Studies on Synthetic Fibers (I)⑴. Decomposition and Synthesis of "Nylon".

By **Kôhei HOSINO.**

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Introduction. Synthetic linear polymers suitable for syntheic fibers are divided into two classes⑵:

(1) A-polymers (Addition polymers), produced by recurring addition of unsaturated monomers. (a) polystyrene, (b) polymethyl methacrylate, (c) polyvinyl alcohol, (d) polyvinyl acetal, (e) chlorinated polyvinyl chloride, (f) copolymer of vinyl chloride and vinyl acetate, (g) polyvinylidene chloride, etc. To this class belong the following synthetic fibers, (a) Styrolflex, (e) Gôsei-1 (Kyoto Imperial University, Japan), Kanebian (Kanegahuti Boseki K.K.), (e) Pe-Ce-Faser (I.G., Germany), (f) Vinyon (Carbide and Carbon Chemicals Corp., U.S.A.), (g) Saran (Dow Chemicals Co., U.S.A.).

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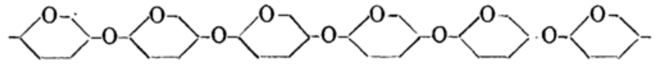
(1) *J. Chem. Soc. Japan*, **61** (1940), 475; **63** (1942), 15.

(2) Carothers, *J. Am. Chem. Soc.*, **51** (1929), 2540.

(2) C-polymers (Condensation polymers), produced by recurring condensation of bifunctional compounds. Celllulose and silk fall in this class as are shown in Table 1.(3)

Table 1.

I		Cellulose (polyacetal from glucose)
II	-NH-R-CO-NH-R′-CO-NH-R-CO-NH-R′CO-	Silk (polyamide)
III	-O-R-CO-O-R-CO-O-R-CO-O-R-CO-	Polyester (from ω-hydroxy acid)
IV	-O-R-O-CO-R′-CO-O-R-O-CO-R′-CO-	Polyester (from dibasic acid and glycol)
V	-O-CO-R-CO-O-CO-R-CO-O-CO-R-CO-O-	Polyanhydride (from dibasic acid)
VI	O-R-CO-NH-R′-CO-NH-R′-CO-O-R-CO-	Mixed polyester-polyamide
VII	-NH-R-CO-NH-R-CO-NH-R-CO-NH-	Polyamide (from ω-amino-acid)
VIII	-CO-R-CO-NH-R′-NH-CO-R-CO-NH-R′-NH-	Polyamide (from ω, ω′-diamine and dibasic acid)

These polymers were studied by Carothers since 1928, and the artificial fiber made of superpolyamide (VIII) has grown up to an industrial product under the trade name of "Nylon."(4)

Decomposition of "Nylon". The sample manufactured by du Pont Company was received in January 1939. Its properties are shown in Table 2.

Table 2.

Young's modulus: 280 kg./mm^2.

Elastic recovery (15% stretch held for one minute, recovery during one minute after release): 7.8% for "Nylon," 2.1% for viscose rayon, 3.3% for acetate rayon, 3.8% for silk.

Melting point in sealed capillary tube: 254° (cor.)

Cor. denier	No. of Filament	Fil. den.	Twist/m.	Tenacity (g./d.)	Wet tenacity (g./d.)	Elongation (%)
44.80	15	2.99	880	5.14	4.67	15.3

Hydrolysis. "Nylon" has great resistance against alkali, but is hydrolyzed with little difficulty by acid. The sample was washed with ether, dissolved in concentrated hydrochloric acid and treated as is shown in Table 3.

Thus "Nylon" yields hexamethylene diamine hydrochloride and adipic acid upon hydrolysis with hydrochloric acid, so it is proved to be polyhexamethylene adipamide. According to the study on X-ray diffraction pattern of "Nylon", its identity period along the fiber axis is 17.0 A. and number of atoms in its structural unit is 14.(5) Found: C, 63.43; H, 9.85;

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(3) Carothers, *J. Am. Chem. Soc.*, **54** (1932), 1579.

(4) A.P. 2130948.

(5) Sakurada, *Jinkenkai*, **7** (1939), 143.

N, 12.52⁽⁶⁾; N, 12.1 (Kjeldahl method); moisture, 3.31. Calculated for $C_{12}H_{22}O_2N_2$: C, 63.06, H, 9.80, N, 12.38%. *Molecular Weight.* Approximate molecular weight is determined by viscosity measurement of *m*-cresol solution of "Nylon" at 20°C. Concentration $c=0.4090$ g./100 c.c. solution, relative viscosity, $\eta_r=1.409$, $\ln\eta_r/c=0.84$. The viscosity of *m*-cresol solution is expressed by the Fickentscher's equation:

$$\frac{\log \eta_r}{c} = \frac{75K^2}{1+1.5Kc}+K\,.$$

From this equation,

$$K = 64.3\cdot 10^{-3}$$

Calculating the limit value $c \to 0$,

$$\lim_{c\to 0}\frac{\ln\eta_r}{c} = \lim_{c\to 0}\frac{\eta_{sp}}{c} = 0.87$$

Using the Staudinger's formula,

$$\lim_{c\to 0}\frac{\eta_{sp}}{c} = K_{\ddot{a}qu.}\cdot n\ ,$$

where $K_{\ddot{a}qu.}$ is a constant, $K_{\ddot{a}qu.}=1.10^{-4}$⁽⁶⁾ and n is the number of chain atoms in one molecule.

If CONH group in a linear molecule is assumed to be equivalent to $(CH_2)_2$ in respect of the contribution to the viscosity of solution,

$$n = 870\,.$$

As the structural unit is $NH(CH_2)_6NH\cdot CO(CH_2)_4CO$, the primary molecular weight $m=226$. Therefore, average degree of polymerisation $P=870/14=62$. Average molecular weight $M=mP=14000$.

Synthesis of "Nylon". (1) *Adipic acid.* 4 kg. of nitric acid (sp. gr. 1.375) with or without catalyst are warmed to 55–60° in a 5l. stainless steel beaker, and then 1 kg. of technical cyclohexanol (b.p. 160–162°) is added dropwise with mechanical stirring. Yield: without catalyst 73.5%, with 0.2% of ammonium metavanadate⁽⁷⁾ 77.3%, m.p. 150–152°.

(2) *Hexamethylene diamine* (a) Adipamide

$$HOOC(CH_2)_4COOH+2/3PCl_3 = ClOC(CH_2)_4COCl+2/3H_3PO_3\,.$$

$$ClOC(CH_2)_4COCl+4NH_3 = H_2NOC(CH_2)_4CONH_2+2NH_4Cl$$

160 g. of phosphorus trichloride (1.16 mol.) is added to 170 g. of adipic acid, then is warmed at 45–50° for 3 hours, and when cooled the upper

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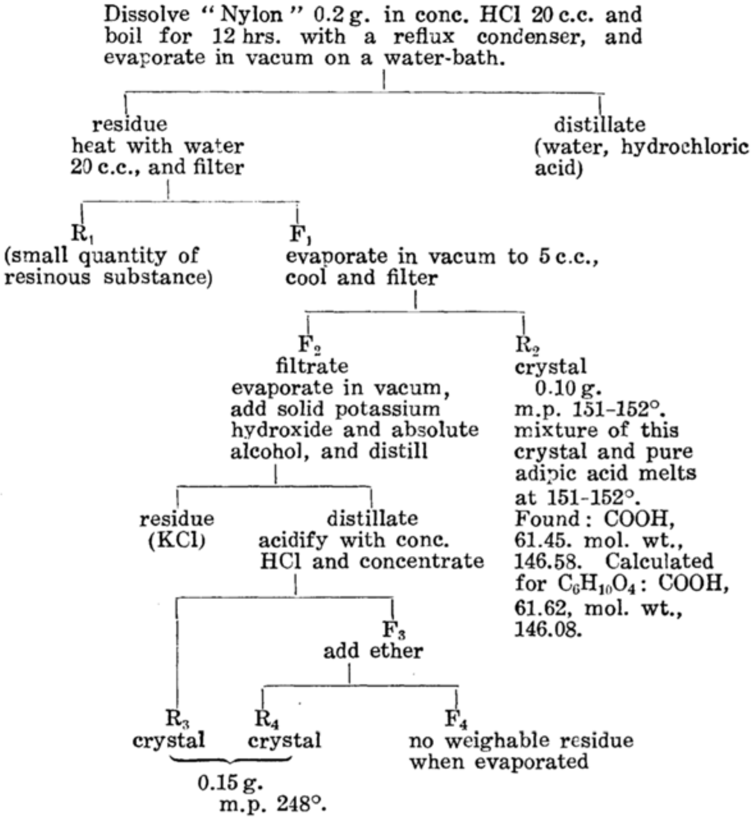
(6) Staudinger, *Melliand Textilber.*, **20**(1939), 631.

(7) "Organic Syntheses" Coll. Vol. 20.

Table 3.



Dissolve "Nylon" 0.2 g. in conc. HCl 20 c.c. and boil for 12 hrs. with a reflux condenser, and evaporate in vacum on a water-bath.

residue
heat with water 20 c.c., and filter

distillate
(water, hydrochloric acid)

R_1
(small quantity of resinous substance)

F_1
evaporate in vacum to 5 c.c., cool and filter

F_2
filtrate
evaporate in vacum, add solid potassium hydroxide and absolute alcohol, and distill

R_2
crystal
0.10 g.
m.p. 151-152°.
mixture of this crystal and pure adipic acid melts at 151-152°.
Found: COOH, 61.45. mol. wt., 146.58. Calculated for $C_6H_{10}O_4$: COOH, 61.62, mol. wt., 146.08.

residue
(KCl)

distillate
acidify with conc. HCl and concentrate

F_3
add ether

R_3
crystal

R_4
crystal

0.15 g.
m.p. 248°.

F_4
no weighable residue when evaporated

Both R_3 and R_4 are hexamethylene diamine hydrochloride.
Picrate (recrystallized from methanol): m.p. 204-205°.
Diacetyl derivative (recrystallized from benzene): needles, m.p. 125.5-126.0°.
Found: N, 13.90; 14.12. Calculated for $C_{10}H_{20}O_2N_2$: N, 13.99%.

layer is added dropwise in 30% ammonia at 15–25°. The precipitate is recrystallised from water. Yield: 68%, m.p. 220°.

(b) Adiponitrile. (i) Adipamide is dehydrated by phosphorus pentachloride in a similar way as in the case of malonitrile(8).

$$H_2NCO(CH_2)_4CONH_2+2PCl_5 = NC(CH_2)_4CN+2POCl_3+4HCl$$

Yield, 70%, b.p. 145–148°/12 mm. (ii) Or according to Lazier(9), this compound is manufactured by passing the mixed vapour of adipic acid and ammonia over heated silica gel packed in a glass tube. The best yield was obtained at 380° when 100 g. of adipic acid is passed over 45 g. of silica gel during 4 hours accompanied by a flow of ammonia with a

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(8) "Organic Syntheses," **10**, 66.
(9) B.P. 494236; A.P. 2144340.

rate of 610 c.c. per minute. Yield, 78%, b.p. 130–133/2 mm., d_4^{25} 0.96092, n_D^{24} 1.438. molecular refraction; observed, 30.0, calculated, 29.9.

(c) Hexamethylene diamine. (i) One and half liters of absolute ethyl alcohol saturated with ammonia and 54 g. (0.5 mol) of adiponitrile are placed in the flask and then 230 g. (10 atoms) of sodium is added in one lot. After all sodium is dissolved, the mixture is acidified with conc. hydrochloric acid and insoluble salts (sodium chloride and ammonium chloride) are filtered.

$$NC(CH_2)_4CN+8Na+8C_2H_5OH = NH_2(CH_2)_6NH_2+8C_2H_5ONa\,.$$

The hexamethylene diamine hydrochloride (m.p. 248–250°) obtained by evaporation of the filtrate is mixed with solid potassium hydroxide and the free diamine is distilled. Yield 50%, b.p. 195–200°; m.p. 38–40°.

(ii) Catalytic reduction(10). One hundred g. of adiponitrile, 100 g. of liquid ammonia, and 10 g. of nickel on kieselguhr catalyst(11) are sealed in a shaking autoclave. Hydrogen is forced into the autoclave until the total pressure reaches 120 kg./cm.² while the temperature is maintained at 120° for 6 hours. The main product of the reaction, hexamethylene diamine, b.p. 90–92°/14 mm., 194–195°, m.p. 39–40°, is 81 g. in yield (78% of the theoretical).

Small quantity of hexamethylene imine, b.p. 136–138°, is also obtained as a by-product. If the nickel catalyst is substituted by cobalt-on-kieselguhr catalyst, 100 g. of the pure di-nitrile is completely hydrogenated in about 4 hours and yields 102 g. of hexamethylene diamine.

(3) *Hexamethylene diammonium adipate* ("Nylon" salt)

$$[{}^{+}H_3N(CH_2)_6NH_3^{+}]\ [{}^{-}OOC(CH)_4COO^{-}]$$

This salt was prepared by mixing hexamethylene diamine and adipic acid in alcoholic solution(3). It melted at 194–195°(12), yield of the twice recrystallized salt: 63%. Found: N, 10.65; 10.47. Calculated for $C_{12}H_{26}O_4N_2$: N, 10.68%.

(4) *Polymerisation*. (i) Polymerisation in solution. A mixture of hexamethylene diammonium adipate and p-xylenol—thymol (1:1) was placed in a glass vessel fitted with a reflux air condenser. The mixture was heated for 6–12 hours in a stream of nitrogen (washed by Franzen's solution) or carbon dioxide or hydrogen (dried over phosphorus pentoxide) in a salt-bath consisting of a mixture of potassium nitrate and sodium nitrate in mol ratio. Syringic acid (4-hydroxy-3, 4-dimethoxybenzoic acid)(13), antioxidant, was synthesized by heating 3,4,5-trimethoxy-benzoic acid(14), which is obtained from gallic acid and dimethyl sulphate, with 48% hydrobromic acid. M.p. 197–203°. On heating the water formed in the reaction was removed as distillate. After 6–12 hours heating, the

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(10) B.P. 490922. Howk, A.P. 2166152; Signaigo, A.P. 2166183.

(11) Adkins, "Reactions of Hydrogen," **19**, Wisconsin (1937).

(12) According to Carothers' description, m.p. 183–184°.

(13) Alimchandani and Meldrum, *J. Chem. Soc.*, **117**(1920), 964.

(14) *Ann.*, **340**(1905), 220.

entire reaction mass was poured gradually with stirring into a large volume of ethyl alcohol. The polyamide precipitated as a white granular powder and was filtered, washed with alcohol, and dried. It dissolved in phenol or *m*-cresol or formic acid after swelling. Found: N, 12.31, 12.24. Calcd. for $C_{12}H_{22}O_2N_2$: N, 12.38%. M.p. 250–253°. The examples are shown in Table 4. A 20% solution of this polyamide in anhydrous phenol was spread on a glass plate and dried at 80°. The film thus obtained had the tenacity of 2.1 kg./mm.^{2} and the elongation of 6%, and could be dyed very satisfactorily with dyes of acid group, e.g., Silk Blue R, Silk Yellow, Brilliant Scarlet 3R, Wool Violet 4B extra, Silk Green, and dyes used for cellulose acetate rayon, e.g., Celliton Fast Red R, Setacyl Direct Blue, etc.

Table 4.

Polyamide No.	3	4	5	9
"Nylon" salt (g.)	40	80	57	100
p-Xylenol-thymol (g.)	50	80	60	150
Syringic acid (g.)	0.3	2	0	0
Bath-temp. (°C.)	230–250	240	230	240–250
Time (hr.)	6	8	7	12
Intrinsic viscosity, $[\eta]$	0.865	1.069	0.684	1.1593
Number of chain atoms in one molecule, n	865	1070	684	1160
Degree of polymerisation, *P*	62	71	49	83
Molecular weight, *m*	14000	16000	11000	18700
Extent of reaction, *p*	0.9835	0.9856	0.9791	0.9877

Extent of reaction, *p*, was calculated by the following equation,

$$p = 1 - \frac{1}{70\,[\eta]}$$

where $[\eta] = \lim_{c \to 0} \frac{\ln \eta_r}{c}$ in *m*-cresol solution at 20°C.

(ii) Polymerisation in a closed vessel in the absence of solvent (Fusion method). A mixture of 135 g. (0.5 mole) of hexamethylene diammonium adipate and 0.7 g. (0.005 mole) of adipic acid (viscosity stabilizer) was placed in a 550 c.c. stainless steel autoclave. Air was removed from the autoclave by evacuation, followed by filling with hydrogen (5 kg./cm.^{2}). The autoclave was heated to 280° in a salt-bath during 1.5 hours. The pressure was then reduced to atmospheric during 0.5 hour and the heating continued for 2 hours. The pressure was then reduced to 10 mm. absolute pressure for 5 minutes. After cooling, the polymer was removed from the autoclave as a white cake. It had an intrinsic viscosity of 1.36 and good fibers were obtained on spinning from melt.

(5) *Spinning.* (a) Wet Process. A 25% solution of polyphexamethylene adipamide in a solvent mixture approximately consisting of 89% phenol and 11% water or in formic acid was spun from a spinneret having 10 orifices of 0.1 mm. diameter into a coagulating bath of a 4% aqueous sodium hydroxide solution. But this did not give a satisfactory result. A spinning-bath consisting of ether, alcohol, or petroleum ether gave the same result. When the spinning solution was dropped on a water surface,

a transparent film was obtained. Fibers were obtainde from this film by stretching ten fold in length (Table 5).

(b) *Dry Process.* A 30% solution of polyhexamethylene adipamide in 95% formic acid was dry spun from an orifice of 0.12 mm. diameter provided at the bottom of a small brass tank (capacity 30 c.c.) in an apparatus used for spinning the cellulose acetate rayon (4 m. in length and 30 cm. in diameter).

The spinning conditions and the properties of obtained fibers are compared with Ex. VII of Carothers' A. P. 2130948 as in Table 6. The cross section of this fiber is a crenellated circle, and approaches to a perfect circle as the fiber cold draws.

Table 5.

Diameter (μ)	Denier (d.)	Tenacity (g./d.)	Elongation (%)
8	0.52	4.8	21.3
24	4.6	1.4	19.3

Table 6.

	Carothers	the author	
Intrinsic viscosity, [η]	1.48	1.01	
Concentration (%)	29.2	30	
Diameter of orifice (mm.)	0.1	0.12	
Spinning pressure (kg./cm².)	10	3	
Temp. (°C.)	70	75	
Spinning speed (m./min.)	25	50	
Cold drawing (%)	145	100	400
Denier (d.)	2.25	4.75	3.23
Denier at break (d.)	0.80	—	2.55
Tenacity (g./d.)	1.68	1.48	4.67
Tenacity at break (g./d.)	4.73	—	5.93
Wet tenacity (g./d.)	—	1.30	3.24
Elongation (%)	180	37.2	26.8

Table 7.

Cold drawing (%)	0	100	200
Denier (d.)	26	13.9	6.3
Tenacity (g./d.)	0.94	2.14	2.44 (wet: 1.75)
Elongation (%)	371.8	148	55.0 (wet: 112.8)
Denier at break (d.)	5.5	5.6	4.1 (wet: 3.0)
Tenacity at break (g./d.)	4.43	5.30	3.78 (wet: 3.73)
Testing machine	K.S. senimeter	K.S. senimeter	Mackenzie

(c) *Melt Process.* Polyhexamethylene adipamide was heated at 270° in a cylindrical brass vessel surrounded by an electrically heated salt-bath (a mixture of potassium nitrate and sodium nitrate in mole ratio) and provided at the bottom with an orifice 0.4 mm. in diameter. The top of the vessel was connected with a tube through which hydrogen is passed under a gauge pressure to 5 kg./cm². The extruded filament was collected on a motor-driven drum having a peripheral speed of 90 m./min. The cold-drawn fiber was lustrous and silky in appearance with the properties as is shown in Table 7. From this polyamide, monofil suitable for fishline was also spun by using a specially made spinning machine. The melted polyhexamethylene adipamide (intrinsic viscosity 0.946) was extruded through the spinneret orifice (diameter 1 mm.) at the rate of 5 g. per minute. The spinning rate was 30 m. per minute and the drawing rate 100 m. per minute, corresponding to 220% cold drawing. The resultant fiber had a denier of 274.4, a dry tenacity of 4.32 g. per denier, and an elongation of 23.3%. The wet strength of this fiber was 3.96 g. per denier and the wet elongation was 29.6%. The cross section of this fiber obtained by melt spinning is perfectly circular whether the fiber is cold drawn or not (Fig. 1). The boundary at the junction between the drawn and the undrawn sections of the filament is shown in Fig. 2. Load-elongation curve of this fiber is similar with that of "Nylon".

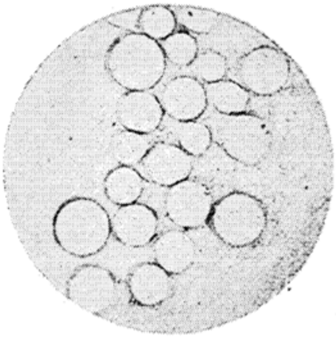

Fig. 1.

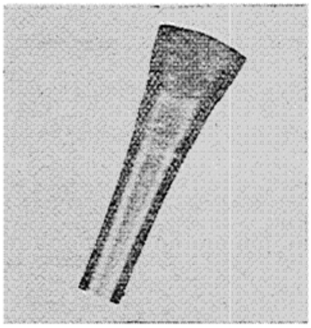

Fig. 2.

Summary.

(1) "Nylon" yields hexamethylene diamine hydrochloride and adipic acid upon hydrolysis with hydrochloric acid, so it is proved to be polyhexamethylene adipamide.

(2) Superpolyamide was synthesized from adipic acid and hexamethylene and an excellent synthetic fiber was spun from this polymer.

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Research Department, Tôyô Rayon Kaisya,
Otu, Japan.