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ADVANCES IN THE CHEMISTRY OF POLYETHYLENEIMINE (POLYAZIRIDINE)†

D. S. Zhuk, P. A. Gembitskii, and V. A. Kargin

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† Since polyethyleneimine is an industrial product, and really a straight-chain compound, it has seemed advisable to retain this name in the translation, while the more systematic *aziridine* is used for the monomer (Ed. of Translation).

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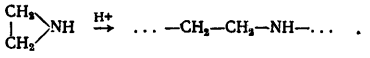
Polyethyleneimine has been produced on the industrial scale since 1938, in Germany by the Badische Anilin- und Soda-Fabrik AG. at Ludwigshafen and in the USA by the Chemirad Corporation. It is used mainly for the water--repellent finishing of paper and textiles[1-4], for conferring dyeability on them[5], in the manufacture of reactive dyes[6], for the production of anion-exchange resins, films, and membranes[7-9], in the foundry industry[10], and as an additive to motor fuels[11].

1. METHODS OF SYNTHESISING POLYETHYLENEIMINE

Polyethyleneimine is obtained mainly by the polymerisation of aziridine. Another simple and convenient method for obtaining it is the thermal decomposition of 2-oxooxazolidine. Polyethyleneimine of low molecular weight (in the form of a mixture mainly of triethylenetetramine and tetraethylenepentamine) — the so-called polyethylenepolyamine — is manufactured in large quantities by the condensation of dichloroethane in ammonia or ethylenediamine[12], and is used as a hardening agent for epoxide resins.

2. POLYMERISATION OF AZIRIDINE

The polymerisation of strained three-membered rings constitutes a special aspect of the more general question of the conversion of rings into linear polymers. Unlike other methods of synthesising compounds of high molecular weight, the polymerisation of rings generally involves no change in electronic structure (provided that the peculiarities of the type of bond in strained three-membered rings are disregarded) or in the number of chemical bonds in the system: only the way in which the bonds are arranged is changed. Although a C–N bond in the ring is cleaved on the polymerisation of aziridine, a similar bond is formed in the linear polyethyleneimine molecule:



Thermodynamically, the possibility of polymerisation of ring monomers is determined by the accompanying change in free energy. The strain in three-membered rings results in the polymer being more stable thermodynamically than the monomer, and their heat of polymerisation (~23 kcal mole^{-1} for aziridine)[13] provides a measure of this strain. Thus, in their tendency to polymerise, three-membered rings are close to a double bond in olefins (heat of polymerisation ~22.5 kcal mole^{-1}).

An aspect, requiring separate consideration, is the kinetic possibility of polymerisation, i.e. the mobility of the relevant bonds under the reaction conditions, since thermodynamically unstable compounds may be quite stable kinetically, and will not polymerise if they contain no labile bond. As example we can cite cycloalkanes, for which, in spite of their fairly considerable thermodynamic instability (e.g. ~25 kcal mole^{-1} for cyclopropane), conditions of polymerisation have not yet been found‡. In this case the complete equivalence of all the bonds in the ring is responsible for the thermodynamic instability of strained alicyclic rings at high temperatures manifesting itself specifically[15] in their homolytic thermal isomerisation into ethylene derivatives.

Three-membered heterocycles (aziridine, oxiran, thiiran) are completely stable kinetically when absolutely pure, owing to the similarity in the energy characteristics of all the cyclic bonds. However, they polymerise in the presence of certain activators (polymerisation catalysts), which act selectively on the carbon–heteroatom bond. In fact it has been shown[16] that absolute dry§ and pure aziridine does not polymerise even at 150°. The most usual polymerising agents are acids[17-24] (including carbon dioxide[25,26], acid salts[18-20], and phenol[27]), alkylating agents[18,28-30], boron trifluoride[18,31-33], anhydrous iron(III) chloride[33], silver nitrate or perchlorate[34], surface-active substances (kieselguhr, activated carbon[20], aluminium oxide, silica gel, etc.[32]), ammonia under pressure[35], and water¶. Any reagent which can convert the ring nitrogen atom into the quadrivalent state (by salt formation, oxidation, or coordination) can act as a polymerisation catalyst for aziridine.

Bases, which are known to catalyse the anionoid polymerisation of oxides, do not cause the polymerisation of aziridine[32]. Peroxides and ultraviolet radiation†, which induce the free-radical polymerisation of vinyl compounds, are also ineffective in this respect[32]. Inhibitors of free--radical polymerisation do not exhibit the polymerisation of aziridine. Sodium, potassium, sodamide, and strontium carbonate exert an inhibiting action[18,32].

Mechanism

There is no consensus of opinion concerning the mechanism of the polymerisation of aziridine. German authors[24,32,39] regard it as a case of polycondensation, which presupposes intermediate formation of an addition product with the catalyst, involving cleavage of the aziridine ring (in the case of hydrochloric acid, for example, 2-chloroethylamine hydrochloride is formed), and its occurrence in two stages

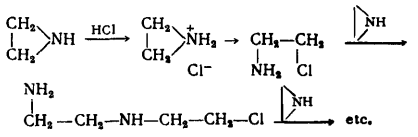
‡ One paper has been published[14], describing the preparation of a polymeric product from phenylcyclopropane under high pressures (up to 2000 atm).

§ A special technique has been worked out[16] for preparing absolutely dry aziridine. The dry product (dried by standing over sodium) is distilled under vacuum and condensed over sodium which has been freshly cut and warmed in a vacuum. On cooling with solid carbon dioxide, the sodium dissolves to form a bright blue solution. The aziridine is distilled off from the resulting solution into a carefully evacuated flask. A solution of sodium is not formed if the aziridine has not undergone preliminary drying.

¶ Water is a peculiar polymerisation catalyst for aziridine. In the presence of water alone[36,37] polymerisation is extraordinarily slow (even at elevated temperatures) and usually ceases at the tetramer stage. Water has been proposed[37] as a specific catalyst for the dimerisation, trimerisation, and tetramerisation of aziridine.

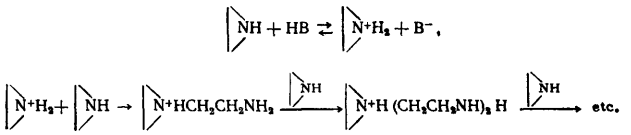
† Results reported by Japanese workers[38], showing the polymerisation of aziridine when irradiated on poly(vinyl chloride), do not contradict the above statement. Careful investigation has established that, in contrast to the radical mechanism of vinyl polymerisation, the polymer is formed in this case by the usual acid polymerisation of aziridine catalyst by OH or COOH groups produced on exposure of the substrate polymer.

– intramolecular version (rate-determining stage) and anionoid fission:



This mechanism is inconsistent with the more thorough and rigorous kinetic investigations of British[16,40] and American[18] workers. No explanation is provided of the fact that the reaction of 2-chloroethylamine hydrochloride with the feebly anionoid aziridine is of the second order, whereas the reaction of this compound with the strongly anionoid caustic potash obeys a different kinetic law. 2-Chloroethylamine hydrochloride was not isolated from reaction mixtures undergoing polymerisation, although it itself was shown to polymerise slowly at room temperature[18].

These workers suggested a mechanism of cationoid additive polymerisation of polar type, involving stepwise reaction of the aziridinium ion with uncharged rings:

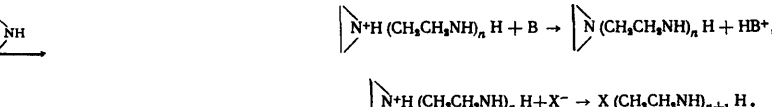


The first of these reactions is reversible, and since the rate of growth of the polymer chain is slower than transfer of a proton, all the protons will be distributed in a definite fashion among the various basic centres in the polymerising mixture. The distribution is a function of the relative concentration and basic strength of these centres. In the early stages most of the protons are combined with monomeric molecules, and the main product of polymerisation is the dimer. When the concentration of the dimer has become considerable relative to that of the monomer, formation of the trimer, tetramer, and higher polymers begins: i.e. as in chain transfer by a radical or by an ion in vinyl (radical or ionic) polymerisation, we have here a protonation transfer equilibrium.

During the progress of the reaction, the degree of polymerisation will increase, and products of low molecular weight will gradually disappear. This is confirmed[16] by the successive chromatography (on paper) of the polymerisation products of aziridine. On the first chromatogram up to seven different spots or bands (up to the octamer) are distinguished, with an unresolvable band due to higher polymers. Two faint spots were also observed, more mobile than the dimeric spots, which were shown to be caused by traces of aminoethanol and 2-2′-aminoethylaminoethanol (a hydrolysis product of the dimer).

It is also possible that two polymeric molecules may combine through their terminal aziridine groups. This is supported by the increase in the degree of polymerisation in mixtures containing no monomeric aziridine[16], and also by the spontaneous polymerisation of the specially synthesised dimer of aziridine[41].

Chain termination (in this case deactivation of the quaternary ion) can occur on abstraction of a proton by a base B (e.g. by a monomer molecule, an amino-group or an aziridinyl group of a polymer, an anion, water, etc.) or when the ring is opened by an anion:

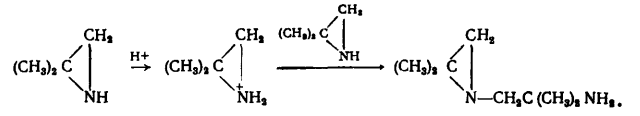


If in the latter reaction X^- represents an aziridinyl group of a polymer, the polymer chain becomes branched.

Thus although aziridine undergoes additive polymerisation, and only a few reactive aziridinium ions are present at any given instant, the general character of the process resembles stepwise polycondensation, in which all molecules contain reactive groups because of the very rapid redistribution of hydrogen ions among the various substances present.

In order to settle the question of the mechanism of this polymerisation, it is of interest to study the behaviour of unsymmetrically substituted derivatives of aziridine, since differences in reaction mechanism, which for unsubstituted aziridine can be revealed only by the kinetic form, lead in this case to structural differences.

It has been shown[42] for the polymerisation of 2,2-dimethylaziridine that the reaction involves fission of the bond between nitrogen and the cyclic methylene group (the dimer was isolated, and its structure established by a separate synthesis):



This direction of ring cleavage corresponds‡ to the bimolecular inversion mechanism S_N2 of interaction between charged and uncharged 2,2-dimethylaziridine rings.

The conclusion that other alkylated aziridines polymerise by an S_N2 type of mechanism is confirmed indirectly by a rough comparison of their rates of polymerisation§. Alkylated aziridines containing a cyclic primary carbon atom (2-methylaziridine, 2-ethylaziridine, 2,2-dimethylaziridine) are found to polymerise as readily as does aziridine itself. In contast, the polymerisation of the

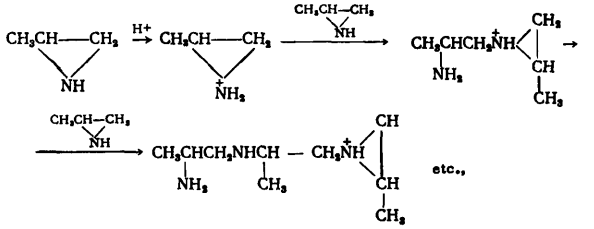
‡ As noted above, preferential rupture of a cyclic bond at a primary rather than a secondary or a tertiary carbon atom indicates an inversion mechanism, whereas preference to a tertiary in relation to a primary atom would indicate an ionisation mechanism [S_N1].

It has been shown[43] that change to a more nucleophilic ion or a donor molecule can produce a bimolecular inversion with structures which are subject to an ionisation mechanism in the presence of less powerful nucleophiles. It must be noted in this connection that the aziridinium nitrogen should exert a considerable effect (through carbon attached to the nitrogen) favouring inversion.

§ Kinetic investigation of the polymerisation of alkylated aziridines is complicated by the solubility characteristics of the polymers. Thus the polymer of 2,2-dimethylaziridine, in contrast to polyethyleneimine, is insoluble in water and soluble in ether. This makes it difficult to use viscometric methods in studying the kinetics of polymerisation. To determine reaction rates the authors distilled unchanged monomer from an alkaline solution of the reaction mixture.

alkylated rings containing no primary carbon atom (*trans*--2,3-dimethylaziridine, 2,2-dimethyl-3-propylaziridine) is extraordinarily difficult.

Polymerisation of the optically active (+)- and (-)-2-methylaziridines (with the ether-BF_3 complex or with HCl) yields[33] solid polymers which soften at ~60–80° and show strong optical rotation (up to ±100°) opposite in sign to that of the monomer. The high degree of optical activity and the considerable rise in softening point compared with polymeric (±)-2-methylaziridine suggest a high degree of preservation of asymmetry during polymerisation. This is compatible only with an S_N2 type of ring cleavage at a primary carbon atom:



since the latter is accompanied neither by the formation nor by the rupture of bonds attached to the asymmetric carbon atom.

Kinetics

Let us discuss briefly the kinetics of the acid polymerisation of aziridine. If the catalyst concentration is assumed to remain substantially unchanged during the reaction, the polymerisation of aziridine, which according to the above mechanism is a second-order reaction (with respect to the aziridine rings), can be represented by the equation

$$\frac{1}{1-p} - 1 = \frac{p}{1-p} = Kt,$$

where p is the fraction of the monomeric aziridine which has reacted. On the further assumption that the molecular-weight distribution resembles that calculated for polycondensation[44] and is independent of temperature, reaction velocity, etc., we obtain $X^{-0.5} - 1 = Kt$,¶ where X is the fraction of the monomer unchanged.

If the time variation of polymerisation with various acids is plotted as $p/(1-p)$ against t (Fig. 1), the progressively diminishing slope of the curves indicates a gradual decrease in rate during the reaction, which is most clearly shown in the early stages. Two types of explanation are possible for this phenomenon: (1) the aziridine nitrogen atom in monomer or polymer is more strongly basic than an amino--nitrogen atom, and as a result competes more vigorously for possession of a proton; and (2) the catalyst is consumed in the course of the reaction.

Careful dilatometric kinetic investigations have shown[16] that the molecular-weight distribution is independent of the nature or concentration of the catalyst. This implies that the relative distribution of protons among the various basic centres (aziridine nitrogen in monomer and polymer, primary and secondary amino-nitrogen in the polymer) is identical. In this case the reaction velocity at any stage

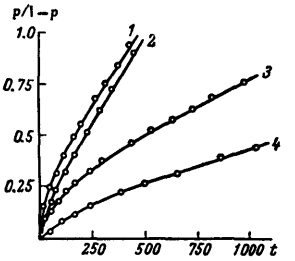


Fig. 1. Polymerisation of aziridine in the presence of various acidic catalysts (dependence of degree of conversion on time): 1) 0.025 M chloroacetic acid; 2) 0.054 M toluene-*p*-sulphonic acid; 3) 1.00 M benzoic acid; 4) 0.88 M dichlorophenol.

in the conversion will be proportional to the concentration of protons, and can be expressed mathematically as

$$-\frac{d[M]}{dt} = \sum^{x,y} K_{xy}[M_x][M_yH^+], \qquad (1)$$

where M_x represents an uncharged terminal aziridine ring in a polymer having a degree of polymerisation of x - 1, and M_yH^+ is a charged aziridinium ring in a polymer having a degree of polymerisation of y - 1, while [M] is the total concentration of aziridine rings.

Thus the hypothesis that the catalyst concentration remains constant during polymerisation is incorrect (at least for the acids investigated), and the slowing down in the early stages of the reaction is caused not by formation of a strongly basic dimer but by diminution in the catalyst concentration†. The consumption of catalyst during polymerisation in the presence of hydrochloric, hydrobromic, and sulphuric acids, whose anions are able to compete with an aziridine molecule in opening a protonated aziridine ring, is not unexpected, since all three acids are capable of reacting with aziridine to form open-chain products.

The polymerisation of aziridine in the presence of perchloric, picric, and other acids having very feebly nucleophilic anions occupies a special position. In this case the original hypothesis, that the catalyst concentration is constant during polymerisation, proves to be correct, and Eqn. (1) remains valid. The only side-reaction in this case can be solvolytic opening of the aziridine rings (by hydrolysis, alcoholysis), which, however, makes no effective difference to the kinetic interpretation.

With the first group of acids considered here, in contrast, the reaction velocity is greatly dependent[16] on the acid used, since the kinetics of the breakdown of catalyst in a side-reaction with the aziridine varies with the different acids. In this case the kinetic interpretation must take into account the differences in the partial consumptions of monomer in the side-reaction. These differences

¶ This equation is of the same form as for a reaction of order 1.5 with respect to the monomer.

† The first hypothesis can also be rejected on the basis of the following simple experiment. Rates of polymerisation in the presence of 10–15% of added strong bases (dimer of aziridine, n-butylamine, piperidine) were compared[16] with the course of reaction in the absence of these additions. The slight retarding effect can be attributed to dilution of the aziridine.

are most definite in form with strong acids (sulphuric, hydrochloric, toluene-*p*-sulphonic) and with weak acids. (acetic and benzoic acids, 2,4-dichlorophenol). Whereas with strong acids the kinetics of catalyst destruction are consistent with their complete ionisation in aziridine solution, the kinetic treatment for weak acids is based on the hypothetical formation of ion-pairs. The kinetic regularities for both cases will be examined in detail below.

Thus, although the polymerisation of aziridine is additive, it differs from vinyl additive polymerisation (radical or ionic) in two main features. Firstly, as a result of the presence of a transfer equilibrium, all monomeric and polymeric molecules are capable of being activated (and deactivated). This produces definite kinetic characteristics resembling those observed in condensation polymerisation. Secondly, the partial consumption of catalyst usually exceeds that of the monomer, whereas the opposite is the case in other types of polymerisation.

Strong Acids

Changing the initial concentration of the strong toluene-*p*-sulphonic acid has no effect[16] on the course of polymerisation (which in all experiments is represented by a single curve relating extent of conversion with time — Fig. 2). Thus although the catalyst is consumed during the reaction, the rate of polymerisation at any instant is proportional to the catalyst concentration:

$$-\frac{d[M]}{dt} \propto [HA]_0. \qquad (2)$$

The similarity in the catalytic activity of all strong acids (for the polymerisation of aziridine) shows that they are practically completely ionised in aziridine. Consequently $\Sigma[BH^+] = [HA]$ at time t. If $[M_yH^+]/[BH^+]$ is independent of the acid concentration, so that $[M_yH^+] \propto [HA]$, substitution of this expression in Eqn. (1) yields

$$-\frac{d[M]}{dt} \propto [HA], \qquad (3)$$

i.e. the rate of polymerisation at time t is proportional to the instantaneous acid concentrations, and consequently the ratio of the fractional decrease in concentration of the monomer to the fractional decrease in concentration of the acid should be constant:

$$\frac{[HA]\, d[M]/dt}{[M]\, d[HA]/dt} = K. \qquad (4)$$

On substituting here the relation (3), we obtain $-d[HA]/dt \propto \propto [HA]^2$ (a relationship of the second order with respect to the acid concentration). It is consistent with the consumption of acid by the reaction

$$\overset{+}{\text{N}}\text{HR} + A^- \rightarrow ACH_2CH_2NHR, \qquad (a)$$

where R = H or a polymer chain of any length.

For this latter reaction, too, we can write

$$-\frac{d[HA]}{dt} = \sum^{\nu} K_{\nu A^-}[A^-][M_\nu H],$$

and if we substitute, in view of the above, $[A^-] = [HA]$ and $[M_yH^+] \propto [HA]$, we obtain the general expression for the rate of polymerisation of aziridine given previously (p. 518). Thus the kinetics of polymerisation catalysed by a strong acid which is able to cause only one side-reaction of type (a) can be regarded as completely elucidated by the case discussed here of toluene-*p*-sulphonic acid. Polymerisation in the presence of hydrochloric and sulphuric acids is also of this type.

Weak Acids

The above kinetic regularities do not occur with weak acids. In the case of benzoic acid the overall rate is greater than would be expected for the first order with respect to the initial acid concentration. The discrepancy is especially clearly marked (see Fig. 3) in the later stages of the reaction, at which with a low concentration of benzoic acid reaction has practically ceased, although the greater part of the aziridine still remains unchanged.

It has already been noted that the catalytic action of weak acids is far weaker than that of strong acids even in the initial stages of the reaction. Strong acids are assumed to undergo complete dissociation in aziridine solution. In order to explain the low catalytic activity of weak acids, we must either assume that they undergo equilibrium dissociation (with considerable quantities of the undissociated form present) or suppose, by analogy with ionic vinyl polymerisation[45], that they form not free ions but ion-pairs of the type $\overset{+}{\text{N}}\text{H}_2A^-$, whose catalytic activity (their tendency to ring-opening) is presumably less than that of the free aziridinium ion.

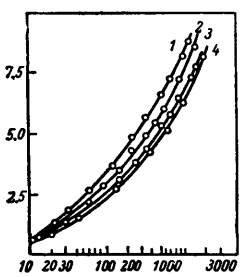


Fig. 2. Dependence of rate of polymerisation of aziridine at 40° on initial concentration (wt.%) of a strong acid (toluene-*p*-sulphonic):
1) 6.1; 2) 3.85; 3) 2.30; 4) 1.30.

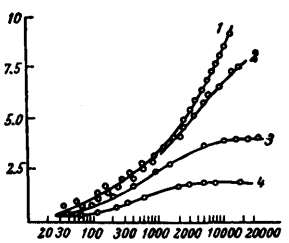
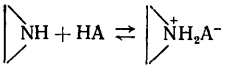


Fig. 3. Dependence of rate of polymerisation of aziridine at 40° on initial concentration (wt.%) of a weak acid (benzoic):
1) 12.25; 2) 5.72; 3) 3.47; 4) 1.53.

If we now accept that the equilibrium in the reaction



is displaced completely to the side of the ion-pair, the kinetic treatment for the case of weak acids will be entirely analogous to that given above for strong acids (with toluene-*p*-sulphonic acid as example) except that the concentration of the free aziridinium ion has been replaced by that of the ion-pairs. The relationship (3) remains valid. However, destruction of the catalyst, which was a second-order reaction with strong acids, becomes a first-order reaction with ion-pairs. Consequently $-d[HA]/dt \propto [HA]$, and Eqn. (4) for strong acids is replaced in the case of weak acids by the equation

$$\frac{[HA]\, d\,[M]/dt}{[M]\, d\,[HA]/dt} = K\,[HA],$$

according to which the fractional decrease in catalyst concentration (and hence the rate of polymerisation), corresponding to the fractional decrease in monomer concentration, will exceed the decrease in the acid concentration. In other words, the initial rates will fall more rapidly for the most dilute solutions of the acids, as actually occurs when benzoic acid is used.

Thus the hypothesis of the existence of ion-pairs provides a good explanation of the difference in kinetic behaviour between strong and weak acids. There may also be intermediate cases.

3. THERMAL DECOMPOSITION OF 2-OXOOXAZOLIDINE

Another important method of obtaining polyethyleneimine is provided by thermal decomposition of the cyclic urethane 2-oxooxazolidine. Thermolysis of this compound in a strongly alkaline solvent (trishydroxyethylamine) yields monomeric aziridine[46]; thermolysis which is uncatalysed or is catalysed by weakly basic catalysts results in polyethyleneimine[47,48]. The simplicity of the synthesis of 2-oxooxazolidine and of its pyrolysis, the absence of complicated catalysts, solvents, or special apparatus, and also the avoidance of the use of the highly toxic[49-51] and mutagenic aziridine have led to the appearance of many theoretical and practical papers on this line of research within a short period[46-48,52-55].

The possibility of obtaining polyethyleneimine while avoiding the use of aziridine was first reported in the patent literature[47], without any data on the properties or composition of the pyrolysis products, only the information being given that the maximum nitrogen content reached in the polymer was 23.7%. A more detailed account[48] showed that polyethyleneimine is not the only product of thermal decomposition, for three substances of low molecular weight (one solid and two liquid) were isolated together with the polymer. One of the liquid products was aminoethanol, which was regarded as produced by the hydrolysis of aziridine formed as an intermediate. The other two substances were considered to be substituted ureas. Infrared-spectroscopic investigation of the polymer showed that it also contained carbonyl groups. Japanese workers have recently described in a series of papers[52-54] a careful investigation of the composition of the thermolysis products of various substituted 2-oxooxazolidines (as well as of 2-oxooxazolidine itself), and the kinetics and mechanism of this reaction.

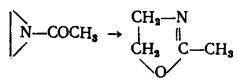
Thermolysis Products

The pyrolysis of 2-oxooxazolidine at 230° and atmospheric pressure in a stream of dry nitrogen is accompanied by the evolution of only ~ 61% of the theoretical quantity of carbon dioxide[53], and hence ~ 39% of the 2-oxooxazolidine is converted into other thermally stable carbonyl compounds. Disappearance of the carbonyl band of 2-oxooxazolidine in the infrared spectrum (at 1760 cm^{-1}) of the pyrolysate is accompanied by the appearance of a new carbonyl band (at 1686 cm^{-1}).

The pyrolysate was separated into four components (Table 1) by careful fractionation. In agreement with the above observations by Jones and his coworkers[48], the first fraction consists of aminoethanol. The structure of 1-2′-hydroxyethyl-2-oxoimidazolidine (second fraction) and of 1-2′-aziridinylethyl-2-oxoimidazolidine (third fraction) was proved by analysis, infrared examination, and comparison with synthetic preparations. The large quantity of products of low molecular weight (~ 62%) is probably explained by the solubility of 2-oxooxazolidine at temperatures above 80° in the pyrolysis products, which increases the likelihood of side-reactions.

The infrared spectrum of the fourth, polymeric fraction contains three amide absorption bands, at 1695, 1495, and 1275 cm^{-1}, which are analogous to bands in the spectra of the second and third fractions. Thus these results suggest that the polymeric products of the pyrolysis of 2-oxooxazolidine consist of a mixture of polyethyleneimine fractions of low molecule weight‡, some of them containing terminal 2-oxoimidazolin-1-yl rings.

The pyrolytic decarboxylation of 3-acetyl-2-oxooxazolidine gives, together with the corresponding polymer, a considerable quantity of 2-methyl-Δ^2-oxazoline[53], probably formed by a rearrangement of *N*-acetylaziridine



resembling the rearrangement of *N*-benzoylaziridine into 2-phenyl-Δ^2-oxazoline[58].

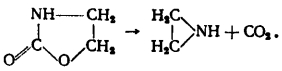
TABLE 1. Composition of pyrolysate of 2-oxooxazolidine.

Fraction	B.p., °C	M.p., °C	Compound	Content, %
1	—	—	aminoethanol	4.76
2	180—185 (3.5 mm)	51.5	1-2′-hydroxyethyl-2-oxoimidazolidine	52.38
3	—	239	1-2′-aziridinoethyl-2-oxoimidazolidine	4.76
4	—	—	polyethyleneimine	38.1

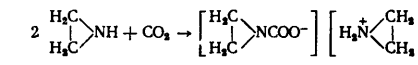
‡ The relatively low molecular weight of polymers obtained by the thermolysis of 2-oxooxazolidine is consistent with investigations of the depolymerisation of polyethyleneimine and its *N*-substituted derivatives. The latter are usually depolymerised at lower temperatures than is polyethyleneimine itself[41]. Thus poly-*N*-phenethylethyleneimine and poly-*N*-n-butylethyleneimine are completely depolymerised to the corresponding piperazines at 150° and 200° respectively. Although polyethyleneimine itself depolymerises to piperazine only at 280°,[56,57] branched-chain polyethyleneimine molecules can be regarded as representing a particular case of *N*-substituted derivatives of polyethyleneimine, so that the temperature of pyrolysis is linked with the structure of the polymer.

Mechanism

According to Jones[48] the mechanism of the thermal decomposition of 2-oxooxazolidines is best explained by the formation of aziridine in the first stage of the reaction

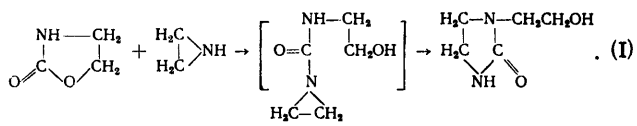


In fact, aziridine, while being extremely stable in strongly alkaline medium, readily polymerises in the presence of acids, forming polyethyleneimine by a stepwise mechanism (p. 517) promoted by aziridinium cations. Initiation of the polymerisation of aziridine by carbon dioxide can be written



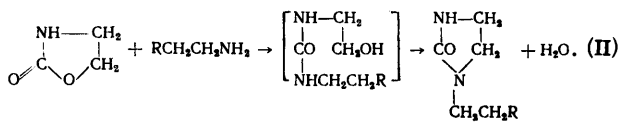
This route and also pyrolytic polymerisation initiated by certain acidic impurities or traces of water probably lead to the formation of polyethyleneimine instead of aziridine in the thermolysis of 2-oxooxazolidine.

The formation of secondary products in pyrolysis can also be explained by the intermediate formation of aziridine. For example, 1-2′-hydroxyethyl-2-oxoimidazolidine results from nucleophilic attack on the 2-oxooxazolidine molecule by aziridine followed by cyclisation of the adduct:



(I)

Similar attack on 2-oxooxazolidine by the terminal group of a polymer with subsequent elimination of water from the adduct leads to the formation of various 1-2′-aminoethyl--substituted derivatives of 2-oxoimidazolidine:



(II)

Actually, the compound in which R = , i.e. 1-2′-aziridinylethyl-2-oxoimidazolidine, and a polymer having the structure (II) represents two other products of the pyrolysis of 2-oxooxazolidine. The water evolved according to Eqn. (II) is probably used up in opening the aziridine rings (to form aminoethanol) and also end-groups in the polymer.

However, the above mechanism of the formation of 1-substituted 2-oxoimidazolidines of low molecular weight and terminal 2-oxoimidazolidinyl groups on polymer chains necessarily presupposes the absence of substituents in position 3 of 2-oxooxazolidine, and consequently in position 1 of aziridine. Thermal decomposition of 3-substituted cyclic urethanes results[53] in the complete evolution of carbon dioxide, and the infrared spectrum of the pyrolysate contains no frequencies due to carbonyl groups. The pyrolysate of 3-*p*-chlorophenyl-2-oxooxazolidine consists entirely of poly-*N*-*p*-chlorophenylethyleneimine of low molecular weight. Even when decomposition of this oxooxazolidine was stopped after the evolution of half the theoretical quantity of carbon dioxide, the band at 1767 cm^{-1} (due to carbonyl in the original oxooxazolidine) could be detected in the pyrolysate at half the intensity observed with the original compound; no new carbonyl absorption bands were observed.

Thus, in contrast to the usual decarboxylative polymerisation, in which decarboxylation and polymerisation occur simultaneously, in the thermolysis of oxooxazolidines these two processes are completely independent reactions.

Kinetics

Study of the rate of the uncatalysed decarboxylation of 2-oxooxazolidine has shown[54] that in this case the decomposition is autocatalytic. It is seen from the graph in Fig. 4 that the rate of conversion dx/dt first increases as reaction proceeds, reaches a maximum, and then decreases. Such a dependence of rate on x represents the characteristic rate curve for autocatalytic reactions. Here it is the principal reaction products — aziridine and its polymer — which develop the autocatalytic properties.

A comparative study of the rates of decarboxylation of various 3-substituted 2-oxooxazolidines has established[54] that the ring is cleaved at the C–N bond, not at C–O (Table 2). In fact the reactivity of a 3-aryl-2-oxooxazolidine is greatly dependent on the electronic character of the substituent in the benzene ring: electron-acceptor groups accelerate decarboxylation, whereas electron-donor groups slow it down.

Thus the cleavage of the C–N bond in oxooxazolidine is the rate-determining stage in the process of decarboxylation.

A kinetic study of the catalytic decarboxylation of 2-oxooxazolidines in the presence of aromatic amines has shown that the resulting pyrolysate exerts a stronger catalytic effect than does the aromatic amine added as catalyst, the rate of conversion being represented by a curve having a maximum, which is characteristic of autocatalytic reactions.

In the presence of high-boiling aliphatic amines, however, the reaction velocity has its highest value at the

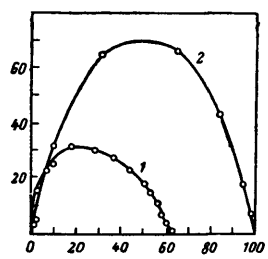


Fig. 4. Variation in rate of uncatalysed decarboxylation of 2-oxooxazolidines during reaction:
1) 2-oxooxazolidine (200°); 2) 3-*o*-nitrophenyl-2-oxooxazolidine (230°).

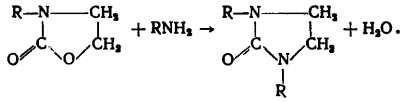
TABLE 2. Relative rates of decarboxylation of 3-substituted 2-oxooxazolidines.

Oxooxazolidine (R–Ox)	Relative rate
C_6H_5Ox	1
p-CH_3—C_6H_4—Ox	0.7
p-Cl—C_6H_4—Ox	1.9
p-O_2N—C_6H_4—Ox	130.0

beginning. The descending curve in Fig. 5 (in contrast to the expected linear dependence of dx/dt on X for this pseudo-first-order reaction) is explained by consumption of the added amine in the side-reactions of ammonolysis of the intermediate aziridine

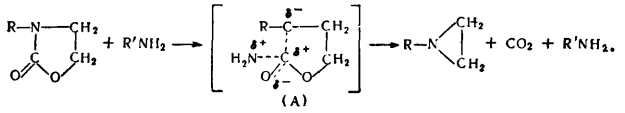


and condensation with the initial 2-oxooxazolidine

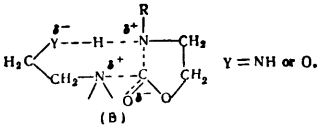


Polyamines and amino-alcohols are still more active decarboxylation catalysts[54]. Since the catalytic effect of the former exceeds the value calculated from the number of amino-groups, while it is generally absent from alcohols, a "push-pull" type of mechanism is suggested. As applied to the decarboxylation of 2-oxooxazolidines, this may consist in simultaneous nucleophilic attack by the amino-group on the positively charged carbonyl carbon atom in the oxooxazolidine and electrophilic attack by hydrogen in another amino-group (or more probably in a hydroxy--group) at the nitrogen in the urethane group of the oxooxazolidine.

Thus whereas the uncatalysed decarboxylation of oxooxazolidines and the reaction in the presence of aromatic amines are autocatalytic, the reactions catalysed by aliphatic amines, polyamines, and amino-alcohols progess in two different ways depending on the structure of the catalyst. If a simple amine is used as catalyst, reaction goes mainly through the transition state (A):



In the reaction catalysed by an amine containing a β-NH_2 or β-OH group, on the other hand, the active transition complex probably approximates to structure (B)



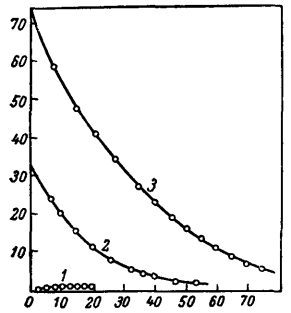


Fig. 5. Type of variation in rate of decarboxylation of 2-oxooxazolidines during reaction at 230° (1 M p-nitrophenyl-2-oxooxazolidine catalysed by different concentrations of n-dodecylamine in dibenzyl ether):
1) no catalyst; 2) 0.5 M; 3) 1 M.

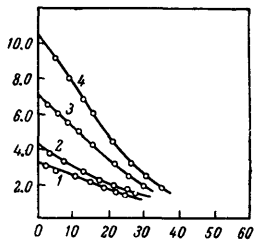
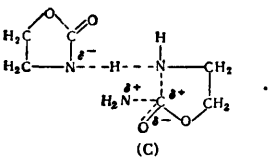


Fig. 6. Nature of variation in rate of decarboxylation at 230° of different concentrations of 2-oxooxazolidine catalysed by different concentrations of n-dodecylamine in dibenzyl ether:
1) 0.5 M + 0.75 M; 2) 0.5 M + 0.5 M;
3) 1 M + 0.75 M; 4) 1 M + 0.5 M.

In the presence of simple aliphatic amines, the decarboxylation of 2-oxooxazolidine follows a peculiar course[54] (see Fig. 6). All curves for rates of conversion with different initial concentrations of 2-oxooxazolidine are seen to converge to a single point (at about 60% conversion). The corresponding kinetic calculations show that in this case the initial rate of decarboxylation is of the second order with respect to the oxooxazolidine and of the first order with respect to the amine. These features can be explained by a peculiar, coordinated mechanism, in which the amine attacks the oxooxazolidine as a nucleophile, while another oxooxazolidine molecule attacks it as an electrophile. The transition state can be represented by the structure (C)



4. PROPERTIES OF POLYETHYLENEIMINE

Molecular Weight

Oligomeric polyethyleneimine, obtained by the acid polymerisation of aziridine, is a viscous, almost colourless resin, which can be freed from fractions of low molecular weight by electrodialysis through cellulose acetate membranes[32]. The molecular weight of polyethyleneimine oligomers has been determined by cryoscopy[18] in diphenylamine, determination of the maximum quantity of dibromoethane necessary for the complete cross-linking of all the aziridine (and amino-) groups in the polymer[59], and viscosity measurements on aqueous solutions[18]. The corresponding Staudinger viscosity constant for a 1% solution of polyethyleneimine in water $K_{\bar{m}} = 2.8 \times 10^{-4}$ was obtained by extrapolation of the relative viscosity curve for purified polyethylenepolyamines. Polyethyleneimine was found to be an oligomer of comparatively low molecular weight.

The degree of polymerisation of polyethyleneimine can be calculated[24] theoretically from the molecular proportions of aziridine and of the catalyst, but the practical values

are always lower owing to the presence in the polymer of fractions of low molecular weight. Polymerisation of aziridine in the presence of the usual acidic catalysts may yield polymers of molecular weight not exceeding[24,32,60] 1000–2200, § the mean-molecular-weight of the polyethyleneimine depending on the conditions of polymerisation[24]: it is increased by increasing the initial concentration of aziridine at constant temperature, and lowered by increasing the catalyst concentration. If polyethyleneimine of as high molecular weight as possible is desired, the initial solutions of aziridine must be as concentrated as possible and a minimum amount of catalyst must be used. In practice this minimum amount is 1 mole % based on the aziridine (because of the consumption of acid in side-reactions[16]).

Theoretically this corresponds[24] to a polymer of molecular weight 4300 (if pure aziridine is used in the absence of solvent). In practice, however, this is impracticable, since increasing the aziridine concentration above 50% greatly increases the rate of polymerisation, which then is often explosive in character[32,63,64]. The explosiveness is due to inadequate removal of the heat of polymerisation at high reaction velocities.

Raising the temperature also increases the rate of polymerisation[24]. The effect of temperature depends substantially on the initial concentration of aziridine: it is considerably greater at high concentrations than with dilute initial solutions.

The comparatively low molecular weight of polyethyleneimine obtained by the acid polymerisation of aziridine in aqueous and alcoholic solutions is probably established when polymerisation ceases owing to the gradual cleavage of the aziridinyl groups at the ends of the growing polymer chains (as a result of solvolysis or side-reaction with the catalyst, see above). Polymerisation of aziridine with catalysts which do not cause ring-opening as a side-reaction (in non-aqueous media), and in the absence of contamination by compounds of low molecular weight, can probably lead to the synthesis of polyethyleneimine of higher molecular weight. Special attentian is being paid to the polymerisation of aziridine in the presence of catalysts of high molecular weight, e.g. surface-active substances or cation-exchange resins.

Degree of Branching

Polyethyleneimine can contain up to 38% of nitrogen in the form of primary amino-groups[65-67]: i.e. it is a strongly branched polymer. The formation of such polymers is observed mostly when polymerisation is continued until the monomer has been almost completely converted. Infrared examination[67] of polyethyleneimine shows it to contain primary, secondary, and tertiary nitrogen atoms (bands at 2.9, 6.3, 9.0, and 9.6 μm). In the polymerisation of aziridine in the presence of 1 mole % of HCl the degree of branching increased with rise in temperature and increase in the acid concentration[66]. It is interesting that at low temperatures (20°) the degree of branching diminishes with fall in the acid concentration (from 38% to 12%);

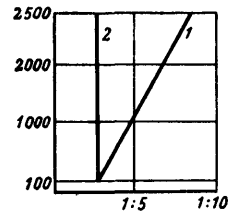


Fig. 7. Dependence of degree of branching of polyethyleneimine on catalyst (HCl) concentration for polymerisation of C = 50% of aziridine at:
1) 20°; 2) 80°. The molar ratio of aziridine to catalyst is plotted as ordinate.

at high temperatures (80°) it is independent of concentration and has the value 38% (see Fig. 7). The complete polymerisation of polyethyleneimine at high temperatures results in the degree of branching again increasing to 38%.

Unbranched polymers can be obtained by the polymerisation of an N-substituted aziridine. Thus the preparation has been described[13] of a straight-chain polyethyleneimine (up to a molecular weight of 2000) by the polymerisation of N-benzenesulphonylaziridine (by heating or in the presence of traces of boron trifluoride).

5. REACTIONS OF POLYETHYLENEIMINE

Ionisation Equilibrium

Three papers have been published[59,67,68] on the use of potentiometric titration to study the ionisation of polyethyleneimine. Although different specimens of the polymer were employed, the results show quite good agreement. The titration curve for polyethyleneimine in aqueous potassium chloride (Fig. 8) resembles that for monoacid bases, except that the pH values fall more sharply than with amines of low molecular weight. This indicates that the NH groups in the polymer have a far smaller ability to combine with acid than have the simpler amines. The basic strength of the NH groups in polyethyleneimine is increased by the presence of a neutral salt (KCl). Thus a 0.01 M solution of the polymer in 1 N KCl has pH 9.89, while the equivalence point is at pH 4.4. The equivalence point is reached at 66% neutralisation: in other words, only two-thirds of the basic groups in polyethyleneimine can be titrated. A similar phenomenon is observed with proteins[68] and with poly-N-vinylimidazole[69].

Similar results have been obtained[67] by the back titration of polyethyleneimine hydrochloride with alkali. Exact neutralisation is achieved after 34% of the hydrochloride HCl has been titrated. The curve representing titration of the hydrochloride with alkali is inverted with respect to the titration curve for the basic polymer.

The acid dissociation constant of polyethyleneimine $K_a \simeq 10^{-9}$ has been calculated[67] by means of the modified Henderson–Hasselbalch equation for polyelectrolytes. This equation is valid only up to a degree of dissociation of $\alpha = 0.5$. Over this range polyethyleneimine conforms to Katchalsky's theory of polyelectrolytes[70]; above $\alpha = 0.5$ it behaves as a monomeric acid.

§ Although the molecular weight of industrial specimens of polyethyleneimine produced by the BASF firm probably lies within or near the above limits, with American specimens[61] M = 30 000–40 000 and even[62] 100 000.

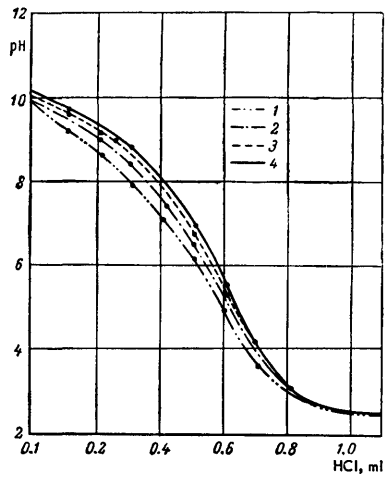


Fig. 8. Curves representing potentiometric titration of a 0.01 M solution of polyethyleneimine with 0.5 *N* HCl in the presence of various concentrations of neutral salt (*N* KCl): 1) 0.1; 2) 0.5; 3) 1.0; 4) 2.0.

British workers succeeded[59] in titrating amino- and aziridinyl groups in the polymer separately, obtaining pK_a values of 9.0 and 10 respectively. Calculation of the constants was based on Katchalsky's equation for chain polyelectrolytes[71].

Very similar results were obtained in a study of the ionisation of polyethyleneimine which had been cross-linked with dibromoethane[72]. Although the titration curves were similar in form to those for the oligomer, a difference was caused by the appearance of new nitrogen atoms which could not be titrated even at pH 1–2, i.e. extremely feebly basic (tertiary) atoms. Their number corresponds exactly with the number of dibromoethane molecules which have reacted. The results of the titration of oligomeric polyethyleneimine become clear when it is remembered that specimens of the polymer usually contain up to 38% of tertiary nitrogen atoms owing to branching.

Salts of Polyethyleneimine, Complex Formation

Viscosity measurements on partly neutralised aqueous solutions of polyethyleneimine[67] show that maximum viscosity occurs at 80% neutralisation. Further addition of electrolyte merely screens the charges on the long-chain polymer molecule. This weakens the electrostatic repulsion between ionised groups, as a result of which the extended filaments of ionised polyethyleneimine pass more and more into random tangles, as with uncharged fibrous molecules.

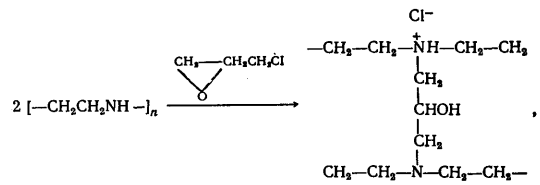
It has also been found that polyethyleneimine salts are strongly hydrolysed in solution (up to 30%). Titration of cross-linked polyethyleneimine with different acids gives the sequence – acetate < chloride < toluene-*p*-sulphonate – for the affinity of the resin for anions. The degree of swelling of the corresponding salts of the cross-linked oligomer in water falls in the same sequence, which indicates increasing association of the ions owing to van der Waals forces of adhesion between the anions and the polymer chains.

Polyethyleneimine has been found[67,72] to absorb copper (and also cobalt and nickel) to form ammines. Complex formation is accompanied by a decrease in the basic strength of the polymer and in the viscosity of aqueous solutions, owing to the weakened hydrophilic character produced by screening of the ionic groups by the complexing copper ions. The ammines of polyethyleneimine with copper and nickel can be completely dried, and the resulting powders, unlike polyethyleneimine itself, are not hygroscopic.

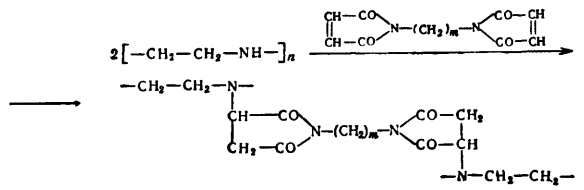
Study of the salts of polyethyleneimine is of interest for the fundamental theory of polyelectrolytes in view of the exceptionally high charge density of the ionic groups.

Cross-Linking of Polyethyleneimine Chains (Hardening Reactions)

The preparation of purely aliphatic anion-exchange resins of extraordinarily high capacity, based on polyethyleneimine networks, has attracted special attention to the study of the cross-linking of this polymer by various substances. Among cross-linking agents which have been used are 2,3-epoxypropyl chloride[73,75]



dichloroethane and dibromoethane[74], formaldehyde[72], and maleimide[75]



(cross-linking by addition to an activated double bond).

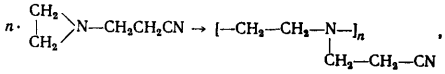
The reaction with dibromoethane has been studied the most thoroughly. The minimum quantity of the latter required to form a gel with polyethyleneimine is[72] 0.028 mole g-equiv.$^{-1}$. To obtain a mechanically stable resin, however, this quantity must be increased fivefold (to 0.16 mole g-equiv.$^{-1}$). Only a small proportion of the dibromoethane was actually found to form cross-links between the polyethyleneimine chains, most of it reacting with nitrogen atoms in the same chain to form small closed loops. Drying the resin at 100° produces further cross-linking (the degree of swelling is diminished). Cross-linked polymers obtained by this method are stable to acids and alkalis for 2–3 months.

N-Substituted Polyethyleneimines

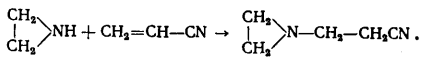
Acetylation of polyethyleneimine with acetic anhydride yields a water-soluble *N*-acetyl derivative, which has been proposed[76] as a blood-plasma substitute. Acylation (acetylation and benzoylation) of polyethyleneimine has been suggested as a method for determining its degree of branching, but the results obtained are not very reliable.

A probably more reliable method is reaction of the terminal amino-groups of polyethyleneimine with nitrous acid by Van Slyke's procedure[65], and also conductimetric titration.

Poly-*N*-cyanoethylethyleneimine has been obtained[77] by the polymerisation of β-aziridinylpropionitrile:



which in turn is readily obtained by the cyanoethylation of aziridine:

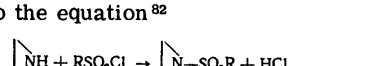


Benzoylation. The Schotten–Baumann benzoylation of polyethyleneimine gives[18] a viscous white product soluble in chloroform, which after reprecipitation in ligroin is obtained as a white powder having a softening point of 110°.

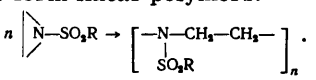
Poly-*N*-nitrosoethyleneimine. This compound has been obtained[18,78] as an insoluble precipitate by the addition of hydrochloric acid to polyethyleneimine in aqueous sodium nitrite solution. The nitrogen content of the resulting polymer differs markedly from the calculated value.

Poly-*N*-sulphonylethyleneimines. These polymers have been obtained both by the reaction of polyethyleneimine with sulphonyl chlorides[79] and by the direct polymerisation[80,81] of *N*-sulphonylaziridines (the methanesulphonyl, benzenesulphonyl, toluene-*p*-sulphonyl, naphthalene-1-sulphonyl, etc. derivatives).

Liquid or low-melting solid *N*-sulphonylaziridines are obtained by the reaction of sulphonyl chlorides with aziridine according to the equation[82]



Polymerisation of the initial aziridine by the hydrogen chloride formed is prevented by carrying out the reaction in the presence of alkali. The monomeric *N*-sulphonylaziridines thus obtained are readily polymerised by heating or by the action of alkali to form linear polymers:



The most effective polymerisation catalysts are organic bases, including aziridine. Polymerisation is inhibited by acids (e.g. arenesulphonic acids and acetic acid).

Poly-*N*-sulphonylethyleneimines are chemically stable solids of high melting point, insoluble in the usual organic solvents and extremely resistant to hydrolysis (by alkalis and acids). Their physical properties can be modified by carrying out polymerisation in the presence of alkaline catalysts. The degree of polymerisation can be controlled to a certain extent by varying the temperature and duration of polymerisation.

N-Sulphonylaziridines are readily polymerised on substrates — textiles, paper, etc.

Methylation. The methylation of polyethyleneimine has been accomplished[83] by the action of dimethyl sulphate on an aqueous solution of the polymer, with subsequent neutralisation with sodium carbonate. The product of exhaustive methylation obtained is a readily water-soluble polymer, which is used for pretreating cellulosic fibres before the application of direct dyes.

A large amount of specialised work has been done on the industrial exploitation of the reaction of polyethyleneimine with cellulose[84,85], and this has been reviewed by Machida[86].

6. COPOLYMERS OF AZIRIDINE

Copolymers with Carbon Monoxide and Carbon Disulphide

Rubberlike solid products are obtained by the copolymerisation of aziridine with carbon monoxide[87] and with carbon disulphide[88,89]. Reaction with the former is carried out at high temperatures (150°) and high pressures of carbon monoxide (~2000 atm). Results of elementary analysis on the product of m.p. 211° correspond to the formula $[(C_2H_5N)_2CO]_n$.

Copolymers with Cyclic Oxides

Depending on the relative proportions of the components, copolymers of aziridine with oxiran and methyloxiran can be obtained as viscous oils of various consistencies[90]. The products have not been investigated in greater detail. They have been used for the processing of textiles. A patent[91] has proposed the use as ion-exchange membranes of copolymers of aziridine with 2,3-epoxypropyl chloride obtained by heating the components (in the proportions 12 : 1) without a catalyst.

A detailed study of the copolymerisation of aziridine with oxides in the presence of various Lewis acids has been made by Overberger and his coworkers[92]. They have shown that even the most active of the catalysts examined (the ether complex of boron trifluoride) gives a product which is not a true copolymer, but consists of a polyamine main chain which has been β-hydroxylalkylated by the epoxides. Actually, the reaction with 1-ethylaziridine, which cannot form side-chains with the oxides, gave a copolymer containing 86 mole % of aziridine residues, while epoxide residues were present only as end-groups (resulting from chain termination). Complex formation between the catalyst and basic polymeric and monomeric aziridine derivatives evidently makes it incapable of catalysing the growth of epoxide chains.

Copolymers with Diisocyanates and Isothiocyanates

Many synthetic resins, from viscous oils to solids, have been obtained[93-99] by the condensation (effected by heating or by the action of acids, alkalis, etc.) of aziridine with aliphatic or aromatic diisocyanates and isothiocyanates, e.g. with 4-methyl-1,3-phenylene diisocyanate.

Copolymers with αβ-Unsaturated Acids, Aldehydes, and Ketones and with Acrylonitrile

The products described in the patent literature[77,98,100,101] are probably polymers of *N*-substituted aziridines, obtained by the addition of aziridine to the vinyl components.

Copolymers with *N*-Sulphonylaziridines

The copolymerisation of mixtures of a sulphonylaziridine and aziridine occurs spontaneously[81], the resulting polymer containing both components. The properties of the copolymers obtained differ from those of polyethyleneimine and of polysulphonylethyleneimines. They depend on the relative proportions of the components. With small amounts of aziridine, resins are obtained which are insoluble in water and in acids. Copolymers containing not less than 5 moles of aziridine per mole of *N*-sulphonylaziridine dissolve in acids, alkalis, and organic solvents. Depending on the contents of the components, the state of aggregation of these copolymers varies from viscous oils to solid resins.

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The growing interest in the chemistry of polyethyleneimine is due not only to the developing fields for its industrial application. The intrinsic interest of this branch of the chemistry of macromolecular compounds is connected both with the peculiar character of the reactivity of functional groups in a polymer chain and with the problem of the special features of multifunctional polymers.

The polyethyleneimine system — the simplest heterochain polymer and polybase — is most convenient for investigations on these lines. This system is formed by replacing one-third of the carbon atoms in polyethylene with nitrogen atoms. While preserving several of the properties of polyethylene (including thermal stability), it is nevertheless highly reactive.

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STEREOCHEMISTRY OF THE HYDROXY-MERCURATION OF ALKENES

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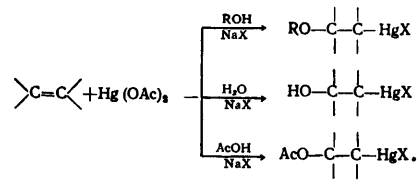
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I. INTRODUCTION

In 1892 Kucherov discovered that mercury(II) salts are capable of addition to a C–C double bond[1]. Eight years later — in 1900 — Hofman and Sand[2] developed this reaction, and in subsequent investigations it was shown that the reaction of alkenes with mercury(II) salts leads to the formation of hydroxyalkylmercury compounds and their derivatives:



Since then, hydroxymercuration has remained a subject widely studied from various viewpoints. Hydroxyalkylmercury compounds, being readily available, find application as pesticides, antiseptics, diuretics, preservatives, seed dressings, etc.

The alkoxyalkylmercury halide derivatives obtained in this way were used to solve several important theoretical problems. Thus the example of electrophilic substitution