SUPPORTING INFORMATION

ICAR ATRP for estimation of intrinsic macro-activation/deactivation Arrhenius parameters under polymerization conditions

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This Supporting Information provides more information concerning the experimental data set used for regression analysis, the strategy employed for the temperature control, the reproducibility of the measurements and the results related to tuning of the intrinsic parameters for activation of the ATRP initiator based on gas chromatography (GC) data.

1. Overview experimental data for regression analysis

Table S1: Overview of polymerization conditions covered in the experimental study of ICAR ATRP of styrene ($[Sty]_0$=8.7 M) with $CuBr_2$/TPMA as deactivator, EtBriB as ATRP initiator and AIBN as conventional radical initiator; isothermal runs; 5% DMF on a volume basis (with respect to monomer)

Entry	Initial molar ratios $[Sty]_0/[EtBriB]_0/[CuBr_2]_0/[TPMA]_0/[AIBN]_0$					ppm[a]	T(^{0}C)
	Sty	EtBriB	$CuBr_2$	TPMA	AIBN		
1	50	1	0.0005	0.0005	0.2	10	70
2	50	1	0.00125	0.00125	0.2	25	70
3	50	1	0.0025	0.0025	0.2	50	70
4	100	1	0.001	0.001	0.2	10	70
5	100	1	0.0025	0.0025	0.2	25	70
6	100	1	0.005	0.005	0.2	50	70
7	200	1	0.002	0.002	0.2	10	70
8	200	1	0.005	0.005	0.2	25	70
9	200	1	0.01	0.01	0.2	50	70
10	500	1	0.005	0.005	0.2	10	70
11	500	1	0.0125	0.0125	0.2	25	70
12	500	1	0.025	0.025	0.2	50	70
13	50	1	0.0005	0.0005	0.2	10	60
14	50	1	0.0025	0.0025	0.2	50	60
15	100	1	0.005	0.005	0.2	50	60
16	200	1	0.002	0.002	0.2	10	60
17	200	1	0.01	0.01	0.2	50	60
18	500	1	0.025	0.025	0.2	50	60
19	50	1	0.0005	0.0005	0.2	10	80
20	50	1	0.0025	0.0025	0.2	50	80
21	100	1	0.001	0.001	0.2	10	80
22	100	1	0.005	0.005	0.2	50	80
23	200	1	0.002	0.002	0.2	10	80
24	200	1	0.01	0.01	0.2	50	80
25	500	1	0.005	0.005	0.2	10	80
26	500	1	0.025	0.025	0.2	50	80
27	100	1	0.005	0.005	0.3	50	80
28	100	1	0.005	0.005	2.0	50	80

[a] ppm of Cu calculated with respect to monomer on a molar basis (ppm level: $10^6 \times [CuBr_2]_0/[Sty]_0$)

2. TEMPERATURE CONTROL

The temperature of the reaction mixture was controlled by a proportional–integral–derivative controller (PID controller). For that purpose, a thermocouple connected to the PID controlled was placed in the reactor flask. Water was employed as coolant and was pumped through a cold finger, which was put in contact with the reaction mixture to generate a localized cold surface. The temperature of the oil bath was set at a constant value and a magnetic stirrer was placed both in the reaction mixture and in the oil bath. A second thermocouple was placed in the oil bath for comparison with the one in the oil bath. Figure S.1 shows the two profiles for one experiment (entry 7, Table 1 main text), *i.e.* the temperature in the reaction flask and the temperature in the oil bath.

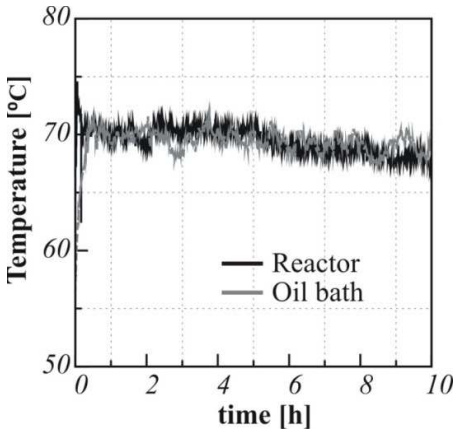

Figure S.1. Temperature profiles for the oil bath and the reaction mixture in ICAR ATRP of styrene mediated by $CuBr_2$/TPMA. (entry 7, Table 1 main text, set point oil bath: 70°C).

3. REPRODUCIBILITY

In order to attest the reproducibility of the experimental procedure gravimetrical and SEC measurements are repeated five times under fixed conditions (entry 6 in Table 1; main text) and analyzed at distinct polymerization times. As shown in Figure S.2 (trial 1-5), a relatively low averaged standard deviation (σ_{av}) value results for the evolution of the conversion, the number-average chain length (x_n) and the dispersity ($Đ$) with time. These averaged standard deviations result by calculating the mean of the standard deviation per reaction time considered.

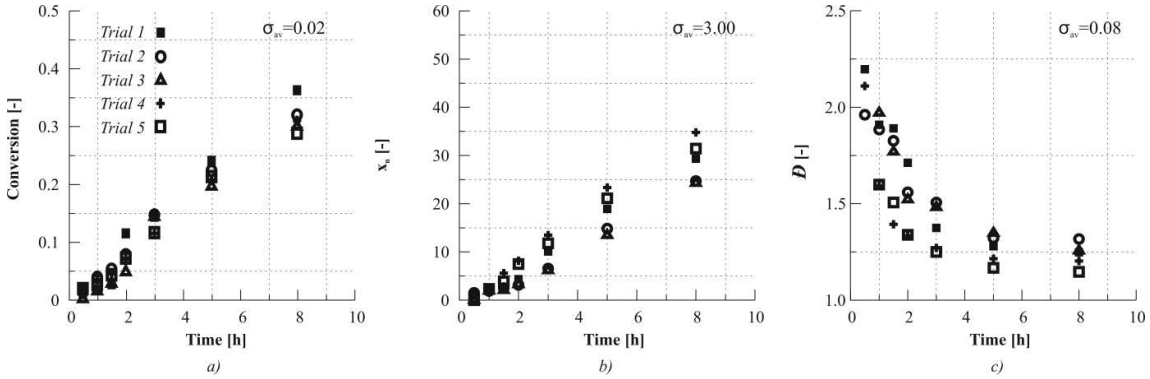

Figure S.2. Reproducibility measurements for the ICAR ATRP of styrene at 70°C; $[Sty]_0/[EtBriB]_0/[CuBr_2/TPMA]_0/[AIBN]_0$: 100/1/0.005/0.2 (Table 1; entry 6:main text); a) conversion profile determined by gravimetric analysis; b) number-average molar mass (x_n) and d) dispersity ($Đ$) determined by SEC using THF as solvent.

Next to the reproducibility of the data obtained by gravimetric analysis and SEC, the accuracy of the measured conversion profile is determined. For this purpose, the consistency of the gravimetric analysis for the determination of the monomer conversion, as compared with the data determined by GC analysis, is verified. Figure S.3 presents the results for two of the five trials in Figure S.2. Clearly, very similar results are obtained using both methods. In fact, the same σ_{av} is obtained. In the figures presented in the main text, for simplicity, only the gravimetric measured conversions are shown.

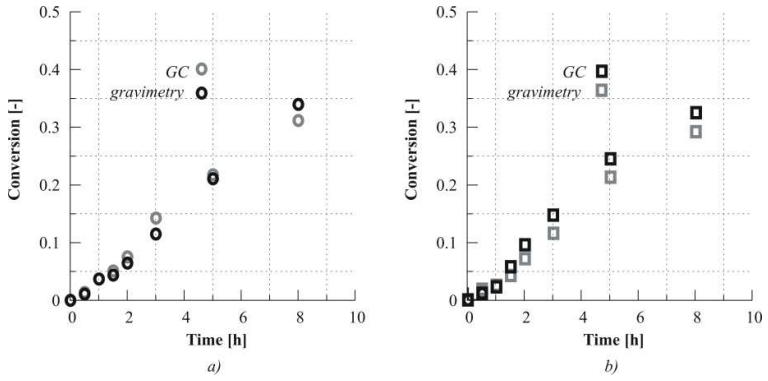

Figure S.3. Comparison of monomer conversion data obtained by GC and gravimetric analysis for ICAR ATRP of styrene (Table 1; entry 6; main text); a) trial 2 and b) trial 5 in Figure S.2; in all cases initially 5 vol% of DMF is present; for the gravimetric analysis an error bar of σ_{av}=0.02 is obtained.

4. IMPROVED ARRHENIUS PARAMETERS FOR ATRP INITIATION

The factor 3 applied for the pre-exponential factor of the ATRP initiator species was selected based on the good description of the experimental data showed in figure S5(a). Figure S5(b) shows the simulated output compared to the experimental data of EtBriB concentration under the assumption $k_{a0}^{chem} = k_a^{chem}$.

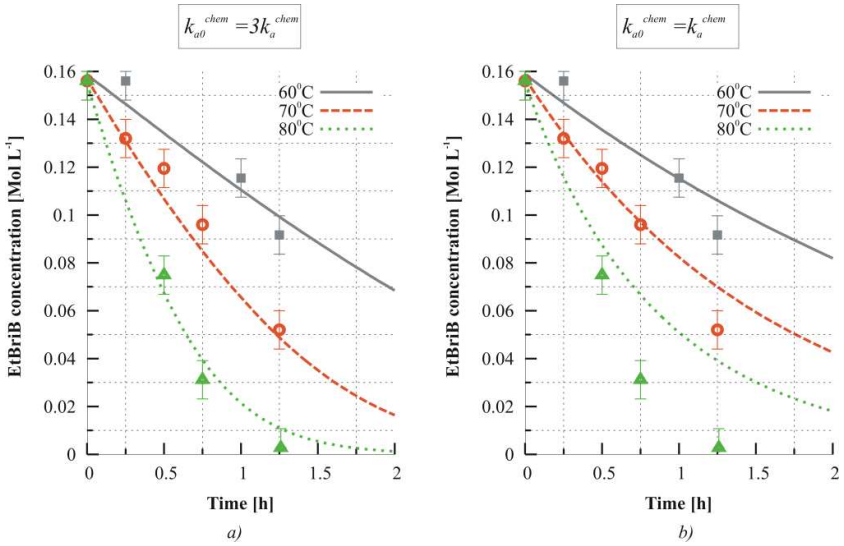

Figure S.4. ATRP initiator concentration as function of time in ICAR ATRP of styrene mediated by $CuBr_2$/TPMA at 60^0C, 70^0C and 80^0C; $[Sty]_0/[EtBriB]_0/[CuBr_2/TPMA]_0/[AIBN]_0$: 50/1/0.0005/0.2; points correspond to experimental data values (Table 1; entry 1, 13 and 19; main text) and lines correspond to simulations assuming that a) $k_{a0}^{chem} = 3k_a^{chem}$ and b) $k_{a0}^{chem} = k_a^{chem}$

5. TYPICAL GC AND GPC PROFILES

A representative GC profile is given in Figure S6 at the start of the polymerization (left) and at 65% conversion (right).

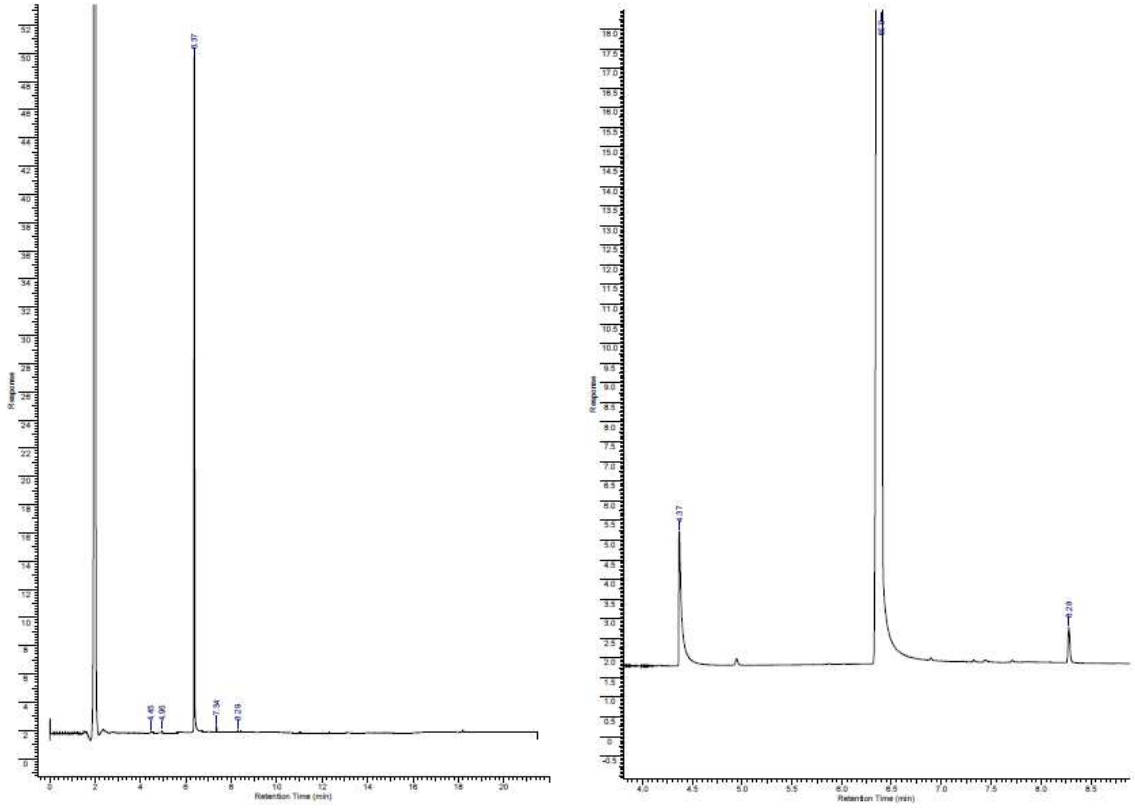

Figure S.5. GC curve at start polymerization and 65% conversion for ICAR ATRP of styrene mediated by $CuBr_2$/TPMA at 70°C; $[Sty]_0/[EtBriB]_0/[CuBr_2/TPMA]_0/[AIBN]_0$: 50/1/0.0005/0.2 (entry 3 Table S1) ; standard ~4.37 minutes; styrene: ~6.37 minutes

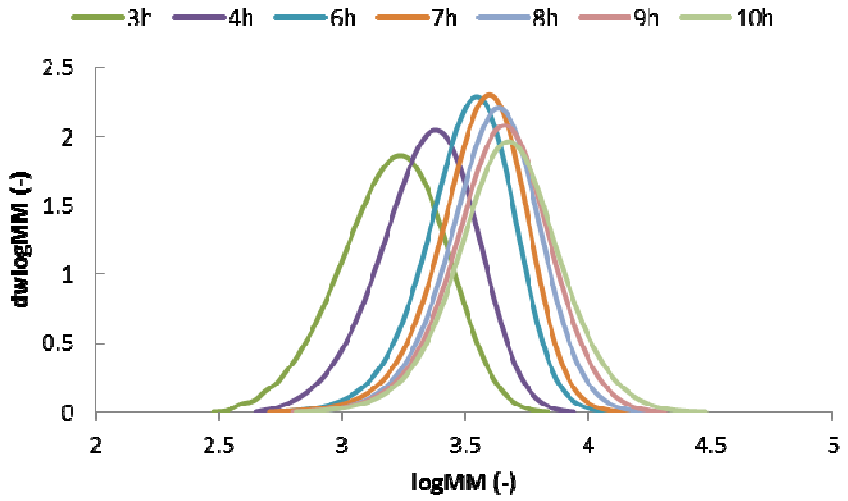

Figure S.6. Evolution of GPC curve for ICAR ATRP of styrene mediated by $CuBr_2$/TPMA at 70°C; $[Sty]_0/[EtBriB]_0/[CuBr_2/TPMA]_0/[AIBN]_0$: 100/1/0.0005/0.2 (entry 6 Table S1); standard ~4.37 minutes; styrene: ~6.37 minutes; MM: molar mass (g mol^{-1}).

6. APPARENT TERMINATION RATE COEFFICIENTS

Apparent "homo-termination" rate coefficients (equal chain lengths) as determined with the so-called composite kt model are used. The parameters of the corresponding correlations are taken from reversible addition-fragmentation chain transfer chain length dependent termination (RAFT-CLD-T) measurements at 90°C (references are given in the main text):

$$i < i_{gel} \text{ and } i < i_{SL} : k_{t,ii}^{app} = k_{t,11}^{app}\, i^{-\alpha_s}$$

$$i < i_{gel} \text{ and } i \geq i_{SL} : k_{t,ii}^{app} = k_{t,11}^{app}\, i_{SL}^{\alpha_l - \alpha_s} i^{-\alpha_l}$$

$$i \geq i_{gel} \text{ and } i < i_{SL} : k_{t,ii}^{app} = k_{t,11}^{app}\, i_{gel}^{\alpha_{gel} - \alpha_s} i^{-\alpha_{gel}}$$

$$i \geq i_{gel} \text{ and } i < i_{SL} : k_{t,ii}^{app} = k_{t,11}^{app}\, i_{SL}^{\alpha_l - \alpha_s} i_{gel}^{\alpha_{gel} - \alpha_l} i^{-\alpha_{gel}}$$

$$i_{gel} = 0.55 w_p^{-2.5}$$

$$\alpha_{gel} = 1.66 w_p - 0.06$$

For apparent "cross-termination" rate coefficients (different chain lengths) following calculation is performed:

$$k_{t,ij}^{app} = \sqrt{k_{t,ii}^{app} k_{t,jj}^{app}}$$