**Post-polymerisation Modification of Bio-based Polymers: Maximising the High Functionality of Polymers Derived from Biomass**

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**ABSTRACT**

The renaissance of the bio-based chemical industry over the last 20 years has seen an ever growing interest in the synthesis of new bio-based polymers. The building-blocks of these new polymers, so called platform molecules, contain significantly more chemical functionality than their petrochemical counterparts (such as ethane, propene and *para*-xylene). As a result bio-based polymers often contain greater residual chemical functionality in their chains, with groups such as alkenes and hydroxyls commonly observed. These functional groups can act as sites for post-polymerisation modification (PPM), thus further extending the range of applications for bio-based polymers by tailoring the polymers final properties. This mini-review highlights some of the most recent and compelling examples of how to make use of bio-based polymers with residual functional groups for PPM. It also looks at how the emerging interdisciplinary field of enzymatic polymer synthesis allows for increased functionality in polymers by avoiding side-reactions as a result of milder reaction conditions, and additionally offers an alternative means of polymer surface modification.

**1. INTRODUCTION**

Since the emergence of the first synthetic polymers in late 19th century, this class of materials has continued to have an enormous impact on society. Although early synthetic polymers, such as nitrocellulose and cellulose acetate, were chemically modified bio-based polymers they were gradually superseded by alternatives from petrochemicals, such as nylon 6,6, poly(ethylene) or synthetic rubber. Today, polymers represent the largest proportion of the chemical industry by volume, but there are well-founded concerns over the sustainability of an industry so reliant on a diminishing non-renewable feedstock. As such the last 20 years has seen a re-emergence of interest in bio-based polymers, with many excellent reviews now covering this rapidly growing area of research.1-4 In the short-term focus has been on preparing bio-based drop-in replacements for current polymers. Examples include the production of 100% bio-based poly(ethylene) from sugar cane, or the continued efforts towards wholly bio-based PET. However, the longer-term view is towards new polymers that on a molecular level may be different to the petrochemical polymers they intend to replace, but whose properties are equivalent or even superior to products current available. At the heart of this approach to new polymers is the synthesis and use of building-block chemicals from biomass, so called platform molecules.5,6 As a definition:

*“A bio-based (or bio-derived) platform molecule is a chemical compound whose constituent elements originate wholly from biomass (material of biological origin, excluding fossil carbon sources), and that can be utilised as a building block for the production of other chemicals.”*

In essence, platform molecules are the bio-based equivalent of the “base chemicals” of the petrochemical industry (i.e. ethene, propene, butenes, benzene, toluene, xylenes and methanol). However, there are some very important differences between traditional base chemicals and bio-based platform molecules, most notably the prevalence of heteroatoms in the latter.5,7 The fossil feedstock for the petrochemical industry is essentially depleted of heteroatoms and so the first building-blocks produced, the base chemicals, are almost entirely comprised solely of hydrogen and carbon. The small amount of functionality present (i.e. C=C or arenes) are used as points to further functionalise via reactions such as oxidations, and in doing so add chemical functionality that can be exploited downstream. One such example is the multiple oxidation of *para*-xylene to terephthalic acid, this required for PET synthesis. However, the pathway from biomass to platform molecules is very different as biomass is inherently comprised of components rich in heteroatoms. The major constituents of biomass; polysaccharide (e.g. cellulose, hemicellulose, starch), lignin, triglycerides and protein are full heteroatoms such as O, N and S. When these constituents are broken down to smaller molecules much of the heteroatom content remains, leaving lots of functionality for further modification. As an example cellulose can be used as a feedstock to produce 5-(hydroxymethyl)furfurfural, and this easily oxidised to 2,5-furandicarboxylic acid (FDCA), a diacid used in the production of the promising PET replacement, PEF.

The presence of greater functionality in bio-based polymers leads to an exciting opportunity for many of the emerging bio-based polymers, the subsequent post-polymerisation modification (PPM) to tailor the polymers properties (figure 1). PPM has arguably existed for as long as the field of polymer science, indeed early examples such as the treatment of natural rubber with sulfur, or production of cellulose acetate and nitrocellulose all represent examples of PPM.8 From the mid-20th century onwards some examples of PPM on synthetic polymers began to emerge, such as the thiol-ene addition of thiols onto butadiene polymers, but the typical low functionality of petrochemical monomers and polymers limited this approach.9 PPM requires the presence of functional groups within the constitutional repeat unit of the polymer to act as a point where further chemical reactions can take place, but where reactions at the sites does not reduce chain length. It therefore follows that the new emerging monomers and polymers from biomass that contain greater functionality compared to petrochemical alternatives, will allow the concept of PPM to be further expanded. The first sections of this mini-review address the need for selective polymerisation methods to be used to ensure the required chemical functionality remains within the polymer to allow for PPM. Chemo-catalytic methods have been demonstrated for many classes of polymers and in some instance prove very effective in producing backbones suitable for subsequent PPM. However, the harsh conditions required to achieve high degrees of polymerisation can also result in undesirable side-reactions such as isomerisation and cross-linking. To address these concerns we also summarise recent developments in the use of milder conditions for polymerisation made possible through the use of enzyme catalysts. Upon successful preparation of functional polymers (i.e. those containing reactive sites for functionalisation) there are several possible routes for PPM. Herein we highlight those most relevant to bio-based polymers: reactions through carbon-carbon double bonds, pendant hydroxyls and chain extension. To complement our discussions around enzymatic polymerisation we have also outlined the emerging field of bio-based polymer surface modification using the same selective enzyme catalysts. The mini review is closed with an outlook that highlights areas where PPM to bio-based polymers has yet to be applied but where this is considerable promise for the future.



**Figure 1.** Diverse possibilities of post-polymerisation modification (PPM) as a result of using functional bio-based monomers.

**2. CHEMO-CATALYTIC SYNTHESIS OF FUNCTIONAL BIO-BASED POLYMERS**

A large proportion of the literature associated with bio-based polymers tends to be focused on the synthesis of polyurethanes,10,11 polycarbonates,12 and in particular, polyesters.13,14 Aside from their extremely useful and diverse properties, one common aspect to all of these materials is that the chemical functionality required to synthesise them can be found in a wide range of bio-based platform molecules (as an example, a particularly good overview on bio-based platform molecules from a lignocellulosic feedstock was given by Becer).1 Many different catalysts and carbonyl activating species have been reported for the synthesis of polymers using di-substituted monomers, where typically, these tend to be identical to those used for the synthesis of crude oil-based plastics.15 However, when aiming to retain reactive functionality found with more complex tri- and tetra-substituted monomers, the range of effective activating agents/catalysts is somewhat restrictive. This is exemplified particularly well through the use of glycerol as a trifunctional monomer; glycerol has received much attention due to its plentiful supply (especially as a by-product from bio-diesel production) and sustainability.16,17

Direct reaction between dicarboxylic acid and glycerol using typical polyesterification catalysts such as (C4H9)2SnO, Sn(Oct)2, Ti(OtBu)4, and Ti(OCH(CH3)2)4 has been shown to result in hyperbranching.18,19 Although this is beneficial when synthesising elastomers for biomedical applications such as scaffolds for tissue engineering, the lack of control and selectivity does not allow for PPM of the elastomers (to enhance characteristics such as water retention capacity) nor allow synthesis of linear functional polyesters.20,21 You et al.circumvented this problem in the synthesis of poly(sebacoyl diglyceride) through the use of ring opening polymerisation rather direct polycondensation of the monomers (scheme 1).22 By first synthesising the diglycidyl sebacate intermediate from the corresponding acid chloride and glycidol, ring opening of the epoxide is possible via the addition of an equivalent of sebacic acid using dioxane solvent and a catalytic quantity of tetrabutylammonium bromide.



**Scheme 1**. Synthetic routes to highly branched poly(glycerol sebacate) and highly linear poly(sebacoyl diglyceride).

Whilst the direct route from dicarboxylic acid and glycerol gave polymer with a high proportion of branching (55%), only 10% branching was found using the diglycidyl sebacate route. As expected, the linear poly(sebacoyl diglyceride) polymer had a reduced dispersity (Đ) of 2.5 compared with the branched poly(glycerol sebacate) with a Đ of 9.3. Mn also varied from 9 kg mol-1 using the direct route to 16.6 kg mol-1 using the indirect route; it should be noted that the two polymers are not directly comparable due to the increased ratio of sebacic acid units used in the indirect route. The idea of pre-activation of sebabic acid to control selectivity was further developed by Taylor et al., using diarylborinic acids as catalytic directing agents for the synthesis of a range of aliphatic and aromatic polyesters, including poly(glycerol sebacate).23 Although use of corrosive dodecanedioyl chloride is still required, glycerol can be used directly in the synthesis without the need to first prepare glycidol. Addition of 1 mol% of diarylborinic acid catalyst (10*H*-dibenzo[*b,e*][1,4]thiaborinin-10-ol) reduced formation of triacylglycerol functionalities to less than 1% (scheme 2, *C*), whilst also showing regioselectivity within diacylglycerol moieties, favouring 1,3-diacylglycerol formation (scheme 2, *A*) over 1,2-diacylglycerol (scheme 2, *B*) at a ratio of almost 13:1. Chain lengths and quantity of linear chain formation were increased over the You method22 giving a GPC Mn of 19.2 kg mol-1 and lower Đ of 1.2.



**Scheme 2**. Synthesis of linear poly(glycerol sebacate) showing different regioselective products, 1,3-diacylglycerol, 1,2-diacylglycerol and triacylglycerol.

Despite promising developments, direct synthesis of bio-based polymers from functional monomers is still largely problematic due to poor selectivity offered by traditional Lewis acid catalysts and the relatively harsh reaction conditions required. Ring opening polymerisation allows preservation of reactive groups to a certain extent, but this is still not absolute and often requires multiple steps to synthesise the necessary precursors employing relatively toxic reagents/solvents and costly reaction conditions. As such, there has been increased focus on the use of enzymes as highly selective polymerisation catalysts, allowing preservation of valuable reactive species.

**3. ENZYMO-CATALYTIC SYNTHESIS OF FUNCTIONAL BIO-BASED POLYMERS**

The enzymatic synthesis of polymers is a broad topic that was extensively covered by several authoritative reviews over the past twenty years.24,25 In this section we will therefore focus our attention only on the bio-catalysed synthesis of functional bio-based polyesters under environmentally-friendly operation conditions. Is it well known that the enzyme-catalysed synthesis of polyesters is not economically competitive with the traditional chemical processes that on lab-scale, are either employing organic or metal-based catalysts.26,27 The major issue of enzymatic polymerisations is the often low molecular masses of the obtained polymers (usually <15 kg mol-1 for aliphatic and <3 kg mol-1 for aromatic polyesters). Additionally, the difficult recovery of the immobilized biocatalyst that, despite being reusable, frequently needs the use of organic media (such as tetrahydrofuran for aliphatic and chloroform for aromatic polyesters) for the separation from the reaction products therefore adding a costly and time-consuming step to the already multi-hour long (usually around 24 h) process. However, the major strength of enzymatic synthesis is the possibility to selectively synthesize polyesters having lateral functionalities that are otherwise difficult to obtain using traditional chemo-catalysis. For example the polymerisation of itaconic acid and its derivatives is susceptible to the high operational temperatures commonly used for polyester synthesis (150-200 °C) that might cause isomerisation to less reactive mesaconic or citraconic acid or crosslinking of the polymeric chains.28 Enzymatic catalysis on the other hand, performed under mild conditions (50 °C, solventless) allows the synthesis of linear chains maintaining the vinyl moiety available for further functionalisations.29,30 A similar situation is subsisting for bio-based monomers having primary and secondary hydroxy groups such glycerol and sorbitol. Obtaining linear polyesters from these monomers is in fact possible only when a lipase-catalysed polycondensation approach is used. The used enzyme, typically lipase B from *Candida antarctica* (CaLB), when operating at mild conditions is extremely selective for the primary hydroxy groups, while the reaction on the secondary hydroxyls is happening at a much slower relative rate due to the remarkable regioselectivity of this biocatalyst.31 The use of elevated temperatures leads to undesired ether formation and dehydration of sorbitol27 or enhances the reactivity of the secondary hydroxy groups leading to the formation of branched polymers as reported in the case of glycerol.32 More recently the utilisation of 9,10-epoxy-18-hydroxyoctadecanoic acid, an epoxy-functional ω-hydroxy-fatty acid extracted from birch bark, for the CaLB-catalysed synthesis of multifunctional oligoesters (yield>80%, 3.4<DP<4.7) was also reported.33 The bio-catalysed synthesis starting from bio-based monomers containing one or more functionalities such as hydroxy, vinyl and epoxy moieties, is a green and sustainable approach when the production of functional pre-polymers having side or end chain functionalities and a limited molecular weight (up to 8-10 kg mol-1) is desired. Moreover enzymatic catalysis was recently used for the modification of poly(hydroxy alkanoates) adding both hydrophilic, such as poly(ethylene glycol), and functional, such as dimethyl itaconate, moieties in order to render the polymer water soluble or suitable for post-polymerisation modification.34 Such polymers reached Mn up to 71 kg mol-1 and Mw up to 75 kg mol-1. Enzymes are therefore ideal catalysts when the synthesis of functional oligoesters with limited molecular weight is desired. This can be reflected in applications such as nanoparticles and resins pre-polymers that will be crosslinked (cured) in a second reaction step, as described below.

**4. POST-POLYMERISATION MODIFICATION (PPM) via C=C**

Alkenes are a common reactive unit found in functional bio-based polymers, with monomers such as itaconic, fumaric and muconic acid (figure 1) often used to incorporate C=C into polyester backbones. Bio-based unsaturated polyesters (UPEs) containing these three diacids are often portrayed as potential replacements to petrochemical derived maleate polyesters, with the electron-deficient nature of the C=C imparting similar reactivity, as will be discussed in later sections.35

**4.1. Curing of Unsaturated Polymers via C=C**

Following the typical uses of fossil-derived maleate UPEs, many of the previous studies into new bio-based UPEs first consider curing through the C=C as the major PPM pathway, producing three-dimensional cross-linked insoluble thermoset networks.36-38 The curing of bio-based UPEs can take two forms (figure 2), either with or without the addition of another curing agent / reactive diluent (acrylates, styrene, methacrylamide, divinylbenzene, *N*-vinyl-2-pyrrolidinone, alkylated epoxidised soybean oil etc.), many of which are not themselves bio-derived.



**Figure 2.** Curing of bio-based unsaturated polyesters (UPEs) either without (**A**) or with (**B**) the addition of a curing agent, resulting in cross-linked thermosets.

Different curing methods are also applied, typically relying on either photo- or thermal activation, the aim to trigger reactions across the C=C within the chain and those of the curing agent. The geminal C=C of itaconic acid is typically more reactive than equivalent counterparts from maleic or fumaric acid, as a result it often proves challenging to synthesise high chain-length (Mn 10 kg mol-1) unsaturated polyesters of IA.28 However, in the case of UPEs for curing thermosets lower chain lengths are more suitable, and indeed often preferred, therefore the increased reactivity of IAs geminal C=C does not hinder its suitability for this particular application. Thermosets produced from bio-based UPEs offer wide potential uses in applications such fiberglass composites, sheet moulding compounds and bulk moulding compounds. Cytotoxicities of thermosets are typically lower than for thermoplastics, and as a result they are often suitable for biomedical applications.39 One such example from Sakuma et al. showed that itaconate-based UPEs can be co-polymerised with methyacrylate polysilsesquioxane to produce biocompatible organic-inorganic frameworks.40 Itaconate UPEs have also been used to enhance the properties of thermoset coatings produced from partially bio-derived acrylated epoxidized soybean oil (AESO, scheme 3). The tensile strength, modulus, glass transition temperature (Tg) and bio-based content of the AESO-based thermosetting resins were improved signiﬁcantly after curing with the itaconate UPEs, with the resultant bio-based UPE-AESO system showing excellent coating properties on glass and tin surfaces.41 The final mechanical properties (hardness, flexibility and adhesion) of the materials were found to be tuneable through the selection of the diols (1,2-ethanediol, 1,4-butanediol or 1,6-hexanediol) and/or glycerol used for the synthesis of the itaconate UPE, and could be extended to waterborne UV-curable system.42



**Scheme 3.** Itaconate UPEs enhancing thermosets of acrylated epoxidised soybean oil (AESO).

Spasojevic et al. very recently demonstrated a one-pot route to fully bio-based thermosets where poly(1,2-propylene itaconate) UPE is first formed as a pre-polymer (Mn 1.3 kg mol-1) and subsequently cured via the use of a range dialkyl itaconates reactive diluents (RD, scheme 4).43 This is an interesting example of how traditional RDs such as acrylate and styrene can be replaced by bio-based alternative, and an additional benefit of itaconates is that the presence of two ester groups allows for fine tuning of the reactivity of RD and the final properties of the thermoset produced by careful selection of the alkyl groups. The cured thermosets in Spasojevic’s study comprised of dense, tight networks, with Tgs and storage moduli in the range of 65-118 °C and 0.37-1.4 GPa respectively. The cured samples also exhibited moderate stiffness (270-660 MPa) and high break stress (21-54 MPa). Increases in the length/size of the itaconate ester group of the RD decreased the mechanical properties as a consequence of lower reactivity of the diluent, resulting in less effective polymer chain packing.



**Scheme 4.** Itaconate UPEs cured via dialkyl itaconate reactive diluents (RDs).

A range of other diols and diacids (such as succinic, adipic and sebacic acid) have been investigated to both increase the bio-based content and to enhance further the properties of the resulting cured material.44,45 One promising example is glucose-derived bicyclic diol isosorbide, which was found to impart increased Tg and strength to the cured material as a results of increased rigidity in the UPE backbone.46-48 Similarly, 2,5-furandicarboxylic acid (FDCA) has also recently been investigated as a co-monomer in fumarate UPEs, and much like isosorbide is found in increase the Tg and thermal stability of resulting resin due to higher rigidity in the polyester backbone.49

*cis*-*cis*-Muconic is another promising renewable unsaturated dicarboxylic acid readily obtainable from both the lignin and sugars, and represents an excellent candidate for the production of bio-based unsaturated polyesters. It is unique from typical bio-based unsaturated diacid monomers (i.e itaconic and fumaric acid) as it contains a diene, with both C=Cs being electron deficient. Beckham et al.recently demonstrated the successful formation of low molecular weight muconate-succinate co-polymers formed with a range of bio-derivable diols.50 A maximum incorporation of 12.8 mol% muconic acid (relative to the other diacid: succinic acid) was achieved in this study, but still resulting in soluble UPEs. Composite fiberglass panels were subsequently produced by infusing a mixture of low molecular weight poly(butylene succinate-co-muconate) and styrene into a woven glass mat and thermally initiating polymerisation (scheme 5). These partially bio-based thermoset composites possessed shear moduli in excess of 30 GPa, a value typical of current commercial petrochemical-derived composites.



**Scheme 5.** *cis*-*cis*-Muconic acid (MA) and succinic acid (SA) co-polyesters for the production of partially bio-based thermoset fibreglass composites.

Electron-rich pendant C=Cs of terpenes and terpenoids can also be used as a reactive site for curing bio-based unsaturated polymers.51 One very recent example by Sablong et al. prepared a moderate molecular weight poly(limonene carbonate) from the reaction of citrus oil derived limonene oxide with CO2, thiscontaining a pendant exocyclic C=C.52 High Tg thiol-ene click networks (TENs) were subsequently produced by addition of either petrochemical-derived trimethylolpropane tris(3-mercaptopropionate), or bio-derived mercaptanized soybean oil. The resultant TENs also showed promising properties such as high transparency, good acetone resistance and high hardness, suggesting their potential application in coatings.

**4.2. Addition of Pendants via C=C**

Due to the periodically located exo-double bond in the polymer backbone, bio-based polyesters derived from itaconic are interesting structures for post-polymerisation reactions via Michael additions.53 As the first example of a reaction of this type Lv and co-workers reported aza- and thio-Michael additions of an amine and different thiols to an itaconic acid-based polyester obtained by means of acyclic diene metathesis (ADMET) polymerisation (scheme 6).54 These post-polymerisation modifications proceeded with high yields of more than 90% at ambient temperatures without the use of any catalyst, resulting in polyester-itaconates with molecular weights up 33 kg mol-1.



**Scheme 6.** Michael addition of different sulfur and nitrogen nucleophiles to an unsaturated polyester-itaconate.

With this method, it is also possible to introduce two different nucleophiles in the polymer backbone via a one-pot sequential addition procedure. However, in both cases a 15-fold excess of the nucleophiles had to be used. Furthermore, the authors were able to show that sterically demanding primary amines, such as sec-butylamine can also be added to the polyester itaconates at low temperatures (scheme 7). Usually primary and secondary amines undergo an intramolecular reaction after the addition to form a lactam, which leads to the cleavage of the polyester.55-57 At temperatures above 37 °C this reaction indeed takes place, providing a material with a temperature-controlled self-degradation with high potential for biomedical applications.



**Scheme 7.** Temperature dependent degradation of amine-modified polyester itaconates.

In a later example Ramakrishnan and co-worker subjected poly(dodecylitaoncate) to a series of Michael additions also with sulfur and nitrogen-based nucleophiles, such as proline and cysteine (scheme 8).58 Again these addition were almost quantitative and only a slight excess of nucleophiles was used in this case, while *N*-propylamine or LiClO4 were added in catalytic amounts. The molecular weights (M*n*) obtained were very high ranging from 15 to 815 kg mol-1 with broad dispersities. This can be explained by undesired crosslinking reactions of the unsaturated double bonds.



**Scheme 8.** Addition of sulfur- and nitrogen nucleophiles to polyester itaconates.

Meier and co-workers followed a similar approach by reacting aliphatic polyitaconates with three different sulfur nucleophiles in the presence of catalytic amounts of hexylamine.59 Again full conversion of the double bond was observed, resulting in substituted polyester itaconates with molecular weights up to 14 kg mol-1. Subsequently, the corresponding polysulfides were oxidized to polysulfones, revealing the potential of itaconic acid-based polyesters to obtain novel types of bio-based polymers (scheme 9).



**Scheme 9.** Synthesis of polysulfones derived from polyesters based on itaconic acid.

So far the only example of a Michael addition of C-nucleophiles was reported by Farmer et al.60,61 With their procedure, they were able to add acetylacetone and dimethyl malonate to the -unsaturated double bond of polyester itaconates and fumarates (scheme 10). The reactions were performed in the presence of a heterogeneous catalyst under microwave radiation without the use of additional solvents. Like in the other cases, the conversion of the PPM was very high (>95%), and could also be controlled (i.e. restricted to ~50%) by reducing reaction times to several minutes. The resulting modified polyesters exhibited metal chelating abilities and an increase in Tg.



**Scheme 10.** Michael addition of acetylacetonate and dimethyl malonate to polyester itaconate.

**4.3. Diels-Alder additions** **(1,3-cycloadditions)**

Itaconic acid-based polyesters can also be modified by means of 1,3-dipolaric cycloadditions. Ritter et al. were able to show that bio-based dinitrones can be used as crosslinking agents of these polyesters, which results in an increase in the mechanical properties of the materials.62 Diels-Alder reactions can also be exploited as a tool for post-polymerisation of bio-derived polymers. Tang and co-workers developed fatty-acid derived poly (meth)acrylates by an transesterification of vegetable oil with ethanol amine.63 The unsaturated fatty acid pendants were modified via thiol-ene click chemistry to introduce furan moieties, which can be used as dienes in Diels-Alder reactions (scheme 11).64 The addition of suitable succinimid-based bis-dienophile allowed for reversible crosslinking resulting in mendable bio-elastomers.



**Scheme 11.** Fatty acid-derived poly (meth)acrylates with furan moieties than can be used as dienes.

A somewhat similar approach using furan moieties derived from furfuryl alcohol was already reported by Gandini and co-workers in 2002.65 However, in this case the furan building blocks were introduced into a polyacrylate backbone by co-polymerisation of hexylacrylate and 2-furfural acrylate, resulting in a polymer with a low percentage of renewable resources. Later, Yoshie and co-workers synthesized polyesters derived from 2,5-furandimethanol and succinic acid resulting in the incorporation of the diene into the backbone of the polymer.66,67 This kind of polyesters can also undergo reversible cross-linking with bismaleinimids by means of a Diels-Alder reaction.

**4.4. Additions to isolated (non-conjugated) pendant C=C-double bonds**

Many of the above examples represent PPM on electron deficient C=Cs, this often as a result of their conjugation with neighbouring esters groups. However there are examples of bio-based polymers containing isolated, non-conjugated, C=Cs and whose mode of PPM is therefore different. A very interesting example for the post-polymerisation modification of an isolated electron-rich C=C double bonds was recently reported by Greiner and co-workers.68 They modified poly(limone carbonate) PLC, which is accessible by a reaction of limonene oxide with CO2.69 They exploited the C=C double bond of the limonene moiety to add different thiols and polyethylene glycol in high conversions up to 99% (scheme 12). This lead to materials with a wide variety of applications, such as rubbers, hydrophilic and antibacterial polymers.



**Scheme 12.** Post-polymerisation modification of PLC.

A similar approach was undertaken by Sablong and co-workers.70 However, in this case two different marcaptoalcohols were added to the double bond to obtain a set of hydroxy-functionalized PLCs. These were then used as polyol components for polyurethane coatings and the curing kinetics was thoroughly examined.

Kleij and co-workers followed a different strategy to functionalize the unsaturated double bond of PLC.71 In a first step the double bond was epoxidized to the corresponding poly(limonene carbonate oxide) PLCO, followed by a ring-opening with CO2 to obtain poly(limone dicarbonate) PLDC (scheme 13). In both cases, full conversions could be obtained. Depending on the molecular weight of the starting material (1.5 to 15 kg mol-1), different PLDC were synthesized with very high Tg up to 180 °C. In addition, the procedure is compatible with the commercially available mixture of *cis/trans*-(+)-limonene oxide as starting material for the PLC.



**Scheme 13.** Synthesis of poly(limone dicarbonate) PLDC.

Polyesters of methylvinyl glycolate (MVG) represent another pathway to bio-based polymers containing a PPM suitable non-conjugated C=C. MVG is accessible through catalytic degradation of mono and disaccharides, and can be co-polymerised with other bio-based monomers such as lactic acid (via the lactide and the lactone of MVG).72-74 The incorporation of vinyl glycolic acid in polylactic acid-based polyesters and subsequent post-polymerisation modification via thiol-ene click chemistry allowed for tunable hydrophilicity (scheme 14), which is otherwise difficult to attain for pure poly(L-lactic acid).75



**Scheme 14.** Tuned hydrophilicity of PLA co-polymers through PPM of vinyl glycolate units.

In a similar approach, Taarning et al. prepared *trans*-2,5-dihydroxy-3-pentenoic acid methyl ester (DPM) from pentoses using a Sn-Beta zeolite catalyst in methanol (33% yield).76 The purified DPM monomer was subsequently co-polymerised with ethyl 6-hydroxyhexanoate (E6-HH) using CaLB as catalyst, this giving polyesters with Mn over the range 5.2-1.8 kg mol-1 with higher chain lengths observed when the proportion of DPM in feed was reduced (22% relative to E6-HH). PPM was applied by reaction on either the hydroxyl (reaction with trifluoroacetic anhydride, 100% functionalisation possible, links to section 5) or the C=C (thiol-ene click, 30-100% functionalisation possible depending on sterics of thiol), this showing an improvement on the MVG study as two possible sites for PPM can be selectively exploited.

**5. PPM via HYDROXY GROUPS**

Within the list of readily available platform molecules are several polyols (glycerol, sorbitol, mannitol, xylitol etc.) each of which can, through the previously described selective reaction of the primary hydroxyl groups, produce bio-based polymers bearing reactive residual hydroxyls as suitable sites for PPM. You et al. demonstrated how free hydroxyls preserved on poly(sebacoyl diglyceride) can react with maleic anhydride to produce poly(sebacoyl diglyceride) maleic monoester (scheme 15, *a*), achieving 80% esterification by 1H NMR, with an Mn of 25.1 kg mol-1 and Đ of 1.4.22 Preservation of α,β unsaturation on the maleate pendant allows further reaction with an aldehyde or ketone enolate via Michael addition, where the terminal acid group may undergo separate esterification or amidation. Similarly, Wang et al. discussed synthesis of poly(glycerol sebacate) succinate monoester (scheme 15, *b*) giving a 13 mol% of tethered carboxylic acid, relative to total repeating units. After having activated the acid groups using *N*,*N*'-Dicyclohexylcarbodiimide (DCC), the material was reacted with different concentrations of tyramine to give two polymers containing 17 mol% and 26 mol% of the corresponding amide (scheme 15, *c*).77 It is postulated that the discrepancy in mol% of tethered succinic acid versus mol% of tyramine functionalisation relates to amine end capping carboxylic acid groups, along with a degree of aminolysis of the polyester backbone to give lower molecular weight oligomers. Nevertheless, the resulting materials were found to have stronger physical bonding capability and enhanced elastic deformation as a result of the tyramine PPM. Taylor et al. demonstrated the ability to enhance the apparent number-average molecular weights of poly(glycerol sebacate) by crosslinking through urethane linkages via reaction with hexamethylene diisocyanate in varying concentrations (0.5 to 20 mol%) relative to polymer OH groups (scheme 15, *d*).23 Further to this, both You and Taylor synthesised glycerinate functionalised polymers by reaction with fluorenylmethyoxycarbonyl-(Fmoc)-protected glycine using *N*,*N*-diisopropylcarbodiimide (DIC), allowing >95% functionalisation of the OH groups, and N-tert-butoxylcarbonyl (Boc)-protected glycine using DCC to give 90% glycination and a Mn and Đ of 25.1 kg mol-1 and 1.4 respectively. De-protection to the free amine would allow the surface properties to be tailored or allow the possibility of bioconjugation through reaction with carboxylates present on amino acids, peptides, proteins, glycans or biotin, (scheme 15, *e* and *f*). Interestingly, Burdick et al. modified poly(glycerol sebacate) with 5-norbornene-2-carbonyl chloride (scheme 15, *g*) as way of preparing the polymer for thiol–ene click chemistry with pentaerythritol tetrakis (3-mercaptopropionate) and subsequently control amount of crosslinking. Three materials were synthesised containing 11, 15 and 19% norbornene determined by 1H NMR spectroscopy (scheme 15, *h*).78 Increased quantities of crosslinker resulted in materials with increased strength, whilst increased elongation was predominant in samples using lower concentrations of crosslinker.

Literature reporting post-polymerisation modification of poly(glycerol sebacate) alone demonstrates the vast array of chemistry that can be performed on any similar bio-based polymer that contains free hydroxyl groups. As long as such functionality is selectively preserved through the polymerisation stage, the resulting material can be extensively tailored to fit a multitude of applications.



**Scheme 15.** a) maleic anhydride, dimethylformamide (DMF), microwave; b) succinic anhydride, dioxane, pyridine, N2; c) tyramine, DCC / *N*-hydroxysuccinimide (NHS), 4-dimethylaminopyridine (DMAP), N2; d) hexamethylene diisocyanate, CHCl3; e) DIC, DMAP, CHCl3; f) DCC, DMAP, CH2Cl2; g) 5-norbornene-2-carbonyl chloride, triethylamine. h) pentaerythritol tetrakis (3-mercaptopropionate), 2,2-dimethoxy-2-phenylacetophenone UV (365 nm, 10 mW cm−2).

**6. PPM via CHAIN EXTENSION**

Another possibility for post-polymerisation modification of polymers is the use of chain extenders. These usually react with a pre-polymer (i.e. a low molecular weight polymer or oligomer) to form larger chains or networks that completely change the properties of the resulting polymer. The most prominent example in this area are polyurethanes, where hydroxyl-terminated pre-polymers (polyols) are reacted with di- or polyisocyanates via a polyaddition pathway. In this field, a lot of research in the last years has been dedicated to increase the renewable content of this class of polymers. Most of the efforts have been placed on polyol components derived from bio-based building blocks. In this respect, vegetable oils,79-81 lignin,82 carbohydrates,83 and polyols from bio-based monomers have been used as polyol components.84,85 However, one of the major drawbacks in this field and the references cited above is the limited choice of diisocyanates that are to date almost exclusively derived from petrochemical resources. Therefore, the bigger challenge is to find bio-based alternatives to conventional isocyanates.

**6.1. Extension Using Diisocyanates**

The most straightforward approach to bio-based diisocyanates is the use of diamines derived from renewable resources. Maybe the most popular example in this field is pentamethylene diisocyanate and other polyisocyanates that are accessible from this component and are also commercially available.86 Pentamethylene diisocyanate is derived from the pentanediamine, which in turn can be obtained from glucose via a bio-technological pathway involving the decarboxylation of lysine (scheme 16).87



**Scheme 16.** Synthesis of pentamethylene diisocyanate from lysine.

However, this approach still relies on the use of phosgene to introduce the isocyanate group. To circumvent the use of this toxic reagent other ways to introduce isocyanate groups into bio-derived molecules have been reported.88 In this respect, the Curtius-rearrangement has been used in to transform di- and poly carboxylic acids derived from renewable resourced into the corresponding isocyanates. This transformation can be performed by two different pathways:

1. By reacting the carboxylic acid with ethylchloroformat or thionylchloride, followed by an addition of sodium azide (scheme 17, *a*).89,90

2. By treatment with hydrazine, followed by a reaction with nitric acid (scheme 17, *b*).91

In both cases an acyl azide is formed, which rearranges to the corresponding isocyanate.



**Scheme 17.** Curtius-rearrangement of carboxylic acids to isocyanates.

However, this method is currently not applied on industrial scale and the reagents used, such as hydrazine, sodium azide, and ethylchloroformate also suffer from rather high toxicity. In addition, the latter is produced by a reaction of ethanol with phosgene, which only deflects the problem of using this critical reagent to a different stage of the process.

**6.2. Non-Isocyanate Extension**

Non-isocyanate polyurethanes (NIPU) have been introduced as a more sustainable alternative, as the urethane group is introduced by other more benign reaction pathways, avoiding critical reagents.

One possible route are polycondensation reactions of dicarbonates or dicarbamates (scheme 18, *a*). Another pathway is the reaction of cyclic dicarbonates with diamines via a polyaddition mechanism (scheme 18, *b*).92-96



**Scheme 18.** Different routes to non-isocyanate polyurethanes.

The ring-opening reaction of these carbonates leads to polyurethanes with hydroxyl-groups in -position to the urethanes. The influence of this structural difference on the properties of the polymers compared to classical polyurethanes has been intensively studied with a significant difference in solubility and Tg to name but a few.93,97,98

A somewhat special case of this transformation is the reaction of a diamine with two equivalents of ethylene carbonate. This results in the formation of a diurethane diol, which can be further reacted with dicarboxylic acids to obtain different kinds of polyester-polyurethanes.99 Using this method NIPUs without a hydroxyl-group in -position to the urethane can be obtained. However, it should be mentioned that this only allows for an ethylene group as linker between the ester and the urethane group (scheme 19).



**Scheme 19.** Synthesis of polyester-polyurethane starting from a polyurethane diol.

**7. CHEMO-ENZYMATIC FUNCTIONALISATION OF SURFACES**

The interest in the chemo-enzymatic functionalisation of surfaces dates to around 10 years ago when with the first reports on bio-catalysed activations of polyesters and lignin-based materials.100,101 Kudanga and co-workers first functionalized beech wood pieces using a laccase-mediated approach in order to couple phenolic amines on the surface, their function to act as anchor point for subsequent coupling of a fungicide molecule.101 A similar approach was used for the coupling of different types of fluorophenols and dimer fatty amines onto flax and coconut fibres using laccase from *Trametes hirsuta*. The authors also noted that by using different mediators it was possible to enlarge the substrate scope and grafting efficiency of the method.102 Later in 2015 the hydrophobic surface functionalisation of jute fibers (having a middle lamella that is rich in lignin) was also achieved. A first laccase-activation step in order to create free radicals on the surface was followed by the grafting of octadecylamine leading to a hydrophobic material having a water contact angle (WCA) of 116.72° and a wetting time of 18.5 min.103 Further considering lignin, a very elegant approach of note is the enzymatic functionalisation of cork surfaces with antimicrobial hybrid biopolymer/silver nanoparticles. The group led by Prof. Tzanov used amino-functional biopolymers as doping agents to stabilize concentrated colloidal dispersions of silver nanoparticles carrying functionalities that were used in a second laccase-mediated reaction for the covalent immobilisation onto cork, this in order to obtain a durable antibacterial effect of the materials’ surface.104

The second commonly investigated polymers for surface reactions are polyesters, which are widely used in a range of applications going from the automotive industry to the biomedical field. In 2009 Donelli and co-workers presented a detailed study including WCA, FTIR and fluorescence spectroscopy characterisation of enzymatically activated poly(ethylene terephthalate) membranes where the free surface carboxylic groups created from the enzymatic attack were coupled with fluorescent alkyl bromide 2-(bromo-methyl)naphthalene. This report underlines how enzymatic treatment allows the surface functionalisation of very thin polymeric layers while maintaining its bulk properties.100 The “limited surface hydrolysis” concept was developed and extended onto another widespread aliphatic polyester, poly(L-lactic acid) (PLA). In this approach (figure 3) a first enzymatic surface activation step creates hydroxyl and carboxyl groups on the polymer surface (leaving the materials’ bulk properties unaltered) followed by a functionalisation step that could be enzymatic (esterification reaction), electrostatic (polymer-drug interactions) or chemical (direct coupling on the newly created reactive surface groups).

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**Figure 3.** Chemo-enzymatic surface functionalisations of poly(L-lactic acid surfaces) via use of the “limited surface hydrolysis” concept.

Also in this case a limited surface hydrolysis of PLA films was used as activation step for the hydrophilisation of the polymeric surface and the creation of hydroxy and carboxyl groups. In a second step several reactions were carried out including enzymatic esterification of the hydroxyl groups with a fluorinated acid,105 the electrostatic coupling of the chemotherapeutic drug doxorubicin (and its subsequent controlled release in conditions mimicking the physiological environment)106 and the production of a superhydrophobic material via the chemical coupling of a stearic acid-based alkylketene dimer leading to a WCA>150° (figure 3).107

Beyond the enzymatic coupling described on polyesters above, a two enzymatic step approach was also used in order to functionalise polyamide fibres with ferulic acid. In a first step, a polyamidase from *Nocardia farcinica* was used to create some amino surface groups on the polymer that, in a second step, were coupled to ferulic acid using the previously reported laccase from *Trametes hirsuta*.108 A recent work from Song et al. focused instead on the potential of proteases for the hydrophilisation of nylon fabrics in order to create ionic groups that were stained with wool-reactive acid and basic dyes investigating the effect of several reaction parameters such as temperature, pH, enzyme concentration and reaction time.109 A recent publication also highlighted the different hydrolysis pattern between poly(ethylene terephthalate) (PET) and its bio-based counterpart poly(ethylene furanoate) (PEF). The authors, while performing the enzymatic hydrolysis of various surfaces (thin films and spin coated) noticed a remarkable 1.7 times faster hydrolysis of PEF and a strong negative effect of the polymer’s crystallinity on the hydrolysis rate.110 The enzymatic functionalization of surfaces is therefore an appealing strategy when the modification of the outer layers of polymer films and micro structures are desired but where maintaining its bulk properties is also necessary. This may not otherwise be achievable by traditional techniques like harsh chemical treatments, such as NaOH that would penetrate into the bulk of the material and deeply affecting the molecular mass and mechanical properties,106 or plasma which cannot reach the farthest corners and regions of complex structures (i.e. the functionalization of the inner part of a cylindric structure).

**8. OUTLOOK**

This review gives and overview of how the inherent chemical functionality of platform molecules (i.e. bio-based building-block chemicals) can be carried through to bio-based monomers and eventually to their polymers. These functional groups act as sites for post-polymerisation allowing for the properties of the final polymers to be fine-tuned to address the needs of the user. As such the increased functionality of bio-based monomers, relative to their petrochemical counterparts, should be embraced and not discarded (as they would be through the short-term view of targeting bio-based drop-in replacements to current fossil-derived monomers). This approach is succinctly captured by the concept of “bio-privileged molecules”, whereby we should be actively seeking to utilise the higher functionality of bio-based chemicals to yield new products with enhanced performance over petrochemical derived equivalents, those that bio-based polymers will eventually supplant.111

The field of PPM on bio-based polymers is rapidly growing and has significant scope for further development beyond the examples highlighted herein. New tools and techniques are continually being developed to assist those trying to exploit the functionality of bio-based polymers, but now greater details are needed on the effects these modifications have to final polymer properties, such as processability, biodegradability and cost.

Although briefly highlighted within this review the authors would anticipate growing prevalence of bio-based composite materials, where bio-based UPEs are cured in the presence of plant fibres to address a range of applications.112 As research continues new bio-based monomers will also become available to polymer producers, further increasing the choice of final polymer properties and options for PPM. One recent area of growing interest is in novel bio-based oxo-norbornene monomers for ring-opening metathesis polymerisation (ROMP).113-115 However, although several examples exist of functional bio-based polymers being produced in this fashion, there is currently no example of the residual C=C functionality being exploited for PPM. The promise for this approach is however clear, as PPM (thiol-ene click and bromination-nitroxide radical coupling) has been applied to petrochemical derived polymers produced from ROMP of norbornenes.116-117 Another emerging bio-based monomer of interest to this field is the diester dimethyl-2,5-dihydroxy-3-hexenedioate (DMDHHD), produced from the metathesis of the aforementioned MVG. DMDHHD has already been used to produce polyesters or polyamides containing C=C as sites from functionalisation, but as yet has not been exploited for PPM studies.118

This mini review also showed a mixture or both fully and partially bio-based polymers, it is indeed currently often found that either the functional group on the polymer, or the reagent it is being reacted with, is petro-chemically derived. Therefore, greater effort is required to ensure that the final polymers are wholly bio-derived, and that any procedure used to produce them is as environmentally benign. Despite this, it cannot be denied the exciting opportunity over the coming years to prepare a diverse range of tuneable polymers through the utilisation of highly functional bio-derived polymers coupled with the application of post-polymerisation modification.

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