Studies on Polymerizaton and Depolymerization of ε-Caprolactam Polymer. VIII. The Solution Viscosity of Poly-ε-capramide of Super-high Degree of Polymerization*

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Several equations have been proposed on the relationship between the intrinsic viscosity $[\eta]$ of poly-ε-capramide in sulfuric acid and the polymerization degree $\bar{P}_n$ or the molecular weight $\bar{M}_n$ as follows:

$\bar{P}_n = 124[\eta] - 5$ [1]

$\bar{P}_n = 119[\eta]$ [2]

$\bar{P}_n = 170[\eta]_{50\%\ H_2SO_4}$ [3]

$\log[\eta] = 0.764(\pm 0.016)\log \bar{M}_n - 3.20$ [4]

These equations were proposed on the polymer with polymerization degrees below 300 and with broad molecular weight distribution, which was polymerized in the presence of water.

Poly-ε-capramide of a super-high degree of polymerization and with the sharp molecular weight distribution can be obtained by the so-called rapid polymerization of ε-caprolactam in the presence of alkali catalyst[5]. It is expected that the behaviour of the solution viscosity of poly-ε-capramide of a super-high degree of polymerization would be quite different from that of poly-ε-capramide polymerized in the presence of water.

Experimental and Results

Polymerization of ε-Caprolactam[6]. — Sodium hydroxide was dissolved in ε-caprolactam at 100°C at the amount of 1/100, 1/500, 1/750 and 1/1000 mol./mol. and then carbon dioxide gas was introduced for 30 min. into the molten ε-caprolactam. ε-Caprolactam containing colloidally dispersed sodium carbonate was heated at 290°C under normal

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* VII, *Makromol. Chem.*, 30, 212 (1959).

[1] A. Matthes, ibid., 5, 165 (1950).

[2] H. Staudinger and H. Schnell, ibid., 1, 43 (1947).

[3] K. Hoshino and M. Watanabe, *J. Am. Chem. Soc.*, 73, 4816 (1957).

[4] J. R. Schaefgen and P. J. Flory, ibid., 70, 2709 (1948).

[5] W. Griehl, *Faserforsch. u. Textiltech.*, 7, 207 (1956).

[6] H. Yumoto and N. Ogata, This Bulletin, 31, 907, 913 (1957).

TABLE I. THE RELATION AMONG C, η_{rel} AND $[\eta]$

Sample No.	Concentration (g./100 cc.)							$[\eta]$
	0.1	0.2	0.5	1.0	1.5	2.0	3.0	
A	1.091	1.185	1.512	2.079	2.752	3.483	5.291	0.91
B	1.151	1.336	1.911	3.340	5.060	6.610	11.48	1·62
C	1.246	1.553	2.634	5.421	8.708	14.34	27.66	2.51
D	1.308	1.689	3.073	7.060	11.45	19.79	39.53	3.09
E	1.383	1.853	3.220	7.260	12.89	23.89	51.29	3.71
F	1.476	1.942	3.789	8.753	15.52	28.18	66.82	4.47
G	1.883	3.008	8.206	19.07	59.05	116.8	357.9	8.32

TABLE II. THE NUMBER OF CARBOXYL AND AMINO GROUPS, AND $\bar{P}_n$ OF THE POLYMER

Sample No.	$-NH_2$		$-COOH$	
	Mol./113 g.	$\bar{P}_n$	Mol./113 g.	$\bar{P}_n$
A	1.300×10^{-2}	77	1.010×10^{-2}	99
B	0.676 〃	148	0.501 〃	199
C	0.415 〃	241	0.189 〃	529
D	0.319 〃	314	0.145 〃	690
E	0.295 〃	339	0.120 〃	833
F	0.289 〃	347	0.098 〃	1025
G	0.155 〃	646	0.053 〃	1910

pressure in a nitrogen atmosphere or at 250°C under the reduced pressure of 250 mmHg in a nitrogen atmosphere. After the polymerization, polymers were quickly cooled and washed with water.

Determination of the Solution Viscosity.—Polymers were dissolved in 98% sulfuric acid at the concentrations of 0.1, 0.2, 0.5, 1.0, 1.5 and 2.0 g./100 cc. and the relative viscosities of the solutions were determined with the Ostwald's viscometer at 25°±0.01°C. The number of carboxyl groups in the polymers was determined by the alkali titration in benzyl alcohol with phenolphthalein as an indicator, and the number of amino groups was determined by potentiometric titration, in phenol-alcohol solvent (1.7/1.0 in volume)[7].

Table I shows relative viscosities η_{rel} of the polymer solutions at various concentrations in 98% sulfuric acid. The number of amino groups in the polymers is about twice as great as that of carboxyl groups, as shown in Table II. Although there have been many discussions on the structure[6,8-12] of the end groups of the alkali-catalyzed poly-ε-capramide, it is assumed that the polymerization degree calculated from the number of amino groups may be correct, since the number of carboxyl groups increases by washing the polymer with water, while that of amino groups does not increase[6,11].

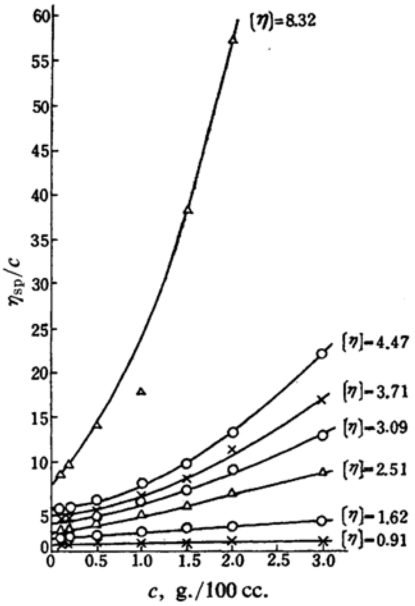

Fig. 1. The relation between η_{sp}/c and c.

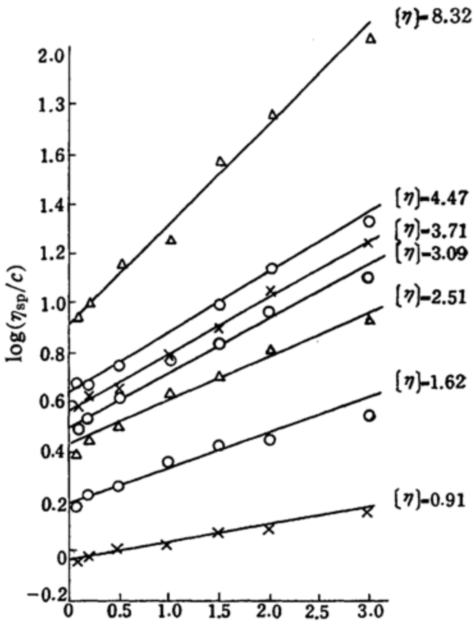

Fig. 2. The relation between log (η_{sp}/c) and c.

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[7] J. E. Waltz and G. B. Taylor, *Anal. Chem.*, **91**, 418 (1947).

[8] D. Heikens, *Makromol. Chem.*, **18**, 62 (1956).

[9] W. Griehl and S. Schaaf, ibid., **32**, 170 (1959).

[10] J. Králicěk and J. Šebenda, *J. Polymer Sci.*, **30**, 493 (1958).

[11] S. Schaaf, *Faserforsch. u. Textiltech.*, **10**, 224 (1959).

[12] A. Hamann, ibid., **9**, 351 (1958).

The relationships between the polymer concentration c (g./100 cc.) in 98% sulfuric acid and η_{sp}/c (η_{sp} means specific viscosity) shift from a straight line as the polymerization degree increases as shown in Fig. 1. However, as shown in Fig. 2, a linear relation between $\log(\eta_{sp}/c)$ and c is found and can be expressed as follows:

$$\log(\eta_{sp}/c) = K \cdot c + \log[\eta] \tag{1}$$

where K is a constant and $[\eta]$ the intrinsic viscosity of the polymer, which is obtained by extrapolation of linear $\log(\eta_{sp}/c)$ vs. c graphs to infinite dilution. The values of $[\eta]$ of the polymers are shown in Table I.

Plotting K against $\log[\eta]$, a straight line is obtained as shown in Fig. 3 and the following equation is obtained.

$$K = 0.33 \log[\eta] + 0.05 \tag{2}$$

From Eqs. 1 and 2, Eq. 3 can be derived.

$$\log(\eta_{sp}/c) = 0.05\,c + (0.33\,c + 1)\log[\eta] \tag{3}$$

Plotting η_r (η_{rel} at $c=1$) against $[\eta]$, a straight line is obtained as shown in Fig. 4, and Eq. 4 is obtained.

$$\eta_r = /2.2[\eta] \tag{4}$$

The relationship between $\log \overline{P}_n$ and $\log[\eta]$ is in a linear function as shown in Fig. 5, and Eq. 5 is obtained.

$$\overline{P}_{n\,NH_2} = 89[\eta] \tag{5}$$

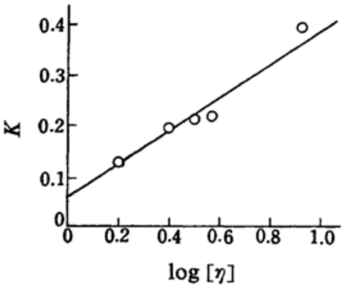

Fig. 3. The relation between K and $\log[\eta]$.

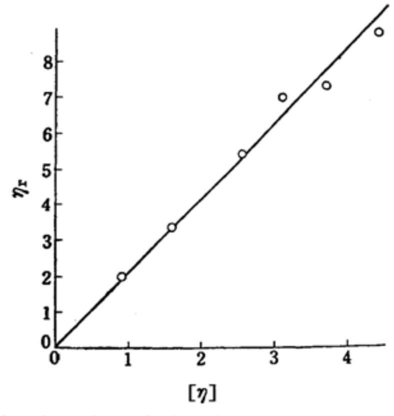

Fig. 4. The relation between η_r and $[\eta]$.

From Eqs. 4 and 5, Eq. 6 can be derived.

$$\overline{P}_n = 40.5\,\eta_r \tag{6}$$

Fig. 6 shows the relationship between $\overline{P}_n$ and η_r at $c=1$.

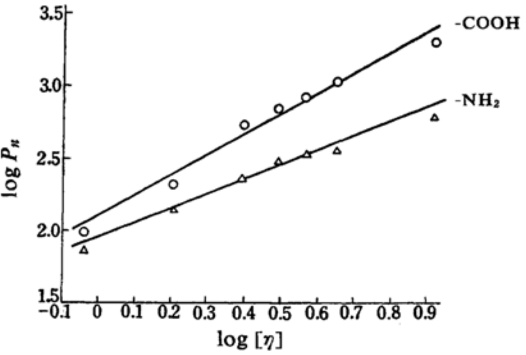

Fig. 5. The relation between $\log \overline{P}_n$ and $\log[\eta]$.

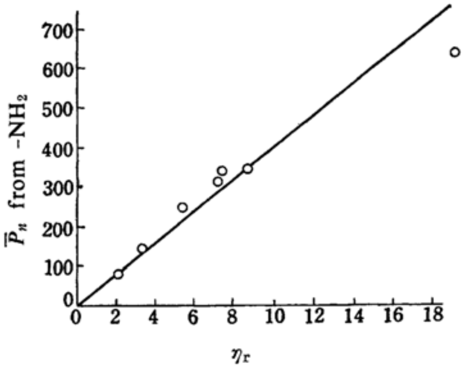

Fig. 6. The relation between $\overline{P}_n$ and η_r.

Change in the Polymerization Degree of the Polymer. — The alkali-catalyzed poly-ε-capramide, which had been washed with water, was preserved in a desiccator with phosphorus pentoxide in a dark place for about 2 years. At that stage, the solution viscosity of the polymers was measured. The polymerization degree of the polymer decreases markedly in comparison with that just after the polymerization and $\overline{P}_n$ becomes about 70, regardless of the initial $\overline{P}_n$.

Discussion

Generally, it is recognized that the solution viscosity of high polymers can be expressed in the following equation proposed by Huggins,

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \tag{8}$$

where k' is approximately constant for a series of polymers in a give solvent. Matthes[1] has recognized that the solution viscosity of poly-ε-capramide in concentrated sulfuric acid is well expressed in Huggins' equation and the same results have been attained by Rybnikář[13].

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[13] F. Rybnikář, ibid., 9, 500 (1958).

TABLE III. CHANGE IN P_n OF THE ALKALI-CATALYZED POLY-ε-CAPRAMIDE

$\bar{P}_n$ of the polymer just after the polymerization	$\bar{P}_n$ of the polymer after 2 years
454	71
254	71
241	64
208	72
190	71

Dawydoff[14] has also reported that the relationships between c and η_{sp}/c or ln η_{sq}/c are in linear functions in the range of the concentrations of less than 0.1 g./100 cc.

Plotting η_{sq}/c against c, a straight line is obtained for the alkali-catalyzed poly-ε-capramide of $[\eta] < 2.5$, while the shift from a straight line becomes greater in the polymers of $[\eta] > 2.5$. However, a linear relation between log (η_{sp}/c) and c can be found for the polymers in the wide ranges of the polymerization degrees.

It is expected that the interactions among chain molecules occur strongly, as the polymerization degree of the polymer increases, and a simple equation between η_{sp}/c and c is not found. The relationship between $\bar{P}_n$ and $[\eta]$ is a simple equation as that derived by Matthes[1] for the polymer polymerized in the presence of water, but the value of the proportionality constant for the alkali-catalyzed polymer is smaller than that derived by Matthes. This is expected to be due to the difference in the molecular weight distribution.

The polymerization degree of the alkali-catalyzed polymer decreases markedly even at room temperature, as stated before, in spite of the fact that the polymers were preserved in a dry state in a dark place. As it is expected that no chemical or photochemical reactions occur in such moderate state, it is very interesting to ascertain whether the amide-interchange reactions would occur in poly-ε-capramide even at room temperature in solid phase, especially in that of a super-high degree of polymerization.

Summary

The solution viscosity of poly-ε-capramide of a super-high degree of polymerization in 98% sulfuric acid has been investigated. A linear relation between log (η_{sp}/c) and c (g./100 cc.) is found for the alkali-catalyzed polymers of $[\eta] > 2.5$, as expressed by the following equation.

$$\log(\eta_{sp}/c) = 0.05\,c + (0.33\,c + 1)\log[\eta]$$

The relationship between $\bar{P}_n$ and $[\eta]$ is expressed by the following equation.

$$\bar{P}_n = 89\,[\eta]$$

The alkali-catalyzed polymer of a super-high degree of polymerization degrades slowly at room temperature in solid phase.

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[14] W. Dawdoff, ibid., 8, 267 (1957).