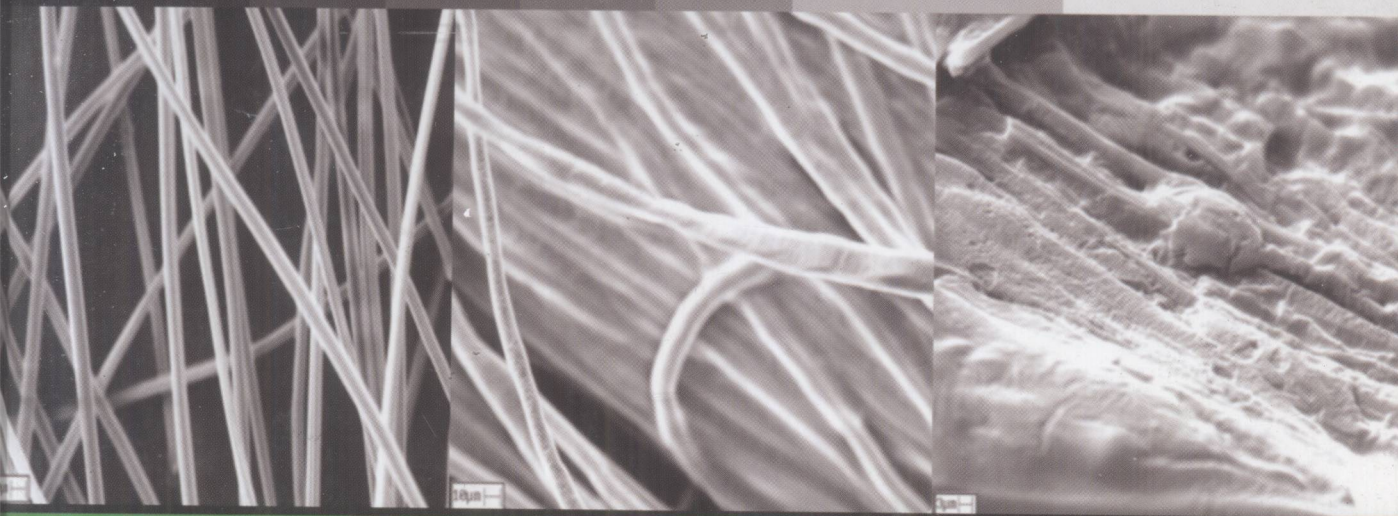


Monomers, Polymers and Composites from Renewable Resources



Edited by
**Mohamed Naceur Belgacem and
Alessandro Gandini**

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Foreword

Expert predictions about the future availability of fossil resources, viz. petrol, natural gas and coal, which are not renewable within a useful time scale, vary between one and three generations. The concern about the geopolitical situation related to these dwindling resources has therefore been increasing steadily in the last decade and has recently reached peak proportions with the apparently unstoppable soaring market prices of petrol.

The primary issue here is obviously energy, considering that more than 90 per cent of these resources are used as fuels, but the fact that the vast majority of organic chemicals and synthetic polymers are derived from them (as a result of the petrochemical 'revolution' of the post-Second World War boom), constitutes an equally serious challenge.

Whereas the energy issue is being vigorously debated through various alternative solutions (nuclear, biomass combustion, aeolian, geothermal, etc.), with the corresponding progressive implementations, the only alternative to fossil resources for the manufacture of commodity chemicals and polymers is the use of renewable vegetable and animal counterparts, that is, the biomass.

As a consequence, research initiatives to this effect are being implemented ubiquitously with a sense of increasing urgency, as witnessed by the growing investments assigned by the concerned ministries, supranational institutions (EU, UNIDO, etc.) and the private industrial sector. This is being accompanied by the dramatic increase in scientific publications, patents and international symposia covering the topic of the rational exploitation of renewable resources to produce commodities alternative to petrochemicals.

The incessant biological activities that the earth sustains thanks to solar energy provide not only the means of our survival, but also a variety of complementary substances and materials which have been exploited by mankind since its inception, albeit with a growing degree of sophistication. Suffice it to mention, as an example, wood as a source of shelter and, later, of paper. In modern times, the exploitation of renewable resources to prepare useful products and plastics was indeed quite prominent between about 1870 and 1940 (natural rubber for tyres, cellulose acetate and nitrate, plant-based dyes, drying oils, etc.). As already pointed out, however, a major shift in industrial chemistry took place, starting from the second quarter of the last century, which led to the supremacy of first coal and then petrol as the basis of its output in terms of most intermediates, commodities and polymers.

This trend witnessed its apex at the end of the last millennium, when competent assessments from various academic and industrial circles begun alerting the community about the need of returning to the exploitation of renewable resources, albeit, obviously, following a more rational and thorough strategy. The concept of the 'biomass refinery' puts forward an approach, similar to that of the classical petrol counterpart, in which each of the different components of a given natural resource is isolated by chemical or biochemical means with the aim of turning them into useful products. Thus, interesting chemicals and monomers for industry and medicine, compounds with a specific useful pristine structure, resins, natural fibres and oils (used as such or after adequate modification), as well as polymers produced by bacteria, could replace progressively petrol-based counterparts. To take wood again as an example, this strategy implies that its various components are separated and valorized, namely: (i) cellulose fibres, essentially for papermaking, but also as reinforcing elements in composite materials; (ii) lignin as a macromonomer for novel plastics, or as a source of valuable chemicals like vanillin; (iii) bark tannins for leather treatment and as components for resins and adhesives; (iv) specific minor chemicals present in knots for medical applications such as neutraceuticals, etc.

In this way, the dependence on fossil resources steadily decreases and every country in the world profits equally from this radical change, since biomass is ubiquitous and the technologies associated with its refinery just have to be adapted to the local species.

Numerous countries have embarked on ambitious programmes devoted to these issues and some of them have already been turned into concrete achievements through collaboration between public and private sectors. This amply justifies the pursuit of further research and development activities.

The purpose of this book is to concentrate exclusively on one topic within this broad issue, namely the use of renewable resources as precursors or aids to novel macromolecular materials. It reflects the concerted effort of a number of specialists to propose a hopefully comprehensive scientific and technological appraisal of the state of the art and the perspectives related to the numerous facets of this realm. In the 15 years that have elapsed since the first, much more modest review on this topic was published by one of us*; progress has been astounding, both qualitatively and quantitatively. Hence, the initiative to prepare this collective volume, which we hope will constitute a useful working or consulting tool for all those involved, associated or simply interested in these important issues.

Given the global context, it does not seem preposterous to us to consider the materials discussed in this book as the *polymers of the future*.

The preparation of this book benefitted enormously from the unfailing editing advice of Joan Gandini, who devoted innumerable hours of her skills to help improve its quality. For this and for other precious heart-warming assistance, we are deeply grateful to her.

We wish to express our most sincere thanks to Vera Fernandes, who played a decisive role, with her secretarial competence and assiduity, in assuring the smooth progress of the different phases of the book construction.

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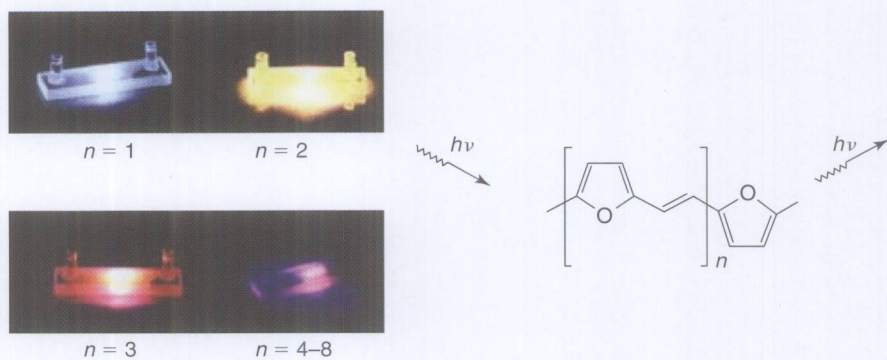


Figure 6.4 Photoluminescence of oligomers oligo(furylene vinylene)s with different lengths [57b].

Contents

Foreword	v
List of Contributors	vii
1 The State of the Art.....	1
<i>Alessandro Gandini and Mohamed Naceur Belgacem</i>	
2 Terpenes: Major Sources, Properties and Applications	17
<i>Armando J.D. Silvestre and Alessandro Gandini</i>	
3 Materials from Vegetable Oils: Major Sources, Properties and Applications	39
<i>Mohamed Naceur Belgacem and Alessandro Gandini</i>	
4 Rosin: Major Sources, Properties and Applications	67
<i>Armando J.D. Silvestre and Alessandro Gandini</i>	
5 Sugars as Monomers	89
<i>J.A. Galbis and M.G. García Martín</i>	
6 Furan Derivatives and Furan Chemistry at the Service of Macromolecular Materials.....	115
<i>Alessandro Gandini and Mohamed Naceur Belgacem</i>	
7 Surfactants from Renewable Sources: Synthesis and Applications	153
<i>Thierry Benvegna, Daniel Plusquellec and Loïc Lemiègre</i>	
8 Tannins: Major Sources, Properties and Applications	179
<i>Antonio Pizzi</i>	
9 Lignins: Major Sources, Structure and Properties	201
<i>Göran Gellerstedt and Gunnar Henriksson</i>	
10 Industrial Commercial Lignins: Sources, Properties and Applications	225
<i>Jairo Lora</i>	
11 Lignins as Components of Macromolecular Materials.....	243
<i>Alessandro Gandini and Mohamed Naceur Belgacem</i>	
12 Partial or Total Oxypropylation of Natural Polymers and the Use of the Ensuing Materials as Composites or Polyol Macromonomers	273
<i>Alessandro Gandini and Mohamed Naceur Belgacem</i>	
13 Hemicelluloses: Major Sources, Properties and Applications	289
<i>Iuliana Spiridon and Valentin I. Popa</i>	
14 Cork and Suberins: Major Sources, Properties and Applications.....	305
<i>Armando J.D. Silvestre, Carlos Pascoal Neto and Alessandro Gandini</i>	
15 Starch: Major Sources, Properties and Applications as Thermoplastic Materials.....	321
<i>Antonio J.F. Carvalho</i>	
16 Cellulose Chemistry: Novel Products and Synthesis Paths	343
<i>Thomas Heinze and Katrin Petzold</i>	

17	Bacterial Cellulose from <i>Glucanacetobacter xylinus</i> : Preparation, Properties and Applications	369
	<i>Édison Pecoraro, Danilo Manzani, Younes Messaddeq and Sidney J.L. Ribeiro</i>	
18	Surface Modification of Cellulose Fibres	385
	<i>Mohamed Naceur Belgacem and Alessandro Gandini</i>	
19	Cellulose-Based Composites and Nanocomposites	401
	<i>Alain Dufresne</i>	
20	Chemical Modification of Wood.....	419
	<i>Mohamed Naceur Belgacem and Alessandro Gandini</i>	
21	Poly(lactic Acid): Synthesis, Properties and Applications	433
	<i>L. Avérous</i>	
22	Poly(hydroxyalkanoates): Origin, Properties and Applications	451
	<i>Ivan Chodak</i>	
23	Proteins as Sources of Materials	479
	<i>Lina Zhang and Ming Zeng</i>	
24	Polyelectrolytes Derived from Natural Polysaccharides.....	495
	<i>Marguerite Rinaudo</i>	
25	Chitin and Chitosan: Major Sources, Properties and Applications.....	517
	<i>C. Peniche, W. Argüelles-Monal and F.M. Goycoolea</i>	
	<i>Index.....</i>	543

The State of the Art

Alessandro Gandini and Mohamed Naceur Belgacem

ABSTRACT

This chapter gives a general introduction to the book and describes briefly the context for which the editors established its contents and explains why certain topics were excluded from it. It covers the main raw materials based on vegetable resources, namely (i) wood and its main components: cellulose, lignin, hemicelluloses, tannins, rosins and terpenes, as well as species-specific constituents, like natural rubber and suberin; and (ii) annual plants as sources of starch, vegetable oils, hemicelluloses, mono and disaccharides and algae. Then, the main animal biomass constituents are briefly described, with particular emphasis on: chitin, chitosan, proteins and cellulose whiskers from molluscs. Finally, bacterial polymers such as poly(hydroxyalkanoates) and bacterial cellulose are evoked. For each relevant renewable source, this survey alerts the reader to the corresponding chapter in the book.

Keywords

Animal biomass, Vegetal biomass, Wood, Cellulose, Lignins, Hemicelluloses, Natural rubber, Suberin, Tannins, Rosins, Terpenes, Annual plants, Starch, Vegetable oils, Hemicelluloses, Mono and disaccharides, Polylactic acid, Algae, Chitin, Chitosan, Proteins, Cellulose whiskers, Bacterial polymers, Poly(hydroxyalkanoates), Bacterial cellulose

1.1 THE CONTEXT

The biosynthesis of macromolecules through enzymatic, bacterial and chemical polymerizations of specific molecular structures constitutes a key step in the evolution of living organisms. Natural polymers have therefore been around for a very long time and always constituted one of the essential ingredients of sustainability, first and foremost as food, but also as shelter, clothing and source of energy. These renewable resources have also played an increasingly important role as materials for humanity through their exploitation in a progressively more elaborated fashion. The ever improving technologies associated with papermaking, textile and wood processing, vegetable oils, starch and gelatin utilization, the manufacture of adhesives, etc. represent clear examples of the progressive sophistication with which man has made good use of these natural polymers throughout the millennia. Concurrently, natural monomers have been polymerized empirically for equally long periods for applications such as coatings, paint and ink setting, leather tanning, etc.

The progress of chemistry, associated with the industrial revolution, created a new scope for the preparation of novel polymeric materials based on renewable resources, first through the chemical modification of natural polymers from the mid-nineteenth century, which gave rise to the first commercial thermoplastic materials, like cellulose acetate and nitrate and the first elastomers, through the vulcanization of natural rubber. Later, these processes were complemented by approaches based on the controlled polymerization of a variety of natural monomers and oligomers, including terpenes, polyphenols and rosins. A further development called upon chemical technologies which transformed renewable resources to produce novel monomeric species like furfuryl alcohol.

The beginning of the twentieth century witnessed the birth of a novel class of materials, the synthetic polymers based on monomers derived from fossil resources, but the progress associated with them was relatively slow up to the Second World War and did not affect substantially the production and scope of the naturally based counterparts. Some hybrid materials, arising from the copolymerization between both types of monomers were also developed at this stage as in the case of the first alkyd resins. Interestingly, both monomers used in the first process to synthesize nylon in the late 1930s were prepared from furfural, an industrial commodity obtained from renewable resources, in a joint venture between Quaker Oats and DuPont.

The petrochemical boom of the second half of the last century produced a spectacular diversification in the structures available through industrial organic chemistry. Among these, monomers played a very significant role, as it transpires from the high percentage of such structures represented in the list of the most important chemical commodities in world production. The availability of a growing number of cheap chemicals, suitable for the production of macromolecular materials, gave birth to 'the plastic age', in which we still live today, with of course greatly enhanced quantitative and qualitative features.

This prodigious scientific and technical upsurge went to the detriment of any substantial progress in the realm of polymers from renewable resources. In other words, although these materials never ceased to exist, very modest investments were devoted to their development, compared with the astronomical sums invested in petrochemistry. As a consequence, although cotton, wool and silk textile are still plentiful, the competition of synthetic fibres has not stopped growing. Likewise, the incidence of natural rubber is very modest today, compared with its synthetic counterparts, not only in relative tonnage, but also in the continuously widening degree of sophistication associated with the properties of the latter materials. In virtually all other domains associated with polymeric materials, the present contribution of structures derived from renewable resources is very modest and has not played an appreciable role in terms of bringing about specific functional properties. On the other hand, paper has resisted all attempts to be replaced by synthetic polymers, although these have been playing a growing role as bulk and surface additives, albeit without modifying the essential constitution of this material, which still relies on the random assembly of cellulose fibres.

We are deeply convinced that this state of affairs has nothing to do with any consideration of relative merits associated with the different structures and chemical processes involved in either context. Its origin is instead to be found in a purely economic aspect (*i.e.* in the enormous difference in investment that favoured petrochemistry for the last half century) which was also the period when the chemical industry witnessed its fastest progress ever. The choice to finance R&D activities in polymers derived from fossil resources in a massive way was to the benefit of the corresponding materials as we know them today. This objective situation, however, does not prove anything against the potential interest of alternative counterparts made from renewable resources, simply because no such investments were ever made to that effect.

Should fossil resources be available for us to exploit for centuries to come, the above arguments would sound like a futile exercise in style. Their validity stems precisely and primarily from the very fact that fossil resources are dwindling and becoming progressively more expensive. Furthermore, they are not a commonly shared richness, since their global distribution is totally uneven, which implies that certain countries are heavily dependent on others in this respect. These problems are of course affecting the energy outlook in the first instance, since some 95 per cent of the fossil resources are used as fuel, but the looming crisis will inevitably affect the corresponding chemical industry as well.

The purpose of this book is to show, through its attempt to cover, as exhaustively as possible, the wide spectrum of materials already potentially available, that renewable resources are perfectly apt to provide as rich variety of monomers and polymers as that currently available from petrochemistry. Implicit in this statement is the condition that substantial investments should be placed in the future to carry out the required research.

All contributors to this volume provided stimulating evidence about the potentials in their own field, but they are also aware that their efforts will turn into industrial realities only with the joint intervention of adequately financed fundamental and applied research, *viz.* the implication of both public and private sectors. If, on the one hand, it is encouraging to see a very impressive increase in this type of activity worldwide, the situation relative to petrochemistry, on the other hand, is still at a very low level of competitiveness. Qualitatively, a change in awareness has indeed taken place, parallel to the preoccupation surrounding the energy issues. This book is intended to amplify these promising initial stirrings by providing very sound examples of what can be achieved thanks to this alternative strategy.

Renewable resources are intrinsically valuable in this realm because of their ubiquitous character, which gives any society precious elements of sustainability, including with respect to polymeric materials. In all the topics covered by this book, emphasis is made, explicitly or implicitly, to the essential fact that the specific sources utilized for the purpose of producing new polymers, are taken neither from food, nor from natural materials, but instead from *by-products* of agricultural, forestry, husbandry and marine activities. One of the best examples of

this strategy is the production of furfural, since it can be carried out industrially virtually anywhere in the world (see Chapter 6), given the fact that any vegetable by-product containing pentoses represents an excellent raw material for its synthesis.

The term 'renewable resource', as used in this book, is defined as any animal or vegetable species which is exploited without endangering its survival and which is renewed by biological (short term) instead of geochemical (very long term) activities.

1.2 VEGETABLE RESOURCES

It is estimated that the world vegetable biomass amounts to about 10^{13} tons and that solar energy renews about 3 per cent of it per annum. Given its fundamental role in the maintenance of the oxygen level, the principle of sustainability limits its exploitation at most to that renewed percentage. With respect to the scope of this book, vegetable biomass can be divided into wood, annual plants and algae.

1.2.1 Wood

Wood is the most abundant representative of the vegetable realm and constitutes the paradigm of a composite material. It displays, on the one hand, a basic universal qualitative composition in terms of its major constituents (cellulose, lignin, hemicelluloses and polyphenols) and, on the other hand, species-specific components which can be polymeric, like poly-isoprene (natural rubber) and suberin, or small molecules, like terpenes, steroids, etc. An example of its morphology is shown in Fig. 1.1, which illustrates the role of the three basic components respectively as the matrix (lignin), the reinforcing elements (cellulose fibres) and the interfacial compatibilizer (hemicelluloses). The middle lamella ($0.5\text{--}2\mu\text{m}$) is mainly composed of lignin (70 per cent), associated with small amounts of hemicelluloses, pectins and cellulose. The primary wall, often hard to distinguish from the middle lamella, is very thin ($30\text{--}100\text{ nm}$) and is composed of lignins (50 per cent), pectins and hemicelluloses. The secondary wall is the main part of the vegetal fibres. Its essential component is cellulose and it bears three layers, viz. the external, S_1 ($100\text{--}200\text{ nm}$), the central S_2 (the thickest layer of $0.5\text{--}8\mu\text{m}$) and the internal or tertiary layer, S_3 ($70\text{--}100\text{ nm}$) situated close to the lumen.

Wood is the structural aerial component of trees. The rest of their anatomy, namely roots, leaves, flowers and fruits, are not relevant to the aim of this book, and will therefore not be dealt with.

Cellulose dominates the wood composition, although its proportion with respect to the other main components can vary appreciably from species to species. Conversely, polyphenols are the least abundant components and moreover, can exhibit quite different structures. As for lignins and hemicelluloses, their relative abundance and their detailed structures are essentially determined by the wood family: softwoods are richer in lignins, whereas hardwoods are richer in hemicelluloses. These three basic polymeric components represent fundamental sources

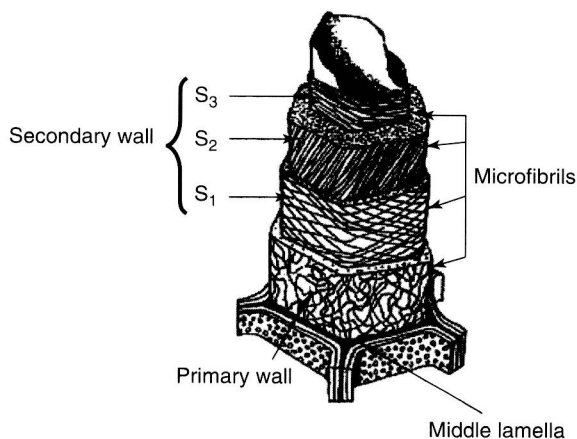


Figure 1.1 Typical morphology of a wood fibre.

of interesting materials and are thoroughly examined in this context, in specific chapters of this book, which focus their attention on the exploitation of these natural polymers after appropriate chemical treatment, with the aim of obtaining novel polymeric materials. The uses of wood itself as a structural material, as a source of furniture or flake boards and as a raw material in pulping, will not be treated here, because these applications call upon the exploitation of this fundamental natural resource through well-established technologies. Obviously, all these processes undergo regular improvement in their chemistry and engineering, but we deemed that their inclusion in the present treaty would have unduly overcharged its contents. The interested reader will find excellent monographs on each topic, going from introductory texts to highly specialized books [1–6].

The only area in which wood-related materials is witnessing important research contributions, concerns its physical and chemical modification, in order to protect it against degradation by various reagents or to obtain novel properties such as a thermoplastic behaviour. These aspects are treated in Chapter 20.

Similar considerations determined our decision not to include here chapters on the traditional uses of cellulose, like papermaking and cotton textiles, whose technologies are very thoroughly documented [7–10]. As for those cellulose derivatives which have been exploited for a very long time, like some cellulose esters and ethers, they will be dealt with in the appropriate chapter (Chapter 16), but again without a systematic treatment of the corresponding processes and properties [11–13].

1.2.1.1 Cellulose

Virtually all the natural manifestations of cellulose are in the form of semi-crystalline fibres whose morphology and aspect ratio can vary greatly from species to species, as shown in Fig. 1.2. The subunits of each individual fibre are the microfibrils which in turn are made up of highly regular macromolecular strands bearing the cellobiose monomer unit, as shown in Fig. 1.3.

The interest of cellulose as a source of novel materials is reflected in this book through four chapters dealing, respectively, with (i) the chemical bulk modification for the preparation of original macromolecular derivatives with specific functional properties (Chapter 16); (ii) the surface modification of cellulose fibres in view of their use as reinforcing elements in composite materials and as high-tech components (Chapter 18); (iii) the processing and characterization of these composites, including the use of nano fibres (Chapter 19) and (iv) the technology and applications associated with bacterial cellulose (Chapter 17). These contributions clearly show that cellulose, the most abundant and historically the most thoroughly exploited natural polymer, still provides new stimulating avenues of valorization in materials science and technology.

1.2.1.2 Lignins

Lignin, the amorphous matrix of wood, is characterized by a highly irregular structure compared with that of cellulose, and is moreover known to vary considerably as a function of wood family (*in situ*) and of the isolation process, which always involves a depolymerization mechanism. Figure 1.4 gives a typical example of the structure of a lignin macromolecule with its most characteristic building blocks. The pulping technology which calls upon a delignification mechanism based on the use of sulphites, yields lignin fragments bearing sulphonate moieties (*i.e.* polyelectrolytes).

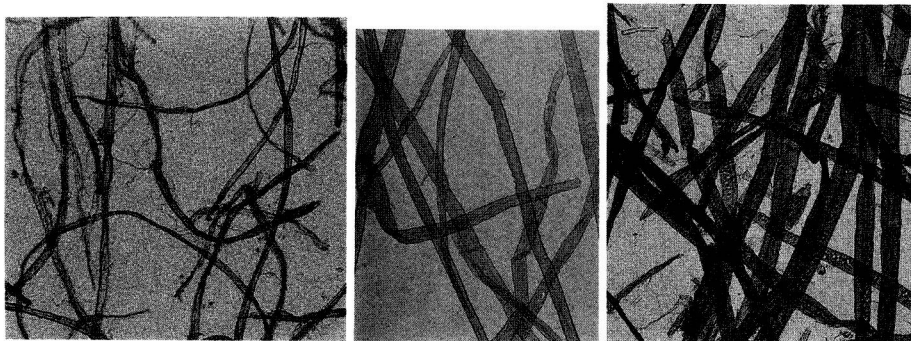


Figure 1.2 Cotton, pine and fir fibres.

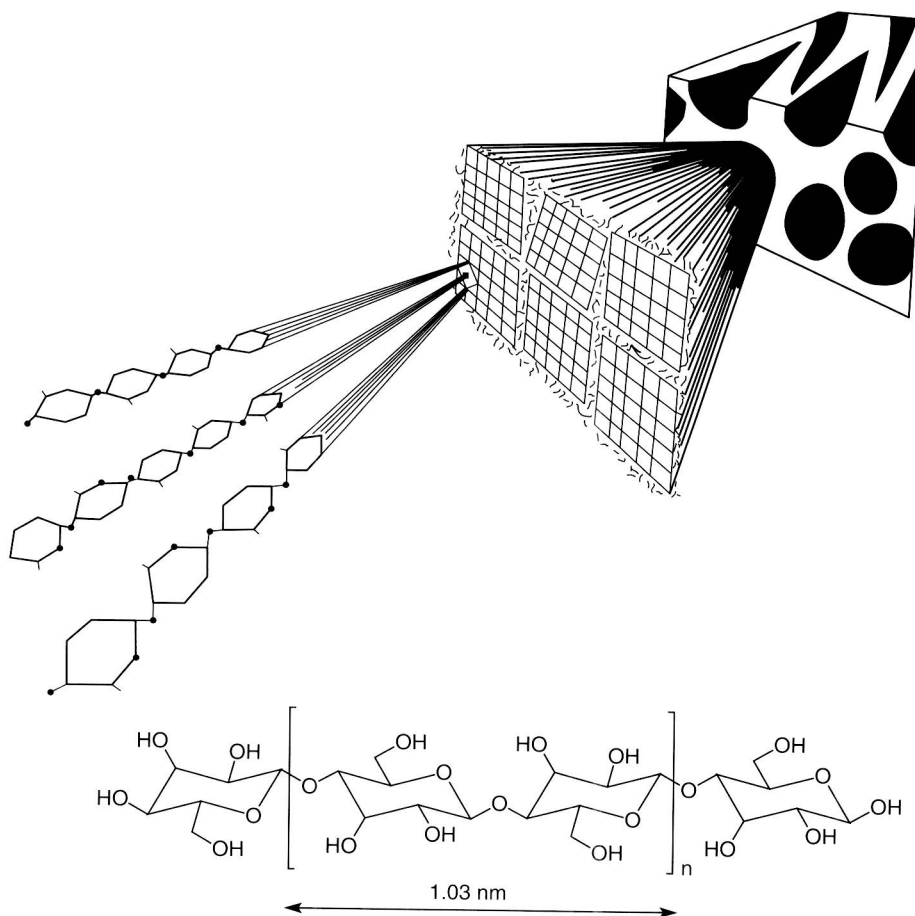


Figure 1.3 Schematic view of the components of cellulose fibre.

Traditionally, the aim of separating the wood components has been associated with papermaking, in which delignification isolates the cellulose fibres. In this context, the dissolved lignins have been utilized as fuel, which provides not only the energy required by the process, but also a convenient way of recovering its inorganic catalysts.

The idea of using these lignin fragments as macromonomers for the synthesis of polymers, by introducing them into formaldehyde-based wood resins, or by exploiting their ubiquitous aliphatic and phenolic hydroxyl groups, began to be explored only in the last quarter of the twentieth century. Given the fact that these industrial oligomers are produced in colossal amounts, it seems reasonable to envisage that a small proportion could be isolated for the purpose of producing new polymers, without affecting their basic use as fuel. Additionally, novel papermaking technologies, like the organosolv processes and biomass refinery approaches, like steam explosion, provide lignin fragments without the need of their use as a source of energy and with more accessible structures, in terms of lower molecular weights and higher solubility. Therefore, lignin macromonomers represent today a particularly promising source of novel materials based on renewable resources.

Three chapters are entirely devoted to lignin, covering (i) sources, structure and properties (Chapter 9), (ii) industrial processes and applications (Chapter 10) and (iii) their physical or chemical incorporation into novel macromolecular materials (Chapter 11). Moreover, its oxypropylation and the interest of the ensuing polyols are discussed in Chapter 12 and the properties of lignosulphonates as polyelectrolytes are dealt with in Chapter 24.

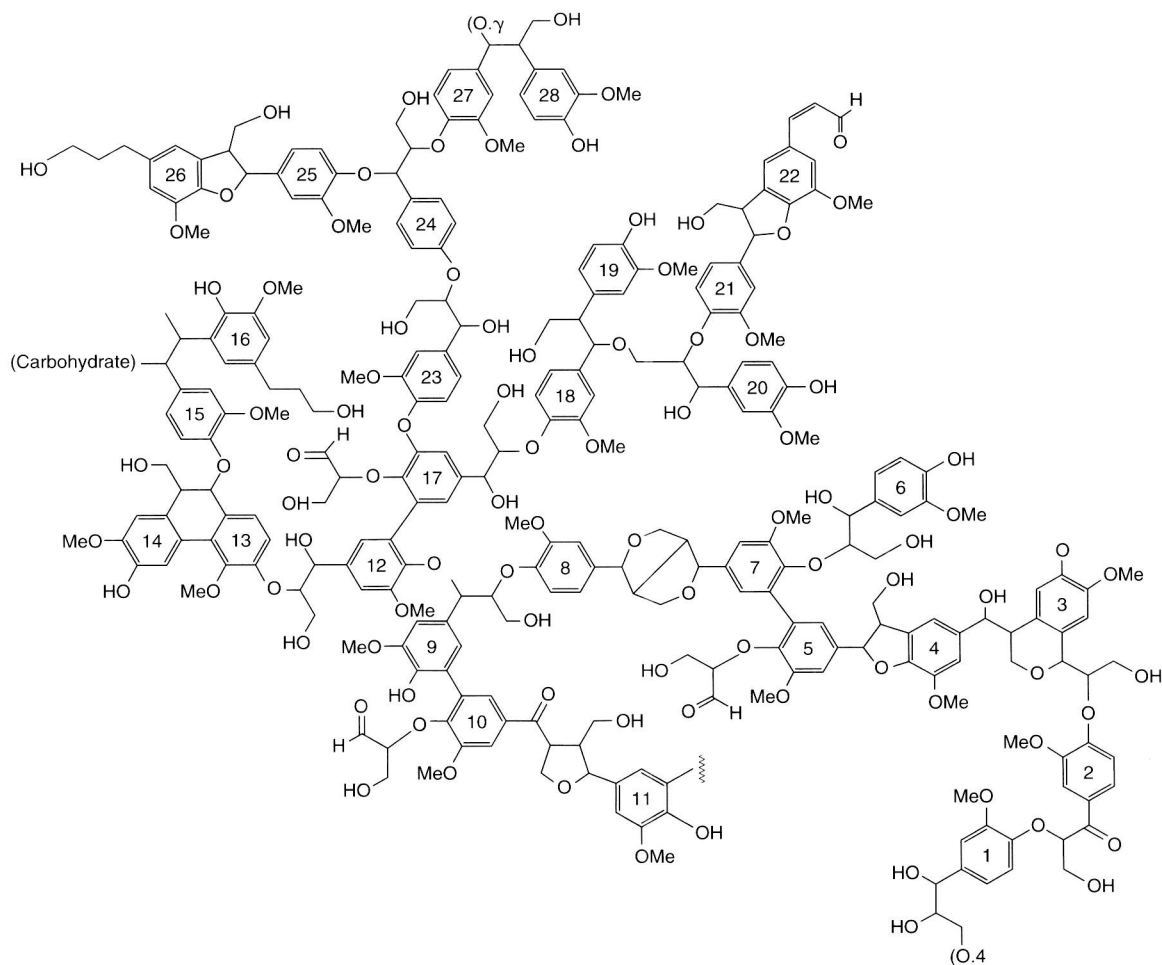


Figure 1.4 Lignin main moieties in a typical macromolecular assembly.

1.2.1.3 Hemicelluloses

Wood hemicelluloses are polysaccharides characterized by a relative macromolecular irregularity, compared with the structure of cellulose, both in terms of the presence of more than one monomer unit and by the possibility of chain branching. Figure 1.5 gives typical examples of such structures.

In papermaking processes, part of the wood hemicelluloses remain associated with the cellulose fibres, which results in the improvement of certain properties of the final material. The rest of these polysaccharides is dissolved together with lignin and in most processes it is burned with it. In some instances, however, particularly in the case of organosolv pulping or steam explosion technologies, the hemicelluloses can be recuperated as such. The utilization of wood hemicelluloses, but also of counterparts extracted from annual plants, has interested several industrial sectors for a long time, in particular that of food additives. In recent years, new possible outlets for hemicelluloses have been and are being explored, as discussed in Chapter 13.

1.2.1.4 Natural rubber

Turning now to more species-specific components, natural rubber is certainly one of the most important representatives. Different tropical trees produce different forms of poly(1,4-isoprene), which are exuded or extracted as an aqueous emulsion (latex) or as a sap-like dispersion, before coagulation. The *cis*-form of the polymer (Fig. 1.6(a)) tends to be amorphous and has a glass transition temperature of about -70°C , which makes it ideally suitable for application

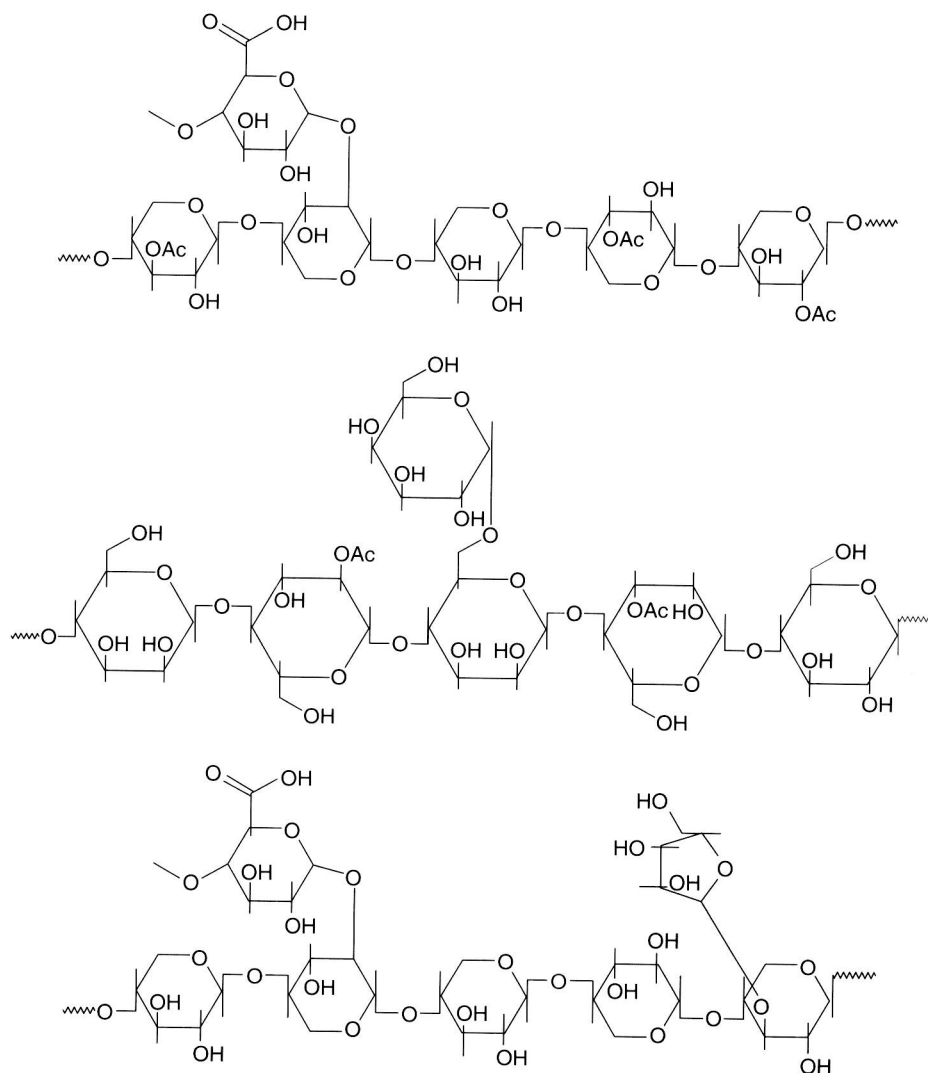


Figure 1.5 Three typical hemicellulose structures.

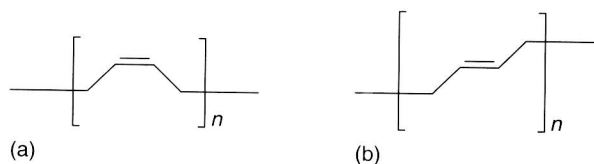


Figure 1.6 The two main structures of poly(1,4-isoprene) in natural rubber: (a) the *cis*-form and (b) the *trans*-form.

as elastomers, following chemical crosslinking (vulcanization) which involves some of its $C=C$ insaturations. Its world production in 2004 was estimated at about 8 million tons. The *trans*-form (Fig. 1.6(b)), called *gutta percha* or *balata*, readily crystallizes forming rigid materials melting at about 70°C . As in the case of papermaking and cotton textile, the extraction and processing technology of these valuable natural polymers, as well as the preparation and optimization of their corresponding materials, represent a well-established and well-documented know-how [14] and is therefore not treated in this book. Examples of interesting recent contributions to the biosynthesis [15]