Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Liquid Crystalline Networks based on Photo-initiated Thiol-ene Click Chemistry

Yuzhan Li[a,1], Yuehong Zhang[b,1], Monojoy Goswami[c]*, Dan Vincent[d], Liwei Wang[d], Tuan Liu[d], Kai Li[e], Jong K. Keum[f], Zhenhua Gao[b], Soydan Ozcan[g], Kyle R. Gluesenkamp[g], Orlando Rios[a,]*, and Michael R. Kessler[h,]*

[a] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
[b] College of Materials Science and Engineering, Northeast Forestry University, Harbin, 150040, China
[c] Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
[d] School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, United States
[e] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
[f] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
[g] Energy and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
[h] Department of Mechanical Engineering, North Dakota State University, Fargo, ND 58108, United States

*1 Bethel Valley Rd, Oak Ridge, TN 37831, United States
Phone: (865) 574-6843. E-mail: goswamim@ornl.gov
*1 Bethel Valley Rd, Oak Ridge, TN 37831, United States.
Phone: (865) 574-3747. E-mail: rioso@ornl.gov.
*1401 Centennial Blvd, Fargo, ND 58108, United States.
Phone: (701) 231-7494. E-mail: Michael.R.Kessler@ndsu.edu.

[1] These authors contributed equally to this work.

Monomer synthesis and LCNs formulation:

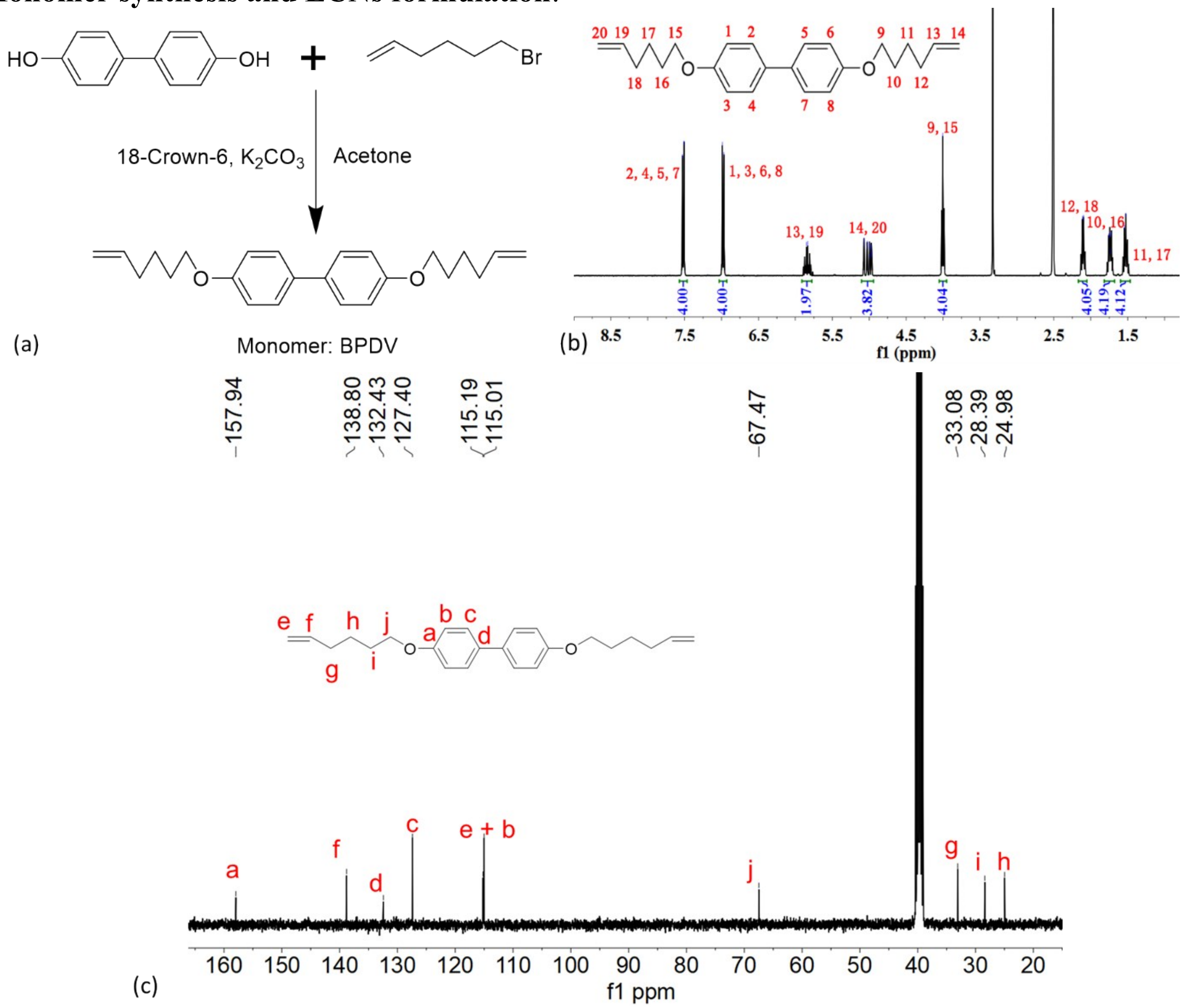

Figure S1. (a) Synthetic route of the biphenyl-based divinyl monomer. (b) ^{1}H NMR spectrum of the synthesized BPDV. (c) ^{13}C NMR spectrum of the synthesized BPDV.

The chemical shift at 4.93-5.10 and 5.75-5.90 ppm were attributed to -CH_2 and -CH of the vinyl groups, respectively. Without further purification after synthesis, the monomer showed a clean NMR spectrum, indicating that the Williamson ether synthesis method provides an efficient way to prepare divinyl monomers with a variety of mesogenic and flexible spacer structures for novel LCNs development.

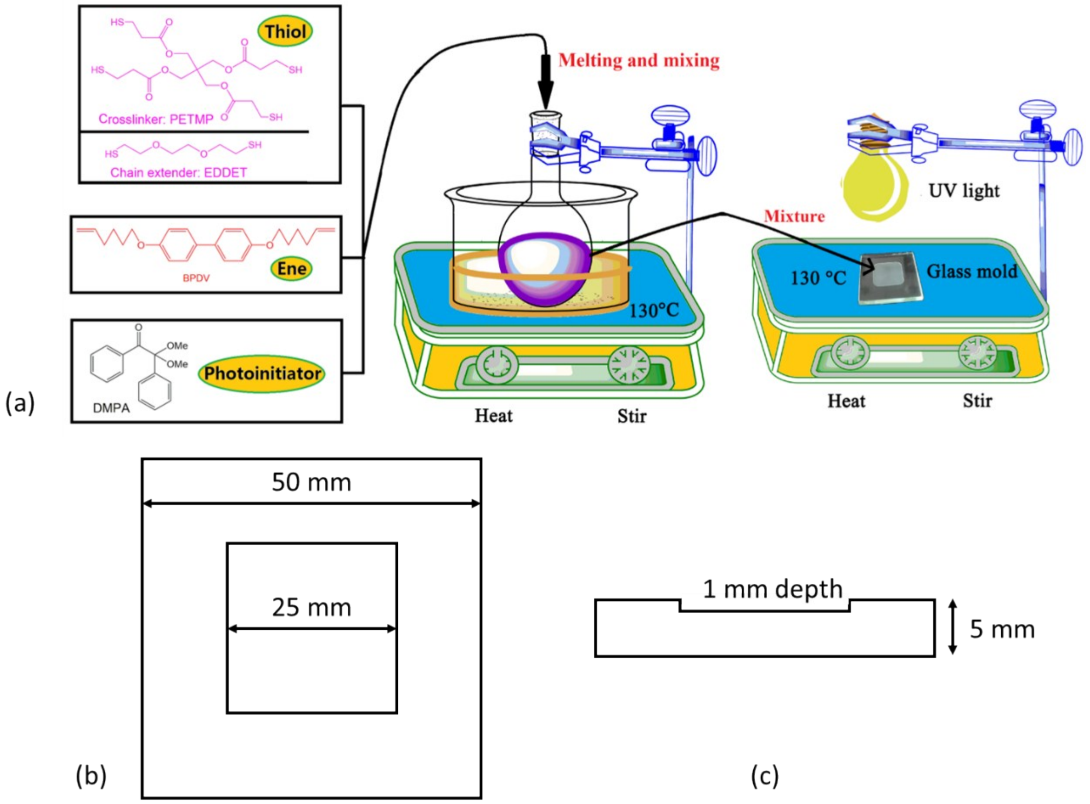

Figure S2. (a) Schematic illustration for the preparation of LCNs. (b) and (c) dimensions of the glass mold used to prepared LCNs.

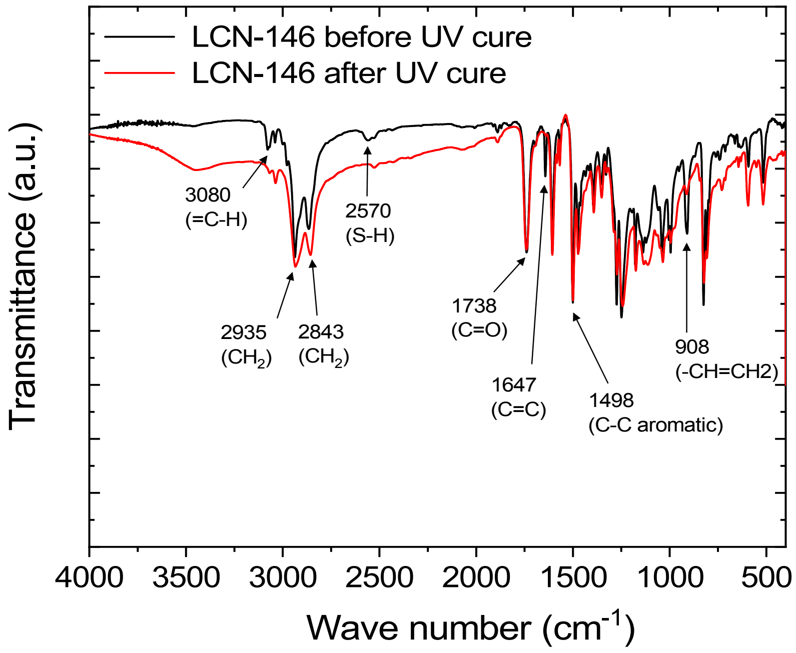

Figure S3. FTIR spectra of a model LCN-146 system before and after UV curing reaction showing the change of S=H and C=C bonds. Major peaks were indicated by arrows and were assigned to different chemical groups.

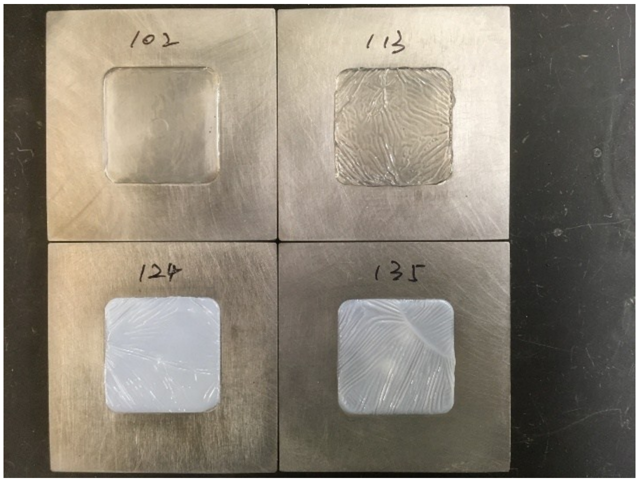

Figure S4. Optical appearance of fully cured LCNs. The variation in composition resulted in different microstructure and crystallinity, affecting transparency of the materials.

Molecular Dynamics Method:

The polymer model is based on the Kremer-Grest bead-spring model, where each monomer bead is connected by spring-like bonds. The bonds between the chains are modeled using finite extensible elastic (FENE) potential:

$$U^{FENE}(r_{ij}) =-\frac{1}{2}KR_0^2\, ln\left(1-\frac{r_{ij}}{R_0}\right)^2$$

Where, *K* is the spring constant and R_0 is the equilibrium maximum extent of the bond.

The angular interactions between the monomers are modeled by harmonic potential given by,

$$U^{ANGLE}(r_{ij}) = K_\theta\,(\theta - \theta_0)^2$$

Where, K_θ, is the prefactor and θ_0 is the equilibrium value of the angle.

The non-bonded interactions are modeled as Lennard-Jones (LJ) potential given by,

$$U^{LJ}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \varepsilon$$

Where, ε is the LJ interaction parameter and σ is the monomer diameter.

Force Field discussion: As stated, these MD simulations are performed using LJ force-field. It is well known that molecular anisotropy influences the long-range orientational ordering of liquid crystals. However, the question of anisotropic repulsive or attractive forces responsible for determining liquid crystalline behavior was not clearly known for many years. Mayer-Saupe theory of nematics established the role of the attractive forces as the determining factor of long-range orientational ordering in LC.[1] Following the attractive force Mayer-Saupe theory, we used LJ attractive forces between the rigid mesogens to model the LC polymer. The flexible monomers interact with each other via LJ repulsive forces. The crosslinkers attract each other with LJ attractive interactions. The anisotropy in the interactions between different monomers of the polymer chain helps develop LC structures in this system as usually observed in LC systems. Typically for spherical or disk-shaped materials Gay-Berne potential is considered as an accurate representation in modeling liquid crystal. However, for polymers a combination of attractive and repulsive LJ forces can be used to represent the anisotropic interactions between the monomers in liquid crystal simulations.[2-5] Therefore, we followed the route of a combination of attractive and repulsive LJ interactions between the monomers to introduce anisotropic interactions in the LC modeling.

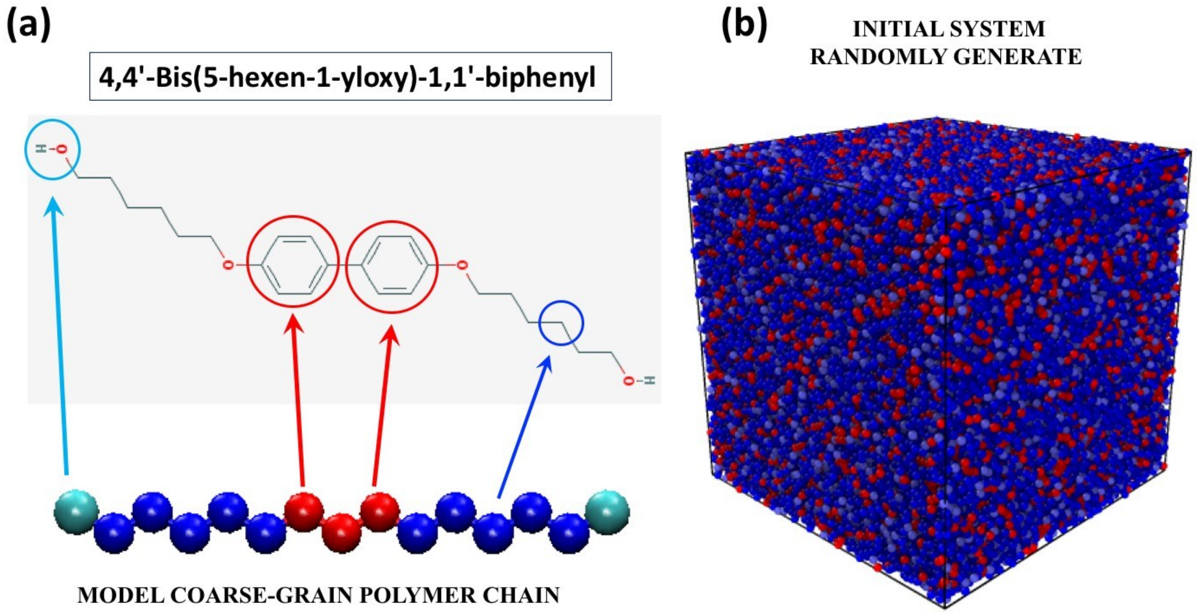

Figure S5: Model polymeric system for MD simulation. (a) coarse-graining of BPDV monomer. The cyan beads are reactive ends. The blue beads are flexible part of the chains. The red beads are the rigid mesogen that form LC structures. (b). The initial simulation box randomly generated. The cyan colors are not seen here, as the system is not crosslinked yet. The dark blue colors are chain end monomers, recolored as cyan after crosslinking.

Model System: The simulations are performed using LAMMPS molecular dynamics package. All numbers are in reduced unit denoted by asterisk. Distance, $r^* = r/s$, where s is the monomer diameter. Temperature, $T^* = k_BT/e = 1.0$ is used, where e is the Lennard-Jones (LJ) interaction parameter. The reduced density of the system = $0.81\ \sigma^{-3}$. The crosslinking is done during MD simulation.

Simulation Snapshots:
All the simulations are equilibrated for 10 million LJ time steps. Once equilibrated, the simulations are further run for 1 million LJ time steps to collect statistics. The snapshots at the end of the simulations are shown in Figure S6. Figures S6(a) and (b) are plotted for the large-chain and small-chain systems respectively. Cross-linking is performed by creating bonds between two crosslinking monomers when they approach a cut-off radius of 1.12 σ, the distance of LJ repulsive cutoff. Cyan colors show crosslinked monomers. Blue are flexible chains and the red are the rigid mesogens, the middle 3 monomers connected by 180° angle. The red color rigid monomers form higher number of clusters in small chain than large chain as can be seen from Figures S6(a) and (b).

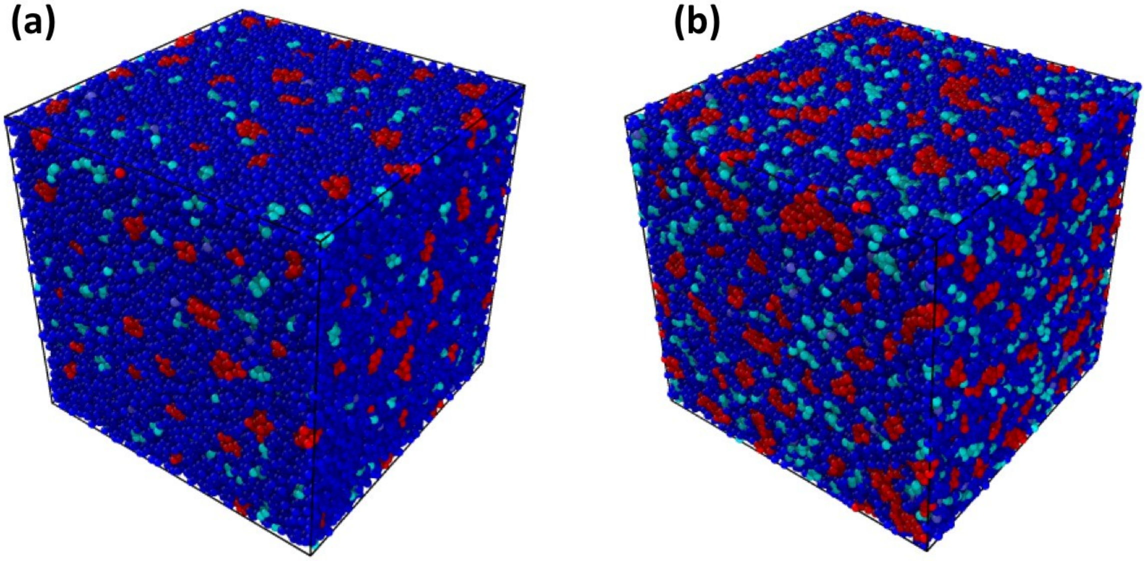

Figure S6: Simulation snapshot for the full system. The blue, red, and cyan colors are flexible, rigid and crosslinker of the polymer chains. (a) large-chain system. (b) small-chain system.

Crosslinking:
Crosslink monomers are shown in Figures S7(a) and (b) for large-chain and small-chain respectively. Crosslinking is achieved in 1 million time-steps. Two crosslinker monomers are considered crosslinked, if they come 1.12 σ distance away from each other. Once they crosslink, they become inactive for the next crosslinking. 96.9% and 97.1% of crosslinking is achieved within 1 million time-steps for large-chain and small-chain systems respectively.

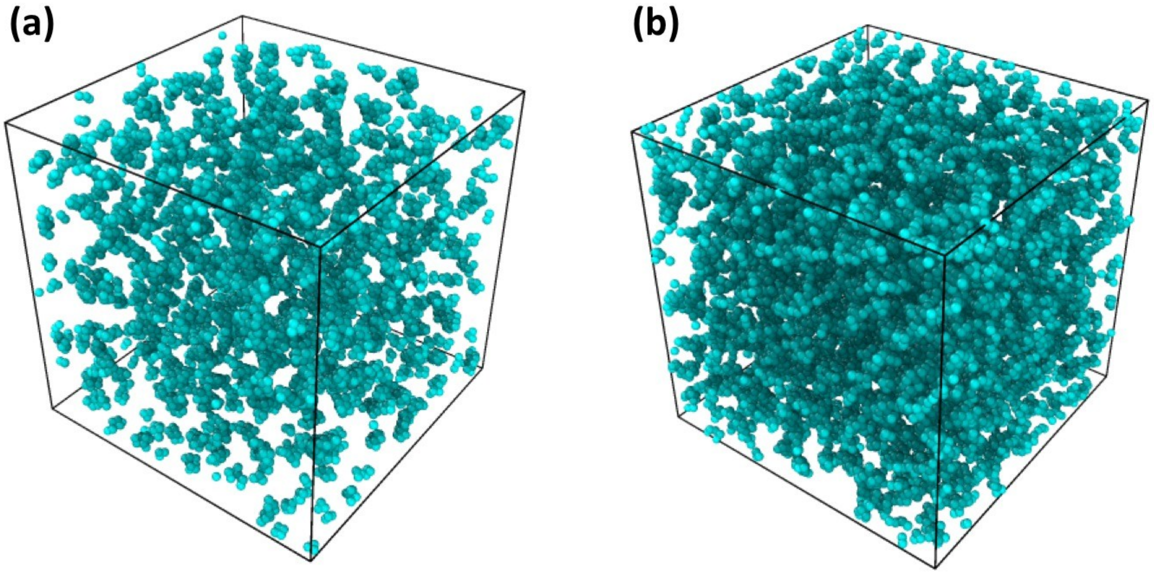

Figure S7: Crosslinking, only the crosslinked monomers are shown. (a) Large chain crosslinking. 96.9% crosslinking achieved in 1 million LJ time steps. (b) small chain crosslinking, 97.1% crosslinking achieved in 1 million LJ time steps. Both the systems show highly crosslinked polymers.

3D structures of LC domain:

In Figure S8, we show the structure of the rigid mesogens of the polymer chains. The long-range orientational ordering of liquid crystal phase can be seen in Figure S8(a) for the large-chain system. While the long-range ordering and strong agglomerated structures is observed in Figure S8(b) for the short-chain polymers, the liquid crystal phases cannot be visualized from this structure.

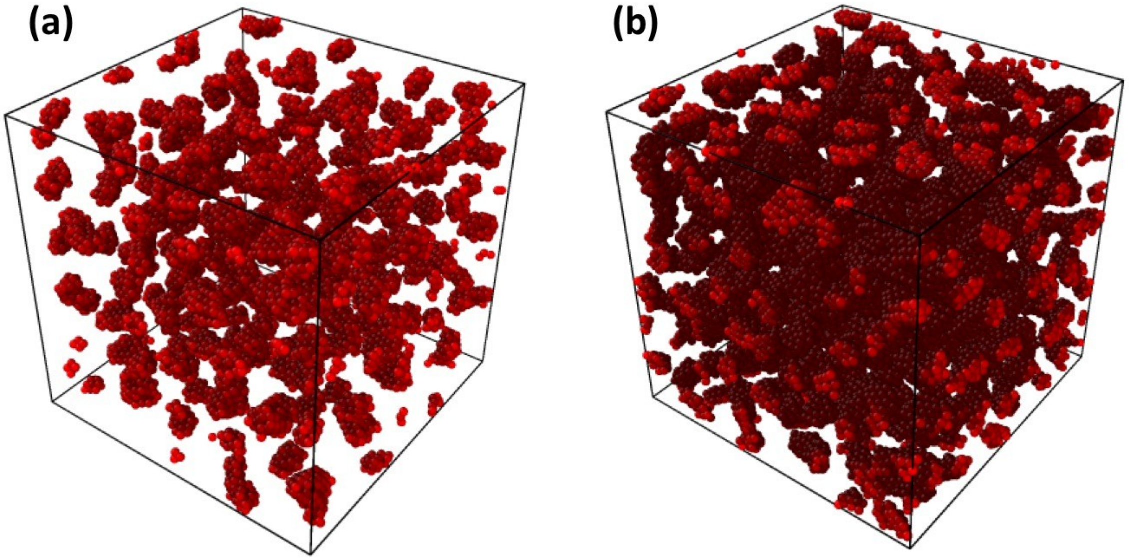

Figure S8: Three dimensional structures of the rigid mesogens at the end of simulation. (a) Self-assembly for the large-chains. The structures show well-arranged LC structures of self-assembled rigid mesogens. (b) Self-assembly for the small-chains. While well-arranged LC ordering can be seen, the agglomeration is so large, the LC ordering is downplayed by agglomeration. The cross-section slices of this structures are shown in Figure 7a and 7b in the main manuscript.

Cross-section of LC domains:
In Figure S9, we show the structure of the rigid mesogens of the polymer chains across the director, z-axis in this case. The well-defined, long-range ordering is observed in Figure S9(a) for the large-chain system. The long-range ordering is broken in Figure S9(b) for the short-chain polymers. There is higher agglomeration in Figure S6(b), that is commensurate with the density profile shown in the main text Figure 7.

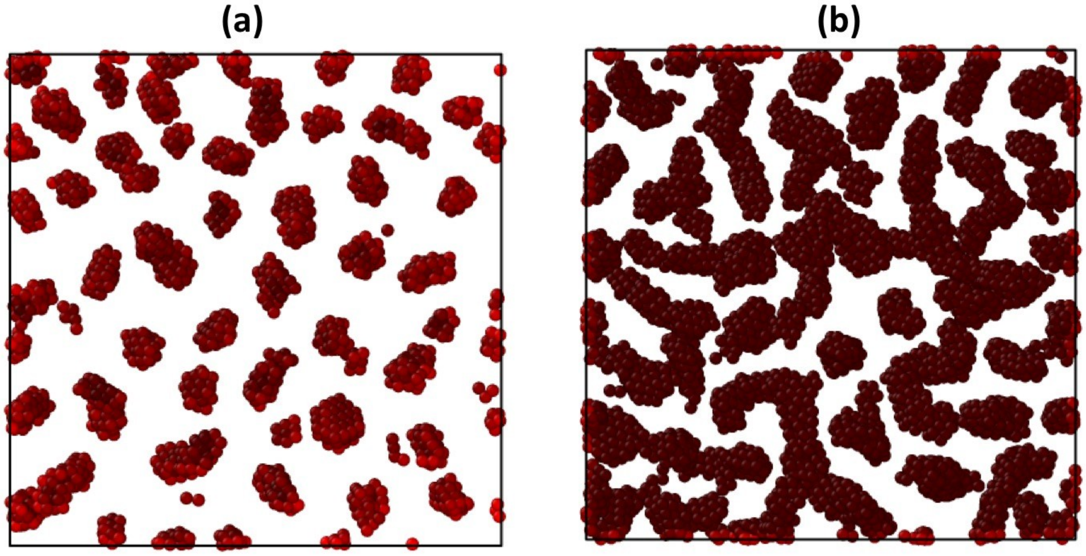

Figure S9: View along the parallel to the axis of the director. (a) large-chain structure, showing excellent LC ordering. (b) small-chain structure, showing mostly agglomeration, not well-defined LC ordering observed.

References

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