Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

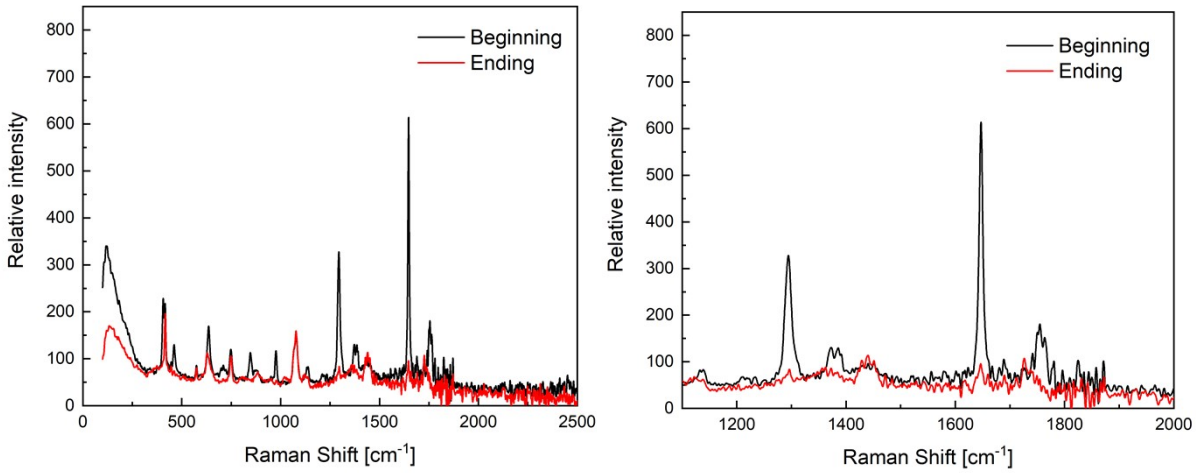


Figure A1: Representative Raman spectrum before initiation (black line) and at the end of the reaction (red line). The whole spectrum is shown on the left and a cut-out of the relevant peak is shown on the right.

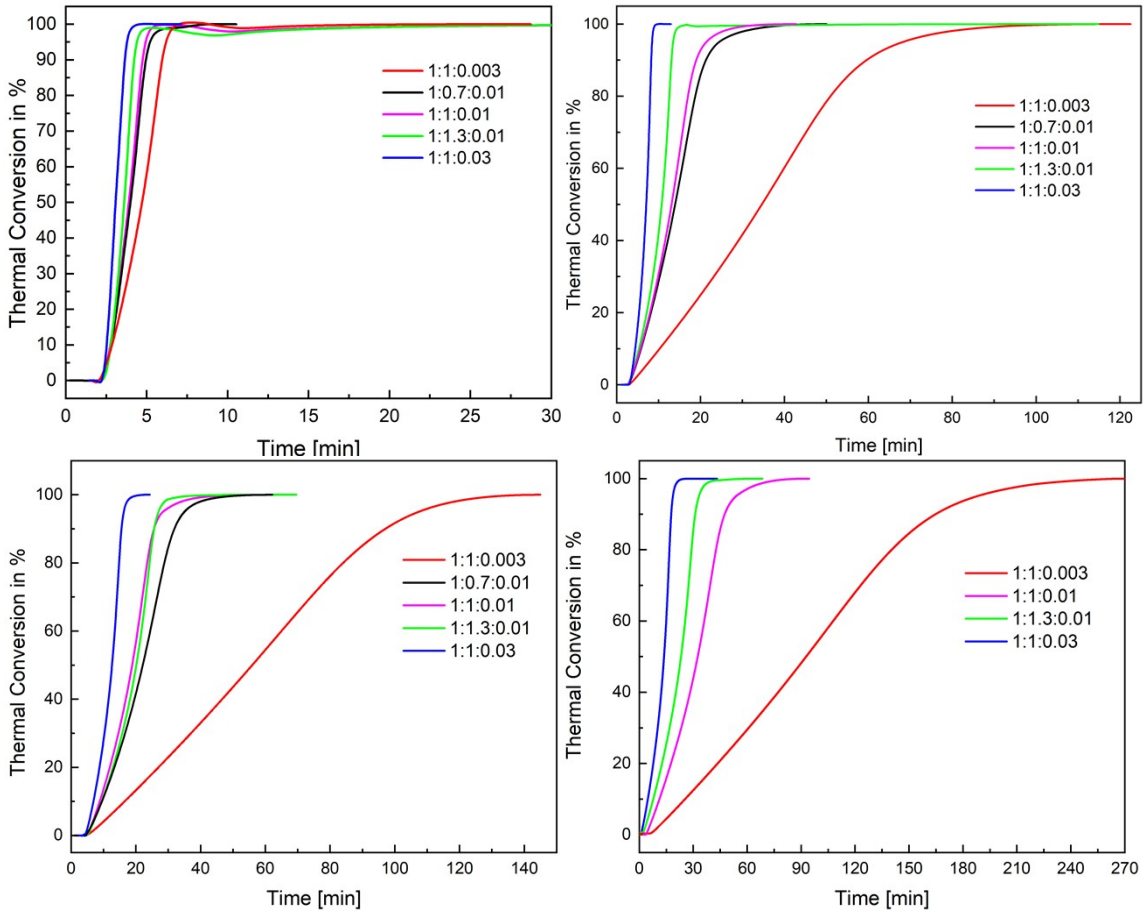


Figure A2: Representation of the thermal conversion as a function of time of all molar ratios at respectively 60 °C (upper left), 25 °C (upper right), 15 °C (lower left) and 5 °C (lower right).

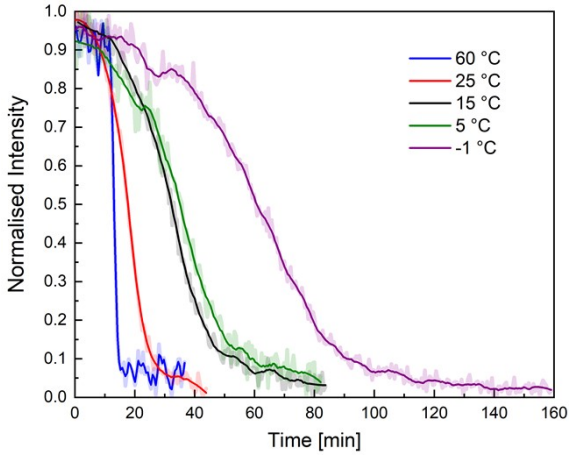


Figure A3: Representation of the normalised Raman conversion as a function of time at different initiation temperatures and a molar ratio of 1:0.7:0.01.

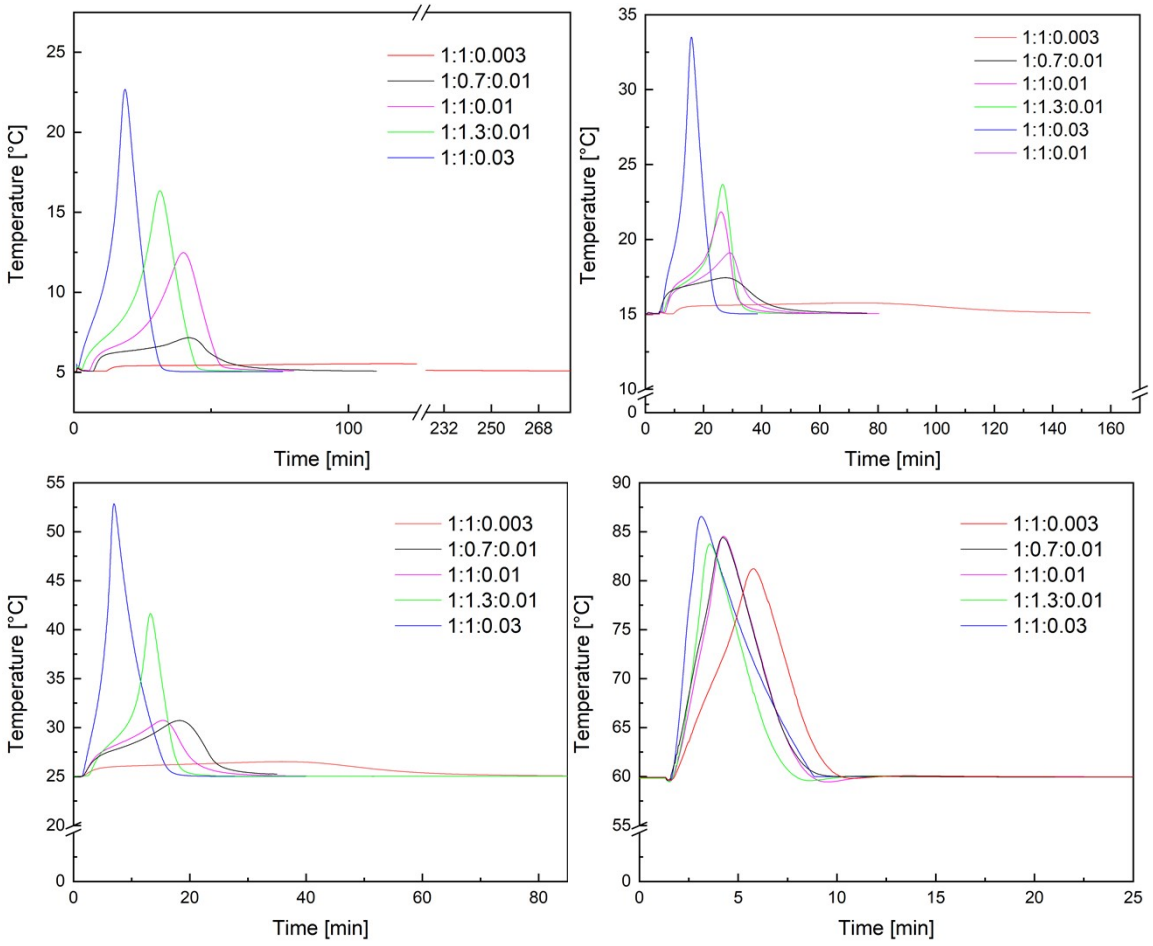
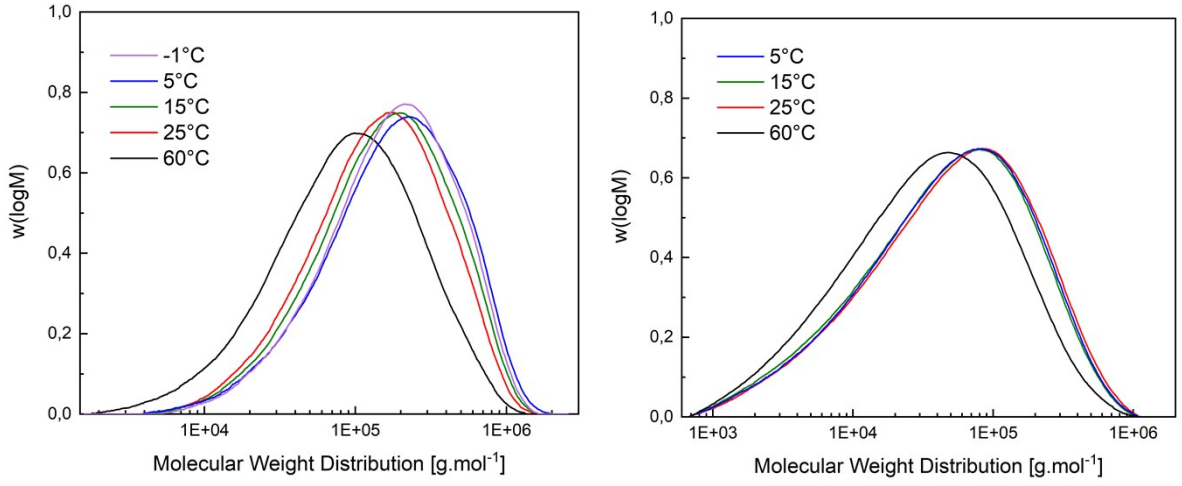


Figure A4: Temperature profile of the emulsion polymerisation.



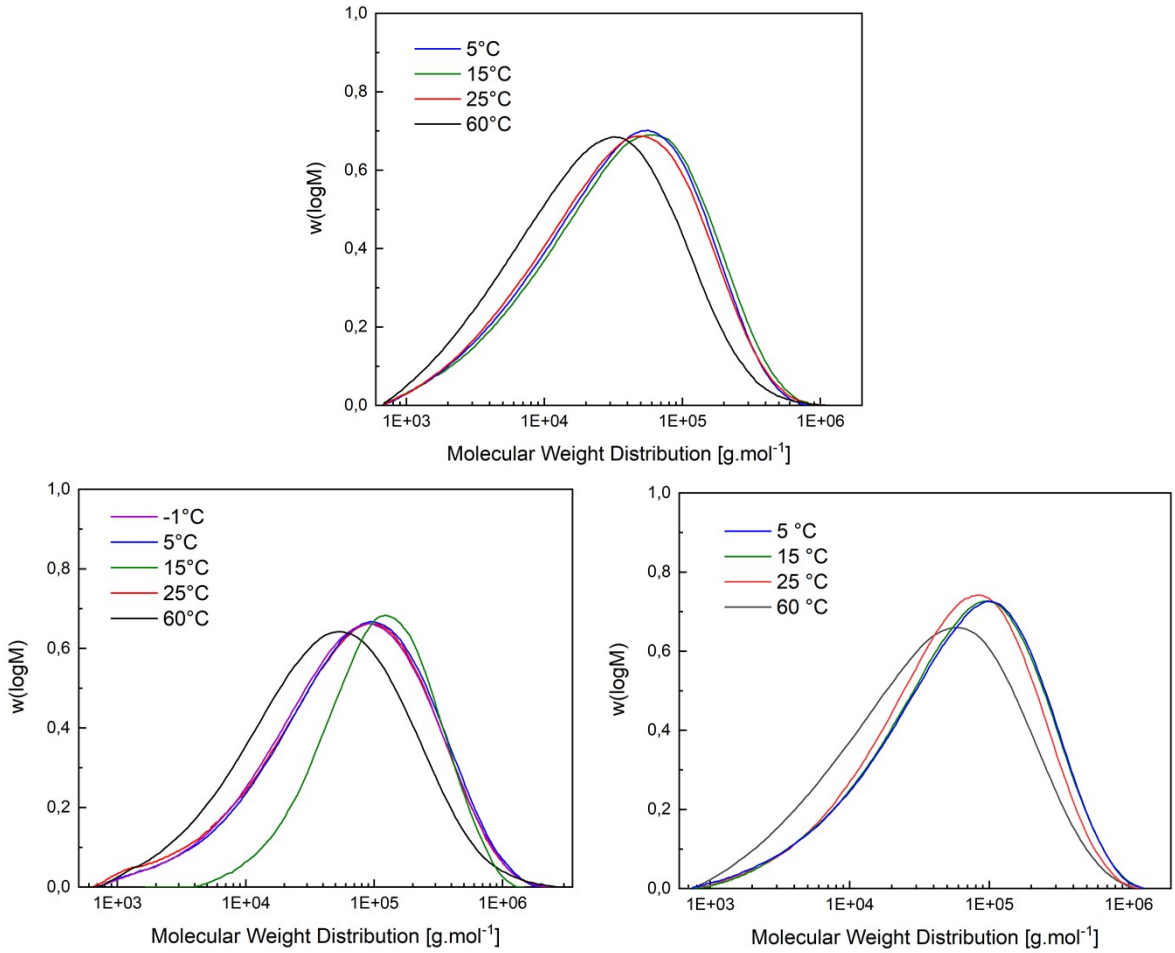
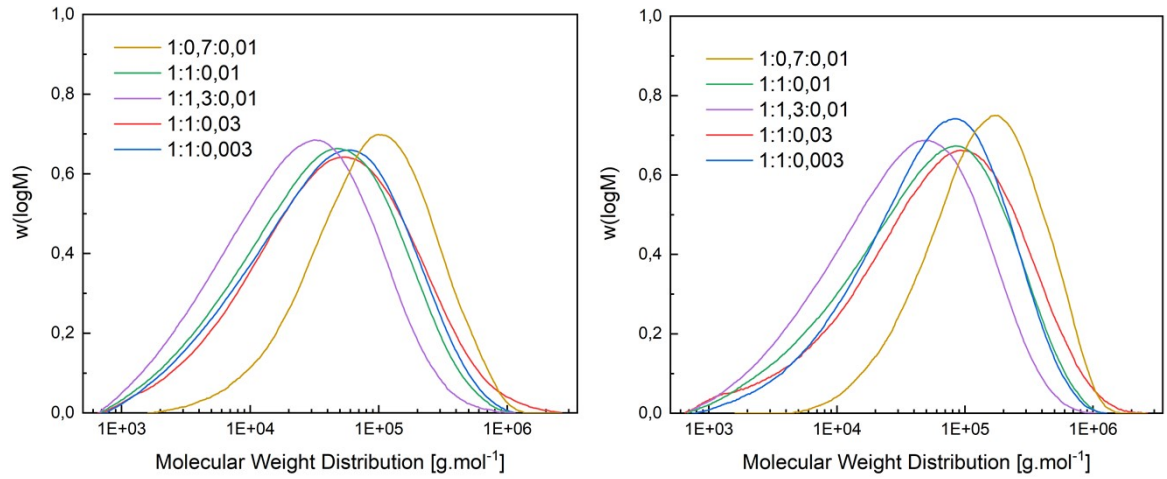


Figure A5: Influence of the initiation temperature on the molecular weight distribution, using different molar ratios of the redox components: 1:0.7:0.01 (upper left), 1:1:0.01 (upper right), 1:1.3:0.01 (middle), 1:1:0.03 (lower left) and 1:1:0.003 (lower right).



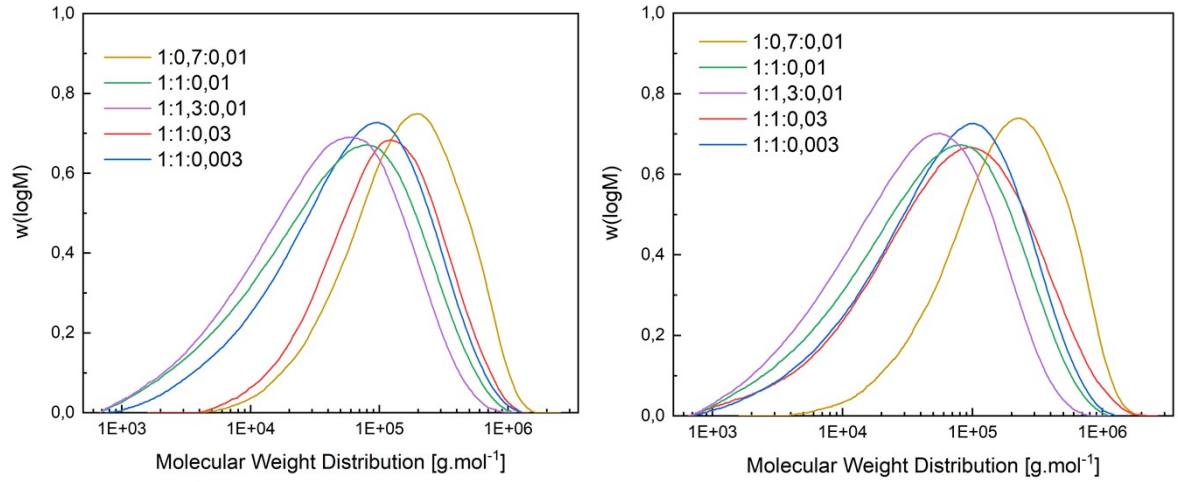
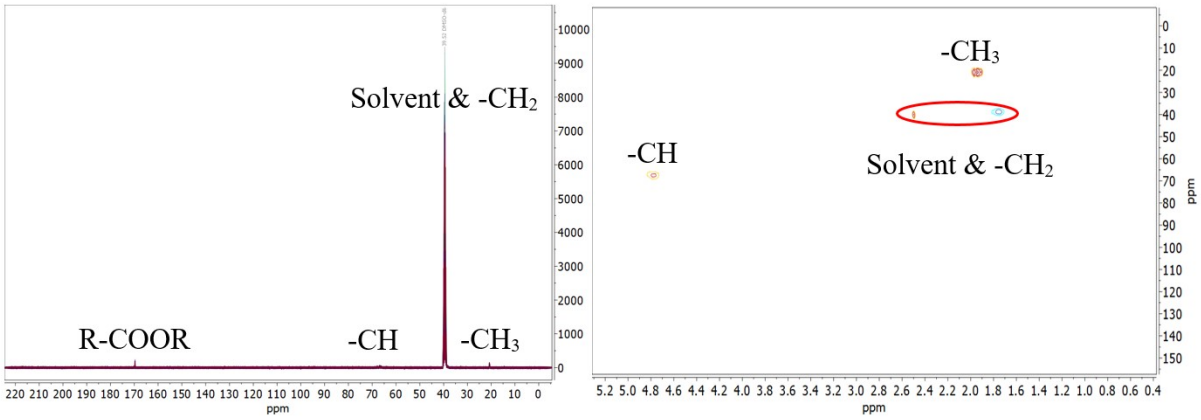


Figure A6: Molecular weight distribution at different operating conditions of the redox components and at different initiation temperatures: 60 °C (upper left), 25 °C (upper right), 15 °C (lower left) and 5 °C (lower right).



(a) *(b)*

Figure A7 : Stacked 1D ^{13}C NMR spectrum of all samples (a) and representative 2D HSQC spectrum (b).

Table A1: Analysis of variance table, model for prediction of M_n.

Model Factor	probability value [-]	F-value [-]	Variance inflation factor [-]
r_{tBHP}	< 0.0001	197.54	1.01
ϑ_0	< 0.0001	93.82	1.01
r_{tBHP}^2	< 0.0001	84.85	1.01

Table A2: Analysis of variance table, model for prediction of M_w.

Model Factor	probability value [-]	F-value [-]	Variance inflation factor [-]
r_{tBHP}	< 0.0001	34.50	1.01
ϑ_0	< 0.0001	48.09	1.01
r_{tBHP}^2	< 0.0001	3.72	1.01

TableA3: Analysis of variance table, model for prediction of $t_{99\%}$.

Model Factor	probability value [-]	F-value [-]	Variance inflation factor [-]
$r_{Fe\text{-}cat.}$	< 0.0001	34.11	1.04
r_{tBHP}	< 0.0001	6.52	1.02
ϑ_0	0.0212	328.4	1.15
ϑ_0^2	< 0.0001	13.54	1.18

Table A4: Overview of the intensities of the signals in all ^{1}H-NMR spectra.

R_{Redox}	Temperature [°C]	Integral CH	Integral OH 1	Integral OH 2	Integral OH 3	Integral CH_3	Integral CH_2	Integral neo-C_9H_{19}
1:0.7:0.01	25	1.05	0.05	0.04	0.14	2.94	2.00	0.89
	15	1.05	0.07	0.05	0.15	2.93	2.00	0.97
	5	1.05	0.07	0.04	0.12	2.98	2.00	0.74
	-1	1.03	0.05	0.03	0.08	2.94	2.00	0.83
	60	1.05	0.07	0.04	0.12	3.01	2.00	0.96
1:1:0.03	25	1.06	0.06	0.04	0.15	3.00	2.00	0.75
	15	1.05	0.06	0.04	0.15	2.95	2.00	0.86
	5	1.03	0.09	0.03	0.11	3.00	2.00	0.71
	-1	1.04	0.05	0.03	0.10	2.99	2.00	0.68
	60	1.07	0.16	0.05	0.19	2.95	2.00	1.18
1:1:0.003	25	1.03	0.06	0.04	0.13	2.90	2.00	1.02
	15	1.02	0.06	0.03	0.10	2.93	2.00	1.00
	5	1.04	0.06	0.03	0.13	2.92	2.00	1.00
	60	1.03	0.07	0.04	0.14	2.95	2.00	1.25
1:1:0.01	25	1.05	0.06	0.04	0.15	2.97	2.00	0.79
	15	1.04	0.06	0.04	0.13	2.97	2.00	0.73
	5	1.04	0.06	0.04	0.15	2.94	2.00	0.80
	60	1.06	0.06	0.04	0.15	2.98	2.00	1.08
1:1.3:0.01	25	1.05	0.06	0.04	0.12	3.01	2.00	0.72
	15	1.05	0.06	0.04	0.12	2.98	2.00	0.74
	5	1.05	0.06	0.04	0.16	2.99	2.00	0.77
	60	1.07	0.09	0.06	0.22	2.99	2.00	1.14