"Looking into Hydrogels":
HR-MAS NMR Spectroscopy as Versatile Tool for Hydrogel Characterization

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INTRODUCTION

The UV curing of vinyl containing hydrogel building blocks results in insoluble polymer networks, which cannot be characterized using conventional ^{1}H-NMR spectroscopy. The NMR spectra of solid samples show considerable line broadening in the NMR spectra obtained. These broad signals can be attributed to the presence of dipolar interactions, chemical shift anisotropy (CSA) and magnetic susceptibility effects. HR-MAS ^{1}H-NMR spectroscopy can be considered as an extension of traditional ^{1}H-NMR spectroscopy towards semi-solid samples. Since HR-MAS NMR spectroscopy enables the recording of quantitative NMR-spectra of solvated networks, the technique is gaining increasing importance as a characterisation tool in solid phase synthesis, polymer chemistry and in the biomedical field.

EXPERIMENTAL METHODS

The line width observed in the NMR spectra of solids can be decreased considerably by swelling the hydrogel samples in a deuterated solvent (e.g. deuterium oxide, D_2O). As a result, the polymer becomes solvated and gains segmental motion, enabling the chains to more closely resemble the conditions they would experience in solution. The latter results in the removal of dipolar interactions and CSA effects, resulting in a decrease in line width to a few kHz. Additionally, the line broadening due to magnetic susceptibility effects can be reduced by rapidly rotating the sample at an angle of 54.7° relative to the static magnetic field (figure 1, left). At this "magic angle" θ, the contribution of the Hamiltonian disappears, effectively removing the line broadening effects. The applied spinning rates are generally in the order of a few kHz. Magic angle spinning NMR (MAS-NMR) spectroscopy thus allows the recording of NMR spectra of solids, with more narrow signals. The combination of the above-mentioned effects thus enables the application of ^{1}H-NMR spectroscopy on semi-solid samples.

RESULTS AND DISCUSSION

In our laboratory, HR-MAS ^{1}H-NMR spectroscopy was applied for the first time to determine the cross-linking degree of methacrylamide-modified biopolymers.[1] By comparing the integration of the signal corresponding to the methacrylic double bonds with the integration of a signal that remains chemically inert during the cross-linking procedure, the cross-linking efficiency can be determined. When the composition of the (bio)polymer is known, the spectroscopic data enable the calculation of the degree of methacrylation (DM).

Interestingly, since the double bonds present in the samples are consumed during cross-linking, it also becomes feasible to calculate the degree of cross-linking (DC) by comparing the intensity of the signals corresponding with the methacrylamide moieties present before and after cross-linking (figure 1, right). Since different samples have to be compared, these intensities should also be normalized using the inert signal. For methacrylamide-modified gelatin (gel-MOD), the following equation has been obtained:

$$DC(\%) = \left[\frac{\left(\frac{I^i_{5,7 \text{ or } 5,45 \text{ ppm}}}{I^i_{0,9 \text{ ppm}} \right) - \left(\frac{I^c_{5,7 \text{ or } 5,45 \text{ ppm}}}{I^c_{0,9 \text{ ppm}} \right)}{\left(\frac{I^i_{5,7 \text{ or } 5,45 \text{ ppm}}}{I^i_{0,9 \text{ ppm}} \right)} \right] * 100\%$$

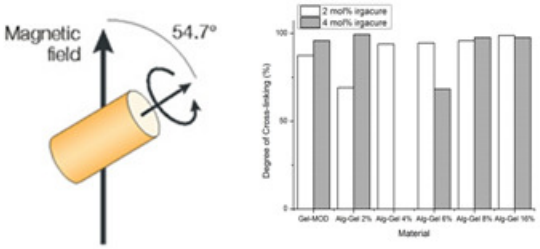

Figure 1: Schematic overview of HR-MAS NMR spectroscopy (left). Cross-linking efficiencies (%) for the various biopolymer derivatives when applying different photoinitiator concentrations obtained using HR-MAS NMR spectroscopy (right).

CONCLUSION

HR-MAS ^{1}H-NMR spectroscopy was shown to be an interesting characterisation tool to correlate the hydrogel crosslinking efficiency with the crosslinking conditions applied. The number of crosslinkable moieties remaining unreacted after UV curing in the presence of a suitable photo-initiator can be easily quantified using this state-of-the-art characterization tool.

REFERENCES

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