Supporting Information

for

Controlling mechanical properties of bio-inspired hydrogels by modulating nano-scale, inter-polymeric junctions

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Further experimental data
**1H NMR data of 6Arm-PEG-NH-catechol and 6Arm-PEG-catechol**

*Figure S1.* Purity confirmation of synthesized 6Arm-PEG-NH-catechol polymer analyzed by 1H NMR. Peaks at 9–10 ppm indicating aldehyde in starting material (up), were successfully disappeared after bound to PEGs (down).

**6Arm-PEG-NH-catechol 1H NMR (300 MHz, CDCl3, δ)**

7.19 (s, 1H, C₆H₂H(OH)₂−), 6.81-6.88 (m, 2H, C₆HH₂−(OH)₂−), 4.09-4.05 (m, 2H, -NH-CH₂-C₆H₃(OH)₂−), 3.95-3.59 (m, PEO), 3.40-3.36 (t, 2H, PEO-CH₂-NH-)

**3,4-dihydroxybenzaldehyde (DHBA, 300 MHz, DMSO-d₆, δ)**

9.56 (s, 1H, CHO), 7.26-7.22 (dd, 1H, C₆H₂H(OH)₂−CHO), 7.18 (d, 1H, C₆H₂H(OH)₂−CHO), 6.87-6.84 (d, 1H, C₆H₂H(OH)₂−CHO)
Figure S2. Purity confirmation of synthesized 6Arm-PEG-catechol polymer analyzed by $^1$H NMR. Peaks at 2–3 ppm, -CH$_2$-CH$_2$- in starting material (up), were successfully shifted with 0.2 ppm after bound to PEGs (down).

6Arm-PEG-catechol $^1$H NMR (300 MHz, CDCl$_3$, δ)
6.71-6.69 (m, 2H, C$_6$HH$_2$(OH)$_2^-$), 6.52-6.49 (dd, 1H, C$_6$H$_2$(OH)$_2^-$), 3.79-3.33 (m, PEO), 2.81-2.76 (t, 2H, C6H3(OH)2-CH2-), 2.49-2.44 (t, 2H, CH2-C(O)NH-)

3,4-dihydroxyhydrocinnamic acid (DHCA, 300 MHz, DMSO-$d_6$, δ)
6.59-6.56 (d, 1H, C$_6$H2H(OH)$_2^-$), 6.55-6.54 (d, 1H, C$_6$H$_2$(OH)$_2^-$), 6.42-6.39 (dd, 1H, C$_6$H$_2$(OH)$_2^-$), 2.62-2.57 (t, 2H, C$_6$H$_3$(OH)$_2$-CH2-), 2.41-2.36 (t, 2H, -CH$_2$-COOH)
GPC data of mPEG-NH-catechol and mPEG-catechol

Figure S3. GPC data of synthesized mPEG-NH-catechol. There were no peaks after 18 min, elution time of synthesized mPEG-NH-catechol product.

Figure S4. GPC data of synthesized mPEG-catechol. There were no peaks after 18 min, elution time of synthesized mPEG-catechol product.
** Calibration curve of our GPC system  

**Figure S5.** Calibration curve of GPC system. Each point means 130 kDa, 30 kDa, 20 kDa, and 5 kDa molecular weight Hyaluronic acid and PEGs. 30 min corresponds to the molecular weight under 100 Da. This means above GPC data of mPEG-NH-catechol and mPEG-catechol have no impurities, molecular weight under 5 kDa to 100 Da.
Quinone tanning reactions of catecholic linear PEG derivatives.

**Figure S6.** A schematic description of quinone tanning (i.e. crosslinking) of catecholic PEGs (Chemical structure: mPEG-NH-catechol (left) and mPEG-catechol (right)) Quinone tanned products of mPEG-NH-catechol and mPEG-catechol as a function of a stoichiometric ratio of NaIO₄ : catechol (0.25 : 1 – 2 : 1) was analyzed by gel permeation chromatography.