Supporting Information

Anisotropic Double Network Hydrogels via Controlled Orientation of a Physical Sacrificial Network

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KEYWORDS: Hydrogels, Semi-rigid polymers, Composite materials, Double network gels, Anisotropic structures, Anisotropic mechanical properties

Appendix A) Calculation of $L_{contour}/L_{mesh}$

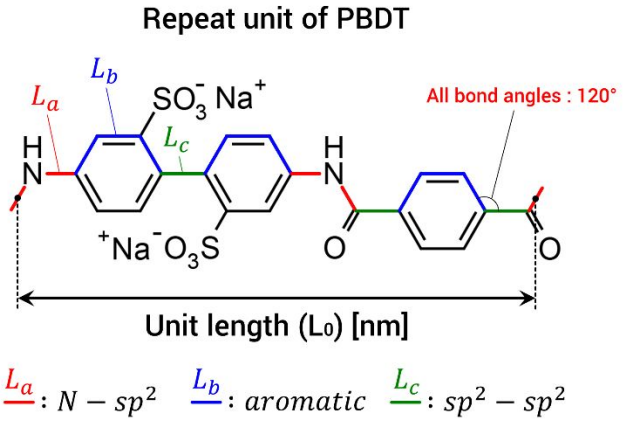

Figure S1. Schematic illustration of the unit length of PBDT.

To estimate contour length of PBDT ($L_{contour}$), we used the following equation,

$$L_{contour} = \left(\frac{M_w}{M_u}\right) \times L_0$$

where M_w, M_u, and L_0 are the molecular weight of PBDT, repeat unit weight of PBDT and unit length of PBDT, respectively. From the GPC experiment and simple arithmetic, M_w and M_u are determined to be ~142,000 and ~518. Assuming that all bond angles are 120° as shown in **Figure S1**, the unit length (L_0) can be obtained as follows;

$$L_0 = \{L_a \times 2 + L_a \times \cos 60° \times 2\} + \{L_b \times 3 + L_b \times \cos 60° \times 6\} + \{L_c \times 3\}$$

$$L_0 = 3L_a + 6L_b + 3L_c$$

where L_a, L_b, and L_c are the bond length of N-sp^2 C, aromatic C and sp^2-sp^2 C, respectively. By taking the value from the reference[1,2]: L_a = 0.133 nm, L_b = 0.140 nm, and L_c = 0.147 nm, the unit length (L_0) is calculated as 1.68 nm. Finally, we obtained L_c as follows.

$$L_{contour} = \frac{142{,}000}{518} \times 1.68 = 460.5\ nm$$

To estimate the mesh size of the PAAm network (L_{mesh}), we use the following equation derived from the affine model:[3]

$$L_{mesh} \approx \left(\frac{3k_bT}{E}\right)^{1/3}$$

Where k_b is Boltzmann Constant, T is temperature (25°C), and E is Young's modulus. Utilizing E=17 kPa from our previous paper[4] results in L_{mesh} = ~9 nm.

Finally, $L_{contour}/L_{mesh} \approx 51$, meaning that the chains of PBDT extend through many units of the PAAm network, effectively locking it in place. This result demonstrates why when stretching force is applied to the PBDT/PAAm gel the PBDT chains align and cannot relax.

References

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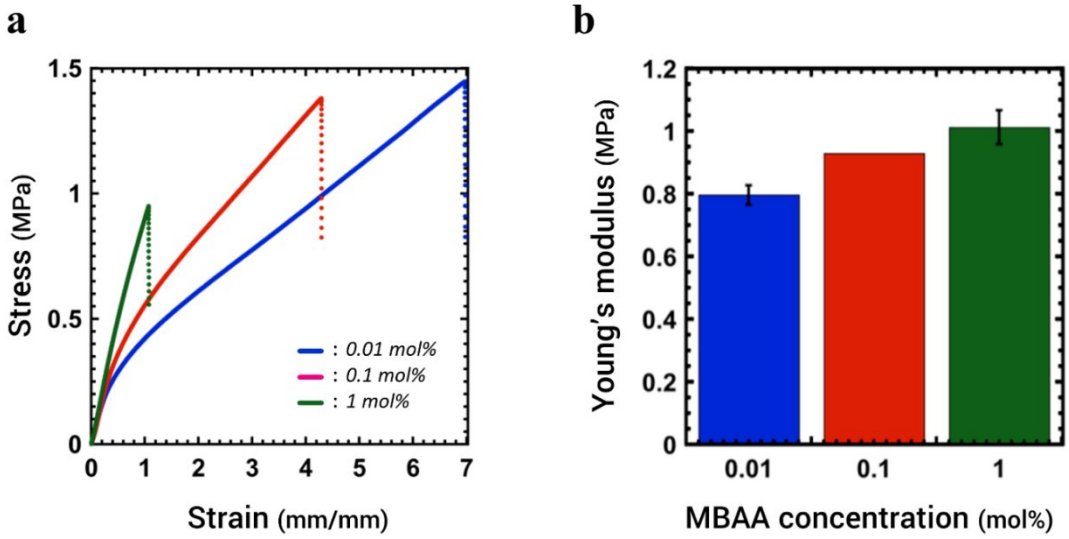

Figure S2. Effect of crosslinking density of the PAAm network on the mechanical properties of the PBDT/PAAm gels crosslinked in 0.15 M $ZrCl_2O$ solution. a) Typical stress-strain curves from uniaxial tensile testing. The blue, green and red line represent the MBAA concentration for 0.01, 0.1 and 1 mol%, respectively. b) Young's modulus of the samples estimated from the initial slopes of the stress-strain curves. The error bars are standard deviation from the results of 3-5 samples. For the 0.1 mol% sample, the error was so small that error bars are not visible.

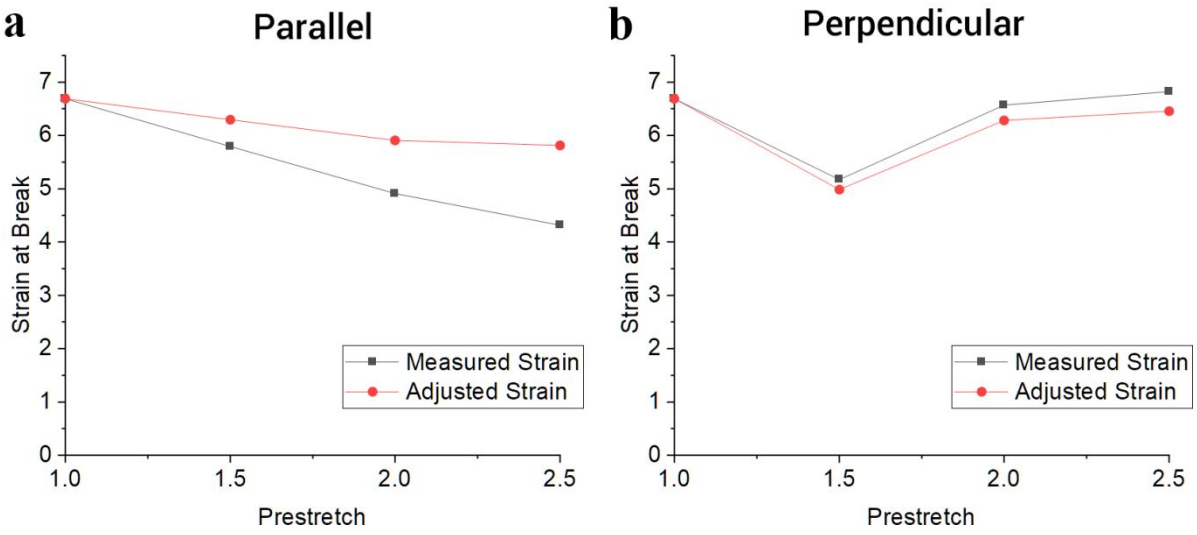

Figure S3. Comparison of measured strain and adjusted strain, accounting for pre-stretching. a) Strain at break in the parallel direction to pre-stretching. Pre-stretching reduces the measured strain at break. b) Strain at break in the perpendicular direction to pre-stretching. Poisson's effects cause the measured strain to be slightly greater than the true strain.