*Studies of the Structure and Properties of Aromatic Polyamide. I. Physical Properties of Poly(m-xylyleneadipamide)**

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It has been reported that *m*-xylylenediamine reacts with various aliphatic dibasic acids to form high molecular weight polyamides(1).

The polymer of *m*-xylylenediamine and adipic acid shows the effects caused by a reversal of the position of the carbonyl groups relative to the amide nitrogen, compared to that of the polymer of isophthalic acid and hexamethylenediamine(2,3). *m*-Xylylenediamine has the characteristic high reactivity of aliphatic diamines mainly due to the side-chain methylene group, which is considerably more reactive than aromatic diamines(4,5). The present investigation was undertaken to study the physical properties of a melt-spun filament of aromatic polyamide obtained from *m*-xylylenediamine and adipic acid; as described herein, studies of the dynamic mechanical properties as well as of the chemical behavior of the polymer reveal that it possesses properties intermediate between poly-ε-capramide and polyethylene terephthalate.

Experimental

Polymerization of *m*-Xylylenediamine and Adipic Acid.—Commercially available *m*-xylylenediamine was distilled under reduced pressure, and the fraction boiling at 114°C/1 mmHg was used for the polymerization. The purified adipic acid (m. p. 133°C) was obtained by crystallization of commercially available dibasic acid from aqueous ethanol. The *m*-xylylenediamine adipic acid salts were prepared according to the following procedure(6): 14.6 g. (0.1 mol.) of adipic acid was added into a solution of 13.6 g. (0.1 mol.) of *m*-xylylenediamine in 28.2 ml. of water in order to obtain a concentrated warm solution of the salt. When the solution had been cooled, a white crystalline solid precipitated out slowly. In order to complete the precipitation of the salt, 113 ml. of isopropanol was added. The white solid was filtered, washed with isopropanol, and dried under vacuum at 60°C. The yield of salt was 93%, m. p. 193∼194°C. The nylon salt thus obtained was polymerized at an elevated temperature with the following procedure: Excess adipic acid (0.075 mol. %) was added as a stabilizer, and the salt was heated at 180 to 190°C in a Claisen flask under a nitrogen atmosphere. Then the polymerization temperature was gradually raised to 260°C over a 1∼1.5 hr. period. The polymer was held at 260°C for 2 hr. at atmospheric pressure before applying a vacuum (1 to 5 mmHg) for 0.5 to 1 hr. to complete the polymerization. The resulting polymer had a melting point of 243°C, $d_4^{25}=1.2059$, and the intrinsic viscosity measured in *m*-cresol at 25°C was 0.96. It showed the typical infrared spectrum of polyamide, indicating a NH band (hydrogen bonding) at 3297 cm^{-1}, an amide I band at 1639 cm^{-1} and an amide II band at 1545 cm^{-1}. Experimental details will be discussed in a forthcoming paper**.

Melt-spinning of Poly(*m*-xylyleneadipamide).—A small scale melt-spinning instrument, composed of a heating cylinder, plunger, spinneret (0.5029 mm. diameter, 0.402 mm. length) and with a

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1) E. F. Carlston and F. G. Lum, *Ind. Eng. Chem.*, **49**, 1239 (1957).

2) F. G. Lum and E. F. Carlston, ibid., **44**, 1595 (1952).

3) A. J. Yu and R. D. Evans, Abstracts of papers, 135th Am. Chem. Soc. Meeting, Boston, Mass. (April 5-10, 1959), p. 23s.

4) P. J. Flory, U. S. Pat. 2244192 (June 3, 1941).

5) W. W. Triggs, Brit. Pat 525516 (Aug. 29, 1940).

** N. Yoda and I. Matsubara, *J. Polymer Sci.* (1962), in-press.

6) W. H. Carothers, U. S. Pat. 2130947 (Sept. 20, 1938).

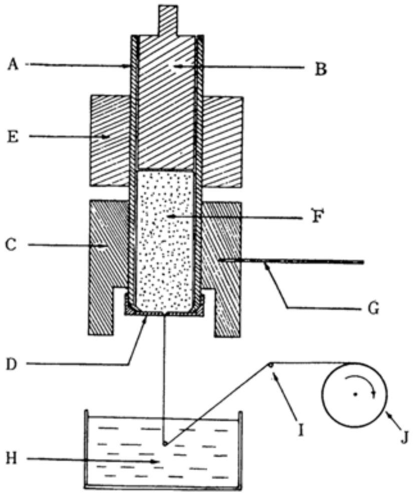

Fig. 1. Melt-spinning apparatus of polymer.

A Heating cylinder
B Plunger
C Heating jacket
D Spinneret
E Cooling jacket
F Polymer block (candle)
G Thermometer
H Cooling bath
I Guide
J Take-up roller

heating and cooling jacket, a cooling bath and a take-up roller, as shown in Fig. 1, was used as the apparatus.

The spinning block of the polymer was prepared by melting the polymer flakes in a sillicone-varnished (DC 20) glass cylinder under dry nitrogen atmosphere under vacuum at an elevated temperature. After pressing the melt with the steel plunger to complete the deairation at 245~250°C, it was cooled gradually to form the polymer block, which was ready to use for spinning.

The following spinning conditions were employed for the melt-spinning of poly(*m*-xylyleneadipamide) shown in Table I.

TABLE I. MELT-SPINNING CONDITIONS OF POLY-(*m*-XYLYLENEADIPAMIDE)

Item	Condition
Spinning temperature	265°C
Diameter of polymer block	27 mm.
Pressing speed	0.260 cm./min. (press, 282 r. p. m.)
Diameter of spinneret	0.5029 mm. (length : 0.402 mm.)
Rate of take up	30 m./min.
Length of air cooling	1.5 m. (at 25°C)
Cooling bath temperature	5°C

Drawing and Heat-setting of the Undrawn Filament. — The undrawn filament thus obtained was heat-stretched in a water bath at 79°C, the draw ratio of 3.4—4.5 was found to be the optimum. (Low speed, 5 m./min., high speed 25 m./min.) The stretched filament was treated either at 180°C for 5 min. or at 187°C for 10 min. in a thermostat drier for the heat setting.

Measurement of Density. — A mixed solvent composed of carbon tetrachloride and toluene was used, and the density was measured by the flotation method7).

Measurement of the Stress-strain Curves of the Filaments.—Stress (g./D) and strain (%) curves were obtained by the use of an Instron tensile-testing instrument.

Measurement of Light Resistance.—The drawn filaments were exposed to light by means of a Atlas Fade-O-meter for a certain period of time and the tensile strength of the irradiated specimens was then measured.

Results and Discussion

Stress-strain Diagram of Poly(*m*-xylyleneadipamide) Mono-filament.—The stress-strain curves of melt-spun mono-filaments are shown in Fig. 2. The stress-strain characteristics change as expected with an increase in the strain rate. The tenacity of the drawn filament is 5.93 g./D., whereas the heat-set filament shows a tenacity of up to 6.79 g./D.

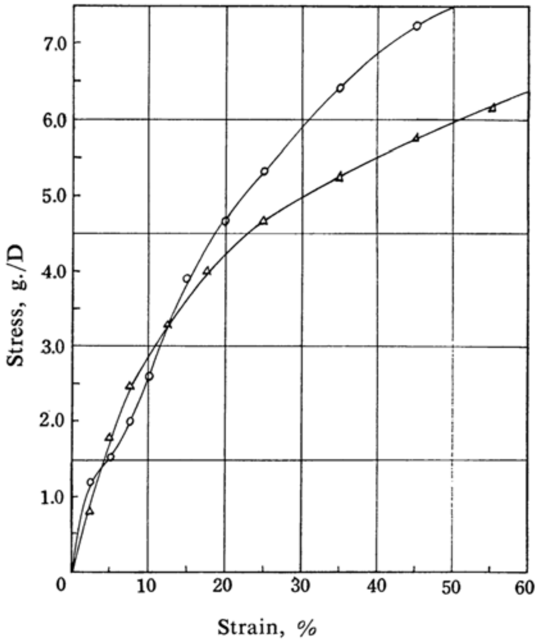

Fig. 2. Stress-strain curve of poly (*m*-xylyleneadipamide) mono-filament.
○ Heat-set filament △ Drawn filament

Wet and Dry Knot, and Loop Tenacity.—The wet and dry knot, and the loop tenacity are compared with those of polycapramide and polyethylene terephthalate in Table II and Fig. 3.

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7) C. E. Black and M. Dole, *J. Polymer Sci.*, **3**, 358 (1948).

TABLE II. DRY AND WET KNOT, AND LOOP TENACITY

Polymer	Dry, knot, and loop tenacity g./D	Wet, knot, and loop tenacity g./D
MXDA-6	5.36	4.18
Polyester	4.5—7.0	4.5—7.0
Polycapramide	4.5—7.0	4.0—6.5

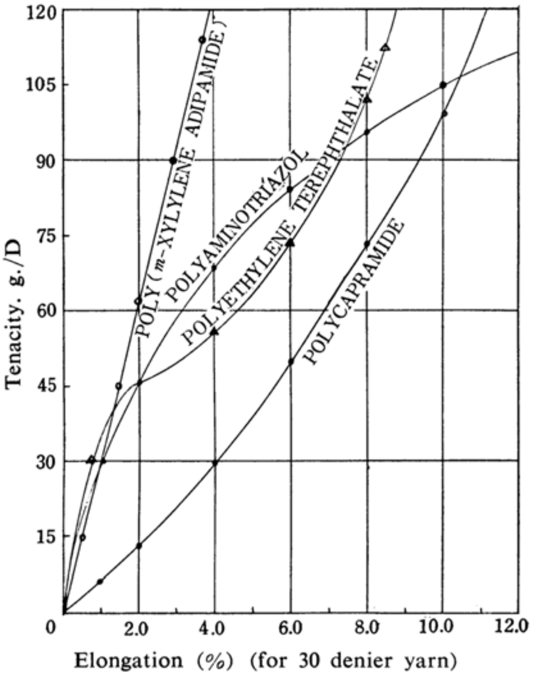

Fig. 3. Relation between elongation and tenacity of poly(*m*-xylyleneadipamide) mono-filament[8].

Measurement of Shrinkage.—The shrinkage of the heat-set filament in boiling water was measured at 4.0%.

Measurement of Light-resistance.—The light-resistance of the heat-set filament was measured by means of an Atlas Weather-o-Meter over the periods of 10, 20, 40 and 80 hr.

The ratio of the tenacity of irradiated to that of unirradiated filament is plotted against the irradiation time in Fig. 4. It can be seen in Fig. 4 that a 25% decrease in the tenacity was observed for 40 hr. irradiation, and 30% for 80 hr. exposure.

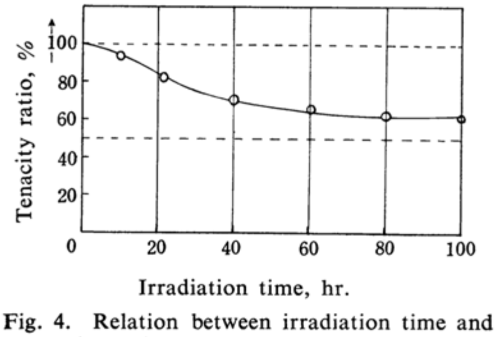

Fig. 4. Relation between irradiation time and tenacity ratio.

Elastic Recovery of the Heat-set Filament.—The elastic recovery was measured by the Instron instrument at a 5% elongation and a 10% elongation, the results are summarized in Tables III and IV respectively.

TABLE III. ELASTIC RECOVERY OF POLY-(*m*-XYLYLENEADIPAMIDE) FILAMENT

No.	Immediate recovery	Delayed recovery	Deformation
1	57/81=0.705	24—20/81=0.0495	20/81=0.247
2	67/80=0.815	15—12/80=0.0376	12/80=0.150
3	54/77=0.700	23—20/77=0.0390	20/77=0.261
$\overline{X}$	0.740	0.042	0.219

TABLE IV. ELASTIC RECOVERY OF POLY-(*m*-XYLYLENEADIPAMIDE) FILAMENT

No.	Immediate recovery	Delayed recovery	Deformation
1	110/197=0.560	87—54/197=0.167	54/197=0.273
2	110/196=0.561	86—55/196=0.158	55/196=0.280
3	110/196=0.561	86—53/196=0.168	54/196=0.270
$\overline{X}$	0.561	0.164	0.274

It was found that the elastic recovery of the filament is 78.2% or better at the 5% elongation and that at the 10% elongation the elastic contribution (immediate plus delayed) drops

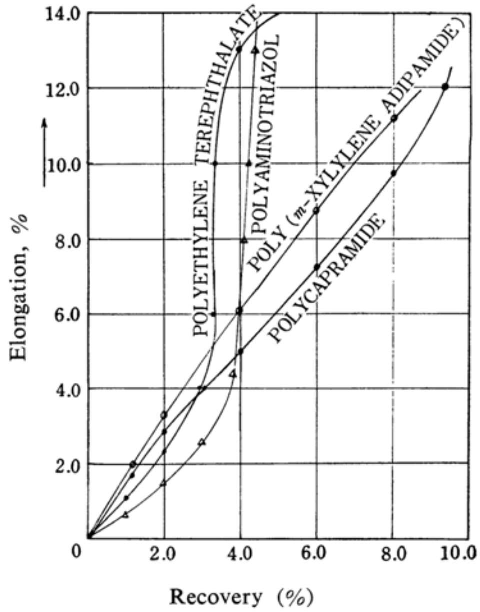

Fig. 5. Elastic recovery and elongation of poly (*m*-xylyleneadipamide) yarn, as compared with other fibers.

to 72.5%. Similar results were obtained from the repeated stress data. The elastic recovery of the poly(*m*-xylyleneadipamide) filament is compared with that of polyester, polycapramide and polyaminotriazole in Fig. 5.

Measurement of the Dynamic Modulus of Elasticity and of the Loss Factor (tan δ).—The dynamic modulus of elasticity, E_2, is expressed in terms of the product of the frequency, ω, and the dynamic coefficient of the viscosity, η, as follows;

$$E_2 = \omega\eta \tag{1}$$

The loss factor, tan δ is expressed in Eq. 2, where E_1 is the modulus of the elasticity.

$$\tan\delta = E_2/E_1 \tag{2}$$

The observed data in Eqs. 1 and 2 are shown in Table V.

TABLE V

Filament	Dynamic modulus of elasticity, $E_2 \times 10^{10}$ dyn./cm^2,	Loss factor tan δ $\times 10^{-2}$
Stretched and nonheat-set filament	5.08	2.2
Stretched and heat-set filament	5.34	1.9

The values thus obtained are compared with those of polycapramide and polyethyleneterephthalate in Table VI.

TABLE VI

Polymer	Dynamic modulus of elasticity, $E_2 \times 10^{10}$ dyn./cm^2	Loss factor tan δ $\times 10^{-2}$
Nylon 6	4.2	10
Nylon 6.10	4.5	4.4
Polyester (×5 drawn)	4.5	1.5
Polyester (×7 drawn)	1.3	1.5

It can be seen from Table VI that the poly(*m*-xylyleneadipamide) filament possesses physical properties intermediate between nylon 6 and polyester.

Measurement of Density.—The density was measured by the floating method, using a toluene/carbon tetrachloride solvent mixture. A modified pycnometer was employed at 25.0°C for the measurement.

The observed values are summarized in Table VII.

TABLE VII. DENSITY OF POLY-(*m*-XYLYLENEADIPAMIDE)

Density	Un-stretched	Stretched	Annealed
d_4^{25}	1.2059	1.2219	1.2248

It was again concluded that the density of poly(*m*-xylyleneadipamide) shows a value intermediate between polycapramide and polyethylene terephthalate, as is shown in Table VIII.

TABLE VIII

Density	Polycapramide	Poly (MXD-6)	Polyethylene terephthalate
d_4^{25}	1.14	1.23	1.38

Viscosity Measurement.—The intrinsic viscosity was measured in *m*-cresol at 25.0°C.

$$[\eta]^{25^\circ\mathrm{C}}_{m\text{-cresol}} = 0.96$$

In a diluted concentration range of the *m*-cresol solution, an abnormal increase in specific viscosity was observed, as is shown in Fig. 6.

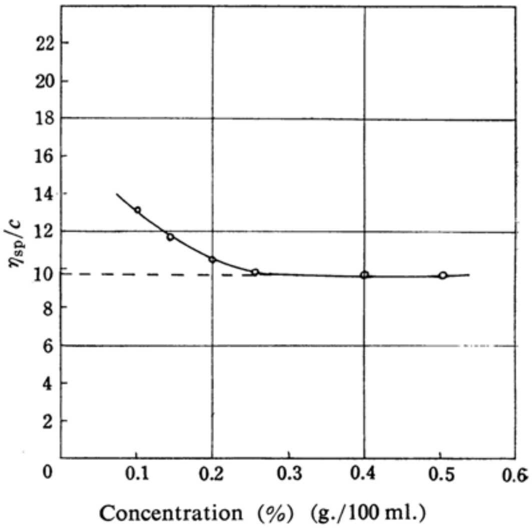

Fig. 6. Relation between reduced viscosity and concentration of poly(*m*-xylyleneadipamide) measured in *m*-cresol at 25°C.

Summary

Poly(*m*-xylyleneadipamide) was synthesized by the polycondensation of *m*-xylylenediamine and adipic acid, and the resulting polymer was melt-spun to afford a mono-filament. The physical properties of the undrawn filament, the stretched filament, and the stretched and annealed filament were investigated. It was found that the dynamic mechanical behavior and the chemical property of the aromatic polyamide are intermediate between poly-ε-capramide and polyethylene terephthalate.

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8) J. W. Fisher, *J. Applied Chem.*, **4**, 212 (1954).

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