Electronic Supplementary Material (ESI) for Polymer Chemistry.

Viscoelastic and Thermoreversible Networks Crosslinked by Non-covalent Interactions Between "Clickable" Nucleic Acids Oligomers and DNA

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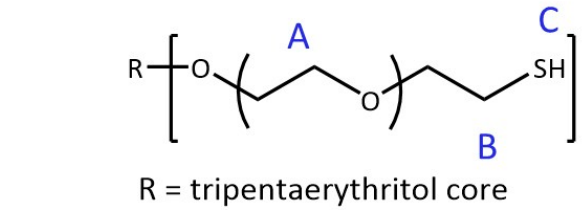
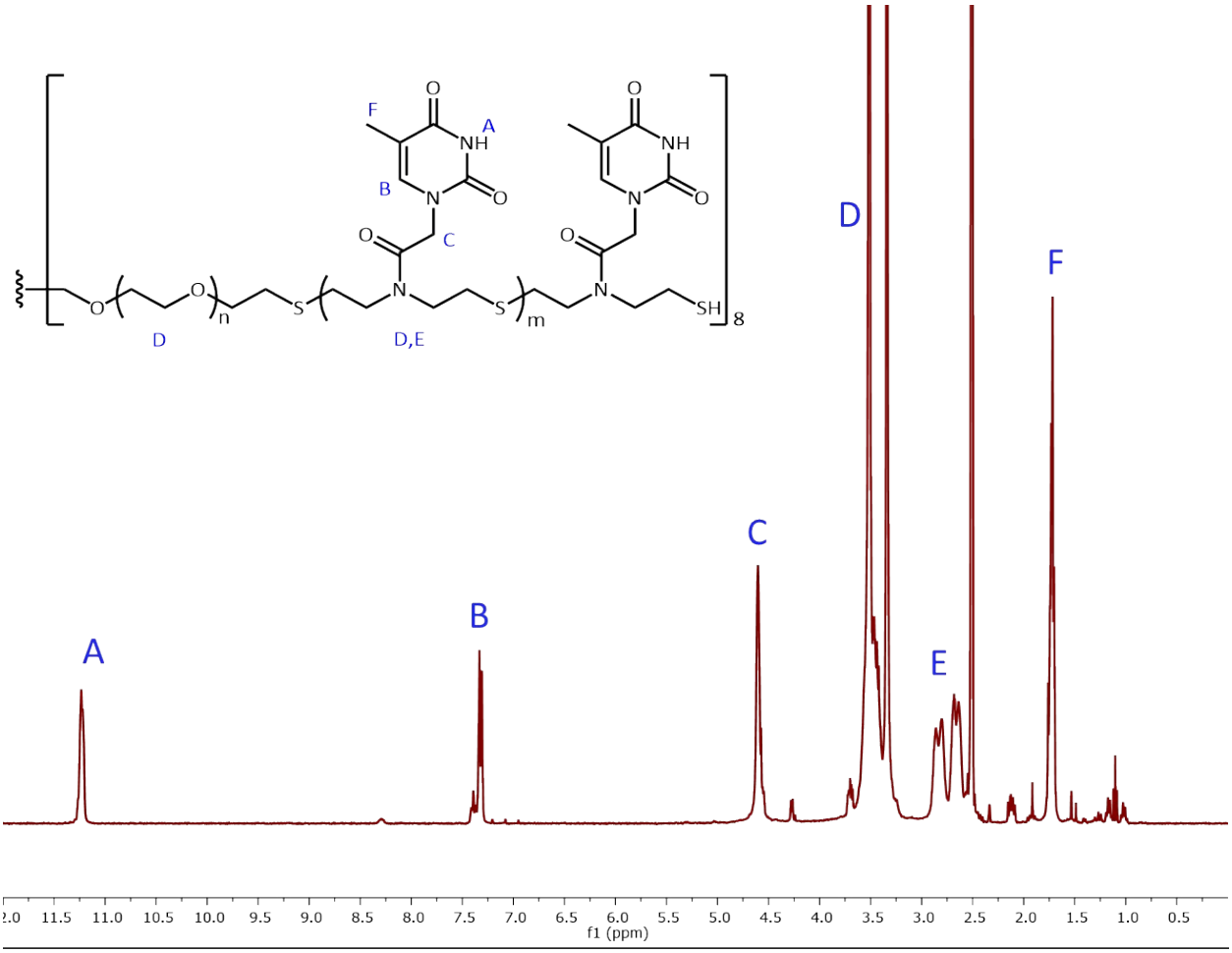
Supporting Information



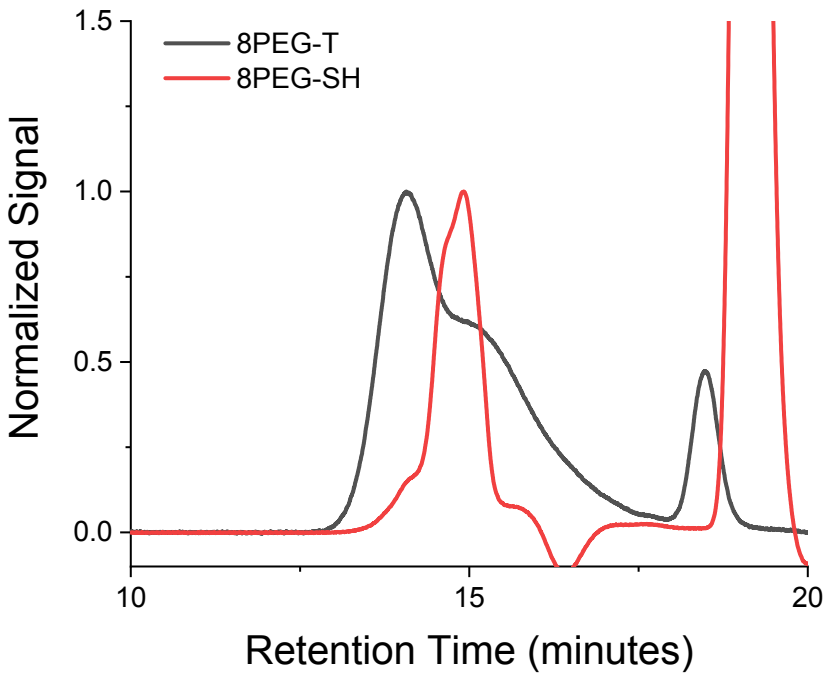
R = tripentaerythritol core

8PEG-SH: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.62 (m, 1816H), 2.62 (q, 16H), 2.29 (t, 8H)

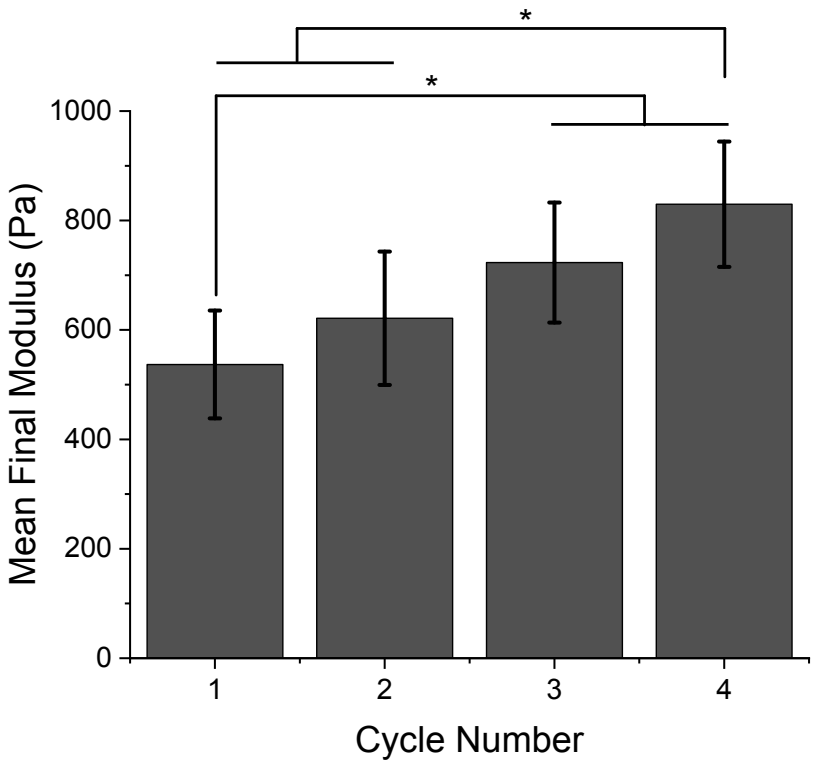


8PEG-T: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.22 (s, 12H), 7.35 (m, 12H), 4.61 (s, 24 H), 3.52 (m, 275H), 2.82 (m, 24H), 2.66 (m, 24H), 1.72 (m, 36 H)

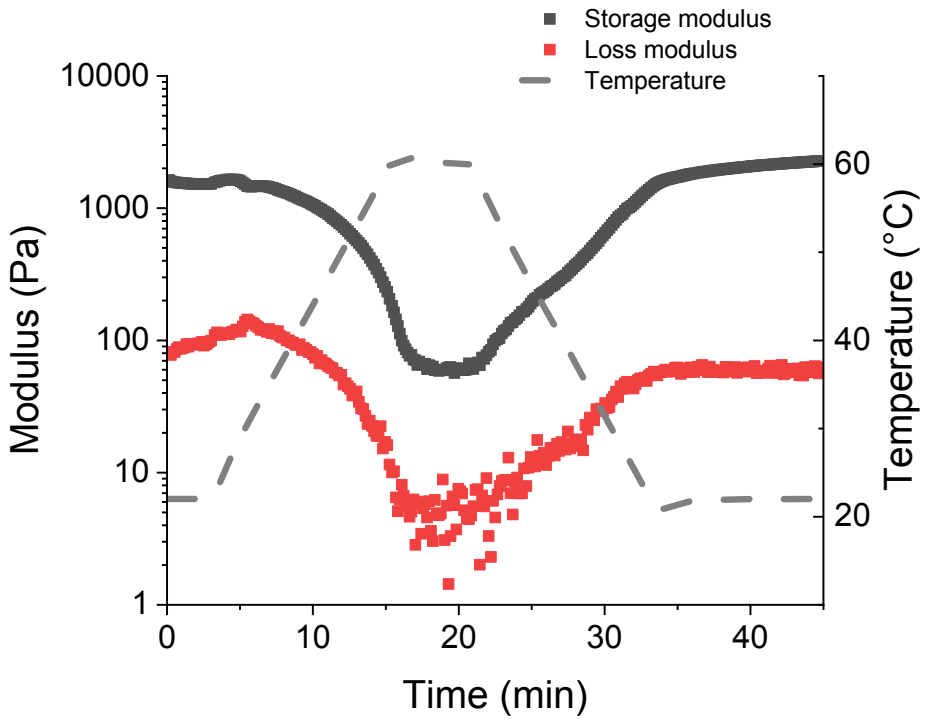
Supporting Figure S1. Representative characterization of fully synthesized 8PEG-T macromers compared to the 8PEG-SH precursor.



Supporting Figure S2. Gel permeation chromatography (GPC) of the unfunctionalized 8-arm poly(ethylene glycol) precursor (red) and the 8PEG-T conjugate (black) following copolymerization. The shift to lower retention times in the primary peak indicates an increase in molecular weight. The shoulder that appears in the 8PEG-T trace is most likely due to the polymer polydispersity, which is a side effect of the quasi-step growth polymerization mechanism, or incomplete separation of smaller molecular weight products. Estimated molecular weights were determined via ^{1}H NMR integration.



Supporting Figure S3. The mean final storage modulus of CNA/DNA gels after 3 heat/cool cycles shows a stiffening of the gel with each cycle number. Gels were made at 5% w/v 8PEG-T, 1:1 A:T ratio, and 20% H_2O in DMSO. One cycle refers to a temperature ramp to 70°C followed by a cooling to 22°C and equilibration for 20 minutes. Statistical significance is denoted by * ($p<0.05$).



Supporting Figure S4. Temperature sweep data from 22°C to 60°C showing that at 60°C, the gel does not melt, indicating melting temperatures are higher than 60°C.

KWW Function

The Kohrausch-Williams-Watts (KWW) function was used to fit stress relaxation data. This model is primarily a phenomenological fitting model, but describes the relaxation of real materials quite well. It modifies the traditional exponential decay function with a stretching factor, β, which gives an indication of the distribution of relaxation times that exist in the material.

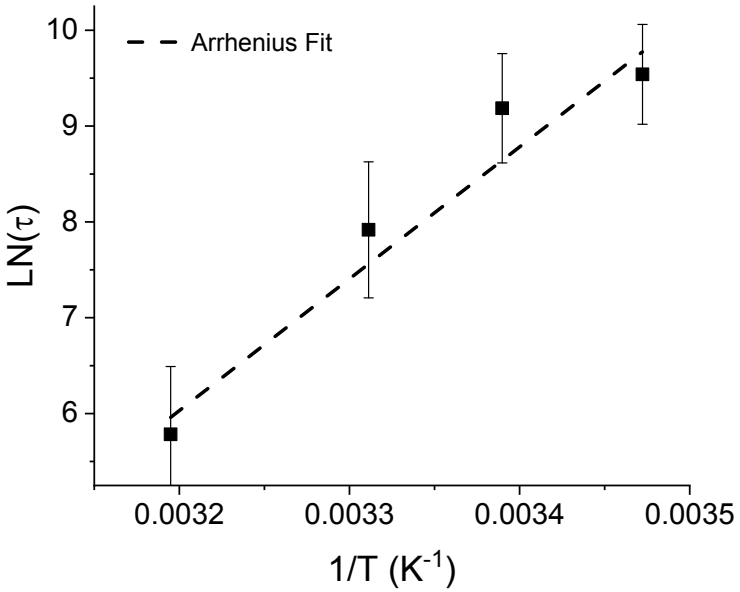
$$G(t) = G_0 \exp\left[\left(\frac{t}{\tau}\right)^{\beta}\right]$$

By plotting the normalized modulus, only two parameters need to be fit: τ, which is the characteristic relaxation constant, and β, which as described above is the stretching factor.

Reversible gel theory predicts that the characteristic time constant, τ, has an Arrhenius dependence on temperature. Thus, by obtaining τ as a variety of temperatures, one can extract out an estimate of the activation energy of the relaxation process and creating an Arrhenius plot from the data.

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad \rightarrow \quad \ln(\tau) = \frac{E_a}{RT} + ln(A)$$

The below graph shows the Arrhenius dependence of the relaxation time constant on temperature for gels crosslinked with A20 ssDNA. The activation energy for the relaxation in these gels, i.e. slope, was



determined to be 110 ± 20 kJ/mol.

Supporting Figure S5. Arrhenius plot of characteristic relaxation times. A linear fit gives an activation energy of 110 ± 20 kJ/mol.