cake was slurried successively with 600 ml. each of water and ethyl alcohol. The combined filtrate was evaporated at 15 mm. pressure by warming on a water-bath (not above 65°). A white solid remained weighing 90.5 g. (86%) after drying in a vacuum desiccator. The crude methylene-bis-acrylamide was recrystallized from a mixture of 300 cc. of acetone and enough water (about 75 cc.) to dissolve the product in the hot solution. The white solid that separated from the cooled solution weighed 71 g. (67.5% yield of purified material), m.p. 185° with polymerization.

Anal. Calcd. for $C_7H_{10}O_2N_2$: N, 18.2; double bonds, 2.0; mol. wt., 154. Found: N, 18.2; double bonds, 2.0, 1.7 (catalytic hydrogenation); mol. wt., 159, 164 (ebullioscopic).

WILMINGTON, DEL. RECEIVED JUNE 22, 1950

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

Acid-catalyzed Reactions of Nitriles. II. Polyamides from Formaldehyde and Dinitriles

BY EUGENE E. MAGAT, LEONARD B. CHANDLER, BURT F. FARIS, JOHN E. REITH AND L. FRANK SALISBURY[1a,1b]

The reaction of adiponitrile with formaldehyde in strong sulfuric acid solution at room temperature has been studied in detail. Infrared, osmotic pressure, end-group determination and solubility data show that the polymer formed is polymonomethylene adipamide (16 nylon). Infrared determinations of –CN end groups suggest that the polymer is highly branched because of the large excess of –CN ends; however, the hydrogenated polymer shows a disproportionately small number of $-NH_2$ ends which arise from hydrogenation of the nitrile ends. The polymer is unusually sensitive to degradation by acids; in 90% formic acid solution at 30° the molecular weight of the polymer is cut to one-half of its original value in one hour. The polymerization has been extended to dinitriles other than adiponitrile and to aldehydes other than formaldehyde.

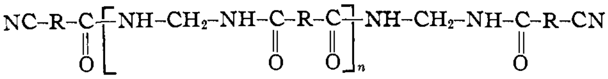
Introduction

In a previous paper[2] it was shown that nitriles react with formaldehyde under the influence of strong sulfuric acid to give methylene-bis-amides

$$2R{-}CN + CH_2O \xrightarrow[H_2O]{H_2SO_4} R{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}R$$

in yields often exceeding 90%. This paper describes work in which the reaction has been extended to the preparation of polyamides from difunctional nitriles and formaldehyde.

$$NC{-}R{-}CN + CH_2O \xrightarrow[H_2O]{H_2SO_4}$$



$$\mathrm{NC{-}R{-}}\underset{\underset{O}{\|}}{C}\left[\mathrm{{-}NH{-}CH_2{-}NH{-}}\underset{\underset{O}{\|}}{C}\mathrm{{-}R{-}}\underset{\underset{O}{\|}}{C}\right]_n\mathrm{{-}NH{-}CH_2{-}NH{-}}\underset{\underset{O}{\|}}{C}\mathrm{{-}R{-}CN}$$

The reaction product is a polymer which corresponds to the polyamide from monomethylenediamine and the parent acid of the dinitrile.

This new method of obtaining polymers[1b] permits the preparation of a type of polyamide which cannot be obtained by the conventional method of heating a diamine with a dibasic acid since monomethylenediamine is unstable in the free state.[3] Aside from yielding a new polyamide structure, this method differs from the usual procedure for polyamide preparations (heating at 200–300°) in that it is exothermic and proceeds rapidly at room temperature. Good solvents for conducting the polymerization are sulfuric and formic acids or mixtures of the two acids; these acids present the advantage of being solvents for both the starting materials and the polyamide end-product.

The polymerization reaction appears to be general and can be adapted to a large variety of dinitriles. Aldehydes other than formaldehyde can be used in the reaction to yield alkylidene-bis-amide polymers. Most of the work reported here deals with the polymerization of adiponitrile and formaldehyde which leads to polymonomethylene adipamide. In the usual nylon nomenclature the polymer is abbreviated as 16 polyamide where 1 stands for the number of carbon atoms in the diamine and 6 stands for the number of carbon atoms in the dibasic acid.

The technique employed in this type of reaction may be illustrated by the following typical polymer preparation. An equimolar solution (22.5 g.) of adiponitrile and trioxane is added over a period of 5 minutes to a solution of 90% aqueous formic acid (81 cc.) and 96% sulfuric acid (30 cc.). The exothermic reaction is maintained at 30 ± 2° by cooling with an ice-bath. After 20 minutes the initial exothermic character of the reaction subsides and the solution becomes increasingly thicker. Forty-five minutes after the start of the reaction, the product is poured into a Waring Blendor and within 3 to 10 minutes the solution assumes the consistency of a clear thick gel. Water is added immediately with rapid stirring and polymer separates as a white powder. Yields vary with the polymerization conditions and range between 30 and 95%.

The following discussion will deal with (a) the evidence for assigning the 16 polyamide structure to this polymer, (b) the evidence that it is a high molecular weight polymer, (c) the effect of polymerization variables on polymer properties and (d) the reactivity of the polymer chain toward various chemical agents.

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[1] (a) Presented before the Division of Organic Chemistry at the April, 1950, Meeting of the American Chemical Society. (b) Since the manuscript was submitted a paper dealing with the preparation of polyamides from azelaonitrile and formaldehyde has been published. Mowry and Ringwald, THIS JOURNAL, **72**, 4439 (1950). This manuscript was revised to include only new evidence for the structure of the polymers which was not presented by Mowry and Ringwald.

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

[3] Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, p. 207.

(a) Evidence for the Polymonomethylene Adipamide Structure.—The elemental analysis for carbon, nitrogen, and hydrogen closely checks that calculated for a 16 polyamide. *Anal.* Calcd. for $(C_7H_{12}N_2O_2)_n$: C, 53.83; H, 7.75; N, 17.94. Found: C, 53.81–54.34; H, 7.65–7.88; N, 17.55–17.93. Hydrolysis of the polymer by refluxing with 45% phosphoric acid gives a quantitative measure of formaldehyde which corresponds to the expected methylenediamine (18.4 to 20.0% as compared to a theoretical value of 19.25%). Upon cooling, the hydrolysis mixture precipitates adipic acid which has been isolated in 83% yield. The infrared absorption spectrum of the polymer from adiponitrile and formaldehyde shows the presence of peptide linkages –CO–NH– which are bonded as in 66 nylon (bands at 3.03, 3.25, 3.42 μ). The absorption spectrum is shown in Fig. 1; that for 66 nylon is shown in Fig. 2. The main difference between the 16 and 66 polyamide spectra is the presence of a nitrile band (–CN) at 4.46 μ which can readily be seen in Fig. 1. This band indicates an abnormally high value for nitrile groups in the polymer. Quantitative estimation of these nitrile groups is based on comparison with the infrared spectrum of adiponitrile which is shown in Fig. 3. A discussion of the high concentration of nitrile groups is given later when polymer end-groups are considered. Solvents for the 16 polymer are phenol, *m*-cresol, formic acid, α-cyanohydrins, methanol–calcium chloride and sulfuric acid, all of which are solvents for 66 nylon. This similarity in solubilities is further evidence for the polyamide structure of 16 polymer.

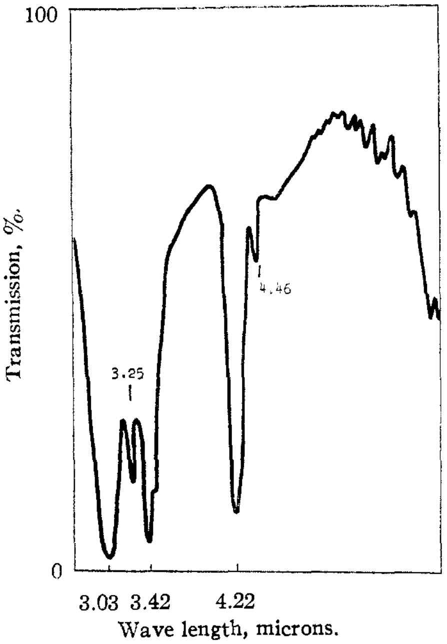

Fig. 1.—Infrared spectrum* of Nylon 16 0.001-inch film.

Fig. 2.—Infrared spectrum* of Nylon 66 0.002-inch film.

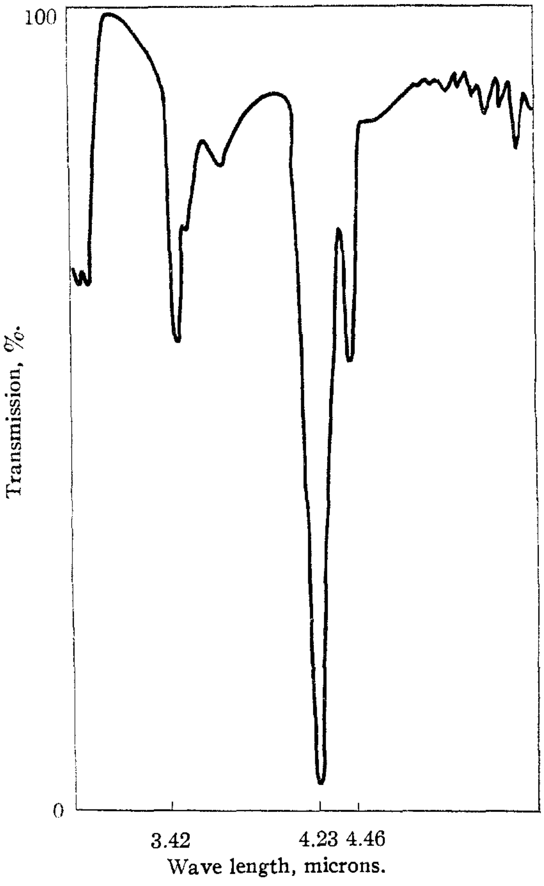

Fig. 3.—Infrared spectrum* of adiponitrile 0.0005-inch liquid cell.

(b) Evidence that the Product of the Reaction of Adiponitrile and Formaldehyde is a Polymer of High Molecular Weight.—Osmotic pressure measurements in *m*-cresol at 85° using a screw-clamped osmometer with reswollen cellophane membrane indicate a molecular weight of 10,000 to 20,000 for 16 polymers of intrinsic viscosity ranging between 1.5 and 2.0. Intrinsic viscosities vary with the preparation of the polymer, but optimum condi-

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* Tracings of spectra recorded on Perkin-Elmer Infrared Spectrometer Model 12B with rock-salt prism in accordance with instruction manual.

tions give values in the range of 1.5 to 2.1. Commercial 66 nylon has an intrinsic viscosity in the range 0.7–1.3. If the molecular weight–intrinsic viscosity relation developed for 66 nylon[4] is applied to 16 polymer without change in constants (M_n 13,000, $[\eta]$ 1.39) the number average molecular weight should be between 22,000 and 34,000. The intrinsic viscosity of 16 polymer in *m*-cresol is independent of temperature in the 25–65° temperature range. A parallel series of determinations with 66 nylon showed a similar behavior. Therefore, it may be assumed that 16 polymer does not exhibit an unduly high intrinsic viscosity because of molecular association in a poor solvent.

Clear, flexible and pliable films can be hot-pressed at 280°. Films can also be cast from solvents such as acetone cyanohydrin.

Analysis of the polymer for $-NH_2$ or $-COOH$ end groups as practiced for 66 nylon[5] showed that both were absent as would be expected from the theoretical structure of the 16 polymer. The only end groups present should be $-CN$; for a molecular weight of 10,000 there should be 54 $[-CO-(CH_2)_4-CO-NH-CH_2-NH-]$ recurring units and two nitrile end groups (200 CN groups per 10^6 g.). Quantitative estimation of nitrile groups by infrared analysis using adiponitrile as a standard shows that on a weight per cent. basis 16 polymer contains approximately 2700–CN groups per 10^6 grams. This result may indicate among other possibilities either a linear 16 polymer of molecular weight 740 or a high molecular weight branched polymer. The former does not appear to be correct in view of the high intrinsic viscosity, the high molecular weight as measured by osmotic pressure and the film-forming properties of the 16 polymer. This anomaly has not received an adequate explanation since upon hydrogenation (see below) the polymer has only 130 $-NH_2$ ends per 10^6 g.

(c) **Effect of Polymerization Variables on Polymer Properties.**—The polymerization reaction of dinitriles with formaldehyde is sensitive to changes in reaction conditions. Polymer properties are dependent on a large number of variables such as reaction time, concentration of the reagents, nature of the acid used as catalyst, temperature, molar balance of reactants, purity of reactants and introduction of extraneous components. Most of these variables have been discussed by Mowry and Ringwald[1b] in their study of the polymerization of azelaonitrile and formaldehyde. Additional data are presented in the experimental section.

(d) **Chemical Behavior of the 16 Polymers.**—The stability of the 16 polyamide toward acids, heat and hydrogenation conditions has been examined and the results are reported below. The polymer contains a multiplicity of methylene-bis-amide groups ($-CO-NH-CH_2-NH-CO-$) and as a consequence is less stable than 66 nylon.

(1) **Stability toward Acids.**—The polymer from adiponitrile and formaldehyde is rapidly degraded by acids at room temperature. This behavior is somewhat unexpected since monomeric methylene-bis-amides are moderately stable in dilute acids even when heated. Since the polymer itself is prepared in a strongly acid solution it is probable that the polymerization reaction is accompanied by a simultaneous degradation reaction.

Solutions of 16 polymer in 90 or 100% formic acid are rapidly degraded at 25° (irrespective of the method of preparation of the polymer). The decrease in intrinsic viscosity of 16 solutions in formic acid solution as a function of time is shown in Table I.

TABLE I

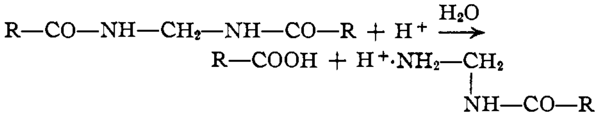
VISCOSITY STABILITY OF 16 POLYAMIDE IN FORMIC ACID SOLUTION AT 25°[d]

Time, min.	$[\eta]$ in 90% formic acid[b]	$[\eta]$ in 100% formic acid[b]	$[\eta]$ in 90% formic acid[c]
Init. polymer	1.31[a]	1.95[a]	0.61[a]
20	0.95	1.14	
50	.74	0.78	
90	.59	.63	.40
110	.52	.51	
250	.35	.30	.33
370	.28	.23	.30
2 days	.06	.10	.17

[a] Intrinsic viscosity measured in *m*-cresol. [b] Polymer prepared in formic–sulfuric acid solution. [c] Polymer prepared in 85% sulfuric acid alone. [d] Intrinsic viscosities in formic acid were determined by using an Ostwald viscometer and timing the solution through the capillary at various intervals of time after addition of the polymer to the formic acid.

In contrast to solutions in formic acid, 16 polyamide solutions in *m*-cresol at 85° show but a slight decrease of viscosity over a period of 3 weeks (drop from 2.16 to 1.76).

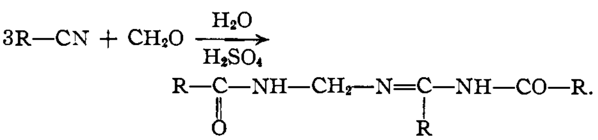
The mechanism of degradation of 16 polymer by acids as weak as formic acid is not clear. Degraded polymers ($[\eta]$ = 0.13) do not exhibit any COOH end-groups; therefore, degradation does not occur by hydrolysis of the methylene bis-amide linkage to form an acid.



$$R—CO—NH—CH_2—NH—CO—R + H^+ \xrightarrow{H_2O} R—COOH + H^+·NH_2—\underset{NH—CO—R}{\underset{|}{CH_2}}$$

Even at elevated temperatures simple methylene-bis-amides are relatively stable to formic acid. Thus methylene-bis-butyramide heated at a reflux (101°) for 19 hours in 90% formic acid yielded approximately 25% butyric acid and 75% recovered methylene-bis-butyramide.

It appears, therefore, that another mechanism must be advanced to explain the rapid degradation by acids at 25°. A plausible explanation is the hydrolysis of segments of the 16 polymer chain which are formed by side-reactions during the polymerization. An example of such a configuration is



$$3R—CN + CH_2O \xrightarrow[H_2SO_4]{H_2O} R—\underset{O}{\underset{\|}{C}}—NH—CH_2—N=\underset{R}{\underset{|}{C}}—NH—CO—R.$$

This compound could give an imide and an amide upon hydrolysis.

$$R—CO—NH_2 + CH_2O + NH_3 + R—CO—NH—CO—R$$

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(4) Taylor, THIS JOURNAL, **69**, 635, 638 (1947).

(5) Waltz and Taylor, *Anal. Chem.*, **19**, 448 (1947).

TABLE II

POLYAMIDES FROM FORMALDEHYDE AND DINITRILES OTHER THAN ADIPONITRILE

Dinitrile	Reaction medium	Reacn. time, min.	$[\eta]$ *m*-cresol	Yield, %	Molding temp. of films, °C.	Analyses, %						Product
						Carbon		Hydrogen		Nitrogen		
						Calcd.	Found	Calcd.	Found	Calcd.	Found	
Sebaconitrile	F–S[a]	65	1.01	75	200	62.3	62.9	9.5	9.4	13.2	13.2	$(C_{11}H_{20}N_2O_2)_n$
Pimelonitrile	F–S	55	Insol.	65	200	56.4	55.9	8.3	8.1	16.4	15.7	$(C_8H_{14}N_2O_2)_n$
p-Xylylene cyanide	S[b]	27	Insol.	80	280	64.7	62.5	5.9	6.2	13.7	12.2	$(C_{11}H_{12}N_2O_2)_n$
Adiponitrile–pimelonitrile (50:50)	F–S	45	0.86	65	220	55.1	54.2	8.0	8.4	17.2	17.0	$(C_{7.5}H_{13}N_2O_2)_n$
Bis-9,9-(β-cyanoethyl)-fluorene	F–S	30	1.63	25[c]	140	75.1	76.7	6.3	6.3	8.8	9.2	$(C_{20}H_{20}N_2O_2)_n$
α-Methyl-adiponitrile	F–S	80	0.28	13	190	56.4	55.0	8.3	8.3	16.4	15.3	$(C_8H_{14}N_2O_2)_n$
β,β'-Dicyanodiethyl ether	S	90	0.23	27	165	48.8	47.0	7.1	6.9	16.3	15.2	$(C_7H_{12}N_2O_3)_n$

[a] F–S contains 57.6% formic acid, 36% H_2SO_4 and 6.4% water. [b] 80 or 85% H_2SO_4. [c] Fraction soluble in acetone, another 40% was insoluble in acetone.

TABLE III

POLYAMIDES FROM ADIPONITRILE AND ALDEHYDES OTHER THAN FORMALDEHYDE

Aldehyde	Reacn. medium	Reacn. time, hr.	Temp., °C.	Yield, %	$[\eta]$ *m*-cresol	M.p., °C.
Butyraldehyde	Concd. H_2SO_4	27	2–4	40	0.36	210
Chloral	Concd. H_2SO_4	4	0–5	50	.10	200–228
Acetaldehyde[a]	Concd. H_2SO_4	3	0–5	13	.14	237–239
Propionaldehyde	Concd. H_2SO_4	3	0–5	27	.14	237–244
Valeraldehyde	Concd. H_2SO_4	2.75	0–5		.08	200–205
Hexahydrobenzaldehyde	Concd. H_2SO_4	3	−3 to 0		.08	205–220
Butyraldehyde (and terephthalonitrile)	Concd. H_2SO_4	3	0		.21	259–267

[a] Analysis of acetaldehyde–adiponitrile polymer. Calcd. for $(C_8H_{14}O_2N_2)_n$: C, 56.12; H, 8.83; N, 16.36. Found: C, 55.31; H, 8.32; N, 16.83.

Since 16 polyamide is unstable to acids it is highly important to stop the reaction at the gel point which marks the time at which the polymerization reaction ceases to predominate over the degradation reaction.

(2) **Stability to Heat.**—The 16 polymer prepared from adiponitrile and formaldehyde melts in the 300 to 325° range with decomposition. Determinations were made by dropping the polymer on a heated block. Films of the polymer were pressed at 275–290° and no degradation was apparent since the films were usually pliable, clear and colorless when prepared from a polymer of intrinsic viscosity above 1.0. However, the heating process rendered the polymer insoluble in *m*-cresol. Probably cross-linking occurred upon heating at these high temperatures. On the other hand films of 16 polymers cast from acetone cyanohydrin solution remained soluble in *m*-cresol after the film-forming process.

In contrast to N-methylolamides which lose formaldehyde upon heating, 16 polymer does not evolve any formaldehyde when it is heated above its melting point under decomposition conditions.

(3) **Stability under Hydrogenation Conditions.**—Since amine end groups can be titrated accurately in nylons,[5] mild hydrogenation of 16 polymer was carried out with the intention of hydrogenating nitrile groups to amino groups without affecting the rest of the chain of the polymer. Free amino groups could then be titrated and could serve as a measure of the initial number of nitrile ends. The initial polymer of $[\eta]$ 1.35 was hydrogenated with Raney cobalt catalyst in *m*-cresol solvent to give a polymer of $[\eta]$ 1.01. The original polymer had no amine ends; the hydrogenated polymer had approximately 1.3 amine ends per 10,000 molecular weight but the number of –CN groups as shown by infrared was not appreciably decreased after the hydrogenation.

The hydrogenation conditions used on the polymer were tried on adiponitrile and methylene-bis-butyramide as model compounds containing either nitrile ends or internal linkages similar to those of 16 polymer. Adiponitrile was 90.3% converted to amine as determined by titration; methylene-bis-butyramide was recovered unchanged and no pressure drop was observed in hydrogenation runs under conditions identical to those used for the hydrogenation of 16 polymer.

Reaction with Components other than Adiponitrile and Formaldehyde.—The polymerization reaction is applicable to other dinitriles. In the case of straight chain aliphatic dinitriles, the melting point of the polymer with formaldehyde decreases with lengthening of the carbon chain of the dinitrile. Thus the polymer from sebaconitrile and formaldehyde, 110 polyamide, melted at 225°. A phenomenon often observed in these polymers was a low melting point (*ca.* 200°) followed by resolidification and remelting above 300°. The reaction has been applied to branched chain dinitriles, aromatic dinitriles and copolymers of various nitriles. Results of these polymerizations are shown in Table II. None of these combinations presented any advantages for study over the 16 polymer system.

Aldehydes other than formaldehyde reacted more slowly with dinitriles and 96 or 100% sulfuric was necessary to effect the polymerization reaction. In general, the resulting polymers were of lower molecular weight and were lower melting than polymers obtainable by the use of formaldehyde. The various polymers prepared are shown in Table III.

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

RECEIVED JUNE 22, 1950

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

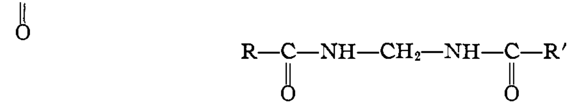
Acid-catalyzed Reactions of Nitriles. III. The Reaction of Nitriles with N-Methylolamides

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

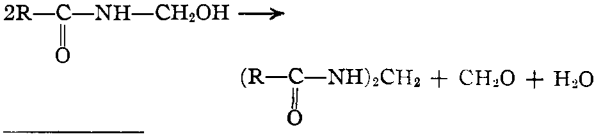
In a previous communication it was shown that nitriles react with formaldehyde in the presence of strong acids to form methylene-bis-amides.[1] The intermediate in that reaction was assumed to be an N-methylolamide carbonium ion. This paper deals with the second step of the reaction of nitriles with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



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

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]



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

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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).