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Graft 1-Phenylethylene Copolymers of Lignin. 1. Synthesis and Proof of Copolymerization

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ABSTRACT: A method of grafting lignin has been developed which allows 1-phenylethylene (polystyrene) graft copolymers of lignin to be quantitatively made. The grafting reaction is a solution polymerization often run in aprotic, polar, organic solvents. The reaction initiates free-radical grafting of lignin by a redox reaction involving hydrogen peroxide and chloride ion. Grafting changes the solubility and surface properties of lignin, converting it to a thermoplastic. The lignins grafted have been obtained from pine by kraft process and hardwoods by base extraction.

Introduction

Technical solutions to social–technical problems, such as the warming of the planet by the greenhouse effect[1,2] and the loss of energy supplies caused by the consumption of fossil fuels,[3,4] often involve the utilization of biomass. There are many sources of biomass ranging from sewage sludge to lobster hulls, but the bulk of this material is one of the two most common natural polymers, cellulose and lignin. Lignin is a biomass processing residue of paper production or ethanol fermentation that is often burned as fuel. Before it can be used either as a part of the solution to environmental problems or as an article of commerce, a great deal of technical information must be known about lignin. Much of this information concerns the nature of the material itself, but equally important is fundamental knowledge of the chemistry for alteration of lignin and the chemistry and physics of the altered products. One such chemistry for the alteration of lignin involves the formation of complex, thermoplastic copolymers of lignin. This is the reaction which will be discussed here.

Lignin has previously been grafted with ethenylbenzene (styrene monomer) by irradiation of lignin/ethenylbenzene mixtures.[5–7] Stannett showed that, on average, only 7% of the lignin was grafted by this technique.[8] We have formed graft copolymer by conducting a free-radical polymerization with ethenylbenzene in nitrogen-saturated, organic or aqueous/organic solvent containing lignin, calcium chloride, and a hydroperoxide. We have used solution polymerization to prepare numerous, laboratory-scale samples of poly(lignin-*g*-(1-phenylethylene)) copolymer. Solution polymerization gives us easy heat control and rapid production of products for testing.

The product is a thermoplastic copolymer. In the following sections, the synthesis procedure, proof of grafting, purification procedures, and characterization results will be described.

Experimental Section

Synthesis: Dimethyl sulfoxide has been used as the solvent for the reactions reported here. This reaction can be successfully run with concentrations or mole ratios of the reactants in the following ranges: (1) polymerizable solids' content of the reaction, 23 wt % or less; (2) hydroperoxide to calcium chloride, 0.25–32; (3) hydroperoxide to lignin (M_n), 21–113; and (4) weight fraction of monomer in polymerizable solids, 0.01–0.95.

Prepare sample A by placing pure ethenylbenzene in a conical flask and bubble it with nitrogen (N_2) for 10 min. Prepare sample B by placing lignin, calcium chloride, and dimethyl sulfoxide solvent in a conical flask, stir until dissolved, and bubble the solution with N_2 for 10 min. Samples A and B are stirred while being purged with nitrogen. Add H_2O_2 to sample B, and bubble it with N_2 for 20 min. Add sample A to sample B. After 5 min of stirring and bubbling N_2 through the reaction mixture, the flask is stoppered and placed in a 30 °C bath for 48 h.

Initial reactions were not stirred while in the 30 °C bath. The reaction was terminated by addition of 1% hydroquinone solution. The reaction mixture was diluted with 100 mL of water and allowed to dialyze against pure water for several days. The phase behavior seen in initial reactions indicated that the reaction should be stirred throughout the synthesis.

The stirring rate and force will depend on (1) the amount of ethenylbenzene monomer in the monomer mixture, with higher mole fractions of ethenylbenzene requiring higher rates of stirring, and (2) the shape and structure of the reaction vessel. High shear rates in the reaction should be avoided because they will cause the formed polymer to mechanically degrade. The preferred stirring rate in the conical flask used in laboratory synthesis is 2–5 Hz. This produces a shear rate of approximately 10–200 s^{-1} in the reaction mixture and is the preferred shear rate for high-yield synthesis. All reactions are terminated by opening the reaction vessel. This terminated slurry can then be added to 10 times its volume of acidified water (pH = 2), and the polymer can be recovered by filtration.

The fractionation of the graft copolymer is diagramed in Figure 1. The reaction product, A, is extracted with benzene for 48 h. The benzene-soluble material is recovered by evaporating the benzene, and the solid is labeled fraction BeEx. The solid not dissolved in benzene is labeled fraction B and is slurried with 0.5 M sodium hydroxide for at least 16 h. This solution is filtered, and the filtrate is dialyzed against water for 3–5 days by using dialysis tubing. The solid filtered from the base is washed with 2 M hydrochloric acid, washed with distilled water, dried, and labeled fraction C. The dilute, dialyzed solution is then dried or freeze dried to recover base-soluble fraction D.

Assays: Analysis procedures for oxidizing equivalents by iodine/thiosulfate titration and elemental composition are given in ref 9.

Materials: Most of the lignin used in these studies is a kraft pine lignin prepared in "free acid" form with a number-average molecular weight of 9600, a weight-average molecular weight of 22 000, and a polydispersity index of 2.29. Ash content of the lignin is 1.0 wt % or less. The material was used as recovered from acidified black liquor. Elemental analysis results are C = 61.66, N = 0.89, H = 5.73, S = 1.57, Ca = 0.08, and Fe = 0.014 wt %.

Yellow poplar lignin from Bioregional Energy Associates of Floyd, VA, was used in some of the reactions. It was extracted from steam-exploded wood with aqueous base and precipitated by addition of mineral acid. It has a molecular weight range of 1000–1200. The elemental analysis results of the lignin are C = 62.15, H = 5.96, N = 0.54, O = 29.64, and S = 0.11 wt %. Some of the lignin used in the copolymerizations described below was extracted with benzene for 48 h at a ratio of 1 g of lignin to 10–15

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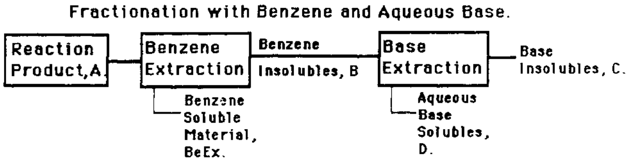

Figure 1. Flow diagram of the copolymer fractionation process.

mL of benzene using a Soxhlet apparatus. This removed the low molecular weight portion of the lignin (approximately 3–5 wt %) and allowed certain fractionation experiments to be done on the product to prove the existence of graft copolymer. This extraction process is not necessary for successful copolymerization of the lignin, however.

A hardwood lignin was recovered as follows. A sample of 300 g of fine hardwood fibers washed from steam-exploded wood pulp by the Masonite Corp., Hardboard Group, P.O. Box 1048, South 4th Avenue, Laurel, MS 39441-1048, was extracted with aqueous 2 M NaOH. The dissolved lignin was precipitated in aqueous HCl and recovered by filtration.

The compound ethenylbenzene was obtained from the Laboratory and Research Products Division of Kodak, Rochester, NY 14650. The ethenylbenzene was purified to remove the stabilizer by washing the monomer three times with aqueous base at a ratio of 1 g of ethenylbenzene to 1 mL of 2 N NaOH. The stabilizer-free monomer was washed with distilled water to pH = 7 and dried with anhydrous calcium chloride for 2 days. It was then distilled under vacuum at 40 °C and 20 mmHg pressure. The central cut was collected in dark bottles and stored in a freezer at −15 °C. Hydrogen peroxide was also from Kodak and was nominally defined as 30% hydrogen peroxide in water. Assays of the two bottles used showed them to be (1) 28.99% H_2O_2 in water, 1.704×10^{-2} equiv/g, 1.907×10^{-2} equiv/mL, and (2) 29.86% H_2O_2 in water, 1.756×10^{-2} equiv/g, 1.947×10^{-2} equiv/mL. Reagent-grade 1,4-dioxacyclohexane, anhydrous calcium chloride, and dimethyl sulfoxide were used in these experiments. Other salts were reagent-grade materials and were used as supplied.

The 2-propenamide (common name, acrylamide) 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. Nitrogen used in the syntheses was commercial-grade bulk gas.

Equipment: Freeze drying was done on a Virtis Model 10-010DA lyophilizer. Weighings were done on a Mettler H6, four-decimal-place balance. All benzene extractions were done in a Soxhlet apparatus. Fourier transform infrared spectroscopy was done on a Nicolet 5DX spectrophotometer controlled by a Nicolet computer and equipped with a Hewlett-Packard ColorPro plotter.

Results and Discussion

A large number of polar monomers, prone to hydrogen bonding, have been added to lignin using this free-radical grafting process, including 2-propenamide,[9-12,24] repeat units of 2-propenoic acid,[13,14] 2,2-dimethyl-3-amino-4-oxohex-5-ene-1-sulfonic acid,[15-17] dimethyldiprop-2-enylammonium chloride,[18,19] (3-oxy-4-oxo-5-methylhex-5-enyl)trimethylammonium methylsulfate,[20,21] (3-oxy-4-oxo-5-methylhex-5-enyl)trimethylammonium chloride,[22] α-(1-methyl-1-oxo-2-propenyl)-ω-hydroxypoly(oxy-1,2-ethanediyl) with an average of 1, 5, or 10 poly(oxy-1,2-ethanediyl) repeat units,[23] and *N*,*N*-dimethyl-2-propenamide.[24] Table I gives results from a series of unstirred reactions run to determine if 1-phenylethylene side chains could be attached to lignin. The reactions were run to optimize synthesis conditions when a nonpolar monomer, ethenylbenzene, was used in place of progressively larger portions of a polar monomer, 2-propenamide. Previous work[5-8] had shown 2-propenamide was extensively grafted by this chemistry. The results of Table I show that yield falls off as the amount of ethenylbenzene in the reaction increases to more than 50% of all monomer. The data show that graft copolymer can be made using this reaction but that yields on the order of 25–40 wt % are common when more than half of the monomer added to the grafting reaction is ethenylbenzene. These yields are low and make this an impractical polymerization technique for forming graft copolymer. Further tests were then run to find solvent, reagent, and reaction conditions that would maximize yield from the reaction. Some of these reactions are listed in Table II.

Table I
Grafting of Yellow Poplar Lignin with Monomer Mixtures[a]

	material added, g			yield	
sample no.	lignin	ethenylbenzene	2-propenamide	g	%
1-1	1.00	0.460	6.077	5.5	73.0
1-2	1.00	0.937	5.757	9.6	125.
1-3	1.00	1.875	5.118	6.6	82.8
1-4	1.00	2.343	4.798	8.0	98.3
1-5	1.00	4.687	3.198	2.3	25.9
1-6	1.00	1.700	0.0	1.1	40.7

[a] All reactions were initiated with calcium chloride and hydrogen peroxide.

The reaction with dimethyl sulfoxide gave the highest yield, so DMSO was chosen for further tests. The next series of tests focused upon which salt to use to provide chloride ion and what amount of solvent to use in the reaction (concentration effects). Some of these data are given in Table III. These reactions were run on a larger scale and showed that calcium chloride was the preferred coinitiator. Other halide salts could be used in grafting, as the data of Table III showed, but yield and conversion of monomer to copolymer were highest when calcium chloride was used in the reaction. Further, these reactions were stirred continuously and gave yields a factor of 2 larger than that shown by similar unstirred reactions.

Reaction 3-5, a blank, shows that a hydroperoxide is critical to the reaction since when the hydroperoxide is omitted, the yield of the reaction drops to about the amount of lignin added to the reaction. This shows that graft copolymerization is not occurring. To show lignin grafting is occurring in the other reactions, however, requires testing of the reaction product. Proof of formation of graft copolymer was completed by mass balance of fractionated reaction product, solubility tests, wetting tests, phase partitioning tests, and FTIR analysis. A set of reaction products were fractionated by benzene and base treatment to determine if lignin and poly(1-phenylethylene) could be separated.

When a mixture of lignin and poly(1-phenylethylene) homopolymer is treated this way, two pure samples are produced. BeEx is pure styrene homopolymer (poly(1-phenylethylene)), and D, the fraction soluble in aqueous base, is pure lignin. For a copolymer reaction product, none of the fractions is pure. Fraction BeEx, the benzene-soluble part of the product, contains poly(1-phenylethylene) homopolymer and the graft copolymer that has long poly(1-phenylethylene) chains on it. Fraction C contains graft copolymer with medium-sized, poly(1-phenylethylene) chains on it. Fraction D is unreacted lignin and graft copolymer with tiny poly(1-phenylethylene) chains on it. Data from typical separations are given in Table IV. Further, analysis by infrared spectroscopy shows that all four fractions of a copolymer sample contain poly(1-phenylethylene) and lignin while fractions from a lignin–poly(1-phenylethylene) mixture are pure.

Spectra were obtained by Fourier transform infrared spectroscopy from reaction product fractions, pure poly(1-phenylethylene), and treated lignin. Data from the

Table II
Use of Different Solvents in the Grafting Reaction

		material added, g				yield	
sample no.	solvent used	lignin	ethenylbenzene	$CaCl_2$	H_2O_2, mL	g	%
2-7	*N,N*-dimethylformamide	2.00	18.79	2.00	2.00	5.17	24.7
2-8	dimethyl sulfoxide	2.02	18.76	2.00	2.00	19.9	95.9
2-9	1,4-dioxacyclohexane	2.00	18.77	2.01	2.00	1.88	9.05

Table III
Use of Different Salts in the Grafting Reaction

	material added, g						yield	
sample no.	salt used	lignin	ethenylbenzene	salt	DMSO	H_2O_2, mL	g	%
3-1[a]	NaCl	2.00	18.76	2.79	20.04	1.9	7.06	27
3-2[b]	NaCl	2.00	18.76	2.87	30.16	1.9	4.75	14.7
3-3[a]	$CaCl_2$	2.00	18.77	2.02	20.75	1.9	19.69	94.3
3-4[b]	$CaCl_2$	2.00	18.75	2.07	30.10	1.9	19.93	94.6
3-5[a]	$CaCl_2$	2.01	18.76	2.00	20.02	0.0	2.12	10.2

[a] Low solvent content reaction. [b] High solvent content reaction.

Table IV
Mass Distribution of Fractions for the Reaction Product[a]

		wt % of total product in fraction			
sample no.	yield, g/(wt %)	A (total)	BeEx (benzene sol)	C (base insol)	D (base sol)
4-A	17.26/83.06	100	86.3	5.46	
4-B	18.16/87.48	100	91.7	1.8	4.8
4-C	18.65/89.75	100	91.4	2.2	4.9
4-D	18.92/91.09	100	90.1	3.6	5.1
4-E	16.87/81.74	100	88.9	4.9	4.7

[a] Lignin content in the reactions (lignin/(lignin + ethenylbenzene)) is 9.63 wt %.

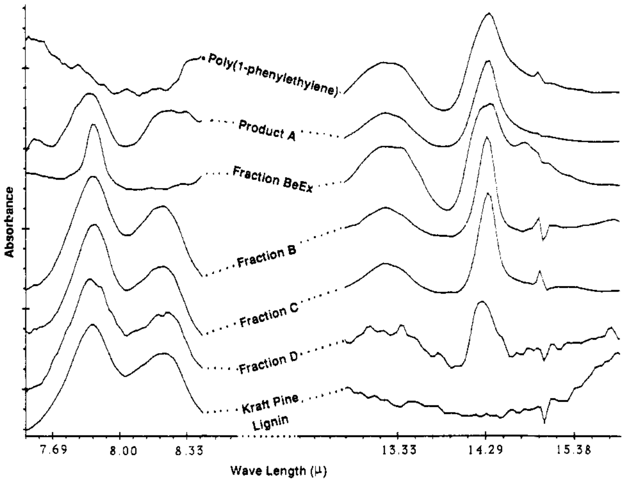

Figure 2. FTIR spectra of the reaction product, its fractions, pure poly(1-phenylethylene), and lignin.

infrared spectra of the materials are presented in Figure 2. Lignin was treated in a blank reaction containing no ethenylbenzene, mixed with poly(1-phenylethylene), extracted with benzene, and tested for infrared absorbance. The lignin shows a characteristic absorbance peak at 7.88-μm wavelength. Poly(1-phenylethylene) shows a strong absorbance peak at 14.35-μm wavelength. The absorbance peaks are distinct and allow the materials to be distinguished. Spectra on all the fractions of reaction product 5-17 show both peaks, as shown by the spectra for the fractions plotted in Figure 2. The spectrum for fraction D is that of reaction 5-18 since fraction 5-17D was too small to analyze. Measurements on other samples of Table IV show the same distribution of both components of the copolymer in all product fractions.

The infrared spectroscopy results show that the two components of the reaction product, lignin and poly(1-phenylethylene), are distributed throughout the product's fractions and thus provide strong evidence that the two components are chemically bound. This would only be possible for a graft copolymer since mechanical and solution mixtures are readily separated by the extraction process. In addition to the infrared data, the following chemical and physical properties of the reaction product also support the hypothesis of copolymer formation:

1. The lignin component in fraction BeEx has been changed from benzene-insoluble to benzene-soluble and, at the same time, from base-soluble to base-insoluble.

2. A large amount of stable emulsion is always formed when a benzene solution of fraction BeEx is fully mixed with aqueous base or water.

3. The lignin component in fraction B has been changed from water-wettable to water-nonwettable.

4. Fraction C cannot be dissolved in benzene or aqueous base. Of course, a mechanical mixture of lignin and poly(1-phenylethylene) does not have the above properties. The different solubility of the fractions of the product in benzene and aqueous base reflects the different size of the grafted poly(1-phenylethylene) chain(s) on lignin. The infrared analyses and the results of the solubility and wettability tests show, when taken together, that the amount of ungrafted lignin is virtually zero.

These data and the size-exclusion chromatography data[25,26] on products from grafting lignin with other monomers by this chemistry all prove that copolymer has been formed.

Data for a spectrum of reactions run to optimize yield and create samples of different molecular weight and composition are given in Table V. All of these reactions were stirred at a rate of about 4 Hz throughout the synthesis.

These products have been shown to be poly(lignin-*g*-(1-phenylethylene))-containing materials by a series of solubility and extraction tests and are formed with almost 100% grafting efficiency for lignin. The results of reactions 5-16–21 show that there is an optimum ratio of peroxide to chloride to lignin that produces maximum yield and ethenylbenzene conversion. The spectrum of mole ratios of hydroperoxide to chloride ion tested in these six experiments is 0.271–1.357, with the optimum yield occurring at a ratio of 0.783. The mole ratio of hydroperoxide to lignin (M_n) at optimum yield is 140. At these ratios, *quantitative* conversion of ethenylbenzene to polymer occurs. The data from a dozen other samples show that there is a broad range of halide ion concentrations that produce high but not maximum yield. Maxi-

Table V
Composition and Yield of Copolymer Reaction Mixtures

	composition, g					
sample no.	lignin	ethenylbenzene	$CaCl_2$	H_2O_2, mL	solvent	yield g/(wt %)
5-16	2.00	18.76	2.02	1.0	20.04	17.80/85.74
5-17	2.00	18.76	2.01	2.0	20.00	20.28/97.69
5-18	2.00	18.76	2.07	3.0	19.99	20.37/98.12
5-19	2.01	18.77	2.02	4.0	20.02	19.10/91.92
5-20	2.01	18.78	2.02	5.0	20.02	18.53/89.13
5-21	3.03	18.78	2.00	2.0	20.00	19.14/87.76
5-26	2.01	4.69	2.04	2.0	20.01	5.68/84.78
5-27	2.01	9.39	2.02	2.0	20.00	10.42/91.40
5-28	2.01	14.07	2.03	2.0	20.10	14.95/92.79
5-29	2.01	18.76	2.03	2.0	20.01	19.52/93.98
5-30	2.02	23.45	2.04	2.0	20.07	23.76/93.29
5-34	8.00	28.15	8.00	8.0	40.02	33.16/91.73
5-35	8.04	18.76	8.00	8.0	40.03	24.14/90.07
5-36	8.01	9.39	8.00	8.0	40.10	15.45/88.79
5-37	8.01	18.74	6.00	8.0	40.04	24.59/91.93
5-38	8.01	18.76	6.00	8.0	40.02	24.36/90.99
5-39	8.04	18.75	6.00	8.0	40.05	15.96/59.57
5-49	0.00	9.39	6.02	8.0	40.0	0.00/0.00
5-53	0.00	23.25	6.0	8.0	40.0	4.97/21.38

mum yield of copolymer can be obtained only when a specific concentration ratio exists between chloride ion, hydroperoxide, and lignin. The data of reactions 5-26–39 show that virtually any combination of lignin and ethenylbenzene can be grafted together to give copolymer. The copolymer's lignin content can thus be varied between 0 and 100 wt % to give any particular lignin content desired. The yields of reactions 5-35 and 5-37–39 are altered by the amount of sodium hydroxide added to the reaction mixture, with the molar concentration of base being 5-35 = 0.00, 5-37 = 0.029, 5-38 = 0.053, and 5-39 = 0.078 M. Comparison of the results of reactions 5-37–39 to that of reaction 5-35 shows that, as the pH of the reaction mixture increases, the yield of the product goes down when the hydroxide concentration reaches 0.078 M. Alteration of pH by introduction of organic bases, such as amines, immediately terminates the reaction since these materials are effective free-radical scavengers. The addition of any acid, such as HCl, to the reaction mixture reduces yield by 35%. Finally, a set of three samples was run to test the effects of changing the sequence of additions in the reaction. The hydrogen peroxide was added to nitrogen-enveloped lignin, the mixture was allowed to sit for 15, 30, or 45 min, and the salt and solvent were added. The reaction was then run as usual. Altering the time between additions had no effect on the reaction or its yield.

Sample 5-49 was run as a blank reaction by placing 6.02 g of calcium chloride in a 250-mL conical flask containing 40.04 g of dimethyl sulfoxide and stirring on a magnetic stirrer for several hours to dissolve the $CaCl_2$. The uniform solution, when formed, had a temperature of over 35 °C. The sample was stirred and bubbled with N_2 for about 10 min before 8.0 mL of 30% aqueous hydrogen peroxide was added to the reaction mixture followed by 9.39 g of ethenylbenzene. The reaction foamed and exploded out of the reaction vessel, resulting in zero yield and recovery of product.

Sample 5-49 was run to see how much polymerization would occur in the absence of lignin in the reaction mixture. It shows a potential problem with the reaction process, however. Reaction reagents that are warm when mixed can cause foaming or an explosion. An altered method was developed to avoid the danger of reaction explosion, and this altered method is illustrated with the following detailed discussion.

A total of 4.00 g of Masonite hardwood lignin, extracted with base from steam-exploded, hardwood pulp and precipitated with HCl, and 3.00 g of calcium chloride were placed in a 250-mL conical flask containing 30.18 g of dimethyl sulfoxide. The solution was cooled to 30 °C to minimize the possibility of explosion or foaming. This solution was stirred and bubbled with nitrogen (N_2) for about 10 min before 4.0 mL of 29.86% aqueous hydrogen peroxide was added to the reaction mixture. N_2 was bubbled through the reaction mixture, and it was stirred for about 5 min more. Next, 14.07 g of nitrogen-saturated ethenylbenzene was added to the reaction. The polymerizable material in the reaction contained 22.1 wt % hardwood lignin. After a short period of stirring and bubbling N_2 through the reaction mixture, the flask was stoppered, placed in a 30 °C bath for 2 days, and stirred continuously. Within 1 h, the unique reactivity of this lignin in this chemistry was evident. The reaction thickened and became turbid. These changes often take 14 h or more with other lignins. The reaction was terminated by adding 7 mL of 1% hydroquinone. The reaction mixture was poured into 1.0 L of acidified water and precipitated. The reaction product from the precipitation was recovered by filtration and found to weigh 17.11 g for a yield of 94.69 wt %.

Other reactions run with the above process; base-extracted, hardwood lignin; and 9.28 or 4.69 g of ethenylbenzene gave yields of 92.08 and 86.16 wt %, respectively. The physical behavior of the reactions during polymerization thus supports the first-order dependence of reaction rate on monomer concentration seen in free-radical reactions[27] and shows that the gel effect can be used to boost yield in these polymerizations.

Comparing the results of the three precooled reactions to those of sample 5-49 also shows the benefit of cooling the components of the reaction mixture to below 30 °C before combining them. There was no foaming or an explosion. The cool lignin solution may fail to exothermically decompose the hydroperoxide, thus avoiding a self-propagating process of decomposition, heating, and decomposition that can result in a spontaneous explusion of the reactor contents from the reaction vessel, as occurred in sample 5-49. Prereaction cooling thus not only promotes high yield but it also increases the safety of the polymerization process.

Sample 5-53, a precooled, blank reaction, shows that the presence of lignin is critical to forming graft copolymer. In sample 5-53, a yield of only 21.38 wt % of polymerizable monomer as poly(1-phenylethylene) homopolymer

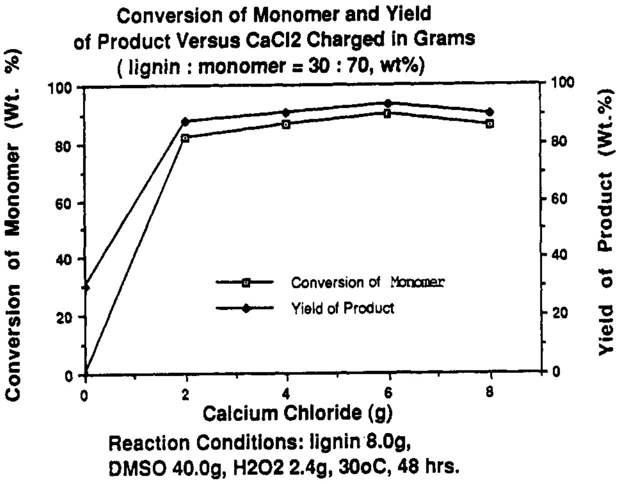

Figure 3. Yield and conversion of monomer for reactions containing different amounts of chloride ion.

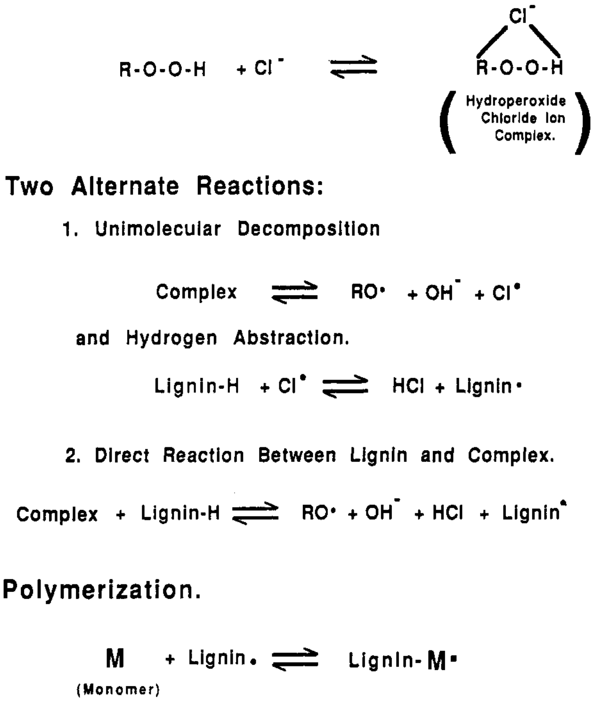

Figure 4. Possible mechanism of the reaction.

is produced when lignin is not added to the reaction mixture. The absence of the backbone sharply reduces yield in the reaction and shows that lignin is apparently critical to the initiation of the reaction.

Additional data on the importance of the several reagents involved in the reaction were gathered by running a series of reactions in which only the chloride ion concentration was varied. A plot of yield versus calcium chloride added to reactions containing 30 wt % lignin and 70 wt % ethenylbenzene as polymerizable materials is given in Figure 3. The plot shows that at constant hydrogen peroxide content, reaction yield rises sharply when chloride ion is introduced into the reaction. Further, the results show that even trace concentrations of chloride ion increase yield by a factor of 2. This implies that the chloride ion must be present to promote the formation of free radicals.

The data of Table V and Figure 3 are coincident with, but not proof of, a possible mechanism for this grafting reaction. The mechanism is outlined in Figure 4. The reaction requires the presence of lignin in the reaction mixture to produce the active, free-radical site of reaction. This observation supports the idea that the reaction might be a concerted reaction between a hydroperoxide–chloride ion complex and lignin rather than the separate reaction steps pictured in Figure 4.

The hydroperoxide and chloride ion react to form a chlorine atom. The chlorine then abstracts hydrogen from lignin to form the free-radical site on the natural backbone and initiate polymerization. Chloride ion could act as a catalyst in this mechanism if the hydrochloric acid formed in the hydrogen abstraction later dissociates. The data of Figure 3 show that such catalytic behavior may be occurring in the reaction.

Solid structure, internal phase behavior, and thermal transitions of these complex plastics will be described in papers discussing the applications of these materials.

Conclusions

By initiation with calcium chloride and hydrogen peroxide in a stirred reaction, a thermoplastic side chain of poly(1-phenylethylene) can be grafted onto lignin via free-radical polymerization. Many halide salts and solvents can be used to conduct the grafting reaction, but calcium chloride and dimethyl sulfoxide have been found most effective for maximizing yield. Stirring the reaction mixture is critical to successful grafting during the reaction. The reaction product is a complex mixture of poly(1-phenylethylene) homopolymer and a broad molecular weight distribution of graft copolymer. The fractionation and spectroscopic analysis of several reaction products confirm the presence of graft copolymer. Mixtures formed by both mechanical mixing and solution evaporation are separated by benzene and base extraction, but reaction products cannot be separated into lignin and poly(1-phenylethylene) fractions by the same procedure. Fourier transform infrared spectroscopy of the fractions confirms the presence of lignin and poly(1-phenylethylene) in all fractions of reaction product. The FTIR data and the results of solubility and wettability tests imply that little if any of the lignin is left ungrafted by the reaction. At a mole ratio of hydroperoxide to chloride ion of 0.783 and a mole ratio of hydroperoxide to lignin (M_n) of 140, *quantitative* conversion of ethenylbenzene to polymer occurs in reactions run in dimethyl sulfoxide. A broad range of halide ion concentrations that produce mole ratios of hydroperoxide to chloride ion between 0.271 and 1.357 produces high but not maximum yield in the reaction. Altering the pH of the reaction mixture by adding free-radical inert bases has no effect until the concentration of base exceeds several hundredths molar. Any addition of acid sharply reduces yield. Reactions initiated with reagents that are above 35 °C when mixed can cause foaming or an explosion. Base-extracted, HCl-precipitated, hardwood lignin reacts more rapidly and completely than other hardwood or softwood lignins tested in this grafting reaction. The gel effect can be used to boost yield in these polymerizations. The data are coincident with, but not proof of, a (hydroperoxide–chloride ion complex) + lignin mechanism for this grafting reaction.

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