Supplementary Information

I. EXPERIMENTAL METHODS

As discussed in the main text, liquid monomer formulations were poured into molds (for DMA specimens the molds were constructed from microscope slides and spacers), and then photo-polymerized using UV light; Figure S1 shows a schematic overview of the process as well as example images of the samples used for the fracture experiments.

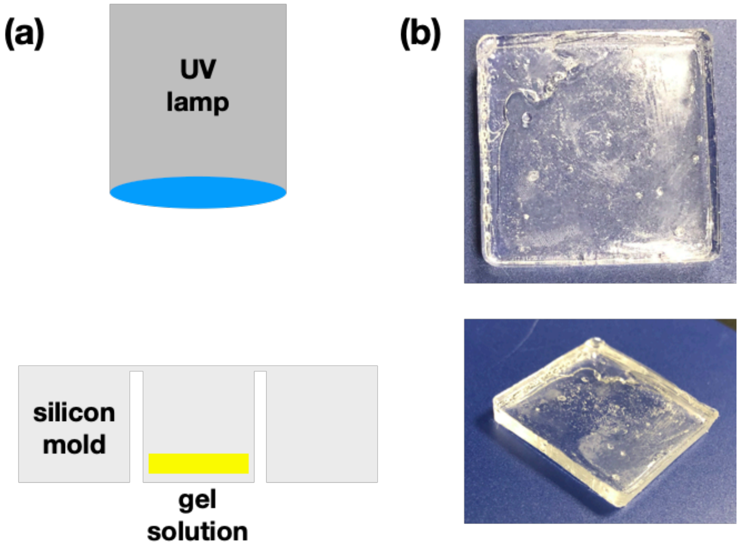

FIG. S1. (a) A silicone mold is partially filled with a monomer formulation and then UV-cured. (b) Example images of fabricated samples; both images depict the same 30 mm × 30 mm × 3 mm sample from different perspectives.

II. SAMPLE CHARACTERIZATION

A. Mechanical properties

During DMA experiments, storage modulus (E'), loss modulus (E'') and tan delta ($tan\delta$) behaviors were collected simultaneously as a function of temperature. The figures below correspond to this data for an unswollen (e.g. virgin) 20 mol percent PEGDA network undergoing a temperature sweep from -50°C to 100°C. A peak in the *tanδ* profile is observed at the start of this temperature sweep (right), indicating a T_g for the network of approximately -42°C, well below ambient temperatures. This is supported by a significant decrease in E'' starting at the same temperature and plateauing at 0°C. The full transition is not captured (e.g. complete *tanδ* peak and decrease in E'), as this would require additional cooling below -50°C which is out of the range for reliable measurements of the equipment employed.

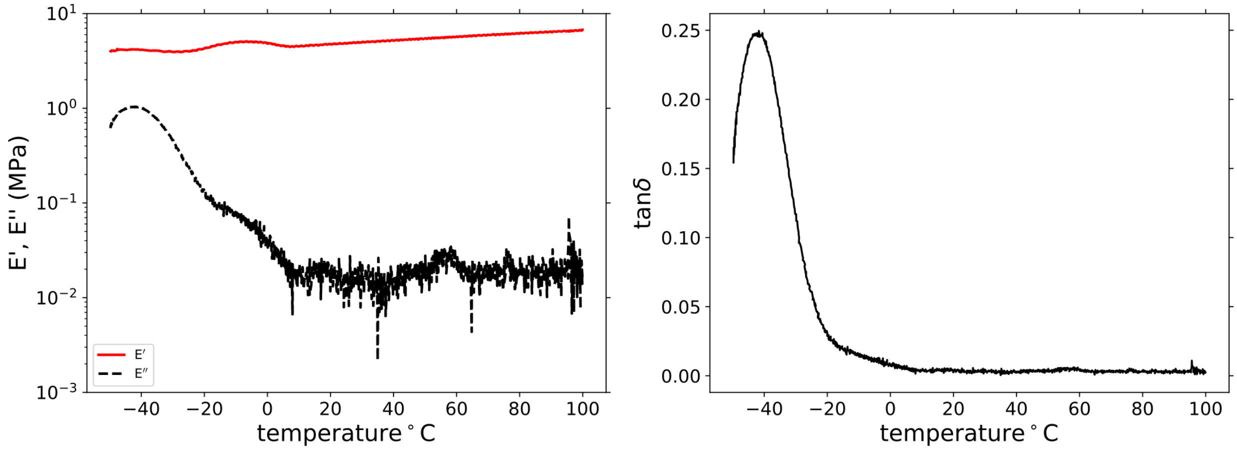

FIG. S2. Left: Loss and storage moduli data for an unswollen, 20 mol percent PEGDA network. Right: the associated tanδ data.

B. Swelling measurements and characterization

Water absorption was measured explicitly in the softest gels, e.g. gels which did not exhibit self-rupture. As shown in Figure S3, the rate of water absorption was rapid and then slowed over time; this is consistent with literature results on similar gels. The inset of Figure S3 shows an enlargement of the early-time swelling. As shown in the Figure, substantial water uptake is observed during the early stages of swelling.

In order to characterize density changes during swelling, samples were immersed in Milli-Q water for 600 seconds, and then sample mass and volume were measured for samples which did not rupture. As shown in Figure S4, a reduction in density of 10-20% was observed for all modulli. We note that our measurements are somewhat basic due to the challenges encountered in this measurement, namely addressing the challenge of self-rupture during

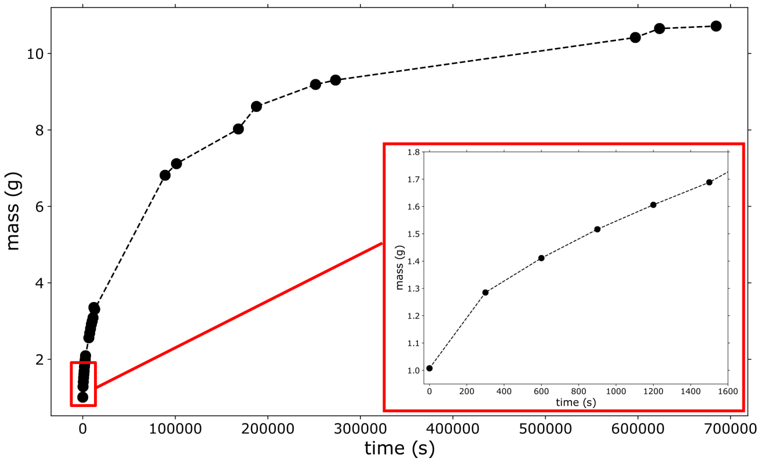

FIG. S3. Swelling of a 0.1:99.9 gel over time; inset shows an enlargement of the mass change at the earliest times.

the swelling process. However, this data clearly shows that density is reduced at a timescale which is relevant to the rupture process.

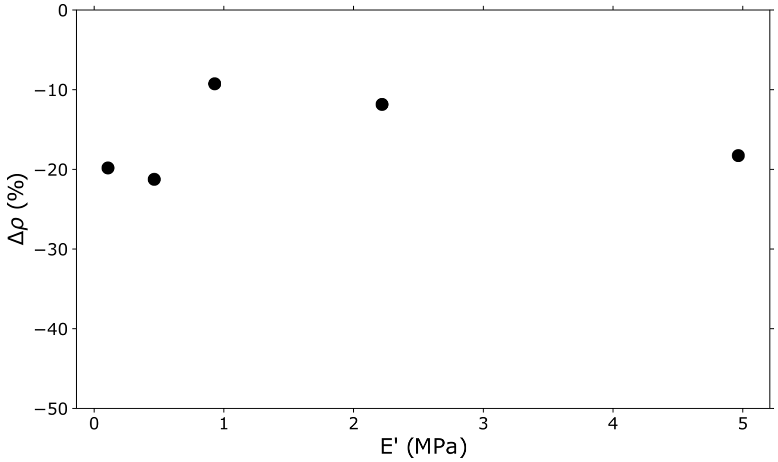

FIG. S4. Change in density after 600 seconds of swelling; a 10-20% reduction in density was observed.

Understanding the stresses that develop during liquid imbibement is complex problem requiring for example the understanding of fluid flux as well as the development of non-homogeneous material properties. Despite these challenges in interpreting the stress field, we believe that the the dominant component of the stress field is compressive. This is to be expected as the diffusion-limited process of fluid imbibement results in material with a ‘skin’ with different properties than the core [1]. Furthermore, before sample rupture occurred,

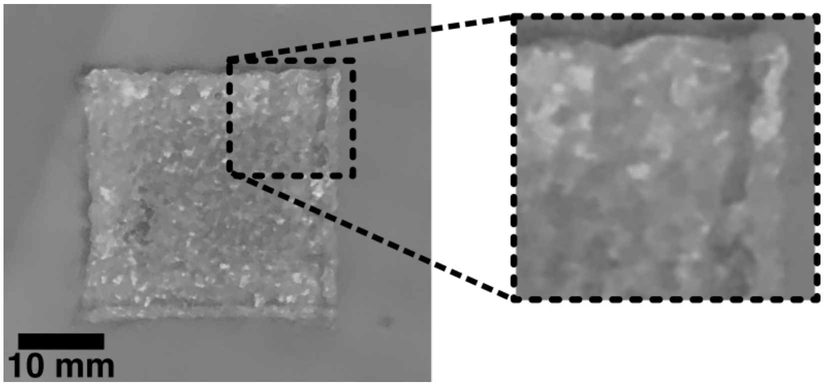

FIG. S5. Wrinkling on the surface of a swollen gel; inset shows an enlargement of the wrinkling pattern.

wrinkles were observed on the gel surface, as shown in Figure S5. Wrinkling of soft-materials is well-studied problem, and is known to result from compressive stresses [2].

III. DYNAMIC FRACTURE

A. Estimate of Griffith length

While a precise measurement of the Griffith length would require extensive experiments beyond the scope of this study, we can provide the reader with an order of magnitude estimate. As indicated in the main text, the Griffith length, l_c, is given by

$$l_c \sim \gamma Y/\sigma^2, \tag{1}$$

where σ is the applied boundary stress, Y is appropriate elastic modulus, and γ is the energetic cost of creating new surfaces. We have directly measured the elongational storage modulus, E', but the other quantities must be taken from literature. The energetic cost of creating new surfaces, often referred to as the fracture energy, has been measured for a wide range of polymeric materials, and is generally found to be of order 1 J/m^2 [3, 4]. The boundary stresses are challenging to estimate, as they depend on nature of imbibement as well as the network architecture. The most relevant literature result is the work of Curatolo et al., a detailed computational study of wrinkling in a hydrogel sphere. This work found that the stress were highly non-uniform throughout the gel, but at the boundary the compressive stress was calculated to be comparable to the hydrogel's elastic modulus [1]. Using these values, we find that $l_c \sim 0.1$ micron; this is comparable to results in materials where brittle fracture is observed.

B. Crack bifurcation

During fracture, bifurcation was observed, and the frequency of bifurcation was found to be correlated with gel modulus, see Figure S6. Bifurcation was observed in all of the 5:95 gel samples, in 60% of the 10:90 gel samples, and was not observed in any of the 20:80 gel samples.

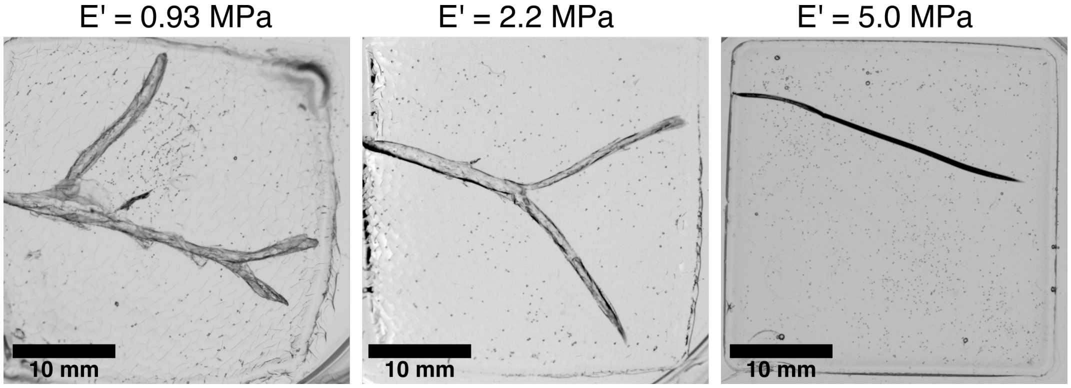

FIG. S6. Snapshots during fracture illustrating the degree of bifurcation at different gel moduli.

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