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Characterization of Polyethylenimine

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SUMMARY

Polymerization of anhydrous ethylenimine proceeds to completion with destruction of the terminal 1-aziridinyl group at relatively low molecular weight. In the absence of evidence for end groups, it is suggested that the chain terminating process is the formation of large rings composed of repeating C_2H_5N units.

Information is given on the various intermediates present in the early stages of polymerization of ethylenimine and on analytical techniques for determining the degree of branching in polyethylenimine.

INTRODUCTION

The mechanism for polymerization of ethylenimine has been fairly well established as far as the initiation and propagation reactions are concerned [1, 2]. These steps may be treated as a special case of a ring-opening reaction of ethylenimine by an amine (Fig. 1).

The protons are, of course, rapidly equilibrated with various amine bases in the system; thus the rate of polymerization slows markedly with increasing conversion or as a greater concentration of the more basic acyclic amine group is produced [3]. The polymerization does proceed to completion [3]. There is little information, however, on the chain termination step for polymerization.

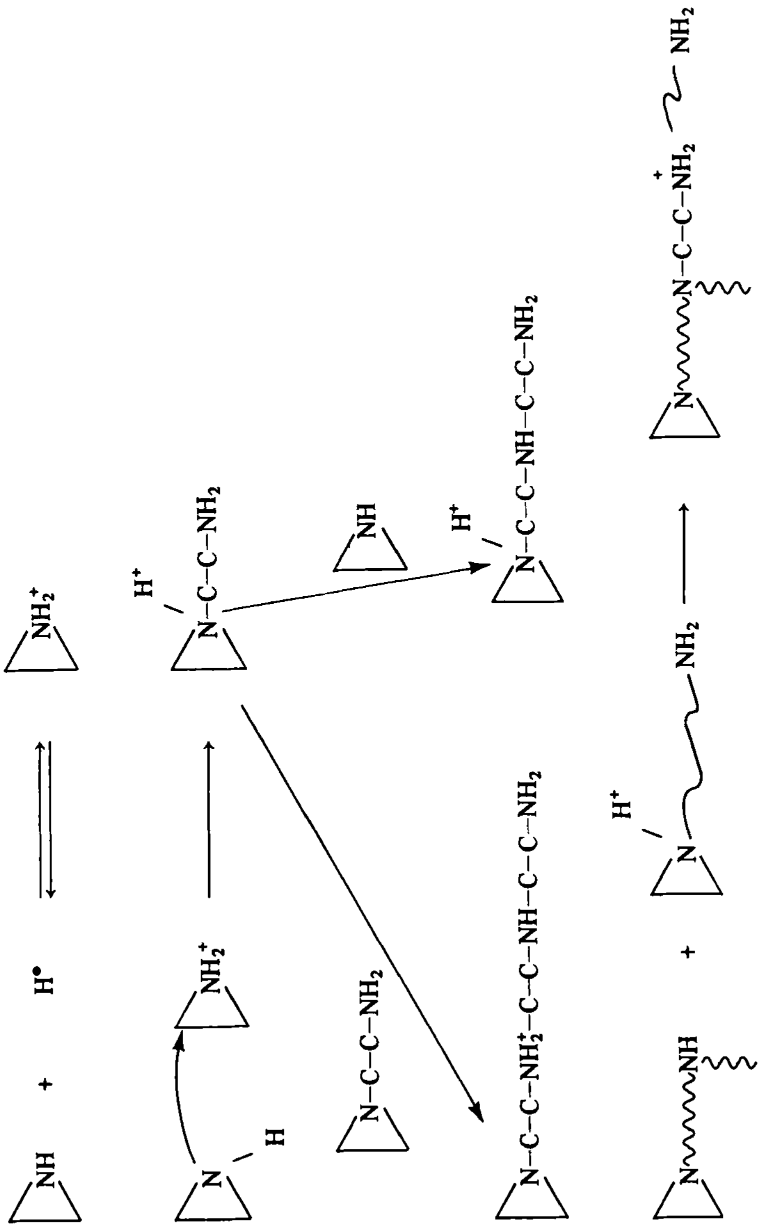

Fig. 1. Initiation and propagation steps in ethylenimine polymerization.

It was recognized early that polyethylenimine was highly branched; considerable work has been directed to this point [1-6]. The work reported in this paper is presented for the purpose of providing more information concerning the end groups and the degree of branching in polyethylenimine.

RESULTS AND DISCUSSION

The acid catalyzed polymerization of aqueous ethylenimine is often very rapid and exothermic in the early stages. For that reason, the polymerization was studied in methanol as a solvent in order to follow the appearance and disappearance of the various intermediates initially formed in the reaction. These results are shown in Fig. 2.

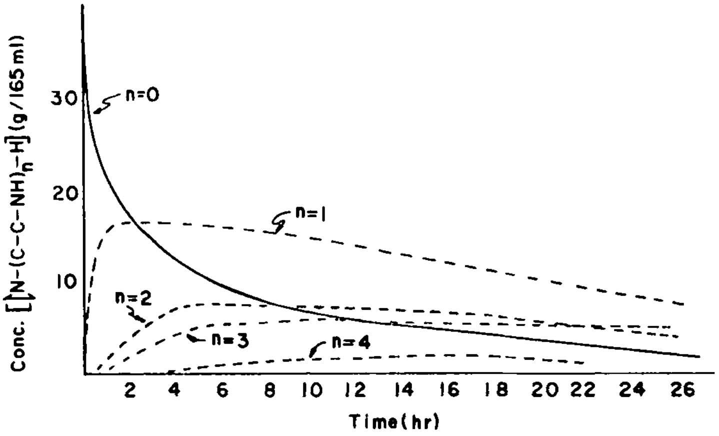

Fig. 2. Intermediates in the early stages of ethylenimine polymerization.

Several interesting observations were made from these data. The tetramer which formed consisted of both linear (I) and branched (II) isomer; thus the reaction of amine with aziridinium ion leading to branching in polyethylenimine occurred at the earliest opportunity (Fig. 3).

The ratio of I:II existing throughout the early stages of polymerization is shown in Fig. 4.

It is not surprising that the linear isomer predominates since there are three reactions which can lead to I versus only one which can lead to II, and the rates for all these reactions would be expected to be similar (Fig. 5).

It is noteworthy that up to about 50% conversion of ethylenimine, the

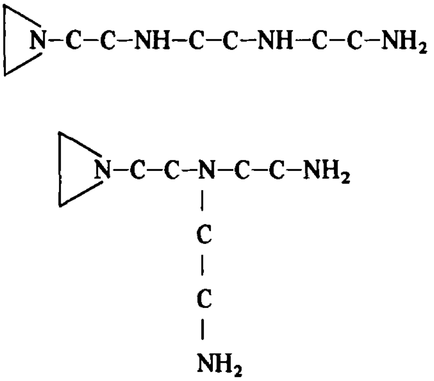

Fig. 3. Isomeric tetramers in ethylenimine polymerization.

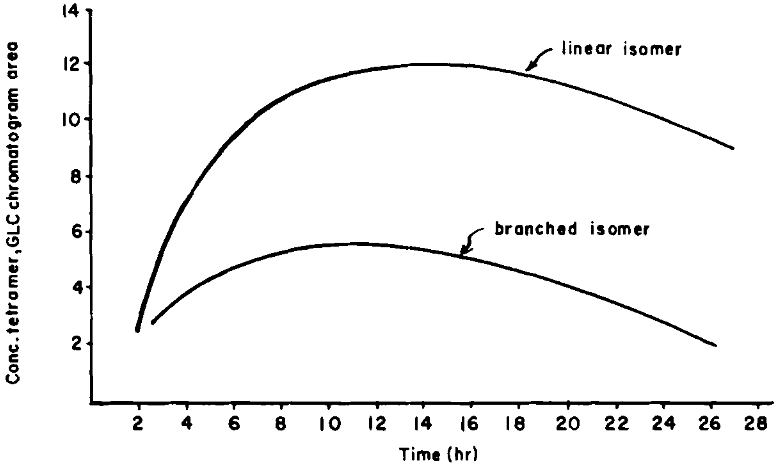

Fig. 4. Linear to branched tetramer ratio existing in early stages of ethylenimine polymerization.

only products formed are dimer, trimer, and tetramer. It is only past 50% conversion of ethylenimine that higher molecular weight products begin to form. This is illustrated in Fig. 6.

At about 96% conversion of ethylenimine the solvent and residual ethylenimine was removed and the molecular weight determined. The value obtained (MW_n) was 720. After standing for 1 month at room temperature,

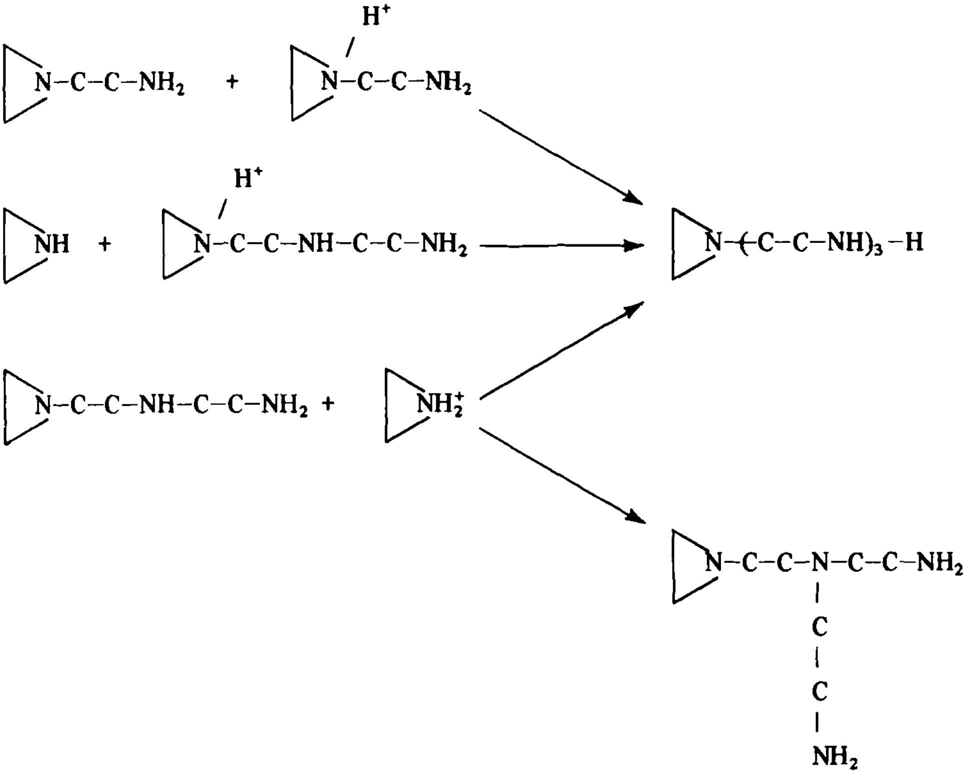

Fig. 5. Reactions leading to branched and linear tetramer.

a condition representing the acid-catalyzed polymerization of pure ethylenimine in the latter stages, the molecular weight was found to be 2700. Continued standing would produce a polymer of a maximum molecular weight around 3000 to about 3500.

Although the polymerization slows to a very, very low rate, this is because the acid catalyst is primarily associated with the more basic acyclic amino groups and not because of a chain terminating reaction. The molecular weight does approach a limiting value, however, and this must be due to some chain terminating reaction. With very low molecular weight polymers of ethylenimine (< 1000 MW_n) the end groups are a 1-aziridinyl group and a primary amino group, as shown in Table 1.

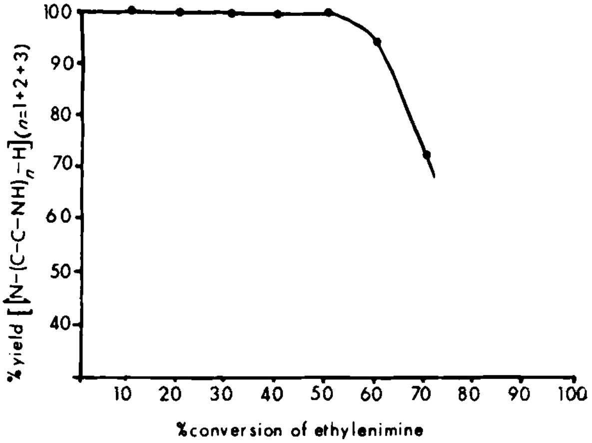

Fig. 6. Composite yield of dimer, trimer, and tetramer vs ethylenimine conversion.

Table 1. Aziridine Group Analysis in Low Molecular Weight Polyethylenimines[a]

	Wt% C_2H_4N	
MW$_n$	Found	Calc
540	7.8	7.4
720	5.7	5.8
900	4.9	4.7

[a] Determination by IR spectral analysis [7].

As the molecular weight increases to higher and higher values, however, the aziridine group content decreases below that corresponding to one aziridine group per polymer chain. This is illustrated in Fig. 7.

With polymers of molecular weight of only about 3000, certain probable end-groups would be readily visible in the IR spectra. However, the spectra indicated practically no hydroxyl group (from polymers made in water as solvent) and very, very low content of piperazine group (detectable to a lower limit of 0.2 wt% as $C_4H_8N_2$ [8].

Polymers of 1-alkyl aziridines prepared in water, although occurring by a reaction which has different kinetic features, also show the absence of

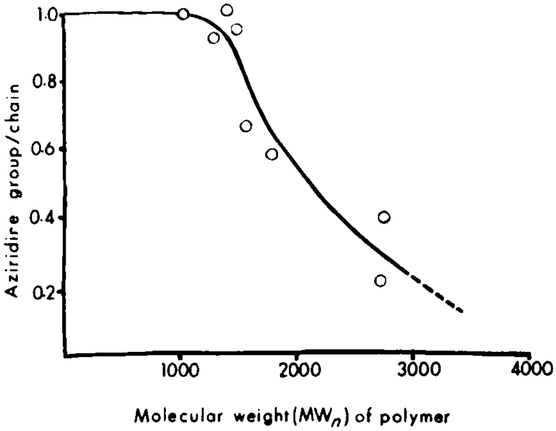

Fig. 7. Ratio of 1-aziridinyl group to polymer chain vs molecular weight of polyethylenimine (anhydrous polymerization).

these groups as well as the low ultimate molecular weights ($MW_n \sim 2000$). It was further shown for these polymerizations that the rate was essentially the same regardless of the choice of $HClO_4$ or HI as catalyst.

It was reasoned that some reaction, although not detectable, was occurring which destroyed the aziridine ring end group at relatively low molecular weights. If some nonpropagating reagent which would react with the aziridine ring could be added to ethylenimine at a rate comparable to the propagation reaction, then it should be possible to prepare polymers of predetermined molecular weights based on the mole ratio of ethylenimine to the added reagent providing the predetermined molecular weight would not be greater than that possible without added reagent. A logical choice for this reagent would be amines of equal or greater reactivity to those existing in the propagation reaction (e.g., vic-diamines). These assumptions were found to be valid, as shown by the results given in Table 2.

Such reaction may be treated either as addition of ethylenimine to the amine or as addition of a "chain-stopper" to the polymerization mixture. Polymers formed from ethylenediamine are then known to have primary amine groups as end groups.

It is of interest that the HCl-catalyzed polymerization of ethylenimine in aqueous solution can produce polymers of considerably higher molecular weights than those produced by polymerization of pure anhydrous ethylenimine. The highest values of MW_n so obtained were about 20,000.

The difficulty in detection of end groups in anhydrous polyethylenimine

Table 2. Polymerization of Ethylenimine in the Presence of an Amine

Amine (wt%)		Polymer MW_n Found	Calc
Ethylenediamine	(20.1)	275	295
Ethylenediamine	(10.1)	620	600
Ethylenediamine	(5.24)	1130	1140
Ethylenediamine	(3.8)	1705	1540
Polyethylenimine[a]	(46.7)	1450	1320
Polyethylenimine[a]	(34.0)	1930	1830
Ethanolamine	(6.1)	914	1015
Diethanolamine	(10.6)	910	980
Benzylamine	(10.7)	1150	1000
Allylamine	(5.7)	1170	1010
n-Butylamine	(7.25)	925	1014
Cyclohexylamine	(9.9)	1050	1008

[a] $MW_n = 617$.

(or poly 1-alkylaziridines) and yet the low ultimate molecular weights obtained has led to the speculation that the major chain-terminating process is the formation of a large cyclic ring. To be consistent with other ring-opening reactions of ethylenimine as well as the propagating reaction for polymerization, this ring formation should occur via an S_N2 reaction requiring the backside approach of a chain amino group to the aziridinium carbon atom. Thus formation of piperazine rings should be precluded (Fig. 8).

As mentioned earlier, branched isomers are formed at the earliest opportunity in the polymerization (i.e., formation of tetramer). It is of interest to note that most of the branching must occur in the early stages of polymerization since in the latter stages the combination of higher oligomers produces the higher molecular weight products and such combination represents fewer reactions which could lead to branching than in the early stages where monomeric ethylenimine is present.

Problems have existed, to some extent, in the determination of the degree of branching in polyethylenimine. From the polymerization mechanism it may be deduced that the final polymer should contain one primary amino group for every tertiary amino group excepting end groups. Thus the problem is simply one of determination of the various amino nitrogen types. Determination of the total nitrogen content by the Dumas method was found to be accurate. Determination of either the primary amino nitrogen

Table 3. Nonaqueous Titration of Polyaziridines

Polymer	% Total Nitrogen by Dumas	% Nitrogen by titration	% Nitrogen neutralized
Polyethylenimine	31.57	25.6	81.0
Poly-1-(2-hydroxyethyl)aziridine	15.89	14.4	90.7
Poly-1-(2-acetoxyethyl)aziridine	10.36	5.64	54.4
Poly-1-allyl aziridine	16.05	13.8	86.0

Table 4. Comparison of Analytical Methods for Amino Groups in Polyethylenimine

Method	% Total nitrogen by Dumas	% Tertiary amino nitrogen	% Primary + secondary amino nitrogen
Acetylation in acetic acid (acid titration of amine)	31.16	7.94	23.22[a]
Acetylation in pyridine (base titration of acetic acid)	31.16	8.12[a]	23.04

[a] Difference between % total N and determined amino nitrogen.

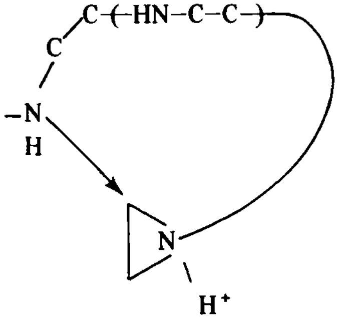

Fig. 8. Proposed chain termination reaction in ethylenimine polymerization.

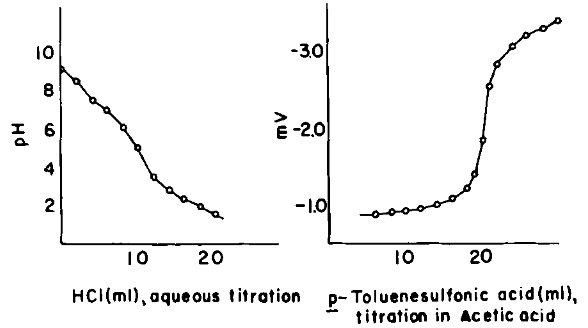

Fig. 9. Comparison of titration curve for polyethylenimine in water with that in acetic acid.

or tertiary amino nitrogen would establish the degree of branching. Early work utilized the Van Slyke analysis for primary amino group [1, 5] and preparation of the benzoylated derivative for comparison of the elemental analysis [4]. The benzoylation was reinvestigated in later work [3] wherein quantitative IR analysis of secondary and tertiary amide content of the derivative was also conducted. The initially formed benzoylated polyethylenimine had to be refluxed with aqueous sodium carbonate solution to remove residual benzoic acid.

Although the benzoylation procedure gave values for the degree of branching [3] which are quite close to the values to be reported here, the procedure appears to be somewhat lengthy. A more direct method was sought.

Table 5. Comparison of Tertiary and Primary Amino Group Analysis in Polyethylenimine

Determination	Result	
	Found	Calc
% Total nitrogen (Dumas method)	33.18	33.10[a]
Molecular weight (ebullioscopic)	1200	1141[a]
% Primary amino nitrogen as end groups		2.3[b]
% Tertiary amino nitrogen	8.00	7.9[c]
% Primary amino nitrogen	10.2	10.3[c]

[a] Calculated from mole ratio of ethylenediamine to ethylenimine used in the polymer preparation.

[b] Assumed primary amino end groups for polymer of MW_n 1200.

[c] Assumed primary and tertiary amino nitrogen values must be equal excepting end groups.

The Van Slyke method for primary amino group determination was shown to be inaccurate when applied to vic-ethylenediamines, giving high results [1]. This was confirmed; for example, purified diethylenetriamine gave values 15.5% too high (% N as $-NH_2$: calc 27.1; found 31.3).

Also, the Van Slyke method always gave values for polyethylenimine which were much higher than the tertiary amino nitrogen content as determined by acetylation and titration in acetic acid by p-toluenesulfonic acid. However, at the time this discrepancy was found, it was not known whether or not the acetylation-titration method was accurate.

It is well known that the titration of aqueous polyethylenimine with an aqueous acid solution, such as hydrochloric acid, gives titration curves with no break suitable for determination of the end point. It was found that titration of polyethylenimine in acetic acid solvent with p-toluenesulfonic acid (or perchloric acid) in acetic acid did give such an inflection. A comparison of these curves is shown in Fig. 9.

It was of particular interest that the end point obtained for polyethylenimine, when titrated in acetic acid, corresponded to only 81% of the nitrogen content of the polymer. Similar titration of several poly(1-alkyl)aziridines showed the same type of fractional neutralization, as shown in Table 3.

Failure to neutralize all of the amino groups was apparently due to reduced basicity of specific amino groups as adjacent amino groups became neutralized.

Polyethylenimine could be acetylated in acetic acid by heating with acetic anhydride (to render the primary and secondary amino groups nonbasic) and the resulting solution titrated with p-toluenesulfonic acid in acetic acid; such would represent a simple direct method for determination of the degree of branching. However, it was uncertain if the results would be accurate because of the above findings.

The polymer could be dissolved in pyridine, acetylated with excess acetic anhydride, the unreacted acetic anhydride hydrolyzed, and the acetic acid titrated with base. The primary + secondary amino nitrogen thus determined subtracted from the total nitrogen gave values for tertiary amino nitrogen content. The precision was poor, however, apparently due in part to magnified error resulting from taking the difference in two relatively large experimentally determined values. The average of tertiary amino nitrogen values for a number of such determiniations was quite close to values obtained by the direct acid titration previously described. Two particularly good sets of data are shown in Table 4. Such good agreement in the two methods should be possible only if it is possible to titrate (in acetic acid) all of the basic nitrogen existing in the completely acetylated polyethylenimine.

An attempt was then made to demonstrate that as the fraction of primary and/or secondary amino groups acetylated increased (by partially acetylating with deficient amounts of acetic anhydride) the fraction of remaining amino nitrogen which could be neutralized approached 100%. The results are shown in Fig. 10.

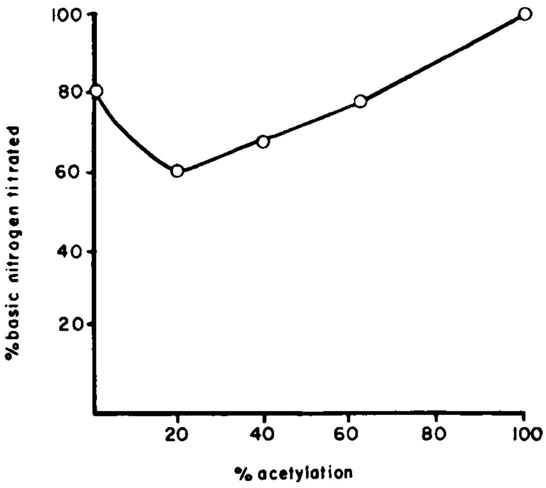

Fig. 10. Fractional neutralization of basic nitrogen in polyethylenimine vs fractional acetylation.

The initial decrease in the fraction of nitrogen which was titratable from 81% to about 58% at only about 15% acetylation was somewhat surprising. It may be due to the same factors that caused the decrease in titratable nitrogen when poly-1-(2-hydroxyethyl)aziridine was acetylated to poly-1-(2-acetoxyethyl)aziridine. Continued acetylation of polyethylenimine did cause an increase in the fraction of remaining nitrogen that could be titrated and appeared to approach 100%.

The above is only an indication that all of the basic nitrogen existing in completely acetylated polyethylenimine can be neutralized since the 100% value for tertiary amino group had to be assumed. Confirmation of this fact was possible after subsequent development of a reliable independent method [8] for primary amino group analysis (based on IR spectral analysis). For these experiments the polymers with known primary amino end groups were used. The results in Table 5 show a very good 1:1 correspondence in primary amino group to tertiary amino group.

The fact that essentially all of the tertiary amino groups in completely acetylated polyethylenimine can be titrated in acetic acid with p-toluenesulfonic acid whereas all such groups in poly-1-alkylaziridines cannot (poly-1-alkylaziridines contain all vic-ethylene tertiary amino groups) strongly suggests that the tertiary amino groups in polyethylenimine (branching sites) largely contain as nearest amino neighbors only secondary amino groups.

For many preparations of polyethylenimine under varying conditions and of different molecular weights, the degree of branching has been found to be about the same. This value is about one branch for every 3 to 3.5 nitrogen atoms existing in a linear unit. This value is in good agreement with that obtained from the benzoylation method previously mentioned [3]. The method is much simpler, however, and more direct.

REFERENCES

[1] G. D. Jones, A. N. Langsjoen, M. M. C. Neuman, and J. L. Zomlefer, *J. Org. Chem.*, **9**, 125 (1944).
[2] W. G. Barb, *J. Chem. Soc.*, **1955**, 2564, 2577.
[3] G. D. Jones, D. C. MacWilliams, and N. A. Braxtor, *J. Org. Chem.*, **30**, 1994 (1965).
[4] W. Kern and E. Brenneisen, *J. Prakt. Chem.*, **159**, 193 (1941).
[5] H. G. Konnecke and M. Heise, *J. Prakt. Chem.*, **9**, 232 (1959).
[6] E. Leibnitz, H. G. Konnecke, and G. Gawalek, *J. Prakt. Chem.*, **6**, 289 (1958).
[7] H. L. Spell, *Anal. Chem.*, **39**, 185 (1967).
[8] H. L. Spell, *Anal. Chem.*, In press.

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