Thermally-functional liquid crystal networks by magnetic field driven molecular orientation

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ABSTRACT: Aligned liquid crystal networks were synthesized by photopolymerization of liquid crystal monomers in the presence of magnetic fields. Grazing incident wide angle X-ray scattering was used to characterize the degree of molecular alignment of mesogen chains and time-domain thermoreflectance was used to measure thermal conductivity. Liquid crystal networks with mesogenic units aligned perpendicular and parallel to the substrate exhibit thermal conductivity of 0.34 W m⁻¹ K⁻¹ and 0.22 W m⁻¹ K⁻¹, respectively. The thermal conductivity and orientational order of liquid crystal networks vary as a function of temperature. The thermal conductivity of liquid crystal networks can be manipulated by a magnetic field at above the glass transition temperature (65 °C) where the reduced viscosity enables molecular reorientation on the time scale of 10 min.

Changes in the thermal conductivity $\Lambda$ of a material with temperature are typically gradual; e.g., in most cases near room temperature, the strongest increase with temperature is the linear $\Lambda(T)\propto T$ temperature dependence of a metal alloy and strongest decrease with temperature is the reciprocal $\Lambda(T)\propto 1/T$ temperature dependence of a dielectric crystal.¹ Recently, materials that have more abrupt changes in $\Lambda(T)$ have been studied for their potential as thermal
regulators. For example, the thermal conductivity of VO₂ increases abruptly by 50% at the metal-to-insulator transition, \( T_{MI} \approx 340 \text{ K} \).²

Materials that respond to a magnetic, electric, or elastic strain field with a change in thermal conductivity are also sought as thermal switches.³ The largest contrast that we are aware of for a solid-state thermal switch near room temperature, a factor of 2, is the giant magnetothermal resistance of Co/Cu multilayers.⁴ We refer to thermal regulators (materials with abrupt changes in conductivity with temperature) and thermal switches (materials with conductivity that responds to an external trigger) as “thermally functional” materials.

Here, we describe thermally functional materials based on liquid crystal networks (LCNs). Liquid crystals (LC) have long been known to have an anisotropic thermal conductivity in the nematic phase which suggests the possibility of manipulating their thermal conductivity through changes in nematic order.⁵ When polymerized, molecular ordering of mesogen units in LCN can be manipulated by external stimuli such as thermal, electric, magnetic and optical fields.⁶ The LCN films we study are synthesized by photopolymerization of liquid crystal (LC) diacylate monomers (1,4-bis-[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzene) (RM257, Wilshire Technologies) with thiol-crosslinker (pentaerythritol tetrakis[3-mercaptopropionate]) (PETMP, Sigma Aldrich) in the presence of a magnetic field. RM257 is a nematic liquid crystal monomer in the temperature range of 67 – 130 °C and can be oriented by magnetic fields due to the anisotropic magnetic susceptibility of the mesogen units (Figure 1).

A LC solution for photopolymerization was prepared by mixing RM257 with PETMP (5 mol%) and photoinitiator (2-hydroxy-2-methylpropiophenone, 0.3 wt%, Sigma Aldrich) at 80 °C. The solution was then cast onto a sapphire substrate that was previously prepared by spin coating with polyimide (PI) film followed by Al thin film deposition by magnetron
sputtering (Supplementary information Figure S1). The PI film provides thermal insulation between the Al transducer and the sapphire substrate that increases the sensitivity of the measurement to the thermal conductivity of the LC layer.\(^7\) We then removed the glass slide. Photopolymerization was performed for 20 min using UV lamps (nominal wavelength 365 nm with a nominal power at the substrate of 3-20 mW cm\(^{-2}\)), forming a randomly crosslinked liquid-crystal network (LCN) film. A magnetic field was applied parallel (\(B_\parallel\)) or perpendicular (\(B_\perp\)) to the Al/PI/sapphire substrate using N52-grade NdFeB permanent magnets during photopolymerization (Supplementary information Figure S2).\(^8\)

The thermal conductivity of aligned LCNs was measured by time domain thermo-reflectance (TDTR).\(^9\) TDTR data were collected as in-phase voltage (\(V_{in}\)) and out-of-phase voltage (\(V_{out}\)) signals measured by a lock in amplifier with a modulation frequency of 9.1 MHz. The heat penetration depth in the LCN polymer layer, \(d = A^{1/2}(\pi f C)^{-1}\) is approximately 60 nm; \(A\) is the thermal conductivity, \(f\) is the modulation frequency of the pump beam and \(C\) is the heat capacity per unit volume. Due to the small thermal penetration depth compared to the laser spot size (10 \(\mu m\)), heat flow in the LCN is nearly one-dimensional in the direction normal to the film surface. Thus, the thermal conductivity we measure by TDTR is for the direction normal to the LCN/substrate interface. During TDTR studies, we manipulate molecular orientation using the magnetic field generated by SmCo permanent magnets, which can operate at elevated temperatures up to 320 °C (Figure 2A).

We fit the data to the thermal model\(^10\) by adjusting the thermal conductivity of the LCN as the only free parameter. Thermal conductivities of sapphire (35 W m\(^{-1}\) K\(^{-1}\)) and PI (0.2 W m\(^{-1}\) K\(^{-1}\)) were obtained from literature and independent measurements, respectively. The Al layer thickness (~ 50 nm) was measured by picosecond acoustics. (Supplementary information Figure S3). The electric resistivity of Al film measured by four-point probes was...
converted to thermal conductivity using the Wiedemann-Franz law. The per-pulse heating and steady state heating by accumulation of pulses are $\Delta T_p = 3.6$ K and $\Delta T_{SS} = 8.4$ K, respectively, by 5 mW pump and probe beams which pass through the sapphire substrate.

Examples of measured and fitted TDTR data are shown in Figure 2B. First, we measured the thermal conductivity of RM257 monomers in the nematic phase at 80 °C and found 0.14 W m$^{-1}$K$^{-1}$ when a magnetic field was applied parallel to the substrate ($B_\parallel$) and 0.24 W m$^{-1}$K$^{-1}$ when a magnetic field was applied perpendicular to the substrate ($B_\perp$) (Supplementary information Figure S4). This degree of anisotropy, approximately a factor of 2, is similar to other nematic LCs. After polymerization, the thermal conductivity increases by 0.1 W m$^{-1}$ K$^{-1}$ in both directions with the formation of chemical bonds: the thermal conductivity of LCNs aligned perpendicular and parallel to the substrate are 0.34±0.05 W m$^{-1}$ K$^{-1}$ and 0.22±0.02 W m$^{-1}$ K$^{-1}$ for 10 samples, respectively. The standard deviation of multiple measurements is 10%.

We carried out grazing incidence wide-angle x-ray scattering (GIWAXS) at the 12-ID-B beamline at the Advanced Photon Source using 14 keV photons to characterize the molecular orientation of our LCNs. The 2D scattering data were collected with a PerkinElmer XRD 1621 CN detector. We mounted the samples on a temperature-controlled sample stage with the incident angle of beam varying from 0.1° to 0.25°. The 1D scattering profiles were generated using Igor-pro based software NIKA.

Figure 3 shows GIWAXS data and corresponding schematics of the mesogenic unit ordering. Note that chains connecting mesogens are omitted in the figure for clarity. We observe scattering peaks typical of magnetically-aligned LCNs. Since three phenyl rings at the core of RM257 are rotated by 24° with respect to each other the primary GIWAXS
peak at \( q \sim 1.53 \ \text{Å}^{-1} \) corresponds to a plane spacing of 4.1 Å, 0.3 Å larger than typical for \( \pi-\pi \) stacking.\(^{15} \) With the magnetic field applied perpendicular to the substrate \((B_z)\) during polymerization, the \( \pi-\pi \) stacking peak appears along the direction parallel to the substrate, indicating the vertical alignment of mesogens in the LCN, see Figure 3A.

Perpendicular and parallel GIWAXS measurements with respect to the magnetic field direction \((B_y)\) were performed to prove in-plane anisotropy of mesogens in LCN films (Figure 3B, 3C). The different features of \( \pi-\pi \) stacking orientation distribution in Figure 3B, 3C reveal the nature of in-plane anisotropic alignment of mesogen units. The long optical axis of mesogens in each domain is aligned in the direction of the magnetic field while \( \pi-\pi \) stacks have no preferential orientation around the optical axis, resulting in the isotropic ring pattern with an incident beam along with the aligned direction (Figure 3C).

We checked that the molecular orientation of LCNs polymerized with a 4 times higher cross-linker concentration (20 mol\% PETMP) is reduced as expected.\(^{14, 16} \) GIWAXS data confirm the loss of orientational ordering at the high cross-linking density (Supplementary information Figure S5). The thermal conductivity is 0.2 W m\(^{-1}\)K\(^{-1}\) independent of magnetic field orientation during polymerization as well.

We also checked the effects of surface interactions on our experiments. Near a surface, mesogenic units can exhibit local orientation that deviates from the bulk. The thickness of the boundary layer can make up a significant portion of the thermal penetration depth of the TDTR measurement.\(^{17} \) We do not observe a significant difference in thermal conductivity for LCNs with or without surface functionalization of substrate by fluorosilane (1H,1H,2H,2H-perfluorodecytrimethoxysilane, Sigma Aldrich) which greatly lowers surface
anchoring energy. The lack of dependence on surface anchoring energy indicates that surface interactions are not driving the changes in thermal conductivity.

We construct an effective medium model to provide insights on the dependence of thermal conductivity on molecular orientation. Our model describes the LCN material as comprised of partially-ordered, cylindrical mesogens embedded in an isotropic amorphous polymer matrix. The fundamental components of the in-plane and out-of-plane thermal conductivity tensors of the mesogen are $\Lambda_{\text{in-plane}}$ and $\Lambda_{\text{out-of-plane}}$. The thermal conductivity of a partially-aligned aggregate of mesogens is a function of the order parameter $S$: \(^{18}\)

\[
\Lambda_{\theta \perp}^{-1} = \frac{1}{3} \left( \Lambda_{\text{in-plane}}^{-1} + 2 \Lambda_{\text{out-of-plane}}^{-1} \right) + \frac{2}{3} S \left( \Lambda_{\text{in-plane}}^{-1} - \Lambda_{\text{out-of-plane}}^{-1} \right) \tag{1}
\]

\[
\Lambda_{B \perp}^{-1} = \frac{1}{3} \left( \Lambda_{\text{in-plane}}^{-1} + 2 \Lambda_{\text{out-of-plane}}^{-1} \right) - \frac{1}{3} S \left( \Lambda_{\text{in-plane}}^{-1} - \Lambda_{\text{out-of-plane}}^{-1} \right) \tag{2}
\]

\[
S = \frac{1}{2} \left( 3 \left\langle \cos^2 \varphi \right\rangle - 1 \right) \tag{3}
\]

where $\varphi$ is the angle between the long axis of the molecules and the magnetic field. \(^{19}\)

\[
\left\langle \cos^2 \varphi \right\rangle = \frac{\int_0^{\pi/2} f(\beta) \cos^2 \beta \sin \beta d\beta}{\int_0^{\pi/2} f(\beta) \sin \beta d\beta} \tag{4}
\]

where the orientational distribution function of the mesogen molecules $f(\beta)$ is obtained from the azimuthal intensity $I(\theta)$ of the primary scattering peak as shown in Figure 2. In both cases, we calculate $S=0.6$ as the order parameters for LCNs aligned parallel ($B_{\parallel}$) and perpendicular ($B_{\perp}$) to the substrate (Supplementary information Figure S6).

We model the flexible chain segments of the mesogens and crosslinkers as an isotropic polymer matrix. An effective medium model for cylindrical LC molecules embedded in an
isotropic matrix predicts that the effective thermal conductivity of LCNs under magnetic field parallel ($B_{//}$) and perpendicular ($B_{\perp}$) to the substrate is:

$$\Lambda_{LCN,B_{//}} = (1 - \Phi)\Lambda_{medium} + \Phi\Lambda_{B_{//}}$$

(5)

$$\Lambda_{LCN,B_{\perp}} = (1 - \Phi)\Lambda_{medium} + \Phi\Lambda_{B_{\perp}}$$

(6)

where $\Phi$ is volume fraction of rigid core of mesogen and $\Lambda_{medium}$ is thermal conductivity of the isotropic polymer matrix. We estimate $\Phi$ by

$$\Phi = \frac{(1-C)(M_{RC} / \rho_{RC})}{(1-C)(M_{LC} / \rho_{LC}) + C(M_{C} / \rho_{C})}$$

(7)

where $M_{LC}, M_{RC}$ and $M_{C}$ are the molecular weights of the LC monomer, rigid core of mesogen, and crosslinker, respectively; $\rho_{LC}, \rho_{RC}$, and $\rho_{C}$ are their mass densities; and $C$ is the crosslinker concentration. The volume fraction taken by flexible chains and crosslinker is $\Phi = 0.6$ for LCN with 5 mol% crosslinker.

Assuming $\Lambda_{medium} = 0.2 \ W \ m^{-1} K^{-1}$, we estimate the fundamental in-plane thermal conductivity, $\Lambda_{In-plane}$, and out-of-plane thermal conductivity, $\Lambda_{Out-of-plane}$, of perfectly aligned rigid core of LCN of 1.5 W m$^{-1}$ K$^{-1}$ and 0.15 W m$^{-1}$ K$^{-1}$. Thus, we conclude that the contrast in the thermal conductivity change can be improved with a larger order parameter $S$ and smaller isotropic component $\Phi$ but the upper limit on the contrast will be a factor of 10. Additional details of the effective medium modeling of thermal conductivity is described in Supplementary information Figure S7.

Due to the thermotropic nature of LCN, the molecular ordering and thermal conductivity of LCNs depends on temperature. Figure 4 shows two sets of TDTR measurement from room temperature to 200 °C for LCNs aligned perpendicular to the substrate. First, individual measurements were done at fixed temperatures (Supplementary information Figure S8) and
converted to thermal conductivity (open squares), see Figure 4. The time between each measurement is 10 min. We also measured the thermal conductivity using a constant heating and cooling rate of 4 °C min⁻¹ (small circles). In this form of TDTR measurement, the time-delay between pump and probe is fixed at 80 ps and the ratio -V_{in}/V_{out} is recorded as a continuous function of temperature and converted to thermal conductivity. Both measurements show a decreasing thermal conductivity at elevated temperature.

We attribute the decrease in thermal conductivity to the loss of molecular order at above glass transition temperature (Supplementary information Figure S9). Figure 5A-B shows GIWAXS data for LCNs aligned perpendicular to the substrate. We observed an isotropic ring at 150 °C suggesting loss of orientational and positional order. LCN maintains its thermal conductivity up to 200 °C when a magnetic field is applied in aligned direction during the measurements (Supplementary information Figure S10).

We examined chain reorientation kinetics of LCNs by switching the magnetic field direction. A LCN aligned perpendicular to the substrate (B⊥) was first heated to 200 °C and slowly cooled to room temperature in the presence of a magnetic field applied parallel to the substrate (B∥). The GIWAXS patterns (Figure 5C) and azimuthal intensity at q ~ 1.53 Å⁻¹ (Figure 5D) show that the scattering peak becomes wider and the center is tilted by 32° with respect to the initial state (Figure 5A).

Figure 6 shows thermal conductivity of LCN during magnetic reorientation. First, LCN polymerized under magnetic field parallel to the substrate (B∥) was heated to 150 °C (Figure 6A) followed by switching the orientation of the magnetic field (B⊥). The thermal conductivity of LCN increases gradually over a time span of 1500 s, see Figure 6B. The thermal conductivity shows pronounced hysteresis upon cooling. After cooling, the room
temperature thermal conductivity is 0.30 W m\(^{-1}\) K\(^{-1}\), comparable to LCNs polymerized under magnetic field \((B_L, 0.34\) W m\(^{-1}\) K\(^{-1}\)). The GIWAXS pattern after reorientation shows vertical molecular alignment as well (Supplementary information Figure S11).

The reorientation kinetics is controlled by the competition between magnetic torque, 
\[
\Gamma_m = -1/2 \mu_0^{-1} \Delta \chi B^2 \sin(2\phi)
\]
and viscous drag, 
\[
\Gamma_{vis} = -\eta \left(\frac{d\phi}{dt}\right)
\]
where \(\mu_0\) is permeability of vacuum, \(\eta\) is the rotational viscosity, \(\Delta \chi\) is the anisotropy of the magnetic susceptibility of the mesogen, and \(B\) is the applied magnetic field.\(^{21}\) The relaxation time constant \(\tau\) is\(^{22}\)

\[
\tau = \left(\frac{2\mu_0 \eta}{\Delta \chi B^2}\right)
\]

(8)

Relaxation times in prior work ranges from a few minutes for liquid crystal elastomers to a few tens of hours for block copolymers.\(^{22b, 2314, 21, 24}\)

In our experiments, \(\tau \sim 700\) s, see Figure 6B. The theoretical value\(^{17}\) of \(\Delta \chi\) of RM257 is \(1.1 \times 10^{-3}\) cm\(^3\) mol\(^{-1}\). We measured the dynamic viscosity of the LCN by rotational oscillatory rheometry at 150 °C and found \(4.5 \times 10^{3}\) Pa s. Equation 7 predicts \(\tau \sim 8 \times 10^{3}\) s (Supplementary information Figure S12), an order of magnitude higher than what we observe in the thermal conductivity measurements. An order of magnitude discrepancy between measurements and the theory has been observed in other liquid crystal polymer systems.\(^{21b}\)

In summary, magnetically aligned LCNs were synthesized via polymerization of LCs in the presence of a magnetic field. Magnetically-aligned LCNs show thermal conductivity of 0.34 W m\(^{-1}\) K\(^{-1}\) and 0.22 W m\(^{-1}\) K\(^{-1}\), respectively, for magnetic fields applied perpendicular and parallel to the substrate during polymerization. The molecular ordering and thermal conductivity of aligned LCNs are correlated and can be manipulated by temperature and
magnetic field at elevated temperature where the reduced viscosity enables chain reorientation on a time scale of minutes.
Figure 1. Chemical structure of RM257.
Figure 2. Thermal conductivity measurement of aligned LCNs by TDTR. A. Schematic illustration of TDTR measurement for LCN/Al/polyimide/sapphire samples under magnetic field $B_L$ applied by a permanent magnet. B. Measured and fitted TDTR data for LCNs polymerized under parallel ($B_\parallel$) and perpendicular ($B_\perp$) magnetic field.
Figure 3. The effect of magnetic field during polymerization on chain alignment. A. GIWAXS data for LCN polymerized with a magnetic field perpendicular to the substrate ($B_\perp$). B. C. GIWAXS data for LCN polymerized with a magnetic field parallel to the substrate ($B_\parallel$). X-ray incident direction is represented as red arrows. In the figure, scattering vector $q$ ($2\pi \lambda^{-1}$) ranged from $-3 \, \text{Å}^{-1}$ to $3 \, \text{Å}^{-1}$ for the $xy$ plane and $0$ to $4 \, \text{Å}^{-1}$ for the $z$ plane.
Figure 4. Temperature effect on thermal conductivity of LCNs. A. TDTR data for perpendicularly aligned LCN ($B_{\perp}$) measured at fixed temperature from room temperature to 200 °C. B. Thermal conductivity at each temperature converted from Figure S7 (open squares) and continuous temperature measured by in situ continuous TDTR with a heating rate of 4 °C min$^{-1}$ (dots). Continuous thermal conductivity is converted from $-V_{\text{in}}/V_{\text{out}}$ at fixed time delay $t = 80$ ps.
Figure 5. Temperature effect on molecular ordering and magnetic field reorientation.
A. GIWAXS data for LCN aligned perpendicular to the substrate ($B_{\perp}$) at 25 °C. B. GIWAXS data for LCN aligned perpendicular to the substrate after heating up to 150 °C. Order-disorder transition was observed. C. GIWAXS data for LCN after magnetic reorientation ($B_{\perp} \rightarrow B_{\parallel}$). LCN aligned perpendicular to the substrate ($B_{\parallel}$) was heating up to 150 °C then cooled down to the room temperature in the presence of magnetic field parallel to the substrate ($B_{\|}$). D. Azimuthal intensity of LCN aligned perpendicular to the substrate at (A), 25 °C, (B) 150 °C and (C) 30 °C after reorientation. Φ represents azimuth angle from the substrate.
Figure 6. Effect of magnetic field on thermal conductivity of aligned LCN. A. Thermal conductivity of LCNs before and after magnetic reorientation. LCN polymerized under a parallel magnetic field ($B_∥$) was heated up to 150 °C with $B_∥$. After magnetic reorientation ($B_∥ \rightarrow B_⊥$) it is slowly cooled down to room temperature. Heating and cooling rate is 4 °C min$^{-1}$. B. Thermal conductivity of a parallel aligned ($B_∥$) LCN in response to an orthogonal magnetic field ($B_⊥$) at 150 °C. The magnetic field was switched to the perpendicular direction ($B_⊥$) at 150 °C at $t = 0$ s.
ASSOCIATED CONTENT

Supporting Information. Sample preparation detail, TDTR sensitivity, thermal conductivity of RM257, additional GIWAXS data, thermal model, DSC and rheological characterization of LCN. This material is available free of charge via the Internet at http://pubs.acs.org.

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