Multi-functionalized hydrogels by a thiolactone-based synthetic protocol

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Supporting Information

Supplementary LC-MS studies

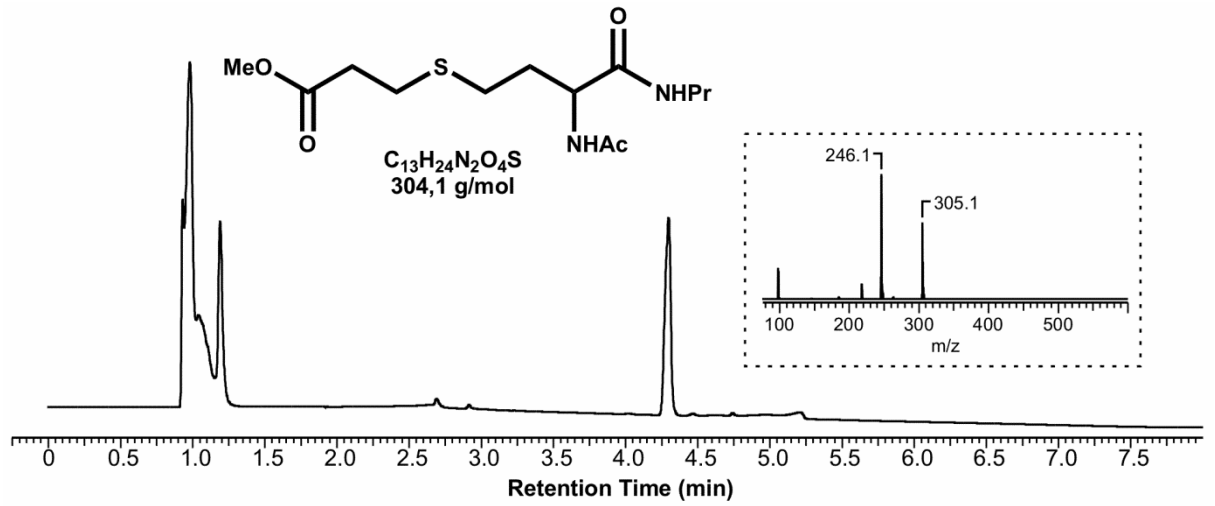

Figure S1. LC trace derived from a mixture of *N*-acetylhomocysteine thiolactone, propylamine and methylacrylate in DCM, which was left to react for one night. The inset shows the mass spectrum of the only detected reaction product.

As supplement to the LC-MS experiment series presented in Figure 2, another reaction was performed in which 232 mg of *N*-acetylhomocysteine thiolactone in 0.8 mL of DCM was reacted with 0.6 mL propylamine in the presence of 0.66 mL methyl acrylate. Analogous to the previously performed reactions, the mixture was left over night and after that, all volatiles were removed *in vacuo* followed by dissolution of the residue in acetonitrile (HPLC grade). Figure S1 shows the corresponding LC-MS trace. As depicted in Figure 2 of the main manuscript, the attack of propylamine on thiolactone leads to a ring opening of the latter, releasing free thiols. Normally those thiol groups would form disulfide bridges or react with DCM if any is present. However, Figure S1 proves that the released thiols react much faster with the methyl acrylate, leaving no opportunity for the thiol to undergo one of the two other reactions. The LC trace exhibits only detectable reaction product, which is the expected thioether originating from the reaction of *N*-acetylhomocysteine thiolactone, first with propylamine and in the second step with methyl acrylate.

Tuning of swelling degrees

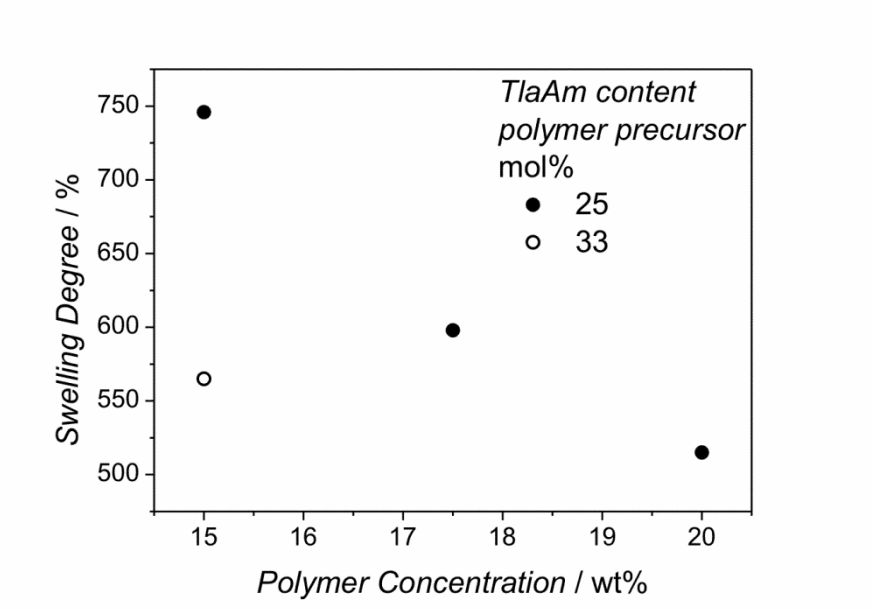

Figure S2. Swelling degree of synthesized gels as a function of polymer concentration in the initial gelation formulation and of the thiolactone content of the polymer; the polymers used were Tla25 and Tla33 (see Table 1, main manuscript) and the ring opening amine 3-morpholinopropylamine.

As mentioned in the main manuscript, crosslinking degrees of the gels can be adjusted by three different means, that is, adjustment of gelation time, precursor concentration and number of available thiol groups. Figure S2 shows how an increasing precursor concentration leads to lower swelling degrees of the resulting gels. Additionally, a data point is added showing how the swelling degree is affected by the thiolactone content of the polymer precursor. More thiolactone groups result in an increasing amount of thiol groups after the ring opening step and therefore in more opportunities for crosslink formation, which in turn leads to a significantly decreased swelling degree.

Dynamic mechanical analysis

Figure S3 shows the storage moduli of a selection of morpholino functionalized pNIPAAm gels at 1 Hz as a function of swelling degrees (extracted from Figure 4, main manuscript). The gel strength clearly drops with increasing swelling degree as expected. It is noted that the measured values show certain error margins as a drying effect is observed during measurement, which cannot be ruled out.

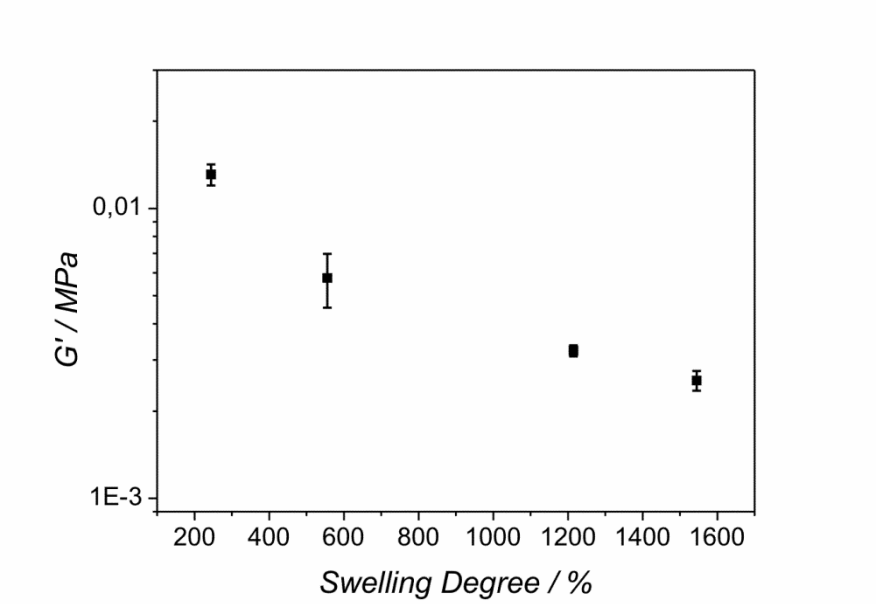

Figure S3. Storage moduli G' of a selection of morpholino functionalized pNIPAAm gels (precursor Tla25, Table 1) plotted as a function of swelling degrees, Force amplitude = 1 N; frequency = 1Hz; displacement amplitude = 200 μm; T = 25 °C.