Studies on Synthetic Polyamide (V).⁽¹⁾
Precipitability and Melt Viscosity.⁽²⁾

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Introduction. The present investigation attempts to find the relation between precipitability and solution viscosity, and the relation between melt viscosity and solution viscosity for the polyamide derived from ε-aminocaproic acid.

Methods.

Materials. Pure ε-caprolactam was prepared, isolated and purified by vacuum distillation as described in my second paper.⁽³⁾ One mole of ε-caprolactam which had dissolved various quantity of pure butyric acid (Takeda Chemicals Co., b.p. 160–162°) was placed in an autoclave and heated at 250–270° under the pressure 15 kg./cm.^{2}of hydrogen for 23 hours. Uniformity of temperature all around the autoclave was established by heating in salt bath of a mixture of potassium nitrate and sodium nitrate in mole ratio. Thus the materials No. 1–17 polymer in Table 1 were prepared, and No. 18, without butyric acid, was prepared by evacuating during the last period of the polymerization.

Solution Viscosity. The solution viscosity was determined on the solutions of the polymer in freshly redistilled *m*-cresol (b.p. 201–202°). The Ostwald viscosimeter was thermostated in a water bath at 30±0.02°. Kinetic energy corrections were never important as the efflux time for about 10 c.c. of the solvent was longer than 120 seconds. The viscosities were all measured at concentration of c=0.4000±0.0020 g. per 100 c.c. of solution. The viscosity of the pure solvent η_0 and that of the solution η_1 are related to intrinsic viscosity $[\eta]$ by

$$[\eta] = \frac{ln\frac{\eta_1}{\eta_0}}{c} \quad .$$

Precipitability. Solutions of 1.0000 (±0.0008) g. of the polyester in 25 c.c. of *m*-cresol were maintained at 20.0° in a thermostat and were slowly titrated, under isothermal conditions, with heptane (Takeda Chemicals Co., b.p. 81–91°) from a calibrated microburette. The nonsolvent, heptane, was added with constant and vigorous agitating during the addition. A translucent turbidity indicated the end-point. The end-points were

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(1) (IV), this Bulletin, **19** (1933), 153; 158.

(2) *J. Chem. Soc. Japan*, **65** (1944), 419.

(3) This Bulletin, **18** (1943), 105.

sharp and could be reproduced within 1%, but the constancy of temperature during the titration was essential, and for instance the titre varied as follows as the temperature varied.

Temperature, °C.	5	10	15	20	25	30
Heptane, c.c.	26.20	28.90	29.60	31.10	32.30	33.70

The precipitability γ is the fraction of the total volume of non-solvent at end-point for a given constant initial weight concentration of polymer.

Melt Viscosity. Small steel spheres carefully selected for uniformity which had been previously heated at desired temperature were dropped into 27 mm.×300 mm. glass tube containing the melt of the polyamide. The tube was placed in a salt bath which was completely within an electric furnace. Observing the ball with strong illumination, its time of fall through 50 mm. distance was measured by means of a stop watch. The temperature was controlled, a sealed mercury regulator and a thermometer and transformers being used. The temperatures of the measurement were (220±0.5°), 240±0.5°, 260±0.5°, and 280±0.5°. The test showed that the polyamide did not decompose nor change during three hours at these temperatures in the atmosphere of carbon dioxide; they were entirely stable over the measuring period. Melts were freed from gas bubbles by standing. Melt viscosities μ were calculated by Dorr and Roberts' equation,(4)

$$\mu = \frac{g}{18}\,\frac{d^2(\rho'-\rho)}{\left(1+2.1\dfrac{d}{D}\right)\left(1+\dfrac{R}{12}-\dfrac{R^2}{960}\right)}\quad ,$$

where g is the gravity constant, d is the diameter of steel balls, ϱ' is the density of steel balls, ϱ is the density of the melted polymer, D is the diameter of the glass tube, v is the velocity of ball fall, and $R\,(=dv\varrho/\mu)$ is Reynold's number. To the data of d and ϱ' at room temperature, corrections were applied by using the thermal expansion constant. From the volume occupied by melted polymer of known weight, ϱ was determined.

$$\rho = 1.083(240^\circ),\ 1.076\ (260^\circ)\ \text{and}\ 1.070\ (280^\circ)$$

Results and Discussions.

The results of titration and viscosity determination are included in Table 1.

(1) $[\eta]-\gamma$ *Relationship.* The sharp dependence of solubility on solution viscosity or molecular weight are seen in Fig. 1. Higher molecular polycapramide has little solubility, and γ and reciprocal of $[\eta]$ are in linearity in the range of $[\eta]<0.8$,

$$\gamma = 0.521+0.0285/[\eta]. \qquad (1)$$

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(4) Dorr and Roberts, *Trans. Am. Inst. Chem. Engrs.* **33** (1937), 106.

In the ragne of $[\eta]>0.8$, this equation is not applicable. It is conceived that $[\eta]$ is proportional to the weight-average degree of polymerization P_w and that P_w is approximately twice the number-average degree of polymerization P_n on highly condensated linear polymers. Therefore equation (1) cán be transformed into

$$\gamma = \alpha + \beta / P_n \,, \qquad (2)$$

where α and β are constants for the given series. This relation has been applied to polystyrene by Schulz,⁽⁵⁾ to polyundecanate by Baker,⁽⁶⁾ and to polyoxyethylene glycol by Hibbett.⁽⁷⁾ Thus it is proved that equation (2) may be applicable to the low molecular weight polycapramide in *m*-cresol when titrated with heptane.

Table 1.

No.	Mole of butyric acid	$[\eta]$	Heptane c.c.	γ	μ poise		
					280°	260°	240°
1	0	0.7058	31.10	0.554	181.0	266.2	550.8
2	1/800	0.6660	32.30	0.564	115 3	163.1	320.4
3	1/400	0.6358	32.60	0.566	63.8	115.1	179.9
4	1/200	0.5876	34.80	0.582	—	—	—
5	1/100	0.4152	36.20	0.590	19.0	29.2	52.2
6	1/50	0.3715	27.70	0.601	8.1	11.2	15.4
7	1/25	0.2936	41.10	0.622	1.4	2.3	2.8
8	1/10	0.1798	53.10	0.680	0.6	0.7	0.9
9	0	0.6808	32.50	0.565	160.5	233.4	323.0
10	1/800	0.6693	32.80	0.567	83.2	162.6	250.3
11	1/400	0.6032	33.30	0.571	61.1	116.4	192.6
12	1/200	0.5891	35.00	0.583	42.2	96.8	124.5
13	1/100	0.3700	35.30	0.585	13.2	18.3	25.6
14	1/50	0.3185	37.70	0.600	4.5	7.2	19.3
15	1/25	0.2465	42.60	0.630	1.6	2.3	2.8
16	1/10	0.1912	52.20	0.676	—	—	—
17	0	0.8865	28.70	0.534	692 3	1017	1363
18	0	1.0665	27.00	0.521	820.4	1218	1576

(2) $[\eta]$-μ *Relationship.* Log μ and $[\eta]^{\frac{1}{2}}$ are in linear relationship as are shown in Fig. 2, and these straight lines are expressed by the following equations:

$$\left.\begin{aligned} &\text{at } 240^\circ,\ \log\mu = -2.5 + 6.2\,[\eta]^{\frac{1}{2}} \\ &\text{at } 260^\circ,\ \log\mu = -2.7 + 6.2\,[\eta]^{\frac{1}{2}} \\ &\text{at } 280^\circ,\ \log\mu = -3.0 + 6.2\,[\eta]^{\frac{1}{2}} \end{aligned}\right\} \qquad (3)$$

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(5) Schulz, *Z. physik. Chem.*, A**179** (1937), 321.

(6) Baker, Fuller and Heiss, *J. Am. Chem. Soc.*, **63** (1941), 2142.

(7) Lowell and Hibbert, *J. Am. Chem. Soc.*, **61** (1939), 1916.

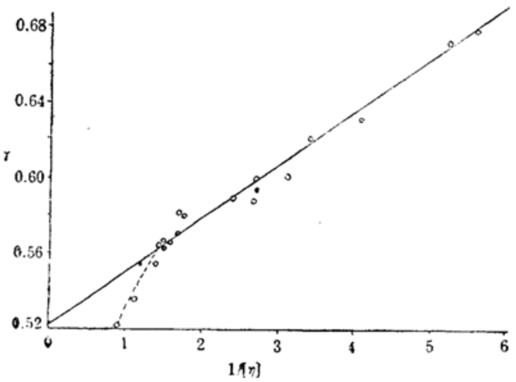

Fig. 1. [η]–γ curve.

Flory⁽⁸⁾ has reported a linear relationship between lnμ and $Zw^{\frac{1}{2}}$ on polyester, when Zw is the number of chain atoms in the molecules of weight-average molecular weight, and has applied to molecular weight determination,

$$\mu = A' \, e^{C'Zw^{1/2}} \qquad (4)$$

where A' and C' are constants.

As it has been proved that Zw approximately proportional to $[\eta]$, the equation (3) may be transformed into (4) and (5),

$$\log \mu = A'' + C[\eta]^{\frac{1}{2}}, \qquad (5)$$

where A'' is a constant dependent of temperature, and $C=6.2$.

(3) *The relation between μ and the absolute temperature T.* Typical data are given in Tables 1 and 2, and the results are included in Figs. 3 and 4, where log μ is plotted against the reciprocal of absolute temperature T. According to the well-known equation,

$$\log \mu = A''' + B/T, \qquad (6)$$

the observed points in Figs. 3 and 4 must lie on straight lines. The slope of these lines ranges from 2100 to 2500, independent of molecular weight.

(4) *μ-T-$[\eta]$ relationship.* From the equations (5) and (6), we obtain

$$\log \mu = A + B/T + C[\eta]^{\frac{1}{2}}, \qquad (7)$$

where A, B and C are constants. According to the theory of Eyring and Kauzmann⁽⁹⁾ on viscosity of large molecules,

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(8) Flory, *J. Am. Chem. Soc.*, **62** (1940), 1057.

(9) Eyring and Kawzmann, *J. Am. Chem. Soc.*, **62** (1940), 3113.

$$\log \mu = ln\frac{Nh}{V} - \frac{\varDelta S^{+}}{R} + \frac{\varDelta H^{+}}{RT}, \qquad (8)$$

where N is Avogadro's number, h is Planck's constant, V is the volume of unit flow of molecule, R is gas constant, $\varDelta S^{+}$ is entropy of activation

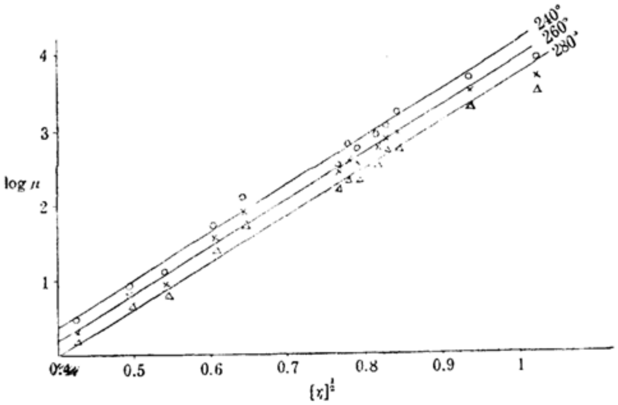

Fig. 2. μ–$[\eta]$ curves.

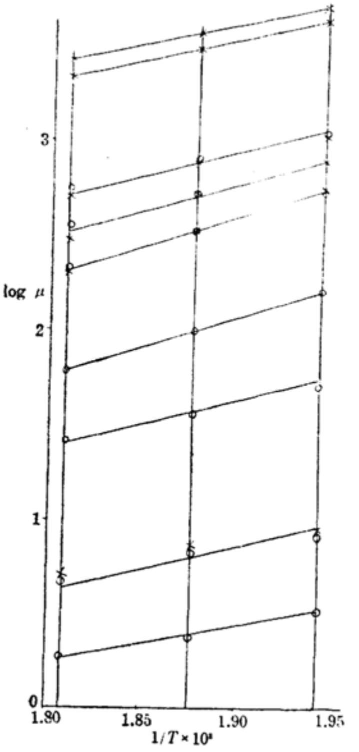

Fig. 3. μ–1/T curves.

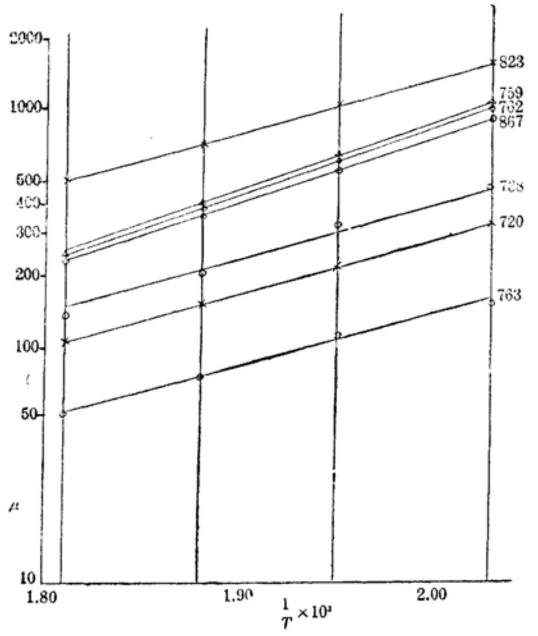

Fig. 4. μ–1/T curves.

for viscous flow, and ΔH^{+} is its energy of activation. Comparing the equations (7) and (8)

$$\Delta H^{+} = 2.3\,RB, \tag{9}$$

and it may be said that $\Delta H^{+}=9.7-11.5$ kcal for polycapramide independent of molecular weight. Flory's data on polyester, $B=1800$ and $\Delta H = 8.0 - 8.5$ kcal(8). For polycapramide,

$$\log \mu = -7.0 + 2300/T + 6.2[\eta]^{\frac{1}{2}} \tag{10}$$

This equation is applicable to the polymer of $[\eta]<1$, and is not applicable to that of $[\eta]>1$ nor to that containing three dimensional links, nor to partially oxidized polymer.

Table 2.

Melt viscosity μ of polycapramide in poise.

No.	220°	240°	260°	280°
738	485	347	209	139
720	320	231	150	108
759	1197	645	403	257
762	1125	642	390	255
763	155	111	783	542
823	1680	1160	760	540
867	928	588	349	246

Summary.

A study of polyamide has been attempted on a series of strictly isochemical linear synthetic polyamide derived from ε-aminocaproic acid.

(1) The polymer molecules have been investigated by "equilibrium" interaction with a non-solvent in solution (precipitability γ), kinetic interaction in a dilute solution (solution viscosity $[\eta]$), and kinetic interaction in a condensed polymer phase (melt viscosity μ).

(2) $[\eta]-\gamma$ relationship is established experimentally.

(3) $\mu-T-[\eta]$ relationships are established experimentally.

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