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Manuscript title: Progress in the Synthesis of Sustainable Polymers from Terpenes and Terpenoids

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Abstract

The imminent depletion of resources derived from fossil fuels is a major concern for today's society. 300 Million tonnes of polymers are used every year in the form of plastics, most commonly derived from fossil fuels, hence the necessity to find new materials based on renewable resources. This review explores the utilisation of monoterpenes; a family of abundant and inexpensive natural products, as promising renewable monomers. Terpenes can be directly used in polymerisations or converted into bespoke monomers through organic transformations. The use of terpenes for the production of renewable plastics has been a prevalent topic of research for the past few decades. Herein an assessment of the future prospects for the use of these small functional molecules to synthesise novel and valuable renewable materials is presented.

1. Introduction

If the consumption of fossil fuels by our society continues at the current rate, our oil feedstocks will be expended within the next century. This, combined with the associated environmental issues around global warming and environmental pollution has resulted in a drive for scientific research to alleviate the dependence of our society on polymers and plastics derived from fossil fuels.[1] The utilisation of fossil fuels in the manufacture of plastics currently accounts for approximately 7% of worldwide oil and gas usage and is likely to strongly increase.[2] Moreover, a recent report clearly demonstrates that polymer wastes are increasing and by 2050 we may have more polymer waste than fish in our oceans.[3] Some of these issues can be addressed through the synthesis of polymers from renewable resources, and also by targeting materials that are naturally degradable into environmentally benign molecules. However, of the 300 million tonnes of plastics produced annually worldwide, renewable polymers contribute less than 1%.[1,4] The key reasons absenting renewable polymers from the commercial market are their high cost, and the relatively poor properties of the materials compared to their petrochemical equivalents.[5–7]

Renewable raw materials have the potential to provide a wide range of monomers arguably as comprehensive as those provided by the petrochemical industry.[8] The increase in academic research, and recently, industrial attention are likely to ensure that society starts to utilise renewable chemicals for the production of plastics.[9,10] As mentioned above the renewable polymers currently on the market cannot compete with petroleum based plastics, and this will not change until the technology is developed further. These advances will require development of novel and truly sustainable polymers, and to achieve all of this, full integration of other essential disciplines is necessary.[11,12]

However, it is important to remember that sustainable polymers are relatively new when compared to petroleum based plastics. The high performance of plastics derived from fossil fuels is the outcome of many years of intensive research and commercial scale optimisation. This will come for the next generation of renewably derived polymers, but will require significant and concerted academic and industrial research in the coming decades.[12]

The synthesis of macromolecules from natural sources is not a new idea. In fact, this area of research was the focus of pioneering explorations in polymer science.[13] However, these studies fell out of favour as the development of oil based synthetic chemicals grew. Only recently, in the light of environmental concerns, the recognition of our finite oil resource, and the need to utilise society’s waste streams has there been a renaissance of research towards synthesis of sustainably produced polymers. This is emphasised and highlighted in the increased number of reviews published recently in this area. [1,8, 14,15]

In recent years considerable research has been devoted to finding renewable monomers for the synthesis of sustainable polymers. These include both new materials entirely derived from renewable feedstocks, and those that combine petroleum based and renewable monomers.[16] In order to successfully shift to sustainable alternatives, the chemical industry must develop both existing and new low cost polymers which, as a minimum are able to compete with current petroleum based plastics on price and more importantly on performance.

A high proportion of the plastics used today accumulate in landfill where they are bulky and pervasive. Polymers from renewable recourses are not inherently biodegradable, however it is now imperative that society considers carefully the end of life issue of our plastics. Since we cannot exist without them, we have to learn to live with the consequences of plastics in our society. New materials are currently being developed to be more easily recycled, degraded to useable by-products or safely incinerated to recover their embedded energy.[17,18]

1.1 Monomers from biomass

Plant biomass is a major potential sustainable source of organic carbon.[19] Biomass-based processes that could replace crude oil could harness enzymatic methods, microbiology, and metabolic engineering to direct the transformation of sugars, lipids, and other biomass-derived molecules to the desired monomers. Monomers derived from biomass can be divided into three categories based on hydrogen, carbon, and oxygen compositions (**Error! Reference source not found.**).[7]

1. Oxygen-rich molecular biomass with a molar ratio of C/O less than an arbitrary number 5.0,(carboxylic acids, polyols, dianhydroalditols, and furans).
2. Hydrocarbon-rich molecular biomass with the ratio of C/O larger than 5.0, (vegetable oils, fatty acids, terpenes, terpenoids, and resin acid).
3. Hydrocarbon molecular biomass with no oxygen (bioethene, biopropene, and bioisoprene).

It is also important to mention opportunities around non-hydrocarbon molecular biomass. A very obvious example is carbon dioxide, which has the potential to be used as both a monomer,[20] and as a solvent for the sustainable synthesis of polymers.[21]

Using the renewable monomers mentioned above, there is now a plethora of polymers which can be synthesised from biomass. These polymers make use of many methods of polymerisation, such as free radical, ring opening, condensation and many other innovative approaches to produce polymers with a range of properties and sustainable characteristics.

Probably the most familiar renewable monomer is lactic acid for the synthesis of poly(lactic acid) (PLA).[22] PLA has received significant commercial attention as it displays suitable properties to replace polyolefins as well as potentially offering sustainability benefits over petrochemical based polymers.[23–26] A major drawback of PLA is the need for high quality land to grow the corn needed to extract the starch. In the future there will be a need to move away from such feedstocks, for example the use of waste CO_2 as an alternate carbon source .[27]

Furans are another group of monomers predominantly obtained from polysaccharides or sugars and encompass molecules such as furfural (**1**), furfuryl alcohol (**2**), 5-methyfurfural (**3**) and 5-hydroxymethylfufural (HMF) (**4**) (**Error! Reference source not found.**).[28] These are well developed monomers which can be used directly in step growth polymerisation or can participate in Diels-Alder reactions to introduce new functional groups into the polymer. [29–32] Furfural (**1**) and its derivatives are a particularly rich source of potential renewable monomers. Moreover, the fact that these can be produced directly from waste biomass is extremely attractive since this overcomes important ethical issues surrounding food *vs* fuel. Because of high production costs, **3** is not yet a high-volume chemical and the potential uses of HMF-derived compounds have currently not been fully exploited.[33] Vegetable oils and fatty acids also represent a large area of opportunity in new sustainable polymers.[34,35]

Within the category of hydrocarbon rich biomass are terpenes and terpenoids, and these represent a vast range of molecules which are of great interest to polymer science. The many desirable properties of terpenes have recently made them very attractive for polymer research and this is highlighted by reviews which have been published within the past five years.[14,36]

This review will focus on the use of monoterpenes and rosin acids as monomers for the synthesis of renewable, thermoplastic polymers. Initial attempts at polymerising the most abundant terpenes (**6**, **10** and **11)** concentrated on using their olefinic moieties for free radical or cationic polymerisation. Although this method showed some success,[37] the data was not compelling and recently attention has shifted to perform synthetic modifications to the terpenes in order to synthesise a terpene based molecule which can more easily undergo polymerisation. This process has been substantially aided by the corresponding advances in sustainable synthetic methodologies that have enabled prefunctionalisation of terpenes in polymer chemistry. This aspect will be covered at length in this review.

Terpenes, terpenoids and resin acids are a group of non-polar molecules and share a building block, isoprene (**5**), as a common elementary unit (**Error! Reference source not found.**). The most common terpenes contain two isoprene units and are known as monoterpenes, these are typically produced biosynthetically by many classes of trees and plants.[38] This class of molecules is grouped under hydrocarbon rich biomass, and contains a vast family of naturally occurring compounds which show enormous structural diversity (**Error! Reference source not found.**). Some common terpenes are limonene (**6**), α-terpinene (**7**), myrcene (**8**), 3-carene (**9**), α-pinene (**11**) and β-pinene (**10**) (**Error! Reference source not found.**). Terpenes are abundant, inexpensive and do not directly compete with food sources, and are therefore ideal small molecule building blocks for many applications.[38] These hydrocarbon based molecules usually contain one or more carbon-carbon double bonds and have a general formula $C_{10}H_{16}$. Turpentine is the volatile fraction isolated from pine resin and is produced on a scale of 330 kilotonnes per annum (KTA).[39]

The composition of turpentine is dependent on the age and species of the tree, among other factors. However, the major components are **11** (45-97 %), **10** (0.5-28 %) and smaller amounts of other monoterpenes.[40] This class of molecules can easily interconvert to give a number of basic monoterpene skeletons starting from many precursors.[41] Monoterpenes are particularly diverse structurally due to the presence of numerous stereogenic centres, but also because of the many oxygenated compounds which can easily be generated from the basic skeletons.[38] Despite the vast range of terpenes available, α-pinene (**11**), β-pinene (**10**), myrcene (**8**) and limonene (**6**) are the most widely studied for polymerisation applications. This is because of their high abundance, low cost and ease of isolation and these terpenes will be the main focus of this review.

2. Direct polymerisation of terpenes

Owing to the exo- and endocyclic carbon-carbon double bonds possessed by many of the terpenes, initial research focused upon polymerisation of terpenes *via* their double bonds through radical or cationic polymerisation.[37,42] These processes include the homopolymerisation of terpenes and also their copolymerisation with other synthetic monomers such as styrene. This section will highlight the direct polymerisation of terpenes through their carbon-carbon double bonds.

*2.1 β-Pinene (**10**)*

Pinenes are the most abundant of the terpenes and are isolated using steam distillation of resinous sap obtained from pine or conifer trees.[38] Perhaps the earliest evidence of the polymerisation of the pinenes was in 1937, however the paper did not report molecular weights and it was not specified which isomer of pinene was used.[43] Early research on terpene polymerisation was largely focused on β-pinene because it was abundantly available from pine trees. β-pinene (**10**) has two alkyl groups on its exocyclic double bond, these have an electron donating effect, thus stabilising carbenium ion **12.** This stabilisation effect combined with the sterically accessible exocyclic double bond in **10** results in β-pinene (**10**) readily undergoing cationic polymerisation.[44]

2.1.1 Homopolymers of β-pinene (**10**)

The first study of the cationic homopolymerisation of β-pinene (**10**) to give homopolymers was carried out in 1950 by Roberts *et al*. under Friedel-Crafts conditions (**Error! Reference source not found.**).[37]

The polymerisation of **10** using $AlCl_3$ as a catalyst was found to be fast and very exothermic, yielding a solid polymer with relatively low molecular weight ($\dot{M}_n$) *ca.* 2 kDa.

This reaction is driven by the high reactivity of the *exo*-methylene double bond, the breaking of the highly strained fused cyclobutane ring and the formation of the relatively stable *para*-menthene carbenium ion **13**. The mechanism for the cationic polymerisation of **10** utilises aluminium trichloride as a Lewis acid (**Error! Reference source not found.**). Aluminium trichloride reacts with water to form a strong proton donor which subsequently protonates the double bond of **10**, the carbenium ion **12** then rearranges to form a *para*-menthene type carbenium ion **13** responsible for the propagation reaction.

Conventional cationic polymerisations have shown that it is possible to homopolymerise β-pinene (**10**). However, the molecular weights obtained are only low to moderate and have a very broad distribution of molecular weights.

The first example of a living cationic polymerisation of **10** was carried out by Lu *et al.* in 1997 to give **22** with a narrow dispersity (Đ) *ca.* 1.3).[46,45] The controlled living polymerisation of **10** was carried out using combinations of α-chlorodiethyl ether as an initiator and [$TiCl_3$(O*i*Pr)] as an activator in the presence of (*n*Bu_4NCl) (**Error! Reference source not found.**). The optimal results were achieved using the above conditions in dichloromethane at temperatures in the range -40 °C to -78 °C, yielding **22,** with again relatively low molecular weight *ca.* 5 kDa, with narrow dispersity Đ *ca.* 1.1-1.2 and high conversion. The living nature of this system was confirmed by the linear increase of $\dot{M}_n$ with monomer conversion.[45–47]

Cationic polymerisation using Lewis acid catalysts such as $AlCl_3$ and $ZnCl_2$ produced homopolymers of **10** with relatively low molecular weights ($\dot{M}_n \leq 1$ kDa).[37] The cationic method has limitations. To obtain polymers with high molecular weights the polymerisation must be carried out at low temperatures (-40 °C to -78 °C) in order to minimise the relative kinetic contribution of the transfer reaction with respect to chain propagation. Even at low temperatures, the molecular weights of **16** obtained were relatively low, and a high concentration of Lewis acid was needed for a satisfactory conversion.

To try and combat the issues commonly associated with cationic polymerisation Lu *et al.* synthesised a Schiff-base nickel catalyst **23** (**Error! Reference source not found.**).[48]

Single site late transition metal-based catalysts are more tolerant of functional monomers and less oxophilic. Their single site nature enables ligand tailoring resulting in a system which can be modified in numerous ways to tune the polymerisation process. Nickel and palladium based catalysts are often chosen for the polymerisation of α-olefins but, nickel is more desirable because of the high cost and low abundance of palladium.[49]

The nickel catalyst alone could not polymerise β-pinene (**10**). However upon addition of an activator, methylaluminoxane (MAO), the catalyst **23** showed very high activity. Using this catalytic system at 40 °C, polymers with a molecular weight $\dot{M}_n$ = 11 kDa and a Đ of 1.70 were obtained. The ratio of MAO to nickel complex **23** determined the rate of polymerisation, and the molecular weight of polymers. Four ligands were synthesised to produce complexes **23a-d** and investigated for catalytic activity (**Error! Reference source not found.**). It was observed that the less rigid aliphatic ligands (complexes **23c** and **23d)** were preferred, suggesting that a more open active site facilitates coordination of the bulky β-pinene (**10**) molecule. This catalyst is a key example of production of high molecular weight poly(β-pinene) (**16**) at temperatures above 0 °C with extremely high productivity, up to 1.25 x10^7 g of **16** / mol of **23c** or **23d**, and these conditions could be utilised on an industrial scale.

More recently Kamigaito and co-workers reported the synthesis of a high molecular weight hydrogenated poly(β-pinene) (**16**) which showed some interesting and useful properties.[50,51] Polymers with high molecular weights $\dot{M}_n > 40$ kDa and $\dot{M}_w$ *ca.* 100 kDa were achieved using $EtAlCl_2/Et_2O$ in a solvent mixture of CH_2Cl_2 and *n*-hexane and a halide **25** as the initiator. The olefinic groups of **16** were then hydrogenated using various catalysts. The optimal conditions for the hydrogenation were found to be using *n*-hexane under molecular hydrogen at 1 MPa pressure with a Pd/Al_2O_3 species as a catalyst, inducing >99 % conversion of the double bonds (**Error! Reference source not found.**).

The hydrogenation of high molecular weight **16** was carried out in an attempt to improve the thermal resistance, durability and optical properties. The increase of the molecular weight resulted in **16** possessing mechanical strength comparable to other commercial polymers and displayed a flexural strength high enough to be classed as a plastic material. This is most likely a consequence of the chair conformation of the less-strained cyclohexane ring in the main chain. This is an example of post modification of polymers derived directly from terpenes in order to improve their properties.

In order to overcome the problems encountered during low temperature polymerisation of β-pinene (**10**), Kukhta *et al.* investigated the use of $AlCl_3$ etherates for the room temperature polymerisation.[52] Using an initiating system of $H_2O/AlCl_3OPh_2$ **16** was synthesised at room temperature with molecular weight in the range of 9-14 kDa and a T_g of 82-87 ^oC. This research demonstrates that it is possible to produce homopolymers of β-pinene (**10**) using ambient temperatures and catalyst systems which are inexpensive and commercially available.

The discussed work has established the potential to synthesise polymers based on **10** and other renewable feedstocks with properties at least equalling current commercially available plastics. For these polymers to become economically viable, more work is certainly needed to create, cheaper, green and sustainable routes to their synthesis.

2.1.2 Copolymers of β-pinene (**10**) and synthetic monomers

A number of copolymers of β–pinene (**10**) and synthetic monomers such as styrene have been synthesised and studied. The incorporation of well-studied synthetic monomers into poly(β–pinene) (**16**) allows tuning of the properties of the resultant polymer, [42,53,54] such as preparation of a random copolymer of **10** and isobutylene [55] which used a common initiating system. Additionally a 1-phenylethyl chloride with a $TiCl_4/Ti(OiPr)_4/nBuN_4Cl$ system was used in dichloromethane at −40 °C.[46] β-pinene (**10**) and isobutylene have similar propagating cationic structures (**Error! Reference source not found.**) and therefore their reactivity was predicted to yield a random copolymer.

Both monomers were consumed at comparable rates, suggesting similar cationic polymerisation reactivity of the two monomers and therefore the formation of random co-polymers under the above conditions. The polymerisation progressed in a controlled manner, yielding high molecular weight polymers ($\dot{M}_n$ *ca.* 25 kDa) with Đ < 1.2. The increase of the β-pinene (**10**) fraction, which offers rigidity to resultant polymers, from 10 % to 30 %, increased the T_g of final polymers by 60 °C. This clearly demonstrates that the properties of polymers containing **10** can be tuned by introducing specific amounts of synthetic monomer to the feed.

*2.2 Homopolymers of α-pinene (**11**)*

α-Pinene (**11**) is the most abundant turpentine component and this has led to numerous attempts of the cationic polymerisation of this compound. The polymerisation of **11** has not been as successful as β–pinene (**10**) largely because of the lack of a reactive *exo*-cyclic double bond. The sterically shielded endocyclic double bond in **11** is obstructed and consequently chain propagation is slowed.[56] However, **11** is readily protonated and can form a tertiary carbenium ion **27**, but the attack of the endocyclic double bond to the isopropenyl cationic site is limited by steric hindrance.

The first polymerisation of **11** was reported in 1950 by Roberts *et al.* and used a Lewis acid to promote the cationic polymerisation.[37] The process was found to be very low yielding (*ca.* 35%), this low conversion was improved by using elevated temperatures, (up to 40 °C), but only resulted in oligomers of **11**. There are two proposed methods for the mechanism of polymerisation of α-pinene, one involves the same *para*-menthene intermediate, **13**, as obtained in the β–pinene (**10**) polymerisation. The second involves the rearrangement of the tertiary pinene carbenium ion **27** to a saturated secondary bornane isomer **28** (**Error! Reference source not found.**).[44] The main chain of poly(α-pinene) consists of two different repeating units, one of which is similar to that of poly(β–pinene) (**29**), the other is a norbornane-like structure **30** (**Error! Reference source not found.**).

Despite the lack of reactivity exhibited by **11**, a considerable amount of research has been devoted to the cationic polymerisation because α-pinene (**11**) is the most naturally abundant terpene, as previously mentioned. Initial attempts at the polymerisation using traditional Lewis acid catalysts proved to be ineffective. However, many groups have successfully produced homopolymers of **11** by combining Lewis acids with $SbCl_3$ as an activator.[57–59] The cocatalytic effect of the $SbCl_3$ is a result of the stabilisation of the growing carbenium ion, which favours the formation of polyterpenes. The polymerisation of **11** was carried out in toluene at -15 °C using an $AlCl_3/SnCl_3$ system produced poly(α-pinene) (**29**) with $\dot{M}_n$ = 1.1-1.6 kDa. These conditions produced a negligible proportion of dimers compared to when $AlCl_3$ was used without the presence of $SnCl_3$.

The polymerisation of **10** was also investigated using these conditions, and interestingly it was found that $SnCl_3$ actually inhibited the polymerisation rate and resulted in a poorer molecular weight distribution.[44,56] Other attempts at the polymerisation of α-pinene (**11**) include the hydrothermal deposit of $AlCl_3$ onto a zirconium mesoporous material and the use of the resultant solid Lewis acid as a catalyst.[60]

Despite the many attempts at polymerisation of α-pinene, most studies have been less than successful, yielding only oligomers. This suggests that even though α-pinene is an abundant, cheap and renewable resource it does not have the required reactivity to be utilised as a renewable monomer, for homopolymerisation.

2.3 Polymers from other terpenes

2.3.1 Limonene (**6**)

Limonene (**6**) containins both chiral centres and carbon-carbon double bonds. The (*R*)-enantiomer is produced on a scale of over 70 KTA as a by-product of the citrus industry.[61]

and the molecule is present in more than 300 plants.[62] The polymerisation of **6** was first carried out by Roberts and Day using Frieldel-Crafts conditions; early attempts were only capable of producing low molecular weight polymers.[37] The cationic polymerisation of limonene (**6**) using $AlCl_3$ as a catalyst was studied by Brum *et al.*[63] The poly(limonene) (**32**) produced had a very low molecular weight (*ca.* 0.5 kDa) and low conversions of only 7% were achieved, this is likely attributed to chain termination via β-elimination. Satoh *et al.* were able to synthesise a copolymer of limonene and malemide *via* radical polymerisation.[64] When the polymerisatation was carried out in a fluroalcohol the polymer spontaneously formed an almost complete 1:2 (limonene:malemide) statistical copolymer. A random copolymer was not produced and this is thought to be due to the bulky structure of limonene.[65] The rigid cyclic structures of the monomer resulted in a polymer with a very high T_g *ca.* 220-250 ^oC, this highly ordered polymer could be used to mimic natural polymers. This material has good structural order and thermal properties however, within the repeating unit of the polymer only a third is composed of a terpene based monomer.

Recently, a study reported the radical homopolymerisation of **6** using benzoyl peroxide as an initiator at 85 °C in xylene.[66] The resultant polylimonene has a glass transition temperature (T_g) of 116 °C. This research indicates that it is perhaps possible to produce high molecular weight homopolymers of **6** through radical polymerisation, but more research is needed to improve the low conversions. Moreover, this research is contradictory to what has been reported previously regarding the radical polymerisation of limonene, and Indeed, **6** has been shown to act as a chain transfer agent for radical polymerisations hence producing very low

M_w polymers.[67,68]

New methods to utilise limonene (**6**) in polymer chemistry are clearly required since it is such an abundant waste stream.[69,70]

2.3.2 Myrcene (**8**)

Myrcene (**8**) is a basic monoterpene that can be readily obtained from the essential oils of plants or from the pyrolysis of pinene.[71] Myrcene (**8**) has three double bonds meaning that there is the possibility for radical or cationic polymerisation at three sites. Myrcene can be functionalised through its double bonds leading to polymers with a range of applications. It was shown by Sarkar *et al.* that **8** can be polymerised through an environmentally benign emulsion polymerisation method.[72] The mild conditions (70 °C for 20 h) yielded polymers of 92 kDa with a T_g of -73 °C. The polymers displayed properties such as a low T_g, and thermal stability makes this polymer a good candidate for biobased elastomers. More recently Kali and co-workers have synthesised polymyrcene using a solvent free controlled radical polymerisation (**Error! Reference source not found.**).[73] This is the first time that myrcene (**8**) has been polymerised in a controlled way, in this case RAFT was used, and this yielded polymers with low polydispersites, typically between 1.1-1.4. The polyterpene had a T_g of -60 °C, and ^1H NMR analysis showed that at least 96% of the polymer consisted of 1,4 polymyrcene.

The use of terpenes to produce ‘green plastics’ has been the subject of a large amount of research in the past decade, however many of the polymers produced using terpenes as monomers have not been able to compete with the current petroleum analogues. Various polymerisation processes lack control over molecular weight and structure, or require undesirable conditions such as high temperatures, toxic solvents or precious metal catalysts.[45,55] Development of controlled living mechanisms has led to the synthesis of terpene derived polymers with high molecular weights and useful properties. However, this was mainly achieved by the introduction of synthetic comonomers into the monomer feed, hence reducing the sustainability of the resulting polymer.[54]

Much of the research into the polymerisation of terpenes in their raw form has resulted in polymers which lack the desired properties to compete with the plastics currently used commercially. It is clear that although the use of renewable and sustainable materials is desirable, this path is futile if the synthesised polymers cannot compete with current plastics both in terms of cost and performance. New approaches are required to utilise terpenes as monomers for renewable polymers. One strategy is to perform controlled and sustainable functionalisation of the terpenes to transform them into monomers that can produce more competitive polymers. The following section will explore this strategy for the production of renewable polymers.

3. Polymers from functionalised terpenes

*3.1 Limonene (**6**)*

A common transformation of limonene is the epoxidation of the internal double bond to produce **35** and **36**. The Coates research group utilised carbon dioxide and **37** and **38** to produce linear polycarbonates based upon prior success of petroleum-based cyclohexane oxide/carbon dioxide copolymerisation (**Error! Reference source not found.**).[74]

β-Diiminate zinc acetate complexes **39** (**Error! Reference source not found.**) were chosen as catalysts due to their high activity towards polymerisation of epoxides and carbon dioxide.

The polymerisation was carried out at 25 °C, regioregular alternating polycarbonates, **37** and **38**, were produced with a high molecular weight $\dot{M}_{n} =$ 25 kDa and a Đ of 1.16. When the temperature was increased to 50 °C the reaction yielded a more random copolymer of polycarbonate with a noticeable decrease of molecular weight and broadened dispersity (Đ = 1.34). Low temperature polymerisation facilitated the stereo- and regioregular ring-opening of **35** and **36**, but this was accompanied by longer reaction times required to yield high molecular weight. One drawback of this synthesis, is the polymerisation of only the *trans* isomer of limonene oxide resulting in a large amount of unreacted starting material.

In an attempt to combat this Greiner and co-workers developed a stereoselective synthesis of limonene oxide, producing little of the *cis* isomer of limonene oxide.[75] Not only was the synthesis more efficient, it also produced high molecular weight polymers (M_n >100 kDa) with attractive thermal properties (e.g. T_g = 130 ^{o}C) by reducing the amount of alcohol impurities, which can act as chain transfer agents, in the monomer feed. The monomer synthesis was scaled up to 1.3 kg of limonene oxide per batch, working in such a way that the organic solvents used could be recycled after use, imparting an additional sustainable aspect to this polymerisation.

Following their previous work, the Coates research group synthesised the single enantiomers of **37** and combined the two amorphous enantiomerically pure polymers together in a 1:1 ratio.[76] These polymers then formed a stereocomplexed, semi-crystalline polymer with enhanced mechanical properties compared to the single enantiomers of the polymer.

Thiol-ene additions are widely used as very efficient transformations since they display click reaction features.[77] Meier and co-workers utilised the high atom efficiency of thiol-ene additions to introduce different functional groups to produce limonene based homopolymers.[61] Limonene (**6**) was reacted with both hydroxyl and methyl ester functionalised thiols to produce monomers which would be suitable for polymerisation through polycondensation (**Error! Reference source not found.**).

Limonene (**6**) has two carbon-carbon double bonds, one of which is exocyclic and the other endocyclic, both mono and bis-addition products were obtained because of the differences in reactivity of the two bonds. When a 1:1 ratio of terpene:thiol was used only a low conversion of the double bonds was achieved <50%. The ratio was therefore increased to 1.2 equivalents of terpene to produce the highest yield of monosubstituted product *ca.* 80%. Reactions were carried out at room temperature, in the absence of solvent and initiator, conditions which can be considered to be 'green'.

The disubstituted monomers were used for condensation polymerisation and 1,5,7-tri-azabicyclo[4.4.0]dec-5-ene (TBD) was chosen as a catalyst due to its high transesterification activity. The steric effect of the bulky cyclic structure of the terpene may hinder the catalyst and prevent access to reactive centres, resulting in the formation of mainly oligomers with the diester and diol despite the fact TBD has a high activity.

Polymerisation between two heterodifunctional monomers produced polymers **40** and **41** with molecular weights $\dot{M}_n$ = 8 kDa and 10 kDa and a Đ of 1.65. It was discovered that high molecular weight polymers could be obtained from the diol or diester monomers with a spacer between limonene units to reduce the steric hindrance. The co-monomers were long-chain fatty acid-based diesters and diols derived from castor oil which can also be classed as a renewable monomer. Condensation polymerisation was carried out at 120 °C under vacuum using the same TBD catalyst. Polymers with a higher molecular weight $\dot{M}_n$ = 9 kDa – 25 kDa were obtained, probably due to the reduction of steric hindrance from the long chain spacers. The T_g of all polymers were ≈ −45 °C and the melting points varied from −15 °C to 50 °C.

More recently the Meier group utilised the thiol-ene click chemistry to synthesise new renewable diamine monomers from (*R*)-(+)- and (*S*)-(−)-limonene (**6**).[78] In order to obtain renewable polyamides, the co-polymerisation of the synthesised diamines with different renewable diesters *via* polycondensation polymerisation was attempted (**Error! Reference source not found.**). This method was also used to obtain isocyanate free polyurethanes.

The synthesis of renewable polyamides **42** with molecular weights up to $\dot{M}_n$ = 12 kDa can be obtained *via* the selective combination of thiol modified limonene.

Work by Meier and co-workers also demonstrates the potential for elegant and efficient chemical functionalisation of renewable monomers.[61,78] The functionalisations were carried out at room temperature without the presence of solvents. However, the use of thiols in polymers can be seen as undesirable because of potential discolouration and bad odours; both are important considerations when developing polymers for commercial applications.

Commodity monomer terephthalic acid (**44**) was synthesised from limonene (**6**) (**Error! Reference source not found.**) in order to form poly(terephthalic acid) (PTA).[79] This is an example of a biobased version of a plastic which is already in use and therefore has properties which are desirable. However, this is a very expensive synthesis of PTA and the method used cannot be described as green. Thus, merely using a renewable alternative as a starting material for a polymer does not necessarily result in a sustainable or commercially viable route to a polymer. There must be a synergetic relationship between the development of sustainable synthetic methods and the advances of novel and imaginative biomaterials.

*3.2 Myrcene (**8**)*

Kobayashi *et al.* prepared high molecular weight poly(3-methylenecyclopentene) (**46**) using a combination of Grubbs metathesis and cationic polymerisation (**Error! Reference source not found.**).[71]

Grubbs second generation catalyst (Grubbs II) was used to convert **8** into 3-methylenecyclopentene (**45**), which was subsequently polymerised *via* cationic polymerisation. This process produced a high molecular weight and regiopure polymer **46**, $\dot{M}_n$ = 22 kDa with a Đ of 1.12. The cationic polymerisation was initiated using an *i*BuOCH(Cl)Me/$ZnCl_2$/Et_2O system at -40 °C in toluene, and demonstrated excellent control of the molecular weight. Low Đs indicated a living process was achieved and these polymers displayed a T_g of 11 °C. However the ring closing metathesis uses an expensive ruthenium metal catalyst, and is a low yielding step (45%).

*3.3 Carvone (**47**) and Menthol (**54**)*

Another common terpene is carvone (**47**), this can be found in both spearmint and caraway oils and is produced on the scale of 10 KTA.[80] Hillmyer and co-workers hydrogenated **47** using Wilkinson's catalyst to give dihydrocarvone (**48**) and carvomenthone (**51**), these monomers could be further modified by the Baeyer-Villiger reaction to produce lactones **49** and **52** which can be polymerised through ROP (**Error! Reference source not found.**).[81]

To avoid epoxidation of the terminal alkene of **48** Oxone® was chosen as the oxidant for the Baeyer-Villiger reaction. The polymerisation was carried out in bulk at 100 °C using diethyl zinc as a catalyst and benzoyl alcohol as the initiator. The ROP yielded carvomenthone-based polymers **50** with high molecular weights $\dot{M}_n$ = 62 kDa, a Đ of 1.16 and a T_g of −27 °C and dihydrocarvone-based polymers **53** with a molecular weight $\dot{M}_n$ = 10.5 kDa, a Đ of 1.24 and a T_g of −20 °C.

Menthol (**54**) is another terpene and is commercially available in its oxidised form, a compound known as menthone (**55**). Hillmyer and co-workers were able to synthesise polymers (**57)** based on menthol using a similar method to the previously mentioned ROP of carvone derivatives (**Error! Reference source not found.**).[82] **55** is readily converted to a lactone monomer, menthide (**56**), by the Baeyer-Villiger oxidation using *m*CPBA as an oxidising agent. The ROP of **56** utilised a highly active zinc alkoxide catalyst which was previously discovered within the Hillmyer group, allowing the polymerisation to run at room temperature in toluene for 8.5 hours. By adjusting the monomer to catalyst ratio, polymers with molecular weights ranging from $\dot{M}_n$ = 3 kDa to 91 kDa with the Ðs below 1.6 were formed.

Using similar principles to Hillmyer, the Winnacker research group utilised the Beckman rearrangement to synthesise lactams **59** and **62** from menthone (**55**) (**Error! Reference source**

not found.).[83,84] Anionic ring opening polymerisation using potassium and benzoyl chloride subsequently produced oligomers (M_w *ca.* 0.5 kDa) of the resulting polyamide **60** and **63** . These oligomers are in the early stages of research and therefore further investigations are being carried out to improve the molecular weight distribution which is currently fairly low. However, this method is a clever use of robust organic chemistry to synthesise a novel terpenoid based polyamide, with a good control of stereochemistry.

Winnacker *et al.* has further developed these polymers through improved synthesis of the polyamide **62**.[85] This was achieved through a one pot synthesis of **62** from **55**, followed by the polymerisation using NaH as a base, a more convenient reagent than elemental potassium. These advances have led to the synthesis of **63** on a larger scale, and hence further analysis has been carried out. M_w 1-5 kDa were achieved with Đ (*ca.* 2). These polymers exhibit crystalline properties and have a high T_m (300 ^{o}C) making them promising for biobased versions of Nylon-6.

3.4 Pinenes

In order to circumvent the lack of reactivity of α-pinene (**11**) towards cationic and radical polymerisation Miyaji *et al.* used a visible light photo-oxidation to quantitatively convert **11** into pinocarvone.[86] Pinocarvone possesses an exocyclic double bond, which is conjugated to a ketone moiety, and can be homopolymerised through a radical ring opening process. The polymerisation was investigated in a number of solvents to yield polyketones with an M_n of 26 kDa and a fairly high T_g (162 ^{o}C). Both enantiomers of α-pinene (**11**) were used as starting materials in order to investigate the effect of chirality on the resulting polymer. The built in chirality is a very interesting aspect of using terpenes as monomers, and resulted in polymers with optical activities.

A recent collaboration between Howdle and Stockman has developed simple chemistry to modify terpenes and create new polymers.[87] Cheap and abundant terpenes, such as α-pinene (**11**), β-pinene (**10**) and limonene (**6**), were transformed into monomers by addition acrylates and methacrylate functionality to create new monomers that can easily undergo free radical polymerisation.

A variety of terpene derived monomers have been synthesised (**Error! Reference source not found.**). **10**, **11** and **6** were functionalised by use of a hydroboration then oxidation sequence in order to install a hydroxyl functionality. In the case of **47**, an alcohol was formed by reduction of the enone functionality with lithium aluminium hydride. The hydroxyl functionalised terpenes were esterified with acryloyl or methacryloyl chloride using Et_3N as a base.

These new monomers **64-71** were polymerised through conventional free radical polymerisation using azobisisobutyronitrile as an initiator. In most cases the polymerisations were successful yielding the polymers **72-78** (**Error! Reference source not found.**). The polymerisations gave polymers with molecular weights up to 106 kDa with high conversions *ca.* 98 %. The Đ was across a large range (1.3-2.2), as expected for FRP which do not use control agents. The polymers also displayed T_g values from -18 °C up to 142 °C, giving them the potential for many applications.

Varying the terpene and acrylic acid starting materials allows tuning of the properties of the resultant polymer, making them excellent candidates for commercially useful polymers from renewable resources. The above synthesis of the monomers is currently neither ‘green’ or sustainable. However, with the evidence of the useful properties of these polymers an effort can be made to optimise the conditions and develop improved routes for both the synthesis of the monomers and the polymerisation process.

With this in mind the synthesis was developed to move away from the toxic acryloyl and methacryloyl chloride and substituting with acrylic and methacrylic acid; both of which will become commercially available from renewable sources. A propyl phosphonic anhydride was introduced to promote ester coupling between terpene alcohols and acrylic acid, producing an environmentally benign water-soluble triphosphate by-product; considerably more sustainable than chloride in any waste stream.

Howdle, Stockman and co-workers looked into a more efficient one step synthesis of the monomers *via* C-H activation, which can be viewed as an efficient way of functionalising alkenes.[87] Methacrylic acid was added to **10** *via* catalytic C-H functionalisation using $Pd(OAc)_2$ as a catalyst (**Error! Reference source not found.**). Optimal conditions were found to be 2 mol% $Pd(OAc)_2$, 2 equiv. benzoquinone under an atmosphere of O_2 and using methacrylic acid as the solvent. The reaction was carried out at 50 °C for 16 h and produced two possible products in 82% (**79** and **80**) in a 10:1 ratio.

C-H activation has been successful in improving the synthesis of acrylate and methacrylate functionalised monomers by reducing the number of steps from one to two, as well as producing new interesting monomers. Though this work is still ongoing, promising results have been demonstrated.

The research highlighted above really emphasises the benefits of collaboration within the scientific disciplines, here the convergence of polymer and organic chemistry has resulted in novel polymers with interesting and useful properties.

The polymers synthesised above are derived from renewable resources and possess required chemical properties which is crucial when developing new green and sustainable plastics. There are still problems to be solved, for example a renewable source of the acrylic and methacrylic acids is required. However, new processes are appearing, and synthetic biology looks set to create a ‘toolbox’ of platform chemicals that could be considered in the future.

3.5 Rosin acids

Gum rosin is the non-volatile fraction of pine resin obtained by tapping living pine trees and is the most common rosin. Production of rosin exceeds 1,000 KTA, consisting primarily of resin acids which include both abietic- and primaric type rosin acids with characteristic hydrophenanthrecene structures (**Error! Reference source not found.**).[36] The synthesis of polymers using rosin acids is a huge area of research and will not be covered in depth here, more comprehensive reviews have been published previously.[88,36]

Main chain polymers derived from rosin acids are most commonly polymerised by step growth polymerisation taking advantage of carboxylic acid functional groups. A range of functional monomers from rosin acids have been synthesised using Diels-Alder reactions.[89]

These monomers lead to the preparation of polyesters, polyamindes, polyamindeimides and polyester polyols.[90] Many of these main chain polymers have low molecular weights and this is due to steric hindrance of the bulky rosin acids, monomer impurities and stoichiometric control.[88]

Rosin acids have been converted into vinyl, acrylic or allyl ester groups that can undergo radical polymerisation (**Error! Reference source not found.**).[91] Controlled radical polymerisation of monomers derived from gum rosin enables the preparation of well-defined polymers with high molecular weight and functionality, these could be developed into advanced materials such as thermoplastic elastomers and composites.

Tang and co-workers have developed a series of well-defined rosin-containing (meth)acrylic polymers by controlled polymerisation.[91] The conversion of the carboxylic acid group of **88** and **86** to acrylate and methacrylate groups respectively resulted in the synthesis of monomers containing a vinyl group which was highly susceptible to radical polymerisation **87a-c** and **89**. Atom transfer radical polymerisation (ATRP) was used to polymerise the (meth)acrylate monomers.

Acryloyloxyl dehydroabieticcarboxylate (ADA) (**89**) in which the dehydroabietic group is connected directly to the vinyl ester group, was prepared from acryloyl chloride and dehydroabietic alcohol, obtained by reduction of dehydroabietic acid (**83**) with sodium borohydride (**Error! Reference source not found.**). For monomers 2-methacryloyloxyethyl dehydroabieticcarboxylate (MAEDA) (**87c**), 2-acryloyloxyethyl dehydroabieticcarboxylate (AEDA) (**87a**), and 4-acryloyloxybutyl dehydroabieticcarboxylate (ABDA) (**87b**), dehydroabietic acid (**83**) was first converted into an acyl chloride using oxalyl chloride followed by the in-*situ* esterification reactions with hydroxyl groups of corresponding (meth)acrylates.

Copper catalysed ATRP of **89** was carried out to give polymers with a broad dispersity indicating the reaction was not controlled. This was most likely due to the dominating steric hindrance of the dehydroabietic moiety. For other acrylates, ATRP allowed the preparation of well-defined rosin-derived polymers with low Đ and controlled molecular weight. The molecular weight of polymers ranged from 10 kDa to 100 kDa with Đ < 1.3. The higher molecular weight was consistent with the longer spacers between the rosin moiety and the vinyl group, further indicating the action of a steric effect. These polymers exhibited tunable thermal properties by simple manipulation of monomer structures and could show potential applications for thermoplastic elastomers or composites.

It is clear that the functionalisation of renewable feedstocks using green and sustainable methods is both an interesting and a commercially exploitable field of research. In particular the transformation of renewable feedstocks to yield small molecules containing functional groups which can be readily polymerised is a very promising area of research and development.[74] The terpenes are particularly interesting because of their wide range of functional groups and chiral centres. They present a significant opportunity in the search for ‘green polymers’ and up untill now it is the lack of a viable commercial scale route to new polymers that can compete with petrochemically derived commodity polymers that is holding back this potential.

4. Conclusions and outlook

There is a long history of the polymerisation of monoterpenes, initially the most common polymerisation technique was to utilise the double bond for cationic polymerisation to produce homopolymers of α- and β-pinene.[37] Radical polymerisation has proven to be ineffective for the polymerisation of terpenes due to their high reactivity and ability to act as chain transfer agents.[67,68] The pinenes, limonene and myrecene are the most abundant terpenes and therefore research has focused on these monoterpenes which is clearly reflected in the literature. The majority of this review focused on the functionalisation of terpenes prior to polymerisation, owing to the success of this approach over recent years. This method has allowed terpene derived monomers to be polymerised through methods other than cationic and radical polymerisation. Techniques such as, ring opening and condensation polymerisations have been utilised to produce novel, terpene derived polyesters, polyamides, polyurethanes and polycarbonates with a range of properties.

Terpenes are currently produced on the scale of 300 KTA with the potential to be produced on a larger scale from waste streams if the demand was high enough. Terpenes are produced by plants through metabolic pathways and as a result have inherent functionality and chirality. The present production of terpenes is not enough to manufacture a new plastic on a large commodity scale, but the functionalised nature of terpenes could enable the synthesis of low volume and valuable speciality materials derived directly from renewable feedstocks.[51]

This review has highlighted the present difficulties surrounding production of terpene homopolymers with useful properties and a range of inventive methods being employed by some research groups to overcome this problem. Most promising perhaps is the direct functionalisation of terpenes into monomers that can be “dropped-in” to established and efficient polymerisation processes. These approaches have the potential to produce sustainable polymers with valuable and tuneable properties, but to be successful the underlying chemistry by which the terpenes are modified needs to be efficient, green and sustainable. To achieve truly sustainable polymers with real world applications the development of collaborations across all scientific disciplines and industry is imperative.

Development of renewable small molecules as novel monomers is a large and ongoing area of research. Currently many renewable feedstocks rely on the allocation of arable land to grow crops specifically for extraction of the useful molecules; an ethically questionable practice comparable to that of the first generation biofuel production processes. For the successful production of useful molecules from biomass the current extraction technology needs to be improved, or alternate carbon sources found. Of the currently available renewable polymers PLA has been the most successful, but only a small proportion of the plastics in the marketplace are developed from this and increasing capacity will rely upon more efficient routes to the continuous extraction of sugar from crops, and more energy efficient and optimised polymerisation processes.[3]

There is currently a trend towards sustainability both in research and in society. Consumers are more willing to pay extra for something that is perceived to be environmentally friendly and it now falls to the scientific community to ensure that there are suitable products on the market. In this review terpenes have been assessed for their potential as renewable monomers for polymer production.

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References

1. Williams C and Hillmyer M (2008) Polymers from renewable resources: A perspective for a special Issue of polymer reviews. *Polymer Reviews* **48(1)**: 1–10.
2. Okada M (2002) Chemical syntheses of biodegradable polymers. *Progress in Polymer Science* **27(1)**: 87–133.
3. WEF (World Economic Forum), EMF (Ellen MacArthur Foundation) and McKinsey & Company (2016) The new plastics economy: Rethinking the future of plastics. Ellen MacArthur Foundation, Crowes, UK
4. Holmberg AL, Reno KH, Wool RP and Epps III TH (2014) Biobased building blocks for the rational design of renewable block polymers. *Soft matter* **10(38)**: 7405–7424.
5. Mooney BP (2009) The second green revolution? Production of plant-based biodegradable plastics. *The Biochemical journal* **418(2)**: 219–232.
6. Anastas P and Eghbali N (2010) Green chemistry: principles and practice. *Chemical Society Reviews* **39(1)**: 301–312.
7. Yao K and Tang C (2013) Controlled polymerization of next-generation renewable monomers and beyond. *Macromolecules* **46(5)**: 1689–1712.
8. Vilela C, Sousa AF, Fonseca AC, Serra AC, Coelho JFJ, Freire CSR and Silvestre AJD (2014) The quest for sustainable polyesters – insights into the future. *Polymer Chemistry* **5(9)**: 3119–3141.
9. Dodds DR and Gross RA (2007) Chemicals from biomass. *Science* **318(5854)**: 1250–1251.

10. Ragauskas AJ (2006) The path forward for biofuels and biomaterials. *Science* **311(5760)**: 484–489.
11. Anastas P (2008) Fusing green chemistry and green engineering: DesignBuild at the molecular level. *Green Chemistry* **10(6)**: 607.
12. Mohanty AK, Misra M and Drzal LT (2002) Sustainable Bio-Composites from renewable resources: Opportunities and challenges in the green materials world. *Journal of Polymers and the Environment* **10(1–2)**: 19–26.
13. Ringsdorf H (2004) Hermann Staudinger and the future of polymer research jubilees - Beloved occasions for cultural piety. *Angewandte Chemie - International Edition* **43(9)**: 1064–1076.
14. Winnacker M and Rieger B Recent (2015) Progress in sustainable polymers obtained from cyclic terpenes: synthesis, properties, and application potential. *ChemSusChem* **8(15)**: 2455–2471.
15. Gandini A and Lacerda TM (2015) From monomers to polymers from renewable resources: Recent advances. *Progress in Polymer Science* **48**: 1–39.
16. Mathers RT (2012) How well can renewable resources mimic commodity monomers and polymers?. *Journal of Polymer Science Part A: Polymer Chemistry* **50(1)**: 1–15.
17. Gandini A (2008) Polymers from renewable resources: A challenge for the future of macromolecular materials. *Macromolecules* **41(24)**: 9491–9504.
18. Hillmyer MA and Tolman WB (2014) Aliphatic polyester block polymers: renewable, degradable, and sustainable. *Accounts of Chemical Research* **47(8)**: 2390–2396.

19. Huber GW, Iborra S and Corma A (2006) Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical Reviews* **106(9)**: 4044–4098.
20. Sugimoto H and Inoue S (2004) Copolymerization of carbon dioxide and epoxide. *Journal of Polymer Science, Part A: Polymer Chemistry* **42(22)**: 5561–5573.
21. Curia S and Howdle SM (2016) Towards sustainable polymeric nano-carriers and surfactants: facile low temperature enzymatic synthesis of bio-based amphiphilic copolymers in $scCO_2$. *Polymer Chemistry* **7(11)**: 2130–2142.
22. Drumright RE, Gruber PR and Henton DE (2000) Polylactic acid technology. *Advanced Materials* **12(23)**: 1841–1846.
23. Yates MR and Barlow CY (2013) Life cycle assessments of biodegradable, commercial biopolymers — A critical review. *Resources, Conservation and Recycling* **7**: 54–66.
24. Mecking S (2004) Nature or petrochemistry?-biologically degradable materials. *Angewandte Chemie - International Edition* **43(9)**: 1078–1085.
25. O’Keefe BJ, Hillmyer MA and Tolman WB (2001) Polymerization of lactide and related cyclic esters by discrete metal complexes. *Journal of the Chemical Society, Dalton Transactions* **(15)**: 2215–2224.
26. Bourissou D, Moebs-Sanchez S and Martín-Vaca B (2007) Recent advances in the controlled preparation of poly(α-hydroxy acids): Metal-free catalysts and new monomers. *Comptes Rendus Chimie* **10(9)**: 775–794.
27. Álvarez-Chávez CR, Edwards S, Moure-Eraso R and Geiser K (2012) Sustainability of bio-based plastics: general comparative analysis and recommendations for improvement.

Journal of Cleaner Production **23(1)**: 47–56.

28. Mascal M and Nikitin EB (2008) Direct, high-yield conversion of cellulose into biofuel. *Angewandte - Chemie - International Edition* **47(41)**: 7924–7926.
29. Gandini A (1997) Furans in polymer chemistry. *Progress in Polymer Science* **22(6)**: 1203–1379.
30. Gandini A and Belgacem NM (2007) Furan chemistry at the service of functional macromolecular materials: The reversible Diels-Alder reaction. *Materials, Chemicals, and Energy from Forest Biomass* **954(18)**: 280–295.
31. Ma J, Pang Y, Wang M, Xu J, Ma H and Nie X (2012) The copolymerization reactivity of diols with 2,5-furandicarboxylic acid for furan-based copolyester materials. *Journal of Materials Chemistry* **22(8)**: 3457–3461.
32. Gandini A, Coelho D, Gomes M, Reis B and Silvestre A (2009) Materials from renewable resources based on furan monomers and furan chemistry: Work in progress. *Journal of Materials Chemistry* **19(45)**: 8656–8664.
33. Chheda JN, Román-Leshkov Y and Dumesic JA (2007) Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chemistry* **9(4)**: 342-350.
34. Refvik MD and Larock RC (1999) The chemistry of metathesized soybean oil. *Journal of the American Oil Chemists' Society* **76(1)**: 99–102.
35. Montero de Espinosa L and Meier MAR (2011) Plant oils: The perfect renewable resource for polymer science?!. *European Polymer Journal* **47(5)**: 837–852.

36. Wilbon P, Chu F and Tang C (2013) Progress in renewable polymers from natural terpenes, terpenoids, and rosin. *Macromolecular Rapid Communicaions* **34(1)**: 8–37.
37. Roberts WJ and Day AR (1950) A study of the polymerization of α- and β-pinene with Friedel—Crafts type catalysts. *Journal of the American Chemical Society* **72(3)**: 1226–1230.
38. Gandini A (ed) (2008) *Monomers, polymers and composites from renewable resources*. Elsevier, Oxford, UK.
39. Erman WF (1985) *Chemistry of the monoterpenes*. M. Dekker, New York, USA.
40. Derfer J.M (1989) *Chemistry of turpentine*. Pulp Chemical Association, New York, USA.
41. Corma A, Iborra S and Velty A (2007) Chemical routes for the transformation of biomass into chemicals. *Chemical Reviews* **107(6)**: 2411–2502.
42. Pietila H, Sivola A and Sheffer H (1970) Cationic polymerisation of *beta*-pinene, styrene and *alpha*-methylstyrene. *Journal of Polymer Science Part A: Polymer Chemistry* **8(3)**: 727–737.
43. Carmody MO and Carmody WH (1937) Polymerization of terpenes. *Journal of the American Chemical Society* **59(7)**: 1312–1312.
44. Lu J, Kamigaito M, Sawamoto M, Higashimura T and Deng Y-X (1996) Cationic polymerization of β-pinene with the $AlCl_3/SbCl_3$ binary catalyst: Comparison with α-pinene polymerization. *Journal of Applied Polymer Science* **61(6)**: 1011–1016.
45. Lu J, Kamigaito M, Sawamoto M, Higashimura T and Deng Y-X (1997) Living cationic isomerization polymerization of β-pinene. 2. Synthesis of block and random copolymers

with styrene or *p*-methylstyrene. *Macromolecules* **30(1)**: 27–31.

46. Lu J, Kamigaito M, Sawamoto M, Higashimura T and Deng Y-X (1997) Living cationic isomerization polymerization of β-pinene. 1. Initiation with HCl−2-chloroethyl vinyl ether adduct/$TiCl_3$(O*i*Pr) in conjunction with *n*Bu_4NCl. *Macromolecules* **30(1)**: 22–26.
47. Lu J, Kamigaito M, Sawamoto M, Higashimura T and Deng Y (1997) Living cationic isomerization polymerization of □-pinene. III. Synthesis of end-functionalized polymers and graft copolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **35(8)**: 1423–1430.
48. Yu P, Li A-L, Liang H and Lu J (2007) Polymerization of β-pinene with Schiff-base nickel complexes catalyst: Synthesis of relatively high molecular weight poly(β-pinene) at high temperature with high productivity. *Journal of Polymer Science Part A: Polymer Chemistry* **45(16)**: 3739–3746.
49. Emsley J (1989) *The Elements*. Clarendon Press, Oxford, UK.
50. Satoh K, Sugiyama H and Kamigaito M (2006) Biomass-derived heat-resistant alicyclic hydrocarbon polymers: poly(terpenes) and their hydrogenated derivatives. *Green Chemistry* **8(10)**: 878–882.
51. Satoh K, Nakahara A, Mukunoki K, Sugiyama H, Saito H and Kamigaito M (2014) Sustainable cycloolefin polymer from pine tree oil for optoelectronics material: living cationic polymerization of β-pinene and catalytic hydrogenation of high-molecular-weight hydrogenated poly(β-pinene). *Polymer Chemistry* **5(9)**: 3222–3230.

52. Kukhta NA, Vasilenko IV and Kostjuk SV (2011) Room temperature cationic polymerization of β-pinene using modified $AlCl_3$ catalyst: toward sustainable plastics from renewable biomass resources. *Green Chemistry* **13(9)**: 2362–2364.

53. Sheffer H, Greco G and Paik G (1983) The characterisation of styrene *beta*-pinene polymers. *Journal of Applied Polymer Science* **28(5)**: 1701–1705.

54. Snyder C, McIver W and Sheffer H (1977) Cationic polymerisation of *beta*-pinene and styrene. *Journal of Applied Polymer Science* **21(1)**: 131–139.

55. Li A-L, Zhang W, Liang H and Lu J (2004) Living cationic random copolymerization of β-pinene and isobutylene with 1-phenylethyl chloride/$TiCl_4$/$Ti(O\textit{i}Pr)_4$/$\textit{n}Bu_4NCl$. *Polymer* **45(19)**: 6533–6537.

56. Lu J, Liang H, Zhang R and Deng Y (1998) Comparison of cationic polymerisation of α and β pinenes and limonene. *Acta Polymerica Sinica* **1(6)**: 698–703.

57. Higashimura T, Lu J, Kamigaito M, Sawamoto M and Deng Y-X (1993) Cationic polymerization of α-pinene with aluminium-based binary catalysts, 2. Survey of catalyst systems. *Die Makromolekulare Chemie* **194(12)**: 3441–3453.

58. Radbil’ AB, Zhurinova TA, Starostina EB and Radbil’ BA (2005) Preparation of high-melting polyterpene resins from α-pinene. *Russian Journal of Applied Chemistry* **78(7)**: 1126–1130.

59. Higashimura T and Deng Y (1992) Cationic polymerization of α-pinene with the binary catalyst $AICl_3$/$SbCl_3$. *Die Makromolekulare Chemie* **193(9)**: 2311–2321.

60. Li L, Yu S, Liu F, Yang J and Zhaug S (2005) Reactions of turpentine using Zr-MCM-41

family mesoporous molecular sieves. *Catalysis Letters* **100(3–4)**: 227–233.

61. Firdaus M, Montero de Espinosa L and Meier MAR (2011) Terpene-based renewable monomers and polymers *via* thiol–ene additions. *Macromolecules* **44(18)**: 7253–7262.
62. Bähr M, Bitto A and Mülhaupt R (2012) Cyclic limonene dicarbonate as a new monomer for non-isocyanate oligo- and polyurethanes (NIPU) based upon terpenes. *Green Chemistry* **14(5)**: 1447–1454.
63. Brum FJB, Laux FN and Forte MMC (2013) Synthesis of hydrocarbon polymers by cationic polymerization and their thermal properties. *Designed Monomers and Polymers* **16(3)**: 291–301.
64. Satoh K, Matsuda M, Nagai K and Kamigaito M (2010) AAB-Sequence Living Radical Chain Copolymerization of Naturally Occurring Limonene with Maleimide: An End-to-End Sequence-Regulated Copolymer. *Journal of the American Chemical Society* **132(29)**: 10003-10005.
65. Matsuda M, Satoh K and Kamigaito, M (2013) Periodically Functionalized and Grafted Copolymers via 1:2-Sequence-Regulated Radical Copolymerization of Naturally Occurring Functional Limonene and Maleimide Derivatives. *Macromolecules* **46(14)**: 5473-5482.
66. Singh A and Kamal M (2012) Synthesis and characterization of polylimonene: Polymer of an optically active terpene. *Journal of Applied Polymer Science* **125(2)**: 1456–1459.
67. Mathers RT, McMahon KC, Damodaran K, Retarides CJ and Kelley DJ (2006) Ring-opening metathesis polymerizations in D-limonene: A renewable polymerization

solvent and chain transfer agent for the synthesis of alkene macromonomers. *Macromolecules* **39(26)**: 8982–8986.

68. Ren S, Zhang L and Dubé MA (2015) Free-radical terpolymerization of *n*-butyl acrylate/butyl methacrylate/D-limonene. *Journal of Applied Polymer Science* **132(47)**: 42821.
69. Mülhaupt R (2013) Green polymer chemistry and bio-based plastics: Dreams and reality. *Macromolecular Chemistry and Physics* **214(2)**: 159–174.
70. Negro V, Mancini G, Ruggeri B and Fino D (2016) Citrus waste as feedstock for bio-based products recovery: review on limonene case study and energy valorization. *Bioresource Technology* **214**: 806–815.
71. Kobayashi S, Lu C, Hoye TR and Hillmyer MA (2009) Controlled polymerization of a cyclic diene prepared from the ring-closing metathesis of a naturally occurring monoterpene. *Journal of the American Chemical Society* **131(23)**: 7960–7961.
72. Sarkar P and Bhowmick AK (2014) Synthesis, characterization and properties of a bio-based elastomer: polymyrcene. *RSC Advances* **4(106)**: 61343–61354.
73. Hilschmann J and Kali G (2015) Bio-based polymyrcene with highly ordered structure *via* solvent free controlled radical polymerization. *European Polymer Journal* **73**: 363–373.
74. Byrne CM, Allen SD, Lobkovsky EB and Coates GW (2004) Alternating copolymerization of limonene oxide and carbon dioxide. *Journal of the American Chemical Society* **126(37)**: 11404–11405.

75. Hauenstein O, Reiter M, Agarwal S, Rieger B and Greiner A (2015) Bio-based polycarbonate from limonene oxide and CO_2 with high molecular weight, excellent thermal resistance, hardness and transparency. *Green Chemistry* **18(3)**: 760–770.
76. Auriemma F, De Rosa C, Di Caprio MR, Di Girolamo R, Ellis WC and Coates GW (2015) Stereocomplexed poly(limonene carbonate): A unique example of the cocrystallization of amorphous enantiomeric polymers. *Angewandte Chemie - International Edition* **54(4)**: 1215–1218.
77. Kolb HC, Finn MG and Sharpless KB (2001) Click chemistry: Diverse chemical function from a few good reactions. *Angewandte Chemie - International Edition* **40(11)**: 2004–2021.
78. Firdaus M and Meier MAR (2013) Renewable polyamides and polyurethanes derived from limonene. *Green Chemistry* **15(2)**: 370–380.
79. Colonna M, Berti C, Fiorini M, Binassi E, Mazzacurati M, Vannini M and Karanam S (2011) Synthesis and radiocarbon evidence of terephthalate polyesters completely prepared from renewable resources. *Green Chemistry* **13(9)**: 2543–2548.
80. De Carvalho CCCR and Da Fonseca MMR (2006) Carvone: Why and how should one bother to produce this terpene. *Food Chemistry* **95(3)**: 413–422.
81. Lowe JR, Martello MT, Tolman WB and Hillmyer MA (2011) Functional biorenewable polyesters from carvone-derived lactones. *Polymer Chemistry* **2(3)**: 702–708.
82. Zhang D, Hillmyer MA and Tolman WB (2005) Catalytic polymerization of a cyclic ester derived from a ‘cool’ natural precursor. *Biomacromolecules* **6(4)**: 2091–2095.

83. Winnacker M, Vagin S, Auer V and Rieger B (2014) Synthesis of novel sustainable oligoamides *via* ring-opening polymerization of lactams based on (−)-menthone. *Macromolecular Chemistry and Physics* **215(17)**: 1654–1660.
84. Winnacker M, Tischner A, Neumeier M and Rieger B (2015) New insights into synthesis and oligomerization of ε-lactams derived from the terpenoid ketone (−)-menthone. *RSC Advances* **5(95)**: 77699–77705.
85. Winnacker M, Neumeier M, Zhang X, Papadakis CM and Rieger B (2016) Sustainable chiral polyamides with high melting temperature *via* enhanced anionic polymerization of a menthone-derived lactam. *Macromolecular Rapid Communications* **37(10)**: 851–857.
86. Miyaji H, Satoh K and Kamigaito M (2016) Bio-Based Polyketones by SelectiveRing-Opening Radical Polymerization of α-Pinene-Derived Pinocarvone. *Angewandte Chemie International Edition* **55(4)**: 1372-1376.
87. Sainz MF, Souto JA, Regentova D, Johansson MKG, Timhagen ST, Irvine DJ, Buijsen P, Koning CE, Stockman RA and Howdle SM (2016) A facile and green route to terpene derived acrylate and methacrylate monomers and simple free radical polymerisation to yield new renewable polymers and coatings. *Polymer Chemistry* **7(16)**: 2882–2887.
88. Maiti S, Ray SS and Kundu AK (1989) Rosin: A renewable resource for polymers and polymer chemicals. *Progress in Polymer Science* **14(3)**: 297–338.
89. Zhang J (2012) *Rosin-based chemicals and polymers*. Smithers Rapra Technology Ltd., Shropshire, UK.
90. Liu X, Xin W and Zhang J (2009) Rosin-based acid anhydrides as alternatives to

petrochemical curing agents. *Green Chemistry* **11(7)**: 1018–1025.

91. Zheng Y, Yao K, Lee J, Chandler D, Wang J, Wang C, Chu F and Tang C (2010) Well-defined renewable polymers derived from gum rosin. *Macromolecules* **43(14)**: 5922–5924.

Figure 1. Categories of natural molecular biomass.[7]

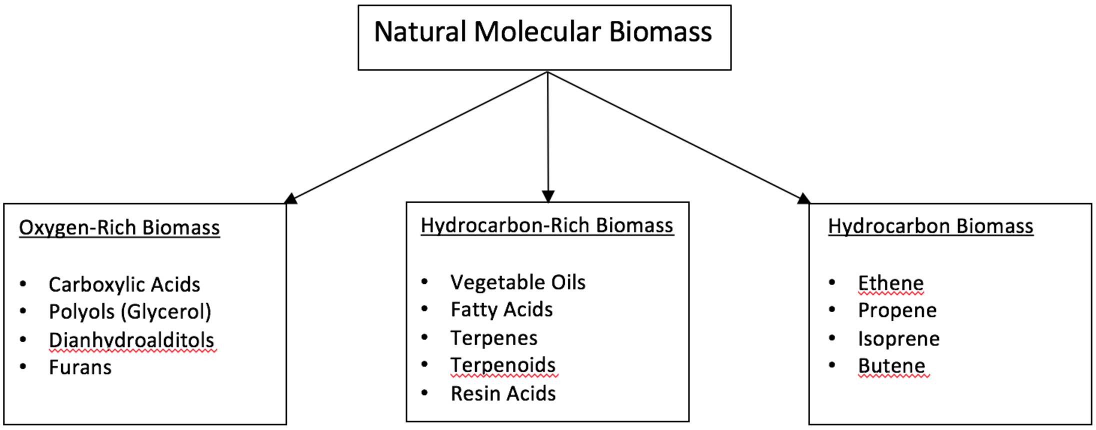
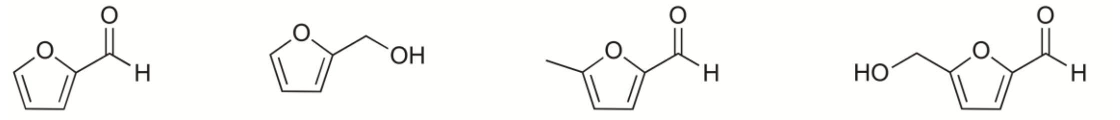


Figure 2. Furfural and some common derivatives.



Furfural 1

Furfural Alcohol 2

5-Methyl Furfural 3

5-Hydroxymethyl Furfural 4

Figure 3. Some common monoterpenes.

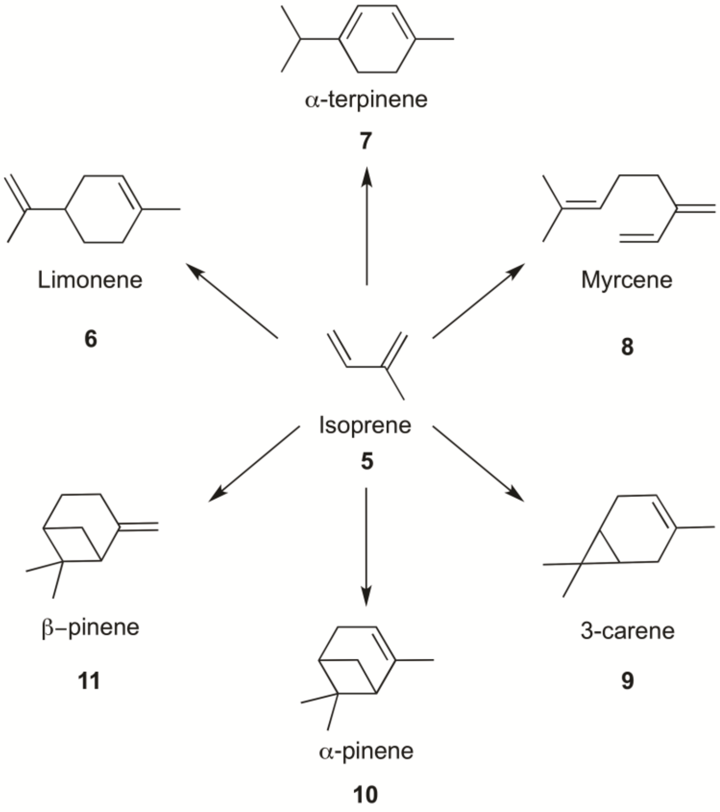


Figure 4. Schiff base nickel catalyst **23**.[48]

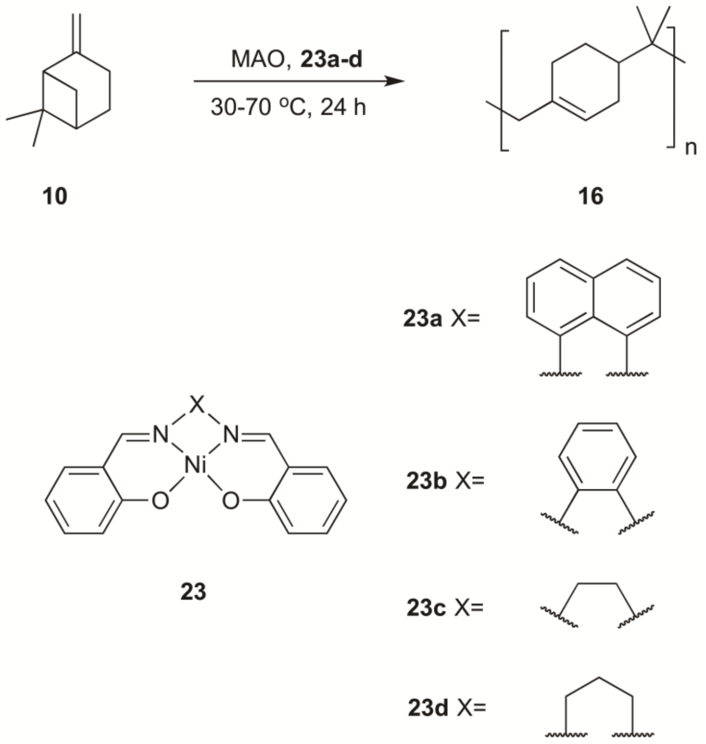
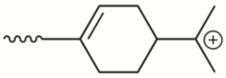


Figure 5. Propagting species of β –pinene (**10**) and isobutene.



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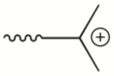

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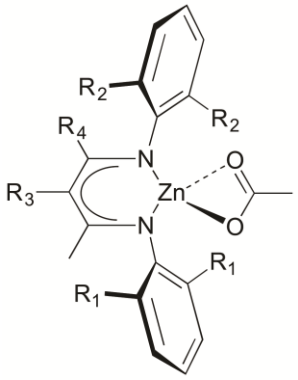
Figure 6. β-Diiminate zinc complex **39** used as a catalyst for the copolymerisation of **35** and **36** with carbon dioxide.[74]



39

Figure 7. Polyamide (**42**) synthesised from limonene (**6**).[78]

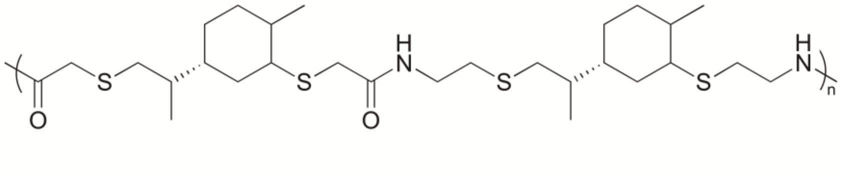


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Figure 8. Monomers derived from terpenes.[87]

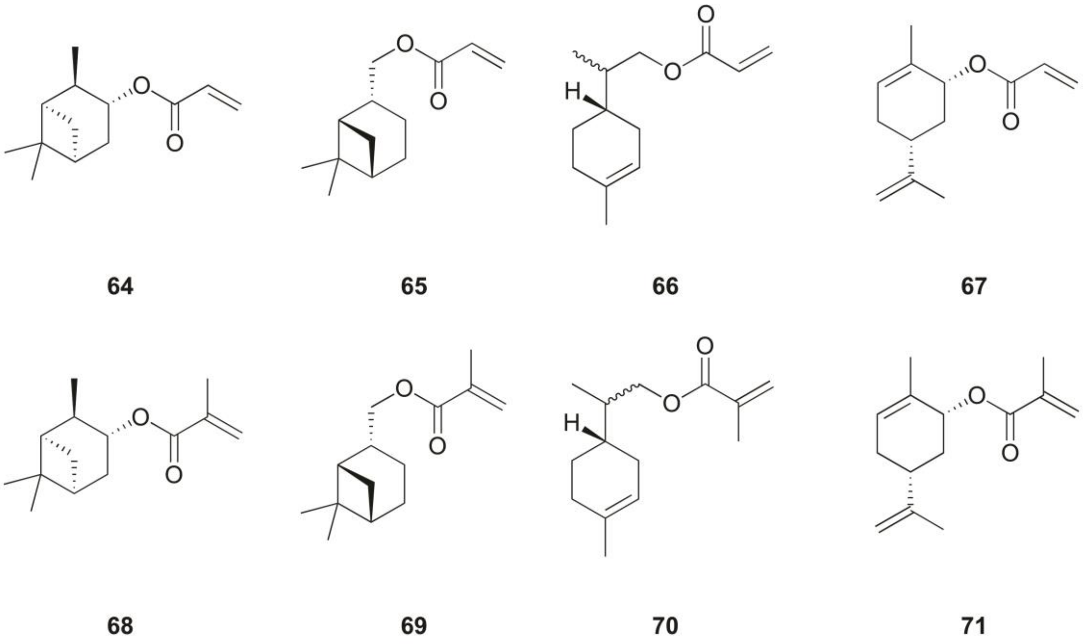


Figure 9. Polymers from acrylate and methacrylate monomers derived from terpenes.[87]

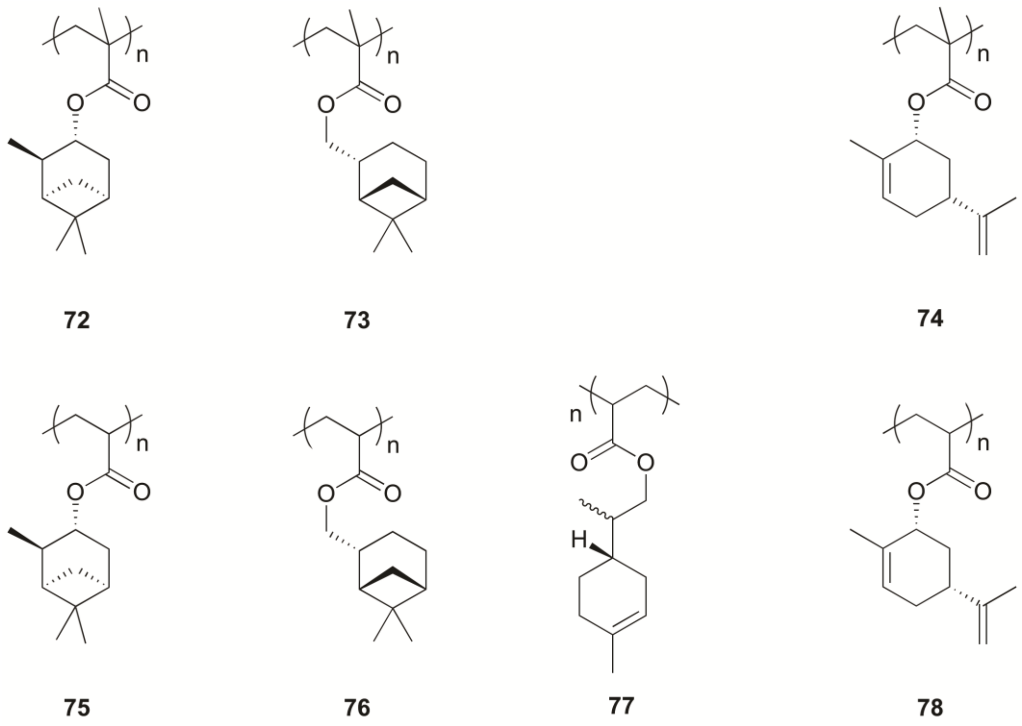
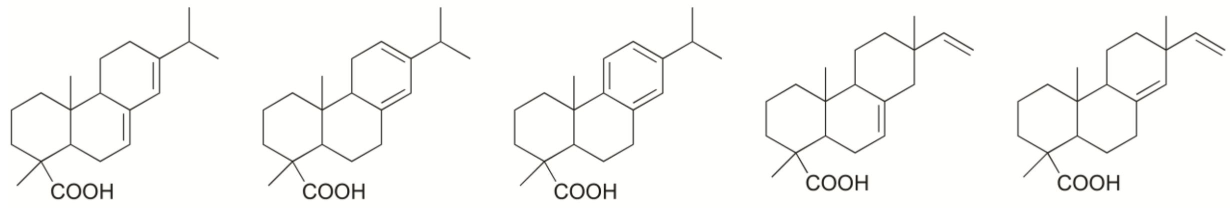
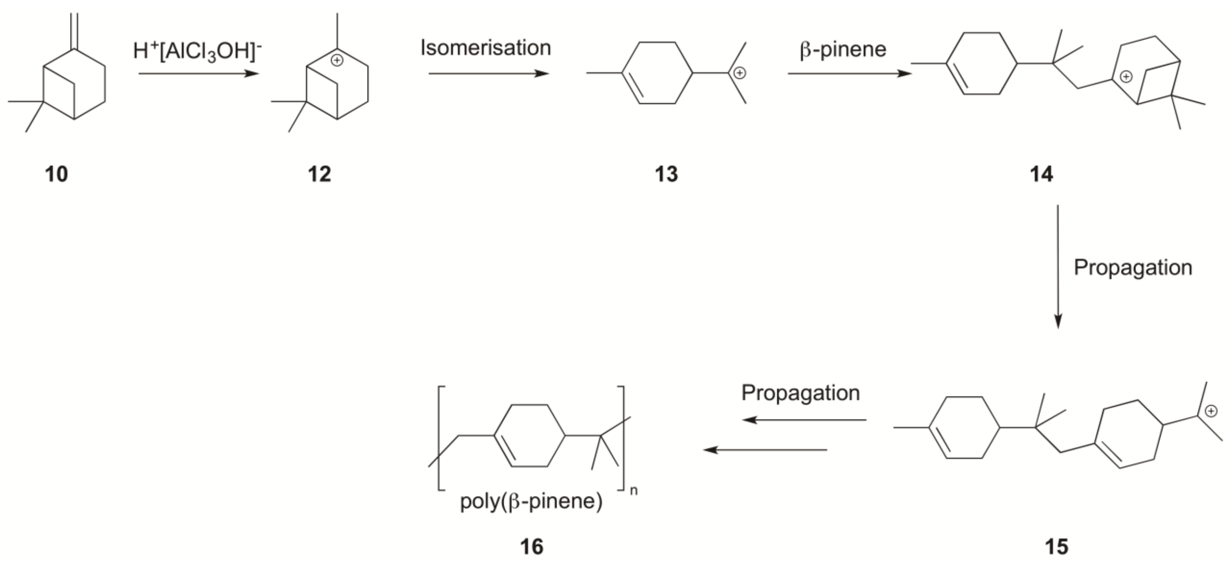


Figure 10. Some common components of pine resin.

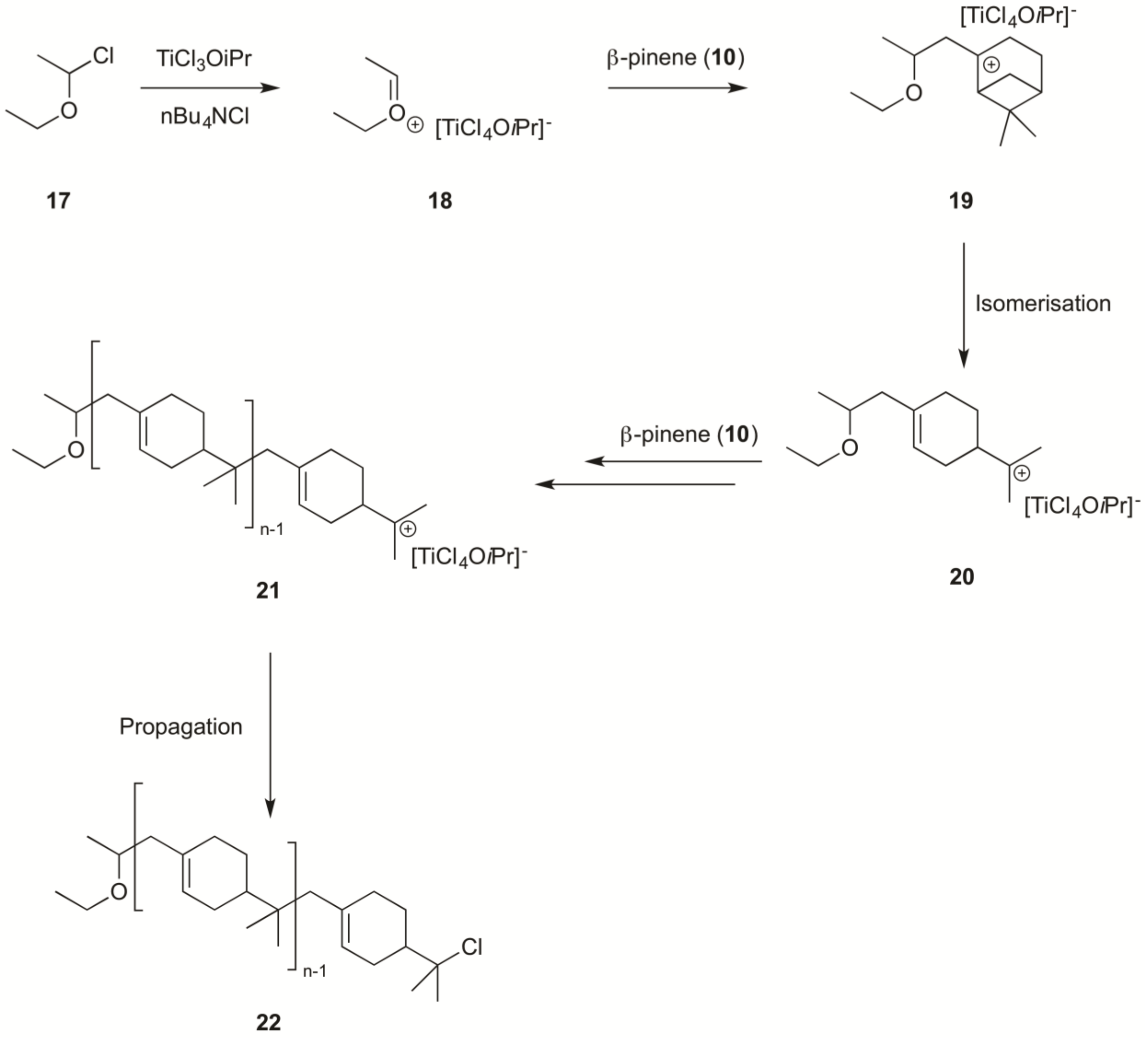


81 **82** **83** **84** **85**

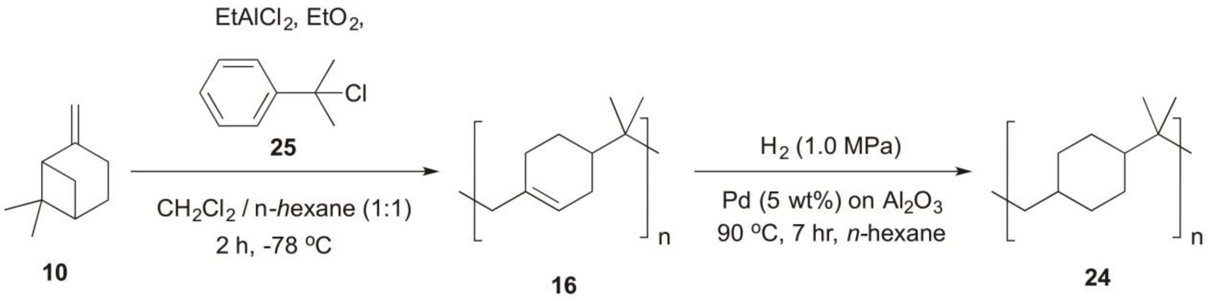
Scheme 1. The cationic polymerisation of β–pinene.[37]



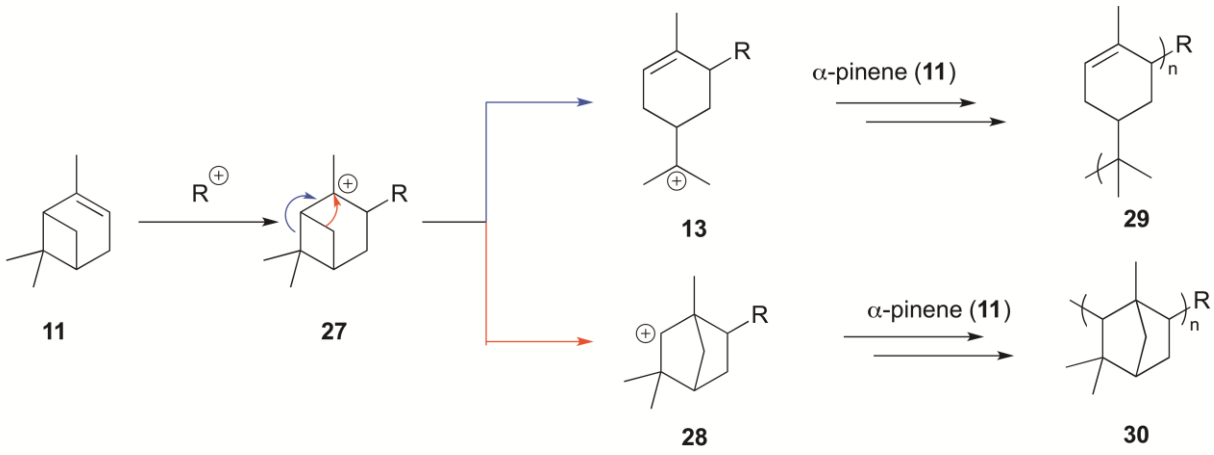
Scheme 2. The living cationic polymerisation of β–pinene (**10**).[45–47]



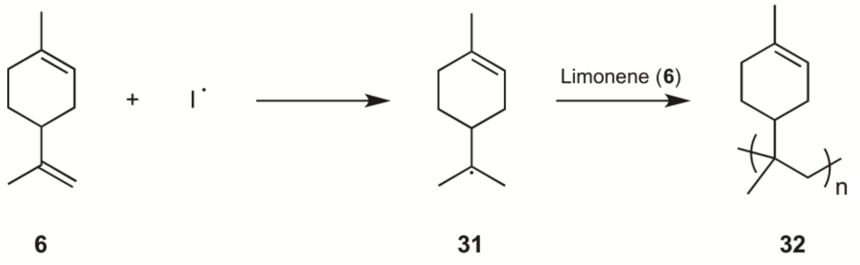
Scheme 3. Hydrogenation of poly(β-pinene) (**16**).[51]



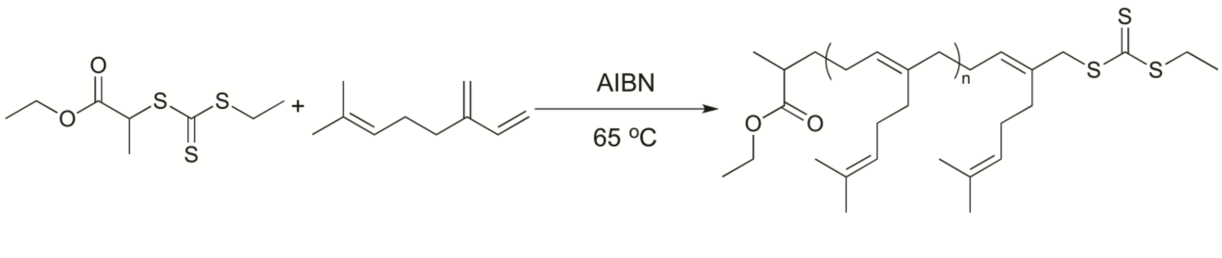
Scheme 4. The two proposed mechanisms of polymerisation of α-pinene (**11**).



Scheme 5. The radical polymerisation of 6 using benzoyl peroxide as an initiator.[66]

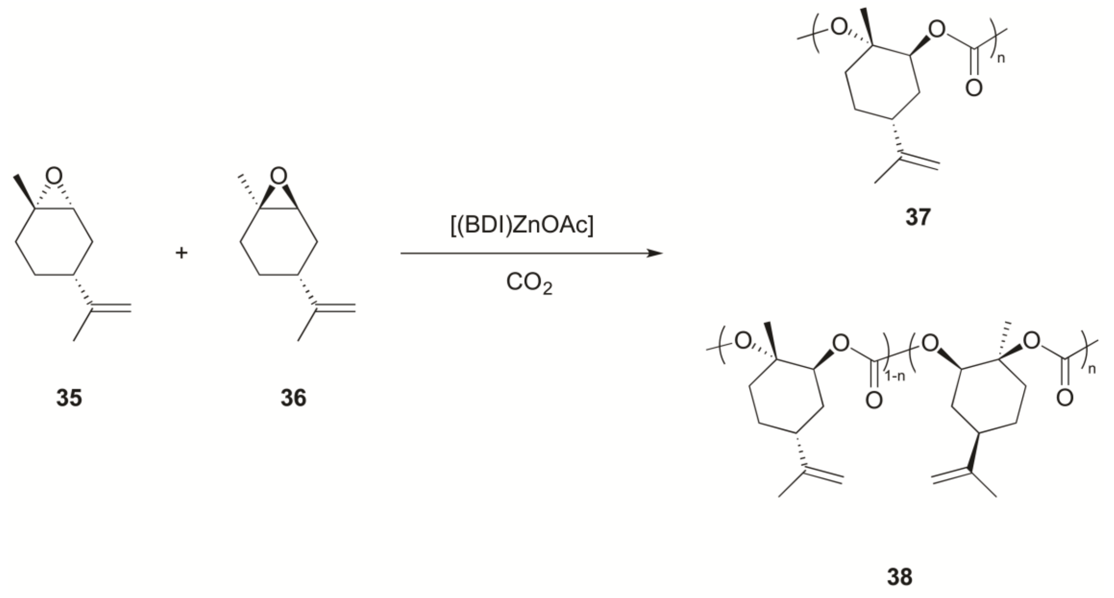


Scheme 6. Syntheis of polymyrcene (**34**) using RAFT.[73]

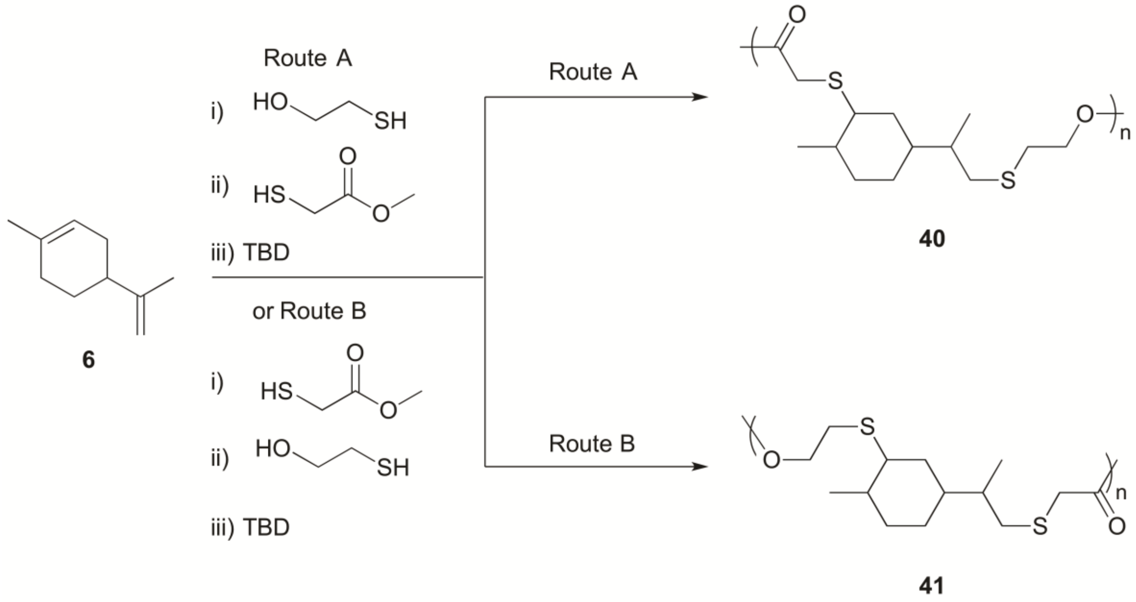


33 **8** **34**

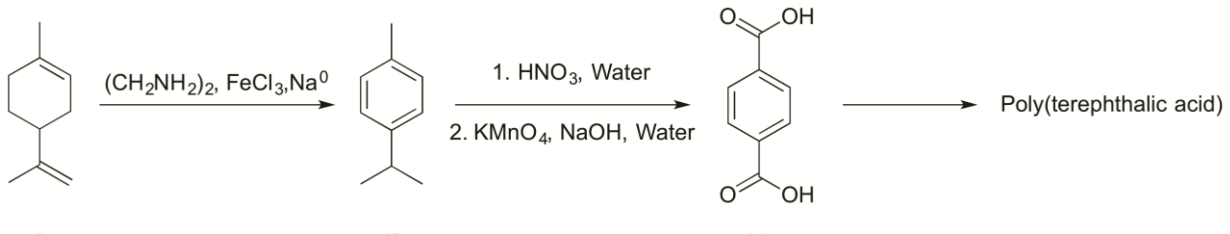
Scheme 7. Copolymerisation of **35** and **36** with carbon dioxide.[74]



Scheme 8. Conversion to polymerisable monomers through thiol-ene click chemistry, and subsequent polymers **32** and **33**.[61]

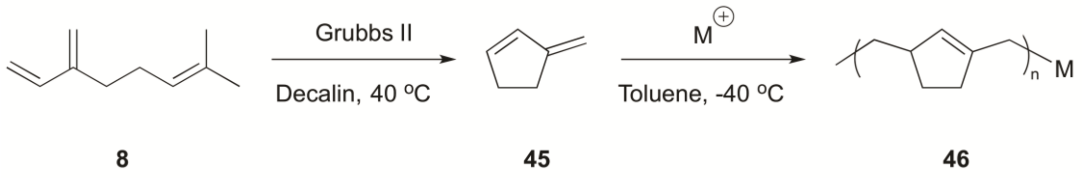


Scheme 9. Synthesis of PTA from limonene (**6**).[79]

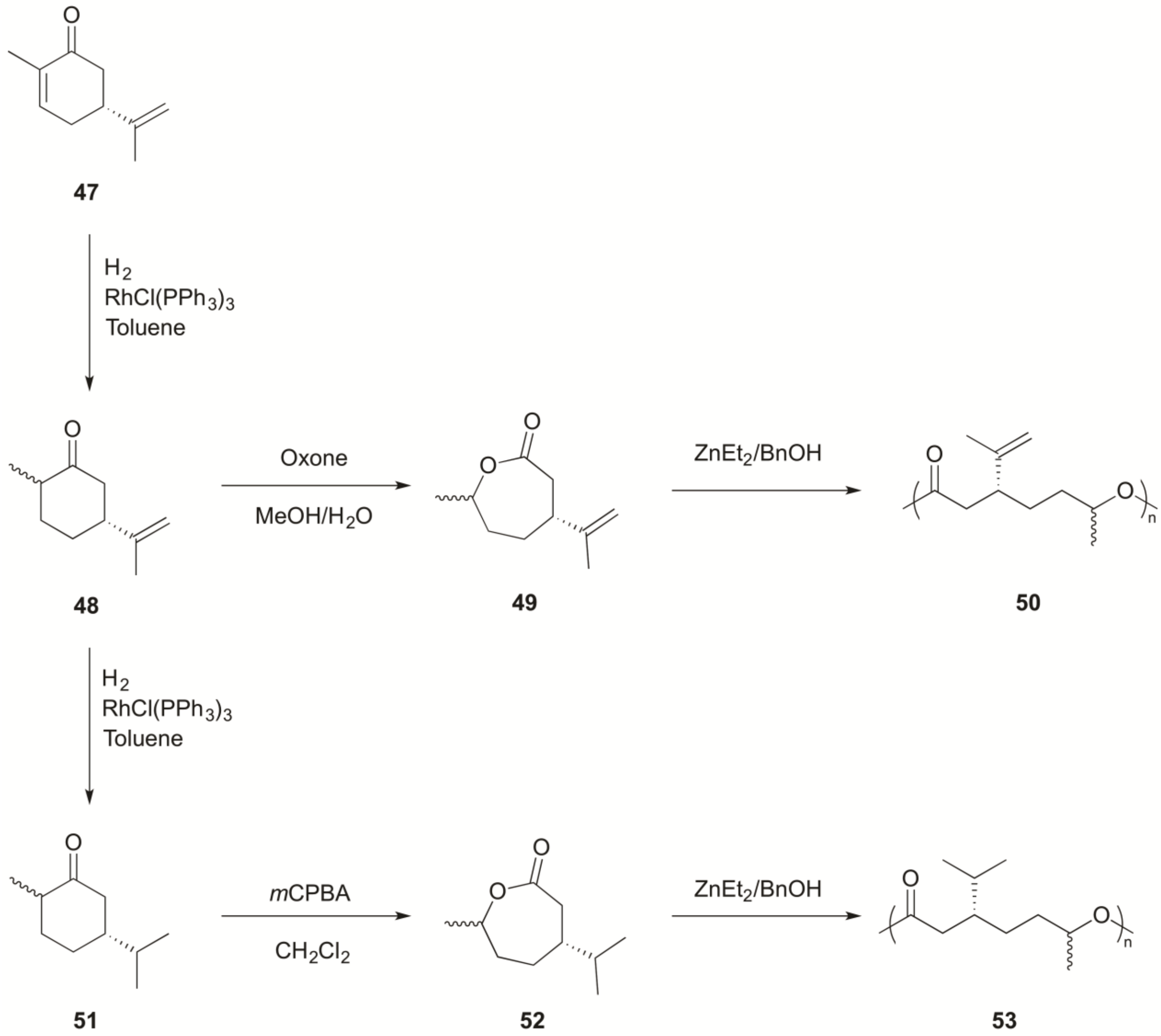


6 **43** **44**

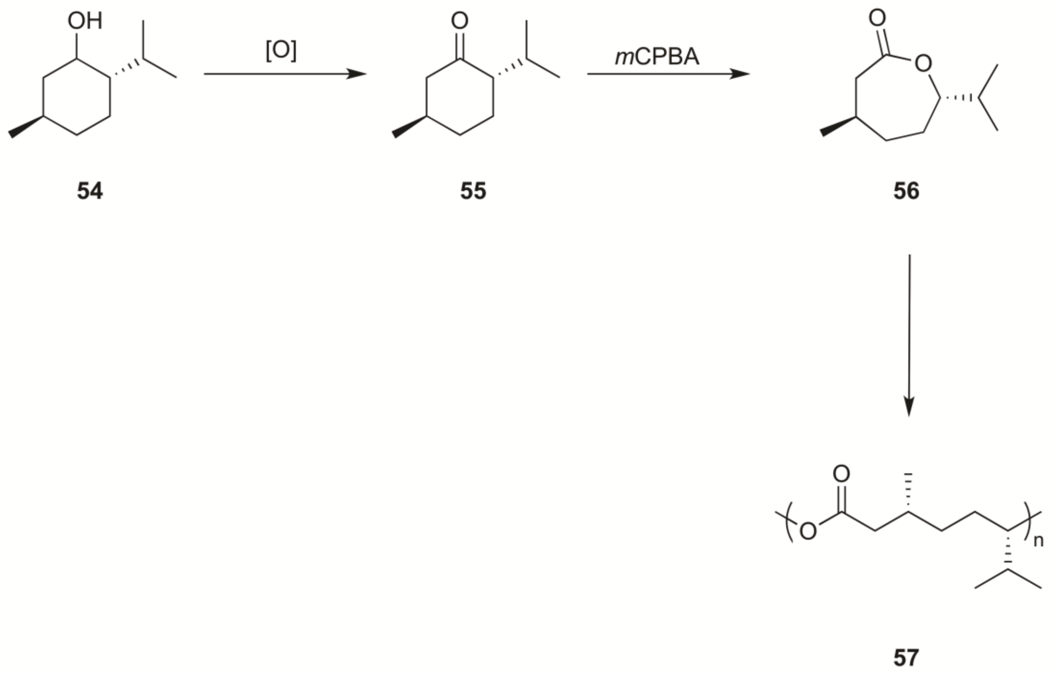
Scheme 10. Polymerisation of myrcene.[71]



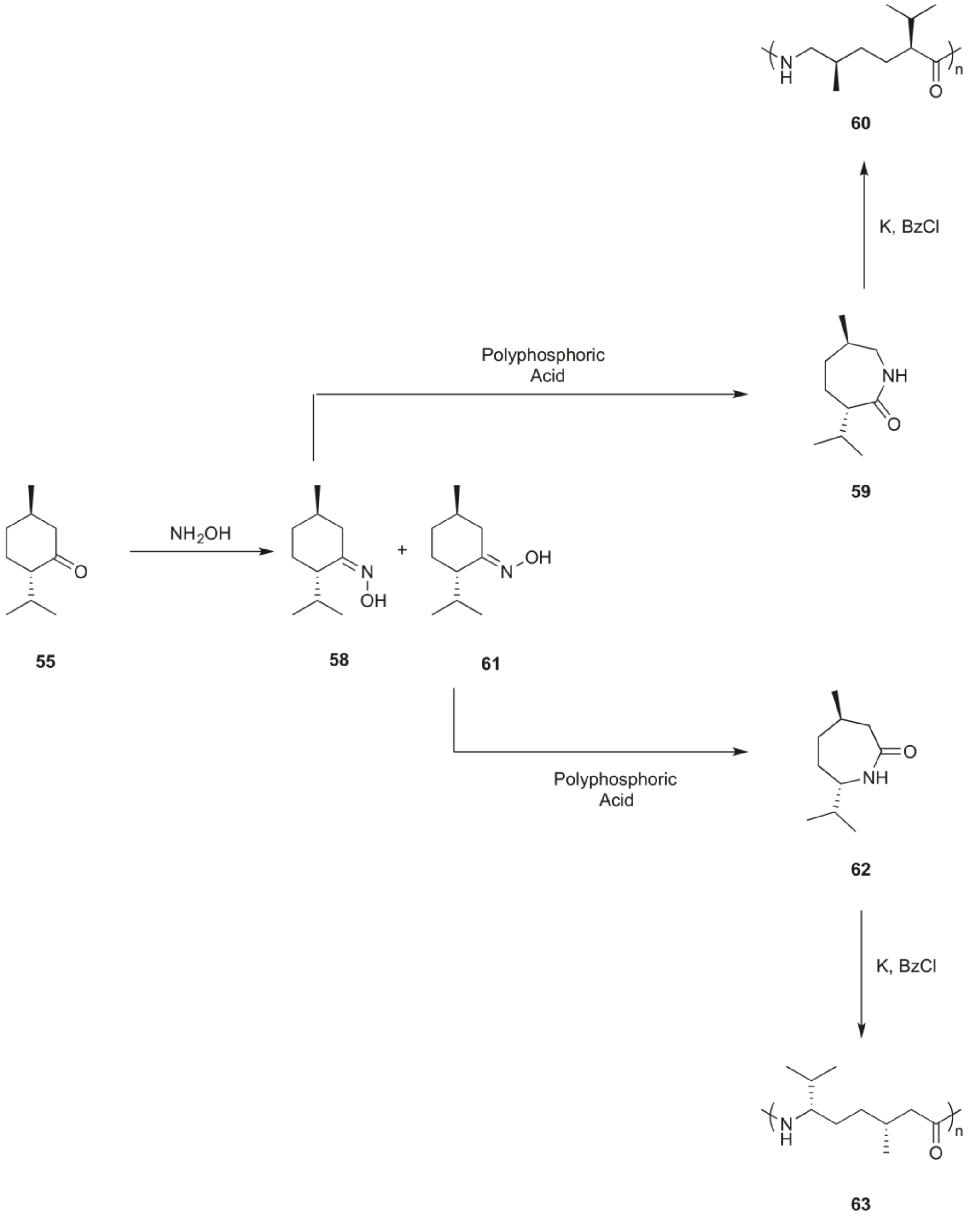
Scheme 11. Ring opening polymerisation of carvone derived monomers **49** and **52**.[81]



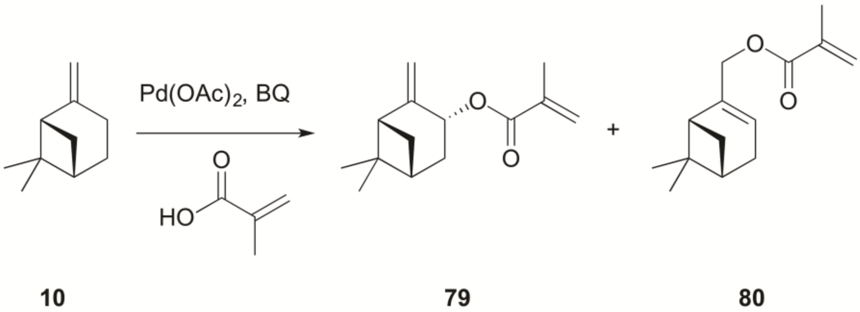
Scheme 12. Synthesis of polymers from menthol (**54**).[82]



Scheme 13. Synthesis of polymers via lactams **59** and **62** obtains using the Beckman rearrangement.[84]



Scheme 14. C-H activation of β-pinene (**10**) using a Pd catalyst to yield functionalised monomers.[87]



Scheme 15. Conversion of rosin acid to acrylates and meth(acrylates).[91]