Supporting information

Switching from Controlled Ring-Opening Polymerization (cROP) to Controlled Ring-Closing Depolymerization (cRCDP) by Adjusting the Reaction Parameters that Determine the Ceiling Temperature

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EXPERIMENTAL SECTION

Equations

Dainton's equation, [SE-1] states that at the equilibrium point i.e., when $\Delta G_p = 0$ there is a critical temperature, referred to as the ceiling temperature (T_c) or floor temperature (T_f), depending on the thermodynamic features of the polymerization. At this point, no conversion of monomer to polymer is obtained.

$$T = \frac{\Delta H_p}{\Delta S_p + R ln([M])_{eq}} \qquad \text{[SE-1]}$$

It is possible to express Dainton´s equation as a function of the equilibrium molar fraction, $\frac{n_m/V}{n_0/V}$, instead of the equilibrium monomer concentration, $[M]_{eq}$, [SE-3] (n_m = molar amount of monomer at equilibrium, and n_0 = starting molar amount of monomer, hence, when $n_m = n_0$, T is equal to T_c.

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$$\ln([M])_{eq} = \frac{\Delta H_p}{R*T} - \frac{\Delta S_p^0}{R} \qquad \text{[SE-2]}$$

$$[M]_{eq} = \frac{[M]}{[M]_0} = \frac{n_m/V}{n_0/V} \qquad \text{[SE-3]}$$

This is possible under the assumption that the volume does not change upon polymerization [SE-4].

$$\text{[SE-3] in [SE-2]} \Rightarrow \ln\left(\frac{n_m}{n_0}\right) = \frac{\Delta H_p}{R*T} - \frac{\Delta S_p}{R} \qquad \text{[SE-4]}$$

Polymerization set-up

Table S1. Polymerization setup for AOMEC different concentrations in DCM

Temperature [°C]	AOMEC [ml]	AOMEC [mmol]	Hex-diol [mmol]	DBU [mmol]	DCM [ml]	[AOMEC] [mol/L]	[AOMEC]:[Hex-diol]:[DBU]
30	2	12.5	0.125	0.625	none	6	[100]:[1]:[5]
30	0.8	5	0.05	0.25	0,45	4	[100]:[1]:[5]
30	0.8	5	0.05	0.25	1.7	2	[100]:[1]:[5]
30	0.8	5	0.05	0.25	4.2	1	[100]:[1]:[5]
30	0.8	5	0.05	0.25	9.2	0.5	[100]:[1]:[5]
30	0.4	2.5	0.025	0.125	19.6	0.125	[100]:[1]:[5]

Table S2. Bulk polymerization of AOMEC at different temperatures

Temperature [°C]	AOMEC [ml]	AOMEC [mmol]	Solvent	DBU [mmol]	[AOMEC] [mol/L]	[AOMEC]:[DBU]
30	0.8	5	None	0.25	6	[100]:[5]
60	0.8	5	none	0.25	6	[100]:[5]
110	0.8	5	none	0.25	6	[100]:[5]
140	0.8	5	none	0.25	6	[100]:[5]
170	0.8	5	none	0.25	6	[100]:[5]
200	0.8	5	none	0.25	6	[100]:[5]

Table S3. Polymerization of AOMEC in different concentrations and temperatures in toluene

Temperature [°C]	AOMEC[(a)] [ml]	AOMEC [mmol]	Toluene [ml]	DBU Stock Solution[(b)] [ml]	[AOMEC] [mol/L]	[AOMEC] :[DBU]
30	0.8	5	0.7	1	2	[100]:[5]
60	0.8	5	0.7	1	2	[100]:[5]
75	0.8	5	0.7	1	2	[100]:[5]
90	0.8	5	0.7	1	2	[100]:[5]
30	0.8	5	3.2	1	1	[100]:[5]
60	0.8	5	3.2	1	1	[100]:[5]
75	0.8	5	3.2	1	1	[100]:[5]
90	0.8	5	3.2	1	1	[100]:[5]
30	0.8	5	8.2	1	0.5	[100]:[5]
60	0.8	5	8.2	1	0.5	[100]:[5]
75	0.8	5	8.2	1	0.5	[100]:[5]
90	0.8	5	8.2	1	0.5	[100]:[5]
30	0.8	5	18.2	1	0.25	[100]:[5]
60	0.8	5	18.2	1	0.25	[100]:[5]
75	0.8	5	18.2	1	0.25	[100]:[5]
90	0.8	5	18.2	1	0.25	[100]:[5]

[(a)]0.8 ml AOMEC is equal to 1 g; [(b)]Containing 0.25 mmol DBU per ml of toluene

Table S4. Polymerization of AOMEC in different concentrations and temperatures in acetonitrile

Temperature [°C]	AOMEC[(a)] [ml]	AOMEC [mmol]	Acetonitrile [ml]	DBU Stock Solution[(b)] [ml]	[AOMEC] [mol/L]	[AOMEC] :[DBU]
30	0.8	5	0.7	1	2	[100]:[5]
45	0.8	5	0.7	1	2	[100]:[5]
60	0.8	5	0.7	1	2	[100]:[5]
75	0.8	5	0.7	1	2	[100]:[5]
30	0.8	5	3.2	1	1	[100]:[5]
45	0.8	5	3.2	1	1	[100]:[5]
60	0.8	5	3.2	1	1	[100]:[5]
75	0.8	5	3.2	1	1	[100]:[5]
30	0.8	5	8.2	1	0.5	[100]:[5]
45	0.8	5	8.2	1	0.5	[100]:[5]
60	0.8	5	8.2	1	0.5	[100]:[5]
0	0.8	5	18.2	1	0.25	[100]:[5]
30	0.8	5	18.2	1	0.25	[100]:[5]
45	0.8	5	18.2	1	0.25	[100]:[5]

[(a)]0.8 ml AOMEC is equal to 1 g; [(b)]Containing 0.25 mmol DBU per ml of acetonitrile

Instruments: Nuclear magnetic resonance (NMR)

^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.62 MHz) spectra were recorded with a Bruker Avance 400 spectrometer at 298 K. For the measurements, either ~10 mg (^{1}H NMR) or ~100 mg (^{13}C NMR) of the polymer was dissolved in 0.8 ml of $CDCl_3$ in a sample tube that was 5 mm in diameter. The spectra were calibrated using the residual proton of the solvent signal (i.e.,7.26 ppm (^{1}H NMR) and 77.0 ppm (^{13}C NMR) for $CHCl_3$).

Size exclusion chromatography (SEC)

The number-average molecular weight (M_n) and dispersity (Đ) of the polymers during and after polymerization were determine using a Verotech PL-GPC 50 Plus equipped with a PL-RI detector and two PLgel 5 µm MIXED-D columns that were 300 × 7.5 mm (Varian, Santa Clara). A PL-AS RT autosampler (Polymer Laboratories) was used to inject the samples, and chloroform was used as the mobile phase at a flow rate of 1 mL/min at 30 °C with toluene as an internal standard. The calibration was created using polystyrene standards with a narrow molecular weight distribution ranging from 160 – 371,000 g/mol.

Determination of the thermodynamic parameters for the polymerization of AOMEC in toluene. [Toluene] = 2M

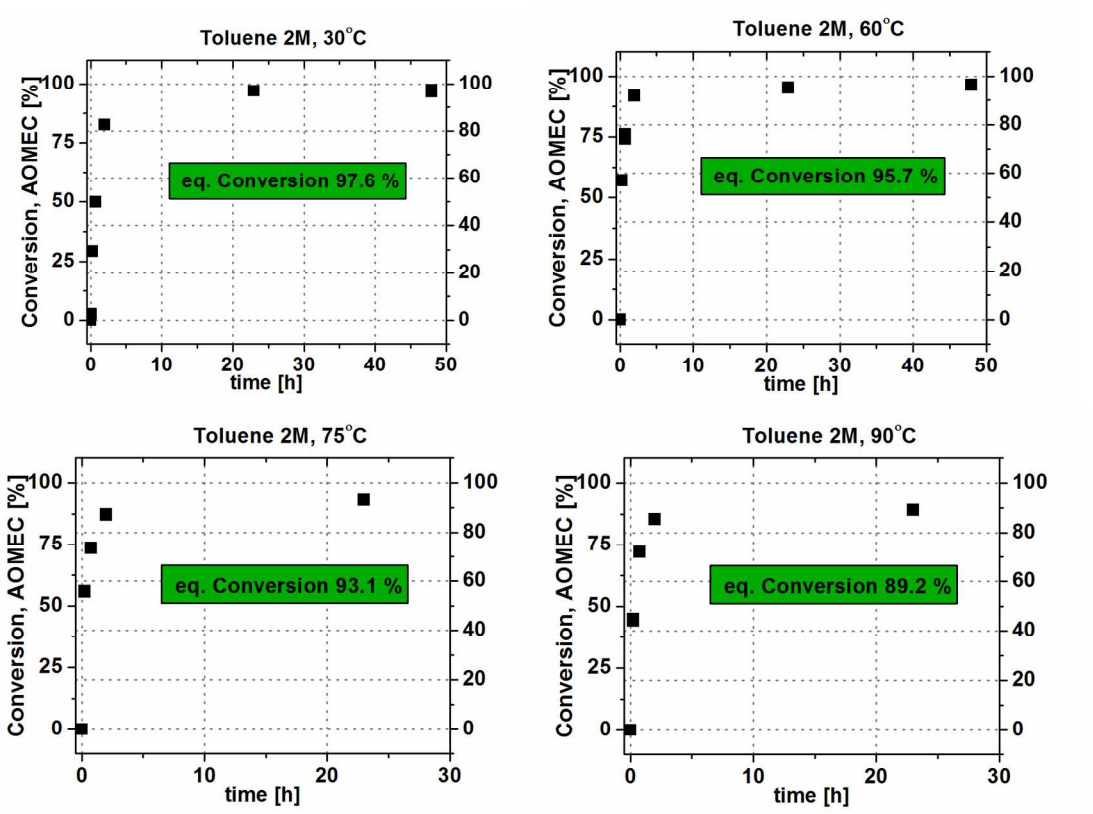

Figure S1. Polymerization of AOMEC in toluene (2M solution) at different temperatures. [DBU] = 5 mol%.

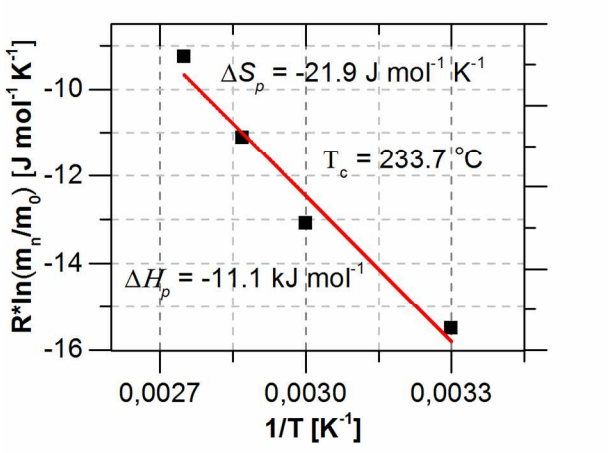

Figure S2. Thermodynamic parameters for the polymerization of a 2M solution of AOMEC in toluene.

[Toluene] = 1M

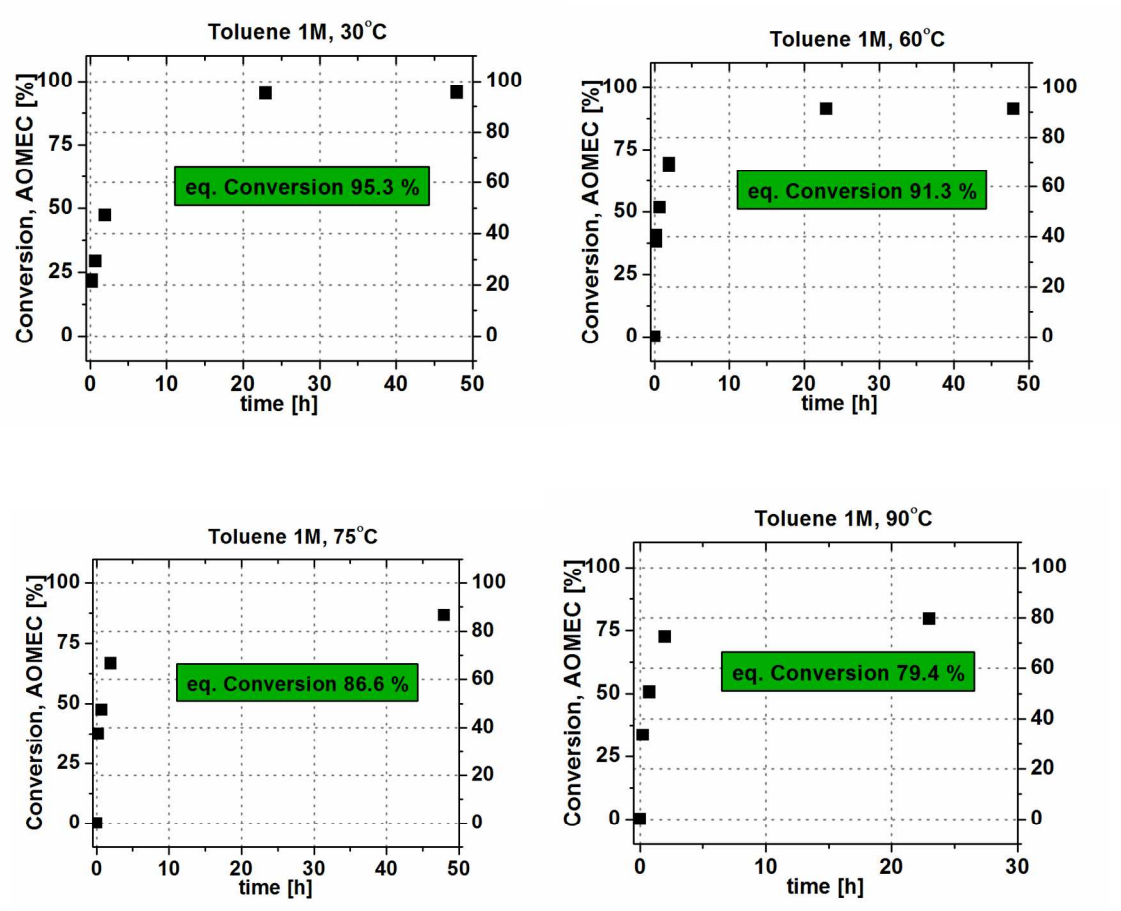

Figure S3. Polymerization of AOMEC in toluene (1M solution) at different temperatures. [DBU] = 5 mol%.

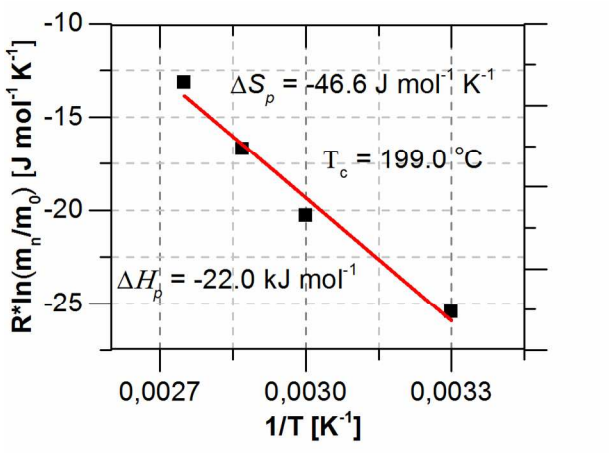

Figure S4. Thermodynamic parameters for the polymerization of a 1M solution of AOMEC in toluene.

[Toluene] = 0.5M

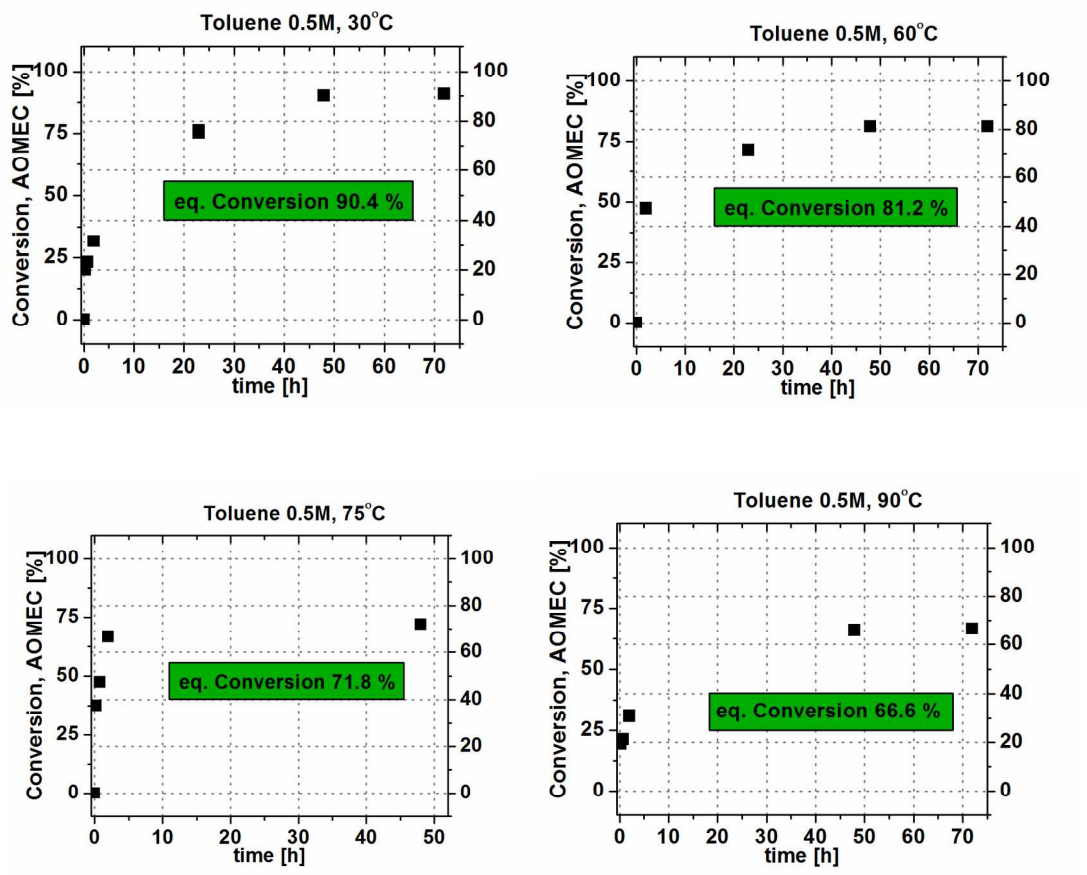

Figure S5. Polymerization of AOMEC in toluene (0.5M solution) at different temperatures. [DBU]=5 mol%.

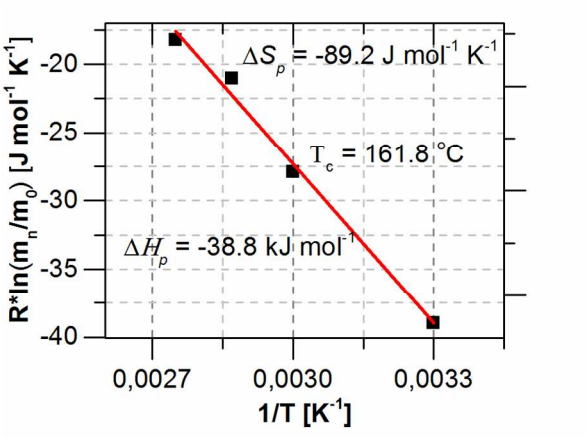

Figure S6. Thermodynamic parameters for the polymerization of a 0.5M solution of AOMEC in toluene.

[Toluene] = 0.25M

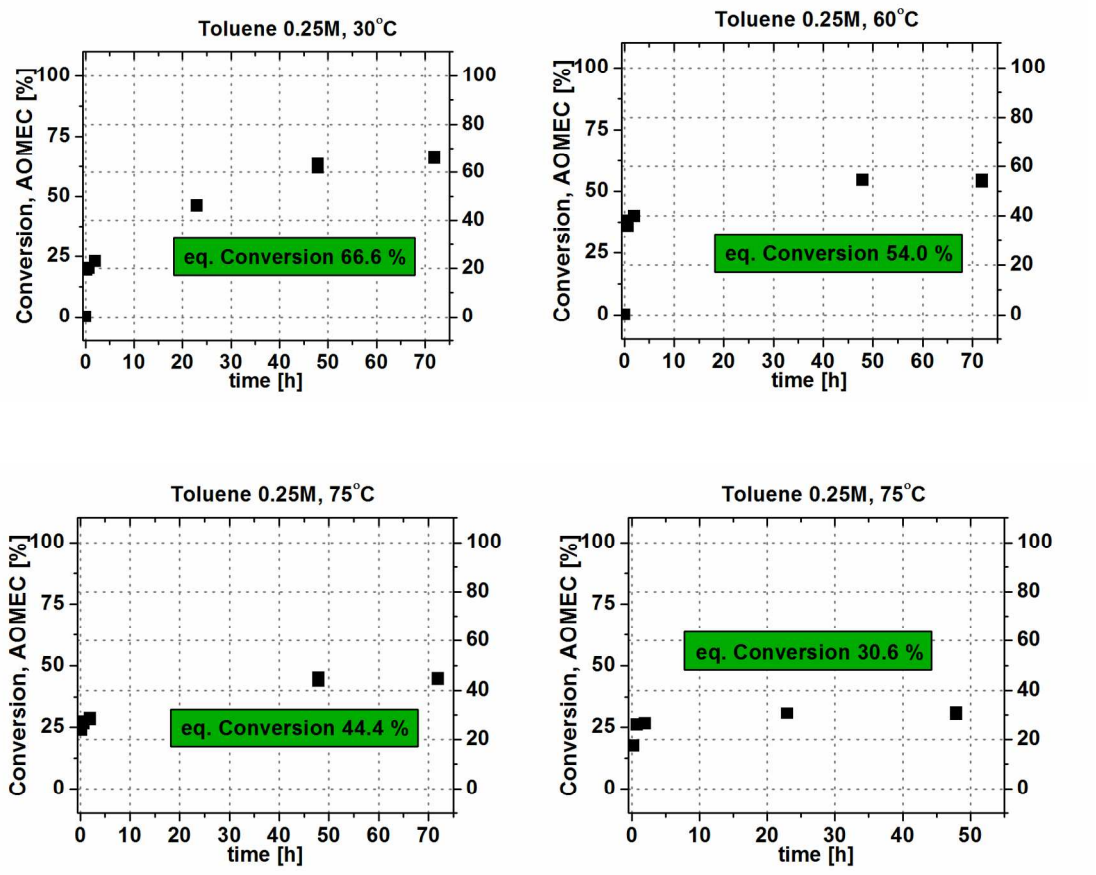

Figure S7. Polymerization of AOMEC in toluene (0.25M solution) at different temperatures. [DBU] = 5 mol%.

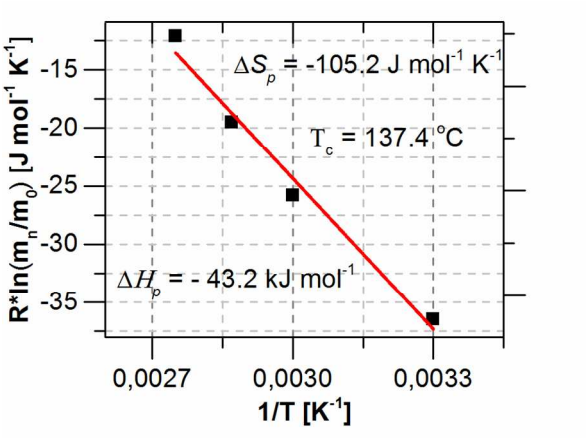

Figure S8. Thermodynamic parameters for the polymerization of a 0.25M solution of AOMEC in toluene.

[Acetonitrile] = 2M

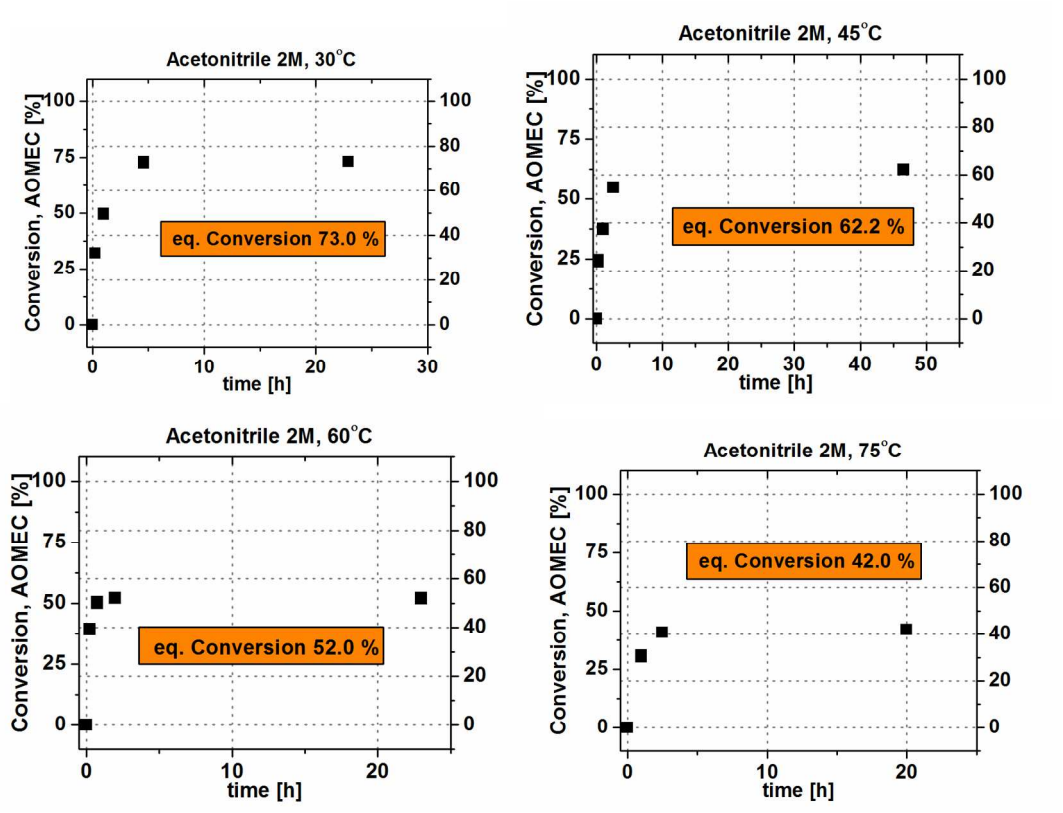

Figure S9. Polymerization of AOMEC in acetonitrile (2M solution) at different temperatures. [DBU] = 5 mol%.

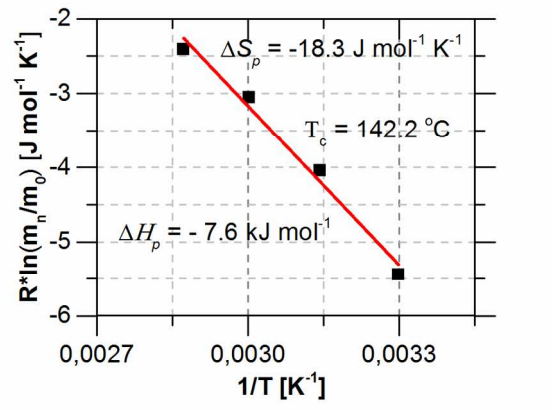

Figure S10. Thermodynamic parameters for the polymerization of a 2M solution of AOMEC in acetonitrile.

[Acetonitrile] = 1M

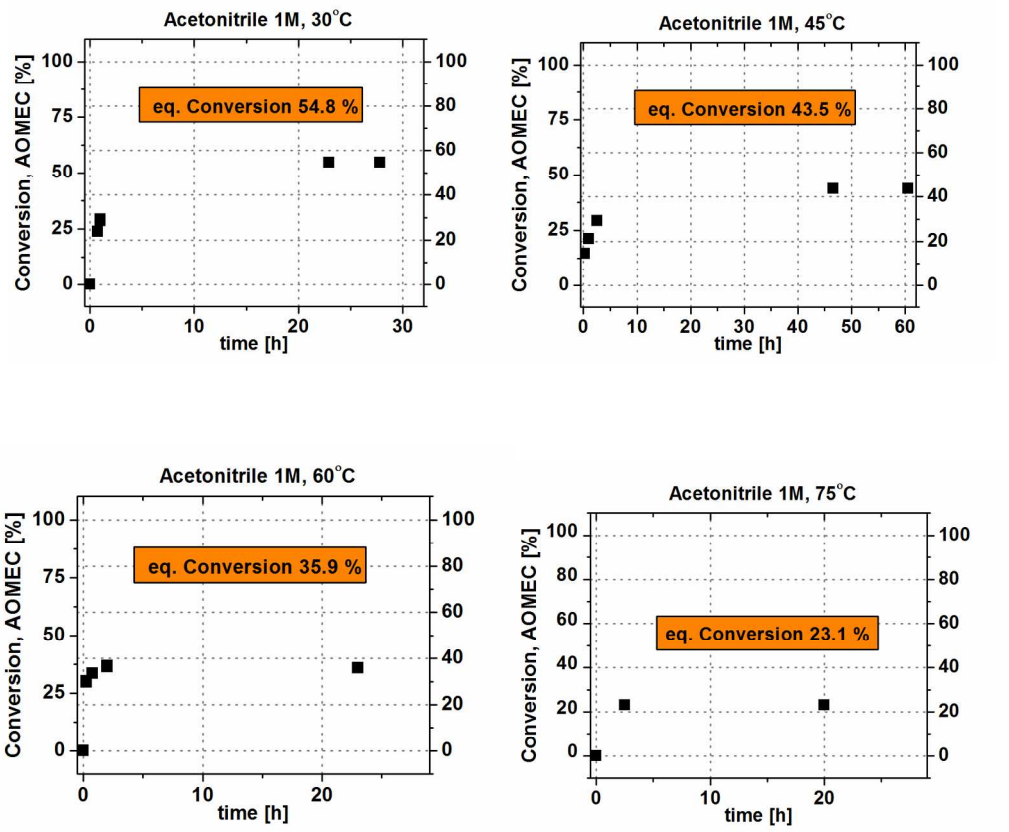

Figure S11. Polymerization of AOMEC in acetonitrile (1M solution) at different temperatures. [DBU] = 5

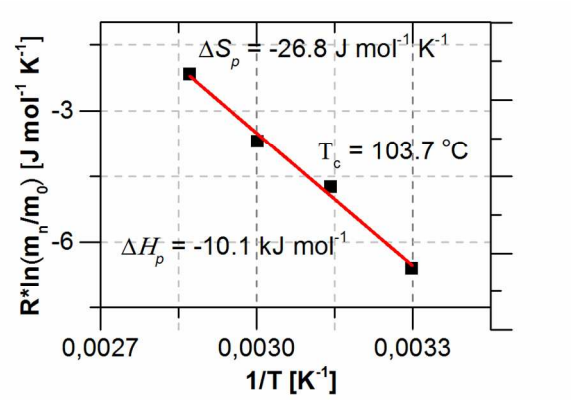

Figure S12. Thermodynamic parameters for the polymerization of a 1M solution of AOMEC in acetonitrile.

[Acetonitrile] = 0.5M

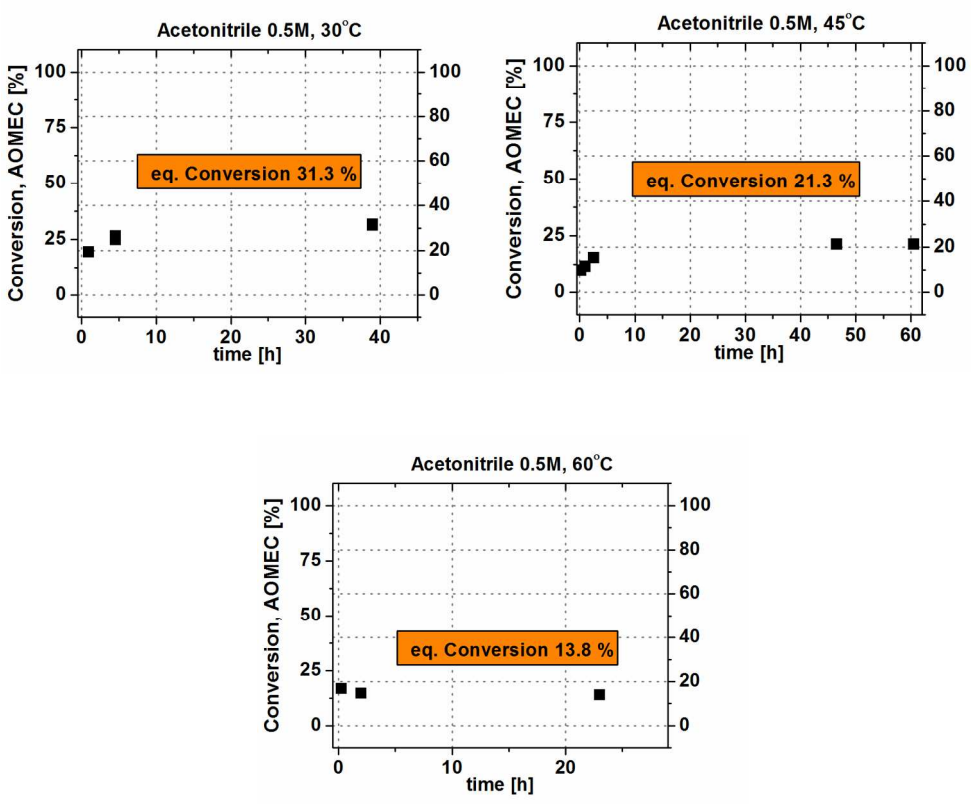

Figure S13. Polymerization of AOMEC in acetonitrile (0.5M solution) at different temperatures. [DBU] = 5 mol%.

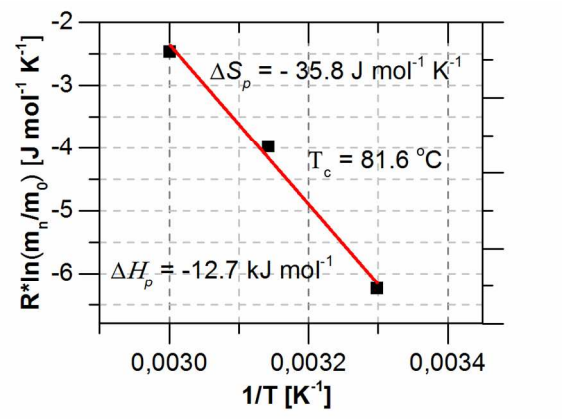

Figure S14. Thermodynamic parameters for the polymerization of a 0.5M solution of AOMEC in acetonitrile.

[Acetonitrile] = 0.25M

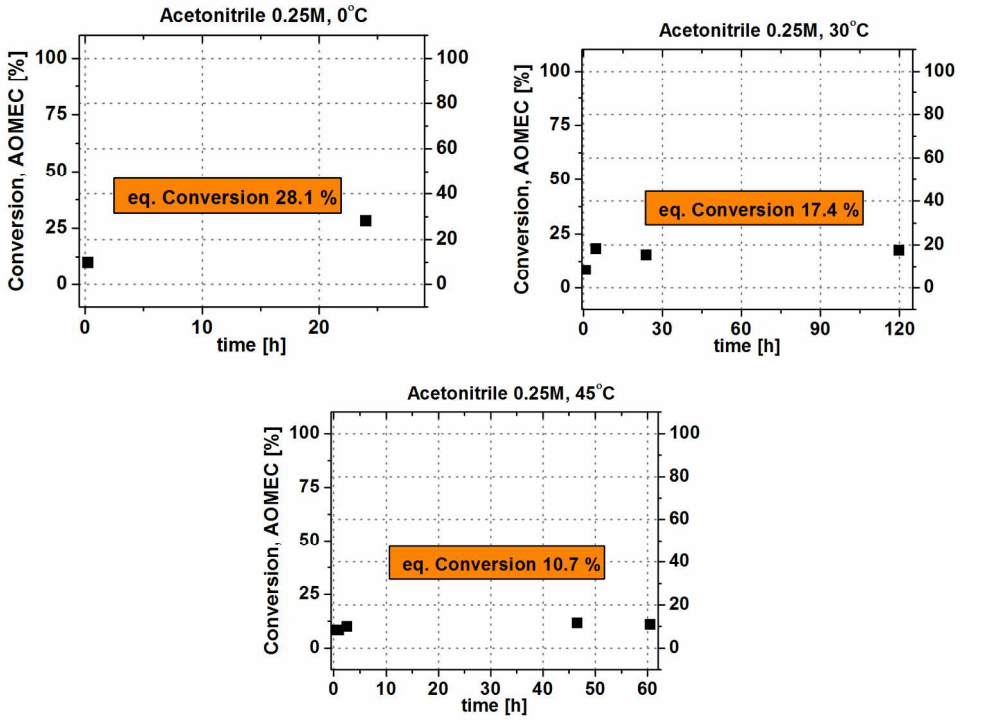

Figure S15. Polymerization of AOMEC in acetonitrile (0.25M solution) at different temperatures. [DBU] = 5 mol%.

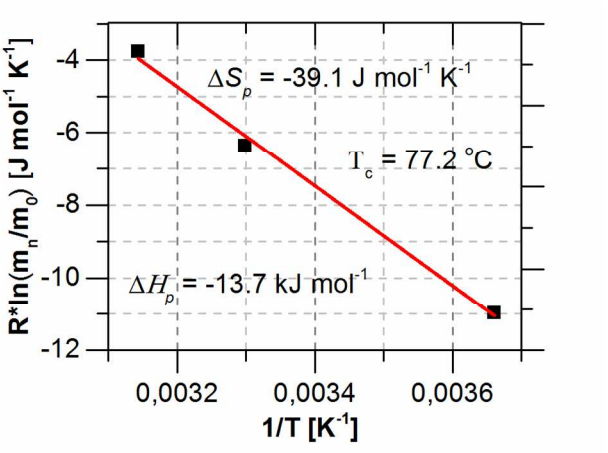

Figure S16. Thermodynamic parameters for the polymerization of a 0.25M solution of AOMEC in acetonitrile.

Table S5. Polymerization of AOMEC in bulk (6 M) at 30 °C

Temperature [°C]	Solvent	Concentration	Time [h]	Conversion [%]	M_n [g*mol^{-1}]*10^{-3}	M_w/M_n
30	none	bulk (6 M)	0	1	0.2	1
30	none	bulk (6 M)	0.0167	3.8	1.27	1.03
30	none	bulk (6 M)	0.05	7.4	1.89	1.09
30	none	bulk (6 M)	0.1	11.5	3.04	1.06
30	none	bulk (6 M)	0.167	17.4	4.37	1.05
30	none	bulk (6 M)	0.333	30.6	6.39	1.08
30	none	bulk (6 M)	0.583	47.1	-	-
30	none	bulk (6 M)	0.833	58.3	11.1	1.08
30	none	bulk (6 M)	1.333	75	12.9	1.09
30	none	bulk (6 M)	1.667	85.3	-	-
30	none	bulk (6 M)	2	88.5	15	1.09

Table S6. Ring-Closing Depolymerization of AOMEC in MeCN (0.5 M) at 82 °C

Temperature [°C]	Solvent	Concentration	Time [h]	Conversion [%]	M_n $[g*mol^{-1}]*10^{-3}$	M_w/M_n
82	MeCN	0.5 M	0.333	89.6	15.2	1.09
82	MeCN	0.5 M	0.5	84.4	14.9	1.09
82	MeCN	0.5 M	0.667	81.1	14.5	1.08
82	MeCN	0.5 M	0.833	78	13.6	1.08
82	MeCN	0.5 M	1	74	12.9	1.10
82	MeCN	0.5 M	1.167	69.6	12.5	1.08
82	MeCN	0.5 M	1.333	66	11.7	1.08
82	MeCN	0.5 M	1.583	60.5	-	-
82	MeCN	0.5 M	1.833	54.8	10.5	1.10
82	MeCN	0.5 M	2.083	47.8	10	1.12
82	MeCN	0.5 M	2.333	43	8.8	1.13
82	MeCN	0.5 M	2.583	37.5	8.4	1.11
82	MeCN	0.5 M	3.083	31	6.8	1.10
82	MeCN	0.5 M	3.333	29.1	6.4	1.12
82	MeCN	0.5 M	3.833	23.4	5.4	1.11
82	MeCN	0.5 M	4.333	17.7	4.6	1.10
82	MeCN	0.5 M	4.833	14.9	-	-
82	MeCN	0.5 M	5.833	12.7	1.7	1.10
82	MeCN	0.5 M	6.833	10.3	-	1.10
82	MeCN	0.5 M	7.833	5.2	0.5	1.03
82	MeCN	0.5 M	8.333	1.5	0.3	1.01

References

(1) Olsén, P.; Odelius, K.; Albertsson, A.-C. *Macromolecules* **2014**, *47*, 6189.

(2) Olsén, P.; Odelius, K.; Keul, H.; Albertsson, A.-C. *Macromolecules* **2015**, *48*, 1703.