

Summary

The pyrolysis method used previously to transform the acetyl derivatives of N,N-dimethylacrylamide into N,N-dimethylacrylamide was applied to the preparation of other N-alkyl acrylamides and methacrylamides. N,N-Diethylacrylamide was obtained in good yield by the thermal decomposition of N,N-diethyl- α -acetoxypropionamide, but pyrolysis of N-methyl- and N,N-di-*n*-butyl-

acetoxypropionamide was less satisfactory for the preparation of the corresponding acrylamides.

N-Methyl- and N,N-dimethylmethacrylamides were made successfully by pyrolyzing the corresponding N-alkyl α -acetoxyisobutyramides. Apparently methacrylamides can be made more readily than acrylamides by the pyrolysis method.

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Preparation and Properties of N-Methylol, N-Alkoxyethyl and N-Alkylthiomethyl Polyamides

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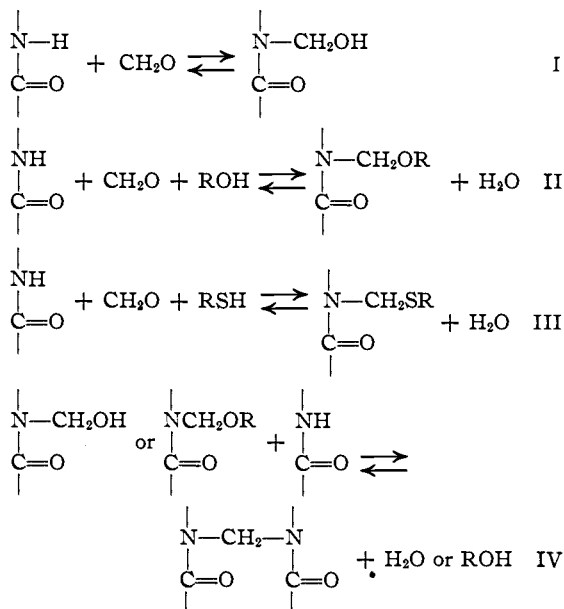
The preparation and properties of high molecular weight, linear polyamides derived from amino acids and from diamine-dibasic acid salts have been studied in detail by Carothers.¹ There has, however, been no report of the chemical reactions which these polymers undergo. Other workers refer to the treatment of polyamides with formaldehyde to give slight modification^{2,4} but the preparation of well-defined chemical entities is not described. This work was undertaken to explore the possible reactions of the high molecular weight polyamides and to study the properties of the derivatives obtained.

The starting materials for this investigation were polyhexamethylenedipamide and polyhexamethylenesebacamide.³ Both of these polymers are high melting solids which show appreciable solubility, without degradation of molecular weight, only in formic acid, phenol, sulfuric acid and solutions of salts such as calcium chloride in methanol. These two polymers are both sensitive to degradation by hydrolysis, alcoholysis, and ammonolysis at elevated temperatures. From consideration of these facts it is evident that the variety of experimental conditions which may be imposed upon these polyamides during a study of their chemical reactions is severely limited.

Preparation

It has been found that these polyamides react with formaldehyde to yield an N-methylol derivative or with formaldehyde in the presence of alco-

hols or mercaptans to yield N-alkoxyethyl (II), and N-alkylthiomethyl (III) derivatives. In addition, a fourth product, probably having the crosslinked methylene structure (IV) has been obtained.^{4,5} These reactions are represented in the following equations where the polyamide chain is indicated simply by the amide group.



The formation of the N-methylol polyamides (I) is brought about in the presence of acids or bases while the formation of II, III and IV is catalyzed by acids but not by bases. The same situation holds also for the reverse reaction: the methylol groups are readily removed by acids or bases

(4) See also Hopff, Weickmann and Ufer, U. S. Patent 2,288,279 (1942).

(5) The following U. S. Patents are related to the work described here: Cairns, 2,393,972 (1946); Cairns, 2,430,860, (1947); Charch, 2,430,910 (1947); Foster and Larchar, 2,430,923 (1947).

(1) (a) H. Mark, "High Polymers," Vol. I, "The Collected Papers of Wallace H. Carothers on High Polymeric Substances," Interscience Publishers, Inc., New York, N. Y., 1940; (b) Coffman, Berchet, Peterson and Spanagel, *J. Polymer Sci.*, **2**, 306 (1947).

(2) (a) Coffman, U. S. Patent 2,177,637 (1939); (b) Fraenkel-Conrat, Cooper and Olcott, *THIS JOURNAL*, **67**, 950 (1945); (c) McCreath, U. S. Patent 2,425,334 (1947).

(3) For convenience these polymers will be referred to as 66 and 610, respectively. The first number refers to the number of carbon atoms in the diamine used and the second to the number of carbon atoms in the dibasic acid.

while the alkoxyethyl and alkylthiomethyl groups and the methylene crosslinks are stable to bases but hydrolyzed easily in the presence of acids. Such behavior is also found with comparable derivatives of monomeric amides and with the formals which are analogs of the substituted amides under consideration here. It is also of interest that mild heat alone causes reversal of eqn. I but not of II or IV.

The N-methylol polyamides (I) may be prepared by the action of aqueous formaldehyde on solutions of 66 in formic acid at temperatures around 60°. In this case the conditions of reaction must be very carefully controlled in order to prevent the formation of the crosslinked structure (IV). This cross-linking manifests itself by a very rapid increase in the viscosity of the solution. In many cases the reaction mixture may change from a smooth solution of moderate viscosity to a tough, intractable, rubbery gel in a few seconds. A more controllable and satisfactory method for the preparation of N-methylol polyamides consists in treatment with formaldehyde in the presence of an inert medium (such as chloroform, dimethylformamide, dioxane or toluene) and a basic catalyst (potassium carbonate) at 120 to 150°. The use of pyridine as an inert medium is advantageous since it also serves as a basic catalyst.

The N-alkoxyethyl and N-alkylthiomethyl polyamides are prepared readily by the action of a solution of formaldehyde in an alcohol or mercaptan on a polyamide dissolved in formic acid at 60°. Prevention of cross-linking is, in these cases, accomplished by using an excess of alcohol or mercaptan. A second method for the preparation of N-alkoxyethyl derivatives involves the treatment of a solid polyamide with an alcohol-formaldehyde solution at temperatures up to 150° in the presence of catalytic quantities of acid. It has been demonstrated that the use of this method at elevated temperatures brings about some reduction in the average molecular weight of the polymer. The products obtained by this method are still true high polymers and exhibit the properties of high strength, elongation and flexibility, and show viscosity effects common to all soluble, high molecular weight, linear polymers.

Degree of Substitution

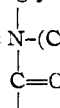
The parent polyamides used in this study ranged in molecular weight up to perhaps 50,000 and were usually about 15,000 to 25,000. For 66 a molecular weight of 22,600 corresponds to a chain having 200 amide groups or 100 repeating units. In the preparation of the derivatives described here it was found possible to effect reaction with practically all of the amide groups under special conditions but major attention has been devoted to products having up to 50% amide substitution. Large excesses of formaldehyde and other reagents are usually required to bring about high degrees of substitution. Thus alkoxyethyl polyamides are

prepared using about 7.5 moles of formaldehyde and 10 to 15 moles of alcohol per unit molecular weight of polyamide,⁶ and of these quantities only about 0.5 to 1 mole of formaldehyde and alcohol appear as part of the final product. All the reactions under consideration here, with the possible exception of the formation of I, involve water as one of the products and it is therefore not surprising that addition of water to any reaction mixture results in a lowering of the degree of substitution. For example, under certain conditions a reaction mixture based on 1 unit mole of 66, 7.5 moles of paraformaldehyde, 11 moles of methanol and 0.4 mole of water yields a N-methoxymethyl-66 of about 45% amide substitution, and a similar mixture containing 4.0 moles of water gives a product of about 31% substitution. The second important factor governing the degree of substitution is the relative amounts of formaldehyde and polyamide used. Increasing the amount of formaldehyde increases the degree of substitution.

Proof of Structure

The structure assigned to these derivatives is based first of all on the method of formation. Further it has been found that acid hydrolysis of a N-methoxymethyl-66 gives rise to formaldehyde in quantities which roughly balance the calculated values based on the methoxyl content of the same polymer as determined by the standard Zeisel method. The differences found between formaldehyde and methoxyl content usually indicate excess of formaldehyde over the calculated quantities. These observations point strongly toward

the existence of groups of the structure $\text{N}-(\text{CH}_2\text{O})_x\text{R}$.



Additional evidence supporting the N-alkoxyethyl structure is found in the fact that polyamides prepared from dibasic acids and N,N'-dialkylated diamines (such as N,N'-dimethylhexamethylenediamine) are apparently unaffected by treatment with formaldehyde. Finally, comparison of the infrared absorption spectra of 66 and N-methoxymethyl-66 indicates a definite reduction in the intensity of certain NH absorption bands in the case of the substituted derivative.⁷ Unequivocal evidence to show that these products are not oxygen alkylated derivatives of the structure $\text{N}-(\text{CH}_2\text{O})_x\text{R}$ has not been obtained.

Physical Properties

The parent polymers from which the alkoxyethyl derivatives are obtained by chemical reaction are hard, high-melting materials of consid-

(6) "Unit molecular weight" is the molecular weight of the recurring unit in the polymer. In the case of 66 this unit is $\text{HN}(\text{CH}_2)_6\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-$.

(7) We are indebted to Dr. J. R. Downing for this observation.

erable strength and are capable of being oriented by the process of "drawing." These polymers are also "crystalline" as evidenced by their opacity when allowed to cool slowly from the melt and the typical sharp patterns obtained by X-ray diffraction of unoriented materials as well as the well-defined fiber pattern shown by oriented products. Most of these properties are almost certainly the manifestation of two structural features of these polyamides: first, they have uniform chains which can pack well into a crystal unit; and second, there is abundant opportunity for the formation of hydrogen bonds between chains which would result in very high interchain forces. The conversion of 66 into a N-alkoxymethyl-66 involves the replacement of some of the amide hydrogens by the CH_2OR group. The removal of the amide hydrogens reduces the opportunity for interchain hydrogen bonds, and the introduction of the large $-\text{CH}_2\text{OR}$ group makes it less probable that the polymer chains can pack well into a crystal unit. The properties of the alkoxymethyl polyamides in comparison with the unsubstituted polymers from which they are derived are best interpreted in the light of these two structural characteristics.

The properties of 66 and the corresponding N-alkoxymethyl derivatives of two different degrees of substitution are listed in Table I.

TABLE I
PHYSICAL PROPERTIES OF POLYAMIDES

	N-Methoxymethyl-66		
	66	35% Amide subst.	50% Amide subst.
Max. concn. in hot 80% ethanol	None	About 40%	>60%
Melting point, °C.	264	150-160°	100-110
Modulus of stiffness in 1000's lb./sq. in.	290	14.2	3.0
Recovery from 100% stretch, %	30-35	70-80	90-95
Tensile strength, lb./sq. in.	8000-10,000	4500-6000	2000-3000

The solubility of the parent 66 and 610 is limited to mineral acids, strong organic acids, phenols and solutions of calcium chloride in methanol. The alkoxymethyl derivatives are soluble in all these solvents and also dissolve readily in the lower alcohols and mixtures of these alcohols with water or chloroform. Methanol and ethanol containing 15 to 30% water are excellent solvents for these polyamides and are much better than the alcohols alone. As the degree of amide substitution increases the solubility in alcohol increases and the stability of solutions toward gelation also increases. The stability of solutions of N-methoxymethyl-66 in aqueous alcohol shows a sharp increase around 30-35% amide substitution. It is interesting to note that Baker and Fuller⁸ found that the related N-methyl polyamides also showed greatly increased solubility at about the same point. Most of these alkoxymethyl polyamides are insoluble in hydrocarbons, chlorinated hydro-

(8) Baker and Fuller, *THIS JOURNAL*, **65**, 1120 (1943).

carbons, esters and ketones. Certain unusual effects were noted in connection with the precipitation of N-methoxymethyl-66 from its alcohol solutions. Addition of acetone causes separation of the polymer from its alcohol solution, and the amount of acetone required to cause precipitation is directly related to the amide substitution. The amount of acetone required, however, is independent of the concentration of polymer in the alcohol solution. In effect, a given polymer shows solubility in a critical acetone/alcohol ratio which is a function of the amide substitution. Addition of water to an alcohol solution of these polymers also causes precipitation but in this case the amount of water is independent of the degree of amide substitution and depends solely on the chemical structure of the base polyamide and the substituent group.⁹ Thus, each of these polymer derivatives may be characterized by a simple test which has roughly the same utility as the melting point of a monomeric compound. These relationships, particularly the acetone precipitation, are also affected to a minor extent by the degree of polymerization. Specific examples of these data are shown in Table II.

TABLE II
PRECIPITATION OF N-ALKOXYMETHYL POLYAMIDES FROM SOLUTION

Polymer	% Methoxyl (a)	Volume of solvent to initiate precipitation, ml.	
		Acetone (b)	Water
N-Methoxymethyl-66	7.21	48	23.5
	9.72	66	22.8
	9.94	81	23.3
N-Methoxymethyl-610	7.86	43	7.0
	8.03	53	7.1
	9.23	96	7.4
N- <i>n</i> -Propoxymethyl-66	9.81	128	7.5
	..	140	13.4
	..	105	11.0
N-Isobutoxymethyl-66	..	105	11.0
	..	350	1.0

^a Acetone added to refluxing, stirred solution of 1.0 g. of polymer in 20 ml. 80% ethanol in case of N-isobutoxymethyl-610 and products based on 66. The other polymers from 610 were measured at concentration of 0.5 g. in 12 ml. of 80% ethanol. ^b Water added to refluxing, stirred solution of 0.5 g. of polymer in 25 ml. of methanol in all cases.

The melting points of the N-substituted polymers decrease as the degree of substitution increases. In the case of N-methoxymethyl-66 the melting point changes from 264° for zero substitution to about 100° at 50% and finally to room temperature and lower at 70 to 80% substitution. The lowering of melting point as the amide hydrogen is replaced has been noted with other series of polyamides.^{8,10}

The modulus of stiffness and of stretching also decreases rapidly as amide substitution increases. At about 50% substitution, products approaching

(9) C. S. Marvel, Office of Publication Board, Report PB 11193, discusses analogous effects in the precipitation of rubber from solution.

(10) Salisbury, U. S. Patent 2,351,074 (1944).

rubber and synthetic elastomers in this respect are obtained. The tensile strength decreases as substitution increases while the total elongation at break remains roughly constant.

One of the most striking changes in physical properties which accompanies substitution on the amide nitrogen is the increase in recovery from stretching. Unsubstituted 66 or 610 when stretched undergoes a deformation ("drawing" orientation—see ref. 1) which is not recovered when the stress is released unless the temperature is raised to a very high value. In the case of the alkoxymethyl polyamides the tendency to recover from stretching at room temperature is pronounced and at 45 to 50% substitution, rapid recoveries of 90–95% from elongations up to 500% of the original length are realized.

Experimental¹¹

N-Methylol-66 (I).—(a) **In Acidic Medium.**—A solution of 60 g. of 66 (0.265 unit mole) in 210 g. of 90% formic acid (sp. gr. 1.20) was prepared by stirring the mixture at 60° for one to two hours. Prolonged exposure of the polyamide to warm formic acid should be avoided since gradual hydrolysis of amide linkages occurs under these conditions. To this solution was added a solution of 60 g. (2 moles) paraformaldehyde in 110 ml. of water, also at about 60°, over a period of eight minutes. Care must be taken at the beginning of the addition since a too rapid rate at first will cause separation of the 66. Twelve minutes later 50 ml. of 60° water was added and after a total time, from the beginning of the aldehyde addition, of thirty-five minutes, the solution was poured into a mixture of 500 ml. of water and 500 ml. of acetone. To the resulting slightly turbid solution, 1500 ml. of water was added over a period of forty minutes causing the N-methylol-66 to separate as a granular powder. This product was washed by reslurrying several times with water, then with aqueous ammonia, water and finally acetone.

*Anal.*¹² Found CH₂O, 5.9. This corresponds to substitution of 23% of the amide groups with CH₂OH groups.

Use of commercial formalin in the above procedure yields an N-methylol polyamide which also contains a few per cent. of methoxymethyl groups derived from the methanol present in the commercial product.

(b) **In Basic Medium.**—A mixture of 100 g. of 66 (pulverized to about 20-mesh size) 100 g. of paraformaldehyde and 300 g. of pyridine was charged into a 1-liter stainless steel tube which was mounted in a device for rocking and heating the tube. The mixture was heated to 130–135°, held at this temperature for thirty minutes and then cooled rapidly to room temperature. The resulting sirupy solution was filtered to remove a small amount of unchanged 66 and foreign material and then poured into a large volume of water. The polymer separated as a soft slime and was freed of solvent and formaldehyde by mechanical working (rubber rolls or dough mixer) in a stream of cold water. The product was air dried in the form of thin sheets. *Anal.* Found CH₂O, 12.6. This corresponds to substitution of 55% of the amide groups with methylol groups.

N-Methoxymethyl-66 (II). (a) **Preparation by Solution Method.**—A solution of 60 g. of 66 in 180 g. of 90% formic acid was prepared by stirring at 60°. To this was added a solution of 60 g. paraformaldehyde in 60 g. meth-

anol¹³ also heated to 60°. The rate of addition was very slow during the first minute in order not to precipitate any of the 66 and then was increased so that it was complete at the end of three minutes. Ten minutes after the aldehyde addition was begun,¹⁴ 60 g. of methanol was added rapidly and the reaction allowed to proceed for a total of thirty minutes. The solution was then poured into 1700 ml. of equal parts (by volume) of acetone-water, and aqueous ammonia was added gradually. The addition of the ammonia caused the N-methoxymethyl-66 to separate as fine white granules. *Anal.* Found: CH₂O (Zeisel), 7.13; CH₂O by sulfite method,¹² 1.4. These values correspond to a total amide substitution of methoxymethyl and methylol groups of 36%.¹⁵

A procedure analogous to that described above but using an anhydrous formic acid/acetic acid mixture (prepared by addition of sufficient acetic anhydride to 90% formic acid to combine with the water present) yielded a higher substituted product. *Anal.* Found: CH₂O (Zeisel), 9.94; CH₂O by sulfite method, 0.30. The combined total amide substitution corresponding to these analyses is 46%.

(b) **Preparation by "Direct" Method.**—In a 1-gallon nickel-lined autoclave equipped with an efficient anchor type agitator and an overhead discharge line was placed 1000 g. of 66 (pulverized to pass a 16-mesh screen), 1000 g. of paraformaldehyde, 30 g. of water and 1500 g. of methanol. This mixture was heated to 139°, and a solution of 20 ml. of 85% phosphoric acid in 50 g. of methanol was forced in by means of nitrogen pressure. The reaction mixture was maintained between 139 and 140° for eight minutes and then discharged very rapidly (forty to fifty seconds) through the overhead pipe into a solution of 1600 ml. of methanol, 400 ml. of water and sufficient ammonia to neutralize the phosphoric acid catalyst. The resulting solution was freed of foreign material and a trace of unchanged 66 granules by filtration using a diatomaceous earth filter-aid, and the clear filtrate poured into water. The polymer was freed of solvent and aldehyde by working in a stream of water in a mixer. Finally treatment with 1% sodium hydroxide at 40° for fifteen minutes served to remove N-methylol substitution, and also caused the polymer to break up into fine granules. In most runs about 980 g. of polymer was obtained but there were, of course, high losses involved in the use of an autoclave with an overhead discharge line. *Anal.* Found CH₂O (Zeisel), 10.53; amide substitution based on CH₂O, 45%. A procedure analogous to the above, using 300 g. of water in the reaction mixture, yielded a lower substituted product. *Anal.* Found CH₂O, 7.8; amide substitution based on CH₂O, 31%.

This direct synthesis of N-alkoxymethyl polyamides has been found to be of wide applicability. The optimum temperature generally varies for each polyamide-alcohol combination. For example, N-methoxymethyl-610 is best prepared at 130–133°, while a copolymer such as 66/610/

(13) Such solutions are best prepared by warming a suspension of paraformaldehyde in methanol to 60° and then adding a trace of solid sodium or potassium hydroxide. Under these conditions most samples of paraformaldehyde dissolve very rapidly to give perfectly clear solutions. Such a solution undoubtedly contains a large proportion of the aldehyde and methanol in the form of the hemiacetal, CH₂OCH₂OH.

(14) The time at which this second quantity of methanol is added is an important factor in determining the total degree of substitution. The longer this time interval, the higher will be the degree of substitution. This is believed to be due to the effect of the water formed by the esterification of the formic acid by the methanol.

(15) Calculation of degree of amide substitution.—Equations have been derived which permit analyses to be simply converted to the per cent. of amide groups substituted. For N-methoxymethyl-66

$$Z - 0.014 ZP = 3.65 P$$

Where Z = % of amide groups substituted, and
P = % methoxyl

Similar relationships may be derived for any combination of substituent groups and kinds of analyses.

(11) We are indebted to Drs. J. W. Stillman and A. H. Hale of these Laboratories under whose supervision many of the analyses reported here were carried out.

(12) The analysis for CH₂O derived from N-methylol groups was carried out by treating a solution of the polyamide in 70% aqueous alcohol with sodium sulfite and titrating the liberated alkali with standard acid.

