

Interpolymer from Starch Xanthate and Polyamide-Polyamine-Epichlorohydrin Resin: Structure and Papermaking Application*

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Synopsis

The efficacy of oxidatively crosslinked starch xanthate for improving wet- and dry-strength properties of paper prompted the present study of an alternative, interpolymeric crosslinking procedure. Sodium starch xanthate of degrees of substitution 0.05-0.25 was reacted with a commercial paper additive (a polyamide-polyamine-epichlorohydrin wet-strength resin) which was found to contain 3-hydroxyazetidinium chloride, epoxypropyl, and chlorohydrin groups (3:1:1) to give an interpolymer crosslinked by both ionic and covalent bonds. Model systems, in conjunction with nuclear magnetic resonance, infrared, and ultraviolet spectral data, served to elucidate reaction mechanisms and structures of the interpolymer and the commercial resin. Reaction conditions that favored formation of either ionic (polysalt) or covalent (xanthate ester) crosslinks were investigated. In preliminary evaluations, incorporation of the interpolymer into paper handsheets resulted in excellent wet- and dry-strength improvements.

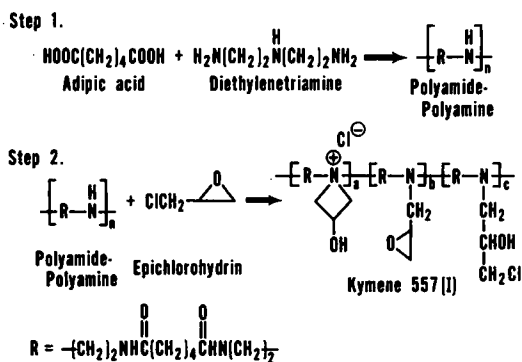
INTRODUCTION

Previous and continuing studies at the Northern Laboratory, directed toward the development of cereal-based papermaking chemicals, have shown that oxidatively crosslinked starch xanthate can be used as a wet-end additive to improve the wet and dry strength of paper.¹ However, alternative procedures for incorporating starch xanthate into paper are desirable for obtaining improved strength properties and simplifying the incorporation process. To this end, the present work describes reactions between Kymene 557 (polymer I, a polyamide-polyamine-epichlorohydrin resin, Hercules Inc., Wilmington, Delaware) and sodium starch xanthate (polymer II) to form an interpolymer crosslinked by ionic and covalent bonds. The nature of the chemical reactions between polymers I and II and structural analysis of polymer I, with the aid of model systems, were investigated. cursory laboratory evaluation of interpolymer formation in situ in papermaking pulp furnishes indicates the good potential of this procedure in achieving the objectives.

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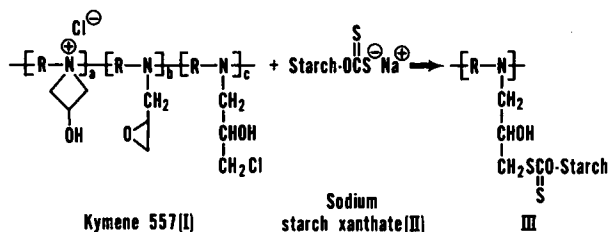
RESULTS AND DISCUSSION

Polymer I is prepared commercially according to scheme 1.² Reportedly, polymer I contains "epoxypropyl and/or 3-hydroxyazetidinium chloride



Scheme 1

groups" which react with nucleophiles.³ Our data show that the polyamino groups of polymer I were about 60% 3-hydroxyazetidinium and about 20% each of epoxypropyl and chlorohydrin (degree of substitution, D.S., of 0.6, 0.23, and 0.17, respectively). The azetidinium and epoxypropyl rings were readily opened by compound II to yield an interpolymer, crosslinked by the xanthate ester bond that is shown by III in scheme 2.



Scheme 2

Model studies indicated that displacement of covalent chlorine by xanthate to yield xanthate ester would be relatively slow, compared to reactions of azetidinium and epoxy rings with xanthate.

Structure of Polymer I

Chlorohydrin Content. Polymer I, in an aqueous solution containing 10% solids, was precipitated quantitatively by addition of its aqueous solution to acetone. Chlorine analyses of the precipitated polymer revealed that it contained 7.3% ionic chlorine and 2.0% covalently bonded chlorine (Table I). Presumably, the covalently bonded chlorine was present as 3-chloro-2-hydroxypropyl groups. Based on these chlorine analyses and on nuclear magnetic resonance (NMR) studies to be discussed, the average

TABLE I
Analysis of Polymer I^a

I	Chlorine, %			Nitrogen, %
	Total	Ionic	Covalent	
Nonpurified ^b	14.7	7.7	7.0	12.7
Purified precipitate ^c	9.2	7.3	2.0	12.3
supernatant	5.6	0.4	5.0	0.4

^a Kymene 557, a polyamide-polyamine-epichlorohydrin resin.

^b Chlorine and nitrogen analyses were made on commercial samples at 10% solids.

^c Polymer of commercial sample was precipitated in acetone.

repeating unit weight of polymer I, which is based on $\langle \text{R}-\text{N} \rangle_n$ in scheme 1,

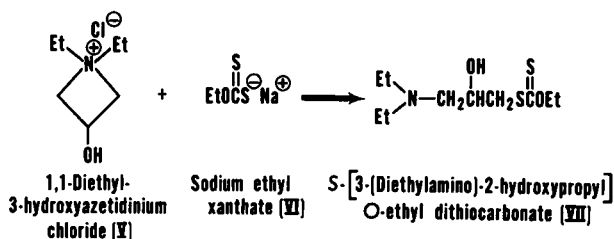
would be about 300 when fully substituted, and 17 units in each 100 units (D.S. 0.17) of polymer I would contain chlorohydrin substituents. The acetone supernatant contained 5.0% covalent chlorine and only 0.4% nitrogen (polymer I, dry basis). Covalent chlorine in the supernatant was probably due to excess epichlorohydrin, used in the commercial preparation of polymer I.

3-Hydroxyazetidinium and Epoxy Rings. NMR spectra of acetone-precipitated samples of polymer I, measured in dimethyl sulfoxide, (DMSO)- d_6 , revealed proton absorption for 2 amide and 8 methylene groups of the polyamide backbone, consistent with the structure shown in scheme 1. These spectra also showed complex multiplets between τ 6.8 and 7.5 (approximately 3 protons), where epoxides absorb, and between τ 5.2 and 6.0 (3 protons). Absorption centered at τ 2.0 (0.6 proton), which is assigned to the azetidinium ring hydroxyl, disappeared rapidly upon addition of trifluoroacetic acid, (TFA)- d_1 , to the DMSO- d_6 solution of polymer I, while absorption between τ 6.8 and 7.5 disappeared gradually. However, the rest of the spectrum remained unchanged except for an additional 3-proton absorption centered at τ 6.5.

Spectra of diethylenetriamine and 2-diethylaminoethanol in DMSO- d_6 showed that absorption of methylene protons attached to tertiary nitrogens were centered at τ 7.5 but shifted to τ 6.7 and 6.9, respectively, when treated with TFA- d_1 . A spectrum of 3-chloro-2-hydroxypropyltrimethylammonium chloride in DMSO- d_6 revealed that absorptions of the quaternary *N*-methylene and of the chlorohydrin protons were centered at τ 6.5 and were unchanged on addition of TFA- d_1 . A spectrum of 3-O-(2,3-epoxypropyl)-1,2:5,6-di-O-isopropylidene- α -D-glucopyranose (IV)⁴ in DMSO- d_6 exhibited absorption for its epoxypropyl group between τ 6.8 and 7.5, an absorption that gradually disappeared on addition of TFA- d_1 . The other regions of the spectrum of compound IV were unchanged except for additional proton absorption centered at τ 6.5. Spectral data obtained from these models suggest that the effect of TFA- d_1 on proton absorption shifts of

I from absorption between τ 6.8 and 7.5 to absorption centered at τ 6.5 was caused by both protonation of the tertiary nitrogens and opening of the epoxy ring. Apparently, protons of methylenes attached to quaternized nitrogen (azetidinium nitrogen) of I in DMSO- d_6 should and, indeed, did absorb in the region centered at τ 6.5, unaffected by addition of TFA- d_1 .

Absorption of I that was centered at τ 5.6 (range τ 5.2–6.0) was compared with the spectrum of 1,1-diethyl-3-hydroxyazetidinium chloride (V)⁵ (see scheme 3). In DMSO- d_6 , the azetidinium ring of V exhibited complex



Scheme 3

multiplets between τ 5.2 and 6.0, centered at τ 5.6 (see experimental section for detailed shift assignments of the 5 protons), which were unaffected by addition of TFA- d_1 . Both the pattern and region coincided with absorption of I between τ 5.2 and 6.0. The spectrum of polymer I between τ 5.2 and 6.0, integrated for 3 protons, which corresponds to 60 azetidinium ring groups per 100 repeating units (D.S. 0.6), based on a maximum of 5 protons that could appear in this region if I contained one azetidinium ring per repeating unit. Since the spectrum of I in DMSO- d_6 showed that, at τ 7.5, proton absorptions of the epoxy ring overlapped with absorptions of methylene groups that were attached to tertiary nitrogens, it was not possible to establish clearly separate absorptions for these two groups at the overlapping region. However, maximum D.S. of epoxypropyl groups by difference from azetidinium and chlorohydrin analyses would be 0.23. The 3-chloro-2-hydroxypropyl (D.S. 0.17) and epoxypropyl (D.S. 0.23) groups represent 2.4 (40% of 6) methylene protons attached to tertiary nitrogens and 0.7 epoxy ring protons for a total of 3.1 protons. This total compares favorably with the 3 protons of I in DMSO- d_6 , found between τ 6.8 and 7.5.

Unit Weight of Polymer I. The D.S. values of azetidinium, epoxypropyl, and chlorohydrin groups of I, which were 0.6, 0.23, and 0.17, respectively, correspond to an approximate ratio of 3:1:1. Based on the repeating units of I (scheme 1, step 2), which contain the azetidinium, epoxypropyl, and chlorohydrin groups in the 3:1:1 ratio, the average repeating unit weight of I is 301. This weight comprises (1) 212.0 for the repeating polyamide-polyamine unit; (2) 34.8, 11.4, and 18.7 for the azetidinium, epoxypropyl, and chlorohydrin structures, respectively; and (3) 24.2 for chloride content, of which 21.3 is associated with the azetidinium group.

Reaction of Polymer I with Compound II

Polysalt Structure. When a solution of I at 1% concentration was slowly admixed with a neutral aqueous solution of II (D.S. 0.13, 0.2% concentration) and maintained at pH 7, precipitation occurred at a dry weight ratio of 0.334 of I to 1.0 of II. The isolated product accounted for 98% of the total of I and II that were added. Sulfur (3.6%) and nitrogen (3.3%) contents of the product were approximately theory for an interpolymeric polysalt formed from reaction of 0.334 part of I and one part of II (Table II). The amount of I that was required to effect precipitation varied according to concentration and pH of the reactants and D.S. of II.

TABLE II
Ratios of Polymer I and Starch Xanthate (II) Required to Precipitate Polysalt^a

II		Amount I required, ^b parts/100 parts II			Yield, Nitrogen, Sulfur, ^c		
D.S.	Concentration %	pH 5	pH 7	pH 9	%	%	%
0.05	0.20	24.0					
0.13	0.01	42.7	58.3	66.8			
	0.05	27.3	36.4	41.0			
	0.10	27.3	34.2	39.2	97	3.3	3.6
	0.20	26.4	33.4	36.4	98	3.3	3.6
0.25	0.50	25.0	32.7	34.6			
	0.20	59.9					

^a I, at 1% concentration, was added to aqueous solutions of starch xanthate (II) with stirring (25°–27°C) until the precipitate formed. D.S. = degree of substitution.

^b The calculated stoichiometric amount of I was based on one amino group of I/xanthate group of II and an average unit weight of I as 300. These amounts were 9.0, 22.3, and 40.2 parts I/100 parts II for 0.05, 0.13, and 0.25 xanthate D.S., respectively.

^c After 24-hr storage and based on product obtained at pH 7.

In support of an interpolymeric polysalt structure, treatment of the fresh undried product (xanthate D.S. 0.13) with acid permitted quantitative recovery of carbon disulfide as expected for a xanthate group. The fresh undried product dissolved in 1*N* sodium hydroxide; whereas the air-dried product was sparingly soluble. When the dried product that contained 3.6% sulfur was treated with acid, generation of carbon disulfide was slow and nonquantitative. Evidence that the product undergoes further reaction to give xanthate ester groups, which would not yield carbon disulfide on acidification, was obtained by infrared (IR) spectroscopy. The dried product exhibited weak IR absorption at 8.3 and 9.4 μm , regions characteristic for a xanthate ester structure.⁶

Xanthate Ester Structure (III). An aqueous solution of II was treated with about one half the amount of I that effects precipitation. The pH of the mixture was adjusted to 7, and then portions were removed periodically to record ultraviolet (UV) spectra. A separate control solution of I at 0.01% concentration had no absorption maximum in the 200–400 nm

region, whereas a control solution of II at 0.05% concentration exhibited a maximum at 305 nm. The mixture of I and II, after 5 min, showed an absorption maximum at 305 nm, equal in intensity to that of the control xanthate solution. After 1 hr, intensity of absorption of the mixture at 305 nm decreased ca. 50%, and a new absorption appeared near 280 nm. When unreacted xanthate in the mixture was destroyed at this time by adjusting the pH to 2, the mixture showed a clearly defined maximum at 280 nm and none at 305 nm. Absorption near 280 nm is characteristic for the xanthate ester structure.⁶ After 4 hr, the intensity at 305 nm had decreased about 75% of the original value, but the intensity of the absorption at 280 nm had not increased over the 1-hr value. After 24 hr, absorptions at both 280 and 305 nm had disappeared, and a new but weak absorption maximum was observed near 320 nm, a region where trithiocarbonates absorb. These spectral data suggest that I and II reacted to yield a xanthate ester structure, which subsequently underwent further reaction to give trithiocarbonate.

Similar observations were made for reactions between I and II at pH 5, 9, and 10. At pH 12, the spectrum of a mixture of I and II showed an absorption maximum at 320 nm but no significant absorption at 280 nm. In addition, at pH 12 a gas that slowly evolved over 24 hr was trapped and identified as carbonyl sulfide.⁷ Xanthates are known to react with epoxides in strong alkaline media to yield carbonyl sulfide and trithiocarbonate.⁸

Reactions between xanthate and azetidinium groups were elucidated by means of model systems.

Model Compound Reactions

Reaction of 1,1-Diethyl-3-hydroxyazetidinium Chloride (V) with Sodium Ethyl Xanthate (VI). An aqueous mixture containing VI (1% concentration) and an equivalent amount of V (scheme 3) was adjusted to pH 7; portions were removed periodically for determining UV absorption. Initially, there was absorption only for ionic xanthate (maximum at 303 nm). This absorption diminished with concurrent formation of a new absorption maximum at 280 nm. After several hours, absorption at both 280 and 303 nm had disappeared and a new absorption maximum was present at 320 nm. These results were analogous to those described for aqueous mixtures of I and II, except that absorption at 280 nm for the model system disappeared more rapidly. Since it appeared difficult to isolate the reaction product of V and VI as a stable derivative from an aqueous reaction mixture, V and VI were reacted in nonaqueous systems. In absolute ethanol, reaction between V and VI was more rapid than in water, as indicated by both iodine titrations of unreacted xanthate and UV spectroscopy, and also resulted in a stabilized absorption at 280 nm (absolute ethanol as solvent for UV). After a reaction period of 1 hr, a yellow oil was recovered in 75% yield. The oil exhibited UV absorption at 280 nm and IR absorption at 8.3 and 9.5 μm , characteristic of the xanthate ester

structure. Also, a small amount of carbonyl absorption was present probably due to slight decomposition of VII caused by the presence of water in both the reaction and recovery systems.

When V and VI were dried, suspended in anhydrous ether, and stirred 6 hr, a yellow oil was recovered in 55% yield (80% in 30 hr) which crystallized on standing overnight. Recrystallization from hexane gave a white solid that had IR absorption at 8.3 and 9.5 μm but none at carbonyl regions. The UV and NMR spectra and analytical data were consistent with the structure of VII.

Derivative VII showed stability in several nonaqueous solvents; however, when VII was dissolved in ethanol and treated with water, UV absorption at 280 nm rapidly disappeared in 1 hr. After 4 hr, five products of decomposition in addition to free sulfur were separated by thin-layer chromatography (TLC). In general, IR spectra of these products showed strong absorptions at 5.7, 5.8, and 5.9 μm (carbonyl), weak to no absorption at 8.3 and 9.5 μm , and no hydroxyl. These components were not further characterized. In addition, UV analyses showed that mixtures of VII and xanthate (VI) yielded carbonyl sulfide and trithiocarbonate.

When VII was converted to the hydrochloride salt, stability in water was greatly increased. When VII was converted to the 3-O-acetyl derivative, this product also exhibited an increased stability in water. The acetyl derivative of VII was also prepared in quantitative yield by reacting VI with the 3-O-acetyl derivative of V. This experiment, demonstrating direct attack on the azetidinium ring, obviates any requirement that the reaction must proceed via the possible epoxide intermediate.

Stability of VII appears to be related to reduced availability of the unshared electrons on both the nitrogen and hydroxyl oxygen. An unstable cyclic dithiocarbonate yields mono- and dithiocarbonates, with elimination of carbonyl sulfide, and a stable trithiocarbonate in the presence of xanthate via an episulfide.⁹⁻¹¹

Reactions of Ethyl Xanthate (VI) with Azetidinium, Epoxy, and Chlorohydrin Structures. The rates of reaction at pH 9 of ethyl xanthate (VI) with (a) Kymene 557 (I), (b) 1,1-diethyl-3-hydroxyazetidinium chloride (V), (c) propylene oxide, and (d) 3-chloro-1,2-propanediol were investigated briefly (Table III). An equivalent weight of 375 was used for I, based on the average unit weight of 300 divided by the total D.S. (0.8) of azetidinium and epoxypropyl groups present.

A solvent system of ethanol-water (9.5:1 v/v) was used for all reactions, except with I. In the 95% ethanol system, the xanthate ester that was formed remained stable during 4 hr. It was necessary that the derivative be stable to eliminate side reactions that could use up unreacted xanthate. A solvent system for I of ethanol-water (2:1 v/v) also yielded a stable derivative up to 4 hr as indicated by UV spectroscopy. The low solubility of I in ethanol prevented the use of a higher level of ethanol, and the model derivatives were unstable in the higher levels of water. For I, 80% of the combined number of azetidinium and epoxypropyl groups reacted in 4 hr

TABLE III
Reaction Rates of Sodium Ethyl Xanthate (VI)
with Polymer I^a and Model Compounds at pH 9

Reaction period, hr	Per cent VI that reacted ^b			
	I	1,1-Diethyl-3-hydroxy-azetidinium chloride (V)	Propylene oxide	3-Chloro-1,2-propanediol
0.12	37	3	7	1
1	72	30	41	1
2	77	48	—	—
4	80	54	58	7

^a Precipitated in acetone.

^b Equivalent amounts of reactants were used. Concentration of reaction mixture was 1% VI, dry basis; unreacted VI was determined by titration with 0.01*N* iodine solution.

at a rate considerably higher than for the models. Only 7% of xanthate (VI) reacted with 3-chloro-1,2-propanediol in 4 hr.

Application of I and II in Paper

Nonpurified solutions of I and II were added sequentially to an unbleached kraft pulp furnish to determine the effects of addition order of I and II, furnish pH (5 or 7), addition level of I (0.25 or 0.50%, dry pulp weight basis), and xanthate D.S. of II (0.13 or 0.25) on wet- and dry-strength properties of the paper handsheets (Table IV). These preliminary data show that (1) polymer I should be added to the furnish before II, (2) dry strength was greater at the lower pH whereas wet strength was independent of pH, (3) dry-strength and, particularly, wet-strength properties were greater for the higher addition level of I, with use of a constant level of II, and (4) strength properties were slightly greater with use of starch xanthate of the lower D.S.

In general, dry-tensile and dry-burst strengths of interpolymer-treated papers were about double those of polymer I-treated control papers; and Concora crush resistance, a property often difficult to improve, was nearly three times greater. Addition of polymer II, alone, had no appreciable effect on paper strength properties.

Probably, II is initially attracted to and retained on the fibers by ionic interactions with I, which is substantive to the fibers. However, covalent bonding between polymers I and II could ensue while handsheets were being formed, pressed, dried, and aged.

EXPERIMENTAL

General

NMR spectra were recorded by a Varian HA-100 NMR spectrometer. Tetramethylsilane was the internal reference standard ($\tau = 10.00$). UV

TABLE IV
Effect of Interpolymer on Strength of Handsheets^a

Additive, %	Furnish pH	Polymer II, D.S.	Burst factor, (g/cm ²)/(g/m ²)	Breaking length, m,		Concora crush, lb.
				Dry	Wet	
Controls						
None	7 ^b		50	6560	140	60
I, 0.25	7 ^b		61 (22) ^c	7750 (18)	1400 (900)	67 (13)
I, 0.50	7 ^b		65 (30)	8250 (26)	1750 (1150)	71 (18)
II, 2.5	7 ^b	0.13	49 (-2)	6670 (2)	175 (25)	61 (3)
Interpolymer Treated						
II, 2.5; I, 0.25 ^d	7	0.13	66 (32)	8230 (26)	980 (600)	74 (23)
I, 0.25; II, 2.5	7	0.13	76 (52)	9400 (44)	1400 (900)	82 (37)
I, 0.25; II, 2.5	5	0.13	78 (56)	9650 (47)	1400 (900)	87 (45)
I, 0.5; II, 2.5	7	0.13	78 (56)	9950 (52)	1800 (1260)	91 (52)
I, 0.5; II, 2.5	7	0.25	76 (52)	9430 (44)	1500 (970)	90 (50)

^a Basis weight of handsheets, 127 g/m² dry basis, addition of I before II.

^b Wet- and dry-strength properties were similar at pH 5.

^c Parentheses, per cent change from untreated control.

^d Addition of II before I.

spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer. IR spectra were determined with a Perkin-Elmer Model 137 spectrophotometer of films cast on silver chloride plates and of potassium bromide discs. Melting points were measured with a Fisher-Johns apparatus. TLC was used for qualitative separations on microscope slides (1 × 3 in.), filmed with Silica Gel G, and the eluent was 4:1 (v/v) ether-tetrahydrofuran. For detection of components by TLC, either 19:1 (v/v) methanol-sulfuric acid spray, Rhodamine 6-G fluorescent spray, or iodine vapor was used.

Chemical Analyses

Carbon, hydrogen, and nitrogen were determined with a Perkin-Elmer 240 elemental analyzer. Chlorine and sulfur were determined by the method of White,¹² except for Kymene 557 (I). Because volatile chlorohydrins were lost during drying of nonpurified samples of I, a special procedure was developed for total chlorine. This procedure is described below.

For ionic chloride determinations, 1-ml portions of (a) purified (acetone precipitated) and nonpurified (commercial stock sample) solutions of I, diluted to 1% solids with distilled water, and (b) nondiluted acetone supernatant of purified I were added to 100-ml portions of 95% ethanol and titrated with 0.01*N* mercuric nitrate at pH 3 (0.1*N* HNO₃) with diphenylcarbazone as the indicator. For total chlorine of I, the 1-ml portions were added to 5 ml of 1*N* sodium hydroxide plus 5 ml of distilled water, heated 15 min (steam bath), cooled to 25°–27°C, diluted to 50 ml with 95% ethanol, and titrated with mercuric nitrate as described above. When 95% ethanol was added to the alkali-treated samples of I, a precipitate formed that was dissolved by adding 25 ml water. This procedure gave accurate results on commercial samples of both 3-chloro-1,2-propanediol and 3-chloro-2-hydroxypropyltrimethylammonium chloride.

Starch content of unreacted xanthate in reaction mixture filtrates of I and II was determined by the Munson-Walker method.¹³

Unreacted xanthate in model reaction mixtures was determined by titrating 1-ml portions of reaction mixtures and of control xanthate solutions (in 50 ml of 95% ethanol) with 0.01*N* iodine solution.

Polymer I

Kymene 557 (I) is a commercial cationic polyamide-polyamine-epichlorohydrin resin sold as an aqueous solution at 10% solids and pH 5. Reported nitrogen content: 12.8%¹⁴; found: 12.7%, dry basis.

NMR Data of I in DMSO-*d*₆. τ 1.7 (2-proton multiplet, amides); τ 2.0 (0.6 to 0.8-proton absorption, which disappeared on deuteration, hydroxyl); τ 7.8 (4-proton multiplet, methylenes α to carbonyl); τ 8.5 (4-proton multiplet, methylenes β to carbonyl); τ 6.5 (7-proton multiplet, which includes methylenes β to nitrogens, methylenes α to quaternary nitrogens, and methylenes of chlorohydrins); τ 6.8–7.5 (3-protons, multiplets that in-

clude methylenes attached to nonprotonated tertiary nitrogens, primarily at τ 7.5, and epoxy rings at τ 6.8–7.5); τ 5.2–6.0, centered at τ 5.6 (3-protons, multiplets that include one multiplet at τ 5.4 and one multiplet at τ 5.8; methylenes and methine of azetidinium ring).

NMR Data of I in DMSO- d_6 + TFA- d_1 . τ 6.5 (10 proton multiplet, which includes all methylenes attached to nitrogens, ring-opened groups of former epoxide, and chlorohydrins). No signal was present at τ 6.8–7.5 (except DMSO- d_6 , τ 7.5) or at τ 2.0. The rest of the spectrum was unchanged from that of I in DMSO- d_6 .

Sodium Starch Xanthate (II)

Commercial pearl corn starch was converted to sodium starch xanthate of D.S. 0.05, 0.13, and 0.25 in a Model 50 Ko-Kneader,¹⁵ diluted to 10% solids, and stored at 1°C.

3-O-(2,3-Epoxypropyl)-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose (IV)

Model IV was obtained from R. E. Wing of the Northern Laboratory and has been previously reported.⁴

1,1-Diethyl-3-hydroxyazetidinium Chloride (V)

Diethylamine and epichlorohydrin were reacted according to the method of Ross et al.⁵ to give an 85% yield of compound V. On the basis that isomeric chlorohydrin and/or epoxypropyl derivatives might also be formed, NMR, IR, and analytical evaluations of V were made.

NMR Data of V in DMSO- d_6 . τ 6.5 (4-proton overlapping quartets, methylenes of ethyl groups); τ 8.9 (6-proton triplet, methyls of ethyl groups); τ 5.2–6.0 centered at τ 5.6 (5-protons, multiplets, consisting of one multiplet at τ 5.5 that includes one methine as determined by decoupling and one multiplet at τ 5.8; absorptions at τ 5.2–6.0 include methylenes and methine of azetidinium ring); τ 3.2 (1-proton doublet that disappeared on deuteration, hydroxyl).

IR Spectrum of V. Showed hydroxyl absorption at 3.1 μ m (in addition to water hydroxyl at 2.9 μ m) and indicated no chlorohydrin, epoxide, or tertiary amine structures.

Elemental Analysis of V. Calculated for $C_7H_{16}ClNO \cdot H_2O$: C, 45.8; H, 9.8; N, 7.6; Cl, 19.3. Found: C, 45.5; H, 9.7; N, 7.6; Cl, 19.1.

Model V was a white, crystalline compound soluble in acetonitrile and absolute ethanol and insoluble in acetone; mp 154°–155°C (reported⁵ mp 154°–155°C).

Sodium Ethyl Xanthate (VI)

Model VI was prepared by adding carbon disulfide to a solution of sodium ethoxide (sodium and ethanol) by the method of Ingram and Toms,¹⁶ except that acetone rather than water was added to the reaction mixture before crystallization in ether.

S-[3-(Diethylamino)-2-hydroxypropyl] O-Ethyl Dithiocarbonate (VII)

A solution of V, containing 165.5 mg in 14.4 ml of either absolute or 95% ethanol, was added to 144 mg of VI and mixed 1 hr at 25°–27°C. After 1 hr, the reaction mixture was added to 50 ml of anhydrous ether and washed with four 25-ml portions of water to remove unreacted V and VI. Ether was evaporated under vacuum (50°C), and VII, a yellow oil, was obtained in 75% yield. Alternatively, 396 mg of V and 345 mg of VI, pre-dried under vacuum over phosphorus pentoxide at 25°C, were suspended in 10 ml of anhydrous ether. The insoluble reactants were mixed in a closed vial by means of a magnetic bar for 6 hr at 25°–27°C. After 6 hr, the ether portion was transferred to a separate vial and evaporated. A yellow oil was recovered in 55% yield (80% in 30 hr), which crystallized on standing overnight in a dry atmosphere at 1°C. After this yellow solid was recrystallized three times from hexane (Dry Ice–acetone bath), a pure white solid was obtained with mp 37.5°C. This product gave $\lambda_{\max}^{\text{ether}}$ 280 nm (ϵ 11,000). See results and discussion for other UV and IR data.

NMR Data of VII in DMSO- d_6 . τ 8.7 (3-proton triplet, methyl of O-ethyl group); τ 5.4 (2-proton quartet, methylene of O-ethyl group); τ 9.1 (6-proton triplet, methyls of *N*-ethyl groups); τ 7.6 (6-proton multiplet that consisted of a doublet as determined by decoupling and a quartet, *N*-methylene of propyl group and *N*-methylenes of ethyl groups, respectively); τ 6.1–7.1 (3-protons, ABC multiplets, methine β to nitrogen centered at τ 6.2 and *S*-methylene centered at τ 6.5 and 7.0); τ 5.1 (1-proton doublet, hydroxyl). A series of decoupling experiments related methyl and methylene groups to their respective ethyl groups.

Elemental Analysis of VII. Calculated for $C_{10}H_{21}NO_2S_2$: C, 47.8; H, 8.4; N, 5.6; S, 25.5. Found: C, 47.9; H, 8.4; N, 5.5; S, 25.5.

Aqueous Treatment of VII

To 40 mg of VII were added 20 ml of absolute ethanol and 20 ml of distilled water (0.1% concentration, 25°–28°C, pH 8). Four hours after aqueous treatment of VII, ethanol and water were removed under vacuum (50°C). The residue was dissolved in chloroform and separated by TLC. Five component zones were sectioned and eluted with chloroform. IR spectra of these components were briefly discussed in the results and discussion section.

Hydrochloride Salt of VII

Hydrogen chloride gas, slowly bubbled into a solution of VII (251 mg) in ether (50 ml), gave a white precipitate in 98% yield that had stable UV absorption at 280 nm in water for 2 hr at 25°–27°C. NMR of the salt in DMSO- d_6 showed that the *N*-methylene protons shifted from τ 7.5 to 6.8.

Elemental Analysis of Hydrochloride Salt of VII. Calculated for $C_{10}H_{22}ClNO_2S_2$: C, 41.7; H, 7.7; N, 4.9; Cl, 12.3; S, 22.3. Found: C, 41.6; H, 7.6; N, 4.8; Cl, 12.3; S, 23.3.

3-O-Acetyl Derivative of VII

To 251 mg of VII, acetic anhydride (310 mg) was added dropwise with mixing. After 30 min, a quantitative yield of the product was obtained following several successive ether (50 ml)-vacuum treatments to remove excess acetic anhydride/acetic acid. IR analysis of the acetylated product showed intense carbonyl absorption at 5.7 μm and no hydroxyl absorption. NMR (DMSO- d_6) gave a signal for one acetyl group at τ 8.0 (3 protons). The remaining NMR spectrum was the same as described for VII, except that the methine proton shifted downfield about 0.4 ppm.

Elemental Analysis of 3-O-Acetyl Derivative of VII. Calculated for $\text{C}_{12}\text{H}_{23}\text{NO}_3\text{S}_2$: S, 21.8. Found: S, 21.5.

3-O-Acetyl Derivative of V

To 165.5 mg of V was added 310 mg of acetic anhydride. No appreciable acetylation occurred as indicated by insolubility of V. Upon addition of perchloric acid (about 200 mg dropwise), acetylation occurred readily. Excess acetic anhydride/acetic acid was removed as described for the acetyl derivative of VII. IR of the white crystalline product showed no hydroxyl but intense carbonyl absorption at 5.7 μm , whereas the remaining spectrum was essentially unchanged from that of V.

NMR (DMSO- d_6) showed no hydroxyl but 3 acetyl protons at τ 7.9. The remaining spectrum was as described for V, except that absorptions of the methine and ring methylene protons were displaced downfield 0.6 ppm and 0.2 ppm, respectively.

Solutions of 208.5 mg of acetylated V in 7.2 ml of 95% ethanol and 144.5 mg of VI in 7.2 ml 95% ethanol were admixed and stirred for 2 hr. Extraction with ether as described for VII afforded a quantitative yield of the 3-O-acetyl derivative of VII. IR, UV, and NMR spectra were identical to those of the acetylated VII previously described.

Polysalt

One-milliliter samples of the stock solution of II (D.S. 0.05, 0.13, 0.25) were diluted with distilled water to concentrations ranging from 0.01 to 0.5 (Table II) and kept at 25°–27°C. Samples of each solution were then adjusted to pH 5, 7, and 9 with 0.1–1.0*N* hydrochloric acid or 0.1–1.0*N* sodium hydroxide. The stock solution of I, nonpurified, was diluted to 1% solids and added dropwise to each solution of II until a precipitate formed. The precipitate was washed successively with water, ethanol, acetone, and ether and then stored at 23°C and 50% relative humidity for 24 hr before analyses for volatiles, yield, nitrogen, and sulfur.

Applications of I and II in Handsheets

To a 1000-g pulp slurry (15 g dry basis, unbleached, kraft pulp in tap water, 560 Canadian Standard freeness), under good agitation, was added 37.5 g of an aqueous solution of II (stock solution diluted to 1% concentra-

tion, 0.375 g, dry basis). The pH was then adjusted to 7.0 with 1*N* hydrochloric acid, and 3.75 g of a solution of I at 1% concentration (0.0375 g, dry basis) was added (mixed 3 min). Levels of I and II were 0.25% and 2.5% dry pulp basis, respectively. The mixture was diluted to 0.35% consistency, pH was adjusted to 7.0, and handsheets (127 g/m² dry basis) were prepared and tested according to TAPPI standards.¹⁷ Control sheets were prepared with (a) no additives, (b) 2.5% of II but no I, and (c) 0.25% of I but no II.

SUMMARY AND CONCLUSIONS

A study, employing model compounds, was made on reactions between Kymeme 557 (I), a commercial polyamide-polyamine-epichlorohydrin resin, and sodium starch xanthate (II). NMR, IR, UV, and chemical analyses revealed that I, which we found to contain 3-hydroxyazetidinium chloride, epoxypropyl, and chlorohydrin groups in the ratio of 3:1:1, reacts with II to form an interpolymer, crosslinked by both ionic and covalent bonds. Xanthate groups of II react with azetidinium and epoxy ring groups of I to form xanthate ester crosslinks, and with cationic amino groups of I to form polysalt crosslinks. In model systems, mixtures of 1,1-diethyl-3-hydroxyazetidinium chloride and sodium ethyl xanthate yielded a xanthate ester, S-[3-(diethylamino)-2-hydroxypropyl] O-ethyl dithiocarbonate.

The effects of pH (5-12), polymer weight ratio (I:II, 0.18-0.67:1) and concentration (II, 0.01-0.5%), and xanthate D.S. (0.05-0.25) on the ratio of polysalt to xanthate ester crosslinks in the interpolymer were studied. Application of the interpolymer as a wet-end paper additive was the primary basis for selection of the range of reaction variables. Incorporation of the interpolymer, in situ, into unbleached kraft handsheet furnish by sequential addition of I and II improved dry-strength properties of paper approximately double those that were obtained with use of I alone, whereas application of II alone was ineffective.

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The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

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