

Controlled Polymerization of Next-Generation Renewable Monomers and Beyond

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ABSTRACT: Natural molecular biomass plays an important role in the field of renewable polymers, as they can be directly used or derivatized as monomers for controlled polymerization, in a way similar to many petroleum-derived monomers. We deliver this perspective primarily based on a monomer approach. Biomass-derived monomers are separated into four major categories according to their natural resource origins: (1) oxygen-rich monomers including carboxylic acids (lactic acid, succinic acid, itaconic acid, and levulinic acid) and furan; (2) hydrocarbon-rich monomers including vegetable oils, fatty acids, terpenes, terpenoids and resin acids; (3) hydrocarbon monomers (bio-olefins); and (4) non-hydrocarbon monomers (carbon dioxide). A variety of emerging synthetic tools (controlled polymerization and click chemistry) are particularly summarized. An overview on future opportunities and challenges, which are critical to promote biorefinery in the production of renewable chemicals and polymers, is given.



1. INTRODUCTION

Although the recent development of renewable polymers has achieved great progress, the small share (<5%) of renewable polymers in the commercial market is largely due to their high cost and inferior performance compared with synthetic polymers produced from petroleum chemicals.^{1–5} Synthetic plastics account for consumption of ~7% of fossil fuels worldwide.^{6–9} Referring to per capita consumption of plastics, the number is even more astonishing. Every person in the U.S. averagely consumed more than 140 kg of plastics in 2010. The development of renewable polymers is driven by a strong desire to reduce carbon footprint and our dependence on fossil fuels as organic material feedstock.^{8,10–17} While novel processing approaches and modifications of existing renewable polymers can be effective, the next stage of growth in this arena will rely on the development of judicious synthetic strategies for next-generation materials that involve the design, preparation, and controlled polymerizations of new monomers from abundant biomass.^{13–15,18–22}

Natural polymers, including cellulose, hemicellulose, polysaccharide, lignin, chitin, and chitosan, are considered as abundant and low-cost feedstock.^{11,12,18,23–29} These natural polymers have been widely used for a variety of applications, which play a significant role in our daily life. Physical blending and modest chemical modifications are common approaches to enhance certain properties of raw materials. More recently, advanced polymerization techniques are being used to manipulate macromolecular structures of these materials to further improve their performance. In contrast, natural resources like vegetable oils, fatty acids, hydroxyalkanoates, and lactic acids are a class of natural molecular biomass, which could be precisely molecular-engineered into renewable

polymers in a way similar to many synthetic plastics manufactured from petroleum chemicals.^{6–8,14,17,19–21,30–37}

It has been a general goal to develop renewable polymers replacing and resembling existing polymeric materials derived from petroleum chemicals.^{1,2} There are a variety of reviews and highlights published over the past decade.^{4,5,7–18,22,38–41} A thorough review of all aspects of renewable polymers is not the intention of this Perspective. Our motivation is to provide a perspective on how to prepare renewable polymers through a monomer approach, especially those from natural molecular biomass, which could achieve the control at a level similar to current petroleum-based monomers and their polymers. This Perspective starts with three main pathways to prepare monomers from natural resources. We then give a critical overview on challenges (and opportunities) that face in the field of renewable polymers. The majority of this Perspective summarizes the preparation of monomers from different classes of natural molecular biomass and their controlled polymerizations. Among natural molecular biomass, vegetable oils (including fatty acids), terpenes, terpenoids, and resin acids belong to hydrocarbon-rich biomass, while carboxylic acids and furans biomass contain significant fractions of oxygen in their structures, and carbon dioxide is a non-hydrocarbon-containing biomass. We critically assemble works on these monomers together based on various methods of controlled polymerizations in conjunction with a few highly efficient and emerging organic functionalization techniques.

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2. GENERAL PATHWAYS TOWARD SYNTHESIS OF RENEWABLE MONOMERS

Generally, there are three major pathways to produce monomers (or their precursors) from natural resources. Since these are small molecules and derived from natural resources, we call them “natural molecular biomass” in order to distinguish from macromolecular biomass (or natural polymers).

2.1. Fermentation. The most-developed pathway is to transform biomass into monomers via fermentation of carbohydrates.^{11,23} Biomass carbohydrates are the most abundant renewable resources. Lactic acid (2-hydroxypropionic acid) can be produced by fermentation of carbohydrates such as maltose, sucrose, lactose, etc. Currently, large-scale commercial lactic acid is mainly produced via the fermentation of glucose. The world production of lactic acid is around 350 000 t/year produced through the fermentation process. It is widely believed that there will be a substantial growth in the next decade. Another well-known example is the fermentation preparation of 1,3-propanediol, the key building block in poly(propylene terephthalate), via a cost-effective fermentation developed by Genencor and DuPont.¹²

It should be mentioned that polymers can be produced directly from sugars or lipids by bacterial fermentation. The most well-known polymers are poly(hydroxyalkanoate)s. There are a few excellent reviews on microbial production of poly(hydroxyalkanoate)s.^{40,42} ICI developed a fermentation pathway to prepare copolyesters from 3-hydroxybutyrate and 3-hydroxyvaleric acid.⁴³ Currently, there is a worldwide interest to scale up the process of poly(hydroxyalkanoate)s. However, this Perspective will not discuss the preparation of these types of polymers or their monomers (e.g., 3-hydroxypropionic acid).

2.2. Chemical Transformation of Natural Polymers. The second pathway involves chemical degradation and transformation of natural polymers. Lignocellulosic biomass is the most abundant renewable polymer and represents a significant sustainable feedstock. Cellulose is primarily built by C6- and C5-sugars (by polymerization of glucose), while hemicellulose is a polymer of glucose and xylose.¹¹ Lignin is a highly cross-linked polymer built of substituted phenols. Besides those components, plants also contain products such as lipids, sugars, and starches as well as other products rich in hydrocarbon including terpenes, resins, steroids, and rubber that are often found in essential oils and resins. The catalytic conversion of biomass into intermediates is an attractive technology. For example, thermal dehydration of pentoses and hexoses in acid media leads to the formation of three important basic nonpetroleum chemicals: furfural (2-furancarboxaldehyde) from dehydration of pentoses, 5-hydroxymethylfurfural (HMF) from hexoses by dehydration, and levulinic acid from hydration of HMF.

2.3. Molecular Biomass Direct from Nature. Different from the above molecular biomass derived from natural polymers or by microorganism fermentation, there is a lot of molecular biomass directly obtained from nature. Vegetable oils are among the most abundant molecular biomass.^{31,33,36,44} Most vegetable oils contain triglycerides, which consist of building blocks of glycerol and fatty acids. A great number of literatures report the use of vegetable oils to make various monomers for polymerization. Another important class of natural molecular biomass is terpenes, terpenoids, and resin acids.^{20,21,30,31}

Since nature-derived molecular biomass has much better defined chemical structures than natural polymers, it is possible to use macromolecular engineering to prepare a variety of polymers with controlled architectures and desirable properties, potentially to the level comparable to petroleum chemical counterparts. The molecular biomass obtained from four different categories will be the major focuses discussed in this Perspective.

3. CURRENT APPROACHES AND CHALLENGES TOWARD RENEWABLE POLYMERS

Great progress has been achieved in the development of renewable chemicals and polymers from natural resources. However, the stark contrast on market shares between petroleum chemicals and polymers and renewable counterparts implies the following: on one hand, the cost and performance of renewable chemicals and polymers are still far behind petroleum products; on the other hand, this indicates there is an optimistically greater potential to explore renewable chemicals and polymers. We believe there are several areas worthy for extensive exploration, which, in many aspects, requires interdisciplinary cooperation among scientists with different backgrounds.

3.1. Improving Monomer Synthesis and Polymerization Techniques. Eventually, the scale of biorefinery should be targeted similar to that of petroleum refinery, although the process of biorefinery may be significantly different. The goal of the biorefinery process is to produce high quality chemicals and monomers, which can be further derivatized into fuels, materials, and polymers. To achieve this ambitious goal, significant efforts are needed to overcome many challenging obstacles. Efficient, economical, and large-scale synthesis of monomers is vital. This will rely on a few key issues: (1) resource pool that should be abundant and easily accessed; (2) process that should be compatible with biorefinery concept; (3) chemistry that is simple, practical, and operational. Catalysts are expected to play an important role. There have been significant efforts in many countries working on catalytic processes to make biodiesels and biofuels. As most of biodiesel and biofuel chemicals are also precursors to make monomers, interdisciplinary cooperation between polymer scientists and catalyst scientists is needed.

There is also a critical need to develop powerful polymerization techniques that can be used for novel bio-based monomers. In the traditional petroleum industry, coordination polymerization, step-growth polymerization, free radical polymerization, and ionic polymerization have observed huge success in making commodity polymers. While similar monomers derived from natural resources can be polymerized by these traditional tools, many other monomers need new polymerization techniques. Controlled polymerization such as ring-opening polymerization, acyclic diene metathesis polymerization, ring-opening metathesis polymerization, and controlled radical polymerization have shown promise to achieve a certain level of success. However, many molecular biomass-derived monomers such as 2-methyltetrahydrofuran, angelica lactone, α -methylene- γ -valerolactone, 2-methylbutyrolactone, and 3-methylbutyrolactone as described in later sections of this Perspective have not been polymerized. More powerful polymerization techniques, which provide versatility, high molecular weight, and tolerance to functionalities and impurities, are essential.

3.2. Developing Highly Efficient Chemistry/Less Purification Process. Although a vast variety of monomers have been developed for precise and controlled polymerization, unfortunately many current technologies could not provide either monomers or polymers in an economical way comparable to petroleum counterparts. Before biorefinery can be achieved in a reasonably large scale,⁴⁵ other strategies need to be developed on the direct utilization of raw materials without sophisticated purification or at least materials without strict requirement on purity. A lot of natural biomass has rather complicated chemical structures but often shares common functional groups. Taking advantage of these functional groups is the key to utilize raw natural biomass. This usually requires the use of highly efficient chemistry for functionalization such as click chemistry. Another alternative pathway is to make a mixture of monomers using raw natural resources. The polymerization of these monomers usually leads to the formation of cross-linked polymers, which are certainly useful for many applications. However, the key is to find strategies to make soluble polymers out of these mixed monomers. One such example is the use of rich double bonds on raw vegetable oils to develop non-cross-linked polymers for various applications. Some groups have reported the synthesis of functionalized monomers out of the double bonds, however ending up with insoluble cross-linked thermosetting polymers.^{46–53} Liu and co-worker developed two strategies to prepare soluble polymers from raw soybean oil with triglycerides as major components using a simple hydrolysis reaction (Figure 1).^{54,55} The first strategy involved the

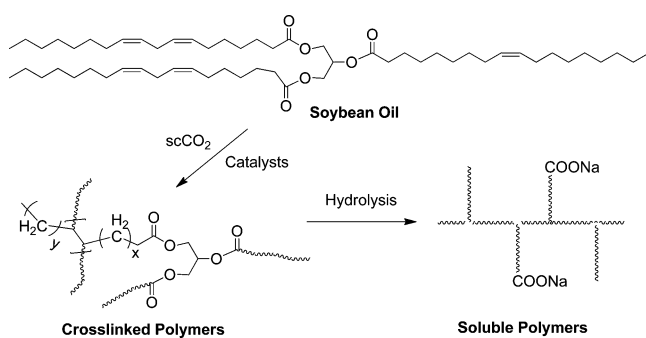


Figure 1. Preparation of un-cross-linked soluble polymers using raw soybean oil.^{54,55}

epoxidation of carbon–carbon double bonds and then underwent catalytic ROP of the epoxidized soybean oil, followed by hydrolysis with a base, giving ionic polymeric surfactant. The second strategy used direct conversion of soybean oil into polymerized soybean oil through polymerization of carbon–carbon double bonds in supercritical carbon dioxide (scCO_2). The polymerized soybean oil was then converted into ionic polymeric surfactants by hydrolysis with a base. Unlike the first strategy, the polymer backbone by the second strategy is a carbon–carbon bond.

3.3. Combining Natural Polymers and Molecular Biomass. Much research has been carried out on the modification of natural polymers with petroleum chemicals or improvement of synthetic petroleum-based polymers with natural products. The combination of natural polymers and natural molecular biomass is much less explored. Such combination would maximize the utilization of natural resources, while improving the overall performance. Most

natural polymers possess a rich functional group for functionalization to target desirable properties. A variety of molecular biomass also has functional groups. These functional groups provide channels to integrate them together (Figure 2).

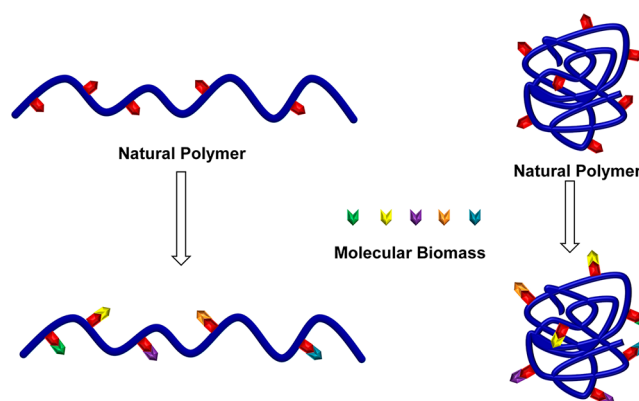


Figure 2. Conjugation between natural polymers and molecular biomass.

For example, chitosan has characteristic amino group around its polymeric framework. However, chitosan is only soluble in few dilute acid solutions due to its crystalline nature. Duan et al. grafted rosin and its derivatives (either molecular rosin or rosin polymers) onto chitosan and showed that there should be a significant improvement in solubility.^{56,57} Both degree of crystallinity and thermal decomposition temperature of chitosan graft copolymers decreased due to the presence of rosin moiety by disrupting the intermolecular hydrogen bonding. The graft copolymers also showed promise as a better carrier for controlled drug release compared to ungrafted chitosan. We have modified hydroxyl-rich lignin with rosin acids through a simple esterification reaction.⁵⁸ Such modification has a significant impact on lignin properties. Contact angle of water droplets on the rosin-grafted lignin films was $\sim 90^\circ$, while that for unmodified lignin films was only 75° . The surface of rosin–lignin composites was rich with rosin components. The enhanced hydrophobicity makes the modified lignin to have excellent water resistance by absorbing less than one-hundredth of water compared to unmodified lignin.

4. MAJOR CLASSES OF MONOMERS AND THEIR POLYMERIZATION

According to their natural molecular biomass origins, we classify monomers into four different categories based on hydrogen, carbon, and oxygen compositions (Figure 3): (1) oxygen-rich molecular biomass with the molar ratio of C/O less than an arbitrary number 5.0, including carboxylic acids, polyols, dianhydroalditols, and furans; (2) hydrocarbon-rich molecular biomass with the ratio of C/O larger than 5.0, including vegetable oils, fatty acids, terpenes, terpenoids, and resin acids; (3) hydrocarbon molecular biomass including bioethene, biopropene, and bioisoprene; and (4) non-hydrocarbon molecular biomass including carbon dioxide.

4.1. Oxygen-Rich Molecular Biomass. Although there is a lot of molecular biomass satisfying $\text{C/O} < 5.0$, this Perspective only covers the most important oxygen-rich molecular biomass such as carboxylic acids and furans. Polyols

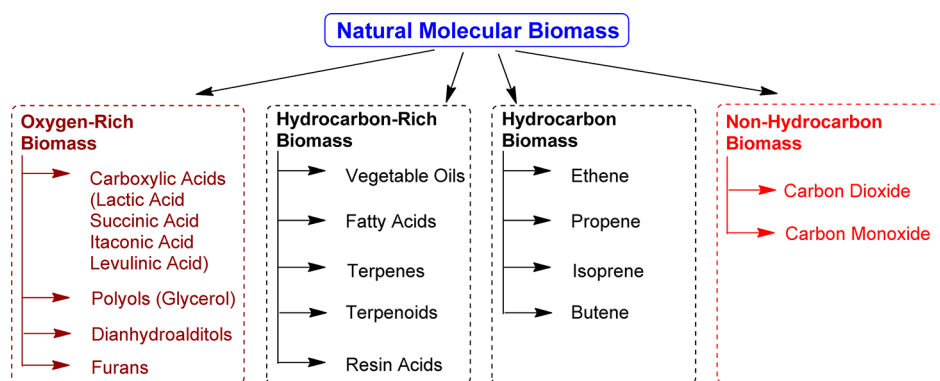







Figure 3. Classification of major natural molecular biomass.

Table 1. Controlled Polymerization of Some Carboxylic Acid-Derived Monomers

Monomer	Polymerization Method	Catalyst/Controlled Agent	M_n (g/mol)	PDI	Comonomer
 Lactide	ROP	Dimethylaminopyridine (DMAP) ⁶³	20,000	< 1.2	
	ROP	Phosphine ⁶⁴	15,000	1.11-1.40	
	ROP	<i>N</i> -heterocyclic carbenes ⁶⁵	27,000	1.16	
	ROP	Thiourea-amine ⁶⁶	42,000	1.05	
 γ -butyrolactone (GBL)	ROP	Aluminium isopropoxide trimer ⁶⁷	30,000		ϵ -CL
	ROP	Tetraphenyl tin ⁶⁸	1,600-145,000	1.3-2.1	ϵ -CL, etc
	Enzyme-catalyzed ROP	Novozyme-435 ⁶⁹	9,600-16,100	1.4-1.8	ϵ -CL
 N-vinylpyrrolidone	RAFT/MADIX	(<i>O</i> -ethylxanthylmethyl)benzene and [1-(<i>O</i> -ethylxanthyl)ethyl]benzene ⁷⁰	26,700	1.36	
	Organostibine-mediated Polymerization	Organostibine/AIBN ^{71, 72}	20,400-74,100	1.05-1.31	Styrene, MMA
	RAFT	Diphenyldithiocarbamate of Diethylmalonate ⁷³	45,800	1.4	Styrene, acrylate
	RAFT	Cumyl dithiobenzoate, Trithiocarbonate ⁷⁴	135,000-97,000	1.6-1.7	2-vinylpyridine
	RAFT	Chloroxanthate (CX) Inifers ⁷⁵	17,400	1.40	
	ATRP-MADIX	Macro xanthate ⁷⁶	16,000	1.5	Styrene
	NMP	TEMPO ⁷⁴	26,000-80,000	1.7-2.2	Styrene
	ATRP	CuCl/Me6Cyclam/methyl 2-chloropropionate ⁷⁷	8,900	1.21-1.37	
 γ -valerolactone (GVL)	Organolanthanide-Initiated Polymerization	SmMe(C ₂ Me ₅) ₂ (THF) ⁷⁹	78,000	1.09	ϵ -CL, MMA
	ROP	BF ₃ ·OEt ₂ ⁸⁰	4,300	1.6	β -butyrolactone
 3-methyltetrahydrofuran (3-MTHF)	ROP	Acetyl hexafluoroantimonate ⁸¹	6,600	N/A	

(glycerol)^{13,18,45,59} and dianhydroalditols⁶⁰ have been well reviewed in recent literature,⁶⁰⁻⁶² thus not included here.

4.1.1. Carboxylic Acids. Most renewable carboxylic acids are prepared by fermentation of carbohydrates such as glucose. Glucose is produced from starch, cellulose, sucrose, and lactose by enzymatic hydrolysis or from woody biomass by chemical transformation. In this section, common acids including lactic acid, succinic acid, itaconic acid, and levulinic acid are critically summarized. There are two major strategies to make carboxylic acid-based monomers: cyclic monomers for ring-opening polymerization (ROP) and difunctional monomers (e.g., diacid, diester, diamine, diol) for condensation polymerization. Both strategies lead to the formation of aliphatic polyesters or polyamides. Step-growth polycondensation of a hydroxyl acid or between a diacid and a diol enables access to a large range of monomer feedstock. Given the limited control of step-growth polycondensation, this Perspective will not target on difunc-

tional monomers for condensation polymerization. ROP can be used to polymerize cyclic esters including glycolide, lactide, 3-caprolactone, δ -valerolactone, and β -propiolactone, resulting in aliphatic poly(ester)s with controlled molecular weight and narrow molecular weight distribution. In addition, *N*-vinyl-2-pyrrolidone is particularly singled out as it can undergo various controlled radical polymerization. Table 1 summarizes some of controlled polymerization of carboxylic acid-derived monomers.

4.1.1.1. Ring-Opening Polymerization. Lactic acid is the most widely studied carboxylic acid from natural resources with the extensive success in commercialization: production of poly(lactic acid) (PLA) by a number of companies worldwide. There are still many challenges to be addressed: (1) brittleness of PLA and (2) low glass transition temperature (T_g) of PLA are the most noticeable weakness of PLA. Many research groups are actively working to improve and overcome these

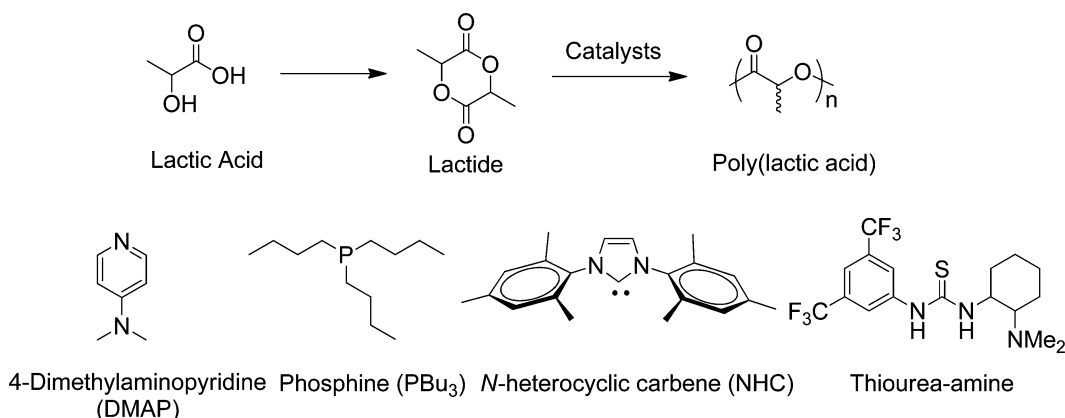


Figure 4. Synthesis of poly(lactic acid) and representative organocatalysts used for ring-opening polymerization of lactide.

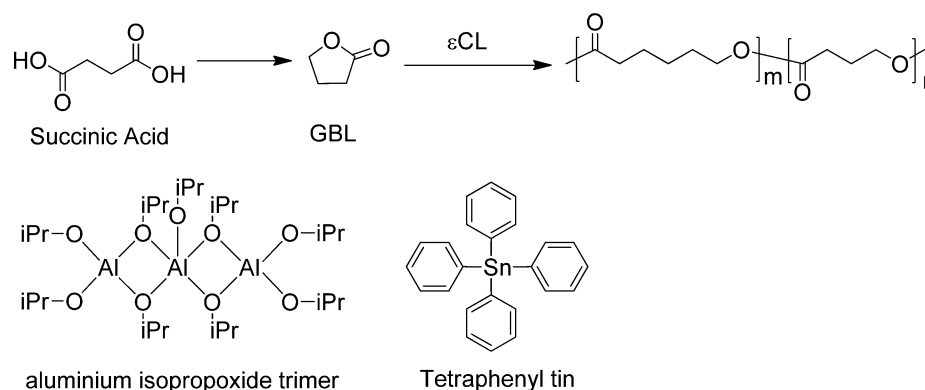


Figure 5. Copolymerization of γ -butyrolactone derived from succinic acid (with ϵ CL as an example) and representative catalysts.

problems.^{82–87} Lactic acid can be converted thermally and catalytically into its cyclic dimer, lactide (LA). There are two major ways to prepare PLA: polycondensation of lactic acid and ROP of lactide.^{6,8,63,65,88–93} ROP is a more widely used technique to prepare high molecular weight PLA. The polymerization undergoes ring-opening of the cyclic lactide in the presence of catalysts. Compared to polycondensation, ROP allows the control of molecular weight as well as stereotacticity of PLA. The choice of catalysts is vital in dictating the control of polymerization and structure of PLA. ROP of lactide can be carried out by cationic, anionic, and coordination–insertion mechanisms, depending on the catalysts. Phenoxy diamine zinc ethoxides, β -diketiminato metal alkoxide complexes, and homoleptic yttrium phenoxides are good catalysts to polymerize lactide at very high rates.^{94–96} Chiral salen Al complexes can polymerize *R,R* enantiomer 20 times faster than *S,S* enantiomer.⁹⁷

We single out organocatalysts for ROP of LA, as there have been tremendous efforts recently in developing this class of catalysts to give excellent polymerization control, high rates, and versatile functional end groups.⁹³ A few widely developed organocatalysts are listed in Figure 4. Dimethylaminopyridine (DMAP) was the first organocatalyst as a Lewis basic amine used for living ROP of lactide.⁶³ PLA with low PDI (<1.2) and molecular weight up to 20 000 g/mol was prepared using ethanol as an initiator at 35 °C in dichloromethane with reaction time ranging from 20 to 96 h. Phosphines were effective ROP catalysts for the preparation of PLA with PDI at 1.11–1.40 and molecular weights targeted up to 15 000 g/mol.⁶⁴ Under a proposed nucleophilic mechanism, the more

basic and nucleophilic alkyl-substituted phosphines were more effective lactide polymerization catalysts than phosphines with one or more aryl groups. Minimal transesterification originating from transesterification of the polymer chain was confirmed by narrow molecular weight distribution. *N*-Heterocyclic carbenes (NHC) are also highly efficient transesterification catalysts for a variety of carboxylic acid esters. In the presence of an alcohol initiator at room temperature, the polymerization of lactide using sterically hindered 1,3-bis(dimethyl)imidazol-2-ylidene (IMes carbene) produced PLA with low PDIs (<1.16) and high end-group fidelity.⁶⁵ The polymerization was well-controlled and exhibited the features of a living polymerization. Polymerization rates were comparable to those of the most active metal catalysts for ROP of lactide. Bifunctional thiourea-amines are suitable for dual activation of an electrophilic lactone and nucleophilic alcohol in ROP of lactones by combining both an electrophile-activating thiourea and a nucleophile-activating amine. A thiourea-amine was used for ROP of lactide in solution and provided PLA with controlled molecular weight, low PDIs, and end-groups defined by the added initiating alcohols.⁶⁶ An interesting feature of the thiourea-catalyzed polymerization is little transesterification of the linear polymer occurs, as evidenced from negligible broadening of the PDI even at near-complete conversion after prolonged reaction time. The high fidelity of end-groups makes chain extension of PLA possible simply by addition of more monomers.

Succinic acid is another important renewable chemical for manufacturing of polymers.^{23,98} Along with many other dicarboxylic acids, succinic acid can be obtained by fermentation of glucose. Succinic acid has been transformed

into γ -butyrolactone (GBL) (Figure 5). GBL can be used for the preparation of biodegradable polymers. However, ROP of GBL has not been studied extensively due to its poor polymerizability. Most polymerization involves the ring-opening copolymerization of GBL. Copolymerization of GBL with ϵ -caprolactone (ϵ CL), initiated with aluminum isopropoxide trimer, led to the formation of copolymers with molecular weight 30 000 g/mol and up to 43 mol % repeating units derived from GBL.⁶⁷ Their molecular weight can be controlled by the concentration of consumed comonomers and the starting concentration of initiator. In addition, copolymerization of GBL and ϵ CL was successfully carried out by enzyme-catalyzed ROP using Novozyme-435.⁶⁹ The increase of [GBL]/[ϵ CL] feed ratio resulted in decrease of molecular weight of copolymers and reaction yield. Nakayama et al. investigated ROP of GBL with cyclic esters. Comonomers included L-lactide, glycolide, β -propiolactone, δ -valerolactone, and ϵ CL.⁶⁸ Tetraphenyltin was used as an initiator. The copolymerization was carried out in bulk at 140 °C for 4 days. The GBL contents of the copolymers varied in the range from 0 to 26 mol %. The number-average molecular weight was from 1300 to 150 000 g/mol. When a small amount of the GBL unit was introduced into the polymer chain, increased flexibility and excellent biodegradability were imparted to the polymer. However, excess GBL resulted in low molecular weight polymers with substantially low yields.

Levulinic acid is a difunctional chemical for preparation of polymers,^{11,23} as shown in Figure 6. Intramolecular dehydration

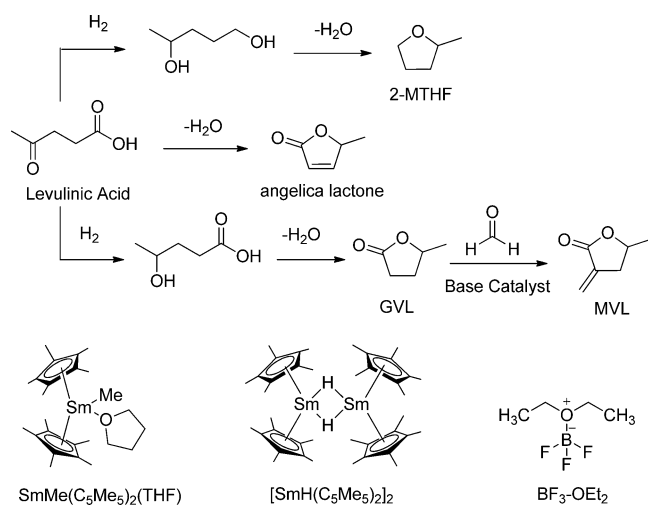


Figure 6. Synthesis of monomers derived from levulinic acid and representative catalysts.

by simple distillation leads to angelica lactone. Levulinic acid can be reduced to 4-hydroxypentanoic acid, which readily dehydrates into γ -valerolactone (GVL). Levulinic acid can be hydrogenated to 1,4-pentanediol, which dehydrates to 2-methyltetrahydrofuran (2-MTHF). A heterogeneous, gas-phase catalytic condensation of GVL with formaldehyde over basic catalysts produces α -methylene- γ -valerolactone (MVL). Organolanthanide complexes such as $\text{SmMe}(\text{C}_5\text{Me}_5)_2(\text{THF})$ and $[\text{SmH}(\text{C}_5\text{Me}_5)_2]_2$ were used to initiate a living ring-opening polymerization of GVL to give high molecular weight polyesters (>70 000 g/mol) with extremely narrow molecular weight distribution (PDI < 1.08).⁷⁹ Copolymerization of GVL with β -butyrolactone and caprolactone was also successfully

carried out using $\text{BF}_3\text{-OEt}_2$ and organolanthanide as catalysts, respectively.^{79,80,99} MVL is an attractive acrylic monomer, which has been of interest due to its similarity in structure to methyl methacrylate.^{41,100} The incorporation of the lactone structure into the polymeric chain confers to the polymer higher thermal stability than that of poly(methyl methacrylate) with the glass transition temperature over 100 °C. However, literature about the polymerization of MVL is scarce. Similarly, ROP of 2-MTHF is rarely reported.

Itaconic acid is an unsaturated dicarboxylic acid and produced via fermentation from carbohydrates. It has a current market volume of about 15 000 t/year.²³ Given the similarity in structure, it may serve as a replacement for petrochemical-based acrylic or methacrylic acid. It is used in the manufacture of synthetic fibers, coatings, adhesives, thickeners, and binders.^{23,101,102} As shown in Figure 7, transformation of itaconic

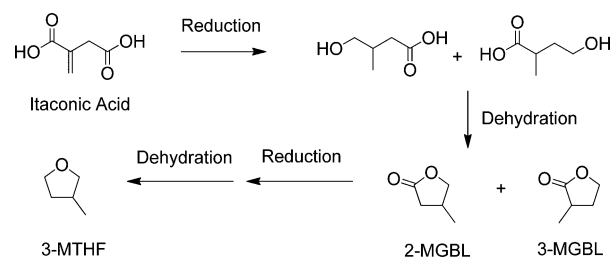


Figure 7. Itaconic acid and its conversion into various monomers.

acid into monomers has been explored with a variety of multifunctional catalyst system.^{23,101,102} The hydrogenation of the carbon-carbon double bond in itaconic acid leads to hydroxyl acids, which undergo intramolecular esterification to produce two regioisomeric monomers 2-methyl butyrolactone (2-MGBL) and 3-methyl butyrolactone (3-MGBL). Further reduction and dehydration give 3-methyltetrahydrofuran (3-MTHF). It was reported that cationic polymerization of 3-MTHF is similar to that of THF.⁸¹ However, the comparatively low value of activation entropy prevents polymerization of 3-MTHF at temperatures above 4 °C. Polymerization of methyl butyrolactones (2-MGBL and 3-MGBL) is rarely investigated. Although 5-member lactones are thermodynamically more stable, these are interesting monomers worthy for more investigation on ring-opening polymerization.

4.1.1.2. Controlled Radical Polymerization. A variety of monomers derived from carboxylic acids can undergo ROP to produce renewable polymers, while *N*-vinyl-2-pyrrolidone (NVP) can be polymerized by various controlled radical polymerization techniques. NVP is an important monomer derived from 2-pyrrolidone, which can be obtained by a reaction between GBL and ammonia. Poly(*N*-vinylpyrrolidone) has found a wide range of applications in pharmaceuticals, cosmetics, textiles, paper, detergents, and beverages. Many controlled polymerization techniques have been used to prepare poly(*N*-vinylpyrrolidone) (Figure 8). NVP is a typical unconjugated monomer that can be polymerized into high molecular weight polymers only by a radical mechanism similar to vinyl acetate.⁷⁰ Kamigaito et al. achieved simultaneous control of the tacticity and molecular weight in poly(*N*-vinylpyrrolidone) by xanthate-mediated radical polymerization in fluoroalcohols. For molecular weight control, xanthates of (*O*-ethylxanthylmethyl)benzene and [1-(*O*-ethylxanthyl)ethyl]benzene were used as RAFT/MADIX chain transfer agents (CTAs). Both led to a controlled/living radical polymerization,

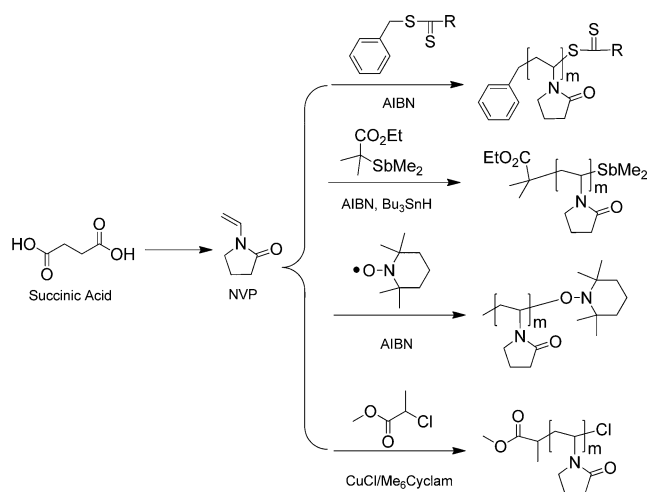


Figure 8. Controlled radical polymerization of *N*-vinyl-2-pyrrolidone.

and the latter showed higher chain transfer ability under the optimal conditions; the molecular weight distribution was 1.36 when the molecular weight was up to 26 700 g/mol. For tacticity control, the polymerization was carried out in fluoroalcohols via a conventional radical process without CTAs to give syndiotactic polymers. The polymer tacticity was dependent on the amount of the fluoroalcohol, and a more acidic and bulkier fluoroalcohol led to a higher syndiotacticity. When the CTA was used in the fluoroalcohols, the living and syndioselective polymerization proceeded to enable the simultaneous control of the molecular weight and the tacticity.

Organostibine-mediated living radical polymerizations have been used to polymerize NVP under mild conditions to reach virtually complete conversion to give well-defined polymers with narrow molecular weight distribution.⁷¹ The molecular weight of poly(*N*-vinylpyrrolidone) increased linearly when the amount of NVP was increased, and the resultant polymers had a molecular weight of 42 100 g/mol and a PDI of 1.22, suggesting that the polymerization proceeded in a living manner. This polymerization technique was further used to prepare poly(*N*-vinylpyrrolidone)-based block copolymers with styrene and methyl methacrylate by successive addition of the corresponding monomers to the organostibine macromediators.⁷² Well-defined poly(*N*-vinylpyrrolidone) and its block copolymers were also prepared by RAFT and nitroxide-mediated polymerization (NMP).^{73,74} In addition, NVP has been successfully polymerized by atom transfer radical polymerization (ATRP), cobalt-mediated radical polymerization, and many others.^{75–78,103} The readers can refer to Table 1 for details.

4.1.2. Furan. Furfural and 5-hydroxymethylfurfural (HMF), two widely developed furan-derived monomers, can be respectively prepared from C5 and C6 carbohydrate resources (Figure 9).^{19,104–106} About 300 000 t/year of furfural are produced from agricultural and forestry wastes such as corncobs and sugar cane bagasse. Most furfural is converted to furfuryl alcohol by reduction.^{107,108} Furfuryl alcohol (FA) is

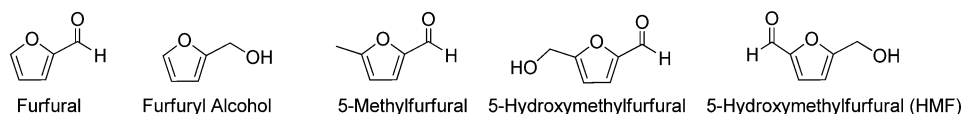


Figure 9. Structures of furfural and a few derivatives.

often used to make different resin materials. By polycondensation reaction, FA can be converted to poly(furfuryl alcohol) (polyFA), which is a precursor for carbonaceous materials including microporous carbon, carbon nanocomposites, carbon films, and foams.^{109–113} PolyFA has also attracted interest in the synthesis of organic–inorganic hybrids materials and bio-based nanomaterials.^{114,115}

4.1.2.1. Diels–Alder Reaction. One of major motivations to study furan-derived monomers is their availability of Diels–Alder (DA) reaction. The reversible DA reaction between furan and maleimide has been well investigated in the past several years for new polymeric materials (Figure 10).^{19,116} Both the

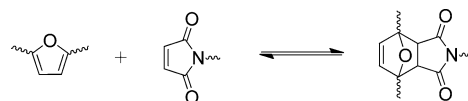


Figure 10. Diels–Alder reaction between furan and maleimide.

DA and retro-DA reactions are straightforward and not affected by side reactions, thus making DA reaction favorable for polymer synthesis. By manipulating the reaction temperature, the DA or retro-DA reaction can be well controlled. Usually the reaction with temperature at about 65 °C can lead to the adduct product, while higher temperature (e.g., ~110 °C) reaction would revert the system to its decomposition stage. Although the adduct product of DA reaction is a mixture of the *exo* and *endo* forms, the final polymer structures and properties are usually not affected since both stereochemical forms exist as chain links in polymer backbones.¹¹⁶ The DA reaction can be widely employed to prepare both linear and branching polymers depending on the number of functionality. For the linear systems, the DA polycondensations of difuran and bismaleimide can generate linear polymers. Gandini et al. reported a new polymer based on DA reactions (Figure 11).¹¹⁷ The difuran monomer and bismaleimide reacted with each other under typical DA reaction conditions to produce a linear polymer. For the nonlinear system, the polymerization usually occurred with one of the monomers that have more than two functionality groups. Either difuran and trimaleimide or bismaleimide and trifuran can form nonlinear polymers under same reaction conditions as the linear polymer synthesis. Depending on the reaction time and cross-linking extent, the nonlinear DA polycondensation can provide either soluble branched polymers or insoluble polymer gels.¹¹⁶ Another very interesting polymerization system involved the use of monomers with a furan heterocycle at one end and a maleimide group at the other end. These monomers are usually first protected in the form of a DA adduct before polymerization. After the retro-DA reaction at high temperature, the monomers will be deprotected and go through a polymerization reaction to form the desired macromolecular molecules (Figure 11 (3)).^{104,118}

Based on the reversible DA condensation, some novel copolymers including furan units have been developed for various applications such as self-healing materials. The Wudl

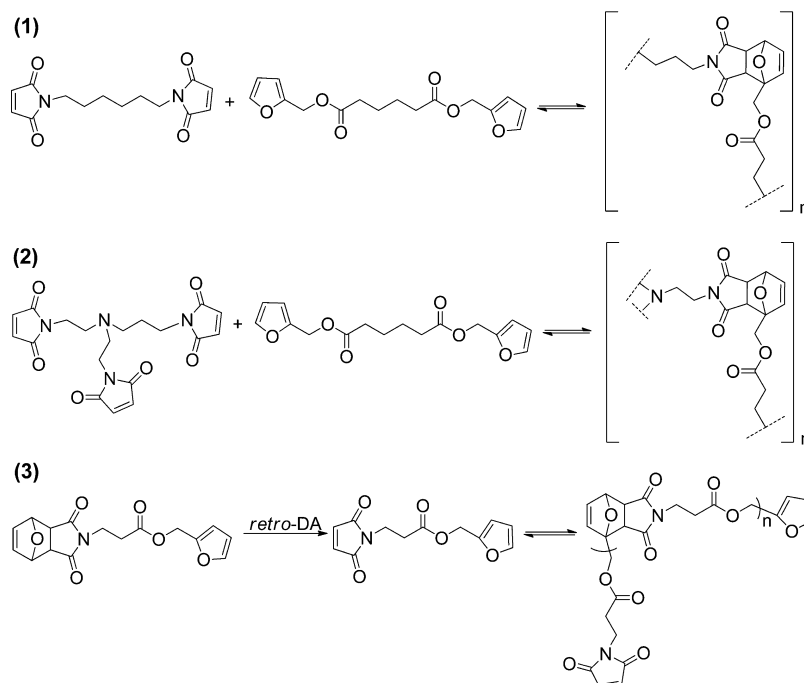


Figure 11. (1) Linear DA polycondensation; (2) nonlinear DA polycondensation; (3) deprotection and reversible DA polymerization.¹¹⁷

group pioneered the use of reversible DA cycloaddition to prepare thermally remendable cross-linked polymeric materials.¹¹⁹ Liu et al. reported a new cross-linked polyamide.¹²⁰ Rong et al. developed a novel epoxy resin with both furan and epoxide units, and this resin material showed good crack healing capability.¹²¹ Broekhuis and co-workers synthesized thermally self-healing polymers based on functionalized furan and bismaleimide.¹²² Also, a new thermosensitive hydrogel based on furfuryl methacrylate and dimethylacrylamide has been prepared via DA reaction by Wei and co-workers.¹²³

4.1.2.2. Controlled Radical Polymerization. Recently, controlled radical polymerization has been used to polymerize furfuryl methacrylate (FMA). Kavitha et al. applied ATRP to polymerize FMA using ethyl 2-bromoisobutyrate as initiator and CuCl/hexamethyltriethylenetetramine as catalysts.¹²⁴ Conventional radical polymerization of FMA led to severe gelation. But PFMA prepared by ATRP was gel free and soluble in many organic solvents. This polymer had controlled molecular weight and low polydispersity index (PDI = 1.31). The reactive furfuryl functionality in the PFMA materials was used to make thermally remendable cross-linked polymer via DA and retro-DA reaction. The Long group successfully carried out FMA polymerization by RAFT with kinetic studies confirming linear molecular weight growth and relatively narrow molecular weight distribution (Figure 12).¹²⁵ They confirmed the DA

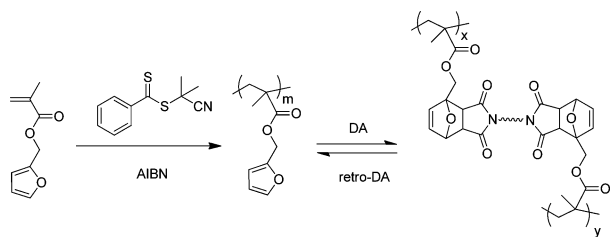


Figure 12. Synthesis of PFMA and thermoreversible cross-linked polymers by DA reaction.¹²⁵

reaction of PFMA with *N*-cyclohexylmaleimide at 60 °C and the retro-DA at 130 °C. They also studied rheological, thermal, and structural properties of thermoreversible cross-linked polymers.

4.2. Hydrocarbon-Rich Molecular Biomass. Based on the above-mentioned arbitrary number, hydrocarbon-rich molecular biomass includes those with C/O > 5.0. It is our intention to cover most abundant and low-cost molecular biomass as described below. A few other biomass, including cholesterol and vitamin, should also deserve attention.

4.2.1. Vegetable Oils and Fatty Acids. Vegetable oils are an important class of abundant natural resources. Vegetable oils are liquid materials at room temperature derived from plants.^{31,39,126–128} Recently, it has become a very attractive research area to develop new polymeric materials from vegetable oil-based monomers for various applications.^{37,44,129–132} Among various vegetable oils, the most commonly used oils for polymer synthesis include linseed, sunflower, soybean, castor, palm, and olive oils.^{36,133} The main components of vegetable oils are triglycerides. Triglyceride usually has three ester bonds, which can be hydrolyzed to form glycerol and three fatty acids (Figure 13). Different vegetable oils have various compositions of fatty acids.^{31,133} The fatty acids take about 95% of the total weight of triglycerides. Most of the fatty acids have natural functional groups such as double

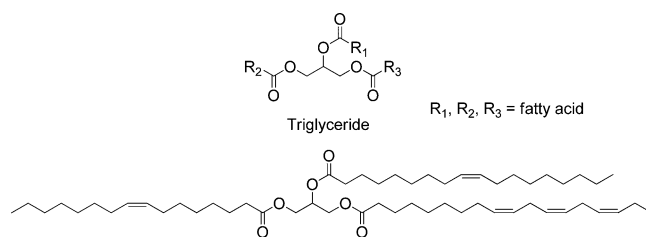


Figure 13. General chemical structure of triglycerides and a typical triglyceride oil molecular structure.

bonds, hydroxyl, and epoxy groups. The degree of unsaturation of fatty acids is the most important parameter to dictate the properties (both physical and chemical) of vegetable oils.^{37,134} There are two major pathways to prepare polymers from triglycerides. The first method involves the use of the original functional groups on the fatty acids to prepare polymers by various polymerization techniques. The second route is chemical modification of triglycerides before polymerization. In the second pathway, natural functional groups with low reactivity (e.g., carbon–carbon double bonds) can be replaced with new functional groups, which are then readily polymerized.^{36,135} We will focus on some interesting monomers derived from triglycerides and fatty acids that can be (co)polymerized to prepare novel renewable polymeric materials.

4.2.1.1. Acyclic Diene Metathesis (ADMET) Polymerization.

Linear monomers from fatty acids are a class of monomers originating from vegetable oils. Fatty acids can be easily obtained by hydrolysis or alcoholysis of triglycerides. Fatty acids can be directly used as polymerizable monomers or building blocks to obtain more advanced monomers, which can be polymerized by different techniques.^{129,136,137} Compared with triglyceride-based monomers, fatty acids are not only renewable resources, but also offering diverse properties to the final polymeric materials. ADMET is an olefin metathesis technique widely used in polymer synthesis.¹³⁸ ADMET polymerization is a step-growth polymerization method usually resulting in a linear polymer with unsaturated double bonds in the main chain.¹³⁹ 10-Undecenoic acid is a special fatty acid with functional double bonds in the end. This unique fatty acid usually comes from castor oil and has been well studied due to its terminal double bonds that can be used as diene monomers for ADMET polymerization.³³ Meier and co-workers have done a lot of work on diene monomer synthesis from 10-undecenoic acid (Figure 14).^{140–144} All of these monomers have same

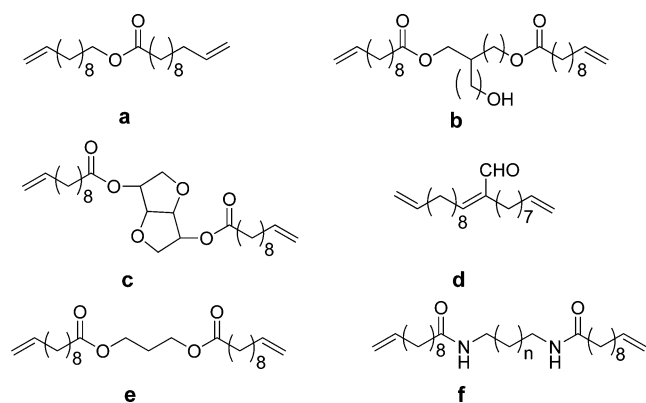


Figure 14. Diene monomers derived from 10-undecenoic acid for ADMET polymerization.^{140–145}

diene end groups and different middle blocks, which can be designed for various polymer preparations. First the monomer **a** was synthesized by the esterification of 10-undecenoic acid and 10-undecenol. This monomer was polymerized by ADMET with the use of Grubbs or Hoveyda–Grubbs second-generation catalysts to yield final polymers with molecular weight $\sim 20\,000$ g/mol.¹⁴⁴ The monomer **d** containing aldehyde groups was polymerized with the aid of metathesis catalysts. After the polymerization, the aldehyde

groups can be further modified and polymerized to obtain cross-linked polymer network.¹⁴⁵

Nonlinear monomers derived from triglycerides can lead to hyperbranched or cross-linked polymers by various polymerization methods. Since triglycerides have three fatty acid components, these monomers can be polymerized in three different locations to give either hyperbranched polymers or cross-linked polymer networks. The triglycerides with abundant double bonds on the carbon chains can be easily utilized to polymerize or copolymerize with other monomers to get hyperbranched polymers by ADMET. Due to the similar reactivity of double bonds, the traditional ADMET technique cannot control the polymerization very well, easily generating cross-linked networks.¹⁴⁶ The Larock group developed a strategy to carry out the ADMET polymerization of triglycerides using Grubbs first-generation catalyst.¹⁴⁷ The high activity of metathesis complex allowed the polymerization with low load of catalysts. The Meier group investigated polymerization of model triglycerides via ADMET in the presence of methyl acrylate as a chain stopper. The combination of Hoveyda–Grubbs II catalyst and chain stopper can efficiently control the polymerization of triglycerides to get non-cross-linked hyperbranched polymers.¹⁴⁸ Later, high oleic sunflower oil was polymerized via acyclic triene metathesis (ATMET) to highly branched and functionalized polyesters (Figure 15).¹⁴⁹ If the Hoveyda–Grubbs second-generation

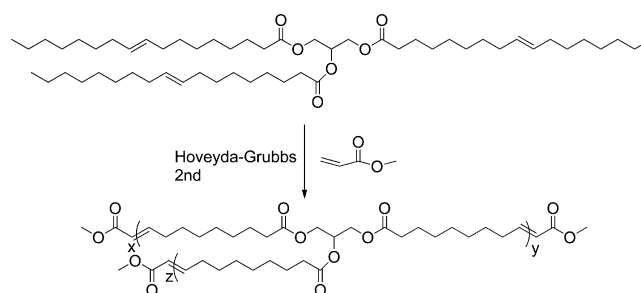


Figure 15. Hyperbranched polymers synthesized from sunflower oil by ATMET polymerization with a chain stopper.¹⁴⁹

catalyst was used and methyl acrylate was introduced as a chain stopper, the molecular weight of the obtained polymers could be tuned by varying the ratio of the triglyceride and methyl acrylate. Using the first-generation Grubbs catalyst for the polymerization of high oleic sunflower oil, no cross-linked polymers were formed, even without the use of a chain stopper.

4.2.1.2. Ring-Opening Metathesis Polymerization (ROMP). ROMP has been used to prepare fatty acid-derived polymers. The Meier group developed a new class of fatty acid-based monomers with different chain lengths (C6, C8, C10, C12, C14, C16, and C18) functionalized by norbornene.^{150,151} The polymerizations of these monomers initiated by Grubbs III catalysts proceeded in a living fashion with good initiation efficiency, and well-defined polymers with low PDI (1.0–1.26) and molecular weight up to $\sim 126\,000$ g/mol were obtained. These polymers show various T_g and T_m depending on the different fatty acid chain lengths (Figure 16).

Interesting work involving functionalized triglyceride monomer synthesis and a commercial norbornyl-functionalized linseed oil (Dilulin) was carried out by the Larock group.^{46,47,51,152} They used castor oils as starting materials to react with bicyclic anhydride to obtain a novel bicyclic

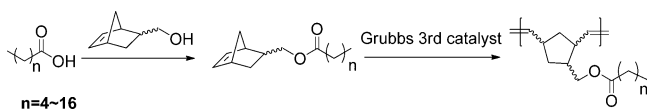


Figure 16. Fatty acid-derived norbornene monomers and their ROMP.^{150,151}

triglyceride monomer. The new monomer was then copolymerized with cyclooctene via ROMP using Grubbs first-generation catalyst to yield rubbery thermosets (Figure 17).

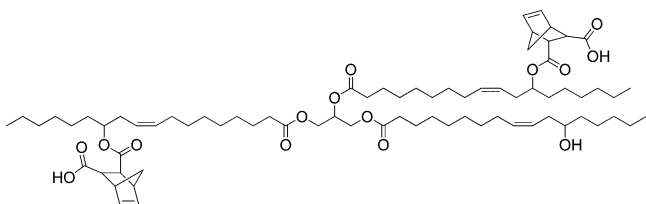


Figure 17. A bicyclic monomer derived from castor oil.⁴⁶

The thermosets range from 55 to 85 wt % oil and are flexible and slightly transparent. The increase of concentration of the modified castor oil in the feed ratio resulted in an increase in the extracted (unreacted or oligomeric) components in the final thermosets. The most effective catalyst concentration was 0.5 wt %. The final polymers are transparent thermosets with low T_g (-14 to 1 °C).

4.2.1.3. Ring-Opening Polymerization. Narine et al. reported the synthesis of lactone monomers derived from 9-hydroxynonanoic acid that can be polymerized via ROP (Figure 18).^{153,154} Monolactone and dilactone were obtained in high purity (>98%) when hafnium salt was used to catalyze the lactonization reaction of 9-hydroxynonanoic acid in xylene under refluxing conditions. ROP of the nonanolactone was carried out using lanthanum chloride or aluminum isopropoxide as catalysts, yielding poly(nonanolactone) with molecular weight in the range 5000–12 600 g/mol. The PDI was in the range 1.2–1.4. This family of polyesters is hydrophobic and crystalline.

The Domb group reported a systematic study on the synthesis, characterization, and polymerization of ricinoleic acid lactone.¹⁵⁵ Polymerization of the ricinoleic acid lactones with catalysts commonly used for ROP of lactones resulted in oligomers. Copolymerization with lactide by ROP, using $\text{Sn}(\text{Oct})_2$ as catalyst, yielded copolyesters with molecular weights in the range 5000–16 000 g/mol and melting temperatures of 100–130 °C for copolymers containing 10–50% w/w ricinoleic acid residues.

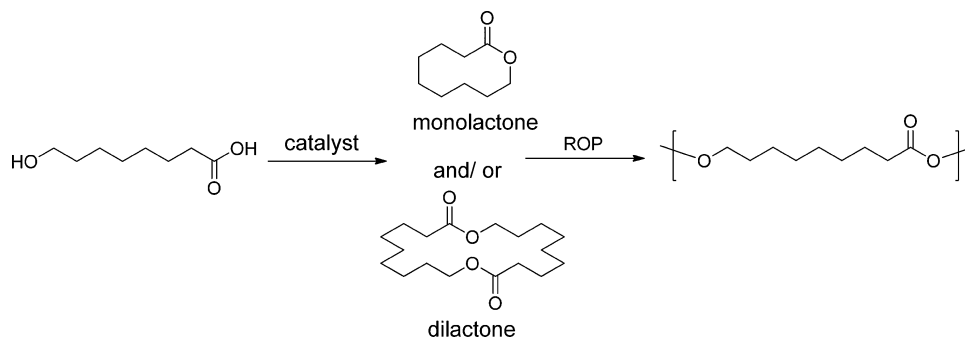


Figure 18. Synthesis of monolactone and dilactone from 9-hydroxynonanoic acid and their ROP.^{76,154}

4.2.1.4. Controlled Radical Polymerization. As shown in Figure 19, alkyd resin-containing different oil side chains have been modified into alkyd macro-RAFT agents, which were used as building blocks for multisegmented acrylic–alkyd homopolymers (one vinyl monomer) or block copolymers (blocks of vinyl monomers).¹⁵⁶ The RAFT agent attached telechelically onto the main chain of the polyester was successful in mediating copolymerization of acrylate and other activated vinyl monomers forming blocks of homopolymers. Different sequences of monomers were used to demonstrate the wide range of applicability for this technique. It should be mentioned that fatty acid-derived (meth)acrylate monomers such as dodecyl acrylate and octadecyl acrylate have been polymerized by RAFT.^{157,158}

The Meier group prepared a series of fatty acid derived methacrylate monomers (Figure 20).¹⁵⁹ Methacrylate monomers with different chain lengths (C10, C12, C14, C16, and C18) of pending alkyl groups were prepared from fatty alcohols (capric, myristic, palmitic, and stearic). They found these methacrylate monomers can be polymerized in bulk at 35 °C through ATRP using $\text{CuCl}/\text{pentamethyldiethylenetriamine}$ (PMDTA)/tricaprylylmethylammonium chloride as the catalyst system and ethyl 2-bromoisobutyrate (EBIB) as the initiator. Optimized polymerization conditions allowed for the synthesis of high molecular weight polymers (13 000–136 300 g/mol) with narrow molecular weight distribution (PDI = 1.2–1.4). The effects of different chain lengths of fatty acids on the polymer properties were also studied. It turned out that as the alkyl chain length of fatty acids increased, the T_m of final polymers increased from -40 to 19 °C.

Cross-linked polymers can be prepared by free radical polymerization of acrylate-based monomer, although not controlled (Figure 21). Acrylates can be prepared by the reaction of acrylic acid with epoxidized triglycerides. The acrylated triglycerides can be utilized in different polymer syntheses. First, they can copolymerize with small molecular weight monomers such as monomethyl maleate, cinnamate, and maleic anhydride to obtain soft viscous polymers with low T_g .^{160–162} Second, they can also react with acrylonitrile via Ritter reaction to obtain acrylamide functionalized vegetable oils.¹⁶³ This monomer was then copolymerized with styrene using radical polymerization to get materials having T_g at 30–40 °C. Third, acrylate-functionalized monomers can react with *N*-bromosuccinimide in the presence of acrylic acid to get bromoacrylated triglycerides, which can be further polymerized with styrene to get thermosetting polymers.¹⁶⁴ Additionally, the acrylated oil monomers have been used to synthesize

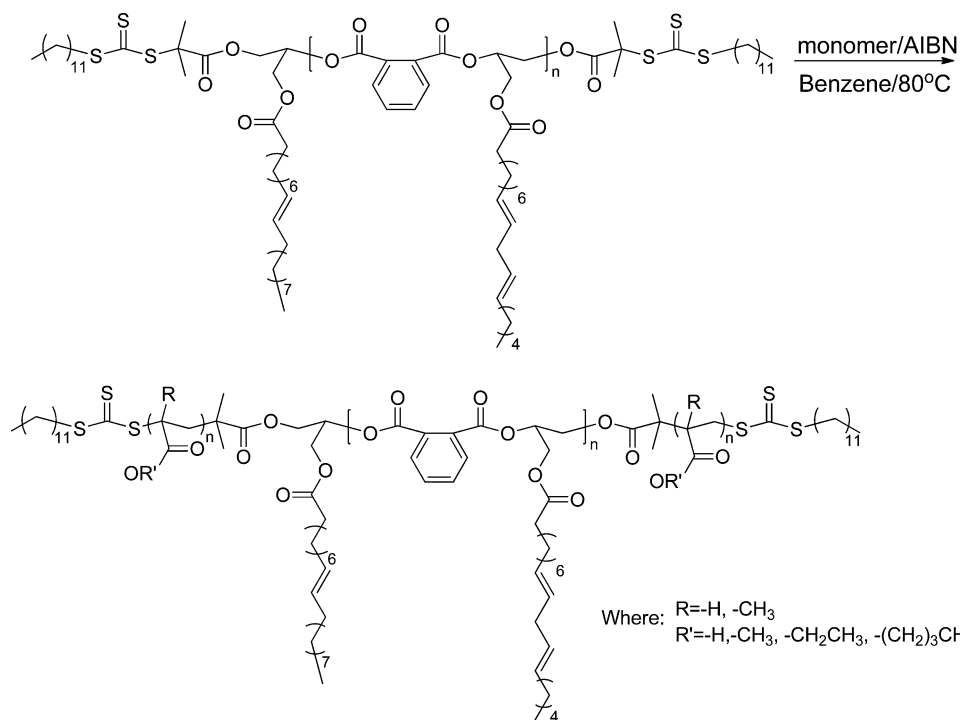


Figure 19. Synthesis of alkyd resin-containing block copolymers by RAFT.¹⁵⁶

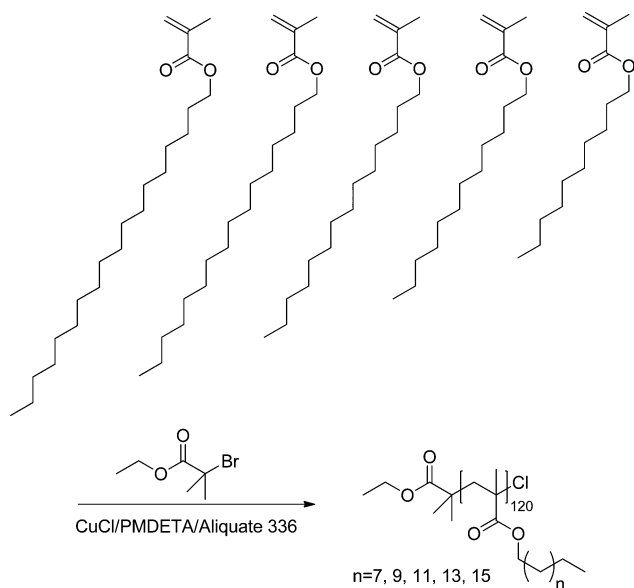


Figure 20. Synthesis of poly(methacrylate)s with different fatty acid-derived alky chains via ATRP.¹⁵⁹ Reproduced with permission from ref 159.

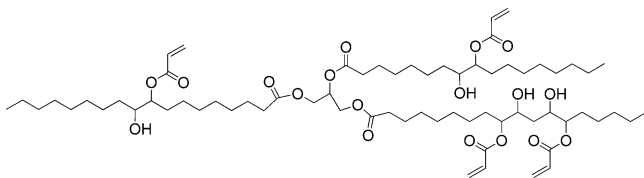


Figure 21. Acrylated epoxidized monomers derived from vegetable oils.¹⁶⁵

composite materials with glass fibers to lower the cost of production and to maintain the properties of fiber materials.¹⁶⁵

4.2.1.5. Thiol–Ene Click Chemistry. The thiol–ene reaction is a well-known click reaction in the field of chemistry. This reaction has been widely used in the preparation of functional polymers.^{166–168} Thiol–ene reaction is also a very powerful synthesis method to obtain monomers from fatty acids. The double bonds from fatty acids can easily react with thiol groups under mild conditions. Figure 22 lists some fatty acid-derived

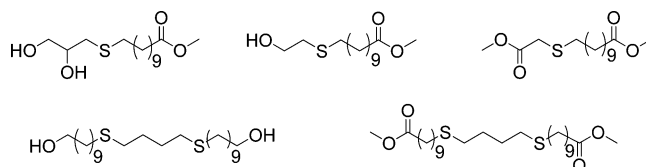


Figure 22. Fatty acid-based monomers derived from thiol–ene reactions.³⁴

monomers prepared by thiol–ene reactions.^{34,36} All these monomers are derived from 10-undecenoic acid. Functional monomers with hydroxyl or ester groups are obtained by the thiol–ene reaction. These monomers were polymerized in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) catalyst to produce various linear or hyperbranched polyesters. These polymers usually have molecular weights from 4000 to 10 000 g/mol and T_m between 50 and 70 °C. Thiol–ene reaction has been used in polycondensation to prepare fatty acid-derived polymers directly. Lluch and co-workers used allyl-10-undecenoate to react with 3,6-dioxa-1,8-octanedithiol.¹⁶⁹ After the thiol–ene polymerization, the end groups of polymers were functionalized with three different thiols. Using this strategy, they obtained a series of telechelic polymers with molecular weight about 1000–3000 g/mol, which can be further used in the synthesis of thermoplastic block copolymers. Compared with the diene monomers for ADMET polymerization, the fatty acid-based monomers derived from thiol–ene reactions have been less studied and reported. New fatty acid monomers

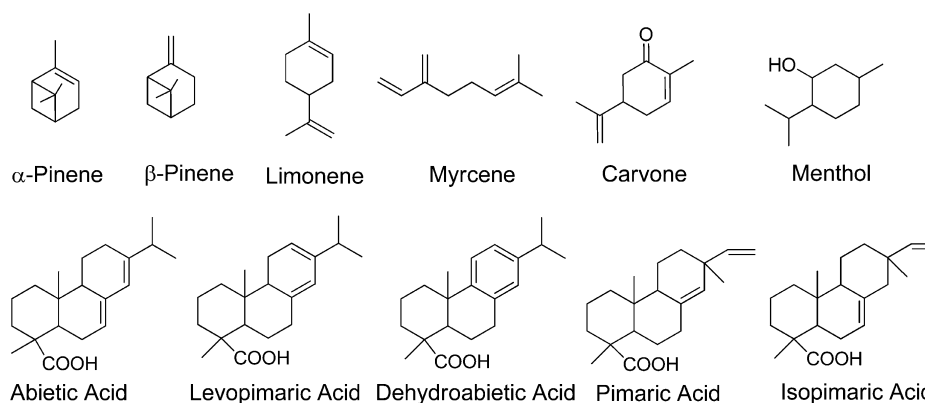


Figure 23. Various terpenes, terpenoids, and resin acids.

obtained from thiol–ene reactions will be of great interest in the future.

4.2.2. Terpenes, Terpenoids, and Resin Acids. Terpenes, terpenoids, and resin acids are a class of hydrocarbon-rich natural molecular biomass (Figure 23). Many plants and trees produce this class of molecular biomass. Particularly, pine and conifer trees produce resin with major components containing terpenes and rosin.^{14,20,21,30,35,170–173} The volatile fraction of resin, turpentine, is composed of a mixture of terpenes. Most terpenes have a basic cycloaliphatic structure with isoprene elementary unit. Terpenes are widely used as solvents and in some cases are reported to be used as chain transfer agents.¹⁷¹ Terpenoids (e.g., carvone and menthol) are considered as modified terpenes, wherein methyl groups have been moved or removed or oxygen atoms added. Rosin is the solid nonvolatile fraction of resin. Rosin consists primarily of abietic- and pimaric-type resin acids (or rosin acids) with characteristic hydrophenanthrene structures. The intrinsic acidity, rigidity, and renowned hydrophobicity, coupled with other chemical properties, enable rosin acids to be converted to a large number of downstream derivatives such as salts, esters, maleic anhydride adducts, and hydrogenated, disproportionated rosins. These are derivatives used in a wide range of applications such as in the manufacture of adhesives, paper sizing agents, printing inks, solders and fluxes, surface coatings, insulating materials, and chewing gums.^{35,170,172–174} Traditionally, most of monomer synthesis involves a Diels–Alder reaction between levopimaric acid and a dienophile such as acrylic acid, maleic anhydride, and maleimide. The preparation of polyesters, polyamides, polyamide-imides, and polyester polyols has been achieved by step-growth polymerization between these monomers and comonomers such as diol, diacid, diamine, etc.^{175–185}




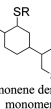







Turpentine's world yearly production amounts to about 350 000 t. The production of rosin is more than 1 000 000 t/year. Terpenes, terpenoids, and resin acids have been used as monomers or derivatized into monomers for various polymerizations, as summarized in Table 2.

4.2.2.1. Cationic Polymerization. Pinene and limonene, two of the most abundant and inexpensive terpenes, are widely used for the synthesis of polymers.^{14,22,30} Due to the electron-donating group on the double bonds through hyperconjugation, many of these monomers can undergo cationic polymerization. Due to the presence of highly reactive *exo*-methylene double bond, β -pinene is the most widely studied monomer for cationic polymerization, while only oligomers of α -pinene (with *endo*-methylene) can be obtained by cationic polymerization.¹⁸⁶ Furthermore, numerous copolymers of pinenes have been

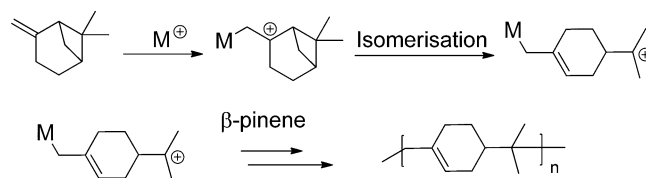
prepared. In the development of cationic polymerization of terpene monomers, the key component is catalysts that allow living and controlled polymerization to achieve high molecular weight. Lewis acids such as aluminum chloride or ethylaluminum dichloride only result in low molecular weight β -pinene polymers ($M_n \leq 4000$ g/mol).^{186,214} The Sawamoto group developed the first controlled and living cationic polymerization of β -pinene using HCl–2-chloroethyl vinyl ether adduct/TiCl₃ in conjunction with *n*Bu₄NCl as catalysts.¹⁸⁷ As shown in Figure 24, a tertiary carbocation was formed with the addition of cationic initiator onto β -pinene. Further isomerization produced a propagating isobutylene-like tertiary carbocation, which is similar to cationic polymerization of isobutene. The existence of the reactive *exo*-methylene double bond, the release of fused cyclobutane ring strain, and the formation of a stable tertiary carbocation make the reactivity of β -pinene based cationic addition much higher than isobutene. The living nature of this polymerization also allows for the synthesis of block copolymers of β -pinene with styrene or *p*-methylstyrene.¹⁸⁸ Kennedy et al. and Kamigaito et al. prepared high molecular weight poly(β -pinene) ($M_n = 40\ 000$ and $21\ 000$ g/mol) by using an H₂O/EtAlCl₂ cocatalyst system at temperature as low as -80 °C.^{189,190} These polymers exhibit a glass transition temperature around 90 °C. Lu et al. synthesized poly(β -pinene) with a molecular weight of $11\ 000$ g/mol and a PDI of 1.70 by cationic polymerization at 40 °C using a combination of Schiff-based nickel complex catalyst and methylaluminumoxane as an activator.¹⁹¹ Kostujk et al. used a low-cost co-initiator system, H₂O/AlCl₃OPh₂ (OPh₂: diphenyl ether), to produce relatively high molecular weight poly(β -pinene) (9000 – $14\ 000$ g/mol) at 20 °C, which has a T_g at ~ 82 – 91 °C.¹⁹²

A random copolymer of β -pinene and isobutylene was synthesized using 1-phenylethyl chloride, titanium tetrachloride, titanium isopropoxide, and tetra-*n*-butylammonium chloride as co-initiating system.¹⁹³ β -Pinene and isobutylene have similar propagating cationic species, thus probably having similar reactivity to produce a random copolymer. The polymerization at -40 °C progressed in a controlled manner. The final polymers had molecular weight as high as $25\ 000$ g/mol with a PDI below 1.2. The increase of β -pinene fraction, which offers rigidity to resultant polymers, from 10% to 30%, increased the T_g of final polymers by 60 °C. Lu et al. prepared random and block copolymers by a combination of living cationic polymerization, ROP, and controlled radical polymerization. Benzyl chloride-capped poly(β -pinene) prepared by cationic polymerization was used as macroinitiator to polymer-

Table 2. Polymerization of Monomers Derived from Terpenes, Terpenoids, and Resin Acids

Monomer	Polymerization Method	Catalyst/Controlled Agent	M_n (g/mol)	PDI	Comonomer
 α -pinene	Cationic Polymerization	Aluminum chloride ¹⁸⁶	1,600	2.3	
 β -pinene	Cationic Polymerization	Aluminum chloride or ethyl aluminum dichloride ¹⁸⁶	6,400	3.2	
		Isopropoxytitanium trichloride, tetra- <i>n</i> -butylammonium chloride ¹⁸⁷	5,000	1.3	
		Isopropoxytitanium trichloride, tetra- <i>n</i> -butylammonium chloride ¹⁸⁸	3,600-4,000	1.1-1.3	Styrene, methylstyrene
		H ₂ O/EtAlCl ₂ ¹⁸⁹	40,000		
		CH ₂ Cl ₂ -Methylcyclohexane/EtAlCl ₂ ¹⁹⁰	54,700	2.18	
		Schiff-based nickel catalyst ¹⁹¹	11,000	1.70	
		H ₂ O/AlCl ₃ OPh ₂ ¹⁹²	9,000-14,000	~2.0	
	Cationic-ROP	AgSbF ₆ /propylene oxide ¹⁹⁴	4,500	1.61	THF
	Cationic-ATRP	CuCl/2,2'-bipyridine (bpy) ¹⁹⁵	3,900	1.31	Styrene
	Cationic-ATRP	CuCl/2,2'-bipyridine (bpy) ¹⁹⁵	33,000	1.51	Styrene
RAFT	2-Cyanopropyl-2-yl dithiobenzoate ¹⁹⁶	18,000	1.15-1.25	<i>n</i> -butyl acrylate	
RAFT	1-Methoxycarbonyl ethyl phenyldithiobenzoate ¹⁹⁷	4,880-38,300	1.10-2.05	Methyl acrylate	
 Limonene	FRP	BPO ¹⁹⁸	42,700	N/A	Acrylonitrile, MMA
		BPO ^{199,200}	N/A	N/A	Styrene, <i>N</i> -phenylmaleimide
	RAFT	AIBN/ <i>n</i> -butyl cumyl trithiocarbonate (CBTC) ²⁰²	8,400	1.48	<i>N</i> -phenylmaleimide
 Limonene derived monomer	Condensation polymerization	1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) ²⁰³	9,000-25,000	1.75-2.47	methyl-10-undecenoate or 10-undecen-1-ol
 3-methylenecyclopentene	Cationic polymerization	<i>i</i> -BuOCH(Cl)Me/ZnCl ₂ /Et ₂ O ²⁰⁴	22,000	1.12	
 menthane	ROP	Zinc alkoxide ²⁰⁵	3,300-91,000	1.6	
 carvomenthane	ROP	ZnEt ₂ /BnOH ²⁰⁶	62,000	1.16	
 dihydrocarvone	ROP	ZnEt ₂ /BnOH ^{206,207}	10,500	1.24	
 Dihydrocarvone derived cyclic lactone	ROP	ZnEt ₂ or Sn(Oct) ₂ ²⁰⁷	5,100-14,900	1.1-1.2	ϵ -caprolactone
 Methyl methacrylate	FRP	AIBN ²⁰⁸	13,400	2.29	Methyl methacrylate
	FRP	AIBN ²⁰⁹	3,900-4,700	1.11-1.14	
	ATRP	CuBr/Me ₆ Tren ²¹⁰	10,000-100,000	<1.3	
	ATRP	CuBr/Me ₆ Tren ²¹¹	8,200-77,000	1.18-1.66	ϵ -caprolactone
	ATRP	CuBr/Me ₆ Tren ⁵⁸	11,600-56,400	1.65-3.31	Graft from lignin
 Graft from lignin	RAFT	Cumyl dithiobenzoate ¹⁷⁴	29,000	1.3	
	Photo polymerization	Photoinitiator ^{212,213}	660,000	N/A	2-ethylhexyl acrylate, butyl acrylate, vinyl acetate, acrylic acid

ize tetrahydrofuran in the presence of AgSbF₆ and propylene oxide at 20 °C. The propylene oxide served as a catalyst to reduce the reaction time from more than 40 h to less than 20 min. A block copolymer of β -pinene and tetrahydrofuran with molecular weight of 4500 g/mol and a PDI of 1.61 was obtained.¹⁹⁴ Using same poly(β -pinene) macroinitiator, block


Figure 24. Cationic polymerization of β -pinene.¹⁸⁷

and graft copolymers of β -pinene and styrene were prepared (Figure 25).¹⁹⁵ The benzyl chloride-capped poly(β -pinene) was used as a macroinitiator for ATRP of styrene. Well-defined block copolymer poly(β -pinene)-*b*-polystyrene was prepared, using a copper chloride catalyst and 2,2'-bipyridine (bpy) as a ligand. A brominated poly(β -pinene) macroinitiator was prepared by reacting poly(β -pinene) with *N*-bromosuccinamide and AIBN. A poly(β -pinene)-*graft*-polystyrene copolymer was prepared through ATRP of styrene using the partially brominated poly(β -pinene) as macroinitiator, copper chloride as catalyst, and bpy as ligand. They obtained a graft copolymer with a molecular weight of 33 000 g/mol and a PDI of 1.51.

Myrcene has been used as starting materials to prepare polymers. Using ring-closing metathesis with Grubbs second-generation catalysts (G-2), myrcene was converted into 3-methylenecyclopentene, which was further polymerized by cationic polymerization to provide high molecular weight regioregular poly(3-methylenecyclopentene) ($M_n = 22\ 000$ g/mol and a PDI of 1.12) using *i*-BuOCH(Cl)Me/ZnCl₂/Et₂O as initiation system (Figure 26).²⁰⁴ The cationic polymerization showed excellent control on the molecular weight and a low PDI, indicated a living process for this new monomer. These polymers displayed a T_g of 11 °C and a T_m of 65 and 105 °C.

4.2.2.2. Radical Polymerization and Controlled Radical Polymerization. β -Pinene with other vinyl monomers have been copolymerized.^{196,197} For the copolymerization of β -pinene and either methyl acrylate or *n*-butyl acrylate, β -pinene exhibited very low reactivity in free radical polymerization and only a small fraction of final copolymers contained β -pinene. In both cases, β -pinene had a reactivity ratio of approximately zero. This indicates that no β -pinene homopolymers were produced and that the random copolymers consisted of large acrylate portions separated by a single β -pinene repeat unit. Reversible addition-fragmentation chain transfer (RAFT) polymerization was attempted to produce copolymers of β -pinene with either methyl acrylate or *n*-butyl acrylate using 1-methoxycarbonyl ethyl phenyldithiobenzoate and 2-cyanopropyl-2-yl dithiobenzoate respectively as the transfer agents. Both copolymerization showed characteristic living and controlled behavior. However, very similar to free radical polymerization, the final compositions again contained a very small fraction of β -pinene.

Free radical copolymerization of limonene with acrylonitrile, methyl methacrylate, or styrene was carried out.¹⁹⁹⁻²⁰¹ Similar to β -pinene copolymerization, limonene cannot self-polymerize, as the reactivity ratio of limonene was zero. Due to chain transfer effect from limonene, the molecular weight of final polymers was lower when molar fraction of limonene in the feed ratio increased. The hydrogen abstraction from the limonene radical was likely to be the cause. If polymerization chain end has a limonene radical, the polymerization would terminate, as this radical can take an allylic hydrogen from the limonene monomer and produce a stable radical that is incapable of reinitiating polymerization. Similarly, copolymer-

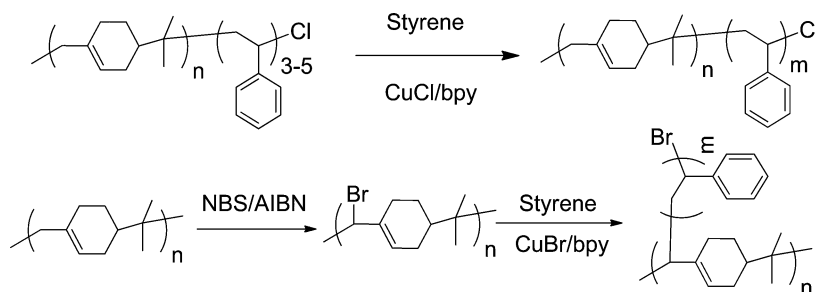


Figure 25. Synthesis of block and graft copolymers of β -pinene and styrene by a combination of living cationic polymerization and ATRP.¹⁹⁵

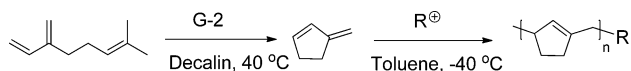


Figure 26. Ring-closing metathesis of myrcene and subsequent cationic polymerization of 3-methylenecyclopentene.²⁰⁴

ization of limonene and *N*-phenylmaleimide by free radical polymerization or RAFT indicates that limonene would not react with itself.²⁰² High molecular weight polymers with a M_n of 9200 g/mol and a T_g of 243 °C were obtained by free radical polymerization when the feed ratio of *N*-phenylmaleimide to limonene was at 2:1 with fluorinated cumyl alcohol as a solvent, indicating that there are interactions between the fluorinated solvent and *N*-phenylmaleimide and the bulky limonene structure. This strong coordination at the chain end enhances the addition of the electron-rich limonene monomer. Polymers with molecular weight up to 8400 g/mol were obtained by RAFT polymerization, which showed good control on molecular weight.

However, a recent study reported the successful radical homopolymerization of limonene using benzoyl peroxide as an initiator at 85 °C in xylene.¹⁹⁸ The weight-average molecular weight of resultant polylimonene is 43 000 g/mol. The T_g of polylimonene is 116 °C. This new study is significantly contradictory to early studies. Thus more exploration should be done to confirm the polymerizability of limonene in the future.

In the development of side-chain rosin-containing polymers, resin acids have been converted to vinyl, allyl ester, or acrylic groups that can undergo radical polymerization (Figure 27). Free radical polymerization was first used to polymerize vinyl ester monomers.^{175,215,216} However, only low molecular weight polymers were obtained due to steric hindrance. Allyl

monomers were synthesized and expected to reduce the steric hindrance.^{217–219} However, only low molecular weight polymers were prepared by free radical polymerization. Superior to vinyl and allyl ester monomers, acrylic monomers have achieved much better success in the preparation of side-chain rosin-based polymers, partly due to the increased reactivity of the unsaturated double bonds. Monomers containing a rosin moiety maleopimaric acid anhydride (MPA) were synthesized from gum rosin.²⁰⁸ Monofunctional acrylic rosin derivatives were synthesized from esterification of MPA and various acrylates, including 2-hydroxyethyl acrylate (HEA), 3-hydroxypropyl acrylate, and 4-hydroxybutyl acrylate. Monofunctional monomers were copolymerized with methyl methacrylate (MMA) by radical polymerization. Using different acrylic monomers, length of spacer group to rosin moiety could be varied. As the length of spacer group was increased, T_g of copolymers decreased, but the molecular weight of copolymers increased. Molecular weight up to 13 400 g/mol and a T_g of 97 °C were obtained for polymers with the longest spacer. Photocuring and photo-cross-linking characteristics of these copolymers as negative photoresists were studied.²⁰⁸ The double bond in rosin structure is expected to contribute to the photo-cross-linking of copolymers by reaction with nitrene produced from bis-arylazide-type photoinitiator by UV radiation. It was noted that the polymers containing rosin moiety have good optical property to be used as photoresist materials. Because the rosin moiety attached as the side chain of copolymers contains anhydride group, these resist polymers could be stripped by NaOH solution. Chu et al. prepared disproportionated rosin β -acryloyl ethyl ester by esterification of disproportionated rosin and HEA.²⁰⁹ Kinetics parameters of bulk polymerization of this monomer in the presence of AIBN

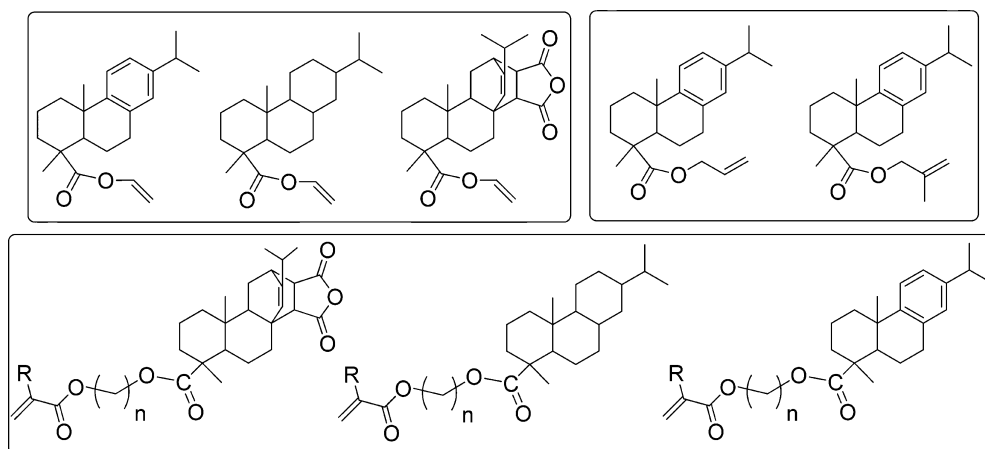


Figure 27. Rosin-derived vinyl ester monomers, ally ester monomers, and (meth)acrylic monomers.

were studied by differential scanning calorimetry (DSC). Final polymers had a molecular weight less than 5000 g/mol and a T_g of ~ 25 °C. The low molecular weight was attributed to steric effect from the rosin moiety. Kim et al. prepared hydrogenated rosin epoxy methacrylate, based on hydrogenated rosin and glycidyl methacrylate.^{212,213} UV-cross-linkable polyacrylates acted as polymeric photoinitiators due to the benzophenone incorporated into their backbones. Hydrogenated rosin epoxy methacrylate was used as a tackifier and blended at different levels with the synthesized, UV-cross-linkable polyacrylates for use as pressure-sensitive adhesives.

The Tang group has developed a series of well-defined rosin-containing (meth)acrylic polymers by controlled radical polymerization.^{174,210,211} They first prepared high quality dehydroabietic acid-derived (meth)acrylate monomers followed by ATRP (Figure 28).²¹⁰ Acryloyloxy dehydroabieticcarbox-

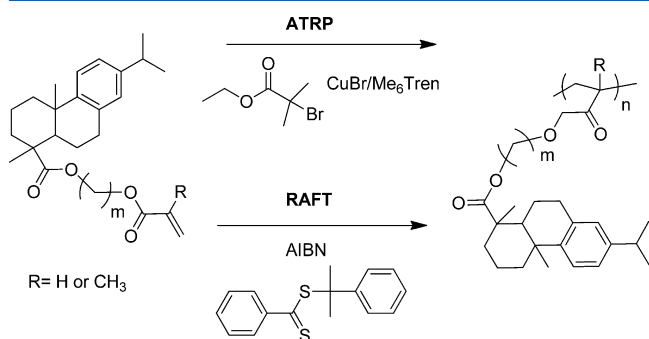


Figure 28. ATRP and RAFT of rosin-based (meth)acrylate monomers.^{174,210}

ylate (ADA), in which the dehydroabietic group is connected directly to the vinyl ester group, was prepared from acryloyl chloride and dehydroabietic alcohol, which was obtained by reduction of dehydroabietic acid with sodium borohydride. For monomers 2-methacryloyloxyethyl dehydroabieticcarboxylate (MAEDA), 2-acryloyloxyethyl dehydroabieticcarboxylate (AEDA), and 4-acryloyloxybutyl dehydroabieticcarboxylate (ABDA), dehydroabietic acid was first converted into acyl chloride under oxalyl chloride followed by in-situ esterification reaction with hydroxyl groups of corresponding (meth)acrylates. For ATRP of ADA, the reaction was not controlled, most likely due to the steric effect of dehydroabietic moiety. For other acrylates, ATRP allowed the preparation of well-defined rosin-derived polymers with low polydispersity and controlled molecular weight. The molecular weight of polymers ranged from 10 000 to 100 000 g/mol with PDIs below 1.3. Higher molecular weight was obtained for polymers with longer spacers between the rosin moiety and the vinyl group, further indicating the steric effect. These polymers exhibited tunable thermal properties by simple manipulation of monomer structures. The polymer with the longest spacer had a T_g of 22 °C (PABDA), while the one with the shortest spacer had a T_g of 90 °C (PMAEDA).

They extended CRP to RAFT polymerization of rosin-based monomers (Figure 28).¹⁷⁴ RAFT polymerization using cumyl dithiobenzoate (CDB) as the transfer agent and AIBN as the radical initiator was carried out. Polymerization of MAEDA in toluene showed a living character with molecular weight up to 20 000 g/mol and PDI < 1.3. For the acrylate monomer, similar conditions were applied for its polymerization. However, resultant polymers had high PDI (>1.5). When the solvent

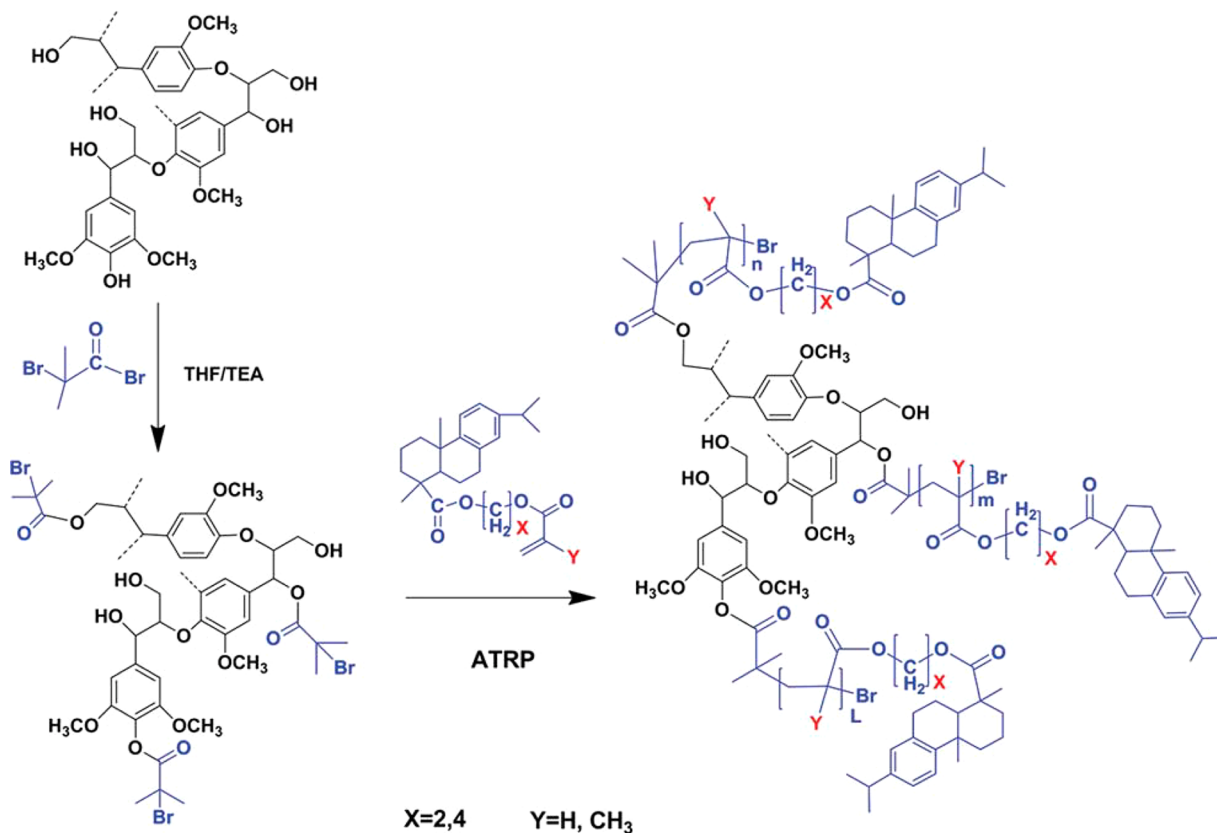


Figure 29. Synthesis of rosin polymer-grafted lignin composites by surface-initiated ATRP.⁵⁸ Reprint with permission from ref 58.

was changed to THF, polymerization led to a polymer with molecular weight 29 100 g/mol and a PDI of 1.3. The polymerization of the acrylate monomer was relatively slow in a polar solvent (THF), however controlled.

The Tang group further prepared rosin acid-degradable caprolactone block copolymers by combining ATRP and ROP.²¹¹ Two-step sequential polymerization using either poly(2-acryloyloxyethyl dehydroabiatic carboxylate)-OH (PAEDA-OH) or poly(ϵ -caprolactone)-Br (PCL-Br) as macroinitiators resulted in well-defined block copolymers with low polydispersity. One-pot polymerization was carried out with three different sequential feeds of AEDA and ϵ -CL monomers. The control of one-pot polymerization depended on the interactions of coexisting ATRP catalysts and ROP catalysts. While the minimal interactions between copper(I) and tin(II) catalysts produced well-defined block copolymers, excess copper(II) or tin(II) led to the formation of block copolymers with polydispersity >1.5. It was suggested that the tin(II) catalysts reduced the persistent radicals copper(II) of ATRP, leading to a poorly controlled polymerization. PCL segments of the block copolymers exhibited excellent degradability under acidic conditions. Thermal behaviors of these block copolymers showed a strong dependence of polymer compositions due to the possible crystallization of the PCL block.

Later, the Tang group used surface-initiated ATRP to graft rosin polymers from lignin, yielding a class of hydrophobic biocomposites (Figure 29).⁵⁸ Lignin is a complex material with characteristic aromatic structures. The major functional groups of lignin consist of hydroxyl, methoxyl, and phenylpropane units. A lignin macroinitiator (Lignin-Br) was prepared by reacting lignin with 2-bromoisobutyl bromide (BiBB) in the presence of triethylamine. The fraction of bromine content in lignin was controlled by changing the feed ratio of starting materials: lignin and BiBB. ATRP was performed using the same ligand and catalyst as the polymerization of rosin (meth)acrylic monomers. All polymerization was living and controlled, as indicated by the kinetic study. A simple esterification reaction was used to modify lignin with resin acids directly. The thermal properties of lignin-rosin composites can be manipulated by the structures of rosin polymers. Graft copolymers exhibited T_g in the range of \sim 20 and 95 °C. The incorporation of rosin moiety significantly enhanced hydrophobicity of lignin, as evidenced by the static contact angle measurement of water droplets on the films of lignin composites. The surface of rosin-lignin composites was dominated with chemical compositions originating from the hydrocarbon-rich rosin moiety, as confirmed by X-ray photoelectron spectroscopy. The rosin-lignin composites showed water uptake below 1.0 wt %, while unmodified lignin had a water uptake at 18 wt %, indicating the impartation of hydrophobicity of rosin into the composites.

4.2.2.3. Ring-Opening Polymerization. Carvone and menthol are two common terpenoids used for starting materials to generate monomers for ROP. Menthol is usually available in its ketone form, a compound called menthone. The Hillmyer group converted menthone to a lactone monomer, menthide, by the Baeyer-Villiger oxidation using *m*-chloroperoxybenzoic acid (Figure 30).²⁰⁵ The ROP of menthide was carried out at room temperature using a highly active zinc alkoxide catalyst. Polymers with molecular weight ranging from 3300 to 91 000 g/mol with the PDI below 1.6 were obtained. The polymerization showed controlled behavior. Polymerization of carvone

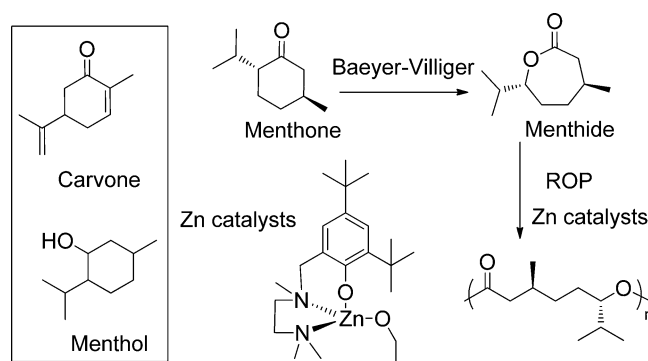


Figure 30. Carvone and menthol and ROP of menthide (derived from menthone).²⁰⁵

derivatives proceeded in a similar fashion.^{206,207} Carvone was hydrogenated into carvomenthone via intermediate dihydrocarvone using Wilkinson's catalyst. The carvomenthone was converted to carvomenthide by the Baeyer-Villiger oxidation. The polymerization of carvomenthide led to polymers with a molecular weight of 62 000 g/mol, a PDI of 1.16, and a T_g of -27 °C, while polymerization of dihydrocarvone led to a molecular weight of 10 500 g/mol, a PDI of 1.24, and a T_g of -20 °C. Copolymers of these two monomers displayed a glass transition temperature between those of the two homopolymers.

The Hillmyer group further modified dihydrocarvone into an epoxidized cyclic lactone monomer and copolymerized it with caprolactone using the same reaction conditions as used for the homopolymerization.²⁰⁶ All polymers showed a low PDI between 1.1 and 1.2. Using either tin-based or zinc-based catalysts, random and cross-linked copolymers were prepared. With the increase of oxidized dihydrocarvone in comonomer compositions, the cross-linked copolymers displayed a decrease in T_m and an increase in T_g , due to the disruption of the crystallization of the ϵ -caprolactone segments by the oxidized dihydrocarvone. The final polymers exhibited shape memory properties, which along with their prospect of biodegradability can find applications in the biomedical field.

4.2.2.4. Click Chemistry. Limonene has been derivatized into desirable monomers for condensation polymerization. Thiol-ene click chemistry has been used to produce limonene-based homopolymers by the Meier group.²⁰³ Both monoaddition product and a mixture of monoaddition and diaddition products were prepared, since there are different reactivities of the terminal and internal double bonds in limonene (Figure 31). Disubstituted monomers were used for condensation polymerization.²⁰³ Due to the steric effect from the bulky cyclic structure, only oligomers were obtained with the diester and the diol, even with the use of TBD as a catalyst, which usually

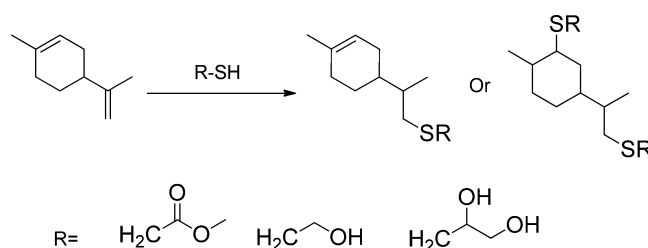


Figure 31. Thiol-ene click chemistry between limonene and thiols.²⁰³

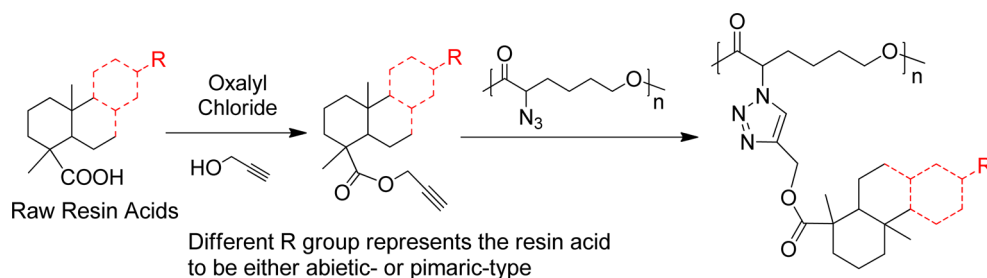


Figure 32. Attachment of raw rosin materials onto PCL side chain through click chemistry.⁵⁸

has high transesterification activity. High molecular weight polymers can be obtained from the diol or diester monomers with a spacer between limonene units to reduce the steric hindrance. Either the self-metathesis or thiol–ene homocoupling was used to prepare the comonomers from methyl-10-undecenoate or 10-undecen-1-ol. Higher molecular weight polymers with molecular weight at 9000–25 000 g/mol and a PDI between 1.75 and 2.47 were obtained by condensation polymerization carried out at 120 °C under vacuum using TBD as catalyst. All polymers have a T_g of ~ -45 °C and varied T_m (-15 to 50 °C). Longer alkyl chains led to higher melting temperature.

Copper-catalyzed azide–alkyne cycloaddition is another highly efficient click reaction that could play a major impact in the utilization of raw natural resources. For example, we have used click chemistry to attach raw rosin onto polycaprolactone to prepare a class of hydrophobic polyesters (Figure 32).²²⁰ Resin acids have more than 10 different isomers, but each one has a carboxylic acid, which can be converted into propargyl esters. These alkyne-containing rosin esters can be clicked onto an azide-substituted polycaprolactone by a typical copper-catalyzed cycloaddition. The hydrocarbon nature of rosin structures provided PCL excellent hydrophobicity with contact angle very similar to polystyrene (85° – 90°) and very low water uptake. Although the addition of rosin side group increased the hydrophobicity, it also disrupted the crystallinity of PCL. Thus, the rosin-substituted PCL still maintained full degradability. This work opens an avenue to prepare novel biocompatible and biodegradable hydrophobic polyesters. The use of raw rosin materials would significantly lower the cost of production. These reactions could be expanded to other natural derived polymers.

4.3. Hydrocarbon Molecular Biomass. Due to their gigantic volume and impact on daily life, olefins like ethylene, propylene, and isoprene are too important to be ignored for exploration of their production from renewable resources. Development of these monomers from renewable natural resources is an important emerging direction and still in its infancy stage. However it has enormous potential. Industry has a lot of interests in developing these monomers, although academic research starts to pick up. We are not aiming at extensively summarizing this important class of hydrocarbon monomers from biomass, as it could serve as an independent topic. Recently, Mathers has written an excellent article on these olefins.¹⁵

Ethylene is one of the most important platform petrochemicals for production of many most important commodity polymers such as high- and low-density polyethylene, poly(vinyl chloride), polystyrene, poly(ethylene terephthalate), etc.²²¹ The large-scale economically attractive steam cracking process makes almost all ethylene production based on

petroleum feedstock. Recently much attention has been focused on renewable feedstock for ethylene production. Conversion of bioethanol (from biomass) to ethylene represents a chemically identical alternative to ethylene.^{15,222} In fact, ethylene was produced by ethanol dehydration prior to the era of petroleum chemical industry. The conversion of bioethanol to ethylene heavily relies on the development of bioethanol precursor. Bioethanol can be obtained by fermentation of different feedstocks such as sugar cane, corn, and lignocellulosic biomass.^{223,224} Production of bioethanol as a transport fuel has been widely pursued in many countries including US, Europe, Brazil, and China. The efficiency of dehydration of bioethanol to ethylene is largely dictated by catalysts such as zeolites and mesoporous silica.^{225–227}

Propylene is the second largest petroleum chemical. There are many pathways developed to convert biomass into propylene.¹⁵ One pathway is to convert bioethanol to ethylene and then to propylene through dehydration, dimerization, isomerization, and metathesis. Biobutanol is another source to prepare propylene through dehydration, isomerization, and metathesis. Fermentation and direct cracking of other biomass such as cellulose, lignin, and sugar are actively being pursued, especially in industry.

Isoprene, isobutene, and butadiene are three most important intermediates for making renewable rubber. Given the huge market of rubber in automobile industry, the development of these intermediates from biomass would play a very positive impact in the field. Microbial fermentation holds promise for making these renewable rubber intermediates.²²⁸ Isoprene is used to make synthetic latex similar to that of the rubber tree. Isobutene and butadiene are four-carbon intermediates used to make butyl rubber and styrene–butadiene rubber. Due to the tightening supply of both natural and synthetic rubber, companies like Goodyear and Michelin have put efforts to make commercial production of these rubber intermediates from sugar. Biotech firm Genencor produced the enzyme isoprene synthase using genetically engineered microbes. They reported the production of 60 g of isoprene per liter of sugar solution using their microbes.²²⁹ Compared to isoprene, both isobutene and butadiene derived from renewable resources are much less explored. Isobutanol produced from carbon dioxide can be further dehydrated into isobutene. Butadiene can be produced from bioethanol using heterogeneous catalysts. Production of these monomers has been elegantly reviewed by Mathers¹⁵ and thus is not necessary to repeat.

Current efforts in this arena are focused on the synthesis of monomers, as most polymerization technologies have matured over the last half-century in the petroleum industry. The challenge exists mainly in the cost-effective production. Technically, more efficient catalysts (including enzymes) and

Table 3. Copolymerization of Carbon Dioxide (CO₂) Using Various Catalysts^a

catalyst	comonomer	M _n (g/mol)	PDI
ZnEt ₂ /H ₂ O ^{238,239}	PO	N/A	N/A
[(BDI)ZnOAc] complexes ²⁴⁰	PO	10000–43300	1.09–1.27
(Salcy)CoX ²⁴¹	PO	9500–19600	1.15–1.31
(Salen)CrX ²⁴²	PO	4700	1.23
(BOXDIPY)MCl ²⁴³	PO	5300–18000	1.12–1.54
β-diiminate zinc ²⁴⁴	CHO	22000	1.09–1.11
(BOXDIPY)MCl ²⁴³	CHO	14000	1.12
dimeric zinc complexes ²⁴⁵	CHO	12000	1.30
(salen)Co(III) complexes ²⁴⁶	CHO	9200–29300	1.06–1.17
(salalen)CrCl complexes ²⁴⁷	CHO	3000–11000	1.05–1.16
β-diiminate zinc acetate complexes ²⁴⁸	limonene oxide	3700–10800	1.12–1.34
(salen)Co(III) ²⁴⁹	epichlorohydrin	4400–25900	1.07–1.22
(salen)Cr(III) chloride complexes ²⁵⁰	oxetane	6700–14500	1.26–1.60
zinc glutarate ²⁵¹	PO, ε-caprolactone	275000	1.54
Co(III)–salen complex ^{252,253}	PO, CHO	50900–82100	1.04–1.14
(salen)CrCl ²⁵⁴	PA, CHO	13000–18000	1.12–1.13

^aPropylene oxide (PO); cyclohexene oxide (CHO); phthalic anhydride (PA).

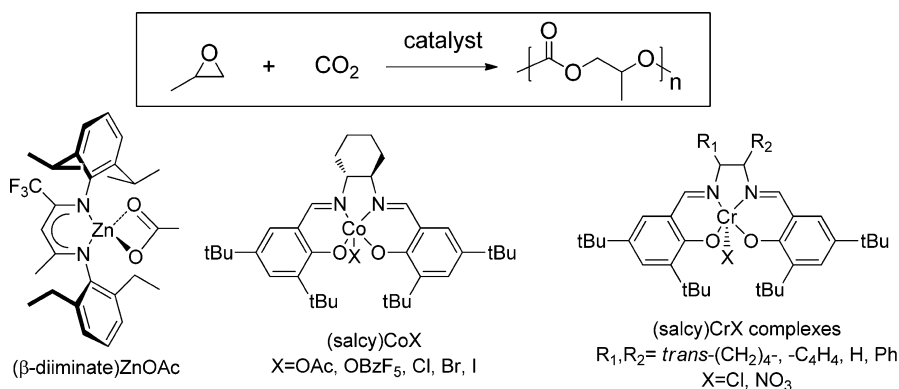


Figure 33. Copolymerization of PO and CO₂ using zinc-, cobalt-, and chromium-based catalysts.^{241,242}

high throughput processes are critically needed in order to compete with petroleum counterparts.

4.4. Non-Hydrocarbon Molecular Biomass (CO₂). Carbon dioxide (CO₂) is an abundant non-hydrocarbon renewable nonflammable gas. It is a C₁ feedstock.^{38,230,231} As a renewable natural resource, CO₂ has low cost and nontoxicity, which makes it a promising resource for chemical synthesis, especially for polymer synthesis.^{232–235} Due to its inertness, CO₂ is usually combined with high reactive reagents, and the reactions are usually carried out with special catalysts. Currently one of the most interesting research areas in the utilization of CO₂ is the synthesis of polycarbonates and polyurethanes. In these processes, CO₂ is used as a monomer and copolymerized with epoxide. Many publications report the reaction of CO₂ with epoxide to form polycarbonates due to their potential applications as packaging materials and engineering thermoplastics.^{236,237} Table 3 lists some of CO₂ copolymerization.

The catalysts used in CO₂ copolymerization can be divided into heterogeneous and homogeneous catalysts. The most widely used catalyst is zinc-based complexes as well as aluminum-, chromium-, and cobalt-based catalysts.²⁵⁵ The first use of CO₂ as monomer in polymer synthesis dated back to 1969. Inoue and co-workers prepared copolymers from CO₂ and propylene oxide (PO) using a mixture of ZnEt₂ and H₂O as catalyst system.^{238,239} The 1:1 ratio of ZnEt₂/H₂O along with 20–50 atm of CO₂ at 80 °C gave poly(propylene

carbonate) (PPC). Following that research, other catalyst systems have been developed to prepare the copolymers from PO and CO₂. The Coates group reported highly active, single-site catalysts based on zinc.²⁴⁰ The final polymers have low PDI, demonstrating that the copolymerization was well controlled. They also developed a cobalt catalyst for the same polymerization (Figure 33).²⁴¹ By adjusting the reaction parameters, they prepared highly regioregular poly(propylene carbonate) with no byproducts. Lu et al. developed chromium Salen complex catalysts, which can be used to control the stereochemistry of copolymerization of PO and CO₂ (Figure 33).²⁴² Very recently, the Nozaki group discovered some tetravalent metal complexes as a new class of catalysts for the copolymerization of PO and CO₂.²⁴³ They found that all the tetravalent metal (titanium, zirconium, germanium, and tin) complexes have activities to copolymerize propylene oxide with CO₂.

Besides PO, CO₂ has been also copolymerized with cyclohexene oxide (CHO) to obtain various polymers. In 1999, Beckman and co-workers first reported the copolymerization of cyclohexene oxide with CO₂ using zinc and aluminum catalysts.²⁵⁶ Then Nozaki et al. developed dimeric zinc complexes for the asymmetric alternating copolymerization of CHO and CO₂.²⁴⁵ In this system, the dimeric zinc species played a crucial role during the copolymerization process. The copolymerization of CHO and CO₂ gave optically active

polymers at 49% ee. Also, SalenCo(III) complexes were found to have activities for the asymmetric CHO–CO₂ copolymerization by Lu and co-workers.²⁴⁶ The final polymer is a highly isotactic semicrystalline polymer with a high melting point at 216 °C and high decomposition temperature at about 310 °C. The similar (Salalen)CrCl complexes for the copolymerization were also reported by Nozaki and co-workers. This catalyst showed very high activity under atmospheric pressure of CO₂.²⁴⁷

Furthermore, many other monomers have been used to copolymerize with CO₂ under metal catalyst system to produce novel polymeric materials. As described in previous sections, Coates and co-workers recently reported a new polycarbonate prepared from CO₂ and limonene oxide.²⁴⁸ β -Diimine zinc acetate complexes were employed to activate the copolymerization of CO₂ and limonene oxide. High monomer/catalyst ratios and long polymerization time led to the formation of high molecular weight polycarbonate (Figure 34). The Coates group

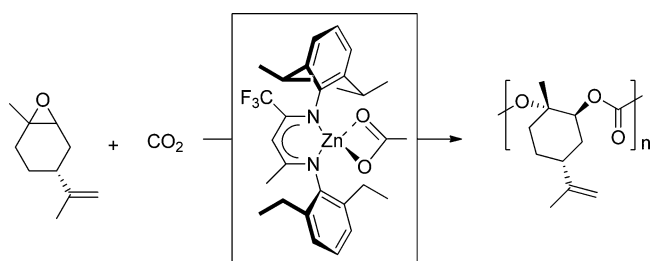


Figure 34. Copolymerization of CO₂ and limonene oxide using zinc catalyst.²⁴⁸ Reproduced with permission from ref 248.

has combined carbon dioxide and limonene oxide to prepare linear polycarbonates. It was found that low temperature polymerization facilitated the stereo- and regioregular ring opening of limonene oxide. Regioregular alternating polycarbonates were obtained with a molecular weight of 25 000 g/mol and a PDI of 1.16 using β -diimine zinc acetate complexes as catalysts at a polymerization temperature of 25 °C. A more random copolymer of polycarbonate with a noticeable decrease of molecular weight and a broadened molecular weight distribution (PDI = 1.34) was obtained when the polymerization temperature increased.

Recently, Lu and Darensbourg reported the cobalt-based catalyst system for the copolymerization of CO₂ and epichlorohydrin.²⁴⁹ Aliphatic polycarbonate composed of oxetane and CO₂ was prepared with a Cr complex catalyst by the Darensbourg group.²⁵⁰ During the development of metal catalyst systems for the copolymerization involving CO₂, some complicated polymerization systems containing more than two comonomers have also been studied. Ree and co-workers reported the terpolymerization of CO₂ with PO and ϵ -caprolactone. The copolymer was obtained at 60 °C and 400 psi pressure under the effect of zinc glutarate catalyst.²⁵¹ Later, asymmetric terpolymerization of PO, CHO, and CO₂ at mild conditions was studied by Lu and co-workers.^{252,253} The T_g of this terpolymer can be manipulated by changing the compositions of cyclohexene carbonate and propylene carbonate linkages. The Darensbourg group developed a new terpolymerization system containing cyclic acid anhydrides, epoxide (cyclohexene oxide), and CO₂.²⁵⁴ This terpolymerization was catalyzed by the (salen)CrCl catalyst. The final copolymer showed a wide range of T_g from –39 to 95 °C, depending on the different epoxide compositions.

Overall, research on CO₂-involved copolymerization has drawn a lot of attention in the past decade. Various well-defined metal catalysts have been developed to activate the copolymerization of epoxide and CO₂. The research of different copolymers containing renewable CO₂ monomer with specific molecular architectures will be of great interest in the future. In addition, there is significant research on using carbon monoxide (CO) as a renewable resource to prepare polymers. Some recent reviews are listed in refs 257–260.

5. CONCLUSIONS

In conclusion, there are a lot of opportunities to develop molecular biomass and monomers for preparation of renewable polymers. A lot of progress has been achieved on the development of oxygen-rich, hydrocarbon-rich, hydrocarbon, and non-hydrocarbon molecular biomass for production of renewable polymers. Controlled polymerization provides a promising platform to produce high-performance polymers with controlled molecular weight, functionalities, and architectures. However, there are a lot of critical challenges to be addressed before biorefinery can achieve its greater potential. These challenges include, but are not limited to, (1) developing a broader pool of monomers and more powerful polymerization techniques that tolerate impurities and functionalities, (2) developing high efficient chemistry process with less purification process to reduce the production cost of renewable polymers, and (3) combining natural polymers and molecular biomass to maximize the utilization of natural resources and to improve material performances. With continuous efforts to develop new technologies, and improved acceptance and conscientious understanding among the public, renewable chemicals and polymers will play an ever-increasing role for future generations and a sustainable society in reducing our dependence on fossil fuel, decreasing carbon emission, and promoting more environmentally benign materials.

■ AUTHOR INFORMATION

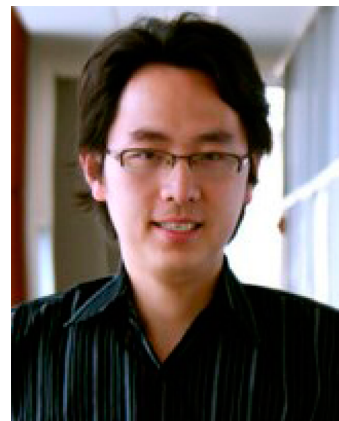
Corresponding Author

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Notes

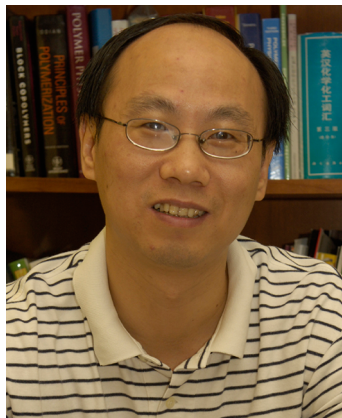
The authors declare no competing financial interest.

Biographies



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