Supplementary Materials for "Solute Transport Dependence on 3D Geometry of Hydrogel Networks"

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Geometrically calculating in-plan mesh size, plane-normalized depth, and mesh radius for each junction functionality (4, 6, 8)

First, the ideal shape of a mesh portal had to be determined from the regular polyhedrons (tetrahedron, hexahedron, octahedron. For the tetrahedrons, the shape was based on a carbon ring chair conformation, which resulted in adjacent tetrahedrons facing each other with a 180° rotation around the normal of their shared plane. Hexahedrons and octahedrons could be tessellated without rotations and still form perfect repeating network structures (see Fig. 4).

Second, the ideal plane for each portal was taken by finding the plane that includes the midpoints of each chain in the portal. To simplify the structures for a solute passing through the portal at the ideal normal angle, mesh sizes were flattened into the plane by taking the cosine between the chain and the plane, and the sine was calculated to find the effective depth of the portal. For the tetrahedron, the face-edge-face angle is $arccos(1/3)$, which means the in-plane mesh size is $\xi * \sin\left(arccos\left(\frac{1}{3}\right)\right) = \frac{2\sqrt{2}}{3}\xi$ and the depth is $\xi * \cos\left(arccos\left(\frac{1}{3}\right)\right) = \frac{1}{3}\xi$. For the hexafunctional network, there was no angle, so the in-plane mesh size was equal to the mesh size and the depth is zero. For the octafunctional network it was a 45° angle, yielding an in-plane mesh size and depth of $\frac{\sqrt{2}}{2}\xi$.

The resulting 2D structures were a hexagon for tetrafunctional networks and two squares. The diameter of an inscribed circle on the hexagon was $\sqrt{3} * side\ length$, so it was multiplied by the in-plane mesh size and divided by two to find the mesh radius. For the two squares, the in-plan mesh size was simply divided by two to find the relevant mesh radius.

A priori calculation of mesh size and mesh radius for multi-arm PEG hydrogels

From the structural parameters of initial polymer volume fraction, degree of polymerization between junctions, junction functionality, and frequency of chain-end defects, mesh size and mesh radius can be calculated by using equilibrium swelling theory and a modified Canal-Peppas equation.[1]

Equilibrium Swelling Equation:

$$\varphi_s^{-\frac{1}{3}}[\ln(1-\varphi_s)+\varphi_s+\chi\varphi_s^2] = -1 * \left(1-\frac{2}{f}\right)(1-\gamma)\frac{V_1\rho_d}{M_r N_j}\varphi_0^{\frac{2}{3}} \#(1)$$

Modified Canal-Peppas Equation:

$$\xi = \varphi_s^{-\frac{1}{3}}\left[\left(1-\frac{2}{f}\right)\bar{l}^2 C_\infty \lambda N_j\right]^{\frac{1}{2}} \#(2)$$

Case-Specific Mesh Radius Calculation:

$$r_m = \begin{cases} \frac{\sqrt{6}}{3}\xi & f = 4 \\ \frac{1}{2}\xi & f = 6 \\ \frac{\sqrt{2}}{4}\xi & f = 8 \end{cases} \#(3)$$

In Eq. 1, V_1 is the molar volume of solvent, 18 mL/mol for water. Polymer specific parameters for PEG were used as previously described:[2]

Symbol	*Value*	*Unit*
χ	0.426	N/A
C_∞	4	N/A
$\bar{M}_r$	44	g/mol
ρ_p	1.18	g/mL
λ	3	N/A
$\bar{l}$	0.15	nm

In Eq. 1, relaxed polymer volume fraction (φ_r) was arbitrarily set to 0.10, based on previous experiments showing that relaxed polymer volume fraction is equivalent to the initial polymer volume fraction in covalently networked, synthetic polymer systems.[2] Frequency of chain-end defects was set to 0, and the degree of polymerization between junctions was set to 60. Junction functionalities were then set to 4, 6, or 8, and the equation was solved for the swollen polymer volume fraction (φ_s). The results of Eq. 1 were used to calculate the mesh size (ξ) in Eq. 2. Mesh radii were calculated from mesh size and junction functionality according to Eq. 3.

[1] N. R. Richbourg, N. A. Peppas, *Prog Polym Sci* **2020**, *105*, 101243.
[2] N. R. Richbourg, M. Wancura, A. E. Gilchrist, S. Toubbeh, B. A. C. Harley, E. Cosgriff-Hernandez, N. A. Peppas, *Science Advances* **2021**, *7*, eabe3245.