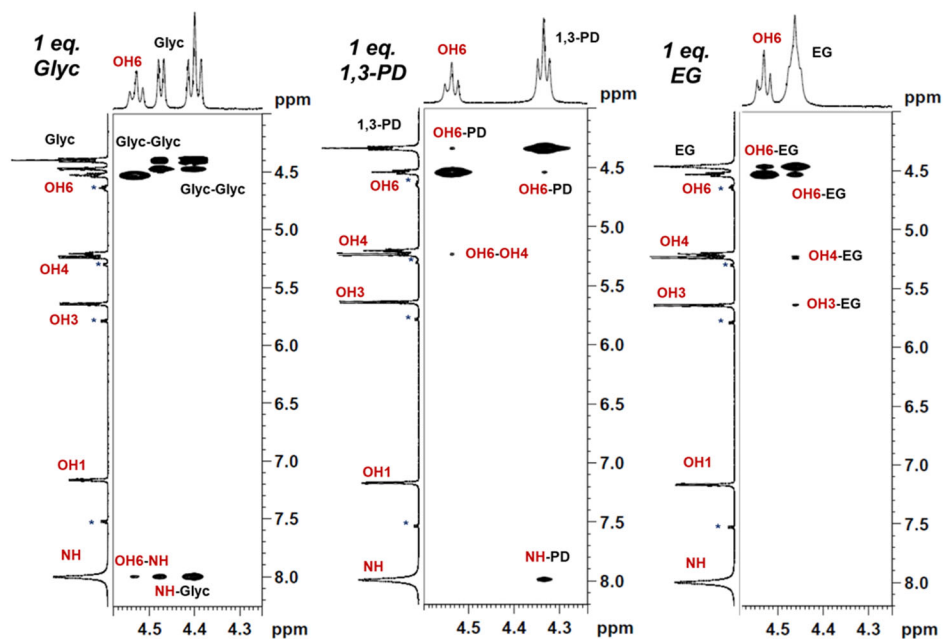


# Supporting Information

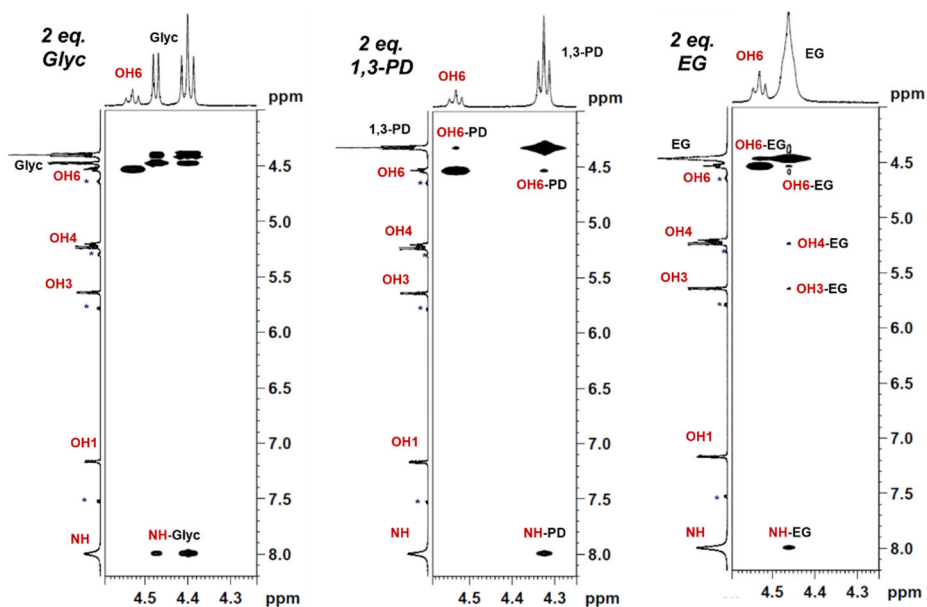
## **The Importance of Primary and Secondary Hydrogen Bonding Interactions of Polyols on the Plasticization of Chitosan**

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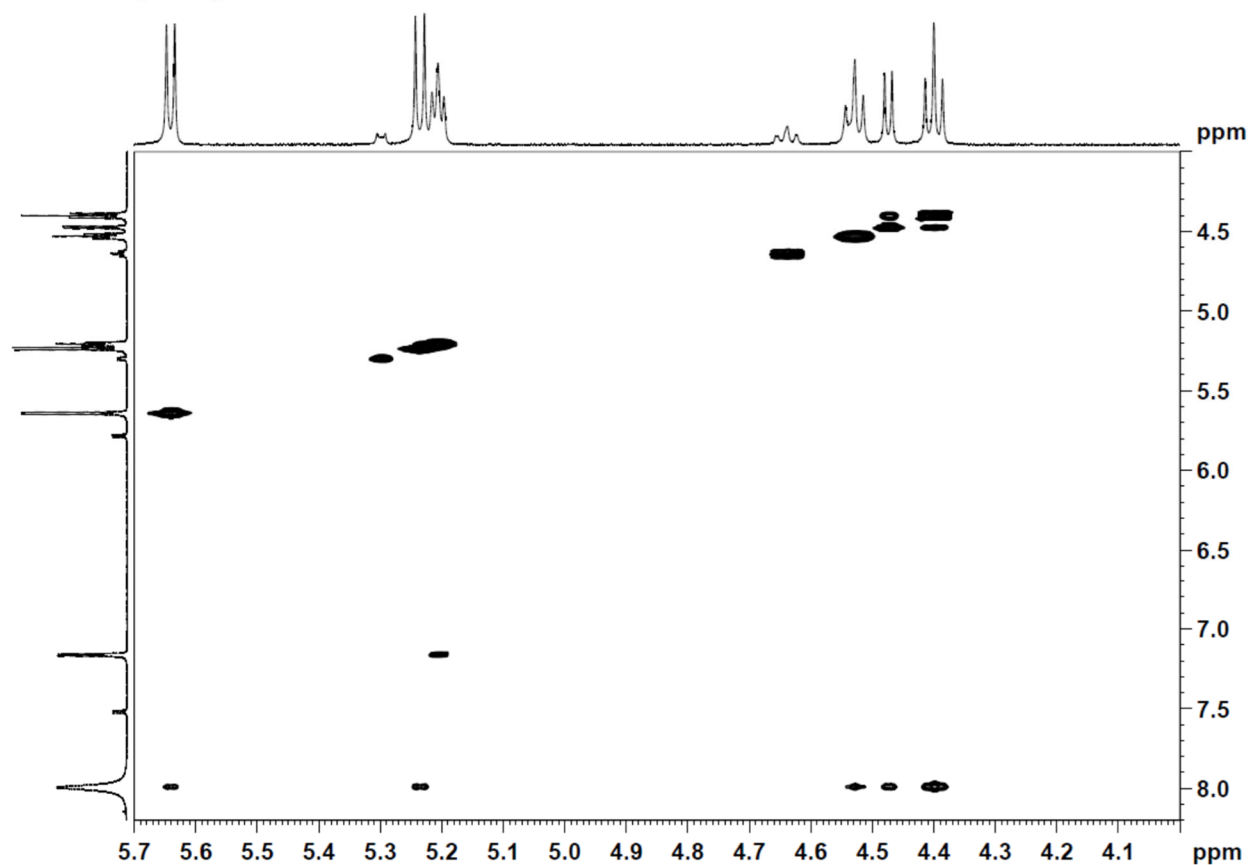


**Figure S1.** Representative cross sections of the 2D NOESY spectra of the polyol OH's at 12.5 mM GlcN and 12.5 mM Glyc (left), 12.5 mM 1,3-PD (middle), or 12.5 mM EG (right) recorded at 400 MHz (9.4 T). Small peaks for the alpha anomer of GlcN are observed in the spectra, and the corresponding peaks are denoted with an asterisk (\*).



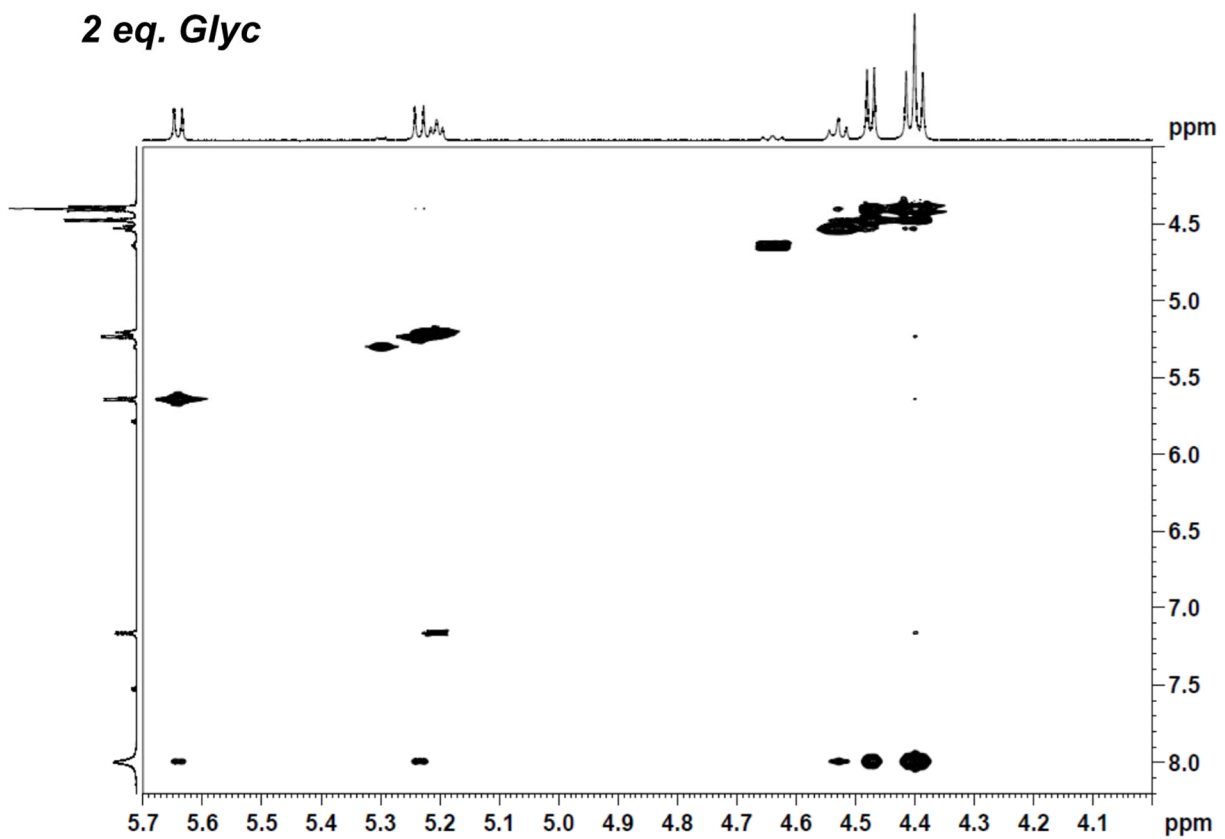
**Figure S2.** Representative cross sections of the 2D NOESY spectra of the polyol OH's at 12.5 mM GlcN and 25 mM Glyc (left), 25 mM 1,3-PD (middle), or 25 mM EG (right) recorded at 400 MHz (9.4 T). Small peaks for the alpha anomer of GlcN are observed in the spectra, and the corresponding peaks are denoted with an asterisk (\*).

**0.5 eq. Glyc**

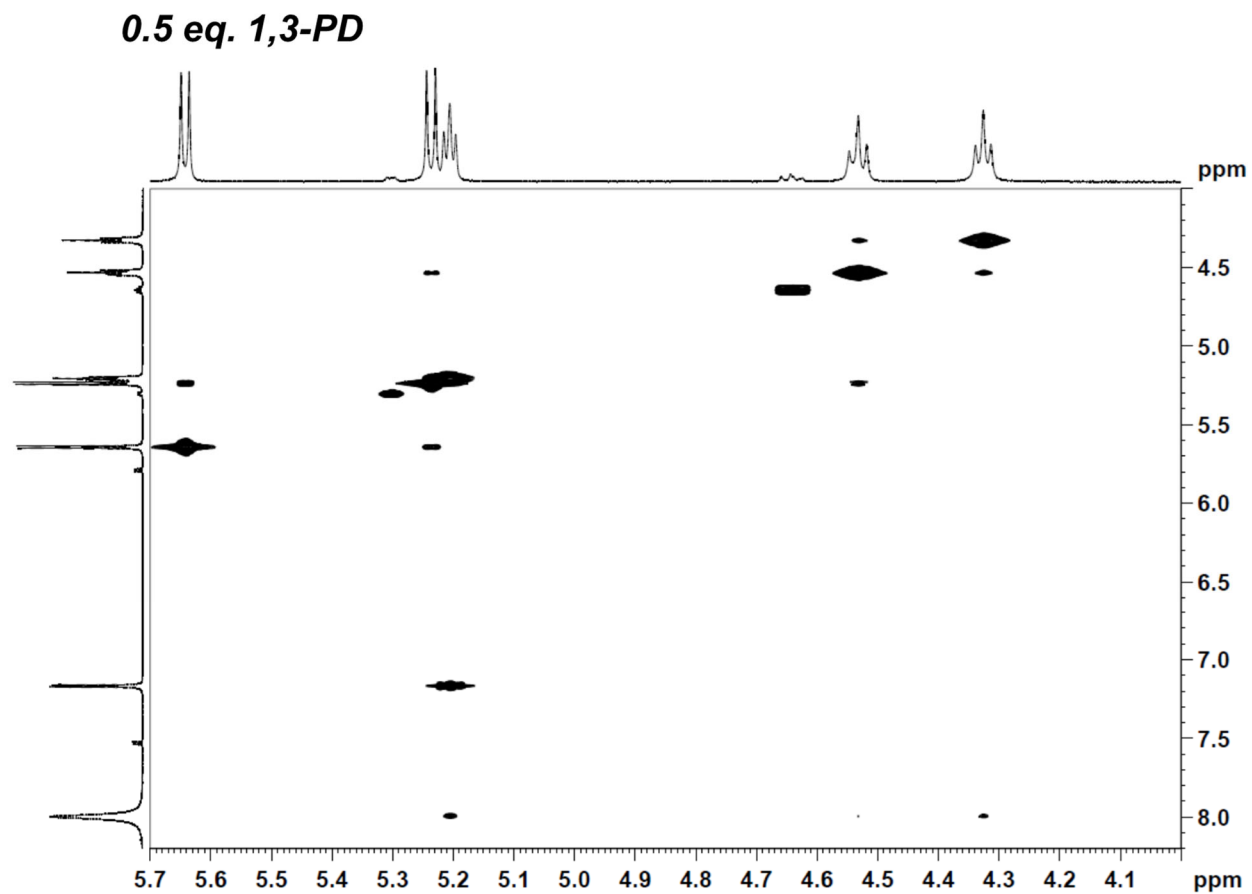


**Figure S3.** Full 2D NOESY spectra of 12.5 mM GlcN and 6.25 mM Glyc in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T). Full 1D NMR spectrum can be found in Figure S17.

**Figure S3a.** We have previously reported the full 2D NOESY spectra of 12.5 mM GlcN and 12.5 mM Glyc in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T) (*Smith, D.R, et. al. ACS Omega* **2021**, *6*, 39, 25227–25234).

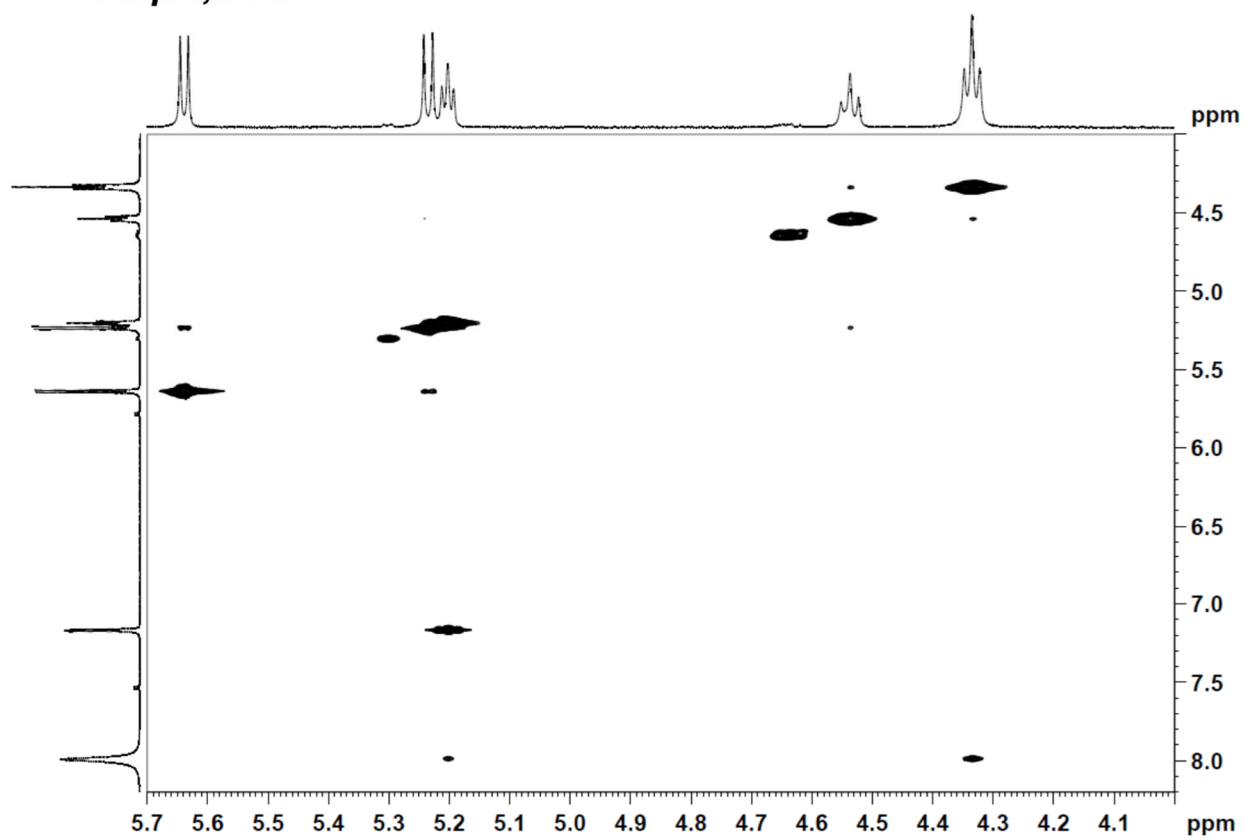


**Figure S4.** Full 2D NOESY spectra of 12.5 mM GlcN and 25 mM Glyc in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T). Full 1D NMR spectrum can be found in Figure S18.

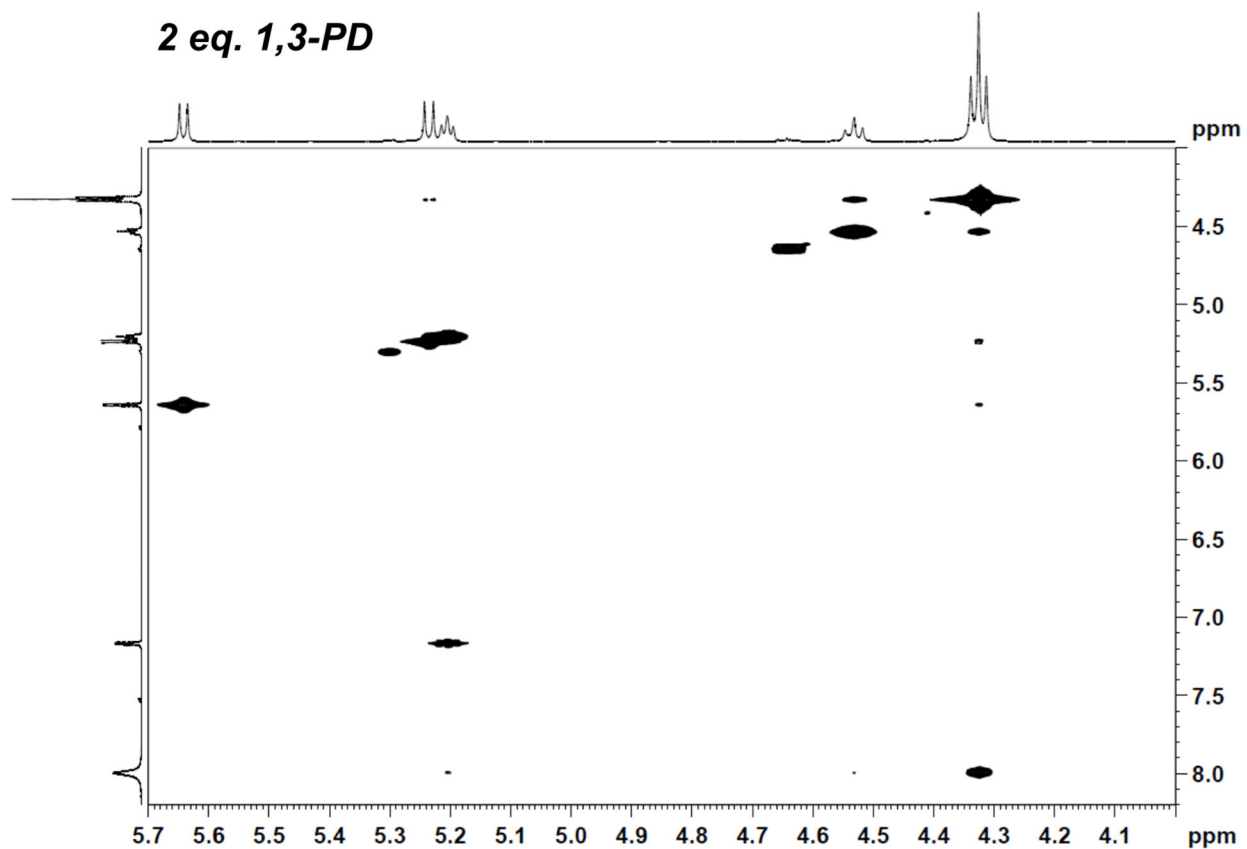


**Figure S5.** Full 2D NOESY spectra of 12.5 mM GlcN and 6.25 mM 1,3-PD in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T). Full 1D NMR spectrum can be found in Figure S19.

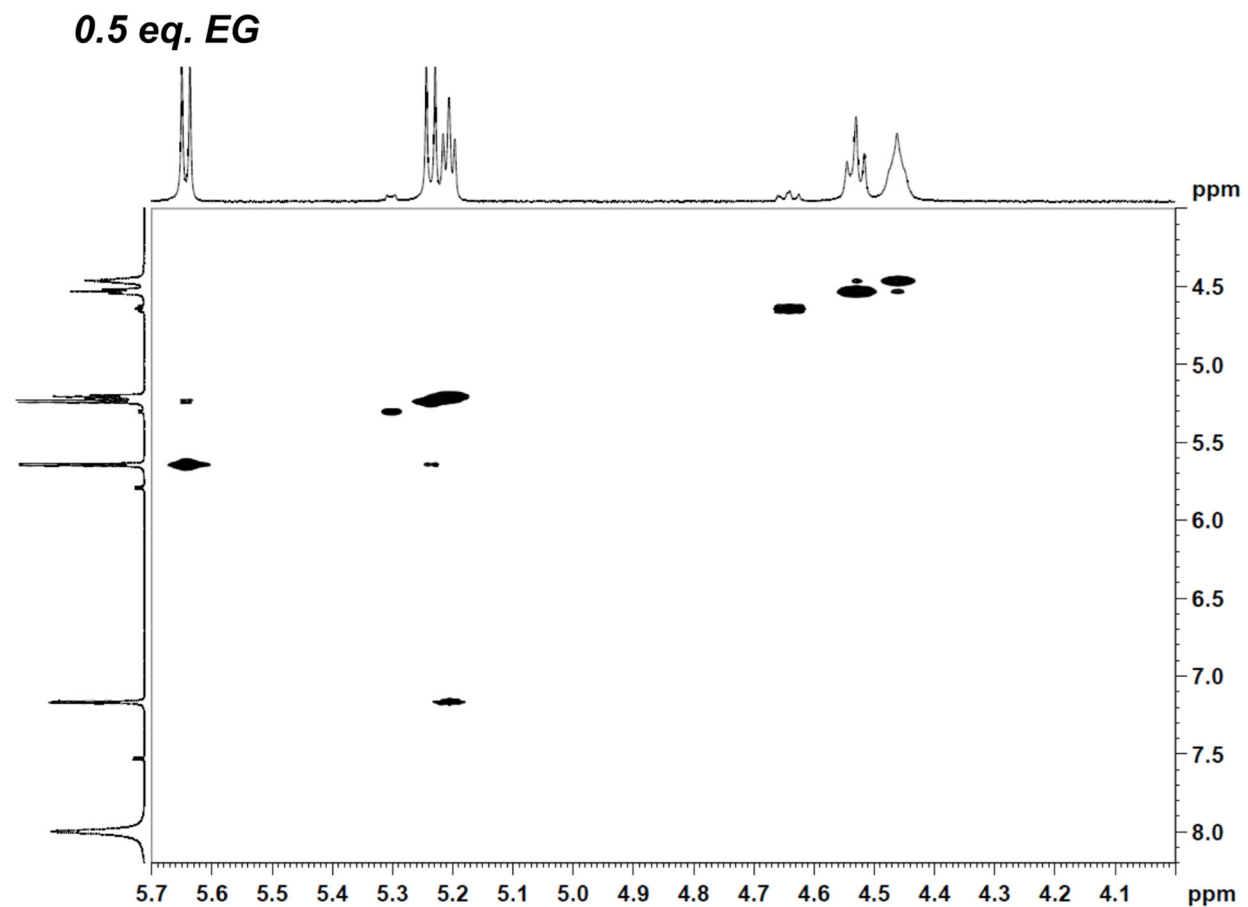
**1 eq. 1,3-PD**



**Figure S6.** Full 2D NOESY spectra of 12.5 mM GlcN and 12.5 mM 1,3-PD in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T). Full 1D NMR spectrum can be found in Figure S20.



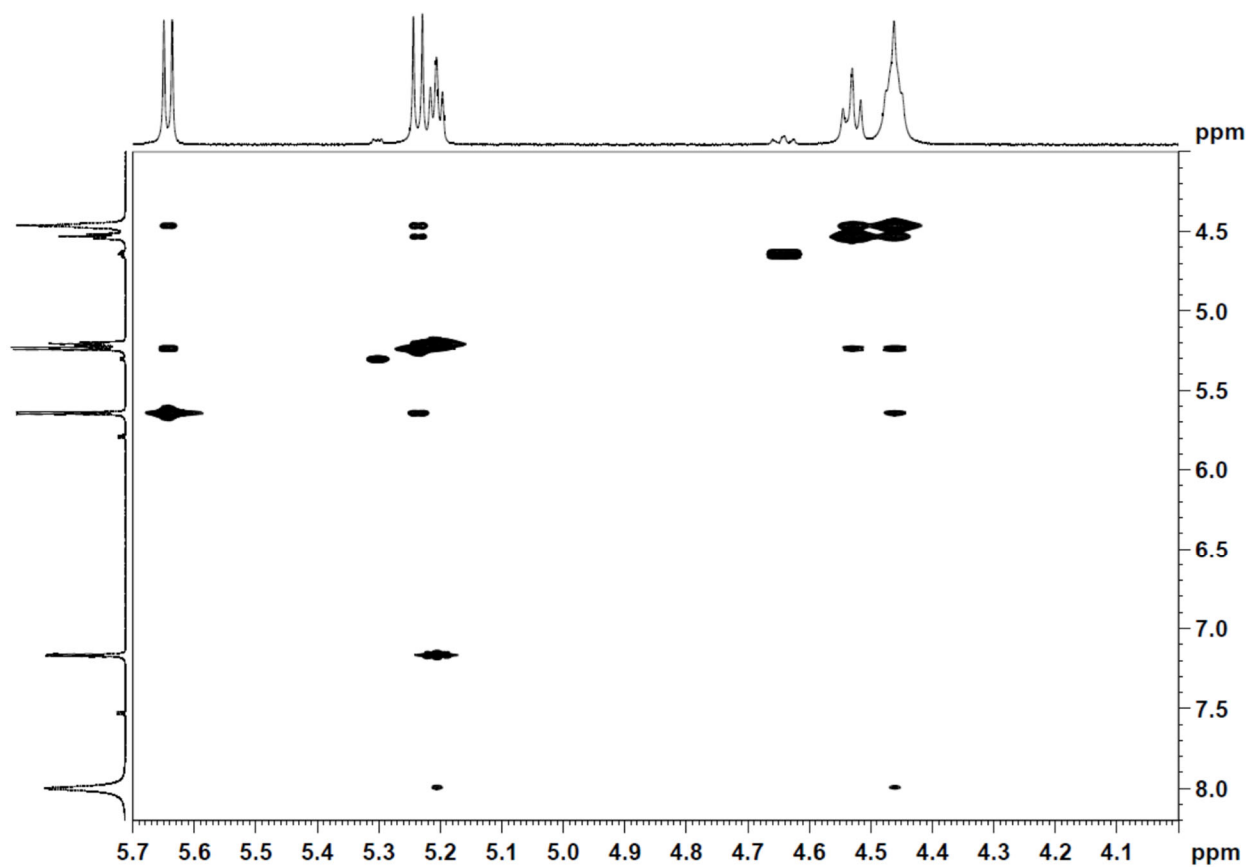
**Figure S7.** Full 2D NOESY spectra of 12.5 mM GlcN and 25 mM 1,3-PD in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T). Full 1D NMR spectrum can be found in Figure S21.



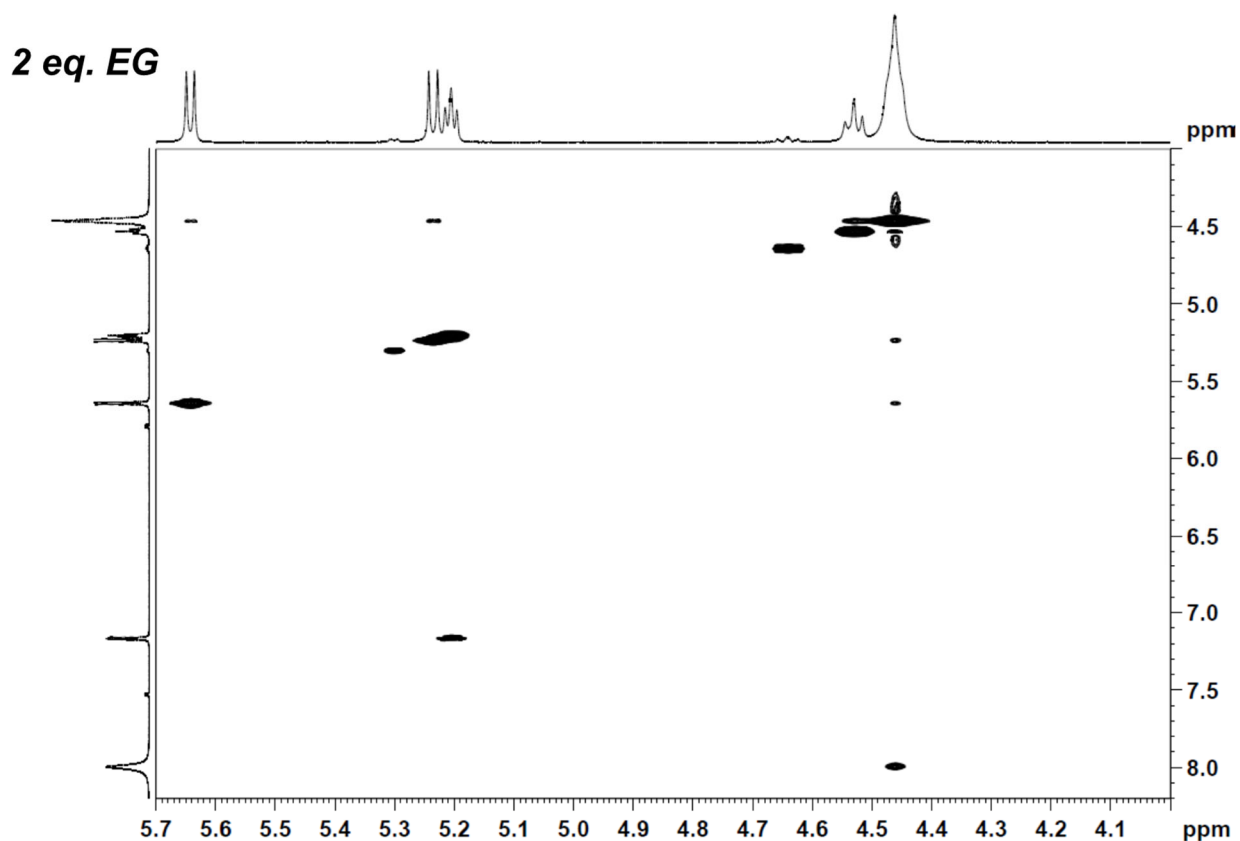
**Figure S8.** Full 2D NOESY spectra of 12.5 mM GlcN and 6.25 mM EG in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T). Full 1D NMR spectrum can be found in Figure S22.



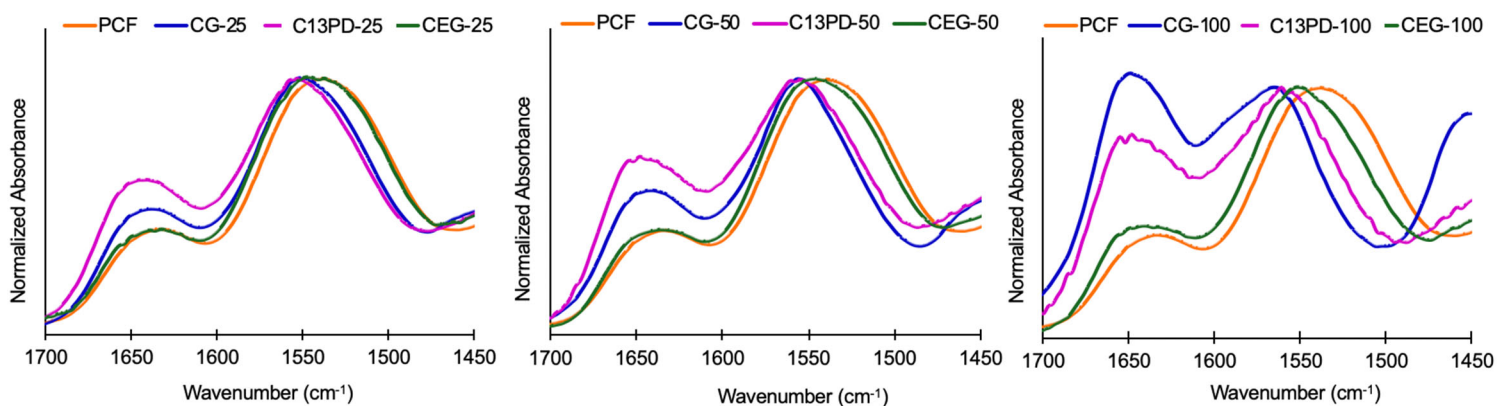
**1 eq. EG**



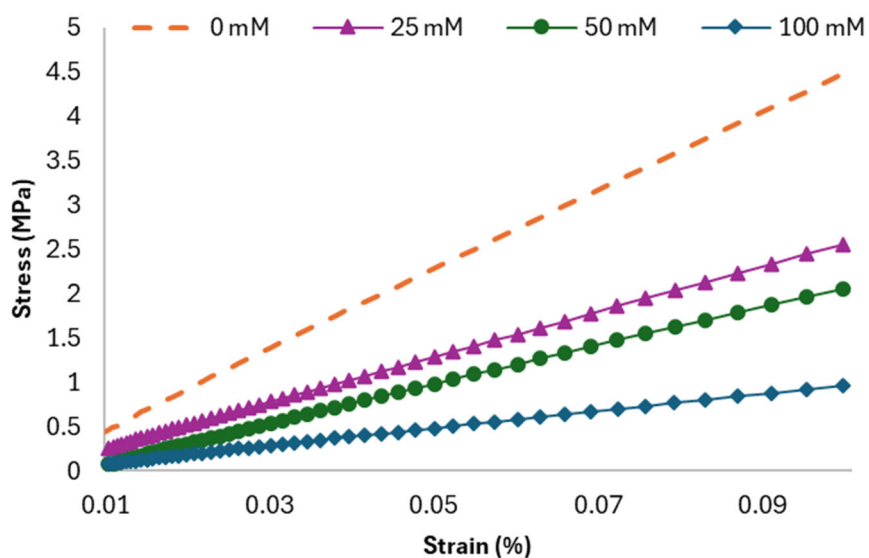
**Figure S9.** Full 2D NOESY spectra of 12.5 mM GlcN and 12.5 mM EG in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T). Full 1D NMR spectrum can be found in Figure S23.



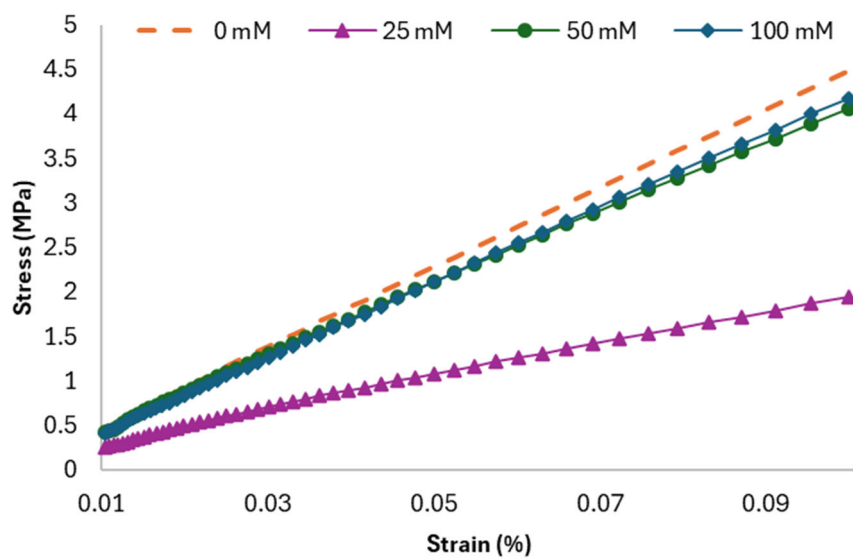
**Figure S10.** Full 2D NOESY spectra of 12.5 mM GlcN and 25 mM EG in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T). Full 1D NMR spectrum can be found in Figure S24.



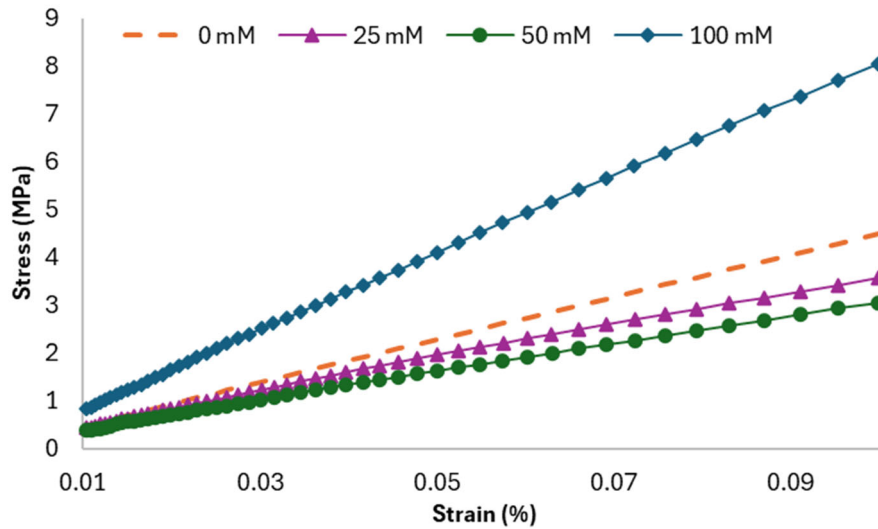
**Figure S11.** ATR-IR spectral overlay of CN/NH and CO-H combination band region from 1700 cm<sup>-1</sup>-1450 cm<sup>-1</sup> PCF (orange), CG (blue), C13PD (fuchsia), CEG (green) with increasing polyol concentration from 25 mM to 100 mM.



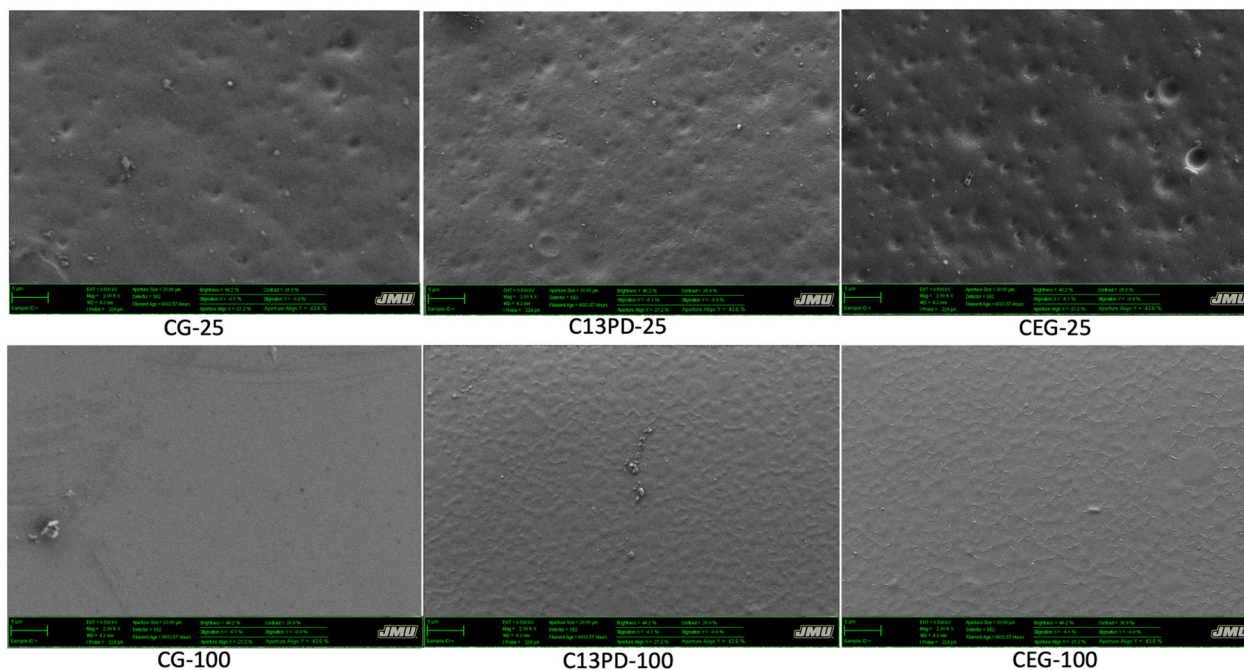
**Figure S12.** Stress-strain curves of 1% chitosan films with 0 mM (orange), 25 mM (pink), 50 mM (green) and 100 mM (blue) Glyc at 25 °C and 1 Hz.



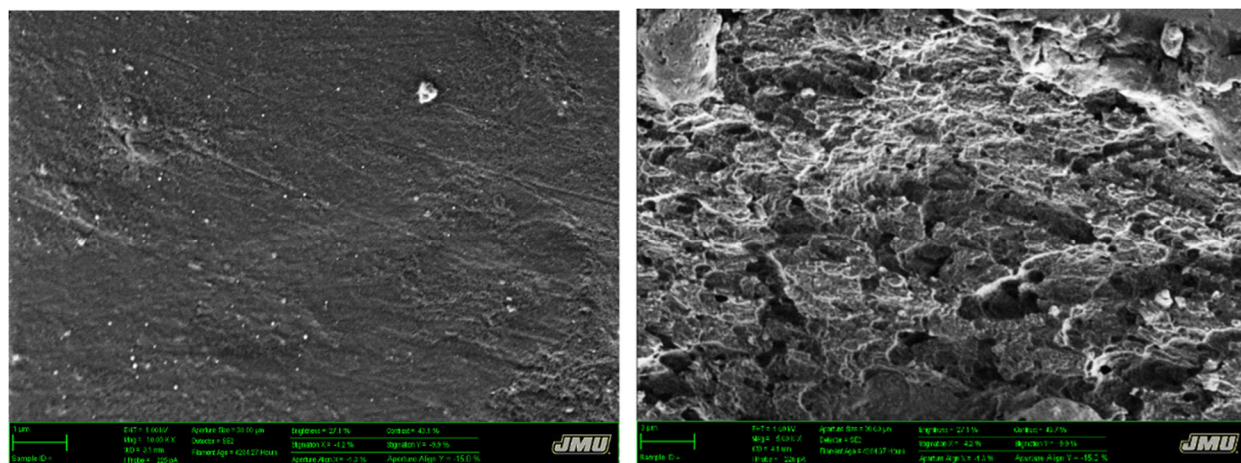
**Figure S13.** Stress-strain curves of 1% chitosan films with 0 mM (orange), 25 mM (pink), 50 mM (green) and 100 mM (blue) 1,3-PD at 25 °C and 1 Hz.



**Figure S14.** Stress-strain curves of 1% chitosan films with 0 mM (orange), 25 mM (pink), 50 mM (green) and 100 mM (blue) EG at 25 °C and 1 Hz.



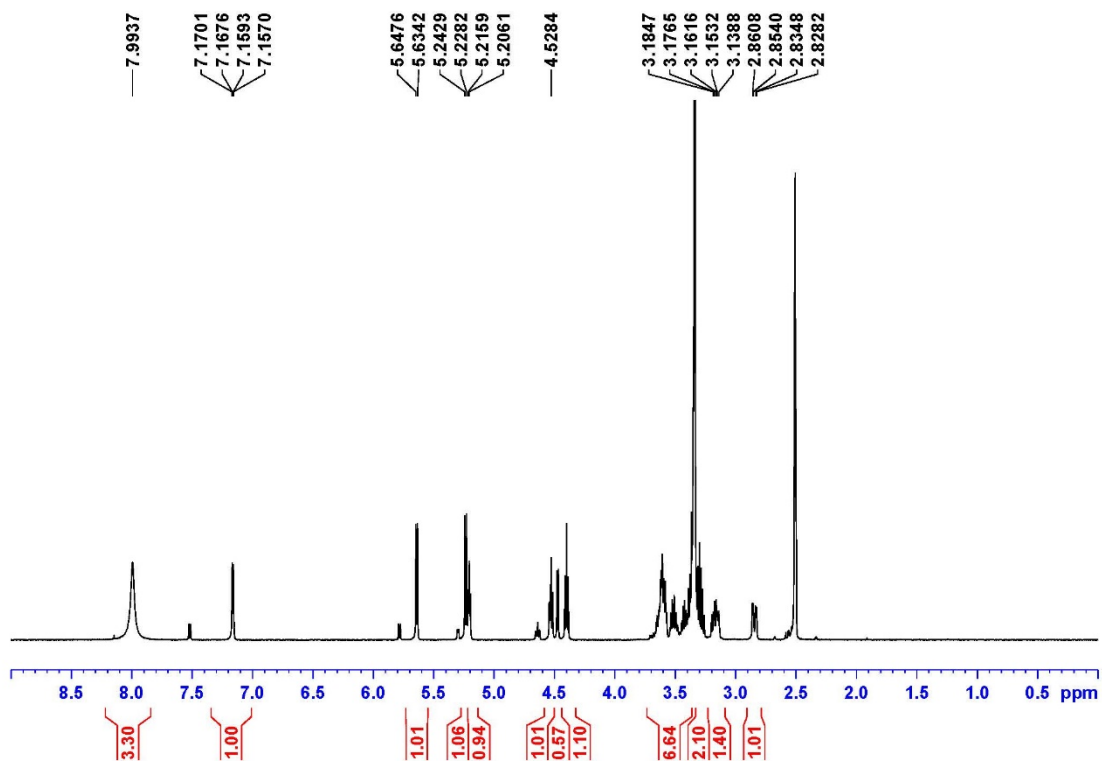
**Figure S15.** SEM surface morphologies of 1% chitosan films at 25 and 100 mM Glyc (CG-25 and CG-100), 1,3-PD (C13PD-25 and C13PD-100) and EG (CEG-25 and CEG-100).



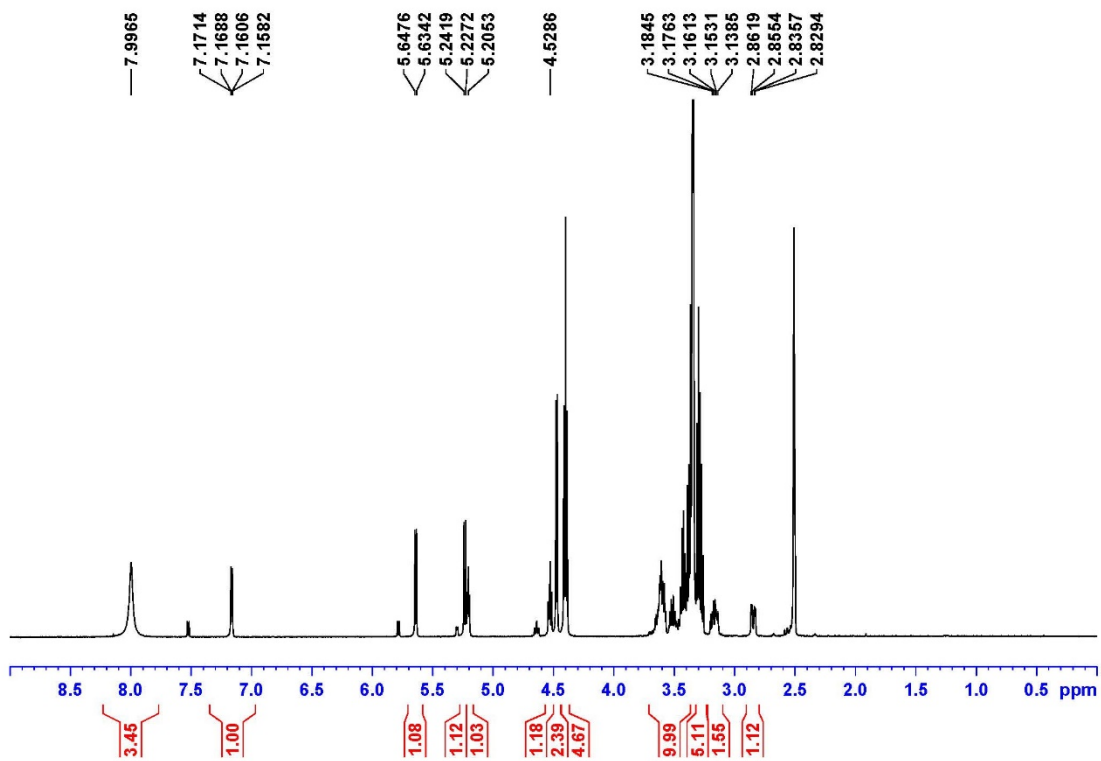
**Figure S16.** SEM surface (left) and cross-sectional (right) morphologies of 1% chitosan films.

Film	T <sub>H20</sub> (°C)	WL (%)	T <sub>max</sub> (°C)	ML (%)
CG-25	21.9	10.7	246.5	48.2
CG-50	21.9	10.9	246.1	40.0
CG-100	23.1	11.2	255.6	42.8
C13PD-25	20.3	10.3	243.9	47.4
C13PD-50	21.6	9.9	247.9	46.8
C13PD-100	21.9	9.7	250.2	46.7
C2M13PD-25	20.3	10.4	244.1	49.8
C2M13PD -50	20.3	9.6	241.9	49.6
C2M13PD-100	24.1	9.3	245.5	51.2
CEG-25	34.4	8.2	245.6	48.4
CEG-50	37.6	8.5	247.5	47.6
CEG-100	37.7	8.4	248.0	47.3
C12PD-25	34.7	7.4	242.4	53.7
C12PD-50	20.7	8.0	239.9	53.2
C12PD-100	35.2	7.7	245.7	50.9

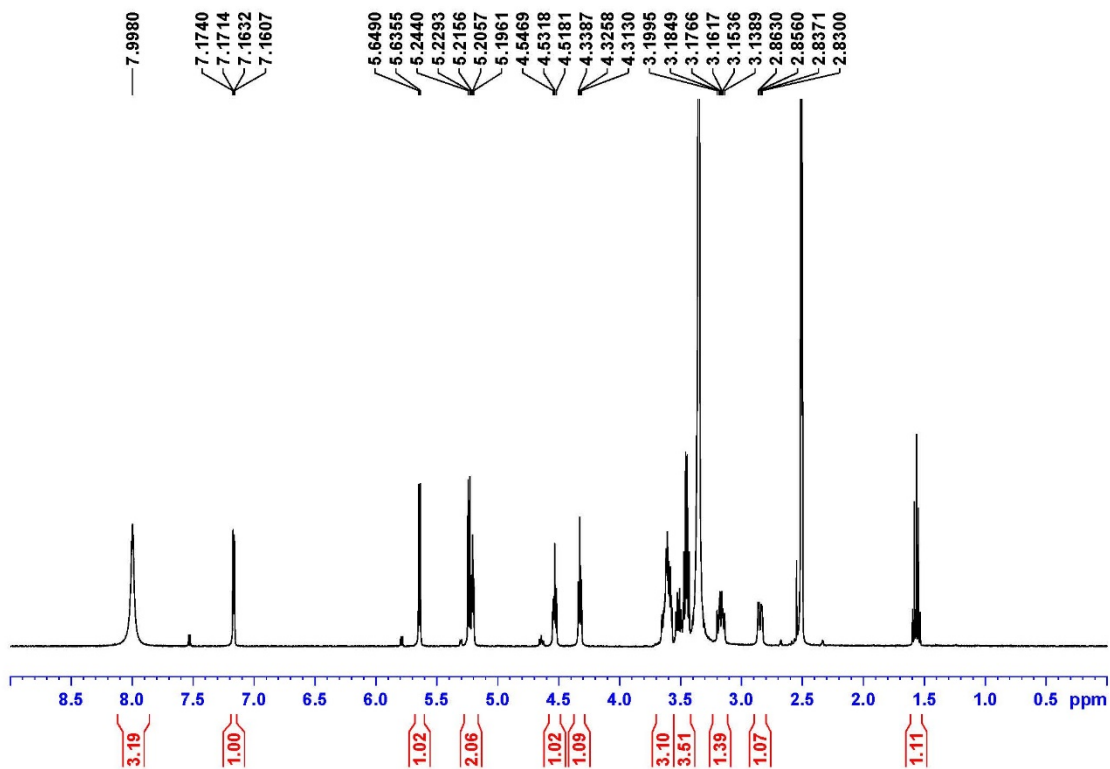
**Table S1:** TGA of the films containing different polyols at 25 mM, 50 mM and 100 mM. Values for water loss temperature and mass percent loss (T<sub>H20</sub>, °C and WL, %) and maximum mass loss temperature and mass percent loss (T<sub>max</sub>, °C, ML, %) are given.



**Figure S17.** Full 1D NMR spectra of 12.5 mM GlcN and 6.25 mM Glyc in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T).

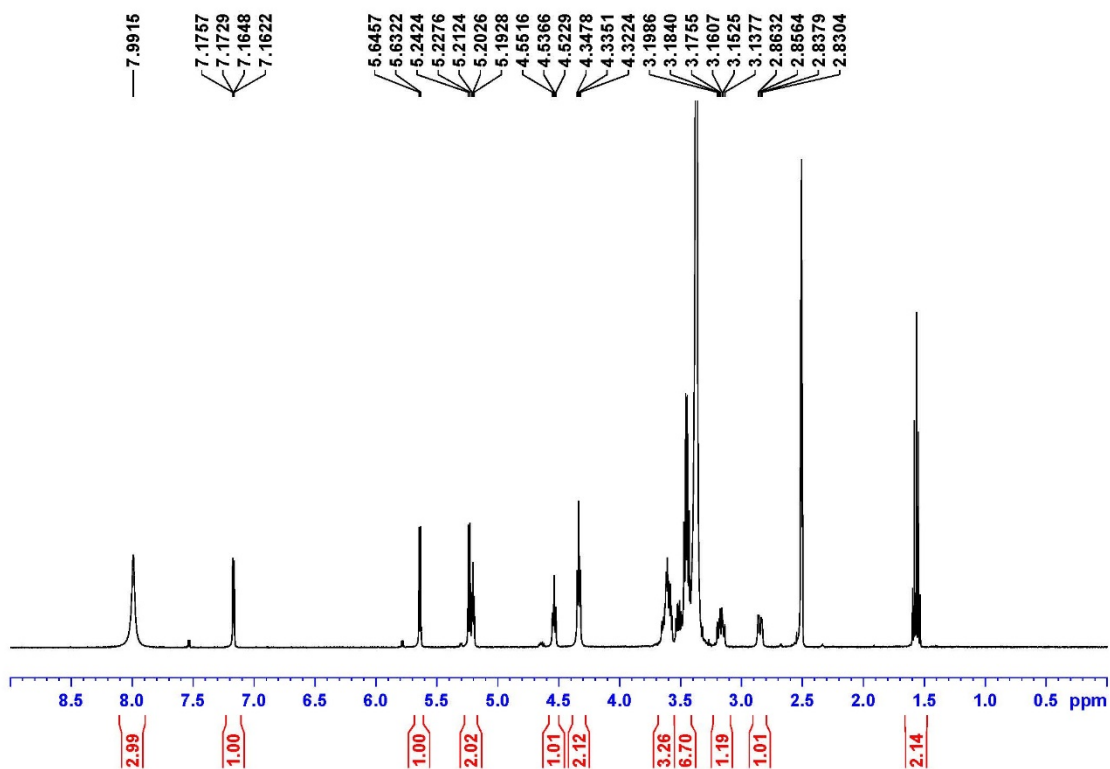


**Figure S18.** Full 1D NMR spectra of 12.5 mM GlcN and 25 mM Glyc in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T).

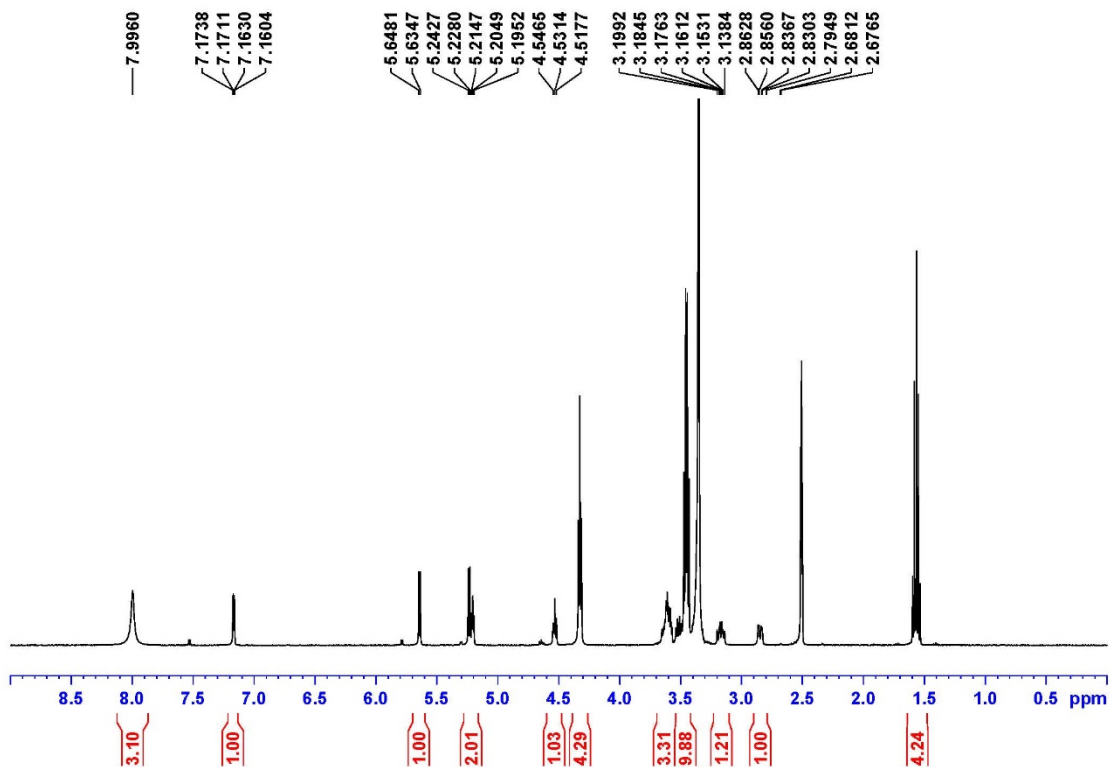


**Figure S19.** Full 1D NMR spectra of 12.5 mM GlcN and 6.25 mM 1,3-PD in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T).

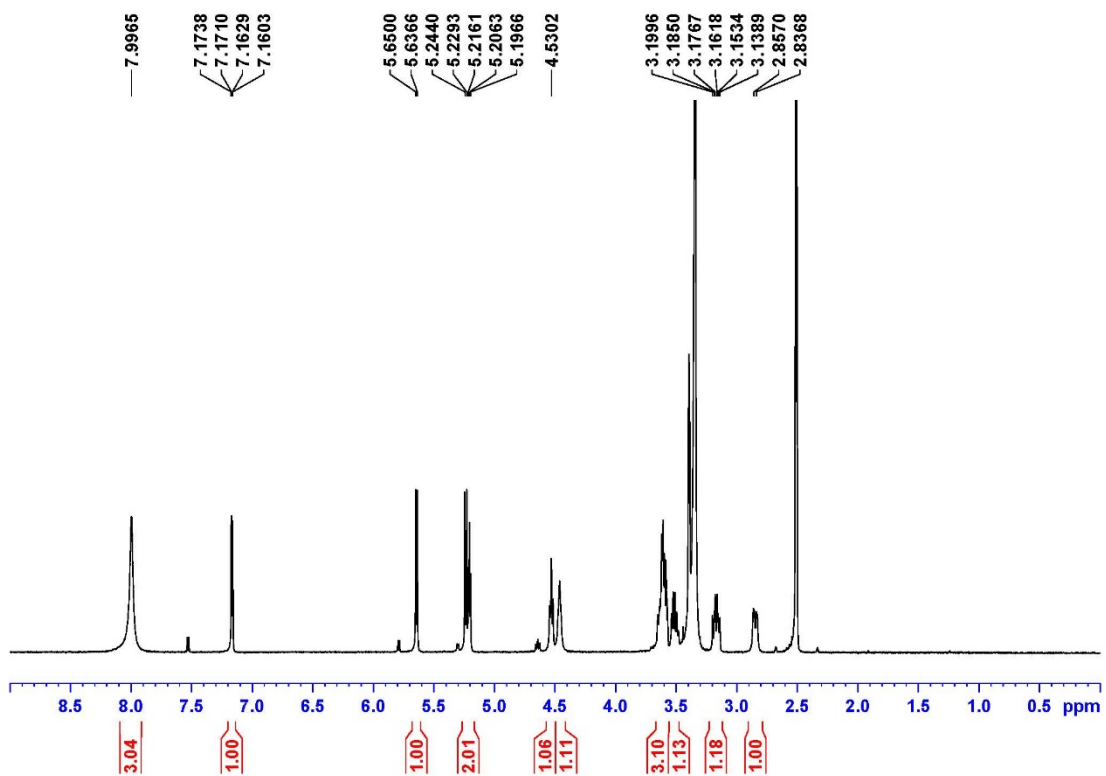




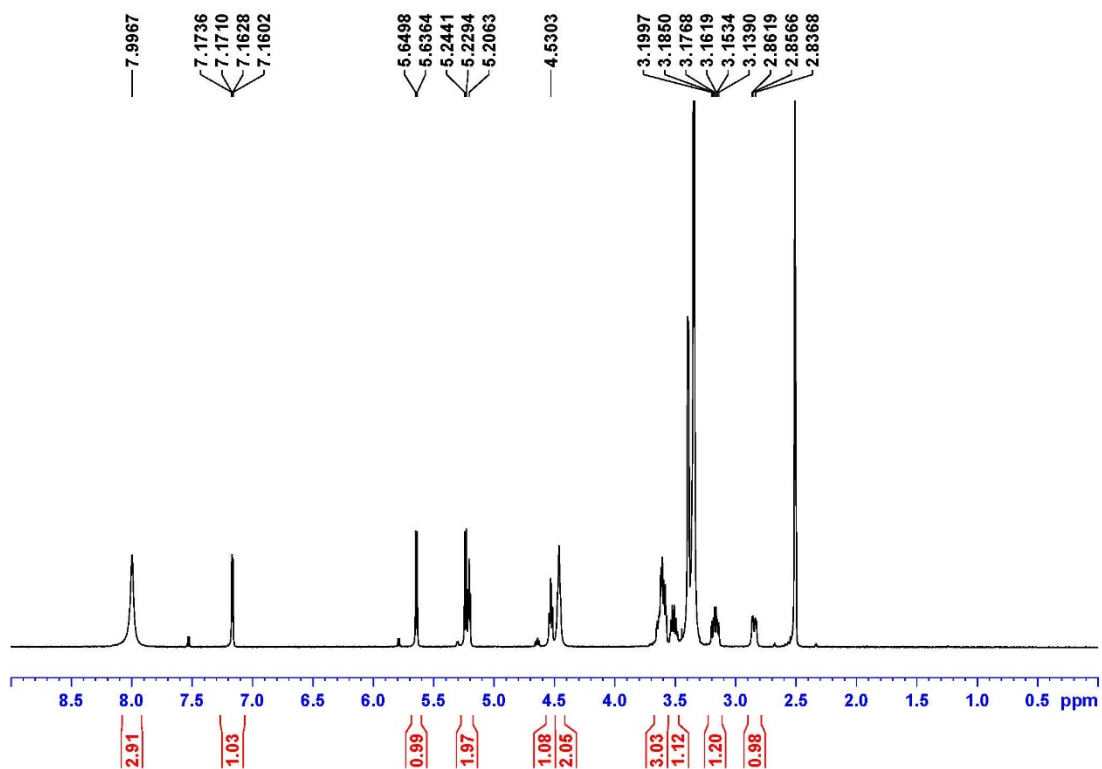
**Figure S20.** Full 1D NMR spectra of 12.5 mM GlcN and 12.5 mM 1,3-PD in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T).



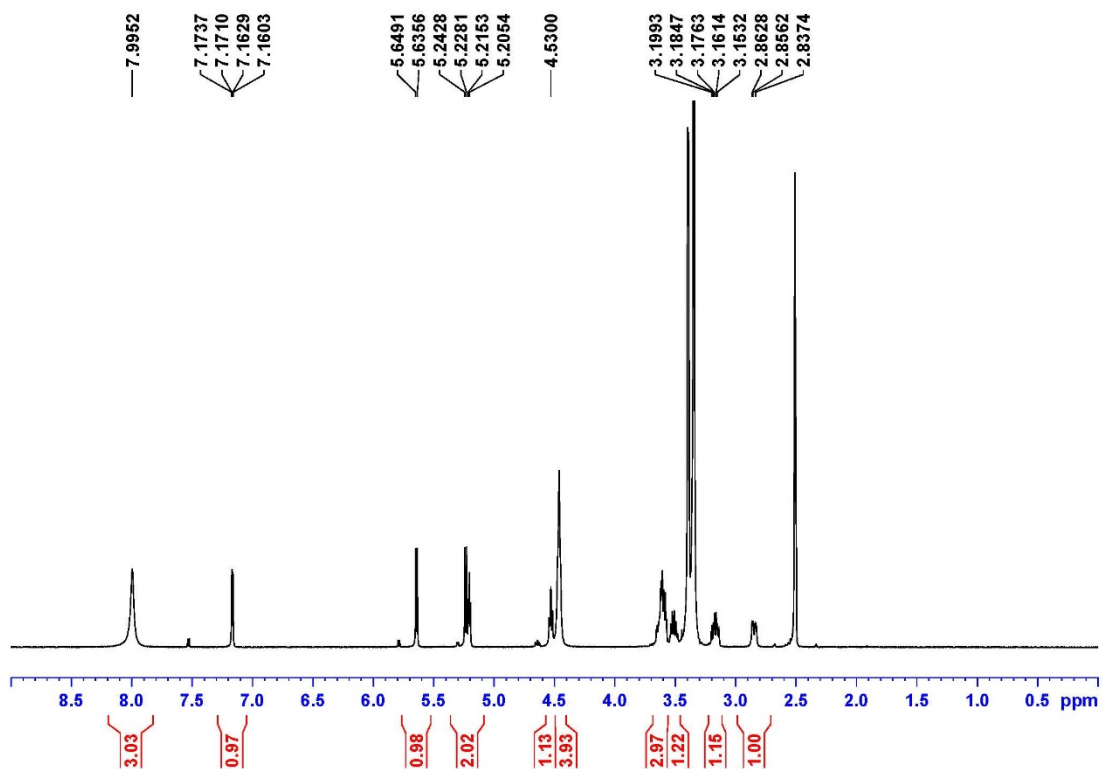
**Figure S21.** Full 1D NMR spectra of 12.5 mM GlcN and 25 mM 1,3-PD in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T).



**Figure S22.** Full 1D NMR spectra of 12.5 mM GlcN and 6.25 mM EG in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T).



**Figure S23.** Full 1D NMR spectra of 12.5 mM GlcN and 12.5 mM EG in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T).



**Figure S24.** Full 1D NMR spectra of 12.5 mM GlcN and 25 mM EG in d<sub>6</sub>-DMSO recorded at 400 MHz (9.4 T).