Lignin. 21. Depolymerization by Bond Cleavage Reactions and Degelation

Johnson F. Yan*[1a,b]

Weyerhaeuser Technology Center, Weyerhaeuser Company, Tacoma, Washington 98477

Fernand Pla,[1c] Ryuichiro Kondo,[1d] Matti Dolk, and Joseph L. McCarthy[1a]

Department of Chemical Engineering, University of Washington,
Seattle, Washington 98195. *Received December 28, 1983*

ABSTRACT: The complex chemical reactions in the delignification of wood are categorized as composed of three main stages: (1) primary degradation in which the native lignin gel is depolymerized into smaller polymeric fragments which dissolve, (2) deactivation or repolymerization of reactive smaller polymer fragments, and (3) further hydrolysis of the dissolved polymers into the ultimate "ω-lignin" containing only uncleavable bonds. In a conventional batch delignification, the first two stages are not separable, while the third may require further reaction. In processes conducted with high liquid-to-wood ratios at the early stage, or with successive incremental batch processes, or with continuous degradation processes conducted using a flow-through reactor, repolymerization (or "condensation") reactions can be eliminated or minimized. In the absence of condensation, the primary degradation process is now formulated as independent depolymerization reactions associated with the cleavage of up to four different types of aryl ether bonds. Experimental data on the rate of dissolving of the gel mass fraction are used to obtain some of the rate constants of these parallel reactions. Flory's postgel relations are used to quantify average molecular weights. These relations are relatively simple when the primary chains in the sol and in the overall system are assumed to be present in the "most-probable" distribution. The change of molecular parameters during delignification is interpreted in terms of a recently proposed molecular theory, and no contradictions to the proposed theory have been found.

Introduction

As a result of many decades of research, much knowledge of the nature and reactions of lignins has been acquired, and this information has been ably summarized by Sarkanen and Ludwig[2] and others. It is well established that gymnosperm lignins are branched chain polymers made up of structural units which are mainly guaiacylpropane-type configurations. These are joined by linkages of several kinds, and Adler[3] has estimated the frequency of occurrence of a number of these. Gierer[4] and others have indicated that some linkages are moderately easily hydrolyzable, and some are not.

The objective of the research to be reported here, and in certain forthcoming papers, is to gain an enhanced understanding of the nature and frequency of occurrence of the several types of linkages joining the structural units in lignin polymers, the kinetics of hydrolysis of those that can be cleaved, and the nature of the lignin fragments which come into being as a result of the cleavage reactions.

Although qualitative studies of the depolymerization of lignins were carried out many years ago by one of the authors[5] as well as by others,[2] quantitative kinetic studies on model compounds have been conducted only recently, for example by Ljunggren[6] and Obst.[7] Complementary to these model compound investigations are the kinetic and molecular approaches carried out by one of the authors[8,9] on the lignin polymer itself, as present in woody tissue or in liquid solution.

Yan[8,9] and Pla[10] view native lignin as a branched chain polymer which has gelled. With this concept (see sketch in Figure 1), the depolymerization of lignin can be considered as consisting of three kinetically different stages: (A) primary degradation or degelation—the native polymer gel is degraded into smaller polymeric fragments which become dissolved and comprise the sol phase, (B) recondensation—the sol polymers, which may still contain reactive groups, may be quenched or deactivated, or may recombine to form new polymers,[11] and (C) posthydrolysis—the sol polymers may be further degraded in an appropriate homogeneous solution until all cleavable bonds are broken, whereby there results the ultimate "ω-lignin".[5] Depending on the extent of recondensation, the ω-lignin may assume different forms as shown as ω_1 and ω_2 in Figure 1.

This paper deals with the molecular aspects of the primary degelation process and mainly *in situations where recondensation is minimized or avoided*. In contrast, in a prior paper,[8] a theory was presented for a batch delignification system in which condensation was considered to occur. In later papers, we expect to report procedures and results obtained relative to depolymerization of lignins under several experimental conditions, along with the results of our efforts to present useful structural and mathematical interpretation.

Kinetics of Bond Cleavage

Mathematical Formulations. We consider that native lignin in the wood is all in the gel phase so the gel fraction by weight = g = 1 at time = t = 0, where g is related, at any time, to the weight fraction of the sol, s:

$$g + s = 1$$

It is assumed that the structural unit in lignins is a C_9 unit, and that each unit has one phenolic hydroxyl (PhOH) group which can be either free or bound as an ether bond.[8] The fraction of C_9 units existing in the linear chain portion of lignin is p'', and that in the branch portion is α'', in accord with the structures in Figure 1. The double prime signs denote that these fractions are in the gel phase. Therefore we have

$$g(t) = p'' + \alpha'' \tag{1}$$

Since the reactivity of the ether bond determines the rate and the extent of bond cleavage reactions, further classification of the ether bonds is needed for the formulation of kinetics. Unlike the theory developed for a batch system allowing recondensation,[8] the scheme that follows is concerned only with the gel portion.

Empirical evaluation of the rate of weight loss of gel lignin may be approached by testing for a first-order process. However, difficulties are encountered because the plot of ln g vs. t deviates from linearity, even at an early

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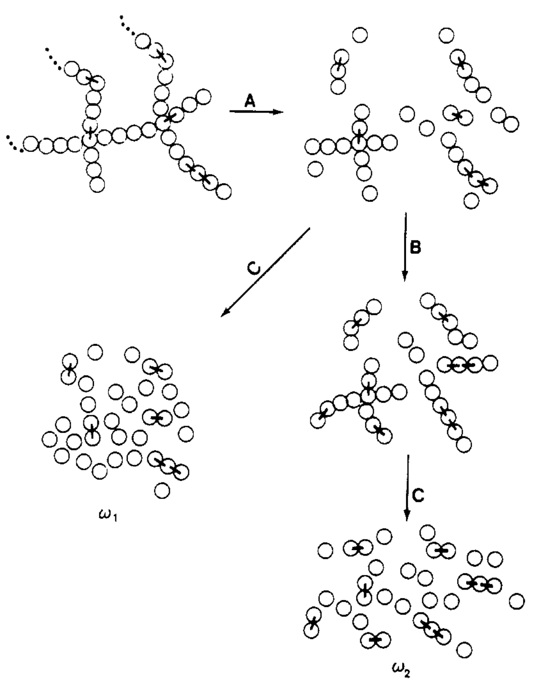


Figure 1. Sketch of depolymerization mechanism of lignin. Circles denote C_9 units; bars are uncleavable bonds.

stage of delignification.[12] Various methods have been devised to account for this deviation or curvature, but none of them are satisfactory from a molecular viewpoint.[8]

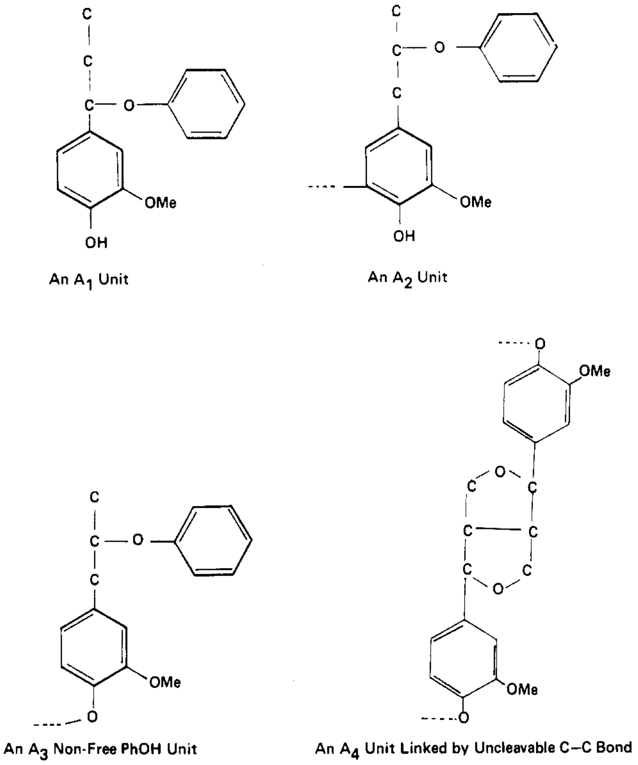
An even more fundamental question is the use of weight or weight fraction in treatment of the degradation kinetics of polymers.[8] In the general case, the molar concentrations needed for kinetic formulation of depolymerization may not properly be replaced by mass or weight of lignin. Even for the degradation of linear polymers, a first-order mass decay relationship is permissible only under limited structural situations for the polymers in question. However, first-order mass decay does result from kinetics[13] if one assumes (1) that the polymer under study has a "most-probable" distribution, (2) that the "zip" length (or the size after degradation) also has a most-probable distribution, and (3) that the zipping frequency has a Poisson distribution such that the zipping reaction is first order. These conditions can be met by considering that the reacting bonds are randomly distributed in the system and that bonds of a given kind are equally reactive. In the case of linear polymers, deviation from first-order weight loss kinetics is still appreciable in the later stage of degradation. This deviation has been attributed to the presence of another bond type but the phenomenon has not been quantified.[13]

For degradation of the lignin gel polymer, the same random distribution and equal reactivity concepts can be applied. However, the lignin gel appears to contain more than one type of cleavable aryl ether bonds, and these are present initially in the wood with different abundances.[3,4] Depending on their location in the lignin macromolecules, the structural units containing the various bond types can be further classified (Figure 2) as follows.

A_1 units: those with α-O-4 ether bonds to rings with *free phenolic* hydroxyl (PhOH) groups and present either as terminal units (chain ends) or as nonterminal units.

A_2 units: those with β-O-4 ether bonds to rings with *free PhOH* groups and present either as terminal units or as nonterminal units.

A_3 units: those with either β-O-4 or α-O-4 bonds to phenyl rings with *non free PhOH* groups and present as nonterminal units. The β-O-4 bonds in this category are the most abundant linkages in lignins, and these may exist in two isomeric forms, as presented in a model dimer.[7] Further complicating this type of unit is the fact that it may be present in the linear chains or in structural units which may comprise branching points.[8]



An A_1 Unit

An A_2 Unit

An A_3 Non-Free PhOH Unit

An A_4 Unit Linked by Uncleavable C–C Bond

Figure 2. Classification of lignin units according to the status of bonding of PhOH groups. See text for symbols used.

A_4 units: those having substantially noncleavable bonds such as the carbon–carbon linkages in pinoresinol.[8] The fraction of these units in the total *PhOH-containing* units is small[3,4] and they may generally be neglected in weight loss studies when the degradation is still far from completion.

On the basis of the above considerations, these aryl ether bonds, assuming they are randomly distributed in the lignin, are considered to be cleaved according to the weight first-order rate law. Kinetically the units may exist as A_1, A_2, and A_3 before cleavage, but all may become dissolved units, A_s, on degradation:

$$A_1 \xrightarrow{k_1} A_s$$

$$A_2 \xrightarrow{k_2} A_s$$

$$A_3 \xrightarrow{k_3} A_s$$

As written, the rate constants refer to those of dissolution reactions. However, a unit may exist in a dissolved polymer fragment without breaking all cleavable bonds. But the cleavage rate constant is proportional to the weight loss constant if the initial and degraded polymers have constant number-average DP.[13] This is indeed the case in delignification because lignin gel has a very large ("infinite" by Flory's theory of gelation) but constant DP.

Since the reactions are simultaneous and parallel with a common product, their mathematical form can be expressed as[14]

$$p'' = p_1 e^{-k_1 t} + p_2 e^{-k_2 t} + p_3 e^{-k_3 t} + p_\infty \qquad (2)$$

where p_1, p_2, and p_3 are the initial fractions of A_1, A_2, and A_3 units in the *linear* chains; p_∞ is the uncleavable fraction.

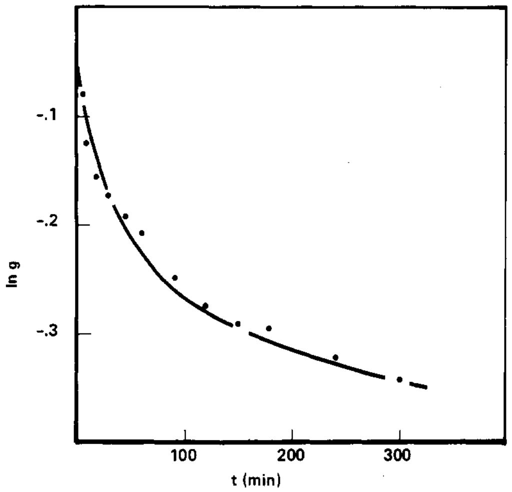


Figure 3. Batch delignification of hemlock wood meal at 120 °C with kraft liquor (10:1 liquor:wood ratio, 30% sulfidity). Only the initial stage of delignification was investigated.[12]

Since a branch unit may also be an A_3 unit (see formula II in ref 8), the cleavage at branch points is expressed as

$$\alpha'' = \alpha_0 e^{-k_3 t} + \alpha_\infty \qquad (3)$$

where α_0 is the initial fraction of A_3 units present as branch units. From eq 1

$$g(\infty) = p_\infty + \alpha_\infty$$

According to the assumed reactivities of the various ether bonds, the rate constants can be listed in the order $k_1 > k_2 > k_3$.

Comparisons of Theory with Experimental Results. Recently three good sets of experimental data have become available, and these may be interpreted in terms of the kinetic schemes outlined above.

Data of Kondo and Sarkanen.[12] In their study of the *initial* phase of delignification by use of the kraft process, Kondo and Sarkanen obtained lignin weight loss data for the digestion of hemlock wood meal at 120 °C as shown in Figure 3. The 12 data points show significant deviation from the first-order behavior. The experiment was designed to study the initial phase of batch delignification, and thus the process was not carried out far enough to allow the evaluation of all rate constants. However, for large values of t (in minutes), the last two points in a ln g vs. t plot can be fitted by use of the equation

$$g \sim 0.78e^{-0.00034t} \qquad (4)$$

The difference between the observed g values and those given by eq 4, i.e.

$$\Delta = g - 0.78e^{-0.00034t}$$

can be evaluated for small t, and a least-squares fit of ln Δ vs. t yields

$$\Delta = 0.16e^{-0.027t}$$

Therefore, the entire set of these data can expressed as a two-term function:

$$g = 0.16e^{-0.027t} + 0.78e^{-0.00034t} \qquad (5)$$

This equation is shown as the solid curve in Figure 3. The sum of the preexponential factors, 0.16 + 0.78 = 0.94, is close to 1 so that no additional terms needed to be evaluated. In other words, this set of data can be used to evaluate two rate constants.

Data of Pla and Robert.[15] These data were obtained by use of an isothermal incremental extractive delignification of spruce wood meal with dioxane–HCl at 70 °C. Using the same technique as described above to calculate the later portion from the last three data points gives (with t in h)

$$g \sim 0.51e^{-0.00367t} \quad \text{for large } t \qquad (6)$$

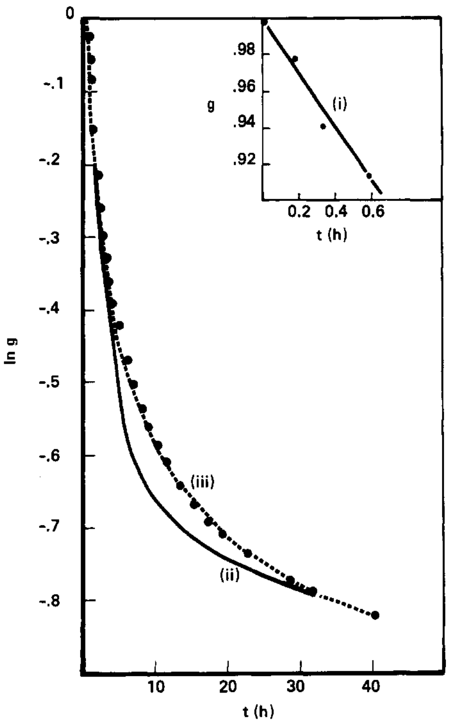


Figure 4. Successive extraction of spruce wood meal with 0.1 M HCl in dioxane[10,15] at 70 °C. See text for detailed explanation of curve numbers.

Twenty-five points are shown in Figure 4. However, unlike the previous case, this set of data allows the evaluation of a rate constant at the early stage by plotting g vs. t (see insert in Figure 4). This may be done because the weight loss is small for small values of t. For $k_1 t < 0.05$ the approximation

$$r^{-k_1 t} = 1 - k_1 t$$

can be used. This yields the line in the insert of Figure 4:

$$g \sim -0.146t + 0.998$$

This is indicated as line i. Obviously, $p_1 k_1 = 0.146$. On this basis, the entire range of data based on two exponential terms is represented as curve ii in Figure 4 and is expressed as

$$g = 0.49e^{-0.298t} + 0.51e^{-0.00367t} \qquad (7)$$

However, a noticeable deviation of curve ii from the experimental curve still exists. Therefore, an additional term is included such that

$$g = ae^{-k_1 t} + (0.49 - a)e^{-k_2 t} + 0.51e^{-0.00367t} \qquad (8)$$

with

$$ak_1 = 0.146$$

Deviations of experiments from eq 7 are large in the median range of t. From original numerical data,[10,15] it can be noted that

$$g = 0.559 \quad \text{at } t = 10 \text{ h}$$

$$g = 0.513 \quad \text{at } t = 15.5 \text{ h}$$

Table I
Rate Constant for the Cleavage of Non-Phenolic β-Aryl Ether Bond at 170 °C

method and system	k_3, min^{-1}	ref
model, kraft	0.0158	6
model (erythro form), soda[a]	0.017	7
theory, kraft	0.018	8
FTR, soda (UV absorption basis)	0.015	16
FTR, soda (weight basis)	0.017	work in progress

[a] Cooking of a 60:40 erythro–threo mixture of veratrylglycerol–β-guaiacyl ether[7] can be expressed as fraction of starting material remained = $0.6e^{-0.017t} + 0.4e^{-0.0038t}$. This result can obviously be obtained by using the technique outlined in this section.

These relationships can be used along with eq 8 to evaluate the three-term rate expression:

$$g - 0.51e^{-0.00367t} = 0.067 = ae^{-1.46/a} + (0.49 - a)e^{-10k_2}$$

$$g - 0.51e^{-0.00367t} = 0.031 = ae^{-2.263/a} + (0.49 - a)e^{-15.5k_2}$$

and these two equations may be solved simultaneously to yield

$$a = 0.22 \qquad k_2 = 0.14\ \mathrm{h}^{-1}$$

Thus the final three-term equation becomes

$$g = 0.22e^{-0.664t} + 0.27e^{-0.14t} + 0.51e^{-0.00367t} \tag{8a}$$

This result is shown as curve iii in Figure 4, and the fit is considered excellent with a root mean square residue of 0.01 in gel fraction. Alternately, a least-squares method may be employed to obtain these rate constants. However, our method outlined here is more deductive with respect to the development of the kinetic scheme.[14]

Data of Dolk et al.[16] In a special effort to avoid the occurrence of recondensation during the primary degradation, Dolk et al.[16] studied delignification by using a "flow-through" reactor ("FTR"), similar to that employed previously by Yean and Goring[17] and others. In their preliminary report on the delignification of thin hemlock wood platelets, these authors described use of a sodium hydroxide solution to delignify at 170 °C, a temperature range of practical importance. The technique of FTR allows frequent or continuous detection and collection of reaction products. Absorbance of radiation in 280 nm is used to estimate the concentration of dissolved lignin in the effluent stream leaving the reactor. An absorbance–time curve is obtained for each run. This curve rises rapidly to a peak absorbance, then decreases exponentially with time. The rate constant obtained in this exponential region[16] is 0.015 min^{-1}. A similar experiment based upon weight fraction of lignin remaining in the gel phase gave a first-order rate constant of 0.017 min^{-1} for the main delignification process. These experiments will be reported in detail in a later paper.

The rate constants obtained in the Dolk et al.[16] experiments should be dominantly representative of the cleavage of β-aryl ether bonds associated with a non free phenolic hydroxide residue, the most frequently occurring type of hydrolyzable bond. These results are seen in Table I to be in moderately good agreement with results reported in the literature by Ljunggren[6] and Obst[7] for the hydrolysis of linkages in model substances and by Yan[8] from theoretical considerations. This agreement suggests that this cleavage rate is independent of alkalinity and the presence of Na_2S and whether the reaction is homogeneous or heterogeneous. A great excess of NaOH present in the reaction vessel would ensure a first-order cleavage rate and, to some extent, would eliminate physical barriers and chemical condensation. However, detailed mechanism of these reactions requires further investigation.

Consideration of Gel–Sol Transition

Mathematical Formulations. The above described kinetic aspects of delignification constitute only part of molecular theory which may be connected to other properties of gel and sol based upon the concepts[8-10] of branched chain structures and the degelation of lignin.

When Flory's notation with the prime sign denoting the sol properties is used, the distribution for sol and gel of the cross-linking density α is given[18] by

$$\alpha = s\alpha' + g\alpha'' \tag{9}$$

Also, according to Flory[18]

$$\alpha' = \alpha u^2/s \tag{10}$$

where u is the extinction probability.[8] Other relations derived by Flory are

$$s = (1 - \alpha)u + \alpha u^2 \tag{11}$$

$$\bar{x}_n' = \bar{y}_n'(1 - \bar{y}_n'\alpha'/2)^{-1} \tag{12}$$

$$\bar{x}_w' = \bar{y}_w'(1 + \alpha')(1 - (\bar{y}_w' - 1)\alpha')^{-1} \tag{13}$$

where $\bar{y}_n'$ and $\bar{x}_n'$ are the number-average DP of the primary chains and of the resultant branched polymers, respectively, and $\bar{x}_w'$ is the weight-average DP of the branched polymers in the sol.

In a prior study,[8] these postgel relations have been used for the evaluation of batch delignification of wood. The sol fraction and DP averages can be measured for each sample collected. The calculation of other parameters is fairly simple provided one makes the assumption that the forms of $\bar{y}_n'$ and $\bar{y}_w'$ are in accord with the most-probable distribution[8] for the primary chains, i.e., that these DP averages are given by

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

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

where p' is the extent of reaction of primary chains in the sol fraction.[8,9]

Equations 12 and 13 can then be transformed into two equations with two unknowns, p' and α'. Each pair of $\bar{x}_n'$ and $\bar{x}_w'$ yields the required p' and α'. Similarly, by combining eq 10 and 11, the result is a quadratic equation in u, with the measured s value and the calculated α' appearing in its coefficients. From eq 9, α'' can be calculated so that the kinetics in eq 3 can be established.

Comparison of Theory with Experimental Results. Published data are usually not detailed and thorough enough to provide a good basis for comparison with theory. The only exception appears to be the work of Pla[10,15] based on the extractive delignification of spruce wood with a dioxane–HCl solution. Using this set of data, detailed calculations have been made by using the procedures shown in the Appendix, and the results are shown in Tables II and III. The kinetic data, shown in Figure 4, are also given in Table III.

The α'' values shown in Table III do not follow an exponential trend at any stage of delignification. In fact, they appear to be fairly constant throughout, as evident from the average value of 0.052 ± 0.006. Comparing this result with eq 3, one concludes that

$$\alpha_0 = 0 \qquad \alpha_\infty = 0.052$$

In other words, the cross-linking density in the lignin gel fraction remains constant at 0.052 as calculated by using Flory's theory. Within the framework of this concept, this

Table II
Sol Properties of Dioxane Lignin[a]

fraction	$\bar{x}_n'$	$\bar{x}_w'$	r'	p'	α'	$\bar{y}_w'$
P1	10.42	19.14	1.84	0.905		20.0
P2	10.58	21.41	2.02	0.904	0.0036	19.8
P3	11.39	23.04	2.02	0.911	0.0032	21.5
P4	11.99	26.36	2.20	0.913	0.0079	22.0
P5	13.09	29.19	2.23	0.920	0.0076	24.0
P6	13.82	31.25	2.26	0.924	0.0076	25.3
P7	14.08	33.09	2.35	0.924	0.0091	25.3
P8	14.06	35.34	2.51	0.923	0.0117	25.0
P9	14.19	36.02	2.54	0.923	0.0123	25.0
P10	14.37	37.04	2.58	0.924	0.0128	25.3
P11	14.55	38.72	2.66	0.925	0.0135	25.7
P12	14.82	41.41	2.80	0.925	0.0154	25.7
P13	15.03	42.88	2.85	0.926	0.0153	26.0
P14	15.23	44.82	2.94	0.926	0.0161	26.0
P15	15.39	46.60	3.03	0.927	0.0171	26.4
P16	15.50	47.41	3.06	0.927	0.0172	26.4
P17	15.65	48.90	3.12	0.927	0.0173	26.4
P18	15.76	50.94	3.23	0.927	0.0183	26.4
P19	15.81	52.25	3.30	0.924	0.0187	25.3
P20	15.89	54.08	3.40	0.927	0.0195	26.4
P21	15.94	54.76	3.44	0.927	0.0200	26.4
P22	16.05	56.23	3.50	0.928	0.0200	26.8
P23	16.02	58.64	3.66	0.927	0.0213	26.4
P24	16.07	59.45	3.70	0.927	0.0215	26.4
P25	16.18	61.44	3.80	0.927	0.0221	26.4

[a] Fraction numbers are those specified by Pla.[10,15] DP are obtained[10] by dividing molecular weight averages by 191. $\bar{x}_n'$ and $\bar{x}_w'$ are measured quantities; r', p', α', and $\bar{y}_w'$ are calculated quantities.

Table III
Calculated Branching Parameters[a]

fraction	t, h	s	u	α	α''
P1	0.17	0.0217			[b]
P2	0.33	0.0570	0.0602	0.0562	0.059
P3	0.58	0.0855	0.0883	0.0346	0.038
P4	1.25	0.144	0.1504	0.0503	0.058
P5	1.75	0.194	0.1999	0.0367	0.044
P6	2.25	0.2292	0.2348	0.0314	0.039
P7	2.75	0.2572	0.2637	0.0338	0.042
P8	3.25	0.2841	0.2921	0.0388	0.050
P9	3.75	0.3045	0.3127	0.0383	0.050
P10	4.25	0.320	0.3283	0.0379	0.050
P11	5.00	0.341	0.3496	0.0377	0.050
P12	6.00	0.371	0.3803	0.0395	0.054
P13	7.00	0.393	0.4019	0.0372	0.051
P14	8.00	0.413	0.4221	0.0373	0.052
P15	9.00	0.429	0.4384	0.0381	0.054
P16	10.00	0.441	0.4502	0.0374	0.053
P17	11.50	0.4565	0.4656	0.0365	0.053
P18	13.50	0.474	0.4833	0.0371	0.054
P19	15.50	0.487	0.4962	0.0370	0.054
P20	17.50	0.498	0.5074	0.0376	0.056
P21	19.50	0.507	0.5165	0.0381	0.057
P22	22.50	0.517	0.5263	0.0373	0.056
P23	28.50	0.538	0.5475	0.0382	0.058
P24	31.50	0.545	0.5544	0.0382	0.058
P25	40.00	0.559	0.5684	0.0382	0.059
average					0.052 ± 0.006

[a] t and s are measured quantities; u, α, and α'' are calculated quantities. [b] Not calculated due to the negative value of α'.

means that about 5% of the structural lignin units remain as cross-linked units in the gel throughout the period of extensive extraction with dioxane–HCl.

In the sol fraction, the cross-linking density, α', increases with delignification so that the measured polydispersity, r', also increases (Table II). It appears that the highly polydispersed molecules can be accounted for only in terms of a branching theory.[8-10]

Also, it is interesting to note that the weight-average DP of the primary chains in the sol fraction, $\bar{y}_w'$, increases to a maximum value of 27. Although this extraction is extensive, complete delignification has not been achieved because dioxane–HCl is a rather mild delignifying agent at the temperature studied. However, the ultimate value of $\bar{y}_w'$ in Table II, in the absence of condensation processes, may never be larger than that originally presented in wood; the latter was estimated to have a value of 28, in the development of the delignification theory for the batch process.[8,9]

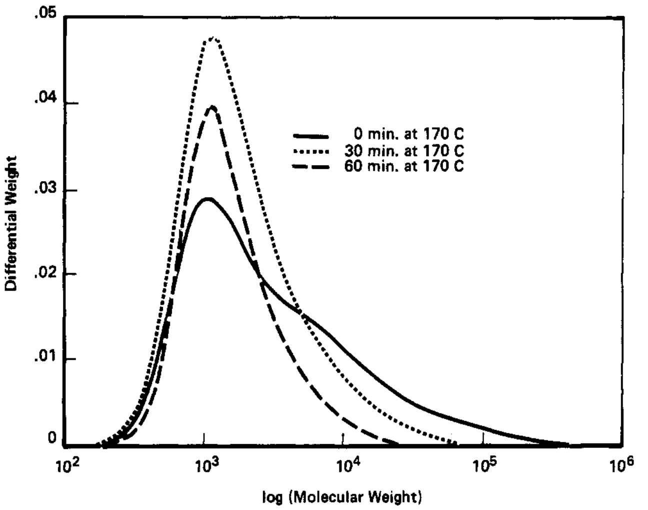


Figure 5. Posthydrolysis of one of the FTR lignins[16] at 170 °C with 1 N NaOH. Molecular weights were measured with previously calibrated size exclusion chromatography using Sephadex G200 in 0.1 N NaOH.

Posthydrolysis

If the cross-links in lignin consist of β-aryl ether bonds, then the ultimate ω-lignin polymers obtained after exhaustive hydrolysis should be linear with a dispersity of 2 according to eq 12 and 13 with $\alpha' = 0$.

Figure 5 shows a preliminary result[16] of posthydrolysis experimentation which indicates the approach to a constant molecular weight distribution, i.e., that of an ω-lignin. It will be interesting and important to characterize ω-lignins in terms of molecular weight and polydispersity. According to Figure 1, condensation may result in the formation of unbreakable bonds (e.g., C–C bond between lignin units) which would cause an increase in the chain length of ω-lignins. The characterization of ω-lignins from various delignification processes, batch and continuous, on softwoods and hardwoods, may reveal the extent of condensation and the constitution of the primary chains.

Conclusions

It appears that no contradiction to the molecular theory of degelation has arisen from the results obtained so far in delignification experiments. Only minor reassignments of gelation parameters have needed to be made to differentiate the continuous delignification from a batch process. Both appear to be in agreement with model compound studies and kinetic observations of the delignification of wood.

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Appendix

The calculation of α' and other parameters may be conducted as follows. Substituting eq 14 into 12 gives α'

expressed as a function of p':

$$\alpha' = 2(1 - p' - 1/\bar{x}_n') \qquad \text{(A1)}$$

which, together with eq 15, is then substituted into eq 13 to yield a quadratic equation in p'. Only the larger root is physically meaningful, and this takes the form

$$[-B + (B^2 - 4AC)^{1/2}]/2A \qquad \text{(A2)}$$

where

$$-B = 5\bar{x}_w' + 1 - 4r' - 2/\bar{x}_n'$$

$$A = 4\bar{x}_w' + 2$$

$$C = \bar{x}_w' - 3 + 2/\bar{x}_n'$$

$$r' = \bar{x}_w'/\bar{x}_n'$$

Values of p' thus obtained are listed in the fourth column of Table II. From eq A1 and 15, α' and $\bar{y}_w'$ can be obtained.

Likewise, α can be eliminated from eq 10 and 11, and the result is a quadratic equation in u with the solution again in the form of (A2). The coefficients are

$$-B = s(1 - \alpha')$$

$$A = 1$$

$$C = s\alpha'$$

Since s is a measured quantity and α' calculated from (A2), the values of u can be calculated. α and α'' are then calculated by using eq 10 and 9, and these are listed in Table III.

Registry No. Lignin, 9005-53-2; dioxane lignin, 8068-03-9.

References and Notes

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Photophysical Studies of a Water-Soluble Copolymer of Methacrylic Acid and 1-Pyreneacrylic Acid

Deh-Ying Chu and J. K. Thomas*[1]

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.

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ABSTRACT: The chromophore pyrene was located in poly(methacrylic acid) in three different ways: (a) as a guest molecule by simple solubilization, (b) covalently attached to the polymer ends, and (c) randomly bound to the chain. The photophysical properties of pyrene, fluorescence, and triplet–triplet absorption were then used to investigate the nature of the chromophore environment on the polymer and the restriction placed by the polymer on movement of reactive molecules to pyrene. pH, which markedly affects the architecture of the polymer (closed coil at low pH (<4), randomly open coil at higher pH (~6)), had a marked influence on the observed kinetics. The effect of pH was interpreted for each probe situation (a, b, and c) as related to the position of the chromophore with respect to the water interface, or the degree of penetration of water into the polymer coil, and the ease of exit of nonbound pyrene (situation a). Some studies on poly(acrylic acid) are also reported and compared to those for poly(methacrylic acid). It is concluded that photophysical methods are powerful techniques for the study of dynamics of polyelectrolytes.

Introduction

The past decade has seen an increasing interest in the effects of organized assemblies on photochemical reactions.[2-4] For the most part micelles and microemulsion systems have been studied where the photosystem of interest is solubilized either partly or completely by the organized assembly. On excitation the micelle or its surface participates in the reaction and directs certain reaction features of interest. Such studies have many applications in model systems for the storage of energy and also as models for the solubilization of organic molecules by biosystems. One of particular interest is the solubilization of carcinogenic materials by DNA.[5] Several other systems serve to solubilize insoluble organic molecules in aqueous systems by providing a vehicle for the molecule of interest; e.g., clay systems or colloidal clays solubilize organic materials in many river systems, while caffeine can effectively solubilize molecules such as pyrene in water.[6] Of immediate interest is the possibility of using polymers for such studies. For example, there are reports of the solubilization