

Supplementary Information

Morpholine-Functionalized Polycarbonate Hydrogel for Heavy Metal Ion Sequestration

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Synthesis of ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-Et): the synthesis was performed similarly to¹; briefly: solution of bis-MPA (22.1 g, 0.165 mol, 1 eq.) in 150 cm³ of ethanol with 6.8 g of Amberlyst 15 (strongly acidic resin) was refluxed 22 h. Next, the resin was filtered off and ethanol was stripped off. Crude product was dissolved in 200 cm³ of CH₂Cl₂ and insoluble part was filtered off. After removal of the solvent colorless, viscous liquid was obtained with yield= 81 %. In second step, into solution of dry ethyl 2,2-bis(methylol)propionate (42.72 g, 264 mmol, 1 eq.) in 800 cm³ of THF (vigorously stirred and immersed in an ice/ water bath) ethyl chloroformate was added (75 cm³, 85.52 g, 788 mmol, 3 eq.) and stirred further 40 min. Next, dry triethylamine (110 cm³, 79.8 g, 788 mmol, 3 eq.) was added dropwise over 40 min. After 1.5 h cooling bath was removed and solution stirred overnight at dry nitrogen atmosphere. Next, precipitate was filtered off and THF removed on rotary evaporator. The crude product was dissolved in 100 cm³ of CH₂Cl₂ and washed with 2·50 cm³ 1M HCl_{aq.}, 50 cm³ saturated aq. solution of NaHCO₃, 25 cm³ of brine and 25 cm³ of aq. dist. Next, organic phase was dried over MgSO₄ and solvent was stripped off after MgSO₄ filtering off. Obtained yellow liquid crystallized after 4 h in a freezer. The product was recrystallized from ethyl acetate until white crystals were obtained. Yield= 24 %.

Synthesis of poly(ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate)-based hydrogel:

Polymerization was carried out similarly to synthesis of P(MTC-Morph)-based hydrogels using MTC-Et (0.1 g, 0.532 mmol, 90 eq.), MTC-PEO-MTC (0.13 g, 0.059 mmol, 10 eq.) and TU (0.0236 g, 0.064 mmol, 11 eq.) in 0.5 g of dry CH₂Cl₂ was prepared in one vial, and a solution of benzyl 2,2-bis(methylol) propionate (0.0013 g, 0.006 mmol, 1.0 eq.) and DBU (0.0090 g, 0.058 mmol; 10 eq.) in 0.27 g of dry CH₂Cl₂. After purification, obtained flexible, transparent, colorless monoblock of gel fraction equaled 78 %.

- 1 K. Fukushima, R. C. Pratt, F. Nederberg, J. P. K. Tan, Y. Yan Yang, R. M. Waymouth, J. L. Hedrick, *Biomacromolecules*, 2008, **9**, 3051.

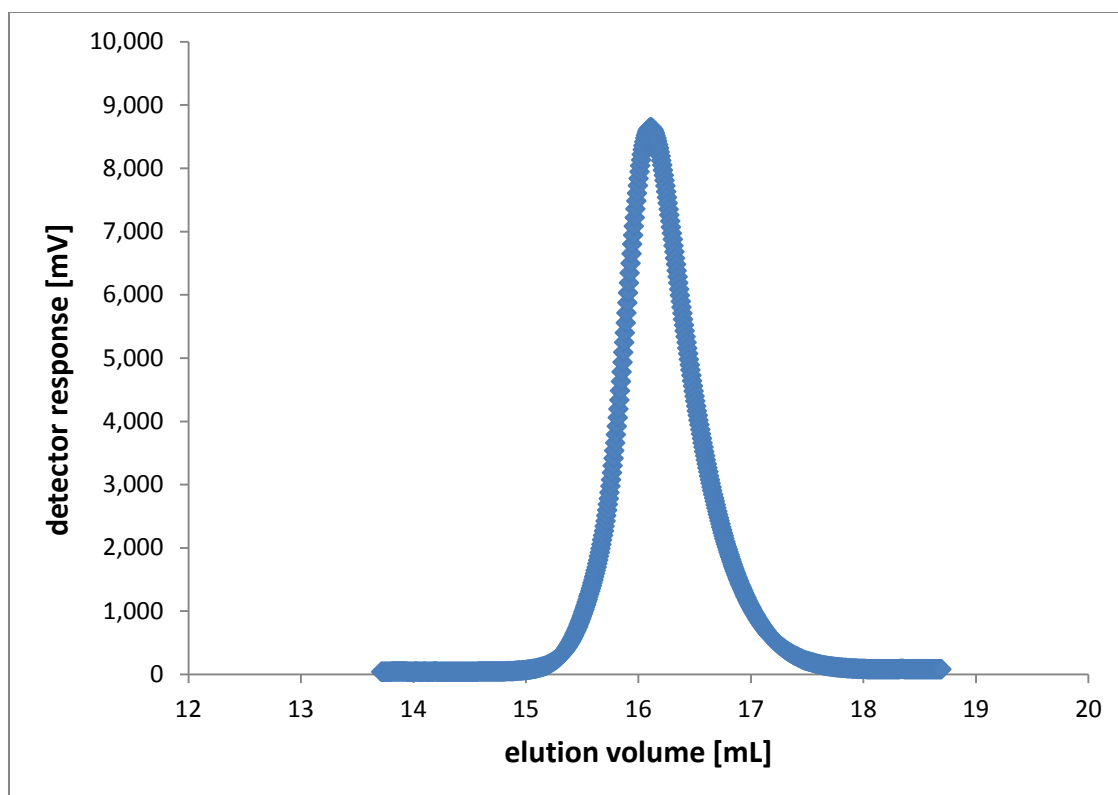


Figure S1. SEC (THF+ 2 % triethylamine) trace of the obtained MeOPEO_{2k}-P(MTC-Morph) copolymer (Table 1, Entry 2)

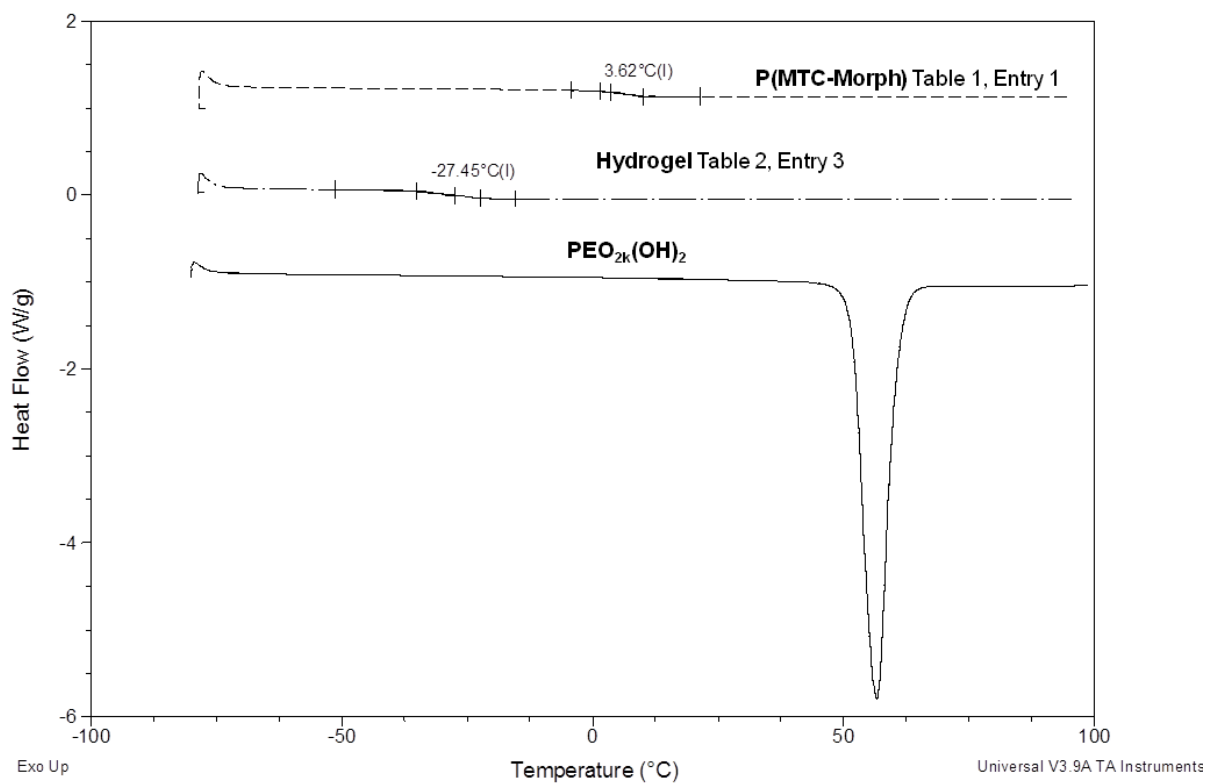


Figure S2. DSC curves of synthesized P(MTC-Morph) (2nd heating cycle), hydrogel with 10% cross-linker (2nd heating cycle) and initial PEO_{2k}(OH)₂ (1st heating cycle), heating rate: 10 °C·min⁻¹

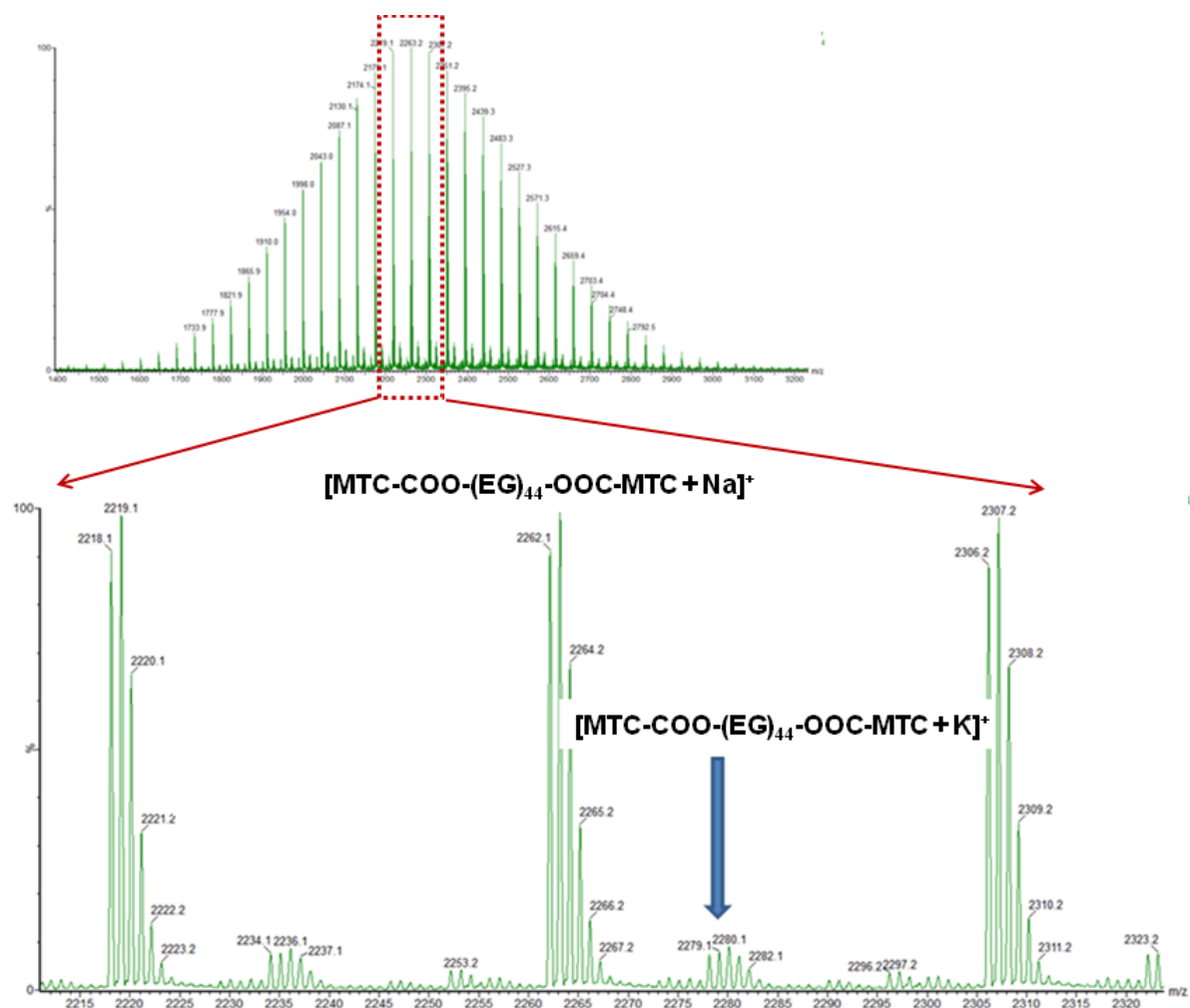


Figure S3. MALDI-ToF MS spectrum of MTC-PEO-MTC cross-linker after treatment with TMSD

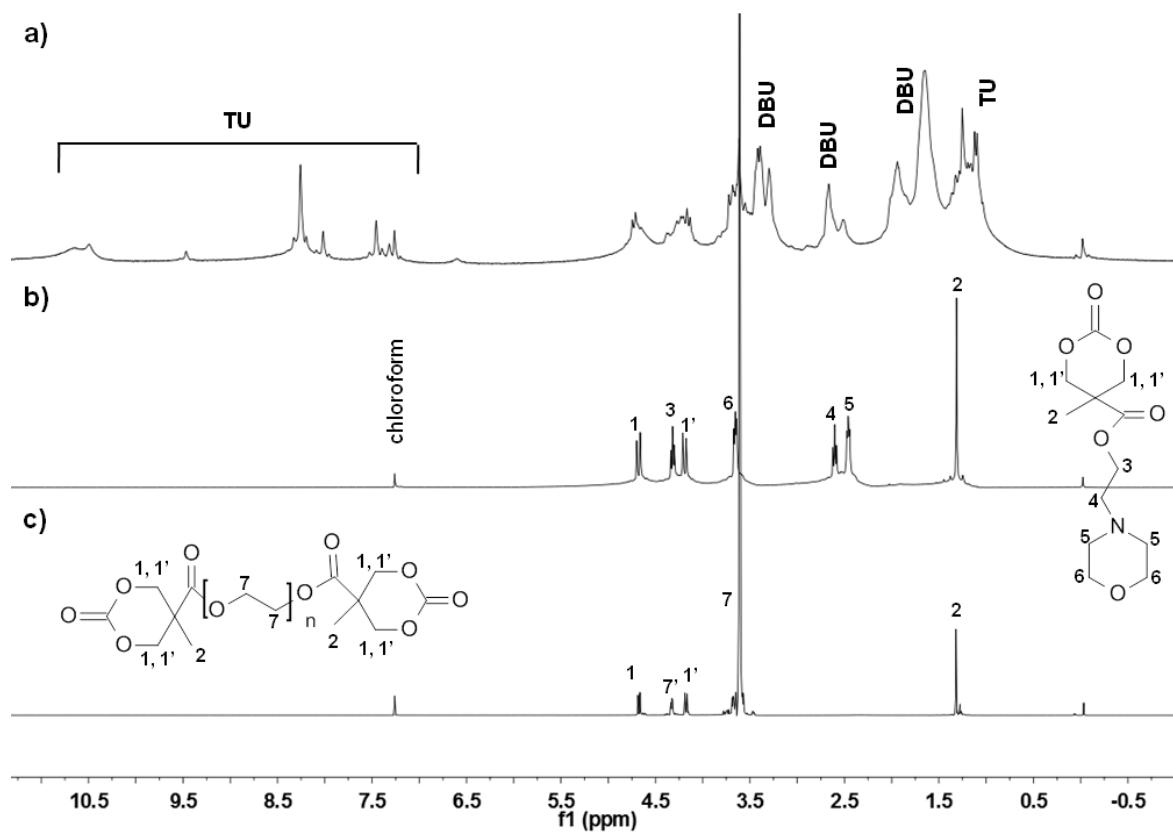


Figure S4. ¹H NMR (300 MHz, CDCl₃) spectra overlay of soluble residue extracted from *net*-P(MTC-Morph-co-PEO) (10% PEO; Table 2, Entry 3) (a), MTC-Morph (b) and ¹H NMR spectrum (500 MHz, CDCl₃) of MTC-PEO-MTC cross-linker (c)