hydrogels with compressive modulus of ~350 Pa best supported the proliferation of hESCs and maintained their pluripotency.

The Corgel® BioHydrogel from Lifecore Biomedical (Table 3) is a typical hydrogel obtained by enzymatic crosslinking reaction with HRP and H_2O_2. Corgel® offers a range of physical properties depending on the tyramine substitution (TS) percentage and the tyramine substituted hyaluronan (TS-NaHy) concentration.

Supramolecular HA Hydrogels

Self-assembling hydrogels are formed through specific supramolecular (noncovalent) interactions between pendant or end group functionalities and do not require the use of triggers such as chemical initiators or heat. Furthermore, because many of these supramolecular interactions are reversible, supramolecular self-assembly allows ease of injection without potential premature gel formation and near-instantaneous reassembly for hydrogel retention at the target site. The use of supramolecular interactions to form HA hydrogels by self-assembly has been explored through guest-host interactions, such as the interaction between or adamantane (Ad, guest) and cyclodextrin (CD, host). Ad associates strongly with CD (association constant on the order of 1×10^5 M^{-1}) by hydrophobic interactions. The Burdick group has separately conjugated HA with Ad (Fig. 1C-xiii) and CD (Fig. 1B-ix) to form injectable HA hydrogels (Rodell et al. 2013). Mixing both components resulted in rapid formation of a supramolecular hydrogel displaying shear-thinning and near-instantaneous self-healing (shear recovering) properties. The hydrogel's physical properties, including mechanics ($G' \approx 300$ Pa at 1 Hz) and flow characteristics, were dependent on crosslink density and network structure, controlled through: macromer concentration; the extent of guest macromer modification and the molar ratio of guest and host functional groups. They have further upgraded these supramolecular hydrogels via the introduction of secondary covalent crosslinking (addition of thiols and Michael-acceptors on HA: e.g., methacrylates, acrylates, vinyl sulfones) to increase hydrogel moduli ($E = 25.0 +/- 4.5$ kPa) and *in vivo* stability (>3.5 fold at 28 days) (Rodell et al. 2015a). Inclusion of proteolytically degradable peptides make these hydrogels responsive to enzymatic degradation *in vitro* and *in vivo* (Rodell et al. 2015b). The rational and selective modification of amino acid residues near the proteolytic site enabled selective protease susceptibility and control over hydrogel degradation kinetics.

The macrocyclic host molecule cucurbituril (CB) was also conjugated to HA to obtain supramolecular hydrogels upon interaction with HA monofunctionalized with polyamines (PAs) of diaminohexane (DAH) or spermine (SPM) (Jung et al. 2014; Park et al. 2012). CB[n] has exceptionally high binding affinity and selectivity toward alkylammonium ions in aqueous solution. In particular, it tightly binds PAs, like DAH or SPM in their protonated forms, to make stable 1:1 host–guest complexes with a binding constant up to 10^{10} or 10^{12} M^{-1}. MonoCB[6]-HA was obtained by thiolene "click" photoreaction between monoallyloxy CB[6] and SH-HA (Fig. 1B-i), while DAH-HA or SMP-HA were obtained by activation of HA carboxyl groups with EDC followed by reaction with amines of DAH and SMP (Oh et al. 2010). MonoCB[6]/DAH-HA or MonoCB[6]/SPM-HA hydrogels were obtained by simply mixing DAH-HA or SPM-HA and monoCB[6]-HA solutions driven by the host–guest interaction