Supplementary Materials for

Probing the in-plane liquid-like behavior of liquid crystal elastomers

Haruki Tokumoto, Hao Zhou, Asaka Takebe, Kazutaka Kamitani, Ken Kojio, Atsushi Takahara, Kaushik Bhattacharya*, Kenji Urayama*

*Corresponding author. Email: bhatta@caltech.edu (K.B.); urayama@kit.ac.jp (K.U.)

Published 18 June 2021, Sci. Adv. 7, eabe9495 (2021)
DOI: 10.1126/sciadv.abe9495

The PDF file includes:

Supplementary Text
Figs. S1 to S11
Legends for movies S1 to S4
References

Other Supplementary Material for this manuscript includes the following:

(available at advances.sciencemag.org/cgi/content/full/7/25/eabe9495/DC1)

Movies S1 to S4
Supplementary Text

Deformation of the nematic elastomer membrane

Consider a flat membrane \( \Omega \) where \((x_1, x_2)\) denotes the coordinates on the membrane. Now, deform the membrane into a three dimensional surface \( S \) in such a way that the point that was at position \((x_1, x_2)\) is now at position \((y_1, y_2, y_3)\). In other words, the deformation is described as the mapping

\[
\begin{align*}
y_1 &= y_1(x_1, x_2) \\
y_2 &= y_2(x_1, x_2) \\
y_3 &= y_3(x_1, x_2).
\end{align*}
\] (A)

This deformation can induce a stretch in the plane of membrane. To calculate the principal stretches, we first calculate the metric tensor associated with the deformation is

\[
\begin{align*}
\mathbf{g}_{\alpha\beta} &= \sum_{i=1}^{2} \frac{\partial y_i}{\partial x_\alpha} \frac{\partial y_i}{\partial x_\beta}. 
\end{align*}
\] (B)

This is positive-definite 2 \( \times \) 2 matrix with two real positive eigenvalues \( \lambda^2_1 \) and \( \lambda^2_2 \) where \( \lambda_1 \geq \lambda_2 \) are positive real numbers. The principal stretches in the plane of the member are \( \lambda_1 \) and \( \lambda_2 \). So a shear of the membrane corresponds to \( \lambda_1 \neq \lambda_2 \). The theory of Cesana et al. (40) for ideal materials say that there is no shear stress as long as \( \lambda_1 \leq r^{1/2} \lambda_2 \). It is easy to adapt the arguments in Plucinsky et al. (47) and Aharoni et al. (48) to show that metrics that satisfy the relationship \( \lambda_1 \leq r^{1/2} \lambda_2 \) can drape a complex array of shapes including domes, saddles, faces and topographies.

Additional information about the numerical method.

We minimize the functional (48) in the main text using a fast Fourier transform-based numerical method introduced in Zhou and Bhattacharya (46) and similar to augmented Lagrangian method of Michel, Moulinec and Suquet (49). We introduce \( F \) as an auxiliary variable and use an augmented Lagrangian to treat the condition \( F = \nabla y \). Specifically, we consider the problem

\[
\begin{align*}
\max_{\lambda} \min_{F, y, n} \int_V W(F, n, \nabla n; n_0) dV + \frac{\nu_F}{2\Delta t} \int_V |F - F^{k-1}|^2 dV + \frac{\nu_n}{2\Delta t} \int_V |n - n^{k-1}| dV \\
+ \int_V \Lambda \cdot (F - \nabla y) + \frac{\rho}{2} |F - \nabla y|^2 dV
\end{align*}
\] (C)

and solve it using the alternating direction method of minimizers (ADMM) which is an iterative method:
Step 1. Minimize over $F, n$. This is a local nonlinear problem which is solved at each finite difference node.

Step 2. Minimize over $y$. This leads to a Poisson’s equation which we solve using fast Fourier transform over the finite difference grid.

Step 3. Update the Lagrange multiplier $\Lambda$. This is a local update at each finite difference node.

Step 4. Check for convergence and iterate if necessary. This is a global update by adding contributions from all finite difference nodes.

This iteration is conducted for each time step.

**Poisson’s ratio of I-MCPNE**

Poisson’s ratio ($\mu$) of I-MCPNE is evaluated from the lateral dimensional variation in uniaxial stretching. In finite deformation, $\mu$ for mechanical isotropic materials is defined by the ratio of longitudinal true strain ($\ln \lambda_x$) to transverse true strain ($\ln \lambda_y$):

$$\mu = -\frac{\ln \lambda_y}{\ln \lambda_x}$$

Figure S1 shows the relation of the true strains in the two directions. The dimensional variations are measured by optical microscopy using a stretching device. Each data point is the average of five measurements. All data points fall on a straight line with a slope of 0.478 in a wide range of stretch ($1 < \lambda_x < 3$) including the stress plateau regime (Fig. 1A). The value of $\mu$ is close to 0.5, ensuring the validity of the assumption of incompressibility ($\lambda_x\lambda_y\lambda_z = 1$) for I-MCPNE.

![Figure S1](image.png)

**Figure S1.** Relation of the true strains in longitudinal and transverse directions in uniaxial stretching of I-MCPNE.
Fig. S2. True stress-stretch relations of I-MCPNE in (a) unequal biaxial stretching with a strain ratio ($\lambda_x/\lambda_y = 5/3$), and (b) equibiaxial stretching. The inset shows the corresponding nominal stress-stretch relations.

Fig. S3. Effects of crosshead speed on the stress-stretch relations in planar extension of I-MCPNE: (a) nominal stress; (b) true stress.
Fig. S4. Biaxial true stresses as a function of area change in the loading plane ($\lambda_x\lambda_y$) in various types of biaxial strain for (a) SBR and (b) I-MCPNE. (a) In conventional elastomers, $t_x-\lambda_x\lambda_y$ and $t_y-\lambda_x\lambda_y$ relations depend on the type of biaxial stretching. (b) In I-MCPNE, $t_x-\lambda_x\lambda_y$ and $t_y-\lambda_x\lambda_y$ relations in all types of biaxial stretching are collapsed into a single master curve. Parts of individual loading curves that deviate from the master curve correspond to the data in the monodomain regime. The master curve indicates that $t_x (= t_y)$ in the polydomain regime is dictated by the area variation $\lambda_x\lambda_y$, (equivalently, by thickness variation $\lambda_z$).
Fig. S5. Theoretical true stress-stretch relations and director distribution for various types of extension obtained by the full-field 3D simulations with the free energy including non-ideal and Frank elasticity and a time-dependent evolution for the director. The theoretical true stress-stretch relations satisfactorily describe the experimental ones in unequal biaxial stretching with a strain ratio $(\lambda_x/\lambda_y)$ of (a) (5/2) and (b) UB(5/3) and (c) equibiaxial stretching. The insets show the nominal stress-stretch relations. The director field in real space and the corresponding diffraction patterns are also displayed. The color represents the angle of the planar component of the director. The calculations in all types of biaxial stretching are made using the same parameter set. (d) The corresponding comparison using nominal stress.

|                | Equibiaxial | UB(5/2) | UB(5/1) | Planar |
|----------------|-------------|---------|---------|--------|
| $\lambda_x$   | (1.3,1.3)   | (1.4,1.2)| (1.5,1.1)| (1.7,1.0) |
| $\lambda_z$   | (1.3,1.3)   | (1.4,1.2)| (1.5,1.1)| (1.7,1.0) |
| $\lambda_z$   | (1.5,1.5)   | (1.75,1.3)| (1.9,1.2)| (2.3,1.0) |
| $\lambda_z$   | (1.8,1.8)   | (2.2,1.5)| (2.6,1.3)| (3.3,1.0) |

Fig. S6. 2d wide-angle diffraction patterns in various types of biaxial strain for I-MCPNE obtained by obtained by the full-field 3D simulations with the free energy including non-ideal and Frank elasticity and a time-dependent evolution for the director. The corresponding experimental data are shown in Fig. 3C.
Fig. S7. Six types of biaxial stretching.

Equibaxial (EB)
\[ \lambda_x = \lambda_y = 1 \]

Planar (PE)
\[ \lambda_y = 1 \]

Unequal biaxial (UB)
\[ (\lambda_x - 1) / (\lambda_y - 1) = 5/1, 5/2, 5/3 \]

Two-step planar (TPE)
\[ \lambda_x = 1.4; \lambda_y = 1 \]
\[ \lambda_x = 1.4; \lambda_y = 1.4 \]
\[ \lambda_x = 1.8; \lambda_y = 1.4 \]

Fig. S8. Uniaxial nominal stress-stretch relations for the specimens at 25 °C subjected to 7 and 10 heating/cooling cycles. The tensile properties are repeatable for multiple heating/cooling cycles.
**Fig. S9.** WAXS experimental setup equipped with a biaxial stretcher at BL05XU at SPring-8. The initial gauge length of a specimen is 10 mm each. Photo credit: K. Kojio (Institute for Materials Chemistry and Engineering, Kyushu University).
b  Unequal biaxial (5/1)

\[(\lambda_x, \lambda_y) = (1, 1)\]  \[(\lambda_x, \lambda_y) = (1.5, 1.1)\]

\[(\lambda_x, \lambda_y) = (1.9, 1.2)\]  \[(\lambda_x, \lambda_y) = (2.6, 1.3)\]

15 nm^{-1}

\[(\lambda_x, \lambda_y) = (1.75, 1.3)\]  \[(\lambda_x, \lambda_y) = (2.2, 1.5)\]

c  Unequal biaxial (5/2)

\[(\lambda_x, \lambda_y) = (1, 1)\]  \[(\lambda_x, \lambda_y) = (1.4, 1.2)\]

\[(\lambda_x, \lambda_y) = (1.75, 1.3)\]  \[(\lambda_x, \lambda_y) = (2.2, 1.5)\]
**Fig. S10.** 2d WAXS patterns of I-MCPNE at various deformations: (a) planar extension, unequal biaxial extension of a strain ratio of (b) (5/1) and (c) (5/2), (d) equibiaxial extension, (e) uniaxial extension. The patterns at each strain are collected at the 5 x 5 or 5 positions around the central position of the specimen in (a)-(d) or (e), respectively.
(a) PE

(b) UB(5/1)
Fig. S11. Azimuthal distribution of scattering intensity for I-MCPNE at various deformations: (a) planar extension, unequal biaxial extension of a strain ratio of (b) (5/1) and (c) (5/2), (d) equibiaxial extension. Each data are obtained from the 2d WAXS patterns in Fig. S10.
Supplementary Movies

Movie S1. Animation of the simulations for texture evolution in uniaxial stretching

Movie S2. Animation of the simulations for texture evolution in planar extension

Movie S3. Animation of the simulations for texture evolution in unequal biaxial stretching (5/1)

Movie S4. Animation of the simulations for texture evolution in equal biaxial stretching
REFERENCES AND NOTES

1. P. J. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, 1953).

2. L. R. G. Treloar, *The Physics of Rubber Elasticity* (Clarendon Press, 1975).

3. M. Rubinstein, R. H. Colby, *Polymer Physics* (Oxford Univ. Press, 2003).

4. M. Warner, E. M. Terentjev, *Liquid Crystals Elastomers (Revised Edition)* (Clarendon Press, 2007).

5. F. Brömmel, D. Kramer, H. Finkelmann, Preparation of liquid crystal elastomers. *Adv. Polym. Sci.* 250, 1–48 (2012).

6. S. W. Ula, N. A. Traugutt, R. H. Volpe, R. R. Patel, K. Yu, C. M. Yakacki, Liquid crystal elastomers: An introduction and review of emerging technologies. *Liq. Cryst. Rev.* 6, 78–107 (2018).

7. T. J. White, D. J. Broer, Programmable and adaptive mechanics with liquid crystal polymer networks and elastomers. *Nat. Mater.* 14, 1087–1098 (2015).

8. M. Warner, E. M. Terentjev, *Liquid Crystals Elastomers* (Clarendon Press, 2003).

9. L. Golubovic, T. C. Lubensky, Nonlinear elasticity of amorphous solids. *Phys. Rev. Lett.* 63, 1082–1085 (1989).

10. P. Bladon, E. M. Terentjev, M. Warner, Transitions and instabilities in liquid crystal elastomers. *Phys. Rev. E.* 47, R3838–R3840 (1993).
11. S. Conti, A. DeSimone, G. Dolzmann, Soft elastic response of stretched sheets of nematic elastomers: A numerical study. *J. Mech. Phys. Solids* **50**, 1431–1451 (2002).

12. J. Schätzle, W. Kaufhold, H. Finkelmann, Nematic elastomers: The influence of external mechanical stress on the liquid-crystalline phase behavior. *Makromol. Chem.* **190**, 3269–3284 (1989).

13. S. M. Clarke, E. M. Terentjev, I. Kundler, H. Finkelmann, Texture evolution during the polydomain-monodomain transition in nematic elastomers. *Macromolecules* **31**, 4862–4872 (1998).

14. K. Urayama, E. Kohmon, M. Kojima, T. Takigawa, Polydomain–monodomain transition of randomly disordered nematic elastomers with different cross-linking histories. *Macromolecules* **42**, 4084–4089 (2009).

15. A. Azoug, V. Vasconcellos, J. Dooling, M. Saed, C. M. Yakacki, T. D. Nguyen, Viscoelasticity of the polydomain-monodomain transition in main-chain liquid crystal elastomers. *Polymer* **98**, 165–171 (2016).

16. N. A. Traugutt, R. H. Volpe, M. S. Bollinger, M. O. Saed, A. H. Torbati, K. Yu, N. Dadivanyan, C. M. Yakacki, Liquid-crystal order during synthesis affects main-chain liquid-crystal elastomer behavior. *Soft Matter* **13**, 7013–7025 (2017).

17. A. Agrawal, A. C. Chipara, Y. Shamoo, P. K. Patra, B. J. Carey, P. M. Ajayan, W. G. Chapman, R. Verduzco, Dynamic self-stiffening in liquid crystal elastomers. *Nat. Commun.* **4**, 1739 (2013).
18. A. Takebe, K. Urayama, Supersoft elasticity and slow dynamics of isotropic-genesis polydomain liquid crystal elastomers investigated by loading- and strain-rate–controlled tests. *Phys. Rev. E.* **102**, 12701 (2020).

19. H. Higaki, K. Urayama, T. Takigawa, Memory and development of textures of polydomain nematic elastomers. *Macromol. Chem. Phys.* **213**, 1907–1912 (2012).

20. J. S. Biggins, M. Warner, K. Bhattacharya, Supersoft elasticity in polydomain nematic elastomers. *Phys. Rev. Lett.* **103**, 037802 (2009).

21. J. S. Biggins, M. Warner, K. Bhattacharya, Elasticity of polydomain liquid crystal elastomers. *J. Mech. Phys. Solids* **60**, 573–590 (2012).

22. N. Uchida, Soft and nonsoft structural transitions in disordered nematic networks. *Phys. Rev. E.* **62**, 5119–5136 (2000).

23. G. Skacj, C. Zannoni, Molecular simulations shed light on supersoft elasticity in polydomain liquid crystal elastomers. *Macromolecules* **47**, 8824–8832 (2014).

24. T. Okamoto, K. Urayama, T. Takigawa, Large electromechanical effect of isotropic-genesis polydomain nematic elastomers. *Soft Matter* **7**, 10585–10589 (2011).

25. K. Urayama, New aspects of nonlinear elasticity of polymer gels and elastomers revealed by stretching experiments in various geometries. *Polym. Int.* **66**, 195–206 (2017).
26. C. M. Yakacki, M. Saed, D. P. Nair, T. Gong, S. M. Reed, C. N. Bowman, Tailorable and programmable liquid-crystalline elastomers using a two-stage thiol-acrylate reaction. *RSC Adv.* **5**, 18997–19001 (2015).

27. J. Kupfer, H. Finkelmann, Nematic liquid single-crystal elastomers. *Makromol. Chemie-Rapid Commun.* **12**, 717–726 (1991).

28. S. M. Clarke, A. Hotta, A. R. Tajbakhsh, E. M. Terentjev, Effect of cross-linker geometry on equilibrium thermal and mechanical properties of nematic elastomers. *Phys. Rev. E.* **64**, 61702 (2001).

29. D. L. Thomsen, P. Keller, J. Naciri, R. Pink, H. Jeon, D. Shenoy, B. R. Ratna, Liquid crystal elastomers with mechanical properties of a muscle. *Macromolecules* **34**, 5868–5875 (2001).

30. A. Petelin, M. Čopič, Observation of a soft mode of elastic instability in liquid crystal elastomers. *Phys. Rev. Lett.* **103**, 77801 (2009).

31. K. Urayama, R. Mashita, I. Kobayashi, T. Takigawa, Stretching-induced director rotation in thin films of liquid crystal elastomers with homeotropic alignment. *Macromolecules* **40**, 7665–7670 (2007).

32. N. P. Godman, B. A. Kowalski, A. D. Auguste, H. Koerner, T. J. White, Synthesis of elastomeric liquid crystalline polymer networks via chain transfer. *ACS Macro Lett.* **6**, 1290–1295 (2017).
33. D. Mistry, P. B. Morgan, J. H. Clamp, H. F. Gleeson, New insights into the nature of semi-soft elasticity and “mechanical-Frédéericksz transitions” in liquid crystal elastomers. *Soft Matter* **14**, 1301–1310 (2018).

34. T. H. Ware, J. S. Biggins, A. F. Shick, M. Warner, T. J. White, Localized soft elasticity in liquid crystal elastomers. *Nat. Commun.* **7**, 10781 (2016).

35. G. C. Verwey, M. Warner, E. M. Terentjev, Elastic instability and stripe domains in liquid crystalline elastomers. *J. Phys. II* **6**, 1273–1290 (1996).

36. S. Conti, A. DeSimone, G. Dolzmann, Semisoft elasticity and director reorientation in stretched sheets of nematic elastomers. *Phys. Rev. E* **66**, 061710 (2002).

37. B. L. Mbanga, F. F. Ye, J. V. Selinger, R. L. B. Selinger, Modeling elastic instabilities in nematic elastomers. *Phys. Rev. E. Stat. Nonlin Soft Matter Phys.* **82**, 051701 (2010).

38. B. Yohsuke, K. Urayama, T. Takigawa, K. Ito, Biaxial strain testing of extremely soft polymer gels *Soft Matter*, 7, 2632–2638 (2011).

39. A. J. Leadbetter, A. I. Mehta, Molecular packing in the nematic phase of cyano compounds with different ring systems. *Mol. Cryst. Liq. Cryst.* **72**, 51–57 (1981).

40. P. Cesana, P. Plucinsky, K. Bhattacharya, Effective behavior of nematic elastomer membranes. *Arch. Ration. Mech. Anal.* **218**, 863–905 (2015).
41. Y. Luo, J. Xing, Y. Niu, M. Li, Z. Kang, Wrinkle-free design of thin membrane structures using stress-based topology optimization. *J. Mech. Phys. Solids* **102**, 277–293 (2017).

42. M. O. Saed, A. H. Torbati, D. P. Nair, C. M. Yakacki, Synthesis of programmable main-chain liquid-crystalline elastomers using a two-stage thiol-acrylate reaction. *JoVE*, e53546 (2016).

43. T.-T. Mai, Y. Morishita, K. Urayama, Novel features of the Mullins effect in filled elastomers revealed by stretching measurements in various geometries. *Soft Matter* **13**, 1966–1977 (2017).

44. P. H. Hermans, P. Platzek, Beiträge zur Kenntnis des Deformationsmechanismus und der Feinstruktur der Hydratzellulose. *Kolloid-Zeitschrift*. **88**, 68–72 (1939).

45. J. S. Biggins, E. M. Terentjev, M. Warner, Semisoft elastic response of nematic elastomers to complex deformations. *Phys. Rev. E*. **78**, 41704 (2008).

46. H. Zhou, K. Bhattacharya, Accelerated computational micromechanics. *J. Mech. Phys. Solids* **153**, 104470 (2021).

47. P. Plucinsky, M. Lemm, K. Bhattacharya, Programming complex shapes in thin nematic elastomer and glass sheets, *Phys. Rev. E* **94**, 010701 (2016).

48. H. Aharoni, Y. Xia, X. Zhang, R.D. Kamien, S. Yang, Universal inverse design of surfaces with thin nematic elastomer sheets. *Proc. Natl. Acad. Sci. U.S.A.* **115**, 7206–7211 (2018).
49. J. Michel, H. Moulinec, P. Suquet. A computational method based on augmented Lagrangians and fast Fourier transforms for composites with high contrast. *Comput. Model. Engr. Sci.* **1**, 79–88 (2000).