Electronic Supporting Information

Determination of degree of substitution (DS) of guar

The DS of guar is defined as the average number of substituted hydroxyl groups per one sugar unit. We can assume that guar is composed of repeating sugar units which each possesses 3 OH groups. Thus the maximum possible average DS equal 3, which would mean that all OH groups from all sugar units are chemically substituted. (D. Risica, M. Dentini and V. Crescenzi, Polymer, 2005, 46, 12247-12255)

Indeed, for repeating unit constituting of one mannose moiety unsubstituted by galactose one, three OH groups can be chemically modified. For repeating unit constituting of mannose unit substituted by galactose one, the mannose unit has 2 OH groups and the galactose unit possesses 4 OH groups, thus there are on average 3 OH groups per sugar able to be esterified. The DS values were determined through $^1$H NMR spectroscopy by considering some protons of ester moieties introduced onto guar backbone as internal reference. These protons were selected because for most of esterified guar derivatives, they can clearly assigned and have no interference with other peaks.

Illustration with the guar derivative acetylated with acetyl chloride (2).

As indicated in Fig. 8 of the manuscript, the signals of protons from 1.65 to 2.2 ppm correspond to methyl protons of acetate group and was set to 3 (internal reference). The resulting integration of all guar protons ($I_0$) was computed. This integral arises from (i) 7 protons of the methyne (C-H) and methylene (CH$_2$) groups of sugar units constituting the guar backbone and from (ii) the (3-DS) protons of residual OH groups non chemically modified
(visible in NMR spectra collected in DMSO-[d6] or CDCl3 since in these solvents they are not exchanged).

As \( DS \) is defined as the number of ester groups per one sugar unit, it can be estimated from the ratio: \( \text{Digital Integration of one proton coming from the introduced chemical moiety introduced onto the guar chain) / (Digital Integration of one proton coming from the guar chain).} \)


So, we obtain:

\[
DS = \frac{3/3}{I_0 / (7 + (3-DS))}\\
DS = \frac{7+3-DS}{I_0}\\
I_0 DS = 10 - DS\\
DS (1+I_0) = 10\\
\]

and \( DS = \frac{10}{1+I_0} \)
**Fig. 1 ESI** Photographs of guar ($M_w = 566$ kDa) solubilised at 5 % wt in EMIMMP (a), BMIMCl (b) and AMIMCl (c).

**Fig. 2 ESI** SEC-traces of native guar and of regenerated guar samples from EMIMMP, EMIMAc, BMIMCl, AMIMCl for guar of $M_w = 299$ kDa.
**Fig. 3 ESI** FT-IR spectra of native guar (126 kDa) (a) and guar regenerated from BMIMCl (b), EMIMMP (c) and AMIMCl (d).

**Fig. 4 ESI** Thermal decomposition profiles of native guar and guar regenerated from ILs. The analysis were performed under nitrogen atmosphere at a heating rate of 10 °C/min.
Fig. 5 ESI $^1$H NMR spectra (250 MHz, 6 mg/mL, D$_2$O, 25 °C) of the starting (top) and of the AMIMCl recycled after the acetylation reaction with acetyl chloride (down).

Fig. 6 ESI FTIR spectra of guar esterified with hexanoyl chloride in AMIMCl (a) and in BMIMCl (b); conditions: 80 °C, 2 h, n esterifying reagent / n sugar unit = 5/1, n pyridine / n sugar unit = 2.5/1.
**Fig. 7** ESI $^1$H NMR spectrum (400 MHz, 10 mg/mL, CDCl$_3$, 25 °C) of guar esterified with hexanoyl chloride ($DS = 2.7$).

**Fig. 8** ESI $^1$H NMR spectrum (400 MHz, 10 mg/mL, DMSO-d$_6$, 70 °C) of guar esterified with acryloyl chloride ($DS = 0.72$).
**Fig. 9 ESI** $^1$H NMR spectrum (400 MHz, 10 mg/mL, CDCl$_3$, 25 °C) of guar esterified with 2-chloropropionyl chloride ($DS = 2.51$).