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Perspective

Polymers from Renewable Resources: A Challenge for the Future of Macromolecular Materials

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ABSTRACT: This perspective article examines the state of the art regarding the field of polymers from renewable resources and attempts to give a critical appraisal of the situation related to a representative number of specific materials, in terms of their interest, present degree of advancement, and prospective development within short- and medium-term projections. The selected examples include polysaccharides and their derivatives, lignin, suberin, vegetable oils, tannins, natural monomers like terpenes, and monomers derived from sugars, with particular emphasis on furan derivatives and lactic acid, bacterial cellulose, and poly(hydroxyalkanoates), ending with a brief assessment of the potential role of glycerol and ethanol as future precursors to monomers.

The Context

The incessant biological activity in living organisms generates a multitude of compounds, including a variety of monomers and polymers. The present essay is exclusively concerned with those renewable structures that can be turned into viable macromolecular materials.[1,2] The equally relevant aspects related to the use of renewable resources to produce a remarkable variety of chemicals (including some interesting monomers) through the implementation of the biorefinery strategy[3] have been recently assessed in a series of comprehensive reviews.[4] The specific area dealing with self-assembled biological soft materials[5] is also gaining relevance but is not dealt with here. Finally, although many of the polymers discussed below are biodegradable, this property is not exclusively associated with materials from renewable resources;[6] hence, its broad area falls outside the purpose of this brief account.

There is nothing particularly novel about the exploitation of renewable resources in this context. Since the inception of human activities, the needs for shelter, clothing, tools, weapons, utensils, and all types of coatings have called upon them, first with a minimum amount of modification and then, progressively, through increasingly elaborate processes aimed at optimizing their specific performance and durability. By the late 19th century, the tanning of leather, papermaking, the conditioning and dyeing of natural fibers, the "mastication" and vulcanization of natural rubber, the use of drying oils in inks, paints, and lacquers, the exploitation of gelatin in photography and other domains, the use of starch and natural resins as adhesives, the chemical modification of cellulose to prepare the first thermoplastic polymers, and the processing of woods for different uses, to quote but some of the most relevant achievements, had reached a high degree of technological sophistication.

However, the relative importance of macromolecular materials based on renewable resources suffered thereafter a gradual setback first with the rapid surge of coal-based chemistry starting from that period and later with the petrochemical revolution of the 20th century. Although certain sectors, like papermaking and the use of drying oils, remained virtually unchallenged; others, like the production of tires and cellulose esters, lost their market primacy, and still others, like the exploitation of natural resins, were relegated to a minimal industrial role. Within a few decades, the realm of polymers prepared from fossil resources literally swamped the world, not only with huge quantities of plastics, elastomers, fibers, adhesives, paints, and packaging materials but also with an astonishing variety of sophisticated macromolecular structures, whose functional role in all aspects of the emerging technologies proved indispensable. There is no point in elaborating further on this all too well-

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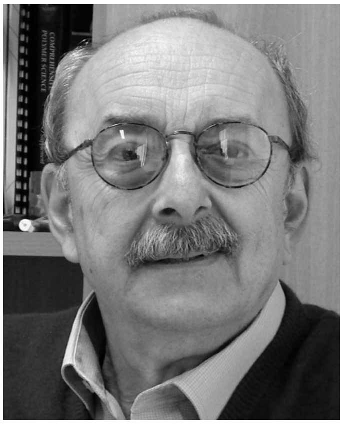

After a first three-year research stint on stereospecific polymerization at Battelle Memorial Insitute (Geneva), Alessandro Gandini moved to Keele University (UK), where he received a PhD (cationic polymerization) in 1965. He then did research and teaching at NRCC, Ottawa, Canada (gas-phase photochemistry and photophysics), the Brookhaven National Laboratory, USA (gas-phase kinetics), Havana University, Cuba (polymer from renewable resources and cationic polymerization), again NRCC Ottawa (UV photochemistry and IR-laser multiphoton isotope enrichment), Grenoble Polytechnic Institute, France (a variety of the above topics plus studies on polymer surfaces and interfaces and on polymer composites), and São Paulo University at São Carlos, Brazil (novel materials from polysaccharides), before landing in Portugal (Aveiro University) 40 years later. His present professional interests are polymers from renewable resources, photochemistry, and the properties of macromolecular surfaces and interfaces.

known picture that characterized the end of the millennium and that holds sway still today.

The reasons why this state of affairs is being challenged with a growing vitality are also extremely well-known, since moreover they are essentially the same as those that underlie the present energy debate. Only their essential aspects will therefore be recalled here, namely (i) fossil resources, particularly petrol and natural gas, are likely to start dwindling within one or two generations, (ii) the price of petrol is skyrocketing and there are no indications that it will return to a small fraction of its present value within any foreseeable lapse of time, (iii) the sense of urgency related to sustainability has finally reached governments' and industries' awareness, and (iv) what was a few years ago the *concept* of a biomass refinery is rapidly becoming a *paradigm*, with sound realizations being implemented throughout the world.

It follows that the challenge is not on the actual macromolecular materials that surround us today, for nothing is really wrong with them per se, but rather on their precursors. Indeed, their lack of renewability on a reasonable time scale and prices which are likely to increase considerably soon make them more questionable with every passing day. Hence, the growing shift of interest to renewable resources (just as with the energy issue[7]) has reached impressive proportions in terms of the number of scientific publications, monographs, books, international symposia, patents, and industrial as well as public investments, although with a still modest output of concrete realizations. It is clear in fact that this upsurge of motivation is not accompanied by the massive financial backing that would translate into a research and development boom, similar to what happened to polymer science and technology in the aftermath of World War II. The story of polypropylene stands out in this comparison, with the extremely rapid growth from its birth in the laboratory to industrial production.[8]

Optimism is de rigueur here, but this should not obscure the fact that the overenthusiastic statements appearing in some recent reviews and other media should blur the real picture, which I consider less rosy, being made up of obviously promising aspects mixed with some wishful thinking. Having worked in this field for several decades, published one of its very first reviews in the early 1990s,[9] and having just coedited what I hope is a comprehensive treatise on it,[1] I wish to put forward a middle-term perspective, insisting on my hope that polymers from renewable resources are indeed the macromolecular materials of the future, but also trying to examine the issues at stake with detachment. Because of the nature of this essay, its coverage will be far from comprehensive, being instead focused on the general realm illustrated by examples, many from recent work the author conducted with many valuable collaborators in Grenoble, France, São Carlos, Brazil, and Aveiro, Portugal where a University–Industry platform was recently set up to investigate novel materials derived from renewable resources. For the reader interested in specific aspects, the book mentioned above[1] provides a thorough coverage of the whole area up to 2007, with a rich set of references.

Natural Polymers and Their Modification

Darwinian selection within vegetable and animal species has given rise to the evolution of a vast array of polymer architectures bearing a great deal of structural sophistication and site-specific chemical moieties. As mentioned above, some of these natural polymers have a very long history of exploitation without major modifications, cellulose being the prime example along with paper and cotton, a history that also applies to more complex macromolecular assemblies like wood, cork, and leather. This section is devoted to a short excursion into the realm of the chemical modification of macromolecular renewable resources, arranged as a function of their basic structures.

Polysaccharides

Unmodified Polymers. Cellulose,[10] chitin,[11] and starch[12] (Figure 1), three heavyweights among natural polymers by their shear abundance and importance, display very different properties, including crystallinity, solubility, and aptitude to chemical modification, and hence quite different applications as macromolecular materials, despite the fact that their basic building blocks are not that different. The different modes of supramolecular assemblies operating with these polysaccharides are influenced by their specific macromolecular architecture, and the ensuing natural morphologies are in the form of fibers for cellulose, films for chitosan, and granules for starch.

To these major representatives, it is essential to add the numerous hemicelluloses,[13] whose resemblance to cellulose is only nominal, since they bear individual structural features (often bearing different glycoside units in their macromolecule as well as branched architectures), which are each associated with specific properties and hence diverse applications, e.g., as films and coatings,[14] polyelectrolytes,[15] food emulsifiers or rheology modifiers, as well as drugs. Although no major *qualitative* breakthrough is likely to occur from materials from hemicelluloses, given the very extensive fundamental and applied research that has been devoted to them, their widespread usefulness as food and medicinal aids is a guarantee of future *quantitative* developments as "green" polymers.

The nanopandemic has also reached the realm of polysaccharides! Cellulose "whiskers" from tunicate, a marine animal also known as sea squirt, are near-perfect cellulose monocrystals, some 15 nm in diameter and ~1 μm long. Additionally, "microfibrils" with diameters ranging from 2 to 10 nm and lengths reaching several micrometers can be isolated from native vegetable cellulose fibers through a combination of chemical

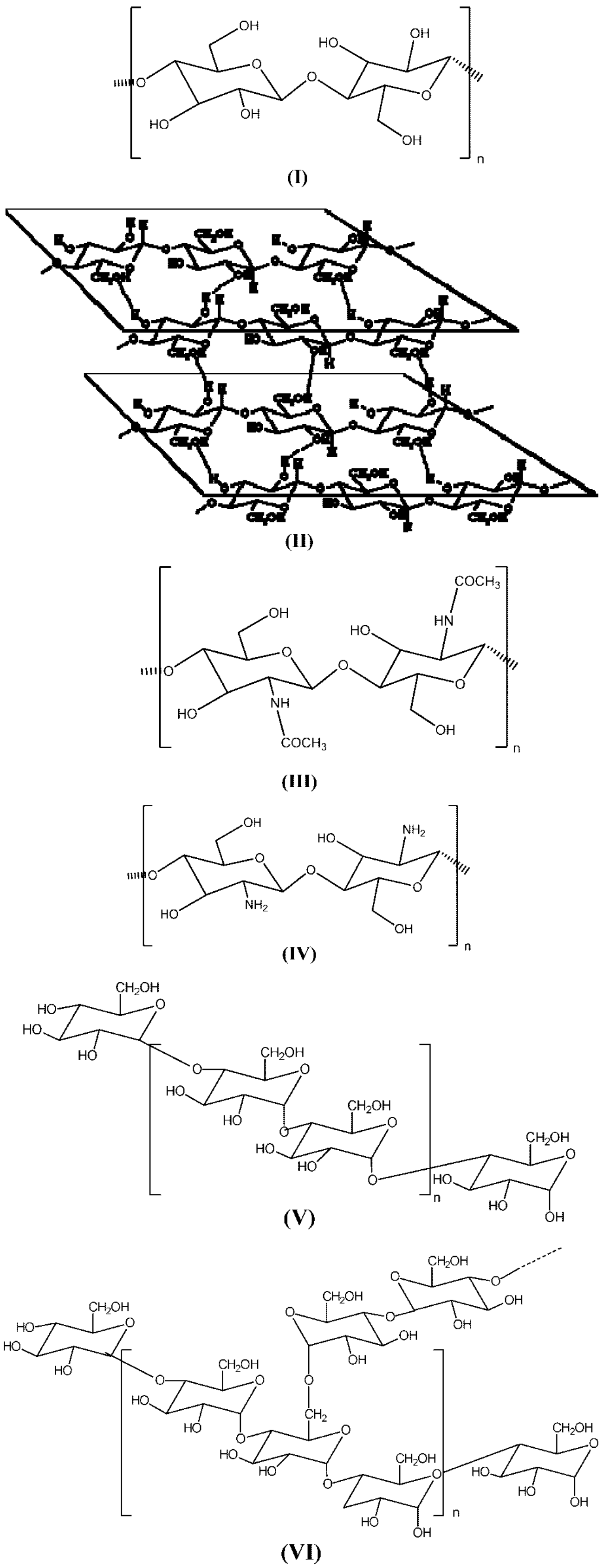

Figure 1. The most abundant polysaccharides in nature: (I) cellulose polymer unit and (II) the inter- and intramolecular hydrogen bondings in its supramolecular assembly; (III) chitin polymer unit and (IV) the predominant unit of chitosan, its fundamental derivative; the two constituents of starches, amylose (V) and amylopectin (VI).

and mechanical means. Their mechanical properties, with a Young's modulus of ~140 GPa, i.e., close to that of Kevlar, make them ideally suited as reinforcing elements in composite materials.[16] They have also been used for manufacturing extremely tough nanopaper,[17] whose tensile strength reaches 214 MPa, viz., the double of the previous record value. Another interesting feature of these nanoobjects is the strong viscosity enhancement they induce when they are suspended in water, even at very low concentrations. Similar nanofibers can be isolated from chitin, whereas the nanoconstitutive building blocks of starch are nanoplatelets some 5 nm thick and a few tens of nanometers for the *x* and *y* directions. Their role in the elaboration of novel composite materials is being actively investigated.

Whereas it seems far-fetched to envisage harvesting cellulose whiskers from tunicates for any large-scale application, the various extraction processes aimed at isolating the polysaccharide nanoparticles from vegetables (cellulose nanofibers from wood and annual plants) and animals (chitin whiskers from the exoskeletons of crustaceans) available in huge quantities at modest prices can become viable technologies in the near future, provided economical solutions are found for their scale-up. This perspective fits most adequately within the broader context of the explosion of the nanosciences and nanotechnologies.

Studies of ultrathin cellulose films constitute another active domain of the nanoworld in which fundamental investigations mingle with more applied features, as recently reviewed.[18]

Another field in which a polysaccharide has become a subject of much research has to do with the family of materials called thermoplastic starch (TPS).[12,19] Their preparation involves the mechanical disruption of the natural granules in the presence of one or more plasticizers, e.g., a mixture of water and glycerol. The interest in this type of plastic stems from a number of elementary considerations, notably the availability of a cheap and abundant renewable resource, its biodegradability, and the relative ease of processing with equipment normally used with conventional thermoplastics. There is however a major drawback associated with the excessive hydrophilicity of starch, which is not reduced appreciably by the common polyol-type plasticizers, since both the dimensional stability and the mechanical properties of TPS are jeopardized in damp environments, not to speak of liquid water. Some applications are indeed possible despite these shortcomings, as in the case of self-destroying wrappings of dishwasher detergent cubes and trays for chocolate boxes, but of course the need to solve or minimize this drawback remains a top priority. Interesting solutions can come from (i) blending the TPS with a hydrophobic polymer, which can itself be a renewable resource, as in the case of natural rubber, (ii) adding appropriate fillers, including nanoparticles, or (iii) chemically modifying the surface of the TPS processed object to render it hydrophobic (see below).

The bulk chemical modification of starch does not fall within these aims, simply because it gives rise to materials with radically different properties, as in the case of cellulose and cellulose acetate. TPS-like materials are already commercially available, but it seems certain that much will be done in the coming years to widen their scope, and not only in the direction of improved hydrophobicity, whose privileged areas of application appear to be packaging and disposable plastics. The research dealing with finding new and better plasticizers is certainly one of the most important aspects related to improve the performance of TPS.[20] Numerous laboratories have tackled the effect of a series of nonvolatile plasticizers, such as glycerol, urea, fructose, xylitol, sorbitol, maltitol, glycols (EG, TEG, PG, PEG), ethanolamine, and formamide. Several criteria concerning the most appropriate structures for this key role have been put forward, although a rough first principle simply predicts, as one would expect, that any substance capable of forming hydrogen bonds would be able to plasticize starch.

Another very active area of starch exploitation is the processing of foamed materials for loose-fill packaging, in which a maximum amount of the renewable polymer is mixed with synthetic counterparts like poly(styrene).[21]

Chitin's future as a material is strongly limited by its intractable character, for it is infusible and sparingly soluble only in some rather exotic media. Given that chitosan[11] is on the contrary readily soluble in mildly acidic aqueous solutions and that it is also much more apt to be chemically modified, it is only too natural that the attention should have been focused much more extensively on this fundamental chitin derivative rather than on its precursor. These aspects are briefly discussed below.

Chemical Modification. The ubiquitous hydroxyl groups in polysaccharides are the most obvious source of chemical modification that has been exploited for over a century, principally in the preparation of cellulose esters and ethers, but also in more subtle alterations, e.g., in order to tune the structure of hemicelluloses for specific applications. These processes, whose optimization in terms of yields and economy is regularly reassessed, constitute a strong basic contribution to the field of polymers from renewable resources, and there is no reason to doubt that they will maintain their important role in the decades to come. What is certainly more relevant here is the fact that a whole host of novel materials based on polysaccharides is being intensely sought, both through bulk and surface modifications.

Bulk Modification. The very extensive research on cellulose derivatives has achieved a high degree of sophistication and a huge horizontal coverage, so that it is not too exaggerated to assert that virtually any moiety has been appended on its backbone.[11,22] This state of affairs is obviously not accompanied by a corresponding flood of materials, for the interest in these modifications stems more frequently from issues related to the need of synthetic intermediates or applications other than as polymeric materials, although some of the ensuing macromolecular structures have found highly useful roles as bioactive products, e.g., for the controlled release of drugs.

The same considerations apply to starch and the multitude of its derivatives;[12,23] i.e., there is little evidence that any of them will be converted into an important macromolecular material.

In contrast to the two latter situations, the chemical modification of chitin to produce chitosan[11] represents a fundamental process within the scope of this essay, since chitosan is one of the most promising materials derived from renewable resources. The interest in these polysaccharides as materials is relatively recent, compared with the age-old exploitation of cellulose and starch. The insolubility of chitin in most common solvents is the principal reason for this delayed attention, despite its abundance in both the animal and fungal kingdoms, and it was only when its transformation into chitosan received close scrutiny that these precious renewable resources began to show their remarkable potentials. This chemical modification is in fact particularly simple, since it just involves the hydrolysis of an amide moiety to generate the corresponding primary amino function (Figure 1-IV). As in all polymer modifications, the ideal 100% conversion is very hard to achieve, and chitosans are therefore a whole family of polymers, characterized by their average molecular weight and their degree of deacetylation, i.e., the percentage of amide groups converted into NH_2 counterparts.

Chitosan can readily be spun into fibers, cast into films, or precipitated in a variety of micromorphologies from its acidic aqueous solutions. The major applications of chitosan are in biomaterials, pharmaceuticals, cosmetics, metal ion sequestration, agriculture, and foodstuff treatment (flocculation, clarification, etc., because of its efficient interaction with other polyelectrolytes).[11] Two basic reasons explain the burgeoning surge of interest in chitosan. On the one hand, its potential applications are far from having been exhaustively assessed, and this includes blends and composites, as well as the processes themselves, like microencapsulation and coextrusion. On the other hand, its chemical modification, through either or both the amino and hydroxyl functions, is also in its infancy (compared for example with what has been done with cellulose) and deserves to be developed in several directions, e.g., water-soluble derivatives, surface active structures, polyelectrolytes with specific charges and charge density, etc.

Recent work in our laboratory has shown that the deposition of chitosan films of different thicknesses on uncoated paper sheets not only improves the optical properties of the ensuing surfaces and their printability but also brings about useful modifications of certain mechanical and permeability properties.[24] The bulk oxypropylation of chitin and chitosan is discussed below within the general context of this process applied to a variety of renewable substrates. Likewise, the preparation of chitosans bearing furan and maleimide moieties is included in the section dealing with the application of the Diels−Alder reaction to thermoreversible polymer systems.

Surface Modification. By far the most actively studied polysaccharide substrates in terms of surface modification are the cellulose fibers in all their diverse morphologies and sizes, and this is mostly explained by the concomitant growing interest in the use of these fibers as reinforcing elements in composite materials with thermoplastic or thermosetting polymeric matrices, in replacement of glass fibers.[16,25] The advantages associated with this substitution include a reduction in density and cost, a lower fiber abrasivity, the ubiquitous availability of lignocellulosic fibers, their renewable connotation, and the fact that the composites can be recycled or burned for energy recovery at the end of their life cycle, operations which cannot be applied to the glass fiber counterparts.

The need for a surface modification of the fibers in this context is primarily connected with the optimization of the fiber/matrix interface in terms of a maximum adhesion, so that the mechanical solicitations (load) applied to the composite through the matrix are properly transferred to the fibers, which can thus provide their reinforcing role. This is particularly necessary with nonpolar matrices like polyethylene because of their obvious incompatibility with the highly polar OH groups sitting on the cellulose fiber surface. A second important reason for the modification has to do with the minimization of the hydrophilic character of the cellulose fibers in order to avoid their loss of strength following moisture absorption.

Given the ineluctable fact that the only moieties which are chemically exploitable are OH groups, the corresponding grafting processes must call upon the typical condensation reactions associated with them, viz., essentially esterification, etherification, and formation of urethanes.[25] All of them have received much attention, including the use of siloxanes, for which the actual condensation *only* takes place at high temperature between the surface cellulose C−OH group and the Si−OH function formed by the partial hydrolysis and subsequent oligomerization of the siloxane.[26] Silylation is more straightforward[27] and has also been applied to cellulose microfibrils.[28]

Interestingly, alkylaluminum and alkylboron compounds have also been successfully tested in this context.[29] A large selection of inert and reactive moieties has thus been appended onto the fibers using approaches with different degrees of sophistication and experimental complexity.

Among the various strategies adopted to satisfy both the requirements discussed above, the ideal solution consists in creating a dense continuity of covalent bonds between the fiber surface and the matrix.[25] This can be achieved by appending specific reactive moieties at the fibers' surface and constructing the matrix around them by a copolymerization involving both its monomer(s) and the appended groups. A typical example consists in reacting the surface of cellulose fibers with an alkenyl isocyanate and thereafter building a matrix from a vinyl monomer, which will copolymerize with the appended alkenyl moieties and thus generate continuous covalent linkages at the fiber/matrix interface.

When the matrix is a condensation polymer, similar tricks can be played by grafting one of its complementary functions onto the fibers, so that it can participate in the chain growth and thus generate covalent bridges at the fiber/matrix interface. Examples of this approach include polyesterifications in the presence of fibers bearing carboxylic anhydride groups and the formation of an epoxy matrix in the presence of fibers bearing NH_2 functions. Simpler procedures have also been shown to give satisfactory results, including the esterification of the fiber surface with a fatty acid,[30] whose long aliphatic chains reduce considerably the polar character of the modified surface and play an adequate compatibilizing role with polyolefin matrices thanks to their structural affinity and chain entanglement by interdiffusion (mechanical adhesion enhancement).

The latter modification has also been exploited in another vein, by carrying it out in polar media (like DMF) which induce some fiber swelling.[31] In this case, the esterification also involves OH groups buried within the amorphous regions of the outer shell of the fibers, thus giving rise to a sleeve of thermoplastic material around the unreacted rigid fiber core. The net result of this operation is that the modified fibers can be hot-pressed into a continuous sheet, which is in fact a composite material in which cellulose is the precursor of both the matrix and the reinforcement. A similar approach has been applied to the oxypropylation of the fibers, as discussed later.

Recent interest in surface modification has extended its purpose to satisfy other material properties and applications. One of these concerns hyperhydrophobicity, and we have been engaged in this challenge for a few years now using two differing approaches, namely the introduction of either highly labile moieties or much more stable ones, but still removable. The choice fell upon perfluoro moieties which were grafted onto the fiber surface by esterification reactions using trifluoroacetic anhydride and the chlorides of 3,3,3-trifluoropropionic (TFP) and pentafluorobenzoic (PFB) acids (Figure 2).[32]

In all instances, the surfaces acquired not only a highly hydrophobic character (water contact angles of ~120°) but also a similar lipophobic property, with diiodomethane contact angles of ~100°. Because of the well-known hydrolytic susceptibility of trifluoroacetates, suspending and stirring the correspondingly modified fibers in neutral water resulted in a rapid loss of trifluoroacetic acid (TFA), with the accompanying restoration of the normal hydrophilic properties of the cellulosic surface within a day at room temperature. Exposure to variably moist air at room temperature showed that 30% relative humidity did not alter the surface properties in weeks, while 100% produced a significant recovery of surface hydrophilicity within about one week.

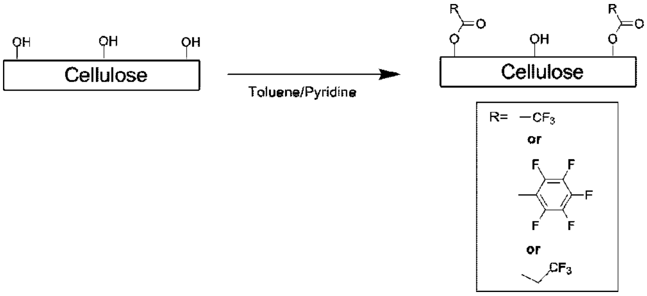

Figure 2. Hydrophobization and lipophobization of cellulose fibers.[32]

Trifluoroacetylation is therefore a good way of preparing hydrophobic and lipophobic papers that must lose these characteristics soon after exposure to water, e.g., in certain packaging or agricultural applications. The fibers modified with TFP and PFB displayed the same surface properties as their TFA counterparts but were stable to hydrolysis with neutral water and only lost their perfluoro moieties when the pH was raised to 9 (slow hydrolysis over weeks) or 12 (fast hydrolysis within days). The applications of these materials are hence associated with the need of permanent hydrophobic and lipophobic properties, but the recycling of the cellulose fibers is still possible, through a preliminary aqueous alkaline treatment, which is in fact the very first step in the paper recycling process.

It is well-known that the surface morphology affects the water contact angle and an increase in microroughness is accompanied by hydrophobic properties. In a recent study, we looked at the combined effect of the deposition of silica microparticles and perfluorosiloxanes (PFS) onto the surface of cellulose fibers and confirmed the roughness effect because the water contact angles went from ~120° with the PFS treatment only to nearly 150° when this was preceded by the silica deposition.[33]

All the surface treatments related to cellulose fibers also apply to the corresponding modifications of wood, albeit with appropriately adapted experimental conditions. This is not surprising, given the similar reactivity of hemicelluloses, which bear the same OH groups, and the fact that lignin is also likely to intervene as a reactive substrate through its aliphatic and phenolic counterparts. The bulk and surface chemical modification of wood has been recently discussed in comprehensive monographs.[34]

A very different strategy was also successfully tested which allowed the modification of cellulose fibers to be attained through admicellar polymerization, although strictly speaking this process did not involve the chemical modification of the fibers' surface.[35] In this approach, the fibers were suspended in water, and a cationic surfactant was added in concentrations sufficient to generate admicellar morphologies around the fibers, i.e., essentially a bilayer sleeve of surfactant, but insufficient to give rise to standard micelles in the aqueous medium. Thereafter, a water-insoluble monomer was added to the suspension, again in concentrations not exceeding the amount required to fill the hydrophobic inner core of the admicelles, and its free-radical polymerization carried out by thermal or photochemical initiation. The final material was therefore made up of fibers covered by a thin polymer coat, which could be incorporated into a matrix possessing the same macromolecular structure.

This process had the obvious advantages of (i) a simple procedure, (ii) a green connotation associated with the use of an aqueous medium, (iii) a good interface compatibilization between the fiber and the polymer deposited at their surface thanks to the presence of the surfactant interlayer, and (iv) a wide choice of monomers, particularly vinyl and acrylic homologues, and hence a correspondingly wide choice of matrices. It therefore deserves further investigation as regards the actual processing and testing of the corresponding composites to verify that indeed the fibers, thus modified, are securely adhered to the matrix.

Further work on building admicelles onto cellulose fibers took another turn during our investigations, and now the purpose became the adsorption of organic pollutants from aqueous suspensions, i.e., the use of the modified fibers for sequestering contaminants from industrial effluents. This was successfully achieved with a number of aromatic molecules.[36]

As for the problem of TPS moisture uptake discussed above, we tackled the need to reduce their hydrophilicity by dipping or suspending TPS films, plasticized with different amounts of glycerol, with a number of reagents in solution in order to render their surface more hydrophobic.[37] Given the fact that once again we were dealing with OH groups, the choice of modifiers included isocyanates, oxiranes, and acid chlorides for the reactive moieties and short or long nonpolar structures to implement the actual change in surface polarity. All of them induced a drastic drop in the polar contribution to the surface energy of TPS with a corresponding increase in the water contact angles, which ranged from 80° to 100° (constant with time), compared with an initial value of 25°−30°, rapidly decreasing to 0°, for the pristine substrates. The simple dipping operation proved quite adequate and thus a good candidate for practical applications.

Whereas the bulk modification of chitosan is a highly topical field of research and development,[38] its surface counterpart has spurred little interest until now and has concentrated on appending polar groups like more NH_2 and COOH on the surface and on oxidizing it with an oxygen plasma or by UV/ozone irradiation, mostly to attain materials better adapted to biological compatibility.[39]

Our ongoing work on chitosan in Aveiro[40] also involves surface modification, but rather in the direction of creating hyperhydrophobic properties through the grafting of perfluoro moieties using the same reagents mentioned above for cellulose, but also perfluorooxiranes, more suited to condense with the chitosan primary amino functions.

In the course of these investigations on the surface modification of chitosan as a source of novel macromolecular materials, we were surprised to find that its surface energy, which had been the object of several studies, had been reported to bear values that were exceedingly low for a polysaccharide, particularly in terms of its polar contribution. We looked into this problem in a systematic way[41] and discovered that its origin stemmed from the poor and variable degree of purity of the chitosan samples used in those laboratories. The culprit was in fact the presence of different amounts of waxes, sterols, and fatty derivatives (i.e., residual natural substances left over from the previous processes involving first the isolation of chitin from the animal substrate and then its conversion into chitosan), which, by virtue of their predominantly nonpolar structures, tended to migrate to the surface of the chitosan films and mask its polar macromolecules. A thorough purification put the record straight with γ_s^d and γ_s^p values close to 30 mJ m^{-2}, viz., similar to those of cellulose, starch, and chitin. In a brief mention of the surface graft polymerization of chitosan with methyl acrylate and styrene,[42] the authors of this wider study reported exceedingly high contact angles with water, measured before the modifications, but did not comment on the anomaly, which suggests that the chitosan surface was contaminated with the type of impurities discussed above.

This is not a trivial matter because polymers isolated from natural substrates are always likely to contain impurities associated with other components, whose structures can be very different from their own, as in the typical case of lignocellulosic fibers isolated from wood or in the less well documented instance of inadequately purified gelatin, which displays a very low apparent surface energy, incompatible with its highly polar structure, because of the migration of even minute proportions of lipids toward the substrate−air interface.

Lignin. Lignin,[43−45] the second major component of wood and annual plants, is a highly branched and irregular macromolecule, whose structure varies with the vegetable species, although its basic building blocks can be schematically simplified into "C9" units made up of a phenolic moiety bearing three aliphatic carbons. The aromatic components are moreover differently substituted by methoxy groups, whereas the aliphatic portions are characterized by the variable presence of C═C unsaturations, OH functions, and other less frequent substituents.[43] Figure 3 shows a hypothetical lignin structure purporting to illustrate how this cross-linked natural polymer exists in situ and to emphasize its glaring irregularity, compared with the repetition of identical glycoside units found in linear cellulose and chitin and in both the linear and the branched macromolecular components of starch. In lignocellulosic renewable materials, lignin plays the role of the matrix which surrounds the reinforcing elements made up of cellulose fibers.

Given its unattractive structure, the interest in lignin as a possible source of macromolecular materials does not arise from a strange desire to isolate it and valorize it, but simply from the fact that its fragments are available in enormous quantities, albeit in different molecular weights and specific structures, as a result of the chemical processes associated with the production of cellulose pulp for papermaking.[44] In most of today's pulping technologies that cleave the native lignin into soluble fragments to separate it from the fibers, the most rational use is to produce energy from the combustion of these fragments and to recover the pulping catalysts at the same time. Considering the colossal amounts of biomass involved in this industry, the isolation of a modest proportion of these lignin oligomers for other utilizations is however perfectly sound. This concept simulates the corresponding situation associated with the small percentage of petrol exploited in the chemical industry, compared with its predominant use as a source of energy. Additionally, some novel technologies based on the biomass refinery imply a more economic energy approach and do not require the recovery of catalysts through combustion,[44] hence justifying the interest in seeking ways to exploit these cheap lignin oligomers in the elaboration of novel macromolecular materials.

Their incorporation into other polymers in the form of blend partners or simply fillers[44] has been investigated for decades, but these efforts have not been translated into any sizable industrial activity, most probably because of the limited advantages obtained in terms of gains in specific properties, coupled with the indispensable, but difficult, issue of ensuring raw materials with reproducible characteristics from one batch to another. This appears to be more a lack of readiness and coordination among potential industrial partners than a real problem because a given pulping mill can indeed provide a lignin with constant characteristics, if required. An example of a tangible improvement in properties achieved with different lignins is illustrated by a study we conducted in Grenoble on

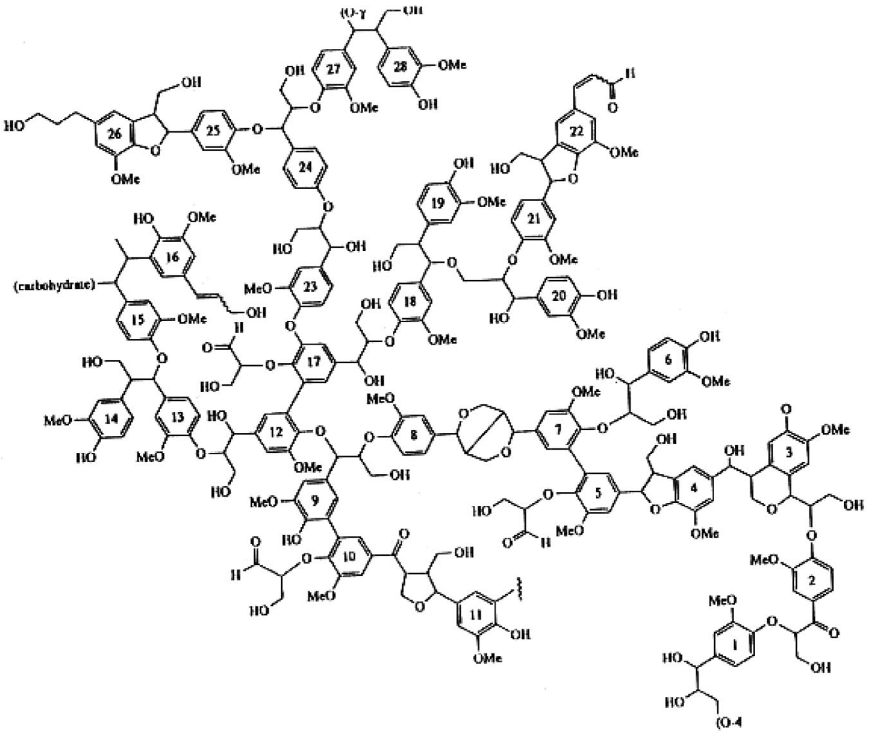

Figure 3. Lignin main moieties in a hypothetical *native* structure.

their inclusion in printing inks and paint vehicles,[46] which showed a drastic reduction in misting, without any accompanying detrimental effects to their other functional parameters.

Lignin has been shown to be a very effective stabilizer against the photooxidative degradation of common polymers like polyolefins,[45] a role which justifies its use to replace more expensive synthetic additives, provided the brown coloration it imparts to these blends does not affect their applications.

The use of lignin fragments as such, or after suitable chemical modifications, as macromonomers has also been extensively investigated through the implication of both their phenolic and aliphatic hydroxyl groups to prepare polyesters and polyurethanes.[45] To the best of my knowledge, none of these polymers have reached a sizable commercial stage, despite their viable properties. As for this disappointing situation, the reasons evoked in the previous paragraph most likely apply here, too.

The one specific category of lignins which have found numerous utilizations in agriculture, drilling wells, animal feed, etc., because of their polyelectrolyte properties are the lignosulfonates produced in the sulfite pulping mills.[44] Their scope will undoubtedly widen as a result of continuing fundamental and applied research aimed at refining the knowledge of their properties and studying novel modifications.

Because of their high contents of aromatic moieties, lignins have also been exploited to prepare carbonaceous materials with interesting results in various forms of activated carbons[45,47] as well as in the preparation of carbon fibers from blends with poly(ethylene oxide).[45,48] Obviously here, the problems of structural irreproducibility vanish by definition, and this realm has, to my mind, a very promising potential industrial development.

Another way to circumvent the problem of compositional variations in lignins and produce potentially attractive polymer precursors consists in their radical transformation into polyether–polyols by oxypropylation, as discussed below.

A different and interesting approach to the exploitation of lignins is their conversion into mixtures of monoaromatic monomers, i.e., to splice them down chemically or enzymatically to their fundamental units.[45] These can be made to bear either C=C unsaturations, and hence be polymerized or copolymerized by chain reactions, or typical polycondensation functional groups for the synthesis of aromatic polyesters, polyethers, polyurethanes, etc. In both instances, the aromatic character of the ensuing polymers would be the key feature, associated with good thermal and mechanical properties and possible liquid crystal connotations.

Recent fundamental studies on the physicochemical features of lignin monolayers deposited on different substrates[49] constitute a valuable contribution to the basic understanding of the role of its diverse moieties in interactions among themselves or with other structures and hence to the more rational and better control of supramolecular materials.

Suberin. Suberin is an almost ubiquitous component of the outer bark cell walls of higher plants, representing typically 20–50% of extractive-free outer bark weight, but is also present in some of their other organs like the roots.[50] This biopolymer is particularly abundant in the very thick bark of cork oak (up to 50%), a species native to the Mediterranean region. This natural aliphatic–aromatic cross-linked polymer plays the fundamental role of a hydrophobic barrier protecting the plant from biological attacks and at the same time preserving its moisture content.

The structure of this macromolecule has been thoroughly investigated, and Figure 4 provides a schematic view of its pristine features. If, on the one hand, the aromatic domains of suberin evoke roughly the structure of lignins, the predominant aliphatic counterparts are, on the other hand, unique with their long nonpolar chains terminated by functional groups.

For a polymer chemist, these structures are particularly interesting, and their isolation by ester cleavage has provided a detailed map of their specific abundance in terms of chain length and nature, number, and position of their polar groups. Figure 5 shows the most significant fragments isolated from the suberin

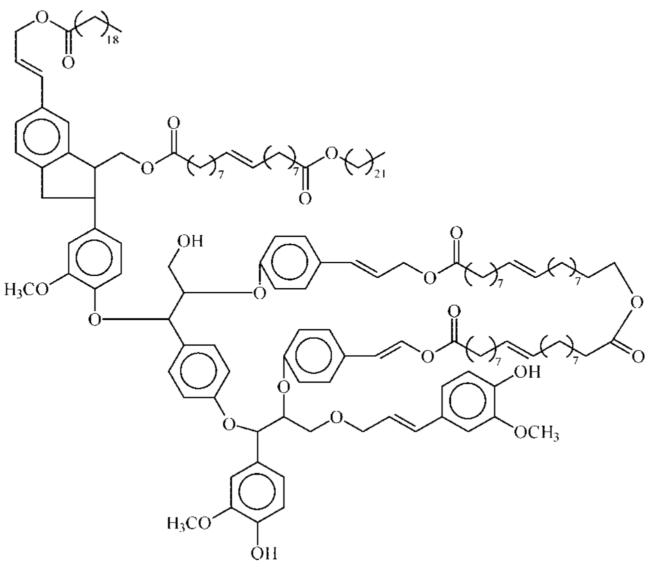

Figure 4. A partial view of the structure of suberin.

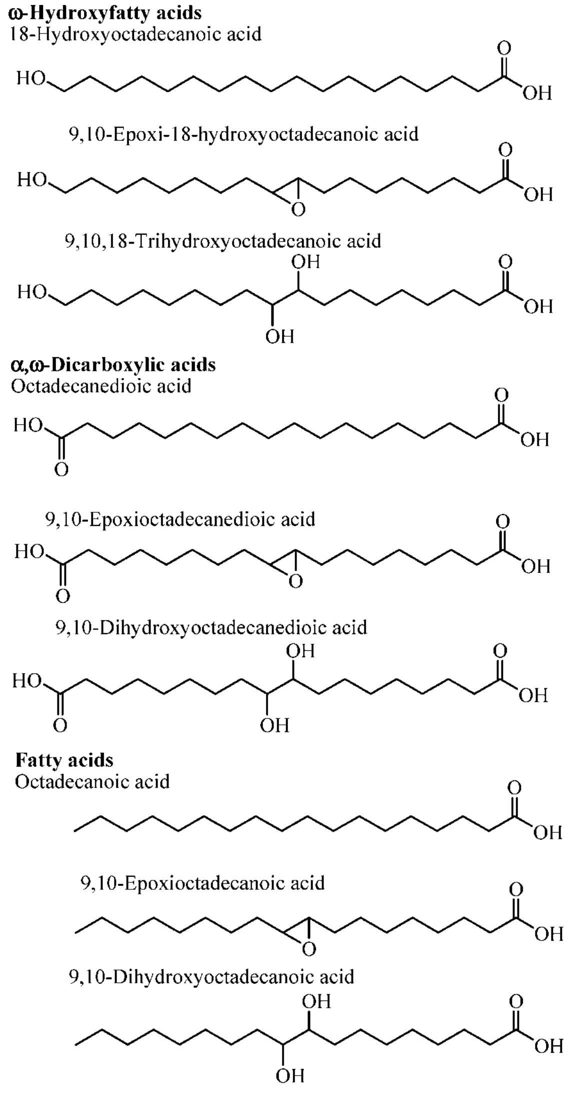

Figure 5. Structure of the most abundant monomeric components isolated from the hydrolysis of suberin.

of cork oak, which are accompanied by numerous homologues. All of them are in fact potential monomers for the synthesis of polyesters with interesting hydrophobic and biodegradable properties.

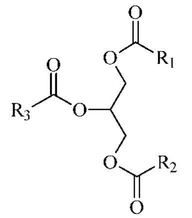

Figure 6. The basic structure of natural triglycerides, where R_1, R_2, and R_3 are fatty acid aliphatic chains, often, but not always, identical.

Our recent study of the polycondensation of these macromonomers, as obtained from the hydrolysis and methanolysis of cork suberin,[51] using various catalytic systems, indicated that low-T_g semicrystalline polyesters are readily obtained and that, not surprisingly, their films displayed a marked hydrophobic character with water contact angles of ~100°. Given the fact that the carboxylic groups exceeded the OH counterparts in these mixtures, better results in terms of yields and molecular weights were obtained when their polycondensation was conducted in the presence of a stoichiometrically added diol. Work is in progress to assess the biodegradability of these novel polyesters from renewable resources.

Natural Macromonomers: Their Modification and Polymerization

Oligomers such as tannins and triglyceride macromonomers are very abundant in the vegetable realm, and research aimed at their valorization as a source of polymeric materials is gaining momentum, particularly with the latter, more varied, compounds, but not excluding some notable novel applications of tannins.

Vegetable Oils. The traditional uses of vegetable oils (triglycerides bearing a large variety of fatty acid moieties, see Figure 6) in paints and inks, both as macromonomers in the preparation of alkyd resins and as natural diluents, represent standard industrial practices, which only undergo periodical upgrading of minor chemical or polymer relevance. The same goes for the mechanism of their oxido-polymerization ("siccativity") associated with the interaction of the unsaturations borne by their aliphatic chains with atmospheric oxygen.

The more stimulating facet of this field is the search for new applications of vegetable oils, based on their preliminary chemical modifications aimed at enhancing their specific reactivity in a given type of polymerization process.[52]

Two distinct sites in triglycerides are available to chemical modification, namely (i) the ubiquitous ester moieties, which can be readily hydrolyzed or transesterfied and then, if required, submitted to further transformations and (ii) the possible presence of one or several reactive functions along the aliphatic chains, the most frequent of which are C=C unsaturations and OH groups.

The exploitation of the first approach usually produces the single aliphatic strands with a terminal reactive site, unless incomplete modification is preferred, in which case one or two OH groups are generated on the glyceric residue. Of course, these processes resemble closely those associated with the production of "biodiesel", but here the pressing need is to achieve original structures capable of responding adequately to polymerization stimuli.

The second approach is much more versatile in that the unsaturations and/or the OH groups are open to a wide variety

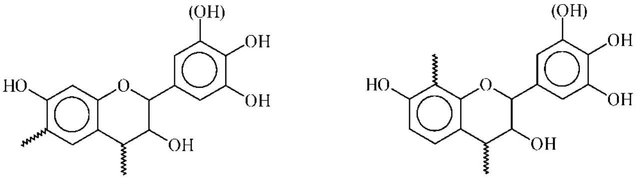

Figure 7. Two typical monomer units found in tannins.

of rather straightforward modifications, e.g., oxidation to oxiranes, but ultimately most of them converge onto the formation of hydroxyls, which can be exploited as such or turned into other reactive moieties, such as polymerizable acrylic or styrenic functions. The most advanced R&D efforts in this context, which in fact have already attained industrial status, like Cargill BiOH based on soybean oil (whose triglycerides contain an average of about five unsaturations per molecule), are related to the preparation of polyols for polyurethane production, in substitution for the petroleum-based polyether-based polyols currently employed.

A recent investigation in Grenoble[53] concentrated on appending acrylic moieties onto epoxidized soybean oil and attained average degrees of substitutions (DS) as high as eight groups per triglyceride. Already with a DS of about 5, these modified oils displayed an excellent photoreactivity in the presence of conventional photoinitiators, suggesting that they can replace adequately the petroleum-based acrylic varnishes currently utilized in fast UV-coating processes.

Important recent contributions in this area include the work at Domb's laboratory on biodegradable polymers based on fatty acids[54] and the use of vegetable oils as precursors for the preparation of polyurethanes.[55]

There is little doubt that the use of vegetable oils as a source of original polymers will increase progressively in the near future both in quantity and in the variety of novel macromonomers, and this will not constitute a problem with respect to changes in the global agricultural strategy because, contrary to what is being perceived with the much more massive biofuel domain, the needs of raw materials will always be very modest relative to the essential food and feed requirements.

Tannins. Tannins are natural phenolic structures present in numerous wood species particularly in the southern hemisphere.[56] They are mostly located in their barks, although, in some instances, they are found in the wood itself. Their traditional use in leather manufacturing has been extended to other applications of which the only relevant example in the present context is the formulation of adhesives and more specifically wood adhesives, a domain which is steadily gaining importance because of its ecological relevance. Tannins are oligomeric compounds characterized by sequences of units bearing two or more OH groups per aromatic moiety as exemplified by the polyflavonoid structures whose monomer units are shown in Figure 7, with DPs varying considerably (from 2 to 30) from species to species.

Extensive research, particularly by Pizzi and co-workers,[56,57] has optimized formulations for wood adhesives in which tannins, together with appropriate cross-linking agents, provide materials displaying properties comparable to those of conventional phenol− and urea−formaldehyde counterparts. These original glues represent two major steps forward in the very important wood processing industry (particle boards, etc.) because they minimize formalderhyde emissions, thus solving a serious ecological problem associated with the use of conventional wood adhesives indoors, while calling upon the exploitation of a readily available renewable resource.

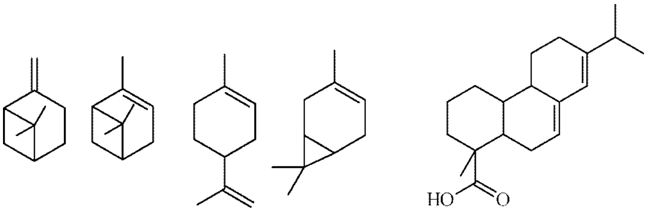

Figure 8. Four common polymerizable terpenes (from left to right: β-pinene, α-pinene, limonene, and 3-carene) and abietic acid.

These ongoing studies have been recently enriched by novel formulations in which starch is also incorporated[58] with promising results and hence the surge of a novel family of adhesives in which two widespread natural resources are the fundamental ingredients. Given the worldwide massive requirements related to wood adhesives, the progressive replacement of the traditional resins by those incorporating tannins, and perhaps also starch, seems a realistic and welcome feature of the near future.

Natural Monomers: Their Modification and Polymerization

Nature produces a number of monomers which have been a long-time source of useful "resins". Terpenes[59] (Figure 8) and rosin[60] (a mixture of unsaturated polycyclic carboxylic acids, of which abietic acid is the major representative; see Figure 8) dominate this sector, but despite recent research aimed at a better control of their polymerization, particularly with terpenes, it is unlikely that in the short term these initiatives will see any major changes in either the quality of the ensuing materials or a significant increase in their production.

The use of sugars as monomers represents an interesting challenge which is being pursued in very elegant and thorough investigations.[61] Whereas the application of some of these polymers in specialized niches, e.g., as biomaterials, seems acquired, their wider spreading into more conventional domains is debatable, mostly because of economic constraints related to the exotic character of both the monomers and their polymerization processes.

Sugars, as well as their natural oligomers and polymers, also play a fundamental role as precursors to other monomers, namely furan derivatives and lactic acid.

Furans. The hemicellulose dominant in virtually all lignocellulosic structures associated with annual plants, and some of their products, is xylan, i.e., a polysaccharide based on C5 glycosidic units. The acid-catalyzed depolymerization and dehydration of these residues of agricultural or forestry activities, available ubiquitously, albeit from different species (sugar cane bagasse, corn cobs, rice hulls, etc.), to produce furfural has been an industrial process for nearly a century and has reached a yearly worldwide output of ∼300 000 tons. Some 85% of this chemical commodity, whose market price is currently around $1 per kilogram, is converted into furfuryl alcohol, a precursor to different types of resins and carbonaceous materials.[62] Furan-based fine chemicals and synthons for pharmaceuticals and other high-added value molecules represent the second most important outlet of furfural.

C6 sugars and polysaccharides can be converted into hydroxymethylfurfural following the same type of process as for furfural, and its industrial implementation will be a reality very soon, following major recent progress in its optimization.[63]

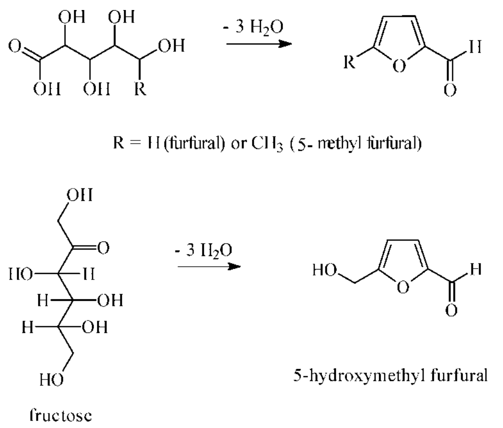

Figure 9. Conversion of C5 and C6 sugars into the two basic furan monomer precursors.

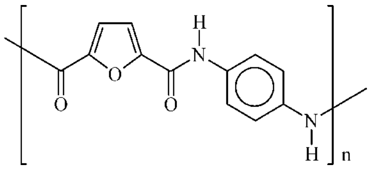

Figure 10. Furan−aromatic polyamide simulating the Kevlar structure and properties.[64]

These two first-generation furan derivatives (Figure 9), obtained directly from renewable resources, represent the starting points of an ambitious strategy[64] that consists of (i) exploring their conversion into polymerizable structures, i.e., monomers for chain and step reactions simulating the well-known petroleum-derived aliphatic and aromatic counterparts, (ii) studying those polymerization processes and establishing their similarities and differences with respect to standard systems, and (iii) characterizing the structure and properties of the ensuing furan polymers and copolymers and assessing their interest, viability, and/or competitiveness as macromolecular materials.

This survey was conducted in a comprehensive fashion over the past few decades, and criteria concerning "good" and "bad" candidates were established.[64] Some of these polymers do represent promising, and sometimes better, alternatives to existing fossil-based materials, like, not exhaustively, (i) the mixed furanic−aromatic polyamide shown in Figure 10, which has properties comparable to those of Kevlar, (ii) polyurethanes with thermoplastic elastomeric properties, coupled with a tendency to graphitize upon pyrolysis, and (iii) the conjugated polymers and oligomers sketched in Figure 11, which display good electronic conductivity when doped, photo- and electroluminescence, and whose dimer, appended on diverse polymer chains, displays an efficient photo-cross-linking aptitude.[64]

More recently, we tackled a very obvious structure, curiously enough neglected over the years, viz., the furan counterpart of poly(ethylene terephthalate), poly(ethylene 2,5-furancarboxylate), and found that it can be readily synthesized in high molecular weights (Figure 12) and that its physical properties are consistent with a wide range of possible applications.[65]

An additional area of polymer science and technology in which furans can provide a substantial contribution is related to the specific chemical properties of this heterocycle. One of them is the propensity and regioselectivity of the 2-substituted furan ring to undergo electrophilic substitution at its C5 position, which was exploited to prepare end-functionalized poly(isobutene) and its block copolymers by cationic polymerization in the presence of a suitable furan derivative.[64]

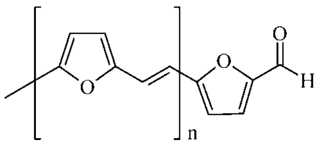

Figure 11. Poly(furylene vinylene).[64]

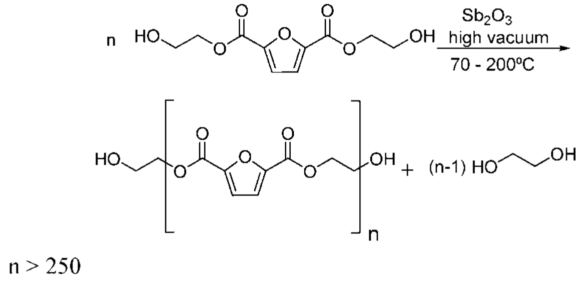

Figure 12. Synthesis of the novel polyester simulating the structure and properties of PET.[65]

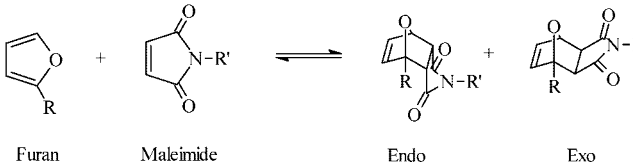

Figure 13. Diels−Alder equilibrium between a monosubstituted furan derivative and an N-substituted maleimide.

Another chemical feature distinguishing the furan structure is its pronounced dienic character, which makes it an ideal partner in Diels−Alder (DA) reactions with dienophiles like maleimides. The DA reaction is a reversible 4 + 2 molecular coupling which generates diastereomeric adducts, as in the example shown in Figure 13.

Typically, the forward reaction dominates up to ~60 °C and the backward decomposition of the adduct becomes preponderant above ~100 °C. The interest here is, on the one hand, the possibility of synthesizing macromolecular structures using complementary monomers bearing more than one reactive moiety and, on the other, to exploit the thermal reversibility of the DA reaction (retro-DA) to induce the controlled depolymerization of those macromolecules.[66] This chemical peculiarity was sporadically applied to polymer synthesis or reticulation up to the end of the past century, when it began to gain impetus both qualitatively, by the different synthetic approaches explored, and quantitatively, by the steadily growing number of studies being published.

A brief survey with examples is in order here to illustrate this situation.[66] Linear macromolecular growth is achieved with either difurans (AA) reacting with bismaleimides (BB) or by using a single monomer molecule incorporating both moieties (AB). Whereas the first type of system has received much attention with respect to polymer synthesis and thermal reversion to the starting monomers, the second, which is more promising because it avoids the problem of functional stoichiometry, was only tackled once in the past[66] with a molecule in which the furan and maleimide moieties were too close to each other. We are presently studying better AB-type monomer structures. Because no kinetic study had been reported on either of these systems, we carried out a preliminary investigation,[67] first with monofunctional model compounds and then with a typical AA + BB linear polymerization (Figure 14), using both ultraviolet

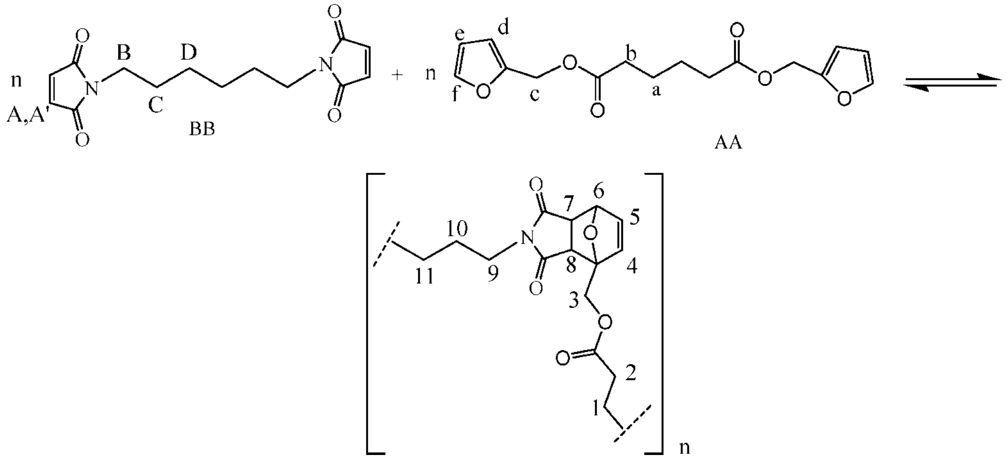

Figure 14. Reversible DA linear polymerization of a bismaleimide with a difuran comonomer.[67]

and ^{1}H NMR spectroscopy. The corresponding retro-DA processes were also followed.

In another vein, the DA/retro-DA strategy has been applied to the synthesis of thermally labile networks and to mendable materials, always using furan/maleimide combinations.[66]

In the first context, various specific solutions were sought, e.g., the use of difunctional molecules as cross-linkers for linear polymers or copolymers bearing the complementary functions as pendant moieties. The return to the starting thermoplastic materials was effectively achieved by heating the networks above 100 °C to promote its progressive retro-DA de-cross-linking and dissolution in a medium containing an excess of the monofunctional DA complement of the cross-linker, so that upon cooling the recovered linear polymer solution, the liberated difunctional cross-linker would couple with the added monofunctional DA reagent instead of reinitiating the network formation. We are presently applying this strategy to prepare thermoreversible chitosan gels by appending either furan or maleimide (or both on different samples) on the linear polysaccharide chains.[40]

The principle of mendable and removable materials calls upon the synthesis of DA-based networks using polyfunctional furan and maleimide monomers. Any fissure or other damage to objects thus prepared can be mended by heating them to promote a local flow induced by the retro-DA adduct openings.[66] Likewise, an adhesive bearing DA adducts in its final macromolecular structure can be readily removed by making it flow at the appropriate retro-DA temperature, which induces the de-cross-linking of the set adhesive.[66] These different approaches to intelligent materials also include the preparation of dendrimers and hyperbranched structures.

Looking at the broader perspective of the role of furans in polymer science and technology in the years to come, it appears that a new chapter has finally opened, which will elevate this domain from the monotonous predominance of furfuryl alcohol resins to a variety of fresh materials from renewable resources, including both those which can potentially replace petroleum-based counterparts and those whose properties are entirely original.

Lactic Acid. One of the outstanding achievements in the realm of polymers from renewable resources is undoubtedly the rapid progress related to the research and development activities for the production of poly(lactic acid) (PLA) or polylactide (Figure 15).[68] This ongoing scenario is too familiar and well documented to require any extensive coverage here, but it is important to emphasize its most important aspect which has to do with the practical relevance of this polymer. PLA has been an industrial commodity with important applications, particularly in packaging and fiber technology, which has reached a global capacity exceeding 250 000 tons per year with a steadily declining price.[69]

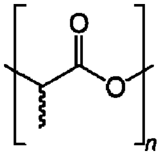

Figure 15. Polylactic acid.

Considering that starch is the precursor for the lactide monomers and that therefore the sources are varied and available virtually everywhere, albeit through the exploitation of different species, PLA represents the very paradigm of the polymer of the future in that it fits perfectly within the biomass refinery concept, within the green chemistry postulates, within the very definition of a polymer from renewable resources, within the biodegradability criteria, and all this accompanied by very adequate mechanical and thermal properties.

Bacterial Polymers

Two very different macromolecular structures, which can be profitably used as polymeric materials, are synthesized by bacteria, namely cellulose[70] and poly(hydroxyalkanoate)s[71] (PHA). For reasons that are not always easy to rationalize and that are not the same for both, neither of these renewable polymers has yet attained a commodity status on the market.

Bacterial Cellulose. At regular intervals for the past two decades, bacterial cellulose has been heralded as the marvel polysaccharide by various specialists, who sung its virtues ("the Rolls-Royce of celluloses"[72]) in such different domains as biomedical applications,[70,73] papermaking,[70] nanocomposites,[70,74] electronic[70] and acoustic devices, and foodstuffs.[70] There is no discussion about its remarkable properties,[70,75] mostly linked to the unique morphology of the fiber bundles generated by the microbes (Figure 16), but what seems to be particularly difficult to achieve is a quantitative upgrading of the corresponding biotechnology and hence the slow progress toward achieving a substantial production and correspondingly lower prices.

As long as this situation remains unresolved, bacterial cellulose will remain elusive because of its poor availability at very steep costs. This translates into a straightforward conclu-

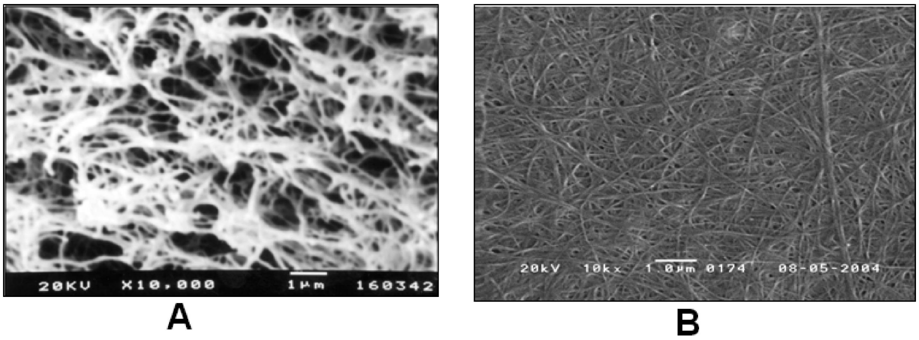

Figure 16. (A) Surface of a membrane of bacterial cellulose prepared by freeze-drying. (B) Surface of a membrane dried in a laboratory oven.

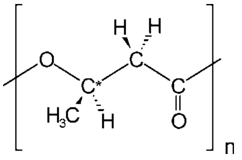

Figure 17. Structure of PHB.

sion: for the time being this very beautiful material is confined to high-tech applications requiring relatively modest quantities. This state of affairs has also brought about an unhealthy mode of operating, whereby the centers producing bacterial cellulose are unwilling to make it available to laboratories that wish to begin research related to its properties and novel materials.

Poly(hydroxyalkanoate)s. Early studies on poly(hydroxybutyrate) (PHB) (Figure 17), which constitutes the homologue "normally" produced by the bacteria, had been confined to its structural characterization and to the reasons why these creatures need to synthesize it.[71] The saga of the PHAs[76] has punctuated the news for some 25 years, indeed since ICI announced the production of a biodegradable polyester by a fermentation process involving the growth of the macromolecules inside the cells of bacteria. Apart from various test trials of packaging and other objects, however, these polymers only reached the market in recent years and in relatively modest outputs, after numerous industrial and commercial ownership changes.

The major reason for this disappointingly slow development is to be found in the uncompetitive price of the various homo- and copolymers which can be readily produced following alternative processes. Considerable progress has been achieved in fine-tuning the properties of the materials through controlled structural modifications, but the corresponding minimization of production costs has not accompanied this trend, despite the high hopes associated with the expected biotechnology revolution. It is therefore difficult for me to assess what the near future promises as regard the impact of these materials on the polymer market.

Oxypropylation of Renewable Polymers

The oxypropylation of natural polymers constitutes a very different approach to the exploitation of the biomass compared with most of the topics discussed above. Cellulose and starch have been modified industrially by this process for years to obtain the corresponding hydroxypropyl derivatives, which find applications as rheology modifiers, food additives, etc. These technologies and the associated materials are well established and thus will not be reviewed or assessed here in terms of bulk transformations but will be examined below in a previously unexplored context based on limiting the transformation to the initial depth of the cellulose fibers and of the starch grains.

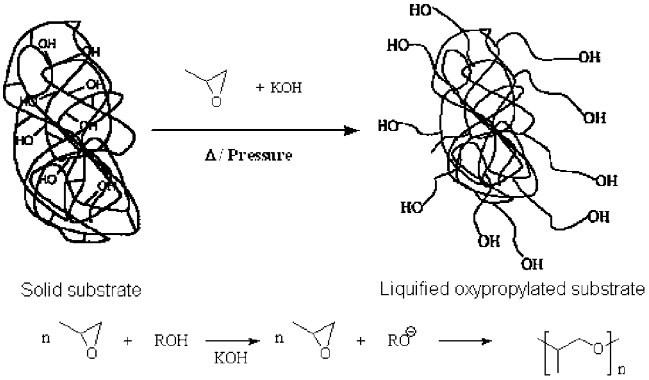

Figure 18. Schematic illustration of the oxypropylation of an OH-bearing polymeric substrate, accompanied by some PO homopolymerization.

What is instead worth some consideration has to do with our ongoing work on the exploitation of nonedible byproduct of various industrial activities related to agriculture, forestry (including papermaking), fishery, and food and beverage production, whose value can be significantly increased by oxypropylation.[77] This strategy started with a comprehensive study of the transformation of sugar beet pulp (an intractable solid mixture of mostly polysaccharides) into a viscous polyol,[78] whose properties made it a suitable macromonomer for the synthesis of polyurethanes and polyesters.

The subsequent extension of this process to other OH-bearing substrates, namely lignins from different pulping technologies,[79] chitin and chitosan residues,[80] cork powder,[81] olive stones,[77] etc., showed its excellent adaptability. In practice, the systematic testing of a very wide variety of biomass residues proved that any renewable resource incorporating hydroxyl groups in its structure can be turned into a polyol in near-quantitative yields, after the appropriate optimization of the reaction parameters, viz., temperature as well as type and amount of basic catalyst. These operations, whose basic mechanism is generalized in Figure 18, are simple and do not require a solvent or a separation process, so that all that goes into the reactor is removed as the desired product at the end. They are therefore good examples of green chemistry processes. The major variable here is the ratio of propylene oxide (PO) to substrate, which governs such polyol properties as its viscosity and OH index, as well as the proportion of PO homopolymer which always accompanies the actual oxypropylated substrate.

The use of these polyols in the replacement of petroleum-based counterparts in typical polyurethane foam formulations gave materials with comparable properties, suggesting that oxypropylation seems a very promising way to give intractable biomass residues, usually burned for energy recovery, a better scope as polymer precursors.

In a totally different vein in terms of the type of material aimed at, we applied the oxypropylation reaction to cellulose fibers using quantities of PO sufficient to attack only their outer sleeve, i.e., to induce an in-depth transformation limited to a modest thickness.[82] This strategy allowed a specific modification to take place, viz., one that created a thermoplastic shell around the fibers, whose core preserved its semicrystalline rigid morphology, so that they could be heat-pressed into continuous sheets made up of an oxypropylated cellulose matrix and unmodified inner fibers as reinforcing elements. In other words, cellulose was the source of both components of the composite.

The same principle was applied to the oxypropylation of the outer shell of pristine (ungelatinized) starch granules,[83] and again the final material morphology consisted of an oxypropylated starch matrix reinforced by the unmodified inner cores of the granules.

The important fact that propylene oxide can be prepared from glycerol (see next section) makes all these processes even more interesting, since both the substrates and the reagent are hence based on renewable resources.

Glycerol- and Alcohol-Based Monomers

The spectacular rise in glycerol production associated with the booming biodiesel industry, and its consequent drop in price down to ~$0.05 per pound, has accelerated very considerably all scientific and technological research aimed at multiplying its uses and new derivatives.[84] Some of them are in fact monomers like diols, diacids, oxiranes, acrylic acid, acrolein, and lactic acid, and this opens a novel perspective of preparing polymers from renewable resources in which well-known structures, traditionally derived from the chemical transformation of fossil resources, become available through the transesterification of triglycerides. DuPont's Sorona poly(trimethylene terephthalate) is among the first industrial materials in which 1,3-propanediol made from glycerol constitutes one of the two starting monomers.

The perspective of the alternative biomass fuel, viz., ethanol from lignocellulosics, also opens novel avenues, since out of the massive quantities envisaged (see the Brazilian version of this strategy) a consequent proportion could be used to produce ethylene, and hence poly(ethylene) would become available from renewable resources. But of course this is for much later!

Conclusion

It is my conviction that there is a pressing need for all parties concerned, whether scientific institutions, industrial R&D sectors, or appropriate government departments, to enhance considerably the implementation of activities aiming at accelerating the development of polymers from renewable resources. Although petroleum, natural gas, and carbon are here to stay for some time to come, it is likely that their price will remain very high and that their reserves will start dwindling within a few decades. It would therefore be particularly wise to prepare the future with a responsible strategy aimed at assessing the potential of both known and novel macromolecular materials through a more systematic and intense research program covering all aspects of their conception, characterization, and possible applications. In other words, what should be done is indeed what was done in the decades of the past century during which petrochemistry, and hence polymer science, witnessed an extraordinary qualitative and quantitative expansion, thanks to a major collective effort, which was made possible by an appropriate financial backing from both the private and the public sectors. I see no reason to doubt that this should not work as well in the case of using renewable resources to prepare polymers because the variety of potential structures is huge and, as in the case of the materials from fossil resources, many of them will prove to be of little interest, but many others will meet the needs of society and will therefore be able to replace gradually their existing counterparts.

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