
Composition of the Brown Material from Oxidized Nylon 6¹

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ABSTRACT

The dark compounds which are formed during the thermal oxidation of nylon 6 have been isolated and analyzed, mainly by thin-layer chromatography. The structures of the dark substances have been tentatively proposed, having assumed that the chemical principles that have been elucidated for the oxidation of pyrrolidine are equally valid for the oxidation of nylon. The ideas that have been developed differ from earlier ideas about the formation of brown materials, in that they are not necessarily based on the formation of derivatives of pyrrole. The new concepts account for the formation of polymers of variable molecular weight which may contain chromophores of variable length and of slightly different chemical compositions.

Introduction

At temperatures greater than 120°C, in oxygen and in air, polyamides will eventually become dark brown. Discoloration is accompanied by a fall in the breaking strength and in the elongation-at-break of the fiber. Similar effects are observed when a polyamide is irradiated at room temperature with ultraviolet light [1, 6-9]. Despite investigations [2, 10, 11] of the thermal oxidation of polyamides, the compositions of the brown compounds remain unknown, and those products which have been identified have not indicated how brown compounds could have been formed. A more recent analysis [3] of the low molecular weight products of thermally degraded polyamides has also

failed to indicate a pathway, but part of the route by which pyrrolidine is oxidized to brown material has been elucidated [4]. (It oxidizes via 2-pyrrolidone to succinimide, which undergoes dimerization. Subsequently, the dimer polymerizes to yield brown material.)

In this study a possible chemical formula for the brown substance derived from oxidized nylon 6 has been deduced by assuming that the chemical principles that have been elucidated for the oxidation of pyrrolidine are valid for the oxidation of nylon.

Experimental

MATERIAL. Nylon 6, free from delustrant and anti-oxidant, was soaked in an aqueous solution of nonionic detergent (0.1% v/v) at 50°C for 20 min. It was then rinsed with water at 80°C until the wash liquor became clear and then transferred to a soxhlet apparatus in which it was washed successively with ethanol and ether for periods of 24 h each. The purified polyamide

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was dried, first in a stream of warm air, and finally by storage in a vacuum desiccator over phosphorus pentoxide.

THERMAL OXIDATION. Purified nylon was placed in a beaker covered with a glass plate and placed in an oven maintained at the predetermined temperature. After the required time had elapsed the fibers were removed from the oven and stored in a vacuum desiccator over phosphorus pentoxide. A sample of nylon 6 which had been oxidized at 160°C for 12 h is referred to as N6 (O₂, 160°, 12).

HYDROLYSIS OF POLYAMIDE. A sample of the degraded polyamide (25 g) was placed in a flask (1000 ml) fitted with a ground glass stopcock and 5*N* hydrochloric acid (500 ml) was added. The mixture was solidified at -78°C, and the flask was evacuated for 1 min. After the mixture had been allowed to liquefy at room temperature under vacuum, the degassing process was repeated. Finally, the flask was sealed under vacuum and maintained at 110°C for 24 h.

FRACTIONATION OF THE HYDROLYSATE. The acidic hydrolysate was evaporated to dryness, the residue was dissolved in the minimum quantity of warm water and poured onto a column containing the cation exchange resin Amberlite C. G. 120 in the H⁺ form. Acidic products were eluted with distilled water (Fraction 1). Amino acids, bases, and the brown compounds were subsequently eluted with 5*N* aqueous ammonia, and the eluate was evaporated to dryness (Fraction 2).

EXAMINATION OF THE DARK SUBSTANCES. When a sample of Fraction 2 was chromatographed on cellulose using *t*-butanol/acetic acid/water (3:1:1) as the eluent, amines and amino acids moved away from the origin, while most of the brown compounds remained there. Subsequently, analytical amounts of the brown material were obtained by preparative thin-layer chromatography in this system, aqueous pyridine (2.5%) being the solvent for extracting the brown material from the substrate. The resulting solution was evaporated to dryness under reduced pressure. To ensure the absence of contaminants of low molecular weight, the brown material was chromatographed and recovered a second time. The brown product was dissolved in the minimum amount of water; a small amount of white, insoluble substance (presumably cellulose) was filtered off, and the brown aqueous solution was placed onto a column of cation exchange resin (Amberlite C. G. 120 in the H⁺ form) which was washed with distilled water. The brown substance was eluted with 5*N* aqueous ammonia. The solvent was removed under reduced pressure, and the brown residue was freeze-dried (48 h) to yield dark brown crystals, the ultraviolet and infrared spectra of which are shown in Figures 1 and 2.

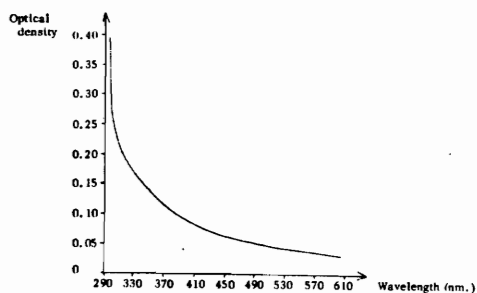


FIG. 1. Ultraviolet absorption spectrum of the brown material from nylon 6 (O₂, 160°, 12); solvent: water; concentration of brown material: 10⁻² g/l; light-path length: 1 cm.

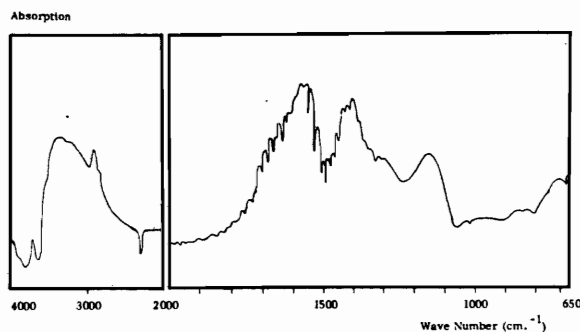


FIG. 2. Infrared absorption spectrum of dialyzed brown material from nylon 6 (O₂, 160°, 12).

Other samples were isolated using a different method for purification, namely dialysis. A sample (2.0 g) of Fraction 2 from a sample of nylon which had been oxidized for 8 h at 170°C, N6 (O₂, 170°, 8), was dissolved in water (100 ml) and continuously dialyzed using tap water. After 50 h the brown solution was evaporated to dryness under reduced pressure and freeze-dried (24 h). The brown product had a very large ash content. Subsequently, a sample was dialyzed first using tap water (50 h, continuously) and then by immersion of the dialysis sac in distilled water (3 × 2 liters, 15 h each). Unfortunately, the ash was never wholly removed, and it was not constant for a given set of conditions; contamination by combination with heavy-metal ions from the tap water should give a constant ash content. Plots of the proportion of each element against ash content, for all the data in Table I, gave reasonable straight lines from which the composition of the ash-free brown material (Table II) was obtained by extrapolation using the method of least squares.

PHYSICAL BEHAVIOR OF THE BROWN MATERIAL. The brown material ceased to be wholly soluble in its normal solvents after it had been dried. It is possible that further polymerization had occurred, but it seems more likely that cohesion between the molecules of the brown material is enhanced by the drying process.

TABLE I. Composition of brown material from oxidized nylon 6.

Origin of sample	C, %	H, %	N, %	Ash, %	Isolation technique
N6 (O ₂ , 160°, 12)	50.70	5.30	5.70	3.0	Column chromatog- raphy followed by thin-layer chromatography
N6 (O ₂ , 160°, 12)	50.20	5.20	6.70 ^a	3.5	
N6 (O ₂ , 160°, 12)	54.00	5.20	5.80	0	
N6 (O ₂ , 170°, 8)	51.80	5.75	5.70	2.0	Column chromatog- raphy followed by dialysis
N6 (O ₂ , 170°, 8)	46.50	4.95	6.00	7.0	
N6 (O ₂ , 170°, 8)	46.80	4.90	6.10	8.0	

^a This value was discounted in the calculation reported in Table II.

TABLE II. Composition of brown material and various postulated model compounds.

Compound	C, %	H, %	N, %	O, %
I	52.74	6.96	5.13	35.17
II	54.55	6.82	5.30	33.33
Repeat Unit A	56.47	6.67	5.49	31.37
Repeat Unit B	53.53	5.58	5.20	35.69
Observed after extrapola- tion to zero ash content using method of least squares	53.79	5.80	5.67	34.74

CHEMICAL BEHAVIOR OF THE BROWN MATERIAL.

Ozonolysis. Ozone-rich air was bubbled through a solution of the brown material (0.01 g) in formic acid (98–100%; 50 ml). After 3 h the brown solution had become appreciably paler. Prolonged treatment with ozone failed to discharge all the color.

Catalytic Hydrogenation. A sample of the brown material in methanol (0.01 g in 50 ml) was hydro-

genated in the presence of Adams' catalyst. After 70 h the brown solution was appreciably paler. Prolonged treatment (300 h) failed to eliminate all the color.

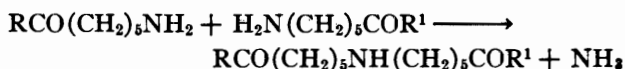
Reduction with Zinc/Mineral Acid. The brown material (0.01 g) was dissolved in 1N hydrochloric acid (10 ml). The hydrogen produced by the addition of zinc to the solution caused the color of the solution to become appreciably paler in a short time (2 h). Prolonged treatment (10 h) with nascent hydrogen failed to produce a colorless solution.

Results and Discussion

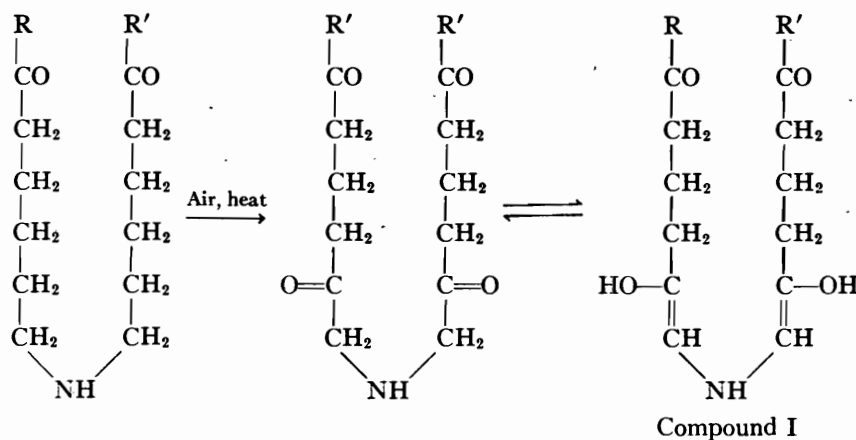
The compositions of various samples of brown material obtained from nylon 6 are shown in Table I.

The uv spectrum and the chromatographic and dialytic properties of the brown material suggest that it is polymeric. Its chemical properties indicate the presence of at least two types of chromophore; one is a conjugated system of carbon-carbon and possibly carbon-oxygen double bonds; the other may be an aromatic system or it may be an inorganic system.

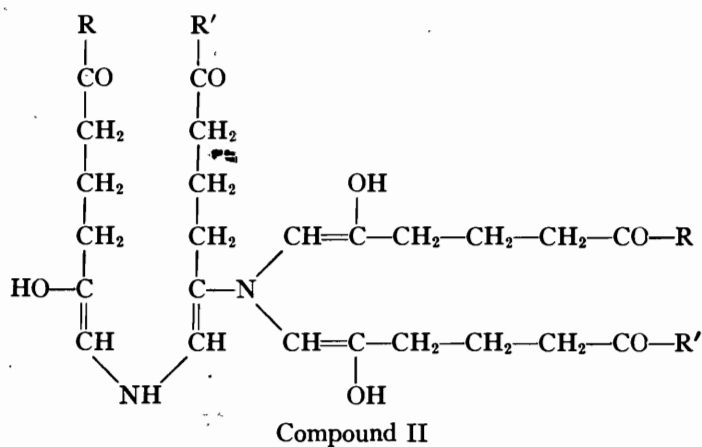
It is known [5] that one of the volatile products obtained by heating nylon is ammonia. The elimination of ammonia from the polymer strongly suggests a reaction leading to the formation of a secondary amine:



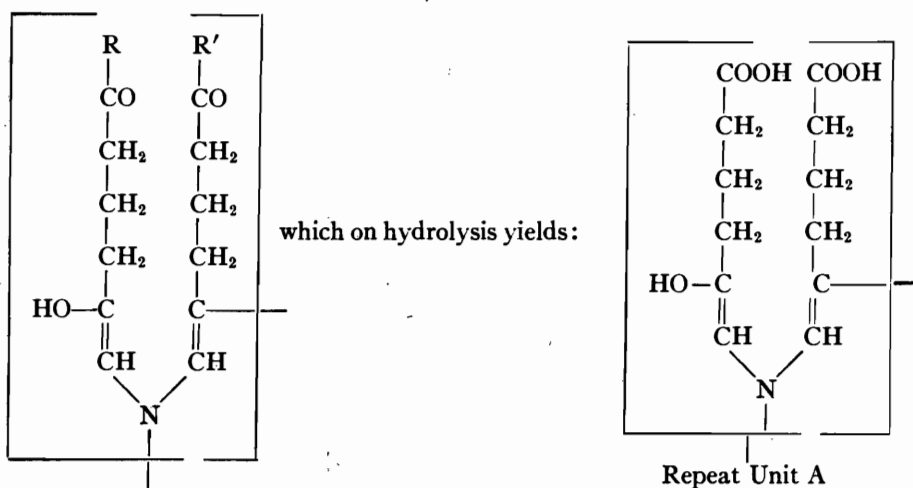
It is assumed that the secondary amine unit is able to oxidize by a route similar to that for pyrrolidine. Indeed, pyrrolidine and piperidine have been identified among the products of oxidized nylons [3]. The oxidation of methylene groups (to carbonyl groups) in the β positions relative to the nitrogen atom is considered to be most likely. (Oxidation of methylene groups adjacent to the nitrogen atom would yield polymers which, after hydrolysis, would not have compositions similar to the composition found experimentally.)



Two units of this type will condense to form:

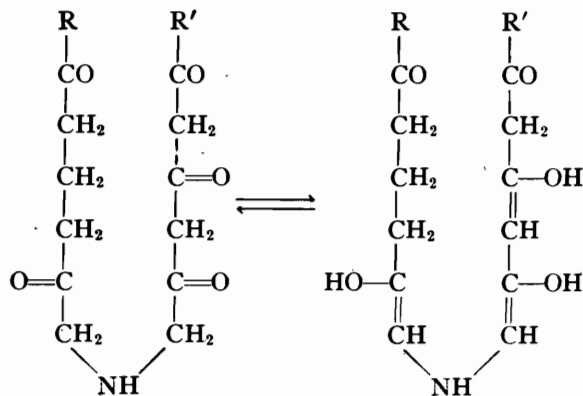


further condensation of which will form a polymer with a repeat unit of:

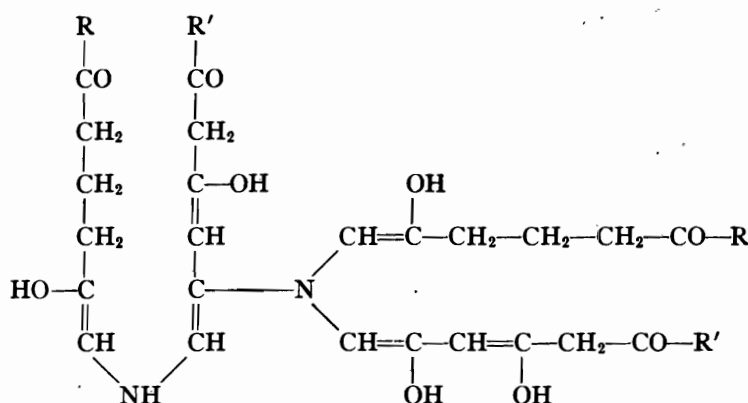


The compositions of compounds I and II after hydrolysis and Repeat Unit A are shown in Table II.

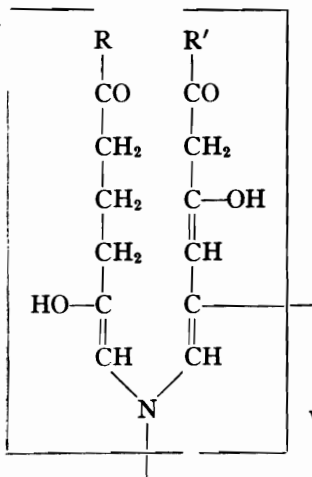
Table II shows that Repeat Unit A contains more hydrogen than the brown material. If a third methylene group in the original secondary amine unit is oxidized,



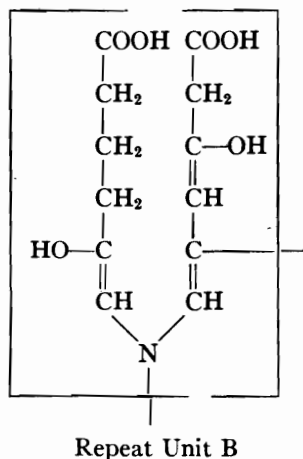
Two units of this type will condense to form:



Further polymerization will yield a polymer with a repeat unit:



which after hydrolysis will become:

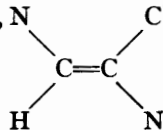


The composition of Repeat Unit B (Table II) is close to the composition calculated from various samples of brown material. It seems that after condensation of two amino groups, three methylene groups (on average)

in the secondary amine unit will oxidize, and one of the carbonyl groups (on average) will condense with another secondary amine group.

Many permutations of the number and position of the active groups as well as variations in the molecular weight are possible. Consequently, the brown material from nylon 6 is not expected to be a homogeneous product. When the postulated structure is in the enol form, the condensed units will be conjugated (by carbon-carbon double bonds and by the lone pairs of electrons on the nitrogen atoms), and the length of a chromophore will depend on the number of units in each molecule. If molecules of this type contain different numbers of secondary amine units, then chromophores of different length will be formed. Thus, the resulting mixture would exhibit a broad spectrum of absorptions in the uv and visible regions and would be brown in color.

The brown material from oxidized nylon 6 is extremely polar. Since the postulated compounds contain two carboxylic acid and two hydroxy groups (on average) in each unit of each molecule, it would be very polar. Ozonolysis, catalytic hydrogenation, and reduction all partially decolorize the brown product. Since the carbon-carbon double bonds encountered in the proposed structure (*i.e.*, N=C) are resistant



to these processes, it too would undergo only partial decoloration.

Summary

The brown compounds from oxidized nylon 6 have been isolated and analyzed. The structures of the dark substances have been tentatively proposed. The ideas that have been developed differ from earlier ideas [11] about the formation of brown materials, in that they are not necessarily based on the formation of derivatives of pyrrole. The new concepts account for

the formation of polymers of variable molecular weight which may contain chromophores of variable length and of slightly different chemical compositions. It is inherent in the new concepts that chromophores which absorb at longer wavelengths are progressively less plentiful than those that absorb at short wavelengths. Consequently, the intensities of absorption in the ultra-violet/visible spectrum must fall progressively with increasing wavelength.

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