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Supplementary Information for ***Elastic Sheath–Liquid Crystal Core Fibres Achieved by Microfluidic Wet Spinning***

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(A) Materials Preparation

(1) Polymer Dopes

For this work, two polymer dope preparation procedures were followed.

First, solutions of 12-14% w/w PI in each of *n*-hexane (99%, Carl Roth GmbH), *n*-decane (Sigma Aldrich), and toluene (99% from synthesis, Carl Roth GmbH) were prepared by dissolving the polymer under constant stirring at not more than 40°C for at least two days, until the solution appeared optically homogeneous without any visible aggregates and with a uniform consistency throughout.

In the other procedure, a dilute solution of the polymer (concentration of 5% w/w or lower) using the same materials was first prepared, then filtered through a 0.20 μm PTFE syringe filter before being reconcentrated through solvent evaporation at 30°C with stirring to the desired final concentration. Both optically and performance-wise, no visible differences were observed between the solution preparation methods, though the procedure involving a direct dissolution of polymer in solvent was easier to control and faster overall.

(2) Cholesteric Liquid Crystal Mixtures

Normal incidence red-reflecting cholesteric liquid crystal mixtures were prepared first by weighing a quantity of the chiral dopant ZLI-3786 in a clean glass vial. RO-TN 615, E55+CB15, or another host nematic liquid crystal was then added dropwise to the vial to achieve a concentration of approximately 25% w/w chiral dopant. This mixture was then heated to isotropic (normally above 70°C), producing a clear liquid, before cooling back into the nematic phase. The coloured Bragg reflection characteristics of the mixture was verified with the unaided eye, both in the bottle and in a cell prepared from two glass slides, before its use in fibre spinning.

(B) Tensile Characterisation of Filled and Unfilled Fibres

A set-up for tensile characterisation was built consisting of two unidirectional micrometre translational stages (ThorLabs) fixed to a steel frame. A hydrophobised glass slide was broken in half with each side fixed using tape to a micropositioner stage, creating an initial gap between the slides of 3 mm that could be extended to a maximum of 25 mm.

(C) Hildebrand and Hansen Solubility Parameters of the Materials Used

Using the method described by Fedors[1], we estimate the Hildebrand parameters for the materials used in both the polymer dopes and the cores as follows:

(1) Polyisoprene and polybutadiene

A proposed equation for determining the solubility parameter of a high molecular-weight polymer is given by

$$\delta = \rho \cdot \frac{\Delta f_{ir}}{M_r} \qquad (1)$$

such that ρ is the polymer density, M_r the molar mass of the repeating unit of the polymer, and Δf_{ir} is the sum of the repeating units' contributions to a "molar attraction constant", which measures the contributions of the functional groups and units of a polymer monomer to their dipole and overall interactions. Inputting the values for each of the groups then gives, for polyisoprene:

$$\delta = \left(0.91 \frac{g}{cm^3}\right) \cdot \frac{(214 + 2 \cdot 133 + 19 + 111)}{68 \frac{g}{mol}} = 16.7\ MPa^{1/2}$$

For polybutadiene, a similar procedure is followed:

$$\delta = \left(0.91 \frac{g}{cm^3}\right) \cdot \frac{(2 \cdot 133 + 2 \cdot 111)\frac{(cal/cm^3}{mol}}{54 \frac{g}{mol}}$$

This shows that both polybutadiene and polyisoprene, having similar Hildebrand solubility parameters, should show similar interactions with the liquid crystal.

(2) Cyanobiphenyl liquid crystals (ex. 5CB) and chiral dopants

Many common liquid crystal mixtures with known compositions, such as E7,[2,3] are prepared from biphenyls and terphenyls. While it is not certain what is contained within the RO-TN mixtures, nor is it possible to find out readily, we can calculate the Hildebrand parameter for a representative liquid crystal, 5CB. To do so, a different equation is proposed by Fedors for a non-polymer material:

$$\delta = \left(\frac{\sum \Delta e_i}{\sum \Delta v_i} \right)^{1/2} \tag{2}$$

such that Δe_i is a contribution of a chemical group to the molar energy density of the molecule, expressed in $\frac{cal}{mol}$, and Δv_i a contribution to its molar volume, expressed in $\frac{cm^3}{mol}$. (This equation can be used for polymers, but is largely impractical due to the large sizes of typical molecules, leading us to prefer instead using equation (1) for polymers instead.) In the case of 5CB, we find the following:

$$\delta = \left(\frac{[(6100) + (2 \cdot 7630) + (4 \cdot 1180) + (1125)]}{[(24.0) + (2 \cdot 52.4) + (4 \cdot 16.1) + (33.5)]\frac{cr}{m}} \right. = 22.4\ MPa^{1/2}$$

For the chiral dopant, ZLI-3786 (Figure 2(d)), we calculate:

$$\delta = \left(\frac{[(10 \cdot 1180) + (2 \cdot 800) + (2 \cdot 7630) + (2 \cdot 4150)}{[(10 \cdot 16.1) + (2 \cdot 3.8) + (2 \cdot 52.4) + (2 \cdot 10.8)} \right. = 9.9\ cal^{\frac{1}{2}} cm^{-\frac{3}{2}} = 20.2\ MPa^{1/2}$$

This suggests miscibility of the dopant in the liquid crystal.

Hansen parameters are often a better predictor of dissolution or miscibility between disparate materials with differing polarities[4], as they account for both polar interactions and hydrogen bonding. Hansen parameters use three components: a London dispersion parameter δ_D, which is often similar to the calculated Hildebrand parameter; a polar parameter δ_P; and an electron transfer parameter δ_H. These three parameters are related to the final solubility parameter δ:

$$\delta^2 = {\delta_D}^2 + {\delta_P}^2 + {\delta_H}^2 \tag{3}$$

For the liquid crystal 5CB, we can use a tabulation method, similar to that used for the Hildebrand parameter, to compute each of the individual Hansen parameter components[1,4,5]:

$$\delta_D = \left(\frac{(0) + (2 \cdot 7530) + (4 \cdot 1180) + (1125)}{(32.0) + (2 \cdot 52.4) + (4 \cdot 16.1) + (33.5)} \right)^{1/2} = 9.4\ cal^{1/2} cm^{-3/2} = 19.3\ MPa^{1/2}$$

$$\delta_P = \left(\frac{(3750) + (2 \cdot 50) + (4 \cdot 0) + (0)}{(32.0) + (2 \cdot 52.4) + (4 \cdot 16.1) + (33.5)} \right)^{1/2} = 4.1\ cal^{1/2} cm^{-3/2} = 8.3\ MPa^{1/2}$$

$$\delta_H = \left(\frac{(400) + (2 \cdot 50) + (4 \cdot 0) + (0)}{(32.0) + (2 \cdot 52.4) + (4 \cdot 16.1) + (33.5)}\right)^{1/2} = 1.5\ cal^{1/2} cm^{-3/2} = 3.0\ MPa^{1/2}$$

Combining these terms, we then obtain:

$\delta^2 = (19.3)^2 + (8.3)^2 + (3.0)^2 = 450.0\ MPa$

$\delta = 21.2\ MPa^{1/2}$

For polyisoprene, the Hansen solubility parameters can be estimated by literature[4,6] as $16.9\ MPa^{1/2}$, $1.\,1\ MPa^{1/2}$, and $-0.4\ MPa^{1/2}$ for δ_D, δ_P, and δ_H, respectively, which can then be summed to obtain $\delta = 16.9\ MPa^{1/2}$. This value is in agreement with the Hildebrand parameters calculated earlier.

We can also quantify a *relative energy difference* (RED), which is a ratio of a parameter calculated from the Hansen solubility parameters to an experimentally-determined "interaction radius" of a polymer (r_0). For polyisoprene, this radius is $9.6\ MPa^{1/2}$[4]. We then calculate a relative radius using:

$$r_a^{\ 2} = 4(\Delta\delta_D)^2 + (\Delta\delta_P)^2 + (\Delta\delta_H)^2 \qquad (4)$$

Inputting the obtained values gives:

$r_a^{\ 2} = 4(19.3 - 16.9)^2 + (8.3 - 1.0)^2 + (3.0 + 0.4)^2 = 86.1\ MPa$

$r_a = 9.3\ MPa^{1/2}$

$RED = \frac{r_a}{r_0} = \frac{9.3}{9.6} = 0.97$

When the RED is less than one, but not substantially so, the condition of swelling is met; this is consistent with our experimental observation of the fibers leaving cholesteric liquid crystal residues on substrates.

The ZLI-3786 can, by using the tabulation methods described above, be found to have a solubility parameter of $19.8\ MPa^{1/2}$ and an RED with polyisoprene of 0.81, which are consistent with the observation of its miscibility in the liquid crystal and the LC swelling the polymer sheath.

(D) Supplementary Information Images

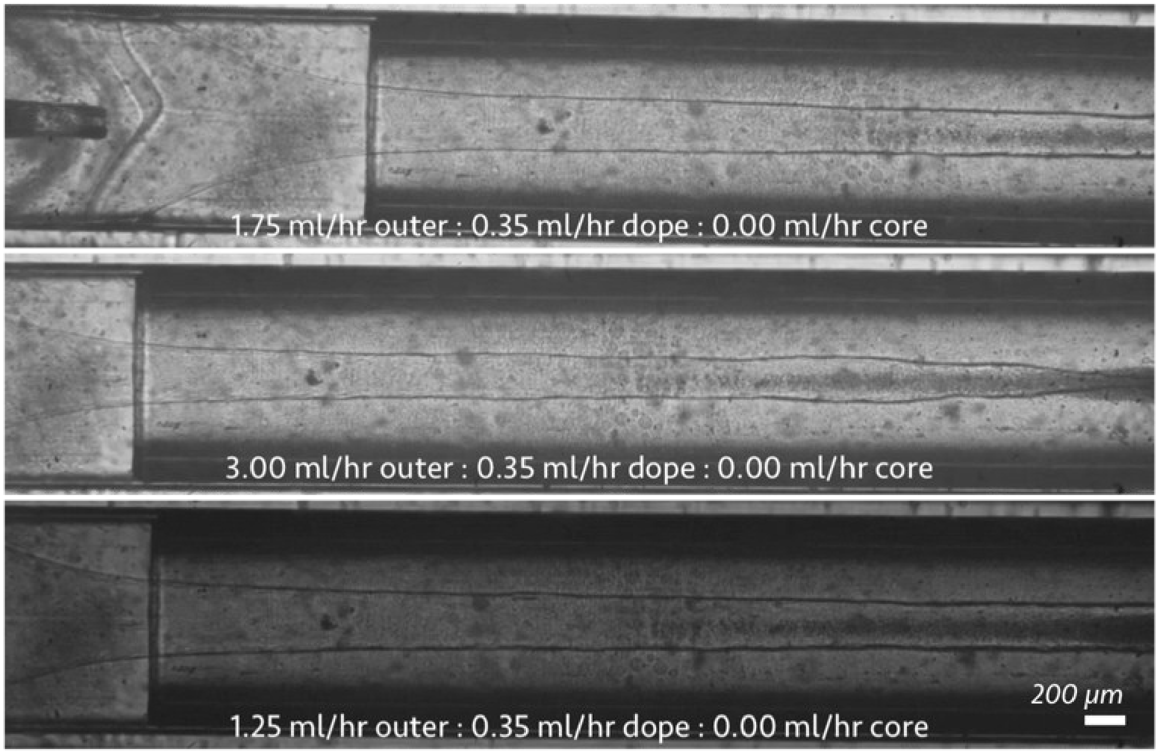

Figure S1. Flow and jetting profiles of different flow rate ratios of polymer dope to bath without a core for 14% w/w polyisoprene in n-hexane as a polymer dope and 10% PVP and 10% LiBr in ethanol as the coagulation bath. Because of the slow solidification of the polymer jet during the flowing process, at higher bath flow rates, pinching off of the polymer jet is observed: the jet becomes extremely thin, which permits Rayleigh instability to develop much more easily in the thinner jet.

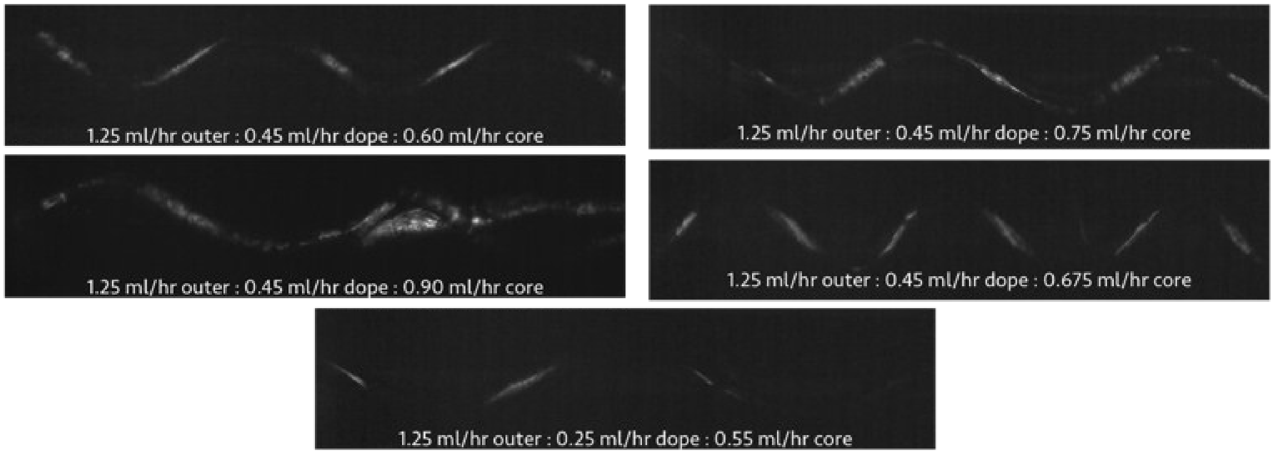

Figure S2. Images taken during the spinning process of a core of RO-TN 615 flowing within a polyisoprene in hexane sheath, as viewed between crossed linear polarisers, at different flow rate combinations. The zig-zagging character reflects the fact that we are observing the *projection into the image plane of an overall helicoidal fibre shape, as observable in Figure 3b) in the main article, that spontaneously forms downstream from the spinneret due to a mismatch of flow speeds.*

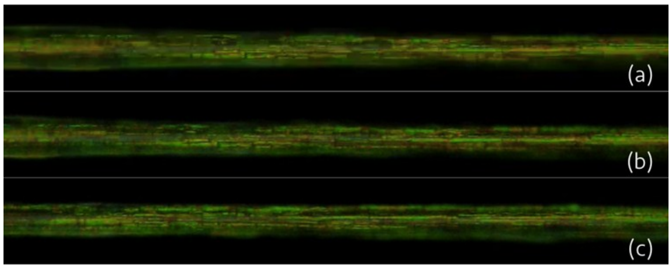

Figure S3. A PI fibre filled with the 25% w/w ZLI-3786 in RO-TN 615 mixture, as viewed in reflection mode between crossed polarisers. The difference between (a), (b), and (c) is stretching the fibre to thin it progressively, with (c) being the most stretched; the stretching induces a colour change that is more obvious between (a) and (c), but is still quite subtle.

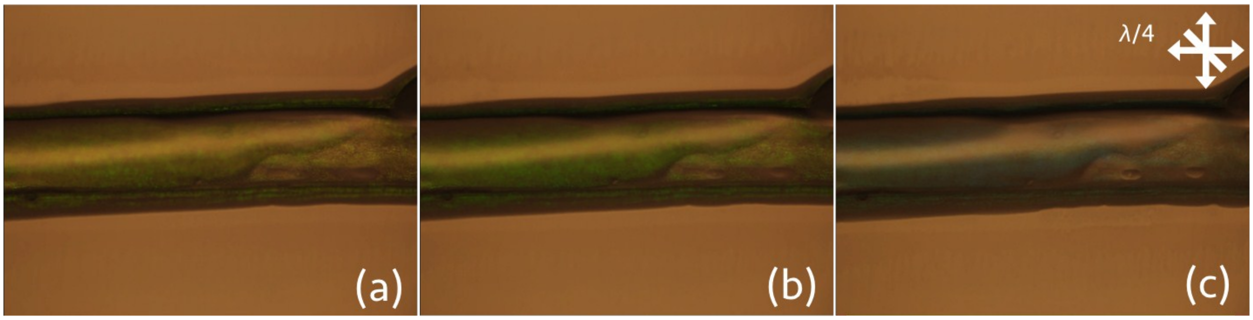

Figure S4. Still frames from Video S6 showing the heating of a polyisoprene fibre filled with 25% w/w ZLI-3786 in RO-TN 615 and mounted on a glass microscopy slide, as viewed in reflection mode between crossed polarizers with a quarter wave plate. The fibre is heated from (a) ~20°C to (b) ~35°C and (c) ~50°C, showing a blueshift in observed colour.

(E) Supplementary Information Videos

Video S1: The jetting of a 14% w/w polyisoprene in hexane dope into a coagulation bath of 10% w/w PVP and 7% w/w LiBr in ethanol.

Video S2: Coaxial jetting of RO-TN 615 and 14% w/w polyisoprene in hexane dope into a coagulation bath of 10% w/w PVP and 7% w/w LiBr in ethanol.

Video S3: Stretching of a pure polyisoprene fibre.

Video S4: Stretching of a polyisoprene fibre filled with a cholesteric liquid crystal (25% ZLI-3786 in RO-TN 615).

Video S5: The change of the reflected colour of the liquid crystal fibre as a function of illumination direction of incident light.

Video S6: The change of colour of the liquid crystal fibre filled with a cholesteric liquid crystal upon heating and cooling. The fibre was heated from room temperature (~22°C) to ~50°C by the use of a heat gun and then allowed to cool under ambient conditions. The fibre is here bounded by unconfined liquid crystal that has most likely escaped from the sheath when the fibre was deposited on the hydrophilic glass substrate, due to the surface forces as the glass substrate tends to be wetted by the liquid crystal. A similar phenomenon was observed by Kim and Lagerwall for electrospun core-sheath fibres deposited on hydrophilic substrates[7]. The escaped liquid crystal originally has a boundary that does not minimise its surface area, most likely due to the high viscosity of the cholesteric liquid crystal. During the heating experiment, as the material changes into an isotropic phase, the reduction in viscosity leads to flow, as is readily seen in the video, redistributing the liquid material such that the surface area is minimized. The fibre itself shows no significant response to the heating/cooling experiment beyond the colour change.

References

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