Progress Toward Sustainable Reversible Deactivation Radical Polymerization

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The recent focus of media and governments on renewability, green chemistry, and circular economy has led to a surge in the synthesis of renewable monomers and polymers. In this review, focussing on renewable monomers for reversible deactivation radical polymerizations (RDRP), it is highlighted that for the majority of the monomers and polymers reported, the claim to renewability is not always accurate. By closely examining the sustainability of synthetic routes and the renewability of starting materials, fully renewable monomers are identified and discussed in terms of sustainability, polymerization behavior, and properties obtained after polymerization. The holistic discussion considering the overall preparation process of polymers, that is, monomer syntheses, origin of starting materials, solvents used, adaptations are made.

1. Introduction

Reversible deactivation radical polymerizations (RDRP) have revolutionized the synthesis of polymers over the last few decades as they offer unprecedented control over the growing chains, allowing for the precise design of polymers. Whether it is the degree of polymerization, the composition, the polymer architecture, or the selective functionalization of the chain ends, RDRPs allow to tune and dictate these parameters and a few high-value industrial applications have already emerged.[1,2] Classically, monomers used for RDRP are based on petroleum as they are easily obtained as side streams from the cracking of crude oil. In light of global warming and pollution caused by single-use plastics, the shift toward renewable resources has gained increased attention from politicians, the media, and governments, as exemplified by the proposed action plan for a circular economy in the European Union.[3] Renewable polymers are promising in this respect as, at least in principle, a closed loop of CO₂ can be obtained if the polymers are made from 100% renewable resources and are burned at the end of their life cycle, releasing no additional CO₂ into the atmosphere. Of course, recycling and/or other material recovery options for the end-of-life of polymers would be even more environmentally benign. In this sense, the progress made in the field of green chemistry[4] over the last 20 years has provided the framework and tools to apply these aspects to monomers for RDRP. However, the extraction or synthesis of renewable-sourced monomers for radical polymerizations is not trivial, as not many natural substances contain polymerizable double bonds.[5–7] Most prominent examples of suitable feedstocks include terpenes, itaconic acid, and lignin (Figure 1). However, the majority of literature-described bio-based monomers are not obtained applying sustainable approaches throughout and often combine non-renewable polymerizable moieties with renewable platform molecules. A typical strategy in this regard is the derivatization of a hydroxy group with (meth)acryloyl chloride to give the respective (meth)acrylate monomer.[8] A multitude of resources have been subjected to this strategy, ranging from the abovementioned terpenes and lignin, to carbohydrates and triglycerides (Figure 1). While this has allowed to prepare a large library of partially bio-based monomers for radical polymerizations, their synthesis most often involves toxic acyl chlorides,[9] harmful to the environment, generating stoichiometric amounts of hydrochloride salt as waste, which is typically neutralized with stoichiometric amounts of base. Additionally, many bio-derived monomers contain a significant fraction of non-renewables and, as herein consider renewability in

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terms of the origin of the respective atoms, the term renewable monomer should be used with caution. An easy way to highlight this is to count the number of atoms originating from renewable and non-renewable resources. For example, while methyl 10-(acryloyloxy)-9-hydroxyoctadecanoate (Figure 1) has a relatively high number of renewable atoms (60 of 90), correlating to 83 wt% renewable content, creosyl methacrylate (Figure 1) contains only 19 renewable atoms out of a total of 29, that is, 67 wt% renewable content. Therefore, the synthesis of such (meth)acrylate monomers does not follow all the 12 principles of green chemistry and is thus not sustainable in most cases. Numerous previous reviews have discussed such partly renewable monomers (red squares – dashed, Figure 1); for instance Fiona L. Hatton recently summarized such monomers used for RAFT polymerizations,[8] and the reader is directed to these reviews for more detailed information on the synthesis and polymerization of such partially and often non-sustainable monomers.[5-7,10-13] The focus of this manuscript lies with fully renewable monomers obtained either directly from plants or via synthetic pathways that can be considered sustainable (green squares – line, Figure 1) and the polymerization of such monomers using RDRP techniques to give fully renewable polymers. It is noted that our aim is to establish a short-term milestone within renewable and sustainable RDRPs and to invite scientists

![Diagram of Renewable Resources](https://example.com/renewable-resources.png)

**Figure 1.** Overview of the types of monomers available from renewable resources that have been polymerized using RDRP techniques. The monomers highlighted by a green square are the subject of this review, while those in a red dashed square are partially renewable and have been summarized elsewhere.[5-8,10-13]
2. Sustainability of RDRP Techniques

Prior to starting the discussion on monomer synthesis and their polymerization, it is important to compare the sustainability aspects of the different RDRP techniques mentioned in this manuscript. This is an important exercise, as the necessary reagents significantly contribute to the overall sustainability, but this has not been considered so far when discussing partially renewable monomers for RDRP. The two techniques most often employed are atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain-transfer (RAFT) polymerization, while nitroxide-mediated polymerization (NMP) and organometallic-mediated radical polymerization (OMRP) have also been used. While the precise mechanism of each technique is outside of the scope of this review—and can be found in other reviews[19–25]—the components of each of these systems and the synthetic pathways will be highlighted. Special emphasis will be put on sustainability in the discussion and the environmental factor (E-factor) is calculated for some of the employed RDRP techniques. The E-factor gives an appreciation for the amount of waste generated compared to that of the product obtained[26] and will be calculated as defined by Sheldon for the different RDRP techniques starting from commercial reagents.

\[
E \text{factor} = \frac{\text{waste (g)} - \text{product (g)}}{\text{product (g)}} \quad (1)
\]

It is worth noting that for the calculation of the E-factor, the sustainability of the reactants and reagents is not taken into account. However, this number is an indication of the sustainability of the process and serves to compare different procedures, among other parameters as discussed above. All the E-factors, 29 in total, were ranked from highest (1886) to lowest (3) and will be highlighted throughout the schemes and tables using a three-color scale using green for the lowest values, orange for the middle ones, and red for the highest ones. If several synthetic steps are involved in the overall synthetic pathway, the accumulated E-factor is also indicated, thus considering all synthesis steps up to that point. All detailed E-factor calculations are provided in the Supporting Information.

2.1. ATRP

ATRP relies on a catalyst, typically copper, a halide-containing initiator, and ligands which stabilize the copper (see Scheme 1 for example), Copper (I) chloride (CuCl) is often employed in ATRP and is industrially produced by reacting metallic copper and chlorine gas at elevated temperatures (450–900 °C).[27] Chlorine is a very toxic gas with an LC50 of 0.65 mg m⁻³ and is also very toxic to aquatic life. CuCl can also be obtained hydrothermally through the reduction of Cu(II) in the presence of chloride ions. Both processes are atom efficient and can be considered as relatively sustainable. CuCl₂ is often employed in ATRP to tune the rate of the reaction and is produced by reacting copper (II) oxide, carbonate, or hydroxide with a hydrochloric acid solution at 120 °C.[27] Both CuCl and CuCl₂ are classified as harmful and have oral LD₅₀ of 336 and 584 mg kg⁻¹ bw, respectively. Depending on the starting copper (II), this process generates a stoichiometric amount of water or hydrogen carbonate as waste, with the former having to be removed from the solution. Hydrochloric acid is produced by dissolving chlorine gas in water while chlorine gas is industrially obtained through the electrolysis of aqueous sodium chloride solutions producing chlorine, hydrogen, and sodium hydroxide.[28] This process is very energy-intensive and requires a constant feed of rock salt, which itself needs to be obtained via mining or evaporation of sea water, but the overall process is still sustainable as all of the side products are valuable platform chemicals. The bromine analogues of the aforementioned copper salts, CuBr and CuBr₂, are obtained analogously to CuCl and CuCl₂, that is, via hydrometallurgy of copper(II) sulfate and sodium bromide or through the reaction of copper(II) oxide with hydrobromic acid.[27] Unlike their chloride analogues, they are not classified as toxic but both CuBr and CuBr₂ are very toxic to the aquatic environment. Alternatively, metallic copper can be directly treated with bromine water.[27] The former process generates a stoichiometric amount of sodium sulfate waste, which needs to be removed from the solution, while the latter two processes produce water or no waste, respectively, and are therefore more sustainable synthetic methods. In addition, sodium sulfate has an oral LD₅₀ of >2000 mg kg⁻¹ bw and an LC₅₀ of >2000 mg m⁻³. Iron (III) chloride is another ATRP catalyst and is readily and cheaply available. It is mainly
produced by the chlorination of iron scraps with chlorine gas (toxic, see above), but is also a by-product of metallurgical and chemical processes.\[29\]

Another commercial ATRP catalyst described in this manuscript is based on iron (III) bromide (FeBr$_3$) with an 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene ligand (Scheme 1). FeBr$_3$ is easily available by reacting iron oxide with hydrogen bromide. The catalyst is obtained by reacting the iron salt with the N-heterocyclic carbene (NHC, here 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in tetrahydrofuran (THF) at room temperature.\[30\] The NHC itself is obtained via a four step procedure.\[31\]

First oxaldehyde is reacted with 2,6-diisopropylphenylamine to yield the corresponding glyoxal imines, which are subsequently reduced by sodium borohydride in THF, followed by an acidification to yield the diamine dihydrochloride salts. Sodium borohydride may damage the fertility of an unborn child, is toxic with an oral LD$_{50}$ of 56.57 mg kg$^{-1}$ and an LC$_{50}$ of 1300–5180 mg m$^{-3}$. It furthermore releases flammable gases upon contact with water. It is obtained by reacting boric acid esters with sodium hydride, with the latter being obtained by the addition of sodium metal to hydrogen gas in paraffin oil.\[32\] The diamine salts are then cyclized through treatment with triethyl orthoformate and subsequently deprotonated with potassium hydride. Potassium hydride is obtained akin to sodium hydride.\[32\] The overall synthesis of this iron-NHC catalyst is thus not based on renewable resources and, given the number of steps often times generating stoichiometric amounts of waste, also not sustainable.

The last type of ATRP catalyst that concerns reactions mentioned in this review is based on ruthenium (II) complex with a cyclopentadienyl, a chloride, and two triphenylphosphine (PPh$_3$) ligands (Scheme 1). Nowadays it is commercially available and is likely synthesized by refluxing ruthenium (III) chloride trihydrate in ethanol (EtOH) in the presence of cyclopentadiene and triphenylphosphine.\[33,34\] Ruthenium chloride, typically in the form of RuCl$_3$·H$_2$O and Ru(OH)Cl$_3$, is obtained by treating ruthenium (IV) oxide (RuO$_4$) with hydrochloric acid. Ruthenium oxide, in turn, is obtained via its distillation from aqueous solutions containing a mixture of platinum group metals.\[35\] It should be emphasized that ruthenium is a rare earth metal and is part of the critical raw material list of the European Union.\[36\] Cyclopentadiene is unstable above –70 °C and readily dimerizes to form dicyclopentadiene, with the reverse process requiring the input of energy, that is, temperatures above 160 °C.\[37\] It is a toxic chemical, with an LD$_{50}$ of 590 mg kg$^{-1}$ bw for oral intake and an LC$_{50}$ of 1972 mg m$^{-3}$ via inhalation, and is hazardous to aquatic life. It is obtained industrially from the C$_5$ fraction of cracked naphtha,\[37\] and is thus neither sustainable nor renewable. Triphenylphosphine (PPh$_3$) is a sensitizer and has LD$_{50}$s of 700 mg kg$^{-1}$ bw for oral routes, >4000 mg kg$^{-1}$ bw for dermal routes, and an LC$_{50}$ of 12500 mg m$^{-3}$. PPh$_3$ is obtained by reacting phosphorous trichloride (PCl$_3$) with chlorobenzene and metallic sodium, generating six equivalents of sodium chloride waste.\[38\] PCl$_3$ is made by reacting elemental phosphorous (P$_4$) with chlorine gas,\[39,40\] while chlorobenzene is obtained by reacting benzene with chlorine gas at 20–80 °C using a Lewis acid catalyst, for example, FeCl$_3$.\[41\] Hydrogen chloride is formed as a side product of this process, but most importantly, benzene and chlorine are both non-renewable chemicals\[28,42–44\] and chlorine is additionally toxic, while benzene is classified as carcinogenic.

Apart from the ligands necessary for the above ruthenium complex, three other ligands will be mentioned in this manuscript, 2,2′-bipyridine (bipy), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), and tributylamine (nBu$_3$N), all

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**Scheme 1.** The chemical structures of catalysts, ligands, and initiators used for ATRP polymerizations reviewed in this article. The oral LD$_{50}$ values in mg kg$^{-1}$ bw are shown for the catalysts, ligands, and initiators where available.
of which are toxic chemicals (Scheme 1a). Bipy has an oral LD$_{50}$ of 100–350 mg kg$^{-1}$ bw and a dermal of 400–600 mg kg$^{-1}$ bw, while PMDETA has an oral, dermal, and inhalatory toxicity of 1330 mg kg$^{-1}$ bw, 200–1000 mg kg$^{-1}$ bw, and 2056 mg m$^{-3}$, respectively. nBu$_3$N has an acute oral toxicity of 420 mg kg$^{-1}$ bw, an acute dermal toxicity of $>$2000 mg kg$^{-1}$ bw, and a toxicity via inhalation of 500 mg m$^{-3}$. Bipy is obtained by dimerizing pyridine in the presence of a Raney nickel catalyst, with pyridine, in turn, being synthesized from acrolein, ammonia, and acetaldehyde at 350–550 °C over solid catalysts, mainly based on silicon oxide and aluminum oxide. While acrolein can be obtained in a sustainable fashion from renewable resources via the dehydration of glycerol, ammonia is still obtained through the Haber–Bosch process, which uses coal- or petrol-based syngas as hydrogen source. Acetaldehyde is industrially produced mainly through the Wacker process from ethylene or via the dehydrogenation of ethanol. Both processes can in principle be renewable if bioethanol and bioethylene are used and produce water or no waste products. Commercially available PMDETA is synthesized from diethylenetriamine, formaldehyde, and formic acid at 120 °C in water. Diethylenetriamine can either be obtained as a side product from the production of 1,2-diaminoethane from 1,2-dichloroethane and ammonia or in a more selective hydrogenation reaction of diaminoethane and hydrogen over a metal catalyst. 1,2-Dichloroethane is commonly obtained from ethylene and chlorine or hydrogen peroxide. While dimethyl-2-chloro-2,4-trimethylglutarate (DCTG) is industrially produced as a side product of the cumene process, as renewable synthetic pathways, for example via fermentation processes, are currently not industrially implemented. Most unsustainable, however, is its reaction with sodium cyanide, a highly toxic chemical with acute oral, dermal, and inhalatory toxicities of 5 mg kg$^{-1}$ bw, 11 mg kg$^{-1}$ bw, and 103 mg m$^{-3}$, respectively, which is also hazardous to aquatic environments. This reaction produces acetone cyanohydrin (Scheme 2), a chemical toxic for aquatic life and humans, with an LD$_{50}$ of 17 mg kg$^{-1}$ bw for oral routes, 16 mg kg$^{-1}$ bw for dermal routes, and an LC$_{50}$ of 223 mg m$^{-3}$, generating a stoichiometric amount of sodium sulfate waste (also toxic, see above). The production of hydrazine, another toxic chemical with an LD$_{50}$ of 108–173 mg kg$^{-1}$ bw and an LC$_{50}$ of 759 mg m$^{-3}$, is more sustainable as it is produced via the oxidation of ammonia using chlorine, oxygen, or hydrogen peroxide. Ammonia is obtained through the Haber–Bosch process, which is currently not renewable as it
relies on hydrogen mainly produced via the syngas process, but itself is a catalytic and sustainable procedure. The subsequent oxidation of ammonia to hydrazine could potentially be renewable and sustainable if oxygen is used as the oxidant releasing only water as waste. Overall, the synthesis of AIBN is therefore currently not sustainable or fully renewable. In addition, AIBN is harmful to aquatic life and is toxic to humans with an LD$_{50}$ of 300–2000 mg kg$^{-1}$ bw for oral routes and $>$2000 mg kg$^{-1}$ bw for dermal routes. Nonetheless, when taking into account the equivalents of AIBN typically needed for RAFT polymerizations, as the CTA and monomer are typically used in 10 to 1000 times excess,[22] the impact is limited.

The 18 different CTAs encountered in this review are shown in Scheme 2. The sheer number of CTAs available makes the detailed analysis of each synthetic pathway impractical—and can also be found in the literature[68]—and thus only the synthetic pathways of a representative and often applied CTA, namely 2-cyanoprop-2-yl dithiobenzoate (CPDB), will be discussed here exemplarily. CPDB can be prepared via two pathways: either by reacting commercially available bis(thiobenzoyl)sulfide with an excess of AIBN in ethyl acetate (EtOAc) under reflux,[69] or by reacting 2-bromo-2-cyanopropane with magnesium benzodithioate (Scheme 2).[70] None of the synthetic pathways for AIBN (see discussion above), bis(thiobenzoyl)sulfide, or 2-bromo-2-cyanopropane are currently sustainable or based on renewable molecules.


<table>
<thead>
<tr>
<th>Entry</th>
<th>Technique</th>
<th>Controlling agent</th>
<th>Solvents</th>
<th>Toxic chemicals (LD$_{50}$/Critical raw materials)</th>
<th>E-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ATRP</td>
<td>DCTG</td>
<td>Hex$^a$</td>
<td>CCl$_4$ (Oral: $&gt;$2000 mg kg$^{-1}$ bw; inhalation: 20 000 g m$^{-3}$) Mel (Oral: 80–132 mg kg$^{-1}$ bw, inhalation: 4011 mg m$^{-3}$)</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>RAFT</td>
<td>CPDB Route 1</td>
<td>THF$^a$</td>
<td>Br$_2$ (Inhalation: 0.7 mg m$^{-3}$)</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>RAFT</td>
<td>CPDB Route 2</td>
<td>THF$^a$, EtO$_2$</td>
<td>CS$_2$ (Oral: $&gt;$2000 mg kg$^{-1}$ bw, inhalation: 10 000 mg m$^{-3}$)</td>
<td>60$^a$</td>
</tr>
<tr>
<td>4</td>
<td>NMP</td>
<td>SG1</td>
<td>EtO$_2$</td>
<td>$^3$Bu$_2$N (Oral: 420 mg kg$^{-1}$ bw, dermal: $&gt;$2000 mg kg$^{-1}$ bw, inhalation: 500 mg m$^{-3}$)</td>
<td>148$^a$</td>
</tr>
<tr>
<td>5</td>
<td>NMP</td>
<td>BB</td>
<td>EtO$_2$, DCM$^a$, H$_2$O$_2$</td>
<td>Bipy (Oral: 100–350 mg kg$^{-1}$ bw, dermal: 400–600 mg kg$^{-1}$ bw)</td>
<td>373$^a$</td>
</tr>
<tr>
<td>6</td>
<td>NMP</td>
<td>NHS-BB</td>
<td>THF$^a$</td>
<td>DCC (Oral: 1110 mg kg$^{-1}$ bw, inhalation: 159 mg m$^{-3}$)</td>
<td>394$^a$</td>
</tr>
<tr>
<td>7</td>
<td>NMP</td>
<td>PE-TIPNO</td>
<td>EtO$_2$, MeOH$^a$, DCM$^a$, H$_2$O$_2$, THF$^a$, CHCl$_3$, Toluene$^a$</td>
<td>Hydrazine (Oral: 108–173 mg kg$^{-1}$ bw, inhalation: 759 mg m$^{-3}$) PbO$_2$ (Oral: $&gt;$2000 mg kg$^{-1}$ bw)</td>
<td>286$^a$</td>
</tr>
<tr>
<td>8</td>
<td>OMRP</td>
<td>Alkylcobalt</td>
<td>DCM$^a$, EtOAc$^+$</td>
<td>Co(acac)$_2$ (Oral: 300–2000 mg kg$^{-1}$ bw, dermal: $&gt;$2000 mg kg$^{-1}$ bw, inhalation: 5090 mg m$^{-3}$) VAc (Oral: 3500 mg kg$^{-1}$ bw, inhalation: 14 000–15 800 mg m$^{-3}$)</td>
<td>13$^a$</td>
</tr>
</tbody>
</table>

Full E-factor calculations are provided in the Supporting Information. $^a$E-factor calculation without column chromatography purification as data not provided in literature report.
both originating from fossil fuels, followed by an oxidation using potassium ferricyanide in a water/ethanol mixture (Scheme 2).\(^{[72]}\) While the Grignard reaction is highly unsustainable, as it requires strong cooling and generates stoichiometric amounts of waste, the chemicals used are also problematic. Bromobenzene has an oral LD\(_{50}\) of 2380 mg kg\(^{-1}\) bw and LC\(_{50}\) of 29 700 mg m\(^{-3}\), and is toxic to aquatic life, while CS\(_2\) is suspected of damaging fertility and has an oral LD\(_{50}\) of >2000 mg kg\(^{-1}\) bw and an LC\(_{50}\) of 10 350 mg m\(^{-3}\). Yet, as both AIBN and bis(thiobenzoyl)sulfide are commercially available, the majority of the synthetic steps are not included in this calculation leading to an E-factor, 6 (entry 2, Table 1), drastically lower than its “true” value. It should be mentioned that due to the lack of information, the column chromatography purification performed for this route is not included in the E-factor and thus again the actual value is anticipated to be much higher than the one calculated here.

A similar E-factor, which however does not consider the purification step, was calculated for the second synthetic route. The second route uses 2-bromo-2-cyanopropane, which can be obtained by reacting 2-cyanopropane with tribromophosphine and bromine (Scheme 2).\(^{[75,76]}\) Not only is bromine extremely toxic, with a respiratory LC\(_{50}\) of 0.7 mg m\(^{-3}\), and hazardous to aquatic environments, but additionally hydrogen bromide is produced as a side product, which is corrosive, making this reaction unsustainable. While 2-cyanopropane can in

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**Scheme 2.** Chemical structures of chain transfer agents (CTAs) used for RAFT polymerizations reviewed in this article, as well as the synthetic pathways to AIBN,\(^{[65,71]}\) bis(thiobenzoyl)sulfide,\(^{[72–74]}\) and CPDB.\(^{[69,70]}\) * E-factor does not include column chromatograph purification. The units for reported oral LD\(_{50}\) values are mg kg\(^{-1}\) bw and mg m\(^{-3}\) for LC\(_{50}\).
principle be obtained renewably by reacting biobutanol with ammonia,[59] neither tribromophosphine nor bromine can be renewably sourced. In addition, tribromophosphine is a toxic chemical with an oral LD$_{50}$ of <50 mg kg$^{-1}$ bw and an LC$_{50}$ of <1000 mg m$^{-3}$. 2-Bromo-2-cyanopropane is then further reacted in THF with magnesium benzodithioate, obtained via a Grignard reaction on bromobenzene, followed by the addition of carbon disulfide, to yield CPDB in 32% overall yield.[70] The E-factor for this synthetic pathway is 61 (entry 3, Table 1), excluding the column chromatography of the last step, and is thus significantly higher than that for route 1, mainly as a result of the significantly lower yield and the need to synthesise these molecules rather than being commercially available.

### 2.3. NMP

NMP is based on the reversible homolytic scission of a carbon-nitrogen bond on an alkoxyamine with the polymerisation control being a result of the persistent radical of the nitroxide-based radical.[23,77] The NMP controlling agents mentioned in this review are based on N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide (SG1; Scheme 3), either bearing isobutyric acid (BB) or its succinimidyl ester–terminated analogue (NHS-BB), and N-tert-butyl-N-(2-methyl-1-phenylpropyl)-O-(1-phenylethyl)hydroxyl-amine (PE-TIPNO; Scheme 3). Both SG1 and PE-TIPNO are commercially available, while BB and NHS-BB are both synthesized from SG1. SG1 is obtained via a two-step reaction starting from 2,2-dimethylpropanal and tert-butylamine to give 2,2-dimethyl-1-(1,1-dimethylethylamino) propyl diethyl phosphonate in the presence of diethyl phosphate. The amine is subsequently oxidised using 3-chloroperbenzoic acid (mCPBA) in dichloromethane (DCM) to give SG1 (Scheme 3).[78,79] Other more sustainable oxidation pathways have also been reported.[80] None of the reagents used are obtained from renewable resources, for example, 2,2-dimethylpropanal is either obtained as a side product in the hydroformylation of isobutene to produce 3-methylbutanal or through the isomerization of 1,1,2-trimethyloxirane,[81] and the synthetic pathway generates a stoichiometric amount of 3-chlorobenzoic acid waste. In addition, tert-butylamine is a toxic chemical with oral and dermal LD$_{50}$ of 464 mg kg$^{-1}$ bw and 2000–3600 mg kg$^{-1}$ bw, and an LC$_{50}$ of 3800 mg m$^{-3}$. Most importantly, however, the isolation of the final product requires the use of column chromatography and the yield of the two synthetic steps is low, 40%, which leads to a high E-factor of 460 (entry 4, Table 1). Since some of the literature reports do not state the exact amounts of silica and solvents needed for the column chromatography, and

![Scheme 3. Synthetic pathways and respective E-Factors for the alkoxyamine controlling agents used for NMP in this review: SG1,[78,79] BB,[82] BB-NHS,[83] and PE-TIPNO.[84] * E-factor reported without column chromatography purification. The units for reported oral LD$_{50}$ values are mg kg$^{-1}$ bw.](image-url)
to allow for a better comparison to other controlling agents, the E-factor without column is also calculated (Table 1).

BB is synthesized by using a copper catalyst to homolytically cleave the C-Br bond in 2-bromo-2-methylpropionic acid, generating a carbon-centered radical which is quickly quenched by SG1. The reaction also requires the use of bipy as ligand and is performed in acetonitrile (Scheme 3). Bipy, as outlined above, is not currently available from renewable resources. 2-methyl-2-bromopropionic acid is most likely obtained by treating isobutyric acid with tribromophosphine and bromine. Isobutyric acid, in turn, is produced through the oxidation of isobutyraldehyde, a side product of the hydroformylation of propene, with renewable alternatives, such as the dehydrogenation of biobutanol, currently not being employed. While the reaction has a decent yield, 87%, the extraction procedure reported for the small scale process leads to a large E-factor of 225 (see Supporting Information, which can likely be decreased on a larger scale. This E-factor is only for the BB synthesis starting from SG1 (see Supporting Information for detail), and if SG1 is considered in the BB E-factor, the overall E-factor increases to 373 without, and 685 with column chromatography purification in the SG1 synthesis (entry 5, Table 1).

NHS-BB is obtained through a dicyclohexylcarbodiimide (DCC) coupling of the acid residue of BB with N-hydroxysuccinimide (Scheme 3). While both DCC and N-hydroxysuccinimide are available commercially, only N-hydroxysuccinimide is at least partially available from renewable resources. DCC is a suspected carcinogen, and has an acute oral, and inhalational toxicity of 1110 mg kg\(^{-1}\) bw, and 159 mg m\(^{-3}\), respectively. DCC is made from dicyclohexylthiourea, which is in turn made from isocyanates, carbon disulfide or phosgene in basic media. Phosgene is a chemical weapon with an acute toxicity via inhalation of 8.6 mg m\(^{-3}\), and thus both DCC and phosgene are not sustainable and need to be replaced by safer alternatives. N-hydroxysuccinimide, on the other hand, is obtained from succinic acid, which in turn can be obtained renewably from the fermentation of glucose. The E-factor for this synthetic step is 21 (see Supporting Information for details) and is kept in THF-x-diethyl ether (Et\(_2\)O), followed by oxidation using ammonium hydroxide and copper acetate in MeOH\(^{a}\) to yield TIPNO (Scheme 3). Both reaction steps use a large excess of zinc or phenylmagnesium bromide generating large amounts of waste which, along with the mediocre yield of 60%, is reflected in a high E-factor of 124 (see Supporting Information for details). It should be mentioned that the column chromatography purifications performed to isolate both the intermediate and TIPNO are not included in this calculation. TIPNO is then reacted with benzyl hydrazine in toluene\(^{a}\) in the presence of lead dioxide to give PE-TIPNO in 73% yield. Lead oxide has an LD\(_{50}\) of >2000 mg kg\(^{-1}\) bw, is very toxic to aquatic life, and may damage fertility, an unborn child and organs through exposure. Benzyl hydrazine is in turn obtained by reacting benzylbromide with hydrazine (toxic, see above) in Et\(_2\)O\(^{a}\), with benzylbromide originating from non-renewable ethylbenzene and bromide (highly toxic, see above). The large amounts of solvents needed and the excess of lead dioxide used lead to a high E-factor of 162 for this step, again not including the column chromatography purification necessary (see supporting information). Therefore, the overall E-factor of the PE-TIPNO synthesis is 286 (entry 7, Table 1).

2.4. OMRP

OMRP is based on the reversible scission of a carbon-transition metal bond and the commonly encountered metals are cobalt, iron, osmium, titanium, molybdenum, and chromium. Unlike ATRP, a stoichiometric amount of the controlling species, that is, the metal complex, is needed as all of the propagating chains need to be end-capped by the controlling agent. Thus the sustainability of the metal complex weighs heavily in the overall sustainability of the polymerization process. An indicative comparison of the abovementioned metals in terms of sustainability can be obtained by comparing the abundance of these metals on earth. Iron and titanium are the most abundant, with abundancies in the earth's crust of 6% and 0.6%, osmium is the least abundant with 10\(^{-7}\)% while chromium, cobalt, and molybdenum lie in between with abundancies of 0.01%, 0.0029%, and 0.00012%, respectively. Evidently, abundance is not the only criterion for sustainability of a metal and factors such as recyclability and ease of recovery also play a key role. Another important aspect of sustainability is toxicity. In terms of toxicity, the exact oxidation state of each metal species strongly impacts the toxicity and thus it is difficult to draw an accurate general conclusion for each metal. We therefore refrain from making oversimplified and possibly misleading statements, as depending on the oxidation state and ligands, each metal used for the controlling agents would have a different toxicity.

The alkylcobalt species mentioned in this review is synthesized from cobalt(II) acetylacetonate (Co(acac)\(_2\)), vinyl acetate (VAc), and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70) (Scheme 4). Both Co(acac)\(_2\) and VAc are toxic agents considered herein (entry 6, Table 1).

The last alkoxyamine discussed in this paper is PE-TIPNO, which is a modified version of TIPNO (Scheme 3). TIPNO is synthesized in a two-step procedure from 2-methyl-2-nitropropane and isobutyraldehyde\(^{84}\) with the latter having oral and dermal LD\(_{50}\)s of 3730 mg kg\(^{-1}\) bw and 5580 mg kg\(^{-1}\) bw, respectively, and an LC\(_{50}\) of 23 000 mg m\(^{-3}\). Both reagents are obtained from non-renewable resources, that is, tert-butylamine, and hydroformylation of propene, respectively. Using water as the solvent and an excess of zinc in the presence of ammonium chloride, the nitrate intermediate is obtained, to which benzene is added through a Grignard reaction in THF-diethyl ether\(^{a}\) (Et\(_2\)O), followed by oxidation using ammonium hydroxide and copper acetate in MeOH\(^{a}\) to yield TIPNO (Scheme 3). Both reaction steps use a large excess of ammonium hydroxide and copper acetate in MeOH\(^{a}\) to yield TIPNO (Scheme 3).
chemicals with Co(acac)₂ having an acute oral, dermal, and respiratory toxicity of 300–2000 mg kg⁻¹ bw, >2000 mg kg⁻¹ bw, and 5090 mg m⁻³, VAc has an acute oral and inhalation toxicity of 3500 mg kg⁻¹ bw, and 14 000–15 800 mg m⁻³. This bulk reaction, using an excess of vinyl acetate and V70, is followed by column chromatography under an inert atmosphere using DCM and EtOAc as eluent. While vinyl acetate can in principle be renewably-sourced from bioethanol and acetic acid in a catalytic process, V70 is obtained in a similar process to AIBN and is not renewably-sourced. In addition to the fact that cobalt is a critical raw material, the vast amounts of solvent and silica needed for the preparation of the R-Co(acac)₂ controlling agent leads to the second highest E-factor of all techniques mentioned in this review, an accumulated waste of 626 kg kg⁻¹ product (entry 8, Table 1).

The above discussion and table clearly highlight the unsustainable and non-renewable nature of the controlling agents discussed herein and typically applied in RDRP techniques. However, recent developments in ATRP using metal-free photocatalysts, decreasing the copper content to a few ppm, as well as the recycling of the metal used in ATRP or OMRP appear to be conducive to more sustainable polymerization techniques. Nonetheless, the unique ability of these RDRP techniques to control the chain growth process, and thus the final characteristics of the polymer, may justify their use even though they are inherently not environmentally friendly.

It is also obvious that a direct comparison of the different synthetic pathways is not always possible, as sometimes the purification data is missing and reagents are commercially available. The latter is especially significant as industrial syntheses of controlling agents, such as SG1 or PETIPNO, are most likely optimized and generate less waste and use less solvent than the academic synthetic routes outlined here, thus lowering the E-factor and improving the sustainability. However, this data is not publicly available. From the E-factors calculated above, the ATRP reagents generate the least amount of waste, mainly because the controlling agents do not rely on column chromatography purification and the ligands needed are commercially available. In contrast, NMP and OMRP appear to generate the largest amount of waste as they require lengthy column chromatography using toxic solvents. However, alternative initiation systems exist, such as a binary Co(acac)₂/V70 system, which solely rely on commercially available compounds and do not require column chromatography, thus drastically lowering the E-factor described above.

However, sustainability is a complex principle and the toxicity of the substances should also be considered. In this aspect, looking only at the chemicals listed in the table, RAFT uses the lowest number of toxic or critical chemicals, while NMP uses the largest number. Again, the individual toxicity and criticality of each chemical would need to be assessed, for example through Life-Cycle Assessments to gain a truly comprehensive picture of the sustainability of each technique. The above discussion should be considered a first important step in this direction and, as it clearly highlights problematic issues, might serve a starting point for the future design of more sustainable controlling agents.

3. Fully Renewable Monomers for Radical Polymerizations

While the agents rendering RDRP controlled polymerization reactions are crucial, the monomer has a significantly higher impact in terms of sustainability, as it is typically used in a 100–1000-fold excess compared to the controlling agent, initiator, and ligands. Thus, it is often considered as the sole parameter of renewability and sustainability, being a too simplistic perspective considering the discussion above. It is however certainly key to closely examine the monomer synthesis, as well as the polymerisation solvent in order to be able to judge the renewability and sustainability of a polymerization. Below, this exercise is performed only for monomers fully derived from renewable resources.

3.1. Terpenes

Terpenes or terpenoids are a major class of compounds, industrially extracted on kiloton scales from coniferous trees and plants, making them an attractive resource for polymerizations. Over 40 000 different terpenoids are known and have historically been used as solvents (turpentine) or as essential oils and fragrances. The most important terpenes in terms of their availability include α- and β-pinene, menthol, and limonene (Scheme 5a). Radical polymerizations of these molecules are rather challenging, as the internal, for example, α-pinene, limonene, and carvone, and sterically hindered double bonds, for example, in β-pinene, are prone to termi-
nation and transfer reactions, such as degradative transfer (Scheme 5b).[106–108] Additionally, polyterpenes are poorly soluble in common organic solvents, for example, tetrahydrofuran or chloroform or chloroform, and require the use of non-polar solvents during polymerization, which are not suitable for some RDRP techniques, such as ATRP.[109] As a result, mainly copolymerizations with more soluble and more reactive comonomers have been performed and are summarized below.

Two different isomers of pinene exist: α-pinene, bearing an internal, endocyclic double bond, and β-pinene, containing a terminal, exocyclic double bond (Scheme 5a). While α-pinene has not been successfully copolymerised so far, several examples of β-pinene copolymers with monomers bearing activated or conjugated double bonds are reported in the literature. Akin to cationic polymerisations, the generated radical isomerizes into its most stable position on the β-pinene molecule, which is the tertiary isopropyl carbon (Scheme 5c). The first reports in 2006 described the copolymerization of β-pinene with acrylonitrile and methyl acrylate using reversible addition fragmentation (RAFT) polymerizations.[110,111] Both acrylonitrile,[112] and methyl acrylate[112] have been recently shown to be available from renewable resources, namely sugars (Scheme 6), and thus, at least in theory, completely renewable copolymers can be obtained using these monomers. It is however important to note that the possible renewability of acrylonitrile and methyl acrylate does not lower their toxicity, which does not comply with the third principle of Green Chemistry, and alternative non-toxic and renewable replacements should be aimed for.

Acrylonitrile is carcinogenic and has oral and alternative non-toxic and renewable replacements should be aimed for. Acrylonitrile is carcinogenic and has oral and alternative non-toxic and renewable replacements should be aimed for. Acrylonitrile is carcinogenic and has oral and alternative non-toxic and renewable replacements should be aimed for. Acrylonitrile is carcinogenic and has oral and alternative non-toxic and renewable replacements should be aimed for. Acrylonitrile is carcinogenic and has oral and alternative non-toxic and renewable replacements should be aimed for.

β-Pinene maleic anhydride copolymerizations were performed using 1-phenylethyl phenyldithioacetate (PEDB, Scheme 2) in THF, 1,4-dioxane, or a mixture of the two at 60 °C.[113] While PEDPTA showed low conversions and high molecular weight dispersities (1.62) in THF, PEDPTA enabled a more controlled chain growth process in THF (D = 1.25). 1,4-dioxane proved to be an efficient way of increasing the conversion to around 30% while maintaining the dispersities below 1.4. Using a 1:9 v/v solvent mixture of THF:1,4-dioxane, the dispersities were further reduced to values below 1.3 for conversions around 20%. Irrespective of the solvent and the β-pinene feed, the copolymer was found to contain 50 mol% of each comonomer. The authors then investigated the self-assembly of such copolymers with an additional non-renewable styrene block and showed that interesting post-polymerization functionalizations are possible on the maleic anhydride monomer. Akin to the above discussion on methyl acrylate and acrylonitrile, styrene is a natural tree sap product but poses serious health hazards (damages unborn child and organs, LC_{50} of 11 800 mg m^{-3}) and is obtained from entirely non-renewable channels at an industrial scale. It should be noted, that the quantities naturally occurring in styx gums are extremely low (<0.42% of the plant mass)[118] and that enzymatic pathways from renewable biomass are also limited by their low yield.[119] Polymerications of β-pinene and N-methyl and N-ethyl maleimide were performed in dichloroethane at 60 °C using...
1-phenylethyl phenyldithiocarbonate (PEPDTA, Scheme 2) as the CTA and were inhibited at low conversion (≈25%) for both. The authors reasoned that the retardation was a result of the poor reinitiation ability of the maleimide-CTA chain end leading to termination and side reactions, which had been previously reported for other copolymerizations.[120] Thus, further improvements are necessary to attain a controlled character for these copolymerizations. While the copolymerization of β-pinene resulted in polymers bearing cyclohexene rings in the backbone, see Scheme 5, polymers based on limonene have a cyclohexene ring as the pendant group. Kamigaito et al. copolymerized limonene and potentially renewable N-cyclohexyl maleimide, N-ethyl maleimide, and N-phenyl maleimide using RAFT polymerization.[121] Using S-butyl S′-cumyl trithiocarbonate (BCT, Scheme 2) as the CTA at 60 °C in 1,1,1,3,3,3-hexafluoro-2-propylpropan-2-ol (BA) type alternating copolymers were obtained for all three N-substituted maleimide limonene copolymers. While high conversions of up to 70% and molecular weight distributions below 1.26 were obtained, the polymerization kinetics were very slow, taking up to 100 h to reach 70% conversion. Further investigations by the same group reported on the terpolymerisation of limonene, N-phenyl maleimide and methyl methacrylate, the latter two both potentially renewable (see above), at 60 °C in 1,1,1,3,3,3-hexafluoro-2-propylpropan-2-ol using S-2-cyano-2-propyl S′-butyl trithiocarbonate (CPBTC, Scheme 2) as controlling agent. Conversions of up to 90% could be obtained while retaining low dispersities (D < 1.43) for targeted degrees of polymerization (DPs) below 40. For higher targeted DPs, and thus molecular weights above 3500 g mol⁻¹, the dispersity increased up to 1.62. MALDI-TOF analysis revealed that the obtained polymer showed a defined sequence of maleimide-limonene-maleimide (BAB), which was randomly copolymerised with methyl methacrylate (BAB-r-C). Yet, as above, the polymerizations were slow and no evidence, such as a first order kinetic plot, was provided to highlight the controlled chain growth process. While both these reports are promising, further examples, particularly dealing with the homopolymerization of limonene, are to date not reported.

The most recent example of the copolymerization of a more complex terpene, namely valencene (Scheme 5), was reported by Satoh et al. using RAFT polymerization.[122] Valencene is commercially available and is present in various citrus fruits with its main use in the fragrance industry.[123] The authors copolymerised valencene with N-phenylmaleimide, a potentially renewable monomer (see above), at 60 °C using S-butyl S′-cumyl trithiocarbonate (BCT, Scheme 2) in 1,1,1,3,3,3-hexafluoro-2-propylpropan-2-ol. While the molecular weights increased linearly with conversion for a 50 mol% copolymerization, the molecular weight distributions were rather broad for the low molecular weights obtained, D > 1.31 for Mₙ < 2800 g mol⁻¹. Nonetheless, the thermal properties of these copolymers, obtained from free radical analogues, indicated high glass transition temperatures as well as high thermal stabilities, highlighting their promise for high-temperature applications.

Kali et al. were the first to report the homopolymerization of a terpene, namely myrcene (Scheme 5), using a RDRP technique.[124] RAFT polymerization with a trithiocarbonate CTA (ethyl 2-[(ethylthio)thiocarbonylthio]propionate (EETP); Scheme 2) was used at 65 °C in the bulk. Although conversions were limited to below 50%, a controlled chain growth process was observed, that is, a linear increase of the molecular weights with conversion and a linear pseudo first order kinetic plot were obtained. Analysis of the formed poly(myrcene) using 1H and 13C NMR spectroscopy revealed a predominant 1,4-addition to the myrcene unit during the polymerisation in both cis and trans conformers, while less than 4% of other insertions were identified, presumably as a result of steric hindrance. Such a high degree of 1,4-additions was previously not possible to attain using Ziegler-Natta, free radical, or anionic polymerizations. Further investigations by the same group complemented these findings and by changing the RAFT agent, radical initiator, and temperature, conversions could be increased to 64%.[125]

In 2017, Marić et al. demonstrated that the polymerization of myrcene was also possible using 2-[(tert-butyl)(1-diethoxyphosphoryl)-2,2-dimethylpropyl]amino(oxy)-2-methylpropionic acid alkoxymine (BlocBuilder, BB; Scheme 3), and the succinimidyl ester terminated NHS-BlocBuilder alkoxymine (NHS-BB; Scheme 3) in nitroxide-mediated radical polymerizations (NMP).[126] The best control over the homopolymerization was observed at 120 °C in the bulk using NHS-BB. While the polymer microstructure was less regular compared to the above RAFT system, 1,4-addition segments were constant at 80% (cf. 96% for RAFT), the NHS-BB system allowed to reach conversions above 80% (cf. 60% for RAFT). The higher conversions obtained for NMP make this polymerization technique more sustainable, while the very high E-factor calculated for the NHS-BB controlling agent could indicate that RAFT polymerization is a more sustainable polymerization technique.

Apart from myrcene, Kamigaito et al. have reported the homopolymerization of a terpene-derived monomer, namely pinocarvone. Pinocarvone is obtained from α-pinene via a neat, catalyst free and sustainable photooxidation reaction (Scheme 7a).[127] The E-factor for its synthesis is 14 (see Supporting Information for details). In an attempt to synthesise bio-based polyketones using RAFT, CTAs with different activities were tested (dithiobenzoates (2-cyano-2-propyl dithiobenzoate (CPDB)), dithiocarbamates (2-cyano-2-propyl pyrrole-1-dithiocarboate (CPDB)), thriothiocarbonates (S-2-cyano-2-propyl S′-ethyl trithiocarbonate (CPET), methyl 2-[(ethylthiocarbonylthio)thio]-2-phenylaceta (MEETP), S-butyl S′-cumyl trithiocarbonate (BCT; Scheme 2), with the latter showing the fastest quantitative conversions (50 h) and the best control over the chain growth process. Similar to the copolymerization of β-pinene discussed above, the polymerization solvent, or absence of it, strongly affected the polymer structure. For bulk polymerizations, a radical ring-opening polymerization (rROP) mechanism was in competition with a conventional...
1.2-radical polymerization mechanism, leading to a polymer with both main chain and pendant 6-membered cyclohexane-ene moieties (Scheme 7b). In fluorinated alcohols, such as 1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-ol, hexafluoro-2-propanol, or 4-(trifluoromethyl)benzyl alcohol, on the other hand, rROP took place almost exclusively to yield a polymer with up to 99% of ketone units in the backbone. The Michael acceptors could be further functionalized using, for instance, thiol as nucleophiles or via reductions and provided a powerful tool for the synthesis of functional, fully renewable polymers. In terms of sustainability, bulk polymerizations are preferred and thus the polymer with a mixture of ketone units is more sustainable compared to the ones synthesized in fluorinated alcohols. These ketone containing polymers could potentially replace polyesters, such as poly(ethylene terephthalate), as a result of their bulky structure and high Tg of around 130 °C. Copolymerizations with potentially renewable butyl acrylate (BA; see discussion for butyrolactones) to form triblock copolymers with up to 30 wt% of pinocarvone showed their possible suitability as microphase separating block copolymers. Moreover, the high Tg of poly(pinocarvone), 130–160 °C, and the high decomposition temperature, 300–325 °C, both depending on the number of ring-opened units, suggest possible applications as thermoplastic elastomers for high temperature applications, as their mechanical properties are maintained up to high temperatures.

Apart from pinenes, limonene, and myrcene, few terpene monomers with reactive double bonds exist. A rare example is pimaric acid (Scheme 5), containing a substituted allylic double bond, which, however, remains extremely difficult to (co)polymerize by radical pathways,[128] and further developments of RDRP techniques are necessary to allow for its polymerisation. Nonetheless, the ease of availability and low cost of terpene monomers clearly highlight their potential and versatility for applications in which rigid and thermally stable polymers are needed. However, more information on their mechanical properties needs to be obtained in order to discuss possible replacements for specific applications. A particular challenge is the poor solubility of the formed polymers, which calls for uneconomical and environmentally harmful solvents[129] to be used during the polymerization and purification, putting into question the scalability of their synthesis and the renewability and sustainability of these polymers. This is particularly true for 1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-ol, hexafluoro-2-propanol, and 4-(trifluoromethyl)benzyl alcohol, which are suspected carcinogens and mutagens with the latter also being toxic, with LD50 of 413 mg kg\(^{-1}\) bw for oral routes, and an LC50 of 1000–2000 mg m\(^{-3}\). Moreover, such fluorinated and chlorinated substances are known to bioaccumulate in the environment and organisms and a shift to bulk polymerizations is key. Moreover, room for improvements remains in light of the slow polymerization rate, the poorly explored applications of such copolymers,[130] and the challenge in controlling their polymerization.

Apart from NMP and RAFT, no other polymerization techniques have been able to control the chain growth process for these non-activated hydrocarbon monomers and other techniques, such as OMRP or ATRP, may allow to address some of the issues mentioned above.

### 3.2. Cellulosic Biomass

Cellulosic biomass constitutes the largest renewable resource available on the planet, with an estimated 170 × 10\(^{12}\) tons available and a regeneration rate of 3% per year—an almost inexhaustible raw material. In comparison, a total of 348 million tons of plastic from all sources were produced worldwide in 2017[112] Apart from its abundance, cellulosic biomass presents a multitude of different functionalities and structures as a result of its different components, such as cellulose, hemicelluloses, and lignin. Over the last few years, these raw materials have been increasingly studied for their effective transformation into monomers for a variety of different polymerization processes.[131–135] Fermentation in particular has led to promising platform chemicals, such as lactic acid, however few of these molecules contain a double bond suitable for radical polymerizations, with itaconates being the most prominent exceptions.

#### 3.2.1. Itaconates

Itaconic acid (2-methylenesuccinic acid) is a dicarboxylic acid (Scheme 2a) industrially produced on the kiloton scale via the bacterial fermentation of carbohydrates,[133,134,136–138] but can also directly be prepared from biomass, for instance beech wood.[139] Due to its structural resemblance to methacrylates it is sometimes referred to as the natural methacrylic acid analogue (Scheme 8a). However, to date, no RDRP technique has been reported to homopolymerize itaconic acid. The presence of two carboxylic acid functionalities allows for the synthesis of a variety of substituted derivatives (Scheme 8b) and several functionalized derivatives have been reported using, in principle, renewable moieties, namely MeOH,[140,141] butanol,[142,143] and cyclohexanol.[144,145] Another frequently utilized transformation of itaconates is its dehydration into itaconic anhydride followed by a ring-opening and ring-reformation using amines to yield N-itaconimidides (Scheme 8c,d).[146,147] The itaconic anhydride derivative can be either obtained by dehydration reactions, which are already implemented industrially for other acids such as succinic acid,[148] or through distillation of citric acid.[149] The literature-reported way of preparing itaconic anhydride (Scheme 8) uses phosphorous pentoxide as dehydrating agent,[146] which is not sustainable as it is used in excess and generates a stoichiometric amount of phosphorus hydroxide.
(P_2O_5(OH)_2), which disproportionates into phosphate oxide and phosphonous acid waste.[150] Particularly N-phenyl itaconimide, which can be obtained from aniline (potentially renewable, see discussion in terpenes) and itaconic anhydride, has been particularly popular as a renewable itaconate-derived monomer.

The first studies on the controlled polymerisation of itaconic acid derived dimethyl itaconate (Scheme 8b) were carried out utilising an unconventional ATRP initiator, p-toluen 2-sulfonyl chloride, CuCl as catalyst, and 2,2’-bipyridine (bipy, Scheme 1) as ligand in the bulk.[151] A low conversion was observed (40%), after which significant deviations from the linear increase of molecular weight with conversion were observed as a result of elimination and termination reactions.

More successful polymerizations of esterified itaconic acid derivatives were performed by Barner-Kowollik et al. using RAFT polymerization.[152] Dibutyl itaconate and dicyclohexyl itaconate (Scheme 8b) were synthesized using acid catalyzed transesterifications[150] and their E-factor is calculated to be 9, assuming a yield of 50% as no yield was reported. Both monomers were subsequently polymerised using dithiobenzoaete, dithioacetate, and trithiocarbonate (cumyl dithiobenzoate (CDB), cumyl phenyl dithioacetate (CPDA), and S,S’-bis(α,α’-dimethyl-α’-acetic acid) trithiocarbonate (BDAT); Scheme 2) as CTAs at 65 °C in the bulk. While the dithiobenzoate led to almost no conversion for the butyl functionalized itaconate and the dithioacetate was limited to low conversions, below 20%, for dicyclohexyl itaconate, the trithiocarbonate CTA reached conversions above 50%. Nonetheless, rather high dispersities were observed (D > 1.5), which was ascribed to the occurrence of a hybrid polymerization behavior between free radical and controlled radical polymerization. Such systems are characterized by a low initial addition rate constant of the growing radical chain to the RAFT agent (k_{AD}) compared to the propagation rate constant (k_p). A rapid increase of the molecular weights at the beginning of the reaction was observed, followed by the linear increase of molecular weight with conversion, resulting in a semi-controlled polymerisation. Nonetheless, chain extensions with non-renewable styrene were possible using the trithiocarbonate CTA.

Similar conversions but slightly lower dispersities (D ≈ 1.5) were reported for dibutyl itaconate (DBI) by Satoh et al. for RAFT polymerizations at 20 °C in the bulk using methyl 4-cyanopentanoate dithiobenzoate (MCPDB; Scheme 2).[153] In addition, the successful block extension of a dibutyl itaconate macroRAFT agent based on cumyl dithiobenzoate (CDB; Scheme 2) with N-phenyl itaconimide in 1,4-dioxane at 50 °C was reported. The authors also prepared telechelic triblock copolymers with a soft DBI block and two hard itaconimide blocks and these showed mechanical properties typical for thermoplastic elastomers and microphase separation.

Previous investigations had already investigated N-phenyl itaconimide as a monomer with the first report in 2005. Therein Choudary et al. attempted the block extension of a methyl methacrylate (MMA, potentially renewable see above) macoinitiator with N-phenyl itaconimide using reverse ATRP.[154] Using FeCl_3·H_2O as catalyst and triphenylphosphine as the ligand, polymerizations were performed at 85 °C in toluene and led to a negligible chain extension of the itaconimide. Copolymerizations of the N-phenyl itaconimide/methyl methacrylate pair were reported later using a traditional CuBr_2/bipy catalyst (Scheme 1a) and a suitable itaconimide-based initiator at 80 °C in anisole.[155] Yet, rather high dispersities (D = 1.3–1.56) were obtained and no comment on the comonomer incorporation was made.

The successful homopolymerization of N-phenyl itaconimide using ATRP was reported a year later in 2015 by Okada et al. using an iron bromide-N-heterocyclic carbene catalyst (Scheme 1).[155] Controlled polymerisations were obtained in anisole at 60 °C up to high conversions (70%) but broad molecular weight distributions were obtained (D > 1.3). The authors also stated that CuBr/amine ATRP catalyst systems were not suitable for the polymerization of N-phenyl itaconimide as they catalyzed the double bond isomerization generating a deactivated non-polymerizable internal double bond. Copolymerizations of phenyl itaconimide were also shown to be possible with non-renewable styrene. Later reports described the synthesis of thermoplastic elastomers based on a lysine-derived monomer and N-phenyl itaconimide.[156] However, the synthesis of the lysine-derived monomer required the use of toxic phosgene and protecting groups and thus yielded an entirely unsustainable polymer.

These reports on renewable itaconic acid-derived polymers demonstrate the difficulty of its controlled polymerization up to quantitative conversions. Neither RAFT nor ATRP have so far allowed perfectly controlled polymerizations and further investigations are necessary to overcome this challenge, which may also lead to the possibility of polymerizing itaconic acid directly. Additionally, tuning the polymer properties via the functionalization of the carboxylate or carboxylic acid functional groups would allow to synthesise well-defined polymers with properties targeting a specific application. Moreover, the synthesis of other renewable itaconic acid-based monomers would allow to expand this monomer library and be suitable for a variety of applications, as already reported for non-renewable analogues.[156,157]

3.2.2. α-Methylene-γ-Butyrolactones

α-Methylene-γ-butyrolactones (MBL) are a class of five-membered lactones with an exo-methylene unit (Scheme 9c) and can be extracted from tulips.[158] Although several synthetic pathways to methylene butyrolactones from renewable resources have been reported (e.g., Scheme 9a,b,[159–161] Fors et al. were
the first to report a one-step procedure for the synthesis of \( \gamma,\gamma\text{-dimethyl-}\alpha\text{-methylene-}\gamma\text{-butyrolactone (Me}\_2\text{MBL)} \) and MBL from itaconic acid, via a reduction and a selective addition, respectively (Scheme 9a).\(^{[163]}\) The E-factors for these pathways are 72 and 1886 for \( \text{Me}_2\text{MBL} \) and MBL (excluding \( \text{SiO}_2 \) chromatography), respectively. The first controlled radical polymerization of the simplest representative of such butyrolactones, \( \alpha\text{-methylene-}\gamma\text{-butyrolactone (MBL)} \), was reported by Matyjaszewski et al. in 2008 using ATRP.\(^{[163]}\) At 50 °C in DMF\(^*\) using a CuBr/bipy catalyst complex and 2-bromopropionitrile as initiator, rapid and controlled polymerizations were observed giving rise to well-defined polymers (\( M_n = 18 \times 200 \text{ g mol}^{-1}, D = 1.09 \)). Chain extensions of an MBL macroinitiator with potentially renewable monomers, such as BA and methyl methacrylate (MMA), were not successful due to the poor solubility of this macroinitiator.

Controlled miniemulsion polymerizations in water of \( \gamma\text{-methyl-}\alpha\text{-methylene-}\gamma\text{-butyrolactone (MeMBL; Scheme 9c)} \) were attempted using RAFT polymerization in order to prepare heat-resistant polymer latexes.\(^{[164]}\) Using oil-soluble 1-phenylethyl phenylidithioacetate (PEPDTA; Scheme 2), cumyl dithio benzocate (CDB; Scheme 2) and cumyl phenylidithioacetate (CPDA; Scheme 2) as CTAs at 70 °C, miniemulsion homopolymerizations of MeMBL led to little success, as latent aggregation and a poor control over the chain growth process were observed.\(^{[164]}\) It should be noted that non-renewable sodium dodecyl sulfate was used as a stabilizer, which has an additional impact on the sustainability of the process. Stable polymer colloids and a more controlled polymerisation could only be achieved through the addition of non-renewable styrene and a subsequent copolymerization with MeMBL.

In an attempt to attain mechanical properties superior to those of commodity polymers currently used in a range of applications, block copolymers based on MBL and butyl acrylate (BA) were synthesized using ATRP.\(^{[165]}\) BA can, in principle, be sustainably obtained from renewable resources by combining butanol, which, as mentioned above, can be obtained through sugar\(^{[142,143]}\) or glycerol\(^{[166,167]}\) fermentation as well as from lactate-derived methyl or ethyl acrylate.\(^{[112]}\) Polymerization of the BA center block was performed using a CuBr/CuBr\(_2\) catalyst with \( N,N,N',N''\text{-pentamethyldiethylenetriamine (PMDETA; Scheme 1)} \) as ligand and a difunctional ATRP initiator (dimethyl 2,6-dibromohexanediololate) (MBHD; Scheme 1) at 80 °C in anisole, while the second MBL block was obtained through the use of a CuCl/CuCl\(_2\) catalyst and bip as ligand at 50 °C in DMF\(^*\). The two blocks were immiscible and, depending on the size of the hard block, different stable phase morphologies were observed by atomic force microscopy (AFM) and small angle X-ray scattering (SAXS). Nonetheless, only slight improvement of the tensile strength and elastic modulus were observed (<50%, compared to a triblock copolymer made of commercial BA and MMA), while the elongation at break was poor for all samples as a result of the brittle MBL blocks. Improvements in the stress at break values were achieved for multi-armed p(BA-b-MBL) star block copolymers, for which the mechanical properties reached values comparable to simple diblock copolymers based on BA and MMA.\(^{[168]}\) Even if the synthesis of the multivalent initiator is cumbersome and not sustainable, and these polymers are thus not real alternatives to commercially available thermoplastic elastomers, such property investigations are crucial if such polymers are to replace fossil-based materials.

The mechanical properties introduced by MBL to the aforementioned thermoplastic elastomers motivated the groups of Tolman and Hillmyer to investigate a renewable ABA triblock copolymer.\(^{[169]}\) Using sequential ROP of menthend followed by chain-end functionalisation with an ATRP initiator, and chain extension with MBL using a CuCl/bipyridine catalyst in DMF\(^*\) at 60 °C, hard-soft block copolymers of varying block lengths were synthesized. Microphase separation of MBL in the poly(menthend) matrix was observed by differential scanning calorimetry (DSC), AFM, and SAXS, independently of the copolymer composition. Triblock copolymers containing more than 15 wt% MBL showed mechanical properties comparable to those of commercial elastomers, for example, poly(styrene-block-butadiene-block-styrene), in terms of Young’s modulus (>6 MPa), while the renewable triblock copolymers were superior in terms of true elasticity (recovery of shape). Additionally, the elongation at break of these renewable copolymers was remarkably high (>730%). Analogous triblock copolymers were prepared from menthend and \( \gamma\text{-methyl-}\alpha\text{-methylene-}\gamma\text{-butyrolactone (MeMBL)} \) by the same group and further improvements of the elongation at break to values >1600% were achieved exceeding the limits of the instrument used.\(^{[170]}\) Their performance in adhesive blends using commercial tackifiers were determined in a preliminary test and the results demonstrated that such triblock copolymers have a fail temperature, that is, the temperature at which the adhesive detaches, higher than those of commercial pressure sensitive adhesives (>150 °C compared to 90–125 °C for commercial duct tapes). Thus, not only were fully renewable materials prepared, but it was clearly demonstrated that such polymers can outperform fossil-based established materials.

In another study, the groups of Higaki and Takahara showed that bio-based PMBL polymer brushes synthesised on a silicon wafer were superior to PMMA brushes synthesised on the same substrate in terms of wear resistance and relative elastic modulus, which are important for potential scratch-resistant coating applications.\(^{[171]}\) PMBL brushes were grown from an ATRP initiator-functionalised silicon wafer using a CuBr/bipyridine catalyst in DMF\(^*\) at 30 °C to give a homogenous polymer layer on the substrate. However, no comment on the effect of the surface-bound initiator on the control of the polymerization, nor the molecular parameters of the copolymers were made.

In a study by Forss et al. Me\(_2\)BL- and MBL-based polymers were synthesized using a dithiobenzoate CTA (2-cyano-2-propyl benzodithioate, CPDB; Scheme 2) for the replacement of fossil fuel-based PMMA in optical fibre applications.\(^{[162]}\) At 80 °C in benzene, well-defined high molecular weight homopolymers with \( T_g \)'s above 190 °C with similar optical properties to PMMA were obtained.

The above examples highlight the potential of renewable MBL-based polymers for the replacement of petroleum-based commodity plastics such as PMMA. While both RAFT polymerization and ATRP are capable of polymerizing this monomer, the choice of solvent typically significantly limits the sustainability of these polymerizations and further investigations are
necessary to optimize these reaction conditions. Surprisingly, no reports on the post-polymerization modification of the butyrolactone repeat units have been reported, which would not only allow for the tuning of the polymer’s properties but also broaden the applications attainable with such polymers.

3.3. Sugars and Carbohydrates

Among polymers based on renewable monomers, carbohydrates are one of the most studied class of molecules as they are abundant, can be easily obtained from non-food resources and are versatile as a result of the multiple functional groups.\textsuperscript{[172]} Especially glycopolymers, that is, polymers bearing carbohydrate pendant moieties, have gained interest since the early 2000s in light of their potential applications as stimuli-responsive materials,\textsuperscript{[173]} for cell recognition, and in drug delivery.\textsuperscript{[174–178]} A more recent trend in this field is the use of enzymes for the synthesis and polymerization of glycopolymers in aqueous media with advantageous low toxicity, sustainability, scalability, and selectivity of the process.\textsuperscript{[174,179]} Yet most of these monomer syntheses rely on unsustainable acrylate functionalizations and so far no fully renewable glycomonomer has been reported.\textsuperscript{[174,180–184]}

3.4. Lignin

Lignin is the third main constituent of biomass after cellulose and hemicelluloses and serves as the rigid and structure-giving segment of cell walls. Made up mainly of three repeating units, para-coumaryl alcohol, coniferyl alcohol, and synapyl alcohol (Scheme 10a) connected via ester, ether, and carbon-carbon linkages, this polymer (as a sulfonated lignin) is obtained as a side product from the papermaking industry at a scale of \( \approx 100 \text{ Mt per year} \) (data from 2015)\textsuperscript{[185]} and is typically directly burned to obtain the energy for the pulping process. Recently, lignin was exploited for the synthesis of a variety of different platform chemicals,\textsuperscript{[186–188]} for example, eugenol, vanillin, guaiacol, or syringol (Scheme 10b), but also polymers.\textsuperscript{[189–194]} The advantages of this feedstock are its non-competitiveness for food and feed as well as its low price. However, issues related to purity, degradation of lignin during pulping, and low yields obtained by novel (non-Kraft) processes, so far hamper the implementation of lignin in large-scale material products, although some progress in addressing these issues has been made.\textsuperscript{[187,195,196]} Indeed, several reports have been published on the RDRP of lignin-derived monomers, but all of the reported examples\textsuperscript{[197–201]} use a methacrylate functionalization to attach polymerisable double bonds, leading to monomers obtained in a non-sustainable fashion with a significant non-renewable content. Nonetheless, these polymers showed interesting properties for a variety of applications, such as adhesives and coatings, warranting the interest in developing other renewable functionalization pathways or establishing the, to date, unreported direct polymerization of lignin-derived molecules, such as eugenol.

3.5. Phenylpropanoids

Closely related to lignin are \( \beta \)-methylstyrenes (Scheme 11a) and vinylguaiacals (VG; Scheme 11b), which can be directly extracted from a variety of plants,\textsuperscript{[204,205]} or obtained through the decarboxylation of ferulic acid, a component of lignin,\textsuperscript{[204,205]} respectively. \( \beta \)-Methylstyrenes are known to homopolymerize radically because of their bulky methyl substituent, preventing successive \( \beta \)-methylstyrene additions.\textsuperscript{[206]} As a result, Kamigaito et al. investigated the polymerization of anethole, \( \alpha \)-methyl isoeugenol, isosafrole, and acetyl isoeugenol (Scheme 11a) with methyl acrylate (MA, potentially renewable, see discussion in terpenes) using 2,2′-(1,3-phenylene)bis[(1,1,1,3,3,3-hexafluoropropan-2-ol)] (m-C\( \text{6} \)H\( \text{4} \)(CF\( \text{3} \))\( \text{2} \)OH), a toluene-derived fluoroalcohol, at 60 °C.\textsuperscript{[207]} A variety of dithio- and trithio-CTAs (cumyl dithiobenzoate (CDB), \( \alpha \)-cumyl \( \beta \)-ethyl trithiocarbonate (CETC), \( \beta \)-cyano-2-propyl \( \beta \)-ethyl trithiocarbonate (CPTC), \( \beta \)-cyano-2-methoxy-4-methyl-2-pentyl \( \beta \)-ethyl trithiocarbonate (CMMETC), and \( \beta \)-1-isobutoxyethyl \( \beta \)-ethyl trithiocarbonate (BEETC); Scheme 2) were used. In all cases, slow polymerisation rates, <25% conversion after 24 h, were observed. Nonetheless, molecular weights of up to 10 000 g mol\(^{-1}\) and dispersities below 1.36 were obtained, except for CETC, for which dispersities were above 1.42. However, no evidence for a controlled chain growth process was provided for these RAFT copolymerizations.

![Scheme 10. Chemical structures of a) the three main repeating motifs found in the structure of lignin, and b) derivatives of lignin, useful as platform chemicals and for monomer synthesis.](image)

![Scheme 11. Possible sources and structures of a) different \( \beta \)-methylstyrenes, b) ferulic acid and its transformation into vinylguaiacol.](image)
Vinyl guaiacol bears only one substituent on the vinyl group, thus is less sterically hindered, and can therefore be homopolymerized. However, the phenol moiety, a well-known antioxidant, quenches radical species and inhibits the homopolymerisation leading to low conversions. Phenol protecting groups have been used in the past, but these contradict the idea of sustainable and green chemistry. Nonetheless, the obtained polymers still provide a renewable route to access functionalised poly(vinyl guaiacol) and poly(vinyl catechol) polymers, otherwise only obtained from petroleum sources.

Cinnamic acid (Scheme 11a) is another example of a phenylpropanoid bearing a polymerizable double bond with the special feature that both a styrenic and acrylic propagating radicals can be formed. Satoh et al. investigated the polymerization of cinnamic acid and cinnamic methyl ester, along with other non-renewable analogues, with methyl acrylate using ruthenium-catalysed ATRP, RAFT polymerization, and NMP. At a 1:1 feed of cinnamic monomers and MA at 60 °C in toluene, using dimethyl-2-chloro-2,4,4-trimethylglutarate as initiator and RuCp*Cl(PPh₃)₂/nBu₃N as catalytic system (Scheme 1), the polymerizations were well controlled but very slow (65% conversion after 56 days). Interestingly, almost exclusive 1,2-addition of the monomer, that is, the formation of a styrenic radical, was observed for the obtained polymers. Slightly faster polymerization rates, 60% conversion after 13 days and 50% conversion after 13 days, were observed for NMP and RAFT polymerizations, respectively, maintaining a similar control. While NMP was performed at 90 °C in the bulk using N-tertbutyl-N-(2-methyl-1-phenylpropyl)-O-(1-phenylethyl) hydroxyl-amine (PE-TIPNO; Scheme 3) as the controlling agent, RAFT polymerizations were conducted at 60 °C in toluene using CPETC (Scheme 2) as the CTA. Unfortunately, no mechanical properties were reported for the copolymers.

These few phenylpropanoid copolymers exemplify the recent interest in this type of monomer as an alternative renewable building block. However, the inability to homopolymerize these monomers and the slow copolymerization kinetics are major drawbacks of these monomers and further investigations are necessary. Moreover, the methoxy or acetyl groups on the benzeno ring could provide handles for the chemical functionalization and allow for the tuning of the copolymer properties.

### 3.6. Triglycerides

Triglycerides are triesters of glycerol with fatty acids, conventionally referred to as fats and oils. Especially plant oils provide a variety of very useful fatty acids for polymer synthesis (Scheme 12). For example, while olive oil consists mainly of oleic acid, castor oil contains up to 90% of ricinoleic acid. Through a simple transesterification or saponification reaction, glycerol and the respective fatty acids or esters can be obtained giving rise to two very versatile renewables with different functionalities. These have been exploited for the synthesis of platform chemicals and polymers, some of which have already been successful in industrial settings. In terms of RDRP of triglycerides and their derivatives, the direct polymerization is challenging as the double bonds of the fatty acid chains are non-activated in terms of radical stability, being non-conjugated and/or internal. Furthermore, crosslinking and termination are present and such monomers have therefore mostly been used for the preparation of thermoset resins via free radical polymerization. Nonetheless, two patents claim that by selecting the right temperatures, controlling agents, and solvents, homopolymers of triglycerides can be obtained with no crosslinking by ATRP while using RAFT polymerization led to hyperbranched polymers. Apart from these two reports, the method of choice for the polymerization of triglyceride-based monomers has been the attachment of a double bond reactive toward radical polymerizations, for example, the incorporation of an (meth)acrylate. Such reactions were either performed on fatty acid derivatives or glycerol. As mentioned above, these functionalizations are inherently non-sustainable and use activated (i.e., acid chloride or anhydride) non-renewable (meth)acrylate moieties to obtain a polymerizable handle. This is especially true for fatty acids, as the need for a spacer between the acrylate and fatty acid, or the reduction of the carboxylic acid to an alcohol prior to acrylate attachment are needed to create polymerizable molecules. Examples of such partially renewable fatty acid-based monomers have been recently reviewed by Caillol et al.

Unlike fatty acids, glycerol is highly hydrophilic with three hydroxyl groups, two primary and one secondary, and the difficulty of the selective functionalization of just one hydroxyl group with a polymerizable function—in order to avoid crosslinking—limits the versatility of glycerol as a starting material. Enzymatic catalysis has proven powerful in circumventing the laborious protection and deprotection steps necessary for the preparation of monofunctional monomers and extending the type of monomers accessible. The polymerization of these monomers using RDRP has already been summarized in 2012 by Lapinte et al. The pendant hydroxyl groups of these polymers have been used for the functionalization of nanoparticles or the preparation of stimuli-responsive polymers. Even though these monomers are glycerol-derived, their renewable content is rather low as the (meth)acrylates are currently not bio-derived. This is unsurprising since the focus of most of these studies were...
novel polymer architectures or polymers targeted for specific applications. Functionality and renewability should, however, not be exclusive and a recent study by Meier et al. combined a sustainable synthesis with renewable resources to develop novel allyl and olefin monomers, which introduce functionalisable pendant side chains once incorporated into polymers.\cite{128} In a solvent-free, one-pot transesterification reaction, functional monomers bearing allylic or olefinic double bonds and a cyclic carbonate were synthesized in a sustainable fashion (Scheme 13a,b), as verified by an E-factor as low as 3 for the overall preparation process. The homopolymerization of these monomers was not possible by organometallic-mediated radical polymerization (OMRP) using an alkyloxybutyl initiator (Scheme 13c), which was attributed to degradative chain transfer. Copolymerizations at 40 °C with vinyl acetate, which can be renewable if synthesized from bioethanol\cite{94} and acetic acid,\cite{95} in the bulk gave rise to copolymers with up to 50 mol% of allylic and olefinic monomer incorporation through a controlled chain-growth process. Although slight deviations from pseudo-first order kinetics were noted and a detailed explanation could not be given, this study is the first to report the RDRP of non-activated allylic double bonds, which drastically expands the library of monomers accessible, as several natural molecules bear an allylic bond, for example, eugenol and pimaric acid. Moreover, the pendant carbonate functionalities should allow for interesting post-polymerization modifications\cite{244–246} to tune the polymer properties.

Overall, triglycerides provide a promising platform for renewably-sourced polymers, as they are abundant, contain multiple, complementary functionalities and can be obtained from non-food sources. This is especially true if the properties of triglyceride-based polymers, which are not fully renewable, are considered as these have already found applications as pressure sensitive adhesives\cite{167} and further applications are expected to be possible with such triglyceride-based (co) polymers.

3.7. CO2

CO2 has attracted immense attention as a C1 building block for synthetic chemistry\cite{248,249} as well as polymer synthesis,\cite{250–255} as it is abundant, cheap, and non-toxic. The transformation of CO2 into monomers with polymerisable double bonds was only recently reported and requires stoichiometric amounts of reagents or functional molecules, which are not renewably sourced.\cite{244,256,257} Thus, the development of catalytic routes transforming or incorporating CO2 into renewable monomers is necessary and while such developments have surged over the last few years for step-growth reactions,\cite{253} the combination of CO2 with a double bond in a sustainable fashion using solely renewable resources remains challenging.\cite{253,258,259} A relevant example is, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one, that is accessible by a Pd(II)/phosphine promoted telomerisation of CO2 and butadiene (which can be fully bio-sourced). The free radical polymerization generated polyesters,\cite{258,260} however it has not been successfully polymerized by RDRP.

4. Outlook and Future of Renewable Polymers via Sustainable Pathways

Going back to Figure 1, and comparing the 16 fully renewable monomers reviewed in this article with the more than 35 representative partially bio-based monomers shown (and even more can be found in the literature), it is obvious that the majority of available bio-based monomers are in fact not completely renewable or have up to date been synthesised using non-sustainable pathways. If fully renewable polymers are to aid in the effort toward a more sustainable and circular economy, several aspects need to be carefully addressed. First, the fully renewable nature of monomers needs to be ascertained, as otherwise the label “renewable polymer” is “greenwashing” and misleading. Special attention needs to be paid to the synthetic pathways used to obtain such monomers from renewable resources and natural molecules as “renewability is not enough.”\cite{261} and otherwise environmental burden shifting is promoted. The whole lifecycle from resource to polymer to application to grave or recycling needs to be considered, ideally with quantitative data, such as life cycle assessment. As this data is difficult to obtain for small scale laboratory processes, the synthetic processes and pathways should at least be guided by the 12 principles of green chemistry and metrics need to be applied whenever possible. The E-factor, first introduced by Sheldon, remains a very useful and easy tool to calculate sustainability metric in this regard, considering the amount of waste compared to product. Since the monomer is the main constituent of both the polymerisation and the final product, its preparation has the largest impact on sustainability. Therefore, the establishment of further functionalization pathways allowing for the sustainable synthesis of fully renewable polymers is of great interest and novel pathways are needed to expand the library of fully renewable monomers. This is especially true for non-acrylate-based polymers, or in general polymers originating from monomers bearing non-activated double bonds, as this (renewable) monomer type is still in its infancy.
Equally important are, however, the use of non-toxic solvents, for example, supercritical \( \text{CO}_2 (\text{scCO}_2) \) and environmentally friendly polymerization techniques. Ideally, such polymerizations avoid toxic, expensive, and scarce metals or use these in a catalytic amount and have a sustainable synthesis pathway. Currently, this is utopic to assume, given the relatively recent discovery of many of the RDRP techniques.

A further aspect, which is often neglected when considering renewable polymers, is polymer purification and, should the conversion not have reached 100\%, the recovery of any unused monomer. The most commonly used purification methods, including precipitation and dialysis, rely on large amounts of volatile, and sometimes toxic solvents. Alternative processes, such as extraction using \( \text{scCO}_2 \) are more and more explored and allow to recover unused monomers from the reaction mixture while being inherently more sustainable.

Finally, the properties of fully renewable polymers need to be investigated and determined in order to bring such polymers out of an academic confinement. This is especially true for fatty acid- and lignin-based monomers, as the non-renewable analogues already showed promising properties for applications such as pressure sensitive adhesives. These not fully renewable polymers may however, from an industrial standpoint, already fulfill the necessary criteria to switch from fossil fuel-based analogues to these materials. Although the ultimate goal should be to stop relying on fossil fuels altogether, such partially renewable polymers could be a step in the right direction. It should be mentioned that while renewable polymers made by RDRP processes are able to cover the majority of currently needed and employed polymers, it is clear that polymers made using other techniques are equally needed for other applications. These other polymerization techniques, that is, polycondensation, ring-opening and step-growth polymerizations, have the advantage that they are often run in the bulk, and require simple or no initiators or controlling agents, thus contributing to significantly lower E-factors compared to RDRP techniques. The complementary properties of these different polymers will allow to cover the total demand of polymers and complete the shift toward a Circular Economy.

The above points clearly highlight that the standards for a monomer to be called sustainable need to be raised. As a first measure, the E-factor for any monomer synthesis, and ideally also polymerisation, should be mentioned per default alongside conversion and yield. This will allow for a first point of comparison with established literature reports and also identify areas for improvements for the authors themselves. Furthermore, a close reflection of the solvents used throughout the synthesis and polymerisation needs to be provided and ideally only solvents which are recommended by the solvent selection guide should be used. Should this not be possible, for instance if an undesirable solvent or reagent is inevitable, an explanation should be provided, and more sustainable alternatives should be evaluated.

5. Conclusions

Renewable polymers are a promising alternative to fossil resource derived polymers. While significant progress has been achieved in renewable polymers made via step-growth polymerizations, the RDRP of renewable monomers is still strongly limited to naturally occurring molecules bearing a suitable double bond, such as terpenes, itaconates, and lignin. The scarcity of sustainable functionalisation pathways attaching double bonds further restricts the number of fully renewable monomers. Efforts into the sustainable synthesis of renewable monomers are necessary to overcome this issue. Moreover, the ability to polymerize renewable monomers bearing less activated double bonds, frequently encountered in natural molecules, for example, lignin or fatty acids, is still difficult by most RDRP techniques and is necessary for the full exploitation of the available renewable feedstock. Once these limitations are overcome and a broader library of renewable polymers is available, the mechanical and other properties need to be investigated in order to fully establish renewable polymers as viable alternatives to fossil fuel-based polymers.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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