Chitosan Hydrogelation with a Phenothiazine based Aldehyde – a Synthetic Approach toward Highly Luminescent Biomaterials

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To calculate the NH_2/CHO molar ratio, the number of moles of glucosamine units into the chitosan has been calculated taking into consideration the degree of deacetylation, using the equation $N = \frac{m}{0.83X162 + 0.17X204} X0.83$ (eq. 1)

where N: number of the glucosamine moles; m: amount of chitosan used in reaction; 0.83: fraction of glucosamine units; 162: molecular weight of the glucosamine unit; 0.17: fraction of N-acetylglucosamine units; 204: molecular weight of the N-acetylglucosamine unit.

To have an insight on the amount of aldehyde transformed into imine bonds during the hydrogelation process, the conversion has been calculated with equation:

$$\eta\%\ (C\underline{H}O \rightarrow C\underline{H}{=}N) = \frac{Mi - Mr}{Mi} x100 \quad \text{(eq. 2)},$$

where Mi is the amount of aldehyde used for hydrogel obtaining, and Mr represents the amount of aldehyde removed during the hydrogels washing, found as the difference between the initial amount of reagents (chitosan and aldehyde) and the amount of xerogel. This calculation supposed the total removal of the aldehyde during the washing and lyophilization processes.

Taking into consideration the conversion of the aldehyde into imine units, the conversion of the amine units into imine units has been calculated with the equation:

$$\eta\%\ (NH_2 \rightarrow CH{=}N) = \frac{\eta\%\ (CHO \rightarrow CH = N)}{100 X n NH2} X100 \quad \text{(eq. 3)},$$

where nNH_2 is the number of glucosamine moles from the NH_2/CHO molar ratio used for hydrogel obtaining.

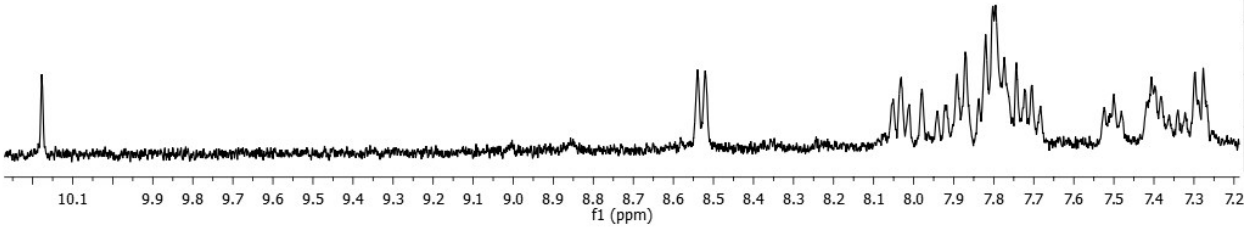
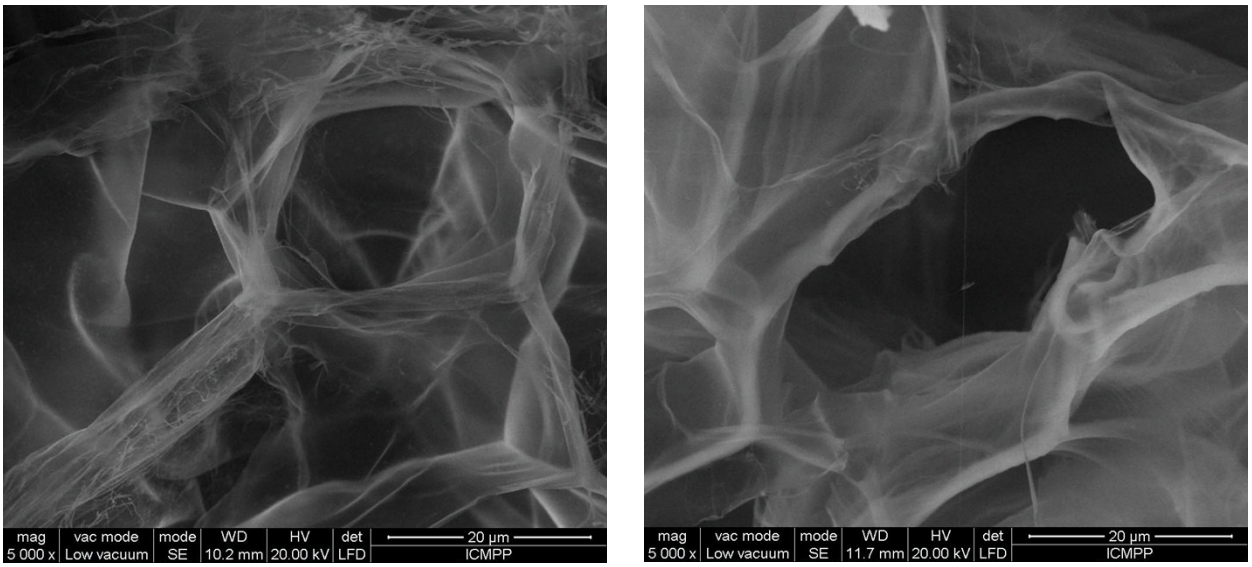


Figure 1s. ^{1}H-NMR spectrum of the **CPA1** hydrogel



CPA1 **CPA5**

Figure 2s. SEM images of the xerogels

Table 1s. Stoks shift of the hydrogels calculated for the three absorption maxima

Code	λ_{abs1} (nm)	λ_{em1} (nm)	Stokes shift 1 (nm)	λ_{abs2} (nm)	λ_{em2} (nm)	Stokes shift 2 (nm)	λ_{abs3} (nm)	λ_{em3} (nm)	Stokes shift 3 (nm)
CPA1	360	523	**163**	395	529	**134**	481	529	**48**
CPA2	360	522	**162**	393	529	**136**	487	527	**40**
CPA3	360	523	**163**	395	525	**130**	484	533	**49**
CPA4	360	524	**164**	390	531	**141**	480	529	**49**
CPA5	360	524	**164**	406	532	**126**	479	537	**58**

Table 2s. Stoks shift of the xerogels calculated for the three absorption maxima

Code	λ_{abs1} (nm)	λ_{em1} (nm)	Stokes shift 1 (nm)	λ_{abs2} (nm)	λ_{em2} (nm)	Stokes shift 2 (nm)	λ_{abs3} (nm)	λ_{em3} (nm)	Stokes shift 3 (nm)
CPA1	360	515	**155**	395	513	**118**	481	551	**70**
CPA2	360	533	**173**	393	508	**115**	487	543	**56**
CPA3	360	500	**140**	395	535	**140**	484	540	**56**
CPA4	360	542	**192**	390	538	**148**	480	529	**49**

CPA5	360	545	**185**	406	544	**138**	479	539	**60**