Acetals for adaptable and pH degradable thermosets and the use of internal acid sources

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Declaration

The work described in this thesis was undertaken at the University of Sheffield under the supervision of Prof. Patrick Fairclough and Dr Sebastian Spain between October 2018 and November 2022 and has not been submitted, either wholly or in part, for this or any other degree. All the work is original work of the author, except where acknowledged.

Signature: ____________________________

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Abstract

Thermosets are a class of polymers with excellent thermal and mechanical properties, which has prompted their use in a wide range of applications and industries. However, thermosets are inherently infusible and insoluble and consequently their recycling is challenging. To address this an acid cleavable, methacrylate cross-linker bearing two acetal groups was synthesised. and used as a cleavable cross-linker in thermosets. ‘H NMR spectroscopy showed the hydrolysis products were HEMA, tri(ethylene glycol) and acetaldehyde and the extent of hydrolysis increased with lower acid pKₐ.

The cross-linker synthesis was then optimised and scaled up for consistency in future thermoset syntheses and mechanical testing, while also improving the sustainability of the process. Acetal-containing methyl methacrylate thermosets formed homogeneous solutions in acidic solvent/H₂O mixtures. The degradation products were found to be p(methyl methacrylate-co-2-hydroxyethyl methacrylate), tri(ethylene glycol) and acetaldehyde, consistent with acetal hydrolysis. Comparison of the rate of acetaldehyde evolution and gravimetric loss of p(MMA-co-A1) showed the rate of degradation related to a complex pathway involving swelling, hydrolysis, and solvation of p(MMA-co-A1). These results showed that acetal cross-linkers may enable chemical recycling of thermosets.

Acid generators were then investigated as internal acid sources for catalysis of acetal hydrolysis and exchange reactions in covalently adaptable networks. Novel polymeric sulfonate thermal acid generators were synthesised and their thermolysis properties comprehensively characterised via thermogravimetric analysis and ‘H NMR spectroscopy. However, upon thermolysis they underwent a cross-linking reaction and consequently are unsuitable for use in degradable thermosets.

Lastly, the cross-linker was used in covalently adaptable networks and exhibited re-processable adhesive behaviour.
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Abbreviations

4-TMA – 4,N,N-trimethylaniline

AIBN - 2,2'-azobis(2-methylpropionitrile)

BPO – benzoyl peroxide

CAN – covalently adaptable network

DCA – dichloroacetic acid

DMSO - Dimethyl sulfoxide

DMA – N,N-dimethylaniline

DSC – differential scanning calorimetry

EGDMA – ethylene glycol dimethacrylate

\( E_a \) – Activation energy

\( E_i \) – Intramolecular elimination

HEMA - 2-hydroxyethyl methacrylate

HPLC-MS – high performance liquid chromatography mass spectroscopy

IR – infrared

MAA – methacrylic acid

MCA – monochloroacetic acid

MEK – methyl ethyl ketone

NITf - N-hydroxynaphtalimide triflate

NMR – nuclear magnetic resonance
PAG – photoacid generator

pTsCl – para-toluene sulfonyl chloride

pTsOH – para-toluene sulfonic acid

RAFT - reversible addition-fragmentation chain-transfer

R.T. – room temperature

SEC – size exclusion chromatography

SOE - spiroorthoester

TAG – thermal acid generator

TCA – trichloroacetic acid

$T_{\text{EI}}$ – temperature of intramolecular elimination

TEG – tri(ethylene glycol)

TEGDVE – tri(ethylene glycol)divinyl ether

TFA – trifluoroacetic acid

$T_g$ – glass transition temperature

TGA – thermogravimetric analysis

THF – tetrahydrofuran

TLC – thin layer chromatography

TMA – 4,N,N-trimethylaniline

vtNMR – variable temperature nuclear magnetic resonance
Chapter 1 - Introduction

1.1. Thermosets

1.1.1. Thermosets, their properties, and synthesis
Thermosets are a class of polymer that harden, cure, via a chemical reaction involving the chemical cross-linking of chains.\textsuperscript{1,2} The product is an insoluble network of infinite molecular weight, meaning it cannot be measured. The curing process of thermosets may be initiated via an external stimulus such as heat or UV and by mixing reactive species such as monomers and a catalyst or monomers and atmospheric moisture. The term curing in the field of thermosets generally refers to polymerisation of a pre-polymer solution. The composition of which can be, polymers, oligomers, mono and multifunctional monomers, and additives such as initiators, antioxidants, and fillers.

At a molecular level the synthesis of thermosets proceeds via step or chain growth polymerisation, sometimes both occur simultaneously, for example hybrid cure adhesives.\textsuperscript{3} A variety of functional groups have been used in thermoset chemistry including poly(urethanes), epoxy resins, poly(benzoxazines), phenolic resins, unsaturated polyesters and (meth)acrylate resins (Figure 1-1).\textsuperscript{4} Collectively, thermosets account for approximately 18 % of all polymers produced\textsuperscript{5} and annual polymer production has increased at a sustained rate since their inception and is expected to continue.\textsuperscript{5-8}
1.1.2. Thermoset properties and application

Thermosets offer excellent thermal stability, good mechanical properties, chemical resistance, and good dimensional stability. This is largely due to the presence of covalent cross-links between polymer chains that form a complex network that is insoluble and cannot be melted. Furthermore, thermosetting polymer synthesis is technically simple and may be used in manufacturing processes unavailable to traditional materials, such as resin vacuum infusion, hand lay-up and pultrusion in composite manufacturing. The favourable properties of thermosets have enabled their use in a range of applications such as, adhesives, composites and coatings within a range of industries such as, aerospace, construction, electronic and automotive.

Adhesives offer advantages over traditional mechanical fasteners such uniform stress distribution, weight reduction, joining different materials and complex geometries. However, their removal for repairs or at the end of life can be challenging compared to a nut and bolt fastener, separation of adhesively joined components may lead to substrate damage, failure or contamination. For low value substrates this may not be financially damaging but creates recycling challenges and negatively effects the environment. For adhesively joined high value substrates such as anisotropic carbon fibre composites or battery cells in electronic vehicles, damaging these materials is financially and environmentally costly. This is also true
of thermoset coatings which are applied to an object to give a finish or protection. However, removal or repairs is challenging due to the infusible and insoluble properties of thermosets.

The role of thermosets in composites is to make up the matrix phase within which a reinforcer is dispersed, thermoset-reinforcer composites have unique properties such as excellent mechanical strength while also being lightweight. However, the infusible and insoluble properties of thermosets mean repairs and end of lifecycle disassembly is challenging. Reinforcers such as carbon fibre are valuable, and their production is resource intensive so recovery for reuse is preferable. Technology enabling the repair of glass fibre composite wind turbine blades could increase their operational lifetime and prevent them from entering landfill at their end of life.\textsuperscript{12,13}

1.1.3. Thermoset Recycling

Thermoset recycling is more challenging than their non-covalently cross-linked equivalents, thermoplastics.\textsuperscript{14} Current end of life options for thermosets and their composites are landfill disposal, mechanical recycling and thermal treatment. Mechanical recycling of thermosets and composites involves grinding to a fine particulate for use as filler, degrading potentially valuable reinforcers and components. Thermal treatment of thermosets and their composites produces different results depending on whether it is performed under aerobic or anaerobic conditions. Aerobic conditions lead to combustion and the opportunity for energy recovery, usually any reinforcer present is reduced to low quality filler. Anaerobic conditions, often referred to as pyrolysis, allow the transformation of thermosets to fuels and enable reinforcer recovery. The effectiveness of thermal treatment depends on the plant and process emission control technology and energy recovery efficiency.\textsuperscript{5,8,13–16}

Chemical recycling of thermosets, often called solvolysis, involves the reactive dissolution of thermosets with cleavable bonds within their backbone or cross-links. During chemical recycling cleavable bonds react with solvent or other chemical species, breaking them and forming lower molecule weight species. The products may then be separated and collected
via processes such as precipitation or distillation for reprocessing into thermosets if the products are monomers or reactive oligomers and polymers. Chemical recycling is mainly performed on a lab scale and there are concerns over the environmental impact and safety of using hazardous solvents.17–22

1.2. Degradable Thermosets

Despite the excellent properties and usefulness of thermosets, their lack of recyclability is an issue. Common thermosets are fossil fuel derived and follow a linear economy model, whereby resources are extracted and become waste which is environmentally damaging.23 Their lack of recyclability and reusability creates further consumption of fossil fuels and more pollution. Conventional thermosets do not biodegrade and landfilled thermoset waste slowly breaks down in particulates accumulating in all major ocean basins, freshwater systems and terrestrial habitats.5,14 As previously discussed the alternatives are mechanical and thermal recycling, however mechanical recycling is likely to delay the release of thermosets into the environment and thermal recycling can create harmful emissions, while both still further demand for fossil fuels.14–18

One solution is the use of renewable feedstocks such as lignin, hemi-cellulose and cellulose however, life-cycle analysis of bio-derived plastics has shown they can embody more CO₂ equivalents than traditional fossil derived plastics.8,14,24 The use of renewable feedstocks doesn’t guarantee that these materials won’t become pollutants, for example poly(lactic acid) requires collection for industrial composting.25 An alternative is materials that can be degraded in response to a stimulus enabling separation and reuse of components or reinforcers. The degradation products may be designed so that they can be reused in a different application or reprocessed to new thermosets.

Degradable thermosets enable removal of thermoset adhesives and coatings without damaging substrates and facilitate reinforcer recovery in composites. There are two main approaches to achieving degradable thermosets via the incorporation of additives that give
physical or chemical degradation or the addition of degradable units to the thermoset). A further category of polymers undergo full depolymerisation to monomers in response to stimuli such as self-immolative polymers\textsuperscript{26,27}, polymers made \textit{via} RAFT polymerisation\textsuperscript{28,29} or in the presence of catalysts or enzymes\textsuperscript{30–32} exists. However, these do not exhibit the mechanical and thermal properties equivalent to conventional thermosets and have been omitted from this introduction.

1.2.1. Additives

Additives may be formulated into thermosets that enable thermoset degradation or component separation. They remain dormant in the network until the joining of substrates is no longer required, upon which a stimulus is applied and debonding achieved. The mechanism of degradation proceeds by a physical change such as rupture, delamination or phase change.\textsuperscript{33,34}

1.2.1.1. Thermally expansive microparticles

Thermally expansive microparticles undergo volumetric expansion when heated. They are composed of a thermoplastic shell, a copolymer of vinylidene chloride, acrylonitrile, meth acrylonitrile and methyl methacrylate (MMA), encapsulating a liquid hydrocarbon such as isobutane or isopentane.\textsuperscript{35} Upon heating two processes occur simultaneously, softening of the thermoplastic shell as it is heated above its $T_g$ and the phase transformation of the liquid hydrocarbon core to a gas, the change in volume is around 50–100 times its original (Figure 1-2).
Upon cooling the thermoplastic core becomes rigid trapping the particle in its expanded state. The overall expansion of a bond joint leads to a reduction in strength and separation. Armes et. al coated thermally expanding microparticles with poly(pyrrole) which has a known absorption peak in the near infrared region. Subsequent irradiation with an infrared lamp led to expansion of the microparticle removing the need for bulk heating. The temperature of expansion varies from 70 to 285 °C. Inorganic thermally expansive microparticles such as graphite, vermiculite, pearlite and mica have been investigated as high temperature alternative to thermoplastic encapsulated hydrocarbons. Kawate and Kanki added expandable graphite microparticles (10-40 wt%) to epoxy resins and observed debonding of substrates after thermal treatment at 250 °C. However, the high wt% used lowered the bonding strength of the epoxy resin.

Of the additive techniques outlined, thermally expansive microparticles have seen the largest industrial use for mainly non-structural applications. Examples of polyurethanes and epoxy-based adhesives utilising thermally expansive microparticles can be found in the literature; however, use of thermally expansive microparticles in (meth)acrylate thermosets are sparse.
1.2.1.2. Nanoparticle additives

Nanoparticles have been used as additives to aid debonding via heat generation. Evonik developed MagSilica, a pressure sensitive adhesive containing silicon dioxide encapsulated iron oxide nanoparticles. Upon exposure to external magnetic fields nanoparticles radiate heat aiding disassembly. However, many substrates act as barriers to external magnetic fields decreasing the disassembly efficiency.\textsuperscript{34,40} ElectRelease is a commercially available debondable epoxy adhesive. When a potential difference (10-50 V) is applied debonding is achieved. However, conductive substrates are required limiting the technology.\textsuperscript{34}
1.2.2. Chemically Modified Thermosets

Thermoset degradation can be enabled by chemical modification with groups that respond to stimuli such as temperature, ultraviolet light (UV) and pH. Ultrasonic, near infrared radiation and electrical current are less popular due to the expense of equipment. Of these pH degradable thermosets are particularly desirable as the reaction products can be reacted with one another via a condensation reaction to yield the original functional group, offering a route to reusable thermosets. pH responsive linkers have been well studied in biomedical polymers such as soft gels, however, their use in degradable thermosets with strong mechanical properties is relatively low and largely confined to epoxy resin chemistry. A brief introduction to functional groups used in degradable thermosets follows; two detailed reviews by Ma and co-workers have recently been published in this area.

1.2.2.1. Lactone modification

Servando et al., Sangermano et al. and Tomuta et al. copolymerised a modified bisphenol A diglycidyl ether resins to incorporate γ-caprolactone in varying amounts as compostable or alkaline degradable materials. The cross-linked networks were synthesised via cationic polymerisation; in all studies the thermal stability was lower than standard epoxy resins. Sangermano et al. studied the hydrolysis of networks containing γ-caprolactone at 0, 2, 5 and 10 wt % over 2 months at pH 7.4 in a buffer solution; increasing γ-caprolactone content increased the hydrolytic weight loss to 5 wt%, compared to 0 % weight loss for the sample with no γ-caprolactone. Tomuta et al. synthesised a hyperbranched pre-polymer from 3,5-dihydroxybenzoic acid and γ-caprolactone, which was subsequently polymerised with bisphenol A diglycidyl ether. The authors used product $T_g$ as an estimate of the extent of hydrolysis in refluxed KOH/EtOH (1 M) solutions; the $T_g$ decreased over time for all networks containing γ-caprolactone segments after 24 hrs. The 10 wt % hyperbranched caprolactone containing sample $T_g$ decreased from 122 to 60 °C. The long degradation times may hinder their use and bisphenol A diglycidyl ether is concerning due to its negative health effects.
1.2.2.2. Hindered ureas

Cheng and co-workers\textsuperscript{48–50} polymerised sterically hindered amines with di- or multifunctional isocyanates, producing sterically hindered poly(ureas) (Scheme 1-1). Traditional ureas are resistant to hydrolysis due to the conjugation within the functional group. However, the presence of steric bulk on the urea bond disrupts conjugation by preventing the orbitals from aligning in a coplanar configuration. Furthermore, the sterically hindered urea bond is dynamic and dissociates to a hindered amine and isocyanate; under aqueous conditions the isocyanate is hydrolysed liberating CO\textsubscript{2} and an amine. The rate of hydrolysis and therefore, thermoset degradation was increased via the use of bulkier amines. For example b) in Scheme 1-1b, poly(ureas) synthesised with \textsuperscript{1}Pr substituents showed no appreciable degradation when incubated at 37 °C in phosphate buffered saline solution for 200 hrs, whereas the \textsuperscript{t}Bu bearing poly(urea) fully degraded in 100 hrs.\textsuperscript{49}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme1}
\caption{Scheme 1-1 – pH degradable sterically hindered poly(ureas).\textsuperscript{48–50}}
\end{figure}

Cheng and co-workers then synthesised a thermoset from hexamethylene diisocyanate and 2-(\textsuperscript{t}ert-butylamino)ethanol which could be hydrolysed in the presence of water or depolymerised in the presence of excess 2-(\textsuperscript{t}ert-butylamino)ethanol and exhibited covalently adaptable behaviour due to the dynamic nature of the hindered urea bond, see Section 1.3 Covalently Adaptable Networks. The hydrolysis of hindered poly(ureas) offers a route to
simple removal of thermosets; however, their application may be hindered by the use of Sn(Oct)$_2$ as a polymerisation catalyst and isocyanate monomers, both of which have environmental and health concerns.$^{51-53}$ Lastly, the materials undergo hydrolytic degradation at neutral pH meaning coatings, adhesives and composites utilising them may undergo premature degradation.

1.2.2.3. Orthoesters

Endo and co-workers developed spiroorthoesters (SOEs) as monomers for pH degradable thermosets synthesised via ring opening polymerisation (Scheme 1-2).$^{54-57}$ Under acidic conditions poly(SOEs) depolymerise to SOE monomers enabling chemical recycling. Initial work developed vinyl functional poly(SOEs) that were cross-linked via thiol-ene reactions with dithiols. The corresponding polymers were depolymerised in dichloromethane/trifluoroacetic acid (TFA) (4 mol %) at 20 °C to yield bifunctional SOE monomers in yields >66 %.$^{54,55}$ Endo and co-workers then synthesised poly(SOEs) from SOE derivatives of common diacid monomers (terephthalic acid, succinic acid and 1,4-cyclohexane dicarboxylic acid) aiming to produce chemically recyclable equivalents of commodity polymers (Scheme 1-2a).$^{57}$ However, polymerisation of these reached low conversions and the formation of cross-linked species was not observed.
Lastly, Endo and co-workers synthesised SOE functionalised copolymers of methyl methacrylate or styrene which were then cross-linked via cationic polymerisation using BF$_3$.OEt$_2$ to yield poly(SOEs) (Scheme 1-2b). The resultant cross-linked thermosets underwent depolymerisation to the starting SOE functionalised copolymers in solutions of dichloromethane/TFA (5 mol %) at 20 °C after 36 hrs.
1.2.2.4. Hexahydrotriazines

García et al.\textsuperscript{58} synthesised degradable thermosets utilising the hexahydrotriazine functional group by the reaction between 4,4′-oxydianiline and paraformaldehyde (Scheme 1-4). The $T_g$ could be tuned between 125-193 °C by changing the equivs. of paraformaldehyde to control the cross-link density. The thermosets were stable in aqueous solutions with a pH >3, whereas in aqueous H$_2$SO$_4$ solutions with a pH <2 they underwent full depolymerisation in 56 min.

1.2.2.5. Diketoenamines

\[
\text{OOC} \quad \text{OOC} \\
\text{NH}_2 \\
\text{H}_2\text{N} \quad \text{N} \quad \text{H}_2\text{N}
\]

\[
\text{R} = (\text{CH}_2)_2, (\text{CH}_2)_4, (\text{CH}_2)_6
\]

Scheme 1-3 - Diketoamine based degradable thermosets.\textsuperscript{59}

Christensen et al.\textsuperscript{59} synthesised three difunctional triketone monomers from adipic, suberic and sebacic acid difunctional triketone that were polymerised with tris(2-aminoethyl)amine producing poly(diketoenamines) (Scheme 1-3). The $T_g$ was between 110-130 °C depending on the equivs. of tris(2-aminoethyl)amine relative to the triketone. The resulting poly(diketoenamines) underwent depolymerisation in H$_2$SO$_4$ solutions (5 M) to the corresponding triketone and tris(2-aminoethyl)amine in yields >90 %. Furthermore, the authors demonstrated methodology for separating the triketone monomer from mixed plastic waste streams and recovery of fibres from composites using poly(diketoenamine) as a matrix. Lastly, the authors used recovered triketone monomer to make new thermosets that had near identical mechanical properties to the virgin thermoset.
1.2.2.6. Imines

A wide range of multifunctional amines, aldehydes and ketones are commercially available and yield poly(imes) with broad properties.\textsuperscript{60} Taynton \textit{et al} synthesised poly(ime) thermosets without the use catalysts from terephthaldehyde, diethylene triamine and triethylene tetramine in organic solvents (Scheme 1-5). The highly cross-linked networks formed were resistant to hydrolysis at up to 90 °C and became malleable and healable; upon loss of water the networks regained rigidity. Carbon fibre reinforced poly(ime) composites could be degraded in acidic solutions and the fibres recovered.\textsuperscript{60-63}

Scheme 1-4 - Hexahydrotriazine based degradable thermosets.\textsuperscript{58}

Scheme 1-5 - Synthesis of cross-linked poly(ime) degradable thermosets.\textsuperscript{60}
1.3. Covalently Adaptable Networks

Covalently adaptable networks (CANs) are another solution to the infusible and insoluble properties imparted on thermosets by chemical cross-links. CANs contain exchangeable chemical bonds that undergo exchange reactions. CANs swell in organic solvents like thermosets but flow like thermoplastics when a stimulus is applied, typically heat. The exchange reactions that give CANs this behaviour can follow associative, dissociative, and concerted reaction mechanisms. CANs that react via an associative pathway are often called vitrimers as their viscosity is governed by exchange reactions at elevated temperatures following the Arrhenius law.

Associative CANs undergo exchange reactions where a reactive intermediate is formed, and subsequent elimination yields a new cross-link, the networks cross-link density remains constant (Scheme 1-7).
Dissociative exchange reactions proceed by first breaking a cross-link and subsequently forming a new cross-link, as the rate of exchange increases the cross-link density of the CAN decreases (Scheme 1-8). Lastly, the concerted mechanism proceeds in a single step where bonds are formed and broken simultaneously, maintaining a constant cross-link density.\(^{65}\)

The type of exchange reaction impacts the macroscopic properties of CANs via the effect on cross-link density. Therefore, the rate of exchange reactions and presence of catalysts and functional group concentration also influences the macroscopic properties of CANs. For example, Leibler and co-workers work on acid-epoxy and anhydride-epoxy resins demonstrated well known epoxy resin thermosets could undergo associative exchange reactions such as transesterification, at >70 °C in the presence of Zn(acac)\(_2\) or Zn(ac)\(_2\)
catalysts. These materials behaved like conventional epoxy resins at room temperature but could be re-molded at elevated temperatures as the rate of exchange increased.\textsuperscript{66} Worrell \textit{et al.} synthesised thiol-thioester associative exchange based CANs that could be reprocessed at 23 °C.\textsuperscript{67}

The rate of exchange reaction is one of multiple properties that influence the macroscopic properties of CANs, meaning introduction of a specific dynamic bond to a network will not give the same stress-relaxation behaviour as in other CANs.\textsuperscript{65} The macroscopic properties of CANs depend on a multitude of factors including \( T_g \), cross-link density, chemical composition of the matrix, impurities, catalysts and network stiffness.\textsuperscript{65,68} Dynamic functional groups used in CANs include disulfides, Diels-Alder cycloadditions, transesterification, transcarbomylation, transamidation, transimination, transalkylation, olefin metathesis, transacetalisation and acetal metathesis.\textsuperscript{69–76} Of the aforementioned functional groups, acetals are of particular interest due to their degradable and dynamic properties.

\section*{1.4. Acetals}

Acetals are commonly used aldehyde and ketone protecting groups in organic synthesis as they can be hydrolysed under acidic conditions.\textsuperscript{77} Their structure is the diether form of geminal diols. Historically the name acetal referred specifically to diethers derived from aldehydes, and ketal was the term for the ketone derivative. However, acetal now refers to both types of geminal diether.\textsuperscript{78}

Acetals can be synthesised by the nucleophilic addition of alcohols to an aldehyde or ketone. This produces water which requires removal from the reaction mixture to drive the equilibrium towards acetal formation. Techniques for the removal of formed water include azeotropic distillation with a Dean-Stark apparatus or the use of water scavenging species such as triethyl orthoformate, boron trifluoride-etherate, hydrogen chloride or molecular sieves.\textsuperscript{79,80}

The reaction mechanism proceeds by nucleophilic addition of an alcohol a protonated carbonyl group (Scheme 1-9). Subsequent proton transfer forms a tetrahedral hemiacetal intermediate.
Elimination of water yields an oxonium ion that undergoes a second nucleophilic addition of alcohol and subsequent proton transfer to form an acetal. The formation of the hemiacetal can be performed under basic conditions, but no further reaction takes place as the OH group cannot be turned into a suitable leaving group. Therefore, synthesis of acetals by this route requires acid catalysis to enable the elimination of water.¹⁷

Other synthetic routes to acetals include transacetalisation of an acetal with another alcohol or an aldehyde or ketone with another acetal under acidic conditions.⁸⁰ This is particularly useful for the synthesis of ketone derived acetals, for which the reaction with an alcohol gives poor results.⁸⁰ It is also possible to synthesise mixtures of acetals by an acid-catalysed metathesis reaction between two or more acetals.⁸¹

Acetals can also be synthesised from an alcohol and vinyl ether under acidic conditions and hemiacetal esters via the acid-catalysed reaction between a carboxylic acid and vinyl ether.¹,⁸²,⁸³ This reaction is favourable to those previously mentioned as it does not require the removal of a by-product to drive the reaction to completion and does not produce a mixture of products as with transacetalisation and acetal metathesis methodologies. However, it is limited by the availability of vinyl ethers, specifically divinyl ethers that are required to synthesise monomers bearing multiple polymerizable groups that can serve as chemical cross-links between polymer chains in thermosets. At the time of writing 1,4-butanediol divinyl ether,⁸⁴ 1,4-cyclohexanediol dimethyl divinyl ether (mixture of isomers),⁸⁵ di(ethylene glycol)
divinyl ether,\textsuperscript{86} poly(ethylene glycol)divinyl ether ($M_n 250$)\textsuperscript{87} and tri(ethylene glycol)divinyl ether are commercially available,\textsuperscript{88} though there are examples of laboratory scale preparations of novel divinyl ethers via a variety of synthetic methodologies.\textsuperscript{89–92}

Nasanit \textit{et al.} synthesised a diepoxyl cross-linker from glycidol and tri(ethylene glycol) divinyl ether, however, the yield was 5 \% (Scheme 1-10).\textsuperscript{93} If the low yield can be improved this could provide a synthetic route to meth(acrylate) cross-linkers with cleavable acetal groups by reaction with hydroxyl functionalised monomers such as 2-hydroxyethyl methacrylate and 2-hydroxyethyl acrylates; this is the focus of Chapter 2.

![Scheme 1-10 - Synthesis of acetal containing diepoxyl cross-linker.\textsuperscript{93}](image-url)
1.4.1. Acetal stability

It is hypothesised that hydrolysis of acetal groups in cross-links will impart methacrylate thermosets with degradable properties. An understanding of hydrolysis conditions and any structure-property relationships is therefore important. Acetals are stable under basic conditions but undergo hydrolysis in acidic media to form an alcohol and aldehyde or ketone.\(^{94-96}\)

Under acidic conditions the acetal oxygen is protonated and subsequently eliminated as an alcohol, forming a carboxonium ion, this is generally rate determining step (Scheme 1-11).\(^{95}\)

Nucleophilic addition of water forms a hemiacetal which undergoes the same series of reactions to form an aldehyde and two alcohols\(^ {94,96}\)

\[
\begin{array}{c}
\text{OR}^1 \text{R}^2 \text{OR}^3 \leftrightarrow \text{R}^1 \text{R}^2 \text{OR}^3 + \text{R}^1 \text{OH} \\
\text{H}_2\text{O} \rightarrow \text{R}^2 \text{OR}^1 \text{H} \leftrightarrow \text{OR}^1 \text{R}^2 \text{OH} \rightarrow \text{H} \rightarrow \text{OR}^1 \text{R}^2 \text{OH} \\
\text{Carboxonium ion} \\
\end{array}
\]

Scheme 1-11 - Acetal hydrolysis mechanism.

The specific substituents \(R^1\), \(R^2\) and \(R^3\) all effect the stability of the intermediate carboxonium ion and therefore the rate of hydrolysis. Liu and Thayumanavan published a comprehensive study of the effect different substituents have on hydrolytic stability of 18 acetal-containing compounds.\(^ {96}\) They performed hydrolysis experiments in CD\(_3\)CN/D\(_2\)O/phosphate buffer solutions at pH 5 and monitored them \textit{via in situ} \(^1\)H NMR spectroscopy. Several trends were observed. Increasing the distance between \(R^1\) and an electron withdrawing amide group increased the half-life \((t_{1/2})\). The effect of increasing CH\(_3\) substitution at \(R^2\) and \(R^3\) was probed; hydrolysis at pH 5 was only observed when \(R^2\) and \(R^3 = \text{CH}_3\), due to the electron donating effect of the CH\(_3\) stabilising the carboxonium ion. Acyclic acetals were less stable than 5-membered cyclic acetals, which were then less stable than 6-membered cyclic acetals. Lastly, upon decreasing the pH from 7.4 to 5, the \(t_{1/2}\) was found to decrease by two orders of magnitude.
Bulmus et al. monitored the hydrolysis of the acetal groups in their benzaldehyde derived cross-linkers via UV-spectroscopy in DMF at 37 °C using buffers to maintain solution pH at 4.5, 5.5, 6.5 and 7.4. They found that all cross-linkers were stable at pH 7.4 over 20 hrs. and had $t_{1/2} < 60$ minutes when at pH 5.5. Cross-linkers synthesised from 4-hydroxybenzaldehyde had shorter half-lives than those synthesised from 4-methoxybenzaldehyde due to the electron donating nature of the methoxy group stabilising the carboxonium intermediate. In summary, electron-donating substituents ($R^1, R^2, R^3$, Scheme 1-11) will stabilise the carboxonium ion giving rise to faster hydrolysis, meaning there is scope to tune the hydrolysis properties of acetal cross-linkers to an industrially-useful timeframe.

1.4.2. Acetals in Polymer Chemistry

Acetals have been used in a variety of polymer systems as a pH responsive functional group, including drug delivery, thermoplastics, thermosets, and CANs. Their use in acrylate/methacrylate cross-linkers is covered in Chapter 2, degradable thermosets in Chapter 3 and CANs in Chapter 5. The acetal group is particularly desirable in polymer networks as it both dynamic and acid degradable. This enables networks to be recycled via mechanical and chemical routes. Furthermore, Ma and co-workers have shown that polymeric hydrolysis products containing alcohol groups can be collected and cross-linked via reaction with divinyl ethers to yield materials with properties similar to that of the virgin material.
1.5. Green chemistry & sustainable synthesis metrics

The driving force behind this PhD research is tackling thermosets and their composite’s contribution to the global pollution problem. However, designing for degradation is just one of twelve green chemistry principles, first proposed by Anastas and Warner, that chemists can use to design green processes and products. A formal definition of Green Chemistry is the “design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances.”

The twelve principles are as follows:

1. Prevention of waste – prevention of waste is better than treating waste
2. Atom economy – incorporation of starting materials into products should be maximised
3. Safe synthesis – substances used and produced in syntheses should pose as little toxicity to humans and the environment as possible
4. Safer chemicals – products should maximise function while minimising toxicity
5. Safer solvents and auxiliaries – substances that are used but not incorporated into the final product should either be eliminated from the process or made innocuous
6. Energy efficiency – Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure
7. Renewable feedstocks – Starting materials and other reagents should be renewable rather than depleting whenever technically and economically practicable
8. Fewer derivatives – The use of derivatisation in a process should be minimised or avoided if possible
9. Catalysis – Catalysts are favourable over stoichiometric reagents and may be recovered and reused
10. Design for degradation – Products should degrade into innocuous by-products in the environment or reusable components for collection
11. Real-time analysis – Real-time monitoring and control of processes can prevent the formation of hazardous substances

12. Safer chemistry for accident prevention – Substances and their form should be chosen to minimise the potential and consequences of chemical accidents

Winterton has added a further twelve principles\textsuperscript{105}, while Anastas and Zimmerman developed the twelve principles of green engineering.\textsuperscript{107} However, quantitatively and qualitatively measuring the greenness of chemical processes is challenging as these are only guidelines. Some techniques such as life cycle assessment determine a product or process’ environmental impact from cradle to grave but require vast amounts of data. This can make the process costly and slow, although there are hybrid systems that look at specific parts of the lifecycle or have lower specificity. However, there are simple metrics available to the synthetic chemist. Three easily calculated metrics are atom economy, E factor, and process mass intensity. Although these do not measure the environmental impact of waste or economic viability of syntheses, they can provide insight into the efficiency and wastefulness of a process.\textsuperscript{106,108}

Atom economy measures the percentage of the reactants incorporated into the product, where a reactant is any building block that forms part of an intermediate or is incorporated into the final product. The atom economy is then calculated using the following equation:

\begin{equation}
\text{atom economy} \, (\%) = \frac{\text{molecular weight of product}}{\text{sum of molecular weights of starting materials and byproducts}} \times 100
\end{equation}

A high atom economy indicates a high amount of incorporation of starting materials in the product. However, the atom economy does not consider the amount of waste generated throughout a process. Therefore, processes with 100% atom economy can be highly wasteful in their use of auxiliaries or through achieving low conversion and selectivity.\textsuperscript{109,110} The E factor
quantifies the amount of waste produced in a chemical process. The ideal E factor is zero. As waste is undesirable in terms of sustainability it provides a more complete quantitative analysis of a process’ greenness. E factor is calculated using the following equation:\textsuperscript{108,111,112}

\begin{equation}
\text{Equation 1-2}

E \text{ factor} = \frac{\text{mass of waste}}{\text{mass of product}}
\end{equation}

Lastly, the process mass intensity considers the mass of all materials used in a process that is omitted in the calculation of E factor such as solvent, silica during purification and desiccants during drying. It is calculated using the following equation:

\begin{equation}
\text{Equation 1-3}

\text{process mass index} = \frac{\text{Mass used in process}}{\text{Mass of product}}
\end{equation}

The metrics and twelve principles will be used to guide and quantify the greenness of dimethacrylate acetal containing cross-linkers synthesised in Chapter 2.
1.6. Acid Generators

Acid generators, sometimes referred to as latent acids, is a collective term for molecules that generate an acid upon exposure to an external stimulus such as light, heat or mechanical force. They are often given a prefix relating to the stimuli they respond to such as photoacid, thermal acid or mechanoacid generator; the latter is a relatively new type of acid generator.\textsuperscript{113–115} Within the context of this research they will be investigated as latent degradation and dynamic bond exchange catalysts. Much of the founding work in the field was related to photolithography and utilising the spatial control they give to selectively cleave acid sensitive polymers.\textsuperscript{116,117} Subsequently they have been applied to degradable thermosets\textsuperscript{118}, as latent catalysts in adaptable networks,\textsuperscript{67,119–121} and as latent initiators in acid catalysed polymerisations.\textsuperscript{122,123} Their proposed role in this research is as latent hydrolysis catalysts within degradable thermosets and latent exchange catalysts in adaptable networks. A brief overview of acid generator development, example chemistries, current state of the art and their application in degradable thermosets and CANs will now be given. For more in depth reviews see Shirai and Masahiro\textsuperscript{116}, Martin \textit{et al.}\textsuperscript{124}, Zivic \textit{et al.}\textsuperscript{117} and Tsuchimura.\textsuperscript{125}

Early photoacid generators were ionic; such as aryl diazonium, diaryliodonium, triarylsulfonium and triarylpophosphonium salts, utilising metal halide counter ions such as BF\textsubscript{4}\textsuperscript{−}, SbF\textsubscript{6}\textsuperscript{−}, AsF\textsubscript{6}\textsuperscript{−} and PF\textsubscript{6}\textsuperscript{−} (Figure 1-3). Upon irradiation with light of a suitable wavelength (200-300 nm), these salts undergo photolysis liberating a free acid. The wavelength of light required can be tuned by incorporating different functionality to the onium component. Onium salts have high thermal stabilities, however, they have low solubilities in organic solvents.\textsuperscript{116,117}

![Figure 1-3 - Examples of onium ions used in ionic acid generators.](image-url)
Alternative non-ionic acid generators were subsequently developed to circumnavigate the low solubility of ionic acid generators. Two categories of ionic acid generators exist, those that require hydrogen donors to generate acids and those that generate acids via a unimolecular process. The former includes \textit{para}-nitrobenzyl sulfonates, sulfones, disulfones, \textit{N}-hydroxyimide sulfonates, phenolic sulfonates, diazonaphthoquinones, and imino sulfonates.\textsuperscript{116,125} As the required acid generator will be present in a polymer matrix, the latter type is favoured for simple acid generation. This criterion limits the pool of available acid generators to \textit{ortho}-nitrobenzyl esters and sulfonate esters (Scheme 1-12).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Scheme_1-12.png}
\caption{Scheme 1-12 - Nonionic acid generators a) \textit{ortho}-nitrobenzyl esters and an example of a sulfonate b) cyclohexyl tosylate.}
\end{figure}

\textit{Ortho}-nitrobenzyl esters of carboxylic and sulfonic acids are thermal and photoacid generators.\textsuperscript{126,127} Upon irradiation with ultraviolet light they undergo a free radical reaction pathway, proceeding via the abstraction of a benzylic hydrogen atom via a nitro group oxygen atom followed by rearrangement and subsequent elimination of an acid, yielding a nitrosoaldehyde.\textsuperscript{116} A complication of using light to drive the acid generation within polymer matrices is significant absorption of light by the matrix. To avoid this, the wavelength of light required to drive photolysis can be tuned by substitution on the aromatic ring and acid group.\textsuperscript{126,128} \textit{Ortho}-nitrobenzyl esters are also known to undergo thermal elimination, the temperature of which is controlled by substituent effect. Interestingly the thermolysis temperature has been found to vary within polymer matrices versus the neat acid generator.\textsuperscript{129} Lastly, the syntheses of \textit{ortho}-nitrobenzyl esters is easily achieved via the reaction between \textit{ortho}-nitrobenzyl alcohols and acid chlorides.\textsuperscript{127,130}
Sulfonates are known thermal acid generators that undergo an intramolecular elimination reaction to produce an alkene and sulfonic acid.\textsuperscript{131} The temperature of acid generation is dependent on substituents enabling the facile synthesis of acid generators with a range of thermolysis temperatures.\textsuperscript{122,123,132,133} Sulfonate acid generators are covered in greater detail in Chapter 4.

Shirai \textit{et. al} have published several examples where thermoset degradation is induced by a photoacid generator (PAG).\textsuperscript{118,134--138} Four (meth)acrylate cross-linkers bearing acetal linkages were synthesised (Figure 1-4). A photo or thermal radical initiator was used to make polymer films. The acetal linkages in films were found to be stable up to 180-240 °C. Films doped with the PAG \textit{N}-hydroxynaphtalimide triflate (NITf) (1 wt%) were irradiated with UV light (366 nm), generating triflic acid, and heated at 100 °C for 10 minutes, after which films were soluble in THF, indicating the degradation of cross-links.\textsuperscript{138} Further work with these monomers, and alternative triflic acid generators, found post baking was not required and films became soluble in methanol upon UV irradiation.\textsuperscript{136} Shirai \textit{et. al} published further work with trifunctional methacrylate acetal cross-linkers that degraded upon acid generation.\textsuperscript{135}
Acid generators have been used to impart CANs with irreversible changes to their dynamic behaviour via catalysis. The first example of this methodology was reported by Worrell et al. who used photobase generators in thioester/thiol dynamic chemistry-based CANs, whereby
irradiation with light caused an irreversible phase change in the CAN from solid to liquid (Scheme 1-13). Unlike previous CAN systems removal of the stimulus did not return the material to its original state. Furthermore, the spatial control offered by using light as a stimulus enabled them to create distinct regions within the CAN in different physical states. The authors then synthesised networks containing both photoacid and photobase generators, that underwent photolysis at different wavelengths of light. Generation of acid neutralised any free base halting the dynamic bond exchange and returning the network to a solid state. Schlögl and co-workers have reported further the use of photoacid in thiol-acrylate and photobase generators in thiol-epoxy based CANs to control the rate of bond exchange and therefore the stress-relaxation properties of the networks.

Scheme 1-13 - Photobase and photoacids used by Worrell et al. to impart CANs with lockable phase change behaviour.
1.7. Research Aims

Despite offering excellent mechanical properties, thermosets infusibility and insolubility hinder their recyclability and as legislation on the use and recycling of plastics may ban traditional thermosets, solutions must be found as they are essential to modern life. There are many literature examples of degradable thermosets, however, many require complicated syntheses of novel monomers, post-polymerisation functionalisation and undergo a step-growth type curing mechanism.

The research aims of this project are to assess the viability of acetal chemistry for use in methacrylate-based thermosets that are pH degradable. Methacrylate-based thermosets are of particular interest to Scott Bader, the industrial funders of this research. Their adhesives, coatings and composite product ranges utilise free radical curing techniques that are compatible with methacrylate-based thermosets. Introducing end-of-life recycling options to their product range is of the utmost importance to the business and acetal containing thermosets are hypothesised to enable this.

To achieve this acetal containing cross-linkers will be synthesised from a divinyl ether and hydroxyl functionalised methacrylate, then scaled up to allow characterisation of their degradation and mechanical properties. Furthermore, acetals undergo dynamic exchange reactions and impart networks with adaptable behaviour which will be investigated. Lastly, it is hypothesised that acid generators can be added to acetal containing networks to give hydrolysis on demand properties.
Chapter 2 – Synthesis and Characterisation of Dimethacrylate Acetal Cross-Linker

2.1. Introduction

As previously discussed, the starting materials for acetals are an alcohol, a nucleophile, and an electrophile such as an aldehyde, ketone or vinyl ether. Within an industrial context it is desirable for starting materials to be commodity chemicals as these will have an established supply chain and appropriate regulatory status allowing their use. Furthermore, from an industrial and sustainability point of view, multistep reactions are undesirable. Therefore, searching for synthetic routes to methacrylate or acrylate-based acetal cross-linkers was limited to the following nucleophile/electrophile pairs: (meth)acrylates bearing an alcohol and a multifunctional aldehyde, ketone or vinyl ether. Alternatively, the pair could be reversed to meth(acrylates) bearing an aldehyde, ketone or vinyl ether and a diol. Unfortunately in the latter scenario no vinyl ether bearing (meth)acrylates are commercially available and in both scenarios the high temperatures required to synthesise acetals from alcohols and ketones or aldehydes are likely to lead to thermally initiated homopolymerisation of (meth)acrylates. There, a route using an alcohol bearing (meth)acrylate and divinyl ether is desirable.

There are few examples of (meth)acrylate cross-linkers containing acetal functional groups in the literature. The majority of examples of degradable thermosets based upon acetal chemistry are epoxy resin materials. Fortunately, acetal chemistry has been utilised in stimuli responsive hydrogels and pH degradable polymers for drug delivery, of these examples all are synthesised from an alcohol and aldehyde or by transacetalisation based syntheses.

Bulmus et al. synthesised a library of acetal containing methacrylates and acrylates by the reaction of 2-hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acrylate and poly(ethylene glycol methacrylate) with 4-methoxybenzaldehyde or 4-hydroxybenzaldehyde (Scheme
Reactions were stirred at 0 °C for 15 hrs using para-toluenesulfonic acid (pTsOH) as an acid catalyst and 3 Å molecular sieves as a water trapping agent. Purification was performed via basic alumina column chromatography producing the acetals in the yields ranging between 30–70%. Burek et al. synthesised a diacrylate cross-linker by a two-step synthetic procedure (Scheme 2-1b). Firstly, acryloyl chloride was reacted with 4-hydroxybenzaldehyde to give an aldehyde functional monomer. The crude product was purified via vacuum distillation, and isolated with 81% yield. The aldehyde group was then reacted with trehalose to yield a diacrylate cross-linker bearing two cyclic acetal groups via refluxing in DMF and benzene for 16 hrs; water was removed via azeotropic distillation. The purification process involved repeated dissolution and precipitation from ethyl acetate and hexane to yield the monomer in 41% yield. Both 4-hydroxybenzaldehyde and trehalose can be sourced from renewable feedstocks.
Further examples of dimethacrylate cross-linkers bearing one acetal group were synthesised by Themistou and Patrickios, Heath et al., and Kim et al. all via transacetalisation reactions (Scheme 2-2). Themistou and Patrickios reacted HEMA with paraformaldehyde using pTsOH as a catalyst in toluene at 80 °C. The crude product was purified via column chromatography to give the dimethacrylate with a yield of 15%, which was then further distilled prior to use (Scheme 2-2a). Heath et al. prepared a dimethacrylate by the reaction of HEMA
with 2,2-dimethoxypropane using pTsOH as a catalyst in benzene to enable the azeotropic removal of methanol; no yields or purification procedures were reported (Scheme 2-2b). Lastly, Kim et al. synthesised a similar dimethacrylate using poly(ethylene glycol) methacrylate (n=6) and 2,2-dimethoxypropane (Scheme 2-2c). Again, pTsOH was the catalyst, however, THF was the solvent and instead of azeotropic distillation, methanol was collected using molecular sieves. No further purification or the yield were described.

\[
\begin{align*}
\text{a)} & \quad \begin{array}{c}
2 \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{CH}_2\text{O}}{\text{CH}_2\text{O}} \quad \overset{\text{OH}}{\text{OH}} \\
\end{array} & \quad \begin{array}{c}
\overset{\text{pTsOH}}{\text{toluene}} \\
\overset{80 \text{ °C}}{\text{}} \\
\end{array} & \quad \begin{array}{c}
\overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \\
\end{array} \\
\text{b)} & \quad \begin{array}{c}
2 \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{CH}_2\text{O}}{\text{CH}_2\text{O}} \quad \overset{\text{OH}}{\text{OH}} \\
\end{array} & \quad \begin{array}{c}
\overset{\text{MeO}}{\text{MeO}} \quad \overset{\text{MeO}}{\text{MeO}} \\
\overset{\text{pTsOH}}{\text{}} \\
\end{array} & \quad \begin{array}{c}
\overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \\
\end{array} \\
\text{c)} & \quad \begin{array}{c}
2 \quad \overset{\text{O}}{\text{O}} \quad \overset{(\text{CH}_2\text{O})_6\text{OH}}{\text{CH}_2\text{O}} \quad \overset{(\text{CH}_2\text{O})_6\text{OH}}{\text{OH}} \\
\end{array} & \quad \begin{array}{c}
\overset{\text{MeO}}{\text{MeO}} \quad \overset{\text{MeO}}{\text{MeO}} \\
\overset{\text{pTsOH}}{\text{}} \\
\end{array} & \quad \begin{array}{c}
\overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{O}}{\text{O}} \\
\end{array}
\end{align*}
\]

Scheme 2-2 - Synthetic routes to (meth)acrylates containing acetal functional groups via transacetalisation.\(^{148-150}\)

Lastly, only one synthetic route to (meth)acrylate cross-linkers utilising the reaction between an alcohol and vinyl ether could be found in the literature (Scheme 2-3). Shirai et al. performed a two-step synthetic procedure first reacting a series of aromatic diols with 2-chloroethyl vinyl ether catalysed by NaOH in dimethyl sulfoxide (DMSO) at 75 °C for 14.5 hrs (Scheme 2-3a). The resultant vinyl ethers were purified via recrystallisation, or column chromatography when \(R^1\) was the triphenyl group, producing a series of divinyl ethers with yields ranging from 46–79 %. The divinyl ethers were reacted with HEMA or 2-hydroxyethyl acrylate using pTsOH as a catalyst in THF for 25 hours at 0–5 °C (Scheme 2-3b). The monomers were purified via column chromatography and insolated in yields ranging 41–72 %.\(^{118,151}\)
It is clear from the literature a variety of acetals with different substituents can be made, meaning there is scope for tuning their hydrolytic behaviours to those required for degradable thermosets. However, the examples discussed require elevated temperatures, multiple steps or produce waste products such as MeOH or HCl that require removal. Within this chapter research was undertaken to develop a simple synthetic methodology for a dimethacrylate cross-linker containing acetal groups from commercially available starting materials and to characterise its hydrolysis products to guide its application in degradable thermosets.
2.2. Results and Discussion

2.2.1. Synthesis of Acetal Cross Linker & Hydrolysis Experiments

2.2.1.1. Synthesis of Acetal Bearing Dimethacrylate Cross-Linker A1

A methacrylate cross-linker bearing two acetal functional groups (A1) was synthesised from tri(ethylene glycol) divinyl ether (TEGDVE) and HEMA using pTsOH as a catalyst (Scheme 2-4) in a process adapted from Nasanit et al, by replacing the glycidol with HEMA. The proposed mechanism proceeds via vinyl ether tautomerisation to an electrophilic oxonium ion and nucleophilic addition by an alcohol followed by proton exchange to yield an acetal (Scheme 2-5). Thin layer chromatography (TLC) confirmed the reaction was complete in 6 h and the 1H NMR spectrum of the crude product showed no residual vinyl ether groups were present, suggesting complete formation of the diacetal product. A1 was purified via column chromatography and isolated in 75% yield. 1H NMR spectroscopy revealed the molar ratio of ethylene bridge protons was higher than expected, due to an oligomerisation side reaction (discussed in detail in section 2.2.2.2).

![Scheme 2-4 - Synthesis of acetal cross linker.](image)

![Scheme 2-5 - Reaction mechanism of acetal formation via reaction of alcohol and divinyl ether.](image)
2.2.1.2. Hydrolysis of A1

The acetal groups of A1 were hypothesised to impart acid-degradable behaviour to A1 cross-linked networks by acting as cleavage point between chains. Therefore, an understanding of the hydrolysis behaviour of A1 was required. The hydrolysis kinetics are important as they will contribute to the stability of A1 cross-linked networks and how easily they are removed when desired. Additionally, the hydrolysis products may become environmental pollutants meaning their identification is paramount to understanding the consequences of their release. A1 was added to a 0.15 M solution of pTsOH in acetone-d6/D2O (9/1 v/v) and stirred at 50 °C for 5 hrs. (Scheme 2-6), these conditions were selected based on acetal containing epoxy thermoset degradation experiments in the literature where the solvent/water ratio was kept high to maintain product solubility.\textsuperscript{152}

\[ \text{Acetone-d6/D}_2\text{O (9/1 v/v)} \]

\[ \text{pTsOH (0.15 M)} \]

\[ 50 \degree \text{C} \]

\[ 5 \text{ hours} \]

\[ \text{Acetaldehyde} \]

\[ \text{HEMA, tri(ethylene glycol)} \]

Scheme 2-6 - Hydrolysis of A1, yielding HEMA, tri(ethylene glycol) and acetaldehyde.

Comparison of the \(^1\)H NMR spectra of A1 with that of the reaction mixture after 5 hrs. revealed quantitative hydrolysis of the acetal groups, as determined by the disappearance of the CH and CH\textsubscript{3} resonances at 4.80 (m, 2H) and 1.31 (m, 6H) ppm, respectively (Figure 2-1). The literature on acetal hydrolysis states the products should be an alcohol and an aldehyde or ketone.\textsuperscript{94} A1 is unusual as it is an asymmetric acetal, the ether groups on either side are different, often a feature of acetals synthesised from a vinyl ether and alcohol.\textsuperscript{70} It was hypothesised that the hydrolysis of A1 would produce HEMA, tri(ethylene glycol) (TEG) and acetaldehyde. Analysis of the \(^1\)H NMR spectrum of the hydrolysis reaction mixture confirmed the formation of acetaldehyde by the emergence of CH\textsubscript{3}C(O)H and CH\textsubscript{3}C(O)H peaks at 9.61 (S, 1H) and 2.01 (M, 3 H) ppm, respectively (Figure 2-1). However, the molar ratios of these peaks were lower than expected, this was attributed to acetaldehyde’s low boiling point, high volatility, and ability to form hydrates causing difficulty in measurements.\textsuperscript{153}
The spectra also showed a shift in the alkene CH peak at 6.11 ppm to 6.03 ppm suggesting the formation of a different methacrylate. The bridging CH$_2$ peaks in the region 4.25–3.25 ppm were assigned to those in HEMA and TEG but could not be assigned individually due to the similarity in the proton environments. The reaction mixture was also characterised by high pressure liquid chromatography mass spectroscopy (HPLC-MS) which confirmed acetaldehyde, HEMA and TEG were the hydrolysis products (Appendices Figure 8-1).

2.2.1.3. Effect of pK$_a$ on Hydrolytic Stability

With the hydrolysis products of A1 determined, its hydrolytic stability with different strength acids was investigated. As before, hydrolysis experiments were conducted in 0.15 M acid acetone-d$_6$/D$_2$O (9/1 v/v) solutions at 50 °C for 5 hrs. Due to the experiments being conducted in organic media, pH could not be used to study the hydrolytic stability, as this is specific to water. The pK$_a$ of various acids in water was used as an empirical measure of acid strength,
as this changes with solvent,\textsuperscript{154} to aid with acid selection. $pK_a$ is the negative log of the equilibrium constant of an acid and its conjugate base; lower values indicate a more dissociated and, therefore, stronger acid.\textsuperscript{154}

It was hypothesised that decreasing $pK_a$ would affect the observed hydrolytic stability of A1. The strength of an acid depends upon the stability of its conjugate base and the HA bond strength. A strong acid may have a stable conjugate base and weak HA bond. Lastly the solvent’s ability to stabilise the ions formed upon dissociation is also important.\textsuperscript{154} A series of structurally similar acids with $pK_a$ values greater than that of pTsOH ($pK_a$ -2.8)\textsuperscript{155} were sought to probe the hydrolytic stability of A1. A variety of sulfonic and carboxylic acids spanning a $pK_a$ range from -2.8 to 4.8 were compiled (Figure 2-2).\textsuperscript{156} Notably, only the sulfonic acids had $pK_a$ values below 0. Three series were identified mono, di, and trichloroacetic acid, 2- and 3-furoic acid and 2-, 3-, and 4-nitrobenzoic acid. Of these, monochloroacetic (MCA), dichloroacetic (DCA) and trichloroacetic (TCA), as well as trifluoroacetic (TFA) acid were chosen due to their cost and $pK_a$ values, 2.86, 1.29, 0.65 and 0.23 respectively. $pK_a$ decreases with increasing chlorine substitution in the $\alpha$ position in the chloroacetic acid series, due to the increase in electronegativity weakening the O-H bond via the inductive effect. This is also true when comparing TCA and TFA, the CF$_3$ group is more electronegative weakening the O-H bond.\textsuperscript{157}
Acetals are generally stable at basic and neutral pH, but at pH < 7 hydrolysis occurs. Under these acidic conditions the weakly basic acetal oxygen is protonated and subsequently eliminated forming an oxonium ion, this is typically, but not always, the rate determining step (Scheme 2-7). Nucleophilic addition of water forms a hemiacetal which undergoes the same series of reactions to form an aldehyde and two alcohols. \( pK_a \) is the pH at which the concentration of acid and its conjugate base are equal, the greater concentration of hydronium ions mean lower \( pK_a \) acids should give a greater extent of hydrolysis if the concentrations and time are kept constant. Therefore, it was expected the extent of hydrolysis of A1 would increase in the order MCA, DCA, TCA and TFA.

![Scheme 2-7 - Mechanism of acetal hydrolysis.](image)

Figure 2-2 - \( pK_a \) of carboxylic and sulfonic acids in H\(_2\)O.
Table 2-1 - Effect of acid $pK_a$ on the extent of A1 hydrolysis in acetone-$d_6/D_2O$ (9/1 v/v) at 50 °C for 5 hrs.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a$</th>
<th>Hydrolysed (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochloroacetic acid</td>
<td>2.86</td>
<td>2</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td>1.29</td>
<td>62</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>0.65</td>
<td>100</td>
</tr>
<tr>
<td>Trifluoroacetic acid</td>
<td>0.23</td>
<td>100</td>
</tr>
</tbody>
</table>

$^a$Determined via $^1$H NMR spectroscopy

Table 2-1 summarises the extent of A1 hydrolysis after 5 hrs. at 50 °C for the acids MCA, DCA, TCA and TFA. As expected lower $pK_a$ values led to quantitative hydrolysis determined by $^1$H NMR spectroscopy. It was thought the greater extent of hydrolysis was due to greater acid dissociation giving rise to a higher concentration of hydronium ions capable of catalysing A1 hydrolysis. A1 in solutions of the weaker acids MCA and DCA was only partially hydrolysed, 2 and 62 % respectively. Upon leaving the MCA and DCA samples for 48 hrs at 50 °C the extent of hydrolysis increased to 86 and 31% respectively. This suggests a $pK_a < 1.29$ is desired if A1 hydrolysis is to occur within a useful timeframe, that will vary depending on application.$^7$

2.2.2. Optimisation and Scale Up of A1 Synthesis

To further characterise the degradation properties and prepare samples for mechanical testing, large batches of A1 were required to minimise batch-to-batch variation and reduce the time spent repeating small scale syntheses. Furthermore, the scalability of the process is industrially and environmentally relevant. As the application of A1 to thermoset chemistry aims to contribute positively to sustainability, so should the synthetic procedure. To achieve this the synthesis of A1 was scaled up and optimised using the twelve principles of green chemistry, proposed by Anastas and Warner, as a framework for improving the process.$^{104}$ Particularly the prevention of waste and using less hazardous materials, safer solvents and catalysis.
Preparation of A1 makes excellent use of TEGDVE and HEMA, as shown by the atom economy of 100%, no side products are produced as it proceeds by proton transfer steps. However, the initial preparation of A1 (Scheme 2-4) used a high pTsOH loading of 5 mol % relative to TEGDVE and tetrahydrofuran (THF) as a reaction solvent, which is expensive, highly flammable and a suspected carcinogen. Furthermore, the work up required back extraction of the product into DCM and subsequent washes, followed by flash column chromatography producing solvent and silica waste. The following parameters were identified for optimisation; acid concentration, solvent, reactant feed rate and the work up procedure.

2.2.2.1. Acid Species and Concentration

To better understand the role of the catalyst pTsOH in synthesising A1 from TEGDVE and HEMA a series of syntheses with varying pTsOH mol % relative to TEGDVE were performed. A solution of TEGDVE and DCM was fed into a reaction vessel containing DCM, pTsOH and HEMA, reagent concentrations and the feed rate were kept constant. The reactions were monitored by $^1$H NMR spectroscopy to characterise the effect of catalyst loading on conversion over 300 min. The disappearance of the HEMA vinyl CH peak at 6.13 ppm was used to follow conversion which had very slight overlap with the shoulder of that of A1 at 6.08 ppm. However, the preferred HEMA CH$_2$ positioned on the β-carbon to the ester at 4.29 ppm coalesced with the equivalent protons in A1. Further to this the vinyl ether CH$_2$ peak at 6.50 ppm could not be used to monitor time conversion as it is susceptible to acid catalysed hydrolysis (see section 2.2.2.2).

The conversion results (Figure 2-3) reveal that the control experiment with no pTsOH did not undergo any reaction during the experiment duration. Interestingly, reducing the pTsOH concentration from 5 to 0.5 and 0.1 mol % led to no observable decrease in conversion during the 2-hour addition of the TEGDVE and DCM solution, meaning the reaction duration can be reduced from 24 to 2 hours. Decreasing pTsOH loading from 5 to 0.1 is a factor of 50 decrease
with no change in the reaction outcome, meaning less catalyst is wasted and subsequently separated from the product.

Interestingly, no appreciable increase in the conversion of HEMA was observed after 3 hours of stirring when using 0.5 and 0.1 mol % pTsOH suggesting a stoichiometric imbalance arising from experimental error causing the reaction to stall or the possibility of side reactions consuming reactants and preventing the reaction from reaching completion. When using 5 mol % pTsOH a decrease in conversion of HEMA to A1 was observed during the 3 hours stirring which was thought to be due to possible hydrolysis of the acetal product at the higher acid loading. Increasing the pTsOH content would increase the concentration of H₂O in the reaction as pTsOH is supplied as the monohydrate.

Alternative acids may be used that are more suitable for industrial handling, such as methane sulfonic acid and TFA, due to their liquid form. Interestingly when investigating other acids, it was found that using TFA at 0 °C gave low conversion that increased to 92 % after removing DCM at 35 °C on the rotary evaporator. This may be a useful acid to pursue for larger scale reactions at ambient temperatures. Furthermore, easily removable, and reusable heterogeneous catalysts such as polymer bound pTsOH may be of interest.

Figure 2-3 - Effect of acid concentration on conversion of HEMA to A1 as determined by 'H NMR spectroscopy.
2.2.2.2. Oligomerisation Side Reactions

Table 2-2 - Effect of pTsOH mol % on HEMA conversion during the synthesis of A1 and the formation of acetaldehyde side product.

<table>
<thead>
<tr>
<th>pTsOH (mol %)a</th>
<th>Conversion at 120 mins (%)b</th>
<th>Conversion at 300 mins (%)b</th>
<th>[Acetaldehyde]:[A1] 300 minsb</th>
<th>Methylene CH₂ Integralb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>94</td>
<td>95</td>
<td>1:75</td>
<td>16.78</td>
</tr>
<tr>
<td>0.5</td>
<td>95</td>
<td>95</td>
<td>1:47</td>
<td>16.87</td>
</tr>
<tr>
<td>5</td>
<td>96</td>
<td>91</td>
<td>1:10</td>
<td>18.33</td>
</tr>
</tbody>
</table>

a Relative to TEGDVE; b determined by ¹H NMR spectroscopy

Upon further examination of the reaction mixture ¹H NMR spectra from reactions performed using different acid concentrations, the emergence of a peak at 9.74 ppm over time was observed. This was assigned as the CH₃C(O)H in acetaldehyde. The difference in shift compared to previous experiments characterising the hydrolysis of A1 was due to the different deuterated solvent systems used.¹⁵⁹ Observing acetaldehyde further supported the hypothesis that hydrolysis of the acetal groups in A1 was occurring during the reaction via the previously discussed mechanism. However, TEGDVE may also undergo hydrolysis of the vinyl ether groups producing TEG and 2 equivalents acetaldehyde (Scheme 2-9).¹⁶⁰

![Scheme 2-8 - TEGDVE hydrolysis mechanism.](image)

If TEG was being generated in situ, it was hypothesised that an oligomerisation side reaction could occur via a step growth mechanism generating oligomeric acetal species end-capped with HEMA. TEG is a diol able to undergo polymerisation with TEGDVE via addition to the vinyl ether groups to form poly(acetals). A similar reaction was described by Tomlinson et al. during the synthesis of polyacetals from poly(ethylene glycol) and TEGDVE. The authors
proposed residual water underwent addition to the vinyl ether group forming a hemiacetal capable of reacting further, creating very hydrolytically unstable diacetal species along the polymer backbone. However, there is little evidence in the literature suggesting significant formation of hemiacetals during vinyl ether hydrolysis. The equilibrium favours the formation of an aldehyde and alcohol. The latter may take part in further reactions with divinyl ethers forming a poly(acetal) under the reaction conditions of A1.

By comparing the ratio of A1 to acetaldehyde in the $^1$H NMR spectra of reactions conducted with different pTsOH concentrations it was found that concentrations increased the prevalence of acetaldehyde (Table 2-2). As proton transfer to the methylene group is the rate determining step of vinyl ether hydrolysis, this was indicative of this pathway contributing to a side reaction. Evidence of a step growth oligomerisation was revealed by the integrals of the methylene CH$_2$. Upon examining the methylene CH$_2$ shifts in the region 3.40-3.90 ppm the integrals were higher than the expected for A1 relative to the vinyl CH. Higher integrals were observed for higher acid concentrations, suggesting acid catalysis was contributing to the reaction pathway of the side reaction. Furthermore, elemental analysis of the product gave values of carbon 57.11 % and H 8.23 % which differed from the expected values of carbon 59.17% and hydrogen 8.58%, suggesting the molecular composition was different.

HPLC-MS was used to study the product of the 0.5 mol % pTsOH reaction to reveal the true reaction product(s) and therefore, the mechanism (Figure 2-4). The chromatogram revealed a distribution of products of varying polarity, with the largest peak appearing over the retention time range of 8.7-9.3 minutes. The mass spectra revealed structures with higher than expect m/z suggesting the formation of oligomers, the structures of which are shown in Figure 2-4 (full assignments – Appendices Table 8-1). HEMA was identified as the chromatogram peak at 4.2 mins. suggesting the formation of the by-product proceeded via vinyl ether hydrolysis as this creates a stoichiometric imbalance that prevents HEMA from reacting. The diol identified at peak 4.8 mins was synthesised by reaction of tri(ethylene glycol) and TEGDVE or tri(ethylene glycol)mono vinyl ether. TEG is synthesised by the hydrolysis of the vinyl ether
groups in TEGDVE; the diol is then created by two possible pathways, addition of TEG to tri(ethylene glycol)monovinyl ether.

![Diagram showing the structure of the diol](image)

Figure 2-4 – (a) HPLC-MS chromatogram showing distribution of products and (b) mass spectrum of chromatogram peak at 10.2 min of the crude reaction mixture of the A1 synthesis.

The other pathway is the addition of tri(ethylene glycol) to TEGDVE and subsequent hydrolysis of the remaining vinyl ether group. The diol attributed to the peak at 5.5 mins is generated by addition of two tri(ethylene glycol) molecules to TEGDVE. The peaks within the boxed region between 6-7.8 mins. in Figure 2-4 all correspond to structures of the general formula shown. Again these species are generated by a reaction of *in situ* synthesised tri(ethylene glycol) and TEGDVE which are then capped by the reaction of HEMA with a vinyl ether. The degrees of oligomerisation in these species was observed to be up to 6. The peak at 8.9 mins corresponded to the desired product A1, and the peak at 10.8 mins was thought to be oligomeric derivatives of A1. The mass spectrum of the peak at 10.8 is shown in Figure 2-4 with all peaks labelled with their difference in m/z to the base ion peak at 817.422 amu. The
spectrum contains species varying in m/z by ~176 amu, this is indicative of molecules of similar polarity varying by a common repeat unit. It was expected that HEMA capped oligomers would vary by an m/z of 150.09 amu or an adduct corresponding to the actual mass of tri(ethylene glycol). However, the closest value to 176 amu was found to be the tri(ethylene glycol) adduct [M+Na]+, 173.09 amu which has a difference of 3 amu units. Therefore, it cannot be definitively stated that these oligomers are similar in structure to A1. This may be resolved by optimising the instrument operating conditions. However, based on the other structures identified and the similarity of these products’ proton environments in 1H NMR spectroscopy, the by-products of the reaction between HEMA and TEGDVE, under acidic conditions, are believed to be mono, dimethacrylate or diol oligomers.

2.2.2.2.1. pTsOH Catalysed Polymerisation of TEGDVE

To investigate if hydrolysis was causing the oligomerisation side reaction, the synthesis of A1 was performed under anhydrous conditions. TEGDVE was first purified via azeotropic distillation of water with toluene and storing over molecular sieves. HEMA and THF were stored over molecular sieves, and all were stored under nitrogen in Schlenk glassware. The reaction was repeated under anhydrous conditions in Schlenk glassware but unexpectedly high integrals for the methylene CH₂ protons in the region 3.40-3.90 ppm were observed suggesting oligomerisation via the previously discussed pathway. The presence of the TEGDVE hydrolysis product acetaldehyde was also observed in the 1H NMR spectrum of the reaction mixture. This suggested oligomerisation was still occurring in the absence of environmental and residual moisture in reagents. It was hypothesised the source of H₂O was pTsOH monohydrate, the catalyst’s commercially available form.

A series of control experiments were performed to verify this hypothesis. The synthesis was performed as before without HEMA present and at various acid concentrations. If water from pTsOH monohydrate was hydrolysing TEGDVE to TEG then a poly(acetal) would form (Scheme 2-9). Furthermore, the molecular weight of the resulting poly(acetal) should increase
with pTsOH monohydrate as this leads to an increase in residual water and, therefore, tri(ethylene glycol) reducing the molar ratio of TEGDVE to TEG.

\[
\begin{array}{c}
\text{O} \text{O} \text{O} \text{O} \text{O} \xrightarrow{\text{pTsOH, DCM}} 0-25^\circ\text{C} \text{O} \text{O} \text{O} \text{O} \text{O} \\
\end{array}
\]

Scheme 2-9 - Synthesis of poly(acetal) via the hydrolysis of TEGDVE.

The reactions were performed with acid concentrations of 0.1, 0.5 and 1 mol % relative to the vinyl ether groups. The reaction was quenched 30 minutes after the addition of TEGDVE by addition of Na₂CO₃ to prevent further reaction, and was worked up. When using 0.1 mol % pTsOH, residual TEGDVE was observed in the "H NMR spectrum of the products. This was thought to be due to the low acid concentrations reducing the rate of vinyl ether hydrolysis. However, when using 0.5 and 1 mol % no vinyl ether was observed in the products and the integrals of the methylene CH₂ protons in the region 3.40-3.90 ppm were found to increase with acid loading, suggesting the formation of longer chains at higher acid loadings.

Table 2-3 - Summary of control poly(acetal) characterisation data.

<table>
<thead>
<tr>
<th>pTsOH mol %</th>
<th>Methylene bridge CH₂ product (^{1}\text{H}) NMR integral(^a)</th>
<th>(M_n) (g/mol)(^b)</th>
<th>(M_w) (g/mol)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>N/A</td>
<td>1200</td>
<td>1300</td>
</tr>
<tr>
<td>0.5</td>
<td>19.12</td>
<td>1500</td>
<td>1900</td>
</tr>
<tr>
<td>1</td>
<td>23.15</td>
<td>2400</td>
<td>3300</td>
</tr>
</tbody>
</table>

\(^a\) Determined via "H NMR spectroscopy (CDCl₃) relative to the acetal CH₃ shift at 1.30 ppm, \(^b\) determined by SEC in THF and relative to p(MMA) standards

Furthermore, the molar masses of the reaction products determined by size exclusion chromatography (SEC) were found to increase with acid concentration (Table 2-3 & Appendices Figure 8-2). This supports the hypothesis that pTsOH monohydrate can act as a water source leading to the formation of oligomerisation side products in the synthesis of A1 and therefore, a compromise between rate of reaction and extent of oligomerisation must be reached by selecting a suitable acid concentration.
2.2.2.2. \textbf{pTsOH Catalysed Copolymerisation of TEGDVE and TEG}

To further support the formation of poly(acetals) from TEGDVE and TEG formed \textit{in situ}, a final series of control reactions was performed (Scheme 2-10). Poly(acetals) were synthesised directly from TEGDVE and TEG under the same reaction conditions for the synthesis of A1. As before pTsOH concentrations of 0.1, 0.5 and 1 mol \% were used to probe the effect on polymerisation and was monitored by product molar mass. Conversely to control polymerisations where only TEGDVE was used, lower catalyst concentrations gave higher molar masses by SEC (Appendices Figure 8-3). As previously discussed, lower catalyst loadings lead to a decreased rate of vinyl ether hydrolysis. In the case of the step growth polymerisation of TEGDVE and TEG this causes a lower stoichiometric imbalance between the A$_2$ and B$_2$ type monomers. Stoichiometric imbalance of monomers in step growth polymerisation is known to retard propagation due to the reactive chain ends having no suitable functional group to react with.\textsuperscript{164} The result of which is lower than expected molar masses of the polymer products. Therefore, an acid concentration of 0.1 mol \% relative to TEGDVE was chosen for future syntheses as it had a lower rate of the competing oligomerisation side reaction and led to no decrease in the rate of conversion of HEMA to A1 over the 6 hrs reaction.

\begin{center}
\begin{align*}
\text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{OH} \\
0-25 ^\circ C & \quad \downarrow pTsOH, DCM & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{O}_n
\end{align*}
\end{center}

Scheme 2-10 - Synthesis of poly(acetals) from TEGDVE and TEG.
2.2.2.1. Effect of TEGDVE Feed Rate on Reaction Kinetics

The effect of the feed rate of the TEGDVE/solvent solution on reaction kinetics was investigated to reduce the overall reaction time and enable efficiency in later screening of reaction conditions. By increasing the feed rate of TEGDVE the effective concentration is increased which should lead to an increase in the rate of reaction. The feed rate was increased by a factor of 5 from 0.5 mol/hr to 2.5 mol/hr, and the conversion followed at regular time intervals by $^1$H NMR spectroscopy (Figure 2-5). At a feed rate of 0.5 mol/hr the conversion reached 94% after 120 min. Upon increasing the feed rate to 2.5 mol/hr, 94% conversion was reached in 20 min enabling faster screening of the effect of solvent on the reaction. Although this increased rate is efficient, it is likely to come with an increased rate of heat evolution that will be unsafe on larger scales due to the decreased rate of heat removal that accompanies reducing the reactor surface area to volume ratio.\(^\text{165}\)

![Figure 2-5 - Effect of TEGDVE feed rate on kinetics of A1 synthesis measured by $^1$H NMR spectroscopy.](image)
2.2.2.2. Choosing a Solvent

When selecting a reaction solvent, it is often important to consider whether they are required to act as a proton source, their ease of removal and whether it eases separation of products and impurities. Furthermore, when performing large scale reactions, toxicity, physical risks and consequences of environmental release are of importance. Previous syntheses of A1 have utilised THF or DCM as the reaction solvent, both of which are unsuitable on a large scale due to cost, volatility, and their respective hazards. Therefore, an alternative solvent was sought using guidelines available in the literature.

The criteria for selection of the replacement solvents were: no alcohols to prevent reaction with the vinyl ether; suitable polarity to enable charge stabilisation of intermediates; and reduced toxicity relative to THF and DCM. Immiscibility with water was also desirable for ease of purification. Previous reactions had reached near quantitative conversions meaning only catalytic amounts of pTsOH had to be removed. It was hypothesised that this could be achieved by washing with saturated aqueous solutions such as brine. Solvents less dense than water were preferred for ease of separating liquid phases. Lastly, boiling points lower than 100 °C were also desirable to enable easy isolation of the product via distillation of the solvent. The chosen solvents and the reaction conversion are summarised in Table 2-4. It is worth noting here that methyl methacrylate is an industrially useful class of solvent known as a reactive diluent. The diluent is then copolymerised with the product in its application. Reactions were performed as before using a TEGDVE/solvent (1/1 v/v) solution feed rate of 2.5 mol/hr into a vessel containing solvent, pTsOH (0.1 mol %) and HEMA. The conversion upon completion of addition and after 30 minutes of stirring was monitored via $^1$H NMR spectroscopy.
Table 2-4: Solvent’s properties and effect on conversion of HEMA to A1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Immiscible with H₂O</th>
<th>Density &lt; H₂O b.p. &lt; 100 °C</th>
<th>Conversion after addition (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conversion after stirring (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl THF</td>
<td>×</td>
<td>✓</td>
<td>78</td>
<td>95</td>
</tr>
<tr>
<td>Acetone</td>
<td>×</td>
<td>✓</td>
<td>98</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>DCM</td>
<td>✓</td>
<td>×</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Dimethyl carbonate</td>
<td>Partially</td>
<td>✓</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>✓</td>
<td>✓</td>
<td>98</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Isopropyl acetate</td>
<td>Partially</td>
<td>✓</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>×</td>
<td>✓</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>No solvent</td>
<td>N/A</td>
<td>N/A</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>THF</td>
<td>×</td>
<td>✓</td>
<td>85</td>
<td>99</td>
</tr>
<tr>
<td>Water</td>
<td>N/A</td>
<td>N/A</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined via <sup>1</sup>H NMR spectroscopy (CDCl<sub>3</sub>) relative to the acetal C<sub>H</sub> at 14 mins and <sup>b</sup>30 mins, samples were quenched with NEt<sub>3</sub>, no residual HEMA or TEGDVE were observed.

The average conversion of two repeats are summarised in Table 2-4, after completion of the addition of the TEGDVE solution and stirring, all solvents gave ≥95% conversion except water. The reactions in water were not expected to proceed due to the hydrolysis of the vinyl ether groups and it will be omitted from further discussion. Interestingly, the conversion after addition was lowest when using coordinating solvents, THF and 2-methyl THF, whereas the remaining solvents had near quantitative conversion. The reduced conversion was thought to be due to
the formation of hydrogen bond between the ethereal oxygen of the furan ring and the hydroxyl of HEMA reducing its nucleophilicity.

All solvents used gave near quantitative conversion after stirring for 30 minutes. The choice of solvent could also be performed based on their sustainability, safety, and cost. When considering the solvents from a sustainability standpoint, the E factor and process mass index would be lowest for the reaction using no solvent, however, in the absence of any calorimeter data and the requirement to remove pTsOH from the product via aqueous/organic solvent extraction, it was deemed unsuitable. Based upon solvent selection guides of GSK, Pfizer and Sanofi, Byrne et al. have published a comprehensive green solvent selection guide\textsuperscript{166} that considers safety and sustainability. Both acetone and ethyl acetate can be sourced renewably and are preferred based upon their safety and environmental scores and were chosen for further scale up work.

2.2.2.3. Optimisation of reaction work up conditions

So far, the reaction optimisation process has been concerned with conversion of the starting materials to A1 and it is understood that quantitative conversion of HEMA is reached within 30 min of completion of the TEGDVE addition when using 0.1 mol % pTsOH. Therefore, a reliable work up process that gave A1 in a high a yield was sought. Initial syntheses of A1 were adapted from a similar process described by Nasanit \textit{et al.}\textsuperscript{93}, in which the purification procedure was column chromatography. The adapted process included removing the reaction solvent (THF), redissolution in DCM and performing a series of aqueous washes (3 × H\textsubscript{2}O and 3 × brine) before being dried over Na\textsubscript{2}SO\textsubscript{4}, this was followed by purification by column chromatography. Problematically, this process was time consuming and produced a lot of aqueous, solvent and silica waste, while achieving 75% yield of pure A1.

Upon examination of the \textsuperscript{1}H NMR spectrum of crude A1 after washing it was found that residual HEMA, DCM and water were present. The amount of HEMA was expected to decrease with the optimised pTsOH mol % as less vinyl ether hydrolysis could occur. Also the DCM could
be removed by increasing the duration of concentration *in vacuo* and the water by improved
drying, although some is to be expected due to the hygroscopic nature of the tri(ethylene glycol)
component in A1. Therefore, the column chromatography purification procedure was deemed
unnecessary and liquid-liquid extraction purification of A1 synthesised in ethyl acetate or
acetone was investigated.

Table 2-5 - Effect of wash volume (%) on yield of A1 synthesised in acetone or ethyl acetate.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wash volume (wt % of organic phase)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>7</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>84</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>7</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>82</td>
</tr>
</tbody>
</table>

Reactions in acetone and EtOAc were performed at a larger scale with a theoretical yield of
23 g. of A1. Upon completion of the reactions, the crude reaction mixtures were split into two
36 mL portions and the effect of wash volume percent on yield was investigated. For the
reactions performed in acetone the wash process was two washes of the organic extract with
saturated brine, as acetone is miscible with water. For reactions performed in ethyl acetate
the wash process was one wash with deionised H₂O and one wash with saturated brine. For
both solvents, the wash volume was either 7 or 10 vol % of the organic phase, the initial
preparation by Nasanit *et al.*³ used ~30 vol %, which generated greater waste and also it was
likely more product was lost to the discarded phases. A higher yield was observed for both
solvents when a lower wash volume % was used, this was thought to be due to loss of A1 into
the aqueous and/or brine phase arising from the hydrophilic tri(ethylene glycol) component
(Table 2-5). The highest yield achieved was 97% when the wash volume was 7% and acetone
was used, however, when performing the washes, a white precipitate formed that made
separation of the phases challenging. Therefore, a wash volume of 7% using ethyl acetate as
the solvent was chosen for scale up as it gave a yield of 92%, although some emulsification of the two phases occurred which slowed the separation process.

2.2.2.4. Scale Up of A1 Synthesis

A scaled-up synthesis of A1 was performed using the optimised conditions. The theoretical mass of A1 was 462.5 g and the yield was 90%, which may be improved by further refining the washing procedure. $^1$H NMR spectroscopy showed no impurities, but a degree of oligomerisation had occurred as the methylene CH$_2$ integral at 3.40-3.90 ppm was 16.73, which is greater than the expected 14 and preventing or reducing the oligomerisation is discussed in the future work.

2.2.2.5. Sustainability comparison of start and final protocols of Scaled Up A1 Synthesis

Table 2-6 - Green metrics for initial and optimised synthesis of A1.

<table>
<thead>
<tr>
<th>Synthetic Procedure</th>
<th>Atom Economy (%)</th>
<th>E Factor</th>
<th>Process Mass Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>100</td>
<td>5.6</td>
<td>443</td>
</tr>
<tr>
<td>Scale up</td>
<td>100</td>
<td>0.42</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The atom economy of the synthesis of A1 is 100% for both the initial and optimised syntheses of A1, however, this provides no insight into the overall wastefulness of the process. The generation of waste was expected to have been significantly reduced when compared to the initial synthesis of A1 that utilised back extraction of the product into DCM, multiple washes, and column chromatography. The E factor for the initial synthesis falls within the expected range for fine chemicals, a large reduction is observed for the scale up synthesis which is within the range for bulk chemicals.$^{108}$ A large reduction in waste is shown in the difference in values of the process mass index for both synthetic procedures. They differ by two orders of magnitude highlighting the usefulness in optimising a process to minimise environmental consequences.
2.3. Conclusions

A novel dimethacrylate cross-linker bearing two acetal functional groups was synthesised from HEMA and TEGDVE. The hydrolysis of A1 was probed by $^1$H NMR spectroscopy and HPLC-MS revealing the products to be tri(ethylene glycol) and acetaldehyde. Further experiments investigated the effect of acid $pK_a$ on the extent of A1 hydrolysis at 50 °C for 5 hrs in 0.15 M acetone-$d_6$/D$_2$O (9/1 v/v) solutions. It was found that the extent of hydrolysis increased with decreasing $pK_a$ over the course of 5 hrs, however 100 % was only achieved when using acids with a $pK_a < 1.29$. This demonstrated the potential to synthesise pH degradable thermosets via the incorporation of A1.

The synthesis of A1 was then optimised and scaled up to reduce batch to batch variation affecting mechanical testing results, reduce the time spent performing and purifying reactions and improve the sustainability. An oligomerisation side reaction related to the pTsOH loading was also identified via $^1$H NMR spectroscopy and HPLC-MS. Under the reaction conditions residual H$_2$O in pTsOH monohydrate is capable of partially and fully hydrolysing the TEGDVE vinyl groups to tri(ethylene glycol) which can react further to with TEGDVE to make mono or di HEMA capped oligomers. The pTsOH acid catalyst loading was reduced from 5 to 0.1 mol% with no considerable reduction in conversion at 120 minutes, alternative reaction solvents and purification processes were investigated, and ethyl acetate chosen and the requirement of column chromatography for purification removed. Finally, the reaction was optimised and scaled up to yield 450 g of A1 (90 % yield) via a process with both a lower E-factor and process mass index than the original.
2.4. Experimental

2.4.1. Materials

pTsOH hydrate (97%) was purchased from Alfa Aesar. Tri(ethylene glycol)divinyl ether was provided by BASF. Acetone (≥99.0%), ethyl acetate (≥99.5%), sodium carbonate anhydrous, sodium chloride (≥99.5%), sodium sulfate anhydrous (≥99%) were purchased from Fisher. 2-MeTHF anhydrous (≥99.0%), acetone-d₆ (99.0%), CDCl₃ (99.8%), chloroacetic acid (99%), D₂O (99.9%), dichloroacetic acid (≥99%), dichloromethane (≥99.9%), dimethyl carbonate (99%), HEMA (97%), hexane (≥95.0%), isobutyl acetate (natural, ≥97.0%), 3Å molecular sieves, trichloroacetic acid (≥99%), triethylamine (≥99 %), tri(ethylene glycol) (99%) and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich. Silica gel (40–63 μm) and THF (HPLC grade) were purchased from VWR. All reagents were used as supplied, unless otherwise stated.

2.4.2. Instrumentation

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at 25 °C. ¹H NMR spectra were recorded at 400 MHz and ¹³C spectra at 101 MHz. Spectra were processed using the MestreNova software. IR spectra were recorded on a PerkinElmer FTIR Spectrum Two equipped with UATR Two diamond. Size exclusion chromatography was performed on an Agilent PL-GPC50 equipped with a refractive index detector and PLgel Mixed-C (7.8 × 300 mm, 5 μm bead size) with an integrated PLgel 5 μm guard column, at a flow rate of 1.0 mL min⁻¹. All the samples were measured relative to a set of ten low-dispersity poly(methyl methacrylate) standards (Agilent, UK) with peak molecular weights ranging from 550 to 1,568,000 Da. The eluent system was THF with 0.025 w/v% butyl hydroxytoluene. Elemental microanalysis (CHN) was performed on an Elementar Vario Micro Cube. HPLC-MS was performed on an Agilent 6530 Q-TOF MS, samples were run in electro-spray ionisation
2.4.3. Initial Synthesis of A1

THF (25 mL), tri(ethylene glycol) divinyl ether (2.50 g, 0.012 mol) and hydroxyethyl methacrylate (3.20 mL, 0.025 mol) were added to an oven dried round bottom flask and stirred on an ice bath for 30 min. To this, pTsOH monohydrate (0.120 g, 0.63 mmol) was added in portions and the mixture stirred in an ice bath for a further 6 hrs. The reaction was monitored by TLC in ethyl acetate/hexane (1:1 v/v). Once complete, saturated aqueous Na$_2$CO$_3$ (10 mL) was added and mixture stirred for a further 10 min. The reaction mixture was filtered and concentrated *in vacuo* to give a white suspension. H$_2$O (15 mL) was added and then washed with DCM (3 × 10 mL). The organic extracts were washed with H$_2$O (3 × 10 mL) and brine (3 × 10 mL) and dried over Na$_2$SO$_4$. Solids were removed by filtration and volatiles removed *in vacuo* to give a colourless oil. The crude product was purified *via* column chromatography using solvent gradient elution of ethyl acetate/hexane (40/60, 50/50, 60/40) with NEt$_3$ (2 vol %) to yield a colourless oil (4.00 g, 8.96 mmol, 75%). δ$_{H}$ (400 MHz, CDCl$_3$): 6.13 (d, 2H), 5.58 (d, 2H), 4.80 (m, 2H), 4.29 (m, 4H), 3.64 (m, 16H), 1.94 (m, 6H), 1.31 (m, 6H). $^{13}$C {$^{1}$H} NMR (CDCl$_3$): δ 167.7, δ 136.6, δ 125.9, δ 99.8, δ 70.7, δ 64.1, δ 62.6, δ 19.6, δ 19.4, δ 18.4. ATR-IR: 2987-2874. cm$^{-1}$ (C-H), 1716 cm$^{-1}$ (COO), 1296 cm$^{-1}$ (COC), 1133 cm$^{-1}$ (COO), 939.99 cm$^{-1}$ (C=C). HPLC-MS C$_{22}$H$_{38}$O$_{10}$, [M]+ theoretical 462.25 amu, experimental [M+Na]$^+$ 485.25.20. CHN calculated (C 59.17%, H 8.58%), observed (C 57.11%, H 8.23%).
2.4.4. Hydrolysis of A1

A1 (0.1 g, 0.2 mmol) was added to an acidic stock solution (1.5 mL, 0.15 M acid) in acetone-
d6/D2O (9/1 v/v) and heated to 50 °C for 6–48 hours. An aliquot (0.7 mL) was taken and its 1H
NMR spectrum recorded. Hydrolysis (%) was calculated using the integrals of the acetal CH
and acetaldehyde CH resonances at 4.80 and 9.79 ppm, respectively, using the following
equation:

Equation 2-1

\[
\text{Hydrolysis} \%(\text{\%}) = \left( \frac{\text{Acetaldehyde CH (4.80 ppm)}}{\text{Acetaldehyde CH (4.80 ppm)} + \text{Acetal CH (9.79 ppm)}} \right) \times 100
\]

2.4.5. Effect of acid on scale up

General procedure

A 50 mL round-bottomed flask was charged with DCM (20 mL), HEMA (6 mL, 0.05 mol) and
pTsOH (Table 2-7). The solution was cooled in an ice bath for 30 min. TEGDVE (5.00 g, 0.025
mol) was added to DCM (5 mL) and added dropwise using a syringe pump at a flow rate of
0.025 mol/hr. Aliquots (0.2 mL) were taken periodically, quenched with NEt3 (2 µL, 0.014 mmol)
and diluted with CDCl3 (0.5 mL). Reactions were quenched by the addition of sat. Na2CO3 (5
mL) after 6 hrs. The transparent solution was washed with H2O (2 × 5 mL) and brine (5 mL),
the organic phase was dried over Na2SO4, filtered, and concentrated in vacuo to yield a
colourless oil. Conversion was calculated using the following equation:

Equation 2-2

\[
\text{HEMA Conversion (\%)} = (1 - \frac{\text{HEMA integral (6.13 ppm)}}{\text{HEMA integral (6.13 ppm)} + \text{A1 integral (6.10 ppm)}}) \times 100
\]
Table 2-7 - Effect of pTsOH on A1 synthesis experiment formulations.

<table>
<thead>
<tr>
<th>pTsOH / mol % of TEGDVE</th>
<th>pTsOH / mg (mmol)</th>
<th>HEMA / mL (mmol)</th>
<th>TEGDVE / g (mmol)</th>
<th>DCM / mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>6 (50)</td>
<td>5.00 (25)</td>
<td>25</td>
</tr>
<tr>
<td>0.1</td>
<td>4.7 (0.0246)</td>
<td>6 (50)</td>
<td>5.00 (25)</td>
<td>25</td>
</tr>
<tr>
<td>0.5</td>
<td>23.5 (0.123)</td>
<td>6 (50)</td>
<td>5.00 (25)</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>235 (1.23)</td>
<td>6 (50)</td>
<td>5.00 (25)</td>
<td>25</td>
</tr>
</tbody>
</table>

2.4.6. Anhydrous Synthesis of A1

Tri(ethylene glycol)divinyl ether was purified via azeotropic distillation with toluene three times and stored over 3 Å molecular sieves under nitrogen. HEMA and THF were stored over 3Å molecular sieves under nitrogen for 24 hours prior to use. To an oven dried Schlenk flask under nitrogen HEMA (3.20 mL, 0.025 mol), pTsOH (0.120 g, 0.63 mmol) and THF (25 mL) were added stirred on an ice bath for 30 minutes. TEGDVE (2.50 g, 0.012 mol) was added dropwise, and the reaction was stirred for six hours. Once complete, saturated aqueous Na<sub>2</sub>CO<sub>3</sub> (10 mL) was added and mixture stirred for a further 10 min. The reaction mixture was filtered and concentrated in vacuo to give a white suspension. H<sub>2</sub>O (15 mL) was added and then washed with DCM (3 × 10 mL). The organic extracts were washed with H<sub>2</sub>O (3 × 10 mL) and brine (3 × 10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Solids were removed by filtration and volatiles removed in vacuo to give a colourless oil.
2.4.7. Control Polymerisation of TEGDVE

General Procedure

To a round-bottomed flask pTsOH and DCM (20 mL) were added and cooled on ice for 30 min. Tri(ethylene glycol)divinyl ether (5.0 mL, 0.025 mol) was added to DCM (5 mL) and added dropwise to the reaction mixture using a syringe pump at 0.25 mol/hr. After 30 min. the reaction was quenched with saturated Na₂SO₄ (5 mL) and stirred for 10 min. The reaction mixture was washed with H₂O (3 × 5 mL) and brine (1 × 5 mL) and the organic extract was dried over MgSO₄, filtered, concentrated in vacuo and dried in a desiccator yielding an oil*. ¹H NMR spectra recorded in CDCl₃.

*Samples synthesised with 0.5 and 1 mol % pTsOH were yellow

<table>
<thead>
<tr>
<th>pTsOH / mol % of TEGDVE</th>
<th>pTsOH / g (mmol)</th>
<th>TEGDVE / g (mol)</th>
<th>DCM / mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0047 (0.0246)</td>
<td>5.00 (0.025)</td>
<td>25</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0235 (0.123)</td>
<td>5.00 (0.025)</td>
<td>25</td>
</tr>
<tr>
<td>1</td>
<td>0.047 (0.246)</td>
<td>5.00 (0.025)</td>
<td>25</td>
</tr>
</tbody>
</table>
2.4.8. Control Polymerisation of TEGDVE and TEG

General Procedure

To a round-bottomed flask pTsOH, TEG (3.71 g, 0.025 mol) and DCM (20 mL) were added and cooled on ice for 30 minutes. Tri(ethylene glycol)divinyl ether (5.0 mL, 0.025 mol) was added to DCM (5 mL) and added dropwise to the reaction mixture using a syringe pump at 0.25 mol/hr. After 30 minutes reaction was quenched with saturated Na$_2$SO$_4$ (5 mL) and stirred for 10 minutes. The reaction mixture was washed with H$_2$O (3 × 5 mL) and brine (1 × 5 mL) and the organic extract was dried over MgSO$_4$, filtered, concentrated *in vacuo* and dried in a desiccator yielding an oil. $^1$H NMR spectra recorded in CDCl$_3$. 

Figure 2-6 – $^1$H NMR Spectra (CDCl$_3$) of reaction products of control polymerisation of TEGDVE.
Table 2-9 - Control polymerisation of TEGDVE and TEG formulations.

<table>
<thead>
<tr>
<th>pTsOH / mol % of TEGDVE</th>
<th>pTsOH / g (mol)</th>
<th>TEG / g (mol)</th>
<th>TEGDVE / g (mol)</th>
<th>DCM / mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0047 (0.0246)</td>
<td>3.71 (0.025)</td>
<td>5.00 (0.025)</td>
<td>25</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0235 (0.123)</td>
<td>3.71 (0.025)</td>
<td>5.00 (0.025)</td>
<td>25</td>
</tr>
<tr>
<td>1</td>
<td>0.047 (0.246)</td>
<td>3.71 (0.025)</td>
<td>5.00 (0.025)</td>
<td>25</td>
</tr>
</tbody>
</table>

Figure 2-7 - $^1$H NMR spectra (CDCl$_3$) of poly(acetal) synthesised from TEGDVE and TEG.
2.4.9. Effect of TEGDVE Addition Rate

A 50 mL round-bottomed flask was charged with DCM (20 mL), HEMA (6 mL, 0.05 mol) and pTsOH (4.7 mg, 0.247 mmol), and stirred on ice for 30 min. A solution of DCM (5 mL) and TEGDVE (5.00 g, 0.0247 mol) was added to a syringe and added dropwise to the reaction mixture using a syringe pump at 0.5 or 2.5 mol/hr. Aliquots (0.2 mL) were taken periodically and quenched with NEt\(_3\) (2 \(\mu\)L, 0.014 mmol) and diluted with CDCl\(_3\) (0.5 mL) for \(^1\)H NMR spectroscopy analysis. Conversion was calculated using the following equation:

**Equation 2-3**

\[
HEMA \ Conversion (\%) = (1 - \frac{HEMA \ integral \ (6.13 \ ppm)}{HEMA \ integral \ (6.13 \ ppm) + A1 \ integral \ (6.10 \ ppm)}) \times 100
\]

2.4.10. Effect of Solvent on Synthesis of A1

A 50 mL round-bottomed flask was charged with DCM (20 mL), HEMA (6 mL, 0.05 mol) and pTsOH (4.7 mg, 0.247 mmol), and stirred on ice for 30 minutes. A solution of DCM (5 mL) and TEGDVE (5.00 g, 0.0247 mol) was added to a syringe and added dropwise to the reaction mixture using a syringe pump at 2.5 mol/hr. Aliquots (0.2 mL) were taken periodically and quenched with NEt\(_3\) (2 \(\mu\)L, 0.014 mmol) and diluted with CDCl\(_3\) (0.5 mL) for \(^1\)H NMR spectroscopy analysis. Conversion was calculated using the following equation:

**Equation 2-4**

\[
HEMA \ Conversion (\%) = (1 - \frac{HEMA \ integral \ (6.13 \ ppm)}{HEMA \ integral \ (6.13 \ ppm) + A1 \ integral \ (6.10 \ ppm)}) \times 100
\]

2.4.11. Effect of work up

**General procedure**

A round-bottomed flask was charged with solvent (50 mL), HEMA (13.0 g, 0.1 mol) and pTsOH (9.5 mg, 0.50 mmol), and stirred on ice for 30 minutes. TEGDVE (10.1 g, 0.05 mol) was added to a syringe and added dropwise to the reaction mixture via a syringe pump at 2.5 mol/hr. Aliquots (0.2 mL) were taken periodically and quenched with NEt\(_3\) (2 \(\mu\)L, 0.014 mmol) and
diluted with CDCl$_3$ (0.5 mL) for $^1$H NMR spectroscopy analysis. Samples (36 mL) of the crude reaction mixture were taken and washed as per table below. The organic extracts were collected, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo.

Table 2-10 - Wash formulations and yield of A1 recovered.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Crude volume / mL</th>
<th>Wash volume / %</th>
<th>H$_2$O / mL</th>
<th>Brine / mL</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>36</td>
<td>7</td>
<td>0</td>
<td>$2 \times 2.5$</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>10</td>
<td>0</td>
<td>$2 \times 3.75$</td>
<td>84</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>36</td>
<td>7</td>
<td>2.5</td>
<td>2.5</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>10</td>
<td>3.75</td>
<td>3.75</td>
<td>82</td>
</tr>
</tbody>
</table>

2.4.12. Synthetic scale up

HEMA (236.5 g, 1.95 mols), ethyl acetate (200 mL) and pTsOH (1.902 g, 0.1 mol) were added to a reactor equipped with an overhead stirrer and cooled on ice until the internal temperature reached 0 °C. TEGDVE (202.3 g, 1 mol) was added dropwise while ensuring the internal temperature was <5 °C. After the addition of TEGDVE was complete the reaction was stirred for 1 hr and allowed to reach room temperature before quenching with saturated aqueous Na$_2$CO$_3$ (10 mL). The organic phase was then washed with H$_2$O (20 mL) and brine (20 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo to yield a clear oil (416 g, 90 %).

2.4.13. Green Metric Calculations

Atom economy was calculated using the following values and equation:

Equation 2-5

$$Atom\ economy\ (\%) = \frac{2 \times (130.14) + 202.25}{462.53} \times 100$$
E factor was calculated using the following equation:

\[
E \text{ factor} = \frac{\text{mass of waste}}{\text{mass of product}}
\]

For the initial synthesis of A1 the following data was used:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Mass / g</th>
<th>Reagent</th>
<th>Product</th>
<th>Waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEMA</td>
<td>3.424</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEGDVE</td>
<td>2.5</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pTsOH</td>
<td>0.12</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>22.23</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>4 (74.6 % yield)</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the optimised and scaled up synthesis of A1 the following data was used:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Mass / g</th>
<th>Reagent</th>
<th>Product</th>
<th>Waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEMA</td>
<td>253.8</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEGDVE</td>
<td>202.3</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pTsOH</td>
<td>0.190</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>180.4</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>425.5 (92 % yield)</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The process mass index was calculated using the following equation:

Equation 2.7

\[
\text{process mass index} = \frac{\text{Mass used in process}}{\text{Mass of product}}
\]

For the synthesis of A1 the following data was used:

Table 2.13 - Process mass index data for initial and optimised synthesis of A1.

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>Initial</th>
<th>Optimised</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Mass / g</td>
<td></td>
</tr>
<tr>
<td>HEMA</td>
<td>3.424</td>
<td>253.8</td>
</tr>
<tr>
<td>TEGDVE</td>
<td>2.5</td>
<td>202.3</td>
</tr>
<tr>
<td>pTsOH</td>
<td>0.12</td>
<td>0.1902</td>
</tr>
<tr>
<td>THF</td>
<td>22.23</td>
<td>180.4</td>
</tr>
<tr>
<td>DCM</td>
<td>39.9</td>
<td>0</td>
</tr>
<tr>
<td>Sat. Sodium carbonate soln.</td>
<td>13.4</td>
<td>26.8</td>
</tr>
<tr>
<td>H₂O</td>
<td>55</td>
<td>20</td>
</tr>
<tr>
<td>Brine soln.</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>Silica gel</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>902</td>
<td>0</td>
</tr>
<tr>
<td>Hexane</td>
<td>655</td>
<td>0</td>
</tr>
<tr>
<td>A1</td>
<td>4 (74.6 % yield)</td>
<td>425.5 (92 % yield)</td>
</tr>
</tbody>
</table>
Chapter 3 – Synthesis and Degradation of Acetal Containing Methacrylate Thermosets

3.1. Introduction

Literature examples of pH degradable thermosets incorporating acetal groups mainly focus on epoxy resins, which are summarised in this introduction with some examples of (meth)acrylate-based acetal resins. Watson et al. synthesised a series of acetal containing epoxy resins from cis-cyclohexane-1,2-dicarboxylic anhydride, a series of three novel diepox monomers and one commercially available cyclic acetal-containing diepox monomer, that degraded via acetal hydrolysis or transetherification (Scheme 3-1). Samples for degradation were prepared as thin film discs of approximately 1 cm diameter, immersed in solutions of ethanol, water and acetic acid (1:1:1 or 2:1:1 by volume) with acid concentrations of 4.8 or 4.4 M at 88 °C. When $R^1$ and $R^2$ were both CH$_3$ the resin was degraded and formed a homogeneous solution in 2-3 minutes, however, when $R^1$ was H and $R^2$ was CH$_3$, only partial degradation was observed over 60 minutes. Furthermore, there was no observed degradation when $R^1$ and $R^2$ were H, or the commercially available cyclic acetal monomer, cyclohexane meta-dioxane, was used. The authors do not say which concentration of acetic acid these experiments were performed in. The authors also showed networks could be degraded via transetherification in solutions of methane sulfonic acid, or pTsOH (0.026-0.5 M) in ethanol or methanol. The previously degradation resistant resins where, $R^1$ and $R^2$ were both H, degraded within 60 mins under these conditions. When $R^1$ was H and $R^2$ was CH$_3$ or $R^1$ and $R^2$ were CH$_3$ was <10 mins.\textsuperscript{171}
Shirai et al., synthesised a series of highly cross-linked (meth)acrylate resins via polymerisation of the di or trifunctional monomers using thermal and photo initiators in the presence of a photoacid. The acetal bearing monomers were synthesised via a two-step procedure first reacting an aromatic di or triol with 2-chloroethyl vinyl ether and subsequent nucleophilic addition of HEMA or 2-hydroxyethyl acrylate. Thin films containing 1 wt % photoacid generator were irradiated at 366 nm and baked at 100 °C for 10 minutes, after which the films became soluble in THF. The photogenerated triflic acid had catalysed acetal hydrolysis, yielding p(HEMA) or p(2-hydroxyethyl acrylate), an aromatic diol or triol and acetaldehyde (Scheme 3-2).\textsuperscript{151}
Heath et al., synthesised an acetal containing diacrylate via transacetalisation of 2,2-dimethoxypropanone with 2-hydroxyacrylate. This was polymerised using a photoinitiator. Films of 1 μm thickness were then degraded in acidic THF solutions at room temperature and 60 °C, the concentration, acid species and cosolvents used are not described (Scheme 3-3).
Hashimoto et al. synthesised acetal containing epoxy resins and carbon fibre composites using tetraethylenepentamine as a curing agent. The acetal functionality was incorporated via reaction between hydroxyl groups on bisphenol A or a phenolic resin and an epoxy functionalised vinyl ether, 4-vinylxybutyl glycidyl ether or cyclohexane dimethanol vinyl glycidyl ether. They were degraded in 0.1 M HCl THF/water (9/1 v/v) solutions at room temperature over 12-24 hours (Scheme 3-4). The authors collected the degradation products bisphenol A or Cresol Novolak and the carbon fibre resin which may be reused. Bisphenol A and Cresol Novolak were characterised by $^1$H NMR and SEC which showed high purity and the Cresol Novolak $M_n$ and $M_w/M_n$ values were similar to those of the virgin material.¹⁷³

Yuan et al. synthesised a dicyclo diacetal degradable component via reacting two equivs. of vanillin with erythritol and subsequent functionalisation of this diacetal with epichlorohydrin to yield a diepoxy monomer. This was polymerised with diaminodiphenyl sulfone yielding a pH degradable resin that formed erythritol and vanillin derivatives (Scheme 3-5). Real time $^1$H NMR spectra of the degradation process were recorded in 0.1 M HCl DMSO-d$_6$/H$_2$O (9/1 v/v) at 50 °C and found to be complete within 5 hrs. The authors found that degradation time decreased from 160 to 55 mins with increasing solvent polarity due to greater ease of hydrogen ion ionisation. Thin film degradation outcome was dependent on the acetone/H$_2$O ratio in 0.1 M HCl solutions. When using 9/1-5/5 v/v solutions thin films degraded within 2 hrs.
However, when the ratio was 4/6-1/9 no degradation was observed, this was thought to be due to the low acetone content reducing the solubility of degradation products. Lastly degradation time was found to decrease with increasing acid strength in 1 M acetone/H$_2$O (9/1 v/v) solutions; HCl, H$_2$SO$_4$ and H$_3$PO$_4$ gave degradation times of 40, 70 and 480 min. respectively.$^{174}$

![Scheme 3-5](image.png)

Scheme 3-5 – Bioderived acetal containing epoxy resins synthesised by Yuan et al.$^{174}$

Li et al. synthesised acetal resins from phenolic resins and 1,4-cyclohexanedimethanol vinyl ether that degraded to the parent phenolic resin, 1,4-cyclohexanedimethanol and acetaldehyde (Scheme 3-6). The authors characterised the network degradation rate gravimetrically and used solvent contact angle on the surface of thermosets to select suitable solvents for degradation, founding degradation rate was increased when contact angles were low in solutions of acetone/H$_2$O. Further to this, the authors found that degradation rate was found to increase in solvents that gave a high swelling ratio. The degradation rate decreased with acid strength and no degradation was observed in acetic and phosphoric acids in 0.1 M acetone/H$_2$O solutions.$^{70}$ Further studies by Wang et al.$^{99}$ on acetal containing epoxy resins, Li et al.$^{72}$ on resins synthesised from epigallocatechin gallate and tri(ethylene glycol)divinyl ether, and Chen et al.$^{73}$ on phenolic resin and tri(ethylene glycol)divinyl ether derived resins found degradation was dependent on acid concentration and type, temperature and solvent.
Lu et al.\textsuperscript{71} synthesised a series of styrene, 2-ethylhexyl methacrylate and HEMA copolymers and terpolymers. During the syntheses, cross-linking was performed \textit{in situ} via reaction of the HEMA hydroxyl and tri(ethylene glycol)divinyl ether to form diacetal cross-links. The acid degradation products yielded linear polymers, tri(ethylene glycol) and acetaldehyde (Scheme 3-7). These cross-links are identical to those generated when cross-linking networks with A1; the cross-links were varied from 0-10 mol %. The authors used swelling ratios to select suitable solvents for degradation. DMF and DMSO gave the greatest swelling ratios for all samples, however, they favoured THF due to its low boiling point. The authors found that the contact angle of various THF/H\textsubscript{2}O solutions and neat THF was lowest when the ratio was THF/H\textsubscript{2}O 9/1 v/v, which also had the highest degradation rate at 50 °C and complete dissolution was achieved in 0.17 hrs. Cross-link density was found to slow the degradation time in 0.1 M HCl THF/H\textsubscript{2}O (9/1 v/v) at 50 °C from 0.17 to 4 hrs when increasing from 2.5 to 10 mol % cross-linker. The authors focussed on styrene copolymers with 5 mol % acetal cross-linker and found that increasing temperature from 25 to 50 °C in 0.1 M HCl THF/H\textsubscript{2}O (9/1 v/v) decreased the degradation time from 21.5 to 0.197 hrs. Changing the solvent in 0.1 M HCl

![Diagram of degradation process](image)
solvent/H\_2O (9/1 v/v) solutions was found to have a large effect on degradation, when using acetone, ethanol, methanol, DMF and DMSO the greatest mass loss was 26.86 % after 12 hours in acetone. Having determined THF to be the most efficient solvent for degradation the authors investigated the effect changing the ratio of THF/H\_2O in 0.1 M HCl at 50 °C had on degradation. Increasing the H\_2O content slowed degradation and, interestingly, decreasing it to 9.5/0.5 THF/H\_2O also increased the degradation time from 0.197 to 0.25 hrs. Lastly, the authors also showed that degradation rate decreased when decreasing the acid concentration.

While acetal containing degradable thermosets have been in the literature since Watson et al. reported them in 1996,\textsuperscript{171} it is only recent examples that have begun to characterise their degradation behaviour and products.\textsuperscript{70,174} Lu et al. synthesised thermosets with identical cross-links to A1, however the cross-link was produced \textit{in situ} during the polymerisation by reacting HEMA with TEGDVE. Within this chapter free radical curing thermosets of methyl methacrylate cross-linked with A1 are synthesised and characterised. Subsequently their degradation behaviour is characterised and compared to that of A1.
3.2. Results and Discussion

3.2.1. Degradable A1 and methyl methacrylate thermosets

3.2.1.1. Synthesis and Thermal Characterisation of p(MMA-co-A1)

Having synthesised A1 and demonstrated its full hydrolysis in 0.15 M solutions of acids with a $pK_a < 1.29$, it was expected that thermosets cross-linked with A1 would be degradable under acidic conditions. A model thermoset was synthesised by bulk polymerisation of MMA and A1 (2 wt%) using benzoyl peroxide (BPO) and $4,N,N$-trimethylaniline (4-TMA) as a redox initiator (Scheme 3-8). MMA, BPO and 4-TMA were selected as they are used in commercial adhesive systems, although MMA use is less prevalent due to regulations controlling the use of volatile organic compounds (VOCs).

\[
\text{Scheme 3-8 Synthesis of acid degradable model adhesive via bulk polymerisation.}
\]

The networks were characterised by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA gives insight into the temperature at which thermal degradation of the thermoset occurs and therefore an understanding of the operating temperatures it can withstand during its processing and application. Furthermore, TGA allows determination of the loss of any volatile components that can indicate residual monomers from the synthesis of the thermoset.
DSC allows measurement of the glass transition temperature \( (T_g) \), the temperature at which polymers undergo a physical transition from the glassy to rubbery state. For thermosets no further transition is observed due to the chemical cross-links in the network.\textsuperscript{177} However, the \( T_g \) provides understanding of the degree of cure (extent of reaction) when synthesising thermosets,\textsuperscript{178,179} and is another useful parameter for processing and application temperatures. Failure to understand the thermal properties of polymers prior to their application can have catastrophic failures, such as the Space Shuttle Challenger disaster.\textsuperscript{180}

TGA revealed a thermal profile inconsistent with that of a cross-linked MMA thermoset (Figure 3-1). Linear poly(MMA) is known to undergo a thermal depolymerisation that gives a rapid loss of mass at temperatures >200 °C, the temperature at which this occurs is influenced by end groups,\textsuperscript{181–183} and the types of linkages present in the backbone (i.e. head-tail, tail-tail, head-head) which each have their own thermal stability and impart the thermal profile with mass loss at different temperatures.\textsuperscript{184–187} Cross-linked p(MMA) exhibits a similar thermal profile to that of its linear equivalent but with a higher thermal stability resulting from the cross-links.\textsuperscript{188} However, the TGA profile of A1 cross-linked MMA model adhesives used in preliminary degradation studies displayed a loss of volatile compounds at ~100 °C which was attributed to residual MMA from the polymerisation. Following this a gradual loss in mass was observed that dropped sharply at 400 °C. The presence of further volatile species was an indication that low conversion was reached during the polymerisation.
DSC characterisation of the model adhesive further supported low monomer conversion. Cross-linking is known to increase the $T_g$,\textsuperscript{189} therefore the $T_g$ was expected to be higher than that of linear p(MMA) which is in the region of 105-120 °C.\textsuperscript{190} However, the observed $T_g$ was much lower than expected ~50 °C (Figure 3-2). Such a low $T_g$ is indicative of the presence of unreacted MMA plasticising the thermoset network.\textsuperscript{189} The evidence of low conversion when making the model thermosets has implications for the future analysis of degradation. Therefore, a more detailed investigation of the thermoset synthesis was undertaken.
3.2.1.2. Effect of Post Curing on glass transition temperature

A bulk polymerisation of MMA to p(MMA) (Scheme 3-9) was used as a model into the cure kinetics and the effect of thermal post curing treatment on the $T_g$ of p(MMA). p(MMA) was chosen as its $T_g$ is well known, ranging from 105-120 °C. Furthermore, the synthesis of linear p(MMA) enabled the reaction to be monitored by $^1$H NMR spectroscopy, preliminary experiments to track conversion gravimetrically were hindered by experimental error due to the volatility of MMA causing the mass to vary.

![Scheme 3-9 Model p(MMA) synthesis.](image)

MMA was polymerised using the same redox initiator system, BPO and 4, N,N-trimethylaniline (TMA) at 2 wt %, as initial model thermosets. Initial attempts to study the kinetics of the bulk polymerisation were unsuccessful due to difficulty in sampling the high viscosity reaction mixture. The experimental setup was changed to a series of batch bulk polymerisations each corresponding to a time point, this leads to greater experimental error but enables the characterisation of the high viscosity and glassy reaction media. Again, initial experiments were unsuccessful due to inconsistent conversion thought to arise from further polymerisation taking place after quenching by exposure to air. To ensure no further polymerisation could occur in the highly concentrated reaction medium each sample was quenched by the addition of acetone-$d_6$/D$_2$O MEHQ solution and immersion of the reaction vessel into liquid nitrogen. Conversion of MMA to p(MMA) was determined by $^1$H NMR spectroscopy (Figure 3-3) and showed the reaction reached ~90 % conversion after 6 hrs. Upon leaving the reaction for 24 hrs no further reaction was observed.
Free radical polymerisation undergoes an auto-acceleration process, also known as the Trommsdorff-Norrish effect, which results from the effect of changing reaction medium on the termination constant $k_t$ of propagating chains, this is observed as three distinct regions (Figure 3-3, labelled i, ii and iii).\textsuperscript{191} Region i falls between 0-40 % conversion and is a low viscosity mixture of $p$(MMA) in MMA, termination occurs by chain transfer, combination, disproportionation or inhibition.\textsuperscript{192} During this region viscosity increases with conversion leading to a decrease in the segmental and translation diffusion that enables chain ends to meet species capable of terminating the propagating chain end.

As the reaction reaches the gel point $k_t$ decreases leading to an increase in the rate of reaction (region ii) and auto-acceleration is observed. Within this region the diffusion of propagating chain ends by translational and segmental motion and reptation occurs over a timescale that is large with respect to the lifetime of a propagating chain. However, low molar mass species such as monomers can diffuse quickly through the gel-like reaction medium. Further reaction leads to the formation of a glassy matrix (region iii) in which the remaining monomer diffuses slowly and $k_t$ and $k_p$ are low.\textsuperscript{191,192} Under the reaction conditions the polymerisation reached $\sim$90 % conversion. Further reaction is unlikely to occur without elevating the temperature of the glassy $p$(MMA) matrix above the $T_g$ of 105 °C, such as to 120 °C, in a process known as post-curing.\textsuperscript{191}
Samples of p(MMA) were again synthesised by the bulk polymerisation of MMA (Scheme 3-9) and the effect of post-cure temperature and time on the \( T_g \) was investigated by DSC (Figure 3-4). When post-cured for 24 hrs at 60 °C and 80 °C the \( T_g \) was much lower than expected at 54 °C and 66 °C, respectively. However, post-curing at 100 °C for 24 hrs and 48 hrs the \( T_g \) was found to be 82 °C and 107 °C, respectively. The increase in \( T_g \) is likely from a combination of thermally-initiated polymerisation, the increased mobility of MMA in the softened p(MMA) matrix and the evaporation of unreacted MMA. A \( T_g \) of 107 °C falls within the expected range for p(MMA), therefore, the reaction conditions in Scheme 3-9 and the post-curing conditions of 100 °C for 48 hrs were chosen for the synthesis of A1 and MMA-based thermoset resins for investigations into thermoset degradation.

\[
\begin{array}{c}
\text{Post-cure temperature (°C)} \\
\hline
50 & 60 & 70 & 80 & 90 & 100 & 110 \\
\hline
0 & 30 & 60 & 90 & 120 \\
\end{array}
\]

\( T_g \) (°C)

- 24 hour cure
- 48 hour cure

![Figure 3-4](Effect of post-cure temperature and time on the \( T_g \) of p(MMA)).

p(MMA-co-A1) was synthesised using the optimised conditions (Scheme 3-10) yielding a glassy resin. Characterisation by TGA (Figure 3-5) showed a sharp mass loss at temperatures \( >200 \) °C consistent with thermal depolymerisation. Unlike previously synthesised p(MMA-co-A1), no observed loss of volatiles was observed. Furthermore, the gel content was determined to be 94% showing a high amount of insoluble material was present, indicating a high degree of cure was achieved. DSC characterisation showed the \( T_g \) was 102 °C (Appendices Figure 8-4), higher than the \( T_g \) of 50 °C that was previously observed for
p(MMA-co-A1). Having found a suitable method for synthesising p(MMA-co-A1), the degradation properties were re-investigated.

Based upon previous A1 hydrolysis experiments it was hypothesised that acetal groups in networks cross linked with A1 would be stable under basic and neutral conditions and some weakly acidic solutions. However, when exposed to 0.15 M solutions of acids with a $pK_a < 1.29$ the acetal groups should be hydrolysed, breaking the chemical cross links and yielding a homogeneous solution of p(MMA-co-HEMA), TEG and acetaldehyde (Scheme 3-11).

Samples of the cured thermoset p(MMA-co-A1) were soaked in a solution of pTsOH (0.15 M)
in acetone/H$_2$O (9/1 v/v) at 50 °C for 6 hrs and visually checked for the formation of a homogeneous solution. Over 6 hrs the glassy thermoset became a swollen gel before forming a homogeneous red solution indicating hydrolysis of the acetal groups. Thus, demonstrating A1 as a suitable cross-linker for acid degradable methacrylate-based thermosets.

![Scheme 3.11 Acid degradation pathway of A1 cross-linked adhesives.](image)

### 3.2.1.4. $^1$H NMR Spectroscopic and Gravimetric Study of Thermoset Degradation

Having previously shown the hydrolysis products of the cross-linker A1 were HEMA, acetaldehyde and TEG, an experiment was designed to ensure A1 cross-linked thermosets followed the same hydrolysis pathway. Samples of p(MMA-co-A1) were ground to a powder and degraded in a stock solution of pTsOH (0.15 M) in acetone-d$_6$/D$_2$O (9/1 v/v) at 50 °C. Residual insoluble p(MMA-co-A1) was removed by filtration. The filtrate was then characterised by $^1$H NMR spectroscopy, and showed the small molecules tri(ethylene glycol) and acetaldehyde were produced with the copolymer p(MMA-co-HEMA). This is consistent with the mechanism of acetal hydrolysis$^{94}$ and shows the hydrolysis of acetal groups in cross-links gives rise to the acid degradation of p(MMA-co-A1).
Using the $^1$H NMR spectroscopy data the evolution of acetaldehyde over time was monitored and the concentration calculated by comparing with the known analyte pTsOH present in the stock solution (Figure 3-6 and Appendix Figure 8-5). The concentration of acetaldehyde reached a maximum after 135 min. However, previous network degradation experiments took 300 minutes to form homogeneous solutions. This suggests the rate of network degradation is dependent upon the solubilisation of the formed p(MMA-co-HEMA) and acetal hydrolysis. This may also be due to the increased surface area of the ground powder being degraded.

Figure 3-6 Evolution of acetaldehyde during the degradation of p(MMA-co-A1) networks in acetone-d$_6$/D$_2$O (9/1 v/v) pTsOH (0.15 M) solutions measured by $^1$H NMR spectroscopy.
The degradation kinetics of p(MMA-co-A1) were then followed gravimetrically. Based upon the previous experiment all acetal groups present in p(MMA-co-A1) are hydrolysed after 135 minutes (Figure 3-7). Consequently, any remaining heterogeneous material is p(MMA-co-HEMA) undergoing solubilisation. This was found to be 29 % of the starting mass after 135 minutes. Therefore, polymer dissolution is contributing to the degradation kinetics of p(MMA-co-A1) thermosets.

![Graph showing degradation kinetics of p(MMA-co-A1) thermoset in acetone/H$_2$O (9/1 v/v) pTsOH (0.15 M) at 50 °C for 6 hours.](image)

Figure 3-7 Degradation kinetics of p(MMA-co-A1) thermoset in acetone/H$_2$O (9/1 v/v) pTsOH (0.15 M) at 50 °C for 6 hours.

3.2.1.5. Effect of Solvent on Degradation

The degradation of p(MMA-co-A1) thermosets was then investigated in different solvent/water (9/1 v/v) pTsOH (0.15 M) solutions at 50 °C (Figure 3-8). Acid degradation rates of epoxy resins bearing acetal groups have been shown to increase with the polarity of the solvent used,\textsuperscript{174} however, no such relationship was observed for p(MMA-co-A1). The epoxy resins in question degraded to small molecules, whereas p(MMA-co-A1) yields p(MMA-co-HEMA). Homogeneous solutions were formed within 5 hrs in all solvents except DMSO (Figure 3-8). Upon leaving the DMSO experiment to run for 24 hours the system remained heterogeneous. This could be due to poor swelling of the thermoset in DMSO resulting in a low diffusion of pTsOH and H$_2$O to the acetal groups, meaning hydrolysis occurs exceedingly slowly.
The swelling ratio of the neat solvents was then determined at room temperature by comparing the initial mass with the swollen mass. In the swollen state the amount of pTsOH and H₂O transported into the thermoset matrix by solvent is expected to be higher. Therefore, it is hypothesised that degradation is more likely to occur in solvents that exhibit a high swelling ratio on p(MMA-co-A1).

The swelling ratios were found to be >150% for all solvents except DMSO which was 26%. It is therefore plausible that the concentration of pTsOH and H₂O is low in p(MMA-co-A1) when exposed to DMSO and hydrolysis of the acetal groups is zero, low or occurring only at the
surface. A second scenario is also possible whereby hydrolysis of the acetal groups occurs producing p(MMA-co-HEMA); the theoretical amount of the comonomer HEMA present would be very low as only 2 wt% A1 is used to cross-link the thermosets. However, upon taking the remaining sample and drying in a vac oven at 100 °C it was found that 101 % of the starting mass remained suggesting no degradation had occurred. Having observed that a high swelling ratio is required for degradation, further experiments were continued in acetone due to its low toxicity, price and potential to be renewably sourced.\footnote{166}

3.2.1.6. Effect of Solvent/Water Ratio on Degradation

p(MMA-co-A1) was degraded in acetone/H₂O solutions of varying v/v ratios. The pTsOH concentration was kept constant at 0.15 M and the temperature was held at 50 °C. It was found that increasing the amount of water led to a qualitative decrease in degradation. After 5 hrs residual p(MMA-co-A1) remained in all but the 9/1 v/v acetone/H₂O pTsOH (0.15 M) solution. Samples treated in 8/2 and 7/3 acetone/H₂O solutions were visibly swollen and the solution had taken on the yellow colour of the thermoset. However, samples in the 6/4 and 5/5 acetone/H₂O solutions remained largely unchanged. Upon filtering and drying \textit{in vacuo} at 100 °C the residual thermoset samples it was found that >80 % of the starting mass remained for all but the 9/1 v/v acetone/H₂O pTsOH (0.15 M) solution (Figure 3-11).

![Figure 3-10 Degradation of p(MMA-co-A1) in acetone/H₂O pTsOH (0.15 M) solutions at 50 °C.](image)
The swelling ratios of p(MMA-co-A1) in acetone and acetone/H$_2$O solutions ranging from 9/1 to 5/5 v/v show a large decrease upon increasing the H$_2$O content of the solutions (Figure 3-11). Coupling this with the degradation experiments, there is further support that the ability of the solution to swell the thermoset has a direct impact on the degradation of p(MMA-co-A1) to a homogeneous solution.

### 3.2.1.7. Effect of Acid Species on Degradation

Previously, the effect of $pK_a$ on the extent of hydrolysis on the cross-linker A1 was investigated (2.2.1.3) and the extent of hydrolysis was found to decrease with increasing $pK_a$. In those experiments, the hydrolysis was monitored by $^1$H NMR spectroscopy. However, the degradation of p(MMA-co-A1) thermosets by acetal hydrolysis is a complex multistep process involving chemical reactions and physical processes which occur on different timescales. Therefore, the effect of $pK_a$ on p(MMA-co-A1) thermoset degradation was investigated to see if the same trend was observed.
It was found previously that complete hydrolysis of A1 occurred in acetone-d$_6$/D$_2$O 0.15 M solutions of pTsOH, MsOH, TFA and TCA after 5 hrs at 50 °C. Samples of p(MMA-co-A1) were soaked in 0.15 M acetone/H$_2$O solutions of pTsOH, MsOH, TFA, TCA, DCA and MCA for 5 hrs at 50 °C to compare the thermoset degradation behaviour to A1. The degradation of p(MMA-co-A1) in the pTsOH, MsOH and TFA solutions was complete within 5 hrs, as was the hydrolysis of A1. However, in the case of TCA it was found that 65 % of the starting mass remained after 5 h, which previously gave complete hydrolysis of A1 (Figure 3-13). This shows the acidic degradation of p(MMA-co-A1) is different to the hydrolysis of A1.
3.2.2. Degradation Mechanism

From the degradation experiments it is clear the mechanism of p(MMA-co-A1) degradation is dependent on a series of physical and chemical processes. Although there is little literature devoted to the degradation process of pH responsive thermosets, the individual processes thought to be involved, (solvent induced swelling of the thermoset, diffusion of active species throughout the network and polymer dissolution) have been subject to theoretical and experimental investigation. Early on in degradation these processes may occur simultaneously but $^1$H NMR spectroscopy has shown the evolution of acetaldehyde reaches a maximum after 135 mins suggesting the final step in p(MMA-co-A1) degradation is dissolution of the produced p(MMA-co-HEMA).

Based upon the experimental findings and available literature, the following mechanism of p(MMA-co-A1) degradation is proposed (Figure 3-14). The physical state of the polymer component of the system transitions from glassy polymer to swollen gel and finally solvated ‘free’ polymer as the system becomes homogeneous. On a molecular scale the process is more complicated as will be discussed. At $t=0$, or prior to immersion in a pTsOH (0.15 M) acetone/H$_2$O (9/1 v/v) solution, the thermoset is a glassy network. Upon immersion solvent diffuses into the thermoset at the interface (i, Figure 3-14). As it diffuses new interfaces are created between solvent and swollen gel, and glassy matrix and swollen gel. Within the swollen gel region hydrolysis of the acetal groups can now occur as pTsOH and H$_2$O diffuse with the solvent. The network composition of this region is complex with cross-linked chains, partially cross-linked chains and newly formed linear p(MMA-co-HEMA) the result of full cross-link hydrolysis. The latter of these can then undergo dissolution once chain entanglements are overcome by movement of the chain, the rate of which is likely to increase as more cross-links are hydrolysed leading to a net increase in mobility. It is assumed the system becomes a swollen gel (ii, Figure 3-14) before $t=135$ minutes (Figure 3-6) when all acetal groups have been hydrolysed as the accompanying pTsOH and H$_2$O, that diffuse into the network with acetone, are required for hydrolysis to occur. The true structure of the network at this point is
a mixture of hydrolysed and cross-link chains, some of the former will have begun to undergo dissolution into the solvent which is observed qualitatively in experiments as a reduction in size of the gel. After 135 mins. the acetal groups are consumed leaving only p(MMA-co-HEMA) to undergo dissolution (iii, Figure 3-14) in the remaining 280 mins, it is therefore clear that the rate of p(MMA-co-A1) degradation is dependent on swelling and diffusion, acetal hydrolysis and dissolution of the formed p(MMA-co-HEMA).

Figure 3-14 Proposed mechanism of p(MMA-co-A1) degradation.
3.3. Conclusions

p(MMA-co-A1) thermosets were used as a model system for degradation experiments, synthesised via bulk polymerisation initiated by the redox system BPO/TMA. However, initial characterisation via TGA and DSC showed loss of low molecular weight species and an unexpectedly low $T_g$ indicating a low degree of cure. To circumnavigate challenges associated with characterising cross-linked networks the curing of a model p(MMA) system was followed by $^1$H NMR spectroscopy using the same reaction conditions. Conversions of MMA were around 80 % which is characteristic of bulk free radical polymerisations. Therefore, the effect of post curing in an oven at different temperatures and durations was investigated. The highest $p$(MMA) $T_g$ was obtained after post-curing for 48 hrs at 100 °C and p(MMA-co-A1) cured under the same conditions had a $T_g$ of 102 °C.

$p$(MMA-co-A1) was found to form homogeneous solutions when soaked in pTsOH (0.15 M) acetone/H$_2$O (9/1 v/v) solutions at 50 °C for 6 hrs, this was then repeated and monitored gravimetrically revealing degradation was complete at 5 hrs. However, $^1$H NMR spectroscopy of degradation filtrates showed acetaldehyde was no longer produced at 2 hrs suggesting the degradation process was dependent on a variety of factors. The effect of solvent, solvent water ratio and acid $pK_a$ on degradation were investigated. The solvent swelling ratio was found to be related whether thermoset samples degraded, and acetone was chosen for further studies. The ratio of acetone/H$_2$O had to be kept at 9/1 v/v for degradation to occur within 5 hrs at 50 °C and was also thought to be due to the lower swelling ratio when using 8/2 v/v or lower. Lastly, the effect of acid $pK_a$ in 0.15 M acid in acetone/H$_2$O (9/1 v/v) solutions at 50 °C over 5 hrs on degradation was investigated using the same acid series in Chapter 2. Interestingly the cross-linker A1 was fully hydrolysed by trichloroacetic acid within 5 hrs, however, only 35 % mass loss was observed in the $p$(MMA-co-A1) thermosets after 5 hrs further suggesting the degradation kinetics are dependent on physical and chemical factors that we propose a mechanism for.
3.4. Experimental

3.4.1. Materials
A1 was synthesised as described in chapter two. Methyl methacrylate (99.0 %) was purchased from Acros Organics. Basic alumina and DMF (≥99.0 %) were purchased from Fisher. Methyl ethyl ketone (laboratory reagent grade) was purchased from Scientific Laboratory Supplies. 4-methoxy phenol (99 %), 4-\(N,N\)-trimethylaniline (99%), benzoyl peroxide (Luperox, 25 % \(\text{H}_2\text{O}\)), DMSO (≥99.9 %), isobutyl acetate (natural, ≥97.0 %) and methane sulfonic acid (≥99 %), were purchased from Sigma-Aldrich. All reagents were used as supplied, unless otherwise stated. Details of other materials can be found in Chapter 2.4.

3.4.2. Instrumentation
DSC was performed on a TA Instruments DSC25, 5-10 mg of sample was placed in an aluminum Tzero pan that was sealed with a Tzero Hermetic lid. Samples were equilibrated at -40 °C for five minutes before the following program, 20 °C/min ramp to 200 °C, 20 °C/min ramp to -40 °C and a final 10 °C/min ramp to 200 °C. The \( T_g \) was determined using the TA Instruments Trios software. TGA was performed on a TA Instruments Q500, ~10 mg of sample was placed in a flame cleaned platinum pan and heated under \( \text{N}_2 \) from 25-800 °C at a ramp rate of 20 °C/min. Details of other instrumentation can be found in Chapter 2.4.

3.4.3. Model Adhesive Synthesis
The following stock solutions were prepared. Methyl methacrylate (82.8 g, 0.83 mol), A1 (1.8 g, 4.0 mmol) and benzoyl peroxide (25 % \( \text{H}_2\text{O} \), 4.8 g, 15 mmol) were mixed. Methyl methacrylate (86.4 g, 0.86 mol) and 4,\(N,N\)-trimethylaniline (3.6 g, 26 mmol) were mixed. The two solutions were added to a 200 mL dual syringe equipped with a static mixer. Adhesives were then dispensed into moulds (0.5 cm\(^3\)) and cured at room temperature for 48 hrs before being placed in an oven preheated to 40 °C oven overnight. The product was a glassy orange cube.
3.4.4. Adhesive Degradation Study

To poly(MMA-co-A1) (~500 mg) a solution of acid (10 mL, 0.15 M) in acetone/water (9/1 v/v) was added and heated to 50 °C for 24 hours. If no solubilisation was observed acetone (40 mL) was added and left for 48 hours at 50 °C.

3.4.5. $^1$H NMR spectroscopy kinetic study of bulk polymerisation of p(MMA)

Methyl methacrylate was purified by passing over a column of basic alumina. BPO (1.49 g, 4.49 mmol) was added to methyl methacrylate (28.2 g, 0.281 mol) and 4, N,N-trimethylaniline (0.575 g, 0.423 mmol) was added to methyl methacrylate (28.2 g, 0.281 mol). Both solutions were degassed with N$_2$ for 30 minutes. 0.5 mL of each solution was added to a sample vial sealed with a septum and mixed on a vortex. The reaction proceeded at room temperature for a fixed time. Reactions were quenched by the addition of an acetone-d$_6$/MEHQ stock solution (1 mL, 0.15 M) followed by immersion of the vial in liquid N$_2$. Samples were diluted with CDCl$_3$ and their $^1$H NMR spectrum recorded. Conversion was calculated using the following equation:

\[
MMA \text{ conversion (\%)} = (1 - \frac{I_{3.55 \text{ ppm}}}{I_{3.55 \text{ ppm}} + I_{3.44}}) \times 100
\]

3.4.6. Post-curing study of p(MMA)

Methyl methacrylate was purified by passing over a column of basic alumina. BPO (1.49 g, 4.49 mmol) was added to methyl methacrylate (28.2 g, 0.281 mol) and 4, N,N-trimethylaniline (0.575 g, 0.423 mmol) was added to methyl methacrylate (28.2 g, 0.281 mol). Both solutions were degassed with N$_2$ for 30 minutes. 0.5 mL of each solution was added to a sample vial sealed with a septum and mixed on a vortex. The reaction proceeded at room temperature for 6 hours. Vials were then placed in an oven preheated to 60-100 °C for 24 or 48 hours.
3.4.7. Synthesis and post curing of p(MMA-co-A1)

The following stock solutions were made up. Methyl methacrylate (82.8 g, 0.83 mol), acetal cross-linker (1.8 g, 4.0 mmol) and benzoyl peroxide (25 % H₂O, 4.8 g, 15 mmol) were mixed. Methyl methacrylate (86.4 g, 0.86 mol) and 4, N,N-trimethylaniline (3.6 g, 26 mmol) were mixed. The two solutions were added to a 200 mL dual syringe equipped with a static mixer. Adhesives were then dispensed into moulds (0.5 cm³) and cured at room temperature for 6 hours before being placed in an oven preheated to 100 °C for 48 hours. The product was a glassy orange cube.

3.4.8. ¹H NMR spectroscopy study of p(MMA-co-A1) degradation

Samples of p(MMA-co-A1) (0.05 g) were ground to a fine powder and added to a pTsOH (1.5 mL, 0.15 M) acetone-d₆/D₂O (9/1 v/v) solution and heated to 50 °C for up to 24 hours. The insoluble fraction of adhesive was removed via filtration through cotton wool and the ¹H NMR spectrum of the filtrate recorded. The relative concentration of acetaldehyde was calculated from ¹H NMR spectra using the integrals of the following peaks pTsOH at δ 7.68 ppm and acetaldehyde at δ 2.07 ppm. The following equation was used:

\[ \text{Conc}_{\text{acetaldehyde}} (M) = \frac{I_{2.07 \text{ ppm}}}{I_{7.68}} \times \frac{\text{No. of protons}_{\text{pTsOH}}}{\text{No. of protons}_{\text{acetaldehyde}}} \times \text{conc}_{\text{pTsOH}} \]

3.4.9. Gravimetric degradation study of p(MMA-co-A1)

To samples of poly(MMA-co-A1) (~500 mg) acetone/water (9/1 v/v) pTsOH (10 mL, 0.15 M) was added and heated to 50 °C for a fixed time between 0-300 minutes. At pre-determined time intervals, the insoluble fraction was collected by filtration and dried in a vacuum oven at 100 °C for 48 hours and the mass recorded. The remaining weight % was calculated using the following equation:

\[ \text{Weight} \% = \left( \frac{\text{initial mass} - \text{final dry mass}}{\text{initial mass}} \right) \times 100 \]
3.4.10. Degradation Studies

General procedure

To poly(MMA-co-A1) (~500 mg) a solution of acid (10 mL, 0.15 M) in solvent/water (9/1 v/v) was added and heated to 50 °C for 24 hours. If no solubilisation was observed solvent (40 mL) was added and left for 48 hours at 50 °C.

3.4.11. Determination of swelling ratios

General procedure

p(MMA-co-A1) (400 mg) was added to a sample vial containing solvent or a solvent/H₂O (9/1 v/v) solution (10 mL). Samples were left at room temperature for 48 hours, removed dried with paper towel and weighed. The swelling ratio was determined using the following equation:

Equation 3-4

\[
\text{Swelling ratio} \, (\%) = \left( \frac{\text{mass of swollen gel} - \text{dry mass}}{\text{dry mass}} \right) \times 100
\]

3.4.12. Determination of gel content

p(MMA-co-A1) (200 mg) was added to a Soxhlet thimble and extracted with refluxing THF (300 mL) for 24 hours. Sample placed in a vacuum oven at 70 °C for 48 hours and weighed. The gel content was determined using the following equation:

Equation 3-5

\[
\text{gel content} \, (\%) = \left( \frac{\text{initial mass} - \text{final mass}}{\text{initial mass}} \right) \times 100
\]
Chapter 4 – Acid Generators

4.1. Introduction

Having demonstrated that methyl methacrylate networks cross-linked with acetal crosslinker A1 could undergo acid-catalysed degradation to form homogeneous solutions of p(MMA-co-HEMA), the use of thermal acid generators (TAGs) and photoacid generators (PAGs) as internal acid sources was investigated. From the results in Chapter 3, the generated acid would need a pKa ≤ 0.25, corresponding to trifluoroacetic acid, the weakest acid that fully degraded p(MMA-co-A1) at 0.15 M in acetone/H2O (9/1 v/v) solutions within 5 hours at 50 °C. Several strategies for the photo release of sulfonic and carboxylic acids exist in the literature.116,117,193 The focus of this chapter is largely the thermally-driven intramolecular elimination (Ei) of sulfonates, the products of which are a sulfonic acid and an alkene (Scheme 4-1).194

![Scheme 4-1 – Intramolecular elimination of sulfonate forming an alkene and sulfonic acid.](image)

The mechanism of elimination is debated and may be concerted, proceeding via 5 or 6 membered transition states,195 meaning multiple pathways are possible in the same substrates.194,195,204,196–203 Corey et al.194 synthesised a series of 8-quinolyl sulfonates and 2-pyridyl sulfonates from the corresponding sulfonyl chlorides and alcohol using NEt₃, pyridine or n-butyllithium in yields of 65-91% (Figure 4-1). Interestingly the pyrolysis products were not consistent with a concerted pathway, suggesting the amine group was acting as an internal base leading to an E2 type elimination. The highest temperatures of Eᵢ (Tₑᵢ) were observed for the 1-octanol sulfonates of 8-quinoline and 2-pyridine, 220 °C and 225 °C respectively, and the olefin yields were <50%. Tₑᵢ was greatly reduced for the 2-octanol sulfonates of 8-quinoline and 2-pyridine, 150 °C and 115 °C respectively, and the olefin yields were >85 %. The temperature of sulfonate elimination was affected by the ester structure showing there is scope
for tuning the temperature, which needs to be above the post-cure of 100 °C and below the onset of p(MMA-co-A1) thermal degradation at 250 °C. $T_{EI}$ is used within this text to refer specifically to the temperature at which cleavage of the sulfonate C-O bond occurs. Within the literature several examples are seen where $T_d$ is incorrectly used to describe temperature of acid generation where it is actually describing the temperature at which mass loss is observed via TGA.

![Chemical structures of 8-quinolyl and 2-pyridyl sulfonates and their elimination temperatures](image)

Figure 4.1 – 8-quinolyl and 2-pyridyl sulfonates and their elimination temperatures.¹⁹⁴

Lee et al.¹²³ synthesised three aryl cyclohexyl sulfonates with differing substituents in the para position on the arene ring (Figure 4-2). Only the nitro derivative’s thermal properties were studied, $^1$H NMR spectroscopy showed it underwent full thermolysis at 90 °C after 128 minutes in C₆D₆, to yield cyclohexene and para-nitrobenzene sulfonic acid. The TAGs were used as latent thermal initiators in the bulk cationic polymerisation of isobutyl vinyl ether. No polymerisation was observed below 50 °C and as thermolysis generated the initiator species this can be taken as the minimum $T_{EI}$. Furthermore, at $T > 60$ °C the rate of polymerisation increased, when R was NO₂. When R was H, a significant increase in polymerisation rate was observed at $T > 80$ °C, whereas the rate was low when R was CH₃ indicating that the electron donating and withdrawing properties of the arene substituents have a direct impact on $T_{EI}$. Of these species only the cyclohexyl para-toluenesulfonate may have a $T_{EI}$ suitable for degradation of p(MMA-co-A1).
Shin *et al.* synthesized a series of thermally cleavable di-epoxide cross-linkers (Figure 4-3) by reacting disulfonyl chlorides with 3-cyclohexene-1-methanol and subsequent formation of the epoxide by reacting the alkene groups with potassium peroxymonosulfate. These cross-linkers were partially thermolyzed to generate free acid species that catalysed the reaction between poly(vinyl phenol) and the remaining epoxy groups to generate a resin. TGA revealed the onset temperature of $E_i$ for Figure 4-3 a, b and c was 157 °C, 162 °C and 183 °C respectively. Interestingly, when the cross-linkers were cast into thin films that contained 30 mol % poly(styrene) and heated to 100 °C for 150 seconds, the disappearance of the sulfonate groups was observed by IR spectroscopy, suggesting a much lower $T_{Ei}$ than observed by TGA.

When using the cross-linker Figure 4-3 a as a source of acid catalyst to cross-link poly(vinyl phenol) films, insoluble fractions were observed at temperatures as low as 70 °C. The authors offer no explanation of the origin of the different thermolysis behaviors observed via different techniques or when the cross-linkers were in different systems.

![Figure 4-3 – Thermally cleavable sulfonate-based epoxide cross-linkers.](image)
Kolomanska et al. synthesized a series 4-styrene sulfonates via a multistep route starting with the synthesis of 4-styrene sulfonyl chloride by the reaction of 4-styrene sodium sulfonate with thionyl chloride (Figure 4-4). The 4-styrene sulfonates were synthesised via the reaction of 4-styrene sulfonyl chloride with the corresponding alcohol. The corresponding series of polymers were synthesised via reversible addition-fragmentation chain-transfer (RAFT) polymerisation and their thermolysis behaviour characterised via TGA. It was found that p(styrene sulfonates) bearing branched alkyl pendant groups underwent Ei elimination at lower temperatures than their linear equivalents by temperature sweep TGA, ranging from 190-230 °C. Further characterisation by isothermal TGA at 150 °C for 2 hrs showed that p(styrene sulfonates) bearing branched alkyl pendant groups underwent 10-13% mass loss suggesting that Ei is occurring at lower temperatures.

![Figure 4-4 – p(styrene sulfonates) synthesised and their T_Ei determined via temperature sweep TGA.](image)

Within the literature Ei is used as a method for the preparation of olefins, latent initiators, thermally degradable thermosets and thermally labile polymers for organic photovoltaics. The latter reported by Kolomanska et al. is the most relevant to the aims of this chapter, the authors synthesise and polymerise 4-styrene sulfonate monomers which produce a polymer bound sulfonic acid group upon heating. The work in this chapter aims to reverse this by creating monomers capable of generating a sulfonic acid via Ei that is released and able to diffuse through A1 cross-linked polymer networks and catalyse the hydrolysis of acetal cross-links.
4.2. Results and Discussion

4.2.1. Preliminary Investigations of Acid Generations

Initially, four types of TAGs were investigated as *in situ* acid catalysts: 2-nitrobenzyl tosylate (2-NBT), *N*-hydroxytosylate-1,8-napthalimide (NHTN), hydroxyethyl ammonium nitrate and *t*butyl trifluoroacetate (Scheme 4-2). 2-NBT and NHTN were chosen as they generate pTsOH and *t*butyl trifluoroacetate generates TFA, both acids have previously been shown to catalyse the hydrolysis of A1 and A1 cross-linked networks. Hydroxyethyl ammonium nitrate was chosen as it thermally generates nitric acid which has a pKa of -1.3$^{155}$ in water. This is within the experimentally determined pKa that are appear optimal for A1 hydrolysis.

Scheme 4-2 - Preliminary acid generators 2-NBT, NHTN, 2-hydroxyethyl ammonium nitrate and *t*butyl trifluoroacetate thermal/photo acid generation schemes.
Nitrobenzyl esters are well known photo and thermoacid generators\textsuperscript{127,207} and 2-NBT was synthesised following literature preparations\textsuperscript{130} from 2-nitrobenzyl alcohol and \textit{para}-toluene sulfonyl chloride (pTsCl) and characterised via \textit{\textsuperscript{1}H} NMR spectroscopy (Appendix Figure 8-6). Interestingly 2-NBT synthesis requires dicyclohexylamine rather than the commonly employed, but weaker, bases pyridine and NE\textsubscript{T}{3}. Their use led to the formation of 2-nitrobenzyl chloride as the major product.\textsuperscript{208} Thermolysis of 2-NBT yields pTsOH and 2-nitrosobenzaldehyde.\textsuperscript{127}

NHTN was synthesised by a two-step process, the intermediate product being \textit{N}-hydroxy-1,8-napthalimide that was subsequently reacted with pTsCl, the products were characterised via \textit{\textsuperscript{1}H} NMR and IR spectroscopy (Appendix Figure 8-7 to Figure 8-10).\textsuperscript{209} Napthalimide esters are photoacid generators proceeding through a radical based mechanism followed by proton abstraction to yield pTsOH, the non-acid product is determined by the reaction solvent.\textsuperscript{210} NHTN was synthesised to probe the viability of thermal acid generation from napthalimide esters.

Hydroxyethyl ammonium nitrate is available commercially as a latent acid catalyst in resin precursor solutions, upon heating the salt degrades producing ethanolamine and nitric acid which catalyses the resin formation. Finally, \textit{\textsuperscript{t}}butyl trifluoroacetate was sought due to the thermally-labile nature of \textit{\textsuperscript{t}}butyl esters that undergo a thermal rearrangement via a six membered transition state that liberates trifluoroacetic acid and isobutylene.\textsuperscript{211–213} However, \textit{\textsuperscript{t}}butyl trifluoroacetate could not be synthesised \textit{via} Steglich or Fischer esterification methods. This was thought to be due to degradation of the product during purification.
4.2.2. TGA Analysis of Acid Generators

Previous work has shown to achieve a good degree of curing in p(MMA-co-A1) thermosets a post curing step at 100 °C is required. Therefore, acid generators present in p(MMA-co-A1) thermosets should be stable at 100 °C. 2-NBT has been shown by TGA to undergo thermolysis to pTsOH from 150 °C onwards.\textsuperscript{126,127,214} NHTN and hydroxyethyl ammonium nitrate were characterised by TGA to ensure they underwent thermolysis above 100 °C to prevent prematurely hydrolysing acetal cross-links (Figure 4-5). The TGA traces of NHTN and hydroxyethyl ammonium nitrate both showed a mass loss at 280 °C and 210 °C, respectively, these were assigned as the temperature of thermolysis. Both underwent thermolysis above 100 °C meaning they are suitable for use in p(MMA-co-A1) thermosets.

![Figure 4-5 - TGA thermograms (N\textsubscript{2}, 20 °C/min) of NHTN and hydroxyethyl ammonium nitrate.](image)

A further criterion is that the temperature of acid generation is prior to the onset of p(MMA-co-A1) network thermal degradation, previously shown to occur from 250 °C onwards. Based upon the TGA data 2-hydroxethyl ammonium is suitable, however, NHTN generates acid above this temperature meaning networks containing it may thermally degrade when generating acid. Despite this, NHTN was used to gauge whether its thermolysis properties varied in networks.
4.2.3. Addition of TAGs to Networks

To assess whether 2-NBT, NHTN and hydroxyethyl ammonium nitrate were suitable in situ acid sources, model thermoset networks were synthesised. Networks were synthesised via bulk polymerisation of MMA, methacrylic acid (MAA), A1 and TAG (1 wt%) using BPO and 4-TMA as a redox initiator system. MAA was incorporated as it is commonly used in adhesives to promote adhesion to metal substrates. Thermosets were be heated above the TAGs $T_E$ generating acid in situ and forming soluble thermoplastics. Initially 2-NBT was investigated as the acid source, however, it was found that adhesives doped with 2-NBT would not cure when using the redox initiator (Figure 4-6).

![Figure 4-6](image.png)

Figure 4-6 - Inverted vials of adhesives doped with 2-NBT, free flowing fluids suggested poor curing.

Radical curing thermosets commonly use redox systems such as BPO and 4-TMA supplied as a two pot system that separates the components until dispensing, ensuring a long shelf life.\(^{215,216}\) However, in the presence of 2-NBT, a solid thermoset was not formed. Inversion of vials containing 2-NBT doped adhesives revealed free flowing liquids, suggesting 2-NBT interacted unfavourably with the initiator system. Previously; Gill & Williams demonstrated the catalytic effect of nitrobenzene on the thermal decomposition of benzoyl peroxide in solutions of benzene and nitrobenzene, favouring the formation of the benzoic acid via a radical pathway.\(^{217}\) Therefore, the rate of termination may be higher in the presence of 2-NBT via a similar pathway accounting for the low conversion.
Subsequent attempts to add NHTN or hydroxyethyl ammonium nitrate to the same adhesive formulation were unsuccessful. Both TAGs were insoluble in the adhesive precursor solution and cured adhesives (Figure 4-7). To overcome the challenges of cure inhibition, solubility and potential leaching when using additive TAGs, a monomeric TAG was sought.

![Figure 4-7 – Vials of NHTN (left) and 2-hydroxyethyl ammonium nitrate (right) doped p(MMA-co-MAA-co-A1) adhesives prior to curing.](image)

### 4.2.4. HPMA and HEMA Tosylates

The desired TAG would need to be capable of undergoing copolymerisation with methacrylates such as A1 and MMA in the thermoset formulation. Commercially available 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxypropyl methacrylate (HPMA) were utilised for their reactive alcohol group (Scheme 4-3). HEMA and HPMA were chosen to investigate the effect of substitution on the α-carbon relative to the sulfonate on $T_{\text{Ei}}$. The tosylates of these monomers were synthesised by reaction with pTsCl using NEt$_3$ as a HCl trap and purified via column chromatography achieving yields of 32% and 37% for the HPMA and HEMA tosylates, respectively. The products were characterised by $^1$H and IR spectroscopy, demonstrating the targeted products had been synthesised (Appendix Figure 8-11 to Figure 8-14). Commercially available HPMA is a mixture of the regioisomers 2-hydroxypropyl methacrylate and 2-hydroxyisopropyl methacrylate, the ratio of which was determined via $^1$H NMR spectroscopy to be 0.7:0.3 (Appendix Figure 8-15). The ratio of the corresponding tosylates was 0.6:0.4; the decrease in the 2-hydroxypropyl methacrylate derivative was hypothesised to be due to the
lower reactivity of secondary alcohols due to steric hindrance or greater solubility in the aqueous phase used during purification.\textsuperscript{77}

\begin{equation}
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{OH} \\
\text{R}
\end{array}
+ \begin{array}{c}
\text{Cl} \\
\text{SO} \\
\text{O} \\
\text{Ph}
\end{array}
\rightarrow
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{R}
\end{array}
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{SO} \\
\text{Ph}
\end{array}
\end{equation}

\text{R} = \text{H, CH}_3

Scheme 4-3 - Synthesis of HPMA and HEMA tosylates by reaction with pTsCl.

4.2.5. Thermal Characterisation of HEMA Tosylate

The tosylates were hypothesised to undergo intramolecular elimination to vinyl methacrylate and pTsOH which has already been shown to have a suitable $pK_a$ to catalyse acetal hydrolysis (Scheme 4-4).\textsuperscript{194,206,219,220} Further to this pTsCl is a cheap and commonly used starting material. The mechanism of intramolecular elimination reaction is known to proceed via 5 and 6 membered transition states depending on the substrate.\textsuperscript{118,122,123,131–133,194,206,219,221}

\begin{equation}
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{S} \\
\text{Ph}
\end{array}
\rightarrow
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\begin{array}{c}
\text{O} \\
\text{SO}
\end{array}
\end{equation}

Scheme 4-4 - Intramolecular elimination of HEMA tosylate to vinyl methacrylate and pTsOH.

HEMA tosylate (HEMAtos) was initially characterised by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). DSC showed that an exothermic thermal event took place at 120 °C, with a shoulder peak at 160 °C (Figure 4-8). It was expected that TGA would show a 40 % mass loss at 120 °C corresponding to the volatilisation of vinyl methacrylate generated via $E_i$ of HEMAtos. However, TGA showed the onset of mass loss at 200 °C and then a sharp drop at 300 °C. In both the DSC and TGA pans a residue was present and it was hypothesised that the DSC peaks may by the thermal initiated polymerisation of HEMAtos or some other thermally driven side reaction that is preventing $E_i$ from occurring.
4.2.6. Optimisation and Scale Up of HPMA and HEMA Tosylate Syntheses

The synthesis of HEMA and HPMA tosylates was optimised and scaled up for further studies of the Ei reactions of the corresponding polymers and model thermosets. The reaction between HPMA and pTsCl was chosen (Scheme 4-5) as the secondary alcohol reacts more slowly. Furthermore, the initial synthesis had a yellow impurity that seemed to form prior to the addition of the alcohol functional monomer. A survey of the literature of tosylation reactions was performed to identify alternative bases, catalysts, order of reagent additions and the stoichiometry of reagents (Table 4-1).

Scheme 4-5 - Synthesis of HPMAtos.
Table 4-1 – Literature conditions of tosylation reactions.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Base</th>
<th>Catalyst</th>
<th>Feed&lt;sup&gt;a&lt;/sup&gt;</th>
<th>[OH]:[Cl]:[Base]&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tipson et al.</td>
<td>Pyridine</td>
<td>-</td>
<td>pTsCl</td>
<td>1:1:1</td>
</tr>
<tr>
<td>Kabalka et al.</td>
<td>Pyridine</td>
<td>-</td>
<td>pTsCl</td>
<td>1:2:3</td>
</tr>
<tr>
<td>Yoshida et al.</td>
<td>NEt&lt;sub&gt;3&lt;/sub&gt;</td>
<td>NEt&lt;sub&gt;3&lt;/sub&gt;.HCl</td>
<td>pTsCl</td>
<td>1:1.5:2.5</td>
</tr>
<tr>
<td>Morita et al.</td>
<td>N,N-dimethylbenzylamine</td>
<td>KOH</td>
<td>pTsCl</td>
<td>1:1.5:0.1</td>
</tr>
<tr>
<td>Kazemi et al.</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>None</td>
<td></td>
<td>1:1.5:36</td>
</tr>
<tr>
<td>Ding et al.</td>
<td>NEt&lt;sub&gt;3&lt;/sub&gt;</td>
<td>4- (dimethylamino)pyridine</td>
<td>pTsCl</td>
<td>1:1.5:1.5</td>
</tr>
</tbody>
</table>

<sup>a</sup>Species fed into the reaction mixture, <sup>b</sup>ratio that authors claim give fastest reaction conditions

Based upon the conditions reported in the literature (Table 4-2) a series of HPMAtos syntheses were performed to improve the yield (32%) and suspected low conversion of the secondary alcohol isomer present in commercial HPMA. The majority of tosylation reactions reported in the literature added pTsCl to a solution of alcohol and base so the initial synthesis of HPMAtos was modified to a pTsCl feed. <sup>1</sup>H NMR spectroscopy was used to monitor the conversion of both isomers, the primary alcohol was found to reach >99 % conversion after 27 hrs, after which the secondary alcohol reached only 32 % which increased to 38 % at 72 hrs (Appendix Figure 8-16 to Figure 8-19). When using pyridine, the primary and secondary alcohols were found to reach >99 % and 40 %, respectively (Appendix Figure 8-20 to Figure 8-23). When using DMAP in reactions with pyridine the primary and secondary alcohols were found to reach >99 % and 35 %, respectively (Appendix Figure 8-24 to Figure 8-27). However, Kabalka et al. reported the rate of tosylation is improved by using a [OH]:[pTsCl]:[pyridine]
molar ratio of 1:2:3. Upon repeating the synthesis of HPMAtos under these conditions an increase in secondary alcohol conversion to 98% in 72 hrs was observed (Appendix Figure 8-28 to Figure 8-30).

Table 4-2 – Experimental conditions of HPMAtos synthesis optimisation experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Base</th>
<th>Catalyst</th>
<th>Feed</th>
<th>[OH]:[Cl]:[Base]</th>
<th>1° OH Conversion (%)^a</th>
<th>2° OH Conversion (%)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NEt₃</td>
<td>pTsCl</td>
<td>1:1.5:1.5</td>
<td>&gt;99</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pyridine</td>
<td>pTsCl</td>
<td>1:1.5:1.5</td>
<td>&gt;99</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pyridine</td>
<td>DMAP</td>
<td>pTsCl 1:1.5:1.5:0.2 (DMAP)</td>
<td>&gt;99</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Pyridine</td>
<td>pTsCl</td>
<td>1:2:3</td>
<td>&gt;99</td>
<td>98</td>
<td></td>
</tr>
</tbody>
</table>

^a Determined via ¹H NMR spectroscopy

However, under these conditions there was a large excess of pTsCl and pyridine to be removed from HPMAtos. Therefore, a series of experiments investigating reactive work up procedures were performed on portions of the crude reaction mixture and monitored via TLC. Propylamine, tBuOH, poly(vinyl alcohol) and sat. sodium bicarbonate were added to the reaction crude mixture and stirred^{227-229}. It was found that after one hour of stirring with sat. sodium bicarbonate no pTsCl was present.
4.2.7. FRP Polymerisation of HPMAEnough and HEMAtos

HPMAEnough and HEMAtos were polymerised to their corresponding polymers via free radical polymerisation initiated by 2,2'-azobis(2-methylpropionitrile) (AIBN) at 70 °C in methyl ethyl ketone (MEK) (Scheme 4-6). After 24 hrs the conversion of HPMAEnough to p(HPMAEnough) and HEMAtos to p(HEMAtos) was determined via ¹H NMR spectroscopy to be 90 and 80 %, respectively. The crude polymers were purified by precipitation into methanol and centrifugation prior to characterisation by SEC. The $M_w$ was 42800 and 65600 g/mol for p(HPMAEnough) and p(HEMAtos) respectively, indicating the formation of polymeric species (Table 4-3, Appendices Figure 8-31). The dispersity (Đ) was determined to be 1.33 and 1.72 for p(HPMAEnough) and p(HEMAtos) respectively (Table 4-3), which are expected for uncontrolled free radical polymerisation where termination of propagating chains is uncontrolled leading to broad molecular weight distributions.¹⁹¹,¹⁹²

![Scheme 4-6 – Free radical polymerisation of HPMAEnough and HEMAtos.](image)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conversion (%)a</th>
<th>$M_w$ (g/mol)b</th>
<th>Đb</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(HPMAEnough)</td>
<td>90</td>
<td>42800</td>
<td>1.33</td>
</tr>
<tr>
<td>p(HEMAtos)</td>
<td>80</td>
<td>65600</td>
<td>1.72</td>
</tr>
</tbody>
</table>

¹°Determined via ¹H NMR spectroscopy after 18 hrs, ²°determined by SEC in THF relative to p(MMA) standards.
4.2.8. Thermolysis of p(HPMAtos) and p(HEMAtos)

p(HPMAtos) and p(HEMAtos) synthesised via free radical polymerisation were characterised by TGA and DSC to investigate the temperature of E_i. A suitable TAG for p(MMA-co-A1) systems must undergo E_i before the onset of thermal degradation of the network, but not at the post-cure temperature of 100 °C. The TGA thermograms recorded under N_2 for both p(HPMAtos) and p(HEMAtos) with p(MMA-co-A1) are shown in Figure 4-9. Interpreting these thermograms it is assumed the drop in mass corresponds to the generation of pTsOH as the remaining mass is non-volatile polymer. p(HEMAtos) undergoes 60 % mass loss, corresponding to pTsOH, at T > 250 °C and is closely followed by a thermal degradation path similar to poly(MMA-co-A1) therefore it is unsuitable as an internal acid source for the acetal group hydrolysis. The DSC thermogram shows an exothermic peak at 240 °C which was attributed to the E_i reaction, supporting the TGA data.

Figure 4-9 – a) DSC and TGA thermograms of p(HPMAtos), b) DSC and TGA thermograms of p(HEMAtos) and c) TGA thermograms of p(HEMAtos), p(HPMAtos) and p(MMA-co-A1).
The TGA thermogram of p(HPMA\textsubscript{tos}) showed a 58% mass loss, corresponding to pTsOH, beginning at 200 °C, which is below the onset of p(MMA-co-A1) thermal degradation. The DSC further supports this showing an exothermic peak at 190 °C. Therefore, p(HPMA\textsubscript{tos}) was thought to undergo E\textsubscript{i} at a suitable temperature to enable \textit{in situ} acid generation for acetal group hydrolysis in p(MMA-co-A1). The difference in E\textsubscript{i} temperature between p(HPMA\textsubscript{tos}) and p(HEMA\textsubscript{tos}) was attributed to the α-methyl group giving a lower energy transition state which will be discussed in detail later.

Having found evidence for a thermally driven process \textit{via} TGA and DSC characterisation, a molecular understanding was sought. The p(HPMA\textsubscript{tos}) and p(HEMA\textsubscript{tos}) residues that remained in the DSC pans were characterised \textit{via} $^1$H NMR spectroscopy, HPLC-MS and IR spectroscopy. The E\textsubscript{i} reaction products were hypothesised to be pTsOH and p(vinyl methacrylate) or p(methylvinyl methacrylate), corresponding to p(HEMA\textsubscript{tos}) or p(HPMA\textsubscript{tos}), respectively (Scheme 4-7). However, attempts to dissolve the residues were unsuccessful suggesting they had cross-linked; the pendent vinyl groups may react \textit{via} a radical process\textsuperscript{196} or Friedel-Crafts type reaction.\textsuperscript{206,230}

![Scheme 4-7 - Proposed E\textsubscript{i} reaction of p(HPMA\textsubscript{tos}) and p(HEMA\textsubscript{tos}).](image)

The DSC pan residues were washed with DMSO-$d_6$ and $^1$H NMR spectroscopy and HPLC-MS was performed on the extract. $^1$H NMR spectroscopy revealed both extracts contained pTsOH, determined by the peaks at 7.48, 7.12 and 2.29 ppm (Figure 4-10 a and b). This was also seen in the HPLC-MS as pTsOH, [M+H]$^+$ 170.93 AMU (Appendices Figure 8-32 & Figure 110)
The insoluble residue was then dried *in vacuo* to remove any residual DMSO-d$_6$ and characterised by IR spectroscopy. The expected vinyl peak at $\sim1650$ cm$^{-1}$ was not observed, supporting that a cross-linking side reaction involving it was taking place at elevated temperatures (Appendices Figure 8-34 & Figure 8-35).

Based upon these studies HPMAtos was chosen for use as an internal acid source in p(MMA-co-A1) as it underwent E$_i$ at $\sim200$ °C based upon the TGA data which is suitable for the thermoset post-curing conditions discovered in Chapter 2 and is below the temperature at which p(MMA-co-A1) thermally degrades. However, the overall goal of introducing HPMAtos to p(MMA-co-A1) is to internally catalyse acetal hydrolysis, thus breaking cross-links; the cross-linking of p(HPMAtos) is orthogonal to this. It is hypothesised that when HPMAtos is
present as a comonomer its effective concentration will be reduced meaning the cross-linking side reaction doesn’t occur as the reactive species will be sufficiently separated.

4.2.9. HPMA\textsubscript{atos} and HEMA\textsubscript{atos} Model Adhesives

Having demonstrated that p(HPMA\textsubscript{atos}) underwent E\textsubscript{i} at \(~200\) °C it was incorporated into a model thermoset network. The model network was a synthesised via bulk polymerisation of A\textsubscript{1}, MMA and HPMA\textsubscript{atos} at 5 wt %, 81 wt % and 10 wt %, respectively using BPO and 4-TMA as a redox initiator system (Scheme 4-8). A control network comprising A\textsubscript{1} and MMA at 5 wt % and 91 wt % was also synthesised. The A\textsubscript{1}/MMA/HPMA\textsubscript{atos} networks were cured at room temperature for 6 hrs and post-cured at 100 °C for 48 hrs Interestingly, the network containing HPMA\textsubscript{atos} was a brown colour, whereas the control was pale yellow; both were colourless solutions prior to the addition of 4-TMA. Pale yellow was previously observed in networks synthesised using BPO and 4-TMA as the initiator system.

![Scheme 4-8 – Synthesis of model MMA, A1 and HPMA\textsubscript{atos} networks.](image-url)
Previous TGA of p(HPMAtos) showed that pTsOH was generated via Eₗ at ~200 °C. The A1/MMA/HPMAtos and control networks were characterised via TGA to ensure pTsOH was generated (Figure 4-11). As HPMAtos was present at 10 wt % it was calculated that the wt % of pTsOH in the degradable network was 5.8 wt %. This was the expected mass loss that would be observed via TGA. However, the TGA thermogram of the 10 wt % HPMAtos network showed no clear mass loss corresponding pTsOH generation when compared with the control; both showed mass loss with an onset around 200 °C. Furthermore, the presence of HPMAtos in the network increased the thermal stability.

![TGA thermogram](image)

**Figure 4-11 – TGA thermogram of HPMAtos network and no HPMAtos control.**

An alternative experiment was designed to observe the generation of pTsOH. The 10 wt % HPMAtos containing network was heated at 180 °C for 3 hours in an oven, soaked in acetone, filtered and the filtrate was concentrated *in vacuo*. The resultant residue was then characterised by ¹H NMR spectroscopy and HPLC-MS. The ¹H NMR spectrum showed the residue contained pTsOH, confirmed by the aromatic CH peaks at 7.89 and 7.45 ppm and the CH₃ peak at 2.54 ppm; this was further supported by the HPLC-MS data (Appendices Figure 8-36 & Figure 8-37).
A second set of networks was synthesised without MMA to ease the analysis of the Ei reaction products and investigate whether the *in situ* generated pTsOH could catalyse the hydrolysis of acetal links in A1 (Scheme 4-9). p(A1-co-HPMAtos) was synthesised by polymerising A1 and HPMAtos at 48 wt % each using 1 wt % of BPO and 4-TMA for 6 hours at R.T., followed by post-curing at 100 °C for 48 hrs. A non-degradable control network using ethylene glycol dimethacrylate (EGDMA) instead of A1 was also synthesised. Samples of the networks were heated to 180 °C in an oven for 18 hrs and the small molecules extracted by Soxhlet extraction and concentrated *in vacuo*, and was analysed by ¹H NMR spectroscopy. Control samples of the networks were not heated and underwent Soxhlet extraction to ensure no pTsOH was generated prematurely.

![Scheme 4-9 – Synthesis of A1/HPMAtos networks.](image)

The ¹H NMR spectra of the Soxhlet extract residues of EGDMA and A1 networks that weren't heated in the oven had peaks corresponding pTsOH. These were also present in the heated
samples; meaning it could not be determined if this was generated prior to or during the heating in the oven. Premature generation of pTsOH is problematic as it may cause unwanted degradation of thermoset network during application.

To probe this further a final series of networks composed of A1, HPMAtos, and MMA was synthesised. A1 was fixed at 2 wt % in all samples and HPMAtos was varied from 5 to 50 wt % and are referred to as HAM-X, where x denotes the wt % of HPMAtos present. (Table 4-4). MMA was used to ensure solubility of HPMAtos in the polymerisation starting mixture. The networks were synthesised as before and characterised by IR spectroscopy. The expected aromatic stretches were observed at 3000-2800 cm\(^{-1}\), the strong ester stretch from the methacrylates at 1725 cm\(^{-1}\), and a strong aliphatic ether stretch at 1160 cm\(^{-1}\) (Figure 4-12). In the HAM-25 and HAM-50 networks spectra an alkene peak at 1600 cm\(^{-1}\) was observed suggesting residual monomer was present.

<table>
<thead>
<tr>
<th>Network</th>
<th>A1 / wt %</th>
<th>MMA / wt %</th>
<th>HPMAtos / wt %</th>
<th>BPO / wt %</th>
<th>4-TMA / wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAM-5</td>
<td>2</td>
<td>89</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>HAM-10</td>
<td>2</td>
<td>84</td>
<td>10</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>HAM-25</td>
<td>2</td>
<td>69</td>
<td>25</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>HAM-50</td>
<td>2</td>
<td>44</td>
<td>50</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>
The generation of pTsOH within the networks was characterised by TGA. An isothermal step was (180 °C for 3 hrs) added to improve the observation of the E₁ reaction. The theoretical mass loss resulting from the generation of pTsOH was calculated using the wt % of pTsOH in the HPMAtos monomer, was calculated as 58 %. It was hypothesized that the mass loss during the 180 °C isothermal step should match the theoretical pTsOH wt % and these are marked on Figure 4-13 with dashed lines.
For the networks HAM-5, HAM-10, and HAM-25 no mass loss was observed until the isothermal step, at which a sharp drop was observed thought to arise from the generation of pTsOH. The observed mass loss was equal to or less than the calculated theoretical amount of pTsOH, supporting that this step was pTsOH generation. However, the TGA thermogram for HAM-50 exhibited unexpected mass loss during the initial temperature ramp from 25-180 °C suggesting the presence of unreacted monomer which was supported by the IR spectrum. Furthermore, the isothermal stage exhibited a greater mass loss than the theoretical amount of pTsOH generated via Eᵢ, further supporting that this network was not fully cured.

Lastly, the TGA thermogram for the temperature ramp from 180-800 °C for HAM-5, HAM-10 and HAM-25 are consistent with cured methacrylate networks, showing a sharp drop in mass from 300 °C onward. However, the HAM-50 outline has a broad and multistep mass loss suggesting that the network has residual unreacted species. Alternatively, the TGA of HAM-50 may arise from the premature generation of pTsOH which subsequently catalysed the hydrolysis of the acetal groups, however, this would only account for an unexpected mass loss of <2 wt %. A detailed understanding of the Eᵢ reaction of p(HPMAtos) was then sought before returning to any model network studies to ensure premature Eᵢ was not taking place.
4.2.10. Isothermal TGA Characterisation of p(HPMAtos)

To gain a further understanding of the solid-state E_i reaction of p(HPMAtos), isothermal TGA studies were performed at 140, 160 and 180 °C. Samples were initially heated to the isothermal target temperature at 10 °C/min and held for 18 hrs before a final 10 °C/min ramp to 800 °C. It was hypothesized that if p(HPMAtos) was undergoing E_i at lower temperatures then mass loss would be observed during the isothermal stage.

The TGA thermograms of the isothermal step at 140, 160 and 180 °C are shown in Figure 4-14. Previous temperature sweep TGA has shown that p(HPMAtos) undergoes E_i at ~200 °C to high conversion; this was also observed under isothermal conditions at 180 °C. Rapid mass loss from 100 to 50 % was observed from 0-210 mins attributed to the generation of pTsO_H.

The residual mass was 45 wt %, the theoretical maximum residual mass of 42 wt % was not reached, this was thought to be due to experimental error and potential generation of pTsOH during the initial temperature ramp to 180 °C.

Unexpectedly, the isothermal TGA at 140 and 160 °C both showed considerable mass loss over 18 hrs indicating E_i was occurring at lower temperatures than previously observed when performing temperature sweep TGA. The residual mass was 79% and 55% at 140 °C and
160 °C, respectively. As previously discussed, a post-cure step was required when synthesising p(MMA-co-A1) networks, the conditions of which were heating at 100 °C for 48 hrs. Based on the isothermal TGA results, it is plausible that when post-curing networks containing HPMAtos, pTsOH is being generated which may be interfering with the post-cure and prematurely degrading the network.

Ideally p(HPMAtos) would have been characterised using isothermal TGA at 120 and 100 °C however, the 18 hrs experimental duration of the isothermal step would probably need to be extended meaning the residence time in the TGA was very long. Therefore, kinetic analysis of the isothermal data was performed to obtain an Arrhenius plot from which the data at 120 and 100 °C could be estimated via extrapolation. This is possible by plotting a linear version of the Arrhenius equation using the natural log:

Equation 4-1

\[ k = Ae^{-\frac{E_a}{RT}} \]

Equation 4-2

\[ \ln k = -\frac{E_a}{RT} + \ln A \]

Where \( k \) is the rate constant at a given temperature, \( E_a \) is the activation energy, \( R \) is the gas constant, \( T \) is the temperature in Kelvin and \( A \) is the pre-exponential factor. By analysing the data from the isothermal TGA it is possible to determine the rate constants of the \( E_i \) reaction of p(HPMAtos) at 140 °C, 160 °C and 180 °C. The remaining unknown terms in the linear Arrhenius equation can then be determined by plotting \( \ln(k) \) versus \( 1/T \) where \(-E_a/R\) is the gradient and \( \ln(A) \) is the y-intercept. As \( E_i \) is an intramolecular reaction the reaction is 1st order. Therefore, to determine the \( k \) at 140 °C, 160 °C and 180 °C, \( \ln(x) \), where \( x \) was the fractional conversion, was plotted versus \( t \) of the isothermal steps, the gradient of which is \(-k\).
When plotting ln(x) versus t of the isothermal step what appeared to be linear plots were obtained for 140 and 160 °C with $R^2$ values of 0.99 and 0.97, respectively (Figure 4-15). However, these plots are likely non-linear and no relationship is observed due to the low conversion of the $E_i$ reaction. At 180 °C the relationship between ln(x) and t was non-linear with an $R^2$ value of 0.80 indicating that the mass loss during the isothermal heating was either incorrectly attributed to conversion of p(HPMAtos) to pTsOH or $E_i$ was occurring alongside another process. To gain an understanding of what the TGA was revealing zero and second order kinetic plots were produced. The zero order plots were non-linear for all temperatures (Appendices Figure 8-38). Interestingly, in the second order plots ($1/x$ versus $t$) a linear relationship was observed with an $R^2$ value of 0.99 for all temperatures (Figure 4-16), this would suggest that the reaction is second order which is inconsistent with the proposed $E_i$ mechanism.$^{219,220}$

![Figure 4-15](image-url) – First order kinetic plots of isothermal TGA of p(HPMAtos), where x is the fractional conversion determined from mass loss.
Upon examining the literature covering TAGs,116,117 and specifically $E_i$ of sulfonates,133,206 it was clear that TGA is the standard technique for characterising thermolysis. However, there is an important criterion for a TGA being suitable, if the $E_i$ takes place at a temperature below the boiling points of the products then it is unsuitable for that system. This is because the temperature at which mass loss is observed is most likely due to the volatilisation of a small molecule product of $E_i$ and not the true temperature at which $E_i$ occurs.

It was hypothesised that p(HPMAtos) and p(HEMAtos) both meet this criterion. This was confirmed by comparing the TGA traces of p(HPMAtos) and pTsOH monohydrate (Figure 4-17). pTsOH exhibited a mass loss at 100 °C due to H$_2$O in the sample, however, a sharp decrease in mass began at ~180 °C that was attributed to the evaporation of pTsOH. This matched well with the trace of p(HPMAtos) which had a sharp decrease in mass with an onset at 180 °C and ended at ~42 % residual mass, corresponding to the loss of all pTsOH in the system. Therefore, previous TGA of p(HPMAtos) and p(HEMAtos) that had been used to characterise the temperature of $E_i$ were showing the evaporation of pTsOH instead. Therefore, an alternative technique was sought to gain a true understanding of the temperature of $E_i$ and insight into the reaction mechanism.
4.2.11. Variable Temperature NMR Spectroscopy Study of p(HEMAtos) and p(HPMAtos) E_i Mechanism

E_i can proceed via 5- or 6-membered transition states depending on the functional groups.\textsuperscript{219,235} The reaction products of sulfonate elimination are an alkene and sulfonic acid (Figure 4-18), therefore, they proceed via a 6-membered transition state. Variable temperature \textsuperscript{1}H NMR (vtNMR) spectroscopy was used to gain insight into the reaction mechanism and products of solution phase E_i of p(HEMAtos) and p(HPMAtos). p(HEMAtos) is discussed first for simplicity as p(HPMAtos) is a mixture of isomers.

a) 5-membered transition state E_i pathway

\[
\text{R} - \text{O} - \text{S}^{\text{tol}} \xrightarrow{\text{x}} \text{R} - \text{C} = \text{O} + \text{O} - \text{S}^{\text{tol}} - \text{OH}
\]

\[
\text{R} = \begin{array}{c}
\text{NC} \\
\text{H}
\end{array}
\]

b) 6-membered transition state E_i pathway

\[
\text{R} - \text{O} - \text{S}^{\text{tol}} \xrightarrow{\text{x}} \text{R} - \text{C} = \text{CH} + \text{HO} - \text{S}^{\text{tol}} - \text{O}
\]

\[
\text{tol} = \begin{array}{c}
\text{N}
\end{array}
\]

Figure 4-18 – a) 5-membered transition state E_i pathway and b) 6-membered transition state E_i pathway of p(HEMAtos).
The predicted Eᵢ reaction products for p(HEMAtos) were p(vinyl methacrylate) and pTsOH. From the NMR spectra recorded at different times (0-18 hrs) at 90 °C, a reduction in intensity of the p(HEMAtos) aromatic ring CH peaks at 7.76 and 7.42 ppm and increase in the intensity of pTsOH aromatic ring CH doublet peaks at 7.55 and 7.16 ppm was observed, confirming that Eᵢ was occurring (Scheme 4-10 b). The presence of pTsOH in the t=0 spectrum is due to the experimental setup as the sample enters the spectrometer preheated to the target temperature resulting in an unavoidable delay between heating and the first spectrum being recorded. Furthermore, the peak corresponding to the CH₂ in the α-position to the sulfonate at 4.25 ppm disappears over time indicating cleavage of the ester group. However, the expected p(vinyl methacrylate) peaks at 7.5, 5 and 4.5 ppm were not observed (Scheme 4-10 b).
An unexpected broad peak was observed that shifted downfield throughout the experiment to 10.85 ppm, this was assigned to a COOH proton. The downfield shift of this peak with time was attributed to the generation of pTsOH as the experiment proceeded. As the dissociation constant of pTsOH is higher the increase in its concentration overtime leads to an increase in the protonated form of COOH. The equilibrium shifts to reduce the amount of free hydronium.
ions in the system, leading to the observation of a previously exchangeable proton.\textsuperscript{153,154,237} Allan \textit{et al.} reported that the gas phase pyrolysis of vinyl benzoate at 400-550 °C resulted in the formation of ethyne and benzoic acid. This is the only example of the synthesis of an alkyne \textit{via} ester pyrolysis\textsuperscript{238,239}. It is proposed that the production of the experimentally observed COOH peaks proceeded \textit{via} a similar pathway, consuming the pendent alkene groups of vinyl methacrylate units to produce the observed poly(methacrylic acid) components and ethyne (Scheme 4-10 a). Furthermore, ethyne has a boiling point of -84 °C\textsuperscript{240} and consequently the majority would be present in the headspace of the NMR tube and therefore not easily observed. However, the peak at 2.03 ppm was assigned as the alkyne CH proton as it appeared and decreased over time as it moved to the vapour/gas phase.

Interestingly, a peak at 9.56 ppm was observed indicating the presence of an aldehyde (Scheme 4-10 b). The intensity of this peak increased with time suggesting it was a by-product of the thermolysis. It was hypothesised that this was the product of vinyl methacrylate hydrolysis due to residual water, the product of which would be the enol derivative of acetaldehyde that would tautomerise to acetaldehyde and p(methacrylic acid). Initially, the peak at 2.02 ppm was assigned as the acetaldehyde CH\textsubscript{3}. However, this peak decreased over time whereas the aldehyde CH remained. Furthermore, no H\textsubscript{2}O peak at 3.33 ppm\textsuperscript{159} was observed in the \textit{t}=0 spectrum. It was also considered that the aldehyde could be formed \textit{via} the 5-membered \textit{E}i pathway (Scheme 4-11), and that the produced para-toluene sulfonic acid was oxidised to pTsOH.\textsuperscript{241} However, there is little evidence in the literature of sulfonates undergoing this type of \textit{E}i.\textsuperscript{194,195,197,219,235,239,242–245}

\[
\begin{align*}
\text{CH}_2=\text{CH}-\text{CO}-\text{O} \quad & \rightarrow \quad \text{CH}_2=\text{CH}-\text{CO}-\text{H} + \quad \equiv \\
\text{R} & \quad \quad \text{R} = \quad \text{NC} \\
\end{align*}
\]

\textit{Scheme 4-11 - Proposed further \textit{E}i of p(vinyl methacrylate) to p(MAA).}
Kornblum et al. and Nace et al. both described the synthesis of aldehydes and ketones from aliphatic and aromatic tosylates via an oxidation reaction with DMSO, typically in the presence of NaHCO$_3$ as a catalyst.$^{246}$–$^{249}$ This reaction proceeds slowly under neutral and weakly acidic conditions. It was hypothesised that any aldehyde in the reaction mixture was formed via this reaction.

It was expected that p(HPMAtos) would also undergo E, via the same pathway as p(HEMAtos), however, the products would be dependent on the isomer. The majority isomer, poly(2-tosylpropyl methacrylate), would produce a ketone pendent group and the minority isomer, poly(tosylisopropyl methacrylate), would produce an aldehyde functional group (Scheme 4-12 a) via the 5-membered pathway. For the 6-membered pathway it was expected that a further reaction producing methacrylic acid components would be observed alongside the product propyne. The ratio of these isomers in the monomer HPMAtos was determined via $^1$H NMR spectroscopy, to be 3:1; however, when polymerised the CH$_2$ peaks used to calculate this coalesced due to the peak broadening in polymeric products (4.00 ppm). Therefore, the two isomers were treated as one when monitoring the reaction, however, their reactivities may be different.
Again, the generation of pTsOH was observed by the presence of the pTsOH aromatic CH doublet peaks at 7.55 and 7.16 ppm which increased in intensity from 0-18 hrs. (Scheme 4-12 b). A reduction in the CH peak at 4.90 ppm and CH$_2$ peak at 4.00 ppm and was observed corresponding to the cleavage of the sulfonate ester bond in both the minor and major isomers. Evidence of the aldehyde forming pathway was observed as the peak at 9.53 ppm assigned
as the CH proton in the pendant aldehyde group. Furthermore, the peak at 2.02 ppm was assigned as the CH proton in propyne. Lastly, an exchangeable COOH peak that shifted downfield overtime to 12.5 ppm was observed suggesting the 6-membered pathway was also taking place. Again, the majority of propyne was thought to be present in the headspace of the NMR tube due to its low boiling of -23.2 °C. The COOH peak was shifted further downfield than in the p(HEMA-tos) experiment due to p(HPMA-tos) having a lower amount of pTsOH per unit mass due to the extra methyl group.

4.2.12. Variable Temperature ¹H NMR Spectroscopy Study of p(HPMA-tos) and p(HEMA-tos) Eᵢ

To probe the temperature of Eᵢ, p(HPMA-tos) and p(HEMA-tos) were characterised via ¹H variable temperature NMR spectroscopy. Both polymers were characterised to verify the previously observed effect of CH₃ and H substitution alpha to the sulfonate ester group on the temperature of Eᵢ where p(HPMA-tos) was found to undergo Eᵢ at a lower temperature via TGA. The samples were heated to 50 °C, 70 °C or 90 °C for 18 hrs in DMSO-d₆, spectra were recorded at 30-minute intervals, and the conversion was monitored using the ring CH peak at 7.75 ppm.

The conversion of tosylate to pTsOH determined by vtNMR at 50, 70 and 90 °C for p(HEMA-tos) and p(HPMA-tos) are shown in Figure 4-19. Interestingly Eᵢ was observed at much lower temperatures than previously observed via TGA, and p(HEMA-tos) was more labile than p(HPMA-tos) based on conversion. For both polymers 100 % conversion of the tosylate to pTsOH was observed after 8 hrs at 90 °C with high conversion observed at 70 °C (93 % and 79 % for p(HEMA-tos) and p(HPMA-tos) respectively). Eᵢ was observed in both polymers at 50 °C which may mean that the pTsOH observed in networks previously was generated prematurely by the exotherm during the cure and when heating to 100 °C during the post-cure step.
To ensure that the generation of pTsOH was taking place via $E_i$, the conversion data was used to generate 1st order kinetic plots. Unlike the isothermal TGA data of p(HPMAtos), a linear relationship was observed for all temperatures indicating the reaction followed the expected pathway (Figure 4-20). As expected, the $k_{obs}$ for both p(HEMAtos) and p(HPMAtos) increased with temperature. However, rates were higher for p(HEMAtos) at all temperatures which contradicts the TGA data that suggested p(HEMAtos) was less reactive than p(HPMAtos).

Due to the high $R^2$ values for all values of $k_{obs}$, it was assumed that p(HEMAtos) and p(HPMAtos) were reacting via the same pathway. If they were undergoing $E_i$ by a combination of 5 and 6-membered transition states then the rate of reaction would vary for both pathways.
This is particularly interesting in p(HPMAtos) as it is a mixture of isomers, but the high $R^2$ values indicate they are both reacting via the same pathway.

4.2.13. The Effect of the R Group and the determination of the $E_i$ Mechanism

As both p(HEMAtos) and p(HPMAtos) were found to undergo $E_i$ at lower temperatures than expected and via an unexpected pathway, a structure-property investigation was undertaken to aid the future design of TAGs and particularly those that undergo $E_i$ at higher temperatures. Using the first order rate constants obtained from the vNMR spectroscopy experiments at 50, 70 and 90 °C for both p(HEMAtos) and p(HPMAtos), the activation energy ($E_a$) for both polymers was determined from their Arrhenius plots (Figure 4-21). The vNMR spectroscopy experiments demonstrated that p(HEMAtos) was more reactive than p(HPMAtos) and this was supported by the calculated $E_a$ of 87 kJ/mol versus 94 kJ/mol. However, what causes the higher energy barrier is unclear.

![Figure 4-21 – Arrhenius plots of a) p(HEMAtos) and b) p(HPMAtos).](image)

The mechanism of $E_i$ is known to proceed via a concerted mechanism through a 5- or 6-membered cyclic transition state (Figure 4-18). Reaction with a hydrogen atom on the $\alpha$ carbon leads to a 5-membered transition state. Alternatively reaction with the hydrogen on the $\beta$ carbon leads a 6-membered transition state. Of the two pathways the 5-membered transition
state proceeds via the more readily abstractable proton, due to its proximity to the strongly electron withdrawing tosylate group. However, gas phase experiments and computational models have shown abstraction of this proton leads to a more energetically unstable transition state, due to the poor charge separation.\textsuperscript{196–204,219} From the vtNMR experiments of p(HEMA\textsubscript{tos}) and p(HPMA\textsubscript{tos}) it was determined that both polymers reacted preferentially via the 6-membered pathway due to the small amount of aldehyde observed compared to free pTsOH. A disparity in these values suggests that the alkene is preferentially formed and undergoes further reaction to p(methacrylic acid). However, determining the ratio of products was challenging due to the exchangeable nature of the COOH proton. Coupling this with the high $R^2$ values for both $k_{\text{obs}}$ and $E_a$ it is assumed both polymers react via the 6-membered transition state.

Therefore, it was assumed that the difference in $E_a$ between p(HPMA\textsubscript{tos}) and p(HEMA\textsubscript{tos}) was due to unfavourable interactions in the transition states arising from the methyl branch point in p(HPMA\textsubscript{tos}). First, the conformation of the 6-membered transition state of p(HEMA\textsubscript{tos}) is considered (Figure 4-22). As the transition state is 6-membered it will adopt a chair-like conformation to minimise strain and thus forcing substituents into pseudo-equatorial or pseudo-axial positions about the ring.\textsuperscript{250,251}

\begin{center}
\includegraphics[width=0.8\textwidth]{fig4_22.png}
\end{center}

Figure 4-22 – Conformational analysis of p(HEMA\textsubscript{tos}) E, 6-membered transition states.

When reacting via the 6-membered pathway there are two possible conformers that may be adopted to give rise to a chair-like transition state (Figure 4-22). However, these conformers
are not equal in stability, in the lowest energy conformation, the R group (polymer backbone) is positioned pseudo-equatorial. In the unfavourable conformation, the R group occupies a pseudo-axial position where it encounters an unfavourable 1,3-diaxial interaction with the pseudo-axial sp\(^3\)-hybridised sulfonate oxygen lone pair orbital.

In the majority isomer of p(HPMAtos), the 6-membered transition states have two favourable conformers, one for each of the enantiomers, \(S\) and \(R\), arising from the chiral centre (Figure 4-23). In the energetically unfavourable transition state conformer for both \(S\) and \(R\) enantiomers, both the R and methyl groups occupy pseudo-axial positions. The R group clashes sterically with the aromatic ring of the tosyl group and the methyl group encounters an unfavourable 1,3-diaxial interaction the pseudoaxial sp\(^3\) hybridised sulfonate oxygen lone pair orbital. The more favourable conformers position both the R and methyl group in pseudo-equatorial positions. However, unlike the p(HEMAros) 6-membered transition state, these groups both encounter 1,2-steric clash which raises the relative \(E_a\) of the p(HPMAtos) major isomer conformer.
Lastly, the minority regioisomer of p(HPMA\text{tos}) also exists as a pair of stereoisomers, S and R, however, the position of the R and methyl group are on the same carbon meaning the higher $E_a$ in these conformers relative to those of p(HEMA\text{tos}) cannot be due to 1,2-steric interactions. The unfavourable conformers are destabilised by the R group in the pseudo-axial position which has greater steric bulk than the methyl group, therefore the steric interaction with the tosyl group aromatic ring destabilises the transition state. Therefore, the lowest energy conformers position the bulkier R group in the pseudo-equatorial position. To summarise the lower $E_a$ of p(HEMA\text{tos}) is due to there being fewer destabilising interactions in the 6-membered transition state compared to p(HPMA\text{tos}).

4.2.14. p(HEMA\text{tos}) solid state $E_i$ $^1$H NMR spectroscopy study

The vtNMR studies found that p(HEMA\text{tos}) was more labile towards $E_i$ than pHMA\text{tos} which contradicts the solid state (TGA and DSC) results. Furthermore, $E_i$ occurred at lower temperatures than expected and the reaction products were soluble in DMSO-$d_6$, whereas solid state studies produced insoluble resins after heating at 140-180 °C.
To investigate the effect of the physical state on the temperature of $E_i$ in p(HEMA) a series of experiments were performed. p(HEMA) was heated in vials for 18 hrs over a temperature range of 50-130 °C before DMSO-$d_6$ was added to allow determination of the conversion of p(HEMA) to pTsOH via $^1$H NMR spectroscopy. However, upon heating the samples became discoloured and formed a swollen gel when DMSO-$d_6$ was added, indicating that the samples had cross-linked and therefore the conversion could not be determined.

The extracts were characterised via $^1$H NMR spectroscopy (Figure 4-25) to gain insight into the structures of any soluble products and therefore, the cross-linking mechanism. The extracts of the samples heated to 50 and 60 °C contained mostly p(HEMA) as confirmed by the ring CH peaks at 7.76 and 7.42 ppm, methylene CH$_2$ peak at 4.25 ppm, aromatic CH$_3$ peak at 2.33 ppm, the backbone CH$_3$ at 1.63 ppm and the backbone CH$_2$ at 0.66 ppm. pTsOH was also present as confirmed by the aromatic CH doublet peaks at 7.47 and 7.11 ppm and the CH$_3$ peak at 2.28 ppm. However, samples heated to 70 °C or higher contained pTsOH and no polymer, suggesting the remaining sample had cross-linked. Consequently, this means p(HEMA) undergoes $E_i$ in the solid state at much lower temperatures than previously thought and is unsuitable for use in A1 cross-linked networks due to the temperatures at which they are post-cured. Furthermore, the unwanted cross-linking will mean A1 cross-linked networks cannot be removed by solvent washing at the end of lifetime.
The cross-linking pathway is unknown; however, four possible mechanisms are proposed. Thermally generated radicals may react with the pendent vinyl groups between two chains creating a cross-link (Scheme 4-13). Another potential pathway is via the reaction between methacrylic acid units created by the further elimination of in situ formed vinyl esters previously discussed, which may undergo acid catalysed nucleophilic addition to a charged carbonyl derivative created by the tautomerisation of the vinyl pendant group, producing a hemiacetal ester type species (Scheme 4-14). However, hemiacetal esters are known to be thermally labile at temperatures >100 °C so cross-links formed via this process are likely to undergo thermolysis forming a soluble product that was not observed in the 1H NMR spectra of extracts of reactions performed at >100 °C.
It is proposed in the literature that p(styrene isobornylsulfonates) undergo a Friedel-Crafts type reaction upon cleavage and the norbornyl cation alkylates the resulting polymer bound pTsOH unit in the meta position.\textsuperscript{206,227,228,253,254} However, no mechanism or detailed structural characterisation are given, it is unclear whether this could lead to cross-linking in p(HEMAtos) and p(HPMAAtos) systems as the pTsOH produced is not polymer bound. Mahindaratne and Wimalasena\textsuperscript{230} described a pTsOH catalysed alkylation of norbornyl, cyclohexyl and 4-methyl-2-pentyl tosylates with toluene, which could lead to cross-linking in p(HEMAtos) and p(HPMAAtos).

Lastly, the formation of cross-linked samples of p(HEMAtos) in the solid state occurs at lower temperatures than expected, vTNMR studies yielded no cross-linked residues at 50-90 °C. It is believed that this is due to concentration effects whereby pendant groups capable of
undergoing cross-linking reactions are sufficiently diluted in solution meaning they do not come within a close enough proximity to react. Whereas in the solid state the effective concentration is high meaning the pendant groups undergo cross-linking reactions.
4.3. Conclusions

Novel methacrylate TAGS, HEMAtos and HPMAtos were synthesised via an optimised route reacting pTsCl with HPMA or HEMA. The corresponding polymers were synthesised via free radical polymerisation and their thermal Eᵢ reaction characterised via DSC and TGA. Initial characterisation suggested p(HPMAtos) generated pTsOH at 180 °C. However, characterisation of solvent extracts from model thermoset networks of A1/HPMAtos/MMA or A1/HPMAtos revealed the presence of pTsOH after the post-curing at 100 °C.

Isothermal TGA characterisation of p(HEMAtos) and p(HPMAtos) at different temperatures was used to determine the reaction kinetics. However, the data showed second order reaction kinetics, when it was expected to be first order. From this it was determined that TGA is only applicable to TAGs that undergo Eᵢ at a temperature greater than the boiling points of one of the products. p(HEMAtos) and p(HPMAtos) were than characterised via v$t$NMR at 50 °C-90 °C in DMSO-$d_6$. This revealed the polymers underwent high conversion to pTsOH at 70 °C and 90 °C, much lower temperatures than desired for inclusion into A1 networks.

Finally, the reaction was conducted in the solid state and the products characterised via $^1$H NMR spectroscopy. Cross-linking of the polymers at 50-130 °C was observed, meaning HPMAtos and HEMAtos are unsuitable for this application.
4.4. Experimental

4.4.1. Materials
1,8-napthalenic anhydride, 2-nitrobenzyl alcohol (97 %), 4-dimethylaminopyridine (≥99 %), AIBN (98 %), dicyclohexylamine (99 %), DMSO-d₆ (99.8 atom % D), HCl (37 wt %), HPMA (97 %, mixture of isomers), hydroxylamine hydrochloride (≥99.9 %), pTsCl (≥99 %), pyridine (99.9 %, anhydrous), 'BuOH (99 %) were purchased from Sigma-Aldrich. MeOH (HPLC grade), MgSO₄ anhydrous, sodium carbonate anhydrous, sodium chloride (≥99.5 %), NaOH (99 %) and toluene (HPLC grade) were purchased from Fisher. All reagents were used as supplied, unless otherwise stated. Other reagents are listed in previous experimental sections.

4.4.2. Instrumentation
All instrumentation is reported in previous experimental chapters.

4.4.3. Synthesis of 2-nitrobenzyl tosylate
2-nitrobenzyl alcohol (6.12 g, 0.040 mol), pTsCl (8.38 g, 0.044 mol) and acetone (20 mL) were added to a round bottom flask and stirred on an ice bath. Dicyclohexylamine (7.95 mL, 0.040 mol) was added dropwise over 30 minutes and the ice bath removed. Mixture stirred for 3 hours and precipitate removed via filtration. Filtrate washed with Na₂CO₃ (2x5 mL), H₂O (5 mL) and brine (5 mL). Organic phase dried over MgSO₄, filtered and concentrated in vacuo to yield off white crystals (11.0 g, 90 % yield) ¹H NMR (400 MHz, CDCl₃) δ 8.12 (dd, J = 8.2, 1.3 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.80 – 7.73 (m, 1H), 7.68 (td, J = 7.6, 1.3 Hz, 1H), 7.55 – 7.46 (m, 1H), 7.39 – 7.34 (m, 2H), 5.47 (s, 2H), 2.46 (s, 3H), 2.17 (s, 3H).

4.4.4. Synthesis of N-hydroxy-1,8-napthalimide
1,8-naphthalenedicarboxylic acid (15.1 g, 76.2 mmol), hydroxylamine hydrochloride (6.46 g, 93 mmol) and DMF (90 mL) were added to a round bottom flask and stirred. To the suspension 48 wt% NaOH solution (8.06 g, 96.7 mmol) was added dropwise. Mixture heated to 30 °C for
one hour and subsequently cooled on ice. HCl (20 mL, 3 M) was added dropwise and stirred for 30 minutes. Yellow precipitate collected by filtration, washed with H$_2$O (3x10 mL) and dried in vacuo at 100 °C for 96 hours (14.0, 86 %). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 10.76 (s, 1H), 8.50 (dd, $J = 14.8, 7.7$ Hz, 2H), 7.89 (t, $J = 7.3$ Hz, 2H). $^{13}$C {$^1$H} NMR (101 MHz, DMSO) δ 161.36, 135.09, 131.88, 131.33, 127.79, 126.74, 122.84. ATR-IR: 3066 cm$^{-1}$ (O-H), 2824 cm$^{-1}$ (C-H), 1701 cm$^{-1}$ (C=O). CHN calculated (C 67.61 %, H 3.31 %, N 6.57 %), observed (C 66.83 %, H 3.55 %, N 6.12 %).

4.4.5. Synthesis of $N$-hydroxytosylate-1,8-napthalimide

$N$-hydroxy-1,8-naphtalimide (2.5 g, 0.012 mol), NEt$_3$ (2.45 mL, 0.018 mol) and THF (30 mL). pTsCl (2.35 g, 0.012 mol) was added to THF (5 mL) and added dropwise. The solution was then refluxed for 4 hours and subsequently cooled. Yellow solid was collected by filtration and washed with cold water (3x10 mL) and dried in vacuo at 100 °C for 24 hours (2.47 g, 57 %). 

$^1$H NMR (400 MHz, DMSO) δ 8.58 (d, $J = 7.4$ Hz, 2H), 8.52 (d, $J = 7.3$ Hz, 2H), 8.00 – 7.89 (m, 4H), 7.55 (d, $J = 8.1$ Hz, 2H), 2.53 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, DMSO) δ 160.13, 147.13, 136.13, 132.21, 132.06, 131.90, 130.65, 129.53, 128.02, 127.22, 122.40, 21.82. ATR-IR: 3125-2970 cm$^{-1}$ (C-H), 1723.3 cm$^{-1}$ (C=O). [M+H]$^+$ theoretical 368.05 amu, experimental 368.1 amu. CHN calculated (C 62.12 %, H 3.57 %, N 3.81 %, S 8.73 %), observed (C 62.22 %, H 3.79 %, N 4.12 %, S 8.98 %).

4.4.6. General procedure for synthesis of TAG doped adhesives

MMA (0.24 g,), methacrylic acid (0.17g,), A1 (0.02 g,), 4-$N$,$N$-trimethylaniline (0.06 g) and acid generator (0.01 g) were added to sample vial and sealed with a septum. MMA (0.48 g,) and BPO (0.02 g,) were added to a sample vial and sealed with a septum. Both mixtures were mixed on a vortex and degassed with N$_2$ for 30 minutes. The mixtures were mixed under N$_2$ and left for 6 hours at room temperature and cured at 100 °C for 48 hrs.
4.4.7. Tosylation of HEMA and HPMA

HEMA (4.68 mL, 0.039 mol), NEt₃ (5.85 mL, 0.042 mol) and DCM (20 mL) were added to a round bottom flask and cooled on an ice bath. pTsCl (6.72 g, 0.35 mol) was added to DCM (10 mL) and added dropwise to the reaction mixture. After 18 hours the mixture was filtered and washed with DCM (3x10 mL). The filtrate was concentrated in vacuo to yield a pale-yellow oil. The crude product was purified via column chromatography in an eluent of hexane/ethyl acetate (6/4 v/v, 2 vol% NEt₃) to yield a white solid (2.97 g, 37 %) ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.78 (m, 2H), 7.37 (dd, J = 8.1, 2.2 Hz, 2H), 6.08 (q, J = 1.2 Hz, 1H), 5.60 (p, J = 1.6 Hz, 1H), 4.37 – 4.23 (m, 4H), 2.47 (s, 3H), 1.92 (t, J = 1.3 Hz, 3H). ATR-IR: 2990 cm⁻¹ (C-H), 1719 cm⁻¹ (C=O), 1363 (S=O).

HPMA (5.88 mL, 0.039 mol), NEt₃ (5.85 mL, 0.042 mol) and DCM (20 mL) were added to a round bottom flask and cooled on an ice bath. pTsCl (6.72 g, 0.35 mol) was added to DCM (10 mL) and added dropwise to the reaction mixture. After 18 hours the mixture was filtered and washed with DCM (3x10 mL). The filtrate was concentrated in vacuo to yield a pale-yellow oil. The crude product was purified via column chromatography in an eluent of hexane/ethyl acetate (6/4 v/v, 2 vol% NEt₃) to yield a white solid (3.34 g, 32 %) ¹H NMR (400 MHz, CDCl₃) δ 7.82 – 7.74 (m, 2H), 7.33 (t, J = 7.8 Hz, 2H), 6.01 (dt, J = 9.8, 1.3 Hz, 1H), 5.54 (dp, J = 3.2, 1.6 Hz, 1H), 5.09 (qd, J = 6.5, 5.2, 4.0 Hz, 0H), 4.84 (pd, J = 6.6, 3.4 Hz, 1H), 4.21 – 4.03 (m, 2H), 2.44 (d, J = 4.1 Hz, 3H), 1.90 – 1.84 (m, 3H), 1.32 (d, J = 6.5 Hz, 2H), 1.26 (d, J = 6.6 Hz, 1H). ATR-IR: 2986 cm⁻¹ (C-H), 1718 cm⁻¹ (C=O), 1362 (S=O).
4.4.8. Synthesis of HPMAtos Method Development Experiments

HPMA (1.5 mL, 0.010 mol), base and DCM (25 mL) were added to a round bottom flask and stirred on an ice bath for 30 minutes. pTsCl was added in portions and the reaction stirred. Samples were taken periodically to monitor conversion via $^1$H NMR in CDCl$_3$ and TLC in ethyl acetate/petroleum ether (1/3 v/v). The conversion of the isomeric alcohols to the corresponding tosylates was calculated from $^1$H NMR spectra using the following equations:

Equation 4-3

$$\text{primary alcohol conversion (\%) } = \left( \frac{i(5.9)}{(i(5.93) + i(6.05))} \right) \times 100$$

Equation 4-4

$$\text{secondary alcohol conversion (\%) } = \left( \frac{i(5.95)}{(i(5.95) + i(6.07))} \right) \times 100$$

Table 4-5 – Bases and molar ratios used in method development experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Base</th>
<th>[HPMA]:[pTsCl]:[Base]:[DMAP]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Triethylamine</td>
<td>1:1.5:1.5:0</td>
</tr>
<tr>
<td>2</td>
<td>Pyridine</td>
<td>1:1.5:1.5:0</td>
</tr>
<tr>
<td>3</td>
<td>Pyridine</td>
<td>1:1.5:1.5:0.2</td>
</tr>
<tr>
<td>4</td>
<td>Pyridine</td>
<td>1:2:3:0</td>
</tr>
</tbody>
</table>
4.4.9. Reactive Workup of HPMA\textsubscript{6}tos Synthesis

HPMA (1.5 mL, 0.010 mol), base and DCM (25 mL) were added to a round bottom flask and stirred on an ice bath for 30 minutes. pTsCl was added in portions and the reaction stirred. Aliquots (5 mL) were taken and added to vials, then stirred. A quenching agent was added (Table 4-6) and monitored by TLC in ethyl acetate/petroleum ether (1/3 v/v).

<table>
<thead>
<tr>
<th>Quenching agent</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEt$_3$</td>
<td>0.24 g</td>
</tr>
<tr>
<td>tBuOH</td>
<td>0.3 g</td>
</tr>
<tr>
<td>Mowiol 8-88</td>
<td>0.5 g</td>
</tr>
<tr>
<td>Sat. Na$_2$CO$_3$</td>
<td>1 mL</td>
</tr>
</tbody>
</table>

4.4.10. Optimised Synthesis of HPMA\textsubscript{6}tos

HPMA (14.0 mL, 0.1 mol), DCM (100 mL) and pyridine (24.0 mL, 0.3 mol) were added to a round bottom flask and stirred at 0 °C for 30 minutes. pTsCl (38.2 g, 0.2 mol) was added in portions over an hour. Reaction allowed to reach ambient temperature and stirred for 72 hours. As reaction proceeded white precipitate formed. Reaction quenched with sat. Na$_2$CO$_3$ (20 mL) and stirred for 20 minutes. Organic phase separated and washed with sat. Na$_2$CO$_3$ (2x20 mL), HCl (3x20 mL, 1 M), H$_2$O (20 mL) and brine (20 mL). Organic phase diluted with toluene (200 mL) and concentrated in vacuo, this was repeated twice more to yield a colourless oil (29.8 g, 98 %) that crystallised upon standing. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 – 7.74 (m, 2H), 7.33 (t, J = 7.8 Hz, 2H), 6.01 (dt, J = 9.8, 1.3 Hz, 1H), 5.54 (dp, J = 3.2, 1.6 Hz, 1H), 5.09 (qdd, J = 6.5, 5.2, 4.0 Hz, 0H), 4.84 (pd, J = 6.6, 3.4 Hz, 1H), 4.21 – 4.03 (m, 2H), 2.44 (d, J = 4.1 Hz, 3H), 1.90 – 1.84 (m, 3H), 1.32 (d, J = 6.5 Hz, 2H), 1.26 (d, J = 6.6 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.85, 144.83, 135.60, 134.09, 130.02, 129.96, 128.00, 127.83, 126.47, 126.20, 77.48, 77.16, 76.84, 76.69, 71.21, 67.97, 66.10, 21.73, 18.25, 17.60, 16.19. $V_{\text{max}}$ (cm$^{-1}$) 2992
(CH), 1719 (C=O), 1614 (C=C), 1348 (S=O), 1175 (S=O), 896 (C=C). $[\text{M+Na}]^+$ theoretical 321.35 amu, experimental 321.1 amu, purity 98 %. Melting point 68 °C.

4.4.11. Free radical polymerization of HEMAtos

To a vial butan-2-one (5 mL, 20 wt %), HEMAtos (1.00 g, 35.0 mmol) and AIBN (5.80 mg, 0.035 mmol) were added and degassed with $N_2$ on ice for 30 minutes. The reaction was heated to 70 °C for 18 hours. Crude reaction added dropwise to cold MeOH (50 mL, 10-fold excess) and white precipitate formed and collected via centrifugation (4500 rpm, 10 minutes). Supernatant decanted and precipitate redissolved in butan-2-one (5 mL) and reprecipitated into MeOH (50 mL, 10-fold excess), collected via centrifugation (4500 rpm, 10 minutes). White solid dried in vacuum oven (30 °C) for 1 week.

![Figure 4-26 - $^1$H NMR spectrum (CDCl$_3$) of p(HEMAtos).](image)
4.4.12. Free radical polymerization of HPMAtos

To a vial butan-2-one (5 mL, 80 wt %), HPMAtos (1.00 g, 33.5 mmol) and AIBN (5.50 mg, 0.034 mmol) were added and degassed with N₂ on ice for 30 minutes. The reaction was heated to 70 °C for 18 hours. Crude reaction added dropwise to cold MeOH (50 mL, 10-fold excess) and white precipitate formed and collected via centrifugation (4500 rpm, 10 minutes). Supernatant decanted and precipitate added to butan-2-one (5 mL) and reprecipitated into MeOH (50 mL, 10-fold excess) collected via centrifugation (4500 rpm, 10 minutes). Orange solid added dried in vacuum oven (30 °C) for 1 week.

Figure 4-27 - ¹H NMR spectrum (CDCl₃) of p(HPMA-tos).
4.4.13. Synthesis of Model Networks

General procedure:

To a sample vial cross-linker, monomer and BPO (0.02g, 2 wt %) were added to a vial following the amounts in Table 4-7, Table 4-8 and Table 4-9 and stirred for 15 mins. 4-TMA (0.02 g, 2 wt %) was added and mixed on a vortex mixer. Samples were left at room temperature for 6 hrs and post-cured in an oven preheated to 100 °C for 48 hrs.

Table 4-7 – Initial A1/MMA/HPMAtos network formulations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A1 / g</th>
<th>MMA / g</th>
<th>HPMAtos / g</th>
<th>BPO / g</th>
<th>4-TMA / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degradable</td>
<td>0.05</td>
<td>0.81</td>
<td>0.1</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Control</td>
<td>0.05</td>
<td>0.91</td>
<td>0</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 4-8 - A1/HPMAtos and EGDMA/HPMAtos network formulations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A1 / g</th>
<th>EGDMA / g</th>
<th>HPMAtos / g</th>
<th>BPO / g</th>
<th>4-TMA / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degradable</td>
<td>0.49</td>
<td>0</td>
<td>0.49</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Control</td>
<td>0</td>
<td>0.49</td>
<td>0.49</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 4-9 – HAM network formulations.

<table>
<thead>
<tr>
<th>Network</th>
<th>A1 / g</th>
<th>MMA / g</th>
<th>HPMAtos / g</th>
<th>BPO / g</th>
<th>4-TMA / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAM-5</td>
<td>0.02</td>
<td>0.89</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>HAM-10</td>
<td>0.02</td>
<td>0.84</td>
<td>0.10</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>HAM-25</td>
<td>0.02</td>
<td>0.69</td>
<td>0.25</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>HAM-50</td>
<td>0.02</td>
<td>0.44</td>
<td>0.50</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Samples of network (0.40 g) were placed in a vial, sealed and added to an oven preheated to 180 °C for 3 hrs. Samples were removed and allowed to cool, acetone (10 mL) was added and left for 30 mins. The network was removed by filtration and the filtrate concentrated in vacuo. $^1$H NMR spectra recorded in CDCl$_3$.

4.4.15. Heating and Soxhlet extraction of A1/HPMAtos

Samples of network (0.5 g) were heated to 180 °C in an oven for 18 hrs. Samples were then placed in a Soxhlet extraction setup and THF at 70 °C for 24 hrs. The Soxhlet extract was concentrated in vacuo, the residue dissolved in DMSO-d$_6$.

4.4.16. Isothermal TGA characterisation of p(HPMAtos) and p(HEMAtos)

Samples (10 mg) were added to a flame cleaned platinum TGA pan. Samples were then heated at 10 °C/min to 140-180 °C and held for 18 hrs. A further temperature ramp from 140-180 °C to 800 °C was performed at 10 °C/min under N$_2$. Conversion was determined using the following equations:

Equation 4-5

$$Conversion(\%) = (1 - \left( \frac{M_0 - M_{w_{PTsoH}}}{M_{w_{HEMAtos}}/M_0} \right) ) \times 100$$

Equation 4-6

$$Conversion(\%) = (1 - \left( \frac{M_0 - M_{w_{PTsoH}}}{M_{w_{HPMAtos}}/M_0} \right) ) \times 100$$
4.4.17. $^1$H vtNMR spectroscopy studies of $p$(HPMA$\text{tos}$) and $p$(HEMA$\text{tos}$)

Samples (40 mg) were added to DMSO-$d_6$ (0.6 mL) and inserted into a Bruker Avance 400 MHz spectrometer at preheated to 50-90 °C. $^1$H NMR spectra were recorded at 400 MHz. Conversion was determined using the following equation:

$$\text{Conversion} (\%) = (1 - \frac{\text{integral (7.75 ppm) } t}{\text{integral (7.75 ppm) } t_0}) \times 100$$

4.4.18. $p$(HEMA$\text{tos}$) solid state $E_i$ $^1$H NMR spectroscopy study

$p$(HEMA$\text{tos}$) (40 mg) was added to a vial and sealed. Vials were immersed in an oil bath preheated to 50-130 °C and left for 18 hrs. Samples were cooled to room temperature, DMSO-$d_6$ was added, insoluble residues were removed via filtration and the $^1$H NMR spectrum of the filtrate recorded.
Chapter 5 – Acetal Methacrylate CANs

5.1. Introduction

The use of acetals as dynamic covalent groups in covalently adaptable networks (CANs) is a relatively recent discovery. Acetals can undergo exchange reactions via two pathways: transacetalisation and acetal metathesis. Transacetalisation is the exchange reaction between an alcohol and an acetal, producing a different acetal and alcohol (Scheme 5-1 a). In acetal metathesis two acetals undergo an exchange reducing producing two new acetals (Scheme 5-1 b). A benefit of these reactions is neither require the presence of a catalyst to impart a network with adaptable properties. Furthermore, the acetal group enables acid degradation of the networks for material recovery and reuse.

Ma and co-workers synthesised the first example of an acetal-based CAN via the thermal addition reaction of a hydroxy-functional poly(styrene) copolymer to 1,4-cyclohexanedicarboxylic acid dimethylene bisphenol diacylate (Scheme 5-2). They found malleability could be controlled via the hydroxyl to acetal ratio and samples could be reprocessed in a hot press at 150 °C for 10 mins; the authors do not mention the pressure used. The tensile properties of the reprocessed materials were similar to the starting material, and they could be chemically recycled via acetal hydrolysis. Further work by Ma and co-workers used this reaction to cross-link other networks such as phenolic resins, p(HEMA-co-styrene) and p(HEMA-co-styrene-co-2-ethylhexyl methacrylate) with 1,4-cyclohexanedicarboxylic acid dimethylene bisphenol diacylate. Further examples in the literature include the cross-linking of HEMA modified p(styrene-
butadiene) with 1,4-cyclohexanediol divinyl ether,\textsuperscript{100} phenolic resin\textsuperscript{73} or lignin with TEGDVE\textsuperscript{74}.

Ma and co-workers also showed neighbouring group participation is possible during transacetalisation, altering the reprocessing properties of acetal CANs.\textsuperscript{72} The presence of a hydroxyl group neighbouring the acetal group in 2-(1-butoxyethoxy)phenol lowered the activation energy from 68.5 ± 3.5 kJ mol\textsuperscript{-1} for (1-butoxyethoxy)benzene to 43.7 ± 1.4 kJ mol\textsuperscript{-1}. This was then used in epigallocatechin gallate and TEGDVE networks (Scheme 5-3).

Lastly, Shuangjian \textit{et al}.\textsuperscript{255} synthesised a spirocyclic acetal containing CAN via a photoinitiated radical thiol-ene reaction (Scheme 5-4). The spirocyclic acetal underwent catalyst-free metathesis to give the network's adaptable properties and improved the thermal stability of the network relative to acyclic acetal examples.
Based upon these reports, we hypothesised that A1 cross-linked networks could undergo transacetalisation and acetal metathesis to create adaptable materials. The research within this chapter focuses on the preliminary synthesis and characterisation of A1 cross-linked network CANs. Focussing on A1/MMA and A1/HEMA/MMA networks to investigate the effect of reaction pathway, metathesis or transacetalisation, on the materials properties.
5.2. Results and Discussion

5.2.1. Lap shears and repressing
Lap shear testing is used to measure the bond strength of an adhesive joining two substrates by pulling them apart.\textsuperscript{3} It was hypothesised that dynamic bonds could enable two substrates to be re-joined by heating under increased pressure. Aluminium lap shear samples were prepared using a P2 etch, A1 (2 wt%), MMA(94 wt%), BPO (2 wt%) and 4-TMA (2 wt%) and their bond strength determined using a tensometer. Commercially available structural methacrylate-based adhesives contain additives such as elastomers, achieving bond strengths >20 MPa.\textsuperscript{3,4} The initial bond strength of A1 cross-linked and EGDMA cross-linked adhesives was 4.4 ± 0.3 MPa and 5.1 ± 0.2 MPa, respectively (Figure 5-1). These values are both much lower than desired and this was thought to be due to the brittleness of the two networks leading to stress concentration and bond failure. Furthermore, the bond failure method was predominantly adhesive, failing at the interface between adhesive and substrate. Therefore, it was hypothesised that the addition of an adhesion promoter could improve the bond strength. The lower bond strength of A1 may be due to the increased viscosity of the cross-linker compared to EGDMA reducing the surface wetting and therefore, the bond strength.\textsuperscript{256,257}
Literature reports suggest that networks containing acetal functionality can react via acetal metathesis, imparting the network with adaptable behaviour.\textsuperscript{70–76} To investigate this A1 and EGDMA lap shears were re-joined in a hot press at 150 °C and 1.5 MPa and their bond strengths recorded. EGDMA lap shears were used as a control, although adaptable behaviour can be achieved via transesterification, free hydroxyls and a catalyst are required.\textsuperscript{66,258,259} A1 cross-linked networks demonstrated adaptable behaviour, upon re-joining the lap shear samples a first, second and third time, bond strengths of 2.6 ± 0.5 MPa, 2.9 ± 0.5 MPa and 2.9 ± 0.3 MPa were achieved, respectively (Figure 5-1). The large standard deviation was thought to arise from the loss of material when pulling apart the lap shears on the tensometer and material being squeezed from the bond line when repressing. The reuse data for EGDMA networks (Figure 5-1) shows one sample exhibited adaptable behaviour. This was thought to be due to unreacted monomer being polymerised upon heating as opposed to transesterification and the sample could not be re-joined a third time.

To improve the bond strength of A1 networks, further lap shears were synthesised incorporating methacrylic acid (MAA) which promotes adhesion by forming carboxylates with the aluminium surface.\textsuperscript{3} The formulation was changed to A1 (2 wt %), MAA (7.5 wt %), MMA
(86.5 wt %); BPO (2 wt %) and 4-TMA (2 wt %) were used as the initiator system. The MAA networks had a bond strength of 10 ± 1 MPa, which is over double of those without MAA. This may be further improved to compete with commercial adhesives via formulation. Finally, the MAA networks also exhibited adaptable behaviour as shown by the bond strengths after repressing the lap shears (Figure 5-2). It is also possible that the additional MAA units may take part in catalysing the acetal metathesis.81,258,260

![Figure 5-2 - Bond strength of A1/MAA/MMA network after lap shear testing and repressing.](image)

5.2.2. Casting panels and cubes

Having found evidence of adaptable behaviour in A1 cross-linked MMA networks via lap shear testing, a series of networks were synthesised for dynamic mechanical analysis, tensile testing, and grinding/reprocessing experiments. The network compositions were varied to investigate the effect of reaction pathway on the reprocessing properties. Networks containing only MMA and A1 were used to probe the metathesis reaction while A1/HEMA/MMA networks were used to probe the transacetalisation reaction and the effect of [OH]:[acetal] group on the macroscopic properties. The formulations of these networks are shown in Table 5-1 and Table 5-2.
Table 5-1 - Formulation of A1/MMA acetal metathesis networks.

<table>
<thead>
<tr>
<th>A1 mol %</th>
<th>MMA mol %</th>
<th>Benox c-50s&lt;sup&gt;a&lt;/sup&gt; mol %&lt;sup&gt;b&lt;/sup&gt;</th>
<th>DMA mol %&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>98</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.5</td>
<td>0.25</td>
</tr>
</tbody>
</table>

<sup>a</sup>Commercially available blend of BPO (50 wt %) and diethylphthalate, <sup>b</sup>mol % of total vinyl groups.

Table 5-2 - Formulation of A1/HEMA/MMA transacetalisation networks.

<table>
<thead>
<tr>
<th>OH/Acetal&lt;sup&gt;a&lt;/sup&gt;</th>
<th>HEMA mol %</th>
<th>A1 mol %</th>
<th>MMA mol %</th>
<th>Benox c-50s&lt;sup&gt;b&lt;/sup&gt; mol %&lt;sup&gt;c&lt;/sup&gt;</th>
<th>DMA mol %&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>10</td>
<td>70</td>
<td>0.25</td>
<td>0.125</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>10</td>
<td>80</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>0.25</td>
<td>5</td>
<td>10</td>
<td>85</td>
<td>0.5</td>
<td>0.25</td>
</tr>
</tbody>
</table>

<sup>a</sup>two moles of acetal per mole of A1, <sup>b</sup>Commercially available blend of BPO (50 wt %) and diethylphthalate, <sup>c</sup>mol % of total vinyl groups.

The networks were synthesised by casting between two glass panels at room temperature (Figure 5-3 a). Upon gelation they were allowed to cool and then post-cured at 100 °C for 48 hrs. Due to the low viscosity of the mixture, glass panels were sealed with silicone sealant prior to casting to ensure no leakage. Throughout the course of casting panels several panels had rough surfaces due to thermal expansion and subsequent contraction resulting from the exotherm and/or shrinkage (Figure 5-3 b). This was avoided by adjusting the ratio of BPO (Benox c-50s) to N,N-dimethylaniline (DMA) to vinyl groups. Tensile bars were then prepared by punching pre-heated panels with a die; samples were obtained for all panels except the 20 mol % metathesis panel (Table 5-1) as the samples crumbled. This was thought to be due to the high cross-linker content making the networks very brittle (Figure 5-3 c).
5.2.3. TGA Analysis

A1/MMA and A1/HEMA/MMA networks were characterised using TGA (Figure 5-4) to ensure they were cured and that thermal degradation took place well above 150 °C, the temperature at which acetal exchange reactions take place.\textsuperscript{70,71,174,72–76,99–101} The TGA thermograms of A1/MMA and A1/HEMA/MMA networks showed no mass loss at T < 200 °C indicating no residual monomer was present. The onset of a sharp mass loss for A1/MMA networks was at 300 °C, well above the expected reprocessing temperature. The order of thermal stability was A1 2 mol % > A1 5 mol % > A1 10 mol %, which was unexpected as cross-linking typically increases thermal stability.\textsuperscript{261} This was thought to arise from the increase in ether and acetal groups at higher A1 mol %, which are less thermally stable than the carbon-carbon bonds in the poly(methacrylate backbone).\textsuperscript{83} The A1/HEMA/MMA networks had similar thermal stabilities.
5.2.4. Reprocessing by Vacuum Compression Moulding and Hot Press

To determine whether the acetal crosslinkers would enable reprocessing, samples of the A1/MMA (10 mol %) and A1/HEMA/MMA ([OH]:[acetal] = 1) networks were ground into a powder then reformed by vacuum compression moulding at elevated temperatures. The conditions chosen for this were based on those described for acetal CANs in the literature.\(^{70-76,99,100,174}\) Samples were heated at 150 °C under vacuum for 15 mins, 30 mins and 60 mins. After reprocessing, the samples were heterogeneous, and particles could be seen within the sample (Figure 5-5). Furthermore, the samples could be easily crumbled by hand and upon immersion in acetone they broke apart whereas a homogeneous network should swell under these conditions. Upon heating to 170 °C and leaving for 15, 30, 60 and 180 min. the same problem was observed. It was hypothesised that this was due to the relatively low pressure exerted on the sample during vacuum compression moulding compared to the hydraulic hot presses used in literature examples. This reduces the interfacial mixing between individual particles and dynamic groups.
Ground samples of A1/MMA (10 mol %) and A1/HEMA/MMA ([OH]:[acetal] = 1) were then compressed under 0.5 or 1 MPa of pressure within a PTFE lined aluminium mould at 150-180 °C for 30-180 min (Figure 5-6). Samples became increasingly discoloured with increased heating duration; this was attributed to oxidation of the network. However, heterogeneous samples were recovered suggesting that something was affecting the dynamic behaviour of the networks and preventing the formation of homogeneous panels. This may be due to the lower pressure used compared to the lap shear repressing that was performed at 1.5 MPa and potential thermal gradient that arose from using a mould.

5.2.5. Potential Issues with A1/MMA and A1/HEMA/MMA Networks

The difficulty in reprocessing the A1/MMA and A1/HEMA/MMA networks could have arisen from network effects, such as high $T_g$, changing the relaxation properties compared to networks described in the literature, side reactions altering the chemical composition of the networks and different synthetic protocols to the networks described in the literature. These will now be discussed.
One possible reason for the network’s reluctance to rearrange is the effect of the matrix on the topological freezing temperature, the lower temperature at which CANs may be reprocessed.\textsuperscript{262,263} It may be that the relatively high melting point of p(MMA), 160 °C\textsuperscript{177} is resulting in slow conformational rearrangement of the network.

A further reason the A1/MMA networks may not be forming the expected homogeneous networks is that previous reports of acetal metathesis polymerisation\textsuperscript{81,159,260,264,265} have shown that acetal metathesis requires an acid catalyst. Kinetic studies by Pemba and Miller\textsuperscript{81} into the transacetalisation reaction show that a protonated acetal acts as the electrophile, driving the transacetalisation reaction, producing products in a statistical mixture. However, conversely to this Zhu and co-workers\textsuperscript{70,101}, Chen \textit{et al.}\textsuperscript{7} and Shuangjian \textit{et al.}\textsuperscript{255} report acid catalyst free acetal metathesis in CANs.

Zhu and co-workers first reported the acid free reaction of 1,1,3,3-tetraethoxypropane and 1,1,3,3-tetra-methoxypropane at 150 °C for 8 hrs (Scheme 5-5).\textsuperscript{101} The reaction mixture was characterised by \textsuperscript{1}H NMR spectroscopy up to 8hrs during which time new peaks formed at 4.72, 4.85 and 4.99 ppm. These were assigned as the products acetal CH.proton but were not specifically assigned. Firstly, it is unclear why this proton would shift downfield when none of the products contain a more electron withdrawing group than any of the starting materials. Secondly, the \textsuperscript{1}H NMR spectra show these products are very much a minority product, whereas acetal metathesis should yield a statistical mixture of products.\textsuperscript{81,260,265} Lastly, if acetal metathesis was taking place then polymeric products would form as both starting materials are difunctional and capable of reacting with one another and themselves.\textsuperscript{81,83,260,265,266}

\[
\text{MeO} \quad \text{MeO} \quad \text{MeO} + \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \\
\text{MeO} \quad \text{MeO} \quad \text{MeO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \quad \text{EtO} \\
150 \degree \text{C} \quad \text{8h.} \\
\]

\text{Scheme 5-5 - Zhu \textit{et al.}'s model acetal metathesis reaction and \textsuperscript{1}H NMR chemical shifts.}\textsuperscript{101}
However, Zhu and co-workers also studied acid free acetal metathesis reactions between 1-(1-isobutoxyethoxy)-4-methylbenzene and (1-isobutoxyethoxy)benzene via GC-MS and the results showed a statistical mixture of products (Scheme 5-6). All but one product was correctly identified by mass spectroscopy.⁷⁰ Shuangjian et al. report the acid free metathesis of cyclic acetals but suggest that atmospheric water takes part in the reaction. They also highlight the effect acetal R groups have on their reactivity towards metathesis²⁵⁵. Chen et al. suggest that metathesis and transacetalisation occur simultaneously in acetal CANs with free hydroxyls⁷. Hydroxyl free CANs synthesised by all authors, however, do show dynamic behaviour, but are synthesised via step-growth polymerisation. Consequently unless high conversion is reached,¹⁶⁴ free hydroxyls will remain in the system and may take part in transacetalisation or act as proton sources for the metathesis reaction.
In the A1/HEMA/MMA networks, the elevated temperatures may be driving a transesterification reaction between HEMA and MMA or A1 (Scheme 5-7). The product of which is a network containing ester cross-links, which require elevated temperatures and catalysis to impart networks with adaptable properties.\textsuperscript{66,258,259} Thus the formation of ester cross-links prevents the networks from forming homogeneous samples.

The lack of adaptable behaviour in A1/MMA networks led to confusion on the origin of adaptable behaviour observed in A1/MMA lap shears. Rahman et al.\textsuperscript{259} showed that phenylboronic pinacol ester functionalised styrene and styrene copolymers will form pinacol ester bonds with silica nanoparticles and hydroxyl functionalised lap shear substrates such as steel and aluminium. It is hypothesised that A1/MMA adhesives may form acetal bonds with the aluminium substrate OH bonds during the repressing step via transacetalisation (Scheme 5-8).

![Scheme 5-8 - Transacetalisation between aluminium substrate and A1.](image-url)
5.3. Conclusions

Recent work has shown acetal containing thermosets are examples of covalently adaptable networks. A1/MMA and A1/MAA/MMA model adhesives exhibited adaptable behaviour, lap shear samples were hot pressed at 1.5 MPa and 150 °C for 15 minutes and found to retain 50-60 % of their original bond strength up to three times. A series of A1/HEMA/MMA and A1/MMA networks were synthesised and characterised via TGA to ensure they were stable at 150 °C, the reprocessing temperature found in the literature. The networks were thermally stable to ~300 °C.

Samples of the networks were ground, and reprocessing was attempted via vacuum compression moulding and hot pressing the samples in a mould. However, these samples did not form the expected homogeneous networks. Multiple potential causes were identified such as lower pressure than previously used, the effect of the p(MMA) components on the network, the disputed metathesis mechanism, and the potential for cross-linking via transesterification in the HEMA networks. However, due to time constraints these questions remain open.
5.4. Experimental

5.4.1. Materials
Iron (III) sulfate hydrate (97 %) and sulfuric acid (95-98 %) were purchased from Sigma-Aldrich. Aluminium strips 26.5x10x1.5 mm were provided by Scott Bader. BENOX-C50s (BPO, phthalates 50 wt %) was purchased from United Initiators. All other reagents are reported in previous chapters.

5.4.2. Instrumentation
Vacuum compression moulding was performed using a MeltPrep VCM with a 10x40 mm bar insert on ground samples (1 g). Hot press moulding was performed using an in-house press, ground samples (5-10 g) were placed into a PTFE lined aluminium mould (80x60 mm) and the press was pre-heated to a target temperature. The charged mould was heated for 15 minutes prior to applying pressure, after which pressure was applied. The mould was cooled prior to opening. Lap shear testing was performed on a Tinius Olsen H5K at a crosshead speed of 1 mm/min, a minimum of five repeats were performed.

5.4.3. Etching aluminium substrates
P2 preparation is described elsewhere. P2 etch solution was added to a vessel and heated to 60-68 °C. Aluminium substrates were degreased by rubbing with propan-2-ol and allowing to dry. Substrates ~5 cm were immersed in the stirred solution for 12 min. Samples were immersed in a deionsied water bath, then placed into a second deionised water bath for 5 mins. Substrates were then placed into an oven preheated to 40 °C for 20-30 mins and used within one hr of being removed from the P2 etch solution.
5.4.4. Synthesis of Lap Shears

The following stock solutions were prepared. Methyl methacrylate (82.8 g, 0.83 mol), A1 (1.8 g, 4.0 mmol) and benzoyl peroxide (25 % H$_2$O, 4.8 g, 15 mmol) were mixed. Methyl methacrylate (86.4 g, 0.86 mol) and 4,N,N-trimethylaniline (3.6 g, 26 mmol) were mixed. The two solutions were added to a 200 mL dual syringe equipped with a static mixer. Adhesives were made up as before and dispensed into a disposable cup, glass beads (212-300 micrometres) were added as spacers and applied to substrates held in a mould that gave a bond area of 25x12 mm. Samples were cured at ambient for 6 hrs before being placed in a preheated 100 °C oven overnight.

5.4.5. Synthesis of Panels

General procedure:

Monomers and BENOX C-50s were added (see Table 5-3 and Table 5-4) to a beaker and stirred until a homogeneous solution had formed. DMA was added and the mixture was stirred until it began to thicken. Solution was poured between to sealed glass plates set to 3 mm apart and left overnight. Glass plates were separated and resulting resin panel cured at 40 °C for 3 hrs then 100 °C for 24 hrs.
### Table 5-3 - A1/MMA network formulations.

<table>
<thead>
<tr>
<th>A1 mol %</th>
<th>A1 / g (mol)</th>
<th>MMA / g (mol)</th>
<th>BENOX C-50s / g (mmol of BPO)</th>
<th>DMA / g (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8.50 (0.018)</td>
<td>90.1 (0.89)</td>
<td>2.27 (9.4)</td>
<td>0.284 (2.4)</td>
</tr>
<tr>
<td>5</td>
<td>19.3 (0.042)</td>
<td>79.4 (0.79)</td>
<td>2.12 (8.8)</td>
<td>0.266 (2.2)</td>
</tr>
<tr>
<td>10</td>
<td>33.5 (0.072)</td>
<td>65.3 (0.65)</td>
<td>1.93 (8.0)</td>
<td>0.241 (2.0)</td>
</tr>
<tr>
<td>20</td>
<td>53.0 (0.12)</td>
<td>45.9 (0.46)</td>
<td>1.67 (6.9)</td>
<td>0.208 (1.7)</td>
</tr>
</tbody>
</table>

### Table 5-4 - A1/HEMA/MMA Network Formulations.

<table>
<thead>
<tr>
<th>[OH]:[acetal]</th>
<th>HEMA / g (mol)</th>
<th>A1 / g (mol)</th>
<th>MMA / g (mol)</th>
<th>BENOX c-50s / g (mmol of BPO)</th>
<th>DMA / g (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.2 (0.094)</td>
<td>43.4 (0.094)</td>
<td>43.8 (0.43)</td>
<td>0.871 (1.8)</td>
<td>0.109 (0.9)</td>
</tr>
<tr>
<td>0.5</td>
<td>5.70 (0.044)</td>
<td>40.5 (0.088)</td>
<td>52.6 (0.52)</td>
<td>1.80 (3.7)</td>
<td>0.226 (1.9)</td>
</tr>
<tr>
<td>0.25</td>
<td>2.67 (0.0205)</td>
<td>38.0 (0.082)</td>
<td>58.2 (0.58)</td>
<td>1.86 (3.8)</td>
<td>0.232 (1.9)</td>
</tr>
</tbody>
</table>
Chapter 6 - Concluding Remarks

Thermosets are a broad class of polymers with excellent thermal and mechanical properties used in a range of applications in industries. However, chemical cross-links create challenges for their recycling and reuse. Two potential solutions to this are chemically recyclable thermosets and covalently adaptable networks, the acetal functional group is suitable for both.

A novel dimethacrylate cross-linker bearing two acetal functional groups was synthesised from 2-hydroxyethyl methacrylate and tri(ethylene glycol)divinyl ether. The extent of acetal hydrolysis was found to increase with decreasing $pK_a$ in 0.15 M acetone-$d_6$/D$_2$O (9/1 v/v) solutions at 50 °C for 5 hrs. However, 100 % hydrolysis was observed only when using acids with a $pK_a < 1.29$. There is scope to create a library of diacetal cross-linkers by changing the divinyl ether and alcohol components for use in (meth)acrylate thermosets and more such as urethane-acrylates.

Model thermosets were synthesised from the acetal cross-linker and methyl methacrylate. Their degradation properties in acidic solvent/H$_2$O solutions at 50 °C for 5 hours were investigated and compared to the neat cross-linker. Homogeneous solutions formed indicating acetal group hydrolysis, however, lower $pK_a$ acids were required for full degradation within 5 hours than compared to the cross-linker. It was hypothesised that the mechanism of degradation was a complex mixture of chemical and physical processes that effect the kinetics.

Structural characterisation of hydrolysis experiments solutions showed the degradation products were p(methyl methacrylate-co-2-hydroxyethyl methacrylate) and the commodity chemicals tri(ethylene glycol) and acetaldehyde. There is scope for synthesis of chemically identical networks from p(methyl methacrylate-co-2-hydroxyethyl methacrylate) and tri(ethylene glycol)divinyl ether which is to be investigated in the future. Furthermore, recovery of tri(ethylene glycol) and acetaldehyde from the degradation solution may enable a synthetic route to tri(ethylene glycol)divinyl ether, heading towards a circular system. Lastly, the long-term stability of acetal containing thermosets will need to be to assessed in a variety of
environments to ensure their suitability for application and prevent unwanted release of degradation products to the environment.

The concept of internalising the acid source for hydrolysis was then researched using conventional acid generators such as 2-nitrobenzyl tosylate, the selection of which was guided by previous investigations of the effect of $pK_a$ on hydrolysis. However, attempts to incorporate acid generators as additives to the prepolymer solution were unsuccessful due to acid generators acting as inhibitors or having poor solubility. To circumnavigate this novel tosylates of 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate were synthesised. The homopolymers were characterised by the field favoured technique of thermogravimetric analysis, however, it was found that the unique structure of these tosylates meant this technique was unsuitable.

Variable temperature nuclear magnetic resonance spectroscopy was used to characterise the thermal elimination of the poly(tosylates) in the solution phase at various temperatures. The poly(tosylates) generated pTsOH however, the expected poly(viny methacrylate) product was not observed, this was attributed to further reactions such as ester pyrolysis and Kornblum oxidation. It was also found that elimination of para-toluene sulfonic acid occurred at <100 °C for both poly(tosylates) meaning they were unsuitable for use in model acetal thermosets. Furthermore, elimination in the solid state formed insoluble residues via hypothesised cross-linking reactions, rendering the tosylates unsuitable for their desired applications. Further work is required to determine the nature of the cross-linking reactions by synthesising model tosylates and investigating alternative acid chemistries such as oxime sulfonates.

Finally preliminary research into the use of the novel dimethacrylate cross-linker in covalently adaptable networks was undertaken, acetal/HEMA/MMA and acetal/MMA networks were synthesised to investigate the acetal metathesis and transacetalisation pathways. Thermogravimetric analysis revealed acetal/HEMA/MMA and acetal/MMA networks were thermally stable to ~300 °C.
Acetal/MMA and acetal/MAA/MMA model adhesives exhibited adaptable behaviour, lap shear samples were hot pressed at 1.5 MPa and 150 °C for 15 minutes and were found to retain 50-60 % of their original bond strength up to three times. However, ground samples of the networks didn’t show any reprocessable behaviour under vacuum compression moulding or in a hot press, the causes of which should be the focus of future work.
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(86) Di(ethylene glycol) divinyl ether 99 764-99-8

(87) Poly(ethylene glycol) divinyl ether average Mn 250 50856-26-3

(88) Tri(ethylene glycol) divinyl ether 98 765-12-8


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Figure 8-1 - Mass spectra of A1 hydrolysis products separated via liquid chromatography.

Table 8-1 - Reaction products determined via HPLC-MS when synthesising A1 with 0.5 mol % pTsOH.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Retention time (min)</th>
<th>m/z / Experimental (theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Molecule 1" /></td>
<td>4.2</td>
<td>[M+Na]⁺ 153.1 ([M+Na]⁺ 153.8)</td>
</tr>
<tr>
<td><img src="image2" alt="Molecule 2" /></td>
<td>4.8</td>
<td>[M+Na]⁺ 349.2 ([M+Na]⁺ 153.8)</td>
</tr>
<tr>
<td><img src="image3" alt="Molecule 3" /></td>
<td>5.5</td>
<td>[M+Na]⁺ 525.3 ([M+Na]⁺ 153.8)</td>
</tr>
<tr>
<td><img src="image4" alt="Molecule 4" /></td>
<td>5.8</td>
<td>[M+Na]⁺ 375.2 ([M+Na]⁺ 153.8)</td>
</tr>
<tr>
<td><img src="image5" alt="Molecule 5" /></td>
<td>6.2</td>
<td>[M+Na]⁺ 329.2 ([M+Na]⁺ 153.8)</td>
</tr>
<tr>
<td><img src="image6" alt="Molecule 6" /></td>
<td>6.8</td>
<td>[M+Na]⁺ 505.3 ([M+Na]⁺ 153.8)</td>
</tr>
<tr>
<td>Molar Mass Distribution</td>
<td>7.1</td>
<td>7.4</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>[M+Na]^+</td>
<td>681.4</td>
<td>857.5</td>
</tr>
<tr>
<td>([M+Na]^+ + 153.8)</td>
<td>153.8</td>
<td>153.8</td>
</tr>
<tr>
<td>Mixture of dimethacrylate cross-linkers</td>
<td>10.2</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 8-2** - Molar mass distributions for poly(acetal) products synthesised from TEGDVE at different pTsOH loadings.
Figure 8-3 - Molar mass distributions for poly(acetal) products synthesised from TEGDVE and TEG at different pTsOH loadings.

Figure 8-4 - DSC of p(MMA-co-A1) cured at 100 °C for 48 hours.
Figure 8-5 - \(^1\)H NMR spectra (acetone-d\(_6\)/D\(_2\)O) of p(MMA-co-A1) degradation supernatant.

Figure 8-6 - \(^1\)H NMR (CDCl\(_3\)) spectrum of ortho-nitrobenzyl tosylate.
Figure 8-7 - 1H NMR (DMSO-d6) spectrum of N-hydroxy-1,8-napthalimide.

Figure 8-8 - IR spectrum of N-hydroxy-1,8-napthalimide.
Figure 8-9 - $^1$H NMR (CDCl$_3$) spectrum of NHTN.

Figure 8-10 - IR spectrum of NHTN.
Figure 8-11 - $^1$H NMR (CDCl$_3$) spectrum of HEMAtos.

Figure 8-12 - IR spectrum of HEMAtos.
Figure 8-13 - $^1$H NMR (CDCl$_3$) spectrum of HPMAtos isomers.

Figure 8-14 - IR spectrum of HPMAtos.
Figure 8-15 - $^1$H NMR (CDCl$_3$) spectrum of HPMA, showing the vinyl peaks at 6.13 ppm and 6.11 ppm used to determine the ratio of the regioisomers.

Figure 8-16 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 3 hrs, using NEt$_3$ as the base and the following reagent ratios [OH$^-$][pTsCl][Base] – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.
Figure 8.17 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 3 hrs, using NEt$_3$ as the base and the following reagent ratios [OH]:[pTsCl]:[Base] = 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.

Figure 8.18 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 27 hrs, using NEt$_3$ as the base and the following reagent ratios [OH]:[pTsCl]:[Base] = 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.
Figure 8-19 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 72 hrs, using NEt$_3$ as the base and the following reagent ratios [OH]:[pTsCl]:[Base] – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.

Figure 8-20 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 3 hrs, using pyridine as the base and the following reagent ratios [OH]:[pTsCl]:[Base] – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.
Figure 8-21 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 23 hrs, using pyridine as the base and the following reagent ratios [OH]::[pTsCl]::[Base] – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regiosomers.

Figure 8-22 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 27 hrs, using pyridine as the base and the following reagent ratios [OH]::[pTsCl]::[Base] – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regiosomers.
Figure 8-23 - $^1\text{H}$ NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 72 hrs, using pyridine as the base and the following reagent ratios $[\text{OH}]:[\text{pTsCl}]:[\text{Base}]$ – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.

Figure 8-24 - $^1\text{H}$ NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 3 hrs, using pyridine as the base with DMAP as a catalyst, and the following reagent ratios $[\text{OH}]:[\text{pTsCl}]:[\text{Base}]$ – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.
Figure 8.25 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 27 hrs, using pyridine as the base with DMAP as a catalyst, and the following reagent ratios [OH]:[pTsCl]:[Base] – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.

Figure 8.26 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 27 hrs, using pyridine as the base with DMAP as a catalyst, and the following reagent ratios [OH]:[pTsCl]:[Base] – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.
Figure 8.27 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 72 hrs, using pyridine as the base with DMAP as a catalyst, and the following reagent ratios [OH]:[pTsCl]:[Base] – 1:1.5:1.5. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.

Figure 8.28 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 3 hrs, using pyridine as the base and the following reagent ratios [OH]:[pTsCl]:[Base] – 1:2:3. Highlighted vinylic protons were used to monitor the conversion of different HPMA regioisomers.
Figure 8.29 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 23 hrs, using pyridine as the base and the following reagent ratios [OH]:[pTsCl]:[Base] – 1:2:3. Highlighted vinylic protons were used to monitor the conversion of different regioisomers.

Figure 8.30 - $^1$H NMR (CDCl$_3$) spectrum of HPMA tosylation reaction mixture after 27 hrs, using pyridine as the base and the following reagent ratios [OH]:[pTsCl]:[Base] – 1:2:3. Highlighted vinylic protons were used to monitor the conversion of different regioisomers.
Figure 8-31 - SEC chromatograms for p(HPMA-tos) and p(HEMA-tos)

Figure 8-32 - p(HEMA-tos) DSC pan extract HPLC-MS chromatogram and spectrum.
Figure 8-33 - p(HPMAtos) DSC pan extract HPLC-MS chromatogram and spectrum.

Figure 8-34 - IR spectra of p(HEMAtos) before and after heating.
Figure 8-35 - IR spectra of p(HPMAtos) before and after heating.

Figure 8-36 - HPLC chromatogram (top) and mass spectrum of 10 wt % HPMAtos/A1/MMA network extract before heating.
Figure 8-37 - HPLC chromatogram (top) and mass spectrum of 10 wt % HPMAtos/A1/MMA network extract before heating.

Figure 8-38 - First order kinetic plot of p(HPMAtos) isothermal TGA.