Supplementary Information for
Load transfer between permanent and dynamic networks due to stress gradients in nonlinear viscoelastic hydrogels

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S1. Supplementary Methods

Digital Image correlation (DIC) for PA tension tests. We use the Ncorr module in MATLAB [1] to analyze DIC data. In Ncorr, the reference image can be updated based on the correlation coefficient, so it can measure large deformation precisely. Details of the DIC procedure are given in our previous works [2,3]. Briefly, we used airbrush to create random speckle patterns on the surface of PA gel. Photographs of these samples were taken 5 times per second during tests. The photos for DIC measurements were acquired using a charged-coupled device (CCD) camera (FLIR Grasshop-per3 4.1 MP mono) with a telecentric lens (Edmund Optics, SilverTL 0.16x). Selected pictures were imported into MATLAB and the strain fields were calculated using Ncorr.

Large strain analysis is activated in Ncorr to update the reference image. The important input parameters are the subset radius, the radius of a circular subset used to correlate sub-images, is set to 20; the subset spacing, the spacing between neighboring subsets, is set to 2; and the strain radius, the size of the region over which displacement data are fitted to a plane to calculate the displacement gradient, is set to 5. The choice of these parameters is determined by the quality of speckle patterns and the strain distribution and may vary from test to test.

Uniaxial tension tests. We use uniaxial tension tests to determine the parameters for our PA models in Eqns. (S4a-c) and (S5a-c) below. These tests are conducted on rectangular PA gel specimens of dimension 30mm (length) x 10mm (width) x 2mm (thickness), as shown in Figure S1. Three cyclic tests and one relaxation test are carried out to determine the parameters for the p-PA and c-PA gels. For cyclic tests, we stretch the sample to a stretch ratio of 3 with stretch rate 1/s, 0.1/s and 0.01/s respectively and then unload them

to their original lengths (stretch ratio = 1) at the same rates. For the relaxation test, we stretch the sample to a stretch ratio of 3 with stretch rate 0.5/s and then hold for a half hour. All tests are done in deionized water to prevent the gels from drying.

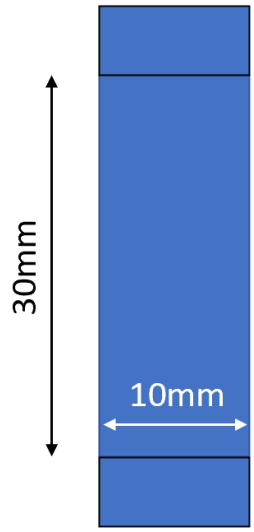

Fig. S1 Schematic of uniaxial tension specimen to determine material parameters for constitutive models

S2. Review of viscoelastic models for PA gels

In this section we summarize our model which describes the constitutive behavior of PA gels. Since this model has been studied in detail in our previous works [4,5], we list equations that are relevant to this work and focus on explaining the physics in the model. Readers who are interested in the connection of this model with statistical mechanics approach are encouraged to read our recent work [6].

c-PA gel model

Let us start with the c-PA gel and consider uniaxial tension. In our model, the 1st Piola or nominal stress *P(t)* is the sum of the stress acting on the permanent network and the stress supported by the dynamic network. The stress acting on the permanent network depends only on the *current* deformation gradient and is given by:

$$\omega_{\text{chem}} \times 2 \left. \frac{dW_0}{dI_1} \right|_{I_1(t)} \left(\lambda(t) - \lambda(t)^{-2} \right) \tag{S1}$$

where ω_{chem} is the molar fraction of chemical crosslinks per unit undeformed volume and W_0 is the strain energy density function for the chemical network. Since the gel is incompressible, we assume W_0 depends only on the invariant of the right Cauchy-Green tensor $I_1(t) = \text{trace}\left[\left(\mathbf{F}^{0\to t} \right)^T \left(\mathbf{F}^{0\to t} \right) \right]$, where $\mathbf{F}$ is the deformation gradient tensor. The superscript $0 \to t$ in the deformation gradient tensor $\mathbf{F}^{0\to t}$ indicates that it is measured from the reference configuration at $t = 0$ when the gel is undeformed. In uniaxial loading, $I_1(t) = \lambda^2(t) + \frac{2}{\lambda(t)}$, where λ is the stretch ratio in the tensile test. Hence eq. (S1) is a direct consequence of hyper-elasticity.

Unlike the chemical cross-links in the permanent network, crosslinks formed from physical bonds in the dynamic network can break and heal. We assume that before loading ($t<0$), the physical crosslinks have reached a state of dynamic equilibrium in which the healing rate is equal to the breaking rate; this steady state healing rate is denoted by χ^{ss}. However, once loading starts (at $t > 0$), the physical bonds can break and heal at different rates. In our model, it is assumed that when a physical bond breaks, it completely unloads and loses all its strain energy. Therefore a newly reformed crosslink at time τ has zero initial energy and the stress carried by it at current time $t>\tau$ depends on $H^{\tau\to t} \equiv \text{trace}\left[\left(\mathbf{F}^{\tau\to t}\right)^T \mathbf{F}^{\tau\to t}\right]$, where the superscript $\tau\to t$ in the deformation gradient tensor $\mathbf{F}^{\tau\to t}$ indicates that deformation is measured with respect to the configuration at τ. For uniaxial tension, $H^{\tau\to t} = \frac{\lambda(t)}{\lambda^2(\tau)} - \frac{\lambda(\tau)}{\lambda^2(t)}$. Note that $H^{t\to t}=0$, consistent with the fact that physical crosslinks carry no load at birth.

Next, we determine the stress carried by the dynamic network at current time *t*. Let $\chi(\tau)$ denote the healing rate at time τ, where $0\le\tau<t$. More precisely, the molar fraction of chains per unit reference volume that are born between τ, $\tau+d\tau$ is $\chi(\tau)d\tau$. Let $\phi_B(\tau,t,H^{\tau\to t})$ denote the survivability function which is the fraction of physical bonds *that survive from the time of their birth at time* τ *to the current time* t. This fraction is equal to 1 at $t=\tau$ and goes to zero for $t>>\tau$. The nominal stress carried by this subpopulation of the chains is

$$\left[\chi(\tau)d\tau\right]\times\phi\left(\tau,t,H^{\tau\to t}\right)\times 2\left.\frac{dW_0}{dI_1}\right|_{I_1=H^{\tau\to t}}\left[\frac{\lambda(t)}{\lambda^2(\tau)}-\frac{\lambda(\tau)}{\lambda^2(t)}\right] \tag{S2a}$$

The stress carried by the bonds that heal or reform for time $t > 0$ (after loading) is obtained by summing the contribution of the stress carried by all subpopulations. This is done by integrating over τ, i.e.,

$$\int_0^t \chi(\tau)\times\phi\left(\tau,t,H^{\tau\to t}\right)\times 2\frac{dW_0}{dI_1}\bigg|_{I_1=H^{\tau\to t}}\left[\frac{\lambda(t)}{\lambda^2(\tau)}-\frac{\lambda(\tau)}{\lambda^2(t)}\right]d\tau \tag{S2b}$$

To this eq. (S2b) we must add the stress carried by the physical bonds that are connected and survive to the current time t before loading, which is

$$2\rho\phi_B(\tau=0,t,H^{0\to t})\frac{dW_0}{dI_1}\bigg|_{I_1(t)}\left(\lambda(t)-\lambda(t)^{-2}\right), \tag{S3}$$

where ρ is the molar fraction of connected physical cross-links before the start of loading. The nominal stress is the sum of eq. (S1), eq. (S2b) and eq. (S3), i.e.,

$$\begin{aligned}P(t)=\omega_{\text{chem}}\times 2\frac{dW_0}{dI_1}\bigg|_{I_1(t)}\left(\lambda(t)-\lambda(t)^{-2}\right)+2\rho\frac{dW_0}{dI_1}\bigg|_{I_1(t)}\phi_B(\tau=0,t,H^{0\to t})\left(\lambda(t)-\lambda(t)^{-2}\right)\\ +\int_0^t\left[\chi(\tau)\phi_B\left(\tau,t,H^{\tau\to t}\right)2\frac{dW_0}{dI_1}\bigg|_{I_1=H^{\tau\to t}}\left[\frac{\lambda(t)}{\lambda^2(\tau)}-\frac{\lambda(\tau)}{\lambda^2(t)}\right]\right]d\tau,\end{aligned} \tag{S4a}$$

In previous works [4] we have proposed that the survivability function $\phi_B(\tau,t,H^{\tau\to t})$ has the form:

$$\phi_B(\tau,t,H^{\tau\to t})=\left[1+\frac{\alpha_B-1}{t_B}\int_\tau^t f\left(H^{\tau\to s}\right)ds\right]^{\frac{1}{1-\alpha_B}}. \tag{S4b}$$

In eq. (S4b), t_B is the characteristic breaking time of physical bonds, $\alpha_B\in(1,\,2)$ is a material parameter that controls the rate of decay of the survivability function and f is a

function which measures the dependence of breaking rate on the stretch experienced by a physical cross-link from its formation at time τ to the current time $t > \tau$ [4]. It is given by

$$f\left(H^{\tau\to s}\right) = \exp\left\{\left(1+\frac{H^{\tau\to s}-3}{I_c-3}\right)^m - 1\right\} \tag{S4c}$$

where I_c is the first invariant of the right Cauchy-Green tensor calculated at the critical stretch λ_c in a tension test, after which the bond breaking kinetics accelerate, and m is a material parameter. Equation (S4c) expresses the fact that when chains stretch beyond their critical strain limit, their breaking rate increase significantly resulting in macroscopic softening of the gel. For a *linear viscoelastic* solid, *f* is the constant function *1* $\left(I_c \to \infty\right)$ so that the survivability function in eq. (S4b) is independent of strain history [7,8].

To complete the model, one needs to supply the healing rate $\chi\left(t\right)$ in eq. (S4a). In our previous works [4,5], we have shown that the healing rate depends on the deformation history and is obtained by solving the integral equation:

$$1-\omega_{\text{chem}} = \chi(t)t_H + \int_{-\infty}^{t} \phi_B(\tau,t,H^{\tau\to t})\chi(\tau)d\tau, \tag{S4d}$$

where t_H is the characteristic time for healing.

p-PA gel model

The model for p-PA gel is almost identical, except that there is no permanent network. This permanent network is replaced by a second dynamic network is added to account for the presence of two phases [5].

With this modification, eq. (S4a) becomes

$$P(t) = \left[\sum_{i=1}^{2} \chi_i^{ss} \frac{t_{Bi}}{2-\alpha_{Bi}} [\phi_{Bi}(\tau = 0, t, H^{0\to t})]^{2-\alpha_{Bi}}\right] \times 2 \left.\frac{dW_0}{dI_1}\right|_{I_1(t)} (\lambda(t) - \lambda(t)^{-2}) +$$

$$\sum_{i=1}^{2} \int_0^t \left[\chi_i(\tau)\phi_{Bi}(\tau, t, H^{\tau\to t}) \times 2 \left.\frac{dW_0}{dI_1}\right|_{H^{\tau\to t}} \left[\frac{\lambda(t)}{\lambda^2(\tau)} - \frac{\lambda(\tau)}{\lambda^2(t)}\right]\right] d\tau \qquad \text{(S5a)}$$

The summation indices $i = 1, 2$ specify the two phases, each has its material parameters, (χ_i^{ss}, t_{Bi}, α_{Bi} , etc.,) , healing rate χ_i and survivability function $\phi_{Bi}(\tau, t, H^{\tau\to t})$. The healing rate of each phase is determined by the integral equation:

$$\omega_i = \chi_i(t) t_{H_i} + \int_{-\infty}^{t} \phi_{B_i}(\tau, t) \chi_i(\tau) d\tau \qquad i=1,2 \qquad \text{(S5b)}$$

where $\omega_1, \omega_2 = 1 - \omega_1$ are the molar fraction of weak and strong bonds in the hard and soft phase respectively.

S3. Determination of model parameters

We used two methods to determine the parameters for the constitutive models for the p-PA and c-PA gels. In both methods, we first define a parameter space for the fitting. The parameter space for the p-PA model is

$C1 \in [0, 5]$ $C2 \in [0, 0.3]$ $C3 \in [0, 0.1]$ $\lambda_c \in [1.05, 1.3]$

$w_1 \in [0.3, 0.7]$ $\alpha_{B1} \in [1.3, 1.9]$ $t_{B1} \in [0, 0.02]$ $m_1 \in [0.3, 0.7]$ $t_{H1} \in [0, 1]$

$w_2 \in [0.3, 0,7]$ $\alpha_{B2} \in [1.3, 1.9]$ $t_{B2} \in [0, 0.2]$ $m_2 \in [0.3, 0.7]$ $t_{H2} \in [0, 1]$

The parameter space for c-PA model is

$C1 \in [0, 5]$ $C2 \in [0, 0.3]$ $C3 \in [0, 0.1]$ $\lambda_c \in [1.05, 3.00]$ $w_{chem} \in [0, 0.15]$

$\alpha_B \in [1.3, 1.9]$ $t_B \in [0, 0.2]$ $m \in [0.3, 0.7]$ $t_H \in [0, 1]$

where $C1, C2, C3$ define the Yeoh's strain energy W_0 in Eqn. (S4a) or (S5a), that is,

$$W_0(I_1) = C1(I_1 - 3) + C1C2(I_1 - 3)^2 + C1C3(I_1 - 3)^3 \qquad \text{(S6)}$$

Specifically, $\mu = 2C1$ is small strain shear modulus of the undamaged PA gel, C1 and C2 controls the strain stiffening characteristic of the network. The fitting results for different PA gels are shown in Table S1-S4.

Method I: **Large dataset computing**

We randomly pick 1 million sets of parameters from the parameter space and calculate the nominal stress using the constitutive model for each test 1 million times based on these 1 million sets of parameters. Using mean square error as criteria, we pick one set of parameters out of these 1 million sets of parameters which fit our experimental data best. The optimal parameters for p-PA and c-PA are shown in Table S1 and S2 respectively. From Figures S2 – S5 we find that the fitting results are good. However, this method takes us several hours to finish even with a powerful workstation.

***Method 2*: Machine learning**

To make the fitting process more scalable, we also developed a machine learning method to determine the parameters. Details of this method can be found in our previous paper [9]. Briefly, we randomly pick 3000 sets of parameters instead of 1 million from the parameter set and then use our model to compute the nominal stress history 3000 times for each test. Then we use machine learning to build metamodels for PA constitutive models based on these 3000 cases. After learning, we use the metamodels to predict the results of constitutive models on 1 million sets of parameters without really computing the constitutive models 1 million times. This method can be implemented in a laptop (CPU – Intel i7-9750H, 4 cores, GPU – Nvidia GTX 1650) in a half hour and the fitting results are just as good as those shown in Figures S2 and S5.

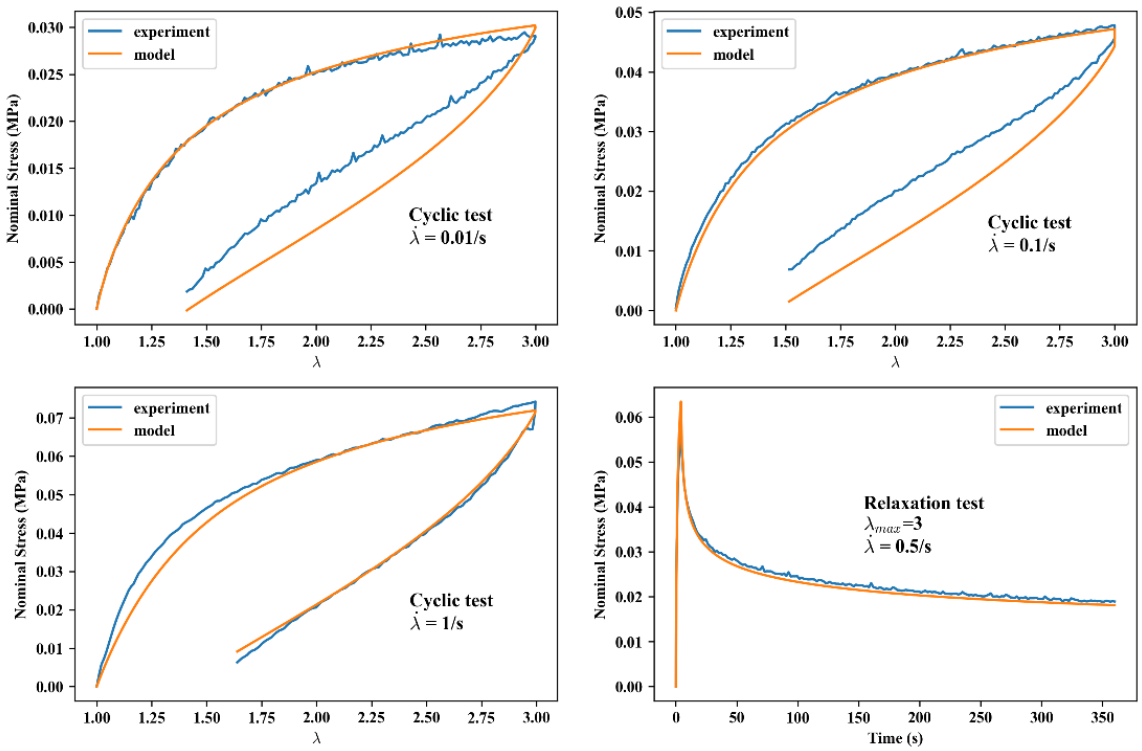

Fig. S2. Fitting results for *p-PA*$_{weak}$. In cyclic test the loading and unloading rates have the same magnitude. In relaxation tests, we first stretch the sample at a rate of 0.5s, then held the stretch ratio constant when it reaches 3.

Table S1. Fitting parameters for *p-PA*$_{weak}$

$C_1 = 0.1000MPa$	$C_2 = 0.0500$	$C_3 = 0.0000$	$\lambda_c = 1.2600$	
$\omega_1 = 0.5729$	$\alpha_{B1} = 1.7448$	$t_{B1} = 0.0058$	$m1 = 0.3635$	$t_{H1} = 0.5301$
$\omega_2 = 0.4271$	$\alpha_{B2} = 1.8404$	$t_{B2} = 0.1529$	$m2 = 0.5277$	$t_{H2} = 0.7351$

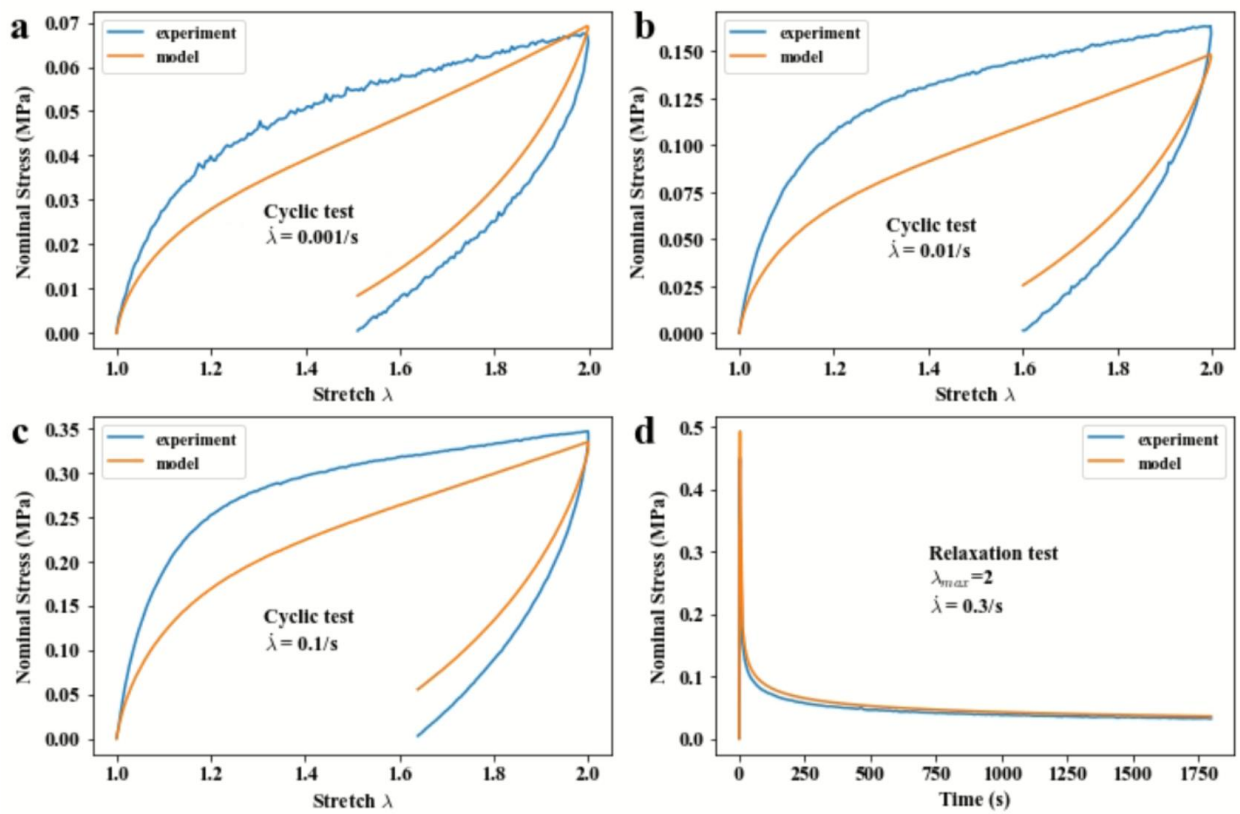

Fig. S3. Fitting results for *p-PA*$_{strong}$. In cyclic test the loading and unloading rates have the same magnitude. In relaxation tests, we first stretch the sample at a rate of 0.3s, then held the stretch ratio constant when it reaches 2.

Table S2. Fitting parameters for *p-PA*$_{strong}$

$C_1 = 3.990MPa$	$C_2 = 0.506000$	$C_3 = 0.0352$	$\lambda_c = 1.1560$	
$\omega_1 = 0.7500$	$\alpha_{B1} = 1.7957$	$t_{B1} = 0.0051$	$m1 = 0.4375$	$t_{H1} = 0.4289$
$\omega_2 = 0.2500$	$\alpha_{B2} = 1.6938$	$t_{B2} = 0.0183$	$m2 = 0.4831$	$t_{H2} = 0.0940$

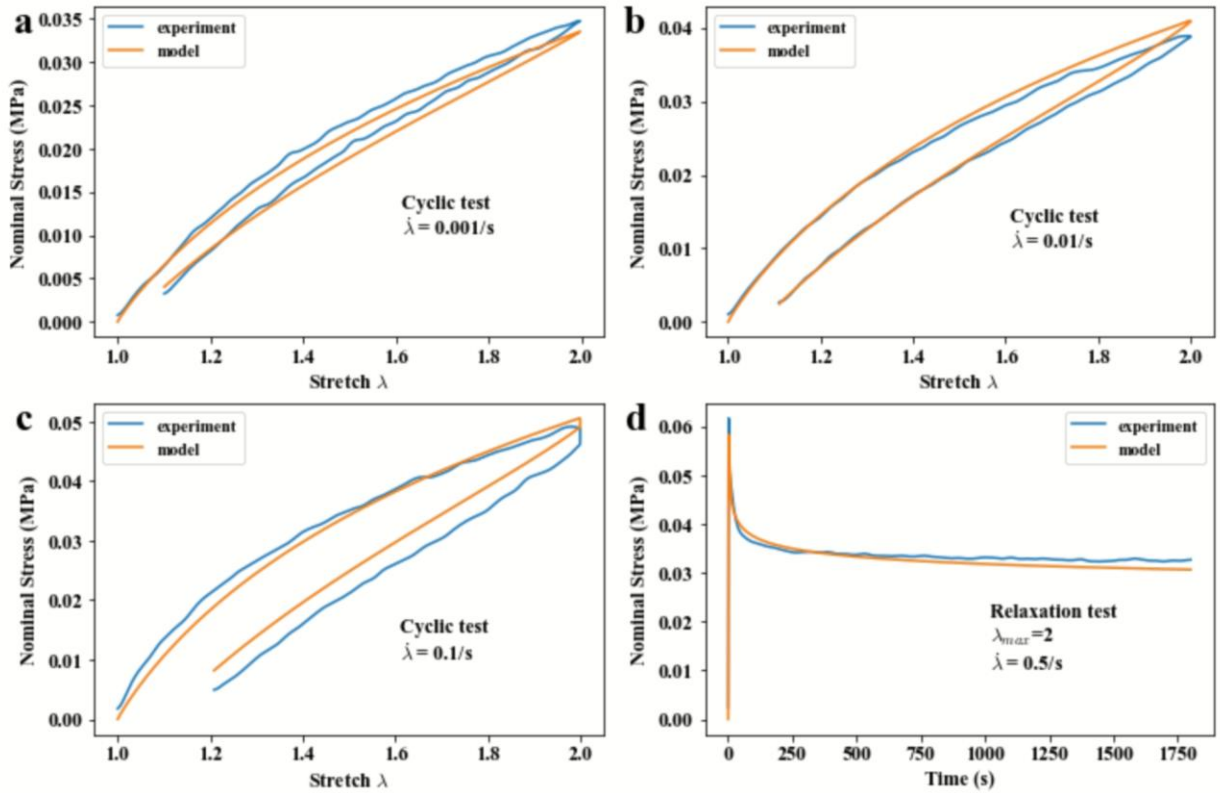

Fig. S4. Fitting results for *c-PA*$_{weak}$. In cyclic test the loading and unloading rates have the same magnitude. In relaxation tests, we first stretch the sample at a rate of 0.5s, then held the stretch ratio constant when it reaches 2.

Table S3. Fitting parameters for *c-PA*$_{weak}$

$C_1 = 0.05682MPa$	$C_2 = 0.0011$	$C_3 = 0.0000$	$\lambda_c = 2.565$	
$\omega_{chem} = 0.0898$	$\alpha_B = 1.8717$	$t_B = 0.0612$	$m = 1.8017$	$t_H = 0.8021$

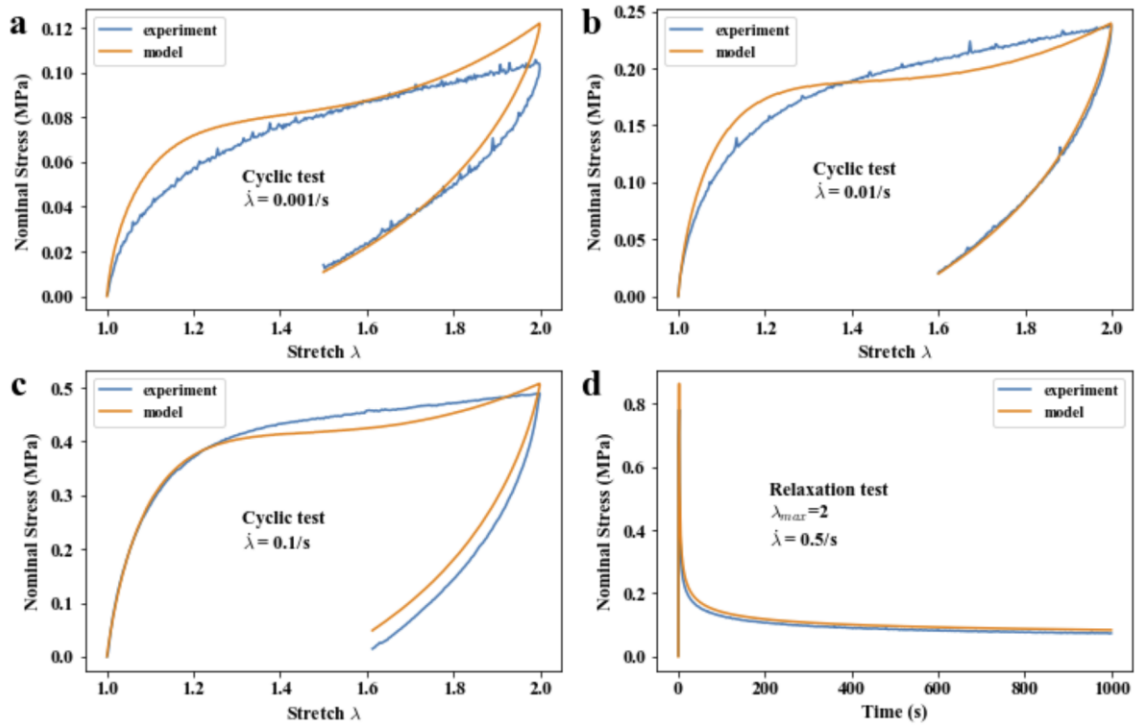

Fig. S5. Fitting results for *c-PA*$_{strong}$. In cyclic test the loading and unloading rates have the same magnitude. In relaxation tests, we first stretch the sample at a rate of 0.5s, then held the stretch ratio constant when it reaches 2.

Table S4. Fitting parameters for *c-PA*$_{strong}$

$C_1 = 2.3416MPa$	$C_2 = 0.1147$	$C_3 = 0.0535$	$\lambda_c = 1.0550$	
$\omega_{chem} = 0.0026$	$\alpha_B = 1.7190$	$t_B = 0.0718$	$m = 0.3079$	$t_H = 0.312$

S4. Model simulation of T-shape specimen test

To simulate the relaxation process, we use eqn. (S4a-d) and eqn. (S5a-b). In our relaxation experiments, the stretch history λ_N at the grip is known, i.e.,

$$\lambda_N(t) = \begin{cases} 1 + 0.1 \times t & 5s > t > 0 \\ 1.5 & t \geq 5s \end{cases} \tag{S7}$$

We assume that the 1st Piola or nominal stress and stretch in each section are uniform and denote them by $P_{ns}, P_{ws}, \lambda_{ns}, \lambda_{ws}$ respectively. Our assumption implies that

$$\lambda_N = \frac{\lambda_{ns} + \lambda_{ws}}{2} \tag{S8}$$

Force balance implies that

$$P_{ns} A_{ns} = P_{ws} A_{ws} = F \tag{S9}$$

where A_{ns}, A_{ws} denote the cross-section area of the specimen in the undeformed state and F is the force acting on the specimen. Equations (S4a-d), (S6-8) allow us to numerically determine the time evolution of stretch ratios $\lambda_{ns}, \lambda_{ws}$ for the c-PA gel. The same procedure, with eq. (S4a-d) replaced by eq. (S5a-b), determines $\lambda_{ns}, \lambda_{ws}$ for the p-PA gel. The numerical algorithm to determine the stress history is based on the fact that the force acting on the two sections is the same. In each timestep, we first guess the length of two sections with the constraint that the sum of their length is equal to the overall length which at each time step is a constant. Then we use our constitutive model e.g., (S4a-d) to calculate the nominal stress on each section at this timestep. The force acting on each section is obtained using these nominal stresses. If the difference between these forces are less than 1Pa, we adopt these lengths and go to next timestep. If not, we re-estimate the length of two parts

according to the difference between the force of two parts. The flow chart of our numerical scheme is shown in Figure S6.

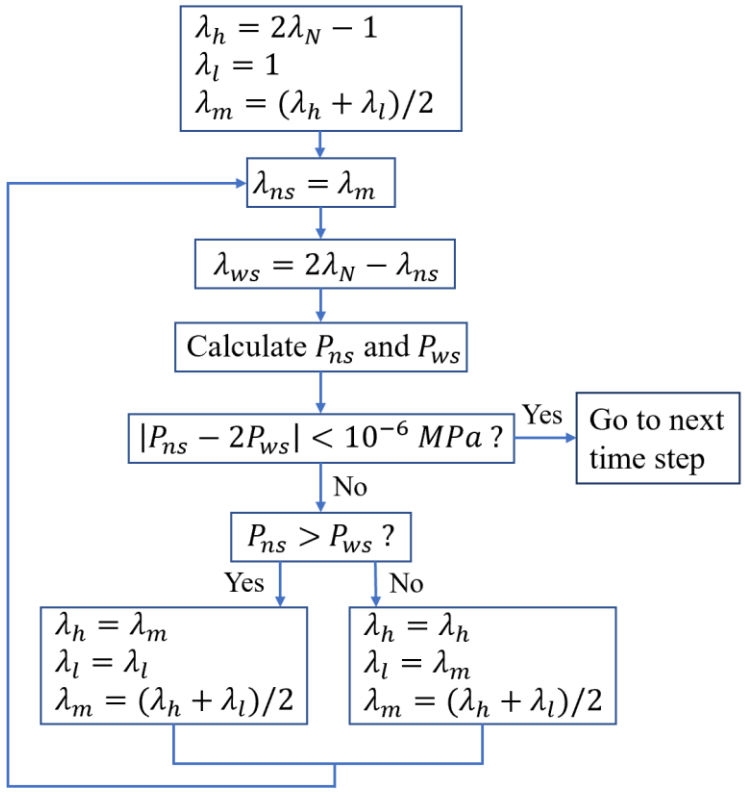

Fig. S6. Flow chart for calculating stretches of T-shape sample in each time step. The subscripts ns and ws denote narrow and wide section respectively. λ_N is the nominal stretch imposed on the specimen. $\lambda_h, \lambda_l, \lambda_m$ are intermediate variables in this algorithm to store relevant stretches.

S5. Relaxation test for T-shape sample in oil

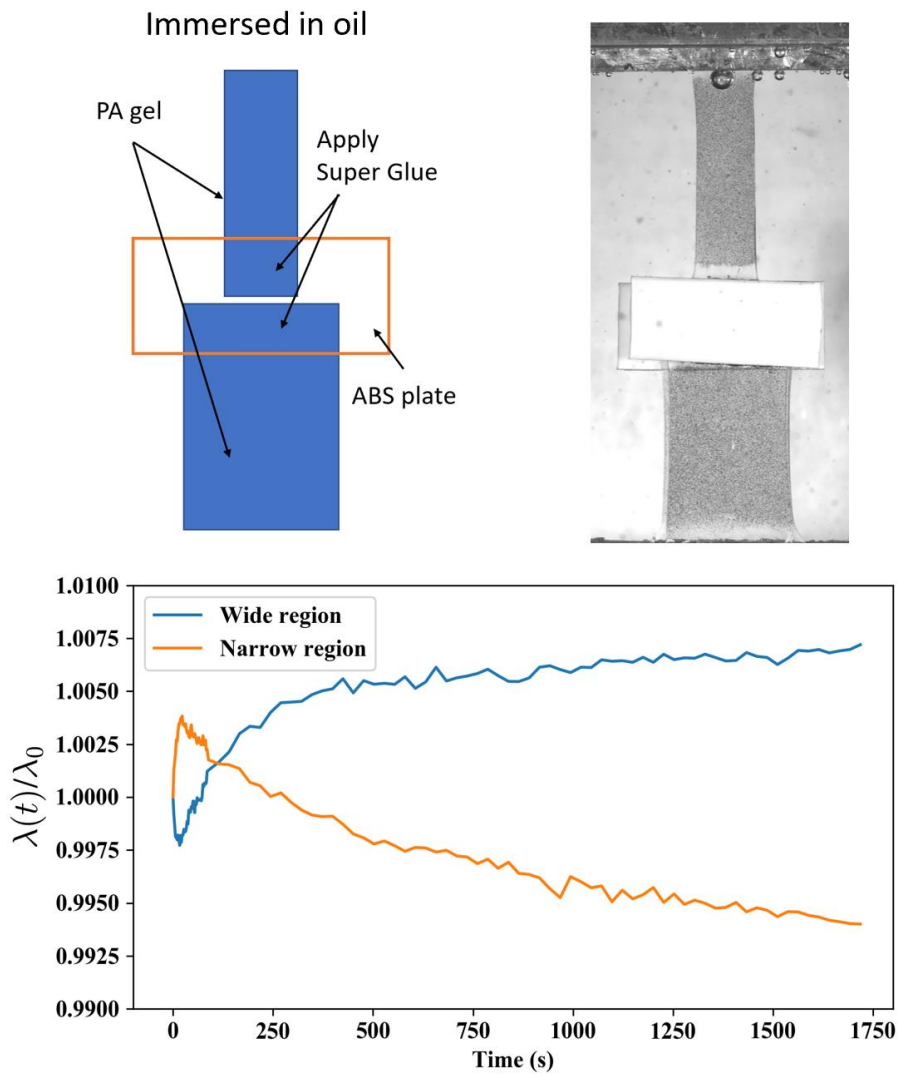

Fig. S6. T-shape test for *c-PA*$_{strong}$ immersed in mineral oil.

The sample is made of two separated parts so there is no water flow within this sample. The sample is stretched to λ_N = L/L$_0$ =1.3 with a fast stretch rate of 0.1/s and then hold it at the deformed length $L = 1.3L_0$ for half an hour. The curves show the time evolution of stretch at narrow and wide sections, which have the same trend as the curve of T-shape test in water.

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