Supporting Text

Using the relationship between the frequency-independent elastic modulus and the effective crosslinking density (or network junction density) (as presented in Calveat *et al.*, ref. 1) based on Flory's theory of rubber elasticity, n_e, the effective crosslinking density is defined as:

$$n_e = \frac{G'}{\left(1-\frac{2}{f}\right)\left(\frac{f}{2}\right)RT},$$

where f is the number of strands linked to a crosslinker. For our calculations, the number is close to 3. (The core of the four-arm polyethylene glycol (PEG) has four strands attached, and the junction between an arm and polylysine has three arms. Therefore, there is one four-arm junction for every four three-armed junctions (between the polylysine and a PEG arm) assuming complete reactivity making f equal to 3.2, however it is very unlikely that all of the arms reacted. Assuming a 75% coupling rate, then f becomes 3.25.) Using f = 3.25 and T = 298 K, and G' = 2,870 Pa.

n_e = 1.85 mol/m^3.

The effective molecular mass between crosslinks is defined by the polymer concentration in kg/m^3 divided by n_e so that M_e = 540 g/mol.

Interestingly, the molecular mass of one PEG arm is supposed to be 2,500 g/mol. The difference in the calculations from the mechanical data and theoretical calculations is likely due to the limitations in the Flory equation, which assumes that the chains are freely jointed. Both the polylysine and PEG exist as α-helices and not as freely jointed chains. This steric hindrance is likely to lead to the difference.

1. Calvet, D., Wong, J. Y. & Giasson, S. (2004) *Macromolecules* **37,** 7762–7771.