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DURHAM UNIVERSITY

**Synthesis and Characterisation of
Degradable Thermosetting Materials**

Shenghui Hou

MSc THESIS

2012

Abstract

Traditional thermosetting materials generally display good durability, yet poor tractability, reworkability, and degradability. This project, however, provides a class of thermoset ring-opening metathesis polymerization (ROMP) materials based on norbornene dicarboximide moieties containing acetal ester group linkage which is degradable when subjected to heat or acidic-catalysis.

In this study, acetal ester linkages were introduced into di-functional monomer by a one-step neat reaction between a functionalised imidonorbornene containing a terminal carboxylic acid group and a 1,4-butanediol divinyl ether. Each monomer and product was characterised by ^1H and ^{13}C NMR analysis, while the obtained polymers were analysed by thermogravimetric analysis (TGA), FTIR, dynamic mechanical analysis (DMA) and oven. The results of TGA indicated that the cross-linked materials started losing weight at 150°C and the extent of the weight loss at 300°C . The IR spectra as it showed the reduction in the intensity of acetal ester band not the complete disappearance. The samples were heated in the oven at 300°C and 250°C . The results showed the higher the DFM content of the cross-linked materials and the heating temperature and the duration of the heating. ^1H NMR analysis of cross-linked sample C11, after the heating treatment in the oven at 300°C for 2hr, indicates the partial formation of linear polymer upon heating. The cross-linked materials were also subjected to acid-catalysed hydrolysis. The samples after hydrolysis in dilute acid were completely soluble in DCM and were therefore characterised by NMR, which shows all the acetal ester linkages were broken down during hydrolysis and that cross-linked polymers changed into linear polymers. Dynamic mechanical analysis was carried out on the cross-linked polymer, linear polymer, polymer after heating, and polymer after hydrolysis, which support that the crosslinking in the polymer were breakdown during heating, but a new kind of network was formed, and the complete breakdown of actela ester linkages after hydrolysis.

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DECLARATION

The work of this thesis was carried out in the IRC Chemistry laboratories of the University of Durham between April 2010 and January 2012. This work has not been submitted for any other degree and is the original work of the author, excepted where acknowledged by reference.

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Chapter 1

General introduction and background

1.1 Thermosetting materials

Thermosetting materials are an important class of materials with excellent thermal and mechanical properties. They have been used in a wide range of applications particularly as coatings, adhesives, and encapsulants.¹⁻³ Thermoset materials are stronger than thermoplastic materials due to their three-dimensional network of bonds. The polymer chains lose some of their ability to move as individual one when they are linked together by cross-links. The cross-link not only brings the polymer toughness, good adhesive and high stable temperature, but also makes the polymer much harder to recycle. Low cross-link densities increase the viscosities of polymer melts; intermediate cross-link densities transform gummy polymers into materials that possess elastomeric properties and potentially high strengths; very high cross-link densities can make materials become very rigid or glassy, for example, phenol-formaldehyde materials. Although, traditional thermoset materials generally display good durability, they exhibit poor tractability, poor recyclability, and poor biodegradability. These characteristics limit their use particularly in applications in where degradability or reworkability are advantageous. For example, it is costly to discard a multi-chip package with a single failed chip. Thus, the use of an adhesive that could decompose to allow chip repair or replacement would be desired for reworkable semiconductor manufacturers. A potential application of reworkable materials lies in packaging areas of electronic devices. A reworkable adhesive could facilitate the repair or reprocessing of individual electronic components.¹ Moreover, there is a great need for adhesives, coatings, and encapsulates to be reworkable in many applications. In order to be reworkable, a material must be removable under controlled conditions, whilst also exhibiting properties that are comparable or exceed those of contemporary materials.²

In recent years, various research groups have been working on the development of thermoset materials. Epoxy resins have been the adhesive of choice in the microelectronics industry and are widely used. This is due to their good unique properties, such as, electric and physical properties, excellent chemical and corrosion

resistance, high adhesion and good thermal stability, and low shrinkage on curing.³ An epoxy adhesive carries the ability to enhance the thermal and mechanical flexibility of components on a circuit board. They are also easy to use, as uncured epoxy resins are able to flow into complex parts of a circuit board before being cured. Once the resins are cured, they display a highly cross-linked three dimensional behaviour with greater adhesive properties. Although the adhesive may be reliable, the difficulty to recycle the material remains an undesirable characteristic of the resins.¹

1.2 Weak linkages in thermosetting materials

Several groups have prepared reworkable materials by introducing cleavable linkages into their respective monomers. These linkages, depending on their nature, can be cleaved chemically or thermally.

1.2.1 Thermally breakable linkages

1.2.1.1 Ester linkage in thermosetting epoxy

The secondary and tertiary ester groups were identified as potential heat-cleavable linking groups, as they could be broken down by heating based on their thermal degradation mechanisms.⁴ A series of cycloaliphatic epoxy monomers incorporated ester groups has been designed by many groups.^{5,6} Some selective examples are shown in Fig. 1.1. The epoxy 1-5 was cured by hexahydro-4-methylphthalic anhydride (HHMPA) as hardener. The curing process uses 1-cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN) as the catalyst. The study of the thermal degradation of the ester linkages showed that they start breaking down between 250°C and 300°C. It should be noted that epoxy resins without ester linkages degraded at 350°C. The crosslink density, T_g (glass transition temperature) and strength of the epoxy decreased at the same time during the degradation test.

Aliphatic esters are very sensitive to hydrolysis. And the electronic packaging needs

good resistance to hydrolysis. Therefore aromatic esters 6 and 7 (Fig. 1.1) were synthesised and cured by HHMPA. This curing process is initiated by 2E4MZ-CN. The thermally degradability behaviour of thermosetting polymers from cured 6 and 7 were studied by TGA. The polymers from cured 6 started breaking down at 330°C, but polymers from cured 7 started decomposing at 250°C. The thermoset materials from 6 and 7 started breaking down at 330°C and 250°C, respectively. This is most likely due to difference between the stability of secondary (material 6) and tertiary (material 7) ester linkages.

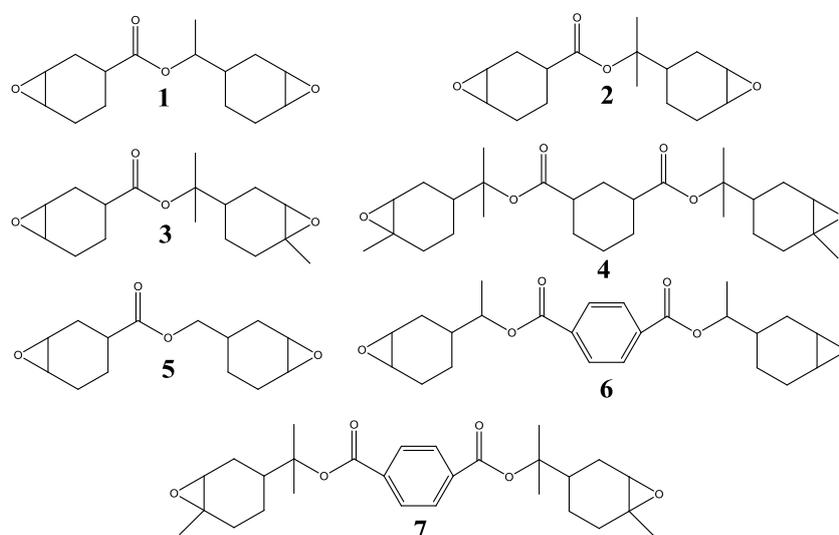


Figure 1.1: Di-epoxide monomers 1-7 containing ester linkages

1.2.1.2 Carbamate linkage in thermally degradable thermosetting epoxy

A series of epoxy monomers containing carbamate linkages were synthesised by some groups,⁷ some examples of which of them are showed in Fig. 1.2. The di-epoxide monomers 8-13 were cured by HHMPA, and the curing process was initiated by 2E4MZCN. The resulting thermosetting polymers started to break down at 250°C -300°C. However, the resins obtained from the commercial cycloaliphatic epoxide which do not contain any carbamate linkages also started breaking down at 350°C. Moreover, the system is further complicated by the fact that the carbamate groups within the di-epoxides can act as an internal catalyst.⁸

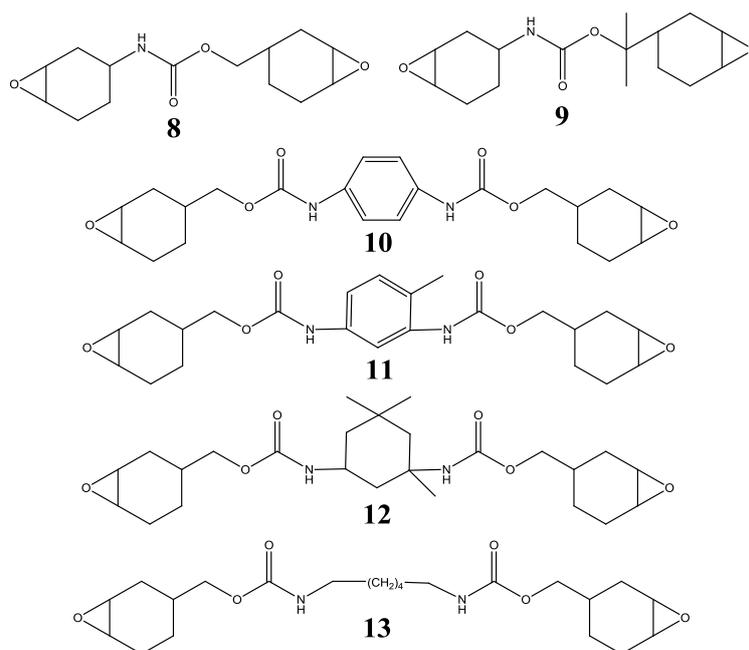


Figure 1.2: Di-epoxide monomers 8-13 containing carbamate linkages

1.2.1.3 Carbonate linkages in thermally degradable thermosetting epoxy

Cycloaliphatic or aliphatic epoxide monomers with carbonate linkages have also been prepared (Fig. 1.3).⁹ Cycloaliphatic di-epoxides monomer 14 contains primary carbonate linkages, 15 contain secondary carbonate group, and 16 contain tertiary carbonate linkage. Although, the synthesis of primary or secondary carbonates with aliphatic groups on both sides were reported to be straightforward, but a carbonate containing tertiary aliphatic groups on one or two sides was much more difficult to prepare.¹⁰ The epoxy monomers 14-16 were cured by HHMPA, and the curing process was initiated by 2E4MZCN. The thermal degradation test, by TGA, showed that the resulting thermoset started to break down at 300°C which is slightly lower than the decomposition temperature of the epoxy resins without carbonate at 350°C.

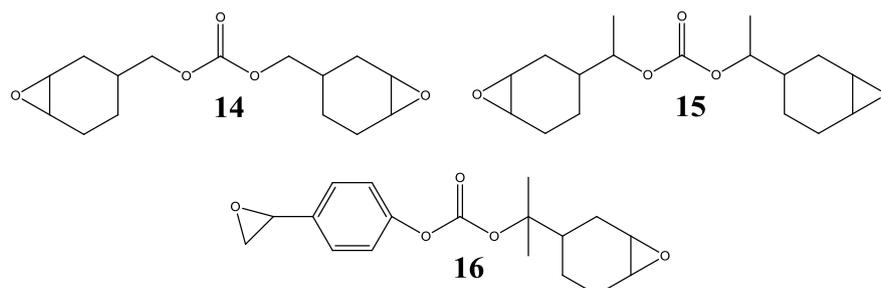


Figure 1.3: Di-epoxide monomers 14-16 containing carbonate linkages

1.2.1.4 Maleimides-based thermosets

Thermosetting resins based on maleimides have been developed for electronic packaging applications.¹¹ The maleimides resin exhibit fast cure speed, better adhesion and low shrinkage after curing.¹¹⁻¹⁴ Maleimide-based functionality not only could be homo-polymerised, but also could be copolymerised with a variety of comonomers (eg, styrenical, acrylate) by free radical processes. However, the resulting thermosetting materials could not be re-worked or recycled. Therefore, attempts have been made to develop thermosetting materials based on maleimide compounds that can provide the advantages offered by maleimide adhesives in a re-workable adhesive system.¹⁴

Multi-functional maleimide monomers have been prepared containing acetal ester linkages 18-22 (Fig. 1.4).¹⁰ Free radical polymerisation process initiated by 1,1-di(tert-amyl peroxy) cyclohexane (USP-90MD) was adopted to polymerise multi-functional maleimide monomers to produce thermosetting materials with acetal ester linkages. DSC, TGA, GC - MS, and hot-stage FTIR were used to analyse the thermal degradation behaviour of the resulting thermosetting materials. The degradation result showed that the acetal ester linkage degraded when the heating temperature reached above 225 °C. Moreover, the re-workability of adhesively bonded substrates was improved when the acetal ester linkage was introduced into the formulation.

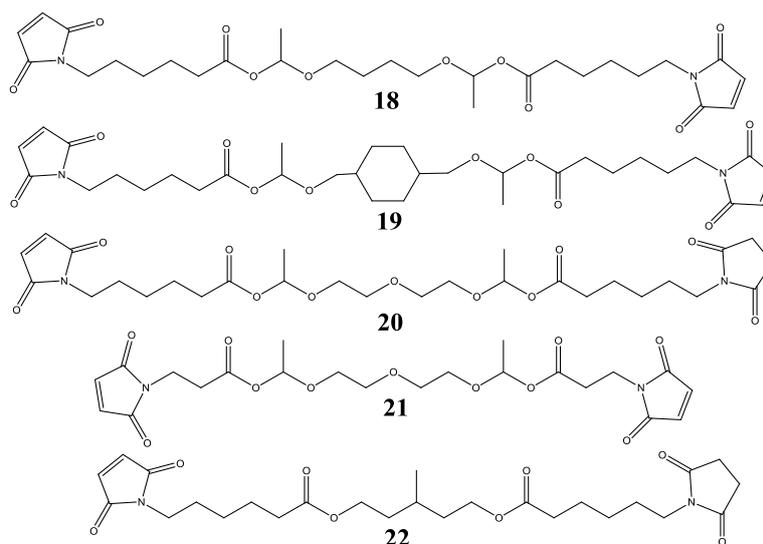


Figure 1.4: Maleimide based monomers 18-22 containing acetal ester groups

1.2.2 Chemically breakable linkages

The chemical cleavage of cross-linked materials based on an acrylic polypropylene oxide polymer network containing urea linkages was investigated.¹⁵ The materials showed complete degradation in hexanol and nonanol at 125°C.

A number of cycloaliphatic di-epoxides with ketal and acetal linkages (Fig. 1.5) were synthesized which were cured with cyclic anhydride to produce thermosetting materials.¹⁶ Thermosets containing ketal linkages (23) dissolved readily and those containing acetal linkages (24) partially in ethanol/water/acetic acid (4.4M) at 88°C. However, thermosets containing both linkages dissolved readily in butyrolactone/water/phosphoric acid (1.5M) at 106°C.

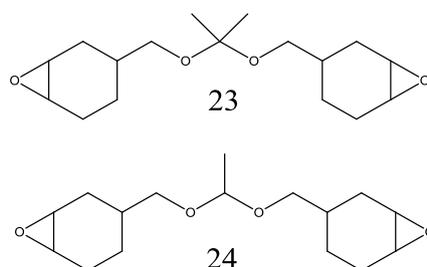
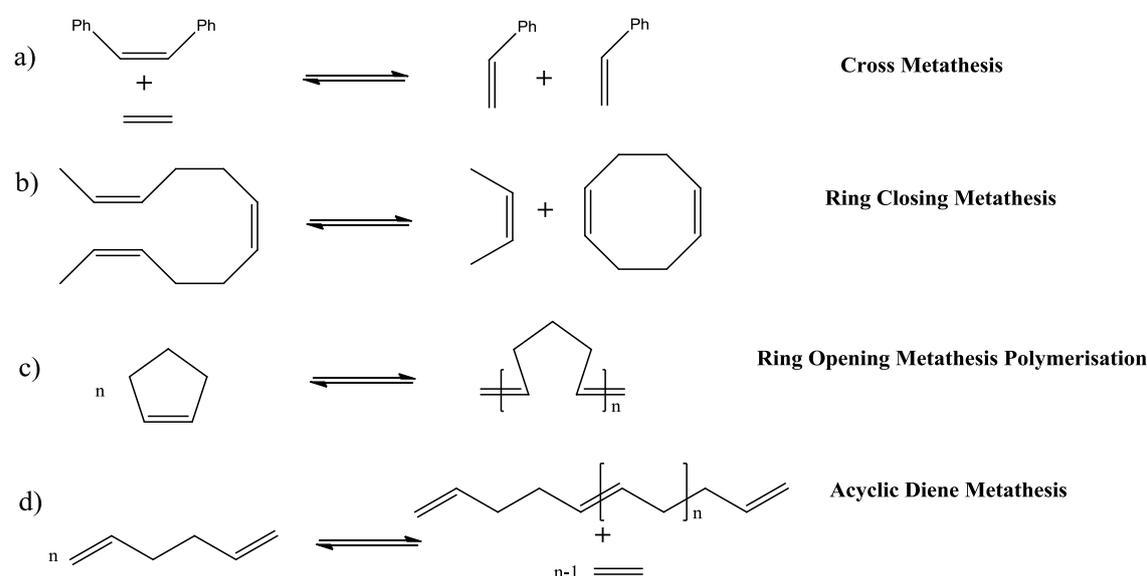


Figure 1.5: Structures of cycloaliphatic epoxides containing ketal and acetal groups

1.3 The polymerisation process

1.3.1 Olefin Metathesis

Olefin metathesis, an organic reaction, refers to redistributing alkylene fragments through the chain scission of C=C double bonds in olefins (alkenes) with the merits of creating fewer side-products and hazardous wastes. Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock shared the 2005 Nobel Prize in Chemistry for their contribution in "The development of the olefin metathesis method in organic synthesis". Metals like nickel, tungsten, rhenium, ruthenium and molybdenum have been used as catalysts in olefin metathesis.¹⁷⁻²⁰

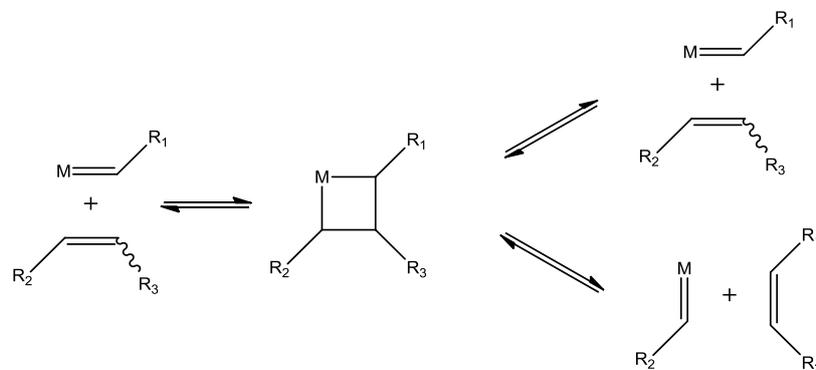


Scheme 1.1: Example of Olefin metathesis

Since its discovery, olefin metathesis has received a broad application and has developed into a mighty technique for both organic and polymer synthesis, such as Cross Metathesis (CM), Ring Closing Metathesis (RCM), Ring Opening Metathesis Polymerisation (ROMP), and Acyclic Diene Metathesis (ADMET), scheme 1.1.²¹

The widely acceptable mechanism for olefin metathesis has been put forward by Herisson and Chauvin in 1971, scheme 1.2.²² The olefinic C=C double bonds reacts with metal alkylidene-species in a reversible [2+2] cyclo-addition, to form a

metallacyclobutane species. The metallacyclobutane ring opens either degeneratively to regenerate the original reagents, or productively to form a new olefin and new metal alkylidene species.

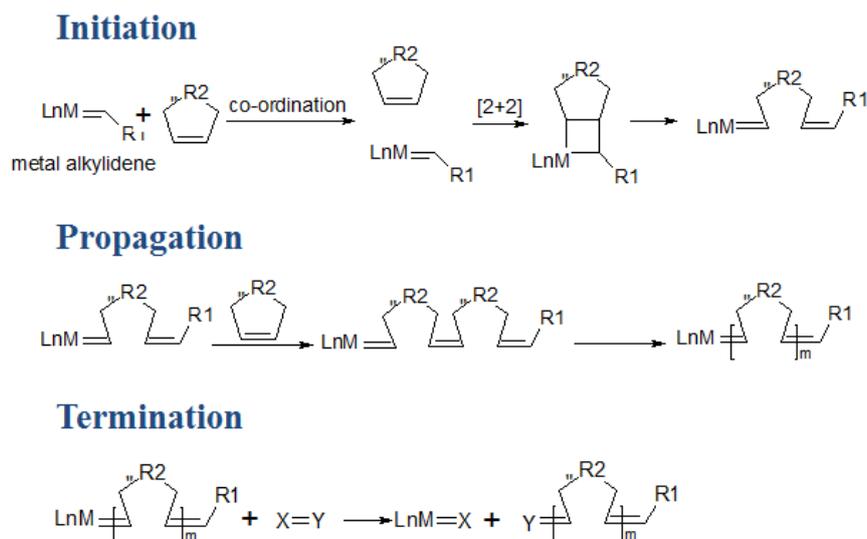


Scheme 1.2: Mechanism of olefin metathesis

Olefin metathesis reactions either do not generate by-products, or only produce a by-product, such as ethane, which can be easily removed by evaporation.²³

1.3.2 Ring-Opening Metathesis Polymerisation

The process of ROMP is an adaptation of olefin metathesis, where strained cyclic olefins are polymerised to form linear polymers using transition metal complexes as initiators. The reaction makes use of strained ring systems, such as norbornenes and their derivatives, to produce an array of stereoregular and monodisperse polymers and copolymers.²⁴ ROMP can be described as a chain growth polymerisation process, and it includes three steps: initiation, propagation and termination (scheme 1.3).



Scheme 1.3: Three steps in ROMP of cyclic olefin

The initiation process begins with the coordination of the transition metal alkylidene complex to the cycloalkene. A [2+2] cycloaddition leads to the formation of a metallocyclobutane intermediate. The productive opening of metallocyclobutane intermediate yields a new metal alkylidene. While the new metal alkylidene is larger due to the inclusion of the monomer, the reactivity towards other monomer molecules remains similar to that of the original metal alkylidene complex. As a result, the propagation process consists of a series of analogous steps, until such a point where polymerisation ends. This termination can be brought about by complete consumption of the monomer, or by deliberately terminating the reaction. In ROMP, the reaction can be terminated via the addition of a particular reagent. The reagent could have two specific roles; to selectively remove the transition metal complex from the end of the polymer chain and to incorporate an easily traceable functional group in its place.²⁵

The ROMP process allows a route to prepare complicated polymers, which might not be possible using other traditional polymerisation techniques.

1.3.3 Living Ring-Opening Olefin Metathesis Polymerisation

ROMP in most cases is a living process and results in polymers with high levels of structure and molecular weight control, whilst retaining very low polydispersity. The

terms “living polymerisation” and “living polymer” were introduced by Szwarc following his ground breaking work on anionic polymerisation in 1956.^{26,27} As stated by Szwarc, a living polymerisation proceeds “without chain transfer or termination”.²⁸ Living polymerisations can afford polymers with narrow weight distributions. These can be determined by considering the polydispersity index (PDI) of the sample,

$$\text{PDI} = M_w/M_n$$

Where M_w represents the weight averaged molecular weight and M_n the number averaged molecular weight. In living polymerisations, the molecular weight is directly proportional to amount of monomer converted to polymer, as all the polymeric chain ends are effectively growing at the same rate. The degree of polymerisation is essentially the average number of monomer units per polymer chain, and it is obtained by the ratio of M_n to molecular weight of the monomer unit.

Control over the polymerisation is the best achieved when the rate of initiation is greater than or similar to the rate of propagation. When fulfilled, the results are the formation of well-defined, monodispersed materials.²⁹

1.4 ROMP Initiators

1.4.1 Ill-defined initiators

It was found that polymers could be formed from ROMP of norbornene using heterogenous initiators based on various transition metal (Ti, Mo, W) halides.^{30,31} In addition, the polymerisation could be enhanced by the introduction of Lewis acidic co-catalysts (Ph_4Sn or Me_4Sn).³²

1.4.2 Well-defined initiators

Though the ill-defined initiator systems did not to give living polymerisations and did not tolerate functional groups, they did provide a valuable insight into the mechanism of ROMP and provided a platform for the development of better defined initiators.³²

1.4.2.1 Titanium-based initiator

The first well-defined initiators for ROMP were based on titanium alkylidenes. Ti initiator provided polymers with narrow polydispersities ($PDI < 1.2$) and molecular weights that were directly proportional to the amount of monomer consumed. However, the initiator suffered from tolerance of the functional groups.³³

The initiator was also found to be reactive towards aldehydes and ketones, which offer a simple way of concluding the ROMP process if needed.³⁴

1.4.2.2 Tungsten- and molybdenum-based initiators

By the late 1980's, Schrock began the development of better defined initiators designed to polymerise strained cyclic olefins and focused on alkylidene complexes based on the structure $M(CH^tBu)(NAr)(O^tBu)$ (where, $M=W$ or Mo , Ar is diisopropylphenyl) (Fig. 1.6).³⁵

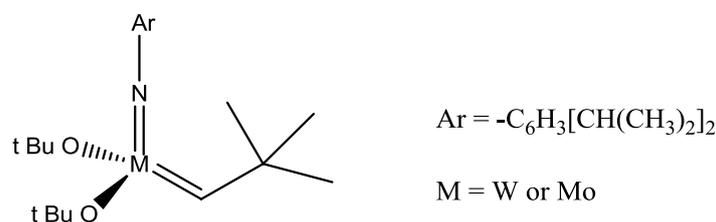


Figure 1.6: The structure of $M(CH^tBu)(NAr)(O^tBu)$

The W-based complex was found to be a good initiator for ROMP of norbornene and polydispersities as low as 1.03 was achieved.³⁶ The ROMP reaction was quenched with benzaldehyde. The tolerance of ROMP initiator towards functional groups was further improved by the development of molybdenum alkylidene complexes. The initiators were found to tolerate a great array of functionalities including molybdenum esters, carbonates, ethers imides, cyano and halo containing groups.³⁷ Another advantage of the Mo initiator was that they were more stable towards decomposition and secondary metathesis reactions than their tungsten analogue.

1.4.2.3 Ruthenium-based initiators

Ruthenium initiators were found to have better functional group tolerance relative to titanium, tungsten and molybdenum based initiators.³⁸ Ruthenium initiator can be used for ROMP of monomers that possess an alcohol, carboxylic acid or an aldehyde. Moreover, the polymerisations could take place in aqueous or protic media.³⁹

The first example of a well-defined Ru complex reported for ROMP was $(PPh_3)_2Cl_2Ru=CH-CH=CPh_2$.⁴⁰ The stability was remarkable; being stable for many weeks in dry and degassed solvents and indefinitely in the solid state. The complex was shown to perform ROMP of norbornene in a living manner.

Although, the initiator was shown to limit secondary metathesis reactions and displayed a large tolerance towards functionality, it was not a very active for ROMP. As a result, the spotlight shifted towards the alteration of ligands on the metal centre to create a more active initiator. It was found that replacement of PPh_3 ligands by bulky, electron rich ligands such as PCy_3 paved the way for more active initiators.⁴¹

Grubbs 1st generation initiator (G-I) was found to be more stable and more tolerant of functional groups than its predecessors (Fig. 1.7). Although these catalysts were shown to ROMP norbornene, the control they showed over the polymerisation was limited.⁴² The complex polymerised a variety of functionalised norbornenes and cyclobutenes in a living fashion, displaying low polydispersities.⁴³

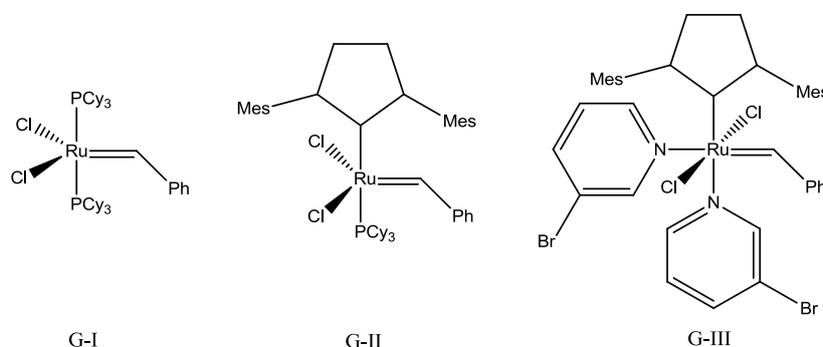


Figure 1.7: Grubbs 1st (G-I), 2nd (G-II), and 3rd (G-III) generation catalyst, (PCy_3 =tricyclohexylphosphine, Mes=2,4,6-trimethylphenyl)

Grubbs 2nd generation initiator (G-II) utilises N-heterocyclic carbenes (Fig. 1.7). These ligands are known to be strong σ -donors, but also less labile than phosphines. Consequently, the ligand is less likely to dissociate from the catalyst, but also stabilises intermediates through possession of a greater electron density.

In some cases, the high steric hindrance present in macromonomers can hinder ROMP initiated by G-I resulting in slow and incomplete polymerisation.⁴⁴ However, this steric hindrance become beneficial for polymerisations initiated by G-II because it lowers k_p relative to k_i and suppresses chain transfer reactions, resulting in well-controlled polymerisations.⁴⁵

The replacement of PCy₃ ligand with two pyridine ligands, in particular 3-bromopyridine (3-BrPyr) in G-II, gave Grubbs 3rd generation initiator (G-III) (Fig. 1.7). Grubbs 3rd generation initiator exhibits high reactivity, fast initiation and high functional group tolerance. In contrast to G-II, the polymerisations, performed by Grubbs-III complex, exhibit much higher values of k_i relative to k_p and result in the formation of polymers with narrow molecular weight distributions (PDI of ~ 1.05).⁴⁶

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1.5 Thermosetting ROMP materials

ROMP, initiated by well-defined ruthenium initiators, has been shown to display excellent functional group tolerance and allow the synthesis of well-defined polymers with controlled architectures, molecular weights, polydispersities, and terminal functionalities. The ROMP process has also been utilised for the formation of thermosetting materials.

Polydicyclopentadiene, widely used in industrial moulding processes and also in heavy machinery manufacturing applications, is a cross-linked polymer yielded by the ROMP of dicyclopentadiene.⁴⁸ Although the polymer is easily produced and possesses good mechanical properties, the ROMP is exothermic and the cross-linking is difficult to control which limits the mechanical properties of the polymer.⁴⁹ (Fig. 1.8)

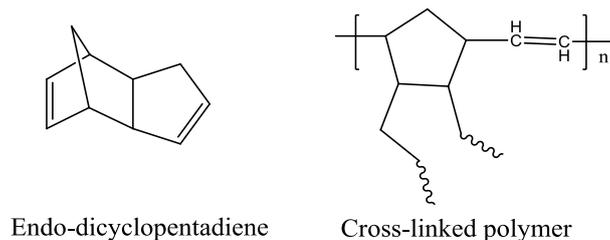


Figure 1.8: The structures of endo-dicyclopentadiene and cross-linked polymer

ROMP processing techniques have also been developed for the synthesis of thermosetting materials with well-defined cross-linked networks from mixtures of mono-functional and di-functional norbornene dicarboxyimide monomers (Fig. 1.9) using ruthenium initiators for applications in Resin Transfer Moulding (RTM) (scheme 1.4) and Reaction Injection Moulding (RIM). By this ROMP processing technique, an excellent level of control over crosslink density and hence over material properties has been achieved. The cross-linked materials produced show high values of yield strength and toughness, which are either comparable or better than the engineering polymer materials, such as polycarbonates which are not easy to synthesize and process.⁴⁹

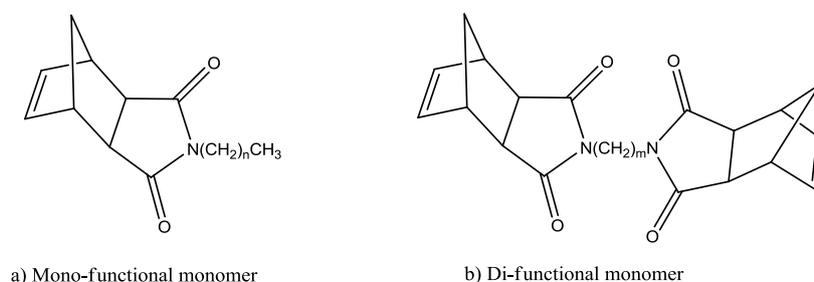
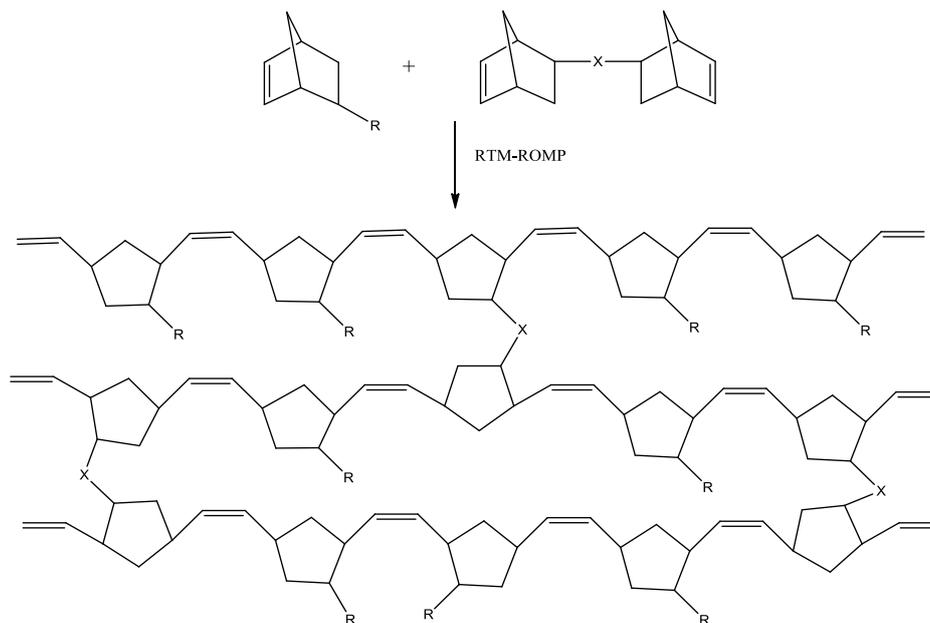


Figure 1.9: Mono-functional *N*-alkyldicarboxyimidonorbornenes and di-functional bis(alkyldicarboxyimidonorbornenes)



Scheme 1.4: RTM-ROMP processing of mono- and di-functional norbornene derivatives giving rise to the synthesis of well-defined cross-linked polymers

1.6 Rheological analysis

Rheological analysis is investigated by dynamic mechanical analysis (DMA) which is a technique used to study and characterise materials. It is most useful for studying the viscoelastic behaviour of polymers. A sinusoidal strain is applied and the stress in the material is measured, allowing one to determine the complex modulus. The temperature of the sample or the frequency of the strain are often varied, leading to variations in the complex modulus; this approach can be used to locate the glass transition temperature (T_g) of the material, as well as to identify transitions corresponding to other molecular motions. There are two kinds of sweep, which are temperature sweep and frequency sweep. Temperature sweep is a common test method that involves measuring the complex modulus at constant frequency while varying the sample temperature, usually at a constant gradient. A prominent peak in $\tan\delta$ (phase angle) appears at the T_g of the polymer. Frequency sweep is that a sample can be held to a fixed temperature and can be tested at varying frequency.

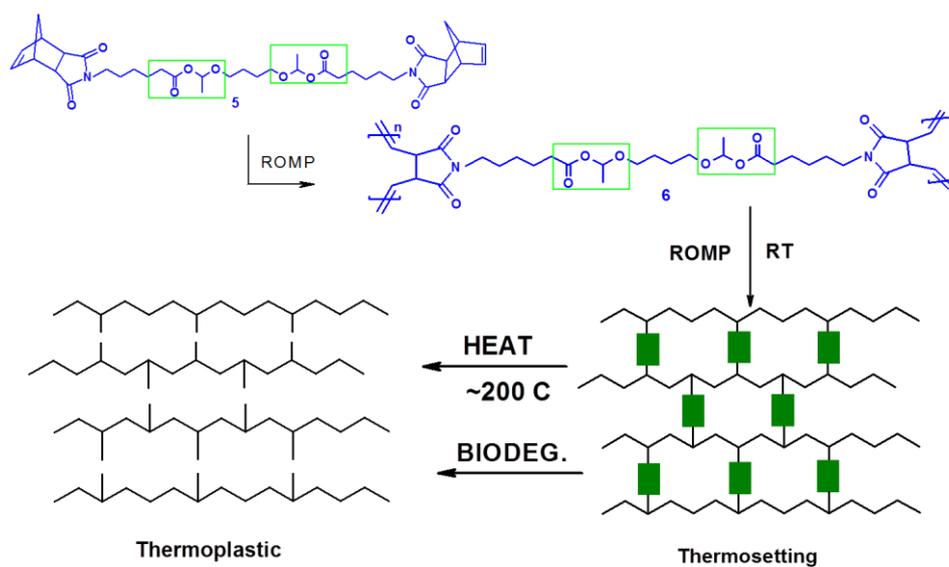
1.7 The aim of this project

Several research groups have reported epoxy-based thermosetting materials containing ester, carbamate and carbonate linkages. The degradation temperature for these resins is reported to be around 350°C. Although these materials might have potential application as re-workable adhesives, they are not biodegradable. Moreover, the resins exhibit 100% weight loss at temperature between 250°C and 350°C which prevent the recycling of the materials into useful products.

The well-defined cross-linked materials synthesized previously by ROMP from the mixtures of mono-functional and di-functional norbornene dicarboximide monomers were very thermally stable, degrading above 400°C.⁵²⁻⁵⁴ So these materials are not ideal as re-workable adhesives and above all they are not biodegradable.

Therefore, the aim of this project was to design and synthesise a range of well-defined thermosetting ROMP materials that are thermally degradable, biodegradable and recyclable. The crucial part of the design of these thermosetting materials was the thermal breakdown or biodegradation of only the linkages, leaving the main chains intact. This would also allow the transition from thermosetting to thermoplastic facilitating the recycling.

We therefore decided to synthesise thermosetting ROMP materials based on poly(norbornene dicarboximide) networks containing acetal ester linkages, Scheme 1.5.⁵⁵ It was anticipated that the combination of well-defined ROMP process and thermal degradation and biodegradability potential of acetal ester groups would enable us to achieve the overall aims of the project.



Scheme 1.5: Schematic representation of the aim of the project

Chapter 2

Synthesis and characterisation of monomers

2.1 Introduction

The focus of this chapter is on the synthesis of di-functional monomers. They are synthesised in three steps. The first step is a Diels-Alder cycloaddition reaction of maleic anhydride and di-cyclopentadiene to give a mixture of exo- / endo-norbornene-5,6-dicarboxyanhydride. This is followed by recrystallization in acetone for several times to give pure exo-norbornene di-carboxyanhydride. The second step is the reaction of the pure exo-anhydride with 6-aminocaproic acid. The third step is the reaction of exo-norbornene imidocaproic acid and 1,4-butanediol divinyl ether.

2.2 Materials and Instrumentation

Maleic anhydride, 1,2-dichlorobenzene, dicyclopentadiene, 6-aminocaproic acid (>99%), 1,4-butanediol divinyl ether (98%), 4-methoxyphenol (99%), amberlyst A21 free base, and 1,2-dichlorobenzene were purchased from Aldrich and used as supplied.

Dichloromethane (DCM) (Analytical Grade, Fisher Scientific), chloroform (HPLC grade, 99.5%, fisher scientific), acetone (analytical grade, fisher scientific), ethyl acetate (analytical grade, fisher scientific) were used as supplied.

Dry toluene was acquired from the departmental solvent purification system.

All monomer synthesis reactions were carried out under an atmosphere of nitrogen.

NMR spectra were either recorded on a Bruker Avance 400 spectrometer at 400.0MHz (^1H) and 100.6MHz (^{13}C); or a Varian Inova 500 spectrometer at 499.8MHz (^1H , COSY, HSQC) and 125.7MHz (^{13}C). All chemical shifts were referenced to the residual proton impurity of the deuterated solvent, CDCl_3 , unless otherwise stated.

2.3 Gel content determination

The gel content of the cross-linked materials were determined by sol-gel extractions.

The cross-linked materials were weighed before extraction to get the initial weight, W_{initial} . The cross-linked polymer was cut into pieces and transferred into a flask equipped and DCM (10ml) was added. The mixture was refluxed for 6 hr. The solid polymer was recovered by filtration. The product was dried in a vacuum oven for 24 hr at 50°C. The product was weighed again after dry to get the final weight, W_{final} . The gel content was therefore calculated by:

$$\text{Gel content (\%)} = \frac{W_{\text{final}}}{W_{\text{initial}}} \times 100$$

2.4 Synthesis of monomers

2.4.1 Mono-functional monomers

Mono-functional monomer 1 (MFM1) and mono-functional monomer 2 (MFM2) used in this work were supplied by EK's group. The structures of mono-functional monomers are shown in figure 2.1. MFM1 and MFM2 were characterised by ^1H NMR and ^{13}C NMR.

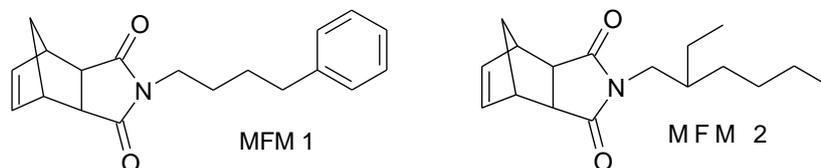
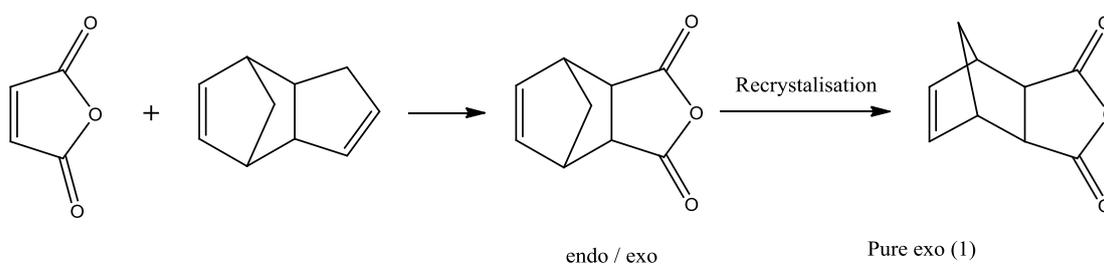


Figure 2.1: Structure of mono-functional monomers used in the project

2.4.2 Di-functional monomer

2.4.2.1 Synthesis of exo-norbornene-5,6-dicarboxy anhydride (I).



Scheme 2.1: Reaction scheme for the formation of the exo-anhydride (I)

Maleic anhydride (49g, 0.5mol) and 1,2-dichlorobenzene (50ml) were placed in a three necked round bottomed flask fitted with a condenser, a dropping funnel and a stirrer bar. The mixture was heated to 180-185°C and dicyclopentadiene (33g, 0.25mol) was added via the dropping funnel over a period of 2 hr. The colour of solution was changed from clear to light yellow. The mixture was heated to reflux for further 6 hr. After which the solution became brown. After that the mixture was allowed to cool down and the yellow crystals were recovered by filtration. The ^1H nmr spectrum showed the product was essentially a mixture of 71% *exo*- and 29% *endo*-isomer. Therefore, the cured product was recrystallised several times from acetone to obtain 100% pure *exo*-isomer as colourless crystals (27g, 0.16mol, 33% yield, mp = 165-167°C).

^1H NMR, (d_6 -acetone, 500 MHz, δ (ppm)): 6.33 (2H, t, H_1), 3.35 (2H, m, H_2), 3.13 (2H, d, H_3), 1.58 (1H, m, H_4), 1.38 (1H, m, H_5)

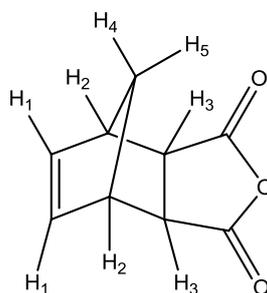


Figure 2.2: Assignment of H atoms in *exo*-anhydride (I)

^{13}C NMR, (d_6 -acetone, 126MHz, δ (ppm)): 173.00 (C_4), 138.68 (C_1), 49.77 (C_3), 47.38 (C_2), 44.59 (C_5).

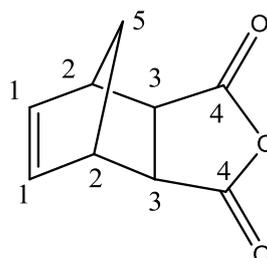
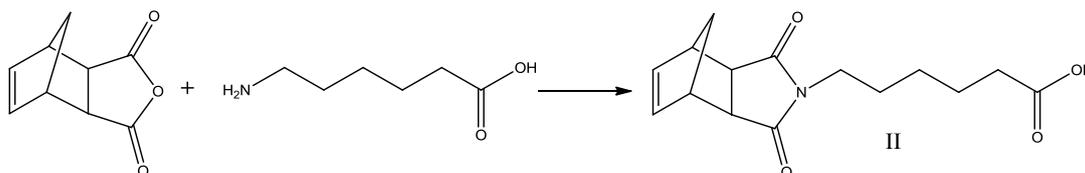


Figure 2.3: Assignment of C atoms in *exo*-anhydride (I)

2.4.2.2 Synthesis of *exo*-norbornene imidocaproic acid (II)

Scheme 2.2: Scheme for the formation of the *exo*-norbornene imidocaproic acid (II)

All glassware were dried in an oven and purged with nitrogen prior to use. *Exo*-norbornene dicarboxylic anhydride (I) (4g, 24.4mmol), 6-aminocaproic (3.5g, 26.9mmol) and a stirrer bar were placed in a two necked round bottom flask fitted with a rubber septum and a reflux condenser. Dry toluene (16ml) was added to the flask by a syringe and the mixture was heated to reflux (115°C) for 17 hr. The reaction mixture was left to cool down to room temperature and the toluene was removed under reduced pressure. The cured product was recrystallized twice in ethyl acetate. The product was dried in a vacuum oven giving the final product as white powder (26.2g, 96.32mol, 89% yield, mp=62-63°C).

^1H NMR, (CDCl_3 , 500 MHz, $\delta(\text{ppm})$): 10.97 (1H, broad, -OH), 6.22 (2H, t, H_1), 3.40 (2H,t, H_4), 3.20 (2H, m, H_2), 2.64 (2H, d, H_3), 2.32 (2H, t, H_8), 1.61 (2H, m, H_7), 1.57 (2H, m, H_5), 1.48 (1H, d, H_9), 1.32 (2H, m, H_6), 1.19 (1H, d, H_{10}).

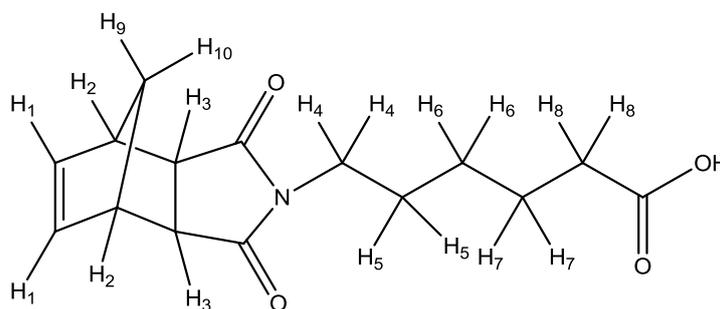


Figure 2.4 Assignment of H atoms in *exo*-norbornene imidocaproic acid (II)

^{13}C NMR, (CDCl_3 , 126 MHz, $\delta(\text{ppm})$): 179.47 (C_{10}), 178.40 (C_4), 138.01 (C_1), 48.00 (C_3), 45.34 (C_2), 42.92 (C_{11}), 38.64 (C_5), 34.03 (C_9), 27.61 (C_6), 26.55 (C_7), 24.37 (C_8).

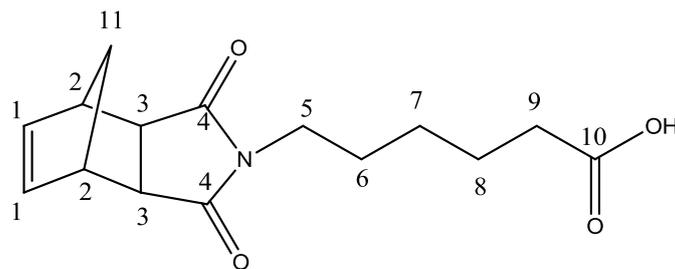
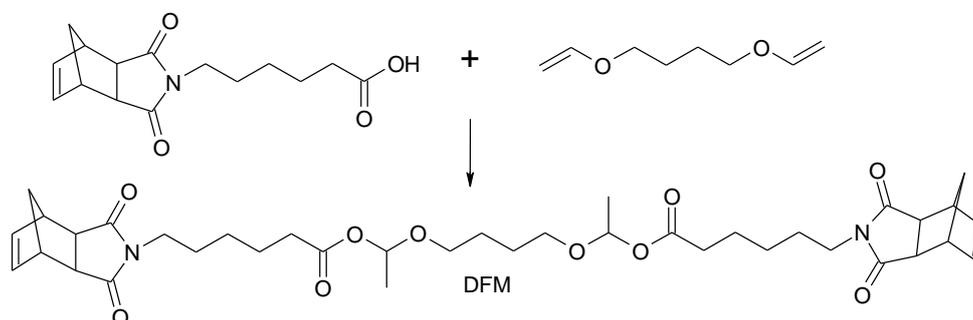


Figure 2.5: Assignment of C atoms in exo-norbornene imidocaproic acid (II)

2.4.2.3 Synthesis of di-functional monomer (DFM)



Scheme 2.3: Reaction scheme showing the formation of DFM

All glassware were dried in an oven and purged with nitrogen prior to use. 1,4-butanediol divinyl ether (2.37g, 16.5mmol), 4-methoxyphenol (0.053g, 0.43mmol) and a stirrer bar were placed into a dry two necked flask fitted with a stopper, and a reflux condenser. The mixture was heated to 90°C and compound II (10g, 36mmol) was added over a period of 2 hr. The clear colour mixture changed into orange upon the addition of the compound II. The mixture was kept refluxing for 21 hr under nitrogen. The reaction mixture was left to cool down to room temperature and toluene (30ml) was added to dissolve the product. Amberlyst A21 free base ion exchange resin (10g) was added, the mixture was thoroughly stirred for 2 hr and the Amberlyst resin was removed by filtration. The toluene was removed under reduced pressure. The product was dried in a vacuum oven, giving a very viscous brown liquid (8.6g, 12.4mmol, 83% yield).

^1H NMR, (CDCl_3 , 500 MHz, $\delta(\text{ppm})$): 6.25 (4H, t, H_1), 5.87 (2H, q, H_{11}), 3.62-3.48 (4H, m, H_{13}), 3.42 (4H, t, H_6), 3.21 (4H, m, H_2), 2.64 (4H, d, H_3), 2.32 (4H, t, H_{10}),

1.61 (4H, m, H₉), 1.60 (4H, m, H₁₄), 1.57 (4H, m, H₇), 1.48 (2H, d, H₄), 1.36 (6H, d, H₁₂), 1.32 (4H, m, H₈), 1.19 (2H, d, H₅).

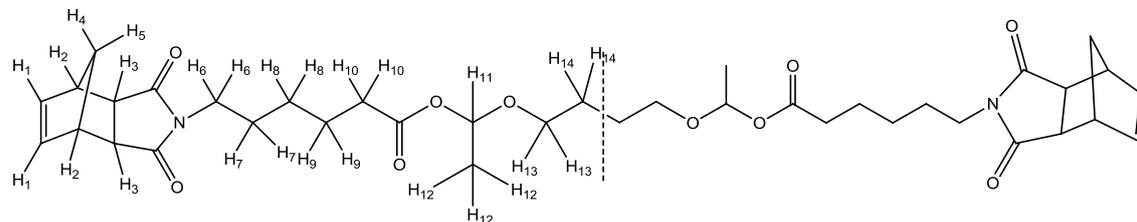


Figure 2.6: Assignment of H atoms in di-functional monomer (DFM)

¹³C NMR, (CDCl₃, 126 MHz, δ(ppm)): 178.25 (C₅), 173.33 (C₁₁), 138.03 (C₃), 96.44 (C₁₂), 68.99 (C₁₄), 48.00 (C₂), 45.36 (C₁), 42.95 (C₄), 38.65 (C₆), 34.46 (C₁₀), 27.66 (C₇), 26.65 (C₈), 26.37 (C₁₅), 24.55 (C₉), 21.01 (C₁₃).

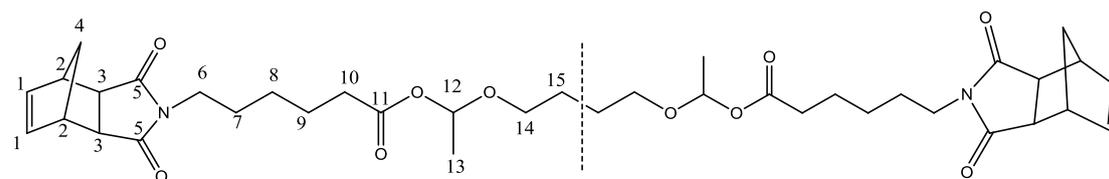


Figure 2.7: Assignment of C atoms in di-functional monomer (DFM)

Chapter 3

Synthesis and characterisation of polymers

3.1 Introduction

The focus of this chapter is on the synthesis of linear polymers via ROMP of mono-functional monomer 1 and 2 and synthesis of cross-linked polymers via co-polymerisation of mono- and di-functional monomers. The thermal degradation behaviour of linear and cross-linked polymers was investigated by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and in the oven.

3.2 Materials and Instrumentation

Mono-functional monomer 1 and 2 (supplied by EK's group), di-functional monomer (prepared in chapter 2), dichloromethane (DCM) (Analytical Grade, Fisher Scientific), chloroform (HPLC Grade, 99.5%, Fisher Scientific), hexane (Analytical Grade, Fisher Scientific), ethyl acetate (Analytical Grade, Fisher Scientific), hydrochloric acid (HCl, 36%, 1.19g/cm³), Grubbs' 1st generation initiator. Dry DCM was acquired from the departmental solvent purification system.

All polymerizations were carried out in an M-Braun glove box.

NMR spectra were either recorded on a Bruker Avance 400 spectrometer at 400.0MHz (¹H) and 100.6MHz (¹³C); or a Varian Inova 500 spectrometer at 499.8MHz (¹H, COSY, HSQC) and 125.7MHz (¹³C). All chemical shifts were referenced to the residual proton impurity of the deuterated solvent, CDCl₃, unless otherwise stated.

Infrared spectra were recorded using a Perkin Elmer RX1 FT-IR machine.

TGA measurements were performed using a Perkin Elmer Pyris 1 TGA in conjunction with a Hiden HPR20, heating from 30 °C to 300 °C at 10 °C/min.

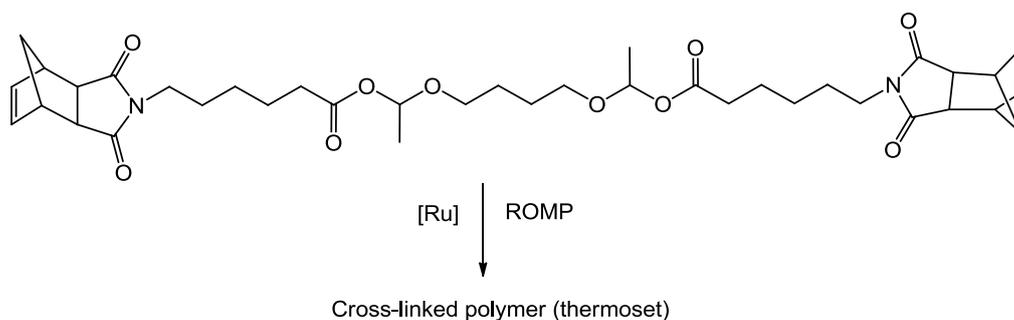
The oven used to investigate the thermal degradability of the materials had a temperature range between 25°C-500°C.

The dynamic mechanical analysis (DMA) was carried out using Texas instrument

AR2000 shear rheology meter.

3.3 Synthesis of polymers

3.3.1 Preparation of cross-linked polymers C4 and C5 from ROMP of di-functional monomer

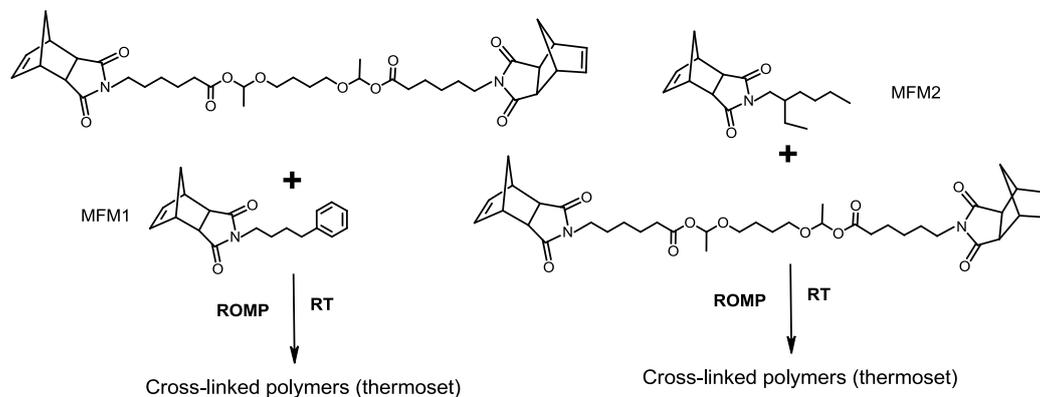


Scheme 3.1: Reaction scheme for the polymerisation of DFM

Di-functional monomer (DFM) (0.422g, 0.606mmol) was dissolved in dry dichloromethane (2ml) in a sample vial. Grubbs' 1st generation catalyst (0.01g, 0.012mmol) was dissolved in dry dichloromethane (0.5ml) in another sample vial containing a stirrer bar. The ratio of monomers to initiator was 50:1. The solution of the monomer was added to the solution of initiator, and stirring commenced. The polymer was formed in the vials. DCM was removed under reduced pressure resulting cross-linked material C4. Gel content was found to be 83%.

Cross-linked material C5 was prepared in a similar manner using di-functional monomer (0.835g, 1.2mmol) and ruthenium initiator (0.01g, 0.012mmol). The ratio of monomer to initiator was 100:1. The gel content of 5 was found to be 78%.

3.3.2 Preparation of cross-linked materials (C6-19) from the co-polymerisation of di-functional and mono-functional monomer



Scheme 3.2: Scheme of co-polymerisation of DFM and MFM

DFM (0.313g, 0.45mmol) and MFM 1 (0.044g, 0.15mmol) were dissolved in dry dichloromethane (3ml) in a sample vial. Grubbs' 1st generation catalyst (0.01g, 0.012mmol) was dissolved in dry dichloromethane (0.5ml) in another sample vial containing a small stirrer bar. Then the solution of the monomers was added to the solution of initiator. Polymer was formed. Dichloromethane was removed under reduced pressure giving cross-linked materials C6. The gel content was found to be 77%. Cross-linked materials C7-13 was prepared similarly using different quantity of MFM1, see table 3.1.

Table 3.1: The quantity of monomer and initiator used in synthesis of cross-linked materials C6-13

Polymer	DFM g, mmol	MFM1 g, mmol	Initiator g, mmol	DFM:MFM1	Gel content %
C6	0.313, 0.45	0.044, 0.15	0.01, 0.012	75:25	77
C7	0.209, 0.30	0.088, 0.30	0.01, 0.012	50:50	81
C8	0.104, 0.15	0.133, 0.45	0.01, 0.012	25:75	82
C9	0.626, 0.9	0.088, 0.3	0.01, 0.012	75:25	89
C10	0.418, 0.6	0.177, 0.6	0.01, 0.012	50:50	74
C11	0.209, 0.3	0.266, 0.9	0.01, 0.012	25:75	77
C12	0.24, 0.34	0.90, 3.06	0.01, 0.012	10:90	85
C13	0.12, 0.17	0.95, 3.23	0.01, 0.012	5:95	74

Cross-linked materials C14-19 were prepared by a similar technique using different quantities of MFM2, see table 3.2.

Table 3.2: The quantity of monomer and initiator used in synthesis of cross-linked materials C14-19

Polymer	DFM g, mmol	MFM2 g, mmol	Initiator g,mmol	DFM:MFM2	Gel content %
C14	1.305, 1.875	0.172, 0.625	0.04125, 0.05	75:25	82
C15	0.87, 1.25	0.344, 1.25	0.04125, 0.05	50:50	86
C16	0.435, 0.625	0.516, 1.875	0.04125, 0.05	25:75	71
C17	1.305, 1.875	0.172, 0.625	0.0206, 0.025	75:25	83
C18	0.87, 1.25	0.344, 1.25	0.0206, 0.025	50:50	82
C19	0.435, 0.625	0.516, 1.875	0.0206, 0.025	25:75	79

3.3.3 Synthesis of linear polymer L20-23.

Mono-functional monomer MFM1 and MFM2 were subjected to ROMP using Grubbs 1st generation ruthenium initiator to prepare linear polymer L20-23. The quantities of monomers and initiator used are shown in table 3.3.

Table 3.3: The quantity of monomer and initiator used in synthesis of linear materials L20-23

Linear Polymer	MFM1 g, mmol	MFM2 g, mmol	Initiator g, mmol
L20	1.000, 3.40		0.0561, 0.068
L21	1.000, 3.40		0.0281, 0.034
L22		1.000, 3.6	0.060, 0.076
L23		1.000, 3.6	0.030, 0.036

In a typical polymerisation reaction a known monomer (known amount) were dissolved in dry dichloromethane (2.0ml), initiator (known amount) was dissolved in dry DCM (0.5ml) in another sample vial containing a small stirrer bar. The monomer solution was added to the vial containing initiator and stirred for 12 hr.

Ethyl vinyl ether (10 fold excess with respect to initiator) was added and the mixture was stirred for further 1 hr. The reaction mixture was then added drop-wise to hexane (10 fold excess). The polymer precipitated which was filtered and dried in an oven to obtain the linear polymer L20-23.

3.4 Thermal degradation of polymer samples

The polymer was weighed and placed in the oven at 300 °C for two hours. The product cooled down to room temperature and weighed again to calculate the weight loss (Table 3.4).

Table 3.4: Thermal degradation result in oven at 300 °C for 2 hr

Sample	DFM %	Before heated mg	After heated mg	Weight loss mg (%)
C4	100	51	33	17.1(34)
C6	75	50	33.5	16.5(33)
C7	50	53.5	42.3	11.2(21)
C8	25	50.6	42.3	8.3(16)
L20	0	51.2	49.7	2.5(5)
C5	100	196.7	127	69.7(35)
C9	75	201.7	133	68.7(34)
C10	50	198.3	141	57.4(29)
C11	25	204.3	165	39.2(19)
C12	10	50.3	44.2	6.04(12)
C13	5	49.8	46.3	3.5(7)
L21	0	48.7	46.3	2.4(5)
C14	75	51.45	35	16.5(32)
C15	50	52.63	37.89	14.7(28)
C16	25	49.89	38.91	10.9(22)
C17	75	53.84	35.53	18.3(34)
C18	50	54.23	37.96	16.3(30)
C19	25	52.85	42.28	10.6(20)

The colour of the samples changed from yellow to black. The product was transferred to a vial and dichloromethane (10ml) was added to test the solubility. The product did not dissolve completely. The mixture was filtrated. The solvent was removed under reduced pressure and a brown solid was obtained. The solid was subjected to ^1H NMR analysis.

3.5 Hydrolysis of cross-linked polymer in hydrochloric acid

3.5.1 Sample preparation

The sample was prepared as a film using a 4cm×5cm Teflon mould. DFM (0.5g, 0.7mmol) and MFM (1.1g, 3.8mmol) were dissolved in dry dichloromethane (1ml) in a sample vial. Grubbs' 1st generation catalyst (0.037g, 0.045mmol) was dissolved in dry dichloromethane (0.5ml) in another sample vial containing a stirrer bar. The ratio of monomers to initiator was 100:1. The solution of the monomer was added to the solution of initiator, and stirring commenced. Immediately, the mixture was injected into a Teflon mould. The polymer was formed in the mould. The mould was left in for dichloromethane to evaporate. The mould then was transferred into a vacuum oven to dry at 50°C for 12 hr. The polymer film formed in the mould.

3.5.2 Hydrolysis test

Table 3.5: Weight loss of the samples during hydrolysis

Sample code	DFM %	Before hydrolysis mg	After hydrolysis mg	Weight loss %
C5	100	94.7	54.9	42
C9	75	99.2	59.2	41
C10	50	379.4	231.4	39
C11	25	501.6	316	37
C12	10	98.6	67.0	32
L21	0	97.8	93.9	4

The degradation of linear and cross-linked materials by acid hydrolysis was investigated. In a typical test, polymer films (known amount) were put into a two necked round bottom flask equipped with a reflux condenser and a stirrer bar. HCl (30ml, pH=3.4) was added and the mixture was refluxed for 24 hr. The flask was cooled down to room temperature. Some small bubbles were observed on the surface of films. The polymer was recovered by filtration, and washed by pure water 3 times. The product was dissolved in DCM and precipitated in hexane. The final product was dried in the vacuum oven. The dried product was weighed to calculate the weight loss.

3.6 Rheological analysis

3.6.1 Sample preparation

The polymer samples were compression moulded at 150 °C into 25mm diameter disks, 1mm thick, to be used with 25mm parallel plate geometry. The samples were annealed at 150 °C for 30 minutes.

3.6.2 Frequency sweep

The material rheology was measured using a TA-AR2000 (Texas instruments) shear rheometer fitted with 25mm parallel plates. Sample degradation was tested and found to not be significant for times up to 4 hours.

A sample could be tested at varying frequency while the temperature was fixed. All the samples were tested at 100°C, 130°C, 160°C, and 190°C. At each temperature, the frequency was varied from 0.01Hz to 100Hz sampling 10 points per decade. And the shear stress was measured at each frequency.

If the sample was subjected to an applied strain; $\gamma = \gamma_0 \sin(\omega t)$. The storage modulus shear stress in phase with the strain, representing an elastic response, and the loss modulus measures the shear stress in phase with the strain-rate, representing a viscous response. The shear storage and loss moduli are defined as follows:⁶⁸

$$\text{Storage Modulus: } G' = \frac{\sigma_0}{\gamma_0} \cos(\delta)$$

$$\text{Loss Modulus: } G'' = \frac{\sigma_0}{\gamma_0} \sin(\delta)$$

$$\text{Phase angle, Tan } (\delta): \tan \delta = \frac{G''}{G'}$$

3.6.3 Temperature sweep

A common test method involves measuring the complex modulus at constant frequency (here 1Hz) while varying sample temperature at a constant negative ramp (here -2 °C/min). In this test mode, δ , where $\tan\delta = G''/G'$, was measure at different

temperatures. A prominent peak in δ appears at the T_g of the polymer.

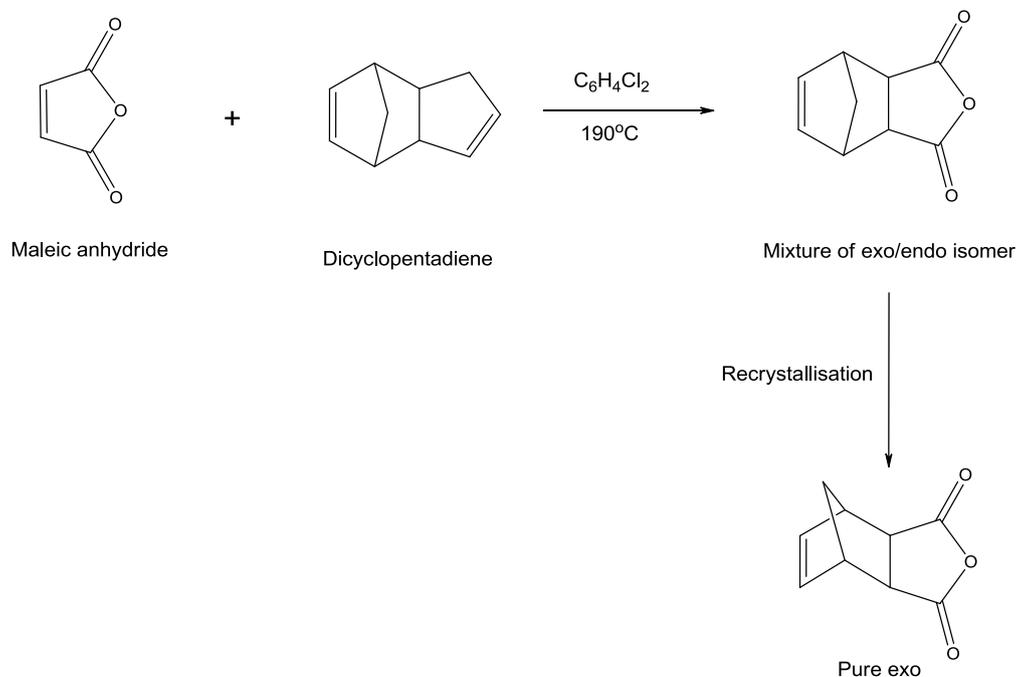
Chapter 4

Results and discussion

4.1 Monomer synthesis

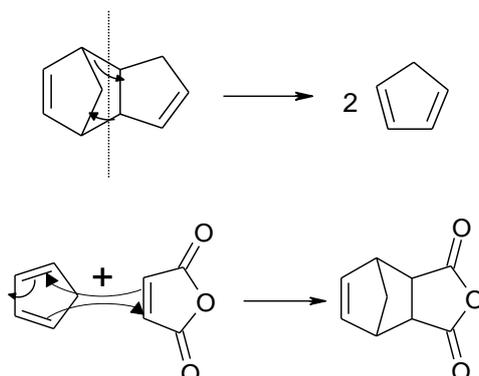
4.1.1 Synthesis of *exo*-norbornene-5,6-dicarboxy anhydride (I)

Pure *exo*-norbornene dicarboxy anhydride was prepared following scheme 4.1.



Scheme 4.1: synthesis route for exo-norbornene-5,6-dicarboxy anhydride (I)

The Diels-Alder reaction between maleic anhydride and dicyclopentadiene was carried out at $190^\circ C$.



Scheme 4.2: The Diels-Alder reaction

The dicyclopentadiene was cracked into cyclopentadiene at the reaction temperature, which then reacted with maleic anhydride to result in a mixture of *exo*/*endo*

nobornene anhydride isomers, scheme 4.2. A temperature above 180 °C was necessary for this reaction in order to obtain more thermodynamically favoured exo-anhydride isomer.

Exo/endo norbornene anhydride was characterised by ^1H NMR in acetone- d_6 and the spectrum is shown in figure 4.1.

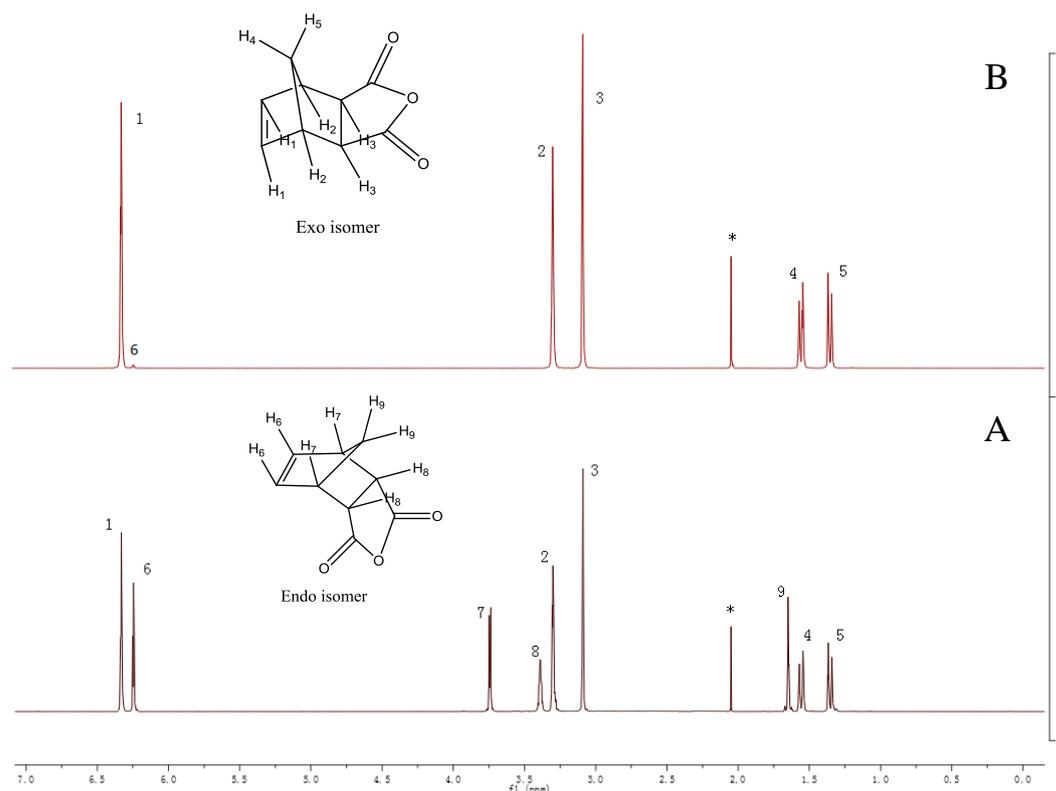


Figure 4.1: ^1H NMR spectrum of exo-(II) and endo-(I) anhydride, in acetone- d_6

A resonance due to exo and endo isomer can be observed, peaks 1-5 and 6-9, respectively (Fig. 4.1.A). The ratio of exo to endo isomer was determined from the ratio of the integration of the resonance due to the olefinic protons of the exo isomer (peak 1) to that of the endo isomer (peak 6). The ratio was found to be 1:0.5, indicating 67% exo and 33% endo isomer.

Although the endo-isomer was preferentially formed in the reaction, unlike exo-isomer it is not very reactive for ROMP using Grubbs' first generation catalyst.

The pure *exo*-isomer was obtained by recrystallization (3 times) from acetone. The ^1H NMR spectrum (Fig. 4.1.B) showed the expected resonance for protons of the *exo*-product. The ratio of the integration of peaks 1 to that of 6 was found to be 1:0.01, indicating the *exo* content of 99%.

The structure of *exo*-isomer was further confirmed by ^{13}C NMR. The ^{13}C NMR spectrum (Fig. 4.2) showed resonance due to the olefinic carbon (a) at 138.68ppm and the carbon (d) at 173.00ppm as expected for pure *exo*-isomer.

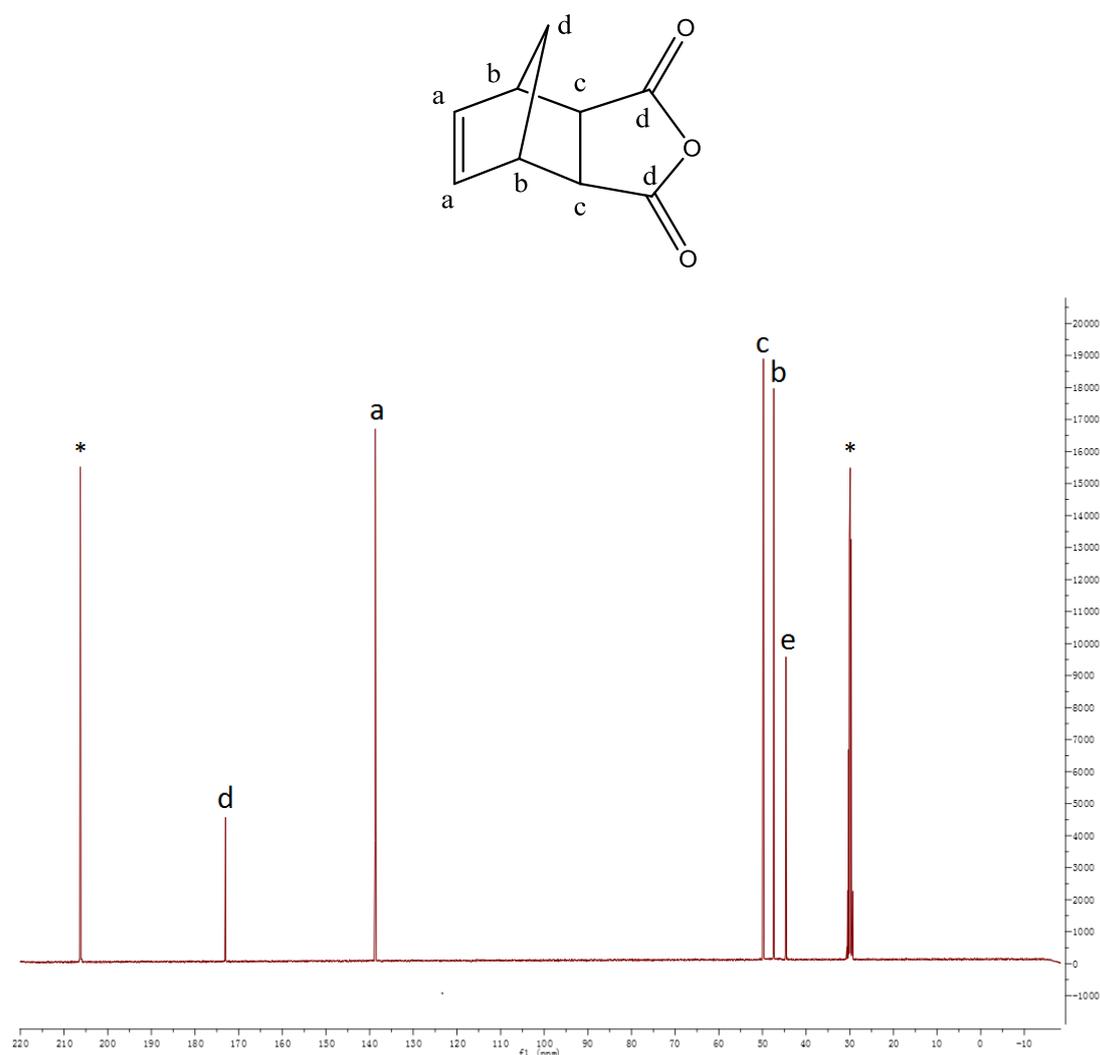
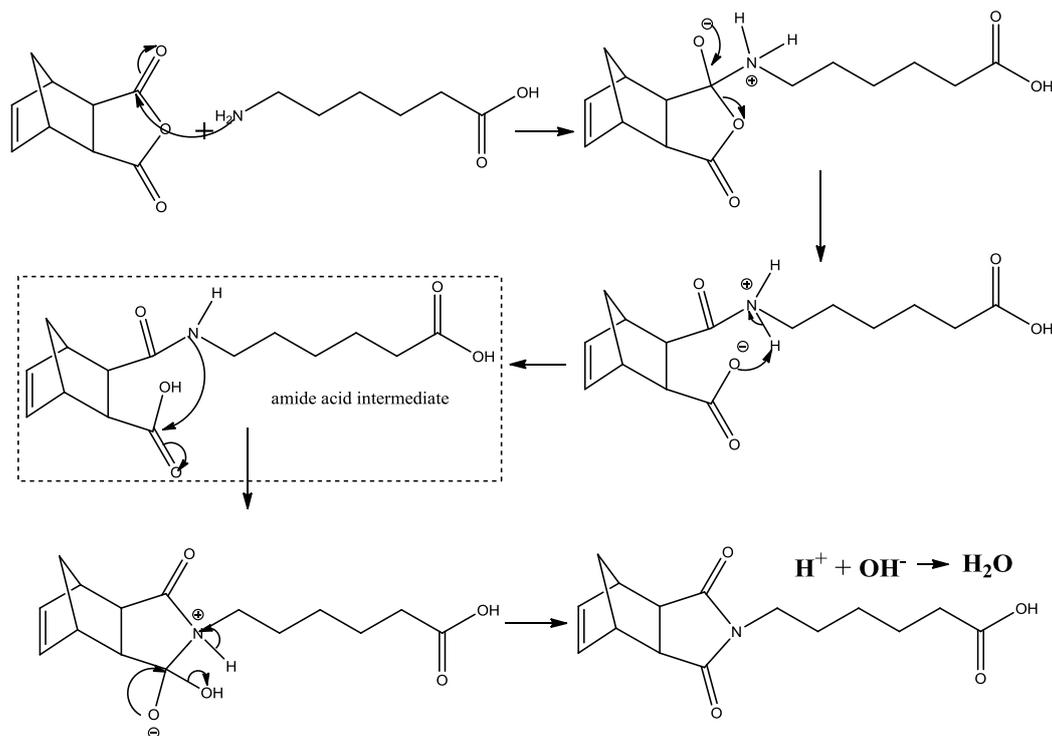


Figure 4.2: ^{13}C NMR spectrum and the structure of *exo*-anhydride, in acetone- d_6

4.1.2 Synthesis of *exo*-norbornene imidocaproic acid (II)

The reaction of *exo*-anhydride norbornene (I) and 6-aminocaproic acid was a one-step reaction in toluene with a yield of 89%. The mechanism of the reaction is shown in scheme 4.3.



Scheme 4.3: Mechanism for the formation of exo-norbornene imidocaproic acid

Both ring opening and ring closing reactions are required before the nitrogen atom can be incorporated into the ring system. The reaction would give amide acid as a crucial intermediate via a ring-opening process. The amide acid intermediate is crucial as it is here that the formation of a good leaving group occurs. In this reaction, the carboxylic acid abstracts a proton from amide creating a good leaving group, H_2O , and thus the ring closing reaction is promoted.

The ^1H NMR spectrum of *exo*-norbornene imidocaproic acid is shown in figure 4.3. All resonances due to the product can clearly be seen in the ^1H NMR spectrum. A resonance due to $-\text{COOH}$ at 11ppm is seen along with the ratio of 1:1 for H_8 : H_1 , indicating the formation of the product. The ratio of the integration of resonance due

to peak 1 and that of peak 4 is 1:1, indicating the formation of dicarboximide (ring has been closed).

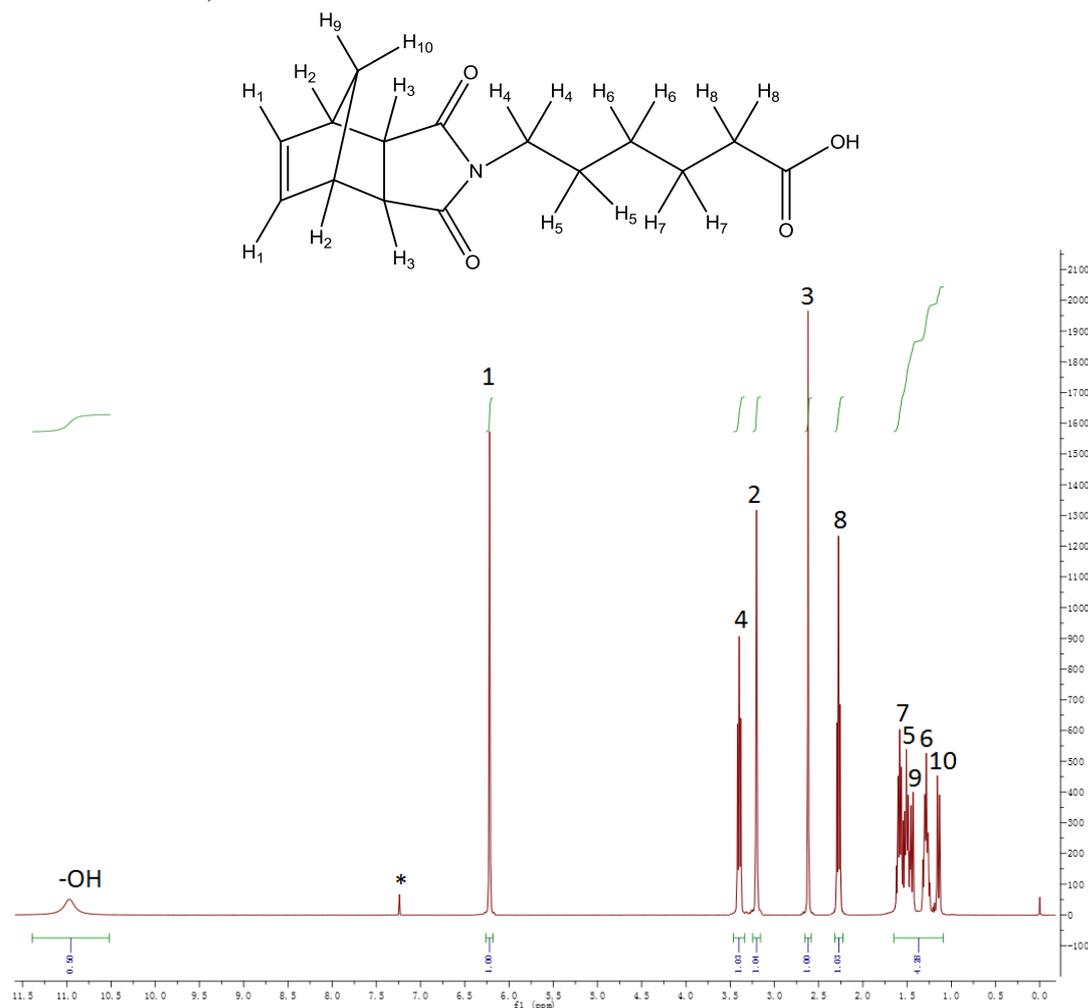


Figure 4.3: ^1H NMR spectrum and structure of *exo*-norbornene imidocaproic acid, in CDCl_3 (II).

The ^{13}C NMR spectrum also shows peaks expected for the product (Fig. 4.4). The spectrum shows characteristic resonance due to $\text{C}=\text{O}$ of the dicarboxylic (d) and the carboxylic acid (j) at 178.40ppm and 179.47ppm, respectively. The olefinic carbon (a) and the $-\text{CH}_2$ next to nitrogen (e) can also be seen at 138.01ppm and 38.64ppm, respectively.

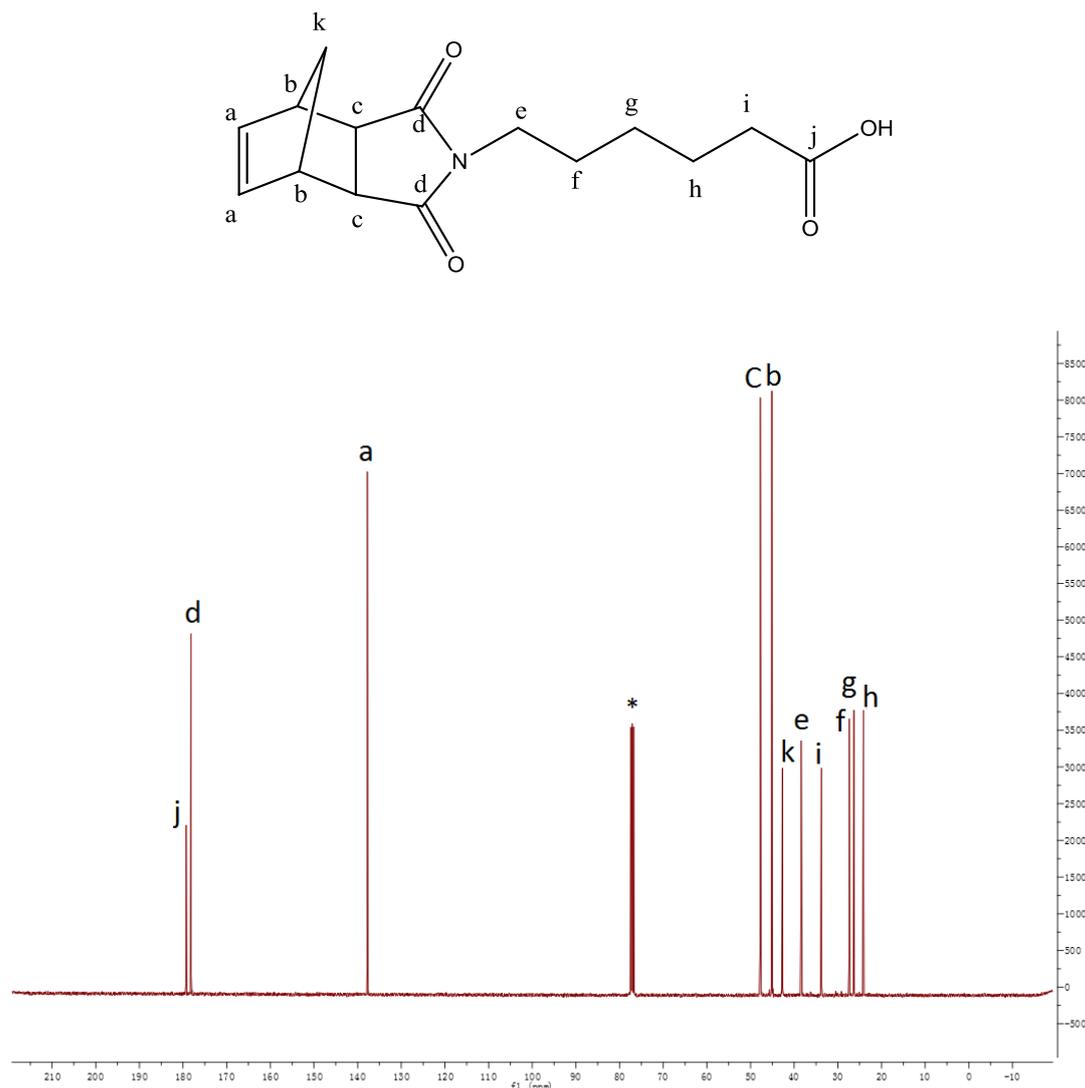


Figure 4.4: ^{13}C NMR spectrum and structure of exo-norbornene imidocaproic acid, in CDCl_3 (II).

4.1.3 Synthesis and characterization of di-functional monomer (DFM)

The di-functional monomer (DFM) containing acetal ester functionalities was synthesised in a one-step neat reaction between exo-norbornene imidocaproic acid (II) and 1,4-butanediol divinyl ether. Exo-norbornene imidocaproic acid (II) possess an obvious acidic character and is able to catalyse the polymerisation of 1,4-butanediol divinyl ether.⁵⁹ In order to prevent the polymerisation of 1,4-butanediol divinyl ether, 4-methoxyphenol was used as inhibitor in this reaction. The pure di-functional monomer (DFM) was obtained in a yield of 83%.

The ^1H NMR spectrum (Fig. 4.5) showed that the product was very pure. The proton spectrum shows clearly resonance due to olefinic protons (H_1) at 6.25ppm. It also shows resonance at 5.87ppm (H_{11}) and 1.36ppm (H_{12}) due to the formation of acetal ester group. The ratio of the integration of resonance due to peak 1 to that of peak 11 and 12 is found to be 4:2 and 4: 6, respectively, indicating the formation of di-functional monomer containing two acetal ester groups as expected.

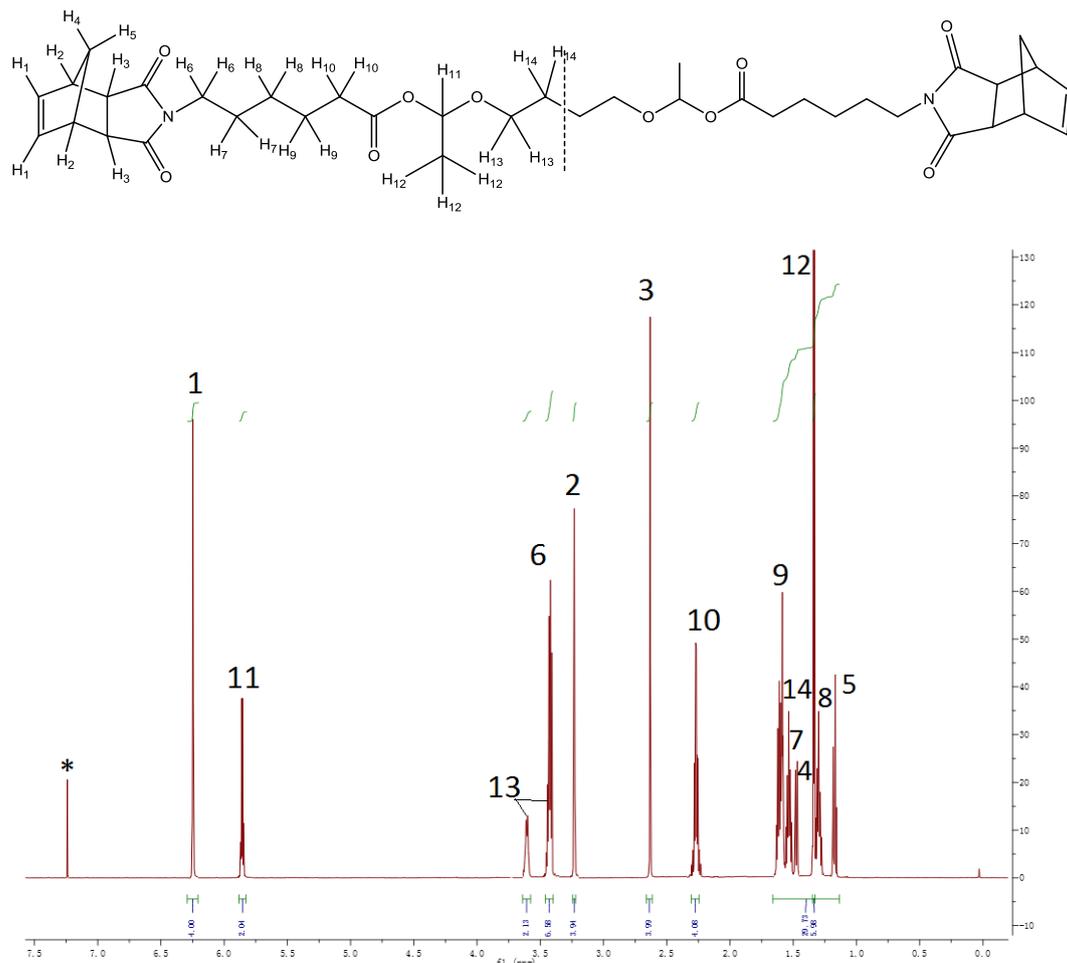


Figure 4.5: ^1H NMR spectrum and structure of DFM, in CDCl_3

The ^{13}C NMR spectrum (Fig. 4.6) shows resonance due to olefinic carbons (a) at 138.03ppm, carbonyl of the dicarboximide (e) at 178.25ppm. It also shows resonance due to carbonyl of the acetal ester group (k) at 173.33ppm. Furthermore, resonance are observed for $-\text{CH}$ (l) and $-\text{CH}_3$ (m) of the acetal ester group at 68.99ppm and 21.01ppm, respectively.

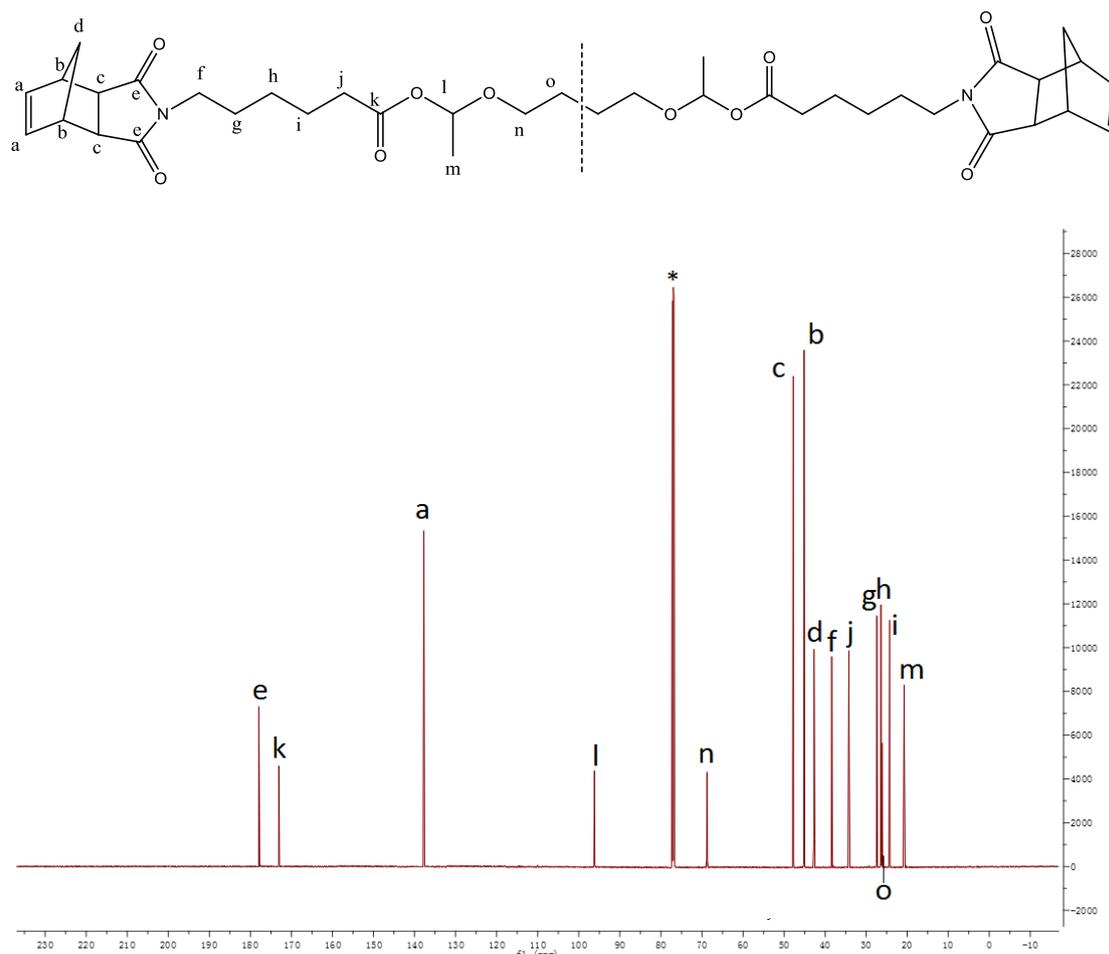
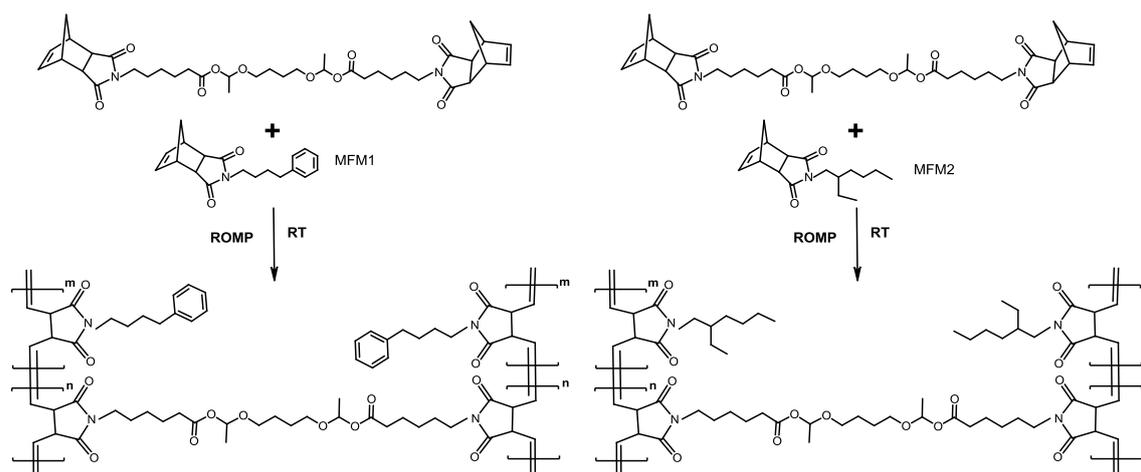


Figure 4.6: ^{13}C NMR spectrum and structure of DFM, in CDCl_3

4.2 Polymer synthesis

All polymers were prepared via Ring Opening Metathesis Polymerization (ROMP) using Grubbs' 1st generation initiator. The di-functional monomer (DFM) and two mono-functional monomers (MFM1 and MFM2) were used in this experiment. DFM was subjected to ROMP to prepare cross-linked materials with a maximum degree of cross-linking.

In order to prepare cross-linked polymer with different degrees of cross-linking, di-functional monomer and mono-functional monomer were co-polymerized in different ratios (scheme 4.4). The linear polymer was also prepared by ROMP of mono-functional monomer to provide samples some comparisons.



Scheme 4.4: Schematic representation of co-polymerisation of DFM and MFM

The summary of homo and cross-linked polymers synthesised for this project are shown in table 4.1.

Table 4.1: Summary of polymers prepared in this project

		Monomers: initiator 50:1	Monomers: initiator 100:1
Cross-linked materials	100%DFM	C4	C5
Cross-linked materials (DFM+MFM1)	75%DFM	C6	C9
	50%DFM	C7	C10
	25%DFM	C8	C11
	10%DFM	N/A	C12
	5%DFM	N/A	C13
Cross-linked materials (DFM+MFM2)	75%DFM	C14	C17
	50%DFM	C15	C18
	25%DFM	C16	C19
Linear homo-polymer (MFM1)		L20	L21
Linear homo-polymer (MFM2)		L22	L23

4.3 Degradation studies

4.3.1 By Thermogravimetric Analysis

4.3.1.1 Weight loss behaviour

The weight loss behaviour for cross-linked samples C4, C6-8 and also linear polymer L20 was investigated by TGA and the TGA thermographs are shown in Fig. 4.7.

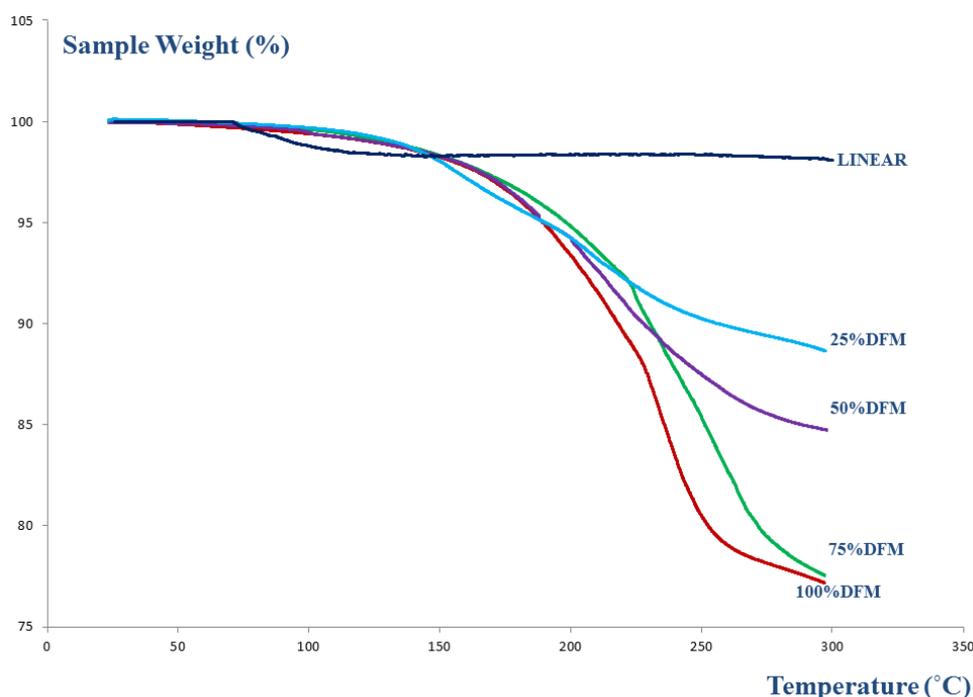


Figure 4.7: TGA thermographs observed for samples C4(100%DFM), C6(75%DFM), C7(50%DFM), C8(25%DFM) and L20(linear polymer).

Table 4.2: Weight loss at 300°C for C4, C6-8 and L20

Samples	C4	C6	C7	C8	L20
DFM %	100	75	50	25	0
Weight loss %	23	22	16	11	2

The percentage weight loss observed during the TGA is shown in table 4.2. The results indicate that the cross-linked material start losing weight at 150°C and the extent of the weight loss at 300°C depends on the level DFM in the samples; the

higher the DMF content the bigger the weight loss. The sample with 100%DMF (C4) show a weight loss of 23% and the weight loss for the sample with 25%DMF content is reduced to 11%. The weight loss is believed to be due to the thermal breakdown of the acetal ester linkages in the cross-linked material as no weight loss was observed for the linear polymer (L20) without any acetyl ester groups. The linear sample only shows 2% weight loss at 100°C due to the moisture in the sample.

The weight loss behaviour for cross-linked samples C5, C9-13 and also linear polymer L21 was investigated by TGA and the TGA thermographs are shown in Fig. 4.8.

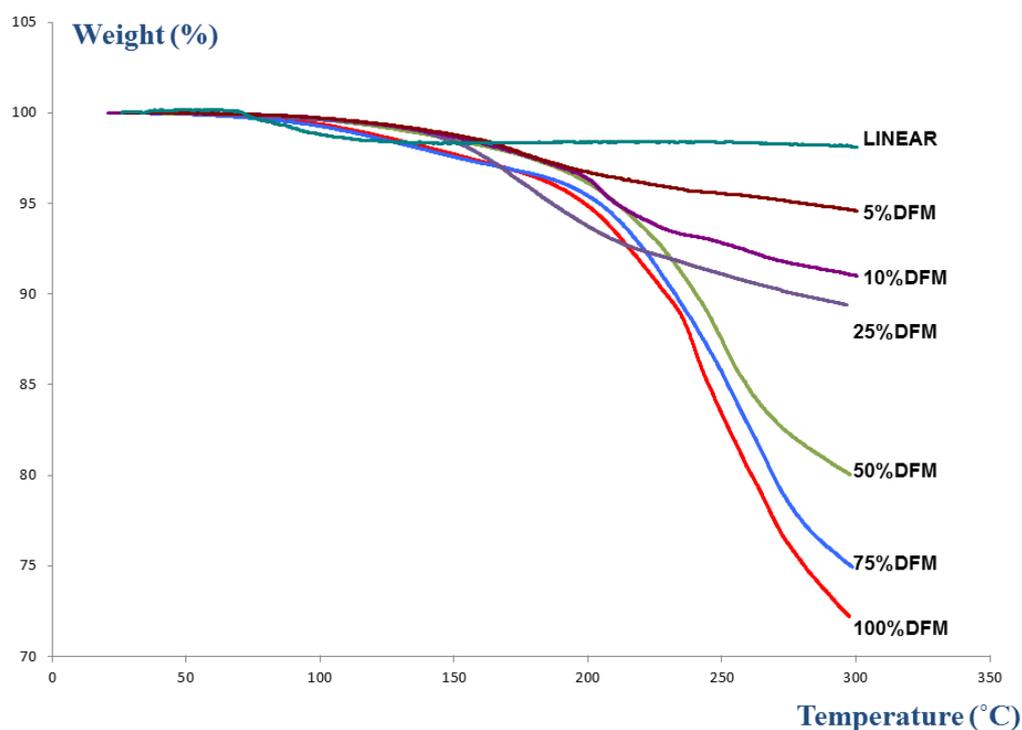


Figure 4.8: TGA thermographs observed for samples C5(100%DMF), C9(75%DMF), C10(50%DMF), C11(25%DMF), C12 (10%DMF), C13 (5%DMF) and L20 (linear polymer).

Table 4.3: The weight loss of C5, C9-C13, L20, and L21 in TGA

Samples	C5	C9	C10	C11	C12	C13	L21
DFM %	100	75	50	25	10	5	0
Weight loss %	28	25	20	9	7	5	2

The percentage weight loss observed during the TGA is shown in table 4.3.

The results also indicate that the cross-linked material start losing weight at 150°C and the extent of the weight loss at 300°C depends on the level of DMF in the samples. The higher the DMF content the bigger the weight loss. The sample with 100%DMF (C5) show a weight loss of 28% and the weight loss for the sample with 5%DMF (C13) content is reduced to 5%. The weight loss is again believed to be due to the thermal breakdown of the acetal ester linkages in the cross-linked material as no weight loss was observed for the linear polymer (L21) without any acetyl ester groups. The linear sample only shows 2% weight loss at 100°C due to the moisture in the sample.

4.3.1.2 Solubility behaviour

Solubility tests were carried out on the cross-linked samples before and after the TGA analysis and the results are shown in table 4.4. The linear materials are completely soluble in DCM and as expected the cross-linked materials are not soluble even at elevated temperature. The cross-linked materials contain acetal ester groups in the network which are expected to breakdown upon heating, Figure4.9.

Table 4.4: The solubility test of cross-linked and linear samples in dichloromethane, before and after TGA

Samples	C4	C6	C7	C8	L20	C5	C9	C10	C11	C12	C13	L21
Solubility before TGA	No	No	No	No	Yes	No	No	No	No	No	No	Yes
Solubility after TGA	No	No	No	No	Yes	No	No	No	No	Partial	Partial	Yes

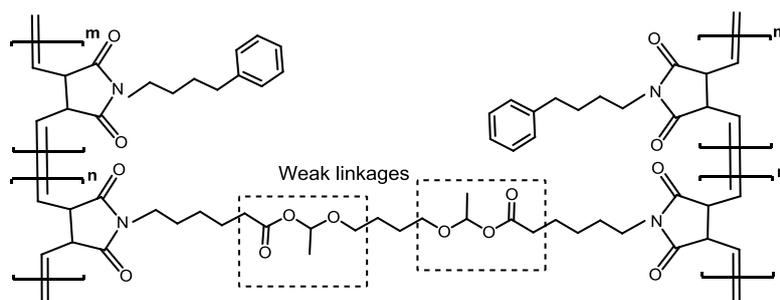


Figure 4.9: The structure of cross-linked materials C4, C6, C7, and C8

The complete breakdown of the acetal ester linkages is anticipated to result in the formation of soluble linear thermoplastic materials. The retrieved materials after the TGA analysis were found to be insoluble in DCM. One plausible reason for the insolubility of materials could be that on the timescale of the TGA measurement there is not enough time for all acetal ester linkages to breakdown.

4.3.1.3 IR investigation

The cross-linked sample C7, containing 50% DFM was subjected to FTIR analysis, before and after TGA, Figure 4.10.

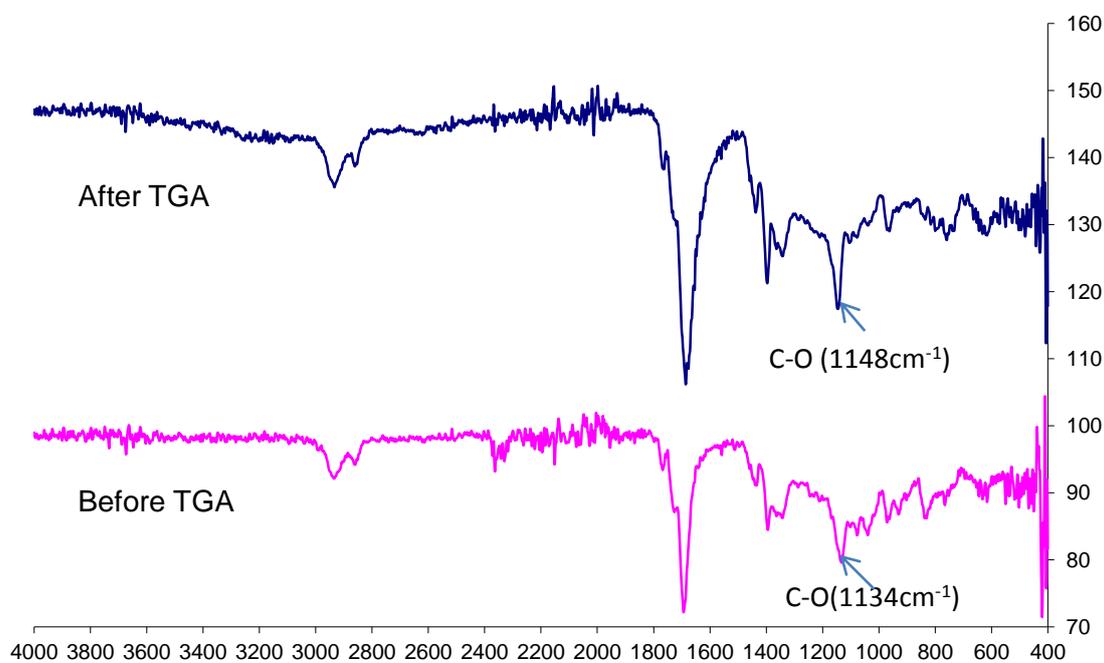


Figure 4.10: FTIR spectra of cross-linked material C7 (50%DFM)

The FTIR spectra show that the C-O vibration at 1134 cm^{-1} to shifted to 1148 cm^{-1} . A considerable reduction in the intensity of C-O bands is also observed for the retrieved materials after the TGA measurement. The reduction is estimated to be about 70% which is comparable to that reported for thermal degradation of maleimide resins containing acetal ester linkages⁸. The presence of the C-O band further confirms that the acetal ester linkages have not been completely broken down.

4.3.2 Oven

The results of TGA investigation showed that the retrieved materials after the TGA analysis remained insoluble in DCM. This was attributed to incomplete breakdown of the acetal ester linkages on the timescale TGA measurements. Therefore the thermal degradation behaviour was investigated in an oven to see the effect of prolonged heating on the degradation of the acetal ester linkages.

4.3.2.1 Weight loss behaviour

The cross-linked materials C4, C6-8 were heated in an oven at 250°C and 300°C for 1-4hr and the resulting weight loss are presented in the Fig. 4.11.

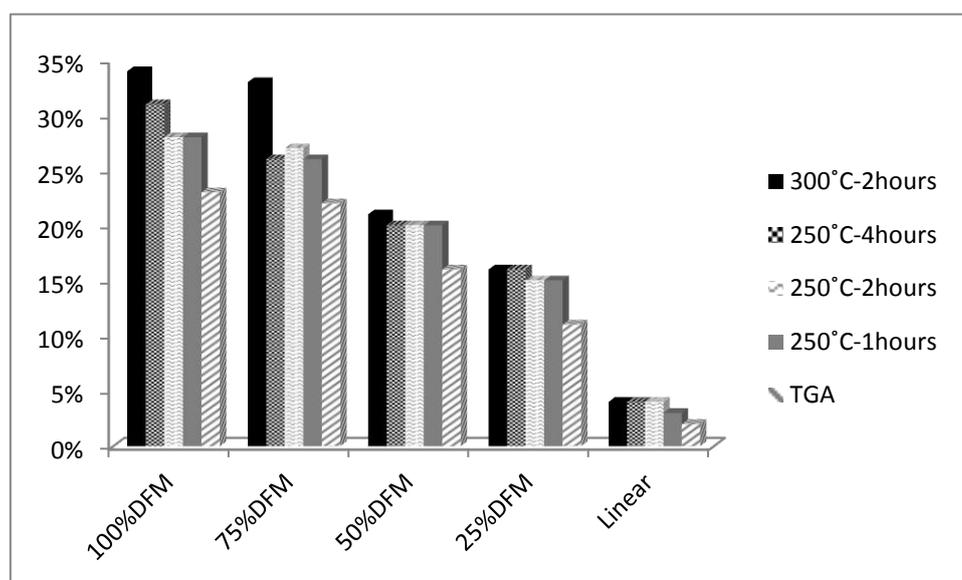


Figure 4.11: Weight loss of polymers (C4, C6, C7, C8, L20) upon heating in an oven

The general trend observed is that samples heated at 300°C for 2hr exhibit the most

weight loss, even more than 250°C for 4 hr. The sample heated at 250°C exhibit more weight loss after 4hr compared to 2hr and 1hr.

The results show a clear correlation between the DFM content of the cross-linked materials and the heating temperature and the duration of the heating; the higher the temperature and the heating duration the more weight loss.

The cross-linked materials C5, C9-13 were also heated in an oven at 250°C and 300°C for 1-4hr and the resulting weight loss are presented in Fig. 4.12. The same general trend to those describe earlier for cross-linked materials C4-C6-8 were observed.

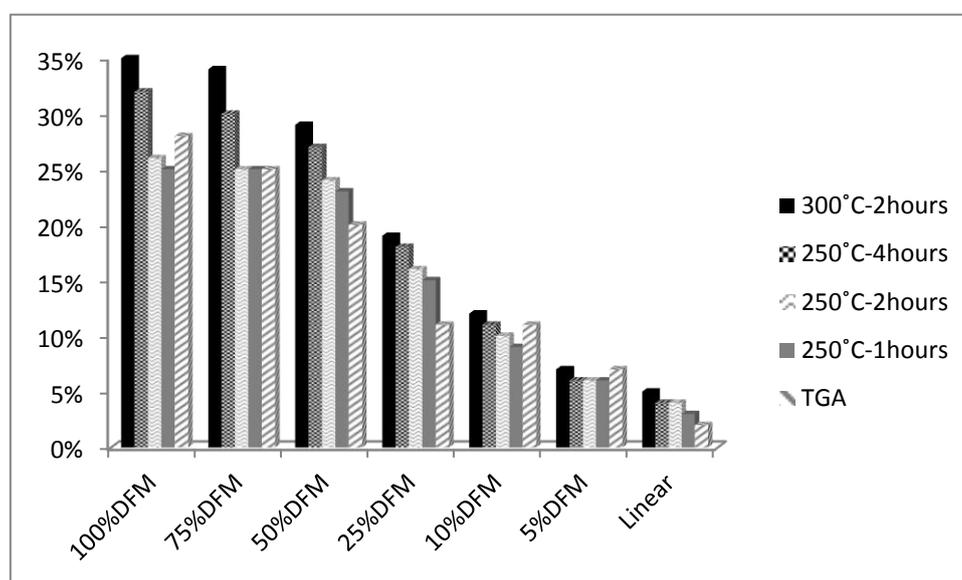


Figure 4.12: Weight loss of polymers (C5, C9, C10, C11, C12, C13, L21) upon heating in an oven

Table 4.5: Weight loss of C4-13, L20, and L21 in oven at 300°C after 2hr and TGA

Sample	DFM %	Weight loss %	
		Oven	TGA
C4	100	34	23
C6	75	33	22
C7	50	21	16
C8	25	16	11
L20	0	5	2
C5	100	35	28
C9	75	34	25
C10	50	29	20
C11	25	19	9
C12	10	12	7
C13	5	7	5
L21	0	5	2

The weight loss observed by heating in an oven are compared to those obtained from TGA are shown in table 4.5 for comparison.

The weight loss observed for heating in an oven at 300°C for a period of 2hr are more than that observed over the timescale of TGA. This indicates that more heating times are required for the breakdown of the acetal ester linkages.

It should be pointed out that no weight loss was observed for the linear polymers L20-21 during the TGA investigation and heating in oven at 250°C and 300°C for 1-4hr, Fig. 4.9 and 4.10. This is taken as indication that the weight losses observed resulted from the thermal breakdown of the acetal ester linkages.

4.3.2.2 Solubility behaviour

The samples of the cross-linked C4-C13 and linear polymer L20-21 became black upon heating in the oven at 300°C for 2hr. Black particles were observed when these samples were dissolved in DCM which were removed by filtration. It appeared that the samples were not completely soluble in DCM and that some polymer residue remained in solution.

Table 4.6: The solubility in dichloromethane before and after oven (300°C after 2hr)

Samples	DFM%	Solubility before oven	Solubility after oven
C4	100	No	Partial
C6	75	No	Partial
C7	50	No	Partial
C8	25	No	Partial
L20	0	Yes	Partial
C5	100	No	Partial
C9	75	No	Partial
C10	50	No	Partial
C11	25	No	Partial
C12	10	No	Partial
C13	5	No	Partial
L21	0	Yes	Partial

The sample of cross-linked material C11 after the heating treatment in the oven at 300°C for 2hr was similarly recovered, re-dissolved in dichloromethane-d and analysed by ^1H NMR, Fig. 4.13A. The ^1H NMR spectrum shows expected characteristic resonances due to the protons of aromatic group (peaks 1-3), vinylic group (peak 4), and $-\text{CH}_2-$ group (peak 5). The spectrum is similar to that of the linear polymer L21 (Fig. 4.13B), indicating the formation of linear polymer upon heating the cross-linked material in oven at 300°C for 2 hr.

The black solid is believed to be the result of the decomposition of ruthenium initiator (unreacted and reacted). When the ruthenium initiator was treated in the oven under similar conditions a black solid was formed.

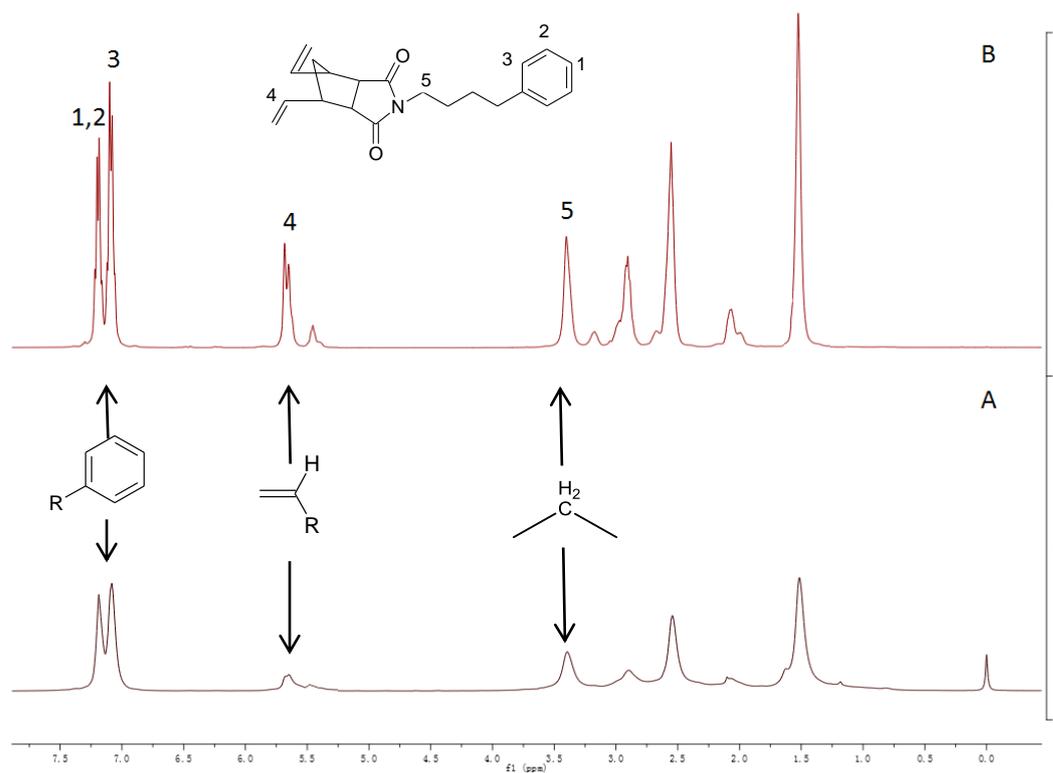


Figure 4.13: NMR spectrum of cross-linked material C11 (25%DFM) degraded in oven at 300 °C during 2 hours (A) and the linear polymer L21 (B), in CDCl₃

4.3.3 Acid-catalysed hydrolysis

The acetal ester linkage is expected to readily undergo acid-catalysed hydrolysis. The acid-catalysed hydrolysis of acetal esters has not been reported.²⁹ However, linear polymers containing ketal and acetal linkages have been reported, Fig. 4.14. The linear polymers have been shown to undergo acid-catalysed hydrolysis forming low molecular weight materials for therapeutics and drug deliveries.

4.3.3.2 Solubility behaviour

The samples of cross-linked material C5, C9-12 after hydrolysis were readily soluble in DCM, table 4.8. The cross-linked sample C11 was dissolved in dichloromethane-d and analysed by ^1H NMR, Fig. 4.15A.

Table 4.8: The solubility of samples after acid-catalysed hydrolysis

Samples	C9	C10	C11	C12	L21
Solubility before hydrolysis	No	No	No	No	Yes
Solubility after hydrolysis	Yes	Yes	Yes	Yes	Yes

The samples after hydrolysis were purified and characterised by ^1H NMR.

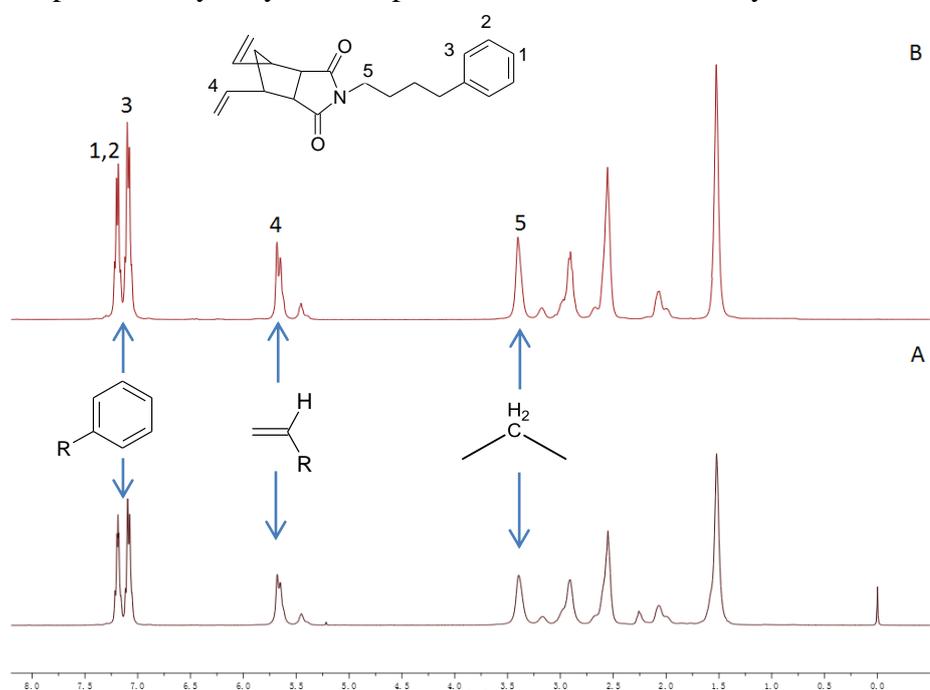


Figure 4.15: NMR spectra of 25%DFM polymer after acid-catalysed hydrolysis (A) and linear polymer (B), in CDCl_3

The ^1H NMR spectrum shows expected characteristic resonances due to the protons of aromatic group (peaks 1-3), vinylic group (peak 4), and $-\text{CH}_2-$ group (peak 5). The spectrum is identical to that of the linear polymer L21 (Fig. 4.15B), indicating the formation of linear polymer upon acid catalysed hydrolysis of the cross-linked material. The ratio of the integration of the resonances due $-\text{CH}_2-$ group (Peak 5) and the vinylic group (peaks 1-3) remained the same as that observed for linear polymer. This indicates that the dicarboximide segments in the cross-linked materials

are resistant to acid-catalysed hydrolysis.

It should be noted that linear polymer L21 remained unchanged after being subjected to acid-catalysed hydrolysis under the same conditions, table 4.8. This further confirms the stability of the dicarboximide segments towards acid-catalysed hydrolysis.

4.4 Rheological analysis

The samples were tested at 100°C, 130°C, 160°C, and 190°C. The results at each temperature were superposed onto a master curve (at one temperature) using “time-temperature superposition”, which was based on Williams-Landel-Ferry (WLF) equation.⁶⁹ We put all master curves at the same reference temperature 130°C which can be seen in figures 4.16 and 4.17. The data was analysed using RepTate software (freeware at www.reptate.com)

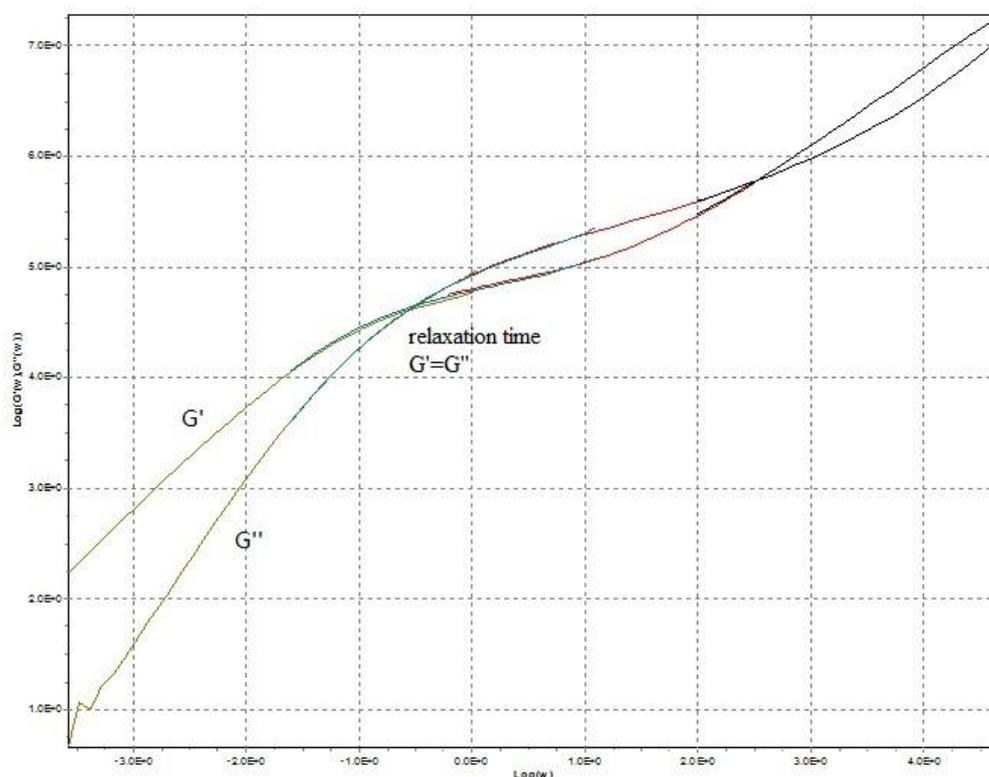


Figure 4.16: Linear rheology ramps of linear polymer sample

In figure 4.16, the elastic modulus G' and viscous modulus G'' were recorded via

frequency sweep. There are two crossover of G' and G'' . The one at low frequencies the crossover of G' and G'' indicated a characteristic the relaxation time, when $G'=G''$. This shows the characteristic time for the whole polymer to relax its stress. The relaxation time is calculated by $\tau = \frac{1}{\omega}$ (where, ω is the crossover frequency). The other one at high frequency, the crossover of $G'=G''$ was the characteristic time scale of the untangent section of the polymer to relax.

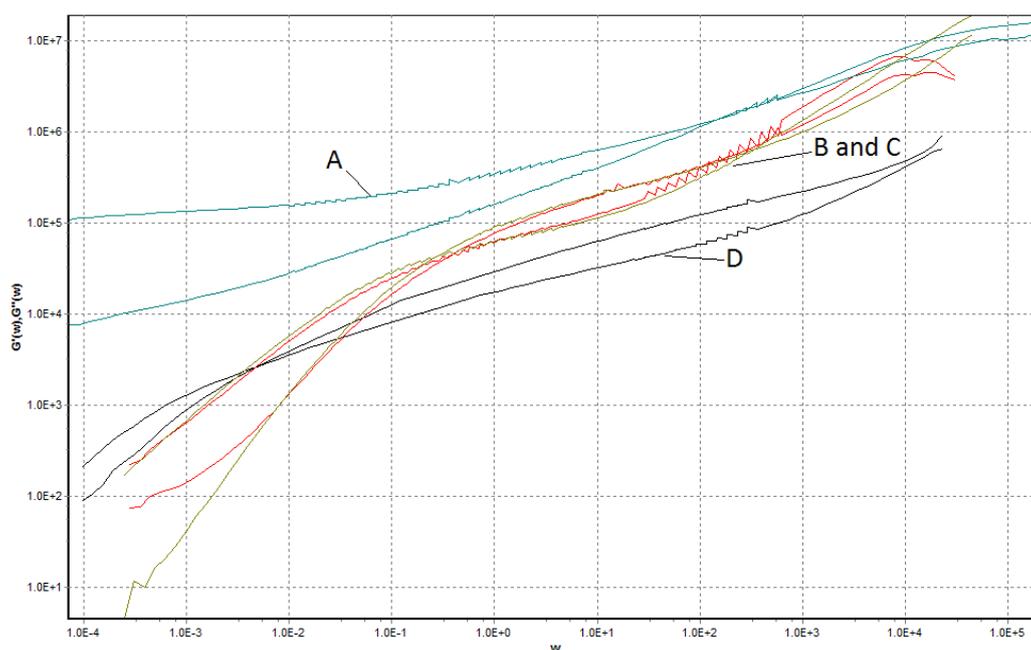


Figure 4.17: Linear rheology ramps of linear polymer (B), 25% cross-linked polymer (D), 25% cross-linked polymer after heating (A), and 25% cross-linked polymer after hydrolysis (C)

In figure 4.17, the relaxation time of linear polymer (B), 25% cross-linked polymer (D), 25% cross-linked polymer after heating (A) and 25% cross-linked polymer after hydrolysis (C) are compared. Curve D has the longest relaxation time of all samples. Curve A does not have a low-frequency cross. The cross-linked polymer after heating was rubber like and the structure (or net-work) of the cross-linked materials changed during heating.

Curves B and C almost superimpose. They had the same relaxation time, that is to say, linear polymer and 25% cross-linked polymer after hydrolysis have the same

characteristics.

The glass transition temperature was measured by temperature sweep (Fig.4.17). Where $\tan \delta = G''/G'$. The peak of the curve represents the phase transition, which was glass transition temperature in this experimental. All the polymers had the similar Tg, which was around 80°C.

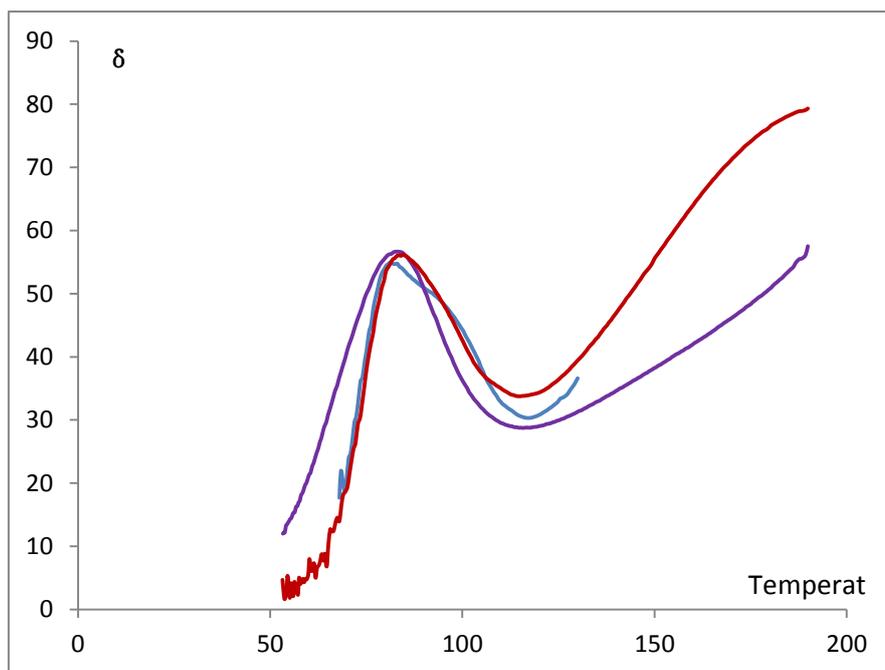


Figure 4.17: Temperature sweep

Chapter 5

Conclusions and future work

5.1 Conclusions

The aim of this project was to design and synthesise a range of well-defined thermosetting ROMP materials that are thermally degradable, biodegradable and recyclable. The crucial part of the design of these thermosetting materials was the thermal breakdown or biodegradation of only the linkages, leaving the main chains intact. This would also allow the transition from thermosetting to thermoplastic facilitating the recycling. In order to achieve the aims, thermosetting ROMP materials based on poly(norbornene dicarboximide) networks containing acetal ester linkages were synthesised.

First, the pure exo di-functional monomer containing acetal ester functionalities was successfully synthesised with a yield of 83% which were fully characterised by ^1H and ^{13}C NMR spectroscopy. Di-functional monomer was subjected to ROMP using ruthenium initiator to prepare thermosetting materials with maximum degree of cross-linking. Second, thermosetting materials with different degrees of cross-linking were also prepared by the ROMP of the mixtures of di-functional and mono-functional monomers.

The results of TGA indicated that the cross-linked materials started losing weight at 150°C and the extent of the weight loss at 300°C depended on the level of di-functional content (DFM) in the samples; the higher the DMF content the bigger the weight loss. The sample with 100%DMF content (C5) showed a weight loss of 28% and the weight loss for the sample with 5%DMF (C13) content was decreased to 5%. The weight loss is attributed to the thermal breakdown of the acetal ester linkages in the cross-linked material as no weight loss was observed for the linear polymer (L21) without any acetal ester groups. The linear polymer sample only showed 2% weight loss at 100°C due to the moisture content in the sample. The retrieved cross-linked samples, after TGA test, did not dissolve in DCM completely, suggesting that the total breakdown of the acetal ester linkages had not been achieved on the timescale of TGA investigation. This observation is supported by the IR

spectra as it showed the reduction in the intensity of acetal ester band not the complete disappearance.

The samples were heated in the oven at 300°C and 250°C. The results showed a clear correlation between the DFM content of the cross-linked materials and the heating temperature and the duration of the heating. The higher temperature and heating duration, the more weight loss would exhibit. The cross-linked samples after heat treatment were not completely soluble in DCM. ¹H NMR analysis of sample C11, after the heating treatment in the oven at 300°C for 2hr, gave a spectrum similar to that of a linear polymer L21. This indicates the partial formation of linear polymer upon heating the cross-linked material in oven at 300°C for 2 hr.

The cross-linked materials were also subjected to acid-catalysed hydrolysis. The weight losses observed were greater than those heated in the oven, indicating more cleavage of the acetal ester linkages upon hydrolysis. The samples of cross-linked material after hydrolysis were readily soluble in DCM. The samples after hydrolysis in dilute acid were completely soluble in DCM and were therefore characterised by NMR. The observed ¹H NMR spectra were the same as those observed for the linear polymer L21. This is a clear indication that all the acetal ester linkages were broken down during hydrolysis and that cross-linked polymers changed into linear polymers.

Dynamic mechanical analysis was carried out on the cross-linked polymer, linear polymer, polymer after heating, and polymer after hydrolysis. Curves for linear polymer and cross-linked polymer after hydrolysis had the same relaxation time. That is to say, linear polymer and cross-linked polymer after hydrolysis had the same characteristic, supporting the complete breakdown of acetal ester linkages. However, curves for cross-linked polymer after heating had no relaxation time at low frequency. It showed that the cross-linked polymer after heating was rubber like. This may indicate the breakdown of the acetal ester linkages followed by the formation of new cross-links.

It is therefore concluded that the complete breakdown of the acetal ester linkages could not be achieved on the timescale of the TGA experiments. Although, the total breakdown is achieved by prolonged heating in the oven, but it appears that other cross-linking processes also takes place. However, complete breakdown of the acetal ester linkages could be achieved by acid-catalysed hydrolysis. This is anticipated to allow the transition from thermosetting to thermoplastic facilitating the recycling and reworking.

5.2 Future Work

The reactions used for the synthesis of monomers have resulted in products with high yields. These routes could be designed to synthesise monomers containing oxygen in 7-position, to improve the bio-degradability of the resulting thermosetting materials. An example of such monomer is shown in Fig. 5.1.

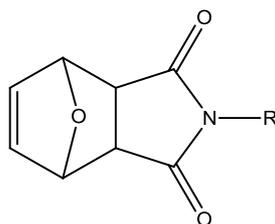


Figure 5.1: Structure of oxanorbornene dicarboxyimides

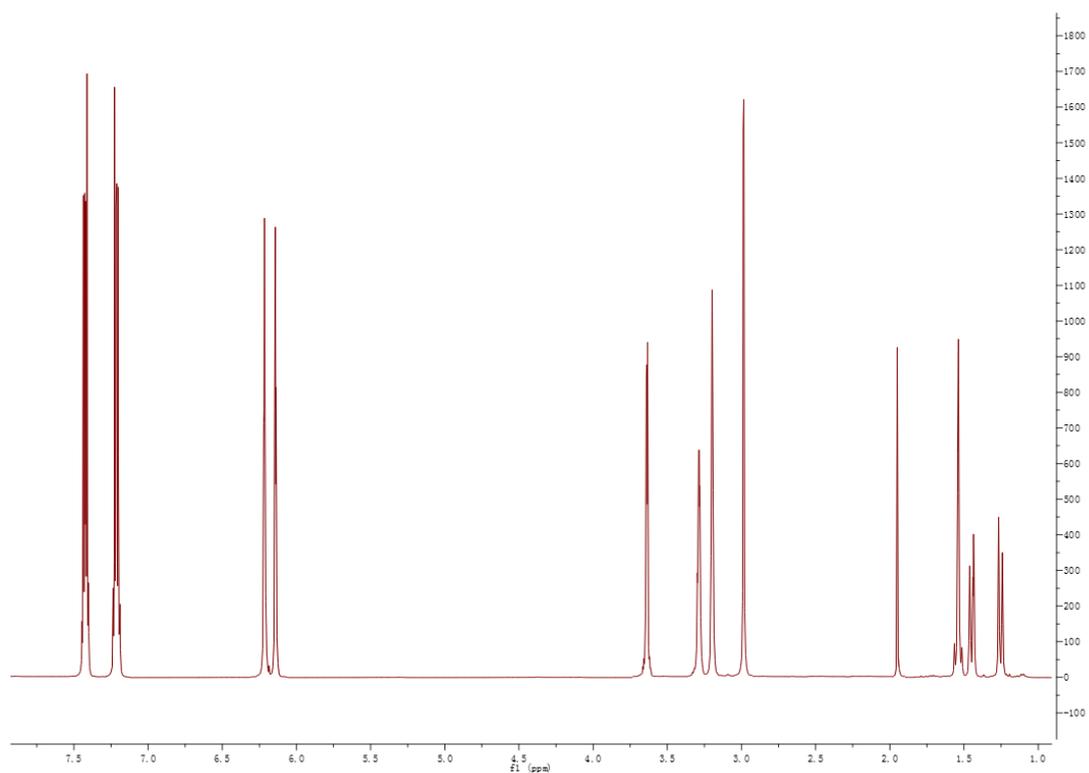
The ROMP of oxanorbornene dicarboxyimides has been described in the literature.

The ROMP polymer used in this experiment have provided a good platform for development of better reworkable materials. The cross-linked ROMP polymers containing acetal ester linkages prepared in this project are expected to have excellent hydrolysis property, therefore, they could be developed as bio-degradable materials.

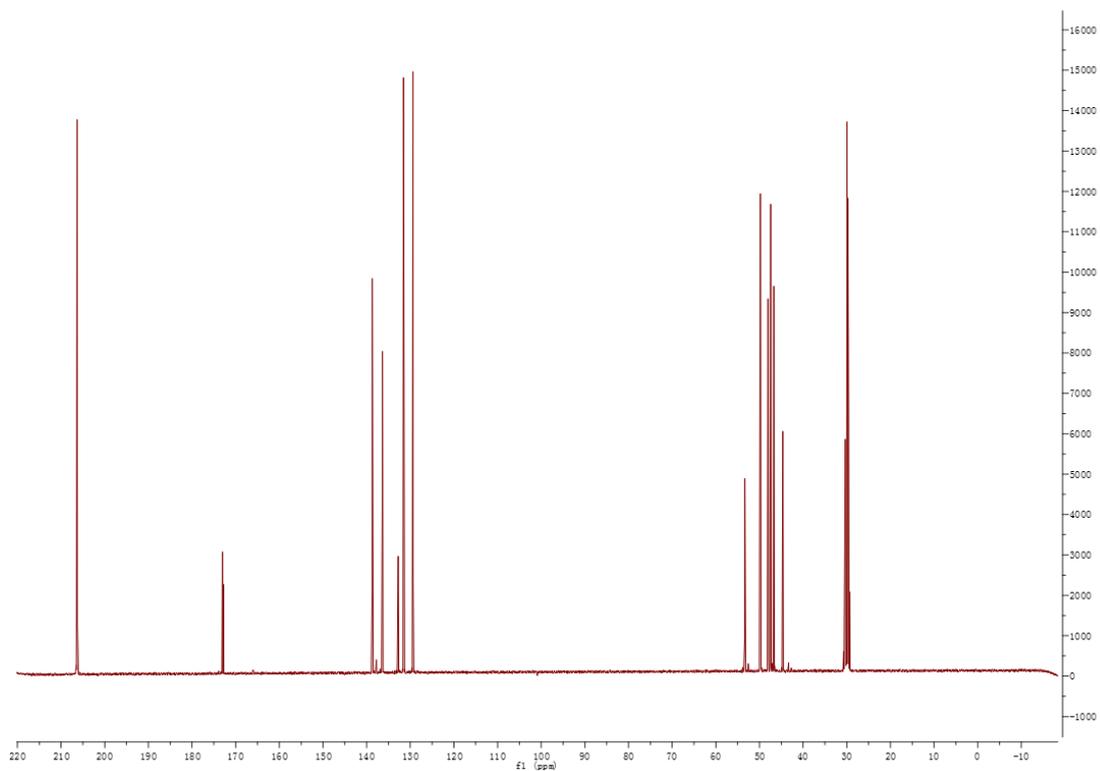
An entire library of di-functional monomers could be synthesized by incorporating different divinyl ethers and amino acids. An area of interest may be the investigation of the properties of monomers and resulting polymers that include cyclohexyl functionalities in their structure.

Thus far, there have not been any reported di-functional monomers incorporating both cleavable linkages and imidonorbornene functionalities. It may be of interest to try to synthesise monomers based on the imidonorbornene formation that contain cleavable linkages. Further study could consider chemical degradation of polymer.

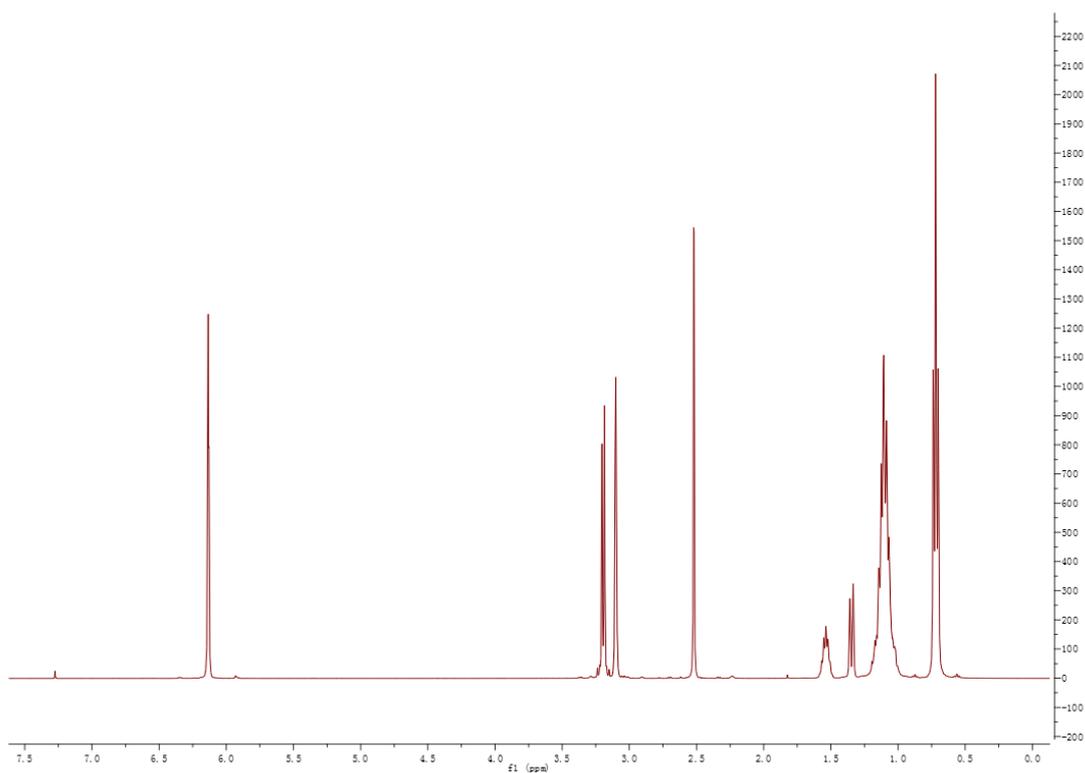
Appendix



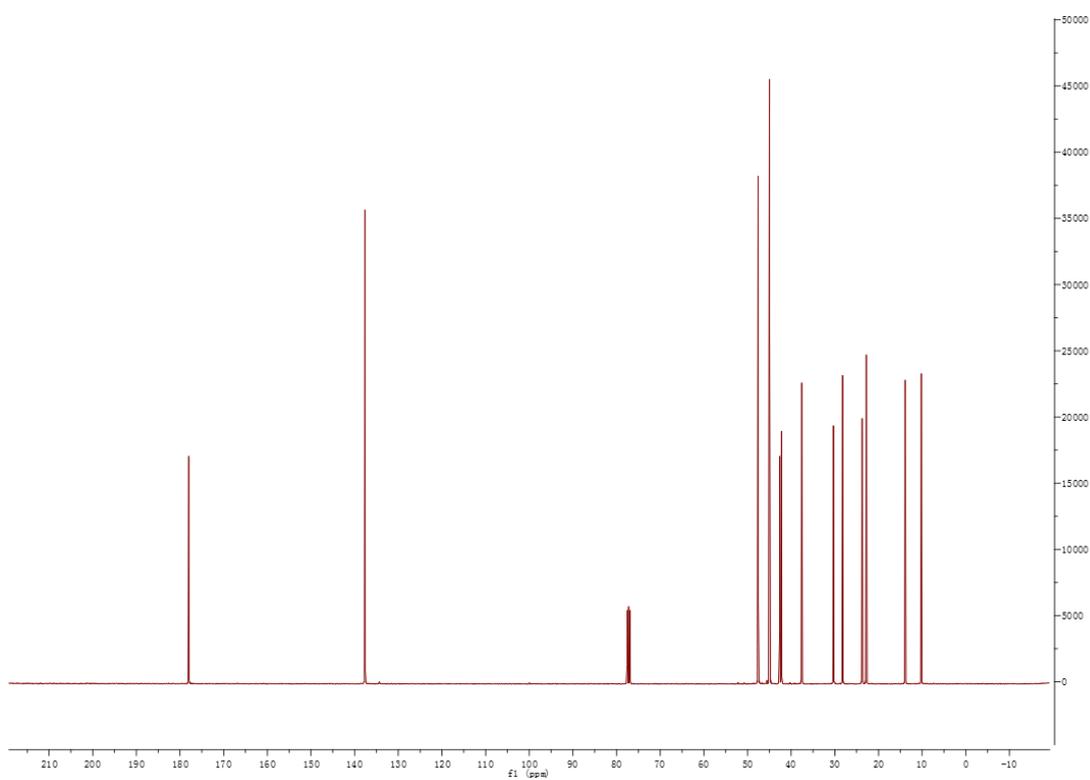
Appendix 1: ^1H NMR spectrum of DFM1



Appendix 2: ^{13}C NMR spectrum of DFM1



Appendix 3: ^1H NMR spectrum of DFM2



Appendix 4: ^{13}C NMR spectrum of DFM2

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