Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information (ESI)

MOLECULARLY IMPRINTED POLYMERS BY THIOL-YNE CHEMISTRY: MAKING IMPRINTING EVEN EASIER

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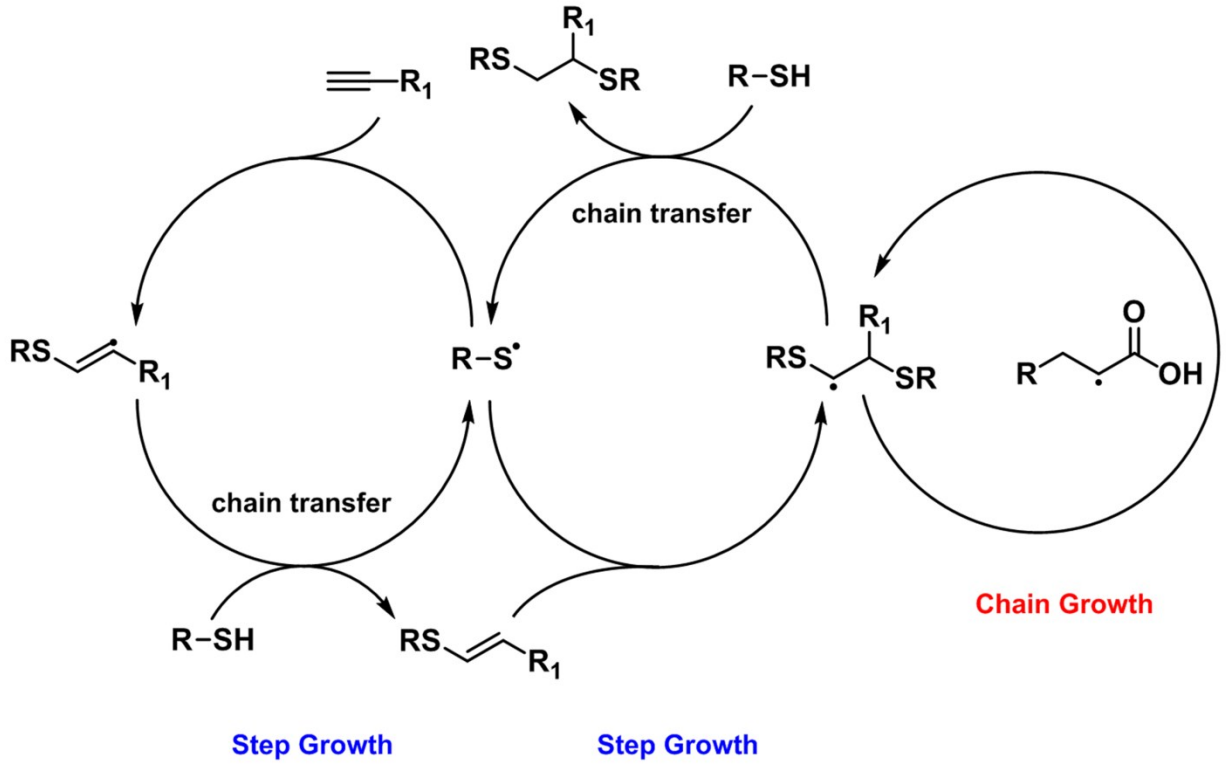

Scheme S1. Proposed mechanism for polymerization via the thiol-yne reaction showing its chain growth and step growth cycles.

Table S1. Alkyne and thiol conversions for thiol-yne polymerized p(AA-co-PETMP-co-DBC) and p(AA-co-diPETMP-co-DBC) as measured by FTIR. Percent conversion was calculated using the following equation:

conversion (%) $= \frac{r_p}{r_m} * 100$, where

$$r_p = \frac{peak\ height\ of\ active\ bond\ in\ the\ polymer}{peak\ height\ of\ C=O\ bond\ in\ the\ polymer} \qquad r_m = \frac{peak\ height\ of\ active\ bond\ in\ the\ monomer}{peak\ height\ of\ C=O\ bond\ in\ the\ monomer}$$

	Monomers			Polymers			
	peak height ≡C-H	peak height C=O	ratio	peak height ≡C-H	peak height C=O	ratio	Conv (%) ≡C-H
p(AA-co-PETMP-co-DBC)	26.5	74.2	0.357	0.9	62.4	0.014	96
p(AA-co-diPETMP-co-DBC)	26.8	74.5	0.360	0.7	41.9	0.017	95
	peak height S-H	peak height C=O	ratio	peak height S-H	peak height C=O	ratio	Conv (%) S-H
p(AA-co-PETMP-co-DBC)	4.1	83.6	0.049	0.7	62.4	0.011	77
p(AA-co-diPETMP-co-DBC)	3.6	79.9	0.045	0.5	41.9	0.012	73

Table S2. Gravimetric conversions for p(AA-co-PETMP-co-DBC) and p(AA-co-diPETMP-co-DBC).

	MIP	NIP
p(AA-co-PETMP-co-DBC)	92 %	94 %
p(AA-co-diPETMP-co-DBC)	>99 %	95 %

Calculation of K_{50} and B_{max}: The binding parameters K_{50} and B_{max} were calculated by fitting with a Langmuir model:

$$\theta = \frac{B_{max}[MIP]}{K_{50} + [MIP]}$$

where θ = fraction of bound template, B_{max} = maximum binding capacity, [MIP] = MIP concentration and K_{50} = apparent binding affinity.

Table S3. Surface area (in $m^2\ g^{-1}$) for p(AA-co-PETMP-co-DBC) and p(AA-co-diPETMP-co-DBC) obtained by BET using dinitrogen as adsorbate at 77 K.

	MIP ($m^2\ g^{-1}$)	NIP ($m^2\ g^{-1}$)
p(AA-co-PETMP-co-DBC)	1.7	2.0
p(AA-co-diPETMP-co-DBC)	2.1	2.5

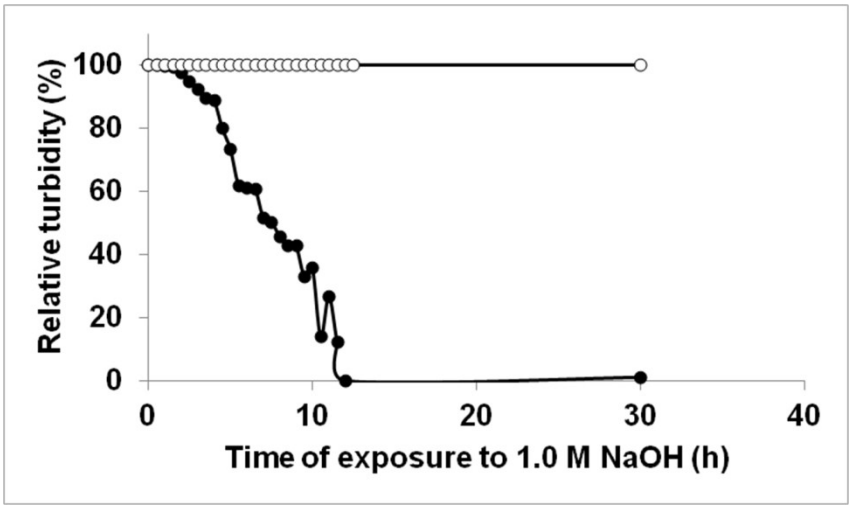

Figure S1. Turbidity measurements over the time for the alkaline hydrolysis of p(AA-co-PETA) (filled circles) and p(MAA-co-EGDMA) (empty circles) in 1.0 M aqueous NaOH.

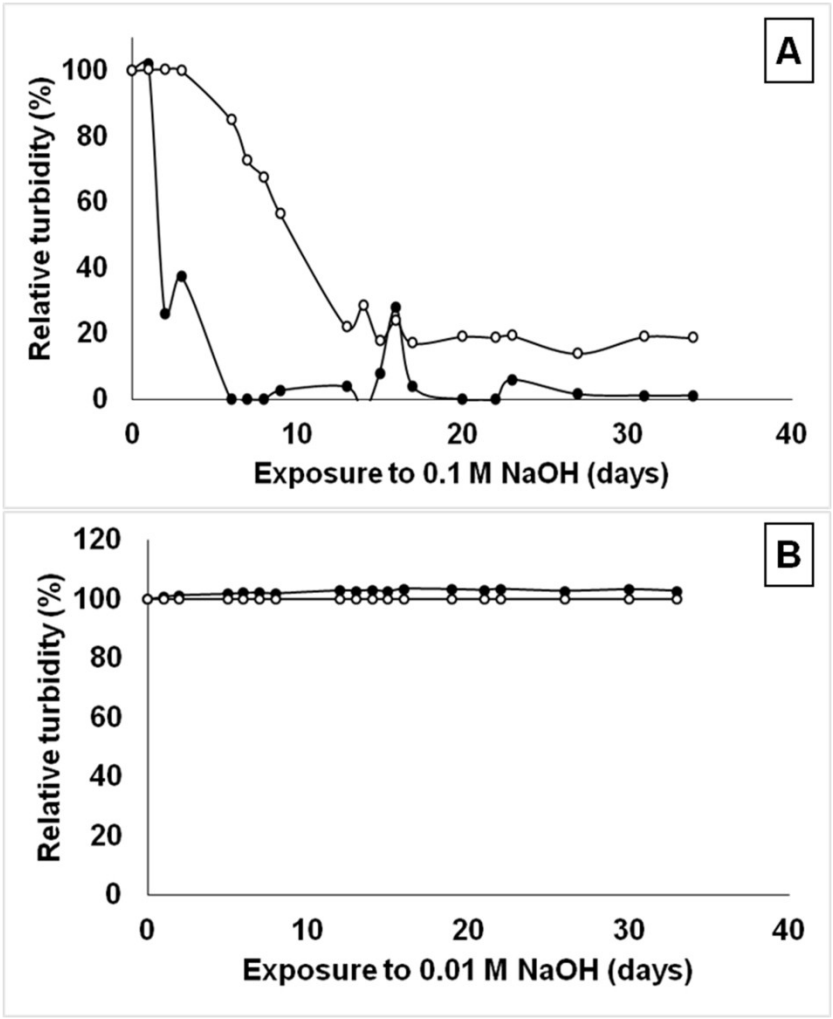

Figure S2. Hydrolytic degradation of p(AA-co-PETMP-co-DBC) (filled circles) and p(AA-co-diPETMP-co-DBC) (empty circles) in 0.1 molar aqueous NaOH (A) and in 0.01 molar aqueous NaOH (B) over time.

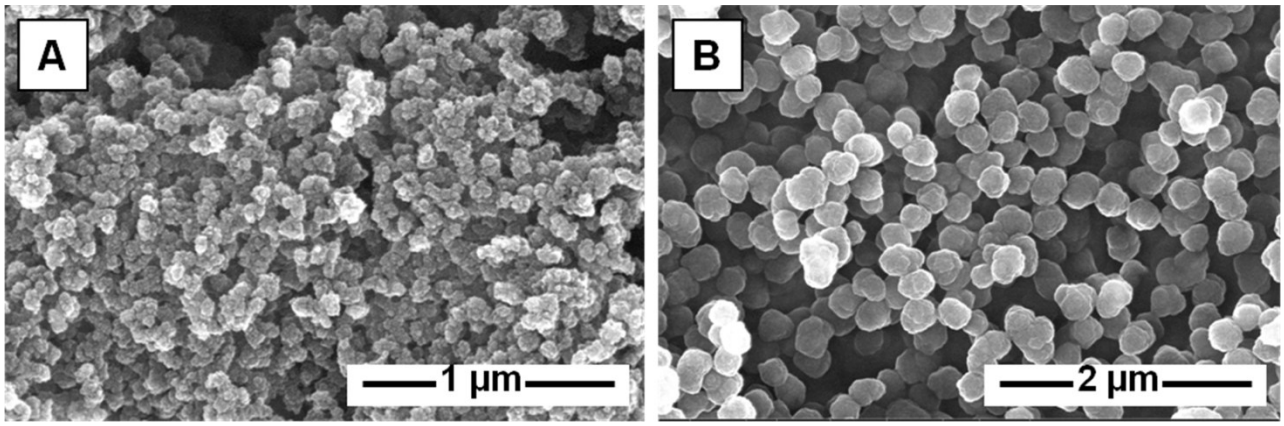

Figure S3. Representative SEM images of (A) p(AA-co-PETA) and (B) p(MAA-co-EGDMA).

Table S4. Mean particles size of the thiol-yne MIPs and NIPs and the FRP polymers as measured by SEM.

Polymer	Mean particle size (nm)
poly(AA-co-PETMP-co-DBC) MIP	2025 ± 446
poly(AA-co-PETMP-co-DBC) NIP	1147 ± 163
poly(AA-co-diPETMP-co-DBC) MIP	1922 ± 370
poly(AA-co-diPETMP-co-DBC) NIP	991 ± 148
poly(AA-co-PETA)	46.72 ± 11.63
poly(MAA-co-EGDMA)	329.7 ± 39.1

Table S5. Exact Mass (Mass), retention time (RT) and putative formula for the compounds identified by the algorythm "Find Bye Moleculare Feature" (MASSHunter, Agilent) on signals generating more than 2000 counts, for p(AA-co-PETA). Corresponding chromatograms are presented in Figure S6.

ESI-						ESI+		
Mass	**RT**	**Formula**	**Mass**	**RT**	**Formula**	**Mass**	**RT**	**Formula**
363.947	0.968		**1589.64**	34.192		**206.118**	1.1	
613.902	1.113		**1259.73**	34.22		**973.801**	32.528	
613.902	1.117		**1589.64**	34.224		**273.12**	34.767	
383.918	1.165		**1453.66**	34.237		**117.078**	34.888	
895.814	1.184		**657.886**	34.309		**157.958**	35.13	
285.939	1.184		**793.859**	34.328		**837.827**	35.21	
649.851	1.188		**1453.66**	34.345		**565.882**	35.306	
379.925	1.188		**987.787**	34.361		**293.934**	35.385	
363.947	1.188		**113.993**	34.386		**480.256**	35.532	C22 H40 O11
1161.75	1.189		**2441.45**	34.43		**157.958**	35.554	
895.815	1.19		**1317.69**	34.438		**429.91**	35.612	
191.952	1.191		**987.787**	34.473		**1031.76**	35.687	
645.859	1.201		**521.914**	34.499		**436.23**	35.743	C20 H36 O10
649.851	1.202		**1317.69**	34.561		**895.785**	35.824	
269.96	1.202		**385.941**	34.685		**392.203**	35.974	C18 H32 O9
285.938	1.203		**1181.72**	34.866		**392.204**	35.978	C18 H32 O9
645.859	1.204		**1511.62**	34.903		**430.912**	36.116	
911.793	1.212		**851.815**	34.904		**623.839**	36.122	
457.884	1.215		**1181.72**	35.097		**348.177**	36.213	C16 H28 O8
911.794	1.217		**1375.65**	35.242		**157.958**	36.472	
629.881	1.219		**1045.74**	35.331		**293.934**	36.541	
535.893	1.219		**1045.74**	35.381		**565.885**	36.635	
629.88	1.221		**1239.67**	35.539		**157.958**	36.647	
551.871	1.221		**579.871**	35.644		**429.91**	36.649	
175.974	1.223		**715.843**	35.651		**429.91**	36.65	
1177.73	1.227		**1103.7**	35.761		**701.861**	36.674	
1177.73	1.233		**579.871**	35.819		**837.836**	36.704	
298.054	1.951		**1103.7**	35.836		**837.836**	36.716	
515.9	2.472		**443.898**	35.843		**701.86**	36.725	
249.967	2.785		**773.799**	35.882		**973.812**	36.737	
365.129	3.492		**969.726**	35.956		**973.812**	36.739	
479.929	9.628		**443.898**	35.987		**1109.79**	36.762	
395.897	10.534		**773.799**	36.019		**1109.79**	36.765	
395.897	10.564		**967.729**	36.038		**1245.76**	36.772	
301.91	10.572		**637.827**	36.044		**1245.76**	36.78	
661.831	10.712		**1163.66**	36.106		**1381.74**	36.784	

661.831	10.722		**637.828**	36.134		**1381.74**	36.788	
927.764	10.852		**1027.68**	36.163		**1517.72**	36.8	
927.764	10.866		**501.856**	36.164		**1517.72**	36.801	
645.859	11.231		**501.856**	36.198		**1653.69**	36.806	
915.787	11.253		**385.943**	36.228		**1653.69**	36.812	
645.859	11.261		**1085.64**	36.243		**1789.67**	36.819	
911.794	11.336		**521.918**	36.587	C18 H2 O19	**1925.64**	36.835	
629.88	11.363		**249.967**	36.631		**1789.67**	36.835	
285.939	11.476		**657.893**	36.635		**2061.62**	36.844	
191.952	11.476		**385.943**	36.648		**2333.56**	36.845	
379.925	11.479		**427.93**	36.65		**2061.62**	36.848	
1443.66	11.53		**155.981**	36.653		**1925.64**	36.848	
379.925	11.532		**657.893**	36.682		**2469.54**	36.85	
1177.73	11.595		**521.918**	36.682	C18 H2 O19	**2197.59**	36.854	
1177.73	11.6		**929.845**	36.698		**2469.54**	36.856	
895.814	11.6		**929.845**	36.708		**2605.51**	36.857	
551.871	11.6		**793.869**	36.719		**2197.59**	36.858	
895.813	11.613		**793.869**	36.721		**2741.49**	36.861	
911.793	11.625		**1065.82**	36.73		**2605.51**	36.862	
649.851	11.626		**1065.82**	36.733		**2333.57**	36.862	
395.898	13.169		**1201.8**	36.753		**460.267**	37.292	
395.898	13.222		**1201.8**	36.754		**273.121**	37.534	
249.967	13.808		**1337.77**	36.763		**172.072**	37.541	C8 H12 O4
365.129	14.312		**1337.77**	36.764		**273.121**	37.614	
365.129	17.497		**1473.75**	36.769		**118.063**	37.806	
287.112	17.786		**1473.75**	36.774		**136.075**	37.829	
508.883	29.14		**1609.72**	36.777		**136.075**	38.118	C5 H12 O4
508.883	29.14		**1609.72**	36.791		**288.156**	38.653	C14 H24 O6
1881.64	31.648		**1745.7**	36.794		**288.156**	38.661	C14 H24 O6
1745.67	31.893		**1881.68**	36.797		**346.198**	39.216	C17 H30 O7
1065.8	33.69		**1745.7**	36.797		**230.08**	41.559	
385.941	33.701		**2561.55**	36.801		**208.098**	41.56	
1667.65	33.78		**2425.58**	36.803		**230.077**	41.726	C10 H14 O6
1531.68	33.847		**2017.65**	36.803		**208.096**	41.729	C8 H16 O6
1395.71	33.881		**1881.68**	36.803		**269.148**	42.203	
249.966	33.892		**2425.57**	36.804		**134.095**	42.997	
1939.6	33.907		**2289.6**	36.805		**116.084**	43.009	
155.98	33.928		**2153.63**	36.805		**134.095**	43.324	C6 H14 O3
1259.73	34		**2153.62**	36.806		**116.084**	43.376	C6 H12 O2
1725.61	34.066		**2289.6**	36.807		**302.099**	48.068	C13 H18 O8
1861.58	34.099		**2017.65**	36.808		**280.117**	48.072	C11 H20 O8

1803.62	34.103		**385.943**	37.354	C12 H2 O15	**341.17**	48.208	
1725.61	34.119		**385.944**	38.439		**280.12**	48.413	
1123.76	34.125		**322.088**	41.492		**302.102**	48.47	
657.887	34.188		**208.094**	41.502		**228.098**	54.766	
1123.76	34.189		**280.116**	48.277		**206.116**	54.818	C9 H18 O5
						206.118	54.836	
						267.169	55.052	

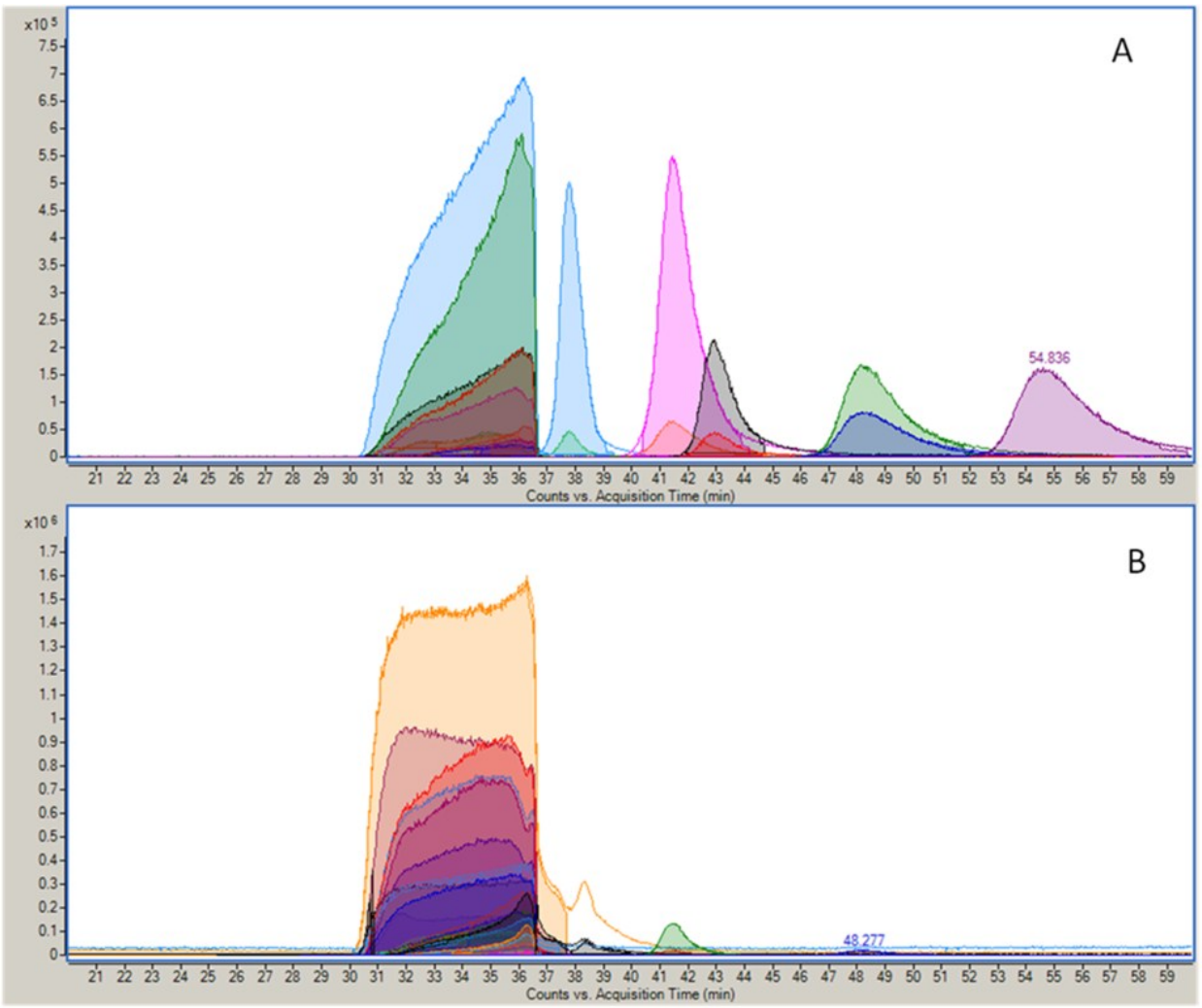

Figure S4. Major compounds fund by SEC/HRMS with positive (A) et negative (B) ionisation for p(AA-co-PETA). Retention time, exact mass and putative formula was reported on Table S5.

Table S6. Exact Mass (Mass), retention time (RT) and putative formula for the compounds identified by the algorythm "Find Bye Moleculare Feature" (MASSHunter, Agilent) on signals generating more than 2000 counts, for p(AA-co-diPETMP-co-DBC). Corresponding chromatograms are presented in Figure S5.

ESI-			ESI+		
Mass	**RT**	**Formula**	**Mass**	**RT**	**Formula**
155.980	34.51		**368.131**	37.96	C14 H24 O11
155.980	34.51		**368.131**	37.96	C14 H24 O11
249.966	34.59		**157.959**	35.44	
249.966	34.59		**157.959**	35.44	
385.941	34.66	C12 H2 O15	**293.936**	35.70	
385.941	34.66	C12 H2 O15	**293.936**	35.70	
113.993	35.03		**429.912**	35.91	C13 H2 O15 S
113.993	35.03		**429.912**	35.91	C13 H2 O15 S
155.980	35.18		**565.886**	35.93	
155.980	35.18		**565.886**	35.93	
249.966	35.25		**701.860**	35.99	
249.966	35.25		**701.860**	35.99	
385.941	35.32	C12 H2 O15	**429.912**	35.99	C13 H2 O15 S
385.941	35.32	C12 H2 O15	**429.912**	35.99	C13 H2 O15 S
521.914	35.39	C18 H2 O19	**565.884**	36.01	
521.914	35.39	C18 H2 O19	**565.884**	36.01	
521.914	35.41	C18 H2 O19	**837.834**	36.03	
521.914	35.41	C18 H2 O19	**837.834**	36.03	
657.887	35.43	C20 H2 O26	**837.834**	36.07	
657.887	35.43	C20 H2 O26	**837.834**	36.07	
427.928	35.46	C14 H4 O14 S	**973.810**	36.08	
427.928	35.46	C14 H4 O14 S	**973.810**	36.08	
657.887	35.46	C20 H2 O26	**701.859**	36.08	
657.887	35.46	C20 H2 O26	**701.859**	36.08	
929.833	35.49		**1109.790**	36.11	
929.833	35.49		**1109.790**	36.11	
929.833	35.51		**973.810**	36.11	
929.833	35.51		**973.810**	36.11	
1065.810	35.61		**1109.790**	36.12	
1065.810	35.61		**1109.790**	36.12	
1201.780	35.61		**1245.760**	36.14	
1201.780	35.61		**1245.760**	36.14	
793.860	35.64		**1245.760**	36.15	
793.860	35.64		**1245.760**	36.15	

1065.810	35.64		**1381.740**	36.15	
1065.810	35.64		**1381.740**	36.15	
793.860	35.68		**1381.740**	36.16	
793.860	35.68		**1381.740**	36.16	
1201.780	35.74		**1517.710**	36.17	
1201.780	35.74		**1517.710**	36.17	
1337.750	35.75		**1517.710**	36.17	
1337.750	35.75		**1517.710**	36.17	
1337.750	35.81		**1789.670**	36.19	
1337.750	35.81		**1789.670**	36.19	
1473.730	35.81		**1789.670**	36.19	
1473.730	35.81		**1789.670**	36.19	
1473.730	35.88		**1653.690**	36.20	
1473.730	35.88		**1653.690**	36.20	
1609.700	35.89		**2061.620**	36.21	
1609.700	35.89		**2061.620**	36.21	
1609.700	35.94		**1925.640**	36.21	
1609.700	35.94		**1925.640**	36.21	
1745.680	35.97		**1653.690**	36.22	
1745.680	35.97		**1653.690**	36.22	
1881.650	35.99		**1925.640**	36.23	
1881.650	35.99		**1925.640**	36.23	
1745.680	36.01		**2197.590**	36.23	
1745.680	36.01		**2197.590**	36.23	
2017.620	36.04		**2061.610**	36.24	
2017.620	36.04		**2061.610**	36.24	
1881.650	36.04		**276.123**	37.89	C12 H20 O7
1881.650	36.04		**276.123**	37.89	C12 H20 O7
2017.620	36.08		**254.141**	37.90	
2017.620	36.08		**254.141**	37.90	
2153.590	36.12		**372.204**	38.04	
2153.590	36.12		**372.204**	38.04	
2153.600	36.13		**394.186**	38.04	C17 H30 O10
2153.600	36.13		**394.186**	38.04	C17 H30 O10
2289.570	36.17		**290.138**	39.21	C13 H22 O7
2289.570	36.17		**290.138**	39.21	C13 H22 O7
			346.164	41.37	C16 H26 O8
			346.164	41.37	C16 H26 O8
			194.027	47.19	C8 H12 Cl2 O
			194.027	47.19	C8 H12 Cl2 O
			450.157	51.56	C15 H30 O15

			450.157	51.56	C15 H30 O15

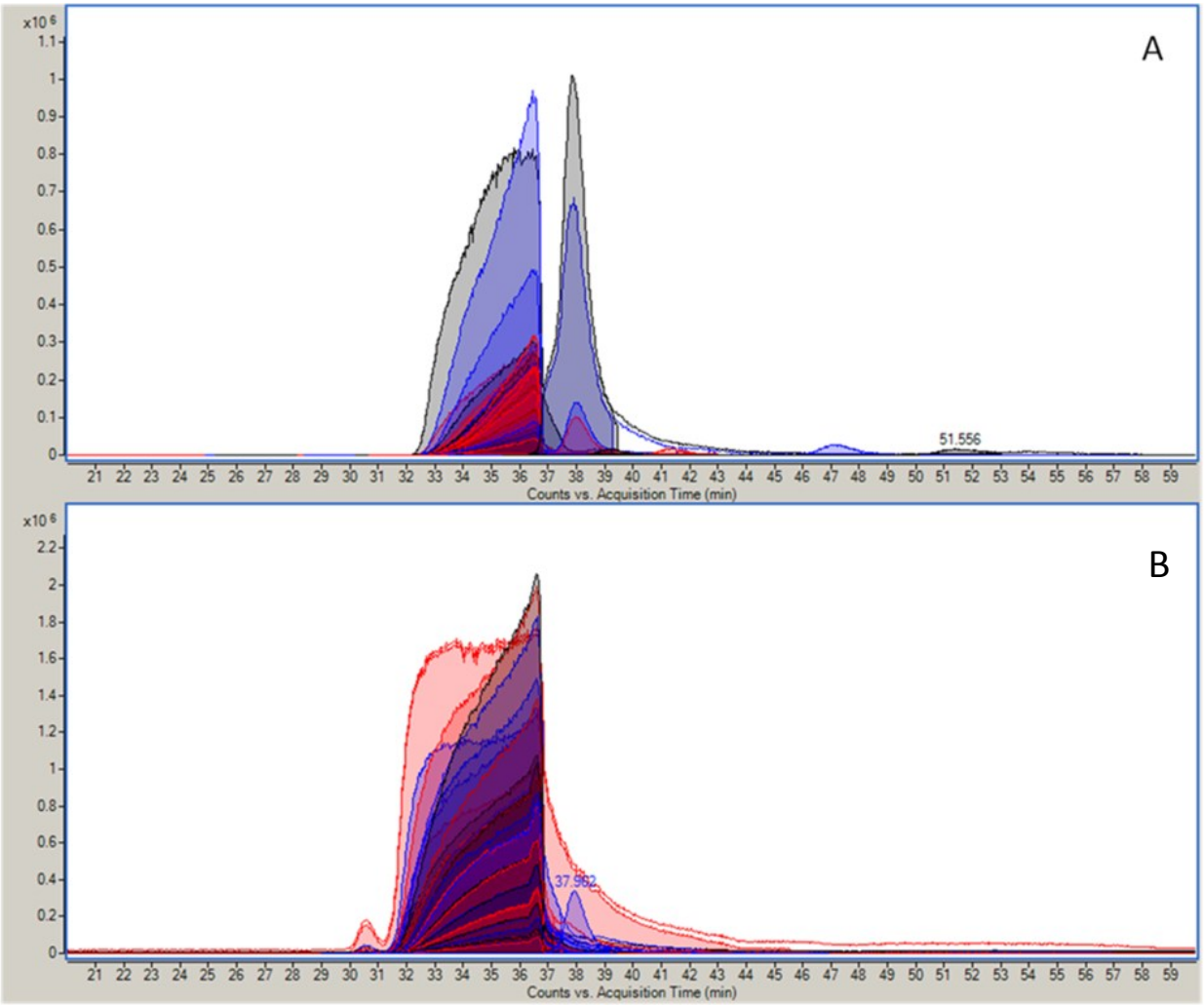

Figure S5. Major compounds fund by SEC/HRMS with positive (A) et negative (B) ionisation for p(AA-co-diPETMTP-co-DBC). Retention time, exact mass and putative formulae were reported on Table S4.

Table S7. Exact Mass (Mass), retention time (RT) and putative formula for the compounds identified by the algorythm "Find Bye Moleculare Feature" (MASSHunter, Agilent) on signals generating more than 2000 counts, for p(AA-co-PETMP-co-DBC). Corresponding chromatograms are presented in Figure S4.

ESI-						ESI+		
Mass	**RT**	**Formula**	**Mass**	**RT**	**Formula**	**Mass**	**RT**	**Formula**
853.811	32.56		**1453.660**	34.92		**1653.680**	33.23	
386.943	32.73		**1375.650**	34.92		**1381.730**	33.28	
1181.720	33.47		**1317.690**	34.95		**1517.700**	33.44	
1201.780	33.94		**249.966**	34.99		**973.804**	34.21	
385.941	34.13	C12 H2 O15	**1045.740**	35.17		**158.961**	34.88	
987.787	34.50		**579.871**	35.59	C15 H13 Cl O12 S5	**429.910**	35.54	
1123.760	34.52		**967.729**	35.73		**759.813**	35.96	
657.886	34.57	C20 H2 O26	**773.800**	35.79		**623.841**	36.07	
1589.640	34.63		**443.899**	35.80	C9 H16 O6 S7	**487.867**	36.15	
1123.760	34.63		**637.828**	35.97	C19 H4 Cl2 O17 S2	**351.893**	36.21	
1395.710	34.64		**385.944**	38.67	C13 H6 O10 S2	**136.075**	37.81	
113.993	34.65		**1653.680**	33.23		**118.063**	37.82	
1259.730	34.68		**1381.730**	33.28		**276.122**	37.91	
657.886	34.69	C20 H2 O26	**1517.700**	33.44		**254.140**	37.92	
793.859	34.70		**973.804**	34.21		**394.185**	38.11	
1511.620	34.71		**158.961**	34.88		**394.185**	38.11	
1259.730	34.71		**429.910**	35.54		**244.095**	38.17	
929.831	34.74		**759.813**	35.96		**206.082**	46.08	
1453.660	34.75		**623.841**	36.07		**194.027**	48.47	
987.787	34.75		**487.867**	36.15		**332.095**	55.60	
793.859	34.75		**351.893**	36.21		**332.095**	55.61	
929.831	34.78		**136.075**	37.81				
1181.720	34.78		**118.063**	37.82				
521.914	34.79	C18 H2 O19	**276.122**	37.91				
1045.740	34.79		**254.140**	37.92				
715.843	34.79	C18 H20 O12 S9	**394.185**	38.11				
1531.680	34.80		**394.185**	38.11				
851.815	34.81		**244.095**	38.17				
521.914	34.85		**206.082**	46.08				
427.928	34.87		**194.027**	48.47				
1065.800	34.89		**332.095**	55.60				
385.941	34.90	C12 H2 O15	**332.095**	55.61				

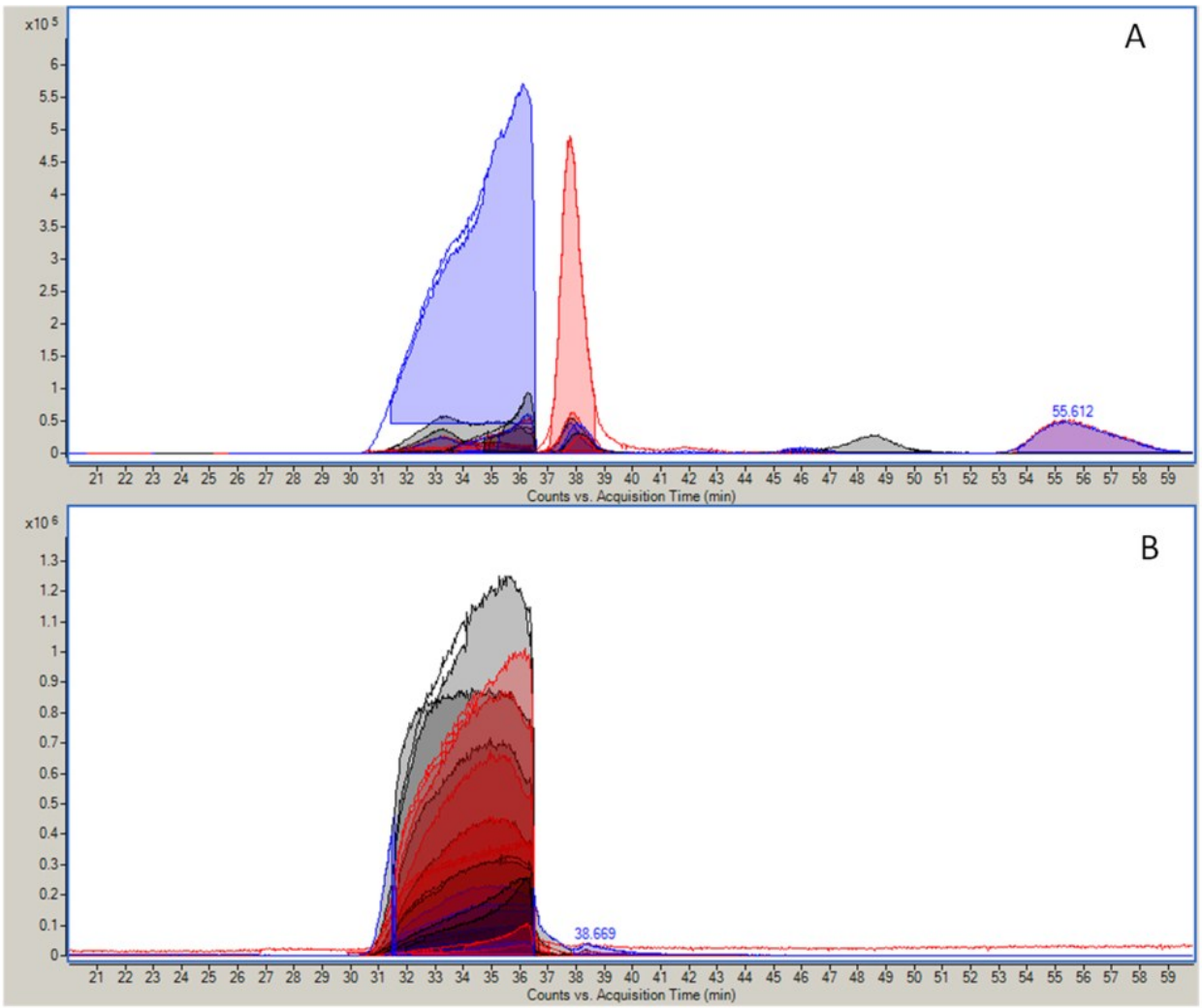

Figure S6. Major compounds fund by SEC/HRMS with positive (A) et negative (B) ionisation for p(AA-co-PETMTP-co-DBC). Retention time, exact mass and putative formulae were reported on Table S3.

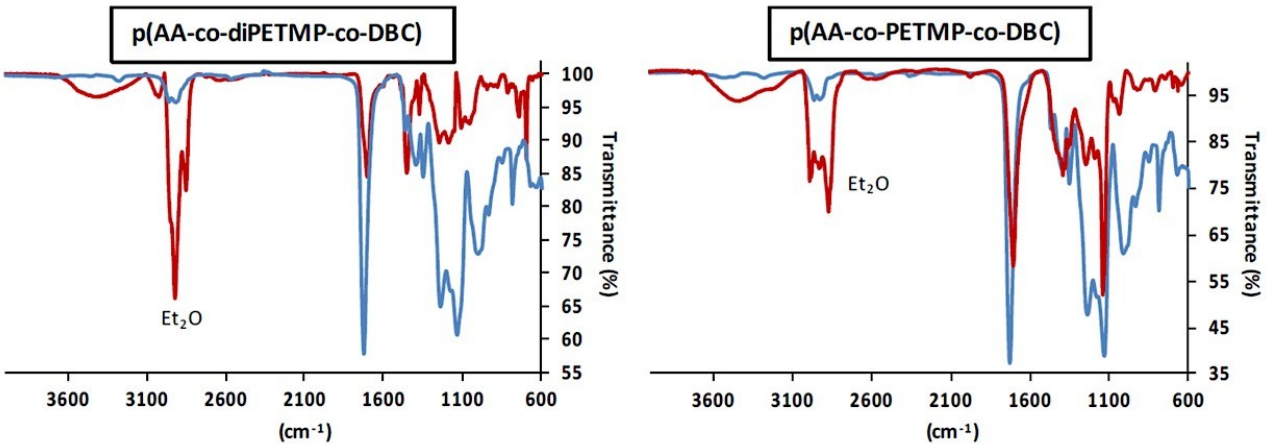

Figure S7. Comparison between the FTIR spectra of the thiol-yne MIPs (blue) and their products of hydrolysis (red) obtained by incubation in 1.0 M NaOH.

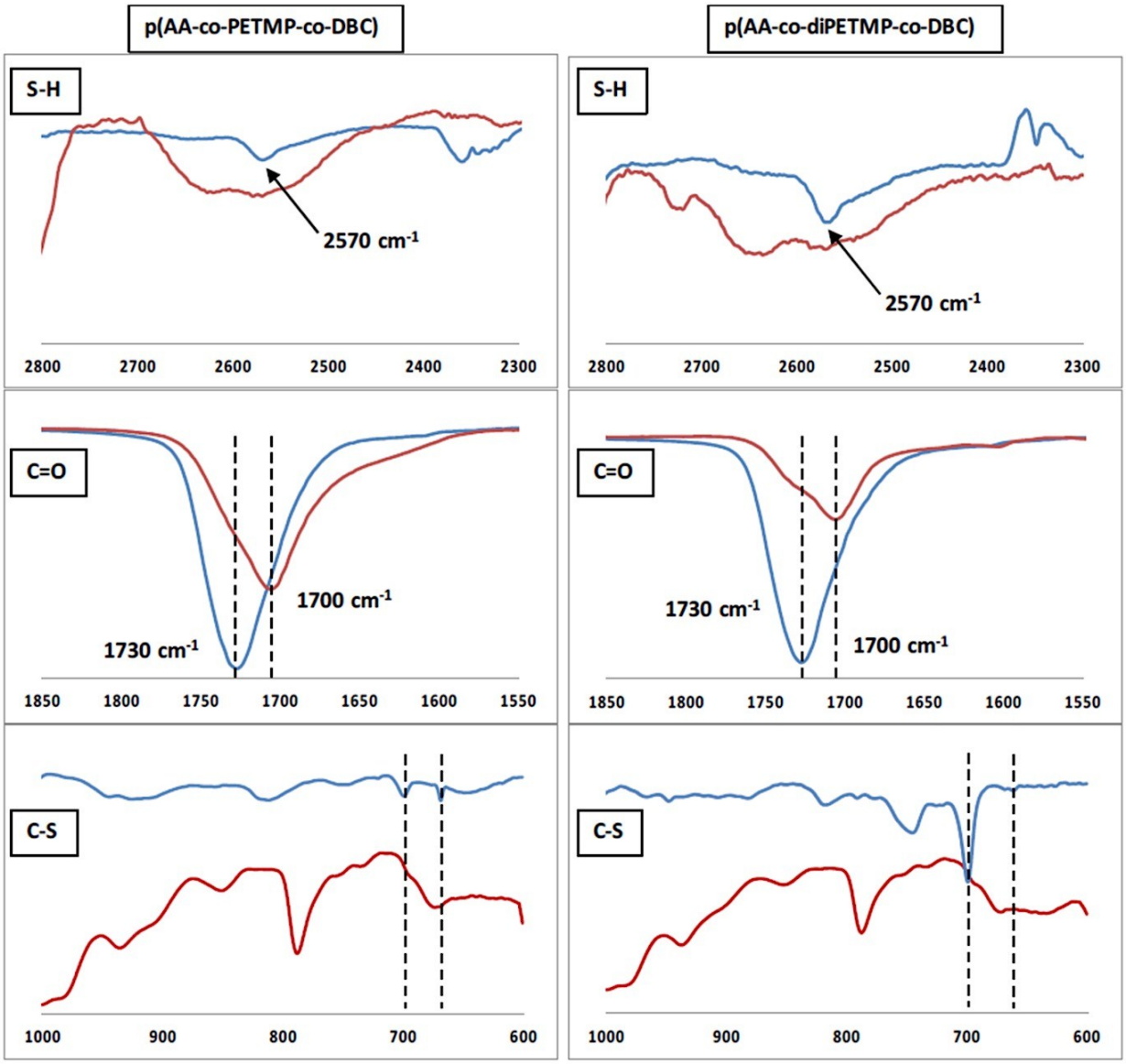

Figure S8. Comparison between the FTIR spectra of the thiol-yne polymer (blue) and their products of hydrolysis (red) for different vibration modes (insets). Wavenumbers are in cm^{-1}.

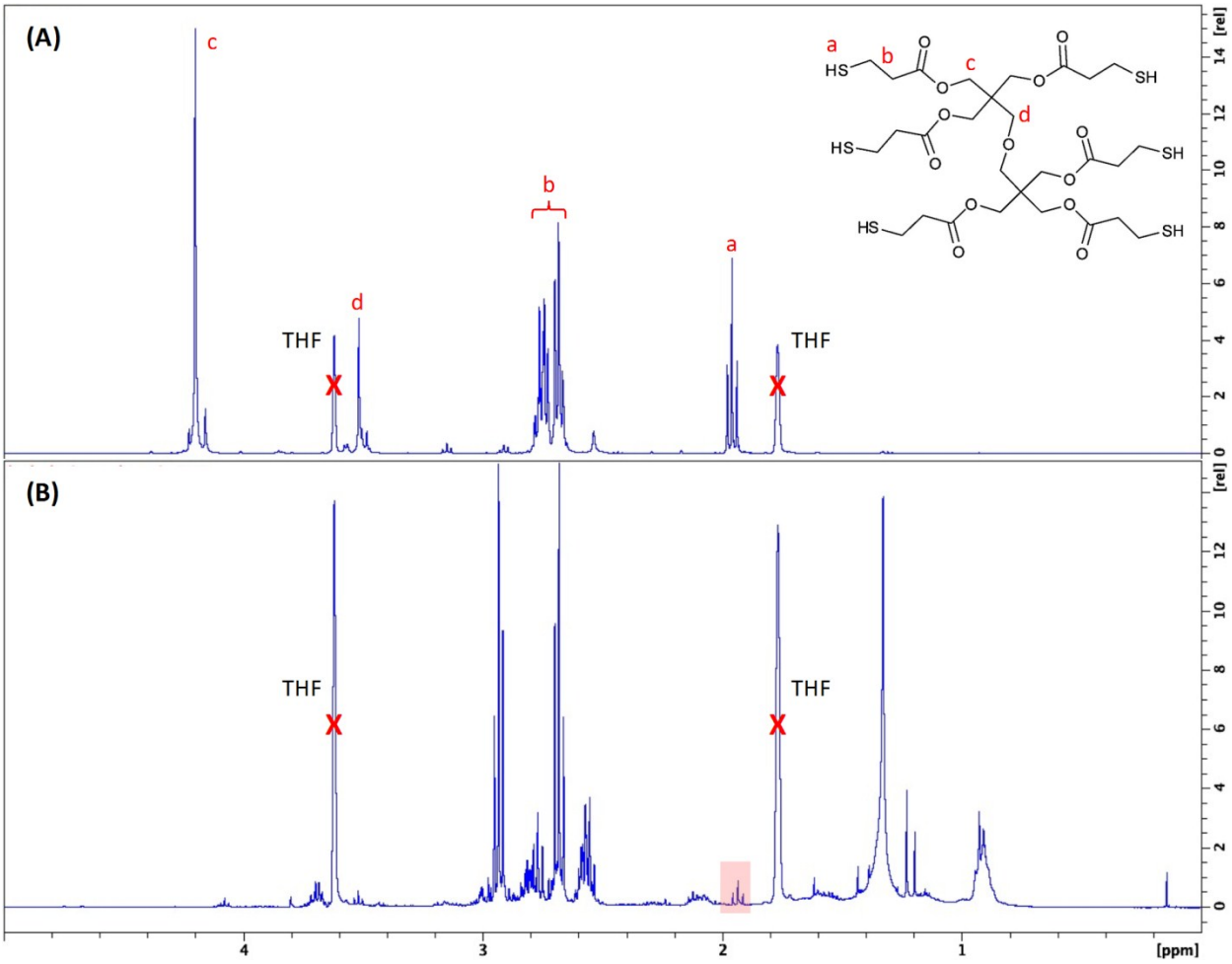

Figure S9. Comparison between the ^{1}H-NMR spectra (in d8-THF) of (A) the polythiol diPETMP and (B) the products of the alkaline hydrolysis (pH = 14) for p(AA-co-diPETMP-co-DBC). The highlighted peaks in B (1.96 ppm) refer to the –SH group.