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Lignin. Structural organisation and fractal properties

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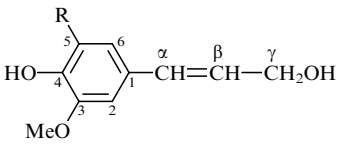
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Abstract. The results of investigations of the topological and supramolecular structures of lignins are considered. The experimental data on the hydrodynamic and conformational properties of dilute solutions of hardwood and softwood lignins are generalised. The relationship between hydrodynamic and fractal properties of lignin macromolecules is analysed and the applicability of various fractal concepts is discussed. Good prospects of using the fractal approach for the study of amorphous polymers with complex topological and supramolecular structures are demonstrated. The bibliography includes 174 references.

I. Introduction

Lignins are polyfunctional biopolymers of plant origin. They are formed upon enzymic dehydrogenation polymerisation of a number of methoxylated derivatives of hydroxycinnamic alcohols (guaiacyl-, syringylpropenol, *etc.*).[1,2]



R = H (guaiacylpropenol), OMe (syringylpropenol).

Two main classes of these biopolymers are distinguished, namely, the guaiacyl type lignin, typical of conifers, and the guaiacyl-syringyl type lignin, which is formed in deciduous plants. The unique character of lignin as a high-molecular-mass compound is due to the diversity of the structural units (dilignols) that constitute the structure and to diverse types of bonds between them.[3,4] More than twenty types of dilignols are currently known. The key types of dilignols incorporated in the lignin structure are shown in Fig. 1. In natural lignins, structural elements with β-O-4-bonds predominate [C(β)–O–C(4), ~25%]. This type of dilignol, 1-(4-hydroxy-3-methoxyphenyl)-2-(2′-methoxyphenyloxy)-1,3-propanediol (**1**, β-guaiacyl ether of guaiacylglycerol), is often used as a dimeric compound modelling the natural softwood lignin.

The rules of distribution of various dilignols in the polymer chain are unknown, most likely, they are non-deterministic, which is due to the absence of genetic control during the biosynthesis, at the stage of assembly of the lignin macromolecule.[1–4] It should, however, be noted that this point of view has lately been criticised. A new concept of lignin biosynthesis based on the view of existence of regio- and stereochemical control of the recombination of monolignols has been proposed.[5]

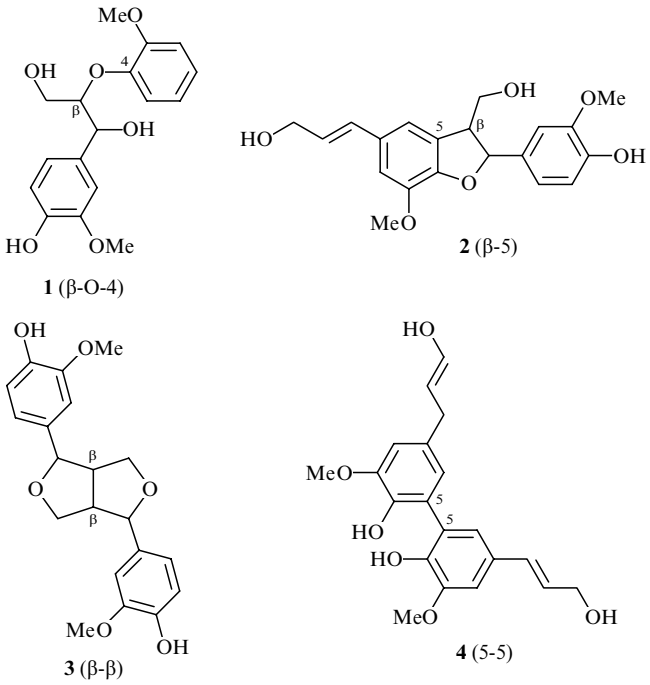


Figure 1. Dimers modelling the microstructural elements of a macromolecule of guaiacyl type lignins:[1] β-O-4-dilignol (**1**); β-5-dilignol (**2**, coumaran structure); β-β-dilignol (**3**, pinoresinol structure); 5-5-dilignol (**4**, biphenyl structure).

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The structural organisation of lignin as a biopolymer can be represented as a set of hierarchical levels differing in complexity, namely, the chemical, topological, supramolecular, and ultrastructural ones.[6] The last-mentioned level is inherent in native lignin. The achievements and problems related to the study of the chemical structure of lignin have been analysed in a review.[7] In recent years, substantial advances have been made in the study of the topological and supramolecular organisation of lignin. This is largely due to the development of new approaches to the research of polymers based on the use of the concepts of deterministic chaos and synergetics, the fractal theory, and non-linear dynamics.

This review gives an analysis of the data accumulated to date on the hydrodynamic and conformational properties of lignin macromolecules in solutions and on the topological structure and properties of lignin as a fractal object.

The topicality of research into lignin is dictated by the significant role it plays in the chemical processing of wood to produce cellulose, paper or cardboard. The production technology of cellulose-containing materials from one or another plant raw material is determined, first of all, by the structure and properties of the lignin it contains. Fragmentation and subsequent dissolution of softwood lignin, composed mainly of guaiacyl type dilignols, require the most drastic pulping conditions. In this case, alkaline delignification procedures are used, in particular, sulfate and soda pulping. Lignin of hardwood trees or herbaceous plants is delignified rather easily, which is due to its specific structural features, namely, the guaiacyl-syringyl structure. Cellulose is produced from these plant raw materials using a number of organosolvate pulping processes.

Depending on the production method, soluble lignins are classified into technical and slightly decomposed lignins. Technical lignins include alkaline lignins resulting from treatment of wood or stalks of herbaceous plants with sodium hydroxide or a mixture of sodium sulfide and hydroxide (alkaline and sulfate pulping) and lignosulfonates,† which are formed as side products upon treatment of the plant raw material with aqueous solutions of oxo compounds of sulfur (the sulfite pulping procedure).[8] The slightly decomposed lignins can be isolated from plant raw materials under relatively mild conditions.

If the reserves of traditional organic raw materials are exhausted, lignin can become the main source for the production of diverse organic compounds,[9] which is due to specific features of the chemical structure of lignin and virtual inexhaustibility of the natural plant resources.

II. Conformational properties and topological structure of lignin

Elucidation of the topological structure of lignin macromolecules is one of the most complicated problems of the physical chemistry of lignin. Historically, the views on the topological structure (configuration) of lignin macromolecules have been based on and have varied to follow the views on its chemical structure. Up to the mid-20th century, it was taken for granted that lignin, like cellulose, is a linear polymer. Later, after the publication of studies by Freudenberg and co-workers on lignin biosynthesis *in vitro* and elucidation of the main principles of the growth of polylignols, the views were revised, and, as a consequence, lignin was assigned to the class of branched polymers (see Ref. 1 and references cited therein). Currently, the concept of a network structure of natural lignin proposed by Goring predominates in wood chemistry.[10–12]

A classical approach to determining the topological structure of polymers includes investigation of the conformational properties of macromolecules in dilute solutions. The conformational properties of macromolecules show themselves, first of all, in the translational and rotational friction processes; therefore, they are studied using methods of molecular hydrodynamics, in particular, velocity sedimentation, isothermal translational diffusion and capillary viscosimetry. These methods allow one to estimate the size and conformation of the macromolecular coils, which are of crucial significance for determination of the topological structure of polymers. Hydrodynamic methods still remain the experimental basis for virtually all studies of the topological structure of lignin.

Previously,[1,2] lignosulfonates (LS) have been considered to be the most appropriate lignin specimens for determination of the macromolecular structure of natural lignin, because only the weakest α- and β-ester bonds are hydrolysed during the nucleophilic sulfitation and the degree of side condensation reactions is low. In addition, unlike many other lignin preparations, lignosulfonates are readily soluble in aqueous solutions. Therefore, many studies dealing with the physical chemistry of lignin have been carried out using LS.

Gardon and Mason have studied the hydrodynamic properties of industrial specimens of guaiacyl type LS (silver fir).[13,14] The measurements of the intrinsic viscosity and the translational diffusion coefficients carried out in brines provided the conclusion that in aqueous solutions, the LS macromolecules occur as the Gaussian impermeable coil conformation. This conclusion was based on analysis of the correlations between the intrinsic viscosity ($[\eta]$), the diffusion coefficient (D), and the molecular mass (M), which were described by Mark–Kuhn–Houwink (MKH) type dependences:

$$[\eta] = K_\eta M^a,$$

$$D = K_D M^b,$$

where K_η and K_D are empirical constants; a and b are the MKH scaling indices. The a and b values equal to 0.47 and -0.56, respectively, point to a a linear topological structure of LS macromolecules. A similar value for b, equal to -0.57, has been obtained for a spruce LS specimen in a 0.02 M solution of NaCl.[15] According to another publication,[16] low-molecular-mass LS fractions ($M < 5 \times 10^3$) consist of linear chains, whereas macromolecules with a higher molecular mass have a branched structure.

Studies performed by Goring and co-workers[11,17] deserve particular attention, because they crucially changed the views on the topological structure of lignins existing at that time. To study the hydrodynamic properties, Goring used LS specimens prepared by laboratory sulfite pulping of spruce wood. It was found that LS has a high polydispersity index [the ratio of the weight-average molecular mass (M_w) to the number-average molecular mass (M_n) reaches 5–7 or even more]. One specimen was fractionated to give nine fractions, whose molecular mass varied from 37.0×10^3 to 1.3×10^6. According to Goring's opinion, aqueous solutions of LS in a 0.1 M solution of NaCl are molecular disperse systems. The Mark–Kuhn–Houwink scaling indices a and b were found to be 0.32 and -0.33, respectively, *i.e.*, the hydrodynamic behaviour of the LS macromolecules corresponded to neither the Gaussian impermeable coil nor the Einstein sphere. The set of obtained results led Goring to the conclusion[11] that LS macromolecules, like those of other soluble lignins, represent fragments of the three-dimensional network of natural lignin *in situ*. The destruction of the three-dimensional network of natural lignin during its isolation from the plant tissue yields microgel particles of an arbitrary shape, whose hydrodynamic behaviour corresponds to the properties of slightly swollen spherical particles. The intrinsic viscosity of LS is fairly low, which is due to the small hydrodynamic radius of cross-linked particles. After the publication of Goring's studies, the concept of the cross-linked structure of natural lignin has gained wide acceptance among researchers; however, no convincing evidence supporting this hypothesis has been obtained so far.

A similar study, but using industrial lignosulfonates has been carried out by Afanas'ev *et al.*[18–20] These publications present the results of measurements of the hydrodynamic characteristics of

† Lignosulfonates belong to the class of polyelectrolytes, due to the presence of strong acidic groups CO_2H and SO_3H in the chain.

Table 1. Hydrodynamic and molecular characteristics of lignosulfonates in a water – salt buffer solution (pH 6.85).[20]

$[\eta]$ /cm^3 g^{-1}	$10^7 D_0$ /cm^2 s^{-1}	dn/dc (see [a])	$10^{-3} M_w$	M_w/M_n
5.4	0.10	0.200	82.0	1.8
4.7	0.13	0.204	38.0	1.7
4.1	0.15	0.220	23.0	1.8
3.8	0.20	0.220	14.0	1.6
3.7	0.21	0.220	12.0	1.8
3.2	0.24	0.239	8.0	1.4
3.0	0.27	0.250	6.0	1.6

[a] Increment of the refractive index.

spruce LS in aqueous and aqueous salt solutions at various pH values (Table 1 presents experimental values for some hydrodynamic parameters of LS obtained at pH 6.85). The researchers demonstrated the satisfiability of the scale invariance principle over a broad range of molecular masses — from 6×10^3 to 82×10^3. Analysis of the viscosimetry ($a = 0.22$) and diffusion ($b = -0.44$) data led to the conclusion[20] that the LS macromolecule is a chaotically branched chain rather than a microgel particle.

Due to the inconsistency of experimental data on the hydrodynamic properties of LS in solutions, the problem of the conformation of LS macromolecules remains debatable. Goring and co-workers[12] believe that LS exists in aqueous solutions as dense globular particles similar to Einstein spheres. However, in this case, the scaling indices a and b should be equal to 0 and -0.33, respectively, which contradicts the experimental data. The viscosimetric properties of samples and the scaling indices $a > 0.2$ imply that the shape asymmetry of the macromolecular coil changes with the growth in the molecular mass and that the macromolecule can be modelled by an ellipsoid of revolution. Rebinder[21] believed that LS molecules exist in solutions as spheroids with fairly large aspect ratios.

Among other reasons, the diversity and inconsistency of the data on the conformations of LS (Table 2) are related to the chemical structure of this polymer, which refers to the class of polyacids (polyanions). The presence of ionogenic groups (carboxy and sulfo groups) capable of a variety of interactions results in LS acquiring some properties atypical of natural lignin. Thus dilution of solutions of lignosulfonates to concentrations of $(1-0.5) \times 10^{-2}$ g cm^{-3} usually entails an increase in the reduced viscosity (η_{sp}/c), instead of the expected decrease, which is due to electrostatic effects.[28] The addition of monomeric electrolytes which shield electrostatic interactions in the chain does not always produce linear dependences of the reduced viscosity on the LS concentration (Fig. 2).[29]

The conformational characteristics of LS are dictated by the degree of ionisation of acid groups, which depends on the nature and properties of the solvent, the type of low-molecular-weight additives, the ion strength of the solution, and so on. The solution temperature and pH are also important factors influencing the hydrodynamic properties of LS. In the pH region of 5.5 – 7.5, the hydrodynamic size of LS molecules dramatically increases as a result of polyelectrolyte swelling; the efficiency of ionisation depends on the molecular masses of fractions according to a complex pattern.[20] Evidently, this is due to the inhomogeneity of fractions as regards the number and the nature of acidic, first of all, sulfur-containing groups. The degree of sulfonation of the fractions for field LS specimens varies over a wide range, namely, from 0.5 to 0.96. Therefore, it is clear that the chemical inhomogeneity of LS has an ambiguous influence on the results of hydrodynamic measurements and the conclusions drawn.

An essential factor complicating the research and interpretation of the results of hydrodynamic measurements for lignosulfonates is the aggregation of macromolecules (even in dilute solutions). According to a publication,[30] the molecular mass of softwood LS measured by the translational diffusion method decreases 6-fold on passing from a 0.1 N aqueous solution of KCl to anhydrous ethanol and decreases 12.5-fold on passing to methanol.

Associates of macromolecules have also been detected in dilute (in particular, aqueous) solutions of LS by velocity sedimentation techniques.[18,20] The hydrodynamic radius of the aggregates determined by these methods is equal to

Table 2. Mark – Kuhn – Houwink parameters for samples of technical lignins isolated from wood.

Lignin specimen	Type of wood	Solvent	MKH parameters			Ref.
			a	b	c [a]	
Lignosulfonate	silver fir	H_2O – NaCl (2 M)	0.47	–	–	14
	"	H_2O – NaCl (0.5 M)	–	−0.56	–	13
	spruce	H_2O – NaCl (0.1 M)	0.32	−0.33	–	17
	"	H_2O – NaCl (0.02 M)	–	−0.57	–	15
	"	H_2O – $BaCl_2$ (0.02 M)	0.19	−0.38	–	22
	"	buffer solution (pH 6.85)	0.22	−0.44	–	20
	hardwood	methanol	0.54	–	–	23
Lignosulfonate amine	softwood	methanol	0.13	–	–	23
Alkaline lignin	spruce	H_2O – NaCl (0.1 M)	0.32	–	0.52	10
	"	dioxane	0.12	–	–	1
	poplar	dioxane	0.29	–	–	24
Sulfate lignin	hardwood	DMSO	0.69	–	–	25
	softwood	DMSO	0.14	–	–	26
	spruce	DMSO	0.15	–	–	27

[a] c is the scaling index in the Mark – Kuhn – Houwink dependence of the sedimentation coefficient on the polymer molecular mass: $S = K_S M^c$.

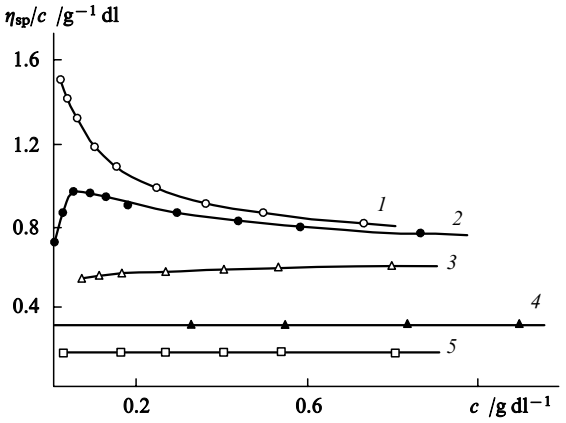


Figure 2. Reduced viscosity of lignosulfonates η_{sp}/c *vs.* concentration upon dilution of solutions of lignosulfonates with brines having different molar concentrations.[29]
NaCl concentration in brine /mol litre^{-1}: (*1*) 0.00001, (*2*) 0.001, (*3*) 0.01, (*4*) 0.1, (*5*) 1.

150–200 nm. Raising the solution temperature to 60 °C induces partial decomposition resulting in a more than twofold decrease in the hydrodynamic radius of the aggregates. It should be noted that the formation of ion associates is a typical feature of not only LS but also other polyelectrolytes.[31]

Lignosulfonates are known to be surfactants. The chains of phenylpropane units form hydrophobic fragments of the macromolecules, while highly acidic sulfo groups constitute the hydrophilic shell. It cannot be ruled out that the hydrophilic properties of LS play a significant role in the structural organisation of the macromolecular coil and, correspondingly, influence the hydrodynamic properties of this polymer in aqueous solutions.

Sokolov and co-workers[27,32,33] have carried out a series of studies dealing with the polymeric properties of alkaline lignins. It was found that both sulfate and alkaline lignins have high polydispersity indices ($M_w/M_n \approx 3-10$). The molecular mass of sulfate lignins varies from 1×10^3 to 34×10^3. As a rule, alkaline lignins isolated from hardwood have a lower molecular mass than softwood lignins. According to Sokolov,[27] the intrinsic viscosity of fractions of sulfate lignin from spruce wood in DMSO varied from 7.4 ($M_w = 1.3\times10^3$) to 13.3 $cm^3\ g^{-1}$ ($M_w = 38.7\times10^3$). The dependence of $\log[\eta]$ on $\log M_w$ is linear (the slope ratio, equal to the scaling index a, is 0.15), *i.e.*, macromolecules of the sulfate lignin are impermeable coils with a high degree of globularity; in the researcher's opinion, they can be modelled by rigid spheres impermeable to the solvent.

This conclusion is at variance with the results obtained by Mayer,[25] who gives a higher value of the viscosimetric parameter for sulfate lignin, $a = 0.69$ (see Table 2). This value corresponds to the conformation of a swollen impermeable coil for a linear macromolecule. It should be noted that this study was performed with hardwood lignin. The differing origin of lignin appears to be the most likely reason for the divergence of results obtained in the studies cited above.[25,27]

Thus, analysis of early publications dealing with the macromolecular structure of lignin attests to a substantial inhomogeneity of sulfate lignins, which is due to specific features of pulping processes.[1–3] A brief survey of publications devoted to technical lignins leads to the conclusion that the use of these polymers for elucidating the topological structure of natural lignin does not give unambiguous results. This is due to the substantial transformation of lignin during isolation from the plant tissue.

More successful studies (as regards gaining information on the structural organisation of natural lignins) have been carried out with another group of specimens, which belong to the class of slightly decomposed lignins. The greatest number of publications deal with the hydrodynamic and conformational properties of dioxane lignins (DL) and milled wood lignins (MWL). These lignins can be isolated from plant tissue under relatively mild conditions, which restricts the undesirable oxidation and condensation processes or modification of the chemical and topological structure of macromolecules. The MWL macromolecules do not contain highly acidic functional groups (see Ref. 24) and this eliminates the influence of the solvent, solution pH, *etc.* on the conformations of the specimens in solutions. Therefore, standard hydrodynamic methods of investigation provide fairly reliable information on the conformational characteristics of slightly decomposed lignins. Analysis of published data[1,2,5] shows that the M_w value for non-fractionated MWL preparations usually does not exceed 30×10^3 for the polydispersity index $M_w/M_n > 1.5$ (the molecular masses of DL are usually higher and the molecular-mass distributions are broader than those of MWL).

The molecular-mass distribution parameters are substantially dependent on the botanical and anatomical origin of lignin as a living natural object. In particular, lignins isolated from different types of wood or even from different parts (the stem, the roots, branches or leaves) of the same plant can differ appreciably in both the chemical structure[5] and the physicochemical properties including the molecular-mass distribution. Detailed studies of macromolecular, in particular, hydrodynamic and conformational, properties of lignins of different taxonomic origins are virtually absent. The necessity of performing such works has not been evident until recently, as it has been generally believed that, irrespective of the origin, natural lignins (and celluloses) are biopolymers with the same topological structure for any plant. However, in recent years, we have obtained new data concerning the macromolecular and conformational properties of slightly decomposed lignins of various botanical origins. This allowed us to hypothesise that the topological structure of natural lignins is polyvariant.

Before proceeding to the analysis of experimental data obtained for different lignin specimens, one should note some specific features of these polymers, which are to be taken into account when interpreting the hydrodynamic results. The first one is relatively low molecular masses of all known types of soluble lignins; therefore, some fractions are classified as oligomers. According to a number of publications (see, for example, Refs 31, 34 and 35), the oligomer molecules, unlike the molecules of high-molecular-mass polymers, are characterised by conformational inhomogeneity (depending on the degree of polymerisation) and an enhanced significance of the terminal functional groups. The excluded volume effects‡ for oligomer fractions can also depend on the degree of polymerisation.[31] These features can, in principle, violate the scaling relationships and bring about certain difficulties in the research of even slightly decomposed lignins.

The macromolecular properties of methanol lignin isolated from poplar wood have been studied.[24] Plotting the dependence of the intrinsic viscosity on the molecular mass showed that the coefficients a present in the MKH equation differ markedly for high and low molecular masses of methanol lignin. For oligomeric fractions, the a value exceeds 0.4 (in a good solvent), while for polymeric fractions, it decreases to 0.3. This regularity also holds in a Θ-solvent, although the values of the coefficients somewhat decrease (by 10%).

An increase in the a values with a decrease in the lignin molecular mass has been noted in several other studies.[36–38] Pavlov *et al.*[39] showed that in the low-molecular-mass region [$M = (0.8-5.8)\times10^3$], the slope of the dependences of $[\eta]$ and D on the molecular mass of MWL fractions increases, the a and b values approaching 0.5 and −0.5, respectively. However, most often, experimental data indicate a straight-line dependence $\log[\eta]-\log M$.

It should be noted that the change in the scaling on passing from one region of characteristic sizes to another is usual for any polymer, which is due, first of all, to conformational transitions.[31,40] Features of the topological structure of some polymers can hamper their transitions from one conformational state to another. In these cases, the region of a universal hydrodynamic behaviour of the molecule is extended. In any case, the macromolecules of soluble slightly decomposed lignins obey the scale invariance principle over a rather wide range of molecular masses $(3-5)\times10^3-100\times10^3$,[41] which justifies the application of traditional approaches to the analysis of conformations of these macromolecules, despite the unique features of the chemical structure of lignins.[42]

The influence of the terminal functional groups on the conformational properties of slightly decomposed lignins is expected to be insignificant, taking into account their chemical structure (the absence of highly acidic functional groups).[2,5] However, some researchers adhere to a different opinion, based on the fact that the Flory linear swelling coefficient for low-molecular-mass fractions of dioxane lignin ($M_w < 3\times10^3$) in a good solvent barely differs from unity.[41] The authors believe that

‡ The excluded volume effect is related to the fact that two polymer chain units should necessarily occupy two physically different sites in space; this effect influences the conformation of the polymer chain in solution.

Table 3. Hydrodynamic characteristics of fractions of milled wood lignins from pine (*Pinus silvestris*) in DMSO.[39]

Fraction	$[\eta]$ /cm^3 g^{-1}	10^7 D /cm^2 s^{-1}	10^{13} S /s	10^{-3} M_{SD}	10^{-3} $M_{D\eta}$	10^{10} A_0 /erg mol$^{-1/3}$ K^{-1}	k_X
1	15.5	2.6	1.7	78	57	4.08	1.1
2	8.1	4.4	0.9	24	23	3.78	2.1
3	8.0	3.5	0.7	24	45	2.99	1.9
4	7.8	6.15	0.5	10.4	8.6	3.93	1.2
5	7.2	7.2	0.4	6.7	5.8	3.87	1.9
6	6.3	7.5	0.3	4.8	5.8	3.45	1.0
7	5.9	7.0	–	–	7.7	–	1.0
8	3.5	15.6	–	–	1.2	–	0.6
9	3.4	15.3	–	–	1.3	–	0.7
10	2.7	15.4	–	–	1.6	–	2.2
11	4.3	16.2	–	–	0.9	–	4.3
12	2.0	21.3	–	–	0.8	–	5.3

this is due to the interaction of the polymer functional groups, resulting in the formation of densely packed weakly solvated coils. The influence of other factors caused by the low molecular mass of the polymers cannot be ruled out either. This influence shows itself as a divergence of the experimental scaling indices obtained by different researchers under analogous conditions. For example it has been noted[37] that the Stockmayer–Fixman dependence of $[\eta] \times M^{-0.5}$ on $M^{0.5}$ at $M \to 0$ found for dioxane lignin isolated from pine wood deviates from a straight line towards higher $[\eta] \times M^{-0.5}$ values, whereas in another publication,[24] an almost perfect straight line was obtained.

The greatest number of publications are devoted to softwood lignins, which belong to guaiacyl type lignins. Some of these studies have been considered in a review.[43] Detailed investigation of lignins from milled pine wood in DMSO has been reported.[39] A sample of this lignin was thoroughly separated into 12 fractions for which velocity sedimentation (S), translational diffusion (D) and intrinsic viscosity ($[\eta]$) coefficients were determined (Table 3).

Attention is drawn by high values and a substantial scatter of the Huggins coefficients (k_H) over the fractions. Earlier studies usually did not report or discuss the k_H values because the interpretation and the physical meaning of the Huggins constant have been and still remain obscure. It is known that typical polymers with a linear topology of macromolecules in good solvents are characterised by $k_H \approx 0.2-0.3$.[44] Guaiacyl lignins differ from guaiacyl-syringyl lignins or linear polymers by great fluctuations of the Huggins parameter (in some cases, by more than an order of magnitude). In our opinion,[45] this is due to the specific fractal structure of the macromolecules of softwood lignins. The relationship between the Huggins parameter and the fractal dimension of macromolecules for a number of flexible- and semirigid-chain polymers in dilute solutions has been analysed by Kozlov *et al.*[46]

Turning back to the discussion of the results obtained by Pavlov *et al.*,[39] it should be mentioned that the dependences of the hydrodynamic characteristics S, D and $[\eta]$ on M_{SD} and $M_{D\eta}$ were approximated by straight lines with a linear correlation coefficient of not less than 0.91. Shkaeva[47] has obtained an unexpectedly high viscosimetric Mark–Kuhn–Houwink parameter for a pine wood lignin ($M_w = 27 \times 10^3$) ($a = 0.79$), which corresponds to the conformation of an impermeable swollen coil for linear polymers in a good solvent. Apparently, this result requires further investigations by sedimentation and diffusion techniques. The Mark–Kuhn–Houwink parameters determined for guaiacyl lignins by different investigators[37,39,43,48–51] are summarised in Table 4.

These results show that the softwood guaiacyl lignins are distinguished by low intrinsic viscosity and low magnitudes of the Mark–Kuhn–Houwink parameter a, which is indicative of compact shape of the lignin macromolecules, related, in all probability, to their branching. The lowest parameter a found is 0.10;[11] however, most often, publications give a value of ~ 0.25 or somewhat higher (see, for example, Refs 48–50). This value coincides with the theoretical value for chaotically branched macromolecules.[31] The parameters b for a variety of softwood lignin specimens in various solvents found from translational diffusion data fall in a rather narrow range, $b = -(0.3-0.4)$.[43]

A number of publications report the values for the Tsvetkov–Klenin hydrodynamic invariant (A_0),[39,50–52] normally calculated using the equation

$$A_0 = (R[D]^2[S][\eta])^{1/3},$$

where R is the universal gas constant; $[D] = D\eta_0/T$, $[S] = S\eta_0/(1-\bar{v}\rho_0)$ ($\bar{v}$ is the specific partial volume of the polymer, ρ_0 is the density of the solvent).

For impermeable spherical particles, the theoretical A_0 value is $\sim 2.9 \times 10^{-10}$ erg mol$^{-1/3}$ K^{-1} (see Ref. 53). For synthetic flexible-chain and moderately rigid-chain polymers, A_0 is normally higher, being equal to $(3.2 \pm 0.2) \times 10^{-10}$ erg mol$^{-1/3}$ K^{-1}. For the milled pine wood lignin, the average value of the Tsvetkov–Klenin hydrodynamic invariant amounts to 3.7×10^{-10} erg mol$^{-1/3}$ K^{-1} (the range is from 2.99 to 4.08, see Table 3).[39] Other researchers reported lower A_0 values for this lignin. For lignin of milled spruce wood, the A_0 values were, on average, 2.95×10^{-10} erg mol$^{-1/3}$ K^{-1} (see Ref. 51). The following values of the hydrodynamic invariant A_0 have been obtained:[50] the average value for the pine wood DL is

Table 4. Mark–Kuhn–Houwink parameters for guaiacyl (softwood) lignins in various solvents.

Specimen	Type of wood	Solvent	10^{-3} M	MHK parameters			10^2 K_η	10^5 K_D	10^{16} K_S	Ref.
				a	b	c				
Milled wood lignin	pine tree (*Pinus silvestris*)	DMSO	4.8–78.0	0.28	−0.41	0.60	0.56	2.5	1.9	39
	"	DMF	3.0–14.6	0.26	−0.43	0.57	0.64	6.5	8.3	37
	spruce (*Picea sp.*)	pyridine	1.9–24.4	0.12	−0.39	0.61	2.6	3.9	3.9	51
Dioxane lignin	pine tree (*Pinus silvestris*)	dioxane	4.3–25.0	0.24	−0.35	0.65	0.65	2.2	2.2	48, 49
	"	DMSO	2.1–100	0.25	−0.40	–	1.27	1.9	–	50
	spruce (*Picea sp.*)	dioxane	1.6–9.8	0.25	–	0.56	–	–	–	43

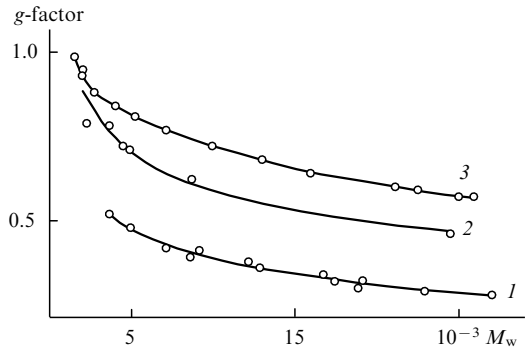


Figure 3. Branching *g*-factor *vs.* molecular mass for fractions of softwood lignins.
(*1*) spruce wood DL;[54] (*2*) pine wood DL-1; (*3*) pine wood DL-2.[55]

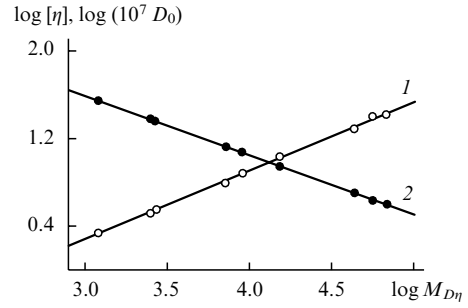


Figure 4. Mark–Kuhn–Houwink dependences plotted for a milled birch wood lignin.[58]
(*1*) $\log[\eta]$ *vs.* $\log M_{D\eta}$; (*2*) $\log D_0$ *vs.* $\log M_{D\eta}$.

2.9×10^{-10} erg mol$^{-1/3}$ K^{-1} and that for MWL in DMF is 3.0×10^{-10} erg mol$^{-1/3}$ K^{-1}. It is noteworthy that published data concerning the experimental determination of A_0 are rather scanty and are actually limited to the above examples.

Generally, analysis of the experimental data on hydrodynamic and conformational properties of slightly decomposed lignins isolated from softwood shows that the macromolecules of these lignins are characterised by high diffusional mobility and low intrinsic viscosity. These features, in combination with data on the Mark–Kuhn–Houwink scaling parameters, the hydrodynamic invariant, and the Huggins parameters, attest to a branched structure of the macromolecules of softwood lignins. Obviously, these lignins refer to the class of chaotically branched polymers.

The degree of branching of a macromolecule can be characterised by the so-called *g*-factor. The magnitude of the *g*-factor is determined by the ratio of the radii of gyration of the branched (R_b^2) and linear (R_l^2) chains with identical molecular masses and thermodynamic flexibilities

$$g = \frac{R_b^2}{R_l^2}.$$

Analysis of the resulting *g*-factors shows [20, 33, 43, 54, 55] that this value depends on the molecular mass of lignin (Fig. 3). The *g*-factor decreases from 1 (for the lowest-molecular-mass fractions) to 0.3–0.5 (for the fractions with $M > 25 \times 10^3$). A similar pattern of dependence of *g* on *M* is observed for synthetic chaotically branched polymers.[31] Running a few steps forward, we would like to note that an absolutely different pattern of dependence has been found for hardwood lignins, in particular, the *g*-factor increases with an increase in the lignin molecular mass.

In recent years, guaiacyl-syringyl type lignins have aroused enhanced interest in researchers;[56, 57] this is related to solution of purely applied problems associated with the involvement of new types of plant raw materials, *i.e.*, annual plants and hardwood, instead of softwood, in the manufacture of cellulose materials. It was found that the polymeric properties of lignins isolated from angiosperms differ appreciably from the properties of lignins isolated from gymnospermous plants, which is related to specific features of biosynthesis and, as a consequence, to differences in the topological structures of macromolecules.

Table 5 contains the hydrodynamic characteristics that we determined for a lignin specimen from milled aspen wood.[58] Comparison of the experimental data demonstrates that the aspen wood lignin has a higher intrinsic viscosity and much lower values of the Tsvetkov–Klenin hydrodynamic invariant compared to those of softwood lignins. Study of a series of samples of guaiacyl-syringyl lignins isolated from birch and aspen wood has shown [58–61] that hydrodynamic characteristics of these lignins follow linear dependences on their molecular masses (Fig. 4). As shown by calculations, the control relations

$$(1 - c) = |b| = \frac{a + 1}{3}, \quad (1)$$

$$K_\eta^{1/3} K_D = \frac{A_0 T}{\eta_0}, \quad (2)$$

$$K_\eta^{1/3} K_S = \frac{A_0 (1 - \overline{v}\rho_0)}{\eta_0 R}, \quad (3)$$

hold for these lignin samples within the bounds confined by the root-mean-square errors of scaling indices. This indicates that the equivalence principle is obeyed in the translational and rotational friction processes. Therefore, it was concluded that, irrespective of the size, the lignin macromolecules are topologically similar, and, hence, the scale invariance principle, fundamental for polymers, holds. Table 6 presents the Mark–Kuhn–Houwink parameters, which allow one to determine the conformation of the macro-

Table 5. Hydrodynamic characteristics of fractions of lignins from milled aspen (*Populus tremula*) in DMF.[58]

Fraction	$[\eta]$ /cm^3 g^{-1}	$10^7 D_0$ /cm^2 s^{-1}	$10^{13} S_0$ /s	$10^{-3} M_{SD}$	$10^{-3} M_{D\eta}$	$10^{10} A_0$ /erg mol$^{-1/3}$ K^{-1}	k_X
1	34.3	3.0	3.57	90.7	98.9	2.5	0.24
2	16.1	5.5	2.11	29.2	34.2	2.4	0.58
3	10.1	8.6	1.89	16.7	14.3	2.7	0.24
4	6.9	12.5	1.52	9.3	6.8	2.8	0.75
5	6.1	13.2	1.03	5.9	6.5	2.5	0.36
6	5.9	14.0	0.88	4.8	5.6	2.4	0.24
7	4.2	19.2	–	–	3.3	–	0.63
8	3.7	20.1	–	–	3.2	–	1.67
9	3.5	22.4	–	–	2.5	–	1.15
10	3.1	24.2	–	–	2.1	–	1.37
Initial specimen	9.3	9.6	–	–	11.9	–	0.88

Table 6. Mark – Kuhn – Houwink parameters for guaiacyl-syringyl (hardwood) lignins in DMF.

Lignin specimen	Type of wood	$10^{-3}\,M$	MHK parameters			$10^{2}\,K_{\eta}$	$10^{5}\,K_{D}$	$10^{16}\,K_{S}$	Ref.
			a	*b*	*c*				
MWL	birch (*Betula verrucosa*)	6.1 – 64.5	0.61	−0.53	0.47	2.78	15.5	19.4	58
MWL	"	6.3 – 21.5	0.69	−0.50	0.50	1.86	9.2	12.7	61
DL	"	4.0 – 49.8	0.57	−0.45	0.55	4.0	21.0	8.5	60
MWL	aspen (*Populus tremula*)	4.8 – 90.7	0.62	−0.55	0.45	2.70	15.9	20.9	58
DL	"	6.9 – 22.5	0.61	–	0.47	3.6	–	20.9	61
ML [a]	poplar (*Populus trichocorpa*)	1.5 – 73.7	0.41	–	–	–	–	–	24

[a] Methanol lignin, 2-methoxyethanol as the solvent.

molecule. For a number of specimens of guaiacyl-syringyl lignins, the scaling indices *a*, *b* and *c* are equal to 0.6 ± 0.1, -0.5 ± 0.05 and 0.5 ± 0.05. These are usual values for linear flexible-chain polymers. Upon analysis of the scaling indices, one can infer that the macromolecules of hardwood lignins in dilute solutions ($c[\eta] \leqslant 1$) acquire the conformation of a swollen impermeable coil. This demonstrates that hardwood lignins belong to a universal class of polymers with a linear macrochain topology. However, the intrinsic viscosities of these specimens are much lower than those for typical linear flexible-chain polymers with the same molecular mass. The average values for the Flory – Mandelkern hydrodynamic invariants [$\Phi^{1/3}P^{-1} = (1.7-2.3) \times 10^{6}$] are lower than the theoretical values for linear Gaussian macromolecules (2.7×10^{6}) and correspond to the hydrodynamic invariants for branched polymers. Noteworthy is the fact [60] that in the case of DL, the pattern of dependence of the hydrodynamic invariant $\Phi^{1/3}P^{-1}$ on the molecular mass is similar to that found for regularly branched polymers, in particular, lactodendrimers (Fig. 5), but differs from the pattern of dependence typical of chaotically branched polymers.

Analysis of the published data dealing with the properties of guaiacyl-syringyl lignins shows that the hydrodynamic behaviour of the macromolecules of lignins isolated from the secondary xylem of deciduous trees differs from the behaviours of both flexible- and rigid-chain linear polymers and also from the behaviour of typical chaotically branched polymers, although some criteria are satisfied. In our opinion, soluble hardwood lignins should be attributed to the class of star polymers. The linear structure of the branches of star macromolecules ensures the maintenance of scaling parameters typical of a linear topology; however, the presence of the branching unit — the star centre — decreases appreciably the hydrodynamic dimensions of the macromolecule. This results in abnormally low intrinsic viscosity and in a decrease in the Flory – Mandelkern and Tsvetkov – Klenin hydrodynamic invariants, which are sensitive to the degree of branching.

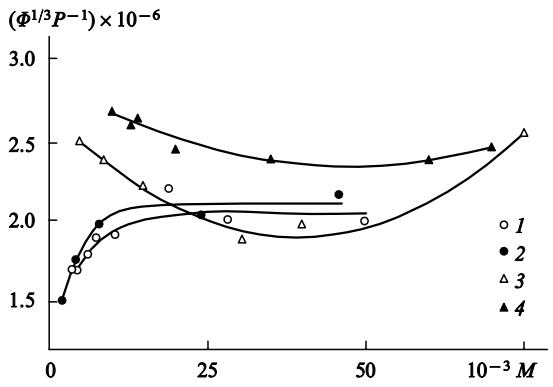


Figure 5. Flory – Mandelkern hydrodynamic invariant *vs*. the molecular mass of polymer fractions with different topological structures.
Polymer: (*1*) birch wood DL,[60] (*2*) dendrimer,[53] (*3*) pine MWL,[50] (*4*) chaotically branched polyphenylquinoxaline.[60]

This assumption is supported by the results of simulation of the growth of polydisperse polymer stars with linear branches within the framework of the self-avoiding random walk (SARW) model.[62] According to this model, one-centre star tri- and tetrafunctional macromolecules form impermeable coils with a Mark – Kuhn – Houwink diffusional parameter *b* close to -0.5 and a fractal dimension d_f equal to 2.§ It is pertinent to recall that Flory [63] has shown theoretically that the viscosimetric parameters *a* for star and linear macromolecules coincide. Later, this result was confirmed experimentally [64] in relation to polystyrenes. A star-like polymer structure in a good solvent should have, in conformity with the logic of the excluded volume effect, the fractal dimension of $5/3 < d_f < 2$. Experimental results reported by Belyaev *et al.*[59] confirm the validity of assignment of the macromolecules of guaiacyl syringyl-lignins to the star type.

III. Lignin macromolecule as a fractal object

The use of classical physicochemical methods of polymer science for the study of dilute solutions of lignin made it possible to elucidate the key hydrodynamic characteristics of its macromolecules, namely, intrinsic viscosity, diffusion and sedimentation coefficients, scaling indices and hydrodynamic invariants. The properties and structure of lignin were found to depend on not only the method used to isolate it from the plant tissue but also on the taxonomic origin. Analysis of the hydrodynamic characteristics of guaiacyl-syringyl lignins showed that the macromolecules of hardwood lignins have a star-like structure, their conformational properties being determined by the linear topology of branches. The hydrodynamic behaviour of guaiacyl lignins differs substantially from the behaviour of polymers with a linear topology of macromolecules.

Despite the long-term studies and a rather vast amount of experimental data on the hydrodynamic properties of lignins of different origin, the task of establishing the topological structure of the macromolecules of natural lignins still remains unsolved. There are grounds for suggesting that traditional approaches and methods are inadequate for obtaining exhaustive information on the structure of macromolecules of natural lignins. The discovery of deterministic chaos, dynamic self-organisation and strange attractor phenomena in the lignin biosynthesis [65 – 67] indicates that solving the problem of structure organisation of lignin generally and its topological structure specifically requires resorting to new approaches.

It has been found in recent decades that the structure of a substance formed under conditions far from thermodynamic

§ The fractal dimension of a macromolecular coil in solution is determined by two types of interaction, namely, the interaction of the coil elements with each other and polymer interaction with the solvent.

equilibrium can be described in terms of the mathematical body of fractal geometry and synergetics.[68–70] The synthesis of polymers, including natural ones, takes place most often under such non-equilibrium conditions. This ultimately results in the formation of fractal structures at one or another level of the polymer structural organisation. It has been stated [71] that any polymer that does not exist in the crystalline state should necessarily have a fractal structure over some scale range. This opinion is confirmed by numerous experimental data.[46, 72, 73] This is why synergetics and fractal analysis are used more and more extensively to study polymers with complex topological structure, for example, cross-linked polymers and chaotically branched polymers.

In 1986, the possibility of describing the supramolecular structure of lignin within the bounds of the fractal concept was hypothesised for the first time.[74] By the end of the 20th century, the fractal theory had gained wide application in natural sciences, including polymer science. Below we consider the main properties of fractal objects of differing nature and discuss the experimental data on the fractal properties of lignin.

1. Structure and fractal properties of polymers

Examples demonstrating the scope and prospects of the application of fractal concepts to description of the macromolecular properties of polymers are documented.[75–80] The key properties of the polymer fractals include self-similarity, fractional dimensions, size dependence of the density, and restricted (regarding the size) domain of existence.[75, 77] Polymers possess statistical self-similarity but over some limited scale range.[71]

A macromolecule is often considered as a fractal cluster assembled from monomer units.[81] The mass M and the density ρ of such a macromolecule are described by the following relation:

$$M = m_0\left(\frac{R}{a_0}\right)^{d_f},$$

$$\rho = \rho_0\left(\frac{R}{a_0}\right)^{D-d_f},$$

where m_0, a_0 and ρ_0 are the mass, the size and the density of a monomer unit; R is the size of the macromolecule; d_f is the mass fractal dimension; D is the dimension of the Euclidean space.

Important characteristics of a macromolecular coil include the radius of gyration R_g and the hydrodynamic radius R_H, which are derived from the results of viscosimetric or diffusion measurements. These parameters depend on the molecular mass (M) and the way it is distributed in space (the latter characteristic is taken into account by the index v, which is equal to 0.5 for the Θ-state)

$$R_g \sim M^v,\ R_H \sim M^v. \qquad (4)$$

The fractal dimension of a single macromolecule is determined by both the topological structure (configuration) and the conformational state. For example, a linear macromolecule can possess different fractal properties depending on the number and the size of monomer units, quality of the solvent, temperature and the concentration of macromolecules, *i.e.*, on those factors that dictate the conformation of the macromolecule.

Baranov *et al.*[82] considered the fractal properties of various conformational states of a linear macromolecule in 3D space (Table 7).

The fractal dimension of a macromolecule is determined by the relation $d_f = 1/v$ (see Ref. 83); thus, the fractal dimension of a macromolecular coil in a Θ-solvent is 2. In a good solvent, $v = 3/5$ and, correspondingly, $d_f = 1.67$.

Table 7. Characteristics of a linear macromolecule as a fractal object.[82]

Conformation	v	a	d_f
Θ-coil	1/2	1/2	2
Swollen coil	3/5	4/5	5/3
Permeable coil	2/3	1	3/2

For the globular state, $v = 1/3$ and $d_f = 3$, *i.e.*, the globular conformation is not fractal. A globule is characterised by a distribution of the 'everywhere dense' type (this does not mean, however, that globular structures are absolutely compact, because the macromolecule bulk contains some amount of the solvent). For a rod-like conformation of the macromolecules, the topological dimension coincides with the fractal dimension and $d_f = 1$; in this conformation, the macromolecule is not a fractal either. Finally, for a permeable coil, $v = 2/3$ and $d_f = 3/2$. In this case, the macromolecule is a fractal.

Thus, the fractal properties of linear polymers are determined by their conformational characteristics and a macromolecule can be a fractal object only in three cases: when it acquires the conformation of a Θ-coil, a permeable coil, or a coil in a good solvent. The main criteria of fractality, namely, a fractional dimension and the scale invariance principle, are satisfied for these conformations. The configuration of macromolecules of natural lignin is not linear, as was shown in Section II; therefore, it is pertinent to consider theoretical models that allow one to study the fractal properties of branched structures.

a. Models of the percolation cluster and 'lattice animals' clusters

The model of percolation cluster (percolation theory) proposed by Broadbent and Hammersley [84] is a mathematical model that allows one to study the regularities of the formation of branched polymeric structures. This model is underlain by a lattice composed of a number of points and bonds. Bonding of the lattice points to each other forms a cluster (a branched macromolecule), which is a fractal characterised by a quite definite fractal dimension dependent on the lattice structure and dimension, the growth mechanism and the p value (p is the probability that a lattice point belongs to the cluster). The percolation cluster model is characterised by universal behaviour of various parameters near the percolation threshold when $p = p_c$ (transition from a finite cluster to an infinite cluster after a critical concentration of points has been attained).¶ The fractal dimension of an infinite critical cluster depends on the lattice dimension and is equal to 1.89 for two-dimensional and 2.5 for three-dimensional lattices.[85] The structure of percolation clusters above the transition point ($p > p_c$) is characterised as uniformly bound, and $d_f = D$, where D is the dimension of the Euclidean space.

When $p < p_c$, there exist a set of clusters that correspond to a universal class of 'lattice animals'. These simulate the statistical behaviour of branched polymers in solutions and represent an ensemble of clusters for which any configuration of a specified size is equally probable. Clusters that refer to the type of 'lattice animals' have the following fractal dimensions:[86] $d_f = 1.55 \pm 0.05$ for the two-dimensional case and 2.00 ± 0.05 for the three-dimensional case. A study of the influence of the mechanism of growth of branched macromolecules on their topological structure and fractal characteristics has been reported.[87] It was found that the applicability of the 'lattice animals' cluster model is limited to particular classes of branched polymers.

b. Models of particle – cluster and cluster – cluster type diffusion-limited aggregation

The model of diffusion-limited aggregation of the particle – cluster type (DLA P – C) is the best known kinetic model of irreversible growth of fractal clusters. This model has been developed by Witten and Sander [88] and has been used subsequently to study the growth of colloid particles of differing nature, electrolysis and polymerisation processes, hydrodynamic structures of the 'viscous finger' type, *etc*. All these processes and structures are subject to the same mathematical description under certain conditions.

¶ The formation of an infinite cluster is a phase transition.

The DLA P–C model has been considered in detail in the books.[76, 80]

If the Brownian (random) motion of particles involved in the Witten–Sander model is replaced by rectilinear motion, the resulting cluster will represent a compact aggregate with a dimension d_f equal to the dimension of the fractal lattice (the Wald–Sutherland model).[89] Compact clusters are also produced in other aggregation models of the particle–cluster type, namely, in the 'rain' model and in the Eden model.[90]

The model of diffusion-limited aggregation of the cluster–cluster type (DLA C–C) is the most plausible model of the growth of aerosol particles.[91, 92] It was also used to study dehydropolymerisation of monolignols.[74]

The fractal dimension of the clusters assembled from monodisperse particles is equal to 1.78 ± 0.05. The polydispersity of particles barely changes the fractal dimension of the cluster. The influence of the growth conditions of clusters (diffusion velocity, the probability of addition upon collision, process reversibility) on their structural characteristics has been studied.[93] A decrease in the probability of addition was found to entail the formation of denser aggregates, the fractal dimension of the clusters being increased to 2.0 ± 0.06.

c. Fractal dimensions

The conformational state of a macromolecule in solution is determined by the solvent quality, the solution temperature, the polymer concentration, *etc*. A change in the polymerisation conditions may entail conformational transitions accompanied by a change in scaling indices, the Mark–Kuhn–Houwink parameters and the critical index ν. The nature of transitions between these states can be different. Some transitions correspond to the 'disorder–disorder' or 'fractal-$d_f^i \leftrightarrow$ fractal-d_f^j' transitions.[82] Determination of fractal dimensions using the scaling indices from data of hydrodynamic measurements allows one to establish reliably the macromolecule conformation. However, it is evident that macromolecules possess not only conformational fractal properties but also configurational fractal properties caused by mutual arrangement of topological elements — knots, side branches, subchains, cross-links, rings, *etc*. Therefore, the use of only Hausdorff type dimensions, applied most often to describe fractal objects, is, apparently, inadequate for unambiguous description of the structural organisation of a polymer molecule because these dimensions do not allow one to have an idea of its configuration.[71] According to Mandelbrot,[94] more accurate description of a complex structure requires the use of a larger number of fractal dimensions.

The connectivity of the structure elements, *i.e*., the configuration of a macromolecule, can be estimated using the so-called spectral (or fracton) dimension d_s, proposed [95] to characterise the natural vibrations of fractals. The fracton dimension can be determined from the equation describing the vibrations of a random network, which differs from the equation describing the random walk of a particle across a fractal lattice (with the dimension d_w) only by the order of the derivative.[85] The d_s value can be found from the relation

$$d_s = \frac{2d_f}{d_w},$$

where $d_w = 2 + \delta$ (δ is the scaling index of abnormal diffusion). For macromolecules with any configuration other than linear, $\delta > 0$.

The fractal and fracton dimensions calculated within the bounds of various cluster models are presented in Table 8.

A specific feature of the fracton dimension is independence of its value of the way of insertion of a fractal object into the Euclidean space. In other words, the fracton dimension, unlike the fractal dimension of the Hausdorff type, does not depend on the conformational state of the macromolecule and is dictated only by its topological structure. The fracton dimension of a linear macromolecule is equal to unity.

Table 8. Fractal (d_f), fracton (d_s) and chemical (d_l) dimensions for branched structures in terms of different cluster models.

Model	D	d_s		d_f		d_l	
		value	Ref.	value	Ref.	value	Ref.
Percolation cluster model	2	1.33	85	1.9	95	1.64	96
	3	1.33	85	2.5	95	1.83	96
DLA P–C	2	1.20	97	1.71	98	1.71	90
	3	1.2–1.4	99	2.50	98	2.50	90
DLA C–C	2	$\leqslant 1.2$	100	1.45	101	1.22	102
	3	$\leqslant 1.26$	100	1.80	93	1.42	102
Model of the 'lattice animals' clusters	2	1.55	86	1.12	86	1.33	90
	3	2.0	86	1.19	86	1.45	90

Along with the fracton dimension d_s, the topology of a macromolecular cluster can be characterised by the chemical dimension (connectivity parameter) d_l which takes into account the arrangement of all chemical bonds occurring between cluster particles. The chemical fractal dimension of the cluster is determined by the expression [103]

$$N \sim l^{d_l},$$

where N is the number of cluster species (monomer units if a polymer fractal is considered); l is the so-called chemical distance, *i.e*., the shortest distance between two knots of the macromolecule. The chemical dimension reflects the internal connectivity in the polymeric fractal; therefore, in some cases, it is called the internal dimension. It follows from the connectivity position that $d_l \geqslant 1$. For a linear polymer chain, the chemical dimension is equal to unity. For a chaotically branched structure formed by the Witten–Sander model (the DLA P–C model), the chemical and fractal dimensions coincide ($d_l = d_f$). As opposed to this, structures formed by the DLA C–C mechanism are less branched, which is manifested as a decrease in the chemical (internal) dimension with respect to the fractal dimension (see Table 8).

d. Multifractal formalism

The models considered above describe objects as monofractals. Biopolymers are usually distinguished by a complicated structural hierarchy with numerous structural sublevels, and each of these can be characterised by particular order parameters. In addition, even at one level of structural organisation, fractal ensembles that reflect the structure of a real compound often require that a spectrum of dimensions rather than a single dimension be used. The differences between them serve as a measure of the degree of inhomogeneity of the object under consideration. This circumstance stipulated the necessity of introducing the concept of the multifractal. A multifractal can be presented as a combination (superposition) of monofractals with different fractal dimensions.

Olemskoi and Flat [104] considered the formalism permitting one to derive the regularities of structure formation from the set of monofractals. The applicability of the multifractal formalism to investigations of structural organisation of objects and physical processes is associated with considering the Renyi dimensions D_q.[72, 75, 105] The Renyi dimensions are determined from the equation

$$D_q = -\frac{\lim_{\varepsilon \to 0} K_q(\varepsilon)}{\ln \varepsilon},$$

where ε is the size of a cell into which the phase space was split; $K_q(\varepsilon)$ are generalised entropies calculated from the equation

$$K_q(\varepsilon) = \frac{\ln \sum P_i(\varepsilon)}{1-q}$$

[$P_i(\varepsilon)$ is the probability that a particle gets into an ith cell]; $q = 0, 1, 2, \ldots, n$.

By definition, D_0 ($q = 0$) is a self-similarity dimension, D_1 ($q = 1$) is the information dimension and D_2 ($q = 2$) is the correlation integral index. For homogeneous sets that obey the relation $P_i(\varepsilon) \sim \varepsilon^D$, the Renyi dimensions of different orders coincide. Apparently, the multifractal formalism concept can prove fairly useful in the study of cross-linked polymers and processes (including chemical ones) accompanied by the formation of temporal fractals.

2. Fractal properties of lignin macromolecules

Due to the progress in the development of fractal theory, it became possible to begin the search for new approaches to the investigation of plant biopolymers with intricate structures, first of all, lignin. It has been demonstrated [106, 107] that the fractal theory can be used to characterise lignin and its biosynthetic analogues, *i.e.*, dehydropolymers. Dehydropolymerisation of monomer precursors of lignin *in vitro* is initiated by the peroxidase–hydrogen peroxide enzymic complex. Freudenberg and co-workers developed two methods for laboratory biosynthesis of lignin, namely bulk and end-wise polymerisation (see references cited in Ref. 1). According to Sarkanen,[1] bulk and end-wise dehydropolymers differ from each other in both the chemical and topological structures. Analysis of the conditions of synthesis of various biosynthetic lignins and comparison of them with the growth conditions of fractal clusters made it possible to hypothesise that the bulk and end-wise polymers correspond to definite universal classes of fractal objects.

The end-wise polymerisation is performed by 100-h continuous feeding of a highly dilute solution of the monomer into a large volume of a fairly dilute (10^{-7} mol litre^{-1}) solution of enzymic complex. The monomer diffusion is considered to be the rate-determining step of the polymerisation of monomeric lignin precursor. Under these conditions, the macromolecule grows through successive addition of the monomer phenoxyl radicals to those few macromolecules that have formed at the initial stages of reaction. Comparison of the end-wise protocol with the known theoretical models of fractal growth led Ozol-Kalnin [74] to the conclusion that end-wise polymers belong to the class of Witten–Sander fractal clusters (the DLA P–C model).

In the case of bulk polymerisation, unlike end-wise polymerisation, a rather concentrated solution of the monomer is injected in the reaction area as one portion. Under these conditions, in the opinion of Ozol-Kalnin and co-workers,[74, 90] numerous polymerisation centres appear immediately and the macromolecules grow according to the DLA C–C model.

In order to verify this hypothesis, we synthesised bulk and end-wise dehydropolymers on the basis of a guaiacyl type monomer precursor, namely, ferulic acid ($C_{10}H_{10}O_4$).[108] The fractal dimension of the macromolecule was determined from the data of hydrodynamic measurements in dilute solutions of dehydropolymers in thermodynamically good solvents (DMSO, dioxane). It was found that the hydrodynamic radius of the macromolecule satisfies scaling relation (4). The fractal dimension $d_f = 1/\nu$ (according to translational diffusion data) for the bulk polymer was found to be 2.35 and that for the end-wise polymer was 1.51. The velocity sedimentation coefficients and the intrinsic viscosity also showed a scaling dependence on the molecular mass of the dehydropolymers. This made it possible to calculate the fractal dimension by two more independent methods. The data [108] indicate that bulk lignin corresponds to the DLA P–C model, while end-wise lignin, to the DLA C–C model, as regards their fractal dimensions (see Table 8).

It is noteworthy that the applicability of the DLA C–C model to the description of fractal properties of end-wise lignin gives rise to certain doubts. The fracton and chemical dimensions of clusters in the DLA C–C model are greater than 1, which implies branching, whereas the Mark–Kuhn–Houwink parameters of the end-wise lignin ($a = 0.8$, $b = -0.58$, $c = 0.45$) and the Flory–Mandelkern hydrodynamic invariant ($\Phi^{1/3}P^{-1} = 2.7 \times 10^{-6}$) obtained in the study cited [108] attest to a linear structure. It is more likely that the fractal properties of this polymer correspond to its conformational state in a good solvent.

One achievement of fractal geometry is elucidation of the relationship between the statistical and fractal properties of polymer chains.[76] It was shown [109] that the equilibrium statistics of linear polymers is adequately modelled by SARW paths, which demonstrate the fractal properties. The key factors that determine the analogy between the descriptions of a macromolecule and the path of a randomly walking particle are the chain structure and the excluded volume effect.

The conformational characteristics of a linear macromolecule depend on only two parameters, the number of units in the chain (N) and the size of the monomer unit (a_0). Thus, according to the Flory theory, the size of the macromolecule (R) is described by the following scaling relation

$$R \sim a_0 N^{\nu_F},$$

where ν_F is the critical index in the Flory theory, which depends on the dimension of the Euclidean space D:[110] $\nu_F = 3/(d+2)$ for $D < 4$ and $\nu_F = 1/2$ for $D > 4$.

According to the SARW model, the average squared distance between the start and the end of the path whose length is N steps obeys the equation

$$\langle R^2(N) \rangle > \sim AN^{2\nu_c},$$

where A is a coefficient depending on the lattice dimension and the length of the walk path; ν_c is the critical index in the SARW model.

Mimicking of the Brownian (random) walk on lattices with different dimensions gave [109] the following values for the critical index ν_c: $\nu_c = 0.749$ for $D = 2$; $\nu_c = 0.592$ for $D = 3$; $\nu_c = 0.5$ for $D > 4$.

It can be easily seen that the critical indices ν_F (in the Flory theory) and ν_c (in the SARW model) virtually coincide. This suggests [76] that the asymptotics of the path of the self-avoiding random walk and the polymeric chain in a thermodynamically good solvent belong to one class of universality, the path itself being a fractal whose self-similar dimension d_f can be determined from the relation

$$\nu_F = \nu_c = \frac{1}{d_f}. \tag{5}$$

Thus, the problem of belonging of the macromolecule of end-wise lignin to fractal objects can be solved unambiguously and refers to metrics, *i.e.*, the mode of arrangement of monomer units in space, rather than to topology ($d_t = 1$). Relations (4) and (5) imply the possibility of determining the fractal dimensions of polymers on the basis of experimentally measurable parameters that characterise, in one way or another, the relationship between the degree of polymerisation N or the molecular mass M and the size of the macromolecule. According to Frenkel' and co-workers,[82]

$$\nu_F = \frac{1+a}{3}.$$

In this case, if the equivalence principle is obeyed in the translational and rotation friction processes, the known equalities (1)–(3) hold between the hydrodynamic scaling indices. Therefore, the fractal dimension d_f of a macromolecule in solution can be estimated by usual molecular hydrodynamics methods.

Analysis of the published data on the hydrodynamic properties of various lignins (Table 9) and comparison of these data with fractal models led to the hypothesis that the supramolecular structure of lignins *in situ* is an infinite network composed of fractal clusters linked to one another.[111] When lignins are isolated

Table 9. Fractal dimensions of some lignins.[90]

Lignin specimen	Solvent	$d_f = 3/(a+1)$	$d_f = 1/\|b\|$
Hydrotropic lignin	dioxane	2.68	–
Dioxane lignin	pyridine	2.61	2.78
Bjorkman lignin	–	–	2.70
Sulfate lignin	–	–	2.56
Alkaline lignin	0.1 M buffer	2.27	–
Lignosulfonate	methanol	1.95	–
	2 M NaCl	2.27	3.0
	0.02 M NaCl	–	1.79

from the plant tissue, the inhomogeneous fractal network is destroyed and its fragments pass to the solution as fractal clusters. Relying on the hydrodynamic characteristics of dioxane lignins in solutions determined by Pla and Yan,[112] Ozol-Kalnin and co-workers [111] concluded that lignin can be assigned to fractals of the DLA P–C type. The fractal dimension calculated from the scaling relation

$$g = CM_w^{3/d-3/2},$$

was equal to 2.439 ± 0.007, which is consistent, in the first approximation, with the dimension of Witten–Sander fractal clusters. However, for other lignin specimens (see Table 9), quite a substantial scatter in the fractal dimensions is observed, which evidently depends on the pre-history and the molecular-mass distribution of the samples under study and on the chosen solvent.

The rather low fractal dimensions of lignosulfonates refer, in the opinion of Ozol-Kalnin *et al.*,[106] to the lignin structure modified upon the chemical reactions that take place during wood cooking rather than to the initial structure of natural lignin. It has also been assumed not without reason [90, 106] that lignins of various classes of universality can be localised in different structural elements of the cell wall, in particular, the possibility of formation of 'dense' Eden type structures with $d_f = d_l = d$ during lignin biosynthesis has not been considered improbable. Thus, the researchers were unable to draw unambiguous conclusions concerning the concordance of the structure of these lignins to particular classes of fractals.

In our opinion, the most reliable data on the fractal properties of lignosulfonates are presented in two publications [113, 114] dealing with lignin obtained by sulfite pulping of softwood. The molecular mass of these specimens was determined by the non-established equilibrium technique and by laser correlation spectroscopy. The fractal dimensions determined by three independent methods were, on average, 2.44 ± 0.18.[115]

The scaling and fractal properties of the macromolecules of MWL isolated from the pine-tree xylem have been studied.[116] The investigation of the macromolecular properties of a number of fractions of this lignin in dilute DMSO solutions confirmed that the main criteria of fractality, namely, the scale invariance principle [in the range of molecular masses $(0.5-64) \times 10^3$] and a fractional dimension, are met. The fractal structure of the macromolecule is manifested in the pattern of mass distribution in space being given by relation (4); this allows one to find the fractal dimension d_f from the plot $\log R_H - \log M$ constructed for each lignin fraction using experimental data (Fig. 6). In the case of MWL, the d_f value proved to be 2.32. The fractal dimensions of MWL specimens calculated from the velocity sedimentation coefficients and intrinsic viscosity were 2.32 and 2.40; thus, they can be classified as fractal objects of the DLA P–C type.

A similar conclusion has been drawn in a study of hydrodynamic and scaling properties of another MWL specimen isolated from pine wood (see Table 4). In this case, the polymer was separated into 9 fractions in the range of molecular masses of $(1.7-14.6) \times 10^3$, for which the scaling principle was found to hold. The results of studies of the molecular hydrodynamics by

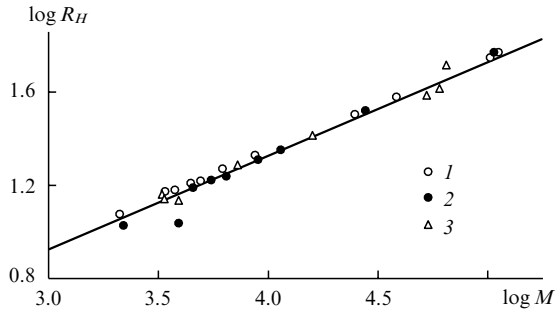


Figure 6. $\log R_H$ *vs.* $\log M$ for pine wood lignin specimens.[116] Specimen: (*1*) MWL in DMSO, (*2*) DL in DMSO, (*3*) DL in dioxane.

different methods proved to be almost identical; the fractal dimension was 2.32 ± 0.02.

The macromolecules of the Pepper lignin (DL-1–DL-4) (Table 10) are also typical fractal objects with a fractional dimension in any of the studied solvents including dioxane, DMF and DMSO. The self-similar properties are obeyed in the range of molecular masses $(3.0-100) \times 10^3$ (Fig. 7).

Thus, the fractal dimensions of slightly decomposed lignins isolated from softwood are mainly in the range of 2.3–2.8, the isolation procedure having little influence on the fractal properties of the specimens. The data reported in the literature indicate that macromolecules of softwood lignins refer to the versatile class of DLA P–C type fractals.

The numerical values of the fractal dimension d_f characterise the growth of the fractal cluster, in this case, the dehydropolymerisation of monolignols. It is of prime interest to study the effects of different factors (for example, the degree of branching, intramolecular cyclisation) on the microstructure of the cluster and to elucidate the relationships between these factors and the fractal dimension, which is known to be a global property of the cluster.

Table 10. Fractal dimension (d_f) of lignin specimens isolated from various types of plants (according to sedimentation and diffusion analysis and viscosimetry).[55, 60, 61, 108, 116, 117]

Specimen	Plant	Solvent	d_f determined by		
			viscosimetry	sedimentation analysis	diffusion analysis
DL-1	pine wood (*Pinus silvestris*)	dioxane	2.54	–	2.56
DL-2	"	dioxane	2.36	–	2.32
MWL	"	DMSO	2.40	2.32	2.32
DL-3	"	DMSO	2.54	–	2.50
DL-4	"	dioxane	2.42	2.86	2.86
LS	spruce (*Picea sp.*)	buffer solution	2.46	–	2.27
MWL	birch (*Betula verrucosa*)	DMF	1.86	1.89	1.89
DL	"	DMF	1.91	2.2	1.75
MWL	aspen (*Populus tremula*)	DMF	1.85	1.82	1.82
DL	"	DMF	2.0	–	1.89
DL	parsnip (*Heracleum sosnovsk.*)	DMF	1.66	2.3	1.64
DL	mountain ash (*Sorbus aucuparia*)	DMF	1.8	1.92	1.85

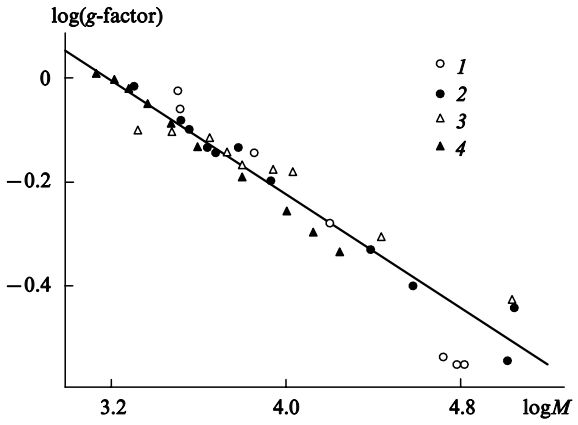


Figure 7. Branching *g*-factors *vs*. molecular mass of lignin.[116]
Specimen: (*1*) MWL, (*2*) DL-1, (*3*) DL-2, (*4*) DL-3 (the digits mean the numbers of fractions).

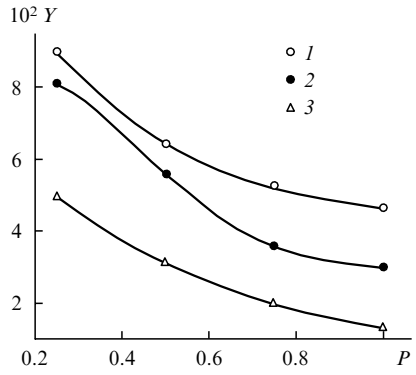


Figure 8. Degree of cyclisation (Y) *vs*. probability of the addition (P) of a particle to the growing cluster for different free paths L.[117]
Free path L: (*1*) 1000, (*2*) 100, (*3*) 5.

It has been proposed[55] to simulate various versions of dehydropolymerisation using a modified model† of the growth of fractal aggregates of the DLA P–C type.

Unlike the classical Witten–Sander model of diffusion-limited aggregation, this model has been supplemented by the parameter P describing the probability of addition of a monomer unit to the growing aggregate upon collision. The probability of addition simulates the chemical reactivity and indicates which process (diffusion or chemical reaction) predominates in the irreversible formation of bonds. The free path of particles in the walk on a lattice, the probability P and the space geometry were shown to influence the formation of the microstructure of the fractal macromolecules constructed in terms of this model.

It has been proposed[111] that, depending on the conditions, one can observe the formation of either a 'fractal forest' or a separate 'tree with bushes', which corresponds to the growth of a branched lignin macromolecule in a cell wall in the narrow space between the cellulose fibrils. Since the growth of branches is restricted by the walls, the resulting cluster will possess a much lower effective branching than that produced in the case of unrestricted growth in all directions. The hydrodynamic behaviour of such a macromolecule, especially if it contains a rather large number of rings, will differ substantially from the behaviour of fractal macromolecules of the Witten–Sander type. The possibility of formation of 'bushes' within the bounds of the fractal growth procedure implies that the presence of the so-called sol fraction in natural lignin (Brauns lignin) cannot serve as evidence supporting the assumption of the network structure of lignin.

An important topological feature of network and branched polymers is the presence of intramolecular rings. It was found that chaotically branched fractal clusters formed in terms of the modified diffusion-limited aggregation model also contain cyclic structures. According to the publication,[117] the procedure of counting intramolecular rings is reduced to counting the number of particles n that close the rings during the growth of the fractal cluster. Figure 8 shows the dependence of the degree of intramolecular cyclisation Y on the probability of addition of a particle to the growing aggregate for several free paths L. The Y value is defined as the ratio of the number of particles n closing the rings to the total number of particles N in this cluster. It should be borne in mind that the Y value defined in this way gives, most likely, a somewhat underestimated degree of cyclisation, because the addition of one particle to the cluster can give rise to two or more (for a lattice with an arbitrary dimension) rings. The number of intramolecular rings depends on various factors including the addition probability P, the free path of particles L and the lattice dimension. The smallest number of rings is found in the clusters formed at $L = 1$ and $P = 1$, *i.e.*, within the framework of the classical DLA P–C model.

It should be noted that accumulation of cyclic structures during the growth of the fractal aggregate obeys the Hurst statistics with an R/S index equal to 0.8 (Fig. 9). This means that simulation of the polymer structure by the diffusion-restricted aggregation technique can give information not only on the structure but also on the dynamics of fractal processes. This aspect is discussed in Section III.3.

In a study of structural features of the fractal cluster,[118] the mechanism of surface diffusion of monomer particles was taken into account. It was shown that the combination of Brownian and surface diffusions with variation of the free walk length allows one to model the growth of aggregates of various universal classes. The fractal properties of the clusters were studied by analysing the generating function (measure) of the cluster‡ within the multifractal approach.

Study of the physicochemical properties of guaiacyl-syringyl lignins has shown[60,61] that the macromolecules of hardwood

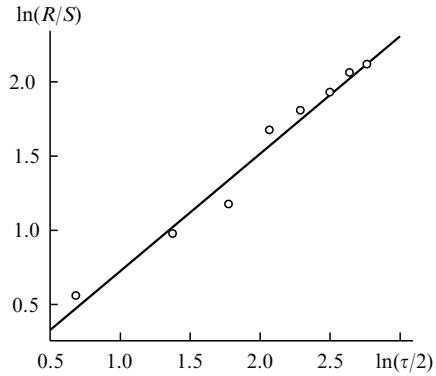


Figure 9. Accumulation of intramolecular cyclic structures during the growth of the Witten–Sander type fractal cluster[62] according to the Hurst equation: $R/S = (A\tau)^H$ (R is the range of the accumulated deviation from the average value, S is the standard deviation equal to the square root of the variance, τ is the time span, A is constant, in this particular case, $A = 1/2$).

† Some other models of this type were also proposed earlier,[78] since the basic Witten–Sander concept is characterised by exceptional versatility and is applicable to investigation of diverse physical phenomena and processes.

‡ Generating functions are used in the probability theory to simulate random processes.

lignins, like those of softwood lignins, are structures with a fractional dimension. The d_f values for the macromolecules of hardwood lignins found by different methods are presented in Table 10.

The dimension of the macromolecule d_f is often determined from the slope of the straight line $\log M = f(\log R_\eta)$, where R_η is the hydrodynamic radius calculated from the equation

$$[\eta] = \frac{10\pi N_a R_\eta^3}{3M},$$

(N_a is the Avogadro number).

On average, the fractal dimensions of hardwood lignins ($d_f = 1.84-1.98$) are much lower than those for softwood lignins ($d_f = 2.3-2.8$). Whereas the fractal dimensions of softwood lignins [116] are consistent with the d_f values for the three-dimensional fractal clusters formed in the Witten–Sander model, the d_f values of hardwood lignins are close to the fractal dimensions of the clusters formed in terms of the SARW models.

Lignins of herbaceous plants have been least studied. Table 11 contains the fractal dimensions of lignins for a monocotyledonous plant family of Gramineae determined from the results of investigation of the hydrodynamic properties of these lignins in dilute solutions in DMF (good solvent).[61] The d_f values of dioxane lignins isolated from the herb stalks occur in the range from 1.5 to 1.8. Judging by these data, the macromolecules of herbaceous and hardwood lignins should be attributed to different universal classes (according to the chemotaxonomic classification generally accepted in lignin chemistry, these lignins belong to the same type of guaiacyl-syringyl lignins).

Table 11. Fractal dimension (d_f) of the macromolecules of dioxane lignins of herbaceous plants of the Gramineae family according to sedimentation and diffusion analyses and viscosimetry (DMF as the solvent).[61]

Plant	d_f determined by		
	viscosimetry	sedimentation analysis	diffusion analysis
Rye (*Secale sp.*)	1.80	1.72	1.50
Oats (*Avena sativa*)	1.72	1.69	1.69
Barley (*Hordeum sp.*)	1.77	1.64	1.69
Wheat (*Triticum sp.*)	1.73	1.64	1.68

It follows from analysis of the macromolecular properties of birch and aspen lignins that the macromolecules are star-like. The simulation of growth of polydisperse polymer stars with linear branches within the framework of the SARW model has shown [62] that one-centre star-like tri- and tetrafunctional macromolecules form impermeable Gaussian coils with Mark–Kuhn–Houwink parameters (a, b, c) close to 0.5 and a fractal dimension of ~ 2 (2.02–2.04). It is noteworthy that these values do not coincide with the values obtained in terms of the SARW model for linear chains ($a = 0.78$, $d_f = 1.67$). Although the results of the theoretical simulation of star polymers remain debatable, they are still consistent with the known statement [63, 64] that the Mark–Kuhn–Houwink parameter a (and, hence, d_f) for these polymers does not depend on the quality of the solvent. Since the d_f values of the hardwood lignins studied differ insignificantly from the value 2.0, which was found for the clusters formed according to the model of 'lattice animals', ultimate determination of the fractal structure of the macromolecules of guaiacyl-syringyl lignins requires further investigations.

Further progress in solving the problem of the fractal structure of lignin is apparently related to estimation of the fracton dimension d_s, which describes the connectivity, *i.e.*, characterises directly the topological structure of the macromolecule.[71, 72] Determination of the fracton dimension is based on the study of the spectra of natural vibrations of fractals. The notion of fractons, *i.e.*, localised vibrational states in fractal materials, was introduced in the study of wave phenomena in fractal materials.[95] The function describing the density of frequency distribution of fractons is a power function,[72] because the scaling principle is obeyed for fractal objects. The mathematical power is determined by the fracton (spectral) dimension, which functions as a space dimension in the low-frequency asymptote of the density of vibrational states.

Using the fracton theory, one can determine the vibrational spectrum of a fractal object and estimate its fracton dimension. The properties of fractons can be studied only in the region of fractal behaviour of real materials. For polymers, the characteristic sizes do not exceed the optical wavelength in the visible spectrum. Therefore, Raman light scattering and inelastic neutron scattering are the key spectral methods used to study fractons. However, these methods have not yet found wide application in the study of polymers. At present, the fracton dimensions have been determined only for proteins,[71] poly(methyl methacrylate) [119] and epoxy polymers.[120] It should be noted that both theoretical and experimental methods for determination of the fracton dimension are at an early stage of development.[104, 121] Probably, this accounts for the inconsistency of obtained results.[71] As regards lignins, their fracton spectra have not yet been studied; however, in view of the complexity of the topological structure of lignins, the necessity of such studies is beyond doubt.

3. Fractal properties of lignin biosynthesis

To continue the discussion of the fractal properties of lignins, one should note that the results of investigations outlined above are based on representing lignins as fractal objects arising in some aggregation processes. However, the concept of fractals has been markedly extended in recent years. Fractal structures of not only objects but also processes have been considered.[122, 123] It was found that many chemical systems can be represented as complex dynamic systems of a finite dimension with a chaotic behaviour.[124–126] The mathematical image of the dynamic (deterministic) chaos is represented by the so-called strange attractor, which is characterised by the fractal structure of its paths in the phase space.[127–130]

In chemistry, the Belousov–Zhabotinskii system is the best known example of a complex system involving any conceivable type of complex dynamic behaviour.[68, 131] Studies of the Belousov–Zhabotinskii reaction revealed diverse chaos and self-organisation phenomena giving rise to periodic space–time structures.

Dynamic self-organisation phenomena have been discovered in the enzymic dehydrogenation polymerisation of monolignols during lignin biosynthesis *in vitro*.[132, 133] Conduction of monolignol dehydropolymerisation under one-dimensional diffusion conditions has been shown [134] to result in space–time dissipative structures.

Chaotic and periodic oscillations of chemiluminescence intensity have been detected [135, 136] in a study of lignin oxidation processes in alkaline media.

Karmanov *et al.*[65] reported the first attempt to study the dynamics of dehydropolymerisation of monomeric lignin precursors in relation to ferulic acid; they demonstrated the possibility of existence of the dynamic mode of the 'strange attractor' type. The process was monitored by the redox method in the 'two-dimensional' variant of the lignin biosynthesis *in vitro*. The redox potentials were determined from the ratio of oxidised and reduced forms of the substrate and the initiator of the polymerisation. This method for determination of redox potentials has been used previously in the study of chemical transformations of the reduced nicotinamide adenine dinucleotide (NADH), ascorbic acid and other compounds.[137] It should be noted that the redox method does not possess sensitivity with respect to any of the compounds

involved in the reaction. Nevertheless, it yields a function of state of the reaction system, which is directly related to the reactant concentrations. The dynamics of the system which undergoes dehydrogenation and thus evolves with time is obtained as a time series of redox potentials, which constitutes a database suitable for analysis and identification of the dynamic behaviour of the system by means of non-linear dynamics methods.

Thus, by obtaining a chronologically ordered series of redox potentials, one can elucidate characteristic features of the process dynamics, identify the presence or absence of nontrivial phenomena (symmetry violation effect, correlations at the macroscopic scales, *etc.*), which can be indicative of the occurrence of dynamic self-organisation processes.

The formation of chaotic modes of dehydropolymerisation has been observed in a study of the dynamics of the coniferyl alcohol – hydrogen peroxide – horse-radish peroxidase system.[66] The dynamic modes implemented during lignin biosynthesis *in vitro* were identified using the strategy of time series analysis based on the deterministic chaos concept.[68–69] This concept is underlain by methods of non-linear dynamics of non-equilibrium systems and the theory of fractal ensembles.[68, 75] It was found that chaotic oscillations can differ in their properties; this leads unambiguously to differences in the structure and properties of the corresponding attractors.[122]

The dynamics of polymerisation of monomer precursors of lignin was studied in several stages. The first stage was the construction of a geometrical image (attractor) of the process in multidimensional phase spaces; this was followed by analysis of multidimensional pseudo-phase paths with identification of the boundaries of the scaling region and the scaling indices (dimensions) and analysis by the attractor topology with estimation of its correlation dimension; subsequently, the dimension of the space of embedding was determined. The research showed [66, 67] that the time dependences of redox potentials during polymerisation of guaiacyl monolignols obey all the main criteria of deterministic chaos, namely, the 'continuous spectrum' criterion and scaling and fractional dimension of the phase paths.

The 'continuous spectrum' criterion (the fast Fourier transform spectrum, FFT) discerns chaotic and periodic spectra, as the former are responsible for a continuous FFT spectrum, while the latter, for a discrete spectrum.

The criterion of a fractional dimension of the phase paths allows one to distinguish between deterministic chaos and structureless chaos. The dimension of the phase path for a process accompanied by dynamic self-organisation is known [138] to be strictly smaller than two (for a two-dimensional case) or strictly smaller than three (for a three-dimensional space). This is due to restriction of the phase space. It can be stated with confidence that polymerisation of monolignols shows an ordered (structured) dynamic behaviour. Structureless chaos is characterised by a distribution of the 'everywhere dense' type; therefore, the phase path dimension coincides with the space of embedding dimension.

The next stage of investigation of the polymerisation of coniferyl alcohol included quantitative evaluation of the phase paths of the process; usually, they are constructed using the Packard time delay method.[139] Figure 10 shows the two-dimensional pseudo-phase portrait of the dynamics of enzymic polymerisation of coniferyl alcohol in the horse-radish peroxidase – hydrogen peroxide system constructed using this method.

The features of the distribution of points in the phase paths in space (point sets, as the path is a set of N points) were estimated and the path convergence to some attractor $C(r)$ was established using the Heaviside integral correlation function [140]

$$C(r) = \frac{1}{N^2} \sum_{i,j=1}^{N} \Theta(r - |x_i - x_j|), \qquad (6)$$

where N is the number of points in the path; $\Theta(r)$ is the Heaviside function; r is the specified distance across which the points are counted; x_i is a point in the phase path with the coordinates $[h(x), h(x+\Delta x), h(x+2\Delta x), \ldots, h(x+(D-1)\Delta x)]$; $|x_i - x_j|$ is the distance from an ith point to a jth point. The function $\Theta(r) = 1$ if $r > 0$ and $\Theta(r) = 0$ if $r \leqslant 0$.

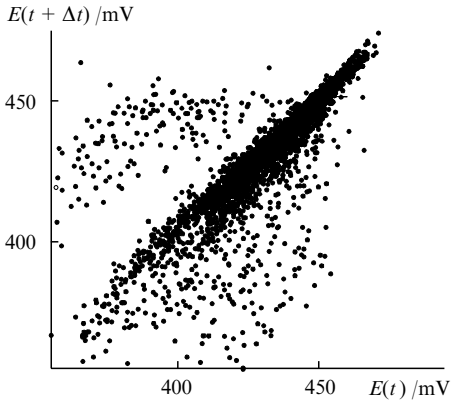


Figure 10. Pseudo-phase portrait of the dynamics of the enzymic polymerisation of coniferyl alcohol in the horse-radish peroxidase – hydrogen peroxide system.
$E(t)$ and $E(t + \Delta t)$ are the redox potentials at instants t and $t + \Delta t$, respectively.

It was found that the Heaviside function is an invariant measure for the systems under study, because in this case, the scaling principle is obeyed. The correlation dimension of the attractor d was determined from the equation $\log C(r) = d \log r$.[141] For polymerisation of coniferyl alcohol, the d index was found to be 1.93 (for another monomeric precursor, ferulic acid, $d = 1.7–1.8$). Since all the criteria of deterministic chaos are fulfilled, it was concluded that the dynamic behaviour of the coniferyl alcohol – hydrogen peroxide – peroxidase and ferulic acid – hydrogen peroxide – peroxidase systems has a certain internal order — a structure with fractal properties. The researchers believe that the last-mentioned circumstance [66, 67] implies that under the chosen conditions, the time evolution of the chemical systems under study is a stable dynamic state called strange attractor.

It is noteworthy that there is a certain relationship between characteristics of the attractor of the dehydrogenation system and the topological structure of the macromolecule of the reaction product (dehydropolymer). It was found that the Mark – Kuhn – Houwink scaling indices calculated from dynamic data are in satisfactory agreement with the results of hydrodynamic measurements.[142] In particular, the parameter a for ferulic acid and coniferyl alcohol is in the range $0.17 < a < 0.38$. These values of scaling indices are normal for the macromolecules of biosynthetic analogues of softwood lignin and correspond to fractal clusters of the Witten – Sander type.

Karmanov and Matveev [143] have studied the dynamic features of lignin biosynthesis using a different approach based on the self-organised criticality theory.[144] A system functioning in the self-organised criticality mode is known to generate so-called flicker-noise vibrations. The main feature of systems with flicker noise is the fact that their power spectrum is described by the dependence [145]

$$A(f) \sim \frac{1}{f^{\nu}},$$

where A is the spectral density of the autocorrelator of the dynamic variable, f is frequency, ν is the mathematical power. The power spectrum ($1/f$ spectrum) is a function that shows how the energy is distributed over frequencies.

It was shown [143] that simulation of polymerisation of coniferyl alcohol is subject to a dependence characteristic of the flicker noise (Fig. 11) with $\nu = 0.8$ (the usual value for a typical flicker noise is $\nu = 0.8–1.3$, see Ref. 146).

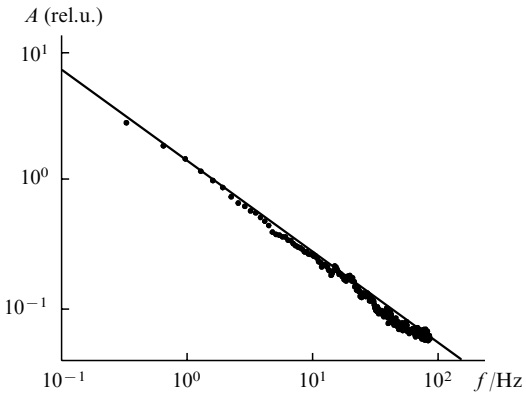


Figure 11. Power spectrum ($1/f$ spectrum) of oscillations of the redox potential during lignin biosynthesis *in vitro* in the coniferyl alcohol–hydrogen peroxide–horse-radish peroxidase system.[143]

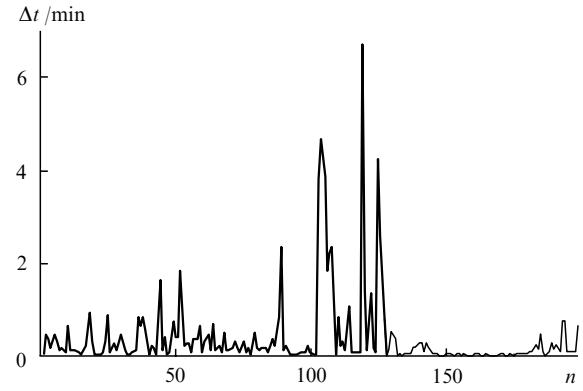


Figure 12. Duration of the laminar phase (Δt) in the dehydropolymerisation of coniferyl alcohol as a function of chronologically ordered fluctuations of redox potentials (n is the ordinal number of the fluctuations).

Yet another feature of the system functioning in the self-organised criticality mode is generation of temporal fractals. Figure 12 shows the dependence of the duration of the laminar phase (Δt is the time delay between fluctuations with numbers $n-1$ and n) of dehydropolymerisation of coniferyl alcohol in the hydrogen peroxide–horse-radish peroxidase system on the function of chronologically ordered fluctuations of redox potentials. Mathematical analysis of this dependence leads to the conclusion that fluctuations of the redox potentials are mutually time-correlated, *i.e.*, in this case, an ordered temporal structure of the fractal type exists. This fact was confirmed by identification of the scale invariance and a fractional dimension of the pseudo-phase portrait of the process dynamics. This proves that the concept of self-organised criticality describes adequately the dynamics of the generation–recombination process of phenoxyl radicals, giving rise to the macromolecules of biosynthetic lignin.

Timashev and co-workers[147] have performed a theoretical investigation of the formation and recombination of radicals. It was shown that the number of free radicals in the steady-state stage of the process fluctuates around some constant value. The Fourier transform spectrum of the temporal series of the number of radicals has a flicker noise characteristic; hence, the process dynamics fits in the self-organised criticality concept. The total dimensions of the attractor of lignin biosynthesis *in vitro* estimated according to the deterministic chaos theory and the self-organised criticality theory are markedly different (Table 12); this means that the dynamics of lignin biosynthesis needs to be further investigated.

The presence of fractal structure in the processes of monolignol polymerisation is confirmed by determination of the H value in the Hurst equation (see the caption to Fig. 9), which is a statistical characteristic of the structure calculated using the equation

$$\frac{R}{S} = \left(\frac{\tau}{2}\right)^{H}.$$

Analysis of the parameters of the Hurst equation (Table 13) confirms that the processes involved in lignin biosynthesis possess a fractal structure.§

Table 12. Characteristics of the chaotic attractor of the lignin biosynthesis *in vitro*.

Dimension of the enveloping space	Correlation dimension d	
	DCT [a]	SOC [b]
2	1.9	1.8
3	2.8	1.9
∞	3.2	2.5

[a] The calculation was carried out using the deterministic chaos theory (DCT).[66]

[b] The calculation was carried out using the self-organised criticality theory (SOC).[143]

§ Systems with deterministic chaos, *i.e.*, those having a fractal ordering, are characterised by $0.5 < H < 1$. For random processes, the Hurst value H is 0.5.

Table 13. Hurst equation parameters for processes related to lignin biosynthesis.

Investigation object	The range of H values	The average H value	Standard deviation	A	Ref.
Lignin biosynthesis *in vitro* [a]	0.67–0.96	0.85	–	0.88	66
Lignin biosynthesis *in vitro* [b]	–	0.87	0.01	–	66
Dynamics of cell membrane lignification	0.63–0.95	0.9	0.2	0.9	142, 148
Dynamics of variation of k_X *vs.* M for fractions of DL and MWL specimens	–	0.79	0.05	−0.08	45
Dynamics of variation of k_X *vs.* M for fractions of dehydropolymer specimens	–	0.82	0.07	0.01	45
Dynamics of accumulation of intramolecular rings in fractal clusters	–	0.85	0.14	−0.08	75
Annual rings of spruce	0.56–0.94	0.79	0.08	–	55
Random processes	–	0.5	0.01	1–1.5	75

[a] Ferulic acid as the monomer. [b] Coniferyl alcohol as the monomer.

IV. Supramolecular structure of lignin

The supramolecular structure of polymers is known to define the mutual arrangement of macrochains and their aggregates. The relevant quantitative characteristics include the size and shape of aggregates and the degree of ordering stipulated by the level of intramolecular interactions. The methods used most often to study the supramolecular structure include X-ray diffraction, electron diffraction and electron microscopy.

Studies dealing with the supramolecular structure of lignins are few. Evidently, the reason is that lignins, which are amorphous polymers, do not usually contain any ordered supramolecular structures such as crystallites, spherulites, *etc*. One more reason is the low efficiency of classical structural methods in the study of amorphous objects.

The wide-angle X-ray scattering provides little information when applied to amorphous polymers. Only in especially favourable cases is it possible to reveal the diffraction effects caused by chemical periodicity of the chain and mutual orientation of the chains. Since lignins are biopolymers with irregular chemical structure, a large set of primary microstructure elements and a rather complex topological structure, the X-ray diffraction pattern obtained for lignins (irrespective of the pre-history of specimens) is expected to represent an amorphous halo. Indeed, this was the case in an X-ray diffraction study of milled spruce wood lignin.[149] Therefore, the results obtained by Pilipchuk *et al*.,[150] who investigated milled wood lignin by electron diffraction, were surprising. These researchers used 2% solutions of lignin in dioxane and acetone and monitored the changes that took place in solutions and films during evaporation of the solvent. After evaporation of dioxane from the solution for 20 h, specific patterns typical of polycrystalline samples were observed on the lignin film thus formed. Further research confirmed the presence of ordering in the structure of films obtained from the dioxane solution; they gave rise to electron diffraction patterns typical of crystalline substances with a long-range order. The pictures of these films obtained by means of an electron microscope showed the presence of symmetrical aggregates consisting mainly of spherical particles of virtually identical sizes. Presumably, during the formation of dioxane films under the experimental conditions, dynamic self-organisation processes take place to give ordered dissipative structures. However, new research is needed to confirm these results. Unlike films obtained from the dioxane solution, the films formed from the acetone solution were fully amorphous.

Most often, the supramolecular structure of lignin is studied using various modifications of electron microscopy. The purpose of a series of studies was to identify individual macromolecules in the photomicrographs obtained by transmission electron microscopy. According to Fengel *et al*.,[2] lignin of milled spruce wood and ethanol lignin form spherical particles (globules 10 to 100 nm in diameter), the particle shape being independent of the sample preparation procedure. It cannot be ruled out that the smallest of the visible particles are single macromolecules; however, they might also be aggregates, as globules tend to form associates.

Study of lignosulfonates revealed the presence of globular structures 20 to 50 nm in diameter and larger aggregates of an irregular shape. Unlike lignosulfonates, sulfate lignin of pine wood forms substantially smaller particles.[2] However, in another study,[151] the formation of much larger globular particles of sulfate lignin, with a size of 40 – 100 nm, has been detected. Taking into account that the molecular mass of this lignin did not exceed 1×10^4, one can suggest that these particles are aggregates composed of several macromolecules. In the presence of electrolytes, sulfate lignin coagulates to give coarse aggregates of an irregular shape. It is clear that to observe separate macromolecules by electron microscopy, new, more rigorous methods for sample preparation need to be worked out. In this connection, noteworthy is the study by Lebedev,[152] who proposed to solve this problem using vacuum atomisation of highly dilute solutions of polymers in mixtures of a solvent and a precipitating agent.

Another group of studies is concerned with the supramolecular organisation of lignins by scanning electron microscopy (SEM). Andersons *et al*.,[153] who studied the spruce MWL, found spherical domains with a size ranging from 0.5 to several micrometers after evaporation of DMSO. It should be noted that the morphology of lignin films depends on a whole series of factors, in particular, the presence of carbohydrates and the nature of the solvent and the support. If the film is prepared by dispersing a dioxane solution of lignin in an aqueous solution of hemicelluloses, no spherical domains are detected after solvent evaporation and removal of hemicelluloses from the film. In a study of biosynthetic lignin [154] obtained by the end-wise method on the basis of ferulic acid ($M_w = 3 \times 10^4$), spherical particles with a size of 3 – 5 μm were detected. Study of the dynamics of formation of the supramolecular particles during polymerisation of coniferyl alcohol, ferulic acid, eugenol and isoeugenol has shown [155] that the growth of macromolecules of the dehydropolymer proceeds through the formation of intermediate supramolecular particles with a size of 0.2 to 1.45 μm. In the presence of hemicelluloses, the size of these particles does not exceed 0.3 μm.

The structure of lignins in a scale range of 0.1 – 10 μm is mainly determined by exogenous factors including temperature and the thermodynamic quality of the solvent used to form the film. It has been found [156] that evaporation of a good solvent gives rise to two types of globular structures in the films of dioxane lignin from pine wood. The diameter of particles of one type does not exceed 1 μm, while that for the other particle type, ~5 μm. When a poor solvent is evaporated, the loose arrangement of particles, typical of the former case, is replaced by a rather dense packing of the polymer with a structure indiscernible by the SEM method. Mechanical drawing of the specimen plasticised by a good solvent induces the formation of pseudo-fibrils, which are aggregates stretched along the drawing direction of the globule. The formation of oblong aggregates from primary globules of the polymer (polyether acrylate) and their adjustment to one another have also been described in other studies.[157, 158]

The supramolecular structure of two types of dehydropolymers based on coniferyl alcohol synthesised by enzymic and photochemical methods has been studied.[159 – 161] The polymer prepared by the traditional method using peroxidase is composed, as shown by raster-tunnel microscopy, of virtually perfect globular microparticles with a rather narrow size distribution with a maximum at about 500 nm. The globular supramolecular structures tend to form regular macrostructures shaped like triangles, hexagons or helices. Apparently, the geometry of the macrostructures is determined by the nature of the substrate. The most perfect structures were formed on the graphite surface. The photochemical procedure also yields globular supramolecular microparticles. However, in this case, no ordered aggregates are formed (irrespective of the substrate type).

A number of publications [162 – 164] are devoted to the supramolecular structure of natural lignin, *i.e*., lignin of the cell walls of the tree xylem. The most weighty results concerning the structural organisation of natural lignin were obtained using transmission electron microscopy combined with the lignin skeleton method. It was found [162] that lignin of the secondary cell wall has a loose network-like structure formed by globular particles bunched into aggregates of different shapes and sizes. In the central layer, the average size of the supramolecular aggregates is equal to 38 nm. In the outer layers of the secondary cell walls, lignin is present as oblong particles ~45 nm wide arranged at right angles to the cell axis. In the primary shell of the pine wood tracheids, lignin occurs as a dense finely grained material,[163] whereas lignin of the central layer consists of oblong particles oriented along the cellulose microfibrils. The results of investigations suggest the formation of lignin with an ordered structure in cell walls, which is related to the formation of various supramolecular structures during lignin biosynthesis, including fibril-like particles, lamellae and globular structures.

Bogomolov and co-workers [164] studied supramolecular structures formed in the pine wood lignin skeletons before and after partial delignification. The research revealed the presence of (i) structureless lignin in all morphological elements of the cell wall and blind pits; (ii) lamellar lignin in the primary shell, blind pits and the inner layers that line the tracheid cavity; (iii) oblong particles of the type of bars in the secondary shell. The researchers noted different behaviours of these supramolecular structures during alkaline delignification. Conversely, according to other researchers,[2, 165] lignin in the wood is totally amorphous and nonstructured, the shape of lignin particles being determined by the shape of spaces between cellulose microfibrils that are filled during lignification of plant cells.

The inconsistency of the results may be due to specific features of the methods used to obtain lignin skeletons. As a rule, this is done by hydrolysis of wood by various acids (sulfuric, hydrochloric or hydrofluoric), the duration of acid treatment needed to dissolve cellulose and hemicelluloses reaching 3–4 months. During the treatment, the acid concentration is gradually increased and, at the final stages, it is brought to 70%–80%. In the opinion of some researchers,[2, 7, 12] high acid concentrations can be responsible for modification of the native structure of lignin.

A promising method for the preparation of lignin specimens is periodate oxidation [166] based on the ability of periodic acid to selectively oxidise and dissolve the polysaccharide components of cell walls. The periodate method for the preparation of lignin skeletons is favourably distinguished from other procedures by mild treatment conditions [neutral pH, low concentration of the reactant (0.08 M), relatively short period (7 days)], which minimise undesirable changes in the structural organisation of the initial lignin.

This method has been successfully used to confirm [55] the globular morphology of lignin in the central layer of the secondary cell wall of the pine wood tracheid. Meanwhile, the outer layers of the cell membrane were found to contain substantial amounts of oblong and fibril-like supramolecular structures. It was found that globular lignin of the central layer, unlike other lignin forms, is readily soluble in acetic acid after cryochemical treatment of the plant material; however, the reasons for the different behaviours of these lignins remain obscure: this may be due either to structural inhomogeneity or to unequal accessibilities of layers in the cell membrane.

Many researchers have mentioned the clearly disordered pattern of the supramolecular organisation and distribution of lignin in all layers of the cell wall including the intercellular layer — the median plate. This circumstance implies the need for extending the range of physicochemical techniques used to study lignin. A study by Raman spectroscopy has shown [167] that the arrangement of the chains of lignin macromolecules in the cell membranes of spruce wood obeys a certain order. The anisotropy of the paramagnetic properties of the natural lignin of spruce wood pointing to predominant orientation of lignin macrochains along the plant cell axis has been detected by EPR spectroscopy.[168] A γ-photon scattering study of the structural organisation of the plant tissue [169] has shown the presence of fractal order in the packing of polymer chains of both cellulose and lignin.

Solution-free diagnostics of the topological structure of polymers based on thermomechanical analysis is a new method in the study of the supramolecular structure of polymers.[170, 171] The data obtained for hydrolytic lignins led Ol'khov *et al.*[172] to the conclusion that lignins contain partly amorphous and partly crystalline supramolecular structures in which the amorphous blocks have a pseudo-network structure with branching points of a physical nature, these roles being played by crystallites. The degree of crystallinity was found to be dictated by the pre-history of lignin specimens.

Yet another procedure proposed [173] for investigating the supramolecular structure of lignin is a combination of electron microscopy and densitometric analysis of photomicrographs of the lignin skeletons of pine wood tracheids. The mathematical processing of densitograms has revealed a certain order in the lignin distribution along the radial direction of the wood cell, which had a self-similarity fractal dimension equal to 1.5.[55] More recent studies [133] indicate that this value is somewhat underestimated. A further development of this method [142, 148] has been the use of non-linear dynamics, fractal geometry and synergetics methods for the analysis of the images obtained by electron microscopy. The following procedure was proposed for the analysis of the electron-microscopy images of lignin polymers. First, so-called spatial series characterising the concentrations of lignin in the radial and tangential directions of a plant cell were constructed and then pseudo-phase portraits were obtained by the Packard method. Second, the integral correlation functions were calculated. Third, the dimensions of the pseudo-phase paths in the spaces with different dimensions were found. The realisation of this algorithm allows one to distinguish between chaotic and ordered structural organisations of the polymer and to establish the order parameters if the system proves to be ordered.

The research showed that the correlation function $C(r)$ of the electron-microscopic images of lignin polymers under analysis is an invariant measure and the distribution function of the ensemble of points in the pseudo-phase space, which reflects the mutual positions of the supramolecular microparticles in the secondary cell wall, is a power function, $C(r) \sim r^d$ (d is a fractional number, $2 < d < 3$). In the researchers' opinion, this implies [148] that the supramolecular organisation of the cell membrane lignin should be described as being scale invariant, *i.e.*, natural lignin has an ordered structure on a scale of 0.01–10 μm.

Table 14 presents some order parameters for the supramolecular structure of lignin, namely, fractal (correlation) dimensions d and the Hurst indices H. A similar fractal type ordering has been established for the supramolecular structure of a number of polyamide acids and polyamides,[71, 174] whose fractal dimension varies in the range of 1.70–1.91 depending on the thermal pre-history of the specimens.

Table 14. Order parameters of the lignins of pine and poplar wood cell membranes.[148]

Plant	Specimen	Hurst parameter H	Correlation dimension d for	
			$D = 2$	$D = \infty$
Pine (*Pinus silvestris*)	xylem tracheid	0.88	1.85	5.17
	xylem tracheid after sulfate pulping	0.90	1.90	5.05
Poplar (*Populus nigra*)	fibre of the xylem libroform	0.74	1.75	–

The results of studies of the supramolecular structure of lignin indicate that lignification of cell membranes is accompanied by dynamic self-organisation processes, giving rise to self-organised structure of the fractal type. It should also be noted that quantitative analysis of the photomicrographs of cell membranes revealed a power size distribution function for the number of supramolecular elements, $N(r) \sim r^{-n}$, which is typical of systems with self-organised criticality.

A topical problem of the wood chemistry is quantitative characteristics of the structural changes of cell membrane lignin during the production of cellulose. A study of the structure of pine wood lignin at different stages of delignification has been reported.[142] The order parameters of the supramolecular structure of lignin before and after sulfate pulping remain virtually the same, indicating that the structural organisation of lignin as a

fractal object is retained during delignification. However, the size of the supramolecular particles varies depending on the degree of wood delignification. These data demonstrate that the chemical processes that accompany the sulfate pulping of wood are not related to any non-linear self-organisation processes.

V. Conclusion

Despite the vast experimental material accumulated in lignin chemistry, the problem of structural organisation of this natural biopolymer still remains topical. The topological structures of lignin macromolecules are studied using traditional methods of polymer chemistry, which are based on the study of conformational characteristics of the macromolecules by molecular hydrodynamics, namely, capillary viscosimetry, velocity sedimentation and translational diffusion. However, analysis of the relevant publications shows that the problem of determining the topological structure of natural lignin remains unsolved in terms of traditional approaches.

In recent years, a new system approach to the study of lignin structure has been proposed. This approach creates the theoretical grounds for further research into not only topological but also chemical and supramolecular structures. The strategy is to elucidate the genesis of the deterministic chaos and to establish the quantitative criteria of the order arising at different levels of lignin structural organisation upon self-organisation during lignin biosynthesis. These experimental and theoretical studies are based on modern concepts of synergetics, non-linear dynamics and fractal theory.

The experimental data on the conformational and fractal properties of macromolecules of natural lignins obtained in this way are inconsistent with the existing view of the network structure of lignin. Study of the topological and supramolecular structure of natural lignins of different taxonomic origins, *i.e.*, softwood, hardwood and herbaceous lignins, demonstrated that macromolecules of guaiacyl (softwood) lignins are chaotically branched fractal structures whose parameters correspond to the universal Witten–Sander class of fractals, while macromolecules of guaiacyl-syringyl (hardwood) lignins are star-like structures whose scaling parameters are determined by the linear topology of branches. This provided grounds for a new concept which defines the topological structure of lignins as polyvariant. It was found that the topological structure of lignins depends on the functional groups of monomer precursors, polymerisation conditions and dynamic self-organisation.

The fractal properties of lignin at both the topological and supramolecular levels are due to non-linear self-organisation and are related to a dynamic mode of a strange attractor type. Reconstruction of chaotic attractors in terms of the non-linear dynamics of non-equilibrium systems within the framework of chemical synergetics provided data on the dimension of enzymic polymerisation of the basic monolignols of the guaiacyl type.

New methods for the study of the supramolecular structure of lignin were developed. Quantitative characteristics for the structural changes of the lignin of cell membranes of plant tissues during the production of cellulose were obtained.

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