The Polymerization of Propiolamide

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IN a manner analogous to the proton-transfer polymerization of acrylamide to 3-Nylon announced by Breslow *et al.*,[1] and more recently extended by Marvel *et al.*,[2] propiolamide has been polymerized to a limited extent to yield a material with unique properties.

Employing dry, inert conditions, a 4% (w/v) solution of propiolamide in dimethylformamide (25 ml.) containing anhydrous sodium cyanide (0·2 mg.) was heated at 135° for 14 days. The black solution was poured into a benzene (150 ml.)–methanol (50 ml.) mixture to give a dark brown precipitate which was reprecipitated from a formic acid solution and recovered by freeze-drying a benzene suspension, (24% recovery), η_{inherent} (formic acid 25°) = 0·07. The infrared spectrum is consistent with a structure containing the repeating unit (I) with no discernible acetylenic absorption.[3] Elemental analysis supports this formula.

Found: C, 52·6; H, 4·3; N, 16·2%.
Calculated: C, 52·2; H, 4·3; N, 20·3%.

However, it is suggested that consistently low values for the nitrogen content of the material can originate by the elimination of ammonia in some form. But it is difficult at this stage to equate this with the matching carbon and hydrogen analyses. It is possible that the nature of the compound renders nitrogen analysis problematical.

The filtrate from the initial precipitation gave a tar upon evaporation, which was triturated with methanol to a pale brown solid. A similar infrared spectrum was recorded but with an additional slight acetylenic absorption.

The compound retained 40% of its original weight on heating to 1000° in a nitrogen atmosphere (20° min.$^{-1}$). No sudden weight loss was noted. The infrared spectrum of the residue still showed the gross features of that of the starting material, which is indicative of chain rather than pendent amide groups. The substance did not melt.

Prolonged hydrolysis by hot, dilute hydrochloric acid liberated acetaldehyde which was detected as the 2,4-dinitrophenylhydrazone. Insoluble residues proved to be unreacted polymer. Alkaline hydrolysis (warm, dilute sodium hydroxide) yielded ammonia. Acid-insoluble residues proved to be a mixture of fragmented starting polymer and an undefined resin presumed

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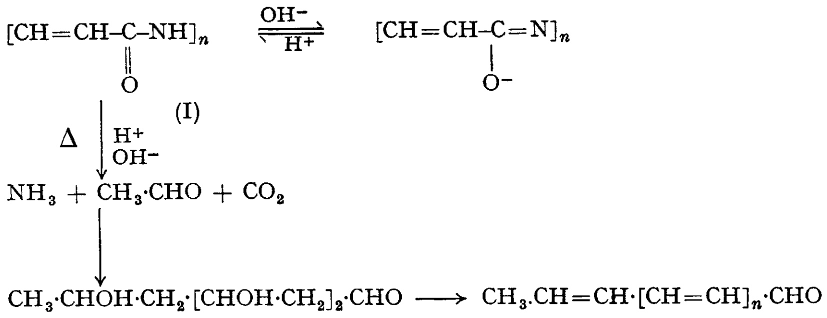

(II)

to result from sequential aldol condensations (II). The polymer is soluble in cold, dilute aqueous sodium hydroxide but is precipitated unchanged upon acidification. These features are displayed schematically.

A single, narrow (5 gauss between derivative peaks), nearly Lorentzian electron spin resonance line was observed in both powdered and dilute solution specimens. The signal strength is seemingly dependent upon the molecular weight of the sample. The maximum unpaired electron density observed was $1{\cdot}1 \times 10^{19}$ g.$^{-1}$. Failure to observe resolved hyperfine structure in dilute solution is attributed to the intramolecular delocalization of the unpaired electrons.[4]

An essentially identical material has been obtained by using combinations of the following solvents and catalysts with propiolamide: dimethylformamide, dimethylacetamide, anhydrous sodium cyanide, sodium thiophenoxide, sodium methoxide, and, in one instance, no added catalyst at all. Temperatures have ranged from 80—135°, times from 90—330 hr.

One preparation of propiolamide yielded a yellow, water-soluble, alcohol-insoluble powder (m.p. > 360°) with an infrared spectrum similar to that of the polymer but containing a prominent acetylenic absorption. This compound was slightly paramagnetic and was polymerized to the same black polymer.

Tetrolamide and *N*-methylpropiolamide have yielded tars under the same conditions of catalyst, solvent, and temperature.

These findings are at present rationalized by assuming anionic delocalization as a result of the system of potentially conjugate double-bonds realized in each polymer molecule. However, propagation is only possible at the amidic anion. A frail analogy is suggested by the "living-polymer" system of Szwarc.[5]

While this manuscript was in preparation, MacNulty's paper[6] appeared in which he described the polymerization of propiolamide using triethylamine. The properties of the polypropiolamide mentioned in his publication are similar to some of those reported here.

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