Temperature-Responsive Supramolecular Hydrogels by Ternary Complex Formation with Subsequent Photo-Crosslinking to Alter Network Dynamics

Lei Zou, Bo Su, Christopher J. Addonizio, Irawan Pramudya, Matthew J. Webber*

University of Notre Dame, Department of Chemical & Biomolecular Engineering, Notre Dame, IN USA *- mwebber@nd.edu

Supporting Data and Characterization

- Figure S1- Detailed schematic of synthesis
- Figure S2- Temperature-dependent ¹H-NMR of F127-BM:CB[8] prior to UV
- Figure S3- Variable temperature rheology of F127-BM without CB[8]
- Figure S4- Strain sweep data of F127-BM:CB[8] hydrogels prior to UV
- Figure S5- Aqueous size-exclusion chromatography before and after UV
- Figure S6- UV/Vis spectroscopic quantification for reduced equivalents of CB[8]
- Figure S7- Temperature-dependent ¹H-NMR of F127-BM:CB[8] following UV
- Figure S8- Comparative rheology data before and after UV treatment
- Figure S9- Strain sweep data of F127-BM:CB[8] hydrogels following UV

Figure S1: Detailed scheme of the reaction to append BM guests on F127 macromers.

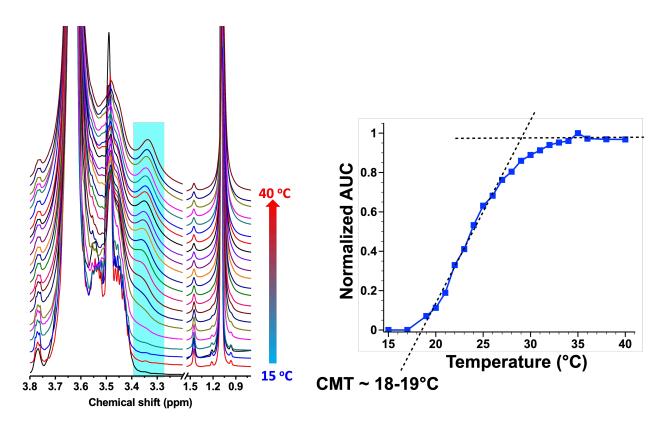


Figure S2: Temperature-dependent ¹H-NMR (left) of F127-BM and one equivalent of CB[8] (1 CB[8] per 2 BM guests), with the area under the curve in the blue-shaded region integrated to estimate the critical micelle concentration (right).

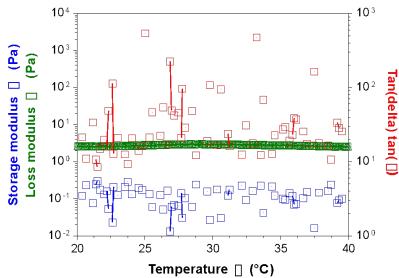


Figure S3: Variable temperature oscillatory rheology of F127-BM without CB[8], with no evidence of gelation over the full temperature range.

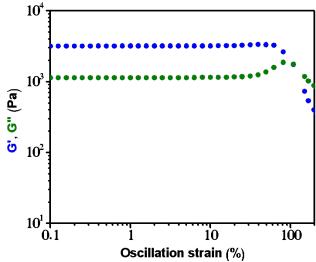


Figure S4: Strain sweep measurements of the gel formed by mixing F127-BM with 1 eq. CB[8] at 37 °C from 0.1% to 200% at 100 rad/s frequency to demonstrate the linear viscoelastic region.

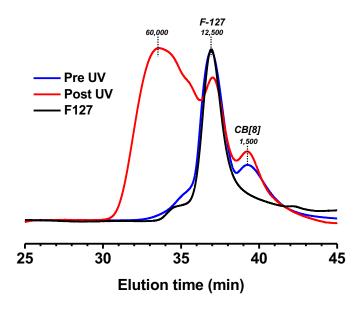


Figure S5: Size-exclusion chromatography of F127-BM with and without CB[8], as well as the sample with CB[8] following photodimerization. Masses for each peak were estimated on the basis of fitting to a PEG/PEO standard curve.

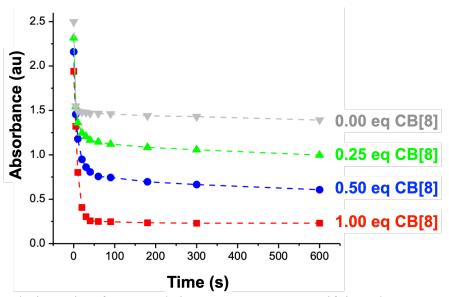


Figure S6: Peak intensity from UV/Vis spectroscopy quantifying the 378-nm absorbance signature serially with different irradiation times.

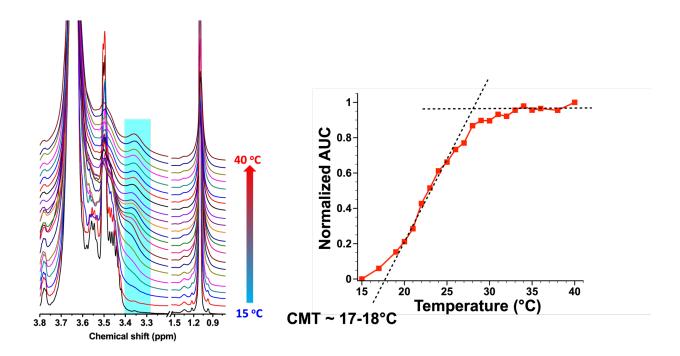


Figure S7: Temperature-dependent ¹H-NMR (left) of F127-BM and one equivalent of CB[8] (1 CB[8] per 2 BM guests) following irradiation of the polymer solution for 6 h with 378 nm light, with the area under the curve in the blue-shaded region integrated to estimate the critical micelle concentration (right).

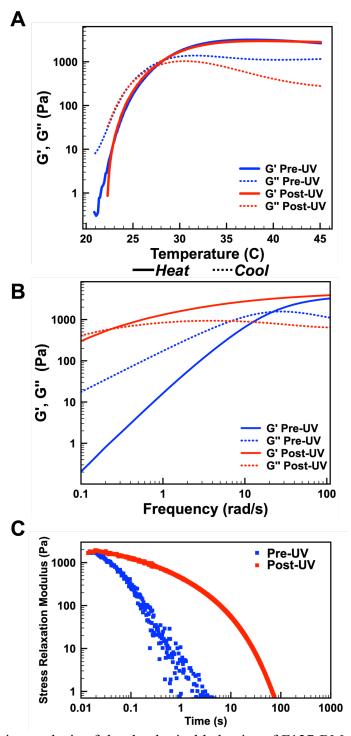


Figure S8: Comparative analysis of the rheological behavior of F127-BM:CB[8] hydrogels both before and after UV treatment to induce BM photo-dimerization, including (**A**) Temperature-dependent measurements, (**B**) Frequency Sweeps, and (**C**) Stress relaxation time-course studies.

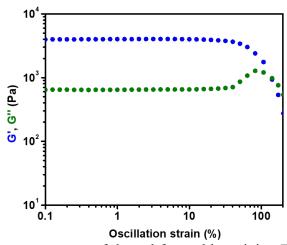


Figure S9: Strain sweep measurements of the gel formed by mixing F127-BM with 1 eq. CB[8] and irradiated for 6 h using 365 nm light, with measurements taken at 37 °C from 0.1% to 200% at 100 rad/s frequency to demonstrate the linear viscoelastic region.