1
Monomers and Macromonomers from Renewable Resources

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1.1
Introduction

Renewable resources constitute an extremely rich and varied array of molecules and macromolecules incessantly produced by natural biological activities thanks to solar energy. Their exploitation by mankind has always been at the heart of its survival as sources of food, remedies, clothing, shelter, energy, etc., and of its leisure as sources of flowers, dyes, fragrances, and other amenities. In the specific context of materials, good use has always been made of cotton, paper, starch products, wool, silk, gelatin, leather, natural rubber, vegetable oils and terpenes, among others, through progressively more sophisticated and scaled-up technologies.

The meteoric ascension of coal and petroleum chemistry throughout the twentieth century gave rise to the extraordinary surge of a wide variety of original macromolecules derived from the rich diversity of monomers available through these novel synthetic routes. This technical revolution is still very much alive today, but the dwindling of fossil resources and their unpredictable price oscillations, mostly on the increase, is generating a growing concern about finding alternative sources of chemicals, and hence of organic materials, in a similar vein as the pressing need for more ecological and perennial sources of energy. The new paradigm of the *biorefinery* [1] represents the global strategic formulation of such an alternative in both the chemical and the energy fields, with progressive implementations, albeit with different approaches, throughout the planet.

Within the specific context of this chapter, renewable resources represent the obvious answer to the quest for macromolecular materials capable of replacing their fossil-based counterparts [2, 3]. This is not as original as it sounds, because, apart from the role of natural polymers throughout our history evoked above, the very first *synthetic* polymer commodities, developed during the second half of the nineteenth century, namely cellulose esters, vulcanized natural rubber, rosin derivatives, terpene 'resins', were all derived from renewable resources. What is new and particularly promising, has to do with the growing momentum that this

trend has been gathering in the last decade, as witnessed by the spectacular increase in the number of publications, reviews, reports, books, scientific symposia and, concurrently, by the correspondingly growing involvement of both the public and the industrial sectors in fostering pure and applied research in this broad field.

The purpose of this chapter is to provide a concise assessment of the state of the art related to the realm of monomers and macromonomers from renewable resources and their polymerization, and to offer some considerations about the prospective medium-term development of its various topics, which are also the section headings. Natural polymers are not covered here, nor are monomers like lactide, which are discussed elsewhere in the book. The reader interested in more comprehensive information on any of these topics, will find it in a recent comprehensive monograph [3].

1.2
Terpenes

The term 'terpene' refers to one of the largest families of naturally-occurring compounds bearing enormous structural diversity, which are secondary metabolites synthesized mainly by plants, but also by a limited number of insects, marine micro-organisms and fungi [4, 5].

Most terpenes share isoprene (2-methyl-1,4-butadiene) as a common carbon skeleton building block and can therefore be classified according to the number of isoprene units. Among the huge variety of structures of terpenes, associated with their different basic skeletons, stereoisomers, and oxygenated derivatives, the only members relevant to the present context are unsaturated hydrocarbon monoterpenes, which bear two such units, *viz.* the general formula $C_{10}H_{16}$, as exemplified in Figure 1.1 for the most representative structures found in turpentine, the volatile fraction of pine resin, which is itself the most representative and viable source of terpenes, whose world yearly production amounts to some 350 000 tons.

Among these molecules, only a few have been the subject of extensive studies related to their polymerization, namely those which can be readily isolated in appreciable amounts from turpentine: α-pinene, β-pinene, limonene and, to a lesser extent, myrcene [5].

Cationic polymerization has been shown to be the most appropriate type of chain reaction for these monomers. Indeed, the very first report of *any* polymerization reaction was published by Bishop Watson in 1798 when he recorded that adding a drop of sulfuric acid to turpentine resulted in the formation of a sticky resin. It was of course much later that the actual study of the cationic polymerization of pinenes was duly carried out, leading to the development of oligomeric adhesive materials still used today, mostly as tackifiers.

The mechanism of β-pinene cationic polymerization is well understood, together with its accompanying side reactions, as shown in Figure 1.2 [5, 6]. As in many other cationic systems, transfer reactions are prominent and hence the
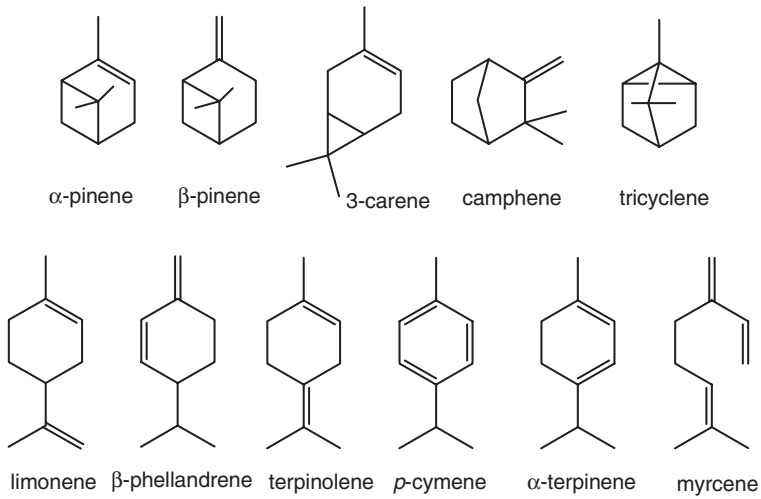
α-pinene   β-pinene   3-carene   camphene   tricyclene

limonene β-phellandrene terpinolene *p*-cymene α-terpinene myrcene

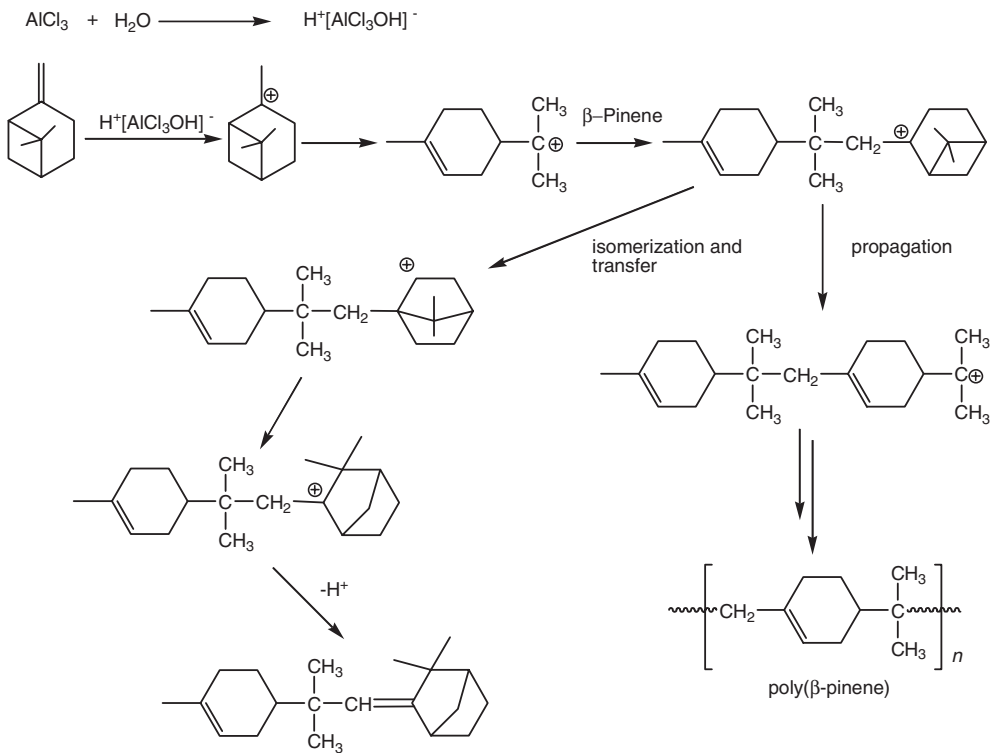**Figure 1.1**   Structure of the most common monoterpenes found in turpentine.

Figure 1.2   The reactions involved in the cationic polymerization of β-pinene.

degree of polymerization (DP) of the ensuing materials tend to be low. The development of cationic initiators capable of providing controlled, or quasi-living, conditions opened a new perspective also for the polymerization and copolymerization of β-pinene, and novel materials were synthesized with higher molecular weight and regular structures [5, 7].

The prevalence of investigations devoted to β-pinene stems from the relative simplicity of its cationic polymerization, compared with the more complex behavior of α-pinene.

The free radical polymerization of pinenes and limonene is of little interest, because of the modest yields and DPs obtained with their homopolymerizations. However, their copolymerization with a variety of conventional monomers has been shown to produce some interesting materials, particularly in the case of controlled reversible addition fragmentation chain-transfer (RAFT) systems involving β-pinene and acrylic comonomers [5].

A recently published original alternative mode of preparing polymeric materials from terpenes [8], makes use of a ring-opening metathesis mechanism in the presence of diclycopentadiene and generates hyperbranched macromolecules bearing a complex structure.

Terpenes epoxides, prepared by the straightforward oxidation of their unsaturation [9], have also been submitted to cationic polymerization [5, 10] and to insertion copolymerization with CO_2 [11], but these studies were not systematic in their approach.

It can be concluded that the advent of both free radical and cationic living polymerizations has brought new life into the area of terpene polymers and copolymers. No study is however known to the author regarding the use of enzymes to induce the polymerization of these natural monomers and such an investigation deserves some attention.

1.3
Rosin

Rosin [12, 13], also known by the name of colophony, is the designation traditionally given to the non-volatile residue obtained after the distillation of volatiles from the resin exuded by many conifer trees, mostly pine. It is therefore the complement of turpentine, which is the major source of terpenes discussed in the preceding section. Rosin played a fundamental role in waterproofing wooden naval vessels in the past and its use declined with the progressive decrease in their construction. Its annual worldwide production is however still more than one million tons and in recent years new uses are being actively sought within the general trend toward the valorization of renewable resources.

All rosins are made up of 90–95% of diterpenic monocarboxylic acids, or 'resin acids', $C_{19}H_{29}COOH$, in different specific molecular architectures. Their most common structures can be subdivided into those bearing two conjugated double

bonds, as in Figure 1.3, and those in which the unsaturations are not conjugated, as in Figure 1.4.

The chemical modifications of these molecules which have been thoroughly studied include [12]:

- the oxidation of one unsaturation to give an endoperoxide;
- the aromatization of the rings through dehydrogenation and the subsequent functionalization of the ensuing aromatic moieties;
- the hydrogenation of one or both unsaturations;
- the isomerization relative to the position of the unsaturations;
- the Diels–Alder (DA) reaction with dienophiles;
- the reactions with formaldehyde and phenol;
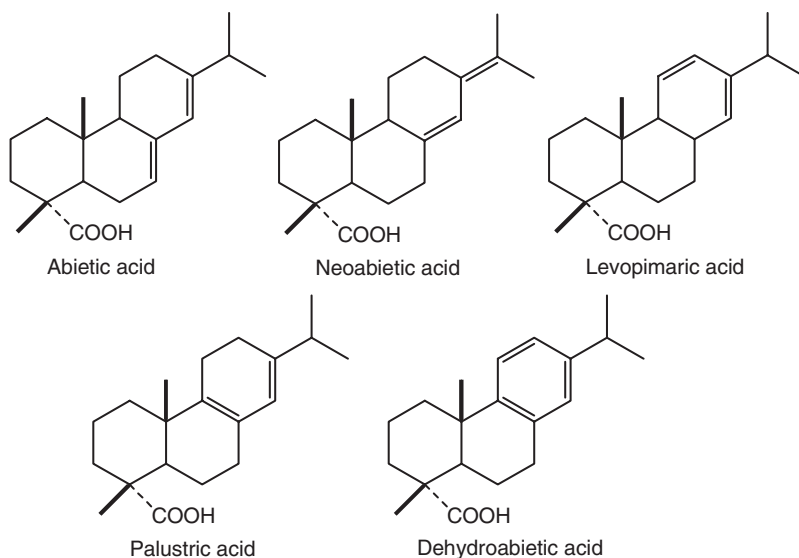- the preparation of salts of the carboxylic acid.

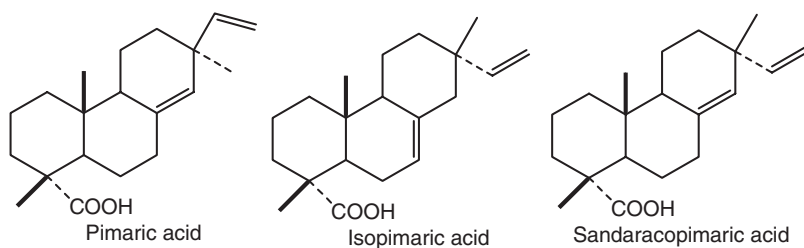**Figure 1.3** Structures of the most common conjugated resin acids.

Figure 1.4 Structures of the most common non-conjugated resin acids.

The aspects relevant to the use of rosin as such, or one of the derivatives arising from its appropriate chemical modification as monomer or comonomer [12–14], have to do with the synthesis of a variety of materials based on polycondensations and polyaddition reactions of structures bearing such moieties as primary amines, maleimides, epoxies, alkenyls and, of course, carboxylic acids. These polymers find applications in paper sizing, adhesion and tack, emulsification, coatings, drug delivery and printing inks.

A recent addition to the realm of rosin derivatives used in polymer synthesis dealt with rosin-based acid anhydrides as curing agents for epoxy compositions [15] and showed that their performance was entirely comparable with that of petroleum-based counterparts, with the advantage of a simple process and, of course, their renewable character.

As with terpenes, there is no record of the use of rosin or its derivatives as monomers in enzymatic polymerizations, a fact that should stimulate research aimed at filling this gap.

1.4
Sugars

Carbohydrates constitute a very important renewable source of building blocks for the preparation of a variety of macromolecular materials, which find key applications particularly in the biomedical field, because of their biocompatibility and biodegradability (see also Chapter 9 and 16). The introduction of sugar-based units into the polymer architecture can be achieved via (i) polyaddition reactions involving vinyl-type saccharides; (ii) functionalizations that append the carbohydrate onto a reactive backbone; or (iii) polycondensation reactions of sugar based monomers. Whereas the first two approaches generate macromolecules in which the carbohydrate moieties are in fact side groups to conventional vinyl or acrylic chains, the latter alternative is more interesting, because it gives rise to *real* carbohydrate-based polymers in which the repeating units of the main chain are the sugar derivatives themselves [16]. This type of polymerization is only briefly discussed here, moreover the coverage is limited to chemical catalysis, since the enzymatic approach is dealt with in Chapter 4.

Sugars as such are polyols and hence if linear polymers are sought from them, the number of OH functions, or indeed of functions derived from them, must be reduced to two, either by adequate protection procedures, or by appropriate chemical modifications.

The three anhydroalditol diols shown in Figure 1.5, resulting from the intramolecular dehydration of the corresponding sugars, are among the most extensively studied sugar-based monomers with different polycondensation systems leading to chiral polymers [16, 17]. Isosorbide is readily prepared from starch, isomannide from D-mannose, and both are industrial commodities. Isoidide is prepared from isosorbide by a three-step synthesis, because L-idose is a rare sugar. Given the diol nature of these compounds, it follows that polyesters, polyurethanes and
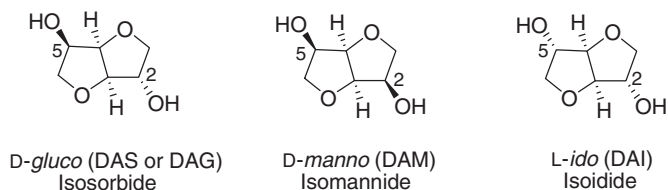
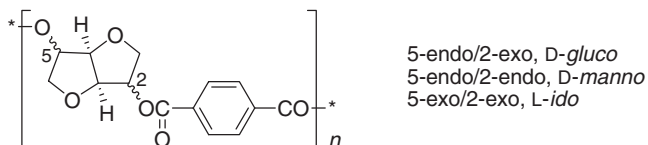**Figure 1.5** Three important anhydroalditol monomers.

5-endo/2-exo, D-*gluco*
5-endo/2-endo, D-*manno*
5-exo/2-exo, L-*ido*

Figure 1.6 Terephthalates based on anhydroalditols [18].

5-endo/2-exo, D-*gluco*
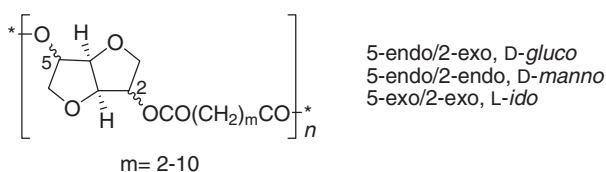5-endo/2-endo, D-*manno*
5-exo/2-exo, L-*ido*

Figure 1.7 Aliphatic polyesters based on anhydroalditols [19].

polyethers are among the obvious macromolecular structures investigated, but polycarbonates and polyester-amides have also attracted some interest. All these materials exhibit higher T_g values than counterparts synthesized with standard aliphatic diols, because of the inherent stiffness of the anhydroalditol structure. The macromolecular rigidity can of course be further enhanced by using similarly stiff complementary monomers, such as aromatic diacids, as in the example of Figure 1.6. The use of aliphatic diacids for the preparation of the corresponding polyesters (Figure 1.7) gives rise to biodegradable materials.

Carbohydrate-based polyamides and polyurethanes constitute two major families of polymers and hence the interest in preparing aminosugars and, from them, the corresponding isocyanates. This wide research field has produced very interesting materials including the first chiral nylon-type polyamides [16].

Typical polyamides and polyurethanes prepared from aminosugars, both from anhydroalditols and protected monosaccharides, are shown in Figures 1.8 and 1.9, respectively.

A new family of linear polyurethanes and poly(ester-urethanes), prepared from both aliphatic and aromatic diisocyanates and isorbide [21] or conveniently protected sugar alditols, has recently been reported and the properties of
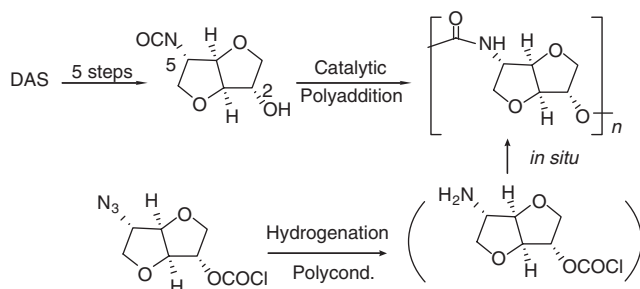
Figure 1.8 Approaches to stiff polyurethanes based on anhydroalditols [20].

D-*gluco* (2-exo/5-endo)
D-*manno* (2-endo/5-endo)
L-*ido* (2-exo/5-exo)

erythro (2-exo/3-exo)
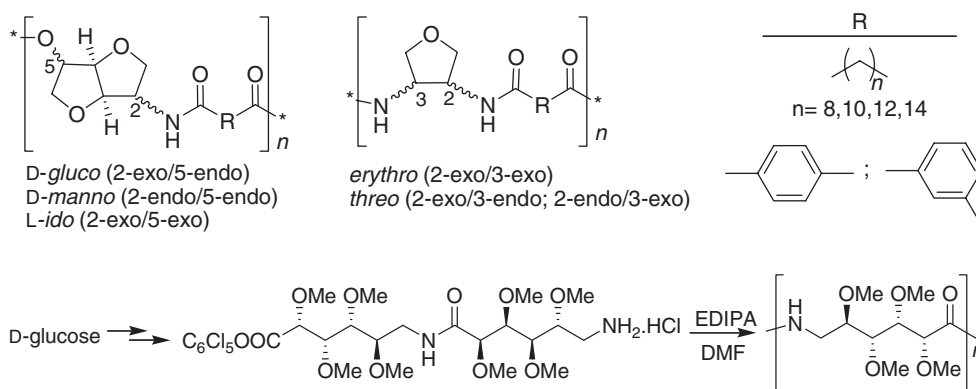*threo* (2-exo/3-endo; 2-endo/3-exo)

n= 8,10,12,14

Figure 1.9 Various polyamide structures derived from sugars [16].

the ensuing materials fully characterized [22]. This interesting investigation has been extended to include aliphatic biodegradable polyurethanes bearing L-arabinitol and 2,2'-dithiodiethanol [23]. Furthermore, the preparation of a novel carbohydrate lactone and its ring-opening polymerization were shown to yield a functionalized cyclic aliphatic polyester [24]. A very thorough study of the synthesis of sugar monoisocyanates [25], aimed at preparing ureido-linked disaccharides, should inspire polymer chemists to extend it to diisocyanate homologs.

1.5
Glycerol and Monomers Derived Therefrom

The current boom associated with biodiesel production from vegetable oils has generated a spectacular rise in glycerol availability, with a yearly world production

estimated in 2008 at 1.8 MT and a correspondingly low price of ~0.6 Euro per kg. The traditional uses of glycerol in pharmaceuticals, cosmetics and personal care products, alkyd resins, etc., are now being progressively complemented with commodities arising from its chemical conversion, as with the examples detailed in the section below.

The clearest indication of the rapidly rising scientific and technological research on chemicals from glycerol is the number of monographs published on this topic in the last few years [26]. Before discussing these aspects, it is instructive to show that glycerol itself is being investigated as a monomer in novel polymerization systems. There are in fact two distinct areas in this context, namely the synthesis of glycerol oligomers and the preparation of its polymers or copolymers using appropriately modified monomers.

The self-condensation of glycerol catalyzed by both homogeneous and heterogeneous basic catalysis yields a mixture of linear and branched oligomers (DPs typically from 2 to 6), mostly linear with the former medium, while mostly branched with the latter [27]. Figure 1.10 shows a schematic illustration of the linear growth, involving only the primary OH groups, since condensation with the secondary ones generates ramifications. The applications of these oligomers include cosmetics, food additives and lubricants. Carboxylic acid oligoglycerol esters [27, 28] are also gaining relevance as materials in similar domains, as well as as emulsion stabilizers and antistatic or antifogging agents.

The preparation of hydroxyesters or hydroxyacids from glycerol and their polycondensation by transesterification has been the subject of recent studies aimed at preparing biodegradable hyperbranched polycarbonates [29] and polyesters
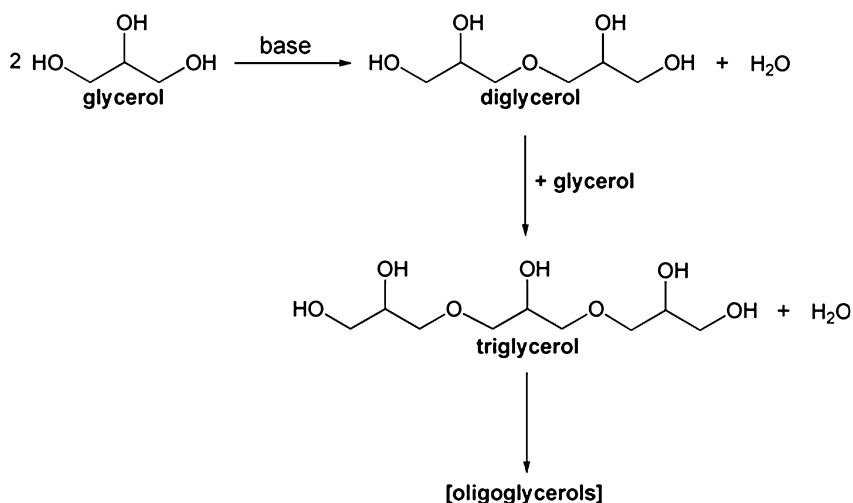

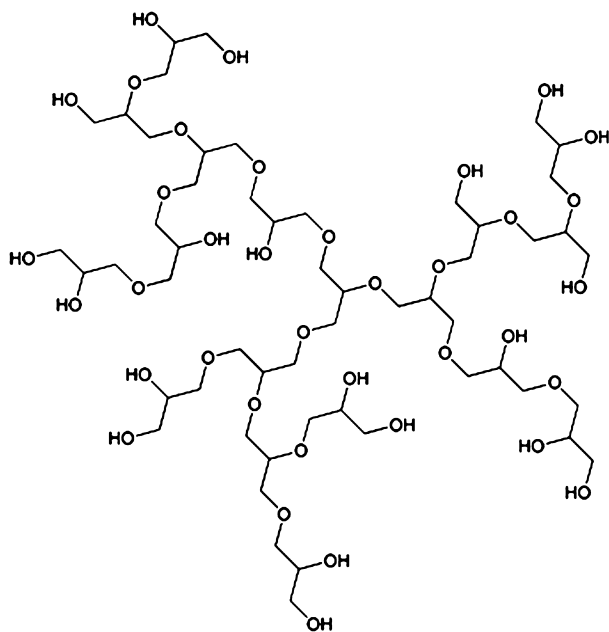**Figure 1.10** Etherification mechanism leading to oligoglycerols.

Figure 1.11 A model structure of hyperbranched polyglycerol.

[30, 31]. Although hyperbranched polyglycerols (Figure 1.11) have not thus far been synthesized directly from glycerol, much work has been devoted to their preparation, because of their interesting properties, including biocompatibility, biodegradability, water solubility and aptitude to easy functionalization. Structures of this type, incorporating poly(ethylene oxide) blocks have been reported, using, for example, glycidyl ethers as monomers [32].

Notwithstanding the promising aspect of investigations related to glycerol-based macromolecules, it is fair to state that much more is to be expected from the wide variety of mechanisms and catalysts being studied in order to convert glycerol into a panoply of chemicals [26] and, in particular, of monomers suitable for both step and chain polymerizations. This is extremely important in the present context, because more and more monomers, which were only available through petrochemical routes, are being reported as accessible through glycerol chemistry, notably diols, diacids, hydroxyacids, oxiranes, acrolein, and acrylic acid, among others. The specific instance of ethylene and propylene glycols [33] is particularly relevant, considering the importance of poly(ethylene terephthalate) (PET), the most important polyester on the market and of the novel poly(trimethylene terephthalate) produced by DuPont under the commercial name of Sorona. These considerations extend to polymers fully derived from renewable resources, as in the case of some of the furan polyesters discussed below.

1.6
Furans

Whereas natural monomers like terpenes and sugars constitute building blocks for a limited number of macromolecular structures, associated with their own peculiar chemical features, the realm of furan polymers bears a qualitatively different connotation in that it resembles the context of petrol refinery, that is, it is open to a whole domain of monomers, whose only specificity is the fact that they all incorporate the furan heterocycle in their structure. This state of affairs stems from the fact that, as in petroleum chemistry, saccharide-based renewable resources are used to produce two first-generation furan derivatives, which constitute the substrates capable of being converted into a vast array of monomers and hence a correspondingly large number of macromolecular structures associated with materials possessing different properties and applications [34].

Furfural (F) has been an industrial commodity for over a century and its production has spread throughout the world reaching a yearly production close to 300 000 Tons (at a price of ~0.5 Euros per kg), with some 70% in China. Its precursors range from agriculture to forestry residues, namely the pentoses present in such different by-products of the food industry as corn cobs, oat and rice hulls, sugar cane bagasse, cotton seeds, olive husks and stones, as well as wood chips. This variety of sources explains why any given country possesses a renewable resource which can be turned into F, considering moreover that the technology associated with its production is particularly simple, being based on the acid catalyzed hydrolytic depolymerization of the hemicellulose and the subsequent dehydration of the ensuing aldopentoses [35]. The dominant xylose component is converted into F, whereas rhamnose, present in modest proportions, gives rise to 5-methylfurfural (MF), as shown in Figure 1.12. The two furan compounds can be readily separated by distillation.
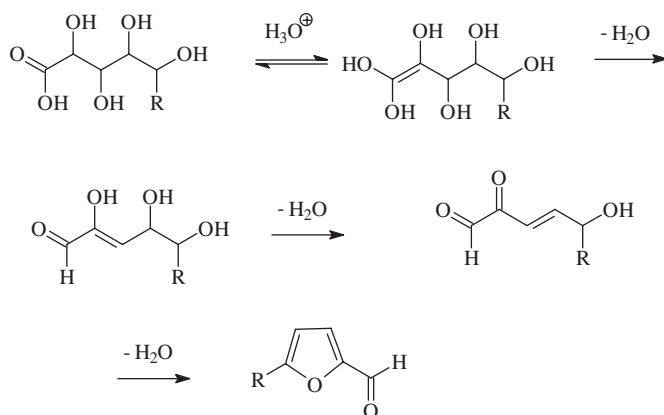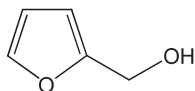

Figure 1.12 Mechanism of F (R=H) and MF (R=CH$_3$) formation from aldopentoses.

Most of the furfural is to-day converted into furfuryl alcohol (FA), which is extensively employed as a precursor to a variety of resins for high-tech applications [34], whose spectrum is constantly broadening.


FA

The second furan derivative which can be prepared from the appropriate C6 polysaccharides or sugars is hydroxymethylfuraldehyde (HMF). The mechanism of its formation from hexoses is entirely similar to that of F, but difficulties associated with the recovery of the product have delayed its industrial production, despite, again, the ubiquitous character of its natural precursors. A very substantial effort has been devoted in recent years to investigate and optimize novel processes and/or catalysts [36] and the ensuing results suggest that HMF will be a commercial commodity very soon. Interestingly, because of its relative fragility, some of these approaches consider the *in situ* conversion of HMF into its very stable dialdehyde (FCDA) or diacid (FDCA) derivatives.
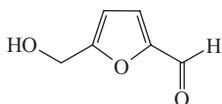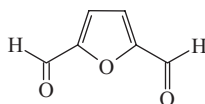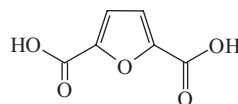
HMF   **FCDA**   **FDCA**

This impressive surge of interest in HMF is yet another clear example of the ferment around the search for original alternatives to petrochemistry, based on the exploitation of renewable resources, in the field of chemicals, materials and energy sources.

This said, the ensuing research strategy, whose implementation began some 40 years ago [34] relies on the following working hypothesis: two first-generation furan derivatives, F and HMF, constitute the starting structures from which two sets of monomers can be synthesized, viz. those suitable for chain polymerizations and copolymerizations, and those associated with step-growth mechanisms. Figure 1.13 shows some of the monomers which have been prepared from F and then assessed in terms of their individual aptitude to the appropriate chain polymerization and copolymerization reactions [34]. Figure 1.14 illustrates a different approach for the exploitation of furfural, and in general monosubstituted furans, but in this case with the purpose of synthesizing byfunctional monomers
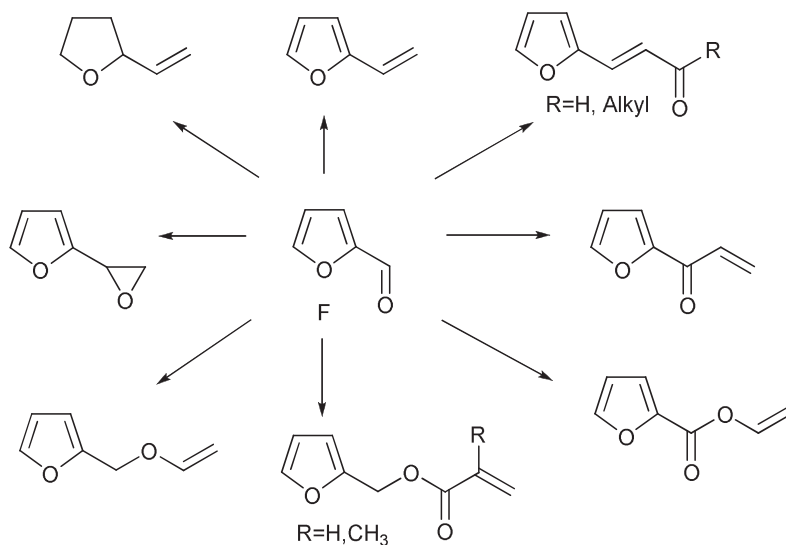
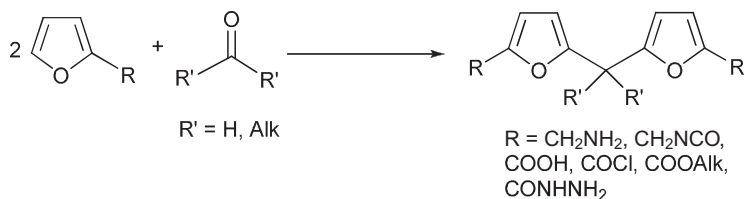**Figure 1.13** A selection of monomers derived from F.

Figure 1.14 Difuran monomers derived from 2-substituted furans (prepared in turn from F).

for polycondensation systems [34]. The ensuing structures incorporate two furan rings, each bearing a reactive group, bridged by a variety of moieties.

Figure 1.15 depicts the type of monomers which have been obtained from HMF, namely, again, structures suitable for step-growth polymerizations [34], but here mostly with a single heterocycle bearing the two reactive moieties.

Only some recent contributions to this large field are discussed here, since thorough reviews are available elsewhere. The most interesting studies relate to two very different approaches to furan polymers, namely the synthesis of novel polyesters and the use of the Diels–Alder reaction to prepare thermoreversible materials [37].

The announced awakening of the 'sleeping giant' HMF has brought furan polycondensates back to the forefront of both fundamental and industrial research. The obvious underlying thought here is the elaboration of macromolecular materials in which aromatic units (fossil resources) are replaced by furan counterparts (renewable resources) and the assessment of the novel structures in terms of their capability of replacing the existing ones advantageously, or at least at par.
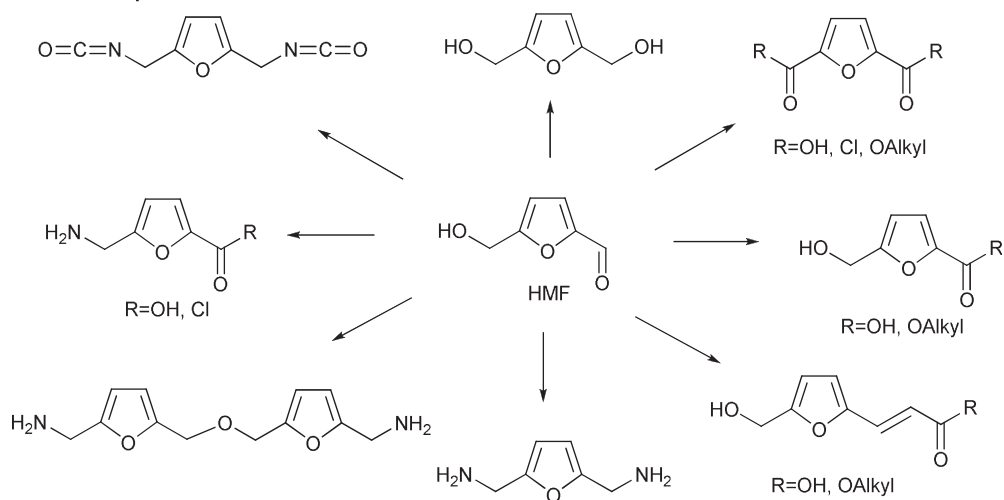
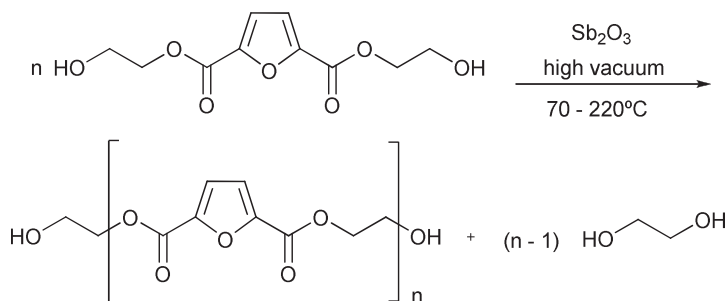**Figure 1.15** A selection of monomers derived from HMF.

Figure 1.16 Polytransesterification mechanism leading to high-DP PEF.

Polyesters come to mind, since PET and some of its more recent homologs play a very prominent role on the polymer market. FDA was therefore used in conjunction with ethylene glycol to synthesize poly(2,5-ethylene furancarboxylate) (PEF), that is, the furan analog of PET [38]. The use of polytransesterification (Figure 1.16) proved particularly effective in generating high-molecular weight semicrystalline polymers.

Interestingly, the replacement of the aromatic ring by the furan counterpart did not alter in any appreciable fashion such polymer properties as glass transition and melting temperature, the high aptitude to crystallize and the thermal stability [37, 38]. The same considerations apply to the polymer homologs bearing 1,3-propylene glycol units [37]. Work is in progress to extend these comparisons to mechanical and processing properties. Given the recent work mentioned above on the synthesis of glycols from glycerol, these novel furan polyesters can be
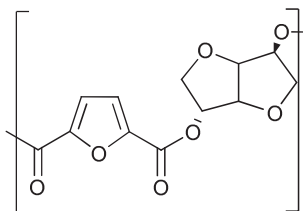
Figure 1.17 Repeat unit of the polyester prepared from FDA and isosorbide.
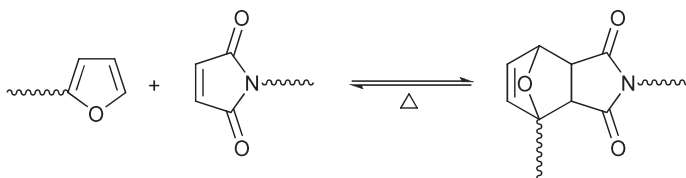

Figure 1.18 The DA equilibrium between growing species bearing respectively furan and maleimide end groups.

considered as being entirely based on renewable resources. The same applies to the combination of FDA and isosorbide (Figure 1.17) which produced, as expected, a much stiffer polyester macromolecule and hence a high T_g [37]. The range of furan polyester structures is currently being widened to include other diols and to study random and block copolymers.

In a very different vein, the purpose of applying the DA reaction to synthesize furan polymers stems from two considerations: (i) the fact that furans are particularly well suited to participate in that coupling interaction, functioning as dienes; and (ii) the thermal reversibility of the DA reaction which opens the way to the preparation of intelligent materials, which are moreover easily recyclable [37, 39, 40]. The most logical complementary function in this context is the maleimide dienophile, because of its excellent reactivity and the fact that multifunctional homologs can be readily prepared. The system therefore can be represented schematically by the reversible interaction shown in Figure 1.18, which depicts any forward/backward DA reaction applied to any polymerization involving furan and maleimide moieties.

Among the different applications of this reaction, the systems which have received most attention are: (i) linear polycondensations involving difuran and bismaleimide monomers (AA + BB) and, more recently, monomers incorporating both moieties (AB); (ii) non-linear polycondensations with at least one monomer with a functionality higher than two; polymer crosslinking, for example, a polymer bearing pendant furan heterocycles reacting with a bismaleimide, or vice-versa. Of course in all these instances, the growth or crosslinking processes are thermoreversible, with temperatures above 100 °C shifting the equilibrium in favor of the reagents, that is, the opening of the adduct, accompanied by the corresponding depolymerization, or decrosslinking. Given the clean-cut nature of
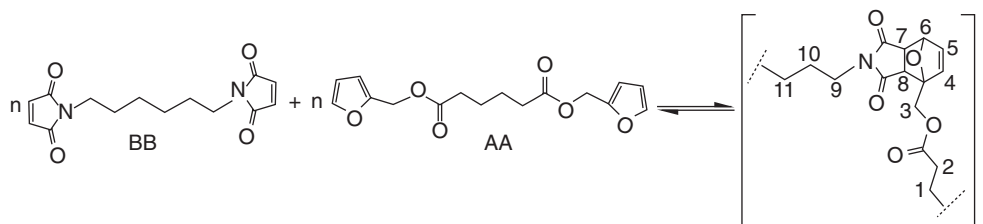
Figure 1.19 Reversible DA polycondensation between complementary bifunctional monomers [40].
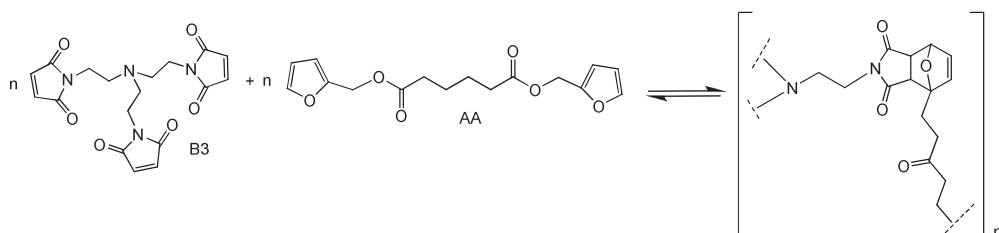
Figure 1.20 Reversible DA non-linear polycondensation between a tris-maleimide and a difuran monomer [37].

the DA reaction, several cycles have been applied to these various systems with reproducible forward and backward features.

A recent example of a thorough study of a linear polymerization using UV and NMR spectroscopy included various monomer combinations [40], like that shown in Figure 1.19.

Similarly, Figure 1.20 shows a typical monomer combination leading to branched and ultimately crosslinked polymers, which are thermally reversible all the way to the initial monomer mixture [37]. Finally, Figure 1.21 shows the reversible crosslinking of a linear furan copolymer by an oligomeric bismaleimide [41].

The present choice of systems based on furan monomers is not exhaustive of course, but hopefully sufficient to illustrate the enormous potential of this area of polymer science, which does justice to the plea for more macromolecular materials from renewable resources.

1.7
Vegetable Oils

The exploitation of vegetable oils, triglycerides of fatty acids, as a source of materials is as old as the inception of civilization, first for coating applications and soap manufacture, then for progressively wider and more sophisticated applications including inks, plasticizers, alkyd resins, agrochemicals, etc. This qualitative and
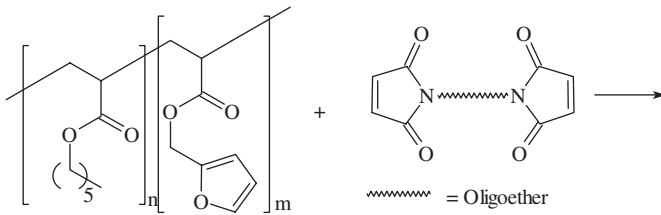
(AcFu)
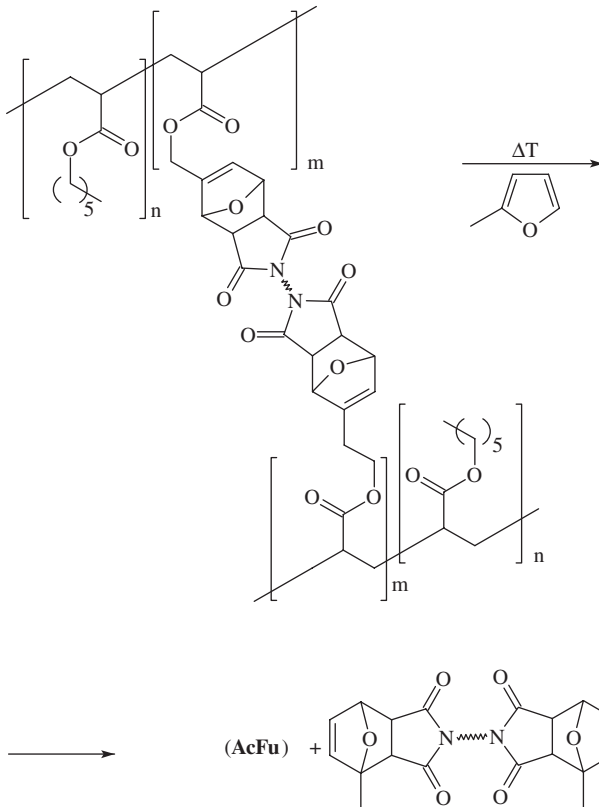
Figure 1.21 Reversible DA crosslinking reaction of a linear furan copolymer [41].

quantitative increase in the realm of materials has been complemented in recent years by the use of vegetable oils for the production of biodiesel. This section highlights briefly recent progress in the use of vegetable oils as macromonomers for the elaboration of novel macromolecular materials, following more thorough reviews published in the last few years [42].

The structure of these natural products can be schematically depicted by the simple generic triglyceride formula given in Figure 1.22, where R_1, R_2 and
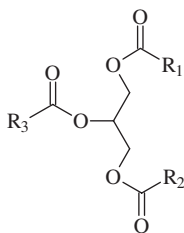
Figure 1.22 Generic structure of a triglyceride.

R_3 represent fatty acid chains, viz. linear aliphatic structures which can vary in length (from C12 to C22) in the number of C=C unsaturations (from zero to 6) and in the possible presence of other moieties, like OH or epoxy groups. Figure 1.23 portrays some of the most characteristic structures of fatty acids prese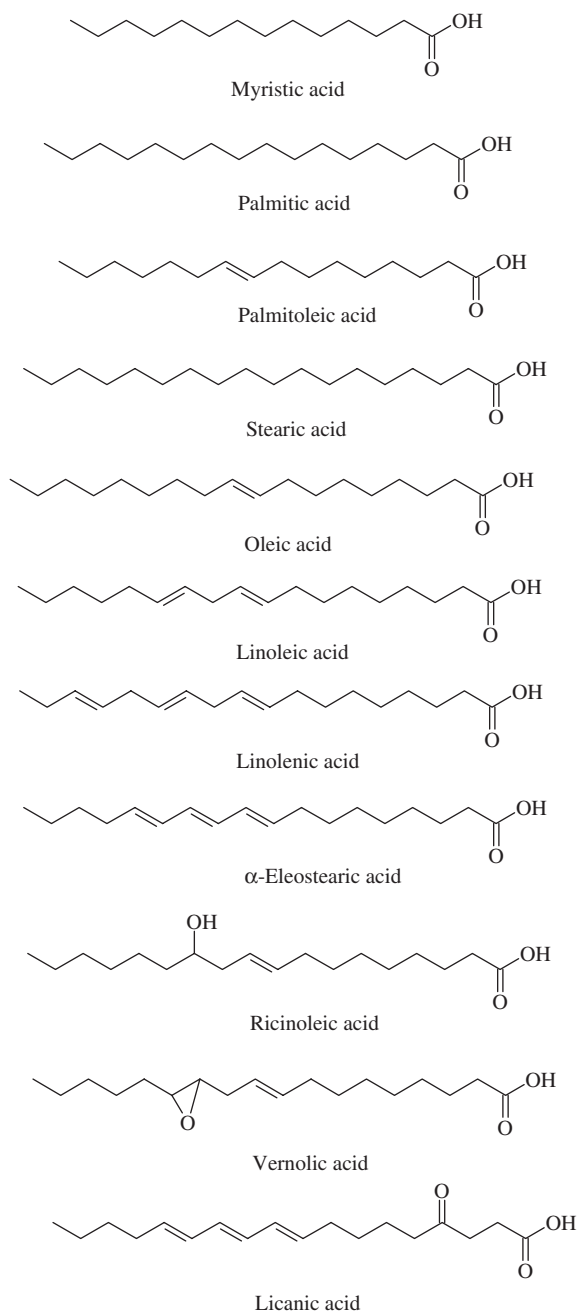nt in triglycerides. A given triglyceride often incorporates identical groups R, but a given oil is always made up of a mixture of triglycerides (typically 3 to 5), frequently with one or two predominant structures making up 70–80% of the composition [42]. The degree of unsaturation of a vegetable oil is perhaps the most relevant parameter in terms of such criteria as siccativity in coatings, lacqers, paints and inks, that is, the drying of the oil by atmospheric oxidopolymerization through a well-established mechanism [42], but also as a source of other types of polymerization and of chemical modification.

The annual global production of vegetable oils is expected to reach some 150 Mt in 2010, of which about 20% is devoted to industrial applications (materials and energy), compared with ~75 and 5% for food and feed uses. Within the combined contexts of this huge amount of renewable resources and of the growing emphasis on their exploitation as alternative precursors to polymers instead of fossil counterparts, it is not surprising to witness a burgeoning research effort in the area, which appears to be set to grow in the near future.

Among the most interesting chemical modifications of oils or fatty acids, epoxidation occupies a privileged position for the number and variety of studies and applications it has spurred [43]. This reaction involves the transformation of C=C alkenyl moieties along the fatty acid chain into oxirane groups using a variety of oxidation systems, for example, that shown in Figure 1.24, although terminal epoxy functions have also been appended to saturated triglycerides [43]. These epoxidized macromonomers have found numerous applications in thermosetting resins using diamines and anhydrides as hardeners, including reinforced nano-hybrid materials and flame retardancy [43].

The other mode of activation of the oxirane moieties is through cationic polymerization, which will generate a network for polyfunctional epoxidized glycerides and thermoplastic materials with fatty acids bearing a single epoxy group [43].

Apart from these direct uses as macromonomers, epoxydized vegetable oils have also been employed as precursors to other polymerizable structures, follow-

Myristic acid

Palmitic acid

Palmitoleic acid

Stearic acid

Oleic acid

Linoleic acid

Linolenic acid

α-Eleostearic acid

Ricinoleic acid

Vernolic acid

Licanic acid

Figure 1.23   Typical fatty acids borne by vegetable oil triglycerides.
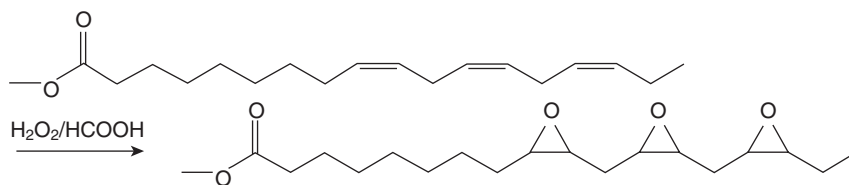
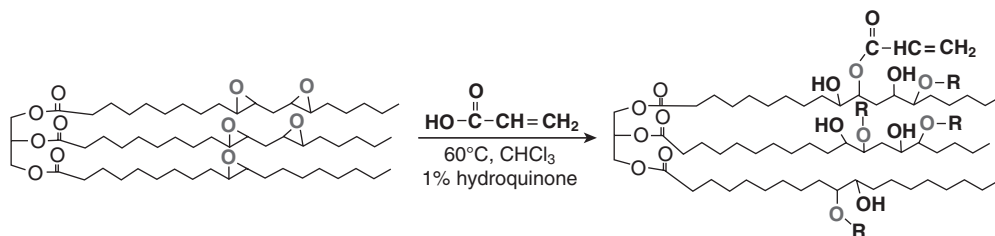**Figure 1.24** The epoxydation of methyl linolenate by performic acid.

Figure 1.25 Hydroxylated and acrylated derivative of epoxidized soy oil.

ing appropriate chemical modifications, namely the formation of polyols for the synthesis of polyurethanes and the insertion of acrylic functions (Figure 1.25) for photopolymerizable structures [42, 43].

Other modifications of vegetable oils in polymer chemistry include the introduction of alkenyl functions, the study of novel polyesters and polyethers and the synthesis of semi-interpenetrating networks based on castor oil (the triglyceride of ricinoleic acid) [42], and also the production of sebacic acid and 10-undecenoic acid from castor oil [44]. Additionally, the recent application of metathesis reactions to unsaturated fatty acids has opened a novel avenue of exploitation leading to a variety of interesting monomers and polymers, including aliphatic polyesters and polyamides previously derived from petrochemical sources [42, 45].

The vitality of this field is further demonstrated by a continuous search for original ways of exploiting vegetable oils. Examples include self-healing elastomers in which fatty acids play a central role [46]; the esterification of cellulose with fatty acids to give thermoplastic materials [47]; the synthesis of a saturated aliphatic diisocyanate from oleic acid and its subsequent use in the preparation of fully biobased polyurethanes in conjunction with canola oil-derived polyols [48]; and novel elastomers from the concurrent cationic and ring-opening metathesis polymerization of a modified linseed oil [49].

Regrettably, all this *chemical* ferment has not yet found a *biochemical* counterpart in the sense that no study on the use of biocatalytic systems has been published in the context of the use of vegetable oils or their fatty acids as sources of polymeric materials.

1.8
Tannins

A large variety of trees and shrubs contain tannins, a term used loosely to define two broad classes of natural phenolic compounds, viz. condensed (or polyflavonoid) tannins and hydrolyzable tannins. Whereas the former are oligomeric in nature, the latter are essentially non-polymeric. The most important varieties of these compounds include the bark of oak and black wattle as well as of pines and firs, and the woods of chestnut, mangrove, and sumach, among others [50]. After millennia of empirical use and a century of intensive industrial exploitation of tannins, particularly in leather tanning, their use began to dwindle after the Second World War up to the 1970s, when new applications were actively sought. This trend saw a considerable boost with the beginning of the third millennium within the more general context of the rational exploitation of renewable resources associated with the paradigm of the biorefinery.

Condensed tannins constitute more than 90% of the total world production of commercial tannins which amounts to about 200 kT per year. Figure 1.26 depicts two typical flavonoid monomer units of condensed tannins, whose average molecular weights vary between 1000 and 4000, depending on the species involved.

Although hydrolyzable tannins are generally considered as being mixtures of phenols, they must be viewed as more complex substances made up of simple structures as those shown in Figure 1.27, together with higher oligomers, some of which contain carbohydrates covalently linked with phenols [50]. Given the relative paucity and poor reactivity of this family of tannins, only flavonoids will be discussed further here.

Within the realm of polymer science and technology, the major application of tannins is in adhesives, mostly for wood, because of their aptitude to react with formaldehyde, although considerable research has been devoted to reduce the use of the latter by optimizing the conditions favoring tannin self-condensation and/or reactions with other aldehydes, as reviewed recently by Pizzi [50], the most authoritative expert in the field.

A major development in the use of tannins in macromolecular materials has taken place in the last few years and again this original contribution comes from Pizzi's laboratory. Condensed tannins were found to crosslink in polycondensation reactions with furfuryl alcohol and small amounts of formaldehyde, thus
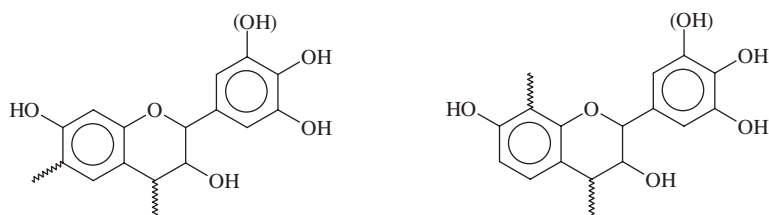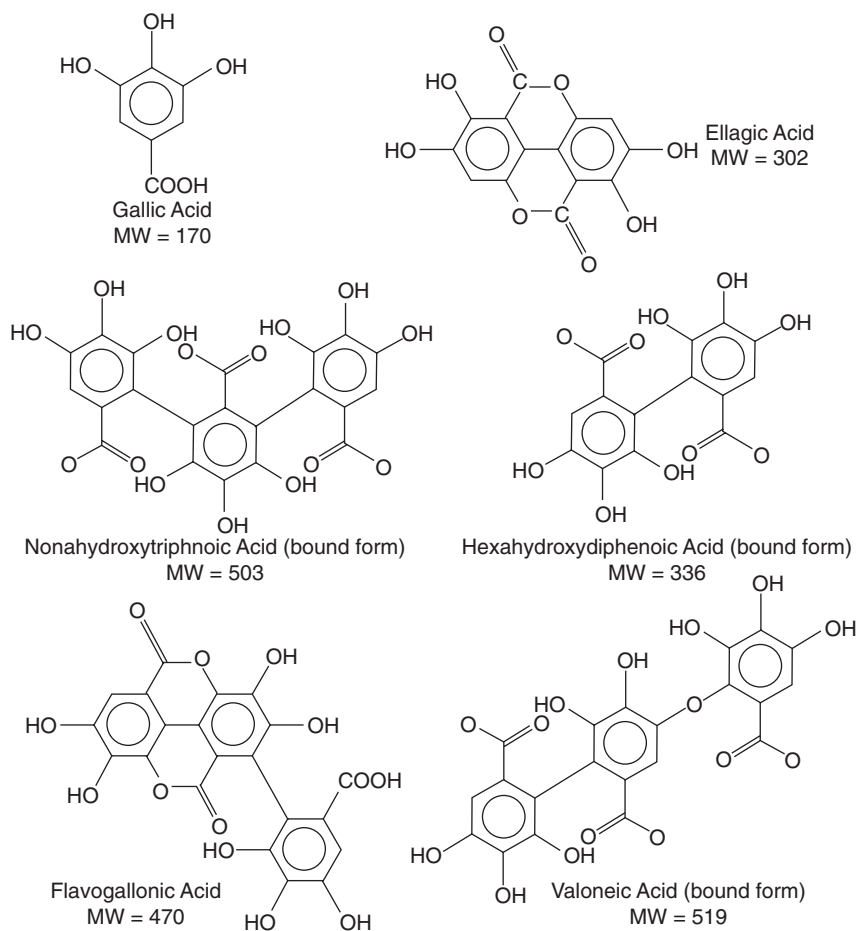

Figure 1.26 The most common monomer units in condensed tannins (polyflavonoids).

Figure 1.27 Low molecular weight components of hydrolysable tannins.

making these compositions almost totally based on renewable resources. When these reactions were conducted in the presence of a volatile additive, foaming took place giving rise to rigid cellular materials [51]. These foams displayed remarkable properties in terms of insulation, fire resistance, chemical inertness and metal ion sequestration [52].

Further work on these remarkable materials involved their carbonization and the thorough characterization of the ensuing carbon foams [53], as well as their subsequent chemical activation, which produced a dramatic increase in surface area, reaching $1800\,m^2\,g^{-1}$ when $ZnCl_2$ was used as promoter [54].

In conclusion, it is heartening to witness the lively rebirth of tannins as precursors of promising materials. As with other natural monomers and macromonomers, it appears that the possible interest of polymer bioprocesses could also be assessed on tannins, a type of study that has not been published thus far.

1.9
Lignin Fragments

Lignin is a fundamental component of plants, where it plays the fundamental role of amorphous matrix around the cellulose fibers and the hemicelluloses in the cell wall to form a supramolecular lignin–carbohydrate structure. Lignin is a phenolic–aliphatic polymer, whose biosynthesis is well documented and whose structure varies as a function of the vegetable species [55]. Figure 1.28 illustrates the typical building blocks found in lignin and the fact that this complex crosslinked macromolecule is also linked to the hemicellulose through occasional covalent bridges.

All chemical pulping processes and, today, all biorefineries applied to woods and annual plants are associated with the chemical splicing of lignin to produce fragments with molecular weights which vary from 1000 to 40000 and possess specific structural features [56]. Notwithstanding this very wide range of features, all these lignin fragments are characterized by a common structural peculiarity, which is particularly relevant to the polymer chemist, namely the ubiquitous presence of both aliphatic and phenolic hydroxyl groups, albeit in different frequencies and proportions.

The exploitation of lignin fragments in macromolecular materials can be divided into three different approaches: (i) as additives in physical blends [57]; (ii) as macromonomers in polymer synthesis; and (iii) as a source of phenolic monomers [58]. Only the latter two aspects are briefly discussed here.

The chemical participation of lignin macromonomers in polymerization or copolymerization reactions has been focussed mostly on the reactivity of both types of OH groups, and hence in the synthesis of polyesters, polyurethanes and polyethers, although some research has also dealt with their intervention through the unsubstituted aromatic sites in different formaldehyde-based resins in partial replacement of phenol [58, 59].

The use of the fragments as such has given contrasting results regarding their reactivity, because of the different topochemical situations in terms of the steric availability of the hydroxyl groups. For obvious reasons of simplicity and economy, the possibility of calling upon lignin macromonomers as produced in industrial operations is nevertheless much more attractive than having to modify them chemically to enhance their reactivity. For this reason, the low molecular weight fragments obtained from organosolv processes are much more interesting lignin macromonomers, owing to their modest steric crowding.

The most important problem associated with lignin macromonomers, as such or after appropriate chemical modifications (mostly aimed at making the OH groups more available), is however the reproducibility of their characteristics, since variations in structural features and molecular weight or molecular weight distribution inevitably induce corresponding variations in the properties of the final materials. A novel biorefinery organosolv process applied to annual plants [60], appears to provide a much better control over the properties of the ensuing low-molecular weight lignin.
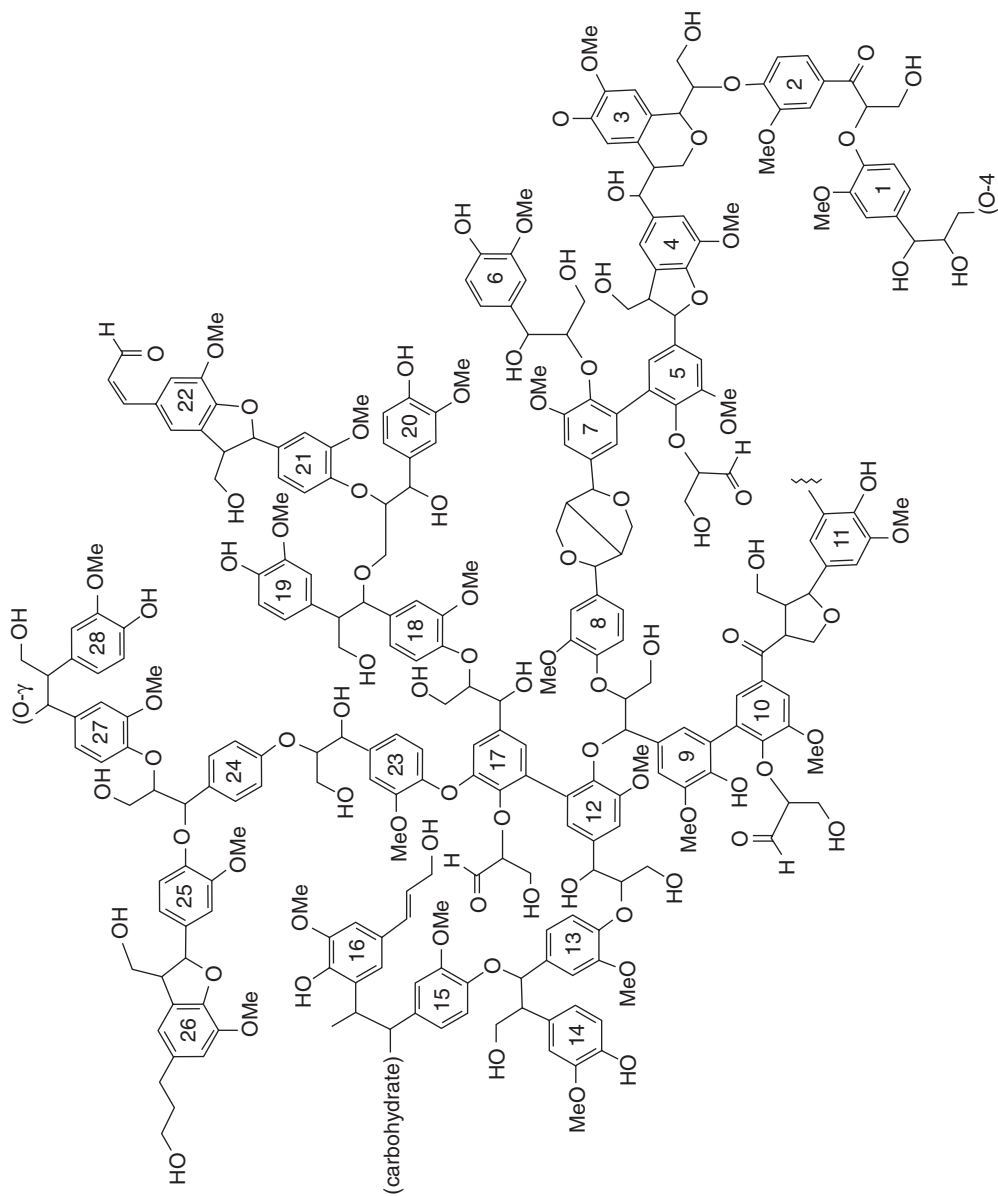
Figure 1.28 An illustration of the typical building blocks in the structure of lignin.

An altogether different strategy of valorization of lignin fragments is their radical conversion to liquid polyols through an oxypropylation reaction induced by the activation of the lignin hydroxyl groups with a Lewis or Bronsted base, followed by the grafting-from oligomerization of propylene oxide initiated by the ensuing oxianions [61, 62]. This process possesses a very wide applicability to OH-bearing substrates, many of them, like sugarbeet pulp, otherwise intractable, with the additional advantage of having a green connotation associated with the fact it does not require a solvent, nor any separation or purification treatment at the end of the reaction.

In essence, its double role is, on the one hand, to bring the OH groups out of the compact macromolecular assembly of the substrate, thus making them more prone to react and, on the other, to enhance the chain flexibility and mobility by appending low T_g grafts, hence turning solid residues into viscous liquids. Figure 1.29 provides a schematic view of this chemical transformation and emphasizes that the grafting reaction is always accompanied by some propylene oxide homopolymerization to give macrodiols, which are themselves potential monomers [61].

Numerous biomass by-products of little use other than combustion, have been valorized in this way, namely poor quality cork powder, olive stones, sugarbeet pulp, chitin and chitosan residues and lignins from different pulping technologies, among others [61, 62]. The ensuing lignin polyols were found to be very appropriate macromonomers for the synthesis of rigid polyurethane foams.
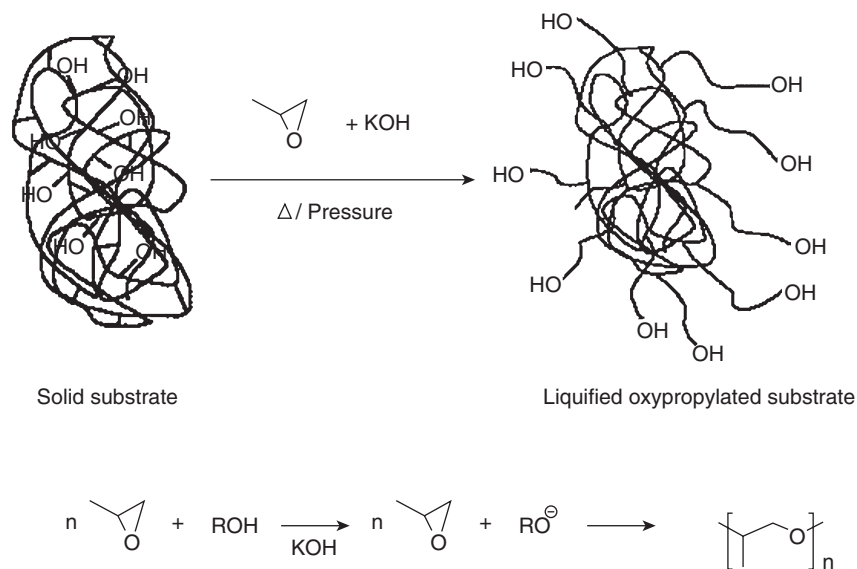

Figure 1.29 Schematic representation of the oxypropylation of solid biomass residues.

The other strategy of lignin exploitation for polymer synthesis revolves around the 'total' splicing of the fragments down to phenolic units [58, 63], which could be used, as such, or after appropriate chemical modifications, as monomers for either step-growth or chain polymerizations. Two major problems are implicit in this approach, namely the optimization of the depolymerization process and, more importantly, the efficient separation of the different ensuing building blocks. This situation has been tackled successfully in a somewhat different context, viz. the production of vanillin from kraft lignin within a biorefinery operation which made use of the remaining lignin as a source of polyurethanes [64]. Similar efforts should be devoted to integrated processes in which some specific monomer structures would be privileged in the lignin depolymerization, leaving the rest for other uses. Biochemical treatments would certainly contribute to the positive outcome of this type of study.

Recent additions to the search of lignin-based polymers include the use of lignin oligomers and vegetable oils to elaborate paper hydrophobic coatings [65] and the preparation of epoxy networks derived from lignosulfonate and glycerol [66].

1.10
Suberin Fragments

Suberin is a natural highly hydrophobic polyester almost ubiquitous in the vegetable realm, where it plays the important role of a protecting barrier between the plant and the environment. The amounts of suberin needed for this protection are very modest and in fact only two trees produce barks which are sufficiently rich in suberin to justify its exploitation, namely *Quecus suber* (cork), a Mediterranean species, and *Betula pendula* (birch), one of the most important hardwood species in Northern Europe. Most of the work on the extraction, hydrolysis and fragment characterization of suberin components has been carried out on cork, which contains between 40 to 60% of this polymer [67]. The suberin structure is made up of crosslinked macromolecules comprising mostly aliphatic polyesters and to a lesser extent a lignin-like network. From a polymer chemist's standpoint, the aliphatic portion constitutes by far the most interesting source of monomers, as clearly suggested by the most representative families of compounds isolated from suberin hydrolytic depolymerization shown in Figure 1.30. The alternative depolymerization by methanolysis yields the same structures with methyl ester moieties instead of COOH groups.

These monomer mixtures have been fully characterized [67, 68] and thereafter submitted to polycondensation reactions with diisocyanates to produce polyurethanes [67] and on their own to prepare polyesters [69]. The preliminary results of the latter study, which called upon both chemical and enzymatic catalyses, showed that the ensuing aliphatic polyesters were interesting materials with
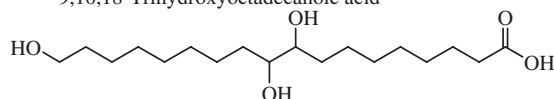
ω-Hydroxyfatty acids
18-Hydroxyoctadecanoic acid
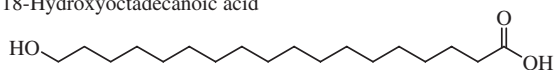
9,10-Epoxi-18-hydroxyoctadecanoic acid
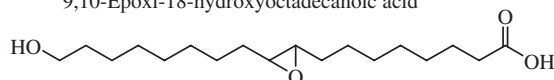
9,10,18-Trihydroxyoctadecanoic acid

α,ω-Dicarboxylic acids
Octadecanedioic acid
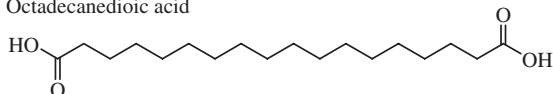
9,10-Epoxioctadecanedioic acid
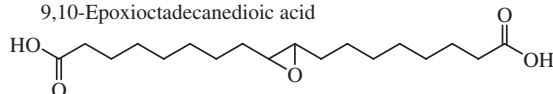
9,10-Dihydroxyoctadecanedioic acid
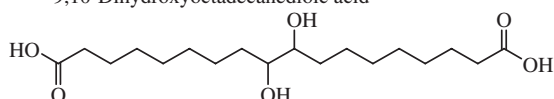
Fatty acids
Octadecanoic acid
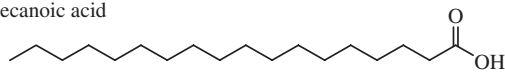
9,10-Epoxioctadecanoic acid
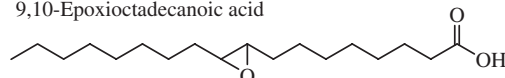
9,10-Dihydroxyoctadecanoic acid
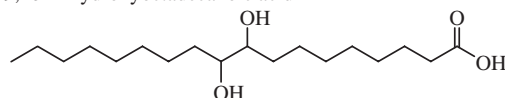
Figure 1.30   The most representative monomers isolated by hydrolyzing suberin.

a marked hydrophobic character. This work is still in progress and the relative merits of the two types of activations are being assessed.

It is important to emphasize that the exploitation of suberin monomers is not done to the detriment of the *noble* parts of cork, since these are extremely useful manifestations of renewable resources. What is used instead are the rejects of cork processing, like powder from stopper manufacturing and irregular morphologies.

1.11
Miscellaneous Monomers

This final section is not intended to cover exhaustively the numerous scattered mentions of the use of different natural monomers, or monomers prepared from natural compounds, in polymerization reactions, mostly because this odd catalog would not reflect the actual potential of these often isolated investigations. The choice was instead placed on a couple of monomers which have received serious attention and produced interesting materials.

Citric acid (Figure 1.31) is a low cost commodity produced industrially via fermentation with an annual production of about 7×10^5 tons. Its use in polymer science was concentrated mostly on its role as a chemical modifier and/or plasticizer of starch, but in more recent years citric acid has been employed as a monomer in the synthesis of polyesters, from crosslinked materials for controlled drug release [70], to oligomers with diol mixtures [71], but particularly of biodegradable polyesters for tissue engineering applications [72]. A different approach was recently proposed [73], in which citric acid was introduced in a polyesterification system with the purpose of enhancing its functionality, following a thorough study of model reactions. The specific role of citric acid was to introduce COOH-terminated branching moieties in an isosorbide-based polyester and thereafter favor its crosslinking with various curing agents in view of preparing high-tech coatings [73].

Tartaric acid (Figure 1.32) is an equally widespread and cheap natural product and its use as a monomer has involved a number of groups, particularly that of Muñoz-Guerra. Among the recent studies, the most interesting deal with the synthesis of biodegradable polycarbonates with anhydroalditols [74], optically active hydrophilic aliphatic polyamides [75] capable of associating themselves to produce supramolecular stereocomplexes [76], and polyurethanes with different diisocyanates bearing COOH side groups, which displayed a unique proneness to degrade with water upon incubation under physiological conditions [77].
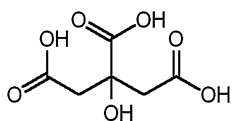

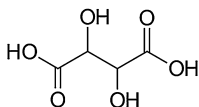
Figure 1.31   Citric acid.

Figure 1.32   Tartaric acid.

Succinic acid, readily available from the fermentation of glucose, is a very prolific molecule that can be usefully exploited in the synthesis of a large spectrum of interesting compounds, including, of course, monomeric structures [78]. Its potential in macromolecular chemistry is awaiting to be intensively exploited.

1.12
Conclusions

Despite the condensed format of this overview, I hope that it manages to convince readers that the interest in monomers from renewable resources is not a passing whim of some polymer chemists led astray by fashionable trends, but, instead, a very sound strategy that should help to shape the future of polymer science and technology. Although obviously not all these studies will reach viable practical realizations in terms of novel macromolecular materials, it is indispensable to build a rich database in preparation for the progressive dwindling of fossil resources, to enable decisions and choices to be made with competence and experience.

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