Supplementary Information

Phase behavior of main-chain liquid crystalline polymer networks synthesized by alkyne-azide cycloaddition chemistry

Yongjian Wang\textsuperscript{a} and Kelly A. Burke\textsuperscript{a,b,c,*}

\textsuperscript{a}Chemical and Biomolecular Engineering, University of Connecticut, 191 Auditorium Road Unit 3222, Storrs, CT 06269-3222

\textsuperscript{b}Polymer Program, Institute of Materials Science, University of Connecticut, 97 North Eagleville Road Unit 3136, Storrs, CT 06269-3136

\textsuperscript{c}Biomedical Engineering, University of Connecticut, 260 Glenbrook Road Unit 3247, Storrs, CT 06269-3247
Differential Scanning Calorimetry and POM of Monomers

Figure S1. Second heating and second cooling differential scanning calorimetry (DSC) traces of (a) 5yMe and (b) 5yH monomer.

The second heating trace for 5yMe (Figure S1.a) shows a small recrystallization exotherm peak at 22°C, and two endothermic valleys at 133°C and 172°C due to the melting and the LC-to-isotropic transitions, respectively. Upon cooling, 5yMe shows two exothermic peaks, with one at 171°C due to the isotropic-to-LC transition and the other at 50°C due to crystallization. The second heating trace for 5yH (Figure S1.b) shows a recrystallization exotherm at 65°C, and two endothermic valleys at 123°C and 227°C due to the melting and the LC-to-isotropic transitions, respectively. Like 5yMe, 5yH shows two exothermic peaks on the cooling trace, with one at 226°C due to the isotropic-to-LC transition and the other at 76°C due to crystallization.

POM of Monomers

Figure S2. Polarized optical microscopy (POM) images of 5yMe cooled from the isotropic melt at 10°C/min at the following temperatures: (a) 170°C, (b) 100°C, and (c) 15°C. POM images of 5yH cooled from the isotropic melt at the same rate at the following temperatures: (c) 220°C, (d) 190°C, and (e) 20°C.
DSC traces of 5yTe films

Figure S3. Second heating DSC traces of 5yTe films: (i) N-5yTe₆-PEO₃₄, (ii) N-5yTe₆-PPO₇₄.

First Heating DSC traces of 5yMe films

Figure S4. First heating DSC traces of N-5yMe₆-PEO₃₄ and N-5yMe₁₂-PEO₃₁₀. The heating trace of N-5yMe₆-PEO₃₄ showed an endothermic valley at 76.8°C and the heating trace of N-5yMe₁₂-PEO₃₁₀ showed an endothermic valley at 66.3°C.
DSC and DMA Data of N-5yMe$_2$PPO$_7$$_4$

Figure S5. (a) DSC and (b) DMA data of N-5yMe$_2$PPO$_7$$_4$. 
Additional DMA Traces of Networks

Figure S6. Comparison of different crosslink density using dynamic mechanical analysis. (a) DMA trace of 5yMe-PEO3 network films, and (b) DMA traces of 5yH-PPO7 network films. (c) DMA trace of 5yH-PEO3 network films.
Figure S7. Second heating DSC trace of 5yMe-PEO3 polymers. Glass transition of 5yMe-PEO3 polymers is at 23°C. Glass transition of 5yTe-PEO3 polymers is at -20.6°C.
Figure S8. Tensile storage modulus and tan delta as a function of temperature for \( \text{N-5yTe}_6\text{-PPO7}_4 \).
Actuation of N-5yMe_{12}-PEO_{310}

Figure S9. Actuation (two-way shape memory cycles) of \textit{N-5yMe}_{12}-\textit{PEO}_{310} using controlled force DMA.
Actuation of $N$-5yMe$_6$-PEO$_3$, $N$-5yH$_6$-PEO$_3$, $N$-5yH$_6$-PPO$_7$, and $N$-5yH$_{12}$-PEO$_{10}$

**Figure S10** Actuation (two-way shape memory cycles) of LCNs measured by DMA in controlled force mode. (a) $N$-5yMe$_6$-PEO$_3$ (b) $N$-5yH$_6$-PEO$_3$ (c) $N$-5yH$_6$-PPO$_7$ (d) $N$-5yH$_{12}$-PPO$_{10}$. Intersection of horizontal tick marks with the traces indicate half actuation strain.
Room Temperature SAXS of LCNs

Figure S11. 2D SAXS patterns acquired at room temperature of: (a) N-5yMe6-PEO34, (b) N-5yMe12-PEO310, (c) N-5yH6-PEO34, (d) N-5yH6-PPO74, and (e) N-5yH12-PPO710.

The SAXS patterns of N-5yMe6-PEO34 (Fig. S10a) and N-5yMe12-PEO310 (Fig. S10b) show one broad halo, indicating both networks display long-range ordering, but that there is no overall alignment to this structure. This was again expected for the polydomain networks. These halos are centered at q=0.054 Å⁻¹ (d=11.57 nm) for N-5yMe6-PEO34 and q=0.064 Å⁻¹ (d=9.76 nm) for N-5yMe12-PEO310 are thought to be related to the aggregation of liquid crystals. The SAXS patterns of 5yH networks synthesized with PEO3 and PPO7 also show bright halos centered at q=0.082 Å⁻¹ (d=7.66 nm) for N-5yH6-PEO34 (Fig. S10c) and q=0.083 Å⁻¹ (d=7.57 nm) for N-5yH6-PPO74 and N-5yH12-PPO710 networks (Fig. S10d and S10e) suggesting that these materials also have longer-range order, but that this is over a shorter distance than the 5yMe networks.
WAXS of Stretched SyH Networks

Figure S12. 2D WAXS pattern and 1D WAXS plot of stretched $\text{N-5yH}_6\text{-PPO7}_4$ (65% strain).

Figure S13. Azimuthal scan of stretched $\text{N-5yH}_6\text{-PPO7}_4$ (65% strain): (i) $2\theta$ at 9.3° (ii) $2\theta$ at 12.35°.
Figure S14. Azimuthal scan of stretched N-5yH6-PEO34 (60% strain): (i) 2θ at 6.50° (ii) 2θ at 8.96° (iii) 2θ at 27.2°.

Figure S15. Azimuthal scan of stretched N-5yH12-PPO710 (140% strain): (i) 2θ at 9.71° (ii) 2θ at 12.52°.