Supporting information

Synthesis and characterization of redox hydrogels based on stable nitroxide radicals

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Table S1. Library of different aspect obtained by free radical polymerization according to two parameters: X_{TEMPO} and X_{CL}.

Fig. S1 Typically ^{1}H-NMR spectra of the supernatant of the polymerisation medium for the investigated P(TMPM-*r*-OEGMA) hydrogels after overnight polymerization. (X_{TEMPO}=0.2; X_{CL}=0.03)

Fig. S2 Typical ^{1}H-NMR spectra for all the non-oxidized P(TMPM-*r*-OEGMA) after overnight polymerization. (Gels are swelled directly in NMR tube to reach equilibrium and homogenous aspect before analysis). (X_{TEMPO}=0.2; X_{CL}=0.03).

Fig. S3 Typical infrared (FTIR) spectra for all the oxidized P(TEMPO+-*r*-OEGMA) (red curve) and all the radical form P(TEMPO-*r*-OEGMA) (blue curve) hydrogels. (X_{TEMPO}=0.4; X_{CL}=0.03).

Fig. S4 Cryo-TEM image for a P(TEMPO-*r*-OEGMA) hydrogel (X_{TEMPO}= 0.2 and X_{CL}=0.03) (sample diluted).

Fig. S5 The equilibrium-swelling factor of the hydrogels for different cross-linker equivalents.

X_{TEMPO} / X_{CL}	0,1	0,2	0,3	0,4
0,014	Liquid	Liquid	Visco-elastic liquid	Visco-elastic liquid
0,02	liquid	liquid	Visco-elastic liquid	Visco-elastic liquid
0,03	Gel	Gel	Gel	Gel
0,04	Gel	Gel	Gel	Gel
0,05	Gel	Gel	Gel	Gel

Table S1. Library of different aspect obtained by free radical polymerization according to two parameters: X_{TEMPO} and X_{CL}.

In Table S1, all the synthetized hydrogels are listed in accordance to the two parameters described: X_{TEMPO} and X_{CL}. A threshold in cross linker seems to be needed to obtain a hydrogel. This threshold is equal to 0.03 for all the tested X_{TEMPO}.
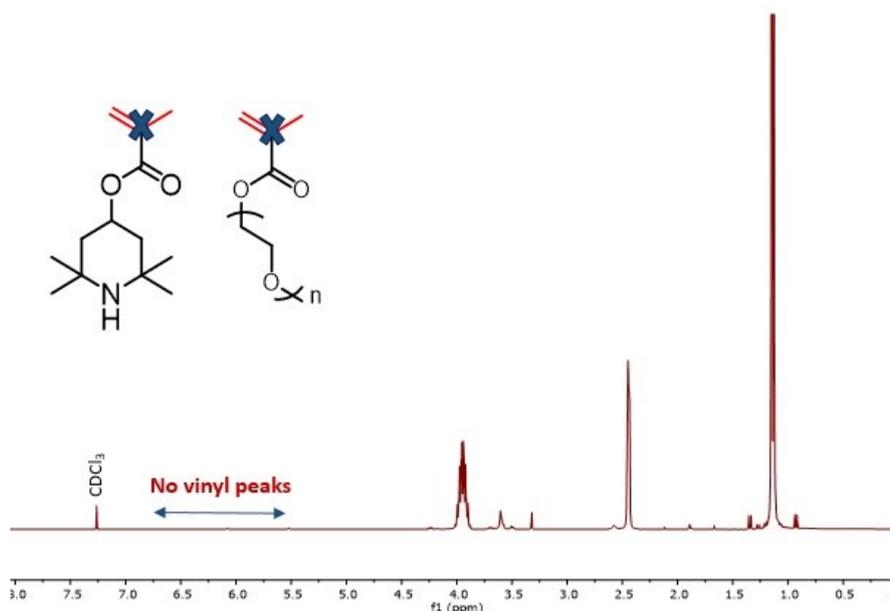
Fig. S1 Typically ^{1}H-NMR spectra of the supernatant of the polymerisation medium for the investigated P(TMPM-r-OEGMA) hydrogels after overnight polymerization. (X_{TEMPO}=0.2; X_{CL}=0.03)

^{1}H NMR experiments were conducted by taking samples from the supernatant of the overnight polymerization medium. The spectrum reveals no vinyl peaks (around 4.6 - 6.5 ppm). This absence of vinyl peaks informs us that the monomers were fully consumed during the polymerization with a conversion rate above 99%. Same results were obtained for all the synthetized networks.
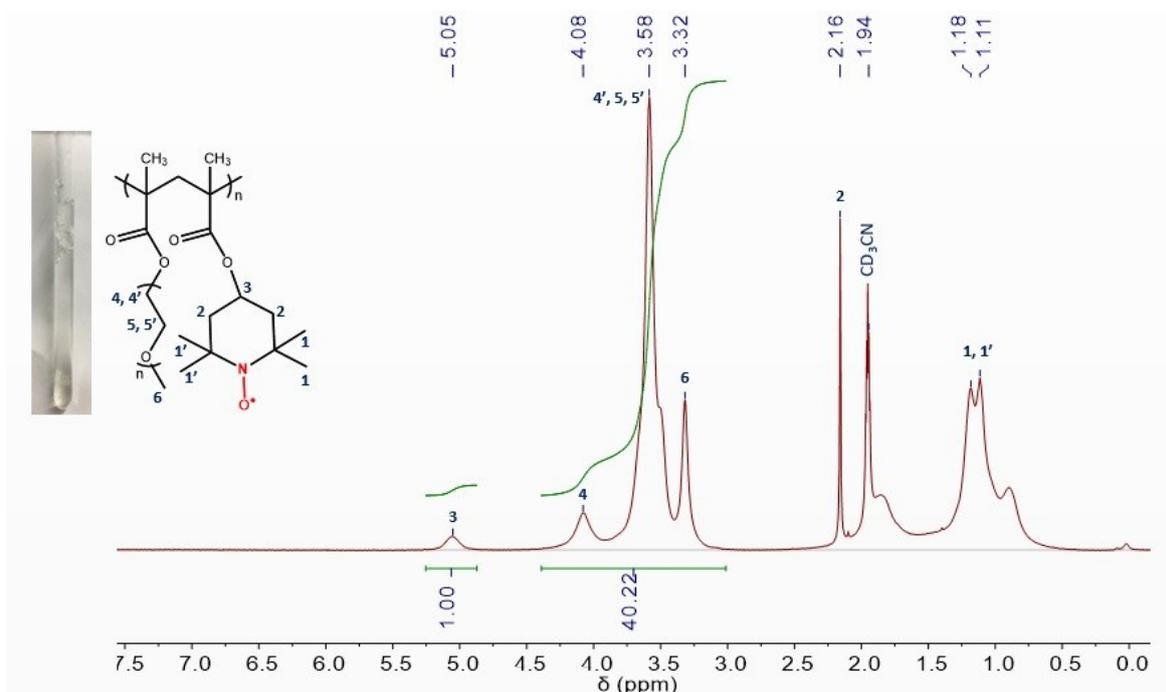
Fig. S2 Typical ^{1}H-NMR spectra for all the non-oxidized P(TMPM-*r*-OEGMA) after overnight polymerization. (Gels are swelled directly in NMR tube to reach equilibrium and homogenous aspect before analysis). (X_{TEMPO}=0.2; X_{CL}=0.03).

^{1}H-NMR (300 MHz, CD$_3$CN) δ(ppm): 5.05 (s, 1H$_3$), 4.08 (s, 2H$_4$), 3.58 (m, 22H$_{4',5,5'}$), 3.32 (s, 3H$_6$), 2.16 (s, 4H$_2$), 1.18 (s, 6H$_1$), 1.11 (s, 6H$_{1'}$).
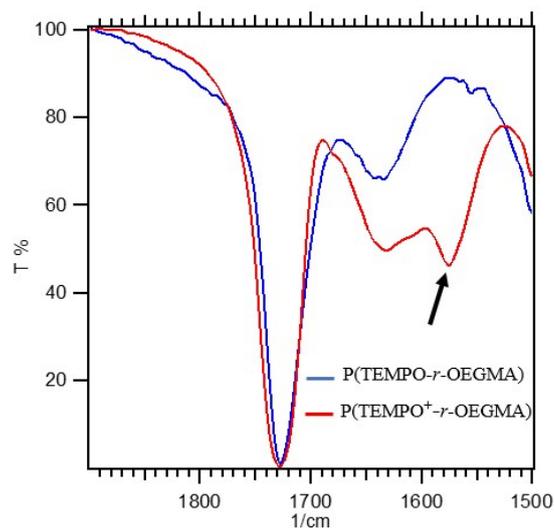
Fig. S3 Typical infrared (FTIR) spectra for all the oxidized P(TEMPO$^+$-*r*-OEGMA) (red curve) and all the radical form P(TEMPO-*r*-OEGMA) (blue curve) hydrogels. (X_{TEMPO}=0.4; X_{CL}=0.03).

Infrared (FTIR) spectra were recorded to confirm the presence of TEMPO$^+$ in our hydrogels. Known in the literature, that nitroso bond (N═O) appear at 1570 1/cm and N-O appear at 1540 1/cm. The IR spectra of our hydrogels in radical and charged state, confirm the value of this peaks.
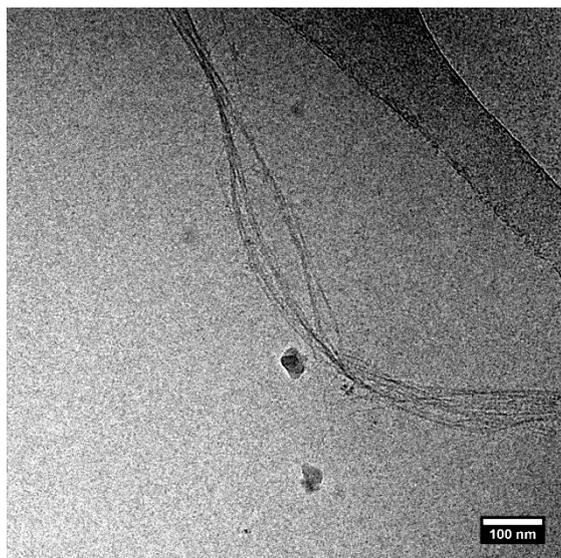
Fig. S4 Cryo-TEM image for a P(TEMPO-*r*-OEGMA) hydrogel (X_{TEMPO}= 0.2 and X_{CL}=0.03) (Sample diluted).

According to the cryo-TEM picture, the TEMPO hydrophobic domains are nanosized with a diameter of a few nanometers. Nevertheless, we have no clue to explain why fibrillar domains have been observed. This could be an artifact resulting from sample preparation since the original hydrogel samples had to be diluted to allow sample preparation for the cryo-TEM experiments.
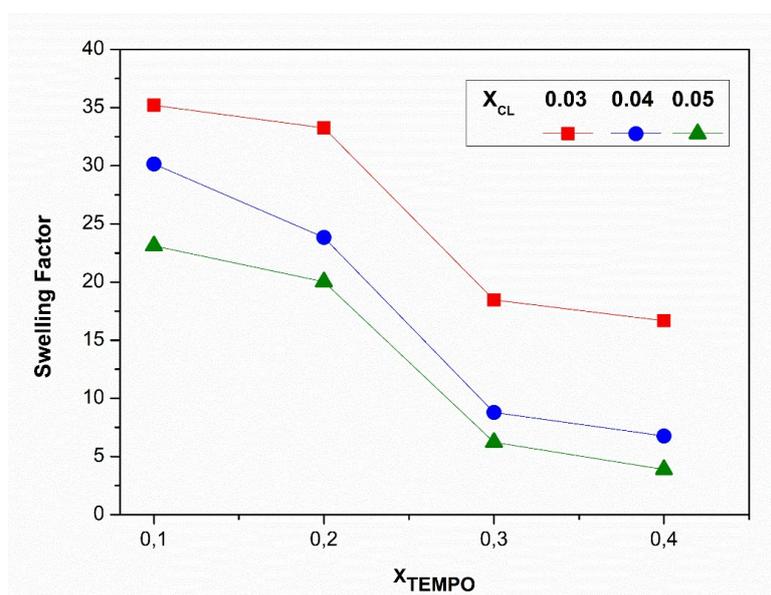
Fig. S5 The equilibrium-swelling factor of the hydrogels for different cross-linker equivalent.

For all the hydrogels tested and shown in Fig. S1, the hydrogels prepared with X_{CL} 0.03 present the best results with a swelling factor around 35. The increase of cross linker ratio leads to a decrease of the capacity of 3D polymer network to retain water. This could be explained by the decrease in the mesh size of the network.