Tools for the design of **Diels-Alder** based reversible polymer systems: Reactivity and reversibility of **Furan/Maleimide adducts**

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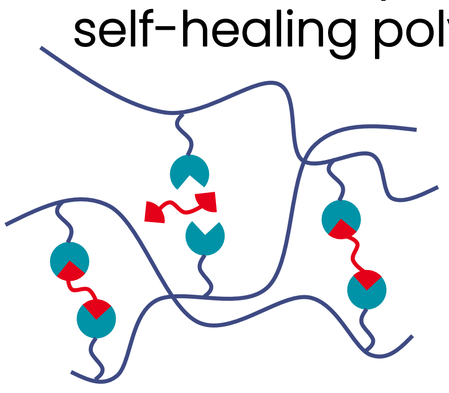
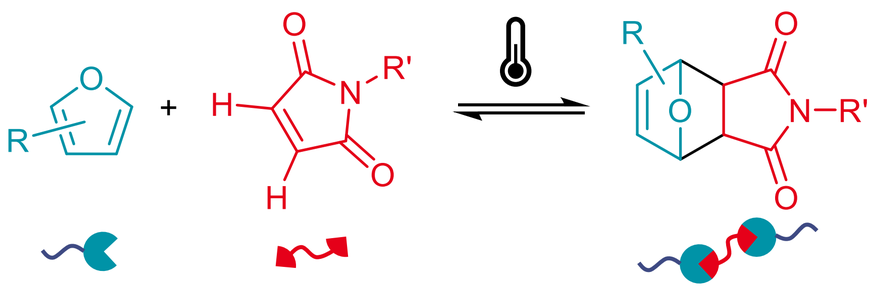
Temperature-stimulated recycling and self-healing polymeric materials



Covalent Adaptable Networks (CAN)[1]

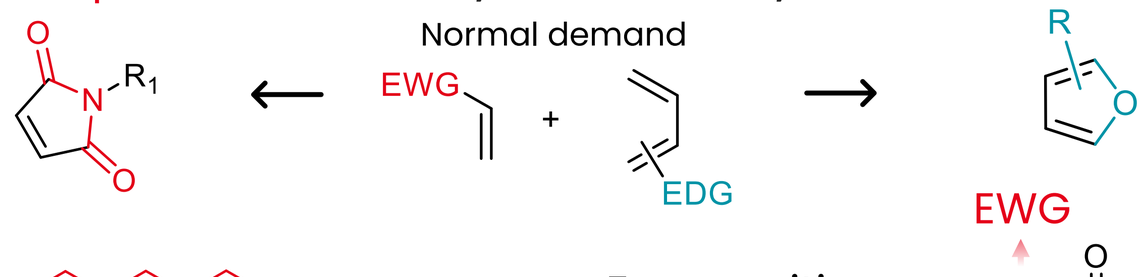
Dynamic Covalent Chemistry (DCC)[2]
Diels-Alder Furan/Maleimide (FMDA)

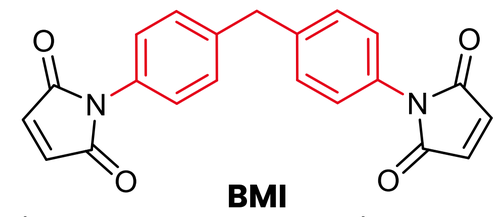


Linear polymers can carry grafted furans that can then react reversibly with a bismaleimide to form a CAN.
⟶ How to select the perfect furan/maleimide duo for your CAN application?

Reactivity/Reversibility[3,4]

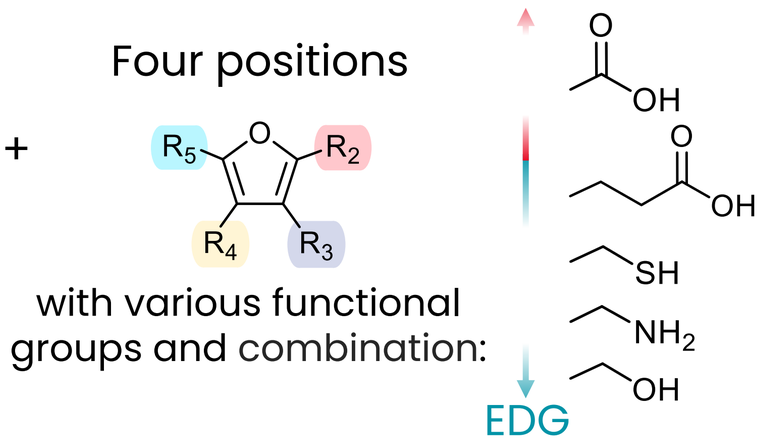
Dienophile ← Normal demand → Diene



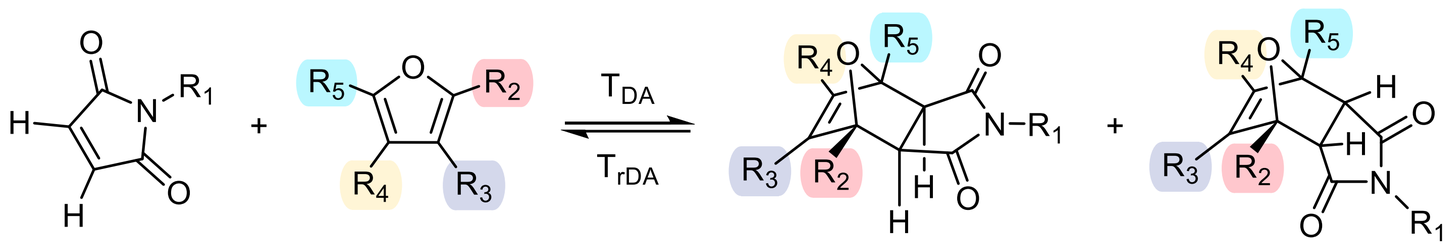


BMI
1,1'-(methylenedi-4,1-phenylene)bismaleimide

Self-polymerization at high temperature (T>80 °C)
(Radical inhibitor in addition)

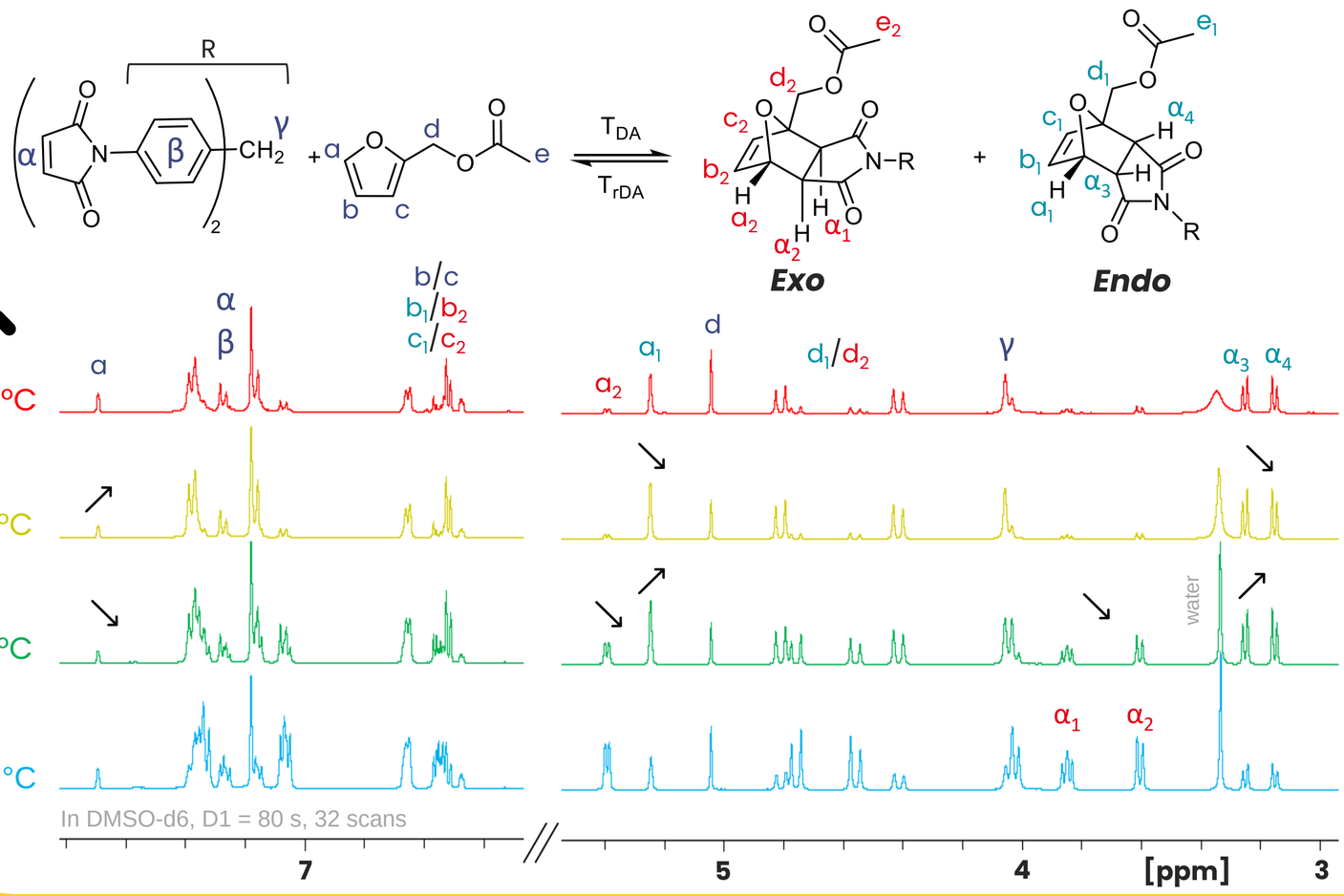


Temperature dependent chemical equilibrium

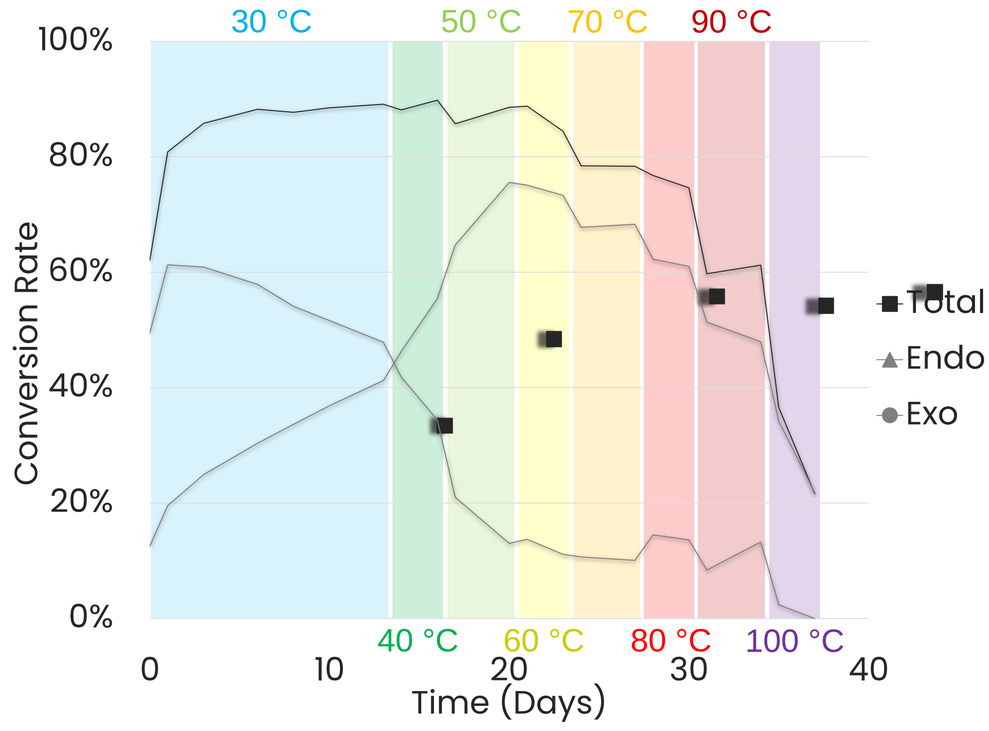


^{1}H-NMR enables monitoring of the equilibrium :

Each Furan are solubilized with BMI (2/1) in DMSO-d_6. The mixtures are maintained at different temperatures until equilibrium and each samples are analyzed by ^{1}H-NMR.

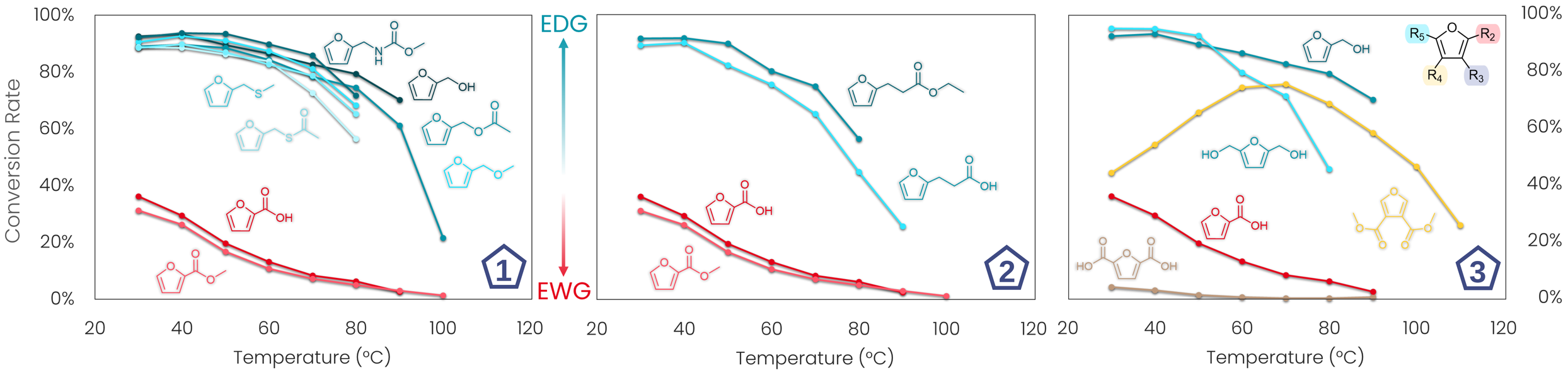


Peaks' integrations enable the determination of the conversion rate at each temperature:



The *Endo* adduct is the first obtained ($T_{DA_{endo}} < T_{DA_{exo}}$) but is less stable than the *Exo* adduct. It is progressively replaced by the *Exo* adduct with time and/or temperature ($T_{rDA_{endo}} < T_{rDA_{exo}}$).

Results and discussion



Under these experimental conditions (30°C to 110°C) and considering that a sufficient quantity of non-reacting BMI can lead to the formation of a gel from 80°C, we observe:

1. Furans with EDG are more reactive and stable than EWG:
   - Higher T_{rDA}
   - Higher conversion rate.

   The grafting function does not change reactivity.
2. The low reactivity of the acid can be compensated by increasing carbon number between function and furan cycle, thus increasing the EDG property.
3. Impact of position and number of functions: Adding a 2nd function in 5-position reduces T_{rDA}
   - In the case of the -CH_2-OH group, the conversion rate is not reduced.
   - For the acid:
     - In 2,5-position, reactivity is near zero.
     - In 3,4-position, the conversion rate is greatly increased, with T_{rDA} from 80°C.

Conclusions:

Importance of the furan selected to adapt the reversibility property and the cross-linking density *vs* T according to the application:

- EDG: high conversion rate, slow reversibility
- EWG: total reversibility, low conversion rate
- Number/position of functions allow to tune T_{DA}/T_{rDA} and conversion rates.

1. Bowman *et al*, Polym. Chem., 2020
2. Rowan *et al*, Angew. Chem., 2002
3. Froidevaux *et al*, RSC Adv., 2015
4. MacKinnon *et al*, Macromolecules, 2024

Article writing in progress

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