Starch Xanthate-Polyethylenimine Reaction Mechanisms

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Synopsis

The chemical nature of starch xanthate (SX)-polyethylenimine (PEI) reaction products has been studied because of their effectiveness as wet-end additives for improving strength properties of paper. Model compounds, in conjunction with ultraviolet, infrared, and chemical analyses, served to elucidate SX-PEI reaction mechanisms. Aqueous solutions of SX (degrees of substitution 0.1-0.5) were titrated with PEI at pH 5-7 (25-30°C) to form SX-PEI flocculent precipitates that were determined to be polyelectrolyte complexes. However, when solutions of SX-PEI were kept at pH 11-12, products were formed that included dithiocarbamic acid salts in major quantities, PEI thioureas, and minor quantities of O-starch PEI thionocarbamate. Acid precipitation of these SX-PEI polymeric reaction products from their alkaline solutions, which contained residual xanthate and PEI, also yielded polyelectrolyte complexes. Model systems suggest that PEI thiranium disulfide and starch xanthide, possible products of air oxidation, could be present in minor amounts and would react rapidly with PEI to yield thioureas and thionocarbamates, respectively. Apparently, mixtures of xanthate and amine gave (1) dithiocarbamic acid salts from both xanthate groups and CS₂ (decomposition from xanthate), (2) thioureas from both dithiocarbamic acid salts and thirium disulfide, and (3) thionocarbamates, principally from xanthate as opposed to xanthide.

INTRODUCTION

Sodium starch dithiocarbonate (starch xanthate, SX), oxidatively crosslinked in papermaking furnish, improves wet and dry strength of paper. In continuing efforts to improve the effectiveness of SX as a wet-end paper-strengthening additive, such ionic polymers as Ky menae 557 and polyethylenimine (PEI), which have sites for ionic and covalent bonding of xanthate [-OC(8)S⁻], have been investigated as alternative crosslinking agents. Our latest work, which involves reactions that occur in aqueous solutions of SX with PEI, was made to facilitate application of SX-PEI products in paper and studies of similar polyelectrolytic systems. PEI, a polycation which contains primary, secondary, and tertiary amine groups in the ratio of 1:2:1, previously has been reacted with polymers of opposite charge to form polyelectrolyte complexes. For example, mercury ion in parts per billion concentration have been substantially removed from wastewater by sequential additions of PEI and SX, forming water-insoluble polyelectrolyte complexes. However, these complexes per se were not...
analytically characterized. In nonpolymeric systems, reactions of primary and secondary amines with xantheate salts in aqueous alkaline solutions can yield thionocarbamates.\(^7\) Reportedly, aqueous solutions of SX and PEI aged at pH 10–12 and room temperature have yielded thionocarbamate \([-\text{OC}(\text{S})\text{N}^-]\) interpolymers.\(^3\) However, others have stated that aqueous alkaline mixtures of cellulose xantheate and PEI on aging yielded dithiocarbamic acid salts \([\text{NC}(\text{S})\text{S}^-]\) and thioureas \([\text{NC}(\text{S})\text{N}^-]\) of PEI but no thionocarbamate product.\(^8\) The PEI dithiocarbamic groups were believed to form from CS\(_2\) of decomposed xantheate. Reportedly, air oxidation of nonpolymeric dithiocarbamic acid salts can yield thiuram disulfides \([\text{NC-(Si)}_2(\text{S})\text{CN}^-]\) and thioureas.\(^9\) The thioureas may be formed readily by reaction of primary and secondary amines with thiuram disulfides. Analogous to air oxidation of dithiocarbamic groups, air oxidation of xantheates can yield xanthides \([-\text{OC}(\text{S})\text{S}(\text{S})\text{CO}^-]\) which readily react with primary and secondary amines to yield thionocarbamates.

Several reaction products including polyelectrolyte complexes were formed in aqueous solutions of SX with PEI at pH ranging from 5 to 12. With the aid of model systems, these products were characterized by ultraviolet, infrared, and chemical analyses. All reactions were at 25–30°C.

**RESULTS AND DISCUSSION**

**SX–PEI Polyelectrolyte Complex**

When a 1%\(_{\text{w/r}}\) aqueous solution of PEI 600 was slowly admixed with a 0.2%\(_{\text{w/r}}\) aqueous solution of SX having a degree of substitution (DS) of 0.15, and when pH was maintained at 7.0, a flocculent precipitate was formed at a dry-weight ratio of 0.145 part PEI/1.0 part SX. Alternatively, when solutions of the alkaline reactants were combined at the same concentrations and ratios, but pH was slowly lowered, precipitation occurred at pH 7. The fresh precipitates, obtained in 95%\(_{\text{w/r}}\) yields (SX–PEI addition basis), had sulfur (4.5%\(_{\text{w/r}}\)) and nitrogen (3.9%\(_{\text{w/r}}\)) contents that were about theory for a product containing 0.145 part PEI/1.0 part of DS 0.15 SX (theory; 4.8% S, 4.1%\(_{\text{w/r}}\) N). When the fresh undried precipitates were treated with acid (pH 1.5) to decompose xantheate groups, CS\(_2\) was recovered\(^{10}\) in amounts corresponding to original xantheate contents. PEI dithiocarbamic acid salts, possible components in the SX–PEI precipitates, also would release CS\(_2\) at pH 1.5. However at pH 11, the fresh undried precipitates readily solubilized and contained 93–97%\(_{\text{w/r}}\) of the theoretical amounts of xantheate, as determined by ultraviolet analysis (\(\lambda_{\text{max}} = 305, \epsilon 17,500\)). These data showed that the fresh undried precipitates were SX–PEI polyelectrolyte complexes. The effects of pH, xantheate DS, and concentration on the amount of PEI required to form these complexes, and analytical data are given in Table I.
TABLE I
Preparation and Analyses of Starch Xanthate (SX)-Polyethyleneimine (PEI) Polyelectrolyte Complexes⁸

<table>
<thead>
<tr>
<th>SX</th>
<th>Amount of PEI required to precipitate SX-PEI complex, parts/100 parts SX</th>
<th>Analyses of precipitated complex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 5</td>
<td>pH 7</td>
</tr>
<tr>
<td>Degree of substitution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DS</td>
<td>Concentration, c_g</td>
<td>pH 5</td>
</tr>
<tr>
<td>0.11</td>
<td>0.10</td>
<td>7.1</td>
</tr>
<tr>
<td>0.15</td>
<td>0.01</td>
<td>9.0</td>
</tr>
<tr>
<td>0.15</td>
<td>0.03</td>
<td>9.0</td>
</tr>
<tr>
<td>0.15</td>
<td>0.10</td>
<td>12.0</td>
</tr>
</tbody>
</table>

⁸ Aqueous PEI (1 c_g) was slowly added to aqueous SX, with stirring, until a precipitate was formed. Sulfur content was determined within 1 hr after precipitation.

Ultraviolet analyses of aged SX-PEI complexes indicated that reactions had occurred similar to those in aqueous SX-PEI solutions at pH 10-12.

Alkaline SX-PEI Solutions

An aqueous solution of SX and PEI at pH 11 was prepared that contained SX of DS 0.22 at 35% concentration and enough PEI 600 to give a ratio of amine to xanthate groups of 2:1, conditions that were previously reported to yield "starch polyethyleneimino thiourethane," an O-starch PEI thionocarbamate. On aging, ultraviolet absorption of this alkaline SX-PEI solution gradually shifted from its xanthate maximum at 305 nm to 300 nm (1-2 days), 292 nm (5 days), and finally 280 nm (28 days) with concurrent formation of a weaker nonshifting absorption at 260 nm. There was poorly defined absorption in the region of 235-245 nm. When acid-treated (pH 1.5), the aged (5-28 days) mixture exhibited an absorption peak at 230 nm but none at 260 and 280 nm. At pH 7-12, absorption by the acid-treated mixture shifted from 239 nm to 237 nm. Ultraviolet spectra of the fresh and 28-day-old mixture before and after acid treatment are reproduced in Figure 1. Absorption at 235-245 nm is partially obscured by overlapping absorptions of alkali at lower wavelengths. SX has a weak absorption at 227 nm.

SX-PEI products in alkaline solution were precipitated in ethanol, isolated, and redissolved at pH 12. The ultraviolet spectra of these redissolved precipitates were similar to those of the solutions from which they were precipitated. Ultraviolet spectra of the SX-PEI solutions in Figure 1 were typical of spectra that contained initial xanthate DS of 0.1-0.5, SX
concentrations of 2.5-10\% and amine:xanthate ratios from 1:1 to 10:1 (pH 10-12).

**Chemical Analyses**

Amounts of CS$_2$ recovered from SX-PEI solutions and their ethanol precipitates that were acid-treated at pH 1.5 are listed in Table II. Yields, sulfur, and nitrogen contents of the precipitates are also given. From the fresh SX-PEI alkaline solution (Fig. 1) containing only xanthate sulfur, CS$_2$ recovery was 97\% of theory, equal to that for an SX (DS 0.22) control.

**TABLE II**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon disulfide recovery, (%)</th>
<th>SX-PEI precipitated product</th>
<th>Yield, (%)</th>
<th>Sulfur, (%)</th>
<th>Nitrogen, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From solution</td>
<td>From EtOH precipitate</td>
<td>Total</td>
<td>As CS$_2$</td>
<td></td>
</tr>
<tr>
<td>SX control</td>
<td>97</td>
<td>60</td>
<td>95</td>
<td>4.7</td>
<td>4.7</td>
</tr>
<tr>
<td>Fresh SX-PEI</td>
<td>97</td>
<td>78</td>
<td>93</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>5-Day-old PEI</td>
<td>80</td>
<td>41</td>
<td>92</td>
<td>3.7</td>
<td>2.9</td>
</tr>
<tr>
<td>28-Day-old SX-PEI</td>
<td>75</td>
<td>33</td>
<td>94</td>
<td>4.6</td>
<td>2.4</td>
</tr>
</tbody>
</table>

* SX-PEI precipitates were formed by addition of the SX-PEI solutions to 95\% EtOH.

* Trapped as CS$_2$-diethylamine complex (Et$_2$NH$\cdot$CS$_2$ $\cdot$ 13,500). Recovery is based on amount of CS$_2$ contained by SX of DS 0.22.

* Theoretical sulfur content for SX of DS 0.22 is 7.8\% and is 7.2\% based on SX + PEI.
Even though the 28-day-old SX-PEI solution contained no xanthate, the yield of CS₂ was still 75% of theory, showing that the acid-unstable derivative (260, 289 nm) was a major component of the aged mixtures. A similar conclusion was reached with the 5-day-old SX-PEI solution. During isolation and drying of the ethanol precipitates, including the SX control, substantial losses of CS₂ occurred. However when total sulfur and CS₂ were determined simultaneously on portions of precipitates from which elemental sulfur had been removed, total sulfur was in excess of the amount that could be removed as CS₂. This excess represented about 10 and 25% of DS 0.22 SX that could be present as the acid-stable components in the precipitates of the 5- and 28-day-old mixture, respectively.

The scheme shown in Figure 2 illustrates reactions and reaction mechanisms of alkaline SX-PEI solutions that are suggested by our work and elucidated in the Model Reactions section.

**Model Reactions**

**Dithiocarbamic Acid Salts.** When CS₂ was combined with aqueous PEI 6 to give an amine:CS₂ ratio of 10:1 and a pH of 12, a water-soluble PEI dithiocarbamic acid salt resulted. A ratio of 2:1 yielded a water-insoluble salt. The fresh soluble PEI salt exhibited absorption maxima at 260 and 289 nm. These absorptions disappeared on acidification (pH 1.5). The aged acid-treated PEI salt solution exhibited absorption only at 237 nm. These results are typical of those from alkaline SX-PEI solutions.

Several model dithiocarbamic acid salts and xanthate-amine aqueous solutions were prepared: (a) N-ethylammonium salt of N-ethyldithio-
carbamic acid (I) and \( N,N \)-diethylammonium salt of \( N,N \)-diethylthiocarbamic acid (II); (b) aqueous, nonisolated sodium salts of dithiocarbamic acids\(^2\) from ethylenediamine, diethylenetriamine, and diethylenetriamine at amine:CS\(_2\) ratios of 1:1; (c) O-ethyl sodium dithiocarbonate (ethyl xanthate, EtX). O-butyl sodium dithiocarbonate (butyl xanthate, BuX), and DS 0.5 SX with nonpolymeric amines; and (d) EtX with PEI. The ratio of amine to xanthate was 2:1, except in the sodium salts of dithiocarbamic acids. In principle, ultraviolet characteristics of fresh, aged, and acid-treated model solutions were the same as those described for SX–PEI solutions and for the PEI dithiocarbamic acid salt. Double peak absorptions of the various xanthate–amine solutions, which developed with age, were identical to those of dithiocarbamic acid salts that were prepared from CS\(_2\) with methylamine (260, 290 nm), ethylenediamine (255, 284 nm), and diethylenetriamine (258, 287 nm). Dithiocarbamic acid salts from both model xanthate–amine and SX–PEI solutions formed more rapidly than could be accounted for on the basis of CS\(_2\) decomposition rate of xanthate control solutions, implying interaction of amine with xanthate groups as well as with CS\(_2\) from decomposed xanthate to form dithiocarbamic groups.

Spectral patterns of the PEI dithiocarbamic acid salt closely resembled those of the model salts of primary amines. Also, the 5-day-old solutions of diethylenetriamine with either xanthates or CS\(_2\) had no appreciable absorptions at 235–245 nm when acid-treated. These ultraviolet data suggest that PEI primary amine groups, rather than secondary, were the principal reactive groups in formation of dithiocarbamic groups. Selected spectra of fresh, aged, and acid-treated solutions of model dithiocarbamic acid salts, PEI dithiocarbamic acid salt, and SX–diethylenetriamine are reproduced in Figures 3 and 4.
Thioureas. In studying thiourea formation in SX-PEI alkaline solutions, the following model compound systems were employed. Aqueous solutions of salts I and II were nitrite-oxidized (pH 4) to N,N'-diethylthiuram disulfide (III) and N,N,N',N'-tetraethylthiuram disulfide (IV), respectively. Addition of ethylamine to a solution of III in ether rapidly gave N,N'-diethylthiourea (V). However, addition of diethyamine to III yielded a small amount of expected side products (i.e., dithiocarbamic acid salt and elemental sulfur) but no appreciable N,N,N',N'-tetraethylthiourea. Thiourea (V) was isolated from crystalline salt I that was aged 2 weeks at 25-30°C. The water-soluble PEI dithiocarbamic acid salt, which was prepared as previously described but at 2% concentration, was nitrite-oxidized to yield a water-insoluble PEI thiuram disulfide, which concurrently reacted with its unreacted amine groups within 15 min to give a PEI thiourea that was soluble in both water and ethanol. In water, the PEI thiourea exhibited absorption at 237 nm at pH 1.5 and 239 nm at pH 7 but at 242 nm in 95% ethanol, a characteristic also of N,N'-diethylthiourea ($\lambda_{\text{max}}$ 237, $\epsilon$ 11,400 and $\lambda_{\text{E100}}^{\text{max}}$ 243, $\epsilon$ 11,670) (Fig. 5).

Apparently, any thiuram disulfide in aged-SX-PEI solutions that might form by air oxidation would immediately react with unreacted primary amine groups to give PEI thiourea. Probably, PEI thiourea was formed principally from dithiocarbamic groups, as solutions of SX-PEI and compound I yielded thioureas even when stored under nitrogen.

Thionocarbamates. Under conditions described earlier for alkaline SX-PEI solutions, thionocarbamates were formed from (1) nonpolymeric xanthates with amines, including PEI, and (2) SX with nonpolymeric amines. However, no appreciable amount of thionocarbamate was formed in SX-PEI solutions. In all cases, dithiocarbamic acid salts also were formed. Several thionocarbamate reference compounds, including an
TABLE III
Aqueous Solutions of Xanthates with Amines Yield Thioncarbamates

<table>
<thead>
<tr>
<th>Thioncarbamates</th>
<th>Concentration of xanthate reactant, %</th>
<th>Amine/xanthate mole ratio</th>
<th>Reaction time, days</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-Ethyl ethylthioncarbamate</td>
<td>50</td>
<td>1.4</td>
<td>2</td>
<td>28.6</td>
</tr>
<tr>
<td>O-Butyl ethylthioncarbamate</td>
<td>40</td>
<td>2.0</td>
<td>4</td>
<td>59.0</td>
</tr>
<tr>
<td>O-Ethyl diethylthioncarbamate</td>
<td>10</td>
<td>2.0</td>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>O-Ethyl diethylthioncarbamate</td>
<td>40</td>
<td>2.0</td>
<td>4</td>
<td>4.0</td>
</tr>
<tr>
<td>O-Ethyl diethylthioncarbamate</td>
<td>50</td>
<td>2.7</td>
<td>2</td>
<td>70.3</td>
</tr>
<tr>
<td>O-Starch ethylthioncarbamate (DS 0.025)*</td>
<td>10</td>
<td>2.0</td>
<td>4</td>
<td>5.0</td>
</tr>
<tr>
<td>O-Starch ethylthioncarbamate (DS 0.06)*</td>
<td>10</td>
<td>10.0</td>
<td>4</td>
<td>12.0</td>
</tr>
<tr>
<td>O-Starch diethylthioncarbamate (DS &lt;0.0005)*</td>
<td>10</td>
<td>2.0</td>
<td>4</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>O-Starch dimethylthioncarbamate (DS 0.036)*</td>
<td>10</td>
<td>2.9</td>
<td>4</td>
<td>7.2</td>
</tr>
</tbody>
</table>

* Prepared from DS 0.5 starch xanthate to give thioncarbamate DS shown in parentheses.

Fig. 5. Ultraviolet absorption spectra of PEI thiourea and N,N'-diethylthiourea (V): (1) PEI thiourea in H2O, pH 7; (2) solution of curve 1 at pH 1.5; (3) PEI thiourea in 95% ethanol; (4) N,N'-diethylthiourea in H2O, no pH adjustment; (5) V in 95% ethanol.

Interpolymeric thioncarbamate of starch and PEI (O-starch PEI thioncarbamate), were prepared by reacting amines with either dithiobis(thiocolformates) (xanthides of corresponding xanthates) or methyl esters of xanthates. The convention chosen for naming thioncarbamate reaction products derived from the various polymers, from several considered, although inadequately defines the polymeric structures precisely, does sim-
plify and provide nomenclature in parallel with that of model thioncarbamates.

Yields are listed in Table III of thioncarbamates from aged solutions of xanthates (EtX, BuX, and SX of DS 0.5) with nonpolymeric amines at various amine:xanthate ratios and at pH 12. Thioncarbamates of non-polymers were extracted as oils and purified by thin-layer chromatography (TLC) in yields up to 70%. The O-starch thioncarbamates from DS 0.5 SX with ethylamine and diethylamine were precipitated in ethanol in yields of only 5 to 12% based on thioncarbamate DS of 0.025-0.06. Diethylamine with either SX or EtX gave low to negligible yields of thioncarbamates. Probably, thioncarbamates of the xanthate-amine mixtures are products principally from xanthate groups, rather than from xanthide that may form by air oxidation, as control solutions of EtX and BuX gave only 0.1-0.2% of the corresponding xanthides.

Aqueous solutions of PEI with either EtX or BuX, aged several days, appeared to yield both thiourea and thioncarbamate groups. Consequently, to determine ultraviolet absorption of pure PEI thioncarbamates, PEI was allowed to react with the methyl esters of EtX and SX to obtain (1) O-ethyl PEI thioncarbamate (XII), which had 0.6 thioncarbamate group/PEI repeating unit and (2) O-starch PEI thioncarbamate, DS 0.18 (XIII). The ultraviolet spectra and extinction coefficients of several thioncarbamates (VI-XIII) from both polymers and nonpolymers are given in Table IV. O-Starch ethylthioncarbamate, DS 0.15 (X), and O-starch diethylthioncarbamate, DS 0.11 (XI), were prepared from starch xanthide of DS 0.25. O-Ethyl PEI thioncarbamate (XII) had considerable solubility in both ethanol and water, exhibiting absorptions at 243 nm in H₂O and 245 nm in ethanol. Partially soluble O-starch PEI thioncarbamate, DS 0.18 (XIII), exhibited a maximum at 243-244 nm. These absorptions correspond to those of X in water at 243 nm and O-ethyl ethylthioncarbamate (VI) in ethanol at 245 nm as compared to the corresponding diethylthioncarba-

<table>
<thead>
<tr>
<th>Thioncarbamate</th>
<th>Solvent</th>
<th>λ Absorption, nm</th>
<th>Extinction coefficient (ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-Ethyl ethylthioncarbamate</td>
<td>EtOH</td>
<td>245</td>
<td>11,400</td>
</tr>
<tr>
<td>O-Butyl ethylthioncarbamate</td>
<td>EtOH</td>
<td>245</td>
<td>10,600</td>
</tr>
<tr>
<td>O-Starch ethylthioncarbamate (DS 0.15)</td>
<td>H₂O</td>
<td>243</td>
<td>11,300</td>
</tr>
<tr>
<td>O-Ethyl diethylthioncarbamate</td>
<td>EtOH</td>
<td>245</td>
<td>11,000</td>
</tr>
<tr>
<td>O-Butyl diethylthioncarbamate</td>
<td>EtOH</td>
<td>245</td>
<td>11,200</td>
</tr>
<tr>
<td>O-Starch diethylthioncarbamate (DS 0.11)</td>
<td>H₂O</td>
<td>249</td>
<td>11,500</td>
</tr>
<tr>
<td>O-Ethyl PEI-thioncarbamate</td>
<td>H₂O</td>
<td>243</td>
<td>12,000</td>
</tr>
<tr>
<td>O-Starch PEI-thioncarbamate (DS 0.18)</td>
<td>EtOH</td>
<td>245</td>
<td>12,000</td>
</tr>
</tbody>
</table>

* 0.6 thioncarbamate group/PEI repeating unit.
* Limited solubility.
mames (XI and VIII) at 249 nm (water) and 251 nm (ethanol). Possibly these ultraviolet data indicate that PEI primary groups as opposed to secondary amine groups were preferentially derivatized.

Although the xanthate–amine model systems strongly suggested that SX–PEI alkaline solutions would yield O-starch PEI thionecarbatate, the reaction is so slow that xanthate was preferentially consumed in formation of PEI dithiocarbamic acid salt.

Infrared Spectroscopy

The thiram, thioureas, and thionecarbamates exhibited strong infrared absorptions between 6.3 and 6.6 μm, which are attributed to C—N stretching vibrations of thiourea, \( \text{NC-S} \) and \( \text{NH-C=S} \). Spectra of selected derivatives, which demonstrate C—N absorptions in the 6.3–6.6 μm region, are shown in Figures 6 and 7. Even with low DS, O-starch thio-

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Fig. 6. Infrared absorption spectra of model compounds: (1) \( N,N' \)-diethylyiourea (V), KBr disk; (2) \( N,N' \)-diethylythiuram disulfide (III), KBr disk; (3) \( O \)-ethyl ethylthionecarbatate (VI), film on Irtran disk; (4) \( O \)-ethyl diethylthionecarbatate (VIII), film on Irtran disk.
Fig. 7. Infrared absorption spectra of polymeric products: (1) PEI thiourea, film on
Irtran disk; (2) PEI, film on Irtran disk; (3) unmodified pearl corn starch (subrate
for xanthation), KBr disk; (4) ethanol precipitate from SX (DS 0.5)-PEI 6 solution aged 6 days, KBr disk; (5) O-starch PEI thionocarbamate, DS 0.18 (XIII), KBr disk;
(6) O-starch ethylthionocarbamate, DS 0.15 (X), KBr disk.

nearbamates, X (Fig. 7, curve 6) and XI (not shown), characteristic C—N
absorptions are readily identified at 6.45 μ and 6.55 μ, respectively. The
C—N absorption of O-starch PEI thionocarbamate, DS 0.18 (XIII), is
centered at 6.6 μ. The C—N absorption of the PEI thiourea, although
centered at 6.3 μ, is quite broad extending into the 6.0 μ region. Infrared
analyses alone were inconclusive for characterizing SX-PEI products (e.g.,
Fig. 6, curve 4).

Weak SX-PEI absorptions at 6.3–6.6 μ were poorly defined because of
several interfering absorptions. These include absorptions on the high
frequency side of 6.1 μ (moisture) and 6.2 μ (NH₂) and absorption on the low
frequency side of 6.8 μ (CH₂).

EXPERIMENTAL

General

Adjustments of pH were made with either HCl, acetic acid, or NaOH.
These with acetic acid are noted in the following sections. Ultraviolet
spectra were recorded with a Perkin-Elmer Model 202 spectrometer. In-
farred spectra were determined with a Perkin-Elmer Model 137 spectrometer from films cast on either I rtran disks, AgCl plates, or KBr disks (see Figs. 6 and 7). Melting points were obtained with a Fisher-Johns apparatus. The method was used for component separations of nonpolymeric models on glass plates filmed with Silica Gel G. Hexane–ethyl acetate (4:1, v/v) was the eluent. Rhodamine 6-G fluorescent spray was used to detect the components. Carbon, hydrogen, and nitrogen of nonpolymeric derivatives were determined with a Perkin-Elmer 240 elemental analyzer. Nitrogen of polymeric derivatives was determined by the Kjeldahl method. Sulfur was determined by the method of White.13

Sodium Salts of Xanthates

Commercial pearl corn starch was converted to SX (DS 0.25 and 0.5) in a Model 50 Ko-Kneader,14 diluted to 10% solids, and stored at 1°C. EtX and BuX were prepared essentially by the method of Ingram and Toms.15 EtX and BuX were dissolved in acetone and recrystallized in ether before use.

Xanthides

Aqueous solutions of SX (0.1% concentration, pH 12) with NaNO2 (2 moles/mole xanthate) were rapidly stirred while pH was slowly lowered to 4-1.5 with glacial acetic acid to obtain starch xanthides as bulky precipitates. The xanthides were filtered and then washed with water (pH 2), 95% ethanol, absolute ethanol, hexane, and ether in that order. The degree of substitution (DS) of each starch xanthide is based on one-half xanthide group hydroxyl group of starch and was about 90%. The degree of substitution of the original SX. Yields were about 95%, starch basis.

EtX and BuX at 10% aqueous concentration were oxidized with NaNO2 as described for SX. These liquid xanthides were extracted with ether, washed with water, and vacuum dried (50°C). Yields were about 80%. The xanthides exhibited strong, broad double-peak infrared absorptions at 7.9 and 9.7 μ for the nonpolymeric xanthides and at 8.1 and 9.7 μ for starch xanthides.

Methyl Esters of Xanthates

SX of DS 0.2, at 5% concentration in water-DMSO (1:1, v/v), and CH3I (2 moles/mole xanthate) were allowed to mix 1 hr. Ultraviolet analyses of the mixture after 1 hr showed only xanthate ester absorption (maximum at 280 nm). The product was precipitated in MeOH and washed with EtOH, hexane, and ether. On the basis of ultraviolet analysis, DS was approximately 0.2; yield, 90%, starch basis: λmax 8.3, 9.4 μ (xanthate ester).

A 20% ether solution of EtX with CH3I (1.5 moles/mole xanthate) was stirred overnight. CH3SH, a reaction product, and excess CH3I were removed by vacuum (40°C) to leave the methyl ester of EtX, which was volatile and fumed when exposed to air. Estimated yield, 75%; λmax 277 nm; λmax 8.20 and 9.45 μ (xanthate ester). Slight carbonyl (C=O) absorption at 5.7–5.9 μ indicated some oxidation of C=S to C=O.
PEI

PEI 6 (98% solids, molecular weight 600) and PEI 600 (33% solids, molecular weight 40,000 to 60,000) were supplied by Dow Chemical Company, Midland, Michigan. Infrared spectra have been reported.4

SX–PEI Products

SX–PEI alkaline solutions, prepared as described above, were aged in screw-capped vials and periodically mixed by inverting the vials. The SX–PEI solutions were stirred into EtOH to give precipitates which were filtered and washed successively with water, ethanol, hexane, and ether. Volatiles were determined on ether-dried samples simultaneously with chemical analyses.

CS Determinations

SX–PEI solutions and precipitates (and SX controls) were treated at pH 1.5 for 4–16 hr at 30–50°C in a closed system swept with nitrogen. The liberated CS2 was trapped in a chilled solution of diethylamine (0.4% in EtOH) having 100 amine groups/original xanthate group.

Salts of Dithiocarbamic Acids

N-Ethylammonium Salt of N-Ethylthiocarbamic Acid (I). A solution of 70% aqueous ethylamine with CS2 (2 mole/mole of amine), when slowly mixed and maintained at 25–30°C for 15 min, gave a light yellow solid on immersing the reaction flask in an ice bath. The solid was further cooled in a Dry Ice-acetone bath, filtered, and washed with cold ether to obtain a pure white solid; yield, 75%: \( \lambda_{\text{max}}^{\text{UV}} 284 \text{ (} \epsilon \text{ 11.870)} \).

Anal. Caled for C_{4}H_{11}N_{2}S_{2}: S, 38.5%. Found: S, 38.2%.

N,N-Diethylammonium Salt of N,N-Diethylthiocarbamic Acid (II). Salt II was prepared from diethylamine and CS2 as described for I. Yield, 70%; mp, 81–82°C; \( \lambda_{\text{max}}^{\text{UV}} 284 \text{ (} \epsilon \text{ 12.460)} \).

Anal. Caled for C_{8}H_{14}N_{2}S_{2}: S, 48.6%; H, 9.9%; N, 12.6%. Found: C, 48.8%; H, 10.0%; N, 12.8%; S, 28.6%.

Thiuram Disulfides

N,N’-Diethylthiuram Disulfide (III). To a 25% aqueous solution of 1 was admixed NaNO2 (2 mole mole 1) and then glacial acetic acid (pH 4) to give a water-insoluble yellow solid. The solid was extracted with ether and washed with water. Evaporation of ether by vacuum (30°C) left a yellow solid which was redissolved in ethyl acetate and recrystallized (twice) in hexane in a Dry Ice-acetone bath to facilitate crystallization. Pure white crystals resulted; yield, 80%; mp, 76.5–77°C; \( \lambda_{\text{max}}^{\text{Ht}} 6.55 \mu \).

Anal. Caled for C_{8}H_{18}N_{2}S_{2}: C, 30.0%; H, 5.0%; N, 11.7%. Found: C, 30.0%; H, 5.0%; N, 11.4%; S, 53.3%.
**N,N,N',N'-Tetraethylthiuram Disulfide (IV).** Compound IV was obtained by nitrite oxidation of II as described for preparation of III from I. Recrystallization in hexane gave pure white crystals; yield, 75%\%; mp. 70.5°C (sharp); $\lambda_{\text{max}}^\text{KBr}$ 6.62 μ, $\lambda_{\text{max}}^{\text{EtOH}}$ 220 (ε 20.615), $\lambda_{\text{max}}^{\text{EtOH}}$ 225 (ε 15.370), and $\lambda_{\text{max}}^{\text{EtOH}}$ 257 (ε 14.465).

**ANAL.** Caled for C$_{16}$H$_{24}$N$_2$S$_2$: C, 40.5%; H, 6.8%; N, 9.5%; S, 43.2%. Found: C, 40.7%; H, 7.2%; N, 9.7%; S, 42.9%.

**Thioureas**

**N,N'-Diethylthiourea (V).** To a 4% solution of thiuram disulfide (III) in ether was admixed 70% aqueous ethylamine (2 mole/mole of disulfide). After 1 hr, the mixture was washed in a separatory funnel with water, and ether was removed by vacuum (30°C) to leave a light yellow solid. The solid was recrystallized twice in hexane as described for III and IV to get pure white crystals; yield, 70%\%; mp. 77.5-78°C; $\lambda_{\text{max}}^{\text{KBr}}$ 6.32 μ (strong absorption also at 6.52 μ); $\lambda_{\text{max}}^{\text{EtOH}}$ 214 (ε 8200), $\lambda_{\text{max}}^{\text{EtOH}}$ 243 (ε 11,400), $\lambda_{\text{max}}^{\text{H}_2\text{O}}$ 213 (ε 11,800), and $\lambda_{\text{max}}^{\text{H}_2\text{O}}$ 237 (ε 11,700).

**ANAL.** Caled for C$_{12}$H$_{24}$N$_2$: C, 44.8%; H, 9.1%; N, 10.2%; S, 24.2%. Found: C, 44.7%; H, 9.3%; N, 10.1%; S, 24.2%.

**Thionocarbamates from Xanthides and Xanthate Esters**

**O-Ethyl Ethylthionocarbamate (VI).** To a solution of 20% ethyl xanthide in ether was admixed aqueous 70% ethylamine (2 mole/mole of xanthide). After 10 min, the mixture was washed with water, and the ether was removed by vacuum (30°C) to leave a dark yellow liquid. Preparative thin-layer chromatography (TLC) gave VI, a light yellow liquid and a trace carbonyl component; yield of VI, 80%\%; $\lambda_{\text{max}}^{\text{EtOH}}$ 6.5 μ; ultraviolet, see Table IV.

**ANAL.** Caled for C$_{11}$H$_{22}$NS: C, 45.1%; H, 8.3%; N, 10.5%; S, 24.1%. Found: C, 44.9%; H, 8.2%; N, 10.2%; S, 24.2%.

**O-Butyl Ethylthionocarbamate (VII).** Compound VII, a nearly colorless liquid, was prepared from butyl xanthide and ethylamine as described for VI; yield, 70%\%; $\lambda_{\text{max}}^{\text{EtOH}}$ 6.52 μ; ultraviolet see Table IV.

**ANAL.** Caled for C$_{14}$H$_{24}$NS: C, 32.1%; H, 9.3%; N, 8.7%; S, 19.9%. Found: C, 32.1%; H, 9.2%; N, 8.3%; S, 19.5%.

**O-Ethyl Diethylthionocarbamate (VIII) and O-Butyl Diethylthionocarbamate (IX).** Compounds VIII and IX were prepared by reacting ethyl and butyl xanthides with diethylamine as described for preparation of VI and VII. Preparative TLC showed that the corresponding monoethyl thionocarbamates (VI and VII) were also obtained with VIII and IX in an approximate ratio of 1:10 even with freshly refluxed, distilled diethylamine to remove any ethylamine. It showed absorptions of carbonyl components at 5.7-5.8 μ removed by tlc. Compound VIII fumed on exposure to air.
Yield of VIII (estimated), 75\%; $\lambda_{\text{max}}^{\text{UV}}$ 6.65 \(\mu\) (film between Irtran disks) ultraviolet, see Table IV; yield of IX, 65\%; $\lambda_{\text{max}}^{\text{UV}}$ 6.62 \(\mu\); ultraviolet, see Table IV.

Due to volatility of VIII, CHNS was not reliable in determining the structure of VIII. The structure of VIII was supported by NMR, infrared, and ultraviolet data.

ANAL. Caled for C\(_6\)H\(_8\)NOS (IX): C, 57.1\%; H, 10.0\%; N, 7.4\%; S, 16.9\%. Found: C, 57.4\%; H, 10.1\%; N, 7.2\%; S, 16.5\%.

**O-Starch Ethylthioncarbamate, DS 0.15 (X), and O-Diethylthioncarbamate, DS 0.11 (XI).**

To aqueous suspensions of DS 0.25 starch xanthide stirred at 15\% concentration were added (a) ethylamine and (b) diethylamine for preparation of derivatives X and XI, respectively. After 16 hr, each mixture was diluted with an equal volume of pyridine and treated with H\(_2\)S to convert any unreacted xanthide to xanthate. The decomposition of xanthide with H\(_2\)S is an extension of a previously reported method of decomposing xanthide with p-chlorothiophenol in pyridine. After the mixture had been treated with H\(_2\)S, xanthate was decomposed at pH 2. In a separatory funnel the mixtures were washed several times with chloroform, so that grayish color and elemental sulfur (acetone=Na\(_2\)S test for elemental sulfur) were removed. The products were precipitated in ethanol; centrifuged; washed successively with ethanol, hexane, and ether; and equilibrated at 73°F, 50\% R.H., to 11.5\% moisture content; yields, approximately 90\% starch basis; $\lambda_{\text{max}}^{\text{UV}}$ 6.4–6.5 \(\mu\); ultraviolet see Table IV.

ANAL. Caled for starch-OC(S)NH\(_2\)\(_2\)H of DS 0.147 based on nitrogen analysis: N, 1.18\%; S, 2.69\%. Found: N, 1.18\%; S, 2.62\%.

Caled for starch-OC(S)(NH\(_2\))\(_2\)H of DS 0.111 based on nitrogen analysis: N, 0.88\%; S, 2.01\%. Found: N, 0.88\%; S, 2.06\%.

**O-Ethyl PEI Thioncarbamate (XII).**

To a 10\% ethanol solution of EtX methyl ester was admixed PEI 6 at 98\% solids to give a mixture containing one ester group/amine group. After 16 hr, the product (soluble in either ethanol or water) was obtained by applying vacuum at 50°C until a solid remained. The solid, washed several times with ether, was hygroscopic; yield, 77\%; based on total primary and secondary groups derivatized; $\lambda_{\text{max}}^{\text{IR}}$ 6.5 \(\mu\) (broad 6.4–6.6 \(\mu\)); ultraviolet, see Table IV. Because the infrared showed appreciable carbonyl absorption at 5.8–5.9 \(\mu\), oxidation of some C=S to C=O probably accounted for the low sulfur content of XII.

ANAL. Caled for C\(_2\)H\(_4\)OC(S)N-PEI containing 0.6 thioncarbamate group/PEI repeating unit based on nitrogen analysis: N, 8.8\%; S, 20.0\%. Found: N, 8.8\%; S, 15.8\%.

**O-Starch PEI Thioncarbamate, DS 0.18 (XIII).**

To a 1\% aqueous slurry of a DS 0.2 methyl ester of SX was admixed PEI 6 to give an amine–ester ratio of 2:1. Uv monitoring of the mixture showed an absorption maximum, initially at 280 nm (xanthate ester), that gradually disappeared with concurrent formation of a new maximum at 243 nm within 1 hr. After
4 hr the partially water-soluble product (XIII) was precipitated in EtOH and washed with EtOH, hexane, and ether; yield 90% both starch basis and DS basis; λKBr 6.50 μ.

Anal. Calculated for starch-OC(S)N—PEI of DS 0.18 based on sulfur analysis and containing 1.5 unreacted amine groups/thioncarbamate group based on nitrogen analysis: N, 3.3%; S, 3.0%. Found: N, 3.3%; S, 3.0%.

Thioncarbamates from Xanthates

Reactions of EtX, BuX, and SX in aqueous solutions with ethylamine, diethylamine, and dimethylamine to yield thioncarbamates are partially described in Results and Discussion. Structures of thioncarbamates from these amines, with xanthates were characterized by comparing their infrared, ultraviolet, and chemical analyses data with thioncarbamate reference compounds (VI—XIII) that were prepared from xanthides and xanthate esters. The O-ethyl- and O-starch dimethylthioncarbamates (Table III) were prepared from xanthates only. Except for H₂S treatments, the starch thioncarbamates from SX (Table III) were acid-treated, isolated, and analyzed as described for derivatives X—XII. There was only a trace of O-starch diethylthioncarbamate from a solution of diethylamine with DS 0.5 SX aged 3 days.

The mention of firm names or trade products does not constitute an endorsement by the U.S. Department of Agriculture over other products or firm names not mentioned.

References

4. PEI—The Versatile Polymer, Dow Chemical Co., Designed Products, Department of Research and Development, Midland Michigan, 1965.

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