

*Some Aspects of the Polymerization and Depolymerization of
N-Substituted Ethyleneimines.*

By W. G. BARB.

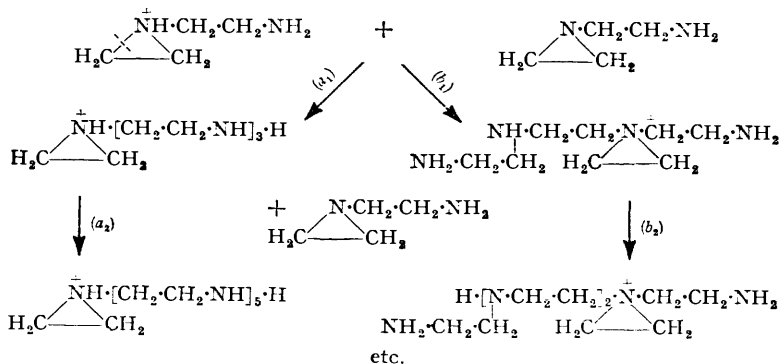
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The polymerization of *N*-substituted ethyleneimines is discussed with special reference to *N*-(2-aminoethyl)ethyleneimine; the products of this polymerization have been examined paper-chromatographically, and by the formation of *o*-chlorobenzoyl derivatives. The latter are 1 : 1 compounds; it is also shown that poly(ethyleneimine) forms a 1 : 1 derivative, and that both polymers must therefore be linear.

The thermal degradation of some *N*-substituted poly(ethyleneimines) has been examined; in certain cases high yields of the corresponding *NN'*-disubstituted piperazine are obtained. The polymers appear to be less thermally stable than the corresponding ethyleneimine monomers.

BARB (preceding paper) pointed out that in the acid-catalyzed polymerization of ethyleneimine growth reactions could occur not only between polymer and monomer, but also between polymer and polymer. An ethyleneimine polymer $\text{H}_2\text{C} \begin{array}{c} \diagup \text{N} \cdot [\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}]_x \cdot \text{H} \\ \diagdown \end{array} \text{CH}_2$ (I) [(*x* + 1)-mer] (I) can be regarded as a special case of an *N*-substituted ethyleneimine, and *N*-substituted ethyleneimines are known to polymerize.

Consideration of the simplest case, the acid-catalyzed reaction of two ethyleneimine-dimer [*i.e.*, *N*-(2-aminoethyl)ethyleneimine] molecules, shows two possible courses of reaction, depending on whether the (hypothetical intermediate) carbonium ion attaches itself to amino- (*a*) or imino- (*b*) nitrogen :



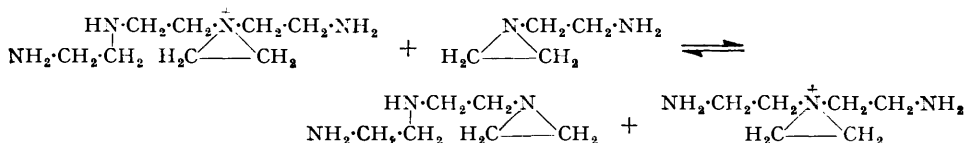
In case (*a*), the dimer of ethyleneimine-dimer is identical with the tetramer of ethyleneimine monomer, the trimer is identical with the hexamer of ethyleneimine, etc. (the protons

will be in equilibrium between all the basic entities). If the reaction follows course (b), the polymers are quaternary iminium ions. We may regard (b) as the fission of an iminium ring and addition of the carbonium ion so formed to the nitrogen of another ring (without necessarily implying that the reaction occurs in two successive steps); in (a), on the other hand, addition occurs at a nitrogen in the side-chain. Whereas course (b) is always possible, (a) would not be expected to occur unless the *N*-substituent of the particular ethyleneimine had a nucleophilic centre of some sort.

Attempts to decide between (a) and (b) were made in two ways: (i) a paper-chromatographic examination of the products, and (ii) benzylation of the polymers and analysis of the product so obtained. As will be shown below, the evidence from these two approaches, though in each case clear-cut, is contradictory and suggests that the actual mechanism is a hybrid of (a) and (b).

Paper-chromatography.—The technique used has been described (Barb, *loc. cit.*). The chromatogram of the product of a polymerization of the dimer (chloroacetic acid as catalyst) was compared with a similarly prepared polymer of ethyleneimine monomer. The positions and colours of the spots of the unpolymerized dimer and of the first polymerization product of ethyleneimine agree. However, the "dimer of the dimer" occurs at the same position as the ethyleneimine trimer and the "trimer of the dimer" coincides with the pentamer of the monomer. Further comparison of spots was impossible owing to inadequate separation, but from the observations cited it is clear that the "dimer-polymers" are not identical with the ethyleneimine polymers of even degree of polymerization; consequently the polymerization of the dimer undoubtedly does not occur entirely as in (a), and we must consider (b) in more detail.

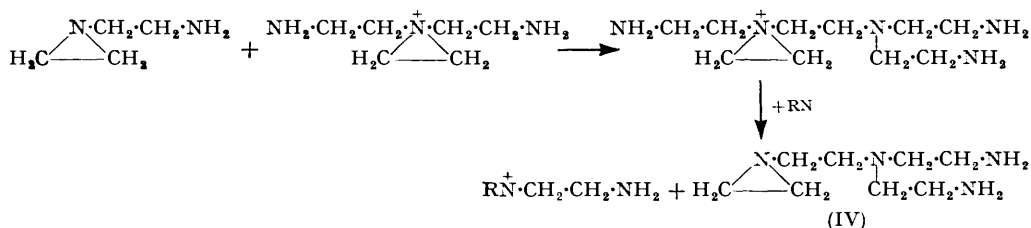
It is extremely unlikely that all the products of the dimer-polymerization are present as quaternary iminium ions. First, the amount of catalyst used is very small, *i.e.*, there would not be one ion available per polymer molecule; secondly, chromatographic comparison of samples taken from a reaction mixture at different times show that the reaction is "stepwise," as in polymerization of the monomer (cf. Barb, *loc. cit.*). These facts suggest that there may be a carbonium-ion equilibrium between active ions and inactive molecules, thus:



This equilibrium would take the place of the hydrogen-ion equilibrium involved in the polymerization of the monomer (cf. Barb, *loc. cit.*). The lowest uncharged polymer which would be formed in the polymerization of the dimer would therefore be identical with ethyleneimine trimer; from this point of view the chromatographic results support mechanism (b). The next species [see reaction (b₂)] would be (II) which is isomeric with the



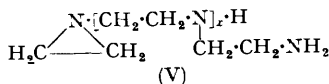
linear pentamer of ethyleneimine, (III), again in keeping with the chromatographic findings. On the other hand the reaction between dimer and the ion from the equilibrium postulated above, *viz.*,



would eventually lead to a tetramer (IV). The chromatograms, however, show no trace of a tetramer. We must therefore conclude that neither mechanism (a) nor (b) fully explains the chromatographic results.

It seemed of interest to test whether this type of equilibrium was only established with ethyleneiminium ions or whether quaternary ammonium ions showed a similar behaviour. Mixtures of tetramethylammonium bromide and triethylamine in alcohol-water solution were kept at 40° for several days and then examined by paper-chromatography, with butanol saturated with water as a running medium. The spots were developed with Dragendorff's reagent for alkaloids, prepared according to Welcher ("Chemical Solutions," D. Van Nostrand Co., Inc., New York, 1942, p. 119); markers of tetramethyl- and tetraethylammonium bromide, trimethylamine and triethylamine gave spots of characteristic colours (chestnut, deep cerise, vermilion, and pink, respectively). It was found that the mixture only contained the original starting materials; no equilibrium had been set up. If the equilibrium postulated for iminium ions is correct, it would be another manifestation of the inherent instability of these ions.

Structure and Derivatives of Ethyleneimine Polymers.—The polymer of ethyleneimine-dimer could in theory have a linear or a branched structure. The same applies to the polymer obtained from ethyleneimine monomer, as is easily shown by writing the various possible reactions. If in actual fact the polymers are of a completely linear structure (I), acylation or benzylation of a polymer of high degree of polymerization should give a 1 : 1 derivative (neglecting the imino-end group). If the polymers are branched, there will be less than one acid group per base molecule of ethyleneimine; for the limiting case of a dimer-polymerization occurring as in case (b) originally discussed, the polymer would have the structure (V) and the acyl derivative would have a 1 : 2 composition.



Existing data on derivatives of poly(ethyleneimine) itself are contradictory. Kern and Brenneisen (*J. prakt. Chem.*, 1941, **159**, 193) acetylated poly(ethyleneimine) in pyridine solution, and purified the water-soluble *N*-acetylpoly(ethyleneimine) by electro dialysis; the compound was of a 1 : 1 composition. Benzylation and *o*-bromobenzylation of poly(ethyleneimine) in pyridine, on the other hand, gave compounds containing too much nitrogen and insufficient halogens compared to a 1 : 1 derivative; the purification of these compounds was described as difficult, but no details were given. Using the Schotten-Baumann method, Jones, Langsjoen, Neumann, and Zomlefer (*J. Org. Chem.*, 1944, **9**, 125) prepared a 1 : 1 polybenzamide, in contrast with Kern and Feuerstein's non-stoichiometric derivative.

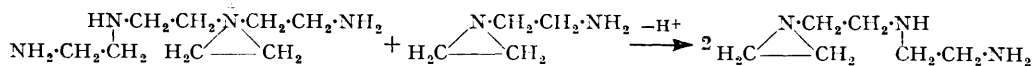
In the present work, poly(ethyleneimine) was made to react with *o*-chlorobenzoyl chloride and *o*-bromobenzoyl bromide, using the procedure described by Jones *et al.* (*loc. cit.*). The derivatives were dried *in vacuo* at room temperature for 18 hr., and contained more halogens and less nitrogen than corresponded to a 1 : 1 compound [*e.g.*, *o*-chlorobenzamide of poly(ethyleneimine) : Found : C, 53.9; H, 4.2; N, 6.65; Cl, 24.45. Calc. for C₉H₈ONCl : C, 59.2; H, 4.95; N, 7.65; Cl, 19.5%]. Since there is no possibility of introducing more than one benzoyl group per nitrogen atom this result was attributed to retention in the polymer of chloroform from which the product had been precipitated by light petroleum; in confirmation, an electrometric titration of the combustion products of the *o*-bromobenzamide with silver nitrate showed a double-inflection curve, indicating that both bromide and chloride ion were present. In view of this retention of solvent there seems little doubt that the anomalous analyses of Kern and Feuerstein's benzoyl derivatives were due to retention of pyridine.

Further attempts to obtain a solvent-free polymer were made, using the more volatile methylene dichloride in place of chloroform, with little improvement. A slight improvement was achieved by drying the polymer *in vacuo* at 60° for 24 hr. The analyses (C, 53.7; H, 4.7; N, 7.0%) are now reasonably close to those for a 1 : 1 compound, the discrepancy corresponding to the retention of less than 10% of methylene dichloride.

The *o*-chlorobenzamide of a polymer of the dimer was prepared by the same procedure. The analyses (C, 51.8; H, 4.8; N, 7.0%) are (except for C) almost identical with those for the derivative of ordinary poly(ethyleneimine), and indicate the compound to be a 1 : 1 derivative.

Since dibenzoylation of primary amino-groups is, under the mild conditions here employed, extremely unlikely, it must be concluded that the "dimer-polymer" has a linear structure, as would be expected from reaction (a).

This conclusion of a linear structure for the dimer-polymer is in direct conflict with the chromatographic results, which indicate that the "dimer-polymers" correspond to ethyleneimine polymers of odd degree of polymerization. The only mechanism embracing all the experimental results is that the first step in the polymerization of dimer occurs as in (b_1); the ion so formed then undergoes the reaction:



to yield the trimer, and subsequent growth of the polymer occurs by reaction of type (a). The theoretical justification for this transition from one type of reaction to another is not obvious.

Depolymerization of N-Substituted Ethyleneimines.—In some experiments on the polymerization of *N*-phenethylethyleneimine, prepared according to Bestian (*Annalen*, 1950, **566**, 210), it was found that if the gummy polymer was heated in a sealed tube at 150° for several hours, the initially brownish material was almost completely converted into a mobile pale amber liquid, which was immiscible with traces of residual polymer and completely set to a crystalline mass on cooling. The material was extremely soluble in most solvents but could be recrystallised from light petroleum (b. p. 40—60°) to give small white crystals, m. p. 80°. The substance was surmised to be 1:4-*di*(phenethyl)piperazine. This compound was prepared from phenethyl bromide and piperazine [by the method employed by Gabriel and Stelzner (*Ber.*, 1896, **29**, 2384) to prepare the corresponding benzyl compound], m. p. 79—80°; mixed with the pyrolytic material, m. p. 79—80° (Found: Synthetic compound: C, 80.6; H, 8.8; N, 9.8; Pyrolytic compound: C, 81.2; H, 8.8; N, 9.4. C₁₀H₁₃N requires C, 81.6; H, 8.85; N, 9.55%). It is particularly interesting that *N*-(phenethyl)ethyleneimine monomer heated under similar conditions to those employed above showed no change. The polymer is thus thermally less stable than the "strained" three-membered ring, possibly owing to the increase in entropy which accompanies the degradation of the polymer to small molecules.

Other polymers examined showed a less clear-cut degradation; the ease of depolymerization and the amount of side-reactions evidently varies greatly with the nature of the *N*-substituent.

A polymer of *N*-(2-cyanoethyl)ethyleneimine, prepared according to Bestian (*loc. cit.*), set to a solid black tar when heated to 200°; further heating, at 280° for four hours, produced a small amount of a mobile liquid which did not crystallize on cooling, but a far-reaching decomposition seemed to have occurred since the tube exploded on being cut open. Similarly poly(ethyleneimine) had to be heated to about 280° before a small amount of a mobile product was formed; this partially crystallized on cooling and was presumably piperazine, but again other decompositions must have occurred since the reaction tubes invariably exploded when cut open. The work of Hutchinson, Collett, and Lazzell (*J. Amer. Chem. Soc.*, 1945, **67**, 1967) on the pyrolysis of polyamines illustrates the variety of compounds which might be formed from poly(ethyleneimine).

Poly(*N*-*n*-butylethyleneimine) proved a more favourable case. When the polymer was heated at 200° for a few hours about one-half of the material was converted into a yellow mobile liquid, immiscible with the residual polymer. After redistillation in a high vacuum, the product was colourless (n_D^{25} 1.4586). For comparison, 1:4-*di*-*n*-butylpiperazine was synthesized from *n*-butyl bromide and piperazine by Gabriel and Stelzner's method (*loc. cit.*); it was a clear viscous liquid, b. p. 110°/8 mm., n_D^{25} 1.4582, in excellent agreement with the value for the pyrolytic material.

Attention is drawn to the close analogy between the depolymerization reactions here described and the decomposition of polysarcosine to 1:4-dimethyldioxopiperazine ("sarcosine anhydride"), discovered by Wessely and Sigmund (*Z. physiol. Chem.*, 1927, **159**, 192).