

# Lignins: Major Sources, Structure and Properties

Göran Gellerstedt and Gunnar Henriksson

---

## ABSTRACT

Lignin is one of the most predominant biopolymers present in plants. Together with cellulose and hemicelluloses, lignin builds up the cell wall in an arrangement which is regulated on the nano-scale and results in lignin-carbohydrate network structures. The molecular complexity of lignin renders all isolation and identification processes difficult and, consequently, many structural questions still remain. In this chapter, our present knowledge about the formation of lignin in plants, its presence in different types of plants as well as several different approaches taken to reveal the chemical structure, is summarized. Furthermore, a brief discussion about the chemical changes introduced in lignin as the result of different types of delignification processes, such as kraft and sulphite pulping and steam explosion, is included.

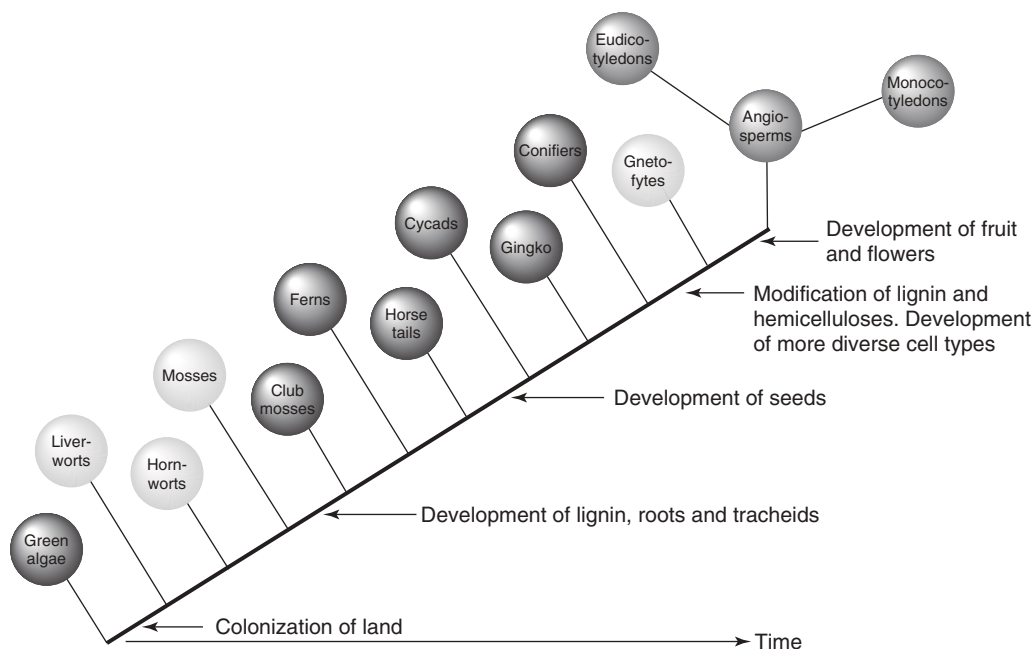
## Keywords

Analytical methods, Annual plants, Cellular structures, Dehydropolymerizate (DHP), Hardwoods, Kraft lignins, Lignification, Lignins, Lignosulphonates, Milled wood lignins (MWL), Softwoods, Steam explosion lignins

## 9.1 INTRODUCTION

Plants are eukaryotic organisms with an ability to utilize light for the fixation of carbon dioxide, having cell walls rich in cellulose and with an ability to use starch as nutrition storage inside the cells. In the evolution of plants, lignin (the term lignin is derived from the Latin word for wood, *lignum*) was introduced some 440 million years ago when the group of vascular plants started to develop. Thereby, a new cell type, the tracheid, was formed typified by its elongated feature and its thick hydrophobic cell wall. In addition to cellulose and lignin, all vascular plants also contain other polysaccharides, hemicelluloses and low molecular mass compounds, extractives. The presence of tracheids permitted an efficient transport of water in the plant and provided the strength necessary for the development of larger species. Simultaneously, the development of root systems took place, thus also allowing plants to grow in dryer environments.

The first vascular plants to develop were vascular cryptogams reproduced using spores and, today, such plants can still be found as the herb families of club mosses, ferns, horsetails and in fern trees. In the further evolution of plants, seed fertilization developed some 360 million years ago and paved the way for an expansion of novel types of trees which successively overruled the vascular cryptogam trees due to a more efficient reproduction system and a greater ability to colonize dryer areas of land. The first trees to develop all had naked seeds often organized in cones and are referred to as gymnosperms. About 150 million years ago, a dramatic new development occurred with plants-carrying flowers, the fertilization being done by insects and with seeds developed inside a fruit body. Such plants, the angiosperms, rapidly took over in importance and, today, more than 90 per cent of all land-living plant species are of this type. Simultaneously, the angiosperms developed more advanced types of leafs and the



**Figure 9.1** A schematic view of the evolution of plants.

cells became more specialized with vessel cells taking care of the water and nutrition transport. The structure of lignin and hemicelluloses was modified in comparison to the gymnosperms. Usually, the angiosperms are divided into two classes, *viz.* the monocotyledons, which include species such as grasses, bamboo and palm trees, and the eudicotyledons represented among others by leaf-carrying trees like birch, aspen and eucalyptus. The woody plants of the latter group are referred to as hardwoods. A simplified schematic representation of the evolution of plants is given in Fig. 9.1.

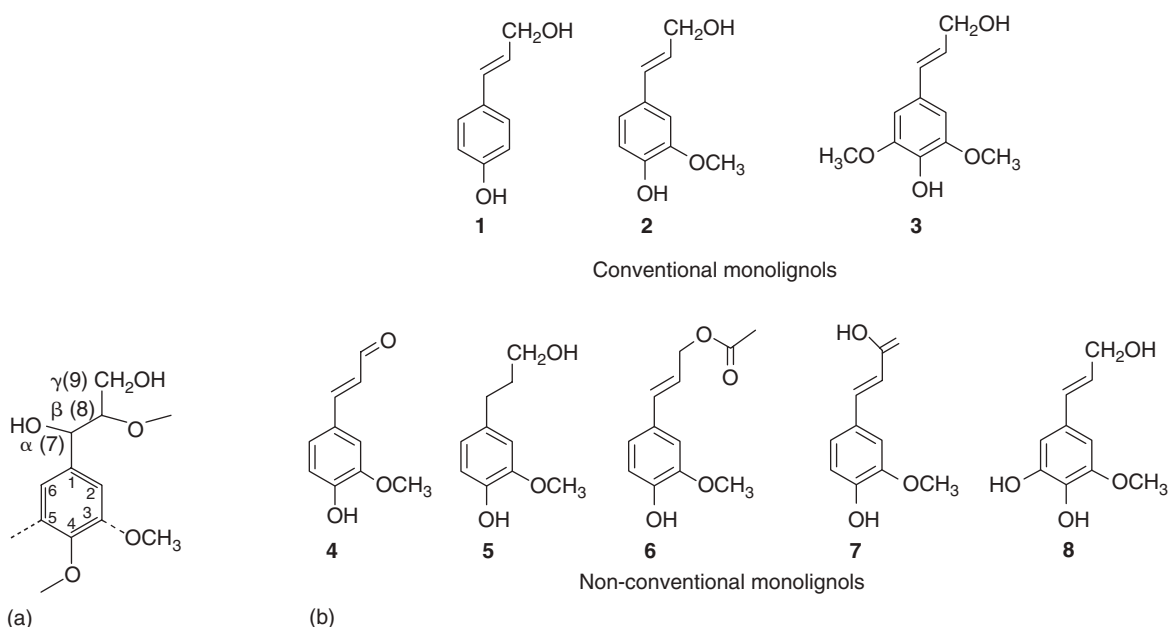
## 9.2 NOMENCLATURE OF LIGNIN

Lignins are formed by polymerization of cinnamyl alcohols (monolignols) which differ in structure depending on plant type. In coniferous wood, the lignin is built up almost exclusively by coniferyl alcohol (G-units) with minor amounts of coumaryl alcohol (H-units) present. The latter is, however, a major constituent in compression wood lignin. In hardwoods, on the other hand, both coniferyl alcohol and sinapyl alcohol (S-units) are used as building blocks and in monocotyledonous tissue, all three alcohols are used as lignin precursors [1–3]. Figure 9.2 shows the numbering system and the structure of the three major monolignols, together with some minor monolignols found as lignin end-groups or present in specific plants [4, 5]. Table 9.1 shows the degree of participation of the major monolignols in different types of plants.

## 9.3 BIOSYNTHESIS OF MONOLIGNOLS AND THE FORMATION OF LIGNIN

The three major monolignols (Fig. 9.2) used to synthesize lignin polymers are formed in the cytoplasm via the shikimate pathway which produces phenylalanine as key intermediate [7–9]. Through further enzyme mediated deamination, hydroxylation, reduction and methylation reactions, the final lignin precursors are formed as depicted in Fig. 9.3.

The further reactions of monolignols in the plant cell wall to form lignin may occur through an initial laccase or peroxidase oxidation of the monolignol giving rise to a resonance-stabilized phenoxy radical as depicted in Fig. 9.4 [10–12]. This step is followed by a coupling reaction and model experiments have shown that the first product, the



**Figure 9.2** (a) Numbering system in monolignols. (b) Types of monolignols found as building blocks in lignin. 1 = *p*-coumaryl alcohol (H-unit), 2 = coniferyl alcohol (G-unit), 3 = sinapyl alcohol (S-unit), 4 = coniferaldehyde, 5 = dihydroconiferyl alcohol, 6 = coniferyl alcohol-9-acetate, 7 = ferulic acid, 8 = 5-hydroxyconiferyl alcohol.

**Table 9.1**

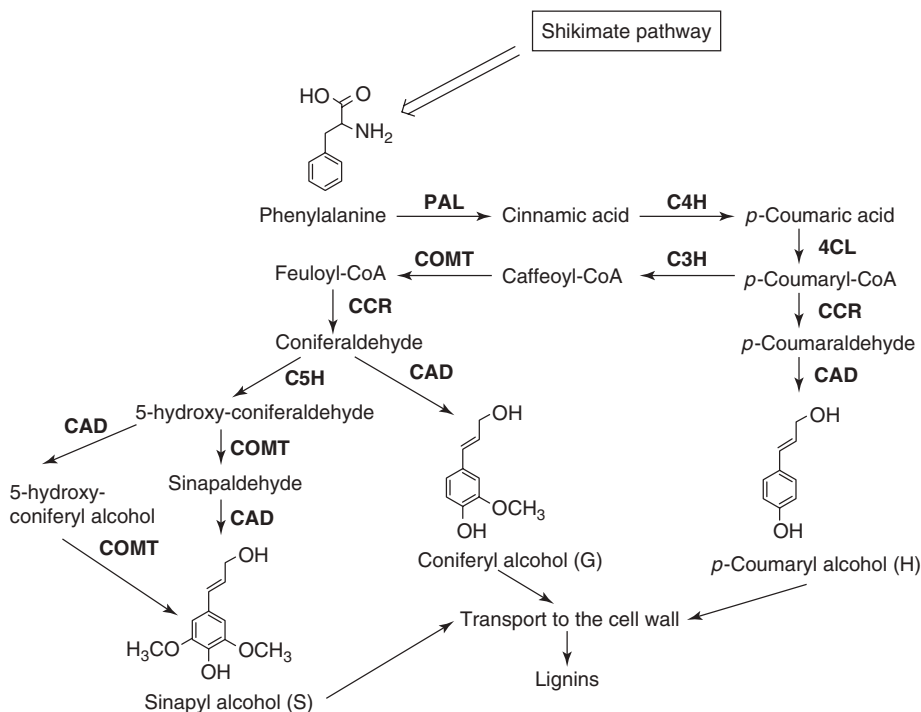
The participation of different monolignols in lignin from various plants

Plant type	<i>p</i> -Coumaryl alcohol	Coniferyl alcohol	Sinapyl alcohol
	(%)		
Coniferous; softwoods	<5 <sup>a</sup>	>95	0 <sup>b</sup>
Eudicotyledonous; hardwoods	0–8	25–50	45–75
Monocotyledonous; grasses	5–35	35–80	20–55

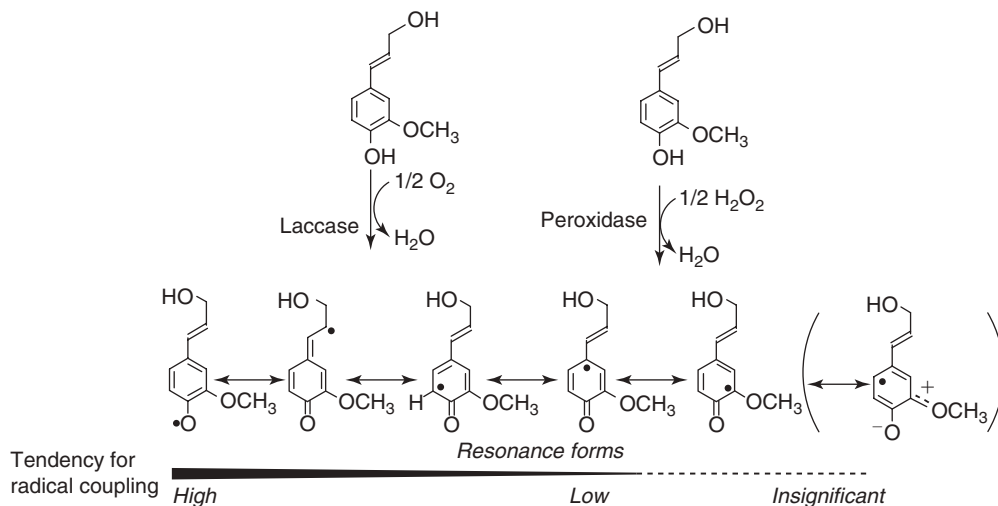
<sup>a</sup> Higher amount in compression wood.

<sup>b</sup> Some exceptions exist [6].

dimer, will be formed by involvement of the  $\beta$ -carbon in one unit and either the phenolic hydroxyl, the aromatic C5 (only in G- or H-units) or the  $\beta$ -carbon in the other [10–12]. It should be noted that the theoretically possible coupling products between two C5 centred radicals or between a phenoxy and a C5 radical are not formed to any noticeable extent. The stepwise further growth of the polymer is thought to involve an end-wise addition of a new monolignol radical to the growing polymer chain. In the latter, however, only the phenolic hydroxyl, the aromatic C5 or C1 positions are available for coupling. Thus, the overall frequency of inter-unit linkages involving the C– $\beta$  carbon can be expected to be completely dominant in any lignin. Coupling in the aromatic C1 position takes place to a low extent and predominantly results in the formation of a spirodienone structure with a secondary lignin fragmentation reaction as an alternative [13]. Other possible modes of coupling may occur if two growing polymer chains are in close proximity, by formation of C5/C5 (in G-units) or phenolic hydroxyl/C5 linkages. Thereby, branching or crosslinking points in the lignin polymer are created. Branching points in the growing lignin polymer are also created by the formation of dibenzodioxocin structures. These are prevalent in guaiacyl lignins and formed by internal trapping after coupling of a C– $\beta$  radical with a 5–5' phenoxy radical [14, 15]. The various types of inter-unit linkages and their abbreviated nomenclature are depicted in Fig. 9.5.

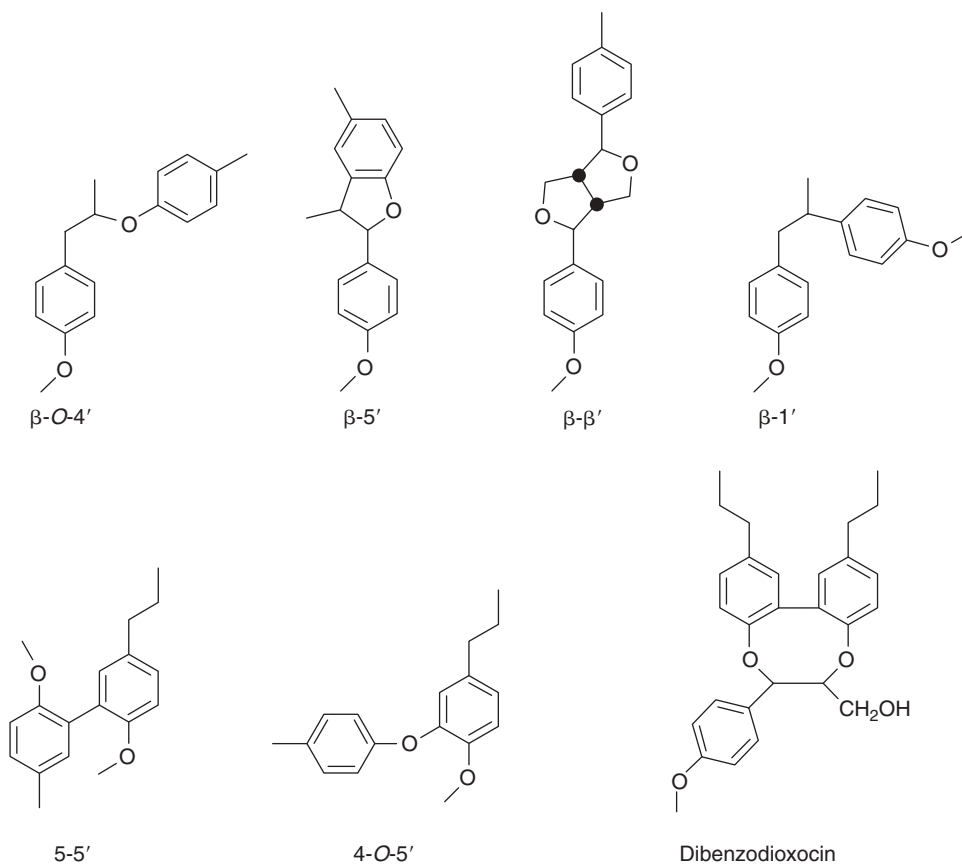


**Figure 9.3** The lignin biosynthesis pathway. Abbreviations of enzymes are: PAL = phenylalanine-ammonia-lyase; C4H = cinnamate 4-hydroxylase; 4CL = hydroxycinnamate:CoA-ligase; C3H = 4-hydroxycinnamate 3-hydroxylase; COMT = S-adenosyl-methionine:caffeate/5-hydroxyferulate-O-methyltransferase; CAD = hydroxycinnamyl alcohol dehydrogenase; C5H = coniferaldehyde-5-hydroxylase.

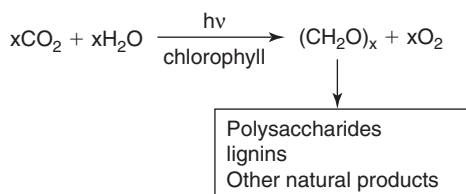


**Figure 9.4** Enzymatic formation of resonance-stabilized monolignol radicals. The relative reactivity in coupling reactions is indicated by the intensity of the line.

Recently, it has been suggested that lignin is not built up by a combinatorial polymerization of monolignols, but has a more ordered structure with a repeating unit larger than that given by the phenylpropane units [16, 17]. Thus, by a template polymerization involving cell wall proteins, oligomeric lignin fragments should be synthesized and added together in a controlled manner. Until now, however, there has been no experimental data to support this theory.



**Figure 9.5** Inter-unit linkage types in lignins and their commonly used denotation.



**Figure 9.6** The fixation of carbon dioxide in nature through the photosynthesis reaction.

## 9.4 MAJOR SOURCES OF LIGNIN

Lignin is present in all vascular plants making it second to cellulose in abundance among polymers in nature. Since lignin, like many other biomass components, is formed via the photosynthesis reaction (Fig. 9.6), it is renewable and it has been estimated that the annual production of lignin on earth is in the range of  $5\text{--}36 \times 10^8$  tons.

In woody plants from the gymnosperm and angiosperm phylum, the lignin content is in the order of 15–40 per cent [18] whereas in herbs, the lignin content is less than 15 per cent [19]. Low lignin content is usually also encountered in annual plants. In Table 9.2, some representative values for the content of lignin in various types of commercially important plants are given.

Many softwood and hardwood species, together with certain types of annual plants, have commercial interest as a source of cellulose fibres for the production of paper and board products. Thus, in technical fibre liberation processes, such as alkaline or sulphite pulping, huge quantities of lignin are dissolved as alkali lignin and lignosulphonates, respectively. With few exceptions (see Chapter 10), these lignins are, however, never isolated, but burnt

**Table 9.2**

Lignin content in various types of plants

Plant Scientific/Common name	Lignin content	Reference
<b>Gymnosperms</b>		
<i>Picea abies</i> , Norway spruce	28	[20]
<i>Picea abies</i> , Norway spruce (compression wood)	39	[21]
<i>Pinus radiata</i> , Monterey pine	27	[22]
<i>Pinus sylvestris</i> , Scots pine	28	[22]
<i>Pseudotsuga menziesii</i> , Douglas fir	29	[22]
<i>Tsuga canadensis</i> , Eastern hemlock	31	[22]
<b>Angiosperms – Eudicotyledons</b>		
<i>Acacia mollissima</i> , Black wattle	21	[22]
<i>Betula verrucosa</i> , Silver birch	20	[23]
<i>Eucalyptus globulus</i> , Blue gum eucalyptus	22	[22]
<i>Eucalyptus grandis</i> , Rose eucalyptus	25	[24]
<i>Populus tremula</i> , European aspen	19	[23]
<i>Corchorus capsularis</i> , Jute	13	[25]
<i>Hibiscus cannabinus</i> , Kenaf	12	[25]
<i>Linum usitatissimum</i> , Flax	2.9	[25]
<b>Angiosperms – Monocotyledons</b>		
<i>Oryza</i> species, Rice straw	6.1	[26]
<i>Saccharum</i> species, Bagasse	14	[26]

together with other wood constituents liberated in the pulping liquor in order to produce the steam required for the process. In all commercial pulping processes, as well as in emerging processes, such as wood hydrolysis for the production of biofuels, the lignin is structurally altered in comparison to the native lignin. Broadly, these types of lignin can be described as being heterogeneous polyphenols with molecular masses in the range of 100–300 000, often with a high degree of polydispersity (see Section 9.6).

In growing plants, on the other hand, the lignin constitutes an integral part of the cell walls with chemical linkages to all types of polysaccharide constituents present. For spruce wood, it has been shown that the major portion of lignin is covalently linked to the hemicelluloses (*i.e.* xylan and glucomannan) with a minor amount being linked to cellulose [27]. The concentration of lignin is, however, not evenly distributed throughout the cell wall and, despite a high concentration of lignin in the middle lamella, the predominant portion is located in the S2 layer of the secondary wall due to its large relative volume [28]. A detailed analysis of the lignin distribution in two wood species, one softwood and one hardwood, has been published and is shown in Table 9.3 [29].

All attempts to isolate lignin from wood or other types of biomass must be preceded by some mechanical disintegration of the material. Usually, intensive milling of the material is employed whereby the structural integrity (*i.e.* cell types), cell layers and any inhomogeneities at the macromolecular level, is eliminated and, from such materials, only an average lignin structure can be obtained. Despite these drawbacks, almost all present knowledge about the structure of lignins is based on comprehensive milling of the plant material, followed by solvent extraction with dioxane and (sometimes) further purification to yield low to moderate yields of lignin. In most isolation procedures, the lignin contains minor impurities of carbohydrates.

#### 9.4.1 Milled wood lignin

In 1956, the first description of the isolation of lignin from spruce wood according to these principles was published and the lignin was denoted as milled wood lignin (MWL) [30]. By employing extremely long extraction times (sequential extraction with dioxane–water, 96:4, for ~6 weeks), around 50 per cent of the lignin could be isolated. The author concluded that ‘MWL is a very useful material for lignin chemists’. In a subsequent paper, several other softwood and hardwood species were used to produce the corresponding MWLs and the similarities

**Table 9.3**

Distribution of lignin in various cell wall layers of softwood tracheids and hardwood fibres

Wood cell	Cell wall layer	Tissue volume (%)	Lignin (% of total)	Lignin concentration (%)
Loblolly pine tracheids (softwood)				
Early wood	S1	13	12	25
	S2	60	44	20
	S3	9	9	28
	ML + P	12	21	49
	CC	6	14	64
Late wood	S1	6	6	23
	S2	80	63	18
	S3	5	6	25
	ML + P	6	14	51
	CC	3	11	78
White birch fibres (hardwood)				
	S	73	60	19
	ML + P	5	9	40
	CC	2	9	85

between various softwood lignins and the differences between hardwood lignins could be clearly demonstrated [31]. Furthermore, it was shown that a second solvent extraction could be used to provide a lignin material still containing substantial amounts of carbohydrates and this was denoted lignin carbohydrate complex (LCC) [32].

As an alternative to the isolation of lignin by solvent extraction, liquid–liquid partition of dissolved wood meal between aqueous sodium thiocyanate and benzyl alcohol has been suggested [33]. In this rather complicated procedure, it was possible to isolate about 40 per cent of the lignin in spruce wood. The lignin still contained some 10 per cent of carbohydrates. In a further alternative to the original method, the milled wood was treated with an enzyme cocktail containing cellulolytic and hemicellulolytic activities, thereby facilitating the subsequent solvent extraction. Fractions of lignin, having different amounts of remaining carbohydrates, could be isolated with a total yield of lignin of 57 per cent from spruce and 68 per cent from sweetgum respectively [34, 35]. An even higher total yield of lignin was obtained by first extracting milled spruce wood with water, followed by extraction with dioxane. After enzymatic hydrolysis of the polysaccharides present in the residue, a second extraction with dioxane was carried out affording a total yield of 84 per cent of the lignin [36]. Enzymatic hydrolysis of extensively milled wood has also been combined with acid hydrolysis employing 0.01 M hydrochloric acid. From both spruce and poplar, around 60–70 per cent of the lignin could be isolated with this method [37]. Table 9.4 gives some data on MWLs from various sources.

Almost all isolation procedures for lignin published till date have been preceded by an intensive milling of pre-extracted wood meal in a vibratory or rotatory mill. In the former type of mill, a milling time of 48 h has frequently been used [30, 34] while in the latter, about 1–2 weeks is required [36, 37]. During the milling, certain types of chemical changes take place in the lignin such as cleavage of  $\beta$ -O-4 linkages and introduction of carbonyl groups [34]. This reaction will result in the formation of new phenolic lignin end-groups with a simultaneous fragmentation of the lignin macromolecule as depicted in Fig. 9.7.

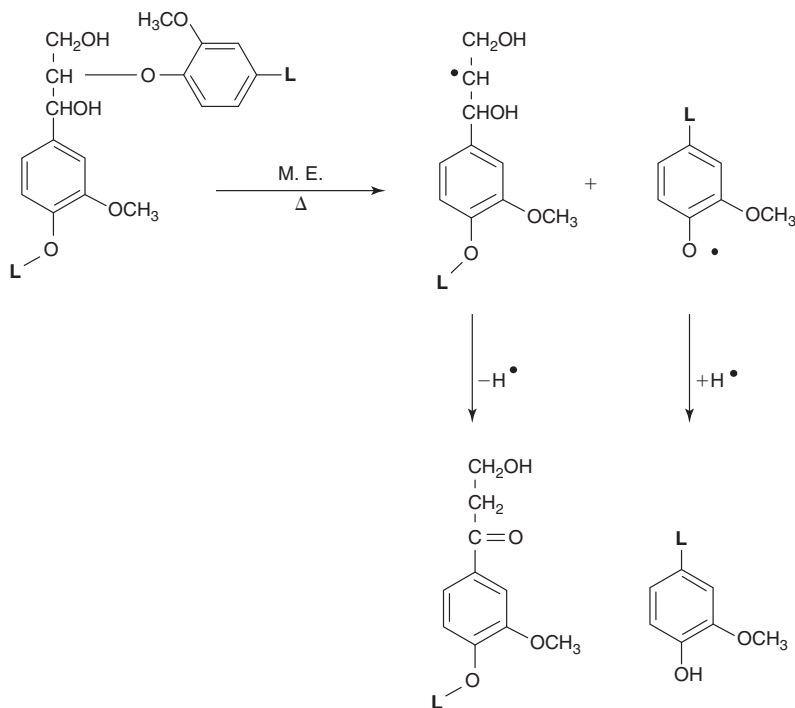
For extractives-free spruce wood, the concentration of free phenolic hydroxyl groups has been determined and values of 10–13 per 100 phenylpropane units have been obtained [38–40]. The corresponding value for spruce MWL is in the order of 20–30 (Table 9.4) depending on the intensity of milling and way of extracting the lignin. Consequently, all published analytical data on the structural composition of native lignin fail to give accurate values for the concentration of  $\beta$ -O-4 structures, since various amounts of this linkage have been mechano-chemically cleaved during the isolation procedure.

In an alternative way of isolating lignin from wood, pre-extracted spruce wood meal has been treated with a commercial mono-component endoglucanase [27, 41]. Thereby, the crystalline structure of cellulose is destroyed and the now amorphous wood can be homogeneously swollen in aqueous urea. By subsequent fractionation of the material in aqueous alkali, all lignin can be recovered as various LCCs (Table 9.5). Also in this case, however, the wood

**Table 9.4**

Representative data on MWL isolated from different wood species

Sample origin	OCH <sub>3</sub> (%)	Phenolic OH (%)	Carbohydrate (%)	Lignin yield (%) <sup>a</sup>	Reference
<i>Picea abies</i> , Norway spruce	15.45	30	1.9	19	[30]
<i>Picea abies</i> , Norway spruce	15.2	20	4.1	17	[34]
<i>Picea abies</i> , Norway spruce, CEL-96 <sup>b</sup>	15.2	20	4.3	28	[34]
<i>Picea mariana</i> , Black spruce	15.41	28	n.a. <sup>c</sup>	n.a.	[31]
<i>Picea mariana</i> , Black spruce	15.3	23	<9.6	25	[37]
<i>Picea mariana</i> , Black spruce, EAL <sup>d</sup>	13.7	21	<7.7	69	[37]
<i>Pinus sylvestris</i> , Scots pine	15.74	27	n.a.	n.a.	[31]
<i>Betula verrucosa</i> , Silver birch	21.51	n.d.	7.5	n.a.	[31]
<i>Liquidambar styraciflua</i> , Sweetgum	21.4	14	3.6	17	[34]
<i>Liquidambar styraciflua</i> , Sweetgum, CEL-96 <sup>b</sup>	21.5	13	3.8	43	[34]
<i>Populus tremuloides</i> , Trembling aspen	19.6	21	<8.0	24	[37]
<i>Populus tremuloides</i> , Trembling aspen, EAL <sup>d</sup>	20.9	21	<4.3	61	[37]

<sup>a</sup> Based on the lignin content in wood.<sup>b</sup> Ball milling of wood followed by enzymatic hydrolysis of polysaccharides prior to extraction of the residue with dioxane–water (96:4).<sup>c</sup> n.a. = not analysed.<sup>d</sup> Ball milling of wood followed by enzymatic hydrolysis of polysaccharides and subsequent acid hydrolysis with 0.01 M HCl of the residue in dioxane–water (85:15).**Figure 9.7** Lignin fragmentation reaction suggested to take place during the milling of wood. M.E. = mechanical energy.



**Table 9.5**

Types of LCC isolated from spruce wood meal after treatment with endoglucanase followed by swelling in urea and fractionation in aqueous alkali [27, 41]

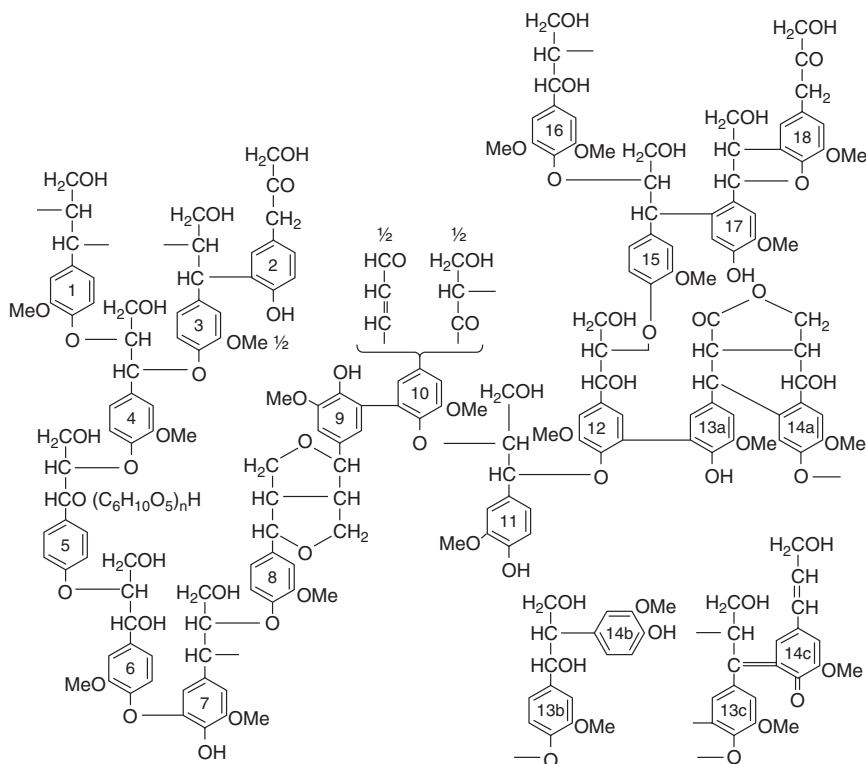
Type of lignin-carbohydrate complex (LCC)	Lignin yield (%)
GalactoGlucoMannan – Lignin	8
Glucan – Lignin	4
GlucoMannan – Lignin <sup>a</sup>	48
Xylan – Lignin <sup>a</sup>	40

<sup>a</sup> Sum of two different fractions.

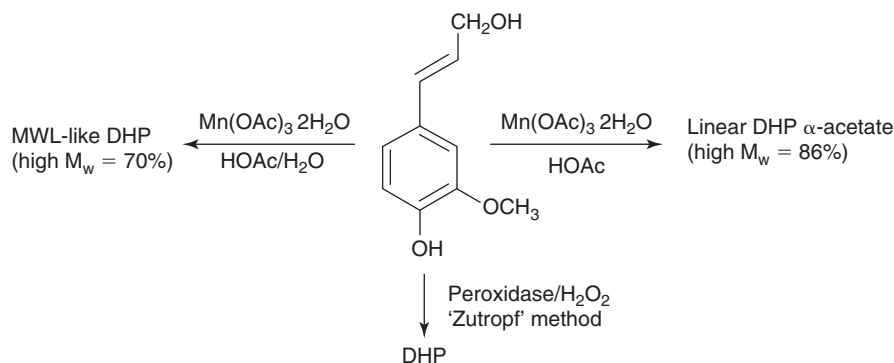
structure must be degraded to some extent prior to enzyme treatment by vibratory ball milling for 3 h and, thus, neither this lignin can be regarded as completely native although the milling intensity has been greatly reduced.

### 9.4.2 Dehydropolymerizate

In the early work on lignin structure, enzymatic polymerization of coniferyl alcohol, employing either laccase or peroxidase together with oxygen or hydrogen peroxide respectively, has frequently been used to produce 'lignin-like' substances denoted dehydrogenation polymers (DHPs) (see Fig. 9.4) [10]. The results from this work were used to construct the first generation of statistical lignin structures in which the then identified relative amounts of different inter-unit linkages were included (Fig. 9.8).



**Figure 9.8** A first generation schematic formula of spruce lignin showing the most important inter-unit linkages between the phenylpropane units [42]. Reproduced by permission of Springer Science and Business Media.



**Figure 9.9** Synthesis of DHP using the ‘Zutropf method’ with peroxidase and hydrogen peroxide or manganese(III)-acetate in acetic acid with or without the presence of water. The biomimetic DHPs were fully acetylated and the high molecular weight fraction obtained after chromatography on polystyrene gel [46].

In the synthesis of DHP, two different modes have been employed, the ‘Zulauf’ and the ‘Zutropf’ methods. The former involves a stepwise addition of enzyme to a solution of coniferyl alcohol whereas in the latter, the reverse is used. From a structural point of view, the two methods give slightly different DHPs but the Zutropf–DHP is considered as being somewhat more ‘lignin-like’ [43]. For both types of DHPs, however, considerable structural differences are encountered in comparison with MWL.

Attempts to improve the synthesis of DHP in order to obtain a more lignin-like polymer have been made. In one such system, coniferin, together with  $\beta$ -glucosidase, peroxidase and hydrogen peroxide, prepared *in situ* from oxygen, glucose oxidase and liberated glucose, were used. Thereby, a very low concentration of hydrogen peroxide could be maintained throughout the oxidation. In different variants of the procedure, the reaction was performed with or without the presence of a polysaccharide and at different pH-values [44]. Based on this model system, it was found that pH, the concentration of monomer radicals and the carbohydrate matrix all affected the structure of the resulting DHP to some extent [45]. Despite these modifications, however, the DHPs were still found to be quite different from MWL.

In alternative ways of preparing DHP by employing biomimetic approaches, a much closer structural resemblance to MWL could be obtained. In one method, manganese(III) acetate was used to polymerize coniferyl and/or sinapyl alcohol [46]. The reaction conditions were found to exert a profound influence on the structure of the resulting polymer and lignin-like, as well as linear polymers, were produced as schematically illustrated in Fig. 9.9. In a similar approach, manganese(III) was produced *in situ* by the oxidation of manganese(II) with manganese peroxidase. Oxidation of coniferyl alcohol was carried out in a two-vessel reaction flask separated by a semi-permeable membrane allowing the manganese(III) to freely move between the vessels, while keeping the enzyme and coniferyl alcohol separated. Again, a lignin-like DHP could be formed as revealed by thioacidolysis in combination with size exclusion chromatography and  $^{13}\text{C}$  NMR spectroscopy [47].

## 9.5 THE STRUCTURE OF LIGNIN

The quantification of lignin present in wood and other plants is usually done indirectly by weighing the solid residue that remains after the complete hydrolysis of all polysaccharides present in the material [48]. The insoluble material, denoted Klason lignin, is thought to be formed by a comprehensive condensation of the original lignin structure by the strongly acidic conditions used in the hydrolysis. In addition, a minor amount of acid-soluble lignin can be determined by measuring the UV absorbance of the hydrolysis liquor, usually at 205 nm [48]. Although the latter value is often added together with the value for Klason lignin to provide the total amount of lignin in a sample, its origin is not known with certainty and, for example, carbohydrates may well contribute degradation products with absorbance in the same region (Gellerstedt, unpublished).

For the quantification of lignin in a large number of similar samples, near-infrared spectroscopy (NIR) is well suited. Once a suitable set of reference samples has been determined using the Klason lignin method, the data can be used to calibrate the NIR signal. Subsequently, the lignin content in unknown samples can be registered in a convenient and rapid way by collecting the respective NIR spectra [49].

Among the early methods for the identification of lignin in a sample, colour reactions have been frequently used [50]. Thus, the treatment of wood or mechanical pulp with a mixture of phloroglucinol and hydrochloric acid results in the development of a reddish colour attributable to a condensation product between coniferaldehyde end-groups in lignin and phloroglucinol.

### 9.5.1 Wet chemistry methods

Today, a large number of wet chemistry methods exist by which lignin can be identified on the basis of its pattern of degradation products. Such methods have also been extensively used to get information about the structural details of different types of lignins. In Table 9.6, some commonly used methods have been collected. Each one of these methods will provide a piece of structural information but in most cases, the information is at best semi-quantitative.

Based on comprehensive work on spruce and birch MWL employing predominantly oxidation with permanganate–hydrogen peroxide and acidolysis respectively as analytical tools, a large number of degradation products has been identified and quantified [51, 56]. Based on these data, the concentration of individual inter-unit linkages present in the two lignins has been calculated and a structural scheme of spruce lignin, similar to that depicted in Fig. 9.8, was constructed [61]. An approach employing catalytic hydrogenation of spruce wood and subsequent identification of the degradation products was found to yield similar results in terms of functional groups and relative frequency of inter-unit linkages [54]. In a similar way, thioacetolysis (*i.e.* acid catalysed condensation of lignin with thioacetic acid), followed by alkaline hydrolysis and reduction with Raney nickel, has been applied on beech wood meal to degrade the lignin into a mixture of monomeric and oligomeric products. Several of these were identified and quantified providing data which formed the basis for a constitutional scheme of beech lignin [62, 63].

### 9.5.2 Nuclear magnetic resonance

Contrary to the wet chemical methods, analysis by nuclear magnetic resonance (NMR) does not degrade the sample and, consequently, all structural features in a lignin can be visualized. Despite the fact that analysis by either proton or carbon NMR results in crowded spectra with a severe overlap of signals, numerous spectra of lignins have been published and a large number of individual signals assigned [64–69]. By the use of spectral editing with, for example, the DEPT-sequence, permitting the separate analysis of CH-, CH<sub>2</sub>- and CH<sub>3</sub>-groups respectively, further details of the assignment of individual signals have been achieved [70]. Furthermore, the use of inverse gated decoupling combined with long delay times between pulses has permitted the quantitative analysis of <sup>13</sup>C NMR spectra thus providing reliable data on the amount of different types of carbon atoms in spruce MWL [71, 72].

Two-dimensional correlation spectra such as the HSQC-sequence can be used to separate the carbon and proton signals, thus permitting a much higher degree of accuracy in signal assignment. Furthermore, such spectra can be integrated in the *z*-direction to give quantitative information provided that a suitable reference signal has been chosen [73]. In Table 9.7, the result of such an integration is shown together with similar data taken from the literature and based on NMR, as well as on wet chemical methods.

**Table 9.6**

Wet chemistry methods for the analysis of lignin and lignin structures

Method	Reaction principle	Reference
Oxidation with KMnO <sub>4</sub> – H <sub>2</sub> O <sub>2</sub>	Oxidative elimination of side chains	[51, 52]
Thioacetolysis	Cleavage of alkyl-aryl ethers	[53]
Hydrogenolysis	Reductive cleavage of ethers	[54, 55]
Acidolysis	Hydrolytic cleavage of ethers	[56, 57]
Thioacidolysis	Hydrolytic cleavage of ethers	[4, 58]
Acetyl bromide – Zinc/Acetic anhydride	Reductive cleavage of ethers	[59, 60]

**Table 9.7**

Frequency of inter-unit linkages in MWL from spruce (*Picea abies*) based on integration of a 2D HSQC spectrum using the aromatic C2 as internal standard

Lignin structure	Number per C9-unit	Reference		
		[74] <sup>a</sup>	[54] <sup>b</sup>	[61] <sup>c</sup>
$\beta$ -O-4'	0.43	0.45	0.45	0.50
$\beta$ -5'	0.12	0.09	0.14	0.12
Dibenzodioxocin	0.05	0.07		
$\beta$ - $\beta$ '	0.035	0.06	0.07	0.02
$\beta$ -1'	0.02	0.01	0.09	0.07
Spirodienone	0.02	0.02		
Coniferyl alcohol	0.02	0.02	0.04	
Coniferaldehyde	0.03	0.04	0.04	
Vanillin	0.02	0.05	0.06	
Dihydroconiferyl alcohol	0.02	0.02	0.04	
5-5'		0.13	0.11	0.11
4-O-5'			0.035	0.04

<sup>a</sup> Based on quantitative <sup>13</sup>C NMR.

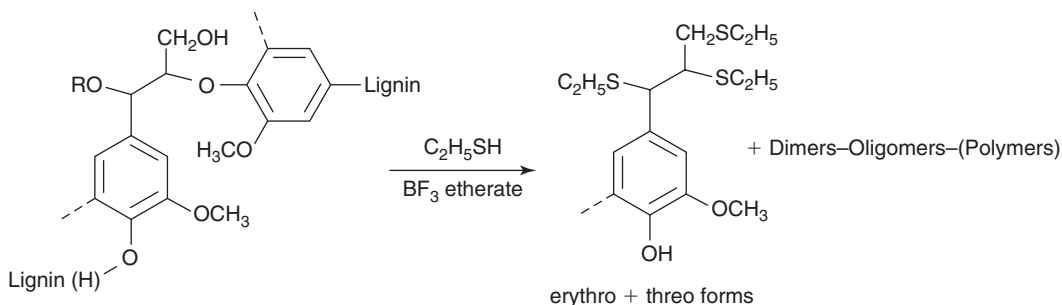
<sup>b</sup> Based on hydrogenolysis of ezomatsu (*Picea jezoensis*) wood.

<sup>c</sup> Based predominantly on permanganate-hydrogen peroxide oxidation.

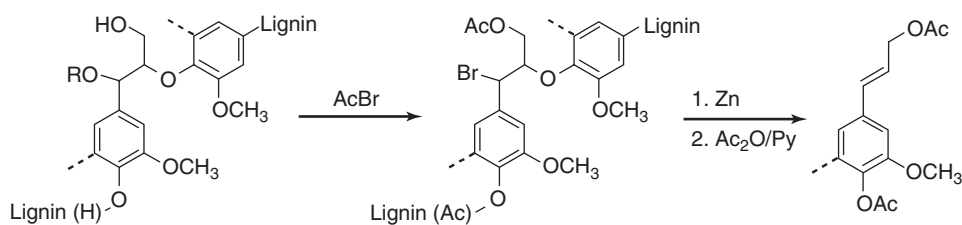
### 9.5.3 Analysis of $\beta$ -O-4 structures

The quantitatively most important inter-unit linkage in lignin, the  $\beta$ -O-4 linkage, can be cleaved in alkaline as well as in acidic conditions. For analytical purposes, alkaline cleavage is used as part of the thioacetolysis reaction sequence [53], whereas acidic conditions can be applied directly to the wood material [75]. In the latter method, hydrochloric acid has been used to afford monomeric and dimeric lignin degradation products which can be identified but, in addition, the reaction also gives rise to products of higher molecular mass, at least in part formed by condensation reactions [56]. Although the method can be used as an analytical tool to give a relative quantification of the number of  $\beta$ -O-4 structures, the presence of condensation reactions is a serious drawback [57]. The chemistry of lignin encountered in acid media, *viz.* the intermediate formation of a benzylic cation, followed by either a proton elimination reaction or an addition of a nucleophilic carbon atom, readily explains the observed behaviour. The presence of an external nucleophile may, however, in analogy to sulphite pulping or analysis by thioacetolysis, prevent any condensation reaction.

In thioacidolysis, a Lewis acid, boron trifluoride etherate, is used together with a strong nucleophile, ethanethiol, to hydrolyse all  $\beta$ -O-4 linkages present in a lignin, wood or pulp sample [20, 58]. The predominant product from the cleavage reaction (Fig. 9.10), a phenylpropane structure (two diastereoisomeric forms) having all side-chain carbons substituted with ethylthio groups, can be readily quantified. Furthermore, several other monomeric degradation products can also be identified, thus providing information about the variability of lignin end-groups [4].



**Figure 9.10** Thioacidolysis of lignin and formation of ethylthio-substituted degradation products.



**Figure 9.11** Analysis of  $\beta$ -O-4 structures in lignin according to the DFRC method (derivatization followed by reductive cleavage) resulting in the formation of cinnamyl alcohol derivatives suitable for quantification. AcBr = acetyl bromide, Ac<sub>2</sub>O/Py = acetic anhydride/pyridine [59].

From wood, the reaction gives a high yield of low molecular mass degradation products (monomers to trimers, with traces of higher  $M_w$  products) and, after treatment, no lignin can be detected in the remaining wood material. Thioacidolysis, when applied to kraft pulps, on the other hand, in addition to monomers–trimers also results in the presence of polymeric material formed as a consequence of pulping reactions [20].

In a later extension of the thioacidolysis reaction, a second step, a Raney nickel reduction, was introduced, thereby also permitting the analysis of dimeric and trimeric degradation products by gas chromatography [20, 76]. By this method, more than 20 different dimeric and 16 trimeric structures, representing all the various inter-unit linkages depicted in Fig. 9.5, except the  $\beta$ -O-4 and dibenzodioxocin structures, have been qualitatively identified from spruce wood. Similar data from birch and aspen wood are also available [23].

A different approach to the analysis of  $\beta$ -O-4 structures involves a two-step procedure with acetyl bromide treatment followed by a reductive cleavage of the  $\beta$ -ether substituent as depicted in Fig. 9.11 [59, 60]. The reaction can be applied to isolated lignins, as well as on cell wall material, and results in the formation of acetylated cinnamyl alcohols which can be readily quantified by gas chromatography. The yield of the major compounds originating from G-, H- and S-units seems, however, to be inferior to the corresponding values obtained from thioacidolysis [20, 60, 76].

Thioacidolysis results in a high yield of the major monomeric degradation product (in two diastereoisomeric forms) from softwoods, as well as from hardwoods. In addition, it is possible to identify several other monomers in minor amounts (Fig. 9.2) [4]. The latter are assumed to constitute lignin end-groups attached to the rest of the polymer through  $\beta$ -O-4' linkages. By pre-swelling of the wood in water prior to the thioacidolysis reaction, an apparent quantitative delignification can be achieved and the yield of the major monomer(s) substantially increased, as shown in Table 9.8. From this table, it is also obvious that the milling used to extract MWL from the wood samples

**Table 9.8**

Yield of the main monomer(s) on thioacidolysis of spruce, birch and aspen wood, spruce TMP and the corresponding MWLs together with the number of phenolic hydroxyl groups per 100 phenylpropane (C9) units [20, 23]

Sample	Yield of the main monomer(s) ( $\mu\text{mol/g}$ Klason lignin)	Content of phenolic OH <sup>a</sup> , Number per 100 C9-units <sup>b</sup>
Spruce wood	1 332	n.a. <sup>c</sup>
Spruce wood (pre-swollen) <sup>d</sup>	1 682 (31%) <sup>e</sup>	13
Spruce MWL <sup>f</sup>	986	20
Spruce TMP <sup>g</sup> (pre-swollen) <sup>d</sup>	1 498	14
Birch wood (pre-swollen) <sup>d</sup>	672 (G) + 2 318 (S) = 2 990 (63%) <sup>e</sup>	7.6
Birch MWL <sup>f</sup>	403 (G) + 809 (S) = 1 212	n.a. <sup>c</sup>
Aspen wood (pre-swollen) <sup>d</sup>	866 (G) + 1 942 (S) = 2 808 (58%) <sup>e</sup>	10
Aspen MWL <sup>f</sup>	609 (G) + 863 (S) = 1 472	n.a. <sup>c</sup>

<sup>a</sup> Determination by periodate oxidation according to [40].

<sup>b</sup> Assumed molecular mass ( $\text{g mol}^{-1}$ ) for one C9-unit: spruce = 183; birch = 210; aspen = 206.

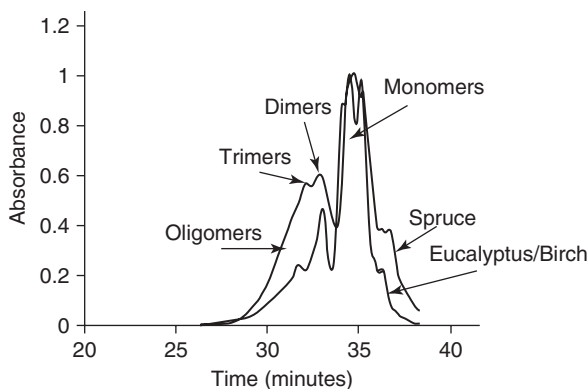
<sup>c</sup> n.a. = not analysed.

<sup>d</sup> Sample pre-swollen in water over-night.

<sup>e</sup> Percentage of the theoretical yield of C9-units per gram Klason lignin.

<sup>f</sup> Yield given as  $\mu\text{mol g}^{-1}$  MWL.

<sup>g</sup> Thermomechanical pulp.



**Figure 9.12** HPSEC on styragel of the acetylated lignin degradation products obtained after thioacidolysis of spruce, birch and eucalyptus wood respectively.

results in substantially reduced amounts of monomeric thioacidolysis products, as discussed above (see Figure 9.7). Simultaneously, the number of phenolic hydroxyl groups is strongly increased. Even the comparatively mild milling procedure used in the production of thermomechanical pulp (TMP), results in an increased number of phenolic hydroxyl groups and a reduction in monomer yield. In the two hardwood samples shown in Table 9.8, the yield of S-units is high and reflects the fact that  $\beta$ -O-4' structures are completely dominant in syringyl type lignins, since the  $\beta$ -5' and 5-5' coupling modes cannot take place. Generally, the content of phenolic hydroxyl groups in hardwoods is lower as compared to softwoods; a result in line with a high abundance of linear  $\beta$ -O-4'-linked syringyl lignin. In guaiacyl lignins, on the other hand,  $\beta$ -O-4' moieties may be present in both linear and branched/crosslinked structures, thus resulting in a considerably lower yield of the monomeric thioacidolysis product.

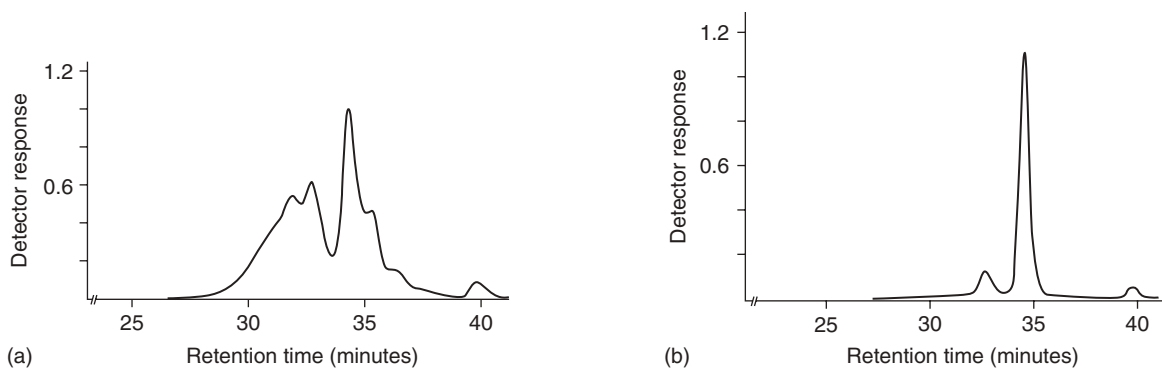
When applied to wood, the thioacidolysis reaction seems to result in a complete dissolution of lignin, since no Klason lignin can be detected in the residue. After acetylation, the degraded lignin fragments can be conveniently analysed by high performance size exclusion chromatography (HPSEC) in tetrahydrofuran [20]. From spruce, as well as from birch and eucalyptus wood, similar chromatograms can be obtained, although the relative intensity of the various peaks is different (Fig. 9.12) (Gellerstedt, unpublished). By the use of calibration substances, it can be shown that no polymeric material is present in the degradation mixture with monomers, dimers and trimers constituting the predominant types of products.

This result is completely in line with the view that the lignin polymer in both softwoods and hardwoods is built up with  $\beta$ -O-4' linkages as the completely dominating type of inter-unit linkage. The number of such linkages has been estimated based on analytical data from MWL, and values of about 50 and 60 per 100 phenylpropane units for spruce and birch, respectively, have been obtained [77]. Obviously, these values must be much higher for the native lignin in wood since, as discussed above, the milling procedure used to produce MWL involves a comprehensive cleavage of  $\beta$ -O-4' linkages (see Fig. 9.7 and Table 9.8).

#### 9.5.4 Lignin heterogeneity

By a selective modification of the cellulose structure in spruce wood, by treatment with an endoglucanase, followed by swelling of the wood in aqueous urea and dissolution in alkali, a subsequent stepwise acidification will result in a complete recovery of all the lignin as different LCCs (see Table 9.5) [27,41]. On thioacidolysis followed by HPSEC of the various LCCs, large differences in the resulting lignin chromatograms were encountered, as demonstrated in Fig. 9.13.

Thus, the thioacidolysis mixture obtained from xylan-linked lignin showed a complete dominance of monomers with only a small amount of dimers present. The glucomannan lignin complex, on the other hand, gave a chromatogram similar to that obtained from wood (Fig. 9.12). A reasonable explanation for these results is the presence of two distinctly different types of lignin in spruce wood; one having a very strong dominance of  $\beta$ -O-4' linkages, being linked to xylan and with a rather linear structure, the other being linked to glucomannan and having a more complex structure comprising the various linkages depicted in Fig. 9.5. The former type of lignin



**Figure 9.13** HPLC of thioacidolysis products obtained from (a) glucomannan-linked lignin, and (b) xylan-linked lignin [41].

**Table 9.9**

Distribution of guaiacyl and syringyl lignin in various morphological regions of white birch (*Betula papyrifera*) [78]

Morphological differentiation	Guaiacyl/Syringyl
Fibre, S2-layer	12:88
Vessel, S2-layer	88:12
Ray parenchyma, S-layer	49:51
Middle lamella (fibre–fibre)	91:9
Middle lamella (fibre–vessel)	80:20
Middle lamella (fibre–ray)	100:0
Middle lamella (ray–ray)	88:12

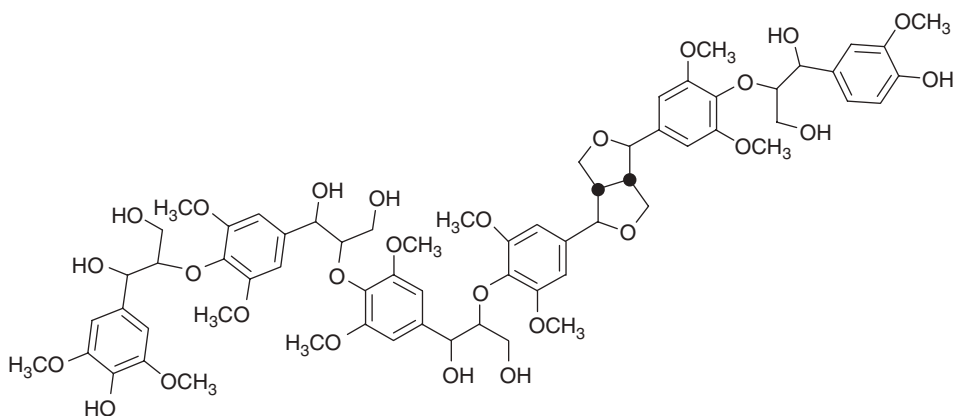
should be expected to be particularly sensitive to milling, resulting in a low yield of thioacidolysis products with a corresponding high amount of free phenolic hydroxyl groups. This has been found to be the case, thus lending further support to the view that a linear  $\beta$ -O-4'-linked lignin is present in spruce wood [41].

For birch wood, it was shown a long time ago, by the use of UV microscopy, that the structure of lignin is not uniform throughout the fibre and vessel elements. Whereas the secondary wall in the fibre fraction was found to contain an almost pure syringyl lignin (*i.e.* a linear lignin with a predominance of  $\beta$ -O-4' linkages) the lignin present in vessels was of the guaiacyl type. Guaiacyl lignin was also found in the middle lamella region [29]. In a further development of the analytical method, more precise data for the presence of G- and S-units throughout the cell walls were obtained (Table 9.9) [78].

By the use of an immunogold labelling technique with specific response for condensed guaiacyl and guaiacyl-syringyl lignin and for non-condensed guaiacyl-syringyl lignin respectively, the data in Table 9.9 have recently been qualitatively confirmed in transmission electron microscopy studies of aspen wood [79]. Further support for the presence of linear lignin structures of the  $\beta$ -O-4' type present in hardwood has also been found by the mass spectrometric analysis of a low molecular mass fraction of eucalyptus lignin, showing the arrangement of S (and G)-units in pentamer and hexamer fragments (Fig. 9.14) [80].

### 9.5.5 The structure of native lignin

The growing awareness that the structure of lignin inside the fibre wall is not uniform, but probably adapted to its site of formation, chemical surrounding and other as yet unknown factors makes the presentation of statistical formulas based on MWL-data alone highly uncertain. The presence of a substantial amount of lignin in spruce, as well as in various hardwood species strongly enriched in  $\beta$ -O-4' structures suggests, however, that linear lignin macromolecules are abundant in both softwood and hardwood lignin. These, as well as other types of lignin macromolecules,



**Figure 9.14** A hexameric lignin fragment from eucalyptus (*E. grandis*) identified by MS-analysis. Further pentamer and hexamer fragments were also found [80].

seem to be chemically linked to the polysaccharides thus forming network structures in the wood tissue. In technical processes, the different types of lignin macromolecules will show different reactivity, thus resulting in inhomogeneous dissolution at the nano-scale [81–83].

The knowledge collected till date on the structure of lignin distinguishes two different types of macromolecules; *viz.* a linear structure predominantly built up by  $\beta$ -*O*-4' linkages in G- as well as in S-units, with minor amounts of  $\beta$ - $\beta'$ ,  $\beta$ -5' and  $\beta$ -1' linkages present. The number of 5-5' and 4-*O*-5' linkages in such lignin is assumed to be very low or zero. As a consequence, the number of free phenolic hydroxyl groups is also very low. In the second type of lignin, a much more branched structure should prevail, 5-5' and 4-*O*-5' linkages being present and the number of phenolic hydroxyl groups quite high. In spruce, this type of lignin should be linked predominantly to glucomannan. The presence of such a lignin requires the formation of chain-like fragments which subsequently are linked together by a secondary formation of 5-5' and 4-*O*-5' linkages (see Section 9.3). The variability of the chain-like fragments can be substantial, thus resulting in lignin macromolecules of considerable difference from each other. Still, the number of  $\beta$ -*O*-4' linkages must be high, however, in order to fulfil all structural requirements concluded from present knowledge. A segment of such lignin is shown in Fig. 9.15.

## 9.6 TECHNICAL LIGNINS

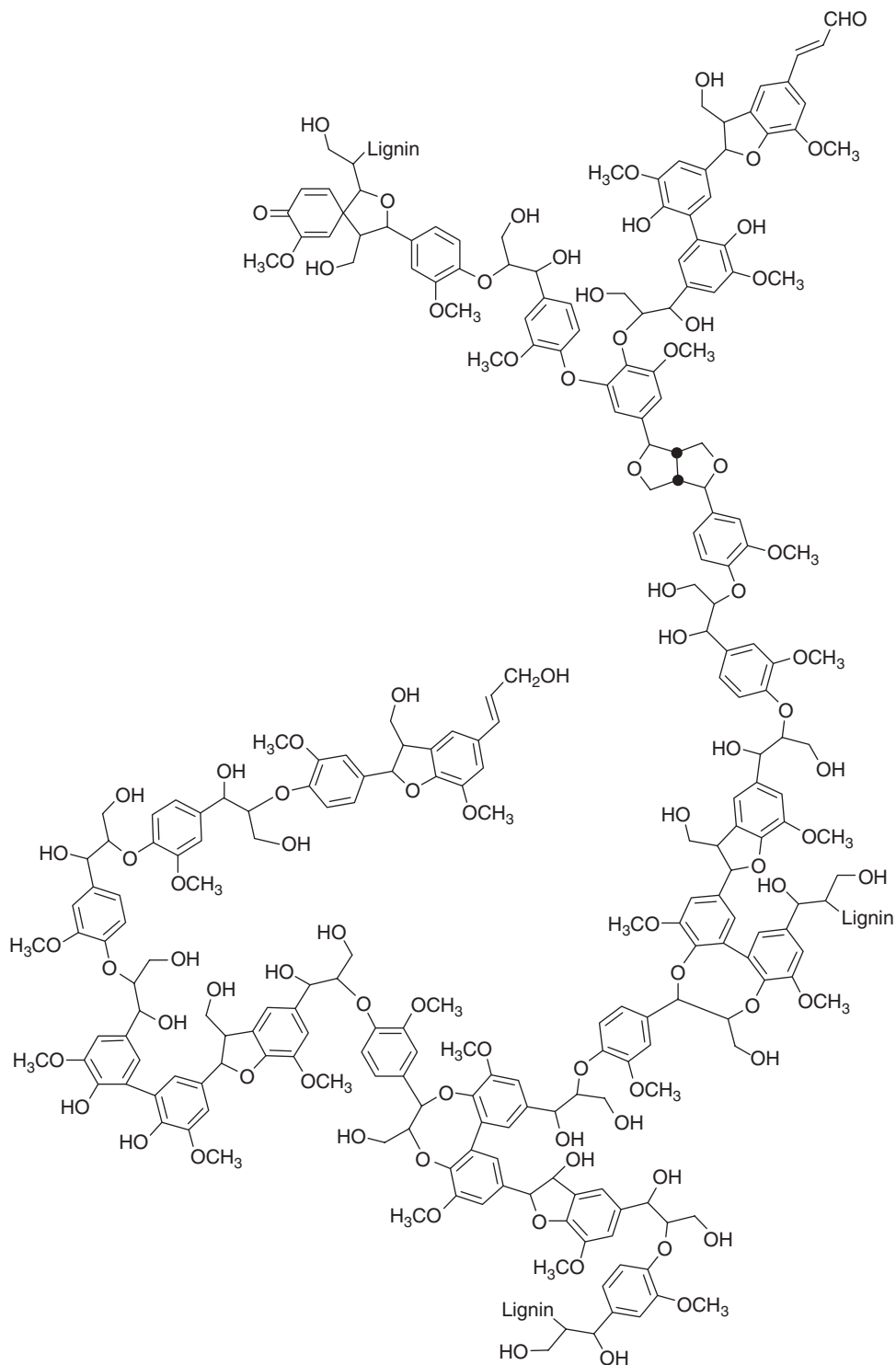
For a more comprehensive discussion of technical lignins, the reader should refer to Chapter 10.

### 9.6.1 Kraft lignins

Delignification of wood and other biomass for the production of kraft pulp involves treatment at high temperature with an aqueous solution of sodium hydroxide and sodium sulphide. Under these conditions, most of the  $\beta$ -*O*-4' structures in lignin are hydrolysed (>95 per cent) and the resulting lignin fragments dissolved in the alkaline solution [84]. Several other degradative lignin reactions also take place under the harsh conditions prevailing in the digester and most of the phenylpropane side-chains are in part eliminated, in part modified. The process results in the dissolution of around 90–95 per cent of all lignin present in the starting material. By acidification of the pulping liquor, the dissolved lignin can be recovered to a great extent as a complex mixture of phenolic structures with molecular mass in the range of ~150–200 000 [85–89].

By solvent fractionation, it has been shown that a predominant portion of softwood kraft lignin is of low molecular mass with a low degree of polydispersity as shown in Table 9.10. The remainder, on the other hand, has both high molecular mass and high polydispersity, presumably due to the presence of both polysaccharides and condensed lignin structures in these fractions [88]. A similar fractionation technique applied to a birch kraft lignin gave the results shown in Table 9.11, again with a high molecular mass tail resulting in a high degree of polydispersity for one of the fractions [89].





**Figure 9.15** Statistical scheme of the glucomannan-linked lignin from spruce. The structure contains 25 phenylpropane units with a total of 4 free phenolic hydroxyl groups. The proportion of inter-unit lignin linkages is: 12  $\beta$ -*O*-4' (2 in dibenzodioxocin), 5  $\beta$ -5', 4 4-5' (2 in dibenzodioxocin), 1 4-*O*-5', 1  $\beta$ - $\beta$ ', 1  $\beta$ -1', 1 coniferaldehyde, 1 coniferyl alcohol.

**Table 9.10**

Analytical data on kraft lignins obtained after solvent fractionation of isolated industrial softwood black liquor lignin [88]

Fraction No <sup>a</sup>	Yield (%)	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub>	Phenolic OH (mmol/g)	Aliphatic OH (mmol/g)	Carboxyl (mmol/g)
1	9	450	620	1.4	5.1	1.0	2.3
2	22	900	1290	1.4	5.0	2.3	1.1
3	26	1710	2890	1.7	4.3	2.1	0.8
4	28	3800	82000	22	3.9	2.4	0.4
5	14	5800	180000	31	3.0	2.4	0.3

<sup>a</sup> Fraction 1 = soluble in methylene chloride.Fraction 2 = residue soluble in *n*-propanol.

Fraction 3 = residue soluble in methanol.

Fraction 4 = residue soluble in methanol/methylene chloride (7:3).

Fraction 5 = residue.

<sup>b</sup> Acetylated lignin fractions.**Table 9.11**

Analytical data on kraft lignins obtained after solvent fractionation of isolated industrial birch black liquor lignin [89]

Fraction no <sup>a</sup>	Yield (%)	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub>	Phenolic OH (mmol/g)	Aliphatic OH (mmol/g)
1	32	650	910	1.4	5.0	1.0
2	38	1320	2110	1.6	4.4	2.2
3	30	3760	87080	23	2.9	3.7

<sup>a</sup> Fraction 1 = soluble in methylene chloride.

Fraction 2 = residue soluble in methanol.

Fraction 3 = residue.

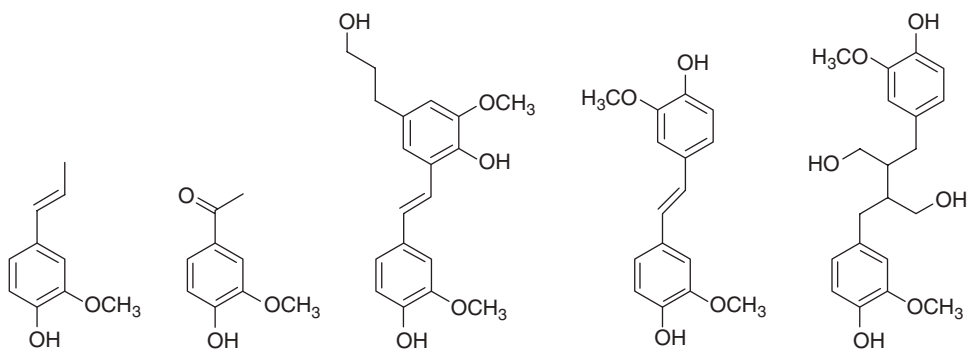
<sup>b</sup> Acetylated lignin fractions.**Table 9.12**

Elemental and methoxyl analysis data for softwood kraft lignin fractions from Table 9.10 together with data for spruce MWL and purified pine kraft lignin [88]

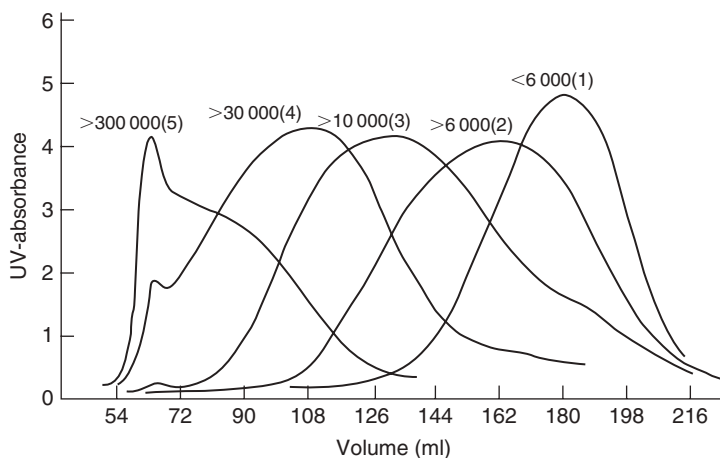
Fraction no	Carbon (%)	Hydrogen (%)	Oxygen (%)	Sulphur (%)	OCH <sub>3</sub> (%)	Sugars (%)
1	67.8	6.43	23.0	2.7	15.4	–
2	65.3	6.48	26.8	1.4	16.0	–
3	64.7	5.96	27.7	1.5	14.9	–
4	64.5	5.73	28.2	1.3	13.9	0.3
5	59.0	5.54	32.8	1.2	11.3	8.7
MWL, spruce <sup>a</sup>	63.8	6.0	29.7	–	15.8	–
Kraft lignin <sup>b</sup>	64.3	6.0	27.9	1.8	13.8	0.9

<sup>a</sup> Reference [30].<sup>b</sup> Reference [91].

NMR analysis of the various lignin fractions from pine/spruce and birch respectively [88, 89], as well as of unfractionated kraft lignin from pine [71], has shown that comprehensive changes of the side-chain structure take place during pulping with a strong reduction of oxygen-linked carbons and a concomitant increase of aliphatic methine, methylene and methyl groups. The content of aromatic rings with free phenolic hydroxyl groups is high, in particular in the low molecular mass fractions. The presence of carboxyl groups (in softwood) is substantial and can be explained by radical coupling reactions between certain fatty acids, present among the wood extractives, and phenolic end-groups in the lignin [90]. Moreover, all the lignin fractions shown in Table 9.10 also contain considerable amounts of sulphur as shown in Table 9.12. Similar data were also found for the birch lignin fractions.



**Figure 9.16** Some representative lignin fragments present in spruce kraft pulping liquor.



**Figure 9.17** Size exclusion chromatography of lignosulphonate fractions after ultrafiltration. Fraction number and approximate molecular mass are shown in the figure [92].

Several hundred low molecular mass lignin-derived components containing one or two aromatic rings have been identified in kraft pulping liquors from spruce and birch respectively [86, 87]. Some prominent structures are shown in Fig. 9.16.

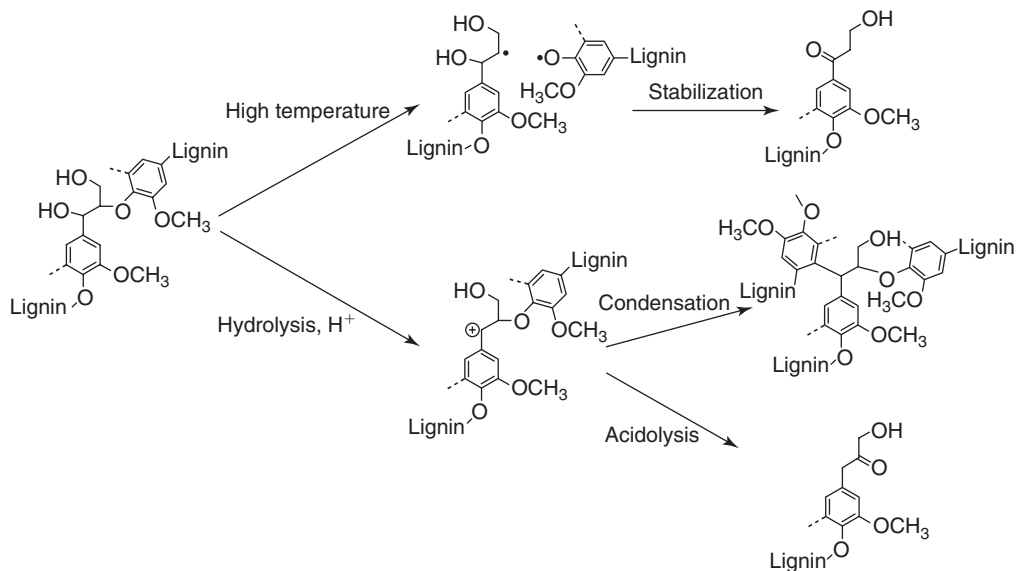
## 9.6.2 Sulphite lignin

The major reaction in sulphite pulping involves the introduction of sulphonate groups in the  $C_\alpha$ -positions in lignin via the intermediate formation of carbo-cations. Thereby, any lignin-carbohydrate linkages present in these positions are cleaved and, together with some hydrolytic cleavage of  $\beta$ - $O$ -4' linkages, the lignin is solubilized. Condensation, predominantly between  $C_\alpha$  and  $C_6$  in adjacent lignin structures, is a major competing reaction, but can be suppressed by having a high concentration of bisulphite ions present in the pulping liquor. The highly water-soluble lignosulphonate can be purified from other substances present in the pulping liquor by ultrafiltration and by using membranes having different  $M_w$  cut-off values, a series of lignosulphonate fractions can be obtained as shown in Fig. 9.17 [92]. By elemental and methoxyl analysis on these fractions, a degree of sulphonation of about 0.4–0.5 per phenylpropane unit has been found. The liberation of phenolic hydroxyl groups, on the other hand, is limited but clearly visible in those lignosulphonate fractions having a low molecular mass distribution (Table 9.13). In comparison with kraft lignins, the side-chains in lignosulphonates are still intact to a high degree, as revealed by  $^{13}\text{C}$  NMR spectroscopy, although some  $\alpha$ -carbon atoms are linked in condensation reactions [93].

**Table 9.13**

Analytical data of lignosulphonate fractions after ultrafiltration of a technical softwood acid sulphite pulping liquor [92]

Fraction no	Yield (%)	M <sub>w</sub>	Phenolic OH (mmol/g)	Sulphonate/Phenylpropane
1	20	590	2.01	0.48
2	29	1 440	0.91	0.52
3	18	3 690	0.65	0.43
4	4	6 500	0.50	0.40
5	6	10 880	0.49	0.39
6	22	21 950	0.51	0.36

**Figure 9.18** Types of lignin reactions encountered during steam explosion. The relative importance may differ depending on the steam treatment conditions.

### 9.6.3 Steam explosion lignin

By subjecting wood or other biomass to high temperature steam treatment, followed by a rapid pressure release, the fibrous mass is 'exploded' and liberated fibres together with fibre bundles are formed. By adjusting the time and temperature, different degrees of wood polymer modification and degradation can be achieved. Although the process is not commercial at present, it has gained much attention as a possible means for simple and cheap separation of wood polymers (*e.g.* for the production of micro-crystalline cellulose and bio-based ethanol). In particular, hardwood species such as aspen are suitable raw materials, since the lignin portion can be extracted, to a large extent, by either aqueous alkali or by organic solvents leaving a residue highly enriched in cellulose [94, 95].

In a pure steam explosion process without any added chemicals, the reaction conditions are weakly acidic, due to the release of acetic acid from the hemicellulose. Thus, the major reaction types are similar to those present in acidic sulphite pulping, *viz.* hydrolysis of polysaccharides and hydrolysis and condensation of lignin. In addition, due to the high temperature usually employed (~200°C), homolytic cleavage reactions of, for example, β-O-4' linkages in lignin can be assumed to take place. The reaction types for lignin are summarized in Fig. 9.18. Altogether, these reactions result in a highly heterogeneous lignin structure containing both degraded lignin fragments and recombined fragments through condensation reactions [96]. Consequently, the number of β-O-4' structures is much lower, as compared with that of the starting material and the content of phenolic end-groups higher. In addition, the number of carbonyl groups is considerably increased due to hydrolytic and/or homolytic cleavage reactions.

## REFERENCES

1. Fengel D., Wegener G., *Wood. Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin, 1984. pp. 132–181.
2. Sjöström E., *Wood Chemistry. Fundamentals and Applications*, 2nd Edition, Academic Press Inc., San Diego, USA, 1993. pp. 71–91.
3. Sakakibara A., Sano Y., Chemistry of lignin, in *Wood and Cellulosic Chemistry* (Eds. Hon D.N.-S. and Shiraishi N.), 2nd Edition, Marcel Dekker Inc., New York, USA, 2001, pp. 109–174.
4. Rolando C., Monties B., Lapierre C., Thioacidolysis, in *Methods in Lignin Chemistry* (Eds. Lin S.Y. and Dence C.W.), Springer-Verlag, Berlin Heidelberg, Germany, 1992, pp. 334–349.
5. Ralph J., Lu F., The DFRC method for lignin analysis. 6. A simple modification for identifying natural acetates on lignins, *J. Agr. Food Chem.*, **46**, 1998, 4616–4619.
6. Chen C.-L., Nitrobenzene and cupric oxide oxidations, in *Methods in Lignin Chemistry* (Eds. Lin S.Y. and Dence C.W.), Springer-Verlag, Berlin Heidelberg, Germany, 1992, p. 301.
7. Higuchi T., Lignin biochemistry: Biosynthesis and biodegradation, *Wood Sci. Technol.*, **24**, 1990, 23–63.
8. Boudet A.-M., Lignins and lignification: Selected issues, *Plant Physiol. Biochem.*, **38**, 2000, 81–96.
9. Donaldson L.A., Lignification and lignin topochemistry – An ultrastructural view, *Phytochemistry*, **57**, 2001, 859–873.
10. Freudenberg K., in *Constitution and Biosynthesis of Lignin* (Eds. Freudenberg K. and Neish A.C.), Springer-Verlag, Berlin Heidelberg, 1968, pp. 47–122.
11. Katayama Y., Fukuzumi T., Enzymatic synthesis of three lignin-related dimers by an improved peroxidase–hydrogen peroxide system, *Mokuzai Gakkaishi*, **24**, 1978, 664–667.
12. Ralph J., Lundquist K., Brunow G., Lu F., Kim H., Schatz P.F., Marita J.M., Hatfield R.D., Ralph S.A., Christensen J.H., Boerjan W., Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenylpropanoids, *Phytochemistry Rev.*, **3**, 2004, 29–60.
13. Zhang L., Gellerstedt G., Ralph J., Lu F., NMR studies on the occurrence of spirodienone structures in lignins, *J. Wood Chem. Technol.*, **26**, 2006, 65–79.
14. Karhunen P., Rummakko P., Sipilä J., Brunow G., Kilpeläinen I., Dibenzodioxocins; a novel type of linkage in softwood lignins, *Tetrahedron Lett.*, **36**, 1995, 169–170.
15. Argyropoulos D.S., Jurasek L., Kristofova L., Xia Z., Dun Y., Palus E., Abundance and reactivity of dibenzodioxocins in softwood lignin, *J. Agr. Food Chem.*, **50**, 2002, 658–666.
16. Lewis N.G., A 20th century roller coaster ride: A short account of lignification, *Current Opin. Plant Biol.*, **2**, 1999, 153–162.
17. Davin L.B., Lewis N.G., Lignin primary structure and dirigent sites, *Current Opin. Biotechnol.*, **16**, 2005, 407–415.
18. Fengel D., Wegener G., *Wood. Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin, 1984. pp. 56–58
19. dos Santos Abreu H., Maria M.A., Reis J.L., Dual oxidation ways toward lignin evolution, *Floresta e Ambiente*, **8**, 2001, 207–210.
20. Önerud H., Gellerstedt G., Inhomogeneities in the chemical structure of spruce lignin, *Holzforschung*, **57**, 2003, 165–170.
21. Önerud H., Lignin structures in normal and compression wood. Evaluation by thioacidolysis using ethanethiol and methanethiol, *Holzforschung*, **57**, 2003, 377–384.
22. Sjöström E., *Wood Chemistry. Fundamentals and Applications*, 2nd Edition, Academic Press Inc., San Diego, USA, 1993, p. 249.
23. Önerud H., Gellerstedt G., Inhomogeneities in the chemical structure of hardwood lignins, *Holzforschung*, **57**, 2003, 255–265.
24. Bassa A., Sacon V.M., da Silva Junior F.G. and Barrichelo L.E.G. Polpacao kraft convencional e modificada para madeiras de Eucalyptus grandis e hibrido (E. grandis x E. urophylla), 35° Congresso e Exposicao Anual de Celulose e Papel, Sao Paulo, Brazil, October 14–17, 2002, Proceedings, p. 5.
25. del Rio J.C., Rodriguez I.M. and Gutierrez A. Chemical characterization of fibers from herbaceous plants commonly used for manufacturing of high quality paper pulps. 9th European Workshop on Lignocellulosics and Pulp, Vienna, Austria, August, 27–30, 2006, Proceedings, pp. 109–112.
26. [http://www.vcn.vnn.vn/sp\\_pape/spec\\_5\\_4\\_2001\\_13.htm](http://www.vcn.vnn.vn/sp_pape/spec_5_4_2001_13.htm).
27. Lawoko M., Henriksson G., Gellerstedt G., Characterization of lignin–carbohydrate complexes (LCCs) of spruce wood (*Picea abies* L.) isolated with two methods, *Holzforschung*, **60**, 2006, 156–161.
28. Fergus B.J., Procter A.R., Scott J.A.N., Goring D.A.I., The distribution of lignin in sprucewood as determined by ultraviolet microscopy, *Wood Sci. Technol.*, **3**, 1969, 117–138.
29. Fergus B.J., Goring D.A.I., The distribution of lignin in birch wood as determined by ultraviolet microscopy, *Holzforschung*, **24**, 1970, 118–124.
30. Björkman A., Studies on finely divided wood. Part 1. Extraction of lignin with neutral solvents, *Svensk Papperstidn.*, **59**, 1956, 477–485.
31. Björkman A., Person B., Studies on finely divided wood. Part 2. The properties of lignins extracted with neutral solvents from softwoods and hardwoods, *Svensk Papperstidn.*, **60**, 1957, 158–169.

32. Björkman A., Studies on finely divided wood. Part 3. Extraction of lignin-carbohydrate complexes with neutral solvents, *Svensk Papperstidn.*, **60**, 1957, 243–251.
33. Brownell H.H., Isolation of milled wood lignin and lignin-carbohydrate complex, *Tappi*, **48**(9), 1965, 513–519.
34. Chang H-m., Cowling E.B., Brown W., Adler E., Miksche G., Comparative studies on cellulolytic enzyme lignin and milled wood lignin of sweetgum and spruce, *Holzforschung*, **29**, 1975, 153–159.
35. Glasser W.G., Barnett C.A., The structure of lignins in pulps. II. A comparative evaluation of isolation methods, *Holzforschung*, **33**, 1979, 78–86.
36. Bezuch B., Polcin J., The structural study of milled wood and enzymatically isolated lignin fractions from spruce wood, *Cell. Chem. Technol.*, **12**, 1978, 473–482.
37. Wu S., Argyropoulos D.S., An improved method for isolating lignin in high yield and purity, *J. Pulp Pap. Sci.*, **29**, 2003, 235–240.
38. Yang J.-M., Goring D.A.I., The phenolic hydroxyl content of lignin in spruce wood, *Can. J. Chem.*, **58**, 1980, 2411–2414.
39. Gellerstedt G., Lindfors E.-L., Structural changes in lignin during kraft cooking. Part 4. Phenolic hydroxyl groups in wood and kraft pulps, *Svensk Papperstidn.*, **87**, 1984, R115–R118.
40. Lai Y.-Z., Guo X.-P., Variation of the phenolic hydroxyl group content in wood lignins, *Wood Sci. Technol.*, **25**, 1991, 467–472.
41. Lawoko M., Henriksson G., Gellerstedt G., Structural differences between the lignin-carbohydrate complexes present in wood and in chemical pulps, *Biomacromolecules*, **6**, 2005, 3467–3473.
42. Freudenberg K., in *Constitution and Biosynthesis of Lignin* (Eds. Freudenberg K. and Neish A.C.), Springer-Verlag, Berlin-Heidelberg, 1968, p. 103.
43. Nimz H., Mogharab I., Ludemann H.-D., <sup>13</sup>C-Kernresonanzspektren von Ligninen, 3. Vergleich von Fichtenlignin mit kunstlichem Lignin nach Freudenberg, *Macromol. Chem.*, **175**, 1974, 2563–2575.
44. Terashima N., Atalla R.H., Ralph S.A., Landucci L.L., Lapierre C., Monties B., New preparations of lignin polymer models under conditions that approximate cell wall lignification. I. Synthesis of novel lignin polymer models and their structural characterization by <sup>13</sup>C NMR, *Holzforschung*, **49**, 1995, 521–527.
45. Terashima N., Atalla R.H., Ralph S.A., Landucci L.L., Lapierre C., Monties B., New preparations of lignin polymer models under conditions that approximate cell wall lignification. II. Structural characterization of the models by thioacidolysis, *Holzforschung*, **50**, 1996, 9–14.
46. Landucci L.L., Reaction of *p*-hydroxycinnamyl alcohols with transition metal salts. 3. Preparation and NMR characterization of improved DHPs, *J. Wood Chem. Technol.*, **20**, 2000, 243–264.
47. Önerud H., Zhang L., Gellerstedt G., Henriksson G., Polymerization of monolignols by redox shuttle-mediated enzymatic oxidation: A new model in lignin biosynthesis, *Plant Cell*, **14**, 2002, 1953–1962.
48. Dence C.W., The determination of lignin, in *Methods in Lignin Chemistry* (Eds. Lin S.Y. and Dence C.W.), Springer-Verlag, Berlin Heidelberg, Germany, 1992, pp. 33–61.
49. Wallbäcks L., Edlund U., Norden B., Berglund I., Multivariate characterization of pulp using solid-state carbon-13 NMR, FTIR and NIR, *Tappi J.*, **74**(10), 1991, 201–206.
50. Nakano J., Meshitsuka G., The detection of lignin, in *Methods in Lignin Chemistry* (Eds. Lin S.Y. and Dence C.W.), Springer-Verlag, Berlin Heidelberg, Germany, 1992, pp. 23–32.
51. Erickson M., Larsson S., Miksche G.E., Gaschromatografische Analyse von Ligninoxidationsprodukten. VII. Ein verbessertes Verfahren zur Charakterisierung von Ligninen durch Methylierung und oxydativen Abbau, *Acta Chem. Scand.*, **27**, 1973, 127–140.
52. Gellerstedt G., Permanganate oxidation, in *Methods in Lignin Chemistry* (Eds. Lin S.Y. and Dence C.W.), Springer-Verlag, Berlin Heidelberg, Germany, 1992, pp. 322–333.
53. Nimz H., Über ein neues Abbauverfahren des Lignins, *Chem. Ber.*, **102**, 1969, 799–810.
54. Sakakibara A., A structural model of softwood lignin, *Wood Sci. Technol.*, **14**, 1980, 89–100.
55. Sakakibara A., Hydrogenolysis, in *Methods in Lignin Chemistry* (Eds. Lin S.Y. and Dence C.W.), Springer-Verlag, Berlin Heidelberg, 1992, pp. 350–368.
56. Lundquist K., Low-molecular weight lignin hydrolysis products, *Appl. Polym. Symp.*, **28**, 1976, 1393–1407.
57. Lapierre C., Rolando C., Monties B., Characterization of poplar lignins acidolysis products: Capillary gas-liquid and liquid-liquid chromatography of monomeric compounds, *Holzforschung*, **37**, 1983, 189–198.
58. Lapierre C., Monties B., Rolando C., Thioacidolysis of lignin: Comparison with acidolysis, *J. Wood Chem. Technol.*, **5**, 1985, 277–292.
59. Lu F., Ralph J., Derivatization followed by reductive cleavage (DFRC method), a new method for lignin analysis: Protocol for analysis of DFRC monomers, *J. Agr. Food Chem.*, **45**, 1997, 2590–2592.
60. Lu F., Ralph J., The DFRC method for lignin analysis. 2. Monomers from isolated lignins, *J. Agr. Food Chem.*, **46**, 1998, 547–552.

61. Adler E., Lignin chemistry – Past, present and future, *Wood Sci. Technol.*, **11**, 1977, 169–218.
62. Nimz H., Chemistry of potential chromophoric groups in beech lignin, *Tappi*, **56**(5), 1973, 124–126.
63. Nimz H., Beech lignin – Proposal of a constitutional scheme, *Angew. Chem.*, **13**, 1974, 313–321.
64. Lundquist K., Proton (<sup>1</sup>H) NMR spectroscopy, in *Methods in Lignin Chemistry* (Eds. Lin S.Y. and Dence C.W.), Springer-Verlag, Berlin Heidelberg, Germany, 1992, pp. 242–249.
65. Robert D., Carbon-13 nuclear magnetic resonance spectrometry, in *Methods in Lignin Chemistry* (Eds. Lin S.Y. and Dence C.W.), Springer-Verlag, Berlin Heidelberg, Germany, 1992, pp. 250–273.
66. Ludemann H.-D., Nimz H., Carbon-13 nuclear magnetic resonance spectra of lignins, *Biochem. Biophys. Res. Comm.*, **52**, 1973, 1162–1169.
67. Nimz H.H., Robert D., Faix O., Nemr M., Carbon-13 NMR spectra of lignins. 8. Structural differences between lignins of hardwoods, softwoods, grasses and compression wood, *Holzforschung*, **35**, 1981, 16–26.
68. Lundquist K., NMR studies of lignins. 2. Interpretation of the <sup>1</sup>H NMR spectrum of acetylated birch lignin, *Acta Chem. Scand.*, **B33**, 1979, 27–30.
69. Lundquist K., Paterson A., Ramsey L., NMR studies of lignins. 6. Interpretation of the <sup>1</sup>H NMR spectrum of acetylated spruce lignin in a deuterioacetone solution, *Acta Chem. Scand.*, **B37**, 1983, 734–736.
70. Bardet M., Foray M.-F., Robert D., Use of the DEPT pulse sequence to facilitate the <sup>13</sup>C NMR structural analysis of lignins, *Macromol. Chem.*, **186**, 1985, 1495–1504.
71. Gellerstedt G., Robert D., Quantitative <sup>13</sup>C NMR analysis of kraft lignins, *Acta Chem. Scand.*, **B41**, 1987, 541–546.
72. Robert D., Chen C.-L., Biodegradation of lignin in spruce wood by *Phanerochaete chrysosporium*: Quantitative analysis of biodegraded spruce lignins by <sup>13</sup>C NMR spectroscopy, *Holzforschung*, **43**, 1989, 323–332.
73. Zhang L. and Gellerstedt G. Quantitative 2D HSQC NMR determination of polymer structures by selecting suitable internal standard references. *Magn. Res. Chem.* **45**, 2007, 37–45.
74. Capanema E.A., Balakshin M.Y., Kadla J.F., A comprehensive approach for quantitative lignin characterization by NMR spectroscopy, *J. Agr. Food Chem.*, **52**, 2004, 1850–1860.
75. Gellerstedt G., Lindfors E.-L., Lapierre C., Monties B., Structural changes in lignin during kraft cooking. Part 2. Characterization by acidolysis, *Svensk Papperstidn.*, **87**, 1984, R61–R67.
76. Lapierre C., Pollet B., Monties B., Rolando C., Thioacidolysis of spruce lignin: GC–MS analysis of the main dimers recovered after Raney nickel desulphuration, *Holzforschung*, **45**, 1991, 61–68.
77. Sjöström E., *Wood Chemistry. Fundamentals and Applications*, 2nd Edition, Academic Press Inc., San Diego, USA, 1993. p. 82.
78. Saka S., Goring D.A.I., The distribution of lignin in white birch wood as determined by TEM–EDXA, *Holzforschung*, **42**, 1988, 149–153.
79. Grunwald C., Ruel K., Kim Y.S., Schmitt U., On the cytochemistry of cell wall formation in poplar trees, *Plant biol.*, **4**, 2002, 13–21.
80. Evtuguin D.V., Amado F.M.L., Application of electrospray ionization mass spectrometry to the elucidation of the primary structure of lignin, *Macromol. Biosci.*, **3**, 2003, 339–343.
81. Lawoko M., Henriksson G., Gellerstedt G., New method for the quantitative preparation of lignin–carbohydrate complex from unbleached softwood kraft pulp: Lignin–polysaccharide networks I., *Holzforschung*, **57**, 2003, 69–74.
82. Lawoko M., Berggren R., Berthold F., Henriksson G., Gellerstedt G., Changes in the lignin carbohydrate complex in softwood during kraft and oxygen delignification: Lignin–polysaccharide networks II., *Holzforschung*, **58**, 2004, 603–610.
83. Lawoko M., Henriksson G., Gellerstedt G., Characterization of lignin–carbohydrate complexes from spruce sulfite pulp, *Holzforschung*, **60**, 2006, 162–165.
84. Gellerstedt G. and Zhang L. Chemistry of TCF-bleaching with oxygen and hydrogen peroxide, in *Oxidative Delignification Chemistry. Fundamentals and Catalysis*, Ed. Argyropoulos D.S., *ACS Symposium Series* **785**, 2001, pp. 61–72.
85. Goring D.A.I., Polymer properties of lignin and lignin derivatives, in *Lignins. Occurrence, Formation, Structure and Reactions* (Eds. Sarkanen K.V. and Ludwig C.H.), Wiley-Interscience, New York, USA, 1971, pp. 695–768.
86. Gierer J., Lindeberg O., Reactions of lignin during sulfate pulping. Part XIX. Isolation and identification of new dimers from a spent sulfate liquor, *Acta Chem. Scand.*, **B34**, 1980, 161–170.
87. Niemelä, K. “*Low-Molecular-Weight Organic Compounds in Birch Kraft Black Liquor*”. Ph.D. Thesis, Helsinki University of Technology, 1990.
88. Mörck R., Yoshida H., Kringstad K., Hatakeyama H., Fractionation of kraft lignin by successive extraction with organic solvents. I. Functional groups, <sup>13</sup>C NMR-spectra and molecular weight distributions, *Holzforschung*, **40**(Suppl.), 1986, 51–60.
89. Mörck R., Reiman A., Kringstad K., Fractionation of kraft lignin by successive extraction with organic solvents. III. Fractionation of kraft lignin from birch, *Holzforschung*, **42**, 1988, 111–116.
90. Gellerstedt G., Majtnerova A., Zhang L., Towards a new concept of lignin condensation in kraft pulping. Initial results, *C. R. Biol.*, **327**, 2004, 817–826.

91. Gellerstedt G., Lindfors E.-L., Structural changes in lignin during kraft pulping, *Holzforschung*, **38**, 1984, 151–158.
92. Lin S.Y. and Detroit W.J. Chemical heterogeneity of technical lignins – Its significance in lignin utilization. *1st International Symposium on Wood and Pulping Chemistry*, Stockholm, Sweden, 1981, Proceedings, Volume 4, pp. 44–52.
93. Hassi H.Y., Chen C.-L. and Gratzl J.S. Carbon-13 NMR spectroscopic characterization of lignosulfonates. *Tappi Research and Development Conference*, Appleton, USA 1984, Proceedings, pp. 249–260.
94. DeLong E.A. Method of rendering lignin separable from cellulose and hemicellulose in lignocellulosic material and the product so obtained. Can. Pat. #1,096,374, 1981.
95. Josefsson T., Lennholm H., Gellerstedt G., Steam explosion of aspen wood. Characterization of reaction products, *Holzforschung*, **56**, 2002, 289–297.
96. Robert D., Bardet M., Lapierre C., Gellerstedt G., Structural changes in aspen lignin during steam explosion treatment, *Cell. Chem. Technol.*, **22**, 1988, 221–230.



# Industrial Commercial Lignins: Sources, Properties and Applications

Jairo Lora

---

## ABSTRACT

This chapter is devoted to review the interest of industrial lignins as materials, rather than fuels. It examines the different industrial technologies related to pulp manufacture in terms of the delignification process and, more importantly, the properties of the corresponding isolated lignins. Sulphite, kraft and soda lignins are therefore reviewed with an emphasis on their structural differences and hence their different domains of applications, including the unique polyelectrolyte features associated with lignosulphonates. Novel emerging technologies related to biomass conversion are also critically discussed, in particular steam explosion and organosolv pulping, with the purpose of illustrating the types of lignins produced and their potential usage.

## Keywords

Lignin, Industrial production, Sulphite pulping, Kraft pulping, Soda pulping, Lignosulphonates, Properties, Applications, Steam explosion, Organosolv technology

## 10.1 INTRODUCTION

Industrial lignins are currently obtained as co-products of the manufacture of cellulose pulp for paper and some chemical derivatives. Although the amount of lignin extracted in pulping operations around the world is estimated to be over 70 million tons per year, less than 2 per cent is actually recovered for utilization as a chemical product. The majority of the lignin extracted in pulp and paper operations is actually burned as part of the treatment of the spent pulping liquors for recovery of energy and regeneration of pulping chemicals.

In this chapter lignins that are available as commercial products in industrial quantities are discussed. The type of pulping process determines the type of lignin industrially available. There are three types of lignins, which correspond to the three dominant chemical pulping processes, namely sulphite, kraft and soda. During pulping the lignin structure is unavoidably modified from that in the original feedstock. For each type of lignin the main reactions and process involved, properties of the resulting lignin and its applications and main producers are reviewed. Chapter 9 of this book addresses the structure and properties of native lignins (*i.e.* as they exist in nature). The reader is also referred to that chapter for information on the type of repeating units normally found in the lignin structure and on the nomenclature used to designate the carbon atoms in the molecule.

In addition to currently available industrial lignins, this chapter includes a discussion on novel lignins that are potentially available in the near future from biorefinery operations, for instance, for the production of ethanol from lignocellulosic biomass.

## 10.2 SULPHITE LIGNIN

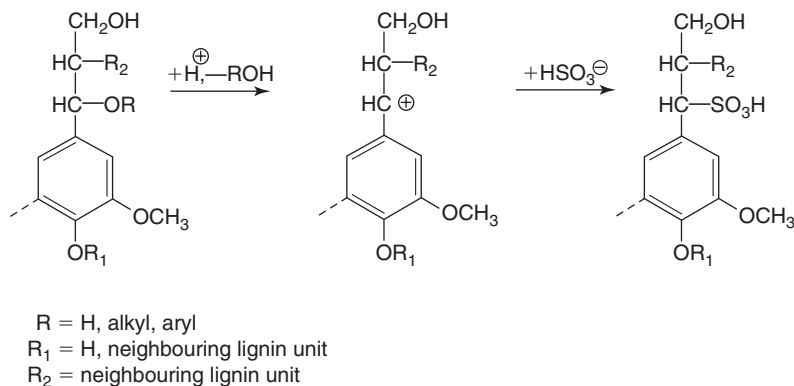
Sulphite lignin is produced in the sulphite pulping process and has historically been the most abundant type of industrial lignin commercially available. About 80 years ago, sulphite was the dominant type of pulping process [1]. It was initially developed based on the use of calcium bisulphite, an inexpensive pulping chemical. The lack of suitable technology for the regeneration of this chemical from the spent pulping liquor precipitated the development of uses for calcium lignosulphonate.

The sulphite pulping technology evolved to encompass the use of other sulphites and bisulphites, such as magnesium, ammonium and sodium. The resulting lignosulphonates found also applications, in some cases specially adapted to a given cation. For these pulping chemicals, recovery systems based on combustion of the organic components of the spent liquor were developed, facilitating environmental compliance without having to rely on lignosulphonate sales. With time, the sulphite pulping process started to lose ground relative to the kraft counterpart, which is more versatile and produces stronger pulps, and has a robust chemical recovery process. Thus, the days of sulphite pulping dominance are long gone and sulphite pulp production has declined from nearly 20 million tons in the 1980s [1] to about 7 million tons nowadays [2]. Current expectations are for continuing decline of sulphite pulp production, since no new sulphite mills have been built in over a quarter of a century and the shut down of antiquated inefficient units will negate small incremental increases that may happen at a few places. In spite of this trend, sulphite lignin production has managed to remain relatively stable, meeting a worldwide demand in which recent declines in consumption in Western Europe, North America and Japan have been offset by increases in China, India and other parts of the world.

### 10.2.1 Process

In the sulphite pulping process, wood is digested at 140–170°C with an aqueous solution of a sulphite or bisulphite salt of sodium, ammonium, magnesium or calcium. The type of salt and its solubility and dissociation characteristics determine the pH of the digestion. For instance, the pulping medium is highly acidic when calcium bisulphite is the pulping agent, but is practiced in highly alkaline environment when using sodium sulphite. During the digestion process, several chemical events take place, including the cleavage of linkages between the lignin and the carbohydrates, the scission of carbon–oxygen bonds that interconnect lignin units, and the sulphonation of the lignin aliphatic chain. The latter reaction is the most critical in sulphite pulping and gives sulphite lignin its main characteristics. This reaction is the result of the attack of the negatively charged sulphite or bisulphite ions on the lignin structure. The targets of such a nucleophilic attack depend on the pH of the sulphite delignification. Thus, at low pH, carbenium (benzylum) ions of phenolic or non-phenolic units are sulphonated at the  $\alpha$  position of the side chain (Fig. 10.1), while at higher pH levels quinone methide structures of phenolic units are the targets [3, 4].

In the acid pH range, weakly nucleophilic sites in the aromatic ring of lignin compete with the sulphite and bisulphite ions for the carbonium ion intermediates, forming condensed structures. Such condensation reactions are detrimental to pulp production and can be minimized by a judicious choice of pulping conditions [4].



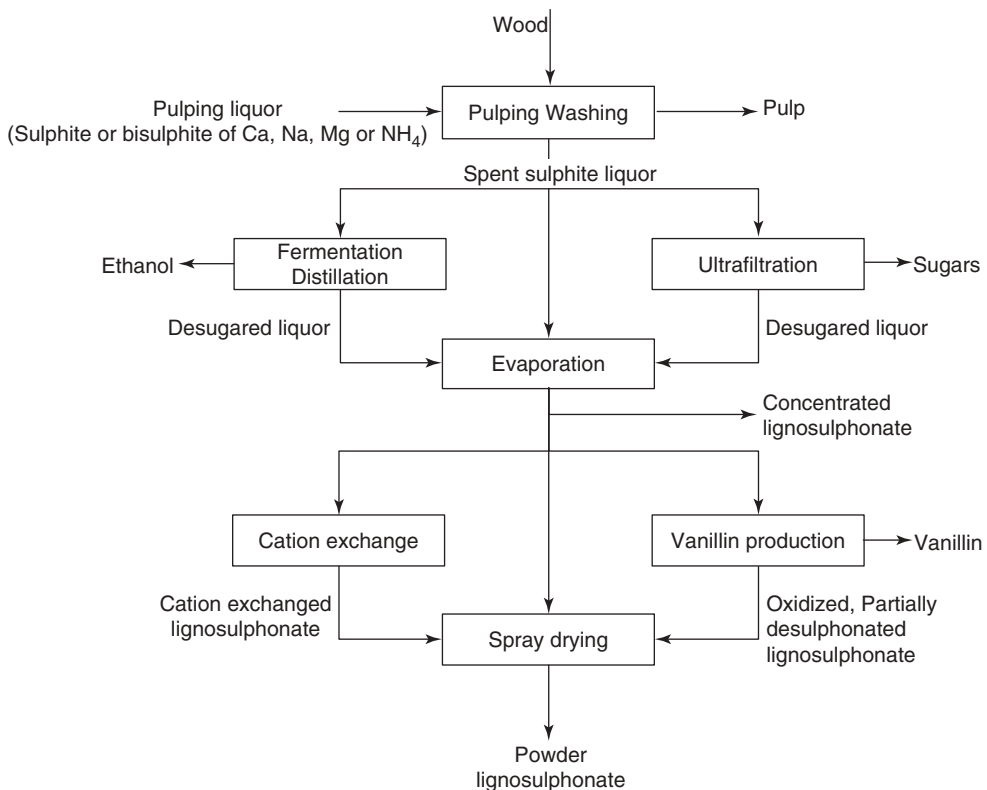
**Figure 10.1** Main reaction scheme for lignosulphonate formation during acid sulphite pulping [3].

During pulping, about 4–8 per cent sulphur is incorporated into the lignin molecules [5, 6], mostly in the form of sulphonate groups. Such groups cause the lignin to become water-soluble and prevent its recondensation, a reaction that is detrimental to pulping as it results in the redeposition of lignin on the fibres. As lignin is removed, the cellulosic fibres are liberated and once the required degree of delignification has been attained, the resulting pulp is separated from the spent pulping liquor by filtration and washing. Most liginosulphonates available in the market today are co-produced with pulps of low lignin content, but some may be obtained in conjunction with the production of pulps with relatively high lignin content, such as pulps used for paper packaging grades. Such a difference in pulping process intensity probably causes variances in the lignin structure.

Sulphite pulping (or any other pulping process, for that matter) does not selectively remove lignin. The carbohydrate components (particularly the hemicelluloses) are solubilized to a considerable extent. As a result, the spent sulphite pulping liquor contains not only liginosulphonate (or sulphonated lignin), but also hemicellulose sugars, and the spent pulping chemicals. Furthermore, carbohydrates appear to be chemically combined with some fractions of the liginosulphonate [7]. All these components are highly soluble in water and are difficult to separate from one another by methods that rely on solubility differences.

Crude spent sulphite liquor in a concentrated form, or as a powder, is available as a product (Fig. 10.2), but purified forms of sulphite lignin have broader applications and higher value [8]. Such purified lignins are obtained by diverse techniques (sometimes involving the simultaneous recovery of co-products) such as:

- Alcoholic fermentation of the sugars in the sulphite liquor and subsequent distillation of the resulting beer, which leaves behind a low sugar content liginosulphonate.
- Sugar removal by chemical destruction.
- Ultrafiltration to remove a sugar-rich permeate, therefore increasing the liginosulphonate content of the retentate fraction.
- Precipitation.



**Figure 10.2** Production pathways for liginosulphonate and selected modified versions.

In addition to purified lignosulphonates, chemically modified lignosulphonates are also produced. The modifications currently in use include:

- Changing the cation (or base) from that originally present in the pulping liquor to a different one, as required for specific applications. This is normally done through the use of ion-exchange resins.
- Oxidation, which is normally done for the production of vanillin. After vanillin recovery, the remaining low sugar, partially desulphonated, oxidized lignosulphonate is recovered and used in specific applications.
- Various other reactions, such as carboxylation, amination, crosslinking, depolymerization and graft copolymerization [9]. Sometimes combinations of these modifications are practiced.

### 10.2.2 Properties

There is a dearth of information on fundamental analysis and characterization of industrial lignins in the published scientific and technical literature, causing many gaps in the detailed understanding of the structure and macromolecular properties of the products industrially available. The situation appears to be worse for sulphite lignins, in spite of the fact that these are the most widely used lignin products. While advancements in modern analytical techniques have made significant contributions to the elucidation of the properties of other lignins (such as native lignin, change in lignin structure during kraft pulping, and lignins from emerging processes, such as organosolv delignification), lignins from the sulphite pulping process have benefited much less from the latest methods. Several factors may explain this, including the declining importance of sulphite pulping, the greater complexity of lignosulphonates as compared to the lignin molecule, (due to the multiple reactions of lignin with the very active sulphite and bisulphite species present in the pulping medium and the possibility to have various counter ions associated with the molecule), the lack of widely accepted standard methods for the preparation of purified lignosulphonates, and the fact that the protocols developed for the lignins that have received more attention require adaptation before they can be applied to lignosulphonates. One exception, which illustrates the complexity of lignosulphonates, is the recent application of two-dimensional  $^1\text{H}$ - $^{13}\text{C}$  NMR spectroscopy to hardwood and softwood lignosulphonates, which has been used to show differences in functional groups for high and low molecular weight fractions, presence of sugar residues, and the nature of methylene moieties [10].

The sulphur content of lignosulphonates is reported in the literature at 4–8 per cent [6, 11, 12]. Most of the sulphur appears in the lignin as sulphonate, but other types of organic sulphur, sulphite and sulphate, are also present. Due to their sulphonate content, lignosulphonates are very soluble in water and are insoluble in organic solvents. According to technical literature from the company Lignotech Borregaard (a leading lignosulphonate producer), the degree of sulphonation in its industrial products ranges from 0.17 to 0.65 sulphonate groups per phenyl propane unit, or about 0.9–3.3 sulphonate groups per 1000 grams of lignin. The high end is represented by de-sugared lignosulphonates extracted from pulping liquors and the low end by modified products, such as oxidized lignosulphonates obtained as co-products in vanillin production [13].

Other functional groups that are present in lignosulphonates include phenolic hydroxyl, aliphatic hydroxyl and carbonyl groups. Their quantity is very dependent on the degree of purity, molecular weight and the production process [14, 15].

Sugar content is an important property of industrial lignosulphonates. The presence of sugars has implications that may be negative in some applications, such as being a retardant in concrete cure. Crude spent sulphite liquor may have reducing sugar contents as high as 35 per cent (solids basis). Low sugar lignosulphonates are produced by fermentation of the sugars, chemical degradation and ultrafiltration [8, 12, 16, 17]. In addition, essentially sugar-free (but oxidized and partially desulphonated) lignosulphonates are obtained as co-products in the manufacture of vanillin from the spent sulphite liquor [13].

The range of values reported in the literature for the molecular weights of lignosulphonates is quite large, from less than 1000 to 150000 and even higher. Polydispersities as high as 7 have been reported [5, 18]. It has been recently proposed that the behaviour of the lignosulphonate molecule in an aqueous medium is better explained by assuming that the macromolecule follows a randomly branched polyelectrolyte conformation [19], rather than the microgel model proposed earlier [18]. In the randomly branched polyelectrolyte model, the backbone of the molecule is less sulphonated than the branches. The use of laser correlation spectroscopy suggests that lignosulphonates are nano-dimensional systems with two domains of particle sizes: one corresponding to individual macromolecules with size  $\sim 10\text{nm}$  and the other to associated macromolecules with 100–200nm size [20].

There is great potential for lignosulphonate characterization based on the application of techniques that rely on hydrophobic interactions. Thus, reversed phase chromatography has been applied to the analytical and preparative fractionation of lignosulphonates on the basis of polarity and has been found to be able to resolve sugar-free lignosulphonates from those covalently bound with carbohydrates [21]. Hydrophobic interaction chromatography, which is extensively used in protein purification and is based on the hydrophobic attraction between a target molecule and a stationary phase, has recently been shown to be useful to classify lignosulphonates according to their hydrophilicity [22, 23]. Inverse gas chromatography (where the stationary phase is the polymer being characterized, which is done by injecting volatile probes of known properties) has been successfully used to characterize the dispersive component of surface free energy (a parameter that for films is evaluated by contact angle measurements) of powder lignosulphonates and other lignins [24, 25].

Regarding the thermal properties of lignosulphonates, when examined by differential scanning calorimetry (DSC), they do not exhibit a glass transition temperature. In high temperature DSC decomposition runs they show two peaks, one at about 320°C and the other at about 450°C. The first peak is associated with the degradation of carbohydrates and the second with lignin itself [26].

### 10.2.3 Applications

The main applications for lignosulphonates are as dispersants and binders and are discussed in greater detail elsewhere [8]. They include:

- *Concrete water reducers:* This is the largest current application for lignins. The dispersant capacity of lignosulphonates (mainly calcium and sodium) is the basis for their use as additives that help increase the workability of concrete and allow a reduction in the amount of water required for proper mixing and handling. By using less water, it is possible to have stronger concrete. Lignosulphonates tend to cause some retardation of concrete setting, particularly when their sugar content is high, and they may also cause air entrainment. Lignosulphonates are also used in the manufacture of grouts and mortars and in cement manufacture by the wet process, where they reduce energy consumption. The use of lignosulphonate in concrete admixtures and other construction-related applications is expected to continue growing significantly in countries such as China and India, which have rapidly expanding economies that require multiple large infrastructure projects and other civil works.
- Other applications that benefit from the tensioactive properties of lignosulphonates include dispersants for gypsum wallboard (where the use of lignosulphonates permits a reduction in the amount of water used for forming the board and consequently a decrease of the drying energy), agrochemicals (for instance, to make water dispersible or wettable powders), dyestuffs (where they may serve as grinding aids as well), bitumen (specially when preparing cold-mix bitumen emulsions), pigments (particularly carbon black used in inks). The dispersing properties of lignosulphonates also make them components of drilling fluids for oil recovery, markets for which in the past chrome and ferrochrome lignosulphonates were extensively used. Currently, a more environmentally friendly alternative is lignosulphonate grafted with acrylates [8, 9]. Other dispersant applications of interest are formulations for scale formation inhibition in industrial waters for a variety of other industrial cleaning purposes. Lignosulphonates are also used as thinning agents for molasses in animal feed.
- *Animal feed binders:* On a volume basis, this is the second most important application of lignosulphonates. Ammonium or calcium lignosulphonate are preferred for the manufacture of pellets, which must be robust enough for handling in industrial equipment without generation of fines and dust. In addition to acting as a binder for the pellets, lignosulphonates provide lubrication in the pelletizing equipment.
- Lignosulphonates are used in other industrial binding applications, such as for green strength improvement of refractories, components in foundry resins, granulation of fertilizers and other agrochemicals, and for briquetting of mineral ores and coal dust. Lignosulphonates have been used in the formulation of thermoset phenol and urea formaldehyde resins used as binders for fibreglass insulation. Because of their high water solubility and low flow when heated, lignosulphonates are less suitable for use in exterior grade resins used as plywood and oriented strand board adhesives. Another major volume utilization (but of a rather low value) is the utilization of crude spent sulphite liquor for soil stabilization and dust control.

- Lignosulphonates are also used in miscellaneous applications, such as additives to stiffen packaging grade papers [27–29], as leather tanning agents [30], and as carriers for agricultural micronutrients [31], among others. Softwood lignosulphonates are catalytically oxidized for conversion to vanillin, a flavour ingredient and pharmaceutical intermediate [32]. The latter process was widely used in the past, but only one facility remains in operation in the world. The residual material that remains after vanillin production is a partially oxidized, low sugar lignin derivative that finds special use as a dispersant for dyes and as an expander for negative pastes of lead-acid storage batteries [13].

#### 10.2.4 Main producers

Borregaard LignoTech is the largest producer of lignosulphonates worldwide. Its 11 manufacturing units in Europe, Asia, Africa and the Americas produce more than 500 000 metric tons (dry basis) of lignin products annually, obtained as co-products from the pulping of hardwoods and softwoods. The manufacture of lignin products by Borregaard LignoTech is integrated in some of their factories with ethanol and/or vanillin production. Their lignin product range consists of more than 200 different offerings, based principally on calcium and sodium lignosulphonates and including full sugar content, fermented, double fermented, ultrafiltered, oxidized and ion-exchanged products [33].

Tembec is the second largest lignosulphonate producer in the world. The company has three sulphite pulp mills in Europe and North America, two of which are major producers of lignosulphonates for sale. Tembec can potentially produce 570 000 metric tons of lignosulphonates per year, but sales are less than that quantity, since the company processes a major fraction of its liquor through its recovery boilers, depending on energy cost and requirements, market conditions and other considerations. The company offers sodium, ammonium and magnesium lignosulphonates from hardwood and softwood in liquid as well as powder form. Complementary processes used by Tembec include alcoholic fermentation (to produce low sugar products) and ion-exchange to produce sodium base lignosulphonate [34].

La Rochette Venizel has one facility in France, which offers sodium, ammonia, magnesium and calcium lignosulphonates. Unlike most other lignosulphonates, which are co-produced with low yield, bleachable pulps, La Rochette Venizel's products are co-produced with high yield, packaging grade pulps, using a milder cooking process [35].

Nippon Paper Chemicals is a Japanese producer of calcium, sodium and magnesium lignosulphonates encompassing a range of properties, including variations in molecular weights and degrees of sulphonation [36].

Cartiere Burgo is an Italian producer of liquid and powder calcium, ammonium and sodium lignosulphonates from red pine, with capacity for about 40 000 tons per year (solids basis) [37].

Domsjö Fabriker AB (formerly part of the MoDo group) has one facility in Sweden with capacity to produce about 25 000 tons of softwood lignosulphonate per year. The facility is integrated with ethanol production [38]. The company has a technology licensing agreement with Nippon Paper Chemicals for the manufacture of concrete additives [36].

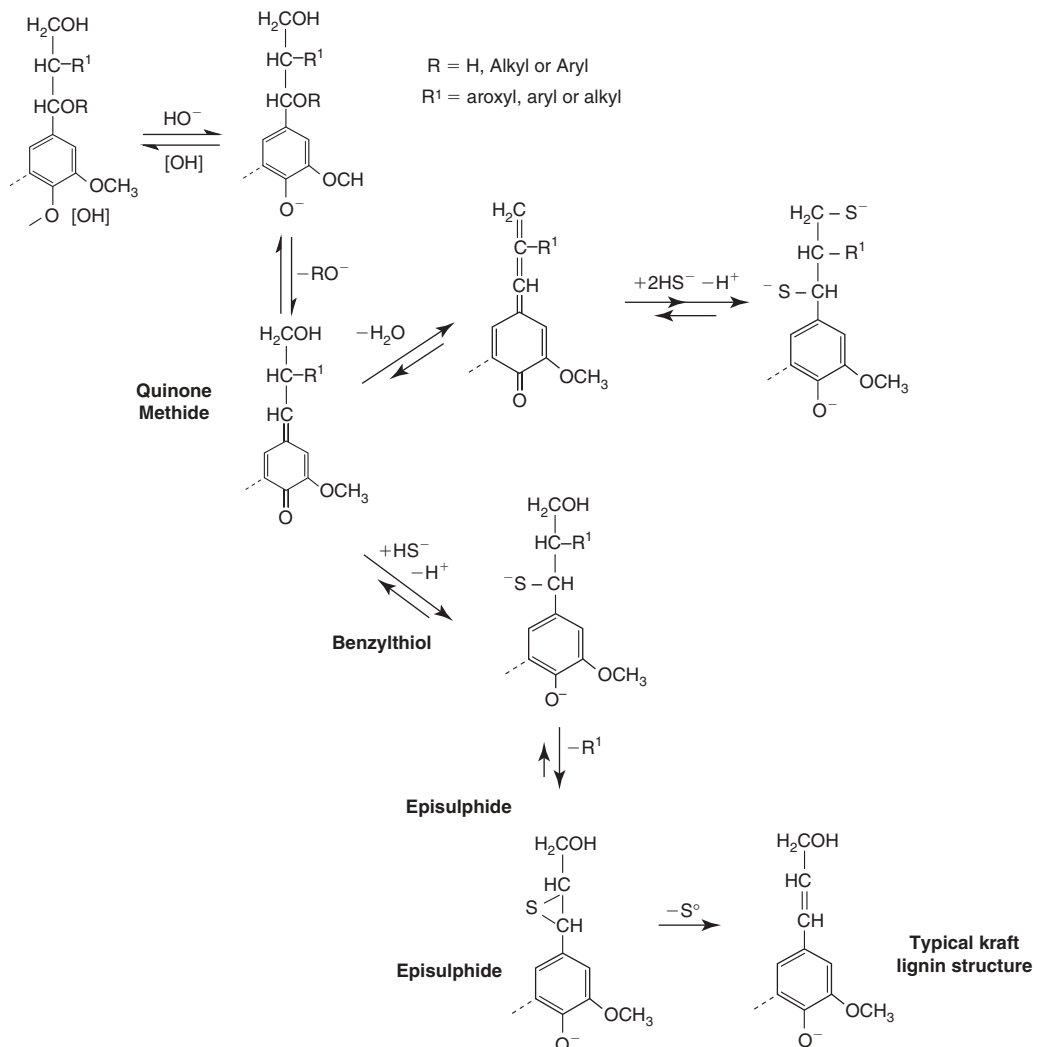
### 10.3 KRAFT LIGNIN

Although the kraft process is the most predominant pulping process worldwide, the recovery of kraft lignin for chemical uses is not practiced broadly at this time. Kraft pulp mills have evolved into very large facilities that are integrated with a highly engineered system for recovery of pulping chemicals and energy which is based on the combustion of the spent pulping liquor (black liquor). The recovery system is essential to the economic and environmental performance of the kraft pulp mill and its use simplifies the business model of pulp and paper producers, allowing them to concentrate on their core paper business. Therefore, relative to sulphite lignin, the quantity of kraft lignin recovered for chemical use is rather small; worldwide only one company is currently practicing it on an industrial basis. This situation may change in the near future, since due to steady efficiency improvements (particularly in Scandinavia), a modern kraft pulp mill nowadays may generate an excess of energy relative to its needs. In addition, the ability to implement incremental kraft pulp production is a desirable goal. Thus, the extraction of lignin has been proposed as a strategy to allow pulp capacity expansion and keep energy production and consumption in balance within the mill. The extracted lignin can then be used inside the mill to generate exportable electricity or outside the pulp mill for energy or other uses.

### 10.3.1 Process

In the kraft process, the fibrous feedstock is digested with a mixture of sodium hydroxide and sodium sulphide at about 170°C. During the digestion several reactions take place, including cleavage of lignin-carbohydrate linkages, depolymerization of the lignin, its reaction with hydrosulphide ion and its recondensation. Lignin depolymerization during kraft pulping occurs principally by the cleavage of  $\alpha$  and  $\beta$  aryl ether bonds, first in phenolic units and in a later phase of delignification in non-phenolic units. Such reactions generate moieties with free phenolic groups, which are soluble in the alkaline environment prevalent during the digestion.

Quinone methide structures are involved as intermediates in kraft delignification, as illustrated in Fig. 10.3. The  $\alpha$  carbon of such intermediates reacts with the hydroxyl, hydrosulphide and sulphide ions present in the pulping medium. Since the sulphide and hydrosulphide ions are much stronger nucleophiles than the hydroxyl group, benzylthiol structures are preferentially formed [4, 39]. This strongly nucleophilic species displaces the aryl ether attached to the  $\beta$  carbon forming an episulphide and causing the depolymerization of the lignin molecule and the formation of a phenolic hydroxyl group in the displaced aryl group, hence increasing lignin solubility in alkali.



**Figure 10.3** Main reaction scheme for the formation of kraft lignin during pulping. Adapted from [39].

The lignin episulphide intermediate in turn can lose elemental sulphur to give conjugated structures. The elimination of sulphur from the episulphide intermediate explains the relatively low sulphur content of kraft lignins. Unlike the sulphonation reaction in sulphite pulping, which produces a water-soluble lignin throughout the entire pH range, the reactions in kraft pulping do not lead to the formation of a lignin soluble in water under acid or neutral conditions.

Kraft pulping appears to be particularly efficient for cleaving dibenzodioxocins, the eight-member rings that have been proposed as a major branching point in wood lignins [40–42]. As a result, 5,5'-biphenyls are formed in high yield and with great selectivity. During alkaline pulping lignin–lignin condensation reactions also take place, therefore counteracting to some extent the lignin fragmentation processes [4]. In this case carbanions formed in the degraded lignin compete for reactive quinone methide sites with the nucleophiles supplied by the pulping liquor. In the case of kraft pulping, the intermediate benzylthiol and episulphide structures may protect the quinone methide intermediates and prevent their participation in such condensation reactions, which would explain the lower amount of condensed diphenyl methane structures observed in kraft pulping relative to soda pulping [42]. Another type of condensation that takes place may involve the formaldehyde released during pulping by the elimination of methylol groups in the lignin side chain. Such formaldehyde may form diarylmethane structures via reactions similar to phenol–formaldehyde (PF) alkaline condensation reactions.

The decreasing water solubility of kraft lignin as the pH is lowered, is the principle used for separation of lignin from the black liquor. As the pH is reduced, the ionization of the molecule is decreased and self-aggregation takes place. Since other components of the black liquor (such as inorganic constituents and the sugars and their degradation products) are soluble in water over a wide pH range, by lowering the pH and precipitating the lignin it is possible to recover it as a product relatively low in ash and carbohydrates.

In carrying out the precipitation, essentially any acidifying medium can be used. However, early on it was recognized that carbon dioxide gas (for instance, from flue gases) was a convenient and cost effective way to accomplish the acidification of alkaline black liquors to a pH of about 9.5 [43]. In the case of kraft wood black liquors at such a pH, the lignin exists as a colloidal suspension that can then be coagulated, that is, heated to about 95–100°C to increase the particle size from ~0.5 to 5 µm or greater and form a more easily filterable material. After filtration, washing with mineral acid of the resulting lignin cake may be applied to reduce the level of contaminants. This can be done by several means, for instance by resuspension in a mineral acid solution followed by filtration [44] or by displacement washing with an acid solution [45] (Fig. 10.4).

Most current commercial applications for kraft lignin involve its chemical derivatives, rather than the lignin as such. The most widely used kraft lignin derivatives are water-soluble sulphonated products, which are used as surfactants. Since the starting lignin material is low in sugars and ash, the resulting sulphonated lignin has high purity and may be used in high value-added applications. The introduction of sulphonate groups into kraft lignin is normally accomplished by sulphomethylation. This reaction can be carried out in a number of ways, such as by reacting the lignin either simultaneously or sequentially with formaldehyde and sodium sulphite [46, 47]. As a result, a methanesulphonate group is introduced at the lignin aromatic ring. Other methods have been proposed to introduce sulphonate groups in kraft lignin, including oxidative sulphonation and sulphonation in oleum, but such methods apparently are not practiced industrially.

Other important derivatives of kraft lignin are lignin amine derivatives prepared by the Mannich reaction [48–50]. Some sulphonated kraft lignins that are used as dispersants are also ethoxylated [51].

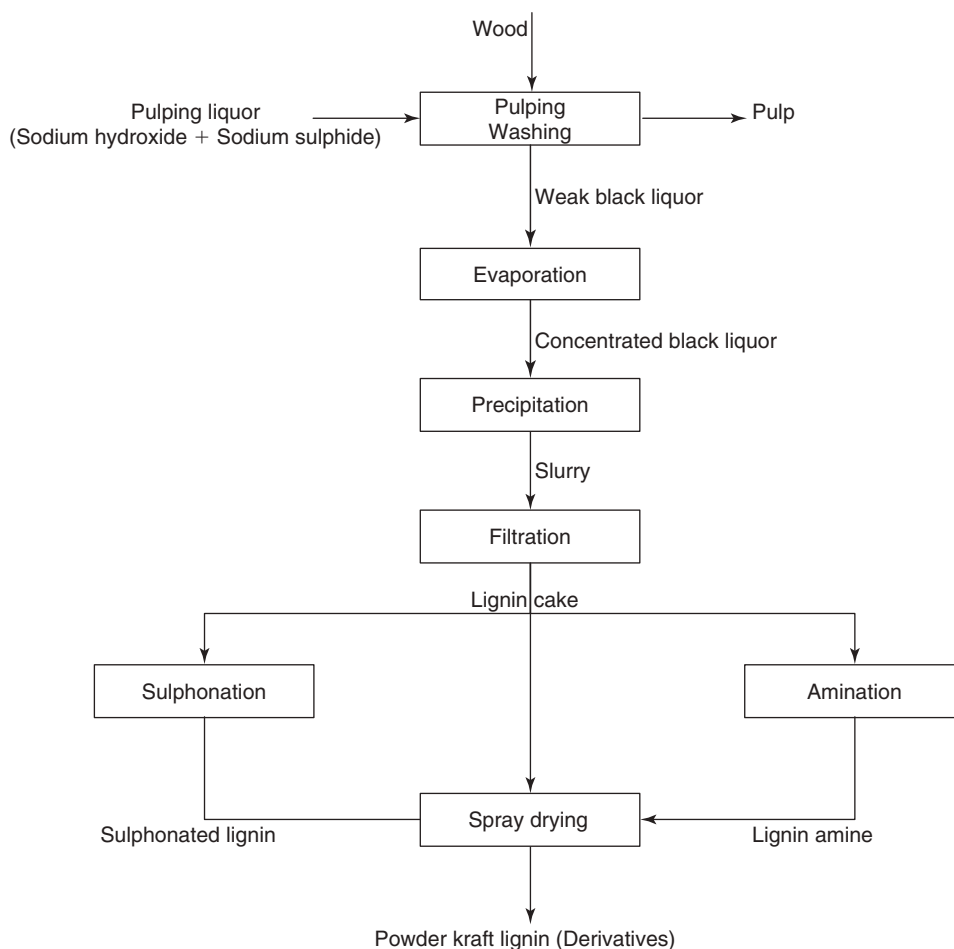
### 10.3.2 Properties

Industrial unmodified kraft lignins (such as Indulin AT produced by MeadWestvaco or Curan 100, formerly produced by Lignotech Borregaard) are characterized by a relatively high degree of purity. Since kraft lignin is not very soluble in water, it is possible to fractionate out water-soluble components, such as sugars and ash, as part of the precipitation process described above. Ash contents are usually below 3 per cent. A recent analytical round robin of lignin samples has reported acid insoluble and soluble lignin contents of about 90 and 3 per cent, respectively, and sugar contents below 2.3 per cent [52]. Carbohydrate moieties in kraft lignin seem to be more predominantly associated with the high molecular weight fraction [53, 54].

Kraft lignins contain 1.5–3.0 per cent sulphur, some of it organically bound and some as elemental sulphur [55]. For softwood kraft lignin, the sulphur content appears to be higher in low molecular weight fractions [53].

The literature has several reports on the molecular weight distribution of kraft lignins. Preparations isolated in the laboratory from industrial black liquors have been reported to have weight average molecular weights ranging from





**Figure 10.4** Diagram for production of kraft lignin and selected derivatives.

2500 to 39000 [53, 54, 55–57]. Measurements done on industrial products suggest a narrower range [5, 52, 58]. Standard methods for molecular weight determination of lignins have not been established as yet, in spite of significant ongoing efforts in that direction [59].

The total hydroxyl content of industrial kraft lignin has been reported at 1.2–1.27 groups per C9 unit, of which 56–60 per cent are phenolic in nature. Kraft lignin does not have aldehyde groups, since these are very labile under alkaline pulping conditions. About 0.15 conjugated and non-conjugated carbonyl groups are present. Other functional groups include benzylic alcohol, carboxylic acids and unsaturated structures. NMR studies indicate that pine kraft lignin has about 2.5 unsubstituted positions in its aromatic rings [60, 61].

Industrial kraft lignin exhibits a glass transition temperature at around 140°C. In high temperature decomposition runs, it exhibits a multiplet peaking at 452°C with two shoulders at 432°C and 482°C. This is in contrast to ligno-sulphonates, which display no glass transition temperature and have a low temperature degradation peak because of their carbohydrate content [26].

Concerning kraft lignin derivatives such as sulphonated kraft lignins (which have more extensive commercial application than the unmodified product), there is relatively little information available. According to their manufacturer, they are available with weight average molecular weights between about 3000 and 15000 and degrees of sulphonation in the range of 0.7 to 3.3 sulphonate group per 1000 g of lignin [62]. The latter is in the range of sulphonation levels exhibited by lignosulphonates produced in sulphite pulping.

Hydrophobic interaction chromatography appears to be promising to classify kraft and other lignins according to their degree of sulphonation [23].

### 10.3.3 Applications

The main applications for kraft lignin derivatives are as dispersants and emulsifiers. They include:

- *Dye dispersants*: Sulphonated kraft lignins are the benchmark for dispersed dyes. Such lignins are made by processes in which the molecular weight, degree of sulphonation or number of free phenolic groups are controlled to get products that meet the requirements of the dyestuff industry, such as grinding efficiency, rheology control, thermal stability, staining and counteracting strength reduction of diazo dyes. The design of kraft lignin based dispersants is a balancing act. For instance, increasing the degree of sulphonation, increases the dispersing efficiency, but reduces heat stability, that is, the adsorption of the dye to the dispersant at a higher temperature. To obtain good dispersion and heat stability, combinations of surfactants used in specific order of addition are sometimes recommended.
- *Agrochemical dispersants*: Sulphonated and ethoxylated sulphonated kraft lignins are used as dispersants for crop protection products formulated in tablets, microcapsule suspensions, wettable powders and produced by pan granulation, spray drying, fluid bed agglomeration and others. The molecular weight and degree of sulphonation can be tailored to the application.
- Sulphonated kraft lignins are also components of air entrainment formulations that give mortar and/or concrete a microstructure that results in better freeze/thaw performance. They are also used as battery expanders (similar to oxidized, partially desulphonated liginosulphonates) to increase the surface of the paste in lead-acid batteries.
- A high-tech application that is in its early stages of development is the production of conductive polymers, in which ethoxylated sulphonated kraft lignin has been used as dopant in the template-guided polymerization of aniline. These materials encounter use in electrostatic dissipative devices, electromagnetic interference shielding of sensitive electronic equipment, production of radar invisible coatings and corrosion protection, among others [63]. Unlike other conductive polymers, those based on sulphonated kraft lignin are more dispersible in water and other solvents and promise to be more versatile and economic.
- *Asphalt emulsifiers*: Unmodified kraft lignins are reported to be good stabilizers for oil-in-water emulsions [64]. Aminated kraft lignin products are particularly effective to prepare asphalt emulsions that are stable at temperatures below water freezing to above water boiling, regardless of dilution or presence of weak acids, bases or salts [30, 50].
- Unmodified kraft lignins have a few applications, principally as anti-oxidant for fat during meat rendering and as carriers, adsorbents and UV screens for active compounds in formulations of crop protection chemicals [62].
- *Production of low molecular weight chemicals*: Dimethylsulphoxide (DMSO) is produced from kraft black liquor by Gaylord Chemical, a US manufacturer [65]. The process involves adding elemental sulphur to concentrated black liquor and reacting at high temperature to form dimethyl sulphide (DMS) and methyl mercaptan. The DMS is oxidized with nitrogen oxide and oxygen to form DMSO [32].

### 10.3.4 Main producer

Mead-Westvaco (who recently acquired Lignotech Borregaard relatively minor kraft lignin business) in the US is the only industrial producer of kraft lignin and derivatives for chemical use worldwide. The company produces mostly low sugar content sulphomethylated lignins from wood at various degrees of sulphonation and molecular weights. Most products are offered in powder form and are used all over the world. The production capacity of the company has been previously reported at 35 000 ton per year (dry basis) [8].

## 10.4 SODA LIGNIN

Soda pulping was industrialized in 1853 [1] and has traditionally been used for non-wood fibres, such as straw, sugarcane bagasse, flax, etc. Such raw materials played a dominant role as sources of pulp up to about a century ago and they still remain an important fibre source for many types of papers in certain developing countries (noticeably China, India and other Asian and South American countries) and for specialty grades in developed countries. Soda pulping is also used to produce high yield hardwood pulps that are employed to make packaging papers and boards.

Non-wood fibre soda pulp mills are normally small in capacity, since the feedstock is bulky and often is not produced at a steady rate all year around. Technology developed for much larger wood pulping operations concerning the processing of the black liquor to recover energy and pulping chemicals is normally not affordable to the typical small non-wood based pulp mill. Lignin recovery is one of the alternatives proposed to handle non-woods soda black liquors. Removal of the lignin reduces the black liquor's chemical oxygen demand (COD) by about 50 per cent and generates a revenue stream from an effluent, effectively enhancing the economic performance of the mill. In recent years, the first two soda lignin recovery facilities were installed in France and India [66], and it is expected that additional facilities will be added in the near future, as this approach to handle non-wood spent lignin gets further established.

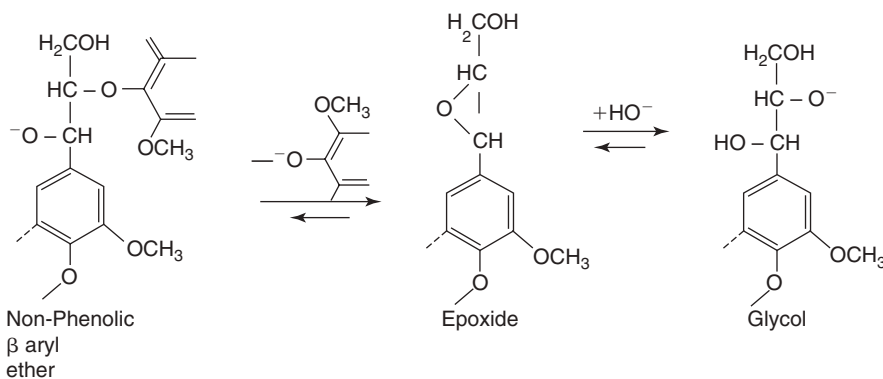
#### 10.4.1 Process

In the soda pulping process the fibrous feedstock is digested with an aqueous solution of sodium hydroxide. Since non-wood fibres have a relatively open and more accessible structure and low lignin content, the pulping temperature can be 160°C or lower. There are some similarities between soda pulping and the kraft process and reactions such as cleavage of lignin-carbohydrate linkages and depolymerization of the lignin and its recondensation take place. Lignin depolymerization during soda pulping also occurs principally by the cleavage of  $\alpha$  and  $\beta$  aryl ether bonds, first in phenolic units and, in a later phase of delignification, in non-phenolic units. The generation of free phenolic groups in such reactions results in lignin fragments that are soluble in the alkaline environment prevalent during the digestion.

Quinone methide structures originating from free phenolic groups are formed in soda pulping, but in this case their nucleophilic attack is not very important, given the relatively weak nucleophilic nature of the hydroxyl group. Instead, there is abstraction of the  $\beta$  proton or elimination of formaldehyde from a methylol group attached to the  $\beta$  carbon, leading to the formation of alkali stable stilbene or styryl aryl structures. In soda pulping, lignin depolymerization takes place mostly in non-phenolic  $\beta$  aryl ether units (Fig. 10.5). In this context, the formation of quinone methide structures is not possible; instead hydroxyl groups in the  $\alpha$  or  $\gamma$  carbon assist in the alkaline elimination of the aryl group with the formation of an intermediate epoxide, which under alkaline conditions opens up to form a glycol [4]. Soda pulping is not as efficient as kraft at cleaving dibenzodioxocins. In the case of wood pulping, in addition to 5,5' biphenyls (which are essentially the only product from the cleavage of such units in kraft pulping), enol ethers and vanillin are formed [40–42].

In soda pulping there are similar condensation reactions as those described above for kraft pulping. In this case, however, the black liquor does not have strong nucleophiles (such as sulphide or hydrosulphide) that might block condensation of the quinone methide intermediates with the carbanions. Hence, lignin condensation may be more prevalent for soda than for kraft pulping.

It should be mentioned that the above mechanisms have been studied in the literature principally from the point of view of pulping of wood, and they may not apply entirely to non-wood soda pulping because of the structural differences in non-wood lignins relative to wood lignins.



**Figure 10.5** Main reactions leading to the formation of soda lignin [39].

As in the case of kraft lignin recovery, the recovery of soda lignin is based on acid precipitation and adjustment of other process variables. An example of a process used industrially to recover non-wood lignins from soda black liquors is the Lignin Process System (LPS). In this case the pH of the black liquor is reduced, usually with a mineral acid, to form a lignin slurry, which is filtered; the lignin cake obtained is washed and dried to generate a high purity lignin powder with less than 5 per cent moisture [67].

### 10.4.2 Properties

Soda lignins are significantly different from lignosulphonates, as they are low molecular weight, insoluble in water, and obtained with low levels of sugar and ash contaminants. They have more in common with kraft lignins, resembling them in molecular weight and hydrophobicity. Among the commercially available lignins, soda lignins are unique in the sense that they are sulphur-free, and therefore can be considered as being closer to lignins as they exist in nature. Another important difference for current commercial products has to do with their genetic origin, which impacts functional groups. Currently available industrial soda lignins are mostly obtained from non-wood plants, while commercial kraft lignins are obtained from woods. In nature, non-wood lignins have structural differences relative to wood lignins. In addition to guaiacyl and syringyl moieties, non-woods have significant amounts of *p*-hydroxyl groups. They also contain etherified phenolic acids that serve as crosslinking bridge with carbohydrates [68, 69]. As discussed elsewhere [70, 71], native lignins from non-woods show structural diversities according to genetic origin, and one would expect such differences to carry on to the corresponding industrial versions.

Similar to unmodified kraft lignins, unmodified soda lignins are available as water insoluble products with relatively low content of ash and sugars. Sugar content for soda lignin recovered by the LPS process has been reported in the 2–3 per cent range. The type of sugars found, however, depends on the species of the pulping feedstock. For instance, straw lignin has predominance of pentoses, while hexoses are more abundant in hemp and flax. This is probably a reflection of the saccharide distribution of the hemicelluloses of the different species. Regarding ash, one of the main components are silicates, which naturally occur in non-wood species. In general, silica contents below 1 per cent have been reported for products offered by a leading soda lignin supplier [72]. Non-wood soda lignins have been reported to contain 0.8–1.6 per cent nitrogen, which is significantly higher than those observed in wood lignins. This nitrogen is assumed to be related, at least in part, to protein residues.

Industrial soda lignins are reported to have total hydroxyl contents in the range of 4.4–5 mmole g<sup>-1</sup> [61, 73], about equally divided between aliphatic and aromatic. As expected for materials of non-wood origin, soda non-wood lignins are polycarboxylates, that is, polymeric materials that contain substantial amounts of carboxylic acid groups (about 2.1–2.3 mmole g<sup>-1</sup>), making them somewhat less hydrophobic than kraft wood lignins.

Recent results on molecular weight distribution of soda lignins obtained using alkaline size exclusion chromatography mention weight average molecular weights in the range of 6900 to 8500 and polydispersities of about 3. These values are in a similar range as those found for kraft wood lignins [52] but, as discussed above, the lack of universally accepted standard protocols for molecular weight determination of a wide range of lignins, compromises their reliability.

Soda lignins do flow when heated and their glass transition temperatures have been reported in the range of 158–185°C [71]. The lack of sulphur gives them some advantage over kraft lignins for applications for which thermal flow is a requirement and volatile sulphurous emissions are undesirable.

### 10.4.3 Applications

Because of their lack of sulphur and closeness to lignin in nature, soda lignins have potential applications that are not available to kraft and sulphite lignins. For instance, they can be used more readily in thermoset binding applications, where use of heat without evolution of sulphurous volatiles is a must. The natural carboxylic acid functionality of non-wood soda lignins gives it the profile of a polycarboxylate-type dispersant. Soda lignins are also better suited in applications for which biological activity is important, such as in the animal feed and nutrition area.

The main applications for soda lignins include the following:

- *Component in PF formulations:* Soda lignins are currently used as partial replacement for phenol in the manufacture of PF resins used as binders in plywood [74], foundry sands and moulding compounds, among others.

With current trends towards reducing dependency on fossil raw materials, it is expected that the use of such high purity lignins as sustainable raw materials will increase in the near future, perhaps expanding to other applications beyond the PF domain [71].

- *Animal health and nutrition:* Lignin in nature is a component of dietary fibre. High purity sulphur-free soda lignins are the industrially available lignins that most closely resemble such native lignins. Products from such lignins have been proposed for the management of enteric disturbances in several animal species, including ruminants and monogastrics [75, 76]. Soda lignins are a natural alternative to the use of antibiotics, which is under increasing regulation in Europe and other places.
- *Dispersants:* Unmodified soda lignins from annual plants have some dispersant ability, given their carboxylic acid content and have been used as dispersants for biological slime control in industrial water circuits [77]. Similar to kraft lignins, soda lignins are converted to high purity, water-soluble derivatives via the introduction of sulphonate groups and the resulting dispersants may be used as concrete additives and other applications [78, 79].

#### 10.4.4 Main producers

GreenValue SA is the main producer in the emerging field of high purity sulphur-free soda lignins. This group has two production facilities, including the largest sulphur-free lignin factory in the world, which is located in Asia. Total capacity is in excess of 10000 ton per year on a dry basis. The group offers lignins derived from non-wood plant sources, such as flax, wheat straw and other grasses. Products are offered in powder and solution form. In addition to unmodified soda lignin, the company also produces modified products, including high purity sulphonated lignins [73].

Northway Lignin Chemical is a small North American producer which offers 50 per cent solids soda liquor, containing soda lignin, ash and sugars and their derivatives. The product is obtained from wood pulping and is used as a low end binder [80].

### 10.5 OTHER FUTURE POTENTIAL SOURCES OF INDUSTRIAL LIGNINS

Lignocellulosic biomass sources are expected to become preferred feedstocks for ethanol biorefineries, since traditional sources of carbohydrates for alcohol conversion (such as grain or sucrose) will not be available in sufficient amounts and under economically competitive conditions to meet increasing demand for sustainable transportation fuels. Fast growth trees and annual non-wood plants will probably be the predominant feedstock for such biorefineries. The use of lignocellulosic biomass as feedstock for ethanol production will generate a lignin-rich stream amounting to more than 60 per cent by weight of the ethanol produced. This lignin fraction has potential use as an energy source and as a chemical intermediate and product. The calorific value of lignin is 93 per cent of the calorific value of alcohol, and therefore the energy content of the lignin co-produced will be more than half of the energy content of the alcohol generated.

Recent projections indicate that the use of alcohol as fuel in the US is going to increase by about 9.5 billion litres by the year 2012 [81]. If 25 per cent of the alcohol increase comes from non-woody biomass, at least 1.1 million tons of lignin could be potentially available. Similar scenarios are expected for Europe and other parts of the world. How this lignin resource is managed is expected to have a significant impact on the economics and ultimate success of the biorefinery.

Biomass conversion technologies typically involve a pre-treatment, which is designed to break down the linkages that exist between lignin and carbohydrate components in the feedstock. Most pre-treatments are either catalyzed by added mineral acid or autocatalyzed by biomass-derived organic acids, as occurs in steam explosion or autohydrolysis. During acid pre-treatments, lignin undergoes depolymerization, caused by scission of  $\beta$ -O-4 and other linkages. Electrophilic attack of side-chain carbenium ions to lignin aromatic rings may to some extent reverse the depolymerization reaction, forming condensed structures linked by carbon-carbon bonds. If conducted under the right conditions of time, temperature and acidity, the acid catalyzed pre-treatments may result in high yields of a partially depolymerized lignin that, although not soluble in water, can be readily extracted with organic solvents or dilute alkali [82–84].

The extraction of lignin from the pre-treated biomass ahead of hydrolysis has its advantages. Lignin binds with enzymes, effectively poisoning these biocatalysts. Thus, if less lignin is present during enzymatic treatment, enzyme requirements decrease. Furthermore, dewatering of the residue after acid or enzymatic hydrolysis is made more difficult by the presence of lignin.

In another category of pre-treatment processes, delignification is actually an integral part of the pre-treatment. This is exemplified by organosolv processes, in which the biomass is treated with an organic solvent at high temperature and pressure to obtain a cellulose solid residue with high carbohydrate content and an extract from which high purity lignin may be recovered. Alkaline delignification pre-treatments have also been proposed in connection with biorefinery operations.

As discussed elsewhere in this chapter, soda delignification is a well-known process widely practiced for the production of pulp and high purity lignin from non-wood fibres [85]. The cellulose fraction could be converted to alcohol by saccharification and fermentation, particularly if the fibre properties of the feedstock are not the most suitable for paper manufacture. In addition to soda delignification, ammonia explosion and lime are among other alkaline processes being considered.

Various biomass conversion technologies have advanced to demonstration and pilot scale, and some lignins originating from such efforts have been available for industrial development purposes. Among these were lignins from steam explosion available in the 1980s, for instance, Sucrolin, offered by a South African company, and Angiolin produced by the US University Virginia Tech in pilot quantities [86].

The Alcell organosolv delignification technology was demonstrated on mixed hardwoods pulping at the semi-commercial level in the latter part of the twentieth century [87] and has been taken over recently by the Canadian company Lignol Innovations, which has incorporated the process into a biorefinery concept. In the Lignol biorefinery process, lignin is recovered from the spent solvent by precipitation (which typically involves adjusting concentration, pH and temperature), filtration and drying [88]. Organosolv lignins are usually high purity, low molecular weight products with narrow molecular weight distributions [89]. These lignins show a low glass transition temperature and exhibit flow when heated. They have high solubility in organic solvents, and are very hydrophobic and practically insoluble in water [71]. Organosolv lignin from the Alcell process has been used industrially at a significant level in the past in various applications and is among the most studied lignins in academic and applied industrial circles in recent times. A very comprehensive review covering the properties, applications and potential of organosolv lignins has been published recently [90].

For a number of years, the Brazilian company Dedini [91] has operated an acid catalyzed organosolv delignification demonstration plant that starting with sugar cane bagasse simultaneously generates a solution of sugars, lignin and other co-products. After separation of the lignin, the sugar solution is co-fermented to alcohol with sucrose from cane juice.

Organic acids (particularly acetic and formic acid) have also received attention as organosolv delignification solvents. The processes of the French organization CIMV [92] and of the Finnish company Chempolis [93, 94] are examples of biorefinery technologies that are currently pursued at pre-commercial level and that claim to recover lignins of high purity with linear structure and very low softening temperatures.

## REFERENCES

1. Ingruber O.V., Kocurek M.J., Wong A.W. (Eds), *Pulp and Paper Manufacture, Volume 4, Sulfite Science and Technology*, 1985, Tappi Press, Atlanta.
2. Sixta H. (Ed.), *Handbook of Pulp*, 2006, Wiley-VCH Verlag GmbH & Co., Weinheim.
3. Gellerstedt G., The reactions of lignin during sulfite pulping, *Svensk Papperstidning*, **79**(16), 1976, 537–543.
4. Gierer J., The reactions of lignin during pulping – A description and comparison of conventional pulping processes, *Svensk Papperstidning*, **73**(18), 1970, 571–596.
5. Glasser W.G., The potential role of lignin in tomorrow's wood utilization technologies, *Forest Prod. J.*, **31**(3), 1981, 24–29.
6. Freudenberg K., Maercker G., Nimz H., *Chem. Ber.*, **97**, 1964, 903.
7. Forss K., Sagfors P.-E., Kokkonen R., The composition of birch lignin. Fractionation of lignosulphonates and lignosulphonate-carbohydrate compounds, *Proceedings International Symposium on Wood and Pulping Chemistry – Poster Presentations*, Vancouver, Canada, 1985 pp. 23–26.
8. Gargulak J.D., Lebo S.E., Commercial use of lignin-based materials Chapter 15, in *Lignin: Historical, Biological and Materials Perspectives*, Eds. Glasser W.G., Northey R.A., Schultz T.P., *ACS Symposium Series*, American Chemical Society, Washington, DC, 1999.
9. Lin S.Y. Graft polymerization of lignosulphonate – An investigation of reaction mechanism and its relation to property modification, *Proceedings Seventh International Symposium on Wood and Pulping Chemistry Volume 1*, Beijing, 1993, pp. 16–23.
10. Lutnaes B.F., Lauten R.A., Myrvold B.O., Ovrebø H.H., Characterisation of lignosulphonates by NMR spectroscopy, *Euromar Conference*, July 16–21, New York, UK, 2006.

11. Shulga G., Solodovniks P., Shakels V., Anisckevicha O., New semi-interpenetrating polymer networks incorporating soluble lignin, *Proceedings of the 7th ILI Forum—Barcelona*, International Lignin Institute, Lausanne, 2005, pp. 159–162.
12. Gasche U.P., Hüslér W., Utilization of spent sulfite liquor – processes now in use and future applications of new methods, *Proceedings International Sulfite Pulping Conference*, Toronto 1982.
13. Anonymous, Lignin chemicals presented by Borregaard – Technical bulletin 600 E, Sarpsborg, Norway, 1980.
14. Alonso M.V., Rodriguez J.J., Oliet M., Rodriguez F., Garcia J., Gilarranz M.A., Characterization and structural modification of ammoniac lignosulfonate by methylation, *J. Appl. Polym. Sci.*, **82**, 2001, 2661–2668.
15. Alonso M.V., Oliet M., Rodriguez F., Garcia J., Gilarranz M.A.R., Rodriguez J.J., Modification of ammonium lignosulfonate by phenolation for use in phenolic resins, *Bioresource Technol.*, **96**, 2005, 1013–1018.
16. Bansal I.K., Wiley A.J., Membrane processes for fractionation and concentration of spent sulphite liquors, *Tappi J.*, **58**(1), 1975, 125–130.
17. Bar-Sinai Y.L., Wayman M., Separation of sugars and lignin in spent sulphite liquor by hydrolysis and ultrafiltration, *Tappi J.*, **59**(3), 1976, 112–114.
18. Goring D.A.I., Polymer properties of lignin and lignin derivatives, Chapter 17, in *Lignins – Occurrence, Formation, Structure and Reactions* (Eds. Sarkanen K.V. and Ludwig C.H.), John Wiley & Sons, New York, 1971.
19. Myrvold B.O., A new model for the structure of lignosulphonates, *Proceedings of the 7th ILI Forum – Barcelona*, International Lignin Institute, Lausanne, 2005, pp. 39–42.
20. Parfenova L., Polyelectrolyte expansion and crossover area in solutions of lignosulphonates modified by membrane methods, *Proceedings of the 9th European Workshop on Lignocellulosics and Pulp*, Vienna, Austria, 27–30 August, 2006, pp. 425–427.
21. Forss K., Kokkonen K., Sagfors P.E., Reversed phase chromatography of lignin derivatives Chapter 13, in *Lignin Properties and Materials*, (Eds. Glasser W.G., Sarkanen S.), *ACS Symposium Series 397*, American Chemical Society, Washington, 1989.
22. Gretland K.S., Gustafsson J., Bråten S.M., Fredheim G.E., Ekeberg D., Characterization of lignosulphonates and sulphonated kraft lignin by hydrophobic interaction chromatography, *Proceedings of the 7th ILI Forum – Barcelona*, International Lignin Institute, Lausanne, 2005, pp. 125–127.
23. Ekeberg D., Gretland K.S., Gustafsson J., Braten S.M., Frdheim G.E., Characterisation of lignosulphonates and kraft lignin by hydrophobic interaction chromatography, *Anal. Chim. Acta*, **565**, 2006, 121–128.
24. Belgacem M.N., Blayo A., Gandini A., Surface characterization of polysaccharides, lignins, printing ink pigments, and ink fillers by inverse gas chromatography, *Journal of Colloid and Interface Sci.*, **182**, 1996, 431–436.
25. Belgacem M.N., Gandini A., Inverse gas chromatography as a tool to characterize dispersive and acid base properties of the surface of fibers and powders Chapter 2, in *Interfacial Phenomena in Chromatography* (Ed. Pefferkorn E.), Marcel Dekker, Inc., New York, 1999.
26. Lora J.H., Creamer A.W., Wu L.C.F. and Goyal G.C., Chemicals generated during alcohol pulping: Characteristics and applications, *Proceedings Volume 2, 6th International Symposium on Wood and Pulping Chemistry*, Melbourne, Australia, 1991, pp. 431–438.
27. Web site of BIOTECH Lignosulfonate Handels-GesmbH [http://www.biot.org/english/index\\_produkte.html](http://www.biot.org/english/index_produkte.html) Visited on October 15, 2006.
28. Web site of La Rochette Venizel Novibond <http://www.novibond.com/novibond/paper.htm> Visited on November 03, 2006.
29. Jopson R.N., Saturation technology for corrugated containers, *Tappi J.*, **76**(4), 1993, 207–214.
30. Hoyt C.H., Goheen D.W., Polymeric products Chapter 20, in *Lignins – Occurrence, Formation, Structure and Reactions* (Eds. Sarkanen K.V. and Ludwig C.H.), John Wiley & Sons, New York, 1971.
31. Adolphson C. and Simmons R.W., Compositions having available trace elements and process of making same and providing for nutrition of plants, shrubs and trees, US Patent 3,244,505, 1966.
32. Goheen D.W., Low molecular weight chemicals Chapter 19, in *Lignins – Occurrence, Formation, Structure and Reactions* (Eds. Sarkanen K.V. and Ludwig C.H.), John Wiley & Sons, New York, 1971.
33. Web site of Lignotech Borregaard <http://www.lignotech.com/> Visited on October 15, 2006.
34. Web site of Tembec Lignosulphonate products <http://www.arbo.ca/pages/en/aboutus.html> Visited on October 15, 2006.
35. Web site of La Rochette Venizel – Novibond products <http://www.novibond.com/novibond/> Visited on October 16, 2006.
36. Web site of Nippon Paper Chemicals <http://www.npchem.co.jp/english/product/lignin/index.html> Visited on October 16, 2006.
37. Web site of Cartiere Burgo [http://www.burgo.com/burgo/Ligninsolfonati\\_en/index.htm](http://www.burgo.com/burgo/Ligninsolfonati_en/index.htm) Visited on November 16, 2006.
38. Web site of Domsjo Fabriker <http://www.domsjoe.com/> Visited on November 12, 2006.
39. Gierer J., Chemistry of delignification, Part 1: General concept and reactions during pulping, *Wood Sci. Technol.*, **1**, 1985, 289–312.
40. Karhunen P., Rummakko P., Sipila J., Brunow G., Kilpelainen I., Dibenzodioxocin: A novel type of linkage in softwood lignin, *Tetrahedron Lett.*, **36**, 1995, 169–170.

41. Argyropoulos D.S., Jurasak L., Kristopova L., Xia Z., Sun Y., Palus E., Abundance and reactivity of dibenzodioxocins in softwood lignin, *J. Agric. Food Chem.*, **50**(4), 2002, 658–666.
42. Argyropoulos D.S., Salient reactions in lignin during pulping and oxygen bleaching: An overview, *J. Pulp Pap. Sci.*, **29**(9), 2003, 308–313.
43. Rinman E.L., Process of treating waste liquors of soda pulp mills, US Patent 1,005,882 1911.
44. Keillen J.J., Ball F.J., Gressang R.W., Method of coagulating colloidal lignates in aqueous dispersions, US Patent 2,623,040 1952.
45. Loutfi H., Blackwell B., Uloth V., Lignin recovery from kraft black liquor: preliminary process design, *Tappi J.*, **74**(1), 1991, 203–210.
46. Adler E. and Hagglund E.K.M., Method of producing water soluble products from black liquor lignin, US Patent 2,680,113 1954.
47. Dillig P., Method for producing low electrolyte lignosulfonates, US Patent 4,740,590 1988.
48. Merton B.J., Cationic bituminous emulsions, US Patent 3,126,350 1964.
49. Ball J.C., Inhibition of corrosion of iron in acids, US Patent 2,863,870 1958.
50. Borgfeldt M.J., Anionic bituminous emulsions, US Patent 3,123,569 1964.
51. MeadWestvaco web site [http://www.meadwestvaco.com/c\\_dir/chempdb.nsf/PDBProductName/REAX%20825E/\\$File/REAX\\_825E.pdf?OpenElement](http://www.meadwestvaco.com/c_dir/chempdb.nsf/PDBProductName/REAX%20825E/$File/REAX_825E.pdf?OpenElement) Visited on November 15, 2006.
52. Abächerli A., Gosselink R.J.A., de Jong E., Baumberger S., Hortling B., Bonini C.D., Auria M., Zimbardi F., Barisano D., Duarte J.C., Sena-Martins G., Ribeiro B., Koukios E., Koullas D., Avgerinos E., Vasile C., Cazacu G., Mathey R., Ghidoni D., Gellerstedt G., Li J., Quintus-Leino P., Piepponen S., Laine A., Koskinen P., Gravitis J., Suren J., Fasching M., Intermediary status of the round robins in the EuroLignin network, *Proceedings of the 7th ILI Forum – Barcelona*, International Lignin Institute, Lausanne, 2005, pp. 119–124.
53. Morck R., Yoshida H., and Kringstad K., Fractionation of kraft lignin by successive extraction with organic solvents. 1. Functional groups, <sup>13</sup>C-NMR-Spectra and molecular weight distributions, *Holzforschung*, **40**(Suppl.), 1986, 51–60.
54. Morck R., Reimann R., Kringstad K., Fractionation of kraft lignin by successive extraction with organic solvents. 3. Fractionation of kraft lignin from birch, *Holzforschung*, **42**, 1988, 111–116.
55. Gellerstedt G., Lindfors E.-L., Structural changes in lignin during kraft pulping, *Holzforschung*, **38**, 1984, 151–158.
56. Shulga G., The coil-to-globule transition of softwood kraft lignin in very dilute aqueous solutions, *Proceedings 9th European Workshop in Lignocellulosics and Pulping*, Vienna, 2006, pp. 510–513.
57. Dutta S., Garvere T.M. and Sarkanen S., Modes of association between kraft lignin components Chapter 12 in *Lignin – Properties and Materials*, (Eds. Glasser, W. and Sarkanen, S.), *ACS Symposium series 397*, Washington, DC, 1989.
58. Gosselink R.J.A., Snijder M.H.B., Kranenbarg A., Keijsers E.R.P., de Jong E., Stigsson L.L., Characterisation and application of NovaFiber lignin, *Indus. Crops and Products*, **20**, 2004, 191–203.
59. Gosselink R.J.A., de Jong E., Abächerli A. and Guran B., Activities and results of the thematic network EuroLignin, *Proceedings of the 7th ILI Forum – Barcelona*, International Lignin Institute, Lausanne, 2005, pp. 25–30.
60. Marton J., Reactions in alkaline pulping, Chapter 16, in *Lignins – Occurrence, Formation, Structure and Reactions* (Eds. Sarkanen K.V. and Ludwig C.H.), John Wiley & Sons, New York, 1971.
61. Cateto C.A., Barreiro M.F., Rodrigues A.E., Brochier-Salon M.C., Thielemans W. and Belgacem M.N., FTIR and NMR studies of lignin acetylation, *Proceedings of the 9th European Workshop on Lignocellulosics and Pulp*, Vienna, Austria, August 27–30, 2006, pp. 192–195.
62. Mead-Westvaco Web Site [http://www.meadwestvaco.com/c\\_dir/chempdb.nsf/search#SearchResults](http://www.meadwestvaco.com/c_dir/chempdb.nsf/search#SearchResults) Visited on November 15, 2006.
63. Berry B.C., Viswanathan T., Lignosulfonic acid – doped polyaniline (Ligno-Pani) – A versatile conducting polymer, in *Chemical Modification, Properties and Usage of Lignin* (Ed. Hu T.Q.), Kluwer Academic/Plenum Publishers, New York, 2002, pp. 21–40.
64. Rojas O., Bullon J., Yaambertt F., Forgiarini A., Argyropoulos D.S., Gaspar A.R., Phase behavior of lignins and formulations of oil-in-water emulsions, *Proceedings 9th European Workshop in Lignocellulosics and Pulping*, Vienna, 2006, pp. 471–475.
65. Gaylord Chemical Inc. web site <http://www.gaylordchemical.com/products/dms0.htm> Visited on November 30, 2006.
66. Lora J.H., Biorefinery non-wood lignins: Potential commercial impact, *92nd Annual Meeting Preprints – Book C*, Pulp and Paper Technical Association of Canada, Montreal, 2006, pp. C3–C6.
67. Abächerli A. and Doppenberg F., PCT WO 98/42912, 1998.
68. Jacquet J., Pollet B., Lapierre C., Mhamdi F., Rolando C., New ether-linked ferulic acid-coniferyl alcohol dimmers identified in grass straws, *J. Agric. Food Chem.*, **43**, 1995, 2746–2751.
69. Lam T.B.T., Iiyama K., Stone B.A., Quantitative determination of lignin polysaccharides associations in wheat internode cell walls: Ferulic acid bridges, in *Appita Proceedings, 6th International Symposium on Wood and Pulping Chemistry, Volume 1*, Melbourne, 1991, pp. 29–33.



70. Lora J.H., Characteristics, industrial sources and utilization of lignins from non-wood plants, in *Chemical Modification, Properties and Usage of Lignin* (Ed. Hu T.Q.), Kluwer Academic/Plenum Publishers, New York, 2002, pp. 267–282.
71. Lora J.H., Glasser W.G., Recent industrial applications of lignin: A sustainable alternative to nonrenewable materials, *J. Polym. Environ.*, **10**(1/2), 2002, 39–48.
72. Gosselink R.J.A., Abächerli A., Semke H., Malherbe R., Käuper P., Nadif A., van Dam J., Analytical protocols for characterization of sulphur-free lignin, *Indus. Crops and Products*, **19**(3), 2004, 271–281.
73. Asian Lignin Manufacturing web site <http://www.asianligninn.com> Visited on 20 November, 2006.
74. Khan M.A., Lora J.H., *Ply Gazette*, August, 2006, 68–77.
75. Montserrat M., Garcia L., Marrero E., Vinardell P., Does lignin affect intestinal morphometry, *6th Internet World Congress for Biomedical Sciences*, Web site <http://www.uclm.es/inabis2000/posters/files/012/session.htm#1>, Visited on 15 November, 2006.
76. Cruz R., Dopico D., Figueredo J., Rodriguez M., Martinez G., Uso de la lignina de bagazo con fines medicinales, *Rev. Med. Exp. INS*, **14**(1), 1997, 67–71.
77. Oberkofler J., Replacement of biocides by special low molecular weight lignin based compounds for bacterial and deposit control of industrial water cycles, *Proceedings of the 7th ILI Forum – Barcelona*, International Lignin Institute, Lausanne, 2005, pp. 79–81.
78. Chang D.Y., Chan S.Y.N., Straw pulp waste liquor as a water reducing admixture, *Mag. Concr. Res.*, **47**(171), 1995, 113–118.
79. He W., Tai D., and Lin S., A comparative study of the reactivities of straw and wood alkali lignin in sulfonation reactions, *Appita Proceedings 6th International Symposium on Wood and Pulping Chemistry I*, Atlanta, USA, 1991, pp. 509–515.
80. Northway Lignin Chemical web site <http://www.duenorth.net/northway/polybind300.htm> Visited on November 15, 2006.
81. Anonymous, 2003 World Ethanol Production, 2003, *F.O. Lichts World Ethanol and Biofuels Report*, **2**(4), October, 28.
82. Wayman M., Lora J.H., Process for depolymerization and extraction of lignin, Canadian Patent No. 1,147,105, 1983.
83. Lora J.H., Wayman M., Delignification of hardwoods by autohydrolysis and extraction, *Tappi*, **61**(6), 1978, 47–50.
84. Wayman M., Lora J.H. and Gulbinas E., Material and energy balances in the production of ethanol from wood, Chapter 13, in *Chemistry for Energy*, (Ed. Tomlinson M.), *American Chemical Society Symposium Series No. 90*, Washington, 1979.
85. Lora J.H., Options for black liquor processing in non-wood pulping, Paper 20, in *Proceedings of International Conference on Cost Effectively Manufacturing Paper and Paperboard from Non-wood Fibres and Crop Residues*, Pira International, Surrey, UK, 2001.
86. Glasser W.G., Davé V., Frazier C.E., Molecular weight distribution of (semi-) commercial lignin derivatives, *J. Wood Chem. Technol.*, **13**(4), 1993, 545–559.
87. Pye E.K., Lora J.H., The Alcell Process: A proven alternative to kraft pulping, *Tappi J.*, **74**(3), 1991, 113–118.
88. Lora J.H., Wu C.F., Cronlund M., Katzen R., Lignin recovery process, US Patent No. 4,764,596, 1988.
89. Lora J.H., Creamer A.W., Wu C.F., Goyal G.C. et al, Industrial scale production of organosolv lignins; characteristics and applications, in *Cellulosics: Chemical, Biochemical and Material Aspects* (Ed. Kennedy J.F.), Ellis Horwood Ltd, 1993, pp. 251–256.
90. Pye E.K., Industrial Lignin Production and Applications, Chapter 5, in *Biorefineries – Industrial Processes and Products* (Eds. Kamm B., Gruber P.R. and Kamm M.), Wiley-VCH GmbH & Co. KGaA, Weinheim Germany, 2006, pp. 165–200.
91. Lahr Filho D., Vaz C.E., Lamonica H.M., Integration of DHR Process (Fast acid Hydrolysis Dedini) with a Typical Sugar and Ethanol Factory, *Abstracts of the ISSCT Co-products Workshop*, Copersucar, Piracicaba, Brazil, 2003.
92. Delmas M., Biomass refining and furanic chemistry, Book of Abstracts, Biomass Derived Pentoses Conference, Reims, 2006.
93. Rousu P., Rousu P., Anttila J., Tanskanen P., A novel biorefinery – production of pulp, bioenergy and green chemicals from nonwood materials. *Proceedings Tappi Engineering Pulping and Environmental Conference*, Atlanta, 2006.
94. Anttila J., Rousu P., Tanskanen J., Chemical recovery in a non-wood pulping process based on formic acid, *Proceedings Tappi Engineering Pulping and Environmental Conference*, Atlanta, 2006.

This page is intentionally left blank.

# Lignins as Components of Macromolecular Materials

Alessandro Gandini and Mohamed Naceur Belgacem

---

## ABSTRACT

This chapter surveys the use of lignin, as such or after modification, as an additive to other polymers, a blend component and a macromonomer. After a brief description of the use of lignin as a filler in different polymeric vehicles, such as inks and paints, the use of this renewable macromolecule as a co-reactant in phenol–formaldehyde and urea–formaldehyde resins, is described. Then, different systems aiming at preparing poly(urethane)s, polyesters, epoxy resins and resins based on lignins and furans are reviewed, and those giving the most interesting materials discussed in some depth. The modification of lignin with alkenyl groups and the polymerization of the ensuing macromonomers are also critically assessed. The following topic is the preparation of lignin-based carbon fibres and activated carbons and their use as reinforcing elements in composites and selective adsorbents, respectively. The preparation of aromatic monomers from lignin and the interest of their polymers conclude the chapter.

## Keywords

Lignins as a filler, Lignins as a macromonomer, Lignins in blends, Resins based on lignins and furans, Chemically modified lignins, Lignin-based polyurethanes, Lignin-based polyesters, Lignin-based epoxy resins, Lignin-containing formaldehyde-type resin, Alkenyl lignins, Lignin-based activated carbon, Lignin-based carbon fibres, Aromatic monomers.

## 11.1 INTRODUCTION

Following the exhaustive preceding monographs on the structure and technology related to the different forms of lignins, their intervention as physical and/or chemical actors in the manufacture of polymers and composites is the subject of this third chapter devoted to that natural polymer. Whereas the role of lignin in wood and annual plant anatomies is always that of the crosslinked matrix surrounding the cellulose fibres, its exploitation as a constituent of synthetic macromolecular materials can only arise from the use of lignin fragments or oligomers, as obtained from the various delignification processes discussed in the preceding chapters. These fragments will simply be called lignins in the course of this chapter, since they represent the only actual sources which intervene in the elaboration of the materials discussed herein. They represent an annual industrial output of some 50 million tons and their use is still today restricted essentially to energy production by combustion in the paper mills. Only a very limited percentage is recovered for other applications. Yet a number of sound arguments have been put forward to show that lignins are very promising sources of materials and chemicals, namely, among others (i) their ready availability in huge amounts at modest prices; (ii) the presence of reactive moieties in their structure which enables chemical modifications, chain extension and polymerizations to be conducted; (iii) the possibility of their controlled chemical or enzymatic splicing into monomeric species or value-added chemicals; (iv) their potential use as components of polymer blends or as fillers in other polymers. These are indeed the topics of the present chapter since they all deal with viable prospects related to the preparation of novel macromolecular materials.

Given the specific vegetable source and the delignification technology used, a large variety of structures and molecular weights are inevitably obtained; hence the chemical and physical properties of lignins can vary considerably. These differences are likely to play a role when they are used as merely physical additives (*e.g.* in composite materials). When lignins, as obtained, or after suitable chemical modification, are instead used as macromonomers participating in the construction of novel polymer architectures, the differences in their structure and molecular weight have no significant impact on the mechanisms associated with these chain growths. Their impact will however be relevant to some properties of the ensuing materials.

All lignins, irrespective of how they are obtained and from which vegetable source, are brown amorphous solids with glass transition temperatures ranging between 70°C and 170°C, depending on their specific structure and molecular weight (and molecular weight distribution). Obviously, a higher degree of aromatic contribution, particularly with inter-aromatic bridges and multiple substitutions, as well as a high molecular weight, will contribute to increase the  $T_g$  and vice versa.

All these lignins possess nevertheless, one universal set of features which is most relevant to the present context and that is the fact that, regardless of the specific structure and molecular weight, they all incorporate aliphatic and phenolic OH groups and unsubstituted aromatic sites. Inevitably, the relative proportions of these three moieties can vary considerably, mostly as a consequence of the precursor species, but their presence is ubiquitous simply because they are totally representative of the general structure of the natural polymer. Other moieties can also be referred to as universal in lignins, such as the typical propyl aliphatic sequence and the methoxy groups attached to the aromatic ring, but they play no role in terms of chemical reactivity for polymerization. Conversely, certain potentially reactive moieties like carboxylic groups and C=C unsaturations, are not ubiquitous in lignins because their presence depends on both the structure of their precursor and the delignification process adopted to fragment it. It follows that if general procedures are to be investigated in order to give lignins a viable status as macromonomers, the universal functional groups will be the only logical choice. In other words, whether lignins are used as macromonomers, as obtained, or after chemical modification, the OH groups and/or the unsubstituted aromatic sites must be considered the only exploitable moieties.

The above considerations are not limited to concepts of chemical modification because even when lignins are considered as additives in the preparation of polymer blends or composites, their hydroxyl functions represent a key structural element in terms of polar contributions and sources of hydrogen bonds which will affect the quality of the interfacial interactions of the ensuing materials, just as the less-polar (ether groups, aromatic rings, etc.) and non-polar (aliphatic sequences) moieties will, in terms of hydrophobic interactions.

The subdivision of this chapter follows the primary criterion based on whether lignins intervene only physically or also chemically in the manufacturing of synthetic polymers. The secondary criterion adopted here has to do with whether the lignins are used as such, that is, as recovered from industrial delignification processes, or after suitable chemical modifications.

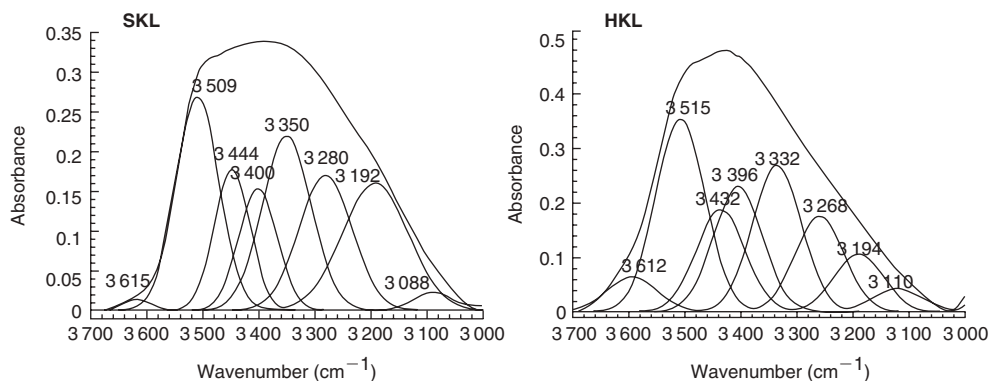
Previous monographs on the use of lignins in macromolecular materials testify to the growing interest in this lively scientific and technological realm since the 1990s, [1] which includes international meetings devoted to it. The establishment in that period of the International Lignin Institute, [2] whose activities are steadily expanding, as well as the increasing number of laboratories involved in this field has generated some exciting achievements and it is the purpose of this chapter to assess them within the framework of previous major contributions.

## 11.2 LIGNINS AS PHYSICAL COMPONENTS

The introduction of lignins, as such or after suitable chemical modifications, as fillers or blend components into natural and synthetic polymers has been the subject of a vast number of studies which cover an impressive selection of materials and vary considerably in both purpose and depth. Feldman is among the most active contributors to this field and has reviewed it thoroughly twice, the second time covering work done up to the end of the second millennium [1c,1f]. One of us carried out similar surveys at the same time [1a,1e]. These monographs should be considered as background bibliography by the interested readers. Since then, numerous original contributions have appeared as discussed below.

### 11.2.1 Unmodified lignins

Notwithstanding their structural fine details, lignins must be considered as relatively polar macromolecules because of the substantial impact of the two types of OH groups borne by all of them, which give rise to inter- and



**Figure 11.1** Deconvoluted FTIR spectra of the  $\nu\text{OH}$  region of two KLs. (Reproduced by permission of American Chemical Society. Copyright 2005. Reprinted from Reference [3]).

intramolecular associations through hydrogen bonding [3] and thus enhance the material cohesive energy, as reflected by the relatively high  $T_g$  of lignins. Figure 11.1 shows the deconvoluted hydroxyl stretching region of the softwood kraft lignin (SKL) and hardwood kraft lignin (HKL). The number of bands contained in the broad OH peak for both SKL and HKL do not vary significantly, except for a change in the relative intensity of several absorptions.

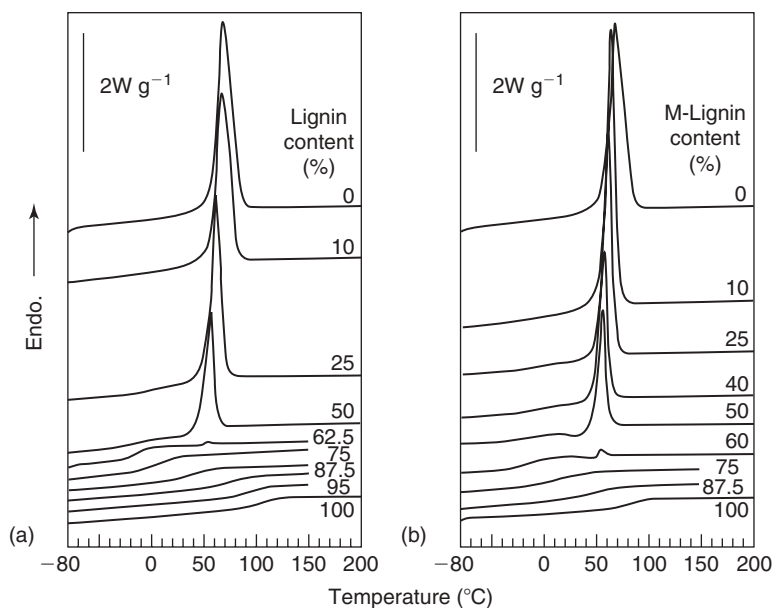
In a more prosaic, but inevitably relevant tone, lignins isolated from industrial or pilot delignification processes are cheap commodities and their direct use in the manufacture of novel materials is therefore particularly attractive, if the operation leads to a viable exploitation.

Before examining the behaviour of macromolecular materials incorporating unmodified lignins, it is worth mentioning a recent interesting study on the plasticization of kraft lignin (KL) [4], which highlighted the existence of two distinct phenomena, one related to small amounts of additives capable of establishing hydrogen bonds with the lignin's OH groups, like water and poly(ethylene glycol) (PEG), and the other involving the conventional interactions based on solubility parameters and associated with high concentrations of plasticizer. It was shown that quantities of water up to about twice the number of lignin OH groups had the same softening effect ( $T_g$  decrease) as that of acetylating them through the progressive reduction in hydrogen bonding. However, further water addition played a minor plasticizing role, whereas additives with a structure similar to that of the lignin monomer units (*e.g.* vanillin and ferulic acid) as well as low degree of polymerization (DP) PEGs, were found to display a high efficiency.

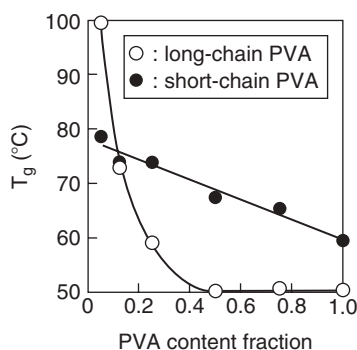
A systematic investigation of materials made up of homogeneous mixtures of kraft or organosolv lignins and high molecular weight poly(ethylene oxide) (PEO) [5] showed that the solubility of lignin in all proportions, as already reported in a different study, [6] was mostly caused by intermolecular hydrogen bonding between the lignin phenolic OH and the PEO ether oxygen atoms, but that other weaker interactions must also occur. The differential scanning calorimetry (DSC) tracings of these blends are displayed in Fig. 11.2.

In the specific instance of organosolv lignin mixtures, [5c] continuous fibres were readily spun from the melt, and although these materials were excessively sensitive to moisture, they found applications as precursors to carbon fibres, as discussed below. These systems are the only example of blends of unmodified lignins with another polymer which are homogeneous over the entire composition range. KL, mixed with poly(vinyl acetate) and two plasticizers, gave homogeneous thermoplastic materials with up to 85 per cent of KL [7]. However, their fragility in aqueous media was a serious handicap towards possible applications.

The surface energy of non-ionic lignins is close to  $70 \text{ mJ m}^{-2}$ , with a dispersive contribution of about  $45 \text{ mJ m}^{-2}$  [8, 9]. It follows that, as in the case of cellulose fibres (whose composites are discussed in Chapter 19), the quality of an interface involving lignin and another polymer will depend on the structure of the latter. Essentially non-polar macromolecules, like polyolefins, will give rise to a relatively high interfacial energy and thus poor adhesion, whereas polymers bearing polar groups, like polyesters and polysaccharides, will establish a much more compatible interface and thus strong adhesion. The degree of dispersion of lignin in heterogeneous polymer blends will therefore depend on both the technique adopted for their preparation and the structural interactions of the two polymers.



**Figure 11.2** DSC tracing of blends of PEO-hardwood kraft lignin (a) before, and (b) after methylation. (Reproduced by permission of American Chemical Society. Copyright 2003. Reprinted from Reference [5a]).

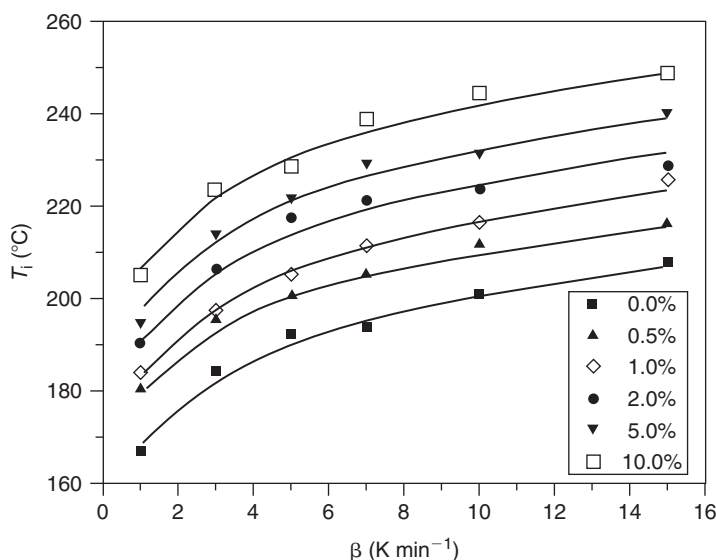


**Figure 11.3**  $T_g$  versus composition curves for the long-chain and short-chain PVA lignin/PVA blends. (Reproduced by permission of American Chemical Society. Copyright 2003. Reprinted from Reference [10]).

Despite the polar character of poly(vinyl alcohol) (PVA) (or perhaps because this feature is too pronounced!), its blends with KL are heterogeneous, but specific intermolecular interactions were shown to exist in these materials, which were melt spun and thoroughly characterized [10]. Figure 11.3 shows the evolution of the glass transition temperature as a function of the PVA/lignin ratios, for two types of PVA.

With another polar polymer, namely a polyurethane elastomer, less than about 10 wt% of lignin apparently give homogeneous blends with interesting mechanical and thermal properties, which become however progressively worse as the lignin content is increased and phase separation enhanced [11]. The intermolecular interactions of lignin blended with various synthetic polymers of different polarity have been examined and discussed in terms of miscibility and the quality of extruded fibres [12]. The addition of a few per cent of lignosulphonic acid into polysulphone gave homogeneous membranes with good proton conductivities (*i.e.* potentially useful in the assembly of fuel cells [13]).

The incorporation of lignins in poly(olefins) and rubbers has attracted much attention within the very important context of polymer stabilization against degradation mechanisms involving free radicals, *viz.* oxidation, photolysis



**Figure 11.4** Experimental and fitted dependence of the onset of oxidation temperatures, as a function of the heating rate for polypropylene stabilized with different amounts of lignin. (Reproduced by permission of Elsevier. Copyright 2005. Reprinted from Reference [14]).

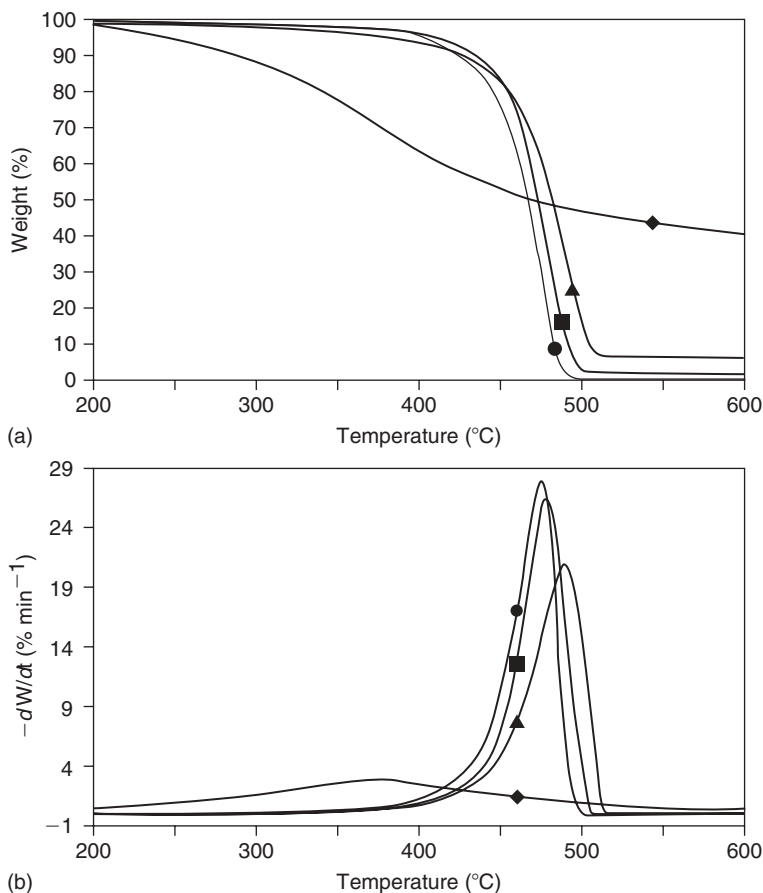
and thermolysis. This approach is entirely plausible, given the abundant phenolic content of all lignins and the well-known role of these structures as radical traps. The contribution of Košíková's group to the study of this topic is fundamental, although other laboratories have occasionally provided additional evidence. The most extensively examined polymer is poly(propylene) (PP), both as pristine and recycled material, for which the stabilization role of small percentages of lignins against photo-oxidation processes has been clearly established [14]. Thus, the onset of the thermal degradation of PP–lignin blends was found to increase with increasing lignin content, as shown in Fig. 11.4.

Higher lignin contents have recently been shown to protect this polymer against thermal degradation, [15] as shown in Fig. 11.5, which illustrates the thermal degradation of PP–lignin blends as a function of the amount of added lignin.

Poly(ethylene) has been recently protected from UV degradation with both a conventional [16] and a novel sulphur-free lignin [17]. When added to natural rubber (1–5 wt%), lignin plays as good a role as a commercial antioxidant [18] and when introduced in styrene–butadiene rubber in significant amounts, it also plays the role of a reinforcing filler [19]. The diffusion of aromatic hydrocarbons through natural rubber was found to be reduced by the incorporation of KL in relatively high proportions [20].

A recent addition to the field called upon the study of the effect of Alcell lignin on the rheological properties of printing inks, varnishes and paints [21]. The lignin particles ( $\Phi < 0.2\mu\text{m}$ ) were incorporated into a series of commercial viscous products and found to be adequately wetted and dispersed. The changes in viscosity and tack of the ensuing suspensions were recorded, on the one hand, as a function of composition and ink source and, on the other hand, as a function of the measuring parameters, *viz.* temperature, tack roller speed and shear rate. It was found that this organosolv lignin (OL) brought about noticeable improvements in the properties of the viscous media used for offset inks and paints, particularly in terms of tack and misting reduction. These positive aspects were not marred by any detrimental effects on their other physical and chemical (drying kinetics) properties. The remarkable suppression of misting is highlighted in Table 11.1 for a variety of commercial inks (alkyd resins), paints and varnishes.

Blends of lignins with biopolymers have also attracted a good deal of attention, from Glasser's pioneering studies with cellulose and some of its derivatives to more recent investigations involving other polysaccharides, proteins and bacterial polyesters [1e,22]. Recent work on starch–lignin films illustrates this aspect adequately; given the growing impact of starch-related materials, as discussed in Chapter 15. Baumberger's group has devoted much effort to the study of the interactions of these two polymers and to the properties of the ensuing blends [23]. Figure 11.6 shows the effect of electron-beam irradiation on the mechanical properties of lignin–starch blends.



**Figure 11.5** (a) TGA, and (b) DTG thermograms under nitrogen atmosphere for (●) pure PP; (■) PP/lignin 95/5; (▲) PP/lignin 85/15; (◆) pure lignin. (Reproduced by permission of Elsevier. Copyright 2006. Reprinted from Reference [15]).

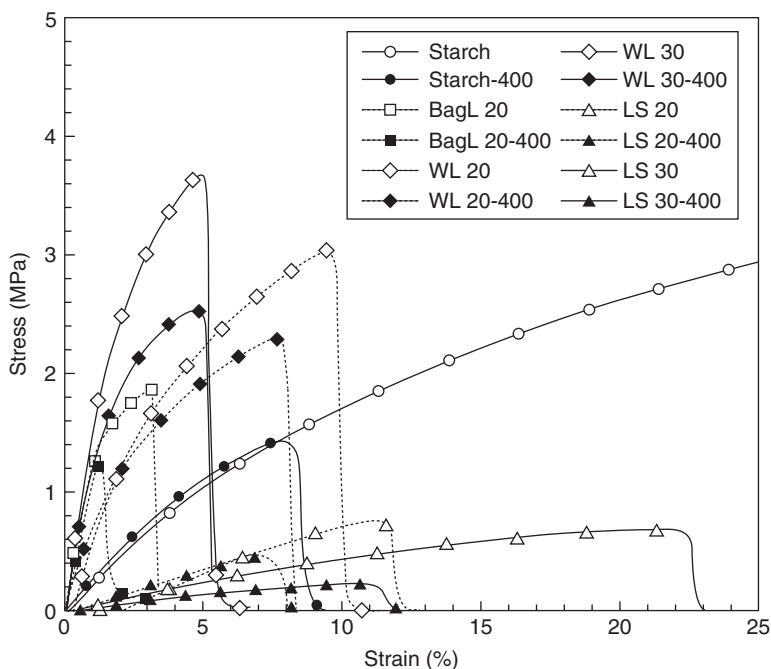
**Table 11.1**

Misting of various commercial resins containing variable amounts of suspended **OL** [21]

	Temperature	% of misting as a function of <b>OL</b> content (% w/w)				
	(°C)	0	2	10	20	40
Suspension						
<b>Alkyd resin B</b>	30	35	33	25	0	0
<b>Alkyd resin C</b>	30	66	63	46	13	0
<b>Paint F*</b>	30	25	24	13	0	0
<b>Paint G*</b>	30	8	0	0	0	0
<b>Varnish E (at 30°C)</b>	30	10	0	0	0	0
<b>Varnish E (at 50°C)</b>	50	63	60	8	0	0
		% of misting as a function of temperature (°C)				
		0	9.2	16.0	20.3	42.0
<b>Alkyd resin A</b>	20	9	0	—	0	0
	30	23	0	0	0	0
	40	45	23	0	0	0
	50	65	—	27	17	0
	60	70	43	33	22	0

\* Paints F and G were commercial paints presenting misting problems.





**Figure 11.6** Effect of the 400 kGy-irradiation on the stress–strain curves (1 mm/min stretching speed) relative to the control and starch/lignins films after storage at 75 per cent RH. (Reproduced by permission of the American Chemical Society. Copyright 2006. Reprinted from Reference [23c].)

The lignins used were from different sources, namely: bagasse alkali (BagL), wheat straw (WL) and lignosulphonate (LS) lignins, incorporated in the starch matrix.

The primary aim of this research was to develop thermoplastic materials in which the hydrophilic character of starch would be reduced by the presence of lignin, but of course the thermomechanical properties of these composites also represented an important issue. All the blends were heterogeneous and the presence of lignin (whatever its source) did not affect the morphology of the amylose and amylopectin phases, although the latter starch component displayed a higher interfacial compatibility with lignin. Moreover, the overall compatibility between the two natural polymers was enhanced by moisture content and lignin lower DPs. LS gave the most intimate interpolymer interactions, but the other lignins, with their more hydrophobic character, improved the water resistance, particularly in cast films. Electron-beam irradiation of these films at high doses produced contrasting results in that their surface water resistance was enhanced to the detriment of their mechanical properties, both properties being affected by the occurrence of crosslinking and degradation reactions involving starch and lignin. This energetic post-treatment, applied in a more controlled fashion, represents a promising tool for the optimization of the functional properties of these materials.

Lignosulphonic acid has found a very appropriate application as a dopant for polyaniline, [24] as already pointed out in the previous chapter of this book. This high-tech material (LIGNO-PANI™) is an excellent illustration of a currently held working hypothesis which purports that lignins can be rationally exploited to give very original value-added commodities. The recently reported composite based on lignin and natural fibres, registered as ARBOFORM<sup>R</sup>, [25] seems to comply with these considerations, although little has been disclosed about its detailed chemistry (composition) and physics (processing).

### 11.2.2 Chemically modified lignins

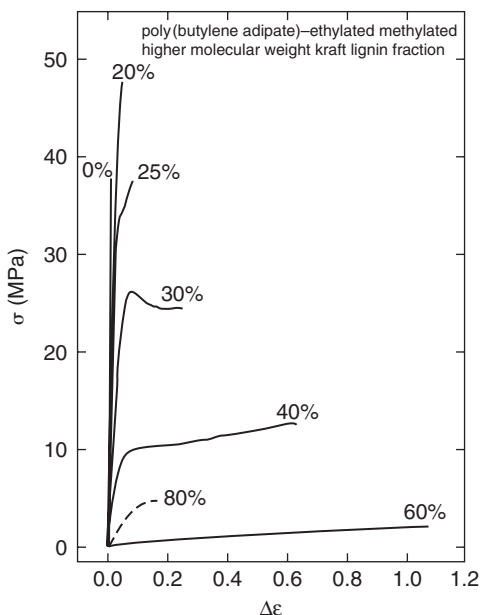
The properties of lignin-based blends and composites can be improved by appropriate chemical modifications aimed at optimizing the interactions between or among the components of these materials, essentially by reducing the corresponding interfacial energy and thus enhancing their compatibility. This logical strategy however, has the inevitable drawback associated with the cost of the modification, which in the case of lignins can alter dramatically

the economic feasibility related to the commercial exploitation of the materials in question. Only those realizations capable of fulfilling a technological requirement of high priority, whether because there is no known alternative, or because the improvements associated with the novel product are particularly noteworthy, will justify such an added cost. These considerations seem entirely obvious to us, but some of the approaches proposed both in this specific context and in the field of lignins as macromonomers discussed below, appear to ignore them or minimize the impact of economic considerations.

Three publications on the use of modified lignins claimed a major breakthrough in developing thermoplastic materials with very high lignin contents. The first [26] reported some properties of '100 per cent KL-based polymeric materials' which were in fact methylated and/or ethylated lignins (*i.e.* lignin ethers prepared by treatments with diethyl sulphate and diazomethane). These materials were not inspected further as such and attention was focused instead on blending them with aliphatic polyesters [27] and to prepare other modified lignins bearing both ether and ester moieties, whose blends with aliphatic esters and PEO were in turn characterized [28]. The mechanical and thermal properties of the blends were thoroughly assessed as a function of composition, plasticizing polymer and modification and were shown to reflect typical features associated with a viscoelastic behaviour in the near- $T_g$  region, often including a semicrystalline component arising from the polyester. These materials are certainly viable in terms of such features, but the basic question is whether they would be economically and ecologically competitive with a wide range of available counterparts, considering the separation procedures applied to obtain the desired lignin fraction, the requirements and reagents associated with the alkylation processes and the cost of the plasticizing polyesters. In other words, the obvious interest of using lignins as the major precursors seems to be negatively counterbalanced by the operations involved in their modification and blending. Figure 11.7 shows the effect of poly(1,4-butylene adipate) on the progressive plasticization of etherified KL samples [27]. A very recent addition to this saga [29] does not provide any results that would alter the above considerations.

The reaction of lignins, including LS, with epichloridrin [30] gives products which have been tested both in blends and in reactive compositions. Blends of these modified lignins with a poly(ethylene)-poly(propylene) mixture, [31] hydroxypropyl cellulose [32] and polyalkanoates [33] have been reported and their properties do not seem to warrant the additional requirements associated with the modification.

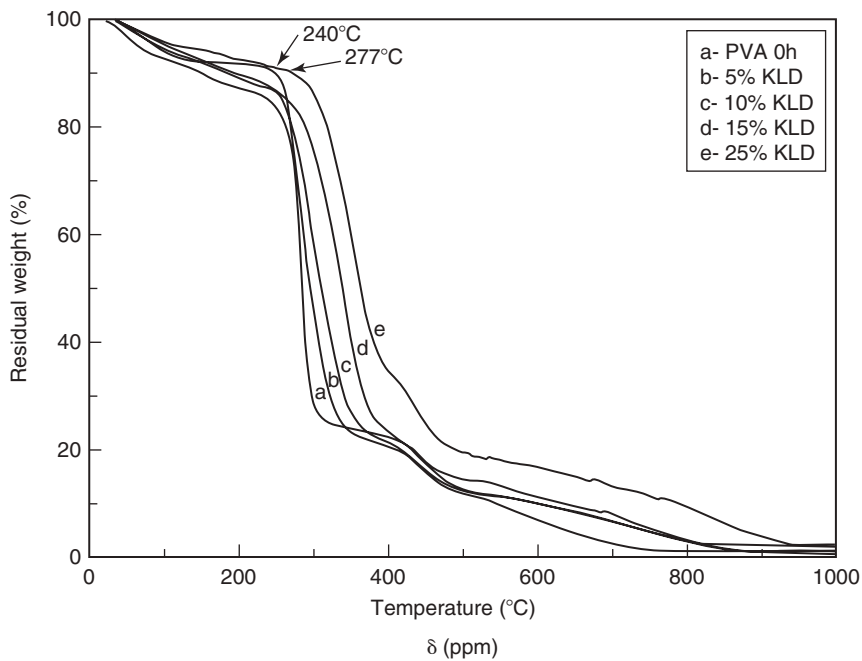
Homogeneous blends of PVA with 5–15 per cent of a KL modified by reaction with a maleimide-substituted aromatic carboxylic acid provided a means to improve the thermal and photochemical stability of the vinyl polymer [34]. Thus, the thermal resistance of the PVA-modified lignin blends increased, as illustrated in Fig. 11.8 [34]. Spectroscopic



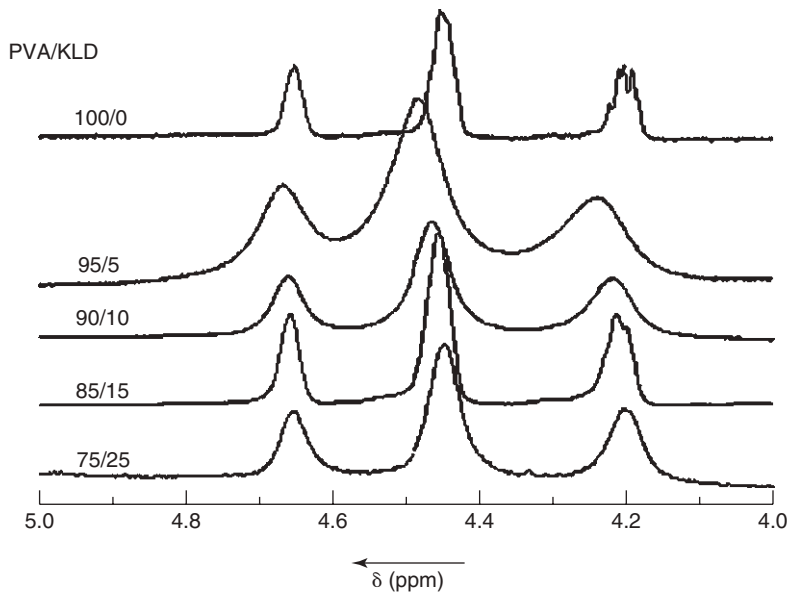
**Figure 11.7** Progressive plasticization of ethylated methylated KL-based polymeric material by poly(1,4-butylene adipate). (Reproduced by permission of American Chemical Society. Copyright 2002. Reprinted from Reference [27]).

evidence of hydrogen bonding interactions between the two polymers was provided in this study, as shown in Fig. 11.9, which shows the chemical shifts of the PVA protons in NMR spectra in the region of 4–5 ppm [34].

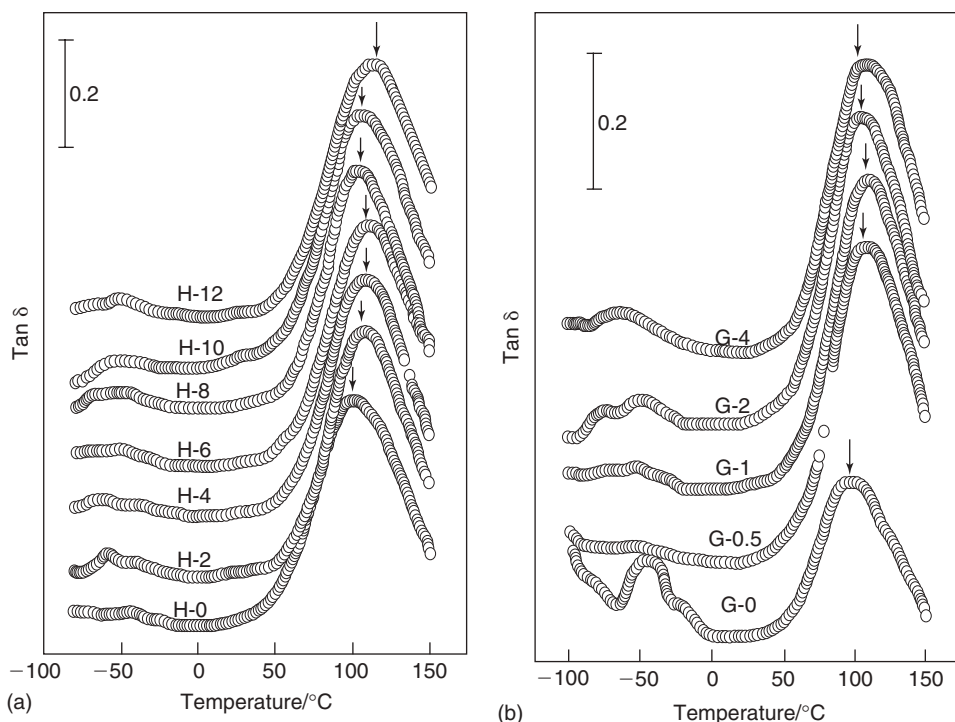
Hydroxypropyl lignin, prepared with propylene oxide (PO) in a basic aqueous medium, was mixed with soy protein to give nano-heterogeneous blends with better mechanical properties and higher glass transition



**Figure 11.8** TGA curves of PVA and blends containing 5–25 per cent kraft lignin derivative (KLD). (Reproduced by permission of Elsevier. Copyright 2006. Reprinted from Reference [34]).



**Figure 11.9**  $^1\text{H}$  NMR spectra (4–5 ppm region) of PVA and blends containing 5–25 per cent kraft lignin derivative (KLD) in  $\text{DMSO-d}_6$ , at room temperature. (Reproduced by permission of Elsevier. Copyright 2006. Reprinted from Reference [34]).



**Figure 11.10** DMTA spectra of the (a) H-series, and (b) G-series sheets plotted in the form of  $\tan \delta$  versus temperature. The arrows indicate  $T_{\alpha}$ . (Reproduced by permission of Wiley Periodicals. Copyright 2006. Reprinted from Reference [35]).

temperatures than those of the pristine protein [35]. Figure 11.10 shows the shifts observed for  $\tan \delta$  in the dynamical mechanical curves demonstrating the improved interface quality. The H-series means a content of hydroxypropyl alkaline lignin corresponding to 0, 2, 4, 6, 8, 10 and 12 wt%. The G-series indicates that 0, 0.5, 1, 2 and 4 mL, corresponding to 0, 1.7, 3.3, 6.6 and 13.2 wt%, respectively, of glutaraldehyde (GA) were added.

Another interesting family of materials involving modified lignins was described by Glasser's group [22] who prepared blends of biodegradable thermoplastics including cellulose esters, polyhydroxybutyrate and a starch-caprolactone copolymer with different lignin esters. The justification for using these lignin derivatives was that the corresponding unmodified organosolv lignin gave unsatisfactory materials. A thorough characterization of all these combinations showed very different levels of interaction between each polymer couple.

In a different vein, the modification of lignins by plasmas generated with different gases was successfully carried out in a rotating reactor [36]. As with other solid substrates, the modifications were confined to the surface of the lignin particles and were therefore suitable for the improvement of the interfacial compatibility in the processing of blends or composites.

Finally, the recent discovery of an accidentally prepared lignin sulphate [37] has opened potentially valuable avenues of medicinal applications.

### 11.3 LIGNINS AS MACROMONOMERS

As with blends and composites, the use of lignins for the synthesis of macromolecular materials has been based either on pristine reagents, as obtained in the delignification processes, or on appropriately modified homologues. The present survey of recent progress covers both approaches separately, as in Section 11.2. Previous reviews on the exploitation of lignins as macromonomers covered the topic more or less systematically up to the pertinent chapters in the book on lignin edited by Hu in 2002 [1].

### 11.3.1 Unmodified lignins

As already emphasized above in the case of physical mixtures of lignins with other polymers, it seems important to us to reiterate that, particularly for polymeric materials which have to compete with low priced existing petroleum-based counterparts, the use of lignins as macromonomers should not be accompanied by their costly modifications. In other words, the ideal situation is obviously that in which lignins can be introduced in the polymerizing medium as obtained from the delignification process. If that optimum approach cannot be applied because of reactivity or other constraints, then the modifications introduced into the lignin structure to solve these problems, should be carefully considered in terms of their economic and ecologic viability.

#### 11.3.1.1 Phenol–formaldehyde and urea–formaldehyde resins

The partial replacement of phenol in the formaldehyde-based (PF) resins appears as one of the most obvious utilization of lignins and indeed much work has been devoted to the synthesis and assessment of these materials [1b,1e]. Given the huge market associated with particleboard, plywood and fibreboard adhesives, the possible incorporation of lignins in their formulation would represent a very profitable operation. Pizzi [38] has analysed the issue from an industrial standpoint and highlighted the advantages and difficulties associated with these systems. The major obstacle to such an industrial development is the limited reactivity of the aromatic sites of lignin compared with that of phenol, because of their higher degree of substitution, which introduces considerable steric hindrance. An interesting way to overcome this relatively slow step is to start the process by methylolating the lignin before mixing it with PF resins and even employing oligomeric aromatic diisocyanates as co-reagents. These process modifications have largely eliminated the problem of the longer pressing times induced by the presence of lignins, making it possible to use more than 50 per cent of methylolated lignins in the resin formulations.

More recent work on this topic include the use of sulphur-free lignins replacing up to 30 per cent of phenol [17] and of 5 per cent of sodium LS into PF–resol resins, which was found to promote condensation reactions [39].

The surface properties of these resins have been determined using both contact angle measurements and inverse gas chromatography [40] and compared with those of a standard PF counterpart. The dispersive contribution to the surface energy increased with the introduction of KL, whereas the polar contribution was not significantly affected. With sodium LS, the major change took now the form of a considerable increase in the donor properties of the resin surface, attributed to the presence of the  $-\text{SO}_3^-$  moieties. A recent interesting addition to this topic deals with lignin-based wood panel adhesives prepared without formaldehyde [41].

The introduction of lignins in urea–formaldehyde (UF) resins has also been extensively investigated [38] and successful industrial applications for particleboard have been operating with about 10 per cent of spent sulphite liquor in the UF formulation. Higher lignin contents have been applied to improve water resistance. In these resins, the lignin does not replace another reagent, as in the case of the PF counterparts, but simply intervenes as a third component, whose reactivity is lower, but whose interests lie in its low price and hydrophobic contribution to the final crosslinked material.

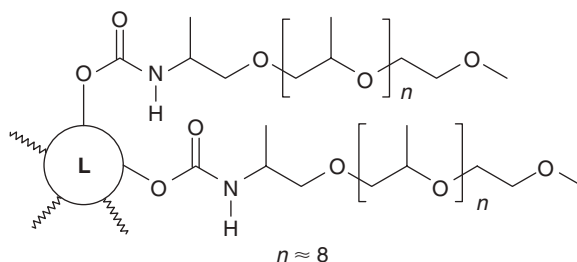
#### 11.3.1.2 Poly(urethane)s

Although the Glasser group's pioneering work on lignin-based poly(urethane)s (PU) was mostly based on modified lignins, and will therefore be discussed in detail below, some of the materials prepared and reported in that systematic series of studies were indeed made up with unmodified lignins, but only for the sake of comparison. The reasons for the modifications were attributed to the modest accessibility of the lignins' hydroxyl groups for their reaction with isocyanate moieties.

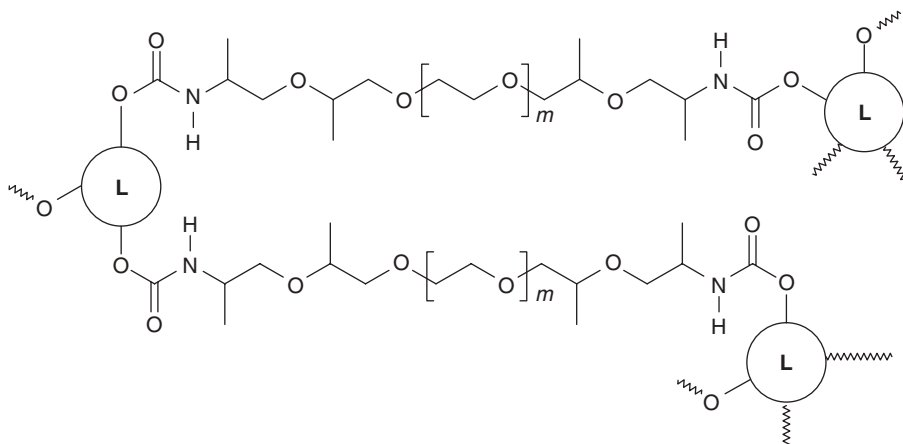
Feldman's group was the first to tackle the possibility of preparing poly(urethane–urea)s to be used as sealing materials in which the oligomeric multiple isocyanate, that is normally the single precursor which crosslinks upon addition of the required amount of water, was mixed with 5–20 wt% of unmodified KL [42]. The characterization of these materials showed unambiguously that the lignin had indeed participated chemically to the construction of the network through some of its OH groups.

Two laboratories have been involved more recently in the synthesis and characterization of PUs based on unmodified lignins. In both approaches, the trick aimed at enhancing the lignins' reactivity consisted in using a diol as third monomer, preferably capable of dissolving the lignin.

Our contribution to this field started with a study of PU foams prepared from KL and hexamethylene isocyanate in the presence of an oligo(caprolactone) macrodiol [43]. In this system, the lignin mass contribution gave viable



Scheme 11.1

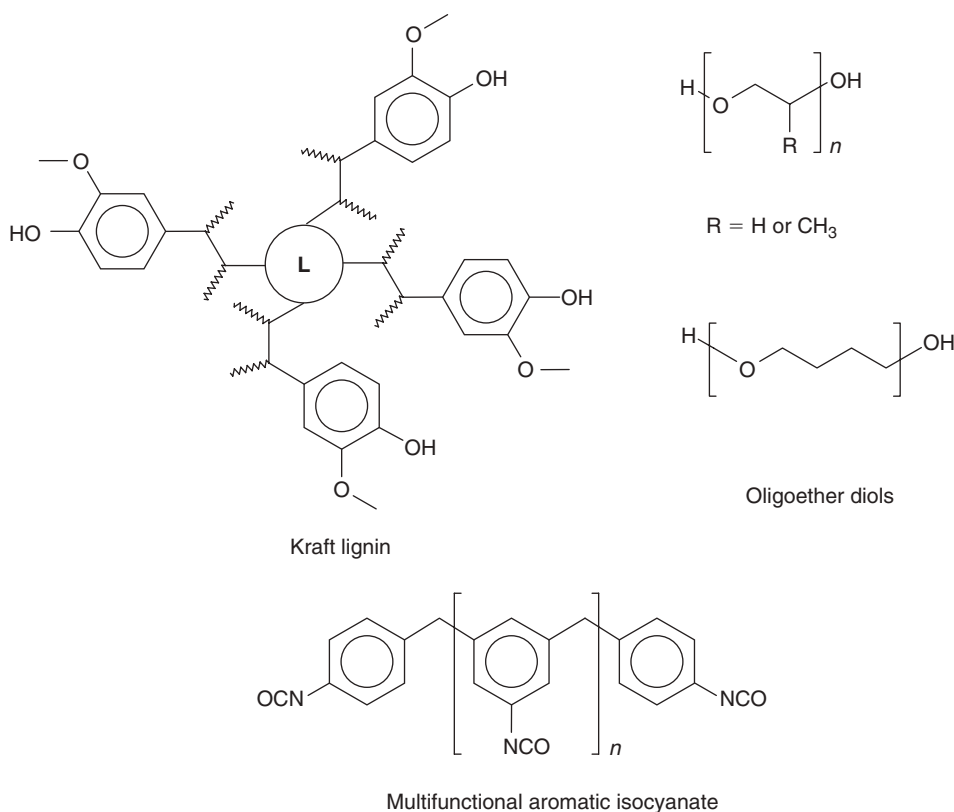


Scheme 11.2

materials up to about 40 per cent. Subsequent studies [44] called upon the use of Alcell lignin (*i.e.* a mixture of oligomers with  $M_n \sim 700$  and  $M_w \sim 1700$  and a  $T_g$  of  $64^\circ\text{C}$ ) whose reactivity was considerably higher than that of KL because of the reduction of steric crowding around the hydroxyl groups. In order to prepare elastomeric PUs we synthesized oligoether isocyanates bearing very low glass transition temperatures. Before carrying out the actual polymer syntheses, various model reactions were studied with the aim of establishing comparative reactivity criteria related to both the difference between phenolic and aliphatic OH groups and the role of steric hindrance around each type. Thus, various lignin models, as well as a model monoisocyanate, were employed together with the actual monomers, *viz.* Alcell lignin, an oligoether monoisocyanate and the corresponding diisocyanate. FTIR and NMR spectroscopy were used to assess these reactivity features and the conclusion was that, although differences existed in terms of the nature of the OH group and its steric availability, all the reactions went to completion, indicating that it was possible in this context to involve every single hydroxyl function. The two types of materials which were then prepared consisted respectively of thermoplastic elastomers or pastes, when the monoisocyanate was used, and partly or fully crosslinked elastomers, when the comonomer was the diisocyanate. The structure of both these low  $T_g$  PUs are shown in Schemes 11.1 and 11.2.

This work was then extended to oxygen-organosolv lignins isolated from spent liquors after delignification of aspen and spruce in different acidic water/organic solvent media [45]. It was found that the nature of the organic solvent used in the delignification process had an effect on the reactivity of the ensuing lignins because it affected their OH content. On the whole however, the properties of the polyurethane networks, prepared with the same diisocyanate shown in Scheme 11.2, were similar to those of the corresponding materials based on Alcell lignin discussed above.

The broad investigation carried out in Hatakeyama's laboratory [46] encompassed various unmodified lignins including Kraft, organosolv and sulphonate varieties which were dissolved into oligoether diols before mixing the ensuing solution with a multi-functional aromatic isocyanate. The strategy here for improving the reactivity of the lignin OH groups consisted in using the macrodiol as both the solvent for lignin and a comonomer. This second

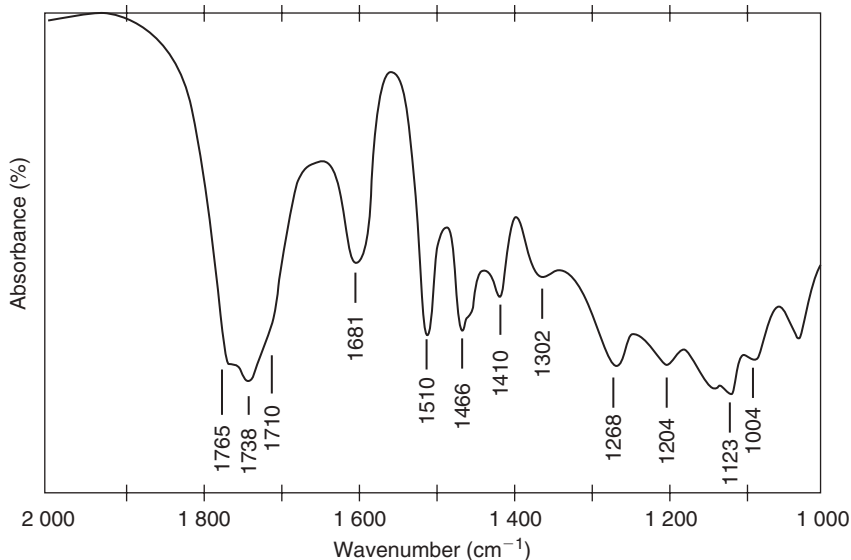
**Scheme 11.3**

role provided a means to reduce the stiffness of the ensuing networks by introducing flexible oligoether sequences as spacers among the rigid aromatic domains formed by the condensation of lignin macromolecules with the isocyanate. All the materials prepared in this study in the form of sheets or foams were thoroughly characterized in terms of thermal transitions and decomposition, as well as mechanical properties. Scheme 11.3 illustrates a typical polymer structure generated by this approach.

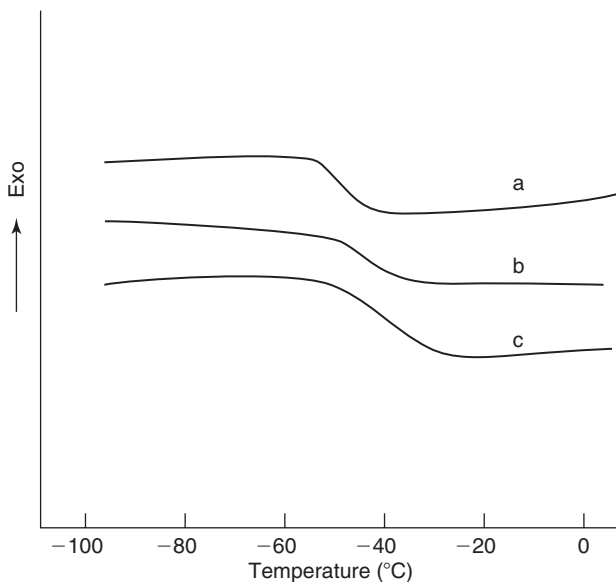
A recent report [47] on the use of steam-exploded straw lignin as macromonomer for the synthesis of PUs, describes systems in which two diisocyanates were tested and in some instances ethylene glycol was employed as comonomer. The results of this investigation are puzzling because molecular weights could be determined for all the ensuing polymers, a fact which is in stark contrast with the expected crosslinked nature of these materials, given the OH multi-functional character of lignin. The other odd aspect of this work is that the amounts of recovered polymers were systematically much lower than the sum of the monomers used, suggesting unaccountable losses, since in principle these types of systems produce a complete yield of polymer.

### 11.3.1.3 Polyesters

Studies related to the synthesis of lignin-based polyesters are few and far between compared with their polyurethane counterparts. This is quite surprising considering that the synthesis and characterization of lignin alkanooates have received close scrutiny [48] and, although these products cannot be considered as interesting materials as such, they certainly represent promising additives in macromolecular compositions (see below). To the best of our knowledge, the first systematic study of the use of unmodified lignins (kraft and organosolv) for the synthesis of polyesters, was carried out some 15 years ago by Guo and Gandini and reported in several publications [6, 44, 49]. In a first series of experiments, the lignins were made to react at low temperature with different proportions of an aliphatic or aromatic acid dichloride in the presence of a proton scavenger. The FTIR spectra of the ensuing polyesters showed unambiguously that both aliphatic and phenolic hydroxyl groups had indeed



**Figure 11.11** FTIR spectra of a typical KL-sebacate (Reproduced by permission of Kluwer Academic. Copyright 2002. Reprinted from Reference [1f]).

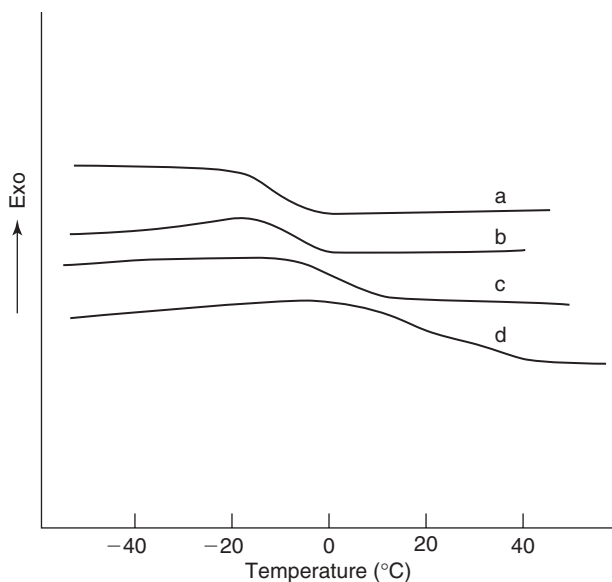


**Figure 11.12** DSC thermograms of three lignin-sebacates with different KL contents. (Reproduced by permission of Pergamon Press. Copyright 1991. Reprinted from Reference [6]).

participated in the polycondensation reactions, as clearly shown in Fig. 11.11. The fact that the highest yield of insoluble polymers coincided with an OH/COCl ratio of unity indicated moreover, that all the OH groups had been involved in the construction of the networks (*i.e.* steric impediments had not played any appreciable role in these processes).

The major difference between the two sets of polyesters had to do of course with their glass transition temperature, which was obviously lower when either the aliphatic diacid had been used or lower proportions of lignin were employed, as shown in Figs 11.12 and 11.13.





**Figure 11.13** DSC thermograms of four lignin–terephthalates with different KL contents. (Reproduced by permission of Pergamon Press. Copyright 1991. Reprinted from Reference [6]).

In order to extend the range of properties and to simplify the synthetic procedures, a second series of experiments was then carried out in which, on the one hand, a third comonomer *viz.* a flexible macrodiol (PEGs of different molecular weights), was added to the systems, and, on the other hand, no solvent was employed because the lignins were thoroughly soluble in the added diol. These bulk copolyesterifications increased the degrees of freedom related to the experimental parameters since it was now possible to vary the proportion of lignin with respect to the diol (degree of chain extension), and the DP of the diol (length of the chain extensions). In this way, the range of  $T_g$  and viscoelastic properties could be amply modulated.

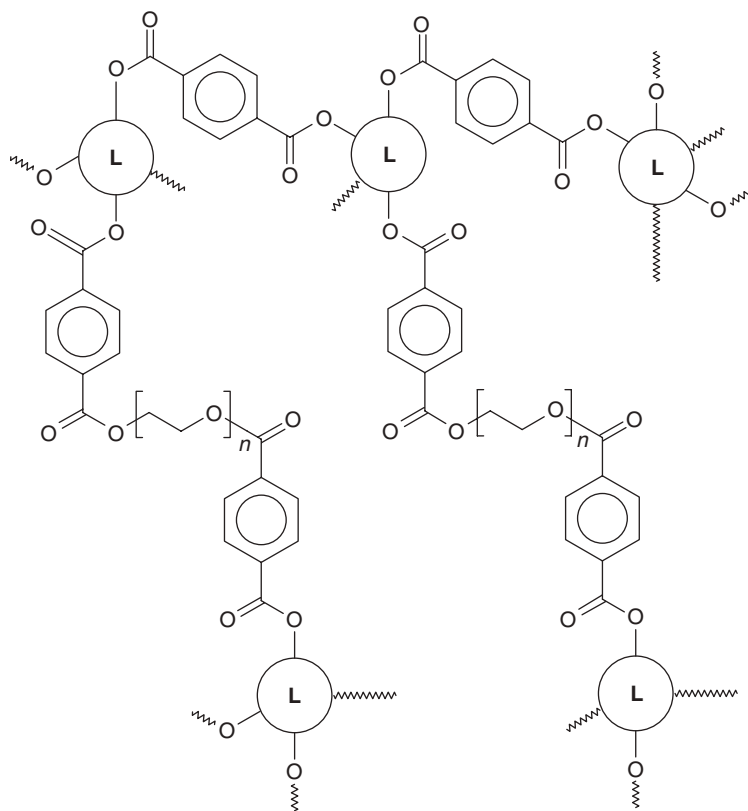
Typical structures of these two families of polyesters are shown in Schemes 11.4 and 11.5.

Figure 11.14 shows some of these effects through typical DSC tracings for a series of polyesters. Figure 11.15 highlights the fact that the higher the KL content in the polyesters, the higher the graphitized residue after their thermal degradation. This is an important observation because it suggests that these polymers should not propagate a flame because of their intumescent character.

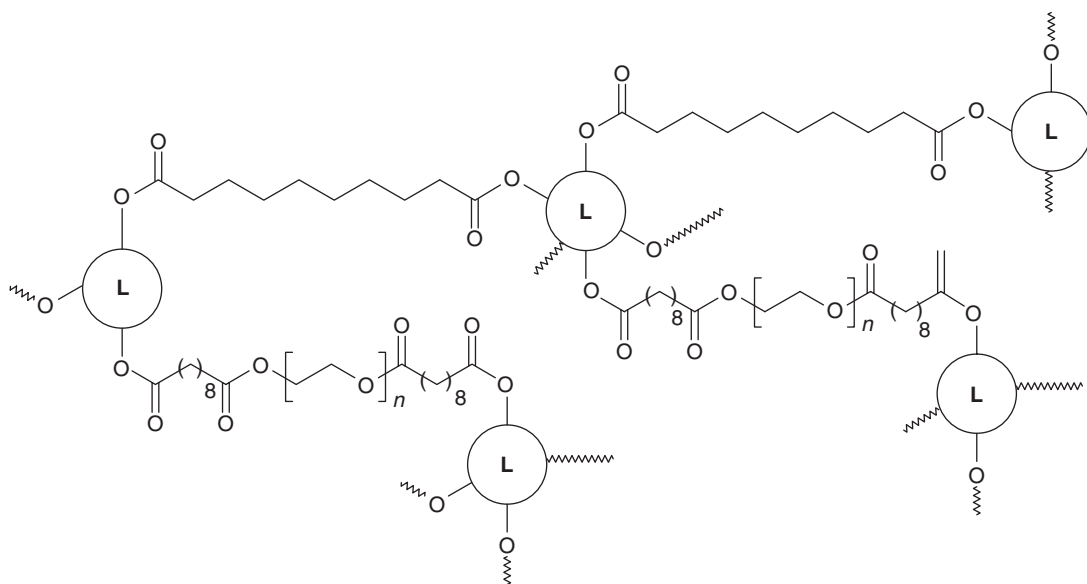
Finally, a morphological analysis of some of these materials showed that it was possible to prepare single-phase networks with more than 50 per cent of KL, since a clear-cut phase separation only became visible in SEM micrographs of polyesters prepared with 65 per cent of lignin.

No substantial difference in behaviour was noticed with either the polymerization systems or the polyester properties between the uses of kraft or oxygen-organosolv lignins. The only quantitative feature favouring the latter was the fact that its reactivity was higher than that of the former as indeed expected because of its lower molecular weight [50].

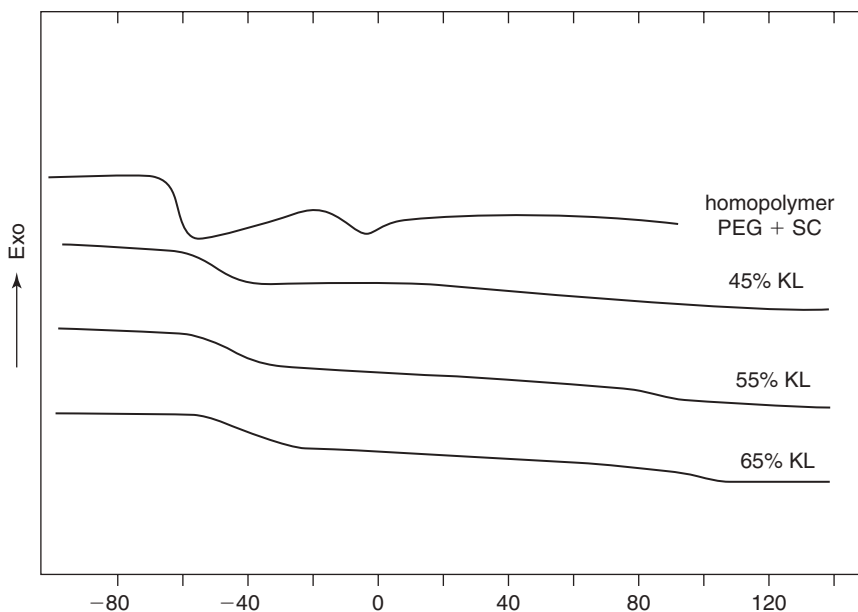
Among the possible applications of these polyesters, one seems to us particularly attractive because it might replace advantageously existing materials and at the same time eliminate a health hazard. The idea is to replace styrene monomer in typical commercial unsaturated polyester compositions by prepolymers synthesized using lignin and an excess of diacid, which could be premixed with the traditional low molecular weight polyesters bearing terminal hydroxyl groups. Given the very low reactivity of carboxylic acids with OH groups, these mixtures would have an adequate pot life at room temperature and could therefore be commercialized as such. Their processing, typically with reinforcing fibres, would be carried out at high temperatures and maybe with an appropriate latent catalyst, thus producing the desired networks because of the numerous  $-\text{COOH}$  groups borne by the lignin pre-polyesters. Presently, the crosslinking of the unsaturated polyesters is ensured by the free radical polymerization of styrene monomer, added to them at the processing stage, which involves the unsaturations by a grafting-through mechanism. In most of the workshops and small industrial concerns, the handling of styrene monomer constitutes



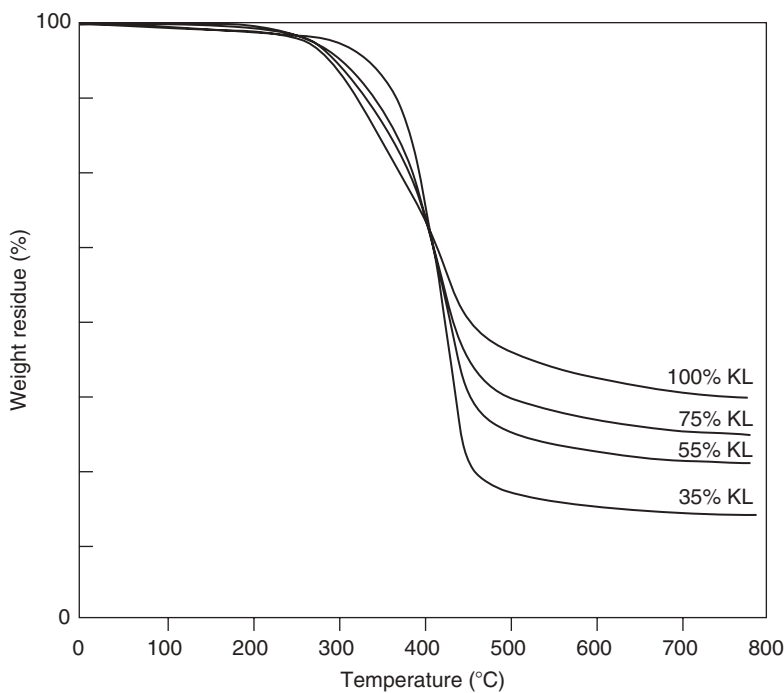
Scheme 11.4



Scheme 11.5



**Figure 11.14** DSC tracings of four KL-PEG<sub>300</sub>-sebacates with different KL contents. (Reproduced by permission of Kluwer Academic/Plenum Publishers. Copyright 2002. Reprinted from Reference [1f]).



**Figure 11.15** TGA thermograms of four KL-PEG<sub>300</sub>-sebacates with different KL contents. (Reproduced by permission of Kluwer Academic/Plenum Publishers. Copyright 2002. Reprinted from Reference [1f]).

an obvious health risk, which would be eliminated by this approach, capable moreover of giving viable materials in which one of the components is a cheap renewable resource.

The only other study of polyesterification involving an unmodified lignin was recently published together with the already discussed study on polyurethanes [47]. Steam-explosion straw lignin was made to react with dodecan-diyl dichloride in different monomer proportions in THF using triethylamine as the acid scavenger. As in the case of polyurethanes, the authors again reported quite surprisingly that the ensuing polyesters were soluble products with quite modest molecular weights. These observations are in contradiction with the normally expected crosslinking associated with systems involving a difunctional monomer (here the acid dichloride) reacting with a partner bearing numerous complementary functions (here the lignin with its multiple OH groups).

#### 11.3.1.4 Epoxy resins

The only published report on the use of unmodified lignins for the preparation of epoxy resins was announced by IBM in the late 1990s and dealt with the solution interaction between Kraft or organosolv lignins and various epoxy monomers, followed by a crosslinking operation induced by aromatic diamines [51]. Although details were scanty, it was announced that these materials were suitable for application in the electronic industry because of their excellent adhesion on copper, very good dielectric properties and temperature stability up to more than 175°C.

#### 11.3.1.5 Grafted lignins

The idea of using lignins as structures capable of generating polymer grafts by a free radical mechanism and the corresponding publications which claim its successful application [52] leave us somewhat perplex, as already explained in detail in previous reviews, [1b,1e] particularly with homogeneous systems using exotic initiators in dimethylsulphoxide (DMSO) (and even radioactive <sup>14</sup>C-labelled styrene [53]). It is in fact difficult to rationalize that styrene or acrylamide can undergo a normal chain growth in the presence of polyphenolic structures, which are excellent radical traps, as indeed emphasized by the numerous studies discussed above on the use of lignins as protecting additives for various commercial polymers. The lack of structural characterization to corroborate the claim of successful grafting and the absence of a study of the materials' properties contribute to generate a puzzled reaction.

#### 11.3.1.6 Resins based on lignins and furans

A recent patent describes the use of adhesive compositions based on mixtures of lignin, furfuryl alcohol and maleic anhydride, whose setting is insured by Lewis acid catalysts [54]. Its text contains a thorough patent survey of other lignin-based resins.

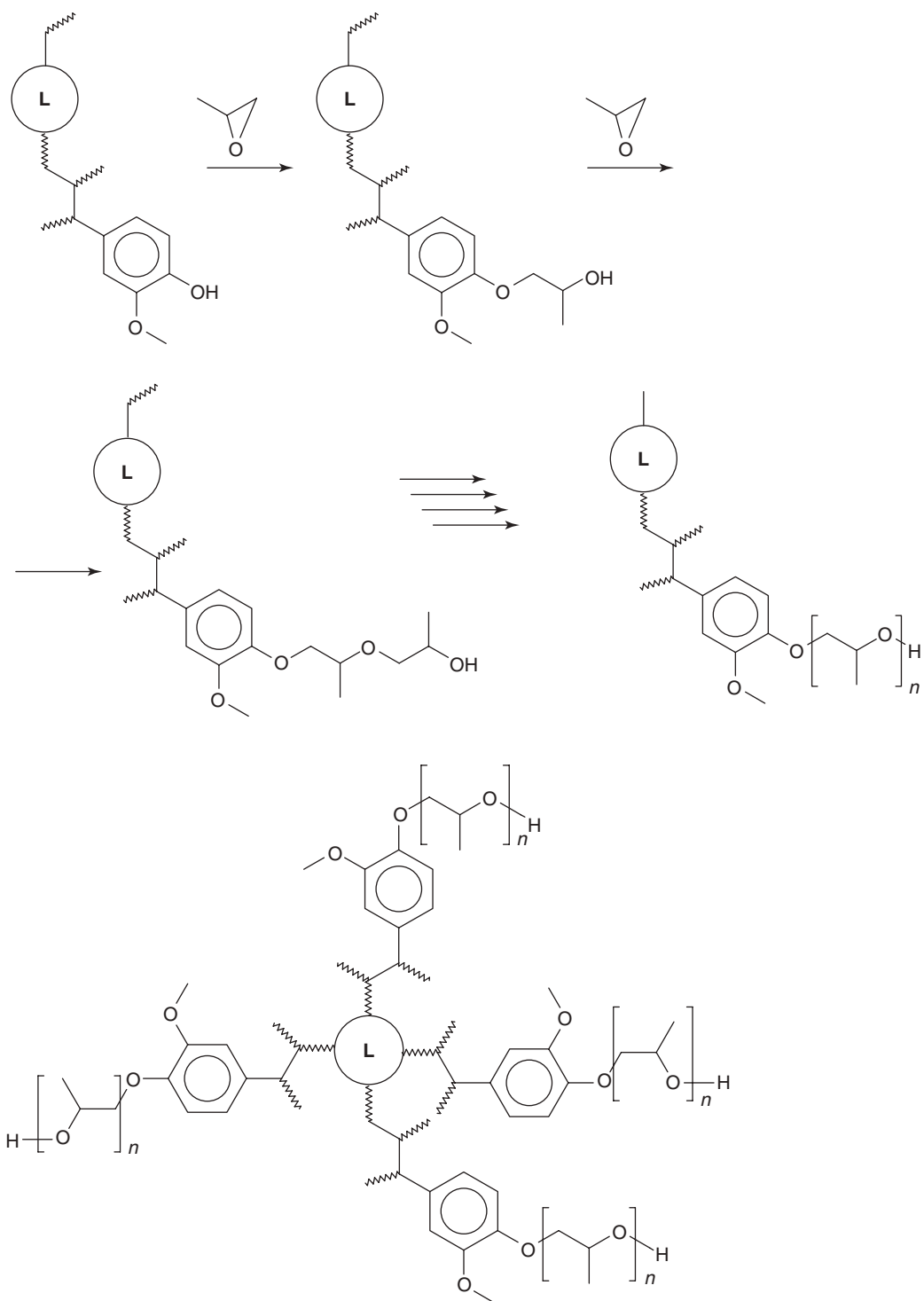
### 11.3.2 Chemically modified lignins

Glasser and co-workers have contributed most significantly to the formulation of two families of lignin-based materials, namely polyurethanes and epoxy resins, in which lignin was modified in order to enhance its reactivity or bear novel functions.

#### 11.3.2.1 Polyurethanes

The modifications of kraft and organosolv lignins were carried out here in order to 'bring out' their OH groups and thus make them more available for condensation with diisocyanates. The techniques used to achieve this goal consisted in blocking first of all part of the OH groups by ethylation with diethyl sulphate and then treating the ensuing lignins with propylene oxide (PO) in order to chain extend the remaining hydroxyl functions with oligomeric PO moieties terminated by primary or secondary OH groups. A variety of these lignin-based polyols (Scheme 11.6) was thus prepared and used as macromonomers in the synthesis of numerous polyurethanes, using aliphatic or aromatic diisocyanates and, in some instances, a macrodiol comonomer, mostly in the form of PEGs of different molecular weights [55].

This systematic study, carried out throughout the 1980s, constituted a very thorough approach to both the synthetic aspects, with their corollary structural characterization, and a whole set of physical and technological properties. Elastomers as well as rigid polymers were prepared and their possible applications carefully examined on the basis of the specific performances determined for each one. Further additions to the basic investigation included the use

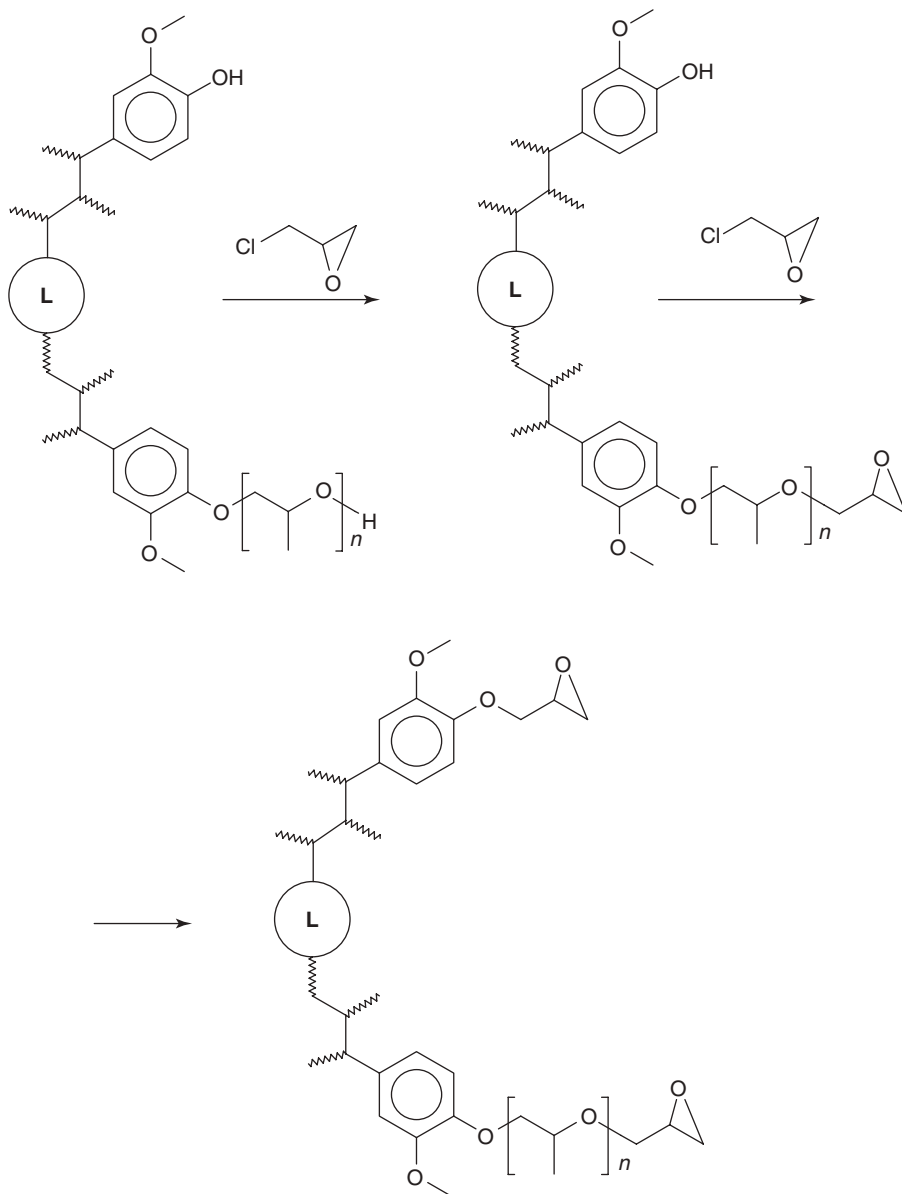

**Scheme 11.6**

of DMTA to follow the crosslinking reactions [56] and the synthesis of interpenetrating networks with acrylic structures [57].

### 11.3.2.2 Epoxy resins

In this context, Glasser's group used the partially oxypropylated lignins described in the preceding section as the substrate for the synthesis of macromonomers bearing multiple oxirane groups by reacting them with epichloridin (Scheme 11.7) [58].

The crosslinking of these polyoxiranes with aromatic diamines using the standard procedures applied to epoxy resins was then studied by DMTA. Reactions proceeded normally, except for the fact that early vitrification, arising from the high aromatic content of these compositions, induced a considerable slowdown of the late curing stages.



**Scheme 11.7**

In a recent addition to the elaboration of lignin-based epoxy resins, calcium LS was treated with epichloridrin to introduce oxirane functions in their structure [59]. Thereafter, these modified lignins were treated with maleic anhydride and the curing reaction leading to these novel epoxy resins was followed by FTIR spectroscopy [60]. More attention was devoted in this work to the kinetics and mechanism of the network formation than to any characterization of the properties of the ensuing materials, but this will probably be followed up.

### 11.3.2.3 Alkenyl lignins

The idea of attaching alkenyl moieties to lignins and use the modified products as macromonomers suitable for chain polymerizations has been put to test on few occasions with unconvincing results in terms of the interest of the materials obtained. The problem intrinsic to this approach is that it is impossible to prepare lignin macromonomers bearing a unique polymerizable moiety, because even when using 1:1 reaction conditions, the distribution of the alkenyl groups cannot be made to reflect that stoichiometry (*i.e.* some lignin macromonomers will contain more than one and others none). It follows that the polymerization of these derivatives will inevitably generate networks, without any straightforward means of controlling their growth.

In both reported syntheses of lignins bearing acrylic moieties, prepared respectively by the reaction of acryloyl chloride [61] and methacrylic anhydride, [62] a high degree of substitution was accompanied by free radical polymerizations or copolymerizations with ill-defined products. In the case of the reaction of lignin with chloroethyl vinyl ether, [63] the ensuing lignins bore an average of five vinyl ether groups per macromonomer and, as could have been easily anticipated, their cationic polymerization produced insoluble crosslinked materials.

### 11.3.2.4 Bulk lignin oxypropylation

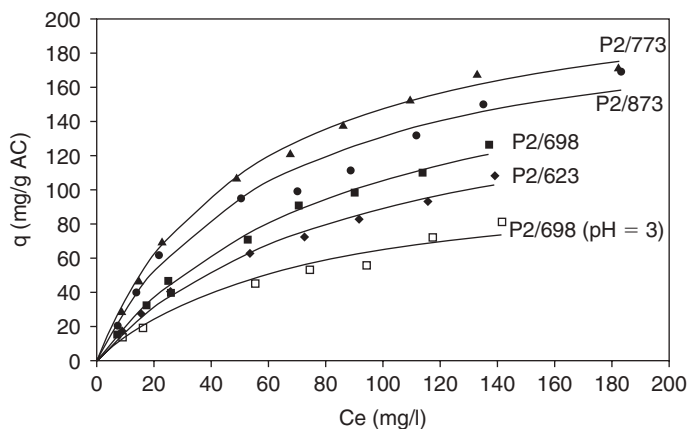
We have carried out an extensive investigation of the oxypropylation of a whole variety of natural polymers using a simple bulk technique which only involves the substrate, PO and a nucleophilic catalyst. Given the general interest of this procedure and of the ensuing viscous polyols, a specific chapter of this book (Chapter 12) is devoted to the issue and therefore the conditions related to the use of lignins as substrate, the results obtained and the exploitation of the corresponding polyols is to be found there. It is important to emphasize that this process differs substantially from that adopted previously by Glasser's group and already discussed above in the context of both polyurethanes and epoxy resins.

## 11.4 CARBON FIBRES AND OTHER GRAPHITIC MATERIALS

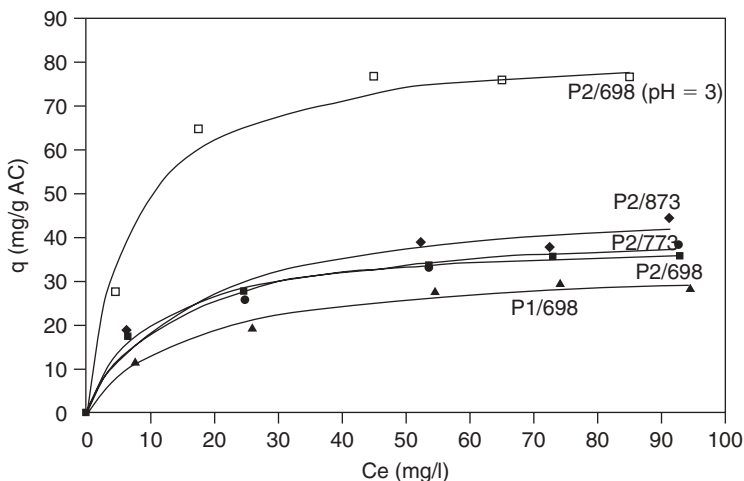
It is reasonable to expect that lignins should be good precursors to graphitic structures, given their high contents of aromatic moieties. Two types of such materials have been pursued in this field, as briefly reviewed below, with particular emphasis on recent advances.

### 11.4.1 Activated carbon

The essence of this research is the result of a systematic study conducted over the last couple of decades by a Spanish laboratory, in which the controlled pyrolysis of KL was optimized to give activated carbons of high quality [64]. Essentially, a precarbonization treatment at 350°C under nitrogen was followed by further carbonization at 700–900°C. Finally, the product was activated either physically by a flow of carbon dioxide, or chemically with ZnCl<sub>2</sub>. Depending on the specific treatment, materials with different properties were obtained, namely with specific surfaces of 1 000–2 000 m<sup>2</sup> g<sup>-1</sup> and a micro/meso/macro porosity distribution which could be readily adapted to the envisaged utilization. These materials possess characteristics which are ideally suited for applications like gas and water purification, liquid–liquid separation, selective adsorption and heterogeneous catalysis [64,65]. The lignin used as a starting material to prepare carbon was isolated from *Eucalyptus Grandis* kraft black liquors by acid precipitation. After purification and drying, it was impregnated by incipient wetting with 85 per cent (w/w) aqueous phosphoric acid at room temperature and dried for 24 h at 333 K in a vacuum dryer. The impregnated lignin was thermally treated under nitrogen at different activation temperatures (623–873 K). For example, the sample P2/698 corresponds to the activated carbon prepared at a phosphoric acid/lignin ratio of 2 and an activation temperature of 698 K. Figures 11.16 and 11.17 show the adsorption isotherms of phenol and Cr (VI), respectively, using carbonaceous substrates obtained under different conditions.



**Figure 11.16** Adsorption isotherms of phenol (298 K) on the activated carbons obtained at different activation temperatures (pH = 6, unless indicated). (Reproduced by permission of Elsevier. Copyright 2004. Reprinted from Reference [65a]).



**Figure 11.17** Adsorption isotherms of Cr(VI) (298 K) on activated carbons (pH = 7, unless indicated). (Reproduced by permission of Elsevier. Copyright 2004. Reprinted from Reference [65a]).

## 11.4.2 Carbon fibres

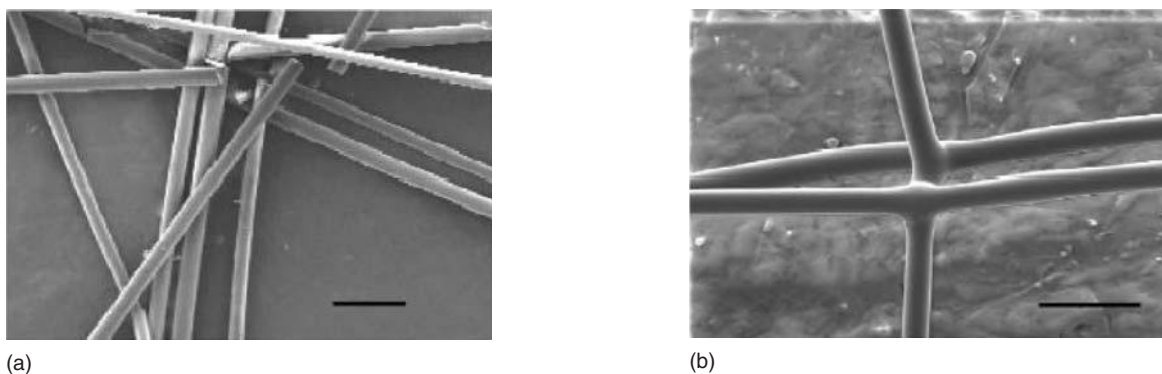
Research on the use of lignins as precursors to carbon fibres started some 40 years ago, but it is only from the 1990s that rational approaches have been pursued. Kadla *et al.* reviewed this topic until the beginning of the millennium [66] and have contributed significantly since then to its progress with valuable investigations.

Some of the lignins they used could be softened and spun into fibres as such, but better results were obtained from their homogeneous blends with PEO [67]. Subsequent carbonization at 1000°C, following thermal stabilization at 250°C, gave carbon fibres with typical diameter of 30–60 μm, tensile strengths of 350–450 MPa, moduli of 30–60 GPa and elongations at break of about 1 per cent. Figure 11.18 shows the effect of increasing thermal stabilization temperature rate on the fibre stability.

Hollow core carbon fibres were also prepared from heterogeneous lignin–poly(propylene) blends, whose morphology was generated by the selective thermal ablation of the polyolefin [68].

Recent additions to these investigations deal with the use of poly(ethylene terephthalate) as the lignin blend component [69] and with the oxidative thermal stabilization of KL fibres [70].





**Figure 11.18** Micrographs of 99 per cent hardwood kraft lignin (HKL)/1 per cent PEO (100 K) fibres after thermal stabilization at temperature rates of (a) 30°C/h and (b) 90°C/h (in both cases the bar represents 100 µm). (Reproduced by permission of Pergamon. Copyright 2002. Reprinted from Reference [67]).

### 11.5 LIGNIN SURFACES AND INTERFACES

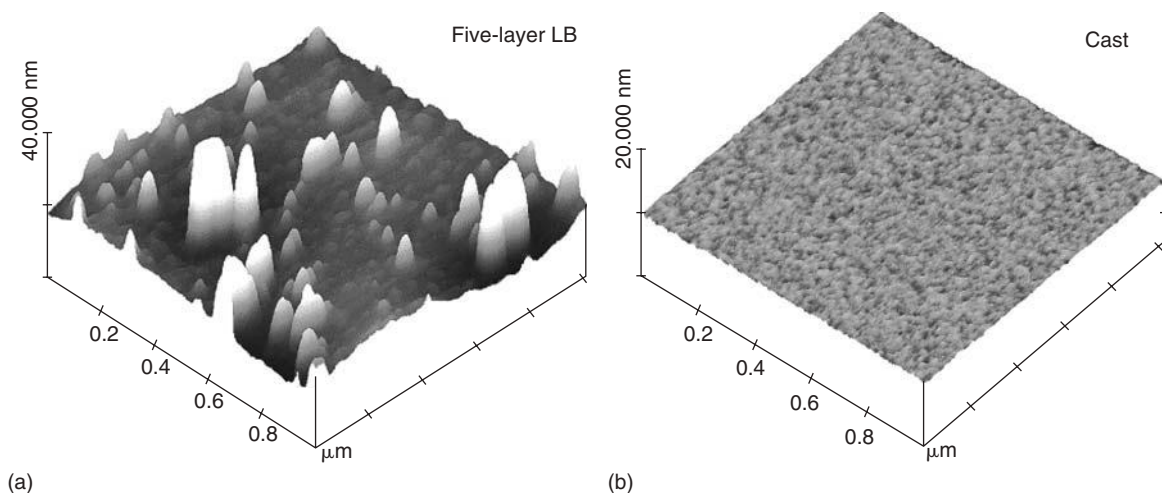
Monolayers of lignin have been examined with a Langmuir trough and the observed intermolecular associations, already well-known in solution systems, point to the possibility of fairly regular extended aggregates in these two-dimensional domains [71]. Figure 11.19 displays the AFM image for a five-layer Langmuir–Blodgett (LB) film of lignin deposited onto mica. The roughness value is 3.8 nm. Figure 11.19(b) shows a lower roughness for the cast film, compared to the LB film (Fig. 11.19(a)), which may be attributed to the absence of molecular orientation in the cast film.

Very recent studies have been devoted to the preparation and characterization of smooth lignin surfaces of extremely thin films spun from solutions [72]. The interaction of these surfaces with a cellulose sphere has been quantified [73] and the corresponding forces found to behave according to the DLVO theory.

These studies open the way to a better understanding of the physical and chemical molecular behaviour of lignins faced with different structures through the construction of LB morphologies and by further studies of interfaces.

### 11.6 AROMATIC MONOMERS FROM LIGNIN AND MODEL POLYMERS

The possibility of degrading lignins in a controlled manner has interested wood chemists for a long time particularly because of their interest in establishing clear-cut lignin structures starting from the isolated fragments. For



**Figure 11.19** AFM images of lignin deposited on mica: (a) LB film, (b) cast film. (Reproduced by permission of the American Chemical Society. Copyright 2002. Reprinted from Reference [71b]).

a polymer chemist, this strategy must be seen in the very different context related to the possibility of preparing well-defined monomers or at least interesting precursors to monomers. This approach is obviously restricted to aromatic structures bearing either functions suitable for polycondensation (*e.g.* OH and COOH groups) or moieties like aldehyde groups that can be readily converted into polymerizable unsaturations.

To the best of our knowledge, this goal has never been attained in terms of reasonable yields of one monomer or a group of homologous structures. This is not surprising considering, on the one hand, the multiplicity of 'monomer units' present in the macromolecular structure of a given lignin and its variety as a function of species and pulping processes and, on the other hand, the complexity associated with their fine-tuned chopping.

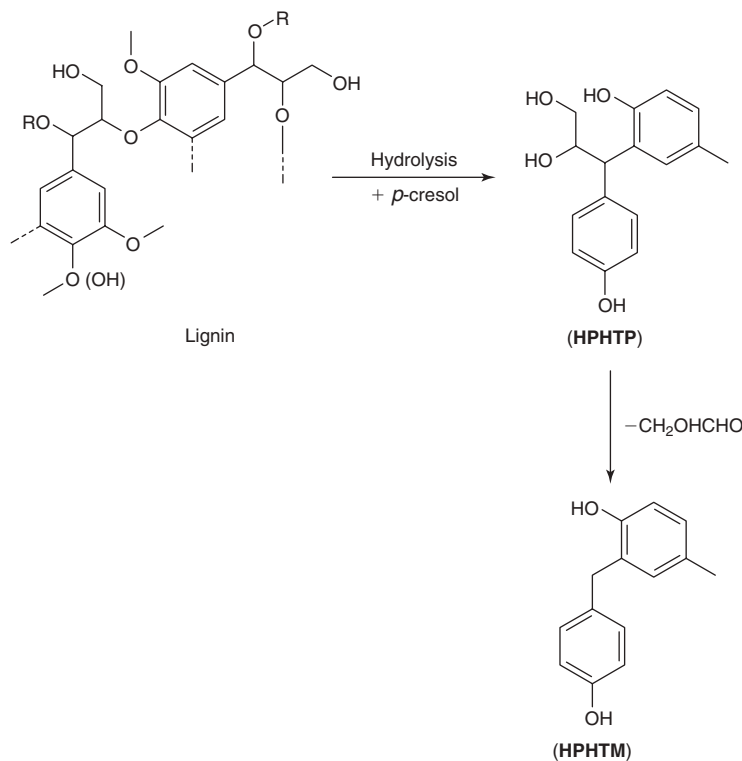
The only viable conversion of lignin into a single aromatic compound is the synthesis of vanillin, which is a very useful commodity, but not in the realm of polymer chemistry. A recent investigation reports its oxidation to vanillic acid [74] and another, the use of this compound for leather tanning [75].

Okuda *et al.* [76] used a solvothermal treatment of organosolv lignin with a water-*p*-cresol mixture to generate a single product, *viz.* 4-hydroxyphenyl-(2-hydroxytolyl)-methane (HPHTM), in yields as high as 80 per cent without any charring. The proposed mechanism for the formation HPHTM, is shown in Scheme 11.8. According to the authors, the HPHTM is produced by the elimination of glycolaldehyde via the formation of an intermediate 'hydroxyphenyl-propane derivative (HPHTP)'.

This bis-phenol could be an interesting monomer for the synthesis of fully or partly aromatic polyesters and polyethers.

In a different vein, Bonini and D'Auria [77] examined the products arising from the degradation of steam-exploded straw lignin induced by a singlet oxygen treatment. As opposed to the solvothermal study mentioned above, this process generated a host of aromatic compounds with various moieties appended to them, such as phenolic and aliphatic OH functions, methoxy groups and  $\alpha$ ,  $\beta$ C=C unsaturations. This lack of selectivity seemed intrinsic to the multiple reaction pathways induced by singlet oxygen and therefore of little use for the purpose of preparing viable monomers.

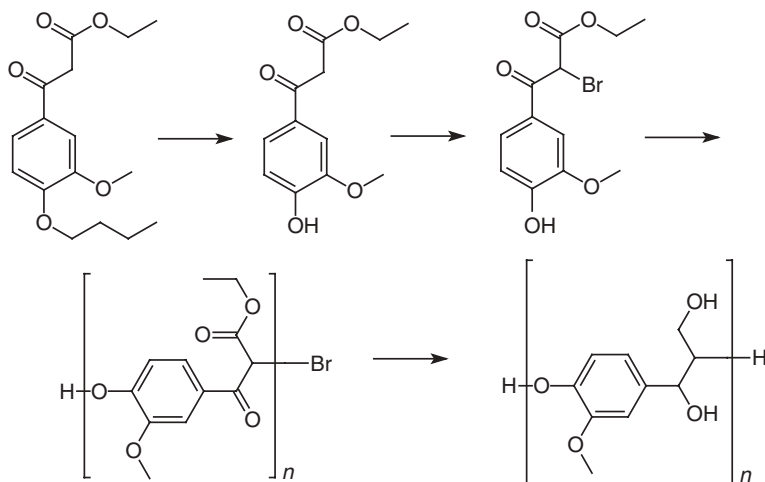
If that quest has up to now eluded researchers, considerable attention has been placed on the synthesis of lignin-like polymers using model monomers. Recent results in this context include the work of Kishimoto's group [78]



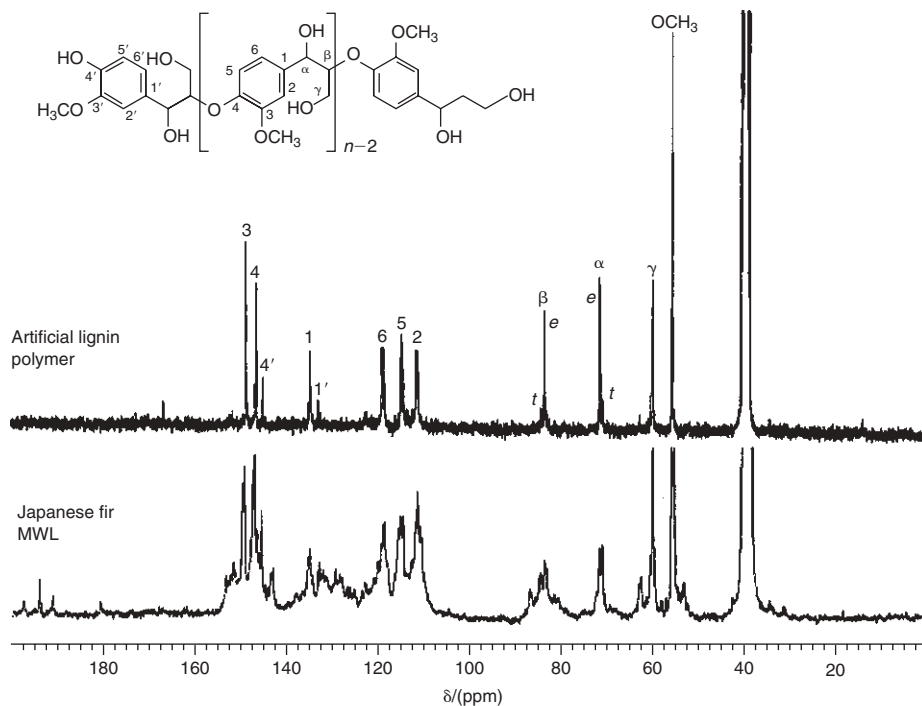
Scheme 11.8

based on the synthesis of ' $\beta$ -O-4 type artificial lignin' through the linear polyetherification of differently substituted phenols bearing a 4-carbonyl-CH<sub>2</sub>Br moiety using the Williamson reaction, as shown in the example of Scheme 11.9. Figure 11.20 shows the NMR spectra of both artificial and natural lignins.

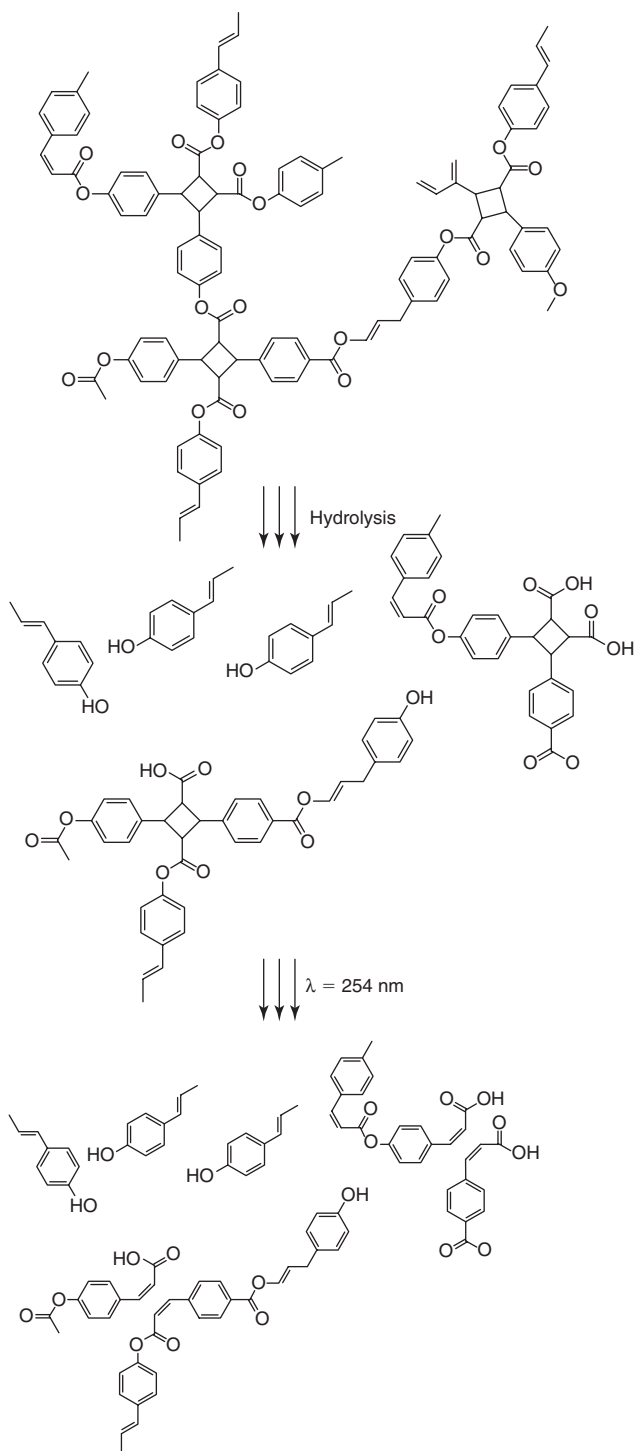
Kaneko *et al.* [79] have prepared hyperbranched structures from the copolymerization of 4-hydroxycinnamic acid with 3,4-dihydroxycinnamic acid (*i.e.* monomers bearing some resemblance to lignin structural units). These



**Scheme 11.9**



**Figure 11.20** <sup>13</sup>C-NMR spectra of artificial and natural milled wood lignins (MWL). (Reproduced by permission of the Royal Society of Chemistry. Copyright 2006. Reprinted from Reference [78b]).



Scheme 11.10

materials displayed liquid crystal features and were moreover readily crosslinked by UV irradiation, giving intermolecular coupling between C=C unsaturations. The degradation of these polyester networks could be carried out in two stages, *viz.* hydrolysis to split the ester group and far-UV irradiation to undo the cyclobutane moieties, as shown in Scheme 11.10.

The use of terms like 'lignin related polymers', 'artificial lignin' and 'phytomonomers' in the two latter studies are clearly overstating the issues at stake, because both the monomers used and the structure of the ensuing polymers have only faint connections with the real counterparts. In other words, the materials obtained are interesting, but their relation with lignins is quite tenuous. This assessment does not imply that such investigations are not relevant, but simply that hopefully further work will come steadily closer to the lignin paradigm.

## 11.7 CONCLUSIONS

Given the vast array of materials and other chemical commodities that can be prepared using lignins and the potential of industrial applications that some of them possess [80], it appears that the meagre figure of some 2 per cent as the proportion of lignins isolated from pulping liquors which is presently exploited for those purposes reflects a very poor state of affairs. A more vigorous interaction between academia and industry is required to make lignins real actors in the biorefinery scene and move from a scientific to a technological status, thus approaching the relevance that other natural polymers like cellulose, chitosan and starch have acquired over the years.

## REFERENCES

1. (a) *ACS Symp. Ser.*, 1989, 397. (b) Gandini A., in *Comprehensive Polymer Science*, Suppl., Eds.: Aggrawal S.L. and Russo S., Pergamon Press, Oxford, 1992, **Volume 1**, p. 527. (c) Wang J., St John Manley R., Feldman D., *Prog. Polym. Sci.*, **17**, 1992, 611. (d) *ACS Symp. Ser.*, 2000, 742. (e) Gandini A., in *Les Polymères Naturels: Structure, Modifications, Applications*, Chapter VI, Editions GFP, Paris, 2000. (f) *Chemical Modification, Properties and Usage of Lignin*, Ed. Hu T.Q., Kluwer, New York, 2002. (g) *ACS Symp. Ser.*, 2007, 954.
2. www.ili-lignin.com.
3. Kubo S., Kadla J.F., *Biomacromolecules*, **6**, 2005, 2815.
4. Bouajila J., Dole P., Joly C., Limare A., *J. Appl. Polym. Sci.*, **102**, 2006, 1445.
5. (a) Kubo S., Kadla J.F., *Macromolecules*, **36**, 2003, 7803. (b) Kubo S., Kadla J.F., *J. Appl. Polym. Sci.*, **98**, 2005, 1437. (c) Kubo S., Kadla J.F., *Macromolecules*, **37**, 2004, 6904. (d) Kubo S., Kadla J.F., *Holzforschung*, **60**, 2006, 245.
6. Guo Z.X., Gandini A., *Eur. Polym. J.*, **27**, 1991, 1177.
7. Li Y., Mlinár J., Sarkanen S., *J. Polym. Sci. Polym. Phys. Ed.*, **35**, 1997, 1899.
8. Lee S.B., Luner P., *Tappi J.*, **55**, 1972, 116.
9. Belgacem M.N., Blayo A., Gandini A., *J. Colloid Interf. Sci.*, **182**, 1996, 431.
10. Kubo S., Kadla J.F., *Biomacromolecules*, **4**, 2003, 561.
11. Cobianu C., Ungureanu M., Ignat L., Ungureanu D., Popa V.I., *Ind. Crops Prods.*, **20**, 2004, 231.
12. Kadla J.F., Kubo S., *Composites A*, **35**, 2004, 395.
13. Zhang X., Benavente J., Garcia-Valls, *J. Power Sources*, **145**, 2005, 292.
14. Gregorová A., Cibulková Z., Kosíková B., Simon P., *Polym. Degrad. Stab.*, **89**, 2005, 553. and references therein.
15. Canetti M., Bertini F., De Chirico A., Audisio G., *Polym. Degrad. Stab.*, **91**, 2006, 494.
16. Toh K., Nakano S., Yokoyama H., Ebe K., Gotoh K., Noda H., *Polym. J.*, **37**, 2005, 633.
17. Gosselink R.J.A., Snijder M.H.B., Kranenbarg A., Keijsers E.R.P., de Jong E., Stigsson L.L., *Ind. Crops Prod.*, **20**, 2004, 191.
18. Gregorová A., Kosíková B., Moravcik R., *Polym. Degrad. Stab.*, **91**, 2006, 229.
19. Kosíková B., Gregorová A., *J. Appl. Polym. Sci.*, **97**, 2005, 924.
20. Iqbal A., Frommn L., Saleem A., Ishaq M., *Polym. Comp.*, **28**, 2007, 186.
21. Belgacem M.N., Blayo A., Gandini A., *Ind. Crops Prod.*, **18**, 2003, 145.
22. Gosh I, Jain RK, Glasser WG, *Reference Id*, p. 331.
23. (a) Baumberger S., *Reference If*, p.1. (b) Lepifre S., Baumberger S., Pollet B., Cazaux F., Coqueret X., Lapierre C., *Ind. Crops Prod.*, **20**, 2004, 219. (c) Lepitire S., Froment M., Cazaux F., Houot S., Lourdin D., Coqueret X., Lapierre C., Baumberger S., *Biomacromolecules*, **5**, 2004, 1678.
24. Berry, B.C., Viswanathan T., *Reference If*, p. 21.
25. Nägele, H., Pfitzer J., Nägele E., Inone R.E., Eisenreich N., Eckl W., Eyerer P., *Reference If*, p. 101.

26. Li Y., Sarkanen S., *Reference Id*, p. 351.
27. Li Y., Sarkanen S., *Macromolecules*, **35**, 2002, 9707.
28. Li Y., Sarkanen S., *Macromolecules*, **38**, 2005, 2296.
29. Chen Y., Sarkanen S., *Reference 1g*, p. 229.
30. Cazacu G., Vasile C., Stoleriu A., Constantinescu G., Pohoata V., *Proceedings of the 7th ILI Forum*, Barcelona 2005, p. 175.
31. Cazacu G., Pascu M.C., Profire L., Kowarski A.I., Mihaes M., Vasile C., *Ind. Crops Prod.*, **20**, 2004, 261.
32. Raschip I.E., Dumitriu R.P., Cazacu G., Vasile C., *Proceedings of the 7th ILI Forum*, Barcelona 2005, p. 167.
33. Cazacu G., Vasile C., Agafitei G.E., Pascu M.C., *Proceedings of the 7th ILI Forum*, Barcelona 2005, p. 171.
34. Fernandes D.M., Winkler Hechenleitner A.A., Job A.E., Radovanovic E., Gómez Pineda E.A., *Polym. Degrad. Stab.*, **91**, 2006, 1192.
35. Chen P., Zhang L., Peng S., Liao B., *J. Appl. Polym. Sci.*, **101**, 2006, 334.
36. Toriz G., Denes F., Young R.A., *Reference Id*, p. 367.
37. Raghuraman A., Tiwari V., Thakkar J.N., Gunnarsson G.T., Shukla D., Hindle M., Desai U.R., *Biomacromolecules*, **6**, 2005, 2822.
38. Pizzi A., in *Handbook of Adhesive Technology*, Eds.: Pizzi A. and Mittal K.L., Marcel Dekker, New York, 2003, p. 589.
39. Turunen M., Alvilä L., Pakkanen T.T., Rainio J., *J. Appl. Polym. Sci.*, **88**, 2003, 582.
40. Matsushita Y., Wada S., Fukushima K., Yasuda S., *Ind. Crops Prod.*, **23**, 2006, 115.
41. El. Mansouri N., Pizzi A., Salvadó J., *Holz Roh. Werkst.*, **65**, 2007, 65.
42. Feldman D., Lacasse M., St. John Manley R., *J. Appl. Polym. Sci.*, **35**, 1988, 247. Natansohn A., Lacasse M., Ban D., Feldman D., *J. Appl. Polym. Sci.*, **40**, 1990, 899.
43. Detoisien M., Pla F., Gandini A., Cheradame H., British Polym. J., **17**, 1985, 260. Cheradame H., Destoisien M., Gandini A., Pla F., Roux G., *British Polym. J.*, **21**, 1989, 269.
44. Gandini A., Belgacem M.N., Guo Z.-X., Montanari S., *Reference 1f*, p. 57.
45. Evtuguin D.V., Andreolety J-P., Gandini A., *Eur. Polym. J.*, **34**, 1998, 1163.
46. Hatakeyama H., *Reference 1f*, p. 41.
47. Bonini C., D'Auria M., Emanuele L., Ferri R., Pucciarello R., Sabia A.R., *J. Appl. Polym. Sci.*, **98**, 2005, 1451.
48. Glasser W.G., Jain R.K., *Holzforschung*, **47**, 1993, 225. Li S.M., Lundquist K., *J. Wood Chem. Technol.*, **17**, 1997, 391. Ralph J., Lu F.C., *J. Agric. Food Chem.*, **46**, 1998, 4616.
49. Guo Z.X., Gandini A., Pla F., *Polym. Int.*, **27**, 1992, 17.
50. Evtuguin D., Gandini A., *Acta Polym.*, **47**, 1996, 344.
51. Shaw J.M., *Print. Circ. Fabr.*, **19**(11), 1996, 38; *New Scientist*, November 29 issue, 1997.
52. Meister J.J., Chen M.J., *Macromolecules*, **24**, 1991, 6843; *J. Appl. Polym. Sci.*, **49**, 1993, 935.
53. Chen M.J., Meister J.J., *Reference Id*, p. 321.
54. Schneider M.H., Phillips J.G., *US Patent 6747076*, 2004.
55. Kelley S.S., Ward T.C., Rials T.G., Glasser W.G., *J. Appl. Polym. Sci.*, **37**, 1989, 2961. Kelley S.S., Glasser W.G., Ward T.C., *Reference 1a*, p. 402. de Oliveira W., Glasser W.G., *Reference 1a*, p. 414.
56. Toffey A., Glasser W.G., *Holzforschung*, **51**, 1997, 71.
57. (a) Kelley S.S., Ward T.C., Glasser W.G., *J. Appl. Polym. Sci.*, **41**, 1990, 2813. (b) Kelley S.S., Glasser W.G., Ward T.C., *Polymer*, **30**, 1989, 2265.
58. (a) Hofman K., Glasser W.G., *J. Wood Chem. Technol.*, **13**, 1993, 73. (b) *J. Adhesion*, **40**, 1993, 229 (c) *Macromol. Chem. Phys.*, **195**, 1994, 65.
59. Zhao B., Chen G., Liu Y., Hu K., Wu R., *J. Mater. Sci. Lett.*, **20**, 2001, 859.
60. Sun G., Sun H., Liu Y., Zhao B., Zhu N., Hu K., *Polymer*, **48**, 2007, 330.
61. Naveau H.P., *Cell. Chem. Technol.*, **9**, 1975, 71.
62. Thielemans W., Wool R.P., *Biomacromolecules*, **6**, 2005, 1895.
63. Dourel P., Randrianalimanana E., Deffieux A., Fontanille M., *Eur. Polym. J.*, **24**, 1988, 843.
64. (a) Cordero T., Rodriguez-Maroo J.M., Rodriguez-Mirasol J., Rodriguez J.J., *Thermochim. Acta.*, **164**, 1990, 135. (b) Rodriguez-Mirasol J., Rodriguez J.J., Cordero T., *Carbon*, **31**, 1993, 53. (c) 87. (d) Gonzalez-Serrano E., Cordero T., Rodriguez-Mirasol J., Rodriguez J.J., *Ind. Eng. Chem. Res.*, **36**, 1997, 4832.
65. (a) Gonzalez-Serrano E., Cordero T., Rodriguez-Mirasol J., Cotoruelo L., Rodriguez J.J., *Water Res.*, **38**, 2004, 3043. (b) Rodriguez-Mirasol J., Bedia J., Cordero T., Rodriguez J.J., *Sep. Sci. Technol.*, **40**, 2005, 3113. (c) Cotoruelo L.M., Marques M.D., Rodriguez J.J., Cordero T., Rodriguez J.J., *Ind. Engin. Chem. Res.*, **46**, 2007, 4982. (d) Suhas P.J.M., Carott P.J.M., Ribeiro-Carott M.M.L., *Biores. Technol.*, **98**, 2007, 2301.
66. Kadla J.F., Kubo S., Gilbert R.D., Venditti R.A., *Reference 1f*, p. 121.
67. Kadla J.F., Kubo S., Venditti R.A., Gilbert R.D., Compere A.L., Griffith W., *Carbon*, **40**, 2002, 2913.

68. Kadla J.F., Kubo S., Venditti R.A., Gilbert R.D., *J. Appl. Polym. Sci.*, **85**, 2002, 1353.
69. Kubo S., Kadla J.F., *J. Polym. Environ.*, **13**, 2005, 97.
70. Braun J.L., Holtman K.M., Kadla J.F., *Carbon*, **43**, 2005, 385.
71. Barros, A.M., Dhanabalan A., Constantino C.J.L., Balogh D.T., Oliveira O.N., *Thin Solid Films*, , **354**, 1999, 215. Pasquini D., Balogh D.T., Antunes P.A., Constantino C.J.L., Curvelo A.A.S., Aroca R.F., Oliveira O.N., *Langmuir*, **18**, 2002, 6593. Pasquini D., Balogh D.T., Oliveira O.N., Curvelo A.A.S., *Coll. Surf. A* **252**, 2005, 193.
72. (a) Norgren M., Notley S.M., Majtnerova G.G., *Langmuir*, **22**, 2006, 1209. (b) Norgren L., Gärdlund L., Notley S.M., Htun M., Wågberg L., *Langmuir*, **23**, 2007, 3737.
73. Notley S.M., Norgren M., *Langmuir*, **22**, 2006, 11199.
74. Munavalli D.S., Chimatadar A., Nandibewoor S.T., *Ind. Eng Chem. Res.*, **46**, 2007, 1459.
75. Suparno O., Covington A.D., Phillips P.S., Evans C.S., *Resour. Conserv. Recycl.*, **45**, 2005, 114.
76. Okuda K., Man X., Umetsu M., Takami S., Adschiri T., *J. Phys.: Condens. Mat.*, **16**, 2004, S1325.
77. Bonini C., D'Auria M., *Ind. Crops Prod.*, **20**, 2004, 243.
78. (a) Kishimoto T., Uraki Y., Ubukata M., *Org. Biomol. Chem.*, **3**, 2005, 1067. (b) **4**, 2006, 1343.
79. Kaneko T., Thi T.H., Shi D.J., Akashi M., *Nat. Mater.*, **5**, 2006, 966.
80. Lora J.H., Glasser W.G., *J. Polym. Environ.*, **10**, 2002, 39.

This page is intentionally left blank.



# Partial or Total Oxypropylation of Natural Polymers and the Use of the Ensuing Materials as Composites or Polyol Macromonomers

Alessandro Gandini and Mohamed Naceur Belgacem

---

## ABSTRACT

This chapter describes the partial and total oxypropylation of different natural polymers and more complex biomass substrates and the use of the ensuing materials as composites or polyol macromonomers, respectively. The total oxypropylation of different lignins, sugar beet pulp, cork, chitin and chitosan and olive pits is then reviewed in terms of its success in converting all these substrates into viscous polyol mixtures, which can be used to prepare polyurethane foams with thermal insulating properties similar to those of conventional industrial counterparts. The chapter finally deals with the *superficial* oxypropylation of cellulose fibres and starch granules (*i.e.* reactions limited to a certain thickness of the substrates) so that the ensuing materials keep their original morphology and properties, but now possess a thermoplastic shell which enables their conversion to single-component composites by simple thermal processing.

## Keywords

Sugar beet pulp, Cork, Chitin, Chitosan, Olive pits, Polyurethane foams, Partial oxypropylation, Total oxypropylation, Cellulose fibres, Starch granules, Single-component composites

## 12.1 INTRODUCTION

The extensive research on the ring-opening anionic polymerization of oxiranes has provided an extremely simple approach to the grafting and chain-extension of macromolecular structures bearing hydroxyl functions [1]. Their activation by a strong Brønsted base generates the corresponding oxianions which function as initiating site for the oxirane propagation reaction. Both ethylene and propylene oxide (**PO**) respond efficiently to this type of polymerization, but the use of the former requires homologated equipment capable of ensuring safety against explosions provoked by sudden uncontrolled exothermic polymerizations. It is therefore much more common to practice oxypropylation reactions.

In the realm of polymer materials, oxypropylation has received considerable attention when applied to both small polyol molecules, like sugars and to polymers bearing multiple OH groups, like cellulose. These chain-extension reactions do not produce any increase in the OH-functionality of the starting substrate, since their role is to transport these groups as chain ends of the inserted polyether segments. The average length of these segments can be modulated as a function of the reaction parameters, but within the limitation imposed by the inevitable transfer reactions that accompany all these systems and give rise to homopolymers of the monomer used, generally in the form of  $\alpha,\omega$ -oligoether diols.

A large variety of functional polymers derived from this approach has been synthesized including, for example, block copolymers in which the polyether sequences stem from a central polymer of a very different nature, like polystyrene [1]. In the same vein, a multitude of non-ionic surfactants are today commercially available thanks to the application of these principles to oligomeric structures bearing a hydrophobic segment, like an aliphatic chain or even a poly(propylene oxide) (PPO) sequence, joined to a hydrophilic counterpart, which is mostly an OH-terminated oligo-ethylene oxide [2]. A third thoroughly exploited approach consists in synthesizing star-shaped macro-molecular materials using, for example, glycerol or pentaerithritol as core molecules which are subsequently decorated with polyether branches. All these applications testify to the degree of sophistication and control reached by the ring-opening polymerization of oxiranes, since the sequence length of the ensuing polyether segments can be predetermined and precisely achieved [1].

The extension of these principles to molecules and macromolecules based on renewable resources has been applied to polymer chemistry and technology, mostly in two areas requiring viscous materials, namely: (i) the preparation of liquid polyols to be used in the manufacture of polyurethanes, and (ii) the synthesis of macromolecular rheology modifiers. A typical polyol for the synthesis of polyurethane foams is obtained industrially from the oxypropylation of sorbitol, [3] whereas hydroxypropyl cellulose represents a major commodity for the rheological control of paints, foodstuff, cosmetics, etc. [4].

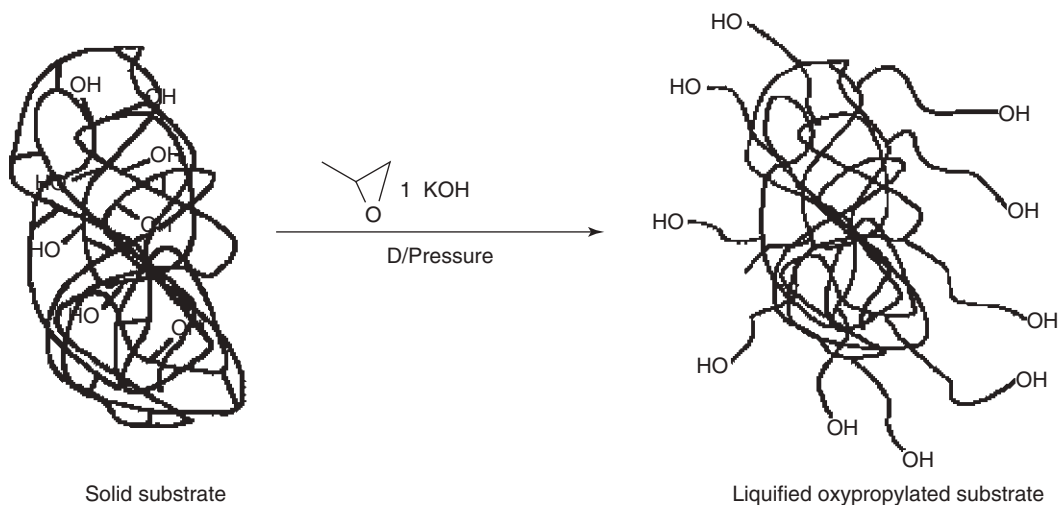
This chapter is devoted to a brief survey of recent work dealing with the oxypropylation of various natural polymeric substrates, all of which, of course, bear OH groups, sometimes accompanied by  $\text{NH}_2$  functions. Whereas the oxyethylation and oxypropylation of cellulose, as well as the oxypropylation of sorbitol, are industrial processes with well-defined parameters and product properties, the studies described here are still at a research stage, although pilot plant development has been reached in some instances. The other relevant difference with respect to the two commercial commodities is that the investigations discussed below deal essentially with substrates which are in fact by-products of major processes (*i.e.* raw materials of little economic impact), but available in very large quantities. In other words, the issue here is two-fold, *viz.* the exploitation of renewable resources and their upgrading through their conversion into value-added materials.

Two distinct processes are used in the oxypropylation of molecular or macromolecular substrates *viz.* systems using a basic aqueous medium and moderate temperatures and bulk reactions in which both high temperatures and pressures are involved. The former approach is particularly suited for the attachment of short branches and has been successfully applied particularly to cellulose and starch. It does not however function satisfactorily with less hydrophilic substrates which tend to be very passive towards activation. For these situations, and indeed in a more general context, the bulk reaction provides an excellent alternative, as emphasized in all the examples discussed in this chapter. Quite apart from the fact that this process can be applied to virtually any OH bearing substrate, it has the added advantage of eliminating any workup at the end of the reaction, since all the PO is used up and the ensuing oxypropylated material, usually in the form of a viscous liquid, is the only product present in the reactor, apart from the catalyst which can be left as such or readily neutralized by contact with the atmosphere. Furthermore, this type of process bears green connotations because of the lack of solvent manipulation and of generation of VOC.

This chapter only deals with the studies that called upon the bulk process because, apart from the positive aspects enumerated above, they produce polyols which are ideally suited for the elaboration of different macromolecular materials, as opposed to the waterborne approach which is more often indicated for modifications associated with rheology modifiers in food and cosmetic technologies.

Most of the investigated systems which are discussed here were based on the idea of producing liquid polyols through the radical transformation of the initial morphology of the corresponding substrates, all of which are rather intractable solids. More recently, a different approach has been envisaged and successfully applied, in which the oxypropylation is limited to a certain thickness of the substrate particles so that the ensuing materials are characterized by an inner pristine core, preserving the original morphology and properties of the substrate, and a thermoplastic shell which enables the processing of a single-component composite by a simple thermal treatment like hot-pressing to produce films. This chapter is thus divided into two sections, following the corresponding different approaches.

In both instances however, the chemistry is the same and its workings can be illustrated by the simplified Scheme 12.1, for which the only difference is the extent of penetration of the oxypropylation reaction within the substrate particles. The number of OH groups involved in this chain-extension reaction, the length of the ensuing grafts, as well as the incidence of homopolymer formation, depend in both strategies on the actual reaction parameters. However, the one common prerequisite, essential for the optimization of this heterogeneous process (except in the case of fibres) is of course the maximum reduction in the substrate particle size compatible with its grinding aptitude.



Scheme 12.1

## 12.2 'TOTAL' OXYPROPYLATION

This section deals with the transformation of different natural polymeric substrates, whose common feature is a high content of OH groups, into viscous polyols through their near-complete oxypropylation. Given the very pronounced similarities associated with all the systems examined below, a detailed description of the process will be provided for the first one and only relevant differences and peculiarities discussed for the others.

### 12.2.1 Lignin

The general structures of this fundamental vegetable polymer, as well as the applications of its various industrial forms, have already been dealt with in detail in the three preceding chapters. As already pointed out, most of the utilizations of lignin as a macromonomer are qualitatively independent of its source and subsequent isolation processes only exploit the omnipresence and relative reactivity of both aliphatic and phenolic hydroxyl groups. Oxypropylation is obviously no exception to this rule and lignin should therefore be considered here as a macromolecular polyol, potentially capable of being grafted with multiple **PPO** chains.

Glasser's pioneering work on the use of lignins as precursors for the synthesis of novel polyurethanes involved, among other approaches already discussed in Chapter 11, their oxypropylation [5]. These studies were carried out with kraft and sulphite lignins (*i.e.* high molecular weight structures) which showed some resilience to a thorough oxypropylation and hence the need of high temperatures and pressures. The authors also found that these rather drastic conditions induced some lignin self-condensation processes and the consequent formation of partly insoluble products.

More recently, this process has been revisited by us in a broader context, particularly in terms of the variety of substrates examined [6, 7]. In this comprehensive study, we called upon kraft (**KL**), ALCELL organosolv (**OL**), soda (**SL**) and an oxygen organosolv lignin (**OOL**). The relevant properties of these substrates are given in Table 12.1.

Reactions were conducted in small stainless steel autoclaves equipped with a stirrer and followed by the temperature increase associated with the onset of polymerization that produced a corresponding increase in pressure which then progressively decreased to zero, indicating the total consumption of **PO**. The parameters which were varied in order to optimize the efficiency of each lignin treatment were the **PO**/lignin ratio (1–10 w/w), the type and amount of catalyst (mostly KOH, but also NaOH and various tertiary amines, used in ratios relative to lignin of 1–10 wt%) and the temperature (140–200°C, associated with pressures of 6–20 bar). Reaction times (*i.e.* the time required for the pressure to return to zero) were found to vary very considerably, ranging from a few minutes

**Table 12.1**

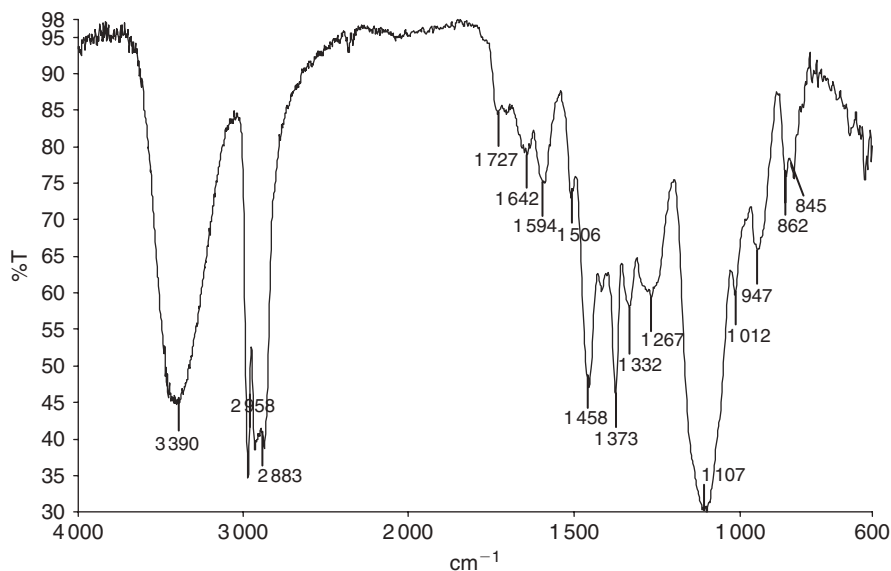
Characterization of the lignins used in our oxypropylation studies [6, 7]

	Lignins			
	KL	OL	SL	OOL
$M_n$	1 220	700	1 100	1 400
$M_w$	11 880	1 700	6 800	4 100
$M_w/M_n$	9.7	2.4	6.2	2.9
Primary aliphatic OH/C9 unit	0.39	0.23	–	0.55
Secondary aliphatic OH/C9 unit	0.27	0.14	–	0.40
Aromatic OH/C9 unit	0.78	0.63	–	0.41
Total OH/C9 unit	1.44	1.00	–	1.36
Average OH/lignin molecule	10	6	9	12

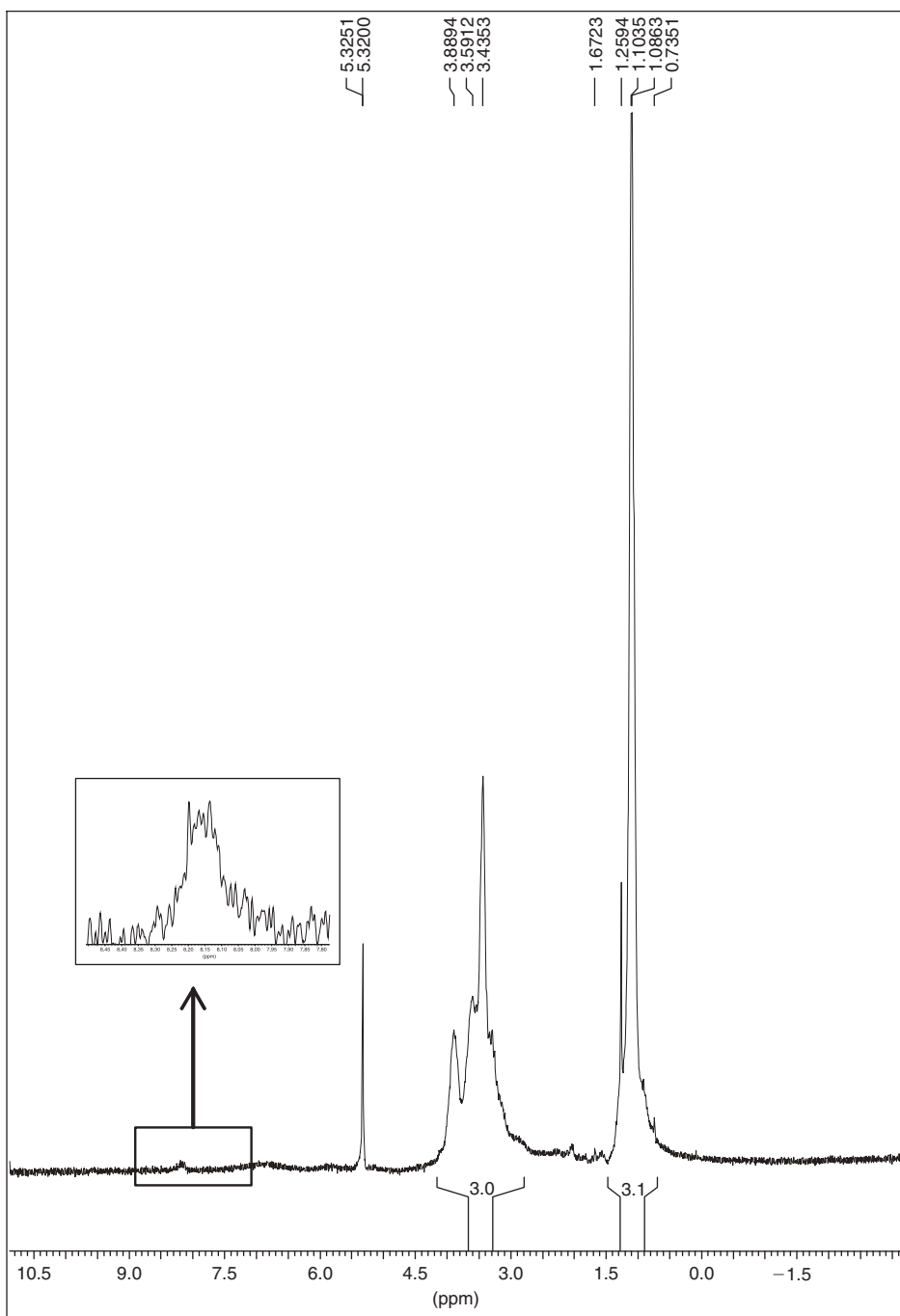
to several hours, particularly as a function of the nature of the catalyst (only KOH displayed a high activity), its concentration, the temperature and the type of lignin.

The characterization of all these products comprised their structural assessment through FTIR and NMR spectroscopy, the determination of the amount of solid residue and **PO** homopolymer and the measurement of their viscosity and hydroxyl index. Figures 12.1 and 12.2 show the FTIR and  $^1\text{H-NMR}$  spectra of the oxypropylated **SL**.

Although all the reactions did in fact proceed to completion in terms of **PO** consumption, not all the corresponding products were made up of 100 per cent liquid polyols, since some solid residue was obtained in several experiments, namely those involving **KL** (20–40 wt%) and **OOL** (20–30 wt%), in contrast to **OL** and **SL** which gave rise to solid-free viscous liquids. These findings confirmed Glasser's observations about the modest reactivity of **KL** [5] and provided a wider correlation between lignin structure and molecular weight and its aptitude to be oxypropylated. Thus, the high average molecular weight of **KL**, coupled with a significant steric hindrance around its OH groups, made this lignin the least reactive in the present context. **OOL** followed and its relative sluggishness



**Figure 12.1** FTIR spectrum of oxypropylated **SL** (30/90 **SL/PO** wt%) (Reproduced by permission of Wiley-VCH. Copyright 2005. Reprinted from Reference [7]).



**Figure 12.2**  $^1\text{H-NMR}$  spectrum of oxypropylated SL (30/90 SL/PO wt%), in  $\text{CD}_2\text{Cl}_2$  (Reproduced by permission of Wiley-VCH. Copyright 2005. Reprinted from Reference [7]).

was attributed to the presence of carbonyl and carboxylic groups in its structure. **OL** and **SL** gave the most satisfactory results in tune with their modest molecular weight.

The extent of **PO** homopolymerization with respect to lignin grafting, was also determined and found to vary between 5 and 75 wt%, the higher values being associated with the less reactive substrates. Thus, for example,

with **PO/OL** = 1 and 5 wt% of KOH, a reaction conducted at 180°C lasted about half an hour and gave a product containing about 20 per cent of homopolymer. It is important to emphasize that this low molecular weight **POP** diol does not constitute a problem in terms of the use of the whole oxypropylation product as a macromonomer mixture for the synthesis of polyurethanes, or for that matter of any other polycondensate, because it must be considered as a difunctional reagent which will participate as a chain extender in the non-linear polymer growth.

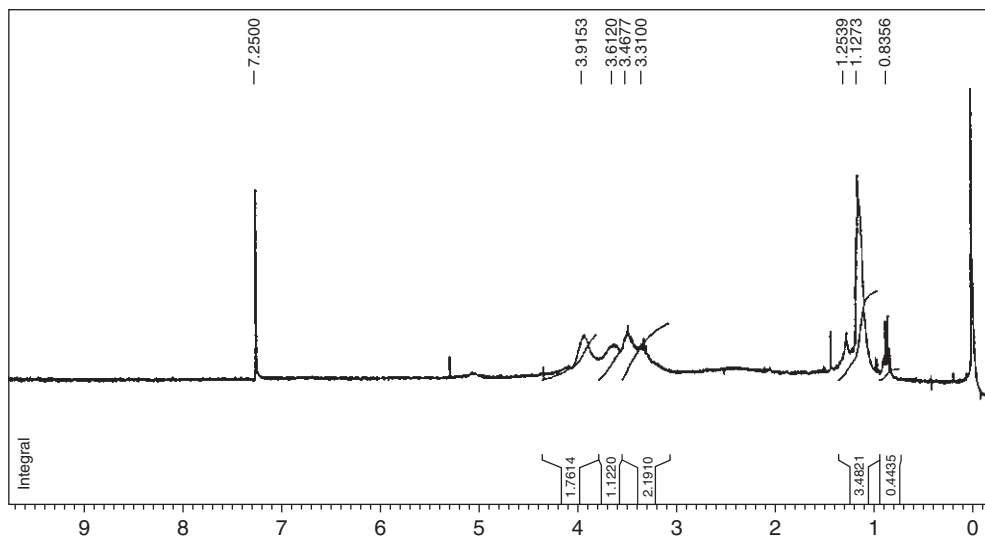
The two most relevant properties of these polyols with regard to their use as polyurethane precursors are their viscosity and hydroxyl index. Values which simulate those associated with commercial counterparts were readily obtained by adjusting the key process parameters, notably the **PO/L** ratio.

The most appropriate polyols arising from this systematic study were employed for the synthesis of polyurethane foams using standard polyfunctional methylenediphenyl diisocyanate (**MDI**) and all the conventional additives required for this technological processing [6, 7]. Additionally, foams were also prepared in which the lignin component was not only the corresponding oxypropylated material but also the lignin itself used as filler. The characterization of these foams, carried out before and after 3 months aging at room temperature and after 10 days accelerated aging at 70°C, included the determination of the foam density, its thermal conductivity and dimensional stability. Compared with the properties of foams prepared with conventional polyols, these novel homologous materials gave very satisfactory performances, particularly when oxypropylated **OL** and **SL** were used as polyols. Both **OL** and **KL** were found to be adequate fillers in proportions of up to about 30 wt%, although the term ‘filler’ is not entirely appropriate in this context since some surface OH groups must have participated in the polycondensation reaction, thus generating covalent links between the polymer matrix and the solid lignin particles, which are hence better defined as ‘reactive fillers’.

In conclusion, it has been shown that it is possible to carry out the straightforward transformation of a cheap solid industrial by-product like lignin into a liquid polyol mixture that can be employed directly as a macromonomer for the fabrication of polyurethane foams, and indeed of any other macromolecular material based on polycondensation reactions involving OH groups.

### 12.2.2 Sugar beet pulp

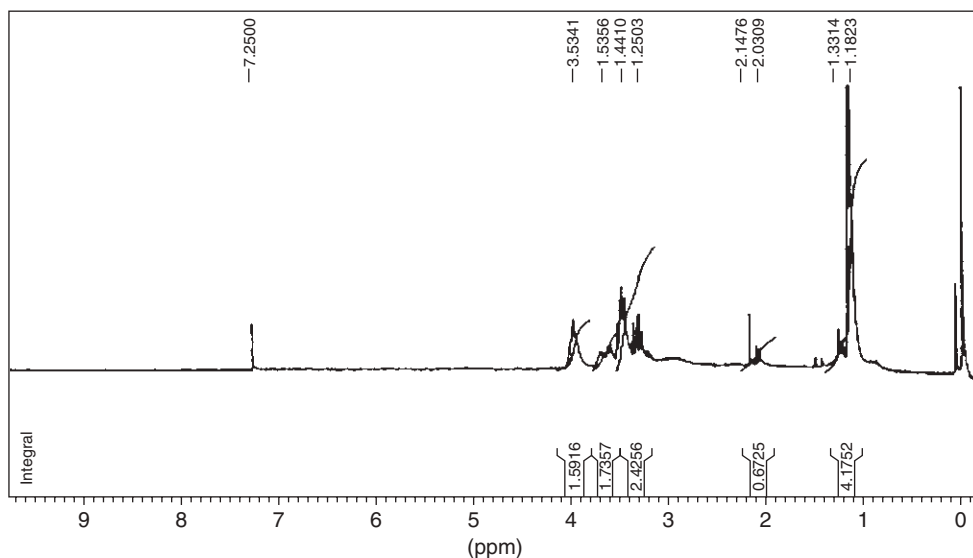
Most of the European sugar production is based on the exploitation of sugar beet (**SB**) and the corresponding industrial process generates enormous amounts of pulp as a by-product. This rather intractable fibrous solid, mostly made up of polysaccharides and pectin, has found some uses as fertilizer and animal feed, but the possibility of converting it into a source of polymeric materials had eluded researchers until it was shown that this remarkably inert natural product could in fact be readily converted into a viscous liquid polyol by a simple bulk oxypropylation treatment [8, 9].



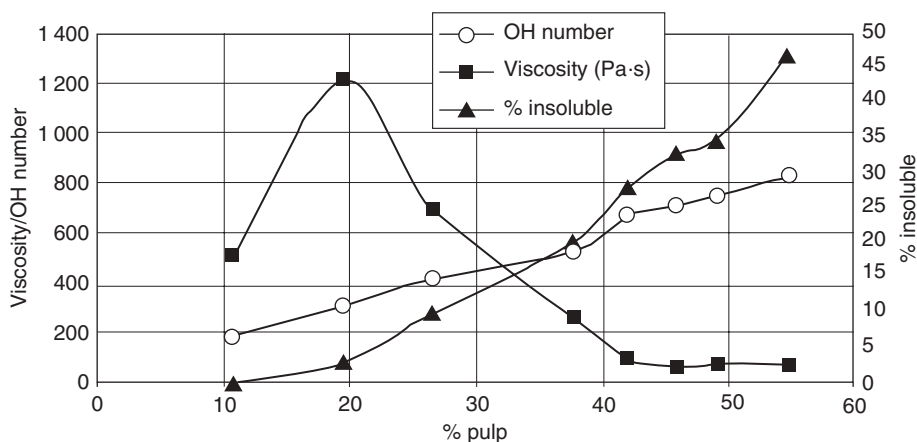
**Figure 12.3** <sup>1</sup>H-NMR spectrum of oxypropylated **SB** (25/75 **SB/PO** wt%) after the extraction of the homopolymer. (Reproduced by permission of Elsevier. Copyright 2000. Reprinted from Reference [9]).

The study of this system in our laboratory preceded that related to lignins and should be considered the second application of bulk oxypropylation after Glasser's work on lignin discussed above. The systematic investigation conducted with **SB** pulp was therefore the first of its kind in terms of the optimization of the oxypropylation reaction aimed at producing a polyol with a minimum amount of solid residue and with properties adequate for its use as a macromonomer mixture in the synthesis of polyurethanes and other crosslinked macromolecular materials. Figures 12.3 and 12.4 show the  $^1\text{H-NMR}$  spectra of the oxypropylated **SB** and of the accompanying **PO** homopolymer.

The relevant parameters that were varied in order to achieve this optimization [8] were the same as those described above for the oxypropylation of lignins, albeit here with only one substrate, namely the **SB** sample provided by the Italian sugar manufacturer Eridania. Likewise, the best results [8] corresponded to conditions quite similar to those established with lignin. All these aspects will therefore not be reported here for the sake of brevity, although it seems appropriate to summarize the work carried out to establish the optimal condition for the oxypropylation of **SB** (Fig. 12.5).



**Figure 12.4**  $^1\text{H-NMR}$  spectrum of the hexane-extracted **PO** homopolymer related to Figure 12.3. (Reproduced by permission of Elsevier. Copyright 2000. Reprinted from Reference [9]).



**Figure 12.5** Variation of the viscosity and the OH number of the  $\text{CH}_2\text{Cl}_2$ -soluble fraction and of the percentage of the  $\text{CH}_2\text{Cl}_2$ -insoluble fraction as a function of the initial percentage of **SB** in the oxypropylation reaction mixture (Reproduced by permission of Elsevier. Copyright 2000. Reprinted from Reference [8]).

The success of this study led to the scale up of the laboratory process to a pilot plant production of tens of kilograms of polyol which were then used in the processing of a number of polyurethane products, [10] including reinforced materials prepared by the RRIM technology [11].

### 12.2.3 Cork

The outer bark of *Quercus suber* known as cork constitutes a dramatic example of excessive Darwinian adaptation in a vegetable species predominant in the Mediterranean basin. The composition properties and applications of cork as a material or of its major component, suberin, are discussed in Chapter 14. When cork is processed (*e.g.* for the manufacture of stop corks) a considerable amount of rejects is produced in the form of small particles and larger unusable pieces. Presently, these by-products are burned to generate energy but, as in the case of lignin, this exploitation is far from satisfactory considering the interesting macromolecular structures associated with cork. Various laboratories have been actively pursuing more rational ways of exploiting this beautiful natural resource and the isolation and use of suberin as a macromolecule mixture, as discussed in Chapter 14. The oxypropylation of cork powder was undoubtedly another promising avenue worth exploring and research on this topic has already given some useful conclusions [12, 13].

Given the fact that polysaccharides and to a minor extent lignin-like structures are present in cork alongside suberin, OH groups are available in this material, even though their contribution to the overall chemical composition is smaller than in other natural polymers like cellulose, starch or lignin. Numerous experiments have shown that this relative paucity of hydroxyl functions does not preclude or indeed reduce the possibility of turning solid cork particles into a viscous liquid polyol by an oxypropylation process [12, 13] whose parameters are very similar to those optimized in the case of previous studies on lignin and **SB** pulp, as detailed above. Interestingly, both the problems and the advantages encountered in those previous studies were again met with cork and an additional improvement in the optimization of the oxypropylation reaction introduced at this point was the pre-impregnation of the substrate with an alcoholic solution of KOH, followed by the evaporation of the ethanol. This pre-treatment enhanced the substrate reactivity by activating a higher number of OH groups.

Both the polyol mixtures [12] and some polyurethane materials obtained from them [13] were thoroughly characterized.

The next step in this venture is the scaling up of the oxypropylation of cork and the processing of a variety of polymers derived from the ensuing polyols.

### 12.2.4 Chitin and chitosan

The increasing relevance of chitin and chitosan as sources of a variety of remarkable materials is highlighted in Chapter 25, dealing with these animal polysaccharides. The possibility of their transformation into liquid polyols arose a decade ago in the context of the search for a film forming polymer electrolyte [14]. Figure 12.6 gives the FTIR spectra of chitosan before and after oxypropylation.

Given the well-known aptitude of chitosan to generate very thin films with good mechanical properties, it was speculated that its oxypropylation might maintain the film-forming behaviour and, at the same time, generate a material capable of solvating high concentrations of lithium ions thanks to the presence of oligoether moieties. This was indeed attained by coupling the viscous oxypropylated chitosan with further ethylene- and propylene-oxide chains.

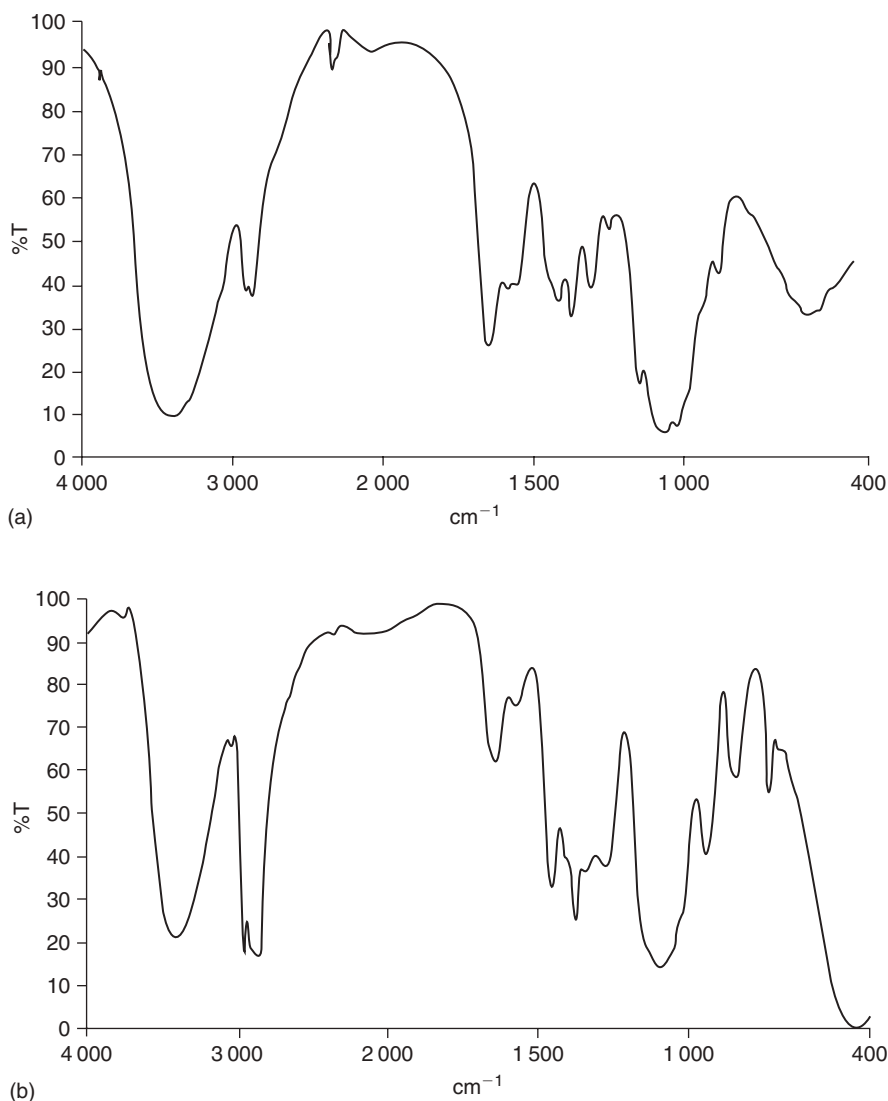
More recently, the study of the oxypropylation of both chitin and chitosan has been revived within the broader context of, on the one hand, optimizing both processes and, on the other hand, of extending the search for applications of the ensuing polyols [15].

As in the case of other natural substrates, this novel investigation is aimed at exploiting what one would define as the lower grades of both chitin and chitosan (*i.e.* the by-products resulting from the processing of both materials) compared with the high grade of the refined counterparts.

### 12.2.5 Olive pits

Another inedible agricultural by-product whose possible exploitation has been thus far limited to combustion for energy recovery is constituted by the olive pits separated from the pomace (which also includes the skin and pulp





**Figure 12.6** FTIR spectra of chitosan (a) before, and (b) after oxypropylation. (Reproduced by permission of Pergamon. Copyright 1998. Reprinted from Reference [14]).

solids) remaining after the oil-pressing process. The hard texture of the pits is made up of a mixture of natural polymers including lignin and polysaccharides (*i.e.* components rich in hydroxyl groups), thus potentially prone to oxypropylation.

Experiments were recently carried out [16] to assess the feasibility of transforming this otherwise intractable material into a liquid polyol following the very same approach described above for all the other studied natural polymers. Finely ground olive pits were thus pre-soaked with a KOH–ethanol solution and then, after the alcohol removal, oxypropylated in bulk at different temperatures within the range of 140–180°C. Preliminary results indicated a very efficient transformation of the substrate since it was turned into a viscous polyol leaving a minimal solid residue. As with all other natural substrates, this liquid product was a mixture of the oxypropylated pit polymers and **POP**.

The complete characterization of these novel polyol mixtures and their use as macromonomers in the synthesis of polymeric materials like polyurethanes and polyesters is in progress.

**Table 12.2**

Experimental conditions for the oxypropylation of different solid substrates

Solid substrate	Experiment number	Solid/PO (w/w)	Catalyst (C)	(C)/solid (%w/w)	T (°C)	Time (mn)	P <sup>a</sup> (bar)	Reference
<b>KL</b>	1	20/80	KOH	5	185	900	10.5	[6, 7]
	2	15/85	KOH	10	195	800	14.2	[6, 7]
	3	10/90	KOH	10	179	900	15.4	[6, 7]
<b>OL</b>	4	20/80	KOH	5	180	19	11.6	[6, 7]
	5	20/80	KOH	7	178	14	11.4	[6, 7]
	6	20/80	KOH	10	170	13	11.1	[6, 7]
	7		NaOH	5	177	21	17.3	[6, 7]
	8		KOH	5	175	20	8.5	[6, 7]
	9	30/70	KOH	5	178	18	8.9	[6, 7]
	10		NaOH	5	177	25	8.4	[6, 7]
	11	40/60	KOH	5	179	30	11.7	[6, 7]
	12		NaOH	5	178	44	18.2	[6, 7]
	13	50/50	KOH	5	183	45	16.2	[6, 7]
<b>OOL</b>	14	20/80	KOH	5	175	500	7.1	[6, 7]
	15	30/70	KOH	5	160	475	9.1	[6, 7]
	16	30/70	KOH	5	180	505	12.7	[6, 7]
	17	40/60	KOH	5	190	330	11.9	[6, 7]
<b>SL</b>	18	25/75	KOH	7.5	174	170	6.5	[7]
	19	25/75	KOH	10	140	180	14	[7]
	20	17/83	KOH	10	156	200	17.5	[7]
	21	30/70	KOH					[7]
<b>SBP</b>	22	30/100	NaOH	3	150	373	10	[8]
	23	30/100	KOH	3	150	330	10	[8]
	24	10/90	KOH	20	155	225	9	[8]
	25	15/85	KOH	20	145	500	8	[8]
	26	20/80	KOH	20	151	360	6	[8]
	27	26/74	KOH	20	140	315	5	[8]
	<b>Cork</b>	28	10/90	KOH	0.5–1	236	102	15.5
29		10/90	KOH	0.5–1	217	130	14.9	[12]
30		10/90	KOH	0.5–1	226	145	15.5	[12]
31		10/90	KOH	0.5–1	217	125	15.0	[12]
32		10/90	KOH	0.5–1	258	99	15.0	[12]

<sup>a</sup> Maximum pressure.

Tables 12.2 and 12.3 summarize the experimental conditions used for the oxypropylation of some of the substrates discussed above, as well as the properties of the ensuing liquid polyols.

### 12.3 POLYURETHANE FOAMS

This section deals with the use of the polyols derived from the oxypropylation of different renewable resources, as macromonomers for the synthesis of rigid polyurethane foams (RPU), calling upon otherwise conventional formulations [6, 7].

**Table 12.3**

Properties of the oxypropylated substrates (see Table 12.2)

Solid substrate	Experiment number	I <sub>OH</sub>	$\eta$ (Pa·s)	Homopolymer content (%)	Solid residue (%)	Reference
<b>KL</b>	1	180	4.2	75	41	[6, 7]
	2	165	3.2	80	36	[6, 7]
	3	148	2.3	83	33	[6, 7]
<b>OL</b>	4	198	6.0	42	0	[6, 7]
	8	203	93	22	0	[6, 7]
	11	250	2860	20	0	[6, 7]
	13	305	–	2	0	[6, 7]
<b>OOL</b>	14	170	4.8	52	25	[6, 7]
	16	178	5.2	39	29	[6, 7]
	17	165	4.1	nd	39	[6,7]
<b>SL</b>	18	15.2	82	25	0	[6, 7]
	19	16.1	85	nd	0	[7]
	20	15.8	nd	30	0	[7]
	21	165	120	18	0	[7]
<b>SB</b>	14	418	710	nd	10	[7]
	15	436	700	nd	9	[8]
	16	260	49	nd	0	[8]
	17	350	305	nd	2	[8]
	18	380	450	nd	6	[8]
19	390	520	nd	12	[8]	
<b>Cork</b>	28	≈130	6	73.2	0.16	[12]
	29	≈130	11.9	69.8	2.50	[12]
	30	≈130	12.4	67.8	4.87	[12]
	31	≈130	13.0	68.7	2.24	[12]
	32	≈130	2.9	75.8	0.22	[12]

nd, not determined.

The procedure concerning the foam preparation consisted in mixing vigorously the polyol (or the mixture of the polyols), the surfactant, the catalysts and the water for about 30 s, followed by the addition of the blowing agent. The commercial polyisocyanate (**MDI**) was then added and the emulsified mixture finally poured into a special mould for free expansion. The RPU foams thus obtained were characterized through their  $T_g$  (DSC) and thermal conductivity, as shown in Table 12.4 [6, 7]. These data are extremely promising, since a large number of these foams gave insulating performances similar to those obtained from petroleum-based counterparts.

## 12.4 PARTIAL OXYPROPYLATION

The strategy behind the idea of limiting the oxypropylation reaction of a natural polymer to the outer shell of its morphology is radically different from that motivating all the bulk oxypropylation reactions described above. Although, as already pointed out, the mechanisms involved in both approaches are identical in nature, the purpose of this limited transformation is not to obtain a polyol to be exploited as a reactive component in polymer synthesis, but, instead, to generate a novel material in which the pristine core and the oxypropylated shell both play an essential role in defining its overall properties.

Two substrates have been tackled in this way up to now within the context of a research project which was started only recently. As outlined below, the aims of these partial transformations were different, but followed the same working hypothesis.

**Table 12.4**

Characteristics of RPU foams before and after ageing

Polyol	T <sub>g</sub> (°C)	Before ageing		After ageing			Reference
		Density (kg/m <sup>3</sup> )	λ (mW/mK)	λ <sup>a</sup> (mW/mK)	λ <sup>b</sup> (mW/mK)	DS <sup>c</sup> (%)	
<b>CP1</b>	58	24.8	15	17	19	+17	[6,7]
<b>CP2</b>	59	26.2	17	18	20	+17	[6,7]
<b>OLOP</b>	60	22.2	16	21	25	+11	[6,7]
	60	24.7	17	21	27	+10	[6,7]
	61	25.1	16	22	29	+15	[6,7]
<b>SLOP</b>	65	30.3	24	29	31	+2	[6,7]
<b>KLOP</b>	66	28.2	29	nd	nd	+29	[6,7]
<b>OOLOP</b>	66	27.9	31	nd	nd	+27	[6,7]
<b>SBPOP</b>	–	37.5	28	nd	nd	–1.8	[11]
	–	46.0	30	nd	nd	–1.9	[11]
	–	37.0	28	nd	nd	–3.4	[11]
<b>Cork-OP</b>	–	28.4	38	nd	nd	–	[12b]
	–	27.4	31	nd	nd	–	[12b]
	–	32.2	24	nd	nd	–	[12b]

<sup>a</sup>After ageing at room temperature for 3 months.<sup>b</sup>After accelerated ageing at 70°C for 10 days.<sup>c</sup>Dimensional stability.

### 12.4.1 Cellulose fibres

The use of cellulose fibres as reinforcing elements in composite materials with polymeric matrices has become a fast-growing topic, as discussed in Chapters 18 and 19. In most instances the appropriate chemical modification of the fibres' surface is an essential requisite imposed by the need of enhancing the interfacial compatibility between fibres and matrix, that is, of ensuring good adhesion and hence optimal mechanical properties of the composite. Of course, the ultimate optimization in this search consists in creating continuous covalent bridges between fibres and matrix which then become, by definition, a single chemical suprastructure in which the two components cannot be disjoined.

The idea of generating a composite material based exclusively on cellulose fibres' precursors arose in recent years through the concept of the partial chemical modification of the fibres, not limited this time to their surface OH groups, but, instead, to an in-depth process, itself limited to a modest thickness. In this way, a material could be generated in which the inner core maintains the original mechanical properties of the unmodified parts of the cellulose fibres, while its outer sleeve could now possess thermoplastic features given a suitable choice of chemical modification. Examples of this approach include esterification with carboxylic acids [17] and etherification with benzyl chloride [18].

Another approach has called upon the coagulation of amorphous cellulose around semi-crystalline fibres (i.e. the preparation of an all-cellulose composite) [19].

All the above systems require a sequence of steps and the use of solvents to attain the final goal, which complicates the process both in terms of economical and ecological soundness. The direct transformation of cellulose fibres into self-reinforced composites by partial oxypropylation was considered a promising alternative to this working hypothesis since it eliminated the use of solvents and could be conducted in a straightforward one-step operation. The study of this system confirmed its viability and produced interesting composite materials [20].

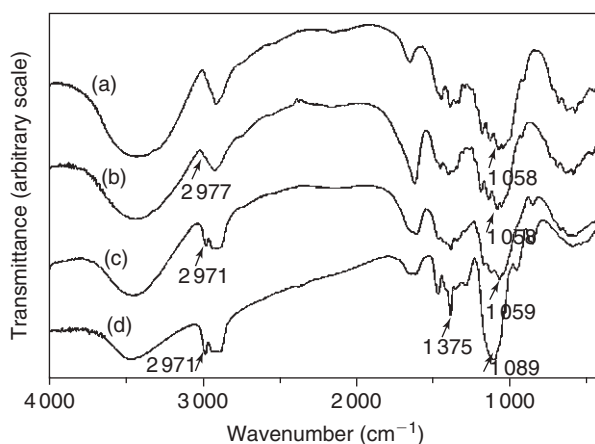
The bulk oxypropylation of cellulose fibres, activated by a strong Brønsted base, was investigated through a systematic study of the role of such variables as the nature of the fibres (different natural types and full cylindrical regenerated filaments), the type and amount of catalyst, the pre-activation conditions, the **PO**/cellulose ratio, the reaction temperature and its duration. In contrast with all the intensive oxypropylation processes described in the preceding section, the amount of **PO** used here was obviously much lower because the purpose of this procedure was to limit the oxypropylation reaction to the outer layers of the fibres. The other major difference with respect

to the synthesis of liquid polyols was the use of more moderate temperatures and hence longer reaction times, in order to minimize the occurrence of reactions deep inside the fibres.

The most relevant results, associated with an adequate thickness of the thermoplastic sleeve surrounding the unmodified fibre cores, gave mass gains comprised between 40 and 90 per cent after the extraction of 5–10 per cent of the **PO** oligomers. These materials were flexible and could be readily converted into films by pressing them at 135°C and 11 ton. A visual and optical microscopy inspection of these semi-transparent films, showed the presence of opaque regions associated with the residual cellulose fibres. In these reactions, the oxypropylation front progressing through the fibre wall (in the case of natural fibres) or the fibre cylinder (in the case of regenerated filaments) obviously attacked preferentially the amorphous cellulose domains.

The extent of oxypropylation was assessed by FTIR spectroscopy, as shown in Fig. 12.7, and its corresponding plasticizing effect from glass transition temperature measurements by DSC. The surface of the modified fibres acquired, as expected, a hydrophobic character, compared with the pristine substrates, as revealed by contact angles of 70–80° and 25–40°, respectively. Figure 12.8 shows the changes in morphology associated with the partial oxypropylation of the fibres and their subsequent pressing to form a composite film arising from their mutual assembly through the plastic flow of their modified sleeves.

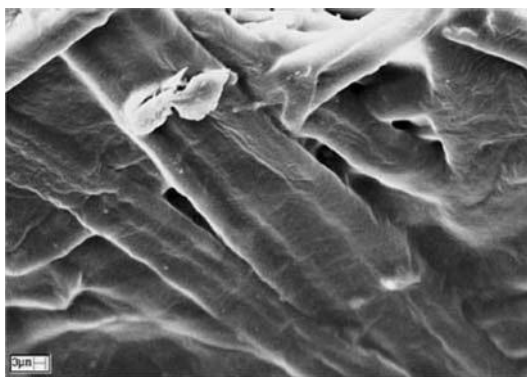
The advantages of this novel system include the extreme simplicity of the process which makes use of all the intervening components and does not require any separation or purification steps as well as the fact of being



**Figure 12.7** FTIR spectra of Avicell powder before (a) and after oxypropylation using [PO]/[cellulose OH] of 1 (b), 3 (c) and 5 (d), and after extraction of the **PO** homopolymer. (Reproduced by permission of Elsevier. Copyright 2006. Reprinted from Reference [20]).

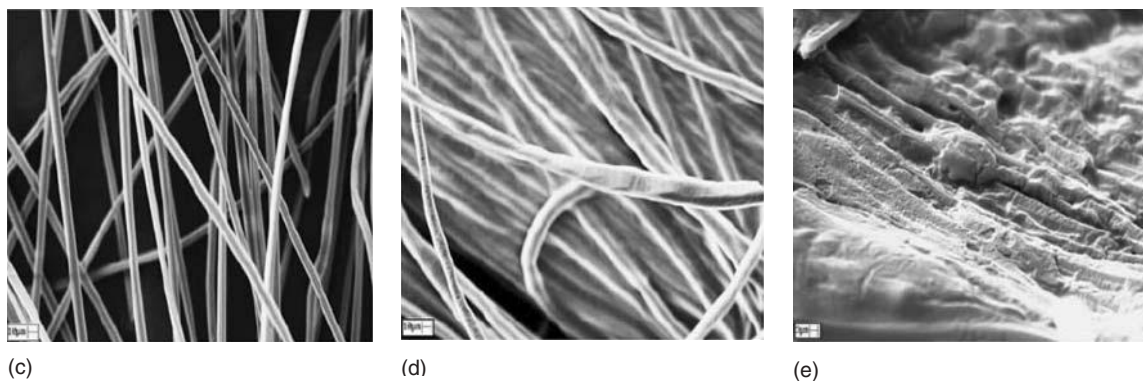


(a)



(b)

**Figure 12.8** SEM micrographs of filter paper fibres (a) before, and (b) after partial oxypropylation.



**Figure 12.8** SEM micrographs of rayon filaments (c) before and (d) after partial oxypropylation and (e) hot-pressing into a film. (Reproduced by permission of Elsevier. Copyright 2006. Reprinted from Reference [20]).

economically and ecologically sound. In addition to these positive engineering aspects, it is important to add the originality and interest associated with the preparation of a composite material in which the dominant role is played by a major and ubiquitous renewable resource.

#### 12.4.2 Starch granules

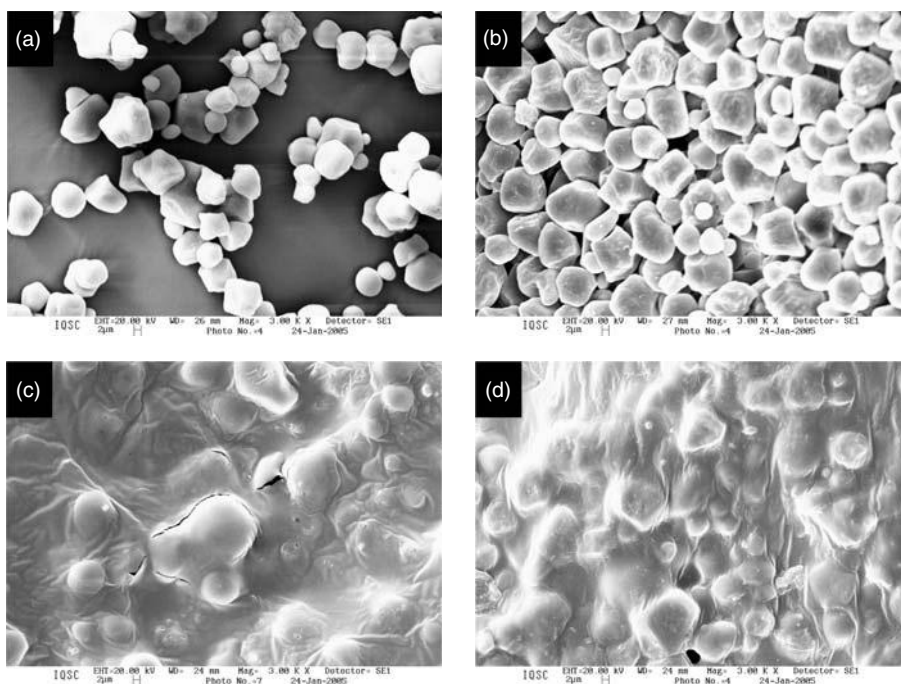
The transformation of starch granules into thermoplastic materials is one of the major issues within the broad field of novel polymers from renewable resources, as highlighted in Chapter 15, because of the ready availability of low cost starch from a variety of agricultural activities throughout the world, albeit in different macromolecular compositions.

That chapter deals comprehensively with the problems facing researchers who are actively engaged in this area which have to do, on the one hand, with the choice of a treatment capable of converting the granules into a processable material (including the actual thermo-mechanical operation and the selection of a suitable plasticizer) and, on the other hand, with ways to reduce the highly hydrophilic character of the ensuing materials. Several interesting solutions are critically discussed there together with an assessment of the state of the art and its short-term prospects for the actual production of viable materials.

The experience acquired during the research on the partial oxypropylation of cellulose fibres discussed in the previous sub-section suggested that a similar approach could be applied to starch granules with the somewhat different purpose of preparing a new form of thermoplastic starch, as such, or as a composite material in which some smaller grains would still be present. The oxypropylation of starch was not a novelty when this project was conceived but, to the best of our knowledge, had only been carried out in aqueous or organic solvent media with purposes related to food and cosmetic applications, rather than the elaboration of novel materials.

The partial oxypropylation of corn starch conducted in bulk was therefore approached [21] by studying the role of the same variables as already mentioned above in the homologous investigation on the partial oxypropylation of cellulose fibres. On the whole, the two systems behaved very similarly as clearly indicated by the characterization of the corresponding products. In particular, FTIR spectroscopy clearly showed a correlation between the amount of **PO** used in the reaction and the extent of grafting of **POP** chains from both amylose and amylopectin. Additionally, the  $T_g$  and the extent of crystallinity were lower, the higher the oxypropylation level, and the corresponding morphologies of the modified granules became increasingly akin to a thermoplastic appearance, as shown in Fig. 12.9.

This ongoing investigation has already pointed to a simple and original way of transforming starch granules by a process which, once again, does not require any separation or purification stage since the single reaction step produces the desired material as such. This new family of thermoplastic starches does not require the addition of a plasticizer since the plasticization is automatically provided by the chemical transformation. Moreover, the grafted **PO** chains bring about a considerable reduction in the hydrophilic character of the original substrate. Whether all these positive aspects are sufficient to justify possible applications of the materials remains to be verified by further research.



**Figure 12.9** SEM micrographs of corn-starch samples: (a) before, and (b), (c), (d) after oxypropylation with increasing PO/starch ratios. (Reproduced by permission of the American Chemical Society. Copyright 2007. Reprinted from Reference [21]).

## 12.5 CONCLUSION

The general applicability of the bulk heterogeneous reaction of **PO** with natural polymers bearing hydroxyl groups in the presence of a nucleophilic catalyst has become an undisputable fact, as testified by the numerous examples given in this chapter. Whether the purpose of this operation is the total conversion of the substrate into a viscous polyol mixture or its partial modification for the preparation of composite or other materials, the only questions that require an investigation in the case of future studies, principally involving unexplored substrates, are confined to quantitative aspects, since it can be safely anticipated that the actual reaction will occur if OH groups are present in the substrate. Whereas the applications of the polyols generated by the bulk processes are clearly oriented towards the synthesis of polyurethanes and polyesters, the partial oxypropylation generates a different type of material, whose direct utilizations are obviously in the realm of composites derived entirely from renewable resources.

## REFERENCES

1. Bailey F.E., Koleske J.V., *Alkylene Oxides and their Polymers*, Marcel Dekker, New York, 1990.
2. Edens M.W., *Surfactant Sci. Ser.*, **60**, 1996, 185.
3. Fis J., *Actualité Chim. (France)*, 2002, n.11–12, 54.
4. Asandei N., Perju N., Nicolescu R., Civica S., *Cell. Chem. Technol.*, **29**, 1995, 261.
5. Wu L.C.F., Glasser W.G., *J. Appl. Polym. Sci.*, **29**, 1984, 1111.
6. Gandini A., Belgacem M.N., Guo Z.X., Montanari S., in *Chemical Modification, Properties and Usage of Lignin*, Ed.: Hu T.Q., Kluwer, 2002, p. 57.
7. Nadji H., Bruzzèse C., Belgacem M.N., Benaboura A., Gandini A., *Macromol. Mater. Eng.*, **290**, 2005, 1009.
8. Pavier C., Gandini A., *Ind. Crops Prod.*, **12**, 2000, 1.
9. Pavier C., Gandini A., *Carbohydr. Polym.*, **42**, 2000, 13.
10. Pavier C., Gandini A., *Eur. Polym. J.*, **36**, 2000, 1653.
11. Pavier C., Doctorate Thesis, Grenoble National Polytechnic Institute, France, 1998.

12. (a) Evtiouguina M., Barros A.M., Cruz-Pinto J.J., Pascoal Neto C., Belgacem M.N., Pavier C., Gandini A., *Bioresour. Technol.*, **73**, 2000, 187. (b) Evtiouguina M., Barros-Timmons A., Cruz-Pinto J.J., Pascoal Neto C., Belgacem M.N., Gandini A., *Biomacromolecules*, **3**, 2002, 57.
13. Evtiouguina M., Gandini A., Pascoal Neto C., Belgacem M.N., *Polym. Intern.*, **50**, 2001, 1150.
14. Velazquez-Morales P., Le Nest J.F., Gandini A., *Electrochim. Acta*, **43**, 1998, 1275.
15. Fernandes S., Freire C.S.R., Pascoal Neto C., Gandini A., *Green Chemistry*, **10**, 2008, 93.
16. Barreiro F., Fernandes S., Gandini A., unpublished results.
17. (a) Mutsumura H., Sugiyama J., Glasser W.G., *J. Appl. Polym. Sci.*, **78**, 2000, 2242. (b) Mutsumura H., Glasser W.G., *J. Appl. Polym. Sci.*, **78**, 2000, 2254.
18. (a) Lu X., Zhang M.Q., Rong M.Z., Shi G., Yang G.C., *Compos. Sci. Technol.*, **63**, 2003, 177. (b) Lu X., Zhang M.Q., Rong M.Z., Yue D.L., Yang G.C., *Compos. Sci. Technol.*, **64**, 2004, 1301.
19. Nishino T., Matsuda I., Hirao K., *Macromolecules*, **37**, 2004, 7683.
20. Gandini A., Curvelo A.A.S., Pasquini D., de Menezes A.J., *Polymer*, **46**, 2005, 10611.
21. Gandini A., Curvelo A.A.S., Pasquini D., de Menezes A.J., *Biomacromolecules*, **8**, 2007, 2047.