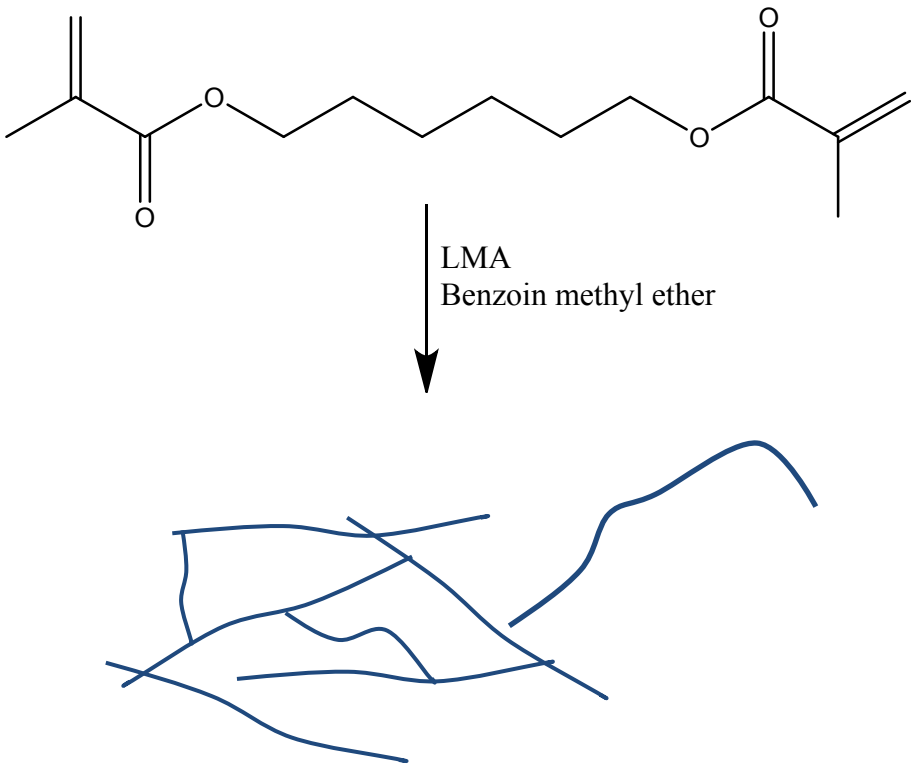
Journal of Materials Chemistry A

Supporting information:

Correlation between scratch healing and rheological behavior for terpyridine complex based metallopolymers

By Stefan Bode, Marcel Enke, Ranjita K. Bose, Felix H. Schacher, Santiago J. Garcia, Sybrand van der Zwaag, Martin D. Hager,* Ulrich S. Schubert*

Schemes:



Scheme S1: Schematic representation of the synthesis of the covalent crosslinked copolymers **CP1** and **CP2**.

Self-healing pictures:

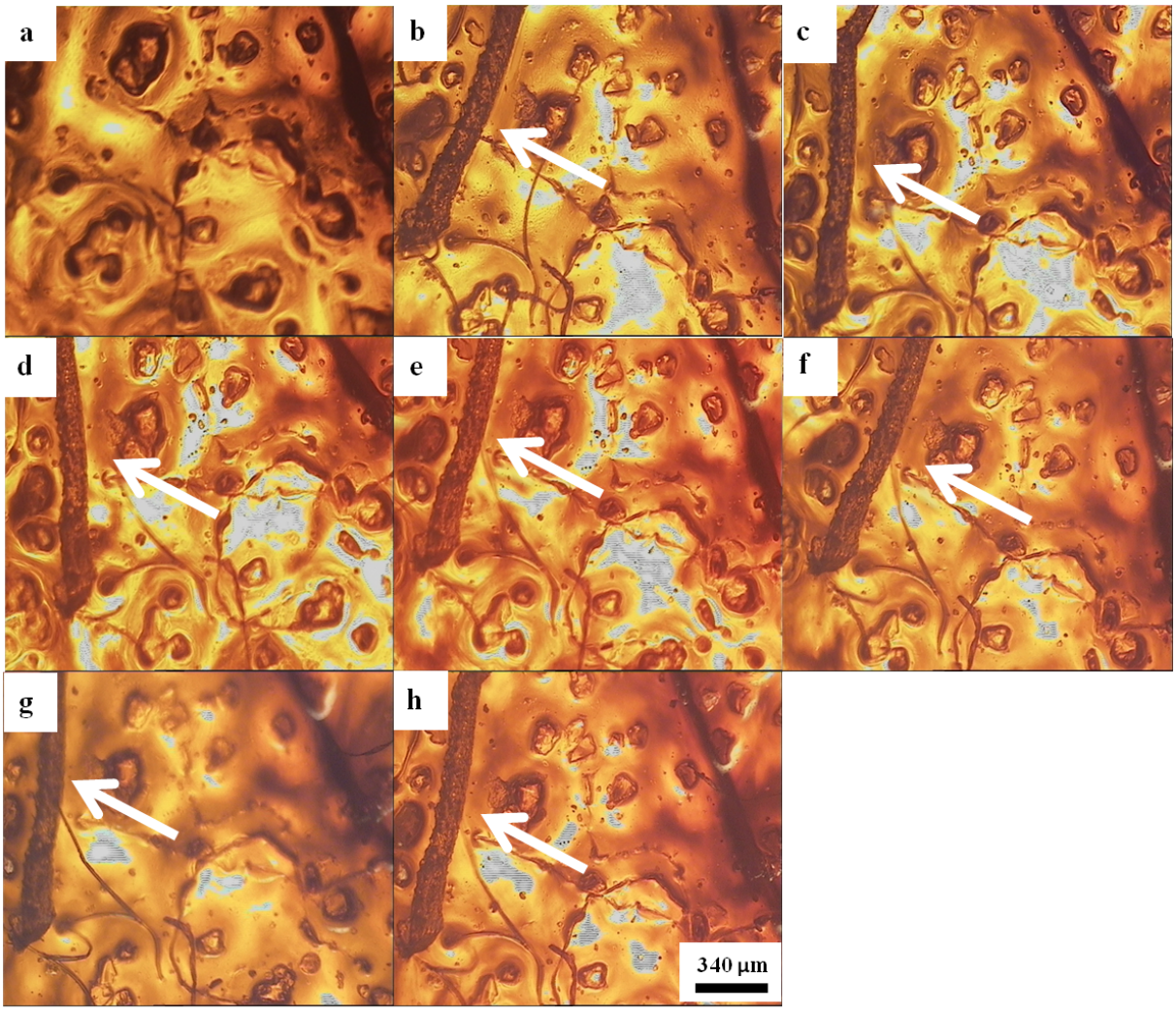


Figure S1: Self-healing studies of the crosslinked copolymer **CP1**: a) Film without a scratch, b) scratch, c) no healing after 17 h at 100 °C, d) no healing after 35 h at 100 °C, e) no healing after 101 h at 150 °C, f) no healing after 115 h at 150 °C, g) no healing after 155 h at 150 °C and h) no healing after 201 h at 150 °C.

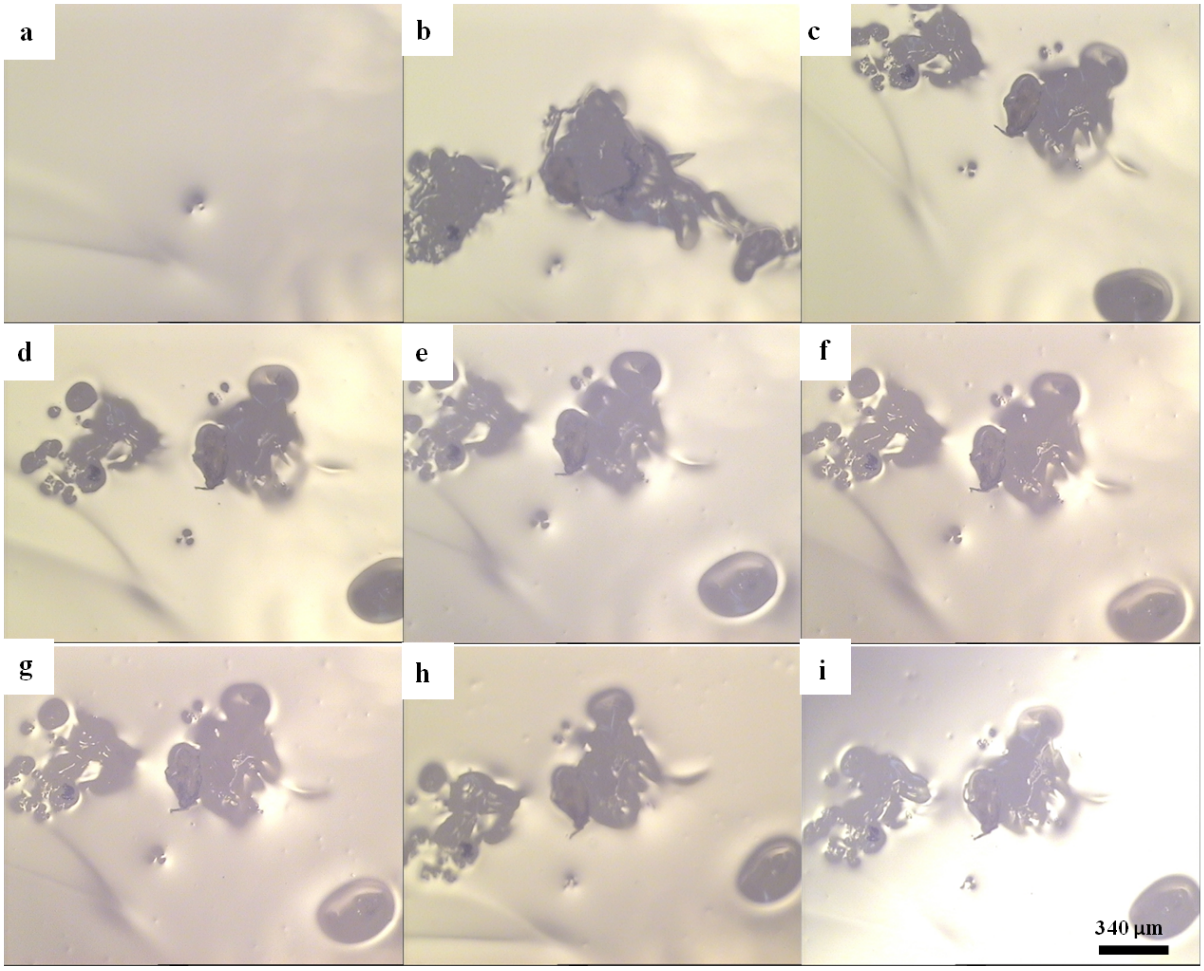


Figure S2: Self-healing studies of the crosslinked copolymer **CP2**: a) Film without a scratch, b) scratch, c) no healing after 20 h at 100 °C, d) no healing after 40 h at 100 °C, e) no healing after 60 h at 100 °C, f) no healing after 80 h at 100 °C, g) no healing after 150 h at 100 °C, h) no healing after 170 h at 150 °C and 190 h at 150 °C.

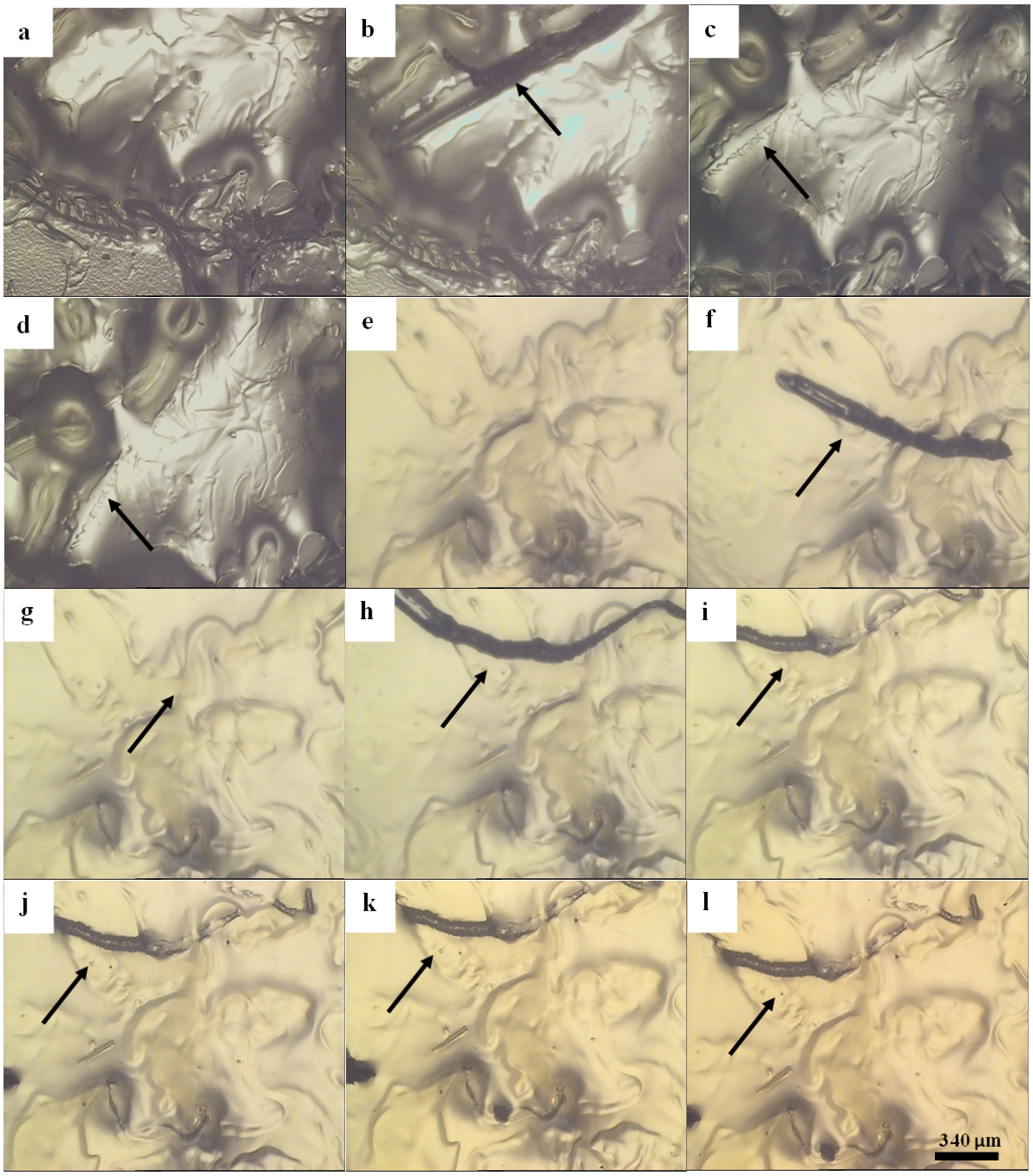


Figure S3: Polymer network crosslinked by the addition of zinc nitrate (**MP1**): a) Film without scratch, b) scratch, c) no healing after 80 h at 100 °C, d) no healing after 210 h at 100 °C, e) film without scratch, f) scratch, g) healing after 17 h at 150 °C, h) 2nd scratch, i) no healing after 20 h at 150 °C, j) no healing after 36 h at 150 °C, k) no healing after 59 h at 150 °C and l) no healing after 74 h at 150 °C.

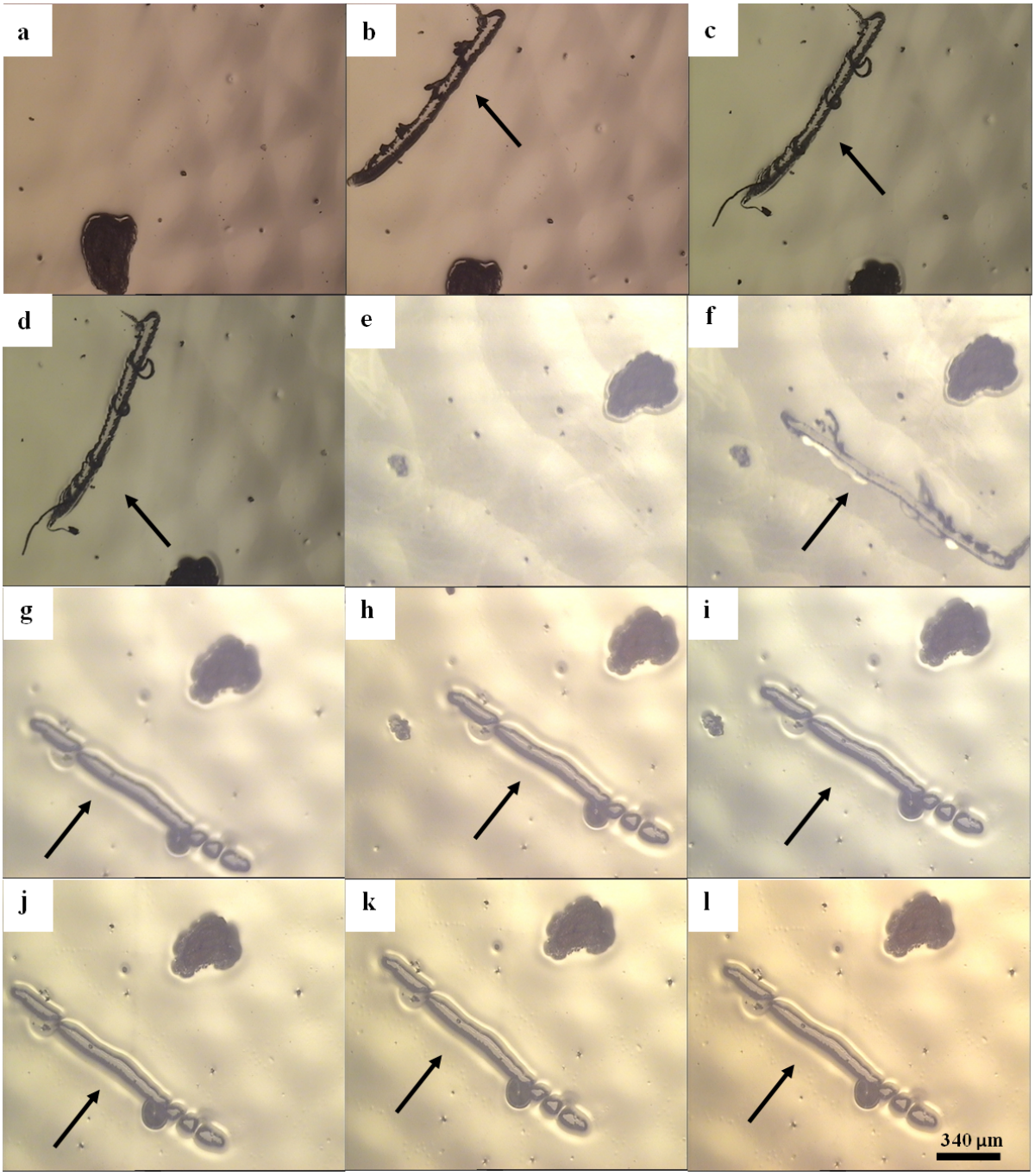


Figure S4: Polymer network crosslinked by the addition of zinc acetate (**MP2**): a) Film without scratch, b) scratch, c) no healing after 80 h at 100 °C, d) no healing after 210 h at 100 °C, e) film without scratch, f) scratch, g) no healing after 17 h at 150 °C, h) no healing after 34 h at 150 °C, i) no healing after 54 h at 150 °C, j) no healing after 70 h at 150 °C, k) no healing after 93 h at 150 °C and l) no healing after 108 h at 150 °C.

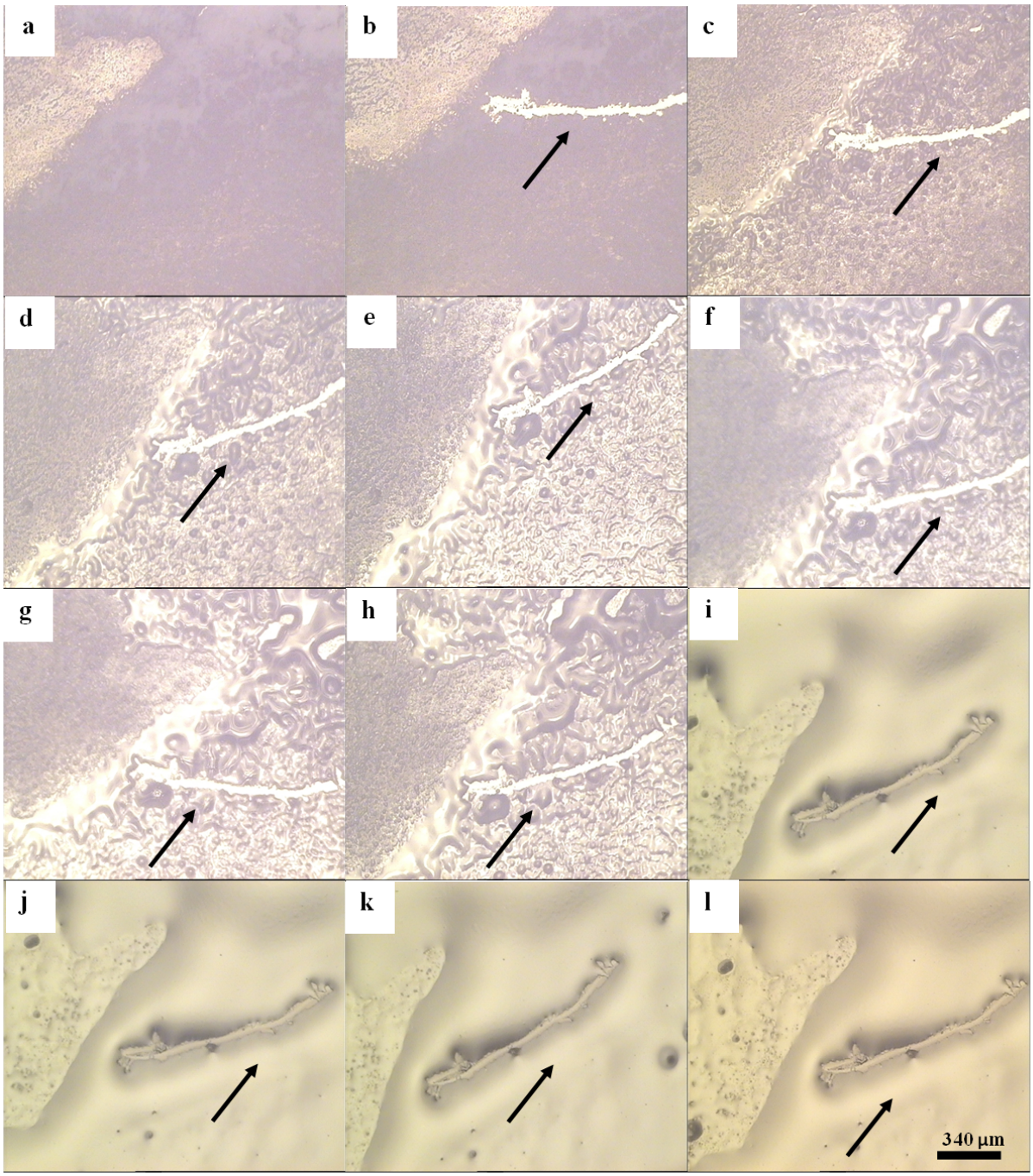


Figure S5: Polymer network crosslinked by the addition of zinc chloride (**MP3**): a) Film without scratch, b) scratch, c) no healing after 22 h at 100 °C, d) no healing after 37 h at 100 °C, e) no healing after 53 h at 100 °C, f) no healing after 72 h at 100 °C, g) no healing after 92 h at 100 °C, h) no healing after 112 h at 100 °C, i) no healing after 17 h at 150 °C, j) no healing after 34 h at 150 °C, k) no healing after 51 h at 150 °C and l) no healing after 68 h at 150 °C.

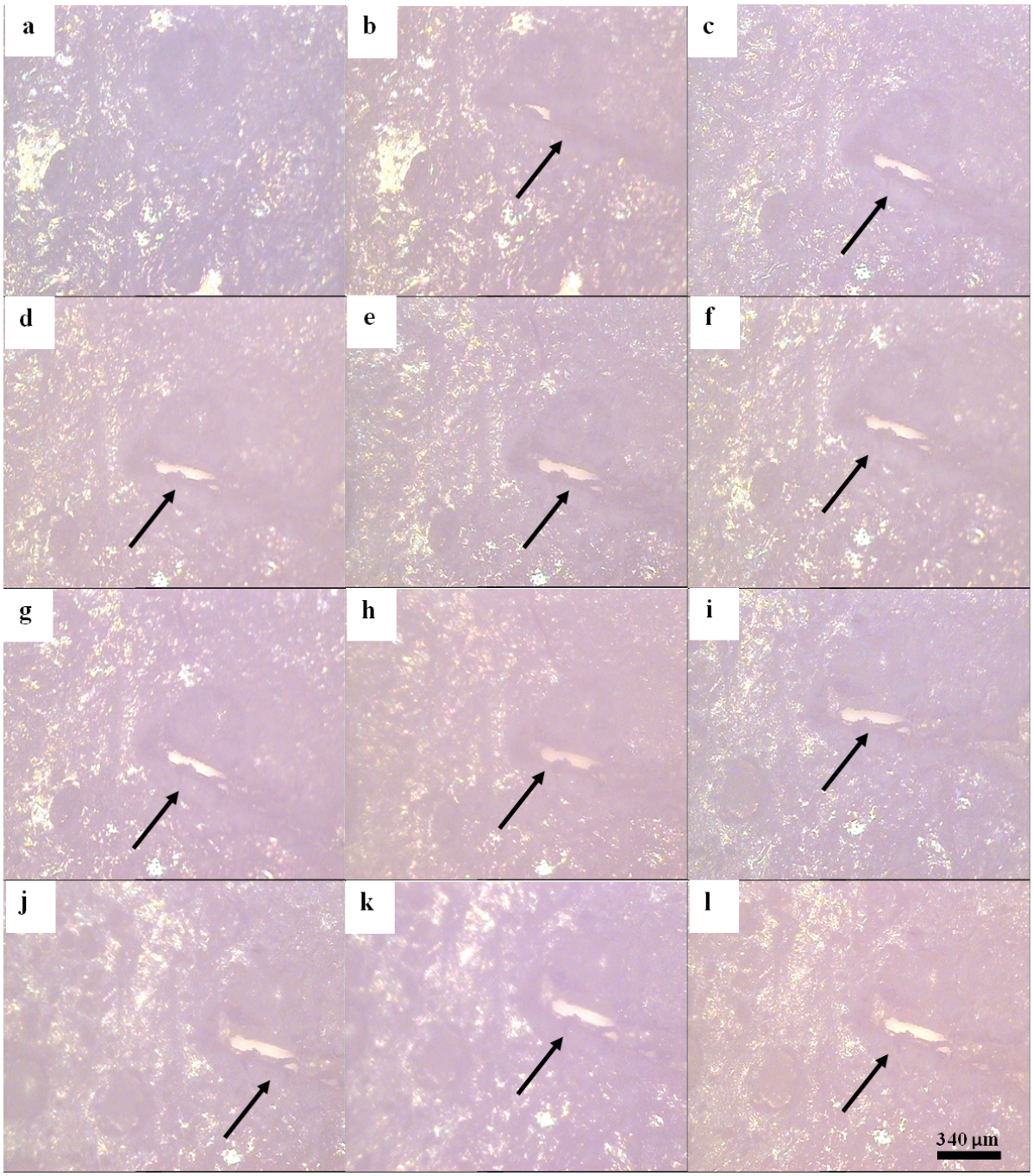


Figure S6: Polymer network crosslinked by the addition of nickel nitrate (**MP4**): a) Film without scratch, b) scratch, c) no healing after 22 h at 100 °C, d) no healing after 37 h at 100 °C, e) no healing after 53 h at 100 °C, f) no healing after 72 h at 100 °C, g) no healing after 92 h at 100 °C, h) no healing after 112 h at 100 °C, i) no healing after 17 h at 150 °C, j) no healing after 34 h at 150 °C, k) no healing after 51 h at 150 °C and l) no healing after 68 h at 150 °C.

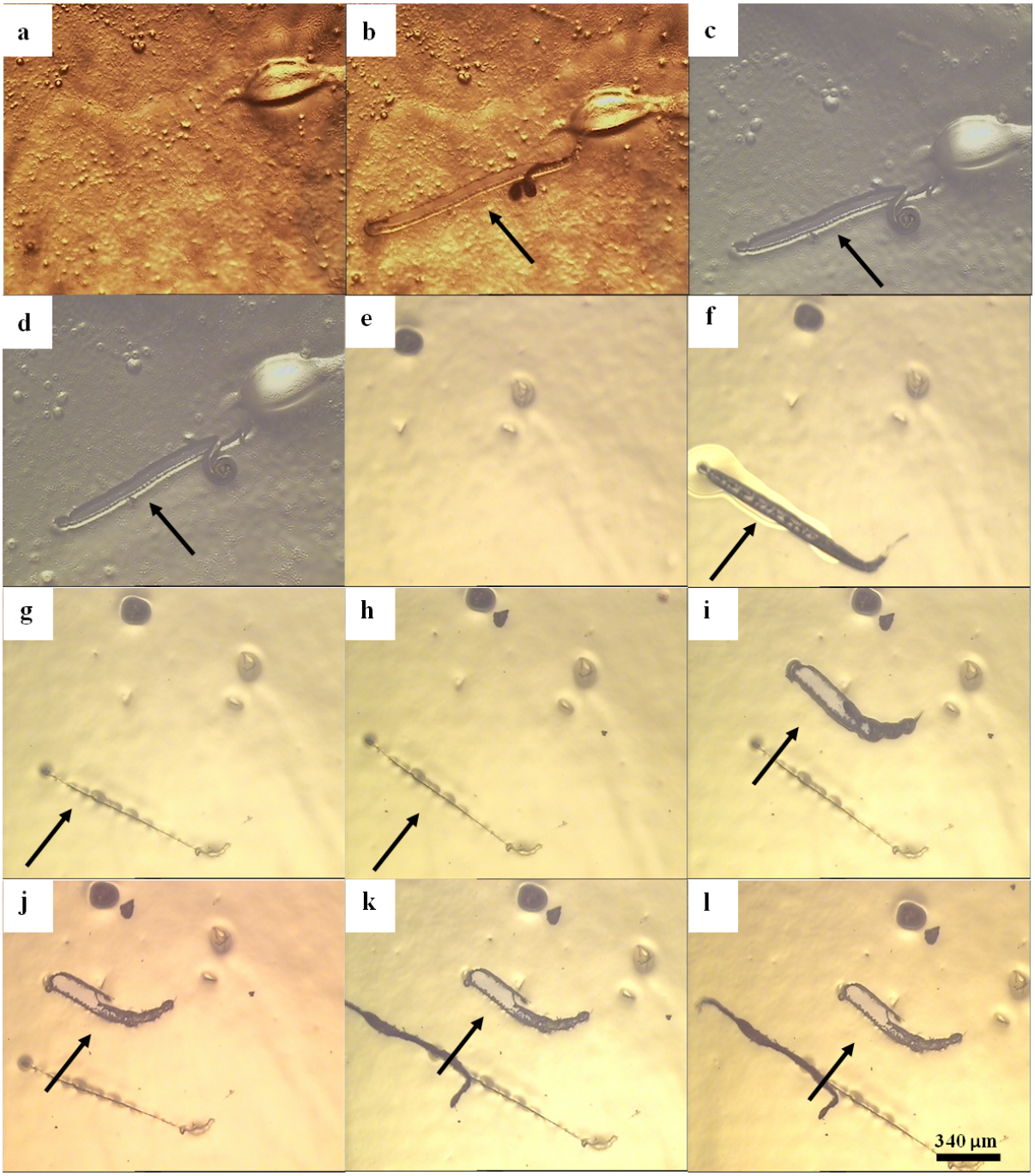


Figure S7: Polymer network crosslinked by the addition of nickel acetate (**MP5**): a) Film without scratch, b) scratch, c) no healing after 120 h at 100 °C, d) no healing after 250 h at 100 °C, e) film without scratch, f) scratch, g) partial healing after 17 h at 150 °C, h) partial healing after 54 h at 150 °C, i) 2nd scratch, j) no healing after 16 h at 150 °C, k) no healing after 39 h at 150 °C and l) no healing after 54 h at 150 °C.

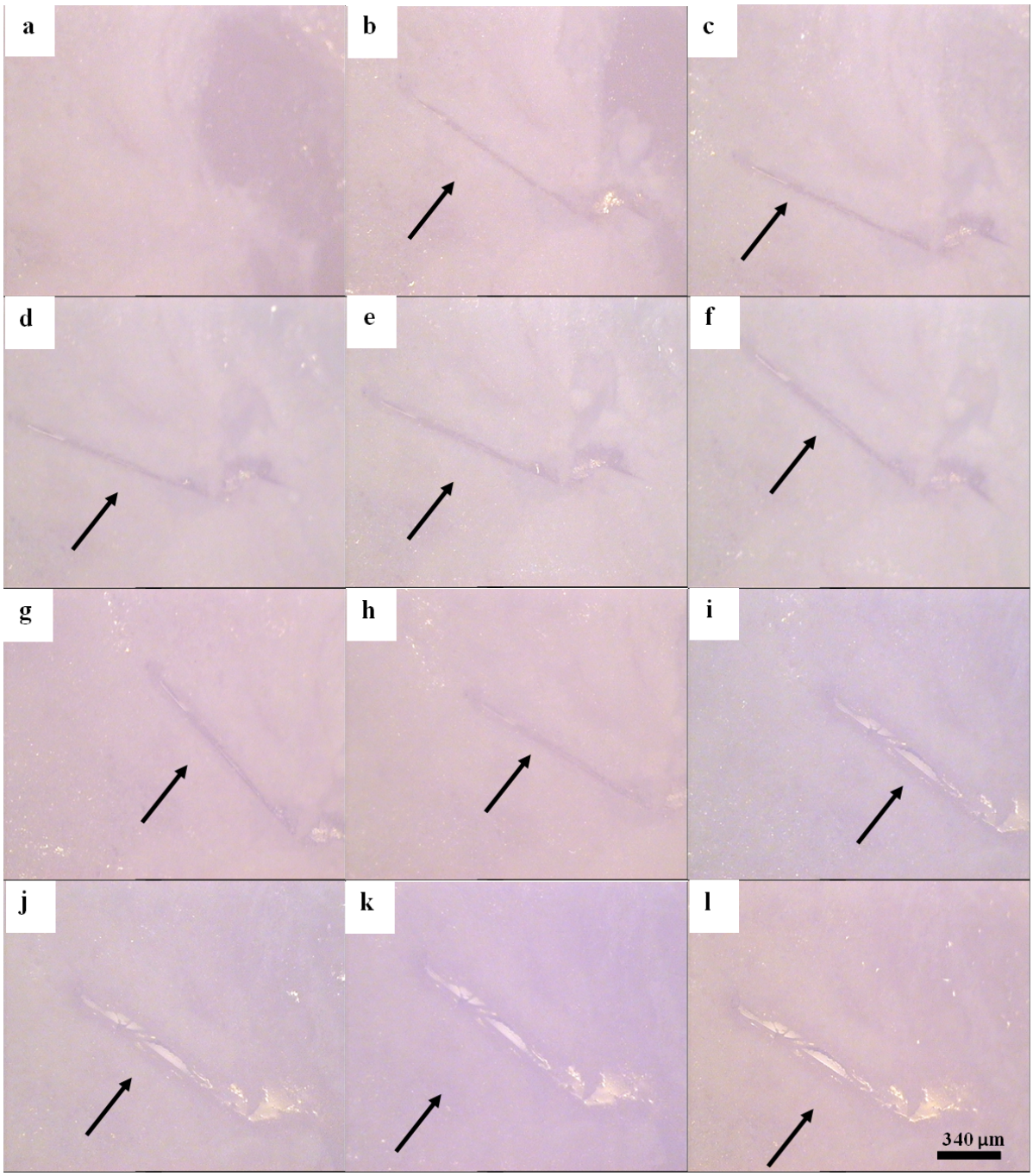


Figure S8: Polymer network crosslinked by the addition of nickel chloride (**MP6**): a) Film without scratch, b) scratch, c) no healing after 22 h at 100 °C, d) no healing after 37 h at 100 °C, e) no healing after 53 h at 100 °C, f) no healing after 72 h at 100 °C, g) no healing after 92 h at 100 °C, h) no healing after 112 h at 100 °C, i) no healing after 17 h at 150 °C, j) no healing after 34 h at 150 °C, k) no healing after 51 h at 150 °C and l) no healing after 68 h at 150 °C.

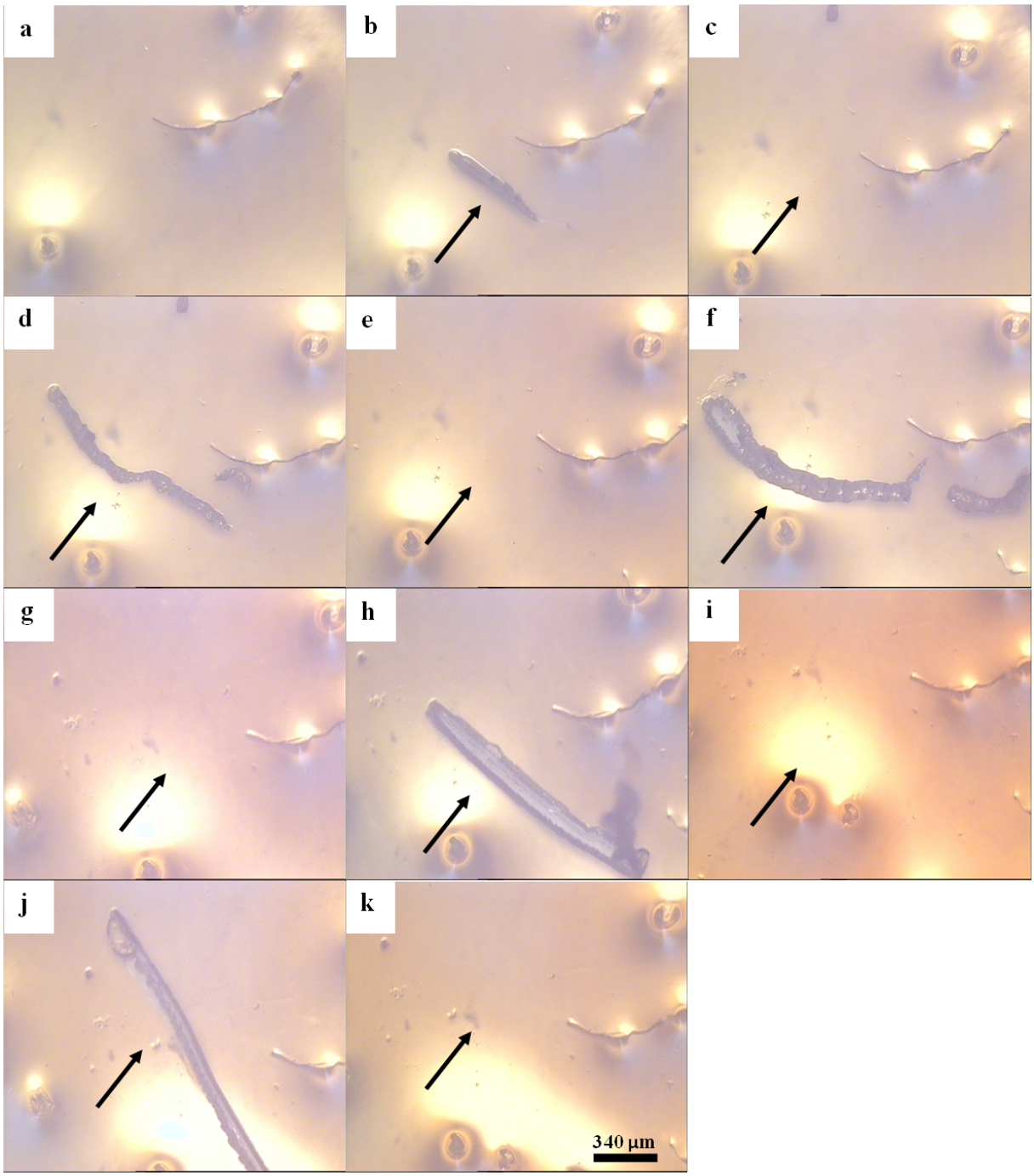


Figure S9: Polymer network crosslinked by the addition of cobalt nitrate (**MP7**): a) Film without scratch, b) scratch, c) healing after 17 h at 150 °C, d) 2nd scrtach, e) healing after 20 h at 150 °C, f) 3rd scratch, g) healing after 16 h at 150 °C, h) 4th scratch, i) healing after 23 h at 120 °C, j) 5th scratch and k) healing after 20 h at 120 °C.

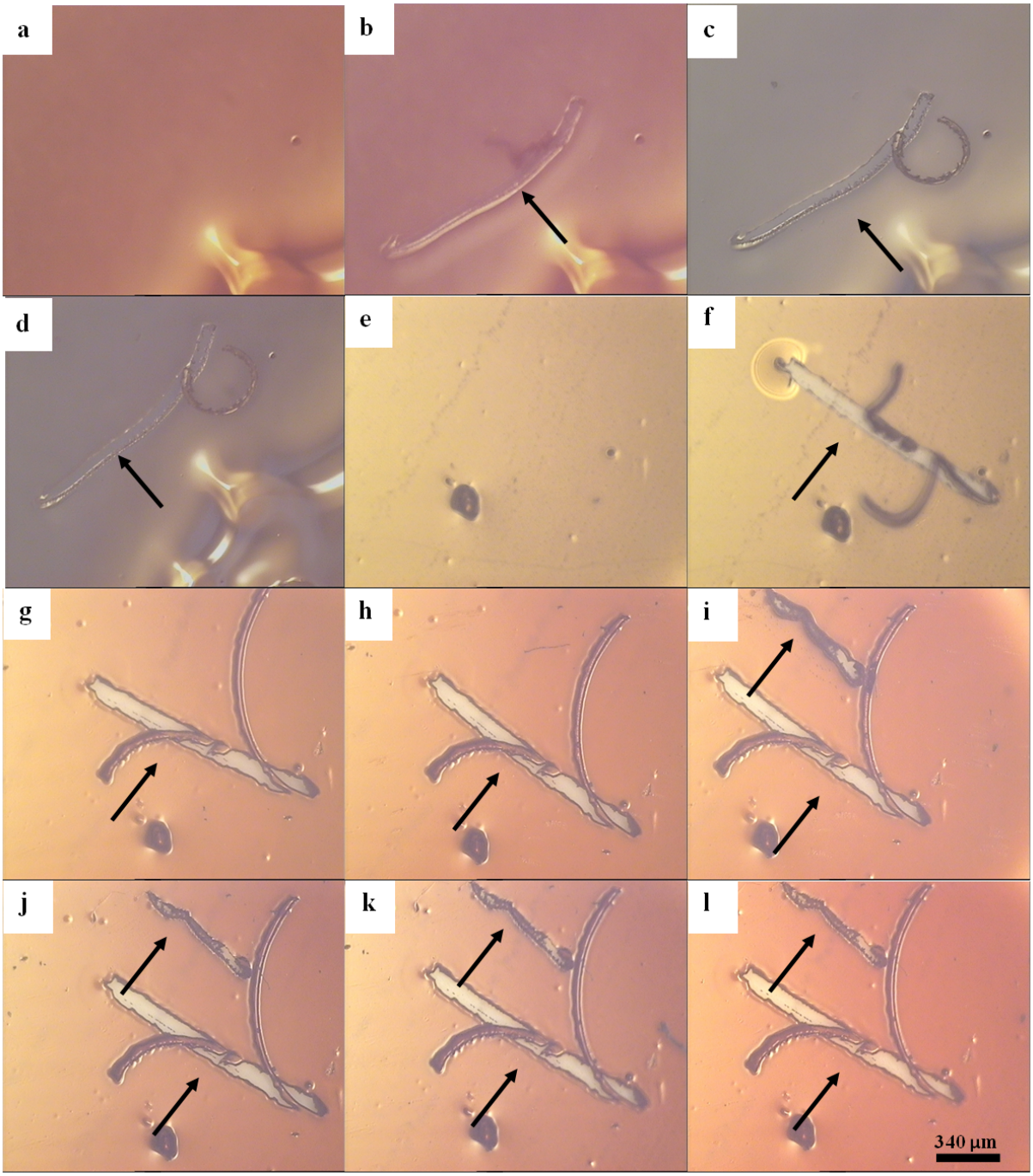


Figure S10: Polymer network crosslinked by the addition of cobalt acetate (**MP8**): a) Film without scratch, b) scratch, c) no healing after 120 h at 100 °C, d) no healing after 180 h at 100 °C, e) film without scratch, f) scratch, g) no healing after 17 h at 150 °C, h) no healing after 34 h at 150 °C, i) 2nd scratch, j) no healing after 20 h at 150 °C, k) no healing after 36 h at 150 °C and l) no healing after 74 h at 150 °C.

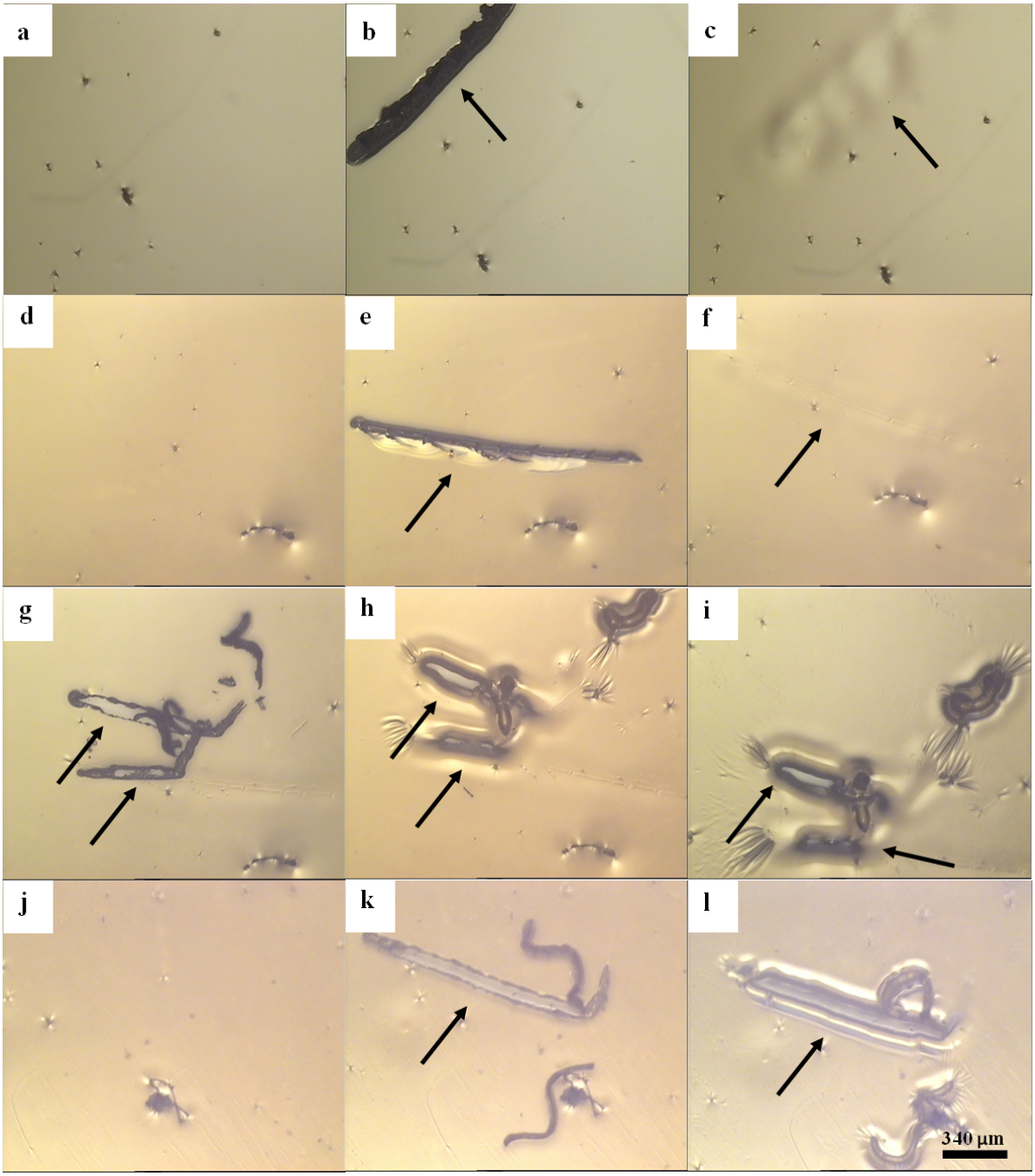


Figure S11: Polymer network crosslinked by the addition of cobalt chloride (**MP9**): a) Film without scratch, b) scratch, c) healing after 20 h at 100 °C, d) film without scratch, e) scratch, f) healing after 17 h at 90 °C, g) 2nd and 3rd scratch, h) partial healing after 16 h at 90 °C, i) partial healing after 96 h at 90 °C, j) film without scratch, k) scratch and l) partial healing after 60 h at 80 °C.

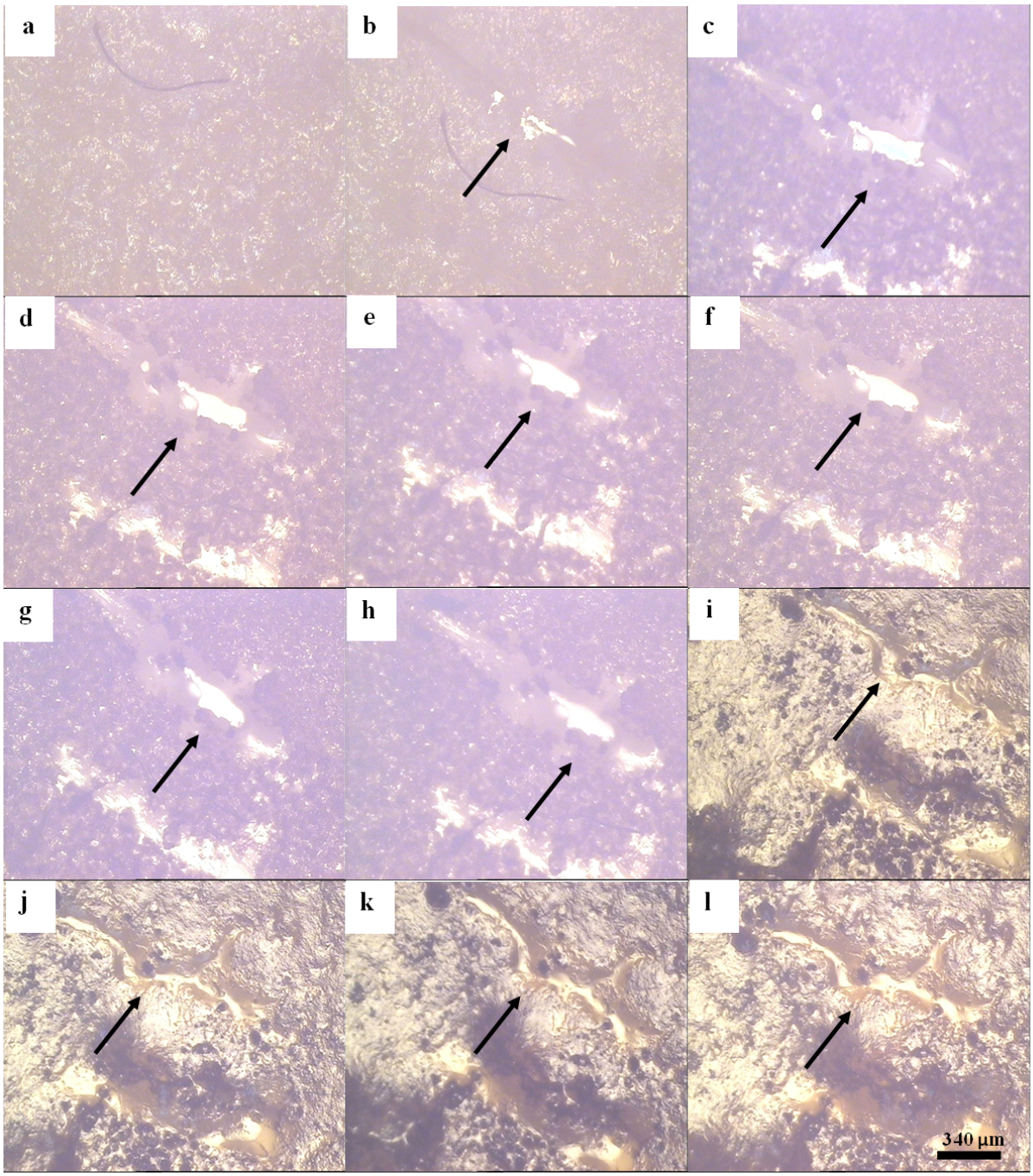


Figure S12: Polymer network crosslinked by the addition of manganese nitrate (**MP10**): a) Film without scratch, b) scratch, c) no healing after 22 h at 100 °C, d) no healing after 37 h at 100 °C, e) no healing after 53 h at 100 °C, f) no healing after 72 h at 100 °C, g) no healing after 92 h at 100 °C, h) no healing after 112 h at 100 °C, i) no healing after 17 h at 150 °C, j) no healing after 34 h at 150 °C, k) no healing after 51 h at 150 °C and l) no healing after 68 h at 150 °C.

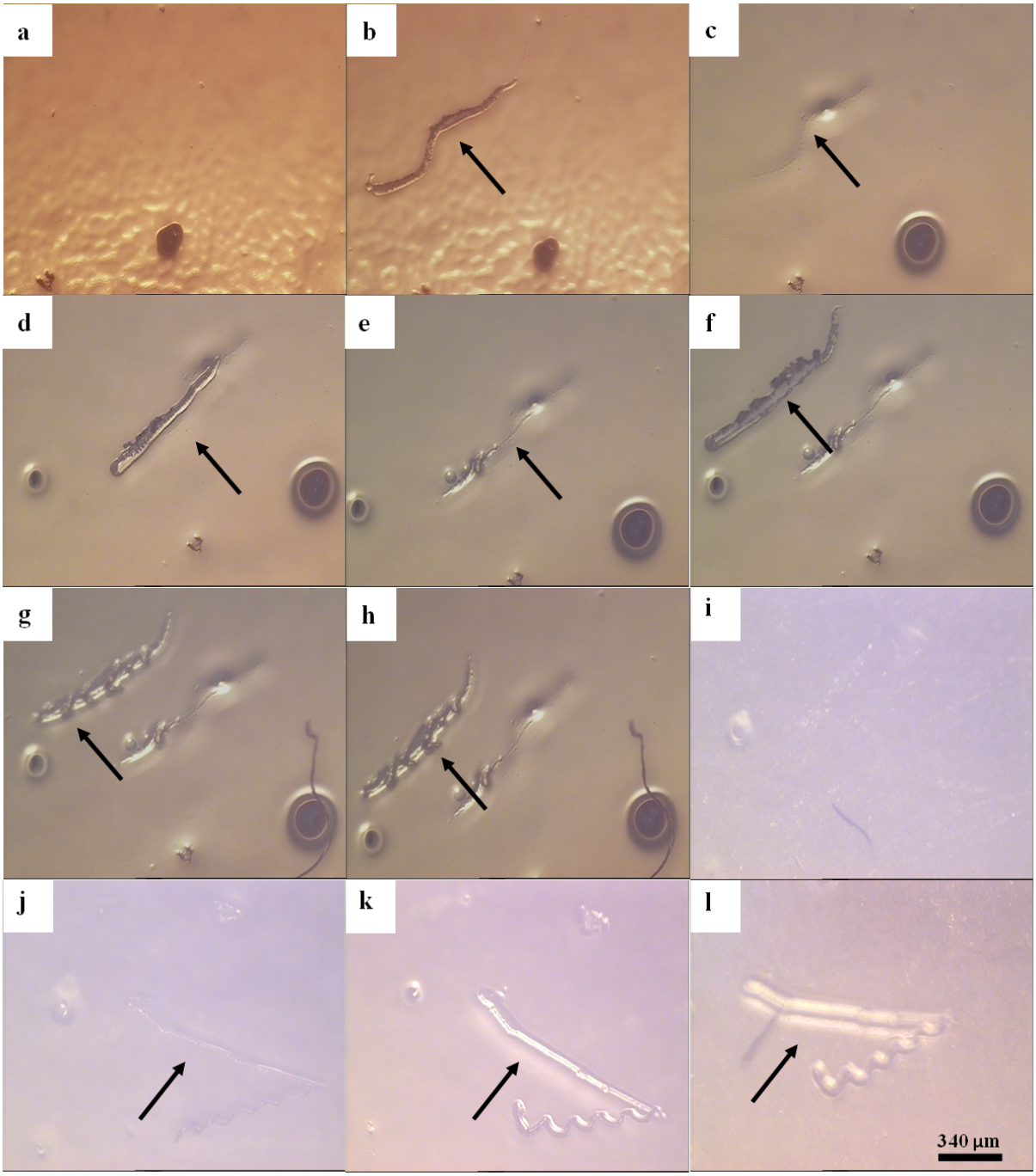


Figure S13: Polymer network crosslinked by the addition of manganese acetate (**MP11**): a) Film without scratch, b) scratch, c) healing after 40 h at 100 °C, d) 2nd scratch, e) partial healing after 80 h at 100 °C, f) 3rd scratch, g) partial healing after 60 h at 100 °C, h) partial healing after 130 h at 100 °C, i) film without scratch, j) scratch, k) no healing after 17 h at 90 °C l) no healing after 97 h at 90 °C.

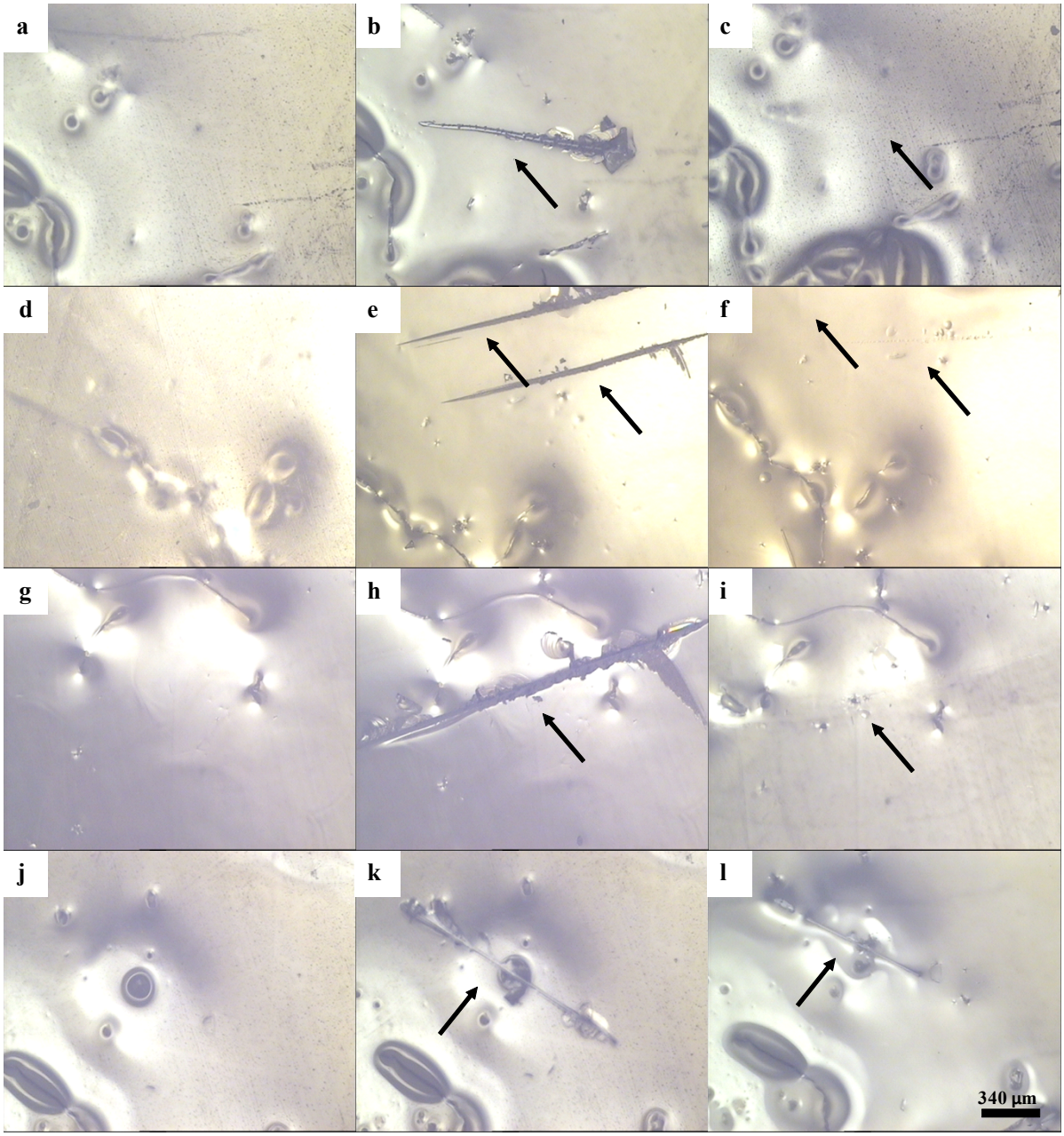


Figure S14: Polymer network crosslinked by the addition of manganese chloride (**MP12**): a) Film without scratch, b) scratch, c) healing after 17 min at 100 °C, d) film without scratch, e) scratch, f) healing after 15 min at 100 °C, g) film without scratch, h) scratch, i) healing after 13 min at 100 °C, j) film without scratch, k) scratch l) partial healing after 11 min at 100 °C.

NMR-spectra

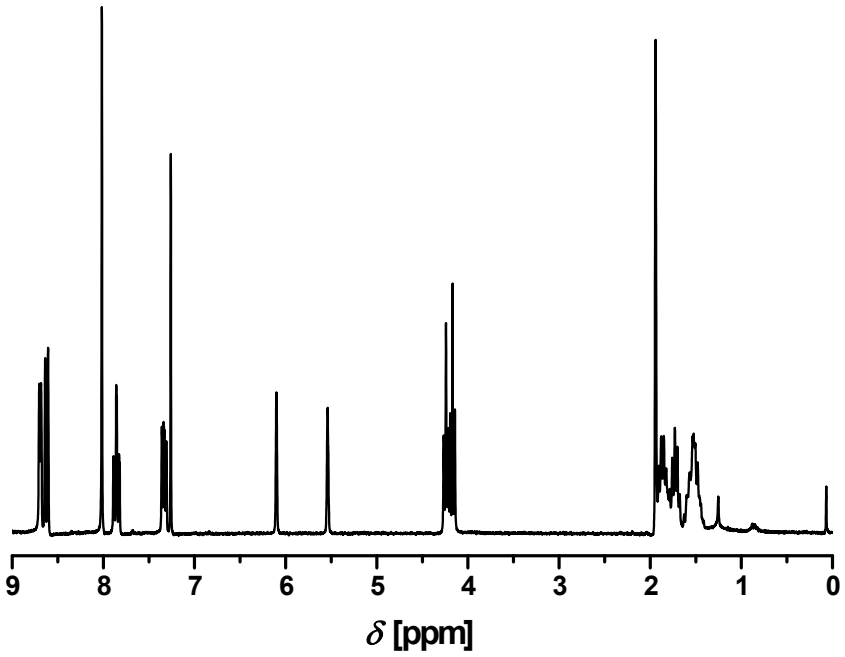


Figure S15: ^{1}H NMR-spectrum of **2** in $CDCl_3$.

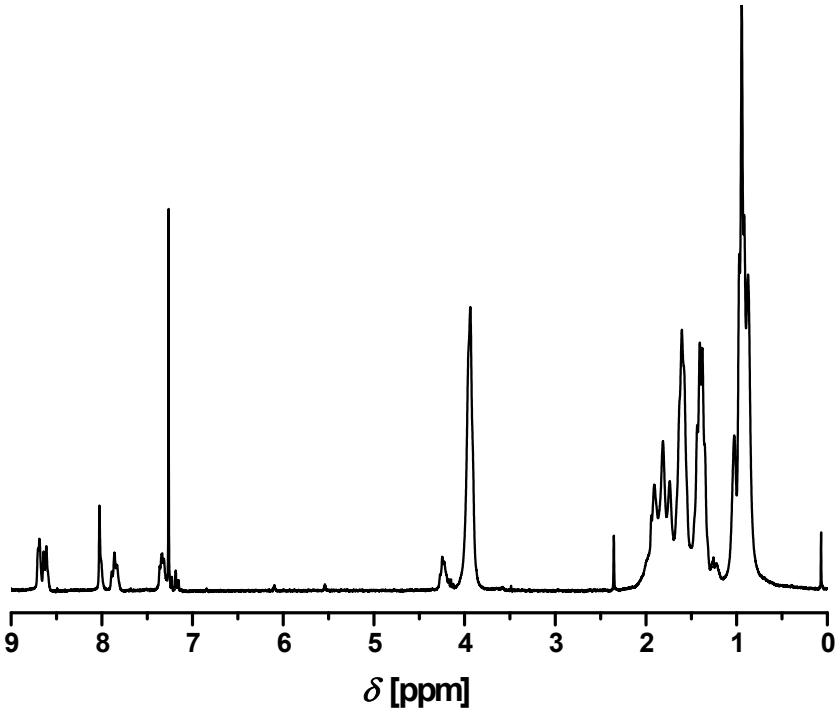


Figure S16: ^{1}H NMR-spectrum of copolymer **P1** in $CDCl_3$.

SEC-curves

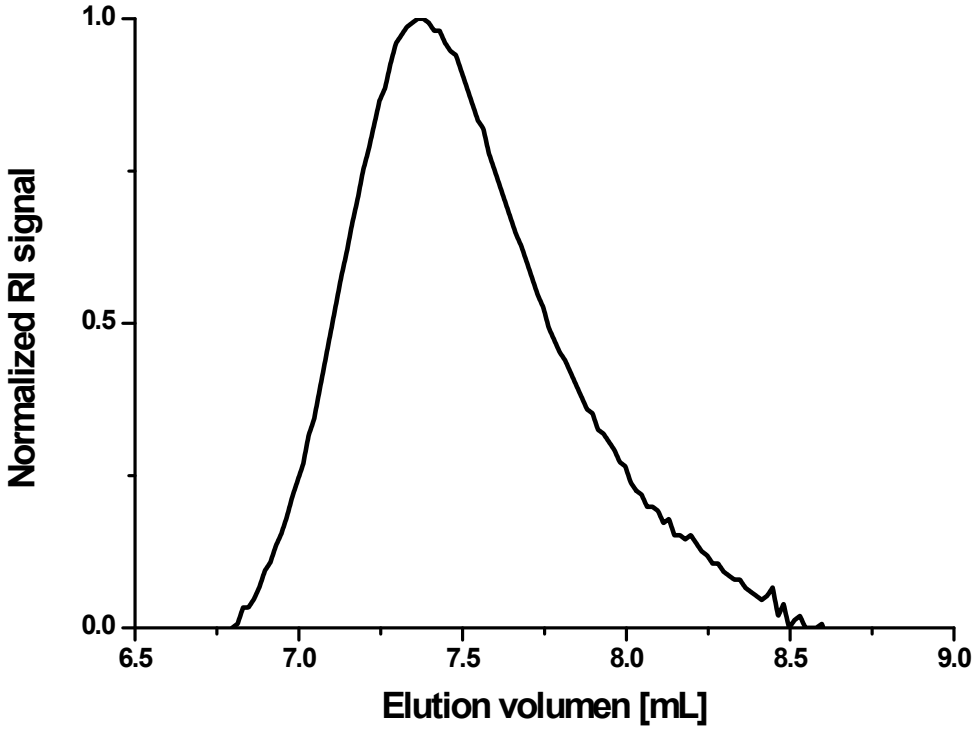


Figure S17: SEC elugram of copolymer **P1** in chloroform/*iso*-propanol/triethylamine [94/2/4].

X-ray data:

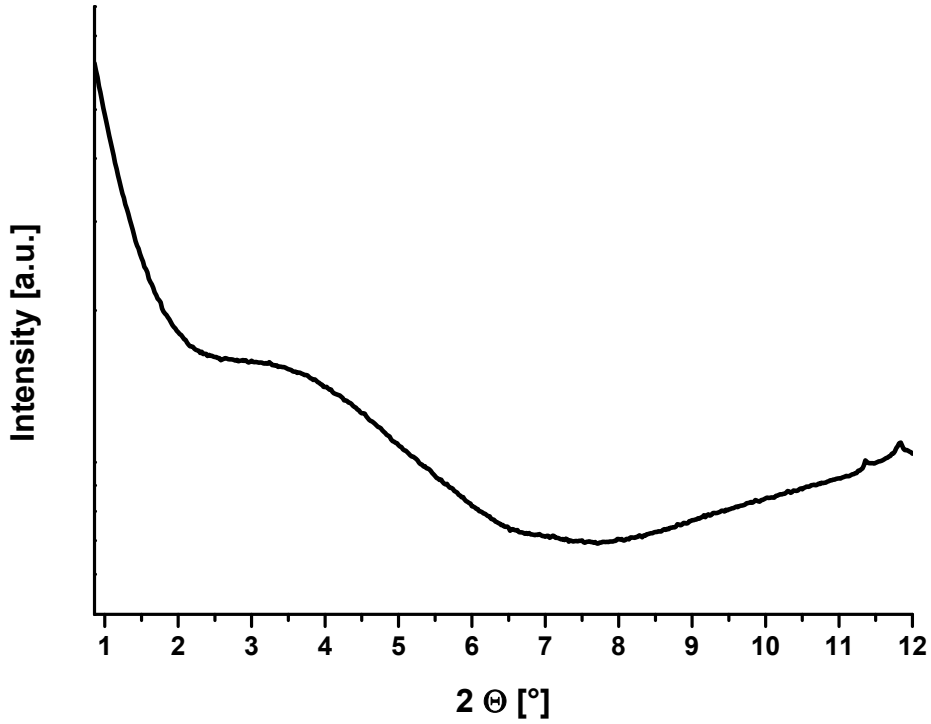


Figure S18: SWAXS pattern of **CP1**.

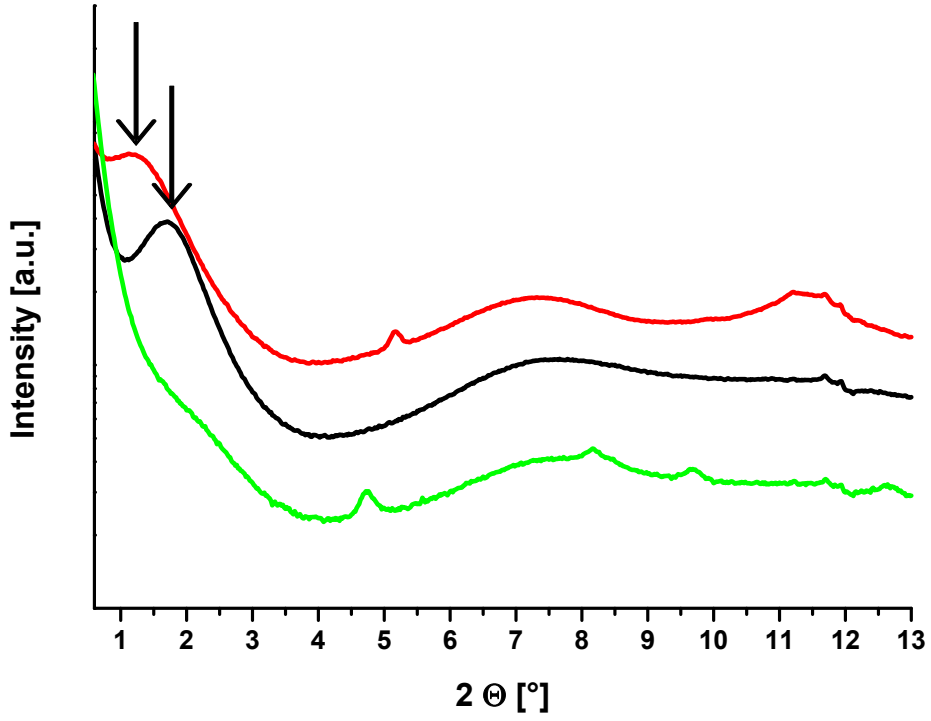


Figure S19: X-ray data of **MP1** (black line), **MP2** (red line) and **MP3** (green line).*

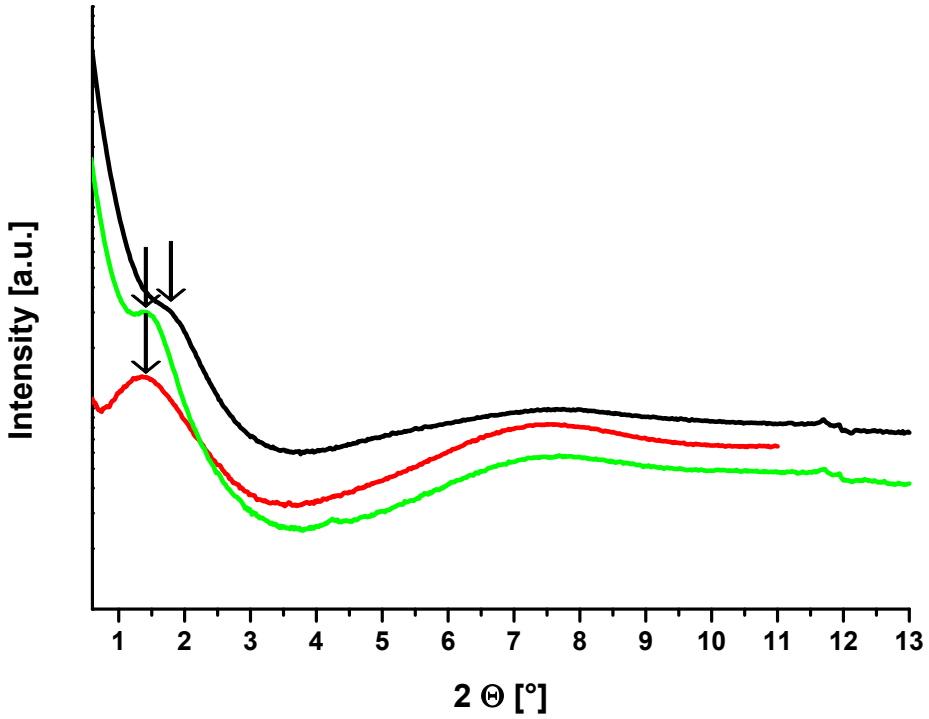


Figure S20: X-ray data of **MP4** (black line), **MP5** (red line) and **MP6** (green line).*

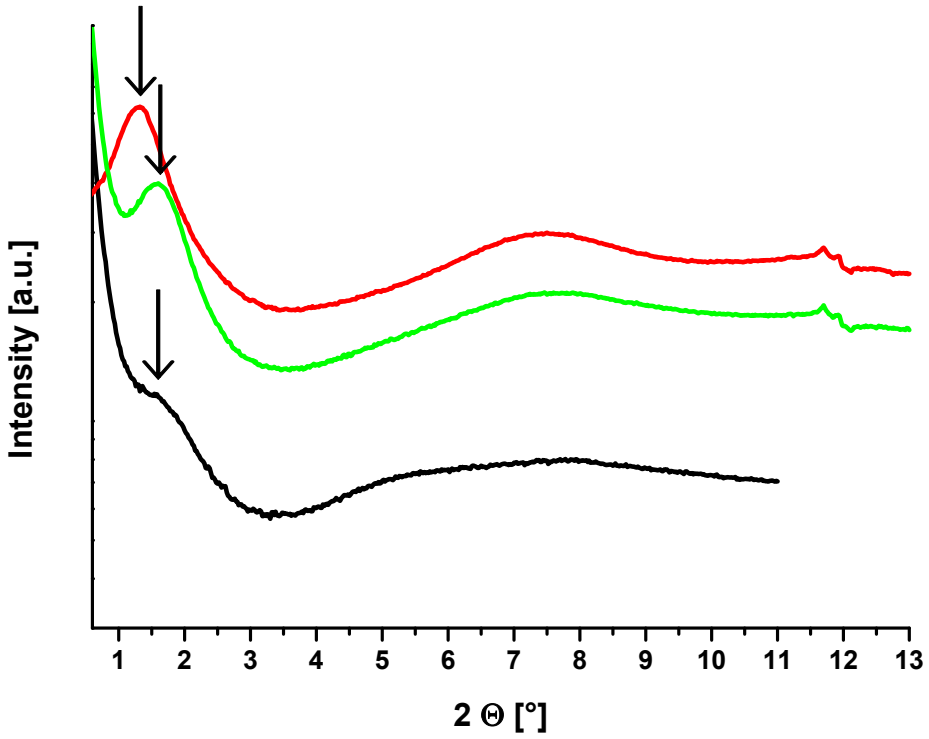


Figure S21: X-ray data of **MP7** (black line), **MP8** (red line) and **MP9** (green line).*

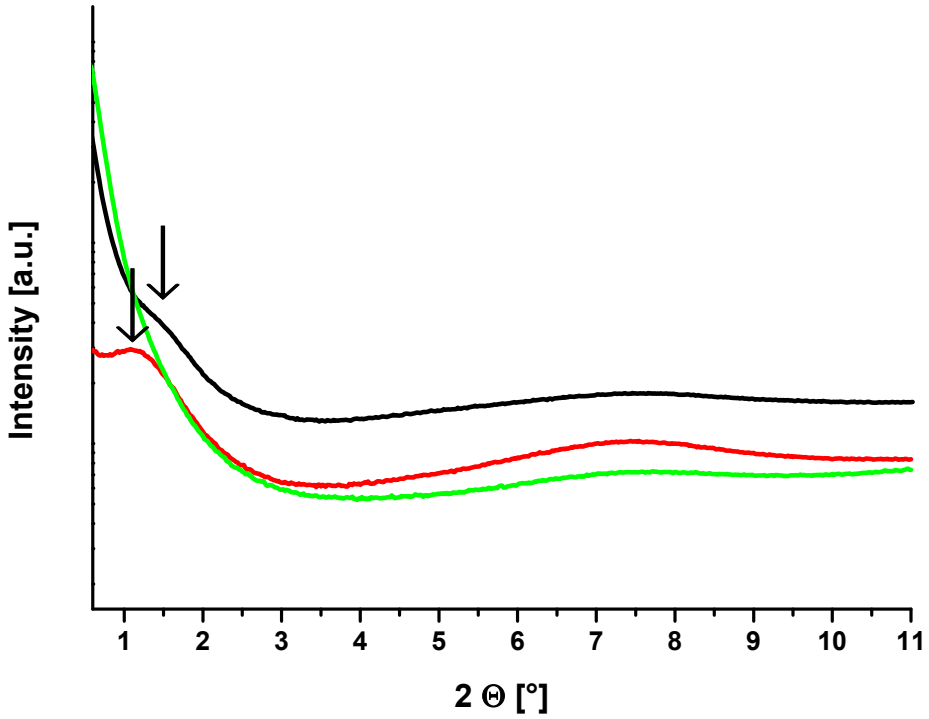
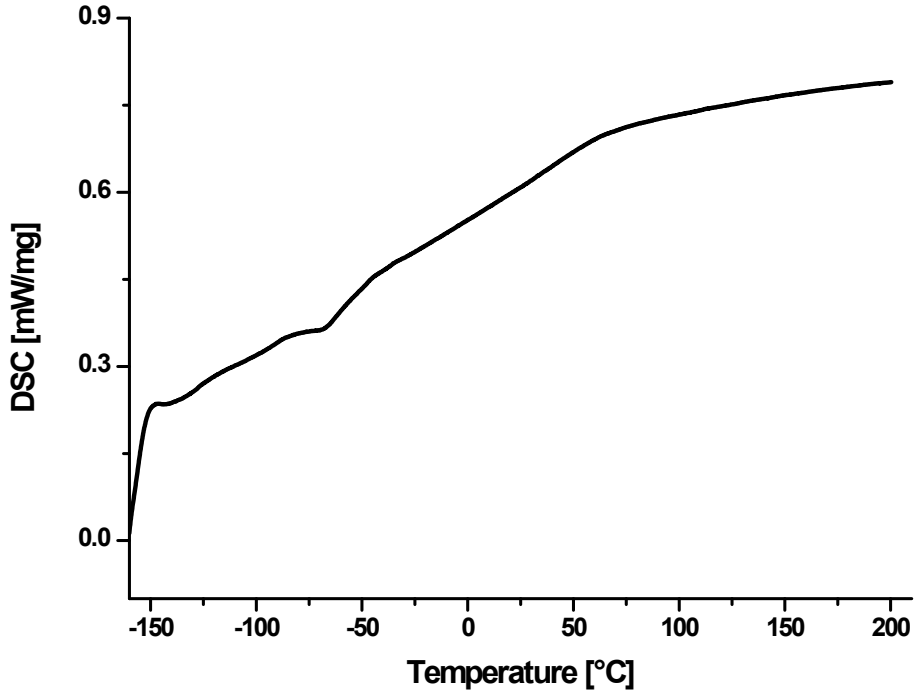


Figure S22: X-ray data of **MP10** (black line), **MP11** (red line) and **MP12** (green line).*

* Additional signals at higher 2Θ values could not be assigned and are of currently unknown origin.

Thermal properties:

a)



b)

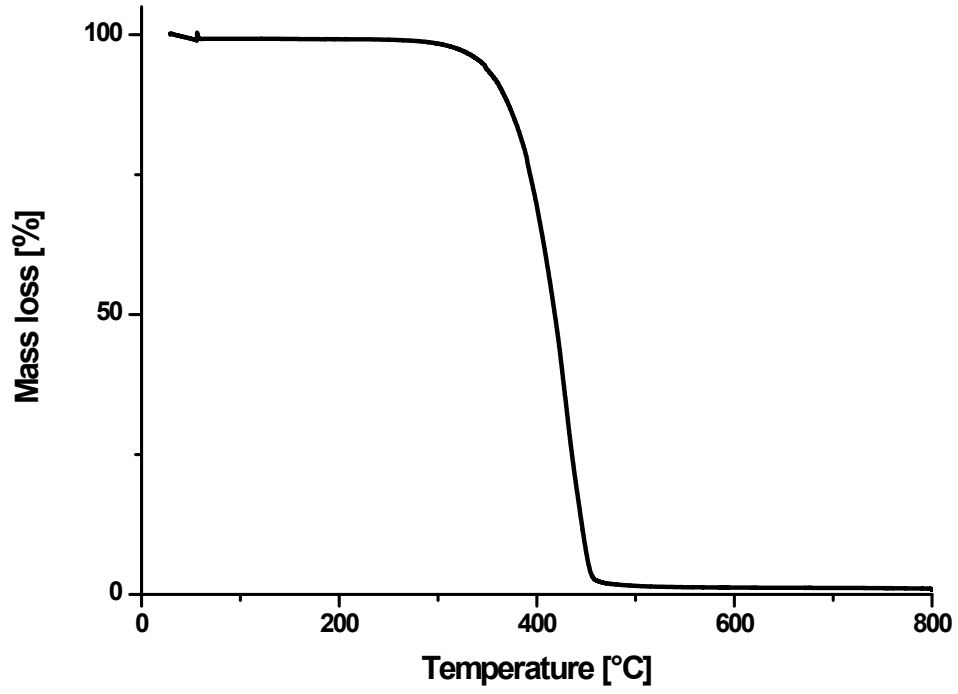
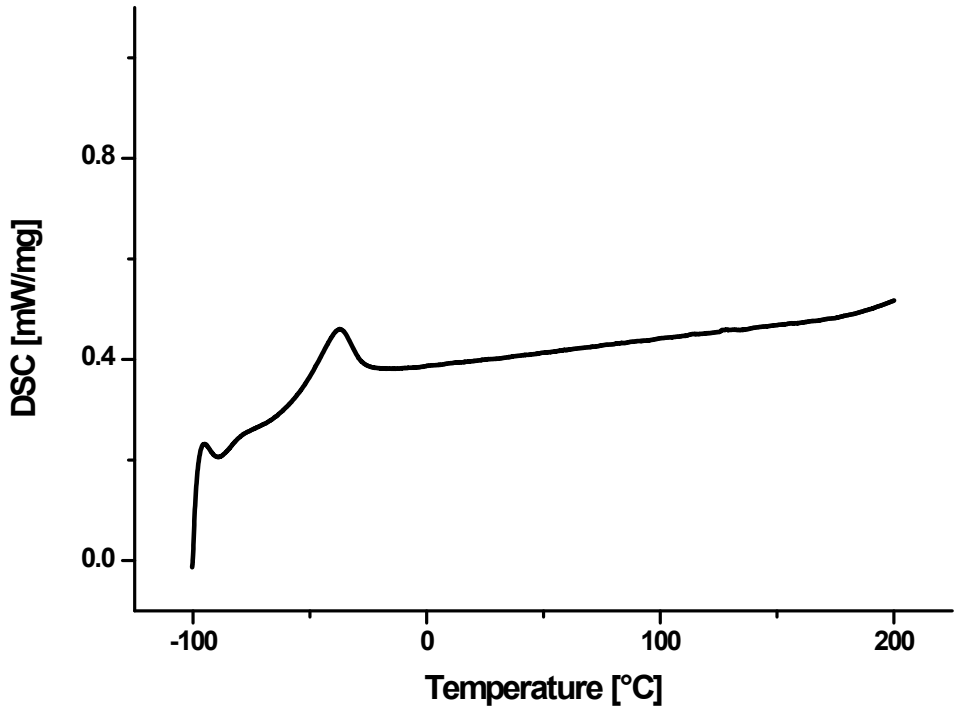


Figure S23: Thermal properties of the polymer network **CP1**: a) DSC and b) TGA.

a)



b)

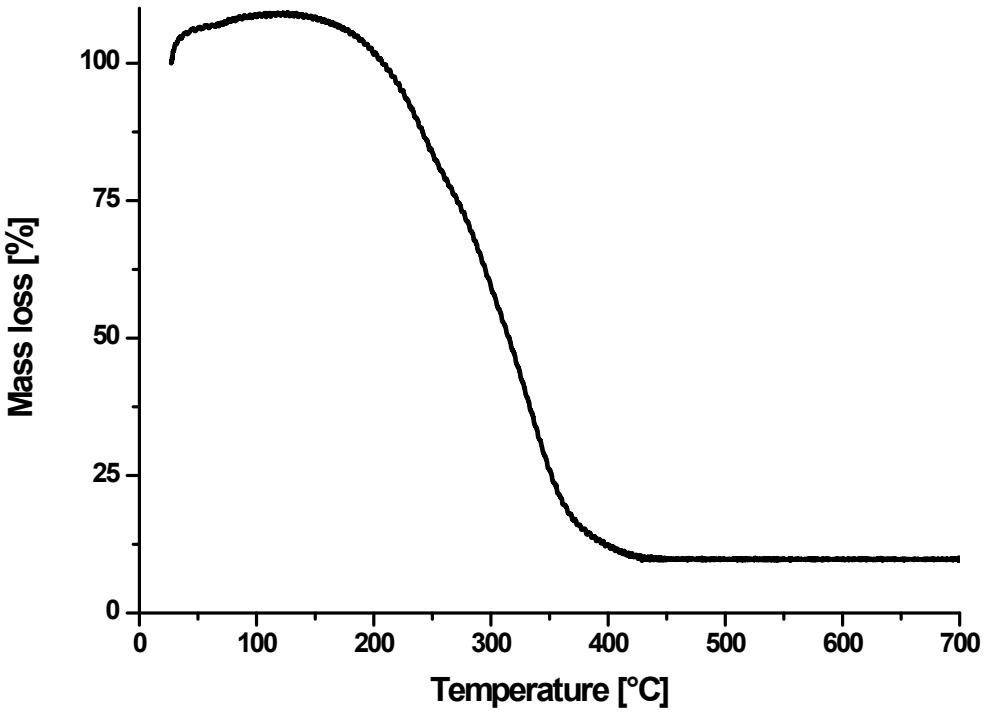
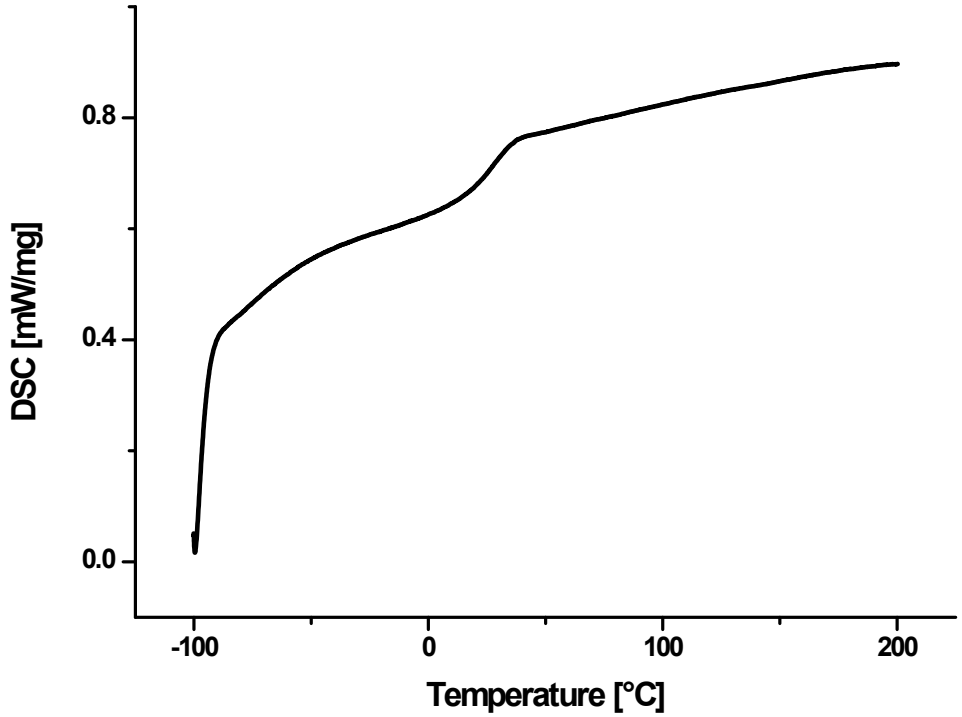


Figure S24: Thermal properties of the polymer network **CP2**: a) DSC and b) TGA.

a)



b)

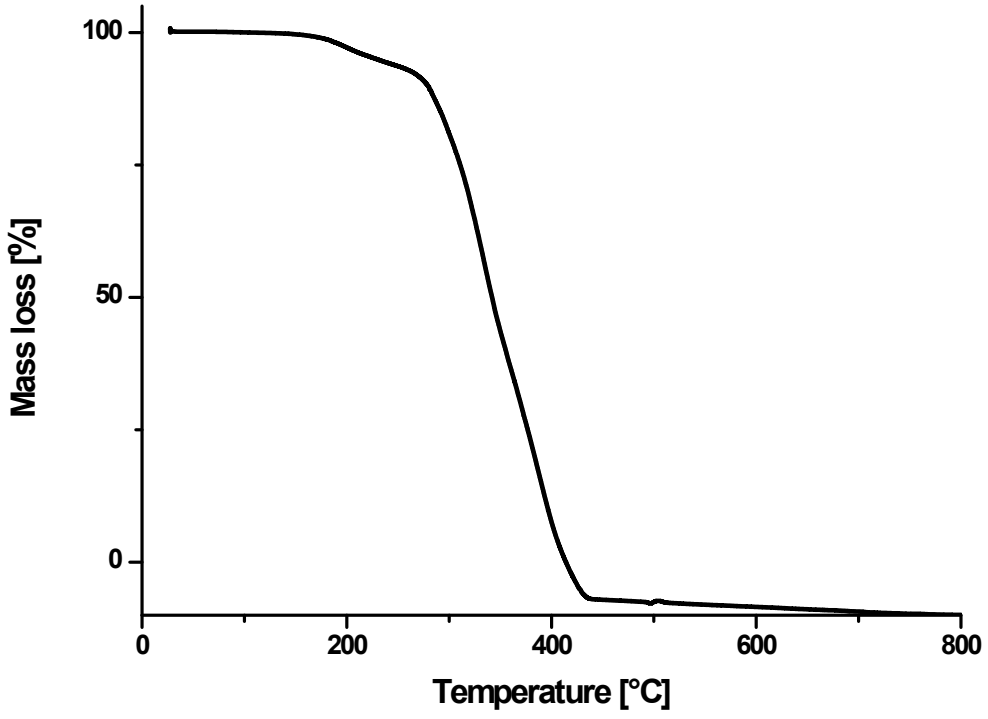
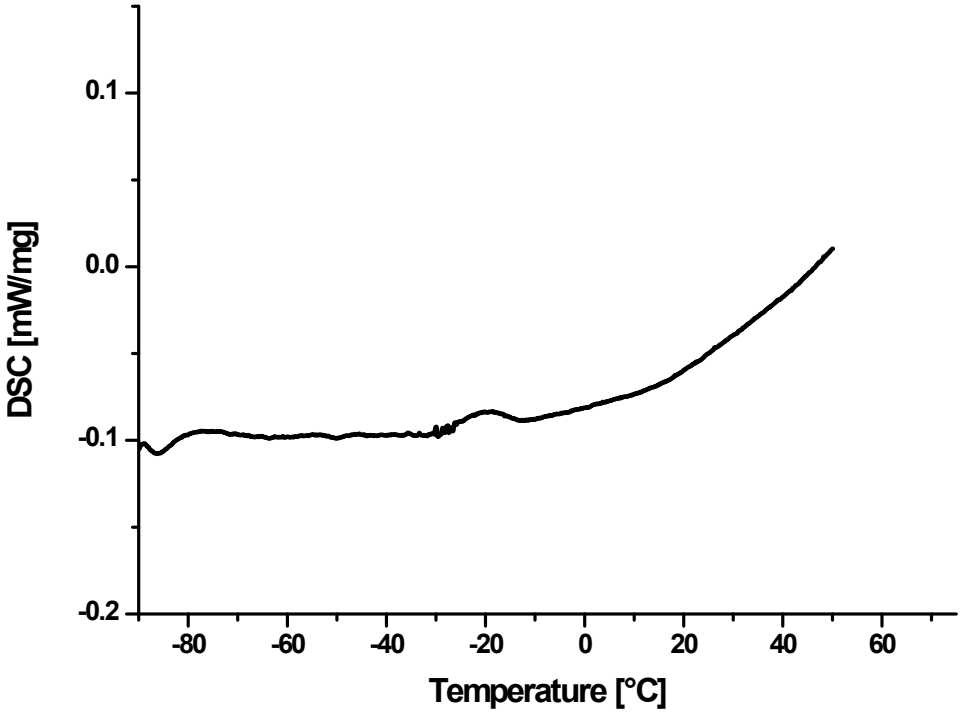


Figure S25: Thermal properties of the copolymer **P1**: a) DSC and b) TGA.

a)



b)

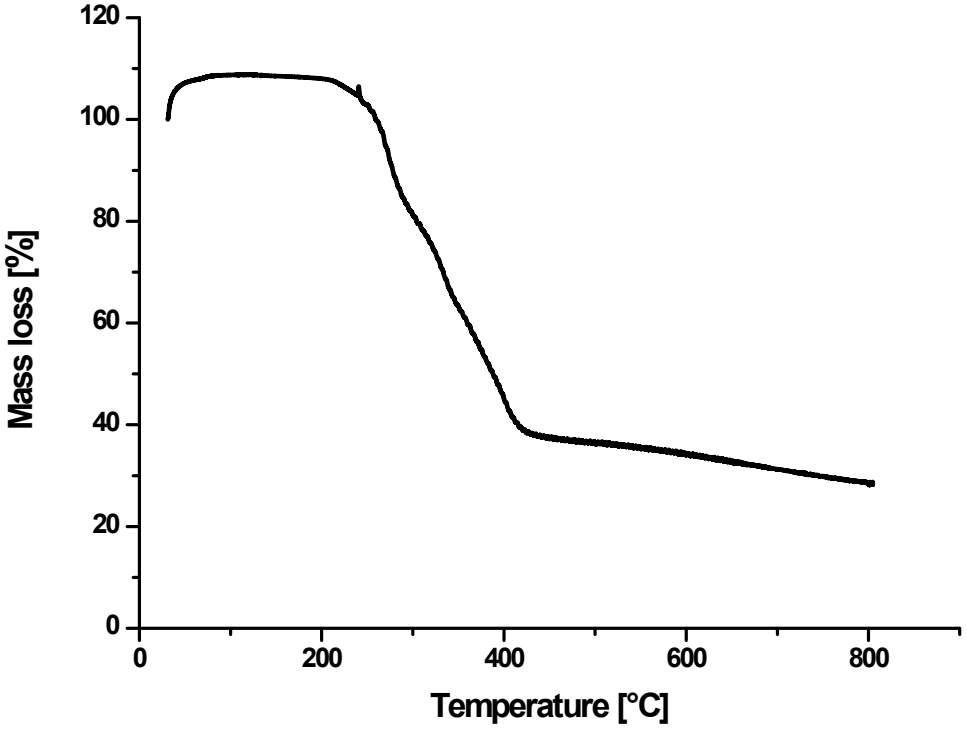
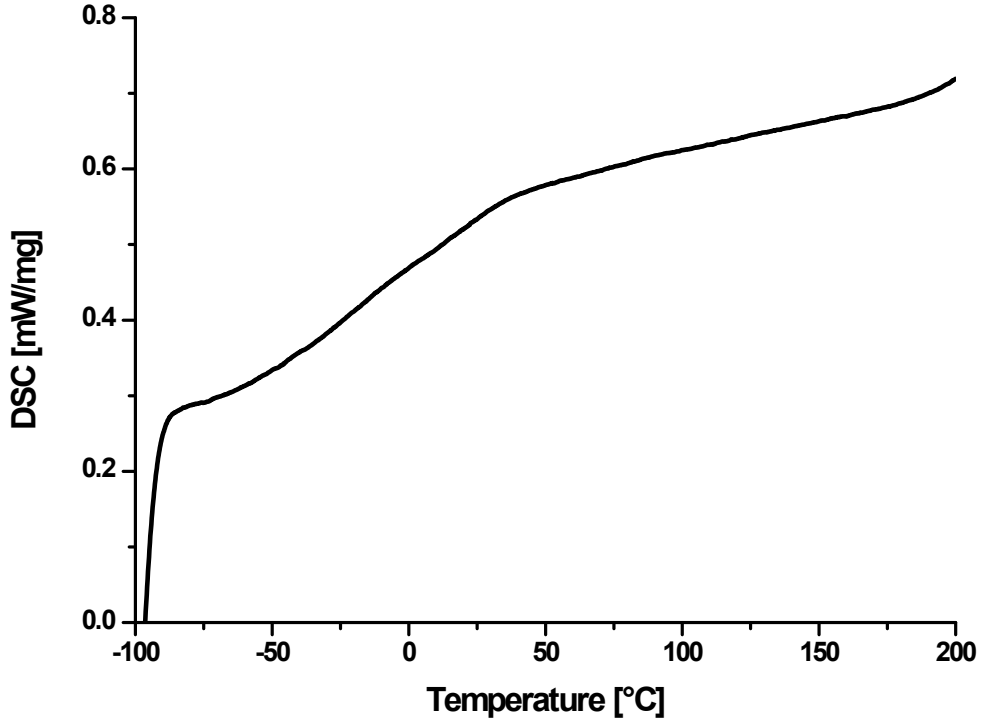


Figure S26: Thermal properties of the polymer network **MP1**: a) DSC and b) TGA.

a)



b)

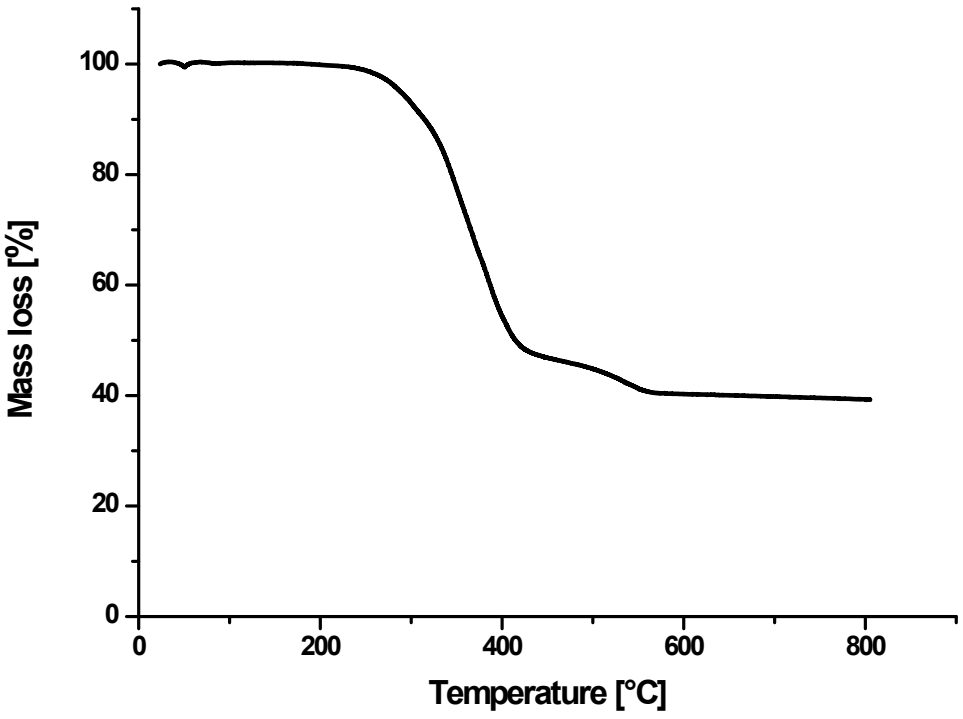
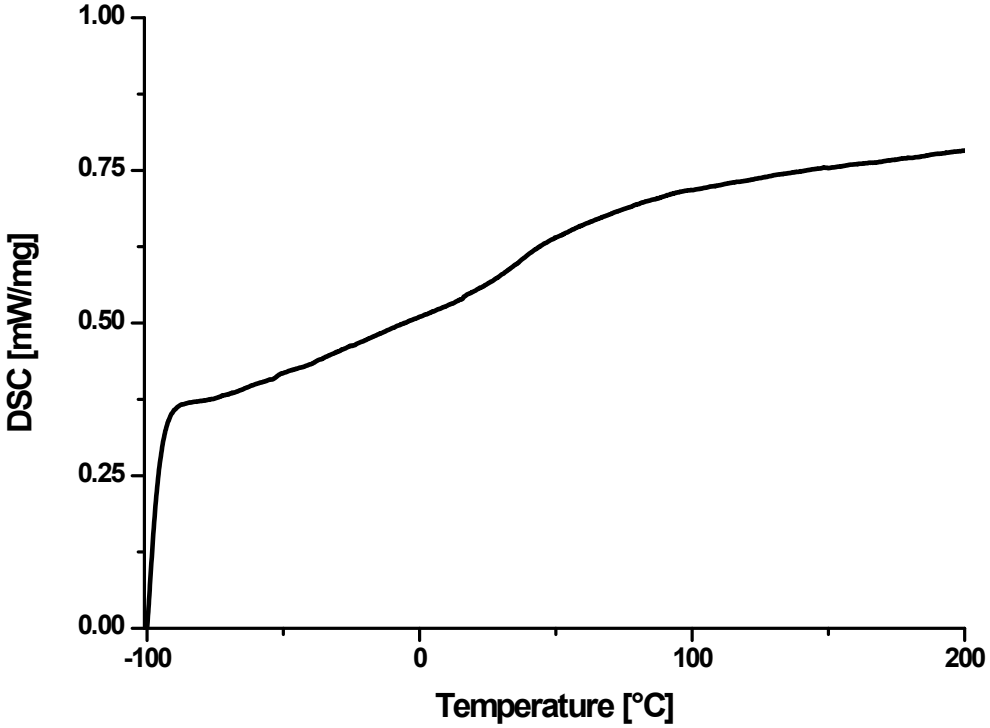


Figure S27: Thermal properties of the polymer network **MP2**: a) DSC and b) TGA.

a)



b)

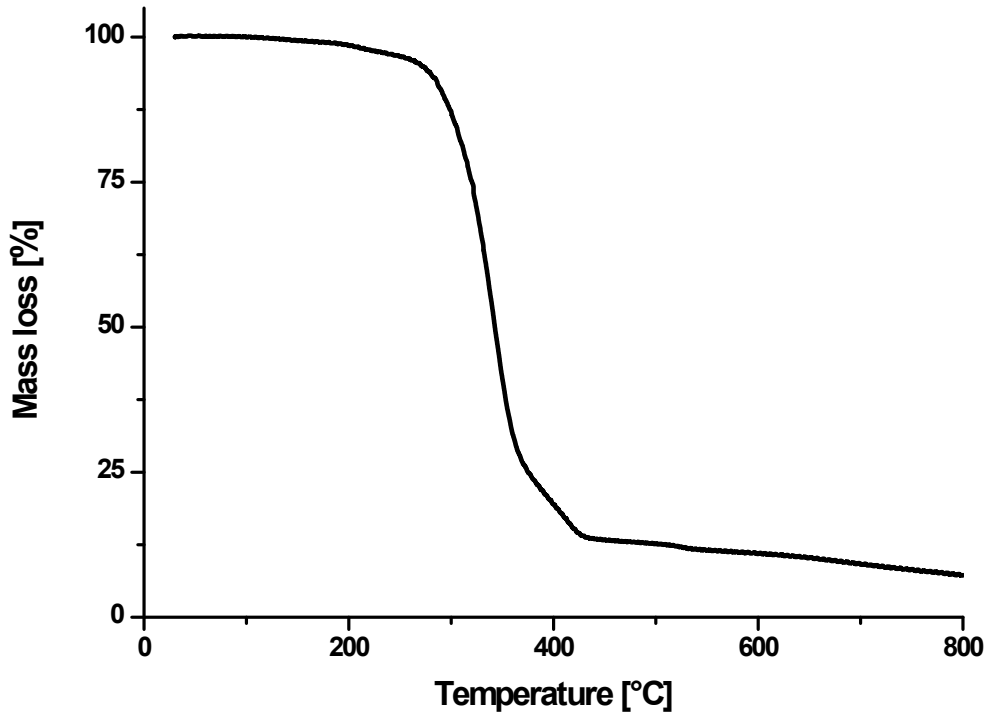
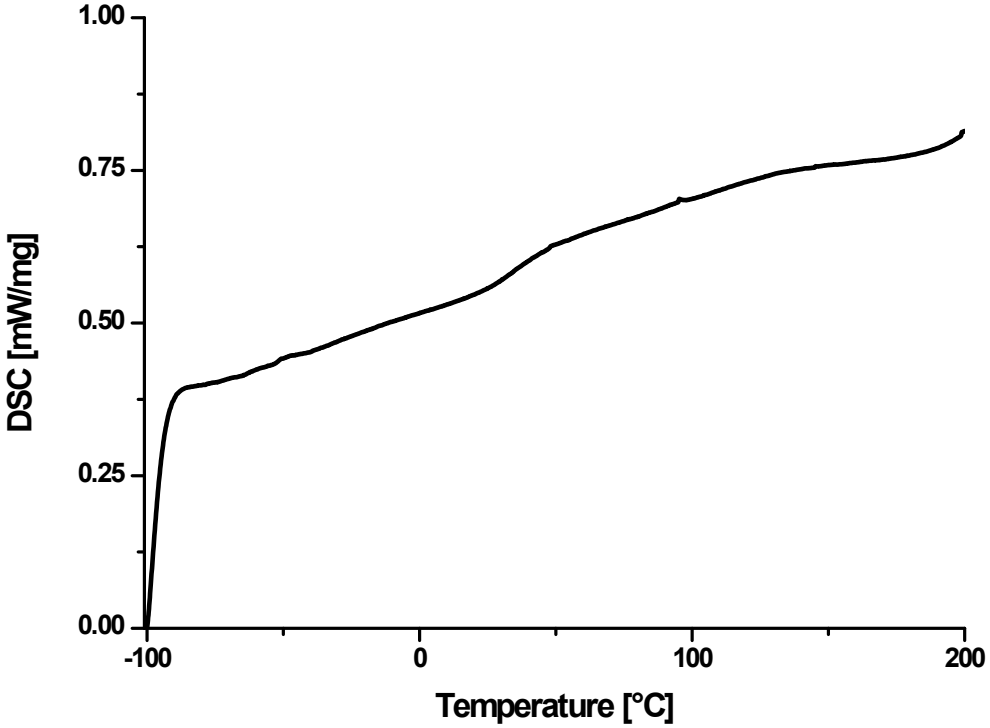


Figure S28: Thermal properties of the polymer network **MP3**: a) DSC and b) TGA.

a)



b)

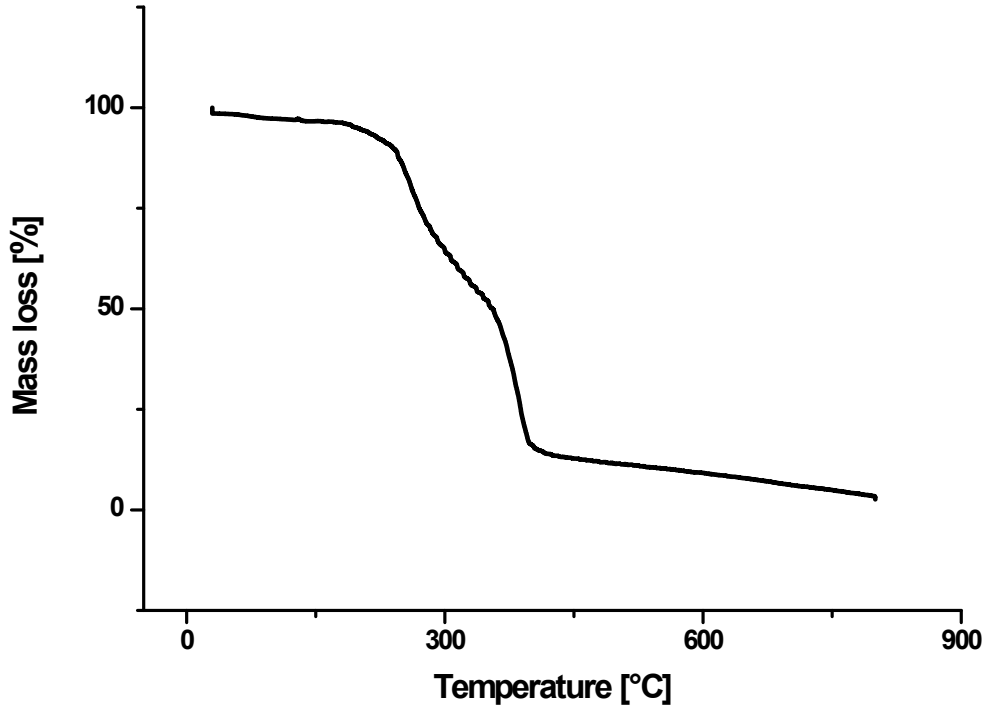
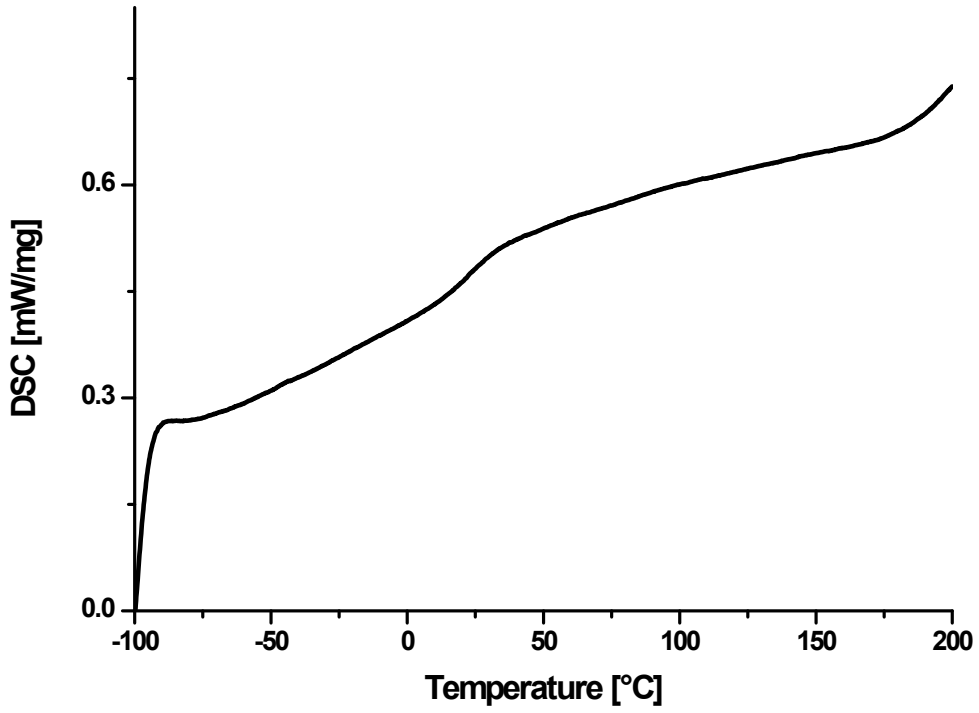


Figure S29: Thermal properties of the polymer network **MP4**: a) DSC and b) TGA.

a)



b)

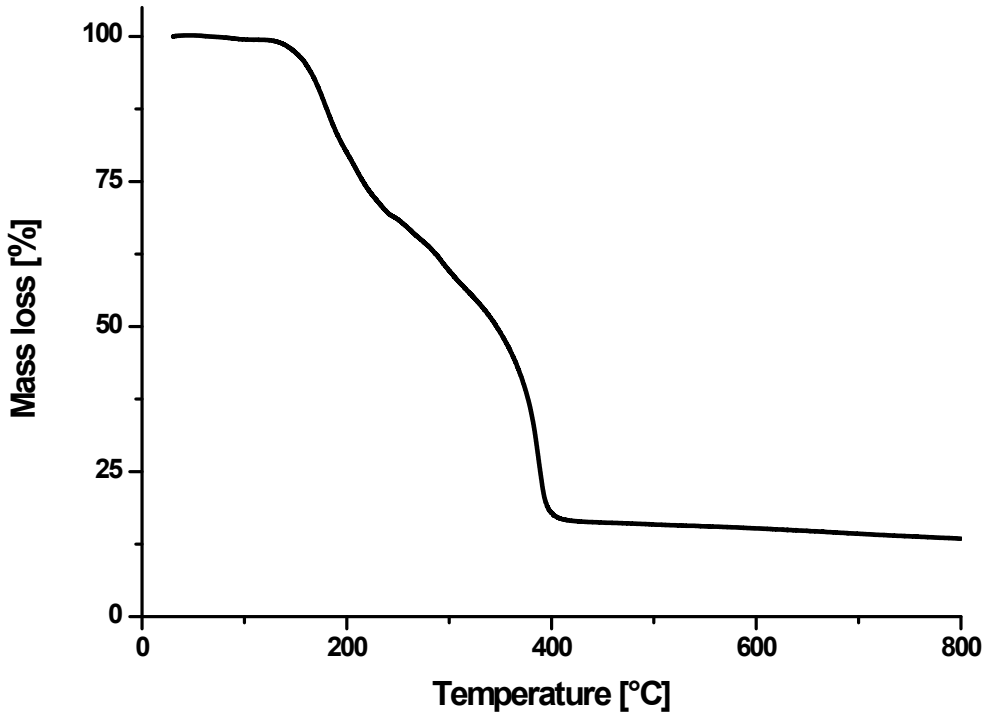
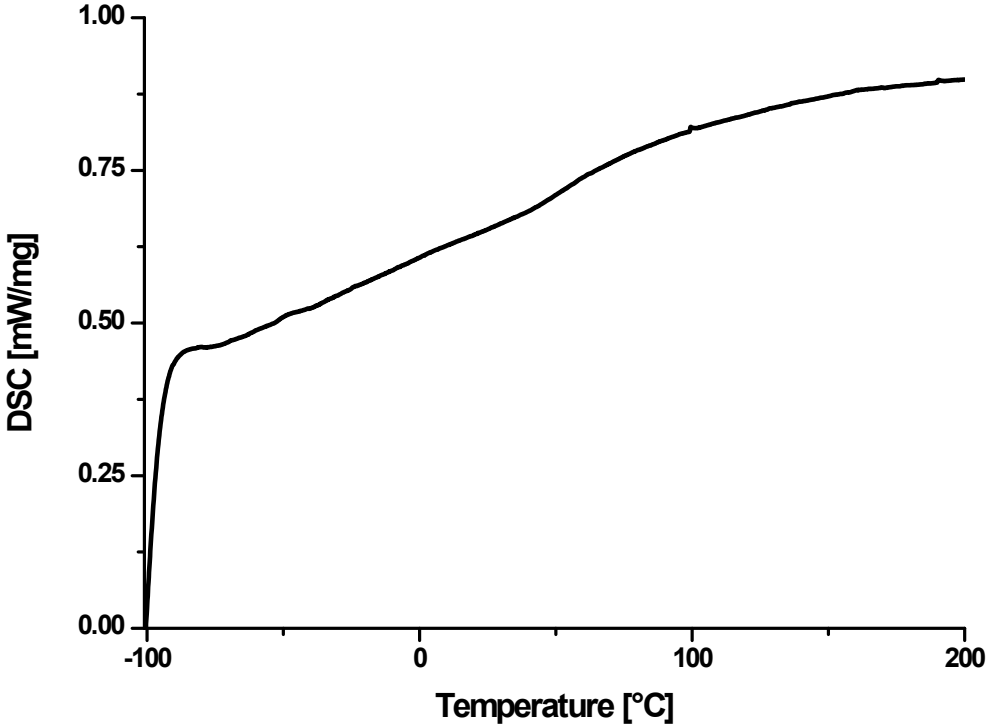


Figure S30: Thermal properties of the polymer network **MP5**: a) DSC and b) TGA.

a)



b)

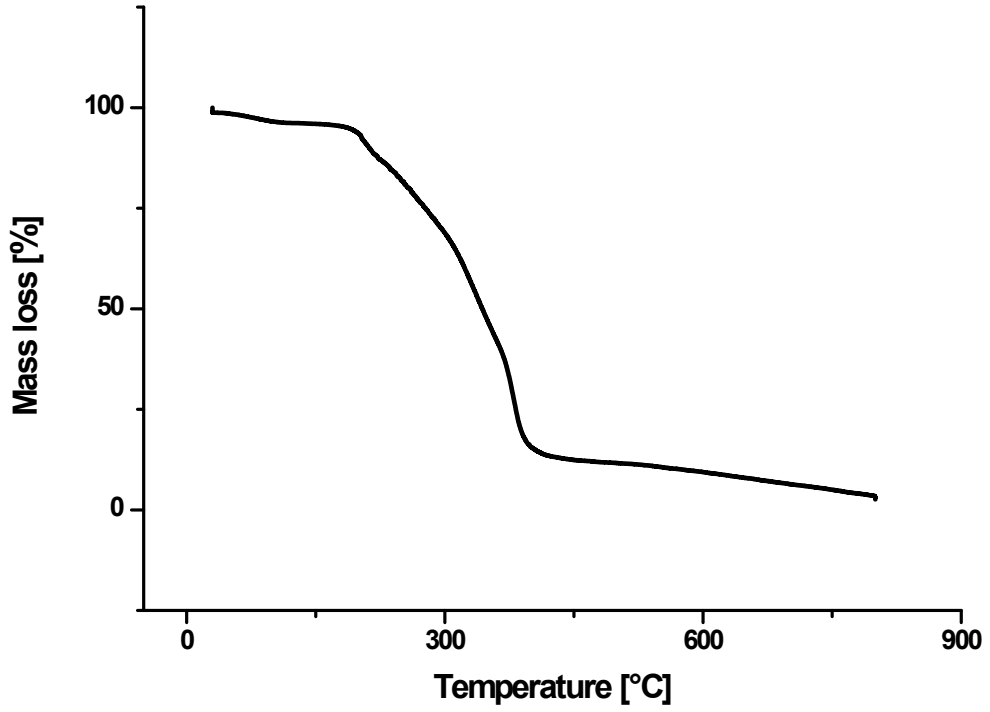
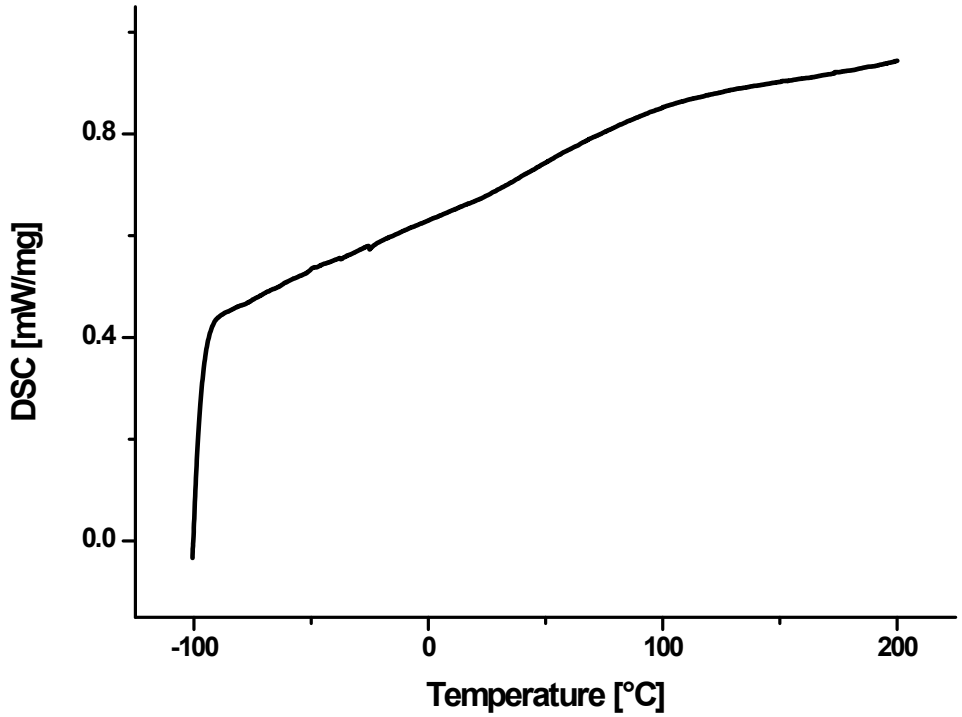


Figure S31: Thermal properties of the polymer network **MP6**: a) DSC and b) TGA.

a)



b)

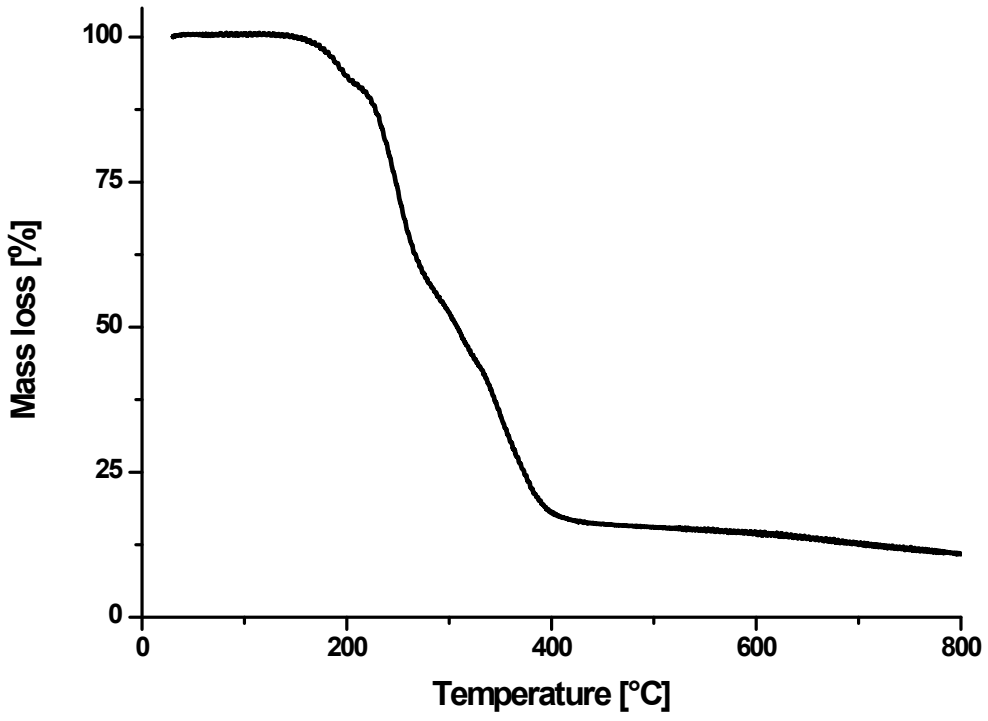
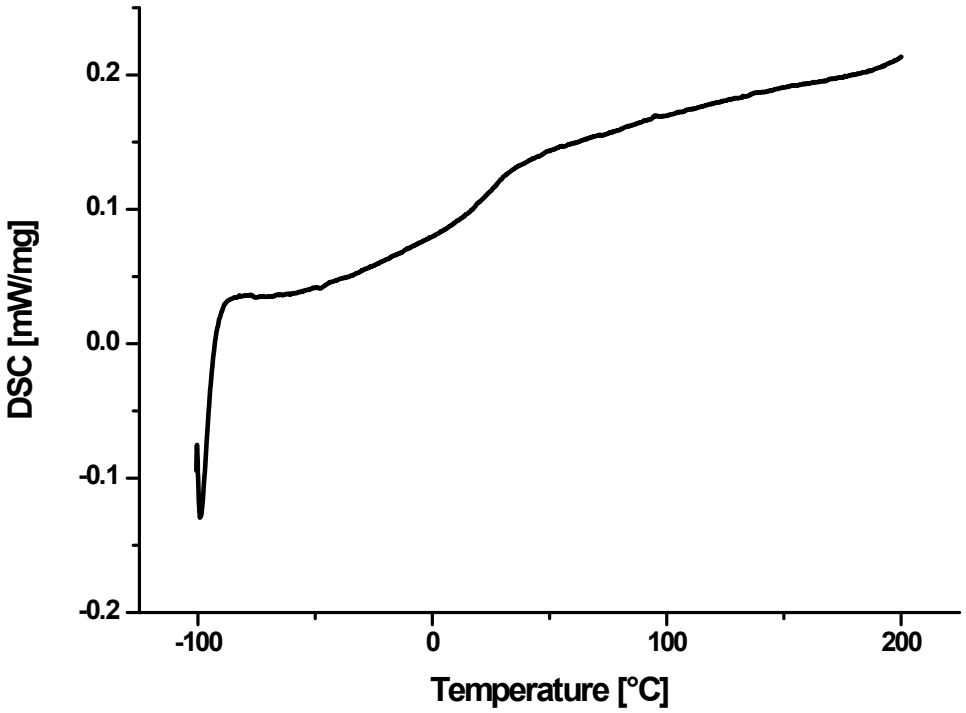


Figure S32: Thermal properties of the polymer network **MP7**: a) DSC and b) TGA.

a)



b)

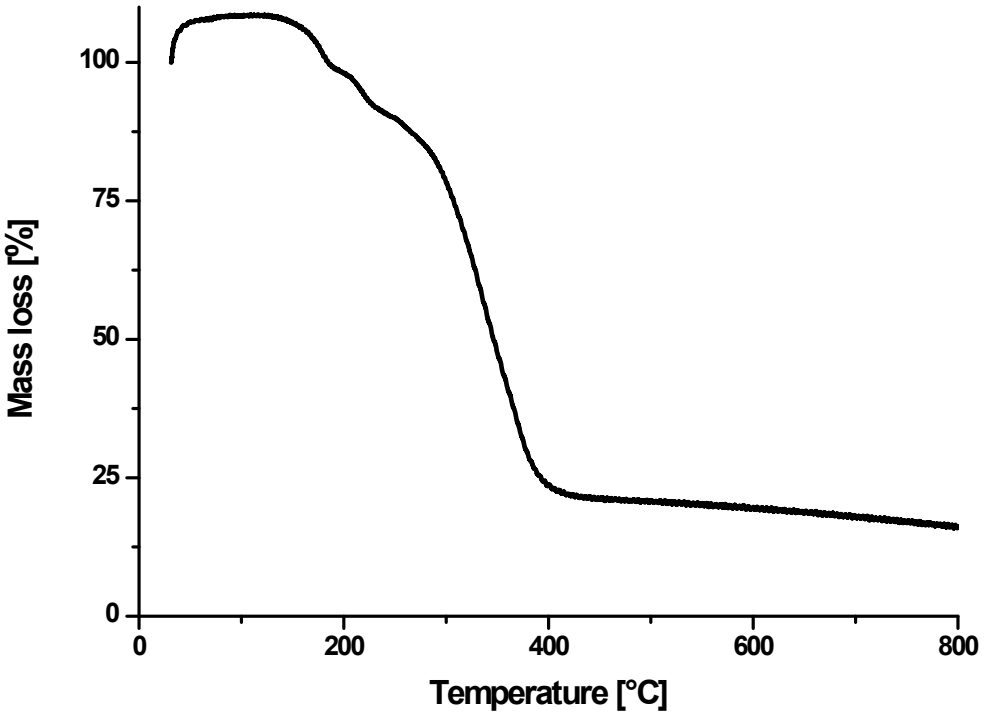
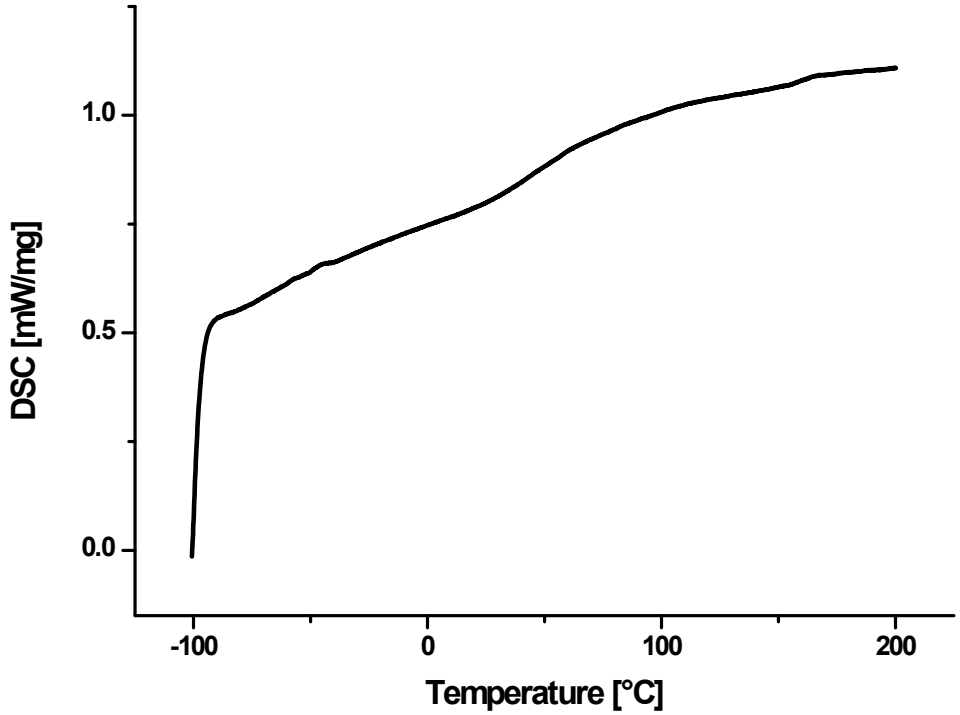


Figure S33: Thermal properties of the polymer network **MP8**: a) DSC and b) TGA.

a)



b)

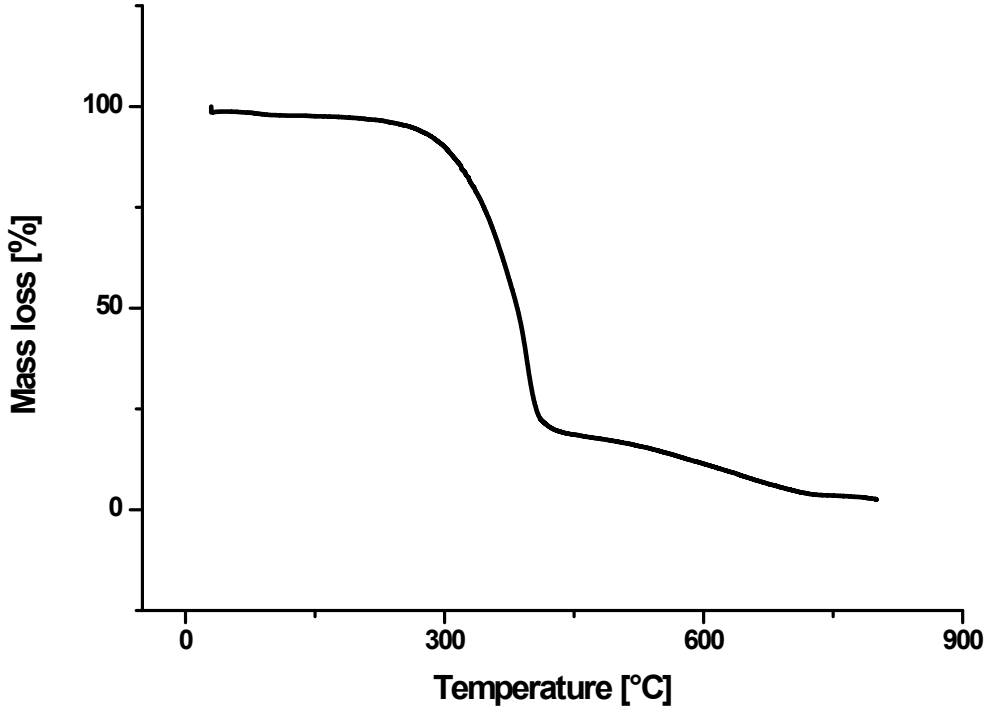
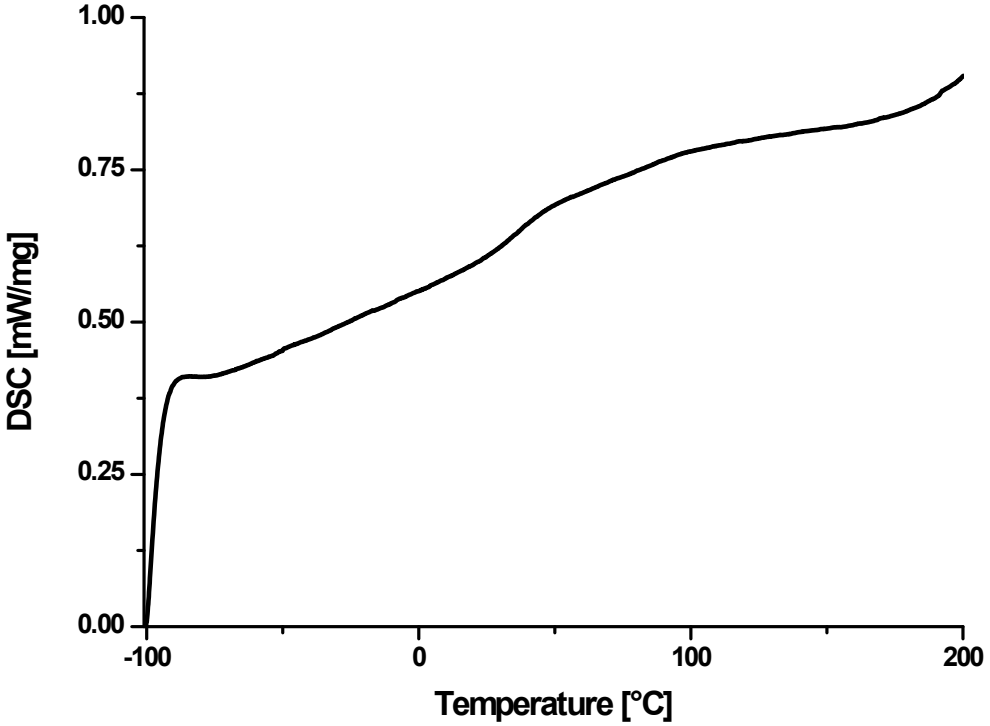


Figure S34: Thermal properties of the polymer network **MP9**: a) DSC and b) TGA.

a)



b)

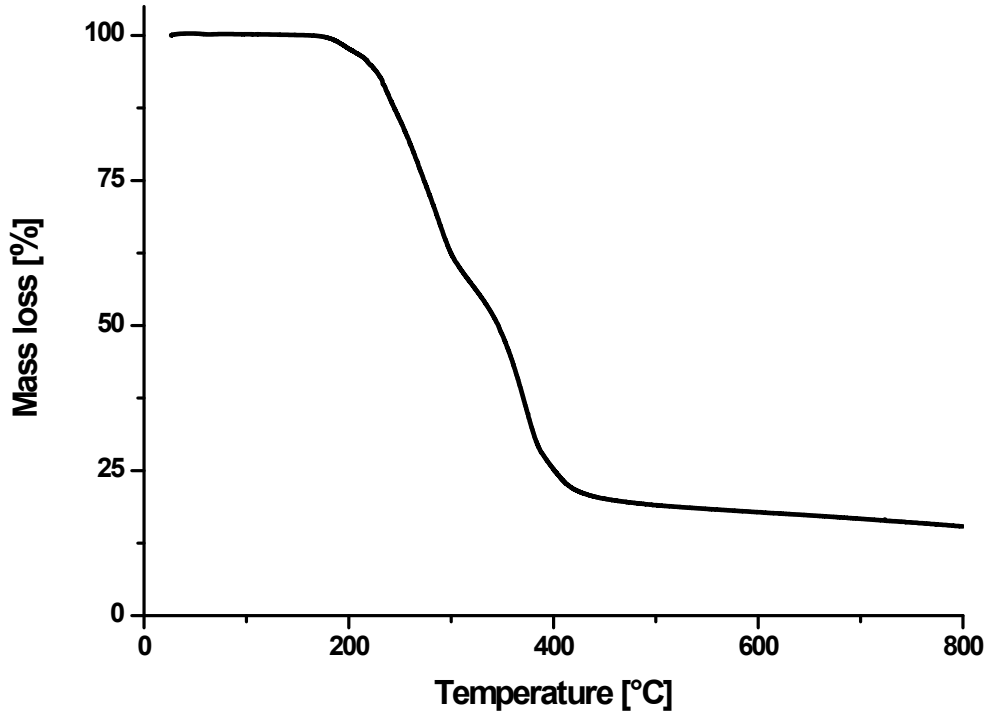
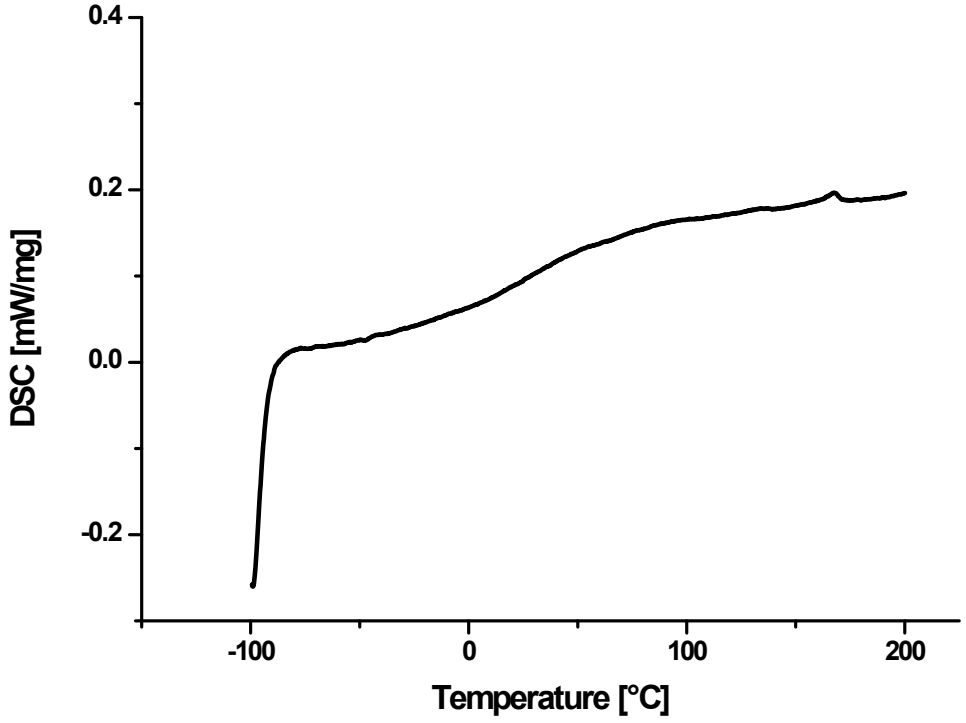


Figure S35: Thermal properties of the polymer network **MP10**: a) DSC and b) TGA.

a)



b)

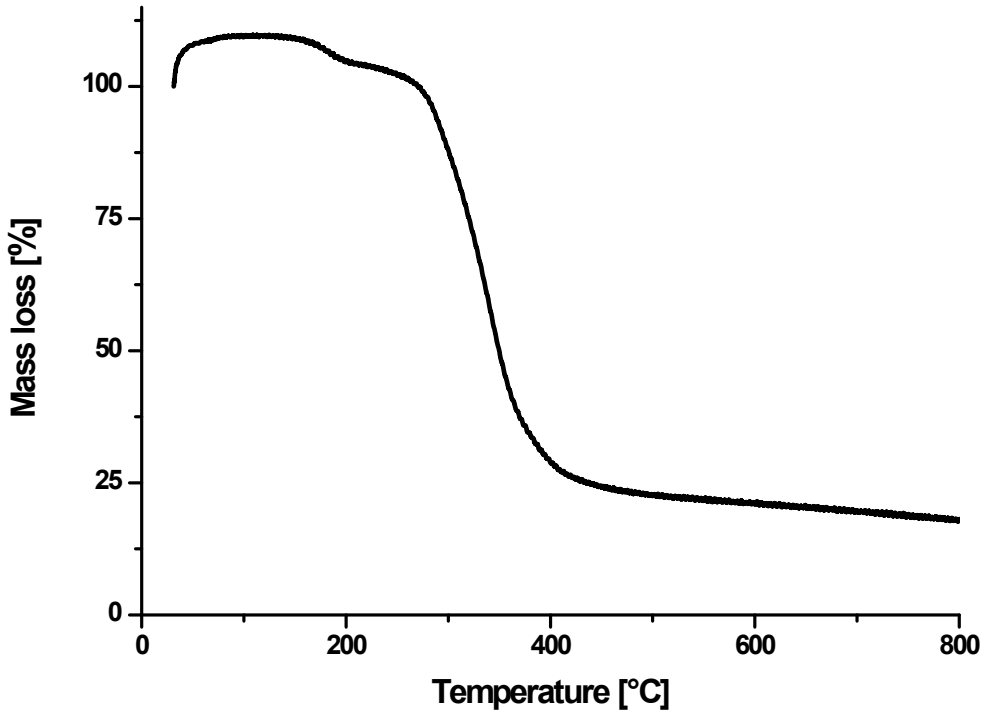
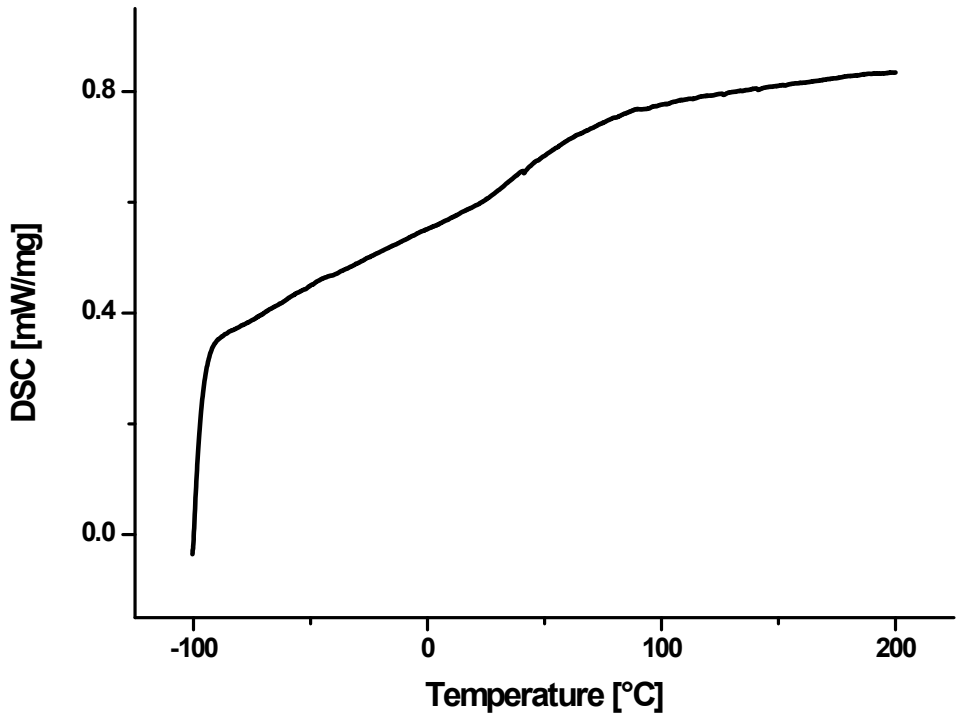


Figure S36: Thermal properties of the polymer network **MP11**: a) DSC and b) TGA.

a)



b)

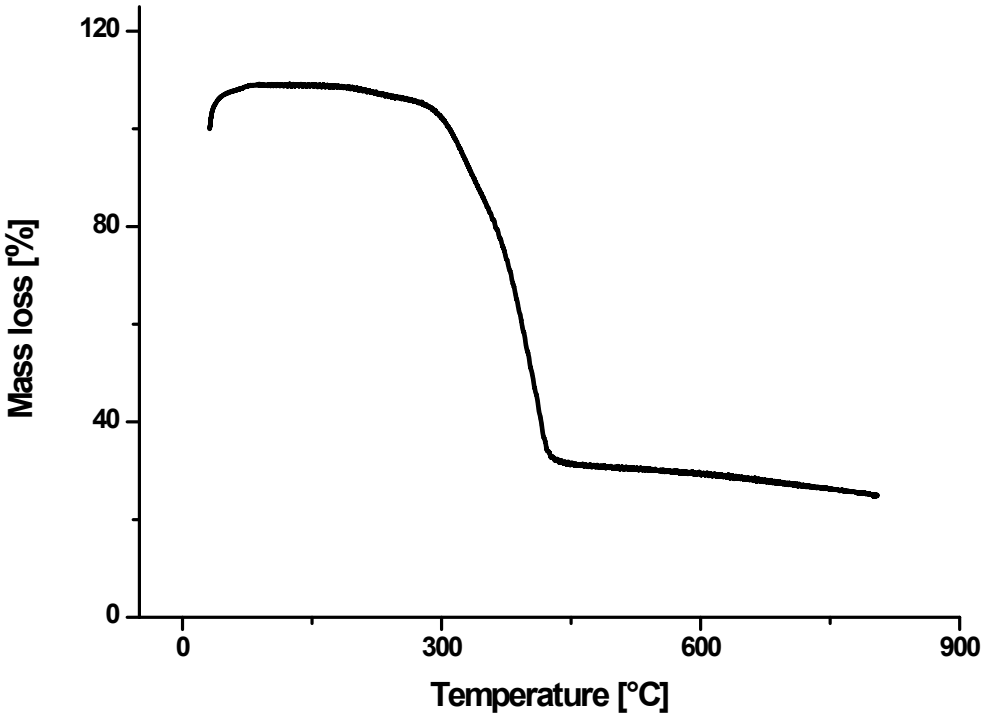


Figure S37: Thermal properties of the polymer network **MP12**: a) DSC and b) TGA.

Rheological results:

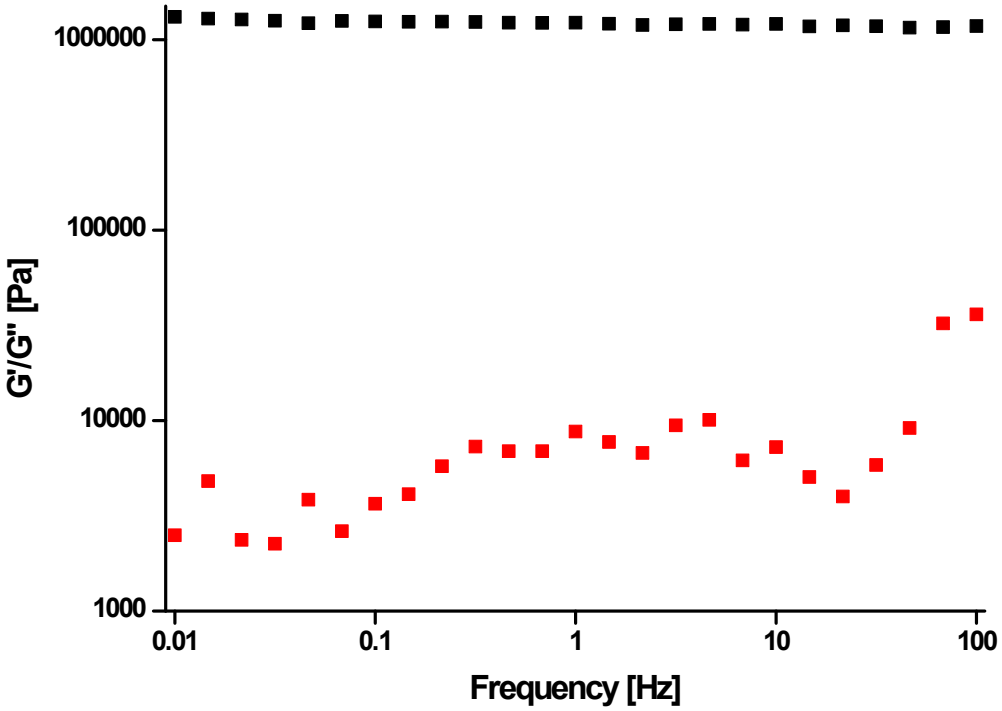


Figure S38: Rheological results of **CP1** at 150 °C (G' in black; G'' in red).

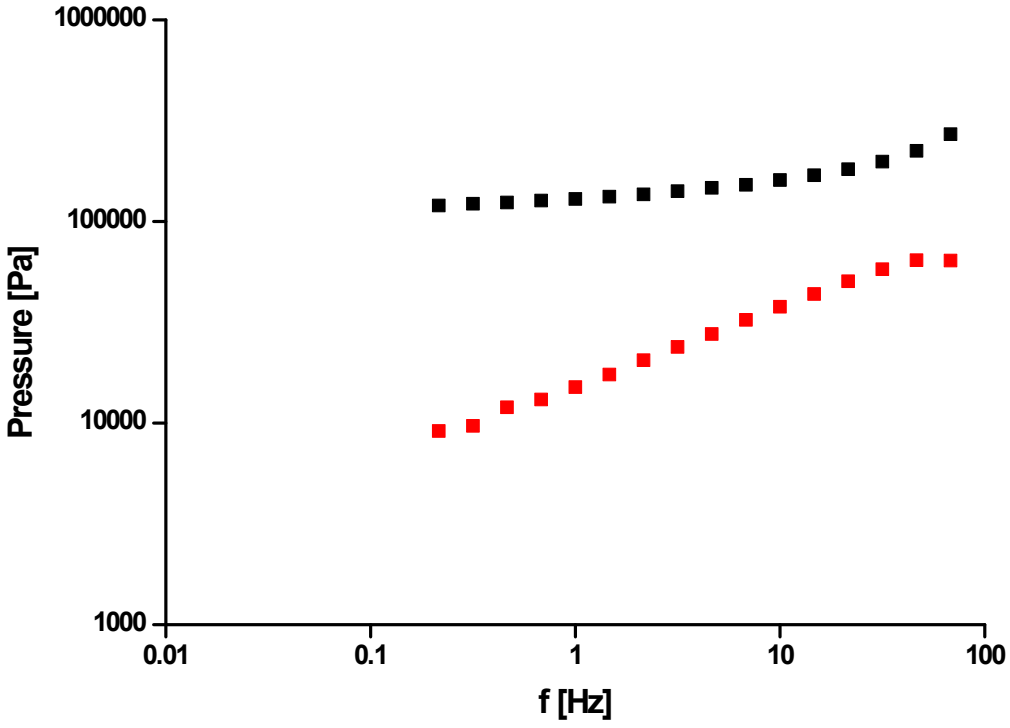
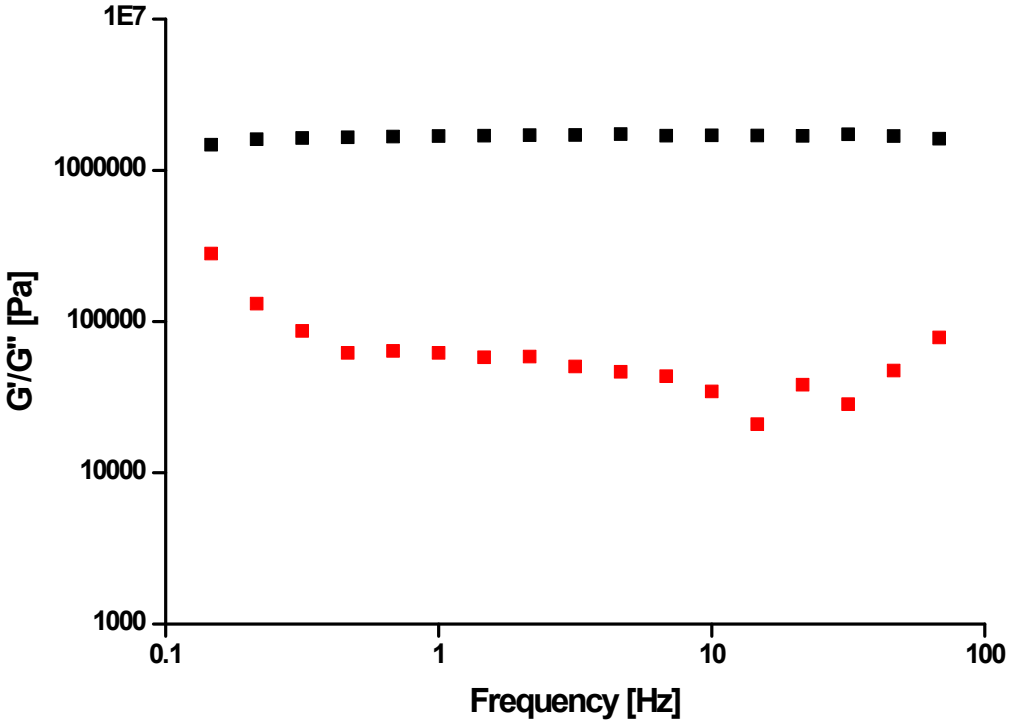
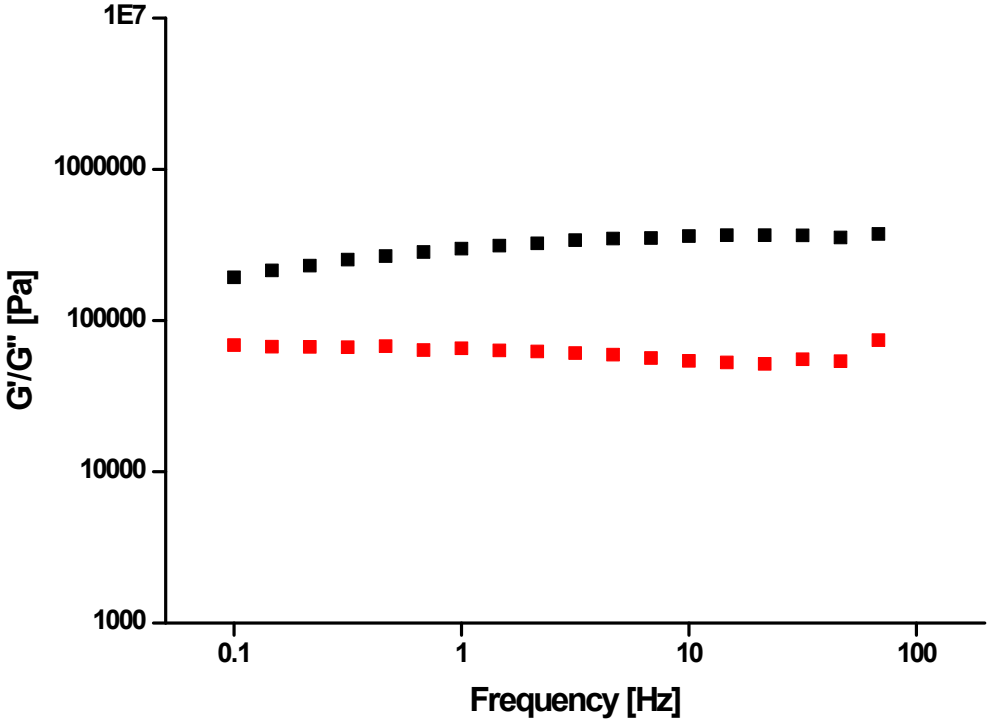


Figure S39: Rheological results of **CP2** at 120 °C (G' in black; G'' in red).

a)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

b)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

c)

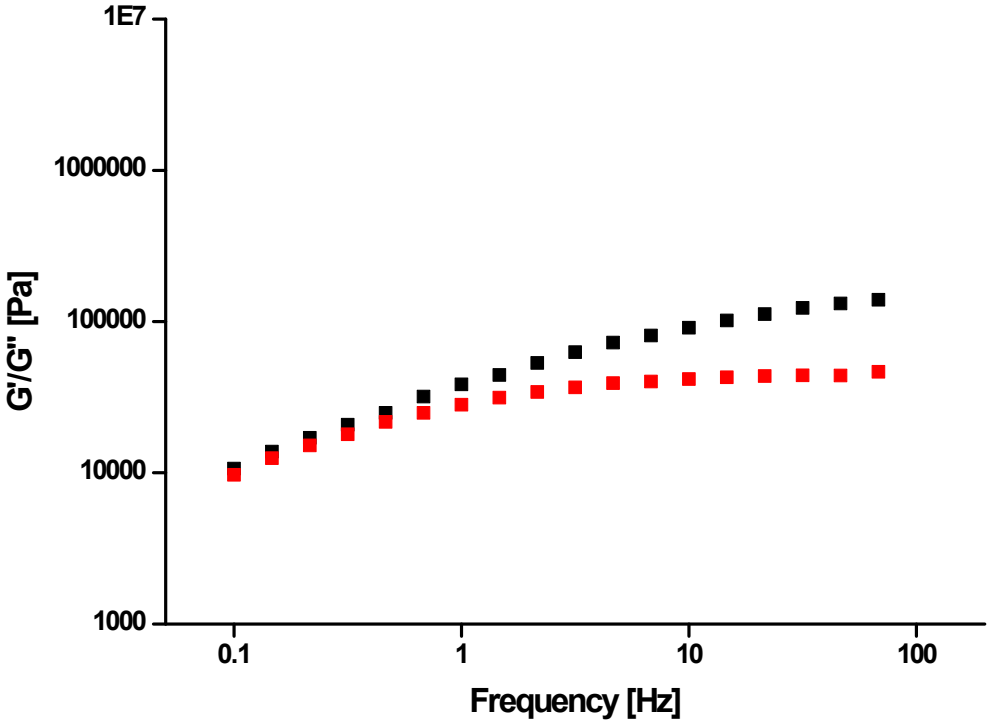
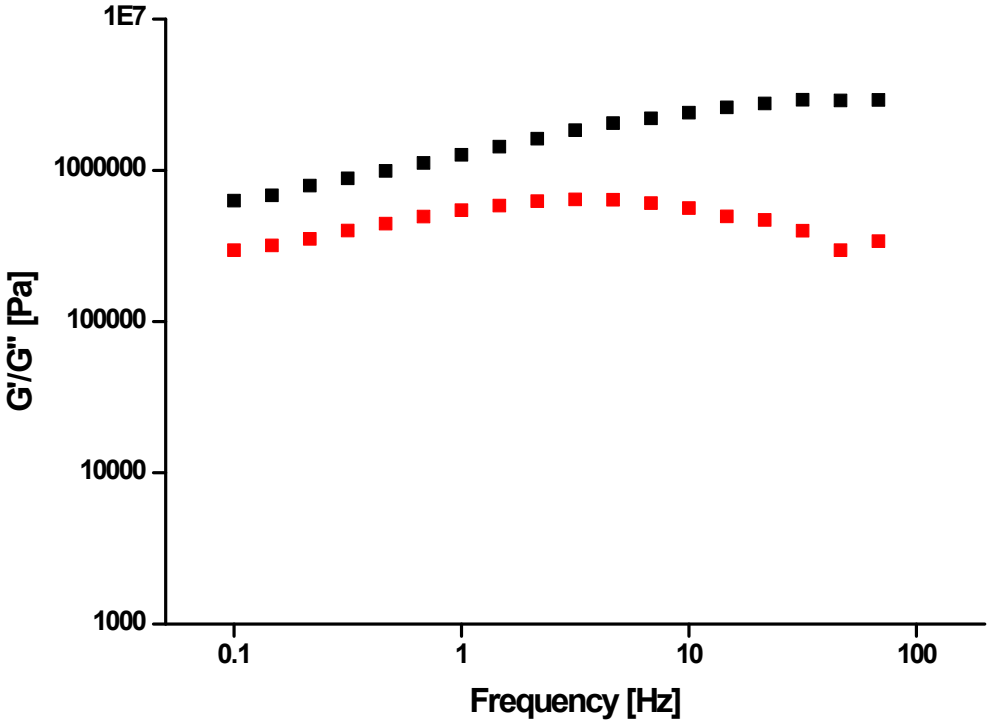
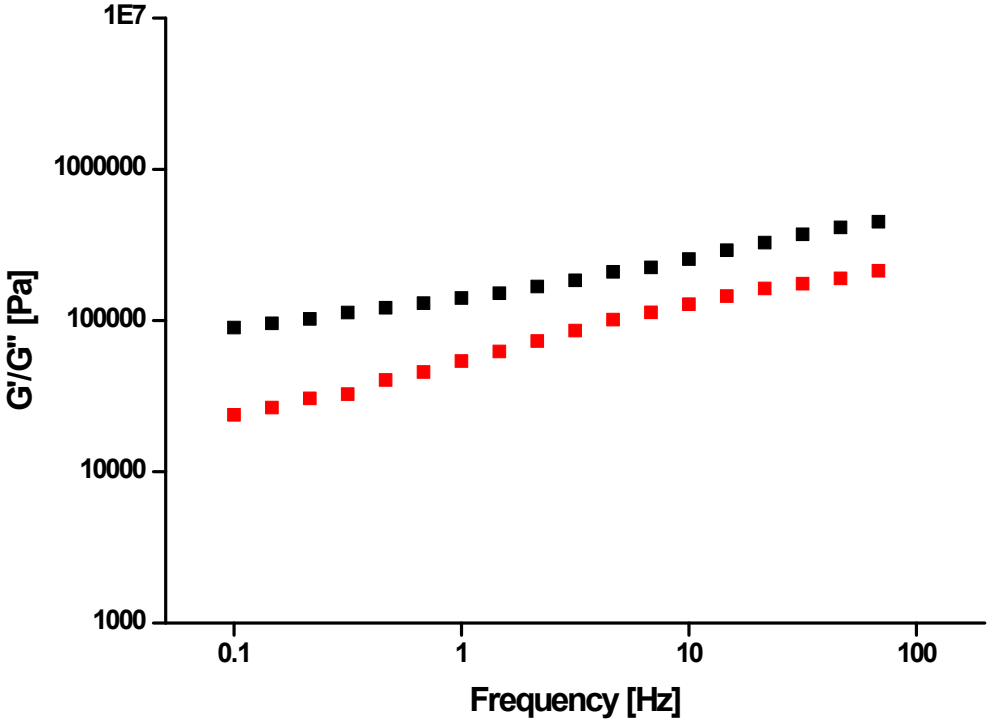


Figure S40: Rheological results of **MP1**: a) 50 °C, b) 100 °C and c) 150 °C (G' in black; G'' in red).

a)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

b)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

c)

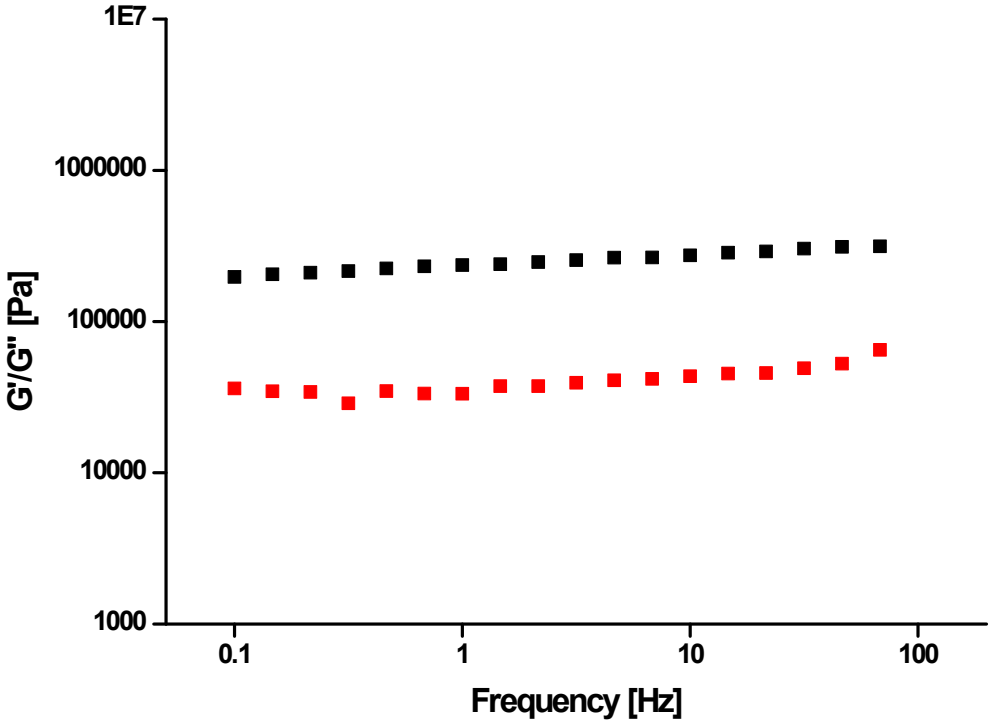
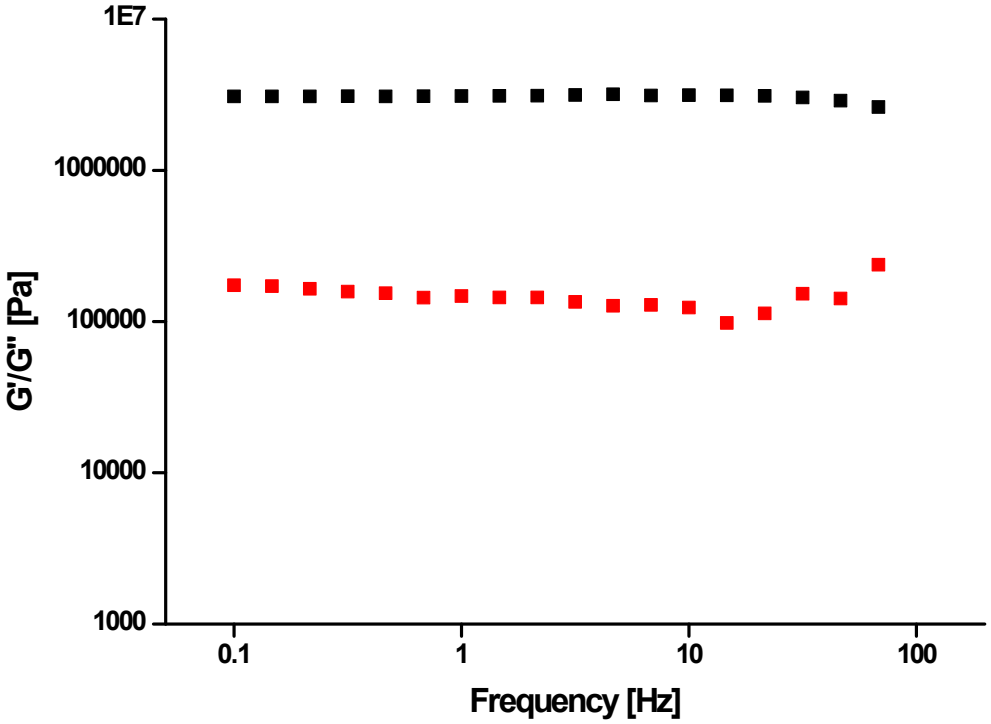
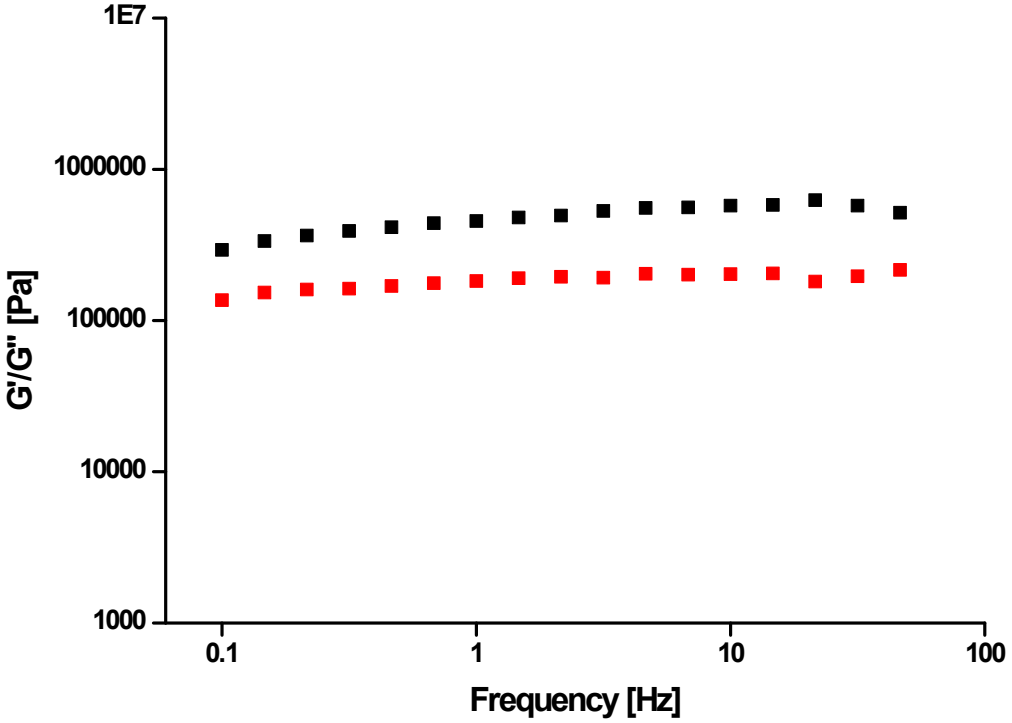


Figure S41: Rheological results of **MP2**: a) 50 °C, b) 100 °C and c) 150 °C (G' in black; G'' in red).

a)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

b)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

c)

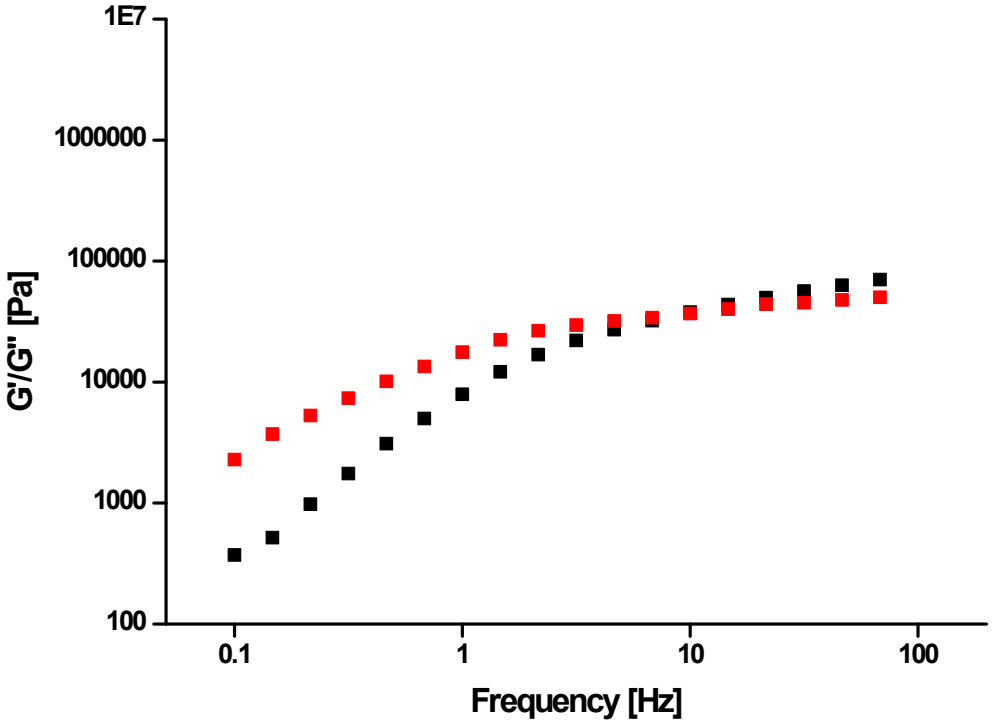
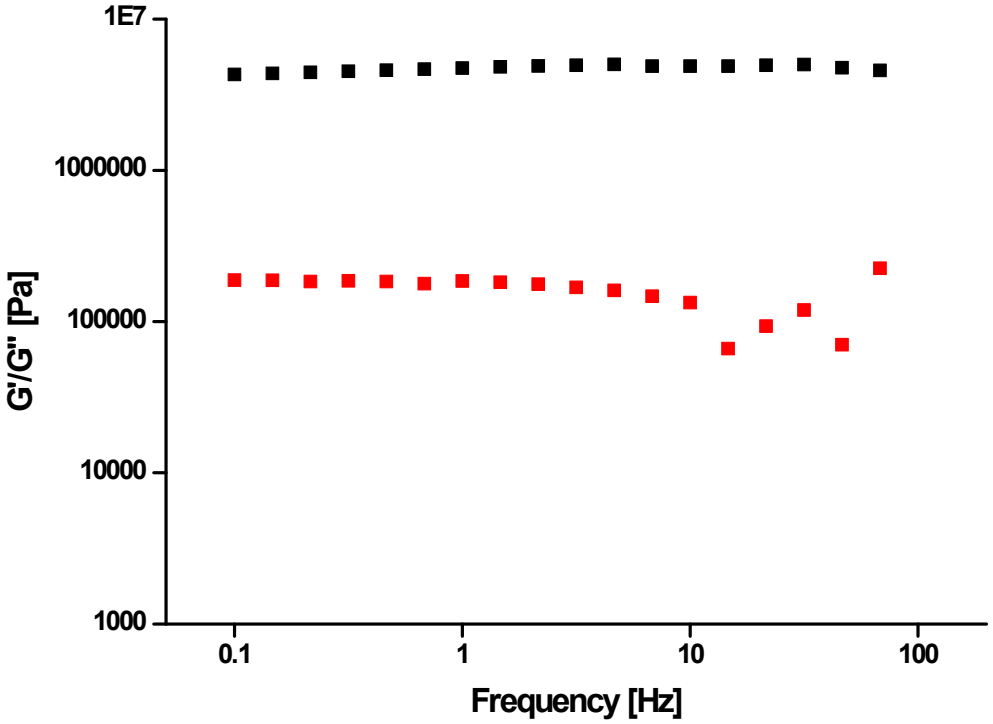
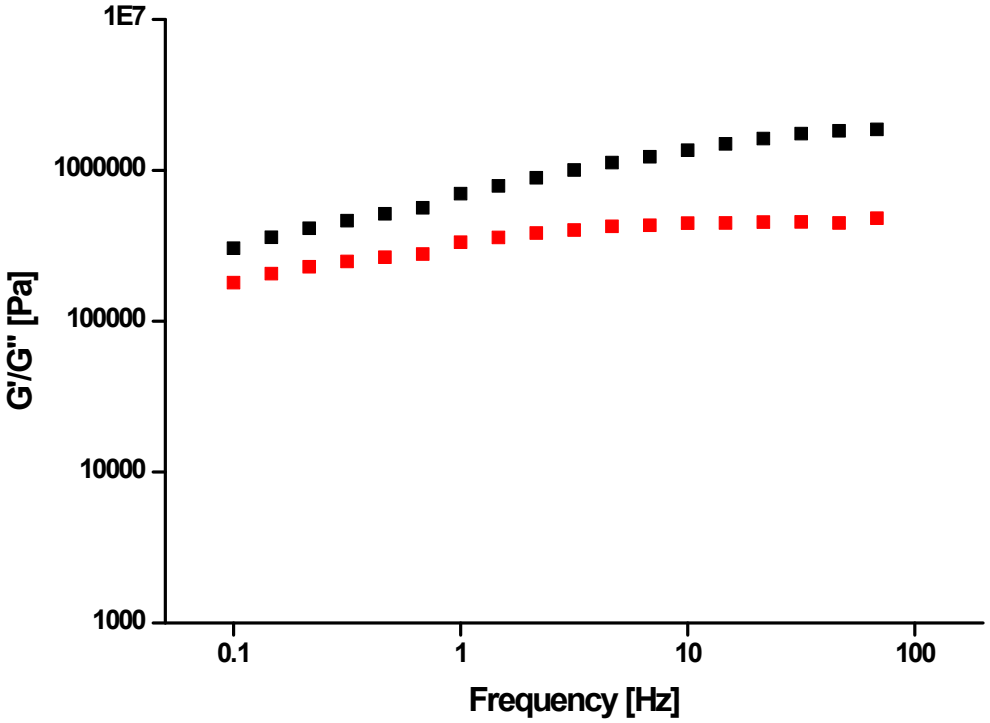


Figure S42: Rheological results of **MP3**: a) 50 °C, b) 100 °C and c) 150 °C (G' in black; G'' in red).

a)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

b)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

c)

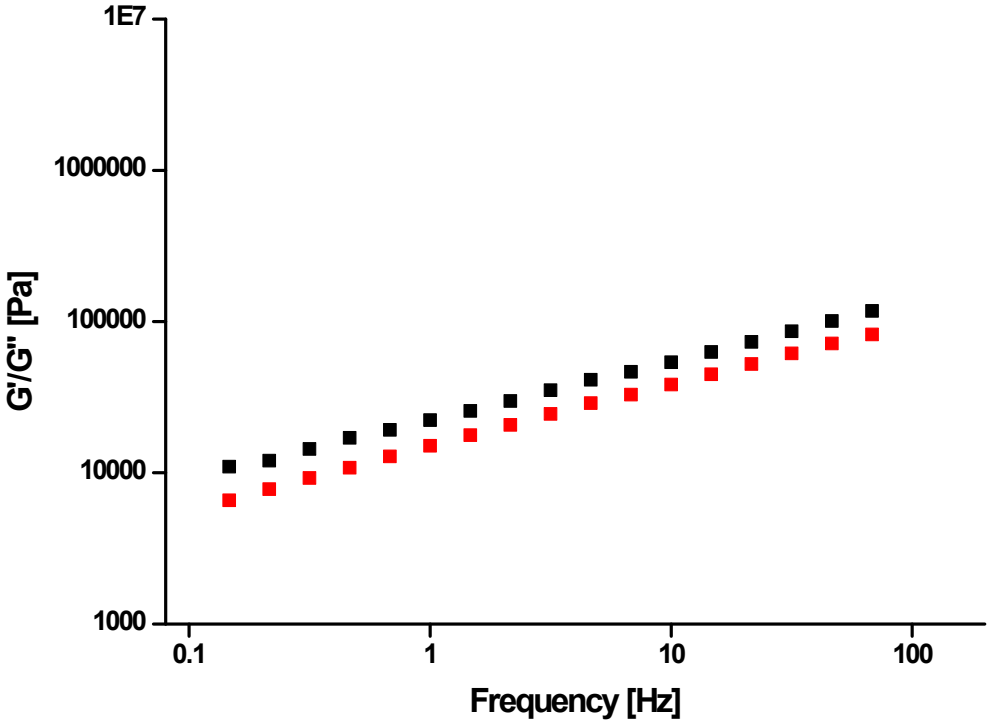
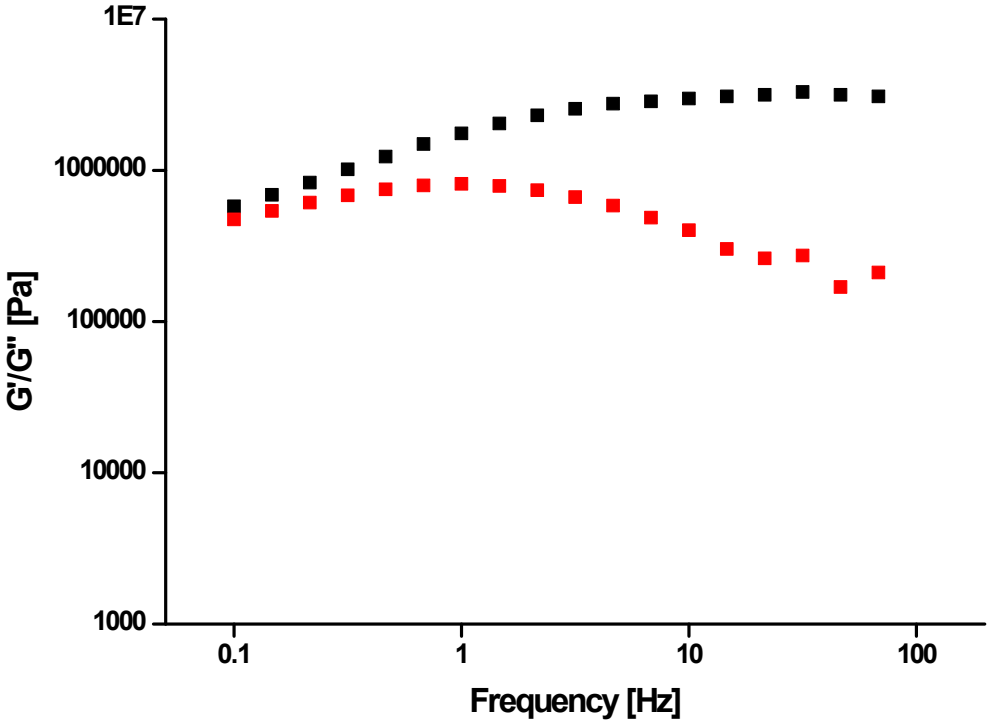
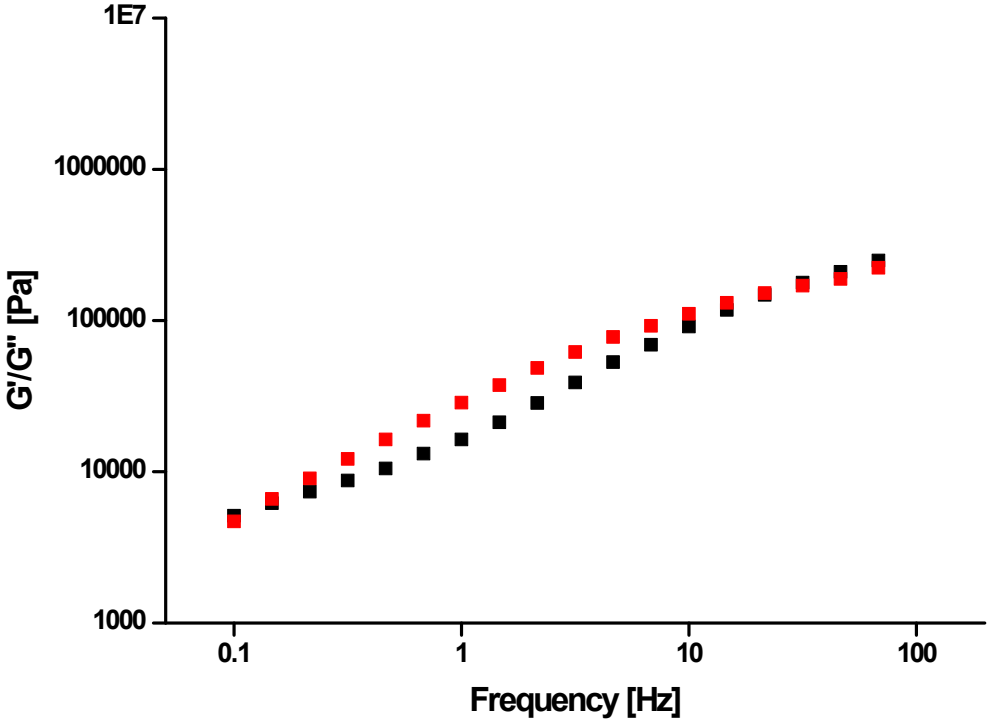


Figure S43: Rheological results of **MP4**: a) 50 °C, b) 100 °C and c) 150 °C (G' in black; G'' in red).

a)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

b)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

c)

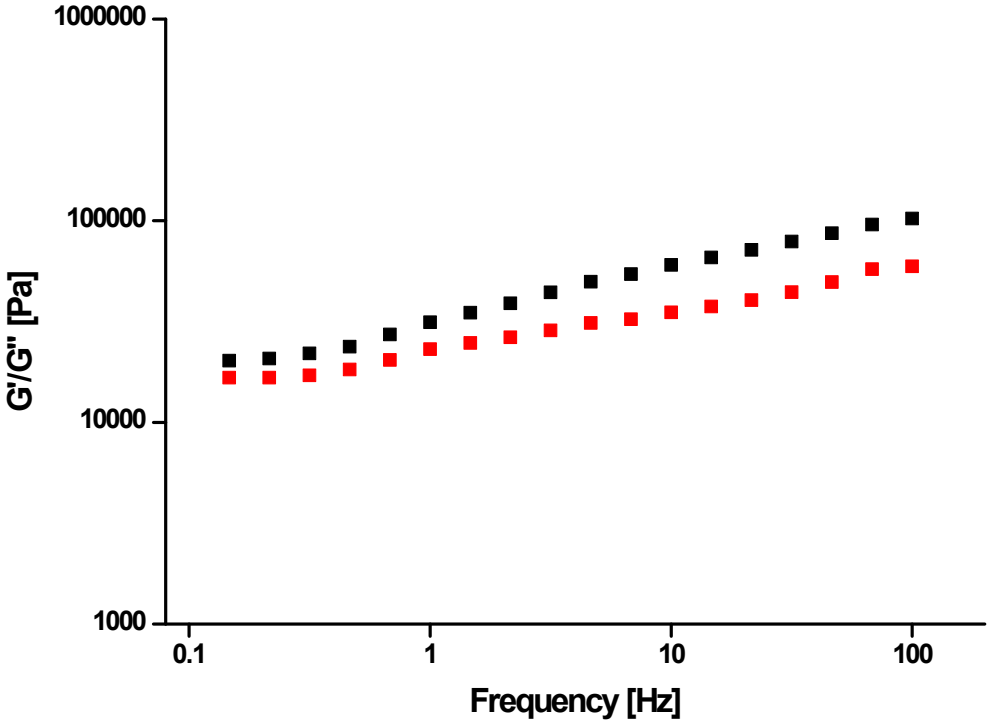
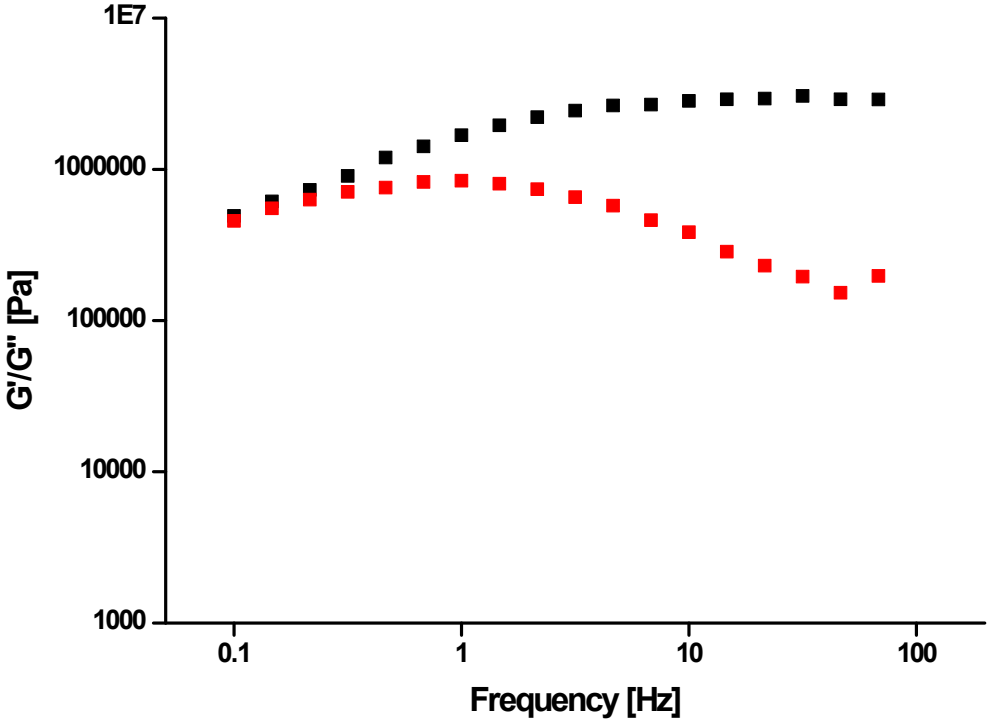
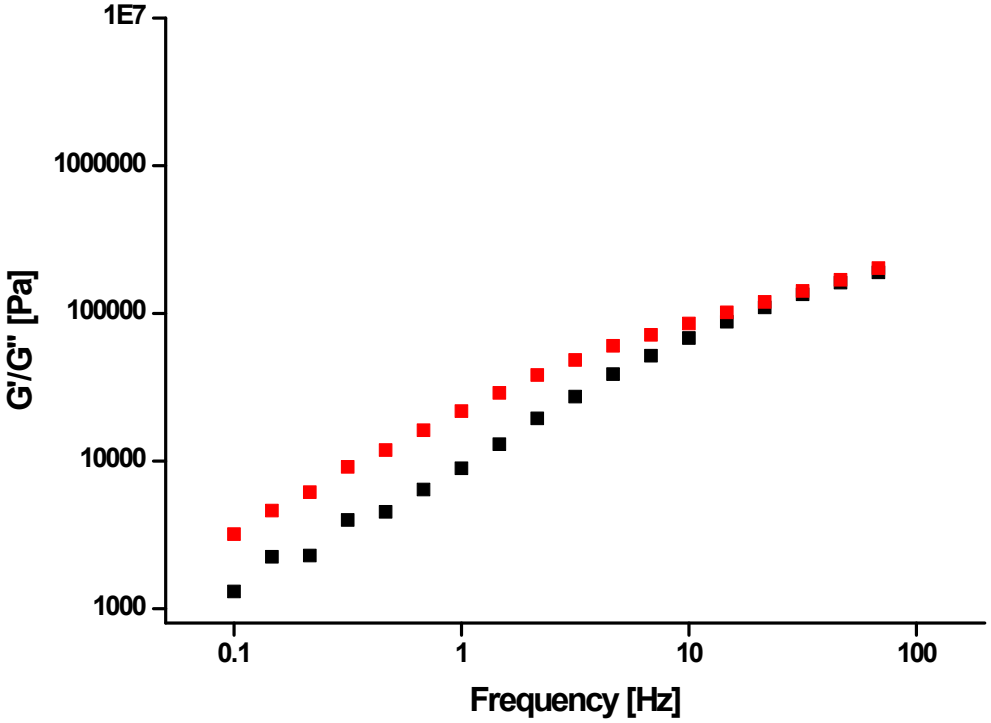


Figure S44: Rheological results of **MP5**: a) 50 °C, b) 100 °C and c) 150 °C (G' in black; G'' in red).

a)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

b)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

c)

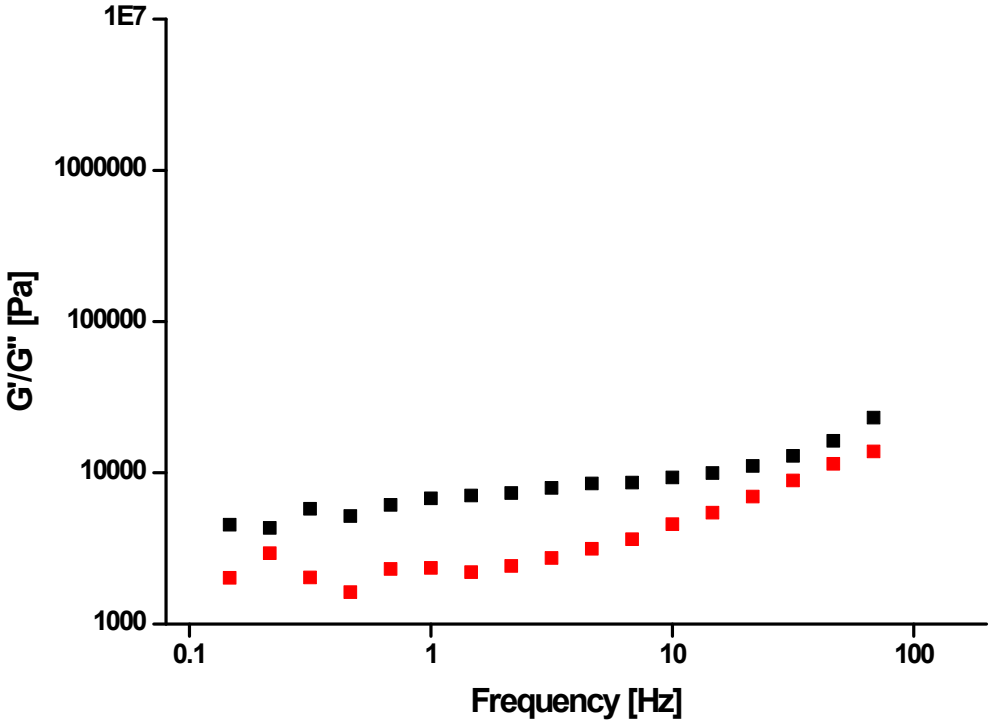
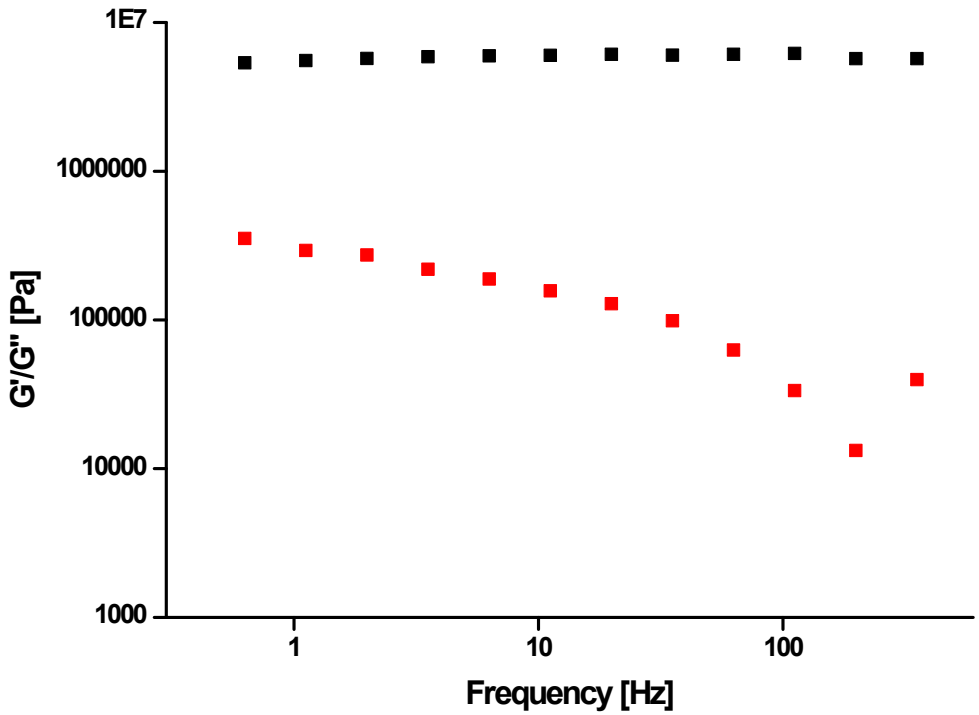


Figure S45: Rheological results of **MP6**: a) 50 °C, b) 100 °C and c) 150 °C (G' in black; G'' in red).

a)



b)

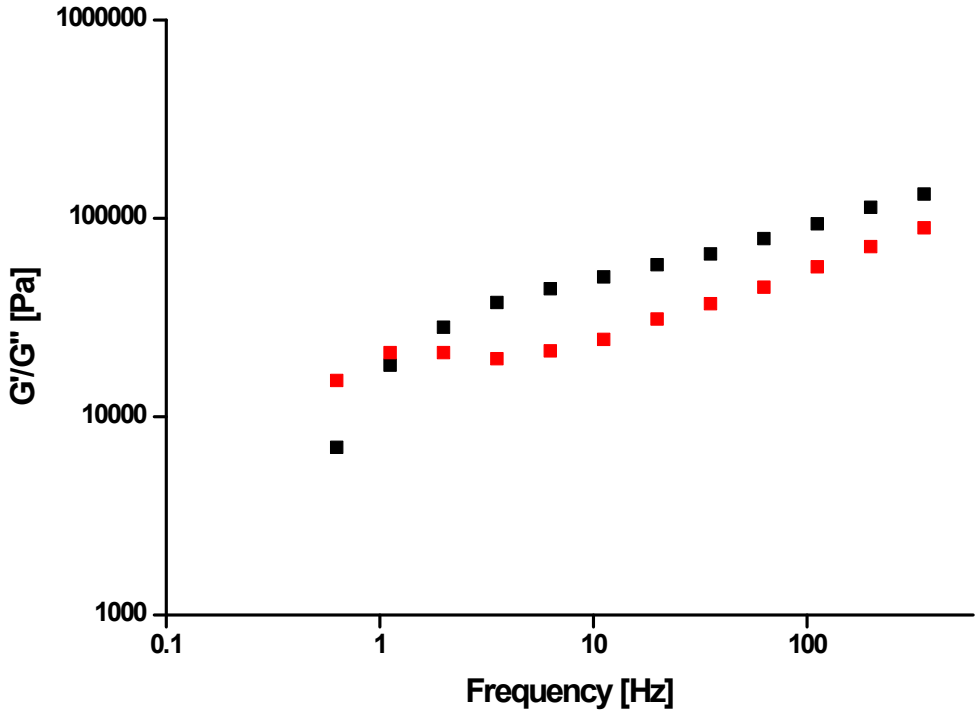
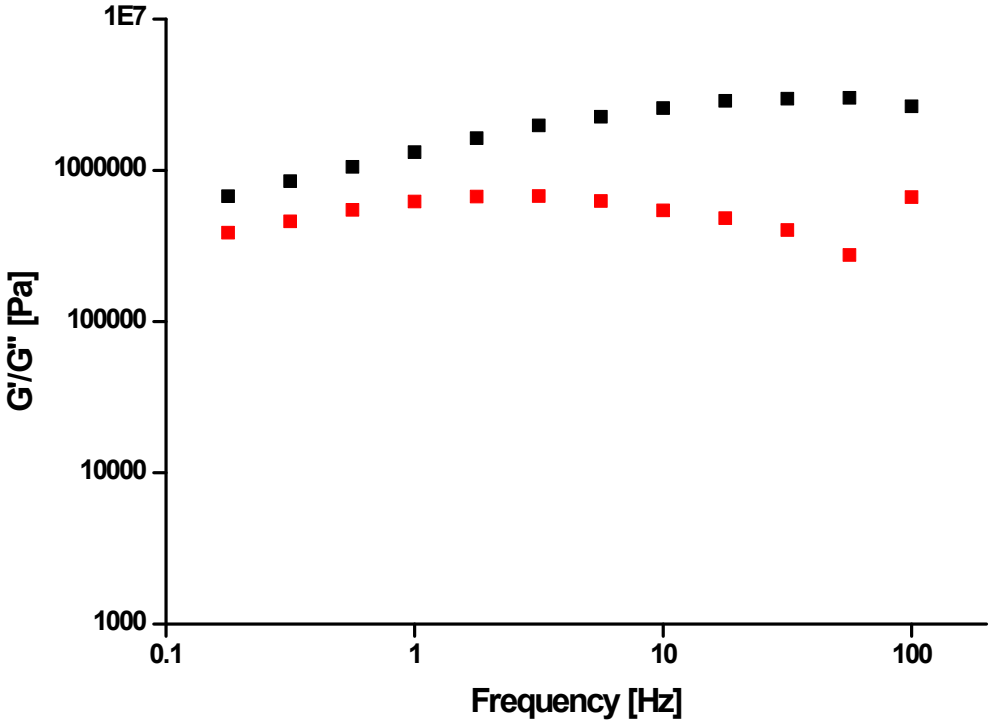
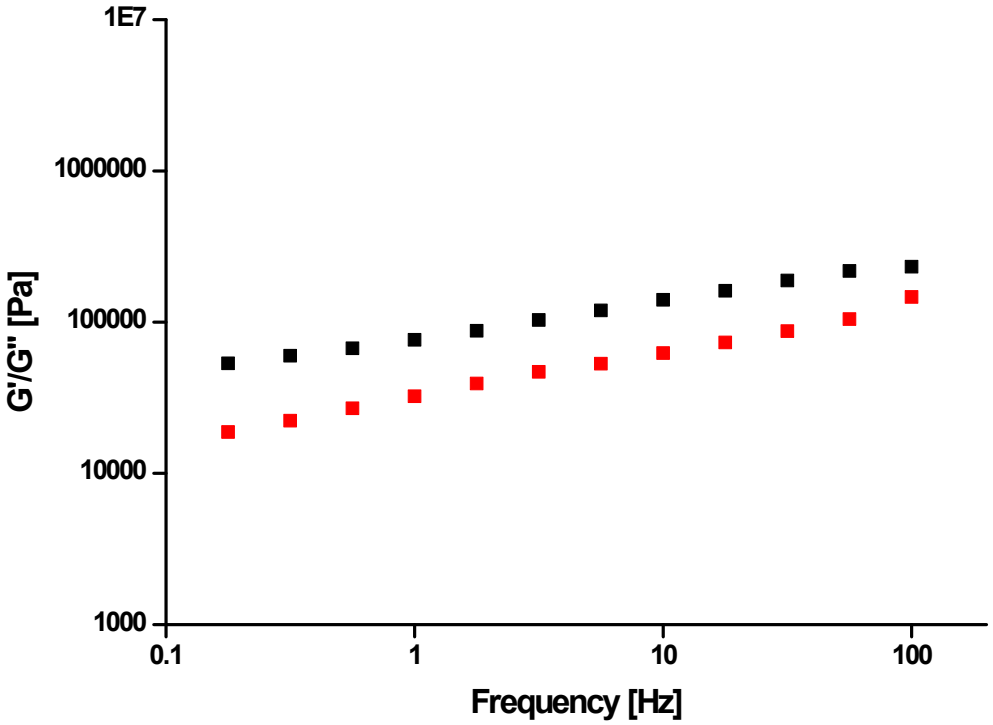


Figure S46: Rheological results of **MP7**: a) 25 °C and b) 120 °C (G' in black; G'' in red).

a)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

b)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

c)

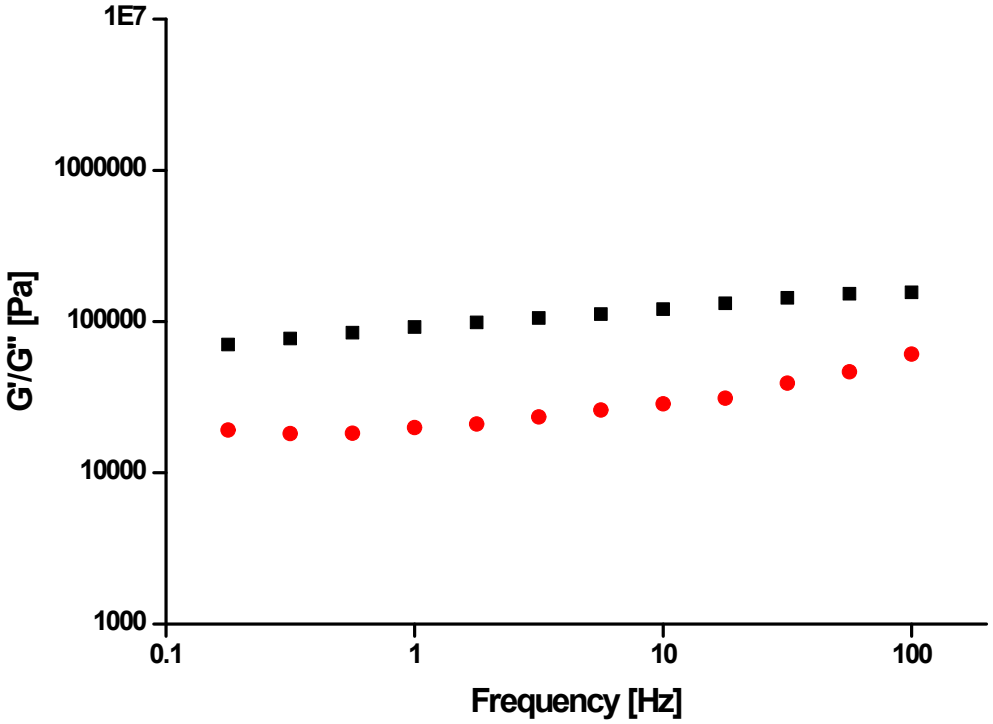
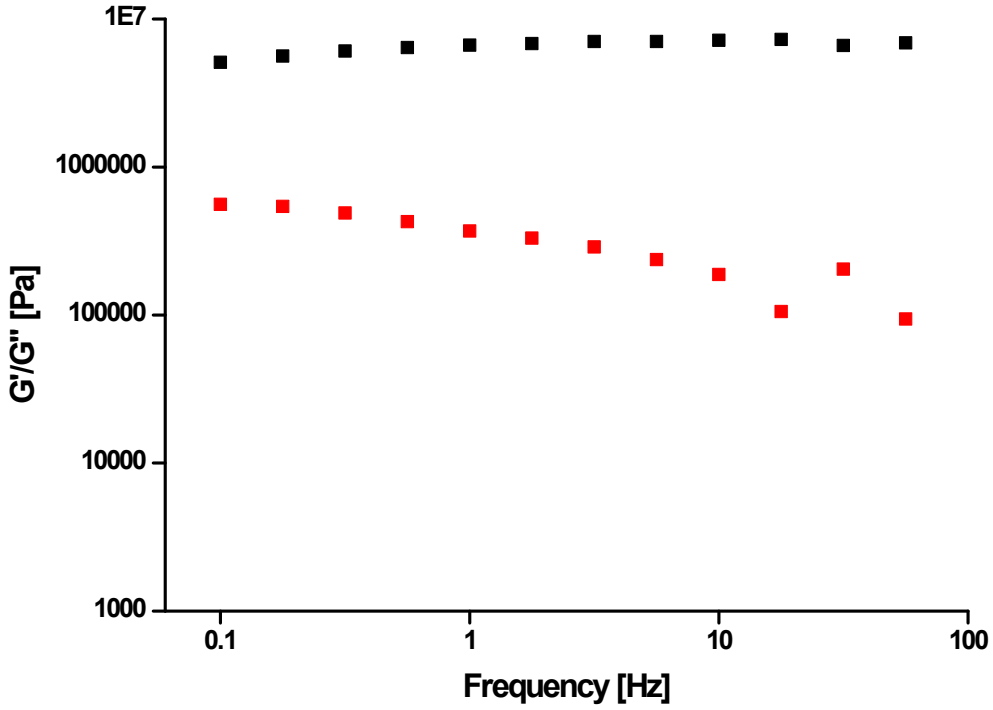


Figure S47: Rheological results of **MP8**: a) 50 °C, b) 100 °C and c) 150 °C (G' in black; G'' in red).

a)



b)

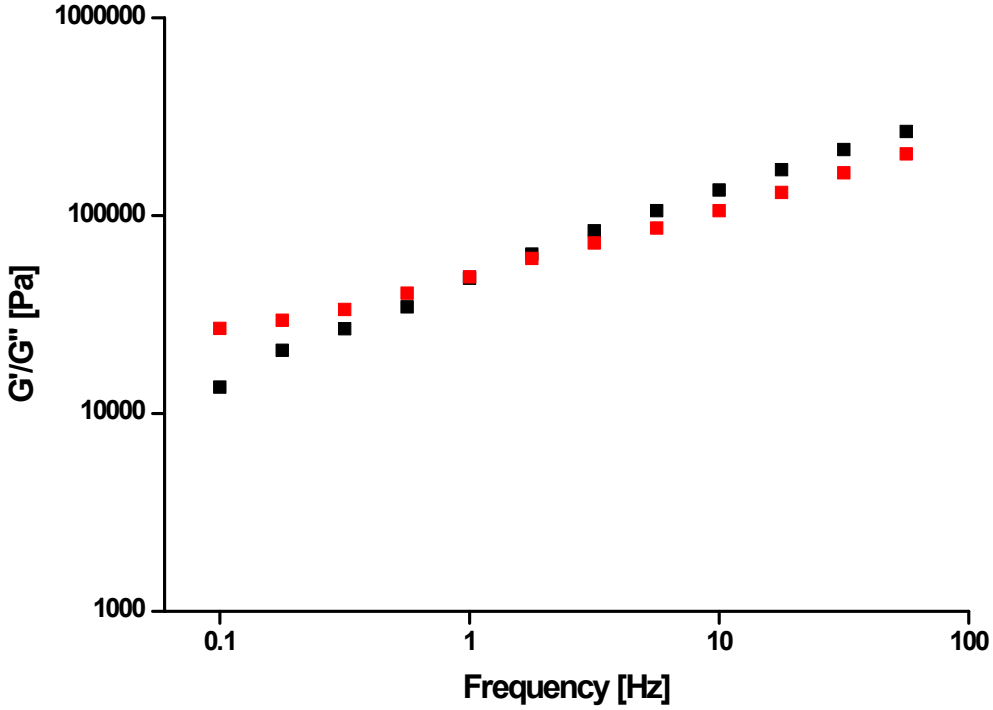
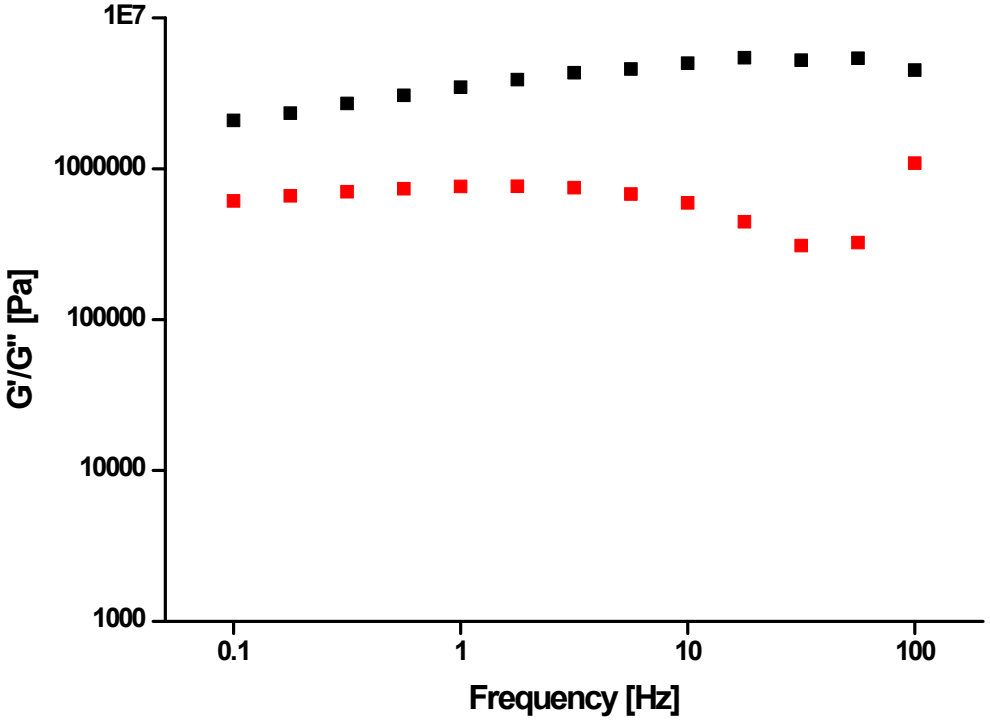
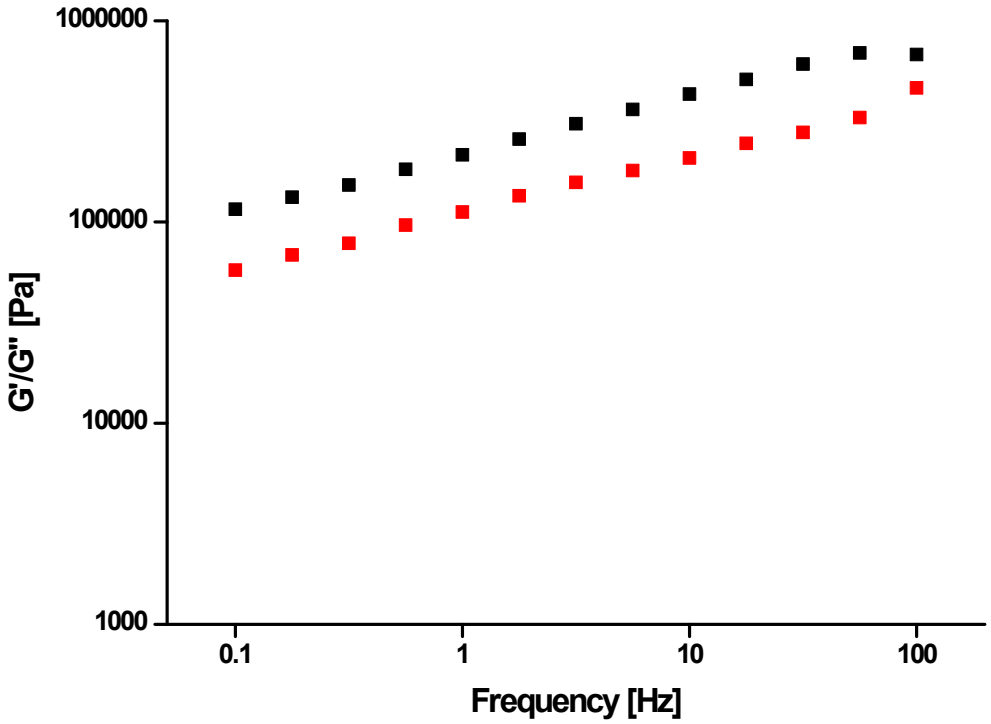


Figure S48: Rheological results of **MP9**: a) 25 °C and b) 100 °C (G' in black; G'' in red).

a)


1E7
1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

b)


1000000
100000
10000
1000
G'/G" [Pa]
0.1
1
10
100
Frequency [Hz]

c)

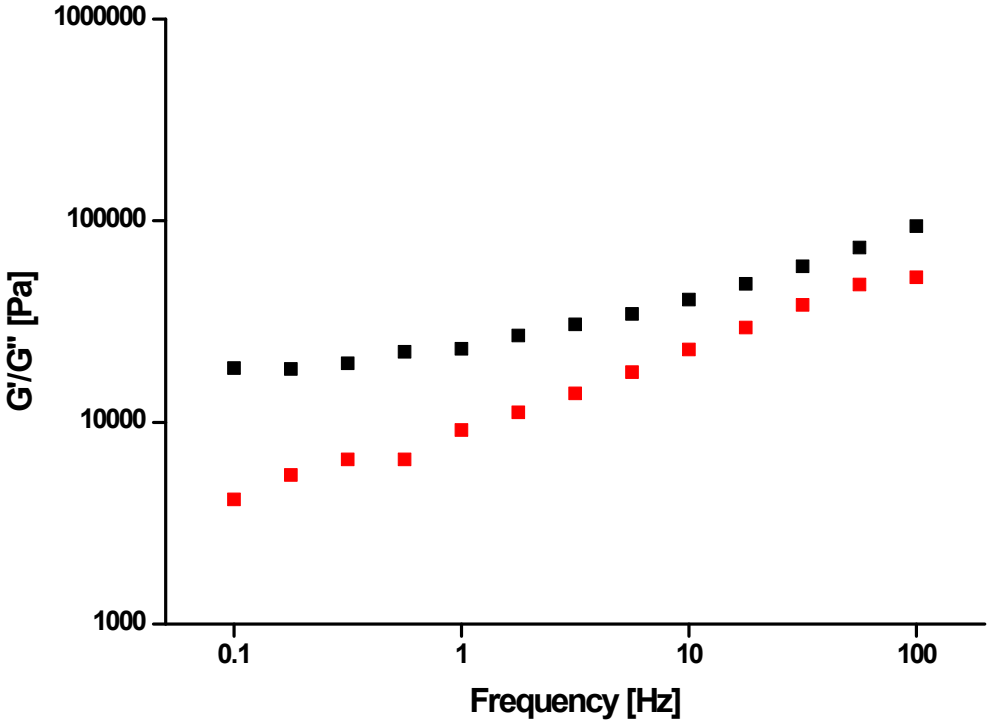
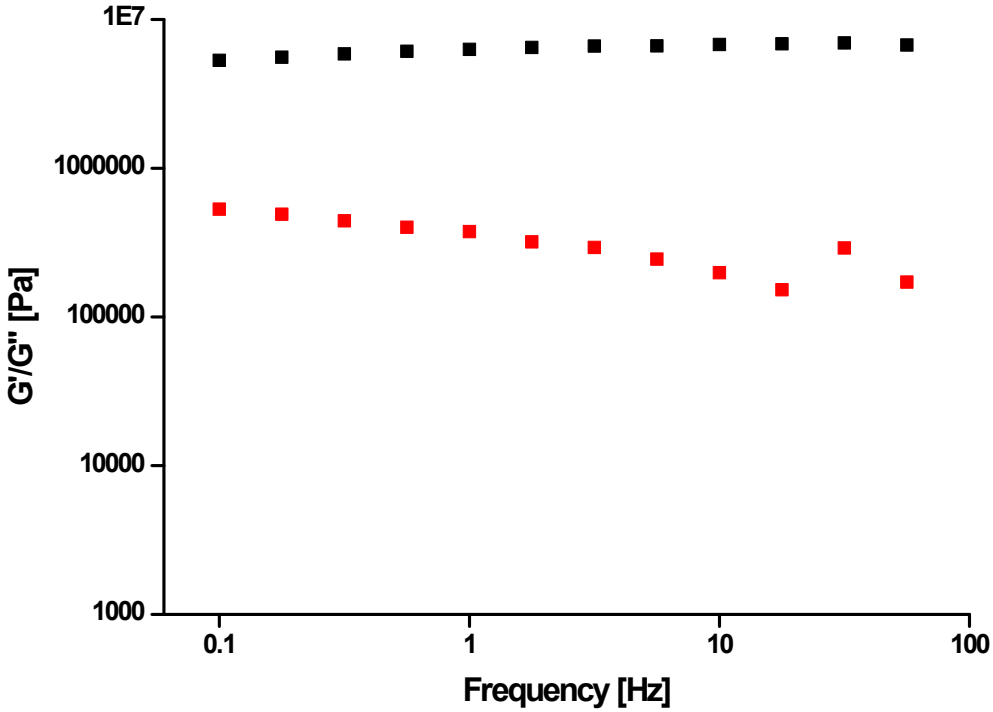


Figure S49: Rheological results of **MP10**: a) 50 °C, b) 100 °C and c) 150 °C (G' in black; G'' in red).

a)



b)

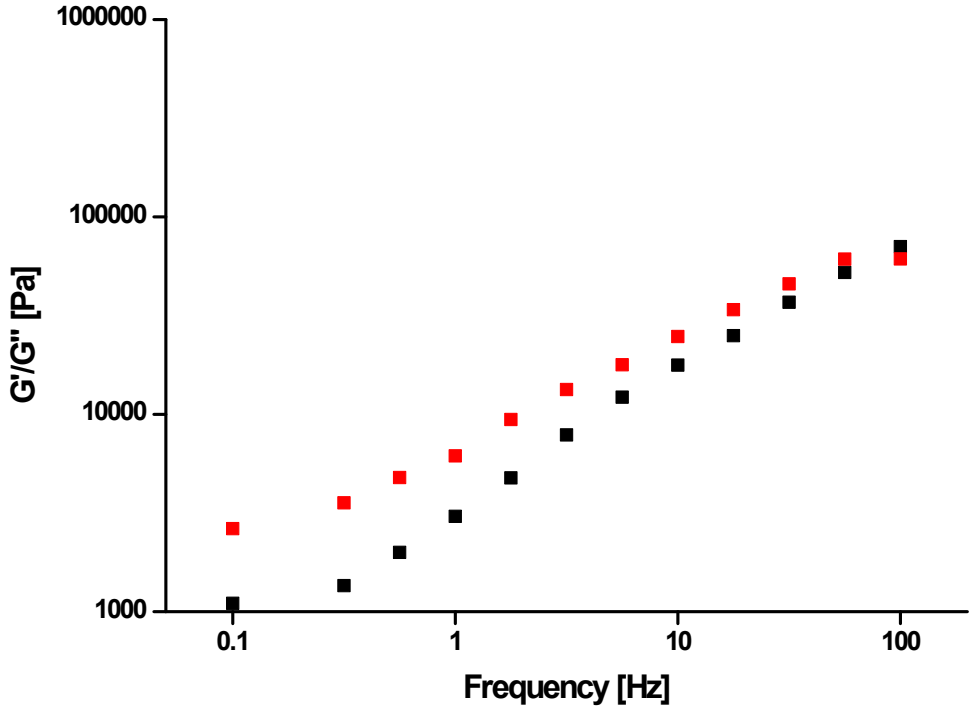
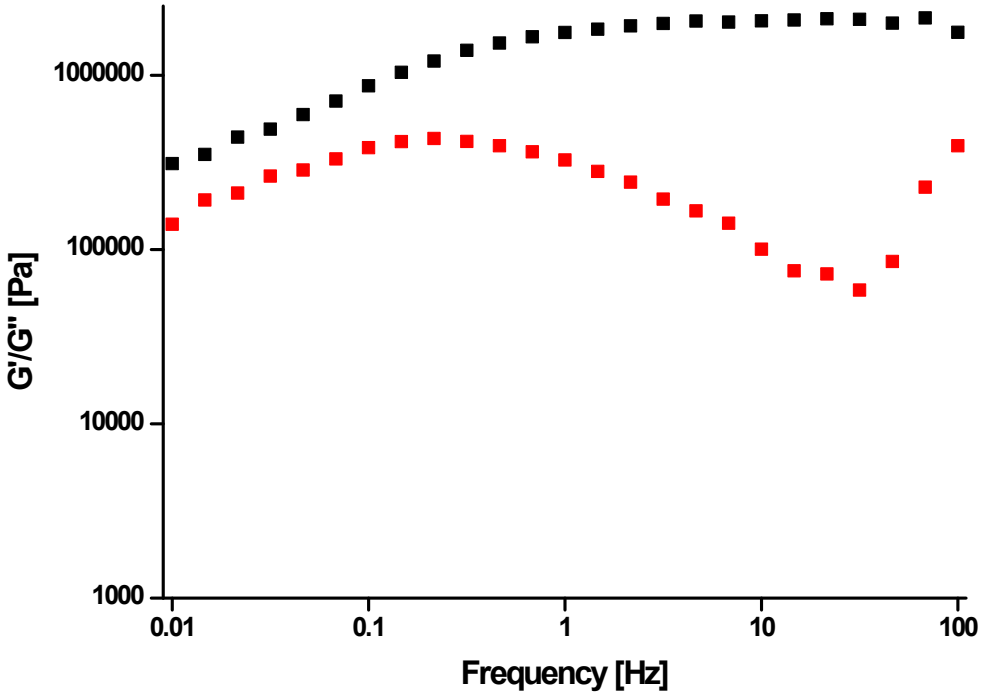


Figure S50: Rheological results of **MP11**: a) 25 °C and b) 100 °C (G' in black; G'' in red).

a)



b)

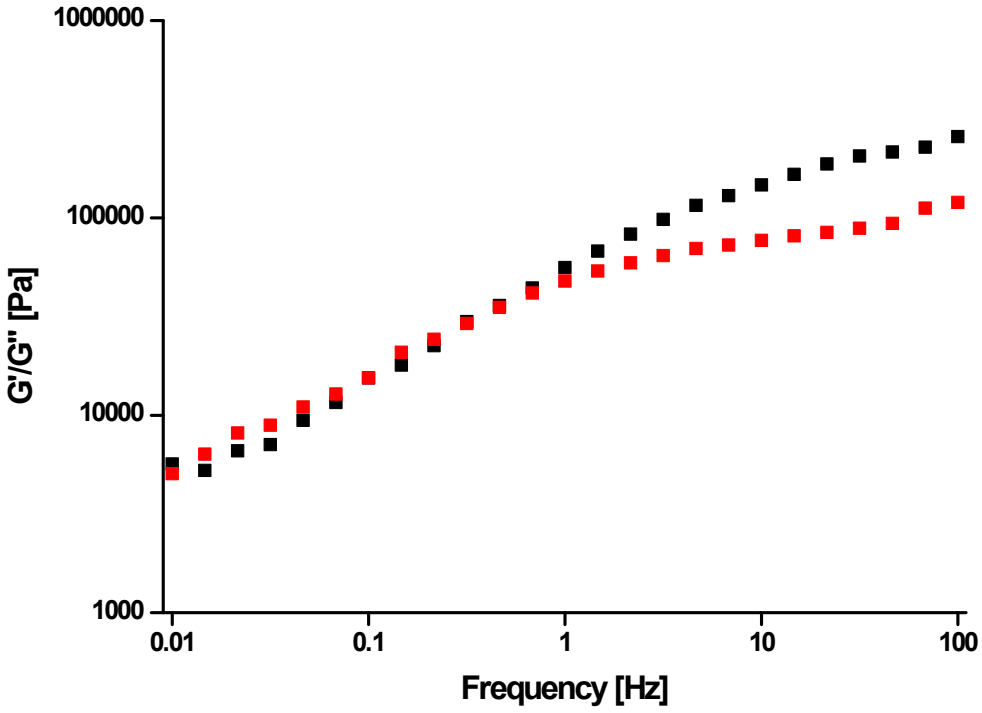


Figure S51: Rheological results of **MP12**: a) 50 °C and b) 100 °C (G' in black; G'' in red).

Summary of selected properties of the metallopolymers:

Table S1: Overview of the elemental analysis results and the thermal properties of metallopolymers **MP1** to **MP12**.

Metallo-polymer	Carbon [%]	Hydrogen [%]	Nitrogen [%]	Chloride [%]	DSC: T_g [°C]	TGA: T_d [°C]
MP1	62.85	8.50	3.13	0.00	no	269
MP2	65.83	8.66	2.13	0.00	no	287
MP3	64.19	8.76	2.07	3.00	39	271
MP4	61.36	8.51	3.11	0.00	37	195
MP5	64.92	8.90	1.98	0.00	23	163
MP6	64.22	8.79	2.04	3.21	53	188
MP7	64.23	8.71	3.07	0.00	64	191
MP8	62.76	8.50	2.04	0.00	24	217
MP9	64.28	8.68	2.06	3.00	51	256
MP10	65.09	8.93	3.01	0.00	35	220
MP11	66.58	9.00	2.12	0.00	33	285
MP12	65.58	8.78	2.38	2.44	42	319

Synthesis of the metallopolymers:

Table S2: Amounts of the polymers and the metal salts for the synthesis of metallopolymer networks.

Metallopolymer	Polymer	Metal salt	m(Polymer)	m(Metal salt)
MP1	**P1**	zinc(II) nitrate	17 mg	1.41 mg
MP2	**P1**	zinc(II) acetate	38 mg	2.35 mg
MP3	**P1**	zinc(II) chloride	56 mg	2.15 mg
MP4	**P1**	nickel(II) nitrate	74 mg	6.06 mg
MP5	**P1**	nickel(II) acetate	44 mg	3.09 mg
MP6	**P1**	nickel(II) chloride	48 mg	3.20 mg
MP7	**P1**	cobalt(II) nitrate	13 mg	1.05 mg
MP8	**P1**	cobalt(II) acetate	50 mg	3.50 mg
MP9	**P1**	cobalt(II) chloride	60 mg	4.02 mg
MP10	**P1**	manganese(II) nitrate	42 mg	2.95 mg
MP11	**P1**	manganese(II) acetate	41 mg	2.80 mg
MP12	**P1**	manganese(II) chloride	16 mg	0.88 mg