Water–Formaldehyde–Hydrogen Sulfide System.
II. Formation and Growth of Thiomethylenic Chains.

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Synopsis

A linear polymer with a high melting point is obtained from the water–formaldehyde–hydrogen sulfide system in the presence of sulfuric acid. This polymer is substantially formed by a polythiomethylene chain with a few oxymethylene units. Its formation involves a topochemical reaction of the mercaptomethanol present in solution on the first separation solid of the system. On heating, the polymer loses oxymethylene units; in the same way, the first solid product separated from the system loses formaldehyde and undergoes a morphological and chemical transformation to polythiomethylene.

INTRODUCTION

Few studies have been reported of the preparation of polythiomethylene $+CH_2S+_n$ (PTM) (I), a linear homopolymer of thioformaldehyde.

Generally two kinds of preparation have been used. The first one involves condensation of methane-dithiol with basic catalysts[1] or polycondensation of α,α'-dichloromethylsulfide[2] or methylene chloride with sodium sulfide or hydrosulfide[3,4] The second one involves cationic polyaddition of cyclic oligomers of thioformaldehyde: 1,3,5-trithiane,[5] 1,3,5,7-tetrathiocane,[6] and 1,3,5,7,9-pentathiocyclodecane.[7]

Generally, PTM obtained by all these methods is insoluble below 190°C. in the usual organic solvents and also in solvents for polyoxymethylene; it shows a high melting range (220–260°C.) and a hexagonal crystalline structure.[8] The only exception is the polymer obtained by polycondensation of alkaline sulfides or hydrosulfides with methylene chloride.[4]

Kohono[9] showed that it is possible to obtain poly(methylene sulfides) of the general formula $(CH_2S_x)_n$ (in which $x = 1-4$) when aqueous formaldehyde solutions react with alkaline sulfides and hydrosulfides.

On the contrary, no methods of preparation of PTM from aqueous formaldehyde solutions in the presence of hydrogen sulfide in acid media are available. In this note we describe the preparation of PTM of high melting point from the $H_2O–CH_2O–H_2S$ system in the presence of sulfuric acid.

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EXPERIMENTAL

Preparation

The reactions were carried out in a thermostatted bath at 20°C. in a three-necked reaction flask provided with a stirrer. Table I reports some typical experiments. The reaction vessel was filled with 1500 g. of an aqueous formaldehyde and sulfuric acid solution with the following composition: CH_2O, 28 wt.-%; H_2SO_4, 4.35 wt.-%. Hydrogen sulfide was bubbled in with stirring from a side arm. After about 30 hr.* the precipitation of a solid product begins. A sample of this first precipitate drawn from the vessel, washed with water, and dried at 55°C. under vacuum, shows a melting range of 90–110°C. and a sulfur content of 49.7 wt.-%. Successive samples with drawn after 150 and 190 hr. show melting ranges of 110–130 and 220–250°C. and sulfur contents of 51.09 and 53.8 wt.-%, respectively. After 190 hr. the reaction was stopped, the solid filtered, washed well with water, and dried at 55°C. under vacuum; 250 g. of solid product was recovered. X-ray analysis showed the presence in the sample of S-trithiane, which was removed in a Soxhlet apparatus with hot benzene. The remaining polymer, 162 g. shows a melting range of 220–255°C., and a sulfur content of 56.5 wt.-%. The soluble product consists primarily of trithiane and low molecular weight polymer.

Annealing

The samples were annealed at 210°C. under vacuum at constant weight. After this treatment the sulfur content rises to values of more than 66 wt.-% [theoretical for $(CH_2S)_n$: 69.5 wt.-%].

RESULTS AND DISCUSSION

It is known[10] that a strong acid media promotes the formation of the cyclic trimer of thioformaldehyde, S-trithiane (II). Kinetic data[10] indicate that the rate of formation of S-trithiane is relatively low and drops with increase of formaldehyde concentration in solution and with decrease of sulfuric acid concentration.

In a previous work[11] we pointed out that aqueous formaldehyde solutions, at their standard pH of 2.5–3.5, absorb hydrogen sulfide proportionally to the amount of formaldehyde present in solution. When the ratio CH_2O-H_2S = 2 is reached, a white solid (III), substantially 1-hydroxy-2-oxa-4,6-dithioheptane-7-thiol (IV) melting 80–82°C., separates

$$HO—CH_2—O—CH_2—S—CH_2—S—CH_2—SH$$
$$IV$$
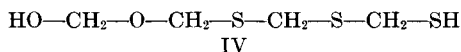
We have ascertained that also at low sulfuric acid concentration a solid (III) substantially formed by IV separates first.

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* This period depends on the composition of solution, stirring and rate of bubbling of hydrogen sulfide.

TABLE I

Starting Conditions and Reaction Products for Experiments on the H_2O–CH_2O–H_2S System; Reaction Temperature 20°C.

Expt. no.	Initial CH_2O concn. in solution, wt.-%	Initial H_2SO_4 concn. in solution, wt.-%	Reaction products	Polymer (V) in the reaction product, %	Characteristics of the obtained products[a]		
					Melting range, °C.	wt.-%	Solubility in hot benzene
1	34.4	0	III	0	97–106	51.3	Soluble
2	34.4	4.16	V	100	220–255	56.4	Insoluble
3	28.0	4.35	II–V	65	220–255	56.5	Insoluble
4	28.0	12.0	II–V	56	230–250	59.9	Insoluble

[a] After separation of trithiane when present (see experimental).

TABLE II
Increase of Sulfur Content and Melting Range at Different Heating Temperatures
of the Product (IV) Obtained in Experiment 1; Heating Time 6 hr.

Heating temperature, °C.	Yield, wt.-%	Characteristics of the polymer recovered	
		Melting range, °C.	S, wt.-%
110	90.0	110–122	56.1
150	85.2	167–187	59.1
180	74.4	213–223	63.5
210	55.0	227–235	67.7

Together with this linear cooligomer, a simultaneous formation of tri-thiane takes place, in an amount proportional to the acid concentration.

After a longer time of reaction and with the solution saturated with hydrogen sulfide, III undergoes a substantial chemical, physical, and structural modification.   The sulfur content rises to values more than 56 wt.-% and the melting range to 200–255°C.   On x-ray analysis this new compound (V) shows a powder spectrum with diffraction peaks corresponding to the interplanar spacings described in the literature[1,2] for hexagonal PTM.[8]

It seems clear that sulfuric acid is a catalyst either for the addition of thiomethylene groups on the first solid of separation (IV) and for the formation of trithiane.

Although cyclization and addition reactions are competitive, the first one may be reduced to very low values or eliminated, increasing the initial CH_2O/H_2SO_4 ratio in the solution.   With a molar ratio of 26.6 we obtained exclusively V.   Nevertheless, sulfuric acid must be present in sufficient quantity to catalyze the addition reaction, while the formaldehyde concentration must be lower than the stability limit[12] of the $CH_2O–H_2O–H_2SO_4$ system to avoid the spontaneous separation of polyoxymethylene.

In Table I the characteristics of the products obtained in some experiments at different starting conditions are reported.

The sulfur content of polymer V obtained in water solution is below the theoretical one for $+CH_2S\frac{}{}_n$ (69.56%), owing to the topochemical attack of thiomethylene groups on compound (IV) containing —CH_2—O— units.
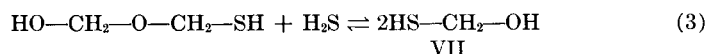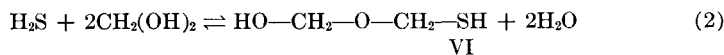
Moreover on annealing of V at a temperature of few degrees below the melting range, it undergoes a limited weight loss, as result of which the sulfur content reaches a value of more than 66 wt.-% and the melting range narrows to 240–255°C.   It seems that the thermal degradation involves the oxymethylene units.   A similar degradtion involving oxymethylene units is observed with product IV, which by a melting process under vacuum, turns to hexagonal PTM, as confirmed by x-ray analysis.   As result of this transformation the melting range and the sulfur content increase proportionally to the heating temperature, as reported in Table II.

In this case, during the melting, together with the degradation of the oxymethylene endgroups, condensation between the oligothiomethylenic residues takes place with formation of polythiomethylene [eq. (1)].
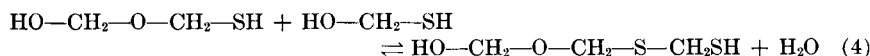
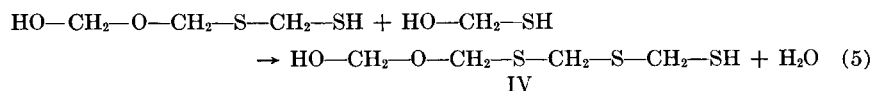$$n\mathrm{HS(CH_2S)_2(CH_2O)_2H} \xrightarrow{\text{Heat}} 2n\mathrm{CH_2O} + (n-1)\mathrm{H_2S} + \mathrm{HS(CH_2S)_{2n}H} \qquad (1)$$
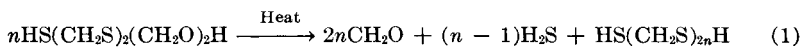
CONCLUSIONS

The experimental data confirm that in the CH_2O–H_2O–H_2S system, in presence of a small amount of sulfuric acid, the absorption of hydrogen sulfide proceeds by a mechanism similar to that reported in absence of the acid catalyst[11]
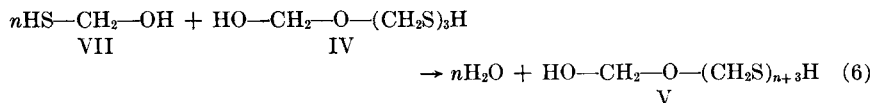
$$H_2S + 2CH_2(OH)_2 \rightleftharpoons \underset{VI}{HO—CH_2—O—CH_2—SH} + 2H_2O \qquad (2)$$

$$HO—CH_2—O—CH_2—SH + H_2S \rightleftharpoons \underset{VII}{2HS—CH_2—OH} \qquad (3)$$

Intermediate VII reacts immediately with VI

$$HO—CH_2—O—CH_2—SH + HO—CH_2—SH$$
$$\rightleftharpoons HO—CH_2—O—CH_2—S—CH_2SH + H_2O \quad (4)$$

and successively the reaction (5) takes place

$$HO—CH_2—O—CH_2—S—CH_2—SH + HO—CH_2—SH$$
$$\rightarrow \underset{IV}{HO—CH_2—O—CH_2—S—CH_2—S—CH_2—SH} + H_2O \quad (5)$$

with formation of IV, the first solid product of the system. The further transformation of IV to V, which takes place in the presence of sulfuric acid, must proceed by a tropochemical addition reaction of a substantially thiomethylenic active species. Therefore the reaction between VII and IV taking place follows eq. (6).

$$n\underset{VII}{HS—CH_2—OH} + \underset{IV}{HO—CH_2—O—(CH_2S)_3H}$$
$$\rightarrow nH_2O + \underset{V}{HO—CH_2—O—(CH_2S)_{n+3}H} \quad (6)$$

From the composition data reported in Table I it appears that $(n + 3)$ in compound V is very low and on the average is approximately 7.

Nevertheless it is possible that the reaction between VII and IV may go with elimination of H_2S. In this case a random formaldehyde–thioform aldehyde copolymer (IX) is obtained

$$\underset{IX}{HO(CH_2O)_x(CH_2S)_yH}$$
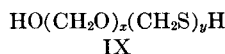
In IX, $x \geq 2$ and $y > 7$, and some oxygen atoms are intercalated in the polythiomethylene chain. According, the annealing of IX would give a product with a sulfur content below the theoretical one for $HS(CH_2S)_nH$, as it happens experimentally.

Therefore all the oxymethylene units are not only at the end of the chain but also intercalated in the polythiomethylene chain; these oxymethylene units are not eliminated by annealing.

In presence of sulfuric acid there is also a formation of trithiane (II) by means of intermediate VII, as proposed by Bogdanski.[10]

We can now conclude that in the CH_2O—H_2O—H_2S system in the presence of H_2SO_4 the following phenomena may happen at the same time: (a) formation and separation of a first solid compound (IV), 1-hydroxy-2-

oxy-5,6-dithioheptane-7-thiol [reactions (2)–(5)]; (b) formation and separation of S-trithiane (II); (g) formation of polythiomethylene by topochemical attack on compound IV [reaction (6)]. In all these processes the active species is mercaptomethanol (VII).

References

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Résumé

Il a été chez nous assuré que par le système eau–formaldéhyde–hydrogène sulfureux en présence de acid sulfurique, on obtient un polymère linéaire avec un point de fusion élevé Ce polymère est substantiellement formé par une chaîne polythiométhylènique avec peu des unités oxyméthyléniques. La formation de ce polymère de la solution aqueuse de formaldehyde intéresse une attaque topochimique sur le première solide de séparation du système, probablement par le mercapto-éthanole présent en solution. Le polymère par réchauffement perd les unités oxyméthyleniques; dans le meme façon le premier produit solide, séparé du système, perd formaldéhyde et subit une transformation morphologique-chimique á polythiométhylène.

Zusammenfassung

Es wurde festgestellt, dass man vom Wasser–Formaldehyd–Schwefelwasserstoff–System in Anwesenheit von Schwefelsaüre eine lineare polymere Substanz mit hohem Schmelzpunkt erhält. Dieses Polymer ist hauptsächlich von einer Polyschwefel-methylenkette bildet, enthält aber auch einige Oximethylengruppen. Dieses Polymer entsteht durch eine topochemische Polymeryzation am anfänglichen festen Produkt des System, wahrscheinlich durch das Athylmercaptan anwesend in der Lösung. Das Polymer verliert mit Erhitzung die Oximethylengruppen; ebenso verliert das erste feste Produkt des Systems das Formaldehyd und verwandelt sich morphologisch und chemisch in Polyschwefelmethylen.