Electronic Supplementary Material (ESI) for Polymer Chemistry

Self-healing metallopolymers based on cadmium bis(terpyridine) complex containing polymer networks

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Supplementary Information:

Tables:

Table S1: Ratio of cadmium salt and terpyridine units in the crosslinked polymer networks **CP1**–**CP9** (determined by elemental analysis).

Crosslinked polymer	ratio of terpyridine : cadmium salt
CP1	1.74:1
CP2	1.09:1
CP3	2.05:1
CP4	1.07:1
CP5	1.71:1
CP6	2.21:1
CP7	1.61:1
CP8	1.96:1
CP9	1.84:1

Figures:

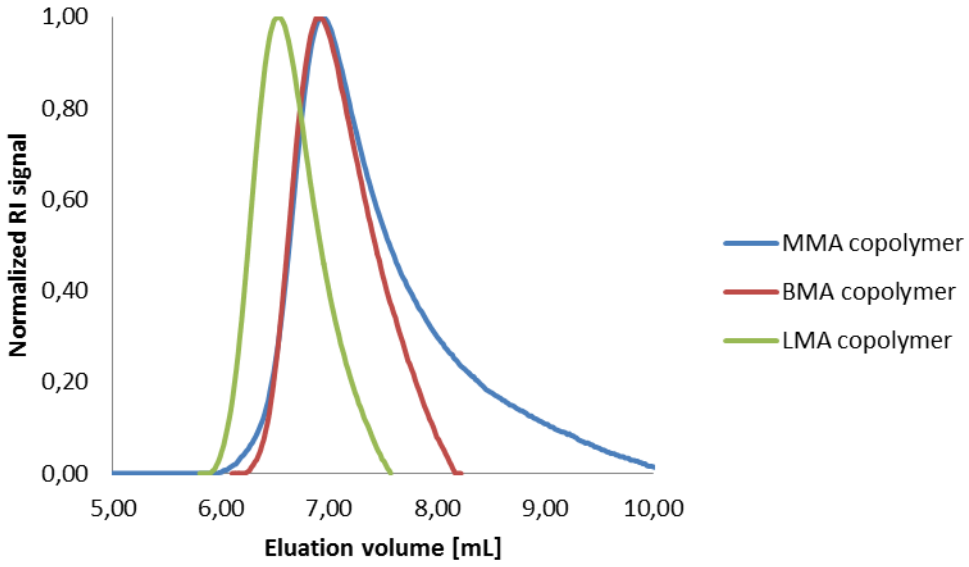


Figure S1: SEC curves of the non-crosslinked copolymers **P1**–**P3**.

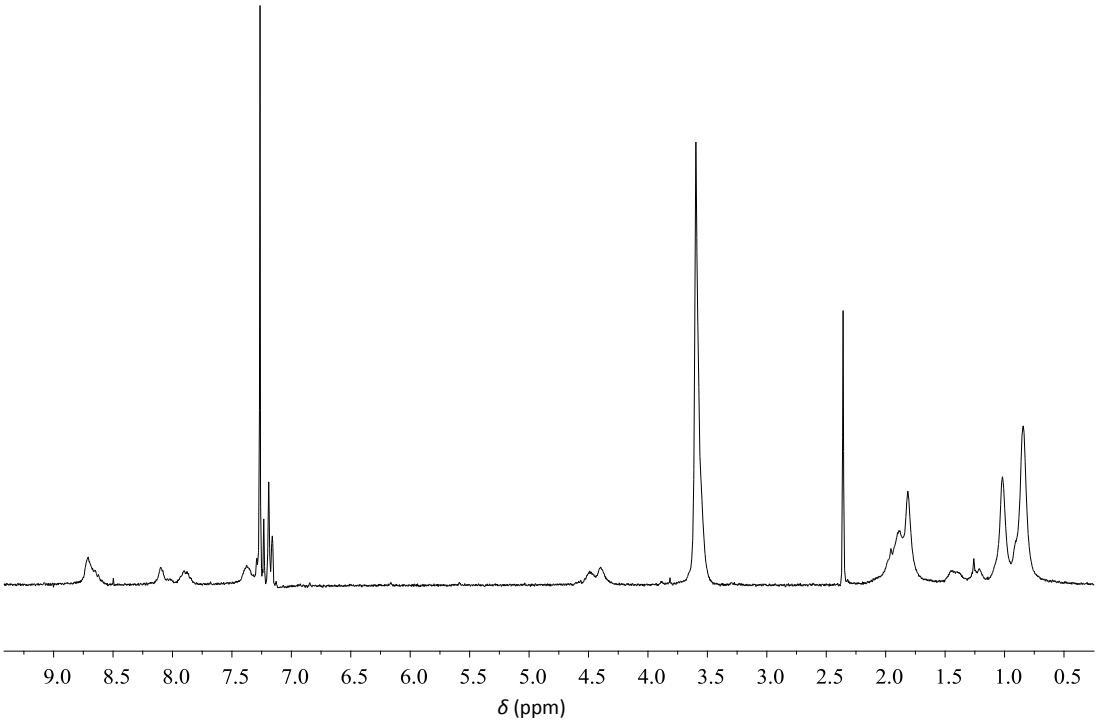


Figure S2: ^{1}H-NMR spectrum of the non-crosslinked copolymer **P1** (in $CDCl_3$).

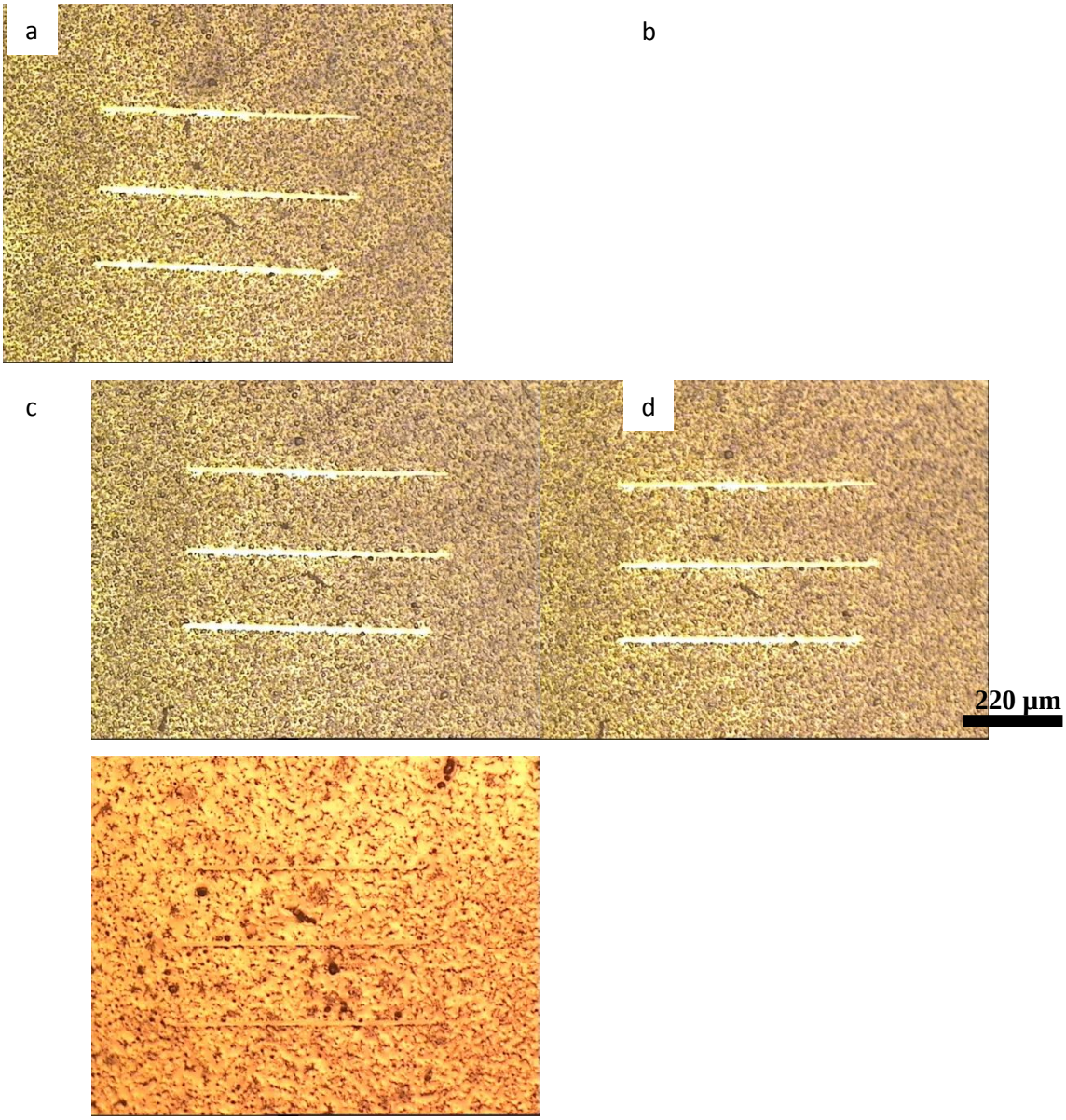


Figure S3: Self-healing studies of the crosslinked polymer **CP2**: a) Scratches, b) no healing after 21 h at 100 °C, c) no healing after 44 h at 100 °C and d) partial healing after 22 h at 150 °C.

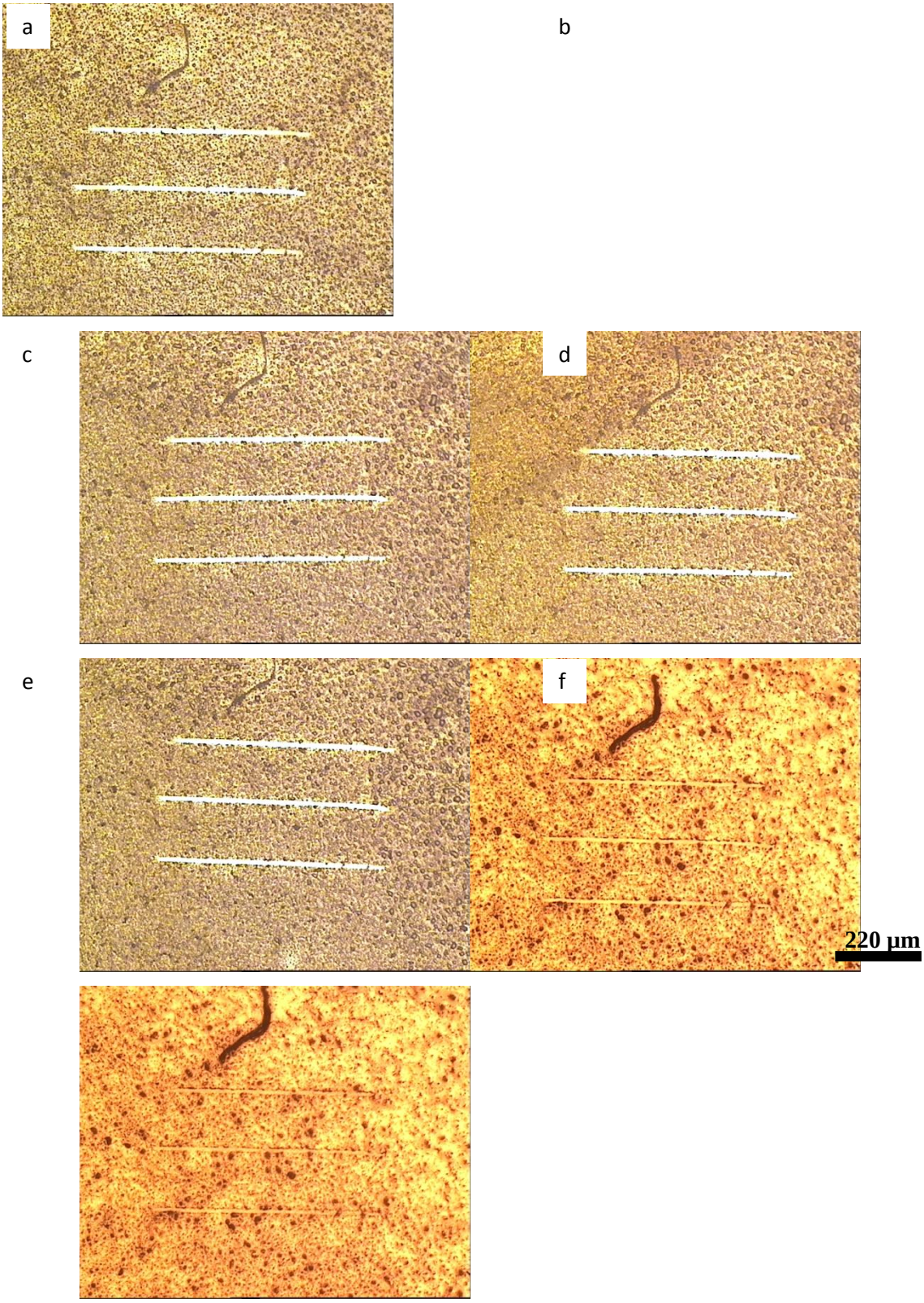


Figure S4: Self-healing studies of the crosslinked polymer **CP5**: a) Scratches, b) no healing after 21 h at 100 °C, c) no healing after 44 h at 100 °C, d) no healing after 118 h at 100 °C, e) partial healing after 22 h at 150 °C and f) partial healing after 91 h at 150 °C.

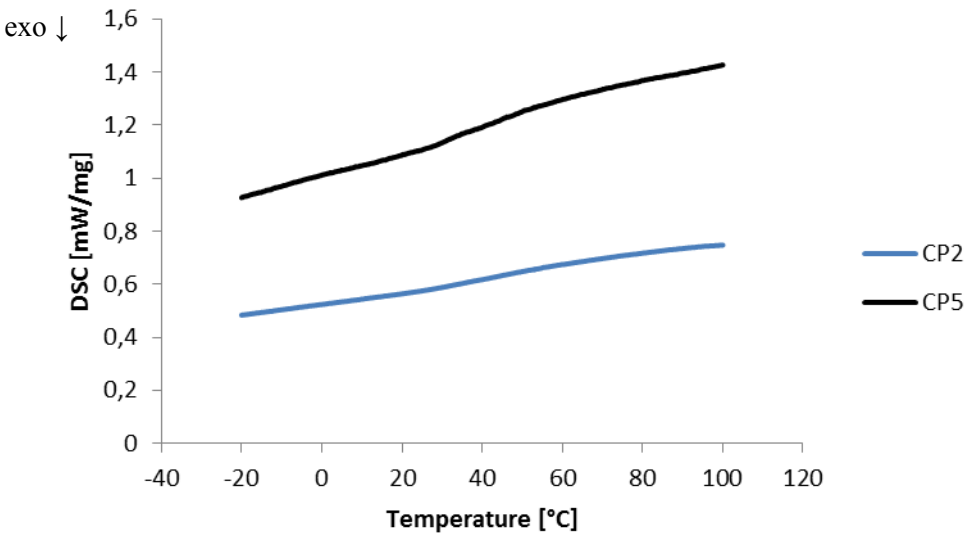


Figure S5: DSC curves of the crosslinked copolymers **CP2** and **CP5**.

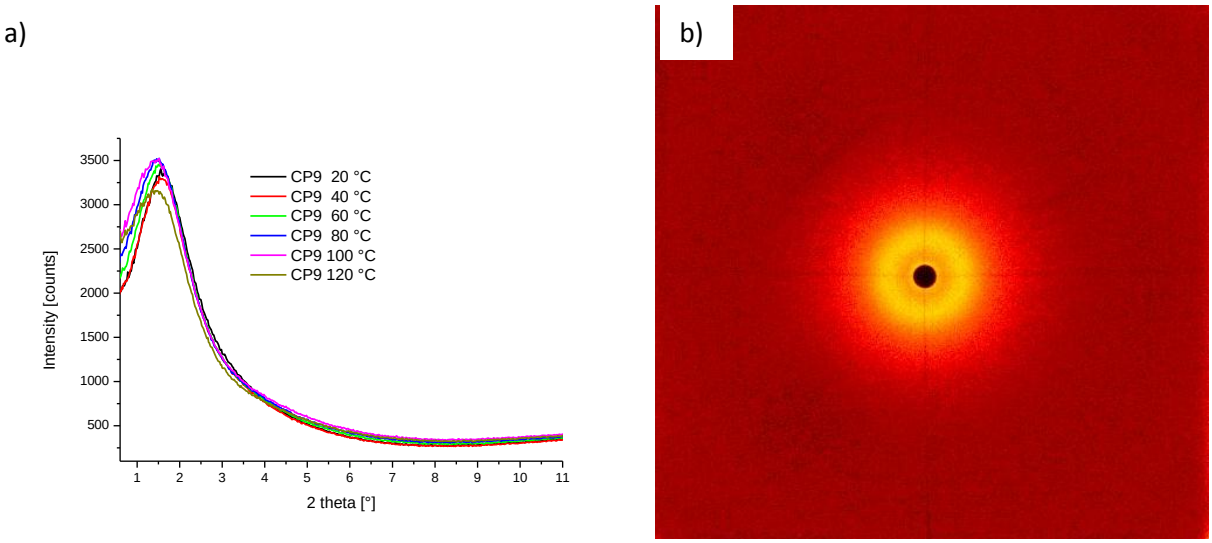


Figure S6: Typical SWAXS curves of the crosslinked copolymers (**CP9**): a) SWAXS data at different temperatures and b) SWAXS signal at the 2D-detector at 20 °C.

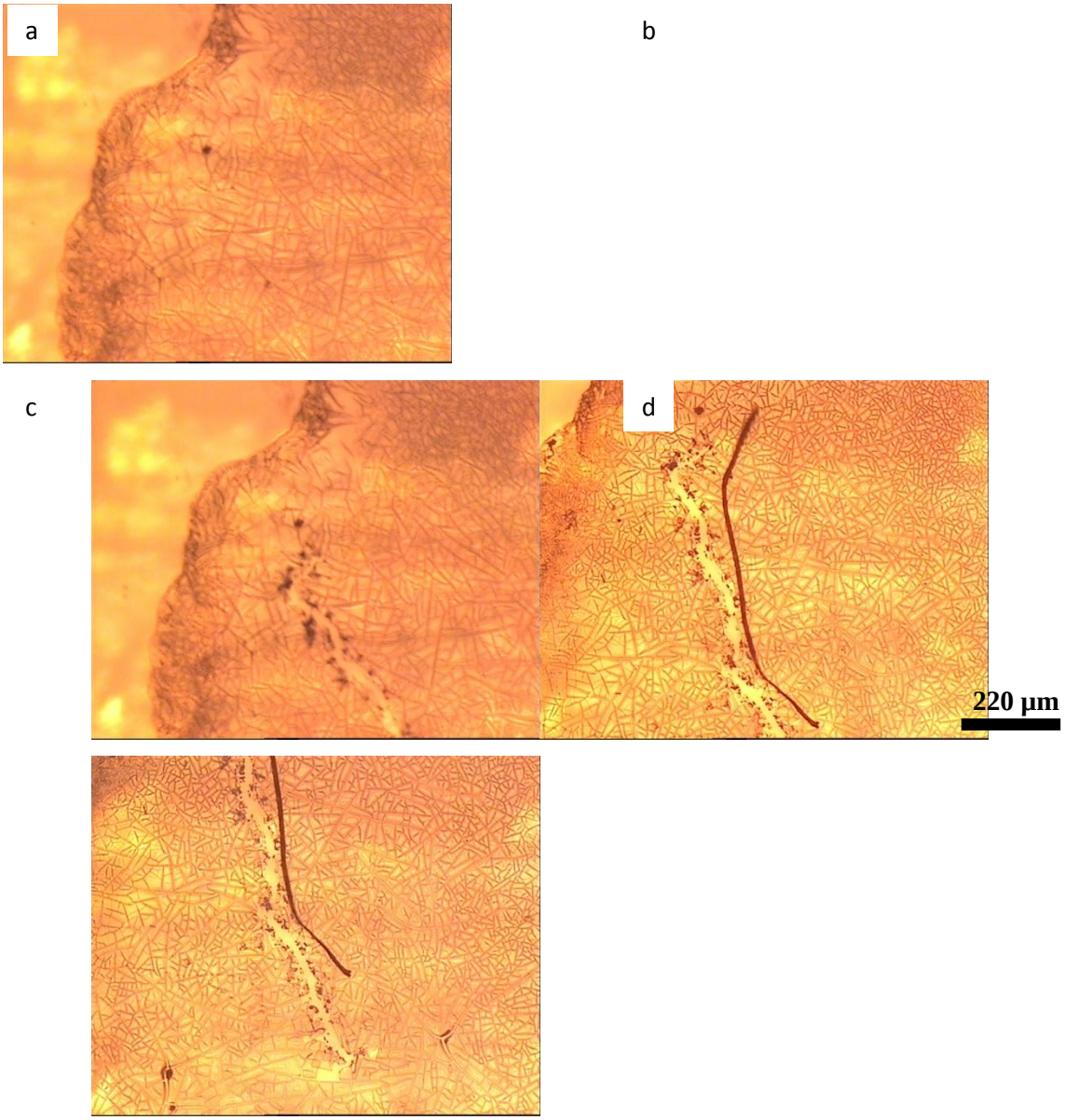
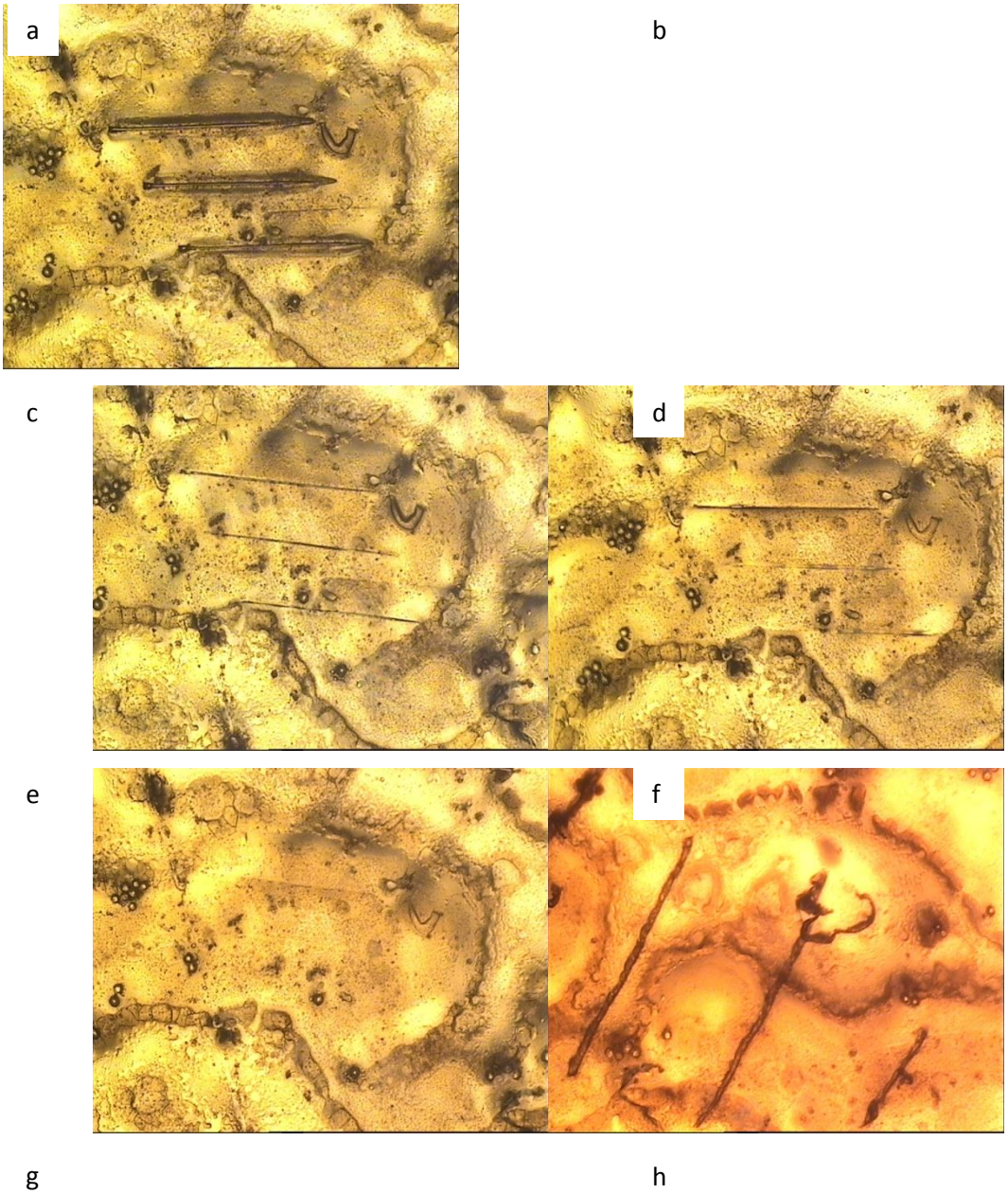


Figure S7: Self-healing studies of the crosslinked polymer **CP10**: a) Film without a scratch, b) scratches, c) no healing after 37 h at 150 °C and d) no healing after 56 h at 150 °C.



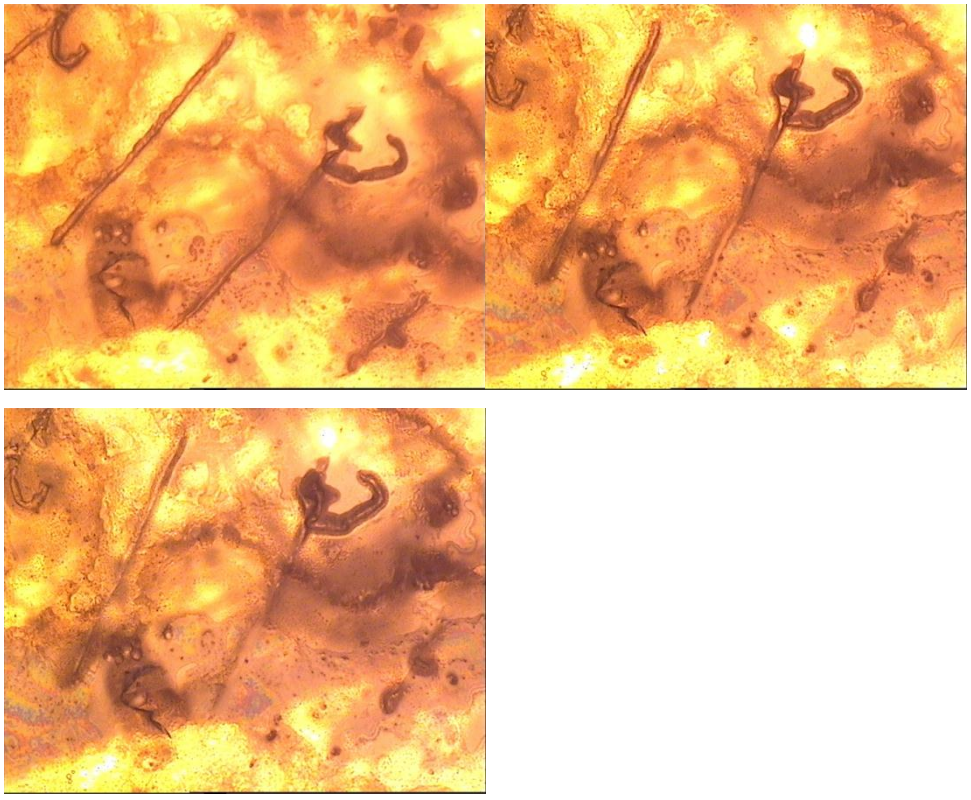


Figure S8: Self-healing studies of the crosslinked polymer **CP11**: a) Scratches, b) partial healing after 4 min at 100 °C, c) partial healing after 90 min at 100 °C, d) healing after 240 min at 100 °C, e) scratches, f) partial after 10 min at 80 °C, g) partial healing after 60 min at 80 °C and h) partial healing after 130 min at 80 °C.

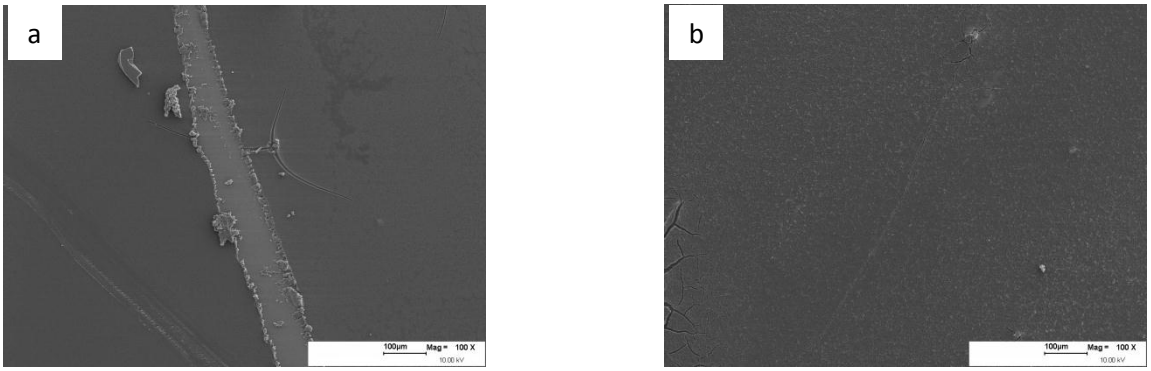
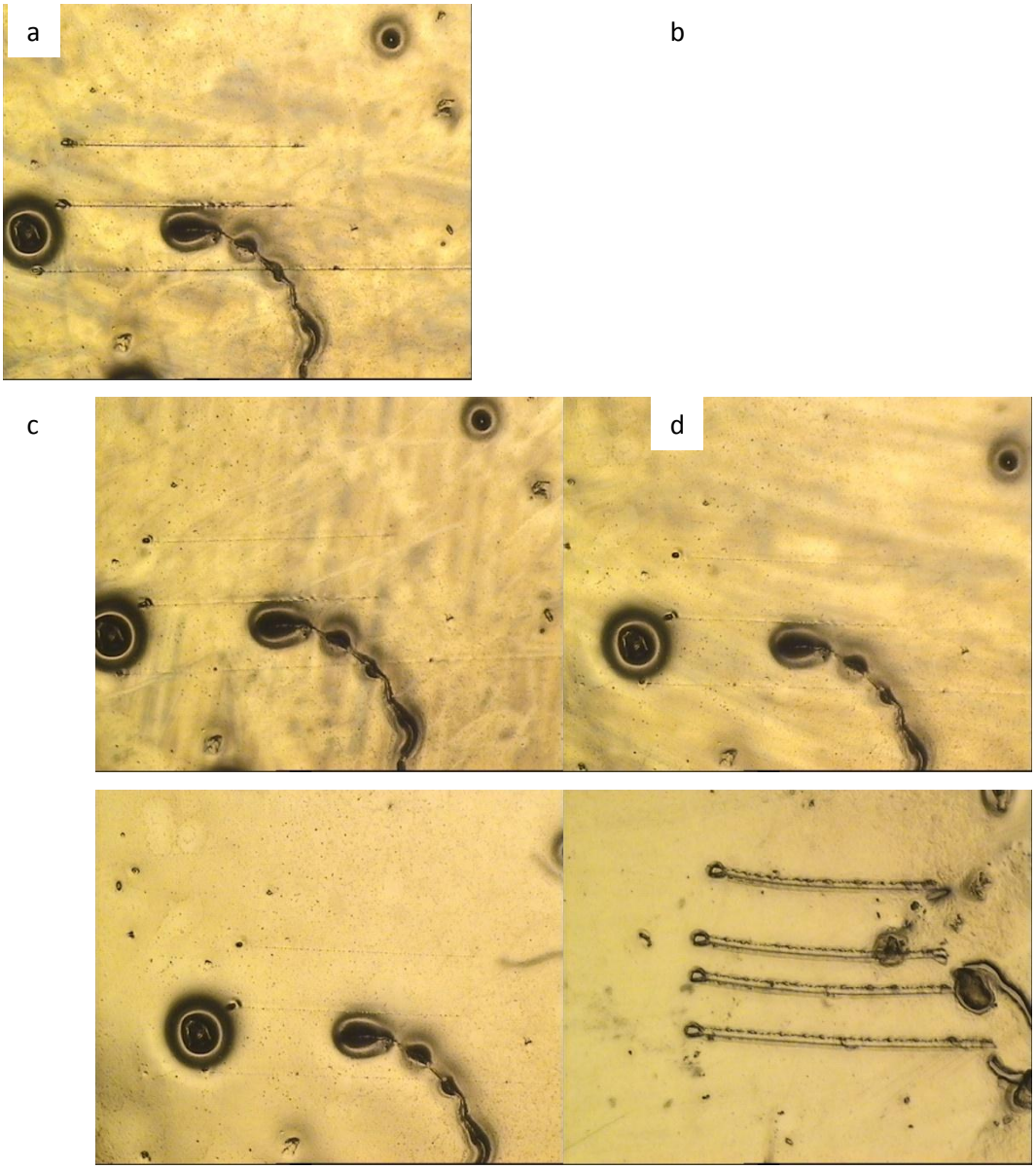


Figure S9: Self-healing studies of the crosslinked polymer **CP11** followed by SEM: a) Scratches and b) healing after 35 min at 100 °C.



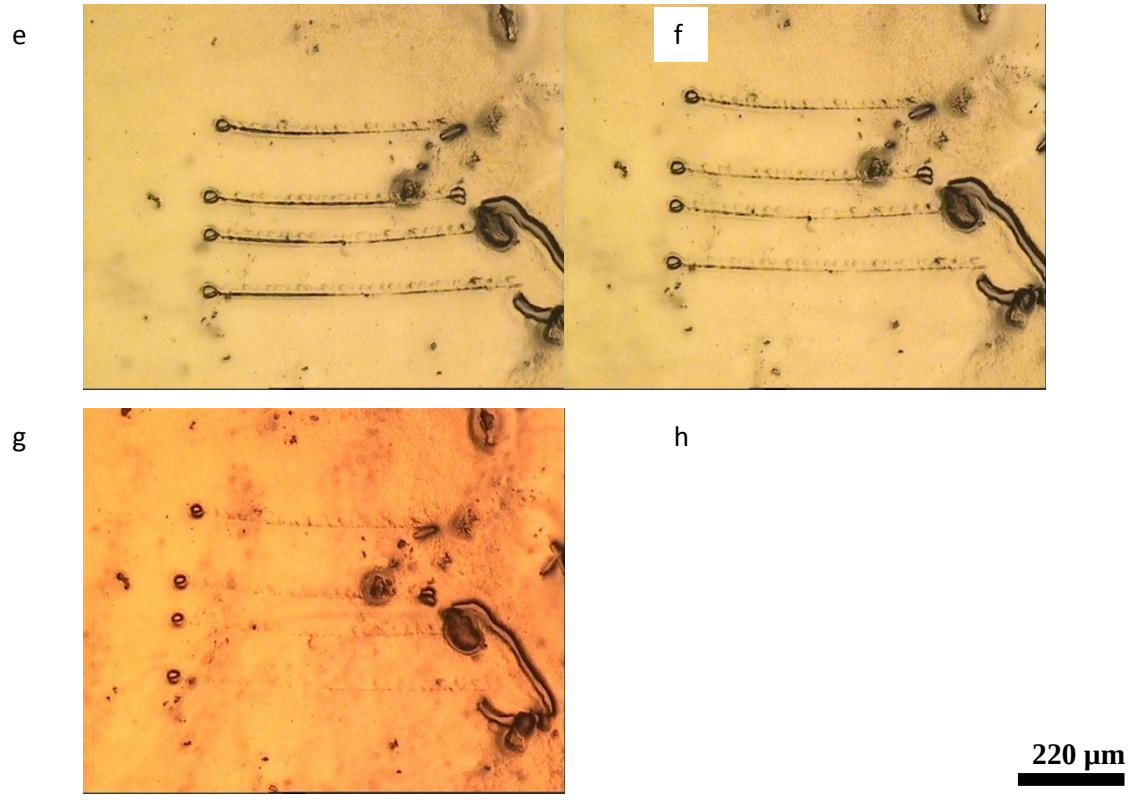


Figure S10: Self-healing studies of the crosslinked polymer **CP12**: a) Scratches, b) partial healing after 2 min at 100 °C, c) partial healing after 10 min at 100 °C, d) healing after 30 min at 100 °C, e) scratches, f) partial after 2 min at 90 °C, g) partial healing after 10 min at 90 °C and h) healing after 170 min at 90 °C.

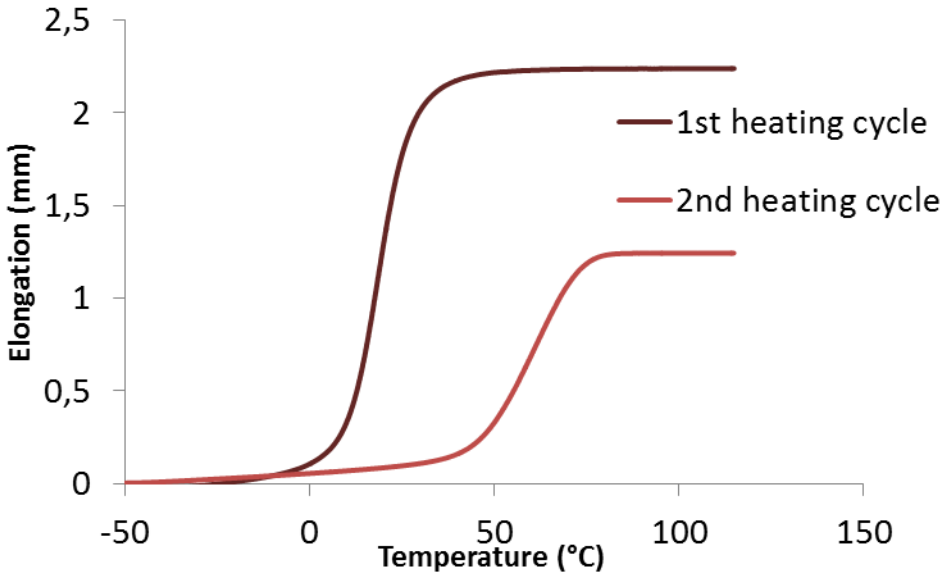


Figure S11: Thermomechanical analysis of the crosslinked polymer **CP11**.

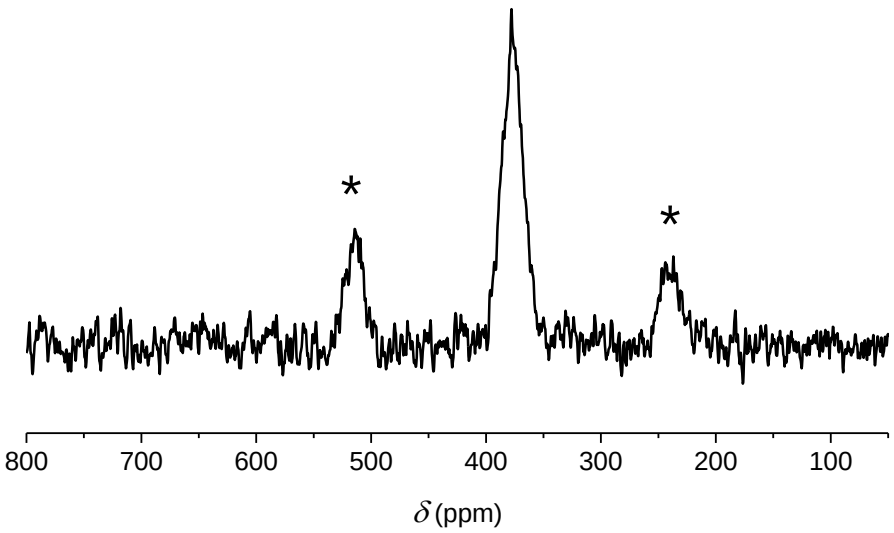


Figure S12: ^{113}Cd- CP-MAS solid state NMR spectrum of **CP5** at room temperature (102400 scans). Spinning side-bands are marked with an asterisk (*).

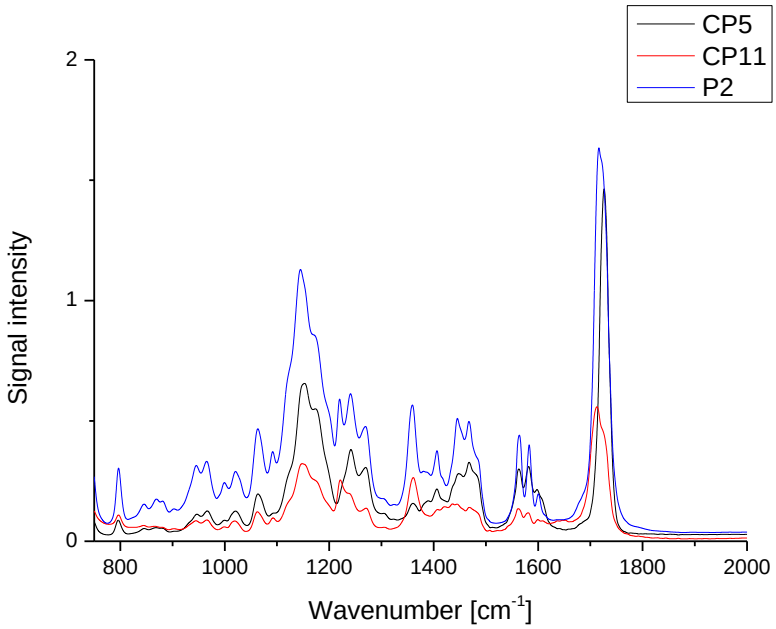


Figure S13: ATR-FTIR-spectra of the polymer **P2** (blue line) and the crosslinked polymer networks **CP5** (black line) and **CP11** (red line).

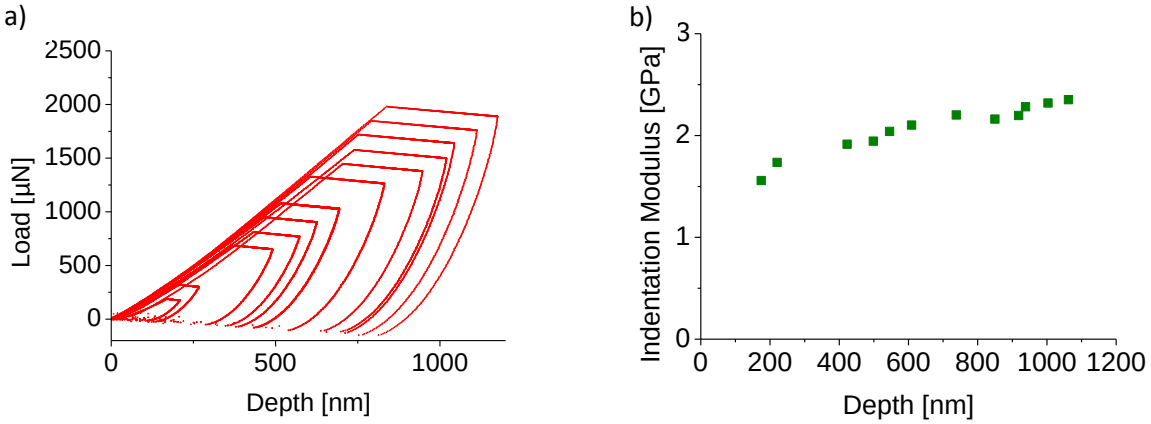


Figure S14: Mechanical properties measured by nanoindentation of **CP11**: a) Load-displacement data and b) indentation modulus.

Experimental Part:

6-(2,2':6',2''-Terpyridin-4'-yloxy)-hexyl methacrylate (1):

A solution of 689 mg of 6-(2,2':6',2"-terpyridin-4'-yloxy)-hexan-1-ol (1.97 mmol) in 25 mL dichloromethane was cooled to 0 °C under nitrogen. 0.9 mL Triethylamine (6.49 mmol) was added and the mixture was stirred for 30 minutes. Subsequently, 0.3 mL methacrylic chloride (3.07 mmol) were slowly added and a gas formation was observed. The solution was stirred for two hours at 0 °C and then the solution was warmed to room temperature. Afterwards the reaction mixture was stirred for 21 hours. After this the solvent and the triethylamine were removed in *vacuo* and the residue was dissolved in dichloromethane. This solution was washed with deionized water (300 mL) and the organic phase was dried over Na_2SO_4. The crude product was purified by silica gel chromatography ($CHCl_3$).

Yield: 650 mg, 79%

^{1}H NMR (250 MHz, $CDCl_3$, δ): 1.48 – 1.94 (m, 11H, -CH_3, $H_{\beta,\gamma,\delta,\varepsilon}$), 4.17 (t, J = 6.5 Hz, 2H, H_α), 4.23 (t, J = 6.5 Hz, 2H, H_ζ), 5.54 (s, 1H, =CH_2), 6.10 (s, 1H, =CH_2), 7.33 (d, J = 4.5 Hz , 2H, $H_{5,5''}$), 7.84 (t, J = 7.5 Hz, 2H, $H_{4,4''}$), 8.00 (s, 2H, $H_{3',5'}$), 8.615 (d, J = 7.5 Hz, 2H, $H_{3,3''}$), 8.69 (d, J = 4.5 Hz, 2H, $H_{6,6''}$) ppm.

^{13}C NMR (62.5 MHz, $CDCl_3$, δ): 18.3 (*C*H_3), 25.7 (C_δ), 25.8 (C_γ), 28.6(C_ε), 28.9 (C_β), 63.6 (C_α), 68.0 (C_ζ), 107.4 ($C_{5,5''}$), 121.3 ($C_{4,4''}$), 123.8 ($C_{3,3''}$), 125.2 (C=*C*H_2), 136.5 (*C*=CH_2), 136.8 ($C_{3',5'}$), 149.0 ($C_{6,6''}$), 156.2 ($C_{2,2''}$), 157.0 ($C_{2',6'}$), 167.3 ($C_{4'}$), 167.5 (*C*O) ppm.

Anal. calcd. for $C_{25}H_{27}N_3O_3$: C 71.92%, H 6.52%, N 10.06%; found: C 71.71%, H 6.51%, N 10.28%

General procedure for the RAFT polymerization:

In a 10 mL microwave vial the corresponding amounts of the two monomers were dissolved in dry toluene. Then the calculated volumes of the stock solutions in toluene of CPDB and AIBN were added. The ratio of [M] to [CPDB] was always 150/1 and the ratio of [CPDB] to [AIBN] 4/1. The exact amounts are listed in **Table S2**.

The reaction mixture was purged with a flow of nitrogen for 30 minutes and the vial was closed. The reaction was performed overnight in an oil bath at 70 °C.

The polymers were purified by precipitation in cold ethanol. The BMA and LMA containing polymers were also purified by BioBeads S-X3 (solvent chloroform).

Table S2: Overview of the amounts and the reaction times of the polymerizations.

Sample	Monomers	m (monomers) [mg]	m (AIBN) [mg]	m (CPDB) [mg]	V (toluene) [µL]	reaction time [h]
P1	**1** MMA	121 357	1.07	5.79	397	16.5
P2	**1** BMA	117 402	0.85	4.59	285	17
P3	**1** LMA	73 447	0.53	2.85	100	17

P1

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.85 – 1.90 (44H), 2.36 (3H), 3.60 – 4.25 (22 H), 6.89 – 7.39 (9H), 7.86 (1H), 8.01 (1H), 8.60 – 8.69 (2H) ppm.

SEC ($CHCl_3$, PMMA-standard): M_n = 15,500 g/mol; M_w = 27,300 g/mol; PDI = 1.76

EA: (calcd. for ratio of both comonomers based on NMR)

calcd.: C: 62.97%; H: 6.67%; N: 2.52%

found: C: 65.74%; H: 7.89%; N: 2.01%; S: 0.00%

DSC: T_g: 74 °C

TGA: T_d: 278 °C

P2

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 – 1.95 (54H), 3.81 – 4.27 (9H), 7.34 (1H), 7.89 (1H), 8.06 (1H), 8.64 – 8.73 (2H) ppm.

SEC ($CHCl_3$, PMMA-standard): M_n = 28,900 g/mol; M_w = 33,300 g/mol; PDI = 1.15

EA: (calcd. for ratio of both comonomers based on NMR)

calcd.: C: 77.12%; H: 10.33%; N: 1.24%

found: C: 69.48%; H: 9.38%; N: 2.34%; S: 0.00%

DSC: T_g: –2 °C

TGA: T_d: 275 °C

P3

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 – 2.02 (180H); 3.94 – 4.28 (14H), 7.40 (1H), 7.88 (1H), 8.04 (1H), 8.64 – 8.72 (2H) ppm.

SEC ($CHCl_3$, PMMA-standard): M_n = 48,500 g/mol; M_w = 54,600 g/mol; PDI = 1.13

EA: (calcd. for ratio of both comonomers based on NMR)

calcd.: C: 75.10%; H: 11.24%; N: 1.21%

found: C: 74.22%; H: 11.35%; N: 1.25%; S: 0.00%

DSC: T_g: –65 °C

TGA: T_d: 280 °C

Table S3: Overview of the elemental analysis results.

Crosslinked polymer	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Halogen (%)
CP1	57.66	7.24	3.17	3.04
CP2	66.36	8.09	2.15	3.32
CP3	60.18	10.82	1.82	1.47
CP4	54.97	6.78	2.72	9.65
CP5	62.24	8.74	2.55	5.55
CP6	68.94	10.95	2.60	4.46
CP7	54.29	6.59	2.78	10.47
CP8	63.92	8.74	2.48	7.57
CP9	68.09	10.89	1.96	6.42
CP10	59.66	7.40	2.94	0.00
CP11	57.88	8.51	2.09	0.00
CP12	64.82	10.12	3.77	0.00