Molecular heterogeneity drives reconfigurable nematic liquid crystal drops

We study NLCO drops, tens of micrometres in diameter, dispersed in water containing sodium dodecyl sulfate (SDS) surfactant. SDS creates a strong preference for homeotropic anchoring, wherein the nematic director (molecular orientation) is perpendicular to the drop surface (Fig. 1a). Each surfactant-stabilized NLCO emulsion drop contains a mixture of 1,4-bis-(4-(6-acryloyloxyhexyloxy)benzoyloxy)-2-methylbenzene (RMS2) monomers and RMS2 oligomers with variable chain lengths (Fig. 1a, details in Extended Data Fig. 1a). Importantly, compared to small-molecule liquid crystals, chain length polydispersity of the NLCOs offers new degrees of freedom which can profoundly affect drop morphology, and the NLCOs are readily crosslinked to lock-in nematic order and morphology.

Essential features of the shape transitions are shown in Fig. 1. At a high temperature (around 90 °C), while in the nematic phase, the drop is spherical (Fig. 1a, c). Here, interfacial energy is large compared to bulk director elastic energy. On cooling, the surface tension and bulk elasticity vary, and excess interface is created. This interplay destabilizes the drop, facilitating spontaneous polymorphic transitions to non-spherical equilibrium structures (see exemplar images in Fig. 1c–h; director configurations in Fig. 1a, b; Supplementary Video 1). These polymorphic shape transitions are reversible and repeatable via temperature cycling (see Extended Data Fig. 2, Supplementary Video 1).

Arguably, the major factor driving these shape transitions is the interfacial tension, which decreases with decreasing temperature. This trend was confirmed in pendant drop experiments using large, millimetre-size NLCO drops (Extended Data Fig. 3), and has been reported in other systems. The decrease in γ is believed to arise from greater molecular ordering at the interface. In our case, surfactant-induced anchoring and the stronger alignment of NLCOs at lower temperatures enhance interfacial ordering. Additionally, NLCO elastic constants increase with decreasing temperature. Thus, with reduction of γ, anisotropic bulk elasticity becomes more important for determining drop shape, increasing the potential for spontaneous shape transitions.

To elucidate the consequences of these effects, we constructed a morphology 'state' diagram from samples that experienced the same heating–cooling cycles. Figure 2a–d exhibits the repeatable drop morphologies: smooth/roughened spheres, flowers, large- and small-diameter filament networks. The state diagram (Fig. 2e) is shown as a function of surfactant concentration and mean oligomer chain length, which increases with total oligomerization time.

Consider the effects of NLCO average chain length. Though all samples are polydisperse, samples prepared with longer oligomerization processing times contain a larger ratio of long-chain to short-chain oligomers and have longer (Fig. 2f, Methods, Extended Data Fig. 4). Larger NLCO elastic constants are expected for longer (Fig. 2e). Additionally, interfacial oligomer assembly with longer tends to reduce (see Extended Data Fig. 3). Larger NLCOs increase oligomer chain hydrophobicity, which induces more interfacial ordering. As temperature is lowered, these trends favour drop morphologies with large surface.

With few exceptions, polydispersity or molecular heterogeneity in matter tends to impede self-assembly and state transformation. For example, shape transformations of liquid droplets with monodisperse ingredients have been reported in equilibrium and non-equilibrium studies, and these transition phenomena were understood on the basis of homogeneous material responses. Here, by contrast, we study equilibrium suspensions of drops composed of polydisperse nematic liquid crystal oligomers (NLCOs). Surprisingly, molecular heterogeneity in the polydisperse drops promotes reversible shape transitions to a rich variety of non-spherical morphologies with unique internal structure. We find that variation of oligomer chain length distribution, temperature, and surfactant concentration alters the balance between NLCO elastic energy and interfacial energy, and drives formation of nematic structures that range from roughened spheres to 'flower' shapes to branched filamentous networks with controllable diameters. The branched structures with confined liquid crystal director fields can be produced reversibly over areas of at least one square centimetre and can be converted into liquid crystal elastomers by ultraviolet curing. Observations and modelling reveal that chain length polydispersity plays a crucial role in driving these morphogenetic phenomena, via spatial segregation. This insight suggests new routes for encoding network structure and function in soft materials.
Fig. 1 | Spontaneous shape transition of NLCO drops. a, b, Schematics depicting a surfactant-stabilized NLCO sphere (a) and filament (b) shown in purple in a background aqueous phase (orange). The red symbols in a represent surfactant molecules. White lines represent the nematic director. The concept of spatial segregation by oligomer chain length is illustrated. The lower inset in a shows how, for simplicity, long-chain/short-chain species are represented by blue/pink solid curves representing hexamers and dimers, respectively (grey ellipses represent monomers). The inset in b shows a magnified view of a filament cross-section. The z axis in b is parallel to (and coincident with) the central filament axis. c–h, An NLCO drop spontaneously (and reversibly) evolves from a sphere to an extended and branched filamentous drop as the temperature is reduced from 90 °C (c) to 20 °C (h). Scale bar in h (for c–h), 20 μm.

Area. More quantitatively, our measurements indicate a crossover transition to non-sphericity when ⟨ℓ⟩ = 1.5 times the monomer length in 0.1 wt% SDS solutions.

Other factors modify surface tension and affect the state diagram. In contrast to work on non-equilibrium liquid crystal filament formation8,9, our experiments were largely carried out below the critical micelle concentration (CMC) of SDS wherein increasing SDS concentration lowers y and helps facilitate interfacial roughening and filament formation (Fig. 2e). Additional experiments confirmed that primary phenomena are not unique to SDS surfactant, nor limited to concentrations below the CMC (Extended Data Figs. 5, 6).

Given this emerging qualitative picture, we sought a more quantitative understanding. To this end, we determined NLCO director configurations using polarization optical microscopy (POM) with a full-wave retardation plate. We then applied simple models to determine their free energies. Here we focus on the two limiting morphologies: spherical versus filamentous drops. Spheres exhibit the classic POM texture corresponding to a radial ‘hedgehog’ director configuration with a central topological charge of +1 (that is, a point defect; Fig. 3a).

Filaments exhibit an escaped-radial director configuration (Fig. 3b, c). For all geometries, the single point defect always remains at the drop centre (Fig. 3a, d, e).

To predict shape transition phenomena, modelling must account for energetics associated with both interfacial tension and elastic bulk free energy of the confined NLCOs. The calculations require knowledge about the splay (K_s), twist (K_t), bend (K_b) and saddle-splay (K_{ss}) NLCO elastic constants, as well as interface anchoring strength. We utilize well-known models for the sphere with radial hedgehog director configuration12 and for cylinders with escaped-radial director configuration18. Importantly, all models assume a homogeneous, monodisperse chain length distribution for the NLCOs. The models employ y from pendant drop experiments, measured drop dimensions, and estimates of elastic constants and interfacial anchoring strength based on small-molecule liquid crystals23. Calculations (see Methods, Extended Data Table 1) yield conditions for the sphere–filament free energy instability.

Surprisingly, we found that free energy instabilities only occur if our system has either an unphysically large saddle-splay elastic constant (K_{ss} > 30K_b), or a value of y that is much smaller (about one-tenth) than those obtained in the pendant drop experiments. Given this discrepancy, we were compelled to consider other effects. In the process, we uncovered the importance of NLCO chain length polydispersity (molecular heterogeneity), which can profoundly affect interface and core energetics.

First, consider elastic free energy gradients in small (about 10–30 μm) drops versus the large (millimetre-size) drops used to obtain y. In small drops, the nematic adopts a single-domain configuration in which the director field experiences large splay distortion near drop centre for spheres, or large splay and bend distortion near the central axis for filaments (see Methods). The millimetre-size drops, by contrast, are composed of many nematic domains, each with different director orientation, and they are filled with many disclination lines. Although director fields in the large drops can be locally non-uniform, most microdomains remain uniformly aligned, and splay/bend elasticity gradients are not large. Thus, the overall elastic gradient effects in millimetre-size drops are small.
experience strong chain-length-dependent driving forces. These forces evolved from a single, central radial ‘hedgehog’ defect, shown schematically at bottom right. A conservative reduction of γ by ten times to approximately 0.1 mN m\(^{-1}\) yields sphere–filament instabilities with reasonable saddle-splay moduli. Importantly, our experiments with bidisperse distributions of monomers and macromers, made by a different chemical procedure\(^{20}\), support this central new insight about the effects of NLCO polydispersity. (See Methods for these latter experiments.) Previously, shape transitions were observed in molecularly heterogeneous systems\(^{20}\), and the phenomenon of segregation by size, broadly defined, has been reported in lipid membrane systems\(^{21}\), near topological defects in liquid crystal simulations\(^{22}\), and in liquid crystal polymer systems mediated by size-dependent nematic/isotropic transition temperatures\(^{23}\). It is perhaps useful to reconsider these phenomena in light of our experiments.

In the micrometre-size drops and cylinders, however, oligomers experience strong chain-length-dependent driving forces. These forces are induced by elastic energy gradients of the director within the drop, that is, higher elastic energy density near the core. To reduce system elastic energy, short chains, which have smaller associated elastic constants, will migrate towards the core, and long chains, which have larger associated elastic constants, will migrate towards the drop surface (Fig. 1a, b). A simple two-component macromer–monomer demixing model with a mean oligomer chain length of \(\langle \ell \rangle = 1.7\) for the outer shell and a mean oligomer chain length in the core of \(\langle \ell \rangle = 1.39\), for example, predicts around a 10% decrease in elastic free energy due to reduced average rod length in the core.

Second, as a result of these elastic free energy gradients, interfacial tension in the small drops is lowered greatly and will differ from that in large drops. Stronger nematic ordering at the interface driven by the greater numbers of long-chain oligomers will decrease \(\gamma\) by a factor of 10 or more compared to drops with homogeneous oligomer distributions (see Extended Data Fig. 3). Thus, spatial redistribution of polydisperse oligomers in the small drops resolves the issues raised by the original homogeneous model. A conservative reduction of \(\gamma\) by ten times to approximately 0.1 mN m\(^{-1}\) yields sphere–filament instabilities with reasonable saddle-splay moduli. Importantly, our experiments with bidisperse distributions of monomers and macromers, made by a different chemical procedure\(^{20}\), support this central new insight about the effects of NLCO polydispersity. (See Methods for these latter experiments.) Previously, shape transitions were observed in molecularly heterogeneous systems\(^{20}\), and the phenomenon of segregation by size, broadly defined, has been reported in lipid membrane systems\(^{21}\), near topological defects in liquid crystal simulations\(^{22}\), and in liquid crystal polymer systems mediated by size-dependent nematic/isotropic transition temperatures\(^{23}\). It is perhaps useful to reconsider these phenomena in light of our experiments.

By contrast, as noted above, spatial redistribution of oligomers is not anticipated in millimetre-size drops. Segregation is driven largely by director distortion near uniformly distributed disclinations and domain walls and will not induce overall migration to the surface. Thus, the surface of the millimetre-size drop is likely to remain a uniform mixture of oligomers with mean chain length set by the initial NLCO distribution. The pendant millimetre-drop \(\gamma\) therefore reflects ‘average behaviour’ of the mixture; it should be much larger than the \(\gamma\) of micrometre-size drops. Possible curvature-induced forces driving segregation will also be less important in large versus small drops.

To harvest these self-assembled morphologies for new functional materials, the NLCOs were ultraviolet-crosslinked into nematic liquid crystal elastomers (NLCEs). Representative scanning electron microscopy (SEM) images of self-assembled NLCEs are shown in Fig. 4a–f. These images were obtained using a focused ion beam to cut through the elastomer, allowing the internal structures to be imaged in three dimensions. The images show thin intertwined filamentous structures grown from several drops (inset shows filaments with different colours grown from different drops). The objects shown in a–c evolved from a single drop and are depicted schematically in the insets; d shows thin intertwined filamentous structures grown from several drops (inset shows intertwined filamentous structures grown from several drops).
microscopy (SEM) images of the NLCEs are in Fig. 4a–d. By comparing POM images of corresponding NLCE and NLCO structures, we confirmed that director configurations are well-maintained.

Last, we show that these NLCE fibres can be densely packed into centimetre-wide and few-micrometres-thick, non-woven, free-standing NLCE mats (Fig. 4e, f) by sedimentation. These structures could find applications in responsive filtration and smart fabrics. A NLCE yarn consisting of well-aligned fibres (Fig. 4g, h) was made by directly pulling fibres out of aqueous solution; these yarn-like objects could find use in artificial muscles24,25 or tunable waveguides. Actuation with the current fibres is under way along these lines. Compared to electrospinning22,23,24 and wet-spinning25, this new approach to making fibrous structures is simple and scalable without the need for sophisticated tools.

Although polydispersity and molecular heterogeneity are often avoided in synthetic systems, here they facilitate equilibrium transitions among dramatically different morphological structures. This feature could be exploited to create soft materials—such as highly branched networks with uniform filament size—simply by tuning chain length distribution, temperature and surfactant concentration. Future studies of branching behaviours may provide new insights into drop assembly and stabilization, and, possibly, could reveal connections to molecular heterogeneity driven segregation and phase separation for function in biological matter29–31. Moreover, the self-assembly processes are reversible, and the network structures can be permanently locked by ultraviolet crosslinking. The simple rules revealed by the experiments offer new concepts for creation of programmed spatio-temporal networks.

Online content
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**Methods**

**Synthesis of NLCO drops**

The NLCO emulsions were made in three steps: (1) preparation of emulsion drops containing monomer/chain-extender mixtures and suspended in an aqueous phase; (2) oligomerization within individual drops to link liquid crystal monomers together into liquid crystal oligomers (LCOs); and (3) creation of final NLCO drop suspensions in water, which are observed by video microscopy as a function of temperature.

**Step 1**

A 1:1 mixture of 1,4-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (monomer RM82, Wilshire Technologies) and n-butylamine (chain-extender, Sigma-Aldrich) was dissolved in chloroform (Fisher Scientific); weight of chloroform is 3× the weight of RM82. A 0.2 wt% (of RM82 concentration) antioxidant, butylated hydroxytoluene (BHT, Sigma-Aldrich), was also added.

The resulting organic phase mixture was then made into a microdroplet emulsion in an aqueous solution. This was achieved by adding surfactant to the mixture of water and organic phase and then shaking to create polydispersed drops with diameters ranging from 10 to 100 μm. Three different surfactants were employed: negatively charged sodium dodecyl sulfate (anionic surfactant SDS, Sigma-Aldrich), positively charged hexadecyltrimethylammonium bromide (cationic surfactant C16TAB, Sigma-Aldrich), and neutral polyoxymethylene (20) sorbitan monolauroate (Tween 20, Fisher Scientific). Although phenomena with the SDS surfactant are reported in the main text, experiments using the other two surfactants exhibited similar behaviour; spontaneous shape transitions are not restricted to a certain type of surfactant. However, in considering surfactants, it is important that homeotropic anchoring of NLCOs is favoured. All chemicals were used as received, without further purification/modification. At this stage, the suspended drops contain unchained monomers.

**Step 2**

The RM82/butylamine (chain-extender)/chloroform–SDS/water droplet suspension is next placed in a water bath at 90 °C for oligomerization. During this process, the organic solvent (chloroform) evaporates completely from each emulsion drop, and then the butylamine begins to link the diacrylate RM82 molecules in chains via a self-catalysed ‘aza-Michael addition’ reaction. Afterwards, emulsion drops are composed of main-chain liquid crystal oligomers, LCOs. The degree of oligomerization, that is, the mean oligomer chain length, ⟨ℓ⟩, is controlled by reaction time.

We note that the NLCO chain length distribution is broad and has a shorter mean oligomer chain length, ⟨ℓ⟩, compared to previous liquid crystal elastomer work.10

**Step 3**

After the reaction, a small volume of the suspension (that is, the NLCO emulsion) is pipetted into a pre-heated glass well, sealed with cover slip and glue, and then cooled to 20 °C on a hotplate at a rate of −1 °C min−1. The suspension is then annealed (that is, quickly reheated to 90 °C and then slowly cooled to 20 °C again) before the drop morphology experiments are carried out.

Note, compared to pure RM82 monomer, which forms a nematic only above 86 °C (it is nematic in the 86–116 °C temperature range), the present LCOs exhibit a wide nematic window that extends below room temperature (that is, at least between 20–90 °C).

**Drop morphology characterization**

Sample cells containing NLCO drops were observed with a Leica DMIR13 inverted optical microscope in bright-field and polarization modes. Leica NPlan10×, Leica PL Fluotar L 63×, and Leica PL APO 100× objectives were used. Crossed-polarizers and full-wave retardation plates were deployed in the microscope to characterize director configurations within the drops.

**Molecular weight measurements of NLCOs**

To further characterize the LCO samples, most of the remaining emulsion solution was centrifuged (2,000 relative centrifugal force, RCF) at 15 °C and washed with deionized water several times to remove surfactant. It was then vacuum dried to remove water.

Part of the resultant bulk sample was then dissolved in tetrahydrofuran (THF; stabilized with 250 p.p.m. BHT, Alfa Aesar) at a concentration of 1.5 mg ml−1 for molecular weight analyses. The molecular weight analyses were performed using standard size exclusion chromatography (SEC, Tosoh Bioscience EcoSEC) with flow rate of 1.0 ml min−1, and with three analytical columns in series: TSKgel G2000HXL, TSKgel G2500HXL and TSKgel G3000HXL. A standard polystyrene sample (MW = 48,100 Da, Sigma-Aldrich) was also added during the SEC measurements for calibration purposes.

**Macroscopic interfacial tension measurements**

The interfacial tension arising between NLCO drop surfaces and background aqueous phase were measured macroscopically using the pendant drop method.13,15 The pendant drop technique works by analysing the shape of a large (millimetre-size) liquid drop hanging from a capillary tube (that is, a flat tip syringe needle), when it is about to detach from the capillary tube. The shape of the hanging drop depends on gravity, on cohesive forces of the drop within the background medium, and on the interfacial tension.

Our pendant drop tensiometry employs a custom-made temperature-regulated chamber, which enabled us to measure the system interfacial tension as a function of temperature. Each NLCO bulk sample was injected into a syringe coupled with a flat tip needle. The pendant NLCO drop was made in a 0.1 wt% SDS water solution in the temperature-regulated chamber. High contrast images of the drop contour were obtained while temperature was slowly decreased. The densities of the bulk NLCO were also measured at the different temperatures. Finally, using the methods and software created by Daer et al.,16 we fitted the drop contour for each sample at each temperature using the density of bulk NLCO and of the surrounding medium. With this information, the interfacial tension can be deduced (see measured interfacial tensions in Extended Data Fig. 3).

**Macromer–monomer mixing experiments**

These experiments were designed to confirm the influence of oligomer polydispersity on the shape transition phenomenology of NLCO drops. Specifically, we investigated how the average chain length of the oligomers in the NLCO mixture affects the shape transitions. For this study, however, we employed a synthetic approach to making the NLCO drop mixtures that was different from the methods in the main text.

We first synthesized a main-chain liquid crystal macromer with a number-average molecular weight of approximately 6,900 Da; following the work by Ware et al., this macromer had a mean chain length, ⟨ℓ⟩, of ~9, that is, a mean chain length roughly 9 times the monomer length. This sample had a polydispersity index (PDI) of 1.3 (for comparison with the NLCOs as described in the main text, see Extended Data Fig. 1). Note, PDI is defined as the ratio between weight-average molecular weight (Mw) and number-average molecular weight (Mn). PDI = 1 implies uniform polymer chain length.

The macromers thus obtained were then mixed with pure RM82 monomer at different weight ratios in chloroform (chloroform:liquid crystal mixture = 3:1 wt/wt). The mixture was then emulsified in 0.1 wt% SDS aqueous solution, and then the chloroform was evaporated in a 90 °C water bath. No further chain growth occurred during this process (confirmed by 1H-NMR) because the chain-extender, n-butylamine, was not added to the mixture. When all chloroform was removed, temperature cycling was carried out following the same protocol described in step 3. The resulting drop shapes and micro-structures were observed in bright-field and polarization optical microscopy (POM).
Upon cooling, the macromer–monomer NLCO drops transitioned from smooth spheres to roughened spheres, flower-like structures, and filamentous structures (see Extended Data Fig. 4). These effects were dependent on the monomer:macromer weight ratio. Specifically, with increased mean oligomer chain length, \((\ell)\), droplet structures with larger surface area are preferred (for example, longer, thinner filaments). The observed phenomenology agrees very well with the observations in the main text. We have argued that the increased bulk elasticity and decreased interfacial tension accompanying increased \((\ell)\) promotes shape transitions. Quantitatively, as shown in Extended Data Fig. 4b, the droplet’s tendency towards non-sphericity commences when \((\ell) = 1.4\). This supplementary macromer–monomer mixing experiment thus exhibits the same tendency as the experiments that employed the synthesis-in-emulsion scheme. In the latter case, the droplet’s tendency towards non-sphericity commenced when \((\ell) = 1.5\). Note, the \((\ell)\) at which non-sphericity commences can vary slightly with drop size.

We also carried out experiments with monomers only. Pure RM82 monomer (\((\ell) = 1\)) crystallizes during cooling; it is nematic only above 86 °C. Thus, shape transitions are not seen with drops containing only monomer. Furthermore, experiments with drops containing only macromers (\((\ell) = 9\), see Extended Data Fig. 1) did not exhibit shape transitions. Evidently, the surface tension in drops with pure macromer is too large to permit shape transitions, presumably due to poor anchoring at the surface. Moreover, the macromer-only system viscosity is much larger than the drops with smaller average chain length, making texture formation/reformation kinetics very slow.

By contrast, the NLCO mixtures we studied maintain good packing at the drop interface, probably because of different formation processes. The NLCOs were synthesized within each SDS stabilized drop. Thus, we expect that homeotropic director ‘pre-alignment’ could already exist at early stages of the oligomerization process in these drops, that is, when most of the oligomer chains are short and the surfactants can induce good anchoring. Thus, importantly, the monomers are approximately locked into their interfacial structure at the outset. Then as the chains grow longer throughout the drop, the longer oligomers spatially segregate to an already partially ordered surface at high coverage and can help increase order at the interface in a perturbative manner. This segregation and greater molecular packing/order reduces interfacial tension and ultimately induces shape transitions when interfacial tension becomes sufficiently small. In principle, the shape transformation process could still happen for a monodisperse system with very small surface tension. Our polydisperse NLCO mixtures, however, provide an easy segregation-driven route to lowering interfacial tension and elastic energy.

**Calculation of system free energy**

Here, we provide details of our model free energy calculations (see also the custom computer codes mentioned in the Code Availability section below). We employ equilibrium models because the effects were reversible with slow temperature cycling, and the structures were stable. Note, for rapid quenching (non-equilibrium) it is possible to generate a transient negative surface tension which could also drive the effect.

The Frank free energy for a nematic liquid crystal is given below; it accounts for the elastic energy associated with spatial distortions of the director \(\mathbf{\hat{n}}\) in the liquid crystal\(^{14}\), that is:

\[
F_\text{F} = \frac{1}{2} \int d^3r \left[ K_{11} (\mathbf{n} \cdot \nabla \cdot \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_{33} (\nabla \times (\nabla \times \mathbf{n}))^2 - K_{23} \nabla \cdot \left[ \mathbf{n} (\nabla \times \mathbf{n}) + \nabla (\nabla \cdot \mathbf{n}) \right] \right]
\]

(1)

Here \(K_{11}\), \(K_{22}\), and \(K_{33}\) are elastic constants for splay, twist and bend deformations, respectively. The final term, with the elastic constant \(K_{23}\), is called the saddle-splay; it is absent from the corresponding Euler–Lagrange equation but contributes to the total free energy. Note, for simple solutions, the so-called splay-bend \(K_{\theta}\) elastic deformation and other second derivatives (or higher-order terms) of the director field\(^{36,38}\) are usually not included—for example, inclusion of \(K_{\theta}\) without higher order terms can lead to paradoxes\(^{36,38}\)—nevertheless, interested readers can find free energy models which include \(K_{\theta}\) and discuss these issues\(^{39}\). To simplify calculations even further, a one-constant limit of the Frank free energy\(^{17}\) is often applied, that is, \(K_{11}, K_{22}\), and \(K_{33}\) are set equal and expressed as a single value, \(K\).

In addition to liquid crystal elastic free energy, our modelling includes interfacial free energy,

\[
F_\text{iso} = \gamma \int dS
\]

(2)

and liquid crystal interface anchoring energy\(^{40}\),

\[
F_\text{aniso} = \frac{1}{2} W_s \int dS \sin^2\Phi
\]

(3)

Here \(\gamma\) is the interfacial tension, \(W_s\) is the anchoring energy coefficient at the interface, and \(\Phi\) is the angle between the liquid crystal director at the interface and the interface normal. Both terms are integrated over the surface.

Starting with these elastic energy expressions, and using well-established elastic models for a sphere (with radial director configuration)\(^{37}\) and for a cylindrical filament (with escaped-radial director configuration)\(^{38,39,41-43}\), one can derive expressions for total system free energy.

For the sphere (one-constant approximation),

\[
F_s = 8\pi \left( K - \frac{1}{2} K_{23} \right) R + \gamma 4\pi R^2
\]

Or, if \(K_{11} \neq K_{33}\),

\[
F_s = 8\pi \left( K_{33} - \frac{1}{2} K_{23} \right) R + \gamma 4\pi R^2
\]

(5)

For the filament (one-constant approximation),

\[
F_I = \pi K \left[ 3 - K_{23} \frac{1}{K} \right] L + \gamma 2\pi R L
\]

(6)

where \(\sigma \equiv \frac{W_f}{K} + \frac{K_{23}}{K_{11}} - 1 > 1\)

Or, if \(K_{11} < K_{33}\),

\[
F_I = \pi K_{11} \left[ 2 + \frac{K}{\sqrt{1 - K}} \tan^{-1} \sqrt{1 - K} - \frac{K}{\sqrt{1 - K}} \tan^{-1} \left( \frac{\sqrt{1 - K}}{\sigma} \right) \right] \frac{K_{23}}{K_{33}} \frac{K_{23}}{K_{11}} L + \gamma 2\pi R L
\]

(7)

Here,

\[
K \equiv \frac{K_{11}}{K_{33}} \text{ and } \sigma \equiv \frac{W_f}{K_{11}} + \frac{K_{23}}{K_{11}} - 1 > 1
\]

Above, \(K\) is the composite elastic constant (that is, in the one-constant approximation) of the NLCO mixture, \(R\) is the radius of the spherical NLCO drop, and \(r\) and \(L\) are the radius and length of the NLCO cylindrical filament, respectively. The twist elasticity, \(K_{23}\), makes no contribution to the free energy of either the sphere or the cylinder, and the anchoring energy term (equation (3)) arises for cylinders with an escaped-radial director configuration, but not for spheres with radial director configurations. Note that in equations (1), (4) and (6), the saddle-splay
\( (K_{ij}) \) term is sometimes ignored, but for our system \( K_{ij} \) is essential. Ignoring saddle-splay would require a negative interfacial tension (\( \gamma \)) for the spontaneous shape transitions, which is inconsistent with our measurements of \( \gamma \) and with the reversible, equilibrium shape transition phenomenology observed.

Since we observed a spontaneous transition from spherical to filamentous drops during cooling, we anticipate that an energetically favourable spontaneous process must have \( F_s < F_e \). We next examine the parameter values needed to favour this spontaneous process.

Among these parameters, \( \gamma \) was measured by the pendant drop technique using large (millimetre-size) drops. For example, the measured \( \gamma \) is 4.64 mN m\(^{-1} \) at 80°C and 2.36 mN m\(^{-1} \) at 30°C for the sample NLCO/2 which had 7 h of oligomerization time (see Methods and Extended Data Fig. 3; see refs. 7, 11, 12, 44, 45 for details of this unusual temperature-dependent trend). In one (typical) sample, \( R \) and \( r \) were measured by bright-field optical microscopy to be 13.0 \( \mu \)m and 0.65 \( \mu \)m, respectively. Because it is difficult to directly measure the elastic constants and anchoring energy coefficients of our NLCOs, we estimate their values at room temperature: \( K_{11} = 6.1 \times 10^{-12} \) N and \( W_s = 10^{-3} \) J m\(^{-2} \). These numbers are chosen based on the values, and on the relationships between parameters, in drops of monodisperse small molecule liquid crystals. When interfacial free energy is dominant (for example, at high temperature or with short \( \ell \)), we expect the NLCO droplets to remain spherical. Then, knowing the interfacial tension, we can compute an estimate for \( K \). Similarly, since the droplet adopts a radial configuration with a hedgehog defect at its centre\(^5\), \( W_s \) is estimated by assuming that the extrapolation length, \( \xi \equiv K/W_s = 1 \) \( \mu \)m, for the spherical drop is much smaller than the drop diameter. Note that \( W_s \) typically ranges from 10\(^{-10} \) to 10\(^{-8} \) J m\(^{-2} \) for weak to strong anchoring. (For reader reference, we list experimental values for important parameters. For thermotropic liquid crystals: (1) SCB has \( K_{11} = 6.2 \times 10^{-10} \) N and \( K_{13} = 8.25 \times 10^{-10} \) N (−25°C); (2) 5CB has \( K_{11} = 6.0 \times 10^{-12} \) N and \( K_{13} = 6.4 \times 10^{-12} \) N (−35°C). For lyotropic liquid crystals: (1) DSCG has \( K_{11} = 10.2 \times 10^{-12} \) N and \( K_{13} = 24.9 \times 10^{-13} \) N (16 wt\%, within −4°C of \( T_{NI} \)); (2) SSY has \( K_{11} = 4.3 \times 10^{-12} \) N and \( K_{13} = 6.1 \times 10^{-12} \) N (29 wt\%, within −2°C of \( T_{NI} \)). For liquid crystal monomers that are molecularly similar to RMB2: \( K_{11} = 2.6 \times 10^{-12} \) N (−97°C)\(^6\). For anchoring energy: (1) SCB/SiO interfaces have \( W_s = 4.0 \times 10^{-3} \) J m\(^{-2} \) (−35°C)\(^6\); liquid crystal mixture (Merck-BDH, MLC 6608)/lecithin interfaces have \( W_s = 4.6 \times 10^{-3} \) J m\(^{-2} \) (23.1°C)\(^5\); 5CB/DMOAP-treated glass interfaces have \( W_s = 1.0 \times 10^{-3} \) J m\(^{-2} \) (−75°C)\(^5\).

The models and criteria above, along with the experimental and estimated parameters, lead to well-defined constraints. A spontaneous shape transition is only possible, for example, when \( K_{11} \geq 2 \times K_{13} \), which is far too large for most liquid crystal materials. Note that abandoning the one-constant approximation does not affect this conclusion. In addition, varying \( K_{11} \) and \( K_{13} \) over a reasonable range—for example, from 5 \times 10\(^{-10} \) to 10\(^{-8} \) N and 5 \times 10\(^{-10} \) to 5 \times 10\(^{-8} \) J m\(^{-3} \)—respectively—does not affect the conclusion (see details in Extended Data Table I). Revisiting the initial comparison between equations (4) and (6) suggests that a smaller ‘true’ \( \gamma \) is needed to greatly increase the probability of a shape transition. We next consider how this situation can be realized through oligomer polydispersity and spatial segregation.

In applying equations (4) and (6), our models treated the bulk NLCO as a homogeneous material with monodisperse chain length. However, the NLCO mixture is polydisperse; it is composed of oligomers with a broad distribution of chain lengths. This new degree of freedom offers the possibility for spatial rearrangement of the oligomers within the drops, wherein the long-chain-length oligomers move preferentially to the interface and the short-chain-length oligomers move to be closer to the drop centre. For micrometre-size NLCO emulsion drops, molecules can easily diffuse and segregate within the confining structure on experimental timescales.

On the basis of simple energy considerations, spontaneous segregation to produce a long-chain-rich shell (near the surface or interface) and a short-chain-rich core (for example, near the sphere centre, or central axis of a filament or cylinder) will lower the system free energy. Consider a quantitative example. For spherical drops of radius \( R \), one can compute the elastic free energy density in the shell and core regions using the relation:

\[ F_{\text{elastic}} = 8\pi K_{11} R \]

If we define the core as the central region with a radius ranging from 0 to \( R/2 \), and the shell as the remainder of the sphere, then the splay elastic energy density in the core is about 7\( \times \) greater than that in the shell. In our experiments, the bulk elastic energy is lowered because short-chain NLCOs, which have smaller elastic constants, preferentially occupy the core regions which have very substantial director distortions (that is, large splay or splay/bend elastic distortions). This phenomenon can be understood as a chain-length-dependent ‘driving force’ due to the elastic energy density gradient within the drop. This energy gradient between core and shell regions leads to spatial rearrangement of oligomers with different chain lengths.

Moreover, the segregation of long-chain oligomers to the drop surface will reduce the interfacial energy of the drop (compared to a drop containing a homogeneous mixture, as is the case for the millimetre-size drops). We thus expect \( \gamma_{\text{true;micro-emulsion}} \) to be less than the corresponding millimetre-size droplet interfacial tension, \( \gamma_{\text{measured;mm-drop}} \), measured in the pendant drop experiments: \( \gamma_{\text{true;micro-emulsion}} < \gamma_{\text{measured;mm-drop}} \). NLCO polydispersity, and its consequences for chain-length-dependent spatial segregation of oligomers within the drop, generates a critical new feature in the microemulsion that influences shape transitions and self-assembly. The resultant reduction of interfacial tension reduces the unphysically large \( K_{11} \) requirement (calculated above) and thus resolves concerns raised by the simple shape instability model calculations for homogeneous, monodisperse liquid crystals. For example, using the same parameters for \( K \) and \( W_s \), but with a reduction of \( \gamma \) by 10\( \times \), we obtain the requirement \( K_{11} > 5.5 \times K_{13} \), which is in an acceptable range for saddle-splay modulus. Of course, further reduction of \( \gamma \) (as long as interfacial energy still dominates at high temperature) decreases the required \( K_{11} \), value even more and renders shape transitions to be even more likely. (Note also that the segregation-induced decrease in bulk elastic energy will further reduce the requirements for \( \gamma \) reduction, because the decrease in elastic free energy in filaments is greater than in spherical drops."

We can estimate the reduction of \( \gamma \) induced by oligomer segregation using a simple bidisperse demixing model (alluded to elsewhere in Methods). In the model, one component of the mixture is a monomer ((\( \ell = 1 \))), and the other component is a macromer with ((\( \ell = 9 \))). As shown in Extended Data Fig. 4c, for a monomer:macromer mixture weight ratio of 1:0.7, the overall mean chain length is \( \langle \ell \rangle_{\text{shell}} = 1.53 \). This condition gives rise to filamentous drop structures. Taking this condition to be exemplary for filament formation, we next show how the macromers and monomers segregate into core and shell regions with uneven chain length distributions in order to lower overall system elastic energy.

Because the total amount of monomer and macromer is conserved during segregation, we readily generate an equation relating the monomer:macromer weight ratio and \( \langle \ell \rangle_{\text{shell}} \) of the initial homogeneously distributed mixture to the final, segregated long-chain-rich shell with \( \langle \ell \rangle_{\text{shell}} \) and the short-chain-rich core with \( \langle \ell \rangle_{\text{core}} \). The resulting relation is:

\[
\langle \ell \rangle_{\text{core}} = 1 - (1 - n) + 2n
\]

Here \( n \) is the number fraction of macromer in the core region, and \( V_{\text{shell}} \) and \( V_{\text{core}} \) are volume of shell and core regions, respectively:

\[
\frac{V_{\text{shell}} + V_{\text{core}}}{V_{\text{total}}} = \frac{V_{\text{shell}}}{V_{\text{total}}} = \frac{6.641(\langle \ell \rangle_{\text{shell}} - 1)}{6.641 + 673(9 - \langle \ell \rangle_{\text{shell}})} = \frac{\langle \ell \rangle_{\text{core}}}{V_{\text{total}}}
\]
Beam/SEM) using a 5.00 kV electron beam. The resulting NLCEs via SEM (dual-beam FEI Strata DB235 Focused Ion Beam) were analyzed using a Hitachi S-4800Field Emission Scanning Electron Microscope (FESEM) equipped with a Noran System X-Lab detection system. The samples were then sputter-coated with gold to enhance the imaging quality.

To quantify how the chain length redistribution within the structure affects the system's overall bulk elastic energy, we take \( \langle \ell \rangle_{\text{core}} = 1.39 \) and \( \langle \ell \rangle_{\text{shell}} = 1.70 \), and we compute the elastic free energy volume integrals over the target geometry (for example, radial/sphere and escaped-radial/filament) using the Frank free energy equation (equation (1)).

We then compare the Frank free energy of the segregated system to that of the homogeneously distributed system with \( \langle \ell \rangle_{\text{whole}} = 1.53 \). For this calculation, we assume that the elastic constant is proportional to oligomer mean chain length\(^{18-22} \). The comparison reveals that this reduction in \( \langle \ell \rangle_{\text{core}} \) will decrease bulk elastic energy by ~5% for the sphere and ~8% for the filament (that is, compared to the homogeneously distributed systems).

Most importantly, as a result of oligomer segregation (for example, an increase of local mean chain length near the interface from 1.53 to 1.70, by ~0.17), the interfacial tension is lowered dramatically. To better appreciate this assertion, consider the homogeneous mixtures NLCO#2 (7 h oligomerization) and NLCO#5 (24 h oligomerization) in Extended Data Fig. 3. For these samples, the interfacial tension (for example, at 30 °C) of the drops made with NLCO#5 (0.12 mN m\(^{-1} \)) is much smaller, by a factor of ~20×, compared to that of NLCO#2 (2.36 mN m\(^{-1} \)).

Hence, our earlier statement in the text that a “conservative reduction of \( \gamma \) by ten times to approximately 0.1 mN m\(^{-1} \) yields sphere–filament distributions.”

Last, we reiterate that in the millimetre-size drops measured by the pendant technique, we expect the chain-length-dependent segregation to be insignificant. Macroscopically, the drop is approximately homogeneous because the millimetre-size drops have many nematic microdomains (each with a director oriented uniformly along a different direction) and many randomly situated disclination lines. The larger drops have lower curvatures too, and therefore director distortion is reduced near their surfaces. The largest distortions that could drive segregation should occur locally near disclinations and at domain walls distributed roughly uniformly throughout the drop; thus, they will not promote net migration to the surface. Moreover, the required molecular diffusion over long distances will be small because of extremely long diffusion times (domain walls would also act as barriers to oligomer diffusion, and so on). Thus, interfacial tension derived from the pendant drop experiments is set by the macroscopic “average” of the whole droplet, that is, \( \langle \ell \rangle \) of the initial (source) NLCO distributions.

**Crosslinking NLCO structures into NLCEs**

To crosslink structural NLCOs into solid NLCE structures, 2 wt% (by RSM82 concentration) of 2,2-dimethoxy-2-phenylacetophenone (radical photoinitiator, Sigma-Aldrich) was added into the initial RSM82/butyllamine/chloroform mixture. Then the same oligimerization–cooling method described above was performed. After the NLCO emulsions reached their final (desired) equilibrium morphologies, the NLCOs were radially crosslinked into elastomers by UV radiation (365 nm) for a few minutes. We then evaporated the background solution, sputter-coated thin metallic films (gold or iridium) onto the structures, and observed the resulting NLCEs via SEM (dual-beam FEI Strata DB235 Focused Ion Beam) using a 5.00 kV electron beam.

**Data availability**

The authors declare that the data supporting the findings of this study are available within the text, including the Methods section, and Extended Data files. Raw data are available from the corresponding author upon reasonable request.

**Code availability**

Custom computer codes associated with modelling in this study are available on GitHub (https://github.com/wei-shao-wei/Molecular-heterogeneity-chooses-reconfigurable-nematic-liquid-crystal-drops).

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**Author contributions**

W.-S.W., Y.X., S.Y. and A.G.Y. conceived the idea and designed the study. Y.X., S.Y. and A.G.Y. wrote the paper, and all authors contributed to the final manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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Extended Data Fig. 1 | Distribution of chain length and molecular weight of NLCO samples measured by size exclusion chromatography. a, The NLCO source samples are shown by size exclusion chromatography (SEC) to be a mixture of monomers, dimers, trimers, tetramers and other oligomers (blue solid line; peaks appearing at longer retention times represent shorter chain lengths). In step-polymerization processes, when the extent of reaction is less than 0.9, monomers dominate the overall molar fraction. For comparison, liquid crystal (LC) macromers (used in the supporting experiment in Methods) synthesized following the schemes of Ware et al. 10 are also included in the plot; these show longer mean chain length and very few (if any) short-chain components (red dashed line). Furthermore, since our system is made in an aqueous solution, the polymerization rate is expected to be slower. For reference, the black dotted line shows the peak for pure RM82 monomer. b, Calculated from SEC data (example in a), the number-average molecular weight ($M_n$, blue solid squares) and polydispersity index (PDI, red filled circles) of the NLCOs are shown as function of oligomerization time. Both $M_n$ and PDI increase with oligomerization time. The dotted (for $M_n$) and dashed (for PDI) curves are to guide the eye. (For comparison, the LC macromer synthesized following the schemes of Ware et al. 10 and used in Methods section ‘Macromer–monomer mixing experiments’ has $M_n = 6,900$ Da and PDI = 1.3.) Bars indicate the spread in $M_n$, which mainly arises from our inability to detect the longer-chain components.
Extended Data Fig. 2 Bright-field optical microscopy images showing reversible shape transitions of NLCO drops during temperature cycling. 

**a–c.** When temperature is increased from room temperature (20 °C) to a higher value (here 90 °C), the NLCO filamentous structures reversibly evolve into spherical microdroplets. 

**c–e.** When cooled from 90 °C to 20 °C, the spherical microdroplets reversibly evolve back into filamentous structures. The drop morphology can be transformed repeatedly, remaining quantitatively similar. Here, multiple small drops evolve in the field of view; data shown earlier (Fig. 1c–h) showed only one large evolving drop. Scale bar in **a** (for all panels), 20 μm.
Extended Data Fig. 3 | Macromolecular interfacial tension of NLCO pendant drops as function of temperature and NLCO oligomerization time. The NLCO drop has homeotropic anchoring at the interface in an aqueous solution consisting of 0.1 wt% SDS. The interfacial tension $\gamma$ decreases with decreasing temperature and increasing NLCO mean oligomer chain length $\langle \ell \rangle$ (consult Fig. 2f for the relation between oligomerization processing time and $\langle \ell \rangle$). Inset, optical image of a NLCO pendant drop hanging from a flat-tip syringe needle (1.26 mm outer diameter) in a 0.1 wt% SDS aqueous solution. The dashed curves are to guide the eye.
Extended Data Fig. 4 | Bright-field optical microscopy images of drop morphologies obtained from mixtures of macromers ($\langle \ell \rangle \approx 9$) and monomers (RM82) at different weight ratios in a 0.1 wt% SDS aqueous solution after cooling. a–e, Images for monomer:macromer weight ratios of 1:0.3, 1:0.5, 1:0.7, 1:0.9 and 1:1, respectively. With a fixed amount of RM82, increasing the concentration of macromers in the drop leads to longer $\langle \ell \rangle$, larger bulk elasticity and lower interfacial tension. The last two factors favour interfacial roughening and filament formation. Images are taken at room temperature after cooling. Scale bar in a (for all panels), 50 μm.
Extended Data Fig. 5 | Bright-field optical microscopy images of NLCO structures in aqueous solutions of different surfactants as a function of the mean oligomer chain length, $\langle \ell \rangle$. 

a–f, NLCO drops in aqueous solutions with different surfactants, that is, with either cationic (a–c; hexadecyltrimethylammonium bromide, C$_{16}$TAB) or nonionic (d–f; Polysorbate 20, Tween 20) surfactants. These systems exhibit a drop morphology evolution similar to that resulting from SDS, that is, with respect to cooling and an increase of $\langle \ell \rangle$. After cooling from 90 °C to 20 °C, a representative NLCO drop in a 0.5 mM C$_{16}$TAB aqueous solution (below the CMC; a–c) and a representative NLCO drop in a 0.03 mM Tween 20 aqueous solution (below the CMC; d–f). Both evolve with increasing $\langle \ell \rangle$ (left to right; consult Fig. 2f for the relation between the oligomerization time (shown at bottom left in all panels) and $\langle \ell \rangle$). For this behaviour to be shown, it is important that NLCOs should favour homeotropic anchoring at the drop interface. Images are taken at room temperature. Scale bars in a–f, 20 μm.
Extended Data Fig. 6 | Bright-field optical microscopy image of aggregated NLCO filamentous structures for an SDS concentration above the CMC. In a 1 wt% SDS aqueous solution (shown here), the NLCO drops exhibit a similar but more complicated shape transition behaviour than that which occurs below the CMC, after cooling from 90 °C to 20 °C. For example, aggregated filamentous structures form and sometimes stick to the substrate due, in part, to micelle-induced depletion. (For comparison, expanded filamentous structures form in aqueous solutions below the CMC, see example in Fig. 1h.) Scale bar, 20 μm.
Extended Data Fig. 7 | Self-assembled NLCE fibrous mat. NLCE fibres can be densely packed into centimetre-wide and few-micrometres-thick, non-woven, free-standing mats by sedimentation. Here we show an image of such a mat (mounted on a hollowed holder) with a diameter greater than 1 cm. Corresponding high-magnification SEM images of this mat are shown in Fig. 4e, f.
**Extended Data Table 1 | Parameter values that permit shape transitions of NLCO drops**

| $\gamma_{\text{measured, mm-drop}}$ (mN/m) | $K$ (N) | $W_a$ (J/m²) | Required $K_{24}$ for shape transition | Reduction factor of $\gamma_{\text{measured, mm-drop}}$ gives $\gamma_{\text{true, micro-emulsion}}$ | Required $K_{24}$ for shape transition with reduced $\gamma$ |
|------------------------------------------|----------|--------------|--------------------------------------|---------------------------------|-----------------------------------|
| 2.36                                     | $5 \times 10^{-11}$ | $5 \times 10^{-5}$ to $5 \times 10^{-4}$ | 60.2 $\times K_{11}$ | 20x                            | $5.7 \times K_{11}$               |
| 2.36                                     | $10^{-10}$ | $5 \times 10^{-4}$ to $5 \times 10^{-3}$ | 31.6 $\times K_{11}$ | 10x                            | $5.7 \times K_{11}$               |
| 2.36                                     | $5 \times 10^{-10}$ | $5 \times 10^{-4}$ | 8.6 $\times K_{11}$ | 2x                             | $5.7 \times K_{11}$               |

This table summarizes parameter values that permit shape transitions (with reasonable saddle-splay elastic constants, $K_{ij}$) based on our model free energy calculations. The calculations fix the interfacial tension ($\gamma_{\text{measured, mm-drop}}$, column 1) at 30°C measured by the pendant drop technique. A fairly wide range of estimated elastic constants ($K$, column 2) and anchoring energy coefficients ($W_a$, column 3) are employed in the calculations. In line with the criteria for a spontaneous shape transition, we require the required saddle-splay elastic constant ($K_{24}$, column 4) to be of the order of ~6 times the splay modulus $K_{11}$ (or less). The calculations show that a smaller ‘true’ interfacial tension, $\gamma_{\text{true, micro-emulsion}}$ (expressed as a reduction factor of $\gamma_{\text{measured, mm-drop}}$, column 5), will relax the saddle-splay requirement (column 6). This reduction of $\gamma$ can be realized through oligomer polydispersity and the resultant oligomer spatial segregation in the elastic stress field. Note that a reasonable range for $K$ is $5 \times 10^{-11} \text{N}$ to $10^{-10} \text{N}$; a value of $K = 10^{-11} \text{N}$ is probably too small, as it is the same order of magnitude as small molecule liquid crystals such as 5CB.