for “good” solvents. Thus, phase separation occurs when \( \chi \) has a value (\( \chi_c \)) that is a little above 0.5.\textsuperscript{21} The \( \chi \) parameter is dependent upon chain length; shorter chains are generally more readily soluble in the solvent mixture. If \( N \) is the degree of polymerization, then the critical value of interaction parameter at which phase separation occurs (\( \chi_c \)) is given by\textsuperscript{23}

\[
\chi_c = \frac{1}{2} + \frac{1}{\sqrt{N}} + \frac{1}{2N} \approx \frac{1}{2} + \frac{1}{\sqrt{N}}
\]  

(2.4)
Gradual addition of non-solvent will cause $\chi > \chi_c$ for the portion of the molar mass distribution, and polymer chains of higher molecular weight will be precipitated out first, followed by shorter chains. The molecular weight distributions of these fractions overlap because of non-ideal separation. Thus every fraction contains a significant amount of lower molecular weight polymer chains ("tail effect"). Thus, if $w_i$ is the weight fraction of the polymer obtained in the $i^{th}$ fractionation step and $\bar{M}_i$ is its average molecular weight, the integral distribution $I(\bar{M}_i)$ is given by equation 2.5 as

$$I(\bar{M}_i) = 1 - \sum_{j=1}^{i-1} w_j - \frac{1}{2} w_i$$

(2.5)

The theoretical curves for the distribution of molecular weights in each fraction is as shown in Figure 2.10.
Figure 2.10  Theoretical curves for the distribution of molecular weights in fractions. (a) Fractional precipitation. (b) Fractional Extraction. The degree of polymerization is $x$.


The polymerization technique used in this study is condensation or step growth polymerization of the AA + BB type, yielding a polydisperse polymer with most probable distribution, leading to an expected $M_w/M_n$ of 2 (assuming 100 % conversion efficiency), when equimolar amounts of A and B monomers are used. In order to obtain polymer fractions with different molecular weights having narrow molecular weight distribution, and to remove unreacted monomers, cyclics, and byproducts of the hydrosilylation reaction, precipitation fractionation was carried out. For all fractionations, toluene was used as a “good” solvent and methanol was used as a poor solvent. Fractionations were performed at room temperature.
2.2 Synthesis

Materials

The following materials were used as received unless and otherwise stated: 2-methylhydroquinone, tert-butylhydroquinone, chlorohydroquinone, allyl bromide, 2-methoxyhydroquinone, terephthalic acid, 4-dimethylaminopyridine (DMAP), and N,N'-dicyclohexylcarbodiimide (DCC) were purchased from Alfa Aesar. Chlorohydroquinone was recrystallized twice from chloroform prior to use. Hydroquinone, 2',5'-dihydroxyacetophenone, and terephthaloyl chloride were purchased from TCI America. Triethylamine was purchased from Baker Analyzed and used as received. 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (F4) (90 %) and 1,1,3,3,5,5-hexamethyltrisiloxane (F3) (99 %), were purchased from Gelest, Inc. Tetrahydrofuran (THF) was distilled from a mixture of Na metal and benzophenone; dichloromethane and toluene were distilled from calcium hydride.

2.2.1 Mesogen Syntheses

2.2.1.1 Synthesis of 4-allyloxyphenol.

The general procedure for the synthesis is shown in Figure 2.11. Hydroquinone (11.1 g, 100 mmol) was dissolved in 100 ml DMSO in a 3-neck round bottom flask under a nitrogen flow in a water bath at ambient temperature. NaH (4.00 g, 100 mmol, 60 % oil immersion) was split into 10 batches of 0.40 g each and was added to the solution of hydroquinone and DMSO after every 10 min. Allyl bromide (12.1 g, 100 mmol) was
added to the reaction mixture with a dropping funnel. The reaction was carried out for 4 hrs. and was terminated by pouring the mixture into distilled water with stirring, after which the product was isolated by extraction with dichloromethane, dried over anhydrous Na₂SO₄, then filtered. The solution was passed through a column packed with silica gel (Grade 9385, 230-400 mesh, 60 Å, Sigma-Aldrich) to remove the oil from the NaH dispersion, and the product was isolated by rotary evaporation of CH₂Cl₂. The 4-allyloxyphenol (7.00 g, 47%) thus obtained was dried in vacuum overnight and further purified by column chromatography using ethyl acetate/hexane (1:3 v/v) as mobile phase. ¹H NMR (400 MHz; CDCl₃; (CH₃)₄Si) δH 4.51 (2H, -CH₂, d), 5.30 (1H, -CH₂, d), 5.39 (1H, -CH₂, d), 6.04 (1H, -CH₂, m), 6.77 (4H, aromatic, m).

![Figure 2.11](image)

**Figure 2.11** Synthesis of 4-allyloxyphenol.

2.2.1.2 Synthesis of terephthalic acid, bis(4-allyloxyphenyl) ester (PPT-H).

The general procedure for the synthesis is shown in Figure 2.12. This synthetic route is similar to that reported by Donnio et al.²⁴ 4-allyloxyphenol (15.01 g, 100.0 mmol), DCC (20.63 g, 100.0 mmol), DMAP (1.22 mg, 10.0 mmol), terephthalic acid (8.30 g, 50.0 moles) and dichloromethane (150 ml) were stirred for 48 hrs. at ambient temperature. The reaction mixture was filtered and washed with 2.0 N aqueous HCl and dried over anhydrous Na₂SO₄, then passed through silica gel using CH₂Cl₂ as mobile phase to get 15.50 g, (60%) H-PPT. The product was isolated by rotary
evaporation of CH₂Cl₂ and was further purified by recrystallizing twice using dichloromethane and ethyl alcohol. H-THP has very low solubility in all solvents. ¹H NMR (Figure 2.13) (300 MHz; CDCl₃; (CH₃)₄Si) δₜ 4.59 (4H, -CH₂, t), 5.34 (2H, -CH₂, d), 5.46 (2H, -CH₂, d), 6.08 (2H, -CH, m), 6.99 (4H, aromatic, d), 7.16 (4H, aromatic d), 8.36 (4H, aromatic s). ¹³C NMR (Figure 2.14) (CDCl₃, 400MHz): δₓ 118.23 (CH₂=), 133.50 (-CH₂-CH=CH₂), 69.65 (-CH₂-CH=CH₂), 156.94 (Cₓ-OCH₂-CH=CH₂), 115.88,122.71 (Cₓ-outer rings), 144.72 (Cₓ-OCO-outer rings), 165.02 (Cₓ-COO-), 134.34 (Cₓ-COO-), 130.629 (Cₓ-central ring ). FT-IR (KBr disk, cm⁻¹): 2875, 2887 (C-H stretch); 3068 (=C-H stretch), 1512 (C=C aromatic stretch), 1730 (C=O stretch).

\[ \text{Figure 2.12 Synthesis of terephthalic acid, bis(4-allyloxyphenyl) ester (PPT-H).} \]
Figure 2.13  
$^1$H NMR of terephthalic acid, bis(4-allyloxyphenyl) ester (PPT-H).
Figure 2.14 $^{13}$C NMR of terephthalic acid, bis(4-allyloxyphenyl) ester (PPT-H).
2.2.1.3 Synthesis of bis(4-hydroxymethylphenyl)terephthalate.

The general procedure for the synthesis is shown in Figure 2.15. The synthetic route reported by Barclay et al.\textsuperscript{13} was followed, but the product was purified by column chromatography using ethyl acetate as mobile phase. Methylhydroquinone (15.27 g, 0.123 mol) was dissolved in 25 mL of pyridine and 75 mL of THF under nitrogen in 3-neck, 1000 ml round bottom flask. This solution was then cooled to 5 °C in an ice bath, and a solution of terephthaloyl chloride (1; 5.00 g, 0.025 mol) in 25 mL of THF was added dropwise over 4 h at 5 °C. The reaction mixture was stirred at room temperature overnight. The mixture was washed with 2 N HCl (NaCl added to aid separation) and water. The THF phase was precipitated into 3500 mL of water at 65-70 °C, and the resulting solid was filtered. The crude product was dissolved in a minimum amount of warm acetone, filtered, and reprecipitated in water at 65-70 °C. The purified yellow precipitate was dried in a vacuum oven at 50 °C overnight, yield 6.88 g (73 %). This synthesis produces a mixture of structural isomers varying in placement of the methyl substituents on the aromatic rings. \textsuperscript{1}H NMR (300 MHz; CO(CD\textsubscript{3})\textsubscript{2}; (CH\textsubscript{3})\textsubscript{4}Si) \( \delta_H \) 2.08, 2.15, and 2.24 (6H, -CH\textsubscript{3}, mixture of isomers), 2.84 and 2.87 (2H, -OH, mixture of isomers), 6.76-7.05 (6H, aromatic, m), 8.33-8.38 (4H, aromatic, m).

![Figure 2.15](image-url)  

\textbf{Figure 2.15} Synthesis of bis(4-hydroxymethylphenyl)terephthalate.
2.2.1.4 Synthesis of terephthalic acid bis(4-allyloxy-2-methyl-phenyl) ester, (PPT-CH$_3$).

The general procedure for the synthesis is shown in Figure 2.16. 37.80 g (100.0 mmol) of bis(4-hydroxymethylphenyl)terephthalate was dried in a vacuum oven at 45 °C, then dissolved in 300 ml DMSO in a 3-neck, 1000 ml, round bottom flask in a water bath held at ambient temperature. NaH (12.00 g) was separated into 10 batches of 1.20 g each, and a batch was added to the reaction mixture every 10 min. under nitrogen flow. After 90 min., 30.0 ml allyl bromide (41.9 g, 347 mmol) was added to the mixture, after which the reaction proceeded for 4 hrs. The reaction was terminated by decanting into 1000 ml distilled water with stirring, and the solid product was isolated by filtration. The product was dissolved in dichloromethane and was stirred with anhydrous Na$_2$SO$_4$ for 2 hrs. then filtered and passed through a silica column using dichloromethane as mobile phase. M-PPT (14 g, 38 %) thus obtained was recrystallized several times using ethyl acetate and hexanes. $^1$H NMR (Figure 2.17) (300 MHz; CDCl$_3$; (CH$_3$)$_4$Si) $\delta_H$ 2.24 (6H, -CH$_3$, m), 4.61 (4H, -CH$_2$, d), 5.32 (4H, -CH$_2$, d), 5.43 (4H, -CH$_2$, d), 6.08 (2H, -CH, m), 6.85 (4H, aromatic, m), 7.08 (4H, aromatic, m), 8.35 (4H, aromatic s). $^{13}$C NMR (Figure 2.18) (CDCl$_3$, 400MHz): $\delta_C$ 117.54 (CH$_2$=), 134.27 (-CH$_2$-CH=CH$_2$), 69.84 (-CH$_2$-CH=CH=CH$_2$), 165.15 (C$_{ar}$-COO-), 134.49 (C$_{ar}$-COO-), 130.87 (C$_{ar}$-central ring ), 143.43, 144.29 (C$_{ar}$-OCO-,outer rings), 155.12, 156.96 (C$_{ar}$-OCH$_2$-CH=CH$_2$), 112.26, 118.08, 122.76, 122.98, 124.16 (C$_{ar}$-outer rings), 16.92 (C$_{ar}$-CH$_3$). FT-IR (KBr disk, cm$^{-1}$): 2866, 2931 (C-H stretch ), 1734 (C=O stretch), 3033 ( =C-H stretch), 1494 (C=C aromatic), 1651 (C=C stretch).
Figure 2.16  Synthesis of terephthalic acid bis(4-allyloxy-2-methyl-phenyl) ester, (PPT-CH₃).
Figure 2.17 $^1$H NMR of terephthalic acid bis(4-allyloxy-2-methyl-phenyl) ester, (PPT-CH$_3$).
Figure 2.18  $^{13}$C NMR of terephthalic acid bis(4-allyloxy-2-methyl-phenyl) ester, (PPT-CH$_3$).
2.2.1.5 Synthesis of bis(4-hydroxychlorophenyl)terephthalate.

The general procedure for the synthesis is shown in Figure 2.19. The synthetic route reported by Barclay et al.\textsuperscript{13} was followed, but the product was purified by column chromatography using ethyl acetate as mobile phase. Chlorohydroquinone (2b; 14.24 g, 0.310 mol), terephthaloyl chloride (1; 4.00 g, 0.020 mol), pyridine (25 mL), and anhydrous THF (100 mL) as solvent. After purification, thin-layer chromatography on silica gel, using ethyl acetate as eluent showed one spot (R\textsubscript{f} = 0.69, yield 5.59 g (69\%). This synthesis produces a mixture of structural isomers varying in placement of the -Cl substituents on the aromatic rings. \textsuperscript{1}H NMR (300 MHz; CO(CD\textsubscript{3})\textsubscript{2}; (CH\textsubscript{3})\textsubscript{4}Si) \(\delta\) 6.7-7.7 (6H, -CH\textsubscript{3}, mixture of isomers), 8.333, 8.34, 8.42 (4H, aromatic, s), 9.00 (2H,-OH).

![Figure 2.19](image)

**Figure 2.19** Synthesis of terephthalic acid bis(2-chloro-4-hydroxy-phenyl) ester.

2.2.1.6 Synthesis of terephthalic acid bis(4-allyloxy-2-chloro-phenyl) ester, (PPT-Cl).

The general procedure for the synthesis is shown in Figure 2.20. This synthesis was essentially identical to that reported in section 2.2.1.4, but 41.92 g (100 mmol) bis(2-chloro 4-hydroxymethylphenyl)terephthalate was substituted for bis(4-hydroxymethylphenyl)terephthalate. Final yield of Cl-PPT after purification was 20 g (40 \%). \textsuperscript{1}H NMR (Figure 2.21) (300 MHz; CDCl\textsubscript{3}; (CH\textsubscript{3})\textsubscript{4}Si) \(\delta\) 2.56 (6H, -CH\textsubscript{3}, s), 4.67 (4H, -CH\textsubscript{2}, d), 5.35 (4H, -CH\textsubscript{2}, d), 5.53 (4H, -CH\textsubscript{2}, d), 6.09 (2H, -CH, m), 7.17 (4H,
aromatic, d), 7.19 (4H, aromatic d), 8.35 (4H, aromatic s). $^1$H NMR (Figure 2.22) (CDCl$_3$, 400MHz): 114.36 (CH$_2$=), 132.86 (-CH$_2$-CH=CH$_2$), 70.57 (-CH$_2$-CH=CH$_2$), 164.59 (C$_{ar}$-COO$^-$), 134.08 (C$_{ar}$-COO$^-$), 130.70 (C$_{ar}$-central ring), 144.41 (C$_{ar}$-OCO$^-$, outer rings), 152.74 (C$_{ar}$-OCH$_2$-CH=CH$_2$), 118.50, 120.92, 123.91, 124.10 (C$_{ar}$-outer rings). FT-IR (KBr disk, cm$^{-1}$): 2862,2914 (C-H stretch), 1730 (C=O stretch), 719 (C-Cl stretch), 1496 (C=C aromatic), 3074 (=C-H stretch), 1649 (C=C stretch).

Figure 2.20 Synthesis of terephthalic acid bis(4-allyloxy-2-chloro-phenyl) ester, (PPT-Cl).
Figure 2.21 $^1$H NMR of terephthalic acid bis(4-allyloxy-2-chloro-phenyl) ester, (PPT-Cl).
Figure 2.22  $^{13}$C NMR of terephthalic acid bis(4-allyloxy-2-chloro-phenyl) ester, (PPT-Cl).
2.2.1.7 Synthesis of 1-(5-allyloxy-2-hydroxy-phenyl)-ethanone.

The general procedure for the synthesis is shown in Figure 2.23. The synthetic route reported by Mmutlane et al.\textsuperscript{25} was followed. Yield was 97%. A mixture of 2,5-dihydroxyacetophenone (7.6 g, 50 mmol), potassium carbonate (6.9 g, 50 mmol) and allyl bromide (6.0 g, 50 mmol) in acetone (100ml) was refluxed for a period of 18 hrs. The reaction mixture was cooled, filtered through Celite (diatomaceous earth) and concentrated in vacuum. The residue was chromatographed on silica gel using 20% ethyl acetate in hexanes eluent to yield 11.2 g (97%) of 1-(5-allyloxy-2-hydroxy-phenyl)-ethanone. \textsuperscript{1}H NMR (300 MHz; CDCl\textsubscript{3}; (CH\textsubscript{3})\textsubscript{4}Si) \(\delta\) 2.62 (3H, -CH\textsubscript{3}, s), 4.52 (2H, -CH\textsubscript{2}, t), 5.33 (1H, -CH\textsubscript{2}, d), 5.45 (1H, -CH\textsubscript{2}, d), 6.06 (1H, -CH, m), 6.92 (1H, aromatic, d), 6.94 (1H, aromatic, d), 7.15 (1H, aromatic d).

![Figure 2.23 Synthesis of 1-(5-allyloxy-2-hydroxy-phenyl)-ethanone.](image)

2.2.1.8 Synthesis of bis(2-acetyl-4-(allyloxy)phenyl)terephthalate. (PPT-COCH\textsubscript{3})

The general procedure for the synthesis is shown in Figure 2.24. 1-(5-allyloxy-2-hydroxy-phenyl)-ethanone (19.22 g, 100.0 mmol) was dissolved in 250 ml of triethylamine and 500 ml of anhydrous THF under nitrogen. This solution was then cooled to 5 °C in an ice bath, and a solution of terephthaloyl chloride (11.50 g, 50.00 mmol) in 250 ml of THF was added drop-wise over 4 hrs. at 5 °C. The reaction mixture
was stirred at room temperature overnight. The mixture was washed with 2 N HCl (NaCl added to aid separation) and water. It was then dried over anhydrous Na₂SO₄ and passed through silica gel using dichloromethane as eluent. Yield was 70%. ¹H NMR (Figure 2.25) (300 MHz; CDCl₃; (CH₃)₄Si) δ H 2.56 (6H, -CH₃, s), 4.62-4.65 (4H, -CH₂, t), 5.35-5.52 (4H, -CH₂, m), 6.06-6.11 (2H, -CH, m), 7.17 (4H, aromatic, d), 7.19 (4H, aromatic d), 8.37 (4H, aromatic s). ¹³C NMR (Figure 3.26) (CDCl₃, 400MHz): δ C 116.51 (CH₂=), 133.29 (-CH₂-CH=CH₂), 69.83 (-CH₂-CH=CH₂), 156.82 (C_ar-OC₂H₂-CH=CH₂), 119.96, 118.62, 124.97 (C_ar-outer rings), 125.24 (C_ar-COCH₃, outer rings), 143.04 (C_ar-OC₂-,outer rings), 165.08 (C_ar-COO-), 134.20 (C_ar-COO-), 130.87 (C_ar-central ring ), 197.34 (C_ar-COCH₃), 29.97 (CH₃-CO-C_ar). FT-IR (KBr disk, cm⁻¹): 1730 (C=O stretch), 2870, 2933 (C-H stretch), 1579 (C=C aromatic), 3101 (=C-H stretch), 1685 (C=C stretch).

![Diagram](image_url)

**Figure 2.24** Synthesis of bis(2-acetyl-4-(allyloxy)phenyl)terephthalate (PPT-COCH₃).
Figure 2.25 $^1$H NMR of bis(2-acetyl-4-(allyloxy)phenyl)terephthalate (PPT-COCH$_3$).
Figure 2.26  $^{13}$C NMR of bis(2-acetyl-4-(allyloxy)phenyl)terephthalate (PPT-COCH$_3$).
2.2.1.9 Synthesis of 2-tert-butyl-4-(allyloxy)phenol

The general procedure for the synthesis is shown in Figure 2.27. This procedure was similar to that followed in section 2.2.1.7, but tert-butyl hydroquinone was used instead of 2', 5'-dihydroxyacetophenone. Yield was 50 %. $^1$H NMR (300 MHz; CDCl$_3$; (CH$_3$)$_4$Si) $\delta$H 1.41 (3H, CH$_3$, s), 4.55 (2H, -CH$_2$, d), 5.27 (1H, -CH$_2$, d), 5.39 (1H, -CH$_2$, d), 6.05 (1H, -CH, m), 6.61 (2H, aromatic, d), 6.91 (1H, aromatic d).

![Figure 2.27](image)

Figure 2.27 Synthesis of 2-tert-butyl-4-(allyloxy)phenol.

2.2.1.10 Synthesis of bis(2-tert-butyl-4-(allyloxy)phenyl) terephthalate (PPT-(CH$_3$)$_3$C)

The general procedure for the synthesis is shown in Figure 2.28. This procedure was similar to that reported in section 2.2.1.2, but (20.62 g, 100.0 mmol) 2-tert-butyl-4-(allyloxy) phenol was substituted for 4-allyloxy phenol. Yield was (45 %). $^1$H NMR (Figure 2.29) (300 MHz; CDCl$_3$; (CH$_3$)$_4$Si) $\delta$H 1.44 (9H, CH$_3$, s), 4.57-4.58 (4H, -CH$_2$, d), 5.32 (2H, -CH$_2$, d), 5.48 (2H, -CH$_2$, d), 6.08 (2H, -CH, m), 6.82 (4H, aromatic, d), 7.05 (4H, aromatic d), 8.39 (4H, aromatic s). $^{13}$C NMR (Figure 2.30) (CDCl$_3$, 400 MHz): $\delta$C 115.15 (CH$_2$=), 133.71 (-CH$_2$-CH=CH$_2$), 69.62 (-CH$_2$-CH=CH$_2$), 156.66 (C$_{ar}$-OCH$_2$-CH=CH$_2$), 112.11, 118.25, 124.96 (C$_{ar}$-outer rings), 143.00 (C$_{ar}$-C(CH$_3$)$_3$, outer rings), 134.64 (C$_{ar}$-OCO-,outer rings), 165.27 (C$_{ar}$-COO-), 133.72 (C$_{ar}$-COO-), 130.84 (C$_{ar}$-central ring ), 30.63 (C$_{ar}$-C(CH$_3$)$_3$, outer rings), 35.08 (-CH$_3$). FT-IR (KBr disk,
cm$^{-1}$): 2873, 2966 (C-H stretch), 1737 (C=O stretch), 1579 (C=C aromatic), 3089 (=C-H stretch), 1652 (C=C stretch).

**Figure 2.28** Synthesis of bis(2-tert-butyl-4-(allyloxy)phenyl) terephthalate (PPT-(CH$_3$)$_3$C).
Figure 2.29 $^1$H NMR of bis(2-tert-butyl-4-(allyloxy)phenyl) terephthalate (PPT-(CH$_3$)$_3$C).
Figure 2.30 $^{13}$C NMR of bis(2-tert-butyl-4-(allyloxy)phenyl) terephthalate (PPT-(CH$_3$)$_3$C).
2.2.1.11 Synthesis of 4-(allyloxy)-2-methoxyphenol

The general procedure for the synthesis is shown in Figure 2.31. This procedure was similar to that reported in section 2.2.1.1, but (14.01 g, 100.0 mmol) 2-methoxyhydroquinone was used instead of hydroquinone. Yield was 44 %. ¹H NMR (300 MHz; CDCl₃; (CH₃)₄Si) δ 3.91 (3H, CH₃, d), 4.55 (2H, -CH₂, d), 5.28 (1H, -CH₂, d), 5.34 (1H, -CH₂, d), 6.09 (1H, -CH, m), 6.30 (1H, aromatic, m), 6.48 (1H, aromatic d), 6.78 (1H, aromatic s).

![Synthesis of 4-(allyloxy)-2-methoxyphenol](image)

Figure 2.31 Synthesis of 4-(allyloxy)-2-methoxyphenol.

2.2.1.12 Synthesis of bis(4-(allyloxy)-2-methoxyphenyl)terephthalate (PPT - OCH₃)

The general procedure for the synthesis is shown in Figure 2.32. This procedure was similar to that reported in section 2.2.1.2, but (18.02 g, 100.0 mmol) 4-(allyloxy)-2-methoxyphenol was used instead of 4-allyloxy phenol. ¹H NMR (Figure 2.33) (300 MHz; CDCl₃; (CH₃)₄Si) δ 3.91 (6H, CH₃, d), 4.66 (4H, -CH₂, d), 5.41 (2H, -CH₂, d), 5.47 (2H, -CH₂, d), 6.15 (2H, -CH, m), 6.78 (4H, aromatic, d), 6.93 (4H, aromatic d), 8.39 (4H, aromatic s). ¹³C NMR (Figure 2.34) (CDCl₃, 400MHz): 114.08 (CH₂=), 134.32 (-CH₂-CH=CH₂), 70.73 (-CH₂-CH=CH₂ ), 146.49 (C₉-OCH₂-CH=CH₂), 106.38, 113.18, 118.54 (C₉-outer rings), 150.48 (C₉-OCH₃, outer rings), 145.04 (C₉- OCO-,outer rings), 164.95 (C₉-COO-), 130.63 (C₉-central ring ), 53.84 (CH₃-O-C₉
outer rings). FT-IR (KBr disk, cm$^{-1}$): 2844, 2912 (C-H stretch), 1512 (C=C aromatic), 3091 (=C-H stretch), 1737 (C=O stretch), 1649 (C=C stretch).

**Figure 2.32** Synthesis of bis(4-(allyloxy)-2-methoxyphenyl)terephthalate (PPT- OCH$_3$).
Figure 2.33 $^1$H NMR of bis(4-(allyloxy)-2-methoxyphenyl)terephthalate (PPT-OCH$_3$).
Figure 2.34 $^{13}$C NMR of bis(4-(allyloxy)-2-methoxyphenyl)terephthalate (PPT-OCH$_3$).
Summarizing, the PPT mesogens having -CH\textsubscript{3} and -Cl substituents on the terminal aromatic rings were mixtures of structural isomers with random placement of the substituents in the 2- or 3- positions of the aromatic rings. The remaining mesogens had substituents placed exclusively in the 2- position of the aromatic rings, as shown in Fig. 2.5. In all cases, careful purification of diallylmesogens by column chromatography and recrystallization prior to polymerization was necessary to obtain high molar mass polymers.

2.2.2 Polymer Synthesis

Step-growth polymerization via hydrosilylation reaction was catalyzed by platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Figure 2.35). Initially solvents like tetrahydrofuran, chloroform, toluene, benzene, and dichloromethane were studied for polymerization based on the capability of solvents to dissolve both mesogens and siloxanes. Temperatures in the range of 40 °C to 90 °C were studied. For example, reaction was carried out at 90 °C in toluene and at 65 °C in THF with reflux. Reactions carried out at lower temperature yielded polymer with higher molar mass due to reduced likelihood of side reactions. Two different catalysts, Karstedt’s catalyst, and cis-dichlorobis(dietylsulfide)platinum(II) were studied for polymerization. The molar masses of polymers synthesized by cis-dichlorobis(dietylsulfide)platinum(II) were less than those of the polymers synthesized by Karstedt’s catalyst.

Based on solvent, temperature and catalyst studies, reaction conditions were chosen to obtain polymers with high molar masses. Alternating copolymers were formed
by AA+BB type polycondensation of the diallyl-mesogens with linear, silane-terminated dimethylsiloxane oligomers \(1,1,3,3,5,5\) hexamethyltrisiloxane (F3) or \(1,1,3,3,5,5,7,7\)-octamethyltetrasiloxane (F4). Polymerizations were conducted in anhydrous dichloromethane (CH\(_2\)Cl\(_2\)) at 45-50 °C for 7 days in a Schlenk flask under stirring. 4.00 g mesogens were dissolved in anhydrous dichloromethane (1.00 mmol mesogen / 2 mL solvent) followed by addition of an equimolar amount of either F3 or F4 co-monomer. After heating to the polymerization temperature and observing dissolution of the monomers, the Pt(0) catalyst (20 parts /10\(^6\) parts mesogen) was added to the clear, slightly yellow solution, resulting in vigorous reaction, evidenced by enhanced refluxing of the solvent for a short time, due to the heat of reaction. During hydrosilylation, platinum (Pt\(^0\)) is reduced to platinum colloids, turning the reaction medium from a yellow color to a dark brown or gray color. After 7 days polymerization, CH\(_2\)Cl\(_2\) was removed by rotary evaporation and the resulting polymer was dried overnight in vacuum.

The crude yield of polymers and oligomers (before fractionation) was close to 100 %. Polymers were subsequently fractionated at ambient temperature by dissolving in toluene (100 mL/g of polymer) in a 4 L Erlenmeyer flask, and precipitating by slow addition of methanol with stirring. Typically, after addition of methanol, 2-3 days were allowed for the polymer-rich phase to collect at the bottom of the flask. Fractions were isolated by carefully decanting the solvent-rich phase and continuing with methanol addition, and a total of 6 fractions were usually recovered. The amount of methanol added to cause polymer precipitation was determined by trial and error and was different for each polymer studied. Fractions were dried under vacuum at 50 °C for 7 days before further analysis. Chemical structures of the fractionated copolymers were verified by
liquid phase $^1$H NMR characterization of the purified samples (third or fourth fraction) using a Bruker DMX300 spectrometer operating at 300 MHz. The NMR samples were prepared in CDCl$_3$ at room temperature, with tetramethylsilane (TMS) added as an internal standard.
a.

\[
\begin{align*}
&\text{Pt(0), CH}_2\text{Cl}_2, 45-50 \, ^\circ\text{C} \\
&\text{R} = -\text{H, -OCH}_3, -\text{C(CH}_3)_3, -\text{COCH}_3, -\text{C(CH}_3)_3
\end{align*}
\]

b.

\[
\begin{align*}
&\text{Pt(0), CH}_2\text{Cl}_2, 45-50 \, ^\circ\text{C} \\
&\text{R} = -\text{CH}_3, -\text{Cl}
\end{align*}
\]

Figure 2.35  Step-growth polymerizations used to prepare copolymers from diallylmesogens and flexible connectors.
Size exclusion chromatography (SEC)

Molar masses of the copolymers were determined as listed in Table 2.1, by size exclusion chromatography (SEC) using a Shimadzu instrument equipped with a series of three Styragel columns (Styragel HR 7.8 X 300 mm columns with 5 µm bead size: (100-10,000), (500-30,000), and (5,000-6,000,000) Da) from Polymer Laboratory, and both refractive index (RI) and ultraviolet absorption (UV, 254 nm) detectors. Measurements were performed in THF at 35 °C with a flow rate of 1 mL/min.
<table>
<thead>
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<th>Polymer</th>
<th>Fraction 2 Mw / PDI (kg/mol)</th>
<th>Fraction 3 Mw / PDI (kg/mol)</th>
<th>Fraction 4 Mw / PDI (kg/mol)</th>
<th>Fraction 5 Mw / PDI (kg/mol)</th>
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</thead>
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<td>F₃-PPT-H</td>
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<td>75/1.7</td>
<td>69/1.3</td>
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<td>46/1.2</td>
<td>39/1.2</td>
<td>29/1.2</td>
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<tr>
<td>F₃-PPT-CH₃</td>
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<td>69/1.4</td>
<td>58/1.2</td>
<td></td>
</tr>
<tr>
<td>F₄-PPT-CH₃</td>
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<td>30/1.2</td>
<td>18/1.2</td>
<td></td>
</tr>
<tr>
<td>F₃-PPT-Cl</td>
<td>16/1.3</td>
<td>9/1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F₄-PPT-Cl</td>
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<td>22/1.3</td>
<td>18/1.3</td>
<td></td>
</tr>
<tr>
<td>F₃-PPT-OCH₃</td>
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<td>33/1.4</td>
<td>28/1.2</td>
<td></td>
</tr>
<tr>
<td>F₄-PPT-OCH₃</td>
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<td>42/1.3</td>
<td>36/1.2</td>
<td></td>
</tr>
<tr>
<td>F₃-PPT-C(CH₃)₃</td>
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<td>62/1.3</td>
<td>49/1.2</td>
<td></td>
</tr>
<tr>
<td>F₄-PPT-C(CH₃)₃</td>
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<td>42/1.2</td>
<td>38/1.2</td>
<td></td>
</tr>
<tr>
<td>F₃-PPT-COCH₃</td>
<td>33/1.3</td>
<td>28/1.4</td>
<td>25/1.2</td>
<td></td>
</tr>
<tr>
<td>F₄-PPT-COCH₃</td>
<td>32/1.4</td>
<td>27/1.2</td>
<td>24/1.2</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.1** Molar masses and polydispersity indices of various polymer fractions obtained.
References


Chapter 3

Characterization of Phase Behavior of Main Chain Liquid Crystalline Polysiloxanes with Low-Temperature Smectic Mesophases.

3.1 Introduction

Experimental methods including differential scanning calorimetry (DSC),¹-³ X-ray diffraction,⁴-⁸ polarized light microscopy,¹,²,⁹-¹² electron microscopy,¹³-¹⁵ nuclear magnetic resonance,¹⁶-²³ electron spin resonance (ESR),²⁴-²⁷ light scattering,²⁶ neutron scattering,²⁸ infra red spectroscopy,²⁹-³² and dielectric relaxation spectroscopy⁸,³³-³⁶ have historically been applied to characterize the phase behavior of liquid crystalline polymers. In the present study, combined evidence from polarized light optical microscopy, DSC, and X-ray diffraction is used to identify phases of the main-chain thermotropic liquid crystalline polymers described in Chapter 2.

3.1.1 Optical Birefringence Textures of Liquid Crystals

A texture is a microscopic image of the defects or singularities in orientational ordering within a thin layer of liquid crystalline material as observed between crossed polarizers. Textures are observed due to formation of characteristic defects or discontinuities in director orientation, which are useful to identify liquid crystalline phases. Various textures commonly observed in nematic and smectic LCs are described in this section.
**Nematic Liquid Crystals:**

Textural features observed in nematic liquid crystals include the monodomain texture, the schlieren texture, disclination lines, nematic droplets and inversion wall.\(^{37}\) Monodomain textures, in which mesogens are aligned in one direction represented by unit vector (director) \( \hat{n} \), are observed on specially prepared substrates prepared by “rubbing”, or by applying an external aligning field to the liquid crystal. The monodomain texture is homogeneously aligned. If the with optical axis lies parallel to the surface of the sample, the monodomain sample will exhibit a homogeneous birefringence color under crossed polarizers, provided the sample is of constant thickness. The homeotropic texture is a variation of the monodomain texture where \( \hat{n} \) is perpendicular to the substrate, which appears black between crossed polarizers.

The schlieren texture is the most commonly observed texture in polydomain nematic liquid crystals. The schlieren texture observed between crossed polarizers displays irregular (wavy), curved brushes (black stripes) originating from point singularities at which two or four brushes coincide. Brushes correspond to extinction positions of the nematic liquid where \( \hat{n} \) is parallel to either polarizer or analyzer. Dark points are the projections of vertically oriented defect lines (disclinations), which represent discontinuities in \( \hat{n} \). When the polarizer and analyzer are turned simultaneously in the crossed position, the disclination brushes move continuously across the area of the picture (rotating about the disclination points), while the disclination positions remain constant. The strength of the disclination is defined as\(^{37,38}\)
\[ |S| = \frac{\text{Number of brushes}}{4} \]  \hspace{1cm} (3.1)

\( S \) is defined to be positive when brushes turn in the same direction as the rotated polarizer and \( S \) is negative when brushes rotate in the opposite direction. At \( S = \pm 1 \), brushes rotate at the same rate as the polarizer (2\( \pi \) line) while at \( S = \pm \frac{1}{2} \), the brushes rotate at twice as fast as the polarizer (\( \pi \) line) as shown in Figure 3.1.\(^9\) The angular distribution \( \Phi \) of the director in terms of polar angle \( \theta_r \), is given as\(^{39}\)

\[ \Phi = S\theta_r + \Phi_0 \]  \hspace{1cm} (3.2)

\( \Phi_0 \) is an additive constant which turns the whole structure by an angle \( \Phi_0 \). Singularities connected by brushes can annihilate or combine leading to growth of domains (“ripening process”)\(^{40}\) if their strengths add up to zero.
Figure 3.1  The schlieren texture of the nematic phase showing singularities with strength $S = \pm \frac{1}{2}$ and $\pm 1$. (PPT-CH$_3$ mesogen synthesized in Chapter 2).

Nematic droplets having bipolar configuration (parallel molecular orientation) or radial configuration (perpendicular molecular orientation) are formed when an isotropic liquid crystal melt is cooled into a biphasic state. The nematic phase formed as droplets is surrounded by isotropic phase at the clearing point.$^{37}$

When an external field is applied orthogonal to the director of a monodomain, characteristic inversion walls form, by $90^\circ$ director reorientation, separating regions of parallel and anti-parallel alignment$^{41}$ as shown in Figure 3.2 Singularities have integral values of strength $S = \pm 1, \pm \frac{1}{2}$. $^{37,38}$
Figure 3.2 Inversion wall observed by polarizing microscope. (Chung T.S.; Cheng S.X.; Jaffe, M. Thermotropic Liquid Crystal Polymers; Technomic Publishing Company: Lancaster, 2001).  

Smectic Phases and Defects

Smectic A ($S_A$):

The smectic A ($S_A$) phase exhibits the homeotropic (pseudoisotropic) and the focal-conic fan texture as shown in Figure 3.3.  

Homeotropic texture can be obtained by substrate treatment (by surfactant) or by using a very clean glass slide and coverslip (by melting LC material on a clean glass slide and allowing the isotropic liquid to run under the coverslip by capillary action). Homeotropic texture appears black under crossed polarizers because $\hat{n}$ is perpendicular to the substrate and does not rotate the polarization of incident light.  

Bright birefringent rings can be observed around air bubbles or impurities due to structural dislocations at the edge of the bubble or impurity.  

The schlieren texture is never observed in a true $S_A$ liquid crystal.
Figure 3.3 Focal conic fan-shaped structure of S\textsubscript{A} phase. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 61, page 188, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

Smectic B (S\textsubscript{B})

The smectic B (S\textsubscript{B}) phase exhibits natural homeotropic and mosaic textures and paramorphotic focal-conic fan textures as shown in Figure 3.4.\textsuperscript{9} “Paramorphotic” fan textures are “inherited” from another LC phase, such as S\textsubscript{A}, remaining when the temperature is lowered into the S\textsubscript{B} phase. On annealing for a long time, the paramorphotic fan texture can form the mosaic texture as shown in Figure 3.5.\textsuperscript{9,11}
Figure 3.4  Focal conic fan-shaped texture of S_B phase. (Ingo Dierking, Textures of Liquid Crystals, Plate 88, page 189, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

Figure 3.5  The mosaic texture of S_B phase. (Ingo Dierking, Textures of Liquid Crystals, Plate 89, page 189, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
Smectic C ($S_C$)

The smectic C ($S_C$), biaxial phase is a tilted analog of the $S_A$ phase in which the molecular long axis is tilted with respect to the layer normal $\hat{n}$. $S_C$ exhibits schlieren textures and focal conic textures. The schlieren structure shows singularities with only four brushes as shown in Figure 3.6.\(^9\) The $S_C$ schlieren is different than nematic schlieren textures, which also show singularities with two brushes. Focal conic defects as shown in Figure 3.7\(^9\) can form naturally or paramorphotically. Paramorphotically formed focal conic defects are lined or broken compared to naturally formed focal conic defects.\(^9,11\)

**Figure 3.6** Schlieren texture of $S_C$ phase exhibiting singularity of $S = \pm 1$. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 71, page 191, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
Smectic D (SD)

The smectic D (SD) appears black (optically extinct) under crossed polarizers as it has body centered cubic lattice structure. SD phase can be distinguished from isotropic SA and crystal B phases nucleating from the nematic phase, as SD phase nucleates in birefringent SC phase in the form of rhombs, hexagons, squares as (shown in Figure 3.8), rectangles and fern type pattern.\(^9,11\)
Figure 3.8 Texture of SD phase exhibiting a square and a hexagon of the growing phase. (Ingo Dierking, *Textures of Liquid Crystals*, Figure 11.1, page 146, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

**Smectic E (S_E)**

The smectic E (S_E) phase exhibits a fan shaped texture with striations (Figure 3.10), a pseudo-isotropic texture, and a mosaic texture. The paramorphotic S_E phase formed by cooling the S_A or the S_B phase exhibits focal conic fan textures with clear lines of arcs and bands. A transparent overlapping platelet (mosaic) texture of S_E phase appears grey-blue to yellowish in color under crossed polarizers.\(^9,^{11}\)
Figure 3.9  Texture of $S_E$ phase exhibiting focal conic defects with striations. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 96, page 203, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

**Smectic F ($S_F$)**

The $S_F$ phase is identified by broken fan shaped (Figure 3.10),\(^9\) schlieren and mosaic texture (Figure 3.11),\(^11\) with sharper lines of discontinuity at the edges of its platelet areas. The fan texture exhibited by the $S_F$ phase is very different from those of the other tilted smectics which also form broken fan textures. The characteristic fan shaped structure of the $S_F$ phase exhibits elongated 'L'-shaped patterns across the backs of the fans.\(^9,11\)
Figure 3.10  Broken fan-shaped texture of S_F phase. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 91D, page 200, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

Figure 3.11  The paramorphotic schlieren-mosaic texture of S_F phase. (Gray, G.W., Goodby J.W.R., *Smectic Liquid Crystals Textures and Structures*, Plate 36, Leonard Hill Publication, 1984).
**Smectic G (S\(_G\))**

The smectic G (S\(_G\)) phase exhibits the natural mosaic texture (Figure 3.12). The paramorphotic texture of S\(_G\) phase formed from S\(_B\) phase on cooling, shows an arced, broken, focal-conic fan texture (Figure 3.13),\(^{11}\) and a weakly colored mosaic texture. S\(_G\) phase obtained by cooling a S\(_C\) or a S\(_F\) phase then the fan texture with a checkerboard appearance.\(^{9,11}\)

![Figure 3.12](image)

**Figure 3.12** The natural mosaic texture of S\(_G\) phase. (Gray, G.W., Goodby J.W.R., Smectic Liquid Crystals Textures and Structures, Plate 43, Leonard Hill Publication, 1984).
Figure 3.13  Paramorphotic broken focal-conic fan texture of S_G phase. (Gray, G.W., Goodby J.W.R., Smectic Liquid Crystals Textures and Structures, Plate 45, Leonard Hill Publication, 1984).

Smectic H (S_H)

The paramorphotic texture of the smectic H (S_H) phase shows fan and mosaic textures (Figure 3.14) with small platelet areas having splintered or 'crinkled' borders. S_H phase can also be identified by the platelet regions with cross-hatched 'zig-zag' lines or grainings.⁹,¹¹
Figure 3.14  The mosaic texture of S_{H} phase. (Gray, G.W., Goodby J.W.R., *Smectic Liquid Crystals Textures and Structures*, Plate 51, Leonard Hill Publication, 1984).

**Smectic I (S_{I})**

The smectic I (S_{I}) phase exhibits a broken focal-conic fan texture and the schlieren texture (Figure 3.15). S_{I} and S_{F} exhibit almost identical structures, however, the S_{I} phase exhibits typical schlieren structure arising from point singularities, while S_{F} shows schlieren areas crossed with mosaic lines, giving schlieren-mosaic texture.\(^9,^{11}\)
Biaxial Smectic A (S_{Ab})

The smectic A_{b} phase exhibits various textures depending on sub type (B_{1}, B_{2}, B_{3}, B_{4}, B_{6} and B_{7}) of the phase. The B_{1} phase exhibits a mosaic texture, however when cooled from the melt, it exhibits dendritic growth (Figure 3.16). The B_{2} phase exhibits focal conic and fan-like texture with striations across the fans (Figure 3.17). The B_{4} phase exhibits weak birefringence with intensive blue color (Figure 3.18). The B_{6} phase exhibits fan-like texture (Figure 3.19). The B_{7} phase exhibits growth of single and double spirals separating from isotropic melt (Figure 3.20).

Figure 3.15  The mosaic texture of S_{I} phase. (Gray, G.W., Goodby J.W.R., Smectic Liquid Crystals Textures and Structures, Plate 79, Leonard Hill Publication, 1984).
Figure 3.16  Dendritic growth of B₁ phase. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 108, page 208, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

Figure 3.17  Focal conic-like texture of B₂ phase. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 110, page 209, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
Figure 3.18  Blue texture of B₄ phase. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 113, page 210, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

Figure 3.19  Blue texture of B₆ phase. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 114, page 211, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
Figure 3.20  Single or double spirals separating from isotropic melt of B7 phase. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 115, page 211, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

**Smectic C\(_A\) (S\(_{CA}\))**

The homeotropically arranged S\(_{CA}\) sample exhibit schlieren textures with singularities of \(S = \pm \frac{1}{2}, \pm 1, \pm \frac{3}{2}, \pm 2\) and perhaps higher strength (Figure 3.21).\(^{42}\) Singularities with \(S = \pm \frac{1}{2}\) are “dispirations”, formed when a wedge dislocation and a screw dislocation combine.\(^{43}\) The S\(_{CA}\) phase also exhibits high birefringence and various schlieren textures. Its schlieren texture exhibits point singularities having two, four, six, or eight dark brushes. These are distinct from those of the S\(_C\) phase, which exclusively show four singularities. Nematic phases exhibit two and four brush singularities, but seldom show higher strength singularities, which are high energy defects in a nematic.
Figure 3.21  Schlieren texture of $S_{CA}$ phase$^{42}$

**Cholesteric Phases**

The cholesteric phases arising from chiral mesogens exhibit “oily streak” texture (Figure 3.22) under planar anchoring conditions. Under homeotropic anchoring conditions, the cholesteric phase exhibits a fingerprint texture from which cholesteric pitch can be calculated distance between the dark lines. The cholesteric phases also exhibit typical Grandjean steps (Figure 3.23), which can be used to determine the value of cholesteric pitch$^{9}$.
**Figure 3.22** Oily streaks texture of cholesteric phase. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 16, page 173, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

**Figure 3.23** Cholesteric phase exhibiting Grandjean steps. (Ingo Dierking, *Textures of Liquid Crystals*, Plate 26, page 176, 2003. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
X-ray Diffraction

X-ray diffraction methods are used for the determination of molecular packing and extent of order in liquid crystalline materials, which are deduced from layer and molecular spacing and correlation lengths. Generally, liquid crystalline polymers studied are of the polydomain type, which exhibit one or more concentric scattering rings. However, polymers and elastomers are easily aligned by drawing or uniaxial extension, which can provide valuable clues to the nature of LC ordering.

The unoriented diffraction pattern of nematic LCPs exhibits a diffuse scattering ring which represents intermolecular correlation, while smectic LCPs exhibit a diffuse outer ring and a sharp inner ring which corresponds to the layer spacing. The X-ray pattern of an oriented nematic polymer is as shown in Figure 3.24.

![Figure 3.24](image)

**Figure 3.24** Schematic of the X-ray diffraction pattern for an oriented nematic phase.

X-ray diffraction pattern of an unoriented S_A phase shows the outer diffuse ring (as lateral packing within the layers is disordered) characteristic of the spacing between mesogens within smectic layers and a sharp inner ring characteristic of lamellar spacing as shown in Figure 3.25. Wide angle reflections lie on the equator indicating that
mesogens are aligned vertically while small angle diffractions lie along meridian indicating layers are horizontal.

![Diagram of X-ray diffraction pattern](Image)

**Figure 3.25** Schematic of the X-ray diffraction pattern for an oriented smectic A phase.\textsuperscript{45}

The X-ray diffraction pattern of an unaligned smectic S\textsubscript{B} phase shows a sharp outer ring and a distinct inner ring.\textsuperscript{11} Aligned samples of S\textsubscript{B} phase exhibits small angle pattern similar to S\textsubscript{A} phase however, wide angle diffraction pattern (Figure 3.26) exhibits sharper arcs along the equator, exhibiting the long range positional order of mesogens in the two dimensions.
The X-ray diffraction pattern of an unaligned SC is similar to that of the smectic A phase exhibiting a sharp inner and a diffuse outer ring, due to one dimensional ordering of the molecules within the layers. As molecules are tilted, the layer spacing is smaller than the molecular length.\textsuperscript{11} Aligned sample of SC phase (Figure 3.27) exhibits wide angle diffraction on the equator, indicating mesogens are aligned vertically, however, low angle diffractions are disposed along axis on either side of meridian indicating that the layers are tilted.

\textbf{Figure 3.27}  Schematic of the X-ray diffraction pattern for an oriented smectic C phase.\textsuperscript{45}
SA, SB and SE are normal phases while SC, SF, SG, SH, and SI are tilted phases. The order of smectic phase sequence from cooling an isotropic melt is\textsuperscript{9,46}

\textit{SA \textbf{-} SC \textbf{-} SB \textbf{-} SI \textbf{-} SF \textbf{-} SG \textbf{-} SE \textbf{-} SH}

The degree of order increases from left to right in the above series.

The X-ray diffraction pattern of an unaligned SD phase shows an outer diffuse ring. Aligned SD phase may show interference patterns at low Bragg angles.\textsuperscript{11} The X-ray diffraction pattern of ordered SE, SI, SG and SH phases exhibit an inner ring and a number of sharp outer rings.\textsuperscript{11,46} SB exhibits a single sharper ring.

Depending upon arrangement of mesogens within layers, X-ray diffraction pattern as shown in Figure 3.28 is observed.\textsuperscript{47}
Figure 3.28  X-ray diffraction patterns of various mesogenic arrangements.47 (Adopted from work of Kricheldorf, H. R.; Probst, N.; Wutz, C. Macromolecules 1995, 28, 7990-7995.)
Figure 3.29 The X-ray diffraction pattern for a $S_C$ polymer network. (Semmler, K.; Finkelmann, H. *Macromol Chem Physic* 1995, 196, 3197-3208).48

Figure 3.29 exhibits splitting of low angle smectic peaks into four peaks, indicating $S_C$ phase.48 The $S_C$ phase exhibiting chevron-like layering is demonstrated by Rousseau et al.49 Braun et al.50 have synthesized F3-PPT-H and F4-PPT-H polymers similar to that in the present study. Based upon existence of inner sharp rings, these polymers were identified as having smectic phases, however these polymers were not characterized further.

$S_{CA}$ phase can be identified from the fiber X-ray diffraction pattern, as it exhibits two characteristic reflections as shown in Figure 3.30. The inner sharp reflection appearing on meridian indicates that the layers are oriented perpendicular to the polymer chain axis. The wide angle reflection splits into two reflections above and below the
equator, indicating that the mesogens with their long axes are tilted with respect to the layer normal and the polymer chain axis.

![X-ray diffraction pattern for an oriented SCA phase.](image)

**Figure 3.30** X-ray diffraction pattern for an oriented SCA phase. (Tokita, M.; Osada, K.; Watanabe, J. *Liq Cryst* **1998**, *24*, 477-480).  

### 3.2 Experiments

#### 3.2.1 Polarized Light Optical Microscopy (POM)

Samples were characterized via orthoscopic observation between crossed polarizers in an Olympus BX51 microscope with UMPlanFL 5x, 20x, or 100x objectives. Two sets of samples were prepared. The first set was prepared by spin casting solution of 3 - 4 mass % polymers in dichloromethane at 5000 rpm. These samples were dried at ambient temperature in vacuum oven for 3 days prior to characterization by optical microscopy. The second set was prepared by depositing films of linear polymers (irregular thickness, typically 1 to 10 µm) on a glass slide by evaporation from a
1.0 mass % solution of acetone or dichloromethane. After air-drying, each sample was annealed on an Instec HS400 hot stage at a temperature (1 °C to 5 °C) above its clearing temperature for 12 h to ensure removal of residual solvent, then ramp-cooled at 2 °C / h until a well-defined optical texture was observed at a final temperature (as specified in the text). No cover slips were used. In some cases, annealing was conducted instead, followed by quick cooling to a specific temperature (where indicated in text). Images were recorded using a 2.0 megapixel Diagnostic Intruments model # 11.2 Color Mosaic digital camera equipped with Spot™ digital imaging software.

3.2.2 Differential Scanning Calorimetry (DSC)

A Seiko Instruments DSC 220 CU equipped with a liquid nitrogen cooling tank was used to characterize thermal transitions in fractionated linear polymers. After crimping 3 to 7 mg of polymer into a TA Instruments aluminum pan, a standard thermal treatment was applied. Samples were first heated above their clearing (isotropization) temperatures to erase previous thermal history, then cooled quickly to 22 °C and allowed to equilibrate for 3 days. DSC heating traces were recorded by initially cooling to -30 °C, then applying a heating ramp at 10 °C/min under a flowing N₂ atmosphere. Indium was used as a calibration standard for both the temperature and heat flow scales. Transition temperatures (T₂, Tᵢ) reported were taken as the temperature at which the peak of the endotherm was observed at a heating rate of 10 °C/min.; uncertainty in the peak position was ± 2 °C or less based upon multiple runs. DSC traces also exhibited the typical inflection associated with the glass transition (T₅), and values reported in Table 3.1 are based upon the midpoint of the inflection at the chosen heating rate.
3.2.3 Wide-Angle X-ray Diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) experiments were performed on samples of 0.5 to 1 mm thickness in transmission using a Rigaku D/MAX Rapid II instrument equipped with graphite monochromator, 300 µm pinhole collimator, and CuK$_\alpha$ source ($\lambda = 1.5418$ Å). Unoriented linear polymers were characterized in transmission after being subjected to the same thermal treatment as the samples studied by DSC. Corrections for polarization and oblique incidence were applied to raw data using Rigaku AreaMax software. No corrections were applied for background scattering or instrumental broadening. Diffractometer scans (intensity vs. 2$\theta$) were obtained by circular averaging of intensity over a range of ($2^\circ \leq 2\theta \leq 30^\circ$). Azimuthal scans (intensity vs. $\chi$) were recorded by averaging the diffracted intensity over a finite interval $\Delta(2\theta)$, which is specified for each sample in the relevant figure captions. Calculated $d$-spacings for smectic layering were estimated by applying the Bragg relationship ($n\lambda=2d\sin\theta$) to the 1st order ($n=1$) layering reflection, based upon the value of (2$\theta$) at which peak intensity was observed. Experimental uncertainty in the calculated $d$-spacings is $\pm 1.0$ Å based upon observations from multiple measurements.

Diffraction patterns for oriented F3-PPT-CH$_3$ were obtained by drawing the sample at room temperature (22 °C). WAXD experiments were conducted immediately thereafter, as well as 2 d and 16 d after stretching. An additional WAXD pattern was obtained after heating this sample to 65 °C. Diffraction patterns for oriented F3-PPT-H were obtained after drawing the sample at 70 °C, allowing 10 minutes at 70 °C, and cooling to 22 °C. An additional WAXD pattern was obtained after re-heating this sample to 100 °C.
3.3 Results

3.3.1 Thermal Behavior: (DSC)

Figure 3.31 and 3.32 represent DSC heating traces for F3-copolymers and F4-copolymers, respectively. In each heating trace, the endotherm designated $T_i$ is the clearing temperature, which corresponds to liquid crystalline to isotropic transition observed in the microscope. In addition, all heating traces exhibit an underlying endotherm (designated $T_2$), due to a transition between liquid crystalline mesophases and an inflection associated with the glass transition, $T_g$. The values of $T_g$ (the midpoint of the inflections), $T_2$ and $T_i$ are reported in the Table 3.1. Cooling traces for some copolymers exhibited an exotherm at a temperature slightly below $T_i$, corresponding to rapid formation of the mesophase, while other cooling traces were poorly defined or featureless.

The thermal transition temperatures and the thermal stability of the liquid crystalline phases are affected by the steric and the dipolar effects of the substituents. In this study, $T_i$ is clearly influenced by the substituents on the aromatic rings of the mesogens, which vary in size, polarity, and structural isomerism. Comparing the -H substituted copolymers to those having larger ring substituents, it appears that placing substituents on the aromatic rings generally lower the value of $T_i$. The depression of $T_i$ with increasing substituent size is well-known in main-chain LCP,\textsuperscript{52,53} and is thought to arise from decreasing the length:diameter ratio and linearity of the mesogens.\textsuperscript{54} An apparent exception to this trend is the thermal behavior observed for F3-PPT-C(CH$_3$)$_3$
and F4-PPT-C(CH$_3$)$_3$ which have endotherms near 125 °C and 128 °C, respectively, a point to be discussed after considering WAXD data.

**Figure 3.31**  DSC traces for copolymers prepared with F3 siloxane spacers.
Figure 3.32  DSC traces for copolymers prepared with F4 siloxane spacers.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g(\degree C)$</th>
<th>$T_m(\degree C)$</th>
<th>$T_i(\degree C)$</th>
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<tr>
<td>F3-PPT-COCH$_3$</td>
<td>-1</td>
<td>31</td>
<td>61</td>
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<tr>
<td>F3-PPT-Cl</td>
<td>7</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>F3-PPT-H</td>
<td>0</td>
<td>52</td>
<td>130</td>
</tr>
<tr>
<td>F3-PPT-CH$_3$</td>
<td>5</td>
<td>30</td>
<td>72</td>
</tr>
<tr>
<td>F3-PPT-OCH$_3$</td>
<td>2</td>
<td>36</td>
<td>45</td>
</tr>
<tr>
<td>F3-PPT-C(CH$_3$)$_3$</td>
<td>-2</td>
<td>-</td>
<td>125*</td>
</tr>
<tr>
<td>F4-PPT-COCH$_3$</td>
<td>0</td>
<td>46</td>
<td>49</td>
</tr>
<tr>
<td>F4-PPT-Cl</td>
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<td>52</td>
</tr>
<tr>
<td>F4-PPT-H</td>
<td>-1</td>
<td>23</td>
<td>89</td>
</tr>
<tr>
<td>F4-PPT-CH$_3$</td>
<td>-8</td>
<td>9</td>
<td>37</td>
</tr>
<tr>
<td>F4-PPT-OCH$_3$</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F4-PPT-C(CH$_3$)$_3$</td>
<td>13</td>
<td>-</td>
<td>128**</td>
</tr>
</tbody>
</table>

* additional endotherms observed at 44 °C and 89 °C.

** additional endotherm observed at 33 °C.

**Table 3.1** Comparison of transition temperatures in F3 and F4 copolymers.
3.3.2 Polarized Light Optical Microscopy (POM)

Optical birefringence textures were observed at ambient temperature (22 ± 2 °C) in thin films deposited from solution. F3-PPT-COCH₃, F3-PPT-H, F3-PPT-Cl, and F3-PPT-CH₃ developed marked optical birefringence with a well-defined threaded texture immediately after spin-coating. Figures 3.33-3.35 show optical birefringence micrographs (1000x) of the textures found in three of the copolymers after three weeks of equilibration at ambient temperature. The characteristic threaded texture consists of interwoven, dark disclinations that differ from the dark brushes of the schlieren texture observed in nematic liquid crystalline polymers. The texture observed was not strongly affected by the molar mass of the fraction studied, although low molar mass fractions of a given copolymer developed well-defined textures more quickly than high molar mass fractions. F4-PPT-COCH₃, F4-H-PPT, F4-PPT-Cl, and F4-PPT-CH₃ developed threaded textures much like the corresponding F3 copolymers, but generally at a slower rate. For example, the F4-PPT-H copolymer gradually became birefringent after several weeks at 22 °C, in contrast to the F3-PPT-H copolymer, which formed the threaded texture almost immediately. F3-PPT-OCH₃ initially appeared amorphous at 22 °C, but heating to 47 °C rapidly produced the familiar threaded texture. F4-PPT-OCH₃ appeared to be amorphous and did not form the threaded texture at any temperature. F3-PPT-C(CH₃)₃ initially appeared amorphous at 22 °C, but slowly developed the threaded texture after several months.
Figure 3.33  Optical birefringence micrographs of spin-coated samples F3-COCH₃ copolymer after three weeks of equilibration at ambient temperature (fraction 5).

Figure 3.34  Optical birefringence micrographs of spin-coated samples F3-Cl copolymer after three weeks of equilibration at ambient temperature (fraction 2).
Copolymers were also studied after heating to an elevated temperature and cooling from the melt. Upon heating, all copolymers exhibited a temperature at which optical birefringence disappeared (isotropization temperature, $T_i$). After melting above $T_i$, samples were cooled by placing in a pre-heated hot stage held at fixed equilibration temperature $T_e$. Figure 3.36-3.38 shows the textures observed in the F3-PPT-H copolymer ($T_i = 125 \, ^\circ C$), after 15 minutes of equilibration at $T_e = 60 \, ^\circ C$, $T_e = 100 \, ^\circ C$, and $T_e = 120 \, ^\circ C$. As the chosen value of $T_e$ approached $T_i$, the threaded texture coarsened and became inhomogeneous, and the density of disclinations decreased. Coarsening of the texture was also noted with increasing time at a fixed $T_e$, suggesting that annihilation of disclinations occurred (all values of $T_e$ were well above the glass transition temperatures determined by DSC).
Figure 3.36  Optical birefringence micrographs of melted and cooled F3-H copolymer (fraction 1), T_c=60 °C.

Figure 3.37  Optical birefringence micrographs of melted and cooled F3-H copolymer (fraction 1), T_c=100 °C.
Interestingly, F3-PPT-Cl, F3-PPT-C(CH₃)₃, and F4-PPT-C(CH₃)₃ formed quasi-spherulitic fan textures at when ramp cooled at 2 °C/hr, to a temperature below their respective isotropization temperatures, as shown in Figures 3.39-3.41.
Figure 3.39 Optical birefringence micrographs of ramp cooled (2°C/hr.) F3-PPT-C(CH$_3$)$_3$ copolymer at 90 °C.

Figure 3.40 Optical birefringence micrographs of ramp cooled (2°C/hr.) F4-PPT-C(CH$_3$)$_3$ copolymer at 90 °C.
**Figure 3.41** Optical birefringence micrographs of ramp cooled (2°C/hr) F3-PPT-Cl copolymer.

### 3.3.3 Wide-Angle X-ray Diffraction (WAXD)

WAXD measurements on unoriented linear polymers were conducted at 22 °C and (2° < 2θ < 30°) in transmission. Linear polymers were subjected to the same thermal history as the samples studied by DSC. Diffraction patterns for all linear polymers exhibited a strong, sharp reflection at 2θ ≈ 3° assigned to smectic layering, a weaker 2nd order reflection, and one or more diffuse halos at higher 2θ as shown in Figures 3.42-3.53. 1 dimensional diffractograms of F3-copolymers and F4-Copolymers are shown in Figures 3.54-3.55. Calculated d-spacings for the smectic layers at 22 °C are presented in Table 3.2; each polymer was below its respective T<sub>2</sub>. F3-PTP-COCH<sub>3</sub>, F3-PTP-C(CH<sub>3</sub>)<sub>3</sub>, and F3-PTP-Cl showed some evidence of three-dimensional ordering,
suggesting that their higher order smectic phases are nearly crystalline. In contrast, F3-PTP-H, F3-PTP-CH₃, and F3-PTP-OCH₃ appeared less highly ordered below T₂.

**Figure 3.42**  Diffraction pattern for an unoriented F3-PPT-COCH₃ at 22 °C after three weeks of equilibration at ambient temperature.
Figure 3.43  Diffraction pattern for an unoriented F3-PPT-Cl at 22 °C after three weeks of equilibration at ambient temperature.

Figure 3.44  Diffraction pattern for an unoriented F3-PPT-H at 22 °C after three weeks of equilibration at ambient temperature.
Figure 3.45  Diffraction pattern for an unoriented F3-PPT-CH$_3$ at 22 °C after three weeks of equilibration at ambient temperature.

Figure 3.46  Diffraction pattern for an unoriented F3-PPT-OCH$_3$ at 22 °C after three weeks of equilibration at ambient temperature.
**Figure 3.47** Diffraction pattern for an unoriented F3-PPT-C(CH₃)₃ at 22 °C after three weeks of equilibration at ambient temperature.

**Figure 3.48** Diffraction pattern for an unoriented F4-PPT-COCH₃ at 22 °C after three weeks of equilibration at ambient temperature.
Figure 3.49  Diffraction pattern for an unoriented F4-PPT-Cl at 22 °C after three weeks of equilibration at ambient temperature.

Figure 3.50  Diffraction pattern for an unoriented F4-PPT-H at 22 °C after three weeks of equilibration at ambient temperature.
Figure 3.51  Diffraction pattern for an unoriented F4-PPT-CH$_3$ at 22 °C after three weeks of equilibration at ambient temperature.

Figure 3.52  Diffraction pattern for an unoriented F4-PPT-OCH$_3$ at 22 °C after three weeks of equilibration at ambient temperature.
**Figure 3.53**  Diffraction pattern for an unoriented F4-PPT-C(CH$_3$)$_3$ at 22 °C after three weeks of equilibration at ambient temperature.
Figure 3.54  WAXD data for F3 copolymers at 22 °C after three weeks of equilibration at ambient temperature.
Figure 3.55  WAXD data for F4 copolymers at 22 °C after three weeks of equilibration at ambient temperature.
WAXD patterns of oriented linear polymers of F3-PTP-COCH3, F3-PTP-Cl, F3-PTP-OCH3 and F3-PTP-C(CH3)3 are compared in Figure 3.56. F3-PTP-OCH3 and F3-PTP-COCH3 exhibit predominantly parallel orientation of smectic layer normals with respect to the axis of extension, whereas F3-PTP-Cl exhibits a perpendicular orientation similar to F3-PTP-H. F3-PTP-Cl formed its higher order smectic structure during the short time allowed after elongation, but F3-PTP-C(CH3)3 was poorly oriented and did not form a highly ordered structure due to slow ordering kinetics at room temperature. Ring-
substitution clearly affects the structure of the higher order smectic state below $T_2$, the texture of the smectic phase, and the alignment of smectic layers after uniaxial extension, although it is not clear that any simple rationalization is possible based upon the size and polarity of the substituents.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$d$ (Å)</th>
<th>Polymer</th>
<th>$d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F3-PPT-COCH$_3$</td>
<td>32*</td>
<td>F4-PPT-COCH$_3$</td>
<td>29*</td>
</tr>
<tr>
<td>F3-PPT-Cl</td>
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<td>F4-PPT-Cl</td>
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<td>29.8</td>
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<td>30*</td>
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<td>-</td>
<td>F4-PPT-C(CH$_3$)$_3$</td>
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</tbody>
</table>

Table 3.2  Calculated $d$-spacings of smectic layers at 22 °C, from value of $2\theta$ at peak intensity. "*" denotes approximate value of $d$-spacing from broad peak. Uncertainties in values are otherwise estimated as ± 1.0 Å.

3.4 Discussion

It was observed that F3-PPT-COCH$_3$ and F4-PPT-COCH$_3$ degrade in air above 50 °C. F3-PPT-OCH$_3$ and F4-PPT-OCH$_3$ have very narrow smectic phase stability. F3-PPT-Cl, F4-PPT-Cl, F3-PTP-C(CH$_3$)$_3$ and F4-PTP-C(CH$_3$)$_3$ exhibit higher order smectic phases or crystallize, which needs to be examined further in future work.
F4-PTP-H and F4-PTP-CH$_3$ exhibit lower mesophase stability compared to F3-PTP-H and F3-PTP-CH$_3$, respectively. Therefore F3-PTP-H and F3-PTP-CH$_3$ copolymers are characterized and discussed further as these polymers present the best opportunity to prepare elastomers with simple smectic phases.

Figure 3.57 presents DSC heating traces for F3-PPT-H and two samples of F3-PPT-CH$_3$ of differing molar mass. The low molar mass sample of F3-PPT-CH$_3$ (M$_w$ = 11 kg mol$^{-1}$) did not have a detectable T$_2$ transition, although an endotherm was detected in the high molar mass sample (M$_w$ = 77 kg mol$^{-1}$) near T$_2$ $\approx$ 30 °C. The measured glass transition temperatures (T$_g$) of F3-PPT-H and F3-PPT-CH$_3$ were each (8 °C ± 2 °C), based on the midpoint of the inflections observed. F3-PPT-H therefore had a substantially larger temperature range between T$_g$ and T$_i$ (≈122 °C) compared to F3-PPT-CH$_3$ (≈64 °C).
After quick cooling from the isotropic melt to any temperature below $T_i$, both F3-PPT-H and F3-PPT-CH$_3$ developed a dense threaded texture with numerous intertwining disclinations (Figure 3.58). Slow ramp-cooling (2 °C/hr.) from the melt produced either schlieren textures with dark brushes emanating from point singularities (Figures 3.59-3.61) or "domain" textures (Figure 3.61-3.62). Schlieren and domain textures could be observed
in different regions within the same sample, due to local differences in thickness and/or orientation. The defect textures formed above $T_2$ persisted upon cooling below $T_2$, with only subtle changes in birefringence colors.

Figure 3.58  Polarized light optical micrographs of threaded texture in F3-PPT-H ($M_w = 85 \text{ kg mol}^{-1}$) quickly cooled to 100 °C from the melt.
**Figure 3.59**  Polarized light optical micrographs of schlieren texture in F3-PPT-H cooled to 100 °C at 2 °C/h from the melt.

**Figure 3.60**  Polarized light optical micrographs of schlieren texture in F3-PPT-CH₃ (Mₚ = 11 kg mol⁻¹) cooled at 2 °C/h to 50 °C from the melt.
Figure 3.61  Polarized light optical micrographs of schlieren and threaded textures in F3-PPT-CH₃ ($M_w = 77 \text{ kg mol}^{-1}$) at 22 °C.

Figure 3.62  Polarized light optical micrographs of domain texture in F3-PPT-CH₃ ($M_w = 11 \text{ kg mol}^{-1}$) at 22 °C.
Figure 3.63  Polarized light optical micrographs of "caterpillar" domain texture in F3-PPT-H at 22 °C.

Schlieren textures can signify either nematic or smectic ordering, and distinguishing between these phases requires closer examination of the singularities observed, in addition to information from X-ray diffraction. Figures 3.60 and 3.61 depict point singularities having two, four, six, or eight dark brushes in F3-PPT-CH3 samples of low and high molar mass. The presence of numerous singularities having more than four brushes is not expected for a nematic phase, as the defect energy scales as $s^2$, where $s$ is the strength of the singularity, equal to $(1/4)$·(number of brushes). (We note that Zhou et al. have observed high-strength disclinations in nematic polymers with "two dimensional" mesogens, however). Figure 3.59 shows the schlieren texture in F3-PPT-H, where point singularities have predominantly two or four brushes. The $S_C$ phase can be ruled out in both F3-PPT-H and F3-PPT-CH3, as the $S_C$ schlieren texture exhibits singularities with exclusively four brushes. The $S_A$ phase also seems
unlikely, as broken fan or homeotropic textures are normally observed.\textsuperscript{58,59} There are at least two known smectic phases that exhibit textures consistent with Figures 3.59 and 3.60. One possibility is the $S_{CA}$ phase, a layered mesophase in which mesogens in adjacent layers tilt in an alternating sense with respect to the layer normals. The $S_{CA}$ phase has been identified in both low molar mass liquid crystals\textsuperscript{60-62} and main-chain thermotropic polyesters,\textsuperscript{63-69} and its schlieren texture exhibits singularities having both two and four brushes. Tokita and Watanabe have recently discussed the nature of defects associated with the two-brush ($s=\pm 1/2$) singularities in $S_{CA}$, main-chain polyesters.\textsuperscript{69} A second possibility is the biaxial smectic-A ($S_{AB}$) phase, which may be indistinguishable from the $S_{CA}$ phase by POM.\textsuperscript{70} However, $S_{AB}$ ordering seems unlikely, as it is rarely found in polymers,\textsuperscript{71} and is usually associated with bent-core mesogens in low molar mass liquid crystals.\textsuperscript{70,72-74}

The "domain" textures in F3-PPT-H (Figure 3.62) and F3-PPT-CH$_3$ (Figure 3.63), which are stable both above and below the respective $T_2$ transition temperatures, suggest smectic ordering rather than nematic. The sharply focused, dark boundaries of the domains are not consistent with nematic textures. The elongated domains in F3-PPT-CH$_3$ exhibit faint, zero-birefringence lines through their approximate mid-sections at room temperature (Figure 3.63). Upon rotation of the sample stage, an elongated domain passes through extinction positions when the long axis of the domain is parallel to either the polarizer or the analyzer, indicating that the optic axis of the domain is equivalent to its long dimension. It is possible that the domains and the four-brush defects in Figure 3.62 are the same defect structures observed with different orientations. The four-brush singularities may correspond to domains that are oriented with the optic
axis perpendicular to the glass slide, whereas the elongated domains could be similar structures having parallel alignment. A markedly different domain texture was observed in F3-PPT-H, especially in thinner regions of the sample, which we named the "caterpillar" texture (Figure 3.63). This texture was characterized by elongated domains, some of which developed numerous transverse dark bands upon cooling. The alternating dark and light bands indicate different orientations of the director with respect to the substrate, with dark bands corresponding to perpendicular alignment. The mechanism of formation of the caterpillar domains and the details of their molecular-level organization merit further investigation.

**X-Ray Diffraction**

F3-PPT-H and F3-PPT-CH$_3$ samples were also characterized in bulk by WAXD at different temperatures. WAXD measurements on unoriented linear polymers (Figure 3.64) were first conducted at room temperature, which is below the T$_2$ transition of each polymer. Both polymers exhibited a low-angle Bragg peak, centered at $2\theta = 3.16^\circ$ ($d = 28.0$ Å) for F3-PPT-H and at $2\theta = 3.15^\circ$ ($d = 28.0$ Å) for F3-PPT-CH$_3$. (Note the log$_{10}$(intensity) scale in Figure 3.64). The presence of a low-angle Bragg peak indicates well-defined positional ordering (layering), so the mesophases occurring below T$_2$ are smectic. Besides the layering peak, a weak 2$^{nd}$ order reflection and two diffuse halos at wide angles were observed in each polymer at $22$ °C (halos centered at approximately $2\theta \approx 13.5^\circ$, 19.5° for F3-PPT-H; $2\theta \approx 13.5^\circ$, 17.5° for F3-PPT-CH$_3$). The presence of two diffuse halos indicates that there are two separate characteristic spacings between the mesogens within smectic layers. Figure 3.64 also compares the diffracted intensity in the
low-angle region for F3-PPT-H and F3-PPT-CH$_3$ at different temperatures above and below their respective $T_2$ transitions. In both cases, the strong layering reflection is still present above $T_2$, confirming that the mesophases above $T_2$ are also smectic phases. Above $T_2$, the $d$-spacing increases only slightly for F3-PPT-CH$_3$ and remains about the same for F3-PPT-H, whereas the wide-angle halos weaken somewhat and broaden, especially for F3-PPT-H. These changes indicate that mesogens gain rotational and/or translational degrees of freedom within the smectic layers above $T_2$, with relatively little change in inter-layer spacing.

**Figure 3.64** Diffracted X-ray intensity vs. $2\theta$ for unoriented F3-PPT-H ($M_w = 85$ kg/mol) and F3-PPT-CH$_3$ ($M_w = 77$ kg/mol) above and below their respective $T_2$ temperatures.
Oriented samples of linear polymers were drawn in the smectic state (refer to Experimental section) and characterized by WAXD. Figure 3.65 shows integrated intensity vs. azimuthal angle ($\chi$), for the low-angle reflection (integrated over $2.5^\circ \leq 2\theta \leq 3.8^\circ$) and the outer wide-angle halo (integrated over $18^\circ \leq 2\theta \leq 22^\circ$) for F3-PPT-H. Well-defined maxima are observed in the low-angle reflection at $(\chi = -90^\circ, 90^\circ)$. The wide-angle halo exhibits four weak maxima at approximately $(\chi = -45^\circ, 45^\circ, 135^\circ, 225^\circ)$. This diffraction pattern is consistent with a S$_{CA}$ phase having a "bookshelf" arrangement of layers, in which the smectic layer normals are predominantly oriented perpendicular to the axis of extension, and mesogens are tilted by about $45^\circ$. 
**Figure 3.65** Diffracted X-ray intensity vs. azimuthal angle ($\chi$) at 22 °C for uniaxially drawn F3-PPT-H linear polymer. The axis of extension lies along $\chi = (0^\circ, 180^\circ)$.

(a) Intensity of low-angle reflection integrated over ($2.7^\circ \leq 2\theta \leq 3.7^\circ$). (b) Intensity of wide-angle halo integrated over ($18^\circ \leq 2\theta \leq 22^\circ$). Data near/behind beamstop are omitted for clarity.
A schematic diagram of the oriented mesophase in F3-PPT-H is shown in Figure 3.66. The chain axis is presumed to be parallel to the layer normals, with the zig-zag tilting of mesogens in adjacent layers that characterizes the $S_{CA}$ state. This model requires the supposition that the chain axes are aligned predominantly perpendicular to the axis of elongation after stretching. However, this "anomalous" alignment of smectic layer normals perpendicular to the axis of elongation is not unusual for drawn smectic main-chain LCP, including those that form a $S_{CA}$ phase. Watanabe et al. suggest that the alignment of the chain axes perpendicular to the axis of elongation could indicate the formation of smectic domains, in which irregular chain folding (hairpin formation) occurs. The domains are thought to slide past one another during elongation, such that their long dimension is aligned with the axis of elongation, while the layer normals (and chain axes) assume the perpendicular orientation. The development of normal (parallel) alignment vs. anomalous (perpendicular) alignment of smectic layer normals with respect to the drawing direction is known to depend on both the strain rate and temperature. We did not attempt to control the strain rate in this study, but the anomalous layer alignment was always obtained for F3-PPT-H under the conditions employed.
Figure 3.66  Diffraction patterns at two temperatures and illustration of $S_{CA}$ ordering with anomalous layer orientation in uniaxially drawn F3-PPT-H. Double-ended arrows designate the axis of extension.
Figure 3.65 also compares diffraction patterns for drawn F3-PPT-H at temperatures above and below its T_2 transition (52 °C). All intensity maxima noted at 22 °C are still present at 100 °C, but the wide-angle halos are significantly broadened at 100 °C. Little change in the tilt angle of the mesogens, if any, is seen upon passing T_2, and changes in the inter-layer d-spacings are also minimal. Based on this evidence, and recalling that the optical textures observed by POM were nearly indistinguishable above and below T_2, we concluded that the phase below T_2 is a higher order smectic state that is structurally similar to the S_{CA} phase. The T_2 transition therefore appears to represent a significant change in chain dynamics, rather than a structural transformation. Chains may undergo a reduction in conformational entropy upon cooling below T_2, as mesogens lose rotational and/or translational degrees of freedom, while the layered structure of the S_{CA} mesophase is essentially preserved.

The flow alignment observed in drawn F3-PPT-CH₃ (M_w=77 kg mol⁻¹) was markedly different (Figure 3.67). Judging by the wide-angle halo, the mesogens are aligned with the axis of elongation, but smectic layer normals are tilted. The separation of the low-angle reflection into four sharp maxima may indicate development of buckling instabilities in the layers similar to those observed in strained S_A liquid crystals\(^{79-81}\) and strained monodomain S_A elastomers.\(^{82}\) (The schematic illustration in Figure 3.66 may be somewhat oversimplified, as buckling instabilities may also generate some regions with disrupted ordering.)\(^{82}\)
Figure 3.67  Diffraction pattern for oriented F3-PPT-CH₃ (Mₙ = 77 kg mol⁻¹) immediately after uniaxial drawing at 22 °C, and illustration of buckled layer arrangement.

The diffraction pattern observed in oriented F3-PPT-CH₃ immediately after stretching was transient, relaxing over a period of several days at 22 °C to yield a new pattern consistent with a S_{CA} phase having the bookshelf arrangement of layers (Figure 3.68).
Figure 3.68  Observed diffraction patterns and illustration of $S_{CA}$ ordering with "bookshelf" layering in oriented F3-PPT-CH$_3$ ($M_w = 77$ kg mol$^{-1}$) 16 days after stretching at 22 °C, and after heating the same to 65 °C. Double-ended arrows designate the axis of extension.

Figure 3.69a depicts the convergence of the four maxima in the inner layering reflection to two peaks centered at $(\chi = 0^\circ, 180^\circ)$ after 16 d of relaxation at 22 °C.
Figure 3.69 Integrated intensity vs. azimuthal angle ($\chi$) for F3-PPT-CH$_3$ ($M_w = 77$ kg mol$^{-1}$) at $22$ °C immediately after stretching, after $2$ d relaxation, and after $16$ d relaxation. Top: low-angle reflection integrated over $(2.5^\circ \leq 2\theta \leq 3.8^\circ)$. Bottom: wide-angle reflection integrated over $(16^\circ \leq 2\theta \leq 19^\circ)$. The axis of extension lies along $\chi = (0^\circ, 180^\circ)$. Data near/behind beamstop are omitted for clarity. Data were rescaled by an arbitrary constant and shifted for ease in comparing line shapes.
Figure 3.69b illustrates the simultaneous resolution of the outer halo into four overlapping maxima after 16 days, due to tilting of mesogens with respect to the original axis of elongation. The azimuthal intensity distribution in Figure 3.69b (bottom curve) could be fit satisfactorily to a sum of two Lorentzian functions and a constant background (Figure 3.70). The center positions of the fitted Lorentzian functions indicate a mesogen tilt angle of approximately 25° with respect to the layer normals (in the relaxed state).

![Diffracted Intensity / AU vs Chi (degrees)](image)

**Figure 3.69** Fit of data from figure 3.69b (bottom curve, 16 d relaxation) to sum of two identical Lorentzian functions plus a constant background.

A proposed model for the structure of the oriented S\textsubscript{CA} mesophase in F3-PPT-CH\textsubscript{3} (after relaxation) is presented in Figure 3.67. The chain axes are oriented in the direction of flow, judging by the positions of the maxima in the low-angle layering reflection. The
parallel alignment of smectic layer normals was always observed in F3-PPT-CH₃, whereas the perpendicular alignment was always observed in F3-PPT-H under the drawing conditions employed here. Although our samples were drawn manually without controlling the strain rate, the orientations observed were repeatable after multiple measurements under similar conditions.

It is interesting to compare the thermal behavior of F3-PPT-H to the similar linear polymer having unsubstituted BHQ type mesogens, first characterized by Ringsdorf et al. in 1983 (structure 4a in Ref. 83), which differs only in the reversal of the ester bridges of the mesogens. The two polymers have virtually identical values of Ti, while Ringsdorf reports a crystallization endotherm at 35 °C that may be similar to our T₂ reported at 52 °C. Unfortunately, the glass transition temperature of the polymer with BHQ type mesogens and the nature of its smectic ordering are not characterized in Ref. 83.
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Chapter 4

Effects of Structural Imperfections on the Dynamic Mechanical Response of Main-Chain Smectic Elastomers

4.1 Introduction and Background

The classical picture of rubber elasticity\textsuperscript{1-5} in polymeric networks is based upon “model” networks which are considered to be ideal or free of structural defects, such as pendant (dangling) chains, loops and trapped entanglements. However, in real networks, such topological defects cannot be neglected, and determination of the number density of elastically effective chains becomes questionable. Elastic chains are those attached to the crosslink junctions at both the ends, while pendant chains are attached to crosslinker only at one end. Several studies\textsuperscript{6-9} examined the effect of structural imperfections on the mechanical and swelling properties of endlinked elastomers. However, the effects of network architecture on the dynamic mechanical response of LCEs have rarely been reported.\textsuperscript{10}

Clarke et al.\textsuperscript{11} observed mechanical loss factor (tan $\delta$) as high as 1.5 to 1.8 for siloxane and acrylate based side-chain nematic LCEs, over wide ranges of temperature and frequency. This high value of loss factor is associated with “soft elasticity”, resulting from internal relaxation of nematic director with zero or little elastic energy cost due to absence of entropy change. However, in the case of side-chain smectic elastomers, which pass into the isotropic state via a nematic state, values of the loss factor reported by the authors, vary from 0.3 to 0.8. These smaller values are associated with rigidity and the
restricting effects of smectic layers. Patil et al. reported higher value of loss factor in the case of main-chain LCEs near the clearing temperature. However, these MCLCEs pass from smectic state directly into isotropic state without passing through nematic state. This high value of loss factor might be due to the more direct coupling between backbone conformation and mesogen orientation in main-chain LCEs compared to side-chain LCEs. However, the possible role of architectural defects, such as pendant chains, in enhancing mechanical damping must be considered.

In order to study the effect of structural imperfections on the mechanical damping of smectic MCLCEs, LCEs with varying amount of structural imperfections are needed. Our work has produced “optimal” and “imperfect” networks having minimum and maximum concentration of topological defects, representing the first reported study of their influence on dynamic mechanical response, for LCE of either the side-chain or main-chain type.

Swelling of Networks

The equilibrium swelling of polymer networks predicted by Flory-Rehner model and the c* Theorem of de Gennes, are developed for ideal networks with no defects. In the thermodynamics of the swollen network system, the change in the Gibbs free energy ($\Delta G$) is replaced by the change in Helmholtz free energy ($\Delta A$), as the pressure-volume product does not change significantly in the swelling. When the network is swollen from the dry state to its equilibrium state, the resulting free energy change, ($\Delta A_{swelling}$), is expressed as.
\[ \Delta A_{\text{swelling}} = \Delta A_{\text{mixing}} + \Delta A_{\text{elastic}} \]  

(4.1)

where \( \Delta A_{\text{mixing}} \) arises from the mixing of polymer chains and solvent molecules, while the \( \Delta A_{\text{elastic}} \) term results from the change in the elastic free energy of the network upon isotropic dilation with the introduction of the solvent molecules. \( \Delta A_{\text{mixing}} \) is given by the Flory-Huggins model:

\[
\Delta A_{\text{mixing}} = kT \left( n_1 \ln \nu_1 + n_2 \ln \nu_2 + \chi n_1 \nu_1 \right)
\]

(4.2)

where, \( n_1 \) and \( n_2 \) are the numbers of solvent and polymer molecules, \( \nu_1 \) and \( \nu_2 \) are the solvent and polymer volume fractions, respectively, and \( \chi \) is the interaction parameter. For a cross-linked network, \( n_2 = 1 \).  

If a rubber network with undeformed dimensions \( L_{x0}, L_{y0}, \) and \( L_{z0} \), undergoes deformation in \( x, \) and \( z \) directions by the factors \( \lambda_x, \lambda_y, \) and \( \lambda_z \), then the dimensions of the deformed network are

\[
L_x = \lambda_x L_{x0}, \quad L_y = \lambda_y L_{y0} \quad \text{and} \quad L_z = \lambda_z L_{z0}.
\]

(4.3)

In the phantom network model, crosslinks freely fluctuate through one another without any hindrance from surrounding chains and entanglements. \( \Delta A_{\text{elastic}} \) for phantom network is given by
\[ \Delta A_{\text{elastic}} = \frac{1}{2} \xi kT(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \] (4.4)

\( \xi \) is the cycle rank, which denotes the number of chains that have to be cut in order to reduce the network to a tree with no closed cycles, \( k \) is Boltzman constant, \( T \) is temperature.

In the affine network model,\(^{21,22} \) the junction points are rigidly embedded in an elastic network.\(^{20} \)

\( \Delta A_{\text{elastic}} \) for affine network is given by

\[ \Delta A_{\text{elastic}} = \frac{1}{2} \nu kT(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) - \mu kT \ln\left(\frac{V}{V_0}\right) \] (4.5)

Where, \( \nu \) is the number of elastic chains per unit volume, \( \mu \) is the number of junctions per unit volume and \( V \) is final volume of the network.

When solvent molecules enters the network system, \( \Delta A_{\text{elastic}} \) increases, due to decrease in entropy of network chains upon dilation, and \( \Delta A_{\text{mixing}} \) decreases due to the increase in the entropy of mixing the solvent molecules with the network chains.

The equilibrium swelling condition is obtained when the two changes balance each other. Thus mathematically,\(^{23} \)
\[
\left( \frac{\partial \Delta A}{\partial n_i} \right)_{T,p} = \left( \frac{\partial \Delta A_{\text{mixing}}}{\partial n_i} \right)_{T,p} + \left( \frac{\partial \Delta A_{\text{elastic}}}{\partial n_i} \right)_{T,p} = 0
\]

(4.6)

Thus from equations, (4.2), (4.4), (4.5) and (4.6)

\[
\ln(1-\nu_2) + \chi \nu_2^2 + \nu_2 = V_1 \nu \left[ \frac{\nu_2}{2} - \nu_2^{1/3} \right] = 0
\]

(4.7)

For the tetrafunctional affine network model and

\[
\ln(1-\nu_2) + \chi \nu_2^2 + \nu_2 = -V_1 (\nu - \mu)\nu_2^{1/3}
\]

(4.8)

for the phantom network model, where \( V_1 \) is the molar volume of solvent and \( \nu_2 \) is the polymer volume fraction at equilibrium swelling. According to constrained junction theory, real networks exhibit properties closer to those of phantom network model, in the highly swollen state. Therefore, equation (4.8) represents equilibrium swelling.

4.2 Results and Discussions

4.2.1 Synthesis of Optimal and Imperfect LCEs

Initially, in order to test the one step, nonlinear polycondensation scheme, we optimized the \((A_2 + B_2 + A_4)\) crosslinking system, using 1,1,3,3,5,5 tetramethylsiloxane as \( A_2 \) molecule, divinyltetramethyldisiloxane as \( B_2 \) molecule and tetra-kis-dimethylsilyloxysilane as \( A_4 \) molecule. Divinyltetramethyldisiloxane was used as \( B_2 \)
molecule as it is readily available and is inexpensive. We established reaction conditions to produce optimal networks, which exhibit minimal swelling and soluble fractions. The mole fraction of A groups (SiH) belonging to crosslinkers is defined as

\[ \rho = \frac{\text{moles A group belonging to branched monomer}}{\text{total moles A groups}} \]

\[ \rho = \frac{4(\text{moles } A_4)}{2(\text{moles } A_2) + 4(\text{moles } A_4)} \]  

(4.9)

\( \rho \) was set to 0.01, 0.02, 0.03, 0.04, 0.06, and 0.08. There are two extremes of crosslink density in this system: zero crosslinking (\( \rho = 0 \)) and maximal crosslinking (\( \rho = 1 \)). The "zero crosslinking" limit (where all flexible connectors are \( A_4 \) molecules) produces linear copolymers, whereas the "maximal crosslinking" limit (where all flexible connectors are \( A_4 \) molecules) produces a rigid solid with thermoset-like characteristics. Intermediate values of \( \rho \) produce elastomers with rigidity that increases as \( \rho \) increases. Higher values of \( \rho \) correspond to higher effective crosslink densities. The mole ratio of total \( A \) groups (SiH) to \( B \) groups (allyl) was calculated as

\[ r = \frac{2(\text{moles } A_2) + 4(\text{moles } A_4)}{2(\text{moles } B_2)} \]  

(4.10)

The \( r \) parameter was varied systematically to identify "optimal" elastomers having the minimum degree of equilibrium swelling in toluene.
Figure 4.1 characterizes the ranges of \( r \) and \( \rho \) that favor gelation in a system where \( B_2 = 1,3 \) divinyl tetramethyl disiloxane, a flexible unit, which is readily available. This system was optimized prior to using any mesogens as \( B_2 \) units, due to the relative difficulty of purifying the bis(allyloxy) terminated mesogens. Here, solid circles represent reaction conditions which produced rubber-like networks, which swelled to equilibrium in toluene. Gray circles represent partial networks which could not completely dissolve in toluene, and open circles represent no network formation (complete dissolution in toluene). Lines are predictions of Flory's non-linear polymerization model, assuming various values for \( p_A \) and \( p_B \).\textsuperscript{25} Swelling experiments in toluene (good solvent) indicate that for this system, optimal networks are formed when \( r \approx 1.04 \) and \( \rho \geq 0.03 \), and suggest that the extent of reaction of the monomers is \( \geq 0.95 \). Optimizing reaction conditions in this fashion defined the maximum molecular weight between crosslinks \( M_c \) (which is limited by the minimum \( \rho \)) accessible through this chemistry.
Figure 4.1 Influence of reaction stoichiometry on network formation by \((A_2 + B_2 + A_4)\) nonlinear polymerization. Lines are predicted upper and lower limits of \(r\) for network formation according to Flory's model.

By systematically varying of \(r\) and \(\rho\) in this way, PPT-CH₃ mesogens are used as \(B_2\) units to obtain optimal and imperfect MCLCEs. Thus, MCLCE were prepared by nonlinear polymerization of PPT-H or PPT-CH₃ mesogens (\(B_2\)), spacer (\(A_2 = F_3\)) and crosslinker (\(A_4\)) by Pt-catalyzed hydrosilylation, similar to a route described by Finkelmann et al.²⁶ Values of 0.04, 0.06, 0.08, and 0.10 were selected for \(\rho\) (mole fraction of SiH units belonging to \(A_4\)), with higher values of \(\rho\) corresponding to higher chemical crosslink densities. For a given series of elastomers having constant \(\rho\), the reaction stoichiometry was further optimized by systematic variation of the \(r\) parameter (mole ratio of SiH groups to allyloxy groups). The elastomers made with PPT-CH₃ mesogens, were synthesized by mixing PPT-CH₃ mesogens in CH₂Cl₂ solution at 45-50 °C, which was necessary to dissolve the (solid) mesogen and homogenize the
immiscible monomers. CH₂Cl₂ represented approximately 65 mass % of the initial reaction mixture in all cases. The elastomers made with PPT-H mesogens, were synthesized by mixing PPT-H mesogens in toluene at 80 °C, due to poor solubility of H-PPT mesogens in CH₂Cl₂. The hydrosilylation polycondensation reaction was catalyzed by platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Alfa Aesar) at a concentration of 1.0 mass % of the total concentration of combined monomers. After 14 days of cure, the CH₂Cl₂ was allowed to evaporate by air drying. Curing proceeded in air at 45-50 °C for an additional 1 day for elastomers made with PPT-CH₃ mesogens, or at 80 °C for PPT-H mesogens, then under vacuum for 1 day.

4.2.2 Swelling and extracting of MCLCEs

The randomly crosslinked networks synthesized by the above scheme always contain significant solubles (extractable material) like unreacted monomers, cyclic species, and free polymeric chains. These solubles act as a plasticizer, which shifts the loss factor peak to lower frequency on loss factor vs. temperature/frequency plot, altering precise determination of damping performance arising from irregular polymeric networks. Solubles, particularly free chains, contribute additional relaxation modes, so MCLCEs synthesized above were swollen and extracted to remove extractables from networks prior to mechanical testing. All MCLCEs were swollen and extracted in toluene for 7 days to measure equilibrium swelling and to remove solubles, during which time the toluene was replaced with fresh solvent daily until a constant equilibrium mass was reached. Swelling is also carried out to determine the equilibrium swelling ratio $Q_s$. 

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(equation 4.10), a metric of the density of elastic chains (ν-μ), according to equation 4.8.

The equilibrium volume swelling ratio, $Q_s$, was calculated according to

$$Q_s = \left( \frac{M_s - M_{ex}}{\rho_1} \right) \left( \frac{\rho_2}{M_{ex}} \right) + 1$$  \hspace{1cm} (4.11)

where $M_s$ is the total mass at equilibrium swelling, $M_{ex}$ is the dry mass of the extracted elastomer, and $\rho_1$ and $\rho_2$ are the densities of toluene and polymer in the solution state, approximated as (0.865 g/cm$^3$ and 1.00 g/cm$^3$), respectively.

Swelling and quantitative extraction (equation 4.12) are measurements of network imperfections. MCLCE swollen in toluene were de-swollen by slow addition of methanol (a poor solvent) to the toluene over a period of a few days, to avoid cracking from rapid evaporation of solvent, followed by air drying and vacuum drying at 50 °C. The soluble fraction was calculated according to

$$W_{sol} = \frac{M_{unex} - M_{ex}}{M_{unex}}$$  \hspace{1cm} (4.12)

where $M_{unex}$ is the dry mass of the elastomer prior to extraction, including solubles.

An optimal value $r_{opt}$ was found for each value of $\rho$, assigned to the value of $r$ producing a network having the minimum equilibrium swelling ratio ($Q_s$) in toluene, a thermodynamically good solvent for the linear polymer. For elastomers made with PPT-CH$_3$ mesogens, the value of $r_{opt}$ observed varied from approximately 1.32 to 1.38, with little dependence on $\rho$ over the range of compositions studied. We did not calculate
the value of $r_{opt}$ for elastomers made with PPT-H mesogens. However, in the case of elastomers made with PPT-H mesogens, value of $Q_s$ was minimum for $r = 2.0$.

All other elastomers having ($r \neq r_{opt}$) exhibited higher $Q_s$ and were termed "imperfect." Compositions having values of $r$ less than about 1.2 did not reach the gel point, forming highly branched polymers or microgels rather than elastomers. Networks having $r$ only slightly above 1.2 are therefore considered highly imperfect and are presumed to contain larger fractions of pendant chains and other defects than the "optimal" networks. The pendant chains in these networks are not necessarily linear, as some pendant structures with branches are also likely to form. Pendant chains are elastically ineffective and do not contribute to the elastic retractive force of the swollen network that balances the osmotic pressure of the solvent at the equilibrium swelling condition, leading to higher $Q_s$. $^{29}$

The observed value of $r_{opt}$ deviated substantially from 1, the value one might expect to be optimal for a polycondensation, where the numbers of "A" groups and "B" groups are equal. In fact, elastomer formulations having $r = 1$ did not even reach the gel point in the present study. Observing $r_{opt} \neq 1.0$ is not unusual for hydrosilylation crosslinking, however. The origin of the deviation has been debated, and appears to have more than one underlying cause. $^{29,30}$ When the amount of crosslinker used is less than optimum amount of crosslinker, the network with higher sol fraction results, implying that appreciable amount of mesogens ($B_2$) failed to get incorporated into the network due to insufficient amount of crosslinker. Side reactions and difference in the site reactivity of the crosslinker are possible reasons for the deviation in the value of $r_{opt}$. Functionality of the tetrafunctional crosslinker can be less than four, if the unreacted site of an $A_4$
molecule is much less reactive than the reactive sites of an A<sub>4</sub> molecule which has reacted at fewer than three sites due to steric hindrance. This would require more crosslinker amount to produce a network with a minimum extent of equilibrium swelling. Side reactions as explained in Chapter 2, may consume silane hydrogen, resulting in deviation in the value of <i>r<sub>opt</sub></i>. Side reaction could result in an increase in the amount of crosslinker required to produce a network exhibiting minimum equilibrium swelling. Substantial deviations from stoichiometric conditions have been previously observed in Pt-catalyzed hydrosilylation end-linking studies with A<sub>4</sub> crosslinker and B<sub>2</sub> = either polydimethylsiloxane (PDMS)<sup>29,31</sup> or poly(diethylsiloxane) (PDES).<sup>32,33</sup>

For each value of <i>ρ</i> studied, the optimal network also exhibited the lowest value of <i>w<sub>sol</sub></i>, in addition to the lowest <i>Q</i><sub>s</sub>. Soluble fractions of the MCLCE studied here ranged from 23 mass % to 52 mass %. Finkelmann et al. also reported relatively high soluble fractions of 18 to 22 mass % for a very similar crosslinking approach (with different mesogens).<sup>26</sup> Even the optimal networks have <i>w<sub>sol</sub></i> values substantially higher than the accepted range for "model" networks, which can have <i>w<sub>sol</sub></i>< 1.0 mass %.<sup>29,32,34,35</sup> Thus, although the "optimal" samples are presumed to have a lower concentration of architectural defects than the "imperfect" networks, they cannot be fairly described as "model" networks. The high soluble fractions may be attributed to intramolecular cyclization reactions, encouraged by the presence of solvent during crosslinking and by the flexibility of the oligosiloxane connectors. The term "optimal" is specific to the crosslinking conditions employed in this study, and does not exclude the possibility that networks with lower equilibrium swelling and/or soluble fractions could be obtained under different crosslinking conditions, e.g. reduced solvent concentration.
4.2.3 Wide-Angle X-ray Diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) experiments were performed on samples of 0.3 mm approximate thickness at ambient temperature (22 ± 2 °C) in transmission using a Rigaku D/MAX Rapid II instrument equipped with graphite monochromator, 300 μm pinhole collimator, and CuKα source (λ = 1.5418 Å). Corrections for polarization and oblique incidence were applied to raw data using Rigaku AreaMax software. To obtain a two-dimensional fiber photo of a drawn MCLCE, the sample was subjected to a uniaxial extension of magnitude λ = (L/L₀) = 2.0, where L and L₀ are the final and initial sample lengths, and the incident X-ray beam was normal to the axis of extension. Diffraction data were converted to grayscale images using commercial image processing software. All MCLCE studied here are randomly oriented, polydomain elastomers prepared by crosslinking in the absence of any external aligning fields. Upon uniaxial stretching to a macroscopic draw ratio of L/L₀ ≈ 2, the smectic layer normals were oriented predominantly in the direction of stretching, judging by the intensification of the low-angle reflection centered at 2θ = 2.8° (Figure 4.2). No evidence of a stable nematic state was found by WAXD, differential scanning calorimetry, or optical microscopy in either the linear polymer or the elastomers at any temperature.
4.2.4 Differential Scanning Calorimetry (DSC)

A Seiko Instruments DSC 220 CU equipped with a liquid nitrogen cooling tank was used to characterize thermal transitions in MCLCP and MCLCE under a flowing N\textsubscript{2} atmosphere. After crimping 7 to 8 mg of sample into a TA Instruments aluminum pan, a 10 °C/min. heating ramp to 195 °C was applied, followed by a -10 °C/min. cooling ramp to -70 °C, followed by a final 10 °C/min. heating ramp to 195 °C. DSC heating traces were recorded during the final heating ramp. Indium was used as a calibration standard for the temperature scale. The clearing temperature (T\textsubscript{si}) reported for the linear polymer was taken from heating traces as the temperature at which the peak of the endotherm was observed at a heating rate of 10 °C/min; uncertainty in the peak position was ± 2 °C. Glass transition temperatures (T\textsubscript{g}) reported are based upon the midpoint of the inflection.
in the heating trace. DSC traces revealed that a linear polymer of moderately high molar mass \((M_w = 77 \text{ kg/mol})\) also forms a higher order smectic phase that melts near \(T_2 \approx 30 ^\circ \text{C}\) after several days of equilibration at \(22 ^\circ \text{C}\). We did not find any evidence of the higher order smectic phase in either the low molar mass linear polymer \((M_w = 11 \text{ kg/mol})\) or the elastomers considered in this study, however. The higher order smectic state may be destabilized by the presence of numerous chain ends (in the low molar mass linear polymer) or by the branched \(A_4\) units (in the elastomers), or the kinetics of its formation may be slowed greatly in the crosslinked elastomers. Figure 4.3 compares DSC traces of a low molar mass, fractionated linear polymer \((M_w = 11 \text{ kg/mol}, M_w/M_n = 1.1)\) and an extracted elastomer having \((r=1.36, \rho=0.08)\). The elastomer has approximately the same \(T_g\) as the linear polymer, but the endotherm expected at \(T_{si}\) is indistinct, despite clear evidence of smectic ordering from WAXD and DMTA. The smectic-isotropic transition is known to be weakly first order, and the endotherm associated with clearing was difficult to detect in these elastomers, regardless of sample size or heating rate. It is possible that the enthalpy change of isotropization in the elastomers differs from that in the fractionated linear polymer. DMTA is better suited for detecting \(T_{si}\) in the elastomers because it is quite sensitive to the changes in storage and loss moduli associated with loss of smectic ordering.
Figure 4.3  DSC heating and cooling traces for linear polymer ($M_w= 11$ kg/mol, $M_w/M_n =1.1$) and crosslinked MCLCE ($\rho=0.08$, $r=1.36$).

4.2.5 Dynamic Mechanical Thermal Analysis (DMTA)

Shear storage moduli of extracted MCLCE were measured using a TA Instruments Q800 DMTA with the shear sandwich fixture. Sample thickness was approximately 0.3 mm. For selected samples, the complex modulus $G'(\omega) = G'(\omega) + iG''(\omega)$ was measured at a small strain (amplitude $\gamma_0 = 0.005$) using a constant temperature frequency sweep, which was repeated at temperature intervals of
5 °C, from -20 °C to 100 °C. Storage and loss moduli were plotted vs. reduced frequency to generate a "master curve" by applying time-temperature superposition (TTS) with shift factors $a_T$ (frequency scale) and $b_T$ (storage and loss moduli). Constant frequency ($\omega = 1 \text{ Hz}$) temperature sweeps were also performed for several samples, from $T = -20 \degree \text{C}$ to 190 °C at a temperature ramp of 10 °C/min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$</th>
<th>$r$</th>
<th>$Q_s$</th>
<th>$w_{sol}$</th>
<th>G/RT (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opt-4</td>
<td>0.040 ± 0.001</td>
<td>1.38 ± 0.05</td>
<td>4.74</td>
<td>31 %</td>
<td>37 ± 4</td>
</tr>
<tr>
<td>Imp-4</td>
<td>&quot;</td>
<td>1.26 ± 0.05</td>
<td>5.96</td>
<td>48 %</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>Opt-6</td>
<td>0.060 ± 0.001</td>
<td>1.32 ± 0.05</td>
<td>5.15</td>
<td>31 %</td>
<td>28 ± 3</td>
</tr>
<tr>
<td>Imp-6</td>
<td>&quot;</td>
<td>1.22 ± 0.05</td>
<td>9.95</td>
<td>52 %</td>
<td>14 ± 1</td>
</tr>
<tr>
<td>Opt-8</td>
<td>0.080 ± 0.002</td>
<td>1.36 ± 0.05</td>
<td>4.72</td>
<td>30 %</td>
<td>34 ± 6</td>
</tr>
<tr>
<td>Imp-8</td>
<td>&quot;</td>
<td>1.22 ± 0.05</td>
<td>7.82</td>
<td>49 %</td>
<td>18 ± 3</td>
</tr>
<tr>
<td>Opt-10</td>
<td>0.100 ± 0.002</td>
<td>1.38 ± 0.05</td>
<td>4.12</td>
<td>23 %</td>
<td>31 ± 3</td>
</tr>
<tr>
<td>Imp-10</td>
<td>&quot;</td>
<td>1.24 ± 0.05</td>
<td>10.3</td>
<td>59 %</td>
<td>11 ± 1</td>
</tr>
</tbody>
</table>

**Table 4.1** Compositions and equilibrium swelling ratios in toluene for all MCLCE. Values of G/RT were determined in the isotropic state at 175 °C and $\omega = 1 \text{ Hz}$. $Q_s$ is the ratio of the equilibrium swollen volume (sol fraction removed) and the dry volume (sol fraction removed).
All networks, optimal and imperfect, were exhaustively extracted in toluene to remove solubles and thoroughly dried before characterization by DMTA in small-strain ($\gamma_0=0.005$) oscillatory shear. Figures 4.4 and 4.5 illustrate constant frequency ($\omega=1$ Hz) temperature ramps for samples Opt-10 and Imp-10 ($\rho=0.10$). (Data at temperatures near and below $T_g \approx 10$ °C may not be reliable, as slippage of a glassy sample is possible in the shear sandwich geometry.) For both samples, $G'(\omega)$ drops sharply above about 30 °C and a maximum in $G''(\omega)$ is noted as the sample passes through the glass transition. Above about 60 °C, the storage modulus drops abruptly, due to the loss of ordering upon clearing of the smectic phase. In contrast, nematic LCE are known to sometimes exhibit an increase in storage modulus above the clearing temperature, an effect which has been attributed in part to the dynamic soft elasticity of the nematic state. For $T >> T_{si}$, the storage modulus in our elastomers increases with temperature, as expected for an isotropic, rubber-like network. Comparing Opt-10 and Imp-10, the storage modulus of the imperfect network is much lower in the isotropic state at $T >> T_{si}$. For example, at $175$ °C and $\omega=1$ Hz, $G' = 0.12$ MPa for Opt-10 and $G' = 0.04$ MPa for Imp-10. For an isotropic, rubber-like network, one expects $G \sim \nu RT$, where $\nu$ is the density of elastically effective chains. Values of $(G/RT)$ determined at $175$ °C and $\omega=1$ Hz, well above the clearing transition temperature, are presented in Table 4.1. The measured values of $(G/RT)$ for the imperfect networks are substantially lower than the values of $(G/RT)$ for the optimal networks in all cases, which is consistent with the higher equilibrium swelling of the imperfect networks. The lower values of $(G/RT)$ and higher equilibrium swelling of the imperfect networks result from higher concentrations of elastically ineffective (pendant) chains.
Figure 4.4  Storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli vs. temperature at $\omega = 1$ Hz for elastomer Opt-10 ($\rho = 0.10, r = 1.38$).
Figure 4.5  Storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli vs. temperature at constant frequency ($\omega = 1$ Hz) for sample Imp-10 ($\rho = 0.10$, $r = 1.38$).
Figure 4.6 illustrates the dependence of \( \tan \delta \) on temperature for optimal and imperfect elastomers with different values of \( \rho \). Regardless of the values of \( \rho \) or \( r \), all imperfect elastomers exhibit markedly higher loss in the isotropic phase compared to the optimal elastomers due to relaxation of pendant chains and other imperfections in the imperfect networks. The contribution of pendant chain relaxation to mechanical damping is not unique to MCLCE, of course. Pendant chains enhance vibration damping behavior of amorphous elastomers as well (e.g. polydimethylsiloxane, PDMS).\(^{31}\) Urayama et al. recently verified experimentally that long linear pendant chains greatly enhance mechanical loss in end-linked PDMS networks, which do not exhibit liquid crystalline or mesomorphic ordering.\(^{36}\) By simply increasing the fraction of long pendant chains, PDMS elastomers having \( \tan \delta > 0.5 \) over several decades of frequency were obtained.
Figure 4.6  Tan δ vs. temperature at constant frequency (ω = 1 Hz) for optimal and imperfect extracted MCLCE.

From Figure 4.6, one can also compare tan δ for optimal MCLCE having different values of ρ. The concentration of A₄ crosslinker units appears to have little effect on either the magnitude of tan δ (in the smectic state) or the temperature at which its maximum value is observed. Little difference in tan δ is noted between the optimal and imperfect networks in the smectic state. At low strains, the mechanical damping in the smectic state arises from segment-level relaxation processes that are insensitive to the
details of chain connectivity, at least at the chosen frequency of observation (ω = 1 Hz). The relaxation of pendant chains occurs on a significantly longer time scale in the smectic state due to the overall slowing of chain dynamics with the constraints imposed by layering.

Networks Opt-8 and Imp-8 were further characterized by constant-temperature frequency sweeps at temperature intervals of 5 °C. Data near T_g and above were collapsed to master curves by temperature-time superposition (TTS). Frequency scale shifting of tan δ data was performed with respect to an arbitrary reference temperature T_ref = 50 °C. Shift factors a_T were first applied to the frequency scale to maximize the superposition of tan δ data across the entire temperature/frequency range. To achieve superposition of G'(ω) and G''(ω) data, an additional shift factor b_T was applied to the moduli. At a given temperature, the value of b_T applied to G'(ω) was constrained to be the same as the value of b_T applied to G''(ω). The superposition of the G'(ω) and G''(ω) data appears to be quite reasonable with this shifting approach, although some regions of imperfect overlap are still seen in tan δ (most obvious in the data obtained at temperatures just above T_g and near T_si). Shift factors applied to the data in Figure 4.7 and 4.8 are plotted in Figure 4.9 for the sake of documenting the shifting procedure. The values of a_T determined for Opt-8 are remarkably close to those determined independently for Imp-8. The dependence of a_T on temperature cannot be satisfactorily represented by the well-known Williams-Landel-Ferry (WLF) expression.37,38
Figure 4.7 "Master Curves" generated by time-temperature superposition for sample Opt-8 ($T_{ref} = 50 \degree C$). Frequency sweeps from $\omega = 1$ Hz to 100 Hz were performed at temperatures between 5 $\degree C$ and 100 $\degree C$.

The failure of TTS is not surprising for a system that undergoes loss of positional ordering with increasing temperature. Attempts to extract physical meaning from the shift factors may be misguided, given that TTS fails for all smectic elastomers studied so far. The shifting approach assumes that the shape of the relaxation spectrum is temperature-independent, which is not true if a change in polymer backbone conformation occurs due to a phase transition. Giamberini et al. report failure of TTS for...
both nematic and smectic MCLCE,\textsuperscript{39} for example. The apparent reasonable superposition obtained for the moduli in Figures 4.7 and 4.8 is therefore probably an artifact of the comparatively narrow frequency range studied at each temperature (1 Hz to 100 Hz). We would expect more obvious deviations from superposition had a larger frequency range been covered at each temperature.

In Figure 4.8, the enhanced mechanical damping due to pendant chains is again seen as a prominent shoulder in tan $\delta$ in the low frequency (high temperature) limit, which is substantially weaker in sample Opt-8. The tan $\delta$ plots for all samples in Figures 4.6-4.8 are also characterized by prominent loss peaks near $T_g$ and $T_{si}$. Tan $\delta$ approaches a peak value of about 1.0 in the transitional region separating the smectic and isotropic states. This temperature range defines the region of steepest decline in the storage modulus, corresponding to the loss of positional ordering associated with smectic layering. The behavior of the MCLCE studied here contrasts with the behavior of side-chain smectic elastomers studied by Clarke et al.,\textsuperscript{11} which exhibited little if any enhancement in tan $\delta$ near the smectic-nematic phase boundary. Clarke et al. observed that the total area under the loss curve between $T_g$ and the clearing temperature appears to be proportional to the total entropy increase associated with the underlying phase transitions. This idea is consistent with the behavior of the MCLCE in this study, which undergo a significant gain in conformational entropy over a comparatively narrow temperature window, perhaps accounting for the strength of the relaxation peak near $T_{si}$. From Figure 4.9, vertical shift is due to the thermal expansion due to broad temperature range over which smectic phase melts.
Figure 4.8  "Master Curves" generated by time-temperature superposition for sample Imp-8 ($T_{\text{ref}} = 50 ^{\circ}\text{C}$). Frequency sweeps from $\omega = 1$ Hz to 100 Hz were performed at temperatures between 5 °C and 100 °C.
Figure 4.9  Shift factors $a_T$ and $b_T$ applied in shifting dynamic mechanical data for networks Opt-8 and Imp-8.
4.2.6 Elastomers made from PPT-H mesogens (E-H)

The DSC heating trace of linear polymer F3-PPT-H exhibits a glass transition temperature ($T_g$) of $8 \pm 2$ °C, endotherm $T_2 \approx 50$ °C (transition between two liquid crystalline mesophases) and clearing temperature (liquid crystalline to isotropic temperature), $T_i \approx 130$ °C. However, the DSC heating traces for E-H was nearly featureless, except for the inflection at $T_g \approx 30$ °C, despite clear evidence of smectic ordering from WAXD and DMA. Thermal behavior of these elastomers was therefore consistent with E-CH$_3$ elastomers, in that the clearing temperature was difficult or impossible to detect by DSC, possibly due to the clearing of the smectic phase over a broad temperature range.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ (r)</th>
<th>r</th>
<th>$Q_s$</th>
<th>$w_{sol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-H4-1.3</td>
<td>0.04</td>
<td>1.3</td>
<td>4.74</td>
<td>31%</td>
</tr>
<tr>
<td>E-H4-1.8</td>
<td>0.04</td>
<td>1.8</td>
<td>5.96</td>
<td>48%</td>
</tr>
<tr>
<td>E-H6-1.3</td>
<td>0.06</td>
<td>1.3</td>
<td>7.24</td>
<td>34%</td>
</tr>
<tr>
<td>E-H6-1.9</td>
<td>0.06</td>
<td>1.9</td>
<td>8.12</td>
<td>58%</td>
</tr>
<tr>
<td>E-H8-1.3</td>
<td>0.08</td>
<td>1.3</td>
<td>6.80</td>
<td>31%</td>
</tr>
<tr>
<td>E-H8-2.1</td>
<td>0.08</td>
<td>2.1</td>
<td>11.26</td>
<td>52%</td>
</tr>
<tr>
<td>E-H10-1.3</td>
<td>0.10</td>
<td>1.3</td>
<td>6.27</td>
<td>27%</td>
</tr>
<tr>
<td>E-H10-1.8</td>
<td>0.10</td>
<td>1.8</td>
<td>10.24</td>
<td>48%</td>
</tr>
</tbody>
</table>

Table 4.2 Compositions and equilibrium swelling ratios in toluene for E-H elastomers studied by oscillatory shear.
Figure 4.10 and 4.11 illustrate constant frequency ($\omega = 1$ Hz) temperature ramps for samples E-H4-1.8 and E-H4-1.3. (Data at temperatures near and below $T_g < 10$ °C may not be reliable, as slippage of a glassy sample is possible in the shear sandwich geometry.) Figure 4.12 exhibits temperature ramp for E-H4-1.3 at various frequencies. For both samples, $G'(\omega)$ drops sharply above about 40 °C and a maximum in $G''(\omega)$ is noted as the sample passes through the glass transition. Above about 100 °C, the storage modulus drops abruptly, due to the loss of ordering upon clearing of the smectic phase as explained above. For $T >> T_{si}$, the storage modulus in our elastomers increases with temperature, as expected for an isotropic, rubber-like network. Comparing E-H4-1.8 and E-H4-1.3, the storage modulus of the imperfect network is much lower in the isotropic state at $T >> T_{si}$ as the modulus does not include any contribution from smectic microstructure above $T_{si}$.

![Graph](image)

**Figure 4.10**  Storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli vs. temperature at $\omega = 1$ Hz for elastomer E-H4-1.3
**Figure 4.11** Storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli vs. temperature at $\omega = 1$ Hz for elastomer E-H4-1.8.

**Figure 4.12** Temperature dependence of storage moduli for elastomer measured by oscillatory shear E-H4-1.3.
Figure 4.13 shows the temperature dependence of the loss tangent for an elastomer E-H4-1.3, measured at frequencies of $\omega = 1$ and 100 Hz. Loss tangents for elastomer E-H4-1.3 exhibit the usual maxima associated with glass transition, which shifts to higher temperatures as frequency increases. In addition, a more pronounced loss peak is observed at high temperature, with maximum values of $\tan \delta \approx 1.2$. A strong maximum in $\tan \delta$ near the clearing temperature has also been noted by Weilepp et al. in polydomain S$_A$ side-chain LCE. In both the present study and in ref 41, the temperature at which the maximum loss occurs corresponds to the region of steepest decline in the storage modulus, which has previously been dubbed the “transition” or “pretransformational” region.\textsuperscript{40,41} The high damping may arise from relaxation of the smectic microstructure on a time scale of order $1/\omega$, corresponding to continuous breaking and re-forming of smectic layers in response to the applied deformation. However, the physical origin of the high mechanical loss is open to question without a precise determination of the changes in mesomorphic ordering occurring within the transition region. The peak in $\tan \delta$ shifts to higher temperatures for higher frequencies of observation, which is consistent with the observations of Weilepp et al. for S$_A$ side-chain LCE. Interestingly, in earlier studies by Clarke et al.\textsuperscript{11} and Gallani et al.\textsuperscript{42} concerning side-chain LCE that pass through a stable nematic state prior to clearing, little or no loss peak was observed at the smectic-nematic phase boundary. Thus, it seems unlikely that the loss peak observed in the transition region for our MCLCE can be attributed to formation of a transient nematic state in the transition region, especially since no stable nematic phase was found in the linear polymer at any temperature.
Figure 4.13 Temperature dependence of mechanical loss factor for elastomer (E-H4-1.3) in oscillatory shear at $\omega = 1$ and 100 Hz.

Figures 4.14-4.17 illustrate the dependence of $\tan \delta$ on temperature for optimal and imperfect elastomers with different values of $\rho$. 
Figure 4.14  Tan δ vs. temperature at constant frequency (ω = 1 Hz) for optimal and imperfect extracted E-H MCLCE.

Figure 4.15  Tan δ vs. temperature at constant frequency (ω = 1 Hz) for optimal and imperfect extracted MCLCE.
Figure 4.16  Tan δ vs. temperature at constant frequency (ω = 1 Hz) for optimal and imperfect extracted MCLCE.

Figure 4.17  Tan δ vs. temperature at constant frequency (ω = 1 Hz) for optimal and imperfect extracted MCLCE.
Regardless of the values of $\rho$ or $r$, all imperfect elastomers exhibit markedly higher loss in the isotropic phase compared to the optimal elastomers due to relaxation of pendant chains and other imperfections in the imperfect networks as explained earlier. However in contrast to E-CH$_3$ elastomers studied above, these elastomers shows shift in $T_g$ and tan $\delta$ peak positions by around $10 \pm 2$ °C. The possible reason for this difference is the narrow range of $r$, for which imperfect and optimal networks are formed for E-CH$_3$ elastomers ($r \approx 1.3$). However, for elastomers made from PPT-H mesogens, $r$ varies over broad range of values from 1.3 to 2.0, due to higher curing temperature. (E-H elastomers synthesized at 45 °C in CH$_2$Cl$_2$ were inconsistent in reaching the gel point.) Also it can be noted that $T_g$ of elastomers for higher values of $r$ is lowered considerably most probably due to more number of siloxane units incorporated by changing stoichiometry.

In order to understand the origin of peak at $T_{si}$, WAXD was carried out at higher temperature on methyl substituted MCLCE ($\rho=0.08$, $r=1.36$) and unsubstituted E-H8-1.3 sample. From Figures 4.18 and 4.19, as temperature increases and approaches $T_{si}$, there is partial melting of unstable domains along the edge, leaving smaller domains and more amorphous material. At lower temperature, there is higher concentration of smectic phase and larger domains, thus rotation of the domains is prohibited by the constraint of the layering. Therefore the idea of soft elasticity does not apply to smectic LCEs, which is consistent with the theoretical predictions of Warner.$^{43,44}$

Domains are connected by layering and domains can not be rotated without breaking layering. There is energetic penalty for breaking layers. Therefore, the storage modulus is high. However, near clearing temperature $T_{si}$, there is biphasic mixture of amorphous rubbery matrix and smectic domains. Clearing temperature happens over the
range of temperatures and once the smaller and less stable domains melt, then the more stable domains remain in the amorphous matrix. These domains now can rotate as the constraints of continuous interconnected layering are removed, and hence high mechanical loss is observed. Thus the storage modulus drops, but the loss modulus does not drop until the smectic phase disappears. Hence, the high damping is observed in the clearing transition range as it is biphasic. Note that Figure 4.18 shows that domain size decreases as temperature increases. However, this observation does not contradict the ideas presented here, as the loss of continuous layering near $T_{si}$ is the key physical change leading to anomalous damping.

Figure 4.18  WAXD at different temperatures of CH$_3$ substituted MCLCE ($\rho = 0.08$, $r = 1.36$).
Figure 4.19  WAXD at different temperatures of H substituted MCLCE ($\rho = 0.08, r = 1.4$).
References


(43) Adams, J. M.; Warner, M. *Phys Rev E* 2005, 72,

Chapter 5

Mechanical Response of Main-Chain Smectic Elastomers at High Elongations

5.1 Introduction

Basic understanding of how smectic elastomers respond to large strains is still emerging. Small angle neutron scattering studies have revealed oblate chain conformation for smectic polymers. Elastic chains in a smectic MCLCE can be envisioned as “hairpinned coils”. Although the mesogens are constrained to stay in layers, an elastic chain can increase its entropy by forming hairpin folds. Under a large uniaxial elongational strain, the polymer backbone conformation is expected to be drastically altered, however, leading to a transition to an extended chain conformation for at least some portion of the chains in the network.

The existence of a plateau in the nominal stress due to polydomain to monodomain transition (P-M transition), in the static stress-strain behavior of side-chain and combined side-chain/main-chain nematic elastomers, was reported by Schätzle et al. The P-M transition has also been observed in nematic side-chain siloxane based LCEs, side-chain polyacrylate and polymethacrylate networks, a main-chain polymalonate, a combination of these to form side-chain/main-chain networks, a main-chain, epoxide based network, and main-chain, semirigid, epoxide based networks. Uchida investigated the elastic effects in the disordered nematic elastomers by considering elastic interactions and random stresses. The authors
concluded that the long range elastic interactions and random internal stresses are responsible for the structural reorganization of the domains, leading to the plateau in the stress-strain curve.\textsuperscript{22} The polydomain to monodomain transition in smectic LCE\textsuperscript{5,23-26} is characterized by a “plateau” of the stress-strain curve as shown in Figure 5.1. Thus smectic LCEs exhibit strong deviations from ordinary rubber elasticity. However, the physical origin of the plateau in smectic MCLCE remains a matter of debate.

According to Ortiz et al.\textsuperscript{5,26} at small strains (region I), there is a linear elastic increase in stress with strain, giving the elastic modulus of the polydomain. At intermediate strain (region II), the curve becomes nonlinear and then quickly exhibits a plateau region, indicative of a P-M transition as shown in Figure 5.1. At large strains (region III), the stress begins to increase again with strain until failure occurs.
Figure 5.1  Stress-strain curve of smectic polydomain LCEs exhibiting polydomain-monodomain transition.

De Gennes\textsuperscript{27} had introduced the concept of hairpins, in which longer chains can increase their entropy by forming hairpins as shown in Figure 5.2. The number of hairpins per chain ($n_h$) and the average contour length between hairpins ($l_h$), are determined by a balance between the tendency to maximize configurational entropy, and the energetic penalty for bending the chain at the hairpins. Thus, based on the concept of hairpins, Adams et al.\textsuperscript{28} have predicted that a main-chain liquid crystalline nematic elastomer shows a plateau in the stress as a function of the elongation imposed along the director, due to unfolding of hairpin chains. During uniaxial stretching of a polydomain,
main-chain elastomer, as shown in Figure 5.1, deformation initially proceeds by re-
arrangement of the smectic microstructure at the domain level via rotations that preserve
the layer spacing (region I). After a threshold strain is reached, the "super-affine"
deformation of chains with hairpins initiates, resulting in a plateau in the stress (region
II). Elongation of chains with hairpins produces little additional retractive force, as the
configurational entropy of these chains is essentially independent of their end-to-end
distance. Shorter chains without hairpins are unable to increase their end-to-end distance
in the same capacity, and thereby deform in a "sub-affine" manner. At larger
deformations, where many hairpins have unfolded, the finite extensibility of elongated
chains produces a steeper increase in the retractive force, a feature that is common to
many isotropic rubber networks as well (region III).

Recently Muresan et al.\textsuperscript{29} have reported a high-resolution X-ray lineshape study
of main-chain smectic polymers. The authors have excluded short range order of smectic
liquid crystals and have proposed formation of hairpins in the smectic LCEs as in nematic
LCEs. Hairpins profoundly affect macroscopic rheological and mechanical response in
main-chain smectic LCPs and LCEs. The idea of hairpin elasticity is quite intuitive for
smectic main-chain elastomers, although little experimental evidence exists to connect
macroscopic mechanical response directly with changes in chain dimensions occurring at
the molecular level.
In this chapter, we vary the chemical composition of MCLCEs by varying the flexible:rigid segment ratio ($r$) and branching parameter ($\rho$). The networks are synthesized at 80 °C in toluene, unlike the E-CH$_3$ elastomers Chapter 4, due to poor solubility of the H-substituted mesogen in CH$_2$Cl$_2$ at 50 °C. The extracted MCLCEs are then utilized to study the effect of chemical composition on the plateau stress ($\sigma_p$) by mechanical characterization at high uniaxial elongation. In addition, we vary the rate of elongation of the samples, the temperature and the nature of the mechanical experiment (force ramp vs. strain ramp), and observe the effect of experimental conditions on the mechanical response.

5.2 Experiments

5.2.1 Elastomer Synthesis

As explained in Chapter 4, MCLCEs were prepared by non-linear polymerization of H-substituted mesogen (B$_2$), spacer (A$_2$) and crosslinker (A$_4$) by Pt-catalyzed
hydrosilylation, similar to the route first described by Finkelmann et al.\textsuperscript{30} The reaction was started by mixing monomers in toluene solution at 80 °C, which was necessary to dissolve the (solid) mesogen and homogenize the immiscible monomers. Toluene represented approximately 50 mass % of the initial reaction mixture in all cases. These networks are different than those studied in Chapter 4, which were cured in CH\textsubscript{2}Cl\textsubscript{2} at 45 - 50 °C. The switch of solvents allowed us to achieve more repeatable results, possibly because toluene is less volatile than CH\textsubscript{2}Cl\textsubscript{2}, or because the PPT-H mesogen has higher solubility under the conditions.

For each value of $\rho$ studied, a series of MCLCE were prepared that had different values of $r$. All MCLCE were swollen and extracted in toluene for 7 days as explained in Chapter 4. Composition and swelling data are presented for all elastomers in Tables 5.1-5.4. ATR-FTIR spectroscopy was carried out to check composition variation in the extracted and unextracted networks as explained in the appendix at the end of this chapter.
Figure 5.3 Chemical structures of monomers and polymers: (a) unsubstituted $B_2$ mesogen (PPT-H); (b) $A_2$ flexible spacer; (c) $A_4$ crosslinker; (d) repeat unit of elastic chains.

5.2.2 Stress-Strain Testing.

Stress-strain behavior of LCEs was determined in tension using controlled force mode. Initially a force of a 0.001 N was applied to the sample and then the force was increased linearly at 0.05N/min. Dogbone shaped samples having total length of 1.5 cm and thickness approximately of 0.5 mm were used for characterization. Experiments were carried out at 30 °C.
Wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) experiments were performed on samples as explained in Chapter 4. To characterize samples by WAXD, uniaxial elongational strain was applied in the smectic state at 30 °C and the elastomer was elongated to various extension ratios \( \lambda = L/L_0 \) of 1, 1.75, 2, 2.25, 2.5, 3.25 and 3.8. The films were elongated in the Q800 instrument under tension at 30 °C by applying a preload force of 0.001N and force ramp of 0.05 N/min. The stretched sample was then mounted on a stainless steel holder using Scotch™ tape. After X-ray diffraction, the sample was heated above \( T_i \) to delete previous mechanical and thermal history, and then stretched to a new extension ratio, and the next WAXD experiment was conducted.

5.3 Results and Discussion

Elastomers were prepared by varying the stoichiometric parameters \( \rho \) and \( r \). Tables 5.1-5.4 summarize elastomer compositions and equilibrium swelling data in toluene. Values of 0.04, 0.06, 0.08, and 0.10 were selected for \( \rho \) (mole fraction of SiH units belonging to \( A_4 \)), with higher values of \( \rho \) corresponding to higher chemical crosslink densities. For a given series of elastomers having constant \( \rho \), the reaction stoichiometry was further varied through the \( r \) parameter (mole ratio of SiH groups to allyloxy groups).

Compositions having values of \( r \) significantly less than about 1.3 did not reach the gel point. Networks having \( r \) only slightly above 1.3 are therefore considered highly imperfect and are presumed to contain larger fractions of pendant chains and other
defects (loops and pendant structure with branches) than the "optimal" networks. Pendant chains are elastically ineffective and do not contribute to the elastic retractive force of the swollen network that balances the osmotic pressure of the solvent at the equilibrium swelling condition, leading to higher $Q_s$.\textsuperscript{31} Unlike networks studied in the Chapter 4, swelling was highest for $r = 1.3$. For constant value of $\rho$, crosslink density increases as $r$ increases and thus concentration of A$_4$ units increases. Swelling decreased as $r$ increased, as the ratio of silicone to mesogen, i.e. ratio of flexible unit to rigid units, is higher. Swelling was minimum for $r = 2.0$ in each series studied at constant value of $\rho$. Elastomers having $r = 1.3$ had the lowest concentration of mesogen among all samples studied.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$r$</th>
<th>$Q_s$</th>
<th>$w_{sol}$</th>
<th>Conc. $A_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Toluene)</td>
<td>%</td>
<td>g ($A_4$)/ g Total</td>
</tr>
<tr>
<td>E-H4-1.3</td>
<td>1.3</td>
<td>14.71</td>
<td>49 %</td>
<td>0.0122</td>
</tr>
<tr>
<td>E-H4-1.4</td>
<td>1.4</td>
<td>12.34</td>
<td>41 %</td>
<td>0.0128</td>
</tr>
<tr>
<td>E-H4-1.5</td>
<td>1.5</td>
<td>11.67</td>
<td>41 %</td>
<td>0.0133</td>
</tr>
<tr>
<td>E-H4-1.6</td>
<td>1.6</td>
<td>8.90</td>
<td>35 %</td>
<td>0.0138</td>
</tr>
<tr>
<td>E-H4-1.7</td>
<td>1.7</td>
<td>9.53</td>
<td>36 %</td>
<td>0.0143</td>
</tr>
<tr>
<td>E-H4-1.8</td>
<td>1.8</td>
<td>9.48</td>
<td>34 %</td>
<td>0.0147</td>
</tr>
<tr>
<td>E-H4-1.9</td>
<td>1.9</td>
<td>9.63</td>
<td>34 %</td>
<td>0.0152</td>
</tr>
<tr>
<td>E-H4-2.0</td>
<td>2.0</td>
<td>4.95</td>
<td>28 %</td>
<td>0.0156</td>
</tr>
</tbody>
</table>

**Table 5.1**  Compositions and equilibrium swelling ratios in toluene at 22 °C for E-H4 series of MCLCEs ($\rho = 0.04$).
<table>
<thead>
<tr>
<th>Sample</th>
<th>$r$</th>
<th>$Q_s$ (Toluene)</th>
<th>$w_{sol}$</th>
<th>Conc. $A_4$ g (A&lt;sub&gt;4&lt;/sub&gt;) / g Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-H6-1.3</td>
<td>1.3</td>
<td>21.91</td>
<td>50 %</td>
<td>0.0184</td>
</tr>
<tr>
<td>E-H6-1.4</td>
<td>1.4</td>
<td>11.45</td>
<td>43 %</td>
<td>0.0192</td>
</tr>
<tr>
<td>E-H6-1.5</td>
<td>1.5</td>
<td>11.49</td>
<td>35 %</td>
<td>0.0200</td>
</tr>
<tr>
<td>E-H6-1.6</td>
<td>1.6</td>
<td>9.12</td>
<td>36 %</td>
<td>0.0208</td>
</tr>
<tr>
<td>E-H6-1.7</td>
<td>1.7</td>
<td>8.10</td>
<td>34 %</td>
<td>0.0215</td>
</tr>
<tr>
<td>E-H6-1.8</td>
<td>1.8</td>
<td>8.32</td>
<td>30 %</td>
<td>0.0222</td>
</tr>
<tr>
<td>E-H6-1.9</td>
<td>1.9</td>
<td>7.35</td>
<td>29 %</td>
<td>0.0228</td>
</tr>
<tr>
<td>E-H6-2.0</td>
<td>2.0</td>
<td>6.11</td>
<td>27 %</td>
<td>0.0234</td>
</tr>
</tbody>
</table>

Table 5.2  Compositions and equilibrium swelling ratios in toluene at 22 °C for E-H6 series of MCLCEs ($\rho = 0.06$).
<table>
<thead>
<tr>
<th>Sample</th>
<th>$r$</th>
<th>$Q_s$ (Toluene)</th>
<th>$w_{sol}$</th>
<th>Conc. $A_4$ g (A₄)/ g Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-H8-1.3</td>
<td>1.3</td>
<td>11.33</td>
<td>43 %</td>
<td>0.0245</td>
</tr>
<tr>
<td>E-H8-1.4</td>
<td>1.4</td>
<td>10.00</td>
<td>38 %</td>
<td>0.0257</td>
</tr>
<tr>
<td>E-H8-1.5</td>
<td>1.5</td>
<td>8.84</td>
<td>34 %</td>
<td>0.0267</td>
</tr>
<tr>
<td>E-H8-1.6</td>
<td>1.6</td>
<td>9.08</td>
<td>37 %</td>
<td>0.0277</td>
</tr>
<tr>
<td>E-H8-1.7</td>
<td>1.7</td>
<td>9.84</td>
<td>33 %</td>
<td>0.0287</td>
</tr>
<tr>
<td>E-H8-1.8</td>
<td>1.8</td>
<td>8.28</td>
<td>31 %</td>
<td>0.0296</td>
</tr>
<tr>
<td>E-H8-1.9</td>
<td>1.9</td>
<td>6.32</td>
<td>26 %</td>
<td>0.0305</td>
</tr>
<tr>
<td>E-H8-2.0</td>
<td>2.0</td>
<td>6.19</td>
<td>27 %</td>
<td>0.0313</td>
</tr>
</tbody>
</table>

**Table 5.3**  Compositions and equilibrium swelling ratios in toluene at 22 °C for E-H8 series of MCLCEs ($\rho = 0.08$).
Table 5.4  Compositions and equilibrium swelling ratios in toluene at 22 °C for E-H10 series of MCLCEs (\(\rho = 0.1\)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(r)</th>
<th>(Q_s)</th>
<th>(w_{sol})</th>
<th>Conc. (A_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-H10-1.3</td>
<td>1.3</td>
<td>10.44</td>
<td>48 %</td>
<td>0.0307</td>
</tr>
<tr>
<td>E-H10-1.4</td>
<td>1.4</td>
<td>8.95</td>
<td>42 %</td>
<td>0.0321</td>
</tr>
<tr>
<td>E-H10-1.5</td>
<td>1.5</td>
<td>8.34</td>
<td>36 %</td>
<td>0.0335</td>
</tr>
<tr>
<td>E-H10-1.6</td>
<td>1.6</td>
<td>6.98</td>
<td>34 %</td>
<td>0.0347</td>
</tr>
<tr>
<td>E-H10-1.7</td>
<td>1.7</td>
<td>7.16</td>
<td>33 %</td>
<td>0.0359</td>
</tr>
<tr>
<td>E-H10-1.8</td>
<td>1.8</td>
<td>6.27</td>
<td>27 %</td>
<td>0.0371</td>
</tr>
<tr>
<td>E-H10-1.9</td>
<td>1.9</td>
<td>6.43</td>
<td>31 %</td>
<td>0.0382</td>
</tr>
<tr>
<td>E-H10-2.0</td>
<td>2.0</td>
<td>5.93</td>
<td>27 %</td>
<td>0.0392</td>
</tr>
</tbody>
</table>

The value of \(r_{opt}\) was not determined for the series of elastomers. For each value of \(\rho\) studied, networks having \(r = 2.0\) exhibited the lowest value of \(w_{sol}\), in addition to the lowest \(Q_s\). Soluble fractions of the MCLCE studied here ranged from 23 mass % to 50 mass %. All networks were exhaustively extracted in toluene to remove solubles and thoroughly dried before characterization by Q 800 instrument.

The segmental orientation of the elastomer E-H6-1.3 (\(\rho = 0.06, r=1.3\)), was studied by WAXD. X-ray diffraction of polydomain unoriented elastomer exhibits two diffuse halos at wide angles, and a sharp reflection at low angle (\(2\theta \approx 2.9^\circ\)) indicating
that the director is randomly oriented as expected for a polydomain. The strong low angle reflection near $2\theta \approx 3^\circ$ is indicative of all smectic phases. Calculated $d$-spacings for the low-angle reflection were $31.4 \pm 1.0$ Å for the elastomers ($r = 1.3$, $\rho = 0.06$) at $22 \pm 2^\circ$C, slightly larger than the values for the linear polymer F3-PPT-H (28 Å) as explained in Chapter 3.

Low angle layering reflection in the X-ray pattern is used to estimate the size of smectic domains in the elastomers studied here. Instrumental broadening was corrected using silver behenate standard at $2\theta = 3.05^\circ$.\textsuperscript{32} This series of elastomers has two layering peaks indicating two possible layer spacing which we are unable to identify spectroscopically. From Figure 5.4 and Table 5.5, as the amount of crosslinker increases, the inter-layer ‘$d$’ spacing increases. This may be because forcing $A_4$ units in the structure frustrates the layering and forces the system to adopt larger inter-layer spacing.
Figure 5.4  WAXD lineshapes for low-angle layering reflection in samples in E-H6 series.
Table 5.5  Domain sizes of MCLCEs. Uncertainty is approximately ±1°.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inter-layer d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Sample</td>
<td>27.8</td>
</tr>
<tr>
<td>r = 1.3</td>
<td>30.5</td>
</tr>
<tr>
<td>r = 1.4</td>
<td>31.0</td>
</tr>
<tr>
<td>r = 1.6</td>
<td>31.8</td>
</tr>
<tr>
<td>r = 2.0</td>
<td>34.5</td>
</tr>
</tbody>
</table>

Uniaxial elongational strain was applied to sample E-H6-1.3 in the smectic state at 30 °C and the elastomer was elongated at various extension ratios (λ = L/L₀) of 1, 1.75, 2, 2.25, 2.5, 3.25 and 3.8 as shown in Figure 5.5. Resulting WAXD patterns at each value of λ are shown in Figure 5.6. Figures 5.7 and 5.8 present integrated azimuthal intensity plots for the low-angle reflections and the diffuse outer halo in E-H6-1.3 (ρ = 0.06, r=1.3) at different extension ratios. From Figures 5.6 - 5.8, it can be observed that very weak layer orientation exists at λ ≈ 1.75. Thus, deformation in region I occurs with minimal domain rotation. The possible reason for this behavior could relate to stretching of amorphous material between smectic domains, although we can not rule out partial disordering of domains (onset of polydomain-monodomain transition). From Figures 5.7 and 5.8, as the strain increases in the confined boundary condition due to clamping, as λ increases through region II, the segmental order parameter increases as smectic layer
normals align with the stress axis. When stretched through region II, smectic domains are transiently disordered as hairpins start to pull out. Once elongation reaches the end of region II, smectic domains are reforming in a monodomain state, i.e. some of the domains having hairpins are pulled out and then they can reorder on neighboring domains and form a globally oriented monodomain with new smectic layers which were absent before. However at $\lambda \approx 3.8$, in region III, once the sample reaches the globally oriented monodomain state, further elongation can occur by undulation instability by buckling of layers,\textsuperscript{33} indicated by splitting of crescents on either side of the meridian.
Figure 5.5  Stress-strain curve (force ramp 0.05 N/min) for X-ray diffraction of E-H6-1.3 elastomer illustrating points at which WAXD data in Figures 5.6 - 5.8 were obtained.
Figure 5.6  Diffraction patterns of elastomer (E-H6-1.3) stretched uniaxially at different extension ratios ($\lambda = L/L_0$).
Figure 5.7  Low angle reflection integrated over \(2.3^\circ \leq \theta \leq 4.2^\circ\) for uniaxially drawn elastomer at different extension ratios at 30 °C. Direction of stretching corresponds to \(\chi = 0^\circ\) and \(\chi = 180^\circ\). Data near/behind the beamstop are omitted for clarity.
Figure 5.8  Wide angle reflection integrated over \((14^\circ \leq 2\theta \leq 25^\circ)\) uniaxially drawn elastomer at different extension ratios at 30 °C. Direction of stretching corresponds to \(\chi = 0^\circ\) and \(\chi = 180^\circ\). Data near/behind the beamstop are omitted for clarity.

5.3.1. Mechanical behavior of MCLCEs

Figures 5.9 and 5.10 show the effect of temperature on the stress-strain behavior of elastomers subjected to uniaxial tension. Dramatic decreases in both nominal plateau stress and the Young’s modulus are observed with increasing temperature. The same temperature dependence was previously observed for the main-chain smectic elastomers\(^5\) and the side-chain nematic elastomers\(^34,35\) As the temperature approaches the isotropization temperature, the polymer backbone between the crosslinks assumes a
random coil conformation to maximize its entropy, exhibiting ordinary rubber-like response. At temperatures below $T_{si}$, hairpins are present in the smectic state. At lower temperature, the volume fraction of smectic material is higher, so the concentration of hairpins is higher, taking up the stress imposed on them and leading to a higher width of plateau (region II). However, in this case, the effect of temperature dominates hairpin elasticity because of gradual melting of smectic material as temperature increases.

**Figure 5.9**  Effect of temperature on the stress-strain behavior of elastomer E-H8-1.4.
Figure 5.10  Effect of temperature on the stress-strain behavior of elastomer E-H8-1.4.

In order to understand the effect of temperature on the plateau stress and the width of the plateau region, the ratio of $\sigma_N/\sigma_P$ was plotted against strain in the Figure 5.10. MCLCEs behave as conventional rubber like materials at 90 °C, when the smectic phase is mostly or entirely melted. At lower temperature, the concentration of smectic phase is higher, leading to higher concentration of hairpins, therefore deviating significantly from ordinary elasticity. At 30 °C, domains acts as a weak physical crosslinks; however at 90 °C, smectic domains melt and region I disappears.

The nominal plateau stress is related to the energy barrier required for transient disordering of smectic domains. From Figure 5.11, the domains get smaller as the
temperature increases, and the energy barrier decreases with increasing temperature. At lower temperature, there is a higher volume fraction of smectic material and larger domains. Big, stable domains require a large amount energy input to allow pulling out of a hairpin because they are more stable. Thus, a larger plateau stress is observed in samples having larger domains. At higher temperature, there is partial melting of the domains. Domains melt along the edge or at defects, leaving smaller domains and more amorphous material. Thus as the temperature increases, the concentration of smectic phase decreases and the nominal stress required to initiate yielding is smaller, exhibiting progressively more rubber-like response.
Figure 5.11  WAXD at different temperatures of MCLCEs ($\rho = 0.08, r = 1.4$).

Low angle reflections of samples were fitted by IGOR Pro 6 software, to sum of Gaussian functions using equation:

$$y = A \exp\left(-\left(\frac{x-x_0}{B}\right)^2\right)$$  \hspace{1cm} (5.1)

where, A and B are height and width of the peak respectively.
Figure 5.12  Fitting of low angle reflection to sum of Gaussian functions ($\rho = 0.06, \ r = 1.4$).

From the values obtained using software, domain sizes of MCLCEs were estimated using the Scherrer equation:

$$D \approx \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (5.2)

where $\lambda$ is wavelength of Cu K$_{\alpha}$ radiation (1.5418 Å), $\beta$ is the full width at half maximum intensity (FWHM) in radians, and $\theta$ is the Bragg angle.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Domain size (D, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Polymer</td>
<td>-</td>
</tr>
<tr>
<td>r = 1.4</td>
<td>200</td>
</tr>
<tr>
<td>r = 1.5</td>
<td>210</td>
</tr>
<tr>
<td>r = 1.6</td>
<td>96</td>
</tr>
<tr>
<td>r = 2.0</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 5.6  Domain sizes estimated using Scherrer equation.

Networks synthesized by varying $r$ and $\rho$ were examined by Q 800 instrument and WAXD in order to deduce the effects of chemical composition on stress-strain behavior. As $r$ increases, approaching 2, the density of elastic chains increases, as shown by the steady decrease in $Q_s$ in all series (Tables 5.1-5.4). Based on their high soluble fractions and swelling ratios ($Q_s$), networks having $r=1.3$ are presumed to contain larger concentration of pendant chains and other defects than the networks having $r=2.0$. The pendant chains in these networks are not necessarily linear, as some pendant structures with branches are also likely to form.

In the dry state, the elastomers contain some volume fraction of smectic materials, some longer chains form hairpins to increase their configurational entropy. However, not all hairpins can uncoil in response to deformation because some are “trapped” by topological constraints. De Gennes\textsuperscript{27} has proved that even in the absence of hairpins, trapped entanglements exist in main-chain nematic LCPs, and one expects the same
situation in smectic MCLCEs. These entangled hairpins are not expected to be removed by uniaxial elongation, so some hairpins exist even at high strains approaching the elongation at break. However, some hairpins are able to uncoil in response to stress, and it is these non-trapped hairpins that lead to some of the characteristic mechanical phenomena in smectic MCLCE at high deformation. As the network is stretched, hairpinned chains begin to unfold at the onset of region II, and the loss of hairpins is accompanied by transient loss of order in the respective smectic domains.

Figure 5.13  Entangled hairpin in main-chain LCPs

Thus, in region I, smectic domains contain loose chain folded structures, and in between them there are amorphous regions that contain crosslink junctions which are largely excluded from smectic domains. We will now consider how the morphology of the elastomers evolves as strain increases in passing through region II. Figures 5.14-5.17 exhibit stress-strain behavior of elastomers in series E-H4, E-H6, E-H8 and E-H10, respectively, at 30 °C. The figures exhibit the classical three-region stress-strain behavior as illustrated in Figure 5.1. As the value of $r$ increases in each series, $\rho$ (crosslink density) increases, which results in smaller smectic micro-domains and lower $M_w$ between crosslinks. From Figures 5.14-5.17 and Table 5.6, samples containing bigger, stable domains ($r = 1.3$) exhibit a higher value of nominal plateau stress than those containing smaller, less stable domains ($r = 2.0$). Thus, as the value of $r$ decreases in each series and
[A₄] also decreases, both the nominal plateau stress and the width of the plateau increase. The yielding seen at the transition from region I to region II is reminiscent of the yield behavior of semicrystalline polymers such as polyethylene and polypropylene, which exhibit necking instabilities in uniaxial extension. Although the morphology of a smectic polydomain elastomer is very different from that in spherulitic semicrystalline polymers, both types of material are thought to contain numerous chain-folded domains. The destruction of folded-chain lamellae found in spherulitic semicrystalline polymers during cold drawing may share some similarities with the transient disordering of the comparatively poorly ordered hairpinned domains in a smectic polydomain MCLCE.
Figure 5.14  Nominal stress vs. macroscopic extension ratios for E-H4 series.
Figure 5.15  Nominal stress vs. macroscopic extension ratio for E-H6 series.
Figure 5.16  Nominal stress vs. macroscopic extension ratio for E-H8 series.
Semicrystalline polymers like polyethylene (PE), isotactic polypropylene (i-PP), polyethylene terephthalate (PET), etc. are two phase mixtures of rubbery amorphous material (consisting of tie molecules, cilia, loops) between chain-folded lamellar crystals. The typical stress-strain behavior for semicrystalline polymers subjected to tensile stress is shown in Figures 5.18-5.19.
Figure 5.18  The change of a spherulite during the cold drawing of a semicrystalline polymer. (Young R J; Lovell P A  *Introduction to Polymers*; Chapman and Hall: New York, 1991)
Figure 5.19  Plastic behaviors of poly vinyl chloride and polyethylene at 22 ± 1 °C.

a) Nominal stress vs. nominal strain curve and b) true stress vs. true strain curve. (G’Sell, C.; Jonas, J. J. Journal of Materials Science 1979, 14, 583.37

Various molecular theories are proposed to explain the macroscopic stress-strain behavior of semicrystalline polymers during cold drawing. According to one conventional approach,38 these polymers exhibit considerable amounts of yield (“cold-drawing”) before failure by a combination of slip and twinning. In the first stage of deformation (elastic deformation, region a), lamellar ribbons slip rigidly past each other
and strain is accommodated by the interlamellar rubbery amorphous region. In the second stage (yielding, region b), the tie chains are highly stretched and slip along the deformation direction. In the third stage (necking, region c), blocks of crystal are pulled out of ribbons and in the fourth stage (strain hardening, region d), blocks which are still attached to each other by tie chains are aligned along the tensile axis giving rise to large macroscopic strains, that produce a fibrillar morphology as shown in Figure 5.20. Finally, when no further chain alignment is possible, the stress increases rapidly and the polymer sample fails by interfibrillar slippage (region e).

![Figure 5.20](image)

**Figure 5.20** Steps in the deformation of semicrystalline polymers. (Schultz J *Polymer Materials Science*; Prentice Hall: 1974)
Similarly, as explained in the introduction, the plateau in the stress-strain curve of smectic MCLCEs in this study could be due to elongation of hairpins combined with transient disordering of smectic domains. In region II where smectic domains are becoming disrupted, chains with hairpins will deform in super-affine fashion\textsuperscript{28} to take up macroscopic shape change. Non-hairpinned chains will not deform appreciably due to their high modulus, compared to hairpinned chains. Once a chain loses its hairpins, it does not contribute further to microscopic elongation and the remaining hairpinned chains take up any additional strain. Thus, the plateau in the stress-strain curve is due to super-affine deformation of hairpinned chains, which is accompanied by transient loss and re-development of smectic ordering. The WAXD data in Figure 5.7 clearly show that an increase in segmental ordering occurs in proceeding through region II \((1.75 < \lambda < 2.75)\). This is attributed to re-orientation of any existing domains, in addition to formation of new domains having layer normals parallel to the axis of extension.

Although the morphology of smectic MCLCP is very different from that of spherulitic semicrystalline polymers, the numerous chain folded domains in both types of materials lead to similar yield behavior in uniaxial elongation. Due to the presence of crosslinks, spherulites are unlikely to form in MCLCEs, so the morphology is better described as small chain folded smectic domains. In semicrystalline polymers there are large spherulitic structures having numerous folded interconnected chain lamellae which are better ordered than smectic polymers, and are interconnected by “tie chains” or intercrystalline bridges.\textsuperscript{38}
Figure 5.21 Force ramp rate dependence of stress-strain behavior of E-H8-1.6 MCLCE.

Figure 5.21 exhibits force ramp rate dependence of stress vs. strain behavior of MCLCE. This behavior is similar to semicrystalline polymers where nominal and plateau stress increases as the force ramp rate increase.

5.3.2 Necking in Smectic MCLCE

The similarities between mechanical behavior of cold-drawn semicrystalline polymers and smectic MCLCE raise the question of whether necking can occur in a smectic MCLCE. No evidence of neck formation has been previously reported in any mesogen-containing LCE system, to our knowledge. However, our samples clearly
exhibit a well-defined, discontinuous contraction similar to that observed in mesomorphic PDES elastomers\textsuperscript{39,40} and cold-drawn semicrystalline polymers (Figure 5.22). The signature of neck formation in a stress-strain plot is a yield stress. In a controlled strain experiment, a maximum in the nominal stress occurs between region I and region II. The nominal stress in region II is thus lower than the observed stress. A decrease in $\sigma_n$ can not be observed by a force ramp, as force is monotonically increasing. Uniaxial elongation of MCLCEs was also studied by strain ramp to observe evidence for necking.

![Image](image.jpg)

(a)                                                                                                                             (b)

**Figure 5.22** Neck formation observed (indicated by arrows) near onset of region III (drawn at 30 °C) using polarized optical microscope.
Figure 5.23  Neck formation for sample E-H6-1.3. Elongation was achieved by a linear strain ramp at a rate of 12.5%/min.

From Figure 5.23, the observed dip in the nominal stress in region II supports the visual confirmation of necking from microscope images. Necking observed is due to intrinsic softening of the MCLCE, where the elastomer undergoes some local structural rearrangement which results in a reduced resistance to deformation. Thus, yielding is initiated by the stress-induced destruction of smectic domains where hairpins are pulled out and smectic order is transiently lost, lowering the modulus (stiffness) locally.

In summary, from Figures 5.14-5.17, stress-strain curves of smectic MCLCEs studied here can be divided into three regions. In region I, at low strain, excluded amorphous material and crosslink junctions in between smectic domains deform without disordering of smectic domains. At the yield stress, domains become transiently
disordered as we go from region I to region II. In region II, deformation of microdomains takes place by hairpin unfolding, stable domains require high stress to disorder as the stabilizing free energy ($\Delta G$) of the smectic mesophase is lost, as domains temporarily pass through a disordered state. Small domains having defects, like crosslink junctions, do not take much stress to break which is similar to the lowering of the melting point of semicrystalline polymers by defects. At the end of region II, smectic domains are reformed in a monodomain state, i.e. some of the domains having hairpins are pulled out and then they can reorder on neighboring domains, forming a monodomain with new smectic layers having global orientation. In region III, at higher strain, hairpins are depleted except for “trapped” hairpins. Since elastic chains can not elongate further, deformation of monodomain takes place by layer buckling.

Finally we consider the curiously slow relaxation of smectic MCLCE upon release of tension, which was noted previously by Ortiz et al.$^{5,26}$ After stretching the sample into region III, the elastomer does not readily return to its initial shape at 25 °C, despite being 15 °C above its $T_g$. After 6 months at room temperature, elastomers in this study remained in a highly oriented monodomain state in the absence of any applied tension. However, upon heating to 50 °C, at which temperature some portion of the sample still remains in the smectic state, the elastomer relax rapidly, returning to their undeformed, polydomain state in less than one minute. When tension is let go after new smectic structure is formed, then there is an energy barrier for breaking those smectic layers, as the system is “stuck” in a local the energy minimum. It has a metastable monodomain state, with a new smectic structure which relaxes so slowly as to appear stable. At high temperature, the energy barrier for breaking smectic domains is smaller
hence the kinetics of the melting of the mesophase is faster and therefore the elastomer contracts faster at higher temperature.

Similar stress-strain behavior has been reported, in the case of endlinked poly(diethylsiloxane) (PDES) networks. Three well defined-regions within the stress-strain curves have been observed. After the initial equilibrium stretching which is similar to the behavior of amorphous elastomers, a discontinuous transition to an ordered mesophase appears as a discrete neck in the sample. The leveling of the stress (region II) is due to the growth of the oriented mesomorphic neck, which results in straightening of elastic chains. Finally, the region III corresponds to further stretching of the oriented chains together with additional reorganization and ordering of the mesomorphic domains. The shape of the stress-strain curve depends upon the rate of deformation and rate of mesophase formation, which in turn depend on temperature. Hedden et al. have reported formation of “neck,” having the quasi-monoclinic mesophase structure (similar to \( \mu \) phase of PDES), due to extended chain, helical backbone conformation. The chain axes of this mesophase are oriented in the direction of extension. Thus, the overall extension ratio of the sample is increased due to growth of mesophase at the expense of amorphous material outside the neck region. Once the entire sample is necked, the neck extension ratio increases minimally due to conversion of amorphous material within the neck to mesophase or due to further orientation of amorphous material. Finally, the sample fails once it reaches an ultimate extension ratio.

The elongation mechanism in PDES is due to a random coil to helix transition. However, in smectic MCLCE, the plateau is due to transition from hairpinned, smectic polydomain state to globally orientated smectic monodomain state, where the population
of hairpins is significantly depleted. Thus, the similarities in their stress-strain curves may be superficial. PDES relaxes quickly when stress is removed, whereas smectic MCLCE get “stuck” due to energy barrier for breaking layers. Once globally oriented smectic domains are formed in the monodomain state, relaxation to the original undeformed polydomain must proceed by disruption of the underlying smectic microstructure. The monodomain state can perhaps be considered a meta-stable state in which the elastic retractive force (entropic driving force) for relaxation is weak compared to the energetic barrier for disruption of the smectic microstructure. At higher temperatures where some of the less stable domains have melted, leaving isolated smectic domains within an amorphous matrix, relaxation of the amorphous parts can occur rapidly upon removal of the tension, producing a rapid contraction. Under these conditions, the energy penalty for contraction is significantly lower, both because less breaking of layers is involved, and because the smectic phase is less stable at higher temperatures.

5.4 FTIR-ATR microscopy of MCLCEs

MCLCEs studied in this thesis have higher concentration of soluble fractions, which were removed prior to mechanical characterization. Therefore, ATR-FTIR spectroscopy is used to check composition variation in the unextracted and extracted networks.

From Figure 5.24, carbonyl absorption at 1732 cm\(^{-1}\) is used as a reference peak to normalize spectra. For both extracted and unextracted networks, we could not conclude whether there was difference between extracted and unextracted networks as no
systematic composition change is observed amongst the samples. Though some spectra showed minor variations in absorbance assigned to Si-CH$_3$ groups, no systematic variation was found to suggest preferential leaching of either siloxane or mesogen from the elastomers during extraction.

Figure 5.24  FTIR spectra of extracted and unextracted networks ($\rho = 0.06$, $r = 1.7$)
Figure 5.24  FTIR spectra of extracted and unextracted networks ($\rho = 0.06$, $r = 1.7$).
References


Vita

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Harshad Patil received his Bachelors of Mechanical Engineering (B.E.) degree from University of Mumbai in 1999. He completed his Master of Science (M.S.) in the Materials science and Engineering from University of Central Florida, Orlando in 2003 under the guidance of Dr. Neelkanth G. Dhere. Harshad joined the Ph.D program in the Department of Materials Science and Engineering at Penn State in 2004. He started his graduate research in the synthesis of polymers and its characterization under the mentorship of Dr. Ronald C. Hedden. During his graduate work, Harshad synthesized, new low molecular weight liquid crystals and main-chain liquid crystalline polysiloxanes having interesting properties. He also carried out fundamental studies investigating how the network architecture affects the small strain oscillatory behavior and large strain uniaxial extension of main-chain liquid crystalline elastomers. His research interests also include non-conventional energy applications like solar cells and fuel cells.