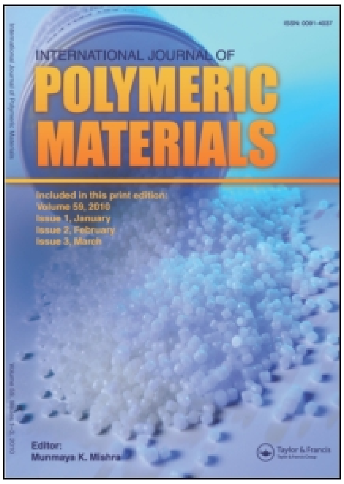

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Hydrodynamic Properties and Structure of Lignin

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Experimental data on hydrodynamic properties of natural and biosynthetic lignins in dilute solutions are reviewed. The results of viscometric, translational diffusion, and sedimentation studies evidence that the macromolecules of lignin are characterized by a complex topological structure. Benefits and limitations of the theoretical approaches used to describe the topology of lignin macrochains are discussed. The relationship between hydrodynamic characteristic and fractal properties of lignin is considered.

Keywords: Lignin; Hydrodynamic properties; Structure

INTRODUCTION

During the long evolutionary period, by self-organization and natural selection nature created a very complex multicomponent polymer composite, namely, wood. Structural organization of lignin, which is one of the essential wood components, controls the performance of its basic functions in wood: mechanical (work on compression and flexure), chemical (lignin as an antioxidant), and biological (protection against pathogenic microorganisms) [1, 2]. According to modern views [3], the biosynthesis of lignin occurs by dehydrogenating free radical polymerization of monolignols catalyzed by an enzymatic system peroxidase - hydrogen peroxide.

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[*] Corresponding author.

The main monolignols are coniferyl, sinapyl, and *p*-coumaryl alcohols. Cinnamic aldehydes and acids, which are biogenetic precursors to the monolignols listed above, can also take part in the biosynthesis. This review is mostly concerned with the topological aspects of the structural organization of lignin.

Lignin is synthesized in plants from monomeric molecules, whose functionality varies from 2 to 4. Thus, both the branched chains and the cross-linked structure (at a gel point) may be formed. In plant tissue, the polymer chains of lignin are surrounded by the macromolecules of noncellulosic polysaccharides, with which they form an amorphous lignocarbohydrate matrix. It is noteworthy that the experimental methods that allow the macromolecules of complex topology in a multicomponent solid composite to be studied are very limited. Therefore, most data were obtained by using theoretical methods developed in polymer chemistry.

Because there are no effective experimental methods for the investigation of lignin *in situ*, the general approach usually involves systematic studies of soluble samples isolated from wood by one of the available methods. Structural studies of lignin chains are essentially similar to the investigation of synthetic polymers, although the specific features of lignin somewhat restrict the variety of experimental methods that can be used.

Detailed investigation of the structure of lignin macromolecules was started by Goring [4–6]. In his studies, Goring used conventional methods: sedimentation, translational diffusion, and viscometry. Hydrodynamic studies are still one of the main sources of data about the structure of lignin macromolecules. Note, however, that these methods do not provide comprehensive information concerning the topics discussed here. Moreover, conventional approaches may be inadequate for the unambiguous characterization of the macromolecular structure of this biopolymer. Quantitative assessment of the parameters of topological structure from experimental data on hydrodynamic properties often leads to controversial inferences. One of the natural causes of this situation is the absence of linear lignin analog. Generally, adequate description of the structure of macromolecules of complex topology presents a complex problem not only to the lignin chemistry. In the absence of reliable data about the nature of branching junctions and the regularities that control their distribution in a chain, quantitative assessment of the structure inevitably depends on the unavoidable assumptions made within the frameworks of various models.

Presently, fractal concepts, which have grown out of the fruitful ideas introduced by De Gennes [7], have become common in the physical chemistry of polymers. It was established that a random walk without crossover, which describes the statistics of polymer chains with excluded volume, possesses a fractal structure. In recent years, the studies of lignin and its biosynthetic analogs have been marked by some progress, which has resulted from the combined use of conventional methods and new approaches related to the application of fractal concepts and computer-aided studies. The results obtained offer a clue to a better understanding of the structure of macromolecules and draw certain prospects for the future studies of the structural organization of lignin.

TOPOLOGICAL STRUCTURE OF LIGNIN MACROMOLECULES

According to Erins [8, 9], the spatial structure of amorphous lignocarbohydrate matrix of wood is described by a superposition of three networks: a network of hydrogen bonds (H-network), which involves both lignin and carbohydrates; a network of lignocarbohydrate valence bonds (LCV network); and a lignin network.

The concept treating native lignin in terms of a network structure has become popular, because this model makes easier the interpretation of complex processes that take place during the technological treatment of wood. The strongest argument in favor of the network model is presented by the insolubility of natural lignin in any "neutral" solvent without preliminary chemical or mechanical degradation [3, 10]. The second argument resorts to the high polydispersity of lignins isolated from plant tissue, because it is distinctly this kind of distribution that is expected to result from network fragmentation [5]. According to [8], this point of view is supported by physicochemical properties of lignin solutions and a rather high content of trifunctional monomer units in lignin chains. Indeed, network polymers are insoluble in any solvents; they do not melt to pass to the flow state, and they contain tri- or tetrafunctional units. At the same time, the fact that a polymer possesses these properties cannot unambiguously prove that it is a cross-linked (network) polymer. Indeed, some uncross-linked polymers were also reported to possess them [11, 12].

According to an alternative viewpoint, lignin *in situ* exists as relatively small branched macromolecules. Within the framework of this concept, the insolubility of native lignin is explained by the fact that it is linked to polysaccharides by either valence and/or hydrogen bonds. For example, Evstigneev *et al.* [13] claim that the dissolution of lignin (delignification) must be preceded by functionalization of the macromolecules of lignin, whose MMD has been specified at the instant the biosynthesis in the cellular wall was completed. Let us consider the results of the studies dealing with the topological structure of lignin.

One of the approaches to solving the problems related to the formation of network topology involves statistical methods, in particular, methods of the theory of branching processes, which are considered the most perfect form of statistical methods [12]. In [14], the parameters describing the gelation of lignin were determined. The known models for the macromolecules of lignin were represented by the graph tree in which the phenylpropane units are positioned at the tops, whereas the bonds between the monomer units are the branches of the graph.

On the basis of the theory of branching processes, the condition for gelation was verified and the mean molecular mass of the sol fraction was calculated. It was demonstrated that all theoretical lignin models (except for models of lignosulfonate from spruce) satisfy Flory's critical condition for gelation, which, in terms of the theory of branching processes, is defined by the inequality

$$(\partial F_1/\partial x)_{x=1} \geq 1,$$

where x is the variable, F_1 is the generating function for the probability of the number of monomer "offspring" in the first generation. The calculated molecular mass of the sol fraction ($1.3 \times 10^3 - 13.8 \times 10^3$) suggests that Brauns lignin (low-molecular-mass lignin, which is isolated from wood by extraction with ethanol without heating or using catalysts) may be identified with the sol fraction of native lignin. Further development of the concept of cross-linked lignin structure allowed the structure of network to be described in greater detail. Using the generating functions for probabilities, Gravitis and Ozol' –

Kalnin [15] calculated the statistical characteristics of lignin network: average chain length between the junctions, number of active chains in the gel fraction, length of active chain. Unfortunately, it is virtually impossible to assess whether the calculated parameters conform to reality. Only the distance between two branching junctions in a chain can be evaluated experimentally from hydrodynamic data, which are considered in the next section of this review. Recall that applicability of the theory of branching processes rests on two rather important assumptions: reactivities of reacting species are assumed to be independent (Flory principle) and intramolecular cyclization is banned.

According to [9], lignin polymer is a cross-linked system of microgel type, that is, it is a heterogeneous network. Factors that account for the different network density involve the formation of lignin from monomers that contain functional groups of different reactivity [1, 3] and the fact that the polymerization takes place in a carbohydrate environment, which is thermodynamically incompatible with the incipient lignin [16]. Heterogeneity of the structure of lignin is confirmed by the analysis of the mobility of a nitroxyl spin label [17]. Broad-line NMR spectra of lignin show broad and narrow components [18]; this feature was interpreted [17] as a manifestation of the different degrees of cross-linking, which results in different mobility of network chains. Theoretical treatment of the formation and the structure of lignin based on the regularities common for cross-linked polymers leads to the conclusion that it is hardly probable that a statistically uniform polymer network may form in different layers of a cell wall [19]. Several factors that give rise to topological heterogeneity of lignin may be listed.

1. Heterogeneity with respect to molecular structure [20, 21]. One may assume that topological heterogeneity is predetermined genetically by the microstructure of chains.
2. An increase in probably of cyclization as the molecular mass of macromolecule increases [22]. This factor follows from general considerations about the feasibility of intramolecular interaction between functional end groups during the growth of a branching tree [12].
3. Microgelation. According to Bobalek *et al.* [23], formation of a cross-linked polymer can proceed *via* the formation of microgel.

> Data on the formation of supermolecular particles during the *in vitro* synthesis of model lignins support the assumption that lignification proceeds *via* microgelation [24].

Of the factors listed above, only the last one may be related to the formation of a cross-linked structure, whereas the first two are not related directly to the topological nature of the polymer formed.

Ozol-Kalnin *et al.* [25] derived the kinetic equation that describes the polymerization on assumption that the reaction proceeds *via* stepwise addition of the monomer of one kind. To describe the formation of a macroscopic network, the criterion for gelation, suggested previously for free radical polymerization of unsaturated compounds

$$dN/dt = dN/dM = 0,$$

(N is the number of propagating polymer chains), was used.

Within the framework of this concept, initially, initiation of polymerization leads to accumulation of the number of propagating chains and makes the dependence of the number of chains more profound. On the contrary, cross-linking reduces the number of chains, and, at the end of the process, the quantity dN/dt decreases to zero. This approach makes it possible to take into account the unsteady character of the polymerization. However, because the mechanisms involved in the propagation of polylignol chains [3] are markedly different from the classical mechanism of free radical polymerization, this variant is hardly pertaining to the lignin formation.

Information about the network structure may be acquired not only in the studies of growth processes, but also in the studies of reverse process, that is, degradation. This approach was first implemented by Szabo and Goring [26], who considered the fragmentation and dissolution of lignin in alkaline pulping as a process reverse to Flory-Stockmayer gelation. However, agreement between experimental and theoretical data was rather poor in spite of the assumption made that two types of gels, localized in different morphological elements of the cell wall, exist. More satisfactory results were obtained for sulfite delignification, which, according to Yan *et al.* [27, 28], involves the degradation of gel (and concomitant formation of sol), which is reverse to the condensation of sol and posthydrolysis of bonds (resulting in the formation of low-molecular-mass ω-lignins).

Studies of Bolker and Brenner [20] also rested on statistical methods. According to the theory, at a certain conversion, probably of any distribution with respect to degrees of polymerization is estimated by the total number of ways Ω by which all N monomer units may be distributed between the molecules at a specified distribution. MMD of a polymer determines the magnitude of Ω. To find this quantity, one has to list all equiprobable ways by which the molecular tree with a specified number of junctions may be drawn. This problem was solved by Bolker for a particular case of a cross-linked system in which only the scission of cross-linkages formed by benzylether bond takes place.

Summarizing the studies using statistical approach to analysis of the structure and behavior of lignin, it is appropriate to note that it was *a priori* assumed that the distribution of all elements of the described by the most probable distribution. This is possible only if the processes that take place are equilibrium. However, one cannot exclude that the polymerization to lignin, which takes place in an open unsteady biosystem which is the cell wall [1, 30], is an essentially irreversible process leading to formation of dissipative structures. The formation of dissipative structure during the *in vitro* biosynthesis was demonstrated in [31]. The fractal properties of lignin [17, 32] and its biosynthetic analogs [33] that were recently discovered also support the important role of non-equilibrium in the biosynthesis of lignin.

One of the promising methods for studying the topological structure of lignin involves computer simulation, which is advantageous over statistical methods in that there is no need to introduce any assumptions concerning the distribution of elements in the system, and information about intramolecular cyclization can be obtained.

Ozol-Kalnin *et al.* [34-36] simulated (by the Monte Carlo method) gradual propagation of lignin macromolecules composed of 50 bi- and trifunctional monomer units. The resulting of simulation, which was performed on a cubic lattice, evidence that the structure of cross-linked macromolecule represents a hierarchic system of rings. Data on the size of rings and their number reveal that small rings usually prevail. On the basis of stereochemical considerations the smaller ring in lignins was assessed to contain four phenylpropane units. The curve that describes the size distributions for the rings in lignins is a rapidly declining function (Fig. 1).

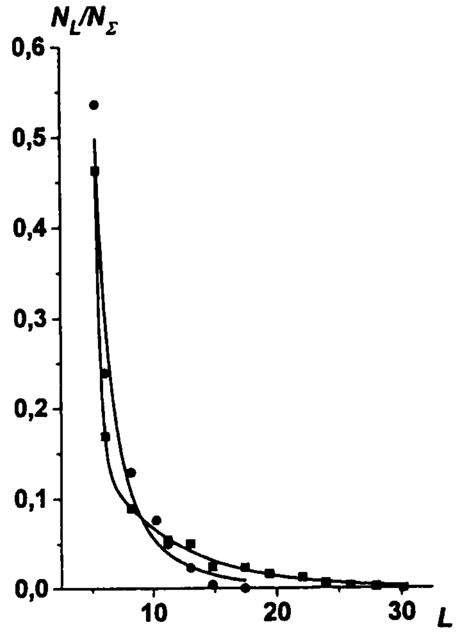

FIGURE 1 Distribution of the rings with respect to size L. N_L is the number of rings of length L, N_Σ is general number of cycles. (1) All units are trifunctional; (2) 5% of the units is trifunctional and 95% is bifunctional [36].

An important characteristic of lignin topology is presented by the so-called bondedness of rings, which is described by the degree of their condensation [35]. If the degree of condensation of the rings is equal to unity, the cycles of the graph are separated from each other. In all cases, the degree of condensation was found to be rather high (Fig. 2), implying that the monomer unit of a ring is at the same time incorporated into several other rings.

For a deeper understanding of the topology of lignin chains, computer-simulated fractal clusters present a topic of special interest. Analysis of the scaling properties of fractals that were grown according to the model for the growth of branched clusters suggested in [37] showed the role of the free path of particles, of the probability of adding a particle on contact, and of the space geometry on the structure (in particular, on the degree of intramolecular cyclization [38] and the fractal dimensionality d_f) [39] of a fractal macromolecule was demonstrated (Figs. 3, 4).

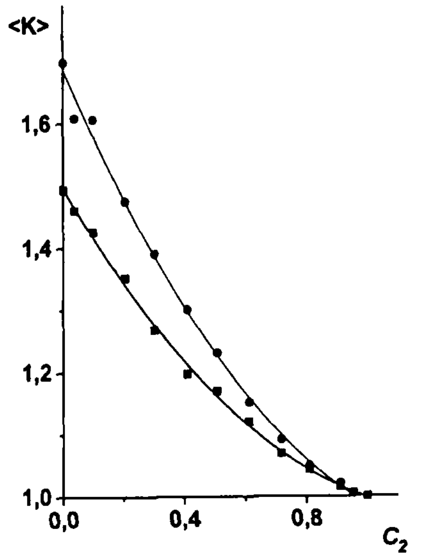

FIGURE 2 Plots of the degree of condensation of the rings (K) *vs.* fraction of bifunctional units C_2. (1) Steric limitations are not taken into account; (2) steric limitations are taken into account, formation of tetrafunctional rings is forbidden [35].

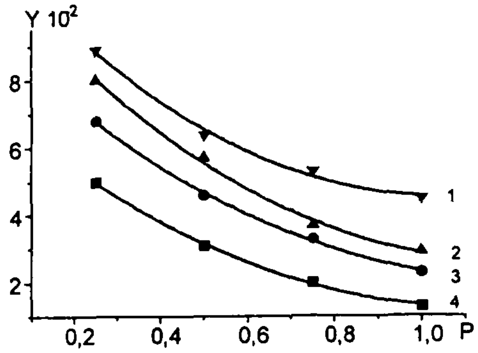

FIGURE 3 Degree of intramolecular cyclization Y as a function of the probability of addition P. The free path L = (1)1000, (2)100, (3)10, (4)5.

The conclusions made on the basis of computer simulation were to some extent confirmed in experimental studies of the properties of wood matter from various species [40]. At the same time, those studies revealed the drawbacks of computer-aided simulations related to the

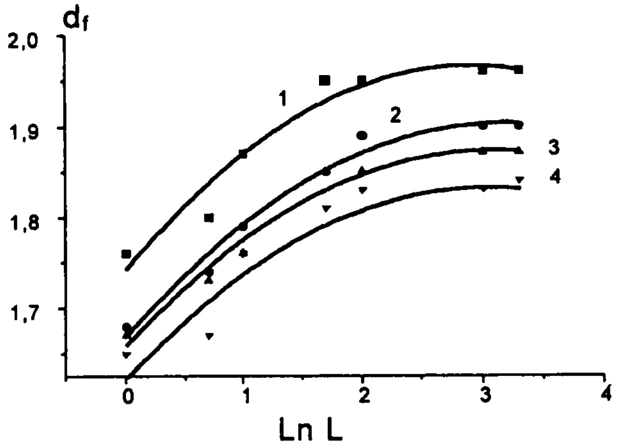

FIGURE 4 Fractal dimensionality d_f as a function of the particles free path L. The probability of addition P = (1)0.25, (2)0.5, (3)0.75, (4)1 [39].

difficulties of making generalizations and limitations on the size of a polymer system, which must not be large.

HYDRODYNAMIC PROPERTIES

Depending on the procedure used to isolate them, soluble lignin polymers may be divided into three major groups [40]: "native" lignins, for examples milled wood lignin (MWL) and dioxane lignin (DL); industrial lignins (sulfate or kraft lignin, lignosulfonate); and biosynthetic lignins (bulk dehydropolymer, bulk-DHP; end-wise DHP).

Present-day views on the structure of lignin macromolecules are mostly based on the studies of lignins of the first group. Naturally, lignins from different sources are also distinguished. Lignins isolated from coniferous wood are the best studied. Studies of biosynthetic lignins (*i.e.*, dehydropolymers synthesized *in vitro* under the conditions reproducing natural biosynthesis [41]) are important for understanding the regularities that control the formation of lignin structure.

Hydrodynamic properties of dilute lignin solutions were perhaps first studied in [42,43]. Gardon and Mason [42,43] investigated industrial lignosulfonates in aqueous NaCl solutions. Based on the measurements of intrinsic viscosity $[\eta]$ and translational diffusion coefficient D, they suggested that, at high ionic strength of solutions, the macromolecules of lignin acquire the conformation of non-draining Gaussian coil. This conclusion was based on the values obtained for the exponents in the Mark–Kuhn–Houwink equations $b_\eta = 0.47$ and $b_D = 0.56$.

$$[\eta] = K_\eta M^{b_\eta}$$

$$D = K_D M^{b_D},$$

However, much lower values of these parameters were reported by Goring with co-workers [5, 44]: $b_\eta = 0.32$, $b_D = 0.33$. Detailed studies of lignosulfonates and other lignins led Goring to a model which treated a lignin macromolecule as a microgel particle [5, 26]. According to this model, the macromolecules of soluble lignins are identified with the fragments of the cross-linked structure of lignin *in situ*. Microgel particles, which may be of any shape including the irregular, possess hydrodynamic properties of slightly swollen spherical particles. This feature explains the low viscosity and the lower values of b_η and b_D as compared with those suggested by the model of non-draining Gaussian coil. It is noteworthy that lignosulfonates are a rather special class of lignin polymers: lignosulfonates are polyelectrolytes. The presence of carboxyl and sulfo groups on the polymer chain and the concomitant ionic interactions give rise to abnormal hydrodynamic properties of lignosulfonates. Suffice it to say that calculations of the Tsvetkov–Klenin hydrodynamic invariant by using the equation

$$A_o = \eta_o D_o (M_w[\eta])^{1/3}/T$$

lead according to [44], to values that are absolutely not typical of polymers: $A_o = (5.2 \pm 1.2) \times 10^{-10}$ erg/(K mol$^{1/3}$). Because of this, using lignosulfonates in the studies of the topological structure of natural lignin is rather limited.

Alkali lignin, which is prepared by treating the wood with aqueous solutions of sodium hydroxide, as a rule, in the presence of sodium sulfide (sulfate lignin) is a more appropriate object for structural studies. This polymer is not a polyelectrolyte and has a rather high molecular mass. In DMSO, the macromolecules of sulfate lignin are compact particles, which are characterized by $[\eta]$ varying from 7.4 ($M_w = 1.3 \times 10^3$) to 13.3 cm^3/g ($M = 38.7 \times 10^3$) and the $\log[\eta]$ *versus* $\log M_w$ plot with the slope $b_\eta = 0.15$.

Hydrodynamic properties of milled wood lignin (spruce) in pyridine were studied in [47]. The molecular masses of fractions isolated by preparative gel permeation chromatography on Sephadexes were determined by sedimentation (according to Archibald) and from the diffusion and viscometric data ($M_{D\eta}$). Logarithmic plots of $[\eta]$, D, and S *versus* M_w are approximated by straight lines (Fig. 5), with parameters $b_\eta = 0.115$, $b_D = 0.39$, and $b_S = 0.61$, respectively. The diffusion coefficients were found to be concentration-independent; polyelectrolyte effects were not observed. The authors claimed that hydrodynamically lignin behaves as a rigid Einstein's sphere. Obviously, this conclusion is not quite rigorous, because the experimental b_η and b_D values are quite different from those characteristic of hard globular particles. The average value of the hydrodynamic invariant A_o was 2.95×10^{-10} erg/(K mol$^{1/3}$).

Similar experimental results (Tab. I) were obtained for milled wood lignin from pine [48]. Note only the higher value of the exponent b_η than that reported in [47]. The fractions examined in this study spanned a broader interval of molecular masses; this usually allows a more reliable determination of hydrodynamic parameters. The average value of A_o, as estimated from sedimentation (according to Svedberg) and viscometry, was 3.1×10^{-10} erg/(K mol$^{1/3}$). The data

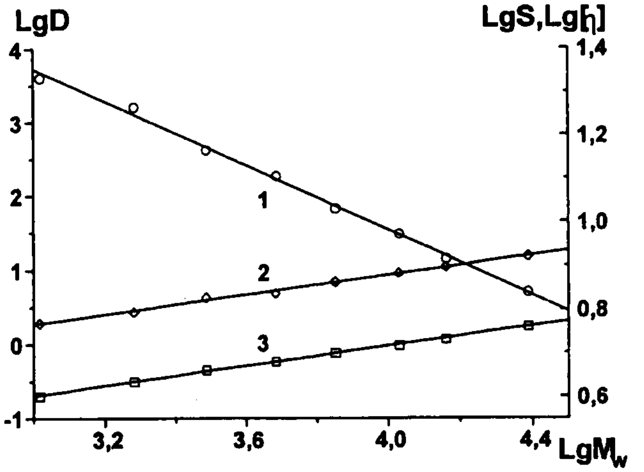

FIGURE 5 (1) $\log[\eta]$, (2) $\log S$, and (3) $\log[\eta]$ *vs.* $\log M_w$ for milled wood lignin fractions (pyridine as solvent) [47].

TABLE I The hydrodynamic properties of lignin (MWL) fractions from wood *Pinus silvestris* [48]*

Fractions	$[\eta]$, cm^3/g	$D_o \times 10^7 cm^2/s$	$S_o \times 10^{13} s$	k'	$M_{D\eta}$	$A_o \times 10^{10}$ $erg/(K\ mol^{1/3})$
1	15.5	2.10	1.67	1.07	64.1	3.54
2	8.1	2.65	0.875	2.08	61.0	2.67
3	8.0	2.80	0.704	1.92	52.4	2.57
4	7.8	4.20	0.528	1.21	15.9	3.04
5	7.2	5.60	0.396	1.86	7.3	3.26
6	6.3	7.60	0.300	0.98	3.3	3.48
7	5.9	7.70	–	0.97	3.4	–
8	3.5	17.20	–	0.56	0.5	–
9	3.4	18.70	–	0.66	0.4	–
10	2.7	21.10	–	2.22	0.4	–
11	2.2	22.40	–	4.33	0.4	–
12	2.0	31.40	–	5.33	0.2	–
H.ф.	4.8	7.90	–	1.20	3.9	–

* Solvent – DMSO.

obtained suggest that $[\eta]$, D, and S conform to some correlation, which is characteristic of homologous polymers; this correlation is not confined to the routine test of the type $|b_D| = (b_\eta + 1)/3 = 1 - b_S$, but involves more elaborate relationships between K_S, K_D, K_η *and* b_D, b_η, b_S [38].

For lignin polymers with an obviously nonlinear chain topology, formulation of the concept of a homologous polymer may present a quite difficult task. At the modern state of knowledge of lignin structure, the fact that the hydrodynamic parameters fit the corresponding uniform Mark–Kuhn–Houwink plots (Fig. 6) suggests that the general pattern of the structural organization of lignin does not change during the growth of its macromolecules, and the principle of scaling invariance, which is a fundamental one for polymer science, is valid during the entire process.

A relatively large number of publications [49–55] deal with dioxane lignins, which are prepared by mild acidolysis of plant tissue in a dioxane–water–HCl mixture. Pla with co-workers [51–54] elaborated on the effect of thermodynamic quality of solvents on the conformational characteristics of lignin macromolecules. These studies may provide valuable information about their structure. Pla and Robert suggested a number of θ-systems of the solvent–precipitant type: dioxane–hexane (100:0.5), THF–hexane (100:6.8), THF–water (100:41.3 vol/vol) at 295.8 K. It was found that using dioxane

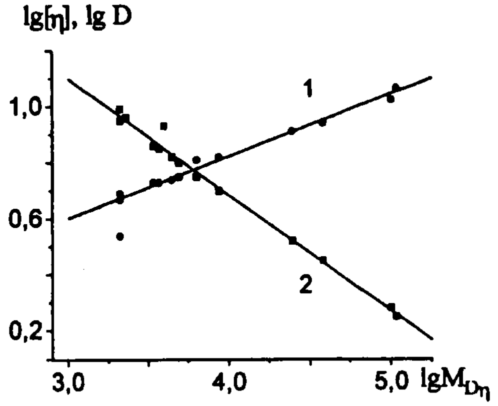

FIGURE 6 (1) log [η] and (2) log D *vs.* log $M_{D\eta}$ for dioxane lignin fractions (DMSO as solvent) [38].

(which is the most common solvent used in lignin chemistry) instead of the θ-solvent had little effect on the conformational parameters and hydrodynamic dimensions of lignin macromolecules (Tab. II). A similar conclusion follows from the data reported in [38, 55], where the temperature was evaluated for the dioxane lignin – dioxane system; it was found that, at $T = 298$ K, the Flory's swelling coefficient is not greater than 1.05. Nevertheless, for the low-molecular-mass range characteristic of lignins, the steric effects related to thermodynamic quality cannot be very important. However, using dioxane as a solvent in the detailed studies of lignin structure is apparently justified because the measurements are conducted under conditions similar to θ-conditions.[1]

It was found that the coefficients of translational diffusion and sedimentation coefficients for lignins are independent of concentration in the concentration range involved in analytical determinations [44, 47].

This fact was also reported in earlier studies [4, 5]. Dioxane lignins, as well as other lignin polymers except for lignosulfonates, are characterized by rather low intrinsic viscosities and exponential coefficients in the Mark – Kuhn – Houwink equations (note that b_η

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[1] For polymers of complex topological structure, the definition of θ-point is ambiguous and requires a special discussion.

TABLE II Parameters of Mark–Kuhn–Houwink equation for different lignin preparations

Lignin preparation 1	*Source* 2	*Solvent* 3	b_η 4	$-b_D$ 5	b_S 6	*Refs.* 7
"Native" lignins						
MWL	Spruce	Piridine	0.12	0.39	0.61	[47]
MWL	Pine	DMSO	0.25	0.43	0.57	[48]
MWL	Aspen	DMFA	0.47		0.61	[48]
DL	Pine	Dioxane	0.28	0.35	0.65	[49]
DL	Spruce	Piridine	0.15	0.36	–	[50]
DL	Spruce	Piridine	0.10	0.40	–	[5]
DL	Pine	Dioxane	0.18	0.39	–	[38]
DL	Pine	Dioxane	0.27	0.43	–	[38]
DL	Pine	Dioxane	0.11	0.37	–	[52]
DL	Spruce	Dioxane-ethanol	0.20	–	–	[52]
DL	Spruce	Dioxane	0.25	–	0.56	[54]
DL	Pine	DMSO	0.18	0.40	–	[66]
DL	Spruce	Dioxane-ethanol	0.23	–	–	[56]
Methanol lignin	Cotton lint	Dioxane-ethanol	0.33	–	–	[56]
Methanol lignin	Cotton lint	Methoxy-ethanol	0.39	–	–	[56]
Industrial lignins						
Alkali lignin	Spruce	Dioxane	0.12	–	–	[3]
Alkali lignin	Spruce	DMSO	0.15	–	–	[46]
Alkali lignin	Cotton lint	Dioxane	0.29	–	–	[56]
Alkali lignin	Spruce	0.1 M buffer	0.32	–	0.52	[4]
Lignosulfonate	Spruce	0.1 M NaCl	0.32	0.33	–	[44]
Lignosulfonate	Larch	0.5 M NaCl	–	0.56	–	[43]
Lignosulfonate	Larch	2 M NaCl	0.47	–	–	[42]
Biosynthetic lignins						
Bulk-DHP		Dioxane-water	0.13	0.35	0.41	[66]
Bulk-DHP		Dioxane-water	0.25	0.46	–	[33]
End-wise-DHP		Dioxane-water	0.78	0.58	0.45	[66]
Computer-simulated macromolecules						
F-1	–	–	0.26	0.42	0.58	[48]
F-2	–	–	0.18	0.40	0.60	[48]

is always smaller than b_D). The lower limit of b_η is 0.1, whereas the upper limit is 0.3. As demonstrated by the data on translational diffusion, for most polymer, the values of the exponent lie in a rather narrow range $b_D = 0.38 \pm 0.05$, that is, the characteristics of translational friction of the macromolecule are almost independent of the lignin source and the solvent used.

There are almost no hydrodynamic data available on lignins isolated from leaves and the grass plants. The only publication [56] worth mentioning reported the properties of lignin isolated from the lint of *Populus trichcarpa* cotton by treating it with an aqueous methanolic solution of hydrochloric acid. This lignin was characterized by higher $[\eta]$ and b_η values than the coniferous lignins; however, the plot of $\log[\eta]$ *versus* $\log M$ was curvilinear.

The Tsvetkov–Klenin invariant for coniferous dioxane lignins is usually not higher than 3×10^3 erg/(K mol$^{1/3}$). According to [49], the value of A_o varied for some fractions in the interval $(2.4-2.9) \times 10^{-10}$ erg/(K mol$^{1/3}$). Lignin polymers were found to show anomalous values of the Huggins parameter k'. In the region of low molecular masses, k' varies from 1 to 3–5 units [48, 38]. At $M > 1 \times 10^4$, the k' values remain at a level 1–1.5.

Thus, analysis of hydrodynamic properties of native lignins reveals that their behavior in dilute solutions is different from that of linear polymers, both flexible- and rigid-chain, in any of the known conformations. Apparently, the macromolecules of soluble lignins are randomly branched chains. Branchings in a chain are known to reduce the hydrodynamic dimensions (*i.e.*, reduce $[\eta]$) and increase the diffusion mobility compared to the linear analog. Theoretical value of b_η in a θ-solvent is 0.25. The branching of the polymer also reduces the hydrodynamic invariant A_o by 15–20% compared to the "standard" value 3.2×10^{-10} erg/(K mol$^{1/3}$) and results in anomalous values of the Huggins parameter.

As emphasized above, an alternative approach treats the macromolecules of lignin as microgel particles which form as a result of fragmentation of the cross-linked natural lignin. Gravitis and Stoldore [57] analyzed the hydrodynamic characteristics of lignin. Within the framework of the concept treating lignin as a cross-linked polymer, the g-factor for branching and the coefficient of bulk swelling q were calculated. The branching density of lignins p was compared with the theoretical branching density calculated on the basis of the existing molecular structures of lignin. It was found that the values calculated on the basis of Freudenberg's structural schemes [3] agree well with the experimental values of the branching density. However, because neither the Freudenberg's structural scheme nor later modifications comply with the topology of network polymers, the cross-linked structure of lignin macromolecules suggested in [57] seems to be arguable. Note that neither the branching density nor the swelling coefficient alone is obviously sufficient to identify the branching or the cross-linking of macromolecules, and take into account the lack of unambiguous relationship between the measured hydrodynamic parameters, the topology and the conformation of macromolecules.

As noted above, studies of biosynthetic lignins which are obtained *in vitro* in a monolignol–peroxidase–hydrogen peroxide system play an important role in gaining a deeper insight into the chemical structure of lignin. As monomeric lignin precursors, coniferyl alcohol [3], ferulic acid [24, 58], and isoeugenol [59] were used in model biosynthesis of coniferous lignin. Two synthetic procedures (and, correspondingly, dehydropolymers of two types) are most commonly used: end-wise polymerization (implemented by continuous addition of monomer) and bulk polymerization (conducted in *n* batch mode). Recently, new procedures for *in vitro* biosynthesis of lignin have been suggested that model both the chemistry and the dynamics of the process [31, 60]. Depending on the conditions and the substrate used, dehydropolymers with different molecular mass distribution may be prepared, although in most cases oligomeric products prevail [61, 62]. Using ferulic acid as a monomer makes it possible to synthesize rather high-molecular-mass ($M_w = 3 \times 10^4$ [63]) biosynthetic lignins.

In [64, 65], a ferulic acid-based bulk polymer was studied. From the linear plots of $\log[\eta]$ *versus* $\log M$ and $\log D$ *versus* $\log M$, coefficients of the Mark–Kuhn–Houwink equation were determined (Tab. II). Hydrodynamic behavior of bulk DHP was found to be similar to that of dioxane lignin. This is not the case with end-wise DHP [66, 67]. At an equal molecular mass, the end-wise DHP is described by a higher $[\eta]$ and comparatively low sedimentation coefficient values. It was found that the exponents in the Mark–Kuhn–Houwink equations for D and $[\eta]$ are greater than 0.5 ($b_\eta = 0.78$, $b_D = -0.58$). Sarkanen [3] suggested that the topological structure of lignins may depend on the supply mode of monomeric phenoxy radical into the reaction zone. In a continuous, endwise mode, formation of linear or slightly branched chains is more probable, whereas in the opposite case, because of the high initial concentration of phenoxy radicals, the formation of randomly branched macromolecules may be expected.

In [66, 67], hydrodynamic properties of two model lignins–synthesized under identical reaction conditions but differing in the mode of monomer supply – were compared. In agreement with theoretical expectations, the end-wise DHP was found to be a linear polymer. The authors claimed that bulk-polymerization led to a randomly branched polymer. It is noteworthy that the validity of this assignment is confirmed by the results reported by Tsvetkov *et al.* [68], who studied polymer with similar characteristics.

In physical chemistry of polymers, the degree of branching is described by the g-factor, which is defined as the ratio between the mean radius of gyration of the branched chain $\langle R^2\rangle_{br}$, and that of the linear chain of the same molecular mass $\langle R^2\rangle_l$,

$$g = \langle R^2\rangle_{br}/\langle R^2\rangle_l$$

A similar approach was introduced into lignin chemistry by Goring [4]. Because there is no linear analog for lignin, it was suggested to determine $[\eta]$ of the "linear analog of lignin" according to equation $[\eta]_l = K_\theta M^{1/2}$, where K_θ is the parameter characteristic of unperturbed chain dimensions. This approach was verified for various lignin polymers. The K_θ value was determined by extrapolation according to a modified Stockmayer – Fixman equation [51 – 55] or by combining a number of similar equations [49].

Apparently, the most reliable value of this parameter, $K_\theta = 0.118\,\text{cm}^3/\text{g}$, was obtained for dioxane lignin by Pla with co-workers [52 – 54], because they conducted the measurements in θ-conditions. However, in other publications, almost identical results were reported: $0.120\,\text{cm}^3/\text{g}$ for dioxane lignin in dioxane [55]; $0.113\,\text{cm}^3/\text{g}$ for dioxane lignin in DMSO [49], $0.119\,\text{cm}^3/\text{g}$ for milled wood lignin in DMSO [49]; $0.125\,\text{cm}^3/\text{g}$ for alkali lignin in 0.1 M buffer [4]; $0.110\,\text{cm}^3/\text{g}$ milled wood lignin in pyridine [47]; $0.119\,\text{cm}^3/\text{g}$ for alkaline lignin from cotton lint in θ-solvent [56]; $0.118\,\text{cm}^3/\text{g}$ for methanol lignin from cotton lint in θ-solvent [56]. It is a remarkable fact that K_θ is independent of the source and history of lignin. Evidently, this may mean that the topological structure of lignin macromolecules is rather uniform and is stable to the effect of various reagents.

Plots of the g-factor *versus* the molecular mass of milled wood and alkali lignins reveal that at $M > 6 \times 10^3$ the dependence reaches a plateau [14]. This was ascribed either to the existing distribution of units with respect to functionality [62] or to the specific features of the topological structure of lignin macromolecules [38]. A similar dependence was reported for dioxane lignins isolated from pine wood [49, 69]. Thus, after a certain molecular mass is attained, increasing the number of side chains does not result in a significantly lower branching factor. Apparently, this situation may occur when the lengths of branches are different and decrease for the branches of later generations. Kogan *et al.* [70] suggested a model to describe the growth of randomly branched macromolecules. This model leads to the same dependence of g-factor on the molecular mass as that observed for lignins. Note that the basic assumptions of the Kogan–Gandel'sman–Budtov model comply with the modern understanding of the regularities of plant tissue lignification. It is important that this conformity is greater than that achieved within the frameworks of other models for macromolecular growth, the Zimm–Kilb model in particular. Calculations according to the Zimm–Kilb theory, which is valid for monodisperse randomly branched chains, demonstrate that each second-fifth phenylpropane unit must represent a junction. This is one of the contradictions between the results of numerical calculations and the model *per se*, which initially assumes that both the chains and the subchains are described by Gaussian statistics.

Karmanov *et al.* [49] compared the branching densities obtained for dioxane lignins according to Zimm–Kilb and Kogan–Gandel'sman–Budtov. The relationship between the branching factor g, parameter a (which quantitatively describes the variation of branch lengths with the variation of ordinal number of generation j), and the number of junctions n is given by the following equation

$$g_n = a - 1/a + (a-1)^2/[a^2(a^n - 1)]^{-1} \times \left\{ n + \sum_{j=1}^{n} 1/(a^i - 1) \right\}.$$

As is seen from Figure 7, for dioxane lignin, the branching density ($\rho = n/M_w$) is approximately two times lower than the p value determined according to Zimm–Kilb. The branching density calculated for coniferous lignins according to the Zimm–Kilb model for polyfunctional branching is 0.3 – 0.4 [51–54] and tends to increase with molecular mass. According to interpretation of the hydrodynamic data suggested in [56, 71], the branching junctions of lignin macromolecules are tetrafunctional.

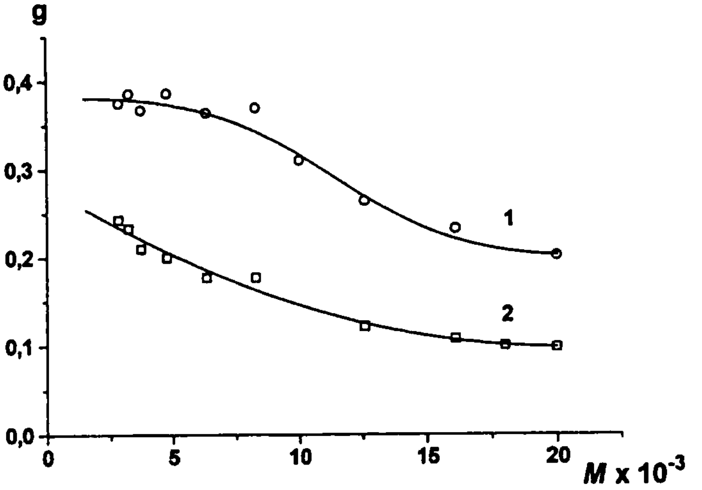

FIGURE 7 Branching density g as a function of the molecular mass of dioxane lignin fractions. (1) Zimm–Kilb model (2) Kogan–Gandel'sman–Budtov model [70].

Analysis of hydrodynamic data for various lignins and their comparison with fractal theories led to a hypothesis [72–74] that considered the supermolecular structure of *in situ* lignins as a network of crosslinked fractal clusters. Within the framework of this hypothesis, the biosynthesis of lignin proceeds as a kinetically unequilibrium diffusion-limited aggregation of the particle–cluster type (Witten–Sander's model) [75]. The fact that the fractal dimensionality d_f of milled wood lignin and dioxane lignin is on the average 2.5 [38, 76] confirms the validity of treating lignins as fractal clusters. The d_f values for lignin polymers were determined from hydrodynamic data according to [17, 38, 76]

$$d_f = 3(b_\eta + 1)^{-1} = (1 - b_S) = b_D^{-1}.$$

According to [17], in some cell wall regions, the crossover of the models describing the structure of lignin is possible (one mechanism of macromolecular growth changes to the other). In particular, a kinetic model of the irreversible growth of compact clusters of unit density (d_f is equal to the dimensionality of the growth space) cannot be excluded [62]. In [77], the hydrodynamic data were used to evaluate the fractal dimensionality of biosynthetic lignins (Tab. III). It was demonstrated that for the branched dehydropolymers d_f can be calculated by the relationship

$$g_\eta \sim 1/K_\theta[M^{3/d_f-1.5}].$$

Comparison of the fractal dimensionalities of lignins and the dehydropolymers revealed that the bulk DHP biosynthetic analog provides an adequate model of the topological structure and polymer properties of the native soluble lignins.

Studies of natural lignin in the cell walls of wood (densitometric analysis of the micrographs) revealed [38] that the lignified secondary cell wall is characterized by fractal structure. This made it possible to suggest that, from the viewpoint of dynamics, the biosynthesis of lignin occurs in the strange attractor mode. According to the definition [78], strange attractors comprise such solutions of the systems of differential equations that do not occupy the phase state compactly, but form a complex lacunar structure possessing fractal properties. In the studies of *in vitro* biosynthesis of lignin [60], several kinds of attractors, including the strange attractor, were discovered. Fractal nature of the dynamic processes of enzymatic dehydropolymerization of ferulic acid was established and some parameters of the random strange attractor in a two-dimensional pseudo-phase space were determined [79]. In particular, fractal self-similar dimensionality was found to be equal to 1.43 and informational dimensionality was equal to 1.61. Studies [76] of the dynamics of monolignol polymerization demonstrate that the nature of fractal properties of lignin lies apparently beyond the concepts involved in diffusion models for the growth of self-similar structures.

TABLE III Scaling characteristics of biosynthetic lignins and theoretical models

	Experiment [77]		*Theory**		
Parameter	*Bulk-DHP*	*End-wise-DHP*	*RWCO*	*DLA-P-Cl*	*DLA-Cl-Cl*
d_f	2.62 ± 0.27	1.66 ± 0.16	1.69	2.44	1.78
b_η **	0.13 ± 0.02	0.78 ± 0.02	0.78	0.23	0.68
ν_F **	0.38	0.60	0.59	0.41	0.56

* Simulated models: random walk without crossover (RWCO), diffusion-limited aggregation of particle-cluster (DLA-P-Cl) and cluster-cluster (DLA-Cl-Cl) types.

** Flory's critical parameter.

CONCLUSIONS

By using conventional methods of polymer science to analyze the topological structure of lignin polymers, a number of important parameters of this structure were reliably determined.

These parameters include hydrodynamic characteristics of the macromolecules: intrinsic viscosity, diffusion coefficients, sedimentation coefficients, coefficients in the Mark – Kuhn – Houwink equations, hydrodynamic invariants. The analysis of hydrodynamic properties revealed that the behavior of lignins in dilute solutions is markedly different from that of linear polymers, both flexible- and rigid-chain, in any of the known conformations. The microgel hypothesis of the structure of lignin macromolecules gained some popularity. According to this hypothesis, the macromolecules of lignin represent fragments of the cross-linked natural lignin, which are obtained by cleavage of the lignin network during the isolation procedure. At the same time, it is also possible that the macromolecules of lignin are common randomly branched chain molecules. Thus, traditional approaches fail to give an unambiguous description of the topological structure of lignin.

An important step towards a better understanding of the structure of lignin was made when fractal properties were discovered. It was found that a lignin macromolecule may be described as a fractal cluster of fractional dimensionality. Fractal dimensionality d_f describes the topological level of structural organization. However, evaluation of d_f is only the first step in studying lignin as a fractal object. In reality, a spectrum of fractal dimensionalities, which serve the invariant measures of that topological characteristic or the other, must be determined. As is known, the concept of a fractal is closely related to the concepts of determinate chaos and the strange attractor. The discovery of random dynamics for the dehydropolymerization of the monomer precursors of lignin in the strange attractor dynamic mode suggests that new procedures and parameters for the description of lignin structure may now be sought.

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