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# Designing End-of-Life Recyclable Polymers via Diels–Alder Chemistry: A Review on the Kinetics of Reversible Reactions

Paul van den Tempel, Francesco Picchioni, and Ranjita K. Bose\*

The purpose of this review is to critically assess the kinetic behavior of the furan/maleimide Diels–Alder click reaction. The popularity of this reaction is evident and still continues to grow, which is likely attributed to its reversibility at temperatures above 100 °C, and due to its biobased “roots” in terms of raw materials. This chemistry is used to form thermoreversible crosslinks in polymer networks, and thus allows the polymer field to design strong, but also end-of-life recyclable thermosets and rubbers. In this context, the rate at which the forward reaction (Diels–Alder for crosslinking) and its reverse (retro Diels–Alder for decrosslinking) proceed as a function of temperature is of crucial importance in assessing the feasibility of the design in real-life products. Differences in kinetics based from various studies are not well understood, but are potentially caused by chemical side groups, mass transfer limitations, and the analysis methods being employed. In this work, all the relevant studies are attempted to be placed in perspective with respect to each other, and thereby offer a general guide is offered on how to assess their recycling kinetics.

thermoreversible click reactions can form and break crosslinks with temperature control. Two popular click reactions are the thiol-ene reaction<sup>[2,3]</sup> and the Diels–Alder (DA) cycloaddition. One particularly popular DA reaction used for this purpose, is the 4 + 2 cycloaddition between maleimide and furan groups. The first reason for its wide usage is assigned to the fact that both maleimide and furan groups are biobased. They can be derived from furfuryl aldehyde, a platform chemical that is abundantly available via oxidation of lignocellulosic biomass.<sup>[4–6]</sup> The maleimide is obtained by first oxidizing furfuryl aldehyde into maleic anhydride, followed by the addition of a maleic anhydride to a primary amine.<sup>[7]</sup> The facile implementation of DA chemistry to polymeric structures is another reason for its popularity. For example, it has been demonstrated how relatively simple modification steps can incorporate furan and maleimide moieties in existing

biobased polymers, such as oils,<sup>[8,9]</sup> chitosan,<sup>[10,11]</sup> gelatin,<sup>[12]</sup> and cellulose.<sup>[13]</sup>

The [4 + 2] cycloaddition between maleimide and furan is shown in **Figure 1**. This DA reaction results in two stereochemically different adducts, known as the endo and exo adduct.


Perhaps the most appealing feature of this specific reaction is the reversible character at mildly elevated temperatures and the fact that it happens at a relatively fast rate compared to other DA reactions.<sup>[14,15]</sup> This is conveniently caused by the planarity of the furan molecule and as it is an electron-rich diene. What stimulates this reaction even more is the electron-deficiency of the bismaleimide double bond and the lack of steric hindrance.<sup>[16]</sup> The building blocks for such materials can vary in functionality and structure but should contain materials with at least three functional groups to form an interconnected network. **Figure 2** illustrates the cradle-to-cradle principle that is an ultimate research goal in this field, with the aim to have a minimal loss of material strength after several recycling steps. The challenge here is to limit or even prevent irreversible side reactions that could harm the reversible character or mechanical properties of these materials.

This chemistry has the potential to be very useful in many applications, such as soft robotics,<sup>[11]</sup> biomedical devices,<sup>[10,12]</sup> slow-release systems,<sup>[17]</sup> and self-healing protective coatings.<sup>[18–21]</sup> In the field of composite and nanocomposite materials, thermally reversible matrices may enhance filler recovery (reinforced fibers) and of the matrix itself.<sup>[22–25]</sup>

## 1. Introduction

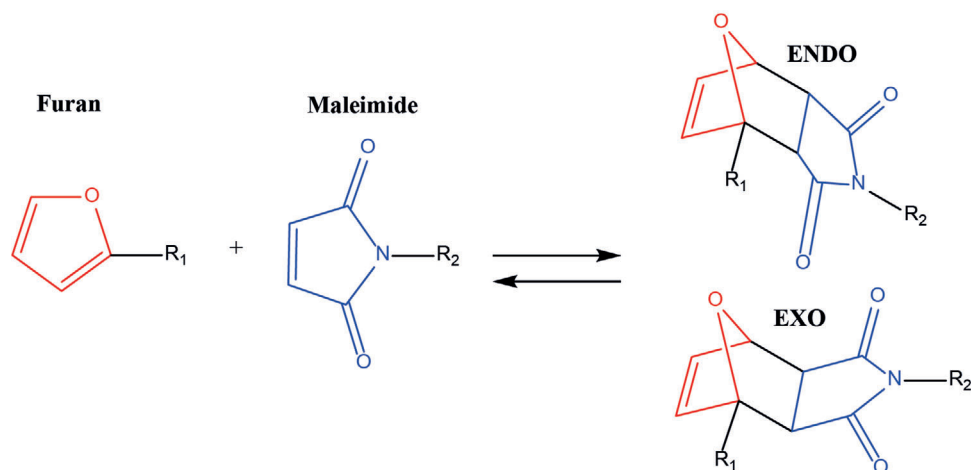
Thermosets are a class of polymers that are highly crosslinked and typically mechanically strong and stiff from a mechanical point of view. There is no doubt that these materials are vital for the modern society. But in contrast to the goal of having a circular economy, these conventional thermosets cannot be easily recycled without heating them to degradation temperatures, or using them as fillers after grinding. However, the use of thermoreversible click reactions allows the end-of-life recycling of strong thermosets. Click reactions are carbon-economical, meaning that they do not produce extra products, or require any other reactants.<sup>[1]</sup> With clever design of a polymer network,

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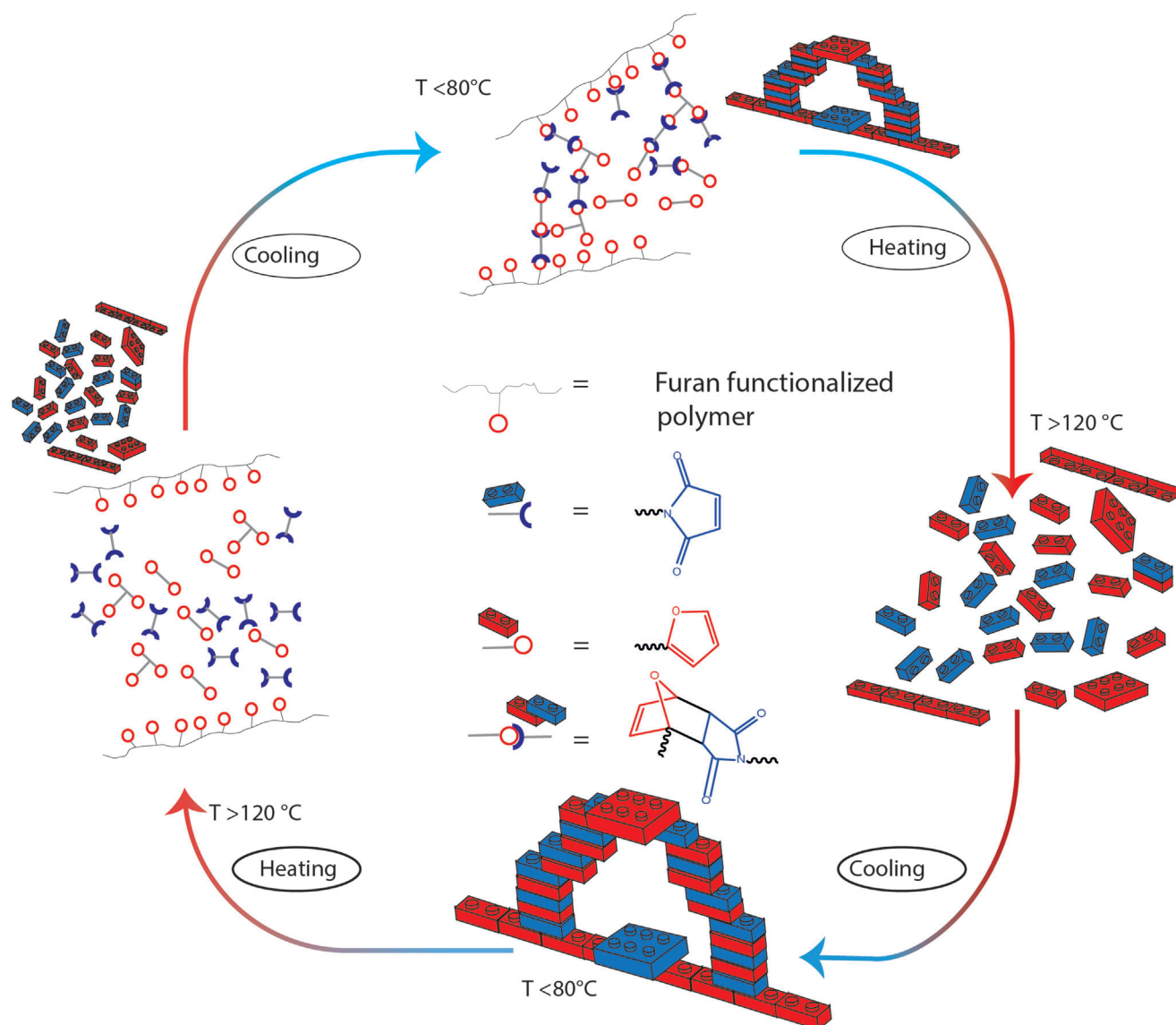
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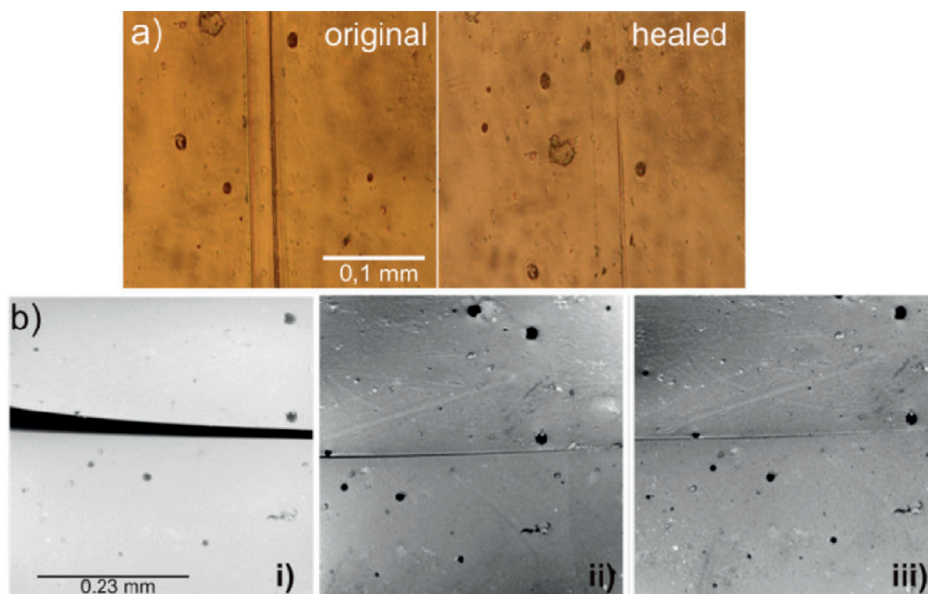
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**Figure 1.** The reaction between a furan and maleimide group.





**Figure 3.** Self-healing study of crosslinked polymer: a) Optimal microscopy of a sample cut with a razorblade (left) and the sample after one day of healing at 50 °C (right). b) Scanning electron microscope images at the healing site of i) the original scratch, ii) the scratch after one day at 50 °C, and iii) scratch after heating at 100 °C for 1 h followed by one day heating at 50 °C. Reproduced with permission.<sup>[35]</sup> Copyright 2014, American Chemical Society.

Naturally, it is also an emerging area of research in processing methods such as extrusion, molding, and additive manufacturing.<sup>[2,26–30]</sup> Several studies also demonstrate their self-healing ability via scratch healing tests (**Figure 3**), albeit requiring mild heating at the damage site.<sup>[31–38]</sup> The self-healing occurs due to the ability to create new covalent bonds at elevated temperatures combined with sufficient chain mobility.

In other words, the potential of furan/maleimide click chemistry in high performance applications is evident. However, an in-depth understanding of the kinetics of the Diels–Alder reaction in polymeric materials is required in order to exploit the thermoreversibility of crosslinked materials to the fullest. The thermal history of said materials critically determines the conversion of the reaction, which is directly linked to material performance. We especially need a clear and accurate view of these kinetics for polymer processing techniques, where reshaping with rapid heating and cooling cycles are playing a key role.<sup>[27]</sup> To the best of our knowledge, a comparable study that is fully dedicated to furan/maleimide Diels–Alder kinetics has not been reported so far. Therefore, we discuss the latest developments in understanding the kinetics of the DA reaction and also critically assess the recent work to push this field further in its path.

### 1.1. Kinetic Equations

The mass balance equations are used to describe and simulate the course of the DA reaction. Despite the fact that most papers consider a stoichiometric ratio of maleimide and furan, here we set up equations for the scenario where this is not necessarily the case. Equation (1) is the mass balance for a furan/maleimide system, with  $[F]$ ,  $[M]$  and  $[A]$  the concentrations of, furan, maleimide, and the cycloadduct respectively. The reaction is first order in

both furan and maleimide.<sup>[32]</sup> Some studies report a total second order fit, but this is only valid for the condition where the initial maleimide concentration equals the furan concentration.<sup>[14,39]</sup>

$$\frac{d[M]}{dt} = -k_{da} [M][F] + k_{rda} [A] \quad (\text{molL}^{-3}\text{s}^{-1}) \quad (1)$$

In this equation,  $k_{da}$  and  $k_{rda}$  are the forward and backward kinetic constant. Note here that we do not distinguish between rates of formation of endo- and exo adducts, although some studies do separate the two rates of formation.<sup>[27,40,41]</sup> We express all concentrations in terms of conversion by applying Equations (2) and (3). In this case, we express the conversion  $x$  for maleimide. We also introduce the addition ratio  $r$ , which is the ratio of the initial molar concentrations of both groups ( $r = [M]_0/[F]_0$ ).

$$x = \frac{[M]_0 - [M]}{[M]_0} \quad (2)$$

$$[M]_0 - [M] = [F]_0 - [F] = [A] \quad (3)$$

Note that the conversion of furan might not necessarily be the same as the conversion of maleimide. They are different when nonstoichiometric amounts are added, or when making allowances for possible side reactions.<sup>[42]</sup> By combining the equations we obtain Equation (4), a relation for the change of maleimide conversion over time.

$$\frac{dx}{dt} = k_{da}[M]_0(1-x) \left( \frac{1}{r} - x \right) - k_{rda}x \quad (4)$$

This equation can be analytically solved for the equilibrium condition, by considering that the change of conversion approaches a value of zero at equilibrium. The resulting quadratic

equation is subsequently solvable for the equilibrium maleimide conversion (Equation (5)).

$$x_{\text{eq}} = \frac{\left(1 + \frac{1}{r} + \frac{k_{\text{rda}}}{k_{\text{da}}[M_0]}\right) - \sqrt{\left(1 + \frac{1}{r} + \frac{k_{\text{rda}}}{k_{\text{da}}[M_0]}\right)^2 - \frac{4}{r}}}{2} \quad (5)$$

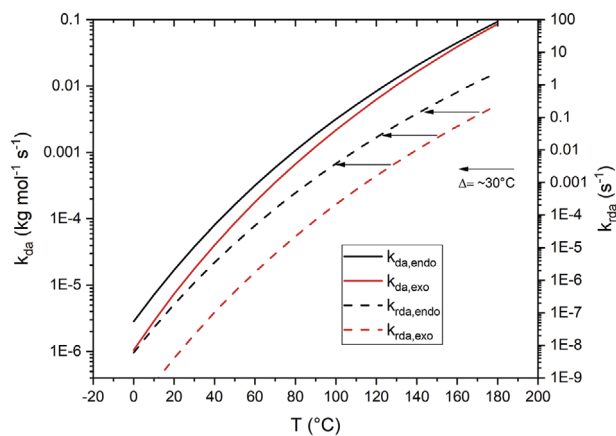
The fact that the equilibrium conversion depends on the concentration is verified experimentally, as Truong et al. found that the equilibrium conversion depends on the concentration of the reactant.<sup>[32]</sup> Equation (5) also tells us that more diluted conditions lead to a lower equilibrium conversion of maleimide, which benefits the reverse DA reaction. Liu et al. monitored the conversion over time at different temperatures, but noticed that the equilibrium conversion started decreasing at 70 °C.<sup>[43]</sup> At higher temperatures the endothermic retro-DA reaction starts to play a more significant role. It is therefore clear that one should consider both the forward and backward DA reaction at these milder temperatures to determine forward and backward kinetic constants more accurately, as also noted by Polgar et al.<sup>[12]</sup> This has been emulated by several publications in recent years, which numerically solve mass balance equations and obtained kinetic data from curve fitting.<sup>[41,44]</sup> In the case that one reactant is present in excess, it acts as functional solvent or plasticizer which can take part in the reaction, although this will limit the strength of the plastic.<sup>[45]</sup>

## 2. Kinetic Comparison between Endo and Exo adduct Formation

In literature there appears to be a general consensus about the endo-adduct being kinetically favored and the exo adduct as the thermodynamically stable diastereomer.<sup>[40,46–49]</sup> The ratio is affected by steric and electrostatic effects which are being exerted on the transition state, and therefore depends on the type of solvent and substituents on the diene (furan) and/or the dienophile (maleimide).<sup>[48]</sup> This is supported by kinetic studies that specifically analyze developments in the endo/exo ratio over time and at various temperatures. Carneiro de Oliveira et al. pointed out that the endo/exo ratio may increase after every cycle, as endo adducts slowly attain the exoconformation.<sup>[46]</sup> Orozco and co-workers indicated that the endo/exo ratio is directly dependent on the polymer chain mobility as well, in case the reaction is used for polymer crosslinking.<sup>[47]</sup> A study by Cuvellier et al. quantifies the ratio of endo and exo stereoisomers in their system by reporting the calculated activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) for both adducts.<sup>[50]</sup> When these values are known, one can apply the Arrhenius equation (Equation (6)) to obtain a forward and backward kinetic constant as a function of temperature.

$$k = A \cdot \exp\left(\frac{E_a}{RT}\right) \quad \text{kg mol}^{-1}\text{s}^{-1} \quad (6)$$

The reported parameters of Cuvellier and co-workers were used to compare the resulting kinetic constants of their endo and exo adducts.<sup>[50]</sup> These forward and backward constants are plotted against temperature in Figure 4. Though at ambient temperatures the formation of endo-adducts dominates over the exo



**Figure 4.** Forward and backward rate constants, derived from data of Cuvellier (2019).<sup>[50]</sup>

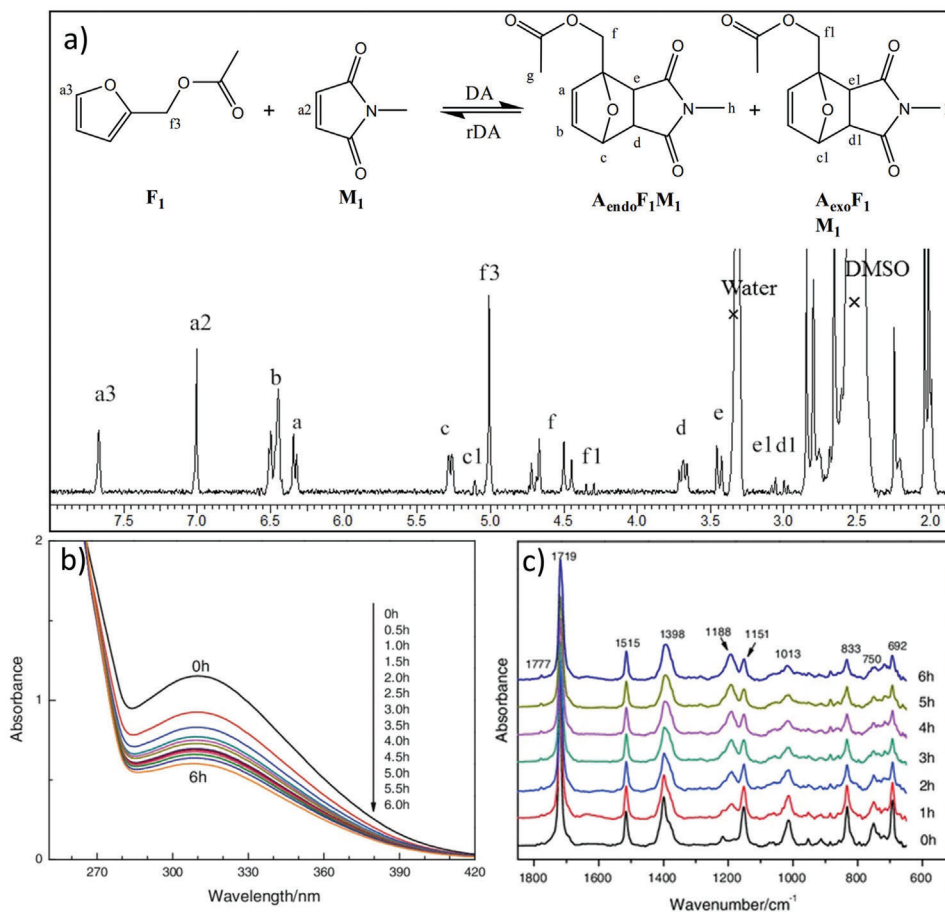
adduct formation, they seem to be almost equal at higher reaction temperatures. This study concludes that the formation of endo adducts is still kinetically more favored, but in other conditions this may not be so clear-cut. Yadav et al. mentions that the exo adduct may sometimes be formed at a faster rate in other solvents.<sup>[51]</sup> For instance, it was observed that exo adducts are kinetically favored in acetonitrile.<sup>[52]</sup> Overall, it is confirmed that the exo adduct is indeed more stable and cleaves at a slower rate, since no claims were found that stated otherwise. Moreover, some researchers point out that the endo/exo ratio has little effect on the unblocking speed,<sup>[49]</sup> while others concluded that the endo adduct is broken faster,<sup>[47]</sup> meaning that it is still not entirely clear which one of these statements is true and under which conditions.

It has also been reported that the difference between the two adducts reacting can be up to 30 or 40 °C to reach the same speed of unblocking, although it varies.<sup>[47]</sup> The same conclusion from literature can be indirectly drawn from Figure 4. The graph of the backward exo-kinetic constant can be superposed with the endo by applying a horizontal translation of approximately 30 °C to the left. In practice, this means that the exo adduct would indeed have to be heated to 30 °C more in order to show the same cleavage rate as the endo adduct. This illustrates the importance of the endo/exo ratio for processing purposes, as well as how much it can vary for different chemical systems. Both thermal history and the polymer system itself have an impact on the endo/exo ratio, and thus directly affects the material behavior and on the desired processing conditions.

## 3. Effect of Methodology on Reported Kinetics

It should be noted that the way in which kinetic studies are carried out affects its results. There are several methods employed in recent kinetic studies to determine an activation energy and the pre-exponential factor. First of all, the presence of maleimide can be quantified by measuring UV absorbance at a wavelength of 310 nanometer.<sup>[10,12,32,43,46,53,54]</sup> The decrease in absorbance indicates the formation of maleimide groups in the DA reaction and vice versa. A second and arguably more accurate method to follow the DA reaction is by <sup>1</sup>H-NMR spectroscopy. Though the





**Figure 5.** a) Example of an  $^1\text{H-NMR}$  spectrum with peak assignment. Reproduced with permission.<sup>[49]</sup> Copyright 2015, Royal Society of Chemistry. b) Development of UV-vis absorbance at 310 nm, indicating maleimide disappearance. c) Example of an IR spectrum, with important peaks assigned. (b,c) Reproduced with permission.<sup>[43]</sup> Copyright 2013, Springer Nature.

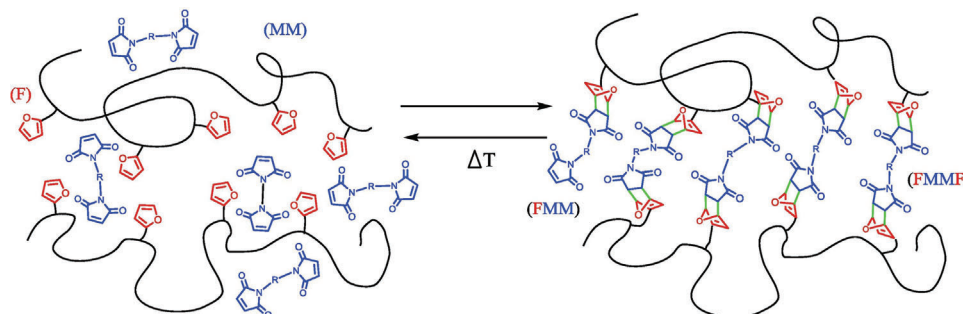
backbone structure may limit the use of this method due to overlapping signals, some can accurately follow the extend of reaction via NMR, and even distinguish peaks corresponding to one of the two stereo-isomers only.<sup>[46]</sup> An example of such an  $^1\text{H-NMR}$  spectrum is shown in **Figure 5a**. Liu et al. discuss how UV results (**Figure 5b**) lead to significantly different observed kinetics with  $^1\text{H-NMR}$  in deuterated dimethyl sulfoxide (DMSO).<sup>[43]</sup> A higher reaction rate is observed in their UV measurements, which was ascribed to the solvent polarity. It is indeed known that polarity of solvents can accelerate the DA reaction due to hydrogen bonding and hydrophobic effects on the transition state.<sup>[48]</sup> However, Carneiro de Oliveira et al. determined kinetic parameters via both  $^1\text{H-NMR}$  and UV-vis using DMSO in both techniques and found that the measured activation energies were quite similar for the reverse reaction, but in the forward reaction they deviate significantly ( $39\text{ kJ mol}^{-1}$  with UV-vis vs  $48\text{ kJ mol}^{-1}$  with  $^1\text{H-NMR}$ ).<sup>[46]</sup> This means that the difference between the values obtained from both techniques is not only caused by solvent polarity and thus remains unexplained.

Several researchers have used IR spectroscopy to determine Diels-Alder conversion using peak intensity ratios, for instance by comparing signals originating from maleimide ( $1436\text{ cm}^{-1}$ , pyrrole stretching) with reference signals from either backbone

or nonreactive parts.<sup>[15,55–57]</sup> An example of such a spectrum is shown in **Figure 5c**. The same can be done with furan peaks, as several clear signals from furan rings are visible at  $1013\text{ cm}^{-1}$  (C–O–C, furan breathing),  $1345\text{ cm}^{-1}$  (furan stretching),<sup>[15]</sup> and furan C–H (out of plane bending) at  $734\text{–}750\text{ cm}^{-1}$ .<sup>[58]</sup> In infrared spectroscopy the material is often analyzed in bulk and we expect that mass transfer limitations play a role at higher conversions, but only for systems that undergo network formation under these conditions. It would perhaps be better to only consider analysis of the initial reaction rate in order to ensure that only reaction kinetics are measured, instead of mass transfer rates.

As an alternative, some studies introduce microcalorimetry or differential scanning calorimetry (DSC) measurements to follow the reaction over time.<sup>[41,44,59,60]</sup> Based on heat requirements to keep the sample pan at either constant temperature (or temperature ramp in case of DSC), it is possible to determine the activation energy and kinetic constant of the reaction.

Rheology experiments are an additional source that tell something about the degree of crosslinking of the material. Polgar et al.<sup>[14]</sup> noted that in contrast to other analysis techniques, this method can distinguish a DA adduct that effectively forms a crosslink in a polymer network (furan-maleimide-maleimide-furan, FMMF) with ones formed only on one side of the dimeric



**Figure 6.** Illustration of two distinguished DA adducts, i.e., half linked (FMM) and crosslinked (FMMF). Reproduced under terms of the CC-BY license.<sup>[14]</sup> Copyright 2017, the Author(s). Published by Elsevier Ltd.

molecule (Furan-maleimide-maleimide, FMM). This is illustrated in **Figure 6**.

The found Diels–Alder conversion can be verified by the Dibeneditto model (Equation (7)), which is an empirical relation between the Diels–Alder conversion and the glass transition temperature:<sup>[41,53,61,62]</sup>

$$\frac{T_g - T_{g0}}{T_{g1} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda) x} \quad (7)$$

In this equation,  $T_g$  is the glass transition temperature,  $T_{g0}$  and  $T_{g1}$  are the glass transition temperature at zero conversion and full conversion, respectively, and  $\lambda$  is a fitting parameter. This equation offers an excellent alternative to verify and compare conversion data obtained by other methods. However, it is challenging to measure  $T_{g0}$  and  $T_{g1}$ , since the materials undergo the DA reaction while measuring  $T_{g0}$ , and  $T_{g1}$  cannot be reached due to mass transfer restrictions that limit the maximum conversion at lower temperatures.<sup>[50]</sup>

In the theory of network formation, the Flory–Stockmayer model is typically introduced (Equation (8)).<sup>[45,63,64]</sup> This model relates functionality of all reactants and the addition ratio of furan and maleimide with a gel conversion, i.e. the conversion at which all molecules have become part of one polymer network.

$$x_{\text{gel}} = \frac{1}{\sqrt{r(1-f_f)(1-f_m)}} \quad (8)$$

The experimental gelation point can be determined as the crossover between the elastic and viscous moduli (via dynamic mechanical analysis) and fits well with the theoretical values obtained with the Flory–Stockmayer model.<sup>[41,60,65]</sup> Together with known kinetics, it gives important insights in processes with temperature variations and it can be predicted if and when a material would be prone to gelation.

#### 4. Effect of Architecture on Reported Kinetics

By now there are many research groups that have analyzed the kinetics of their own furan/maleimide system. The question remains how the kinetics are affected by the structure and architecture of the polymer, for instance whether mass transfer limitations result in lower measured reaction kinetics. In this sec-

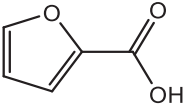
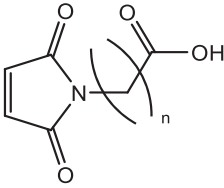
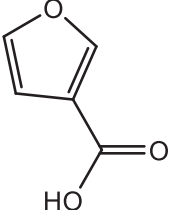
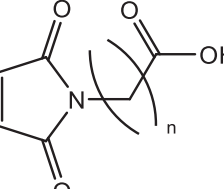
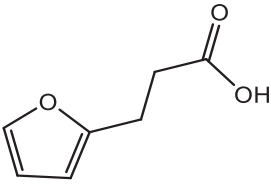
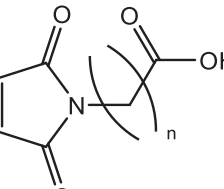
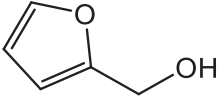
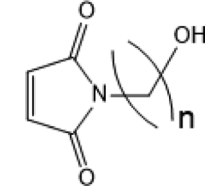
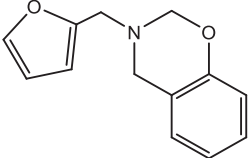
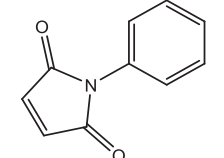
tion, we distinguish three ideas of how to exploit the DA reaction for the construction of polymer networks. We consider linear systems, multifunctional clickable networks (building blocks of low molecular weight), and crosslinked polymers. The former only includes bismaleimides and difurans, which results in a linear step-growth polymerization. Multifunctional clickable networks are a collective term, taking into account chemical systems containing building blocks with a functionality higher than two. Lastly, polymer crosslinking research is mainly focused on strengthening already existing polymer chains, which are not built from DA adducts itself. We separate networking systems built from low molecular weight systems (with at least a functionality of three) as we foresee mass transfer limitations playing a more prominent role in the systems containing larger prepolymer chains. In order to structurally assess the effect of macromolecular and intramolecular structure, we expand the discussion to these three systems.

##### 4.1. Nonpolymerization Kinetics

The reaction kinetics of the DA reaction was first studied in non-polymerization reactions, where mass transfer limitations do not play a role. This means that the reaction is kinetically limited, leaving only the reaction rate between a maleimide and furan to be measured. Effects of side groups and positions have been studied via different approaches. The results of the systematic studies on this topic are listed in **Table 1**. Štirn et al. examined the kinetics of Diels–Alder using two solvents, and determined kinetics via IR.<sup>[67]</sup> They concluded that the absence of solvent is a better option to prepare the materials. After all, the reaction conversion could be followed in pure molten state, and the reaction equilibrium in solution is affected. Koehler and co-workers compared activation energies of carboxylic acid containing furan and maleimide moieties, which were positioned at different sites on the furan.<sup>[66]</sup> A carboxylic acid at the three-position was found to cause an increased reaction rate and equilibrium conversion, therefore facilitating the forward DA reaction. However, a carboxylic acid group is electron-withdrawing and results overall in lower reaction rates, keeping in mind that the participating diene in the DA reaction should be electron-rich to facilitate a fast reaction.<sup>[48]</sup>

The aliphatic spacer length between the maleimide and carboxylic acid was found to have a significant effect on the activation

**Table 1.** Activation energies for various maleimide/furan derivative couples.

Furan	Maleimide	$E_a^a$ [kJ mol <sup>-1</sup> ]	Ref.	Comments
		$n = 1:115$ $n = 2:62$ $n = 5:99$	[66]	By <sup>1</sup> H-NMR, different solvents
		$n = 1:89$ $n = 2:123$ $n = 5:110$	[66]	By <sup>1</sup> H-NMR, different solvents
		$n = 1:99$ $n = 2:110$ $n = 3:95$	[66]	By <sup>1</sup> H-NMR, different solvents
		$n = 1:48$ $n = 2:32$	[46]	<sup>1</sup> H-NMR in d-DMSO
		$48^b$ ; $52^c$	[67]	

<sup>a)</sup>  $n$  is the number of CH<sub>2</sub> spacer groups, as indicated in the maleimide structure; <sup>b)</sup> in chloroform; <sup>c)</sup> in acetonitrile.

energy as well, as observed in Table 1. In the work of Koehler et al. the trend in a minimum activation energy with an ethylcarboxy side group, and higher values for methylcarboxy and pentylcarboxy side groups is most likely attributed to the use of a different solvent in NMR measurements.<sup>[66]</sup> With a similar approach, Carneiro de Oliveira also investigated effect of spacer length on reaction kinetics.<sup>[46]</sup> Besides the activation energies being much lower compared to furan derivatives bearing a carboxylic acid group, it was only shown how activation energies with an ethylhydroxy group was lower than the methylhydroxy counterpart. In all cases it is expected that a longer aliphatic spacer will lead to a slightly higher activation energy, considering that heat dissipates into kinetic bending and stretching motions of aliphatic chains. On the other hand, the presence of more alcohols in a bulk system may have the same stabilizing effect as water does, and thus could result in an even lower activation energy as well.

Still, as other solvents are being used in these studies, these hypotheses are not convincingly proven.

#### 4.2. Linear and Multifunctional Clicking Networks

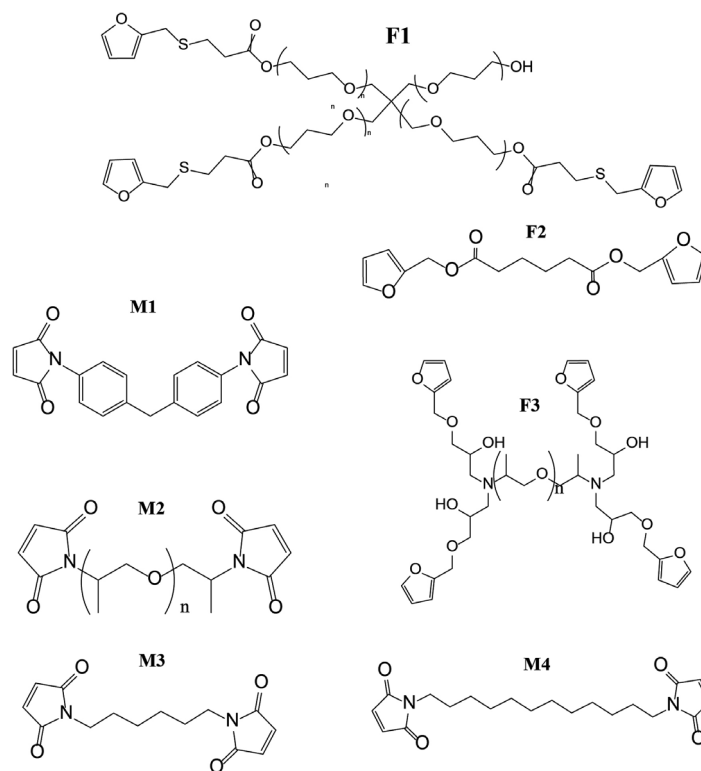
Dimeric furan/maleimide systems form linear polymers only and therefore lack mechanical strength compared to crosslinked systems.<sup>[13,59]</sup> Nevertheless, ample examples of studies analyzed some form of linear thermoreversible polymerizations and demonstrated their useful self-healing properties.<sup>[12,53,54,68–72]</sup> So far, there appear to be two studies analyzing kinetics of such a dimeric system.<sup>[43,54]</sup> Alternatively, a tris-furan and/or trismaleimide can be introduced to form diamond-shaped networks.<sup>[73]</sup> Other studies dealing with network formation via such multifunctional molecules are listed in **Table 2**, with the



**Table 2.** Reported kinetic data from literature, discussing multifunctional click networks.

Furan	Maleimide	$E_{a_f}$ [kJ mol <sup>-1</sup> ]	$\ln(A_f^{a_1})$	$E_{a_b}$ [kJ mol <sup>-1</sup> ]	$\ln(A_b^{a_2})$	Ref.	Comment
F1	M1	48	9.7	88	22.4	[65]	IR, at 20–80 °C
F2	M3	40	5.9 <sup>b)</sup>			[54]	
F3	M1	55.7	13.1	94.2	25.8	[57]	IR
F3	M2	58.5 (endo) 62.6 (exo)	13.1 (endo) 13.6 (exo)	113.0 (endo) 122.6 (exo)	31.0 (endo) 31.5 (exo)	[50]	Determined with microcalorimetry
F3	M2	53.9	11.7	105.7	28.3	[60]	IR

<sup>a)</sup> Units either in kg mol<sup>-1</sup> s<sup>-1</sup> or in L mol<sup>-1</sup> s<sup>-1</sup>. Densities are not known from these studies, but it is assumed that the values do not change significantly <sup>b)</sup> Calculated from data given in the publication.



**Figure 7.** Multifunctional furans and maleimides used in kinetic studies.

corresponding molecular structures of furans and maleimides shown in **Figure 7**.

Gandini et al.<sup>[54]</sup> found an activation energy, but used an excess of one reagent to determine the value of the kinetic constant. Besides the latter study, all other kinetic studies discussed here are performed in bulk. The combination of reported forward and backward pre-exponential factors ( $A_{da}$  and  $A_{rda}$ , respectively) and activation energies ( $E_{a_f}$  and  $E_{a_b}$ ) give all the information required to compare the kinetics of network formation obtained in several studies. All these studies show results within the same order, but there are some notable differences. For instance, it is clear that the combination **F1 M1** gives higher reaction rates than the combination **F3 M1**. Both studies are carried out in bulk and with IR spectroscopy, so here the faster kinetics of **F1** can only be

attributed to the architecture of the furan. Entanglement effects of the tetrafunctional crosslink points may cause more limitations in mass transfer, or it may just be the acidic sulfide of **F1** leading to a higher reaction rate than alcohol groups of **F3**. The discussion whether mass transfer played a role in some studies has been ignored in most cases. However, new studies have investigated the effects of vitrification on the development of a DA reaction in bulk, and noticed that the reaction (and self-healing) can still occur in the vitrified state.<sup>[59,74]</sup> We suggest that we should distinguish mass transfer limitation as a direct consequence of the material being below its glass transition temperature, and the contribution of molecules being part of the polymer matrix and therefore bear immobilized but unreacted groups. We expect that the latter plays a role above the gelation point.

**Table 3.** Summarized kinetic data from studies discussing reaction rate for polymer crosslinking.

Polymer	Crosslinker	Kinetic data	Ref.	Comments
Furan grafted PEG <sup>a)</sup>	M1	$E_{a_f} = 42.1 \text{ kJ mol}^{-1}$ , $\ln(A_f) = 7.2 \text{ L mol}^{-1}$	[55]	IR
Furan grafted EPM <sup>b)</sup> (50 kg mol s <sup>-1</sup> )	M4	$E_{a_f} = 7 \text{ kJ mol}^{-1}$ , $E_{a_r} = 35 \text{ kJ mol}^{-1}$ $\ln(A_f) = 16.1$ $\ln(A_r) = 57.9$	[14]	Rheology and IR
PFS-PBS <sup>c)</sup> multiblock ( $\approx 9.3 \text{ kg mol s}^{-1}$ )	M1	$E_{a_f} = 54.2 \text{ kJ mol}^{-1}$ $\ln(A_f) = 12 \text{ L mol}^{-1} \text{ s}^{-1}$	[58]	IR and DSC
<i>p</i> -Styrene- <i>r</i> -vinylfuran	M1	$E_{a_f} = 18.3 \text{ (endo)}$ ; $34.9 \text{ (exo) kJ mol}^{-1}$ $E_{a_r} = 174 \text{ kJ mol}^{-1} \text{ (endo)}$	[75]	Variable temperature NMR in <i>d</i> -DMSO
Furan grafted EPM <sup>b)</sup>	M3 and M4 and M1	M3: $E_{a_f} = 42.7 \text{ kJ mol}^{-1}$ , $\ln(A_f) = -7.5$ M4: $E_{a_f} = 40.9 \text{ kJ mol}^{-1}$ , $\ln(A_f) = -7.5$ M1: $E_{a_f} = 84.9 \text{ kJ mol}^{-1}$ , $\ln(A_f) = -21.4$	[76]	Rheology
One-system DA polymer containing furan, maleimide and lauryl groups		$E_a = 64.8 \text{ kJ mol}^{-1}$	[77]	Rheology and IR

<sup>a)</sup> Poly ethylene glycol <sup>b)</sup> Maleated ethylene-propylene rubbers <sup>c)</sup> Poly(2,5-furandimethylene succinate)-*b*-poly(butylene succinate).

Similarly, It turns out that **M1**, a maleimide containing two phenylene groups, shows much faster reversible kinetics than with a more flexible maleimide, such as **M2**. This is concluded by comparing the results of Scheltjens and Cuvellier.<sup>[50,57]</sup> As more energy will be stored in the dangling linear part of this maleimide, more energy has to be applied in order to reach the same effect, hence resulting in a higher activation energy for **M2**. Alternatively, this difference in kinetics may be related to the electron delocalization on the phenyl rings. The studies of Cuvellier et al.<sup>[50]</sup> and Diaz et al.<sup>[60]</sup> show the difference in results between a study that distinguishes the endo and exo ratio, and one that does not. This collected data provides a clear overview of expected kinetics for these types of multifunctional systems. Compared to activation energies of nonpolymerization DA reactions summarized in Table 1, the activation energies for multifunctional systems are reported to be similar (leaving chemical effects of carboxylic acid side groups from Koehler et al. out of this discussion).<sup>[66]</sup> However, due to incomplete data of pre-exponential factors in Table 1, no final conclusion can be drawn about mass transfer limitations playing a role in these systems.

### 4.3. Polymer Crosslinking

Furan/maleimide chemistry has been used to crosslink rubbers,<sup>[14,76,78]</sup> poly sacharides,<sup>[5,10,13]</sup> carbon-nanotubes,<sup>[79]</sup> poly ketones,<sup>[47]</sup> polyacrylates,<sup>[80]</sup> and poly ethers<sup>[55]</sup> to yield recyclable thermosets. The studies discussed in this section cover solely systems for which the kinetics were analyzed, The collected data are listed in **Table 3**.

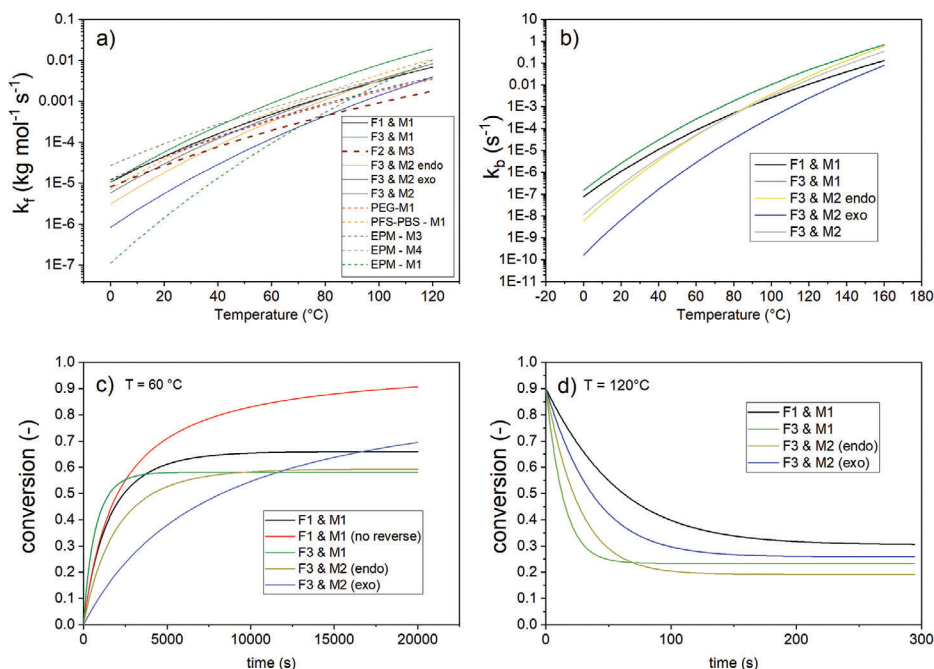
When we put this data next to the kinetic studies that were performed for multifunctional systems, then it can be concluded that the data deviates more than in previous sections, and sometimes even shows values that are not in agreement with other lit-

erature. For instance, two studies discussing polymer crosslinking kinetics of Furan grafted ethylene-propylene rubber (EPM) are not in agreement in terms of reported kinetics.<sup>[14,76]</sup> Liu and co-workers<sup>[67]</sup> reported kinetics for various maleimides (**M1**, **M3**, and **M4**), but the activation energy found with **M1** is much higher than the ones found with **M3** and **M4**, and is in contrast with the values that were found in section 3.2. This gives the impression that the lower measured kinetics of **M1** are not attributed by molecular structure, but instead caused by mass transfer limitations as a consequence of the rigidity of the phenyl rings.<sup>[76]</sup>

Based on the found kinetic data from Tables 2 and 3, forward and backward kinetic constants were plotted against temperature via Equation (6) for the purpose of comparing these kinetics. The resulting plots are shown in **Figure 8**. From the forward kinetic constants (Figure 8a) it appears that there is especially some deviation at lower temperatures.

Figure 8b gives a comparison between reverse DA rates of several combinations. Even though these differences do not appear to be significant, it is clear from Figure 8c,d that conversion developments over time do vary significantly per combination. In Figure 8c we highlight the importance of incorporating both the forward and backward reaction at lower temperatures (in this example 60 °C), by including a result from the combination **F1 M1** where the reverse reaction was not taken into account. Figure 8d shows how the material (in this case starting with 90% curing conversion) can be cleaved in the order of minutes, but not completely due to the equilibrium conversion being reached. This analysis highlights the fact that minor deviations in kinetic values can play a major role in reprocessing steps, and thus the kinetics should be accurately determined for each different system.

It is worth mentioning that sample preparation plays a key role as well. Zhang and co-workers heat the material to 160 °C to re-



**Figure 8.** Kinetic constants plotted based on data from Tables 2 and 3, using Equation (6). a) Forward kinetic constants. b) Backward kinetic constants. c) Conversion plotted over time at 60 °C. d) Conversion plotted over time at 120 °C, typically starting at a conversion of 90%.<sup>[43]</sup> Figure 3c,d is obtained by solving Equation (4) with data from Tables 2 and 3, taking a stoichiometric ratio and a concentration of 1 mol L<sup>-1</sup>.

move a thermal history, but the material can maintain a significant conversion if cooling down rates from this high temperature are too slow.<sup>[58]</sup> When subsequently cooling down the material with an indefinite amount of time, the material is allowed to react already during this interval. When subsequently placing the material for the first fourier transform infrared (FTIR) measurement, the conversion will not be zero at the defined starting time. If the material is still hot from the pre-heating step to 160 °C when being placed in the IR, this naturally leads to a different measured kinetics compared to others.

Having put the recent kinetic studies in perspective, it is clear that we should be careful in terms of sample preparation and method to accurately determine kinetics of a system. There are two accepted methods to ensure a zero conversion at a certain time. One is to directly measure kinetics after mixing maleimide and furan at low temperatures, and the second is to delete the thermal history at higher temperatures (e.g., 160 °C), followed by a quick cooling step with an extra stimulus such as liquid nitrogen.

## 5. Additional Catalytic Stimuli

The aforementioned kinetic studies did not attempt to accelerate the DA reaction, but it can be further stimulated with additional external or internal factors. Back in 1993, Pindur and co-workers gave a broad overview on acceleration of the DA reaction in general.<sup>[81]</sup> Since then, some specific examples appeared in literature with promising new insights on catalysis of this reaction.

Karami et al. demonstrate a method how ultrasonic radiation can be applied on crosslinked DA networks with furan and maleimide.<sup>[82]</sup> DSC and FTIR analysis proved that ultrasonica-

tion was able to cleave the weaker  $\pi$ -bonds in the cycloadducts to a certain extend at room temperature. In comparison with thermal treatment up to 140 °C, it does not cause complete de-crosslinking. Ultrasound can still be used to ease the reverse DA reaction and to prevent elevated temperatures causing extra irreversible side reactions, such as maleimide homopolymerization.<sup>[42]</sup>

Some researchers took the approach of applying UV irradiation. They demonstrated this using anthracene as diene instead of furan.<sup>[83–85]</sup> Unfortunately the use of UV light on furan/maleimide systems has not been reported so far, possibly because the furan is too unstable and may cause undesired reactions, instead of enhancing the DA reaction rate.

Concerning homogeneous or heterogeneous catalysts, it is known that Lewis acids activate the maleimide by complexation to carbonyl oxygen lone pairs. Ions such as tin, zinc, and copper, complexed with an ether are capable of increasing the reaction rate to a significant extent.<sup>[48]</sup> In the recent years no work was found on catalysis of polymer crosslinking with furan/maleimide chemistry, leaving much to be studied in this field. However, an ionic liquid was previously used to enhance the DA rate between anthracene and bismaleimide, and similarly ionic liquids can be incorporated in DA reactions to function as catalyst.<sup>[86]</sup>

Lastly, there are many hints that mechanical stress on the material causes the DA adducts to break faster. Under high stress, some expect that the relatively weak  $\pi$ -bonds (calculated from the adduct enthalpy of formation to be  $-51.8$  kJ mol<sup>-1</sup>) are preferably broken, hence facilitating the reverse reaction and leading to off-equilibrium situations.<sup>[59,60,87,88]</sup> However, so far this effect has not been proven to be significant. This leaves us with the conclusion that there is much to investigate for the furan/maleimide

Diels–Alder reaction, which makes it an attractive topic to study for the coming years.

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## 6. Conclusion

This review covers the kinetics of the furan/maleimide reaction in thermoset polymers. This knowledge is crucial for engineering end-of-life recyclability directly into the materials design. With kinetic data being available, it is possible to predict at which moment a thermoreversible resin undergoes a transition in heating or cooling cycles, such as gelation. This allows us to repurpose end-of-life rubbers and thermosets for the same use as it originally did, instead of heating them to degradative temperatures or using them as fillers. The recent publications on kinetics of this Diels–Alder reaction were reviewed and the developments were discussed in detail. Recent publications considering endo and exo cycloadducts opened up a path to determine crosslinking speeds more accurately, as the difference in reactivity between the two can be significant for some systems. By performing an analysis of kinetic data from other studies, it is highlighted that the differences in measured kinetics are worth mentioning, though this is rarely brought up in literature. In the perspective, the differences in reported kinetics may likely have been caused by molecular architecture, and due to effects caused by the applied methodology. Because of the variable solvents, analysis techniques and sample preparations, it is challenging to quantify effects of mass transfer and chemical structure on observed kinetics of network formation. There are some hints that mass transfer limitations perhaps play a role in more densely networked systems, and the functionality of the building block thus has a direct effect on this. Although this reaction is biobased and has the potential to be a faster reaction with help of catalysis, the subject of furan/maleimide Diels–Alder catalysis has received negligible attention, and could be explored in the future in the field of polymer processing techniques. In summary, this review offers a detailed overview of the kinetics behind the popular furan/maleimide Diels–Alder reaction, and highlights the challenges ahead in the field of self-healing and recyclable polymers.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

click chemistry, Diels–Alder, furans, kinetics, maleimides, recycling

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