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Molecular Theory of Delignification

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ABSTRACT: A method to describe the branched-chain structure of lignin is presented. In a molecular model, the delignification is treated as degelation. Molecular and kinetic parameters are estimated for the kraft process of delignification, which is specific to certain cleavable aryl ether linkages. The cleavage is allowed to occur along the primary chains and at the cross-links. Delignification curves thus obtained are in agreement with experiments. The kinetics and the molecular weight averages of the lignin sol support a treelike model for the lignin macromolecule.

Separation of lignin from wood by chemical means is known as delignification. Alternatively, delignification can be regarded as a major operation in the purification of cellulose, i.e., chemical pulping. Although originating from the same source, cellulose has attracted most of the attention and plays a key role in the development of polymer chemistry, whereas lignin technology has been plagued with ambiguities in its chemistry. The most noticeable example is the lack of "molecularity" in a delignification process.[1,2]

The pulping process, in one form or another, has a long history that dates back to the beginning of civilization.[3] Because of its antiquity and practical emphasis, this process has traditionally been treated as a "craft", which appears to hinder its development as a scientific technology. Small molecules obtained from degraded lignin provide a fertile ground for organic chemistry. Unfortunately, studies on small "model compounds", especially in kinetics, have never exerted a great impact on pulping technology. Although it has been well recognized that lignin, in a natural or degraded state, is a polymer, techniques in polymer chemistry have seldom been used in the studies of lignin.

A pulping process is usually described with a "delignification curve", which depicts the rate of weight loss of insoluble lignin. This description is almost as old as the major pulping processes.[4] It was in the 1940s that the delignification curve began to be formulated in terms of chemical kinetics.[5] Since then, massive amounts of data have been generated for all the pulping "kinetics" and physicochemical terms, such as activation energy, entropy, etc., have been collected, calculated, and compared.[5-8] These delignification curves, and the physicochemical parameters derived from them, are obviously very important in the design and control of a pulping process.

The lack of molecularity of these "master curves" is reflected by the fact that their chemical concentrations are expressed in weight instead of number of molecules.[1,2] Weight-concentration expressions are particularly suspect for polymeric materials.[9-11] Usually the temperature dependence of degradation rate in the form of Arrhenius parameters does not make molecular sense. For example, it is difficult to comprehend an activation energy of, say, 32 kcal per *mole* of polymer[9] or lignin,[5,6] cellulose,[11] or even wood.[10]

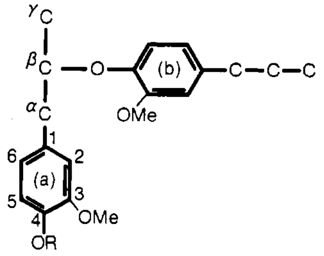
Polymers always have a molecular weight distribution (MWD). In a polymerization or depolymerization process, both the MWD and average degree of polymerization (DP) change with reaction time. Chemical kinetics, when properly expressed in number concentrations, is the most powerful tool to express this process. It is also very powerful in deriving the MWD expressions of polymers.[12,13] For this reason, a polymerization process must satisfy both the MWD and kinetic arguments.

The recognition that lignin is a polymer naturally leads to attempts to measure its MWD.[14-17] Usually these measurements were made under static or equilibrium conditions, without attempting to examine their time dependence. Conversely, kinetics of lignin degradation have seldom been accompanied by MWD measurements. This lack of coordination between equilibrium and kinetic characterizations also contributes to the loss of molecularity in pulping processes.

Following a series of recent publications,[1,2,17-20] this paper is a continued effort to establish the molecularity of the delignification process. In the next section, a new and simplified description of lignin structure—based on the treelike model—will be presented. After that, theories of degradation, chemical reactivities of functional groups, the kinetics of delignification, and the MWD of degraded lignin will be discussed.

Lignin as a Branched Polymer

Model compound studies have suggested that the basic segment of lignin is the phenylpropane (C_9) unit.[3,21,22] In softwood lignin, the majority of C_9 units have a methoxy group adjacent to the phenolic hydroxyl (PhOH) group, as shown in I, which is considered as a "dimer" containing two C_9 units. The other C_9 units may contain two methoxy groups, both adjacent to the PhOH group, or contain no methoxy group at all. On the average, there is 0.95 OMe per C_9 unit in softwood lignin.[21]



(I)

Alternatively, the phenylpropane unit can be regarded as a phenylglycerol. The ether linkage joining two C_9 units, shown in I, is a β-aryl ether bond, which is by far the most abundant linkage in softwood lignin.[21,22]

A C_9 unit in lignin may be linked monofunctionally, bifunctionally, or trifunctionally. Our definition of functionality and linkages is a broad one: When two C_9 units are linked, there may be more than one bond involved, but they are counted as one linkage between the two units. An example is when two glycerol parts interlock to form a hexagonal ring with three bonds between them, as in the case of pinoresinol;[21] the entire ring is counted as one linkage. A trifunctionally linked unit is one that is linked to three other C_9 units, regardless of the number of bonds.

Obviously, each C_9 unit has more than three linking sites. However, a tetrafunctionally linked *unit* is highly improbable, if not impossible, because of stereochemistry. In addition to the β-aryl ether linkage are the α-aryl ether linkage, diaryl ethers, and C–C bonds. Gierer has discussed the stability of various linkages in different "cooking" media.[21] The fissionability of a linkage is defined as the ability of two linked units to separate. For kraft pulping, which is the most widely studied process, a fissionable bond is either a β-aryl or an α-aryl ether bond.

In the case where R = H in I, the C_9 unit (a) is phenolic. If R = Me or another C_9 unit, it is a nonphenolic phenylpropane unit.[21] A β-aryl ether linkage has different reactivities toward cleavage, depending on whether the parent C_9 unit is phenolic or nonphenolic. An α-aryl ether bond is cleavable in the kraft medium when it is in a phenolic unit. This ether bond can be one of the two bonds joining two units; the ether bond may be cleaved, but the other bond stays intact. In this case, the breaking of the α-aryl ether bond does not result in the separation of two units, and the linkage with two such bonds is considered noncleavable.

In the kraft process, phenolic and nonphenolic β-aryl ether bonds and phenolic α-aryl ether bonds are cleavable. The mole fraction of all these cleavable bonds, based on a C_9 unit, is estimated[21,22] to be 0.42–0.46. Taking this fraction as 0.45, the uncleavable fraction is 0.55, which is to be defined as the ultimate "extent of reaction" p_∞, an important parameter in our calculation for the kraft lignin.

Because of the polyfunctionality of each unit, lignin is obviously a branched polymer. The broad MWD of degraded lignin and the insolubility of native lignin also suggest that it is a branched polymer that gels.[14–17,23,24] Attempts to describe the branched-chain structure of lignin naturally lead to the application of the theory of Flory[12] and Stockmayer[25] (F–S theory). Among the physical and chemical properties tested, F–S theory is used mainly to describe the MWD of degraded lignin in the sol fraction. Less widely applied is the kinetic aspect of F–S theory. The identification of linkages associated with the kinetics is occassionally made, but only vaguely. Generally speaking, the branched lignin molecule is considered to be obtained by cross-linking primary polymers with a MWD.

These primary molecules of lignin were first assumed by Szabo and Goring to be trifunctional monomers.[23] The functional groups involved were not specified, but identical reactivity was assumed. The resulting lignin was considered as the product of self-condensation of the RA_n type of monomers, with $n = 3$. Szabo and Goring also suggested kinetic schemes, applicable to two forms of lignin gel, for delignification.

Later, the model was modified by Bolker and Brenner.[24] The primary chain concept was introduced, but the MWD of the primary chain was assumed to be uniform in sulfite and dioxane lignins. Bolker and Brenner identified the α-aryl ether bonds as the linkage broken in these "acid" processes of delignification.

A primary size distribution was assigned by us,[2,17] using an extended version of the Stockmayer distribution.[19,20] For "alkaline" lignins, we identified the β-aryl ether bond as the one that is responsible for degradation.

In addition to the above published accounts, there are two important thesis works related to gel degradation.[26,27] In Pla's work,[26] elaborate measurements of the MWD were made for dioxane lignin. The mechanism developed from this work was much like the one used by Bolker and Brenner[24] and Bolker et al.[28] In Gardner's thesis, reference to delignification was made, but the experiments involved the degradation of dextran gel.[27]

All these works involve the application of the F–S theory of cross-linking and gelation. In most of the studies of delignification and lignin structure, the application of F–S theory was not developed to its full potential. For this development, we impose three stringent molecular factors in delignification: (i) the identification of cleavable linkages, (ii) the MWD of the lignin sol, and (iii) the kinetic schemes associated with the delignification process.

Perhaps the most important of all is the applicability of F–S theory itself. This is usually described briefly in the studies described above, but the theoretical background has not been thoroughly examined. F–S theory is the "ideal gas law" in branched polymers. The formation and breaking of a bond occurs at random. In the RA_n type of condensation polymers, this theory assumes equal reactivity for functional groups A and no intramolecular reaction (ring-free). In other words, this theory amounts to assuming a treelike molecule. Numerous papers have been devoted to criticizing, revising, or verifying this theory and will not be cited here. A recent review of this theory can be found in ref 29.

The most severe challenge to this theory comes from percolation theory,[30,31] which has its origin in the critical phenomena and phase transition. However, the scaling law arguments used in the percolation theory are applicable only in the vicinity of a critical point. The MWD aspect of F–S theory is usually outside the applicability range of the scaling law. It is generally agreed that for the cross-linking of preformed chains, the treelike approximation is a good one, even better than that for the RA_n condensation polymers.[29,31]

A more serious question arises as to the applicability of F–S theory beyond the gel point. The entire process of delignification occurs in this "postgel" region. Early extensive studies made by Flory[12] have developed into several working equations beyond the critical point. In the postgel stage, these equations suggest a violation of the ring-free assumption in the theory.[12,25] This violation is not a serious, but a welcome, one in most cases. Moreover, massive data generated from irradiation studies of polymers have quantitatively supported these equations.[29,32] Therefore, these postgel relations will be used for the overall degradation process in the present study. For easy reference, the symbols used here are listed in Appendix I.

Delignification and Degelation

Previously we introduced the term "degelation" for gel degradation.[2,17] The MWD[17] and kinetic[2] aspects of delignification have been shown to be in complete analogy with degelation. In the kinetic scheme,[2] it was assumed that cleavable β-aryl ether bonds are also the cross-links. Breaking these cross-links leads to the fragmentation and dissolution of lignin. This assumption is too narrow because it represents only one extreme in the degradation of cross-linked gel.[33,34] However, the previous kinetics are partially correct, as will be demonstrated with a more flexible and realistic model.

In addition to the applicability of a molecular theory, we need to examine the experimental conditions and data that are required to substantiate a kinetic scheme. Unlike the degradation of pure polymers, in the solid or gel state, delignification has to be carried out in the presence of the carbohydrate component of wood. The carbohydrates contribute a physical factor in delignification. This factor is usually ignored in the degelation theory of delignification.[2,17,23,24]

In addition to the degelation concept, there is another theory of delignification[35,36] which emphasizes this physical factor. In essence, this theory visualizes that delignification occurs in two steps: (i) cooking chemicals degrade and dissolve the hemicellulose in the cell wall, thus creating a porous structure in wood fibers; (ii) lignin is then degraded and diffuses through these pores. There is a correlation between pore size and molecular weight of degraded lignin. The pores exert a "sieving" effect in which *smaller* lignin molecules diffuse earlier through the smaller pores. Larger lignin molecules come out to the wood matrix only after the pores are correspondingly increased in size. Unfortunately, it is impossible to study an undegraded lignin in the absence of cellulose fibers. Therefore, this sieving effect is difficult to verify or dispute.

However, it is equally difficult to visualize that pore size is a controlling factor in delignification. First, the fibrils and their constituent cellulose chains may not be rigid under the pulping conditions. It is doubtful that they can confine the degraded lignin molecules effectively. Secondly, the sieving effect appears to be in contradiction to the principle of gel permeation chromatography (GPC). When a solution of polymers (linear or branched) is allowed to elute through a porous GPC column, it is the *larger* molecules that are excluded first during the run.

In view of the contradictory sieving and exclusion effects, it is difficult to quantify a physical model such as this one. On the other hand, the degelation theory, based on F–S theory, is a chemical model which considers only the existence or nonexistence of a chemical bond or linkage. Because F–S theory is known to neglect some important geometrical and physical factors, its application to delignification has to be limited to the interpretation of chemical factors.

The presence of cellulose fibers and an initially insoluble lignin do create heterogeneity in delignification kinetics. It is well-known that yield loss on pulping occurs before substantial delignification takes place. In the very early stage of pulping, the cooking chemicals are believed to react and dissolve a portion of hemicellulose. The presence or absence of such a reaction may not affect the reaction of delignification, provided that proper experimental conditions are used. These reactions can be considered as parallel, competitive reactions. In the presence of excess cooking chemicals (which is always the case in practice), delignification can be separated from the dissolution of carbohydrate and treated as an independent reaction.[2]

Heterogeneity does not affect the formulation of chemical kinetics, so long as the reaction is carried out under an isothermal condition. In the case of thermal degradation of linear polymers, solid samples have been used to establish the kinetics.[33,37,38] Chemical degradation is essentially a thermal degradation. This means that the reaction rate is determined by the relative value of the bond dissociation energy and k_BT. The bonds are specific to the chemicals used. Their rate of cleavage is controlled by temperature, but independent of heterogeneity.

Phenolic Hydroxyl Group

Once an aryl ether linkage is cleaved, a phenolic hydroxyl group (PhOH) is liberated. In prolonged kraft cooking, the α-aryl ether bond in a phenolic C_9 unit and the β-aryl ether bond in phenolic or nonphenolic units are quantitatively cleaved.[21] In the "soda" process, the β-aryl ether bond in a nonphenolic unit is cleaved to a smaller extent. This extent has been estimated, but the estimation is less certain than that for the kraft process.

The change in concentration of the PhOH group has been noted for alkaline processes.[39] This change has also been studied kinetically,[40] but the starting material is a milled wood lignin—a lignin sol prepared with severe mechanical degradation. The milled wood lignin was cooked with kraft and soda "liquors". The kinetic data points obtained by Gierer et al.[40] are shown in Figure 1, where α is the fraction of PhOH groups liberated. The curves are calculated theoretically, using our previous reversible kinetics:

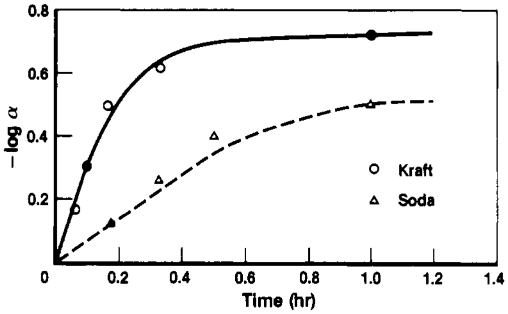


Figure 1. Kinetics of the liberation of PhOH groups in milled wood lignin, in the form of log α vs. t.

$$\mathrm{d}\alpha/\mathrm{d}t = k_1\alpha - k_2(1-\alpha)^2 \qquad (1)$$

The initial condition is $\alpha = 1$ at $t = 0$. Gierer et al. calculated k_1 from the slope of the very first straight line portion of the entire curve. The model shown in eq 1 allows the evaluation of k_2, in addition to k_1. The rate constants at 170 °C are calculated as

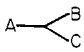
	k_1, h^{-1}	k_2, h^{-1}
kraft	6.8	2.0
soda	1.8	0.9

The minimum value of α at $t \rightarrow \infty$ is estimated to be 0.188 for the kraft process. This is the uncleavable fraction of PhOH groups in the total concentration of this group available in milled wood lignin.

The measured concentration in this kinetic example is the total concentration of PhOH groups, without specifying from which aryl ether bond this group is liberated. The classification of aryl ether bonds as phenolic or nonphenolic is the one used in organic chemistry. For our particular purpose, it is more convenient to classify them according to the functionality of the unit. As stated earlier, we can classify the units as those that are linked monofunctionally, bifunctionally, or trifunctionally. The last one is obviously a nonphenolic unit. The free PhOH groups measured at any stage of reaction are contributed by units in the linear chains and chain ends.

Since we define the monomeric unit as a C_9 unit, our description of the lignin molecule depends on how we describe this basic unit as the repeating unit in the lignin polymer. This can be regarded as an RA_3 unit,[12] as did Szabo and Goring;[23] but this is not realistic because the functional groups are obviously different from each other. Alternatively, the monomeric unit can be regarded as an ARB_2 (or AB_2) type,[12] where A can only react with B. This type of condensation polymer does not gel. However, Gardner[27] has used this condensation polymer as a primary chain instead of a monomeric unit. Final branched polymers can then be obtained by cross-linking the primary chains, which can be linear or branched.

Even an



type of condensation polymer does not lead to gelation, provided that A can only react with B or C and that all other possible reactions are forbidden.[41] Condensation of this type of monomeric unit without restricting the reactivities is mathematically too complicated to handle because the probabilities of A–A, A–B, A–C, B–C, B–B, and C–C reactions are too cumbersome. With Greek letters and numerals designating the carbon atoms as shown in I, possible linkages of groups are found for β–O–4 (β-aryl ether), α–O–4 (α-aryl ether), 5–5, β–β (together with γ–O–α), β–5, 4–O–4 (diaryl ether), etc., with different frequencies of occurrence.[22]

To overcome such a complexity, alternate ways of describing the final branched molecules should be explored. In these, the concept of cross-linking primary chains appears to be the simplest.[17-20] In our new model, which is a revised and simplified version of the previous one,[2] it will be assumed that lignin is made up of primary chains with a "most probable" distribution:

$$w(y) = (1 - p)^2 y p^{y-1} \qquad (2)$$

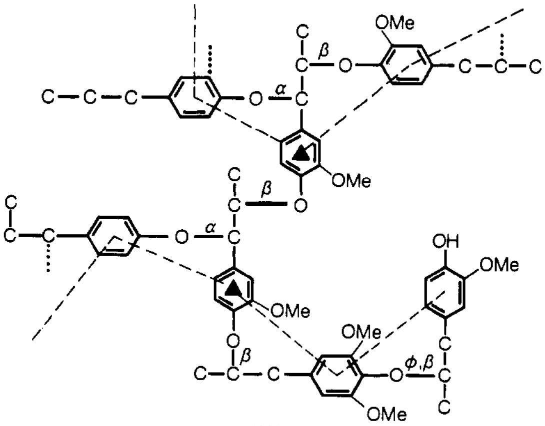
Again the monomeric units in the linear chains are C_9 units. Cross-linking then takes place between the linear chains to form branched-chain lignin and eventually leads to an insoluble gel.[2] In eq 2, p is the fraction of C_9 units that reacted monofunctionally and bifunctionally, regardless to the linkages involved. Evidently the fraction of cleavable linear chains is $p - p_\infty$.

This simple definition of p and primary distribution has been supported experimentally and theoretically. For our application to lignin, the most probable distribution of a majority of primary chains has been established.[2,17,18] Even if the primary chains are otherwise distributed, in a degradation process the chains rapidly assume a most probable distribution.[32,33] In this sense, it is superfluous to assign two chain size distributions for two forms of lignin gel.[2]

Branching Probability and Cross-Linking Density

When two sufficiently long chains react, nonterminal units are linked, thus creating a branch point.[18] This branch point is tetrafunctional in the sense that there are four chains issued from it. A tetrafunctional branch point contains a pair of trifunctionally linked C_9 units.

An arbitrary arrangement is shown in II. The linear chains are defined by the dashed lines. The aryl ether bonds are marked as α or β to designate them as the *nonphenolic* α-aryl or β-aryl ethers. φ,β designates a *phenolic* β-aryl ether. The dotted lines are continuations of chemical bonds. Benzene rings with solid triangles indicate trifunctionally linked units. Shown in II is a pair of trifunctionally linked units joined by a heavy line. This line is the cross-link referred to in this study and is a nonphenolic β-aryl ether bond. The pair of units with triangles defines a tetrafunctional branch point[18] which has the appearance of the letter "H". In this pair, the nonphenolic α-aryl ether bond is stable toward alkali.[21]



(II)

The branching probability is defined as the probability that a chain issued from a branch point will end in another branch point. This probability is designated as α_4 to denote that the branch point is tetrafunctional. The cross-linking density ρ is the fraction of trifunctionally linked C_9 units[25] and is related to α_4 by

$$\alpha_4 = p\rho/[1 - p(1 - \rho)] \qquad (3)$$

Since the critical value (gel point) of α_4 is $^1/_3$, we obtain from eq 3 the critical extent of reaction:

$$p_c = (1 + 2\rho)^{-1} \qquad (4)$$

These relations were obtained by Stockmayer,[25] who assumed a fixed value of ρ. For our application to delignification, these quantities (α_4, ρ, and p) change with time. The critical point is reached at $t \rightarrow \infty$ when there is no gel.[2] Thus, we have

$$p_c = (1 + 2\rho_c)^{-1} \qquad (4a)$$

Delignification Kinetics

Our previous model[2] uses eq 1 to describe the breaking of cross-links and the reverse cross-linking. The second-order cross-linking term is necessary for isothermal degradation.[32,33] This reverse reaction is closely related to the treelike model,[2,29,32] although it has only been speculated in lignin.[42] Since α in eq 1 is normalized with respect to the total PhOH groups, to transform it to the trifunctionally linked C_9 units we replace it with ρ:

$$\mathrm{d}\rho/\mathrm{d}t = k_1\rho - k_2(1 - \rho)^2 \qquad (1a)$$

which has a solution[2]

$$\tau + C = (2/B) \tanh^{-1} [(r + 2 - 2\rho)/B] \qquad (5)$$

where $\tau = k_2 t$, $r = k_1/k_2$, $B = [r(r + 4)]^{1/2}$, and C is the integration constant evaluated at $\tau = 0$, $\rho = \rho_0$.

The ratio r is a measure of the driving force for the first-order cleavage of cross-links. At a given weight-average DP of primary chains $\bar{y}_w = \lambda + 1$, this ratio is evaluated[2] at an equilibrium with a specified value of λ:

$$r = (\lambda - 1)^2/\lambda \qquad (6)$$

As discussed earlier, this model is too restrictive in that it allows only for the breaking of cross-links. A more realistic and flexible model should also allow for the cleavage of primary chains (chain scission). With a most probable distribution, the chain scission is kinetically described by[27,33,37,38]

$$-\mathrm{d}p/\mathrm{d}t = k(p - p_\infty) \qquad (7)$$

A residual term p_∞ is added to the simple model of first-order degradation of linear chains[27,38] because our definition of p suggests an unbreakable fraction p_∞. The integrated form is

$$p = p(t) = p_0 e^{-kt} + p_\infty \qquad (8)$$

This kinetic scheme also fits the theoretical curves in Figure 1, provided that α is replaced with p and $p(0) = 1$, $k = 8\ \mathrm{h}^{-1}$ (kraft) and $2.5\ \mathrm{h}^{-1}$ (soda), and $p_\infty = 0.188$ (kraft).

Therefore, the kinetics described by Figure 1 can be explained either by chain scission eq 8 or by the breaking of cross-links, eq 5. Our new delignification kinetics encompass both processes in these two equations. The kinetics should hold true for the sum of eq 5 and 8. However, the extent of reaction p based on C_9 units actually includes the cross-linked fraction.[12,25] Otherwise, taking the sum $p + \rho$ would result in counting a branch unit twice because this unit belonged to a linear chain before branching occurred.

The values of p's used to fit Figure 1 should not be used for the ones based on C_9 units. For the latter purpose, we use another set of boundary conditions:

$$p(0) = p_0 + p_\infty \qquad p_\infty = 0.55$$

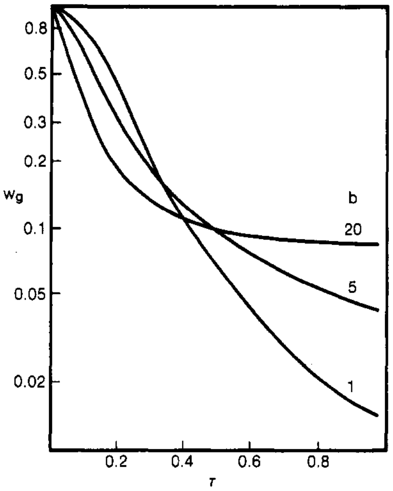


Figure 2. Delignification curves in the form log w_g vs. τ, with values of b specified.

Table I
Delignification Data Calculated by Using $\lambda_0 = 27, p(0) = 0.93, \rho_0 = 0.86$, and $b = 5$

τ	p	λ	ρ	u	w_g
0.05	0.84	11.0	0.29	0.19	0.85
0.1	0.78	7.1	0.25	0.46	0.61
0.15	0.73	5.4	0.26	0.62	0.43
0.3	0.64	3.5	0.33	0.85	0.20
0.6	0.57	2.6	0.40	0.94	0.08
1.0	0.55	2.5	0.41	0.97	0.04

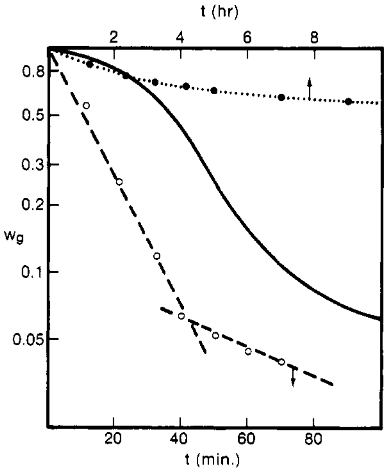


Figure 3. Delignification data in the log w_g vs. t plot. Dashed lines: kraft, drawn as two intersecting lines by Kleinert.[7] Dotted curve: dioxane. The solid curve is the theoretical curve in the previous model (in arbitrary time scale).

The choice of 0.55 for p_∞ has been discussed earlier.

The relationship of chain scission to cross-link breaking reactions is provided by eq 6. For the most probable chain size distribution, we also supplement with

$$\lambda = 2p/(1-p) \tag{9}$$

To provide the same time base for these two degradation processes, let

$$b\tau = kt \tag{10}$$

The gel fraction w_g is calculated from

$$1 - w_g = w_s = (1-\rho)u + \rho u^2 \tag{11}$$

where u is the probability that a unit selected at random belongs to the sol.[12] Dobson and Gordon called it the "extinction probability".[43] Its calculation has been given elsewhere.[20]

Delignification Curve

Calculation of a delignification curve requires the following boundary conditions:[2] At $t = 0$, $p(0) = p_0 + p_\infty$, $\lambda = \lambda_0$, $\rho = \rho_0$, and $w_g = 1$. At $t \rightarrow \infty$, $p(\infty) = p_c = p_\infty$, $\lambda = \lambda_c$, $\rho = \rho_c$, and $w_g = 0$. A residual nonzero ρ_c is used to designate uncleavable cross-links that are formed by diaryl ether, C–C, and other bonds.

We need three parameters for our calculation. First, the value of λ_0 given in the literature[17] has a range 11–27. We choose[17] $\lambda_0 = 27$. Second, given λ_0, $p(0)$ can be calculated by using eq 9, which gives $p(0) = 0.93$. From eq 2, the mole fraction of monomers at the beginning of degradation is 0.07. Since monomers, dimers, and trimers are not considered as cross-linked, we arbitrarily choose twice the value, 0.14, as the minimum non-cross-linked fraction. The maximum cross-linked fraction is therefore $\rho_0 = 1 - 0.14 = 0.86$. This value may be an overestimate because lignin in wood may not be that densely cross-linked.[26]

The third parameter is b. If $b = 0$, we have the breaking of cross-links, but no chain scission. This is the case treated in the previous model.[2] The choice of nonzero values of b is also arbitrary. The calculated delignification curves shown in Figure 2 correspond to $b = 1$, 5, and 20.

It should be emphasized that the choice of the three parameters is arbitrary. More accurate values may be used in the calculation when they are experimentally available.

A typical calculation can be described as follows: A set of parameters λ_0, ρ_0, and b is chosen. The dimensionless time τ is assigned a value, which gives p by eq 8. Equation 9 gives λ, from which r and B can be calculated. The cross-linking density ρ is calculated from eq 5. The cross-linking index at time τ is $\gamma = \lambda\rho$. The calculation of the extinction probability u has been given elsewhere.[20] Alternatively, for the most probable distribution of primary chains, u can be calculated by using the Charlesby–Pinner equation:[45]

$$u + u^{1/2} = 2/\gamma \tag{12}$$

(Charlesby and Pinner[45] actually derived their equation as

$$w_s + w_s^{1/2} = 2/\gamma$$

which has been shown[20] to be a result of using the approximation $w_s \sim u$).

The gel fraction w_g is then calculated from eq 11. Selected values of variables calculated in this way are shown in Table I.

Figure 3 contains actual delignification curves for kraft[7] (170 °C) and dioxane–HCl[26] (40 °C) processes. For comparison, a previously calculated curve using the one-gel model[2] is also included. The degradation curves of dextran gel, obtained theoretically and experimentally by Gardner,[27] have also a similar curve shape in the initial stage to the "theoretical" curve in Figure 3.

Most noticeable is that the experimental curves show an initial rapid rate of weight loss of lignin gel. This weight loss decelerates with increasing time. The previous theoretical curve shows an accelerating trend in the rate of weight loss. This trend persists even for the two-gel model using the breaking of cross-links as the sole kinetics.[2] The disagreement between the decelerating experimental curve and the accelerating theoretical one has been criticized[46] as a discrepancy in the degelation theory. This criticism is apparently valid because a theoretical delignification curve, although not concerned with the fitting of detailed data, should be at least correct in its general shape.

Table II
Calculated Properties of the Sol
(Same Parameters as Table I)

τ	s	$\bar{y}_w'$	$\bar{x}_w'$	R	R(dioxane)[a]	α_4'	α_4'(dioxane)[b]
0.05	0.77	4.7	7	2.2	2.2	0.12	0.28
0.1	0.86	5.2	13	3.3	2.9	0.21	0.29
0.15	0.91	4.9	20	4.9	3.9	0.26	0.31
0.3	0.95	4.0	43	11		0.31	
0.6	0.98	3.5	108	27		0.32	
1.0	0.99	3.4	275	68		0.33	

[a] Dispersion ratios of dioxane lignin at the corresponding w_g values are those obtained by Pla.[26] [b] Branching probabilities of dioxane lignin are those recalculated[18] from Pla's data.[26]

The new delignification curves shown in Figure 2 have successfully removed this discrepancy, although detailed data fitting has yet to be done. As can be expected, lower values of b tend to exaggerate the cross-linking part of the kinetics. Thus, for $b = 1$, a small accelerating effect is noticeable. For even smaller values of b, the delignification curves approach the case where $b = 0$, which corresponds to the complete neglect of chain scission.[2]

Properties of the Sol

Postgel properties of the sol fraction can be calculated with the equations listed in Appendix II. These equations are those derived by Flory[12] and made explicit by us.[20] It should be noted that expressions for the postgel DP averages and the MWD in the sol are obtained by replacing p in the corresponding pregel expressions with ps, where

$$s = 1 - \rho + \rho u \tag{13}$$

For the primary chains, the postgel DP averages are given by

$$\bar{y}_n' = (1 - ps)^{-1} \tag{14}$$

$$\bar{y}_w' = 2ps(1 - ps)^{-1} + 1 \tag{15}$$

The calculated postgel properties are given in Table II, using the same set of parameters as Table I. For comparing general trends by use of these calculations, we also listed the measured dispersion ratios and branching probabilities of dioxane lignin.[26] The comparison of a set of calculations for kraft lignin and the data for dioxane lignin appears unfair. Unfortunately, similar measurements on kraft lignin are not available. On the other hand, we do not attempt to calculate the delignification curve and postgel properties of dioxane lignin on the recognition that the cleavable bonds and their extents of cleavage in the dioxane process are not well defined.

It is surprising that similar measurements of solution properties have not been made for kraft lignin, despite its wide application and long history. Key polymeric parameters needed for lignin characterization are the weight-average DP, the MWD of branched lignin in the sol (or its dispersion ratio), and its branching probability. Another important parameter is the initial chain length λ_0. This parameter is dependent on wood (species, age, location, etc.) but not on the process. It may remain as a speculative parameter for some time to come.[2] When the measuring technique for λ_0 is available, it may serve as an important factor in characterizing wood.

Discussion and Conclusions

Isothermal delignification data in the early stages are usually depicted as a straight line in a semilog plot, first order in w_g.[5,7] To account for the curvature in the later stages, an additional first-order line is drawn. These two lines intersect at the onset of "residual" delignification.[7] Alternatively, the curvature is accounted for by increasing the "order" of reaction.[8] Since the weight-loss "kinetic" schemes are nonmolecular,[1,2] these methods of expressing delignification curves are considered as biased. However, isothermal delignification data do show a trend with a specific curve shape throughout the entire range, as shown in Figure 3. With respect to this trend, the theoretical curves in Figure 2 are in complete agreement with the unbiased data.

Higher values of b have an effect on the curve shape similar to that of higher temperature as we compare the curves in Figure 2 with raw data.[7] It may be tempting to assume an Arrhenius type of temperature dependence for b, using an activation energy of an appropriate model compound. As the kinetics of a model compound retains its molecularity,[2] the activation energy thus calculated may be used with confidence. Such activation energies are available[44] for both phenolic and nonphenolic β-aryl ether bonds, which have the same value of 32 kcal/mol. However, even if this activation energy can be assigned to the Arrhenius relation for b, the relation for k_2 remains undetermined.

Molecular data calculated for the kraft lignin sol, shown in Table II, agree qualitatively in every aspect with our previous argument.[17] The comparison of calculated data with measured properties of dioxane lignin should be made with caution, as similar systematic measurements for kraft lignin are still lacking. The calculated weight-average DP at a given w_g also agrees well with that measured for the kraft lignin.[47] In general, these averages are lower than those for sulfite and dioxane lignins[17,24,47] at the corresponding values of w_g. Molecular parameters such as λ_0 and ρ_0 are characteristic of the starting material (wood) used. Process parameters p_∞ and ρ_c and rate constants k, k_1, and k_2 are obviously dependent on the chemicals used, which determine the bond type and extent of cleavage in delignification. The rate constants are also temperature dependent.

Both the kinetic and MWD data are needed to determine the structural properties of lignin. It has been shown theoretically that the structural interpretation and gelation process are not separable in a treelike model.[29] The same can be said about the branched-chain lignin structure and the delignification process. Obviously, this implication may be extended to lignification, a process practiced by nature.

The power of the degelation theory is due to the fact that it is basically a molecular theory. For delignification, specific conclusions can be summarized as follows: (i) Lignin, in natural or degraded form, may be treated as a branched polymer; the natural form exists as an insoluble polymeric gel. (ii) This branched-chain structure can be described as a cross-linked, treelike molecule. (iii) The primary chains cross-linked have the most probable distribution, or quickly assume this distribution on degradation. (iv) Delignification is analogous to degelation by which specific linkages in the linear chain and at the cross-links are cleaved. (v) The kraft process is specific for the liberation of PhOH groups from the cleavable aryl ether bonds. This specificity determines the rate and extent of cleavage. (vi) The basic unit in softwood lignin is the phenylpropane (C_9) unit. A trifunctionally linked unit is cleaved through the nonphenolic β-aryl ether bond in the kraft process. (vii) Process parameters and rate constants have been estimated. The estimation may be rough but has qualitatively interpreted the delignification curves and the molecular properties of the lignin sol. (viii) The applicability of the treelike model to lignin macromolecules implies that both lignification and delignification occur largely at random. Isothermal kinetics support this implication.

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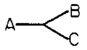
Appendix I. Symbols

A, B, C	functional groups in polyfunctional monomers RA_n, AB_2, and 
B	$=[r(r+4)]^{1/2}$ in eq 5
b	$=kt/\tau$ in eq 10
C	integration constant in eq 5
k, k_1, k_2	rate constants in eq 1, 1a, and 7
k_B	Boltzmann constant
n	number of functional groups in RA_n
$p = p(t)$	extent of reaction of linear polymer at time t
p_c	critical extent of reaction at the gel point
p_0	integration constant in eq 8
p_∞	extent of reaction at $t \rightarrow \infty$
R	dispersion ratio in the sol, defined in eq A4
r	defined by eq 6
s	defined by eq 13
T	absolute temperature
t	time
u	extinction probability
$w(y)$	weight distribution of linear y-mers = weight fraction of the y-mer
w_g	weight fraction of the gel
w_s	weight fraction of the sol
$\bar{x}_n'$	number-average DP of cross-linked molecules in the sol
$\bar{x}_w'$	weight-average DP of cross-linked molecules in the sol
y	DP of primary chains
$\bar{y}_n'$	number-average DP of primary chains in the sol
$\bar{y}_w'$	weight-average DP of primary chains in the sol
α, β, γ	position of carbon atom in I
α	fraction of liberated PhOH groups in eq 1
α_4	branching probability of a tetrafunctional branch point
α_4'	branching probability in the sol
$\gamma = \lambda\rho$	cross-linking index
λ	$\bar{y}_w - 1$
λ_0	initial value of λ at $t = 0$
ρ	cross-linking density
ρ_0	initial cross-linking density at $t = 0$
ρ_c	critical cross-linking density at the gel point
ρ'	cross-linking density in the sol
$\tau = k_2t$	dimensionless time
ϕ	symbol used in II to designate a phenolic aryl ether

Appendix II. Postgel Relations in the Sol

After the gel point ($\rho > \rho_c$), the sol has a cross-linking density given by[12,20]

$$\rho' = \rho u^2/w_s \qquad \text{(A1)}$$

The DP averages of the primary chains in the sol are given by eq 14 and 15. The averages of cross-linked molecules are

$$\bar{x}_n' = \bar{y}_n'(1 - \bar{y}_n'\rho'/2)^{-1} \qquad \text{(A2)}$$

$$\bar{x}_w' = \bar{y}_w'(1 + \rho')[1 - (\bar{y}_w' - 1)\rho']^{-1} \qquad \text{(A3)}$$

These expressions give the dispersion ratio in the sol fraction:

$$R = \bar{x}_w'/\bar{x}_n' \qquad \text{(A4)}$$

The branching probability of a tetrafunctional branch point in the sol is obtained by replacing ρ and p in eq 3 with ρ' and ps, respectively:

$$\alpha_4' = p\rho's/[1 - ps(1 - \rho')] \qquad \text{(A5)}$$

Model Calculations

$$\lambda_0 = 27 \qquad p(0) = 0.93 \qquad \rho_0 = 0.86 \qquad b = 5$$

Define

$$r_0 = (27 - 1)^2/27 = 25.04$$

$$B_0 = [r_0(r_0 + 4)]^{1/2} = 26.96$$

$$X_0 = (r_0 + 2 - 2\rho_0)/B_0$$

We have $X_0 = 0.9388$ (instead of C).

Assume $\tau = 0.1$. From eq 8, $p = (0.93 - 0.55)\exp(-0.1 \times 5) + 0.55 = 0.78$, from eq 9, $\lambda = 2 \times 0.78/(1 - 0.78) = 7.1$, and from eq 6, $r = (7.1 - 1)^2/7.1 = 5.24$ and $B = [r(r + 4)]^{1/2} = 6.96$.

Equation 5 is the same as

$$\left(\frac{1 + X}{1 - X}\right)\left(\frac{1 - X_0}{1 + X_0}\right) = \exp(\tau B)$$

We have $X = 0.9691 = (r + 2 - 2\rho)/B$ or $\rho = 0.248$.

$$\gamma = \lambda\rho = 1.76$$

From eq 12, $u = 0.456$ and from eq 13, $s = 0.864$.

$$w_s = su = 1 - w_g = 0.394 \qquad \text{or} \qquad w_g = 0.61$$

From eq 15, $\bar{y}_w' = 5.2$, from eq A3, $\bar{x}_w' = 13$, from eq A4, $R = 3.3$, and from eq A5, $\alpha_4' = 0.21$.

The procedure is described in the text. In addition, two versions of computer programs give the same result.

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(18) When two sufficiently long chains react, they may be linked in three ways: (i) end-to-end, thus forming a longer chain; (ii) end-to-nonterminal unit, thus creating a trifunctional branch point; (iii) nonterminal unit to nonterminal unit, thus forming a tetrafunctional branch point. Our assumption of a most probable distribution of primary chains implies that branch points are tetrafunctional. Pla calculated the branching probabilities based on trifunctional branch points from the measured "*g* factors" in the sol fraction of dioxane lignin.[26] We recalculated, from the same *g* factors, these probabilities based on tetrafunctional branch points. The relationships between branching probability and the *g* factor are given by Zimm and Stockmayer (Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301).

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Volume Dependence of the Elastic Equation of State. 2. Solution-Cured Poly(dimethylsiloxane)

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ABSTRACT: Vapor sorption measurements for solution-cured poly(dimethylsiloxane) + cyclohexane are reported. The Flory–Huggins interaction parameter χ is found to be $\chi = 0.433 - 0.010v_2$, where v_2 is the volume fraction of polymer. Differential solvent vapor sorption by cross-linked and un-cross-linked PDMS is reported as a function of volume fraction of solvent in the cross-linked PDMS. The elastic component of the solvent chemical potential is investigated as a function of the degree of dilation. Qualitative differences between bulk-cured and solution-cured samples are apparent, and Flory's recent theory of rubber elasticity accounts qualitatively for this behavior.

Introduction

The behavior of solvent-swollen elastomers is dependent upon the thermodynamics of both the mixing process and the elastic restoring forces. If one assumes, with Flory,[1] that these two contributions to the free energy are additive, it follows that the chemical potential of the diluent consists of additive contributions and that the thermodynamic activity of the diluent is the product of two separable components. If $a_{1,c}$ and $a_{1,u}$ represent, respectively, the activities of solvent in cross-linked and un-cross-linked, but otherwise identical polymers, then the ratio $a_{1,c}/a_{1,u}$ at equal polymer volume fractions is the elastic contribution to the solvent activity. Accordingly, this ratio of activities should be comprehensible solely in terms of the elastic equation of state.

Experiments to test this prediction were conducted some years ago by Gee, Herbert, and Roberts[2] on natural rubber (NR) + benzene and more recently by Yen and Eichinger[3] on poly(dimethylsiloxane) (PDMS) + benzene, poly(styrene-*co*-butadiene) (SBR) + benzene, and SBR + *n*-heptane. In all cases the quantity $\lambda \ln (a_{1,c}/a_{1,u})$ exhibits a maximum when plotted against λ^2, where $\lambda^3 = (V/V_0)$ is the ratio of the volume V of the isotropically swollen elastomer to the dry volume V_0 (swelling ratio). The magnitude of the maximum appears to be system dependent, but the fact of its presence in the four systems investigated to date can scarcely be questioned.

The authors of the experiments cited above were unable to account for this result with conventional theories of elasticity and resolved that the assumed additivity of contributions to the free energy was questionable. This conclusion was rejected by Flory,[4] who showed that the swelling behavior is encompassed by his treatment of the constraints which act to limit the range of configurations available to cross-linkages. He predicted that if experiments were performed with solution-cured polymers, their behavior would be qualitatively different from that observed with the bulk-cured samples that had preoccupied the previous investigators.

With the urging and assistance of Professor J. E. Mark, we have undertaken a series of measurements to test this prediction.

Experimental Section

Polymer. The poly(dimethylsiloxane) (PDMS) used for this study was kindly supplied by Professor J. E. Mark. The un-cross-linked polymer contains 0.5 mol % (methylvinyl)siloxane

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