Supporting information

Metallopolymer-Based Block Copolymers for Perfluorinated Substances (PFAS) and Ion Removal

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Directory

1.-Polymers and Nomenclature

Table S1: Summarized molar masses and block segment content (weight content (wt.%), $P_{XX\ wt\%}$) of P*t*BAEMA and PCoE*t*BAEMA) of synthesized polymers calculated by SEC measurements and ^{1}H NMR spectroscopy.

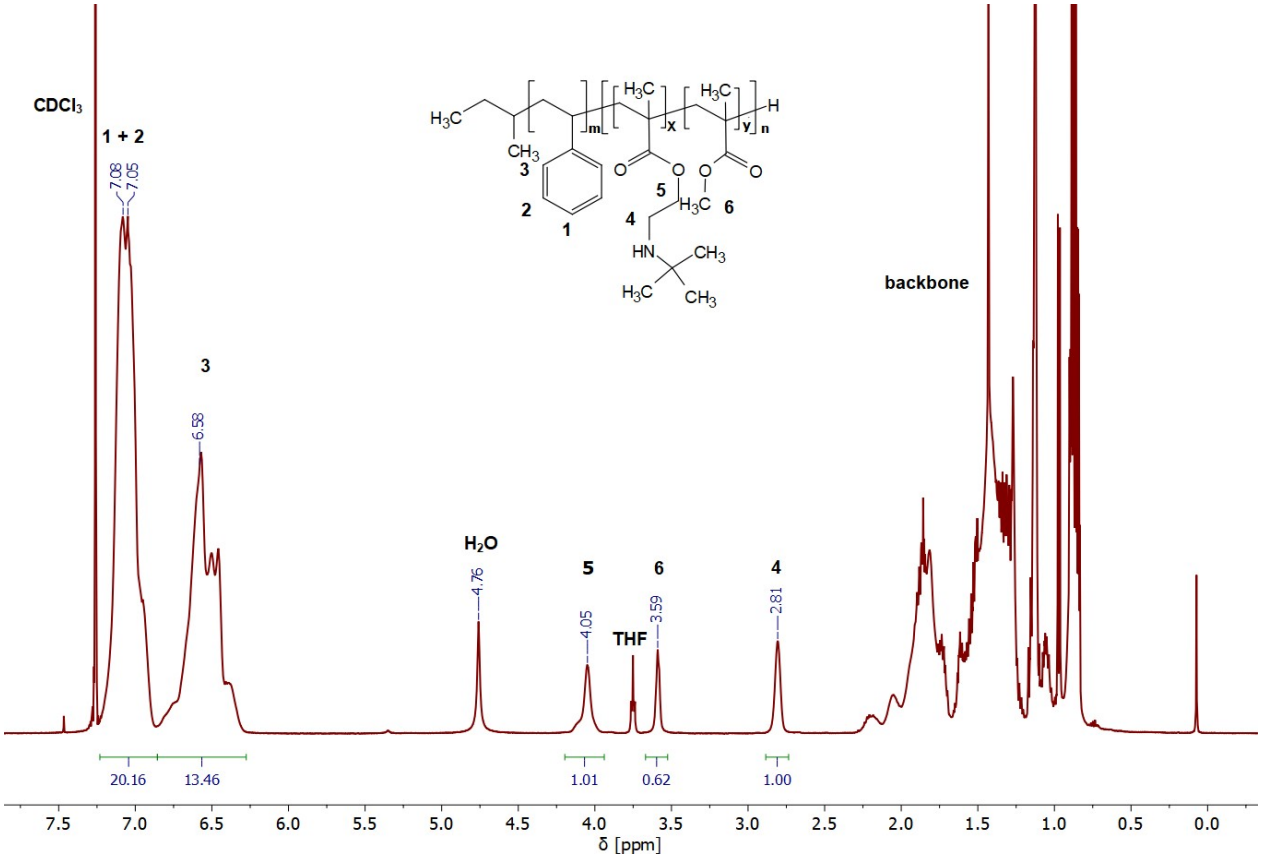
Sample	Polymer	$M_{n,\ NMR}$ [a)]	Đ[b)]	$wt.\%_{PCoEtBAEMA(UV\text{-}Vis)}$[c)]
$P_{6.2}$	PS_{797}-*b*-($PCoEtBAEMA_{7}$-*co*-$PMMA_{8}$)	87.8	1.08	6.2
$P_{20.1}$	PS_{773}-*b*-($PCoEtBAEMA_{31}$-*co*-$PMMA_{12}$)	98.7	1.08	20.1
$P_{27.5}$	PS_{908}-*b*-($PCoEtBAEMA_{65}$-*co*-$PMMA_{28}$)	134.4	1.10	27.5
$P_{31.1}$	PS_{773}-*b*-($PCoEtBAEMA_{57}$-*co*-$PMMA_{27}$)	114.4	1.11	31.1
$P_{33.3}$	PS_{874}-*b*-($PCoEtBAEMA_{88}$-*co*-$PMMA_{48}$)	143.3	1.10	33.3
$P_{40.1}$	PS_{776}-*b*-($PCoEtBAEMA_{80}$-*co*-$PMMA_{30}$)	127.0	1.10	40.1
$P_{92.6}$	$PCoEtBAEMA_{387}$-*b*-$PMMA_{133}$	225.5	1.07	92.6[d)]

[a)] PS molar masses were determined by SEC in THF (kg mol^{-1}, PS standards) and used to calculate NMR values for the corresponding block copolymers; [b)]Dispersity of polymers prior to functionalization measured by SEC in DMF with styrene standard [c)] Weight content of PCoE*t*BAEMA in % calculated by UV-Vis spectroscopy in THF at 489 nm [d)] Weight content determined by ^{1}H NMR data of the block copolymers.

Polymer synthesis and data:

A detailed description of the synthetic and analytical procedure, including the composition calculation, can be found in the supporting information of our previous work under DOI:10.1039/D4PY00780H. All newly synthesized polymers for this work ($P_{27.5,}$ $P_{33.3,}$ and $P_{92.6}$) were analyzed accordingly, and relevant data (NMR and SEC) is presented in the following.

2.-Proton Nuclear Resonance Spectroscopy (^{1}H-NMR) of prepared Polymers



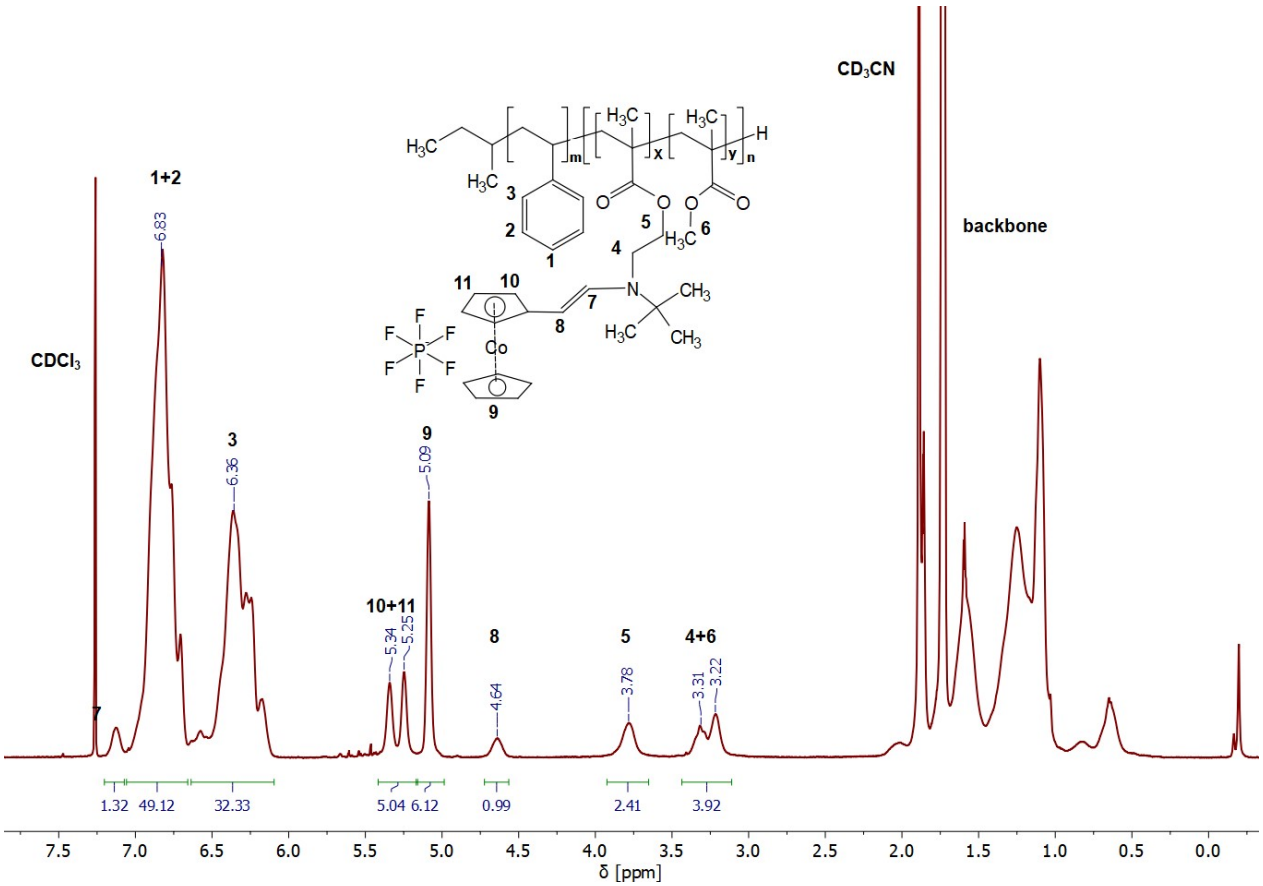


Figure S1: ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm) of PS_{908}-*b*-(P*t*BAEMA$_{65}$-*co*-PMMA$_{28}$)

Figure S2: ^{1}H-NMR (500 MHz, $CDCl_3$/CDCN, δ in ppm) of PS_{908}-*b*-(PCoE*t*BAEMA$_{65}$-*co*-$PMMA_{28}$)

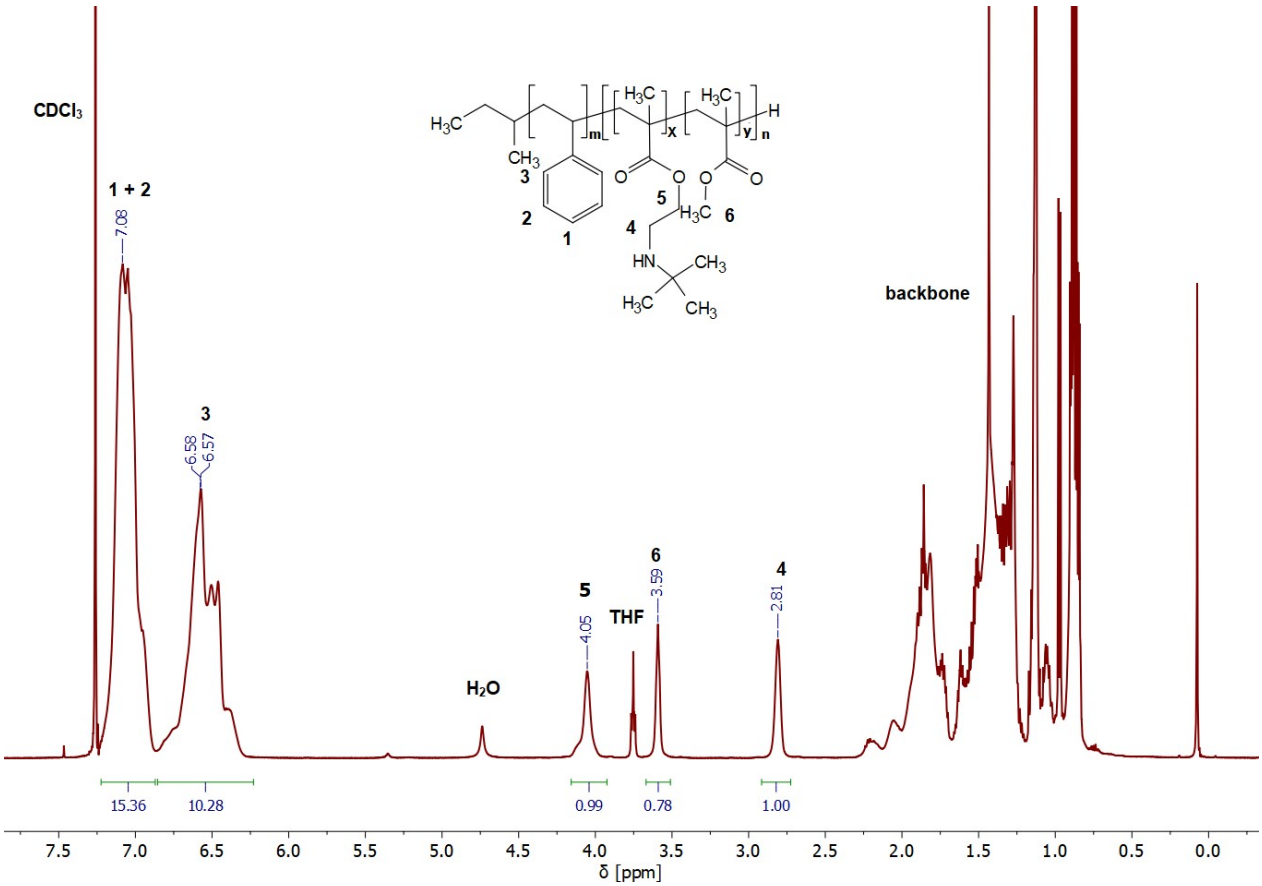


Figure S3: ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm) of PS_{874}-*b*-(P*t*BAEMA$_{88}$-*co*-$PMMA_{48}$)

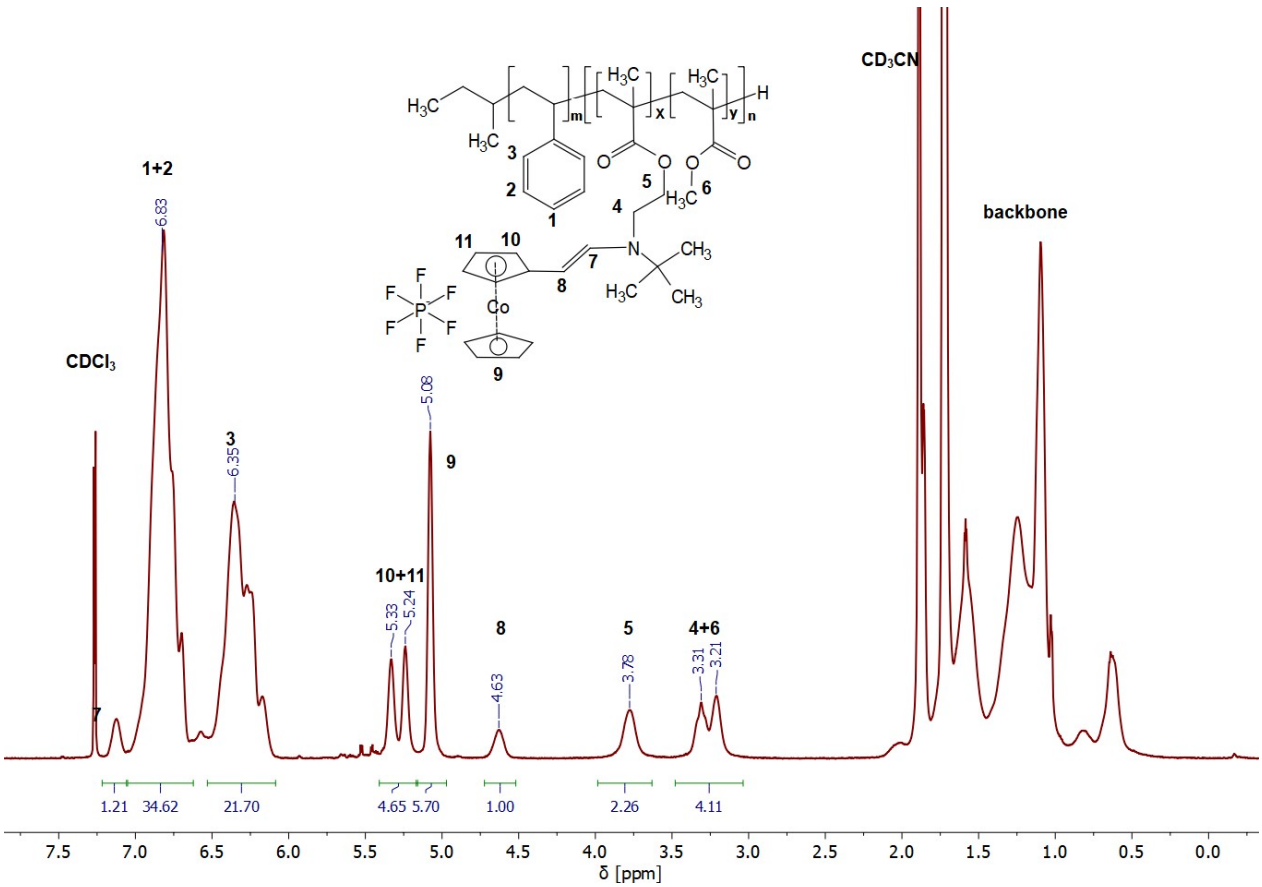


Figure S4: ^{1}H-NMR (500 MHz, $CDCl_3$/CDCN, δ in ppm) of PS_{874}-*b*-(PCoE*t*BAEMA$_{88}$-*co*-PMMA$_{48}$)

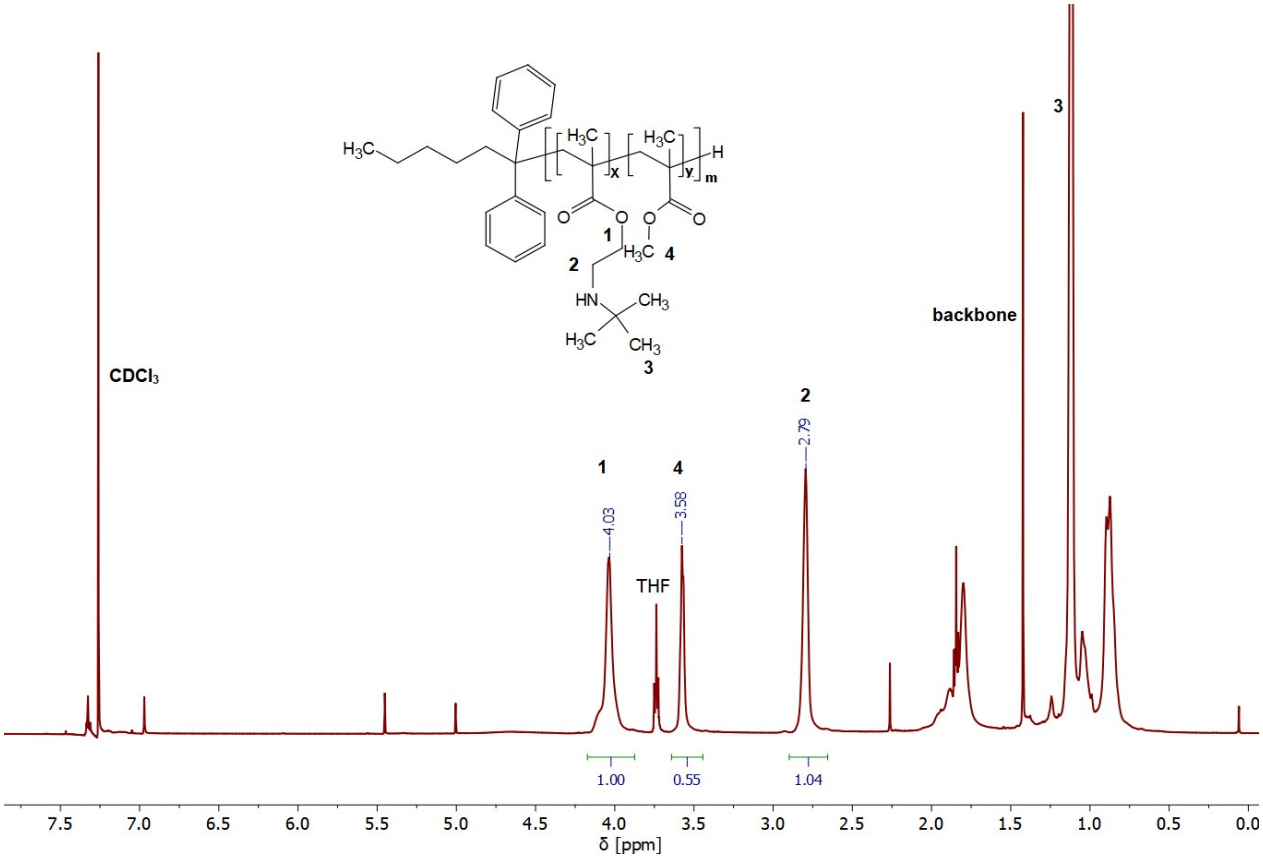


Figure S5: ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm) of P*t*BAEMA$_{387}$-*b*-PMMA$_{133}$

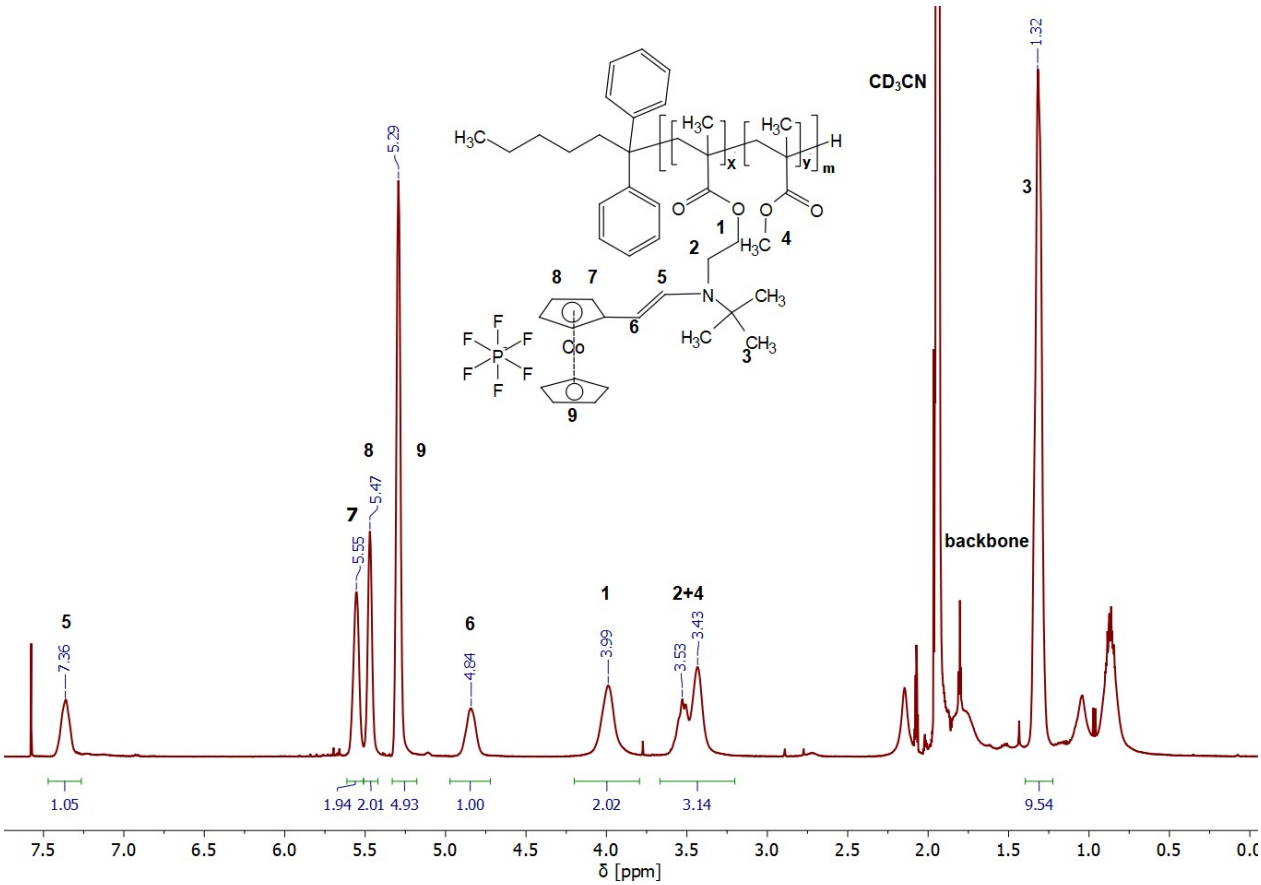


Figure S6: ^{1}H-NMR (500 MHz, $CDCl_3$/CDCN, δ in ppm) of PCoE*t*BAEMA$_{387}$-*b*-PMMA$_{133}$

3.-Size Exclusion Chromatography (SEC) of prepared Polymers

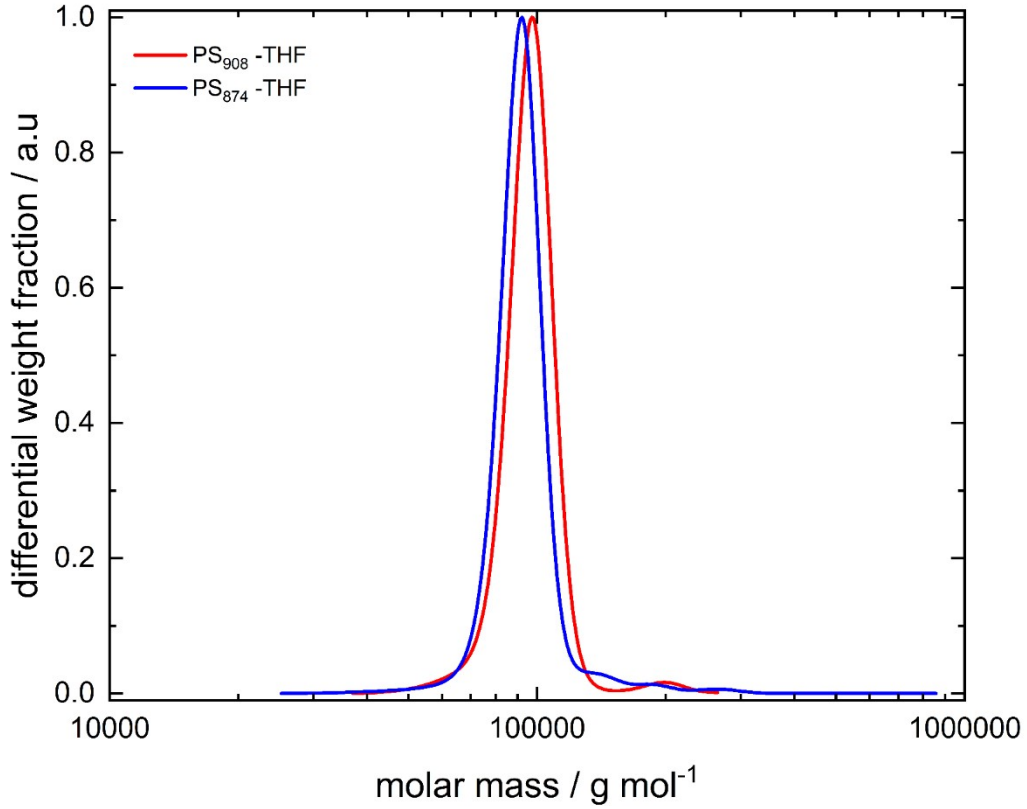


Figure S7: SEC (THF, polystyrene standard) of PS_{908} and PS_{874} first polystyrene block for calculation

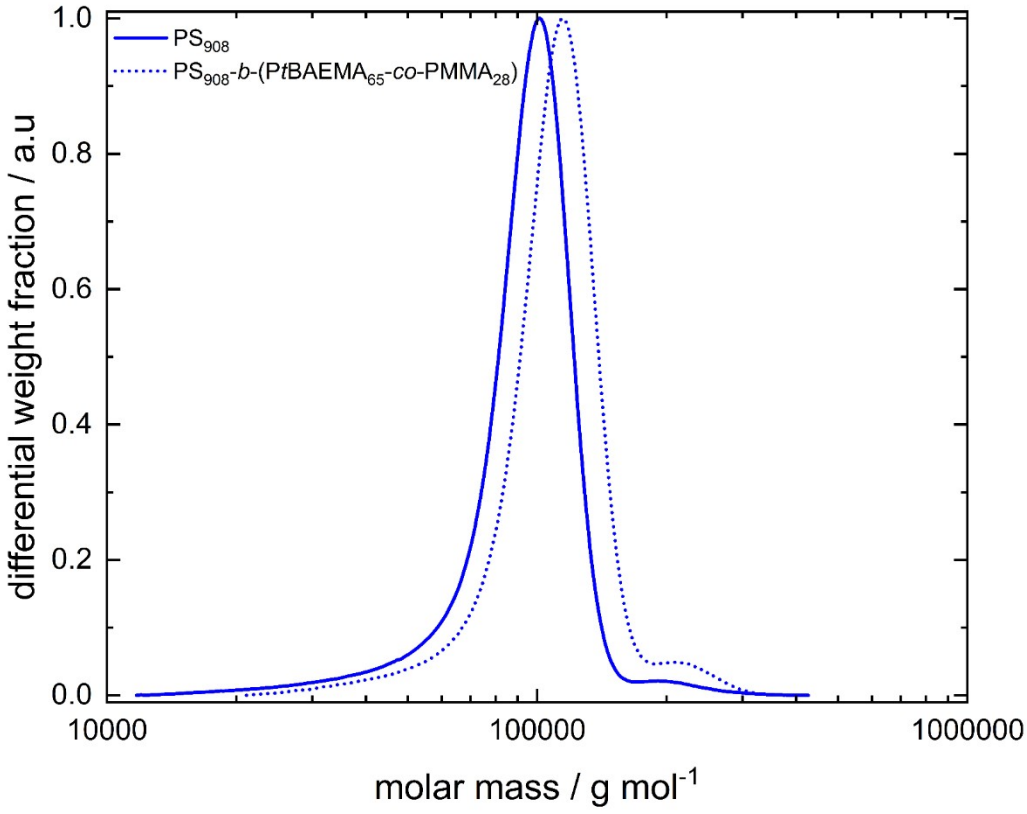


Figure S8: SEC (DMF, PMMA standard) of PS_{908} and PS_{908}-*b*-(P*t*BAEMA$_{65}$-*co*-PMMA$_{28}$)

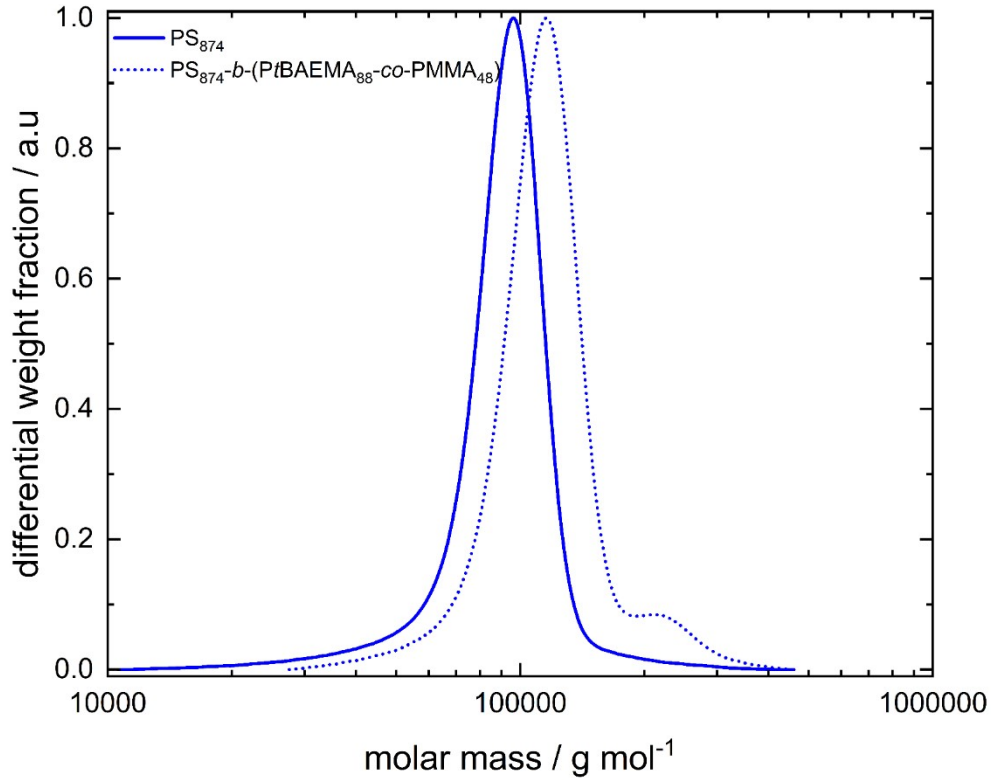


Figure S9: SEC (DMF, PMMA standard) of PS_{874} and PS_{874}-*b*-(P*t*BAEMA$_{88}$-*co*-PMMA$_{48}$)

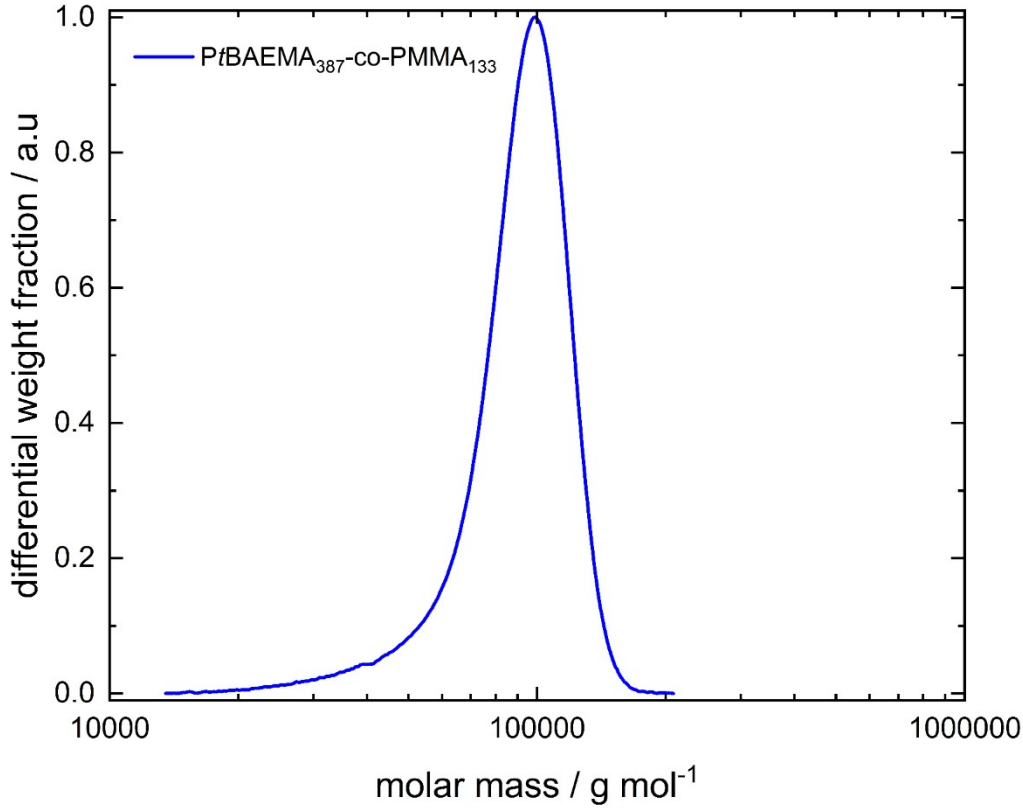


Figure S10: SEC (DMF, PMMA standard) of P(*t*BAEMA$_{88}$-*co*-MMA$_{48}$)

4.-Photographs of Prepared Membranes and SEM Images of the Membrane Surface

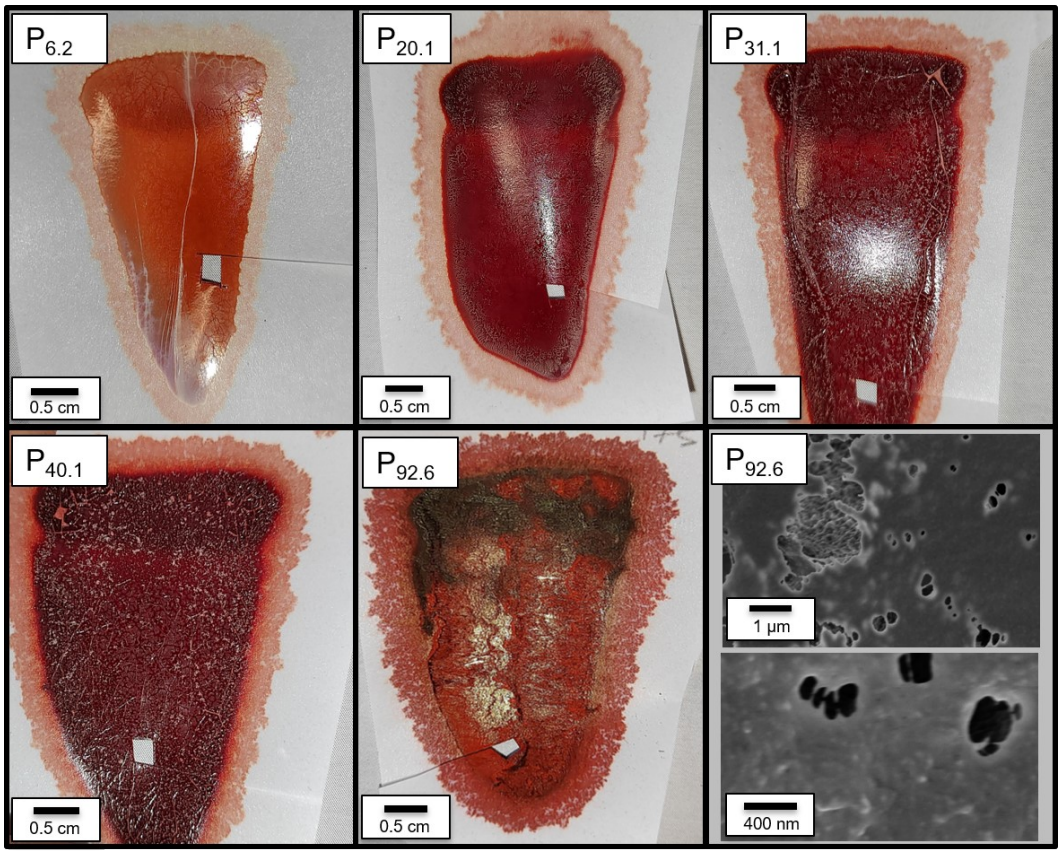


Figure S11: Images of prepared membranes from NMP solution with increasing amount of cobaltocenium containing PtBAEMA in weight percent (P_{XX} wt%) and scanning electron microscopy images of $P_{92.6}$.

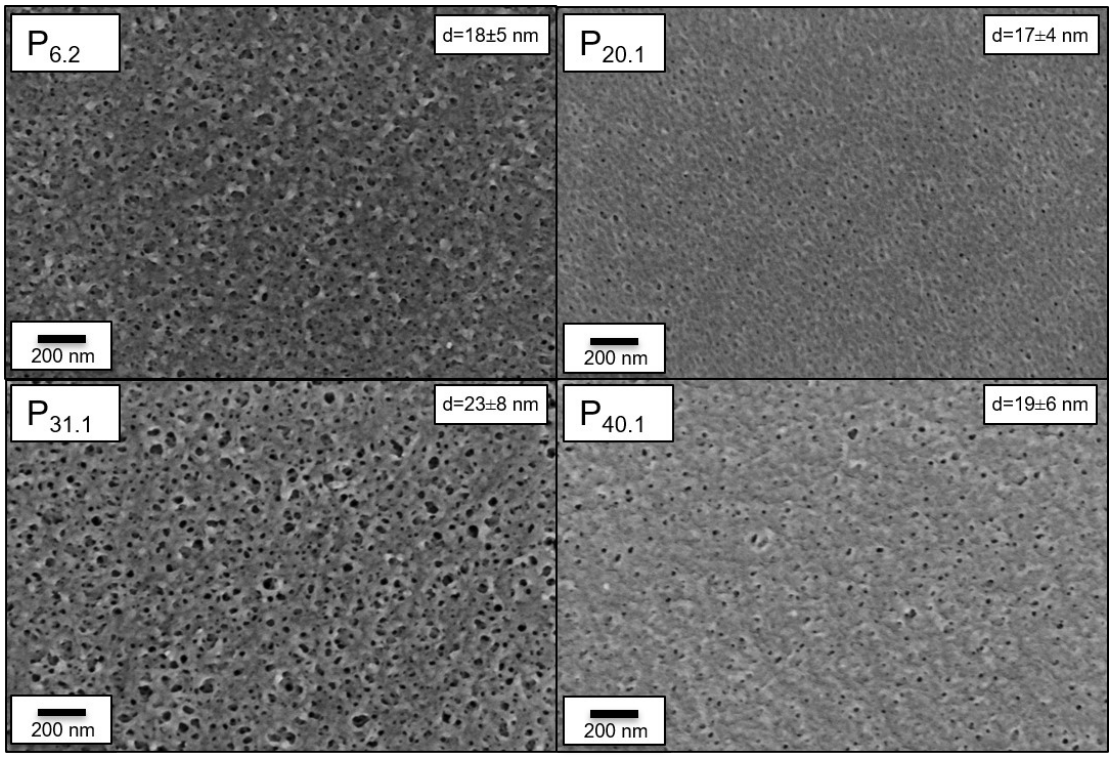


Figure S12: Scanning electron microscopy (SEM) images of membranes from NMP solution with increasing amount of cobaltocenium containing PtBAEMA in weight percent (P_{XX} wt%)

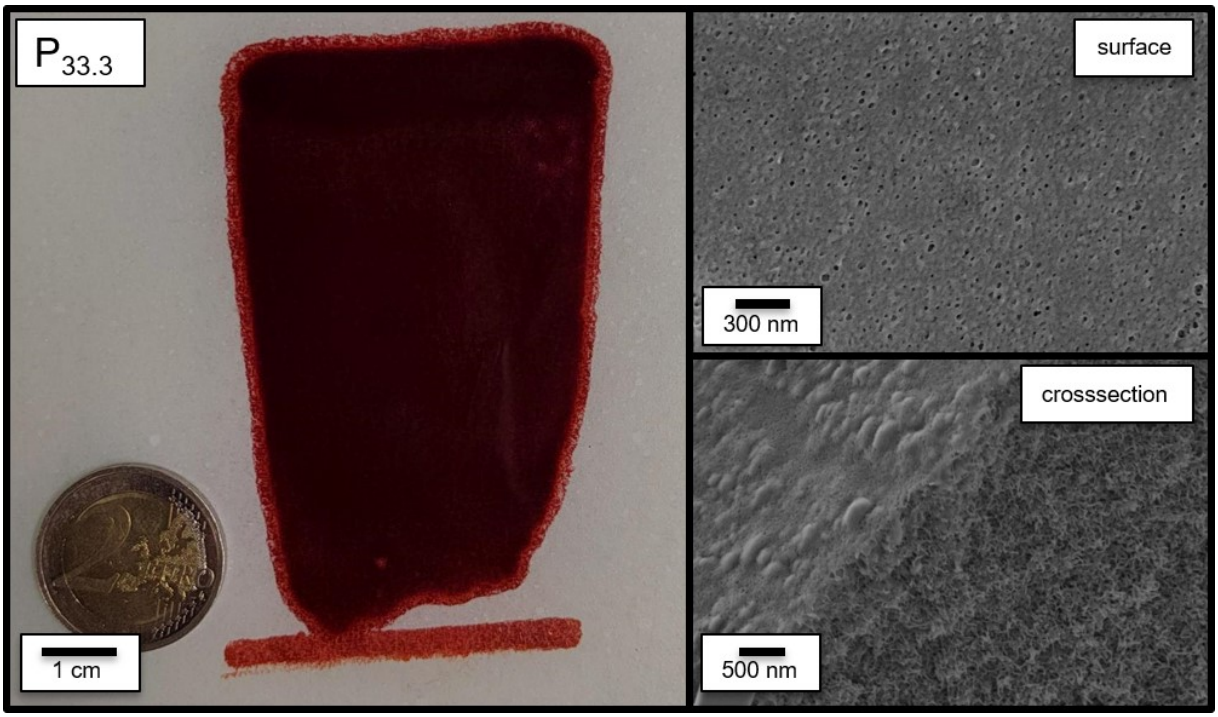
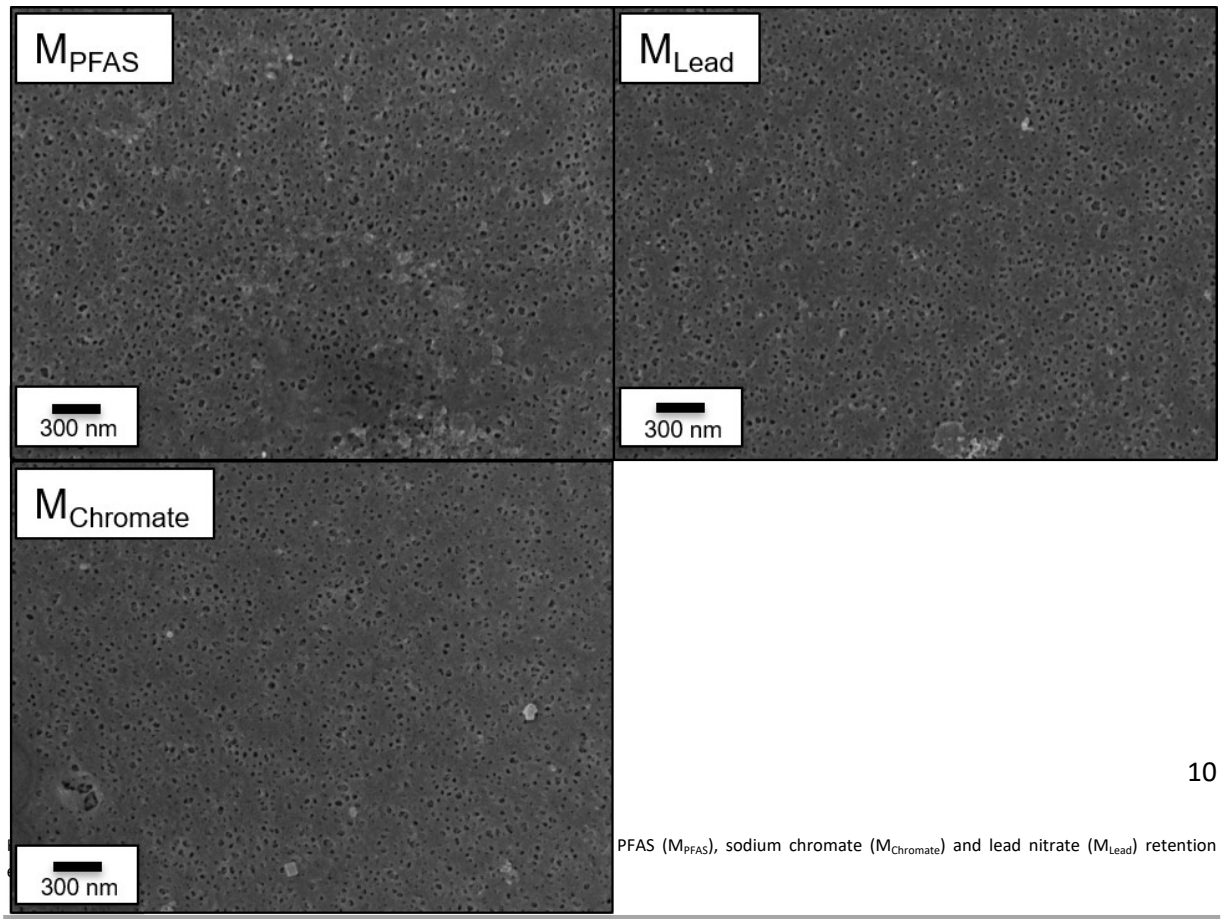


Figure S13: Image of large membrane formed from a DMAc solution of $P_{33.3}$ and respecting scanning electron microscopy images of the surface and crosssection.



PFAS (M_{PFAS}), sodium chromate ($M_{Chromate}$) and lead nitrate (M_{Lead}) retention

5.-Additional Permeance Experiments in Simulated Seawater

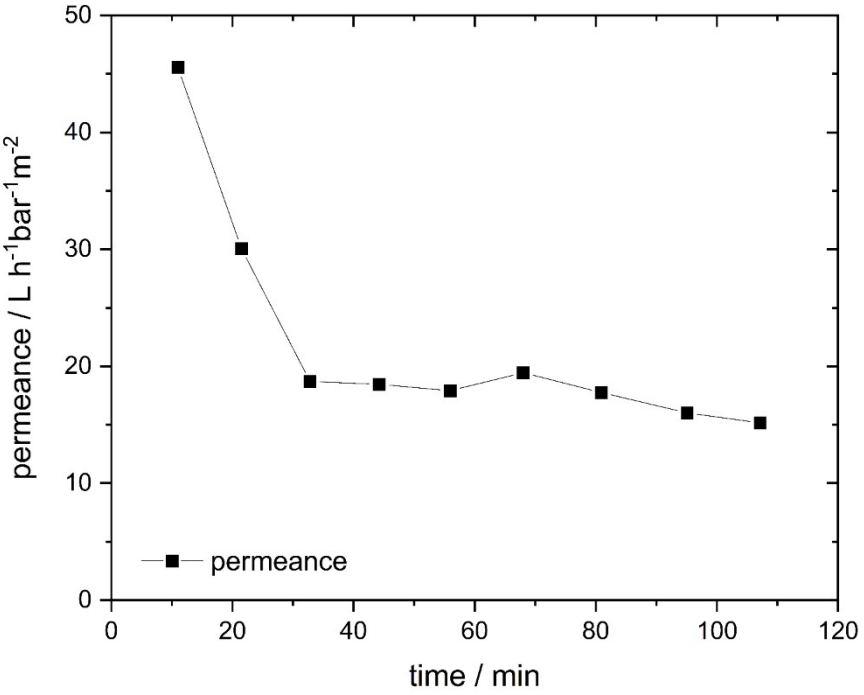


Figure 15: Water flux experiment with a sodium chloride concentration of 3.5 wt% and a pressure of 0.4 bar

6.-Cyclic Voltammetry Data

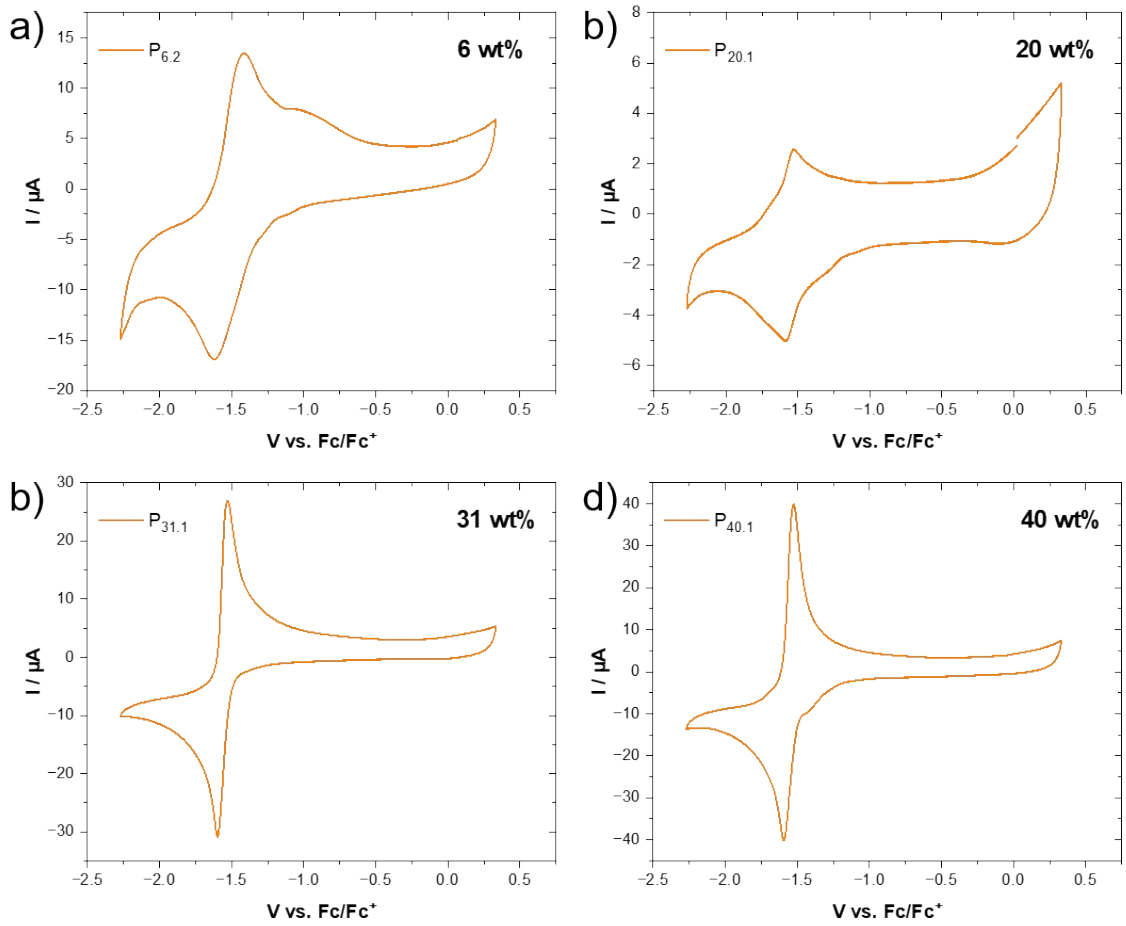


Figure S16: Cyclic voltammetry (CV) investigation of cobaltocenium containing BCP- films in acetonitrile with 0.1 M TBAPF6 at a scan rate of 200 mV s^{-1}, Pt working, and Ag/AgCl reference electrode containing increasing cobaltocenium amounts (P_{XX} wt%): a) $P_{6.2}$. b) $P_{20.1}$. c) $P_{31.1}$. d) $P_{40.1}$.

7.-Thermogravimetric Analysis Data and Ceramic in Synthetic Air

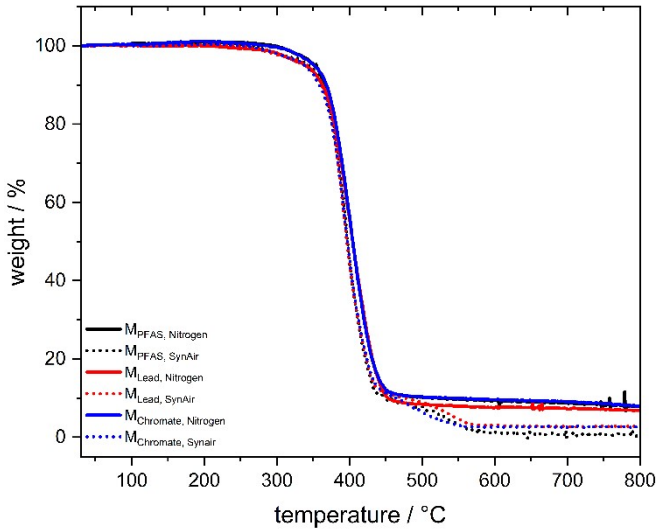


Figure S air up to 800°C with 10 K min^{-1}.

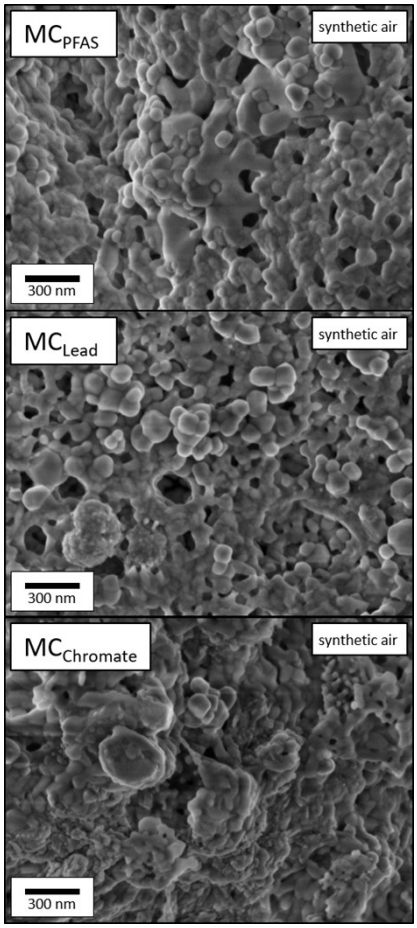


Figure S18: Scanning electron microscopy (SEM) images of the ceramic membrane after calcination in synthetic air up to 800°C with 10 K min^{-1}of PFAS (M_{PFAS}), sodium chromate ($M_{Chromate}$) and lead nitrate (M_{Lead}) retention experiments.

8.-Ceramic Composition and Mapping via Energy-dispersive X-ray Spectroscopy (EDS)

Table S2: Summary of elemental composition of membrane ceramic formed after calcination in nitrogen and synAir up to 800°C with 10 K ^{min1} determined by energy-dispersive X-ray spectroscopy (EDS)

Sample	Atmosphere[a)]	Ceramic yield / wt%	C / wt%	O / wt%	P / wt%	Co / wt%	Cr / wt%
$M_{PFOA\cdot N2}$	nitrogen	7.9	56.2	19.0	8.3	16.5	0
$M_{PFOA.\ SynAir}$	synAir	[0.47]	15.5	44.0	14.8	25.8	0
$M_{Lead.\ N2}$	nitrogen	6.9	65.9	19.4	4.8	9.9	0
$M_{Lead.\ SynAir}$	synAir	2.8	16.3	34.9	14.7	34.1	0
$M_{Chromate.\ N2}$	nitrogen	7.9	69.9	18.8	3.1	6.7	1.5
$M_{Chromate.\ SynAir}$	synAir	2.7	12.3	36.5	14.2	31.4	3.2

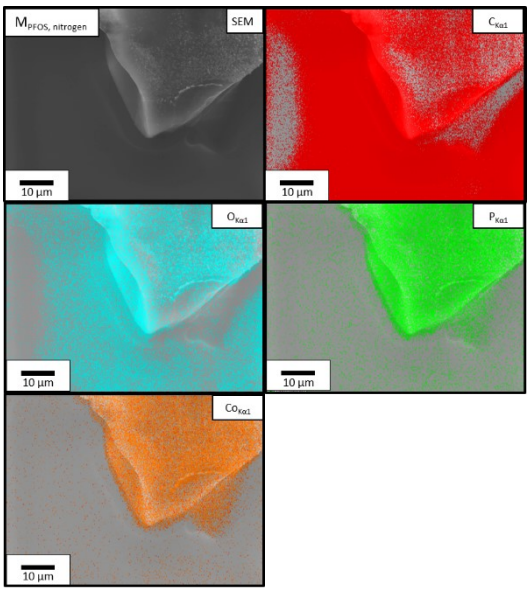


Figure S19: Energy-dispersive X-ray spectroscopy (EDS) images of respective elements found for M_{PFOS} made in a nitrogen atmosphere

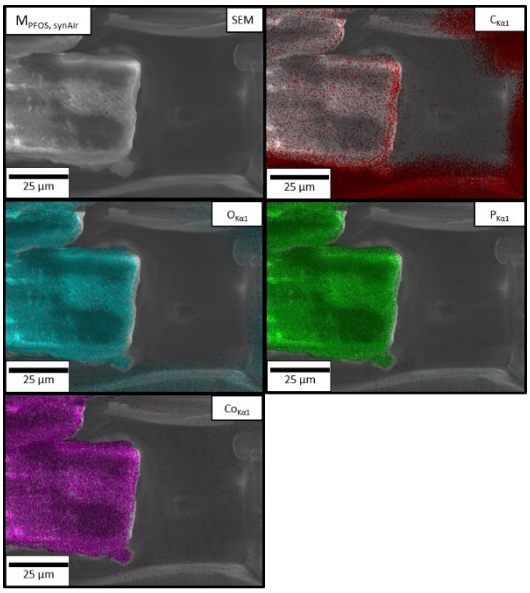
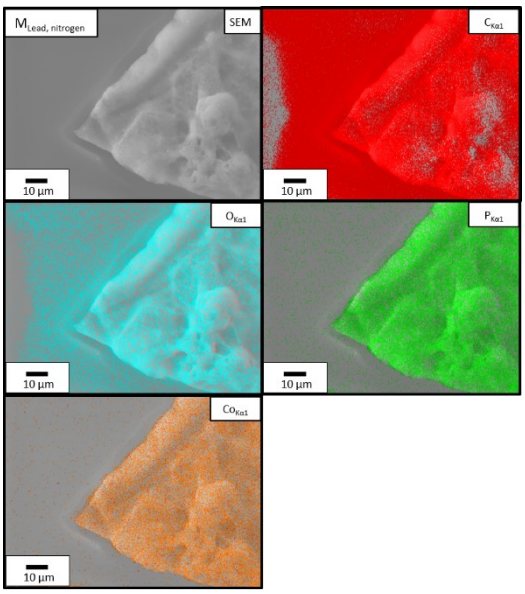


Figure S20: Energy-dispersive X-ray spectroscopy (EDS) images of respective elements found for M_{PFOS} made in an oxidative atmosphere



[a)] synAir is a mixture of nitrogen and oxygen (80/20).

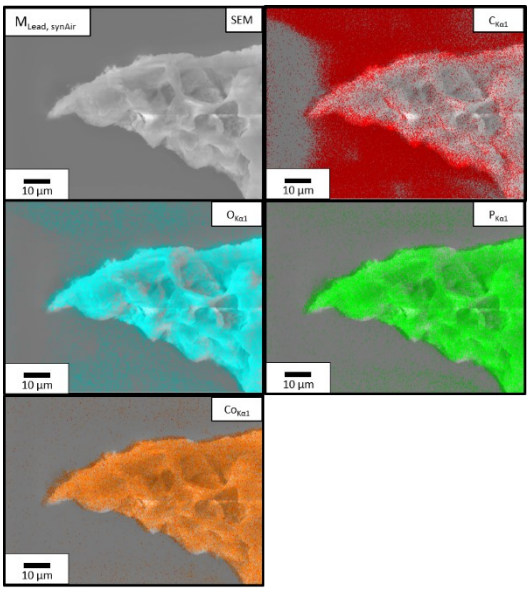


Figure S21: Energy-dispersive X-ray spectroscopy (EDS) images of respective elements found for M_{Lead} made in a nitrogen atmosphere

Figure S22: Energy-dispersive X-ray spectroscopy (EDS) images of respective elements found for M_{Lead} made in an oxidative atmosphere

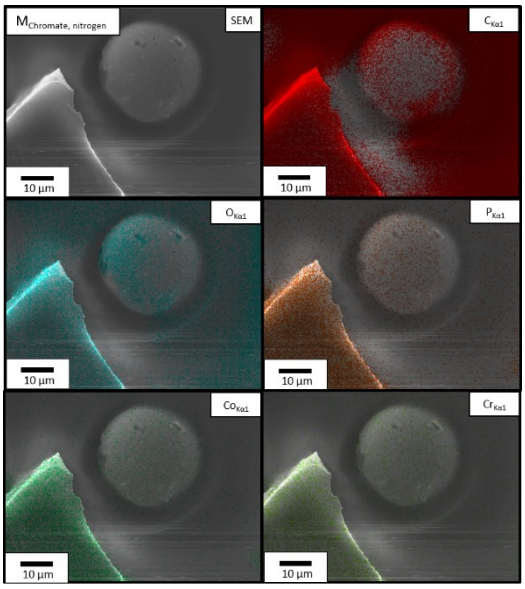


Figure S23: Energy-dispersive X-ray spectroscopy (EDS) images of respective elements found for $M_{Chromate}$ made in a nitrogen atmosphere

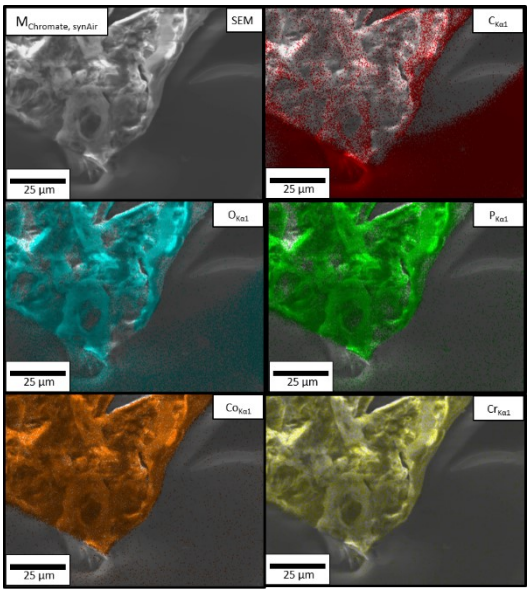


Figure S24: Energy-dispersive X-ray spectroscopy (EDS) images of respective elements found for $M_{Chromate}$ made in an oxidative atmosphere