Degradation of nylon-6 in ethylene glycol: 2. Mathematical illustration of degradation

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(Received 2 February 1979, revised 29 May 1979)

Glycolysis of nylon-6 under pressure at 200–300°C was studied. Reduction of the reaction time and a decrease of the yield of oligomers was observed with the temperature increase. The most advantageous conditions for obtaining oligoamides with $\bar{M}_n \simeq 1000$ were calculated. It was found that in the experimental area investigated linear regression equations describe the course of degradation adequately.

INTRODUCTION

In the previous paper[1] the degrading action of ethylene glycol on nylon-6 was investigated. The glycolysis reaction results in oligoamides with $-OH$ and $-NH_2$ end-groups, of molecular structure:

$$H_2N-(CH_2)_5\left[CO-NH-CH_2)_5\right]_n COO\cdot CH_2CH_2OH$$

We stated then[1] that oligoamides with $\bar{M}_n \simeq 1000$ (capable of reacting with maleic anhydride in order to obtain unsaturated oligoamides of the 'endene' type) were formed after 34 h of glycolysis when sodium glycolate was used as catalyst. In order to shorten the degradation time it was decided to study the course of reaction in an autoclave at 200–300°C under increased pressure.

EXPERIMENTAL

Materials

Nylon-6 was dried at 60°C/4 mm Hg, $\bar{M}_v$ = 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 mm Hg, n_D^{20} = 1 3406.

Measurements

Molecular weights of the initial nylon-6 and of the oligoamides with degree of polymerization $\bar{P} > 90$ were determined viscometrically by Matthes' method[2], while for oligomers with $\bar{P} < 90$ the molecular weights were determined potentiometrically by Waltz and Taylor's[3] method, titrating amino end-groups.

Glycolysis of nylon-6

113 g (1 mole calculated per basic caprolactam unit) of nylon-6, 62 g (1 mole) of glycol and 1.1 g of sodium glycolate were placed into a 350 cm^3 autoclave. The reaction mixture was blown through with dry, oxygen-free nitrogen. A number of degradations with or without sodium glycolate as catalyst were carried out at 200, 250 and 300°C. After finishing every experiment the reaction products were washed out from the glycol several times with acetone and water, centrifuged and dried at 60°C/4 mm Hg. $\bar{M}_n$ and the yield of the obtained oligoamides were determined.

RESULTS AND DISCUSSION

Based on the preliminary experiments we stated that an increase in temperature shortens the reaction time necessary to obtain oligomers with $\bar{M}_n \simeq 1000$ but simultaneously a decrease in yield was observed. This may be attributed to depolymerization of nylon-6 to ε-caprolactam. This effect was seen very clearly in the case of glycolysis carried out in the presence of a catalyst.

A mathematical method of designing the experiment was applied in order to choose the most advantageous conditions of nylon-6 degradation (glycolysis) at 200–300°C which ought to result in oligoamides $\bar{M}_n \simeq 1000$ in the shortest time and with good yield.

M (the number average mol. weight of the degradation product $\bar{M}_n$) and Y (the total yield of oligomers) were taken as dependent variables. In order to state the influence of the independent variables:

T – reaction temperature [°C]
t_d – degradation time [h]
s – catalyst amount [%]

on the course of nylon-6 degradation, the process was investigated for two values of each independent variable.

To obtain the mathematical model of the process the linear course of functions M and Y in the experimental area was established. To avoid a large error when replacing the non-linear function $\bar{M}_n = f(t_d)$ by a linear regression equation the following system of division of the experimental area was taken:

Experimental area I	T (°C)	t_d (h)	s (%)
Upper level	300	14	1
Lower level	250	4	0
Base level	275	9	0.5
Experimental area II			
Upper level	250	24	1
Lower level	200	14	0
Base level	225	19	0.5

The full experiment type 2^3 was applied and the results are given in *Table 1*.

0032-3861/80/010086-03$02.00

Table 1 The matrix of designing the experiments (type 2^3), the observed values of functions M, Y and the estimated values of function $\hat{M}$, $\hat{Y}$ in the experimental areas I and II

				Observed				Estimated			
	Designed			I area		II area		I area		II area	
No.	x_1	x_2	x_3	M	Y	M	Y	$\hat{M}$	$\hat{Y}$	$\hat{M}$	$\hat{Y}$
1	−1	−1	−1	10480	96.8	10820	95.9	10380	99.6	10020	99.9
2	+1	−1	−1	3570	70.1	7800	95.0	3340	71.9	8600	93.2
3	−1	+1	−1	7800	95.0	7200	95.3	7890	92.2	7230	94.5
4	+1	+1	−1	2330	66.4	5840	89.2	2560	66.4	5810	87.7
5	−1	−1	+1	3820	87.6	2140	85.3	3910	88.5	2540	85.4
6	+1	−1	+1	1120	51.4	1520	82.0	1350	45.9	1120	78.6
7	−1	+1	+1	1520	82.0	1480	83.4	1420	91.1	1840	79.9
8	+1	+1	+1	810	33.1	770	67.4	600	38.6	410	73.1

The coefficients of the linear regression equation (1) were calculated from the results obtained by means of the following formulae:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \quad (1)$$

e.g.

$$b_i = \sum_{u=1}^{N} x_{iu}y_u/N \quad (2)$$

where N is the number of experiments;

x_1 is the value of the reduced independent variables in the N^{th} experiment (*Table 1*)

y_u is the value of the dependent variable (result of the experiment, *Table 1*)

Statistical evaluation of the significance of the regression coefficients was tested by means of Student's t-distribution After elimination of insignificant regression coefficients the following regression equation with reduced parameters were obtained:

in experimental area I

$$M = 3931 - 1974x_1 - 816x_2 - 2114x_3 + 429x_1x_2 + 1121x_1x_3 \quad (3)$$

$$Y = 72.80 - 17.55x_1 - 3.67x_2 - 9.27x_3 - 3.72x_1x_3 \quad (4)$$

in experimental area II

$$M = 4696 - 714x_1 - 874x_2 - 3219x_3 + 521x_2x_3 \quad (5)$$

$$Y = 86.56 - 3.41x_1 - 2.74x_2 - 7.28x_3 \quad (6)$$

The values of functions M and Y calculated respectively on the basis of equations (3–6) are placed in *Table 1* and compared with the experimental data.

The obtained equations (3–6) were transformed into natural parameter equations introducing the following relations:

$$X_1 = \frac{T - 275}{25} \quad (7)$$

$$X_2 = \frac{t_d - 9}{5} \quad (8)$$

$$X_3 = \frac{s - 0.5}{0.5} \quad (9)$$

$$X_1 = \frac{T - 225}{25} \quad (10)$$

$$X_2 = \frac{t_d - 19}{5} \quad (11)$$

$$X_3 = \frac{s - 0.5}{0.5} \quad (12)$$

Thus equations (13–16) were obtained; these determine the degradation time $t_d = f(\bar{M}_n, T, s)$ and the yield of oligoamides $Y = f(t_d, T, s)$

$$t_{d\text{I}} = \frac{\bar{M}_n - 50053 + 154.7T + 28890s - 89.68Ts}{3.432T - 1107} \text{ [h]} \quad (13)$$

$$Y_{\text{I}} = 240.81 - 0.553T - 0.734t_d + 63.3s - 0.289Ts \text{ [\%]} \quad (14)$$

$$t_{d\text{II}} = \frac{\bar{M}_n - 19642 + 28.56T + 10398s}{208.4s - 279} \quad (15)$$

$$Y_{\text{II}} = 134.94 - 0.1364T - 0.548t_d - 14.56s \quad (16)$$

The expected degradation time t_d of nylon-6 was calculated from equations (13) and (15), necessary to obtain oligomers with $\bar{M}_n \simeq 1000$ at specified temperature T and assumed concentration of catalyst ($s = 1\%$). From equation (14) and (16) the expected yield of degradation products was calculated.

The results of calculations in the experimental areas I and II are shown in *Table 2.*

Calculations 1–4 for domain I were carried out based on equations (15) and (16) while 5–8 for domain II were based on equations (13) and (14). It can be seen from these results that the most advantageous temperature of glycolysis reaction is 250°C. It is expected that in the case of glycoly-

Table 2 The expected yields $\hat{Y}$ and $\hat{M}$ of oligomers calculated on the basis of equations (14, 16) and (13, 15) respectively

			II area			I area			
	No	1	2	3	4	5	6	7	8
	T [°C]	200	230	240	250	270	280	290	300
	t_d [h]	35.9	23.7	19.7	15.6	14.1	13.1	11.7	8.5
1% of catal.	$\hat{M}$	M = 1000 in all cases as assumed in equation 13							
	$\hat{Y}$	73.4	76.0	76.8	77.7	63.8	56.0	48.7	45.6
no catal.	$\hat{M}$	3910	6460	7290	8150	5740	4820	3820	2980
	$\hat{Y}$	87.9	90.6	91.4	92.3	81.1	76.3	71.8	68.7

sis carried out at 250°C, 80% of oligomers ($\bar{M}_n \simeq 1000$) should be obtained after 16 h. By carrying out the process at higher temperatures (300°C) the degradation time can be reduced, but simultaneously a marked decrease in yield will take place.

As a result of glycolysis carried out at temperatures lower than 250°C, oligomers $\bar{M}_n \simeq 1000$ of higher yield ought to be obtained but after a much longer reaction time. A comparison of calculations for glycolysis with and without catalyst (*Table 2*) shows that after the same degradation time in the case of reaction without catalyst, products with much higher $\bar{M}_n$ should be obtained. Without catalyst, the required oligoamides will need a longer reaction time than in the case of glycolysis carried out with sodium glycolate as a catalyst.

CONCLUSIONS

It can be stated that the most advantageous values of the independent variables (T, t_d and s) for glycolysis of nylon-6 under increased pressure in the given experimental area T = 200–300°C, t_d = 4–24 h, s = 0–1% are: T = 250°C, t_d = 16 h, s = 1% of $HO/CN_2/_2ONa$ in ratio to nylon-6.

The control experiments carried out at the most advantageous conditions calculated previously proved the adequacy of the assumed mathematical model of glycolysis reaction in the above experimental area.

Control experiment No.	$\bar{M}_n$	Yield (%)
1	1130	75.3
2	1270	78.0
3	1040	77.1
4	1180	80.6
5	1240	76.0

ACKNOWLEDGEMENTS

This work was possible thanks to the grant from the Department of Polymers of the Polish Academy of Sciences, 41-800 Zabrze.

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