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# Exploration of diene-dienophile pairs for Diels-Alder- based thermoreversible crosslinked polymers

## **BSc Thesis**

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This BSc thesis has been carried out during the COVID-19 global pandemic (spring-summer 2020). In order to comply with all the learning goals specified for the BSc final project in Chemical Engineering at the University of Groningen, (some of) the results presented in this thesis were not experimentally obtained but provided by the main supervisor based on previous unpublished data and personal experience, or obtained from published literature. The source of data has also been specified explicitly or referenced wherever they appear in this text.

## Abstract

Depletion of natural resources has influenced the rise in demand of synthetic polymers. However, the use of these polymers, especially those that are difficult to recycle, is resulting in extensive pollution. Thermosets are such an example of widely used polymers, offering good mechanical properties, yet recycling them while maintaining these properties is near impossible. It is for this reason that the modification of thermosets is done to allow them to exhibit thermoreversibility, which is the cleavage and reconnection of crosslinks induced by heat. This allows them to be recycled or reworked, and is of great importance in the bid to make the earth more sustainable. In this thesis, the introduction of thermoreversibility to a thermosetting aliphatic polyketone through the addition of diene and dienophile pairs capable of the Diels-Alder reaction is studied. Thermoreversibly crosslinked polyketones based on the diene-dienophile pairs: furan-maleimide, cyclopentadiene-cyclopentadiene, anthracene-maleimide and fulvene-maleimide are the main focus. Their preparation is proposed to be done through addition of the diene functionality in steps, which include Paal-Knorr reaction of the polymeric backbone. Subsequently, crosslinking is carried out using the dienophile. Through literature-based rheological measurement predictions, it is found that the pairs exhibit thermoreversibility at different temperatures, with the fulvene-maleimide having the lowest range (-25°C to 65°C). The results, with the support of thermogravimetric analysis, suggest that the anthracene-maleimide-based incorporated in the polyketone decomposes instead of exhibiting reversible crosslink repair. The cyclopentadiene-cyclopentadiene pair also demonstrates the highest thermal stability (temperature ranging from 150°C - 250°C). The outcome presents a positive outlook of the role of Diels-Alder-based thermo-reversible crosslinked polymers in reworking and recycling thermosets.

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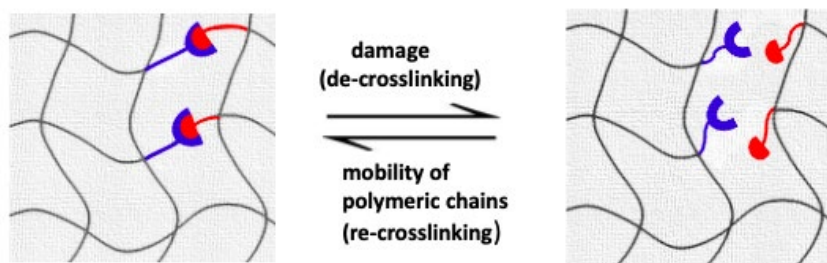
# 1 Introduction

Approximately 50 out of several thousands of synthetic polymers are being produced commercially to replace natural materials in various applications. Properties of these polymers (such as strength, thermal and solvent resistance, etc.) allow for a wide spectrum of industrial applications including fabrics, packaging, coatings, etc. Such polymers, in their usage, are advantageous in terms of costs, processability and versatility [1]. The most important classification of polymers is by their thermal behavior, which brings forth two main groups namely, thermoplastics and thermosets. Upon heating, thermoplastics become fluid and solidify by cooling, which can be performed repeatedly. On the contrary, thermosets are unable to exhibit similar behavior after the curing following their synthesis [2].

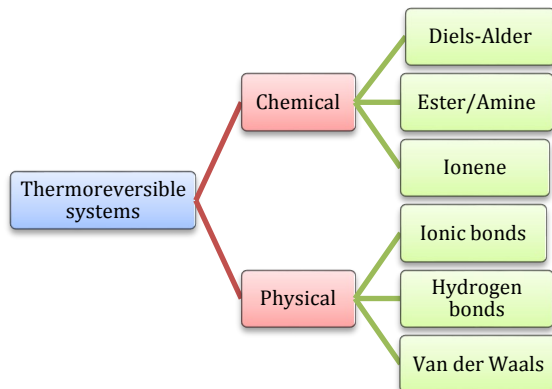
Thermosets are characterized by their network structure which arises from irreversible crosslinking after curing, granting them several desirable properties such as high mechanical strength, thermal resistance and solvent resistance [3]. However, they are prone to developing micro cracks and other forms of damage during their usage, which due to the crosslinks, is difficult to repair. The same phenomenon also renders them difficult to recycle. Reversible polymeric networks shine a new light into the reprocessing and recycling of thermosets as they enable continuous repair of joints within the polymer matrix with the application of external stimuli such as heat, pressure and light [4]. Thermoreversible crosslinking (heat-stimulated) in polymers is of particular interest due to the selectivity offered in cleaving bonds on the crosslinking points [3]. Thermoreversibility implies the capability of thermosets to become fluid upon heating, similar to thermoplastics, making their remolding and recycling possible [5].

## 1.1 Thermoreversible polymers

Thermoreversible crosslinking, as the term implies, is the process whereby crosslinks can repeatedly separate and rejoin as a result of heat stimulus, allowing the polymer to recover its original mechanical properties [3] (**Figure 1**). The phenomenon is also applied in self-healing. To achieve this, there is a need to incorporate various molecular interactions in the polymer matrix, which can be cleaved at high temperatures and reconnected upon cooling to lower temperatures [6]. The interactions are separated into two main categories namely, chemical and physical, as shown in **Figure 2**. Chemical interactions are based on covalent bonding, whereas physical is based on non-covalent interactions such as hydrogen bonding and  $\pi$ - $\pi$  staking [6].



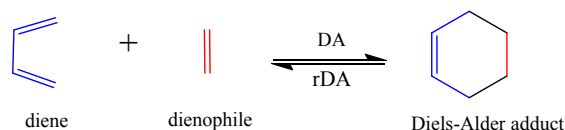
*Figure 1. Schematic representation of thermally-induced reversible crosslinking, adapted from Hermosilla [4]*



**Figure 2.** Thermoreversible systems split into different categories adapted from Toncelli et al [3]

## 1.2 The Diels-Alder reaction

In the ‘chemical’ category of thermoreversible crosslinking, one of the most studied systems is that involving Diels Alder reactions [3]. The Diels-Alder (DA) reaction, shown in **Figure 3**, was discovered to synthesize cyclic compounds in the 1920s by Otto Diels and Kurt Alder. The reaction is a [4 + 2] cycloaddition of an electron rich 1,3 conjugated compound (a  $4\pi$  electron system), known as a diene, and an electron poor compound (with a  $2\pi$  electron system), known as a dienophile. The cyclic DA adduct formed can separate back to the constituent diene and dienophile at elevated temperatures, a process known as retro DA (rDA), rendering the reaction thermally reversible [6]. The DA adduct formed is usually a mixture of two stereoisomers namely; endo and exo. The endo configuration is favoured kinetically, whereas the endo is more stable thermodynamically [7]. However, analysis into such behavior is beyond the scope of this thesis.



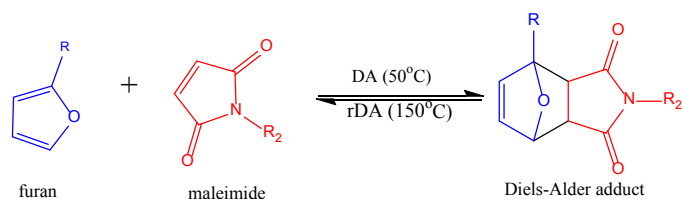
**Figure 3.** The Diels-Alder reaction, adapted from Peterson & Palmese [7]

The Diels-Alder reaction is an equilibrium reaction, meaning the reaction mixture does not exist in a state where only the DA adduct or reactants exist [6]. However, an increase in temperature shifts the equilibrium, allowing the diene and dienophile to have higher concentration, and vice versa. The equilibrium also depends on the diene and dienophile concentrations as the forward and backward reactions follow different order kinetics (DA - second order and rDA - first order) [7]. The implication of this is that an increase in diene and dienophile concentration leads to higher rDA temperatures. This fact can be utilized in manipulating the temperature ranges of application of thermoreversible crosslinking polymers. Another advantage of the Diels-Alder reactions is that they are self-contained, as the adduct produced contains all the atoms in the diene and dienophile [3]. In polymeric systems, various small compounds with diene and dienophile functionalities have been introduced in crosslinks to illustrate thermoreversibility. Four such pairings of dienes and dienophiles are explored in this thesis, both theoretically and experimentally.

### 1.2.1 Furan-maleimide

The system consisting of the furan functional group, as the diene, and the maleimide group, as the dienophile (**Figure 4**), has been the most studied DA-based system for polymers since its first recording in

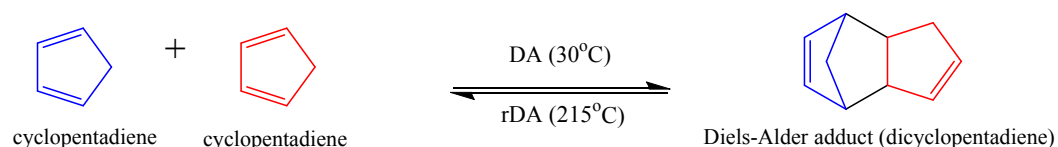
1969 [3]. Furans have electron rich  $\pi$ -bonds connected to electron-donating elements, making them good dienes. Their locked cis-conformation, which is less stable thermodynamically due to steric repulsion, is also a contributing factor for their suitability in this role. Maleimides have  $\pi$ -bonds connected to electron-withdrawing C=O groups, thus their electron deficiency makes them very reactive in DA reactions as dienophiles [8]. Maleimide groups are prone to Michael addition reactions in the presence of amines and they homopolymerise at high temperatures [9]. Therefore, precaution is necessary when involving them in reactions. The combination of furans and maleimides therefore has a low energy of reaction, with the forward reaction generally occurring around 50°C and the retro-DA around 150°C [5]. The work of Zhang et al [5] with the pair in polyketones, achieved a re-crosslinking (self-healing) efficiency of 100%.



**Figure 4.** The Diels-Alder reaction for furans and maleimides, adapted from Zhang et al [5]

### 1.2.2 Cyclopentadiene-cyclopentadiene

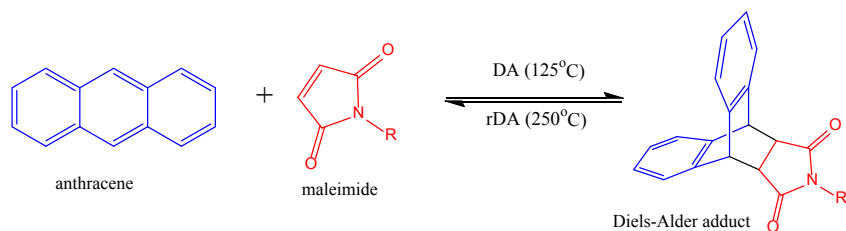
The dimerisation of cyclopentadiene (CPD) is a thermoreversible DA reaction in which CPD acts as both the diene and dienophile (**Figure 5**). The formed dicyclopentadiene (DCPD) can also undergo a DA reaction with CPD (trimer formation). The forward DA reaction occurs at temperatures ranging from 25°C to 120°C, while the backwards, rDA, occurs between 130°C and 215°C [3], [10]. These varying temperatures are influenced by the formation of trimers (and other higher aggregates). The trimer formation is also the main contributing factor to the system having higher softening (rDA) temperatures, making it more thermally stable than the furan-maleimide system [11]. CPD-based cross linkers have been used for halide-containing polymers, such as poly(vinyl chloride), as by the work of Chen et al [12]. They performed the DA reaction between room temperature and 130°C and the rDA at approximately 195°C. Toncelli et al [11] modified this work for application in polyketone systems.



**Figure 5.** The Diels-Alder reaction for cyclopentadiene, adapted from Halteren [10]

### 1.2.3 Anthracene-maleimide

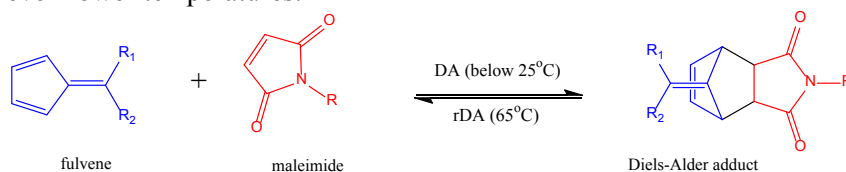
The middle ring of anthracene is electron rich due to the presence of an extensive  $\pi$ -system, making anthracene a good diene. It is able to react with various dienophiles, but interest is with its reaction with maleimides. The forward reaction (**Figure 6**) occurs around 125°C [3]. However, the rDA reaction using this system has not yet been achieved experimentally, according to the literature review done. The system exhibits slow reaction rates, as recorded by Jones et al [13]. Nevertheless, the system has been able to show repair of cleavage done by mechanical stress through the forward DA reaction at temperatures below 120°C, as indicated in the work by Yoshie et al in 2011 [14]. This implies that the system is capable of self-healing mechanical damage; however more research into the retro-Diels-Alder reaction is needed.



**Figure 6. Diels-Alder reaction for anthracene and maleimide, adapted from Halteren [10]**

### 1.2.4 Fulvene-maleimide

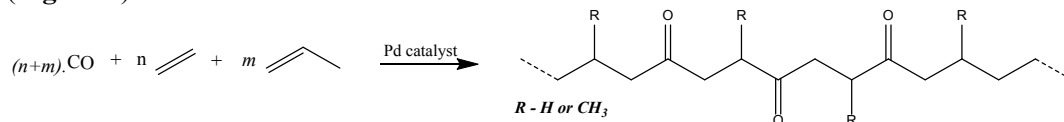
Fulvenes are a form of substituted cyclopentadienes and react with maleimides via a DA reaction, with the fulvenes as dienes and maleimides as dienophiles (**Figure 7**). Fulvenes are similar to cyclopentadiene, but are more reactive due to the presence of the additional  $\pi$ -bond, which makes them more electron rich. In a patent from 1967, Reeder [15] showed that the forward DA reaction between fulvenes and maleimides occurs at room temperature and the resulting product (DA adduct) had a softening temperature of around 60°C, which can be considered as the expected rDA temperature. There is a limited amount of literature on the system, however, work on the DA reactions between fulvene and cyanoolefins, such as that by Boul et al in 2005 [16], suggests that systems based on fulvenes may have the DA and rDA reactions occur at even lower temperatures.



**Figure 7. Diels-Alder reaction for fulvene and maleimide, adapted from Halteren [10]**

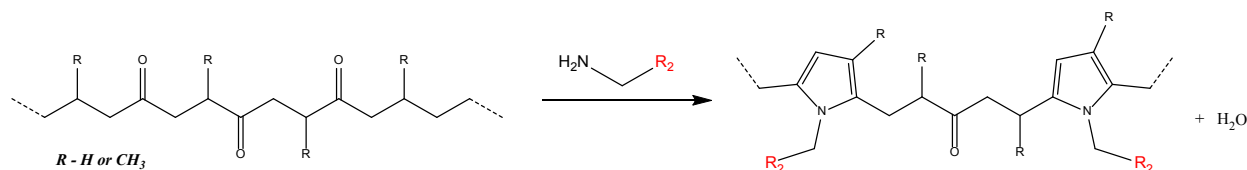
### 1.3 The alternating polyketone

The alternating aliphatic polyketone is employed for research in this thesis due to its relatively easy modification for grafting diene functionalities [5]. The alternating polyketones are produced by the polymerisation of propylene, ethylene and carbon monoxide in the presence of a palladium catalyst [4] (**Figure 8**).



**Figure 8. Synthesis of the alternating polyketone based on ethylene and propylene, adapted from Zhang et al [5]**

Using various amines, these polyketones can be modified through the Paal-Knorr reaction, a condensation reaction between a primary amine and a 1,4 dicarbonyl group [17], (**Figure 9**). This introduces a pyrrole ring to the backbone, which can be attached to different functionalities (the 'R<sub>2</sub>' group) such as furan.

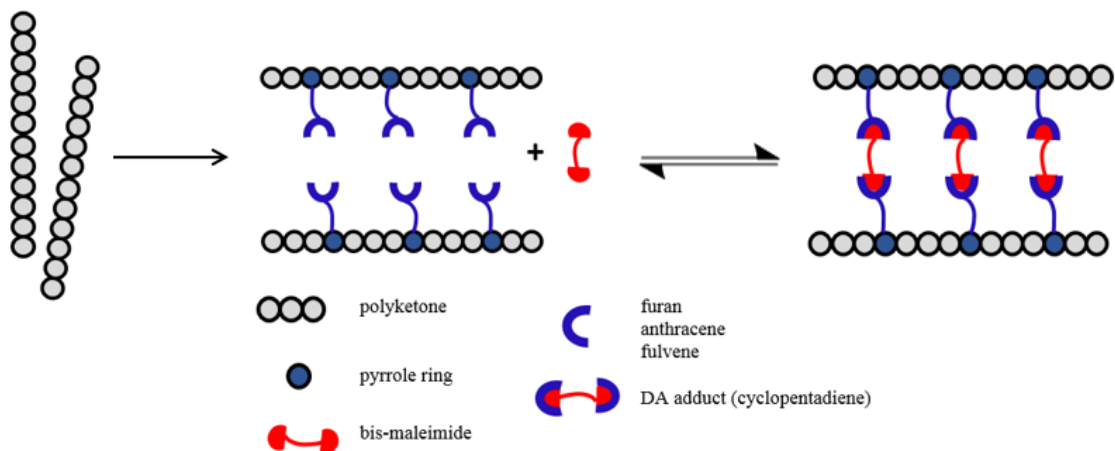


**Figure 9. Schematic representation of the Paal-Knorr reaction used to chemically modify polyketones, adapted from Zhang et al [5]**



## 1.4 Aim

The aim of this thesis is to investigate different chemistries that can facilitate thermoreversibility in thermosets. The focus is on reversibility based on the temperature-dependent Diels-Alder reaction. Using the thermosetting alternating polyketone as the polymeric backbone, four systems of compounds, diene-dienophile pairs used for crosslinking, are synthesised, as shown in **Figure 10**, and characterised in order to assess their performance in thermoreversibility.



**Figure 10.** General scheme of the reactions proposed to create DA-based thermoreversible polymeric systems, constructed from the experimental plan based on literature review

## 2 Experimental

As mentioned in the disclaimer on page 2, the experiments described in this thesis were not actually carried out. However, the following provides details on the proposed experimental procedure, as shown in **Figure 10**. For all the four systems of diene-dienophile pairs, the alternating polyketone based on 70% propylene, 30% ethylene and carbon monoxide, known as PK-30, is used. In the three systems requiring a maleimide to crosslink, the same 1,1'-(methylene-di-1,4-phenylene)bis-maleimide is used. This is in order to maintain similar reaction conditions so that comparisons are objective.

### 2.1 Furan-maleimide

The experiment was based on the work of Zhang et al [5]. The first step is using furfuryl amine, to graft the PK-30 with furan through a Paal-Knorr reaction, targeting 20% carbonyl conversion. This is followed by crosslinking using the bismaleimide. The experimental procedure is briefly described in the following:

#### *Paal-Knorr reaction with furfurylamine to graft furan onto the polyketone*

30g of PK-30 were heated to 100°C until it liquified in a sealed 250ml round bottom flask placed in an oil bath, equipped with a reflux condenser and a U-type anchor impeller. To the flask, 4.43g (0.2equiv, 0.0456mol, calculation in Appendix A) of furfurylamine were added dropwise for the first 10 minutes while stirring at a constant speed of 500rpm. Maintaining all stated conditions, the reaction was carried out for 4 hours. The presence of pyrrole was detected by brown colouring of the reaction mixture which was then cooled to room temperature. Washing was done with deionized water to remove unreacted amines. The

product was filtered and dried by freezing. NMR (solvent: chloroform) and FTIR spectroscopy were performed on the product, PK-furan.

#### DA (crosslinking) reaction between PK-furan and bis-maleimide

In a 100 mL round-bottomed flask equipped with a magnetic stirrer, 7g of PK-furan and 1,71g (4.77mmol, 0.5 equiv. [calculation in Appendix A]) of the bis-maleimide were added. 47ml of chloroform (70g, to have the polymer as 10% w/w of solvent) were used as solvent. Reaction mixture was heated and stirred at 50°C for 24h to perform the Diels-Alder reaction. The polymer gel was dried under vacuum at 50°C to obtain the crosslinked polymers. The resulting crosslinked polyketone was characterised using FTIR spectroscopy.

## 2.2 Cyclopentadiene-cyclopentadiene

The experiment was based on the work of Toncelli et al [11]. First, a chloride functional polymer (PKCl) is prepared by reacting amino-propyl chloride with the PK-30 via a Paal-Knorr reaction, targeting 20% carbonyl conversion. The PKCl can then be reacted with lithium cyclopentadienyl to replace chloride groups with cyclopentadiene. This is followed by crosslinking the cyclopentadiene-grafted polyketone by exposing it to the DA temperature. The procedure is described in the following (determination of mass in Appendix A):

#### Paal-Knorr reaction to prepare polyketones with chlorine groups (PKCl)

60g of PK-30 were added to a 250ml round-bottomed flask equipped with a reflux condenser and mechanical stirrer. 8.53g (0.0912mol, 0.2 equiv. w.r.t. the reacting unit) of 3-chloropropylamine was dissolved in 109ml methanol (to have the amine as 10% w/w of solvent) and NaOH (0.0912mol, 3.64g). The chloropropylamine solution was added to the flask dropwise, for an hour while stirring at 110°C. The reaction was done for a total of 4 hours and then the solvent was evaporated. The reaction product was ground, filtered and washed with demi-water to remove unreacted amines. The light brown product, PKCl, was placed in a freezer for 24 hours to dry. NMR (solvent: chloroform) and FTIR spectroscopy were performed on the product.

#### Addition of the cyclopentadiene functionality to the polyketone

To a 150ml round-bottomed flask equipped with a magnetic stirrer, 10g of PKCl and 1.095g (1 equiv. w.r.t chloride groups) of lithium-cyclopentadiene were added. This was followed by 112.7ml THF (100g, to have the polymer as 10% w/w of solvent) and reaction mixture was stirred. The reaction took place under an inert atmosphere (using nitrogen) at 30°C for 18 hours. Reaction mixture was precipitated in excess demi-water and centrifuged. Aqueous phase was decanted and the product dried overnight in an oven at 150°C, removing unreacted cyclopentadiene, as well as remaining water. The dark brown product was characterised using NMR (solvent: chloroform) and FTIR spectroscopy.

#### DA (crosslinking) reaction between 2 PK-cyclopentadienes

Crosslinking via DA reactions of the cyclopentadiene may already occur during chloride substitution reaction. However, to ensure it occurs, the reaction was done on a small sample. 27.3ml of DMSO was heated to 160°C and 3g of the PK-CPD was dissolved in it, in a 50ml beaker. The crosslinking was achieved by cooling down to and maintaining the solution at 30°C overnight. The product was then filtered, washed with demi-water and freeze-dried. Characterisation was done using FTIR spectroscopy.

### 2.3 Anthracene-maleimide

The first step is the preparation of PKCl as described for cyclopentadiene. Introduction of anthracene functionality to the polyketone can be based on work by Gacal et al. [18]. The PKCl can undergo Williamson ether synthesis with OH group of 9-anthracenemethanol. Crosslinking via DA reaction is done afterwards using the bis-maleimide, in a similar procedure to that carried out for the furan-maleimide system [5]. The procedure is described in the following (determination of mass in Appendix A):

#### Addition of the anthracene functionality to the polyketone

To a 250ml round bottomed flask, equipped with a magnetic stirrer and reflux condenser, placed under inert (nitrogen) atmosphere, 6.33g (1 equiv. w.r.t chloride groups) of 9-anthracenemethanol in 135mL of dry THF (120g, to have the polymer as 16.67% w/w of solvent) were added. To the flask, 1.1 equiv (1.3g of the dispersion) of sodium hydride (dispersed in mineral oil, with 60% w/w) were subsequently added. The reactants were stirred for 30 minutes at room temperature. 20g of PKCl were added to the flask and refluxed at 65°C for 12 hours. The reaction mixture was cooled to room temperature and the solvent evaporated. The product was precipitated into excess methanol and dried in a vacuum oven at 50°C for 24 hours. NMR (solvent: chloroform) and FTIR spectroscopy were performed on the product.

#### DA (crosslinking) reaction between PK-anthracene and bis-maleimide

7g of PK-anthracene and 1,9g (5.3mmol, 0.5 equiv.) of bis-maleimide were added to a 100ml round-bottomed flask equipped with a magnetic stirrer. 47ml of preheated chloroform (70g, to have the polymer as 10% w/w of solvent) was used as solvent. Reaction mixture was heated and stirred at 125°C, under inert atmosphere, for 24h to perform the Diels-Alder reaction. The product was dried under vacuum at 125°C to obtain the crosslinked polymers. A crosslinking density of 21% was expected. Characterisation done using FTIR spectroscopy.

### 2.4 Fulvene-maleimide

The first step is the preparation of PKCl as described for cyclopentadiene. The fulvene used is 3-(cyclopenta-2,4-dien-1-ylidene)butan-1-ol, whose preparation was based on work by Stone and Little [19]. The PKCl can undergo etherification with the OH group on the fulvene, as was done with the anthracene-based system. If this is successful, the product can be reacted with the bis-maleimide. The reaction can be carried out according to the patent by Reeder [15]. The procedure is described in the following (determination of mass in Appendix A):

#### Addition of the fulvene functionality to the polyketone

4.14g (1 equiv. w.r.t chloride groups) of the fulvene was added to a 250ml round bottomed flask, equipped with a magnetic stirrer and reflux condenser, placed under inert (nitrogen) atmosphere. To the flask 135mL of dry THF (120g, to have the polymer as 16.67% w/w of solvent) and 1.1 equiv (1.3g of the dispersion) of sodium hydride (dispersed in mineral oil, with 60% w/w) were also added. The reactants were stirred for 30 minutes, at room temperature. 20g of PKCl was added to the flask and refluxed at 65°C for 12 hours.

Mixture was then cooled to room temperature and the solvent evaporated. The product was then precipitated into excess methanol and dried in a vacuum oven at 60°C for 24 hours. NMR (solvent: chloroform) and FTIR spectroscopy was performed on the product.

DA (crosslinking) reaction between PK-fulvene and bis-maleimide

7g of PK-fulvene and 1,9g (5.3mmol, 0.5 equiv.) of bis-maleimide were added to a 100 mL round-bottomed flask equipped with a magnetic stirrer. Using 47ml of chloroform (70g, to have the polymer as 10% w/w of solvent) as solvent, the reaction mixture was stirred at room temperature, under inert atmosphere, for 24h to perform the Diels-Alder reaction. The mixture was then precipitated in acetone, filtered and dried under vacuum, at room temperature, to obtain the crosslinked polymers. A crosslinking density of 21% was expected. Characterisation was done using FTIR spectroscopy.

**2.5 Rheology**

The rheology was carried out according to the procedure outlined by Orozco et al, 2020 [20]. The four different crosslinked polymers were ground separately and placed in a cylindrical mold (dimensions: 8mm diameter, 1.5mm thickness). The samples were then molded at 40 bar for 20 minutes according to the different de-crosslinking (rDA) temperatures of the different systems discussed in the introduction section. Thermomechanical behavior of the samples was followed by a rheometer in oscillation mode with a strain percentage of 0.2 %, frequency of 1 Hz, and axial force of 10N. The same heating rate of 3K/min was used for every sample for temperature scans using the range between the DA and rDA reactions specific to each system, shown in **Figures 6 to 9**. The data obtained was in terms of  $G'$  (storage modulus) and  $G''$  (loss modulus) and thermomechanical behavior can be evaluated through the complex modulus,  $G^*$ , where:  $G^* = \sqrt{G'^2 + G''^2}$  [21]. The data was normalised (according to equation 1) and the rate determined through a hyperbolic fit, which also removed noise in the data (according to equation 2a and 2b).

$$G^*_{norm} = \frac{G^* - G^*_{min}}{G^*_{max} - G^*_{min}} \quad (\text{equation 1})$$

- $G^*_{norm}$  - normalised complex modulus
- $G^*_{min}$  - complex modulus value when the material is softest
- $G^*_{max}$  - maximum complex modulus value

$$G^*_{norm} = P_1 + P_2 \cdot \tanh(P_3 \cdot \text{time} + P_4) \quad (\text{equation 2a})$$

$P_i$  - the best fit parameters

$$\text{Rate} = dG^*_{norm}/dt \quad (\text{equation 2b})$$

An example of these calculations using the furan-maleimide system in Appendix B.

From rheometry, the anthracene-maleimide system exhibited irregular behaviour (**Figure 16**) thus further investigation of its thermal properties was done using thermogravimetric analysis (TGA). Approximately 10mg powder of the crosslinked polymer based on anthracene-maleimide was placed in a

thermogravimetric analyser. The analyser was run with a temperature ramp of 10°C/min under air conditions to assess decomposition in the presence of oxygen.

### 3 Results and Discussion

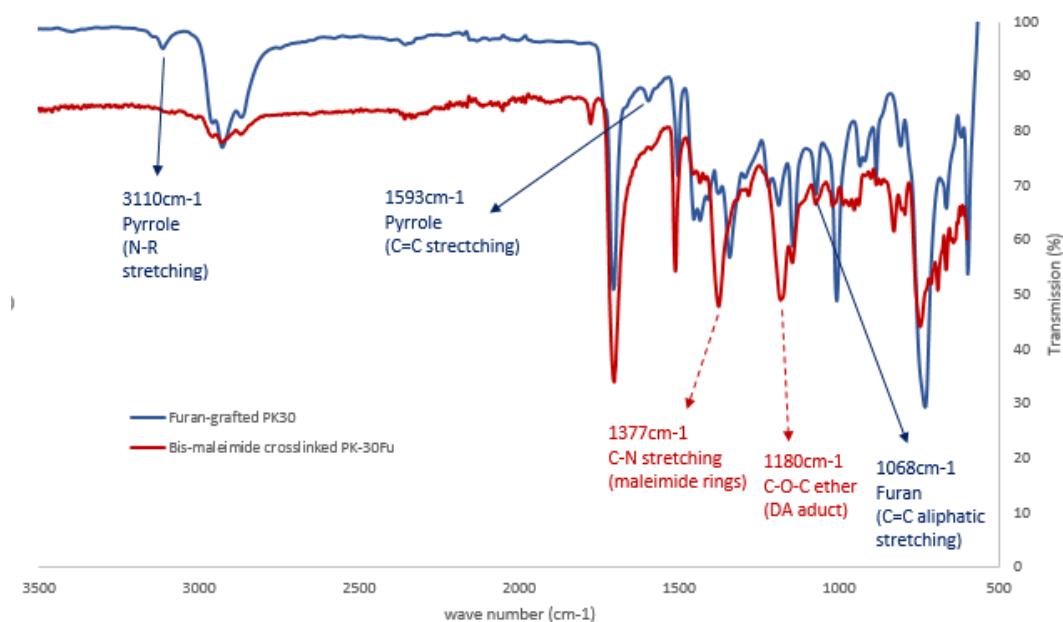
The working assumption in this thesis is that the outlined experimental procedure would have been 100% effective in terms of yield and conversion. Therefore, the results presented in the following are the expectations from trends obtained from literature review of sources already mentioned in this thesis or those found by the daily supervisor. This is with the exception of the results for the furan-maleimide system, where results shown are from previous experiments executed by other researchers.

#### 3.1 Synthesis and characterisation of the crosslinked polyketones

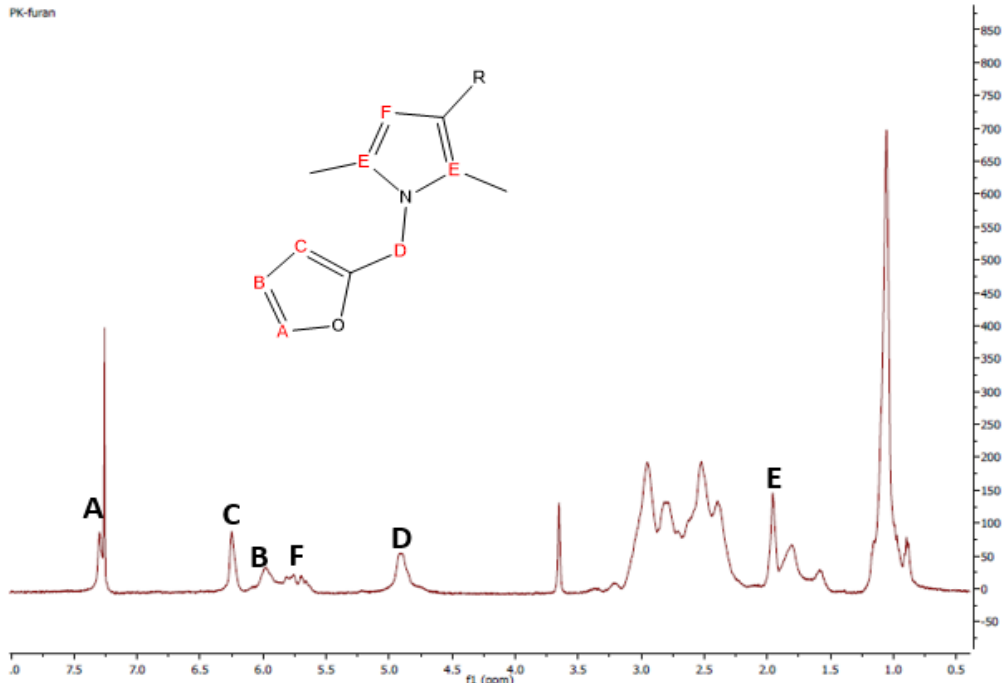
##### Furan-maleimide

The FTIR spectrum for the furan-grafted PK-30, in **Figure 11**, shows the presence of pyrrole rings represented by the peak at 1593cm<sup>-1</sup> and the furan rings shown mainly by the strong peak at 729cm<sup>-1</sup>, which implies the grafting of the furan onto the polyketone. <sup>1</sup>H-NMR spectrum, **Figure 12**, confirms this showing peaks, as indicated in the image, consistent with the furan and pyrrole groups attached to the polymer backbone. The <sup>1</sup>H-NMR spectroscopy, in collaboration with elemental analysis, was used to determine the carbonyl conversion. It was found that the average conversion from both elemental analysis and NMR is 18% , giving a conversion efficiency of 90%. (Calculations in Appendix C)

After successful grafting, the polyketone was then crosslinked using bis-maleimide. The product was characterised by FTIR spectroscopy, the spectrum shown in **Figure 11**. From this, the presence of the adduct's C-O-C ether stretching at 1180cm<sup>-1</sup> is testament to the formation of crosslinks via Diels-Alder reaction.

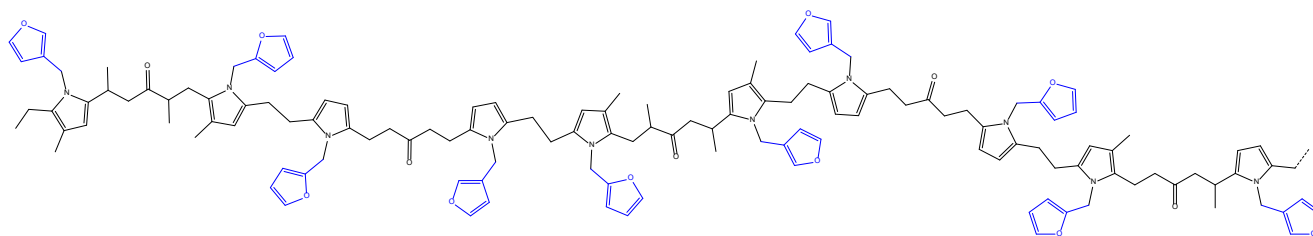


**Figure 11.** FTIR spectra of the furan-grafted polyketone before and after crosslinking with bis-maleimide, based on data obtained from previous lab work provided by the supervisor



**Figure 12.** NMR spectrum of the furan-grafted PK-30, based on data obtained from previous lab work provided by the supervisor

<sup>1</sup>H-NMR predictions of the furan-maleimide-based system were made to assess the proficiency of using MestreNova for the spectra of the other dienes grafting on the polyketone. As shown in **Figure 13(a&b)**, the prediction manages to illustrate the protons also shown in the spectrum from real experimentation. The main difference in the two spectra (**Figure 13(b)**) is the peak multiplicities, as the prediction does not show noise from impurities and the complex interactions of the polymer with itself from the actual experiment. Therefore, using MestreNova for predicting NMR spectra provides a representative visualization of the structural characterization for the diene-grafted polyketones.



**Figure 13(a).** The structure of PK-furan used for MestreNova prediction

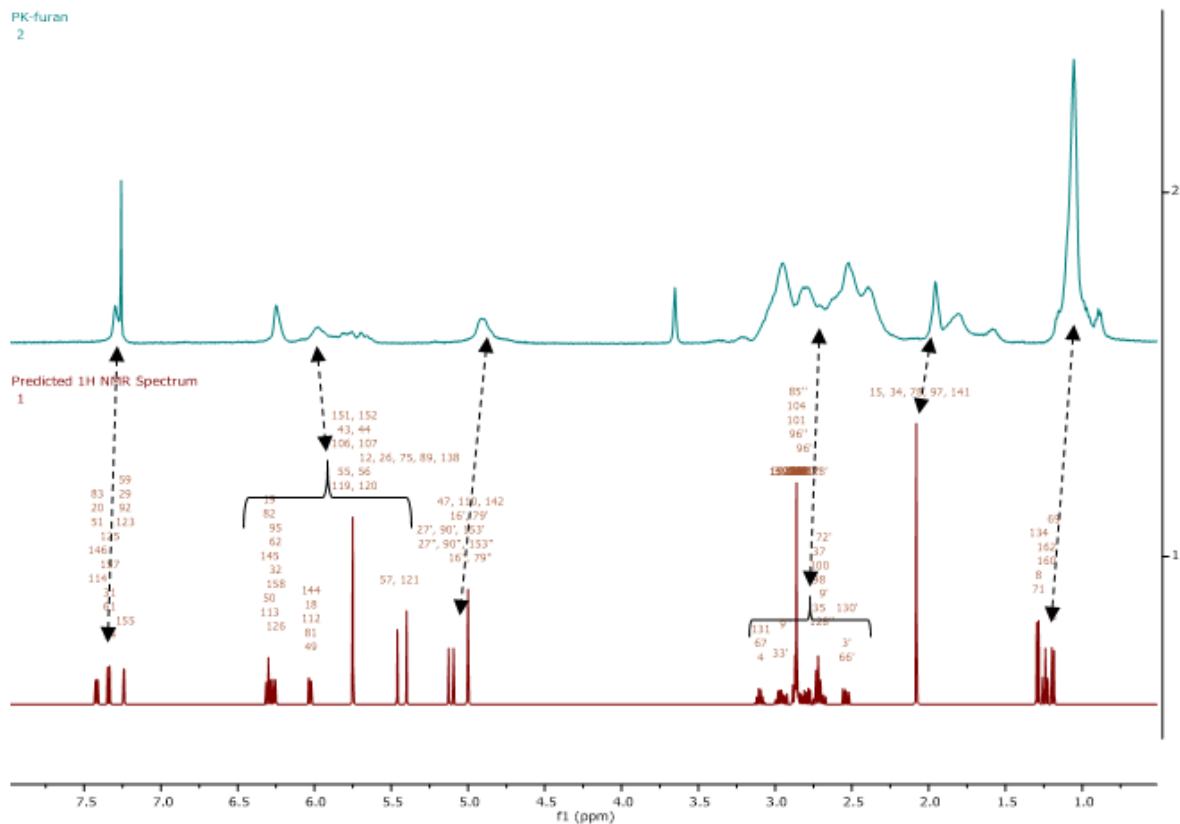


Figure 13(b). A comparison of the MestReNova predicted spectrum (bottom) and with one obtained from experimentation using data provided by the supervisor (top)

Paal-Knorr reaction to prepare polyketones with chlorine groups (PKCl)

Table I shows the agreement between the MestReNova prediction (also in Appendix D) and the peaks obtained experimentally by Toncelli et al [11] for the chlorine-grafted polyketone. The variations may be arising from the different ethylene:propylene ratio and contributions of impurities to the spectrum. The main functionalities of the PKCl would be represented in peaks as shown in Table II for the FTIR spectrum.

Table I. NMR peak assignment for PKCl, using chloroform as solvent, courtesy of Toncelli et al, compared to those in the MestReNova prediction [11]

Chemical shift ( $\delta$ /ppm)	Peak assignment	Corresponding chemical shift in prediction ( $\delta$ /ppm)
1.04	$\text{CH}_3\text{-CH}$ aliphatic	1.25
1.83	$\text{CH}_3\text{-CH}$ aromatic	1.80
1.94	$\text{Cl-CH}_2\text{-CH}_2$	2.05
2.2-3.1	$\text{CH}_2$ aliphatic	2.5-3.2
3.50	$\text{CH}_2\text{-Cl}$	3.40

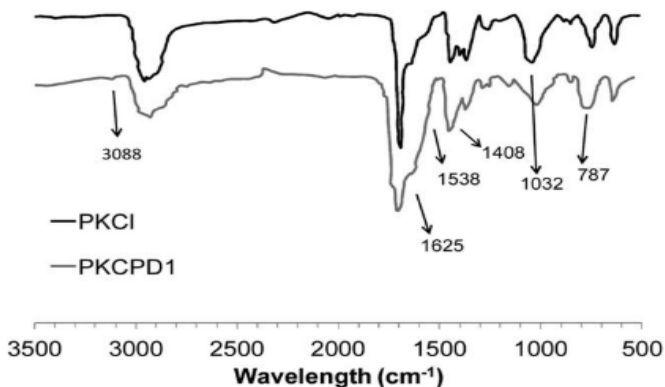
3.87	N-CH <sub>2</sub>	4.00
5.45	CH aromatic	5.47

**Table II. FTIR peak assignment for PKCl, courtesy of Toncelli et al. [11]**

Wavenumber (cm <sup>-1</sup> )	Assignment
667	C-Cl bending
749	C-Cl stretching
1039	C-H in plane deformation
1339	C-N ring stretching
1457	C=C stretching
1704	C=O carbonyl stretching
2875-2935	C-H aliphatic stretching
2969	C-H stretching (pyrrole)

### Cyclopentadiene-cyclopentadiene

The results presented for the cyclopentadiene-cyclopentadiene system are mostly taken from the work done by Toncelli et al [11]. The predictions for the NMR spectrum of the cyclopentadiene-grafted PK-30 are shown in Appendix D. The FTIR spectra shown in **Figure 14** were taken from their work and represent the results expected for this thesis. Characteristic peaks of the C-H ring bending in the CPD dimer at 787cm<sup>-1</sup> and the C=C stretching of the CPD dimer at 1538cm<sup>-1</sup>, indicate that the polymer already starts crosslinking during the introduction of cyclopentadiene. This also implies that a similar spectrum is likely to be observed for the cyclopentadiene-crosslinked polyketone.



**Figure 14. The FTIR spectra for the chlorine- (PKCl) and cyclopentadiene-grafted (PKCPD1) courtesy of Toncelli et al [11]**

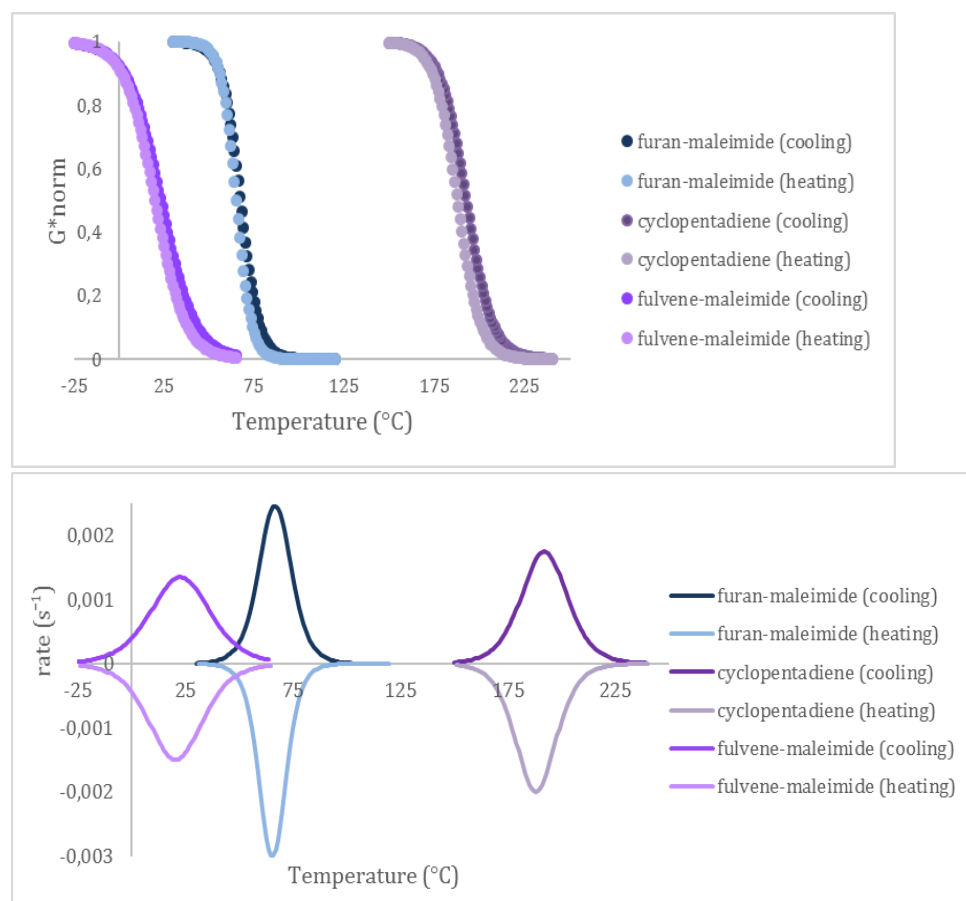


### Anthracene-maleimide and fulvene-maleimide

The results for the experiments for anthracene-maleimide and fulvene-maleimide systems were unavailable, therefore predictions for NMR and FTIR spectra were done using MestreNova and IR tables, respectively. This data is in Appendix D.

## 3.2 Rheology

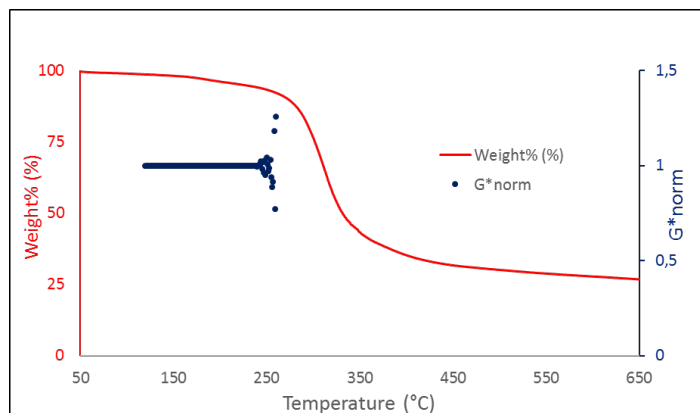
The (predicted) rheological measurements of the Diels-Alder based thermoreversible crosslinked polymers have the main results shown in **Figure 15**. They allow for a comparison of changes in mechanical properties with temperature for three of the four systems based on different diene-dienophile pairs. The  $G^*$ norm demonstrates the two main states of the polymers; crosslinked and de-crosslinked. Values close to one indicate the state of highest crosslinking (when the forward DA reaction is favoured by the equilibrium), and those close to zero denote the state of lowest crosslinking. From **Figure 15**, it can be observed that the systems based on furan, cyclopentadiene and fulvene, all exhibit such thermoreversible behavior, albeit at different temperatures.



**Figure 15.** Rheological result prediction in terms of rate and complex modulus versus temperature, used to compare the diene-dienophile pairs, obtained from data provided by the supervisor

Anthracene shows different behavior in its complex modulus thus the rate could not be determined. This behavior indicated that the bis-maleimide-crosslinked PK-anthracene might be decomposing. This was

confirmed by TGA, as shown in **Figure 16**, the sample appears to be losing mass above 150°C, which can be attributed to decomposition products that have high volatility, or remains of the solvent. At approximately 260°C, the slope starts being the steepest ( $T_{\text{onset}}$ ), the rest of the sample decomposes [22]. This behavior accounts for the ‘noisiness’ in the anthracene-based system’s graph for complex modulus. Therefore, the anthracene-based system failed to exhibit thermoreversibility with PK-30.



**Figure 16.** The predicted rheological and TGA results for the anthracene-based system, from data provided by the supervisor

Hardening of the polymer is the simultaneous process of cooling and increase in viscosity which results in crosslinking whereas softening is vice versa. The (predicted) rheological data in **Figure 15** presents a difference in the hardening and softening rates, as well as varying temperature ranges of thermoreversibility of the samples. The cyclopentadiene-based system exhibits a broader temperature range of thermoreversibility, which may be due to trimer formation. The fulvene-maleimide-crosslinked polyketone shows the slowest rate of thermoreversibility, which could be attributed to the occurrence of crosslinking below the glass transition temperature ( $T_g$ ) of the polyketone, which is around 15°C [23]. Molecular motion is known to slow down below the  $T_g$  [1]. This may be why the hardening and softening rates for the fulvene-maleimide system are slow as polymer mobility is limited, even though it is the most reactive system. The furan-maleimide crosslinks have the fastest hardening and softening rates, as illustrated by the steepest slopes in both graphs in **Figure 15**, due to the thermoreversibility occurring above  $T_g$  and activated nature of diene and dienophile.

The grafting of PK-30 with furan is straightforward, as it requires the Paal-Knorr reaction alone and with water as the only by-product [4]. According to the proposed experimental plan, the other three diene-dienophile systems, require an additional reaction after the Paal-Knorr, to nucleophilically substitute the chloride groups. The electrophilic carbonyl group on the polyketone backbone is thus prone to reaction in this stage. Therefore, use of amine-substituted fulvene, anthracene and cyclopentadiene, which can directly undergo grafting via the Paal-Knorr reaction would be preferred.

There are some advantages and disadvantages to each diene-dienophile system presented by exhibition of thermoreversibility at different temperatures. The crosslinking reaction using cyclopentadiene might be difficult to control due to the formation of trimers. On the other hand, it broadens the thermoreversibility temperature range, implying high temperature stability compared to the other systems [11]. This high temperature application comes at a cost, which is high input of energy required. Therefore, although the

system based on cyclopentadiene is stable at high temperatures, its application in industry may not be economic. The fulvene-based system is the most reactive, evidenced by thermoreversibility at low temperatures, thus it would have lower energy requirements than the other systems [16]. However, its applications are limited as the system would be prone to de-crosslinking at temperatures above 65°C, which would negatively affect the polymer's mechanical properties. The apparent disadvantage with the furan-based system would be that it is not suitable for applications above 150°C [4], however this is due to the homopolymerisation of maleimide thus would also be true for the other two systems using maleimide.

### 3.3 Future perspectives

The furan-maleimide system has been the most extensively studied system of the four, having already achieved a self-healing efficiency of approximately 100% with the polyketone [5]. However, the other three systems require more exploration. For the fulvene-based system, the use of a different polymer with a lower  $T_g$  is recommended. An example of such a polymer is poly(ethylene glycol), PEG, which has a  $T_g$  of around -60°C [24]. Variations of the polymer have been used in the work of Reutenauer et al [25] and Wei et al [26] on fulvene-cyanoolefin systems to produce thermoreversible dynamic elastomers and hydrogels, respectively. Therefore, applying fulvene-maleimide systems to PEG might provide improved mechanical properties. Investigation into the DA crosslink repair of mechanically cleaved crosslinks may be done for the anthracene-maleimide system, as done by Yoshie et al with poly(ethylene adipate) [14]. The study can start with the incorporation of the polyketone used in this thesis. In addition, other polymeric frames such as polyurethane can also be used, as according to the work of Heo et al [27], which showed that although the system does not show thermoreversibility, it had high thermal stability. For the cyclopentadiene system, a different polymer matrix might be less demanding energetically, as the formation of trimers would not increase the thermoreversibility temperature as much as with PK-30. Murphy et al [28] presented this, where trimer formation was the target for crosslinking using dicyclopentadiene-based monomers. This resulted in a rDA temperature of 120°C. Cyclopentadiene is also capable of acting as a diene while reacting with maleimide. This was illustrated by Stegall et al [29], whose work suggests that monosubstituted cyclopentadienes can result in adducts capable of rDA around 140°C. However, experimentations with cyclopentadiene mentioned above both result in thermoreversibility temperatures which coincide with those of the furan-maleimide system.

## 4 Conclusion

The preparation of thermo-reversibly crosslinked polyketones based on the diene-dienophile pairs: furan-maleimide, cyclopentadiene-cyclopentadiene, anthracene-maleimide and fulvene maleimide was proposed in a procedure where the functionalities of the dienes are added to the polyketone backbone via mechanisms including the Paal-Knorr reaction, followed by crosslinking using the dienophile. Investigation of the mechanical properties was done through literature-review-based predictions of the polymers' rheology. Results suggest that the anthracene-maleimide-based pair does not exhibit de-crosslinking at elevated temperatures with PK-30, it decomposes instead. However, it might repair mechanical fracture with temperature treatment as reported with other polymeric systems. Polyketones crosslinked with furan-maleimide Diels-Alder adducts were shown to display the fastest thermoreversibility at intermediate temperatures (30 - 120°C). Those crosslinked with cyclopentadiene come second while presenting wider thermoreversibility temperature range between 150°C and 250°C. With the slowest thermoreversibility rate

is the polyketone crosslinked with the fulvene-maleimide pair, occurring at low temperatures (-25 - 65°C). However, use of a polymer with a lower glass transition temperature than PK-30 presents potential for the system. Regardless of the hardening and softening rates, this thesis implies that, with further research into the polymers' processability, thermo-reversibly crosslinked polymers based on Diels-Alder reactions offer a wide range of temperatures, from -25°C to 250°C, which might be adapted for application in various industries.

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## 7 Appendix

### A. Mass calculations for experimental procedure

#### **Furan-maleimide**

i) In order to determine the amount of furfurylamine required to react with 30g of PK-30, stoichiometric calculations have to be done. First, the average molar mass of the reacting unit is calculated (each reacting unit contains 2 carbonyl groups):

1. With propylene:  $C_8H_{12}O_2$ ,  $M_w = 140\text{g/mol}$

2. With ethylene:  $C_6H_8O_2$ ,  $M_w = 112\text{g/mol}$

Since PK-30 has 70% propylene and 30% ethylene, the weighted average molar mass of the reacting unit can be calculated as:

$$(0.7 \cdot 140) + (0.3 \cdot 112) = 131.6\text{g/mol.}$$

With this, the amount of moles in the reacting unit is:

$$30(\text{g})/131.6(\text{g/mol}) = 0.228\text{mol.}$$

To achieve 20% carbonyl conversion, the amount of furfurylamine ( $M_w 97.117\text{g/mol}$ ) required is:

$$20\% \cdot 0.228\text{mol} = 0.0456\text{mol}$$

$$0.0456\text{mol} \cdot 97.117\text{g/mol} = 4.43\text{g}$$

ii) In order to determine amount of the bismaleimide required to react with the PK-furan:

Molar weight of reactive species =  $131.6\text{g/mol}$

$n(\text{reactive species}-7\text{g}) = 0.053\text{mol}$

Ratio of furan to maleimide = 2:1

Moles of furan (7g)  $\sim 9.54\text{mmol}$  (*18% carbonyl conversion*)

Amount of bis-maleimide required =  $1.71\text{g}$  ( $M_w = 358.35\text{g/mol}$ )

#### **Cyclopentadiene-cyclopentadiene**

i) In order to determine the amount of 3-chloropropylamine required to react with 60g of PK-30, stoichiometric calculations have to be done. First, the average molar mass of the reacting unit is calculated (each reacting unit contains 2 carbonyl groups):

1. With propylene:  $C_8H_{12}O_2$ ,  $M_w = 140\text{g/mol}$

2. With ethylene:  $C_6H_8O_2$ ,  $M_w = 112\text{g/mol}$

Since PK-30 has 70% propylene and 30% ethylene, the weighted average molar mass of the reacting unit can be calculated as:

$$(0.7 \cdot 140) + (0.3 \cdot 112) = 131.6\text{g/mol.}$$

With this, the amount of moles in the reacting unit is:

$$60(\text{g})/131.6(\text{g/mol}) = 0.456\text{mol.}$$

To achieve 20% carbonyl conversion, the amount of 3-chloropropylamine ( $M_w 93.55\text{g/mol}$ ) required is:

$$20\% \cdot 0.456\text{mol} = 0.0912\text{mol}$$

$$0.0912\text{mol} \cdot 93.55\text{g/mol} = 8.53\text{g}$$

ii) The reaction of PKCl with cyclopentadiene:

Molar weight of reactive species =  $131.6\text{g/mol}$

$n(\text{reactive species-10g}) = 0.076\text{mol}$   
 $n(\text{Cl in PKCl}) = 0.076\text{mol} * 20\% = 0.0152\text{mol}$  (20% conversion)  
Mw Li-CPD = 72.04g/mol  
Amount required =  $0.0152 * 72.04 = 1.095\text{g}$

### **Anthracene-maleimide**

i) Amount of 9-anthracenemethanol required:  
Molar weight of reactive species = 131.6g/mol  
 $n(\text{reactive species-20g}) = 0.152\text{mol}$   
 $n(\text{Cl in PKCl}) = 0.152\text{mol} * 20\% = 0.0304\text{mol}$  (20% conversion)  
Mw 9-anthracenemethanol = 208.25g/mol  
Amount required =  $0.0304 * 208.25 = 6.33\text{g}$   
0.8g NaH = 1.1equiv.

ii) In order to determine amount of the bismaleimide required to react with the PK-anthracene:  
Molar weight of reactive species = 131.6g/mol  
 $n(\text{reactive species-7g}) = 0.053\text{mol}$   
Ratio of anthracene to maleimide = 2:1  
Moles of anthracene (7g) ~ 10.6mmol (20% carbonyl conversion)  
Amount of bis-maleimide required = 5.3mmol = 1.9g (Mw = 358.35g/mol)

### **Fulvene-maleimide**

i) Amount of 3-(cyclopenta-2,4-dien-1-ylidene)butan-1-ol required:  
Molar weight of reactive species = 131.6g/mol  
 $n(\text{reactive species-20g}) = 0.152\text{mol}$   
 $n(\text{Cl in PKCl}) = 0.152\text{mol} * 20\% = 0.0304\text{mol}$  (20% conversion)  
Mw 3-(cyclopenta-2,4-dien-1-ylidene)butan-1-ol = 136.19g/mol  
Amount required =  $0.0304 * 136.19 = 4.14\text{g}$   
0.8g NaH = 1.1equiv.

ii) In order to determine amount of the bismaleimide required to react with the PK-fulvene:  
Molar weight of reactive species = 131.6g/mol  
 $n(\text{reactive species-7g}) = 0.053\text{mol}$   
Ratio of fulvene to maleimide = 2:1  
Moles of fulvene (7g) ~ 10.6mmol (20% carbonyl conversion)  
Amount of bis-maleimide required = 5.3mmol = 1.9g (Mw = 358.35g/mol)

## **B. Normalising and removing noise from rheological data**



The  $G^*$  norm, and rate were calculated according to equations 1, 2a and 2b resulting in the shown. The best fit parameters were obtained using the Excel 'SOLVER' function, and were modelled according to the hyperbolic function in equation 2a.

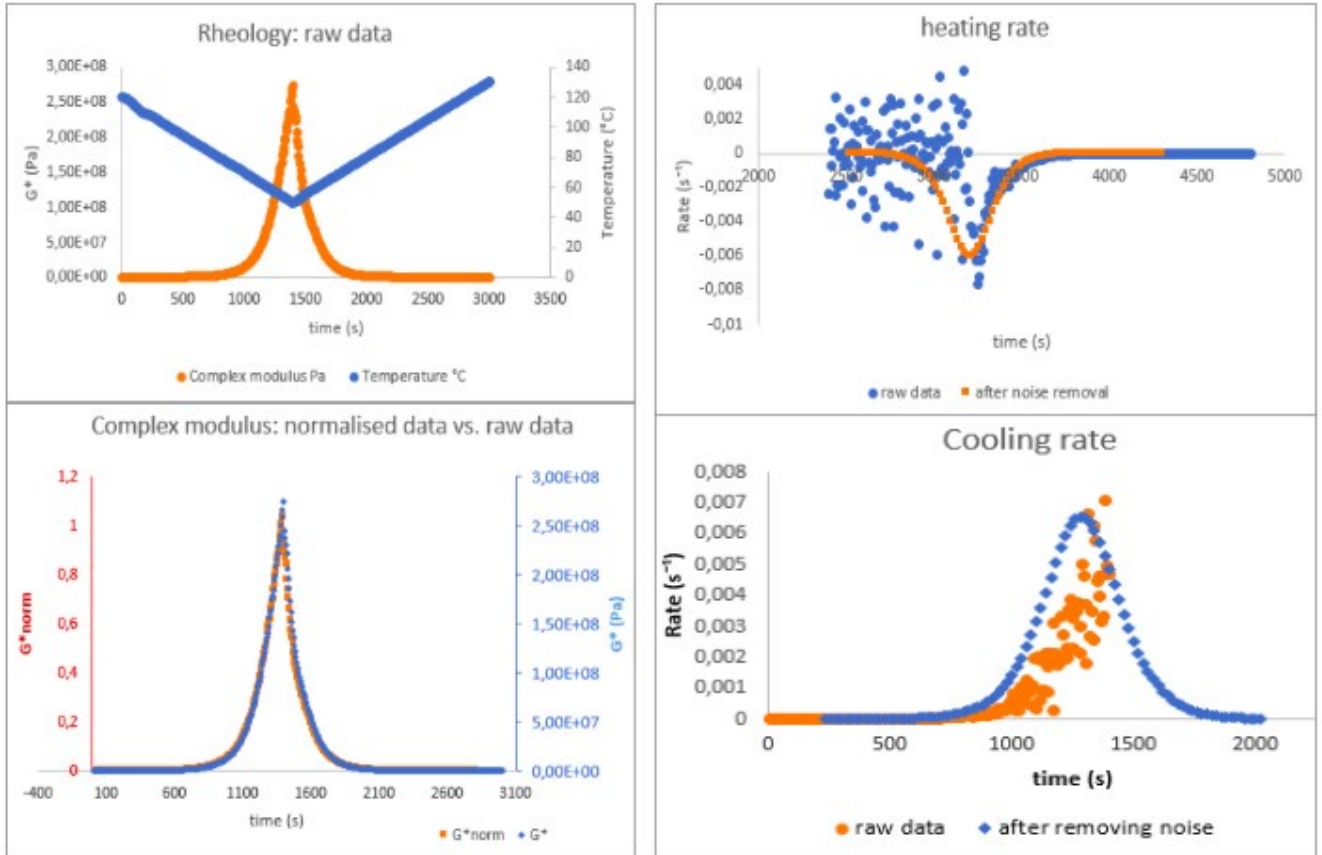
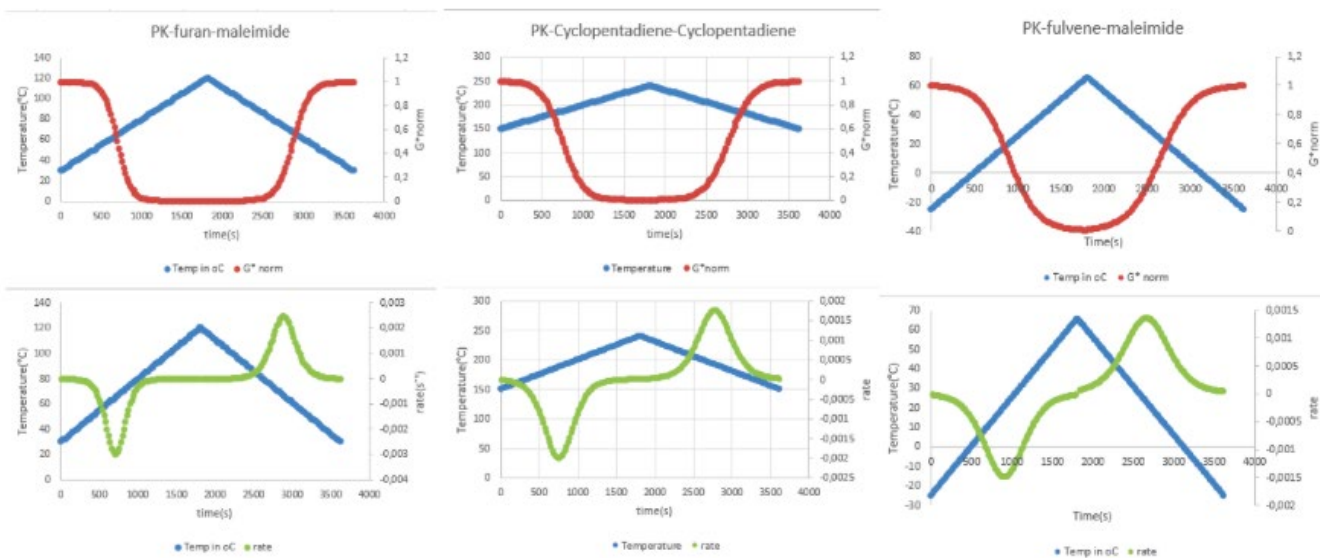


Figure A1: The overall rheological data transformation after the application of equations 1, 2a & 2b.



**Figure A2.** The predicted rheological results for furan-, cyclopentadiene- and fulvene-based systems including the normalised complex modulus, temperature and rate

C. Calculation of carbonyl conversion for the PK-furan

i) *Elemental Analysis*

N% w/w obtained = 1.72 %

Using the value of N weight percentage of 1.72% found.

Theoretically, N w/w% = 1.985%

Thus deviation of obtained value from theoretical = 13.35%

Theoretical conversion of carbonyls = 20%

Including the deviation, conversion of carbonyl:  $(100-13.35)\% * 20\% = \underline{17.33\%}$

ii) NMR

Conversion: finding peaks and taking note of their integrals.

Amount of protons =  $\frac{\text{□□□□□□□□ □□ □□□□}}{\text{□□□□□□ □□ □□□□□□□□ □□□□ □□ □□□□□□□□ □□□□□}}$

Conversion (in terms of number of protons) =  $\frac{\text{□□□□□□□□}}{\text{□□□□□□□□ + □□□□□□□□}}$

Peak assignment	Chemical shift/ppm	Integral	Expected H atoms	number of protons	conversion (%)
D	1,03	143	3	47,66666667	
F	4,9	21,93	2	10,965	18,7015
C	5,98	10,9	1	10,9	18,61127
B	6,25	12,42	1	12,42	20,67014
A	7,3	10,21	1	10,21	17,64096

Table A1. Calculation of the carbonyl conversion via NMR

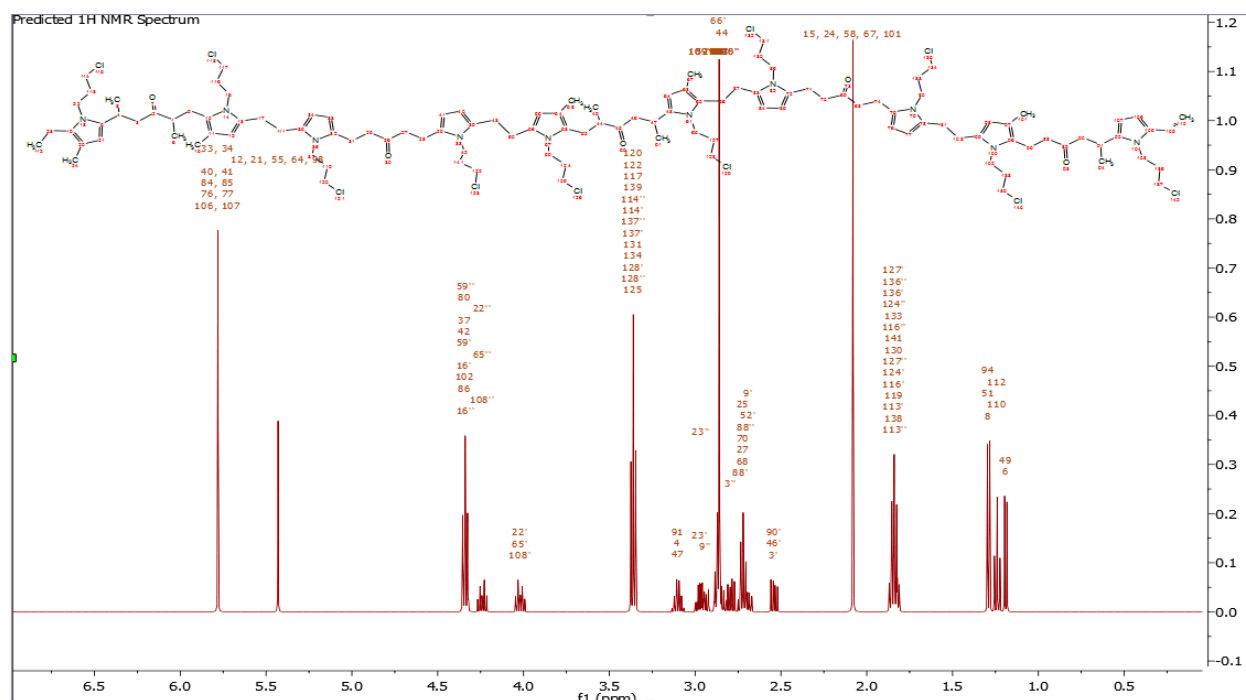
Efficiency = obtained/expected = 18.0675/20 = 90.3375%

D. Characterisation results and predictions

Wavenumber (cm <sup>-1</sup> )	Assignment	
729	C-H bending	furan

1068	C=C aliphatic stretching	furan
1338	C-O stretching	furan
1438	C=C stretching	pyrrole
1593	C=C stretching	pyrrole
3110	N-R stretching	pyrrole

**Table A2. Peak assignments for the furan-grafted PK-30**



**Figure A3. NMR prediction of the PKCl by MestreNova**

Wavenumber (cm <sup>-1</sup> )	Assignment
787	C-H ring bending (CPD dimer)
1408	C-H bending (CPD)
1538	C=C stretching (CPD dimer)

1625	C=C stretching (CPD)
3088	C-H stretching (CPD)

Table A3. FTIR peak assignment for PK-CPD, according to Toncelli et al. [9]

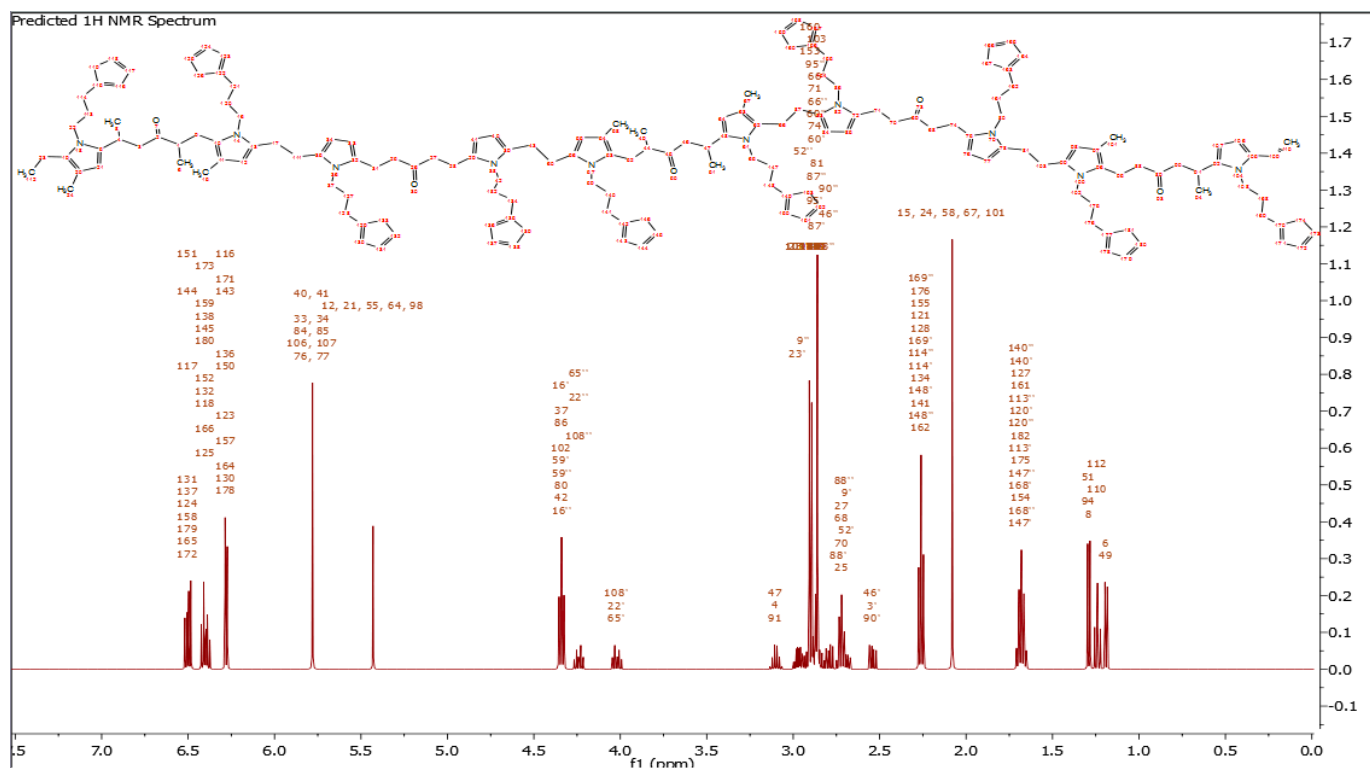


Figure A4. NMR prediction of the PK-CPD by Mestrenova

Wavenumber (cm <sup>-1</sup> )	Assignment
787	C-H ring bending (DA adduct)
1408	C-H bending (CPD)
1538	C=C stretching (DA adduct)
1625	C=C stretching (CPD)
3088	C-H stretching (CPD)

Table A4. FTIR peak assignment for crosslinked PK-CPD, according to Toncelli et al. [9]  
Anthracene-maleimide

i) Substitution of the Cl group by the anthracene functionality

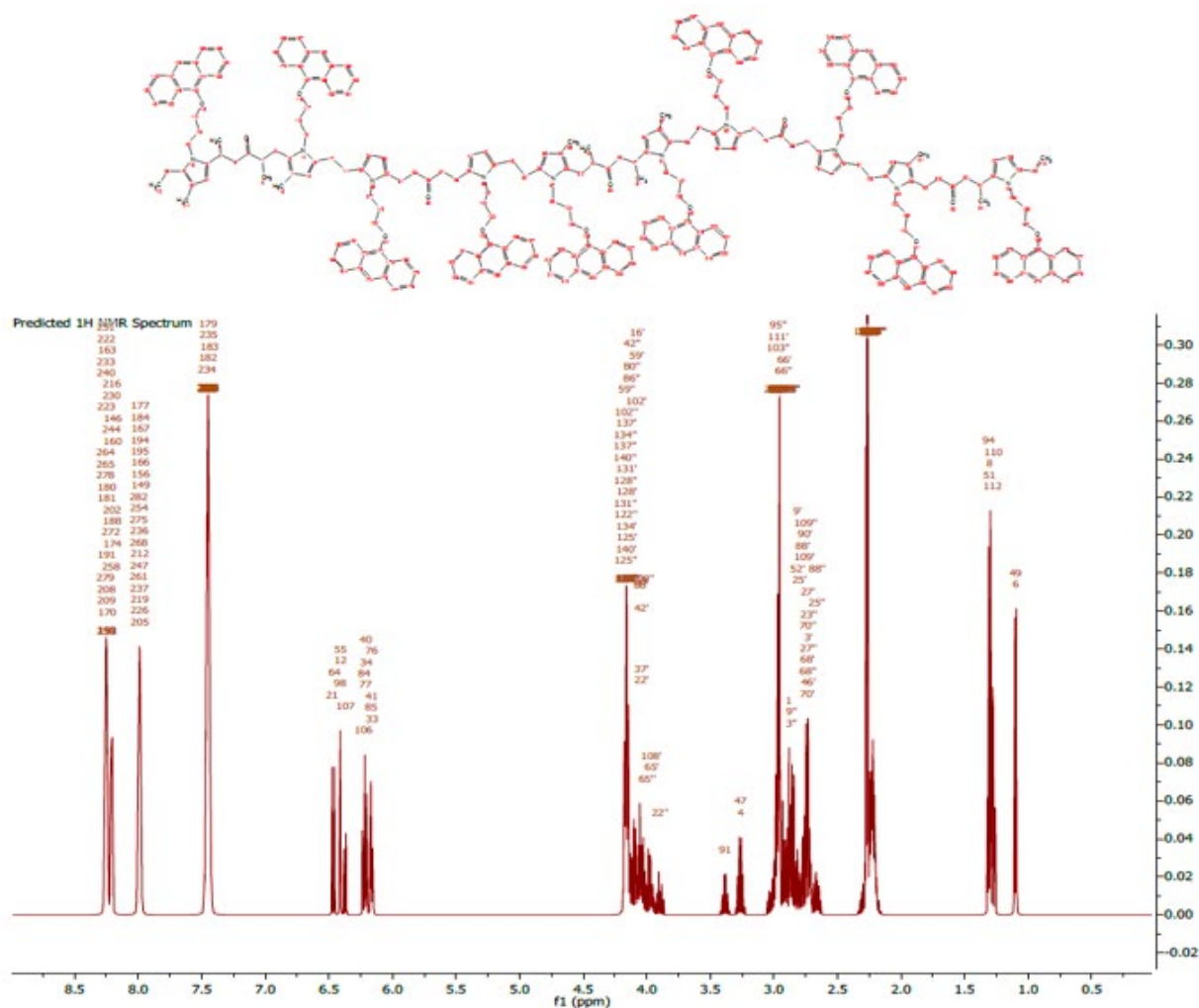


Figure A5. NMR prediction of the PK-anthracene by Mestrenova

Wavenumber (cm <sup>-1</sup> )	Assignment	Intensity
860	C-H ring bending (pyrrole)	strong
1330	C-N ring stretching (pyrrole)	strong
1550	C=C aromatic stretching (anthracene)	weak
1150	C-O-C stretching (ether)	strong

Table A5. FTIR peak assignment prediction for PK-anthracene

ii) Crosslinking of the anthracene-grafted PK30 by bismaleimide

Wavenumber (cm <sup>-1</sup> )	Assignment	Intensity
1350	C-N ring stretching (pyrrole)	strong
1050	C-N stretching (maleimide)	medium
1180	C-O-C stretching (ether)	strong
1570	C=C aromatic stretching (anthracene)	medium, weak
1400	C-H ring bending (DA adduct)	variable
1650	C=C aliphatic stretching (DA adduct)	medium, weak

Table A6. FTIR peak assignment for bis-maleimide crosslinked PK-anthracene

### Fulvene-maleimide

i) Substitution of the Cl group by the fulvene functionality

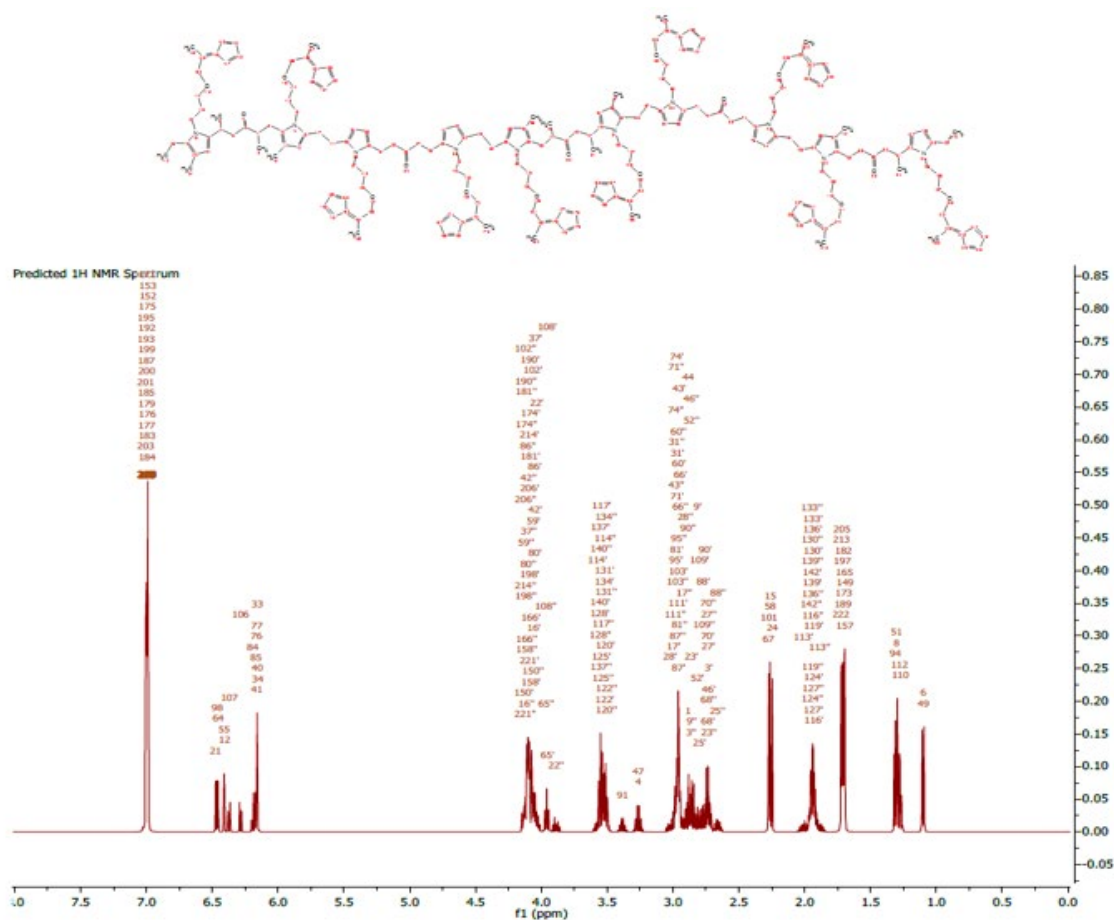


Figure A6. NMR prediction of the PK-fulvene by Mestrenova

Wavenumber (cm <sup>-1</sup> )	Assignment	Intensity
860	C-H ring bending (pyrrole)	strong
1330	C-N ring stretching (pyrrole)	strong
1630	C=C aliphatic stretching (fulvene)	variable
1150	C-O-C stretching (ether)	strong

*Table A7. FTIR peak assignment for PK-fulvene*

ii) Crosslinking of the fulvene-grafted PK30 by bismaleimide

Wavenumber (cm <sup>-1</sup> )	Assignment	Intensity
1350	C-N ring stretching (pyrrole)	strong
1050	C-N stretching (maleimide)	medium
1180	C-O-C stretching (ether)	strong
1650	C=C aliphatic stretching (fulvene)	medium, weak
1400	C-H ring bending (DA adduct)	variable
1615	C=C aliphatic stretching (DA adduct)	medium, weak

*Table A8. FTIR peak assignment for bis-maleimide cross linked PK-fulvene*