

Ionic polymer absorbents inspired by deep eutectic solvents to recover cobalt and nickel

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Table S1. Polymer compositions used in this work, describing the HBA and HBD used as well as the HBA:HBD molar ratio of each component.

Polymer name	HBA	HBD	HBA:HBD molar ratio
polyMETAC:Gly	METAC	Gly	1:2
polyMETAC:EG		EG	1:2
polyMETAC:BdOH		BdOH	1:2
polyMETAC:BuOH		BuOH	1:2
polyMETAC:PCA		PCA	2:1
polyMETAC:PGA		PGA	1:1
polyMETAC:TA		TA	20:1

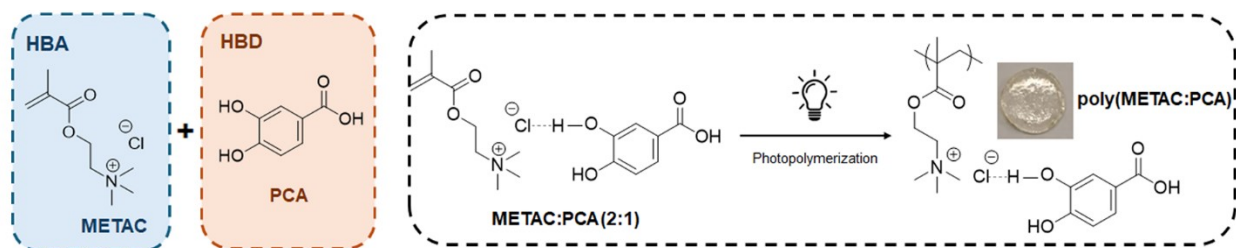


Figure S1. Schematic representation of the interaction between the HBA (METAC) and HBD of the monomer through hydrogen bonding of chloride of METAC and the OH-moiety of HBD, resulting in an ionic polymer after photopolymerization. In this case PCA is used as an example of HBD, although the same logic applied to the other polymers used in this work.

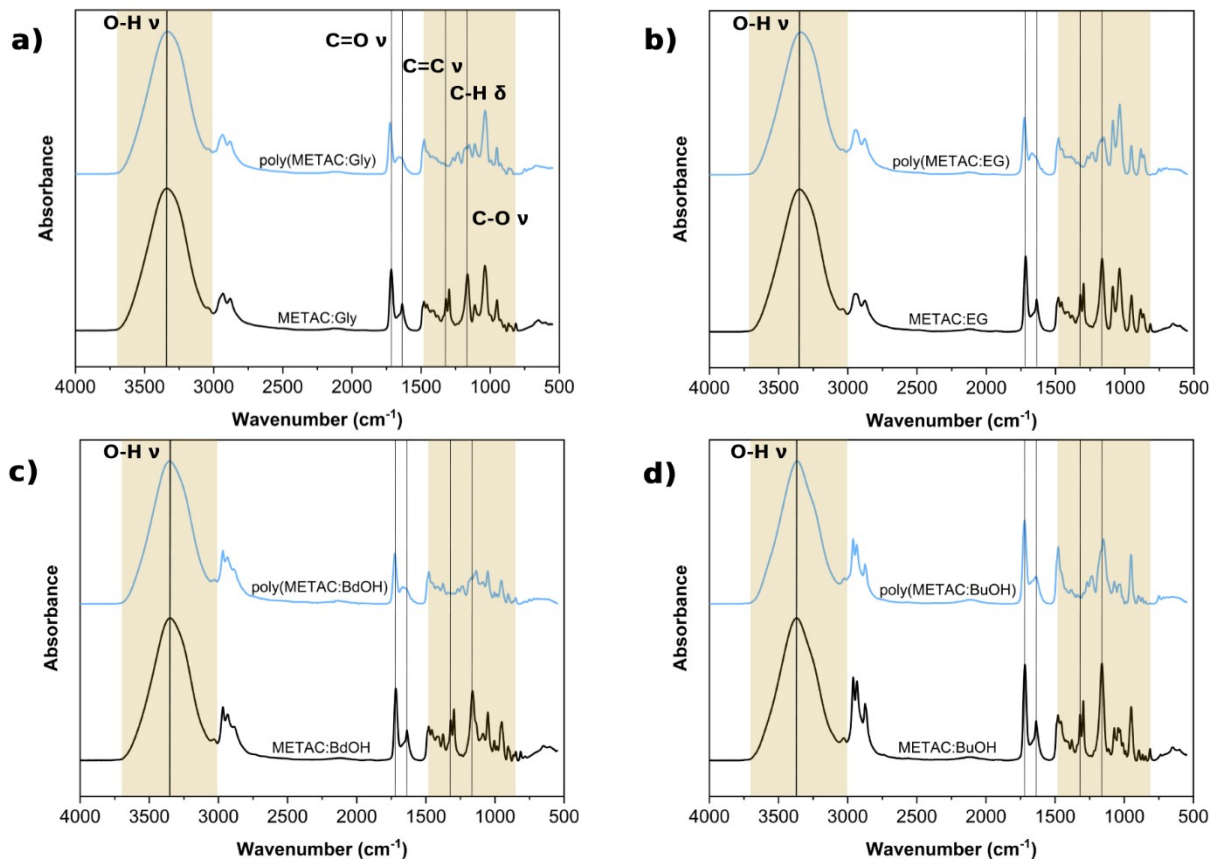


Figure S2. FTIR spectra of the monomers (bottom spectra), i.e. mixtures of METAC and hydroxylated solvents in a 1:2 molar ratio, and after their photopolymerization (poly, top spectra), with highlighted bands related to the polymerization process. The represented polymers are polyMETAC:Gly (a), polyMETAC:EG (b), polyMETAC:BdOH (c) and polyMETAC:BuOH (d).

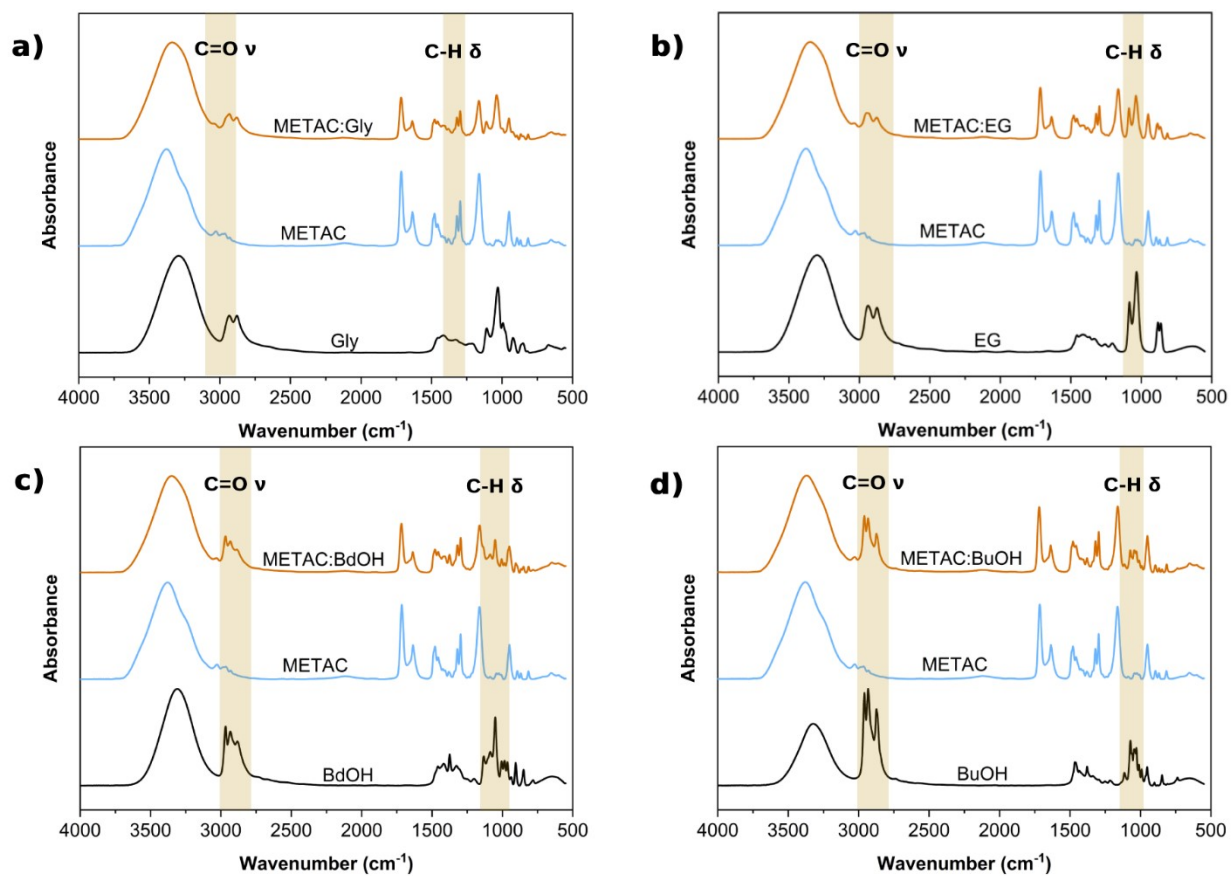


Figure S3. FTIR spectra of each monomer component, i.e. METAC or an hydroxylated solvent, and after mixing both components in a 1:2 molar ratio (METAC:hydroxylated solvent).

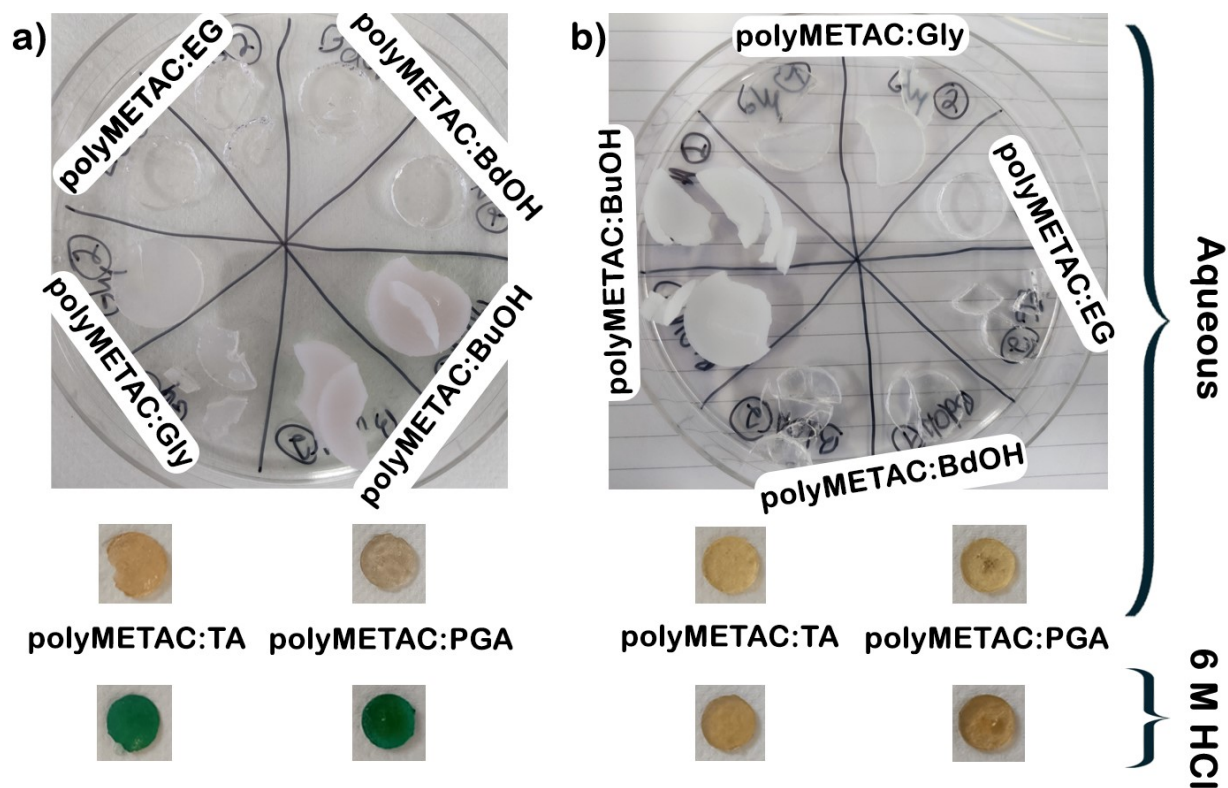


Figure S4. polyMETAC:Gly, polyMETAC:EG, polyMETAC:BdOH, polyMETAC:BuOH, polyMETAC:TA and polyMETAC:PGA polymers after preliminary metal absorption assays – 48 h contact with either 50 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (a) or 50 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (b) in aqueous solution (top) or 6 M HCl (bottom).

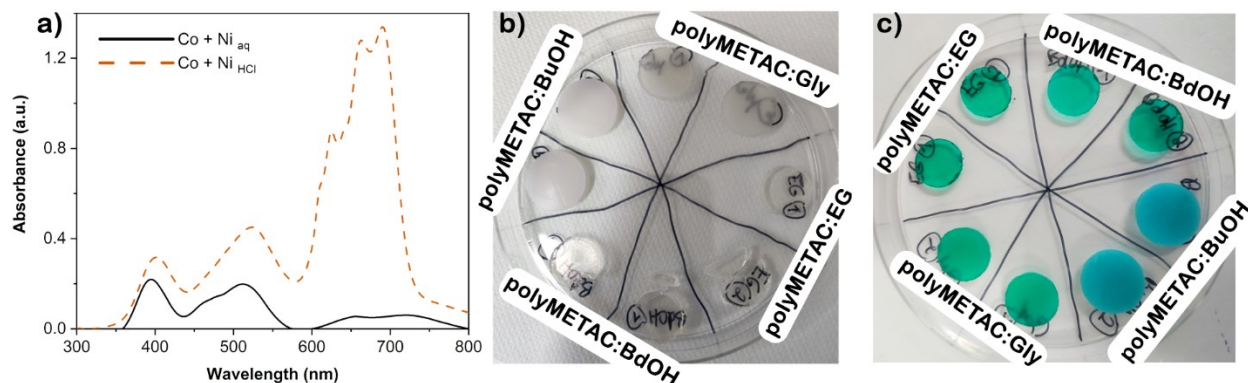


Figure S5. a) UV-Vis spectra of mixed $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in either aqueous solution (aq) or in 6 M HCl (HCl), showing both Co and Ni species showed in the individual metal solutions. **b,c)** polyMETAC:Gly, polyMETAC:EG, polyMETAC:BdOH and polyMETAC:BuOH polymers after preliminary metal absorption assays – 48 h contact with 50 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 50 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in either aqueous (b) or in 6 M HCl (c) solution.

Table S2. Fraction of carbon, hydrogen and nitrogen from CHN elemental analysis of selected polymers following metal uptake process in mixed Co-Ni solutions in 6 M HCl. The absorption capacity q_e was used to determine the nitrogen/absorbed metal ratios for discussion of the effect of the trimethylammonium moiety of METAC in the overall absorption capacity of the polymers.

Sample	% C	% H	% N	Absorbed Co/Nitrogen	Absorbed Ni/Nitrogen
polyMETAC:Gly	40.11 ± 0.11	7.36 ± 0.36	4.45 ± 0.02	0.55	0.52
polyMETAC:EG	39.96 ± 0.32	7.37 ± 0.02	4.61 ± 0.08	0.53	0.49
polyMETAC:PGA	39.78 ± 0.15	7.34 ± 0.04	4.55 ± 0.04	0.35	0.31
polyMETAC:TA	43.72 ± 0.03	7.08 ± 0.17	4.07 ± 0.08	0.57	0.53

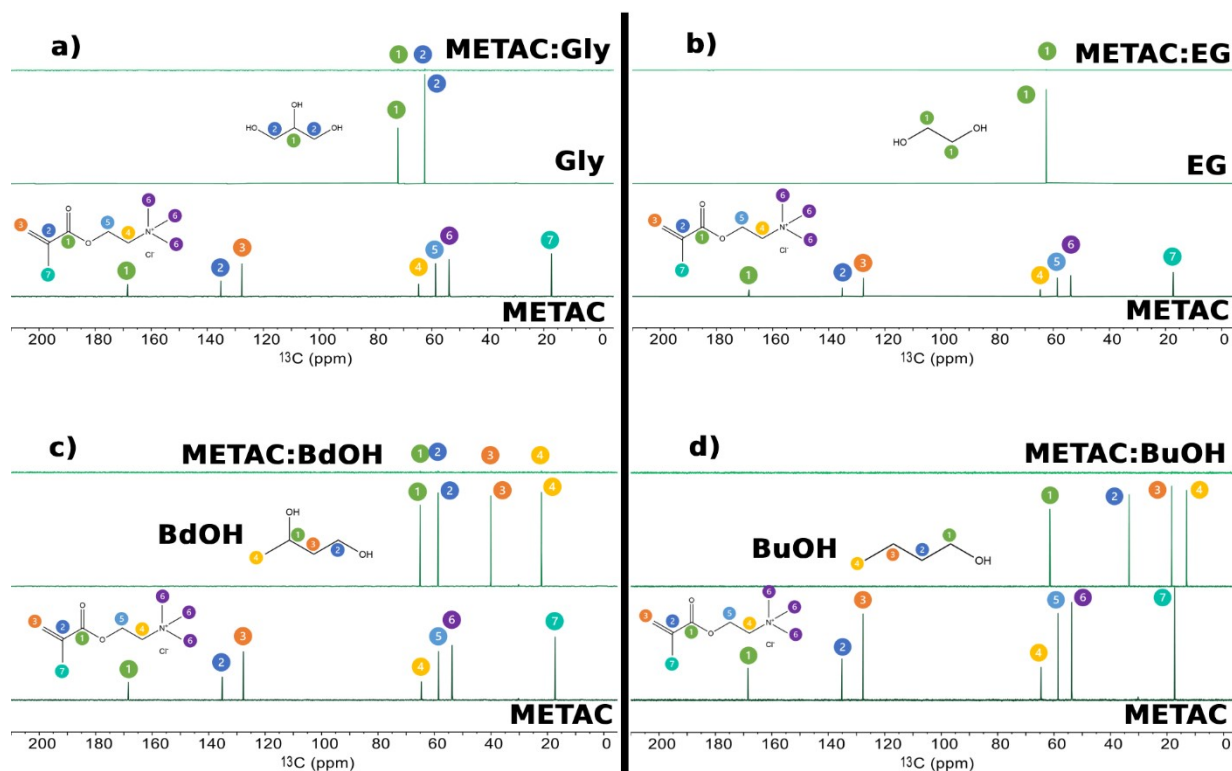


Figure S6. ^{13}C -NMR spectra of remaining media after 48 h contact time of the polymers polyMETAC:Gly (a), polyMETAC:EG (b), polyMETAC:BdOH (c) and polyMETAC:BuOH (d) with 6 M HCl media. All samples were diluted in D_2O in the same ratios prior to analysis.

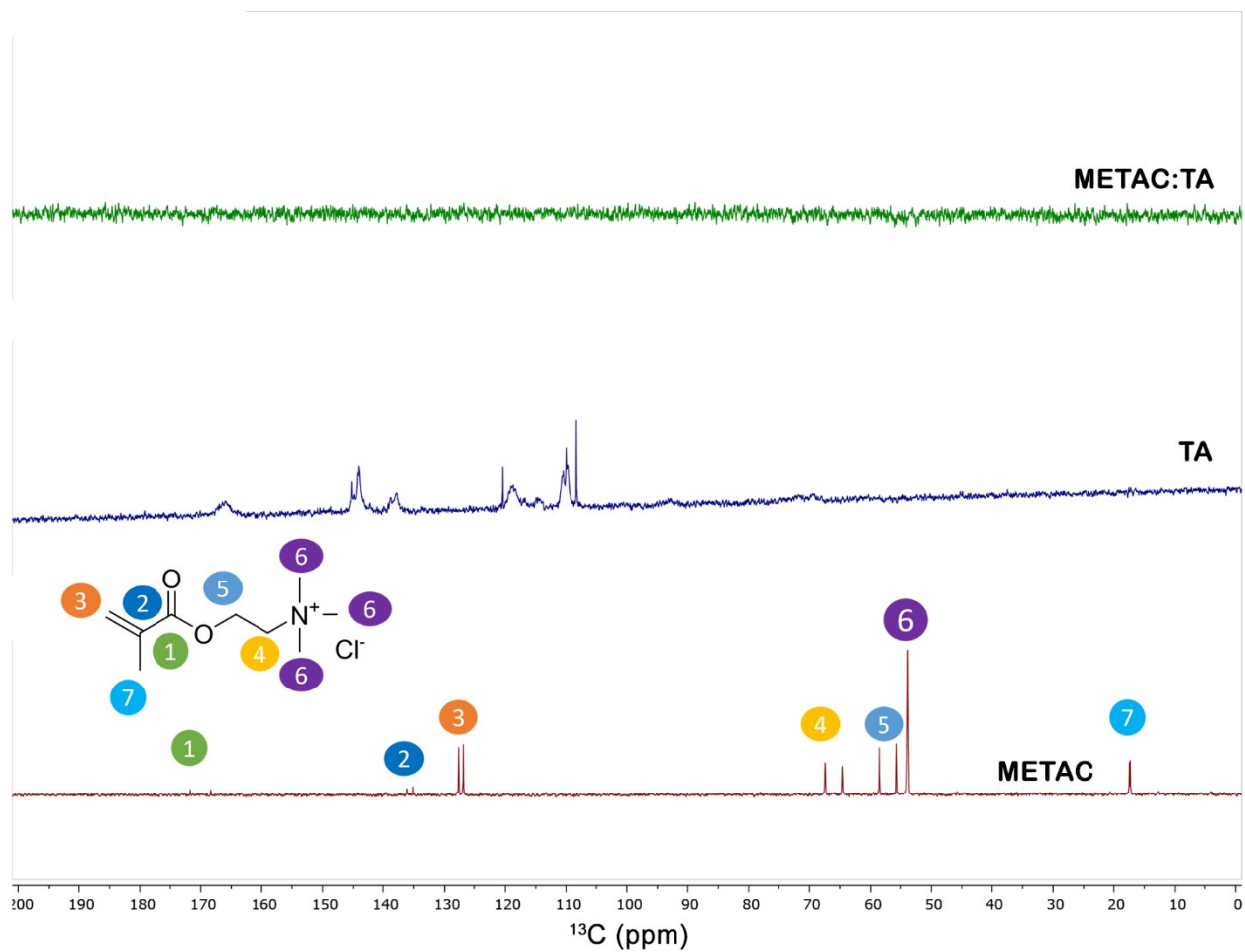


Figure S7. ^{13}C -NMR spectra of remaining media after 48 h contact time of polyMETAC:TA with 6 M HCl media. The samples were diluted in D_2O in the same ratios prior to analysis.

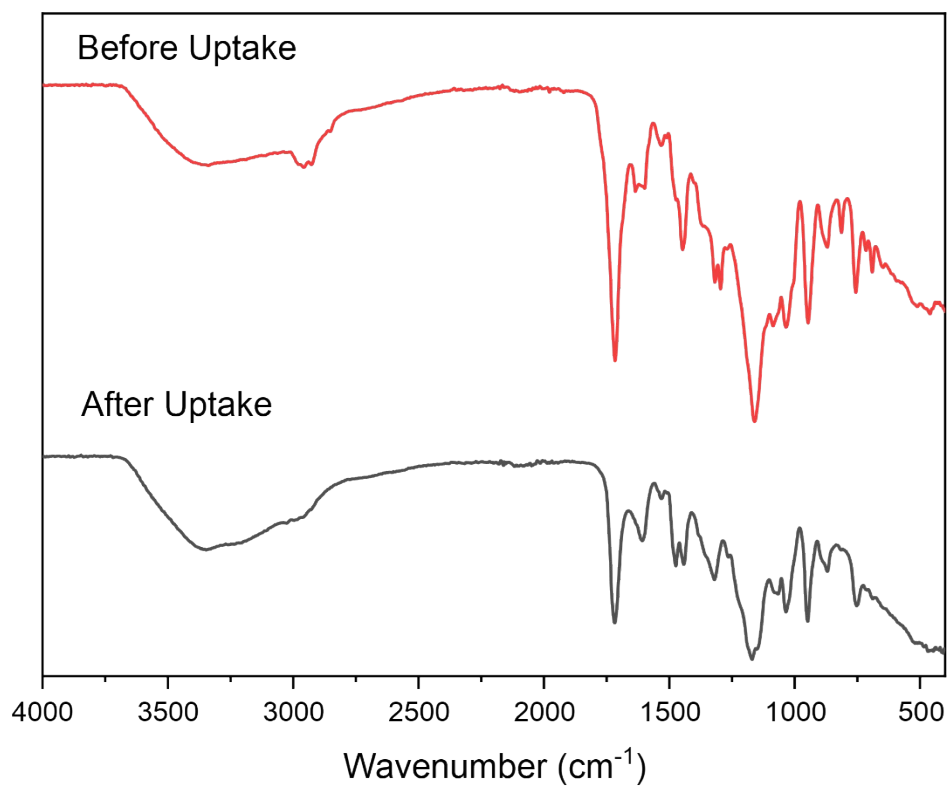


Figure S8. FTIR spectra of polyMETAC:TA before (top) and after (bottom) metal uptake, suggesting the maintenance of the polymeric structure.

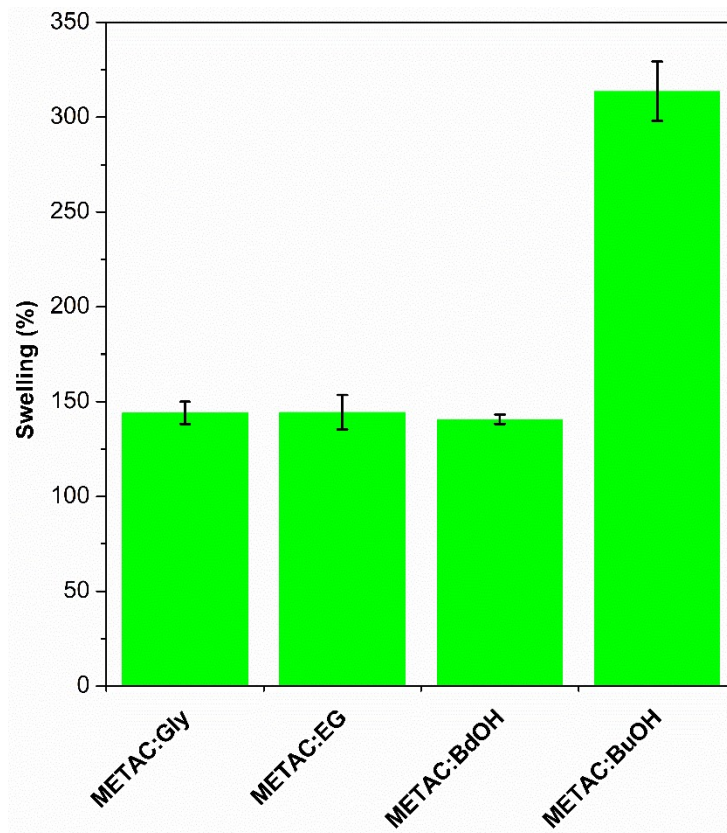


Figure S9. Swelling (%) of METAC:alcohol polymers after contact for 48 h with a mixture of Co and Ni, using 50 mM of each metal in 6 M HCl solutions and after a pre-equilibration step using 6 M HCl.

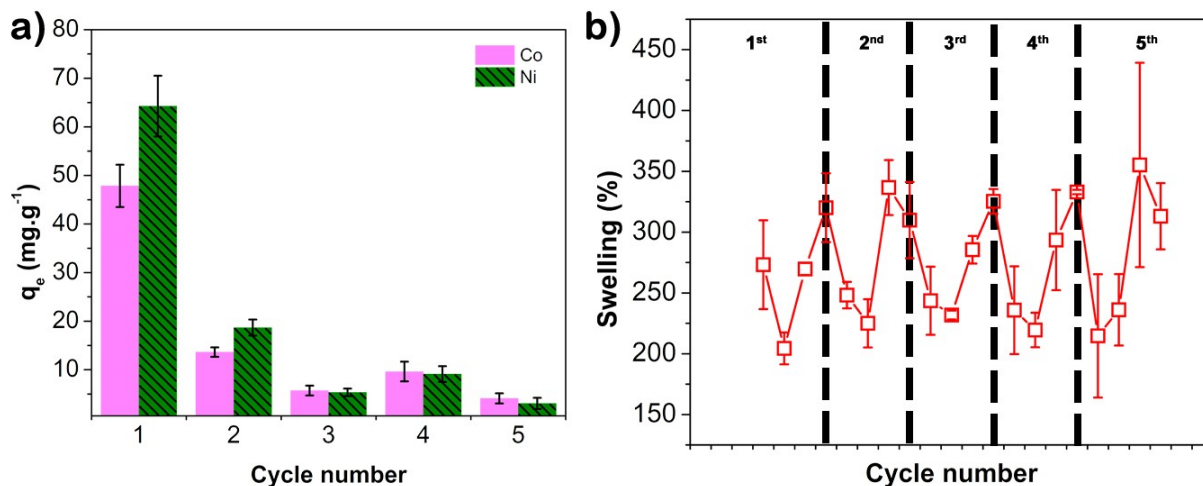


Figure S10. a) Absorption capacity of polyMETAC:EG in each of the five cycles after contacting a 50 mM $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ solution in 6 M HCl. b) Progression of the swelling degree of the METAC:EG polymers in each cycle, either after absorption of the metals or after each of the three water washes carried out in each cycle.

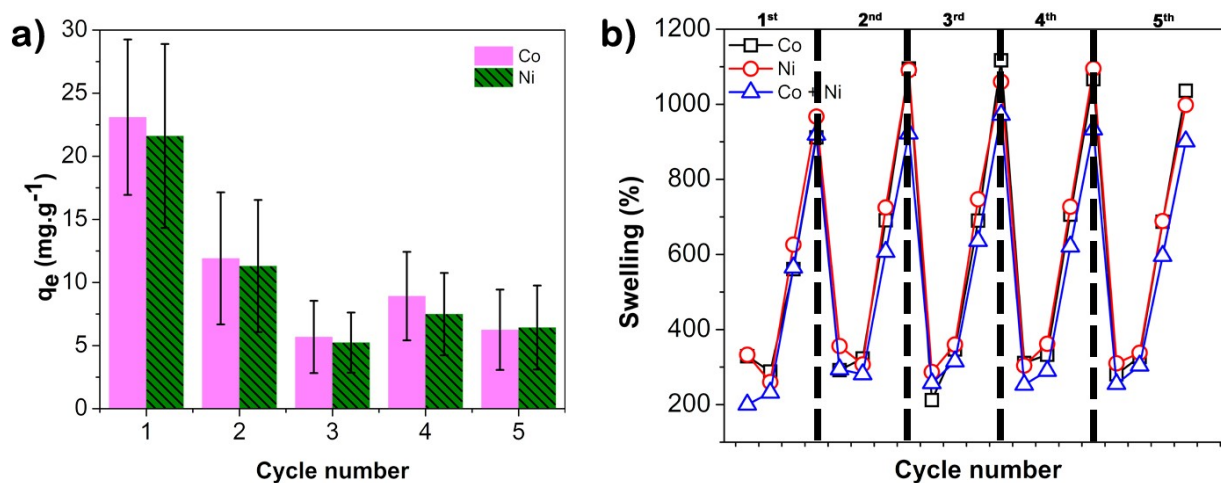


Figure S11. a) Absorption capacity of polyMETAC:TA in each of the five cycles after contacting a 50 mM $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ solution in 6 M HCl. b) Progression of the swelling degree of the METAC:TA polymers in each cycle, either after absorption of the metals or after each of the three water washes carried out in each cycle. Three different scenarios are shown, depending on the metal solution that was used during absorption, either individual 50 mM $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (Co,

black square), individual 50 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Ni, red circle) or a mixture of both (Co + Ni, blue triangle).