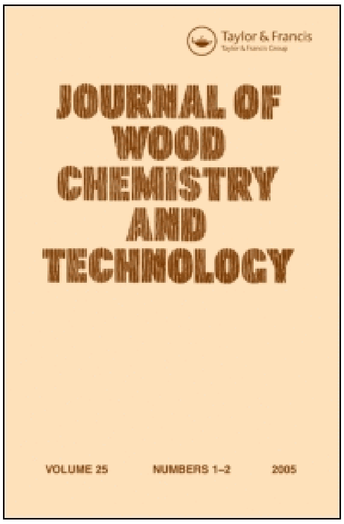

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Branching and Functionality of Lignin Molecules

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BRANCHING AND FUNCTIONALITY OF LIGNIN MOLECULES*

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ABSTRACT

Two models of lignin structure are compared and discussed with respect to experimentally measured molecular weight data. The model of polycondensation of f-functional monomers appears to give incorrect results. A generalized model is presented based upon the concept of a crosslinked polymer formed with randomly distributed pre-polymers. Molecular weight data support a tetrafunctional

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*Dedicated to Professor J. L. McCarthy on his 70th birthday.

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branch point in the lignin preparation studied. However, viscometry data do not support a tetrafunctional or trifunctional functionality. Number- and weight-average DP measurements give important information concerning the characteristics of degraded lignin fractions.

INTRODUCTION

Because its constituent phenylpropane (C_9) units are polyfunctional, lignin exists as a branched polymer. The insolubility of native lignin suggests that it is in a gelled state. Recently the authors have made several attempts to quantify lignin structure and reactions based on the available branching theory[1-7]. Ironic in the development of this "macromolecular chemistry of lignin" is the fact that, while delignification and lignin utilization are of high practical importance, the elucidation of its polymeric structure requires an abstract theory.

This paper is a further attempt to develop the theory of chain branching in lignin. It will be demonstrated that, once the basic molecular parameters are properly established, their evaluation can be readily carried out.

THEORY

Most of the groundwork for branching theory was developed long ago by Flory[8] and Stockmayer[9]. Branched, or non-linear, molecules can be built up randomly by using one of the following models.

Polycondensation

The polymerization that leads to gelation is the self-condensation of A_f type monomers, where f is the functionality. Theoretical development in greater detail can be found in the original publications[8,9], but the following expressions for number-average ($\bar{x}_n$) and weight-average ($\bar{x}_w$) degrees of polymerization (DP) are of considerable importance:

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

$$\bar{x}_w = (1 + \alpha)/[1 - (f - 1)\alpha] \tag{2}$$

where α is the fraction of functional groups that have reacted. All these properties refer to the sol (soluble) fraction of the branched polymer (see the Appendix for the list of symbols used in this paper).

Crosslinking

By randomizing the functionality, f, the result is a crosslinked polymer[10] formed by pre-polymers with the number-average DP = $\bar{y}_n$, and the weight-average DP = $\bar{y}_w$. The averages for the crosslinked polymer are[8]:

$$\bar{x}_n = \bar{y}_n\ (1 - \bar{y}_n\rho/2)^{-1} \tag{3}$$

$$\bar{x}_w = \bar{y}_w\ (1 + \rho)/[1 - (\bar{y}_w - 1)\rho] \tag{4}$$

In this case, ρ is the crosslinking density, and each linear y-mer has y functional groups capable of crosslinking. Self-condensation is a special case in which the pre-polymer is a monomer with f functional groups. Likewise, the random linear polymer is a special case of f = 2 in Eqs. (1) and (2).

Polymers with distribution defined by Eqs. (1) and (2) are said to manifest the "most probable" distribution. One of the important characteristics of these polymers, linear or branched, is that their size distributions are uniquely defined by these two averages[11]. This is a simple and very useful concept in the characterization of dissolved lignin; because it says that, once the number- and weight-average DP are determined, the molecular size distribution, functionality and branching density can be evaluated.

An even more useful and general technique developed by us[7] involves the use of a pair of measured DP averages to evaluate crosslinking density in Eqs. (3) and (4), when the primary chains are assumed to have a most probable distribution.

Branch Points

A lignin branch point may have a functionality of $f \geq 3$; i.e., a C_9 unit may be linked to three or more other units. However, a tetrafunctionally linked unit may be ruled out for structural consideration because of stereochemistry. Therefore, Szabo and Goring[12] made a direct substitution of $f = 3$ in the self-condensation of A_3 in the Flory-Stockmayer theory. This assumption turns out to be incorrect, as is demonstrated below with calculations based upon experimental data.

On the other hand, Bolker and Brenner[13] attempted to generalize the structural description of lignin by considering it as a crosslinked polymer. Unfortunately, their assumption of uniform length of the pre-polymers reduces the utility of this generalization.

Random crosslinking involves the formation of branch points. A linear polymer is formed by end-to-end linking of two smaller linear segments. A trifunctionally linked unit is formed by reacting a linear chain-end with a non-terminal unit in another chain. However, a tetrafunctional branch point, constituted by a pair of trifunctional units, is formed by linking the non-terminal units from two pre-polymer chains. In other words, a trifunctional branch point (shaped like the letter Y) is also a trifunctional unit, but a tetrafunctional branch point (the X shape) is a pair of trifunctional units (see formula II in ref. 5 and Fig. 2b in ref. 6). The concept of this distinction has been discussed thoroughly by Flory (ref. 8, pp. 359-360).

Furthermore, Flory also showed that the condensation of a tetrafunctional unit with a bifunctional one (i.e., $A_4 + A_2$; A_2 is a linear polymer with variable length) is equivalent to the crosslinking of pre-polymers with a "most probable" distribution. Quantitative expressions have also been derived by Flory. If the extent of reaction of the linear polymers is denoted by p, then the DP averages are given by:

$$\bar{y}_n = (1 - p)^{-1} \tag{5}$$

$$\bar{y}_w = (1 + p)(1 - p)^{-1} \tag{6}$$

which are the special cases of Eqs. (1) and (2) with $f = 2$, $y = x$ and $p = \alpha$.

This important conclusion has been applied to lignin[5,6]. The equivalence of the $A_4 + A_2$ condensation and random crosslinking naturally implies that the branch points formed by crosslinking are tetrafunctional (or X points)[8]. Thus when pre-polymers with the DP averages given by Eqs. (5) and (6) are crosslinked, the branching probability α_f is given by:

$$\alpha_f = p\rho/(1 - p(1 - \rho)) \tag{7}$$

This equation does not depend on the functionality of branch points. In fact, it applies for both α_4 and α_3. Flory's equivalence argument automatically suggests that it is α_4.

Functionality

The functionality of the branch point is implied in the argument just described. It can also be determined by viscometry measurements on dilute solutions of branched polymers[14,15].

As a result of branching, the radius of gyration of a branched polymer is reduced as compared with the unbranched counterpart. The contraction factor, g, is a measure of such a reduction in the radius of gyration:

$$g = \bar{R}_{b,\theta}^{2}/\bar{R}_{1,\theta}^{2} \tag{8}$$

where $\bar{R}_{b,\theta}^{2}$ is the mean square radius of gyration of the branched polymer measured under the θ-condition, and $\bar{R}_{1,\theta}^{2}$ is that of the linear chain of the same DP. Viscometry gives the ratio of the intrinsic viscosities, also under the θ-condition:

$$g' = (\eta)_{b,\theta}/(\eta)_{1,\theta} \tag{9}$$

There are several relationships between g and g'. In particular, Zimm and Kilb[15] obtained:

$$g' = g^{1/2} \tag{10}$$

which has been used in our previous work for lignin[1,3]. However, a more generalized form has recently been suggested[16]:

$$g' = g^{\nu} \tag{11}$$

Under the assumptions that the chains (in linear polymers as well as in the branched polymers) are very long, with a Gaussian configuration in the θ-solvent, Zimm and Stockmayer derived for the g-factors for trifunctional and tetrafunctional branched polymers as, respectively:

$$g_3 = \frac{3(1-2\alpha)}{\alpha}\left(\tfrac{1}{2}\left(\frac{1-\alpha}{\alpha}\right)^{1/2}\ln\left(\frac{(1-\alpha)^{1/2}+\alpha^{1/2}}{(1-\alpha)^{1/2}-\alpha^{1/2}}\right)-1\right) \tag{12}$$

$$g_4 = \frac{1 - 3\alpha}{2\alpha}\ln\left(\frac{1 - \alpha}{1 - 3\alpha}\right) \tag{13}$$

where α is the branching probability defined by Eq. (7).

If the proper value of ν is known, the g values can be calculated from the measured values of g' by using Eq. (11). With a knowledge of the functionality, the calculated g values can be used in Eqs. (12) or (13) to evaluate the branching probability α. Alternatively, if α can be evaluated from other sources, such as the molecular weight method to be shown below, then Eqs. (12) and (13) yield the values of g, which on correlating with the measured g' values, gives the value of ν in Eq. (11).

In a semiempirical treatment of viscosities of branched polymers, Bohdanecky[16] obtained a relationship between g' and the weight-average molecular weight $\bar{M}_w$:

$$1/g' = A + B\,\bar{M}_w^{1/2} \tag{14}$$

where A and B are constants and values of A yield information on the degree of functionality[16].

EXPERIMENTAL

Extensive measurements were made on lignin samples prepared from spruce wood meal[1-3], briefly described as follows.

D-Fractions - The spruce meal was extracted with a solution composed of 1000 mL dioxane and 10 mL HCl (sp. gr. = 1.19) at the boiling temperature. The dissolved lignin was then fractionated by size exclusion chromatography (SEC) to obtain narrowly dispersed fractions.

F-Fractions - Same as above except that dioxane-H_2O-HCl (800 mL, 200 mL, 100 mL) was used as the extracting agent. These are also narrow fractions.

P-Fractions - The wood meal was extracted successively at 70°C with the same solution as that used for the D-fractions. The P-fractions are broadly distributed. Each fraction was collected at a different time. These fractions were characterized by laser light scattering and vapor pressure osmometry to obtain their average molecular weights.

Intrinsic viscosity measurements were also carried out, in suitable θ-solvents, for all D-, F- and P-fractions. For more detailed descriptions on the choice of solvents and methods of characterization, original publications should be consulted[1-3].

RESULTS AND DISCUSSION

Using the DP averages obtained for the P-fractions, we can test the two models described above with these data.

Condensation Model - Branching from Molecular Weight Data

For a condensation polymer, one can eliminate α between Eqs. (1) and (2), and the result is an expression for f:

$$f = 2(\bar{x}_n - 1)(\bar{x}_w - 1)/(\bar{x}_n \bar{x}_w + \bar{x}_n - 2 \bar{x}_w) \qquad (15)$$

Using only a few of the measured DP averages, the results shown in Table I are obtained:

Table I. Test of Condensation Model

Fraction	f
P-1	1.99
P-2	2.12
P-10	2.04
P-20	2.06
P-25	2.07

It is evident from Table I that the functionality of the lignin studied is not 3. This appears to invalidate the condensation model of Szabo and Goring[12]. Similarly, the "crosslinking" model of Bolker and Brenner[13] seems not satisfactory because they assumed that $\bar{y}_n = \bar{y}_w$ = constant in Eqs. (3) and (4), which, in effect, reduces to a condensation model with a large but constant value of f.

Crosslinking Model - Branching from Molecular Weight Data

The more generalized crosslinking model proposed by us[5-7] provides for the evaluation of ρ from each pair of measured $\bar{x}_n$ and $\bar{x}_w$, and a detailed procedure for calculation of ρ is given in our previous paper[7]. The corresponding value of α can be calculated from Eq. (7). The results are shown in Table II, together with the measured values of $\bar{x}_w$ and other parameters to be discussed below.

The functionality of the dioxane extracted lignin can be evaluated from the definition of the gel point for which the branching probability is given[8-9] by:

$$\alpha_c = (f - 1)^{-1} \tag{16}$$

and thus $\alpha_c = 1/3$ if $f = 4$; and $\alpha_c = 1/2$ if $f = 3$. Also at the gel point the weight-average DP diverges[8-9]:

$$\bar{x}_w(\alpha_c) \rightarrow \infty \tag{17}$$

Empirically, one can plot the values of α, as calculated from Eq. (7) and listed in Table II, against $1/\bar{x}_w$ and the intercept at $\bar{x}_w \rightarrow \infty$ is the value of α_c. This plot turns out to be linear, as shown in Figure 1, with an intercept at $\alpha_c = 0.35$. Thus we conclude from molecular weight considerations that the branch points are tetrafunctional, in agreement with previous conclusions[5-7].

Table II: Properties of Lignin Fractions

Fraction	$\bar{x}_n$	$\bar{x}_w$	α	g'	g_3	g_4	g
P-1	10.42	19.14	-	0.7235	-	-*	0.697
P-2	10.58	21.41	0.0324	0.7053	0.986	0.966	0.678
P-3	11.39	23.04	0.0311	0.6928	0.987	0.967	0.665
P-4	11.99	26.36	0.0763	0.6669	0.966	0.912	0.638
P-5	13.09	29.19	0.0799	0.6485	0.964	0.908	0.618
P-6	13.82	31.25	0.0840	0.6388	0.962	0.902	0.608
P-7	14.08	33.09	0.1005	0.6284	0.953	0.879	0.597
P-8	14.06	35.34	0.1227	0.6194	0.940	0.845	0.587
P-9	14.19	36.02	0.1292	0.6156	0.937	0.834	0.583
P-10	14.37	37.04	0.1345	0.6111	0.933	0.825	0.578
P-11	14.55	38.72	0.1421	0.6037	0.929	0.812	0.571
P-12	14.82	41.41	0.1593	0.5924	0.917	0.781	0.559
P-13	15.03	42.88	0.1603	0.5868	0.917	0.779	0.553
P-14	15.23	44.82	0.1681	0.5795	0.911	0.763	0.545
P-15	15.39	46.60	0.1770	0.5738	0.905	0.745	0.539
P-16	15.50	47.41	0.1790	0.5708	0.904	0.741	0.536
P-17	15.65	48.90	0.1812	0.5654	0.902	0.736	0.530
P-18	15.76	50.94	0.1893	0.5591	0.896	0.718	0.524
P-19	15.81	52.25	0.1928	0.5546	0.893	0.710	0.519
P-20	15.89	54.08	0.1990	0.5493	0.888	0.696	0.514
P-21	15.94	54.76	0.2035	0.5466	0.885	0.685	0.511
P-22	16.05	56.23	0.2042	0.5428	0.884	0.683	0.498
P-23	16.02	25.64	0.2127	0.5363	0.877	0.661	0.500
P-24	16.07	59.45	0.2147	0.5343	0.876	0.656	0.498
P-25	16.18	61.44	0.2194	0.5295	0.871	0.643	0.493

*Not calculated because of a negative value of ρ, which is a result of the uncertainty in polydispersity of this very first fraction.

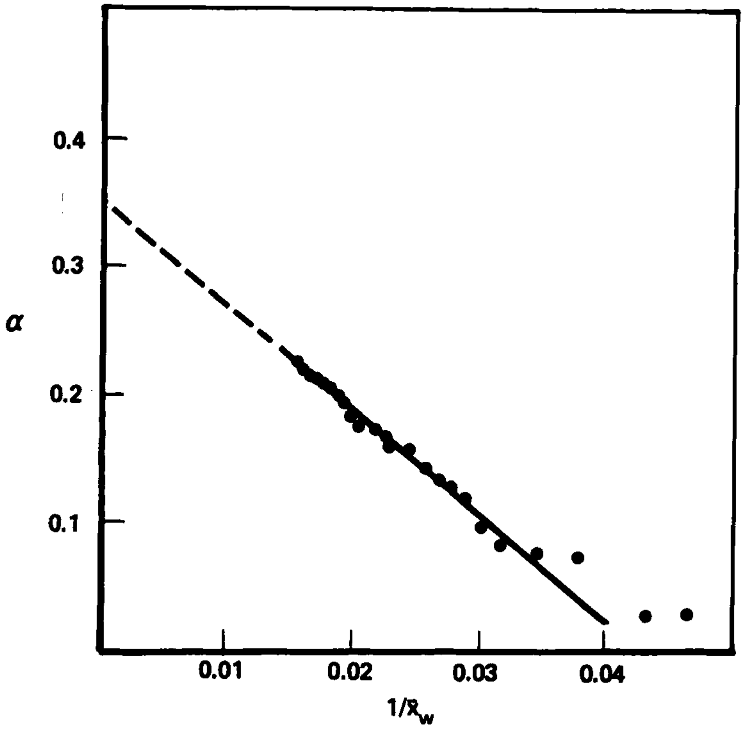

Figure 1: Plot of branching probability (α) against the reciprocal of the weight-average DP. The intercept at the ordinate yields the gel point at α = 0.35.

Chain Branching Evidence from Viscosity Measurements

The g' values determined from intrinsic viscosity measurements on the P fractions are also shown in Table II. Like the weight-average DP, the g' value in a given fraction is the cumulative value over all the previous fractions, with the mass fractions as their weighting factors[1-3]. In this sense, the reported g' values are weight-averages.

The values of g_3 and g_4 shown in Table II were calculated from α by using Eqs. (12) and (13), respectively. These are the g-factors calculated from the molecular weight (DP averages) data as illustrated in the last section and our recent work[7].

From the original values[1-3] of g' and $\bar{M}_w$ obtained for the D and F fractions, we find with high correlation coefficients ($r^2 = 0.99$) in the form of Bohdanecky's equation (7), that:

$$\text{D-fractions:} \quad 1/g' = 0.76 + 0.0108\ \bar{M}_w^{1/2} \tag{18}$$

$$\text{F-fractions:} \quad 1/g' = 0.82 + 0.0083\ \bar{M}_w^{1/2} \tag{19}$$

The intercept values, 0.76 and 0.82, are well in the range given by Bohdanecky[16]. Thus we arrived at an estimated value of $\nu = 0.85$ for both trifunctional and tetrafunctional branch points.

When a similar correlation is performed for the P fractions, and here with a correlation of $r^2 = 0.99$, we obtain:

$$1/g' = 0.72 + 0.0108\ \bar{M}_w^{1/2} \tag{20}$$

This gives an estimation of $\nu = 0.9$ using the Bohdanecky technique. With this value of ν, Eq. (11) is used to calculate the g-factor from the <u>viscosity</u> data. The result is also shown in Table II.

There is an appreciable deviation between these derived g-factors and the values of g_3 and g_4 calculated from the <u>molecular weight</u> data. Although the viscosity g values are closer to g_4 than g_3, again suggesting a tetrafunctional branch point, this deviation cannot be ignored. Perhaps the theories on the g-factors and viscometry have invoked assumptions and conditions that may not be substantiated in the lignin molecules now studied. For example, the measured chain length of lignin pre-polymers[7] is less than 28, which does not satisfy the long chain and Gaussian conditions required in the development of these theories[14-16].

Furthermore, recalling that the P-fractions are highly polydisperse, the empirical relationship in Eq. (19) may not be suitable for use with these fractions despite the observed high correlation coefficient. In addition, the weight-average values of the g' factors may not be fully representative of the cumulative values.

CONCLUSIONS

Molecular weight data suggest that the structure of the dioxane lignin studied can be modeled as a crosslinked polymer with tetrafunctional (X-type) branch points. The observed DP averages yield information sufficient to permit estimates of the crosslinking density and the functionality of branch points of a presumed tree-like lignin polymer[5-6]. Most of the characteristics of the lignin preparation studied can be interpreted based on the simple concept of characterization of lignin by number- and weight-average DP measurements. Viscosity data do not clearly favor a tetrafunctional branch point over a trifunctional one because of the lack of a suitable hydrodynamic theory for relatively short and stiff chains in lignin macromolecules.

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REFERENCES

1. F. Pla, Ph.D. thesis, "Etude de la Structure Macromoleculaire des Lignines," University of Grenoble, France, 1980.
2. F. Pla and A. Robert, Holzforschung (1984) in press.
3. F. Pla and A. Robert, Holzforschung (1984) in press.

4. J. F. Yan and D. C. Johnson, J. Agric. Food Chem. 28 850 (1980).

5. J. F. Yan, Macromolecules, 14, 1438 (1981).

6. J. F. Yan, Science, 215, 1390 (1982).

7. J. F. Yan, F. Pla, R. Kondo, M. Dolk and J. L. McCarthy, Macromolecules (1984) in press.

8. P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y. 1953, Chapter IX.

9. W. H. Stockmayer, J. Chem. Phys. 11, 45 (1943).

10. J. F. Yan, Macromolecules, 12, 260 (1979).

11. J. F. Yan, Macromolecules, 11, 648 (1978).

12. A. Szabo and D.A.I. Goring, Tappi 51 (10), 440 (1968).

13. H. I. Bolker and H. S. Brenner, Science 170, 173 (1970).

14. B. H. Zimm and W. H. Stockmayer, J. Chem. Phys. 17, 1301 (1949).

15. B. H. Zimm and R. W. Kilb, J. Polym. Sci. 37, 19 (1959).

16. M. Bohdanecky, Macromolecules 10, 971 (1977).

APPENDIX

A prime sign (') is usually used for symbols designating properties in the sol fraction[1-8]. In this paper, only the sol fraction is discussed, the prime is omitted without causing confusion with properties of the gel fraction.

A,B	Constants in Eq. (14)
A_2	Bifunctional (linear) monomer or polymer
A_f	Monomer with f functional groups
f	Number of functional groups in a monomer = functionality

g	Contraction factor defined by Eq. (8)
g'	Viscosity ratio defined by Eq. (9)
g_3	Contraction factor of a trifunctionally branched polymer
g_4	Contraction factor of a tetrafunctionally branched polymer
$\bar{M}_w$	Polymer weight-average molecular weight
p	Extent of reaction in linear pre-polymers = fraction of reacted functional groups in pre-polymers
$\bar{R}^2$	Mean-square radius of gyration
$\bar{x}_n$	Number-average DP of branched lignin molecules
$\bar{x}_w$	Weight-average DP of branched lignin molecules
$\bar{y}_n$	Number-average DP of linear pre-polymers
$\bar{y}_w$	Weight-average DP of linear pre-polymers
α, α_f	Branching probability of a f-functional branch point = probability that a linear arm issued from a branch point will end in another branch point
α_c	Critical value of α
ρ	Crosslinking density = fraction of trifunctionally linked units in lignin molecules
(η)	Intrinsic viscosity
θ	Subscript indicating θ-conditions
ν	Exponent defined by Eq. (11)