Synthesis and properties of polyamide polyelectrolytes with phenolic side groups

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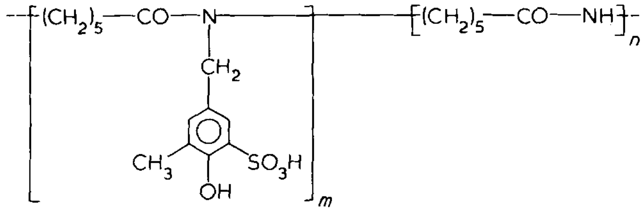
Condensation of nylon-6 with *o*-cresolsulphonic acid CSA and formaldehyde gives *N*-substituted nylon-6 derivatives with *N*-sulphocresylmethylene side groups (IV), responsible for the polyelectrolytic properties of the derivatives. In a strong acid medium the reaction mechanism is as follows: (1) condensation of amide groups with CSA and formaldehyde; (2) elimination of a number of sulphonic groups with the formation of methylene phenol side chains (II, III); (3) degradation of the polyamide chain. A kinetic description of this complex condensation, corresponding well with the proposed mechanism, and calculations in agreement with the experimental data are presented.

INTRODUCTION

In previous papers[1,2] the condensation products of 2-hydroxy-3-methyl-benzenseulphonic acid (*o*-cresolsulphonic acid, CSA) with nylon-6 and formaldehyde were described. These proved to be polyelectrolytes, typical acids, readily soluble in dilute alkali and ammonia. The residue in the polymer chain responsible for the polyelectrolytic properties was found to be:



I

The main drawbacks of the condensation method[1] were: (a) the use of formic acid (toxic, volatile and aggresive) as the reaction medium; (b) the necessity of removing the sulphuric acid always present in the CSA; (c) poor yield, 50% with respect to nylon-6.

Here, an attempt to achieve better yields of similar polyelectrolytes, avoiding use of formic acid as a reaction medium, is described. The following methods were examined:

(1) *N*-hydroxymethyl nylon-6 previously obtained in a separate process was condensed with CSA;

(2) nylon-6 was hydroxymethylated with CH_2O in H_2SO_4 and then, without separating the product, CSA was introduced;

(3) CSA was previously hydroxymethylated with CH_2O and without separating the product, nylon-6 was introduced;

(4) a solution of CSA and nylon-6 in H_2SO_4 was condensed with formaldehyde.

EXPERIMENTAL

Materials

Nylon 6, $\bar{M}_v = 34\,000$, was obtained in powder form.

o-Cresolsulphonic acid (*CSA*). To 324 g of *o*-cresol (3 mol) was added 459 g of conc. H_2SO_4 (4.5 mol) slowly and with cooling to 20°C. Sulphonation was complete in a week. 261 g of the mixture contained 1 mol of the CSA, and was used in this form in further reactions without separation.

Condensation of nylon-6:CSA:$CH_2O = 1{:}3{:}4$ *mol*

11.3 g of nylon-6 (0.1 mol caproamide unit) was left for 24 h together with 78.3 g of CSA–H_2SO_4 solution (0.3 mol). After stirring for 48 h, the nylon-6 had dissolved and 33.3 g of 36% formaline were added slowly, with continuous stirring at the desired temperature. The reaction was slow at room temperature (*Figure 1*). The reaction time could be shortened from 7 weeks to 30 min by increasing the temperature but the sulphur content in the products then decreased after passing through a maximum (*Figure 2* and *Table 1*, columns 2 and 5).

Reaction products (viscous, plastic) were precipitated on adding 200 cm^3 of water. Excess acids (unreacted CSA and H_2SO_4) were removed by kneading repeatedly with water at 50°C until no SO_4^{2-} could be detected in the aqueous medium. Drying the product under vacuum at 50°C resulted in a spongy mass, easy to powder.

Analysis

For analysis the polyelectrolytes were dissolved in methanol/20% ammonia (4:1), centrifuged from unreacted nylon-6, precipitated with 5% HCl, washed with water and dried under vacuum. Analysis of the product obtained after 45 min condensation at 55°C (formula IV where $m = 4$, $n = 2$). Calculated: C, 64.46%; H, 6.81%; N, 3.81%; S, 4.98%. Found: C, 65.22%; H, 6.26%; N, 3.92%; S, 4.70%.

Molecular weights were calculated from the carboxyl end-group concentration, which is the difference between the total acid group concentration titrated with NaOH (1.90 mmol g^{-1}) and SO_3H concentration calculated from the sulphur content (1.55 mmol g^{-1}). The molecular weight thus obtained was: $\bar{M}_n = 1/0.35 \times 10^{-3} = 2860$. M_{calc} for formula IV was 2569.

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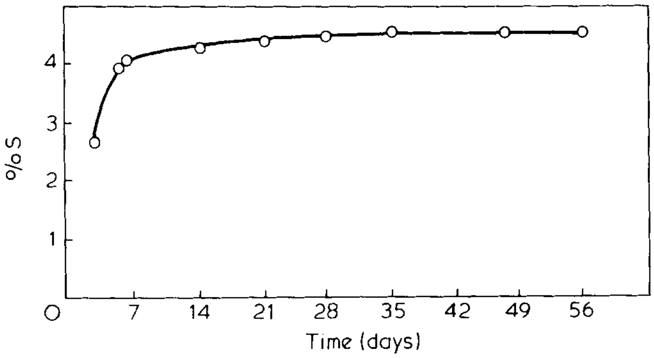


Figure 1 Dependence of the sulphur content in polyamide polyelectrolytes on the condensation time at 20°C

Degradation during condensation

It has been established experimentally that the degradation of the polyamide during the condensation is caused by the action of formaldehyde.

To a stirred solution of 5 g nylon-6 in 45 g conc. H_2SO_4, was added water or water–formalin at 55°C, keeping the same water concentration in each experiment, as shown below:

Curve	Formalin (g)	Water (g)
A	–	17.6
B	3.6	15.3
C	9.2	11.7
D	18.5	5.0
E	27.5	—

Samples of degraded nylon-6 were taken from these solutions at different time intervals, precipitated with cold water, washed and dried. $\bar{M}_v$ for each sample was determined in conc. H_2SO_4 (Figure 3).

Low molecular weight is responsible for a difference between the properties of the polyelectrolyte solutions and those of polyelectrolytes (I) described in refs. 1 and 2 (*Figure 4*). However, maximum η_{sp} is reached for these solutions when all the functional groups are neutralized and the chain is completely stretched, as in the case of polyelectrolytes (I).

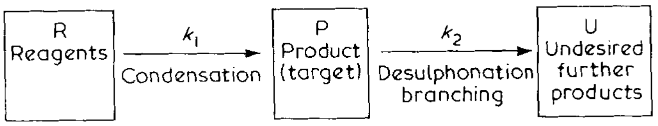
Kinetics of the process

The kinetics of the condensation were investigated by determining the sulphur content. Changes in sulphur content in the reaction products (*Figures 1* and *2*) prove that the condensation is a complex process. It should be noted that:

(1) at room temperature the condensation proceeds like other polycondensation reactions (*Figure 1*);

(2) at higher temperatures (*Figure 2*), two different mechanisms control the process: (a) condensation of nylon-6 with CSA and CH_2O with reaction rate constant k_1; (b) desulphonation and branching[3] to undesired products with reaction rate constant k_2 (see reactions II and III presented in the Discussion).

The above process can be considered as a two-step reaction:



Let r, p and u denote the concentrations of R, P, U respectively and suppose that at the time $t=0$: $r(0)=r_0$ (constant in all our experiments); $p(0)=u(0)=0$. Thus the process can be described by:

$$\frac{dr}{dt}=-k_1r \tag{1}$$

$$\frac{dp}{dt}=k_1r-k_2p \tag{2}$$

$$\frac{du}{dt}=k_2p \tag{3}$$

The solution of these equations for p gives:

$$p=\frac{k_1r_0}{k_2-k_1}\left[\exp(-k_1t)-\exp(-k_2t)\right] \tag{4}$$

The concentration of p can be followed by determining the sulphur content [S] which decreases when branched, undesired products U are formed. Thus

$$p=r_0[S] \tag{5}$$

Comparing (4) and (5) results in:

$$[S]=\frac{k_1}{k_2-k_1}\left[\exp(-k_1t)-\exp(-k_2t)\right] \tag{6}$$

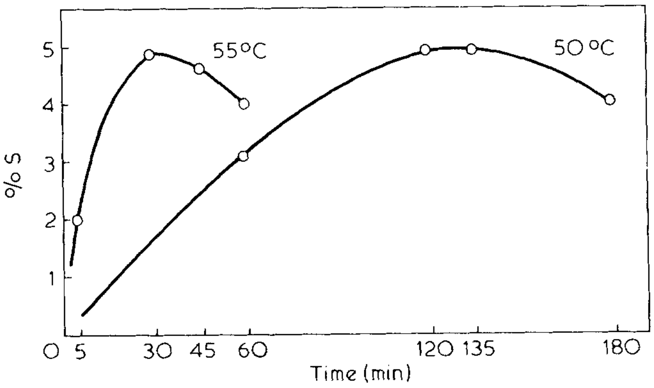


Figure 2 Dependence of the sulphur content in polyamide polyelectrolytes on the time and temperature of condensation

Table 1 Sulphur contents in polyamide polyelectrolytes, found and calculated from equation (6)

	Temperature			
	50°C		55°C	
a	0.059812		0.059264	
k_2	0.022191		0.100126	
k_1	0.001327		0.005934	
Time of the condensation (min)	S (%)		S (%)	
	Found	Calc.	Found	Calc.
5			2.05	2.30
30			4.96 max	4.96
45			4.70	4.75
60	3.17	4.19	4.12	4.40
120	4.96	4.98	2.98	3.09
135	5.00 max	5.00		
180	4.07	4.89		

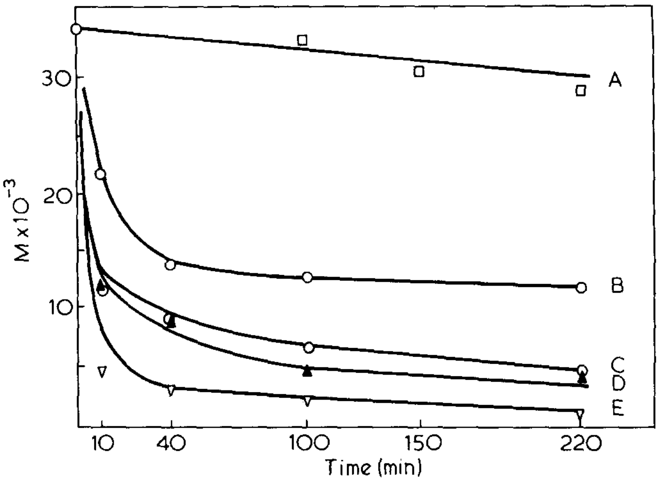


Figure 3 Dependence of the nylon-6 degradation on temperature and on formalin concentration in the presence of H_2SO_4 at 55°C

Equation (6) can be used to predict the sulphur content after different condensation times and always at the same concentration of nylon-6 (0.1 mol), CSA (0.3 mol) and CH_2O (0.4 mol). The following steps are necessary to find k_1 and k_2.

Analysis of equation (6) enables us to expect a maximum p_{max} at time t_{max}. These maxima are related to the reaction rate constants by the following equations:

$$\ln p_{max} = \frac{1}{1-a} \ln a \qquad (7)$$

$$t_{max} = \frac{-\ln a}{k_2(1-a)} \qquad (8)$$

where

$$a = \frac{k_1}{k_2} \qquad (9)$$

From the experimental values, p_{max} and t_{max}, we can successively calculate the reaction rate constants, as shown below. Equation (7) can be solved by the Newton–Raphson algorithm:

$$a_{i+1} = a_1 - \frac{f(a)}{f'(a)} \qquad (10)$$

where

$$f(a) = \frac{1}{1-a} \ln a - \ln p_{max} \qquad (11)$$

$$f'(a) = \frac{1}{1-a}\left[\frac{1}{a} + \frac{1}{1-a}\right] \ln a \qquad (12)$$

When a is known from equations (10), (11) and (12), k_2 can be calculated from equation (8) and k_1 from equation (9).

A comparison of p, calculated from equation (6) at selected times with experimental data, illustrates how this function describes the condensation in strong acidic medium (*Table 1*, *Figure 2*).

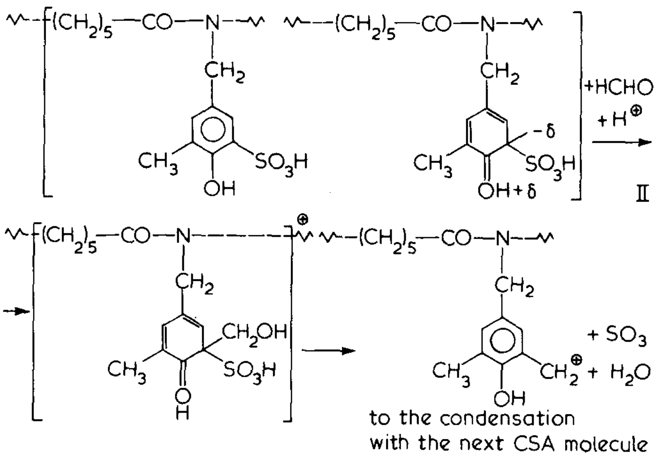
RESULTS AND DISCUSSION

Only method (IV) proved successful. Condensations via the hydroxymethyl derivatives of nylon-6 or CSA failed. On examining the reaction conditions for method (d) more closely it was found that:

(1) at least 3% of the sulphur content in the condensation products is necessary to obtain products soluble in alkali;

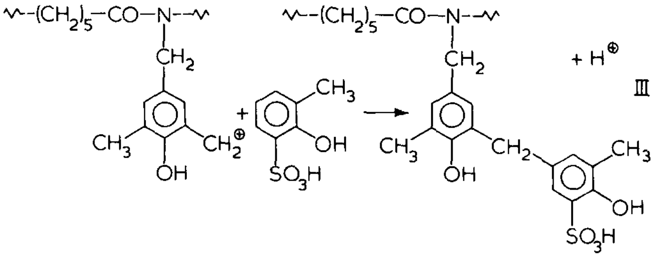
(2) at temperatures higher than 50°C long-branched, dark-coloured and less soluble derivatives are formed.

In a strong acidic medium this seems to be the result of elimination of SO_3H groups under the action of an excess of formaldehyde in the course of the following reactions:



to the condensation with the next CSA molecule

According to ref 3, the intermediate carbocation reacts subsequently with the next CSA molecule to form (III):



The repeated reaction with formaldehyde and CSA increase the amount of phenolic side chain without increasing the sulphur content. The products obtained, when compared with the polyelectrolytes described in refs 1 and 2 (equation 1) are of much lower molecular weight. It was shown in separate reactions that the degradation of nylon-6 was accelerated by the action of formaldehyde, possibly due to increased solvation resulting from the

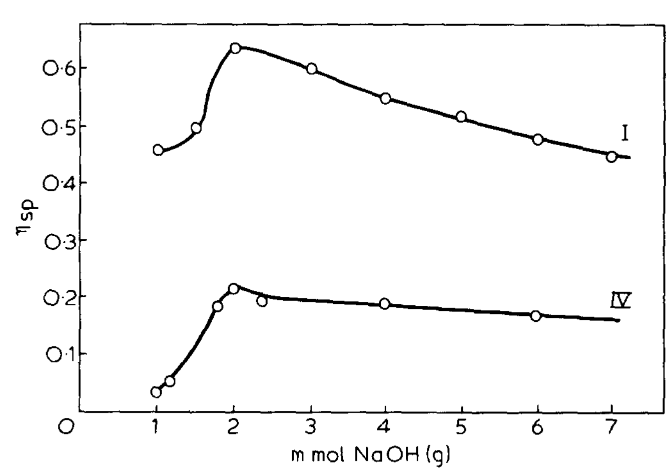


Figure 4 Dependence of η_{sp} of the polyamide polyelectrolytes on the rate of neutralization (formulae I and IV)

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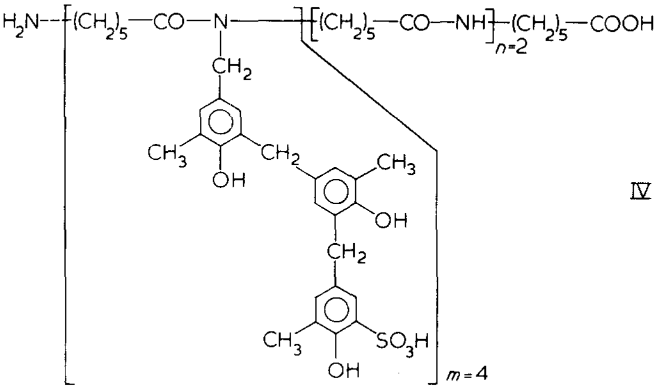
* An example of the iteration is given in the Appendix.

sulphuric ester of methylene glycol $HO.CH_2.OSO_3H$ (formaldehyde + H_2SO_4). The general formula of the polyelectrolyte is thus:



IV

which corresponds satisfactorily with analysis. Several additional similar structures were considered and it was shown that CHNS content varies only slightly when the indices change by one and $m = 4$–5, $n = 2$–3. A side branch longer by 1 phenolic ring is possible which does not change the CHNS content markedly.

REFERENCES

1 Kapko, J. *Bull. Acad. Pol.* 1964, **XII**, **2**, 99
2 Kapko, J., *Bull. Acad. Pol.* 1964, **XII**, **11**, 747
3 Polak, F. and Bortel, E., *Przemysl Chemiczyn* 1958, **37**, 651

APPENDIX A

Example of the iteration for $p_{\max} = 5\% = 0.05$
$\ln p_{\max} = 2.99573$

$$f(a) = \frac{1}{1-a} + 2.99573$$

$$f'(a) = \frac{1}{1-a}\left[\frac{1}{a} + \frac{1}{1-a}\ln a\right]$$

START: for example $a_i = 0.1$

i	a_i	$f(a)$	$f'(a)$	$\frac{f(a)}{f'(a)}$	a_{i+1}
1	0.1000000	0.437302	8.268413	+0.052888	0.047112
2	0.047112	−0.210557	18.910770	−0.011134	0.058246
3	0.058246	−0.023190	15.024783	−0.001543	0.059789
4	0.059789	−0.000329	14.602370	−0.000023	0.059812
5	0.059812	-6×10^{-8}	14.596371	-4×10^{-9}	0.059812

Thus $a = 0.059812$