Properties and Applications of Lignin–Acrylamide Graft Copolymer

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Synopsis

Free-radical, graft polymerization of acrylamide onto lignin occurs in photolysed, distilled dioxane containing calcium chloride and trace quantities of ceric ion. The yield of the reaction is controlled by the amount of oxygen present during dioxane photolysis, the duration of photolysis, and the amount of calcium chloride in the reaction mixture. Polyacrylamide homopolymer is formed during the reaction and can be removed from the graft copolymer by base dialysis. Side chains of the reaction product can be hydrolyzed to partially hydrolyzed polyacrylamide by solution in aqueous base. Hydrolysis raises the limiting viscosity number of the product by a factor of up to 47. As a drilling mud additive, the ability of the reaction product to lower yield point, lower gel strength, or lower API filtrate volume increases with increasing degree of hydrolysis.

INTRODUCTION

Both lignin, a natural polymer obtained from cellulosic plants, and polyacrylamide, a synthetic polymer formed from 2-propenamide, are used in a number of industrial products or processes. Lignin or its derivatives are used in drilling muds or cements as dispersants/viscosity control agents and in water purification as metal ion sequesterants.[1] Polyacrylamide is used in drilling muds as a dispersant/viscosity control agent, in cements as a water loss control agent, and in water purification as a flocculant.[2] In applications where both polymers are used, physical or chemical processes such as selective absorption, precipitation, or complexation can remove one polymer from a treatment system but leave the other behind.[3] One way to avoid this "chromatographing" of a polymer mixture is to chemically link the two polymeric parts into a copolymer. Such a reaction also allows the copolymer to be applied in industrial processes where physical properties incompatible with the process, such as one polymer's insolubility or low molecular weight, are beneficially altered by copolymerization.

For these reasons, a number of groups have performed extensive studies of the grafting of vinyl monomers onto lignin using initiation by either chemicals or irradiation.[4-8] However, all efforts to attach 2-propenamide to lignin to form a lignin–polyacrylamide graft copolymer have failed.[7,9] Failure to synthesize lignin–2-propenamide graft copolymer is chemically significant because 2-propenamide is a highly reactive monomer, similar in reactivity to styrene,[5,8] methyl methacrylate,[10] and acrylonitrile,[11] all of which have been successfully grafted to lignin.

A process for grafting acrylamide to lignin has now been developed. The method permits quantitative polymerization of acrylamide to form lignin–acrylamide graft copolymer and up to 49 wt % polyacrylamide homopolymer.

In the following sections, the experimental methods used in this work, the variables which control reaction yield, product properties, proof of copolymer, and results of testing the reaction product in drilling mud will be described.

EXPERIMENTAL

Materials

Lignin used in these studies is Indulin AT, a commercial product of the Westvaco Corp. The material is a Kraft pine lignin prepared in "free acid" form. The ash content of the product is one weight percent or less. Indulin AT is essentially insoluble in water at pH = 7 but dissolves readily in aqueous solutions at a pH above 9.

2-Propenamide used in all reactions was reagent grade monomer, which was recrystallized from trichloromethane after hot filtration and dried under vacuum ($P < 1$ mm Hg) at room temperature for 24 h. Initiator solution was 0.050M ceric sulfate in 1.00M aqueous sulfuric acid. Dioxane was stabilized reagent grade material which 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 was Spectrapor 2 (12,000 upper molecular weight cutoff) or 3 (3500 upper molecular weight cut off), cellulose, 45–55 mm diameter, membrane tubing made by Spectrum Medical Industries, Los Angeles, Calif.

The lignin–acrylamide reaction products are tested for effectiveness in a base mud containing 28 ppb (pounds per barrel) of Wyoming bentonite and 40 ppb of Revdust, a commercial clay mixture used to represent solids generated by drilling.

Polyacrylamide used in blanks and mixture tests was synthesized by free radical polymerization under nitrogen using a glucose/ceric ion initiator. Molecular weight, as determined using the Mark–Houwink equation,[12,13]

$$[\eta] = 6.31 \times 10^{-5} M_w^{0.80} \tag{1}$$

was 6.0×10^4.

Methods

Acrylamide is grafted onto lignin by free radical reaction in dioxane. Procedure for the synthesis is as follows.

An aliquot of 20 mL of freshly distilled dioxane is placed in a 125-mL, conical flask, bubbled with air or, optimally, oxygen for 5 min and then exposed to the output of a 1000-W xenon lamp to produce photolysis products. Samples undergoing photolysis are mounted 2–4 cm from the lens face

of the lamp housing and are stirred continuously during irradiation. Optimum exposure time is 3 h. Lignin and anhydrous, finely ground calcium chloride are added to the irradiated dioxane solvent, and the mixture is stirred for 20 min. Acrylamide is added while nitrogen gas is bubbled into the mixture. After 10 min a volume of $0.05M$ ceric sulfate in $1.0M$ aqueous sulfuric acid is added, the flask is sealed under nitrogen, and the slurry is stirred for 10 additional minutes. Thickening will start immediately, and the flask contents will become a viscous mass.

The reaction flask is placed in a 30°C bath and allowed to sit for 2 days. Reaction is then terminated with 0.5 mL of 1 wt % hydroquinone in water. Reaction mixture is diluted with 100 mL of water and stirred until uniform. Reaction product is precipitated by adding the dilute reaction mixture dropwise to 1 L 2-propanone. The solid is recovered from 2-propanone by filtration and dried under vacuum at 40°C. Yield is calculated from the formula

$$\text{wt \% yield} = \frac{\text{g polymer recovered}}{\left(\begin{array}{c}\text{g lignin} \\ \text{added}\end{array} + \begin{array}{c}\text{g acrylamide} \\ \text{added}\end{array}\right)} \times 100\%$$

Hydrolyzed samples[14] are prepared from aqueous solutions containing between 1.0 and 2.5 g/dL of reaction product. A stoichiometric amount of sodium hydroxide that will produce the desired percent hydrolysis is added to the solution, and it is heated to 50°C with stirring and maintained there for 1 h. Product solution is precipitated in 5 times its volume of 2-propanone, recovered by filtration, and dried to constant weight.

Dialyze samples by placing the sample to be dialyzed into a tubular sack of dialysis membrane, sealing the membrane opening, and immersing the packaged sample in water or the solution against which dialysis is to occur. Exterior dialysis solution is changed at least once a day.

Assays

Oxidizing equivalents in irradiated dioxane are determined with the following redox procedure.

Place 20 mL of irradiated dioxane in a 600-mL beaker and add 50 mL of water. Add a freshly prepared solution of 3 g of KI and 5 mL of $6M$ HCl in 50 mL of water. Swirl gently, cover the beaker with a watch glass, and let it stand in a dark place for 5 min. Add 200 mL of water by pouring it down the inside of the beaker. Titrate with $0.1N$ thiosulfate solution to a faint yellow color of iodine. Add 5 mL of starch indicator. Titrate until the blue color of starch disappears.

Formula for calculating equivalents of oxidizing agent present is

$$\text{oxidizing agent (eq)} = \left(\begin{array}{c}\text{volume of} \\ \text{thiosulfate} \\ \text{solution (L)}\end{array}\right) \times \left(\begin{array}{c}\text{normality of} \\ \text{thiosulfate} \\ \text{solution (eq/L)}\end{array}\right)$$

The procedure[15] for the lignin analysis is to dissolve a 0.01–0.1-g sample of dried reaction product in 25 mL of $0.5M$ sodium hydroxide solution. A

10-mL aliquot of this solution is diluted to 100 mL total volume with distilled water. An ultraviolet spectrum (400–200 nm) is taken of this solution against a blank of 10 mL of $0.5M$ sodium hydroxide solution diluted to 100 mL with distilled water. The amount of lignin in the sample is determined from the sample absorbance at 287 nm in 1-cm cells. There is, however, a small interference from polyacrylamide at this wavelength. To compensate for the additive effect of polyacrylamide absorbance in a sample, the absorbance due to polyacrylamide is subtracted from the spectrophotometer reading before calculation of lignin content in the sample. Polyacrylamide content of the sample is determined using a Kjeldahl assay for nitrogen.[16] Hengar nitrogen-free paper is used in the Kjeldahl assay.

The equation for obtaining wt % lignin, PL, from the analyses is

$$PL = \frac{A_T - 4.121(WUV \times TN/WK) + 9.821 \times 10^{-3}}{0.9332 \times WUV - 5.389 \times 10^{-4} \times WUV}$$

where A_T = absorbance reading from ultraviolet spectra, WUV = weight (g) of reaction product used for UV assay, WK = weight, (g) of reaction product used in Kjeldahl assay, and TN = weight (g) of nitrogen found in Kjeldahl assay sample.

The weight percent polyacrylamide in the assay sample, PA, is found from the equation

$$PA = \frac{[TN/(WK \times 10^{-2})] - 1.308 \times 10^{-2} \, PL}{0.19706}$$

Since up to 4 wt % of the reaction mixture was calcium chloride, several samples of product were tested for calcium content. A 0.0500 g sample of reaction product was dissolved in water and pH was adjusted to 10 using $0.1M$ potassium hydroxide solution. To the solution were added 1 mL of 3 wt % potassium cyanide in water, 1 mL of 3 wt % hydroxylamine hydrochloride, and a few crystals of CalRed indicator. The sample was then titrated using $0.01M$ ethylenediaminetetraacetic acid.

Calcium and iron content of a series of samples was also determined using atomic absorption spectroscopy. Samples weighing 0.015 g were dissolved in 25.0 mL of $0.5M$ sodium hydroxide, and diluted with $0.1M$ HCl and distilled water to a volume such that calcium concentration was between 0 and 5.0 ppm and pH was 8. Calcium concentration was determined using both calibration curve and standard addition methods for absorption measurements at 422.7 nm. Iron concentration was determined by standard addition method using absorbance measurements at 248.3 nm.

Since some calibration curve and standard addition results did not match, samples of reaction product contained in 125 mL Pyrex flask were heated at 400°C for 24 h, digested for 1 h in 100 mL of boiling hydrochloric acid, and the resulting solution diluted to 250 mL with distilled water. The ashed samples were then assayed using atomic absorption spectroscopy at the wavelengths given above.

Partially hydrolyzed polyacrylamide can be precipitated with copper

(Cu^{2+}) and quantitatively determined by testing the precipitate for copper content. To 2.00 g of dilute (200 ppm) aqueous solution of partially hydrolyzed polyacrylamide in a centrifuge tube is added 1.0 mL of 0.10M cupric sulfate in water. The sample is mixed and centrifuged at 3000 rpm for 30 min. The supernate of the sample is decanted, and the precipitated solids carefully washed twice with 1-mL portions of water. Water is decanted after each wash.

The polymer precipitate is dissolved in a mixture of 5 mL of 10 wt % hydroxylamine hydrochloride and 5 mL of 33 wt % sodium citrate. The solution is diluted to 50 mL total volume in a volumetric flask, mixed, and tested for copper content using a Chemetrics[17] copper test kit. The amount of polymer or degree of hydrolysis is determined by reference to identical tests on polymer standards.

Limiting viscosity number of the reaction product in distilled water was determined at 30°C using a Cannon-Fenske no. 75 capillary viscometer. Viscosities were measured at reaction product concentrations of 0.1–1.0 wt % in 0.1 wt % steps. The data set was extrapolated to zero product concentration using the Huggins equation,

$$(\eta - \eta_0)/C \times \eta_0 = [\eta] + Q_H[\eta]^2 C$$

where η and η_0 are solution and solvent viscosity, C is polymer concentration (g/dL), $[\eta]$ is limiting viscosity number, and Q_H is the Huggins constant of the polymer.

Elemental analyses for carbon, hydrogen, nitrogen, oxygen, and sulfur were performed by Canadian Microanalytical Services, 5074 University Blvd., Vancouver, B.C. Assays for sodium were performed by Galbraith Laboratories, P.O. Box 4187, Knoxville, Tenn.

For lignin–acrylamide graft copolymers tested for drilling mud applications, the concentration of reaction product in the base mud is usually fixed at 0.5 pounds per barrel (ppb). Reaction product is added to base mud that has been aged 24 h at room temperature to hydrate the clays. Sample viscosity at four shear rates, apparent viscosity, plastic viscosity, yield point, gel strength after 10 s and after 10 min of setting, and API filtrate volume are then determined on the sample. The sample is hot-rolled in a pressurized bomb for 16 h at 250°F to simulate exposure to wellbore conditions, after which the same series of tests are run on the hot-rolled mud samples. Drilling mud tests were performed according to American Petroleum Institute (API) specifications with viscosity and gel strength performed according to Sec. 2 of Ref. 18 and filtration tests performed according to Sec. 3, Ref. 18.

Equipment

The photolysis device used is a 220-V Oriel Model 8540 power supply driving a #6269, 1000-W xenon lamp held in a Model 6140 lamp housing.

Atomic absorption assays were run on a Perkin-Elmer Model 4000, double beam, atomic absorption spectrophotometer.

Viscosities were measured with a #75 Cannon-Finske capillary viscometer.

Drilling muds were prepared with a Model 9B multimixer. Mud properties were tested with a Fan Model 35A motor-driven viscometer. Samples were hot rolled in Model 760-12 stainless steel aging cells contained in a Baroid Model 701 roller oven.

RESULTS AND DISCUSSION

Reaction Variables

Yield and product characteristics of the graft copolymer depend upon (1) gas mixture used to saturate the dioxane solvent and duration of saturation with gas, (2) duration of photolysis of the dioxane solvent, (3) calcium chloride concentration, (4) acrylamide concentration, and (5) the salt used as an additive to the reaction. Changes in these reaction variables and the resulting effect on yield and product properties will be described in the following sections.

Photolysis products in the dioxane solvent are critical to the graft copolymerization. Photolysis products needed in dioxane to produce the copolymerization can be prepared quickly by saturating the dioxane with an oxygen-containing gas and exposing the solvent to a 1000-W xenon lamp. Table I shows data on reaction products produced by bubbling dioxane with air for 5 min and then photolyzing with the xenon lamp for 1.0 h. Table II contains data on reaction products produced by bubbling dioxane with oxygen for 5 min and then photolyzing by xenon lamp for different times. All reactions of Tables I and II are run by using the general procedure given in the Methods section. Yields of reactions produced by oxygen saturation of the dioxane and subsequent photolysis are greater than those produced by air saturation of the dioxane and subsequent photolysis. These data imply that oxygen is a critical component in forming part of the initiator needed to produce lignin–acrylamide, graft copolymer.

Length of time that the dioxane is exposed to light from a given source partially controls yield, as shown by data of Table II. All of the previous data imply that photolysis of dioxane reaction solvent is critical to success

TABLE I
Product Produced from Solvent Bubbled with Air for 5 Min and Photolyzed with Xenon Lamp for 1.0 h[a]

Sample no.	Composition, CaCl$_2$ (g)	Yield	
		g	%
1	1.0	1.90	59.4
2	0.50	2.05	64.1
3	0.2	2.24	70.0
4	0.05	1.50	46.9
5	0.01	0.32	10.0
6	0.005	0.80	25.0

[a] Each sample contained 20 mL of air-bubbled, irradiated dioxane, 0.50 g lignin, 3.20 g acrylamide (0.0451 mol), and 0.15 mL of 0.05M Ce(SO$_4$)$_2$ (7.5 $\times$ 10^{-6} mol of Ce^{4+}). Oxidizing equivalents in the dioxane were 6.9 $\times$ 10^{-4} eq/20 mL sample.

of the graft polymerization. Photochemical autooxidation of dioxane yields[19,20] 2-hydroperoxidedioxane [eq. (2)] and 2,3-bis(hydroperoxide) dioxane [eq. (3)]:

$$
\begin{array}{c}
\text{(structure of 2-hydroperoxidedioxane)} \qquad (2)
\end{array}
$$

$$
\begin{array}{c}
\text{(structure of 2,3-bis(hydroperoxide)dioxane)} \qquad (3)
\end{array}
$$

These products are detectable by iodine–thiosulfate assay, a determination which detects hydroperoxides.[21–23] Results of iodine–thiosulfate assay show that photolysis of dioxane under the conditions used in these studies produces oxidizing agents. Distilling the dioxane to remove stabilizer before bubbling with air and photolyzing increases the level of oxidizing equivalents produced more than threefold. Bubbling distilled dioxane with oxygen instead of air before photolysis increases the oxidizing equivalents produced by another factor of 2. The yield of reactions containing 0.50 g lignin, 2.0 wt % calcium chloride, and 0.045 mol acrylamide increased when the number of oxidizing equivalents in the dioxane solvent increased. Since the oxidizing equivalents in dioxane increase as larger amounts of oxygen are placed in the solvent before irradiation, there is a strong possibility that the initiator in the lignin–acrylamide graft copolymerization is a peroxide.

Oxidizing capacity of dioxane bubbled with oxygen and irradiated in a Pyrex flask peaks at 3 h of irradiation and then declines. 1,4-Dioxane absorbs ultraviolet radiation at wavelengths of 220 nm or less.[24] The xenon lamp used in this irradiation produces 0.8 μW/cm^2 · nm at a 50 cm distance from the lamp at 220 nm.[25] There is, therefore, a significant radiation flux to form excited states in the 1,4-dioxane undergoing irradiation. The actual amount of radiation reaching the dioxane is reduced by the glass wall of the vessel. Transmittance of optical glass decreases sharply between 300 and 280 nm.[26] However, the oxidizing capacity of dioxane irradiated for 3 h in a glass container is over 3 times larger than the oxidizing capacity of dioxane irradiated for 30 min in a quartz* container. Since the yield of reaction product has been shown to increase as the oxidizing capacity of the dioxane solvent increases, irradiation in glass for 3 h after bubbling with oxygen is the preferred procedure for the reaction.

Anhydrous calcium chloride concentration is a controlling variable of yield in this synthesis. A tabulation of reaction yield as a function of weight percent calcium contained in the reaction mixture is part of Table II. For all three irradiation times, yield peaks at 2.0 wt % calcium chloride in the reaction mixture. There is a general trend at each calcium concentration toward higher yield at longer irradiation times, up to a maximum of 3 h irradiation time. On the basis of these data, 3 h of irradiation for oxygen-bubbled dioxane solvent and 2.0 wt % calcium chloride in the reaction mixture were chosen as standard conditions for preparation of initial mud-test samples.

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* The transmittance of quartz is above 80% for light between 170 and 1000 nm wavelength.[26]

TABLE II
Yield and Limiting Viscosity Number for Lignin-Acrylamide Reactions[a]

Sample no.	Anhydrous calcium chloride in reaction mixture (wt %)	g	%	Limiting[b] viscosity number (dL/g)	Wt %			Calcium	
					Lignin	Polymerized 2-propenamide		Before ashing	After ashing
A.1. 1,4-Dioxane irradiated for 3 h and containing 0.045 mol (3.2 g) of acrylamide); OE $= 2.96 \times 10^{-3}$ eq[c]									
1	4.0	3.36	90.8	0.59	7.5	67.6		2.8	4.91
2	2.0	3.64	98.4	0.46	6.92	73.4		—	2.25
3	0.8	2.88	77.8	0.49	8.68	71.6		0.8	1.90
4	0.2	2.57	69.5	0.49	10.0	79.5		0.5	0.48
5	0.04	2.22	60.0	0.51	11.2	77.7		—	0
6	0.02	1.80	48.6	0.38	17.7	82.0		—	0
A.2. Reactions containing 0.028 mol (2 g) of acrylamide									
7	4.1	1.90	76.0	0.33	8.50	57.0			
8	2.1	2.37	94.8	0.28	11.7	65.3			
9	0.85	1.46	58.4	0.15	10.9	69.3			
10	0.21	1.74	69.6	0.40	8.09	77.8			
11	0.04	1.5	60.0	0.17	15.9	75.7			
A.3. Reactions containing 0.014 mol (1 g) of acrylamide									

12	4.3	2.1	—	0.08	18.5	37.4	—	10.6
13	2.2	1.5	100	0.21	12.4	48.3	—	6.94
14	0.9	1.17	78	0.22	12.2	55.2	—	3.83
15	0.22	1.35	90	0.16	20.9	60.0		
16	0.04	0.93	62	0.27	15.7	61.6		
B. 1,4-Dioxane irradiated for 2 h; OE = 2.14×10^{-3} eq								
17	4.0	2.57	69.5	0.81	7.28	65.6		
18	2.0	3.42	92.4	0.71	10.4	69.8		
19	0.8	2.5	67.6	0.60	6.54	71.1		
20	0.2	2.8	75.7	0.30	7.18	79.4		
21	0.08	2.25	60.8	0.51	7.03	82.4		
22	0.02	2.37	64.1	0.85	7.10	81.9		
C. 1,4-Dioxane irradiated for 1 h; OE = 8.2×10^{-4} eq								
23	4.0	3.08	83.2	0.53	5.31	69.1		
24	2.0	3.10	83.8	0.67	5.60	75.8		
25	0.8	2.60	70.3	0.497	6.61	71.1		
26	0.2	2.20	59.5	0.32	8.13	77.7		
27	0.04	1.80	48.6	0.468	8.83	79.1		
D. 1,4-Dioxane irradiated for 30 min in a quartz flask; OE = 8.8×10^{-4} eq								
28	4.0	2.40	64.9	0.41				

[a] All reaction mixtures contained 20.0 mL of oxygen-bubbled, irradiated dioxane, 0.5 g of lignin, and 0.15 mL of ceric sulfate solution. Pyrex flask and 3.2 g (0.045 mol) of acrylamide used unless noted otherwise.

[b] Measured at 30°C in distilled water.

[c] OE oxidizing equivalents found in the 20 mL of dioxane after irradiation.

Limiting viscosity number of the product, a measure of molecular size also given in Table II, does not correlate with calcium chloride concentration. The role of calcium chloride in this synthesis is complicated since the salt does not completely dissolve in the reaction mixture. A repeat of sample 2 of Table II in unphotolyzed, distilled dioxane that was centrifuged to remove solids just after being sealed under nitrogen had 66 wt % calcium chloride in the reaction mixture present as solids.* This sample, which has the maximum yield of all formulations tested, had the majority of the salt present as solid.

The effect of reducing acrylamide monomer concentration on yield and properties of reaction product was determined by running a series of reactions using 0.028 or 0.014 mol acrylamide in the reaction mixture. Results of these reactions are given in Table IIA.

These reactions were run to determine if product of lower molecular size could be produced from the reaction. Such materials would be more effective thinners in drilling muds. Limiting viscosity numbers of the reaction products, a measure of molecular size, are lower than those of corresponding reactions run with 0.045 mol acrylamide in the reaction mixture. These data imply that the molecular size of the reaction product in water can be controlled by controlling the amount of acrylamide added to the reaction mixture.

The effect of ceric ion on the reaction product can be seen from the results contained in Table III of reactions run with and without ceric ion. Comparing the results in Table III shows that reactions run with ceric ion usually have a higher yield, have a larger fraction of reaction product soluble in water, and usually produce a product which has a higher viscosity number than do reactions run without ceric ion.

Ceric ion is known[27] to produce hydroperoxide radical by reaction with hydrogen peroxide,

$$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + H^+ + HO_2^{\cdot} \tag{4}$$
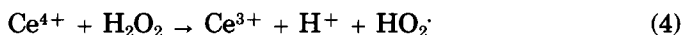
This type of reaction with the oxidizing agents produced by photolyzing dioxane may produce radical sites important in polymerization.

Other salts may act as a reaction promoter in photolyzed dioxane. Equal weights of sodium chloride, calcium chloride dihydrate, and lithium chloride were used in place of anhydrous calcium chloride in repeating the synthesis of sample 2, Table II. Sodium chloride and calcium chloride dihydrate produced a 100 wt % yield of a reaction product which contained 5.0 and 2.6 wt % water-soluble lignin, respectively. Although reaction and solution behavior of these products support the hypothesis that graft copolymer was formed, graft copolymer formation cannot be completely guaranteed since aqueous size exclusion chromatography was not run on these products.

Lithium chloride produced a 52.7% yield of polymer which contained no water-soluble lignin fraction. Lithium chloride was therefore ruled out as a promoter of graft copolymerization.

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* Determined by EDTA titration.

TABLE III
Results for Reactions[a] Run with and without Addition of Ceric Ion, Ce^{4+}

Sample no.	Anhydrous calcium chloride added (g)	Yield		Solution test[b]		
		g	wt %	Solubles (g)	Insolubles (g)	$\eta_{sp/C}$ (dL/g)
A. Reactions run without ceric ion						
1	0.20	1.25	33.8	0.1212	0.0531	0.40
2	0.50	1.74	47.0	0.1400	0.0347	0.51
3	1.00	1.94	52.4	0.1689	0.0091	1.10
B. Reactions run with the addition of 0.15 mL ceric ion						
4	0.20	2.24	70.0	0.1572	0.0253	1.06
5	0.50	2.05	64.1	0.1524	0.0153	0.91
6	1.00	1.90	59.4	0.1718	0.0123	0.84

[a] All reactions run in air-bubbled dioxane that had been irradiated for 60 min. Reactions contained 0.50 g lignin, 3.20 g acrylamide, and different amounts of calcium chloride.
[b] A 1.00-g/dL solution of reaction product made in distilled water, stirred for several days, centrifuged to remove insolubles, tested for viscosity number $\eta_{sp/C}$, and dried to determine solution concentration.

Since much of the work characterizing this reaction is based on yield or solution data, a reproducibility test was run to determine the consistence of these properties of the reaction and product. The reactions run were duplicates of reaction 2 of Table II.

Data from the test are summarized in Table IV. One of the five reactions run failed. The other four produced a consistent yield, but the molecular size of the products as measured by limiting viscosity number changes by a factor of 2. Therefore, the product can be synthesized consistently, but its characteristics are not completely controlled. We have no data which indicate a cause for failure of reaction 3 of Table IV.

Product Properties

Reaction product is a hard, brown solid which can be crushed into a fine tan powder with mortar and pestle. The product can be dissolved in distilled water to form aqueous solutions useable in analysis of the product by ultraviolet spectroscopy, nuclear magnetic resonance, atomic absorption spectroscopy, and wet chemical methods.

When some reaction products are dispersed in water, a portion of the product forms a gelatinous, swollen aggregate which does not dissolve. This gel may be due to entanglement of the lignin fraction of the graft copolymer since it does dissolve in $0.5M$ sodium hydroxide.

Analysis of solutions of reaction product for lignin content by ultraviolet absorbance analysis gave the results shown in Table IIA. Amount of reaction product present as 1-amidoethylene repeat units,

$$-CH_2 - CH - $$
$$\mid$$
$$C = O$$
$$\mid$$
$$NH_2$$
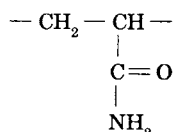
can be determined using Kjeldahl analysis on the reaction product or any of its fractions. Results of these assays are also given in Table IIA. Reaction product solids were tested for contained calcium using both EDTA titration[28] and atomic absorption spectroscopy methods. The complex titration indicated that the calcium content of the reaction products was less than 0.08 wt %. Analysis of the reaction product ash by atomic absorption spectroscopy gave calcium contents as high as 4.9 wt %, however. Several calcium concentrations are given in Table IIA.1.

TABLE IV
Yield and Characterization Data of Reaction Product

Sample no.	Yield		Limiting viscosity number	Analysis results lignin (wt %)
	g	%		
1	3.70	100	0.75	9.7
2	3.70	100	0.34	9.5
3	0.80	21.6	—	—
4	3.67	99.2	0.50	8.6
5	3.64	98.4	0.46	9.4

Peak no.	Polyacrylamide standard	Assigned	Sample 2 (Table IIA)	
1	178.1	C=O	178.3	178.4
2	40.8		41.1	41.1
3	40.5		40.8	40.8
4	40.4	—C—H	40.7	40.7
5	40.2		40.5	40.5
6	34.5		34.8	34.6
7	33.5		34.6	33.8
8	33.3		34.3	33.6
9	32.7	CH_2	33.7	33.2
10	32.5		33.5	33.0
11	28.9		32.7	

[a] All spectra run in water with methanol (47.35 ppm vs. TMS) as a C-13 standard. All peaks listed in ppm.

The sharply different results given by these three assays would occur if calcium were bound in a lignin complex in the reaction product and not present as a free salt. Since lignin is known to bind up to 7 wt % calcium, calcium is apparently bound in the reaction product as a sequestered ion.

Verification of the structure of the side chain was made by performing ^{13}C-NMR on aqueous solutions containing 5 g/dL reaction product of polyacrylamide homopolymer. Chemical shifts of the two polymers are given in Table V. With the exception of peak 11, the spectra match to within 1 ppm.

Two portions of sample 2 of Table IIA were hydrolyzed by preparing 1.0 g/dL aqueous solutions of the sample and adding sufficient sodium hydroxide to produce 25% or 50% hydrolysis. Percent hydrolysis was determined from nitrogen loss in the hydrolyzed product when compared to the original, unhydrolyzed sample.

Elemental analyses, percent hydrolysis, and limiting viscosity number in distilled water for sample 2 and two hydrolysis products, samples 7 and 8, are given in Table VI. The 47-fold increase in limiting viscosity number upon hydrolysis is the characteristic behavior of a polyelectrolyte in water and implies that the product of reaction of lignin and acrylamide in irradiated dioxane is not anionically polymerized acrylamide.[29] The side chains and homopolymer in the reaction product are free radical polymerized acrylamide.

Proof of Copolymer

Polyacrylamide homopolymer is water soluble while the lignin used in these tests, Indulin AT, is water-insoluble. A critical property of the reaction product is that it is water-soluble and that the lignin contained in the product does not precipitate from solution. This change in solubility behavior suggests that the lignin may be chemically bound to a poly(1-amidoethylene) chain, forming a water-soluble copolymer.

This hypothesis was further tested by dialyzing aqueous solutions of reaction product against 0.1M hydrochloric acid solution. The dialysis mem-

TABLE VI

Elemental Assay, Percent Hydrolysis, and Limiting Viscosity Number of Partially Hydrolyzed Copolymer Used in Mud Tests

Sample no.	Elemental Assay (wt %)						Degree of hydrolysis from assay[a]	Limiting viscosity number (dL/g)
	C	H	N	S	O	Na		
				Batch 1				
2	50.19	7.30	16.19	0.24	29.02	0.095	0	0.32
7	43.73	5.97	10.45	0.14	34.13	7.40	24.8	15.2
8	41.52	5.03	6.37	0.18	38.74	12.49	51.4	15.1
				Batch 2				
9	48.49	7.51	12.76	0.43	28.40	0.02	0	0.13
10	45.69	6.07	8.63	0.57	33.04	7.85	26.6	1.31
11	43.17	5.60	7.14	0.67	33.33	9.72	38.0	4.09
12	46.05	5.94	5.69	0.28	31.47	10.13	50.4	3.84

[a] Based on nitrogen loss from samples 2 or 9.

brane was permeable to molecules with molecular weights of less than 3500 so that low molecular weight materials such as calcium chloride, dioxane, or contaminating cations could be removed from the reaction product solution. Such contaminants could aid in dissolving Indulin AT in water since several of the salts of this product are water-soluble. After several days of dialysis, all the cations in the reaction product solution would be exchanged to hydrogen, forming the acid of Indulin AT. The acid form of the lignin is not water-soluble and should precipitate if it were not attached to a water-soluble poly(1-amidoethylene) chain. No precipitate is obtained from these tests, providing support for the hypothesis that copolymer has been formed. Further, dialysis against $10^{-3}M$ hydrochloric acid of a 20.15 wt % mixture of unreacted lignin and polyacrylamide produced 22.5 wt % of the dissolved polymeric solids as precipitate. Ultraviolet assay of the precipitate showed it contained 69.1 wt % of the lignin originally dissolved in the mixture. During dialysis, 10.6 wt % of the polymeric solids were lost.

Samples of reaction product were tested by aqueous size exclusion chromatography and found to migrate as a single material with a molecular size significantly greater than that of pure lignin starting material.[30] Mixtures of lignin and polyacrylamide dissolved in base were readily separated by the size exclusion process. From these data it was concluded that the reaction of lignin and acrylamide in photolyzed dioxane produces graft copolymer of polyacrylamide on lignin with the remainder of the reaction product being homopolymer.

These data show that lignin–acrylamide graft copolymer is formed during the reaction of lignin and acrylamide in dioxane.

Separation of Homopolymer

Polyacrylamide homopolymer can be separated from graft copolymer by dissolving in aqueous base and dialyzing. This separation process also partially hydrolyzes the polyacrylamide as shown by the results of copper precipitation assay given in Table VII. Sample 1, pure polyacrylamide, is a blank for the assay while sample 2, the sodium salt of 100% hydrolyzed polyacrylamide, is the standard. From the result on sample 3, base dialysis procedure used in the separation of homopolymer from graft copolymer produces 53% hydrolyzed polyacrylamide.

Homopolymer is separated from copolymer by preparing a 2.5 g/dL solution of reaction product in 0.5M sodium hydroxide. The solution is stirred for 7 days, dialyzed using Spectrapor #2 tubing against water for 3 days and dialyzed against 0.01M hydrochloric acid for 3 days.

Upon dialysis against 0.01M hydrochloric acid, a precipitate forms inside the dialysis bag. Results of representative base dialysis treatments of three 1.000-g portions of sample 2 of Table IIA are given in Table VIII. An average of 46.1 wt % reaction product precipitates as copolymer-rich solid during the base dialysis and is found to contain virtually all of the lignin originally in the reaction product. An average of 36 wt % reaction product is recovered from the dialysis solution inside the dialysis membrane, and it is found to contain traces of lignin amongst partially hydrolyzed polyacrylamide. Base dialysis of other samples shows that the copolymer-rich precipitate from

TABLE VII
Assay for Degree of Hydrolysis of Polyacrylamide Using Copper Precipitation Test

Sample no.	Material analyzed	Concentration in aqueous solution (ppm)	Copper precipitated (g)	Degree of hydrolysis
1	Pure polyacrylamide	240	0.003	0.0
2	Pure sodium polyacrylate[a]	240	0.330	100
3	Pure dialyzed polyacrylamide	210	0.180	53

[a] Solution made with Alcar 600, a poly(1-sodium carboxalate-ethylene) polymer produced by Allied Colloids.

the dialysis constitutes between 44 and 80 wt % reaction product. Base dialysis may not completely separate graft copolymer and homopolymer, however. A blank, sample 4 of Table VIII, consisting of unreacted lignin and polyacrylamide, produced three times as much precipitate as would be expected if all polyacrylamide were removed from the lignin. These and similar separations show the reaction product may be contaminated with up to 49 wt % polyacrylamide homopolymer.[30]

Tests of Reaction Product in Drilling Muds

Data for the samples prepared for drilling mud tests are given in Table VI. Each batch of material was made up from repeated reactions which produced product in several gram lots. All reaction product samples forming a given batch were combined into one sample, thoroughly blended, and then broken into equal mass samples for hydrolysis. Batch 1 was the result of five duplications of sample 2, Table IIA. Batch 2 was the result of 14 repetitions of sample 13 of Table IIA.

Drilling mud test data for the three samples of batch 1, Table VI, which differ in the fraction of the acrylamide side chain that has been hydrolyzed are given in Table IX.

Similar mud test data for mud samples containing the lower molecular weight samples of Batch 2, Table VI, are given in Table X. These data show that the reaction product produces the desirable effect of lowering yield point, lowering gel strength, and lowering API filtrate volume as degree of hydrolysis of the reaction product increases. This is true for both batches of reaction product.

After hot rolling, the reductions in the above three variables are only significant for the two reaction products that are 50% hydrolyzed, samples 8 and 12 of Table VI.

Though the data is limited, batch 2 samples, which probably have lower molecular weights and appear to give greater yield point lowering and lower gel strength than do samples synthesized with more acrylamide in the reaction mixture (batch 1, Table VI).

CONCLUSIONS

In the series of lignin–acrylamide reaction products tested as drilling and additives, ability of the reaction product to lower yield point and lower gel strength improves with increasing degree of hydrolysis or with decreasing

TABLE VIII
Base Dialysis Results

Sample no.	Reaction product dissolved	Percent of Reaction product solids in		Composition of Fractions (wt %)			
				Supernate		Precipitate	
		Supernate	Precipitate	Lignin	Acrylamide	Lignin	Acrylamide
1	Sample 2, Table I[a]	45.5	41.0	1.4	36.5	13.0	27.0
2	Sample 2, Table I[a]	44.1	35.0	1.4	36.7	11.5	30.5
3	Sample 2, Table I[a]	48.7	32.0	1.4	37.0	10.0	30.0
4	0.2022 g Lignin + 0.8039 g poly-acrylamide	12.9	66.2	—	—	18.8	31.3

TABLE IX
Properties of Test Muds before and after Hot Rolling

Property	Base mud		Sample (Batch 1, Table VI) Reaction product					
			#2		#7		#8	
	Before	After	Before	After	Before	After	Before	After
Viscosity (cP) at a shear rate of								
600 s^{-1}	78	80	94	102	86.5	98	94	68
300 s^{-1}	58	50	70	75	59	74	62	41
200 s^{-1}	49	38	60	64	48	64	50	31
100 s^{-1}	39	24	48	51	34	52	34	20
Gel strength (lb/100 ft^2) after mud has set for								
10 s	29	4.0	32	28	10	41	6.5	3.0
10 min	54	5.5	58	68	41	78	31	4.0
Apparent viscosity (cP)	39	40	47	51	43	49	47	34
Plastic viscosity (cP)	20	30	24	27	28	24	32	27
Yield point (cP)	36	20	46	48	32	50	31	14
API filtrate volume (mL)	11	8.0	11	12.3	7.4	13	6.8	7.2

TABLE X
Properties of Test Muds before and after Hot Rolling

	Base mud		Sample (Batch 2, Table VI)							
			Reaction product							
			9		10		11		12	
Property	Before	After	Before	After	Before	After	Before	After	Before	After
Viscosity (cP) at a shear rate of										
600 s^{-1}	79	80	76	103	78	75	67	68	67	63
300 s^{-1}	58	50	57	77	52	46	44	41	43	38
200 s^{-1}	50	38.5	48	66	42	35	35	32	33	28
100 s^{-1}	39	24.5	38	51	29	22	23	19	22	18
Gel strength (lb/100 ft^2) after mud has set for										
10 s	18	4	9	20	7	4	5	3	3	3
10 min	38	6	44	70	35	5	25	4	12	4
Apparent viscosity (cP)	40	40	38	52	39	38	34	34	34	32
Plastic viscosity (cP)	21	30	19	36	26	29	23	27	24	25
Yield point (cP)	37	20	38	41	26	17	21	14	19	13
API filtrate volume (mL)	12.4	8.0	12.8	12.6	10.0	10.4	10.0	10.0	9.2	9.7

amount of acrylamide in the synthesis mixture of the reaction product. Ability to lower API filtrate volume also increases with increasing degree of hydrolysis within each batch of reaction product tested.

Reaction of lignin and acrylamide in irradiated, calcium chloride-containing dioxane produces graft copolymer and up to 49 wt % polyacrylamide homopolymer. This product can be hydrolyzed to a polyanion by reaction with sodium hydroxide in water. Hydrolyzed reaction products have limiting viscosity numbers in water that are up to 47 times larger than the unhydrolyzed precursors. Grafting of acrylamide onto lignin was confirmed by solubility, dialysis, and aqueous size exclusion experiments.

The grafting reaction is critically dependent on the presence of photolysis products in the dioxane solvent. A hydroperoxide may be the photolysis-produced reagent which takes part in the grafting reaction. Calcium chloride concentration controls reaction yield and maximum yield is obtained at a calcium chloride concentration of 2.0 wt %. Reducing the acrylamide concentration of the reaction mixture reduces product molecular size.

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