On the Reaction of Aromatic Dinitriles and Formaldehyde

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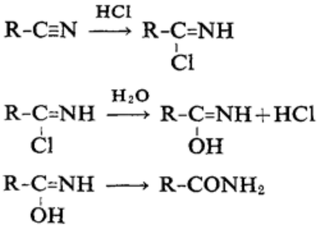
The nitrile group is known to be hydrolysed to acid amide according to the following mechanism,



$$R\text{-}C\equiv N \xrightarrow{HCl} R\text{-}\underset{\displaystyle Cl}{C}\text{=}NH$$

$$R\text{-}\underset{\displaystyle Cl}{C}\text{=}NH \xrightarrow{H_2O} R\text{-}\underset{\displaystyle OH}{C}\text{=}NH+HCl$$

$$R\text{-}\underset{\displaystyle OH}{C}\text{=}NH \longrightarrow R\text{-}CONH_2$$

the reaction being caused by the polar structure of nitrile group. Therefore it is possible to synthesize the compounds having amide linkage by the reaction between nitrile compounds and the compounds which form carbonium cation readily. If the compounds having two nitrile radicals in a molecule are used as the starting material, it is possible to synthesize macromolecules having amide linkages.

Magat(1) and Ritter(2) have studied such

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(1) E. E. Magat, *J. Am. Chem. Soc.*, 73, 1028, 1367 (1951).

(2) J. J, Ritter, ibid., 70, 4045 (1948).

reactions. Magat synthesized the polyamide known as 1,6-nylon having the following structure by reacting adiponitrile and formaldehyde in concentrated sulfuric acid at normal temperature

$$n\,\mathrm{CN(CH_2)_4CN} + n\,\mathrm{CH_2O}$$
$$\rightarrow \mathrm{CN{-}(CH_2)_4{-}}\left[\mathrm{{-}CONHCH_2NHCO(CH_2)_4 \cdot CONHCH_2NHCO(CH_2)_4{-}}\right]_n\mathrm{{-}CN}$$

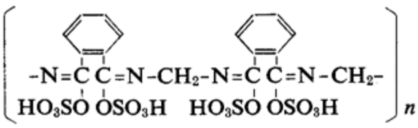
It is reported that this compound had the following properties: m. p. 225°C, mol. wt., 10,000~20,000 (by the osmotic pressure method) and the intrinsic viscosity $[\eta_{sp}/c] = 0.7 \sim 1.3$ (solvent: *m*-cresol). Magat also reported that this compound had good solvent resistance and fiber-forming ability. In his study on the dinitriles, aliphatic dinitriles have been used, but aromatic dinitriles have not been studied. However, it is probable that a new characteristic polyamide having a benzene nucleus and -CONH- linkage will be obtained by the reaction of the aromatic dinitrile and the formaldehyde.

In the present paper the reaction of aromatic dinitriles such as ortho-, iso-, tere-phthalonitrile and *p*-xylylene cyanide, with the formaldehyde has been investigated by means of Magat's method and as a result the author has been able to synthesize a new polyamide having benzene nucleus and -CONH- linkages.

The condensation polymers having -CONH- linkages in the molecule are obtained from all the above dinitriles except orthophthalonitrile. Condensation polymer from terephthalonitrile and formaldehyde has the largest intrinsic viscosity.

Results and Discussion

In the reaction of aromatic dinitriles and formaldehyde in concentrated sulfuric acid, the effect of the substituted position of two nitrile groups is shown in Table I. In the case of orthophthalonitrile, it does not react with formaldehyde. This is believed to be due to the steric hindrance of the neighboring two nitrile groups in the intermediate polymer in the sulfuric acid.



In the case of terephthalonitrile on the other hand, it reacts easily with formaldehyde without the effect of steric hindrance and the product which has the highest condensation polymerization degree is formed. Further, *p*-xylylene cyanide with difficulty causes condensation polymerization reaction with formaldehyde. This is believed to be due to the high reactivity of the methylene hydrogen between the nitrile groups and the benzene nucleus of *p*-xylylene cyanide, which easily causes the side reaction with formaldehyde.

The infrared absorption spectra of the isophthalonitrile and the terephthalonitrile condensation polymer is shown in Fig. 1.

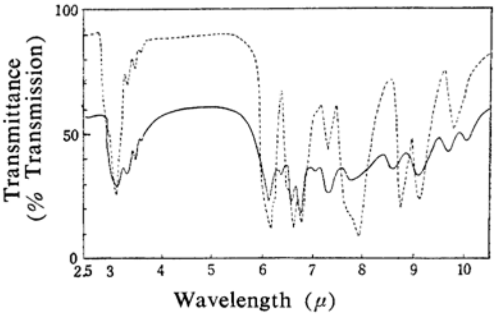


Fig. 1. Infrared spectra

—— Isophthalonitrile + $(\mathrm{HCHO})_n$ polymer
---- Terephthalonitrile + $(\mathrm{HCHO})_n$ polymer

As shown in Fig. 1, a C≡N stretching vibration at 4.5 μ disappears and an N-H stretching vibration at 3.05, 3.30, 3.45 μ, an N-H deformation vibration at 6.6 μ and a C=O stretching vibration at 6.1 μ appears as in 6,6-nylon. Furthermore, a $-\mathrm{CH_2}-$ deformation vibration at 6.75 μ is observed. So it is now clear that both of these polymers have $-\mathrm{CONH{-}CH_2{-}NHCO}-$ linkages, as expected. The result of elementary analysis indicated that these polymers have the following structures;

TABLE I. REACTION CONDITIONS AND RESULTS

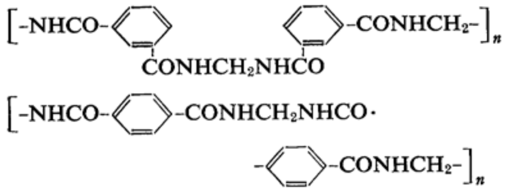
Nitriles (g.)	HCHO (g.)	95% $\mathrm{H_2SO_4}$ (g.)	React. temp. (°C)	React. periods (hr.)	Product (g.)	η_{sp}/c
Ortho- 11.30	2.75	90.70	20	3	No product	—
Iso- 11.30	2.75	90.70	20	3	Condensation polymer 15.0	0.258
Tere- 11.30	2.75	90.70	20	3	Condensation polymer 15.0	0.443
p-Xylylene 4.70	1.00	30.00	20	3	Condensation polymer 6.1	—

TABLE. II. SOLUBILITY

Solvents	Isophthalonitrile polymer		Terephthalonitrile polymer		*p*-Xylylene cyanide polymer	
	Under room temp.	Under heating	Under room temp.	Under heating	Under room temp.	Under heating
95% Sulfuric acid	Sol.	Sol.	Sol.	Sol.	Sol.	Sol.
85% Phosphoric acid	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.
90% Formic acid	Insol.	Insol.	〃	〃	〃	〃
Acetic acid	〃	〃	〃	〃	〃	〃
Monochloroacetic acid	〃	〃	〃	〃	〃	〃
Methyl alcohol	〃	〃	〃	〃	〃	〃
Acetone	〃	〃	〃	〃	〃	〃
Ethyl ether	〃	〃	〃	〃	〃	〃
Chloroform	〃	〃	〃	〃	〃	〃
Chlorobenzene	〃	〃	〃	〃	〃	〃
Benzene	〃	〃	〃	〃	〃	〃
n-Hexane	〃	〃	〃	〃	〃	〃
Phenol	〃	Sol.	〃	〃	〃	〃
m-Cresol	〃	Sol.	〃	〃	〃	〃
Carbon disulfide	〃	Insol.	〃	〃	〃	〃
Dimethyl formamide	Sol.	Sol.	〃	〃	〃	〃
Dimethyl sulfoxide	Sol.	Sol.	〃	〃	〃	〃
Aniline	Insol.	Insol.	〃	〃	〃	〃
Pyridine	〃	〃	〃	〃	〃	〃

TABLE III. EFFECT OF ADDITION CONDITION

Addition condition	η_{sp}/c
Adding terephthalonitrile into the sulfuric acid solution of formaldehyde.	0.229
Adding paraformaldehyde into the the sulfuric acid solution of terephthalonitrile.	0.174
Adding the mixture of terephthalonitrile and paraformaldehyde into the sulfuric acid.	0.428



From these findings, it is understood that the aromatic dinitrile compounds are also capable of forming polyamide as in the case of aliphatic dinitrile compounds.

As benzene rings and –NHCO– linkages are arranged alternately in such polyamide, the crystallization will be accelerated by the intermolecular hydrogen bonds between –CONH– groups and the molecules will be oriented easily. The insolubility of these condensation polymers in almost all organic solvents as shown in Table II and the higher decomposition point above 300°C without melting or softening may be attributed to this crystalline structure.

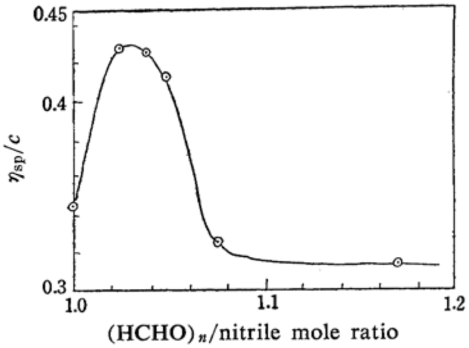


Fig. 2. Effect of the molar ratio of formaldehyde to terephthalonitrile.

In concentrated sulfuric acid, aromatic dinitrile is easily hydrolysed into acid amide and formaldehyde forms carbonium cation and becomes very reactive. Therefore, it is believed that the molar ratio between these two reagents greatly influences the condensation polymerization reaction in sulfuric acid. As shown in Fig. 2 and Table III, the product which has the highest condensation polymerization degree is obtained when the equimolecular mixture of terephthalonitrile and formaldehyde is added into sulfuric acid.

When terephthalonitrile is added into the sulfuric acid solution of formaldehyde and when the molar ratio of formaldehyde to terephthalonitrile is large, formaldehyde is always in excess to the dinitrile in the reaction solution. In this condition the side reaction with activated formaldehyde becomes so predominant that the condensation polymerization reaction is impeded and consequently the intrinsic viscosity of the reaction product becomes low. Similarly when formaldehyde is added into the sulfuric acid solution of terephthalonitrile and the molar ratio is small, the intrinsic viscosity of the reaction product becomes low. It is considered that this fact is due to the hydrolysis of terephthalonitrile into terephthalamide. It is probably for the same reason that the condensation polymerization product of great intrinsic viscosity can not be obtained when the concentration of sulfuric acid is lower than 95% and the reaction temperature is higher, as shown in Figs. 3 and 4.

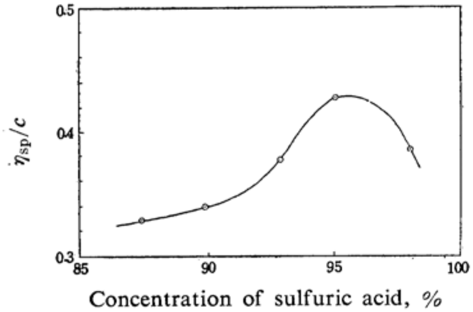


Fig. 3. Effect of concentration of sulfuric acid.

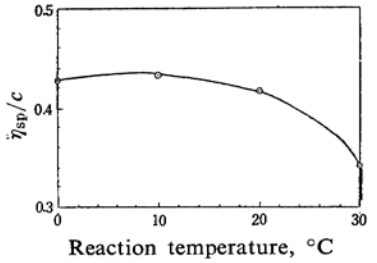


Fig. 4. Effect of reaction temperature.

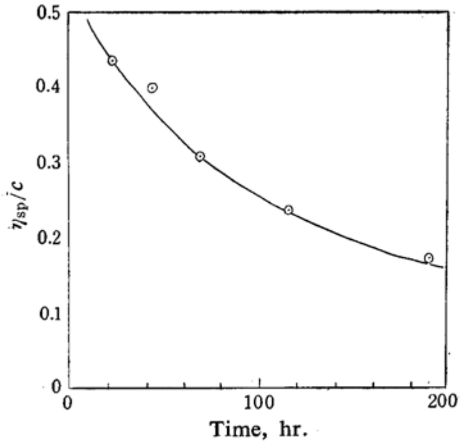


Fig. 5. Degradation by sulfuric acid.

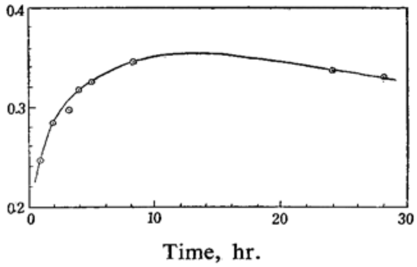


Fig. 6. Effect of reaction time.

The condensation polymer from terephthalonitrile and formaldehyde rapidly degrades in the presence of sulfuric acid at room temperature as shown in Fig. 5. This behavior is somewhat unexpected since the condensation polymer itself is prepared in the concentrated sulfuric acid. Although the mechanism of degradation is not clear, –CONH– linkage may be hydrolysed by acid. As it is probable that the condensation polymerization reaction is accompanied by a simultaneous degradation reaction, the degree of condensation polymerization of the product becomes lower when the reaction time is longer, as shown in Fig. 6.

On the other hand no condensation polymer can be obtained by reacting terephthalamide with formaldehyde under the same reaction conditions as in the case of the terephthalonitrile. Thus it is clear that the mechanism of this reaction is not considered as the formation of acid amide by the hydrolysis of nitrile group in sulfuric acid followed by the methylol condensation as in urea resins, but is considered as follows.

$$CH_2O + H_2SO_4 \rightarrow CH_2OH^+ + HSO_4^-$$

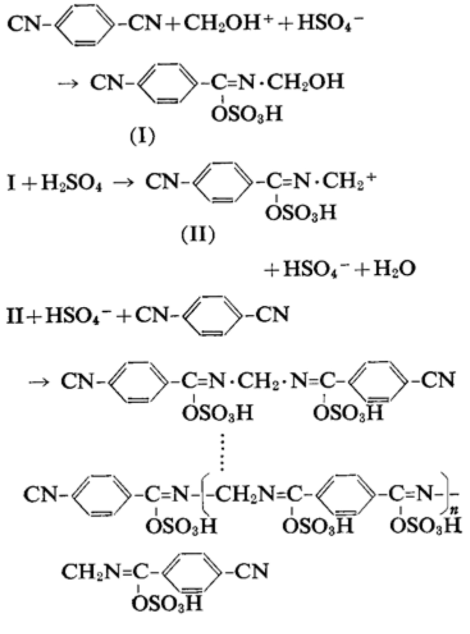
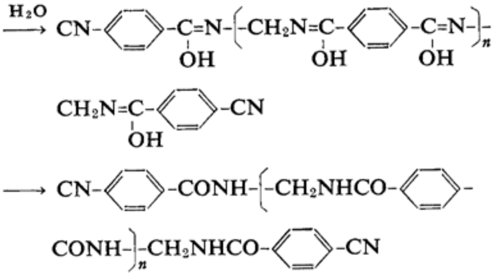


TABLE IV. ELEMENTARY ANALYSIS

Dinitrile	Found C	Found H	Found N	Calcd. C	Calcd. H	Calcd. N	
Isophthalonitrile	58.6	4.7	15.5	61.4	4.6	15.9	for $(C_9H_8N_2O_2)_n$
Terephthalonitrile	58.9	4.7	16.6	61.4	4.6	15.9	for $(C_9H_8N_2O_2)_n$
p-Xylylene cyanide	62.3	6.0	13.0	64.7	5.9	13.7	for $(C_{11}H_{12}N_2O_2)_n$



Experimental

Synthesis of Orthophthalonitrile. — Phthalamide was prepared from phthalic anhydride and aqueous ammonia by the standard method, and then phthalamide (68 g.) was dehydrated to phthalonitrile with acetic anhydride (425 g.) in chlorobenzene (88 g.) by the known method[3]. Yield 26.5 g. (50% of theoretical yield). After recrystallizing from water, a colorless crystal was obtained, m. p. 141~142°C.

Sntheysis of Isophthalonitrile. — Isophthalyl chloride was prepared from isophthalic acid and thionyl chloride, and transformed to isophthalamide with aqueous ammonia. Isophthalamide (32.8 g.) and phosphorus pentachloride (41.6 g.) were mixed in chlorobenzene (200 g.) and the mixture was heated gradually. It was heated for an hour at 98°C. until a homogeneous solution was obtained. After pouring the solution into ice water, 20 g. of crude isophthalonitrile was obtained with 78% yield. The crude material was recrystallized from water. The pure material melted at 160.5°C.

Synthesis of Terephthalonitrile.—Terephthalyl chloride was prepared from terephthalic acid and phosphorus pentachloride and transformed to terephthalamide with aqueous ammonia and then terephthalamide was dehydrated to terephthalonitrile with phosphorus pentachloride in chlorobenzene, using the same methods as in the case of the isophthalonitrile. The crude terephthalonitrile was recrystallized from benzene to needle crystals, m. p. 221.5~222.0°C.

Synthesis of *p*-Xylylene Cyanide.—A solution of potassium cyanide (13 g.) in 25 g. of water was added dropwise into a solution of *p*-xylene bromide (13 g.) in 200 cc. of ethanol at 80°C and the mixture was heated under reflux for three hours. After the reaction was completed, ethanol was distilled off and the residue was poured into ice water and filtered. The precipitate was recrystallized from ethanol and hot water to get pure *p*-xylylene cyanide (4.7 g.), m. p. 96~97.5°C.

Condensation Polymerization of Aromatic Dinitriles and Formaldehyde.—A mixture of paraformaldehyde and dinitriles was added in small portions with stirring at a constant temperature into sulfuric acid which was placed in a 100 cc. three-necked flask equipped with thermometer and stirrer. External cooling was necessary to maintain the constant temperature at 0°C because the reaction was exothermic. After the exothermic reaction was over, the mixture began to thicken gradually. The stirring was continued for two hours after the nitrile was added, to complete the reaction. The reaction product was poured into ice water with stirring to precipitate the condensation polymer. The precipitate was washed with water and the remaining acid was removed by washing with sodium bicarbonate solution (1%), then it was dried at 60°C until it was posssible to get constant weight under reduced pressure. The result of the elementary analysis is shown in Table IV.

Infrared Absorption Spectrum.—A specimen film of the condensation polymer of isophthalonitrile was prepared by evaporating the *m*-cresol solution of the polymer under reduced pressure. The specimen film of the condensation polymer of terephthalonitrile was prepared by squeezing the viscous reaction product between the two glass plates followed by washing the thin layer of polymer with water. The clear thin film thus obtained was dried under reduced pressure. The infrared absorption spectra were observed on these films using a Perkin-Elmer Model 21 spectrophotometer.

Intrinsic Viscosity.—Four hundred milligrams of the condensation polymer was added into 1000 cc. of 85% sulfuric acid and dissolved completely. This was left at 11~12°C for 24 hr. with shaking. The specific viscosity was measured on this solution by using Ostwald's viscosimeter at 30°C and the intrinsic viscosity was calculated.

The Reaction of Terephthalamide and Formaldehyde.—A mixture of terephthalamide (8.2 g.) and paraformaldehyde (1.5 g.) was added into concentrated sulfuric acid (98%, 75 g.) with stirring at 20°C. Although the stirring was continued for two hours after addition, the viscosity of the reaction mixture did not increase. When the reaction mixture was poured into the ice water, white precipitates (8.0 g.) were obtained.

Found: C, 58.41; H, 4.99; N, 17.10. Calcd. for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.07%

Summary

1. Like aliphatic dinitriles, polyamide having benzene nucleus and -CONH- linkages was synthesized by condensation polymerization reaction of aromatic dinitriles and formaldehyde in concentrated sulfuric acid.

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[3] E. Koike; *J. Chem. Soc. Japan. Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 57, 925 (1954).

2. The condensation polymer obtained from terephthalonitrile had the greatest intrinsic viscosity among ortho-, iso-, tere-phthalonitrile and *p*-xylylene cyanide. A product of the highest condensation polymerization degree was obtained, by adding the 1.025 : 1 molar mixture of paraformaldehyde and terephthalonitrile in small portions into ten molar amounts of 95% sulfuric acid at 0°C and then stirring for ten hours at the same temperature.

3. These condensation polymers were insoluble in almost all organic solvents and had no melting and softening point. They decomposed above 300°C.

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