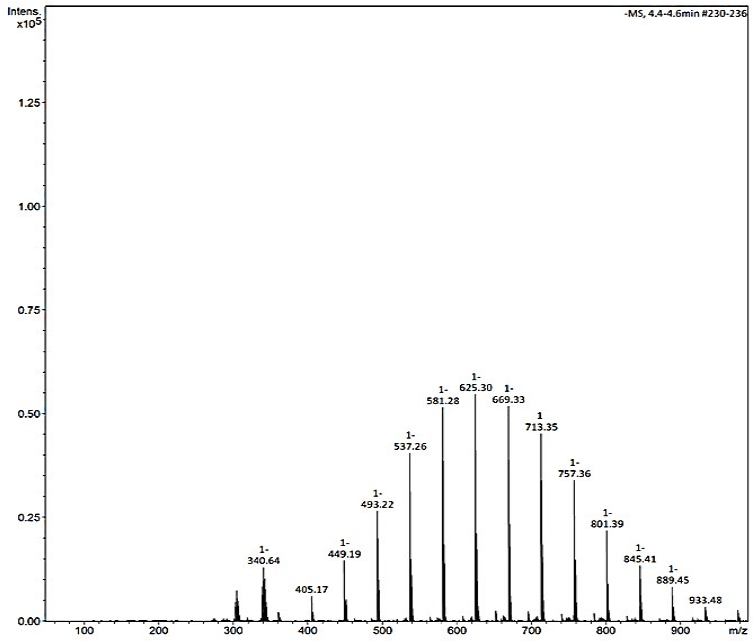
Basic physicochemical properties of PEG-600.

Polydispersity of the PEG-600 sample has been measured and is presented in the figure below:



Polydispersity of PEG-600 as obtained by ESI-MS. The maximum is located at 635.30 m/z.

Data from Merck website: Density at 20 °C : 1.13 gcm^{-3}. Melting point: 17 – 22 °C

Table S1: [P_{44414}] Cl / HCl / H_2O at 25 °C *(turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
13.7	*45.2*
13.9	*42.9*
14.5	*39.4*
14.7	*37.6*
14.8	*36.4*
15.1	*35.0*
15.2	*34.0*
15.3	*33.1*
15.5	*32.3*
15.5	*31.7*
15.7	*31.0*
15.7	*30.3*
15.9	*29.5*
16.0	*29.1*
16.0	*28.6*
16.2	*28.1*
16.1	*27.8*
16.3	*27.3*
16.3	*26.9*
16.3	*26.5*
16.4	*26.2*
16.5	*25.9*
16.6	*25.4*
16.7	*24.9*
16.7	*24.5*
16.8	*24.3*
16.9	*23.9*
16.8	*23.6*
16.9	*23.3*

Table S2: [P_{44414}] Cl / HCl / $CrCl_3$ / H_2O [Cr(III)] = 2.60 g/L at 25 °C *(turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
0.0	*74.8*
13.1	*40.6*
13.4	*38.4*
13.7	*36.4*
13.9	*34.9*
14.1	*33.3*
14.3	*31.9*
14.5	*30.6*
14.7	*29.4*
14.9	*28.4*
15.0	*27.4*
15.2	*26.4*
15.3	*25.5*
15.4	*24.6*
15.6	*23.9*
15.7	*23.1*
15.8	*22.4*
15.9	*21.8*
16.0	*21.2*
16.1	*20.7*
16.2	*20.2*
16.3	*19.7*
16.4	*19.2*
16.5	*18.8*

Table S3: [P_{44414}] Cl / HCl / $CrCl_3$ / H_2O [Cr(III)] = 5.11 g/L at *25 °C* *(turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
0.0	*72.2*
12.7	*40.4*
13.0	*37.8*
13.4	*35.9*
13.6	*33.8*

13.9	*32.2*
14.1	*30.7*
14.3	*29.5*
14.5	*28.5*
14.6	*27.3*
14.8	*26.1*
15.0	*25.1*

15.2	*24.3*
15.3	*23.3*
15.4	*22.6*
15.6	*21.8*
15.7	*21.2*
15.8	*20.5*
15.9	*19.9*

16.0	*19.4*
16.1	*18.9*
16.2	*18.4*
16.2	*18.0*

Table S4: [P_{44414}] Cl / HCl / $CrCl_3$ / H_2O [Cr(III)] = 10.0 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
0.0	*72.1*
11.7	*41.8*
12.1	*39.4*
12.4	*37.0*
12.7	*34.8*
13.0	*33.0*

13.2	*31.4*
13.4	*30.0*
13.5	*28.5*
13.6	*27.4*
13.8	*26.5*
14.0	*25.5*
14.1	*24.7*
14.2	*23.9*

14.3	*23.2*
14.4	*22.5*
14.5	*21.9*
14.6	*21.3*
14.7	*20.5*
14.8	*19.7*
14.9	*19.1*

Table S5: [P_{44414}] Cl / HCl / $CrCl_3$ / H_2O [Cr(III)] = 15.33 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
0.0	*71.7*
10.5	*43.8*
10.9	*40.9*
11.3	*38.6*
11.6	*36.2*
11.9	*34.0*
12.1	*32.4*

12.4	*30.7*
12.6	*29.2*
12.8	*27.8*
12.9	*26.8*
13.1	*25.7*
13.3	*24.7*
13.4	*23.9*
13.6	*23.1*
13.7	*22.2*

13.9	*21.5*
14.0	*20.9*
14.1	*20.3*
14.2	*19.7*
14.3	*19.2*
14.4	*18.6*
14.4	*18.1*
14.5	*17.6*
14.6	*17.2*

Table S6: [P_{44414}] Cl / HCl / $NiCl_2$/ H_2O [Ni(II)] = 2.51 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
13.4	*40.8*
13.6	*38.8*
13.9	*36.8*
14.1	*35.0*
14.3	*33.4*
14.5	*32.1*
14.7	*31.0*

14.9	*29.7*
15.1	*28.6*
15.2	*27.6*
15.4	*26.7*
15.5	*25.9*
15.6	*25.0*
15.8	*24.1*
16.0	*23.4*

16.1	*22.6*
16.2	*22.0*
16.3	*21.4*
16.4	*20.7*
16.5	*20.1*
16.6	*19.6*
16.7	*18.9*
16.8	*18.2*

Table S7: [P_{44414}] Cl / HCl / $NiCl_2$ / H_2O [Ni(II)] = 5.01 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
12.9	*41.8*
13.2	*39.8*
13.5	*37.0*
13.8	*35.3*
14.0	*33.6*

14.3	*32.2*
14.5	*30.9*
14.6	*29.7*
14.8	*28.7*
15.0	*27.6*
15.2	*26.6*
15.3	*25.8*

15.4	*24.9*
15.6	*24.1*
15.7	*23.4*
15.8	*22.7*
15.8	*22.0*
16.1	*21.2*

Table S8: [P_{44414}] Cl / HCl / $NiCl_2$ / H_2O [Ni(II)] = 10.00 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
11.9	*43.5*
12.3	*40.4*
12.6	*38.0*
12.8	*35.9*
13.2	*34.2*

13.4	*32.5*
13.7	*30.9*
13.9	*29.3*
14.1	*28.1*
14.3	*27.0*
14.5	*25.9*
14.7	*24.8*

14.8	*23.9*
15.0	*22.8*
15.2	*21.9*
15.3	*21.1*
15.5	*20.3*
15.6	*19.7*
15.6	*19.6*

Table S9: [P_{44414}] Cl / HCl / $NiCl_2$ / H_2O [Ni(II)] = 15.05 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
11.0	*46.1*
11.4	*42.9*
11.7	*40.5*
12.1	*38.3*
12.4	*36.2*
12.7	*34.4*
13.0	*32.6*
13.2	*31.1*
13.3	*29.9*
13.6	*28.4*
13.8	*27.0*
14.0	*25.9*
14.2	*24.9*
14.3	*23.9*
14.5	*23.0*
14.6	*22.2*
14.8	*21.4*
14.9	*20.7*
15.0	*20.0*
15.1	*19.3*
15.2	*18.6*

Table S10: [P_{44414}] Cl / HCl / $FeCl_2$ / H_2O [Fe(II)] = 1.05 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
13.1	*44.7*
13.5	*42.7*
13.7	*40.1*
14.3	*38.5*
14.4	*37.0*
14.5	*35.8*
14.8	*34.7*
15.0	*33.9*
15.1	*33.4*
15.1	*33.2*
15.2	*32.3*
15.2	*31.7*
15.4	*31.1*
15.5	*30.4*
15.7	*29.6*
15.7	*29.1*
15.8	*28.5*
16.0	*28.1*
16.0	*27.8*
16.1	*27.5*
16.0	*27.1*
16.1	*26.7*
16.2	*26.3*
16.3	*26.0*
16.3	*25.7*
16.4	*25.4*
16.4	*25.0*
16.5	*24.7*
16.5	*24.3*
16.7	*24.0*
16.7	*23.8*
16.7	*23.4*
16.8	*23.1*
16.8	*22.9*
16.8	*22.6*
16.9	*22.5*
16.9	*22.2*
16.9	*22.0*
16.9	*21.8*
17.0	*21.5*
17.0	*21.3*
17.1	*21.1*
17.1	*20.8*
17.2	*20.4*
17.2	*20.2*
17.2	*19.9*
17.4	*19.6*
17.4	*19.3*
17.4	*18.9*
17.5	*18.4*
17.6	*18.0*
17.7	*17.6*
17.7	*17.3*
17.8	*17.1*
17.8	*16.8*
17.9	*16.6*
17.9	*16.4*
18.0	*16.0*
18.0	*15.8*
18.1	*15.4*
18.1	*15.1*
18.2	*14.8*
18.2	*14.6*
18.2	*14.4*
18.3	*14.2*
18.3	*13.9*
18.4	*13.7*
18.4	*13.5*
18.5	*13.4*
18.5	*13.2*
18.5	*13.0*
18.6	*12.8*
18.6	*12.6*
18.6	*12.4*
18.6	*12.2*
18.8	*12.0*
18.6	*11.7*
18.7	*11.6*
18.7	*11.4*
18.7	*11.3*
18.7	*11.1*
18.7	*11.0*
18.8	*10.9*
18.8	*10.8*
18.8	*10.6*
18.8	*10.5*
18.8	*10.3*
18.9	*10.2*
18.9	*10.1*
18.9	*10.0*
18.9	*9.9*
19.0	*9.8*
19.0	*9.7*
19.0	*9.6*
19.0	*9.6*
19.0	*9.5*
19.0	*9.4*
19.0	*9.4*
18.9	*9.3*
19.0	*9.2*
19.0	*9.1*
19.0	*9.0*
19.0	*9.0*
19.0	*8.9*
19.0	*8.8*
19.0	*8.7*
19.0	*8.7*
19.0	*8.6*
19.0	*8.5*
19.0	*8.5*
19.1	*8.4*
19.1	*8.3*
19.1	*8.2*
19.1	*8.2*
19.1	*8.1*

Table S11: [P_{44414}] Cl / HCl / $FeCl_2$ / H_2O [Fe(II)] = 10.0 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
12.5	*39.8*
12.6	*38.1*
13.0	*36.3*
13.2	*35.0*
13.3	*33.9*
13.5	*32.5*
13.7	*31.7*
13.8	*30.7*
14.0	*29.9*
14.0	*29.2*
14.1	*28.4*
14.2	*27.8*
14.2	*27.0*
14.3	*26.6*
14.4	*25.8*
14.5	*25.2*
14.5	*24.6*
14.6	*24.1*
14.3	*10.2*
14.4	*9.8*
14.2	*9.7*
14.2	*9.4*
14.1	*9.1*
14.1	*8.9*
13.7	*8.5*
13.7	*8.2*
13.6	*8.0*

Table S12: [P_{44414}] Cl / HCl / $FeCl_2$ / H_2O [Fe(II)] = 15.0 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
11.7	*42.5*
11.9	*41.0*
12.0	*39.6*
12.1	*38.7*
12.2	*37.9*
12.3	*36.7*
12.5	*35.7*
12.5	*34.9*
12.6	*34.1*
12.6	*33.5*
12.8	*32.7*
12.9	*32.0*
12.9	*31.4*
13.0	*30.8*
13.1	*30.2*
13.2	*29.4*
13.3	*28.7*
13.3	*28.2*
13.4	*27.9*
13.5	*27.5*
13.6	*27.0*
13.6	*26.6*
13.6	*26.2*
13.6	*25.9*
13.8	*25.6*
13.8	*25.1*
13.8	*24.8*

Table S13: [P_{44414}] Cl / HCl / $FeCl_2$ / H_2O [Fe(II)] = 20.0 g/L at *transition temperature: 25 to 50 °C (battle ship method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
27.0	*23.0*
13.9	*10.0*
6.9	*10.0*
13.9	*30.0*
13.9	*20.0*
17.5	*50.0*
4.9	*12.0*
7.0	*20.0*
10.4	*20.0*
10.7	*5.0*
7.9	*20.4*
7.0	*5.0*
7.4	*17.9*
5.4	*18.5*
17.5	*39.6*
21.0	*39.9*
7.1	*49.8*
7.0	*30.0*
4.5	*12.5*
8.7	*30.0*
10.4	*30.0*
12.2	*30.0*
11.1	*30.0*
3.5	*10.0*
7.1	*44.9*
3.5	*30.2*
5.2	*24.8*
5.1	*35.1*
7.1	*39.3*
10.6	*49.5*
3.5	*20.0*
8.7	*50.0*
5.2	*5.0*
17.4	*50.0*
13.9	*50.0*
4.2	*10.0*
1.9	*14.9*
3.5	*39.9*
1.8	*24.9*
1.8	*10.0*

Always biphasic points: green
Transition points: yellow
Always monophasic points: blue

Table S14: [P_{44414}] Cl / HCl / $FeCl_3$ / H_2O [Fe(III)] = 2.5 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
10.9	*47.3*
12.0	*41.0*
12.6	*37.9*
13.0	*35.0*
13.4	*32.6*
13.5	*30.4*
13.9	*28.6*
14.2	*27.4*
14.3	*26.1*
14.5	*25.3*
14.5	*24.4*
14.7	*23.5*
14.9	*22.6*
15.0	*21.8*
15.0	*21.0*
15.0	*20.3*
15.1	*19.7*
15.1	*19.0*
15.1	*18.4*
15.1	*18.0*
15.0	*17.3*
15.1	*16.6*
15.0	*16.0*
14.9	*15.2*
14.8	*14.5*
14.7	*13.8*
14.4	*12.7*

Table S15: [P_{44414}] Cl / HCl / $FeCl_3$ / H_2O [Fe(III)] = 5.17 g/L at *25 °C (turbidity method)*

HCl (wt%)	*[P_{44414}]Cl (wt%)*
12.1	*51.3*
12.4	*49.2*
12.5	*47.2*
12.6	*45.7*
12.7	*43.9*
12.8	*41.7*
13.1	*38.8*
13.4	*37.6*
13.2	*36.1*
13.4	*34.7*
13.5	*33.6*
13.7	*32.1*
13.8	*31.4*
13.7	*30.1*
13.8	*29.3*
13.7	*28.3*
13.7	*27.6*
13.8	*27.0*
13.7	*25.6*
13.5	*24.5*
13.6	*23.9*
13.5	*23.0*
13.1	*21.4*
13.1	*20.8*
12.9	*19.3*
12.1	*51.3*
12.4	*49.2*

Table S16: [P_{44414}] Cl / HCl / $FeCl_3$ / H_2O [Fe(III)] = 10.2 g/L at *25 °C (turbidity method)*

HCl (wt%)	$[P_{44414}]Cl$ (wt%)
12.5	45.2
12.6	42.7
12.7	40.7
12.6	38.7
12.8	37.2
12.7	35.5
12.8	33.8
12.7	32.8
12.6	31.3
12.5	30.2
12.4	29.2
12.2	28.2
12.1	27.0
11.7	25.7
11.5	24.4
11.2	23.3
10.6	21.5
9.9	19.7
9.5	18.4
8.7	16.7
7.8	14.9
7.3	13.5
6.1	10.7
5.5	9.3
4.9	7.9
4.6	7.1
12.5	45.2

Table S17: $[P_{44414}]$ Cl / HCl / $FeCl_3$ / H_2O [Fe(III)] = 15.1 g/L at *25 °C (turbidity method)*

HCl (wt%)	$[P_{44414}]Cl$ (wt%)
10.5	46.6
11.7	40.0
11.5	36.6
10.7	31.9
10.2	28.0
9.2	24.5
8.1	21.2
7.1	18.2
5.4	13.6
4.9	11.9
4.5	10.5
4.0	8.9
3.8	8.0
10.5	46.6
11.7	40.0
11.5	36.6
10.7	31.9
10.2	28.0
9.2	24.5
8.1	21.2
7.1	18.2
5.4	13.6
4.9	11.9
4.5	10.5
4.0	8.9

Table S18: PEG-600 / HCl / $FeCl_3$ / H_2O [Fe(III)] = 10 g/L at *25 °C (turbidity method)*

HCl (wt%)	PEG-600 (wt%)
17.9	27.5
18.8	24.5
19.5	23.4
19.7	21.9
19.8	20.9
20.0	20.0
20.4	19.1
20.7	18.1
20.8	17.4
21.0	16.5
21.4	15.9
21.5	15.5
21.5	15.1
21.6	14.4
21.9	13.7
22.0	13.1
22.1	12.4
22.6	11.7

Table S19: PEG-600 / HCl / $FeCl_3$ / H_2O [Fe(III)] = 10 g/L at *50 °C (turbidity method)*

HCl (wt%)	PEG-600 (wt%)
18.3	20.4
18.8	18.4
19.1	16.9
19.3	15.7
19.6	14.6
19.8	13.6
19.9	12.7
20.1	11.8
20.3	10.8
20.5	9.9
21.0	9.2
21.0	8.7
21.4	8.1
21.8	7.4

Table S20: PEG-600 / HCl / $FeCl_3$ / H_2O [Fe(III)] = 40 g/L at *25 °C (turbidity method)*

HCl (wt%)	PEG-600 (wt%)
11.8	29.8
13.4	26.7
13.6	25.5
13.9	24.4
14.1	23.3
14.3	22.3
14.5	21.4
14.6	20.3
14.9	19.3
15.0	18.5
15.4	17.7
15.4	17.2
15.5	16.5
15.5	15.6
15.8	15.2
15.9	14.5
16.1	13.8
16.2	13.2
16.4	12.5
16.6	11.9
16.7	11.6
17.2	10.9
17.2	10.5
17.4	10.0
17.5	9.6
17.5	9.4
17.3	8.9
17.5	8.6
17.5	8.4
17.5	8.3
17.6	8.2
17.6	8.1
17.7	8.0
17.7	8.0
17.8	7.9
17.8	7.8
17.8	7.7
17.9	7.6
17.9	7.5
17.8	7.3
17.9	7.2
17.9	7.1
17.9	7.0
18.0	7.0
18.0	6.9
18.0	6.8
18.1	6.7
18.1	6.6
18.1	6.5
18.1	6.4
18.2	6.3
18.2	6.2
18.2	6.0
18.3	5.9
18.3	5.7
18.3	5.6
18.5	5.5
18.5	5.3
18.5	5.2
18.6	5.1
18.7	5.0
18.7	4.8

11.8	29.8
13.4	26.7
13.6	25.5
13.9	24.4
14.1	23.3
14.3	22.3
14.5	21.4
14.6	20.3
14.9	19.3
15.0	18.5
15.4	17.7
15.4	17.2
15.5	16.5
15.5	15.6
15.8	15.2
15.9	14.5
16.1	13.8
16.2	13.2
16.4	12.5
16.6	11.9
16.7	11.6

17.2	10.9
17.2	10.5
17.4	10.0
17.5	9.6
17.5	9.4
17.3	8.9
17.5	8.6
17.5	8.4
17.5	8.3
17.6	8.2
17.6	8.1
17.7	8.0
17.7	8.0
17.8	7.9
17.8	7.8
17.8	7.7
17.9	7.6
17.9	7.5
17.8	7.3
17.9	7.2
17.9	7.1

17.9	7.0
18.0	7.0
18.0	6.9
18.0	6.8
18.1	6.7
18.1	6.6
18.1	6.5
18.1	6.4
18.2	6.3
18.2	6.2
18.2	6.0
18.3	5.9
18.3	5.7
18.3	5.6
18.5	5.5
18.5	5.3
18.5	5.2
18.6	5.1
18.7	5.0
18.7	4.8

Table S21: PEG-600 / HCl / $FeCl_3$ / H_2O [Fe(III)] = 40 g/L at *50 °C (turbidity method)*

HCl (wt%)	*PEG-600 (wt%)*
12.9	22.2
13.1	20.7
13.3	19.7
13.4	18.9
13.6	18.2
13.7	17.6
13.8	17.0

13.9	16.4
14.0	15.9
14.1	15.2
14.2	14.6
14.3	14.1
14.4	13.6
14.5	13.1
14.6	12.6
14.6	12.0

14.8	11.4
15.0	10.9
15.1	10.4
15.2	9.8
15.3	9.3
12.9	22.2
13.1	20.7
13.3	19.7
13.4	18.9

Table S22: PEG-600 / HCl / $FeCl_3$ / H_2O [Fe(III)] = 40 g/L at *50 °C (battle ship method)*

HCl (wt%)	*PEG-600 (wt%)*
12.9	25.0
14.1	18.8
15.5	10.6
12.5	30.3
12.4	40.6
13.7	46.2
12.6	44.9
12.4	35.2
10.9	30.0
13.4	19.2
11.9	19.0
11.0	20.0
14.0	10.0
13.0	9.8

9.4	10.0
3.2	89.9
6.3	79.8
9.4	70.0
12.5	59.9
4.7	85.0
7.9	74.9
11.0	65.0
14.1	55.0
17.3	44.8
18.8	40.0
20.3	35.0
14.1	35.0
14.0	40.1
15.7	29.7
14.0	29.7

17.6	29.2
17.4	22.1
17.5	12.6
15.7	20.0
18.8	10.1
21.7	10.6
18.5	30.7
22.0	29.8
24.8	20.7
28.2	10.0
15.2	30.3
18.6	31.0
14.0	30.0
17.0	20.5
17.2	10.1

Monophasic points: blue
Biphasic points: green

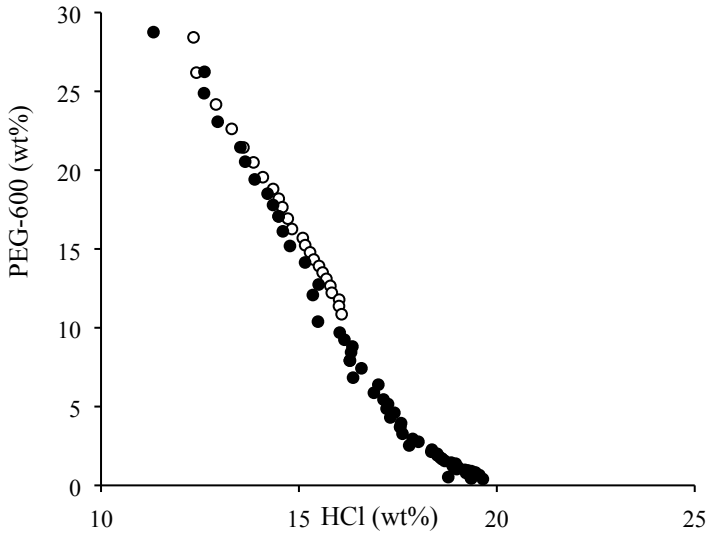


Figure S1: Binodal curves of the system PEG-600/[Fe(III)+HCl 37wt%]/H_2O [Fe(III)] = 40 g/L at 25 °C obtained using two different HCl providers, Fluka (●) and Sigma Aldrich (○).

Biphasic Inducer →	**PEG-600**		**$[P_{44414}]Cl$**	
Fe(III)	B	B	B	B
Fe(II)	M	M	B	B
Ni(II)	M	M	B	B
Cr(III)	M	M	B	B
Co(II)	M	M	-	-
Cu(I)	M	M	-	-
Working temperature →	**25 °C**	**50 °C**	**25 °C**	**50 °C**

Table S24: Table of experiments performed in this work. Six different ions were tested with PEG-600 and $[P_{44414}]Cl$ in HCl 12M and at two working temperatures, 25 and 50 °C. M = monophasic system. B = biphasic system.

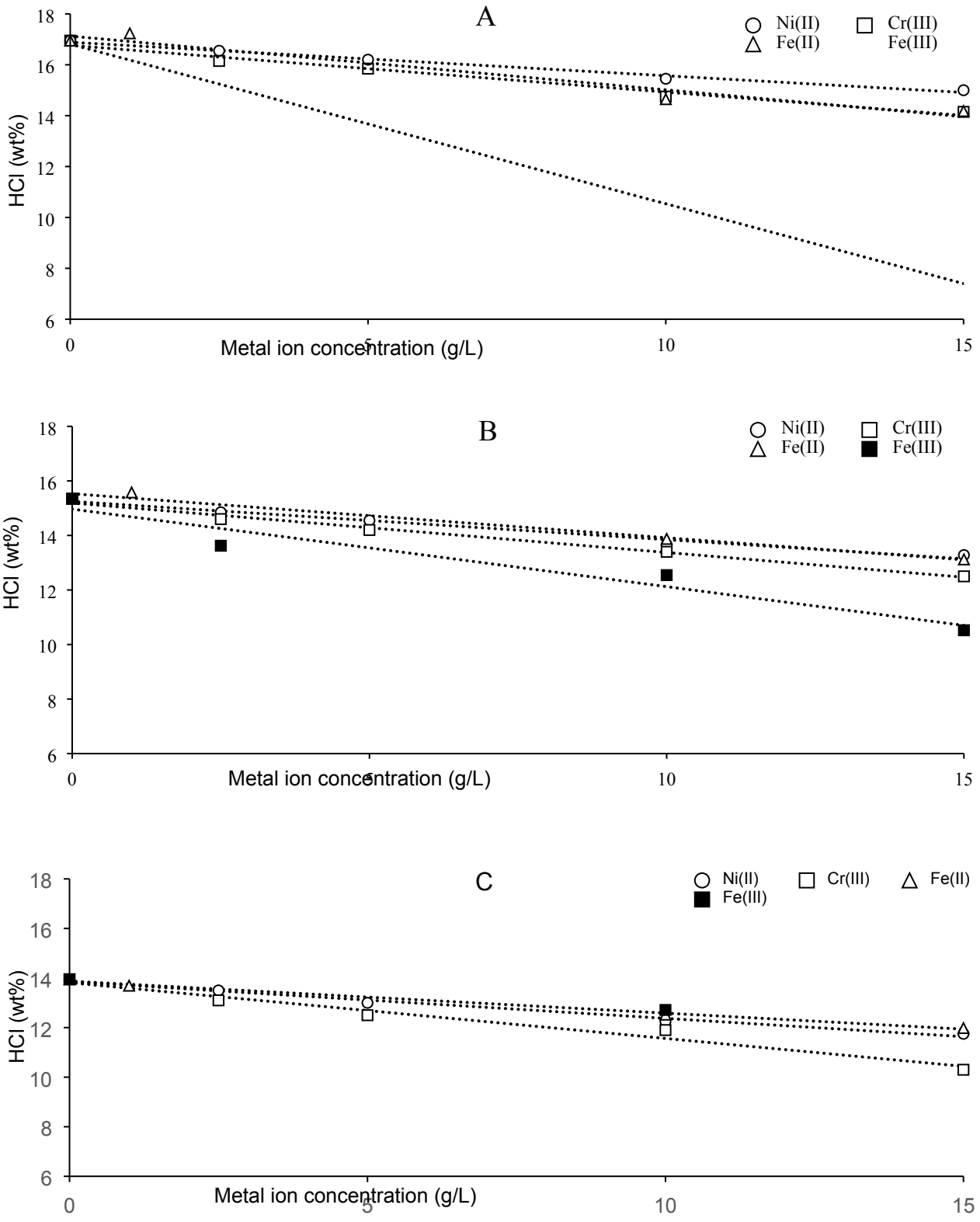


Figure S2: HCl amount (wt%) as a function of metal ion concentration at: A) 20 wt%, B) 30 wt% and C) 40 wt% of IL.

Considering the contribution of metal ions as a function of the acid concentration (in wt%), the binodal curves for the systems containing Ni(II) and Cr(III) are parallel, while for Fe(II) and Fe(III), the curves do not present a parallel tendency. This can be confirmed by plotting HCl concentration at the binodal curve as a function of

metal concentration at different IL wt% (20/30/40). The plots are straight lines with slopes almost identical for Ni and Cr, while slopes differ markedly for Fe(III) and Fe(II) (see Figure S2 of the supplementary materials).

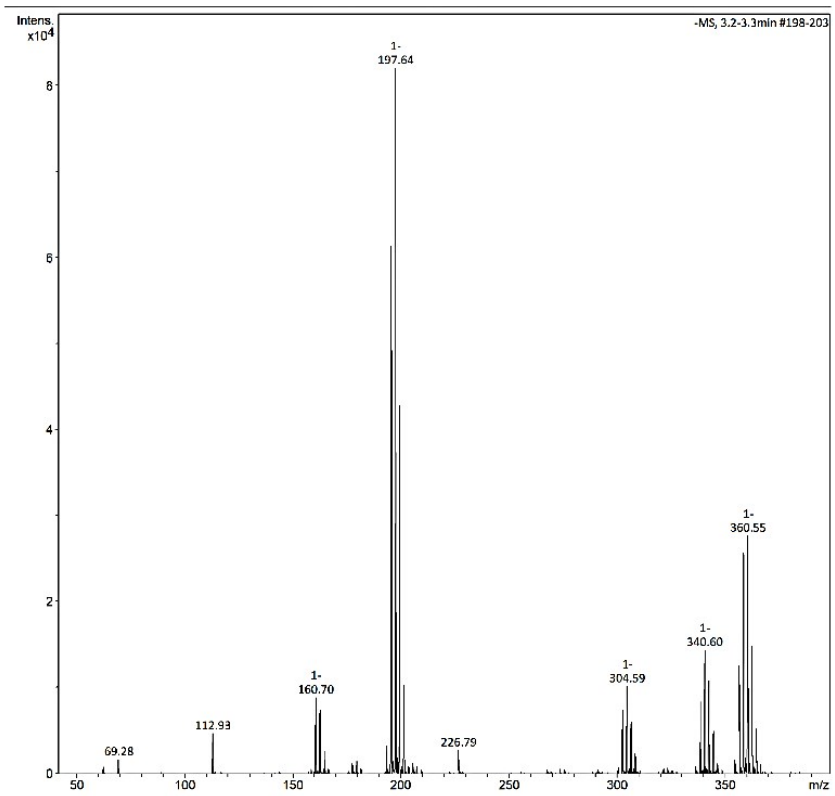


Figure S3: ESI-MS results of the acidic solution Fe(III) + HCl (37 wt% = 12M). Peaks at 197.64 m/z are the characteristic peaks of $[Fe(III)Cl_4]^-$ (molecular weight of the species).

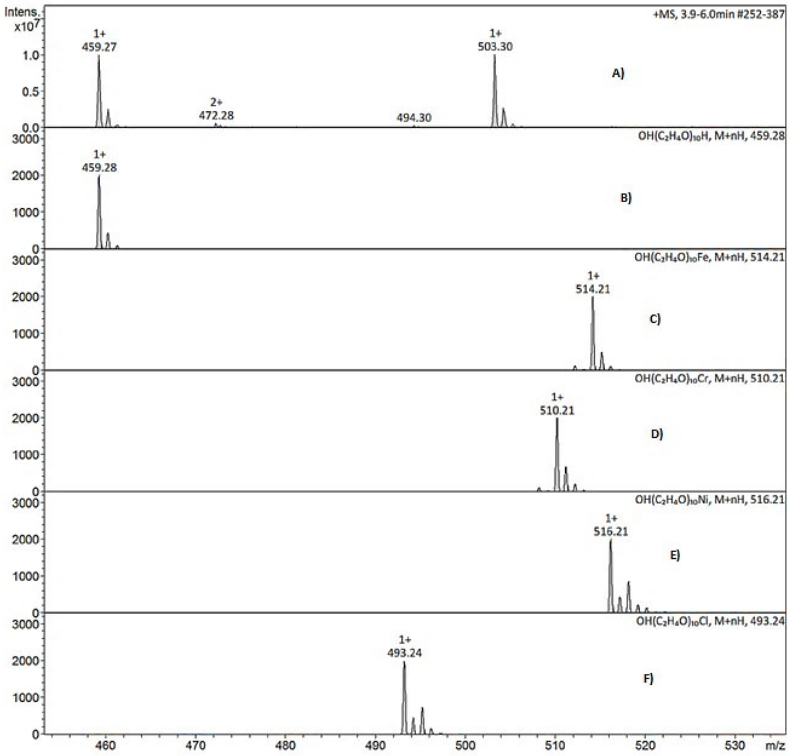


Figure S4: Polymer investigation by ESI-MS. A: polymer phase analysed after mixing 80wt% of stock solution Fe(III) 35 g/L in 12M HCl and 20 wt% of PEG-600, B: fresh polymer PEG-600; Simulation with the software of the ESI-MS machine to show the form of peaks of PEG-Fe (C), PEG-Cr (D), PEG-Ni (E), PEG-Cl (F).