

## The influence of the hydroxyl type on crosslinking process in cyclodextrin based polyurethane networks

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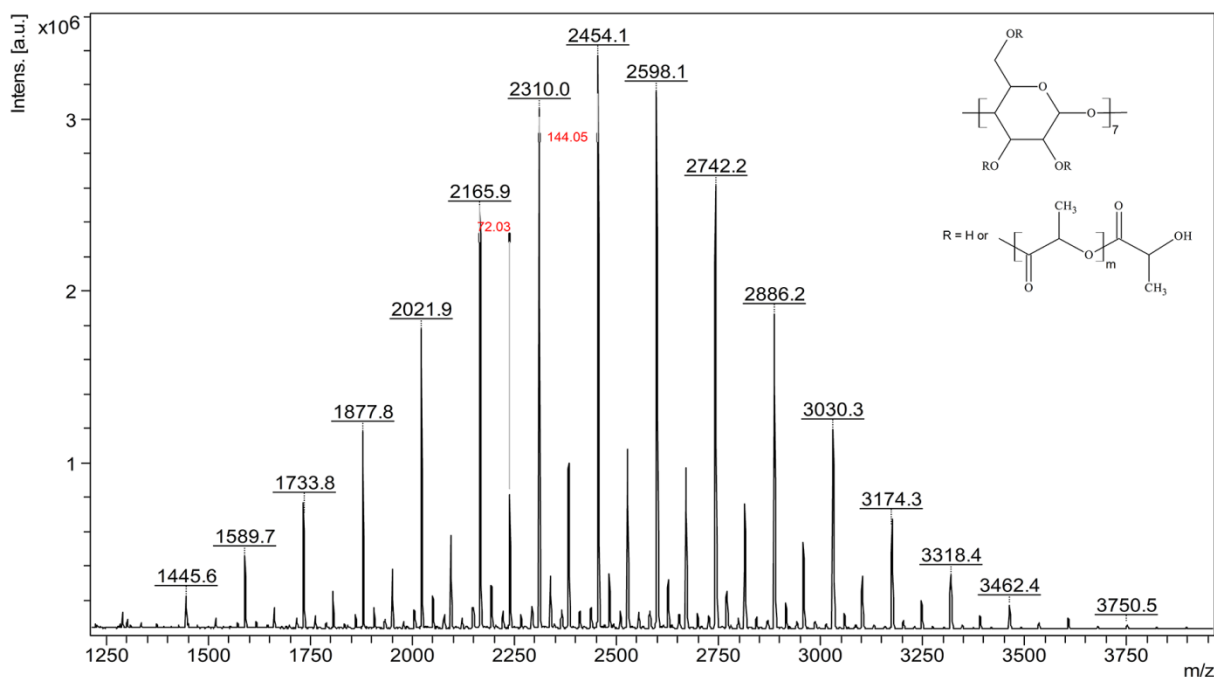
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### Contents:

- CDLA characterization - **Figs. S1** - page S2
- Synthesis of PEG-(NCO)<sub>2</sub> – **Scheme S1**– page S3
- FTIR spectra of hydrogels – **Fig. S3** – page S4
- The degradation curves for CDLA, PEG, hydrogels G, hydrogels B – **Figs. S3-S16, Table S31** – pages S5-S9
- Dependence of swelling degree on temperature – **Fig. S7** – page S10
- Degradation of hydrogels – **Figs. S8, S9** – pages S11, S12
- References – page S13

## CDLA synthesis and characterization

In the MALDI-MS spectrum of CDLA product employed in our study, presented in **Figure 1**, there may be observed two types of peaks: a series of intense peaks, with a difference between two consecutive peaks of 144 Da, corresponding to one lactide unit (or 2 lactate units) and a second series of peaks, of lower intensity, located between the more intense peaks, at a difference of 72 Da from the neighboring peaks. The high intensity peaks represent CDLA species with  $m/z = 1134 (\beta\text{-CD}) + n \cdot 144 (\text{bi-lactate}) + 23 (\text{Na})$  and the low intensity peaks represent also CDLA species with  $m/z = 1134 (\beta\text{-CD}) + n \cdot 72 (\text{lactate}) + 23 (\text{Na})$ , where  $n$  has odd values.

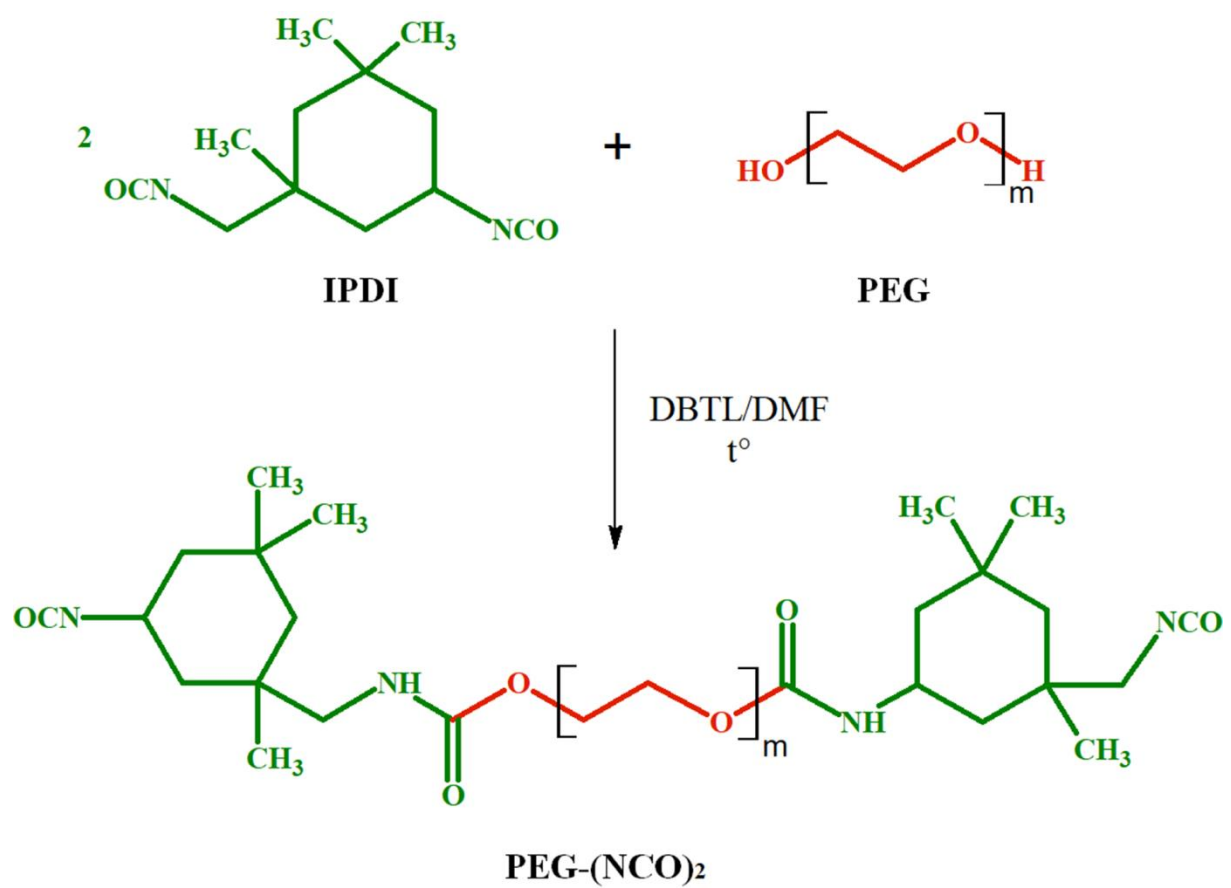


**Figure S1.** MALDI MS spectrum of CDLA

Based on the acquired MS spectrum it was possible to determine the numerical average molecular weight,  $M_n = 2443$  g/mol, the gravimetric average molecular weight,  $M_w = 2526$  g/mol, and the dispersity index,  $\bar{D} = 1.033$ . This is corresponding to a CDLA product with approximately 8 units of LA, covalently linked to CD.

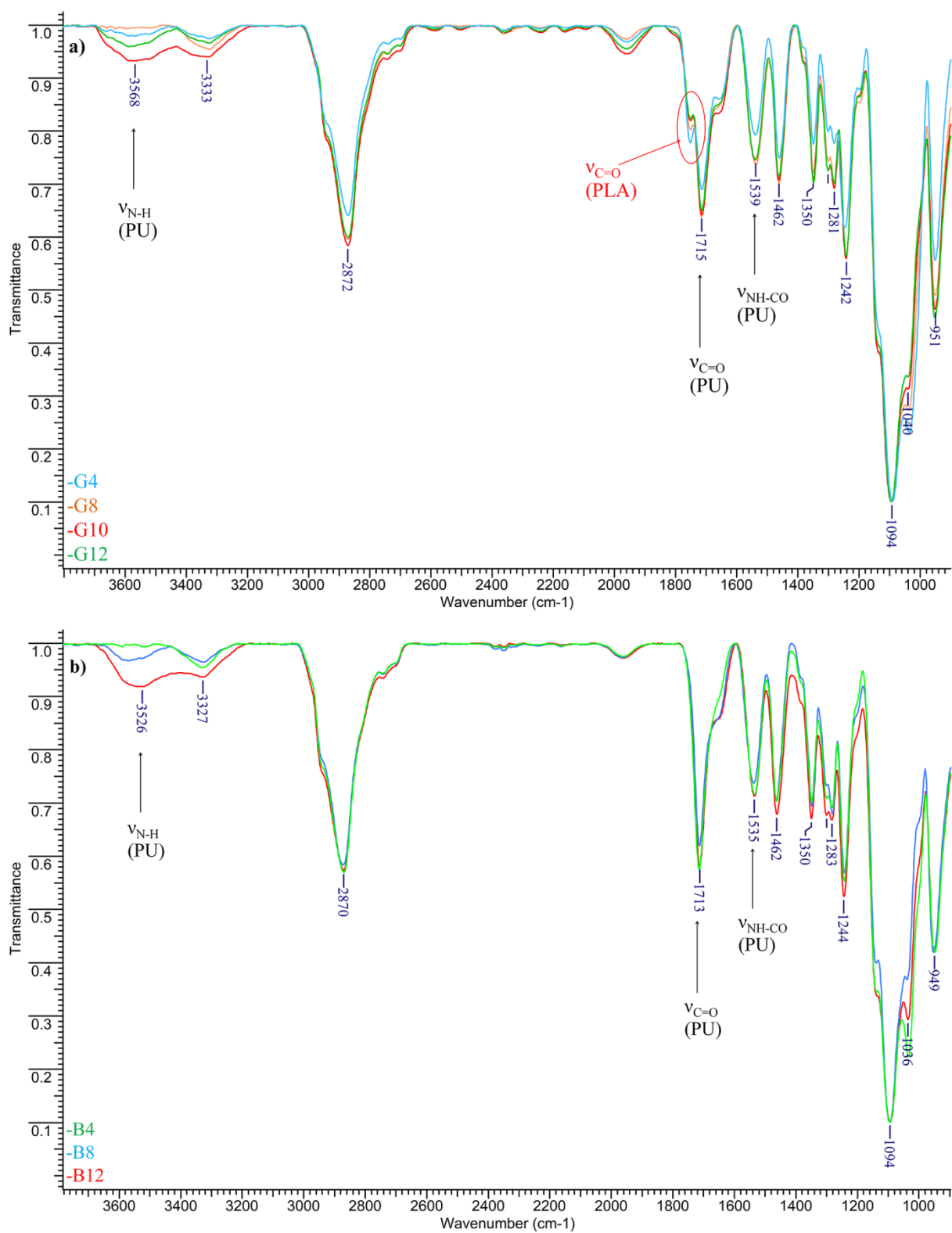
### **Synthesis of PEG-(NCO)<sub>2</sub>**

**Scheme S1** shows the reaction between PEG and IPDI with the formation of the desired compound (PEG-(NCO)<sub>2</sub>), 2 molecules of IPDI bound to a molecule of PEG (functionalized PEG containing 2 isocyanate groups, required for the subsequent cross linking reaction).



**Scheme S1.** Synthesis of PEG-(NCO)<sub>2</sub> prepolymer

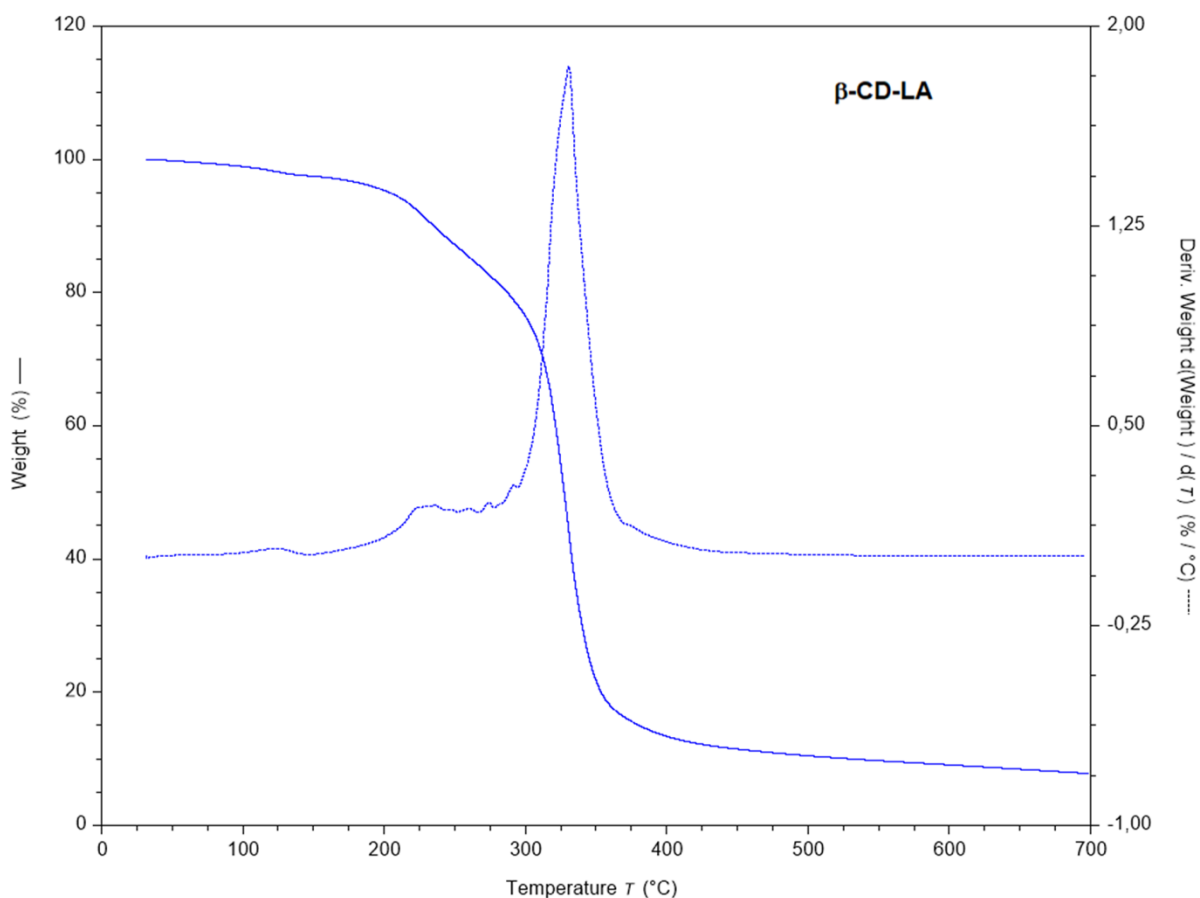
FTIR spectra of hydrogels



**Figure S2.** FTIR spectra of CDLA-PEG (a) and CD-PEG (b)

**The thermal degradation curves**

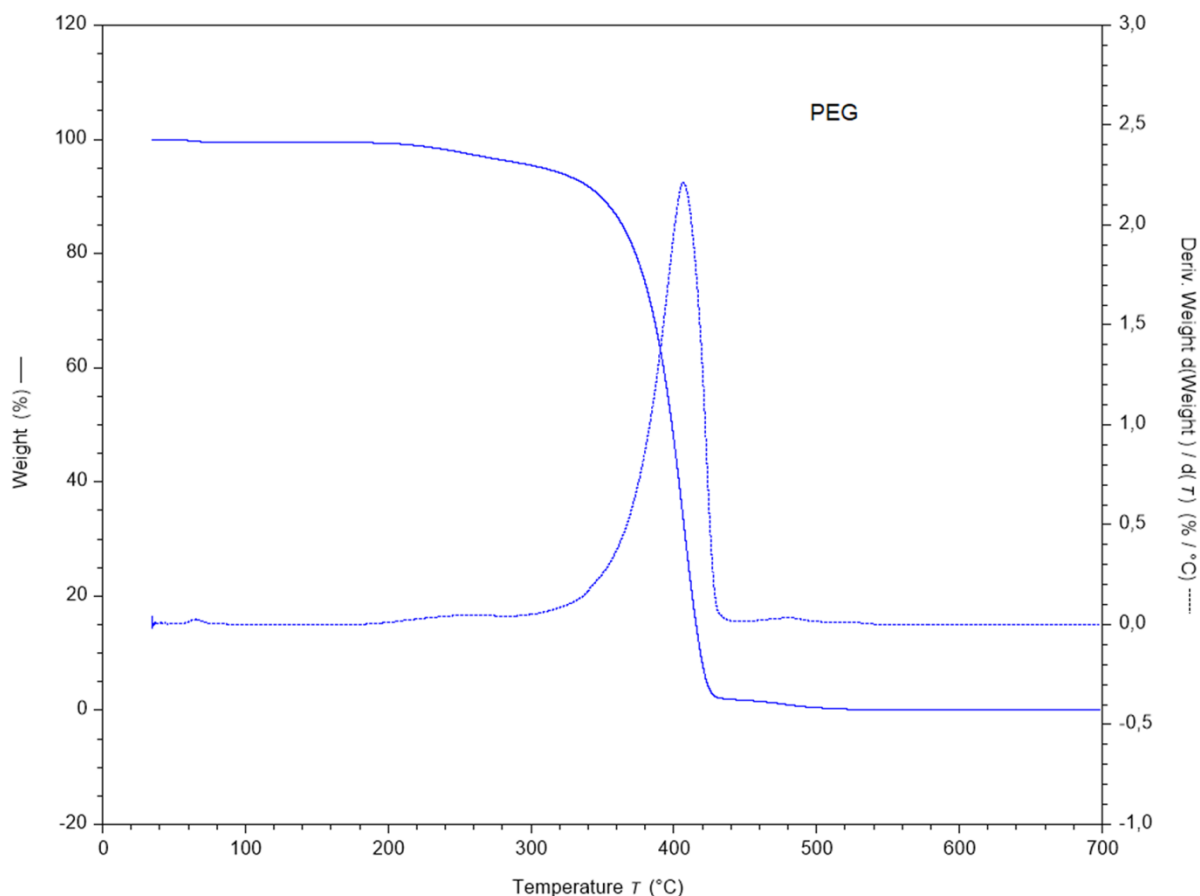
Usually, thermal degradation of  $\beta$ -CD occurs in two steps. The first region corresponds to water vaporization (60-100 °C or even above 100 °C), while the second region is attributed to the decomposition of cyclodextrin itself ( $T > 270$  °C) [2,3]. **Figure S3** depicts the thermal behavior of the CDLA synthesized in the first stage of the reaction and details are found in the **Table S1**.



**Figure S3.** The degradation curves for the CDLA precursor

The onset of thermal degradation of PLA depends on its nature and processing method and is reported to be around 325 °C.

The PEG used in the synthesis starts to degrade close to 400 °C (**Figure S4**, **Table S1**).



**Figure S4.** The degradation curves for the PEG used in the synthesis

The interpretation of the TGA spectra of the samples was done considering the above preliminary information.

**Table S1** contains all the degradation data for the samples B4, B8, B12, G4, G8, G10, G12, CDLA and PEG:

- the temperature range of the degradation steps and the peak of the corresponding derivative, equivalent with the maximum rate of mass loss;
- the decomposition temperatures  $T_5$  and  $T_{10}$ , that express the point where 5% and 10% of the total mass is lost from the sample; currently, the degradation temperature is considered to be  $T_5$ .

- the mass loss at 275 °C, 375 °C, 650 °C; the values of temperatures are chosen in order to reflect the behavior after the main degradation steps.

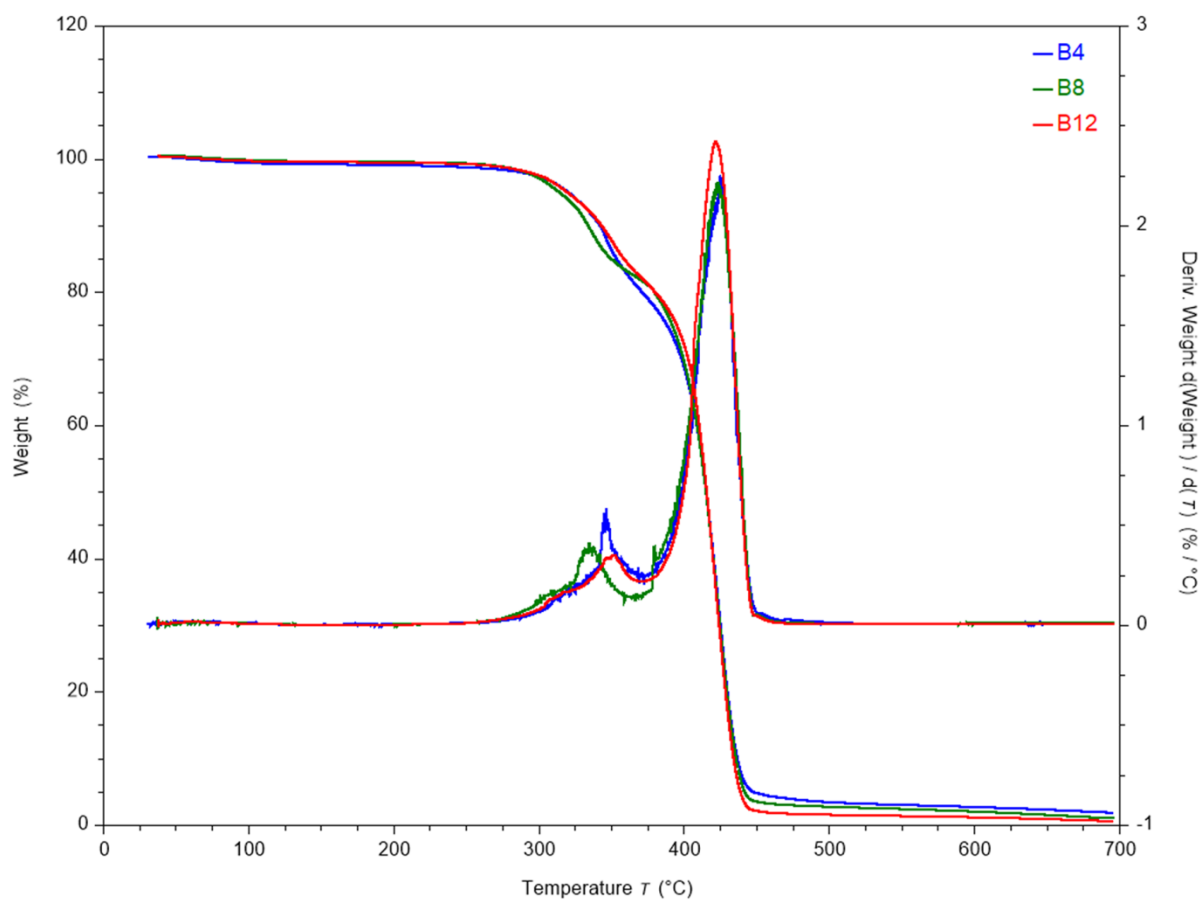
**Table S1.** Degradation data from TG and DTG curves.

#Sampl e	Degradation range		Peak	T <sub>5</sub>	T <sub>10</sub>	weight loss (%)		
		(°C)	(°C)	(°C)	(°C)	275 °C	375 °C	650 °C
CDLA	Step 1	190 – 250	223.1	<b>204.1</b>	235.3	17.46	84.35	91.56
	Step 2	275 - 370	330.8					
PEG	Step 1	310 - 440	329,3	<b>308.3</b>	348.7	3.41	21.18	99.99
B4	Step 1	-	-	<b>320.2</b>	342.5	1.63	20.92	97.73
	Step 2	285 - 370	345.9					
	Step 3	375 - 450	425.6					
B8	Step 1	-	-	<b>314.3</b>	334.2	1.17	18.89	98.51
	Step 2	270 - 360	335.0					
	Step 3	360 - 460	423.3					
B12	Step 1	-	-	<b>319.7</b>	343.3	1.24	18.77	99.14
	Step 2	290 – 370	351.1					
	Step 3	370 - 470	422.2					
G4	Step 1	200 – 260	249.0	<b>282.0</b>	319.2	4.37	26.1	98.16
	Step 2	267 – 375	344.4					
	Step 3	375 - 460	422.4					
G8	Step 1	190 – 245	228.2	<b>294.8</b>	323.6	3.65	22.83	98,92
	Step 2	270 – 365	346.2					
	Step 3	365 - 456	421.9					
G10	Step 1	**	-	<b>283.6</b>	316.0	4.38	25.4	98.6
	Step 2	280-361	334.0					

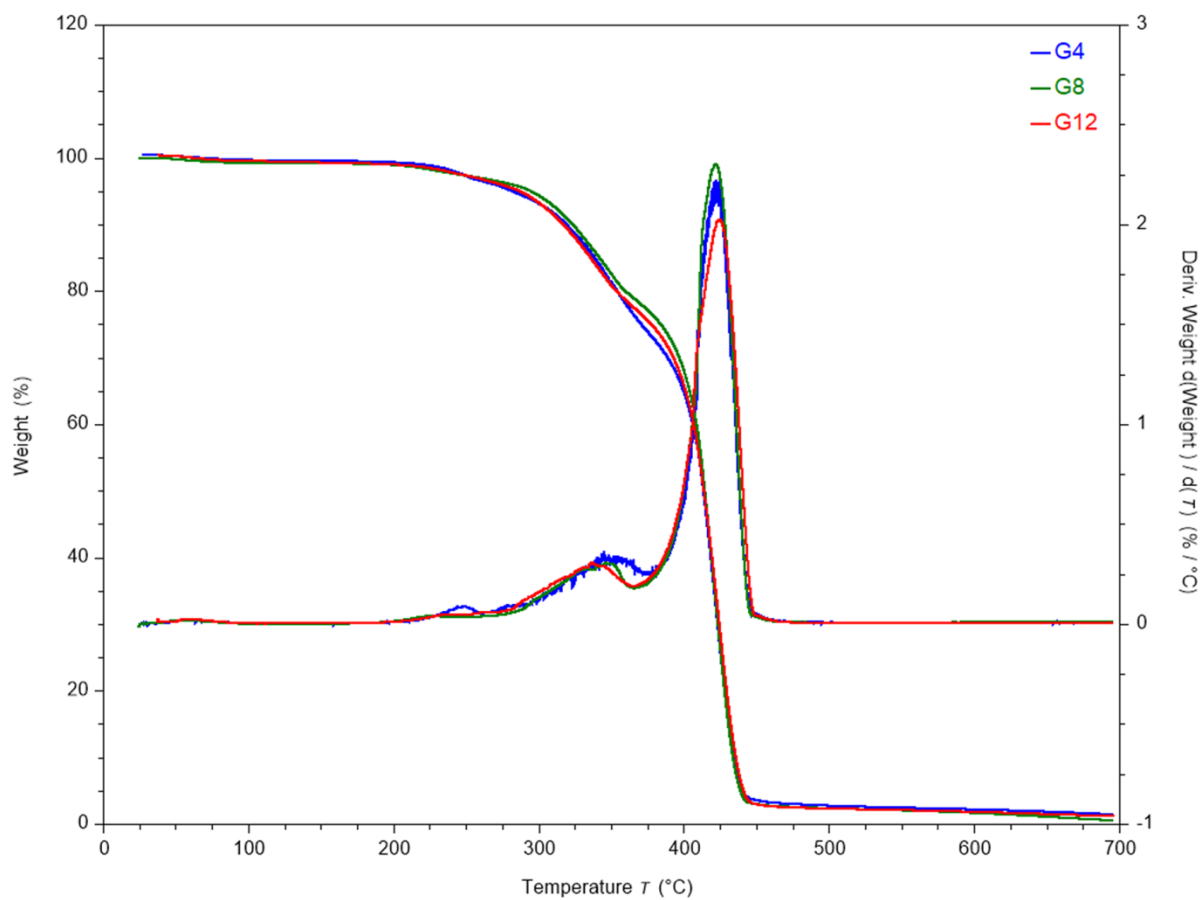


	Step 3	369-451	423.5					
	Step 1	**	239.4					
G12	Step 2	275 -365	337.4	287.2	317.0	4.06	24.4	98.52
	Step 3	365 - 450	424.7					

\*\*faint shoulder in derivative TGA

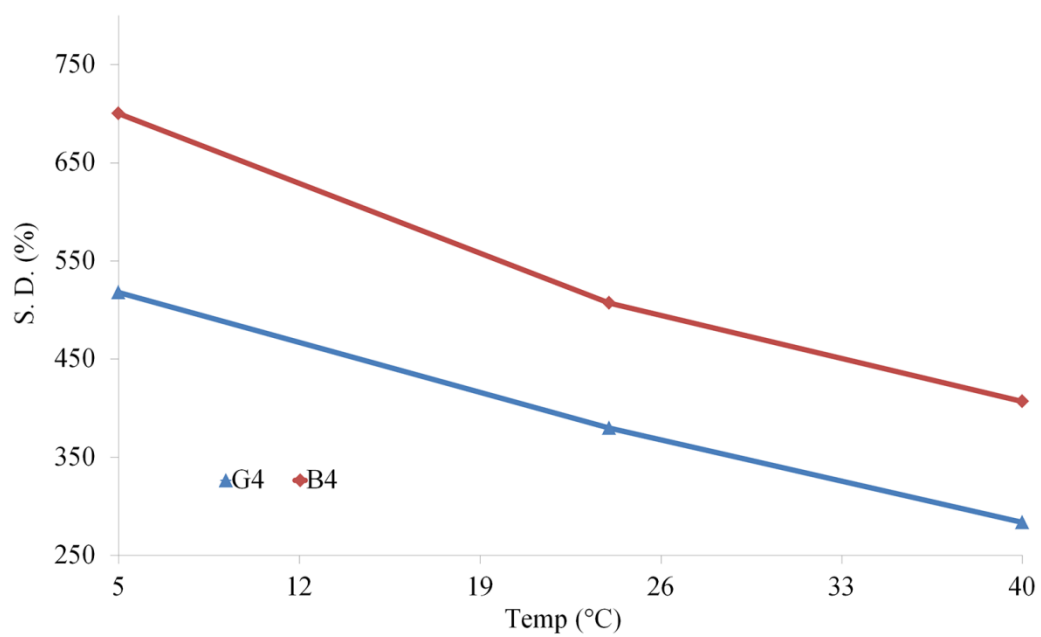


**Figure S5.** The thermal degradation curves of CD-PEG samples



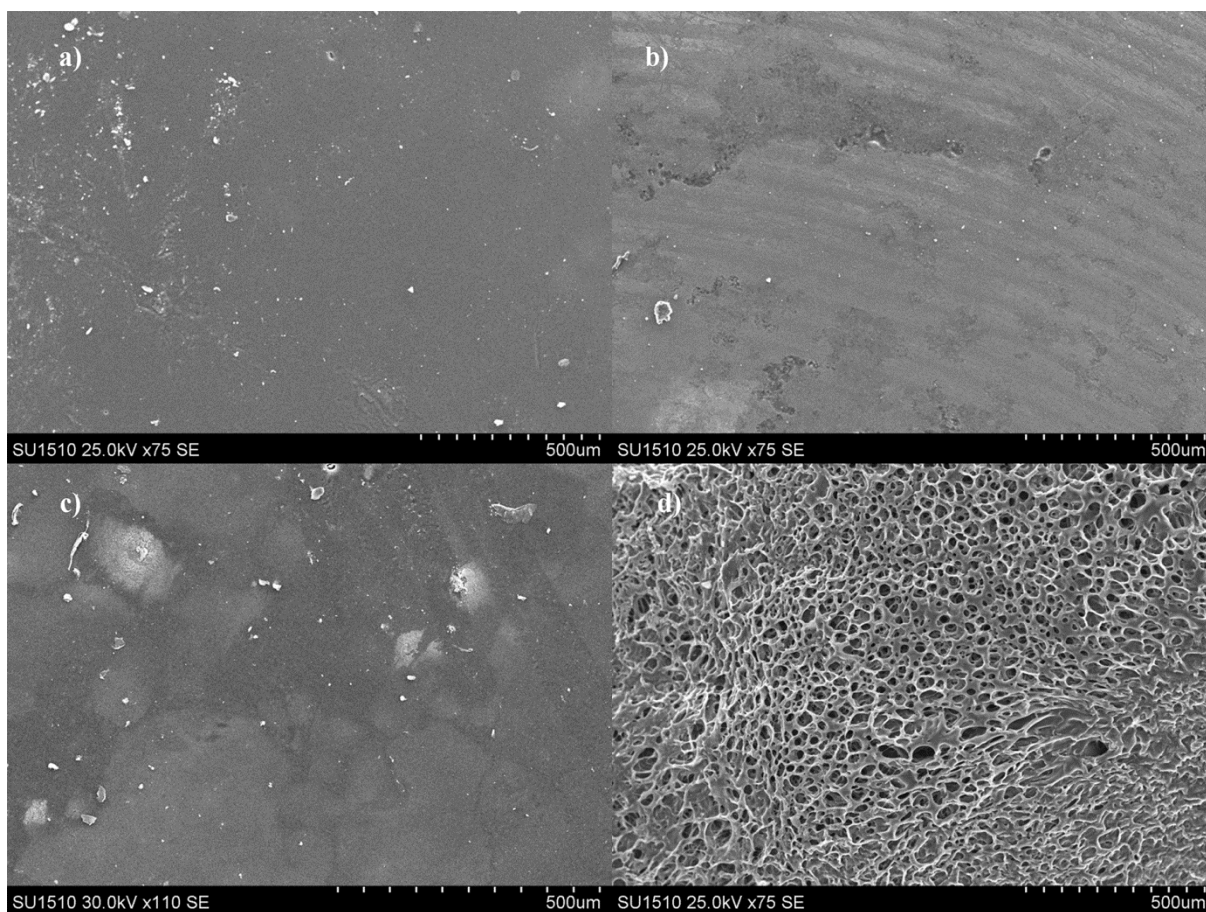
**Figure S6.** The thermal degradation curves obtained for the CDLA-PEG samples

### Dependence of swelling degree on temperature

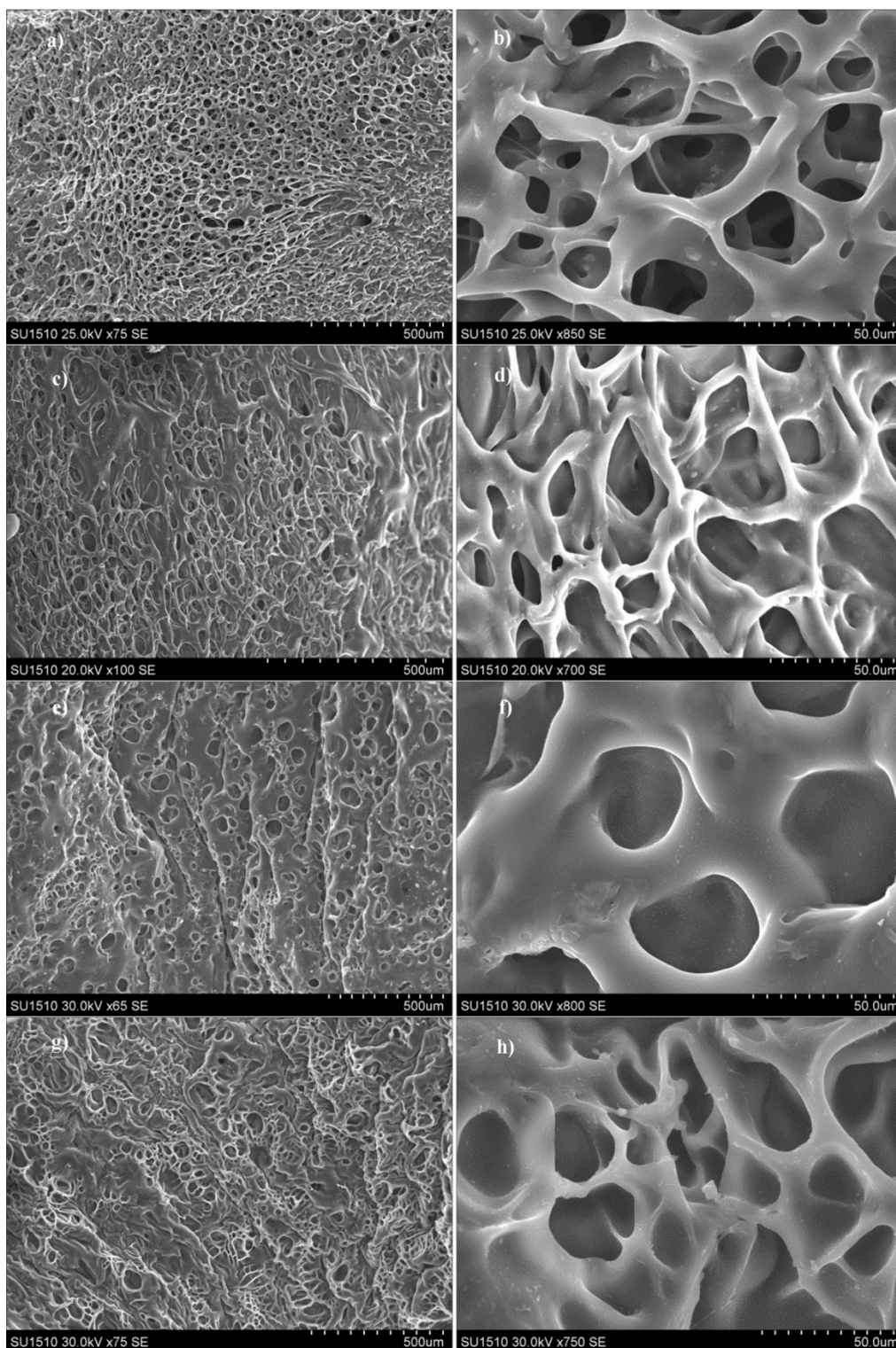


**Figure S7.** Dependence of swelling degree on temperature of CD-PEG (B4) and CDLA-PEG (G4) hydrogels

## Hydrolytic degradation of hydrogels



**Figure S8.** Surface micrographs for CD-PEG – (a) B8 initial, (b) B8 after 193 days, and CDLA-PEG – (c) G4 initial, (d) G4 after 193 days



**Figure S9.** Surface micrographs after 193 days of degradation for CDLA-PEG: G4 at (a) 500μm and (b) 50μm, G8 at (c) 500μm and (d) 50μm, G10 at (e) 500μm and (f) 50μm, G12 at (g) 500μm and (h) 50μm

## References

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