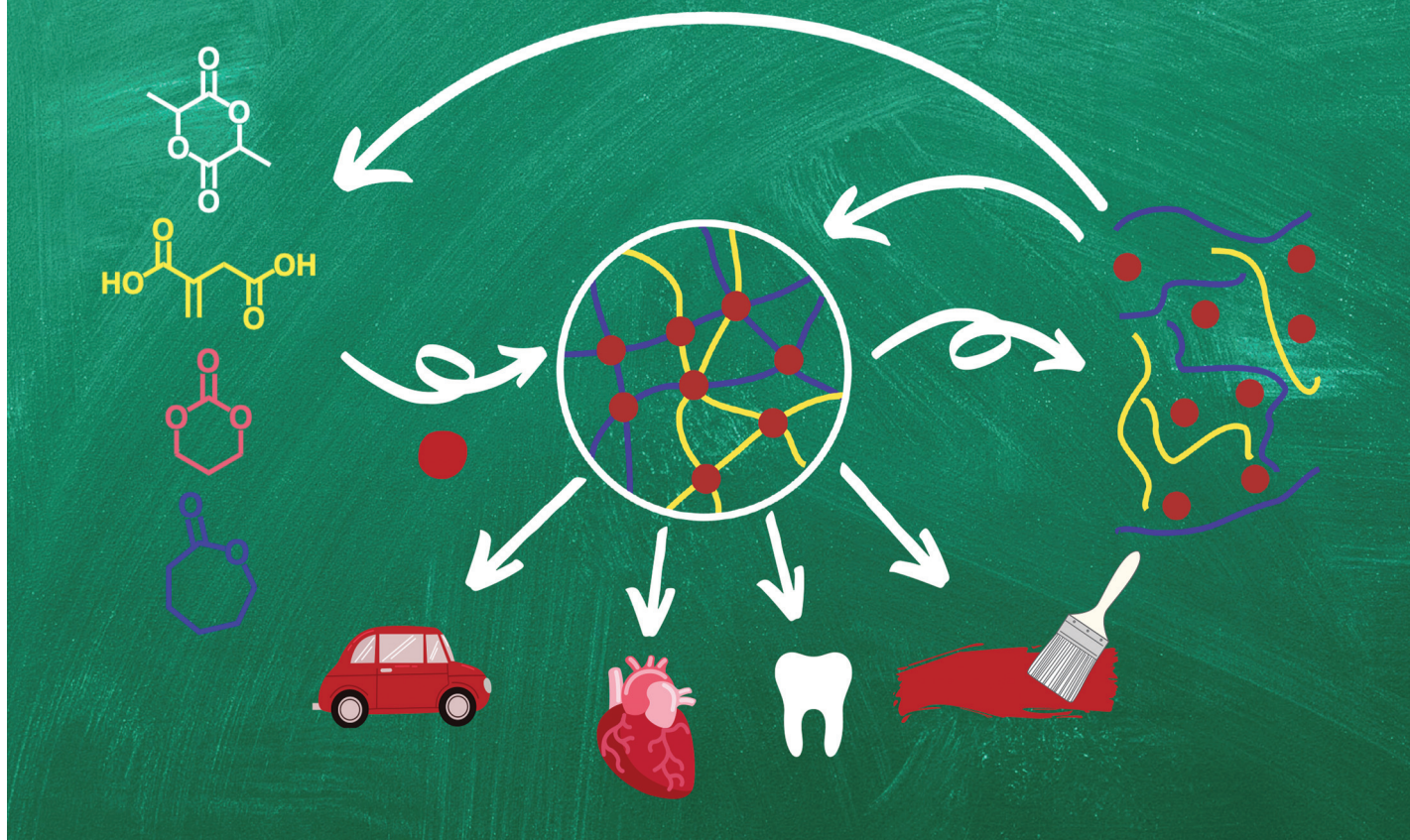


RESINS TO BE CHEERFUL



Highlighting a review from Professor Mike Shaver's team in the Sustainable Materials Innovation Hub at the Henry Royce Institute, University of Manchester, UK.

Inherently degradable cross-linked polyesters and polycarbonates: resins to be cheerful

This review captures the most recent advances in the synthesis and characterisation of degradable thermosetting polyester and polycarbonates, including partially degradable systems derived from itaconic acid and isosorbide, and highlights the potential importance of (bio)degradation at end-of-life for these challenging materials.

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Inherently degradable cross-linked polyesters and polycarbonates: resins to be cheerful

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Thermosets are an important class of materials that provide excellent temperature and solvent resistance; however, their high dimensional stability precludes degradation or reprocessing. While traditional thermoplastics can be mechanically and chemically recycled, these pathways are often elusive for resins due to their intrinsic structure. The renewed demand for sustainable polymers from public, industry and government stakeholders has increased research into (bio)degradable thermoplastics, but thermosets have often been overlooked. Aliphatic polyesters and polycarbonates are the cornerstone of biodegradable polymers, yet offer an arguably greater potential in thermosets as end-of-life options are more limited for these materials. This review summarises the most recent advances in the synthesis and characterisation of degradable thermosetting polyester and polycarbonate materials, including partially degradable systems derived from renewable resources such as itaconic acid or isosorbide. The review is organised by synthetic methodology including one-pot reactions and multi-step approaches making use of pre-polymers. Photo-cross-linking and high-energy irradiation are also discussed as emerging synthetic strategies.

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1. Introduction

The global demand for thermoplastics and thermosets continue to grow; production reached 359 million tonnes 2018.¹ The low cost and versatility of these materials, arising from their light weight, intrinsic durability, ease of synthesis and resistance to degradation, drives market growth. These factors have created an inherent societal dependence on “plastics”, a term public and government stakeholders have used to classify both types of polymeric materials. The manufacture and use of most modern plastics rely on petroleum feedstocks, a non-renewable resource with politically-charged market dynamics, while their resilience and the lack of recycling infrastructure results in the generation of unprecedented amounts of waste, much of which is poorly managed.

For thermoplastics, significant research on biodegradable polymers, such as poly(lactic acid), have promised superior environmental performance through both source, as they are derived from biological feedstocks, and end-of-life, through degradation or depolymerisation.^{2,3} Just as with mechanical recycling, however, this process requires careful control. Exposure to heat, light, ultrasound, microorganisms or certain chemicals such as acids or bases can all trigger degradation, alter chemical composition and progressively decrease the

molecular weight of polymer chains.^{4,5} The inherently complex process and slow degradation in the environment of release means that for “green” credentials to be realised this is best done in a managed process.⁶ However, if degradation is enabled in the environment of release, ecotoxicological impacts of both plastics and their degradation products are understood, and application underpinned by life cycle assessment, these can be exceptionally sustainable materials. Comparison to traditional mechanical and emerging chemical recycling pathways for thermoplastics remain a challenge.

Thermosets, however, cannot be mechanically recycled. The high dimensional structure of thermosets precludes reprocessing. Degradation – biological or otherwise – thus represents potentially sustainable end-of-life pathway for these resins. As such, this review explores the recent developments in the design, development and understanding of degradable cross-linked polyester and polycarbonate resins as an essential part of a sustainable plastics future.

2. Polyesters and polycarbonates

Some of the most prevalent thermoplastics are polyesters and polycarbonates. Poly(ethylene terephthalate), PET, and bisphenol-A bridged polycarbonates, PC (Fig. 1a) are two such oxygen-containing polymers, with applications spanning packaging to rigid plastic to engineering materials. The rigid aromatic functionalities in the polymer backbone can impart superior physical and chemical properties such as high glass

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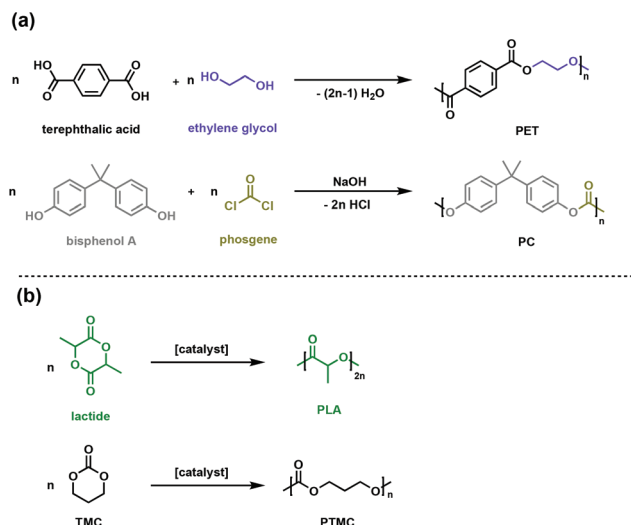


Fig. 1 Synthesis routes for (a) conventional polyesters (PET) and polycarbonates (PC) (b) aliphatic biodegradable polyesters (PLA) and polycarbonates (PTMC).

transition temperature (T_g) and gas impermeability. Environmental degradation of these commodity plastics is not facile, necessitating managed mechanical or chemical recycling infrastructure for which there is inconsistent global access.^{7–9}

One of the goals of contemporary polymer research is to develop alternative polymers that are durable and fit-for-purpose, yet more easily degraded in the environment of release. In pursuit of such materials, the synthesis of biodegradable polyesters and polycarbonates, particularly when generated from renewable resources, has garnered significant attention. Monomeric precursors to polyesters and polycarbonates can be sourced from biomass or waste gas through a variety of biological or chemical transformations.^{10–12} A variety of polymerisation methods are now available to synthesise polymers with an array of backbone topologies and side-chain functionalities. Compared to petroleum-derived polyesters and polycarbonates, for which degradation kinetics are exceedingly slow, the ester and carbonate linkages in the novel polymer backbones can be enzymatically or chemically degraded, offering new options for the life cycle of these materials.^{10,13,14} Poly(lactic acid) (PLA) is the most commercially viable sustainable polyester and is produced through the ring opening polymerisation of renewable lactide (Fig. 1b).¹⁵ PLA has suitable mechanical and physical properties as a sustainable substitute for packaging and textiles, while its ability to be absorbed and degraded *in vivo* enables numerous biomedical applications.^{15–17}

Polycarbonates typically have the high impact strength and excellent mechanical properties needed for challenging engineering applications like airplane windows and safety glass. The



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conventional synthesis of polycarbonates involves the use of toxic and energy-intensive phosgene (Fig. 1a).^{18,19} New synthetic strategies use dialkyl carbonates, which are easily synthesised through a dehydrative condensation of alcohols and CO₂.^{19,20} While useful industrially, the energy cost and lack of control have given rise to the ROP of cyclic carbonates (such as trimethylene carbonate, TMC, Fig. 1b) as an attractive method to achieve well-defined polycarbonates with high molar masses.²¹

Due to their synthetic versatility and diverse properties, aliphatic polyesters and polycarbonates have been some of the most widely studied compounds of rather great potential as degradable thermoplastics. The decomposition of labile linkages could enable recovery of the starting materials or formation of different smaller molecules that could be readily metabolised or environmentally processed. Degradation of these compounds can be either hydrolytic or enzymatic. While both ester and carbonate groups are susceptible to hydrolysis, polyesters usually undergo bulk degradation whereas surface erosion predominates for polycarbonates.²² The short chains between ester or carbonate moieties enable faster degradation profiles for these polymers, although they are rarely completely assimilated into the environment. Enzymatic degradation is a viable alternative to hydrolysis, but it is usually less effective in highly crystalline systems. While promising, there remain concerns with synthetic degradable thermoplastics. As degradation profiles depend upon reaction conditions, biodegradable materials are often incorrectly disposed, rejected from composting facilities and landfilled or worse littered. This suggests that, for thermoplastics, a balance between environmental pollution, fossil-fuel depletion, plastic leaching and cost are needed to ensure sustainability.

The permanent molecular architecture of thermosets precludes reprocessing and mechanical recycling. The lack of traditional waste management, coupled with the higher value potential applications, suggest that degradable materials could more readily offer a sustainable pathway at end-of-life. There is thus an urgent need to extend these linear frameworks and synthetic strategies to degradable cross-linked polymers, enabling new applications (*vide infra*).

3. Cross-linked polymers

Conventional linear polymers become malleable and flow at their T_g and when the temperature is reduced, they retain their new form and are therefore known as *thermoplastics* (Fig. 2a). In contrast, cross-linking polymers set their form during synthesis, as the bonds that form between the individual chains cannot be re-moulded. These are referred to as *thermosets* (Fig. 2b); the term *plastic* now traditionally encompasses both *thermoplastics* and *thermosets*.

Thermosets can be created in one of two ways: in a one-pot reaction, through the copolymerisation of monomers with cross-linker or through the addition or presence of cross-links to a thermoplastic (Fig. 2), as is demonstrated in the curing of



Fig. 2 (a) Schematic representation of polymers (b) schematic of cross-linked polymer architecture.

natural rubbers.²³ The thermoset industry continued to grow, with cross-linked polymers now constituting 15–20% of all polymers produced.²⁴ Their high dimensional stability, along with high thermal, mechanical and environmental resistance have found application as insulators, adhesives, coatings, foams and automotive parts.²⁵ This stability is a challenge at end of life, as functions such as shape reconfiguration, self-healing and recycling are elusive for traditional cross-linked polymers.²⁶

Why pursue research at the interface between these well-developed fields? Aliphatic polyesters and polycarbonates have excellent mechanical and thermal properties for linear polymers, and offer a unique advantage of hydrolytic or enzymatic degradation at end-of-life. Their poor solvent resistance, low thermal stability and significant stress softening mean that some applications are often impossible.²⁷ Cross-linking these degradable systems could impart additional dimensional stability to the polymers, enhancing tensile and impact strength,²⁸ producing materials with improved elasticity and shape retention with reduced creep.²⁹ Research in this area lags behind other cross-linked systems like epoxy resins and polyurethanes, which are explicitly outside the scope of this review. This review will thus provide a detailed summary of the recent developments in the synthesis and characterisation of degradable cross-linked polyesters and polycarbonates from fundamental challenges to potential applications. Components are identified by monomer ($M\#$), cross-linking agent ($C\#$) and polymer ($P\#$), recognising that a single monomer and cross-linker may produce several polymeric structures, sometimes in sequence.

3.1. One-step methodologies to degradable cross-linked polymers

Cross-linked polyesters have been extensively studied by Hillmyer and coworkers, who employed different types of bifunctional cross-linking agents in tandem copolymerisation and cross-linking processes.³⁰ One-step methodologies eliminate processing steps and allow for the direct conversion of





Fig. 3 Synthesis of cross-linked **P1** using cross-linker **C1**.³⁰

monomers to cross-linked polymers. A bis(cyclic carbonate) (**C1**, Fig. 3) was used to synthesise cross-linked elastomers prepared from poly(β -methyl- δ -valerolactone) (**P1**), using a triaza-bicyclodecene (TBD) catalyst. The monomer, β -methyl- δ -valerolactone, (**M1**) and cross-linker were predicted to have similar reactivity, which would improve the cross-linking efficiency. Because of **C1**'s solubility in **M1**, the reaction was performed in bulk. As the reaction proceeded, the mixtures formed gels, whose thermal properties were investigated. Issues arose with monomer equilibrium concentration, so residual **M1** had to be extracted before the samples were subjected to any tests. **C1** incorporation did not affect the thermal properties of the new cross-linked materials, the T_g for all resins being between -47 and -49 °C, comparable with the value of -52 °C measured for linear **P1**. Remarkably, at low cross-linking densities, the materials exhibited higher tensile strength and elongation, along with substantial strain hardening compared to conventional elastomers such as vulcanised natural rubber. When increasing the cross-linking density, the materials showed similar extension properties to common elastomers, followed by a decrease in tensile strength. Moreover, higher plateau moduli along with better hysteresis recovery were observed at higher cross-linker loading. There was, however, no clear correlation between the cross-linking content and ultimate tensile strength. The synthesised elastomers were shown to be chemically recyclable, with 91% recovery of the pure **M1** monomer. The materials were resilient to degradation under physiologically relevant conditions, whereas an acidic environment (HCl, 1 M) promoted network degradation at elevated temperatures (60 °C). Basic conditions (NaOH, 1 M), perhaps counterintuitively, did not prove to be optimal for degradation, suggesting that the carbonate moieties imparted by the cross-linker contributed additional chemical resistance in the cross-linked polymer. However, the recyclability and degradation under specific acidic conditions, along with the superior mechanical properties suggest promise for the sustainability and viability of these materials as rubber replacements.

In related work, Yang *et al.* investigated the *in vivo* enzymatic degradation of poly(ϵ -caprolactone) (**P2**) networks prepared by cross-linking with the aforementioned **C1**, as described in Fig. 3.³¹ The enzymatic degradation was performed using *Thermomyces lanuginosus* lipase. Cross-linking

allowed for increased form-stability and decreased crystallinity compared to the homopolymer, while affording a decreased rate of degradation. Previous studies have shown that the degradation rate of cross-linked polyesters such as **P2** and poly(*D,L*-lactide-*co*- ϵ -caprolactone) (**P3**) is reduced compared to the homopolymers, due to a decrease in the water molecule penetration into the networks.³² This can be exploited when targeting cross-linked **P2** implants as controlled drug release agents, since the amount of acidic degradation products is reduced.³¹ The same group reported the synthesis of poly(trimethylene carbonate) (**P4**) networks through a one-step methodology involving the ring-opening copolymerization of **C1** with trimethylene carbonate (**M2**) and/or ϵ -caprolactone (**M3**) using tin(II) 2-ethylhexanoate, Sn(Oct)₂, as catalyst, as shown in Fig. 4. The networks were touted as biodegradable, but no study was reported in this paper to confirm this property.³³

An important class of cross-linkers are bis(ϵ -caprolactone)s, with two such comonomers studied in detail for the synthesis of degradable cross-linked polymers. Originally patented by Starcher and coworkers in 1963,³⁴ Pitt, Palmgren and coworkers have further investigated bis(ϵ -caprolactone-4-yl) (**C2**) and a related molecule, 2,2-bis(ϵ -caprolactone-4-yl)propane (**C3**) as cross-linking agents for the synthesis of elastomers.^{35,36} These molecules allow for *in situ* cross-linking, thus eliminating prepolymer synthesis. Cross-linked aliphatic polyesters obtained through the Sn(Oct)₂ catalysed ROP of 1,5-dioxepan-2-one (**M4**) in the presence of tetrafunctional **C2** and **C3** (Fig. 5) were investigated.³⁶ Efficient cross-linking was highly dependent on the reactivity ratios of the comonomers,



Fig. 4 Synthesis of cross-linked **P4** networks.³³



Fig. 5 Synthesis of cross-linked **P5** polymers using **C2** cross-linkers.³⁶



with **C2** being more reactive than **C3** towards **M4**. Monomer solubility was problematic, leading to high concentrations of cross-linkers (8–28 mol%) being required, thus restricting the ability to fully control the mechanical properties.^{36,37} The incorporation of **C2** and **C3** in the growing polymer chain resulted in the formation of multifunctional cross-links, allowing the synthesis of strong elastomeric polymers (Fig. 5). The T_g of the cross-linked poly(1,5-dioxepan-2-one) (**P5**) increased compared to its homopolymer. This is anticipated, since cross-linking reduces the available free volume and the chain requires more energy input to become mobile, shifting the T_g to higher values. **C3** exhibits a more flexible structure compared to **C2**, hence imparting a longer physical cross-link and increasing the relative amount of free volume available. Therefore, the **C3** cross-linked **P5** demonstrated a lower T_g than the **C2** cross-linked analogue. These properties demonstrated clear potential for applications where degradable elastomeric biomaterials are desirable, although environmental degradation remains unexplored.

The “design to degrade” approach may tackle resin accumulation in the environment, but the functionality in the cross-links can also facilitate direct reprocessing or mechanical recycling. The incorporation of dynamic bonds in the polymer network can undergo associative exchange reactions such as vulcanisation, olefin metathesis, urethane exchange, siloxane exchange or boronic acid exchange.^{38–42} The most promising, and relevant, chemistry to promote recyclability is the transesterification of esters in the presence of free alcohols, typically catalysed by organocatalysts or Lewis acids.⁴³ It has been postulated that Brønsted acids, known to catalyse the transesterification in small molecules, could also be utilised as catalysts in dynamic covalent bond exchange. These reprocessable networks are often called vitrimers, and can additionally promote reformability and self-healing. Bates and coworkers developed a one-pot synthesis of polyester vitrimers using **C2**, that enables *in situ* cross-linking (Fig. 6).⁴⁴ This approach does not

rely on post-polymerisation reactions and the networks are exclusively formed of ester linkages, preventing competitive exchange reactions in the cross-links, such as urethanes.⁴⁵ While typical thermally-activated transesterification reactions catalysed by Lewis acids occur at temperatures higher than 100 °C, Brønsted acids promote facile exchange at temperatures as low as 25 °C. The comonomer, γ -methyl- ϵ -caprolactone (**M5**), gives rise to an amorphous polymer with a very low T_g of –55 °C. This allows dynamic mechanical thermal analysis (DMTA) study of the cross-linked polymer to be performed above the topology freezing transition temperature (T_v) and T_g at room temperature. A variety of Brønsted acid catalysts with pK_a values ranging from –12 to 0.81 were embedded in the polyester vitrimers. A higher pK_a allowed for faster stress relaxation times and lower activation energies. Overall, this quantitative study on the associated kinetics and thermodynamics of the system should prove foundational for novel acid-catalysed vitrimer systems.⁴⁴

Pennings and coworkers reported the cross-linking of lactones such as **M2**, **M3** and L-lactide (**M6**) using a tetrafunctional spiro-bis-dimethylene-carbonate (**C4**) (Fig. 7).³⁷ **C4** was prepared from diethylene carbonate and pentaerythritol.⁴⁶ Copolymerisations were carried out in bulk at 110 °C, employing $\text{Sn}(\text{Oct})_2$ as a catalyst to obtain a novel class of cross-linked materials, ranging from rubbery to strong and tough semi-crystalline networks.³⁷ Molecular architecture, degree of cross-linking and chain branching impact chain mobility and possible conformations. An increase in cross-link density reduces the available free volume and chain mobility is hindered. Consequently, crystallisation was impeded in **P6**, as the cross-linked materials showed a large melting point depression, from 192 to 177 °C. A significant reduction in heat of fusion was also observed with increasing cross-linking density. With increasing chain interconnectivity, tensile strength of **P6** networks was measured at 65–70 MPa depending on the **C4** concentration, versus 60 MPa for the homopolymer. The same trend was observed for impact strength values. The changes in the melting point and heat of fusion resulting from cross-

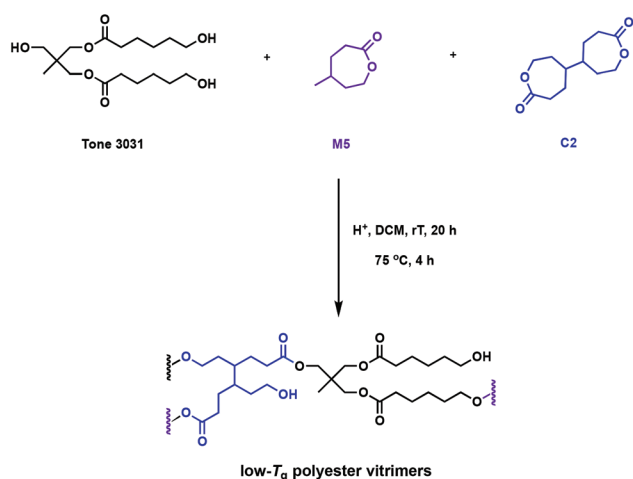


Fig. 6 Synthesis of polyester vitrimers from **M5** using cross-linking agent **C2**.⁴⁴



Fig. 7 Synthesis of cross-linked **P2**, **P4** and **P6** employing **C4** as a cross-linking agent.³⁷



linking with **C4** were not as significant when **M2** and **M3** were used, implying a heavy dependence on the chosen comonomer. Furthermore, because **C4** and **M3** exhibit a significant difference in reactivity, cross-linking was found to be inefficient. Copolymerisation of **C4** with **M2** led to tougher and stronger cross-linked polycarbonate networks compared to the homopolymer counterparts, thus reinforcing the need for a reactivity match between the monomers. Their degradation products were found to be non-toxic and therefore showed promise for biomedical applications. The cross-linked materials, however, did not lose mass within 20 weeks, and 88% of the initial mass was still present after 47 weeks. The resultant degradation times are thus too long for biomedical applications, causing similar *in vivo* issues as **P6**,⁴⁷ although this may open up other applications outside the biomedical realm where robustness is an asset.



Fig. 8 Synthesis of cross-linked **P6** using **C5** as a cross-linker.⁴⁸

3.2. Multi-step approaches to cross-linked polymers

An alternative approach to synthesise cross-linked polymers is through a multi-step approach with a prepolymer that further reacts with a multifunctional cross-linker. This methodology allows fine-tuning of the prepolymer in order for specific properties to be imparted to the final material, but it is in general more time-consuming. Dove and coworkers explored an alternative way to make **P6** networks by employing a flexible, bicyclic lactide derivative (**C5**) as a cross-linking agent.⁴⁸ **C5** was synthesised through a thiol-ene reaction (*i.e.* radical addition of the thiol across the alkene moiety) between an allyl-functionalised **M6** and 1,6-hexanedithiol. In the presence of 1,1,3,3-tetramethylguanidine (TMG), linear or branched **P6** prepolymers were cross-linked with the bifunctional lactide derivative **C5** (Fig. 8). Notably, the networks displayed low T_g values of only 30 °C, contradicting expectations that reduced mobility would lead to a higher T_g upon cross-linking.⁴⁸ This observation was attributed to the long aliphatic chain in **C5**, which imparts greater mobility than classic shorter linkers such as disulfide, thus reducing T_g compared to the original **P6** oligomers.^{48–50} Compared to **P6**, the thermosets showed reduced tensile strength (1.4 to 3.9 MPa vs. 59 MPa) and Young's moduli (13 to 34 MPa vs. 3500 MPa) due to the amorphous nature of the cross-linked network. Notably, the materials' elongation at break values were found to be between 26 and 268%, higher than the 7% for **P6**. The networks were thus applicable where highly ductile **P6** networks are desired, such as fibres, a remarkable accomplishment for a notoriously brittle homopolymer.

Amsden and collaborators employed **C2** and **C3** in a two-step strategy to synthesise polymer networks using 3-arm **P3** (Fig. 9).⁵¹ The **P3** star polymers were previously reported to have lower melt viscosities compared to their linear counterparts. Injection moulding at lower temperatures is thus more facile, requiring less energy and aiding processing.⁵² The desired applications for these systems were drug delivery and tissue engineering. The target elastomers consequently required a $T_g < 37$ °C in order to be rubbery, a property commonly associated with amorphous polymers. Therefore, a copolymer between **M3** ($T_g = -60$ °C) and D,L-lactide, **M7**, ($T_g =$



Fig. 9 Synthesis of cross-linked elastomers employing **C2** and **C3** as cross-linkers.⁵¹



68 °C) was prepared through ROP using glycerol as an initiator and $\text{Sn}(\text{Oct})_2$ as a catalyst.^{51,53} As the crystalline regions in the cross-linked polymer would likely increase both the network degradation time and the rate of bioabsorption,³⁵ crystallinity was not a highly desired property for this study.^{45,46} Installing a C3 cross-link reduces the P3 crystallisable sequences, therefore allowing the cross-linked polymer to be enzymatically degraded. Release began within two weeks and approached 80% completion in 100 weeks, making biodegradation of the cross-linked polymer more efficient than for the linear crystalline homopolymer that undergoes long induction periods prior to mass loss.^{51,54,55}

The C2 and C3 cross-linked polymers synthesised by both Amsden *et al.* and Pitt *et al.* displayed either a low degree of crystallinity or were amorphous.^{35,56} Different ratios of C3 and prepolymers were used to synthesise four elastomers with different mechanical properties. With physical properties such as Young's modulus (0.55–1.55 MPa), ultimate stress (0.21–0.60 MPa) and ultimate strain (65–154%) of the same order as elastin,⁵⁷ this family of elastomers has been suggested as potential tissue engineering scaffolds for soft tissues. The cross-linking efficiency improved with increasing C3 content, forming a tough elastomer, whereas a low cross-linking density promoted faster degradation. *In vitro* degradation studies were performed in phosphate buffer solutions at pH = 7.4, and showed that no sample had degraded completely after 12 weeks. However, as the ultimate tensile stress showed a logarithmic decrease it was suggested that the degradation kinetics are first order.

Hillmyer and coworkers also used a bifunctional bis(β -lactone), C6, in their complementary studies.⁵⁸ C6 was synthesised through carbonylation of the diepoxide derived from 1,5-hexadiene. The lactone comonomer, M5, as well as the C6, can potentially be obtained from renewable feedstocks, hence addressing the circular economy goals.^{58,59} The polyester elastomers were prepared in two steps: first, a star-shaped poly(γ -methyl- ϵ -caprolactone) (P7) was prepared through ROP catalysed by $\text{Sn}(\text{Oct})_2$ in the presence of pentaerythritol initiator, followed by cross-linking with C6 using the same tin catalyst (Fig. 10). Even though $\text{Sn}(\text{Oct})_2$ is not reported as a particularly active catalyst for the ROP of butyrolactones,^{60,61} it generated β -hydroxyesters at the junctions between star-shaped P7, opening the β -lactone through the hydroxy end groups. Reminiscent of the above-mentioned elastomers, the properties of this cross-linked elastomer were competitive with a commercial rubber band. Degradation was tested under environmentally-relevant conditions, with full hydrolysis of the samples observed across a range of temperatures.

Snyder *et al.* designed and prepared polycarbonate vitrimers using an inexpensive Ti(IV) catalyst.⁶² In the same way that transesterification can be exploited with polyesters, carbonates undergo transcarbonation. Consequently, polycarbonate vitrimers could potentially develop into a sustainable class of degradable, reprocessable cross-linked polymers. In order for the networks to undergo transcarbonation, both carbonates and primary hydroxyl groups have to be incorporated in the



Fig. 10 Synthesis of polyester networks using a bifunctional linker, C6.⁵⁸

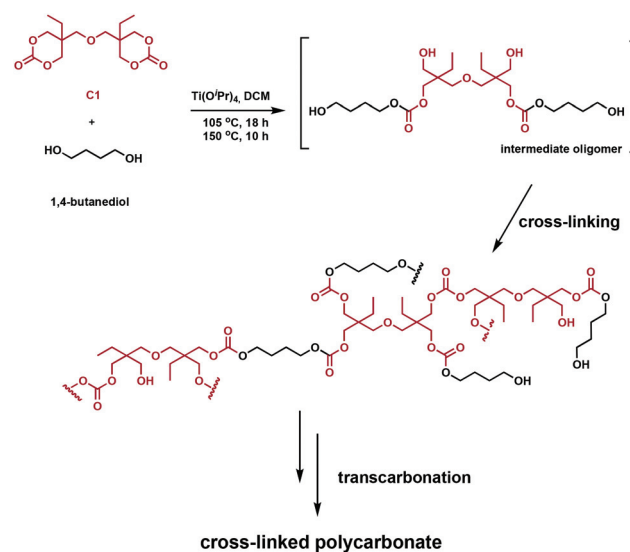


Fig. 11 Synthesis of a cross-linked polycarbonate network from C1 and 1,4-butanediol.⁶²

polymer, achieved in one step using C1 and 1,4-butanediol in the presence of titanium(IV) isopropoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$) (Fig. 11). The starting materials solution cast into molds; solvent evaporation afforded transparent colourless networks. The stress relaxation rates were similar to polyester vitrimers, whereas the activation energy of stress relaxation was found to vary as a function of cross-linking density. These networks were ground and reprocessed at various temperatures and pressures (140–160 °C, 5–10 MPa). Higher reprocessing temperatures led a significantly lower T_g in the final materials, whereas a lower temperature retained the T_g for the yielded networks. Recovery of the tensile strength and plateau storage modulus were used to assess their reprocessability. Values between 71–133% after reprocessing support these claims. Acid-catalysed hydrolysis of the networks recovers 80% pure di(trimethylolpropane) and



induces $\text{Ti}(\text{O}^i\text{Pr})_4$ hydrolysis to form non-toxic TiO_2 .⁶² Although room-temperature T_g values and initiator volatility remain challenges, both polyester and polycarbonate vitrimers are materials that could feasibly tackle the end-of-life challenges of conventional thermosets.

Zhao *et al.* translated these polycarbonate vitrimers into paper composites, that are synthesised *via in situ* cross-linking inside cellulose networks.⁶³ Vitrimeric paper composites with various cross-linker to diol ratios exhibited enhanced fracture strengths of 20 to 42.7 MPa, compared to 8 MPa for untreated paper. Comparable strain values were observed over a wide temperature range (25–120 °C). Moreover, the vitrimeric component imparts reprocessability, shape-memory and self-healing properties to the paper. Both the polycarbonate precursors and cellulose can be easily recovered under mildly acidic conditions. This novel material has since been further explored as transparent coatings for silver nanowire conductive paper, offering improved thermal stabilities compared to the analogues produced through traditional methods.⁶³

3.3. Photo-induced cross-linking

In soft tissue engineering, drug delivery and dentistry, photo-cross-linking has gained a lot of interest due to fast curing rates at ambient temperatures. *In vivo* studies of biodegradable resins have shown facile, controlled material solidification along with important, beneficial clinical outcomes such as minimal scarring, risk of infection or treatment costs.^{29,64,65} Different groups employed a multi-step approach to photo-cross-linked networks by using telechelic degradable prepolymers. These could be synthesised through the ROP of **M6** in the presence of $\text{Sn}(\text{Oct})_2$, with various alcohols (glycerol, hexanediol, sorbitol) as initiators. Following functionalisation of the hydroxy end-groups with acrylates, cross-linking was performed through radical polymerisation, giving rise to novel **P6**-based tissue engineering scaffolds.^{66–68} A similar methodology was used by Seppälä and coworkers who reported the synthesis of cross-linked **P3** elastomers (Fig. 12).⁶⁹ Telechelic **P3** star-shaped oligomers were synthesised, followed by chain-end functionalisation with methacrylic anhydride. Cross-linking afforded elastomers with excellent form stability, particularly when a 1 : 1 molar feed of **M3** : **M7** was used. *In vitro* hydrolytic degradation rates depend on the oligomer composition, with networks containing high amounts of **M3** showing slower kinetics compared to the copolymers having higher **M7** contents. There remains untapped potential for these random copolymers in biomedicine,⁶⁹ although complementary toxicity studies are essential.

Introduction of acrylate end groups does introduce non-degradable components and the potential for trace acrylate impurities, with the associated toxicity risk.^{66,70} However, Storey *et al.* reported that methacrylate-terminated **M3** and **M7**-based prepolymers can be homopolymerised or copolymerised with methyl methacrylate, styrene and 2-methylene-1,3-dioxepane (**M8**) to yield non-toxic networks suitable for implantation.⁷¹ A high degree of cross-linking was reported, with <10% sol contents in all cases, reducing the hazard from



Fig. 12 Synthesis of double-bond-cured **P3** elastomers.⁶⁹

residual olefinic monomers; degradability studies were not performed.

Polyesters are typically hydrolysed to afford acid products, which, depending on application, can be problematic due to potential side effects. In contrast, carbonates usually degrade into carbon dioxide and compounds containing hydroxyl moieties, enabling the design of materials that break down into bioactive molecules.^{72–75} To exploit this, high molecular weight **P4** films of pentaerythritol triacrylate and a photo-initiator (Irgacure 369) were photo-cross-linked to give porous flexible scaffolds.⁷⁶ Human mesenchymal stem cells were shown to readily adhere and proliferate on these scaffolds, highlighting the exciting potential of these materials for biomedical applications.⁷⁶ Similarly, low molecular weight methacrylate-terminated **P4** oligomers were synthesised and used as cross-linking aids along with Irgacure 2959.⁶⁶ Upon UV irradiation, transparent films formed and it was found that the cross-link density was easily tuned by varying the exposure time (30–300 min), while maintaining high gel contents. The elasticity of these materials was found to be between 7.1 and 7.5 MPa, similar to 6.5 MPa for the non-cross-linked **P4** scaffolds. These materials are cyto-compatible and while their erosion times are longer than for the linear counterparts, the degradation products were rendered non-toxic.⁶⁵ In order to improve creep resistance, **P4** oligomers were end-functionalised with fumaric acid monoethyl ester and further photopolymerised (Fig. 13).⁷⁷ The resulting networks had low T_g values between –14.7 and –18.1 °C and were flexible, with Young's moduli varying between 1.25–2.12 MPa and 0% permanent deformation under cyclic loading experiments. While **P4**-type networks do degrade enzymatically,^{78,79} no detailed degradation studies were presented for this system. End-functionalisation was analogously employed for 3-armed hydroxyl-terminated **P2**, **P4** and **P6** oligomers. Photo-cross-linking with a 2,2-



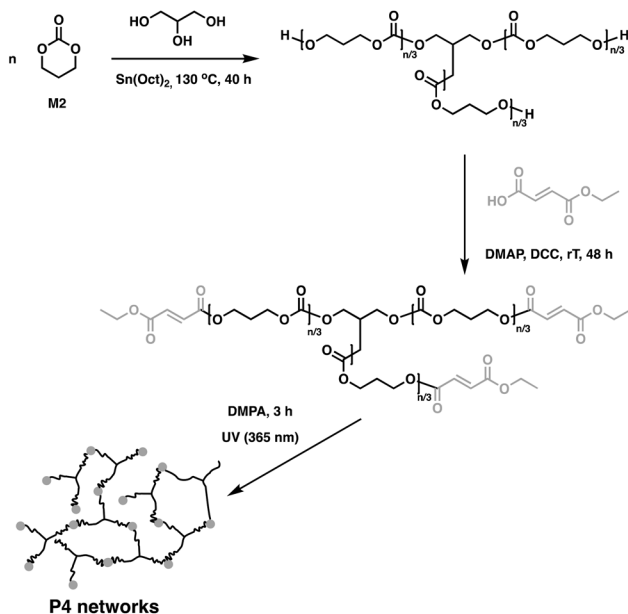


Fig. 13 Synthesis of **P4** networks through UV cross-linking of fumaric acid monoethyl ester-functionalised **P4** oligomers.⁷⁷

dimethoxy-2-phenylacetophenone (DMPA) initiator yielded networks with high gel contents up to 96%.⁸⁰

Further functionality is challenging to incorporate, as no sites for grafting traditional moieties, such as poly(ethylene glycol) (**P8**), heparin or collagen, exist on the linear polymer precursors. Timbart and Amsden circumvented this challenge with a novel star polymer, prepared *via* melt ROP of 2-oxepane-1,5-dione (**M9**) and **M3** in the presence of Sn(Oct)₂ and glycerol (Fig. 14).⁸¹ The acrylated star-copolymers were photo-cross-linked in the presence of DMPA. Post-polymerisation functionalisation through the remaining ketone **M9** was realised through hydrazine modification of the networks was successful, producing elastomer films containing both hydroxyl and amine functional groups. This gives anchors for a variety of



Fig. 14 Synthesis of biodegradable photo-cross-linked elastomers based on **M9** and **M3**.⁸¹

functional groups to load molecules, vary hydrolytic degradation rates or tune hydrophilicity.

3.4. Cross-linking through gamma and electron beam irradiation

Gamma and electron beam irradiation have been widely applied to modify the properties of polymers and biomaterials.^{82–84} These high-energy irradiation methods modify the surface and bulk properties of the materials, with the bonus of simultaneously sterilizing them.⁸² While these methodologies proved ineffective for polymers **P2**, **P6** or poly(propylene carbonate), biodegradable elastomeric **P4** networks can efficiently form using this strategy.^{85–88} High molecular weight **P4** was synthesised through the conventional ROP of **M2** with Sn(Oct)₂ as catalyst, followed by compression moulding under an inert atmosphere to afford films. ⁶⁰Co gamma-irradiation at doses of 25, 50 and 100 kGy was used to cure the **P4** films, yielding flexible bioelastomers.⁸⁹ Grijpma demonstrated that the resulting networks had gel contents between 50–70%, an increase proportional to the irradiation dose. The degree of swelling decreased with increasing irradiation dose, allowing the study to conclude that the cross-linking density increased with an increasing irradiation. Materials with moduli between 4.6 and 5.8 MPa were obtained, lower than the 6.8 MPa observed for non-irradiated **P4**. Yield stress of 1.1–1.6 MPa and a high elongation at break of 580 to 820% were obtained, with the results being of the same order of magnitude to that of the **P4** homopolymer. It was found that cross-linking improves the permanent deformation values, from 4.1% for the homopolymer, to values between 0.2 and 1% for the resins. Furthermore, increasing the irradiation dose causes an increase in gel contents and modulus, whereas the maximum tensile stress and elongation at break do not show significant changes. The elastic networks were used as a substrate for culturing various relevant cells, such as human umbilical vein endothelial cells, smooth muscle cells or mesenchymal stem cells. As expected, the biocompatibility of the gamma-irradiation-cured **P4** elastomeric networks was bolstered. Furthermore, tubular, porous scaffolds were prepared using these materials with the flexibility and elongation at break allowing the materials to be used in blood vessel constructs, as shown in Fig. 15.⁸⁹

In later works by Bat *et al.*, pentaerythritol triacrylate was introduced during the ⁶⁰Co gamma-irradiation curing of high molecular weight **P4**.⁹⁰ Degradation studies were carried out *in vitro* with cholesterol esterase, an enzyme which catalyses cholesterol esters hydrolysis.⁹¹ The degradation rate of the cross-linked polymer was found to be much slower than for typical networks not containing pentaerythritol triacrylate, with a mass loss of 13% *vs.* 64% over three weeks. Cross-linking trials were extended to poly(3-hydroxyalkanoate)s (PHAs), employing electron beam irradiation to cure a microbial PHA produced using *Pseudomonas oleovorans* on a mixture of *n*-octane and 1-octene. The moduli and cross-link density of the networks were varied by altering the ratios of the carbon sources, along with using an extensive range of elec-



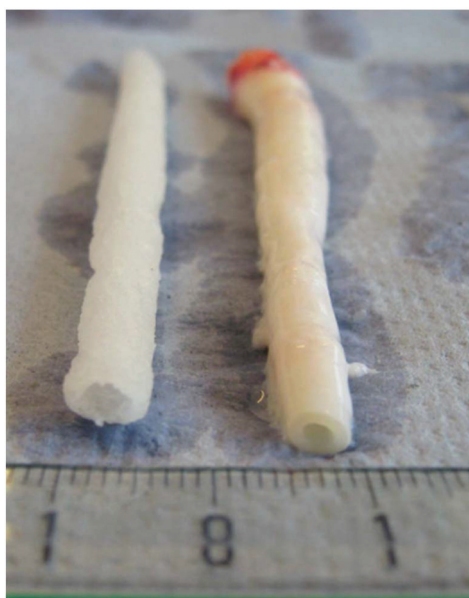


Fig. 15 Porous scaffold (left) synthesised from cross-linked **P4** and porcine carotid artery (right).⁸⁹ Reprinted from ref. 89, Copyright 2020, with permission from Elsevier.

tron beam irradiation doses, between 30 and 500 kGy. The resins are shown to degrade *via* enzymatic hydrolysis and subsequent surface erosion, a degradation mode resembling that of crystalline PHA.⁹²

4. Degradable resins from itaconic acid

An emerging route to novel renewable resins is the use of bio-based polysaccharides or lignocellulosic feedstocks as platform molecules.^{93,94} An economically viable building block that was extensively studied is itaconic acid (**M10**). On industrial scale, this aliphatic dicarboxylic acid building block is synthesised *via* carbohydrate fermentation aided by *Aspergillus terreus*.^{95,96} Owing to its two carboxylic acid moieties, α,β -unsaturated double bond and short chain, it has proven to be a precursor for a myriad of applications, such as flame retardants, coatings, paints and latexes.^{97,98}

With the global unsaturated polyester resin market being valued at 11.63 billion USD in 2019,⁹⁹ there is plenty of room for itaconic acid to expand its scope as a sustainable alternative.⁹³ This platform molecule was recently employed by Hillmyer and collaborators in a variety of high yielding, catalytic transformations to afford a saturated diol and diester and an unsaturated diester.⁹³ All three monomers synthesised were easily purified and employed in step-wise polymerisations to yield high molecular weight polyesters in high yields. The fully **M10**-derived triblock polymer was cross-linked using thiol-ene “click” chemistry with the potentially renewable cross-linker, pentaerythritol tetrakis(3-mercaptopropionate) (**C7**) (Fig. 16).



Fig. 16 Cross-linking of **M10**-derived triblock polymers using **C7**.⁹³

This afforded resins with mechanical properties dependant on the proportion of saturated and unsaturated diols used. The synthesised networks also displayed promising base-catalysed hydrolysis at ambient temperature, hinting at the potential of these degradable, high-value polymers.⁹³ Dai *et al.* reported the use of **M10** along with other bio-based platform chemicals, 2,5-furandicarboxylic acid (**M11**), succinic acid (**M12**) and 1,3-propanediol (**M13**), to afford a range of fully bio-based unsaturated polyesters *via* melt polymerisation.¹⁰⁰ Notably, **M11** is obtained through the oxidation hydroxymethylfurfural, which is derived from sugars or polysaccharides,^{101,102} and its structural rigidity imparts superior thermomechanical properties to the resultant polyesters.¹⁰³ These polyesters were thermally cured to give T_g values between 73.5–141.7 °C and flexural strengths of 41.9–116.8 MPa, matching fossil-fuel derived polyester networks.¹⁰⁰

M10 has also been employed in a biobased vulcanised unsaturated aliphatic polyester elastomer in order to toughen the brittleness of **P6**.¹⁰⁴ The bio-based unsaturated polyester elastomer was synthesised through a polycondensation esterification reaction between four aliphatic monomers: **M10**, **M13**, 1,4-butanediol (**M14**) and sebacic acid (**M15**). A thermoplastic vulcanizate was then prepared, facilitated by the double bond moieties of the **M10** components. Dynamic vulcanisation of the unsaturated polyester, using dicumyl peroxide (DCP) as the initiator in a melted **P6** matrix, gave a well dispersed system. Significantly, **P6** chains were grafted onto the vulcanised unsaturated polyester elastomer, improving the compatibility between the vulcanised phase and the matrix. Dynamic vulcanisation led to a decrease in tensile toughness of the **P6** blend, from 110 MJ m⁻³ to 84 MJ m⁻³. However, the impact toughness of this material was enhanced up to 586.6 J m⁻¹, a 31-fold increase compared to the homopolymer. These materials were suggested to have the potential to replace some conventional petroleum-based plastics, arguing that the monomers were fully bio-based,¹⁰⁴ but an investigation into the fate of these



products at end-of-life would be complementary to these claims. Although the ester bonds in the polymer backbone are labile and they have been shown to hydrolyse under specific conditions, the cross-links may inhibit degradability.

The resemblance of **M10** to (meth)acrylic acids, commonly used cross-linkers in UV-cured coatings opens up new applications.¹⁰⁵ By exploiting multiple distinct bio-based monomers such as **M10**, **M14** and D,L-lactic acid (**M16**), Harlin and co-workers employed condensation polymerisation protocols to synthesise barrier coatings for commercial cardboard (Fig. 17).¹⁰⁶ The double-bond functionality of **M10** allows the free-radical cross-linking of poly(D,L-lactic acid-co-1,4-butenediol-co-itaconic acid) (**P9**). The cross-linking efficiency was tested with a variety of acrylate and methacrylate cross-linkers, along with radical and UV initiators. Using a **P8** diacrylate together with dilauroyl peroxide yielded a cross-linked **P9** with 77% gel content in only 15 minutes. An aqueous dispersion of the synthesised resin was coated on commercial folding boxes. The water vapor transmission rate was measured, showing 50% smaller values than the commercially available extruded **P6** coatings. These coatings are completely oil-resistant and their use has been implemented on pilot scales using line coaters, suggesting that this material could therefore offer exciting applications in the food packaging sector.¹⁰⁶ A more straightforward methodology for synthesising **M10**-based polyester coatings was reported by Brännström *et al.*¹⁰⁷ A series of bio-based unsaturated polyesters were synthesised through polycondensation in bulk using **M10**, **M12** and **M14**. The polyester films were UV-cured and the variation of molecular weight and amounts of residual **M10** and **M12** were assessed to tune the properties of the cross-linked coatings.¹⁰⁷ A challenge with **M10** is that isomerisation to 2-methyl fumaric acid occurs at temperatures of 180 °C.¹⁰⁸ This inhibits effective polymerisation, because the 2-methylfumaric acid isomer is significantly less reactive than **M10**; the polymerisation conditions must thus be well-controlled to reach high monomer conversion and avoid isomerisation.^{107,108} DMA studies indicated that cured **M10**-based polyesters show increased storage modulus and hardness with increasing molecular weights. Compared to **M12**, **M10** has a lower reactivity due to the conju-

gated carboxylic acid moiety, resulting in a faster reaction rate for higher mole ratios of **M12**. However, **M12** incorporation into the polymer led to materials with lower modulus and hardness compared to the UV-cured **M10**-based coatings.¹⁰⁷

A similar approach was described by Dai *et al.* who reported the synthesis of unsaturated polyesters from **M10** and three different diols, namely **M14**, ethylene glycol (**M17**) and 1,6-hexanediol (**M18**). These polyesters were UV-cured to afford bio-based waterborne coatings with excellent water resistance for this type of **M17**-based coating.¹⁰⁹ This study, however, was lacking information regarding the degree of curing and comparisons with the unsaturated polyesters. The same group published a more comprehensive report on cross-linked networks based on the same aforementioned unsaturated polyesters.^{109,110} The thermosetting resins were prepared following a copolymerisation of the unsaturated polyesters with acrylated epoxidized soybean oil (**M19**), another bio-based platform molecule, allowing the coatings to have superior flexibility compared to what was previously reported. The two coatings were taken further in a paper that reports the aim to improve the adhesion of the previously reported coatings by incorporating glycerol (**M20**) in the unsaturated polyester chain.¹¹¹ Moreover, through further incorporation of **M19**, bio-based, UV-curable and water dispersible coatings were afforded, with outstanding flexibility, high adhesion and hardness along with excellent solvent resistance.¹¹¹

While there has been considerable work on itaconic acid-based resins, materials with competitive prices and consistent performance remain elusive. Trying to meet these industrial requirements, Panic *et al.* used esters of **M10** as reactive diluents, whereas the prepolymers were synthesised using **M10** and 1,2-propylene glycol (**M21**) through a polycondensation reaction. The cured networks showed T_g values in the range of 65–118 °C and displayed moderate stiffness (270–660 MPa), whereas the storage moduli were found to vary between 370 and 1400 MPa. Compared to the resins synthesised using styrene as a reactive diluent, the dimethyl itaconate (**M22**) resins had lower elastic moduli, with comparable other properties. There is thus potential for **M10** and its derivatives to be used as bio-based resources for unsaturated polyester resins.¹¹²

5. Isosorbide-based resins

While aliphatic polyesters like **P6** show great potential as biodegradable polymers, bio-based feedstocks such as sugars also hold promise for materials development due to their high functionality and large scale production capability.¹¹³ A key platform chemical derived from sugars is isosorbide (**M23**), a fused bi-heterocyclic diol that thanks to its high stability and functionality has reached industrial scale production^{114–116} through glucose hydrogenation to sorbitol, followed by a selective dehydration step to afford **M23**.^{114,116–119} The bicyclic monomer has been incorporated in a plethora of different polymers including the commercial plastic Durabio™, a **M23**-based non-biodegradable copolycarbonate for use in their



Fig. 17 Three component cross-linked networks for coating applications.¹⁰⁶



automotive parts.^{120–126} While most work has focussed on linear polymers, **M23**-based cross-linked resins have also been explored.

Copolyesters of **M23** with **M10** and **M12** have been made *via* polycondensation in toluene at 140 °C using microwave irradiation.¹²⁷ These fully bio-based cross-linked polyesters showed shape memory properties following cross-linking with **M22** in the presence of a free radical initiator (2,2-azobis(2,4-dimethylvaleronitrile, V65).¹²⁷ Copolyesters of **M10**, **M14**, **M15** and **M23** have also been synthesised and characterised (Fig. 18).¹²⁸ The prepolymers had low T_g values, varying between –51 and –35 °C and T_m values between 34 and 60 °C. With the double bond functionality in **M10**, the polyesters were cross-linked in the presence of DCP. The bio-based networks gave improved shape memory properties, with recovery rates near 100%. Moreover, these materials were bio-compatible in cytotoxicity studies paving the way for medical implants.¹²⁸

M23-containing polyester and polycarbonate resins have also been employed in the coatings industry. Copolyesters of **M12**, **M23** (18–36 wt%) and various diols (**M13**, **M14**, **M20** and 1,2-propanediol, **M24**) were synthesised, with T_g values of 3 to 30 °C. Melamine was used to cross-link the prepolymers and while the T_g values of the novel networks were low, the coatings showed high resistance to photodegradation and hydrolysis.¹²⁹ **M23** was also incorporated at 10–70 mol% in polyester coatings containing **M11**, **M15** and various diols, with the T_g increasing from –46 to 35 °C with increasing **M23** content.¹³⁰ **M23**-based copolycarbonates have also been reported by Noordover *et al.*, in a study exploring the melt polycondensation of **M23** with **M13** or **M14**, using triphosgene and diphenyl carbonate.¹³¹ Curing the synthesised copolycarbonates using conventional polyisocyanate cross-linkers yielded coatings with good mechanical properties. While the polymer architecture and composition were carefully tailored in these reports, (bio)degradation was largely unexplored, and needs to be critically evaluated to support potential sustainability and closed-loop life-cycle applications.



Fig. 18 Shape-memory cross-linked copolyesters synthesised using **M10**, **M14**, **M15** and **M23**.¹²⁸

Thiol-ene chemistry has been used to cross-link **M23**-based resins through allyl ether-functionalisation of the monomer, followed by subsequent polymerisation with a multifunctional mercaptopropionate.^{132–135} This atom economic methodology afforded potentially biodegradable elastomers with variable T_g values, ranging from –10 to –2 °C.^{132,134,135} Backbone degradability can also be introduced in a polymer through carbonate linkages through the synthesis of poly(thioether-*co*-carbonate) (**P10**) networks using quinic acid. An alloc-functionalisation strategy of the quinic acid lactone (**M25**) was exploited, along with a photocatalysed thiol-ene methodology to synthesise polycarbonate networks.⁷⁵ Wooley and coworkers have since used the potential of previous studies as impetus to report the synthesis of a **M23**-based cross-linked polycarbonate (Fig. 19).^{132,136} Isosorbide dialloc (**M26**) was synthesised from **M23**, and it was copolymerised with trimethylolpropane tris(3-mercaptopropionate) (**C8**) through thiol-ene cross-linking. The alloc group, an allyl carbonate, imparted degradability to **M23** along with providing the double bond for cross-linking. Post-cure thermal treatment (at 100 °C) did not impact thermo-mechanical properties, suggesting post-cure heating was unnecessary. The optically transparent elastomers had T_g values below room temperature, moduli of 1.9–2.8 MPa and elongation at break of 220–344%. In terms of degradation, the materials demonstrated a 92% mass loss under basic conditions (1 M NaOH) at elevated temperatures (60 °C), but only a 4% mass loss under physiologically-relevant conditions over 60 days. These novel cross-linked systems have the properties to be good candidates for both biomedical applications and renewable plastics.¹³⁶

M23 can also be used in unsaturated polyesters as a reactive diluent, after chemical modification.¹³⁷ Most examples of renewable unsaturated polyester systems report styrene as reactive diluent for cross-linking, due to its low viscosity, high reactivity and good miscibility. Replacing this suspected carcinogen is a key target for bio-based unsaturated polyester



Fig. 19 Synthesis of **M26** from **M23**, along with the formation of cross-linked networks using **C8** as a cross-linking agent.¹³⁶



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