nature portfolio

Peer Review File

A supramolecular non-mesogenic route towards autonomous liquid crystal elastomer soft robots

Corresponding Author: Professor Tao Xie

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
He et al. reported that smectic liquid crystalline elastomers (LCEs) can be obtained through the polymerization of non-mesogenic monomers composed of an oxime-ester group. Compared to LCEs synthesized via the polymerization of conventional mesogenic monomers, these LCEs are easier to synthesize and orientation control of the mesogens, while also showing superior mechanical properties. Consequently, the design of the LCEs reported by the authors is expected to find applications in novel soft actuators. Therefore, I think the work deserves publication in the journal, however, I feel that the manuscript may be properly revised by taking following comments.

Comment 1: In Supplementary Fig. 1a, the authors show that the monomer is crystalline state and does not exhibit any LC phase based on the POM image. However, this image does not rule out the possibility of a higher-order LC phase. Therefore, the authors should also show a 2D-WAXD image or its 1D pattern.

Comment 2: In Figs. 2f and g, the authors explain that POE-6 shows smectic LC phase based on the 2D-WAXD image and its 1D pattern at 20 °C. Generally, in the smectic phase, higher-order reflections such as second- and third-order reflections are also observed, but no distinct peaks are visible in these images. The authors should also consider the possibility of other LC phases, such as nematic phase.

Comment 3: In Fig. 3b, the authors explain that POE-12 shows only Cr-Iso phase transition. If that is the case, the authors should present 2D-WAXD images or the 1D patterns for that material at each temperature.

Comment 4: In the 2D-WAXD image shown in Fig. 4b (bottom; after program), no diffraction ring or arc corresponding to the smectic LC phase appeared at the small angle region. The authors should explain the reason for the WAXD result.

Reviewer #2

(Remarks to the Author)
This manuscript is highly intriguing in that it demonstrates LCE-like actuation behavior derived from non-mesogenic molecular precursors. In particular, achieving >118% actuation strain at near-ambient temperatures represents a remarkable advancement.

However, the manuscript lacks a sufficiently rigorous mechanistic foundation that rationalizes how the non-mesogenic precursors give rise to LCE-like molecular chain behavior. Simply stating that annealing induces “cooperative ordering” leading to a smectic phase is not convincing. The manuscript does not clearly discuss how this supramolecular ordering provides reversible actuation without strain loss, nor does it articulate the mechanistic similarity to conventional LCEs.

Moreover, several essential experimental checks are missing. At this stage, I cannot recommend publication. The authors must address the major points above, as well as the specific questions below, before a publication decision can be made.

1. As indicated in Figure 1b, annealing plays a critical role in triggering the mesophase. Therefore, WAXD and POM

comparisons "before vs. after annealing" are required.

2. The image shown in Figure 2e appears much more like a *typical nematic Schlieren texture* rather than a smectic Schlieren pattern. This contradicts the claim of a smectic phase. Please reconcile these conflicting observations.

3. The smectic peak in Figure 2g ($q \approx 0.17$ Å^{-1}) is extremely weak compared to conventional smectic LCEs. Combined with the POM in Figure 2e, the system appears nematic-dominant and the smectic assignment remains questionable. Please provide clearer evidence that the phase is truly smectic.

4. In Figure 3a, POE-6 shows a small additional transition at approx. 5–7 °C. Please examine WAXD across this transition and clarify whether POE-6 maintains a single uniform smectic phase in this temperature window.

5. In programming route (1) of Figure 4a, it is unclear how a macroscopic alignment can be maintained when the sample is strained above T_SI and then allowed to contract back to its original length. Please clarify the mechanism by which alignment is retained.

6. The authors claim that annealing converts an amorphous POE-6 into a smectic-phase LCE. However, heating above T_SI generally increases chain mobility, which should erase the annealing-induced supramolecular alignment. How, then, is fully reversible contraction-expansion possible across cycles?

7. Figure 4c shows actuation on timescales approaching ~90 minutes per cycle, which is extremely slow. Please explain the origin of this slow response.

8. The authors should include a video demonstrating multiple cycles (e.g., 10 cycles as in Figure 4c) to support the reversibility and reliability of the actuation.

9. Finally, I strongly encourage the authors to revise the manuscript to improve clarity, consistency, and overall scientific writing style.

Reviewer #3

(Remarks to the Author)
In this manuscript, the development and characterization of liquid crystal elastomers achieved from nonmesogenic monomer containing dynamic covalent bond. The authors have characterized the liquid crystalline property using traditional techniques of POM, DSC and XRD. The mechanical property of the elastomers has also been characterized. The authors provide sufficient logic as to why the nonmesogenic monomers in the network are able to induce LC phase. Most of the conclusions are supported by experimental data except for the smectic phase. The authors ought to establish which type of smectic phase is in the elastomers, Smectic A, Smectic C or different?.

Other points that need addressing:
How does the layer spacing of the elastomer compare with the dimension of the nonmesogenic monomer ?
In figure 3d, the authors present elastic plateau, plateaus are generally observed in aligned samples and more so in nematic phases. Did the authors align the samples and measured and compared with its polydomain sample ?

The authors should compare and contrast the mechanical property e.g Young's modulus of the present elastomers with typical nematic and smectic liquid crystal elastomers for the sake of the completeness of the study.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors revised properly the manuscript by taking my comments. Therefore, I think the work deserves publication in the journal.

Reviewer #2

(Remarks to the Author)
The authors have addressed most of the major concerns raised in the previous review, and the revised manuscript has been significantly improved in clarity and supporting data.
It is almost ready to be published. Before publication, I just want to further make sure one more imfortant issue related to work capacity in this paper as below.

1. While the actuation strain is thoroughly characterized, the manuscript does not quantify the actuation work capacity of the material. Given that practical actuator performance depends not only on strain but also on output stress and work density, it would be important to evaluate the mechanical work generated during actuation.
Can the authors provide a quantitative assessment of the actuation work density (e.g., $\int \sigma \, d\varepsilon$ or blocking-force measurements)

and compare it with representative nematic and smectic LCEs reported in the literature?
Such analysis would allow a more complete evaluation of the actuator performance and clarify whether the high strain observed here translates into competitive mechanical work output.

Reviewer #3

(Remarks to the Author)
The Authors have addressed the concerns, I have raised, in the revised manuscript. The revised manuscript can be accepted for publication.

Version 2:

Reviewer comments:

Reviewer #2

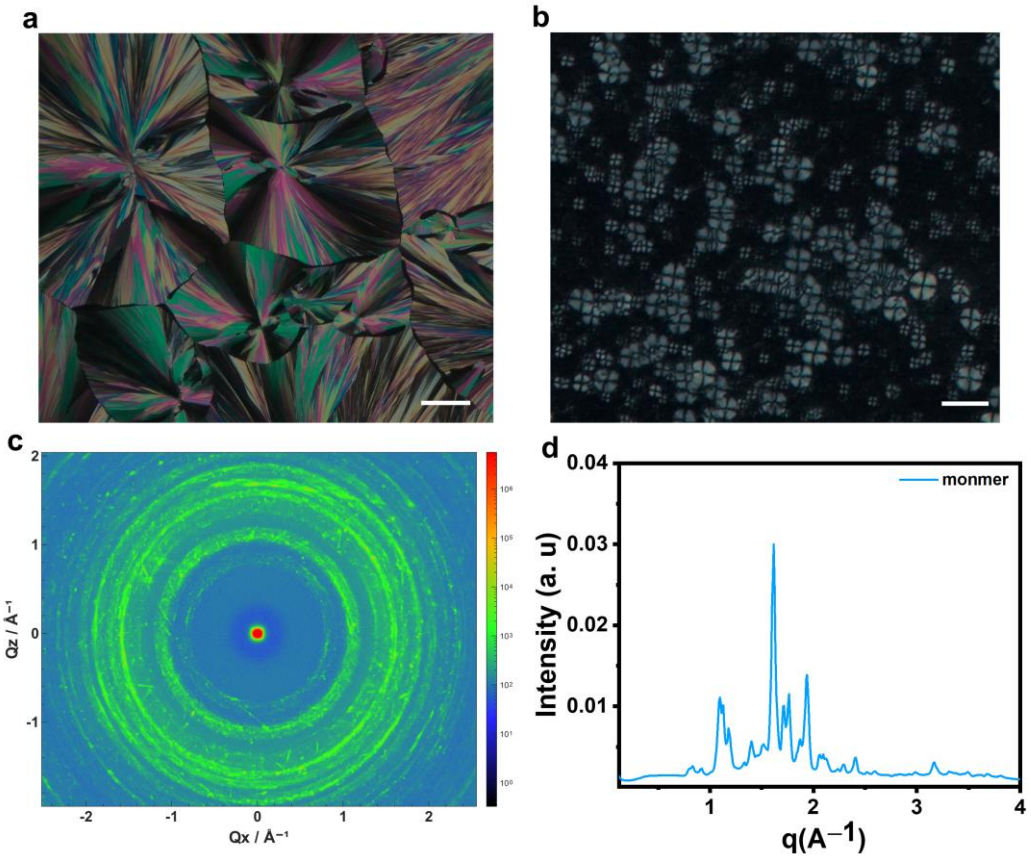
(Remarks to the Author)
It seems to be ready to be published.

Reviewer #1 (Remarks to the Author):

He et al. reported that smectic liquid crystalline elastomers (LCEs) can be obtained through the polymerization of non-mesogenic monomers composed of an oxime-ester group. Compared to LCEs synthesized via the polymerization of conventional mesogenic monomers, these LCEs are easier to synthesize and orientation control of the mesogens, while also showing superior mechanical properties. Consequently, the design of the LCEs reported by the authors is expected to find applications in novel soft actuators. Therefore, I think the work deserves publication in the journal, however, I feel that the manuscript may be properly revised by taking following comments.
Response: We thank you for the positive comments and specific suggestions that help us strengthen the manuscript.

Comment 1: In Supplementary Fig. 1a, the authors show that the monomer is crystalline state and does not exhibit any LC phase based on the POM image. However, this image does not rule out the possibility of a higher-order LC phase. Therefore, the authors should also show a 2D-WAXD image or its 1D pattern.
Response: Agree. We verified the microstructure of monomer via 2D-WAXD experiments. From the WAXD results (Supplementary Figs. 1c and 1d), it can be seen that oximer-ester-6 does not show laminar ordered scattering peaks in the small-angle region and short-range ordered π-π stacking peaks, instead, many narrow peaks (crystalline peaks) can be seen in the range of 1~3 A^{-1}. This rules out that the liquid crystal nature of oximer-etster-6. The result is provided in Supplementary Fig. 1 and the following discussion is added on page in paragraph 7 on page 4.

"The absence of peaks at smectic regions and short-range ordered scattering peaks of π-π stacking further verifies the non-liquid crystalline nature of the monomer (Supplementary Fig. 1)."



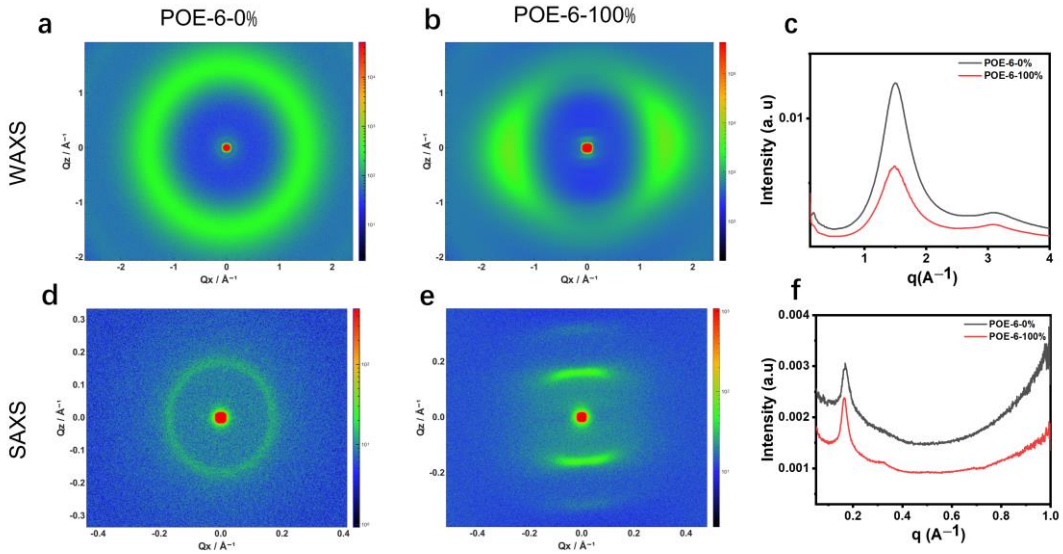
Supplementary Fig. 1 | Microstructure of oxime-ester-6 monomer and linear POE. POM images of **a,** Oxime ester-6 monomer, scar bar: 200 μm **b**, Linear POE-6, scar bar: 20 μm, after cooling from its melting temperature to 20 °C. **c**, 2D-WAXD images of oxime-ester-6 at 20 °C. **d**, 1D X-ray data derived from (c). As illustrated in the figure, during the cooling process, neither the monomer nor the linear POE exhibits any liquid crystal features. Instead, spherical crystals are observed, indicating that the structures do not transition into liquid crystalline states. From the WAXD results, it can be seen that oximer-ester-6 does not show laminar ordered scattering peaks in the small-angle region or short-range ordered π-π stacking peaks, instead, many narrow peaks (crystalline peaks) can be seen in the range of 1~3 A^{-1}. This rules out that the liquid crystal nature of oximer-etster-6.

Comment 2: In Figs. 2f and g, the authors explain that POE-6 shows smectic LC phase based on the 2D-WAXD image and its 1D pattern at 20 °C. Generally, in the smectic phase, higher-order reflections such as second- and third-order reflections are also observed, but no distinct peaks are visible in these images. The authors should also consider the possibility of other LC phases, such as nematic phase.

Response: We agree that higher-order reflection peaks are typically visible in the smectic phase in liquid crystal monomers. However, for liquid crystalline elastomers, the internal random field of distortions due to the crosslinking process can lead to disorder, especially at relatively high crosslink density. This potentially disrupts the quasi-long-range order necessary for observing higher-order reflections (*Eur. Phys. J.*

E 2007, 24, 399–409). In order to determine the liquid crystal phase of POE-6, we did WAXD and SAXS experiments in the unaligned and aligned states. The results (Supplementary Fig. 3) show diffraction ring or arc in the small-angle region ($0.17A^{-1}$) of both 2D WAXD and 2D SAXS images. This indicates the presence of smectic layered order in POE-6. After alignment, the small-angle scattering ring form two symmetrical arcs perpendicular to the stretching direction, further confirming that this is the smectic A phase. Additionally, a faint second-order reflection peak is observed in the SAXS image of the aligned sample, further confirming this layered-ordered smectic A phase. We add the following discussion in paragraph 7 on page 4.

"The small-angle scattering ring form two symmetrical arcs is perpendicular to the aligned direction after alignment (Supplementary Fig. 3). Based on this, the smectic phase is assigned as smectic A."

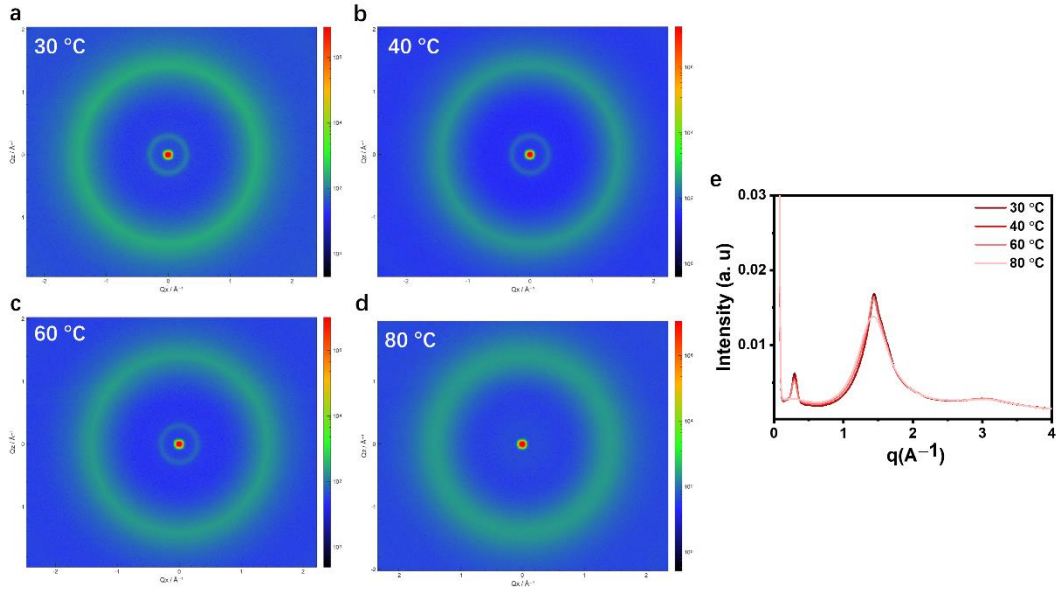


Supplementary Fig. 3 | WAXD/SAXS of polydomain and monodomain POE-6 at 20°C. WAXD images of polydomain POE-6 (**a**) and monodomain POE-6 (**b**). **c**, 1D X-ray data derived from (a) and (b). SAXS images of polydomain POE-6 (**c**) and monodomain POE-6 (**d**). **f**, 1D X-ray data derived from (c) and (d). Alignment was achieved by stretching the samples to 100% engineering strain before analysis. The stretching direction is perpendicular. Diffraction ring or arc observed in the small-angle region ($0.17A^{-1}$) of both 2D WAXD and 2D-SAXS images indicate the presence of smectic layered order in POE-6. After alignment, the small-angle scattering ring form two symmetrical arcs perpendicular to the stretching direction, further confirming that this smectic phase is the smectic A phase.

Comment 3: In Fig. 3b, the authors explain that POE-12 shows only Cr-Iso phase transition. If that is the case, the authors should present 2D-WAXD images or the 1D patterns for that material at each temperature.

Response: We performed WAXD tests of POE-12 from 30 °C to 80 °C and the results are shown in Supplementary Fig. 4 (see below). The WAXD results reveal that POE-12 exhibits not only a Cr-Iso phase transition but also, similar to POE-6, a peak within the smectic region. This indicates that POE-12 similarly forms a layered-ordered liquid

crystal phase, differing from our previous assessment. The reason for this discrepancy is that crystallization masks the macroscopic reversible deformation of POE-12. Therefore, we have revised the description of POE-12 in paragraph 8 on page 5.
"Conversely, if the spacing is too long, the π conjugating moieties become too independent, leading to high segmental mobility. This promotes long-range ordering, not only generating layered smectic phases but also facilitating crystallization. (Supplementary Fig. 4)."



Supplementary Fig. 4 | Phase behavior of POE-12 with varying temperature. a-d, 2D WAXD images of POE-6 at different temperatures. **e**, 1D X-ray data derived from (a)-(d).

Comment 4: In the 2D-WAXD image shown in Fig. 4b (bottom; after program), no diffraction ring or arc corresponding to the smectic LC phase appeared at the small angle region. The authors should explain the reason for the WAXD result.
Response: Agree. The reason is that this signal appears very weak in the 2D-WAXD image, resulting in low resolution in the two-dimensional image and making it difficult to observe. In fact, from its one-dimensional curve below, we can see a faint reflection peak in the small-angle region.

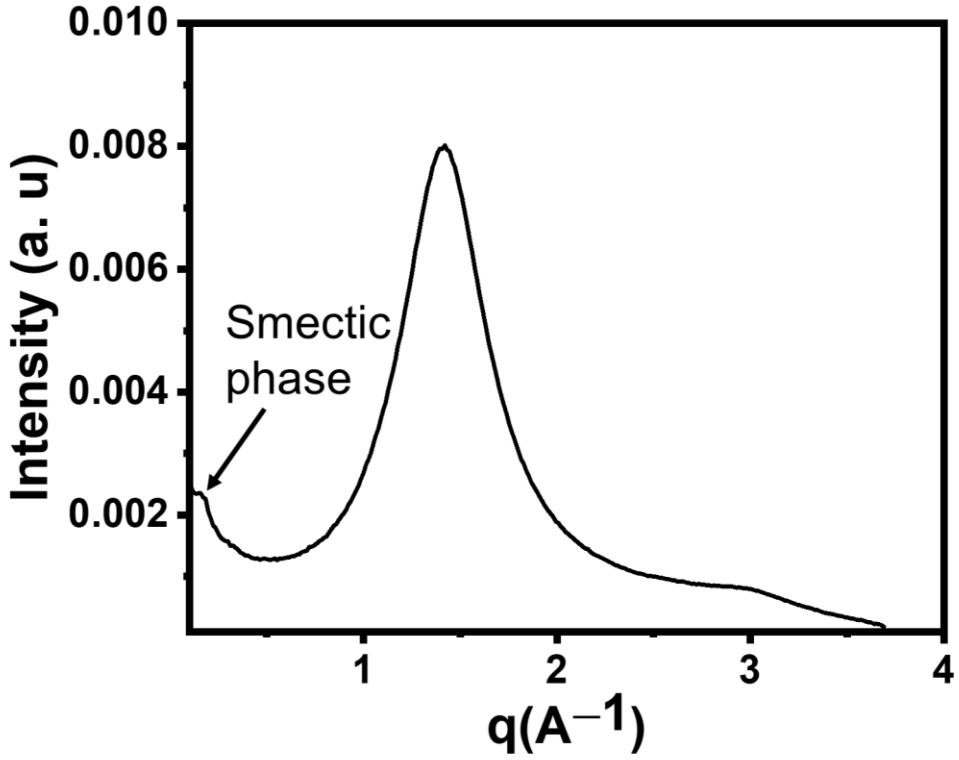


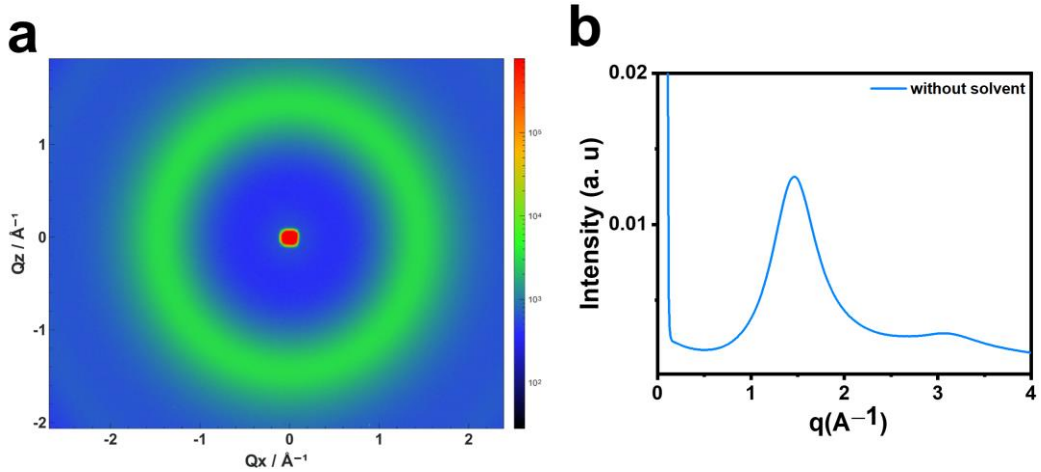
Fig. R1 1D X-ray data derived from Fig. 4b (bottom; after program).

Reviewer #2 (Remarks to the Author):

This manuscript is highly intriguing in that it demonstrates LCE-like actuation behavior derived from non-mesogenic molecular precursors. In particular, achieving >118% actuation strain at near-ambient temperatures represents a remarkable advancement.

However, the manuscript lacks a sufficiently rigorous mechanistic foundation that rationalizes how the non-mesogenic precursors give rise to LCE-like molecular chain behavior. Simply stating that annealing induces "cooperative ordering" leading to a smectic phase is not convincing. The manuscript does not clearly discuss how this supramolecular ordering provides reversible actuation without strain loss, nor does it articulate the mechanistic similarity to conventional LCEs.

Response: As for a more detailed mechanism, this is indeed a critical issue. The liquid crystalline order in POE-6 is formed after the polymerization and solvent evaporation (80 °C, 1 h). By comparison, if the POE-6 is polymerized in the molten state (without a solvent), it fails to form the layered SmA phase (Supplementary Fig. 6). Therefore, solvent evaporation plays an essential role. Our non-liquid-crystalline monomer is a rod-coil-rod tri-block molecule containing a flexible aliphatic spacer, an allylic terminal segment, and a rigid unit of π-conjugating moieties. The interactions between the solvent and the three segmental blocks differ. Consequently, solvent evaporation after the polymerization results in the microphase separation because of the distinct solvent interactions. This process is aided by the dynamic exchange of the oxime-esters that provides the necessary network mobility. The above mechanistic discussion is now discussed on page 5.



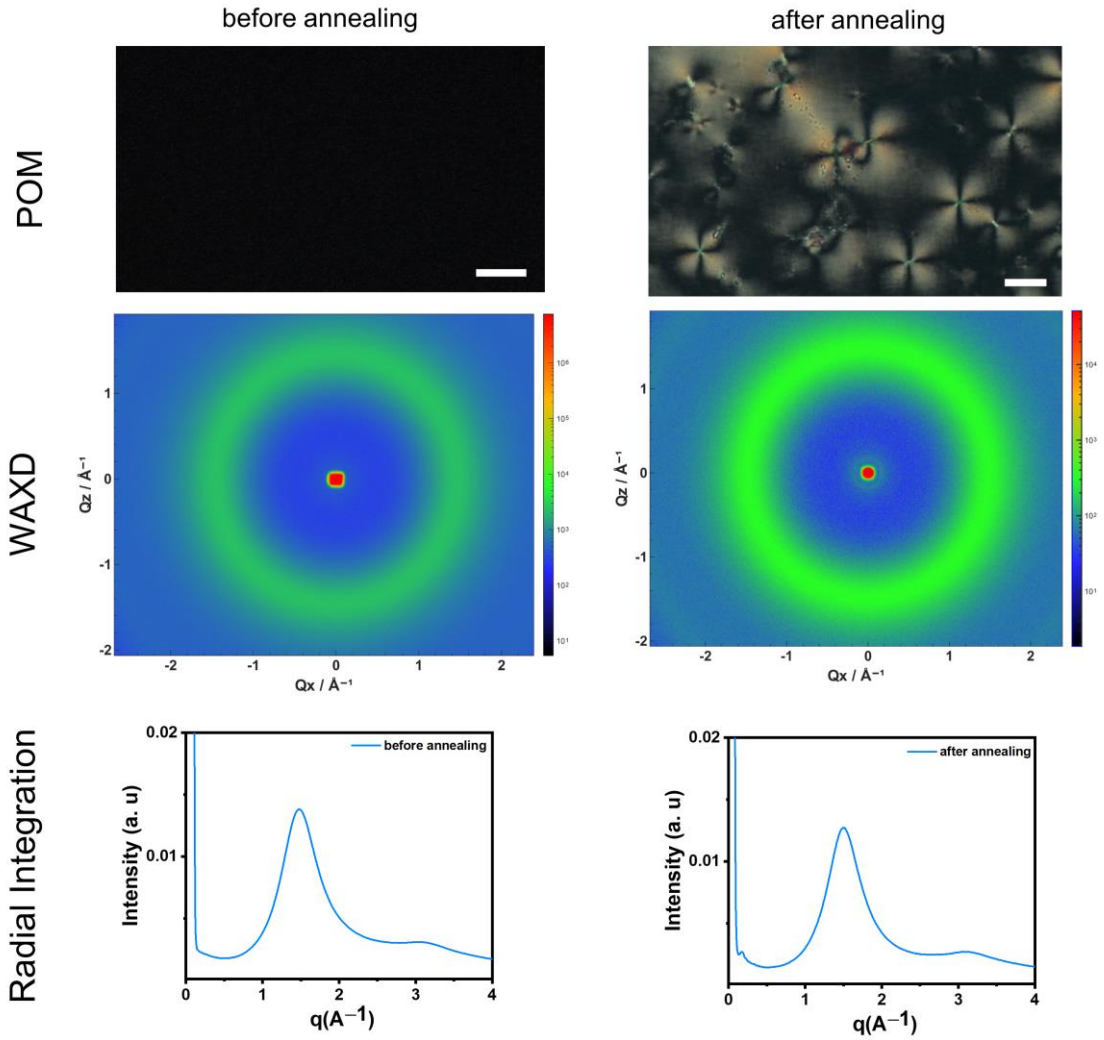
Supplementary Fig. 6| **a**, 2D WAXD pattern of polymerized POE-6 without solvent at 20 °C. **b**, 1D X-ray data derived from (**a**).

As for why the supramolecular ordering provides reversible actuation without strain loss, this is mainly due to the reduction of T_{SI} without sacrificing the liquid crystalline order. For conventional LCE, reducing the transition temperature is typically accomplished by introducing structural defects. This inevitably compromises the

degree of ordering, consequently the actuation strain. This is now discussed on page 8.

Moreover, several essential experimental checks are missing. At this stage, I cannot recommend publication. The authors must address the major points above, as well as the specific questions below, before a publication decision can be made.

1. As indicated in Figure 1b, annealing plays a critical role in triggering the mesophase. Therefore, WAXD and POM comparisons "before vs. after annealing" are required.
Response: The WAXD and POM comparisons of POE-6 before and after annealing are now presented in Supplementary Fig. 5. The results show that no significant birefringence is observed in POM images prior to annealing. However, after annealing, abundant focal conic fan-shaped textures with well-defined four-brush (Maltese cross) extinction patterns becomes visible. Concurrently, WAXD analysis showed no diffraction rings in the smectic region before annealing. Following annealing, distinct diffraction rings appeared in the smectic region, indicating the formation of a layered, ordered smectic phase.



Supplementary Fig. 5 | POM images and WAXD patterns of POE-6 before and after annealing.

2. The image shown in Figure 2e appears much more like a *typical nematic Schlieren texture* rather than a smectic Schlieren pattern. This contradicts the claim of a smectic phase. Please reconcile these conflicting observations.

Response: Agree. In fact, the pattern observed under polarized light microscopy in Figure 2e is stress-induced. Therefore, we re-examined the polarized patterns of POE-6 in both the unaligned and aligned states. In the unaligned sample, typical focal conic fan-shaped textures with distinct four-brush extinction are observed (Fig. 2e top), indicating the presence of a layered smectic mesophase. After alignment, these focal conic domains evolve into a quasi-uniform, well-organized striped pattern (Fig. 2e bottom). This behavior is consistent with the SmA phase, in which the molecular long axis remains perpendicular to the smectic layers. We have revised Figure 2e and the corresponding description in the manuscript.

"Under POM, the unaligned POE-6 exhibits a focal conic fan-shaped textures, while the aligned sample displays a well-organized layered pattern (Figure 2e), indicating the formation of a smectic A phase."

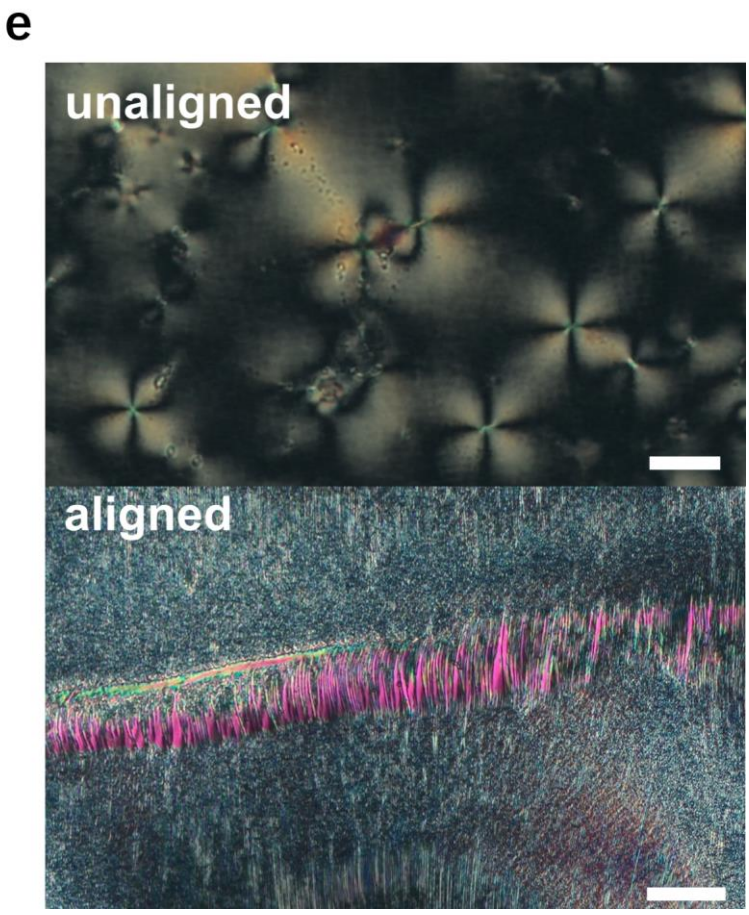
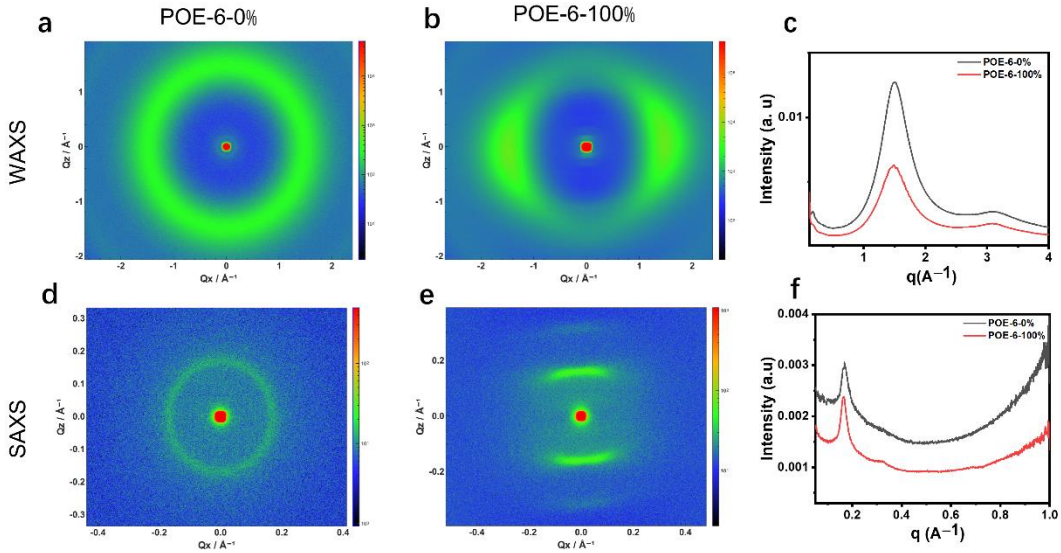


Fig. 2 | e, POM image of unaligned and aligned POE-6 at 20 °C. Scale bar: 50 μm.

3. The smectic peak in Figure 2g ($q \approx 0.17$ Å^{-1}) is extremely weak compared to conventional smectic LCEs. Combined with the POM in Figure 2e, the system appears nematic-dominant and the smectic assignment remains questionable. Please provide

clearer evidence that the phase is truly smectic.

Response: We have now provided a detailed explanation of the polarized light images in point 2 of the review comments. The polarization data strongly supports the formation of the SmA phase, consistent with the WAXD and SAXS data (Fig. S3) Diffraction ring or arc observed in the small-angle region ($0.17A^{-1}$) of both 2D-WAXD and 2D-SAXS images indicate the presence of smectic layered order in POE-6. After alignment, the small-angle scattering ring form two symmetrical arcs perpendicular to the stretching direction, further confirming that this smectic phase is the smectic A phase. Additionally, a faint second-order reflection peak is observed in the SAXS image of the alignment sample, further confirming this layered-ordered smectic A phase.



Supplementary Fig. 3 | WAXD/SAXS of polydomain and monodomain POE-6 at 20°C. WAXD images of polydomain POE-6 (**a**) and monodomain POE-6 (**b**). **c**, 1D X-ray data derived from (a) and (b). SAXS images of polydomain POE-6 (**c**) and monodomain POE-6 (**d**). **f**, 1D X-ray data derived from (c) and (d). Alignment was achieved by stretching the samples to 100% engineering strain before analysis. The stretching direction is perpendicular. Diffraction ring or arc observed in the small-angle region ($0.17A^{-1}$) of both 2D WAXD and 2D-SAXS images indicate the presence of smectic layered order in POE-6. After alignment, the small-angle scattering ring form two symmetrical arcs perpendicular to the stretching direction, further confirming that this smectic phase is the smectic A phase.

4. In Figure 3a, POE-6 shows a small additional transition at approx. 5–7 °C. Please examine WAXD across this transition and clarify whether POE-6 maintains a single uniform smectic phase in this temperature window.

Response: The transition observed around 5-7 °C is the glass transition, representing the temperature at which polymer segments begin to move. Since current instruments cannot perform WAXD testing at such low temperatures, we are unable to provide relevant WAXD data. However, we have reason to believe that POE-6 maintains a uniform smectic phase within this temperature range.

5. In programming route (1) of Figure 4a, it is unclear how a macroscopic alignment can be maintained when the sample is strained above T_{SI} and then allowed to contract back to its original length. Please clarify the mechanism by which alignment is retained.
Response: The mechanism of POE-6 alignment is as follows: When $T > T_{SI}$, the smectic phase melts, and POE-6 transforms into an isotropic cross-linked network. Upon application of an external force, polymer segments align along the force direction, and correspondingly, π-conjugating moiety also align along the force direction. Simultaneously, due to the presence of dynamically exchangeable oxime-ester bonds in our system, the network topology aligned with the external force is fixed. When the temperature cools below $T < T_{SI}$, POE-6 reassembles into a new layered, ordered smectic phase aligned with the external force.

6. The authors claim that annealing converts an amorphous POE-6 into a smectic-phase LCE. However, heating above T_{SI} generally increases chain mobility, which should erase the annealing-induced supramolecular alignment. How, then, is fully reversible contraction-expansion possible across cycles?
Response: Indeed, heating may erase the annealing-induced supramolecular alignment during contraction-expansion cycles. However, this depends on the temperature. In our system, due to the nature of dynamic oxime-ester bonds, higher temperatures accelerate the rate of dynamic exchange reactions. Consequently, the amount of mesogens generated through self-assembly decreases, leading to a reduction in reversible strain. For POE-6, however, its phase transition temperature is quite low, its reversible strain exhibits only a slight decrease after multiple cycles (from first cycle 133% to 10^{th} cycle 130%), which is nearly negligible.

7. Figure 4c shows actuation on timescales approaching ~90 minutes per cycle, which is extremely slow. Please explain the origin of this slow response.
Response: This is mostly related to the tests. In our DMA testing, the heating and cooling rates are 10 °C/min. One cycle includes the time required for the heating process (from -30 to 55 °C), the isothermal time (5 minutes), the cooling process (from 55 to 30 °C), and the isothermal time (15 minutes). The total cycle time is 37 minutes, not 90 minutes. In fact, the actual actuation response of POE-6 is rapid, as demonstrated in the supplementary Video 2.

8. The authors should include a video demonstrating multiple cycles (e.g., 10 cycles as in Figure 4c) to support the reversibility and reliability of the actuation.
Response: We have now recorded a new video (Supplementary Video 2) showing the actuation process over 10 continuous cycles, consistent with the data presented in Figure 4c.

9. Finally, I strongly encourage the authors to revise the manuscript to improve clarity, consistency, and overall scientific writing style.
Response: We have carefully revised the entire manuscript to enhance clarity, consistency.

Reviewer #3 (Remarks to the Author):

In this manuscript, the development and characterization of liquid crystal elastomers achieved from nonmesogenic monomer containing dynamic covalent bond. The authors have characterized the liquid crystalline property using traditional techniques of POM, DSC and XRD. The mechanical property of the elastomers has also been characterized. The authors provide sufficient logic as to why the nonmesogenic monomers in the network are able to induce LC phase. Most of the conclusions are supported by experimental data except for the smectic phase. The authors ought to establish which type of smectic phase is in the elastomers, Smectic A, Smectic C or different?.

Response: We thank you for the constructive comments that help us strengthen the manuscript. To determine the liquid crystal phase in the elastomer, we supplemented the POM images and the WAXD and SAXS results of the unaligned and aligned POE-6. In the unaligned sample, typical focal conic fan-shaped textures with distinct four-brush extinction are observed (Fig. 2e top), indicating the presence of a layered smectic mesophase. After alignment, these focal conic domains evolve into a quasi-uniform, well-organized striped pattern (Fig. 2e bottom). This behavior is consistent with the SmA phase. Diffraction ring or arc observed in the small-angle region ($0.17A^{-1}$) of both 2D-WAXD and 2D-SAXS images indicate the presence of smectic layered order in POE-6 (Supplementary Fig. 3). After alignment, the small-angle scattering ring form two symmetrical arcs perpendicular to the stretching direction, further confirming that this smectic phase is the smectic A phase. Additionally, a faint second-order reflection peak is observed in the SAXS image of the alignment sample, further confirming this layered-ordered smectic A phase. Based on the above results and analysis, we can confirm that the liquid crystal phase in the elastomer is smectic A.

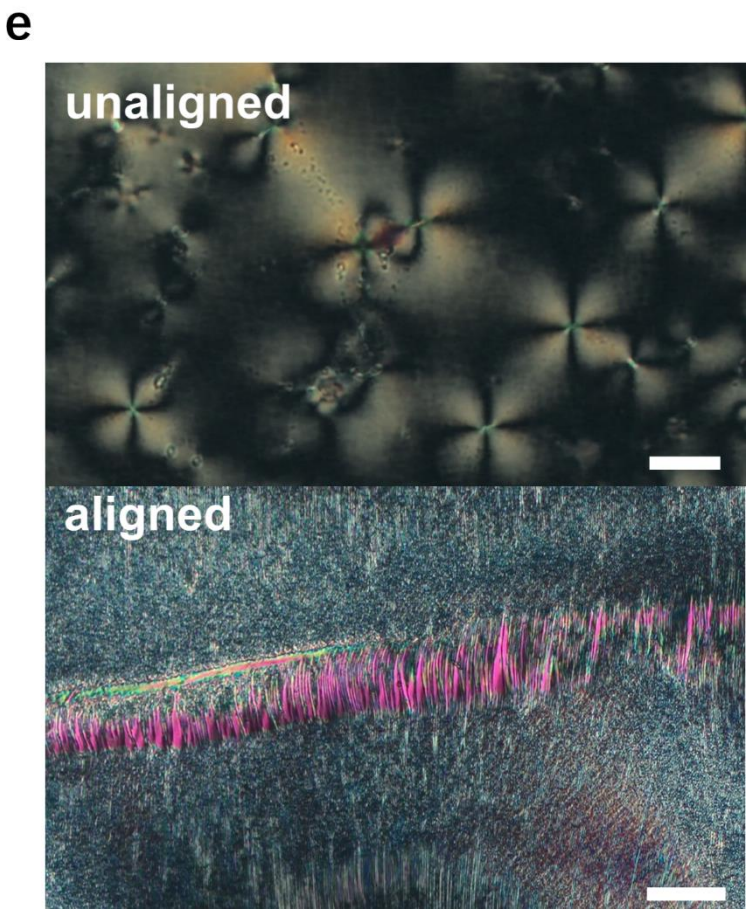
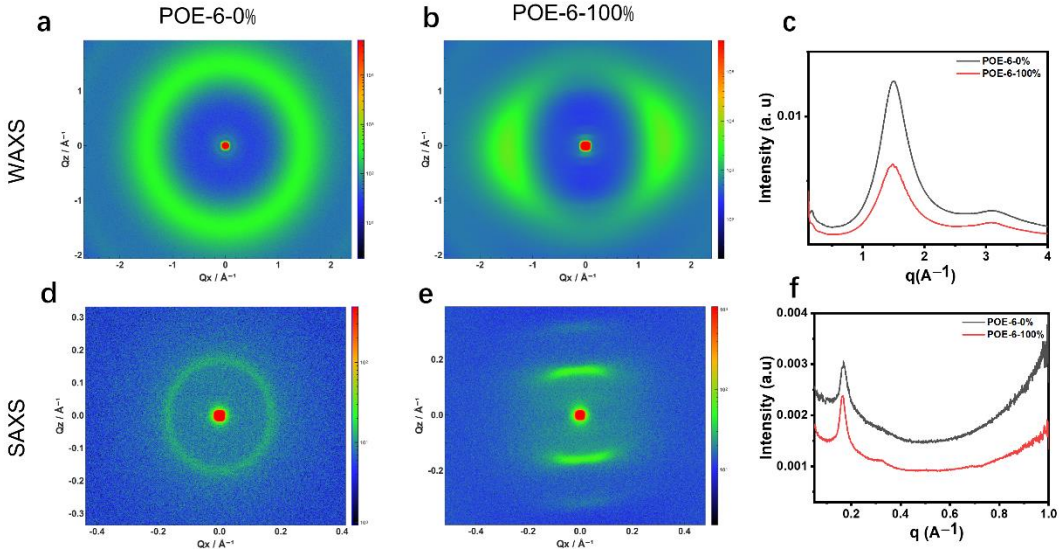


Fig. 2 | e, POM images of unaligned and aligned POE-6 at 20 °C. Scale bar: 50 μm.



Supplementary Fig. 3 | WAXD/SAXS of polydomain and monodomain POE-6 at 20°C. WAXD images of polydomain POE-6 (**a**) and monodomain POE-6 (**b**). **c**, 1D X-ray data derived from (a) and (b). SAXS images of polydomain POE-6 (**c**) and monodomain POE-6 (**d**). **f**, 1D X-ray data derived from (**c**) and (**d**). Alignment was achieved by stretching the samples to 100% engineering strain before analysis. The

stretching direction is perpendicular. Diffraction ring or arc observed in the small-angle region ($0.17A^{-1}$) of both 2D WAXD and 2D-SAXS images indicate the presence of smectic layered order in POE-6. After alignment, the small-angle scattering ring form two symmetrical arcs perpendicular to the stretching direction, further confirming that this smectic phase is the smectic A phase.

Other points that need addressing:
How does the layer spacing of the elastomer compare with the dimension of the nonmesogenic monomer ?
Response: The molecular length of the nonmesogenic monomer is 29.4 Å (calculated via ChemBio 3D simulation), while the layer spacing of the resulting LCE is 36.9 Å. This is now stated in the manuscript on page 3.

In figure 3d, the authors present elastic plateau, plateaus are generally observed in aligned samples and more so in nematic phases. Did the authors align the samples and measured and compared with its polydomain sample?
Response: The samples measured in Figure 3d were in polydomain states. This is now stated clearly in the text.

The authors should compare and contrast the mechanical property e.g Young's modulus of the present elastomers with typical nematic and smectic liquid crystal elastomers for the sake of the completeness of the study.
Response: The modulus of the initial elastic region and threshold stress to enter the soft plateau vary strongly with chemistry (main-chain vs side-chain), crosslink density, temperature relative to phase transitions, sample state (mono-/polydomain), and loading geometry. However, for room-temperature uniaxial tensile tests at the polydomain state, values typically fall within the range shown in Supplementary Table 1 (see below). Compare with nematic and smectic liquid crystal elastomer, despite the smectic ordering, the modulus and the threshold stress are close to nematic liquid crystal elastomer, which is beneficial for actuation efficiency. This is now discussion in the text on page 7.

Supplementary Table 1. Comparison of the modulus and threshold stress of nematic, smectic liquid crystal elastomer and POE-6.

	Nematic	**Smectic**	**POE-6 (this work)**
Modulus of the initial elastic region E_1 **(MPa)**	**0.1~5**	**1~20**	**0.11**
Threshold stress to enter the soft plateau σ_s **(MPa)**	**0.01~0.2**	**0.2~5**	**0.05**

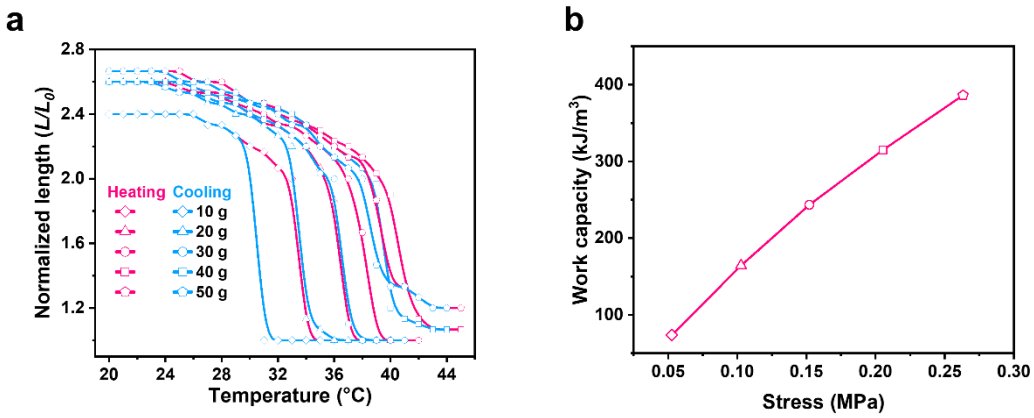
Reviewer #1 (Remarks to the Author):

The authors revised properly the manuscript by taking my comments. Therefore, I think the work deserves publication in the journal.
Response: Thank you.

Reviewer #2 (Remarks to the Author):

The authors have addressed most of the major concerns raised in the previous review, and the revised manuscript has been significantly improved in clarity and supporting data.
It is almost ready to be published. Before publication, I just want to further make sure one more imfortant issue related to work capacity in this paper as below.

1. While the actuation strain is thoroughly characterized, the manuscript does not quantify the actuation work capacity of the material. Given that practical actuator performance depends not only on strain but also on output stress and work density, it would be important to evaluate the mechanical work generated during actuation.
Can the authors provide a quantitative assessment of the actuation work density (e.g., $\int \sigma \, d\varepsilon$ or blocking-force measurements) and compare it with representative nematic and smectic LCEs reported in the literature?
Such analysis would allow a more complete evaluation of the actuator performance and clarify whether the high strain observed here translates into competitive mechanical work output.
Response: We evaluated the work capacity of this LCE through a weight lifting experiment between 20 to 45 °C with results shown in Figure S13. Under a stress of 0.26 MPa, POE-6 reached a maximum work capacity of 386 $kJ \cdot m^{-3}$. Also, we have compared our material's work capacity, actuation strain, and actuation temperature with those of representative nematic and smectic LCEs reported in the literature, as shown in Supplementary Table 4. Compared to most LCEs reported in the literature, POE-6 exhibits a relatively high work capacity, attributable to its elevated actuation strain. Concurrently, POE-6 actuates at a very low actuation temperature, indicating that minimal energy input suffices to achieve its high-work-capacity actuation. This is now discussed on page 8.



Supplementary Fig. 13 | Evaluation of mechanical work capacity generated during actuation under different stress. a, Strains vs temperature diagram of POE-6 film bearing a load from 10 gram to 50 gram. **b**, Corresponding work capacity of POE-6 under different stress.

Supplementary Table 4 | Comparison of the work capacity, actuation strain and actuation temperature of LCE reported in the literature and POE-6.

Sample	Work Capacity (kJ·m^{-3})	Actuation strain (%)	Actuation Temperature (°C)
POE-6	**386**	**147**	**45**
Ref. 1	1427	45	120
Ref. 2	1267	40	140
Ref. 3	730	87	150
Ref. 4	440	82	83
Ref. 5	~160	32	90
Ref. 6	100	12	120
Ref. 7	262	525	150
Ref. 8	140	40	130
Ref. 9	102	32	110

Reviewer #3 (Remarks to the Author):

The Authors have addressed the concerns, I have raised, in the revised manuscript. The revised manuscript can be accepted for publication.
Response: Thank you.