POLYMERIC AMINES AND AMMONIUM SALTS

Edited by

E. J. Goethals

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY
(Macromolecular Division)
in conjunction with
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POLYMERIC AMINES AND AMMONIUM SALTS

Invited Lectures and Contributed Papers
Presented at the
International Symposium on Polymeric Amines
and Ammonium Salts
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PREFACE

This volume is composed of the twelve main lectures and twentynine communications presented at the International Symposium on Polymeric Amines and Ammonium Salts, which was held in Ghent on September 24-26, 1979. The symposium was, to our best knowledge, the first one solely devoted to the subject of polymeric amines.

The symposium and therefore also this volume was devoted to the synthesis, the study of the properties and the - real or potential - applications of polymeric amines and ammonium salts. In the program, one day was devoted to each of these subdivisions. However, the authors, especially the invited speakers, were asked not to restrict themselves to one of these subdivisions but on the contrary, where possible, to extend their paper so that a broad overview of the subject is presented. In this book therefore, the subdivisions have been omitted but it will be remarked that the book begins with synthesis-oriented subjects and progresses with property-oriented papers to end with the papers in which emphasis is put on applications.

The synthetic methods for the polyamines described in this volume include ring-opening polymerizations, polyadditions, reactions on polymers, vinyl polymerization and copolymerization of unsaturated amino compounds etc. A few papers report new synthetic ways for polyampholytes. Although the overview cannot be claimed to be complete, we think that the most important methods are covered.

The properties of polymeric amines are concerned with their ability to form complexes with different metal ions, their behavior as polymeric bases (or nucleophiles) and their water-solubility in the form of ammonium salts. A relatively large part of the subjects is devoted to the synthesis and physicochemical properties of block- and graft copolymers with polyamine blocks or grafts, and to polymer-polymer complexes, including complexes with biopolymers.

The uses of polymeric amines and ammonium salts are naturally in close relation with their properties. They include topics such as chelating polymers, ion exchange resins (also thermally regenerable resins) purification of waste waters, flocculation, biomedical and pharmaceutical applications, emulsifiers, polymeric catalysts, polymeric reagents, textile auxiliaries, paper fabrication, photographic applications etc...

A look at the literature of the last decade shows that research on the synthesis, properties and uses of polymeric amines is increasing in academic as well as industrial institutions. It is therefore believed that these compounds have a considerable potential as new useful materials. We hope that this book will contribute to the understanding and the significance of the field and will stimulate new, and ongoing research on this exciting class of compounds.

The editor wishes to express his heartfelt thanks to the symposium participants for the work involved in presenting the papers at Ghent and preparing the manuscripts included herein. I also thank the members of the scientific and organizing committee for their help in the preparation of the symposium program and their referee work for the present publication. Finally I wish to thank the different organizations who have helped in one way or an other to make this symposium possible: the International Union of Pure and Applied Chemistry, the Belgian National Science Foundation, the Belgian Ministry of National Education, the University of Ghent, the Flemish Chemical Society.

Eric Goethals
University of Ghent
Belgium.

January 23, 1980.

CONTENTS

*Invited Lecture

Invited Lecture

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*Invited Lecture

POLYMERIZATION OF AZIRIDINES

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The Dow Chemical Company, Freeport, Texas 77541, USA

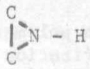
Abstract - A brief review of the reaction steps involved in the polymerization of different types of aziridines is presented. Data are reported on the acid catalyzed polymerization and acid catalyzed cyclooligomerization of 1-alkylaziridines.

The acid catalyzed polymerization of 1-ethylaziridine and 1-(2-hydroxyethyl)-aziridine in water at 25°C proceeds rapidly to about 35-45% monomer conversion, then only very slowly to higher conversions. The polymers produced are low molecular weight (1500-2000) and contain quaternary ammonium groups in the polymer. Neither the rate nor the molecular weight is affected by the counter ion of the acid catalyst used. The same reaction performed at a higher temperature causes only cyclooligomerization of the aziridines. A series of cyclic tetramers of various 1-alkylaziridines were prepared and very limited data is reported on the effect of conditions on these cyclooligomerizations.

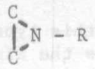
A reaction scheme is suggested which shows the relationship of the polymerization to the cyclooligomerization.

INTRODUCTION

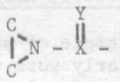
Aziridines may be broadly divided into three groups of compounds for the purpose of considering their reactions, particularly polymerization. These groups are 1-unsubstituted aziridines, (I), 1-substituted basic aziridines, (II) and "activated" aziridines, (III).



Secondary Amines
I

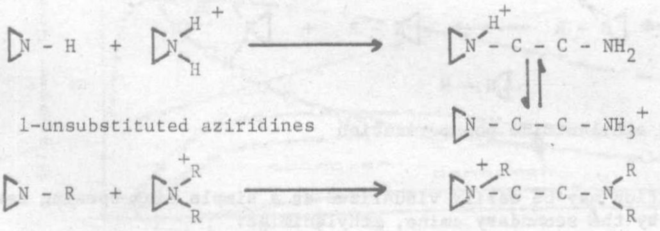


Tertiary Amines
II



Tertiary Amides
III

Compounds in all three groups have the common property that they undergo ring-opening reactions readily and are susceptible to a ring-opening polymerization. Compounds in each group, however, have specific reaction features which are characteristic of that group. Thus 1-unsubstituted aziridines, like secondary amines, may undergo typical amine reactions which lead to nitrogen-substituted derivatives classified here as group II or III compounds. 1-Substituted basic aziridines, being tertiary amines, are similar in that they are basic and undergo typical tertiary amine reactions such as quaternization by alkylating reagents.



1-unsubstituted aziridines

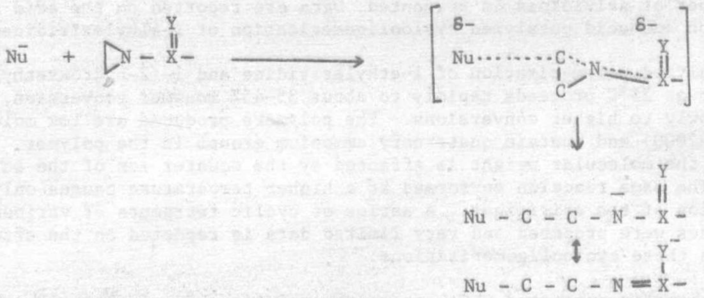
1-substituted basic aziridines

In polymerization of ethylenimine, the initial step is simply a ring-opening reaction of the protonated ethylenimine to make 1-(2-aminoethyl)aziridine along with equilibration of the proton. Such equilibration allows all aziridine rings to eventually undergo reaction.

The first step in polymerization of 1-alkylaziridines, catalyzed by alkylating agents, only produces another alkylated aziridine (quanternary aziridinium group) and no such equilibration is possible under polymerization conditions. Thus when a ring-opening reaction does occur with a nucleophile other than a 1-alkylaziridine, e.g., tertiary amine in the polymer, the polymerization ceases.

Since polymerization of basic aziridines (I or II) depend on making a catalytic amount of the aziridine into an alkylating agent by addition of an acid or a different alkylating agent, a description which distinguishes between groups I and II is whether or not the "catalyst" may equilibrate at a rate more rapid than the ring-opening polymerization reaction (1).

Activated aziridines (III) have been defined as compounds possessing a nitrogen substituent which is able to stabilize a negative charge formed on the aziridine nitrogen in the transition state when that aziridine reacts with a nucleophile (2).



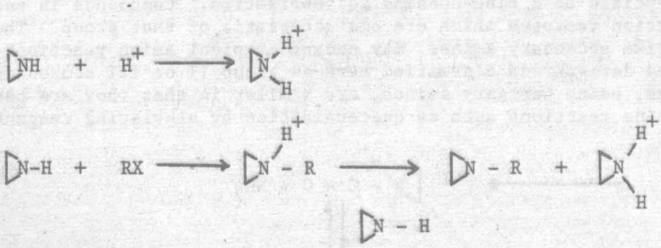
As such, these compounds are more susceptible to anionic polymerization than to cationic polymerization. Also, a variety of complications (e.g. isomerizations) are possible due to and depending on the nitrogen substituent.

Because of different reaction characteristics mentioned above, each type of aziridine (I, II or III) will be reviewed separately.

1-UNSUBSTITUTED AZIRIDINES

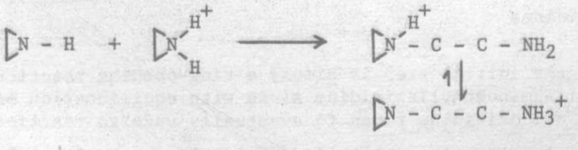
The most studied example of polymerization with this type of aziridine is the polymerization of ethylenimine. Early work was directed towards the kinetics of the polymerization which shows that the polymerization slows markedly with increasing conversion and towards degree of branching present in polyethylenimine (3-7).

Addition of a small amount of acid catalyst converts ethylenimine to an alkylating agent which is the initiating specie. Although a different alkylating agent may be used, it is soon converted to an acid which creates the same initiating specie.



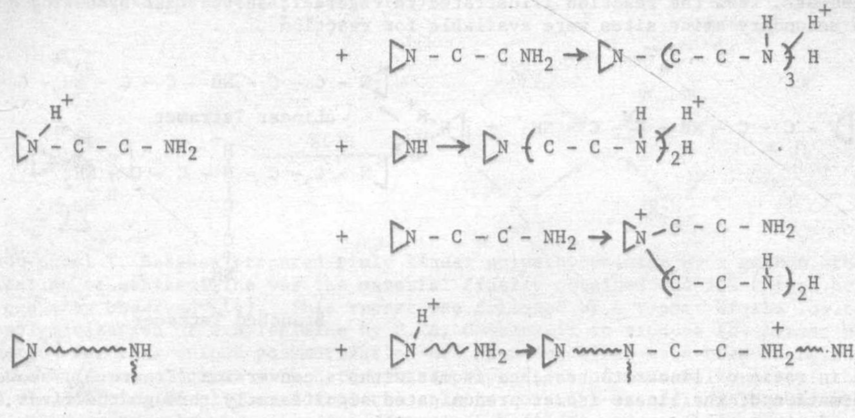
Initiation step in ethylenimine polymerization

The initial propagation reaction may be easily visualized as a simple ring-opening reaction of the protonated aziridine by the secondary amine, ethylenimine.



Initial propagation in ethylenimine polymerization

Subsequent reaction of the aziridine ring with primary and secondary amine groups represent continuing propagation.



Continuing propagation in ethylenimine polymerization.

Reaction of secondary amine groups or aziridine tertiary amine groups represent branching reactions in ethylenimine polymerization.

Formation of the various oligomeric species has been studied in aqueous solutions using computer simulation of the degree of branching based on estimated second-order rate constants for the various oligomer-forming reactions derived from model compounds (8). Reasonable rate constants could be used in the simulation to achieve a degree of branching corresponding to about one branch for every three linear nitrogen atoms (or a primary/secondary/tertiary amino nitrogen ratio of 1/2/1), the experimentally determined value. This same approximate experimental value was obtained in a later study wherein the polymerization was conducted in methanol as solvent (9). In this solvent the rate of polymerization is lower than that in aqueous solution, thus allowing the appearance and disappearance of initially formed intermediates to be measured accurately. These results are shown in Figure 1.

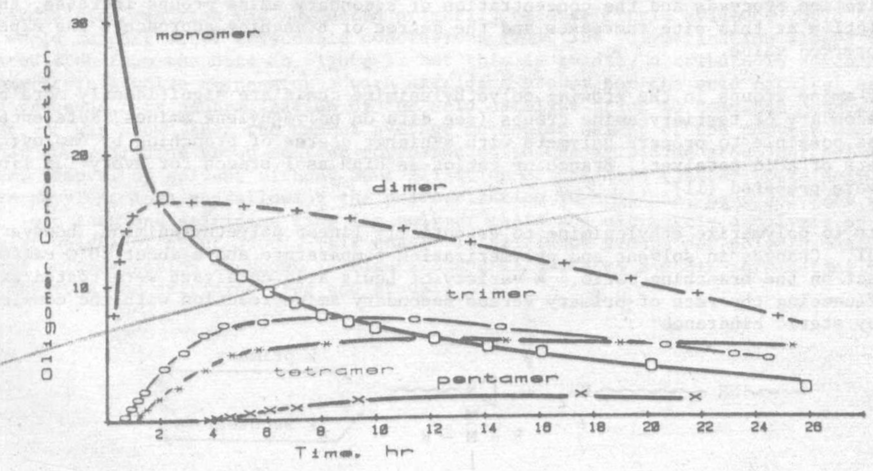
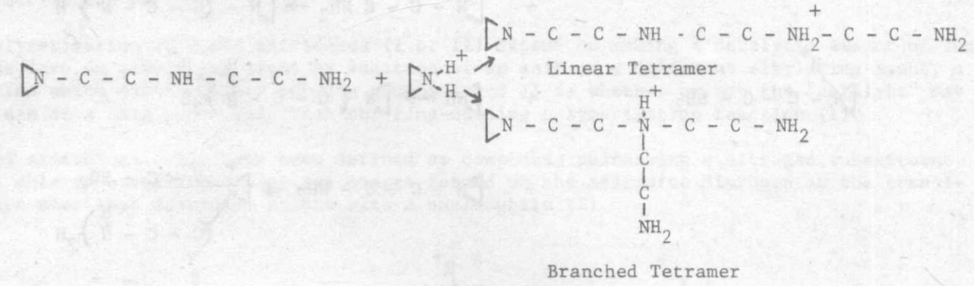


Fig. 1. Rate of formation and subsequent reaction of oligomers in the polymerization of ethylenimine.

Much research has been devoted to accurate methods for measuring the degree of branching in polyethylenimine (9) and attempts made to alter the degree of branching. Isolation of the tetramer isomers, from the reaction illustrated in Figure 1, showed that branching occurred as soon as secondary amine sites were available for reaction



The change in ratio of linear to branched isomer with conversion (Figure 2), showed that rate of formation of the linear isomer predominated significantly through the first 60-70% conversion of ethylenimine, then remained essentailly constant as the tetramer continued to react.

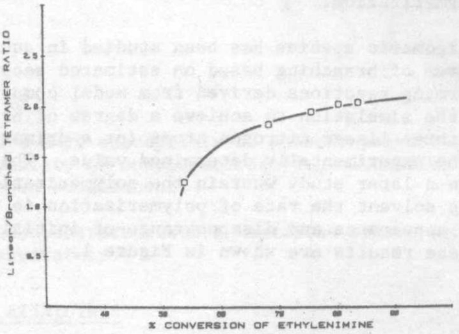
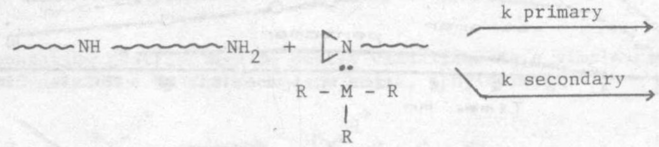


Fig. 2. Change in ratio of linear tetramer to branched tetramer in early part of ethylenimine polymerization (<100% conversion of ethylenimine).

As polymerization proceeds and the concentration of secondary amine groups increase, the rate of reaction at this site increases and the degree of branching approaches the experimentally observed value.

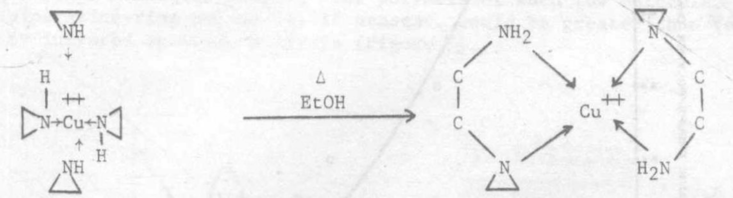
The primary amine groups in the growing polyethylenimine chain are significantly more basic than the secondary or tertiary amine groups (see data on polyethylene amines, Reference 10). Thus, it was possible to prepare polymers with a higher degree of branching by employing large amounts of acid catalyst. Branching ratios as high as 1 branch for every 1.9 linear nitrogens were prepared (11).

Our attempts to polymerize ethylenimine to essentially linear polyethylenimine, however, were unsuccessful. Changes in solvent and polymerization temperature above about 50°C caused little effect on the branching ratio. A variety of Lewis acid catalysts were tested with the idea of influencing the rate of primary versus secondary amine reaction with the complexed aziridine by steric hindrance.

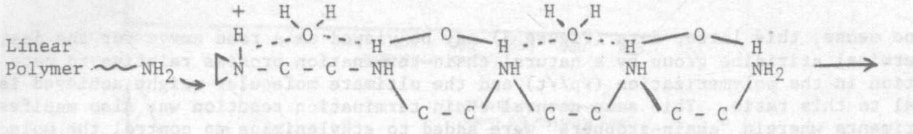


This led only to higher molecular weight oligomers wherein the degree of branching was essentially the same as in protonic acid catalyzed polymerizations (12).

Attempts to polymerize ethylenimine which was complexed to metal ion salts also produced only low molecular weight oligomers and actually formed the basis for a procedure to obtain high yields of 1-(2-aminoethyl)aziridine (13).

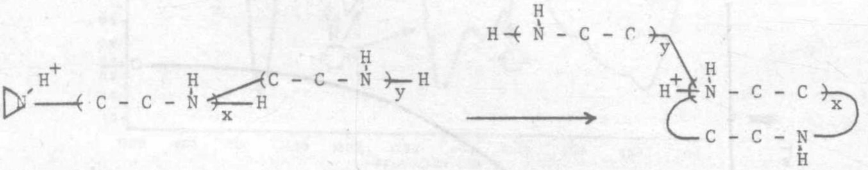


It was not until T. Saegusa prepared truly linear polyethylenimine by a method other than polymerization of ethylenimine was the material finally obtained and its unique crystalline hydrate property observed (14). This report was followed by a report of the low temperature aqueous polymerization of ethylenimine by P. A. Gembitskii to produce the linear polymer (15). The mechanism for this unique polymerization has been described as a head-to-tail polymerization of the hydrated oligomer with heterophase propagation of macromolecules of the crystal hydrates via addition of oligomers from the aqueous solution or addition between the hydrated forms of the polymer molecules containing terminal aziridine rings (16). This propagation has been visualized as:



Solid oligomer hydrate

The chain-terminating reaction in the polymerization of ethylenimine has been described as a probable intramolecular cyclization reaction, comparable to the intermolecular propagation reaction, to form large (greater than six members) cyclic rings (2,9).



Termination step in ethylenimine polymerization

This termination reaction was suggested primarily because little evidence could be obtained which would support other reasonable conclusions (2). The polymerization slowed very rapidly, as can be seen from the data in Figure 1, but this is readily attributable to competition of the more basic acyclic amine groups with aziridine groups for the acid catalyst as polymerication proceeds. By neutralization of the acid catalyst prior to complete consumption of monomer, it was shown that the number average molecular weight of the polymer was low (<1000) and that the aziridine group content corresponded to one aziridine group per polymer chain. However, removal of solvent without neutralization of the acid (latter stage polymerization of pure ethylenimine) and allowing the polymerization to continue, gave polymers which contained less than one aziridine ring per polymer chain and ultimately a polymer of maximum molecular weight of about 3500. This change in aziridine groups per polymer chain with increasing polymerization is shown in Figure 3 and illustrates a chain-terminating process which destroys the aziridine ring end group.

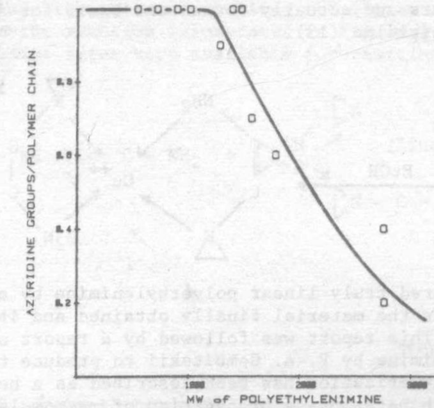


Fig. 3. Dependence of aziridine group content on molecular weight of polymer (polymerization of pure ethylenimine).

In one sense, this latter data (Figure 3) may be viewed as a rate curve for the destruction of terminal aziridine group by a natural chain-termination process relative to rate of propagation in the polymerization ($\sqrt{p}/\sqrt{t}$) and the ultimate molecular weight achieved is proportional to this ratio. This same natural chain-termination reaction was also manifested in experiments wherein "chain-stoppers" were added to ethylenimine to control the molecular weight of the polymer formed (17,18). Amines of comparable reactivity (e.g. ethylene diamine or diethylene triamine) to the amino groups propagating the polymerization were employed. The results, shown in Figure 4, also illustrate the natural chain-termination process.

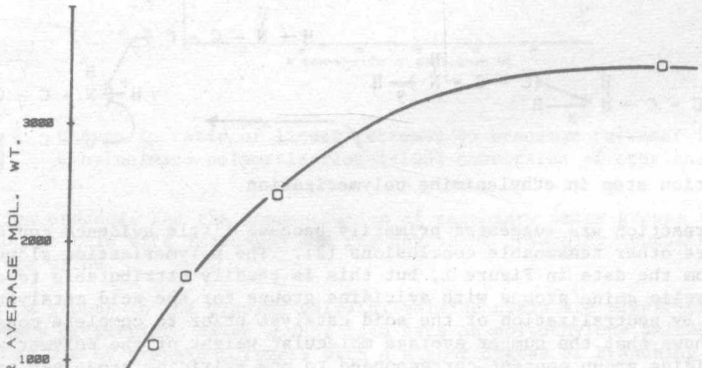


Fig. 4. Effect of amine concentration on molecular weight in polymerization of ethylenimine-amine mixtures.

The suggestion that the natural chain-termination reaction in the polymerization of ethylenimine is an intramolecular cyclization reaction is supported by experiments with 1-substituted basic aziridines wherein polymers might have been expected but high yields of cyclic polyamines were formed instead.

It is noteworthy, however, that the cyclic polyamine end-group must be of larger ring size than six members since such piperazine ring could not be detected in polymers of about 3500-4000 number average molecular weight. For polymers of such low molecular weight, the weight percent of piperazine-ring end-group, if present, would be greater than ten times the detectable limit by infrared spectral analysis (Figure 5).

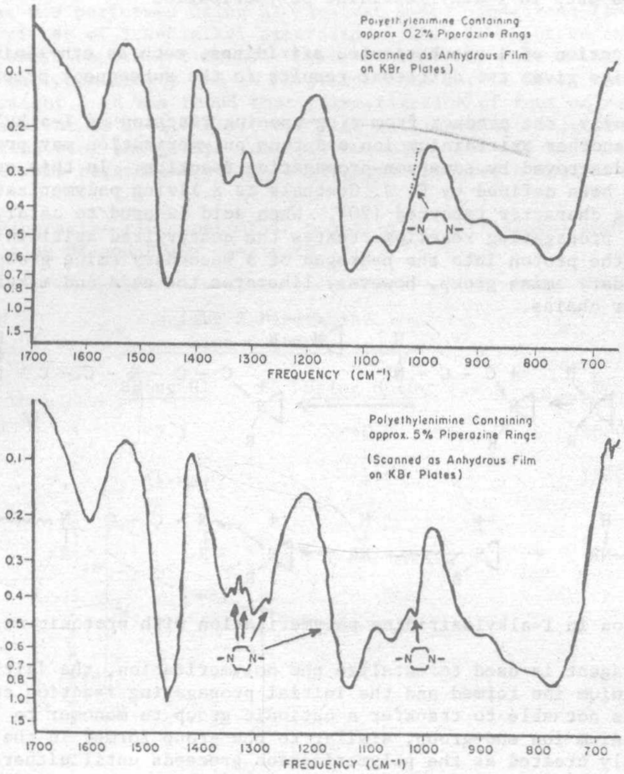
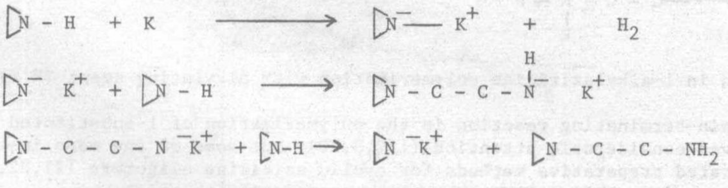


Fig. 5. Infrared spectra of polyethylenimine containing 0.2 wt. % (top) and 5 wt. % (bottom) piperazine ring ($C_4H_8N_2$).

No mention has been made concerning the anionic polymerization of basic aziridines and indeed no such polymerization to high molecular weight polymer has been observed. The first step in such polymerization has been achieved, however (19), and represents a method for the preparation of 1-(2-aminoethyl)aziridine from ethylenimine.



1-SUBSTITUTED BASIC AZIRIDINES

The initiating specie for the polymerization of this group of aziridines is the alkylating agent derived from addition of an acid or a different alkylating agent to the 1-substituted basic aziridine.