

THE PHYSICAL CHEMISTRY OF LIGNIN

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INTRODUCTION

Perhaps we may begin with a rather naïve view of the physical nature of lignin. Wood is an intimate mixture of polymeric components which interpenetrate each other to form a three-dimensional structure. It has been shown with a fair degree of certainty that the lignin moiety in wood is comprised of chains of phenylpropane units¹. The chains are probably crosslinked to each other in a number of different ways to give an extensive network². When the lignin is made soluble, fragments of the degraded network enter into solution as macromolecules of various sizes.

From this simplified picture it can be seen that there are two broad aspects to the physical behaviour of lignin. The first is concerned with the molecular properties of soluble lignins. Here, techniques such as viscometry, sedimentation, light-scattering and diffusion yield information on the size and configuration of the macromolecule in solution. The second type of investigation deals with the bulk properties of the solid or solvent-swollen polymer.

In recent years the behaviour of lignin derivatives in solution has been the subject of increasing study. Outstanding in this respect is the pioneering work of Gardon and Mason^{3,4} and McCarthy *et al.*^{5,6} on the lignin sulphonates. In contrast, scant reference can be found in the literature to measurements on isolated lignins of properties such as specific volumes or heats, accessibility, second-order transitions, softening or tack temperatures, viscoelasticity, adhesion and fracture energies. No doubt the dearth is due to the difficulty of isolating from wood a reasonably unchanged lignin in a form suitable for such studies.

The present paper is an outline of some of the work and ideas of my colleagues and myself on the physico-chemical behaviour of isolated lignins. Most of the results and conclusions are for softwood lignins and highlight the need for similar studies on lignins from deciduous trees. Many references to the results of others are included but no attempt has been made to review the entire field.

THE POLYDISPERSITY OF SOLUBLE LIGNINS

It is immediately apparent in reviewing the literature that the molecular weights reported for soluble lignins cover an immense range. McCarthy *et al.*⁶ fractionated lignin sulphonates and found molecular weights as low as 260. In contrast, a weight average molecular weight of 50,000,000 was determined on a high molecular weight fraction of alkali-cooked periodate lignin⁷. Evidently, there can exist in solution, under the name of

lignin, molecules small enough to be well-defined chemical entities and others large enough to be regarded as colloidal particles.

A wide range of molecular size is also found when individual samples of soluble lignins are fractionated. This is illustrated in *Table 1*. Data for several fractionations of various types of soluble softwood lignins are given. Work on the sulphonates predominates but polydispersity is also apparent for organosolv lignins prepared by the dioxan-HCl extraction described by Pepper *et al.*¹⁰. Thus it seems likely that polydispersity may be a prominent feature of soluble softwood lignins regardless of the manner in which they are made soluble. In routine measurements of the molecular weights of soluble lignins, this property produces certain difficulties to be discussed in a later section.

Table 1. Molecular weight polydispersity of softwood lignins

<i>Wood</i>	<i>Method of isolation</i>	<i>Method of fractionation</i>	<i>Range of molecular weight</i>	M_w/M_n	<i>Ref.</i>
Balsam and fir	Sulphonation	Dialysis and ultrafiltration	3,700→58,000	2.2	3
Hemlock and fir	Sulphonation	Elution from column	400→150,000	7.0	6
Hemlock	Sulphonation	Precipitation with non-solvent	440→58,000	6.4	6
Hemlock	Sulphonation	Precipitation with non-solvent	1,400→96,000	3.3	6
Hemlock	Sulphonation	Precipitation with non-solvent	490→70,000	5.8	6
Spruce	Sulphonation	Successive cooking	1,700→24,000	3.3	8
Spruce	Alkali cook of periodate lignin	Precipitation with Ba ²⁺	35,000→17,000,000	5.7	7
Spruce	Dioxan and HCl	Successive extraction	2,900→50,000	2.7	9

It is interesting to remember that marked chemical differences have seldom been reported between fractions of any particular sample of a soluble lignin derivative isolated from the wood of gymnosperms. Changes have been noted in the methoxyl content³, ultra-violet light absorption⁶ and C, H and O analysis¹¹, but in general such variations are relatively small^{7,8,9,12,13}. Thus, soluble softwood lignins may be regarded as complex polymeric macromolecules, built up of the familiar lignin building blocks¹⁴, differing only slightly in detailed chemical structure but showing large differences in molecular size.

Detailed results for the molecular weights of fractions of soluble hardwood lignins, analogous to the data for softwood lignins summarized in *Table 1*, have not been published. Therefore, it is not possible to draw conclusions on the polymolecularity of soluble lignins from deciduous wood. The few determinations available suggest that soluble hardwood lignins have lower molecular weights than softwood lignins. For example, McCarthy *et al.*¹⁵ estimated that the molecular weights of lignin sulphonates from maplewood were between 800 and 2,100. The corresponding range for spruce lignin sulphonate was 2,800 to 14,000.

It is instructive to compare the molecular dispersity of soluble lignins with that of certain other macromolecules derived from biological tissue.

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Many proteins, such as enzymes or seed globulins, are monodisperse or show an extremely narrow distribution of molecular weights¹⁶. On the other hand, linear polysaccharides like cellulose, amylose or certain hemicelluloses are invariably isolated in a polydisperse state. Usually the degree of polydispersity is not great. The ratio of the weight average molecular weight M_w to the number average molecular weight M_n is approximately 2. This is the ratio expected for molecular weight distribution produced by the random degradation of a linear polymer¹⁷. Some values of M_w/M_n derived from recently published data on cellulose nitrate, xylans and amylose are given in *Table 2*.

Table 2. M_w/M_n for several naturally-occurring macromolecules

Macromolecule	Source	$M_w \times 10^{-5}$	M_w/M_n	Ref.
Cellulose nitrate	Birch	27 ^a	1.9 ^b	18
Cellulose nitrate	Ramie	24 ^a	1.7 ^b	19
Amylose	Potato	8.8 ^c	1.9 ^c	20
Xylan	Birch	0.8 ^a	2.3 ^d	21
Xylan	Elm	0.7 ^a	2.4 ^d	21
Amylopectin	Waxy corn	1,700 ^a	116 ^e	22
Hydrolysed amylopectin	Waxy corn	15 ^a	25 ^e	22
Glycogen	Sweet corn	190 ^a	15 ^e	22
Hydrolysed glycogen	Sweet corn	20 ^a	6.3 ^e	22
Glycogen	Rabbit liver	390 ^a	6.6 ^f	23

^a M_w by light scattering.

^b M_n by viscometry from $[\eta] = 0.0091$ D.P.

^c Calculated from fractionation data.

^d M_n by osmometry.

^e M_n from the alkali number.

^f M_{ww} from sedimentation and diffusion used instead of M_n ; usually $M_w > M_{ww} > M_n$.

There exists a third class of soluble macromolecule which is produced either by the synthesis or degradation of a three-dimensional network. Two examples which have been studied extensively in recent years are amylopectin and glycogen. These materials are made in plant and animal tissue by the enzymic coupling of glucose monomers. In this respect, glucose is polyfunctional and contains an aldehydic group and two alcohol groups (4 and 6) capable of bonding to a second glucose unit. In solution, amylopectin and glycogen are characterized by an extremely wide polydispersity. Some examples of M_w/M_n are given in *Table 2*. It is seen that in contrast to the linear polysaccharides, M_w/M_n can exceed 100. Erlander and French²⁴ have evolved a quantitative treatment of the degradation of such branched polymers and have related the polydispersity to the relative reactivities of the functional groups in the glucose monomer.

The wide polydispersity of the soluble softwood lignins suggests that they fall into the same category as the amylopectin or glycogen systems. The M_w/M_n ratios given in *Table 1* all exceed 2 and in one case the ratio is 7.0. These values were computed statistically from the weight percentage and molecular weights of the individual fractions obtained by fractionation of a particular source of lignin. Undoubtedly M_w/M_n would be even higher if weight and number average molecular weights were measured directly on the original unfractionated lignin.

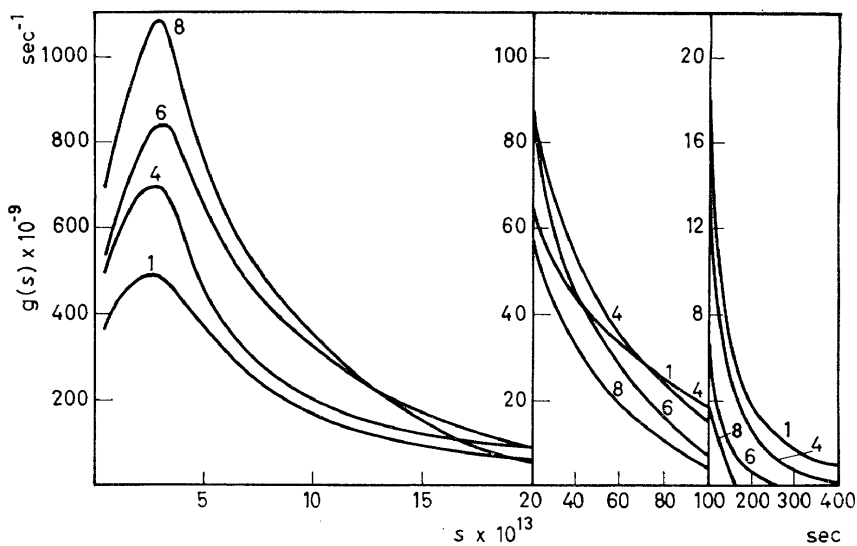


Figure 1. Distribution of sedimentation coefficients for alkali lignin fractions B-1, B-4, B-6 and B-8 described in Reference 25

The excessive polydispersity of soluble lignin is also demonstrated in the ultracentrifuge²⁵. Distribution of sedimentation coefficients, s , for fractions of alkali periodate lignin is shown in Figure 1. Values of s from 0.5×10^{-13} to over 400×10^{-13} sec. were recorded. The low molecular weight material was distributed relatively closely about a sedimentation coefficient of 3×10^{-13} sec. The heavier molecules were present as a long, polydisperse "tail". Fractions of successively lower molecular weight had smaller proportions of the heavy tail. Strikingly similar results have been obtained in degradation studies of glycogen^{23,26,27} and amylopectin²⁷.

THE CONFIGURATION OF SOLUBLE LIGNINS

A characteristic feature of soluble lignin derivatives is the low viscosity which the macromolecule imparts to the solution. In Table 3, the intrinsic viscosity, $[\eta]$ which corresponds to a molecular weight of 50,000 is given for lignin sulphonate and dioxan-HCl lignin from sprucewood. Included for comparison are data for cellulose nitrate, xylan and two synthetic polymers. It is quite evident that the lignins give rather small intrinsic viscosities compared with other polymeric materials. The intrinsic viscosity is a measure of the effective hydrodynamic volume (per unit weight of dry solute) which the macromolecule presents to the shear field in the solvent. For a hard, non-swelling sphere $[\eta]$ in 100 ml/g is given by the Einstein equation

$$[\eta] = 0.025\bar{V} \quad (1)$$

where \bar{V} is the specific volume of the material of the sphere. When the sphere is a macromolecule comprised of a porous, solvent-swollen network, \bar{V} in equation (1) becomes the volume of the swollen macromolecules per

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unit weight of solute. Thus \bar{V} , and therefore $[\eta]$, increases with increased swelling or extension of the macromolecule in the solvent. A low value of $[\eta]$ at a given molecular weight indicates that the molecule is compact and takes up relatively little volume in the solution. The data in *Table 3* show that, for a molecular weight of 50,000, soluble lignins occupy about 1/15 the volume of cellulose nitrate and about 1/3 the volume of poly(α -methylstyrene).

Table 3. Intrinsic viscosities corresponding to a molecular weight of 50,000 for lignins and other macromolecular systems

<i>Macromolecule</i>	<i>Solvent</i>	$[\eta]$ 100 ml/g	<i>Ref.</i>
Dioxan-HCl lignin	Pyridine	0.08	9
Sodium lignin sulphonate	0.1M NaCl	0.10	8
Poly(methyl methacrylate)	Benzene	0.23	28
Poly(-d-methylstyrene)	Toluene	0.24	29
Xylan	Dimethyl sulphoxide	0.5	21
Cellulose nitrate	Ethyl acetate	1.4	30

Polymer configuration is also elucidated by the variation of parameters such as the intrinsic viscosity, diffusion constant or sedimentation coefficient with molecular weight. The exponent, a in the familiar relation:

$$[\eta] = K_{\eta} M^a \quad (2)$$

can vary between 0 and 1 depending on the configuration of the macromolecule¹⁷. In *Table 4* exponents obtained for some soluble lignins are compared with theoretical values for model particles and also with results found for cellulose nitrate and other macromolecules. It is seen that

Table 4. Values of exponents a , b and c for lignins and other macromolecular systems

<i>Macromolecule</i>	<i>Solvent</i>	a	b	c	<i>Ref.</i>
Einstein sphere	—	0*	0.33†	0.67†	—
Dioxan-HCl lignin	Pyridine	0.1	0.4	—	9
Alkali lignin	0.1M buffer	0.32	—	0.52	7
Lignin sulphonate	2M NaCl	0.47	—	—	4
Lignin sulphonate	0.5M NaCl	—	0.56	—	4
Lignin sulphonate	0.02M NaCl	—	0.57	—	5
Lignin sulphonate	0.1M NaCl	0.44	0.48	—	8
Non-freedraining coil	—	0.5-0.8	0.5-0.6	0.4-0.5	17
Poly(α -methylstyrene)	Toluene	0.71	—	—	29
Poly(methyl methacrylate)	Benzene	0.73	0.57	0.43	28
Cellulose nitrate	Ethyl acetate	0.99	0.86	0.17	31
Freedraining coils	—	1	1	0	32

* Equation (1).

† From Stokes' law.

a for soluble lignins lies between the expected value for an Einstein sphere and a non-freedraining random coil. This is in marked contrast to the behaviour of cellulose nitrate where a is 0.99, near the value expected for a completely freedraining coil.

Similar relationships may be established for D , the diffusion constant¹⁷,

$$D = K_D M^{-b} \quad (3)$$

and for s , the sedimentation coefficient¹⁷,

$$s = K_s M^c \quad (4)$$

The values of b and c for the lignins shown in *Table 4* lie between those expected for a non-freedraining random coil and an Einstein sphere.

The variation in hydrodynamic parameters with molecular weight suggests that soluble lignins are not hard, solvent-impermeable spheres. Yet they do not show fully the Gaussian behaviour expected of linear polymers. A suitable model for such a macromolecule would be a compact microgel (33-35) made up of crosslinked material, completely non-freedraining but capable of limited swelling. The compactness of such a macromolecule would produce the low values of $[\eta]$ shown in *Table 3*. Also the wide polydispersity in *Table 1* would be expected whether microgel was formed by random degradation of a network in the wood or by a polymerization reaction during the isolation of the lignin.

A diagrammatic representation of a water-soluble sulphonate microgel is shown in *Figure 2*. The bulk of the molecule is assumed to be made up

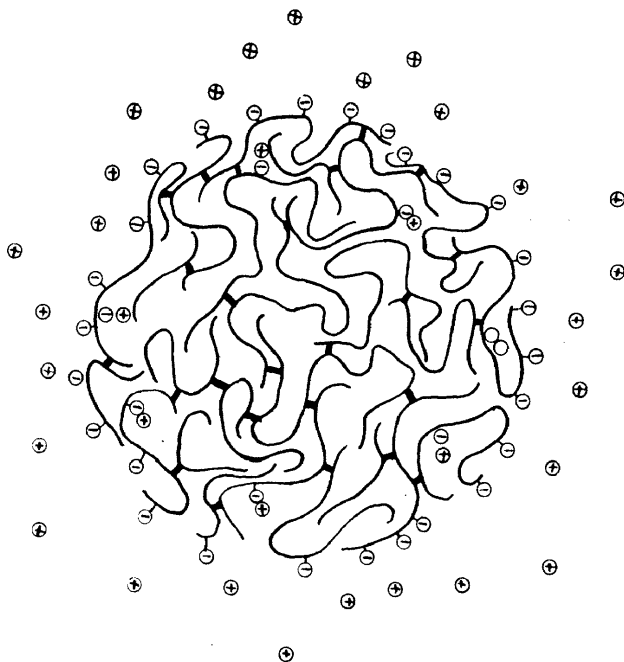


Figure 2. Idealized spherical model of the spruce lignin sulphonate macromolecule

of crosslinked, polyaromatic chains which are randomly coiled. The negatively charged sulphonate groups, near the surface of the particle, maintain its solubility in water. A double layer of counter ions is present in the solvent in the characteristic Boltzmann distribution.

The model shown in *Figure 2* was originally proposed to permit a quantitative theoretical treatment of the polyelectrolyte expansion of certain high molecular weight lignin sulphonates³⁶. The data in *Tables 3* and *4* suggest that all high molecular weight, soluble lignins from softwoods may have a configuration approximated by the microgel model. One would expect differences in the degree of crosslinking, charge and swelling, depending on the method of isolation. Some such variations are indicated by the trends of the data for various lignins in *Tables 3* and *4*. In practice, the microgel particles would not be spheres but irregularly shaped, submicroscopic "hunks" of gell in a wide polydispersity of size. Also, for molecular weights lower than 5,000, it is unlikely that the model shown in *Figure 2* would be applicable. In spite of these reservations it seems probable that the microgel model is appropriate for high molecular weight, softwood lignins in organic or aqueous solvents.

MOLECULAR WEIGHT DETERMINATIONS

A common requirement in the routine characterization of polymers is a simple and reliable method of measuring the molecular weight. In this respect the soluble lignins present a special problem. Many references to the determination of number average molecular weights exist, and here the definitive work of Gross, Sarkanen and Schuerch³⁷ may be mentioned. In the present section a brief discussion of the determination of weight-type averages for lignins is given and the limitations of certain of the methods are discussed.

It may be said at once that the widely used method of measuring $[\eta]$ and then determining M from a relationship such as equation (2) is not to be recommended for the soluble lignins. The intrinsic viscosity of a particular lignin will be influenced not only by the molecular weight but also by the ability of the microgel to swell. Differences in the degree of crosslinking or charge density (in aqueous solutions) will affect \bar{V} and thus $[\eta]$ in equation (1). Hence, it is not feasible to establish a unique relationship between M and $[\eta]$ for a particular lignin derivative in a given solvent. A further objection to such use of the intrinsic viscosity is its relative insensitivity to changes in molecular weight. This is particularly evident from the low value of a for the dioxan-HCl lignins in *Table 4*.

Similar reservations may be made for the use of the diffusion coefficient to measure the molecular weight by means of a relationship such as equation (3). McCarthy *et al.*^{5,6,12,15} and Benko³⁸ have characterized lignin sulphonates in this manner and the latter author has made it clear that the molecular weights so obtained are only relative. The diffusion coefficient is given by³⁹:

$$D = \frac{kT}{f} \quad (5)$$

where k is the Boltzmann constant, T the absolute temperature and f the

frictional constant of the macromolecule. If the molecule is approximately spherical in shape³⁹:

$$f = 6\pi\eta_0 r \quad (6)$$

in which $[\eta_0]$ is the viscosity of the solvent and r the radius of the sphere. The volume of the sphere is related to its hydrodynamic specific volume, \bar{V} by:

$$\frac{4}{3}\pi r^3 = \frac{\bar{V}M}{N} \quad (7)$$

where N is the Avagadro number.

Thus, the relationship between D and M for a spherical molecule is obtained by combining equations (5), (6) and (7) to give:

$$D = \frac{kT}{\eta_0} \left(\frac{N}{162\pi^2 \bar{V}M} \right)^{1/3} \quad (8)$$

It is evident from equation (8) that variations in D will be linked not only to changes in M but also to the previously mentioned dependence of \bar{V} on the swelling capacity of the microgel. A unique relationship between D and M may not be generally valid. However, it is interesting to note that the effect is small in the case of diffusion since $D \propto \left(\frac{1}{\bar{V}}\right)^{1/3}$ in equation (8) in contrast to the direct proportionality of \bar{V} and $[\eta]$ in equation (1).

Elimination of \bar{V} is possible by combining equations (1) and (8) to give:

$$M = \left(\frac{kT}{\eta_0} \right)^3 \frac{N}{6480\pi^2 [\eta] D^3} \quad (9)$$

Equation (9) provides a method of determining M by measurement of $[\eta]$ and D in the same solution. Uncertainties due to the degree of swelling are eliminated. The assumptions involved are as follows:

- (a) The macromolecule is non-freedraining and approximately spherical.
- (b) The Einstein (equation 1) and Stokes (equation 6) relationships are valid.

From arguments advanced in the previous section it seems likely that assumption (a) is justified for soluble softwood lignins. Both the Einstein³⁹ and the Stokes⁴⁰ equations have been verified for macroscopic spherical particles and Polson^{41,42} and Edward^{43,44} have suggested, in recent work, that the approximate validity of equation (9) extends to proteins and even smaller molecules. Thus, assumption (b) is probably also valid in the range of precision usually required for characterization of soluble lignin derivatives.

By a measurement of the diffusion constant and sedimentation coefficient on any given sample the molecular weight can be computed from Svedberg's⁴⁵ well-known equation:

$$M = \frac{sNkT}{D(1 - \bar{v}\rho)} \quad (10)$$

in which ρ is the density of the solution. In equation (10), \bar{v} is the partial specific volume, *i.e.*, the volume of solvent displaced per g of dry macromolecule; thus \bar{v} does not include solvent immobilized by a swelling microgel, in contrast to the term \bar{V} in equations (1) and (8).

Although a mean diffusion constant for lignins is fairly easily obtained, measurement of the sedimentation coefficient is complicated by the wide polydispersity of the macromolecule. An extreme example of this was found for the alkali lignins^{25,46}. The maximum ordinate sedimentation coefficient was found to decrease by factors of up to 10 when the speed of rotation was increased from 12,000 to 60,000 rev/min. The explanation was that different fractions of the same sample were contributing to the peak at the two speeds. The anomaly could probably be resolved by use of a synthetic boundary cell and a suitable integration procedure for determining a weight average value of s . Such methods tend to be laborious compared with the simple procedure of measuring the velocity of the peak.

A more promising method for soluble lignins is the short column, sedimentation equilibrium technique proposed by Van Holde and Baldwin⁴⁷ and by Yphantis⁴⁸. The technique has all the advantages of the classical equilibrium method but precision is sacrificed for speed by working with liquid columns of only 1 mm in depth. Equilibrium is then reached in a few hours instead of days as with the older method³⁹. Weight average molecular weights are obtained from

$$M_w = \frac{RT}{\bar{r}c_0\bar{\omega}^2 (1 - \bar{v}\rho)} \left(\frac{dc}{dr} \right)_{r=\bar{r}} \quad (11)$$

in which c_0 is the initial concentration, $\bar{\omega}$ is the angular velocity and r is the distance from the centre of the rotor. The radius, \bar{r} corresponds to the point in the column at which $c = c_0$. For a short column ($c = 1$ mm) this point is half-way between the meniscus and base of the column. Thus, with the customary Schlieren optics, a determination is made simply by measurement of the gradient dc/dr at the mid-point of the column when equilibrium has been established. Results obtained with the equilibrium technique on soluble softwood lignins are currently being compared with molecular weights based on diffusion and viscometry, and calculated by means of equation (9).

The light scattering method has been extensively used for the determination of weight average molecular weights of macromolecules in solution^{5,7,18,19,21}. The method is reproducible and can be reasonably precise when care is taken in preparation and handling of the solutions⁴⁹. The problem of the removal of dust has been completely solved by the

elegant ultra-centrifugation technique of Dandliker and Kraut^{21,49,50}. Even the presence of deep colour and strong fluorescence as found with soluble lignins can be accommodated with relatively minor refinements⁷. There remains, however, a basic characteristic of the technique which makes it unsuitable for routine molecular weight determinations of the soluble lignins.

From light scattering one obtains a "comprehensive" weight average molecular weight which includes all the particles in solution. With the type of distribution indicated by the sedimentation data in *Figure 1* for alkali lignin, a comprehensive weight average will be characteristic only of the high molecular weight part of the heavy tail. The molecular weight obtained will refer to a small proportion (perhaps < 5 per cent) of the sample and will be unaffected by changes in molecular weight of the major part of the material. Any clarification technique which is applied will tend to cause drastic changes in the light scattering molecular weight, M_{LS} , although only a small proportion of the sample is removed by the purification²¹.

This objection to the light scattering technique is particularly apt for aqueous solutions in which aggregates of large particle size are readily produced and removed only with difficulty. In a recent paper on poly-anhydroglucose addition polymers, Abe and Prins have noted ratios up to 15 for M_{LS}/M_w where M_w was determined by a sedimentation technique⁵¹. A similar discrepancy has also been obtained for aqueous solutions of carb-oxymethylcellulose⁵². Until some way around the problem is found, the comprehensive weight average molecular weight given by light scattering is likely to be unrepresentative of the molecular weight of the bulk of the sample of lignin.

The question now remains as to what method can be used to give a weight average which is representative of the greater part of the sample. The answer would be a technique which is not affected by the small proportion of very high molecular weight material. Short-column, sedimentation equilibrium falls into this category, because the very large particles are sedimented as a layer to the bottom of the cell before equilibrium is reached. The diffusion-viscosity method also would be expected not to be affected by a small proportion of very large particles. The type of average obtained for M will depend on the type of average for D substituted in equation 9. A weight average M will be given by a D corresponding to a weight average frictional constant. In a recent investigation⁹, it has been shown empirically that if the so-called "area" diffusion constant D_A ⁵³ is substituted in equation 5, an f value is obtained which approximates to a weight average f . Thus, substitution of D_A in equation (9) yields a value of M which approaches a weight average. At the same time the presence of a small proportion of very heavy particles will have a negligible effect on the shape of the diffusion patterns obtained.

It should be noted that the data from References 8 and 9 in *Tables 1 3* and *4* are based on molecular weights obtained by the diffusion viscosity method. On the other hand, the results in *Tables 1* and *4* from Reference 7 as well as the data in *Figure 6* are based on light scattering molecular weights.

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POLYELECTROLYTE BEHAVIOUR

Gardon and Mason⁴ first pointed out that lignin sulphonates behaved as swelling polyelectrolytes in aqueous solution. A characteristic feature of a polyelectrolyte is that the molecule expands when the concentration of counter-ion is decreased. When a solution of a polyelectrolyte in water is diluted with water (or 10^{-5} M NaCl) there is a marked increase in the reduced viscosity, due to the swelling of the molecule by the reduction in the ionic strength. In contrast, use of a high ionic strength aqueous

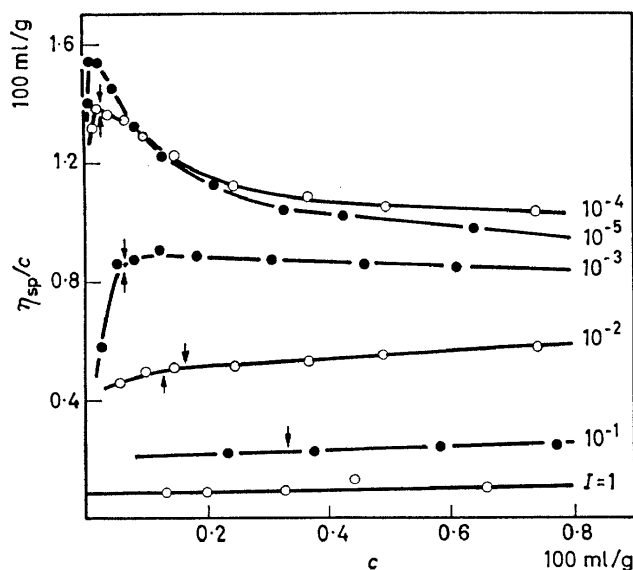


Figure 3. η_{sp}/c v. c for a sodium lignin sulphonate (fraction S-7, Reference 54) at ionic strengths from 1M to 10^{-5} M NaCl. The upward pointing arrows are theoretical predictions of the point of maximum bending while the downward pointing arrows correspond to the experimentally determined maxima

solvent such as 1M NaCl results in the linear graphs of η_{sp}/c v. c usually found for synthetic polymers in non-polar solvents. This behaviour is shown in Figure 3 for a high molecular sodium lignin sulphonate from spruce periodate lignin³⁶. The maxima in the graphs have been shown to be due to intermolecular interaction which predominates at dilutions so low that the expansion has virtually ceased⁵⁴.

To obtain a linear plot of η_{sp}/c v. c at low values of the ionic strength (I_E) it is necessary to dilute the solution so that the Na^+ counter-ion concentration remains constant^{55,56}. The graphs of η_{sp}/c v. c over the range of ionic strengths shown in Figure 4 were determined by such an iso-ionic dilution³⁶. From this data the variation of $[\eta]$ with ionic strength was measured for values I_E down to 0.00002 M. It was in order to explain certain unusual features of the dependence of $[\eta]$ on I_E that the idealized model of the lignin sulphonate macromolecule shown in Figure 2 was proposed³⁶.

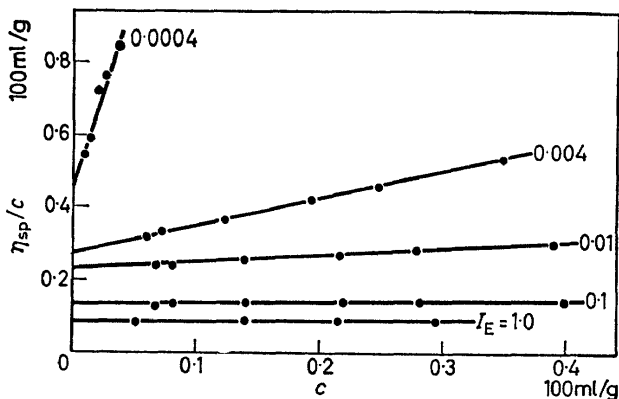


Figure 4. η_{sp}/c v. c by iso-ionic dilution at various values of the ionic strength I_E for a sodium lignin sulphonate (fraction PS-5, Reference 36)

It is probable that the crosslinked, polyaromatic structure of lignin must acquire hydrophilic, charge-bearing groups in order to become water soluble. Thus any water-soluble lignin would be expected to show polyelectrolyte properties⁵⁷. In this respect results similar to those in *Figure 3* have been obtained for alkali lignin prepared by cooking spruce periodate lignin in sodium hydroxide⁵⁸.

It is interesting to note that the lignin can acquire polyelectrolyte properties without becoming soluble. If the process of attaching charge groups to the lignin does not rend the network into soluble fragments, it will then become a polyelectrolyte gel showing the bulk properties of swelling or contracting in aqueous media, depending on the pH or ionic strength. It seems likely that the residual lignins, left on the fibres in the various semi-chemical or high yield pulping processes, would be in this category.

DISPERSING PROPERTIES

For some time water-soluble lignins have been used as cheap dispersing agents in colloidal systems. In a recent study of this effect⁵⁹ rather pronounced differences were found in the dispersing capacity of certain fractions of lignin sulphonate and alkali lignin.

Dispersion was measured by the decrease in viscosity produced in an aqueous suspension of titanium oxide (TiO_2) by the addition of 0.15 per cent lignin to the aqueous phase. Measurements were made with a Drage rheometer, and a standard dispersion number (SDN) was defined at a given rate of shear by

$$SDN = \frac{\text{shear stress of control suspension}}{\text{shear stress of dispersed suspension}} \quad (12)$$

The results showed that some lignins were good dispersants whereas others were not dispersants at all for the conditions under which the standard dispersion numbers were measured. Several SDN values were greater

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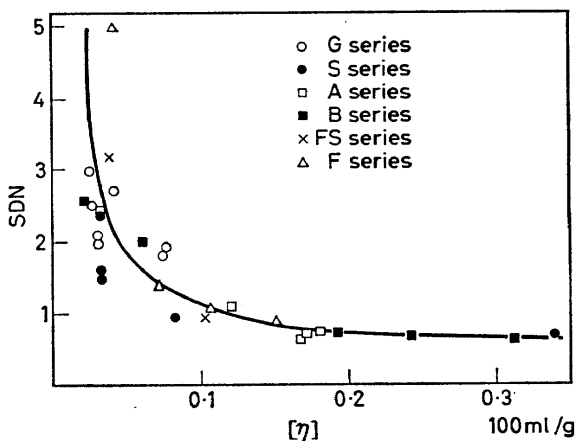


Figure 5. Standard dispersion number *v.* intrinsic viscosity for soluble lignin derivatives. The F-series are alkali lignins (see Reference 58) while all the others are lignin sulphonates described in Reference 59

than 5, while certain samples had SDN less than unity, *i.e.*, addition of the lignin increased the viscosity of the suspensions.

As shown in Figure 5, a well-defined, hyperbolic relationship was found between SDN and the intrinsic viscosities of the lignins. As expected from the correlation of $[\eta]$ and M shown in Table 4, a similar dependence of SDN on molecular weight was noted. The maximum in the graph of SDN *v.* M in Figure 6 was caused by the abrupt drop in the dispersing power of the *D* series of fractions. These were separated by dialysis through a cellophane bag. All lignins were adsorbed on the titanium oxide to a mean value of 95 per cent, with the exception of the *D* series which were adsorbed to only 60 per cent. This smaller degree of sorption may have been the cause of the unexpectedly low SDN values found for these fractions.

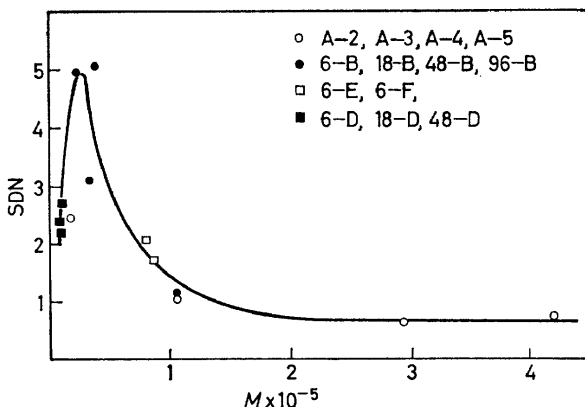


Figure 6. Standard dispersion number *v.* light scattering molecular weight, for some fractions of lignin sulphonate

The mechanism of dispersion was explained by the classical concept of a protective colloid, shown in *Figure 7*. The titanium oxide particles in water possessed a structure-forming tendency which produced aggregation in the slurry. Low molecular weight lignin microgels adsorb on to the particle, promote inter-particle repulsion, break down the structure and thus reduce the viscosity. With lignins of higher molecular weight, the coverage is not as great and thus the dispersion effect is less at a given lignin concentration. When the microgels are very large, inter-particle

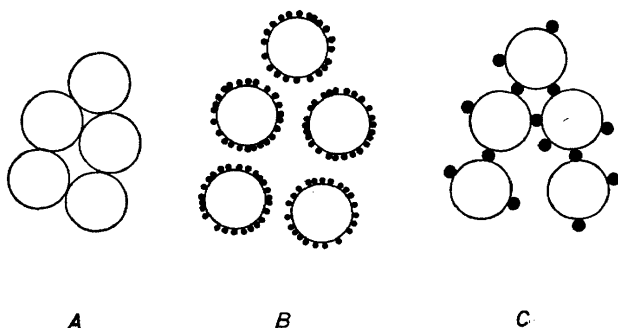


Figure 7. Pictorial illustration of the dispersion of titanium oxide by a lignin microgel. The large empty circles are the titanium oxide particles. The black circles are the lignin macromolecules

- A*—an aggregate in the undispersed suspension
B—dispersion on adsorption of a low molecular weight lignin
C—failure of a high molecular weight lignin to disperse the aggregate

adsorption occurs and the viscosity of the suspension is increased. Although certain detailed points remained unexplained, it seemed that the results in a general way fitted this simple colloidal theory.

ADHESIVE AND THERMOPLASTIC PROPERTIES

It is not known for certain whether lignin contributes to the strength of wood. Recent papers by Stone^{60,61} and Kallmes⁶² suggest that the lignin provides only a minor component of the shear strength of birch wood. On the other hand, one would expect that if lignin exists in wood as a three-dimensional network, comprising up to 30 per cent of the material in the cell wall, it must affect markedly the fibre-fibre adhesion in the wood. To answer such questions, more knowledge of bulk properties, such as softening or tack temperatures of solid or solvent-swollen lignins, is required. The results now to be discussed are taken from a recent study⁶³ of the conditions under which lignin will adhere to itself or to cellulose in the form of sheets of paper.

Several lignins were studied, their common characteristic being that they were insoluble in water. Samples included dioxan-HCl lignins, a Bjorkman lignin⁶⁴, periodate lignins and certain water-insoluble residues from soda and sulphite cooks.

The method consisted of sandwiching the powdered lignin between two small pieces of paper. Bond-strength was then measured as the force

required to pull the "sandwich" apart. Some sandwiches were made up dry. Some were made up with lignin and paper, soaking wet. In all cases, however, the sandwiches were dried before testing. Thus bond-strengths reported refer only to lignin and paper dried and equilibrated to ambient humidity at room temperature.

Normally, lignins did not bond to paper when the sandwiches were made up in the dry or wet state. However, a small but measurable bonding was found when spruce periodate lignin was soaked in a weak solution of NaOH, the sandwich made up wet, then dried and tested. As shown in

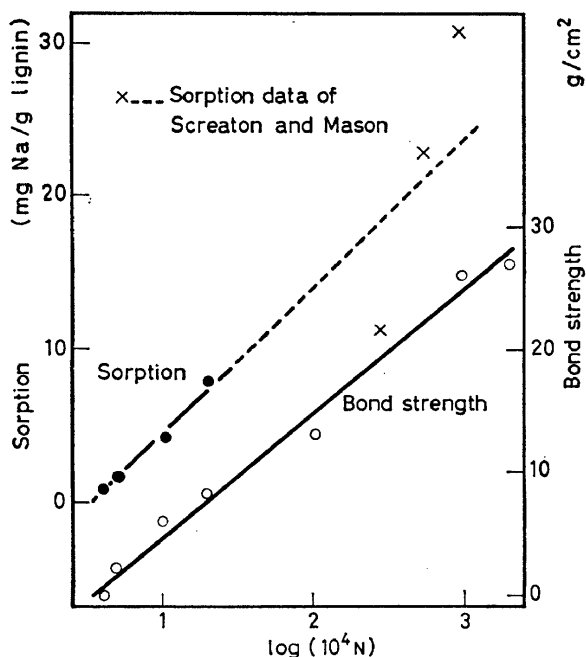


Figure 8. The lower line gives the increase in bond strength with increase in the concentration of alkali used for soaking. The upper line is the sorption of Na^+ on the periodate lignin. The points denoted by crosses are from the sorption data of Scream and Mason⁶⁵

Figure 8, the bond strength increased with the alkali concentration, as also did the sorption of sodium ion on the lignin.

The alkali induced bonding may probably be attributed to the mildly polyelectrolyte nature of the periodate lignin. As shown by Scream and Mason⁶⁵, the sorbed alkali neutralizes the weakly acidic groups in the periodate lignin, thereby permitting their ionization. The free charges thus produced cause the lignin to swell like a neutralized polyelectrolyte gel. The lignin then develops adhesive properties and bonds when dried, in a manner analogous to the behaviour of other alkali-based adhesives⁶⁶. When similar experiments were tried with insoluble residues from an alkali or sulphite cook, extremely strong bonds were formed, presumably because of the greater swelling tendency of such lignins.

As pointed out in an earlier section, the residual lignin left on the fibres in the various high yield or semi-chemical processes, will probably have acquired groups capable of ionization. This lignin, even though insoluble, will possess the swelling characteristics of a polyelectrolyte gel. It seems likely that under certain conditions, such lignin will contribute appreciably to the bonding characteristics of the fibres in the dry sheet of paper.

A study was then made of the effect of temperature on lignin bonding. The paper-lignin-paper sandwiches were pretreated by pressing at temperatures ranging from 25° to 250°. Pressing was done on dry sandwiches and also on sandwiches made up soaking wet. But, as before, all bond-strength tests were made on the dried sandwiches at room temperatures.

The way in which the temperature of pressing affected the bonding of dioxan lignins is shown in *Figure 9*. Pressing dry caused no bond to be formed until temperatures between 125° and 200° were reached. However, when the sandwich was pressed soaking wet and then dried, a bond was formed at a considerably lower temperature than when the pressing was made on a dry sandwich. Similar results were found for the spruce Björkman lignin, but a complete analysis over a range of temperature, as shown in *Figure 9*, was not possible because of the small size of the sample.

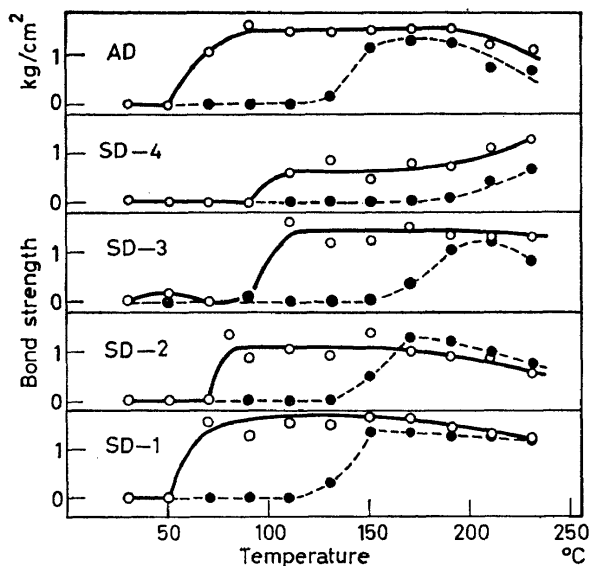


Figure 9. The effect of temperature of pressing on the bond strength of dioxan lignins. Dotted lines and filled circles represent dry pressing while full lines and empty circles correspond to wet pressing. The notation of the lignins is given in *Table 5*

The results for periodate lignins are shown in *Figure 10*. Here the bonding produced by dry pressing occurs at a higher temperature. Also there is a larger decrease of the bonding temperature with wet pressing. Measurements on Wiley milled wood gave results remarkably similar to those obtained for periodate lignin, except that in the case of spruce there

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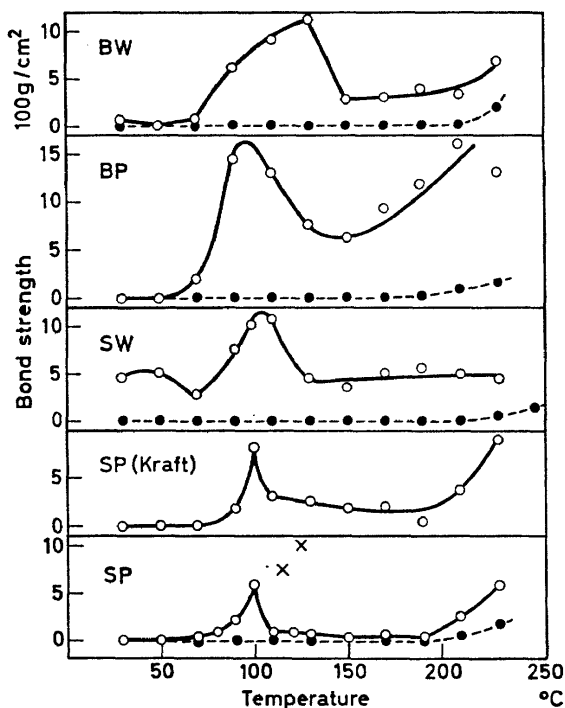


Figure 10. The effect of temperature of pressing on the bond strength for periodate lignins and for woods. Dotted lines and filled circles represent dry pressing while full lines and empty circles correspond to wet pressing. The notation of the lignins is given in Table 5. The two points indicated by crosses in the SP graph were for sandwiches pressed under steam pressure at 115° and 124°. The data labelled SP (Kraft) were for spruce periodate lignin sandwiched between 1/2 inch circles cut from a double weight kraft hand sheet

was a constant "base-line" of bonding at lower temperatures, which was probably due to the cellulose component of the milled wood. The maxima found in the bonding of wet-pressed periodate lignin could not be explained unambiguously. It is interesting to note that in this respect, the periodate lignins rather than the dioxan lignins parallel the behaviour of the milled woods.

It was desirable to ascertain the temperature at which bonding began to occur. This was arbitrarily taken to be the temperature at which a bond-strength of 200 g/cm² was first reached. Bonding temperatures for dry and wet pressing, T_1 and T_2 are given in Table 5. Also included is the sorption of water by the lignin from a saturated solution of sodium chloride at room temperature.

The bonding temperature, as measured in the present work, is analogous to the tack temperature found in polymeric materials. McLaren, Li, Rager and Mark⁶⁷ have pointed out that tack temperatures along with brittle points, softening temperatures and second order transition points belong to the category of non-equilibrium properties of high polymers. These effects all arise from the same basic molecular behaviour and are

Table 5. Bonding temperatures, water sorption and β for various lignins

Sample	Notation	(T_1) °C	(T_2) °C	($T_1 - T_2$) °C	Sorption (mg/g)	β
Spruce dioxan	SD-1	125	50	75	71	0.51
Spruce dioxan	SD-2	140	70	70	75	0.45
Spruce dioxan	SD-3	165	90	75	84	0.43
Spruce dioxan	SD-4	200	95	105	96	0.53
Aspen dioxan*	AD	130	50	80	86	0.45
Spruce periodate	SP	235	90	145	151	0.46
Spruce wood	SW	255	90	165	—	—
Birch periodate†	BP	235	70	165	119	0.67
Birch wood	BW	320	75	155	—	—

* Kindly supplied by Professor J. M. Pepper.

† Kindly supplied by Mrs P. A. Bradley and Professor C. B. Purves.

associated with increased freedom of molecular movement with increase in temperature. At temperatures below the softening temperature of an amorphous polymer the chains are "frozen" and the bulk polymer is a brittle solid. Above the softening temperature the chains acquire enough energy to move readily with respect to each other. The polymer then becomes soft, deformable and sometimes tacky. In the temperature range in which the change occurs there are usually variations in the rate of change of volume or heat content with temperature, giving rise to the so-called second order transitions⁶⁸.

If the polymeric solid absorbs a low molecular weight diluent, the chains are separated by the molecules of the absorbate and therefore require less energy to migrate with respect to each other. Second-order transitions or softening will then occur at a lower temperature. The diluent is said to "plasticize" the polymer⁶⁸.

If lignin in wood is made up of chains of phenyl propane units, cross-linked to give an amorphous, three-dimensional structure, it would be expected to undergo second-order transitions with increase in temperature, and thus to show a softening point. The postulate here is that the bonding temperature, T_1 , can be regarded as the softening temperature of the lignin. The decrease of T_1 to T_2 on wet pressing is, therefore, a measure of the degree to which the lignin is plasticized by the presence of absorbed water.

An approximate quantitative treatment of the decrease in softening temperature with sorption of water is possible in terms of a relationship proposed by Fujita and Kishimoto⁶⁹. If C is the concentration of diluent in g per g of polymer, the lowering of the transition temperature is given by

$$T_1 - T_2 = C \frac{\beta}{\alpha_2} \quad (13)$$

where α_2 is the difference between the thermal expansion coefficient above and below the transition temperature, and β is a parameter representing the contribution of the diluent to the free volume within the bulk polymer.

Williams, Landel and Ferry⁷⁰ have shown α_2 to have a constant "universal" value of $4.8 \times 10^{-4} \text{ deg.}^{-1}$. Substituting for C the sorption of water shown in *Table 5*, the values of β were calculated by means of equation 13.

In spite of fairly marked changes in the water uptake and in $T_1 - T_2$, β in *Table 5* is relatively constant. If the unaccountably high figure for the birch periodate lignin is omitted, the average value of β is 0.47 ± 0.03 . Under the conditions used for wet pressing, the uptake of water by the lignin corresponded to 100 per cent relative humidity. The sorption in *Table 5* was measured at 75 per cent relative humidity over saturated brine. Thus the values of β are too high by the ratio of the sorption at 100 per cent relative humidity to that at 75 per cent relative humidity. If an approximate correction is made based on the sorption isotherm for water on periodate lignin published by McKnight and Mason⁷¹, the average β becomes 0.31. With water as diluent, Fujita and Kishimoto found β for poly(vinyl acetate) and poly(methyl acrylate) equal to 0.37 and 0.30, respectively.

A number of workers have previously discussed the thermoplastic behaviour of lignin. Kleinert and Tayenthal⁷² have noted softening and melting of alcohol lignin in hot water. Lagergren, Rydholm and Stockman⁷³ have considered the effect of lignin softening in the defibring of wood by different methods. The softening and steam plasticizing of lignin has been recognized for some time in the various processes for making board and dimensionally stabilized wood^{74,75,76} and Higgins⁷⁷ has shown that the compressive strength of various types of veneer is markedly temperature dependent. The significance of lignin softening for mechanical pulping has been pointed out by Luhde⁷⁸ and for sulphite pulping by Bjorkman and Person⁷⁹. It seems likely that both in the production of mechanical pulp⁷⁸ and in the drying of newsprint, temperatures and moisture conditions are reached which could cause the lignin to soften. Such softening of a major component must have an appreciable effect on the physical behaviour of the wood or the pulp. In a recent study of the fracture of wood, Atack *et al.*⁸⁰ have shown that at elevated temperatures the wood breaks as if the lignin has been softened. In chemical pulping, the wood is subjected to elevated temperatures in aqueous media. It is probable that the lignin will exist as a semi-molten phase before it is dissolved. Thus much of the loss of reactivity produced by the so-called "condensation" of lignin at high temperature may be due simply to physical coalescence of the molten lignin microstructure in the wood. Marraccini and Kleinert⁸¹ are currently investigating the closely related phenomenon of the loss of lignin surface in the initial stages of the cooking process.

CONCLUDING REMARKS

This paper has been written around the concept of the lignin network proposed in the first paragraph. It must be admitted that none of the evidence gives an unambiguous answer to the important question of the molecular state of lignin in wood. With regard to the polydispersity of the softwood lignins, it is true that a considerable range of molecular weights would be produced by the degradation of a lignin network, in a fashion analogous to the degradation of a branched polymer such as amylopectin.

It is also true that appreciable polydispersity could arise from the synthesis of a branched network by polyfunctional radicals, such as are believed to be the precursors of lignin wood. In fact, the statistical polymer treatment of Erlander and French²⁴ was based on the condensation of polyfunctional glucose monomers. The concept was applicable to the acid hydrolysis of amylopectin and glycogen because the degradation reaction was found to be the reverse of a random condensation. Thus, the polydispersity of soluble softwood lignins may arise either from the degradation of a network already formed in the wood or from the induced syntheses of branched type macromolecules from reactive, low molecular weight molecules present in the wood⁸². Pronounced aggregation of low molecular weight units as suggested by Lindberg would also produce polydispersity⁸³.

The evidence supporting the network theory is more indirect. The universal insolubility of lignin is likely to be due to its extensive branched or crosslinked structure in wood. A network structure of protolignin would explain the well-known difficulty of separation from the carbohydrate moiety. Wardrop⁸⁴ has shown that lignification takes place at a comparatively late stage in the development of the cell wall. If the protolignin is laid down as a three-dimensional network, part of this material is likely to grow around individual carbohydrate molecules. The resulting entanglement of molecular chains could make separation difficult or impossible as in the case of the synthetic "snake cage" polymer mixture⁸⁵. Thus it may not be necessary to postulate covalent linkages between lignin and carbohydrate molecules to explain their difficulty of separation⁸⁶.

If lignin is markedly polymerized by the usual methods and for delignification, one might expect an increase in the molecular weight of a lignin derivative made soluble by a relatively mild treatment and then re-cooked for a longer time. As yet there has been no demonstration of such an increase. In the case of sulphonation it has been shown that already soluble lignin sulphonates are degraded by further sulphonation^{13,87}.

Continuing definitive investigations on the physical chemistry of the lignins will eventually support definite conclusions concerning the molecular state of the lignin in the wood.

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