

## Supplementary material

### Data reduction of the kinetic recordings of the exhausted isobutene from thermal deprotection at different temperatures

In order to investigate the kinetics of thermolysis of grafted *tert*-butyl esters, The isobutene release from the grafted silica in an oven under argon carrier gas at 248°C, 265°C, and 290°C was measured as a function of time by recording the signal of a FID detector directly connected to the oven exhaust. The detector signal provided a measurement of the instantaneous quantity of isobutene released as a function of time:  $\frac{d[\text{isobutene}]}{dt}$ .

After the cold crucible containing the silica sample has been introduced in the hot oven and a delay corresponding to the dead volume of the transfer tubing, The FID detector signal started a transient step as the sample was heating up to the control setting, and finally provided a decaying signal showing the reaction kinetics when the sample reached the constant temperature of the oven. The delay was slightly less than 10 minutes. The recorded signal was given in arbitrary units. Although the experimental conditions (gas flow rate, FID detector settings) were identical for each record, the detector sensitivity might slightly vary when it measured gases flows at different temperatures. The decaying part of the signal was exponential, showing that the kinetics was first-order with respect to *tert*-butyl ester. The measured signal significantly departed from the exponential decay of first-order kinetics at long time for the record at 290°C. The measured signal was above the theoretical exponential, showing that supplementary materials evolving from the thermal degradation of the grafts was observed in this case. Owing to the first-order kinetics (Eq 4), the FID signals were normalized by the area under the curve that gives the total amount of release isobutene related to the starting concentration [ester](0). Equation S1 giving the detector signal (*FID*) as a function of time contains a pre-factor *A* that depends on the detector sensitivity

$$FID = A \times k \times [\text{ester}](0) \times e^{-kt} \quad (\text{Eq S1})$$

The area under the curve is  $\int_0^{\infty} FID dt = A \times [\text{ester}](0)$ , so that the normalization of the recorded signal by the area removes the instrumental constant *A* and the total concentration of ester on the surface [ester](0):

$$\text{Normalized signal} = \frac{FID}{\int_0^{\infty} FID dt} = k e^{-kt} \quad (\text{Eq S2})$$

Calculation of the area under the curve made of equally spaced data points was done using a numerical integration by the classical trapezoidal rule. Precise knowledge of starting time  $t = 0$  was not necessary since the signal was zero at the beginning. The records ended at a final time,  $t_{\text{max}}$ , so that the data was truncated at large time. According to the first-order kinetics, the missing area is

$$\int_{t_{\text{max}}}^{\infty} FID dt = A \times [\text{ester}](0) \times e^{-kt_{\text{max}}} \quad (\text{Eq S3})$$

Its contribution to the normalization factor is  $e^{-kt_{\text{max}}}$ , which is a truncation error of less than 2% of the full area according to the present data and rate constant derived from the slope of the semi-log plot. This correction has been neglected. The recorded signals after normalization with respect to the area are shown in Figure 8 of the main text.

The precise definition of the starting time  $t = 0$  was done from the recorded signal itself. The cumulated signal,  $Int$ , is

$$Int(t) = \frac{\int_{t_{\min}}^t FID \, dt}{\int_{t_{\min}}^{t_{\max}} FID \, dt} \approx \frac{\int_0^t FID \, dt}{\int_0^{\infty} FID \, dt} = 1 - e^{-kt} \quad (\text{Eq S4})$$

A plot of  $\ln[1-Int(t)]$  as a function of  $t$  is linear in the decaying part of the FID signal and the extrapolation of the linear part to  $\ln[1-Int(t)] = 0$  (to  $Int(t) = 0$ ) provides an experimental determination of  $t = 0$  as shown in Figure S1. Departure from the first-order kinetics is observed for long times at 290°C.

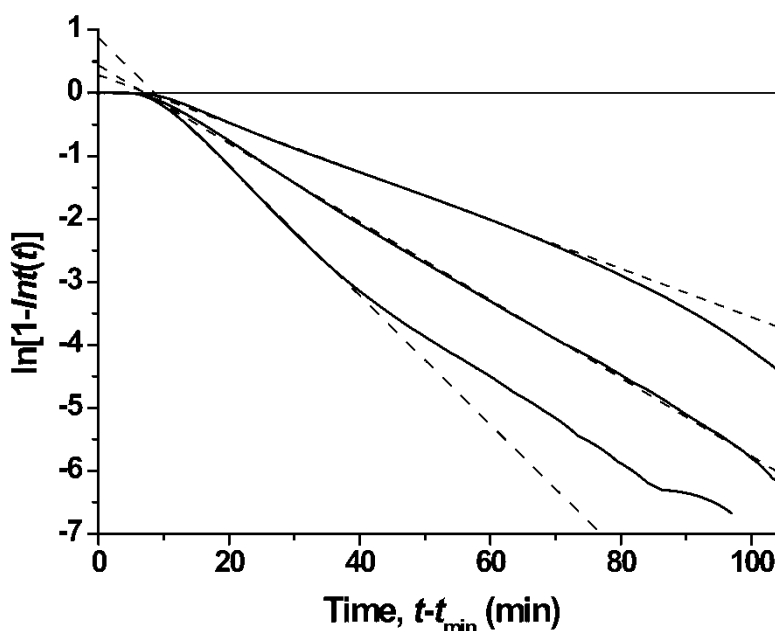


Figure S1: Plot of  $\ln[1-Int(t)]$  as a function of time between  $t_{\min}$  and  $t_{\max}$ , and extrapolation of the linear part (dashed lines) to  $Int(t) = 0$ . From top to bottom, 248°C, 265°C, 290°C.

The plot of  $\ln(\text{Normalized signal})$  vs  $t$  gives  $k$  from the slope and  $\ln k$  as the extrapolation to the starting time  $t = 0$  (Figure S2); the slope of  $\ln[1 - Int(t)]$  vs  $t$  (Figure S1) also gives  $k$ . The three following determinations of  $k$  agreed with each other within  $\pm 5\%$ .

Figure S2: Plot of  $\ln(\text{Normalized signal})$  as a function of time for the kinetics at 3 temperatures 248°C, 265°C, and 290°C (from top to bottom).

Table S1. Starting times and the three independent determinations of the rate constants.

Temperature (°C)	Starting time (min)	Rate constant, $k$ (s <sup>-1</sup> )		
		slope of $\ln(FID)$ vs $t$	extrapolation to $t = 0$ of $\ln(FID)$ vs $t$	slope of $\ln(1-Int)$ vs $t$
248	7.46	0.0061	0.0063	0.0064
265	7.05	0.0103	0.0104	0.0103

290	8.58	0.0018	0.0019	0.0017
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