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Solvent Effects and Initiation Mechanisms for Graft Polymerization on Pine Lignin

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ABSTRACT: Graft copolymerization of 2-propenamide onto Kraft pine lignin, previously initiated with hydrogen peroxide and 3,3-dimethyl-1,2-dioxabutane, can be initiated with 2-hydroperoxy-1,4-dioxacyclohexane, an autoxidation product of 1,4-dioxacyclohexane. Graft copolymer is formed by free radical polymerization in dimethyl sulfoxide containing lignin, calcium chloride, and cerium(IV) ion. Initiation mechanisms based on hydroperoxide reaction with cerium(IV) or chloride ion were tested. The cerium ion/hydroperoxide mechanism does not explain the results of a series of test reactions. However, direct reaction of chloride ion and hydroperoxide did not occur and while chloride ion content of the reaction did correlate with product properties, so did chloride:hydroperoxide mole ratio and lignin:chloride mole ratio. This implies an initiation process involving chloride ion, hydroperoxide, and lignin may produce grafting.

Introduction

Every year the U.S. paper industry produces over 33 million metric tons of Kraft lignin.[1] Most of this biomass is burned as fuel but small amounts are used as binders, asphalt additives, or cement additives. Larger fractions of this waste would be used in other industrial or commercial processes if an economical way existed to convert lignin into a product useful for something more than a fuel.

A possible way to make such a conversion has now been produced.[2,3] The transformation converts Kraft pine lignin to a water-soluble copolymer by graft polymerization. Graft copolymer is formed by conducting a free-radical polymerization of 2-propenamide in nitrogen-saturated, 1,4-dioxacyclohexane containing lignin, calcium chloride, cerium (IV) ion, and 1,4-dioxacyclohexane autoxidation products. Further studies on this reaction have shown that improvements in the reaction process, product solubility, and product physical properties are possible by changing the solvent for the reaction. Further, a mechanism for initiation can now be postulated based on further studies of reaction and products.

Previously prepared graft copolymers have been made by producing 1,4-dioxacyclohexane autoxidation products directly in pure solvent and using autoxidation products without isolation. In this work, we show that the critical autoxidation product, 2-hydroperoxy-1,4-dioxacyclohexane, can be isolated, purified, and used to initiate this grafting reaction in other solvents.

We have also performed further tests to determine the relationship between product properties and reaction conditions. In the following sections, the synthesis procedure, product solubility properties, use of other solvents, possible mechanisms of initiation, mechanism tests, and syntheses run to define how product properties vary as a function of synthesis conditions will be described.

Experimental Section

In the graft polymer synthesis, oxidized 1,4-dioxacyclohexane is vacuum-distilled to separate 1,4-dioxacyclohexane and its autoxidation products. Autoxidation products are then purified and/or used directly to initiate the grafting reaction in another solvent.

Synthesis. To prepare 2-hydroperoxy-1,4-dioxacyclohexane, the time required to produce a maximum concentration of oxidizing equivalents in 1,4-dioxacyclohexane must be determined. Autoxidation is conducted by refluxing 250 mL of freshly distilled 1,4-dioxacyclohexane while bubbling the contents of the reflux vessel with air at a rate of 4.3 mL/s. Optimum duration for this treatment must be determined by conducting an iodine/thiosulfate titration on aliquots of solvent reflux and bubbled for different times.

After 1,4-dioxacyclohexane (I) is refluxed and aerated for the optimum time, unreacted I is removed at 0.27-kPa nitrogen pressure and 23 °C temperature. The isolated white solid is stored at 4 °C in a refrigerator. It is purified by saturating an equal volume mixture of hexane and 3-oxy-2-oxopentane with the solid and chilling to 0 °C. Precipitate is separated from supernate by cold filtration and the purified 2-hydroperoxy-1,4-dioxacyclohexane is stored at 4 °C.

The grafting reaction is run by adding lignin and calcium chloride to a nitrogen-flushed 125-mL flask containing 20 mL of solvent. The mixture is bubbled with nitrogen for 3 min, oxidation products of I are added, and the flask contents are bubbled with nitrogen for an additional 2 min. Flask contents are stirred for 20 min and bubbled with nitrogen for 4 min. The 2-propenamide is then added, flask contents are bubbled with nitrogen for 10 min while being stirred, 0.15 mL of 0.05 M cerium(IV) sulfate in 1 M aqueous H_2SO_4 is added, the sample is stirred and bubbled for an additional 10 min, and the flask is then capped with a septum stopper.

After 2 days of storage in a 30 °C constant-temperature bath, the reaction is terminated and product recovered.

Three recovery methods can be used to recover reaction product. In all methods, the sample is first terminated with 0.5 mL of 1.0 wt % aqueous hydroquinone solution and then diluted with twice its volume of distilled water. When uniform, the sample is treated in one of the following ways. In purification method 1, the graft copolymer is precipitated dropwise in 10 times the sample volume of 2-propanone, recovered by filtration, washed with 2-propanone, and dried to constant weight. This drying step was to determine purity and yield and was dropped from the procedure when the solids were found to be contaminated. Crude product is dissolved in 20–40 times its weight of water and dialyzed against distilled water for 7 days. Product is recovered by freeze-drying.

In the second method, product solution is dialyzed against distilled water for 7 days and solids are recovered by freeze-drying. This method has the disadvantage that unreacted lignin is not removed from the sample, a purification step that occurs in precipitation of graft copolymer in 2-propanone.

In purification method 3, solids are recovered in the same way as in method 2. These solids are then used to make a 5 wt % aqueous solution, which is added dropwise to 10 times its volume of 2-propanone. Product free of ungrafted lignin is recovered by filtration and dried to constant weight.

Assays. Analysis procedures for oxidizing equivalents by iodine/thiosulfate titration, lignin content by UV assay, 1-amidoethylene repeat unit content by Kjeldahl assay, limiting viscosity number, and elemental composition are given in ref 3.

Calcium content of product is determined by atomic absorption measurements performed on solutions of ashed product. Analytically weighed, 0.2-g samples were placed in 125-mL Pyrex flasks and heated to 400 °C for 24 h. The cool ash was digested for 1 h in 100 mL of boiling 10 M hydrochloric acid, and the resulting cooled solution was diluted to 250 mL with distilled water. Solutions were analyzed for calcium in an air/acetylene flame using a 422.7-nm absorption wavelength. Calcium content was determined from a calibration curve made from solutions prepared from 0.020-g samples of calcium carbonate treated in the same way as the product samples. All assays were performed on nonsolvent-precipitated product.

Spectra of ^{13}C resonances were made on 5–10 wt % solutions of product in D_2O using methanol as an internal standard. Infrared spectra were run in both trichloromethane and Nujol using sodium chloride plates.

Chloride ion content of the sample is determined by combusting a 0.50-g sample of product, analytically weighed, in a 400 °C oven for 20 h. After cooling, the ash in the 125-mL Pyrex flask is dissolved in 10 mL of water, 0.10 g of dextrin is added, and 5 drops of fluorescein indicator is added.[4] Solution is then titrated with 0.05 M silver nitrate solution to the pink end point of the indicator.

Insoluble solids in product from the grafting reaction are detected by gravimetric analysis. A 0.20-g sample of product, analytically weighed to 5 decimal places, is dissolved in 20.0 mL of water. After 4 days of stirring, the solution is centrifuged at 2500 rpm on a 5-cm rotor arm in a test tube weighed to constant weight. Solution is decanted and pelleted solids are dried for 2 days at 40 °C and <1.3-Pa pressure. The tube is weighed and drying is continued until a weight constant to 0.1 mg is obtained. Insoluble solids are taken as the weight gain of the test tube.

Materials. Lignin, which makes up the backbone of the graft copolymers, is a cross-linked, oxyphenylpropyl polymer that acts as a glue in woody plants.

Lignin used in these studies is a commercial product. The material is a Kraft pine lignin prepared in "free acid" form with a number-average molecular weight of 9600 and a weight-average molecular weight of 22 000. The ash content of the product is 1 wt % or less. Kraft pine lignin is essentially insoluble in water at pH 7 but dissolves readily in aqueous solutions at a pH >9.

2-Propenamide (common name acrylamide) used in all reactions was reagent grade monomer that was recrystallized from trichloromethane after hot filtration and dried under vacuum ($P < 1.3$ Pa) at room temperature for 24 h. 1,4-Dioxacyclohexane was stabilized reagent grade material that was freshly distilled before use. Calcium chloride and other salts used were reagent grade materials and were used as supplied. Gases used in the syntheses were standard commercial grade cylinder gases.

Dialysis membrane used is Spectrapor no. 3, a 3500 upper molecular weight cutoff cellulose, 45-mm diameter, membrane tubing made by Spectrum Medical Industries, Los Angeles, CA.

Equipment. The atomic absorption spectrophotometer used was a Perkin-Elmer Model 4000 with Model HGA-400 furnace and programmer attachments. Lignin spectra were run on a Perkin-Elmer Lambda 3, UV–vis spectrophotometer. Infrared spectra taken on a Perkin-Elmer Model 283 with infrared data station. Nuclear magnetic resonance spectroscopy was run on an IBM-Bruker WP200Sy multinuclear spectrometer. Freeze-drying was done on an FTS Systems Model FDX-1-84 lyophilizer. Weighings were done on a Mettler B6, 5-decimal-place balance.

Results and Discussion

2-Hydroperoxy-1,4-dioxacyclohexane (HPCH) was made by refluxing 1,4-dioxacyclohexane for 14 h as described. HPCH content of solution was 1.2 wt % and yield of crude solid was 1.0 wt %. By iodine/thiosulfate titration, crude solid was 88.3 wt % pure.

Crude solid was recrystallized and a melting point of 54–55 °C found for the purified solid. The literature value for the HPCH fusion is 53–56 °C.[5] Iodine/thiosulfate titration showed the product to be 99.0 wt % pure when all equivalents were assumed to be from HPCH.

Product infrared spectra in Nujol had a broad OH absorption at 3350 cm^{-1}. Peaks at 1135 and 1085 cm^{-1}, possibly from C–O asymmetric stretching, and at 880 cm^{-1}, possibly due to –OO– vibration, were sharp in a trichloromethane solution spectrum but broad in a spectrum of product in Nujol.

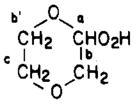
A 90-MHz proton spectrum of product in D_2O gave the peak pattern shown in Table Ia. There is a close match for all proton resonances with those found for HPCH,[6] save for that attributed to peroxide proton. Since hydroxyl protons change chemical shift as a function of solvent more than do aliphatic protons, this difference in chemical shift may be due to solvent effects. A 200-MHz, carbon-13 NMR spectrum of the same sample gave the peaks listed in Table Ib. These peaks show the expected deshielding and splitting pattern for HPCH. Results from a graft copolymerization run using purified HPCH are given in Table II. These data show that 2-hydroperoxy-1,4-dioxacyclohexane is an initiator of graft copolymerization of 2-propenamide onto lignin.

Solvent Effects. Not all of the reaction product from reactions run in I is readily soluble in water. Portions of product swell but do not dissolve in water while all portions of the product are found to be soluble in 0.5 M sodium hydroxide. This solubility behavior indicates that non-water-soluble portions of the product are probably untangled polymer rather than a cross-linked, insoluble product.

Both the sequence of events in the synthesis and the characteristics of the product support the idea that I is a poor solvent in which to run this reaction. Reaction samples containing 2.4 wt % lignin (a common reaction concentration) are two-phase slurries rather than being solutions. During the initial stages of the reaction, the lignin slurry becomes a homogeneous solution but then rapidly thickens, clouds up, and becomes a slurry again.

A hypothesis that will explain this solution behavior is that the growth of a poly(1-amidoethylene) side chain on

Table I
Absorption Peaks in Nuclear Magnetic Resonance Spectra of a 10 wt % Solution of 1,4-Dioxane Autoxidation Products in Deuterium Oxide



(a) Proton Spectrum

		peak location, ppm	
peak set no.	label	2-hydroperoxy-1,4-dioxane[a]	1,4-dioxane autoxidation product[b]
1	leading multiplet	3.59	3.58
2	pentuplet	3.75	3.76
3	multiplet	4.20	4.12
4	triplet	5.05	5.00
5	singlet	5.13	5.12
6	doublet		8.13
6′	broad singlet	9.78	

(b) Carbon-13 Spectrum

	peak location,[c] ppm				
peak no.	decoupled spectrum	assigned	coupled spectrum peak center	pattern	coupling constant, ppm
1	58.47	c	58.43	triplet	2.95
2	64.05	b′	64.03	triplet	2.93
3	64.52	b	64.48	triplet	2.86
4	96.67	a	96.66	doublet	1.73
pure dioxane	65.69				

[a] With respect to tetramethylsilane in trichloromethane at ambient temperature. [b] With respect to DHO ($g = 4.67$) in D_2O at 22 °C. [c] With respect to methanol in D_2O at 22 °C.

Table II
Composition and Product Properties for Reactions Initiated with Purified Peroxide

reacn comp	recryst hydroperoxide reacn (99.0)%	crude hydroperoxide solids reacn (88%)
lignin, g	0.50	0.50
2-propenamide, g	3.2	3.2
dimethyl sulfoxide, mL	20.0	20.0
$CaCl_2$, g	0.1	0.1
Ce(IV), mL	0.15	0.15
hydroperoxide, g	0.15	0.15
	Product Properties	
lignin, wt %	5.62	5.5
1-amidoethylene repeat units, wt %	71.0	68.4
yield		
crude	4.08	4.07
purified	2.90 (70.97 wt %)	3.31 (89.4 wt %)
limiting viscosity, dL/g	0.56	0.62

lignin makes a soluble intermediate which precipitates as its molecular weight increases. Parts of the reaction product that dissolve only in basic aqueous solution would be produced if the lignin particles in the reaction mixture did not completely dissolve during the reaction and were precipitated as a lignin core enveloped in a grafted poly(1-amidoethylene) sheath. Further, if these explanations are correct, using a more effective lignin solvent for the reaction would produce more uniform grafting of lignin and less water-insoluble material in the product.

The first test on solvent improvement was run by adding 3.29 g (0.045 mol) of propanamide to reactions run in irradiated I. Propanamide was added to the reaction because of its chemical similarity to the monomer, 2-propenamide, which appeared to act as a solubilizing agent for the lignin in I. Results of these and comparison reactions are contained in Table III. These data show that reactions run in mixtures containing propanamide have a 40 wt % higher yield and contain less than one-seventh of the water-insoluble product found in samples prepared without propanamide in the reaction mixture. Thus, a solvent that swells or dissolves the lignin molecule is critical to the formation of a high yield of molecularily dispersed graft copolymer.

To find a better solvent for the reaction, seven solvents or solvent mixtures were tested as media in which to conduct the graft copolymerization. The results of these solvent tests are given in Table IV. More than 3.7 g of material, the total mass of lignin and 2-propenamide, are recovered from these syntheses. This mass excess and the calcium and chlorine analysis results show that product from other solvents is not purified by the precipitation procedure used for products synthesized in 1,4-dioxacyclohexane.[2]

The amount of polymeric solid recovered in sample IV-2 was determined by dissolving 0.5052 g of product in 20 mL of distilled water and dialyzing the solution against distilled water using a 3500 molecular weight (maximum) permeable dialysis membrane. After 3 days, dialyzed solution was freeze-dried and 0.3003 g of product was recovered.

A total of 59.4 wt % of the solids recovered from the reaction did not pass through a membrane with a 3500 molecular weight permeability limit. The yield of polymeric product from the dimethyl sulfoxide reaction is thus 75.7 wt %. The amount of water-insoluble material contained in the reaction products formed an alternate solvent is less than one-tenth of that usually found in products formed in dioxane. Further, the reaction run in dimethyl sulfoxide contains a single-phase, viscous fluid at the end of the reaction. A uniform, fluid reaction mixture is a desirable state for the final reaction product because precipitate, formed in three of the solvent mixtures, usually does not entrap living polymers and thus promotes termination of the polymer. A precipitation reaction thus controls product properties by solubility of the product in the reaction mixture. Reaction in solvent, however, allows the product properties to be controlled by mole ratios of reagents in the solution and by monomer reactivity. Specific benefits of solution polymerization will be (1) the opportunity to produce high-molecular-weight polymer since polymerization is not terminated by precipitation and (2) to take advantage of the gel effect that might occur in solvents such as dimethyl sulfoxide (II).

A reaction was run in II to see if the treatment of lignin without polymerization would change its solubility properties. The reaction was a duplicate of test IV-2 but no 2-propenamide (monomer) was added. Method 1 without dialysis was used to recover 0.15 g of product from the reaction. Analysis showed this solid to be 37.3 wt %, water-insoluble lignin. The other 1.25 g of solids from the reaction was dissolved by the 2-propanone.

These results show that the polymerization of 2-propenamide produces the water-soluble lignin product obtained from reaction IV-2, a product previously shown by aqueous size exclusion chromatography, dialysis, and solubility to be graft copolymer. Since reactions run in II provide a more soluble product and greater flexibility in changing product properties, additional work to define the mechanism of this grafting process will be done using II as solvent.

Table III
Results of Reactions Run in the Presence of Propanamide

sample[a]	yield, g	yield, wt %	limiting viscosity[b], dL/g	limiting viscosity[b], corr coeff	precipitation test: wt of reacn product used, g	precipitation test: wt of solids recd, g	precipitation test: wt % insol reacn prod
				Plus Propanamide			
1	3.7	100	49.2	0.998	0.2003	0.0022	1.1
2	3.7	100	56.0	0.999	0.50032	0.0063	1.26
3	3.7	100	62.8	0.998	0.50010	0.01145	2.29
				No Propanamide			
4	2.24	60.5	68.0	0.996	0.50065	0.0566	11.3
5	2.20	59.5	61.5	0.999	0.5003	0.0467	9.3

[a] All samples contained 0.5 g of lignin, 3.20 g of 2-propenamide, 0.15 mL of ceric sulfate solution, and 0.50 g of calcium chloride in 20 mL of 1,4-dioxane that had been bubbled with O_2 for 5 min and irradiated with a 10^3-W Xe lamp for 3 h. [b] In distilled water at 30 °C.

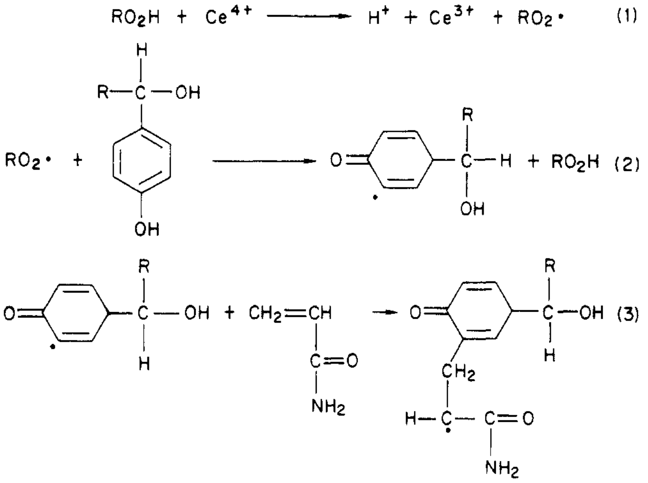
Table IV
Results of Syntheses[a] Run in Different Solvents

sample	solvent	yield, g	reacn prod comp, wt %: lignin	reacn prod comp, wt %: 1-amido-ethylene	reacn prod comp, wt %: Ca	reacn prod comp, wt %: Cl	limiting viscosity, dL/g	precipitation test: wt of reacn prod used, g	precipitation test: wt of solids recd, g	precipitation test: wt % insol in water	phases in reacted mixt
1	1-methyl-2-pyrrolidinone	4.4	4.74	75.36	3.11	2.85	14.2	0.20075	0.002	1.0	precipitate
2	dimethyl sulfoxide	4.71	6.5	76.73	2.79	2.07	32.2	0.20065	0.001	0.5	gelled solution
3	dimethylacetamide	4.13	5.61	57.43	2.77	1.85	27.6	0.20065	0.0018	0.9	precipitate
4	dimethylformamide	4.25	7.18	73.75	2.82	1.90	32	0.20015	0.0023	1.1	precipitate
5	50:50 (v/v) dimethyl sulfoxide–dioxane	4.19	5.13	72.14			53	0.2005	0.00175	0.9	precipitate
6	50:50 (v/v) dimethyl sulfoxide–water	4.28	6.27	71.52			66	0.2005	0.00585	2.9	two fluid phase sample, gelled bottom layer
7	pyridine	4.00	5.42	71.67			47	0.2001	0.001	0.5	precipitate

[a] Each reaction contained 0.50 g of lignin, 3.2 g of 2-propenamide, 0.4 g of 1,4-dioxane autoxidation product, 0.15 mL of ceric sulfate solution, and 20.0 mL of solvent.

Mechanism Studies. The grafting initiator is suspected to be 2-hydroperoxy-1,4-dioxacyclohexane oxidized to a cycloalkoxy or peroxyl radical. This radical or another oxidation product may then abstract a hydrogen atom from lignin or react with lignin to form a grafting site on that backbone. Potential sites of hydrogen abstraction are the 30 phenol groups, the 85 hydroxymethylene groups, or the 5 *p*-hydroxybenzyl alcohol groups that are contained in every 100 repeat units of lignin.[7,8] The lignin radical is then assumed to react with a 2-propenamide molecule to start graft copolymerization. A peroxide/cerium(IV) reaction is the first possible initiation mechanism and is shown in the following reaction mechanism:

Mechanism 1

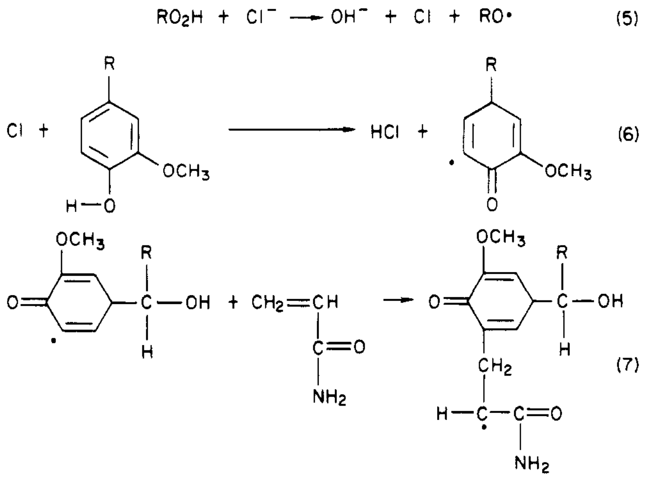


An alternate mechanism for the action of the hydroperoxide is that it oxidizes chloride ion to produce free chlorine in the reaction mixture. This is an electrochemically allowed reaction in water

$$H_2O_2 + 2H^+ + 2Cl^- \rightarrow 2H_2O(l) + Cl_2(g) \qquad E° = 0.417\ \mathrm{V} \quad (4)$$

and may also occur in a polar solvent such as I or II. The native chlorine may then initiate polymerization by proton abstraction from lignin or radical attack on the biopolymer.

Mechanism 2



These alternative explanations of the initiation process were tested by varying mole ratios of reagents in a grafting

Table V
Graft Copolymerization Reactions Run Using *tert*-Butyl Hydroperoxide as Initiator[a]

	initiator added								
	tert-butyl hydroperoxide		Ce(IV)			yield		compd, wt %	
product	g	mol × 10^3	g × 10^3	mol × 10^5	Ce(IV):RO_2H mol ratio × 10^3	g	wt %	lignin	1-amidoethylene
1	0.254	2.82	1.05	0.75	2.66	2.37	64.1	13.9	70.9
2	0.508	5.64	1.05	0.75	1.33	2.70	73.0	9.26	70.8
3	0.135	1.50	1.05	0.75	5.0	2.70	73.0	9.54	68.6
4	0.254	2.82	3.15	2.25	7.98	2.71	73.2	8.2	71.0
5	0.254	2.82	5.25	3.75	13.3	2.16	58.4	9.76	68.9
6	0.254	2.82	0.21	0.15	0.53	2.36	63.8	7.88	68.1
7	0.508	5.64	3.15	2.25	3.99	2.3	62.2		
8	0	0	1.0	0.75	∞	0	0		
9	0.254	2.82	1.05	0.75	2.66	2.60	70.3	9.15	64.9
10	0.254	2.82	1.05	0.75	2.66	1.80	48.6	11.9	58.1
11	0.254	2.82	1.05	0.75	2.66	2.3	62.2	10.0	64.9

[a] All reactions save no. 8 contained 0.5 g of lignin, 3.2 g of 2-propenamide, and 0.5 g of calcium chloride in 20 mL of distilled dioxane. Reaction 8 was similar to the other reactions but contained only 0.2 g of calcium chloride. Products purified by method 1.

Table VI
Reaction and Product Data from Lignin/2-Propenamide Grafting Reactions Run in Dimethyl Sulfoxide

	yield					product comp, wt %				
sample no.	before dialysis, g	after dialysis, g	wt %	$CaCl_2$ added, mmol	limiting viscosity, dL/g	lignin	1-amido-ethylene units	Ca^{2+}	insol material in prod, wt %	Cl^- ion: hydroperoxide mol ratio × 10^3
			A. Reactions Run with 0.045 mol of 2-Propenamide[a]							
1	4.40	3.34	90.4	4.50	0.44	6.03	65.8	2.86	0.27	1.11
2	4.07	3.30	89.4	0.901	0.62	5.48	68.4	0.76	2.0	0.812
3	3.90	3.13	84.5	0.451	0.67	4.94	68.9	0.40	0.77	0.406
4	3.46	2.86	77.4	0.0901	0.80	4.16	69.4	0.09	0.73	0.81
			B. Reactions Run with 0.028 mol of 2-Propenamide							
5	3.10	2.12	84.8	4.50	0.37	6.88	59.1	3.54	1.09	1.11
6	3.04	2.09	83.6	0.901	0.40	6.26	58.8	1.01	0.55	0.812
7	2.68	2.11	84.4	0.451	0.48	8.13	66.4	0.558		0.406
8	1.84	1.44	58.0	0.0901	0.57	6.54	71.4	0.330		0.081
			C. Reactions Run with 0.014 mol of 2-Propenamide							
9	2.14	1.10	73.6	4.50	0.19	12.2	39.5	5.45	2.19	1.11
10	1.12	1.06	70.9	0.901	0.293	13.7	57.5	1.65	8.06	0.812
11	1.49	0.857	57.1	0.451	0.28	15.0	53.0	0.88	2.92	0.406
12	1.25	0.920	61.3	0.0901	0.28	15.5	57.4	0.325	4.20	0.081

[a] All reactions contained 0.50 g of lignin, 0.15 mL of Ce(IV) in 1 M H_2SO_4, 20.0 mL of dimethyl sulfoxide, and 0.15 g of 1,4-dioxacyclohexane oxidation product.

reaction and determining how properties of the products varied in response. In the first series of reactions, mechanism 1 was tested by adding an excess of 3,3-dimethyl-1,2-dioxabutane, $CH_3C(CH_3)_2OOH$, and differing amounts of Ce(IV) ion in 1.0 M aqueous sulfuric acid to a synthesis mixture dispersed in I. Results are given in Table V.

These data show that yield does not change when the cerium ion:peroxide ratio is changed by a factor of 4, as shown by samples V-2, -3, and -4. High levels of cerium(IV) lower yield, as shown by sample V-5. In an absence of hydroperoxide, no reaction occurs, as shown by reaction V-8, but reaction does occur in the presence of hydroperoxide and absence of cerium(IV).[9] These data imply that mechanism 1 is not a valid explanation of the graft initiation in this reaction.

To define the variability of results for syntheses of the type given in Table V, results of three repeats of test V-1 are given as samples V-9, -10, and -11. The mean yield of samples V-1, -9, -10, and -11 is 2.27 ± 0.34 g for a variability of 9 wt %.

Calcium chloride or a similar chloride-containing salt is a necessary reagent in this reaction. Previous tests (ref 4, Table 2, and ref 9) show that reactions run in the absence of such salt produce little if any graft copolymer. To determine if the critical role played by chloride ion in this synthesis was described by mechanism 2, a series of reactions were run with the amount of calcium chloride present in the reaction pot reduced from 4.5 to 0.1 mmol. Results of these tests are given in Table VI.

These data show that yield decreases as the chloride ion: hydroperoxide mole ratio decreases. Further, limiting viscosity number increases as this mole ratio decreases. In graft copolymers, increasing $[\eta]$ means increasing molecular size, normally the result of reduced numbers of grafts per backbone molecule and increasing degree of polymerization. These results thus support the initiation process proposed in mechanism 2. If chlorine abstracts a hydrogen atom, as shown, to produce hydrogen chloride, the chloride ion is a needed catalyst for this reaction. If chlorine attacks a structure in pine lignin to form a chlorine adduct, then chlorine is a controlling reagent.

Digestion studies to remove the backbone and leave a side chain for molecular weight characterization will be needed to determine grafting frequency. Values of N_g, the number of grafts per backbone molecule, will further refine a possible mechanism.

The reaction of hydroperoxides and chloride salts in I was tested by titration. Solutions of 3,3-dimethyl-1,2-dioxabutane or hydrogen peroxide in I were titrated by the iodine/thiosulfate technique. The ratio of equivalents

Table VII
Synthesis Data and Results from Reactions Run with Varied Hydroperoxide:Lignin:Chloride Ion Mole Ratios

sample	comp of reacn,[a] g		yield			comp of prod, wt %			$[\eta]$, dL/g	insol material in prod, wt %	mol ratios of reactants in reacn[c]		
	$CaCl_2$	Hy[b]	before analysis, g	after dialysis, g	wt %	lignin	1-amidoethylene units	Ca^{2+}			Cl/Hy	lignin/Hy × 10^2	lignin/Cl × 10^2
1	0.50	0.4	4.71	2.75	74.2	6.5	76.7	2.79	0.32	0.50	2.7	1.56	0.576
2	0.10	0.4	3.30*	2.56	69.3	5.38	67.4	0.73	0.56	0.87	0.54	1.56	2.88
3	0.05	0.4	2.72*	2.14	57.8	4.94	67.9	0.42	0.69	1.0	0.27	1.56	5.76
4	0.01	0.4	3.16	2.59	70.1	4.60	76.0	0.14	0.77	0.90	0.054	1.56	28.8
5	0.50	0.25	4.31	3.30	89.4	7.00	67.0	2.39	0.35	0.72	4.28	2.47	0.576
6	0.50	0.15	4.40	3.34	90.4	6.03	65.8	2.86	0.44	0.27	7.2	4.15	0.576
7	0.50	0.80	4.73	3.28	88.7	7.21	62.3	2.48	0.31	1.50	1.35	0.779	0.576

[a] Each reaction contained 0.5 g of pine lignin, 45 mmol of 2-propenamide, 0.15 mL of 0.05 M Ce(IV), and 20.0 mL of dimethyl sulfoxide. [b] Hy = 2-hydroperoxy-1,4-dioxacyclohexane. [c] Number-average molecular weight, M_n = 9600, used for lignin.

found to equivalents expected from five determinations was 1.028 ± 0.089 and 1.022 ± 0.0079, respectively. These tests showed the redox titration could be successfully run in I.

Titrations in the presence of 9.0 mmol of chloride ion were then run on the hydroperoxides. Titration detected 98% of the organic hydroperoxide and 99.7% of the hydrogen peroxide. These results were not affected by the presence or absence of oxygen.

Since virtually all of the peroxide is present in the sample, after equilibration with chloride, the titration results show that direct reaction of hydroperoxide with chloride is not occurring. Thus, if mechanism 2 is a basic part of the initiation of graft copolymerization, it does not involve the direct attack of hydroperoxide on chloride ion shown in reaction 5 but instead involves a multistep reaction of hydroperoxide, chloride, and lignin.

The effect of combined variation of hydroperoxide, chloride, and lignin is tested in a series of reactions which gave the results of Table VII. These data show the following functional dependencies between reactant mole ratio and product properties. As chloride:hydroperoxide ratio decreases, there is a decrease, with scatter, in yield, a decrease in product lignin content, and an increase in $[\eta]$. As lignin:chloride ratio decreases, there is no pattern in yield response, lignin content of the product increases, and $[\eta]$ decreases. As lignin:hydroperoxide ratio decreases, there is no response in the above-cited, three product properties.

Since chloride:hydroperoxide and lignin:chloride ratios are correlated reaction variables, these data provide some support for a three-component initiation process for the graft copolymerization. Other three-component initiation systems are known.[10-12]

Conclusions

Graft copolymerization of 2-propenamide onto Kraft pine lignin can be initiated by 2-hydroperoxy-1,4-dioxacyclohexane, an autoxidation product of 1,4-dioxacyclohexane. Grafting can also be produced by hydrogen peroxide or 1,2-dioxa-3,3-dimethylbutane. Graft copolymer is formed by free radical polymerization of 2-propenamide in 1,4-dioxacyclohexane containing lignin, calcium chloride, cerium(IV) ion, and a hydroperoxide.

Reaction was attempted in 1-methyl-2-pyrrolidinone, dimethyl sulfoxide, dimethylacetamide, dimethylformamide, pyridine, and some mixtures of these solvents. Reactions run in dimethyl sulfoxide showed the best yield, product properties, and opportunity to make use of the gel effect during synthesis.

Blank reactions show that the reaction conditions and treatment do not alter lignin but the polymerization sharply alters solubility and molecular size. This confirms grafting. Two possible mechanisms for the reaction are reaction of hydroperoxide with (1) cerium(IV) or (2) chloride ion. The cerium ion initiation process appears to have been eliminated by these tests. Direct reaction of hydroperoxide with chloride ion in 1,4-dioxacyclohexane or dimethyl sulfoxide does not occur either, however. Correlation of chloride:hydroperoxide mole ratio and lignin:chloride mole ratio to product properties implies that a multistep initiation process involving chloride ion, hydroperoxide, and lignin produces grafting.

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