Hydrogels have been found in a variety of biomedical applications ranging from 3-D cell cultures and stem cell differentiation to regenerative medicine, controlled drug delivery and tissue engineering. Polymer gels made of flexible chains have been thoroughly studied to understand the relationship between the physical and functional properties. In contrast, the thermodynamic behavior of supramolecular hydrogels, composed of entangled nanofibers is largely unknown. These systems are formed by self-assembly of small molecules via non-covalent interactions. Enzyme instructed self-assembly allows us to make nanofibers with uniform diameter and infinite length. We investigate the self-assembly of two typical hydrogelators using dynamic light scattering (DLS) and NMR. Measurements have been made on both systems as a function of the concentration and temperature. DLS yields information on the initial stage of fiber formation. Small angle neutron scattering (SANS) is used to determine the structural characteristics (cross-sectional radius of the fibers, average mesh size of the network, etc.) of the nanofibers. We believe a better understanding of the self-assembly process will help us to design supramolecular nanofibers/hydrogels for applications in biology and medicine.