

## Supplementary information

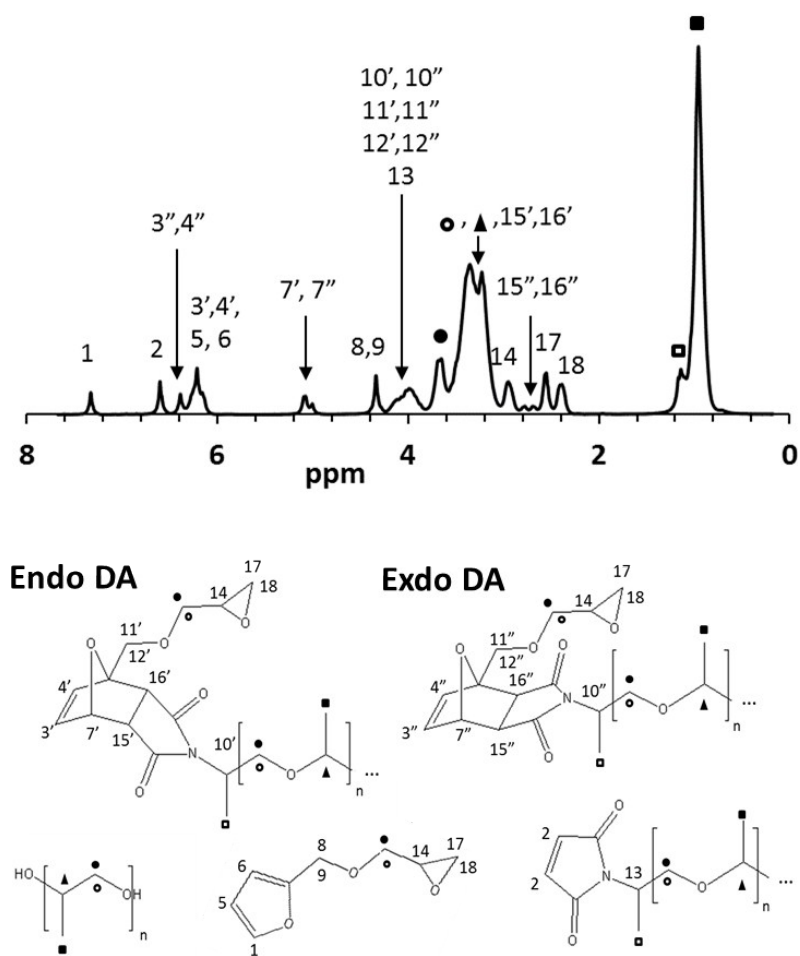


Figure 1: Peak assignment on FGE-M400-PPG425 liquid <sup>1</sup>H NMR spectrum (without solvent) taken after 1 h of reaction at 56.6 °C. Peak assignments were done combining ChemDraw predictions and literature<sup>1,2</sup>.

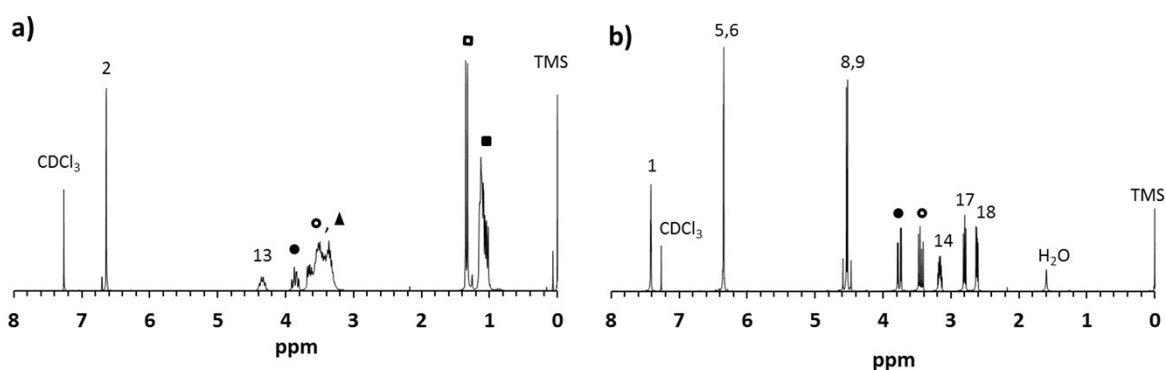


Figure 2: Peak assignment of the monomers: a) M400 and b) FGE.

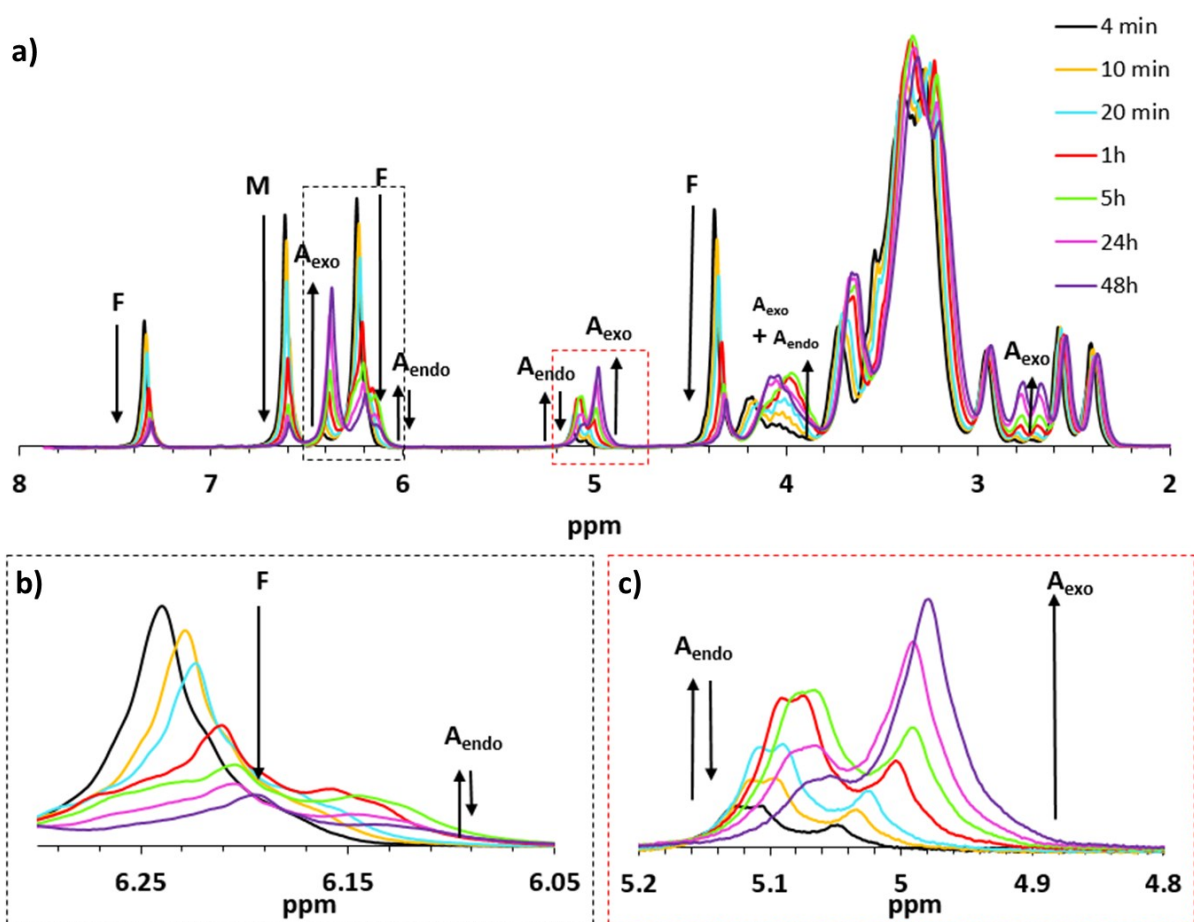
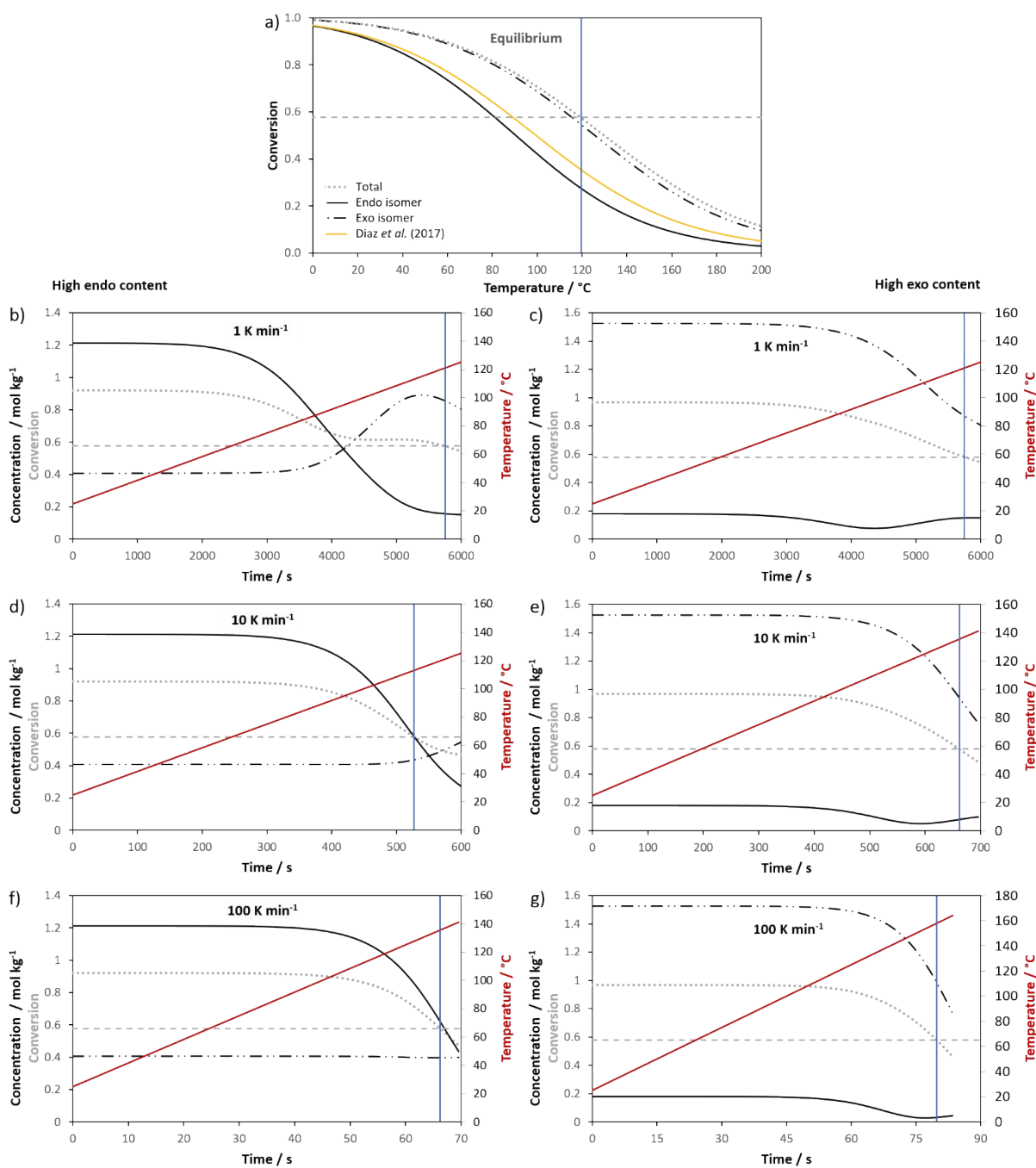


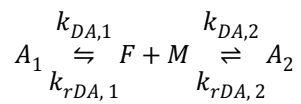
Figure 3: a) Overlay of the FGE-M400-PPG425 liquid <sup>1</sup>H NMR spectra as a function of time with indication of the main changes in peak intensity with arrows due to the decrease in FGE (F) and M400 (M) during reaction, the rapid increase followed by a decrease in endo adduct ( $A_{\text{endo}}$ ) and the increase in exo adduct ( $A_{\text{exo}}$ ) with b) zoomed in on the section between 6.05 and 6.30 ppm and c) zoomed in on the section between 4.80 and 5.20 ppm.

The overlay is only shown between 2 and 8 ppm since the peak at 1 ppm does not change intensity and not taking that one into account allows zooming more on the peaks with lower intensity seeing the spectra in more detail.



**Figure 4:** The total Diels-Alder conversion (grey dots) and concentrations of the endo (black solid lines) and exo (black dash double dotted lines) isomers are simulated of various temperature programmes: a) equilibrium; b) and c) heating at 1 K min<sup>-1</sup>; d) and e) heating at 10 K min<sup>-1</sup>; f) and g) heating at 100 K min<sup>-1</sup>. The equilibrium simulation includes a comparison to the theoretical pure endo (black solid line) and pure exo (black dash double dotted line) isomer kinetics and to the kinetics based on the parameters from Diaz *et al.* 2017 (yellow). The blue lines in all graphs denoted the gel transition, where the total conversion (grey dotted lines) crosses the gel conversion line (grey horizontal dashed line).

Derivation of the equation for the total equilibrium Diels-Alder conversion:



$$\frac{d[F]}{dt} = \frac{d[M]}{dt} = -\frac{d[A_1]}{dt} = -\frac{d[A_2]}{dt} = -k_{DA,1}[F][M] - k_{DA,2}[F][M] + k_{rDA,1}[A_1] + k_{rDA,2}[A_2]$$

For  $r = [M]/[F] = 1$ :

$$K_{tot} = K_1 + K_2 = \frac{[A_1]_e + [A_2]_e}{[F]_e[M]_e} = \frac{x_{eq}}{(1 - x_{eq})^2 [F]_0}$$

$$x_{eq} = \frac{2K_{tot}[F]_0 + 1 - \sqrt{(2K_{tot}[F]_0 + 1)^2 - 4K_{tot}^2[F]_0^2}}{2K_{tot}[F]_0}$$

Derivation of the chemical relaxation time constant for the formation of two stereoisomer adducts, following two parallel, dependent Diels-Alder reactions:

*Perturbation on the concentrations:*  $\Delta[A_1] + \Delta[A_2] = -\Delta[F] = -\Delta[M]$

$$\frac{d([F]_e + \Delta[F])}{dt} = \frac{d([M]_e + \Delta[M])}{dt} = -\frac{d([A_1]_e + \Delta[A_1])}{dt} - \frac{d([A_2]_e + \Delta[A_2])}{dt}$$

$$-\frac{d([A_1]_e + \Delta[A_1])}{dt} - \frac{d([A_2]_e + \Delta[A_2])}{dt} = -(k_{DA,1} + k_{DA,2})([F]_e + \Delta[F])([M]_e + \Delta[M]) + k_{rDA,1}([A_1]_e + \Delta[A_1]) + k_{rDA,2}([A_2]_e + \Delta[A_2])$$

$$-\frac{d[A_1]_e}{dt} - \frac{d\Delta[A_1]}{dt} - \frac{d[A_2]_e}{dt} - \frac{d\Delta[A_2]}{dt} = -(k_{DA,1} + k_{DA,2})([F]_e[M]_e + k_{rDA,1}[A_1]_e + k_{rDA,2}[A_2]_e - (k_{DA,1} + k_{DA,2})([F]_e\Delta[M] + [M]_e\Delta[F] + \Delta[F]\Delta[M]) + k_{rDA,1}\Delta[A_1] + k_{rDA,2}\Delta[A_2])$$

$$\text{with } -\frac{d[A_1]_e}{dt} - \frac{d[A_2]_e}{dt} = -(k_{DA,1} + k_{DA,2})([F]_e[M]_e + k_{rDA,1}[A_1]_e + k_{rDA,2}[A_2]_e)$$

and for small perturbations:  $\Delta[A_i] \ll [A_i]$

$$-\frac{d\Delta[A_1]}{dt} - \frac{d\Delta[A_2]}{dt} = (k_{DA,1} + k_{DA,2})([F]_e + [M]_e)(\Delta[A_1] + \Delta[A_2]) + k_{rDA,1}\Delta[A_1] + k_{rDA,2}\Delta[A_2]$$

$$\tau_{DA} = -\frac{\Delta[A_1] + \Delta[A_2]}{\frac{d\Delta[A_1]}{dt} + \frac{d\Delta[A_2]}{dt}} = \frac{1}{(k_{DA,1} + k_{DA,2})([F]_e + [M]_e) + \frac{k_{rDA,1}\Delta[A_1] + k_{rDA,2}\Delta[A_2]}{\Delta[A_1] + \Delta[A_2]}}$$

For mechanical perturbation:  $\frac{\Delta[A_1]}{\Delta[A_2]} = \frac{K_1}{K_2}$  \*

$$\tau_{DA} = \frac{1}{(k_{DA,1} + k_{DA,2})([F]_e + [M]_e) + \frac{k_{rDA,1}K_1 + k_{rDA,2}K_2}{K_1 + K_2}}$$

\* This assumption is reasonable for mechanical activation of the Diels-Alder adduct bonds with sufficient mechanical force to break both isomer adducts without discrimination, in equilibrium conditions.

## References

- 1 J. Canadell, H. Fischer, G. De With and R. A. T. M. Van Benthem, *J. Polym. Sci. Part A Polym. Chem.*, 2010, **48**, 3456–3467.
- 2 B. Froidevaux, V. , Borne, M. , Laborbe, E. , Auvergne, R. , Gandini, A. , Boutevin, *RSC Adv.*, 2015, **5**,

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