Investigation of liquid crystal polymer structure-property relationships between crystal orientation and dielectric behavior

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Abstract. Liquid crystalline polymers (LCP’s) make up a class of performance materials that derive favorable mechanical, chemical, and electrical characteristics from their long-range molecular ordering. This unique microstructure gives rise to anisotropic bulk behavior and an understanding of the driving forces behind this morphology is essential to the design of manufacturing processes for isotropic material production. In this investigation, the preferred crystal orientation in injection molded LCP plaque samples was measured using wide-angle x-ray scattering (WAXS) and the degree of order in the material was quantified using an order parameter and an anisotropy factor. Additionally, the dielectric constant of the samples was measured with respect to the mold direction (MD) and transverse direction (TD). Specimens were analyzed both as-injection-molded and with the skin layer removed, to investigate the effects of hierarchal structure on material properties. It is shown that preferred orientation along the shear direction in the LCP samples corresponds to dielectric anisotropy, and mechanically removing the shear-aligned layer results in a more isotropic dielectric response.

1. Introduction
Liquid crystalline polymers (LCP’s) constitute a class of performance materials that exhibit high mechanical strength, chemical inertness, inherent flame retardancy and frequency-stable dielectric response [1, 2]. Due to these favorable properties, LCP’s are ideal candidates for various engineering applications, such as high strength-to-weight ratio components, semiconductor packaging and high-frequency electronics. The unique LCP microstructure, which in contrast to conventional amorphous polymers consists of long-range molecular ordering to form crystalline domains, gives rise to anisotropic bulk properties [3-5]. This directionally-dependent behavior can be problematic from an industrial perspective, and thus an understanding of the driving forces behind this morphology, both inherent to the material and induced during manufacturing, is essential for isotropic material production.

Typical manufacturing processes for thermotropic LCP’s include injection molding and cast film extrusion. Both processes expose the polymer to high shear and temperature gradients that ultimately drive the formation of the hierarchal LCP morphology [6]. During injection molding, shear gradients along the flow direction compete with extensional forces in the transverse direction as the material flows from the gate into the mold cavity [7]. Crystallization of the polymer is initiated at the cooler mold surface, forming the skin layer, and shear stresses arise from flow of the LCP bulk over this frozen skin, aligning the crystals along the flow direction [8, 9]. In the center of the mold cavity, transverse extensional gradients compete with the shear forces, producing a core with a more isotropic
state, or a preferred alignment perpendicular to that of the skin [8-10]. A schematic illustration of the LCP flow during injection molding, and the resulting morphology is shown in Figure 1.

![Figure 1](image)

**Figure 1.** a) Injection molding flow behaviour [11], b) hierarchal structure from injection molding [6]

The hierarchal structure that results from the injection molding process ultimately drives the anisotropic LCP behavior. In this investigation, the structure-property relationship between LCP morphology and dielectric response was probed for an injection molded thermotropic LCP. The orientation state in the polymer was determined and compared to the measured dielectric constant along the mold direction (MD) and the transverse direction (TD). This analysis was conducted for LCP plaque samples, both as-injection-molded and with the skin layer mechanically removed, to understand the contributions of the hierarchal microstructure to the macroscopic polymer properties. It was hypothesized that preferred orientation along the shear direction in the LCP samples would correspond to dielectric anisotropy between MD and TD, and that removal of the shear-aligned layer would result in a more isotropic dielectric response.

The LCP orientation state was determined by wide-angle x-ray scattering (WAXS) in transmission mode. The thickness-averaged measurement of direction and degree of preferred orientation has been a common tool for investigating LCP morphology [12-16]. Due to the ordering of rod-like LCP molecules, shown in Figure 2a, typical scattering is manifested as intensity peaks perpendicular to the direction of average molecular orientation, shown in Figure 2b, where MD runs north to south in the representative 2D WAXS pattern (thickness direction normal to the plane shown) [3]. Because of the non-polar nature of the molecules, scattering is symmetric about the orientation axis.

![Figure 2](image)

**Figure 2.** a) Schematic LCP orientation and b) resulting WAXS pattern

In addition to the direction of average orientation in the material, the degree of order in the material may be quantified by integration of the intensity data to calculate a scalar order parameter [17]:
\[ S = \frac{1}{2} \langle (3 \cos^2 \theta - 1) \rangle \]  

where \( \theta \) is the angle between an individual molecular axis and the direction of preferred orientation (the director) and \( \langle \ldots \rangle \) denotes the average over all molecules [18]. Mitchell and Windle have performed an average over all molecular orientation angles, TX, USA). The analysis was referred orientation parameters to quantify the bulk injection molded LCP material [17]. The scalar order parameter may be used for plaque samples with a single mode of orientation, or to describe the degree of preferred alignment in a single regime of the hierarchal structure. An additional metric to quantify bulk LCP order that does not make an assumption about the orientation state in the material is calculated from the tensorial description of the material orientation. Following the work of Rendon et al., this anisotropy factor (AF) may be calculated as:

\[ AF = \sqrt{(\langle \cos^2 \theta \rangle - \langle \sin^2 \theta \rangle)^2 - 4(\sin \theta \cos \theta)^2} \]  

where \( \theta \) is the angle with respect to the flow direction, and \( \langle \ldots \rangle \) denotes the average over all molecules [9]. This quantity, like the scalar order parameter, ranges between 0 and 1 for the isotropic and perfectly aligned cases, respectively, making it an ideal metric for comparing overall degrees of orientation in different materials.

The dielectric behavior of the plaques was measured using the resonant cavity perturbation (RCP) method. This non-contact technique determines the complex permittivity of the material:

\[ \varepsilon = \varepsilon_r' + i\varepsilon_r'' \]  

where \( \varepsilon_r' \) is the dielectric constant (also noted as \( \varepsilon_k \)), and describes the material’s ability to elastically store energy in an applied electric field, and \( \varepsilon_r'' \) is the dielectric loss, which describes the energy dissipated as heat in the applied field [19]. The non-polar LCP main chains, and reduced molecular mobility resulting from the crystalline order, result in both low \( \varepsilon_k \) and low dielectric loss, making LCP’s ideal insulators in high-frequency signal-carrying devices where they reduce crosstalk and power dissipation [19, 20]. The dielectric constant was measured with respect to MD and TD and compared to the orientation state in the material, both as-injection-molded and with the shear layer removed, to illuminate the structure-property relationship in the LCP.

2. Experimental

2.1. Sample Preparation

The material system utilized in this investigation was a commercially-available thermotropic LCP. Plaque samples were injection molded with a Sodick Plustech Model TR40EHV IM machine (Schaumburg, IL, USA). The specimens were prepared in a rectangular mold with a midpoint gate, the cavity measuring 76.2 mm along MD, 50.8 mm in TD, and 0.5 mm along the thickness. Samples for WAXS and dielectric testing were (27.1 mm)² square samples, punched approximately two-thirds of the way from the gate end in the middle of the plaque to minimize entrance and wall effects. For the skin versus core analysis, the outer shear layer of the samples was identified visually by color and texture change apparent in micrographs of the plaque cross-sections, and was found to be approximately 65 \( \mu \)m thick. This region was mechanically removed using a Buehler Ecomet IV polisher (Lake Bluff, IL, USA).

2.2. Wide-Angle X-Ray Scattering

The 2D WAXS orientation measurements were performed on the samples using a D/MAX-RAPID II by Rigaku (The Woodlands, TX, USA). The analysis was performed in transmission mode at 40 kV and 20 mA with a Cu K\( \alpha \) x-ray generator. A 0.5-mm collimator was used in the analysis and the exposure time for each sample was 10 minutes. Azimuthal scans were performed to measure the
degree of orientation with respect to an external frame of reference. For each sample, MD was oriented at 0 degrees and the scattering intensity was then measured as a function of angle in the plane of the sample (rotation axis parallel to the thickness direction), as shown in Figure 3.

![Figure 3](image-url)  
**Figure 3.** a) 2D WAXS pattern with angular convention, and b) resulting intensity versus angle used in the order parameter and anisotropy factor calculations below.

Visual inspection of the 2D WAXS pattern demonstrates the direction of average molecular orientation, with an isotropic state depicted by a uniform ring, and an oriented state showing poles of higher intensity. The degree of order in the samples was quantified using a scalar order parameter by integrating the intensity data [15]:

$$ S = \frac{\int_0^{\pi/2} I(\beta) P_2(\cos \beta) \sin \beta \, d\beta}{\int_0^{\pi/2} I(\beta) \sin \beta \, d\beta} $$

where $S$ is the scalar order parameter, $I$ is the intensity, and $P_2(\cos \beta)$ is the second Legendre polynomial of $\cos \beta$. Rendon et al. provide a detailed implementation of this methodology which was utilized in this investigation [9]. The resulting value provides a metric of the degree of isotropy (or anisotropy) from 0 to 1.

Following a similar method provided by Cinader and Burghardt, the degree of order in each sample was also found through the tensorial description of orientation [12]. Beginning with $u$, a unit vector representation of a point on the azimuthal intensity scan, where $u_1 = \cos \beta$ and $u_2 = \sin \beta$, the second moment tensor of $u$ is given by:

$$ \langle uu \rangle = \begin{bmatrix} \langle u_1 u_1 \rangle & \langle u_1 u_2 \rangle \\ \langle u_1 u_2 \rangle & \langle u_2 u_2 \rangle \end{bmatrix} = \begin{bmatrix} \langle \cos^2 \beta \rangle & \langle \sin \beta \cos \beta \rangle \\ \langle \sin \beta \cos \beta \rangle & \langle \sin^2 \beta \rangle \end{bmatrix} $$

where $\langle \ldots \rangle$ is the weighted azimuthal intensity distribution $I(\beta)$, with $\langle \cos^2 \beta \rangle$ calculated as:

$$ \langle \cos^2 \beta \rangle = \frac{\int_0^{\pi} \cos^2 \beta \, I(\beta) \, d\beta}{\int_0^{\pi} I(\beta) \, d\beta} $$

The anisotropy factor was finally calculated as described above in Equation 2.

2.3. Dielectric Constant Measurement

The dielectric constant was calculated for the injection-molded specimens using the RCP method, in which a sample is placed in a resonant cavity, perturbing the center frequency ($f$) from the empty cavity state. The shift in $f$ and the known sample and cavity volumes then can be used to calculate the dielectric constant of the material:
\[ D_k = \frac{V_c(f_c - f_s)}{2V_s f_s} + 1 \]  

(7)

where \( V_c \) is the volume of the resonant cavity, \( V_s \) is the volume of the sample, \( f_c \) is the center frequency of the empty cavity, and \( f_s \) is the center frequency with the sample in the cavity. The dielectric measurements were taken along MD and TD using an Agilent Technologies 8722ES vector network analyzer (VNA) and a rectangular waveguide operated at an empty cavity center peak of approximately 8.8 GHz [21].

3. Results and Discussion

The orientation results from this investigation are shown in Figure 4, with the as-injection-molded sample in (a) and the sample with the skin layer removed in (b). For both samples, a single mode of orientation along MD is seen, corresponding to a preferential alignment with the flow direction. Visual inspection of the 2D WAXS pattern alone does not conclusively show a change in scattering intensity between the two samples, however, calculation of the order parameter showed a value of 0.70 in the as-injection-molded sample and a value of 0.65 in the sample with the shear layer removed. A similar drop in the anisotropy factor between samples from 0.72 to 0.68, respectively, was also seen. Because a single mode of orientation is observed in both samples, it is expected that the scalar order parameter and the anisotropy factor would give similar results. The reduction in both order metrics with removal of the shear layer is indicative of a skin morphology that is aligned along the flow direction; by removing this highly-oriented region, the degree of order in the material is reduced. However, a uniaxial orientation along MD still exists in the sample with the skin layer removed, demonstrating that shear gradients dominated over transverse extensional gradients through the material thickness during the injection molding process. This is likely due to the thin plaque geometry.

![Figure 4. WAXS patterns for, a) as-injection-molded sample, and b) sample with skin layer removed](image)

The corresponding sample dielectric behavior in MD and TD is presented below in Figure 5. In accordance with the orientation results, dielectric anisotropy is seen in both samples, with a greater spread between MD and TD in the as-injection-molded sample. Removal of the skin layer resulted in a decrease in dielectric constant along both MD and TD, however as illustrated in Figure 6, the percent change along MD was greater, thus the dielectric response became more isotropic. As with the reduction in order metrics, this again results from removal of the highly-aligned skin morphology, ultimately reducing the contribution of this region to the bulk material anisotropy.
4. Conclusions
The orientation state and dielectric constant of injection molded thermotropic LCP samples were presented in this investigation. The complex rheological and thermal conditions present during processing give rise to a hierarchical structure in the LCP morphology that results in macroscopic anisotropy of the material behavior. To better understand the structure-property relationships in LCP’s, molecular orientation was analyzed using WAXS in transmission mode, and the dielectric constant, measured along MD and TD, was found using the non-contact RCP method. An order parameter and anisotropy factor were used to quantify the degree of order in the material, and the values were compared to the dielectric results. The LCP plaque samples were tested as-injection molded, and with the skin layer mechanically removed to illustrate the contributions of the hierarchical LCP morphology to the overall orientation state and macroscopic dielectric response.

It was found that the samples showed a single mode of orientation aligned with the flow direction, resulting from shear stresses through the material thickness during processing. Removal of the skin layer resulted in an expected reduction in the order parameter and anisotropy factor, as well as a decrease in the dielectric anisotropy between MD and TD. These results demonstrated the anisotropic contribution of the skin layer to the overall orientation state, and demonstrated the capability of the orientation metrics to predict approximate dielectric behavior. The observed structure-property relationship in the LCP injection molded plaques provides insight into the fundamental driving factors behind bulk material behavior. The subsequent understanding of how the structure develops as a function of processing presents an opportunity to predict the macroscopic LCP properties resulting from a given manufacturing process, and could eventually enable the design of improved manufacturing methods for the production of isotropic LCP materials.

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References
[1] Cox M K 1987 Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics 153 (1) 415
[2] Thompson D C et al. 2004. IEEE Transactions on Microwave Theory and Techniques 52 (4) 1343
[3] Donald A M, Windle A H, Hanna S 2006 Liquid Crystalline Polymers, New York Cambridge University Press.
[4] Donald A M, Viney C and Windle A H 1983 Polymer 24(2) 155
[5] Bedford S E and Windle A H 1990 Polymer 31 (4) 616
[6] Zhong G J and Li Z M 2005 Engineering & Science 2005 45 (12) 1655
[7] Fang J et al. 2010 *Polymer Engineering & Science* **50** (9) 1864
[8] Weng T, Hiltner A and Baer E 1986 *Journal of Materials Science* **21** (3) 744
[9] Rendon S et al. 2007 *Journal of Applied Polymer Science* **106** (4) 2502
[10] Rendon S et al. 2004 *Polymer* **45** (15) 5341
[11] Partlow W 2005 Injection Molding, in *Civil Engineering Handbook* 543
[12] Cinader D K and Burghardt W R 1999 *Journal of Polymer Science Part B: Polymer Physics* **37** (24) 3411
[13] Cinader D K and Burghardt W R 1998 *Macromolecules* **31** (25) 9099
[14] Rendon S, Burghardt W R, and Bubeck R A 2007 *Rheologica Acta* **46** (7) 945
[15] Mitchell G R and Windle A H 1988 Developments in Crystalline Polymers-2, Basset, D. C., Ed.; Elsevier London, 115
[16] Reyes-Mayer A et al. 2016 *Polymers for Advanced Technologies* **27** (6) 748
[17] Hermans P H P P 1939 *Kolloid-Zeitschrift* **88** (1) 68
[18] De Gennes P-G and Prost J 1995 *The Physics of Liquid Crystals* **83** 83. Oxford; New York Book: Clarendon Press.
[19] Ahmad Z 2012 *Polymer Dielectric Materials*, Dielectric Material, Dr. Marius Alexandru Silaghi (Ed.) InTech DOI: 10.5772/50638. Available from: [https://www.intechopen.com/books/dielectric-material/polymer-dielectric-materials](https://www.intechopen.com/books/dielectric-material/polymer-dielectric-materials)
[20] Tummala R R, 2001 Fundamentals of microsystems packaging, New York: *McGraw-Hill*
[21] Agilent 2006 Basics of Measuring Dielectric Properties of Materials, *Agilent Technologies*