Macromolecules **1992,** *25,* 611–616 **611**

Synthesis and Properties of Several Cationic Graft Copolymers of Lignin

John J. Meister*

Department of Chemistry, University of Detroit, 4001 West McNichols Road, Detroit, Michigan 48221-3090

Chin Tia Li

Bychem, Inc., 312 Conococheaque Street, P.O. Box 219, Williamsport, Maryland 21795

Received August 6, 1990; Revised Manuscript Received October 8, 1991

ABSTRACT: A method of grafting lignin has been developed which allows water-soluble, cationic graft copolymers of lignin to be made. The grafting reaction is a solution polymerization often run in aprotic, polar, organic solvents. The cationic copolymers are made by conducting the reaction with dimethyldiprop-2-enylammonium chloride, (5-methyl-4-oxo-3-oxahex-5-enyl)trimethylammonium methyl sulfate, or (5-methyl-4-oxo-3-oxahex-5-enyl)trimethylammonium chloride. The lignins grafted have been obtained from pine by the kraft process.

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 if 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 a 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 copolymers of lignin. This is the reaction which will be discussed here.

The reaction converts lignin to a water-soluble copolymer by graft polymerization. Graft copolymer is formed by conducting a free-radical polymerization with 2-propenamide and a series of cationic monomers in nitrogen-saturated, organic, or aqueous/organic solvent containing lignin, calcium chloride, and a hydroperoxide. We have used solution polymerization to prepare laboratory-scale samples of copolymer. We have shown grafting can be done using any of the fluids of Table I. Solution polymerization gives us easy heat control and rapid production of products for testing. Names, structures, and acronyms of the monomers are given in Table II.

The product is a cationic copolymer with a limiting viscosity number in the range of 0.2–90 dL/g. The products increase the viscosity of aqueous solution and act as flocculating/deflocculating agents, thinning agents, and dispersing agents. In the following sections, the synthesis procedure, purification procedures, characterization results, and proof of grafting will be described.

Experimental Procedures

Materials. Lignin, which makes up the backbone of the graft copolymers, is a cross-linked, oxyphenylpropyl polymer that acts as an intercellular glue in woody plants. 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 is C = 61.66, N = 0.89, H = 5.73, S = 1.57, Ca = 0.08, and Fe = 0.014 wt %.

Table I
Liquids Useful in Solution Polymerization of Graft Copolymers

dimethyl sulfoxide[a] (DMSO)
1,4-dioxacyclohexane
water
dimethylacetamide
pyridine
dimethylformamide
1-methyl-2-pyrrolidinone

[a] Most frequently used liquids given in bold print.

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. The monomer hexammonium methyl sulfate was obtained from CPS Chemical Co. as 80 wt % monomer in water. The monomer hexammonium chloride was obtained from Alcolac Specialty Chemicals as 75 wt % monomer in water. Both of the cationic monomers were purified by freeze-drying to remove water and recrystallized from ethanol–2-propanone mixture (20:80 (v/v)) to ensure purity. The purified crystals were dried under vacuum and stored in a freezer. Dimethyl sulfoxide was stabilized, reagent grade material. Calcium chloride and other salts were reagent grade materials and were used as supplied. Gases used in the syntheses were standard commercial grade cylinder gases.

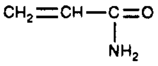
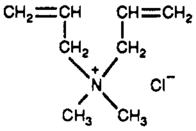
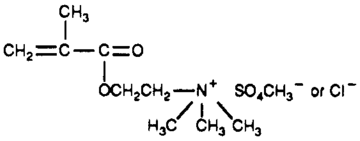
The dialysis membrane used was Spectrapor no. 6, a 1000 upper molecular weight cutoff cellulose, 45-mm-diameter, membrane tubing made by Spectrum Medical Industries, Los Angeles, CA.

Synthesis. The polymerization can be run in any one of several solvents, as illustrated by Table I. Dimethyl sulfoxide or water was used as the solvent for the reactions reported here. In other solvents, the product often precipitates as the reaction proceeds. This reaction can be successfully run with concentrations or mole ratios of the reactants in the following ranges: (1) reactable 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; (4) weight fraction of monomer in reactable solids, 0.01–0.95.

The procedure was as follows. To a dry Erlenmeyer flask of appropriate size was added half of the reaction solvent. All reactants, including the dry mass of hydroperoxide, should not constitute more than 23 wt % of the reaction mixture or an insoluble product may be produced. Dry lignin and dry calcium chloride were added to the reaction vessel, and the vessel was

0024-9297/92/2225-0611$03.00/0

Table II
Nomenclature, Structures, and Acronyms for the Monomers

name	structure	acronym
2-propenamide	 $CH_2{=}CH{-}C(=O)NH_2$	propenamide
dimethyldiprop-2-enylammonium chloride		dipropene chloride
(5-methyl-4-oxo-3-oxahex-5-enyl)trimethylammonium methyl sulfate	 $CH_2{=}C(CH_3){-}C(=O)OCH_2CH_2{-}N^+(CH_3)_3\ SO_4CH_3^-$ or Cl^-	hexammonium methyl sulfate
(5-methyl-4-oxo-3-oxahex-5-enyl)trimethylammonium chloride		hexammonium chloride

capped with a septum or rubber stopper. In a separate vessel, 2-propenamide was dissolved in about one-quarter to one-half of the solvent, and in a third vessel a second monomer was dissolved in the final one-quarter of the solvent. Both monomer solutions and the lignin solution were saturated with N_2 by bubbling with the gas for 10 min. The hydroperoxide was added to the lignin mixture, N_2 was bubbled through the mixture for 5 min, the flask was capped, and the mixture was stirred for 10 min. While the lignin reaction solution was stirred, the monomer solutions were further saturated with N_2. The 2-propenamide solution was added to the lignin solution was stirring under an N_2 blanket, and 1 min was allowed to pass. The second monomer solution was added to the reaction vessel in the same way. The reaction vessel was placed in a 30 °C bath for 48 h. The reaction was terminated with a small volume of aqueous, 1% hydroquinone solution, and a volume of water equal to one-third of the reaction solution volume was added to the product.

This solution can be added to 10 times its volume of 2-propanone and the polymer recovered by filtration. The solids are then redissolved in water. The preceding precipitation step is optional and can be skipped. It was used in the minority of syntheses described here. To remove calcium ion from the product, an amount of $Na_2C_2O_4$ equal to the moles of $CaCl_2$ added to the reaction placed in the solution. The CaC_2O_4 precipitate is removed by filtration. The filtered solution is dialyzed against distilled water for 3–5 days using dialysis tubing. The dilute, aqueous solution is then freeze-dried to recover the product.

Assays. Analysis procedures for (1) oxidizing equivalents by iodine/thiosulfate titration, (2) lignin content by UV assay, (3) 1-(aminocarbonyl)ethylene content by Kjeldahl assay, (4) limiting viscosity number, and (5) elemental composition are given in ref 5. Elemental assay for sulfur was done by ASTM method D 3177-82 with a correction that in step 7.3 the solution is brought to pH $\approx$ 3.8 with 6 M HCl rather than 2.5 M NaOH as incorrectly specified in the procedure. Size exclusion chromatography was done with a mobile phase of pH = 13, 0.1 M NaCl. All solutions were filtered through an 8-μm Nucleopore filter before use. Flow rate was 0.5 mL/min and the mobile phase was not degassed. Injected sample size was 10 μL and the columns were maintained at 43 °C during all separations. Spectra were taken from 200 to 420 nm, and absorbance at 220 nm was plotted versus time for chromatograms. Total permeation volume of the columns was 31 mL, and total permeation time was 62 min.

The number of equivalents of hydrogen peroxide in the aqueous hydroperoxide solution used in synthesis was determined by redox titration as 8.383 mequiv/mL. The graft copolymer Cl^- content was measured by potentiometric titration of chloride ion with silver nitrate ($AgNO_3$) using a calomel electrode as reference and silver electrode as indicator electrode.[6] The end point is determined graphically from the plot of derivative of electrochemical potential with respect to titrant volume, $\partial E/\partial V$, versus volume of $AgNO_3$ added. The content of cationic monomers and propenamide in copolymer is calculated based on the result of elemental analyses for nitrogen, chloride, and sulfur and use of the repeat unit structure of the monomer. Note that this procedure will underrepresent the content of cationic repeat units in the copolymer and overrepresent the 1-(aminocarbonyl)ethylene repeat unit content because of chloride ion loss in dialysis.

Solution Properties. The viscosities of diluted solutions of graft copolymers were measured with a no. 50 capillary viscometer at 30 ± 0.5 °C. The limiting viscosity number of copolymer in pure water is determined using the Fuoss equation[7,8] for ionic copolymer (eq 1) and the Huggins equation[9] for nonionic copolymer (eq 2) to extrapolate four or more viscosity measurements on diluted polymer solutions to zero polymer concentration:

$$\eta_{sp}/C_p = 1/[\eta] + Q_f C_p^{1/2} \tag{1}$$

$$\eta_{sp}/C_p = [\eta] + Q_h[\eta]^2 C_p \tag{2}$$

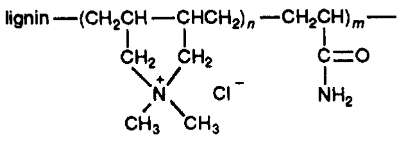
where η_{sp} = specific viscosity (dimensionless), Q_i = the viscosity factor for the fitting equation (i = f, h), C_p = concentration in units of g/dL, and $[\eta]$ = limiting viscosity number (dL/g).

Equipment. Lignin spectra were run on a Beckman DB UV-visible spectrophotometer. Freeze-drying was done on a Virtis Model 10-010DA lyophilizer. Weighings were done on a Mettler H6 4-decimal-place balance. Viscometers used in fluid property measurement were Cannon-Fenske capillary viscometers. Size exclusion separations were performed with a Varian Model 5000 high-performance liquid chromatograph equipped with a Rheodyne 50-μL, fixed-loop injector. Columns used in this work were (1) a Toya Soda TSK-Gel guard column, (2) a TSK-4000-pw column, and (3) a TSK-5000-pw column, all plumbed in sequence. The detector for the chromatography was a Hewlett-Packard HP-1040A high-speed spectrophotometric detector with its supporting computer, the HP-85, containing 16K bytes of additional memory. This detector can perform absorbance measurements at wavelengths from 190 to 600 nm and can detect and store an entire spectrum of the contents of the detector cell over the above wavelength range every second. This capacity allows spectra to be taken at numerous times during the elution of a chromatographic peak and is critical to prove the existence of graft copolymers by multivariate curve resolution.[10]

Results and Discussion

Data from three cationic copolymers will now be presented.

1. **Poly(lignin-*g*-((1-(aminocarbonyl)ethylene)-*co*-(methylene-*N*,*N*-dimethyl-1-azoniocyclopenta-3,4-diylmethylene chloride))) (Lignin–Propenamide–Dipropene Chloride).** Lignin was reacted with dipropene chloride monomer to make a cationic graft copolymer. The structure of the copolymer is illustrated by the formula



$$\text{lignin}{-}(CH_2CH{-}CHCH_2)_n{-}CH_2CH)_m{-}$$

Table III
Synthesis Data of Cationic Lignin Graft Copolymer
Poly(lignin-*g*-((1-(aminocarbonyl)ethylene)-*r*-(methylene-*N,N*-dimethyl-1-ammoniocyclopenta-3,4-diyl-methylene chloride)))[a]

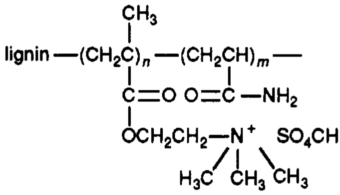
	reaction mixture							reaction parameter					
sample no.	lignin, g	$CaCl_2$, g	A, g	B, g	DMSO, g	EDTA, mmol	E, mL	Cl, mmol	mole ratio	Cl/g	Cl/L	Cl/H	yield, %
3-1	0.66	0.33	2.35	1.03	29.28	1.30	0.65	12.34	83.8/16.2	0.35	18.70	2.26	68.43
3-2	0.65	0.33	2.25	1.25	28.23	1.50	0.65	13.59	80.4/19.6	0.39	20.91	2.49	63.78
3-3	0.66	0.33	2.07	1.55	28.82	1.90	0.65	15.69	75.4/24.6	0.43	23.77	2.88	51.37
3-4	0.66	0.33	1.93	1.88	33.25	2.30	0.65	17.61	70. /30.	0.43	26.68	3.23	49.61
3-5	0.68	0.34	2.69		25.26		0.65	6.13	100/0	0.21	9.01	1.12	95.37

[a] A = 2-propenamide, B = dimethyldiprop-2-enylammonium chloride, mole ratio = mole ratio of monomer A to monomer B, E = 30% hydrogen peroxide (equivalent weight = 8.383 mequiv/mL), Cl/g = chloride content per unit weight of total reaction mass (mmol/g), Cl/L = chloride content per unit weight of lignin (mmol/g), Cl/H = molar ratio of chloride to hydrogen peroxide. The concentration of Na_2EDTA is 200 ppm based on cationic monomer.

and this compound, poly(lignin-*g*-((1-(aminocarbonyl)ethylene)-*co*-(methylene-*N,N*-dimethyl-1-azoniocyclopenta-3,4-diylmethylene chloride))), will be referred to as copolymer 1. The composition, reaction conditions, and yield of copolymer 1 are shown in Table III. The content of dipropene chloride in the reaction ranges from 0 to 30 mol % of total monomer content. The concentrations of lignin, calcium chloride, and monomer in the reaction are around 1.8, 0.9, and 9.5 wt % of total reaction mass, respectively. In the reactions listed in Table III, the ratio of lignin to calcium chloride is 2:1 by weight. The yield of reaction ranges from 49.61 to 95.37 wt %. By comparing yield to reaction chloride ion content, these results indicate that yield of reaction decreases when content of chloride ion (on a molar basis) increases. Simultaneously, however, the yield increase when content of 2-propenamide increases. Physical properties and characterization data are compared below with those from two other copolymers.

Other cationic copolymers can be made using this chemistry. Two alternate cationic copolymers which differ from copolymer 1 in structure, stability, charge density, and molecular size were made. These copolymers are based on hexammonium methyl sulfate and hexammonium chloride. These two monomers were used to make two cationic copolymers which will be referred to as copolymer 2 [poly(lignin-*g*-((1-(aminocarbonyl)ethylene)-*r*-(1-methyl-1-(1-oxo-2-oxabutylenetrimethylammonio)ethylene methyl sulfate)))] and copolymer 3 [poly(lignin-*g*-((1-(aminocarbonyl)ethylene)-*r*-(1-methyl-1-(1-oxo-2-oxabutylenetrimethylammonio)ethylene chloride)))].

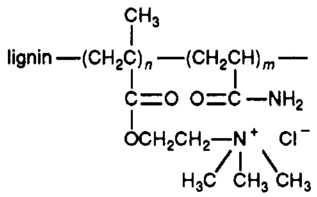
2. Poly(lignin-*g*-((1-(aminocarbonyl)ethylene)-*r*-(1-methyl-1-(1-oxo-2-oxabutylenetrimethylammonio)ethylene methyl sulfate))) (Lignin–Propenamide–Hexammonium Methyl Sulfate). Copolymer 2 has the structure



A series of reactions, similar to those run with the diene monomer, were run with hexammonium methyl sulfate. For the reactions used to make copolymer 2, the compositions, yields, and reaction conditions are shown in Table IVA. The content of the methyl sulfate monomer ranges from 24.3 to 100 mol % of the total monomer content, and the concentrations of lignin, calcium chloride, and monomer are approximately 1.8, 0.9, and 16.5 wt % of the total reaction mass, respectively. The weight ratio of lignin to calcium chloride is also 2:1 by weight. The yields range from 32.19 to 69.62%. The lower yield of sample 4-5 might be due to the absence of propenamide.

On the basis of the above results and the optimum salinity found with the production of poly(lignin-*g*-2-propenamide),[14,15] a new reaction series for copolymer 2 was run at 2.4 wt % of calcium chloride while keeping the monomer content at 1.10 mmol per unit weight of total reaction mass. The composition, reaction conditions, and yield are listed in Table IVB. The yield increases at least 10%.

3. Poly(lignin-*g*-((1-(aminocarbonyl)ethylene)-*r*-(1-methyl-1-(1-oxo-2-oxabutylenetrimethylammonio)ethylene chloride))) (Lignin–Propenamide–Hexammonium Chloride). Copolymer 3 has the structure



For copolymer 3, the reaction composition, conditions, and yield of an initial series of reactions are given in Table VA. The content of hexammonium chloride ranges from 0 to 100 mol % of total monomer content. The concentrations of lignin, calcium chloride, and monomer in the reactions are around 1.5, 0.8, and 15 wt %, respectively. The ratio of lignin to calcium chloride is 2:1 by weight. The same change in yield as a function of chloride ion content in the reaction mixture was seen when chloride ion content in these reactions increased, except when water was used as cosolvent.

The incorporation of water in the solvent system significantly increases yield with yields of up to 90 wt % common in the mixed solvent. In the mixed-solvent reactions, however, these high yields are obtained when the chloride ion content of the reaction is well above the optimum ion content which will produce a high yield in a reaction run in pure DMSO. This boost in yield could be due to the increased solubility of monomer and copolymer in the mixed solvent, since water is the best solvent for both monomer and the cationic polyelectrolyte. The result of the above experiments clearly indicates that yield of graft copolymerization is highly dependent upon reaction content of chloride ion and solvent. The chloride ion for these reactions comes from either calcium chloride or the counterion from chloride-containing monomers. Both sources of chloride ion must be considered in designing a synthesis for maximum yield. To distinguish the chloride ion effect between calcium chloride and chloride counterion, the lignin–propenamide–hexammonium chloride reaction to make copolymer 3 was run at

Table IV
Synthesis Data of Cationic Lignin Graft Copolymer 2[a]

	reaction mixture						reaction parameter					
sample no.	lignin, g	$CaCl_2$, g	A, g	C, g	DMSO, g	E, mL	Cl, mmol	mol ratio	Cl/g	Cl/L	Cl/H	yield, %
						Part A						
4-1	0.67	0.33	2.26	1.58	29.41	0.65	5.95	75.8/24.2	0.17	8.90	1.09	63.40
4-2	0.68	0.34	1.62	3.17	29.37	0.65	6.13	59.9/40.1	0.17	9.01	1.12	61.83
4-3	0.67	0.33	1.34	4.74	29.16	0.65	5.95	45.2/54.8	0.16	8.90	1.09	69.62
4-4	0.68	0.34	0.63	6.36	29.34	0.65	6.13	22.4/77.6	0.16	9.01	1.12	67.78
4-5	0.67	0.33		7.84	29.42	0.65	5.95	0/100	0.15	8.90	1.09	32.19
						Part B						
4-6	0.51	0.88	2.56	2.55	30.06	0.50	15.86	79.7/20.3	0.46	31.10	3.79	77.22
4-7	0.50	0.93	1.92	5.15	30.72	0.50	16.76	59.7/40.3	0.42	33.52	4.08	80.18
4-8	0.50	0.99	1.29	8.36	29.28	0.50	17.84	38.1/61.9	0.43	35.68	4.26	70.44
4-9	0.50	1.02	0.64	10.21	31.40	0.50	18.38	20.0/80.0	0.42	36.76	4.39	91.46
4-10	0.50	1.07		12.77	30.71	0.50	19.28	0/100	0.42	38.56	4.60	70.91

[a] A = 2-propenamide, C = (5-methyl-4-oxo-3-oxahex-5-enyl)trimethylammonium methyl sulfate, mol ratio = mole ratio of monomer A to monomer B, E = 30% hydrogen peroxide (equivalent weight = 8.383 mequiv/mL), Cl/g = chloride content per unit weight of total reaction mass, Cl/L = chloride content per unit weight of lignin, Cl/H = molar ratio of chloride to hydrogen peroxide.

Table V
Synthesis Data of Cationic Graft Copolymer 3[a]

	reaction mixture							reaction parameter				
sample no.	lignin, g	$CaCl_2$, g	A, g	C, g	DMSO, g	H_2O,[b] g	E, mL	Cl, mmol	molar ratio	Cl/L	Cl/H	yield, %
						Part A						
5-1	0.69	0.34	2.45		30.59		0.65	6.12	100.0/0	8.87	1.12	89.65
5-2	0.67	0.34	2.63	0.83	30.46		0.65	10.12	90.2/9.8	15.10	1.86	86.32
5-3	0.68	0.34	2.27	1.68	31.20		0.65	14.21	79.8/20.2	20.90	2.61	83.43
5-4	0.68	0.34	1.70	3.33	47.85		0.65	22.16	59.9/40.1	32.59	4.07	72.22
5-5	0.67	0.34	1.12	4.93	62.89		0.65	29.87	39.9/60.1	44.58	5.48	40.31
5-6	0.67	0.34	0.29	7.40	28.02	3.18	0.65	41.77	10.3/89.7	62.34	7.67	93.27
5-7	0.68	0.34		8.21	26.67	3.55	0.65	45.67	0/100	67.16	8.38	96.20
						Part B						
5-8	0.50	0.38	2.58	1.94	31.08		0.50	16.19	79.5/20.5	32.38	3.86	91.60
5-9	0.50	0.26	2.25	2.82	34.82		0.50	18.27	70/30	36.54	4.36	94.07
5-10	0.50	0.11	1.93	3.37	39.40		0.50	19.95	60.2/39.8	39.90	4.76	91.23
5-11	0.50	0.01	1.61	4.67	45.31		0.50	22.68	50.2/49.8	45.36	5.41	90.71

[a] A = 2-propenamide, C = (5-methyl-4-oxo-3-oxahex-5-enyl)trimethylammonium chloride, E = 30% hydrogen peroxide (equivalent weight = 8.383 mequiv/mL), Cl/L = chloride content per unit weight of lignin, Cl/H = molar ratio of chloride to hydrogen peroxide. [b] The water content is 3 wt % of total solvent.

constant chloride ion content. The reaction composition, conditions, and yield are given in Table VB. Note that the amount of calcium chloride decreases when the amount of hexammonium chloride increases because the total chloride ion content in these reactions is kept at 0.4 mmol per unit weight of reaction mass. This is equal to the chloride concentration when calcium chloride is 2.41 wt % of the total reaction mass, an optimum chloride concentration cited above. The yield increases at least 10% under these conditions. The data of Table VB show that the yield is scattered between 90 and 95 wt % for all of the optimum chloride content reactions. This puts yield at optimum chloride content in the same range as that obtained from the two reactions of Table VA that contain water. These results indicate that the chloride ion content is a critical parameter in controlling the yield of lignin graft copolymer. Further, chloride counterion from dipropene chloride and hexammonium chloride also has the same effect on the yield as calcium chloride salt added to the reaction.

Assays of Cationic Lignin Graft Copolymer. The elemental assays for the series of graft copolymers are given in Table VI. The copolymer nitrogen content will increase when the 1-(aminocarbonyl)ethylene repeat unit content increases. Also, the chloride content will increase when the content of dipropene chloride or hexammonium chloride repeat units increases. In the same pattern, the sulfur content increases when the content of hexammonium methyl sulfate repeat units increases. The elements from counterion content, chlorine and sulfur, are lower than the value expected on the basis of reaction yield. This is apparently due to chloride or methyl sulfate anion loss during purification of copolymer by dialysis. To determine the effect of dialysis on counterion content, a chloride-containing graft copolymer was synthesized and different fractions were purified for different lengths of dialysis time. The results for chloride and nitrogen assays on purified samples of copolymer as a function of dialysis time are given in Table VII. The chloride ion content of the recovered copolymer decreases with increase of dialysis time while the nitrogen content is scattered but essentially constant with increase of dialysis time. This evidence corroborates the hypothesis of counterion loss during dialysis.

Solution Properties of Graft Copolymers. These lignin copolymers are highly water soluble. Since the lignin backbone is insoluble in water, the water solubility of the copolymer is caused by the molecule's side chain. The viscosity of copolymer solutions was measured with a Cannon-Fenske capillary viscometer at 30 ± 0.5 °C. The concentration of solution tested varies from 0.1 to 0.01 wt %. The solution volume taken for testing viscosity is 10 mL. The limiting viscosity number of each copolymer is obtained by using either the Fuoss equation[7,8] (cationic) or the Huggins equation[9] (nonionic), given in eqs 1 and 2.

The limiting viscosity numbers of the copolymers are given in Table VI. For copolymer 1, the limiting viscosity number of the copolymer increases with increasing cat-

Table VI
Elemental Assays of Lignin Copolymer and Limiting Viscosity Number ([η]) in Water at 30 °C

sample no.	N, wt %	Cl, wt %	S, wt %	lignin, wt %	[η], dL/g
		Data for Copolymer 1			
3-1	14.68	2.63		22.17	3.76
3-2	13.78	3.70		15.47	4.02
3-3	13.30	3.88		11.09	2.32
3-4	13.02	3.85		10.70	1.20
3-5	16.37			23.35	0.31
		Data for Copolymer 2, Part A			
4-1	13.15		0.12	10.06	0.46
4-2	8.68		1.69	11.68	1.79
4-3	6.23		3.82	11.40	39.36
4-4	5.61		5.58	8.86	32.36
4-5	3.06		3.72	12.21	15.36
		Data for Copolymer 2, Part B			
4-6	11.77		0.24	7.01	5.07
4-7	8.78		2.99	5.12	23.41
4-8	7.26		3.88	2.44	41.73
4-9	6.29		5.10	4.45	55.03
4-10	5.23		6.35	3.77	85.64
		Data for Copolymer 3, Part A			
5-1	14.79			13.80	0.44
5-2	13.16	0.92		11.30	2.86
5-3	10.69	3.02		9.79	7.09
5-4	7.23	5.97		10.60	12.99
5-5	6.19	4.81		4.60	7.30
5-6	5.68	10.65		6.31	34.97
5-7	5.49	11.48		4.36	36.6
		Data for Copolymer 3, Part B			
5-8	11.62	2.86		5.70	13.07
5-9	10.36	6.21		5.59	16.71
5-10	9.09	8.64		3.00	37.84
5-11	7.76	11.49		5.30	39.85

Table VII
Relationship of Repeat Unit and Counterion Content to Dialysis Time

	elem anal.		
sample no.	N, wt %	Cl, wt %	duration of dialysis, h
7-1	11.39	3.03	0
7-2	10.67	1.28	24
7-3	11.37	0.76	48
7-4	11.41	0.46	72
7-5	11.25	0.32	96
7-6	11.32	0.31	120

Synthesis of Bulk Sample of 5-3[a]

reactant	wt, g	vol, mL
lignin	3.0	
$CaCl_2$	1.50	
propenamide	10.06	
cationic monomer[b]	7.48	
DMSO		137.35
H_2O_2		5.3

[a] The copolymer used for the dialysis test is synthesized as a large-volume repeat of sample 5-3. The reaction is scaled up 4.47-fold. [b] Cationic monomer is (5-methyl-4-oxo-3-oxahex-5-enyl)trimethylammonium chloride.

ionic monomer content in the synthesis reaction. It reaches a peak when cationic monomer content is 19.6 mol % of monomer charge to the reaction and then decreases with a further increase of monomer content. The limiting viscosity number of these copolymers increased with an increase of yield and reaches a maximum at a yield of 63.78 wt %. It then decreases with further increase of yield.

When reactions were run at lower chloride ion content (<0.4 mmol/g, Table IVA), the limiting viscosity number of copolymer 2 goes through a maximum at a cationic monomer content of 54.8 mol %. The same change in limiting viscosity number as a function of yield and cationic monomer content in the reaction mixture was observed in lower chloride ion content reactions to produce copolymer 3. However, when the reactions were run at optimum chloride ion content (Tables IVB and VB), the limiting viscosity of copolymer 2 and copolymer 3 increased linearly with increase of monomer content. The limiting viscosity number does not show a clear relationship with yield for copolymer 2 and copolymer 3 but is a strong function of monomer content and ionic bond content.

Table VIII
Conditions and Results of Size Exclusion Chromatography

		sample no.				
	lignin	3-1	3-2	3-3	3-4	3-5
concn, wt %	0.243	0.502	0.500	0.509	0.512	0.585
init effluent retention time, min	33.0	26.0	26.0	27.0	28.0	24.0
limiting visc no., dL/g		3.76	4.02	2.32	1.20	
retention time to absorbance peak, min	37.0	33.0	34.0	33.0	33.0	30.0

Size Exclusion Chromatography. Size exclusion chromatography (SEC) was first tried on the cationic copolymers in phosphate buffer of pH = 7.40. However, the cationic copolymer would not elute from the column at this pH. An alternate, alkaline brine, mobile phase was tried to eliminate the absorption between column and cationic side chain.[15] A mobile phase of pH = 12.5 and 0.2 N sodium chloride eliminated absorption and allowed size-based elution of the analyte. Table VIII shows SEC results for copolymer 1. The pressure drop across the column was 22 atm, and elution was monitored by plotting absorbance of the detector cell contents at 220 nm. All of the copolymers showed an initial elution at 24–28 min and reached an absorption peak at 30–33 min under the same conditions. The pure lignin sample showed an initial elution at 33 min and reached a maximum at 37 min.

Within the limits of the experimental accuracy of these chromatograms, all of the copolymer samples are larger than the lignin from which they were synthesized. All of the chromatograms show a broad single peak with minimal trailing. Unlike the pure lignin, the copolymers show a more broad elution which indicates that the molecular size of the copolymer is widely distributed. The initial elution represents the polymer molecules of largest size in the sample. These fractions in each sample will have the greatest contribution to the limiting viscosity number. Initial elution times of the different samples of copolymer 1 are shown to be inversely related to limiting viscosity number by the data of Tables VI and VIII. This is exactly the trend that would be expected since, as noted above, (1) the high molecular weight tail of a copolymer's distribution contributes disproportionately to the rheological behavior of the product and (2) SEC causes large molecules to elute first. Therefore, comparing the preceding and peak elution time gives an accurate comparison of the relative size of the copolymers. By this means, the relative size of copolymer can be ranked in a decreasing manner as 3-1 > 3-2 = 3-3 > 3-4 > lignin. The UV spectra taken during elution show that lignin is uniformly distributed throughout the peak. The use of this technique to prove copolymerization and characterize copolymers is described in ref 10.

Copolymers 2 and 3 elute earlier than lignin but show no trend as a function of limiting viscosity number. This is because the strongly basic mobile phase partially hydrolyzes the copolymer during size exclusion.

Conclusions

By initiation with calcium chloride and hydrogen peroxide, a cationic polyelectrolyte side chain can be grafted onto lignin via free-radical polymerization. The assays of lignin, chlorine, nitrogen, and sulfur confirm the presence of backbone and cationic polymer. Ultraviolet spectroscopy and size exclusion chromatography verify the formation of graft copolymer. For chloride-containing monomer, such as dipropene chloride and hexammonium chloride, the chloride counterion has the same effect as calcium chloride on yield and product properties. In the case of dipropene chloride, product limiting viscosity number is decreased with an increase of reaction mixture chloride ion content, or monomer content. However, in the case of hexammonium chloride, the limiting viscosity increased with an increase of reaction chloride ion content and leveled off when the chloride content reached or exceeded 4.5 mmol per gram of reaction mass. For the chloride-ion-free monomer, hexammonium methyl sulfate, the magnitude of the limiting viscosity number depends upon the chloride ion added as a salt, $CaCl_2$. The limiting viscosity numbers range from 5.07 to 85.64 for copolymer 2.

The elution volume of copolymers under size exclusion chromatography in a basic, aqueous mobile phase is smaller than that of lignin. For copolymer 1, the elution volume decreases with increasing dipropene chloride monomer content in the synthesis reaction, which implies that addition of this monomer into the polymer increases molecular size. Furthermore, the elution volume of copolymer 2 is larger than that of copolymer 3 and that of copolymer 1 prepared at the same monomer content. Among the copolymers, the elution volume decreases with an increase of chloride content in the synthesis reaction. These graft copolymers are highly water soluble, will increase the viscosity of aqueous solutions, and can be used as thickening agents and dispersing agents.

Acknowledgment. This work was partially supported by the National Science Foundation under award no. CPE-8260766 and under National Science Foundation Grant CBT-8417876. Support of the copolymer testing program by A and R Pipeline Co. is gratefully acknowledged. Nancy Chew, Thomas Buchers, and others helped in a sizable portion of this work, and their aid and effort are greatly appreciated and acknowledged.

References and Notes

(1) "Global Warming", Hearing Proceedings of the National Ocean Policy Study, Committee on Commerce, Science, and Transportation, U.S. Senate, 11/14/89, U.S. Government Printing Office: Washington, DC, 1990; Shipping List no. 90–263–P.

(2) "Climate Surprises", Hearing Proceedings of the Subcommittee on Science, Technology, and Space of the Committee on Commerce, Science, and Transportation, U.S. Senate, 5/08/89, U.S. Government Printing Office: Washington, DC, 1989; Shipping List. no. 89–501–P.

(3) "Energy Security", Hearing Proceedings of the Committee on Energy and Natural Resources, U.S. Senate, 5/20/87, U.S. Government Printing Office: Washington, DC, 1987; Shipping List no. 87–515–P.

(4) Masters, C. D. *Global Oil Assessments and the Search for Non-OPEC Oil*; U.S. Department of the Interior, Geological Survey, U.S. Government Printing Office: Washington, DC, 1986; Shipping List no. 86–373.

(5) Meister, J. J.; Patil, D. R.; Channell, H. In *Proc. Int. Symp. Oilfield Geotherm. Chem.*, Soc. Petrol. Eng. Paper no. 13559, Phoenix, AZ, Apr 9–11, 1985.

(6) Skoog, D. A.; West, D. M.; Holler, D. M. *Fundamentals of Analytical Chemistry*; Saunders College: New York, 1988; Chapters 7 and 12–15.

(7) Fuoss, R. M.; Strauss, U. P. *J. Polym. Sci.* **1948**, *3*, 246, 602.

(8) Fuoss, R. M. *Discuss. Faraday Soc.* **1951**, No. 11, 125.

(9) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, *64*, 2716–2718.

(10) Nicholson, J. C.; Meister, J. J.; Patil, D. R.; Field, L. R. *Anal. Chem.* **1984**, *56*, 2447–2451.

(11) Negi, Y.; Harada, S.; Ishizuka, O. *J. Appl. Polym. Sci.* **1967**, *5*, 1951–1985.

(12) Shinde, B. M.; Jagdale, S. M.; Gahatge, N. D. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3585–3591.

(13) Lancaster, J. E.; Baccei, L.; Panzer, H. P. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 519.

(14) Meister, J. J.; Li, C. T. In *Oilfield Chemistry, Enhanced Recovery and Production Stimulation*; Borchardt, J. K., Yen, T. F., Eds.; ACS Symposium Series 396; American Chemical Society: Washington, DC, 1989; pp 169–203.

(15) Meister, J. J.; Patil, D. R.; Augustin, C.; Lai, J. Z. In *Lignin, Properties and Uses*: Sarkanen, S.; Glasser, W., Eds.; ACS Symposium Series 397; American Chemical Society: Washington, DC, 1989; pp 294–311.

Registry No. 1 (copolymer), 137236-31-8; 2 (copolymer), 137236-32-9; 3 (copolymer), 127475-92-7.