Studies on Synthetic Polyamides (III)⁽¹⁾
Syntheses of Some Polyamides⁽²⁾

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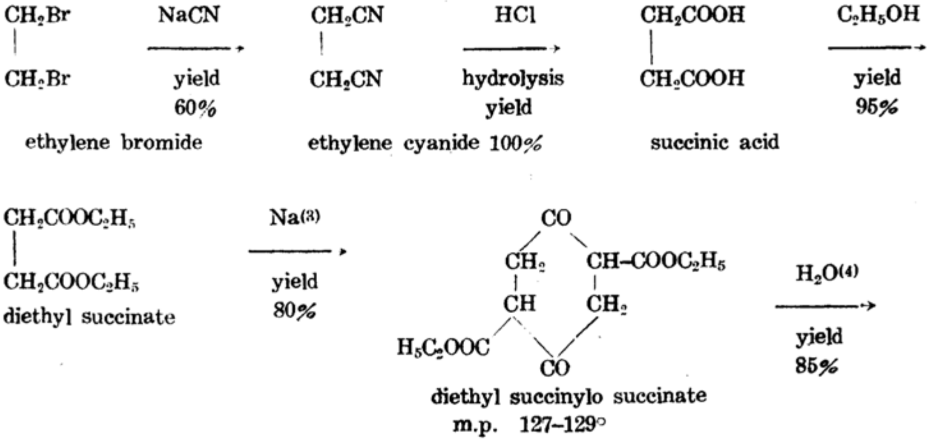
Introduction. "Nylon" manufactured by the du Pont Co. is a synthetic fibre which is made of polyhexamethylene adipamide and has no cyclic ring in its molecular structure and is not made of copolymer as "Vinyon" is. Therefore the synthesis of linear polyamides which contain cyclohexane ring, the preparation of polyamide copolymers and the study of differences between their properties and those of "Nylon" were attempted. For cyclic components of the structural unit of polyamides, *m*- and *p*- diamino derivatives of cyclohexane were selected; phenylene diamines were not suitable, for the basic strength of amino group attached to benzene ring is too weak to form salt with carboxyl group of dibasic acids. The present paper reports the data on polycyclohexylene-1,4-adipamide and polycyclohexylene-5,5-dimethyl-3,1-adipamide. Also an example of polyamide copolymer, copolymers of adipic acid, hexamethylene diamine and ε-caprolactam, were prepared and their properties are described.

Polycyclohexylene-1,4-adipamide. (1) *1,4-Diamino cyclohexane.* The methods of synthesis of 1,4-diamino cyclohexane were as follows.

[The first method]



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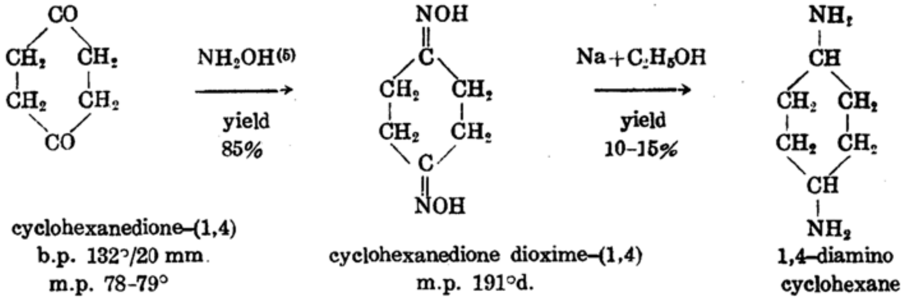
(1) The title of the author's first and second reports [this Bulletin, **18** (1943), 97, 105] was changed.

(2) K. Hosino, *J. Chem. Soc. Japan*, **62** (1941), 190, 599; **63** (1942), 1182.

(3) Vanino, "Präparativ Chemie", II, 3. Aufl., 361.

(4) Vincent, Thompson and Smith, *J. Org. Chem.*, **3** (1939), 606.



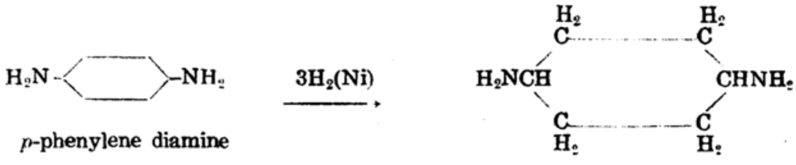
cyclohexanedione-(1,4)
b.p. 132°/20 mm.
m.p. 78-79°

cyclohexanedione dioxime-(1,4)
m.p. 191°d.

1,4-diamino cyclohexane

The reduction of the dioxime to the diamine was proceeded as follows: In a solution of 40 g. of cyclohexanedionedioxime-(1,4) in 700 c.c. of absolute alcohol, 110 g. of metallic sodium was added. As the reduction proceeded, large quantity of insoluble products accumulated. As soon as the sodium had dissolved, the contents of the flask were steam-distilled. The free diamine boiled at 181–183°, and this was a mixture of cis and trans compound.

[The second method]

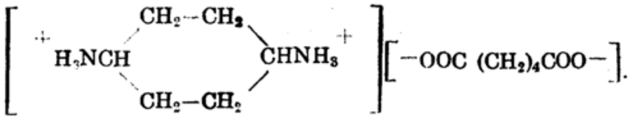


p-phenylene diamine

trans-1,4-diamino cyclohexane

Fifty g. of *p*-phenylene diamine, 50 c.c. of methyl cyclohexane and 5 g. of a reduced nickel catalyst supported on kieselguhr were charged into an autoclave. The reaction mixture was heated at 180°C. under 105 kg./cm.^{2} of hydrogen pressure with constant shaking for 8 hours. As the reaction mixture cooled, most of the hexahydro derivative crystallized out. The product consisted of 28 g. of primary amine (b.p. 170–220°), 11 g. of secondary amine and unchanged phenylene diamine (b.p. 220–270°) and 7 g. of polymerized resinous product. Redistillation of the product gave 40% of the hexahydro-*p*-phenylene diamine (b.p. 92–94°/20 m.m., m.p. 58–60°) as colourless large plates. This compound was identified as trans compound which Curtius(6) had prepared from azide of *trans*-hexahydroterephthalic acid.

(2) *Cyclohexylene-1,4-diammonium adipate,*



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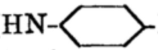
(5) Baeyer and Noyes, *Ber.*, **22** (1889), 2170.

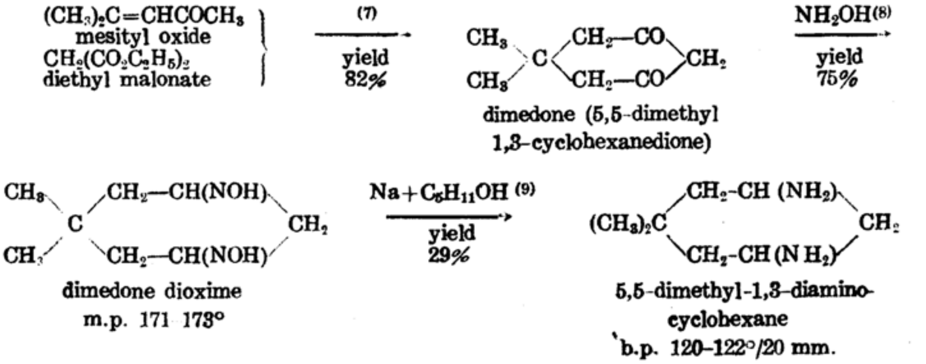
(6) Curtius, *J. prak. Chem.* [2], **91** (1915), 1.

1,4-Diaminocyclohexane and adipic acid form salt in alcoholic solution. Upon heating at 200°, this decomposed with evolution of water. Found: N, 10.49. Calculated for $C_{12}H_{22}O_4N_2$: N, 10.82%.

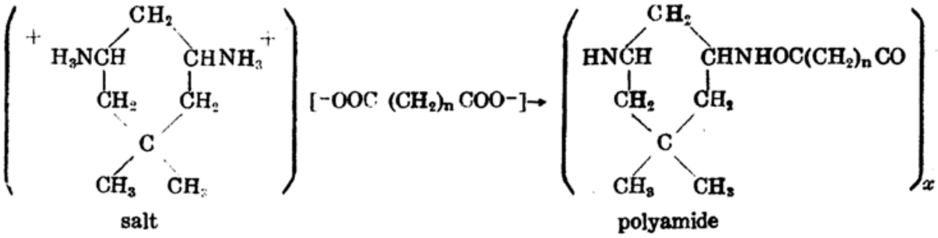
(3) *Polycyclohexylene-1,4-adipamide.* Heating the salt derived from the mixture of *cis-* and *trans*-diamine and adipic acid in thymol at 250°, water was distilled and the salt became insoluble and its melting point became about 400°. Fibre was spun from its melt with glass rod, but it was brittle. The structure of this polymer is supposed to be [HN--NHOC$(CH_2)_4$CO$]_n$. The polyamide derived from the trans diamine and adipic acid did not melt at 500° but decomposed. Its suitable solvent did not exist. The interpolymer of hexamethylene diammonium adipate and cyclohexylene-1,4-diammonium adipate was easily obtained by heating the mixture of these salts in thymol in the stream of hydrogen. Its melting point is higher than that of "Nylon", but it was more difficult to spin fibre from its melt than in the case of "Nylon".

Polycyclohexylene-5,5-dimethyl-1,3-adipamide. This polymer was obtained from adipic acid and diamine derived from dimedone.

(1) *5,5-Dimethyl-1,3-diaminocyclohexane.*



(2) *Cyclohexylene-5,5-dimethyl-1,3-diammonium adipate and polymer.*



The salt was obtained as crystalline precipitates by mixing the equivalent quantities of the diamine and the dibasic acid in alcoholic solution.

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(7) Shriner and Todd, "Organic Syntheses," **15** (1935), 14.

(8) "Organic Syntheses," **11** (1931), 54.

(9) Ruzicka, Goldberg und Hurbin, *Helv. Chim. Acta*, **16** (1933), 1339.

For dibasic acids, three kinds of dibasic acids shown in Table 1 were selected. The properties of these salts and polymers are shown in Table 2. Polymerization was effected in thymol-xylenol by heating the salts at 250–260° for about 12 hours. The three kinds of polyamide from these dibasic acids and 5,5-dimethyl-1,3-diaminocyclohexane melt without decomposition, and filaments formed by extrusion of molten polymer yields oriented fibres upon cold drawing, and its tenacity and elongation range 2–3 g. per denier and 30–40%.

Table 1.

Dibasic acid $HOOC(CH_2)nCOOH$	n	Method of preparation	Melting point	COOH% Found	COOH% Calcd.	Molecular weight Found	Molecular weight Calcd.
Adipic acid	4	By oxidation of cyclochexanol with nitric acid	151–152°	61.45	61.62	146.48	146.08
Azelaic acid	7	By oxidation of ricinus oil with potassium permanganate(10)	104–106°	46.91	47.85	191.86	188.13
Sabasic acid	8	(Kahlbaum)	134–135°	43.85	44.53	205.23	202.14

Table 2.

Dibasic acid	m.p. of salt	yield of salt, %	m.p. of polyamide	N% of polyamide Found	N% of polyamide Calcd.
Adipic abid	237–238°	88	279–282°	10.32	11.10
Azelaic acid	190–191°	75	165–170°	9.07	9.52
Sebasic acid	187–188°	83	173–176°	8.75	9.08

Copolymer. For the sake of brevity, let us denote ε-caprolactam as L, ε-aminocaproic acid as A, hexamethylene diammonium adipate as N (1 mol=131 g.). Copolymers of L or A and N were prepared as follows: The intimate mixture of both compounds was heated at 250° for 3 hours in an autoclave under the pressure 30 kg./cm.^{2} of hydrogen. The pressure was then reduced to the atmospheric, and the mixture was heated at 255° under this pressure to allow the water to distill off. Polymerization was completed by heating for 2 hours at 255° under 10 mm. pressure. Intimate mixtures of polyhexamethylene adipamide and polycapramide in various proportions were prepared by dissolving the known quantities of the two superpolyamides in *m*-cresol and precipitating them therefrom by the addition of ethanol. This gave a quantitative yield of mixed polymer in the form of a white powder. The behavior of the mixed polyamide described above is quite different from that of interpolymer prepared by co-polymerization of hexamethylene diammonium adipate and ε-caprolactam. The melting point data are presented in Figs. 1 and 2 with the data of the yield of polymer from their monomer and the intrinsic viscosities of the copolymers. From these data we can conclude that the polyamides prepared from ε-aminocaproic and that prepared from ε-caprolactam are identical and that the copolymer of the lower melting point are

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(10) "Organic Syntheses," **13** (1933), 4.

obtained when the mol ratio of L or A to N is 2:1, i.e., the ratio of the number of each structural unit is as

$-NHCO\ (CH_2)_5\ NHCO-$	4
$-CONH\ (CH_2)_6\ NHCO-$	1
$-NHCO\ (CH_2)_4\ CONH-$	1

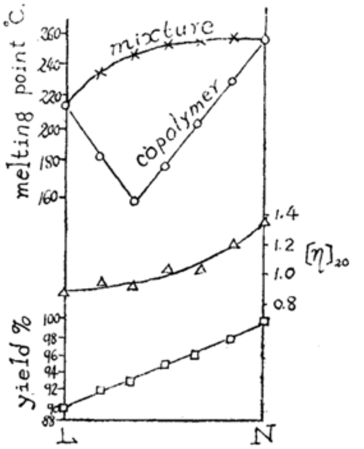

Fig. 1 L-N Copolymer

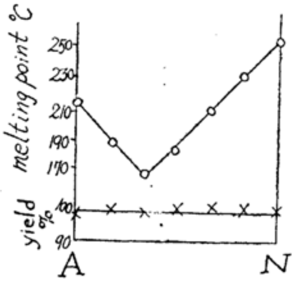

Fig. 2. A–N Copolymer.

The fibre spun from the melt of copolymer is weaker in tenacity than that spun from polycapramide or polyhexamethylene adipamide when the intrinsic viscosities of both polymers are equal. For this reason, it is conceivable that the van der Waals' force between molecular chains of copolymer, which is attributed to the hydrogen bond force of amide groups, is weaker than the force between the molecular chains of polycapramide or polyhexamethylene adipamide polymer, as the repetition of the number of the methylene group between amide linkage is irregular in the case of the former, while it is regular in the case of the latter, so the possibility of formation of hydrogen bonding is greater. The data on X-ray fibre diagram are shown in Table 3. The spots I_0 and I_1 of polycapramide are not observable in the diagram of the copolymer CS-1.

Table 3.

	Polycapramide		Copolymer CS–1 (mole ratio L:N=5:1)	
Spots	plane distance Å	fibre period Å	plane distance Å	fibre period Å
A_1	4.35	—	4.32	—
A_2	3.82	—	3.76	—
I_0	8.19	8.19	—	—
I_1	6.05	8.32	—	—
III_0	2.44	7.32	2.43	7.29

Summary

The syntheses and properties of polycyclohexylene-1,4-adipamide and polycyclohexylene-5,5-dimethyl-1,3-adipamide and copolymer of hexamethylene diamine-adipic acid-ε-caprolactam are descri

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