6,[16] which is soluble in methanol, may be converted to an alkoxymethyl derivative at temperatures around 50°. Higher alcohols require higher temperatures than does methanol; *n*-butyl alcohol reacts smoothly at 150°.

N-Ethylthiomethyl-66.—A solution of 60 g. of 66 (0.265 unit mole) in 150 ml. of 90% formic acid was prepared at room temperature. A solution of formaldehyde in ethyl mercaptan was prepared by the gradual addition of paraformaldehyde (60 g., 2 moles) to 120 g. (1.93 moles) of well cooled ethyl mercaptan containing a trace of sodium hydroxide. This solution was added to the 66 solution at room temperature. After one hour, during which time the temperature rose to 40° and the solution separated into two phases, 1200 ml. of acetone was added slowly to yield a homogeneous solution. Addition of aqueous ammonia to this solution caused the polymer to separate as white granules. This product was found to dissolve readily in warm ethanol. *Anal.* Found: S, 7.39; amide substitution based on sulfur content, 31%.

Summary

The preparation and properties of representative examples of N-methylol, N-alkoxymethyl and N-alkylthiomethyl polyamides by the treatment of linear polyamides with formaldehyde in the presence of acids of bases, or with formaldehyde and alcohols or mercaptans in the presence of acids, respectively, have been described.

WILMINGTON, DELAWARE RECEIVED JULY 20, 1948

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[16] This copolymer is prepared from 40 parts hexamethylenediammonium adipate, 40 parts hexamethylenediammonium sebacate, and 30 parts caprolactam. For details see Brubaker, Hanford and Wiley, U. S. Patent 2,285,009 (1942).

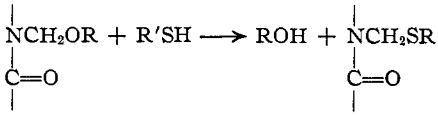
[CONTRIBUTION NO. 250 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

The Reactions of N-Alkoxymethyl Polyamides

BY THEODORE L. CAIRNS, HUGH W. GRAY, ALLAN K. SCHNEIDER AND RICHARD S. SCHREIBER

The previous paper has described the preparation and properties of the N-alkoxymethyl polyamides.[1] This report[2] is concerned with the chemical changes which these polymers undergo.

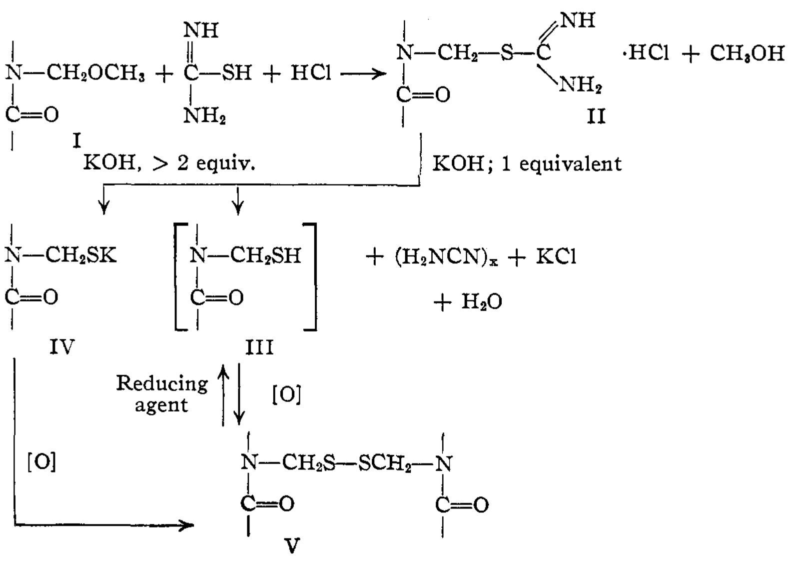
It has been found that the N-alkoxymethyl polyamides condense with compounds containing the thiol group to yield the corresponding N-alkylthiomethyl polyamides according to the equation



$$\overset{|}{\underset{\underset{|}{C=O}}{NCH_2OR}} + R'SH \longrightarrow ROH + \overset{|}{\underset{\underset{|}{C=O}}{NCH_2SR'}}$$

The reaction proceeds at room temperature in the presence of strong acids, such as hydrochloric acid, without the necessity of using large excesses of the mercaptan. In this respect it is greatly superior to the method for the preparation of these sulfur derivatives which was described earlier,[1] and permits the preparation of polyamide derivatives from difficultly available mercaptans such as octadecylmercaptan, 1-thiosorbitol and N,N'-diethyl-β-mercaptoethylamine.

An analogous product may be derived by condensation with thiourea. If one equivalent of concentrated hydrochloric acid is added to a methanol solution of N-methoxymethyl-66 and thiourea (1 mole thiourea per mole of methoxymethyl group) the polymer is very rapidly converted to a water-soluble form. The addition of sufficient alkali to neutralize the hydrochloric acid causes the solution to be converted into a rubbery gel, while the addition of about 2.2 equivalents of alkali for each equivalent of acid produces no apparent change in viscosity and the polymer remains water-soluble. Addition of oxidizing agents (*e. g.*, hydrogen peroxide) to this alkaline solution results in immediate gelation or, in the case of very dilute solutions, precipitation of the polymer. These observations may be explained as the result of a series of reactions represented by the following equations.



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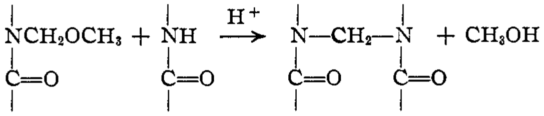
[1] Cairns, Foster, Larchar, Schneider and Schreiber, THIS JOURNAL, **71**, 651 (1949).

[2] Cairns, U. S. Patent 2,430,859 (1947), and 2,430,860 (1947), are related to this work.

Treatment of I with thiourea and acid yields first, the S-alkyl isothiourea salt II, which is water-soluble. Action of an equivalent amount of alkali on this salt results in the formation of the N-mercaptomethyl polyamide III. This first step has an analogy in the reaction of monomeric N-methylol amides[3] while the formation of II is analogous to the well-known method for the preparation of mercaptans from the S-alkyl isothioureas.[4] The N-mercaptomethyl polyamide is very sensitive to oxidation and in the presence of atmospheric oxygen yields the cross-linked polymeric structure V which causes gelation of the solution. Addition of excess alkali to II forms the potassium salt of the mercaptomethyl polyamide (IV). This product is water soluble and is much less readily oxidized by air than is the free mercaptan III but yields the same product (V) when treated with oxidizing agents such as hydrogen peroxide or iodine. The potassium salt (IV) may be isolated as such and, if stored under nitrogen, remains water soluble for several days at least. Neutralization of a solution of II with sodium acetate results in the formation of an insoluble, sulfur-free product, which is probably the original unsubstituted polyamide. This series of reactions presents a useful route for the preparation of high polymers having a controllable number of cross-linkages between chains.

The action of aqueous acid on the alkoxymethyl polyamides results in hydrolysis of the substituent group with the regeneration of the unsubstituted amide group and is, in fact, the reversal of the synthetic method used for the preparation of these polymers. When heated with acid, in the absence of water or any solvent, an interchain condensation takes place as shown in the equation



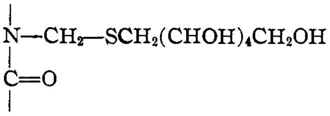
$$\begin{array}{l} | \\ \mathrm{NCH_2OCH_3} \\ | \\ \mathrm{C{=}O} \\ | \end{array} + \begin{array}{l} | \\ \mathrm{NH} \\ | \\ \mathrm{C{=}O} \\ | \end{array} \xrightarrow{H^+} \begin{array}{lll} | & & | \\ \mathrm{N} & \mathrm{—CH_2—} & \mathrm{N} \\ | & & | \\ \mathrm{C{=}O} & & \mathrm{C{=}O} \\ | & & | \end{array} + \mathrm{CH_3OH}$$

The evidence in support of this reaction is a decrease in methoxyl content and conversion of the original alkoxymethyl polyamide into an insoluble and infusible form. Insolubility and infusibility are the prime criteria of a three-dimensional, cross-linked polymer. Conditions under which the hydrolytic regeneration of the polyamide and the acid catalyzed cross-linking may be carried out are given in the experimental section.

Experimental[5]

N-Alkylthiomethyl Polyamides. (a) Reaction with Octadecyl Mercaptan.—A solution of 20 g. of N-methoxymethyl-66 (% CH_3O = 9.72) and 19 g. of crude octadecyl mercaptan in 100 ml. of absolute alcohol was prepared at 60–65°. The mercaptan mixture contained about 85% octadecyl mercaptan (0.066 mole). A solution of 1 ml. of concentrated hydrochloric acid in a few milliliters of absolute alcohol was added and after two hours at 60° the polymer was precipitated as a granular powder by the addition of acetone. After thorough washing with acetone the polymer was dried in air and finally over phosphorus pentoxide. *Anal.* Found: S, 3.72, 3.87; CH_3O, 1.20, 1.16. This octadecylthiomethyl derivative was found to have greatly reduced affinity for water as evidenced by the fact that it was not completely soluble in 80% aqueous ethanol but was readily soluble in absolute alcohol, whereas the original N-methoxymethyl-66 was more soluble in 80% alcohol than in absolute alcohol.

(b) **Reaction with 1-Thiosorbitol.**—A solution of 25 g. of N-methoxymethyl-66 (% CH_3O = 11.5) and 32 g. of 1-thiosorbitol (0.16 mole) was prepared in 100 ml. of 80% aqueous methanol at 50°. A mixture of 1 ml. concentrated hydrochloric acid in about 5 ml. of methanol was added and the solution heated at 50° for two hours and then allowed to stand at room temperature for sixteen hours. Alcoholic alkali was added to neutralize the acid, and the polymer was precipitated as a soft plastic mass by pouring the solution into a large volume of water. The polymer was freed of impurities by working with water and was dried in the form of a thin film. *Anal.* Found: S, 6.42. The sulfur content corresponded to an amide substitution of 21% calculated on the basis of the formula



$$\begin{array}{l} | \\ \mathrm{N—CH_2—SCH_2(CHOH)_4CH_2OH} \\ | \\ \mathrm{C{=}O} \\ | \end{array}$$

The introduction of large amounts of the hydrophilic thiosorbityl radical resulted in a polymer of greatly increased affinity for water. The product described above was found to be completely soluble in 30% ethanol–70% water (by volume) while the original N-methoxymethyl-66 did not dissolve in any alcohol–water mixture containing more than 50% water.

N-Mercaptomethyl-66. (a) Reaction of N-Methoxymethyl-66 with Thiourea.—A solution of 30 g. of N-methoxymethyl-66 (% CH_3O = 9.72) and 6.0 g. of thiourea (0.079 mole) was prepared by stirring with 70 g. of aqueous methanol (80% methanol by volume) at 55–60° for about one hour. This solution was cooled to 30–35° and 6.35 ml. of concentrated hydrochloric acid (0.079 mole) in 15 ml. methanol was added. After about one minute a drop of this solution added to water gave no precipitate. After three minutes a solution of 0.84 g. potassium hydroxide (0.158 mole) in 10 ml. of water and 25 ml. of methanol was added. During the next few seconds the solution changed in color from pale yellow to pink and set to a transparent tough rubbery gel (V).

If the neutralization with potassium hydroxide was carried out in the presence of hydrogen sulfide, gelation did not take place. Further, addition of more than 2.0 moles of alkali per mole of acid used did not cause gelation of the solution, while any quantity less than 2.0 moles resulted in immediate gelation.

(b) **Isolation of the Disulfide of N-Mercaptomethyl-66 (V).**—A solution of 120 g. of N-methoxymethyl-66 (% CH_3O = 6.46) and 36 g. of thiourea (0.47 mole) was prepared in 500 ml. of aqueous methanol (80% methanol by volume) at 60° and then cooled to room temperature. To this was added 36 ml. of concentrated hydrochloric acid (0.40 mole) in 50 ml. of methanol. After fifteen minutes this solution was poured into a mixture of 60 g. of potassium hydroxide (1.06 moles) dissolved in 25 ml. of water and 150 ml. of methanol with vigorous agitation. The precipitate which formed was separated by pressure filtration and the clear yellow, viscous filtrate was stored in an atmosphere of nitrogen.

A portion of this filtrate was diluted with a large volume of water and an excess of 3% hydrogen peroxide added. This caused the precipitation of a white curdy product—the disulfide of N-mercaptomethyl-66 (V). This polymer was washed free of all traces of alkali with water, finally

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[3] (a) Albrecht, Frei and Sallman, *Helv. Chim. Acta*, 233E (1941); (b) Austin and Frank, U. S. Patent 2,323,111 (1943).

[4] "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., p. 345.

[5] We are indebted to Dr. J. W. Stillman and Dr. A. H. Hale of these Laboratories under whose supervision the analyses reported here were carried out.

washed with acetone and dried first in air and then in vacuum over phosphorus pentoxide. *Anal.* Found: S, 4.90; CH_3O, 3.08; ash (calcd. as K_2SO_4), 0.31. This disulfide was insoluble in hot aqueous ethanol and treatment with an excess of a mercaptan caused reduction to a soluble form. Addition of lead acetate to an aqueous solution of the potassium salt of N-mercaptomethyl-66 described above caused formation of a yellow precipitate.

Hydrolysis of N-Methoxymethyl-66 by Aqueous Acid.—The hydrolysis of the methoxymethyl group to CH_3OH, CH_2O and the unsubstituted amide group may be carried out in a controllable fashion and thus is an additional method for obtaining any given degree of methoxyl content.

Small strips of film (0.002″ thick) of N-methoxymethyl-66 were suspended in a solution of 10 ml. of concentrated hydrochloric acid in one liter of water at 50° for various lengths of time. The strips were removed, washed thoroughly in water, soaked in aqueous ammonia, washed in water and finally dried in vacuum over phosphorus pentoxide.

Time in acid solution, minutes	CH_3O, %
0	7.13
1	6.61
2	5.41
3	4.57
4	2.77

Acid Cross-linking of N-Methoxymethyl-66.—A 20% solution of N-methoxymethyl-66 in methanol–water (80% methanol by weight) was prepared by stirring under reflux at 60°. To this was added maleic acid (1% based on the polymer) and the mixture stirred for thirty minutes to dissolve the acid. This solution was filtered under pressure, allowed to stand two hours at 60° to permit the air bubbles to rise out of the solution and was then cast into films on glass plates. The solvent was allowed to evaporate at room temperature for about twenty hours.

The pliable, transparent film prepared in this manner analyzed for 8.53% methoxyl. Baking this film (on the glass plate) for six hours at 60° gave a product of 6.94% methoxyl content; one hour at 100° gave a product of 6.31% methoxyl content. Both these baked films were found to be insoluble (although highly swollen) in hot 80% methanol, and they did not melt at any temperature but charred gradually about 295°. A film of the same N-methoxymethyl-66 prepared in a similar manner but without added acid melted at about 155° and was readily soluble in hot aqueous methanol even after baking for one hour at 100°.

Summary

The conversion of N-alkoxymethyl polyamides to alkylthiomethyl and mercaptomethyl polyamides by treatment with mercaptans or thiourea in the presence of strong acids has been described.

WILMINGTON, DELAWARE RECEIVED JULY 20, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Perylene, a By-product from Some 1-Naphthyl-metallic Compounds

BY HENRY GILMAN AND CECIL G. BRANNEN

Incidental to the preparation of some substituted silanes using 1-naphthyllithium, perylene was isolated from several different mixtures. Mr. L. Miller[1] isolated this hydrocarbon from the reaction between 1-naphthyllithium and silicon tetrachloride, while we have found it in some reactions of 1-naphthyllithium with ethyl silicate and hexachlorodisilane, as well as with silicon tetrachloride.

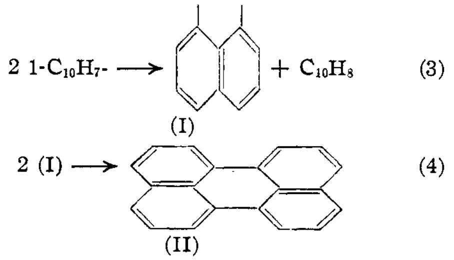
In order to determine if a silicon compound is essential for the formation of perylene, 1-naphthyllithium was made from 1-bromonaphthalene of the highest purity available, hydrolyzed, and the residue examined chromatographically. Pure perylene in a yield of 3% was isolated from the mixture.

There is no evidence in the literature that 1,8-dibromonaphthalene is formed during the bromination of naphthalene and even if traces are formed, it is improbable that perylene in the yield of 3% could have come from that source. To reduce further the possibility that perylene might have resulted from a dibromo isomer, 1-naphthyllithium was prepared from the halide obtained from a Sandmeyer reaction and the mixture examined as before. A 2.8% yield of perylene was found.

Among the mechanisms by which perylene might be produced in this reaction are: (1) the formation and disproportionation of free radicals, followed by coupling; and (2) a ring closure, by dehydrogenation, of an intermediary biaryl, 1,1′-binaphthyl. Free radical formation and disproportionation have been advanced by several investigators,[2] and in this case the mechanism may be as shown by the following set of reactions

$$1\text{-}C_{10}H_7Br + Li \longrightarrow 1\text{-}C_{10}H_7\text{-} + LiBr \qquad (1)$$

$$2\ 1\text{-}C_{10}H_7\text{-} \longrightarrow 1,1'\text{-}C_{10}H_7\text{-}C_{10}H_7 \qquad (2)$$



Some organometallic compounds are known to effect dehydrogenation[3] and such dehydrogenation

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(1) Unpublished studies, Iowa State College.

(2) (a) Gilman and St. John, THIS JOURNAL, **52**, 5017 (1930) (b) Kharasch and Fields, *ibid.*, **63**, 2316 (1941). (c) Wuis and Mulder, *Rec. trav. chim.*, **57**, 1385 (1938); Nauta and Mulder, *ibid.*, **58** 1062 (1939); Gomberg and Bachmann, THIS JOURNAL, **52**, 2455 (1930); Blicke and Powers, *ibid.*, **51**, 3378 (1929); Bachmann and Clarke, *ibid.*, **49**, 2089 (1927). For a discussion with leading references, see Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 540.

(3) Gilman and Bradley, THIS JOURNAL, **60**, 2333 (1938).