

SUPPLEMENTARY INFORMATION for

Application of online infrared spectroscopy to study the kinetics of precipitation polymerization of acrylic acid in supercritical carbon dioxide

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ESI 1

The ATR-IR device for the online monitoring of the polymerization of AA in toluene is displayed in figure S1.

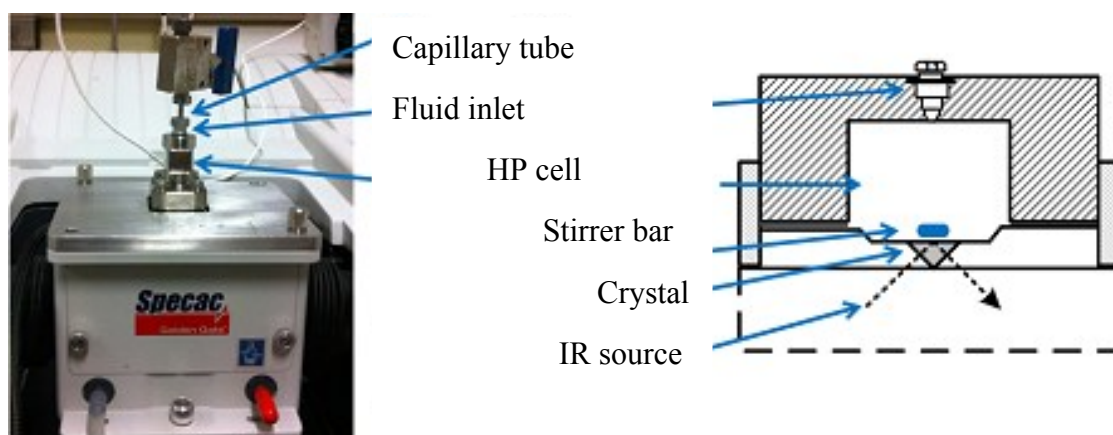


Figure S1. ATR-IR device for the online monitoring of the polymerization of AA in toluene

ESI 2

In the initial FTIR spectrum of AA in scCO₂, we observed some AA peaks at 1620, 1639, 1950 and 2664 cm⁻¹ with a good signal to noise ratio that we can use for a quantitative follow up of the monomer concentration during the polymerization. Thus in order to confirm that these peaks are specific contributions of the AA monomer, we have reported on figure S2 the evolution as a function of time of the intensity of these four peaks during a precipitation polymerization of AA performed at T=72°C, P=160 bar, [M]₀=0.128 M and [AIBN]₀=6.38 mM. It clearly appears from this figure that the same kinetic behaviour is found from these four peaks that allows to confirm that all these peaks are characteristic of AA monomer. We emphasize that at this relatively high temperature (72°C), the initial increase is related to a period of homogenization of the mixture and the following decrease is due to the AA polymerization that starts almost immediately after equilibration without any induction period.

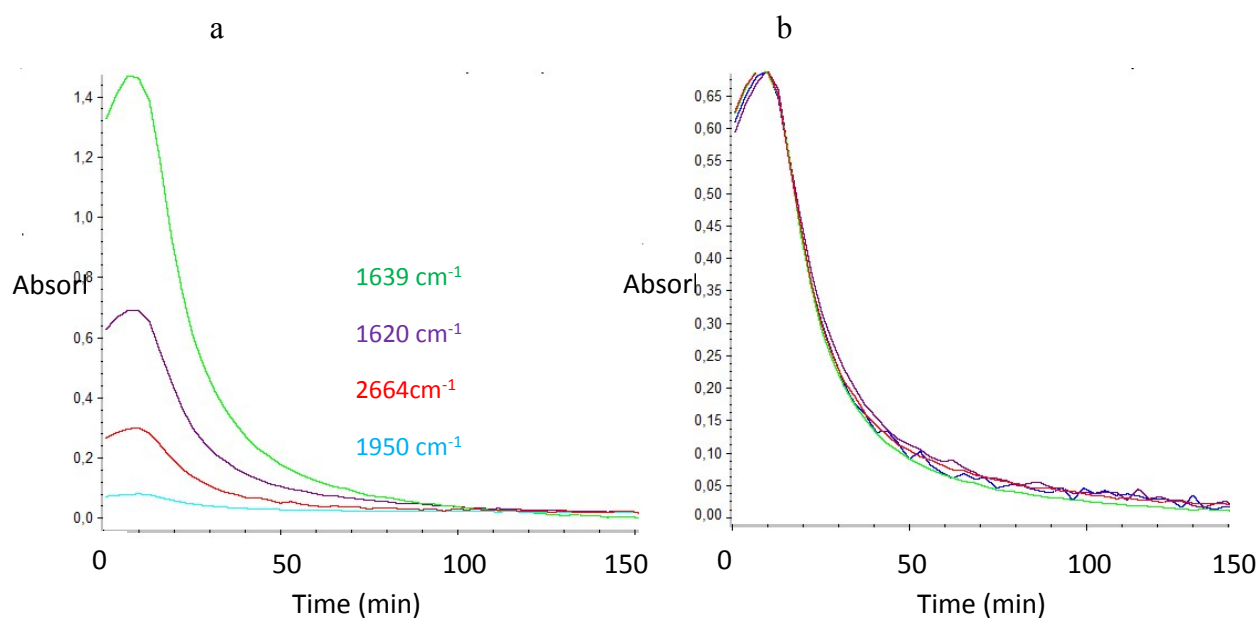


Figure S2: Kinetic monitoring with different characteristic absorption bands of AA: a) - before normalization; b) - after normalization. Experimental conditions: [M]₀=0.128 M, [AIBN]₀=6.38 mM, P = 160 bar, T = 72°C

ESI 3

Figure S3 displays the evolution as a function of time of the FTIR spectra of AA in scCO₂ at T=62°C, P=160 bar, [M]₀=0.71 M and [AIBN]₀=6.38 mM where we notice in particular the decrease of the peak around 1960 cm⁻¹ used for the analysis. However, during the precipitation polymerization, the apparition of polymer particles lead to an inhomogeneity of the mixture that is clearly indicated by a shift of the baseline of the IR spectra toward higher absorbance resulting from an increased scattering of the near infrared light.

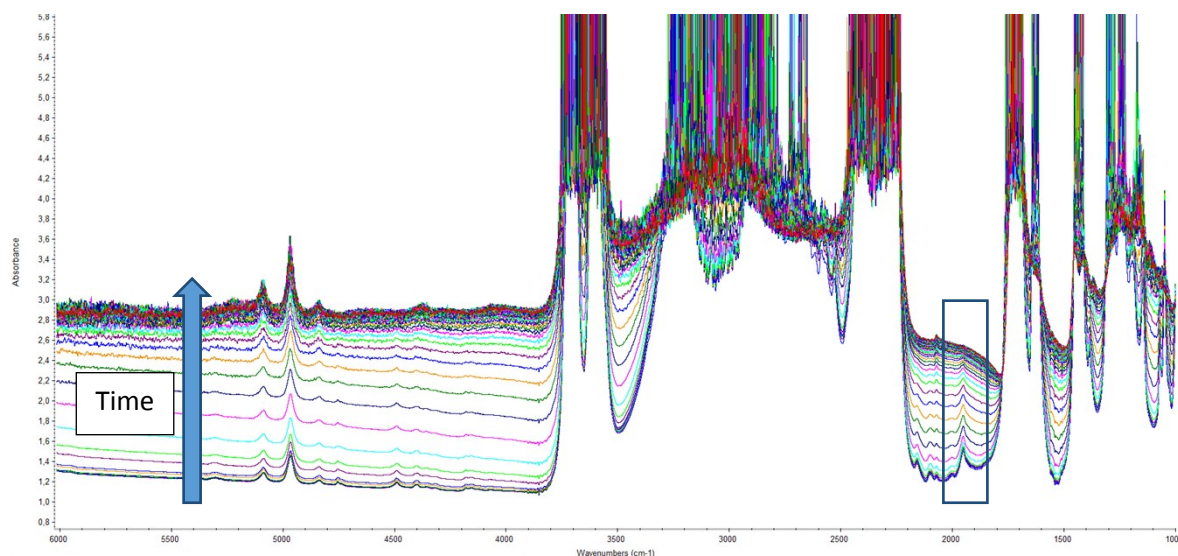


Figure S3. Change as a function of time of the FTIR spectra of AA in scCO₂ at T=62°C, P=160 bar [M]₀=0.71 M and [AIBN]₀=6.38 mM

ESI 4

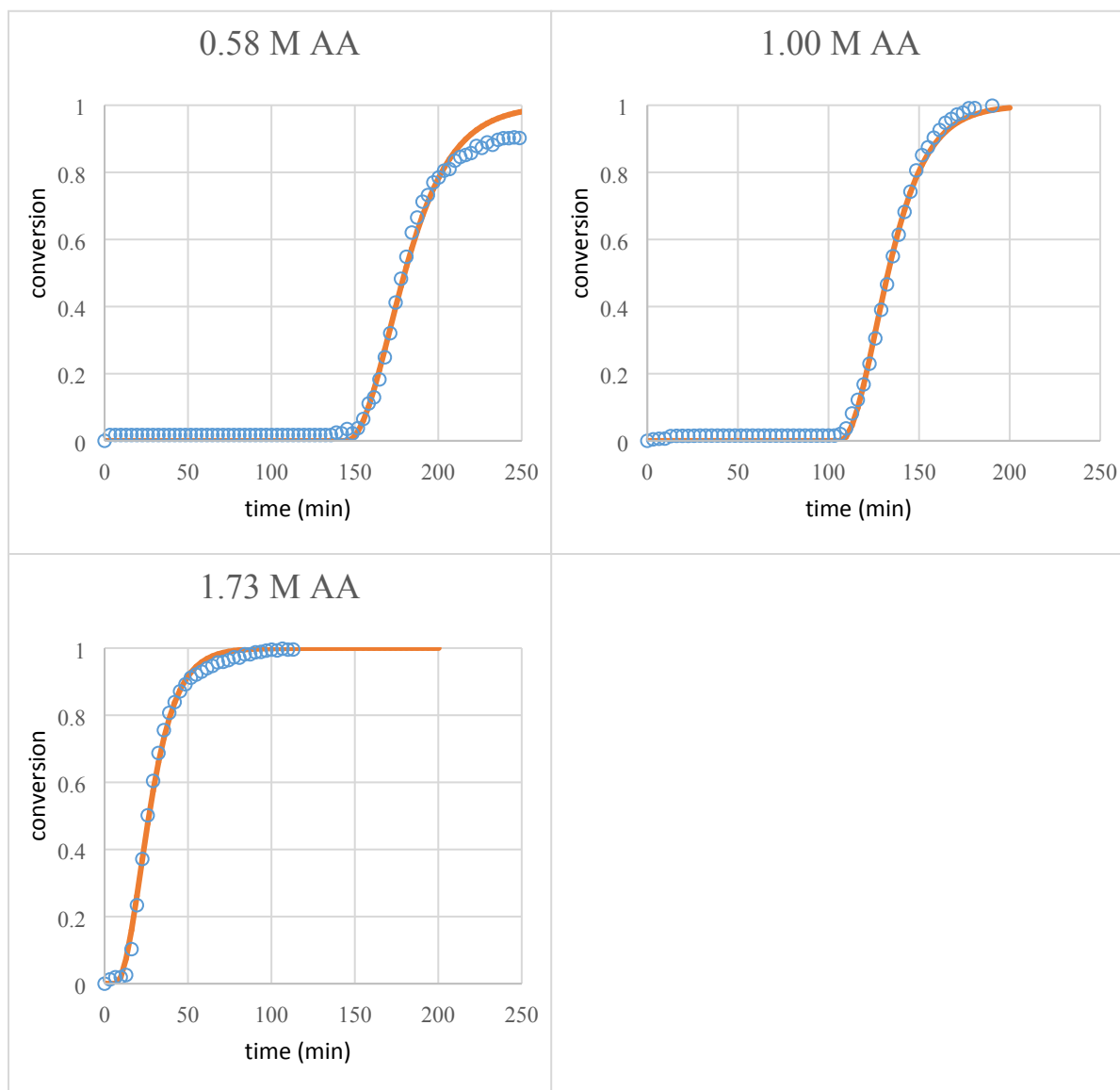
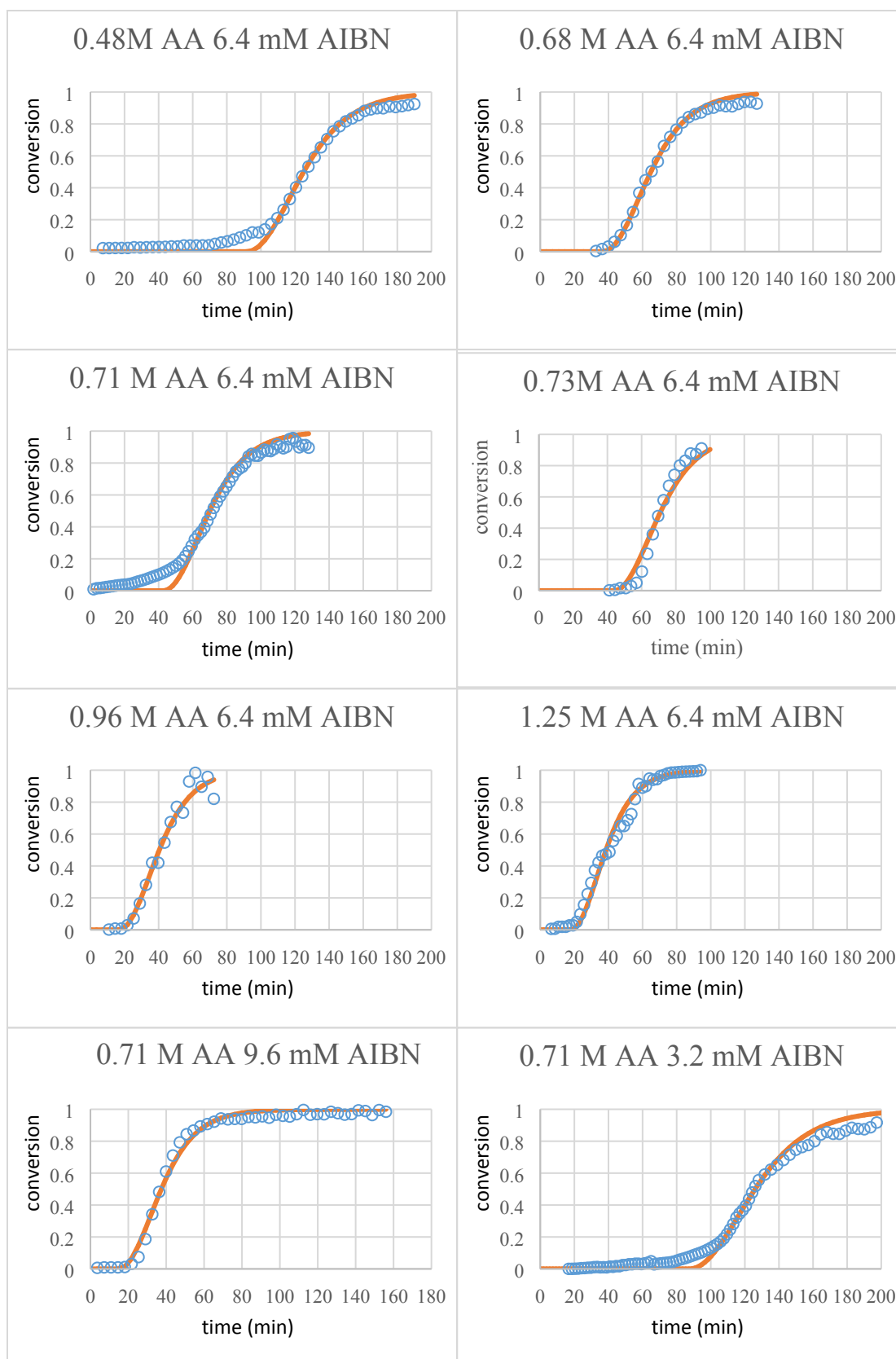


Figure S4. Combined fit to polymerizations in toluene. $k = (0.84 \pm 0.14) \times [\text{AA}]_0^{0.5} \times [\text{AIBN}]^{0.5}$. $t_i = 145 \pm 6$ (0.58 M), 106 ± 5 (1.0 M) or 6.5 ± 3.9 min (1.73 M).



ESI 5, Figure S5. Combined fit to polymerizations in scCO₂. $k = (0.96 \pm 0.11) \times [\text{AA}]_0^{0.5} \times [\text{AIBN}]^{0.5}$. $t_i = 92 \pm 7$ (0.48 M AA, 6.4 mM AIBN), 37 ± 5 (0.68 M AA, 6.4 mM AIBN), 43 ± 6 (0.71 M AA, 6.4 mM AIBN), 44 ± 4 (0.73 M AA, 6.4 mM AIBN), 17 ± 3 (0.96 M AA, 6.4 mM AIBN), 18 ± 4 (1.25 M AA, 6.4 mM AIBN), 15 ± 5 (0.71 M AA, 9.6 mM AIBN), or 87 ± 10 min (0.71 M AA, 3.2 mM AIBN).

Table S1. Parameters of the PAA synthesis in toluene and scCO₂

Solvent	[AA]₀ (M)	[AIBN]₀ (mM)	time (min)	Max. Conv.	M_w^a (kg.mol⁻¹)	Đ^a	Sample recovery^a (%)
Toluene	0.58	6.38	365	0.963	213	2.3	91
Toluene	1.00	6.38	180	0.991	407	2.5	79
Toluene	1.73	6.38	113	0.996	421	2.2	83
scCO ₂	0.48	6.38	190	0.924	781	2.2	82
scCO ₂	0.68	6.38	127	0.927	951	2.1	63
scCO ₂	0.96	6.38	72	0.958	1105	2.5	nd
scCO ₂	1.25	6.38	94	1.00	1310	2.5	nd
scCO ₂	0.71	3.20	230	0.912	1310	2.5	48
scCO ₂	0.71	6.38	128	0.896	968	2.6	57
scCO ₂	0.71	9.60	156	0.985	830	2.2	55

^a determined by aqueous SEC RI-MALS