Electronic Supporting Information

Hierarchically structured, hyaluronic acid-based hydrogel matrices via the covalent integration of microgels into macroscopic networks

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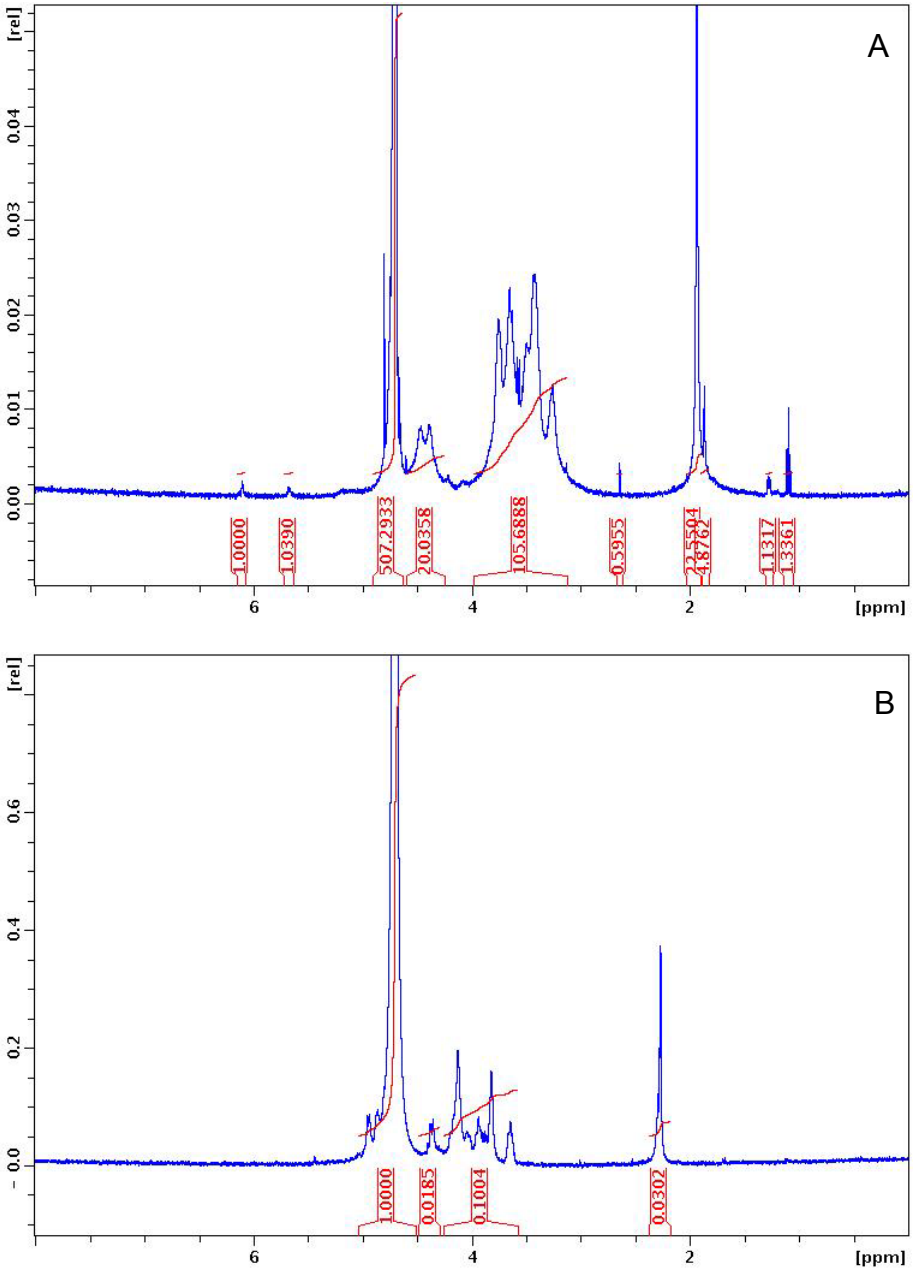
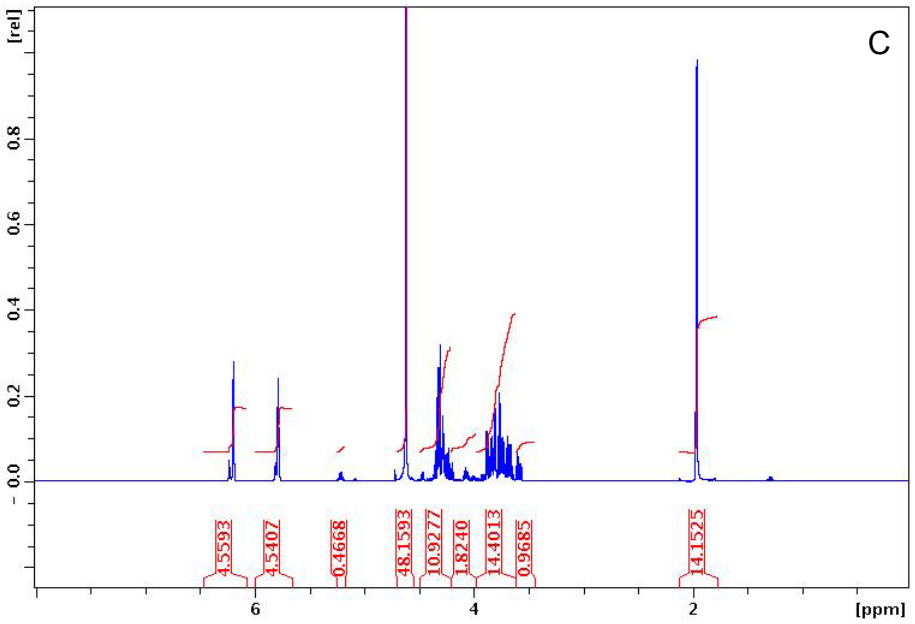
Characterization of crosslinkable HGPs. To confirm the presence of unsaturated double bonds in HGP-GMA, particles were degraded in HCl (6N in H_2O) overnight. After neutralization with NaOH (6 N in D_2O), the degraded product was lyophilized and re-dissolved in D_2O for ^1H NMR analysis. Control experiment under the same condition was performed on GMA to ascertain the absence of an addition reaction between HCl and the methacrylate group during degradation. The crosslinkability of HGP-GMA was confirmed further by radical polymerization of acrylamide in the presence of HGP-GMA. Specifically, to a 0.1 mL acrylamide solution (25 wt% in DI H_2O) was added 1 mg of HGP-GMA, tetramethylethylenediamine (TEMED, 0.5 μL) and 1.0 μL of ammonium persulfate (APS, 64 mg/mL in DI H_2O). Upon thorough mixing, the solution was transferred to a 96-well plate for polymerization at room temperature overnight. A control experiment was carried out under the same conditions in the absence of HGP-GMA.

Figure S1: (A) ^{1}H NMR spectrum of HA-GMA without any treatment. (B)-(D): ^{1}H NMR spectra of HGP (B), GMA (C) and HGP-GMA (D) after HCl treatment.

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6
4
2
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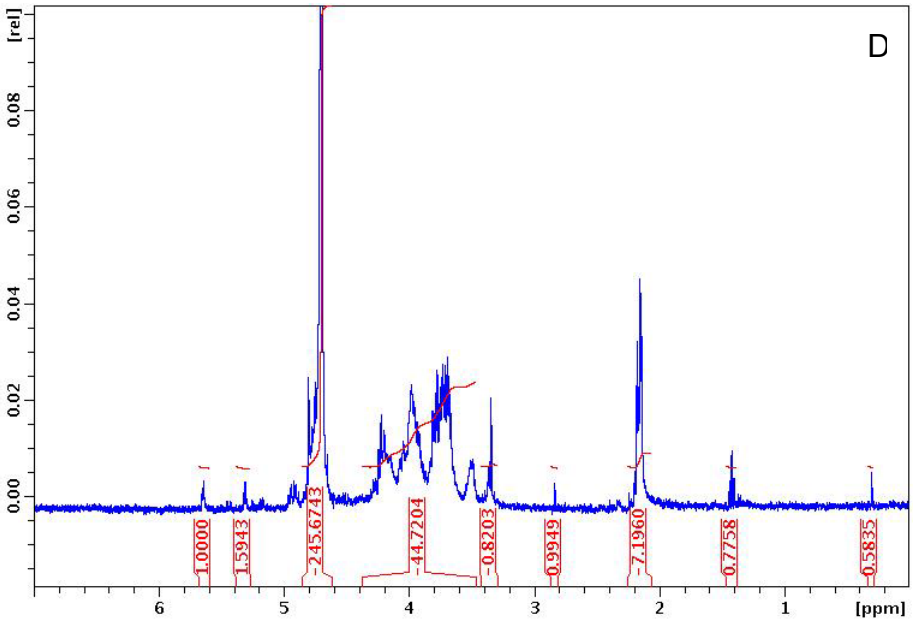
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- 44.7204
- 0.8203
0.9949
- 7.1960
0.7758
0.5835
6
5
4
3
2
1
[ppm]

Figure S2. Vial inversion experiment demonstrating the crosslinkability of HGP-GMA. (A) Radical polymerization of acrylamide without any crosslinker resulted in a polymer solution that flowed (right); (B) Radical polymerization of acrylamide in the presence of HGP-GMA resulted in a viscoelastic gel that did not flow (left).