Supplementary Information

Directional Actuation and Phase Transition-Like Behavior in Anisotropic Networks of Responsive Microfibers

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S1. Uniform Cartesian networks analysis

Figure 2 in the main text depicts two networks with uniform node-to-node distances. The network depicted in Figure 2A exhibited a shape-preserving morphing behavior. The reciprocal slenderness for the responsive PNcG fibers is 0.07 (± 0.01). The maximum deflection of the segments, ψ, is $0\ \mu m$ in this network. The network depicted in Figure 2B exhibited a buckling-governed morphing behavior. The reciprocal slenderness for the responsive PNcG fibers in this network is 0.014 (± 0.002), and the average deflection amplitude ψ is 147 ($\pm 27 \mu m$), showing the large distribution of values, as expected for the ensemble of buckling segments. The reciprocal slenderness and deflection for both systems well-agrees with the analysis performed on the systems with an ununiform distribution of node-to-node distances.

S2. Flory-Rehner equation

The Young modulus of the PNcG polymer cannot be determined directly; hence, it was deduced indirectly from the swelling ratio of the fibers using the Flory-Rehner equation. For a typical swollen polymer network, the fraction of the polymer in the swollen gel, ϕ, defined as $\phi = \frac{V_{us}}{V_s}$, where V_{us} is the unswollen volume of the gel and V_s is the swollen volume of the gel. The Young modulus can be extracted from the Flory-Renher model:[1]

$$E = \frac{3k_BT}{\alpha^3 N_{gel}}\phi^3, \tag{S1}$$

where k_B is Boltzmann constant, T is the temperature that is set to be the room temperature, $\alpha = 6.7\text{Å}$ is the monomer length, and N_{gel} is the number of monomers between two crosslinkers, which is calculated to be 50.2. Using this equation, an estimate for E was established for every fiber that was described in the article.

S3. Using phase transition formalism for describing the buckling of a beam

To develop the phase transition description for the buckling of segments, we followed the formalism suggested by Salvel'ev and Nori for considering beam buckling under an external force as a modified Landau theory problem. The general expression for the mechanical energy, F, of a beam with a Young modulus E, radius r, and length L , as a function of an applied stress σ, is given in Eq. 2 in the main text.3 The beam contour depends on the boundary conditions of the system: in the case of a pinned beam (y =0 and y''=0 at l =0 and l = L) the contour can be expressed as $y = \psi sin\left(\frac{n\pi l}{L}\right)$, while in the case of a clamped beam (y =0 and y'=0 at l =0 and l = L), the contour is described as $y = \psi\left(1 - \cos\left(\frac{2n\pi l}{L}\right)\right)$ .in both cases, the amplitude, ψ, indicates the extent of buckling, and hence can be regarded as an order parameter for the buckling. From the solution of the critical buckling, the critical stress at which buckling occurs is given by:

$$\sigma_c(n) = \frac{a^2n^2E\pi^2r^2}{4L^2}, \tag{S2}$$

where a is a column effective length factor; $a = 1$ in the case of pinned ends, and $a = 2$ for clamped ends, n is the mode order, E is the young modulus, r is the beam's radius, and L is the beam's length.

Substituting the equations of the beam contour into Eq. 2 in the main text, developing the expressions as a Taylor series of ψ, and integrating, one obtains the following expression for the energy as a function of the stress:

$$F = \frac{a^2\pi^3n^2r^2}{4L}(\sigma_c(n) - \sigma)\psi^2 + \frac{a^4\pi^5n^4r^2}{64L^3}(4\sigma_c(n) - 3\sigma)\psi^4 + O(\psi^6), \tag{S3}$$

which, by substituting $\sigma_c(n)$ from Eq. 1 yields Eq. 4. To find the minimum of the energy with respect to ψ, we differentiate Eq. S3 and set to 0. As we focus on the region of order transition ($\psi \to 0$), the higher terms can be disregarded, obtaining:

$$\frac{dF}{d\psi} = 2\frac{a^2\pi^3n^2r^2}{4L}(\sigma_c(n) - \sigma)\psi + 4\frac{a^4\pi^5n^4r^2}{64L^3}(4\sigma_c(n) - 3\sigma)\psi^3 = 0. \tag{S4}$$

From this, we get the deflection that minimizes the energy:

$$\psi_m = \sqrt{-\frac{(\sigma_c(n) - \sigma)}{\frac{a^2\pi^2n^2}{8L^2}(4\sigma_c(n) - 3\sigma)}}, \tag{S5}$$

and this is indeed a minimum, because $\frac{d^2F}{d\psi^2}(\psi_m) > 0$.

In proximity to σ_c ($\sigma \to \sigma_c$), the expression further simplifies to:

$$\psi_m = L\sqrt{-\frac{8(\sigma_c(n) - \sigma)}{a^2\pi^2n^2\sigma_c(n)}}, \tag{S6}$$

The derivation above is general for a single beam and shows that the beam buckling indeed follows the extended Landau theory, with the stress (or force) acting as equivalent to the temperature in thermodynamic systems.

While Eqs. S4-S6 usually focus on a single beam with a known and constant σ_c and a varying external stress. They are also used for describing a system with varying critical stress that is under constant external stress, σ^*. For example, in the ununiform networks described in the article, the same stress is imposed on segments of different critical stresses and affects their buckling extent.

The critical stress depends entirely on the dimensions and mechanical properties of the segments, the Young modulus E, the segment's radius, r, and its length, L, as shown in Eq. 1. Hence, if two of these parameters are constant for all the segments, a Landau-like expression can be developed for the third parameter. For example, for segments along a single fiber, both the Young modulus and the radius are constant, while the segment length can change. Under these assumptions, Eq. S5 can be written in terms of the single-segment properties:

$$\psi_m = \sqrt{-\frac{\left(\frac{1}{4}a^2n^2\pi^2E\left(\frac{r}{L}\right)^2 - \sigma^*\right)}{\frac{a^2\pi^2n^2}{8L^2}\left(4\cdot\frac{1}{4}a^2n^2\pi^2E\left(\frac{r}{L}\right)^2 - 3\sigma^*\right)}}, \tag{S7}$$

taking into account the radius and Young modulus, according to Eq.1, there is a critical length, L^*, above which the segment will buckle under the applied stress. Substituting this into Eq. S7 yields

$$\psi_m = \sqrt{-\frac{\left(\frac{1}{L^2} - \frac{1}{L^{*2}}\right)}{\frac{a^2\pi^2n^2}{8L^2}\left(\frac{4}{L^2} - \frac{3}{L^{*2}}\right)}}. \tag{S8}$$

If we examine the system very close to this critical length ($L \to L^*$) then:

$$\psi_m = \sqrt{-\frac{\left(\frac{1}{L} + \frac{1}{L^*}\right)\left(\frac{1}{L} - \frac{1}{L^*}\right)}{\frac{a^2\pi^2n^2}{8L^2}\left(\frac{4}{L^2} - \frac{3}{L^{*2}}\right)}} \approx \sqrt{\frac{16L^{*3}\left(\frac{1}{L^*} - \frac{1}{L}\right)}{a^2\pi^2n^2}} \tag{S9}$$

where L^{-1} acts as the effective temperature.

When examining a single network, all the responsive fibers are made of the same polymer (i.e., they have the same Young modulus), but in this case, both the radius and the length of the segments can change along the network. In this case, the critical stress yields a critical slenderness ratio, $\overline{S^*} = \sqrt{\frac{4\sigma^*}{a^2n^2E\pi^2}}$, and Eq. S3 can be expressed as a function of the reciprocal slenderness, $\bar{S}$, yielding Eq. 5 in the main text. Deriving the minimum of the energy with respect to ψ (similar to the derivation shown above) yields:

$$\psi_m \approx L\sqrt{\frac{16(\overline{S^*}-\bar{S})}{a^2\pi^2n^2\overline{S^*}}}, \tag{S10}$$

whereby multiplying by $\frac{\bar{S}}{\bar{S}}=1$ can be revised as:

$$\psi_m \approx r\sqrt{\frac{16(\overline{S^*}-\bar{S})}{a^2\pi^2n^2\left(\overline{S^*}^3\right)}}, \tag{S11}$$

leading to Eq. 6 in the main text.

Eqs. S8 and S9 indicate that for all segments, the order parameter ψ should exhibit the same square root dependence on the governing parameter $\bar{S}$, typical of Landau's theory. However, the proportionality coefficient will be different for each segment. Dividing Eq. S8 by L and Eq. S9 by r leads to a unified expression, which is similar for all the segments in the networks as long as E is constant, as portrayed in Figure 4C in the main text.

S4. Shearing within buckling-governed morphing regimes

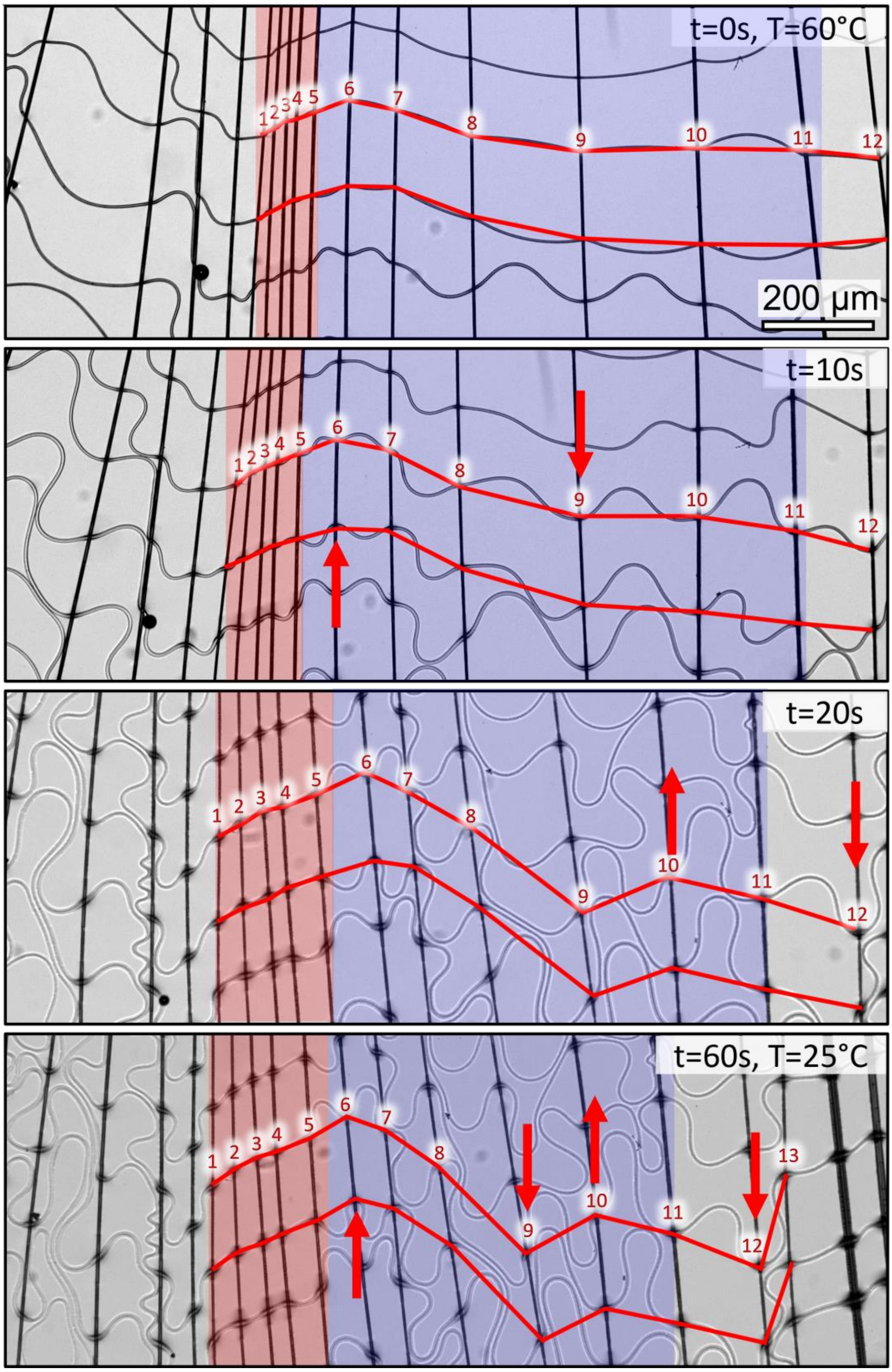

Figure S1. Node-to-node path of two fibers portrayed in Figure 3 in the main text, showing the shearing of the network as the swelling progresses. The nodes along the fibers are numbered from left to right. Major shearing occurred in nodes 6, 9, 10, 12, and 13.

References

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