crystals

MDPI

Communication

Synchrotron Microbeam Diffraction Studies on the Alignment Within 3D Printed Smectic-A Liquid Crystal Elastomer Filaments During Extrusion

Marianne E. Prévôt [1], Senay Ustunel [1,2,†], Benjamin M. Yavitt [3,†,‡], Guillaume Freychet [3], Caitlyn R. Webb [1,4], Mikhail Zhernenkov [3], Elda Hegmann [1,2,4,5,6,*] and Ron Pindak[3]*

[1] Advanced Materials and Liquid Crystal Institute, Kent State University, Kent OH 44242-001, USA; mprevot1@kent.edu (M.E.P.); sustunel@kent.edu (S.U.); cwebb14@kent.edu (C.R.W.)
[2] Materials Science Graduate Program, Kent State University, Kent, OH 44242-001, USA
[3] National Synchrotron Light Source-II, Brookhaven National Laboratory, Upton NY, 11973, USA; benjamin.yavitt@stonybrook.edu (B.M.Y.); gfreychet@bnl.gov (G.F.); zherne@bnl.gov (M.Z.);
[4] Department of Biological Sciences, Kent State University, Kent, OH 44242-001, USA
[5] Brain Health Research Institute, Kent State University, Kent, OH 44242-001, USA,
[6] Biomedical Sciences Program, Kent State University, Kent, OH 44242-001, USA
* Correspondence: ehegmann@kent.edu (E.H.) and RP rpindak@bnl.gov (R.P.)

Synthesis of Liquid Crystal Elastomer

LCEs were prepared similarly to our earlier work with some modifications, as described below.[1,2,3] First, we prepared a 6-arm star block copolymer (6SBC-2αCl) following a ring opening polymerization of the monomers ε-caprolactone (ε-CL), modified ε-caprolactone (α-chloro-ε-caprolactone (α-Cl-ε-CL), and (*D,L*)-lactide (*D,L-LA*). We proceeded to replace a Cl halogen atom from this, which was then substituted for an azide group (-N3) obtaining the 6-SBC-2αN3 that enabled us to attach cholesterol (cholesteryl hexynoate, the LC moiety), using the alkyne-azide Huisgen cycloaddition reaction ("click" reaction) obtaining 6SBC-2αCLC. Fourier transform infrared (FTIR) spectra were used to confirm the appearance of the 2100 cm^{-1} band due to replacement of the Cl by the azide group. The cycloaddition of the LC moiety was also confirmed using FTIR spectra by the disappearance of the azide band and appearance of a new band at 3260 cm^{-1} corresponding to the triazole ring. Prior to UV curing, a methacrylate addition was performed to make 6SBC-2αCLC suitable for photocrosslinking, as described in our previous work[47]. Proton Nuclear Magnetic Resonance (^{1}H-NMR) was also used to characterize the 6-arm star block copolymer.

6-arm star poly(ε-CL-co-2α-Cl-ε-CL-co-D,L-LA), 6SBC-2αCl

In a dry and silanized ampule Dipentaerythritol (1.27 g, 0.005 mol), ε-CL (4.56 g, 0.04 mol) and α-Cl-ε-CL (2.96 g, 0.002 mol) were mixed using a vortex mixer for about a minute, then *D,L*-LA (7.21 g, 0.05 mol) was added and mixed again using a vortex mixer. The mixed solution was flushed with nitrogen and placed in the oven at 140°C for 2 hours. After that tin(II) 2-ethylhexanoate (60 mL, 0.185 mmol) was added and mixed in a vortex mixer. The ampoule was flushed with nitrogen and vacuum sealed and left in the oven for 24 hours at 140°C. As a next step, the liquid mixture was dissolved in cold dichloromethane and centrifuged for 15 minutes at 10000 rpm to collect supernatant. The solvent was removed under reduced pressure and dried in the high vacuum before further characterization and the next steps.

Synthesis of 6-arm star poly(e-CL-co-2α-N3-ε-CL-co-DL-LA), (6-SBC-2αN3)

In a round-bottom flask 6SBC-2αCl (3.8 g, 15 mmol) was dissolved in dry dimethylformamide (DMF) under nitrogen. Then, sodium azide (1.94 g, 30 mmol) was added and stirred under nitrogen at 55˚C for four days. Toluene was added after DMF was removed under reduced pressure, then dissolved solution was centrifuged at 10000 rpm for 15 minutes to remove the salt formation. The supernatant was collected and evaporated under reduced pressure and dried under high vacuum before further characterization and the next steps.

Synthesis of 6-arm-star-poly(e-CL-co-2α-cholesteryl 5-hexynoate-ε-CL-co-DL-LA), (6SBC-2αCLC) by click reaction

Modification cholesterol (LC moiety), cholesteryl 5-hexynoate, was completed exactly according to previously reported work[45]. 6SBC-2αN3 (1.93 g, 10 mmol) was dissolved in DMF: toluene (75:25) and cholesteryl 5-hexynoate (3.86 g, 8 mmol), copper iodide (0.095 g, 0.5 mmol) and triethylamine (0.10 g, 1 mmol) were added and stirred for 4 days at 40°C under nitrogen. Then, the solvent was evaporated under reduced pressure and cold methanol was added to remove unreacted materials and side products. The solution was centrifuged thrice at 10,000 rpm for 10 minutes and the supernatant was collected. The solvent was removed under reduced pressure and dried under high vacuum.

Small Angle X-ray Diffraction (SAXD)

The radial μ-SAXD profile shows two sharp peaks (q_1 = 0.16 Å^{-1} and q_2 = 0.32 Å^{-1}) corresponding to a smectic-A (Sm-A) phase with interdigitated cholesterol moieties (Figure S1a). The radial μ-SAXD profile was recorded during the extrusion process. Figure S1b shows the evolution of the radial profile in the function of printing time and length of the filament. The beam stop was obstructing the peak at q_1 = 0.16 Å^{-1} explaining the difference between the signals observed at 0.16 Å^{-1} and 0.32 Å^{-1}.

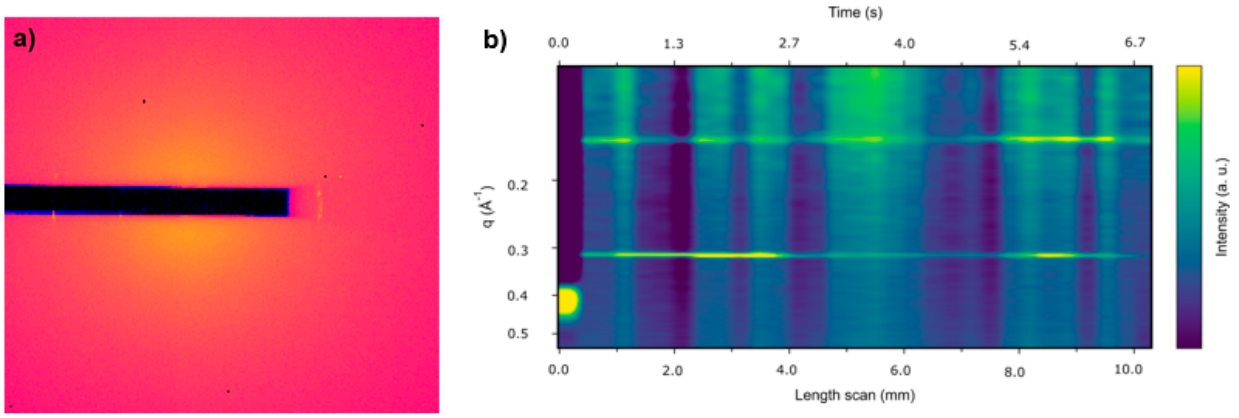


Figure S1. **a**) 2D pattern at the substrate interface and **b**) real-time radial μ-SAXD profile taken during the filament extrusion.

Figure S2 depicts 1D linecuts of azimuthal integration around q = 0.32 Å^{-1} at certain points of the length (L) scan, namely L = 6 mm, L = 7.66 mm, and L = 9mm. The prevalence of azimuthal angle 90^{o} can be seen throughout the sample. However, off-90^{o} structures are identified in the 1D linecut taken at L = 9 mm.

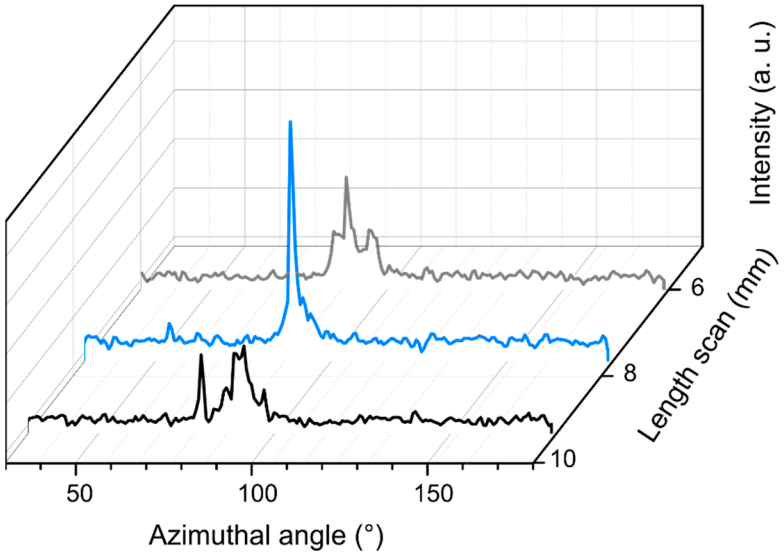


Figure S2. 1D linecut representations of μ-SAXD azimuthal angle versus intensity at three different points of length scan (L = 6 mm in grey, L = 7.66 mm in blue, L = 9 mm in black).

Similarly, the radial μ-SAXD profile was recorded on the filament height. Figure S3 shows the evolution of the radial profile taken every 9 μm during height scan. The beam stop was obstructing the peak at q_1 = 0.16 Å^{-1}, explaining the difference between the signals observed at 0.16 Å^{-1} and 0.32 Å^{-1}.

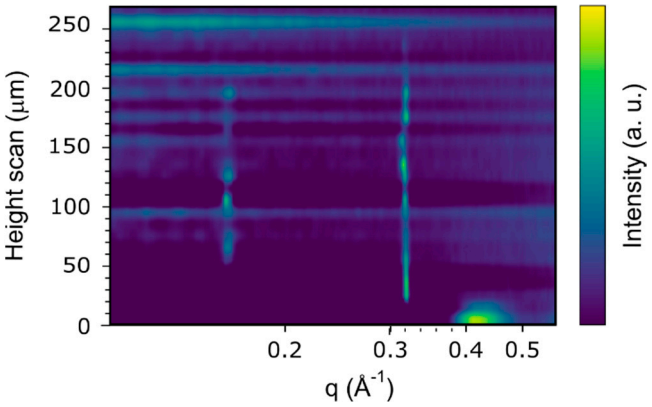


Figure S3. Real-Time radial SAXD profile across the filament height.

Figure S4 is the representation of azimuthal angle versus intensity at different heights (h) around q = 0.32 Å^{-1} as 1D linecuts. In the vicinity of the substrate interface, the layers are aligned parallel to the print direction with an approximate distribution of ± 2°. As h increases, the distribution becomes wider, to approximately ± 3.5° at a height of h = 50 μm, and a distribution of ± 10° h = 150 μm.

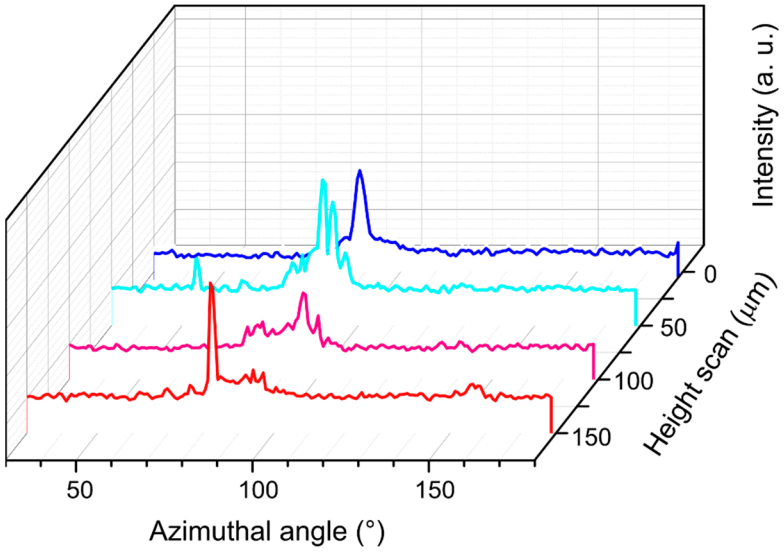


Figure S4. Representative 1D linecuts of azimuthal integration around q = 0.32 Å $^{-1}$ versus intensity at different heights through the filament: at h = 5 μm (dark blue) close to the substrate interface, h = 50 μm (cyan), h = 100 μm (pink), and h = 150 μm (red).

Reference

1 Sharma, A.; Mori, T.; Mahnen, C.J.; Everson, H.R.; Leslie, M.T.; Nielsen, A.d.; Lussier, L.; Zhu, C.; Malcuit C.; Hegmann, T.; McDonough, J.A.; Freeman, E.J.; Korley, L.T.J.; Clements, R.J.; Hegmann, E. Effects of structural variations on the cellular response and mechanical properties of biocompatible, biodegradable, and porous smectic liquid crystal elastomers. *Macromol Biosci.* **2017**, *17*, 1600278. doi:10.1002/mabi.201600278

2 Sharma, A.; Neshat, A.; Mahnen, C.J.; Nielsen, A.d.; Snyder, J.; Stankovich, T.L.; Daum, B.G.; LaSpina, E.M.; Beltrano, G.; Gao, Y.; Li, S.; Park, B.-W.; Clements, R.J.; Freeman, E.J.; Malcuit, C.; McDonough, J.A.; Korley, L.T.J.; Hegmann, T.; Hegmann, E. *Macromol. Biosci*., **2015**, 15, 200-214. doi:10.1002/mabi.201400325

3 Prévôt, M.E.; Ustunel, S.; Freychet, G.; Webb, C.R.; Zhernenkov, M.; Pindak, R.; Clements R.J.; Hegmann, E. Physical models from physical templates using biocompatible liquid crystal elastomers as new morphologically programmable inks for 3D printing, *Journal of Applied Physics*, **2021**, submitted, under peer review.