

pyridine-water (3:2, 30 ml) and pH was adjusted to 8.4 by the addition of N sodium hydroxide. Phenyl isothiocyanate (4 ml) was added with stirring and pH was kept at 8.4 by the addition of N sodium hydroxide. After seven hours the reaction mixture was extracted three times with equal volumes of benzene, which were then discarded. The aqueous phase was brought to pH 2.7 and exhaustively extracted with ethyl acetate (90 ml). The extracts were combined and the ethyl acetate was evaporated *in vacuo* (temperature not above 30° C). To the oily residue water (20 ml) was added and pH was adjusted to 8 by the addition of N sodium hydroxide. A small precipitate was removed and the filtrate then extracted with ethyl acetate (30 ml), which was discarded. The solution was acidified to pH 2 by the addition of 4 N hydrochloric acid which resulted in an oily precipitate. After 24 hours the oil had crystallized (1.8 g). Recrystallization twice from ethanol-petroleum ether. M. p. 164°.

Paper chromatography: Solvent A, decomposition with the appearance of several spots; solvent B,  $q = 0.23$ ; solvent C,  $q = 0.98$ .

Analyses. N (Dumas) 9.30; S (Cuck and Grim<sup>8</sup>) 21.3.  $C_{12}H_{12}O_3N_2S_2$  requires: N 9.45; S 21.6.

5 - (Potassiummethylsulfonate) - 3 - phenyl - 2-thiohydantoin. A solution of L-cysteic acid (1.7 g) in pyridine-water (3:2, 30 ml) was brought to pH 8.6 by the addition of N potassium hydroxide. Under stirring phenyl isothiocyanate (4 ml) was added and pH was then kept at 8.6 by the continuous addition of N potassium hydroxide. After three hours the reaction mixture was extracted three times with equal volumes of benzene, which were then discarded. The aqueous phase was brought to pH 1 by the addition of 4 N hydrochloric acid and the solution was left overnight at room temperature. The solution was then brought to pH 4.2 with N potassium hydroxide and concentrated *in vacuo* to dryness. The residue was dried in a desiccator over phosphorus pentoxide and the dry product extracted with aqueous acetone which left the potassium chloride undissolved. The acetone solution was concentrated *in vacuo* to a viscous solution. On addition of acetone crystallization set in and was completed in the ice box (2.2 g). The product was taken up in a small volume of water and pH adjusted to 5 with potassium hydroxide. On the addition of abs. ethanol the preparation crystallized in fine needles. Recrystallization twice from water-ethanol. The product was highly hygroscopic and was dried *in vacuo* over phosphorus pentoxide at 110°. M. p. 193—7° (decomp.).

Paper chromatography: Solvent A,  $q = 0$ ; solvent B,  $q = 0$ ; solvent C,  $q = 0.11$ .

Analyses: N (Dumas) 8.62; S (Cuck and Grim<sup>8</sup>) 19.4.  $C_{10}H_8O_4N_2S_2K$  requires: N 8.64; S 19.8.

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## Note on the Reaction between Linear Polyamides and Ethylene Carbonate

SVEN SÖNNERSKOG

A-B Svenskt Konstsilke, Borås, Sweden

In connection with an investigation on the interaction between polyamides and cyclic esters the observation was made, contrary to earlier statements elsewhere<sup>1</sup> that ethylene carbonate may act, under particular conditions, as a hydroxyethylating agent upon homopolymers of  $\epsilon$ -aminocaproic acid or hexamethylenediammonium adipate. The reaction is observable just in the temperature range, where the polymers are dissolved by the cyclic ester (approximately 180—185° C). At still higher temperatures (200—220° C) water soluble derivatives are obtained by heating the polymer in a tenfold excess of ethylene carbonate for 4 hours. An inert gas, such as dry carbon dioxide, should be present to prevent side reactions (oxidation, depolymerization).

In a system, containing an unstabilized polymer, no simple kinetic scheme can be

suggested *a priori*. At least the following five steps must be considered:

1. Decomposition of ethylene carbonate into ethylene oxide and carbon dioxide.

2. Etherification of the polyamide at unstabilized end groups.

3. Formation of graft polymers by etherification at the amide links.

4. Ester interchange between polymer and solvent. (The incorporation of small amounts of carbonate ester unit is already reported from an analysis of infrared spectra<sup>1</sup>).

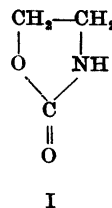
5. The formation of pure polyethylene oxide (linear polyether) by thermal or ionic polymerization in the anhydrous system.

Preliminary studies have been carried out on the water soluble compounds obtained from nylon 6 and nylon 66 polymer. Solubility is not limited to pure water, in fact it seems clear that when once water solubility is reached, a similar solubility in organic solvents such as methanol, acetone, and several aliphatic esters is also obtained, which is in contrast to the insolubility of the parent polymers. Fractional precipitation with a nonsolvent has thus not been feasible up to now. The only successful method for the separation of polymer has been the addition of strong sodium hydroxide solution until the polymer appears as a *coacervate*, which can be collected as an upper layer. Since homopolymers of ethylene oxide of the moderate molecular weight possible in a synthesis carried out at the actual high temperature do not show this behaviour, it is believed that the *coacervate* (in the most complex case) represents a mixture of graft polymer and block copolymer (steps 2 and 3 in the scheme above). The remaining part of the sodium hydroxide is easily removed from the polymer phase by separating the two layers in a small funnel, adding water and deionising with a hydrogen saturated ion exchanger.

Water soluble ethylene oxide "adducts" from fatty alcohols, fatty amines and alkyl phenols are known to give well defined precipitates with ferrocyanic acid<sup>2</sup>. The actual derivatives from nylon 6 and nylon 66 show the same behaviour. If the purified aqueous solution of the *coacervate*, mentioned above, is acidified with hydro-

chloric acid, a slight yellow precipitate is immediately obtained on adding potassium ferrocyanide. Nylons of low molecular weight give a highly dispersed precipitate, passing most filter papers. At higher molecular weight (*e.g.* plastic grades of polymer) the precipitate gradually coalesces to a yellow mass of pronounced rubbery character. A modified Zeisel analysis (according to Morgan<sup>3</sup>) indicates large, but varying amounts of accessible hydroxyethyl groups in the polymers, and it remains to be seen if a more detailed picture of the distribution of the etherifying agent can be obtained.

In this connection it should be mentioned that oxazolidone (I) dissolves polyamides above 80° C. On heating to 170° C it slowly decomposes into carbon dioxide and ethylene imine<sup>4</sup>, thus representing a potential source for the analogous grafting of the polyamide with ethylene imine monomer. In this case, however, solubility in water is never reached, but water soluble polyethylene imine can be isolated by condensing the escaping gases on a "cold finger". The carbon dioxide apparently serves as a gaseous phase activator, similar to its action in aqueous systems<sup>5</sup>.



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