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Supplementary Information

Efficient *N*-sulfopropylation of chitosan with 1,3-propane sultone in aqueous solutions: neutral pH as the key condition

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EQUATIONS

Eqs. S1 and S2. Determination of the degree of acetylation (DA) for chitosan (CS)

Elemental analysis:

$$DA\ (\%) = \left(\frac{W_{(C/N)} - (C/N)_{GlcN}}{(C/N)_{GlcNAc} - (C/N)_{GlcN}}\right) \times 100 \qquad \text{Eq. S1}$$

where $W_{(C/N)}$ is carbon/nitrogen mass ratio obtained by elemental analysis, $(C/N)_{GlcN}$ and $(C/N)_{GlcNAc}$ are the carbon/nitrogen ratios of GlcN and GlcNAc, respectively, equal to 5.145 and 6.861.[1]

^{1}H NMR method:

$$DA\ (\%) = \left(\frac{I_{CH3}/3}{I_{H2-6}/6}\right) \times 100 \qquad \text{Eq. S2}$$

where I_{CH3} and I_{H2-6} are the integrals of the acetyl proton signal in GlcNAc and proton signals of H2-6 in GlcN and GlcNAc units, respectively.[2]

FIGURES

Figure S1. ^{13}C NMR spectra of N-(3-sulfopropyl)chitosan salt (SPCS) purified by different methods

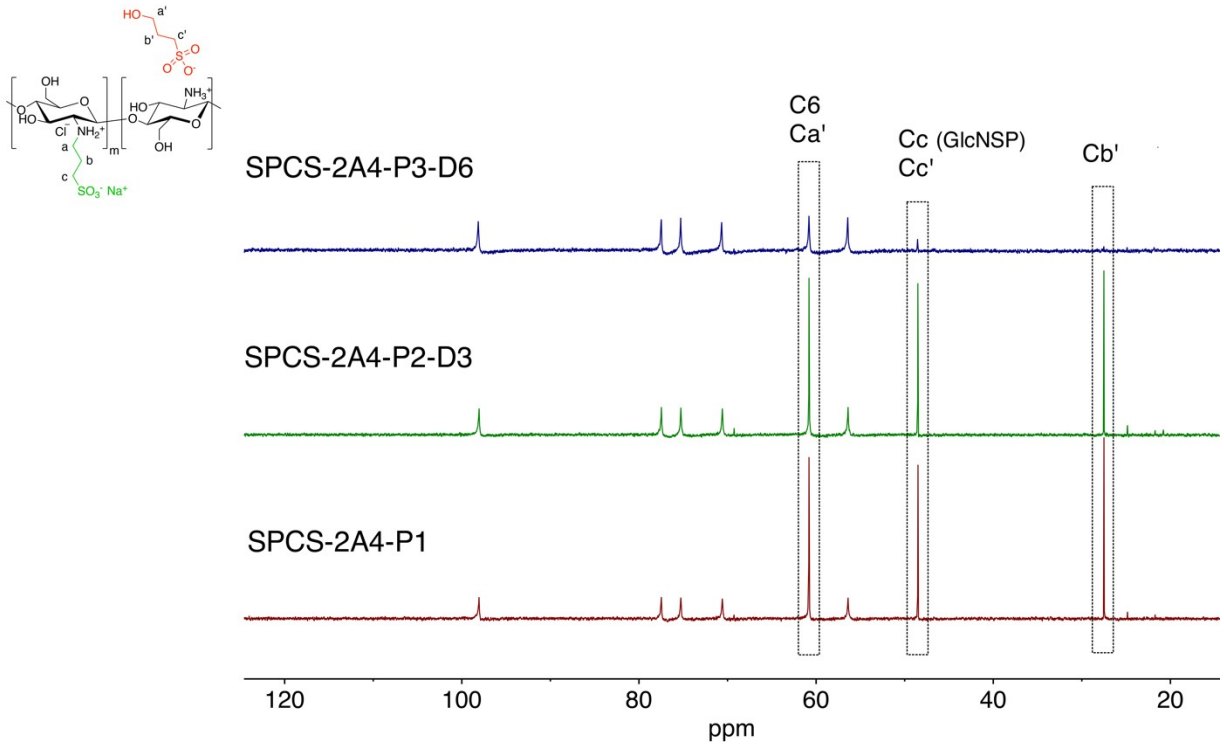

Figure S1. ^{13}C NMR spectra of SPCS-2A4 in D_2O/DCl (100 MHz, pH ~ 3.0, 65 °C). SCPS was purified by precipitation (P1), dialysis against water at pH 6.5 (P2), and dialysis against water at pH 9 (P3). The representative carbon signals are labeled in the spectra.

Figure S2. ^{13}C NMR spectra of 1,3-propane sultone in D_2O

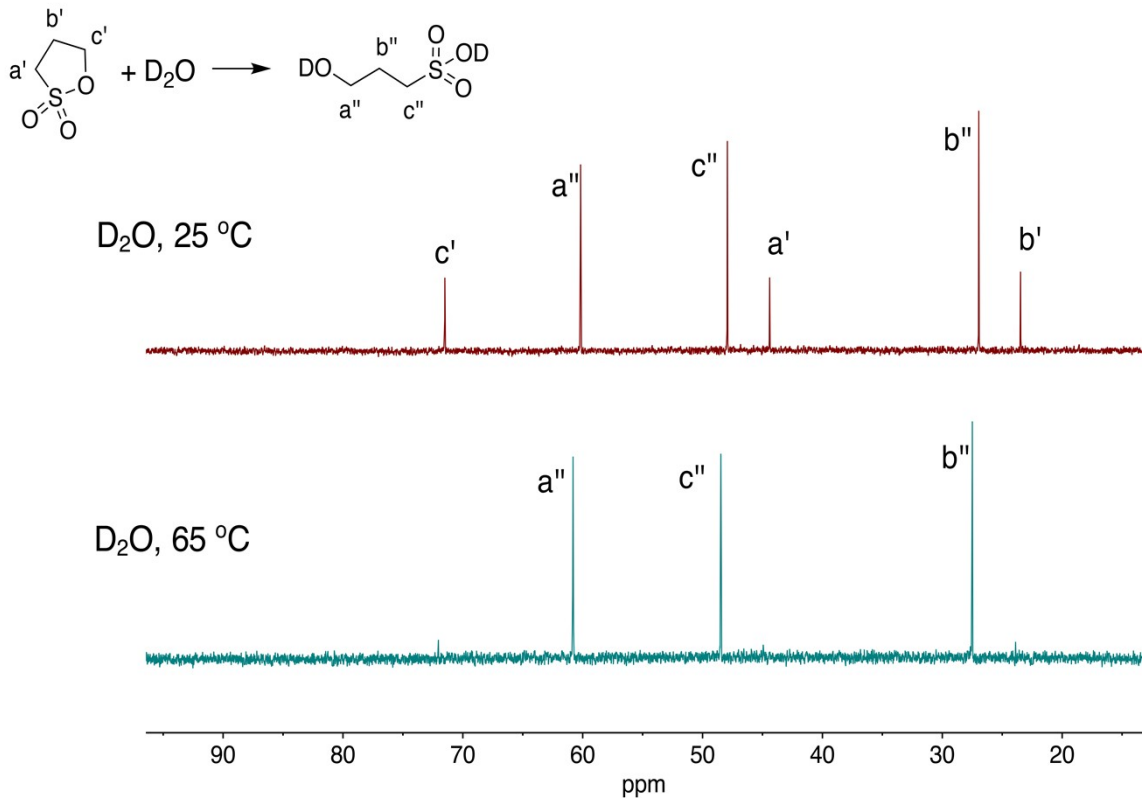

Figure S2. ^{13}C NMR of PrS in D_2O (100 MHz) measured at 25 and 65 °C. PrS was dissolved around 2 h before performing NMR analysis and stored at ambient temperature. The spectra at 65 °C were measured after 30 min exposure of PrS to this temperature (by setting the acquisition time to 30 min).

Figure S3. HMBC spectrum of N-(3-sulfopropyl)chitosan salt (SPCS)

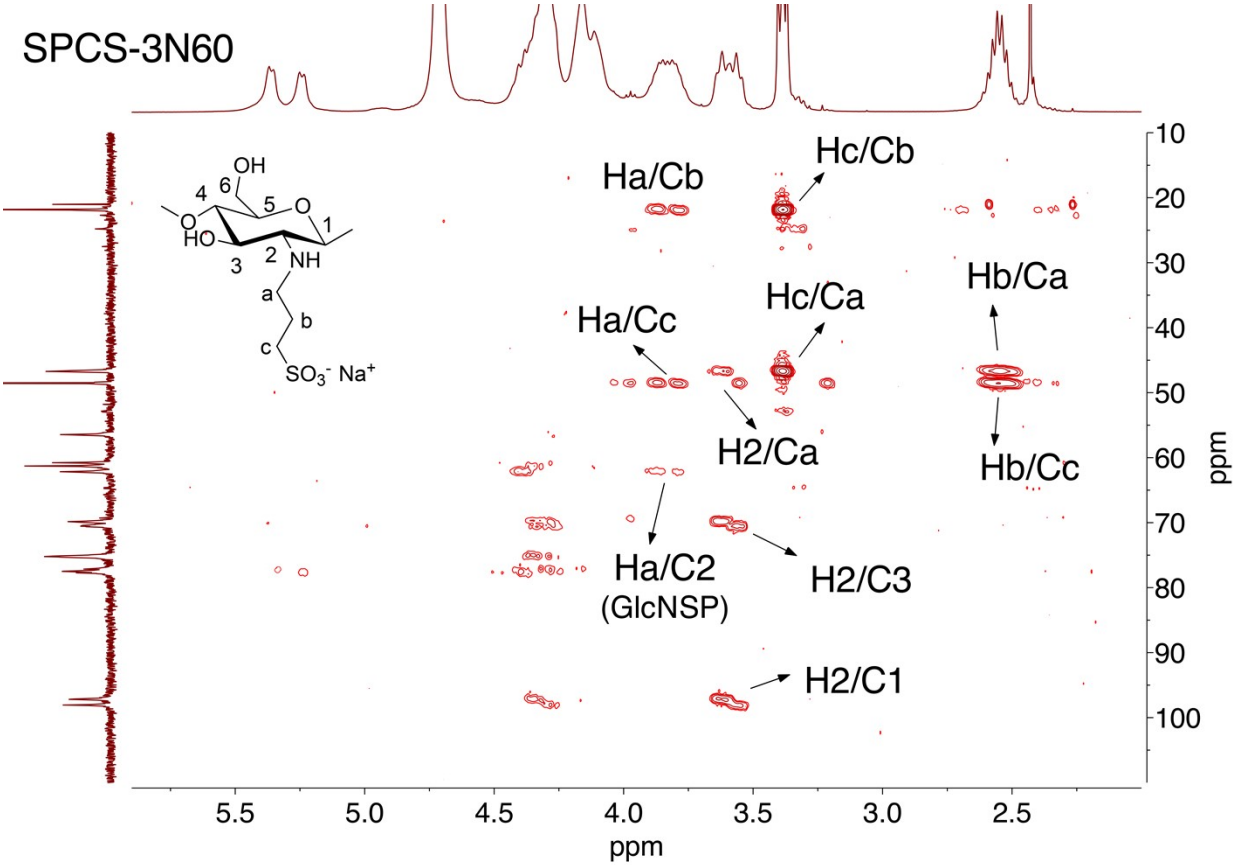

Figure S3. ^{1}H-^{13}C HMBC spectrum of SPCS-3N60 (400 MHz, D_2O/DCl, p*H* ~3.0, 65 °C). The representative cross peaks are labeled in the spectrum.

Figure S4. ^{13}C NMR spectra of N-(3-sulfopropyl)chitosan salt (SPCS) containing sulfopropyl salt

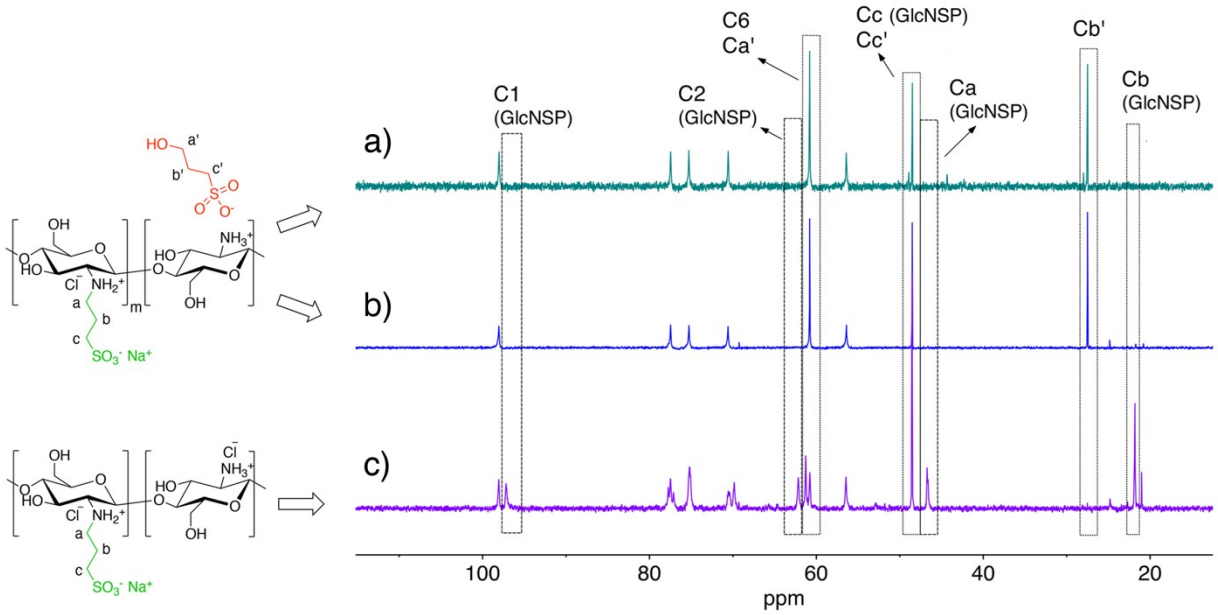

Figure S4. ^{13}C NMR (100 MHz) (a) CS@PrS (weight ratio of 1 : 1) in D_2O after 30 min exposure of the solution to this temperature (by setting the acquisition time to 30 min), (b) SPCS-2A4@sulfopropyl salt in D_2O/DCl, and (c) SPCS-3N60 in D_2O/DCl.

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1. Kasaai, M. R.; Arul, J.; Charlet, G., Intrinsic Viscosity-Molecular Weight Relationship for Chitosan. *J Polym Sci Pol Phys* **2000,** 38, (19), 2591-2598.

2. Hirai, A.; Odani, H.; Nakajima, A., Determination of degree of deacetylation of chitosan by 1H NMR spectroscopy. *Polym Bull* **1991,** 26, (1), 87-94.