

Cross-linked Polystyrene-Dithiocarbamate Polymers: Use in Heavy Metal Removal

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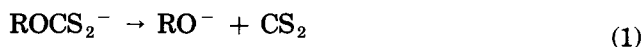
Synopsis

Cross-linked polystyrene polymers were converted to dithiocarbamate polymers. These polymers were used to remove heavy metal cations from water. Dithiocarbamate polymers can be understood to be inherently more stable toward hydrolysis than xanthate polymers.

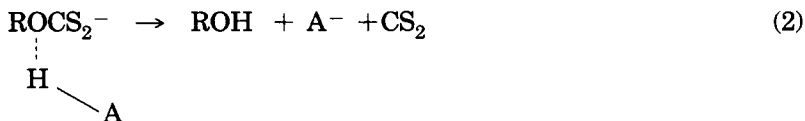
INTRODUCTION

Soluble and insoluble starch xanthates have been used for the removal of heavy metal cations from aqueous solution.¹⁻⁴ These products have been plagued by the instability of the resins themselves and efforts to increase shelf life of these resins by reducing their moisture content or changing the counterion from sodium to magnesium or adjusting the pH have been only partially successful.³

On the basis of our work on the breakdown in water of xanthates of simple alcohols of varying pK_a s, we believe that xanthates are inherently unstable in water solution and probably should not be used in commercial processes for heavy metal removal.^{5,6} This instability stems from the fact that xanthates can decompose by two pathways, shown in eqs. (1) and (2):



Uncatalyzed decomposition



Concerted general acid-catalyzed decomposition

The process summarized by eq. (1) is not dependent on acid catalysis and will occur at all pH values. The process summarized by eq. (2) will be enhanced by the presence of all general acids, but it is quite sensitive to the acidity of these acids and thus it can be minimized by adjustment of pHs to higher values. These ideas are illustrated by the data in Figure 1.

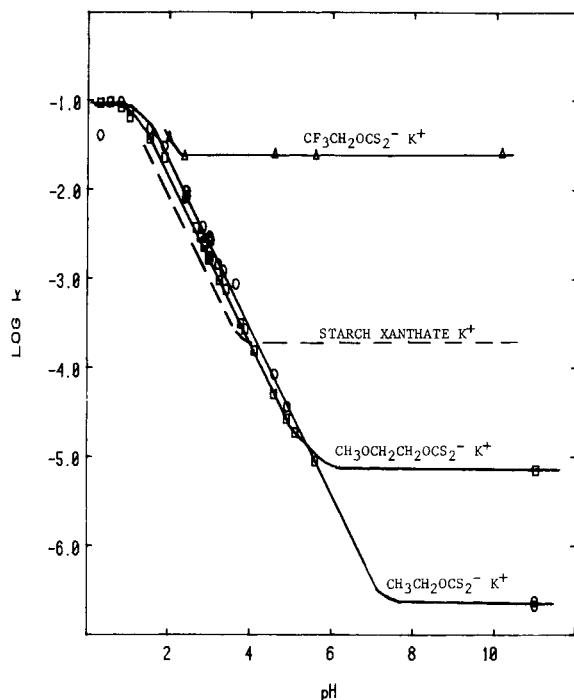
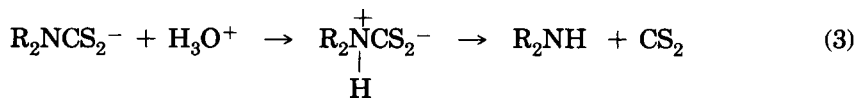


Fig. 1. pH-rate profiles of xanthates and probable profile for xanthates of ring hydroxyl positions for starch. Circles: Ethyl xanthate; squares: methoxyethyl xanthate; triangles, trifluoroethyl xanthate. Conditions 25° C. $\mu = 1.00$ (RCl).

A xanthate formed at the position 6 hydroxyl in starch or cellulose polymers would break down at a rate approximately that for methoxyethyl xanthate. The rate of breakdown of the xanthate formed from the more acidic ring hydroxyl positions can be estimated to occur at the rate indicated by the dashed line in Figure 1.^{5,6}

Since dithiocarbamates are known to break down via a stepwise specific acid-catalyzed mechanism [see eq. (3)] and an uncatalyzed breakdown analogous to eq. (1) is unknown because of the great instability of R_2N^- , polymers based on these resins should possess inherently greater stability to hydrolytic breakdown.



EXPERIMENTAL

Breakdown of Xanthates and Dithiocarbamates in the Presence of Zinc Cation

Kinetic experiments were performed using techniques previously described⁵ except that KCl-HCl solutions at various pHs also contained zinc II acetate. The results are shown in comparison to decomposition rates

in the absence of zinc for two xanthates in Figure 2. The results for the dithiocarbamates studied, are plotted in Figure 3 for benzyl dithiocarbamate and trifluoroethyl dithiocarbamate and in Figure 4 for *N-n*-propylbenzyl dithiocarbamate.

Synthesis

Chloromethylated polystyrene cross-linked by 2% divinylbenzene was heated with 30 mL benzyl amine until a smooth slurry formed and was allowed to stir overnight; then the swollen polymer was isolated by filtration. To 2 g of this polymer was added 20 mL 1,4-dioxane followed rapidly by 1.0 *N* potassium hydroxide in water until the pH of the mixture reached 11. Then carbon disulfide (10 mL) was added and the resulting three-phase mixture was stirred overnight. The polymer was isolated by filtration and was washed with water. In the analysis, the calculated value was 5.48% S, and the value found was 5.72% S. The reaction was run on a larger scale starting with 25 g chloromethylated polystyrene (2% cross-linked). The product of this and the benzylamine was added to 250 mL dioxane followed quickly by sufficient 1.0 *N* potassium hydroxide and 125 mL carbon disulfide; analysis: calculated, 5.48% S, found, 11.98% S. The analysis was repeated 3 months later and 10.92% S was found after drying. This polymer (10 g) was stirred overnight with 100 mL toluene and reisolated and dried. Microanalyses: calculated 5.48% S, found, 9.43% S; calculated, 1.19% N,

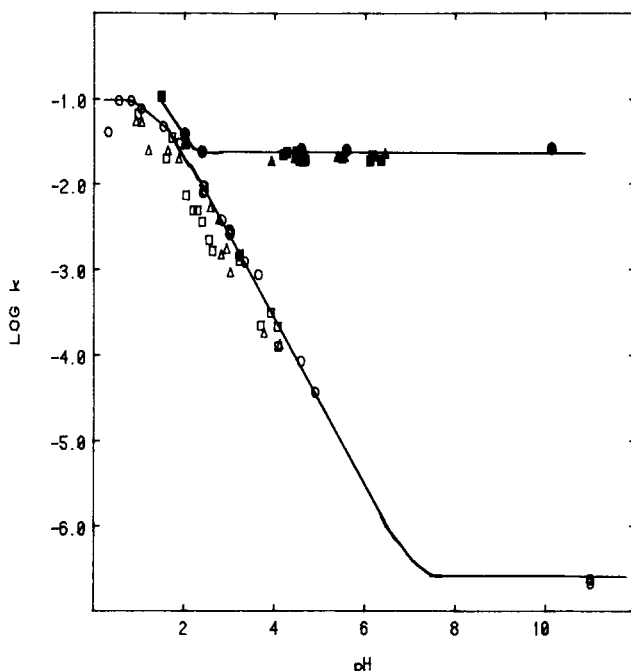


Fig. 2. pH-rate profile for ethyl xanthate; Circles, no added $\text{Zn}(\text{OAc})_2$; squares, 0.1 *M* $\text{Zn}(\text{OAc})_2$; triangles, 0.01 *M* $\text{Zn}(\text{OAc})_2$. pH-rate profile for trifluoroethyl xanthate; closed circles, no added $\text{Zn}(\text{OAc})_2$; closed squares, 0.1 *M* $\text{Zn}(\text{OAc})_2$; closed triangles, 0.01 *M* $\text{Zn}(\text{OAc})_2$.

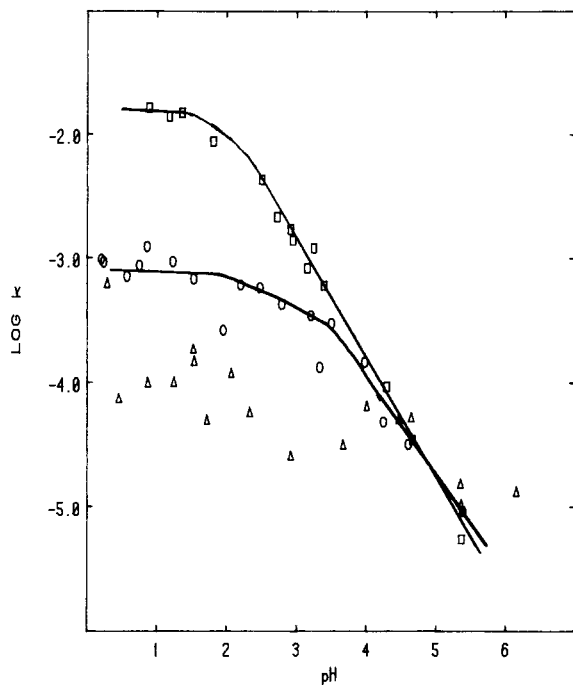


Fig. 3. pH-rate profile for benzyl dithiocarbamate; Circles, no added $\text{Zn}(\text{OAc})_2$; triangles, 0.1 M $\text{Zn}(\text{OAc})_2$. pH-rate profile for trifluoroethyl dithiocarbamate; squares, no added $\text{Zn}(\text{OAc})_2$.

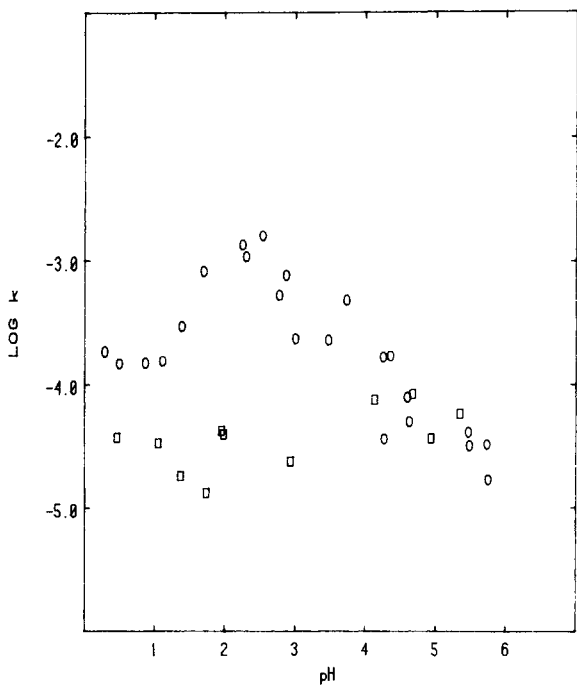


Fig. 4. pH-rate profile for *N-n*-propylbenzyl dithiocarbamate; circles, no added $\text{Zn}(\text{OAc})_2$; squares, 0.1 M $\text{Zn}(\text{OAc})_2$.

found, 4.81% N. If all the sulfur is present as dithiocarbamate, then an excess of moles of nitrogen is present. The polymer removed stoichiometric amounts of zinc based on the sulfur analysis from dilute aqueous solutions of zinc nitrate at neutral pHs.

Atomic absorption analyses for Pb^{++} , Hg^{++} , and Cd^{++} were run using a graphite furnace.

Each of three 40-mL solutions of lead II, mercury II, or cadmium II nitrates was treated with 2 g of the above polymer (11.98% S) and stirred for 1 h. After filtering the solutions were analyzed at Cook College, Rutgers University, by atomic absorption spectroscopy. The results were as shown in Table I. Further atomic absorption and plasma emission analyses were run on solutions treated by the polymer (9.43% S) after aging.

The polymer was washed with water and then filtered under vacuum before weighing. Samples (150 mg) were shaken with 50 mL of a solution of metal salts for 30 min on a Burrell wrist-action shaker. The mixtures were filtered through glass fiber filter paper, and the solutions were then analyzed (Table II).

Proton-Induced X-Ray Emission Spectroscopy

Trace element analysis of the samples was performed by external beam proton-induced x-ray emission analysis (PIXE).

Nanopure water (100 mL) was added to a 250-mL borosilicate bottle. Subsequently the bottles were spiked with 10 elements so that the final concentration was 1 ppm. Polymer resin (50-60 mg) was added to each bottle, and the samples were shaken for 30 min on a mechanical shaker. Subsequently, the samples were vacuum filtered through a 0.45 μm Nuclepore membrane filter, and the collected polymer was dried in air. The filter was then mounted on a 35-mm cardboard slide frame and irradiated with 3.8 MeV protons from the Rutgers Nuclear Physics tandem van de Graaff accelerator for 6 min. The x-ray spectrum of polymer (9.43% S) after treatment with the metal ion solutions is shown in Figure 5. A list of the quantitative recovery of the elements is shown in Table III. The polymer retains the elements beyond and including zinc. Total analysis time for the sample including preparation was 35 min. The method is quick, and detection limits for a 100-mL sample are about 1 ppb. The water is preconcentrated by a factor of 2000.

RESULTS AND DISCUSSION

The results for the breakdown of the two xanthates studied in the presence and absence of zinc cation (see Fig. 2) show that the presence of the transition metal does not add much stability to the xanthate system. This result

TABLE I
Atomic Absorption Analyses of Water Treated with Polymer (11.98% S)

Heavy metal cation	Conc $\mu\text{g/L}$ (ppb)	
	Before	After
Pb^{++}	110	<0.5
Hg^{++}	2600	400
Cd^{++}	690	0.35

TABLE II
Atomic Absorption and Plasma Emission Analyses of Water Treated
with Polymer (9.43% S)

Heavy metal cation h	pH	Concentration $\mu\text{g/L}$ (ppb)	
		Before	After
Zn ⁺⁺	5,950	1000	30, 10, 20
Cu ⁺⁺	5,950	1001	20, 10, 10, 0
Pb ⁺⁺	6.0	686	<20.0 ^a
Cd ⁺⁺	6.0	1120	<5.00 ^a
Cu ⁺⁺	6.0	885	<2.00 ^a
Ni ⁺⁺	6.0	1070	<2.00 ^a
Zn ⁺⁺	6.0	1160	<6.00 ^a

^a These analyses were run on the plasma emission spectroscopy unit at EPA laboratories in Edison, New Jersey, by analyst Bruce Wagner.

is independent of the mechanism of xanthate breakdown. For example, the breakdown of ethyl xanthate goes primarily by the acid-catalyzed mechanism shown in eq. (2), whereas trifluoroethyl xanthate breakdown proceeds almost exclusively through the uncatalyzed reaction pathway [eq. (1)] in the pH region 2–10.

Both benzyldithiocarbamate and benzyl *N-n*-propyldithiocarbamate are stabilized in the presence of zinc cation (see Figs. 3 and 4). Because the reactions are very slow, the breakdown rate for benzyldithiocarbamate was

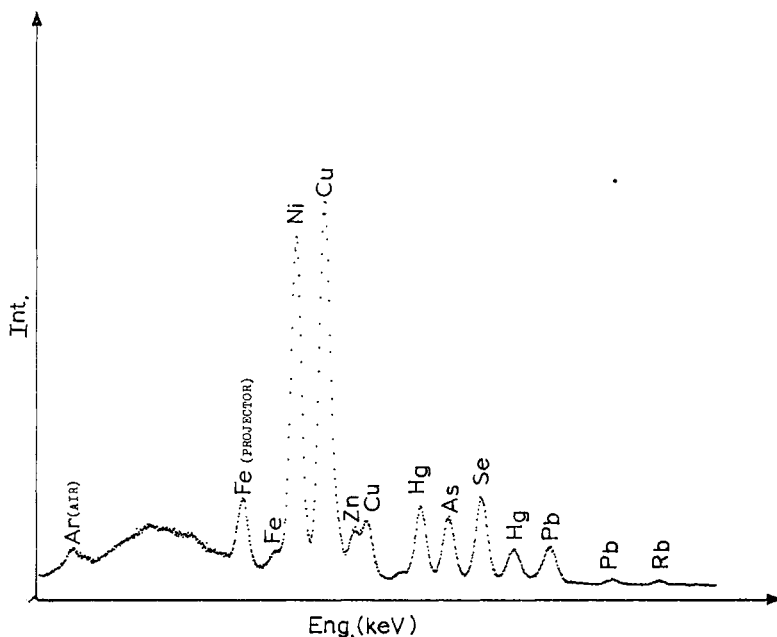


Fig. 5. Dithiocarbamate polymer; S, 9.43%; N, 4.81%, treated with nanopure water spiked with 1 $\mu\text{g/ml}$ (ppm) of K⁺, Cd⁺⁺, Ca⁺⁺, Mn⁺⁺, Fe⁺⁺⁺, Zn⁺⁺, Cu⁺⁺, Ni⁺⁺, Ag⁺, Cr⁺⁺⁺, Se, Pb⁺⁺, Hg⁺⁺, Rb⁺. Control experiments treated the polymer with nanopure water and showed a natural background of the Fe⁺⁺⁺ and Zn⁺⁺, which has been taken into account for the tabulated data in Table I.

TABLE III
Element Recovery Measure by PIXE^a

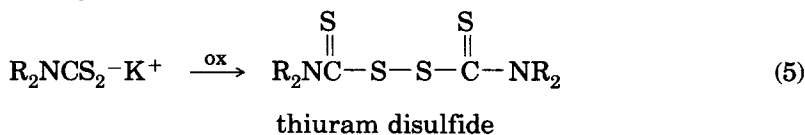
Element	Amount added (ppm)	Amount recovered (ppm)
K	1	ND
Ca	1	ND
Mn	1	ND
Fe	1	ND
Zn	1	0.97
Cu	1	0.98
Ni	1	0.95
As	1	0.94
Cr	1	ND
Se	1	0.96
Pb	1	0.95
Hg	1	0.95
Cd	1	0.92
Rb	1	0.94

^a ND = none detected; below the detection limit of PIXE. Note: Estimated error = $\pm 10\%$. Data expressed in Figure 5.

not measured at sufficiently high pH that the dithiocarbamic acid was completely deprotonated. A good value for k_H from the rate equation (3) for the specific acid-catalyzed breakdown reaction could not be measured. The rate equation is

$$k_{\text{obs}} = k_H [\text{H}^+] \quad (4)$$

for the mechanism shown in eq. (3). Given this result, it is unlikely that the rate measured earlier for *N-n*-butyldithiocarbamate at pH 4.58 can be used to calculate k_H . The value for k_H is probably higher than the $0.35 \text{ M}^{-1} \text{ s}^{-1}$ reported.⁷ If this is true, the sharp dependence of k_H on the $\text{p}K_a$ of primary amines used to form the dithiocarbamates is somewhat less than the -0.6 value for β_{1g} than can be calculated from the original data for *N-n*-butyldithiocarbamate and trifluoroethyldithiocarbamate.⁷ This would bring the behavior of these compounds more in line with the aromatic dithiocarbamates and cyclic secondary amine dithiocarbamates.⁷⁻⁹ That these polymers exhibit higher S and N analyses than theory (based on the original Merrifield polymer analyses for Cl) indicates that these polymers may contain benzyldithiocarbamates in the polymer cavity, and since the molar ratio of sulfur to nitrogen is less than 2:1, the polymer cavities may also contain benzylamine. The polymers can be washed repeatedly with water or toluene without losing their ability to sequester Zn^{++} cation. Treatment with acetone water followed by water washing renders them ineffective. This may be the source of the polymer's stability. The dithiocarbamate groups are protected from acid-catalyzed breakdown and from air oxidation to thiuram disulfides, as illustrated in eq. (5)¹⁰ and from breakdown to isothiocyanates.¹¹



Seven methods for the preconcentration of trace elements in water have been evaluated, and it was determined the dibenzylidithiocarbamate was the most useful.¹² The methods included the use of dithiocarbamate groups immobilized on pore glass.¹³

Cellulose piperazinedithiocarbamate has been synthesized for use as a preconcentrating agent, but the procedure cites storing the resulting polymer under ammonia gas.¹⁴ Leyden and Wegscheider have discussed other preconcentration methods for trace element determination.¹⁵

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