Supporting Information

Amphiphilic tri- and tetra-block co-polymers combining versatile functionality with facile assembly into cytocompatible nanoparticles

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**Figure S1.** The synthetic scheme for the production of tert-Butyl (2-oxo-1,3-dioxan-5-yl)carbamate (tBSC).
Figure S2. Representative $^1$H NMR graph (400 MHz, CDCl$_3$) for the ROP of lactide and tBSC initiated by mPEG5000 (P2), showing quantitative polymerisation of both lactide and tBSC after 15 minutes. (A) time = 0 minutes, (B) time = 15 minutes, and (C) post purification.
Figure S3. $^1$H-NMR and $^{13}$C-NMR spectrum with integrations of P2 (mPEG$_{5000}$-(LA)$_{50}$-(tBSC)$_{50}$) as model polymer.
Figure S4. ATR-IR spectra of the five PEGylated ester-carbonate copolymers showing typical peaks of both ester and carbonate functionalities. In particular, C-H stretching in the region between 2900 -2800, C=O<sub>ester</sub> and C=O<sub>carbonate</sub> in the region of 1750 -1680 and the C-O-C bending of the ester and ether (PEG) functionalities at 1100 cm<sup>-1</sup>.
Figure S5. (main) PEGylated copolymers TGA loss profiles. It can be observed three weight loss regions for all the polymers varying according to the length and stability of the PEG chains. (inset) P2 TGA thermogram with derivate-analysis showing three loss weight contributions.
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Figure S15. Cellular effects of (A and C) protected (B and D) and de-protected polymer nanoparticles. Metabolic activity (A and B) of MCF7 cells was determined by PrestoBlue assay, and plasma membrane integrity by the LDH release assay (C and D). Data represents mean ± S.D of triplicates coming from three independent experiments.