

Degradation of nylon-6 in ethylene glycol

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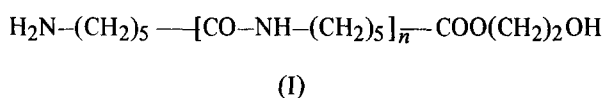
Glycolysis of nylon-6 in boiling ethylene glycol was studied. Oligoamides with amino- and hydroxyl-end-groups were obtained. The following catalysts were examined: zinc acetate, sodium glycolate and poly(phosphoric acid). The reaction rate constants found for first order reaction proved that the amino-groups formed during the degradation take part in acceleration or slowing of the reaction velocity. The reaction rate constants did not change in the polymerization degree range of $\bar{P} = 150-20$. Beginning from the polymerization degree $\bar{P} = 20$ in case of zinc acetate, sodium glycolate and without the catalyst the reaction rate constants increased, the reverse effect was observed when poly(phosphoric acid) was used.

INTRODUCTION

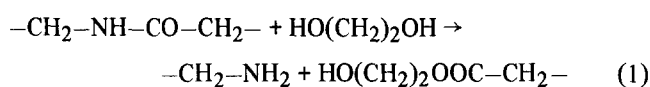
Good solubility of polyamides in strongly polar solvents has been well elaborated in the literature¹. At room temperature they are soluble in inorganic acids²⁻⁴; strong organic acids^{2,4,5}, phenol and its homologues^{3,5,6}, chlorinated aldehydes^{7,8} and concentrated solutions of metal halides in aliphatic alcohols^{6,9}. Less effective are ethylene glycol, glycerol¹⁰, benzyl alcohol⁶, formamide, *N,N*-dimethylformamide and acetamide¹¹ which dissolve polyamides at raised temperatures.

Simultaneously with polyamides dissolution particularly at higher temperatures, degradation processes take place as the result of the amide group hydrolysis, acidolysis, aminolysis or alcoholysis. Degrading action on nylon-6 of such agents as water¹², sulphuric acid¹³, acetic acid, organic bases was carefully examined and described in numerous papers, while there is only little information about their alcoholysis. Saunders¹⁴ examined the influence of butanol fission rate of the polyamide chain, but alcohol was used only as an accelerator. Degradation was carried out in an aqueous medium, butanol acting slower than the other catalysts as for example acids. Włodarczyk¹⁵ proved the degrading action of chloroalcohols on nylon-6, in this case the reaction is catalysed by hydrogen chloride formed during heating.

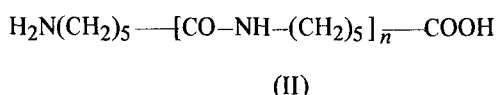
It seemed interesting to examine the degrading action of ethylene glycol on nylon-6. The glycolysis reaction is expected to lead to oligoamides of the following molecular structure:



according to the reaction:



These oligomers differ basically by hydroxyl end-group from linear, conventional oligomers of the structure:



The main purpose of this research was to obtain oligomers (I) with $-\text{OH}$ and $-\text{NH}_2$ end-groups, capable of reacting with maleic anhydride in order to obtain unsaturated oligoamides, 'endene' type analogous to unsaturated polyester resins which are described in Szayna's¹⁶ and Jedliński's¹⁷ papers.

EXPERIMENTAL

Materials

Nylon-6 was dried at 60°C/4 mmHg, $\bar{M}_v = 28\,000$, m.p. = 217°–219°C. Ethylene glycol was distilled under vacuum, the main fraction was dried with Na_2SO_4 and redistilled b.p. 92°C/10 mmHg, n_D^{20} , 1.3406.

Measurements

C, H and N content was analysed using a Perkin-Elmer 240 analyser. I.r. spectra were recorded with a Karl Zeiss spectrophotometer (KBr tablets). Molecular weights were determined viscosimetrically by means of a Ostwald viscometer and potentiometrically using a Mera Elmet N5122 pH-meter. The melting point was determined using Boetius apparatus

Glycolysis of nylon-6

620 g (10 mole) of fresh distilled glycol, 113 g (1 mole calculated per basic caprolactam unit) of nylon-6 was placed into a 1 litre reactor. Degradation was carried out at glycol boiling point (197°C) in dry nitrogen atmosphere. Samples of the degradation product were collected every 2 h, washed from glycol several times with acetone and water, centrifuged and dried at 60°C/4 mmHg. The molecular weight, melting point, i.r. spectra and CHN analysis were determined.

Molecular weights of the initial nylon-6 and of the oligomers with polymerization degree $\bar{P} > 90$ were determined viscosimetrically by Matthes's¹⁸ method while for oligomers with $\bar{P} < 90$ the molecular weights were determined potentiometrically by Waltz's and Taylor's¹⁹ method, titrating amino end-groups.

Analogous degradations were carried out for systems containing the following catalysts: zinc acetate, sodium glycolate and poly(phosphoric acid). In every case the amount of

all catalysts was 1% of the whole reaction mixture. The results are shown in Tables 1–5 and in Figures 1 and 2.

RESULTS AND DISCUSSION

Calculations of reaction-rate constants

The reaction-rate constants were calculated according to the equation for first-order reactions:

$$k = \frac{1}{t} \ln \frac{1 - s_0}{1 - s} \quad (2)$$

Table 1 Glycolysis of nylon-6 without catalyst

No.	Degrada- tion time (h)	Oligoamides			$k \times 10^5$ (min ⁻¹)	$\frac{1}{\bar{P}} \times 10^2$
		\bar{M}_V	\bar{P}	M.p. (°C)		
* 1	0	†28 000	†248.0	†217–19	—	0.40
2	6	16 630	147.2	217–19	0.78	0.68
3	12	11 130	98.5	216–18	0.86	1.01
4	24	6770	59.9	215–18	0.89	1.67
* 5	36	5360	47.4	215–18	0.80	2.10
6	48	4070	36.0	212–16	0.84	2.78
7	72	3020	26.7	209–13	0.79	3.74
* 8	96	2280	20.2	202–07	0.81	4.95
9	120	1570	13.9	193–97	0.98	7.19
10	192	840	7.4	164–71	1.23	13.51
*11	240	700	6.2	162–69	1.19	16.12
12	300	450	4.0	149–56	1.56	25.00

* CHN analysis and i.r. spectra of these samples are shown in Table 5 and Figure 2.

† Data of initial nylon-6 are taken for comparison. $\bar{k}^I = 0.82 \times 10^{-5}$ calculated as arithmetical means of $k_2 - k_8$

Table 2 Glycolysis of nylon-6 with (CH₃COO)₂Zn as catalyst

No.	Degrada- tion time (h)	Oligoamides			$k \times 10^{-5}$ (min ⁻¹)	$\frac{1}{\bar{P}} \times 10^2$
		\bar{M}_V	\bar{P}	M.p. (°C)		
1	6	12 840	113.6	216–18	1.34	0.88
2	12	8130	71.9	215–18	1.39	1.39
3	24	4790	42.4	213–17	1.38	2.36
4	30	3900	34.5	212–17	1.41	2.89
5	36	3290	29.1	210–15	1.43	5.44
6	48	2670	23.6	204–10	1.36	4.24
7	72	1720	15.2	194–99	1.48	6.58
8	96	1270	11.2	186–92	1.56	8.93
9	120	1060	9.4	172–80	1.51	10.64
10	192	660	5.8	164–70	1.61	17.24
11	216	530	4.7	152–59	1.81	21.28

$\bar{k}^{II} = 1.38 \times 10^{-5}$, calculated as arithmetical means of $k_1 - k_6$

Table 5 CHN analysis of the initial nylon-6 and oligoamides from glycolysis without catalyst

Sample	\bar{M}_V		C (%)		H (%)		N (%)	
	*Calc.	Found	*Calc.	Found	*Calc.	Found	*Calc.	Found
Nylon-6	28 042	28 000	63.67	63.54	9.73	9.67	12.38	12.30
Oligoamides no 5	5373	5360	63.43	63.36	9.73	9.61	12.24	12.13
Oligoamides no 8	2322	2280	63.05	62.76	9.73	9.70	12.06	11.88
Oligoamides no 11	740	700	61.62	61.06	9.73	9.62	11.35	10.94

* Calculated on the basis of the molecular structure

where: k is the reaction-rate constant, t is the degradation time, $s = 1/\bar{P}$, is the degree of glycolysis, $s_0 = 1/\bar{P}_0$ is the degree of glycolysis of the initial nylon-6, \bar{P}/\bar{P}_0 are number-average polymerization degrees.

Calculations of the results by means of equation (2) for disorder degradation show that the reaction-rate constant in the case of glycolysis without catalyst is comparatively small ($\bar{k}^I = 0.82 \times 10^{-5}$) and it does not change its value up to the polymerization degree $P \approx 20$. As the glycolysis proceeds the reaction-rate constant increases rather markedly. This may be caused by autocatalytic action of amino end-groups which are formed during degradation (Table 1).

An analogous effect is observed in the case of glycolysis catalysed by zinc acetate (Table 2) and by sodium glycolate (Table 3).

A reverse effect was observed when poly(phosphoric acid) was used as a catalyst, in this case after achieving the degree

Table 3 Glycolysis of nylon-6 with HO-(CH₂)₂-ONa as catalyst

No.	Degrada- tion time (h)	Oligoamides			$k \times 10^5$ (min ⁻¹)	$\frac{1}{\bar{P}} \times 10^2$
		\bar{M}_V	\bar{P}	M.p. (°C)		
1	2	10 660	94.3	216–18	5.54	1.06
2	4	6610	58.5	215–18	5.51	1.70
3	6	4800	42.5	212–16	5.49	2.35
4	8	3730	33.0	213–16	5.57	3.03
5	10	3100	27.4	210–15	5.52	3.65
6	12	2610	23.1	205–12	5.58	4.33
7	24	1330	11.8	188–93	5.87	8.47
8	36	840	7.4	167–72	6.54	13.51
9	48	670	5.9	160–66	6.30	16.95

$\bar{k}^{III} = 5.53 \times 10^{-5}$, calculated as arithmetical means of $k_1 - k_6$

Table 4 Glycolysis of nylon-6 with poly(phosphoric acid) as catalyst

No.	Degrada- tion time (h)	Oligoamides			$k \times 10^5$ (min ⁻¹)	$\frac{1}{\bar{P}} \times 10^2$
		\bar{M}_V	\bar{P}	M.p. (°C)		
1	2	9310	82.4	216–18	6.83	1.21
2	4	5540	49.0	216–18	6.92	2.04
3	6	4020	35.6	211–17	6.80	2.81
4	8	3160	28.0	208–12	6.74	3.57
5	10	2590	22.9	202–08	6.77	4.36
6	12	2220	19.6	203–09	6.71	5.10
7	24	1700	15.0	193–98	4.51	6.66
8	48	1410	12.5	190–97	2.75	8.00
9	72	1210	10.7	187–94	2.17	9.34

$\bar{k}^{IV} = 6.79 \times 10^{-5}$, calculated as arithmetical means of $k_1 - k_6$

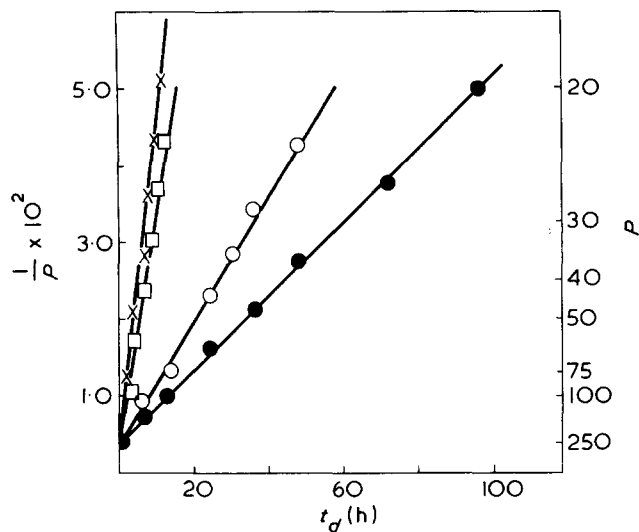


Figure 1 The reciprocal of degree of polymerization $1/\bar{P}$ plotted versus degradation time t_d : ●, without catalyst; ○, with $(\text{CH}_3\text{COO})_2\text{Zn}$; □, with $\text{HO}(\text{CH}_2)_2\text{ONa}$; X, with $(\text{HO})_2\text{OPO}$ $[\text{P}(\text{OH})(\text{OOP})(\text{OH})\text{O}]_n\text{OPO}(\text{OH})_2$

of polymerization $\bar{P} < 20$ the reaction-rate constant decreased. This phenomenon can be explained by the deactivating action of basic amino groups on acidic catalyst (Table 4).

The linear relationship between the reciprocal of number-average degree of polymerization and glycolysis time up to $\bar{P} \approx 20$ is shown in Figure 1. The calculated arithmetical mean values of glycolysis rate constants: $\bar{k}^I = 0.82 \times 10^{-5}$, $\bar{k}^{II} = 1.38 \times 10^{-5}$, $\bar{k}^{III} = 5.53 \times 10^{-5}$, and $\bar{k}^{IV} = 6.79 \times 10^{-5}$ are much lower than the hydrolysis-rate constant in 98% H_2SO_4 ($k_n = 1.20 \times 10^{-4}$), determined by Staudinger¹².

CHN analysis

The results of CHN analysis of oligoamide samples collected during the degradation prove to be in good agreement with the found polymerization degrees. During glycolysis the content of carbon and nitrogen decrease from 63.54% ($\bar{P} \approx 248$) to 61.06% ($\bar{P} \approx 6$) and 12.30% to 10.94% respectively while the hydrogen percentage remains constant within the limits of experimental accuracy.

I.r. spectra

The original i.r. spectrum of nylon-6 with characteristic absorption bands 3300 (vs, NH), 1650 (vs, C=O) and 1560 cm^{-1} (s, NH, C-N) is presented in Figure 2 and compared with the spectra of oligoamide samples collected during the degradation. The spectra of oligomers show the same characteristic absorption bands for nylon-6. For the sample with $\bar{P} \approx 50$ the band at 1740 cm^{-1} (vs, C=O) originating from vibrations of carbonyl group of the ester end-groups formed during glycolysis becomes noticeable.

The intensity of this band increases with the decrease of number-average molecular weight of oligomers this being caused by the increase of the amount of the ester end-groups. In the spectrum of the sample with $\bar{P} \approx 6$ an extension of 3300 cm^{-1} absorption band towards wavenumber 3400 cm^{-1} can be noticed this being associated with absorption of alcohol group 3550–3450 cm^{-1} (s, OH).

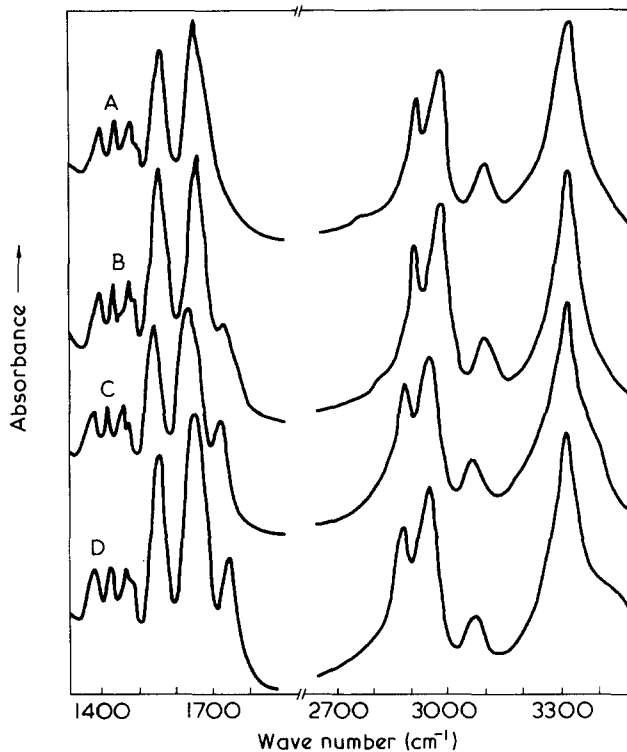


Figure 2 I.r. spectra of the initial nylon-6 and oligoamides from glycolysis without catalyst: A, nylon-6 $M_v = 28\,000$; B, oligoamides no 5 $M_v = 5360$; C, oligoamides no 8 $M_v = 2280$; D, oligoamides no 11 $M_v = 700$

CONCLUSIONS

This paper proves that nylon-6 degrades under the influence of ethylene glycol at boiling temperature. This process can be described by kinetics equation for first-order glycolysis up to $\bar{P} \approx 20$.

Catalysts such as sodium glycolate and poly(phosphoric acid) increase the reaction rate in that range of polymerization degree seven and eight times, respectively.

Anhydrous zinc acetate often used as a catalyst in transesterification processes has only a slight effect on glycolysis.

The results of potentiometric titration of amino end-groups of oligoamides, i.r. spectra and CHN analysis confirm the molecular structure of the degradation products presented in this paper.

ACKNOWLEDGEMENTS

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