Studies on Synthetic Polyamides. (IV).(1)
Solution Viscosity(2)

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Introduction. The synthetic linear polyamides prepared by Carothers and his co-workers are of two kinds: those formed from amino acids and those formed from diamines and dibasic acids. Polycapramide is an example of the former type of polymers, and polyhexamethylene adipamide is one of the latter type. The present paper offers the results of an analysis of the relation between the average molecular weight and the solution viscosity of polyhexamethylene adipamide and some discussions on depolymerization reaction of polycapramide.

1. Molecular Size Distribution in Linear Condensation Polyamides.

(1) *Distribution Functions.* The polymerization of ε-aminocaproic acid or of hexamethylene diamine and adipic acid may be formulated as

$$x\,H_2N(CH_2)_5COOH \longrightarrow H_2N(CH_2)_5CO[HN(CH_2)_5CO]_{x-2}HN(CH_2)_5COOH$$

$$x/2\ H_2N(CH_2)_6NH_2 + x/2\ HOOC(CH_2)_4COOH \rightarrow$$
$$H_2N(CH_2)_6NH[CO(CH_2)_4CONH(CH_2)_6NH]_{\frac{x-2}{2}}OC(CH_2)_4COOH$$

where x represents the total number of reactant molecules combined in the polymer molecule. Three fundamental assumptions for the treatment are as follows:(3)

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(1) The third paper, this Bulletin, **19** (1944), 153.

(2) K. Hosino, *J. Chem. Soc. Japan*, **61** (1940), 545: **62** (1941), 602.

(3) Flory, *J. Am. Chem. Soc.*, **58** (1936) 1874.

(i) The reactivity of a functional group, NH_2 or COOH, is independent of the size of the molecule to which it is attached.

(ii) If the polymer degradation occurs by hydrolysis, all amide links have equal reactivity with respect to the reverse reaction.

(iii) The formation of cyclic compounds, the oxidation by air and the formation of three dimensional linkage (as well as other side reactions) do not occur to an appreciable extent.

Let a "segment" be defined as one amino acid or one diamine or one dibasic acid residue as contained within a polymer molecule. The term "x-mer" will denote a polymer composed of x segments and the extent of reaction p will represent the ratio of the number of amide groups to the number of amide plus unreacted carboxyl groups. And the following notation Π_x will be used.

$$\Pi_x = \frac{\text{Total number of segments which exist as components of } x\text{-mers}}{\text{Total number of segments}}$$

$\simeq$ weight fraction of x-mer, for high molecular weight polymer. According to Flory,

$$\Pi_x = xp^{x-1}(1-p)^2. \qquad (1.1)$$

As p is zero at the beginning of the reaction, $\Pi_x = \begin{cases} 1, (x=1) \\ 0, (x=2, 3, \ldots) . \end{cases}$

The relative number of x-mer molecules is given by

$$N_x = \frac{\Pi_x}{x} = p^{x-1}(1-p)^2. \qquad (1.2)$$

Specially $\qquad N_1 = \Pi_1 = (1-p)^2.$

It must hold that

$$\sum_{x=1}^{\infty} \Pi_x = 1\,. \qquad (1.3)$$

This relation may be derived from (1·1), because

$$\sum_{x=1}^{\infty} \Pi_x = (1-p)^2 \sum_{x=1}^{\infty} xp^{x-1} = (1-p)^2 (\sum_{x=1}^{\infty} p^{x-1})^2 = 1\,.$$

As the number of linkages in x-mer molecule is x-1, the relative number of linkage may be given by

$$\sum_{x=2}^{\infty} (x-1) \frac{\Pi_x}{x} = p\,. \qquad (1.4)$$

This is also derivable from (1·1) :

$$\sum_{x=2}^{\infty} (x-1) \frac{\Pi_x}{x} = (1-p)^2 \sum_{x=2}^{\infty} (x-1) p^{x-1} = (1-p)^2 \sum_{y=1}^{\infty} yp^y = (1-p)^2 p \sum_{y=1}^{\infty} yp^{y-1} = p\,.$$

In order to locate the x-value which gives a maximum in Π_x, let $\partial \Pi_x / \partial x = 0$. The solution is

$$x_{\max.} = -1/\ln p \simeq 1/(1-p) = \text{average value of } x, \text{ when } p \sim 1 . \quad (1.5)$$

At the maximum,

$$\Pi_{x\max.} = -\frac{(1-p)^2}{\ln p} e^{-(1+\ln p)} \cong \frac{1-p}{e}, \text{ when } p \sim 1 . \qquad (1.6)$$

(2) *Molecular Weight Averages.* The "number average" molecular weight M_n, which may be obtained by osmotic pressure measurement or freezing point depression, and the "weight average" molecular weight M_w which may be determined by means of Staudinger viscosity method, are defined by the equations,

$$M_n = \sum M_x N_x / \sum N_x \qquad (1.7)$$

$$M_w = \sum M_x^2 N_x / \sum M_x N_x , \qquad (1.8)$$

where M_x is the molecular weight of an x-mer molecule and N_x is the number of x-mers. By substituting the equation (1·2) for N_x, and xM_0 for M_x, where M_0 is the segment weight (for polyhexamethylene adipamide or polycapramide, $M_0=113$),

$$M_n = M_0/(1-p) \qquad (1.9)$$

$$M_w = M_0(1+p)/(1-p) \qquad (1.10)$$

$$M_w/M_n = 1+p . \qquad (1.11)$$

Degree of polymerization P_n or P_w defined as the average number of segment per molecule which has the molecular weight of M_n or M_w respectively will be given by

$$\left.\begin{aligned} P_n &= M_n/M_0 = 1/(1-p) \\ P_w &= M_w/M_0 = (1+p)/(1-p) . \end{aligned}\right\} \quad (1.12)$$

2. Molecular Weights and Solution Viscosity.

(1) *Viscosity and Concentration.* Viscosities of polyhexamethylene adipamide in m-cresol are expressed satisfactorily by the Fickentscher equation⁽⁴⁾

$$\frac{\log \eta_r}{c} = \frac{75K^2}{1+1.5Kc} + K , \qquad (2.1)$$

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(4) Fickentscher, *Cellulosechem.*, **13** (1932), 58.

where η_r is relative viscosity, c concentration g. per 100 c.c. of solution and K a constant ("Eigenviskosität"). The equation (2·1) is applicable also to cellulose nitrate in acetone, cautschouc in benzene, cellulose in cuoxam, and polyvinyl acetate in benzene. For the limit value of c,

$$\left.\begin{aligned}[\eta] &= \lim_{c\to 0}\frac{\ln\eta_r}{c} = 2.303K(75K+1)\\ K &= \frac{\sqrt{1+130.3[\eta]}-1}{150}\,.\end{aligned}\right\} \qquad (2.2)$$

The function specific viscosity η_{sp} divided by c, i.e. η_{sp}/c, decreases monotonously and the function $\ln\eta_r/c$ increases monotonously as c decreases, both possessing a straight line parallel to horizontal axis as their assymptote, as is shown in Fig. 1.

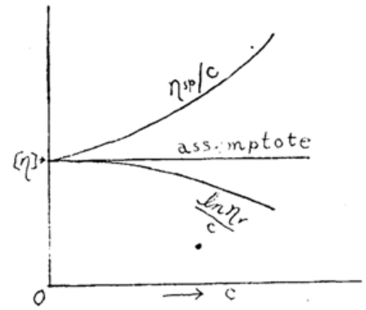

Fig. 1

(2) *Staudinger viscosity relation.* Staudinger has advocated the following relation for the determination of the average molecular weight of linear polymeric substances,

$$\lim_{c\to 0}\frac{\eta_{sp}}{c_m} = K_m M\,, \qquad (2.3)$$

where c_m is base molecular concentration, K_m is the Staudinger constant, and M is average molecular weight. If K_m is determined from osmotic pressure measurement of monodisperse system or of fractionated polymer, M must be "weight-average" molecular weight. In this case the equation (2·3) transforms into

$$\lim_{c\to 0}\frac{\eta_{sp}}{c} = 10K_m\frac{1+p}{1-p} = 20K_m\left(\frac{1}{1-p}-\frac{1}{2}\right), \qquad (2.4)$$

where $$c_m = 10\frac{c}{M_0}\,.$$

Intrinsic viscosity of E. O. Kraemer(5) $\frac{\ln \eta_r}{c}$ coincides to "Grenzviskosität" of K. H. Meyer(6) $\lim\limits_{c\to 0}\frac{\eta_{sp}}{c}$ at $c\to 0$.

Denoting this limit value by $[\eta]$,

$$\lim_{c\to 0}\frac{\eta_{sp}}{c}=\lim_{c\to 0}\frac{\ln \eta_r}{c}=[\eta]\,.$$

The value $[\eta]$ is easily determined by the slope of $\ln \eta_r - c$ curve, as this is almost a straight line passing the origin in the range $0 \leqq c < 1$.

From (2·4),

$$\left.\begin{aligned}\frac{1}{1-p}&=\frac{1}{2}\left(\frac{[\eta]}{10K_m}+1\right),\\ [\eta]&=20K_m\left(\frac{1}{1-p}-\frac{1}{2}\right).\end{aligned}\right\}\qquad(2.5)$$

If K_m is determined from the osmotic pressure measurement of polydisperse system and the ratio M_w/M_n is almost constant for high molecular weight polymers, M in equation (2·3) must be "number average" molecular weight, and equation (2·3) becomes

$$[\eta]=\frac{10K_m}{1-p}=10K_mP_n\,. \qquad (2.6)$$

This is equivalent to the following equation,

$$[\eta]=10K_{\text{äqu}}\cdot Z_n\,, \qquad (2.7)$$

where $K_{\text{äqu}}$ is a constant, and Z_n is the number of chain atoms in the "number average" molecular weight polymer, when $K_{\text{äqu}}$ is determined by osmotic pressure measurement and M_w/M_n is almost constant. He determined the $K_{\text{äqu}}$ constant for the m-cresol solution of polyamide from the measurement of osmotic pressure and the viscosity of chloroform solution of polyamide derived from disobutylhexamethylene diamine and sebacic acid and from the measurement of viscosity of the m-cresol solution of that polyamide.(7)

$$K_{\text{äqu}}=1.2\times 10^{-4}\,. \qquad (2.8)$$

For polyhexamethylene adipamide, the number of chain atoms in one segment is 7.

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(5) Kraemer, *Ind. Eng. Chem.*, **30** (1938), 1200.

(6) Meyer and Wolff, *Kolloid-Z.*, **89** (1939), 194.

(7) Staudinger and Jörder, "Jentgen's Kunstseide und Zellwolle" (1943), 88.

$$Z_n = 7P_n = 7\frac{M_n}{113} = \frac{M_n}{16.15}\,.$$

Substituting this value in (2·7),

$$[\eta] = 7.5 \times 10^{-5} M_n \tag{2.9}$$

$$\simeq 3.8 \times 10^{-5} M_w\,,\ (p \sim 1)\,. \tag{2.10}$$

Using relations (2·9), (1·5) and (1·6), the values of p, M_n, p, $x_{\max}$ and $\Pi x_{\max}$. for various values of $[\eta]^{20^\circ}$ were calculated and are shown in Table 1.

The Staudinger relation is applicable approximately only on high molecular weight polymers and not applicable in the range of low molecular weight as is shown in next paragraph.

(3) *$[\eta]$-M_w relations from freezing point depression measurement.*

Materials.—Polyhexamethylene adipamide of low degree of polymerization was prepared by heating pure hexamethylene diammonium adipate (m.p. 194°, Found: N, 10.56; Calcd.: N, 10.68%) at 200–250° for 10–60 minutes in a stream of hydrogen. The obtained polyamide was pulverized and dried over phosphorus pentoxide in a vacuum desiccator for one week. Adipamide was prepared by passing ammonia in melted adipic acid and recrystallized twice from ammonical water and dried as above.

Solution viscosity.—This was determined on solutions of the polymer in *m*-cresol at 20°, 25° and 30±0.02° using Ostwald viscosimeter. The efflux time for 10 c.c. of these solutions was greater than 150 seconds.

Freezing point depression.—As camphor, borneol or bornyl amine does not dissolve polyamide, phenol was used as solvent. Pure phenol (Takeda Chemical Co.) was dried for one week over anhydrous calcium chloride at 50° and distilled. The middle fraction which melted at 40.93° was used. This sample was weighed in the bottom of a test tube and as soon as 8 or 9 c.c. of melted phenol was introduced, the upper part of the tube was fused and weighed. Perfect solution was attained by maintaining the mixture at 45°. The freezing point of the solution was determined by means of Beckmann thermometer dipped in the solution which gradually cooled across air space in a thermostat maintained at 35.0°. Moisture was removed by passing a gentle flow of air dried over the powder of phosphorus pentoxide. The extent of reaction p and the average molecular weights M_n and M_w were calculated by the following equations,

$$\left.\begin{aligned} p &= 1 - \frac{113}{M_n - 18} \\ M_n &= 7270\frac{S}{L\Delta} \\ M_w &= 2M_n - 131\,, \end{aligned}\right\} \tag{2.11}$$

where S is the weight of the polyamide, L the weight of phenol, and Δ the freezing point depression.

Results.—The experimental results are shown in Tables 2 and 3. The $[\eta]$-M_w relations are expressed by straight lines as is shown in Fig. 2.

$$\left.\begin{aligned}[\eta]^{20^\circ} &= 5.9\times10^{-5}M_w+0.09\\ [\eta]^{25^\circ} &= 5.4\times10^{-5}M_w+0.085\\ [\eta]^{30^\circ} &= 5.1\times10^{-5}M_w+0.08\,.\end{aligned}\right\}\quad(2.12)$$

Discussions.—Eisenschitz, Kuhn and Guth[(8)] proposed the following equation for the solution viscosity of linear polymers.

$$\eta_{sp}=\left[\frac{5}{2}+\frac{1}{16}\left(\frac{l}{d}\right)^2\right]\frac{\varphi c}{100}\,,\qquad(2.13)$$

where φ is the volume in c.c. occupied by one gram of the solute in solution, and l and d are the length and the width of the polymer molecule.

Introducing $[\eta]$ for η_{sp}/c in (2·13),

$$[\eta]=\frac{\varphi}{1600}\left(\frac{l}{d}\right)^2+\frac{2.5}{100}\,\varphi\,.\qquad(2.14)$$

Assuming the shape of the polymer is similar, whether the degree of polymerization is large or small, φ is a constant and by comparing the second terms of (2·12) and (2·14),

$$\frac{2.5\varphi}{100}=0.09\qquad\therefore\ \varphi=36\quad\text{at}\quad20^\circ\,.\qquad(2.15)$$

For a molecule, which has molecular weight of M_w,

$$\frac{\varphi M_w}{N_A}=\frac{\pi d^2 l}{4}\quad\text{or}\quad\frac{\varphi}{d^2}=\frac{\pi l N_A}{4M_w}\,,$$

where N_A is Avogadro number, $N_A=6.06\times10^{23}$.

If we put

$$\Gamma\equiv[\eta]-\frac{25\varphi}{100}=\frac{\varphi}{1600}\left(\frac{l}{d}\right)^2,\qquad(2.16)$$

we have

$$\left.\begin{aligned}\Gamma&=\frac{\pi l^3}{6400M_w}=2.974\times10^{20}\frac{l^3}{M_w}\\ l^3&=3360M_w\Gamma\qquad\text{in Å}^3\text{ unit.}\end{aligned}\right\}\quad(2.17)$$

From (2·12) at 20°,

$$\Gamma=5.9\times10^{-5}M_w\qquad(2.18)$$

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(8) Meyer-Mark, "Hochpolymere Chemie," Bd. I. (1940), 290.

$$l = 0.585 M_w^{2/3} \qquad \text{in Å unit.} \tag{2.19}$$

Denoting the average length for one segment of the polyamide by l_m,

$$l = l_m M_w / M_0 \,,$$
$$l_m = 65.8 M_w^{-1/3} \qquad \text{in Å unit.} \tag{2.20}$$

According to Sakurada,⁽⁹⁾ the degree of bending κ is calculated;

L = the length of segment when stretched
= the half of the fibre period = 8.65 Å

$$\kappa = \frac{L}{l_m} - 1 = 0.131 M_w^{1/3} - 1 \,. \tag{2.21}$$

The $[\eta]$-M_w relations for other polymers are presented: for polydecamethylene adipate in diethyl succinate or chlorobenzene by Flory⁽¹⁰⁾ for pure polyoxyethylene glycol in carbon tetrachloride by Hibbert,⁽¹¹⁾ and for polyundecanate in chloroform by Baker.⁽¹²⁾

Table 1.

$[\eta]^{20}$	M_n	p	x max.	$\Pi_{x\max}$.
0.3	4000	0.9717	35.8	0.0104
0.4	5340	0.9789	47.3	0.0078
0.5	6670	0.9831	59.0	0.0062
0.6	8000	0.9859	70.8	0.0052
0.7	9340	0.9879	82.6	0.0045
0.8	10560	0.9893	93.5	0.0039
0.9	12000	0.9905	105.1	0.0035
1.0	13340	0.9915	118.0	0.0031
1.1	14660	0.9923	130.0	0.0028
1.2	16000	0.9930	141.6	0.0026
1.3	17340	0.9935	153.5	0.0024
1.4	18660	0.9940	165.3	0.0022

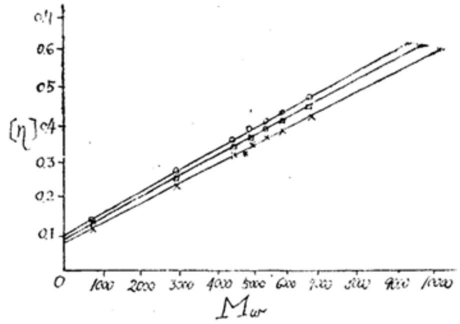

Fig. 2. $[\eta]$—M_w curves.

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(9) Sakurada, *Z. physik, Chem.*, B **38** (1938), 407.

(10) Flory, *J. Am. Chem. Soc.*, **62** (1940), 3032.

(11) Fordyce and Hibbert, *J. Am. Chem. Soc.*, **61** (1939), 1912.

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

Table 2.

No.	Sample	S g.	L g.	Δ°c.	$M_n=7270\frac{S}{\Delta L}$	M_n (mean)
8	" " " 60 "	0.1526	9.414	0.034	3460	145
		0.2105	9.595	0.050	3180	
7	" " " 30 "	0.1879	9.064	0.050	3060	488
		0.1548	8.431	0.046	2920	
6	" " " 20 "	0.2041	8.982	0.061	2690	1590
		0.1779	9.915	0.044	2890	
5	" " 250° 10 "	0.1924	8.518	0.065	2540	2410
		0.1712	8.719	0.057	2480	
4	" " 210° " "	0.2148	9.046	0.071	2450	2510
		0.1405	9.559	0.045	2370	
3	" " " 30 "	0.1850	9.564	0.088	1580	2740
		0.2026	9.444	0.099	1600	
2	"Nylon" salt 200° 10 min.	0.1243	8.655	0.216	483	2990
		0.2113	9.226	0.338	493	
1	Adipamide	0.1404	7.896	0.881	146	3320
		0.119	7.614	0.671	144	

Table 3.

No.	$[\eta]$ 20°	$[\eta]$ 25°	$[\eta]$ 30°	p	M_w
1	0.067	0.055	0.051	—	145
2	0.127	0.125	0.113	0.760	750
3	0.262	0.259	0.238	0.928	3050
4	0.380	0.264	0.339	0.593	4690
5	0.404	0.385	0.353	0.960	4890
6	0.421	0.406	0.378	0.961	5350
7	0.443	0.423	0.394	0.962	5850
8	0.485	0.443	0.409	0.966	6510

3. Depolymerization of Polyamide.

(1) *Theory on depolymerization of linear condensation polymers.* The mol fraction of x-mer molecule in linear condensation polymer derived from bi-functional compounds is given by

$$n_x = \frac{N_x}{\sum N_x} = p^{x-1}(1-p) \,. \tag{3.1}$$

If the bonds of all chains in the mixture at any given time are equally accessible to reaction independent of their position in a chain and independent of the length of their parent chains, and the degree of depolymerization (i.e. the ratio of the total number of bonds cut to the total number of bonds in the parent system) is denoted by α, the total number of t-mers N_t (α) is calculated by Montroll.⁽¹³⁾

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(13) Montroll, *J. Am. Chem. Soc.*, **63** (1941), 1215.

$$N_t(a) = Nn_t(1-a)^{t-1} + N\sum_{x+1=t+1}^{\infty} n_{x+1}a(1-a)^{t-1}[2+(x-t)a]\,, \qquad (3.2)$$

where N is the number of polymer molecules before depolymerization. It is necessary to know the weight average degree of polymerization P_w, if we determine the degree of depolymerization of polymer by the masurement of solution viscosity:

$$P_w = \frac{\sum\limits_{t=1}^{\infty} N_t \cdot t^2}{\sum\limits_{t=1}^{\infty} N_t \cdot t} = \frac{1}{\mu_1 a^2}\Big[a\mu_1(2-a) - 2(1-a)\Big(1-\sum_{t=1}^{\infty} n_t(1-a)^t\Big)\Big]\,, \qquad (3.3)$$

where $\mu_1 = \sum\limits_{x=1}^{\infty} xn_x\,,\ \sum\limits_{t=1}^{\infty} N_t \cdot t = N\mu_1\,,\ \sum\limits_{t=1}^{\infty} n_t = 1.$

Using the facts that

$$\mu_1 = \frac{1}{1-p}$$

and

$$\sum_{t=1}^{\infty} n_t(1-a)^t = \frac{(1-p)(1-a)}{1-p(1-a)}\,,$$

we have

$$P_w = \frac{1+p(1-a)}{1-p(1-a)}\,. \qquad (3.4)$$

If we put $\beta = 1-a$ and $p(1-a) = p\beta = p'$, β denotes the number of uncut bonds divided by the total number of bonds in undegraded system. Letting P_w° be the weight average degree of polymerization before depolymerization,

$$P_w^0 = \frac{1+p}{1-p}\,.$$

Time Dependence of a.—To express the time dependence of a, we shall assume that the rate of depolymerization is proportional to the number of uncut bonds.

$$\frac{dB}{d\tau} = -\lambda B\,,$$

where B is the number of uncut bonds at time τ and λ is the degradation constant.

Thus $$B = Ne^{-\lambda\tau}(\mu_1 - 1)\,, \qquad (3.5)$$

since

$$B_{\tau=0} = N(\mu_1 - 1)\,.$$

Therefore

$$\alpha = \frac{B_{\tau=0}-B}{B_{\tau=0}} = 1-e^{-\lambda\tau}$$

and

$$\lambda = \frac{1}{\tau} ln \frac{1}{1-\alpha} = -\frac{ln\beta}{\tau} \tag{3.6}$$

(2) *Results.* The material for measurement was uncold-drawn fibre spun from the melt of polycapramide which had been prepared by polymerization of ε-aminocaproic acid. Its intrinsic viscosity in *m*-cresol at 20° was $[\eta]=0.9413$. Therefore,

$$P_w^0 = 150[\eta]-14 = 127.2\,,^{(14)}$$

$$p = 0.9845\,.$$

As an example of depolymerization reaction, hydrolysis in 50% sulphuric acid at 30°, 40° and 50° was traced by viscosity measurement. For the determination of P_w, the following equations were adopted. In the equations the proportional constants in the first term were calculated from the ratio $\frac{[\eta]\text{ in }50\%H_2SO_4}{[\eta]\text{ in }m\text{-cresol}}$ of undegraded material, assuming that the value of the second term is constant, for this value is small as compared with that of the first term.

$$\left.\begin{array}{ll} 30^\circ & P_w = 289.3[\eta]-14 \\ 40^\circ & P_w = 294.0[\eta]-14 \\ 50^\circ & P_w = 314.1[\eta]-14 \end{array}\right\} \tag{3.7}$$

Then

$$\beta = \frac{P_w-1}{p(P_w+1)} = \frac{P_w-1}{0.9845(P_w+1)}\,. \tag{3.8}$$

Table 4 (30°).

τ (hr.)	$[\eta]$	P_w	β	$-\frac{\log\beta}{\tau}$
0	0.4881	127.2	1	—
22	0.4383	112.8	0.9975	5.0 $\times 10^{-5}$
29	0.4100	104.6	0.9966	5.2
47	0.3860	97.7	0.9952	4.5
53	0.3762	94.8	0.9936	5.3
70	0.3406	84.6	0.9920	5.0
94	0.3102	75.7	0.9892	5.0
118	0.2889	69.6	0.9870	4.8
148	0.2718	64.6	0.9851	4.4
166	0.2583	60.7	0.9829	4.5
214	0.2374	54.7	0.9793	4.3
290	0.2205	49.8	0.9752	3.8
			mean	4.71×10^{-5}

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(14) Hosino and Noisiki, *J. Chem. Soc. Japan*, **63** (1942), 1175.

The results were shown in Tables 4~7. The value of λ of polyamide is about one hundredth of that of cellulose in sulphuric acid, and $ln\lambda$ is in linear relationship to the reciprocal of reaction temperature in absolute scale (Fig. 3). From the Arrhenius equation, the apparent energy of activation for this reaction is about 25.0 kcal/mole.

Table 5 (40°).

τ (hr.)	$[\eta]$	P_w	β	$-\frac{\log \lambda}{\tau}$
0	0.4803	127.2	1	—
2	0.4637	122.3	0.9993	15.0 $\times 10^{-5}$
18	0.3633	92.8	0.9940	14.0
25	0.3366	85.0	0.9922	13.6
40	0.2966	73.2	0.9883	12.7
43	0.2887	70.9	0.9876	12.6
80	0.2261	52.5	0.9775	12.1
105	0.2118	48.3	0.9748	10.6
110	0.1939	43.0	0.9694	12.1
120	0.1874	41.1	0.9672	12.0
			mean	12.75 $\times 10^{-5}$

Table 6 (50°).

τ (hr.)	$[\eta]$	P_w	β	$-\frac{\log \lambda}{\tau}$
0	0.4495	127.2	1	—
1.1	0.4200	117.9	0.9986	54.5 $\times 10^{-5}$
2	0.4018	112.2	0.9979	45.0
3	0.3885	107.9	0.9972	40.0
5.5	0.3527	96.8	0.9952	38.3
8.0	0.3213	86.9	0.9927	40.0
22.5	0.1878	45.0	0.9716	55.4
27.5	0.1749	40.9	0.9674	52.3
31	0.1630	37.2	0.9625	53.6
52	0.1487	32.7	0.9557	37.8
			mean	46.3 $\times 10^{-5}$

Table 7.

temp. °C.	λ
30	1.085 $\times 10^{-4}$/hr.
40	3.697 $\times$ "
50	10.66 $\times$ "

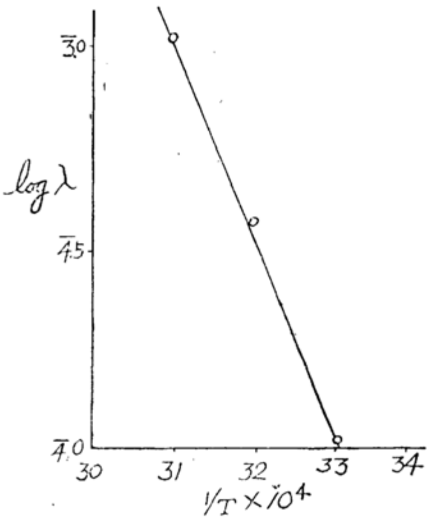

Fig. 3 log λ—$1/T$ curve.

Summary

1. Flory's theory on molecular size distribution in linear condensation polymers was applied to linear synthetic polyamides.
2. Viscosities of polyhexamethylene adipamide or polycapramide in m-cresol are expressed by Fickentscher's equation.
3. The application of the Staudinger viscosity relation to polyamide was discussed.
4. The relations between intrinsic visocisty and "weight average" molecular weight were established experimentally from Flory's theory and the freezing point depression measurement of phenolic solution.
5. The time dependence of the degree of depolymerization was discussed under the assumption that the rate at which bonds are cut is proportional to the number of uncut bonds in the system.

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