Experimental

The experimental procedures used to prepare the various polymers from dinitriles and aldehydes did not vary to any great extent from the following standard preparation of 16 polyamide from adiponitrile and formaldehyde.

Polymerization of Adiponitrile and Formaldehyde.—A solution of trioxane (49 g., 1.63 moles) in adiponitrile (176 g., 1.62 moles) was added with stirring at 30° to a solution of concentrated sulfuric acid (550 g., 300 cc.) in 90% formic acid (970 g., 810 cc.) contained in an 8-liter stainless steel beaker. The reaction mixture was stirred at a low speed and cooling was applied to maintain the temperature at 30°. After approximately 20 minutes the exothermic part of the reaction was over and the reaction mixture began to thicken gradually. After 45–50 minutes the mixture became very viscous and reached the gel-point. Cold water (4000 cc.) was added immediately and stirring was increased to quench the polymerization rapidly. A white powder was precipitated which was filtered and reslurried twice in water to remove all the acid. The last two washes consisted of a sodium carbonate wash followed by a final water wash. Under these conditions a 40% yield of 16 polyamide was obtained (90 g.) which exhibited an intrinsic viscosity in the range of 1.5 to 2.0 in *m*-cresol.

With aldehydes other than formaldehyde similar experimental conditions were employed except for the use of concentrated sulfuric as a solvent and a temperature of 0° to minimize self-condensation side-reactions of aldehydes.

Effect of Polymerization Variables on Polymer Properties. (a) **Effect of Acids.**—The intrinsic viscosity, reaction time and yields of polymer using a number of acid solvent-catalysts are shown in Table IV.

(b) **Effect of Temperature.**—The rate of polymerization of adiponitrile and formaldehyde is a direct function of the temperature. The polymerization is usually carried out at 30°, since at higher temperatures there is a greater danger of hydrolysis of nitrile groups in the acid solvent. At 0° the polymerization reaction is slow and polymers do not seem to exhibit any advantage over polymers prepared at 30°. However, the salient feature of polymers prepared at low temperature (0°) is their ability to yield clear flexible films even when the polymer intrinsic viscosity is as low as 0.23, whereas films from polymers prepared at 30° are brittle up to an intrinsic viscosity of 0.70.

TABLE IV

CATALYSTS FOR THE PREPARATION OF 16 POLYMER

Polymerization medium	[η] *m*-cresol	Yield, %	Reaction time, min.	Gel time, min.
H_2SO_4 (83%)	0.51	64	20	20
H_2SO_4–HCOOH–H_2O	2.16	37	50	50
H_2SO_4–HCOOH–C_2H_5OH	1.52	37	35	35
H_2SO_4–CH_3COOH	0.40	60	10	10
H_3PO_4 (85%)	.23	78	2 days	Did not gel
C_2H_5–SO_3H	.51	..	10	10
p-Toluenesulfonic acid–HCOOH	< .10	44	2 days	Did not gel
HCOOH (100°)	< .10	52	5 hr.	Did not gel

Acknowledgments.—We are indebted to Dr. J. A. Andreen of the Pioneering Research Section, Rayon Technical Division, E. I. du Pont de Nemours and Company, Inc., for carrying out the polymerizations with aldehydes other than formaldehyde and to Dr. J. R. Downing of the Chemical Department, E. I. du Pont de Nemours and Company, Inc., for the interpretation of the infrared data.

WILMINGTON, DELAWARE

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[CONTRIBUTION FROM THE CAROTHERS RESEARCH LABORATORY, RAYON TECHNICAL DIVISION, E. I. DU PONT DE NEMOURS & CO., INC.]

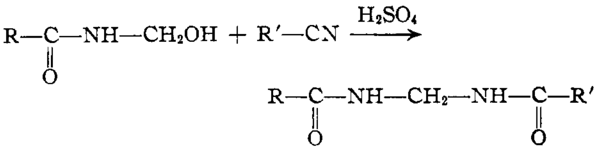
Acid-catalyzed Reactions of Nitriles. III. The Reaction of Nitriles with N-Methylolamides

BY EUGENE E. MAGAT AND L. FRANK SALISBURY

The scope of the reaction, in strong sulfuric acid at room temperature, of N-methylolamides with nitriles to give methylene-bis-amides has been extended to include the preparation of polyamides from N,N'-dimethylolamides and dinitriles. The polymer formed from N,N'-dimethyloladipamide and adiponitrile is similar to that prepared from adiponitrile and formaldehyde (16 nylon). Competitive rates of reaction of N-methylolamides and formaldehyde with nitriles to yield methylene-bis-amides show that the nitrile reacts preferentially with the N-methylolamide.

Introduction

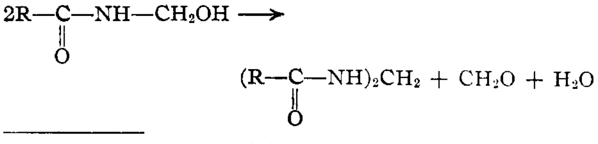
In a previous communication it was shown that nitriles react with formaldehyde in the presence of strong acids to form methylene-bis-amides.[1] The intermediate in that reaction was assumed to be an N-methylolamide carbonium ion. This paper deals with the second step of the reaction of nitriles with formaldehyde, the reaction of N-methylolamides with nitriles to form methylene-bis-amides.



$$R-\underset{\overset{\|}{O}}{C}-NH-CH_2OH + R'-CN \xrightarrow{H_2SO_4} R-\underset{\overset{\|}{O}}{C}-NH-CH_2-NH-\underset{\overset{\|}{O}}{C}-R'$$

The reaction of nitriles with N-methylolphthalimide and N-methylolbenzamide has been reported previously by Buc,[2] but the scope and mechanism of the reaction have received no general consideration. This reaction has been reinvestigated since it has been found that the scope of the reaction can be extended to include the preparation of polyamides by the reaction of N,N'-dimethylolamides and dinitriles.

Monomeric Reaction.—The reaction of N-methylolamides and nitriles is exothermic and is rapid at room temperature. The reaction medium is usually 80 to 100% sulfuric acid or mixtures of sulfuric and formic acid and yields of methylene-bis-amides often exceed 90%. A competing reaction is the self-condensation of certain N-methylol amides in the presence of acids which also gives a methylene bis-amide.[3]



$$2R-\underset{\overset{\|}{O}}{C}-NH-CH_2OH \longrightarrow (R-\underset{\overset{\|}{O}}{C}-NH)_2CH_2 + CH_2O + H_2O$$

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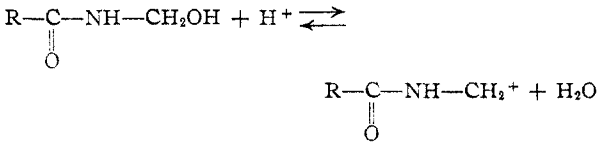
[1] Magat, Faris, Reith and Salisbury, THIS JOURNAL, **73**, 1028 (1951).

[2] Buc, THIS JOURNAL, **69**, 254 (1947).

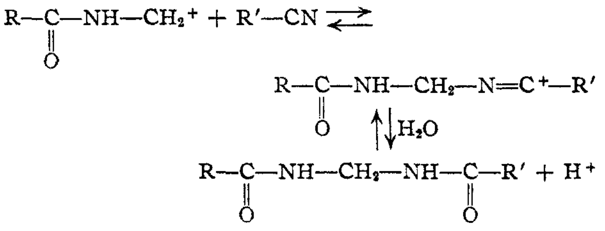
[3] Einhorn, *Ann.*, **343**, 207 (1905).

Thus N-methylolbenzamide dissolved in concentrated sulfuric acid for 2 hours at 30° gave upon reprecipitation with water a 25% yield of methylene-bis-benzamide.

The mechanism of the reaction of methylolamides and nitriles may be represented by the series of equations



$$R-\underset{\underset{O}{\|}}{C}-NH-CH_2OH + H^+ \rightleftarrows R-\underset{\underset{O}{\|}}{C}-NH-CH_2^+ + H_2O$$

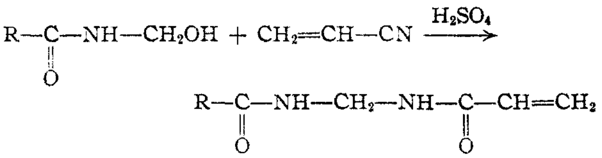


$$R-\underset{\underset{O}{\|}}{C}-NH-CH_2^+ + R'-CN \rightleftarrows R-\underset{\underset{O}{\|}}{C}-NH-CH_2-N{=}C^+-R'$$

$$\uparrow\downarrow H_2O$$

$$R-\underset{\underset{O}{\|}}{C}-NH-CH_2-NH-\underset{\underset{O}{\|}}{C}-R' + H^+$$

A number of new acrylamides can be prepared by this type of reaction from acrylonitrile and various N-methylolamides.



$$R-\underset{\underset{O}{\|}}{C}-NH-CH_2OH + CH_2{=}CH-CN \xrightarrow{H_2SO_4} R-\underset{\underset{O}{\|}}{C}-NH-CH_2-NH-\underset{\underset{O}{\|}}{C}-CH{=}CH_2$$

Thus from N-methylolbenzamide, N-(benzamidomethyl)-acrylamide has been prepared in 60% yield.

To compare the relative rates of the reaction of nitriles with formaldehyde *vs.* methylolamides, a chlorine containing nitrile (*p*-chlorobenzonitrile) was added to a mixture of N-methylolbenzamide and formaldehyde in a formic-sulfuric acid mixture. After stirring for 45 minutes at 30°, the reaction mixture was poured into water and the precipitated product was filtered and dried. If *p*-chlorobenzonitrile reacted preferentially with formaldehyde, $(Cl-C_6H_4-CO-NH)_2CH_2$ would be formed containing 22% Cl (Equation 1); if the *p*-chlorobenzonitrile reacted preferentially with the N-methylolamide, $Cl-C_6H_4-CO-NH-CH_2-NH-CO-C_6H_5$ would be formed containing 12.3% Cl (Equation 2). Intermediate values would be obtained for a mixture of both reaction products.

$$(1)\quad 2Cl-C_6H_4-CN + CH_2O \xrightarrow[H_2SO_4]{H-COOH} (Cl-C_6H_4-CO-NH)_2CH_2$$

$$(2)\quad Cl-C_6H_4-CN + C_6H_5-CO-NH-CH_2OH \xrightarrow[H_2SO_4]{H-COOH} Cl-C_6H_4-CO-NH-CH_2-NH-CO-C_6H_5$$

The resulting product had 12.2% Cl indicating that the nitrile reacted faster with the N-methylolamide than with formaldehyde (Equation 2). This result is in accord with reaction mechanism proposed for the formation of methylene-bis-amides from a nitrile and formaldehyde in acid solution, that is, a slow reaction leading to a N-methylolamide followed by a fast reaction of the N-methylolamide with the nitrile.

Polymeric Reaction.—When the reaction of N-methylolamides and nitriles is extended to N,N'-dimethylolamides and dinitriles the reaction product is a polymeric linear polyamide.

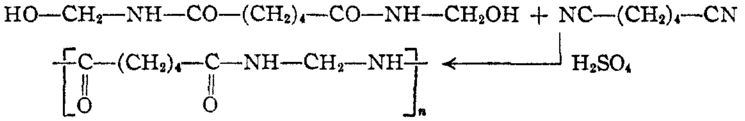
$$HO-CH_2-NH-CO-R-CO-NH-CH_2-OH + NC-R'-CN \longrightarrow$$

$$HO\text{-}CH_2\text{-}NH\text{-}\left[CO\text{-}R\text{-}CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}CO\text{-}R'\text{-}CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}\right]_n CO\text{-}R\text{-}CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}CO\text{-}R'\text{-}CN$$

If R and R' are identical the resulting polyamides correspond to the polyamides derived from methylenediamine and the parent acid of the dinitrile. These polymers are similar in character to polyamides prepared from dinitriles and formaldehyde.[4] When N,N'-dimethylolamides and dinitriles are used, the polymer end-groups consist of N-methylol ($-NH-CH_2-OH$) and cyano groups, whereas in the polymers prepared from dinitriles and formaldehyde all ends are essentially cyano groups.

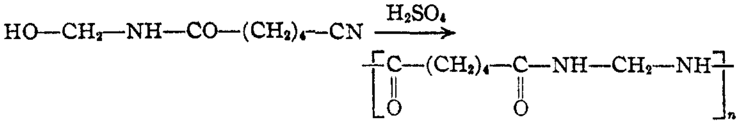
Most of the work reported here deals with the preparation of 16 polyamide, the polyamide theoretically derived from adipic acid and methylenediamine. This polyamide can be prepared by either of the two following methods involving the reaction of nitriles with N-methylolamides.

(A)



$$HO-CH_2-NH-CO-(CH_2)_4-CO-NH-CH_2OH + NC-(CH_2)_4-CN \xrightarrow{H_2SO_4} \left[-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-NH-CH_2-NH-\right]_n$$

(B)



$$HO-CH_2-NH-CO-(CH_2)_4-CN \xrightarrow{H_2SO_4} \left[-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-NH-CH_2-NH-\right]_n$$

According to Method A, a polymer of [η] 0.60 has been prepared in 69% yield in one hour at 30° from N,N'-dimethyloladipamide and adiponitrile using a solution of 96% sulfuric acid and 90% formic acid (in a 1:2.7 volume ratio) both as a solvent and as a catalyst. This method is especially valuable for the preparation of interpolymers in a known structural ratio if other nitriles are substituted for adiponitrile. According to Scheme B, a perfect balance between the N-methylolamide and nitrile groups is obtained by the use of one single reagent. N-Methylol-5-cyanovaleramide in aqueous solution was polymerized in a solution of formic acid and sulfuric acid in 2 hours at 30° to give a 65% yield of 16 polymer of [η] 0.49.

Polyamides prepared by this method exhibit the same instability to 90% formic acid at room temperature as that shown by 16 polyamide prepared

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(4) Magat, Chandler, Faris, Reith and Salisbury, THIS JOURNAL, 73, 1031 (1951).

from adiponitrile and formaldehyde.[4] The extent of degradation is shown in Table I.

TABLE I

STABILITY OF 16 POLYMER IN FORMIC ACID SOLUTION (AT 25°)

Time, min.	[η] *formic acid* of polymer prepared from N,N′-dimethyloladipamide and adiponitrile	[η] *formic acid* of polymer prepared from adiponitrile of formaldehyde
0	0.60	0.61
10	.45	
23	.43	
33	.40	
63	.37	
93	.32	.40
123	.32	
20 hr.	.10	.17

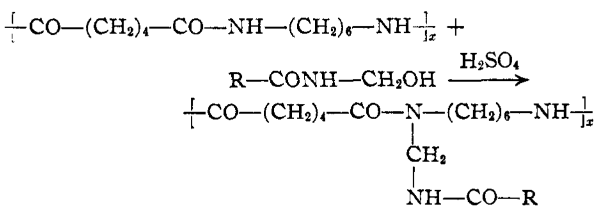
These results indicate that linkages sensitive to the action of acids (possibly due to side reactions) which occur in polymers prepared from adiponitrile and formaldehyde also occur in polymers prepared by the N,N′-dimethylolamide–dinitrile polymerization process.

The competing disproportionation reaction of N-methylolamides to yield methylene-bis-amides in acid solution mentioned above also occurs in the process of preparing polymers from N,N′-dimethylolamides and dinitriles. This side reaction may itself lead to polyamides by treating an N,N′-dimethylolamide alone with an acidic reagent.

$$n\mathrm{HO{-}CH_2{-}NH{-}CO{-}R{-}CO{-}NH{-}CH_2{-}OH} \xrightarrow{\text{acid}} \left[\mathrm{CO{-}R{-}CO{-}NH{-}CH_2{-}NH}\right]_n + n\mathrm{CH_2O} + n\mathrm{H_2O}$$

N,N′-dimethyloladipamide dissolved in concentrated sulfuric acid in a shaker tube under an atmosphere of carbon monoxide at 30° gave upon dilution with water a polymer of [η] 0.15. However, this polymerization method is relatively inefficient since degradation of the polymer is rapid under these experimental conditions.

In the preparation of polyamides from N-methylolamides in acid solution, an additional side reaction may be the reaction of N-methylolamides with the –NH– groups of the polyamide. If this reaction occurs to any appreciable extent, N-methylolamides should react with 66 polyamide to



$$\left[\mathrm{CO{-}(CH_2)_4{-}CO{-}NH{-}(CH_2)_6{-}NH}\right]_x + \mathrm{R{-}CONH{-}CH_2OH} \xrightarrow{\mathrm{H_2SO_4}} \left[\mathrm{CO{-}(CH_2)_4{-}CO{-}\underset{\underset{\mathrm{NH{-}CO{-}R}}{|}}{\underset{\mathrm{CH_2}}{\underset{|}{N}}}{-}(CH_2)_6{-}NH}\right]_x$$

form N-amidomethyl derivatives. To determine the extent of this side reaction N-methylol trichlorobutyramide was added to a 66 polyamide solution in formic or sulfuric acid. Upon reprecipitation, the polymer was analyzed for chlorine, which served as a measure of the frequency of the side-reaction. In concentrated sulfuric acid the above reaction occurred with only one –NH– group for every linear chain of 6800 in molecular weight; in formic-sulfuric acid solution the reaction occurred once for every 15,000 in molecular weight. This side reaction is therefore slow as compared to the main reaction leading to the formation of 16 polyamide from N,N′-dimethyloladipamide and adiponitrile.

Experimental

Reaction of Acrylonitrile and N-Methylolbenzamide.—A mixture of N-methylolbenzamide (0.05 mole, 7.6 g.) and acrylonitrile (0.07 mole, 3.7 g.) was added slowly to 96% sulfuric acid (50 cc.) with stirring. The temperature was kept at 30° by cooling. At the end of 1 hour the reaction mixture was poured into 200 g. of ice and water. The crystalline product which precipitated was filtered and recrystallized from water to give 6.0 g. (60% yield) of N-(benzamidomethyl)-acrylamide. This compound polymerized in the melting point tube when it was heated above 150°.

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: N, 13.7; double bonds, 1.0. Found: N, 13.5; double bonds, 1.0 (catalytic hydrogenation).

Polymonomethylene Adipamide.—A. From N,N′-Dimethyloladipamide and Adiponitrile. A mixture of N,N′-dimethyloladipamide (14.1 g., 0.069 mole) and adiponitrile (5.8 g., 0.054 mole) was added to a solution of 96% H_2SO_4 (20 cc.) and 90% formic acid (54 cc.) slowly with stirring. The reaction temperature was maintained at 30° for one hour. The solution was poured into an excess of water to give a white precipitate of 16 polymer of [η] 0.60. The yield was 13.8 g. (69%).

B. **From N-Methylol-5-cyanovaleramide.**[5]—5-Cyanovaleramide (7.2 g., 0.057 mole) was mixed with 37% aqueous formaldehyde (4.85 cc., 0.06 mole) and potassium carbonate (0.1 g.) was added as catalyst. The solution was heated to 70° on a steam-bath for one-half hour. No precipitate of N-methylol-5-cyanovaleramide was obtained upon cooling the solution. This solution theoretically contained 8.9 g. of N-methylolamide and 3.15 g. of water. To this solution 100% formic acid (28.4 g.) was added so that the total amount of formic acid corresponded to 31.5 g. of 90% formic acid. Concentrated sulfuric acid (96%, 12 cc.) was then added while the solution was stirred and cooled to 30°. Stirring was continued for an additional 75 minutes at which time the solution was poured into an excess of water. The precipitated polymer was filtered and washed with water. The yield was 5.8 g. (65%) of 16 polyamide of intrinsic viscosity 0.49.

C. **From N,N′-Dimethyloladipamide.**—N,N′-Dimethyloladipamide (0.1 mole, 20.4 g.) was dissolved in 96% sulfuric acid (100 cc.). The solution was shaken in a shaker tube in an atmosphere of carbon monoxide at 30° for 6 hours. The reaction mixture was poured into an excess of ice and water to give a white precipitate of 16 polymer of intrinsic viscosity 0.15.

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[5] Wiley and Morgan, *J. Org. Chem.*, **15**, 800 (1950).