

Supplementary Material

Modulating Biofunctional starPEG Heparin Hydrogels by Varying Size and Ratio of the Constituents

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1. Real Time Gelation Behavior of the Hydrogels

Gel cure experiments were performed in real time using small deformation oscillatory rheometry (mechanical spectroscopy) with a MCR301 rheometer (Anton Paar, Austria) with a conical geometry (cone CP50-1-SN1290; 50 mm/1 ° cone plate) [1,2]. Upon mixing all components (see *Preparation of starPEG heparin gels*), 570 μ L of the liquid gel mixture were pipetted onto the bottom plate, and the upper plate was then lowered to a measuring gap size of 0.052 mm. All samples were reacted isothermally at 23 °C in a humidified atmosphere, unless otherwise specified. The evolution of the storage (G') and loss (G'') moduli at a constant frequency of 5 rad/s and strain amplitude of 3% was recorded as a function of time (time sweep). All experiments were performed three times.

Representative results for hydrogel formation between heparin ($M = 14,000$ g/mol) and starPEG ($M = 10,000$ g/mol) in a molar ratio of 1:4 are shown in Figure 1. At the beginning of the experiment, G'' is orders of magnitude larger than G' , and at completion of the reaction, this order is reversed. Both storage and loss moduli increased as a result of the increasing cross-linking density, until a plateau region was reached when cross-linking reaction was completed. The higher the molar ratio of starPEG to heparin the faster the plateau was reached.

The time taken to achieve the gel point conversion is defined as the gel time. The gel point characterizes the transition from liquid to solid state. It can be estimated from the point of crossover of

G' and G'' [3,4]. However, it is only an estimate, because as the gel network structure forms stress relaxation also occurs.

Figure 1. Rheometric characterization of the gelation rate. Evolution of storage (G' ; solid symbol) and loss modulus (G'' ; open symbol) during the crosslinking reaction of starPEG ($M = 10,000$ g/mol) and heparin ($M = 14,000$ g/mol) (ratio 4:1) at 22 °C and a frequency of 5 rad/s.

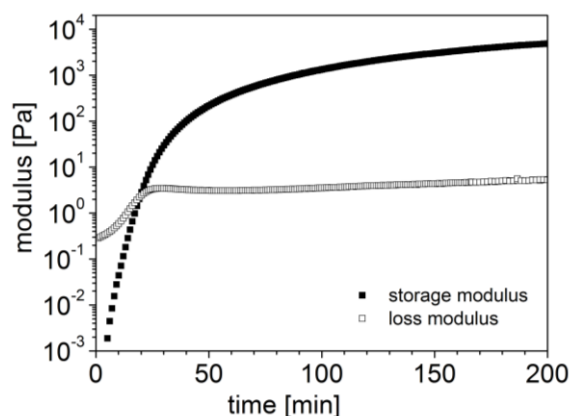
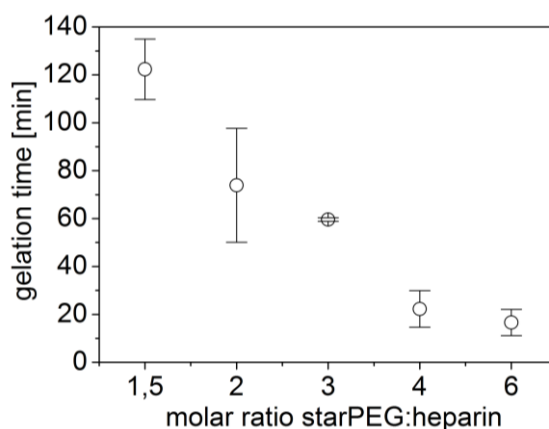


Figure 2 shows the gelation times determined for hydrogels of the PEG10HEP14 series. Shorter gelation times were observed with increasing starPEG concentration in the initial reaction mixture. Thus, hydrogel formation time for the highest cross-linked gel (molar ratio of starPEG to heparin: 6) was below 15 minute and increased up to 122 minutes for gels with 1.5 fold molar excess of starPEG.

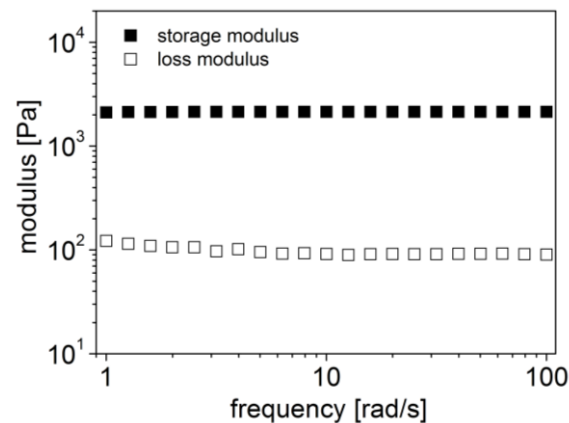
Figure 2. Rheometric characterization of the gelation rate for hydrogels of the PEG10HEP14 series. Plot of gel formation time (gel point) as a function of molar starPEG to heparin ratio.



2. Frequency Dependence of Storage und Loss Modulus

Figure 3 exemplarily shows the result of one rheology experiment for a PBS swollen hydrogel disk of the series PEG19HEP14 (molar ratio of starPEG to heparin: 4). The data for the other gel types look similar in principle.

Figure 3. Frequency dependence of storage und loss modulus for a PBS swollen hydrogel disk of the series PEG19HEP14 (molar ratio of starPEG to heparin: 4).



References

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