# Trends in Diels Alder in Polymer Chemistry

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**Abstract**

Diels Alder (DA) reaction is regarded as a quite useful strategy in organic and macromolecular syntheses. The reversibility of this reaction and the advent of self-repair technology, as well as other applications in controlled macromolecular architectures and crosslinking, have strongly boosted that research activity, that is still undergoing a huge interest for both academic and industrial research. DA reaction is a simple and scalable toolbox. Though it is well-established that the furan/maleimide is the most studied diene/dienophile couple, this perspective article reports strategies using other reversible systems with deeper features on other types of diene/dienophile pairs being either petro-sourced (cyclopentadiene, anthracene) or bio-sourced (muconic and sorbic acids, myrcene and farnesene derivatives, eugenol, cardanol). That Perspective is composed of four sections. The first one briefly recalls the background on the DA reactions involving cyclodimerizations, dienes and dienophiles, parameters affecting the reaction while the second part deals with the Furan/Maleimide reaction. Third, petro-sourced and bio-sourced (or products becoming bio-sourced) involved in DA reactions are also listed and criticized. Finally, the authors' opinion is given on potential future of the crosslinking-decrosslinking reaction, especially regarding the process (e.g., key temperatures of decrosslinking) or possibly monocomponents. It presents both fundamental and applied research on DA reaction and their applications.

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## 1. Preamble

Although the Diels Alder reaction has been known for many decades, the literature has become more and more abundant from the 90ies. Deeper studies based on weak bonds describe original strategies to synthesize new molecules or macromolecules. One of the unexpected examples deals with reversible deactivation radical polymerizations (RDRP) **Durmaz, Colakoglu, Tunca and Hizal [1], [2]** which offer the design of macromolecules with controlled architectures (as block, graft and star copolymers).

Such reactions arise from various challenges developed in both academia and industry with either environmental or economic concerns.

Specific topics involving Health (case of drug delivery), packaging (case of recycling), coatings (case of self-repairing) and electronic packaging where cracking occurs due to differences in thermal expansion index need a better control of the chemical reactions, especially on their reversibility.

However, the domains of applications require various reaction temperatures and eventually these of reversed reactions. For example, in Health, the temperatures can range from room temperature to ca. 50 °C while for paints and varnishes, they can reach up to 120 °C and, for industrial post-crosslinking (oven painting, coatings, composites and 3D materials) **[3]**, they may be raised up to 200 °C.

In the last few years, Health (2.4.10 DA in health) has more attracted the researchers' interest rather than conventional paints, coatings, hybrids **[4]**, and adhesives. In addition, and more recently, the topic related to self-healing has been even more attractive in the scientific community and many strategies of synthesis have been reported (2.4.5 DA for self-healing.

As summarized in this preamble, Diels Alder (DA), is one of the most used methodology, well-developed and scaled up in industry thanks to the thermal stimuli which can be suitably applied in many applications.

Mainly, Gandini's team **[5-7]** has been the pioneer in that area and has comprehensively reviewed the maleimide-furan couple in 2013.

Due to our specific interest in many topics involving DA reaction: *self-curing on demand* technology (SCOD) to cure elastomers **[8]**, repairing coatings **[9, 10]** and adhesives **[11]** , The growing importance of the use of bio-based and low-toxic molecules, and a massive bibliographic search, we decided to update the actual trends and knowledge of DA reaction.

This present review does not aim at updating Gandini's reviews **[5-7]** or the literature on that topic by reporting many articles and patents, but it plans to revisit the Diels Alder reaction globally in the organic and polymer field. This manuscript supplies an overview on the use of new molecules (such as dienes or dienophiles) involved in such a reaction, with a specific part devoted to bio-sourced molecules. Another objective aims at updating the knowledge of the reaction temperatures whatever the DA or retro DA (rDA) reactions, when reported. However, the rDA has not been so comprehensively investigated **[12]**. Finally, several applications will be proposed, highlighting their advantages and limitations. Hence, a critical balance appraisal of the overall situation of such a reaction will be given, with the perspectives of new couples able to bring new insight on the temperature range in DA and retro DA reactions.

## 2. Generalities

### 2.1 Introduction

The Diels Alder (DA) reaction is a cycloaddition between a diene and a dienophile and has been known for a long time **[13-17]** .The purpose of this reaction, which was initially used in organic synthesis, i.e. to get new cyclic molecules, has evolved over time. In addition, the Diels-Alder reaction has then been required to prepare thermostable polymers, and polyimides, using the addition of bismaleimides on furans, followed by aromatization reaction to stabilize the molecules **[18, 19]**. The application of the DA reaction into polymer synthesis constitutes a recent research topic, and the number of studies on DA reaction is still growing constantly (**Figure 1**).

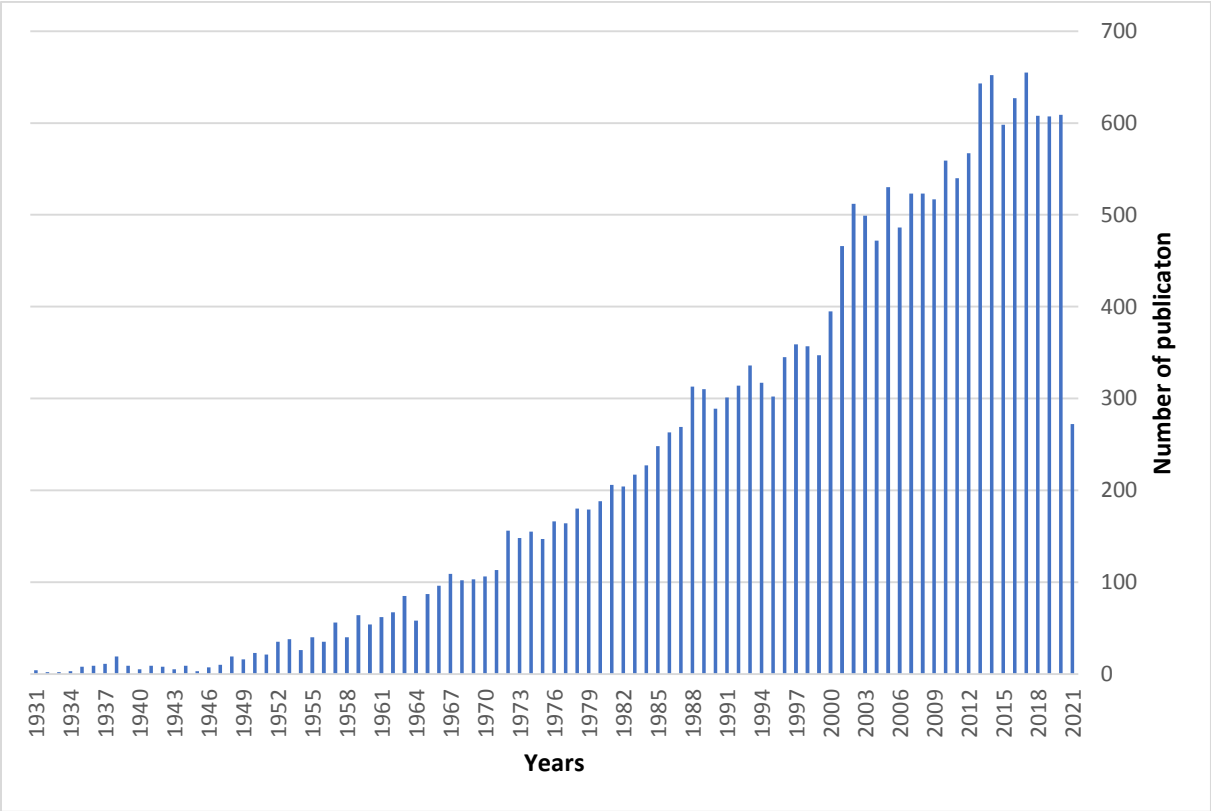



**Figure 1: number of publications on Diels Alder per year, taking all subjects into account from 1930 up to now. Source from SCI Finder.**

More recently, these reactions have been looked not for molecules stabilization but for their ability of heat reversion with the aim at preparing smart polymers **[20].** Ideally, the idea is to enable that the first reaction could be achieved at room temperature and then, could be undone by a moderate temperature heating. The temperature, here, acts as a stimulus in the construction/deconstruction process. Lastly, along the same line, many applications appear based on the concept of self-repairing, recycling materials and the control of the cross-linking. Thus, it completely makes sense to note the concept of reversibility being nowadays developed in polymer chemistry. In this topic, the DA reaction is probably the most known and studied pathway. Especially, the furan-maleimide reaction (F-M) has almost been comprehensively investigated. In the specific F-M field, though particularly well-documented, updating Gandini's reviews **[5-7]** would be of interest. However, in order to use the thermal reversibility behavior of the DA reaction into the polymer industry, it is worth controlling and adapting the building block and the stimuli with regard to the need of the user.

The purposes of this present review aim at i) showing that the DA reaction is omnipresent in the field of polymer and ii) proposing new diene/dienophile couples other than

furan/maleimide, thus being able to enlarge the range of heat reversion and its application in polymer industry. First, after a brief recall of DA background, the F/M couple will be presented and used as an example for the application of DA reaction in the area of Polymer Science. Many different strategies will be highlighted, developed and recent use of FM reaction for high performance polymers will be described. In a second part, to underline some possible and recent alternatives ofF/M couple, other dienes and dienophiles, which can be either petro- or bio-sourced, will be developed and criticized in order to try to complete Gandini's reviews **[5-7]** and articles, and to broaden the scope to all systems of cycloaddition. A special attention will be paid on the availability of these building blocks and examples of their uses in DA polymer chemistry will be added if they exist. Then, a discussion will open toward the future of DA reactions in self-healing, crosslinking-decrosslinking and further applications, especially regarding the process and the industry expectations. In addition, our contribution will not deal with the Huisgen "click" chemistry **[21]**, in contrast to many reviews.

## 2.2 Cycloaddition

The cycloadditions represent a powerful strategy in organic chemistry, and it implements many products classified according to two digits [x + y]. x and y identify both the number of π electron involved in the electronic rearrangement and the number of atoms originating the unsaturated six-membered ring. The cycloaddition of two molecules by π orbital can be [2 + 2], [2 + 4], and [4 + 4] (**Figure 2**). These reactions are broadly irreversible but can sometimes be reversible through thermal or photochemical treatment. By far, the most used method is the [4+2], diene-dienophile, of Diels-Alder reaction.

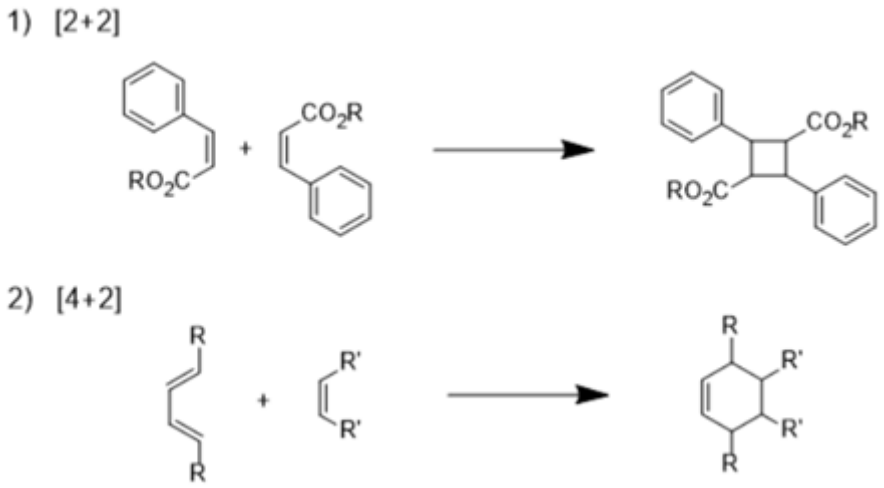
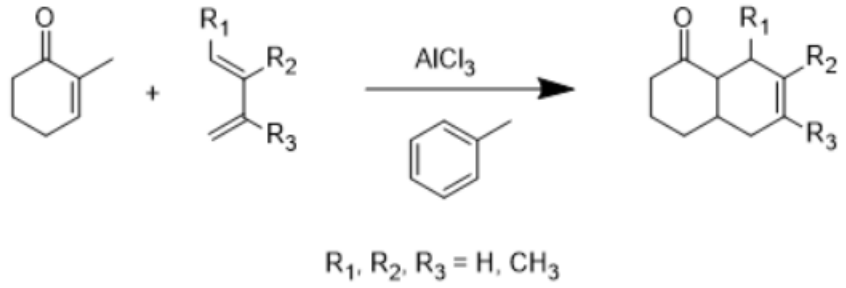



**Figure 2 : Example of cycloaddition reactions [2+2] and [4+2]**

However, the other less-known cycloadditions are more and more frequently used to complete the range of temperature or of the wavelengths applied to reverse the system, such as the case of anthracene [4+4] that occurs at 366 nm and dismantles to 254 nm **[22, 23]**. The cycloaddition reaction can be intramolecular or extramolecular. The most classic ones remain the [4+2], called Diels Alder, that has been the subject of many publications and a comprehensive book written by Fringuelli and Taticchi **[24-30]**. However, the Gandini's update **[5]** on both the selective furan/maleimide couple and the resulting applications on polymers is currently the reference in this area. A first step briefly recalls the basic knowledges, as reported in the Fringuelli and Taticchi's book **[24-30].**

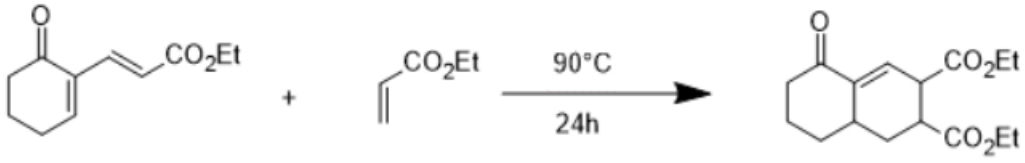
## 2.3 Electronic effects of the Diene/Dienophile in Diels-Alder Reactions

As reported in the Fringuelli and Taticchi's book **[24-30]**, the electronic effects of the Diene/Dienophile induce a huge influence on the cycloaddition rate. Most of the time, during the Diels-Alder (DA) reaction, the electron-donating substituted diene accelerates the cycloaddition with an electron-withdrawing substituted dienophile. This reaction is called a *"normal electron-demand DA reaction"* **[31]** (**Scheme 1).**




**Scheme 1 : Normal electron-demand Diels-Alder reaction between a diene and a dienophile**

Another case exists in which the electron-withdrawing group of the diene enhanced the D-A reaction with an electron-donating dienophile **[32]** (**Scheme 2**). This reaction is called *"inverse electron-demand DA reaction".*




**Scheme 2 : Inverse electron-demand Diels-Alder reaction [32]**

This reverse reaction has changed the overall thinking of the D-A reaction and leads to reflect on the different possible diene/dienophile couples for the synthesis of the polymers. The diene/dienophile couple is essential to promote the DA reaction and the nature of the couple affects the experimental condition of its success. Some of well-known dienes (**Figure 3**) and dienophiles (**Figure 4**) have been already involved in the cycloadditions of DA, well-described by Fringuelli and Taticchi **[24-30].**

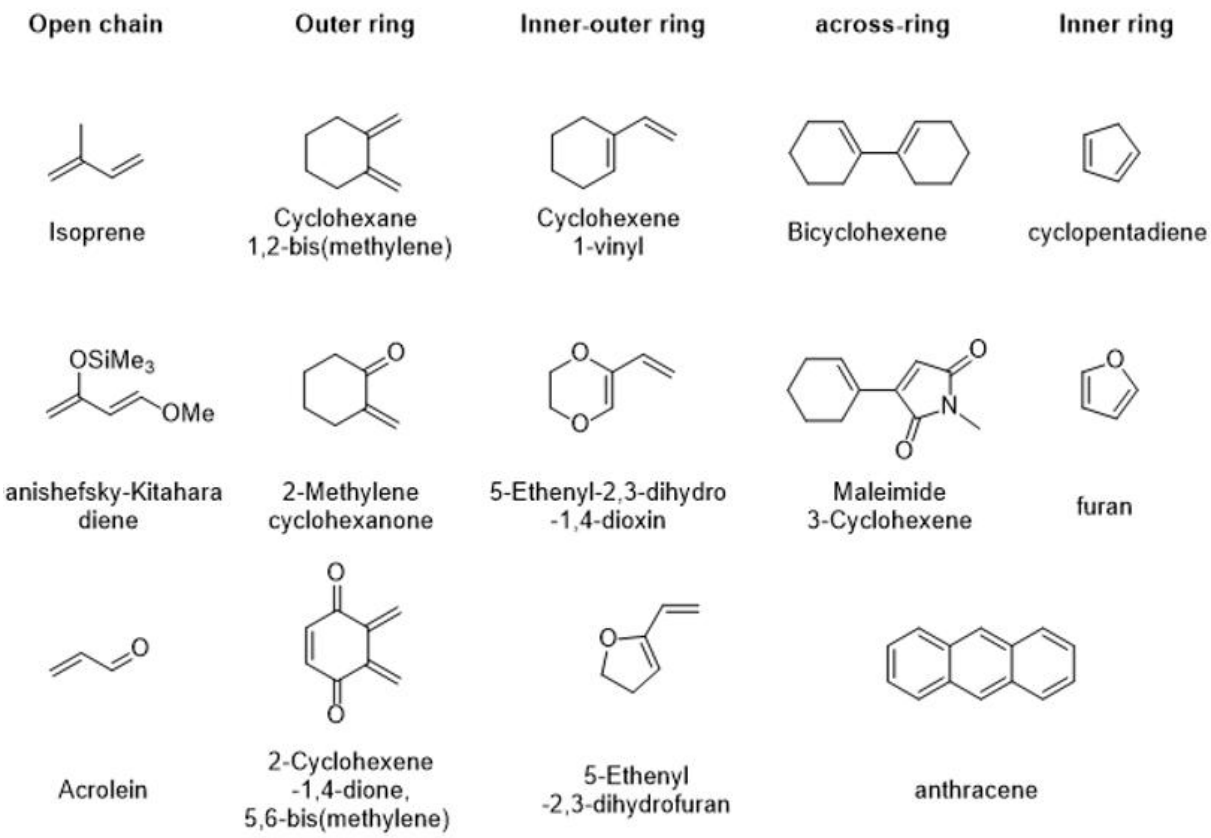



**Figure 3 : List of well-known representative diene structures involved in DA reactions**

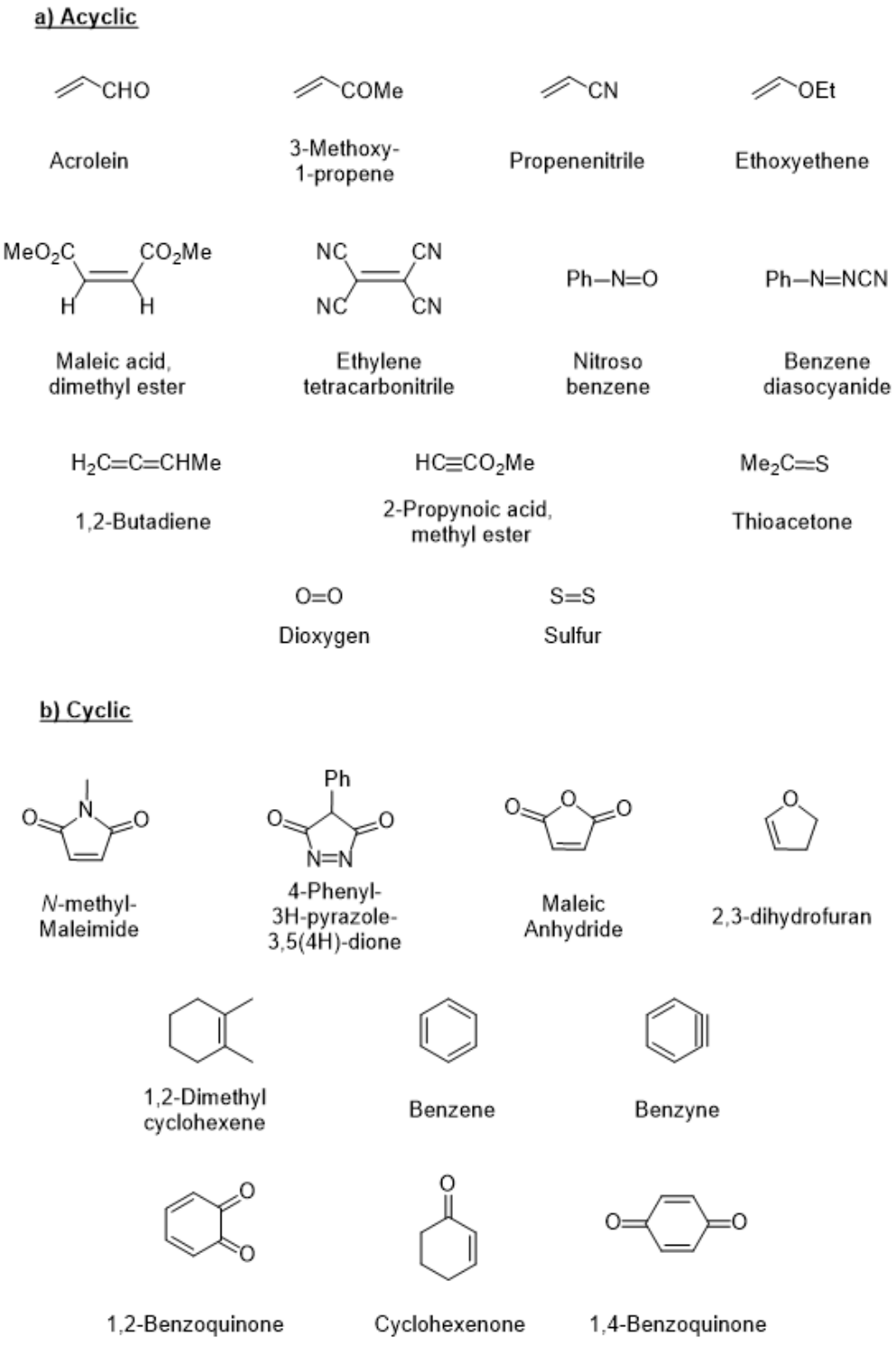



**Figure 4 : List of well-known representative dienophile structures ranked between a) acyclic and b) cyclic molecules**

The lists supplied in **Figure 3 and Figure** 4 are quite relevant. However, they deserve to be updated with, for example, the addition of biomass products which have been increasingly popular nowadays. Indeed, recently, thanks to the gain of growing interest for bio-based building-blocks, new dienes and dienophiles, even if they existed before for other

applications, are now started to be involved in the Diels-Alder reaction such as cyclopenta-1,3-diene **[33]** (**Figure 5a**) which was already used before **[34, 35]** or like anthracene **[36, 37]** (**Figure 5b**). Sorbic acid, bio-based, **[38, 39]** (**Figure 5c**), myrcene **[40, 41]** (**Figure 5d**) its homologue farnesene **[42]** (**Figure 5e**) or 3-hydroxy-2-pyrone **[43, 44]**( **Figure 5f**), just to cite some of them, have gained more interest in the DA community.

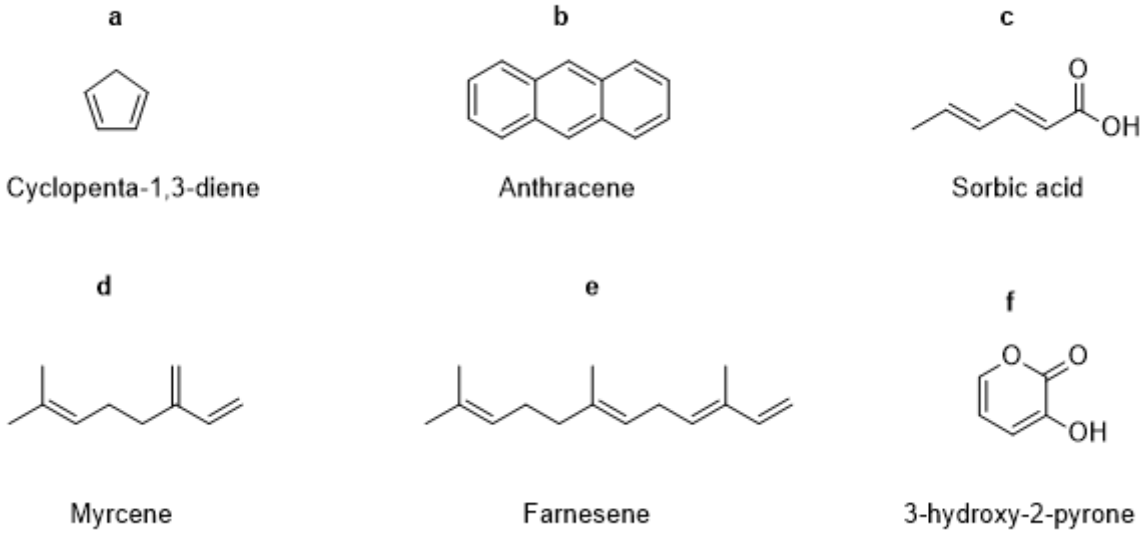



**Figure 5 : Examples of diene structures nowadays used**

As for dienophiles, maleimides **[5]** (**Figure 6a**) as still leaders in this field. However, new challengers emerge like citraconic acid and derivatives **[45, 46]** (**Figure 6b**), itaconic acid and derivatives **[47, 48] (Figure 6c**) or vinyl ketones **[49, 50] (Figure 6d**). A special section will be dedicated to these new or reused dienes/dienophiles building blocks and their applications.

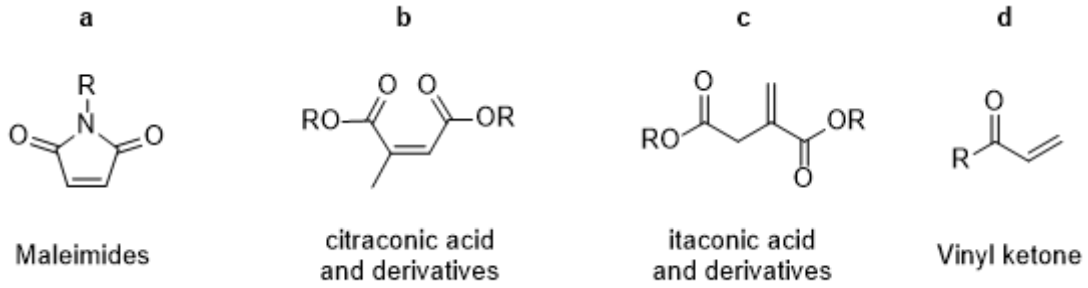


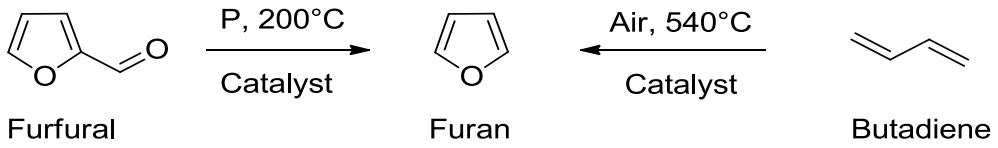

**Figure 6 : Example of structures of dienophiles used nowadays**

## 2.4 Furan/Maleimide (F/M) couple.

### 2.4.1 Generalities about furan and maleimide

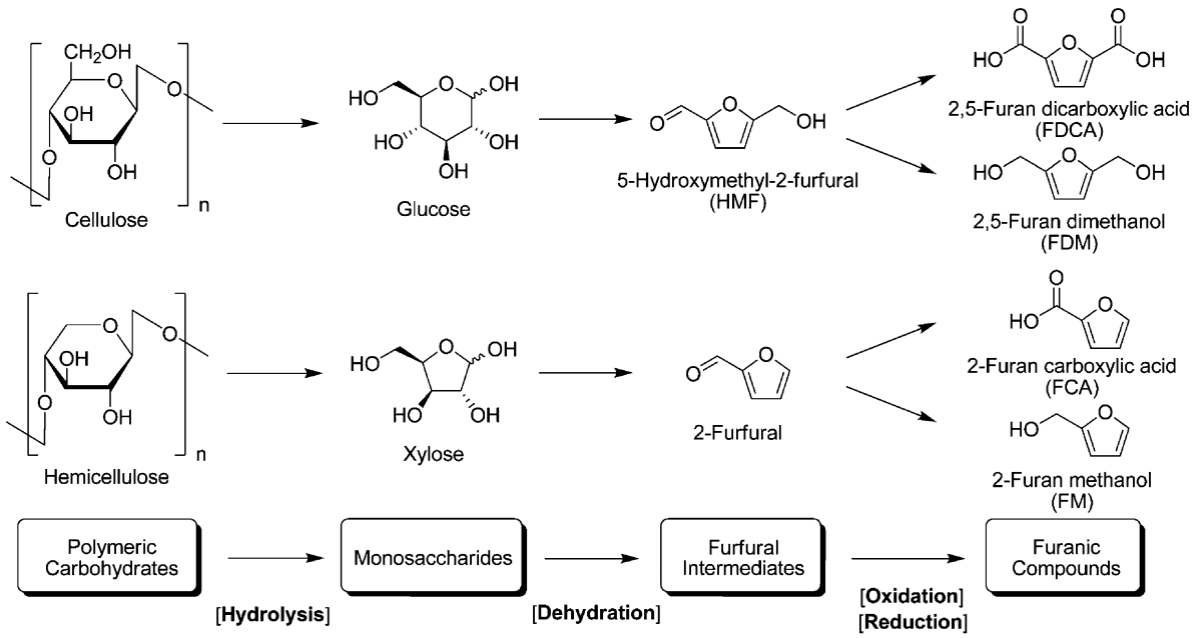
One of the most commonly and largely described diene/dienophile couples is the combination of furan and maleimide **[8]**.

Furan is a pseudo aromatic heterocycle containing four carbon atoms and one oxygen. In 1870, Limpricht **[51]** pioneered its synthesis. Furan is mainly obtained from furfural, a bio-based aldehyde resulting from the distillation of cereals. In the middle of the 20$^{th}$ century, the Du Pont de Nemours Company developed industrial ways (**Scheme 3**) to produce furan from the reaction between furfural and water steam catalyzed by Zn-Fe or Mg-Fe chromite **[52, 53]**. Later, that company proposed to synthesize furan from the oxidation of butadiene **[54]**. They also improve the furfural process by using a palladium catalyst which permits to avoid the use of steam in the reaction. Therefore, furfural decomposes into furan and carbon monoxide at 200 °C under pressure. **[55]**. Furan and its derivatives **[56, 57]** (**Scheme 4**) can be involved in metalation and can react as an aromatic molecule in electrophilic substitutions, as an ether for ring opening reactions, as well as in DA reaction as a diene **[58]**.



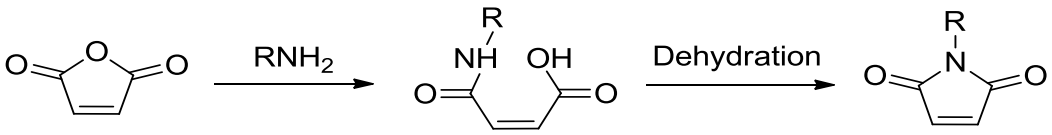

**Scheme 3 : Industrial pathways from furfural or butadiene to produce furan [52, 53] [54]**

Several other furan derivatives produced from biomass have also been quite used. Cho et al. **[57]** supplied a comprehensive and interesting overall scheme for the production of various functional furans from biomass (cellulose and hemicellulose) (**Scheme 4**). Both types of furans, monosubstituted (in 2-position) and disubstituted (in 2-5 positions) have been used. The former ones are mainly involved in polyadditions between α,ω-bis(furan)s and telechelic bismaleimides. The latter ones enable to crosslink polymers bearing furanic groups located in the main chain. That case requires bis(maleimide)s to favour that crosslinking. In addition for further details on this matter, a complete overview on furan and its derivatives was published in 2020 **[59]**.

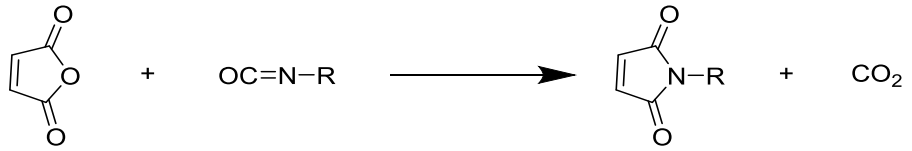



**Scheme 4: Synthetic pathways of furanic compounds prepared from biomass-based polymeric carbohydrates [57] (reproduced from ref [57] with permission from ACS, copyright 2013)**

The term "maleimide" can concern an unsaturated imide and all the associated derivatives, commonly used as building blocks for many organic reactions. Maleimides can be mainly obtained in a two-step synthesis from the reaction of maleic anhydride with amines followed by a dehydration step (**Scheme 5**). Actually, in contrast to aliphatic ones, aromatic maleimides have already reached the industrial scale obtained by dehydration from acetyl anhydride and sodium acetate **[60]**. The former ones have been prepared by academic teams only, one example being from $ZnBr_2$ and silanes **[8]** (**Figure 7**) or from isocyanates **[61-64] (Scheme 6)**.




**Scheme 5 : Synthetic way for the preparation of maleimides from maleic anhydride [61, 62]**




**Scheme 6 : Synthesis of maleimide from maleic anhydride and isocyanate compound [61-64]**

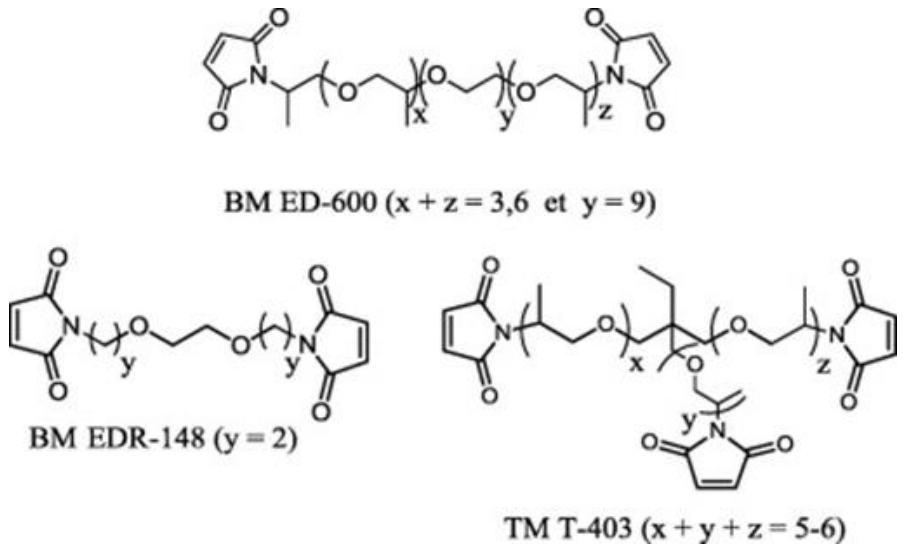
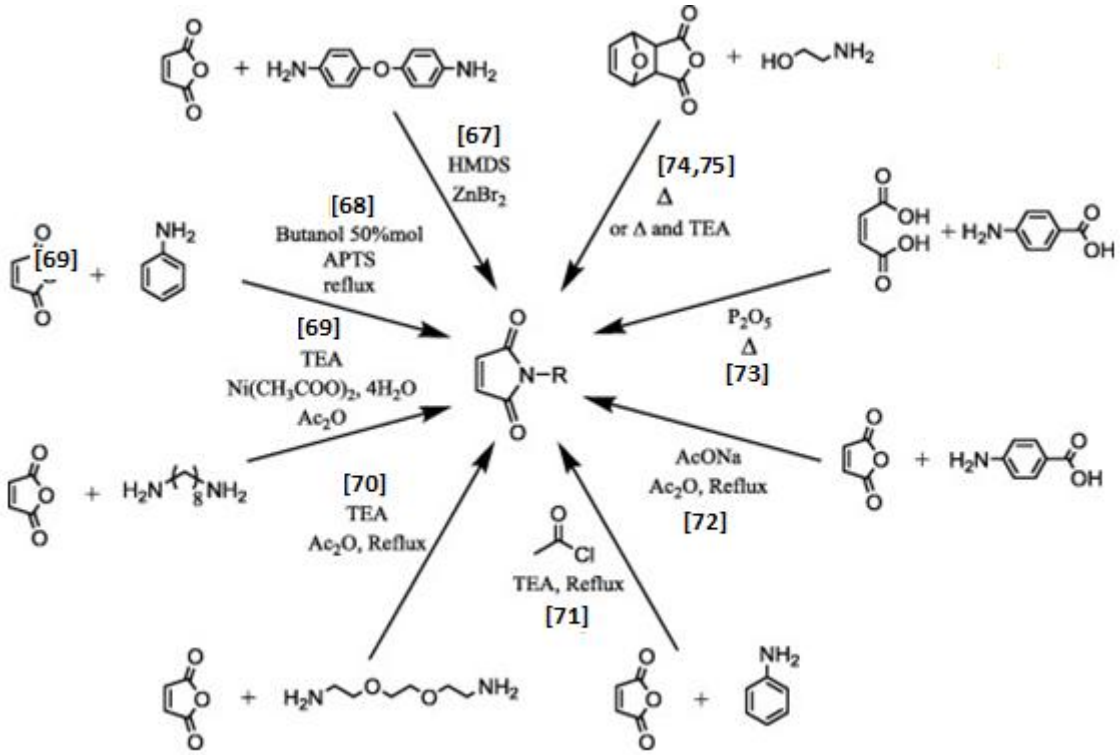


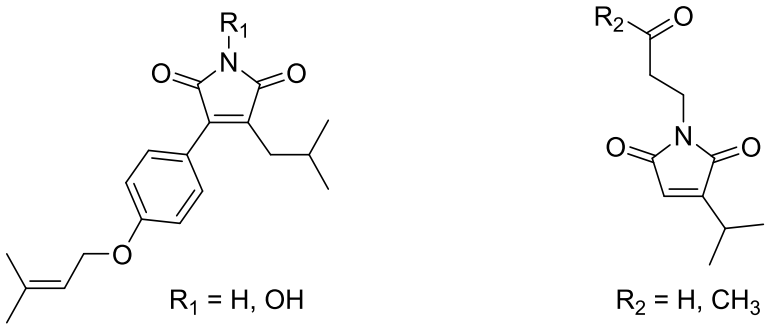

**Figure 7 : Various structures of telechelic and grafted maleimide structures based on PPG and PEG [8]**

The desired maleimide derivatives can be targeted by selecting the amine involved in the reaction **[60, 65]** (**Scheme 5 and Scheme 7**). Another advantage deals with the easy synthesis of bis-maleimides **[66]**.




**Scheme 7 : Various synthetic routes for the preparation of maleimides derivatives [67-75]**

It is also possible to find natural maleimides with complex structures produced by fungi, as in the case of *antrodia camphorata* **[76, 77]** able to produce several maleimides and maleic anhydrides or for *Paecilomyces farinosus* yielding farinomalein **[78]** (**Scheme 8**).




**[76,77]** **[78]**

**Scheme 8 : Examples of natural maleimide compounds**

This keen interest of this specific diene/dienophile couple is due to the fact that the pair furan/maleimide (F/M) DA reaction occurs commonly at room temperature and this couple displays a moderately low temperature for its retro-DA reaction (around 110 °C). This smooth thermal reversibility, applied in polymer synthesis, opens an attractive way for recycling, self-healing, and internal crosslinking processes. It should be noted that the value of the temperature of the retro-DA depends on the diene/dienophile couple used, here F/M, but is also influenced by the structure and the possible substituents born by these molecules. Such a retro-DA happens at an average temperature of around 100-110 °C. However, there are many examples in the literature when the retro-DA of the F/M couple occurs from ca. 80-90 °C **[5, 79, 80]** to 150-160 °C **[81, 82]**. DA reaction is also subjected to kinetic and thermodynamic controls. Indeed, the reaction between two cyclic compounds leads to two diastereoisomers: one called “endo” dominates (as the kinetic product that is faster formed) while the other one, named “exo”, is thermodynamically favourited at higher temperature. The formation and quantification of these both diastereoisomer can be evidenced by NMR spectroscopy. The *endo* adduct is always unblocked (unprotected) at lower temperature than the *exo* one **[83, 84]**, which is thermodynamically more stable. For example the retro-DA, monitored by DSC, could start from 60 °C for some endo adducts or 100 °C for the exo adducts **[8]** Therefore, it is coherent to think that these phenomena are commonly applicable at some other

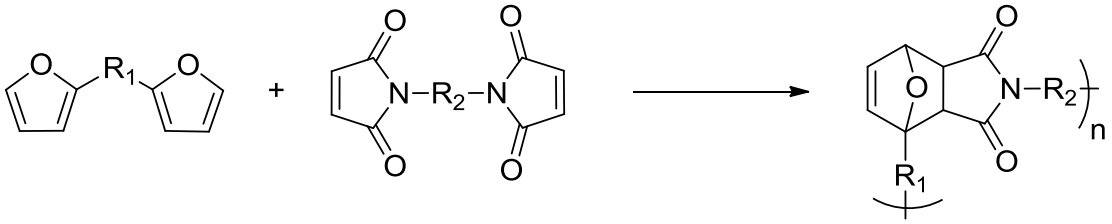
diene/dienophile couples and enlarge the range of DA/retro-DA temperatures achievable for a wider field of application**[85]**.

In the case of maleic anhydride, Eggelte et al. **[86]** studied the reaction involving furan onto this anhydride and its derivatives. These authors showed that the endo isomer was quite difficult to be produced because of the very low temperature of $r_{DA}$.

The versatility of the use of furan and maleimide moieties in polymer synthesis is also a major advantage. Indeed, as very well-described in Gandini's review **[5]**, the F/M couple takes action in different ways to the development of polymer materials by polycondensation strategies. More recently, some pertinent reviews **[87, 88]** have reported the wide variety of polymer architectures obtained from DA and other stimuli-responsive polymers.

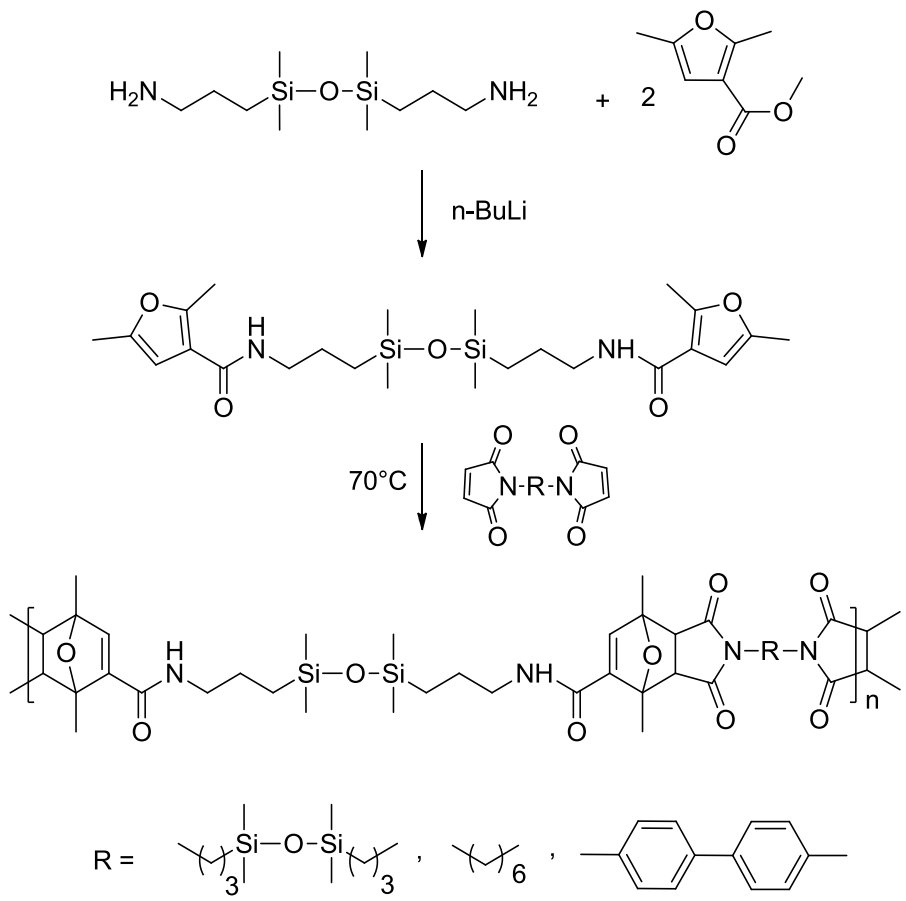
### 2.4.2 Polyaddition of furan-maleimide

It is possible to synthesize telechelic diene and dienophile monomers in the purpose to produce polymers by thermally reversible linear polyaddition. (**Scheme 9**). In 1961, Stille pioneered the first DA polyaddition that did not involve any bisfurans but telechelic bis(cyclopentadiene)s and various bis(dienophile)s as di(maleimide)s **[89]**.



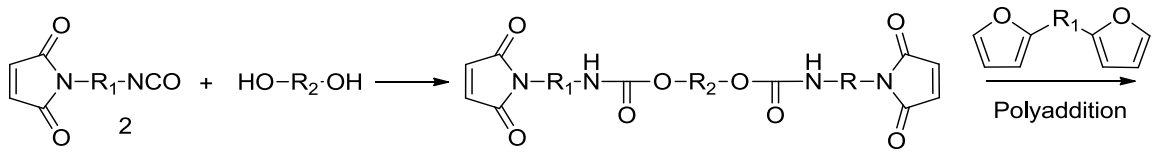

**Scheme 9: Polyaddition of telechelic bis(furan) onto bis(maleimide)**

It took 25 years before DA polyaddition involved the F/M pair. In his article, Tesoro and Sastri **[90]** functionalizes a siloxane with two furan functions and then initiates polyaddition using a bis(maleimide) (**Scheme 10**).



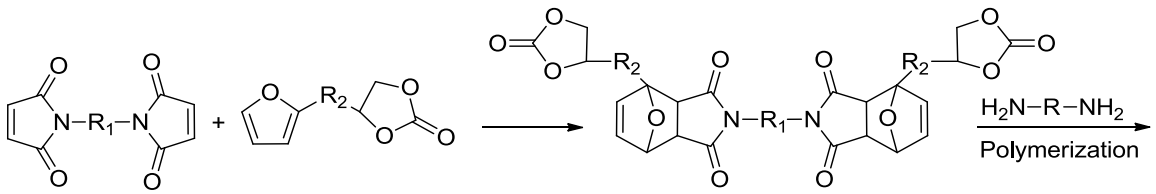

**Scheme 10 : Functionalization and DA polyaddition containing siloxane moities [90]**

That pioneered strategy has inspired many authors for the synthesis of well-known polymers **[91-93]**. This route consists in functionalizing one or more units of a polymer by a member of the F/M couple to obtain an A-A monomer. The polyaddition is then initiated using another B-B monomer (**Scheme 11**). For example, in order to produce polyurethanes, Gaina et al. synthesized original compounds in which the furan moieties are surrounding a urethane bond **[80]** while Shibata succeeded in the production of high performance hybrid polyesters **[94]**. Plenty of different A-A and B-B monomers such as poly-L-lactide **[95]**, non-isocyanate hydroxyurethane **[96]** or epoxy **[97]** can be designed from this way and some of them do not necessary involve the functionalization of an existent monomer **[68]**. Then, it is possible to undo and redo the desired hybrid polymer, facilitating its recycling or increasing its lifespan thanks to a self-healing behavior.



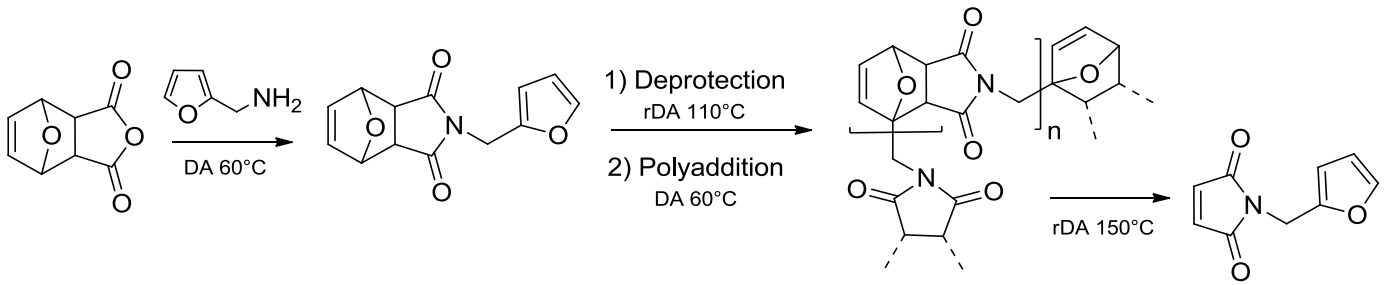

**Scheme 11 : DA polyaddition of bismaleimides containing urethane moities and bisfuran**

Another technique consists in developing polyfunctional polymers using the DA reaction between a first moieties of monomer comprising a furan and another one containing a maleimide group (**Scheme 12**). Once the monomer has been synthesized by DA reaction, polymerization can then take place like is the case of telechelic bis(cyclocarbonate)s and bis(amine)s for non-isocyanate polyurethane (NIPU) synthesis **[79]**.




**Scheme 12: Polymerization of telechelic bis(cyclocarbonate)s with bisamines to yield non-isocyanate polyurethane (NIPU) from F/M DA adduct [79].**

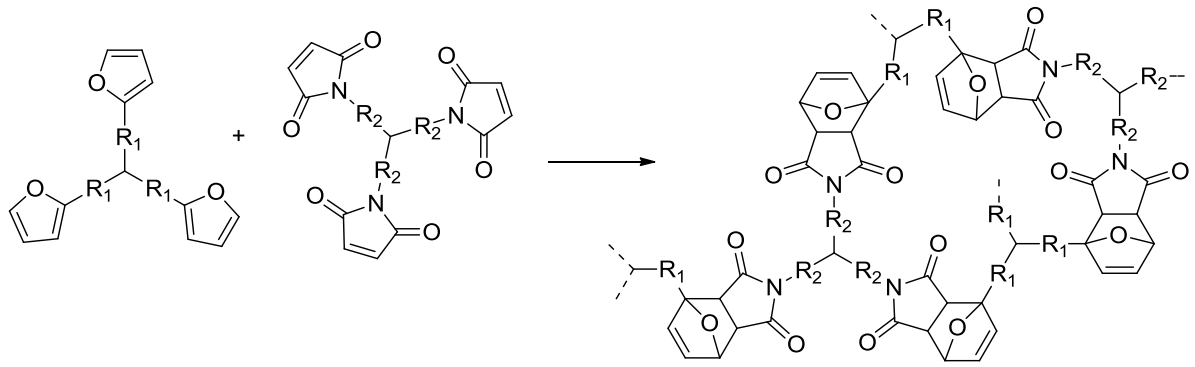
Furthermore, it is possible to directly functionalize a DA adduct to obtain the monomer of interest such as a polyol for the synthesis of polyester **[98, 99]** or some epoxy prepolymer **[100]**. As with the first strategy, the reversibility of the DA reaction makes it possible to plan recycling or self-healing applications. In addition, this technique is versatile and allows to design the monomer involved in the synthesis of the polymer of interest with more possibilities. The same strategies can also be applied by functionalizing a monomer bearing both furan and maleimide functions (types A-B). During the preparation of these monomers, it is therefore necessary to go through protection-deprotection steps to avoid early side-polymerization. (**Scheme 13**) **[101, 102]**.




**Scheme 13 : Synthesis and DA polyaddition of an AB furan/maleimide monomer [102].**

### 2.4.3 Networks

By increasing the number of furan **[103, 104]** and maleimide **[8, 105]** functions born by the monomers, it is also possible to synthesize non-linear polymers leading to more or less densely crosslinked networks (**Scheme 14**).



**Scheme 14: Example of a crosslinked F/M network pathway**

The F/M pair can also be used in the polymer field as a crosslinking agent in order to crosslink polymers. The thermally reversible faculty of the DA reaction associated with crosslinking is widely studied and exploited in industry. As a model, Chen et al. obtained crosslinked hard and transparent monoliths from tetrafurane and tris(2-maleimidoethyl) amine **[106]** , monitoring the DA reaction by UV and solid state NMR spectroscopies at various temperatures. At 24 °C, a DA portion up to 60-70 % required 5 days while at 75 °C, only 3 hrs were enough to reach completion. Solid state reversibility was tested via a series of heating cycles at different temperatures and then quenching in liquid nitrogen. **Figure 8** illustrates fives cycles and the sample was noted to be irreversible below 120 °C while at 130 and 150 °C, ca. 12% and 25% of the DA adduct disconnected.

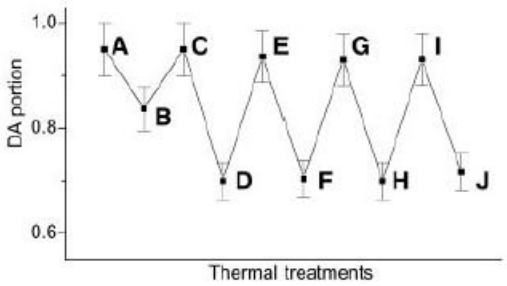
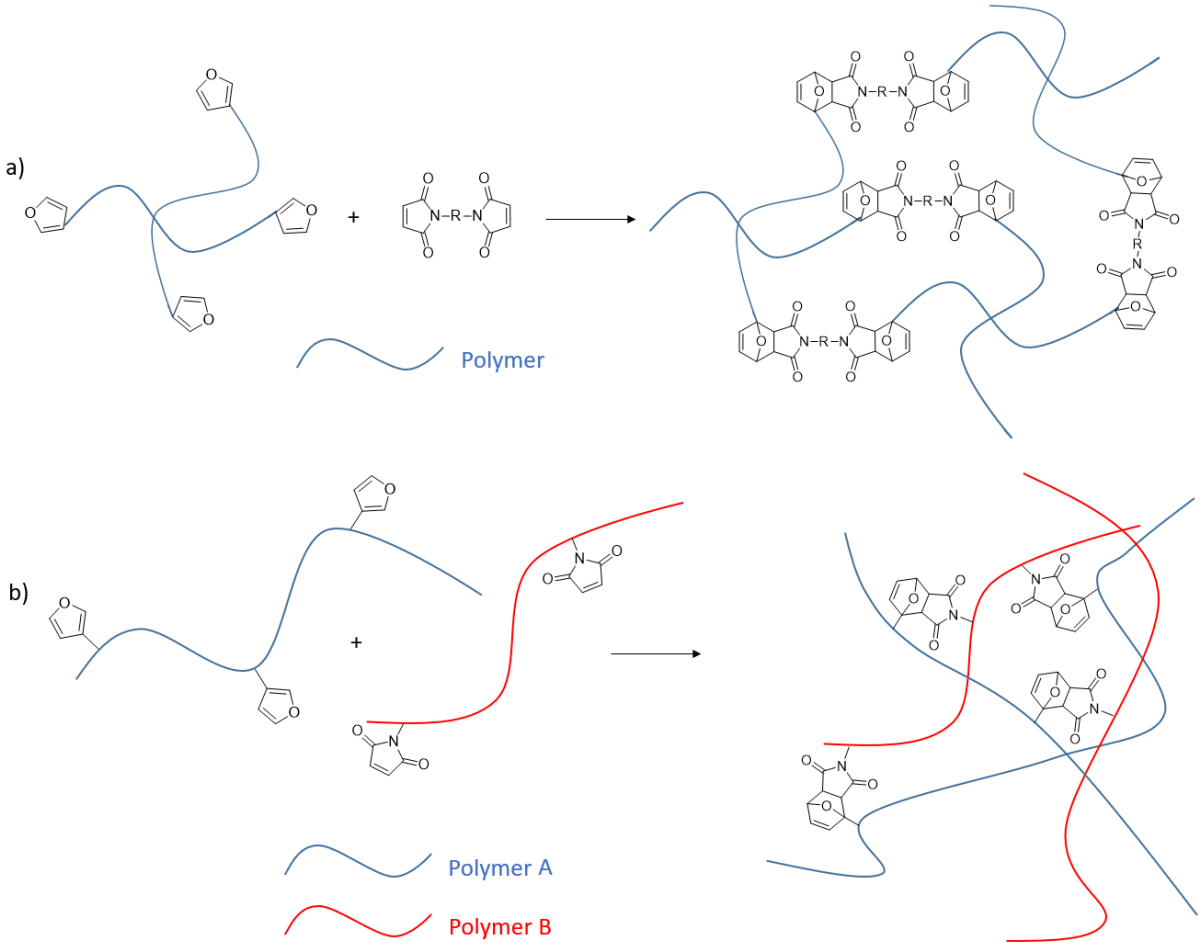



**Figure 8 : Thermal reversibility of polymer resulting from DA of a tetrafurane with a tris(2-maleimidoethyl) amine. (A) to (B), 130 °C for 25 min, followed by quenching in liquid nitrogen. (B) to (C), (D) to (E), (F) to (G), and (H) to (I), 80 °C for 1 hour. (C) ) to (D), (E) to (F), (G) to (H), and (I) to (J), 150 °C for 15 min, followed by quenching in liquid nitrogen. (reproduced from [106] with permission from Sciencemag, copyright 2002).**

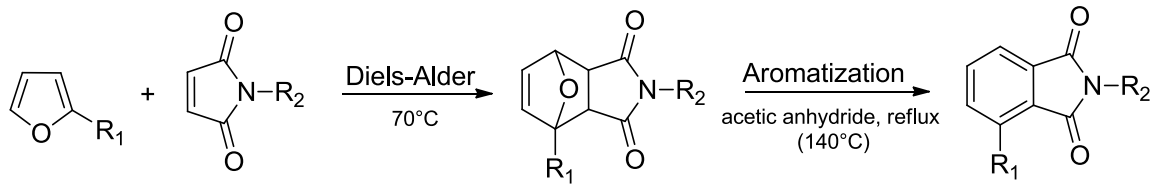
It is also possible to modify any polymer chains with a diene or a dienophile and to use the appropriate maleimide **[107-116]** or furan **[117-119]** as a crosslinking agent (**Scheme 15a**). In addition, the polymer chains can also be functionalized with both dienes and dienophiles functions which by DA reaction, will favor the crosslinking **[82, 119-123]** (**Scheme 15b**). It is also worth noting that a polymer with pendant moieties, instead of being crosslinked with a polyfunctional agent, can simply be grafted **[124, 125]**. Thus, many possibilities are easily anticipated for potential reversible grafting for coatings, electronics, aerospace, decontamination, or medical applications.




**Scheme 15 : Examples of reversible DA crosslinked material a) with a bis(maleimide) crosslinking agent b) thanks to an internal reaction between furan and maleimide-containing polymers.)**

### 2.4.4 Miscellaneous and different uses of furan-maleimide couple and DA reaction

Sometimes, during the synthesis of these polymers, the reversibility of the DA reaction is not desired. If necessary, it is possible to stabilize the DA F/M adduct by an aromatization with acetic anhydride **[90],** with $H_2SO_4$ **[126]** (**Scheme 16**) or a thiol-ene reaction step **[127]** ( **Scheme 17, vi)**).Thus, they prevent (without the double bond) the retro-DA from occurring. As expected, polymer materials which have undergone an aromatization step demonstrate better thermal stability **[19, 90, 128]**.




**Scheme 16 : DA reaction followed by further aromatization of the furan/maleimide adducts [90].**

Thanks to the researcher's imagination, functionalizing polymer chains with diene/dienophile moieties is a powerful tool for molecular design. For example, located at the end-group of a polymer, different polymer blocks can be linked with reversible DA adduct, allowing an easy path to do and undo the structure obtained. **[1, 2]**(**Figure 9**).

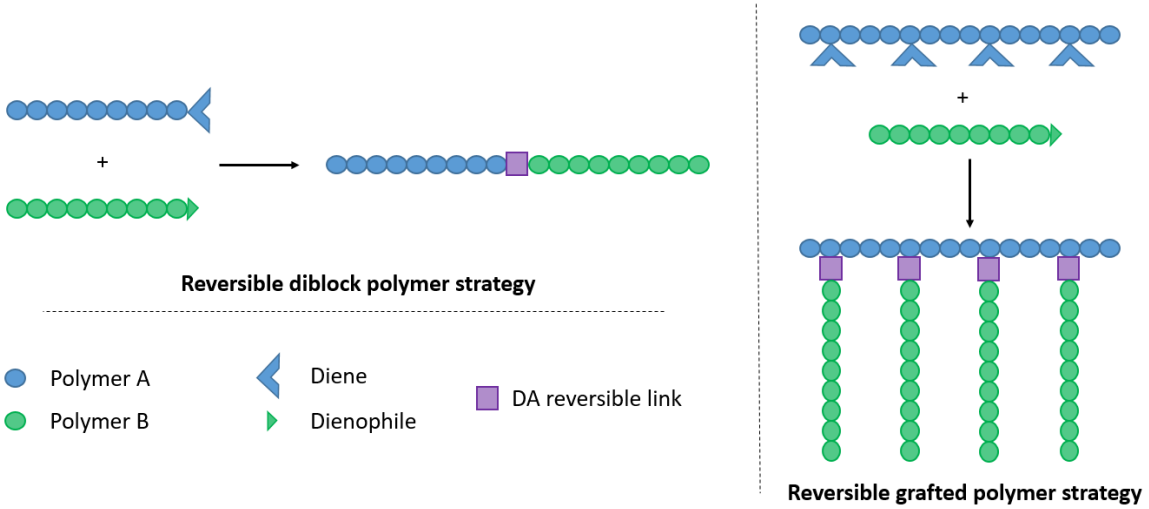
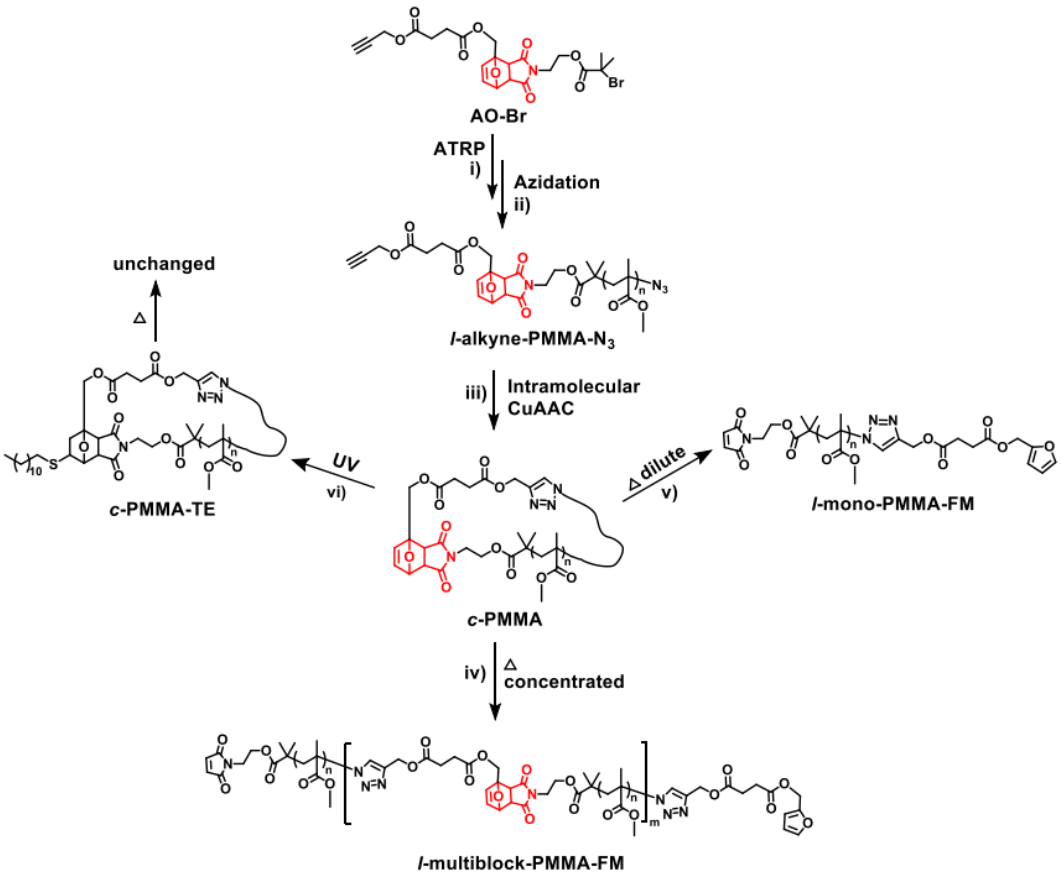


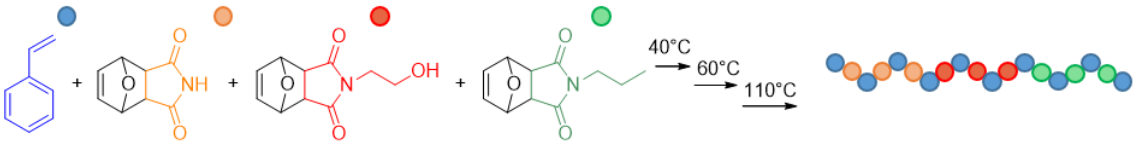

**Figure 9 : Reversible diblock and grafted polymer strategies with anthracene in presence of a dienophile**

Li et al. **[127]** showed that if the DA adduct is a part of a cyclic polymer backbone, its retro-DA allows a facile modification from cyclic to linear topology. **(Scheme 17)**



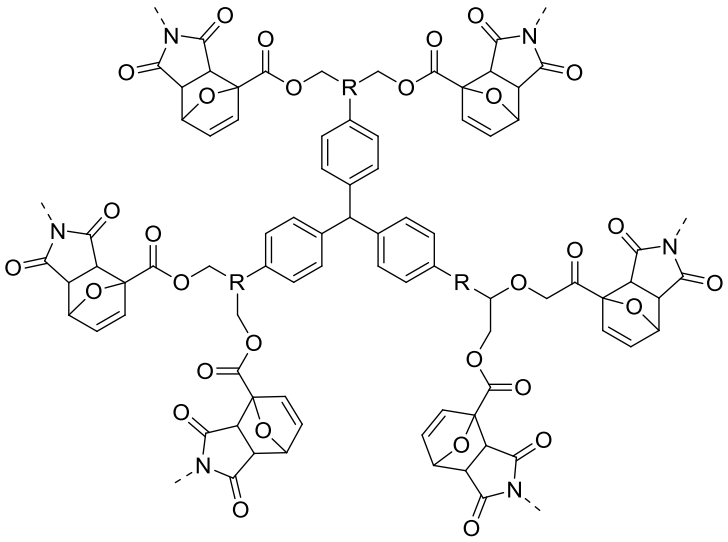

**Scheme 17 : Schematic illustration for the preparation of a reversible cyclic PMMA containing a F/M DA adduct (i) AO-Br:MMA:CuBr:CuBr2:PMDETA = 1:100:0.1:0.01:0.25, acetone as solvent, 50 °C, 2.5 h; (ii) l-alkyne-PMMA-Br:NaN3 = 1:30, DMF as solvent, 30 °C, 24 h; (iii) CuBr:PMDETA = 1:2, toluene as solvent, dilute condition, 50 °C; (iv) toluene as solvent, concentrated condition, 110 °C for 24 h and then 60 °C for 5 days; (v) toluene as solvent, dilute condition, 110 °C, 24 h; (vi) c-PMMA:1-dodecanethiol:TPO = 1:5:0.4, 1, 4-dioxane as solvent, 365-nm UV irradiation, 5h. [127] (reproduced from ref [127] with permission from Elsevier, copyright 2017)**

Lastly, in order to synthesize sequence-controlled copolymer, Han et al. **[129]** smartly used a F/M cycloadduct-based protected form to perform latent monomer for RAFT polymerization. For instance, maleimide is frequently introduced into polymers prepared via a radical mechanism under its furan-cycloadduct form, and easily deprotected by thermal and/or pressure treatment **[21].** Monomers reported by Han et al. **[129]** were DA adducts obtained from furan and different functionalized maleimides. The difference of the retro-DA temperature of each different endo-exo F/M couples was monitored between 40 °C and 110 °C to unprotect, one at the time, each monomer involved in the reaction. (**Scheme 18**).

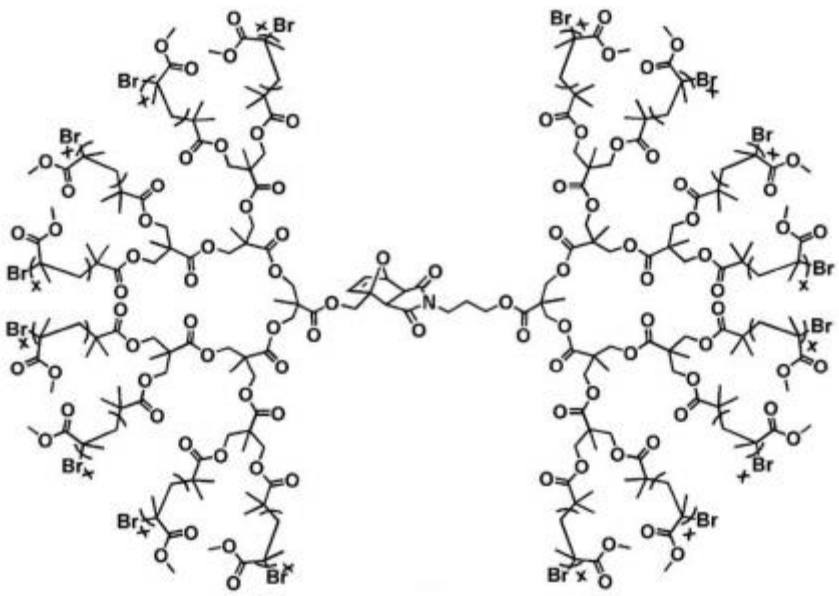



**Scheme 18 : Sequence-controlled RAFT quaternary polymerization of styrene and functionalized maleimide monomers using the F/M DA adduct as latent monomer [129]**

Finally, each polymer or molecular block attached to a F/M moieties can begin a larger elementary building block able to design more complicated structures such as reversible star-like polymers or dendrimers **[5] (Scheme 19), [130, 131]** (**Scheme 20**).



**Scheme 19: Example of the structure of a dendrimer based on furan/maleimide reversible DA reaction [5].**



**Scheme 20 : Structure of furan–maleimide core containing 32-arm dendritic initiators synthetized by Munkhbat et al. [131]. (reproduced from ref [131] with permission from Wiley, copyright 2017)**

Another pertinent use of DA was achieved by Hawker's team. They used a norbornadiene, DA adduct of cyclopentadiene and acetylene, which is also a dienophile, as chain-end functional polymers **[132]** and then ii) the coupling of two polymers (being synthesized by RDRP or ROMP, via a cascade click strategy at room temperature yielding block copolymers (BCPs) **[133]**. Then, a selective and rapid deprotection in the presence of tetrazine enabled to introduce, into synthetic polymers, highly reactive "masked" cyclopentadiene (Cp) functionalities as chain-end groups in an efficient manner. However, and surprisingly, no retro DA was investigated, possibly the BCP being quite stable or from the presence of the $C_5H_{11}$ group.

### 2.4.5 DA for self-healing

Self-healing materials have the ability to auto-repair suffered damages themselves or thank to an external stimulus. A lot of methods to induce self-healing properties have been proposed, using non-covalent bonds **[134]** and covalent bonds of low bond energy **[135]** and **[136]**, as summarized by **Figure 10.**

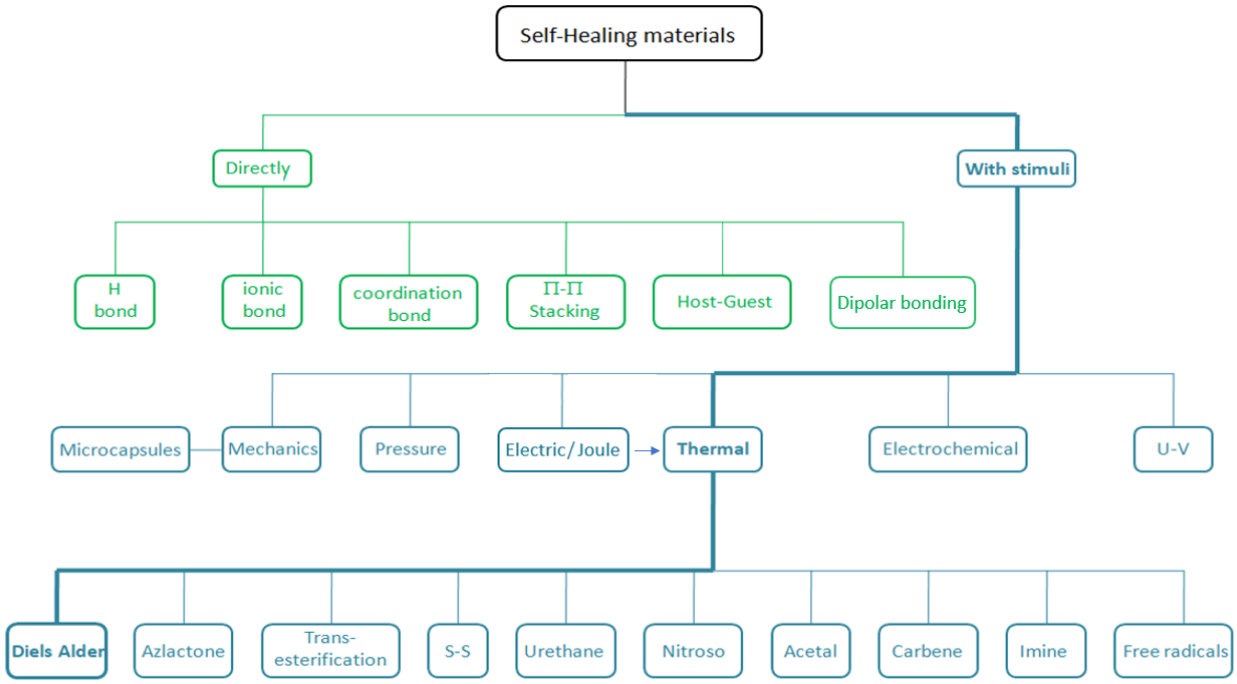


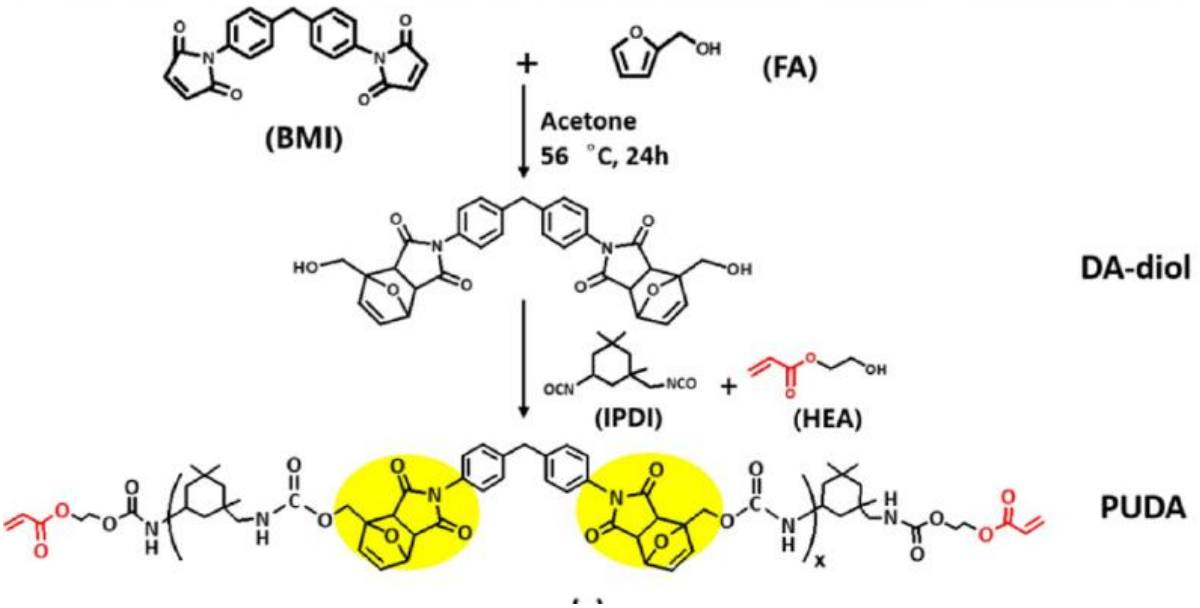

**Figure 10 : Wide variety of strategies to prepare Self-Healing Materials**

The DA reaction, thanks to its ability to do or undo covalent bonds of playing by the temperature, is an effective way to design self-healing or self-repairing materials. Many studies and reviews about self-healing **[20, 137-141]** have already considerably described the subject and it is still considered as a hot topic in polymer chemistry. Reversible covalent chemistries have been harnessed to create covalent adaptable networks (CANs), enabling new applications and insights **[142]**. It is a recent methodology based on efficient associative exchange mechanisms which involve the topologic reconfiguration of networks without the loss of network integrity **[143]**. The field of CANs has become a chemical playground where molecular reactivity and mechanistic principles meet polymer properties. Dynamic covalent linkages within and between polymer chains brings new properties to classical thermosetting polymer formulations, in particular in terms of thermal responses, processing options and intrinsic recycling abilities**.[144]**

### 2.4.6 Shape-memory strategies

One of the usefulness getting crosslinked networks from DA adducts is the ability to tune the temperature of the DA and retro DA to recycle the materials. Another way to take advantage

of this special behaviour is to use it for the development of shape memory materials. The concept of shape memory consists of the possibility for a material to be stably deformed within a certain temperature range and its capacity to turn back to its original shape after heating. Very recently, Li et al. **[145]** developed a polyurethane telechelic bis(acrylate) of high mechanical performances, excellent recyclability, and shape memory properties with the objective to process deformable and recyclable objects for 3D printing. Polyurethane acrylate was synthesised from isophorone diisocyanate, hydroxyethyl acrylate and a DA adduct (**Scheme 21**).




**Scheme 21 : The synthetic strategy of polyurethane acrylate based on DA dynamic reversible bonding (PUDA) [145] (reproduced from ref [145] with permission from Elsevier, copyright 2020)])**

Due to the rigidity of DA adduct in the polyurethane acrylate and the flexibility of hydroxyethyl acrylate, the photopolymer resin forms a two phase-morphology after curing, which makes it an ideal structure to get shape memory property.

The shape memory performance of the obtained materials was investigated through fold-deploy tests (**Figure 11**) **[145]** and shape memory cycles measurements (**Figure 12**) **[145]**.

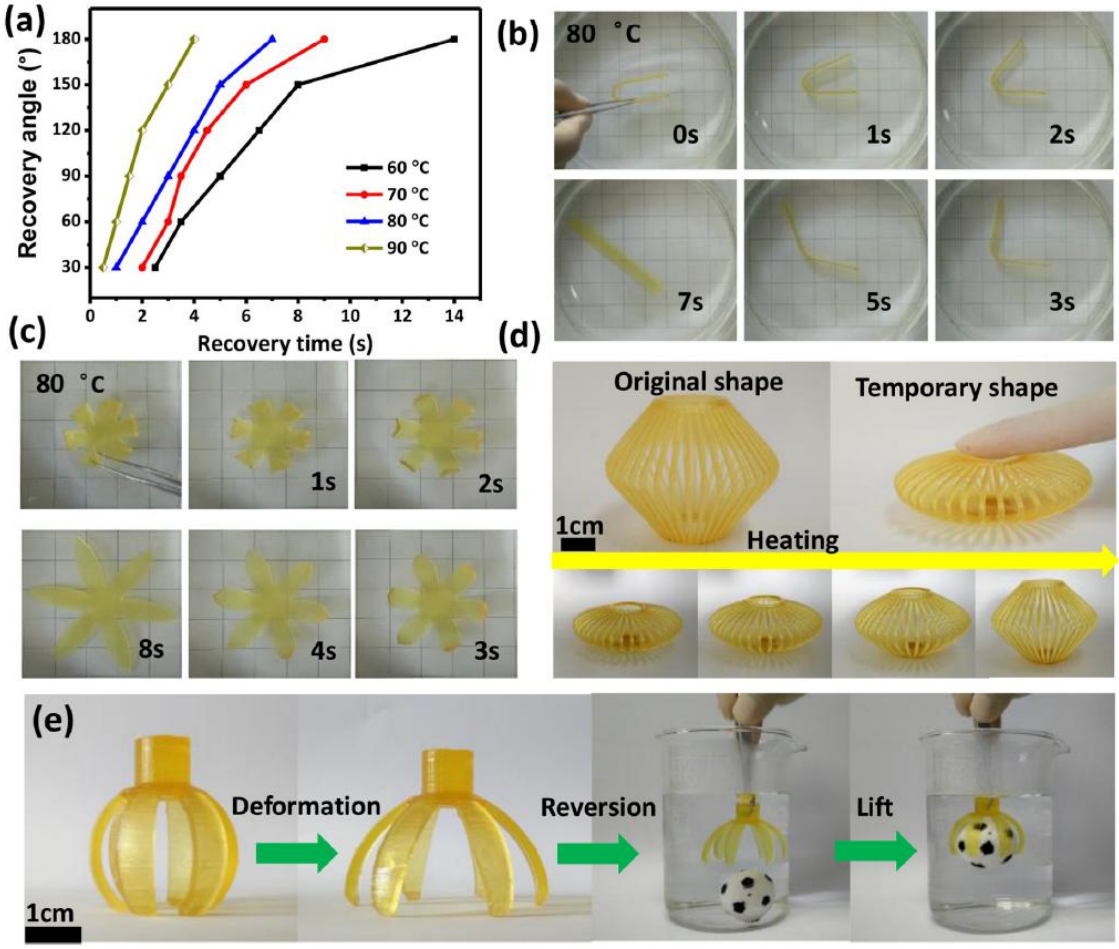



**Figure 11 : Fold-deploy experiment results for the printed samples with polyurethane acrylate (PUDA)-40: (a) recovery angle of the printed sample with time in a water bath at different (b) the recovery process of the sample in an 80 °C water bath; (c, d, e) visual demonstration of shape recovery processes of the printed petal, lamp-chimney and gripper in a water bath or with a dryer. [145] (reproduced from [145] with permission from Elsevier, copyright 20202).**

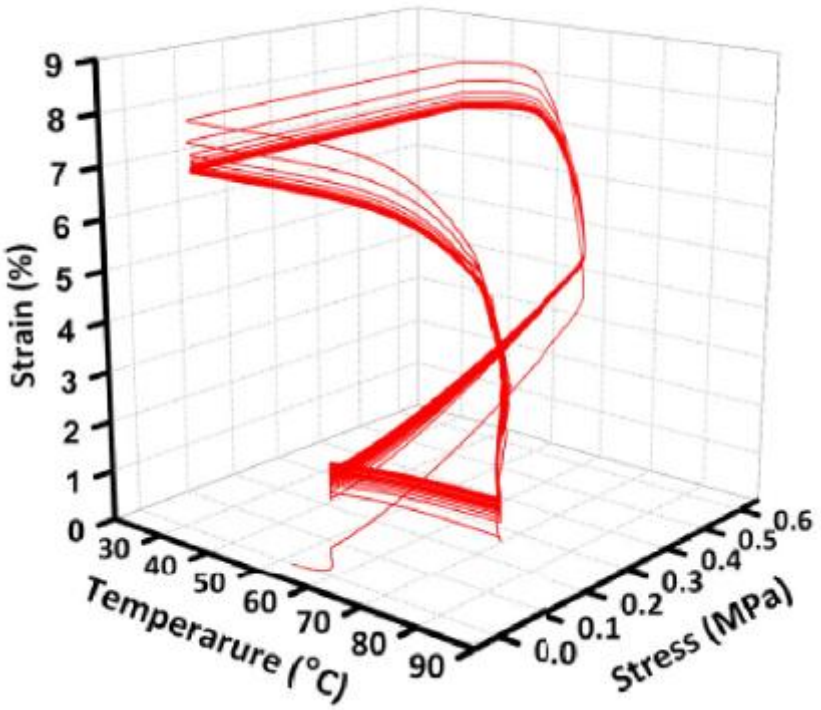



**Figure 12 : Stress-strain-temperature diagram from SMC test of the printed samples with the photopolymer resin PUDA-40 [145] (reproduced from [145] with permission from Elsevier, copyright 2020).**

In addition to this example, more and more studies have reported the use of DA adducts for the fabrication of shape memory materials, either from polyurethane **[110]**, PLA**[146]**, polyester **[147]**, polycaprolactone**[148]**or epoxy resin **[149-151].**

Self-Healing and Shape memory can be combined. Rodriguez et al.**[152]** introduced the Shape Memory Assisted Self-Healing (SMASH) concept on ε-caprolactone, while a comprehensive review was reported by Raquez-Dubois' team in 2016 **[153]**

### 2.4.7 H-Bonding strategy

Furthermore, hydrogen bonding is also useful for DA reactions. As an example, from trifurans and 3-maleimide-propanol, Nguyen et al. **[154]** reviewed the importance of these bonds and synthesized polyurethanes (PUs) in which such bonds are preserved during the heating and are still inducing some structuration (**Figure 13**). Indeed, after a first decrosslinking around 95 °C, these polymers display mobility enough to enable a new crosslinking at 75-85 °C whereas the next decrosslinking starts at higher temperature than the first one (around 110-115 °C).

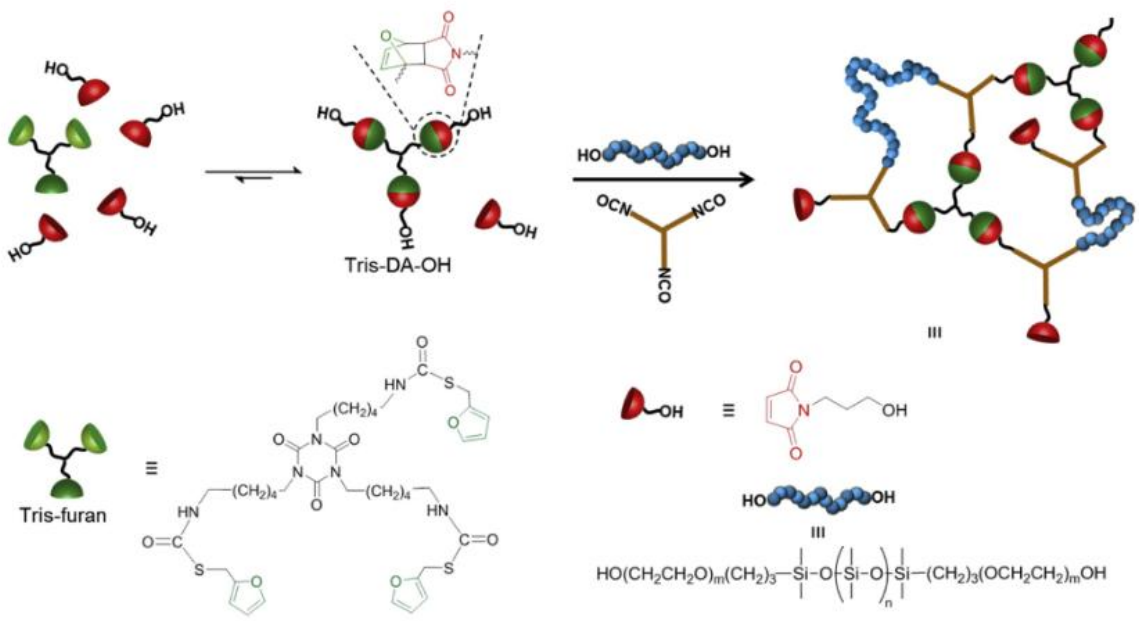



**Figure 13 : Schematic representation of a thermoreversible network based on polydimethylsiloxane [154].**

In 2014, Zhang et al. **[155]** also studied the thermally reversible cross-linked PUs endowed with comprehensive remarkable mechanical properties as reported in their previous survey **[156]**. The microphase-separated structure and heterogeneous segmental dynamics were highlighted by T2 relaxometry experiments, also used to in situ monitor the reversible cross-linking associated with DA and rDA reactions. Based on the T2 relaxometry results, these authors determined the actual temperature of (r)DA reaction as well as the corresponding activation energies of the motion of soft segments.

### 2.4.8 DA reversible thermoset (DART) for 3D

Smaldone's group **[157]** suggested a DA reversible thermoset (DART) process for a first generation of printable DART resins. These resins displayed thermoset properties at use temperatures, ultralow melt viscosity at print temperatures, smooth part surface finish, and as-printed isotropic mechanical properties, hence enabling further erasable surface decoration on micron-scale on the printed parts in a post processing setup.

### 2.4.9. Sealant cured on demand

Sealant cured on demand (SCOD) concept deals with the reaction monitoring at a given temperature to solve a technical issue which is often applied **[158]** . The post-crosslinking consists in processing a polymer and then to launch the crosslinking when this macromolecule is processed. The desired applications encompass the coatings, adhesives, hybrids, composites, etc...

A major application of SCOD concerns materials called "*monocomponents*" for which the action of a thermal or photochemical stimulus **[158]** favors the curing and one reversibility occurs, only. Among them, a classical example deals with masked polyurethanes which can be illustrated as follows: when heated, these polymers release an isocyanato function that reacts with moisture. Delebecq et al. **[159]** comprehensively reviewed how to choose appropriate blocking agents to regulate the deblocking temperature.

Actually, that concept was used for DA reaction by our team to block maleimides by various furans (acetoxy furans and other furoic esters bearing long chain in order to avoid any bubbles in the final material) in the presence of various mercaptans **[160]**. Increasing the temperature (up to 80 °C) enables to unlock the endo compound and spontaneously reacts onto polythiols *via* a conventional thiol-ene reaction. Moreover, we also observed the presence of the exo isomer that needed to reach 110 °C to be unlocked. Further, aromatic and aliphatic bismaleimides were compared to optimize the retro DA reaction (**Figure 14**)**[161].** Aromatic maleimides led to the best compromise to reach a good conversion and easy process.

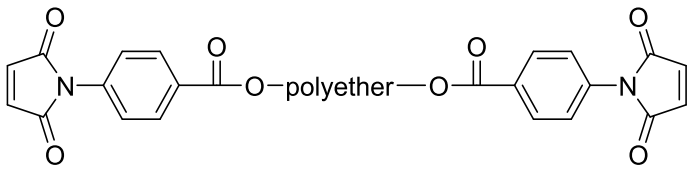



**Figure 14 : aromatic telechelic bis(maleimide) poly(ether) [161]**

All possible uses of the F/M couple in the synthesis of polymers is not only applied to this couple. Indeed, they are all transposable to other combinations of dienes and dienophiles. By tuning the reactivity of the diene/dienophile couples toward the property of the resulting product and on their DA and retro DA temperatures, a wide variety of materials can be offered as well as applications. Therefore, it is important, before describing about the current application trends of such a reaction, not to be limited to the simple F/M couple but to suggest a non-exhaustive list of other potential diene/dienophile candidates involved in the DA reaction.

### 2.4.10 DA in health

As demonstrated, DA reaction plays a massive role in the future of synthetic organic and polymer chemistry. Accordingly, its importance for pharmaceutical or biomedical applications is steadily increasing. DA is present in the synthesis of biomolecules**[162],** for drug delivery **[163, 164]**, fluorescent sensor **[165]** and vaccines **[166].** it is easy to quickly find excellent recent reviews describing the use of the DA tool in the field of drug delivery **[167]** and more generally in chemical biology **[168, 169]** confirming the interest of this reaction in this specific field.

# 3. Other diene/dienophile couples

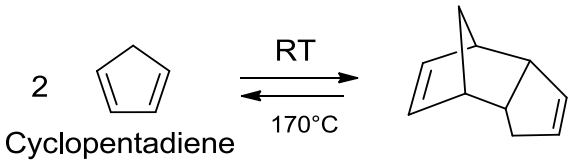
Even if F/M couple has been widely described for the DA reaction through the years, it would be a mistake to limit ourselves to only this one couple. Indeed, as stated in the introduction, many dienes and dienophiles have already been reported for a long time in the DA community. In addition, because of the nowadays renewed and growing interest for renewable building-blocks, new dienes, and dienophiles, although they were involved in other applications several decades ago, are starting to be more and more used in DA reaction. Thus, these molecules, able to perform the DA reaction, increase the possibilities drastically and may permit to consider the potential limits of F/M couple. It is therefore necessary to present these potential candidates before getting involved with the significant applicative fields of DA features.

## 3.1. Petro-based dienes

At the beginning of the 20$^{th}$ century, the industrialization of oil led to a massive generation of molecules. These new petro-based products have influenced and improved the chemical industry. At the same time, the DA reaction was also discovered. Among all dienes, cyclodienes, cyclopentadiene and anthracene have been quite used in DA reaction and are described hereafter.

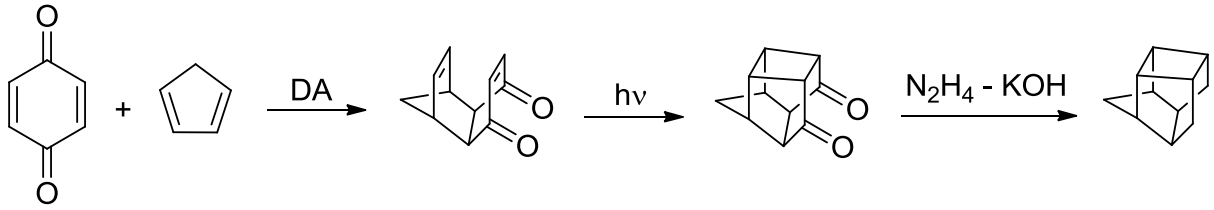
### 3.1.1 Cyclodienes and cyclopentadienes

Cyclodienes also play an active role in DA reaction. Indeed, furan and its derivatives are commonly employed as dienes. However, other cyclodienes are worthy of interest such as cyclopentadiene (CPD) which is the second most famous cyclodiene in the DA community. CPD is obtained from coal tar, by steam cracking of naphtha or from other hydrocarbon products **[170, 171]**. CPD dimerizes via DA reaction into dicyclopentadiene **[172]**. This dimerization is still studied **[173]** and it is possible to re-obtain CPD via retro-DA above 170 °C **(Scheme 22).** Indeed, pure CPD must be stored at low temperature (-20 °C) to prevent from a spontaneous and highly exothermic dimerization. Thanks to the dimer adduct and its retro-DA, it is suitable to generate CPD *in situ* to avoid safety issues linked to the use of free CPD **[174]**.




**Scheme 22 : Dimerization of cyclopentadiene [173]**

Since the beginning of the 20$^{th}$ century, many DA reactions involving CPD have been reported with a lot of dienophiles **[175]**, such as quinones **[176]**, unsaturated trihalosilanes **[177]**, acrylate derivatives **[178]**, vinyl ketones **[179]** or fullerenes **[180]**. DA reaction with CPD is well-documented and many articles focus on the *ab initio* calculations with plenty of dienophiles and solvents for a better understanding of the reactivity of CPD and to anticipate some possible reactions **[181-183]**. Other studies have been devoted to the elaboration of original catalysts **[184, 185]** or on the impact of the possible function borne by CPD on the reactivity of the resulting diene **[186]**. Very recently, reactions of CPD with hexadienone **[187]** and benzoquinone have been reported **[188, 189]** (**Scheme 23**), enhancing the major role of CPD in the DA field.




**Scheme 23 : Synthesis of "cage" from DA reaction between benzoquinone and cyclopentadiene [189]**

Other cyclodienes, such as cyclohexadiene **[190, 191]** or cycloheptadiene **[192]** have also been involved in DA reactions. They have a lower reactivity than those of furan or CPD. However, a recent study has shown an improvement in the reactivity of some cyclodienes with hetero-dienophiles, which is a hopeful perspective for further use of these dienes. **[193]**.

Besides the furan described above as a diene or cyclopentadiene reactive in hetero Diels Alder **[194]**, some hetero-cyclopentadiene can be involved in DA reactions such as thiophene or pyrrole (**Figure 15**). Thiophene can be used as a diene or dienophile, but it is not very reactive **[195]**. In order to overcome this lack of reactivity, it is possible to substitute it **[196]** or to oxidize the sulfur atom of the molecule **[197]** (**Figure 15**). Pyrrole, a nitrogenous cyclopentadiene, also suffers from a lack of reactivity for DA reactions acting as a dienophile **[198, 199]**. It can be noted that pyrrole can also behave as diene in [4+3] cycloaddition reactions. **[200]**

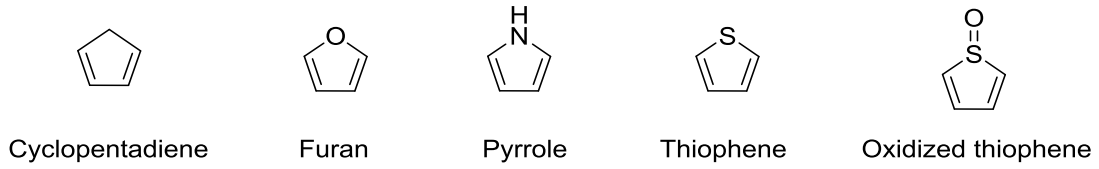
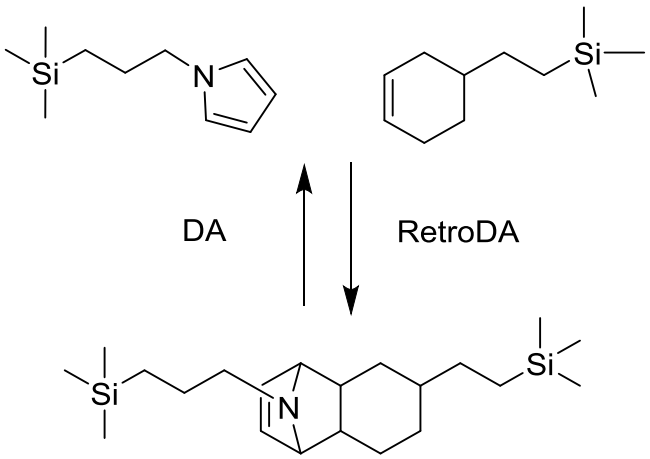



**Figure 15 : Structure of cyclopentadiene and hetero-cyclopentadiene**

Less studies have been developed utilizing pyrrole as the diene. Hwang's group **[201]** reported self-healing ladder-like structured polysilsesquioxane copolymers and terpolymers from a DA reaction between pyrrole and cyclohexenyl-containing silicon moieties. First, the functionalization of both diene and dienophile were achieved on the double-stranded siloxane backbone bearing n-alkyl soft groups inducing some chain mobility **(Scheme 24**).




**Scheme 24: DA and rDA reactions involving pyrrole and cyclohexenyl-containing polysilsesquioxane copolymers [201].**

The DA curing time was optimized to be 90 °C. Then, these authors studied the effect of chain mobility and the chemical structure on self-healing and mechanical properties. All such self-repaired hybrid materials exhibited fast healing times (ca. 5 min) and their decrosslinked adducts displayed remarkably high retention of solubility in conventional organic solvents for good reusability. They also exhibit high thermostability and optical transparency.

Inglis and Barner-Kowollik **[202]** provided a critical review on recent developments in the area of ultra-rapid and mild conjugation chemistries used in polymer chemistry, as an interesting guide to help the formulation of design strategy for novel functional materials. For example, the DA conjugation between cyclopentadiene-functional polymers and those prepared by RAFT polymerization **[203]** can be simply achieved under ambient conditions of atmosphere and temperature within a few minutes hence yielding block copolymers (**Figure 16**).

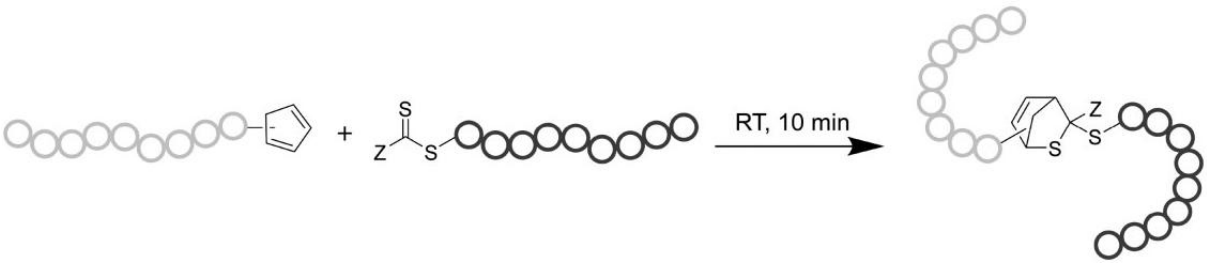



**Figure 16 : Ultra-rapid RAFT-HDA click chemistry [202] (reproduced from [202] with permission from Wiley, copyright 2010)**

.

The same authors also proposed the inverse electron demand Diels–Alder (IVED-DA) reaction between electron-deficient tetrazine derivatives and various alkenes (trans-cyclooctene). Although non-regioselective, these reactions are quite efficient, rapid and occur under mild chemical transformation **[203]**. One example, supplied from **Figure 17** involves tetrazines and strained alkenes, as more recently reported by Hawker's group from a similar strategy **[132, 133]**.

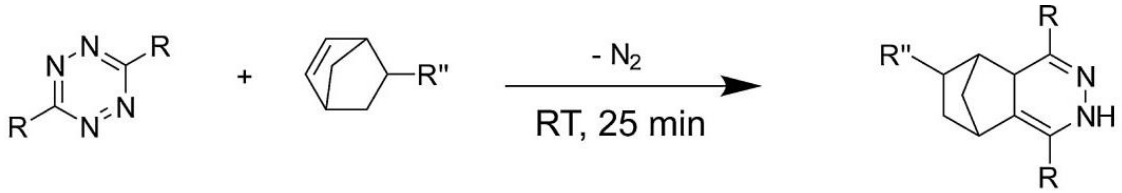



**Figure 17 : Inverse electron-demand Diels–Alder reaction between tetrazines and strained alkenes**

### 3.1.2 Acyclic dienes

Acyclic dienes take an active part in the DA area. Butadiene, which is the simplified model of a diene, can react readily with maleic anhydride, acrolein, quinone and many other dienophiles **[175]**. In addition, the Huntsman (formerly Viking) company uses that strategy to produce telechelic bis(epoxycycloaliphatic) monomers by addition of butadiene onto acrylic acid as UV cationic resins.

It is possible to represent the other acyclic dienes as substituted butadiene with a wide variety of $R_i$ groups (**Figure 18**) and a lot of acyclic dienes can perform DA reactions **[204-206]**.

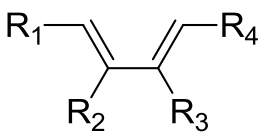
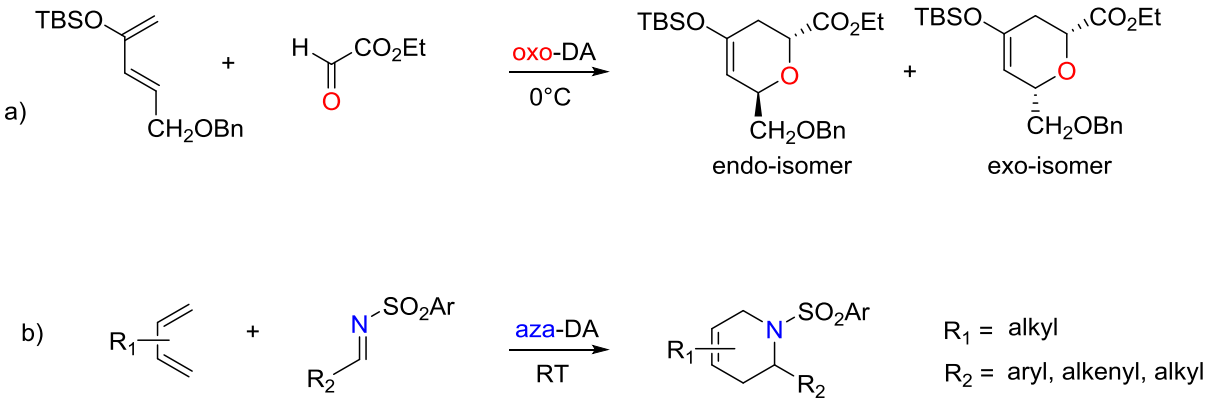



**Figure 18 : Model of dienes structure from butadiene.**

In addition, many articles have reported the use of acyclic dienes in hetero-DA **[207]** such as Aza **[208]**, or Oxo. **[209]** (**Scheme 25**)




**Scheme 25 : a) Oxo [209] and b) Aza [208] DA involving acyclic dienes.**

In general, acyclic dienes have a lower reactivity than those of cyclodienes. However, some of acyclic dienes with a specific structure, can be more reactive than the others. This is the case of an electron-rich diene so-called "Danishefsky's diene", reported in 1974 **[210](Figure 19a)**.These reactants can be used to synthesize molecules of interest such as Xestocylamine **[211]** or involved in hetero-DA as oxo-DA **[212, 213]**(**Figure 19b**) or aza-DA **[214]**(**Figure 19c**).

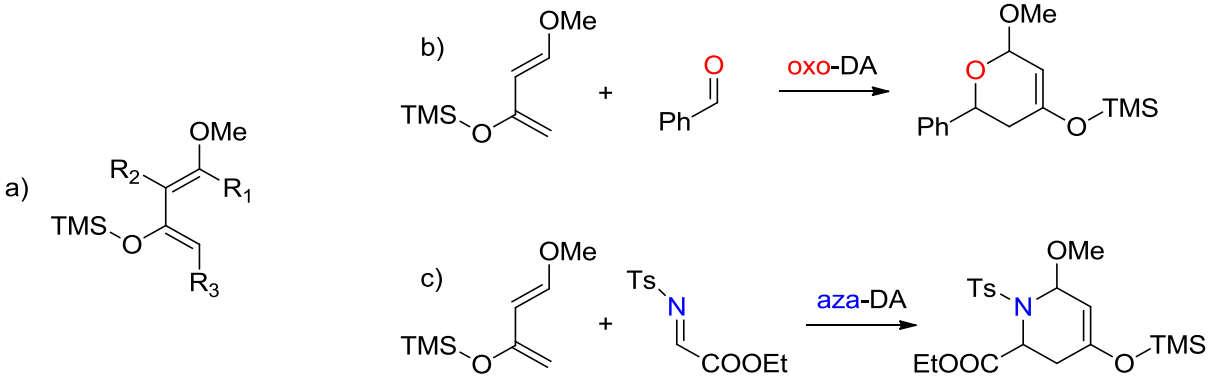
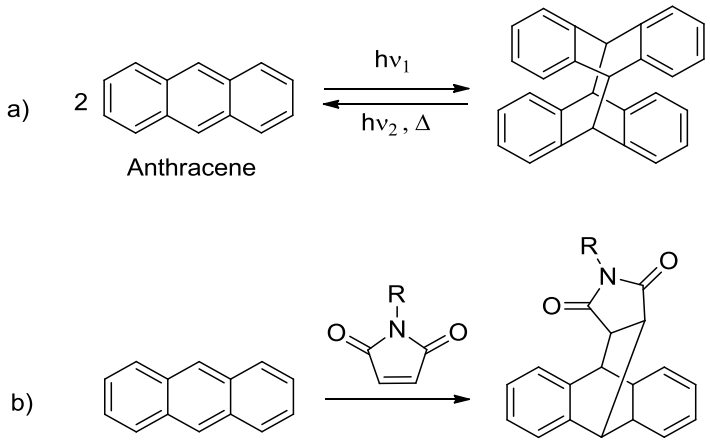



**Figure 19 : a) Structure of a Danishefsky's diene (where TMS stands for trimethylsilyl; [210]. b) Example of an oxo-DA involving a Danishefsky's diene [213]. c) Example of an aza-DA involving a Danishefsky's diene. [214]**

### 3.1.3 Anthracene

Anthracene is a solid polycyclic aromatic hydrocarbon consisting on three benzene rings (**Scheme 26**) which was first isolated in 1832 by Dumas and Laurent **[215]**. It is worth mentioning that anthracene tends to dimerize under photo-irradiation as shown in **Scheme 26a [216, 217]**. The use of anthracene for industrial aromatic chemistry started with the

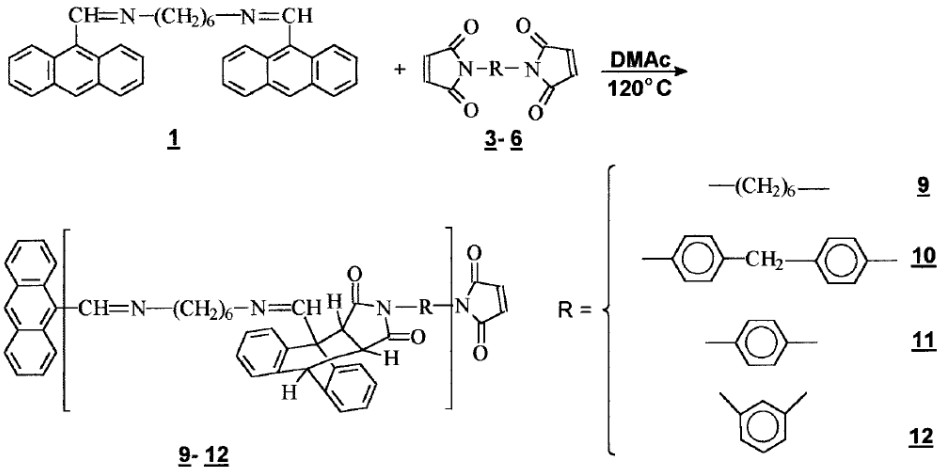
synthesis of the dyestuff alizarin by Graebe and Liebermann as well as by Perkin in 1868 **[218]**. This product can be extracted from coal **[219]** and specific syntheses for functionalized anthracenes have been developed over the years **[220, 221].**




**Scheme 26 : a) Photo-dimerization of anthracene [216], b) Diels-alder reaction between anthracene and maleimide**

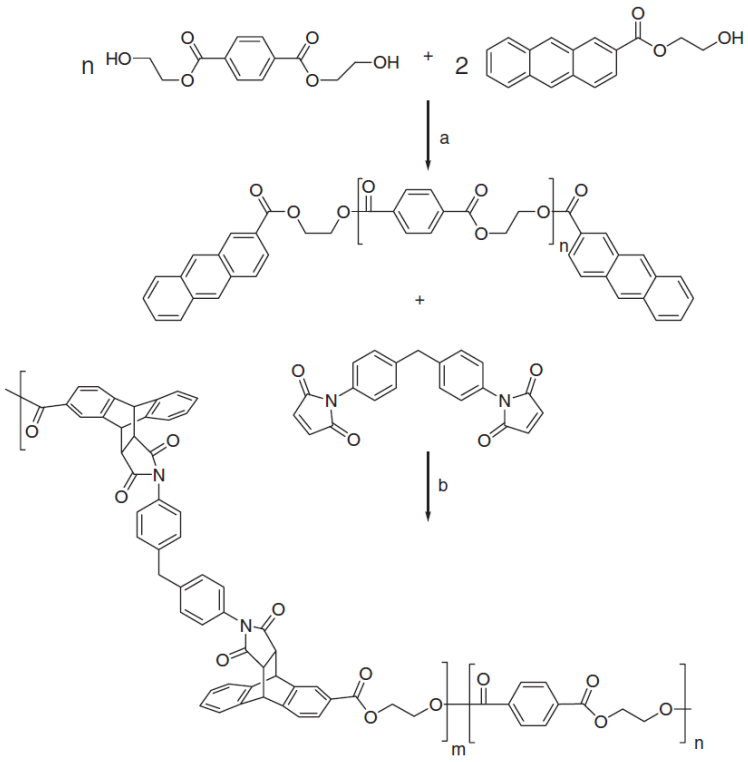
In 1942, anthracene was quickly used in DA reaction **[175] Scheme 26b**. This compound and its derivatives can react with many dienophiles such as maleic anhydride and derivatives **[222]**, carbonyls **[23]** or fumarates **[33]** and are often used in the production of polyester **[223]**, polyethylene **[220, 224]**, or new DA adduct polymers **[225].** Its ability to perform retro-DA and the impact of the substituent of the cycloadduct were well-studied by Chung et al. **[226]** while Snyder's group used this behavior to develop chiral anthracene template as recyclable stereocontrolling elements **[227, 228]**. In addition, several teams reported the use of anthracene to replace furans as highlighted by Liu and Chuo in an interesting review mainly devoted to AD **[20]**. Simionescu et al. **[229]** pioneered the reaction between unsaturated monomers bearing anthracenic moieties and electron deficient-monomers (e.g. acrylates, methacrylates and maleimides). In 1985, these authors highlighted the formation of a charge transfer complex, K, between maleimides and anthracenic group (K=0.05 as a high value compared to those of conventional acceptor-donor systems). Two examples of copolymerization have been reported: i) from 9-anthrylmethyl methacrylate and *N*-phenyl maleimide **[229]** and ii) from methacrylate anthracene and the corresponding acrylate. **[230]** Indeed, from the acrylate, only DA occurred while with the methacrylate, both radical polymerization and DA were concomitantly observed. In another study, the same authors **[231]** showed that *N*-(1-anthryl) maleimide in a thermal reaction led to AD while by anionic initiation, homopolymerization only was noted. From these initial features, Schiraldi's group

**[220]** revisited these reactions and evaluated the retroDA and evidenced that this occurred at high temperature (250-300 °C). In 2001, Grigoras and Colotin **[225]** synthesised polyimines from the DA reaction between anthracene-based dienes and four telechelic dienophiles containing bismaleimide functions (**Scheme 27**). The polycondensation reaction was performed in *N*,*N*- dimethylacetamide at 120 °C yielding polymers, soluble in polar solvents, with molar masses ranging between 3500 and 5600 g $mol^{-1}$. From TGA analysis, these authors observed a two-step decomposition: i) the first one at 250-300 °C ($r_{DA}$) while the second one, starting from 450 °C, corresponds to the decomposition of the imine function.




**Scheme 27 : Synthesis of Diels–Alder polymers from the addition of dienes containing anthracene groups and telechelic bismaleimides [225]**

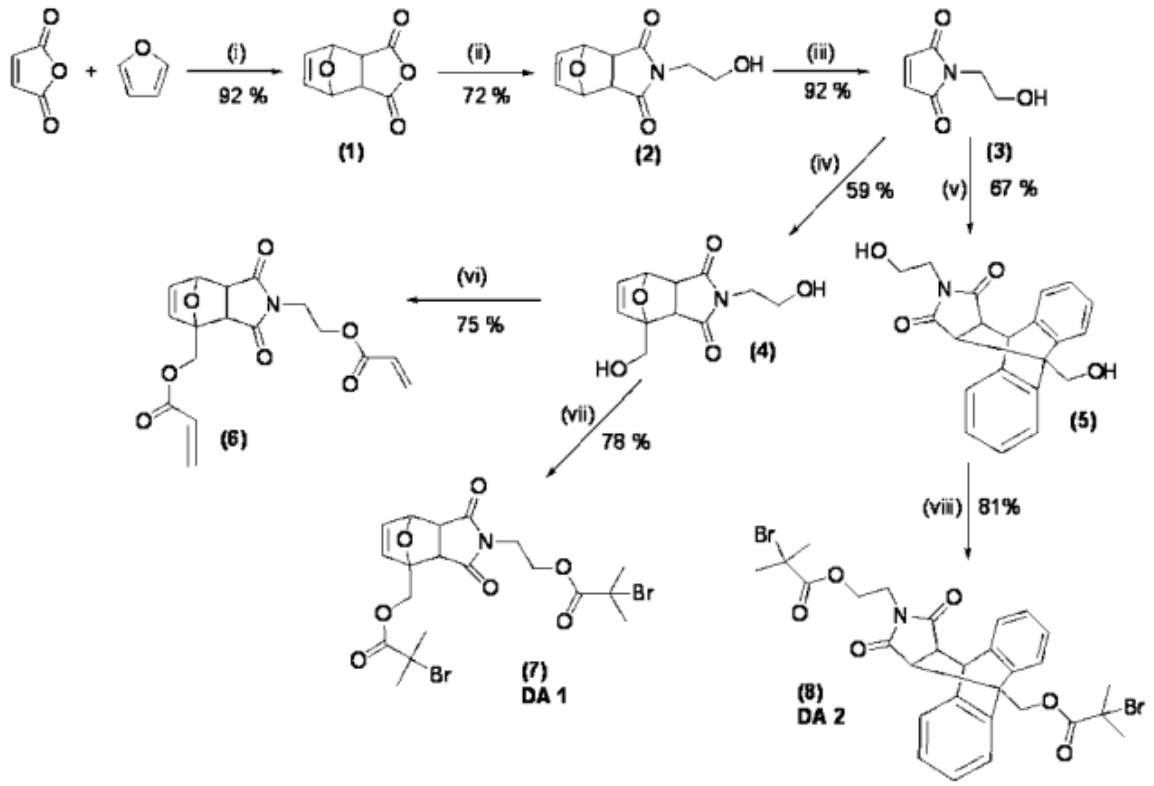
A further interesting survey achieved from Schiraldi's team **[223]** deals with the polytransesterification of bis(2-hydroxyethyl) terephthalate with 2-hydroxyethyl 2-anthracenecarboxylate (in a small amount) leading to low molar mass anthracene-terminated macromonomers (**Scheme 28**). Their anthracene end-group functionality ranged between 1.66 and 1.85. These macromonomers underwent a rapid chain extension with di(4-maleimidophenyl)methane via Diels-Alder cycloadditions resulting in consumption of the anthracene and maleimide end groups to generate polymers with Mn >$2.0*10^4$ g $.mol^{-1}$.



**Scheme 28 : Polytransesterification of bis(2-hydroxyethyl) terephthalate with 2-hydroxyethyl 2-anthracenecarboxylate yielding telechelic macromonomers bearing anthracene end-group followed by chain extension with di(4-maleimidophenyl)methane [223]**

Interestingly, these authors also reported a model study from anthracene methyl carboxylate and phenyl maleimide and the reversibility was monitored by $^{1}$H NMR spectroscopy at 260 °C. Thus, they determined a constant of reversibility but with the polymers, even at 350 °C, they could only conclude that partial degradations occurred even if reversion also happened. Hence, for self-healing, the reversion temperature, is too high, especially for this polymer.

In an interesting article, Haddleton's team studied and compared the efficiency of AD furan-maleimide and anthracene **[74]** by synthesizing well-defined linear and star PMMA polymers bearing DA adducts in their macromolecular backbone. They also reported a preliminary evaluation of their ability to cleave and reform it under external thermal stimuli (**Scheme 29**).



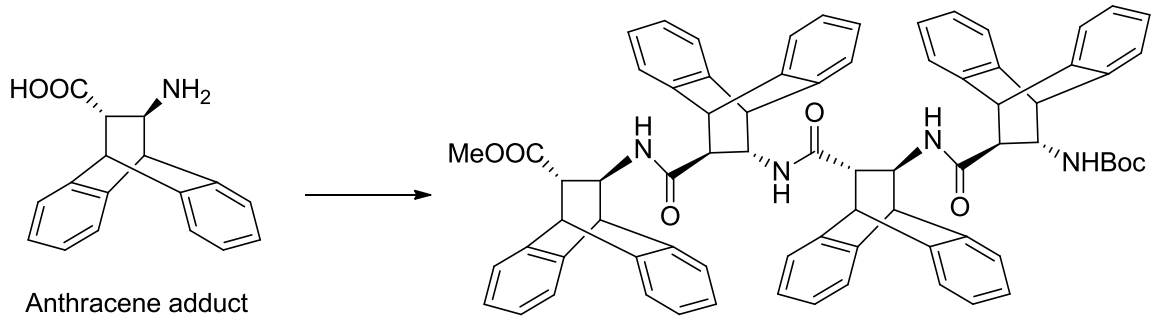

**Scheme 29 : Synthesis of telechelic bis(acrylate) and original ATRP initiators from furan/maleimide and anthracene/maleimide adducts [74]**

From the furanic derivative, 100% reversion was obtained in THF reflux for 24 hr and 50% at 60 °C for 24 hr. From the anthracene compound, this is not as easy and the authors, within the reversion at 200 °C in DMSO, used rhodamine to block the reaction. They noted a 20%-decrease of the molar mass that suggested some Diels Alder reactions.

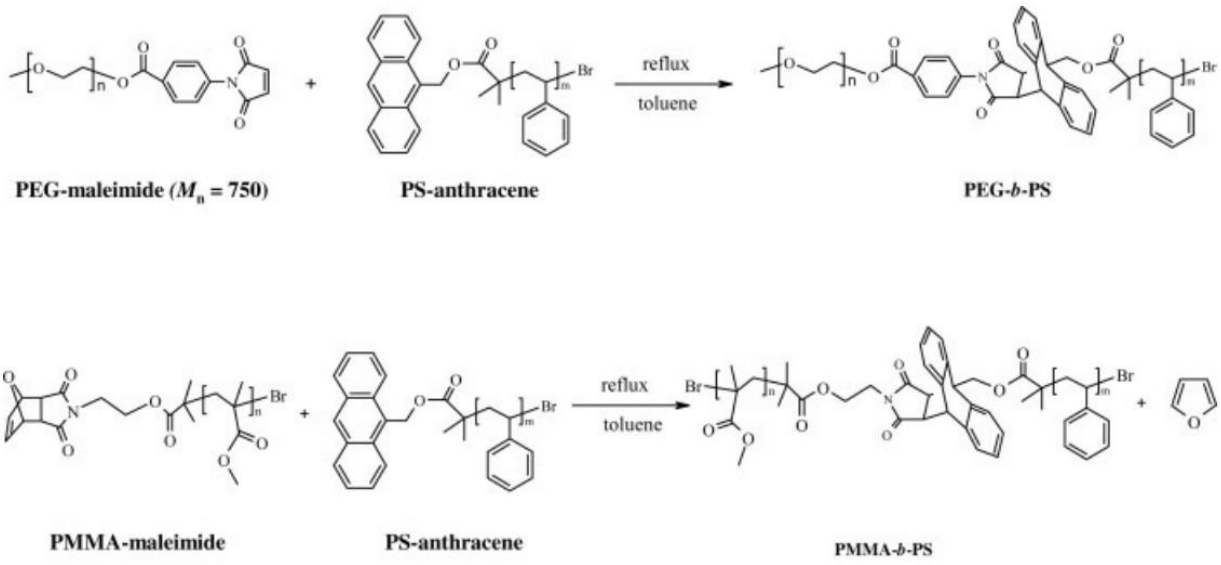
Some other articles describe that anthracene was brightly involved in the synthesis of aromatic polyamides containing anthracene units by tuning with its aptitude for retro DA **[232]**, or in the synthesis of foldamer **[233]** (**Scheme 30**). Another smart use of anthracene was also reported by Durmaz, Hizal, Tunca et al. These authors pioneered the use of anthracene and maleimide functional polymers to generate well-controlled architectures encompassing block copolymers, **[1, 234]** (**Scheme 31),** star copolymers, **[235, 236]** graft copolymers **[2, 237]** and even more complex structures. **[238]** Although making use of readily available materials without any catalyst, elevated temperatures (>110 °C) and extended reaction times (36–120 hr) appear as severe limitations.

Sun et al. demonstrates the versatility of anthracene in DA reaction for the synthesis of amphiphilic or hydrophobic block, comb copolymers, segmented hyperbranched polymers

and star polymers **[239] (Figure 20).** All these examples show that anthracene plays a significant role in the DA area and may still have hidden potential for future applications.




**Scheme 30 : Formation of a foldamer from anthracene adducts [233]**




**Scheme 31 : Reversible diblock PS-*b*-PEG or PS-*b*-PMMA block copolymers linked with anthracene maleimide DA adduct [1] (reproduced from [1] with permission from Wiley, copyright 2006))**

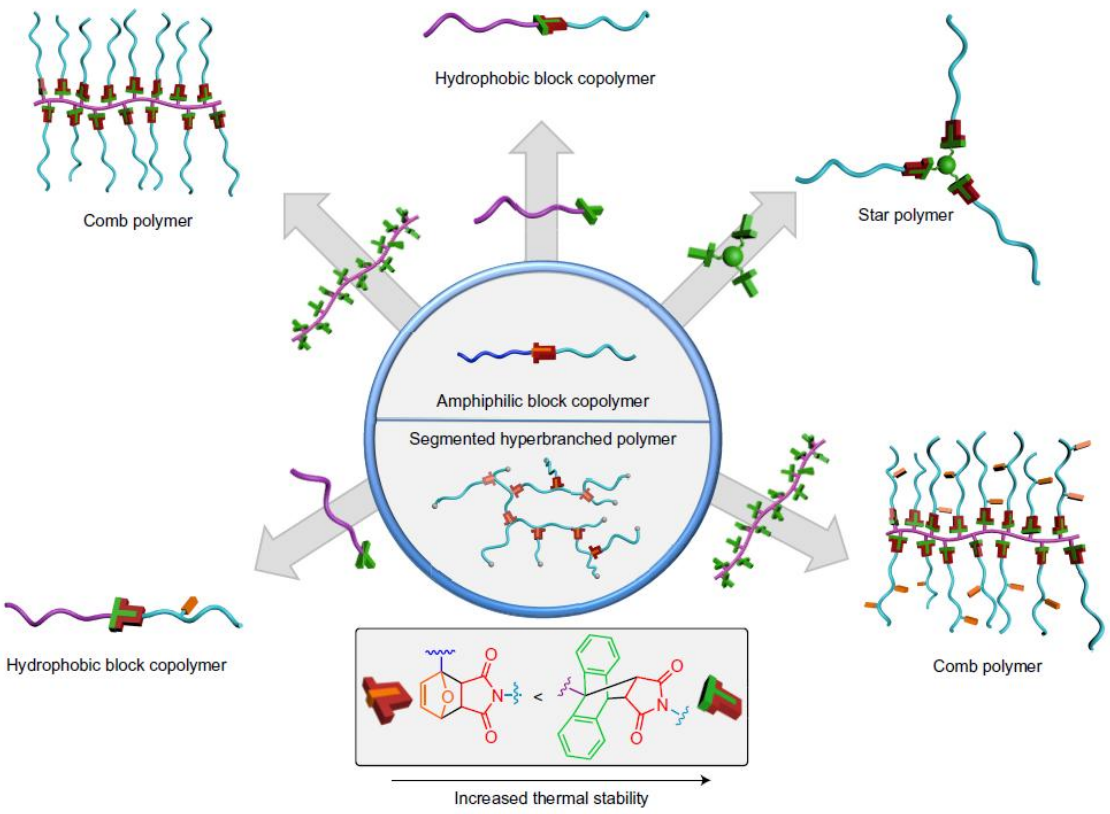
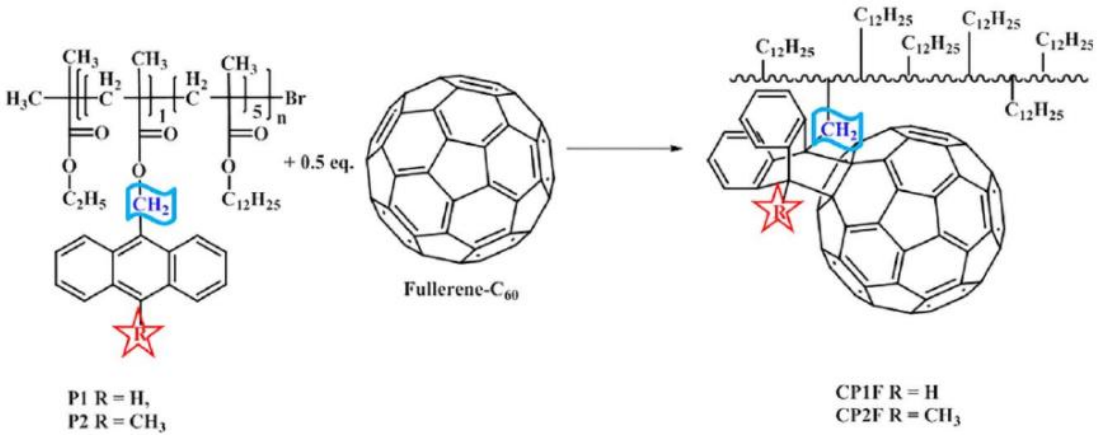



**Figure 20 : Transformation of an amphiphilic block copolymer and a segmented hyperbranched polymer into various macromolecular architectures via diene (furan or anthracene) displacement reactions [239] (reproduced from [239] with permission from Nature Publishing Group, copyright 2017)**

Schubert *et al*. **[240]** synthesized terpolymers based on original (meth)acrylates containing anthracene side groups which were further used in DA cycloaddition with fullerene $C_{60}$. (**Scheme 32**) The copolymer bearing methacrylate was identified as the most reactive combination. The self-healing efficiency, assessed by 3D microscopy, interestingly showed that these new fullerene-containing copolymers feature a peculiar low healing temperature (40-80 °C and in 15 min only, at that upper temperature) when compared to other DA-based self-healing polymers. Additionally, in other studies, the concept could be particularly useful self-healing studies of DA-based semiconductors achieved for low temperature. These unexpected results are quite interesting since previous authors reported that healing polymers bearing anthracene occurred at rather high temperatures (250 °C).




**Scheme 32 : Schematic representation of the DA reaction of poly(methacrylate) copolymers bearing anthracene functions with C60-fullerene resulting in CP1F and CP2Fmaterials (only one possible fullerene anthracene adduct is depicted, crosslinks are also possible) [240] (reproduced from [240] with permission from Wiley, copyright 2018)**

## 3.2 Bio-sourced dienes

Currently, the use of sustainable raw materials and eco-responsible processes is becoming more and more frequent and increasingly searched in the world of the polymer industry. Therefore, in this context, it is relevant to list and show a growing interest in the bio-sourced dienes which can be used in the DA reaction. Several candidates have already demonstrated their efficiency, such as sorbic acid and its derivatives, muconic acid, myrcene, farnesene, eugenol and cardanol (**Figure 21**). Vegetable oils will be not mentioned in this part even if they are currently described when related to bio-based molecule. Indeed, despite the abundance of unsaturation in the alkyl chain of common oil, the lack of conjugated double bond does not allow to use them as dienes but as dienophiles. However, it is worth noting that some conjugated vegetable oil exceptions exist such as conjugated linoleic acid. **[241]**

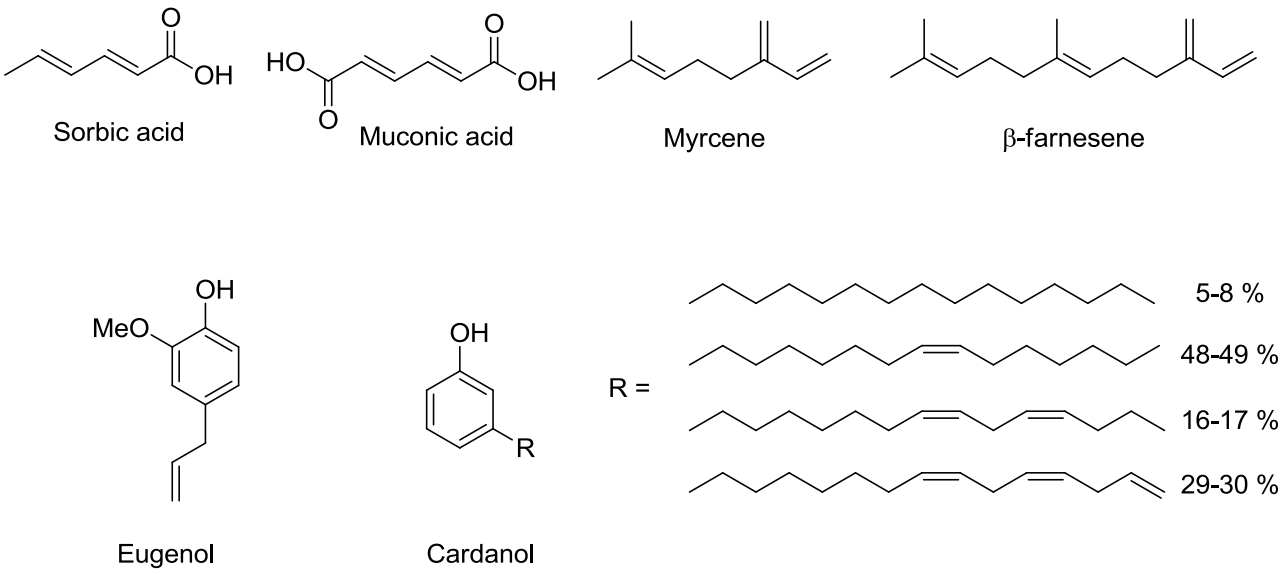
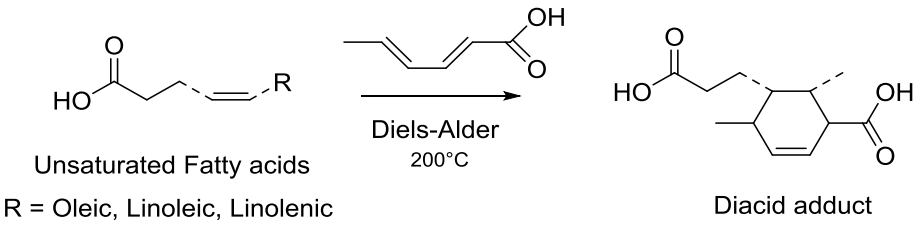



**Figure 21 : Structures of different bio-based dienes used for the DA reactions in polymer fields**

### 3.2.1 Sorbic acid and derivatives

Sorbic acid was isolated in 1859 by distillation of rowanberry oil by Von Hofmann. Once the oil distilled, the lactone of sorbic acid, parasorbic acid, is obtained. It is then necessary to go through a hydrolysis step to yield the desired acid. Sorbic acid and its salts are antimicrobial agents often used as preserves in food and drinks to prevent the growth of mold, yeast, and fungi **[242]**. Since the 1950s, sorbic acid, its aldehyde and ester derivatives have demonstrated their ability to react with styrenic compounds via the DA reaction **[243, 244]**. In the 1980s, sorbic acid was used with maleimide compounds **[245, 246]** or with benzoquinones **[247]**. More recently, numerous articles have reported a renewed interest in sorbic derivatives being able to react with any type of dienophiles, from $O_2$ to 4-phenyl-1, 2, 4-triazoline-3, 5-dione (PTAD) **[248]**, or other triazolines **[249]**, acrylonitrile **[250]**, aryne **[251]**, acrylate **[252]** and benzophenone **[253]**. Reinecke and Ritter **[254]** used sorbic acid in the forms of mono, bi and tetra amide for crosslinking unsaturated polyesters modified with maleic anhydride. More recently, diacids were obtained by DA reaction of sorbic acid with fatty acids for the synthesis of polyamide **[255](Scheme 33)**. In that reaction, the high temperature (200 °C) may induce some aldolization of the oil in addition to the DA on that diene.




**Scheme 33: Synthesis of diacid adduct from unsaturated fatty acids and sorbic acid [255].**

### 3.2.2 Muconic acid

Muconic acid is a telechelic bis(carboxylic acid) with two conjugated double bonds. Muconic acid exists in the form of three isomers (**Figure 22**) and is of growing interest both its synthesis process and for its numerous applications. **[256]**

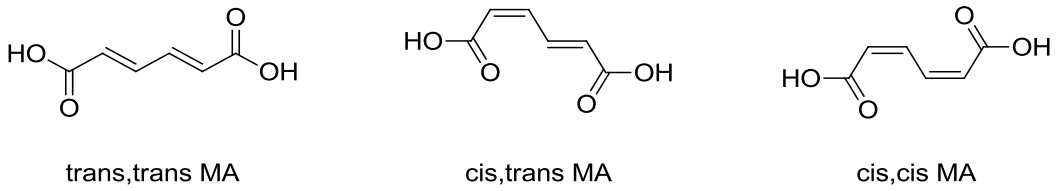



**Figure 22 : Structures of the three isomers of muconic acid (MA)**

Muconic acid can be obtained from a transformation step of catechol using biotechnology. The sourcing can arise from aromatic compounds such as toluene, benzoates, **[257-260]** or from glucose **[261]**.

Isomers of muconic acid are of real interest as a chemical platform for the synthesis of molecules or bio-based monomers **[262].** For example, it is involved in the synthesis of adipic acid **[261, 263]**. By intramolecular cyclization of muconic acid, it is possible to obtain lactones **[264]** or ε-caprolactam after steps of hydrogenation and amidation **[265]** (**Figure 23**).

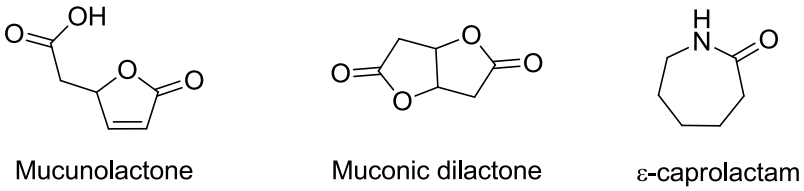
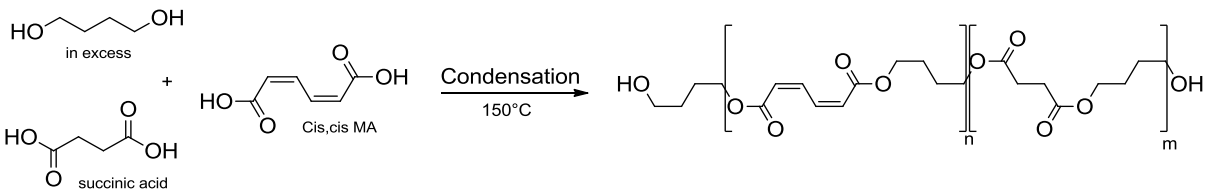


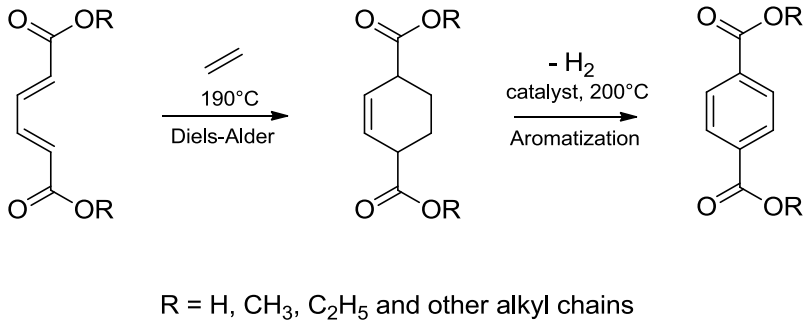

**Figure 23 : Structures of lactones and ε-caprolactam obtained from muconic acid**

This acid is also well-known in the field of polymers as a bio-sourced precursor agent of Nylon 6,6 **[258]**. It can be used as a monomer in the synthesis of polyester by polycondensation with succinic acid **[266, 267]**( **Scheme 34**) or for the production of (co)polymers under radical polymerization. **[268]**



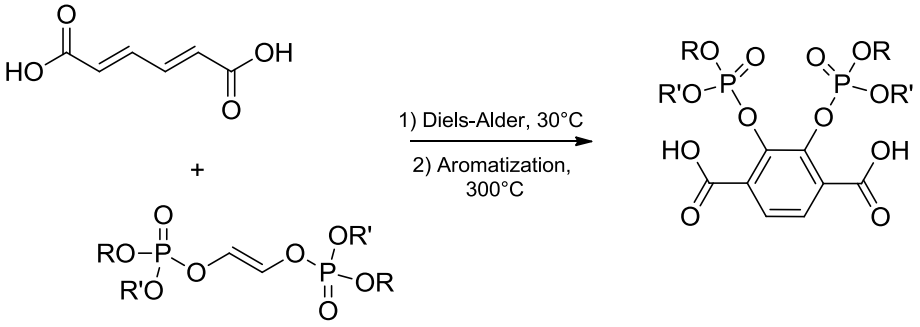

**Scheme 34 : Polycondensation of MA with succinic acid in excess of diol [266]**

Thanks to its two conjugated double bonds, muconic acid has been used for the DA reaction as a diene since the 1950s **[269]**. The steric effect of cis,cis muconic acid and cis,trans muconic acid prohibits the DA reaction reacting these isomers. The use of trans, trans muconic acid under DA reaction is mainly focused on the production of terephthalic acid **[270]** (**Scheme 35**).




**Scheme 35 : Trans,trans muconic acid (or esters) transformation into terephthalic acid (or esters) via Diels-Alder and subsequent dehydrogenation reactions [270].**

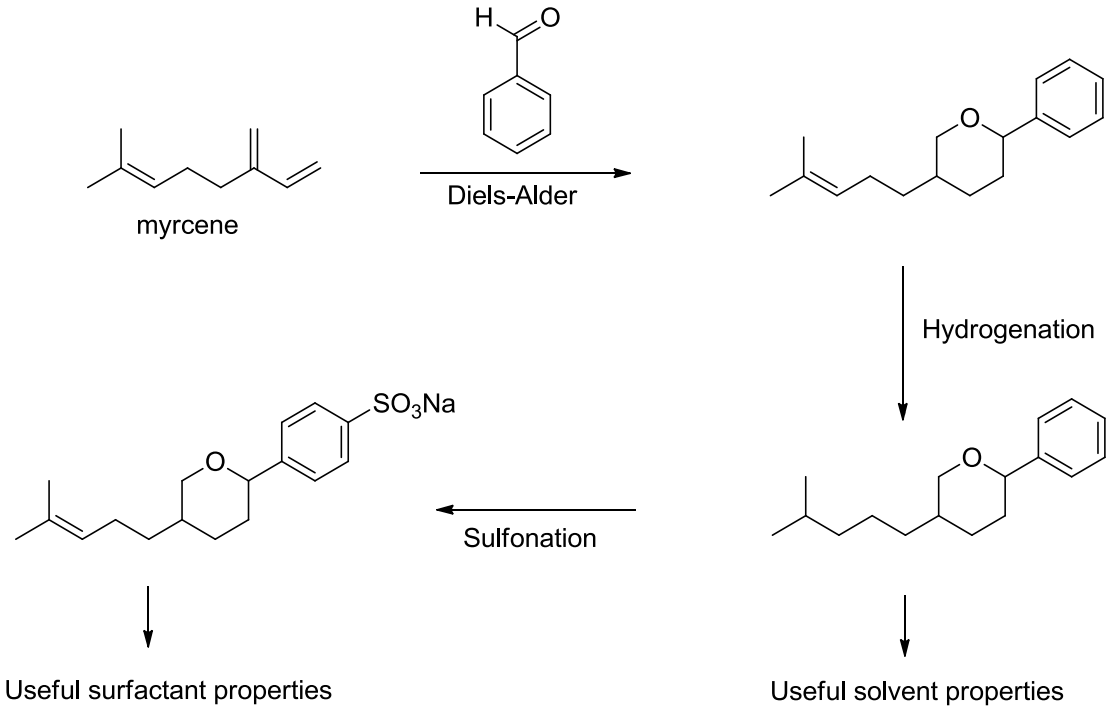
Monomers from DA reaction between muconic acid and maleic anhydride, butene or acrylonitrile **[271],** or phosphonate-based flame retardant reactant **[272]** has also been synthesized (**Scheme 36**).




**Scheme 36 : Two-step synthesis of flame retardant compounds from MA and phosphate derivatives [272]**

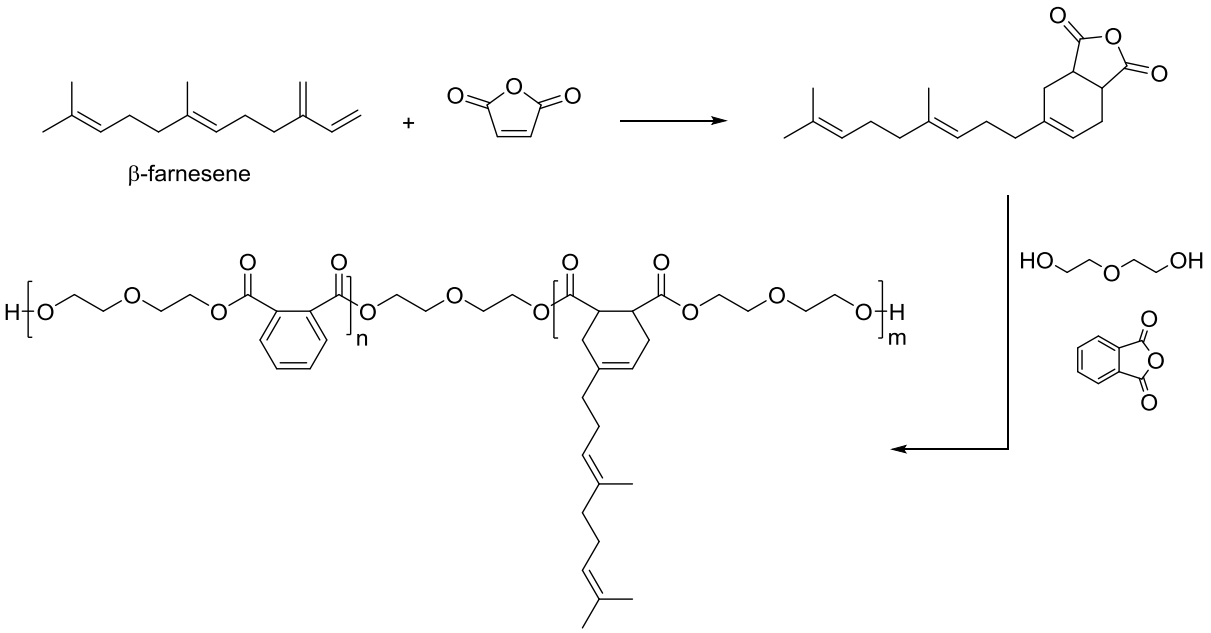
### 3.2.3 Myrcene and Farnesene

The naturally β-myrcene is a colourless oil available in several plants. It can be found in essential oils of wild thyme, ylang-ylang, bay leaf, juniper berries, lemongrass, carrot leaf and jambu flower **[273]**. However, myrcene is mostly industrially produced from turpentine, the distillate of pine resin **[273]**. Myrcene is an acyclic monoterpene (**Figure 21**) that has been currently used in pharmaceutical and cosmetic industries in formulation of flavouring substances and fragrances **[274]**. Since the first reaction between myrcene and maleic anhydride in 1929 **[14]**, numerous DA reactions of myrcene have been reported with acrolein **[275]**, quinone **[276, 277]**, acrylic acid and other various dienophiles **[278]**. In 2013, the Stepan Company **[279]** claimed the synthesis of solvent and surfactant from DA reaction of myrcene and farnesene with a variety of dienophiles (**Scheme 37**).




**Scheme 37: Example of the use of myrcene adduct for solvent and surfactant applications [279]**

As myrcene, farnesene, cited above, can be found in the list of essential oils, in particular in *alpina galanga* oil as much as 18% of the total source **[280]**. In Nature, farnesene is used by numerous species as an alarm pheromone against insect attack. Thus, is it not surprising that a 1982 patent describes the synthesis of crop protections from DA reaction of farnesene with some various dienophiles **[281]**. Other patents claim farnesene DA adducts used as high boiling point-solvents **[282]**, plasticizers for PVC **[283]** or in the synthesis of polyester polyols as polyurethane reactants **[284] (Scheme 38)**. Recently, farnesene has also been used in the synthesis of bio renewable amphiphilic polysaccharides **[42]**.




**Scheme 38 : Example of the use of β-farnesene-maleic anhydride DA adduct for the synthesis of aromatic polyester polyols [284]**

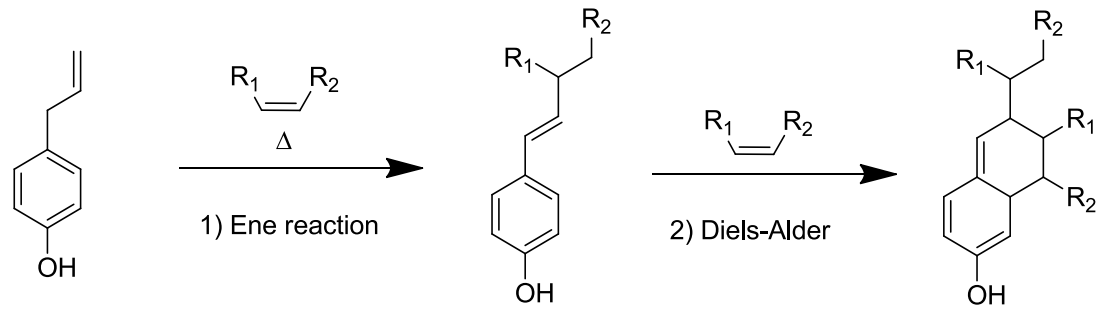
### 3.2.4 Eugenol and Cardanol

Eugenol is a natural allylic phenol (**Figure 21**) which can be found in bay leaves, Jamaican pepper, in certain varieties of cinnamon and in cloves. It is mainly extracted from essential oil of cloves as the aroma molecule. More interestingly, the depolymerization of lignin is a very promising strategy for the production of eugenol **[285].** In addition, its depolymerization by ionic liquids is widely studied **[286, 287]**.

Furthermore, Eugenol is currently used in the pharmaceutical industry for its antiseptic and analgesic properties **[288]**, and is also a precursor for vanillin synthesis **[289]**.

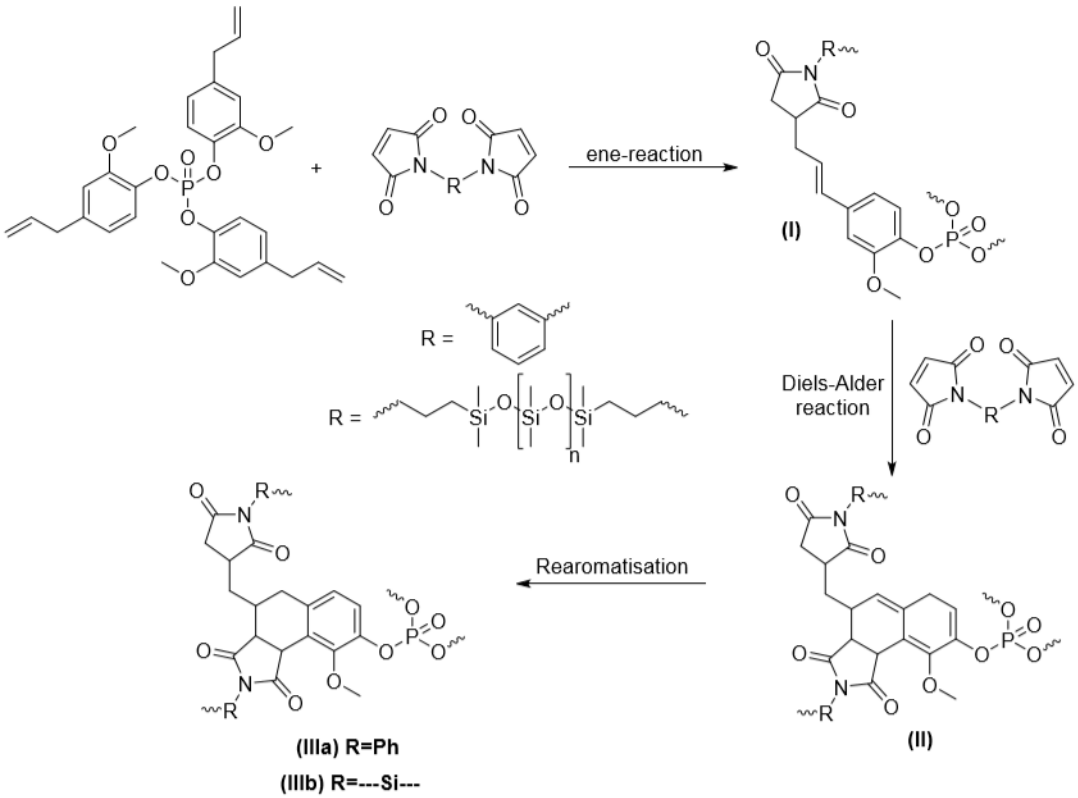
Very versatile, it is well-known in the field of polymer for the preparation of phenolic resins **[290]**, epoxy resins **[291, 292]** or as crosslinking agents **[293]**. Eugenol can act as both a diene and a dienophile. Recently, the synthesis of fluorinated norbornene monomer from eugenol as a dienophile with cyclopentadiene has been reported **[294]**. The reaction of a dienophile onto allyl phenol has been studied **[295-297]**.

To succeed the DA reaction between allylphenol and dienophile, a first ene-reaction between both these reactants occurs allowing the formation of a diene moiety on the molecule (**Scheme 39**).



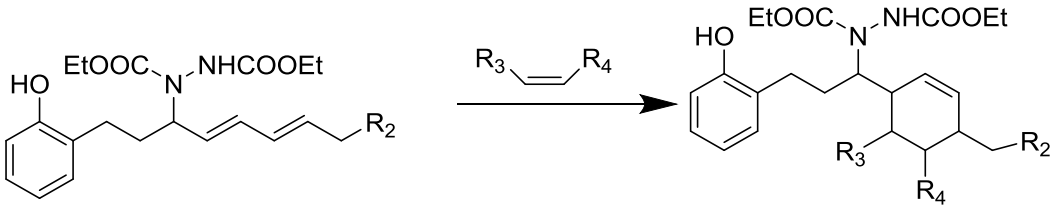

**Scheme 39 : Two-step DA reaction of dienophiles with allyl phenol.**

Then, another dienophile can react onto the formed diene and enables the DA reaction. The same type of reaction of eugenol with maleimide compounds has been described for the syntheses of new polyesters **[298]** and phenolic thermosets **[299-303]** (**Scheme 40**).




**Scheme 40: Synthetic pathway for the formation of the Eugenol derivative/Bismaleimide thermosets [302]. (reproduced reproduced from [302] with permission from Elsevier, copyright 2019))**

As eugenol, cardanol is also a phenol naturally available. Cardanol is obtained from cashew nutshell liquid (CNSL), directly extracted from the shell of the cashew nut, *Anacardium occidental* growing in China, India, Viet-Nam, Nigeria and Brazil. **[304]**. Cardanol is composed of a mixture of at least four constituents diff ering in the unsaturated side chain, namely saturated (5–8%), monoene (48–49%), diene (l6–17%) and triene (29–30%) as illustrated in **Figure 21.** Cardanol and its derivatives can be found in many area of materials **[305]** such as additives (antioxidants **[306]**, surfactants **[307, 308],** plasticizers **[309, 310]**) or as building blocks for polymers **[311]**, epoxy curing agents **[312]**, coatings **[313]**, composites **[314]** or phenolic thermosets **[315, 316]**. Thanks to the same mechanism involving eugenol, some DA reactions on cardanol as a diene have been reported for the synthesis of novolac thermosets with maleimides **[317]**, and the synthesis of coating binders **[318]**, epoxy resins **[319]**, or reactive amides **[320]** with anhydride maleic. Recently, Biswas et al. **[321]** have shown that cardanol can also have a dienophile role in DA reaction. Indeed, after a first ene-reaction with diethyl azodicarboxylate (DEAD), the double bonds of cardanol are conjugated. Then, the cardanol-DEAD adduct allows a self-condensation with the free cardanol (**Scheme 41**). In this particular case, cardanol acts as both a diene and a dienophile.



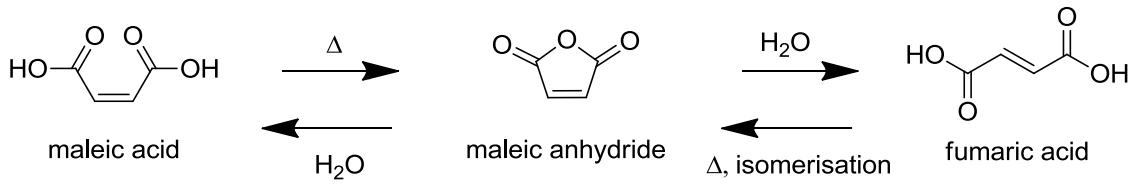

**Scheme 41 : An example of a Diels-Alder self-condensation reaction from cardanol-DEAD adduct [321].**

Of course, this enumeration of other dienes involved in DA reaction is not exhaustive. For example, as explained in the introduction of this section, also some vegetable oils or levopomaric acid have demonstrated a real potential in DA application. Levopomaric acid is specially used with acrylic acid and is described in section **3.3.2.** Acrylic acid and derivatives

## 3.3 Dienophiles.

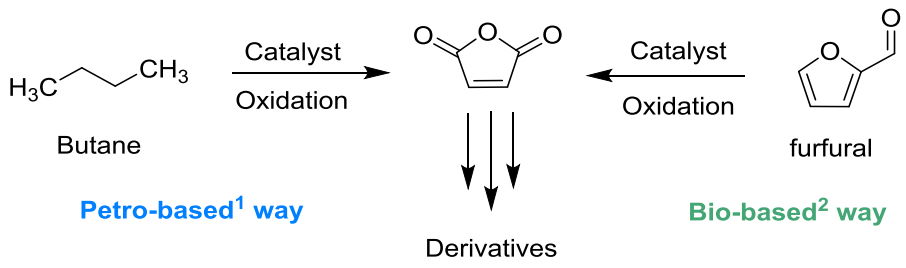
### 3.3.1 Maleic anhydride and derivatives.

Maleimide and its derivatives are the most common dienophiles for the DA reaction. However, other dienophiles have also widely been used. Maleimides are prepared from maleic anhydride which is a quite useful dienophile too. Maleic anhydride and its two diacid isomers, maleic and fumaric acids (**Scheme 42**), were first prepared in 1830 **[322]** and industrially produced one hundred years later. Initially manufactured from benzene, the increasing price and the recognition of benzene as a hazardous molecule have led to its production from butane in 1974 **[322]**.




**Scheme 42 : Chemical structures of maleic anhydride and its two diacid isomers**

Many examples of DA reactions involving maleic anhydride and its derivatives as dienophiles have been described with piperylene **[323]**, furan **[324]**, some vegetable oils **[325, 326]**, cyclopentadiene, acrolein, oxazole **[327]**, and numerous other dienes **[328]**. Nowadays, finding a sustainable and eco-friendly production has been more and more attractive. Maleic anhydride and its derivatives, as important raw materials in the polymer field, do not escape the rule **[329].** With the aim to substitute hazardous and petro-based products from the synthesis of these dienophiles, several studies have been implemented on maleic anhydride and derivatives. An interesting review summarizes the current work on the bio-based synthesis of maleic acid and anhydride from furfural, furan and 5-hydroxymethylfurfural (HMF) **[330]**. (**Scheme 43**). Fumaric acid is already present in many plants; for example *Fumaria officinalis*, as the plant from which it was first isolated, while it could also be produced by sugar fermentation from fungi **[331]**.




**Scheme 43 : Petro-based[1] [322] and bio-based[2] [330] pathways to obtain maleic anhydride**

### 3.3.2. Acrylic acid and derivatives

Acrylic acid is industrially synthesized from the oxidation of propane (or propene) or acrolein, its aldehyde derivatives **[332]**. Acrylic acid and its derivatives (**Figure 24**) are greatly widespread for the synthesis of polymers such as poly(acrylic acid) **[333]**, poly(acrylate)s **[334]**, poly(methacrylate)s **[335, 336]**.

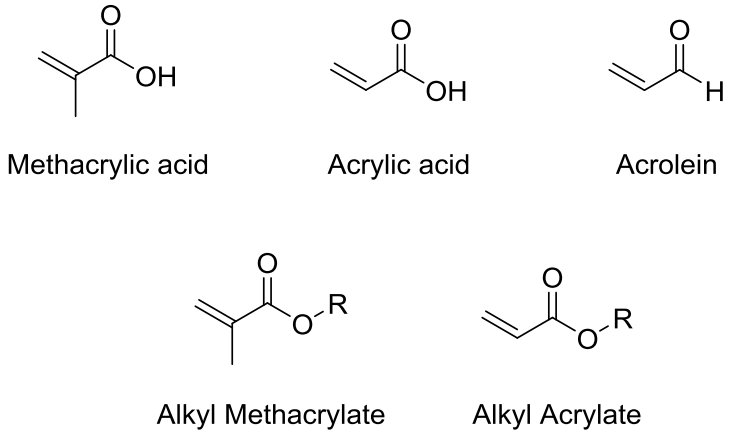



**Figure 24 : Structures of (meth)acrylic acid and its derivatives**

The presence of the double bond on these molecules allows the opportunity to react with some dienes via the DA reaction. Indeed, acrylic derivatives can react with cyclopentadiene, hexadiene **[337, 338]** or with conjugated fatty acid **[339]**. Another example deals with the synthesis of benzoic acid from the DA reaction between acrylic acid and furan **[340]**. More recently, several studies have described adduct (**Figure 25**) from a DA reaction between acrylic acid and levopimaric acid (LPAA) **[341]** for the synthesis of polyketones **[342]**, polyesters **[343],** a bio-based pressure-sensitive adhesives **[344]** and as a crosslinking agent for poly(epoxide) **[345]**, showing the renewed interest of acrylic acid and its derivatives in the DA field.

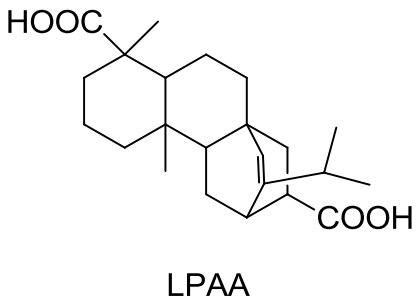
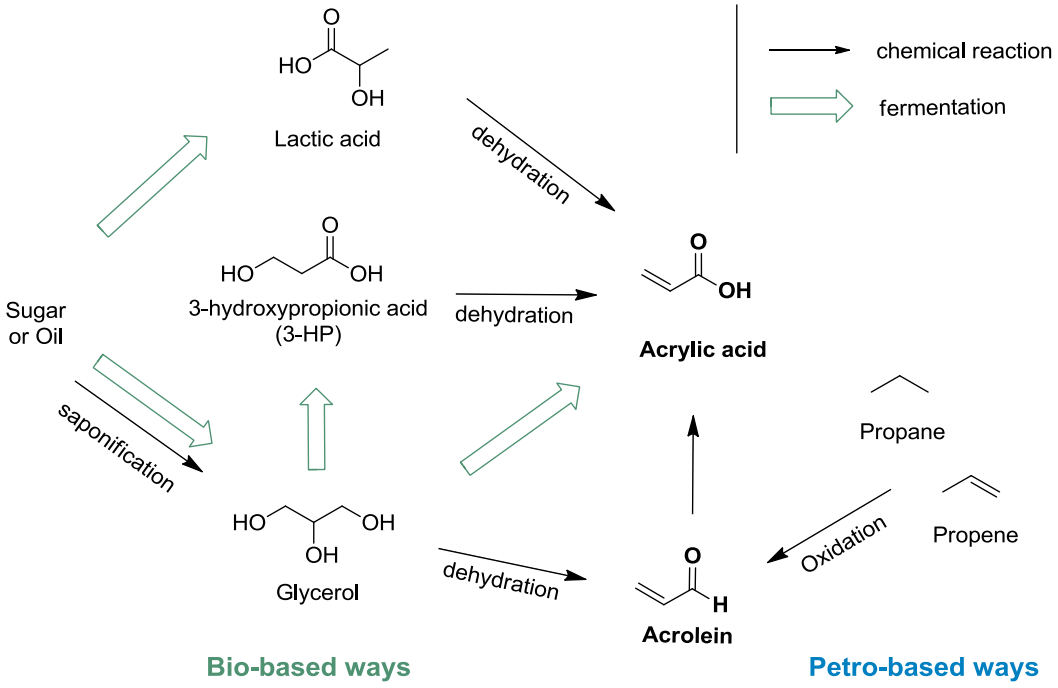



**Figure 25 : Structure of Diels-Alder adduct of levopimaric acid with acrylic acid (LPAA)**

Moreover, these monomers could be synthesized from renewable raw materials as lactic acid **[346]**, glycerol *via* the 3-hydroxypropionic acid (3-HP) **[347],** via dehydration into acrolein **[348]**, or from direct fermentation of sugar **[349]**, strengthening its position in the industry during the current conjectures. The different pathways to obtain acrylic acid are detailed in **Scheme 44**.




**Scheme 44: Different bio-based and petro-based pathways to produce acrylic acid and acrolein**

### 3.3.3 Vinyl ketones

Vinyl ketone compounds (**Figure 26**) are ketones bearing double bonds which enable DA reaction. The most famous and used is the methyl vinyl ketone. Several ways have been reported to obtain methyl vinyl ketone from i) methyl ketone **[350]**, ii) thermal elimination of

β-keto sulfoxide **[351]**, iii) addition of vinyl lithium onto carboxylic acid **[352]** or iv) pyrolysis of propargyl esters **[353]**. However, the most common strategy is the cross aldolization condensation of acetone with formaldehyde **[354]** or with methanol **[355]**, that is less dangerous that the previous one.

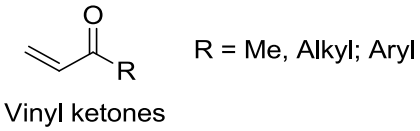
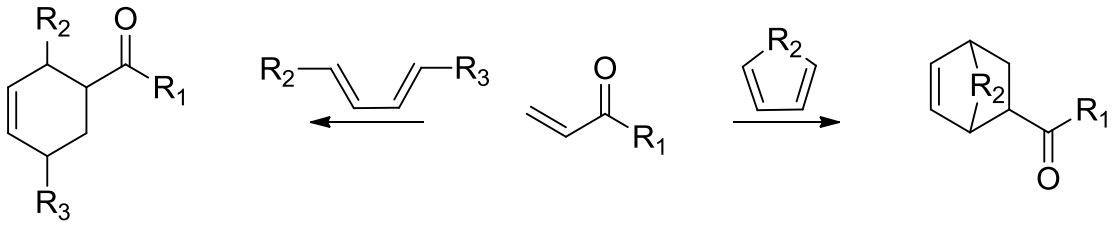



**Figure 26 : Structure of vinyl ketones**

Methyl vinyl ketone can react with plenty of dienes as cyclodienes (**Scheme 45**) **[356, 357]**, furan **[358]** and anthracene **[359]**. Recently, the reaction of methyl isopropenyl ketone with myrcene has been reported **[360]** while some alkyl and aryl vinyl ketones in DA reactions are well studied **[361, 362]**.




**Scheme 45: Examples of DA reaction involving a vinyl ketone and aryl or alkyl dienes [361, 362]**

### 3.3.4. Itaconic acid, citraconic acid and their derivatives

Itaconic acid is largely produced from citric acid **[363]** but can also be obtained by the fermentation of glucose with fungi *Aspergillus itaconicus* **[364]**. Itaconic acid and its derivatives (**Figure 27**) have been lately used for DA purposes.

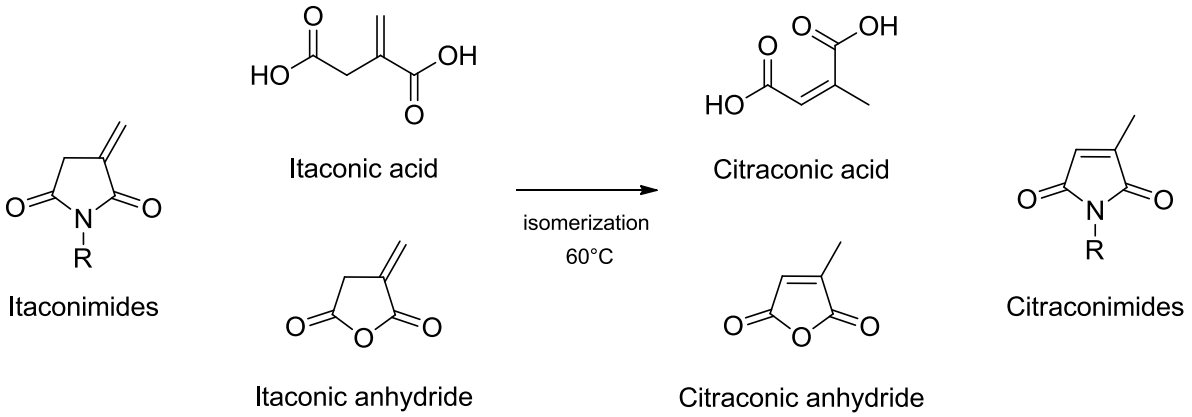
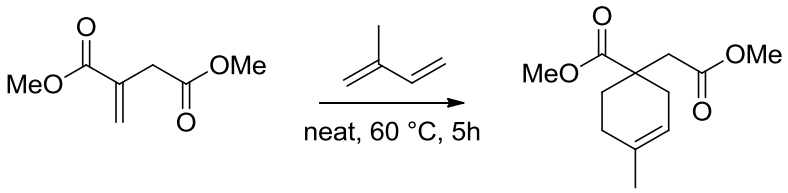



**Figure 27 : Structures of itaconic acid and citraconic acid, and their derivatives**

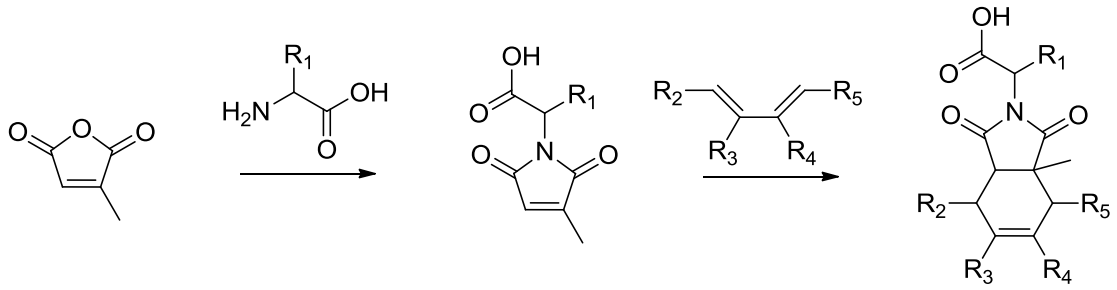
Some articles describe the dienophile behaviour of itaconimides present in the formulation of PVC plasticizers **[365, 366].** Thanks to these compounds, a DA reaction occurs during the degradation of the plasticized PVC and the resulting product stabilises the polymer from a further degradation. Since this finding, the DA reaction between itaconic acid and cyclopentadiene **[367]** has been reported for the synthesis of polyols for polyesters **[368]**. Other itaconic derivatives in DA reactions have been suggested as itaconimides with benzofuran for the synthesis of benzoisoquinoline **[369]**, or with oxazolones **[370]**, itaconic anhydride with furfuryl alcohol **[48]**, or, more recently, with isopropene **[371]** or furan **[372]** for bio-thermoset synthesis (**Scheme 46**).




**Scheme 46 : Diels-Alder reaction between isopropene and itaconic methylester [371]**

Citraconic acid could also be synthesized from citric acid as itaconic acid by thermal isomerization of this previous acid or anhydride and vice versa **[373, 374]**. DA reactions between citraconic acid or anhydride is possible with furan, and with enough reactivity for an intra DA reaction **[46]**. However, most articles about DA reactions with citraconic derivatives

(**Figure 3**) are devoted to citraconimide molecules. In the 90s, the crosslinking reaction of citraconimides with rubber during the reversion process was described and revealed its role as an anti-reversion agent **[375]** and comparative studies about such a crosslinking with squalene as a model system were investigated by Datta **[365, 376]**. The synthesis of azasteroides was reported **[377],** involving maleimides and citraconimides on dihydronapht alene while Gaina described the preparation and polymerization via DA reaction of monomers containing citraconimide or maleimide groups with allyphenyl group **[298]**. Wang and Welker **[378]** achieved the DA reaction between boron diene and some dienophiles, including citraconimides. Recently, a patent has claimed the syntheses of polyfunctional hydrophthalimide monomers from DA citraconimide adducts for polyester resins **[379]**, underlining the real interest for DA reaction with citraconimides (**Scheme 47**).




**Scheme 47 : Synthetic way to obtain polyfunctional hydrophthalimide monomers from Diels-Alder adduct of citraconimide [379]**

Of course, this enumeration of other dienophiles involved in DA reaction is not exhaustive. Other studies report quinones **[247, 277]**, cycloalkenones **[380]** and triazolines **[249]** as potential dienophiles. Some vegetable oils and saturated fatty acids can also be used as dienophiles **[255, 381]** or as diene **[382]**. This abundance of possible dienes and dienophiles and the current growing interest for DA reaction in the polymer area permits to open up a wide range of possibilities for further applications.

## 4. Discussion and outlooks

Through this review, we aimed to highlight the wide variety of reagents involved in the Diels-Alder reaction. The Furan/Maleimide pair is mostly described in the literature **[5-7]** and is used here as a reference for the other diene/dienophile pairs presented in the section 3. Other diene/dienophile couples (**insertion**). The emergence and success of increasingly specialized fields of application such as health drug delivery (p31), smart or self-repairing materials (p24) and 3D printing (p29), and an increasingly growing environment is a fertile ground for DA's

reaction and its versatility. These different activities bring with them their share of constraints that the F/M couple, alone, cannot fully meet.

The Self-Healing aspect or the recyclability of materials enabled by the reversibility of the diene/dienophile system via the retro-DA maintains this reaction as a hot topic and a relevant solution to the locks of tomorrow. However, special attention should be paid to the origin of dienes and dienophiles. They must be bio-sourced, as less toxic as possible and the synthetic route in which they are used must be sustainable **[383]**. As described in the section 3. Other diene/dienophile couples, today, many molecules are studied through the reaction of DA. This is the case of sorbic acid, muconic acid, myrcene, farnesene, eugenol and cardanol as diene and maleic acid, itaconic and citraconic as dienophile to name just some of them. Of course, this is without counting on vegetable oils and other natural raw materials which will, tomorrow, be a source of new compounds of interest for DA reaction.

Despite this increased interest in bio-based compounds, a great deal of information is still lacking on the reactivity and DA and retro-DA temperatures of these compounds. Indeed, even with the couple F/M, certain article omits to specify the temperatures of retro-DA. As discussed in the section 2.4.1 Generalities about furan and maleimide, the temperature of DA and retro-DA depends both on the compounds, on the functionalization of these compounds, on their associations between them and on the kinetic or thermodynamic forms of DA adducts obtained.

The subject is complex and sorely lacking in data. In addition, various studies use DA strategy to allow the coupling without claiming on possible reversible reaction which causes a hole in the data because the reaction of retro-DA does not interest these authors and therefore does not appear in these articles. Especially since these DA and retro-DA temperatures are particularly important to know depending on the intended application.

For example, all studies achieved on F-M couple that displays a reparation temperature close to 110 °C while the exo structure is mainly obtained. However, that temperature leads to controversies for desired applications since it is too high for biomedicine and too low for materials. Thus, revisiting other couples mentioned above should open news trends and opportunities.

In the case of anthracene, a molecule well-known since a lot of time, the results obtained are not always in agreement between different papers, and in various cases, led to controversies

because of different values of retro-DA temperature (50 to 200 °C). As mentioned above, it is requested to adapt the temperatures of DA and retro-DA to the desired application, and this is not the only F-M couple which able to achieve this. Hence, deeper research on various dienes-dienophiles couples to establish a real temperature scale of retro-DA (when available) between room temperature and ca. 200 °C will be pertinent and useful.

Besides the temperature values of DA and retro-DA, one of the added values of DA is the fact that it is much more than a simple reaction. DA, thanks to its reversibility, is revealed as a real toolbox for the organic and polymeric field.

In the last few years, "reparation" of materials and recycling have been of growing interest. In addition, "self-healing" is a quite fashionable trends especially for coatings, car industries, composites, adhesives, and biomedical applications.

In case of reparation, huge efforts have been made to find out solutions to limitations, by varying the structure of the polymers as well as the DA groups either well-dispersed in the matrix or within the polymer backbone or for both. The chain length and the nature of reactants between DA groups have also been studied to optimize the properties of the resulting materials. Sometimes, other concepts have also been included such as shape memory, intramolecular bonds, etc.. All these strategies have been used to obtain a material that recovers its initial properties after damage. Furthermore, many authors have investigated successive degradations-reparations to get an everlasting healed material. The resulting materials were able to be reprocessed multiple times still retaining similar properties (Tg, thermal stability, mechanical responses) as those of the pristine material. For this, a great work has been accomplished on the technical part by using several methods to tune the properties and to improve the quality of the materials after several reparation-degradation cycles. These contributions have led to huge progress whereas none of these systems is adaptable to all materials and many approaches and studies required to be investigated.

By leaving space for the creativity of researchers, this ability to make and break on demand has enabled, in addition to its use in self-healing and shape memory materials, the development of certain technologies such as DART (section 2.4.8 DA reversible thermoset (DART) for 3D) or SCOD (section 2.4.9. Sealant cured on demand), in particular, one of interest to use DA reactions with SCOD concept deals on the possibility in obtaining one K component formulation. This permits to protect a reactive starting material with another reactive component in one composition. It also allows the development of a whole bunch of

new applications described in the section (section 2.4.4 Miscellaneous and different uses of furan-maleimide couple and DA reaction**)** as Sequence-controlled RAFT quaternary polymerization **[129].**

Hence, aspects of reparation and recycling, as well as DART or SCOD to some extent, are real targets for applications from DA reactions in materials. In these fields, many articles for furan/maleimide couple are encompassing the whole area of polymers including elastomers, thermoplastics, and thermosets, that it is not possible to be exhaustive in citing all of them.

We can therefore imagine in the near future that with a more in-depth study of biobased dienes and dienophiles, a scale of known DA and retro-DA temperatures and the growth of applications linked to reversibility behaviours, the interest of researchers and industrialists for DA's reaction will only increases and be the source of new innovative technologies of tomorrow.

## 5. Conclusion

Though discovered in 1928, DA reaction has been studied for several decades by many of academic and industrial researchers and is still of growing interest. This review summarizes non-exhaustive strategies in DA ranging from basic and fundamental methodologies to industrial applications. Beside conventional and well-known Furan/Maleimide couple, a wide variety of dienes and dienophiles reactants have been studied whatever they are petro-sourced or bio-sourced. A huge resurgence of articles for F-M involve main variety as elastomers, thermoplastics and thermosets. For the diene family, first petro-sourced were cyclopentadiene and furan but also not so well studied as pyrrole, thiophene or oxidized thiophene, as well as acyclic dienes and anthracene, whereas emerging bio-sourced dienes have recently been involved in DA reactions: sorbic and muconic acids and derivatives, myrcene, eugenol and cardanol to cite a few. Regarding the dienophile series, maleimides, maleic anhydride and derivatives, acrylic acid and derivatives, and vinyl ketones as petro-sourced have led to many surveys while itaconic and citraconic acids and their derivatives, as well as levopimaric acid as bio-sourced reactants, have also been approached a few times. This list of possible diene and dienophile reactants opens up and enlarges the possibilities about DA reaction.

Furthermore, many efforts must be done on bio-based derivatives and sustainable process due to the actual environmental crisis we are facing.

However, from a fundamental aspect, many articles do not report the presence of both exo and endo isomers which are usually produced. In addition, for most new products obtained, temperatures of DA and retroDA ($r_{DA}$) reactions are not well-known or even controversies have been reported.

By tuning the reactivities of the diene/dienophile couples toward the properties of the searched product and on the DA and retro DA temperatures, a wide variety of possible uses can be offered as well as applications. However, for most of these new products, temperatures of DA and $r_{Da}$ are not known or not yet reported.

In addition, and more and more noted in the literature, that DA reaction has also played a crucial role to offer self-healing materials via crosslinking/decrosslinking strategies. To use the thermal reversibility behavior of such DA reaction in the polymer industry, it is essential to control and adapt both the building blocks and the stimuli towards the needs of the applications. For example, biomedical applications require low temperature (ca. 40 °C) for $r_{DA}$, while many efforts still deserve to be made to find out suitable higher temperatures for high performance materials involved in specific applications (car and aerospace industries). Furthermore, these reactions also enable to design well-architectured polymers (block and graft copolymers, including amphiphilic block copolymers, dendrimers and networks as well as shape memory polymers). Moreover, the smart choice of the diene or dienophile allowed researchers to tune the searched applications (e.g., incorporating PDMS for low Tg elastomers or non-isocyanate polyurethanes for green coatings and adhesives). Finally, SCOD concept as a possibility to obtain one K component formulation appears as a relevant strategy.

It is expected that the design of DA reaction has the potential to be a promising growing pathway to generate new materials with unique properties and will certainly play a significant role in the future of polymer science in the coming years, hence attracting the interest of academic and industrial scientists and engineers, as well as end users.

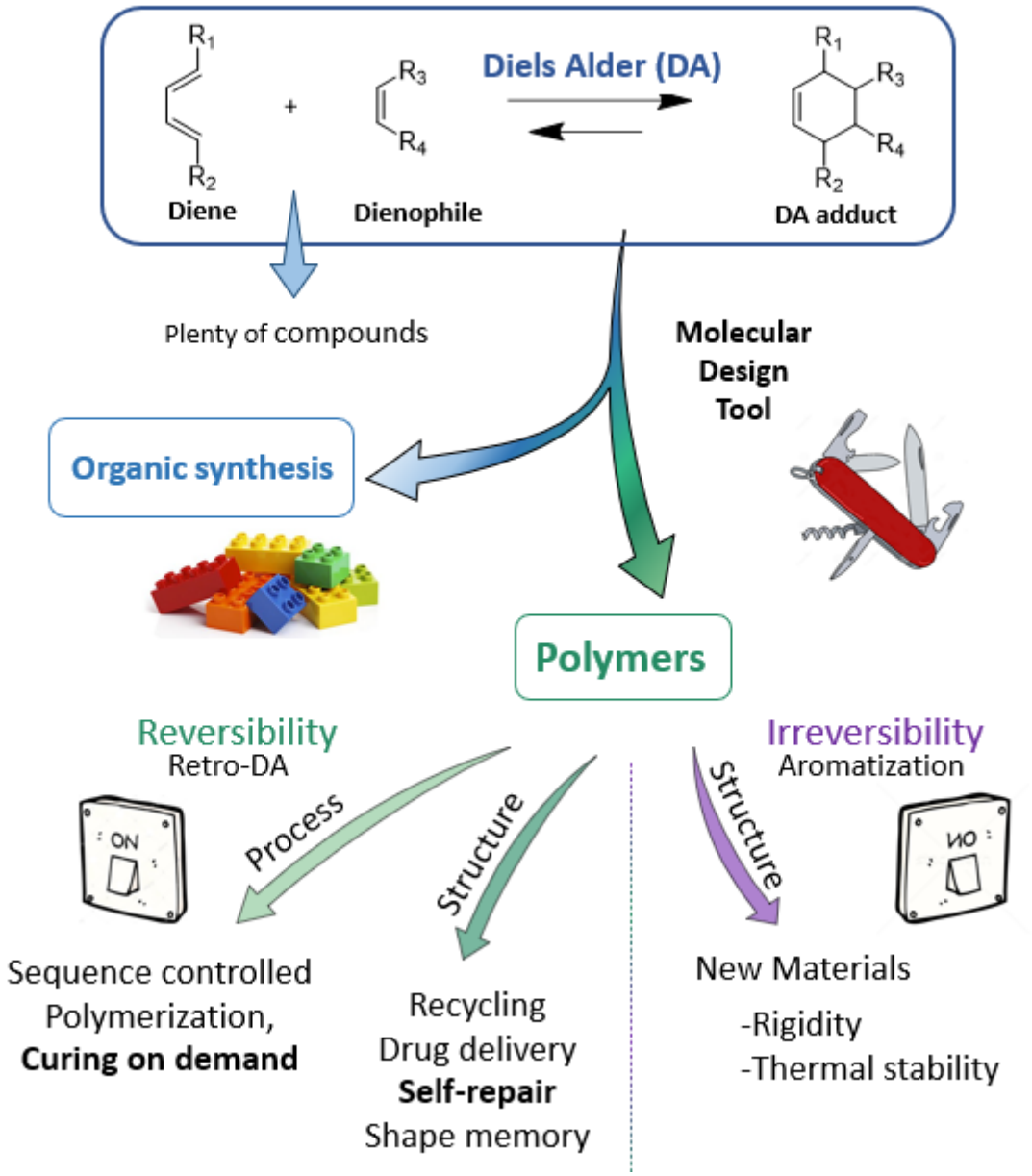



**Figure 28 : Graphic overview of the DA reaction**

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