Supporting Information for:

Poly(2-ethyl-2-oxazoline)-*block*-polycarbonate block copolymers: From improved endgroup control in poly(2-oxazoline)s to chain extension with aliphatic polycarbonate through a fully metal-free ring-opening polymerisation process

Victor R. de la Rosa^b, Sarah Tempelaar^a, Philippe Dubois^a, Richard Hoogenboom^{b,*}, and Laetitia Mespouille^{a,*}

^a Centre of Innovation and Research in Materials & Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials, HEALTH and MATERIALS Research Institutes University of Mons, Place du Parc 23, B-7000 Mons, Belgium. Email: Laetitia.Mespouille@umons.ac.be

^b Supramolecular Chemistry Group, Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281 S4, B-9000, Ghent, Belgium. Email: Richard.hoogenboom@ugent.be



Figure S1. ¹H-NMR spectra of two different hydroxyl-terminated poly(2-ethyl-2-oxazoline)s (PEtOx_nOH) showing the presence (a) or absence (b) of amine ester end-groups. The peak at 4.0 - 3.5 ppm is ascribed to the methylene group in omega, adjacent to the –OH group.



Figure S2. SEC traces wherein a minor increase of the high molecular weight distribution is observed at high temperatures. Eluent: *N*,*N*-dimethylacetamide. Calibrated against PMMA standards.



Figure S3. SEC data: PEtOx₂₃ (—), PEtOx₂₃-*b*-P(MTC_{Br})₁₄ (—), PEtOx₂₃-*b*-P(MTC_{morph})₂₆ (—), PEtOx₂₃-*b*-PMAC₃₀ (—), PEtOx₂₃-*b*-PMPC (—), PEtOx₂₃-*b*-PMBC₂₇ (—), PEtOx₂₃-*b*-PMPC (_), PEtOx₂₃-*b*-PMBC₂₇ (_), PEtOx₂₃-*b*-PMPC (_), PEtOx₂₃-*b*-PMBC₂₇ (_), PEtOx₂₃-*b*-PMBC₂₇ (_), PEtOx₂₃-*b*-PMPC (_), PEtOx₂₃-*b*-PMBC₂₇ (_), PEtOx₂₇ (_), PEtOx₂₇ (_), PEtOx₂₇ (_), PEtOx₂₇ (_), PEtOx₂₇ (_), PE



Figure S4. SEC data: PEtOx₄₃OH, PEtOx₄₃-*b*-PTMC₄₇ (LD1), PEtOx₄₃-*b*-PMAC₅-*b*-P(MTC_{morph})₅₀ (LT1), PEtOx₄₃-*b*-P(MTC_{morph})₁₉ (LD2), PEtOx₄₃-*b*-P(MTC_{morph})₂₉ (LD3), PEtOx₄₃-*b*-P(MTC_{morph})₄₅ (LD4), PEtOx₄₃-*b*-P(MTC_{morph})₆₀ (LD5).



Figure S5. ¹H NMR data: PEtOx₂₃- block copolymers with (from top to bottom): PTMC, PMBC, PMAC, PMPC and $P(MTC_{morph})$.