DAEHAN HWAHAK HWOEJEE
(Journal of the Korean Chemical Society)
Vol. 17, No. 1, 1973
Printed in Republic of Korea

용융상태에서의 Poly-ε-Caproamide의 후중합과 해중합

李 東 鎬·金 昌 洙·安 泰 玩
서울대학교 공과대학 응용화학과

(1972. 8. 23 접수)

Afterpolymerization and Depolymerization of Poly-ε-Caproamide in Molten State

Dong-ho Lee, Chang-soo Kim and **Tae-oan Ahn**
Department of Applied Chemistry, Engineering College, Seoul National University, Seoul, Korea

(Received Aug. 23, 1972)

요 약 Nylon 6의 후중합 반응을 질소흐름, 밀봉 및 감압의 세조건하에서 행하였다. 각 조건에 있어서 점도와 중합물의 감량은 반응온도 및 반응시간에 따라 증가하였고, 같은 반응온도에서의 점도는 감압, 밀봉, 질소흐름의 순서로 증가하였다. 후중합의 activation energy는 10.5 kcal/mole로 계산되었다.

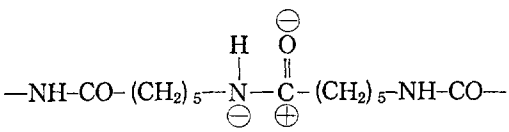
Abstract. The afterpolymerization of nylon 6 was carried out in three different reaction conditions, nitrogen flow, sealing and evacuation.

The viscosity and reduced weight of polymer were increased by increasing the reaction time and temperature, and viscosity of polymers at constant reaction temperature was decreased as the following order: nitrogen flow>sealing>evacuation.

The activation energy of afterpolymerization was 10.5 kcal/mole.

Introduction

Poly-ε-caproamide has the following structure, and the bond between the nitrogen atom and the carbonyl carbon is distinctly polar owing to the polarizing effect of the oxygen atom:



This polar nature of the bond makes poly-ε-caproamide undergo the depolymerization reaction by hydrolysis[1], acidolysis[1], aminolysis[1], amidolysis[2], etc. This property is industrially utilized for the recovery of monomer from poly-ε-caproamide[3].

Besides the depolymerization reaction, poly-ε-caproamide has thermal degradation at high temperature[4]. It has known that the degree of thermal degradation increases with reacton temperature[5] and the products of their degradation reaction are water[6], ammonia[6,8], carbon dioxide[6], amine compounds[6] and monomer, ε-caprolactam[1,6], etc.

In addition to the depolymerization reaction and thermal degradation, poly-ε-caproamide is also expected the reaction of afterpolymerization owing to the condensation reaction of the end

groups of two polymeric molecules so that the degree of polymerization is increased. This phenomenon of afterpolymerization of poly-ε-caproamide is seen during the spinning process and drying process of chips in the preparation of man-made fibre, nylon 6, but the details of afterpolymerization have not been studied yet.

It has been carried out the afterpolymerization of poly-ε-caproamide in this paper in order to explain their mechanism by changing the reaction conitions.

Experimentals

Materials. ε-Caprolactam (Ube Industrial Co. Japan) was recrystallized several times in cyclohexane before use. Sulfuric acid (96 %, Mallinckrodt Chemical Works, U. S. A.) and phosphorous pentoxide (Extra Pure Reagent) was used without further purification. Formic acid and methanol was distilled twice just before use.[7]

Polymerization of ε-Caprolactam. ε-Caprolactam was polymerized with 0.26 % water as a stabilizer at 260 °C by the described methods. After polymerization, poly-ε-caproamide was dissolved in formic acid and then added dropwise in the beaker which contained 10 times of methanol. Oligomer and monomer were dissolved in methanol and the insoluble poly-ε-caproamide was precipitated. A small amounts of 3 *N* HCl was added as a coagulating agent. Poly-ε-caproamide was filtered and dried at 50 °C to constant weight under vacuum. The intrinsic viscosity of poly-ε-caproamide was 0.93 dl/g at 25 °C in 96 % sulfuric acid.

Determination of Reduced Weight of Poly-ε-Caproamide After Reaction. The reacted poly-ε-caproamide was dissolved in formic acid and then was reprecipitated with methanol.

The reprecipitated poly-ε-caproamide was filtered with glass filter (1G3) and was dried at 50° C to constant weight under vacuum. The reduced weight of poly-ε-caproamide was calculated from the difference of weights between before and after reaction.

Measurement of Viscosity. The Ostwald viscometer was used for the measurement of viscosity with concentrated sulfuric acid and all openings of viscometer were connected with silica gel tubes to eliminate the influence of atmospheric humidity. The flow time t was meaured in the thermostat which was maintained at 25±0.05 °C and the specific viscosity η_{sp} was calculated.

Results and Discussions

To study the afterpolymerization of poly-ε-caproamide (nylon 6) in molten state, afterpolymerizations were carried out in the following three different reaction conitions: 1) under nitrogen flow, 2) sample tubes were sealed, 3) evacuation of sample tubes during reaction time.

1. Nitrogen Flow. Sample tubes were continually flushed with the prepurified nitrogen during reaction and afterpolymerizations were carried out in three different temperatures, 220, 230 and 256 °C. The results were summarized in *Table* 1, which was shown the reduced weight of poly-ε-caproamide after reaction and *Fig.* 1 was shown the dependence of the viscosity on the reaction time.

It could be shown in *Fig.* 1 and *Table* 1 that the viscosity and the reduced weight of poly-ε-caproamide were increased by increasing the reaction time and temperature. The reduced weight of poly-ε-caproamide with reaction time and temperature could be explained by the formations of oligomer[1,2], water[6], carbon dioxide[6], ammonia[6,8] and amine compounds[6] at high temperatures by the following reactions: 1) hydrolysis[1], 2) acidolysis[1], 3) aminolysis[1], 4) exchange amidolysis[2].

For hydrolysis as an example:

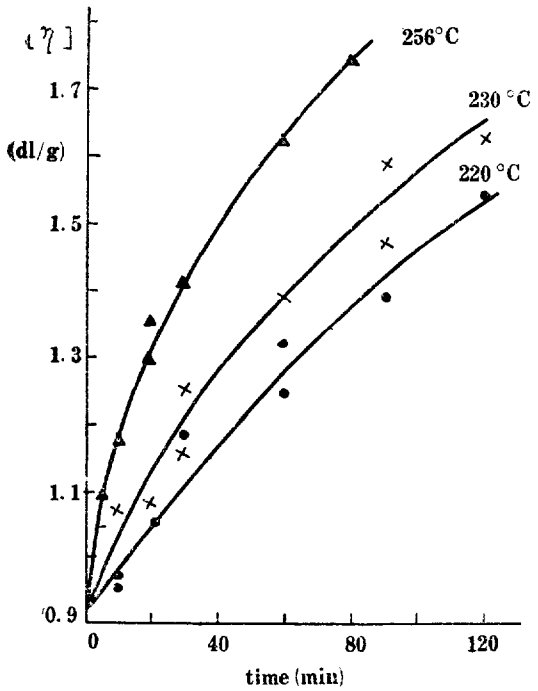


Fig. 1. Variations of intrinsic viscosity with time and temperature in reaction condition of nitrogen flow

$$\text{——NH—CO—}(CH_2)_5\text{—NH—CO—}(CH_2)_5\text{—}$$
$$\text{—}NH_2+H_2O \rightleftharpoons \text{——NH—CO—}(CH_2)_5\text{—}NH_2$$
$$+\text{HOOC—}(CH_2)_5\text{—}NH_2$$

$$\text{HOOC—}(CH_2)_5\text{—}NH_2 \rightleftharpoons \left[\begin{array}{c}\text{—}(CH_2)_5\text{—}\\ \text{—NH—CO—}\end{array}\right] + H_2O$$

The increased viscosity with the reaction time in *Fig.* 1 might be explained by the condensation reaction between the end groups of two polymeric molecules.

$$\text{——NH—CO—}(CH_2)_5\text{—}NH_2+\text{HOOC—}(CH_2)_5$$
$$\text{—NH—CO——} \rightleftharpoons \text{——NH—CO—}(CH_2)_5\text{—NH}$$
$$\text{—CO—}(CH_2)_5\text{—NH—CO——} + H_2O$$

Another reaction which was also expected to increase the viscosity might be the formations of ammonia[6,9], amine compounds[6] and carbon dioxide[6]. These compounds could be formed between two polymeric molecules by the following reaction[8]:

Table 1. The reduced weight of poly-ε-caproamide in reaction condition of nitrogen flow

Temp. (°C)	Time (min.)	Reduced weight (wt. %)
220	10	0.13
	10	0.57
	20	0.96
	30	0.71
	60	2.03
	90	1.75
	90	2.31
	120	3.47
230	10	0.92
	20	1.18
	30	1.24
	30	1.38
	09	2.63
	90	3.47
	90	2.85
	120	4.41
256	5	1.11
	5	0.53
	10	1.08
	20	2.08
	20	2.59
	30	3.23
	60	4.11
	90	6.87

$$\text{——NH—CO—}(CH_2)_5\text{—}NH_2+H_2N\text{—}(CH_2)_5$$
$$\text{—NH—CO——} \rightleftharpoons \text{——NH—CO—}(CH_2)_5\text{—}$$
$$\text{—}(CH_2)_5\text{—NH—CO——} + NH_3$$

To calculate the activation energy of afterpolymerization, we used the Griskey's method[9].

$$\frac{dx}{dt} = kt^n \qquad (1)$$

in which x is $[\eta]$, k reaction rate constant and t reaction time. By integration of Equ. (1), we obtained Equ. (2):

$$\ln(x-x_0) = [k/(n+1)] + (n+1)\ln t \qquad (2)$$

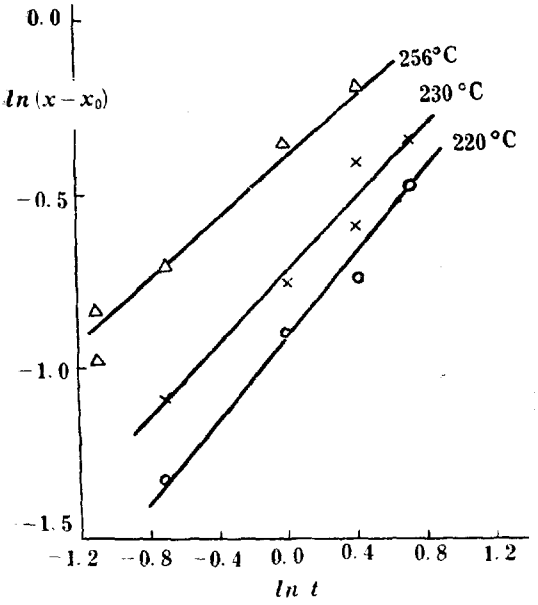


Fig. 2. Plot of ln $(x-x_0)$ against ln t

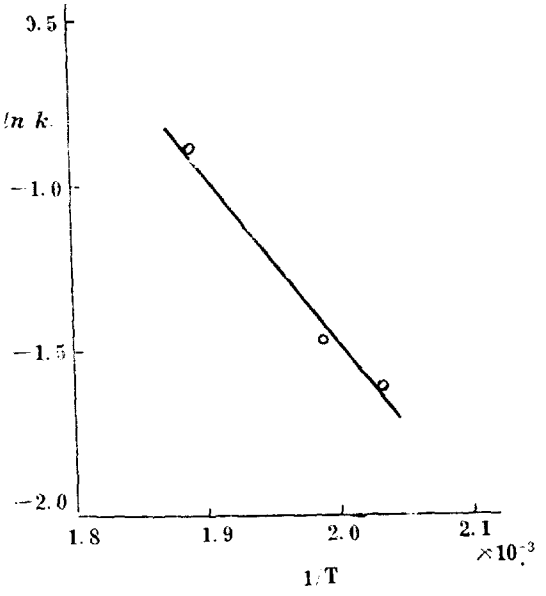


Fig. 3. Arrehnius plot for activation energy

Table 2. Values of n and k

Temp. (C)	n	k
220	−0.46	0.1987
230	−0.48	0.2306
256	−0.52	0.4087

By the plotting ln $(x-x_0)$ against ln t in *Fig.* 2, n and k could be determined from the slope and intercept of straigh tline. The determined values of n and k were shown in *Table* 2.

From the straight line by plotting ln k against $1/T$ in *Fig.* 3, the activation energy could be calculated and was 10.5 kcal/mole which was slightly lower than 12.9 kcal/mole for nylon 66[9].

2. Sealed Condition. After the sample tubes were degassed on a vacuum line by repeated freezing, evacuating and thawing, they were sealed under nitrogen flow. And then afterpolymerizations were carried out at 230 and 256 °C.

The changes of viscosity and the reduced weight of poly-ε-caproamide after reaction were given in *Fig.* 4 and *Table* 3.

From these figure and table, it could be known that the viscosity and the reduced weight of poly-ε-caproamide were also increased with the reaction time and temperature. The reasons of the increase of viscosity and the reduced weight of poly-ε-caproamide might be also explained by the reactions which were already discussed.

The rate of reaction under this condition was lower than that under nitrogen flow. The reason of this phenomenon could be explained by assuming that the equilibrium state between poly-ε-caproamide and oligomer formed was achieved under sealed condition and oligomer formed remained in reaction tubes, but in the case of nitrogen flow, the oligomer and other low molecular weight components formed during reaction could be removed from the reaction tubes and so the reaction could be continued to be reached the equilibrium state.

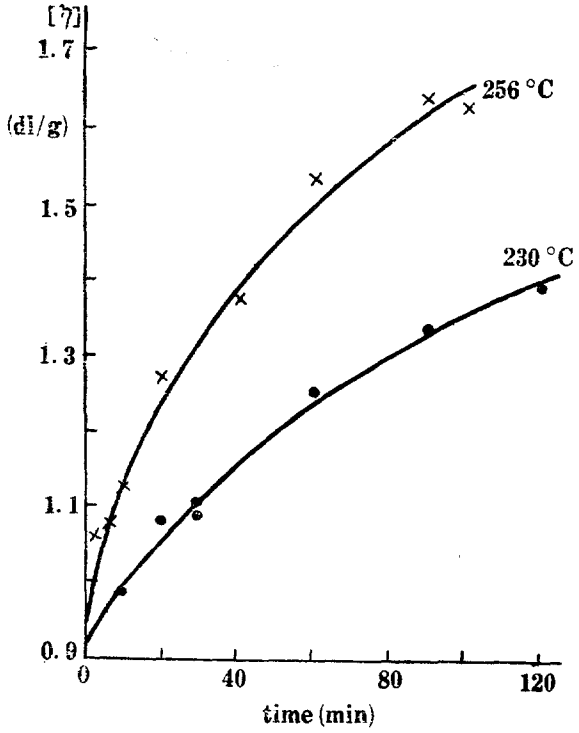


Fig. 4. Variation of intrintsic viscosity with time and temperature in sealed condition

Table 3. The reduced weight of poly-ε-caproamide in reaction condition of sealing

Temp. (°C)	Time (min.)	Reduced weight (wt. %)
230	10	0.85
	20	0.68
	30	1.63
	30	1.24
	60	2.71
	90	2.93
	120	3.01
	150	4.22
256	2	0.64
	5	0.88
	10	1.76
	20	2.03
	40	3.32
	60	3.45
	90	4.37
	120	4.35

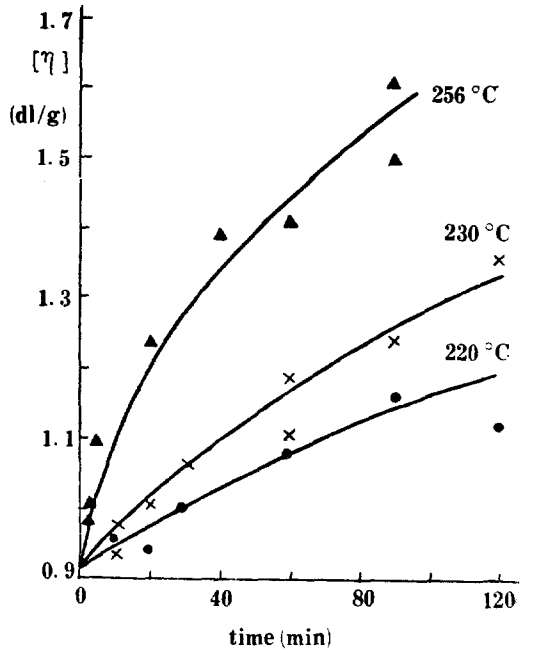


Fig. 5. Variation of intrinsic viscosity with time and temperature in reaction condition of evacuation

3. Evacuation of Sample Tubes. It was known that the rate of reaction under nitrogen flow was faster than that under sealed condition due to the removal of reaction products from the tubes. In order to know the effects of evacuation, the sample tubes were continually evacuated during reaction. As results, the viscosity and the reduced weight of poly-ε-caproamide were given in *Fig.* 5 and *Table* 4.

The viscosity and the reduced weight of poly-ε-caproamide were also increased with the reaction time and temperature, but the rate of reaction under this condition was lower than those under the former two conditions nitrogen flow and sealed condition.

In general, it was known that the contraction of volume was expected during the polymerization reaction and the increase of reaction rate. The decrease of reaction rate under this condition in *Fig.* 5 by comparing with the former two

Table 4. The reduced weight of poly-ε-caproamide in reaction condition of evacuation

Temp. (°C)	Time (min.)	Reduced weight (wt. %)
220	10	0.67
	20	0.48
	20	1.34
	30	0.93
	60	2.48
	90	3.29
	120	2.99
	150	4.38
230	10	0.56
	10	0.45
	20	1.61
	30	2.15
	60	3.02
	60	3.61
	90	3.89
	120	5.17
256	2	0.38
	2	0.99
	5	1.64
	20	2.32
	40	5.14
	60	5.85
	90	7.07

conditions, nitrogen flow and sealed condition, could be explained by decreasing the pressure in sample tube due to the evacuation. The increase of reaction rate due to the removal of reaction products was not observed in this case.

To compare the increase of viscosity for three different reaction conditions, the viscosity was plotted in *Fig.* 6 at constant reaction temperature, 230 °C.

From *Fig.* 6, it could be known that the rate of afterpolymerization was increased as the following order:

evacuation<sealing<nitrogen flow

It could be concluded that the jumping of viscosity in drying or spinning process of nylon 6 could be reduced by using the vacuum system.

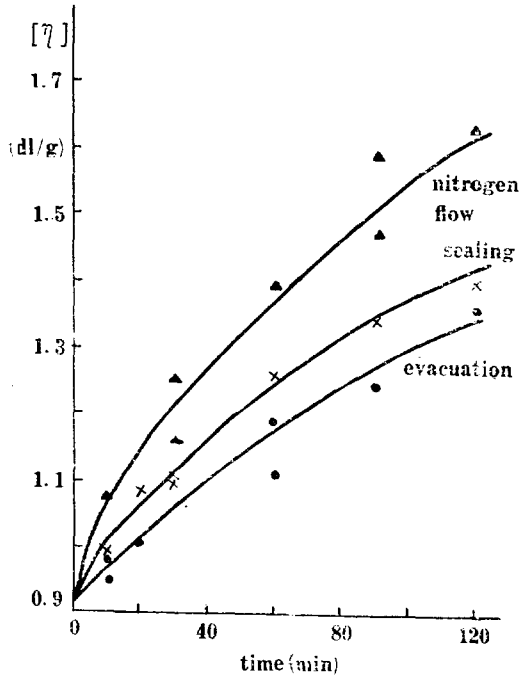


Fig. 6. Effect of reaction condition on intrinsic viscosity at 230 °C

References

1. S. Smith, *J. Polymer Sci.*, **30**, 459 (1958).
2. O. Wichterle, *Makromol Chem.*, **35**, 174 (1960).
3. Otani, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **65**, 1641 (1962).
4. S. Schaaf, *Faserforsch. u. Textiltechnik*, **20**, 224 (1959).
5. G. N. Harding, and B. J. MacNulty, Symposium High Temperature Resistance and Thermal Degradation of Polymers, London, 21-23. Sept., 1960.
6. B. Kamerbeek G. H. Kroes and W. Grollo, Symposium High Temperature Resistance and Thermal Degradation of Polymers, London, 21-23. Sept., 1960.
7. D. Braun, H. Chedron and W. Kern, "Praktikum

der Makromolekularen Organische Chemie", p. 157 (a), Dr. Alfred Hüthig Verlag Gmbh, Heidelberg, Germany, 1966.

8. G. Meacock, *J. Appl. Chem.*, **4**, 172 (1954).
9. R. G. Griskey, and B. I. Lee, *J. Appl. Polymer Sci.*, **10**, 105 (1966).