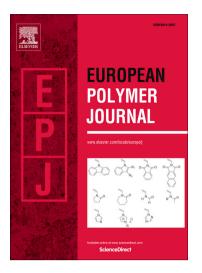
### Accepted Manuscript

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## ACCEPTED MANUSCRIPT

# Tunable hydrophilicity of redox D-mannitol-based polyurethanes modulates glutathione response

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#### ABSTRACT

Disulfide bond-containing polymers are the most widely explored stimuliresponsive materials used as drug delivery carriers, especially in cancer therapeutics. However, they are conditioned by a process of biodegradation under hypoxic physiological microenvironments of cancer cells, where higher levels of the reductant glutathione are present. Furthermore, it is well known that hydrophilicity enhances degradation of disulfide linkage-containing materials in aqueous media, such as physiological conditions. In this context, a series of disulfide bond-containing homoand co-polyurethanes has been synthesized by the polyaddition reaction of 3,4-Oisopropylidene-D-mannitol and/or 2,2'-dithiodiethanol to 2,2'-dithiodiethyl diisocyanate, in THF at room temperature, in good yields. The obtained polyurethanes have average molecular weights in the 23000-97000 g mol<sup>-1</sup> range, with narrow polydispersities. Hydrophilicity of these materials is provided by the content of free hydroxyl groups in the polymer backbones, in partially or totally unprotected D-mannitol moieties, which could be achieved by copolymerization followed by O-deprotection processes. Glutathione-mediated degradation studies of these materials showed how the ratio of hydroxyl to disulfide groups modulates the response of this bio-redox regulator.

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