Supporting Information:
Impact of Molecular-level Structural Disruption on Relaxation Dynamics of Polymers with End-on and Side-on Liquid Crystal Moieties

Diego Becerra,*† Yang Xu,† Xiaoguang Wang,†‡ and Lisa M. Hall*†

†William G. Lowrie Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH 43210, USA
‡Sustainability Institute, The Ohio State University, Columbus, OH 43210, USA

E-mail: becerra.39@osu.edu; hall.1004@osu.edu
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S1  Nonbonded and bonded interactions

S1.1  Bond and angle interactions

The intramolecular potentials comprise interactions within the polymer backbone and the spacers, between the polymer backbone and spacers, and between the spacers and liquid crystals moieties.

The interactions within the polymer (main backbone and spacers) are the following:

\[
U_{\text{bond}} + U_{\text{angle}} + U_{\text{twist}} + U_{\text{align}}
= \frac{k_b}{2} \sum_{i=1}^{N_b-1} (\ell_i - \ell_{b,0})^2 + k_\beta \sum_{i=1}^{N_b-2} [1 - \cos(\beta_i)]
+ k_\omega \sum_{i=1}^{N_b-1} [1 - \cos(\omega_i)] + k_\psi \sum_{i=1}^{N_b-1} [1 - \cos(\psi_i)],
\]

(1)

where \(\ell_i = |r_{i+1} - r_i|\) is the distance between adjacent sites, \(k_b\) is the bond force constant, and \(\ell_{b,0}\) is the equilibrium bond length; \(\cos(\beta_i) = \hat{r}_{(i)(i+1)} \cdot \hat{r}_{(i+1)(i+2)}\) is the angle between adjacent bonds with angle force constant \(k_\beta\); \(\cos(\omega_i) = \frac{\hat{r}_{i+1} \cdot \hat{r}_{i+1} \cdot \hat{u}_i}{1 + \hat{u}_i \cdot \hat{u}_{i+1}}\) is the twist around the polymer backbone between adjacent sites and \(k_\omega\) is the corresponding twist force constant. The last term, \(U_{\text{align}}\), constrains \(\hat{u}_i\) of each site to be aligned with the bond vector, \(\hat{r}_{(i)(i+1)}\), where \(\cos(\psi_i) = \hat{u}_i \cdot \hat{r}_{(i)(i+1)}\) and \(k_\psi\) is the corresponding force constant.

Note that through \(k_\beta\) we can set the stiffness of the polymer.

For the bonded potentials regarding polymer main backbone (PB)–spacer (SP) interactions and spacer (SP)–liquid crystal (LC) interactions we have adopted the notation \(U_b(\ell; k, \ell_0) = \frac{k}{2} (\ell - \ell_0)^2\) for the corresponding bonds, and \(U_0(\hat{x}, \hat{y}; k, \theta_0) = \frac{k}{2} (\theta - \theta_0)^2\) for the corresponding angles, where \(\cos(\theta) = \hat{x} \cdot \hat{y}\), and \(k\), \(\ell_0\), and \(\theta_0\) are the corresponding force constant, equilibrium bond length, and equilibrium angle.
To attach the spacers to the main backbone while ensuring their syndiotacticity, we have adopted a bond potential and an orientational potential as follows

\[
U_{\text{bond}} + U_{\text{orient}} = U_b(\ell_{(PB)(SP)}; k_b, \ell_{b,0}) + U_o(\hat{r}_{(PB)(SP)}, \hat{\sigma}_{PB}; k_a, 90^\circ) + U_o(\hat{r}_{(PB)(SP)}, \hat{\sigma}_{SP}; k_a, 90^\circ) + U_o(\hat{\omega}_{PB}, \hat{\omega}_{SP}; k_a, 180^\circ) + U_o(\hat{r}_{(PB)(SP)}, \hat{\omega}_{PB}; k_a, 90^\circ) + U_o(\hat{\omega}_{SP}, k_{\xi}, 90^\circ) + U_o(\hat{\omega}_{PB}, \hat{\omega}_{SP}; k_{\xi}, 90^\circ).
\]

(2)

where the angles are those between the unit orientational vectors specified.

Finally, the interactions between the terminal mesogenic group that represents a liquid crystal unit to the spacers, which set the liquid crystal type of attachment (end-on side-chain (EOSC) and side-on side-chain (SOSC) configurations).

For the EOSC configuration, the potential is given by

\[
U_{\text{bond}} + U_{\text{orient}} = U_b(\ell_{(SP)(LC)}; k_{b,\text{EOSC}}, \ell_{b,0,\text{EOSC}}) + U_o(\hat{f}_{SP}, \hat{f}_{LC}; k_{\xi}, 90^\circ) + U_o(\hat{r}_{(SP)(LC)}, \hat{u}_{SP}; k_{\xi}, 90^\circ) + U_o(\hat{r}_{(SP)(LC)}, \hat{u}_{LC}; k_{\xi}, 0^\circ) + U_o(\hat{u}_{PB}, \hat{u}_{SP}; k_{a}, 90^\circ).
\]

(3)

For the SOSC configuration, the potential is given by

\[
U_{\text{bond}} + U_{\text{orient}} = U_b(\ell_{(SP)(LC)}; k_{b,\text{SOSC}}, \ell_{b,0,\text{SOSC}}) + U_o(\hat{\omega}_{SP}, \hat{\omega}_{LC}; k_{\xi}, 180^\circ) + U_o(\hat{r}_{(SP)(LC)}, \hat{u}_{SP}; k_{\xi}, 0^\circ) + U_o(\hat{r}_{(SP)(LC)}, \hat{u}_{LC}; k_{\xi}, 90^\circ).
\]

(4)

For more detailed information, the reader should refer to the original source.\textsuperscript{S1}
S1.2 Bonded and nonbonded parameter values

Table S1: Parameter values for nonbonded and bonded interactions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>1</td>
<td>Generic polymer</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>1</td>
<td>Generic polymer</td>
</tr>
<tr>
<td>$m$</td>
<td>1</td>
<td>Generic polymer</td>
</tr>
<tr>
<td>spherical shape</td>
<td>(1, 1, 1)</td>
<td>Generic value</td>
</tr>
<tr>
<td>aspherical shape (ellipsoid)</td>
<td>(1, 1, 3)</td>
<td>Generic value</td>
</tr>
<tr>
<td>$\left(\kappa, \kappa', \mu, \nu\right)$</td>
<td>(3, 5, 1, 3)</td>
<td>Berardi et al. [54]</td>
</tr>
<tr>
<td>$k_b$</td>
<td>$200 k_B T / \sigma^2$</td>
<td>Chen et al. [53]</td>
</tr>
<tr>
<td>$l_{b,0}$</td>
<td>$1 \sigma$</td>
<td>Chen et al. [53]</td>
</tr>
<tr>
<td>$k_\beta$</td>
<td>$1.5 k_B T$</td>
<td>Dietz et al. [54], Ethier and Hall [55]; Faller et al. [56]</td>
</tr>
<tr>
<td>$k_\omega$</td>
<td>$20 k_B T$</td>
<td>Brackley et al. [57]</td>
</tr>
<tr>
<td>$k_\psi$</td>
<td>$90 k_B T$</td>
<td>Brackley et al. [57]</td>
</tr>
<tr>
<td>$k_\alpha$</td>
<td>$90 k_B T / \text{deg.}^2$</td>
<td>Generic parameter to maintain topology</td>
</tr>
<tr>
<td>$k_{b,\text{OSC}}$</td>
<td>$200 k_B T / \sigma^2$</td>
<td>Chen et al. [53]</td>
</tr>
<tr>
<td>$f_{b,0}$</td>
<td>$1 \sigma$</td>
<td>Chen et al. [53]</td>
</tr>
<tr>
<td>$k_{\text{OSC}}$</td>
<td>$200 k_B T / \sigma^2$</td>
<td>Chen et al. [53]</td>
</tr>
<tr>
<td>$f_{\text{OSC}}$</td>
<td>$2 \sigma$</td>
<td>Geometric consideration</td>
</tr>
<tr>
<td>$k_\xi$</td>
<td>$90 k_B T / \text{deg.}^2$</td>
<td>Generic parameter to maintain topology</td>
</tr>
</tbody>
</table>
S2 High T chain structure relaxation

We first calculate the backbone’s end-to-end vector autocorrelation function (ACF$_{ee}$) defined as $\frac{\langle R_{ee}(t) \cdot R_{ee}(0) \rangle}{\langle R_{ee}^2 \rangle}$, where $R_{ee}$ is the vector from the first backbone bead to the last backbone bead. The function was calculated for time blocks of 30,000 $\tau$ with starting times spaced 2,000 $\tau$ apart. These block-averaged functions were then averaged over 15 trials with different starting configurations. To ensure proper relaxation of SCLCP systems, equilibration times are at least 3 times the end-to-end vector relaxation time (estimated as the intersection of the curve with $1/e$). Our results also show that the composition of mesogen type of attachment have no effect on the end-to-end autocorrelation time.

![Figure S1](image)

**Figure S1**: (a) End-to-end vector autocorrelation function (ACF$_{ee}$) and (b) mean-squared internal backbone distance as a function of monomeric units $N_m$, $\langle R^2(N_m) \rangle / N_m$; the internal distance is that from an end backbone bead to the backbone bead starting the $N_m^{th}$ monomer. All SCLCP systems containing different compositions of side-on versus end-on LC moieties are at $T = 8.0 \, \epsilon / k_B$ and $P = 1.0 \, \epsilon / \sigma^3$.

The mean-squared internal distances as a function of monomeric units are shown in Figure S1b for every system studied, where each $\langle R^2(N_m) \rangle / N_m$ point (with $N_m$ the number of monomeric units) is the mean-squared distance from the end backbone bead to the first backbone bead of the monomer $N_m$ where a monomer in the SCLCP model is defined as two consecutive backbone beads and the corresponding side chain that is attached to one
of them. This result is calculated by averaging over all of the chains of 10 melt configurations, spaced 9,000 τ from each other and from the last 90,000 τ of simulation. In all cases, a plateau in the $\langle R^2(N_m) \rangle / N_m$ vs. $N_m$ curve is obtained. Similar to the autocorrelation function for end-to-end vector, the plateau value of the mean squared internal distances is independent of the composition of mesogen type of attachment.
Figure S2: The filled volume from equilibrium simulations as a function of (a) polymer backbones, (b) spacers, and (c) LC moieties is shown for the purely end-on SCLCP system at $T = 1.0 \varepsilon/k_B$ and $P = 1.0 \varepsilon/\sigma^3$. Additionally, the filled volume as a function of (a) polymer backbones, (b) spacers, and (c) LC moieties is shown for the purely side-on SCLCP system at $T = 1.0 \varepsilon/k_B$ and $P = 1.0 \varepsilon/\sigma^3$. Voids are obtained by constructing a surface mesh using the alpha-shape method in OVITO.
Figure S3: Snapshots of purely end-on and purely side-on SCLCP systems (top and front views are comprised in the same image for visualization purposes) from equilibrium simulations at different thermodynamic states (with $P = 1.0 \epsilon / \sigma^3$) for $k_\beta = 0.0$ at the left side of the image and for $k_\beta = 1.5$ at the right side of the image. From top to bottom, mesophases from isotropic to crystalline order can be observed. Cyan represents liquid crystal moieties attached in an end-on manner, yellow represents liquid crystal moieties attached in a side-on manner, scarlet represents spacers, and dark scarlet represents polymer backbones.
S4  Structural Observables of Simulated SCLCP Systems.

S4.1  Radial distribution function of liquid crystals moieties

The radial distribution function of liquid crystals moieties, $g_{\text{LC-LC}}(r)$, was calculated using the standard method, as the average number of times an LC unit would observe another LC unit at a distance between $r$ and $r + \Delta r$ from itself, normalized by the expected number at uniform density (i.e., the number of other LCs in the system divided by the volume of the system). The range of $g_{\text{LC-LC}}(r)$ is from 0 to large positive numbers. A value of 1 indicates a random distribution, a higher value denotes an enrichment, and a value less than 1 signifies a depletion of mesogens in a given separation range.

![Figure S4: Liquid crystal radial distribution function, $g_{\text{LC-LC}}(r)$, at different temperatures obtained from equilibrium simulations with liquid crystal moieties attached in a side-on manner to the polymer backbone with varying percentages as follows: (a) 0% (purely end-on configuration), (b) 20%, (c) 40%, (d) 60%, (e) 80%, and (f) 100% (purely side-on configuration).](image)

At high temperatures ($T > 3 \epsilon/k_B$), the $g_{\text{LC-LC}}(r)$ curves show a consistent random dis-
tribution for all systems, regardless of the composition of LC moieties of different types (see Figure S4). This observation is in agreement with the isotropic state already seen in Figure 3 in the Main Document. However, at lower temperatures, differences become more noticeable, and the first $g_{\text{LC-LC}}(r)$ peak for each system appears at $\sim 1.15 \sigma$ due to the implementation of potentials, but the peak values vary between systems. The overall $g_{\text{LC-LC}}(r)$ trends for purely end-on and purely side-on have been analyzed at length in our prior work for different architectural parameters S1.

The features of the purely end-on system at low temperatures (see Figure S4a) include: (i) the highest peak at $T \sim 1.15 \epsilon/k_B$ corresponding to the largest LC packing, (ii) the second peak is split in the middle, which is characteristic of a hexagonal lattice arrangement, as shown in the top view of Figure 4a, and (iii) at low temperatures, an undulation extending along the computational box can be observed, reflecting the lamellar smectic B-like order in the end-on SCLCP systems. On the other hand, the low-temperature features in the $g_{\text{LC-LC}}(r)$ measurements for side-on SCLCP systems (see Figure S4f) include: (i) first and second peaks much smaller when compared to purely end-on systems due to the absence of smectic B-like order, (ii) the second $g_{\text{LC-LC}}(r)$ does not show a bifurcation, and (iii) the undulations are also visible at low temperatures for long distances, which are related to the quasi-hexagonal shape with columnar structures caused by the LC moieties surrounding and isolating the polymer chains.
S5  Dynamic Observables of Simulated SCLCP Systems.

In Figure S5, the complete $G_{xy}(t)$ curves are shown, including shorter timescales where stress relaxation occurs primarily due to bond and local vibrations. Additionally, longer timescales with reduced resolution, which are not displayed in Figure 6 in the Main Document, are also included.

Figure S5: Relaxation modulus, $G_{xy}(t)$, calculated from the $xy$ component of the stress tensor at different temperatures obtained from equilibrium simulations with liquid crystal moieties attached in a side-on manner to the polymer backbone with varying percentages as follows: (a) 0% (purely end-on configuration), (b) 20%, (c) 40%, (d) 60%, (e) 80%, and (f) 100% (purely side-on configuration). A power law of $-1/2$ is drawn as a guide to the eye. Liquid crystal to isotropic temperatures $T_{LC-I}$ are given in purple in all plots for every case. Curves above $T_{LC-I}$ are shown in various shades of red, while curves below $T_{LC-I}$ are shown in different tonalities of blue.
In Figure S6, the $G(t)$ curves without truncation from the off-diagonal components that include the parallel axis to the LC director $z$ are averaged to obtain the relaxation modulus $G(t) = (G_{xz}(t) + G_{yz}(t))/2$. Interestingly, the same trends discussed in the Main Document for Figure S3 are largely maintained here.

Figure S6: Relaxation modulus, $(G_{xz}(t) + G_{yz}(t))/2$, calculated from the $xz$ and $yz$ components of the stress tensor at different temperatures obtained from equilibrium simulations with liquid crystal moieties attached in a side-on manner to the polymer backbone with varying percentages as follows: (a) 0% (purely end-on configuration), (b) 20%, (c) 40%, (d) 60%, (e) 80%, and (f) 100% (purely side-on configuration). A power law of $-1/2$ is drawn as a guide to the eye. Liquid crystal to isotropic temperatures $T_{LC-I}$ are given in purple in all plots for every case. Curves above $T_{LC-I}$ are shown in various shades of red, while curves below $T_{LC-I}$ are shown in different tonalities of blue.
To provide more specificity and demonstrate that intermediate profiles could be observed in all the systems, although at different temperatures, we conducted another simulation for a purely side-on SCLCP system at $T = 1.72 \varepsilon / k_B$, which is slightly higher than the transition point and some orientational order of the LC moieties can be observed. The resulting new $G(t)$ curve is highlighted in yellow in Figure S7. It is evident that the curve is not flat and deviates from the Rouse-like behavior ($t^{-1/2}$) as well.

Figure S7: Relaxation modulus, $G_{xy}(t)$, calculated from the $xy$ component of the stress tensor at different temperatures obtained from equilibrium simulations for purely side-on SCLCP system. A power law of -1/2 is drawn as a guide to the eye. Liquid crystal to isotropic temperatures $T_{LC-I}$ is given in purple.
References


