Supporting Information

# Physically Associated Synthetic Hydrogels with Long-Term Covalent Stabilization for Cell Culture and Stem Cell Transplantation

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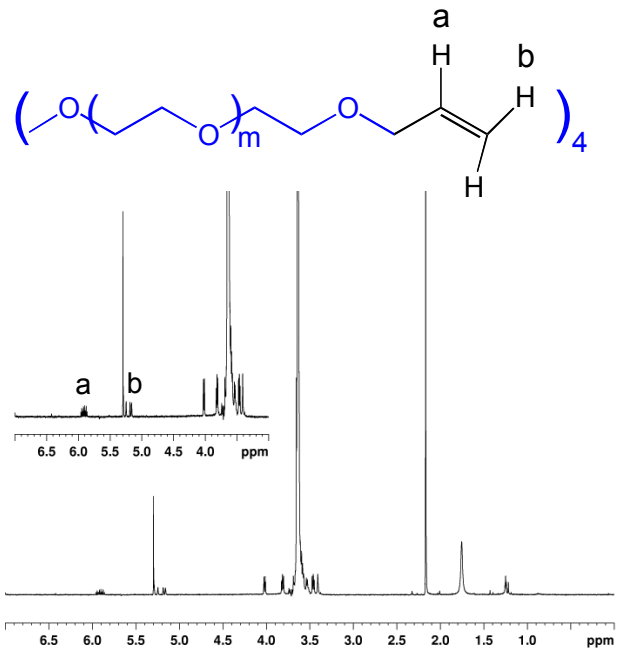



**Figure S1.** $^{1}$H NMR spectra of PEG-allyl ether using $CDCl_3$ as solvent. δ=3.39-3.89 (broad, PEG chain protons), 5.85-5.98 (m, 1H, -$CH_2OCH_2C\mathbf{H}$=$CH_2$), 5.15-5.30 (m, 2H, -$CH_2OCH_2CH$=C$\mathbf{H}_2$).

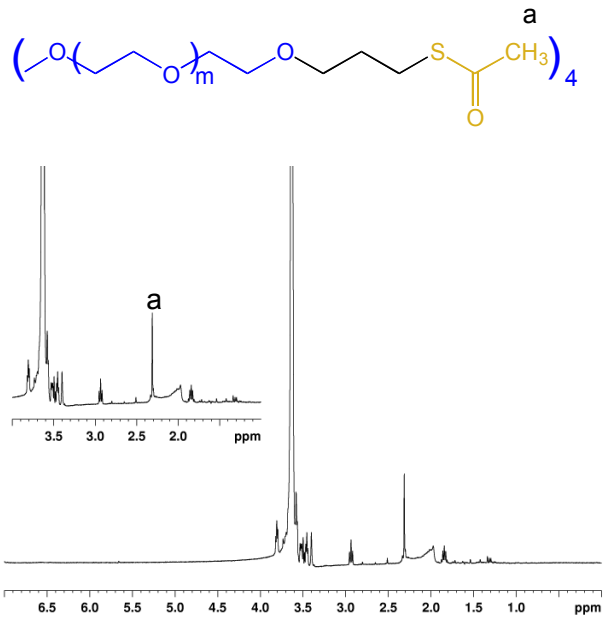



**Figure S2.** $^{1}$H NMR spectra of PEG-thioacetate using $CDCl_3$ as solvent. δ=1.81-1.9 (q, 2H, -$OCH_2C\mathbf{H}_2CH_2S$-), 2.35 (s, 3H, -$SCOC\mathbf{H}_3$), 2.92-2.97 (t, 2H, -

$OCH_2CH_2C\mathbf{H}_2S$-), 3.39-3.89 (broad, PEG chain protons).

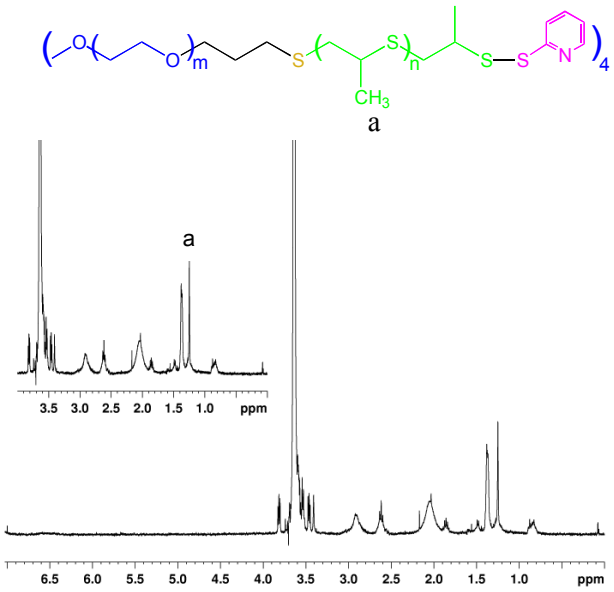
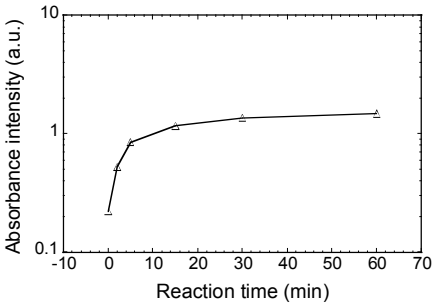
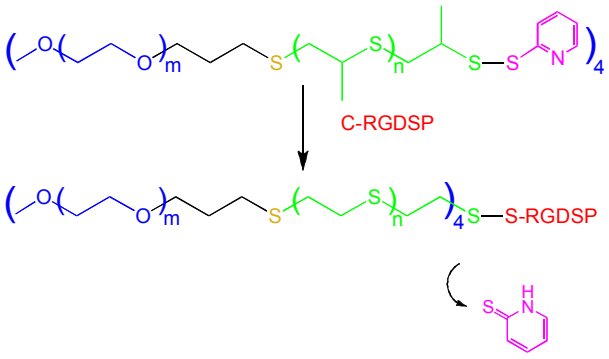



**Figure S3.** $^1$H NMR spectra of PEG-PPS (i.e. $(PEG_{113}\text{-}PPS_5)_4$) using $CDCl_3$ as solvent. δ=1.35-1.45 (d, CH3 in PPS chain), 1.81-1.9 (broad q, 2H, $-OC\mathbf{H}_2CH_2CH_2S$), 3.6-3.7 (broad PEG chain protons).

Note: Depending on the moles of polypropylene sulfide monomer used, PEG arms were modified with 5 or 8 PPS (i.e. $(PEG_{113}\text{-}PPS_5)_4$ or $(PEG_{113}\text{-}PPS_8)_4$, respectively). However, since the solubility of $(PEG_{113}\text{-}PPS_8)_4$ was extremely low and could not be used to consistently form homogeneous bulk hydrogels.




$$\frac{\Delta A_{342nm} \times \text{Mw of Polymer}}{8080 \times \text{mg/mL of Polymer}} = 0.626$$

**Figure S4.** The degree of modification of RGD onto PEG-PPS was monitored by the release of 2-pyridine dithione (absorbance at 342nm), and calculated using the above formulation. The reaction reached a plateau after 1 hour and the coupling efficiency of RGD on four-arm PEG-PPS was ~15%.

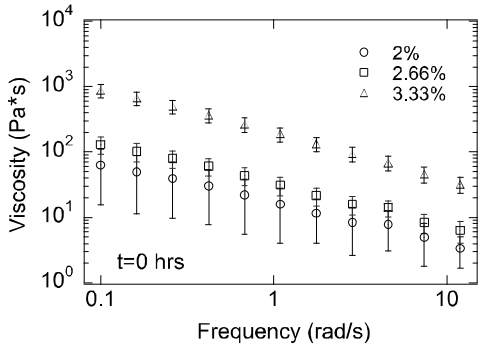



**Figure S5.** The viscosity of $(PEG_{113}\text{-}PPS_5)_4$ hydrogels was obtained as a function of shear rate using a strain-controlled Physica MCR Anton Paar rheometer. Although increasing copolymer concentration was found to increase the viscosity, viscosity decreased with increasing shear rate for all copolymer concentrations, indicating a shear-thinning fluid.

**Table S1.** Network structure parameter of PEG-PPS hydrogels with incubated in cDMEM in the presence of cells for various time.

| PEG-PPS | G (Pa) | $\upsilon_0$ (mol / $m^3$) | Mc ($10^4$ g / mol) |
|---|---|---|---|
| 2%-0h | 17.28 | 0.0069 | 289.85 |
| 2%-336h | 701.73 | 0.2833 | 7.06 |
| 2.66%-0h | 30.25 | 0.0122 | 218.03 |
| 2.66%-12h | 206.45 | 0.0833 | 31.93 |
| 2.66%-72h | 572.73 | 0.2312 | 11.50 |
| 2.66%-168h | 789.45 | 0.3187 | 8.34 |
| 2.66%-336h | 989.64 | 0.3995 | 6.65 |
| 3.33%-0h | 193.28 | 0.0780 | 42.69 |
| 3.33%-336h | 1492.70 | 0.6026 | 5.5260 |

**Equation 1**

$$Mc(g/mol) = \frac{\rho(g/m^3)}{\upsilon_0(mol/m^3)}$$

**Equation 2**

$$\upsilon_0(mol/m^3) = \frac{G(Pa)}{k(J/K) * NA(/mol) * T(K)}$$

$$\upsilon_0(mol/m^3) = \frac{G(Pa)}{1.38*10^{-23}(J/K) * 6.02*10^{23}(/mol) * 298.15(K)}$$

$$= \frac{G(N/m^2)}{1.38*10^{-23}(N*m/K) * 6.02*10^{23}(/mol) * 298.15(K)}$$

From dynamic shear rheology of data taken in the plateau temperature regime, an equilibrium modulus can be determined. Through the theory of rubber elasticity a average molecular weight between cross-linking points can be determined by using equation 1 and 2. Here, Mc is the average molecular weight between cross-linking points, $\rho$ is the polymer densities in the hydrogel, $\upsilon_0$ is the effective network chain density, G is the equilibrium modulus (in the calculation, we used average storage modulus G' as the equilibrium modulus), k is Boltzmann constant, $N_A$ is Avogadro's number.

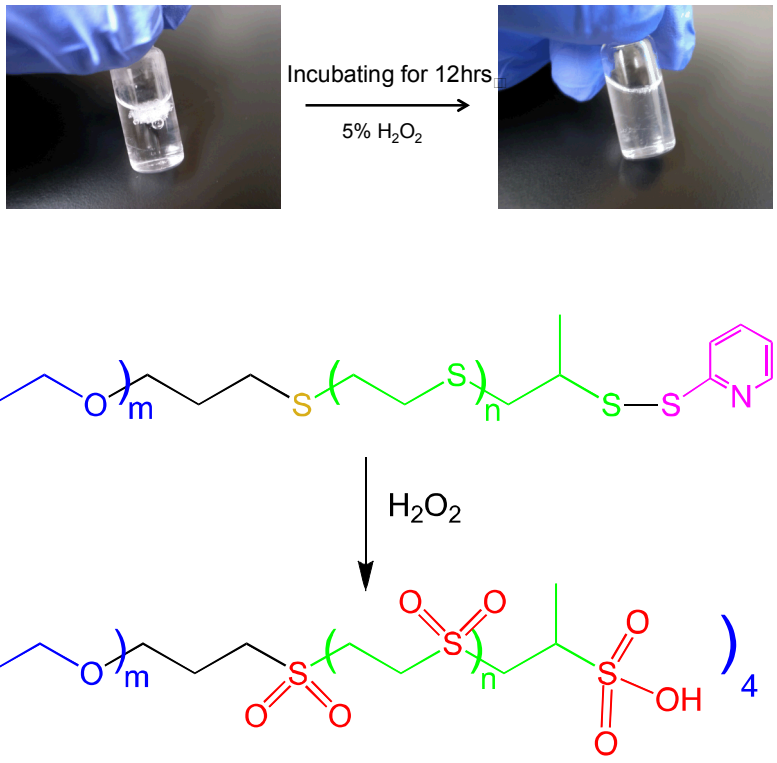



**Figure S6.** 2.66% $(PEG_{113}\text{-}PPS_5)_4$ hydrogels previously incubated in PBS for 336 hours were treated with hydrogen peroxide ($H_2O_2$). The hydrogels degraded completely in 12 hours. Oxidation resulted in hydrophilic sulfones which were not able to self assemble.