

# Thermally self-healing polymeric materials

Based on Diels-Alder and retro Diels-Alder model reaction

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## Summary

Estimations suggest a worldwide production of plastics of more than 300 million tons per year. These include thermoplastic polymers and thermoset polymers. Almost all polymer material which is produced in the world, is waste that is going to landfills or is being reused in relatively expensive ways. These numbers are an indication of what the potential of success is for a polymer with the material properties of a thermoset polymer and can guarantee 100% recyclability.

Reason enough to develop a new method. A new method is already discussed in the thesis of Zhang. That research will be continued in this topic: thermally self-healing materials based on Diels-Alder and retro-Diels-Alder model reactions. To study this system, model compounds with furan groups and different maleimide groups have been synthesized and these have been cross-linked. The used maleimides were: ethyl-, cyclohexyl-, phenyl- and benzyl maleimide. After making pyrrolic furan, a reaction between a furan- and a Reactions were performed in NMR-tudes and the conversions were determined with H-NMR spectroscopy.

Subsequently, when the right parameters were determined, a batch reaction was made of pyrrolic furan and ethyl maleimide. The obtained product was studied with H-NMR spectroscopy and the conversion was determined. The fractions in the batch were separated by column chromatography. The products consists an endo and an exo adduct. These fractions were studied by H-NMR spectroscopy and DSC. Finally hyperchem calculations were performed in order to calculate the diene and dienophile. Also the free energy and the energy cap (dE) was calculated.



# Acknowledgements

I would like to thank everyone with whom I have worked during my master research project for their support and the good atmosphere within the department. This has made the research a very enjoyable and interesting year of my life. I would especially like to thank professor A.A. Broekhuis to provide me with this research project and for his continuous support. I hope the research I did is useful for the future. I would like to thank Claudio Toncelli for the daily supervision, interpretation of the many H-NMR peaks and the informal atmosphere in the lab. Also I would like to thank Jan Henk Marsman and Gert Alberda who provided me a lot of help with the chromatography and the thermal measurements. Unfortunately the column chromatography did not proceed without any troubles and took a lot of time. Thanks to Henk van de Bovenkamp and his robot, the automatically controlled column, all expectations were exceeded. The column was a success and the fractions were separated. Although I spend too much time at the university, I had a great time. I would never forget the non-work related activities at the Bernoulli-lounge like building a new bar and having great Friday afternoon drinks.

Thanks everyone,

Anton



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# Chapter 1

## Introduction

### 1.1 *Aim and Scope*

The main goal of this thesis is to obtain a deeper understanding of the thermoreversible cross-linking and Diels-Alder and retro-Diels-Alder model reactions. Thermally self-healing polymeric materials can be made on the basis of furan-functionalized, alternating thermosetting polyketones (PK-furan) and bis-maleimide by using the Diels-Alder (DA) and retro-Diels-Alder (RDA) reaction sequence. PK-furan can be easily obtained under mild conditions by the Paal-Knorr reaction of the polyketones with furfurylamine. The highly cross-linked polymers can be thermally remoulded to complete recovery in fracture loading, whereas the remoulding process can be repeated multiple times without any loss in mechanical properties. These model reactions are performed in order to get more knowledge about the thermodynamic and kinetic behavior of polyketones. This research covers the model reactions between pyrrolic furan and different maleimides. In order to perform different reactions in H-NMR tubes the conversions can be obtained and a large amount can be made under ideal circumstances. Also is known that during Diels-Alder reactions two products can be formed: the endo- and exo adduct. This is already briefly mentioned in the thesis of Zhang *et al* in 2009 [1], and this research builds upon the results of the furan-maleimide system. But in this thesis the focus will be more on the forming of the adducts and their thermal behavior. The goals are to obtain more information about the DA- and rDA temperatures and their thermodynamic and kinetic behavior. Also a separation of the pure components is very favorable because the properties of these adducts and its H-NMR spectroscopy can be determined.

Furthermore an explanation will be given about Hyperchem calculations. In this way determination of the diene and dienophile of the DA reaction can be determined in advance. Also calculations of the energy gap and the free energy can be used before the reaction is performed. This can be very useful and saves a lot of time. More knowledge of these kind of computer simulations is needed because the results are very reliable.

## 1.2 Thermosetting polymers

A thermosetting plastic, also thermoset, is polymer material that irreversibly cures. Thermosetting polymers have material properties that are highly desirable for many products and applications. The most appreciated material property of thermoset polymers is that they do not deform at high temperatures. The material has a high modulus, a high creep resistance and a relatively high chemical resistance. These material properties are caused by the way of producing.

Thermoset materials in general are usually liquid or malleable prior to curing and designed to be moulded into their final form, or used as adhesives. Others are solids (powder) like moulding compounds used in semiconductors and integrated circuits [2].

Thermosetting plastics can be produced by condensation reaction or by grafting cross-linking material to a polymer backbone. Therefore the specific molecular structure is often highly cross linked in 3 dimensions by intermolecular attractions or covalent bounds. The curing process transforms the resin into a plastic or rubber by a cross-linking process. Energy and or catalysts are added so the molecular chains react at chemically active sites linking into a rigid, 3-D structure. The cross-linking process forms a molecule with a larger molecular weight, resulting in a material with a higher melting point. Once the product is formed, it cannot easily be reversed without decomposition. It can only be recycled as filler material [3].

Some methods of moulding thermosets are [4]:

- Reactive Injection Molding (Bulk Moulding Compounds) [5]
- Powder Injection Molding ( high densities) [2]
- Extrusion Moulding (Pipes and insulation for electrical cables)
- Compression moulding (used to shape most thermosetting plastics)
- Spin Casting (fishing lures, gaming miniatures, figurines)

These moulding methods are all based on an input of the prepolymer, and an output of the thermosetting polymer in its final form. In this way a very wide variety of products can be produced for numerous applications.

### 1.2.1 Types of thermosetting systems

The most common types are epoxy, phenolics, bis-maleimide, and fluoropolymers.

Epoxy resins are known for their toughness and resistance to chemical and environmental damage. Also they will barely shrink during curing. Most epoxy systems are cured at room temperature from two part resins. They are frequently used as laminating resins in fiberglass and binders. They can also be used as electrical conductors and adhesives in structural bonding applications.

Phenolics are known for their strong bonds that provides good resistance to high temperatures. Phenolics are molding compounds usually made from a phenol group and formaldehyde and are available in liquid or solid form. Phenolics can harden at low temperatures and rapidly. Urea formaldehyde resins do not have the same properties as phenolic resins.

Bismaleimide resins are aromatic polyimides with a high resistance to high temperatures and increased toughness. Epoxy blends with bis-maleimide can handle temperatures of 205° to 245 °C. Fluoropolymers including polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) are used in applications requiring higher chemical resistance. PTFE is used in applications requiring high chemical resistance or low friction.

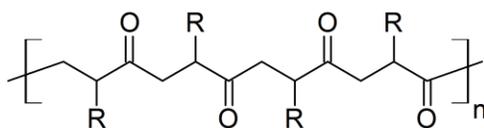
Vulcanized Thermosets Vulcanization is a thermosetting reaction that uses a cross-linked compound or catalyst. In rubber-like materials, vulcanization results in greatly increased strength, stability, and elasticity. Traditionally, sulfur is used as the vulcanizing agent for natural rubber. Thermosets and thermoset materials may contain filler materials such as powders or fibers to provide improved strength and/or stiffness.

Filled or reinforced products consist of resins and modifiers such as pigments, plasticizers, or chopped fibers. By contrast, unfilled resins, base polymers, and raw materials do not contain additives. Typically, raw materials are available as pellets, powders, granules, or liquids. Fibers can be either chopped or wound, and commonly include glass, fiberglass, or cloth. Some products contain solid lubricant fillers such as graphite or molybdenum disulfide. Others contain aramid fibers, metal powders, or inorganic fillers with ceramics and silicates.

### 1.2.2 Aliphatic polyketones

Aliphatic compounds are open-chain compounds and those cyclic compounds that resemble open-chain compounds. Aliphatic hydrocarbons, alkanes, alkenes and their cyclic analogs, undergo chiefly addition and free-radical substitution: addition at multiple bonds and free-radical substitution at other points along the aliphatic chain. These reactions take place in the hydrocarbon portions of other aliphatic compounds. The reactivity of these hydrocarbon portions is affected by the presence of other functional groups, and the reactivity of these other functional groups is affected by the presence of the hydrocarbon portions.

Polyketones are polymers with ketone groups in the backbone chain as can be seen in picture 1.1. Carbonyl groups are very polar thus the oxygen is electronegative and draws electrons away from the carbon atom. So oxygen has a slight negative charge and the carbon has a slight positive charge. Due to the strong bonding of the carbonyl groups the polyketone doesn't melt until 255°C while polyethylene melts at approximately 140°C [6].



**Figure 1.1:** Polyketones from substituted ethylene and carbon monoxide.

Random polyketones can be synthesized in this way, now days most produced polyketones are alternating polyketones. Aliphatic polyketones such as Shell Chemical's Carilon [7] are relatively easy and cheap to produce. Carilon is made from ethylene and carbon monoxide with palladium catalyst.

### 1.2.3 Modification of polyketones

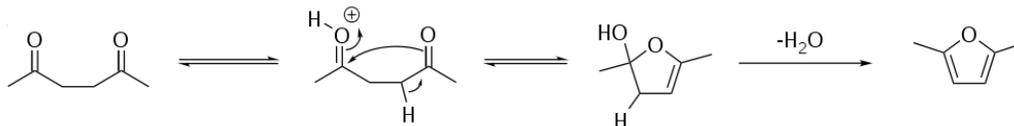
Polyketones can be used in a very wide range of applications and materials. It's possible to replace a small fraction of ethylene, with for instance propylene, to change the melting point. An incorporation of propylene will reduce the cristallinity and thus reduces the melting point. The product is easier to process while the important properties, such as functionalization, are still maintained [8] [9].

Besides the carbonyl groups achieve strong bonding, these polymers have other interesting engineering properties. Due to the high concentration of carbonyl groups the polymer can easily be functionalized. The carbonyls can

react towards many other groups like alcohols or amines. Alternating ketones can also react towards furan or via the Paal-Knorr reaction. The Paal-Knorr Synthesis is a reaction that generates either furans, pyrroles, or thiophenes from 1,4-diketones and is a very promising synthesis.

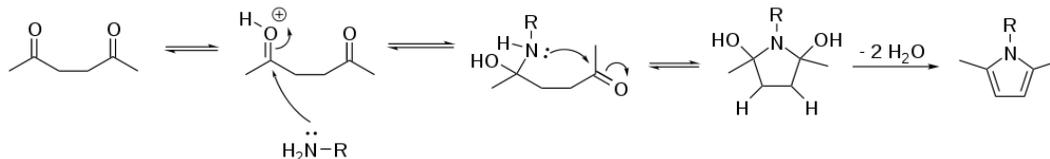
The ethyl group, attached to the amine, will form a bond with the nitrogen of a pyrrole group. The pyrrole group is due to its aromatic structure very stable and soluble in many solvents. Many groups can be attached to the amine and therefore a lot of different functional groups can be grafted onto polyketones. A wide range of variety concerning the material properties is thus possible and makes it interesting for science. Also because the Paal-Knorr reaction is usually the preferred reaction and catalysts or solvents are not needed. Finally a high conversion can easily be achieved due to preventing a reaction between single ketones and the formed pyrroles.

Some Paal-Knorr examples [10] [11] [12]:



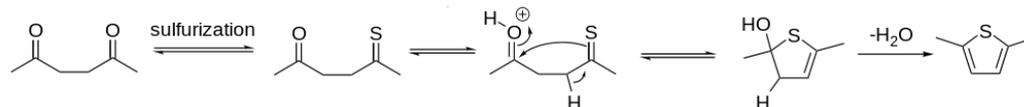
**Figure 1.2:** Furan synthesis mechanism [13].

The acid catalyzed furan synthesis proceeds by protonation of one carbonyl which is attacked by the forming enol of the other carbonyl. Dehydration of the hemiacetal gives the resultant furan. Hemiacetals are compounds that are derived from aldehydes [14].



**Figure 1.3:** Pyrrole synthesis mechanism.

The protonated carbonyl is attacked by the amine to form the hemiaminal. The amine attacks the other carbonyl to form a 2,5-dihydroxytetrahydrofuran derivative which undergoes dehydration to give the corresponding substituted pyrrole [15].



**Figure 1.4:** Thiophene synthesis mechanism.

Thiophene synthesis is achieved via a mechanism very similar to the furan synthesis. The initial diketone is converted to a thioketone with a sulfurizing

agent, which then undergoes the same mechanism as the furan synthesis. Most sulfurization agents are strong dehydrators and drive completion of the reaction.

Zhang *et al* used furan functionalized polyketones to prepare thermoreversible thermosets. These polymers were based on the Diels-Alder reaction. These polyketones can be de-cross-linked at high temperatures, which provide opportunities to recycle them on the material level [16].

### **1.3 Advantages thermosetting polymers**

Thermosetting plastics have a number of advantages. Unlike thermoplastics, they retain their strength and shape even when heated. This makes thermosetting plastics well-suited to the production of permanent components and large, solid shapes. Additionally, these components have excellent strength attributes, although they are brittle, and will not become weaker when the temperature increases. Some material properties which are specifically attributed to thermosetting polymers are the following:

- Very good fire & heat resistance
- Low creep resistance
- Very good mechanical properties
- Very good electrical properties
- No corrosion
- High chemical resistance
- Low weight
- Few limitations in form and design
- Competitive price for many applications

Due to the chemical structure of thermosetting polymers, they do not soften when heated. Before reaching a melting point, they decompose. This results in the product having a decomposition temperature instead of a melting point. The inability of reforming the materials is both an advantage and a disadvantage. Indeed once cured, thermoset polymers have a resistance to deformation, even when heated. This is a beneficial property in their practical use because the products which are made from thermoset polymers can withstand high impact forces without deforming.

The chemical structure of thermoset polymers is appreciated in their practical use, but it is seen as a disadvantage when trying to recycle them.

The cross-linked structure makes them unable to remold after their prior use. This is in contrast to thermoplastics, which soften when heated and harden and strengthen after cooling. A good example is the vulcanized rubber of which car tires can be made from. They can be heated to temperatures between 200°C and 300°C without melting or deforming. At even higher temperatures they will decompose. The decompositions of the unvulcanized material becomes significant at about 300 °C , whereas for the vulcanized polymer it can reach 400°C before dramatically decomposing. Although the composite is vulcanized with only 1%wt of sulfur, the temperature of the vulcanized composite can become much higher before the decomposition of the material occurs. Next to that, it has also to be taken into account that the linear composite is already surpassed the melting point (163°C) before decomposition occurs.

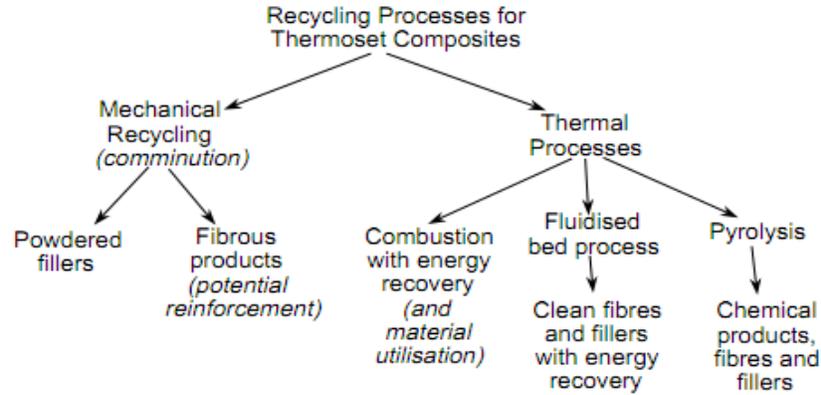
#### ***1.4 Problem of thermosetting polymers***

It is a good property in the practical use of these polymers that thermosets do not deform after they are cured. At the other hand it is not a very favorable property when recycle is desired. Some thermosetting polymers can be depolymerized or de-cross-linked. It's possible to crack polymers with supercritical CO<sub>2</sub> or supercritical H<sub>2</sub>O. The downside of this method is that the use of supercritical fluids is very costly and it does not yield the original monomers. Although there are exceptions, nearly all of the thermosetting polymers such as epoxies or polyester, cannot be simply depolymerized or de-cross-linked to recycle them. Most polymers cannot be remolded for new applications. These thermosets have high chemical resistance, which was a good property in the first place, thus chemically conversion towards reusable materials is not easy.

Biodegradable is a very trending topic. Where the thermosetting polymers first gain ground, now the tremendously amount of the waste causes criticism. For these reasons, thermosetting polymers are either crushed and end up as filling material in other polymers or they end up in landfills. Unfortunately these so called "solutions" are not really desirable since there is no unlimited need for filler material. Also landfills, where polymer waste is directly dumped into the environment cause pollution.

The recycling methods which are mostly used can be divided in two main categories: mechanical recycling and thermal recycling. Mechanical recycling yields a product of the same molecular structure which can be used as a filler material or as a matrix for other materials. Thermal recycling yields can yield many products with lower molecular weight or thermal energy. The most

used recycling methods for thermosetting polymers are summarized in Figure 1.5



**Figure 1.5:** Recycling processes used for thermosetting polymers <sup>[17]</sup>

As can be seen in Figure 1.5, the recycling processes for thermoset composites are either mechanically processed and mixed up with other materials or they are thermally processed to end up with decomposition components. The following list shows the methods of waste management in decreasing order of desirability.

- Prevent waste
- Reuse a product
- Recycle material
- Incinerate waste
- Landfill

The last decades polymers were dumped as landfills. Because they are not biodegradable these polymers will stay as a landfill indefinitely. These days new developments are depicted towards more environmentally friendly recycling methods. A European Union Directive from 1999 is aimed towards a reduction in the amount of plastics which end up in landfills. The idea sounds promising but cannot be realized without new recycling methods. Figure 1.5 show already some better methods than dumping the material in the environment, but they cannot always be applied. For example, the needed processes for mechanical recycling often result in too expensive polymers which cannot compete against the same polymer that is made from original

material. Thermal recycling methods yield a range of products which are hard to separate into useful chemicals and expensive.

Some cross-linked rubbers can be de-cross-linked but unfortunately degradation will occur and the material properties will decrease. Moreover a lot of these polymers have very short life cycles. Most of the thermoset polymers have a life cycle of 3 – 10 years. Some electronic components have maximum life cycles of 15 months, for example computer components. The world's production of electronics waste (E-waste), which consists largely of thermosetting polymers, is estimated to be 20-50 million tons per year.

For comparison: estimations suggest a worldwide production of plastics of more than 300 million tons per year. These include thermoplastic polymers and thermoset polymers. Almost all polymer material which is produced in the world, is waste that is going to landfills or is being reused in relatively expensive ways. These numbers are an indication of what the potential of success is for a polymer with the material properties of a thermoset polymer and can guarantee 100% recyclability.



# Chapter 2

## Thermoreversible cross-linking

In this chapter the available literature of reversible cross-linking using the formation of covalent bonds will be reviewed with the focus on the Diels-Alder reaction. Extra attention will go out to the chemistry used to make thermoreversible cross-links, and on how this influences the obtained material properties.

### **2.1 Introduction**

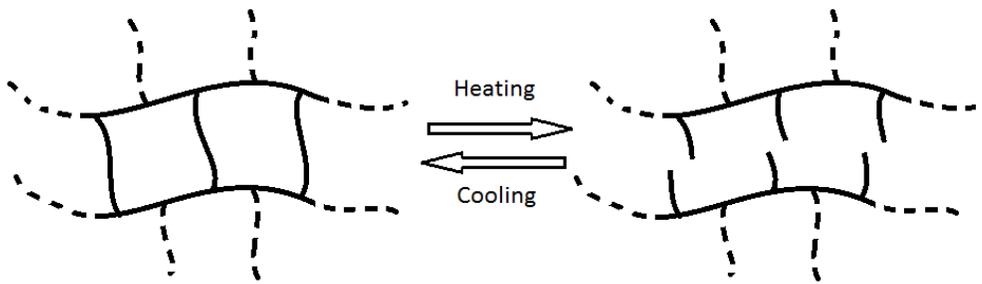
Thermoset polymers are cross-linked and cannot be remolded; this is in contrast to thermoplastic polymers which can be melted and reshaped. Still, thermosetting materials are often used because they have many desirable properties that are not found in thermoplastic materials. Many of these materials are known to have for example a high modulus, high fracture strength, and good solvent resistance. In addition, because cross-linked materials do not melt, they can be applied in a broad temperature range. Unfortunately, these properties also make it very difficult to process, recycle, reshape or repair cross-linked materials.

A thermally reversible cross-linked polymer can be processed as a thermoplastic material at high temperature, while the material will behave like a thermoset at lower temperatures. Therefore, reverse cross-linkable materials are easier to process, can be remolded, and have a higher potential to be recycled and repaired compared to traditional thermosetting polymers. Not all cross-links are broken during the process. However, the reduced amount of cross-links provides enough thermoplasticity to the polymers for reworking or removal. Also, the equilibrium is a dynamic process. Thus, although the material is not completely de-cross-linked, chains can move

because cross-links are detaching and reattaching continuously, and because the equilibrium shifts towards the de-cross-linked state. Some commercial applications of these systems are: adhesives, resins and rubbers.

### 2.1.1 Reversible cross-linking

Thermoset polymers can be reused or recycled by reversing the polymer to a de-cross-linked state. This can be done by stimulating polymers with an external stimulus like UV-light or shear stress. There are also polymers that have a backbone with cross-linking bridges which are thermally reversible. A polymer with such a backbone has the material properties of a thermoset polymer and due to an external stimulus, like heat, the backbone structure will be de-cross-linked.



**Figure 1:** de-cross-linking of a thermally reversible thermoset polymer<sup>[17]</sup>

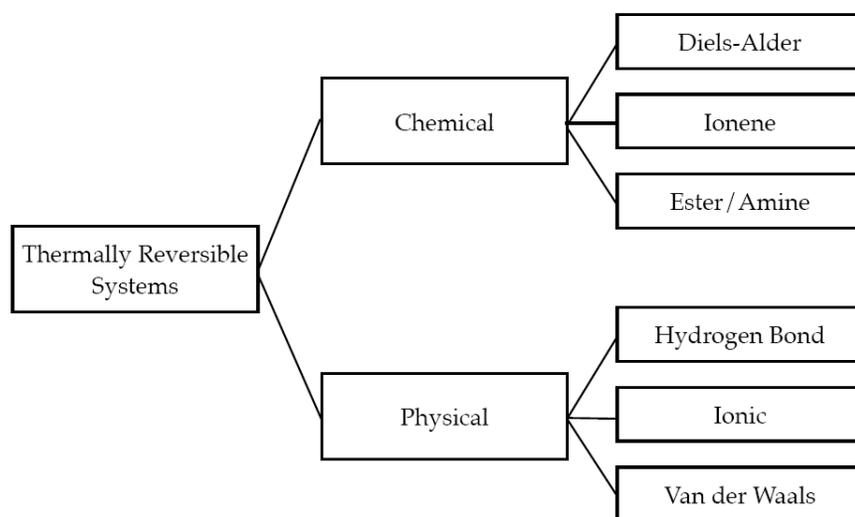
As can be seen in Figure 2, when the material is above the de-cross-linking temperature the polymer reverts to a normal branched polymer. The material then behaves like a thermoplastic polymer and can be reformed to a new shape.

Thermal reversibility of polymer cross-links can be achieved in several ways. They distinguish from each other in the type of bonding. Reversibility can be achieved by either physical bonds or chemical reactions.

Examples of reversible physical cross-links are Van-der-Waals interactions<sup>[18]</sup><sup>[19]</sup>, ionic interactions, or hydrogen bonds<sup>[20]</sup><sup>[21]</sup> (see Figure 3). These are not covalently bonded which usually result in lower de-cross-linking temperatures around 40°C to 80°C.

Chemically reversible cross-links are based on the covalent bonds that can be broken by external influences like shear stress, uv-light and heat. Chemically bonded cross-links are usually more energetic and have a higher temperature for de-cross-linking. With thermal reversibility a change in

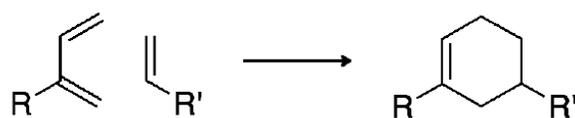
temperature changes the cross-link-state into a de-cross-linked state or vice versa. As covalent bonds are usually stronger than hydrogen- or ionic bonds, polymers using these systems have higher de-cross-linking temperatures. Examples of such chemical systems are sulfur bridges, ionene bond formation, amine or ester bonds and the often used Diels-Alder reaction. The Diels-Alder reaction is the most studied system for thermally reversible thermoset polymers. More elaboration on these systems and examples will be discussed in the next paragraph.



**Figure 2:** Categories thermally reversible cross-links <sup>[22]</sup>

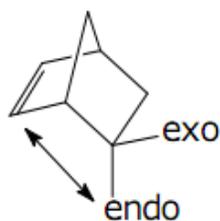
## 2.2 *Diels-Alder reactions*

Otto Paul Hermann Diels and Kurt Alder first documented the novel reaction in 1928 for which they were awarded the Nobel Prize in Chemistry in 1950 for their work on the eponymous reaction. The Diels- Alder reaction is one of the most common organic reactions. It is a so called 6 electron [4+2] cycloaddition <sup>[23]</sup>. The reaction is between a conjugated 1, -3-diene and a  $\pi$ -bound alkene, also called dienophile, to form a new ring which contains one  $\pi$ -bond and two new  $\sigma$ -bonds <sup>[24]</sup>. The reaction can also proceed if some of the atoms in the newly formed ring are not carbon.



**Figure 3:** Typical [4+2] cycloaddition Diels-Alder reaction. <sup>[25]</sup>

The reaction results in two stereo-isomers: an endo-product and an exo-product. The endo product substituent, former dienophile (see Figure 4), is pointed towards the newly formed double bond. The exo product substituent is pointed away from the double bond. This is shown in Figure 5. Also is clear that the endo product has an additional intermolecular interaction (shown by the arrow). At room temperature, kinetic reaction control prevails and the less stable endo isomer is the main reaction product. At higher temperatures and after long reaction times, the chemical equilibrium can assert itself and the thermodynamically more stable exo isomer is formed. The exo product is more stable by virtue of a lower degree of steric congestion, while the endo product is favored by orbital overlap in the transition state. More detail of this intermolecular interaction will be explained later in this chapter.



**Figure 4:** Endo- and Exo orientation of the Diels Alder reaction product

The Diels- Alder reactions are also known for their reversibility. The decomposition reaction of the cyclic system can also be called the retro-Diels-Alder reaction. Retro-Diels-Alder reactions are usually observed when a DA-product is analyzed via mass spectrometry.

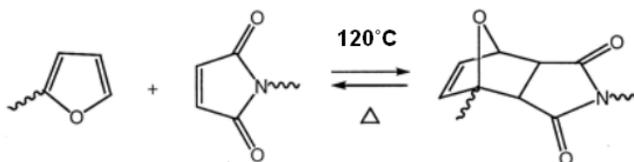
Typically for the Diels-Alder reaction is the equilibrium that exists between two components in a bounded state at lower temperatures and an unbound state at higher temperatures [26], [27] [28]. The temperature where the

equilibrium mainly shifts from the bonded state to the unbonded state is also known as the retro-Diels-Alder temperature (TrDA). As the Diels-Alder adduct and the separate unbonded components are always in equilibrium, the TrDA represents the temperature where the separate components are mainly present. The TDA on the other hand, represents the temperature where the Diels-Alder adduct is mainly present. Heating or cooling only shifts the equilibrium towards the right or the left side of the reaction.

As discussed when the temperature increases, the equilibrium shifts to the rDA reaction. But because of this there is a range of temperature where both the adduct, diene and dienophile are available in significant amounts. The DA reaction follows second order kinetics and the rDA reaction follows first order reaction. Because of this the equilibrium will not only depend on temperature, but also on the concentrations of the diene and dienophile. According to equation 2.1 the de-cross-linking temperature will increase with increasing concentrations of the diene and dienophile.

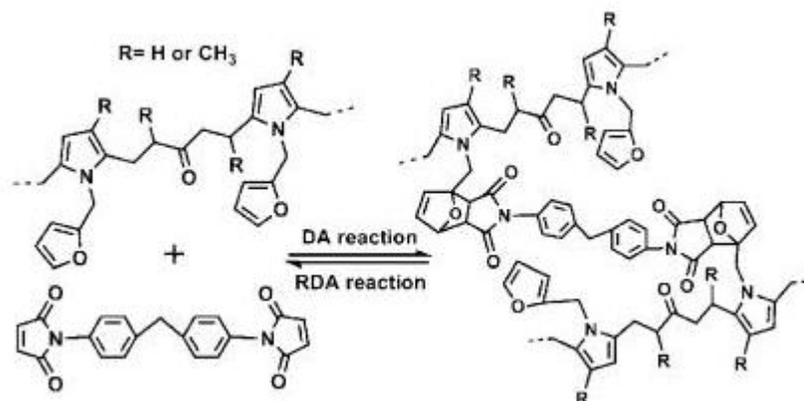
$$K = \frac{[DA - adduct]}{[diene] * [dienophile]} \quad (2.1)$$

There are multiple methods employed to make thermoreversible polymers with the DA system. It's possible to make, from small molecules with multiple dienophiles and diene functionalities, a thermoreversible network via a cross-linked system. For example a thermally reversible DA cycloaddition of a multi-furan and multi-maleimide can be used to prepare polymeric material (See Figure 5). An excellent review on the retro Diels-Alder reaction is given by Chen, X *et al* [29], [30].



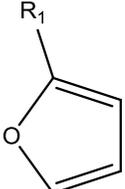
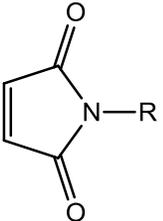
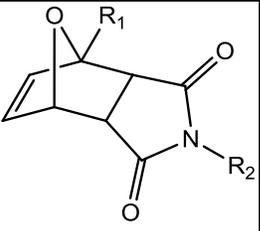
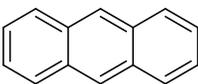
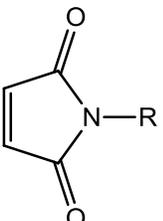
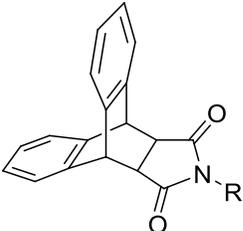
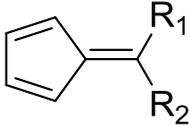
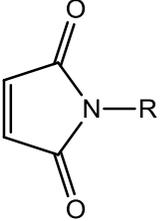
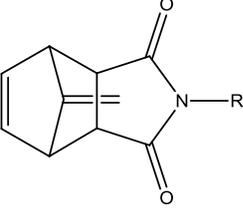
**Figure 5:** A thermally reversible DA cycloaddition of a multi-furan and multi-maleimide [31] Also the dienes and dienophiles can be attached to a polymer backbone. The polymers can be crosslinked with a crosslinker, like bis-maleimide, or a polymer. The polymer will attach via the same functionality as the crosslinker maleimide [32], [33], [1]. This polymer will behave as a thermoset polymer at lower temperatures and as a thermoplastic polymer at higher temperatures. As can be seen in Figure 4 the Diels-Alder reactions do not produce any by-products (self-contained reaction). In thermally reversible polymers, this means that the retro-Diels-Alder reaction will be performed

without the need of any reagents other than the polymer and the cross-linking material.



**Figure 6:** Scheme of the Diels-Alder (DA) and Retro-Diels-Alder (RDA) reactions between PK-furan and bis-maleimide [1].

In Figure 6 the DA and r-DA is shown. This is an example how alternating thermosetting polyketones (PK-furan) and a cross-linker (Bis-maleimide) react and form a cross-linked polymeric structure. This work has been done by Zhang *et al* and more of his study will be discussed later in this chapter.

Diene	Dienophile	Adduct	T <sub>DA</sub>	T <sub>rDA</sub>	Source
 <i>Furan</i>			<b>50-80</b>	<b>110-170</b>	[29] [34] [31] [35]
 <i>Anthracene</i>			<b>125</b>	<b>250</b>	[36]
 <i>Cyclopentadiene</i>			<b>25-120</b>	<b>150-215</b>	[37] [38]
 <i>Fulvene</i>			<b>30</b>	<b>50-100</b>	[37] [39]

**Table 2.1:** Overview of the most used reversible Diels-Alder systems<sup>[22]</sup>

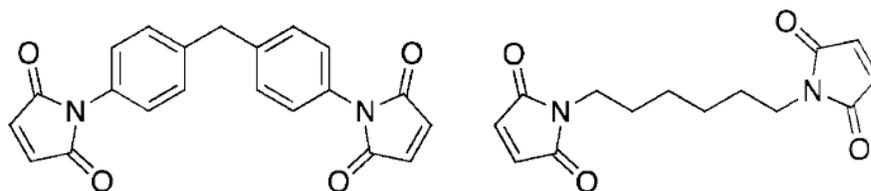
Because the retro-Diels-Alder reaction will be performed without the need of any reagents and it can be used in a wide temperature range, the DA reaction makes it a very suitable system to make thermoreversible polymers. Currently the most used and studied system is the DA reaction of furan with a maleimide compound. Besides this system others are the coupling between two cyclopentadiene, dienophile and anthracene and the reaction between dienophile and fulvene. All these systems are discussed in this chapter. An excellent overview of several Diels-Alder reactions is given by Peterson *et al*<sup>[37]</sup> and is shown in Table 2.1 above.

## 2.2.1 Furan-Maleimide systems

Thermally reversible thermosets polymers have been examined over the last decades. The furan-maleimide system is the best studied system so far. Also is this system relatively easy to characterize because of the specific UV-absorption of the maleimide moiety. In Figure 3 the different thermal reversible systems are shown. The differences between physical and chemical bonding are explained. This thesis will focus on polymers/ models with chemical bonding, in particular the cross-linking of Diels-Alder systems. In the next paragraph a few examples will be discussed.

As mentioned before, the most used system for Diels-Alder reactions is the combination of furan with a maleimide compound. Furan is a very good diene because of its very electron rich  $\pi$ -bonds. Furan is usually derived from furfural. A modification on the second position is relatively easy. For Diels-Alder reactions many furans compounds are used [22].

Maleimides are very good dienophiles because of the electron poor  $\pi$ -bond. Maleimides are synthesized from a primary amine and maleic anhydride. For Diels-Alder reactions a small number of maleimides is used. There are two bis-maleimides who are frequently present in literature. Those are methylenedi-p-phenylene bis-maleimide, the cross-linker Zhang used in his work, and hexamethylene bis-maleimide.



**Figure 7:** methylenedi-p-phenylene bis-maleimide and hexamethylene bis-maleimide

Also mentioned in Table 2.1, the Diels-Alder reaction with furan and maleimide is usually performed by RT to 70 °C. The rDA usually above 80°C. The bond strength between furan and maleimide groups is much lower than other covalent bonds. Thus bond cleavage can be achieved by the rDA reaction. This bond cleavage (rDA) indicates the possibility of thermoreversibility. Via the DA reaction most micro-cracks can be healed. [40]

## Low molecular weight compounds

Cross-linked networks can be synthesized from molecules that have multiple furan and maleimide functionalities. These systems have the capability to de-cross-link completely into low molecular weight compounds. Because of increased cross-linking, the movement of the chains will be more complicated. Therefore equilibrium has been reached between the DA- and rDA reaction. The reaction cannot reach a full completion. The molecules need more than two functionalities to obtain a high molecular weight polymer or network.

A systematic study on the application of the DA and retro-DA reactions was performed. First to model monofunctional systems, then linear polymerizations and non-linear systems. Linear polymerizations with difurans (A-A) and bis-maleimides (B-B) [41] and non-linear systems using A<sub>3</sub> and B-B monomers [42]. Gousse and Gandini, prepared, characterized, and polymerized monomer I (see Figure 2.8). The single methylene bridge joining the two complementary DA moieties made the molecule difficult to handle, and the study was not pursued. An article published by Gandini *et al* describes the synthesis of a low molecular weight compound with the use of A-B monomers. The use of A-B monomers represents for furan-maleimide DA-systems an interesting alternative for linear polymerizations because it ensures the ideal initial stoichiometry. More workable and flexible AB structures (II) have now been synthesized using aminoacids as precursors providing more stable monomers and the possibility of using both precursors derived from renewable resources [43].

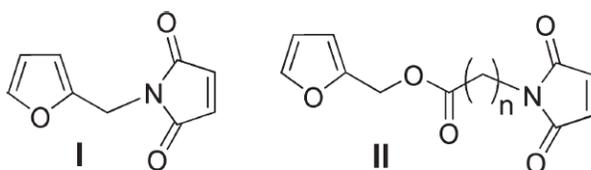
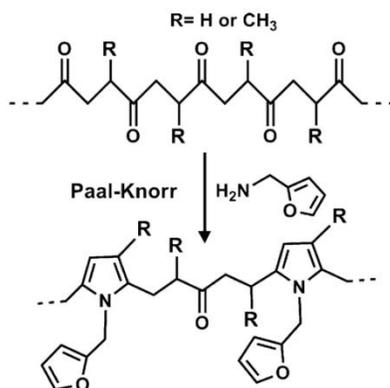


Figure 2.8: Single component furan-maleimide polymer precursor

## Thermoreversible networks from polymers with furan- maleimide groups

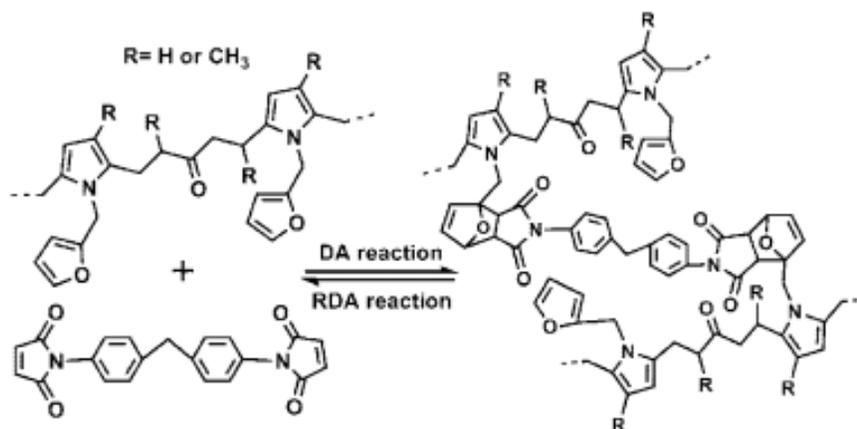
A Thermally reversible cross-linked polymer based on the furan-maleimide system was first mentioned by Craven in 1969. Already discovered were the synthesis, cross-linking and remolding of different polyester, polyureas and polyamides. All these polymers, with

pending furan groups, were cross-linked with different maleimides and mixed at a temperature of 140°C. Subsequently the mixture was molded and cooled to RT. The mixture is cross-linked. Also the reversibility was tested by repeating the procedure several times at temperatures around the 120-140°C [44].

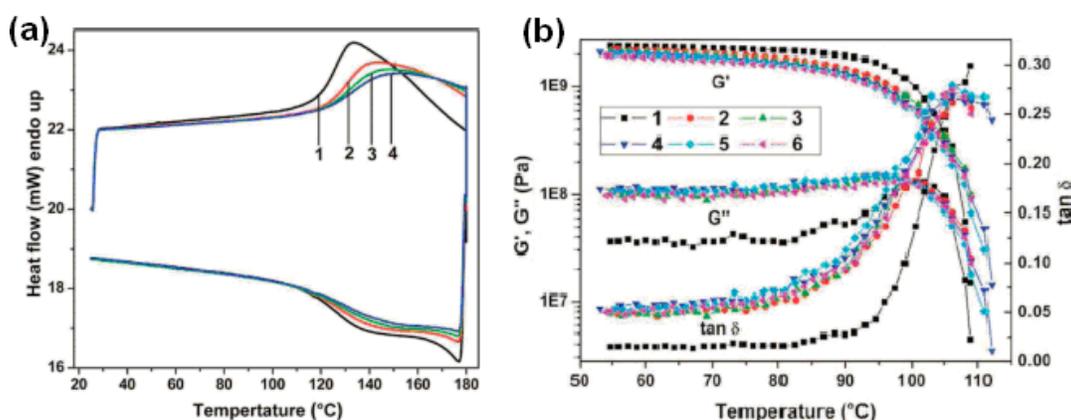


**Figure 2.9:** Polyketone modification by the Paal-Knorr reaction.

It's possible to prepare thermally reversible thermoset polymer with pending furan groups. In 2009 Zhang *et al* did this with polyketons and bis-maleimide. Polyketone is produced by a co- and ter-polymerization reaction of ethylene and carbonmonoxide with a palladium catalyst. A small amount of ethylene is replaced by propylene to reduce the melting point [45]. The reaction takes place at high pressure and high temperature. It's possible to regulate the amount of the methyl side -groups in the polymer by using ethylene and propylene in different proportions during the reaction. Polyketones can then be modified by the Paal-Knorr reaction between polyketone and furfurylamine. During this reaction the polyketone will be transformed in a polypyrrole backbone with water as a side product.



**Figure 2.10** Diels-alder reaction and retro-Diels-Alder reaction between PK-Furan and bis-maleimide.



**Figure 2.11** Thermal behavior of PK-furan with bis-maleimide cross-links. (a): DSC scan with 4 repeating cycles. (b): Dynamical mechanical thermal analysis with 6 repeating cycles.

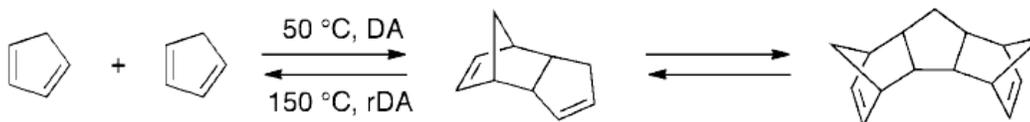
The results can be displayed in a DSC. This method makes very clear how reversible the reaction is. Figure 2.10 makes it very clear that the retro-Diels-Alder reaction lies around the 130°C. Because the lines 1-4 are quite similar the thermo reversibility is a fact. This means PK-furan with bis-maleimide cross-links can be healed without losing mechanical properties. Besides DSC also DMTA confirms this. During the cooling time the Diels-Alder reaction will take place. This will take approximately 20 minutes. A re-cross-link was established at 50°C for 24 hours. The new DMTA shows full recovery of the Diels-Alder adducts. The polymer can almost be totally healed.

One of the most recent studies about this topic was carried out by Canadell *et al* last year. This is about the effects in thermo-remendable polymer

networks based on Diels-Alder cross-link reactions. Structurally varied model compounds, polymeric and network architectures containing DA adducts from furan and maleimide groups have been synthesized. In all cases a mixture of *endo* and *exo* stereoisomers were recorded by  $^1\text{H}$  NMR spectroscopy. The *endo* and *exo* stereoisomers show significantly different thermal responses: the rDA of the *endo* DA-adducts typically takes place at 20-40 °K lower than the corresponding *exo* DA-adduct [46].

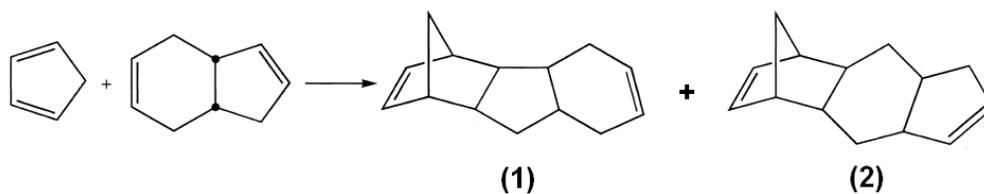
## 2.2.2 Cyclopentadiene systems

Cyclopentadiene is used in cross-linking systems but unless it shows a lot of potential, not many publications are available concerning thermoreversibility. Cyclopentadiene is also a well-known diene- dienophile in Diels-alder reactions (Table 2.1). Cyclopentadiene groups can act both as diene and dienophile so it can react with itself. Then the adduct dicyclopentane will be formed. Subsequent, because the adduct contains dienophilic double bond, trimers can be formed (See Figure 2.12).



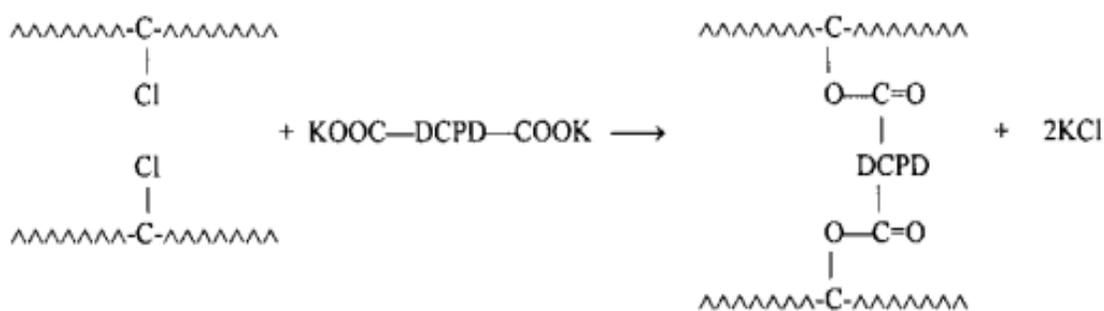
**Figure 2.12:** DA-reactions with two cyclopentadienes

Biesemans *et al.* investigated in 2002 the Diels-Alder reaction between dicyclopentadiene and bicyclononadiene which give three major reaction products out of eight possible structures. They are all three *endo*-isomers. There is no preference observed for the DA-reaction of either the cyclopentene or cyclohexene ring of the starting bicyclononadiene. When the DA-reaction will be performed between cyclopentadiene and cyclohexene both isomers of cyclopentene with the ring up and down is obtained. Only one isomer is obtained during the DA-reaction cyclopentadiene and cyclopentene [47].



**Figure 2.13:** Diels–Alder reaction of dicyclopentadiene and bicyclononadiene

Chen and Ruckenstein have reported cyclopentadiene functionalized polymers. Chlorine containing polymers were reacted with potassium dicyclopentadiene-dicarboxylate to functionalize the polymer with cyclopentadiene side groups (Figure 2.14). This reaction can be characterized as an esterification.



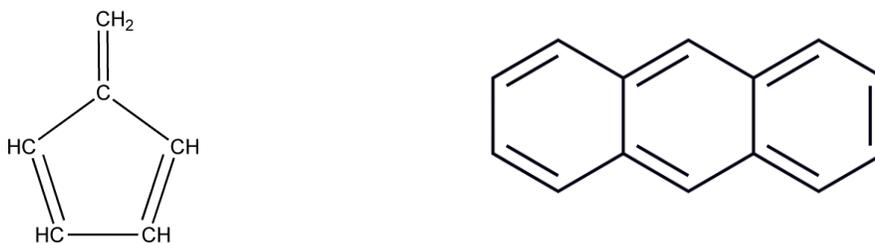
**Figure 2.14:** Esterification reaction between potassium dicyclopentadienedicarboxylate and chlorine containing polymer

Cyclopentadiene functionalized polymers were obtained with 3, 5, 16 cyclopentadiene groups per chain. Also in this reaction the cyclopentadiene groups act both as diene and dienophile in this reaction. These polymers were assumed to have a TrDA of 195°C since the temperature needed for the retro-Diels-Alder reaction of dicyclopentadiene carboxylic acid is between 195°C and 220°C [48].

## 2.2.2 Other systems

Besides the Furan-maleimide- and the cyclopentadiene systems two other systems can be described; Fulvenes and anthracene. Fulvenes are quite similar as cyclopentadiene and take part in the Diels-Alder reaction. Anthracene can also be used for thermoreversible networks. An advantage of this system is that a wide range of temperature can be used. This is dependent of the substituent on the anthracene and dienophile. The disadvantage is the difficulty of modification. The introduction into polymers is very difficult.

For these systems there is plenty of room for research.



**Figure 2.15:** Fulvene and Anthracene

## 2.3 *Molecular orbital calculations*

There can be as many as two electrons in each component atomic orbital, making a total of 4 electrons; 2 molecular orbitals are required to accommodate them. In bonding orbital, electrons are concentrated in the region between the nuclei, where they can be attracted by both nuclei. The increase in electrostatic attraction lowers the energy of the system. In an antibonding orbital electrons are not concentrated between the nuclei; electron charge is zero in the separated atoms. There is a decrease in electrostatic attractions, and an increase in repulsion between the nuclei. The energy of the system is higher than that of the separated atoms. Where electrons in a bonding orbital tend to hold the atoms together, electrons in an antibonding orbital tend to force the atoms apart. The bond of dissociation energy is a stronger electrostatic attraction in the separated atoms. There are

also non-bonding orbitals. Electrons in these orbitals neither strengthen nor weaken the bonding between atoms.

An aromatic molecule is flat, with cyclic clouds of delocalized  $\pi$  electrons above and below the plane of the molecule. For benzene the molecular orbitals that permit this delocalization. But delocalization alone is not enough. For that special degree of stability, aromaticity, the number of  $\pi$  electrons must conform to Huckel's rule: there must be a total of  $(4n+2)$   $\pi$  electrons. A chemical reaction involves the crossing of an energy barrier. In crossing this barrier the reacting molecules seek the easiest path: a low path, to avoid climbing any higher than is necessary; and a broad path, to avoid undue restrictions on the arrangement of atoms. As reaction proceeds there is a change in bonding among the atoms, from the bonding in the reactants to the bonding in the products. Bonding is a stabilizing factor; the stronger, the more stable the system. If a reaction is to follow the easiest path, it must take place in the way that maintains maximum bonding during the reaction process. Now, bonding, results from overlap of orbitals. Overlap requires that portions of different orbitals occupy the same space, and that they be of the same phase.

### 2.3.1. HOMO-LUMO

To give more sight into the reaction mechanism of the Diels-Alder reaction and the differences between the EXO and ENDO adduct, molecular orbital calculation will be given in the next paragraph.

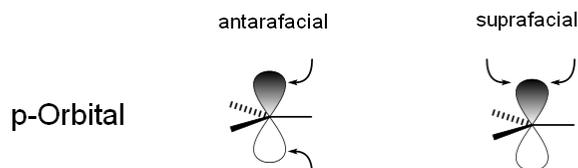
During the experiments describes in this thesis the assumption was the EXO form of the system where furan/ maleimide groups have been used for cross-links should result in a higher  $T_{\text{RDA}}$  than the ENDO form of the system. The effects can be checked by calculating the energy levels of the molecular orbitals of the involved components. For the Diels-Alder reaction the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of both the diene and dienophile are the most important because these exchange electron during the reaction. These orbitals are the pair that lies closest in energy of any pair of orbitals in the two molecules, which allows them to interact most strongly. These orbitals are sometimes called the frontier orbitals, because they lie at the outermost boundaries of the electrons of the molecules.

In 1952, Kenichi Fukui published a paper in the Journal of Chemical Physics titled "A molecular theory of reactivity in aromatic hydrocarbons"<sup>[49]</sup>. Due to his work a good estimation for reactivity could be found by looking at the frontier orbitals.

The three main observations of molecular orbital theory as two molecules interact are:

- The occupied orbitals of different molecules repel each other.
- Positive charges of one molecule attract the negative charges of the other.
- The occupied orbitals of one molecule and the unoccupied orbitals of the other interact with each other causing attraction (HOMO – LUMO)

The Woodward–Hoffmann rule for thermal pericyclic reactions is: A ground state pericyclic change is symmetry-allowed when the total number of  $(4q+2)s$  and  $(4r)a$  components is odd. Where  $q$  and  $r$  are integers and the subscripts  $s$  and  $a$  denote suprafacial and antarafacial respectively. If the total number of these systems is odd then the reaction is thermally allowed<sup>[50]</sup>. Suprafacial and antarafacial refer to modes of bond formation that is respectively on the same face and on opposite faces of a molecular component.



**Figure 2.16:** Antarafacial and suprafacial approach

### 2.3.2 Cycloadditions

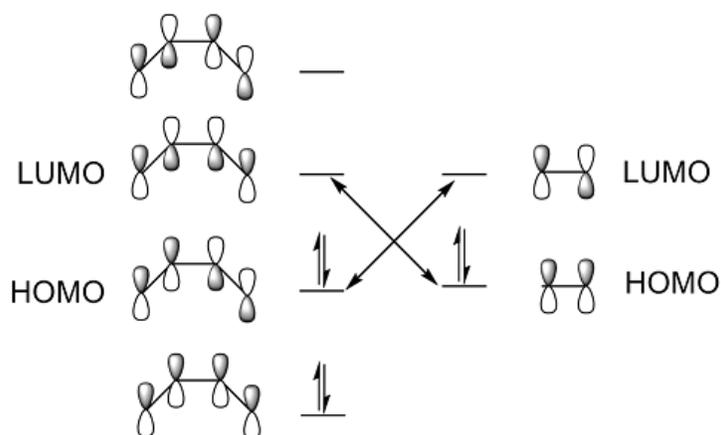
Cycloadditions are the largest class of pericyclic reactions. In cyclization, two  $\pi$  electrons of the polyene form the new  $\sigma$  bond of the cycloalkene. Important is to consider which electrons. The attention lies on the highest occupied molecular orbital (HOMO) of the polyene. Electrons in this orbital are the valence electrons of the molecule. They are tightly held and the most easily pushed about during reaction. The highest occupied molecular orbital of a conjugated diene is  $\psi_2$ . It is the electrons in this orbital that will form the bond that closes the ring. Bond formation requires overlap. To bring these lobes into position for overlap, there must be rotation about two bonds. This rotation can take place in two different ways. There can be conrotatory motion, in which the bonds rotate in the same direction, or there can be disrotatory motion, in which the bonds rotate in opposite directions.

Conrotatory motion brings together lobes of the same phase; overlap occurs and a bond forms. Disrotatory motion, on the other hand, brings together lobes of opposite phase; here interaction is antibonding, and repulsive. It is conrotatory motion that produces the stereochemistry actually observed. On absorption of light one electron from  $\psi_2$  can be raised to  $\psi_3$ . Now the highest occupied orbital is  $\psi_3$ . Now it is the disrotatory motion that brings together lobes of the same phase, and the stereochemistry is reversed.

By making a pericyclic reaction the transition state for these reactions involving electrons of the molecules moving in continuous rings. These reactions can be predicted by the Woodward–Hoffmann rules and thus are closely approximated by Frontier Molecular Orbital theory. The FMO indicates the HOMO of one component and LUMO of the other.

For example, the Diels-Alder has two components, one of four  $\pi$  electrons and one of two. They both undergo reaction in a suprafacial sense. The diene with four electrons can be expressed as  $[4r]$ , and the dienophile can be expressed as  $[4q+2]$ . Thus, the total components that are  $[(4q+2)s]$  and  $[(4r)a]$  is one, because there are  $(4q+2)s$  and  $(4r)s$  only. This means that the reaction occurs between the HOMO of the diene and the LUMO of the dienophile. The four  $\pi$ -orbitals of the diene and the two  $\pi$ -orbitals of the dienophile shift to form two new  $\sigma$ -bonds and a new  $\pi$ -bond. The HOMO and LUMO of a molecule are different orbital phases. They differ in the way how they overlap, and thus in energy. Because there is one  $(4q + 2)_s$  component and no  $(4r)_a$  component the Diels-Alder reaction is thermally allowed. It is typically described as a  $[4s+2s]$  cycloaddition. This can be further improved by describing the location of the electrons in question – both  $\pi$  orbitals in this case, so the reaction becomes  $[\pi 4s + \pi 2s]$  <sup>[10] [51]</sup>.

FMO theory also finds that this reaction is allowed and goes even further by predicting its stereoselectivity, which is unknown under the Woodward-Hoffmann rules. Since this is a  $[4 + 2]$ , the reaction can be simplified by considering the reaction between butadiene and ethene. The diene as well as the dienophile can be the HOMO and the LUMO. These two reactions can occur both, but depends on the electrons. Since diene is often more electron rich, the electrons will flow from the HOMO of the diene to the LUMO of the dienophile. On the next page these calculations will be made. These calculation will show which of the reactions, shown in Figure 2.17, will occur <sup>[52]</sup>.



**Figure 2.17:** Butadiene- Ethene cycloaddition, which reaction will occur?

The calculations of  $\Delta E$  and a  $\Delta E'$  are in this situation necessary. The energy cap between the HOMO of one reactant and the LUMO of the other can be calculated by the ab-initio calculation method. This calculation is based on quantum chemistry and is the best available method to determine the energy caps. In Table 2.1 an example of the energy-gap calculation is presented. The X is an electron rich molecule, the Y an electron poor. So expected; the X will usually be the diene and the Y usually the dienophile.

	X	Y
LUMO	0,191843	-1,18949
HOMO	-8,44817	-10,2195

$\Delta E$	homo X - lumo Y	7,258678	eV
$\Delta E$	homo Y - lumo X	10,41132	eV

Table 2.1: Energy gap between LUMO Dienophile and HOMO of Diene

As can be seen in the Table above the assumption was right. The reaction is facilitated if the  $\Delta E$  (energy gap) is as low as possible. HOMO X will react with LUMO Y.

This reaction cap is also very important for the rDA reaction because this will cause the  $T_{rDA}$ . The first step in reverse reaction is the excitation of the electron of the adduct facilitated by heating. Electrons in HOMO state will go the excited state when enough energy is added. The excited state is the same state as the LUMO state of the same molecule. When the energy cap between HOMO and LUMO is larger, the  $T_{rDA}$  becomes higher. The HOMO LUMO energy gap of two reactions are listed in Table 2.2.

<i>Diels-Alder system</i>	$\Delta E$ [eV]	$\Delta E_{adduct}$ [eV]
Furan/Bis-maleimide	58.90	18.12
Cyclopentadiene/Cyclopentadiene	14.27	22.59

table 1.2: HOMO - LUMO energy gaps, for Diels-Alder reactions calculated by ab-Initio simulation; a: Energy gap between HOMO of Diene and LUMO Dienophile, b: Energy gap between HOMO of adduct and LUMO of adduct.

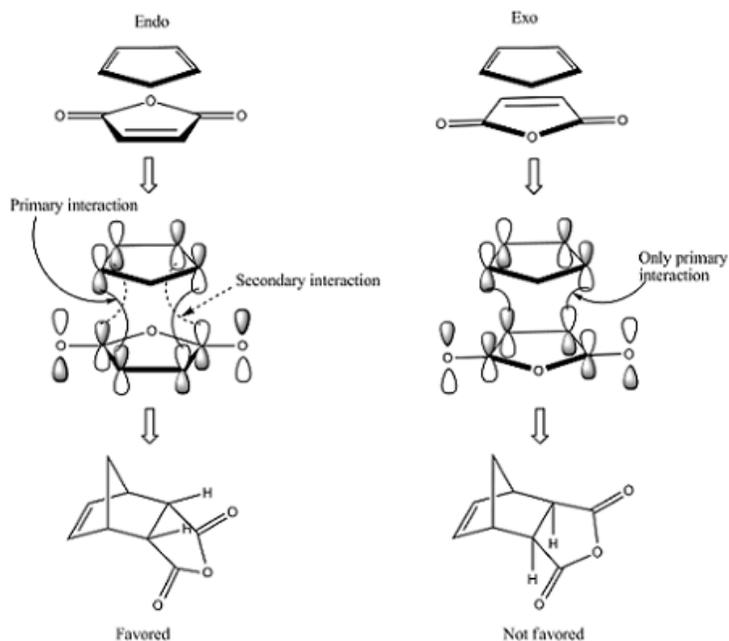
From the energy cap values can be seen that the cyclopentadiene reaction need less energy than the reaction of Furan with Bis-maleimide. This is also studied in previous work on retro Diels-Alder reactions. The  $T_{DA}$  temperature of Furan/Bis-maleimide [53] [54] [35] [34] is higher than  $T_{DA}$  of the cyclopentadiene system [55] [38] [56]. Furthermore the energy cap of the reverse reaction is larger. This will result in a higher  $T_{rDA}$  for dicyclopentadiene.

Not all cycloaddition reactions are allowed. [2+2] reactions for example are not. This because the kinetic barrier. A four membered ring from two alkenes is thermo-dynamically favorable, but kinetically impossible.

### 2.3.3 Endo Exo attack

Electron-donating groups on the diene and electron-withdrawing groups on the dienophile can accelerate the reaction. Also, the more powerful the electron-donating or withdrawing substituents are, the more regioselective the reaction. Important is that the diene must have the cis- conformation to react. A trans- conformation of the diene would lead to a trans- double bond in a ring which costs too much energy to form. As with all pericyclic reactions, the path is determined by thermodynamics. That's why the rDA- reaction is very important for determination of the product.

Already described in this chapter is the yield of two diastereomers formed during the Diels-Alder cycloaddition. There are two possible ways of attacking suprafacially. These are described as ENDO and EXO. These two reactions are allowed by the W-H rules. The ENDO and EXO diastereomers are formed due to a certain approach. The approach is illustrated in Figure 2.17.



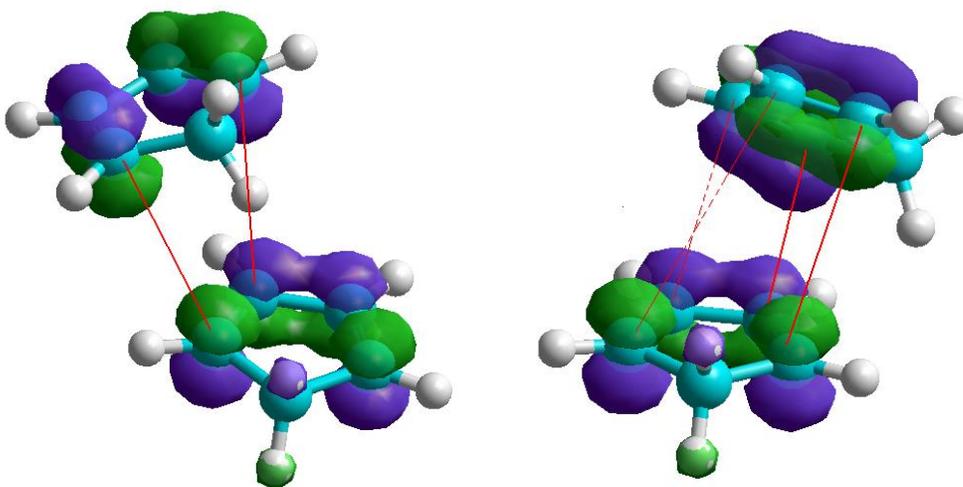
**Figure 2.18:** Endo and Exo approach of Diels-Alder cycloaddition reaction

Transition structures with electron withdrawing substituents are more favored in a hindered environment. Nevertheless they are thermodynamically less favored. This can be explained by the Frontier Orbital approach. As can be seen in Figure 2.18 besides the primary interaction a secondary interaction is possible with the ENDO- approach. This leads to a conflict between kinetics and thermodynamics depending on conditions.

For example a reaction between maleic anhydride and cyclopentadiene: The maleic anhydride is an electron-withdrawing component that makes the dieneophile electron deficient, forcing the regular Diels-Alder reaction. Thus, only the reaction between the HOMO of cyclopentadiene and the LUMO of maleic anhydride is allowed. The secondary (non-bonding) orbital interactions in the ENDO- transition state will lower its energy. Therefore the reaction towards the ENDO-product will go faster and therefore kinetically more favorable.

The preference for kinetic formation of the endo- adduct has not been described really convincingly by secondary orbital overlap. This is a

stabilizing interaction of in-phase orbitals in the transition state that does not lead to new bonds. In cases where the reaction reverses, the exo adducts can be obtained. This can happen when the resulting endo product can easily dissociate back into the starting material. In such reactions, the exo product predominates with extended reaction times because the exo product is thermodynamically favored. Possible is that charge transfer from the nucleophilic diene to the electrophilic dienophiles leads to the possibility for maximum coulombic interaction when the electronegative activating group is folded under the diene. This is still a matter of debate.



**Figure 2.19:** HOMO-LUMO interactions in the Diels-Alder addition of two cyclopentadienes (left: Exo attack, right: Endo attack).

In Figure 2.19 an example has been given. Endo isomers are thermally favored and that can be shown by comparing the reaction enthalpies of two reactions. The reaction enthalpies can be derived from FMO calculations and Hess' law. Here a reaction with two (HOMO-LUMO) cyclopentadienes is illustrated. The two cyclopentadiene can attack themselves in two different ways. In both attacks the molecule under is the LUMO and above the HOMO. The dotted lines are the secondary interactions. Using the calculations methods, the following reaction enthalpies are calculated:

$$\boxed{H_r^o = H_f^o(\text{products}) - H_f^o(\text{reactants})} \quad \text{eq. 1}$$

Where:

$H_r^o$  = reaction enthalpy

$H_f^o$  = free energy

kCal/mol	Activation energy		Reaction Enthalpy $H_r^\circ$	
	endo	exo	endo	exo
AM1	34.21	33.17	-22.69	-24.43
PM3	37.40	36.61	-19.34	-21.20

Table 2.3 Reaction enthalpies ENDO/EXO for cyclopentadiene

As can be seen, there are different calculations methods possible. In this case the semi-empirical AM1 and the PM3 calculations according Hyperchem. It is based on quantum chemistry and is the best available method to use for calculating reaction enthalpies. As can be seen, the reaction for the exo-adduct is more exothermic than the reaction for the endo-adduct. Therefore, higher temperatures favor the dissociation of the endo-adduct more than the dissociation of the exo-adduct. This explains the selectivity for the endo- or exo-adduct at different temperatures, and specifically the favored endo-reaction at low reaction temperatures.

# Chapter 3

## Diels-Alder and retro Diels- Alder

Already mentioned in the previous chapter, Zhang *et al* described thermally self-healing materials. These are developed on the basis of furan-functionalized, alternating thermosetting polyketones (PK-furan) and bismaleimide by using the Diels-Alder and Retro-Diels-Alder reaction sequence. It is found that the achieved self-healing ability of this easily accessible system provides recyclability and reworkability. The simplicity of the synthesis, the broad range of available polyketones precursors and the striking healing ability of this system has led to a wider exploration of this topic. In this case investigation of the model component reaction of different maleimides with a furan group. These experiments will focus on the reaction temperatures of the Diels-Alder and Retro-Diels-Alder and conversions. Afterwards it is observed that the reaction product contains an *endo* and an *exo* form. These two forms are separated and studied because they should have different material properties and thermal behavior.

### 3.1 Introduction

Because of the promising results of self-healing polymeric materials a new area and wide range of research can be developed. The Diels-Alder and its Retro-Diels-Alder analogue represent highly promising methods to introduce self-healing properties into polymeric systems. The last decades two different strategic applications of this reaction sequence have been studied<sup>[1]</sup>: (i) the polymerization of multifunctional monomers like di- or tri-functional furan derivative and bis-maleimide; (ii) the formation of cross-linked polymer networks from linear thermoplastics bearing pendant furan and/or maleimide groups. Both these strategic approaches show limited thermal reversibility and expensive synthesis. This will impede their practical applications as self-healing materials. For this reason new approaches are developed to solve these problems, referring to the work of Zhang *et al.* the

starting materials consist of alternating polyketones obtained by co- or terpolymerization of carbon monoxide, ethylene and propylene using homogeneous palladium-based catalysts. The polyketones can easily be converted into furan derivatives (PK-furan) via the Paal-Knorr reaction with furfurylamine. The PK-furan can then be converted by the DA-reaction with bis-maleimide, resulting in a high cross-linked polymeric network. Furthermore an dissociation of the polymeric network is possible at elevated temperature by the Retro-Diels-Alder reaction. This leads to an environmentally friendly route towards the commercial bulk synthesis of reworkable polymers.

Commencing at these new developments and to obtain a deeper understanding of this system, the experiment can be adjusted to obtain even better results. A model component reaction was used for this study in order to facilitate the structure characterization for the 'tuned' polymeric materials. Thermal and mechanical tests can be performed while varying the maleimide functionalities. The results would give more insight about the reworkability of the eventually produced polyketones.

During the model component reaction 2,5-hexanedione and furfurylamine is used. via the Paal-Knorr reaction it is possible to obtain a high yield of pyrrolic furan. Pyrrolic furan will be used as the furan group which can react with the maleimide. For the maleimide group different attachments were made. In this way the differences in conversions and thermal behavior can be studied. Furan and maleimide will be synthesized according to the DA system. This is possibly the most used system for reworkable polyketones. The DA system is especially useful because it works with many alkenes and dienes. This makes it possible to tune the  $T_{DA}$  and  $T_{rDA}$  for specific applications. This is already discussed in chapter two.

Subsequently the product can be occur in two different forms; the *endo* and the *exo* form. The difference between these two forms is also discussed in chapter 2. Essentially of these two forms is the difference in  $T_{rDA}$ . To obtain more knowledge about the  $T_{rDA}$  of the *endo* and *exo* adduct is an important issue in this thesis and will be mentioned with great respect.

## **3.2 Experimental**

### **3.2.1 Materials**

Paal knorr reactions were performed with 2,5-hexanedione (Aldrich,  $\geq 95\%$ ) and furfurylamine (Aldrich,  $\geq 95\%$ ) to make pyrrolic furan. Dichloromethane (Lab-Scan, 99.8%) Sodium Sulfate. Diels-Alder reaction: Ethylmaleimide (Aldrich, crystalline  $\geq 98\%$  HPLC), Cyclohexylmaleimide (Aldrich, crystalline  $\geq 98\%$  HPLC), Phenylmaleimide (Aldrich, crystalline  $\geq 98\%$  HPLC), Benzyl maleimide (Aldrich, crystalline  $\geq 98\%$  HPLC). Acetonitrile (Acres, pure) Chloroform-*d* (Aldrich 99.8 atom % -*d*) DMSO-*d*<sub>6</sub> (Aldrich 99.8 atom % D) Iodine (Aldrich, 99,99% metals basis).

### **3.2.2 Model compound reaction pyrrolic furan**

The reaction between 2,5-hexanedione ( 5 g, 44 mmol) and furfurylamide (4.26 g, 44 mmol) without solvent was performed in a 50 ml round bottom flask equipped with magnetic stirrer. The reaction was performed at 70°C for 20 hr. under vigorous stirring. After the reaction, the mixture was diluted with dichloromethane (150 ml) and dried over sodium sulfate. The solvent was removed in the rotor- vacuum to yield pyrrolic furan (7.1 g, 95% yield)

### **3.2.3 Model Diels-Alder reaction**

The Diels-Alder reaction of pyrrolic furan (0.5 g, 2.85 mmol) and ethylmaleimide (0.5 g, 3.99 mmol) was performed in acetonitrile (10 ml) in a 50 ml round bottom flask equipped with a magnetic stirrer. The reaction was performed at 80°C for 24 hr. with vigorous stirring. After the reaction the solvent was removed under vacuum and the product was kept cool.

### **3.2.4 Thin layer chromatography**

The Diels-Alder adduct will be examined with aluminum plate TLC (silica gel 60/kieselguhr F<sub>254</sub> tlc plates without fluorescent indicator, Aldrich). The dots were adjusted via capillary pipettes. Product was solved with ethanol. Eluent was ethyl-acetate and pentane (ratio 30:70). The dots were detected with iodine.

### 3.2.5 Separation *endo-exo* adduct

Separation was performed with equipment of Henk v.d. Bovenkamp. The adduct was solved in ethanol. Subsequently 5 ml was added on top of the column filled with silica gel. The used eluent was ethyl acetate and pentane (ratio 30/70). The eluent was added via a pump with a flow of... The fractions were detected with an HPLC. In the first run the peaks are detected. The second run are the fractions separated. These are collected in different round bottom flasks. Afterwards the eluents are evaporated under vacuum and the samples are characterized by NMR.

### 3.2.5 Characterization

H-NMR spectra was recorded on a Varian Mercury Plus 400 MHz using CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> as a solvent. Differential scanning calorimetry (DSC) was performed by Mr Albada on a Perkin Elmer differential scanning calorimeter Pyris 1 under N<sub>2</sub> atmosphere. The DSC was weighted ( approx. 6 mg) in an sealed aluminum pan. The samples were heated from 20 to 180 °C followed by cooling to 20°C. Different amount of cycles were performed and the cooling rates were 1°C per minute throughout the DSC measurements.

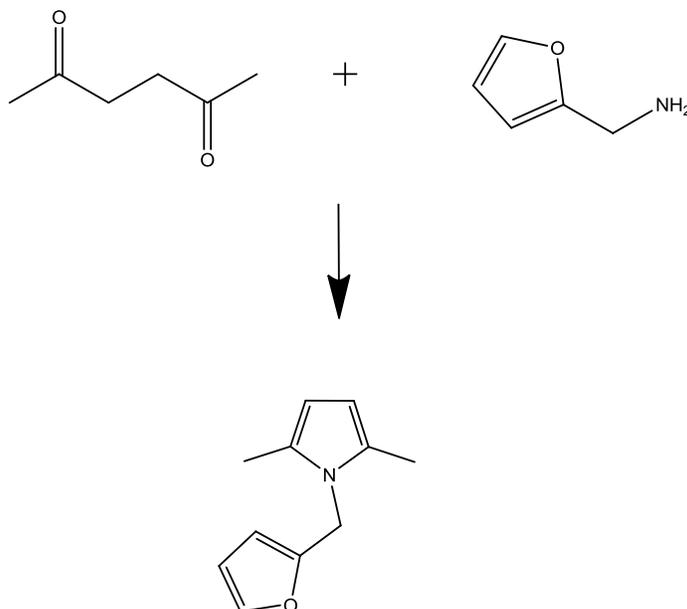
Usage of the robot of Henk vd Bovenkamp. This is an column-chromatograph with an HPLC detector behind it. The different fractions are detected by the HPLC and separated in different flasks performed by a automatically controlled arm. In this way it's possible to separate fractions by column chromatography during the night.

## 3.3 *Results and discussion*

### 3.3.1 Synthesis of pyrrolic furan

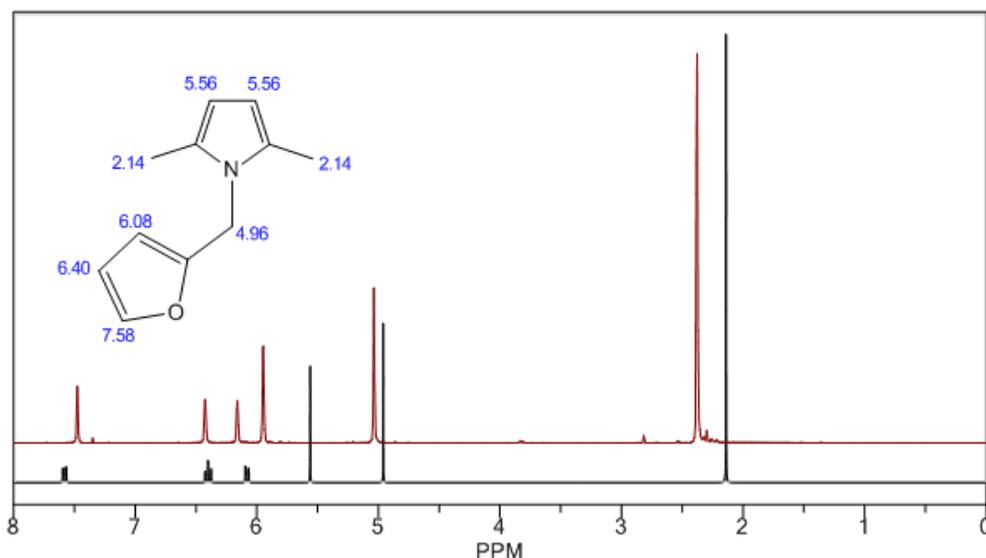
This reaction is performed with the classic Paal-Knorr reaction. A model compound reaction between 2,5-hexanedione and furfurylamine was performed. From this product a great batch is made several times because of its frequent use in this research. The pyrrolic furan is each time

characterized by NMR. The results are compared with the results of Zhang [16]. NMR results are compared with before and after the Paal-Knorr reaction.



**Figure 3.1:** Scheme of the reaction between 2,5-hexanedione and furfurylamine.

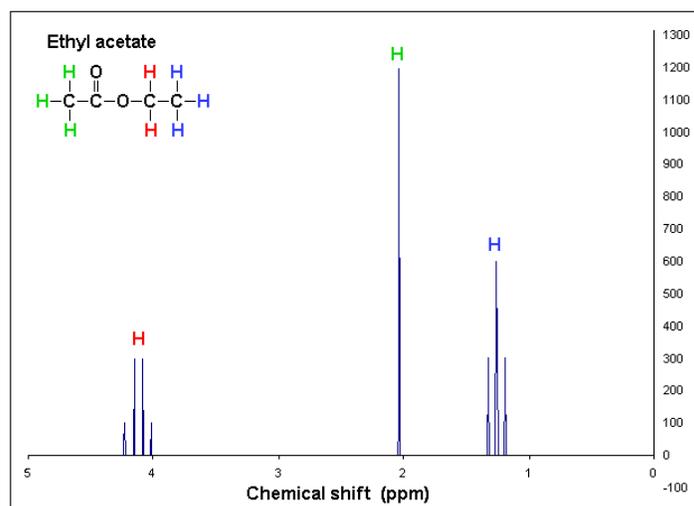
After the Paal-Knorr reaction the appearance of new signals of the pyrrole ring, CH<sub>2</sub> group and the down shifting of the furan ring show the formation of the formed adduct. This is showed in Figure 3.2. It's possible to calculate the conversion of the pyrrolic furan by the intensity of the peak at 4.9 ppm (CH<sub>2</sub> group of the converted furfurylamine) and 3.8 ppm (HH<sub>2</sub> group of the unreacted furfurylamine). The development of the conversion through time is not determined. This is documented by Zhang. He found out that the conversion increase slowly with reaction time. It reached a 64% conversion after a 12 hr. reaction time. At elevated temperature (70°C) the model reaction proceeded almost a 100% conversion at a reaction time of 20hr. But even at low temperatures (50°C) the Paal-Knorr reaction can easily take place.



**Figure 3.2:** red line:  $^1\text{H-NMR}$  spectra of pyrrolic furan, black line: simulation

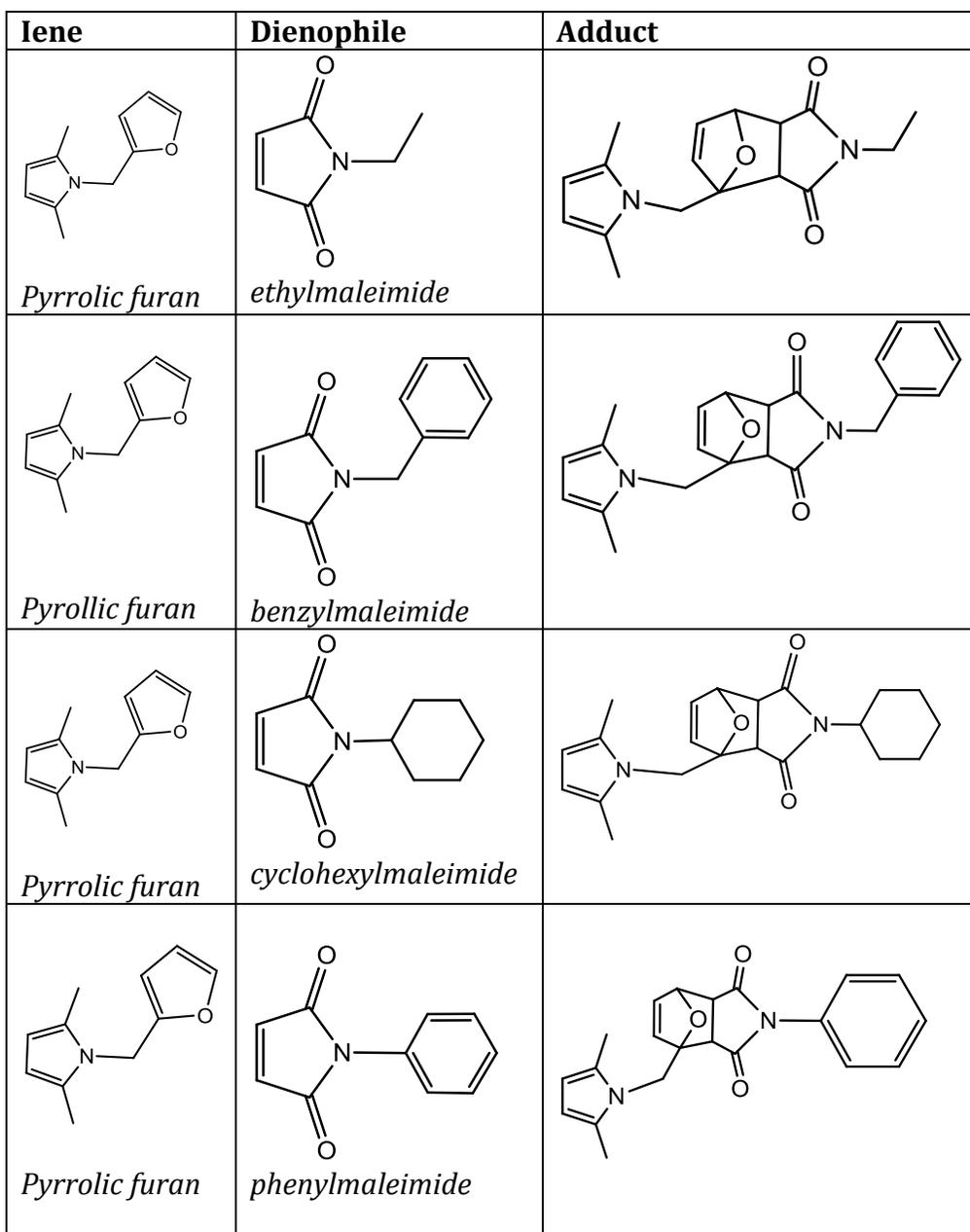
In Figure 3.2 the NMR spectrum and the simulated NMR spectrum is pictured. The black lines are from the simulated spectrum ( $^1\text{H-NMR}$  shifts from ChemBioDraw) and the red line from the product ( $^1\text{H-NMR}$  shifts from Varian Mercury Plus 400Mhz). As can be seen the made product is very pure because almost all other peaks are disappeared. The structure of pyrrolic furan is also added in order to characterize all peaks. Because pyrrolic furan is one of the main component of all reactions a large batch is also made (approximately 40 ml).

NMR-peaks can be present in different ways (singlet, triplet, quartet etc.). The character of the peak depends on the hydrocarbons lying next to him:



### 3.3.2 Model Diels-Alder reaction

The cross-linking of pyrrolic furan and different maleimides via the Diels-Alder reaction was studied as a function of initial molar ratio between maleimide and furan groups achieved by Zhang *et al.* In order to investigate different attachments on the maleimide group concerning the  $T_{DA}$  and  $T_{rDA}$ , different molecules are used.

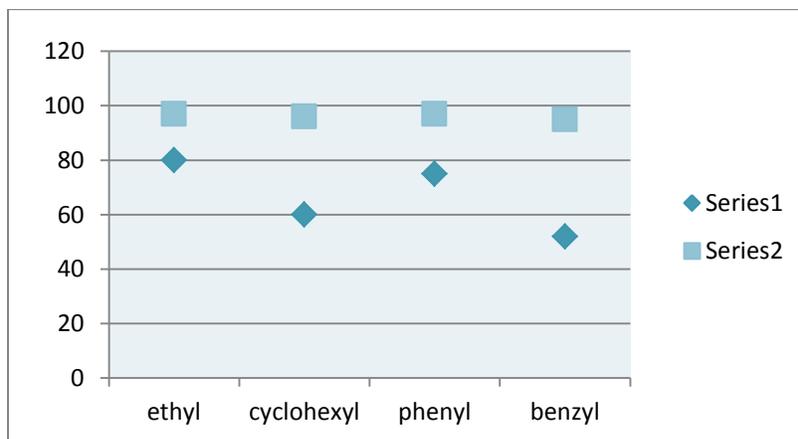


**Figure 3.3:** Scheme of model furan + maleimides and DA-adducts

In this phase of the investigation only the model reaction is performed. Discussed are the differences and get more insight into this matter. First different model adducts with DA functionality are selected. These are selected on functionality, expected  $T_{DA}/T_{rDA}$  and commercial availability. Finally the next maleimides are selected: ethylmaleimide, benzylmaleimide, cyclohexylmaleimide and phenyl-maleimide (see Figure 3.3).

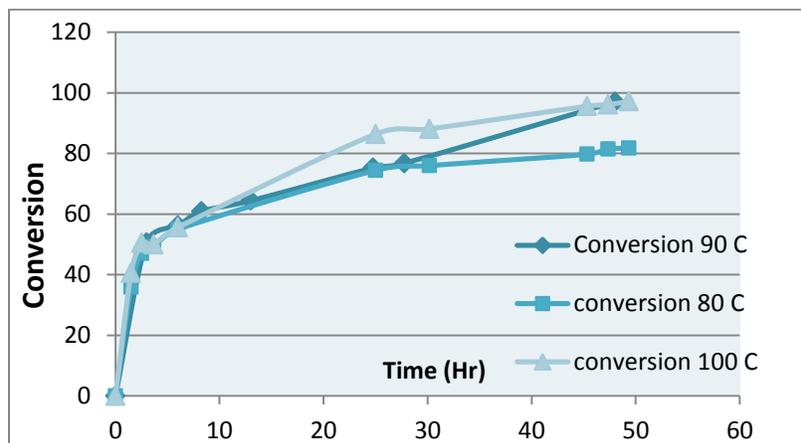
The following procedure describes a typical procedure of modification via DA reaction of the pendant furan rings with monofunctional maleimides: stoichiometric amounts of furan and maleimide were dissolved in acetonitrile. The solution was heated at 80°C from 24 to 48 hours and the ensuing products purified by chromatography on a silica gel column using ethyl-acetate/ *n*-pentane as eluent.

The first step was to investigate the conversions and mono-functionalities of the maleimides. Therefore the reactions were performed in NMR-tubes. These NMR-tubes were heated in the oven for several hours while NMR-spectra were recorded. In this way a trend for the conversion can be plotted. As a solvent DMSO was used because of the high boiling point. This is shown in Figure 3.4.



**Figure 3.4:** Conversions maleimides. Dot: 24hr, square: 48hr.

In Figure 3.4 the conversions of the different model functionalities show no difficulty to reach near 100%. Although ethyl-maleimide will reach 80 % already after 24hours. This reaction will occur more easily than the others.

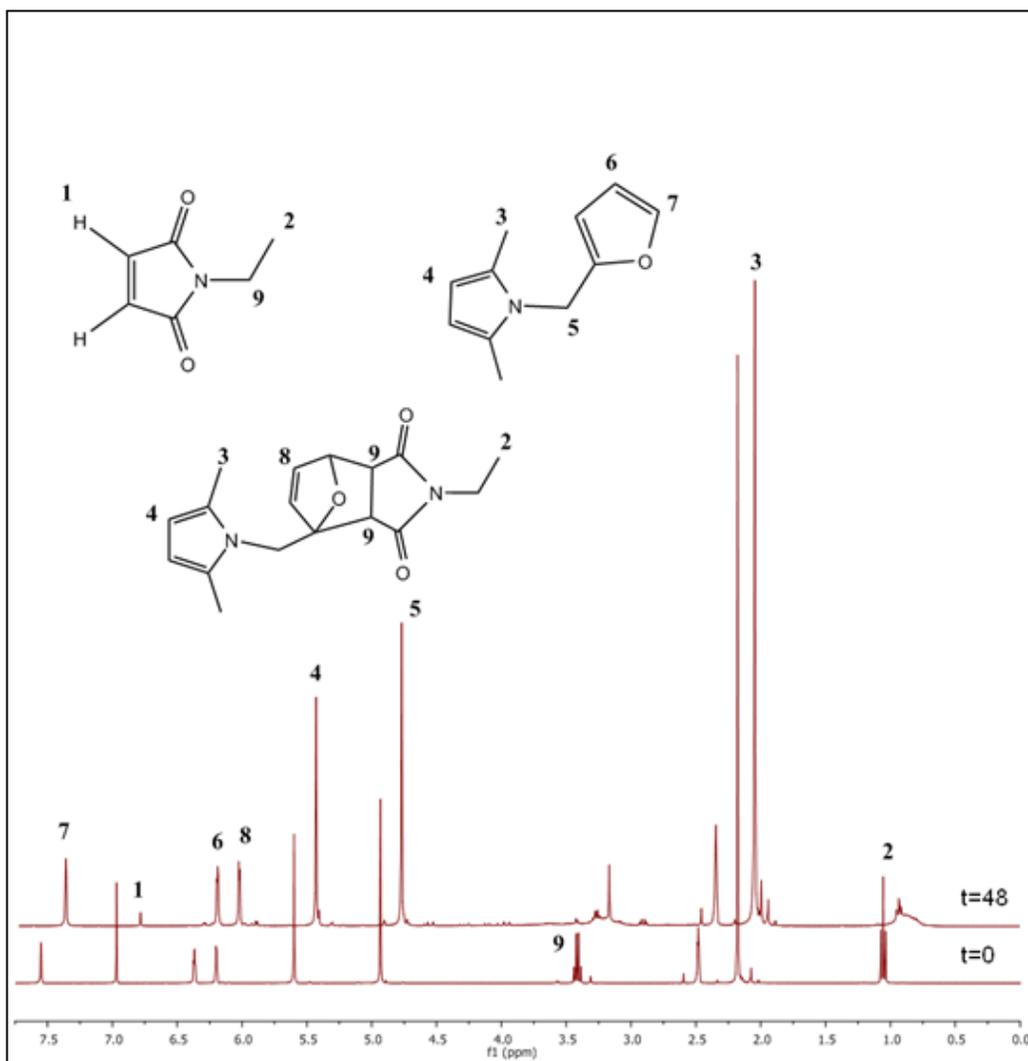


**Figure 3.5:** Conversion ethyl maleimide – pyrrolic furan

In Figure 3.6 an overview of the NMR-spectrum is given from the simulation of ethyl-maleimide and pyrrolic furan and its product. The other red lines are the H-NMR-spectra performed from the samples at time 0 and after 48 hours. When one would measure its conversion more options are possible.

The initial-compounds are in stoichiometric amounts thus the conversion can be measured by integral calculation. The conversion was based on the integral under the peak at 7.0 (peak 1) because this peak is not present in the product. The decrease of the peak indicates a reaction is taking place. In the simulation an overview of the characterization of the peaks is given. The area under the NMR resonance is proportional to the number of hydrogens which that resonance represents. In this way, by measuring or integrating the different NMR resonances, information regarding the relative numbers of chemically distinct hydrogens can be found. Also a conversion can be measured by comparing peaks before and after the reaction. Because not all hydrogens have a different place in the molecule after the reaction. Only there where the reaction take place or a shift in H-NMR-resonance is illustrated.

Another option is the triplet under PPM: 1.22. This ethyl peak is present in the ethyl-maleimide but also in the adduct. If those two peaks are visible in the H-NMR-spectrum, then a conversion can easily be determined by integral calculation using Mestrenova. Unfortunately this method was not applicable due to the unclear peaks after 48 hours. At this moment the conversions are maybe not 100% certain, but nevertheless the choice is made to continue this approach and start with making a larger batch of the reaction ethyl-maleimide and pyrrolic furan. The peaks around 3.5 and 5 are not visible in the H-NMR-spectra. These peaks will be discussed in the next paragraph. The peak at 2.5 PPM is a remainder of a solvent DMSO.



**Figure 3.6:** H-NMR-spectra at 90°C of reaction ethyl-maleimide and pyrrolic furan performed in NMR-tubes.

### 3.3.3 Batch reaction ethyl-maleimide + pyrrolic furan

The batch reaction is performed in a round-bottom flask equipped with a magnetic stirrer. This reaction was performed at various temperatures and with different solvents. Theoretically, the usage of other solvents will only change the boiling temperature and thus the reaction temperature. Nevertheless during these experiments not all reactions went well. The experiments with toluene and DMF gave wrong H-NMR results. The peaks on

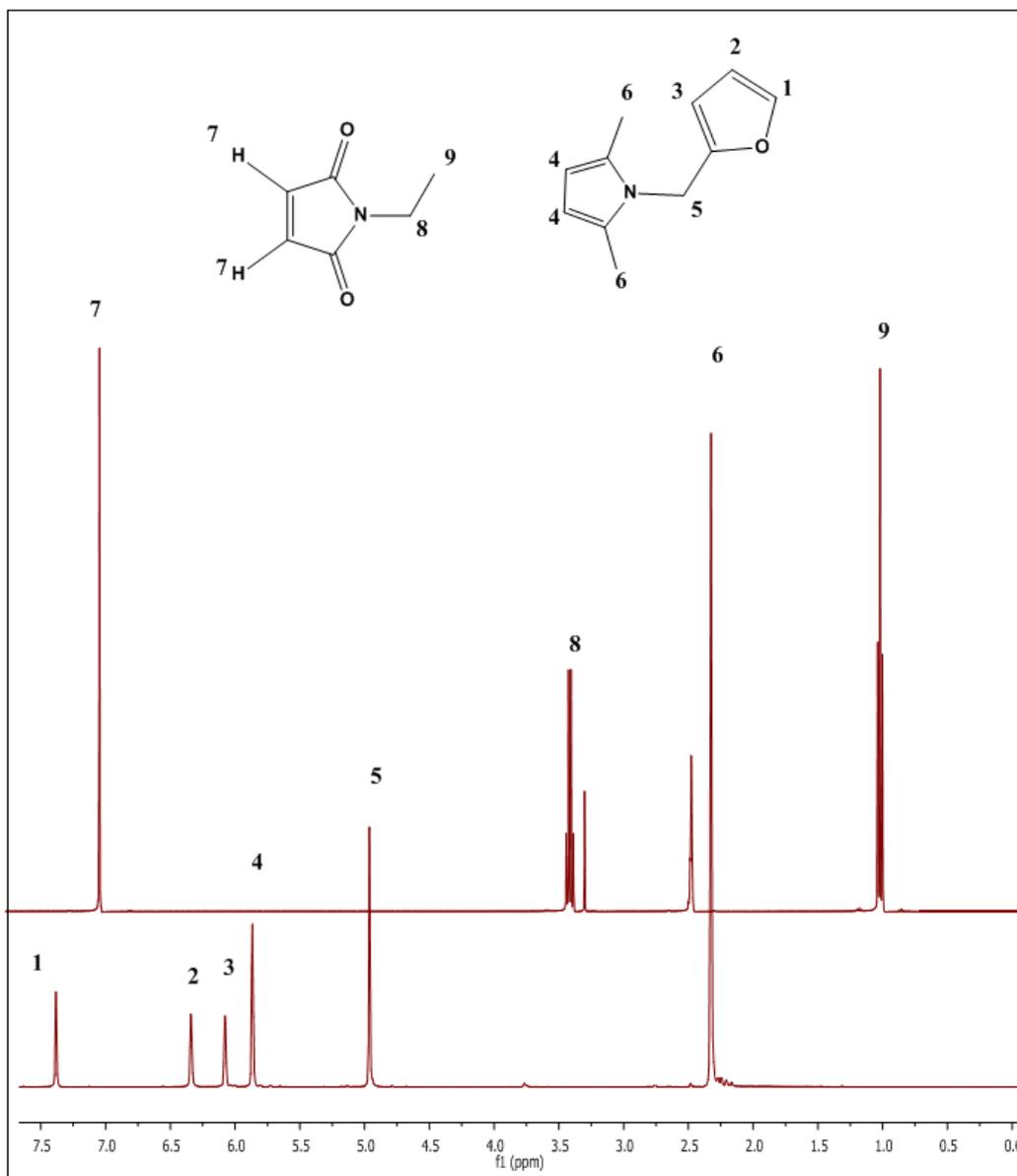
the spectra were unrecognizable, even after several tests and at different temperatures and reaction time. Contamination is probably not the problem because the H-NMR spectra looked clean. The reason why is not further investigated because other solvents also can be used and is not part of this research. H-NMR spectroscopy was also used to study all components and solvents are separately. In this way the H-NMR spectra can be interpreted reliable because sometimes the NMR-simulation give small shifts of the peaks. The other batch experiments were performed with acetonitrile.

Acetonitrile has a boiling point of 82°C. And according to the previous experiments this temperatures must be sufficient for high conversions. Furthermore it is important to remove the solvent completely under vacuum after the reaction, thus solvents with high boiling points are undesirable.

In Figure 3.9 the H-NMR spectrum and the NMR simulation of the batch reaction is shown. The conversion of this reaction is around the 40%. This is lower than expected but can be attributed by the reaction temperature. Because acetonitrile has an boiling point of 82°C, the reaction temperature is around the 75°C. Longer reaction time has no further influence on the conversion since the maximum was reached after less than 24 hours. The total r.t. was 48 hours and the conversion was not further increased.

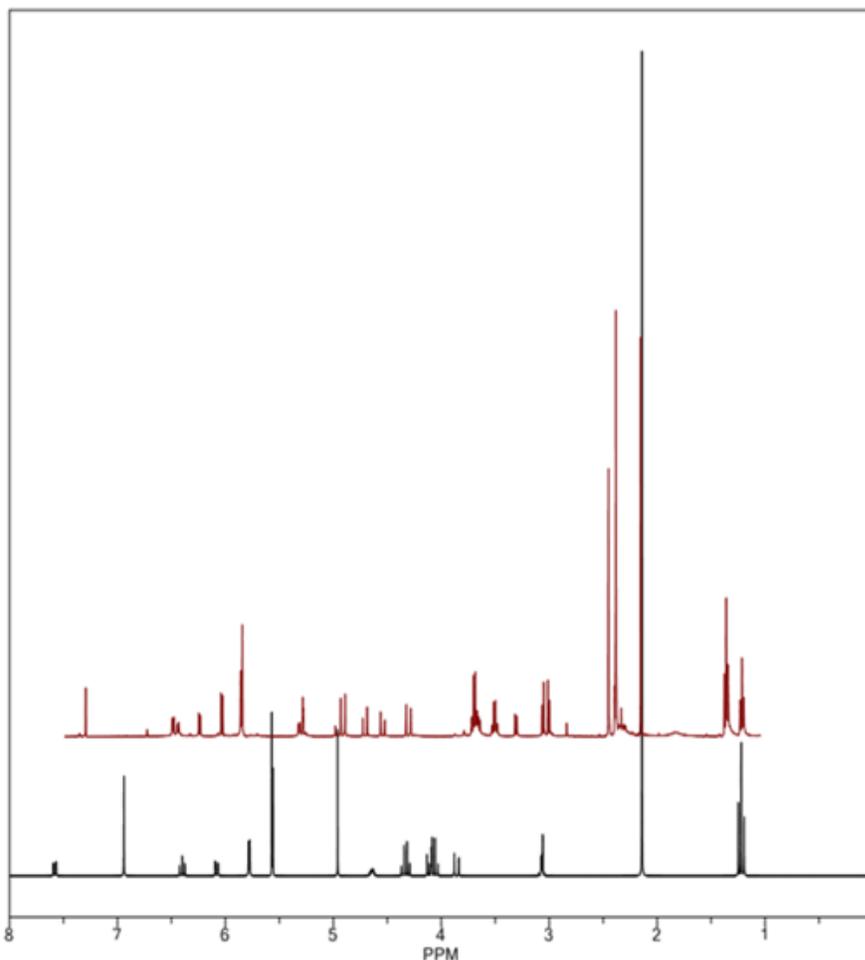
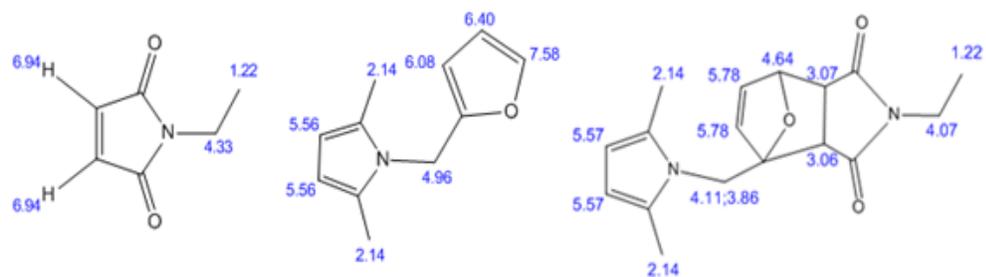
From theoretical models the endo form will yield at relatively low temperatures and short reaction time because this is the more stable form. The exo form will be more present after long reaction time at elevated temperatures. After the batch reaction both endo- and exo forms will be present. All the peaks from ethyl maleimide and pyrrolic furan are recognizable, but the product has some unrecognizable peaks. These peaks are probably the endo and exo form which can arise from the reaction. Because of that an NMR-spectra comparison is made of the batch and the simulation (Figure 3.10). This picture makes clear that all ethyl- maleimide is gone because of the absence of the peak at 6.94 PPMN. This means that the ratio endo/ exo can be calculated from the two triplets around 1.0 PPM.

Unfortunately Chembiodraw cannot simulate both endo- and exo adducts. Also the peaks between 3 and 5 PPM of the H-NMR spectroscopy and the simulation do not correspond. The next experiment will be the separation of all components. With column-chromatography it is possible to separate all the fragments when the right eluent is used. After the separation a new H-NMR spectroscopy of all fragments can be applied. In this way the difference between the spectra of the endo and exo adducts will be made clear. This will be discussed in the next paragraph.



**Figure 3.9:** H-NMR results batch acetonitrile with from top to bottom: Product, ethyl maleimide and pyrrolic furan.

The peak at 2.5 PPM is solvent dmsd, the peak at 3.4 PPM is a HOD peak. NMR spectra of “neat” deuterated solvent always exhibit a peak due to H<sub>2</sub>O in addition to the residual solvent peak. When the exchange rate between H<sub>2</sub>O and HDO is slow on the NMR timescale the water peak appears as two peaks, a singlet corresponding to H<sub>2</sub>O and a 1:1:1 triplet corresponding to HDO.



**Figure 3.10:** H-NMR results batch acetonitrile (red) compared with NMR-simulation (black)

In Figure 3.10 the red line represents the product and the black line the simulation of the product and the reactants. The two triplet peaks around 1 PPM indicates there are two forms of the product present. It cannot be  $\text{CH}_3$  of ethyl-maleimide because that reactant is not present anymore due to the reaction with pyrrolic furan. If this can be separated the differences between endo and exo can be interpreted. This is discussed in the next paragraph.

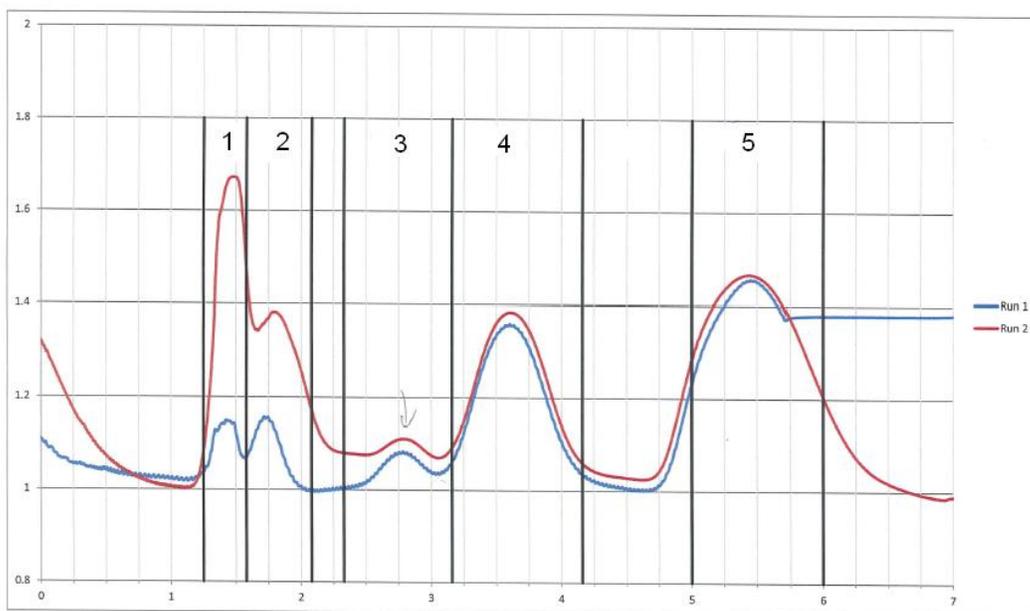
### 3.3.4 Separation components

Stereochemical effects are well documented for the DA and the rDA reactions in molecular and synthetic organic chemistry studies [57]. The distinction between endo/exo stereoisomers has not been made very often. Also their physical separation and thermal behavior is quite unknown. In literature endo/exo stereoisomers were recognized on H-NMR spectra but not physically separated. This can be a great attribution to science because it will explain the thermal behavior of the DA and the rDA adduct. Also a partial thermal reversibility at lower temperatures can be beneficial for reducing internal stresses of cross-link thermosets during Diels-Alder reactions. In this way the influences of the properties of the endo/exo stereoisomers of furan-maleimide DA-adducts on the thermal reversibility of model compounds can be investigated. Also can be established whether stereochemical effects can help explain the temperature differences between model reactions and polymer networks.

When good separation is desired first the right eluent should be obtained. After the batch reaction a small sample was taken from the product. This was dried over vacuum to evaporate all the solvent. To determine the right eluent, the product was solved in methanol (0.1M) and a dot is placed on a silica gel coated aluminium sheet for TLC procedure. Different solvents and different solvent combinations are used. Finally the eluent ethyl acetate/ n-pentane (ratio 1:3) was the best combination. If the substances being separated are colored, the spots can be seen without any further effort. However many substances are colorless and do not show up on the white silica gel unless steps are taken to make them visible. During these experiments iodination was used. The dry plate is placed in a chamber containing a few crystals of iodine. The iodine vapor in the chamber oxidizes the substances in the various spots, making them visible to the eye. After iodination all the 4 dots were visualized (ethyl-maleimide, pyrrolic furan and endo/exo adduct). When the separation is not working use other ratio eluent, other eluent or a different kind TLC-plate. There are also TLC-plates coated with aluminum-oxide, cellulose (fibrous, microcrystalline) and polyamide 6.

From this result can be concluded that the endo and exo must be present in the batch product. Now the fractions must be separated via a column chromatography. A column was packed with silica gel and a small sample of the product (5ml 0.1 M) was dropped at the top of the column. Subsequently, when the solution was sank down, the eluent was added gently. This procedure was performed over and over again but when the samples must be collected by hand, the change of error is simply too high. One must conclude that the fractions of the endo and exo adduct are very close to each other in the column and too small. Finally another possibility was tried thanks to Henk vd Bovenkamp. His so called "robot" has an packed column with an HPLC at the end. The sample was injected at the top where a pump is

responsible for the flow rate of the eluent. Subsequently a HPLC detect the fractions and will plot them against time. If this procedure can be repeated under the same conditions a time scheduled program can be installed in the “robot”. The different fractions will be automatically collected by the “robot” and will be collected in different Erlenmeyer flasks. This makes separation less difficult and more accurate, particularly when the fractions take more than 6 hours to flow through the column. That all conditions are exactly the same is of great importance. The packed material must be clean and the HPLC calibrated. The total system must be repeated several times until the HPLC-plots are totally repeatable. The HPLC-plot against time is shown in Figure 3.10. In this plot the peaks are at the same time schedule. Now one can assume the third line will be identical and the system can be used.



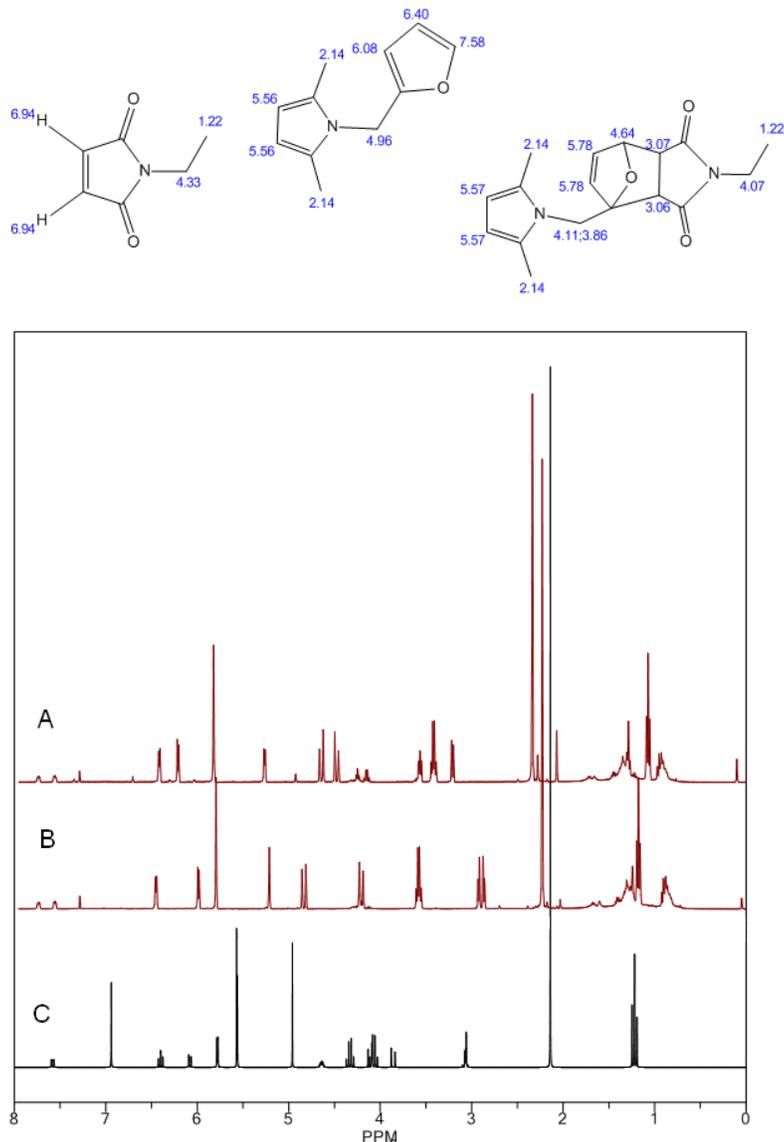
**Figure 3.11:** HPLC-plot after packed column

As can be seen in Figure 3.10 the system is reproducible and thus the peaks can be selected separately. At the horizontal axis the time is plotted and the numbered peak can be selected automatically. The results are presented and discussed in the next paragraph.

### 3.3.5 Results separation components

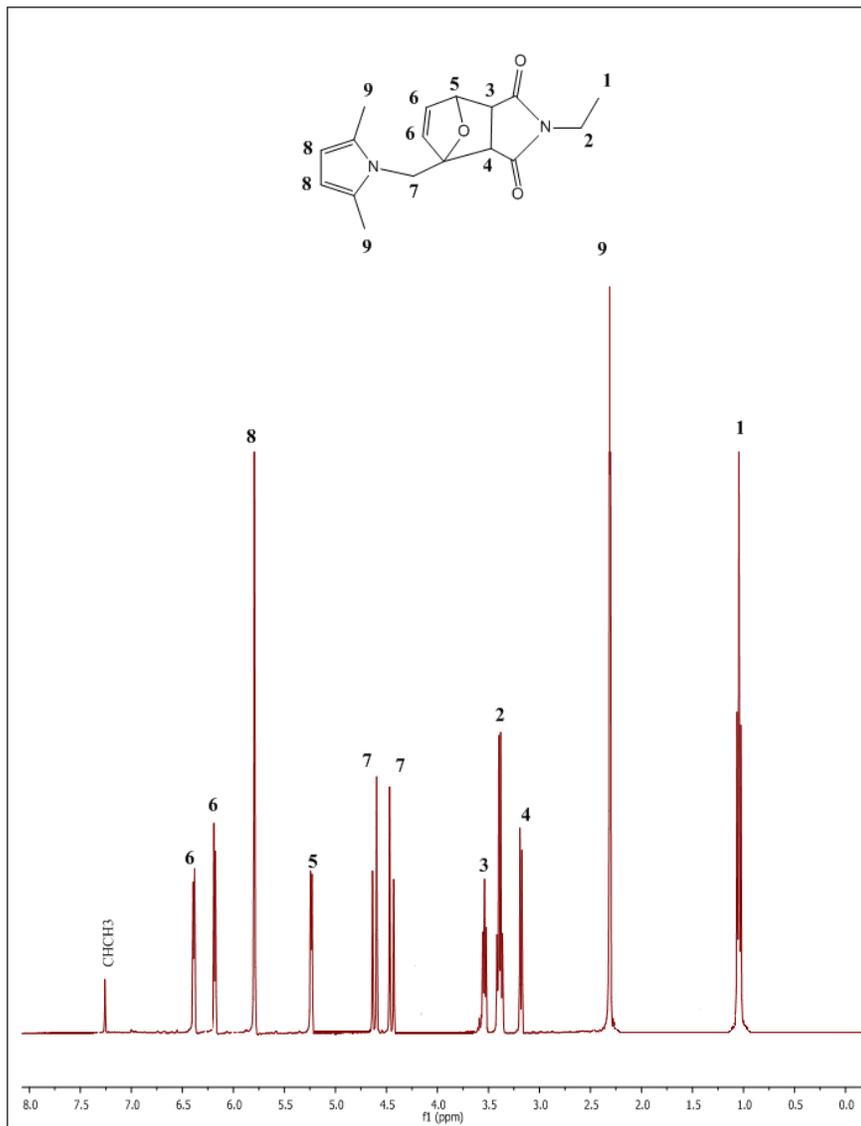
After the separation the eluent of the samples was removed under vacuum. H-NMR spectroscopy was used to study the components. The samples taken in area 1, 2 and 3 gave not a clear H-NMR spectrum. The peaks were not

recognizable as one of the substrates (ethyl-maleimide/pyrrolic furam) or the endo, exo adduct. Nevertheless samples 4 and 5 do show great similarity of the product produced in the batch. Also with each other, but some peaks are shifted. In figure 3.11 both H-NMR spectra are showed.



**Figure 3.12:** endo and exo after separation

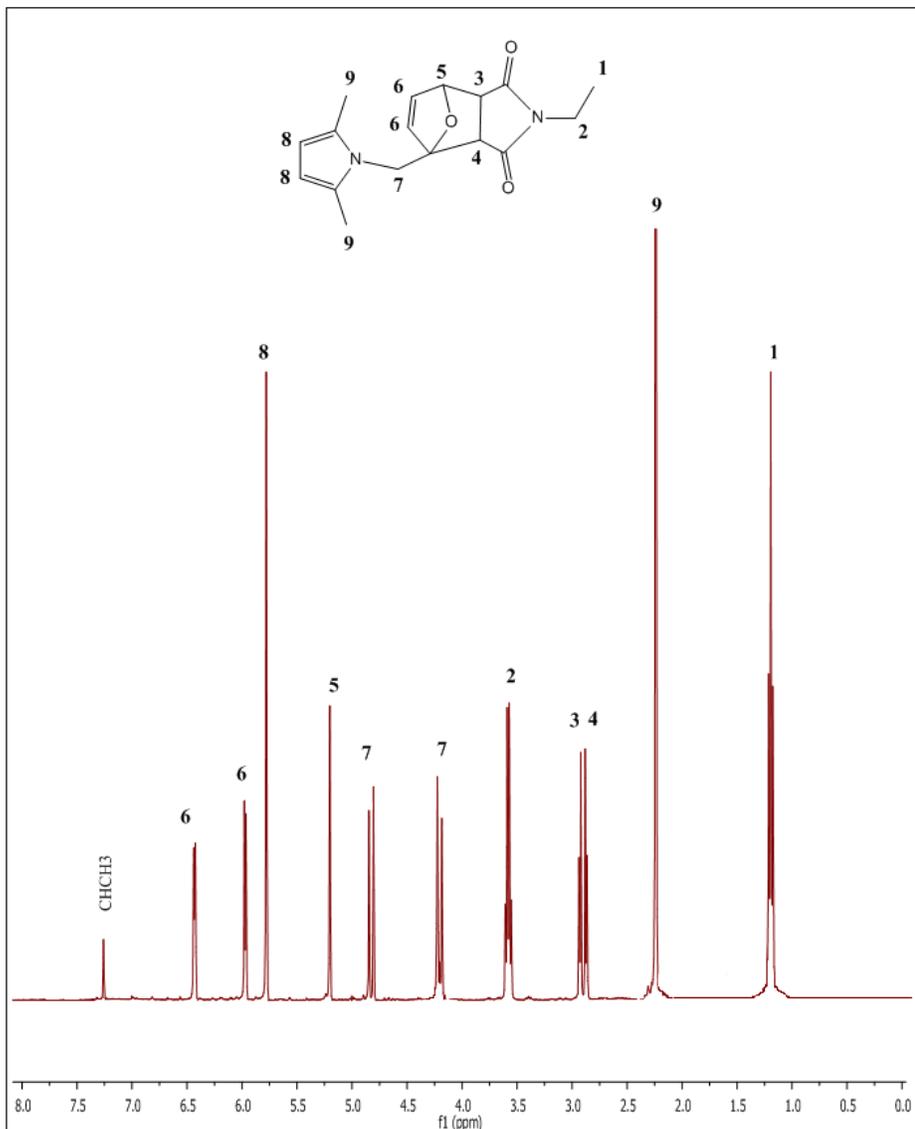
The results of the separation can be found in the Figure above. The lines A and B represent the fractions 3.11, 4 and 3.11, 5. Line C is the simulated line from the reactants and product which are shown above the graph. The next two pictures (Figure 3.13 and 3.14) will illustrate the endo and exo form separately. Here the peaks are interpret and numbered.



**Figure 3.13:** Sample 3.11,4 endo or exo form?

After long consultation is concluded that the spectra above must be the exo form of the adduct. The first proof will be given by counting the protons of all peaks. There must be 20 protons in total. There are peaks with 1, 2, 3, and 6 protons. In order to compare this with the spectrum above an integration of all peaks has been performed. A peak with 2 protons must be twice as large than a peak with one proton. When all peaks are accurately determined the total amount of protons is indeed 20. This gives prove to the theorem that this on of the endo or exo form of the adduct.

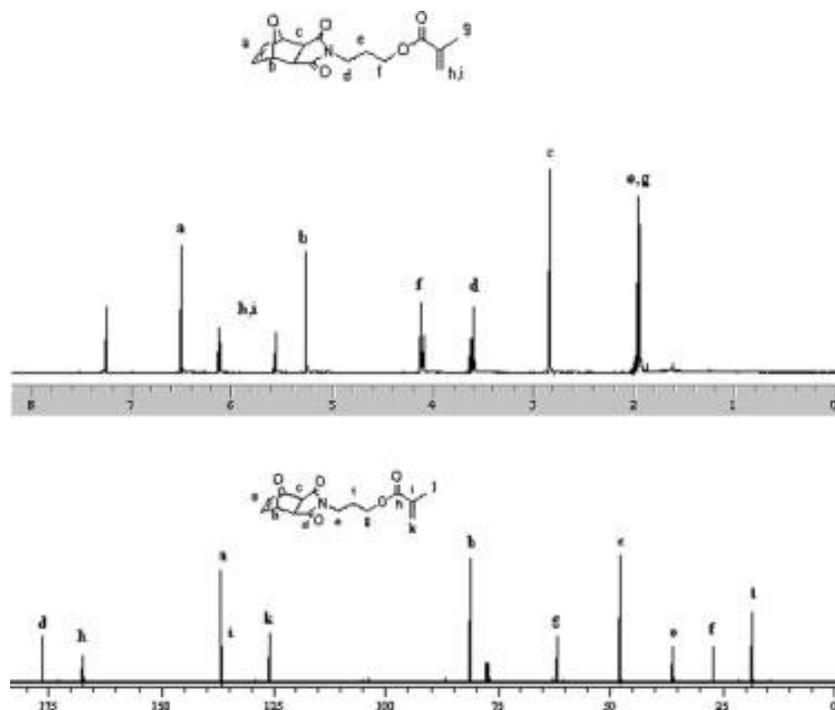
Now will be determined whether this NMR-spectrum is endo or exo form of the adduct. When we take a look at peak nr 5, we concluded that this peak is coupled. This makes sense because with an exo form this proton lies next to 3 and 4 because these are facing upwards in contrast to the endo form were they are facing downwards. Therefore the NMR-spectrum indicates an exo form of this adduct.



**Figure 3.14:** endo form adduct

The sample of Figure 3.14 is the endo form of the adduct. Now the ratio of endo and exo can be calculated after integration. Endo/ exo ratio is 60:40.

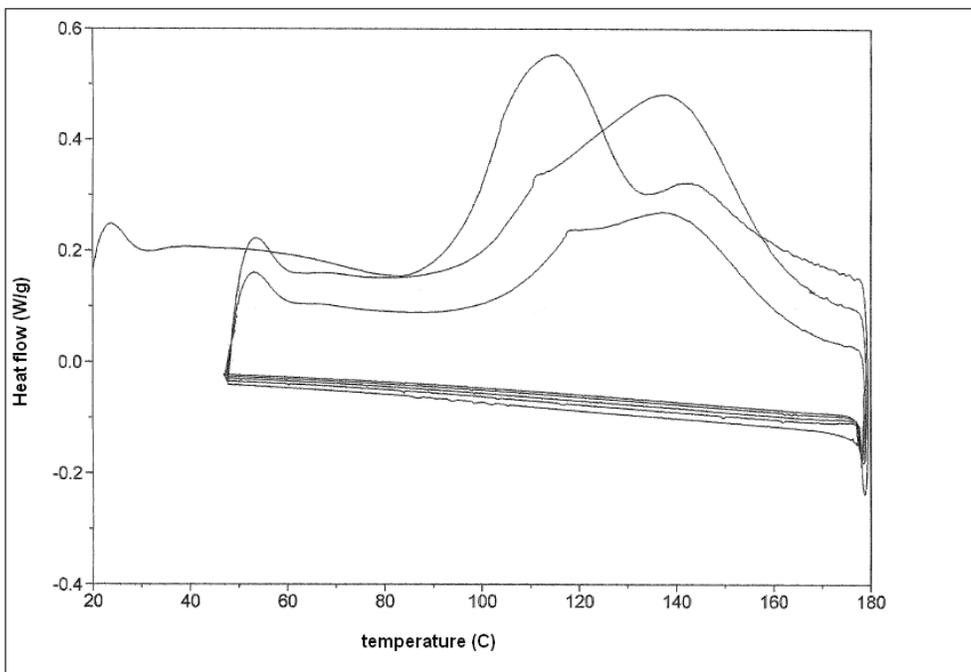
Pearson *et al* [58] describes cycloaddition reaction between furan and maleimide with also two possible diastereoisomers. These two adduct has great resemblance of the endo and exo adduct described in this thesis. They have accomplished to separate them as well. It would be very nice to compare these two H-NMR spectroscopy. Also T. Dispinar *et al* [59] describes in "A Diels-Alder/retro Diels-Alder strategy to synthesize polymers bearing maleimide side chains" a monomer which can be compared with the product mentioned above.



**Figure 3.15:** H-NMR spectroscopy Dispinar *et al*

In this picture the peaks A,B and C can be compared with the monomer described in Figure 3.13 and 3.14. In that Figure the peaks are 6, 5 and 3. Peak nr 3 is in endo form exactly the same, in exo form it shifts a little to the right. The assumption here can be made that the monomer in Figure 3.15 would be an endo form.

In order to create another proof for the statement above a DSC measurements over the components is performed. In this way the endo and exo can be observed according to the melting point. The endo adduct will have an lower melt point than the exo adduct. Also according to the endo and exo hyperchem calculations presented in figure 3.14, the exo product is more exothermic because of its free energy. In figure 3.13 DSC measurements are given from fraction 3.11, 5



**Figure 3.13:** DSC measurements endo adduct

As can be seen is the first cycle has an peak around 115°C. In the next cycles this peak will move towards 140°C. The DSC measurements are set to cool really slow. Thus the total cycle will be warm for a long time. What can be seen in the graph is the endo adduct transforms into a exo adduct. Because after long reaction time and at higher temperatures the endo will form into an exo adduct. Also the exo adduct is more exothermic. This will explain the decrease of the height of the line. Because of the exothermic behavior of the product, the system doesn't have to add more heat. As a result an increase of the lines in every cycle is presented. If more cycles were measured the lines were probably increased even further because of the formation of more exo adduct. As a result of this conclusion the other peak, 3.11, 4, must be the exo adduct. The associated H-NMR structures are now also identified. In figure 3.12 the red line above is exo adduct and the red line underneath is endo adduct.

### 3.3.6 Results Hyperchem calculations

Finally, some assumptions were made during the reactions. In this thesis the diene is pyrrolic furan and the dienophile is ethyl maleimide. This was already confirmed by several literature but, what is also discussed in chapter 2, can be proved by calculation. In order to do so the calculations were performed in hydrochem. First the reactants and product are drawn and the calculation can begin. According to literature <sup>[60]</sup> the energy gap must be calculated with the ab initio method. The energy calculation are presented in table 3.1

	<i>pf</i>	<i>em</i>	
LUMO	7,569285	4,913963	eV
HOMO	-5,98211	-7,853	eV
dE	homo pf - lumo em		10,89607 eV
dE	homo em - lumo pf		15,42228 eV

**Table 3.1:** HOMO/LUMO calculations pf and em

According to these calculations the pyrrolic furan is the HOMO and the ethyl maleimide is the LUMO because it has the lowest energy cap. This outcome is in line with the literature used for this thesis. In the next table the same calculations are made in order to find which adduct has the highest melting point. These calculations are also performed with ab initio method and with an RMS gradient of 0.00001 and unlimited cycles.

	<i>endo</i>	<i>exo</i>	
LUMO	7,13468	7,106537	eV
HOMO	-5,94778	-6,091701	eV
dEadduct	HOMO endo – LUMO endo		13,08246 eV
dEadduct	HOMO exo - LUMO exo		13,19824 eV

**Table 3.2:** HOMO/LUMO calculations endo and exo

As can be seen in the calculations the exo product has an higher energy gap than the endo product. This means it costs more energy to break it down. The exo product has an higher melting point.

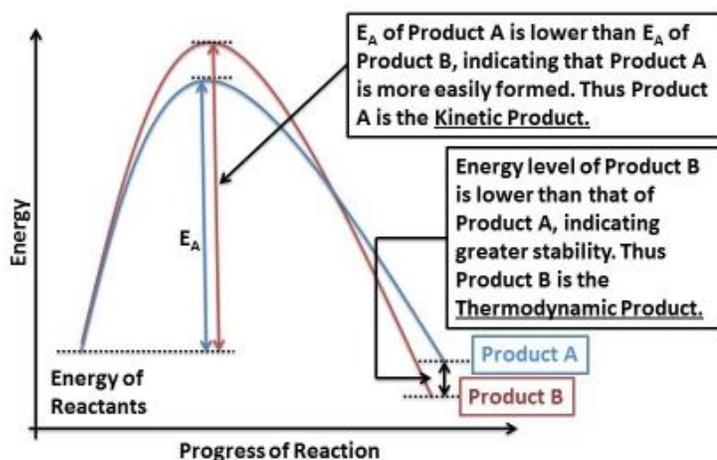
In Table 3.3 calculations are made of the free energy. In this way the thermodynamics can be measured. The calculations must can be performed with hypercam and with the semi empirical pm3 method. According to this calculations the exo adduct is more exotherm than the endo adduct. This is also what is mentioned in literature.

free energy	<i>pf</i>	<i>em</i>	<i>endo</i>	<i>exo</i>
	-45164,2	-36161,5	-81337,8	-81338,5
$dH_{\text{reaction}}$			-12,1	-12,8
$dH_{\text{dissociation}}$			12,1	12,8

**Table 3.3:** Calculation of free energy

Finally A Figure is given which explains the thermal behavior of endo/exo adducts. The energy of activation for product a is lower than product B. this means that the amount of energy required is lower. Also A will form faster and thus is product A the kinetically favored product.

Product B has an higher activation of energy and costs more energy to make. Also it will form slower but once the product is formed the overall energy of the molecule is lower than product A. this means more stability and more thermodynamically favored. When a reaction will take place for longer time at elevated temperatures, more thermodynamically favored product, exo, will be formed because this is the more stable one. The equilibrium moves to exo side of the reaction. And since the exo product is also more exothermic the reaction generates more and more heat.



**Figure 3.14:** Energy behavior endo/exo

A brief summary of kinetic and thermodynamic products [61] [62]:

To Get Kinetic Product:

A kinetic product is favored under non-equilibrium conditions.

- Shortening the reaction time – this will ensure that there is not enough time for a reversible reaction to occur to lead to the formation of more stable thermodynamic product.
- Use of strong base (or strong reagents) – This will ensure that the process is not reversible at the intermediate step.
- Try doing the reaction at lower temperatures – that way you do not provide more energy to cross the EA of the thermodynamic product. But keep in mind, that lowering the temperature may also allow equilibrium conditions to make the reaction reversible and hence allowing formation of thermodynamic conditions.
- Use of hindered base - This point refers to the above example of 2-methylcyclohexanone – where abstraction of less hindered proton would result in formation of kinetic product. If therefore, we use a hindered or bulky base, the more hindered proton would not be readily taken up by the base, thus pushing the kinetic control into the reaction.

To Get Thermodynamic Product:

In order to get thermodynamic control, you need conditions of reversibility at some stage of the mechanism. If that exists then you can try the following:

- Lengthening the reaction time – longer reaction times will ensure that the equilibrium favors formation of more stable product
- Use of milder base (or milder reagents) – This will ensure a greater equilibrium stage allowing reactions to occur in a reversible manner in the mechanism.
- Use of higher temperatures

### 3.4 Conclusions

All assumptions made during these experiments are concluded in the last paragraphs. At first the diene and dienophile were right according to the hyperchem calculations. Also the assumption what is the endo and what is the exo adduct was also right interpreted. This was proven by the DSC.

Finally after many attempts the separation of the endo and exo adduct is performed successfully. Because the fractions are so small and probably so next each other in the column, chromatography by hand was not a success. Fortunately Henk van de Bovenkamp constructed a very handy "robot" which will do the job for you. Now when it is possible to separate the fractions the H-NMR spectroscopy are known and new interpretations about these matters can be done more easily. The demonstration of the computer tool Hyperchem can be used in the further future with Diels-Alder reactions and endo/exo determinations, to check which component is the diene and which is the dienophile. Also an estimation of the Diels-Alder temperature and the retro-Diels-Alder temperature can be made.

Finally the mechanical properties stated in literature of the endo and exo adduct are proven. But also with the components ethylmaleimide and pyrrollic furan all the data is within reach.

Pearson *et al* [58] describes cycloaddition reaction between furan and maleimide with also two possible diastereoisomers. These two adduct has great resemblance of the endo and exo adduct described in this thesis. They have accomplished to separate them as well. It would be very nice to compare these two H-NMR spectroscopy. An email was written to professor Douglas Phil but unfortunately he didn't send the files yet. Maybe this will be of great interest for my successor master student. Fortunately another article, written by Tugba Dispinar *et al*, was found. This article showed some H-NMR spectra of a monomer with great resemblance as the one mentioned in this thesis.

So after all this information from literature, the interpretations of all the peaks of the made adduct, endo and exo, and the DSC results of the endo form can with reasonable certainty be concluded the product is correctly separated. This gives also new understanding towards the peak interpretations of H-NMR spectra concerning endo and exo forms.

In the future more research can be done about this topic and investigate more components and try a higher conversion of the endo/exo. This will make the separation way more easy. Also research towards new components with higher DA- and rDA temperatures can be established.

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