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POLYETHYLENIMINES: THEIR STRUCTURE, BASICITY, AND BIFUNCTIONAL CATALYTIC ACTIVITY IN \( \alpha \)-HYDROGEN EXCHANGE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Robert Louis Flachskam, Jr., B.A.

The Ohio State University

1973

Approved by

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INTRODUCTION

Enzymes and Bifunctional Catalysis

An enzyme increases the rate of a reaction by forming a complex with the substrate(s), transforming the substrate(s) into products(s), and then dissociating from the product(s).

\[ E + S \rightleftharpoons E--S \rightleftharpoons E--P \rightleftharpoons E + P \]

The complex between enzyme and substrate must be strong enough to hold the substrate in the proper orientation for reaction, but, on the other hand, must allow the product to dissociate once the reaction has occurred. This may be accomplished through covalent, hydrogen, hydrophobic, or electrostatic bonding.

Enzymes may be considered as polyfunctional catalysts since several functional groups in the enzyme are ordinarily involved in binding with the substrate and bringing about the transformation of substrate into product. The simplest form of polyfunctional catalysis is bifunctional catalysis, in which two functional groups in the catalyst act on a substrate: Hence the study of bifunctional catalysis is the logical starting point in the understanding of more complex systems.

One of the earliest examples of bifunctional catalysis
is the mutarotation of $2,3,4,6$-tetramethyl-$D$-glucose in the presence of 2-hydroxypyridine.\(^1\) After a hydrogen-

\[
\begin{align*}
\text{CH}_3O & \quad \text{CH}_2O\text{CH}_3 \\
\text{CH}_3O & \quad \text{O} \quad \text{H} \quad \text{O} \quad \text{N} \\
\text{OCH}_3 & \quad \text{CH}_3O
\end{align*}
\]

bonded complex is formed between the substrate and catalyst, two groups in the catalyst act simultaneously in the transfer of the two protons.

Recently there was reported an example of internal bifunctional catalysis.\(^2\) The hydrolysis of hexachlorophene monosuccinate proceeds via the anion 1 and is catalyzed by

\[
\begin{align*}
\text{O} & \quad \text{CH}_2\text{CH}_2 \\
\text{O} & \quad \text{G} \quad \text{O} \\
\text{Cl} & \quad \text{Cl} \quad \text{CH}_2 \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\end{align*}
\]


simultaneous formation of an intramolecular hydrogen bond by the phenolic hydrogen and nucleophilic attack by the succinate carboxylate group. Hence this is an example of combined nucleophilic and general acid catalysis. However in this case the two functional groups are present in the starting molecule. Therefore this example gives no information on the formation of the initial complex in enzyme catalysis.

Hine and coworkers\textsuperscript{5-15} have studied the $\alpha$-deuterium exchange of carbonyl compounds \textit{via} imine formation. Bifunctional catalysts of the type B-R-NH$_2$ have been studied.\textsuperscript{11,18-20} The amino group transforms the carbonyl group into an imine, which is in equilibrium with the corresponding iminium ion (2), and the basic group B then removes the deuterium internally \textit{via} transition state 3.\textsuperscript{3}

\[
\begin{align*}
\text{C} & \equiv \text{NH} \\
\text{C} & \equiv \text{NH} \\
\text{D} & \text{B} \\
\text{C} & \equiv \text{NH} \\
\text{C} & \equiv \text{NH} \\
\text{D} & \text{B}
\end{align*}
\]

Reprotonation of the enamine (4) and eventual regeneration of the carbonyl compound have the net result of exchanging the $\alpha$-deuterium for an $\alpha$-hydrogen. This is quite similar to the operation of enzymes because the imine formation is analogous to the formation of the substrate-enzyme complex, the deuterium exchange is analogous to the transformation
of the complexed substrate into complexed product, and the regeneration of carbonyl compound is analogous to the separation of the product from the enzyme.

Several classes of enzymes, such as decarboxylases, transaminases, and transhydroxymethylases have been shown to use imine intermediates either in the formation of substrate-enzyme complexes or in the transformation of substrate into product. For example, acetoacetate decarboxylase (AAD) catalyzes the decarboxylation of acetoacetic acid by way of a Schiff base (imine) formed from the active $\epsilon$-amine group of a particular lysine residue and the carbonyl group.$^3$

\[
\text{CH}_3\text{C}-\text{CH}_2\text{CO}_2\text{H} + \text{H}_2\text{N}--\text{AAD} \rightarrow \text{CH}_3\text{C}-\text{CH}_2\text{C}=\text{O}
\]

**Bifunctional Catalysis of $\alpha$-Hydrogen Exchange**

A considerable amount of work has been done on the dedeuteration of isobutyraldehyde-2-d. This compound has several advantages as a model for $\alpha$-hydrogen exchange. The aldehyde is soluble enough in water to allow direct nmr analysis of the reaction solution, and the nmr spectrum is easy to interpret since there is only one $\alpha$-deuterium. At

---

35° 69.4% of the aldehyde remains in the unhydrated form.\(^4\) The equilibrium between free and hydrated aldehyde is established prior to deuterium exchange.\(^5\) Assuming that

\[
\text{Me}_2\text{CDCHO} + \text{H}_2\text{O} \rightleftharpoons \text{Me}_2\text{CDCH(OH)}_2
\]

isotope effects are negligible, this means that the deuterium content of both species is the same throughout the reaction.

With moderate concentrations of a primary amine salt and a buffer, it has been shown that the dedeuteration of isobutyraldehyde-2-d is largely a third order reaction, first order in aldehyde, first order in buffer base, and first order in amine salt.\(^6-9\) Evidence was described which showed that the reversible transformation of deuterio-aldehyde into the corresponding N-alkyliminium ion was followed by removal of deuterium by the buffer base (B) to

---

4. L. R. Green, unpublished observation, The Ohio State University.


give an enamine. To learn whether bifunctional catalysis

\[
\text{Me}_2\text{CDCHO} + \text{RNH}^+ \rightleftharpoons \text{Me}_2\text{CDCH=NHR}^+ + \text{H}_2\text{O}
\]

\[
\text{Me}_2\text{CDCH=NHR}^+ + \text{B} \rightleftharpoons \text{Me}_2\text{C=CHNHR} + \text{BD}^+
\]

would occur, the dedeuteration was carried out in the presence of several compounds of the type \(\text{B-R-NH}_2\), which contain both a primary amine salt and a basic group.

\[
\begin{align*}
\text{Me}_2\text{CCH=NHR}^+ & \rightleftharpoons \text{Me}_2\text{C=CHNHR} + \text{BD}^+
\end{align*}
\]

Amino acids of the type \(\text{H}_2\text{N(CH}_2\text{)}_n\text{CO}_2\text{H} (n = 1 \text{ to } 5)\) were used. The reaction conditions were such that the amino acids existed largely in the zwitterionic form \(\text{H}_2\text{N(CH}_2\text{)}_n\text{CO}_2^-\). Catalysis did proceed via formation of iminium ions but there was no evidence found for the internal attack of the carboxylate anions.

The reaction was also carried out in the presence of diamines of the type \(\text{Me}_2\text{N(CH}_2\text{)}_n\text{NH}_2 (n = 2 \text{ to } 5)\).\(^\text{11}\) These diamines have an advantage over the amino acids since they contain a more basic dimethylamino group rather than a weakly basic carboxylate anion; in addition, the tertiary dimethylamino group seemed attractive since unhindered

---


tertiary amines were found to be the most reactive for their basicity, toward isobutyraldehyde-2-d\(^{12,13}\) and its iminium ion formed from methyl amine.\(^9\) The pH of the reaction solutions was kept at a value where the diamines were largely monoprotonated in order that the concentration of ammonium ion be the highest and yet have the tertiary amino group largely unprotonated. The Bronsted plot of the logarithms of the second-order rate constants versus the logarithms of the acidity constants of the diprotonated amines gave a straight line. If bifunctional catalysis had occurred the value of the logarithm of the rate constant for the compound with the optimum distance between the two amino groups would have fallen above the Bronsted line.

The failure of the amino acids and the diamines to act as bifunctional catalysts probably lies in the fact that the iminium ion exists in the trans form. Imines derived from isobutyraldehyde and certain primary alkyl amines have been shown by nmr studies to be trans with no detectable amount of cis isomer present.\(^{14,15}\) It is quite unlikely that

---

the imines formed from isobutyraldehyde and the amino acids and diamines exist in the cis form to any appreciable extent. The stereoelectronic requirements for dedeuteration via the trans iminium ion are illustrated in the Newman projection (5). The carbon-nitrogen double bond and its

\[ \text{Me} \quad \text{Me} \]

four substituents all lie in the same plane. The carbon-deuterium bond is eclipsed by the p orbital of the iminium carbon atom so that the p orbital being formed by the removal of the deuterium can effectively overlap the p orbitals of the carbon-nitrogen double bond. In order that the base can most effectively remove the deuterium, the C-D-B bond angle is drawn as 180°. Molecular models show that the R group in 5 (the number of atoms between the iminium nitrogen and the base) would have to contain at

least seven or eight atoms if the C-D-B bond angle were close to 180° and if there were no extensive eclipsing or unfavorable van der Waals interactions. If the iminium ion were in the cis form only four atoms would be needed. Thus the amino acids and diamines (which have two to six and two to five atoms in the R group, respectively) could have been large enough to catalyze the reaction internally through the cis form but not through the trans form.

There is also evidence against catalysis through the cis form itself. Studies on catalysis of the dedeuteration of isobutyraldehyde-2-d by various secondary amines have shown no catalysis via intermediate iminium ion (6) formation presumably because one of the alkyl groups bonded to the iminium nitrogen is cis to the isopropyl group.13 This steric problem in the aldehyde could be solved by using less bulky aldehydes, such as acetaldehyde or n-butyraldehyde; but additional problems, such as the formation of aldols or α,β-unsaturated aldehydes, would complicate the reaction.

The problem of the iminium ion being in the trans form was eliminated by using acetone-d₆ as the carbonyl com-
pound. Internal catalysis can occur from either side of the iminium ion. Since the nmr technique would be too complicated owing to partially deuterated species, a mass spectral technique was developed to follow the reaction.\(^\text{17}\) The dedeuteration of acetone-\(\text{d}_6\) in the presence of diamines of the type \(\text{Me}_2\text{N(CH}_2\text{)}_n\text{NH}_2\) (\(n = 2\) to 5) was carried out at pH values where the diamines were monoprotonated.\(^\text{11}\) The logarithms of the second-order rate constants plotted versus the logarithms of the acidity constants of the diprotonated amine (Brønsted plot) gave a fairly straight line for \(n = 2\), 4, and 5; however the point for \(n = 3\), i.e., 3-dimethylaminopropylamine, fell above the line. The amount that it fell above the line corresponded to it being about seven times as good a catalyst as if it were acting monofunctionally. The transition state for the bifunctional catalysis is shown in the Newman projection (7). There are only three atoms between the imine nitrogen and the nitrogen that removes the deuterium, giving an eight-membered ring for the transition state. The C-D-N bond angle is probably distorted from 180° to about 150° and carbon atoms 1 and 2 of the diamine are eclipsed. Cis- and trans-2-(dimethylaminoethyl)cyclopentylamine (8) were found to be more effective catalysts.\(^\text{11}\) The cis isomer was found to be

about 100 times as effective a catalyst as expected if it were acting as a monofunctional base; the trans isomer was found to be almost as effective a catalyst as the cis isomer. In these two compounds the two carbon atoms that are eclipsed in \( \text{Me}_2(\text{CH}_2)_3\text{NH}_2 \) are held rigid since they are part of the five-membered ring. Thus in energy is not needed to achieve this eclipsing and there is less flexibility between the nitrogens; these two factors probably account for such effective catalysis.

Additional work has been done on trying to find a catalyst that could act bifunctionally even through the trans iminium ion formed from isobutyraldehyde. Diamines with long carbon chains between the nitrogens were investigated. Three diamines of the type \( \text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2 \) (\( n = 6, 11, 12 \)) all had about the same catalytic activity.\(^{18}\)

Although the diamines with n = 11 and 12 could reach the deuterium atom from the trans iminium ion, the number of unreactive conformations must have been too great because of the long saturated carbon chain.

Another diamine, 1-dimethylamino-8-amino-2-octyne \( [H_2N(CH_2)_5C=CCH_2\text{Me}_2] \), was used in the dedeuteration of isobutyraldehyde-2-d.\(^{18}\) This amine has an advantage over the saturated diamines since four of the carbons are rigidly held in a linear configuration by the triple bond. Molecular models show that there should not be any great amount of eclipsing of carbon-hydrogen bonds, bond stretching, or unfavorable van der Waals interactions. Bifunctional catalysis was indeed found; the term in the kinetic equation that was first order in monoprotonated diamine and first order in aldehyde was about 7.7 times as large as would be expected in the absence of bifunctional catalysis (from comparisons with the activities of the monofunctional catalysts, HC=CCH_2\text{Me}_2 and MeC=CCH_2\text{Me}_2). This diamine has eight atoms separating the two nitrogens and thus would have a thirteen-membered ring in the transition state for bifunctional catalysis.

Perhaps other compounds with more of the intermediate atoms held rigidly in place by unsaturation or rings could be found to give even greater bifunctional catalysis. However there is another approach to the problem. A cata-
lyst could be used that contained several basic groups at various distances away from the primary amino group. The compounds used in this "shotgun" approach were polymers of ethylenimine commercially available from the Dow Chemical Company. These polyethylenimines (PEI's) contain alternating amino and \(-\text{CH}_2\text{CH}_2-\) groups with branching at the amino groups so that about 25% of the amino groups are primary, 50% are secondary, and 25% are tertiary. The PEI's are of molecular weights 600, 1200, and 1800 and are designated by PEI-X where X is the molecular weight.

These polymers could act as bifunctional catalysts by forming an imine with isobutyraldehyde-2-d and one of the primary amino groups, and since the imine would be in equilibrium with the corresponding iminium ion, an amino group in the surroundings could remove the deuterium atom.
Evidence was found that the PEI's did act as bifunctional catalysts in the dedeuteration of isobutyraldehyde-2-d. The first-order rate constant for the dedeuteration of 0.053 M aldehyde by PEI-1800 at pH 8.35 and 35° was found to increase with increasing PEI concentration and then to level off at a value of about $15 \times 10^{-5}$ sec\(^{-1}\) at 0.4 N. This suggested that the exchange was taking place through a complex formed from aldehyde and polymer. The reaction rate increased initially due to more and more aldehyde being complexed; when all the aldehyde was tied up, any further increase in PEI concentration had no effect on the rate. This was supported by absorbance measurements of the aldehyde maximum (285 nm). The absorbance of the aldehyde decreased with increasing concentration of PEI-1800 up to a value of about 0.4 N, the same concentration of polymer at which the rate leveled off. This interpretation was also supported by the behavior of N,N-dimethyl-ethylenediamine, a diamine that can only act as a monofunctional catalyst. The first-order rate constant did not level off but increased almost linearly to a value of $30 \times 10^{-5}$ sec\(^{-1}\) at an amine concentration of 1.4 N; however,


the aldehyde was almost completely complexed at an amine concentration of 0.7 N, as shown from absorbance measurements. Thus in contrast to PEI-1800, in which further addition of polymer has no effect on the rate once all the aldehyde is complexed, further addition of Me₂NCH₂CH₂NH₂ continues to increase the rate even after all the aldehyde is complexed. In the diamine case, one molecule transforms the aldehyde into imine (and thus iminium ion) while another molecule removes the deuterium; further increase in the concentration of diamine continues to increase the rate. On the other hand, in the PEI case, one primary amino group in the polymer transforms the aldehyde into imine while a second amino group in the same molecule removes the deuterium; therefore further increase in PEI concentration has no effect on the exchange rate.¹⁹

The pH-rate plot of the exchange of 0.053 M isobutyraldehyde-2-d by 0.97 N PEI-1800 at 35° shows a maximum of \[15 \times 10^{-5} \text{ sec}^{-1} (k_p)\] at a pH between 8.0 and 8.5. This is consistent with the reaction mechanism. At high pH values not enough of the imines are protonated to give iminium ions; at low pH values too many of the amino groups are protonated and those that remain unprotonated are too weakly basic to provide effective catalysis.¹⁹

Additional evidence that PEI's act as bifunctional
catalysts comes from comparison with other compounds that can act only as monofunctional catalysts. In the dedeuteration of 0.053 M isobutyraldehyde-2-d at 35 ° and pH 8.5 the three PEI's (0.1 N) all had about the same rate constant (7.5 x 10^{-5} sec^{-1}). Ethylenediamine and its N-ethylated derivatives, which can be considered as sections of the polymers, had rate constants of 0.2 x 10^{-5} sec^{-1} to 0.55 x 10^{-5} sec^{-1} at 0.1 N. Thus the PEI's are 12 - 36 times as effective as catalysts as they would be if they were acting monofunctionally. 20

The stoichiometry of complex formation between isobutyraldehyde and PEI was investigated by measuring the absorbance of solutions 0.200 N in PEI-1800 with increasing concentrations of aldehyde. From comparisons of the absorbance of aldehyde in the absence of PEI it was estimated that at 35 ° and pH 8.5 about 0.30 mole of aldehyde was complexed per equivalent of amine in the presence of excess aldehyde. The complex formed between aldehyde and PEI is mainly in the form of imines and imidazolidines. Imidazolidines can be formed from any section of the polymer in which there are primary and secondary amino groups or two secondary amino groups adjacent. 20
Royer and Klotz\(^{21}\) have shown that lauroylation of PEI-600 increases its reactivity toward acid esters of \(p\)-nitrophenol, presumably through hydrophobic bonding.\(^{22}\) Hence PEI-1800 was lauroylated to increase the effectiveness of complexing the aldehyde. However it was found that lauroylation of the polymer decreased its activity slightly.\(^{20}\)

Another attempt to increase the rate of dedeuteration was made by the addition of disodium phosphate to the reaction solution. It was hoped that the doubly charged \(\text{HPO}_4^{2-}\) ion would be attracted to the multiply positively charged polymer and hence increase the rate. However no increase was observed. Another external base, 1,4-diazabicyclo[2.2.2]octane (Dabco), was found to increase the rate by attack on the complexed aldehyde.\(^{20}\)


The present study is concerned with determining the structure of polyethylenimines in order to obtain information on which amino groups are removing the deuterium atom and the number of atoms involved in the transition state.

Polymerization of Ethylenimine

The mechanism of the polymerization of ethylenimine (EI) has been reviewed by Hauser and Dermer and Ham. The polymerization was first described in 1888. It was not until 1941, however, that Kern and Brenneisen proposed three possible mechanisms for the polymerization. The catalysis of the reaction by acids suggested a polycondensation involving initial ring opening, as with hydrobromic acid, to give 2-bromoethylamine (9) and subsequent self-condensation of the bromoamine.

\[ \text{NH} + \text{HBr} \rightarrow \text{H}_2\text{NCH}_2\text{CH}_2\text{Br} \]


25. A. Ladenburg and J. Abel, Ber., 21, 758 (1888).

The second possibility was that the bromoamine initially formed might react with EI in a condensation process.

\[ \text{etc.} \]

The third mechanism involved a chain polymerization in which the catalyst promoted ring opening to produce an active intermediate diradical, which then reacted with EI.

\[ \text{etc.} \]

Observations on catalysis and inhibition in the polymerization reactions led the authors\(^\text{26}\) to conclude that the mechanism was a polycondensation or condensation process and not a chain polymerization. The polymerization exhibi-
ated acid catalysis which was common in condensations and not in chain or vinyl polymerizations. Catalysts that were effective in vinyl and chain polymerizations did not catalyze ethylenimine polymerization. The polymerization was also not catalyzed by vinyl initiators nor inhibited by vinyl inhibitors.

In 1944, after a thorough study of the kinetics and mechanism of ethylenimine polymerization, Jones proposed the following mechanism.\(^\text{27}\) The protons are, of course,

\[
\begin{align*}
\text{NH} + H^+ & \rightarrow \text{NH}_2^+ \\
\text{NH}_2^+ + \text{NH} & \rightarrow \text{NCH}_2\text{CH}_2\text{NH}_2^+ \\
\text{NH} & \rightarrow \text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2^+ \\
\text{NCH}_2\text{CH}_2\text{NH}_2 & \rightarrow \text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2^+ \\
\end{align*}
\]

distributed in a rapid equilibrium among the various nitrogens according to their respective base strengths.

The concentration of protonated aziridine species

\[\text{27. G. D. Jones, A. N. Langsjoen, M. M. C. Neuman, and J. L. Zomlefer, } \textit{J. Org. Chem.}, \text{ 9, 125 (1944).}\]
decreases as the polymerization proceeds to produce the more basic acyclic amino groups, and thus the rate decreases.\textsuperscript{27-29} In the early stages of the polymerization the concentration of monomeric aziridine is relatively high and the propagation reaction occurring is mainly eq 2. However, as the concentration of dimer increases the concentration of trimer and tetramer becomes important (eq 3). Subsequent reaction of these species yields polymer.\textsuperscript{27,28} This mechanism was originally deduced from kinetic measurements and the isolation or detection of low molecular weight oligomers, i.e., dimer, trimer, and tetramer. Recently more sophisticated gas-liquid chromatography techniques have been used to detect the oligomers.\textsuperscript{30,31} It was found that up to about 50\% conversion of E1 the only products formed are dimer, trimer, and tetramer; after this stage higher molecular weight products are formed.

Studies on the polymerization of optically active

\begin{itemize}
\end{itemize}
2-alkylaziridines into optically active polymers gave further evidence that the polymerization is a ring opening reaction; thus ring opening occurs without affecting the optically active center which is consistent with an $S_N^2$ mechanism.$^{32-34}$

Ring opening reactions subsequent to eq 3 provide a path for producing branching in the polymer (eq 4). As

\[
\begin{align*}
\text{PEI} &\quad \text{NH}_2 \\
\downarrow &\quad \downarrow \\
\text{PEI} \quad \text{PEI} &\quad \text{PEI} \\
\text{NH} &\quad \text{NH} \\
\text{PEI} &\quad \text{PEI}
\end{align*}
\]

secondary amino groups are produced, they compete with the primary amino groups in attacking aziridinium ions.


Even though secondary amino groups are less reactive than primary amino groups, a relatively large amount of reaction occurs with the secondary amino groups owing to their high concentration.

Branching may also result from ring opening of aziridinium ions by tertiary aziridine nitrogens (eq 5).

\[
\begin{align*}
\text{NCH}_2\text{CH}_2\text{NH}_2 + & \quad \text{N}^+\text{CH}_2\text{CH}_2\text{NH}_2 \\
\rightarrow & \quad \text{N}^+\text{CH}_2\text{CH}_2\text{NH}_2 \quad (\text{CH}_2\text{CH}_2\text{NH})_2\text{H}
\end{align*}
\]

Attack of an amino group on the resulting quaternary nitrogen would convert it into a tertiary nitrogen. However it is difficult to determine how important eq 5 is in the reaction mechanism. In a computer simulation of the polymerization of E1 it was suggested that this reaction was more important in the initial stages of the polymerization and reaction of secondary amino groups (eq 4b) was dominant in the later stages.²⁹

There has been disagreement over the degree of branching in PEI because of the difficulty in determining the number of primary, secondary, and tertiary nitrogens.²⁷,²⁸,³⁵ Van Slyke analysis for primary nitrogen

has been shown to be unsatisfactory for PEI.\textsuperscript{31} Several different preparations of PEI have been found to contain primary, secondary, and tertiary amino groups in a ratio of approximately 1:2:1.\textsuperscript{29,31} Consistent with this result are the rate constants obtained for ring opening of the various aziridine ions by various types of amino groups in the computer simulation of the polymerization of E1 mentioned previously.\textsuperscript{29}

The nature of the termination reaction in the polymerization has not been resolved. The rate of the reaction decreases as the polymerization proceeds, but this may be due to the progressively lower concentration of aziridinium ions. This could be called kinetic termination and would not represent chain termination. However there is no doubt that chain termination does occur since limiting values of the molecular weight of PEI are obtained.\textsuperscript{31,35,36} With anhydrous E1 the number-average molecular weight (ebulliscope) of the polymers is about 3000 to 3500; with aqueous E1 higher molecular weights are obtained.\textsuperscript{31} To be consistent with eqs 2-4, the termination mechanism would involve destruction of the aziridinium ions by reaction with some nucleophile present in the solution. Termination by hydrolysis

seems unlikely since no hydroxyl groups could be detected in the infrared spectrum of polymers made with water as the solvent. The molecular weight is not greatly influenced by the choice of mineral acid used as catalyst. Thus ring opening by the anion of the acid catalyst is of little importance since anions of different nucleophilicity were used. Polyamines, such as diethylene triamine and triethylenetetramine, have been used as "chain stoppers" in the polymerization of EI. Another possibility for a termination reaction is the formation of macrocyclic rings (eq 6). The value of n would have

$$\text{(CH}_2\text{CH}_2\text{NH})_n \rightarrow \text{NH-CH}_2\text{CH}_2$$

(6)

to be large enough to allow a back-side attack of a chain nitrogen on the aziridinium ring. The infrared spectrum of commercial PEI indicated the presence of 0.2% to 5% (by weight) piperazine rings depending on the method of preparation. However these polymers were probably formed with ethylene dihalides used as initiators.

The preparation of linear-crystalline PEI has recently been reported. The alkaline hydrolysis of

poly(N-formylethylenimine), obtained by the isomerization polymerization of unsubstituted 2-oxazoline initiated by BF$_3$·OEt$_2$ in dimethylformamide at 80°, yields the polymer. 38

\[ \text{N} \]
\[ \text{O} \]
\[ \text{N} \]
\[ \text{O} \]
\[ \text{CHO} \]
\[ \text{NaOH} \]
\[ \text{H}_2\text{O} \]

RESULTS AND DISCUSSION

General Structure of Polyethylenimines

The polyethylenimines used were products of the Dow Chemical Company. The molecular weight ranges of the polymers, as reported in a publication by Dow,\(^1\) are 450-750, 1050-1350, and 1650-1950. Therefore the molecular weights were taken to be 600, 1200, and 1800.\(^2\) The polymers are not of the purely linear type, such as

\[
H_2N-(CH_2CH_2NH)_n-H
\]

but instead contain a large degree of branching. Therefore a better structure for the polymers is

\[
H_2N-(CH_2CH_2NH)_x-(CH_2CH_2NH)_y- \quad \text{with } x+y > n
\]

\[
\text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2
\]

\[
\text{-N-}
\]


2. The Dow tradename for their polyethylenimines is Montrek-N, where 100N is the number-average molecular weight. They will be referred to in this work as PEI-X where X is the molecular weight.
The ratio of primary to secondary to tertiary nitrogens is reported to be approximately 1:2:1. The polymers are also acyclic and have primary amino end groups, and therefore must contain one more amino group than ethylene group per molecule. The reaction solution was said to have contained a source of the extra nitrogen (per molecule of polymer), such as ammonia or ethylenediamine. The amount of quaternary nitrogen was found to be less than 1% even when ten times the usual amount of hydrogen chloride catalyst was used in the preparation of the polymers. Therefore the number of primary nitrogens must be two greater than the number of tertiary nitrogens. By determining the number of either the primary or tertiary nitrogens in each of the polymers, the number of secondary nitrogens could easily be calculated.

**Determination of the Percent Tertiary Nitrogen in Poly-ethylениmines**

The percent of each polymer that is tertiary nitrogen was determined following the method described by Dow.

---


5. Reference 1, p. 16.
The primary and secondary nitrogens were acetylated in an acetic anhydride-acetic acid mixture and the remaining tertiary nitrogens were then titrated potentiometrically (standard calomel and glass electrodes) with standard p-toluenesulfonic acid in acetic acid. A titration curve for PEI-1800 is plotted in Figure 1. The titration of PEI-600 and PEI-1200 gave essentially the same type of curve. The percent of each polymer that is nitrogen was determined by elemental analysis. The percent tertiary nitrogen was then calculated (Table 1).

**Computer Generation of Polyethylenimines**

Polymers of three molecular weights, matching the molecular weights of the actual polymers as closely as possible (Table 2), were generated on an IBM 360 computer. In order to form an acyclic polymer with primary end groups, the polymerization was started with ethylenediamine and one \(-\text{CH}_2\text{CH}_2\text{NH}\)- unit was added at a time to simulate attack on protonated EI.

---

6. Since in the remainder of this study we will be concerned mainly with the number and types of nitrogens in the polymers, the percent tertiary nitrogen will be defined as the percent of the nitrogens that are tertiary nitrogens, i.e.,

\[
\frac{\text{number of tertiary nitrogens}}{\text{total number of nitrogens}} \times 100
\]
Figure 1. Titration of 0.0049 M PEI-1800 in 62% acetic acid - 38% acetic anhydride at room temperature.
### TABLE 1

PERCENT TERTIARY NITROGEN IN POLYETHYLENIMINES

<table>
<thead>
<tr>
<th>PEI</th>
<th>% of Polymer That Is Nitrogen</th>
<th>% of Polymer That Is Tertiary Nitrogen</th>
<th>% Tertiary Nitrogen&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>34.00</td>
<td>7.27</td>
<td>21.4</td>
</tr>
<tr>
<td>1200</td>
<td>32.20</td>
<td>8.01</td>
<td>24.9</td>
</tr>
<tr>
<td>1800</td>
<td>31.89</td>
<td>8.10</td>
<td>25.4</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reference 6.

\[
\begin{align*}
H_2NCH_2CH_2NH_2 + &NH_2^+ \\
\rightarrow &H_2NCH_2CH_2NHCH_2CH_2NH_2
\end{align*}
\]

At this point, however, either the secondary or one of the primary amino groups of diethylenetriamine can attack leading to two possible products.

\[
\begin{align*}
\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 + &H^+ \\
\rightarrow &\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 + &N\text{(CH}_2\text{CH}_2\text{NH}_2)_3 \\
\rightarrow &K_p \text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2
\end{align*}
\]

The addition of subsequent \(-\text{CH}_2\text{CH}_2\text{NH}^-\) groups can lead to
<table>
<thead>
<tr>
<th></th>
<th>Actual PEI's</th>
<th></th>
<th>Computer Generated PEI's</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average Molecular Weight</td>
<td>Average Number of Nitrogens (^a)</td>
<td>Molecular Weight (^b)</td>
</tr>
<tr>
<td>600</td>
<td>14.6</td>
<td>576</td>
<td>14</td>
</tr>
<tr>
<td>1200</td>
<td>28.5</td>
<td>1178</td>
<td>28</td>
</tr>
<tr>
<td>1800</td>
<td>42.4</td>
<td>1780</td>
<td>42</td>
</tr>
</tbody>
</table>

\(^a\) Determined by comparison of the molecular weight of the actual PEI with the molecular weight of the corresponding computer generated PEI.

\(^b\) Calculated from the formula \(H_2N-(CH_2CH_2NH)_n-H\).

A variety of products depending on whether a primary or secondary amino group attacks and depending on what was formed in the previous step. Using the letters P, S, and T for the three types of amino groups, the following scheme can be devised.
Since the polymers contain less than 1% quaternary nitrogen, attack by $T$ was neglected.\textsuperscript{4}

This mechanism is somewhat different from the one that occurs in the actual polymerization. In the computer simulation one starts with one ethylenediamine molecule and essentially adds one molecule of $E_1$ at a time. In the actual polymerization all of the $E_1$ necessary to obtain the correct molecular weight is present initially. Thus the ratio of $E_1$ to ethylenediamine is quite high and the $E_1$ molecules react primarily with one another according to the mechanism discussed in the introduction. Hence unlike the mechanism used in the computer program, the early stages of the reaction form mainly dimer, trimer, and tetramer; in the later stages these oligomers combine to give higher molecular weight molecules. This means that one of the $P$'s in the computer simulation would be replaced by an aziridine ring, which is later converted into an $S$ by attack of an
amino group. Also in the early stages of the actual polymerization attack by tertiary aziridine nitrogens on aziridinium ions to give intermediate quaternary nitrogens is probably important. Thus an S in the computer simulation would be replaced by a quaternary nitrogen which is later converted into a T by attack of an amino group. Destruction of the aziridinium ion results from attack by ethylenediamine.

\[
\begin{align*}
\text{N--PEI} + \text{P-P} & \rightarrow \text{P-S-S--PEI} \\
\text{N--PEI} + \text{P-P} & \rightarrow \text{P-S-T--PEI} \\
\text{N--PEI} + \text{P-P} & \rightarrow \text{P-S--PEI}
\end{align*}
\]

Even if these differences did make some changes in the final polymer, the computer program (as will be described) is still a way to randomly make PEI's with a certain degree of branching.

If we make the common polymer assumption that the reactivity of the end groups depends only on the nature of the end groups and is not affected by any other groups further down the chain, the ratio of the rate of attack by P \( (k_p) \) to that by S \( (k_s) \) is constant. Hence attack by P forms one S and does not change the number of P's.
\[ \frac{\text{d}P}{\text{d}t} = k_s S \left[ C_2H_4NH_2^+ \right] \]

\[ \frac{\text{d}S}{\text{d}t} = \left( k_p P - k_s S \right) \left[ C_2H_4NH_2^+ \right] \]

\[ \frac{\text{d}T}{\text{d}t} = k_s S \left[ C_2H_4NH_2^+ \right] \]

If the ratio of P to S to T is taken to be 1:2:1, as would be the case for an infinitely large polymer, the following would hold

\[ 2 \frac{\text{d}P}{\text{d}t} = \frac{\text{d}S}{\text{d}t} = 2 \frac{\text{d}T}{\text{d}t} \]

Therefore

\[ 2k_s S \left[ C_2H_4NH_2^+ \right] = \left( k_p P - k_s S \right) \left[ C_2H_4NH_2^+ \right] \]

or

\[ 3k_s S = k_p P \]

Since \( S = 2P \)

\[ \frac{k_p}{k_s} = 6 \]

This would predict that the rate of attack by P is six times as fast as the rate of attack by S. Hence for a
first approximation attack by P was made to be six times as likely as attack by S in the computer program.

Each polymer molecule was considered to consist of a main chain and side chains which resulted from branching, i.e., at tertiary nitrogens. Side chains could be off the main chain or other side chains. Each nitrogen in the molecule was assigned a number and these numbers were stored in the computer. Numbers assigned to primary, secondary and tertiary nitrogens were stored in the P, S, and T arrays, respectively. Each row of an array corresponded to the position of one nitrogen in the polymer. The first element of each row designated the position of the particular nitrogen on the main chain. The second and subsequent elements of each row were used in describing nitrogens off the main chain which resulted from branching.

The program began with diethylenetriamine (P-S-P) and a number was assigned to each of the nitrogens, i.e.,

80 - 81 - 82

The primary nitrogens 80 and 82 were stored in the first elements of the first and second rows of the P array. The secondary nitrogen 81 was similarly stored in the first element of the first row of the S array. Therefore initially the three arrays were
Which one of the three nitrogens in the trimer that attacked ethyleniminium ions to form tetramer was then determined by a random number produced in the computer. To make attack by P six times as likely as attack by S, six times as many numbers were assigned to each of the rows of the P array as those assigned to the rows of the S array. If the random number corresponded to attack by the primary nitrogen 80 the new tetramer would be P-S-S-P or

79 - 80 - 81 - 82

Now there is an additional nitrogen that must be stored in the arrays. The primary nitrogen 80 in the trimer is now a secondary nitrogen in the tetramer and a new primary nitrogen, 79, is present. Therefore in order to change the arrays to correspond to the new molecule the 80 in the P array would be changed to 79 and 80 would be added to the first element of the second row of the S array. The three arrays at this stage would be
On the other hand, if the random number had corresponded to attack by the secondary nitrogen 81 the new tetramer would have been P-T-P or

\[
\begin{array}{c}
80 - 81 - 82 \\
\mid \\
81,1
\end{array}
\]

Here the primary nitrogen that is off the main chain is designated by the number of the tertiary nitrogen on the main chain to which it is attached (81) followed by the number 1. In this case the secondary nitrogen 81 would have been removed from the S array while the new tertiary nitrogen 81 would have been added to the T array. The new primary nitrogen 81,1 would have been added to the first two elements of the third row of the P array. The three arrays would therefore have been

\[
\begin{array}{ccc}
P & S & T \\
79 & 0 & 0 \ldots & 81 & 0 & 0 \ldots & 0 & 0 & 0 \ldots \\
82 & 0 & 0 \ldots & 80 & 0 & 0 \ldots & 0 & 0 & 0 \ldots \\
0 & 0 & 0 \ldots & 0 & 0 & 0 \ldots & 0 & 0 & 0 \ldots
\end{array}
\]
This process of adding one nitrogen at a time was continued until the correct number of nitrogens was obtained for each polymer. Table 3 shows the completed arrays for a typical polymer of molecular weight 576 (14 nitrogens), which corresponds to the following structure

\[
74 - 75 - 76 - 77 - 78 - 79 - 80 - 81 - 82
\]

\[
\downarrow
\]

\[
78,1
\]

\[
\downarrow
\]

\[
81,1 - 81,1,1
\]

\[
\downarrow
\]

\[
81,2 81,1,2
\]

or

\[
P - S - S - S - T - S - S - T - P
\]

\[
\downarrow
\]

\[
P
\]

\[
\downarrow
\]

\[
T - S
\]

\[
\downarrow
\]

\[
P
\]

For a particular ratio of \( \frac{k_p}{k_s} \) 25 polymers of molecular weight 576, 1178, and 1780 were generated. When a different set of 25 polymers was needed for the same ratio of \( \frac{k_p}{k_s} \) a different value was given to IX, the number that starts the random generator.  

The program counted the number of tertiary nitrogens and calculated the percent tertiary nitrogen for each of the three types of polymers. Since the distance between

---

7. The random number generator used on the IBM 360 computer is called IRANU. It produces uniformly distributed random integers between specified limits, ILOW and IHIGH. IX is an old integer between these limits which starts the generator and IY is the resulting random integer between ILOW and IHIGH (inclusive).
TABLE 3

COMPUTER OUTPUT FOR A TYPICAL POLYMER OF MOLECULAR WEIGHT 576

<table>
<thead>
<tr>
<th>PEI 576 # 1</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RANDOM NUMBERS USED</strong></td>
<td>27</td>
<td>42</td>
<td>30</td>
<td>581</td>
<td>90</td>
<td>39</td>
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<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
a primary (which forms the imine) and any other amino group (which may remove the deuterium) is important in determining the size of the transition state for dedeuteration, the computer program also counted the number of P, S, and T amino groups at (CH$_2$CH$_2$N) unit distances away from each P. The counting was done by examining the completed arrays. By comparing the numbers assigned to the two nitrogens involved, the distance between them could be determined. For nitrogens on the main chain, i.e., those having only the first element of their rows non-zero, the distance between them was simply the absolute value of the difference between their numbers. For example for the two nitrogens

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>74</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>80</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

the distance was simply six (CH$_2$CH$_2$N) units. However, if one or both of the nitrogens involved was on a side chain the counting procedure became more complicated. In these cases the second and some of the subsequent elements of their rows were non-zero and had to be used in determining how far off the main chain they were. One example of these cases is the following two nitrogens on different side chains
Here the distance between them is the sum of the absolute value of the difference of their first two elements
(|78 - 81| = 3) and the sum of all the other elements
(1 + 0 + - - - + 1 + 2 + - - - = 4) or a total of seven
(CH₂CH₂N) units. After this was done for each P in the
25 polymers the number of nitrogens at each (CH₂CH₂N)
unit distance were totaled. These totals were divided
by the total number of P's in the 25 polymers in order to
give the number of nitrogens per primary, i.e., the
number of nitrogens away from the average primary. The
number of P, S, T or total nitrogens could then be
plotted against the number of (CH₂CH₂N) units away from
the average P (see Figures 4 and 5).

The values of the percent tertiary nitrogen for the
computer generated polymers can be compared to the values
for the actual polymers. The computer should give an
accurate picture of the polymers when these two values
are in close agreement. The results for the initial
$k_p/k_s$ ratio of six gave values of the percent of the
nitrogens that are tertiary for polymers of molecular
weight 576, 1178, and 1780 much smaller than the experi-
mental values for PEI-600, 1200, and 1800. This meant
that the computer polymers did not contain enough
branching and therefore smaller values of $k_p/k_s$ were used. Table 4 lists the results for several $k_p/k_s$ ratios and the averaged values are plotted along with the experimental results in Figure 2. The computer program for generating the polymers is given in Appendix A.

**Titration of Model Compounds**

In the titration of the acetylated polymers it is quite unlikely that all of the tertiary nitrogens were titrated due to the considerable number of positive charges being added to the molecules. For example, it is questionable if all the nitrogens in the following group of tertiaries would be titrated.

\[ T_1 - T_2 - T_3 - T_4 - T_5 - T_6 \]

Considering only nearest neighbors, titration of all the nitrogens would result in three positive charges adjacent to $T_3$.

Therefore model compounds containing adjacent tertiary nitrogens (separated by ethylene groups) were obtained and titrated under the same conditions as the acetylated polymers to see just how many of the nitrogens could be titrated. Pentamethyldiethylenetriamine (1) and hexamethyltriethylenetetramine (2) were commercially available and served as model compounds for
<table>
<thead>
<tr>
<th>$k_p/k_s$</th>
<th>IX$^a$</th>
<th>576</th>
<th>1178</th>
<th>1780</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>399</td>
<td>28.6</td>
<td>33.3</td>
<td>34.2</td>
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<tr>
<td>2.5</td>
<td>101</td>
<td>22.9</td>
<td>27.0</td>
<td>28.0</td>
</tr>
<tr>
<td>2.5</td>
<td>399</td>
<td>21.7</td>
<td>27.4</td>
<td>28.0</td>
</tr>
<tr>
<td>3.0</td>
<td>101</td>
<td>23.1</td>
<td>25.0</td>
<td>25.7</td>
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<td>399</td>
<td>22.6</td>
<td>25.1</td>
<td>27.4</td>
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<tr>
<td>4.0</td>
<td>101</td>
<td>19.4</td>
<td>25.3</td>
<td>26.1</td>
</tr>
<tr>
<td>4.0</td>
<td>399</td>
<td>19.7</td>
<td>23.0</td>
<td>24.5</td>
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<tr>
<td>6.0</td>
<td>399</td>
<td>16.3</td>
<td>19.1</td>
<td>21.1</td>
</tr>
</tbody>
</table>

$^a$Number that started the random number generator on the IBM 360 computer.
Figure 2. Percent tertiary nitrogen vs. molecular weight: • experimental; ○ \( k_p/k_s = 2.5 \); \( \triangle k_p/k_s = 3.0 \); □ \( k_p/k_s = 4.0 \).
T-T-T and T-T-T-T.

As a model for T-T-T, tris(2-dimethylaminoethyl)amine (3)
was prepared from tris(2-aminoethyl)amine (4) by treat-
ment with formaldehyde and formic acid (Eschweiler-Clark
procedure). 8

These compounds should be good models for the groups of
tertiary nitrogens in the acetylated polymer because
they differ only in having -CH₃ groups rather than
-CH₂CH₂NCOCH₃ groups (R = H, (CH₂CH₂N)ₙ) bonded to the
nitrogens.

The model compounds were titrated under the same

Adams, Ed., John Wiley and Sons, Inc., New York,
N. Y., 1949, Chapter 7, p. 323.
conditions as the acetylated polymers. The shape of their titration curves was essentially the same as that of the acetylated polymers (Figure 1) except that the endpoints of the model compounds were slightly steeper. In the titration of 2 and 3 slightly less acetic anhydride was used in the solvent mixture to account for the amount of acetic anhydride used up in acetylating the polymers.

The results in Table 5 show that three and four tertiary nitrogens in a row can be titrated but that only three of the four nitrogens in T-T-T can be titrated. Thus the results from compounds 1 and 2 show that a $T^+$ can have two $\alpha$ and one $\beta$ $T^+$ nitrogens. With the results from compound 3, however, a $T^+$ can have two but not three $\alpha$ $T^+$ nitrogens. From these results two different rules may be written to predict the number of nitrogens that cannot be titrated in various groups of tertiary nitrogens. Rule #1 considers only $\alpha$ T's and states that a T cannot be protonated if there are three $\alpha$ $T^+$ nitrogens. Thus any number of $\beta$ $T^+$ nitrogens are allowed. Rule #2 considers both $\alpha$ and $\beta$ T's. It is known that a T can be protonated if it has two $\alpha$ and one

---

9. The symbols $\alpha$ and $\beta$ refer to the nearest and next-nearest nitrogens, i.e., neglecting intermediate ethylene groups.
<table>
<thead>
<tr>
<th>Amine</th>
<th>Model For</th>
<th>(\text{[Amine]}_N)</th>
<th>(\text{[p-TsOH]}_M^b)</th>
<th>Number of Nitrogens Titrated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T-T-T</td>
<td>0.067(^c)</td>
<td>0.200</td>
<td>2.99</td>
</tr>
<tr>
<td>2(^d)</td>
<td>T-T-T-T</td>
<td>0.028(^e)</td>
<td>0.100</td>
<td>3.96</td>
</tr>
<tr>
<td>3(^d)</td>
<td>T-T-T</td>
<td>0.026(^e)</td>
<td>0.100</td>
<td>3.00(^f)</td>
</tr>
<tr>
<td>4(^g)</td>
<td>P-T-P</td>
<td>0.107(^c)</td>
<td>0.200</td>
<td>1.02(^h)</td>
</tr>
</tbody>
</table>

\(^a\)Titrated potentiometrically (standard calomel and glass electrodes) at room temperature.

\(^b\)In glacial acetic acid.

\(^c\)In 62% acetic acid - 38% acetic anhydride.

\(^d\)Purified prior to titration by recrystallization of the hydrochloride from ethanol - water.

\(^e\)In 64% acetic acid - 36% acetic anhydride.

\(^f\)A 3.7% impurity of 2 in 3 was assumed to take up four equivalents of protons.

\(^g\)This amine was acetylated in the same manner as the polymers prior to titration.

\(^h\)A 13.2% impurity of triethylenetetramine was assumed to be completely acetylated and therefore take up no protons.
\( \beta T^+ \) nitrogens. However it is not known how many additional \( \beta T^+ \) nitrogens are needed to prevent protonation. Hence it is not known whether two \( \alpha \) and two or more \( \beta T^+ \) nitrogens prevent protonation. In the case of only one \( \alpha T^+ \) nitrogen it would be helpful to know how many \( \beta T^+ \) nitrogens would have the same effect as one \( \alpha T^+ \). From Table 15 it is estimated that the protonation of a nitrogen three atoms away (\( \alpha \)) from another nitrogen decreases the \( pK_a \) of the latter about 2.6 \( pK_a \) units at 25°. The effect of a protonated nitrogen six atoms away (\( \beta \)) only decreases the \( pK_a \) by about 0.7 \( pK_a \) units. Therefore four \( \beta T^+ \) nitrogens have about the same effect on the \( pK_a \) as one \( \alpha T^+ \) nitrogen (2.8 vs. 2.6).\(^{10}\) Since two \( \alpha \) and one \( \beta T^+ \) nitrogens are allowed it seems reasonable to allow one \( \alpha \) and five \( \beta T^+ \) nitrogens, but the effect of one \( \alpha \) and six \( \beta T^+ \) nitrogens would be unknown. Finally if there are no \( \alpha T^+ \) nitrogens any number of \( \beta T^+ \) nitrogens is allowed since the maximum number of \( \beta T^+ \)'s is only six. Table 6 summarizes the

---

10. If the fall-off factor of 2.8 for inductive effects\(^{11}\) is used the effect of a \( \beta T^+ \), which is three atoms farther away than an \( \alpha T^+ \), should have \( 1/2.8^3 \) or 1/22 the effect of one \( \alpha T^+ \).

**TABLE 6**

**EFFECT OF PROTONATED $\alpha$ AND $\beta$ TERTIARY NITROGENS ON THE PROTONATION OF TERTIARY NITROGENS**

<table>
<thead>
<tr>
<th></th>
<th>$T^+$ Allowed</th>
<th>$T^+$ Unknown</th>
<th>$T^+$ Not Allowed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$  $\beta$</td>
<td>$\alpha$  $\beta$</td>
<td>$\alpha$  $\beta$</td>
</tr>
<tr>
<td>Rule #1</td>
<td>0-2</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>2  0-1</td>
<td>2  2-6</td>
<td>3  0-6</td>
</tr>
<tr>
<td>Rule #2</td>
<td>1  0-5</td>
<td>1  6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0  0-6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
number of \( \alpha \) and \( \beta \ T^+ \) nitrogens that are allowed and not allowed for protonation and also the unknown cases.

Table 7 lists some of the various groups of tertiary nitrogens that are obtained from the computer programs and the number of tertiaries in each group that would not be titrated. In Table 7 the combinations of \( \alpha \) and \( \beta \ T^+ \) nitrogens which were unknown according to Rule #2 were assumed for the moment not to allow protonation in order to see the maximum difference between the two rules.

In addition, compound \( J_f \), which is a model for \( P-T-P \), was acetylated in the same manner as the polymers in order to block the primary nitrogens and then titrated with \( p \)-toluenesulfonic acid. The results in Table 5 show that only the tertiary nitrogen in \( J_f \) was titrated. Hence the primary nitrogens were completely acetylated and none of the acetylated nitrogens were titrated. This tends to support the assumption that only the tertiary nitrogens are being titrated in the acetylated polymers.

**Correction of the Percent Tertiary Nitrogen in Poly-ethylenimines Generated by Computer**

By knowing the number of nitrogens that cannot be titrated in each of the groups of tertiary nitrogens and by knowing how many of these groups were formed from the
### TABLE 7

**EXAMPLES OF GROUPS OF TERTIARY NITROGENS IN POLYETHYLENIMINES GENERATED BY COMPUTER AND THE NUMBER OF NITROGENS NOT TITRATED IN EACH GROUP**

<table>
<thead>
<tr>
<th>Group</th>
<th>Number of Nitrogens Not Titrated&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Group</th>
<th>Number of Nitrogens Not Titrated&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-T</td>
<td>0</td>
<td>T-T-T-T-T-T</td>
<td>1</td>
</tr>
<tr>
<td>T-T-T</td>
<td>0</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>T-T-T-T</td>
<td>0</td>
<td>T-T-T-T-T-T</td>
<td>1</td>
</tr>
<tr>
<td>T-T-T-T-T-T</td>
<td>1</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>T-T-T-T-T-T&lt;T</td>
<td>0 (1)</td>
<td>T-T-T&lt;T-T</td>
<td>1 (2)</td>
</tr>
<tr>
<td>T-T-T-T</td>
<td>1</td>
<td>T-T-T-T&lt;T</td>
<td>1</td>
</tr>
<tr>
<td>T-T-T&lt;T</td>
<td>1</td>
<td>T-T&lt;T-T</td>
<td>T-T&lt;T-T-T-T&lt;T</td>
</tr>
<tr>
<td>T-T-T&lt;T-T&lt;T</td>
<td>1</td>
<td>T-T&lt;T-T</td>
<td>T-T&lt;T-T-T&lt;T</td>
</tr>
<tr>
<td>T-T-T&lt;T-T&lt;T&lt;T</td>
<td>1</td>
<td>T-T&lt;T&lt;T</td>
<td>T-T&lt;T-T-T&lt;T</td>
</tr>
<tr>
<td>T&lt;T-T-T</td>
<td>1</td>
<td>T-T&lt;T&lt;T</td>
<td>T-T&lt;T-T-T&lt;T</td>
</tr>
<tr>
<td>T-T-T&lt;T&lt;T&lt;T</td>
<td>1 (2)</td>
<td>T-T&lt;T&lt;T</td>
<td>T-T&lt;T-T-T&lt;T</td>
</tr>
<tr>
<td>T-T&lt;T&lt;T&lt;T&lt;T</td>
<td>0 (1)</td>
<td>T-T&lt;T&lt;T</td>
<td>T-T&lt;T-T-T&lt;T</td>
</tr>
</tbody>
</table>

<sup>a</sup>Values obtained using Rule #1; values in parenthesis obtained using Rule #2 when different from value using Rule #1 (see Table 6).
PEI's generated by computer, the total number of nitrogens not titrated can be determined. For example, Table 8 lists the number and type of groups that were formed in 25 polymers of molecular weight 1178. The number of nitrogens in each group that would not be titrated was determined by using Rules #1 and #2. The total number of tertiary nitrogens not titrated in 25 polymers was therefore known and subtracted from the total number of tertiary nitrogens. Knowing the total number of nitrogens in the 25 polymers, a corrected percent tertiary nitrogen was calculated. The results for the polymers generated by computer with $k_p/k_s$ ratios of 2.5, 3.0, and 4.0 are listed in Table 9. The values obtained using Rule #2 were in most cases identical to those using Rule #1 for the polymers of molecular weight 576; the values obtained using Rule #2 for the larger polymers were only about 1% smaller than the values obtained using Rule #1. Therefore the averaged values obtained using Rule #1 for each $k_p/k_s$ ratio were plotted in Figure 3. A $k_p/k_s$ ratio of 3.0 gives the best correlation with the experimental results. The number of primary, secondary, and tertiary nitrogens and the total number of all types of nitrogens at $(\text{CH}_2\text{CH}_2\text{N})$ unit distances from the average primary nitrogen are plotted in Figures 4 and 5.
TABLE 8

GROUPS OF TERTIARY NITROGENS AND THE NUMBER OF TERTIARY NITROGENS NOT TITRATED IN 25 POLYMERS OF MOLECULAR WEIGHT 1178 GENERATED BY COMPUTERa

<table>
<thead>
<tr>
<th>Group</th>
<th>Number of Nitrogens Not Titrated Per Groupb</th>
<th>Total Number of Groups</th>
<th>Total Number of Nitrogens, Not Titratedb</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-T</td>
<td>0</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>T-T-T</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>T-T-T-T</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>T-T-T-T</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>T-T-T-T-T</td>
<td>0 (1)</td>
<td>2</td>
<td>0 (2)</td>
</tr>
<tr>
<td>T-T-T-T-T-T</td>
<td>0 (1)</td>
<td>1</td>
<td>0 (1)</td>
</tr>
<tr>
<td>T-T-T-T-T-T</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>T-T-T-T-T-T-T</td>
<td>0 (1)</td>
<td>1</td>
<td>0 (1)</td>
</tr>
<tr>
<td>T-T-T-T-T-T-T</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>T-T-T-T-T</td>
<td>1 (2)</td>
<td>2</td>
<td>2 (4)</td>
</tr>
<tr>
<td>T-T-T-T-T-T</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Total 7 (13)

a$k_p/k_s = 3.0$, IX = 399.

bValues obtained using Rule #1; values in parenthesis obtained using Rule #2 when different from value using Rule #1 (see Table 6).
<table>
<thead>
<tr>
<th>$k_p/k_s$</th>
<th>IX$^a$</th>
<th>Number of T</th>
<th>% T</th>
<th>Number of T Not Titrated$^b$</th>
<th>Corrected % T$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td><strong>Molecular Weight 576:</strong></td>
<td></td>
<td></td>
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<tr>
<td>2.5</td>
<td>101</td>
<td>80</td>
<td>22.9</td>
<td>1</td>
<td>22.6 (22.3)</td>
</tr>
<tr>
<td>2.5</td>
<td>399</td>
<td>76</td>
<td>21.7</td>
<td>1</td>
<td>21.4</td>
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<td>101</td>
<td>81</td>
<td>23.1</td>
<td>2</td>
<td>22.6 (22.3)</td>
</tr>
<tr>
<td>3.0</td>
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<td>79</td>
<td>22.6</td>
<td>1</td>
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</tr>
<tr>
<td>2.5</td>
<td>101</td>
<td>189</td>
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<td>25.6 (24.4)</td>
</tr>
<tr>
<td>2.5</td>
<td>399</td>
<td>192</td>
<td>27.4</td>
<td>9</td>
<td>26.1 (24.9)</td>
</tr>
<tr>
<td>3.0</td>
<td>101</td>
<td>175</td>
<td>25.0</td>
<td>8</td>
<td>23.9 (23.0)</td>
</tr>
<tr>
<td>3.0</td>
<td>399</td>
<td>176</td>
<td>25.1</td>
<td>7</td>
<td>24.1 (23.3)</td>
</tr>
<tr>
<td>4.0</td>
<td>101</td>
<td>177</td>
<td>25.3</td>
<td>10</td>
<td>23.9 (23.7)</td>
</tr>
<tr>
<td>4.0</td>
<td>399</td>
<td>161</td>
<td>23.0</td>
<td>6</td>
<td>22.1 (21.1)</td>
</tr>
<tr>
<td>$k_p/k_s$</td>
<td>IX&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Number of T</td>
<td>% T</td>
<td>Number of T Not Titrated&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Corrected % T&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>----------</td>
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<td>------------</td>
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<td>-------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Molecular Weight 1780</strong>:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>101</td>
<td>294</td>
<td>28.0</td>
<td>21</td>
<td>26.0 (25.1)</td>
</tr>
<tr>
<td>2.5</td>
<td>399</td>
<td>294</td>
<td>28.0</td>
<td>22</td>
<td>25.9 (24.9)</td>
</tr>
<tr>
<td>3.0</td>
<td>101</td>
<td>270</td>
<td>25.7</td>
<td>14</td>
<td>24.4 (23.2)</td>
</tr>
<tr>
<td>3.0</td>
<td>399</td>
<td>288</td>
<td>27.4</td>
<td>18</td>
<td>25.7 (24.3)</td>
</tr>
<tr>
<td>4.0</td>
<td>101</td>
<td>274</td>
<td>26.1</td>
<td>15</td>
<td>24.7 (23.8)</td>
</tr>
<tr>
<td>4.0</td>
<td>399</td>
<td>257</td>
<td>24.5</td>
<td>13</td>
<td>23.2 (22.3)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Number that started the random number generator on the IBM 360 computer.

<sup>b</sup> Values obtained using Rule #1; values in parenthesis obtained using Rule #2 when different from value using Rule #1 (see Table 6).
Figure 3. Corrected percent tertiary nitrogen (Rule #1) vs. molecular weight: • experimental; ○ $k_p/k_s = 2.5$; △ $k_p/k_s = 3.0$; □ $k_p/k_s = 4.0$. 
Figure 4. Number of primary, secondary, and tertiary nitrogens vs. \((\text{CH}_2\text{CH}_2\text{N})\) units from the average primary \((k_p/k_g = 3.0)\) for polyethylenimines of molecular weight: ○ 576; △ 1178; □ 1780.
Figure 5. Total number of nitrogens vs. (CH₂CH₂N) units from the average primary (k_p/k_s = 3.0) for polyethylenimines of molecular weight: ○ 576; △ 1178; □ 1780.
Number of Primary, Secondary, and Tertiary Nitrogens in Polyethylenimines

The values of the percent tertiary nitrogen in PEI-600, 1200, and 1800 (21.4, 24.9, and 25.4%, respectively, Table 1) that were experimentally determined reflect only the tertiary nitrogens that can be titrated in the acetylated polymers. However it was shown that not all tertiary nitrogens in the acetylated polymers can be titrated. In the preceding section the computer polymers were corrected for the number of tertiary nitrogens that would not be titrated in order that they could be compared with the experimental results. The values of the percent tertiary nitrogen for a $k_p/k_s$ ratio of 3.0 (which gave the best correlation with the experimental results) had to be corrected by subtracting 0.4, 1.0, and 1.5% in PEI-576, 1178, and 1780 (Table 9). Therefore more accurate values of the percent tertiary nitrogen in the actual polymers were obtained by correcting for the number of tertiary nitrogens not titrated in the acetylated polymers, i.e., by adding these same factors to the experimental values. The resulting values of the percent tertiary nitrogen (21.8, 25.9, and 26.9%, respectively) should be more accurate than the original values obtained from the titrations. From these values and the average number of nitrogens in each of the polymers
TABLE 10

NUMBER AND FRACTION OF PRIMARY, SECONDARY, AND TERTIARY NITROGENS IN POLYETHYLENIMINES

<table>
<thead>
<tr>
<th>PEI</th>
<th>Average Number of Nitrogens</th>
<th>Number</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>600</td>
<td>14.6</td>
<td>5.2</td>
<td>6.2</td>
</tr>
<tr>
<td>1200</td>
<td>28.5</td>
<td>9.4</td>
<td>11.7</td>
</tr>
<tr>
<td>1800</td>
<td>42.4</td>
<td>13.4</td>
<td>17.6</td>
</tr>
</tbody>
</table>

(Table 2) the number and fraction of all three types of nitrogens were calculated (Table 10).

Estimation of the Type of $\alpha$-Nitrogens in Polyethylenimines

In order to estimate the type of $\alpha$-nitrogens it is convenient to introduce the concept of bond-halves and the idea of a bond-half leading from one atom to another atom. For example, we will say that a P-S bond contains two bond-halves, the one nearer P and the one nearer S. The former is said to lead from S to P and the latter from P to S. Let us use a notation in which the fraction of the total number of bond-halves that lead from S's to P's is $P_s$. $P_p$, $P_t$, $T_p$, $T_s$, and $T_t$ are defined analogously. Secondary nitrogens are broken down into further
classifications in which we are concerned with what type of nitrogen is on either side. Thus $p_{St}$ is defined as the fraction of the total number of bond-halves that lead from T's to S's that are attached to P's. $p_{Sp}$, $p_{Ss}$, $s_{Sp}$, $s_{Ss}$, $s_{St}$, $t_{Sp}$, $t_{Ss}$, and $t_{St}$ are defined analogously.

The fact that the polymers contain no ethylenediamine means that $P_p$ equals zero. Also since there is no diethylenetriamine, $p_{Sp}$ equals zero. Hence there are 13 non-zero fractions remaining.

Primaries: $P_s$, $P_t$

Secondaries: $p_{Ss}$, $p_{St}$, $s_{Sp}$, $s_{Ss}$, $s_{St}$, $t_{Sp}$, $t_{Ss}$, $t_{St}$

Tertiaries: $T_p$, $T_s$, $T_t$

Eqs 1-4 can be written from symmetry.

\[
\begin{align*}
T_p &= P_t & (1) \\
s_{Sp} &= p_{Ss} & (2) \\
t_{Sp} &= p_{St} & (3) \\
t_{Ss} &= s_{St} & (4)
\end{align*}
\]

Also

\[
\begin{align*}
P_s &= p_{Ss} + p_{St} & (5) \\
T_s &= t_{Sp} + t_{Ss} + t_{St} & (6)
\end{align*}
\]

Therefore

\[
p_{St} = P_s - p_{Ss} & (7)
\]
\[ Ts = Ps - pSs + sSt + tSt \]  
\[ (8) \]

Since six of the unknowns are expressed in eqs 1-4, 7, and 8, this leaves the following seven unknowns: Ps, Pt, pSs, sSs, sSt, tSt, and Tt.

Now Px is the fraction of the total number of bond-halves that lead from any nitrogen to P's and Sx and Tx are defined analogously. Px, Sx, and Tx can be calculated from the fractions of P's, S's, and T's (FP, FS, and FT, respectively) in PEI-600, 1200, and 1800 from Table 10.

\[ Px = \frac{FP}{FP + 2FS + 3FT} \]  
\[ (9) \]

\[ Sx = \frac{2FS}{FP + 2FS + 3FT} \]  
\[ (10) \]

\[ Tx = \frac{3FT}{FP + 2FS + 3FT} \]  
\[ (11) \]

Therefore

\[ Px = Ps + Pt \]  
\[ (12) \]

\[ Sx = sSp + tSp + pSs + sSs + tSs + pSt + sSt + tSt \]  
\[ (13) \]

\[ Tx = Pt + pSt + sSt + tSt + Tt \]  
\[ (14) \]

Since a P may be attached to any T or any S (except a pS), we assume that the relative amounts attached will be proportional to the relative amounts available, i.e.,
\[
\frac{Ps}{Sx - Ps} = \frac{Pt}{Tx}
\]

Substituting for \(Pt\) from eq 12 and rearranging gives

\[
Ps^2 - (Px + Sx + Tx) Ps + PxSx = 0
\]

Since

\[
Px + Sx + Tx = 1
\]

(15)

\[
Ps = \frac{1 + \sqrt{1 - 4PxSx}}{2}, \quad 1 - \frac{\sqrt{1 - 4PxSx}}{2}
\]

(16)

Only the second solution to the quadratic equation gives a reasonable value for \(Ps\). \(Pt\) can now be calculated from eq 12.

Since a \(pS\) may be attached to any \(S\) or \(T\) (but not \(P\)), we assume that the relative amounts attached to each is proportional to the relative amounts available. Thus allowing for those that are unavailable because they are attached to \(P\),

\[
\frac{pSs}{Sx - Ps} = \frac{pSt}{Tx - Pt}
\]

Substituting for \(pSt\) from eq 5 gives

\[
pSs = \frac{Ps(Sx - Ps)}{Tx - Pt + Sx - Ps}
\]

(17)

This leaves \(Px\) primaries, \(Sx - Ps - pSs\) secondaries, and \(Tx - Pt - pSt\) tertiaries. The fraction of all avail-
able nitrogens that are primary is

\[ \frac{Px}{Px + Sx - Ps - pSs + Tx - Pt - pSt} \]

Substituting for pSt from eq 5 and using eq 12 and eq 15 gives

\[ \frac{Px}{1 - Px - Ps} \]

Similarly the fraction that are secondary is

\[ \frac{Sx - Ps - pSs}{1 - Px - Ps} \]

and the fraction that are tertiary is

\[ \frac{Tx - Px + pSs}{1 - Px - Ps} \]

We assume that they are attached to sS, tS, and T in these ratios. Therefore

\[ \frac{sSp}{\frac{Px}{1 - Px - Ps}} = \frac{sSs}{\frac{Sx - Ps - pSs}{1 - Px - Ps}} \]

\[ \frac{sSp}{\frac{Px}{1 - Px - Ps}} = \frac{sSt}{\frac{Tx - Px + pSs}{1 - Px - Ps}} \]
\[
\frac{t_{Sp}}{1 - Px - Ps} = \frac{t_{St}}{1 - Px - Ps}
\]
\[
\frac{Tp}{1 - Px - Ps} = \frac{Tt}{1 - Px - Ps}
\]

Using eqs 1, 2, and 5

\[s_{SS} = \frac{p_{SS}(Sx - Ps - p_{SS})}{Px} \] (18)

\[s_{St} = \frac{p_{SS}(Tx - Px + p_{SS})}{Px} \] (19)

\[t_{St} = \frac{(Ps - p_{SS})(Tx - Px + p_{SS})}{Px} \] (20)

\[Tt = \frac{Pt(Tx - Px + p_{SS})}{Px} \] (21)

Thus by using eqs 1-4, and 7-8 all of the fractions can be calculated. The results for PEI-600, 1200, and 1800 are summarized in Table 11.

**pK\textsubscript{a} Values of the Nitrogens in Polyethylenimines**

The pK\textsubscript{a} values of the conjugate acids of the primary, secondary, and tertiary nitrogens in PEI were estimated by studying the effect of -NR\textsubscript{2} and NHR\textsubscript{2}\textsuperscript{+} substituents (R = H, alkyl) on the pK\textsubscript{a}'s of simple compounds. Table 12 lists the pK\textsubscript{a}'s of the conjugate acids of several amines at zero ionic strength. The majority of the
<table>
<thead>
<tr>
<th>Fraction of Bond-Halves</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Px</td>
<td>0.191</td>
<td>0.170</td>
<td>0.162</td>
</tr>
<tr>
<td>Sx</td>
<td>0.458</td>
<td>0.427</td>
<td>0.425</td>
</tr>
<tr>
<td>Tx</td>
<td>0.351</td>
<td>0.403</td>
<td>0.413</td>
</tr>
<tr>
<td>Ps</td>
<td>0.0967</td>
<td>0.0790</td>
<td>0.0743</td>
</tr>
<tr>
<td>Pt, Tp</td>
<td>0.0938</td>
<td>0.0914</td>
<td>0.0875</td>
</tr>
<tr>
<td>pSS, sSp</td>
<td>0.0565</td>
<td>0.0417</td>
<td>0.0385</td>
</tr>
<tr>
<td>pSt, tSp</td>
<td>0.0402</td>
<td>0.0373</td>
<td>0.0358</td>
</tr>
<tr>
<td>sSS</td>
<td>0.0905</td>
<td>0.0749</td>
<td>0.0743</td>
</tr>
<tr>
<td>sSt, tSs</td>
<td>0.0644</td>
<td>0.0670</td>
<td>0.0690</td>
</tr>
<tr>
<td>tSt</td>
<td>0.0458</td>
<td>0.0599</td>
<td>0.0641</td>
</tr>
<tr>
<td>Ts</td>
<td>0.150</td>
<td>0.164</td>
<td>0.169</td>
</tr>
<tr>
<td>Tt</td>
<td>0.107</td>
<td>0.147</td>
<td>0.157</td>
</tr>
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</table>
TABLE 12

\( p_{Ka} \) VALUES OF THE CONJUGATE ACIDS OF AMINES IN WATER AT ZERO IONIC STRENGTH\(^a\)

<table>
<thead>
<tr>
<th>No.</th>
<th>Acid</th>
<th>( p_{Ka}^{25\degree} )</th>
<th>( p_{Ka}^{35\degree} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtNH(_3)(^+)</td>
<td>10.645(^b)</td>
<td>10.320(^b)</td>
</tr>
<tr>
<td>2</td>
<td>Et(_2)NH(_2)(^+)</td>
<td>10.946(^b)</td>
<td>10.641(^b)</td>
</tr>
<tr>
<td>3</td>
<td>Et(_3)NH(^+)</td>
<td>10.75</td>
<td>10.45</td>
</tr>
<tr>
<td>4</td>
<td>EtNHMe(_2)(^+)</td>
<td>10.02(^c)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>H(_2)NCH(_2)CH(_2)NH(_3)(^+)</td>
<td>9.627(^b),(^d)</td>
<td>9.346(^b),(^d)</td>
</tr>
<tr>
<td>6</td>
<td>( +)H(_3)NCH(_2)CH(_2)NH(_3)(^+)</td>
<td>7.149(^b),(^e)</td>
<td>6.891(^b),(^e)</td>
</tr>
<tr>
<td>7</td>
<td>Me(_2)NCH(_2)CH(_2)NHMe(_2)(^+)</td>
<td>8.72(^c),(^d)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( +)Me(_2)NHCH(_2)CH(_2)NHMe(_2)(^+)</td>
<td>5.92(^c),(^e)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Et(_2)NCH(_2)CH(_2)NHEt(_2)(^+)</td>
<td>9.25(^d),(^f)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>( +)Et(_2)NHCH(_2)CH(_2)NHEt(_2)(^+)</td>
<td>6.83(^e),(^f)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>n-PrNH(_3)(^+)</td>
<td>10.543(^b)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>H(_2)N(CH(_2))(_3)NH(_3)(^+)</td>
<td>10.08(^b),(^f),(^d)</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>( +)H(_3)N(CH(_2))(_3)NH(_3)(^+)</td>
<td>8.69(^b),(^f),(^e)</td>
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</tr>
<tr>
<td>14</td>
<td>n-BuNH(_3)(^+)</td>
<td>10.609(^b)</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>H(_2)N(CH(_2))(_4)NH(_3)(^+)</td>
<td>10.35(^b),(^d)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>( +)H(_3)N(CH(_2))(_4)NH(_2)(^+)</td>
<td>9.49(^b),(^e)</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>n-C(<em>5)H(</em>{11})NH(_3)(^+)</td>
<td>10.63</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>H(_2)N(CH(_2))(_5)NH(_3)(^+)</td>
<td>9.95(^d)</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>( +)H(_3)N(CH(_2))(_5)NH(_3)(^+)</td>
<td>9.49(^d)</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 12 (Continued)

<table>
<thead>
<tr>
<th>No.</th>
<th>Acid</th>
<th>$pK_a^{25°}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>$\text{H}_2\text{N}\text{C}_2\text{H}_4\text{O}\text{C}_2\text{H}_4\text{NH}_3^+$</td>
<td>9.44&lt;sup&gt;b,d&lt;/sup&gt;</td>
</tr>
<tr>
<td>21</td>
<td>$^{+}\text{H}_3\text{N}\text{C}_2\text{H}_4\text{O}\text{C}_2\text{H}_4\text{NH}_3^+$</td>
<td>9.08&lt;sup&gt;b,e&lt;/sup&gt;</td>
</tr>
<tr>
<td>22</td>
<td>$\text{H}_2\text{N}\text{C}_2\text{H}_4\text{N}\text{H}\text{C}_2\text{H}_4\text{NH}_3^+$</td>
<td>9.50&lt;sup&gt;b,d&lt;/sup&gt;</td>
</tr>
<tr>
<td>23</td>
<td>$^{+}\text{H}_3\text{N}\text{C}_2\text{H}_4\text{N}\text{H}\text{C}_2\text{H}_4\text{NH}_3^+$</td>
<td>9.04&lt;sup&gt;b,e&lt;/sup&gt;</td>
</tr>
<tr>
<td>24</td>
<td>$(\text{H}_2\text{N}\text{C}_2\text{H}_4)^2\text{N}\text{C}_2\text{H}_4\text{NH}_3^+$</td>
<td>9.55&lt;sup&gt;b,g&lt;/sup&gt;</td>
</tr>
<tr>
<td>25</td>
<td>$\text{H}_2\text{N}\text{C}_2\text{H}_4\text{N}(\text{C}_2\text{H}_4\text{NH}_3^+)_2$</td>
<td>9.13&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>26</td>
<td>$\text{N}(\text{C}_2\text{H}_4\text{NH}_3^+)_3$</td>
<td>8.33&lt;sup&gt;b,h&lt;/sup&gt;</td>
</tr>
<tr>
<td>27</td>
<td>$\text{Me}_2\text{N}\text{C}_2\text{H}_4\text{O}\text{C}_2\text{H}_4\text{NHMe}_2^+$</td>
<td>9.32&lt;sup&gt;c,d&lt;/sup&gt;</td>
</tr>
<tr>
<td>28</td>
<td>$^{+}\text{Me}_2\text{N}\text{H}\text{C}_2\text{H}_4\text{O}\text{C}_2\text{H}_4\text{NHMe}_2^+$</td>
<td>8.34&lt;sup&gt;c,e&lt;/sup&gt;</td>
</tr>
<tr>
<td>29</td>
<td>$\text{Et}_2\text{N}\text{C}_2\text{H}_4\text{O}\text{C}_2\text{H}_4\text{N}\text{Het}_2^+$</td>
<td>9.72&lt;sup&gt;c,d&lt;/sup&gt;</td>
</tr>
<tr>
<td>30</td>
<td>$^{+}\text{Et}_2\text{N}\text{H}\text{C}_2\text{H}_4\text{O}\text{C}_2\text{H}_4\text{N}\text{Het}_2^+$</td>
<td>8.53&lt;sup&gt;c,e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>


<sup>b</sup>Interpolated from data at higher and lower temperatures.


<sup>d</sup>0.301 has been subtracted as a statistical correction.

<sup>e</sup>0.301 has been added as a statistical correction.
data was at 25° although a few values at 35° were estimated from data at other temperatures. From the data in Table 12 the effect of substituents three to six atoms away from the nitrogen in question was determined; the results are given in Table 13.

The values for the change -H to -NR₂ (R = H, Me, Et) three to six atoms away are summarized in Table 14. The values at 25° for the change -H to -NR₂ (R = H, Me, Et) three atoms away were averaged (1.27 ± 0.17). Since the one value at 35° for the change -H to -NH₂ (0.974) was 0.044 units smaller than the corresponding value at 25° (1.018), the change at 35° was taken to be 0.044 smaller than the average value at 25°, i.e., 1.23. The remaining values at 25° four to six atoms away are all due to the single change -H to -NH₂. The value six atoms away (0.68) did not seem reasonable when compared to the values for the change three to five atoms away, which decreased steadily from 1.27 to 0.46 to 0.26.
### TABLE 13

**EFFECT OF SUBSTITUENTS ON THE pKₐ VALUES OF THE CONJUGATE ACIDS OF AMINES IN WATER FOR THE CHANGE**

\[ H⁻⁻⁻N⁻⁻⁻(Z_n)⁻⁻⁻⁻⁻⁻⁻A \rightarrow H⁻⁻⁻⁻N⁻⁻⁻(Z_n)⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻㈠-Nazi...
Therefore the value at six atoms away was assumed to be in error. A new value was estimated by assuming that the change in $pK_a$ was a function of the energy of interaction between the positively charged nitrogen and the dipole set up between the other nitrogen and the carbon atom. Since the energy of a charge-dipole interaction is proportional to the inverse of the square of the distance between them, $pK_a$ was plotted against $1/d^2$, where $d$ is the distance. For example, for the charge three atoms away

$$H-\text{CH}_2\text{CH}_2^+\text{NH}_3 \rightarrow \text{H}_2\text{N}-\text{CH}_2\text{CH}_2^+\text{NH}_3$$

$d$ was taken to be 2.5. The change in $pK_a$ was also taken to be zero at an infinite distance ($1/d^2 = 0$). A smooth curve was drawn through the points and a value of -0.17
<table>
<thead>
<tr>
<th>Number of Atoms Away, n</th>
<th>$-\Delta pK_a^{25^\circ}$</th>
<th>$-\Delta pK_a^{35^\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.27 ± 0.17</td>
<td>1.23</td>
</tr>
<tr>
<td>4</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.17&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>From data in Table 13.

<sup>b</sup>See text.
was obtained for $\Delta pK_a$ six atoms away ($d = 5.5$).

The values for the change $-\text{NR}_2$ to $\text{NHR}_2^+$ ($R = H, \text{Me}, \text{Et}$) three to six atoms away are summarized in Table 15. The values at $25^\circ$ for the change $-\text{NR}_2$ to $\text{NHR}_2^+$ ($R = H, \text{Me}, \text{Et}$) three atoms away were averaged $(2.57 \pm 0.16)$. Since the one value at $35^\circ$ for the change $-\text{NH}_2$ to $-\text{NH}_3^+$ $(2.455)$ was $0.023$ units smaller than the corresponding value at $25^\circ$ $(2.478)$, the change at $35^\circ$ was taken to be $0.023$ smaller than the average value at $25^\circ$, i.e., $2.55$.

The values at $25^\circ$ four and five atoms away are due to the single change $-\text{NH}_2$ to $-\text{NH}_3^+$ while the value six atoms away is the average of seven changes of the type $-\text{NR}_2$ to $-\text{NHR}_2^+$. The value six atoms away $(0.68 \pm 0.27)$ can be compared with values that can be calculated from the statistically corrected $pK_a$'s of compounds $1$ and $3$.

\[
\begin{align*}
\text{Me}_2\text{N} & \quad \text{Me} & \quad \text{N} & \quad \text{NMe}_2 \\
\text{Me}_2\text{N} & \quad \text{N} & \quad \text{NMe}_2 & \\
\text{Me}_2\text{N} & \quad \text{N} & \quad \text{NMe}_2 & \\
\text{Me}_2\text{N} & \quad \text{N} & \quad \text{NMe}_2 & \\
\text{Me}_2\text{N} & \quad \text{N} & \quad \text{NMe}_2 & \\
\text{Me}_2\text{N} & \quad \text{N} & \quad \text{NMe}_2 & \\
\text{Me}_2\text{N} & \quad \text{N} & \quad \text{NMe}_2 & \\
\end{align*}
\]

$1$  
$pK_{a1} = 9.03^{12}$  
$pK_{a2} = 8.82^{13}$  

$3$  
$pK_{a1} = 8.95^{14}$  
$pK_{a2} = 8.58$  
$pK_{a3} = 7.69^{15}$

12. $0.30$ has been subtracted as a statistical correction.
TABLE 15
EFFECT OF SUBSTITUENTS ON THE pKₐ VALUES OF THE CONJUGATE ACIDS OF AMINES IN WATER FOR THE CHANGE

\[ \text{H}^\text{+} - \text{N}^- (\text{Z}_{n-1}) - \text{NR}_2 \rightarrow \text{H}^\text{+} - \text{N}^- (\text{Z}_{n-1}) - \text{NHR}_2^+ \ (R = \text{H, Me, Et})^a \]

<table>
<thead>
<tr>
<th>Number of Atoms Away, n</th>
<th>(-\Delta pK_a^{25^\circ})</th>
<th>(-\Delta pK_a^{35^\circ})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.57 ± 0.16</td>
<td>2.55</td>
</tr>
<tr>
<td>4</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.68 ± 0.27</td>
<td></td>
</tr>
</tbody>
</table>

^aFrom data in Table 13.

13. 0.30 has been added as a statistical correction.
14. 0.48 has been subtracted as a statistical correction.
15. 0.48 has been added as a statistical correction.
The values for $-\Delta pK_a$ are from $10.21$ and from $30.37$ and $0.63$. The average value of $0.40 \pm 0.15$ is within the range of the value in Table 15.

From the data in Tables 14 and 15 the $pK_a$ values at $35^\circ$ of the conjugate acids of the amino groups in PEI were estimated. The following terms were defined as follows.

\[
\begin{align*}
  p^+ t &= H_3NCH_2CH_2N^- \\
  p^+ Ss &= H_3NCH_2CH_2NHCH_2CH_2NH- \\
  pS^+ s &= H_2NCH_2CH_2NH_2CH_2NH- \\
  pS^+ s &= H_2NCH_2CH_2NHCH_2CH_2NH_2- \\
  p^+ Ss^+ &= H_3NCH_2CH_2NHCH_2CH_2NH_2^+
\end{align*}
\]

Similar terms were defined analogously. First of all the effect of $\alpha$-nitrogens (three atoms away) on the $pK_a$ values was considered. Assuming the effect of $-NR_2$ substituents to be the same as the effect of $-NH_2$, the $pK_a$ of primary nitrogens was taken as the statistically corrected $pK_a$ of $H_2NCH_2CH_2NH_3^+$ ($9.35$). For secondary nitrogens the $pK_a$ of $Et_2NH_2^+$ ($10.64$) was corrected for two $\alpha$-nitrogens ($2 \times 1.23$), giving a value of $8.18$. Likewise for tertiary nitrogens the $pK_a$ of $Et_3NH^+$ ($10.45$) was corrected for three $\alpha$-nitrogens ($3 \times 1.23$), giving a
value of 6.76. The $pK_a$ values were further corrected for both protonated and unprotonated $\beta$-nitrogens (six atoms away). Since only the values at 25° for $-\Delta pK_a$ were known, the respective values of 0.68 and 0.17 were used. For example, the $pK_a$ of $\text{p}^+\text{Ss}$ was estimated by correcting for one $\beta$-nitrogen ($9.35 - 0.17 = 9.18$). However for some of the species the number and type of $\beta$-nitrogen were unknown. For example, in $\text{P}^+\text{t}$ there must be two $\beta$-nitrogens but the type and state of protonation of these nitrogens is unknown. Therefore it was assumed that each of the $\beta$-nitrogens was protonated to the same extent as the polymer as a whole at pH 8.5. The fraction of all the nitrogens protonated ($FN^+$) at this pH was determined experimentally by titration of PEI solution with hydrochloric acid (Table 16). Hence for $\text{P}^+\text{t}$ the $pK_a$ was estimated by correcting for two $\beta$-nitrogens and further correcting for the $\beta$-nitrogens being protonated $[9.35 - 2(0.17) - 2(0.68)(FN^+)]$. In estimating the $pK_a$ values it was also assumed that unknown nitrogens were not protonated if the adjacent known nitrogen was already protonated. For example, in $\text{pSs}^+$ the nitrogen $\alpha$ to $\text{s}^+$ (to the right) was not allowed to be protonated although the $\beta$-nitrogens were allowed to be protonated. In $\text{pSs}^+$ the number of $\beta$-nitrogens (to the right) was taken to be the average of the minimum (0) and maximum (2).
### TABLE 16

**FRACTION OF NITROGENS PROTONATED AT pH 8.5**

<table>
<thead>
<tr>
<th>PEI</th>
<th>FN⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.301</td>
</tr>
<tr>
<td>1200</td>
<td>0.252</td>
</tr>
<tr>
<td>1800</td>
<td>0.212</td>
</tr>
</tbody>
</table>

* Determined in the titration of 0.1 N PEI solution with 1 M hydrochloric acid at 35°C.
number possible, i.e., 1. Thus the pKₐ of pS⁺ was estimated by correcting for two β-nitrogens and one β-nitrogen protonated to the same extent as the polymer as a whole \([8.18 - 2(0.17) - 1(0.68)(FN⁺)]\). Finally in estimating the pKₐ value of species such as p⁺S⁺, a factor of 2.55 was used to correct for the protonated α-nitrogens.

The pKₐ values of the conjugate acids of only two types of tertiary nitrogens were estimated. The first, Tnnn⁺, is a tertiary nitrogen with one protonated and two unprotonated α-nitrogens of any type; the second, Tnnn, is a tertiary nitrogen with three unprotonated α-nitrogens. The pKₐ values were corrected for only one β-nitrogen. Thus the acidities of T⁺nnn⁺ and T⁺nnn were underestimated (and the basicities of Tnn⁺ and Tnn overestimated) because additional β-nitrogens are likely and the protonation of some β-nitrogens is also likely.

Table 17 lists the number of β-nitrogens and protonated α and β-nitrogens for various groups of nitrogens. Table 18 summarizes the resulting pKₐ values for the nitrogens in PEI-600, 1200, and 1800.
# TABLE 17

NUMBER OF β-NITROGENS AND PROTONATED α AND β-NITROGENS IN VARIOUS GROUPS OF NITROGENS

<table>
<thead>
<tr>
<th>Acid²</th>
<th>pK</th>
<th>Number of α-N⁺</th>
<th>Number of β-N⁺</th>
<th>Number of β-N⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primaries:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P⁺⁺t</td>
<td>P1</td>
<td>0</td>
<td>2</td>
<td>(2xFN⁺⁺)</td>
</tr>
<tr>
<td>p⁺⁺S⁺⁺, p⁺⁺St</td>
<td>P2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>p⁺⁺S⁺⁺⁺</td>
<td>P3</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>P⁺⁺⁺⁺</td>
<td>P4</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Secondaries:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pS⁺⁺s</td>
<td>S1</td>
<td>0</td>
<td>1</td>
<td>(1xFN⁺⁺)</td>
</tr>
<tr>
<td>pS⁺⁺⁺⁺, sS⁺⁺⁺⁺, s⁺⁺St</td>
<td>S2</td>
<td>0</td>
<td>2</td>
<td>(2xFN⁺⁺)</td>
</tr>
<tr>
<td>sS⁺⁺⁺⁺</td>
<td>S3</td>
<td>0</td>
<td>3</td>
<td>(3xFN⁺⁺)</td>
</tr>
<tr>
<td>tS⁺⁺⁺⁺</td>
<td>S4</td>
<td>0</td>
<td>4</td>
<td>(4xFN⁺⁺)</td>
</tr>
<tr>
<td>pS⁺⁺⁺⁺, s⁺⁺S⁺⁺⁺⁺, s⁺⁺St</td>
<td>S5</td>
<td>0</td>
<td>2(1-3)</td>
<td>(1xFN⁺⁺)</td>
</tr>
<tr>
<td>s⁺⁺S⁺⁺⁺⁺</td>
<td>S6</td>
<td>0</td>
<td>2(1-3)</td>
<td>1+(1xFN⁺⁺)</td>
</tr>
<tr>
<td>p⁺⁺S⁺⁺⁺⁺</td>
<td>S7</td>
<td>1</td>
<td>1</td>
<td>(1xFN⁺⁺)</td>
</tr>
<tr>
<td>pS⁺⁺⁺⁺⁺⁺</td>
<td>S8</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>p⁺⁺⁺⁺⁺⁺⁺</td>
<td>S9</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>p⁺⁺⁺⁺⁺⁺⁺⁺</td>
<td>S10</td>
<td>1</td>
<td>2</td>
<td>(2xFN⁺⁺)</td>
</tr>
<tr>
<td>s⁺⁺⁺⁺⁺⁺⁺⁺</td>
<td>S11</td>
<td>1</td>
<td>2</td>
<td>(1xFN⁺⁺)</td>
</tr>
<tr>
<td>s⁺⁺⁺⁺⁺⁺⁺⁺⁺</td>
<td>S12</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>s⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺</td>
<td>S13</td>
<td>1</td>
<td>3</td>
<td>(2xFN⁺⁺)</td>
</tr>
</tbody>
</table>
### TABLE 17 (Continued)

<table>
<thead>
<tr>
<th>Acid&lt;sup&gt;a&lt;/sup&gt;</th>
<th>pK</th>
<th>Number of α-N&lt;sup&gt;+&lt;/sup&gt;</th>
<th>Number of β-N&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Number of β-N&lt;sup&gt;+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sup&gt;+&lt;/sup&gt;n.nn&lt;sup&gt;+&lt;/sup&gt;</td>
<td>T1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>T&lt;sup&gt;+&lt;/sup&gt;n.nn</td>
<td>T2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup>For loss of a proton from underlined nitrogen in ambiguous cases.

<sup>b</sup>Values in parenthesis are the minimum and maximum number possible. The average value was used.
### TABLE 18

**pK\textsubscript{a} VALUES OF THE CONJUGATE ACIDS OF THE NITROGENS IN POLYETHYLENIMINES AT 35\degree\ AND ZERO IONIC STRENGTH**

<table>
<thead>
<tr>
<th>Acid\textsuperscript{a}</th>
<th>pK</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primaries:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(p^+t)</td>
<td>P1</td>
<td>8.60</td>
<td>8.67</td>
<td>8.72</td>
</tr>
<tr>
<td>(p^+S_s, p^+St)</td>
<td>P2</td>
<td>9.18</td>
<td>9.18</td>
<td>9.18</td>
</tr>
<tr>
<td>(p^+S_s^+)</td>
<td>P3</td>
<td>8.50</td>
<td>8.50</td>
<td>8.50</td>
</tr>
<tr>
<td>(p^+S^+)</td>
<td>P4</td>
<td>6.63</td>
<td>6.63</td>
<td>6.63</td>
</tr>
<tr>
<td><strong>Secondaries:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(pS^+s)</td>
<td>S1</td>
<td>7.80</td>
<td>7.84</td>
<td>7.87</td>
</tr>
<tr>
<td>(pS^+t, sS^+s)</td>
<td>S2</td>
<td>7.43</td>
<td>7.50</td>
<td>7.55</td>
</tr>
<tr>
<td>(sS^+t)</td>
<td>S3</td>
<td>7.06</td>
<td>7.16</td>
<td>7.24</td>
</tr>
<tr>
<td>(tS^+t)</td>
<td>S4</td>
<td>6.68</td>
<td>6.82</td>
<td>6.92</td>
</tr>
<tr>
<td>(pS^+S_s, S^+S_s, s^+St)</td>
<td>S5</td>
<td>7.64</td>
<td>7.67</td>
<td>7.70</td>
</tr>
<tr>
<td>(s^+S_s^+)</td>
<td>S6</td>
<td>6.96</td>
<td>6.99</td>
<td>7.02</td>
</tr>
<tr>
<td>(p^+S^+s)</td>
<td>S7</td>
<td>5.26</td>
<td>5.29</td>
<td>5.32</td>
</tr>
<tr>
<td>(pS^+s)</td>
<td>S8</td>
<td>5.46</td>
<td>5.46</td>
<td>5.46</td>
</tr>
<tr>
<td>(p^+S^+s^+)</td>
<td>S9</td>
<td>2.91</td>
<td>2.91</td>
<td>2.91</td>
</tr>
<tr>
<td>(p^+S^+t)</td>
<td>S10</td>
<td>4.88</td>
<td>4.95</td>
<td>5.00</td>
</tr>
<tr>
<td>(s^+S^+s)</td>
<td>S11</td>
<td>5.08</td>
<td>5.12</td>
<td>5.15</td>
</tr>
<tr>
<td>(s^+S^+s^+)</td>
<td>S12</td>
<td>2.74</td>
<td>2.74</td>
<td>2.74</td>
</tr>
<tr>
<td>(s^+S^+t)</td>
<td>S13</td>
<td>4.71</td>
<td>4.78</td>
<td>4.83</td>
</tr>
<tr>
<td>Acid&lt;sup&gt;a&lt;/sup&gt;</td>
<td>pK</td>
<td>PEI-600</td>
<td>PEI-1200</td>
<td>PEI-1800</td>
</tr>
<tr>
<td>-----------------</td>
<td>----</td>
<td>---------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>Tertiaries:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T^+ \text{n} \text{n} \text{n}^+ )</td>
<td>T1</td>
<td>4.04</td>
<td>4.04</td>
<td>4.04</td>
</tr>
<tr>
<td>( T^+ \text{n} \text{n} \text{n} )</td>
<td>T2</td>
<td>6.59</td>
<td>6.59</td>
<td>6.59</td>
</tr>
</tbody>
</table>

<sup>a</sup>For loss of a proton from underlined nitrogen in ambiguous cases.
Estimation of the State of Protonation in Polyethylenimines at pH 8.5

The state of protonation in the polymers at pH 8.5 was estimated by solving for the terms on the right side of eqs 22-34.

\[
\begin{align*}
    P_{s_o} &= P^+ s + P^+ s + P_s \\
    P_{t_o} &= P^+ t + P_t \\
    p_{Ss_o} &= p^+ Ss + p^+ S^+ s + pSs^+ + p^+ Ss^+ + pSs \\
    p_{St_o} &= p^+ St + p^+ S^+ t + pSt \\
    s_{Sp_o} &= s^+ Sp + s^+ S^+ p + sSp^+ + s^+ Sp^+ + sSp \\
    s_{Ss_o} &= s^+ Ss + s^+ S^+ s + sSs^+ + s^+ Ss^+ + sSs \\
    s_{St_o} &= s^+ St + s^+ S^+ t + sSt \\
    t_{Sp_o} &= tS^+ p + tSp^+ + tSp \\
    t_{Ss_o} &= tS^+ s + tS^+ s + tSs^+ + tSs \\
    t_{St_o} &= tS^+ t + tSt \\
    T_{p_o} &= Tp^+ + Tp \\
    T_{s_o} &= Ts^+ + Ts \\
    T_{t_o} &= Tt
\end{align*}
\]

The values for the terms on the left side of these equations, with subscript zeros, were taken as the fraction of bond-halves listed in Table 11. The right hand side of these equations break these terms down into their various states of protonation. Protonation of tertiary nitrogens was neglected because of their low
basicity (Table 18). Also adjacent nitrogens were not protonated because of the low basicity of nitrogens with α-nitrogens protonated.

From symmetry the following equations may be written.

\[
\begin{align*}
  s^+Sp &= pSs^+ \\
  s^+Sp &= pS^+s \\
  sSp^+ &= p^+Ss \\
  s^+Sp^+ &= p^+Ss^+ \\
  sSp &= pSs \\
  tS^+p &= pS^+t \\
  tSp^+ &= p^+St \\
  tSp &= pSt \\
  tS^+s &= sS^+t \\
  tSs^+ &= s^+St \\
  tSs &= sSt \\
  Tp^+ &= F^+t \\
  Tp &= Pt \\
  sSs^+ &= s^+Ss
\end{align*}
\]

Equations may also be written for the acidity constants of the protonated nitrogens (Table 18).

\[
K_{p1} = \frac{H Pt}{p^+t}
\]
\[ K_{P2} = \frac{H \ pSs}{p^{+}Ss} = \frac{H \ pSt}{p^{+}St} \]  
\[ (50) \]

\[ K_{P3} = \frac{H \ pSs^{+}}{p^{+}Ss^{+}} \]  
\[ (51) \]

\[ K_{S1} = \frac{H \ pSs}{pS^{+}s} \]  
\[ (52) \]

\[ K_{S2} = \frac{H \ pSt}{pS^{+}t} = \frac{H \ sSs}{sS^{+}s} \]  
\[ (53) \]

\[ K_{S3} = \frac{H \ sSt}{sS^{+}t} \]  
\[ (54) \]

\[ K_{S4} = \frac{H \ tSt}{tS^{+}t} \]  
\[ (55) \]

\[ K_{S5} = \frac{H \ pSs \ F}{pS^{+}s} = \frac{H \ sSs \ F}{s^{+}Ss} = \frac{H \ sSt \ F}{s^{+}St} \]  
\[ (56) \]

\[ K_{S6} = \frac{H \ s^{+}Ss \ F}{s^{+}Ss^{+}} \]  
\[ (57) \]

In the above equations \( H \) is the hydrogen ion concentration and \( F \) is the fraction of nitrogens adjacent to secondary nitrogens that are neutral. Also

\[ Ps = pSs + pSs^{+} + pSt \]  
\[ (58) \]

\[ Ps^{+} = pS^{+}s + pS^{+}t \]  
\[ (59) \]

\[ P^{+}s = p^{+}Ss + p^{+}Ss^{+} + p^{+}St \]  
\[ (60) \]

\[ Ts = pSt + p^{+}St + sSt + s^{+}St + tSt \]  
\[ (61) \]
Finally because the number of bonds to $S^+$ must equal the number of bonds from $s^+$

$$sS^+p + tS^+p + pS^+s + sS^+s + tS^+s + pS^+t + sS^+t + tS^+t = Ps^+ + pSs^+ + p^+Ss^+ + sSs^+ + s^+Ss^+ + tSs^+ + Ts^+$$

Eqs 26, 29, 30, and 32 can be neglected for the moment because of the identities (eqs 35-47). Eq 34 is already solved. Eqs 23, 25, and 31 can easily be solved. Solving for $P^+t$ in eq 49 and substituting into eq 23 gives $Pt$.

$$Pt = \frac{Pt_0}{1 + \frac{H}{K_{P1}}}$$

$P^+t$ can then be calculated from eq 23. Likewise solving for $tS^+t$ in eq 55 and substituting into eq 31 gives $tSt$.

$$tSt = \frac{tSt_0}{1 + \frac{H}{K_{S4}}}$$

The value for $tS^+t$ can then be calculated from eq 31. Finally solving for $p^+St$ and $pS^+t$ in eqs 50 and 53, respectively, and substituting into eq 25 gives $pSt$. 

$$Ts^+ = pS^+t + sS^+t + tS^+t$$

(62)
\[
p_{St} = \frac{p_{St_0}}{1 + \frac{H}{K_{P2}} + \frac{H}{K_{S2}}} \quad (66)
\]

The values for \( p^{+}\text{St} \) and \( p^{+}\text{St} \) can then be calculated from eqs 50 and 53, respectively.

The remaining five equations (eqs 22, 24, 27, 28, and 33) can be solved in the following manner. Using the symmetry equations and substituting for \( \text{Ps}^{+} \) and \( \text{Ts}^{+} \) from eqs 59 and 62, respectively, eq 63 can be rewritten in the following form.

\[
p^{+}\text{S}s + s^{+}\text{S}s + s^{+}\text{St} = p^{+}\text{S}s + p^{+}\text{S}s + s^{+}\text{S}s + s^{+}\text{S}s + s^{+}\text{St} \quad (67)
\]

Also solving for \( s^{+}\text{S}s \) in eq 56 and substituting into eq 57 gives eq 68.

\[
s^{+}\text{S}s^{+} = s\text{S}s \left( \frac{H^2 F^2}{K_{S5} K_{S6}} \right) \quad (68)
\]

Now substituting for all the protonated terms (using eqs 50-54, 56, and 68) in eqs 24, 27, 28, and 67 gives the following four equations.

\[
p\text{S}s \left[ 1 + \frac{H}{K_{P2}} + \frac{H}{K_{P1}} + \left( \frac{H F}{K_{S5}} \right) \left( 1 + \frac{H}{K_{P3}} \right) \right] = p_{Ss_0} \quad (69)
\]
\[
s_{SS} \left[ 1 + \frac{H}{K_{S2}} + \frac{H}{K_{S5}} \left( 2F + \frac{HF^2}{K_{S6}} \right) \right] = s_{SS_0} \tag{70}
\]

\[
s_{St} \left( 1 + \frac{H}{K_{S3}} + \frac{HF}{K_{S5}} \right) = s_{St_0} \tag{71}
\]

\[
p_{SS} \frac{F}{K_{S5}} + s_{SS} \frac{F}{K_{S2}} + s_{St} \frac{F}{K_{S3}} = p_{SS} \left( \frac{F}{K_{S5}} \right) \left( 1 + \frac{H}{K_{P3}} \right) + \\
s_{SS} \left( \frac{F}{K_{S5}} \right) \left( 1 + \frac{HF}{K_{S6}} \right) + s_{St} \left( \frac{F}{K_{S5}} \right) \tag{72}
\]

Solving for \( p_{SS}, s_{SS}, \) and \( s_{St} \) in eqs 69-71, substituting into eq 72, and simplifying gives eq 73.

\[
\frac{p_{SS_0} K_{P2} \left[ K_{P3} (K_{S5} - K_{S1}F) - HK_{S1}F \right]}{K_{P3} K_{S5} \left[ K_{P2} K_{S1} + H(K_{P2} + K_{S1}) \right] + HK_{P2} K_{S1} F (K_{P3} + H)} + \\
\frac{s_{SS_0} \left[ K_{S6} (K_{S5} - K_{S2}F) - HK_{S2}F^2 \right]}{K_{S5} K_{S6} (K_{S2} + H) + HK_{S2} F (2K_{S6} + HF)} + \\
\frac{s_{St_0} (K_{S5} - K_{S3}F)}{K_{S5} (K_{S3} + H) + HK_{S3}F} = 0 \tag{73}
\]

The only unknown in eq 73 is \( F \) since \( p_{Sc_0}, s_{SS_0}, \) and \( s_{St_0} \) are known from Table 11, the acidity constants are known from the corresponding \( pK \) values in Table 18, and \( H \) is taken to be the hydrogen ion concentration at \( pH \ 8.5 \).
Eq 73 is of the fourth degree and was solved using the Newton Raphson Method. In the solution initial estimates of the value of F had to be made. Since F is the fraction of nitrogen adjacent to secondaries that are neutral, F had to be between 0 and 1. The values of F obtained for PEI-600, 1200, and 1800 were 0.495, 0.512, and 0.544, respectively, regardless of whether the initial estimates were 1.0, 0.7, or 0.

With the value of F known for each of the polymers, values for pSs, sSs, and sSt were calculated from eqs 69-71. The remaining terms in eqs 24, 27, and 28 were then calculated using the appropriate acidity equation (eqs 49-57). The terms in eqs 22 and 23 were subsequently solved using eqs 58-62. Using the identity equations (eqs 35-48), all the unknowns in eqs 22-34 are known.

The resulting values are, however, in terms of bond-halves since the terms of the left sides of eqs 22-34 were taken from Table 11, and must be converted so that they are expressed in terms of nitrogens. The Ps+ term, for example, represents the fraction of the total number of bond halves that lead from protonated second-


17. The equation was solved using a computer program written by Dr. William H. Sachs.
aries to primaries. Division by $P_x$ (Table 11), which is the fraction of the total number of bond-halves that lead from any nitrogen to primaries, gives the fraction of the primary bond-halves that come from protonated secondaries. Multiplication by $F_P$ (Table 10), which is the fraction of all nitrogens that are primaries, then gives the fraction of all nitrogens that are primaries and have adjacent protonated secondary neighbors, listed in Table 19 as $P_s^+$. The secondary terms were converted in the same manner, dividing by $S_x$ and multiplying by $F_S$. The results for all primary and secondary terms are given in Table 19.

When the terms involving tertiary nitrogens were defined, two of the three nitrogens were not specified. Thus $T_p$ is the fraction of the total number of bond-halves that lead from primaries to teritiaries with any two other adjacent nitrogens. An assumption was made that each tertiary nitrogen could have only one protonated adjacent nitrogen. Thus, of the three bond-halves that lead to teritiaries, only one may come from a protonated nitrogen. $T_n^+$ is defined as the sum of $T_p^+$ and $T_s^+$ or the fraction of the total number of bond-halves that lead from protonated nitrogens to teritiaries. Since each tertiary nitrogen that has one bond-half coming from a protonated nitrogen must have two other bond-halves coming from unprotonated nitrogens, the
TABLE 19

STATE OF PROTONATION OF POLYETHYLENIMINES AT pH 8.5 AND 35°

<table>
<thead>
<tr>
<th>Fraction</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primaries:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P^+s$</td>
<td>0.145</td>
<td>0.122</td>
<td>0.116</td>
</tr>
<tr>
<td>$P^+s^+$</td>
<td>0.00456</td>
<td>0.00407</td>
<td>0.00416</td>
</tr>
<tr>
<td>$P^+s^+$</td>
<td>0.0311</td>
<td>0.0263</td>
<td>0.0250</td>
</tr>
<tr>
<td>$P^+t$</td>
<td>0.0975</td>
<td>0.105</td>
<td>0.107</td>
</tr>
<tr>
<td>$P^+t^+$</td>
<td>0.0773</td>
<td>0.0714</td>
<td>0.0641</td>
</tr>
<tr>
<td><strong>Secondaries:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P^+s^+,s^+Sp^+$</td>
<td>0.0411</td>
<td>0.0313</td>
<td>0.0291</td>
</tr>
<tr>
<td>$P^+s^+,s^+Sp^+$</td>
<td>0.00174</td>
<td>0.00143</td>
<td>0.00141</td>
</tr>
<tr>
<td>$P^+s^+,s^+Sp^+$</td>
<td>0.00058</td>
<td>0.00049</td>
<td>0.00052</td>
</tr>
<tr>
<td>$P^+s^+,s^+Sp^+$</td>
<td>0.00058</td>
<td>0.00049</td>
<td>0.00052</td>
</tr>
<tr>
<td>$P^+s^+Sp$</td>
<td>0.00860</td>
<td>0.00654</td>
<td>0.00608</td>
</tr>
<tr>
<td>$P^+s^+Sp$</td>
<td>0.0305</td>
<td>0.0293</td>
<td>0.0283</td>
</tr>
<tr>
<td>$P^+s^+Sp$</td>
<td>0.00054</td>
<td>0.00061</td>
<td>0.00067</td>
</tr>
<tr>
<td>$P^+s^+Sp$</td>
<td>0.00054</td>
<td>0.00061</td>
<td>0.00067</td>
</tr>
<tr>
<td>$P^+s^+Sp$</td>
<td>0.00638</td>
<td>0.00612</td>
<td>0.00592</td>
</tr>
<tr>
<td>$s^+s^+,s^+s^+$</td>
<td>0.00467</td>
<td>0.00436</td>
<td>0.00483</td>
</tr>
<tr>
<td>$s^+s^+$</td>
<td>0.00588</td>
<td>0.00574</td>
<td>0.00636</td>
</tr>
<tr>
<td>$s^+s^+$</td>
<td>0.00007</td>
<td>0.00007</td>
<td>0.00009</td>
</tr>
<tr>
<td>$s^+s^+$</td>
<td>0.0690</td>
<td>0.0578</td>
<td>0.0565</td>
</tr>
</tbody>
</table>
TABLE 19 (Continued)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s^+ St, tSs^+$</td>
<td>0.00367</td>
<td>0.00436</td>
<td>0.00505</td>
</tr>
<tr>
<td>$sS^+ t, ts^+s$</td>
<td>0.00195</td>
<td>0.00261</td>
<td>0.00323</td>
</tr>
<tr>
<td>$sSt, tSs$</td>
<td>0.0543</td>
<td>0.0577</td>
<td>0.0591</td>
</tr>
<tr>
<td>$tS^+ t$</td>
<td>0.00064</td>
<td>0.00117</td>
<td>0.00162</td>
</tr>
<tr>
<td>$tSt$</td>
<td>0.0420</td>
<td>0.0567</td>
<td>0.0610</td>
</tr>
<tr>
<td><strong>Tertiaries:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tnnn$^+$</td>
<td>0.104</td>
<td>0.114</td>
<td>0.118</td>
</tr>
<tr>
<td>Tnnn</td>
<td>0.114</td>
<td>0.145</td>
<td>0.151</td>
</tr>
</tbody>
</table>
fraction of the total number of bond-halves that lead
to tertiaries with one protonated and two unprotonated
neighbors is $3 \times Tn^+$. Division by $T_x$ then gives the
fraction of the tertiary bond-halves that lead to ter-
tiaries with one protonated and two unprotonated neigh-
bors. Multiplication by $F_T$ gives $T_{nn}^+$, the fraction of
all nitrogens that are tertiaries and have one protonated
and two unprotonated adjacent nitrogens. The remaining
tertiaries therefore have no adjacent protonated nitro-
gens, i.e., $T_{nn} = F_T - T_{nn}^+$. The results for tertiaries
are also listed in Table 19.

The fractions of $P$'s and $S$'s protonated at pH 8.5
were calculated from eqs 74 and 75.

$$FP^+ = \frac{P^+S + P^+t}{FP}$$  \hspace{1cm} (74)

$$FS^+ = \frac{2pS^+s + 2pS^+t + sS^+t + 2sS^+t + tS^+t}{FS}$$  \hspace{1cm} (75)

The fraction of all types of nitrogens was then calcu-
lated from eq 76

$$FN^+_{\text{calc}} = FP^+ \times FP + FS^+ \times FS$$  \hspace{1cm} (76)

and compared to the experimentally determined values
from Table 16. The results are summarized in Table 20.
TABLE 20
FRACTION OF PRIMARY, SECONDARY, AND ALL TYPES OF NITROGENS IN POLYETHYLENIMINES THAT ARE PROTONATED AT pH 8.5 AND 35°

<table>
<thead>
<tr>
<th></th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP⁺</td>
<td>0.682</td>
<td>0.691</td>
<td>0.705</td>
</tr>
<tr>
<td>FS⁺</td>
<td>0.0351</td>
<td>0.0393</td>
<td>0.0448</td>
</tr>
<tr>
<td>FN⁺ \text{calcd}</td>
<td>0.257</td>
<td>0.243</td>
<td>0.241</td>
</tr>
<tr>
<td>FN⁺ a</td>
<td>0.301</td>
<td>0.252</td>
<td>0.212</td>
</tr>
<tr>
<td>% Deviation \textsuperscript{b}</td>
<td>14.6</td>
<td>3.42</td>
<td>-13.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From Table 16.

\textsuperscript{b}\% Deviation = \frac{\text{FN⁺} - \text{FN⁺}_{\text{calcd}}}{\text{FN⁺}} \times 100
Reactivity of Mono- and Diamines in α-Hydrogen Exchange

In order to estimate the catalytic ability of the primary, secondary, and tertiary nitrogens in PEI it was necessary to study some simple amines that act as mono-functional catalysts. Table 21 lists the catalytic constants, $k_B$, for the removal of deuterium from isobutyraldehyde-2-d for several mono- and diamines and the corresponding $pK_b$ values at 35° and zero ionic strength.

The $k_B$ value for methylamine, $k_m$, cannot be obtained directly because it is impossible to differentiate experimentally between attack of methylamine on uncomplexed deuteroaldehyde (AD) and attack of hydroxide ion on the N-methyliminium ion. However the term containing these two rate constants,

$$
(k_m + \frac{k_h'Kw}{KIH}) K_{MH}
$$

where $k_h'$ is the catalytic constant for the attack of hydroxide ion on the N-methyliminium ion, $K_w$ is the ion product constant of water, and

$$
K = \frac{[Me_2CDCH=NMe]}{[AD][MeNH_2]}
$$

$$
KIH = \frac{[H^+][Me_2CDCH=NMe]}{[Me_2CDCH=NMe^+]} 
$$
### TABLE 21

**CATALYTIC AND IONIZATION CONSTANTS FOR MONO- AND DIAMINES AT 35°**

<table>
<thead>
<tr>
<th>Amine</th>
<th>$\log k_B$</th>
<th>$\log k_B'$</th>
<th>$pK_b^{ab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeNH$_2$</td>
<td>2.0</td>
<td>0.59</td>
<td>3.37</td>
</tr>
<tr>
<td>Me$_2$NH</td>
<td>6.8</td>
<td>1.7</td>
<td>3.19</td>
</tr>
<tr>
<td>Me$_3$N</td>
<td>16</td>
<td>3.4</td>
<td>4.10</td>
</tr>
<tr>
<td>EtNH$_2$</td>
<td>1.6±0.04</td>
<td>0.50±0.09</td>
<td>3.36</td>
</tr>
<tr>
<td>Et$_2$NH</td>
<td>3.1</td>
<td>0.85</td>
<td>3.04</td>
</tr>
<tr>
<td>Et$_3$N</td>
<td>0.77</td>
<td>0.27</td>
<td>3.23</td>
</tr>
<tr>
<td>Piperidine</td>
<td>7.6±1.3</td>
<td>1.8±0.3</td>
<td>2.86</td>
</tr>
<tr>
<td>N-Methylpiperidine</td>
<td>1.45</td>
<td>0.45</td>
<td>3.66</td>
</tr>
<tr>
<td>Morpholine</td>
<td>0.76</td>
<td>0.26</td>
<td>5.59</td>
</tr>
<tr>
<td>N-Methylmorpholine</td>
<td>0.183</td>
<td>0.079</td>
<td>6.61</td>
</tr>
<tr>
<td>Piperazine</td>
<td>1.55</td>
<td>0.48</td>
<td>4.40</td>
</tr>
</tbody>
</table>
TABLE 21 (Continued)

<table>
<thead>
<tr>
<th>Amine</th>
<th>$10^3 k_B$, M$^{-1}$sec$^{-1}$</th>
<th>log $k_B$</th>
<th>$k_B'$, M$^{-1}$sec$^{-1}$</th>
<th>log $k_B'$</th>
<th>$pK_b$$^a$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Diazabicyclo-[2.2.2]octane</td>
<td>3.25$^i,m$</td>
<td>-2.49$^m$</td>
<td>0.89$^m$</td>
<td>-0.05$^m$</td>
<td>5.20$^{m,n}$</td>
</tr>
<tr>
<td>3-Quinuclidinone</td>
<td>0.49$^o$</td>
<td>-3.37</td>
<td>0.16</td>
<td>-0.79</td>
<td>6.75$^o$</td>
</tr>
</tbody>
</table>

$^a$At zero ionic strength.

$^b$p$K_b$ values obtained by subtracting p$K_a$ from p$K_w$ of water at 35$^o$ and zero ionic strength (13.68).


$^e$Extrapolated from data at 30 and 40$^o$.


$^g$Estimated; see text.

$^h$Extrapolated from data at 20 and 40$^o$. 
<table>
<thead>
<tr>
<th>TABLE 21 (Continued)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i Determined in this study.</td>
</tr>
<tr>
<td>k Extrapolated from data at 30 and 59.6°.</td>
</tr>
<tr>
<td>m k or k has been multiplied by a statistical factor of ½.</td>
</tr>
</tbody>
</table>
\[ K_{\text{MH}} = \frac{[H^+][\text{MeNH}_2]}{[\text{MeNH}_3^+]} \]

has been determined in the presence of 2,6-lutidine\textsuperscript{18} and methylamine\textsuperscript{18,19} buffers. The respective values are
6.25 x 10\textsuperscript{-14} sec\textsuperscript{-1} and 9.7 x 10\textsuperscript{-14} sec\textsuperscript{-1}. Hine et al.\textsuperscript{20} have shown that by assuming that 91\% of this term is due to the \( k_m \) component and 9\% due to the \( k_h' \) component, the correlation of \( \log (k_B'K_{\text{MH}}/K_{\text{IH}}) \) vs. \( \log k_b \), where \( k_B' \) is the catalytic constant for removal of deuterium from the N-methyliminium ion by a base, is optimized, especially for the hydroxide ion part.\textsuperscript{21} Therefore using the average of these two values and the value for \( K_{\text{MH}} \) (at 35\(^\circ\) and an ionic strength of 0.5 M\textsuperscript{20}), the value of \( k_m \) was calculated.

\[ k_m = \frac{(8.0 \times 10^{-14} \text{ sec}^{-1})(0.91)}{3.57 \times 10^{-11} \text{ M}} \]
\[ = 2.0 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}. \]

---

21. Reference 20 has some errors in this same calculation in the last paragraph of the Discussion.
The $k_B^*$ values listed in Table 21 were calculated in the following manner. The plot of $\log \left( \frac{k_B^* K_{MH}}{K_{IH}} \right)$ vs. $\log k_B$ is a straight line of slope 0.84. N-Methylmorpholine falls on this line and was used to calculate a y-intercept of 0.44. Therefore

$$\log \frac{k_B^* K_{MH}}{K_{IH}} = 0.84 \log k_B + 0.44$$

Substitution of the appropriate values at 35°C for the equilibrium constants ($K = 93.4 \text{ M}^{-1}$ using 53 M as the concentration of water, $K_{MH} = 3.57 \times 10^{-11} \text{ M}$ at an ionic strength of 0.5 M, and $K_{IH} = 1.32 \times 10^{-7} \text{ M}^{-2}$) the following equation was obtained.

$$\log k_B^* = 0.84 \log k_B + 2.04$$

The log $k_B^*$ value for each amine was calculated by substitution of the corresponding log $k_B$ value.

The $k_B^*$ values (for the attack of bases on N-methyliminium ion) should be more relevant to the removal of deuterium from the iminium ions derived from isobutylaldehyde and PEI than the $k_B$ values (for the attack of bases on the aldehyde itself). A Bronsted plot of $\log k_B^*$ vs. $\log K_b$ is given in Figure 6. The line drawn


Figure 6. Brønsted plot of catalysis constants for deuterium exchange of Me₂CDCH=NHMe⁺ in water at 35°. O primary amines; △ secondary amines; □ tertiary amines.
is the least squares line through the points for piperidine, piperazine, and morpholine.

The value of log $k_B'$ for ethylamine was estimated by comparison of the values for the methyl- and ethyl-substituted series. The amount by which the log $k_B'$ value for diethylamine lies below the log $k_B'$ value for dimethylamine was calculated to be 0.337 after correction for the difference in their basicities was made (using the slope of 0.311 for the line drawn in Figure 6). If the steric effect of two alkyl groups is twice the effect of one alkyl group, then the log $k_B'$ value for ethylamine would be $0.337/2$ or 0.168 units below the log $k_B'$ value for methylamine (neglecting a difference of only 0.01 in their $pK_B$ values). However if the steric effect from methylamine to ethylamine is negligible, then the log $k_B'$ value for the two would be identical. A value halfway between these two extremes was therefore used with an uncertainty large enough to cover both extremes. Hence log $k_B'$ for ethylamine should be $0.168/2$ or 0.084 below the value for methylamine, i.e., $(-0.23 - 0.084)$ or $-0.31 \pm 0.08$. 
Reactivity of Primary, Secondary, and Tertiary Nitrogens in Polyethylenimines

The rate constants for the removal of deuterium from the N-methyliminium ions derived from isobutyraldehyde by the various amino groups in PEI were estimated by using the Bronsted plot of \( \log k_B' \text{ vs. } \log K_b \) (Figure 6). The \( pK_b \) values for the nitrogens under consideration (see Table 18) were calculated from the \( pK_w \) at \( 35^\circ \) and zero ionic strength (13.68)\(^{24} \) and the estimated \( pK^a \) values of the conjugate acids of these species (Table 18). From the \( pK_b \) value for each type of nitrogen the \( k_B' \) value was obtained from Figure 6. The \( \log k_B' \) values for the amino groups in PEI were calculated from lines through the points for the three ethyl-substituted amines. The slope of a plot of \( \log k_B \text{ vs. } \log K_b \) was found to be 0.50 when steric effects were minimized, such as in the case of pyridines lacking 2- and 6-substituents (0.49) and phenoxide ions (0.53).\(^{25} \)

Multiplying this value by 0.84 (the slope of a plot of \( \log (k_B'KK_{MH}/K_{IH}) \text{ vs. } \log k_B \)\(^{20} \) to convert from \( \log k_B \) to \( \log k_B' \), a value of 0.42 was obtained for the slope

---


of the lines through the ethyl-substituted amines. For example, for primary nitrogens in PEI the log $k_B^*$ values were obtained from the $pK_b$ values and a line of slope 0.42 through the point for ethylamine. Therefore, for the primary nitrogen Pt in PEI-600 a value of -1.03 was calculated for log $k_B^*$ ($k_B^* = 9.29 \times 10^{-2} \text{ M}^{-1}\text{sec}^{-1}$) from the $pK_b$ of Pt (5.08) obtained from the $pK_a$ of $P^+$t (8.60). The log $k_B^*$ values for secondary and tertiary nitrogens were similarly obtained from lines of slope 0.42 through diethylamine and triethylamine, respectively.

The estimated contribution of each type of unprotonated nitrogen to the total reactivity was then calculated by multiplying the fraction (Table 19) by the corresponding rate constant (Table 22). For example in PEI-600 the primary nitrogen Pt is estimated to have a reactivity of $7.18 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$ obtained by multiplying its fraction, 0.0773, by its rate constant, $9.29 \times 10^{-2} \text{ M}^{-1}\text{sec}^{-1}$. However, the reactivity of Ps had to be estimated in a different manner since no $pK_a$ value was estimated for the conjugate acid, $P^+$s, and thus no rate constant could be estimated for Ps. The reactivity of Ps was therefore calculated by summing the individual reactivities of the primaries in pSs, pSs$^+$, and pSt. The fractions of these three species in Table 19 are in terms of secondary nitrogens and were therefore multi-
TABLE 22

ESTIMATED RATE CONSTANTS FOR THE DEDEUTERATION
OF Me₂CDCH=NHMe⁺ BY NITROGENS IN
POLYETHYLENIMINES AT 35° AND pH 8.5

<table>
<thead>
<tr>
<th>Nitrogen&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primaries:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>92.9</td>
<td>99.1</td>
<td>104</td>
</tr>
<tr>
<td>pSS, pSt</td>
<td>163</td>
<td>163</td>
<td>163</td>
</tr>
<tr>
<td>pSS⁺</td>
<td>84.3</td>
<td>84.3</td>
<td>84.3</td>
</tr>
<tr>
<td>pS⁺</td>
<td>13.8</td>
<td>13.8</td>
<td>13.8</td>
</tr>
<tr>
<td><strong>Secondaries:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pSS</td>
<td>54.9</td>
<td>56.7</td>
<td>58.2</td>
</tr>
<tr>
<td>pSt, sSS</td>
<td>38.2</td>
<td>40.7</td>
<td>42.9</td>
</tr>
<tr>
<td>sSS</td>
<td>26.6</td>
<td>29.3</td>
<td>31.7</td>
</tr>
<tr>
<td>tSt</td>
<td>18.5</td>
<td>21.1</td>
<td>23.4</td>
</tr>
<tr>
<td>p⁺SS</td>
<td>4.66</td>
<td>4.81</td>
<td>4.94</td>
</tr>
<tr>
<td>pSS⁺</td>
<td>5.68</td>
<td>5.68</td>
<td>5.68</td>
</tr>
<tr>
<td>p⁺SS⁺</td>
<td>0.482</td>
<td>0.482</td>
<td>0.482</td>
</tr>
<tr>
<td>p⁺St</td>
<td>3.24</td>
<td>3.46</td>
<td>3.65</td>
</tr>
<tr>
<td>s⁺SS</td>
<td>3.95</td>
<td>4.08</td>
<td>4.19</td>
</tr>
<tr>
<td>s⁺Ss⁺</td>
<td>0.409</td>
<td>0.409</td>
<td>0.409</td>
</tr>
<tr>
<td>s⁺St</td>
<td>2.75</td>
<td>2.94</td>
<td>3.09</td>
</tr>
</tbody>
</table>

<sup>a</sup> Nitrogen labels: P, S, T represent different types of nitrogens.
TABLE 22 (Continued)

<table>
<thead>
<tr>
<th>Nitrogen&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tnnn&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.547</td>
<td>0.547</td>
<td>0.547</td>
</tr>
<tr>
<td>Tnnn</td>
<td>6.44</td>
<td>6.44</td>
<td>6.44</td>
</tr>
</tbody>
</table>

<sup>a</sup>Rate constants for underlined nitrogen in ambiguous cases.
plied by a factor of 2 to obtain fractions in terms of primary nitrogens. Multiplying each of these fractions by the corresponding rate constant for the primary nitrogen (Table 22) and summing the three resulting reactivities, gives the reactivity of Ps. The estimated reactivities for the nitrogens in PEI-600, 1200, and 1800 are summarized in Table 23.

The reactivities of all primary, all secondary, and all tertiary nitrogens were summed to obtain the reactivity of each of the three types of nitrogens. The resulting value for each type was then divided by the respective fraction in the polymer (FP, FS, and FT from Table 10) to obtain the reactivity per P, S, and T. The reactivities relative to tertiary nitrogens in each of the PEI's and relative to tertiary nitrogens in PEI-1800 were calculated and are given in Table 24.
TABLE 23

REACTIVITY OF THE NITROGENS IN POLYETHYLENIMINES IN THE DEDEUTERATION OF Me$_2$CDCH=NHMe$^+$ AT 35$^\circ$ AND pH 8.5

<table>
<thead>
<tr>
<th>Nitrogen$^a$</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primaries</strong>:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ps$^+$</td>
<td>6.30</td>
<td>5.63</td>
<td>5.75</td>
</tr>
<tr>
<td>Ps</td>
<td>497</td>
<td>420</td>
<td>399</td>
</tr>
<tr>
<td>Pt</td>
<td>718</td>
<td>708</td>
<td>669</td>
</tr>
<tr>
<td><strong>Secondaries</strong>:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p$^+$$S_s$,s$^{Sp}$</td>
<td>19.2</td>
<td>15.1</td>
<td>14.4</td>
</tr>
<tr>
<td>p$S_s$,$s^+$$Sp$</td>
<td>0.329</td>
<td>0.278</td>
<td>0.295</td>
</tr>
<tr>
<td>p$^+$$S_s$,$s^+$$Sp$</td>
<td>0.0280</td>
<td>0.0236</td>
<td>0.0251</td>
</tr>
<tr>
<td>p$S_s$,$sSp$</td>
<td>47.2</td>
<td>37.1</td>
<td>35.4</td>
</tr>
<tr>
<td>p$^+$$St$,$tSp$</td>
<td>9.90</td>
<td>10.1</td>
<td>10.3</td>
</tr>
<tr>
<td>p$St$,$tSp$</td>
<td>24.4</td>
<td>24.9</td>
<td>25.4</td>
</tr>
<tr>
<td>s$^+$$S_s$,$sS_s$</td>
<td>1.85</td>
<td>1.78</td>
<td>2.02</td>
</tr>
<tr>
<td>s$^+$$S_s$</td>
<td>0.00286</td>
<td>0.00286</td>
<td>0.00368</td>
</tr>
<tr>
<td>s$S_s$</td>
<td>264</td>
<td>235</td>
<td>243</td>
</tr>
<tr>
<td>s$^+$$S_t$,$tS_s$</td>
<td>1.01</td>
<td>1.28</td>
<td>1.56</td>
</tr>
<tr>
<td>s$S_t$,$tS_s$</td>
<td>144</td>
<td>169</td>
<td>187</td>
</tr>
<tr>
<td>t$S_t$</td>
<td>77.7</td>
<td>119</td>
<td>143</td>
</tr>
</tbody>
</table>

$^a$ Reactivity, M$^{-1}$sec$^{-1}$
### TABLE 23 (Continued)

<table>
<thead>
<tr>
<th>Nitrogen&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tertiaries</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tnnn&lt;sup&gt;+&lt;/sup&gt;</td>
<td>5.67</td>
<td>6.22</td>
<td>6.44</td>
</tr>
<tr>
<td>Tnnn</td>
<td>73.5</td>
<td>93.5</td>
<td>97.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reactivity of P, S, and T and not p, s, and t.

### TABLE 24

RELATIVE REACTIVITIES OF THE NITROGENS IN POLYETHYLENIMINES IN THE DEDEUTERATION OF Me<sub>2</sub>CDCH=NHMe<sup>+</sup> AT 35° AND pH 8.5<sup>a</sup>

<table>
<thead>
<tr>
<th>Nitrogen</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>9.47 (8.92)</td>
<td>8.95 (8.93)</td>
<td>8.81</td>
</tr>
<tr>
<td>S</td>
<td>5.40 (5.09)</td>
<td>5.51 (5.50)</td>
<td>5.86</td>
</tr>
<tr>
<td>T</td>
<td>1 (0.94)</td>
<td>1 (1.00)</td>
<td>1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Values in parenthesis are relative to tertiary nitrogens in PEI-1800.
Catalytic Abilities of Polyethylenimines in the Dedeuteration of Isobutyraldehyde-2-d

The dedeuteration of isobutyraldehyde-2-d was carried out in the presence of 1.00 N PEI-600, 1200, and 1800 at pH 8.5. The first-order rate constants obtained are listed in Table 25. The rates relative to PEI-1800 were also calculated.

Since the dedeuteration actually takes place via the iminium ions derived from the aldehyde and the primary nitrogens in PEI and since the fraction of primary nitrogens differs from polymer to polymer, the PEI with the highest fraction of primary nitrogens should have the most iminium ions and therefore have the fastest rate. The magnitude of this effect was determined by the addition of an external base to the reaction solution and noting the resulting increase in rate due to the external base attacking the iminium ions.26

Because unhindered tertiary amines have been shown to be the most effective catalysts for their basicity in \( \alpha \)-hydrogen exchange,25 1,4-diazabicyclo[2.2.2]octane (Dabco) was chosen as the external base. The results

26. Different amounts of iminium ions present may not be the only factor involved. The reactivity of the complex formed from aldehyde and PEI may differ from polymer to polymer because of a change in conformation, for example.
TABLE 25

KINETICS OF THE DEDEUTERATION OF 0.054 M ISOBUTYRALDEHYDE-2-d IN THE PRESENCE OF 1.00 N PEI AND 1.00 N PEI, 0.200 N DABCO\textsuperscript{a} AT 35° AND pH 8.51 ± 0.03

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>pH</th>
<th>10^5 (k_p) sec(^{-1})</th>
<th>Relative (k_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-600</td>
<td>8.49</td>
<td>10.2</td>
<td>0.810</td>
</tr>
<tr>
<td>PEI-600 + Dabco</td>
<td>8.50</td>
<td>24.1</td>
<td></td>
</tr>
<tr>
<td>PEI-1200</td>
<td>8.51</td>
<td>12.1</td>
<td>0.960</td>
</tr>
<tr>
<td>PEI-1200 + Dabco</td>
<td>8.48</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td>PEI-1800</td>
<td>8.54</td>
<td>12.6</td>
<td>1</td>
</tr>
<tr>
<td>PEI-1800 + Dabco</td>
<td>8.51</td>
<td>23.5</td>
<td></td>
</tr>
</tbody>
</table>

Dabco Rates:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>10^5 (k_p) sec(^{-1})</th>
<th>Relative (k_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-600</td>
<td>13.9</td>
<td>1.28</td>
</tr>
<tr>
<td>PEI-1200</td>
<td>12.5</td>
<td>1.15</td>
</tr>
<tr>
<td>PEI-1800</td>
<td>10.9</td>
<td>1</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Total concentration of bases, without regard to the state of protonation.
for the deuteriation in the presence of 1.00 N PEI's and 0.200 N Dabco are given in Table 25. The difference between the values of the rate constants with and without Dabco for each PEI gives the rate constant for attack of Dabco on the complexed aldehyde. Division by the value for Dabco attacking the complex formed from PEI-1800 gave the relative rate constants of 1.28, 1.15, and 1 for Dabco attacking the complexes formed from isobutyraldehyde and PEI-600, 1200, and 1800, respectively.
Transition State for Bifunctional Catalysis

In Table 24 the reactivities of primary, secondary, and tertiary nitrogens in the dedeuteration of the iminium ion formed from isobutyraldehyde-2-d and methylamine (Me₂CDCH=NHMe⁺) were given. However, in the bifunctional catalysis by PEI's, the iminium ions involved are formed from the aldehyde and each of the polymers; the concentration of these iminium ions also varies from polymer to polymer. In the previous section an external base (Dabco) was observed to have relative rate constants of 1.28, 1.15, and 1 for attacking the complexes formed from the aldehyde and PEI-600, 1200, and 1800; this was said to reflect the relative amounts of iminium ions present. These differences in the fractions of aldehyde present as iminium ions or in the relative reactivities of the iminium ions should also affect the relative efficiencies of catalysis via attack of the internal amino groups in PEI's. Therefore to correct for the varying concentrations of iminium ions, the reactivities of the three types of nitrogens in the dedeuteration of Me₂CDCH=NHMe⁺ were converted into values for the dedeuteration of the PEI iminium ions by multiplying by 1.28, 1.15, and 1 for PEI-600, 1200, and 1800, respectively. The resulting reactivities are given in Table 26.

In Figure 4 a plot was made of the number of pri-
RELATIVE REACTIVITIES OF THE NITROGENS IN POLYETHYLENIMINES IN THE DEDUERATION OF THE IMINIUM IONS FORMED FROM ISOBUTYRALDEHYDE-2-d AND POLYETHYLENIMINES AT 35° AND pH 8.5

<table>
<thead>
<tr>
<th>Nitrogen</th>
<th>PEI-600</th>
<th>PEI-1200</th>
<th>PEI-1800</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>9.47 (11.4)</td>
<td>8.95 (10.3)</td>
<td>8.81</td>
</tr>
<tr>
<td>S</td>
<td>5.40 (6.52)</td>
<td>5.51 (6.33)</td>
<td>5.86</td>
</tr>
<tr>
<td>T</td>
<td>1 (1.20)</td>
<td>1 (1.15)</td>
<td>1</td>
</tr>
</tbody>
</table>

Values in parenthesis relative to tertiary nitrogens in PEI-1800.

The reactivity of each type of nitrogen at each distance away from the average primary was calculated by multiplying the number of each type by the corresponding reactivity (relative to tertiary nitrogens in PEI-1800) from Table 26. The resulting curves are given in Figure 7. These curves show that the majority of the dedeuteration is being done by primary and secondary nitrogens. The contribution of the tertiary nitrogens to the catalysis is actually less than shown in the curves since the basicity, and hence the reactivity, of Tmmn⁺ and Tmmn were overestimated.
Figure 7. Reactivity of the nitrogens in polyethylenimines vs. (CH₂CH₂N) units from the average primary: O primary nitrogens; △ secondary nitrogens; □ tertiary nitrogens.
The reactivity of the three types of nitrogens in each polymer at each distance was then summed to obtain the reactivity of all the nitrogens in the polymer. In Figure 8 the reactivity predicted for PEI-600, 1200, and 1800 at each distance is shown.

In order to compare the curves in Figure 8 with the relative rate constants for the three PEI's determined experimentally and listed in Table 25 (0.810, 0.960, and 1 for PEI-600, 1200, and 1800, respectively), the estimated reactivities of PEI-600 and 1200 were divided by the estimated reactivity of PEI-1800 at each \((\text{CH}_2\text{CH}_2\text{N})\) unit. The difference between the experimental and calculated reactivities (relative to PEI-1800) at each \((\text{CH}_2\text{CH}_2\text{N})\) unit was plotted in Figure 9. Distances at which the experimental and calculated reactivities are in close agreement should be the optimum distances for bifunctional catalysis. Five to seven \((\text{CH}_2\text{CH}_2\text{N})\) units between the primary nitrogen, which forms the iminium ion, and the nitrogen that removes the deuterium, seem to give the best correlation between the two reactivities. This corresponds to transition states consisting of 19, 22, and 25 atoms.
Figure 8. Reactivity of polyethylenimines vs. (CH$_2$CH$_2$N) units from the average primary:

- O PEI-600;
- △ PEI-1200;
- □ PEI-1800.
Figure 9. Reactivity relative to PEI-1800 (exptl - calcd) vs. (CH₂CH₂N) units from the average primary: ○ PEI-600; △ PEI-1200.
Catalysis by PEI-50,000

Since the rate constants increase on going from PEI-600 to 1200 to 1800, a polymer of much greater molecular weight was studied to see if the rate constant eventually levels off. The polymer chosen was reported to have a molecular weight of 40,000 to 60,000 and hence was called PEI-50,000.¹ Unlike the other three PEI's, which were available neat, PEI-50,000 is supplied as an aqueous solution reported to be at least 33% C₂H₅N by weight.¹,²

The dedeuteration of isobutyraldehyde-2-d was carried out in the presence of 1.00 N PEI-50,000 at several pH values. The resulting first-order rate constants are plotted vs. pH in Figure 10. Also plotted are previous data on PEI-600²⁻ and PEI-1800.²⁹ At pH 8.5 the rate constant for PEI-50,000 is not significantly different from the rate constant for PEI-1800. However at pH 8 and lower, the rate constant for PEI-50,000 is about 50% greater than the rate constant for PEI-1800. The increases

²⁷. Elemental analysis gave values of 19.52% C, 11.28% H, and 11.11% N. The percentage of chloride ion in the PEI solution was determined by the Volhard Method and found to be 0.86%. From these values 34-35% C₂H₅N was calculated.

²⁸. F. E. Rogers, unpublished observations, The Ohio State University.

Figure 10. First-order rate constants for the deuteriation of 0.054 M isobutyraldehyde-2-d at 35° vs. pH: O 1.01 N PEI-600; □ 0.97 ± 0.03 N PEI-1800; ◇ 1.00 N PEI-50,000.
in rate constant with an increase in molecular weight does tend to level off at the lower pH's however. A threefold increase in molecular weight from PEI-600 to PEI-1800 is enough to produce a 50% increase in rate, whereas a 28-fold increase in molecular weight from PEI-1800 to PEI-50,000 is required to produce an additional 50% increase in rate. Thus the additional nitrogens in PEI-50,000 are at too great a distance to do any large amount of catalysis.

The effect of the concentration of PEI-50,000 on the first-order rate constant was also studied. The results for the dedeuteration of 0.054 M aldehyde at pH 8.5 and 35° are given in Table 27 and plotted in Figure 11 along with previous data on PEI-1800. The rate constant for PEI-1800 was found to increase with increasing PEI concentration and then level off at about 0.4 N, i.e., at about eight amino groups per aldehyde molecule. The points for PEI-50,000 suggest the same type of behavior as those for PEI-1800 with the rate leveling off at a slightly higher value. Thus PEI-50,000 has about the same ability in forming complex with aldehyde as PEI-1800 does.

The percent tertiary nitrogen in PEI-50,000 was

TABLE 27
KINETICS OF THE DEDEUTERATION OF 0.054 M
ISOBUTYRALDEHYDE-2-d IN THE PRESENCE OF
PEI-50,000 at 35°

<table>
<thead>
<tr>
<th>[PEI-50,000]</th>
<th>pH</th>
<th>$10^5 k_p$, sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>8.60</td>
<td>6.53</td>
</tr>
<tr>
<td>0.300</td>
<td>8.51</td>
<td>11.5</td>
</tr>
<tr>
<td>0.600</td>
<td>8.52</td>
<td>15.0</td>
</tr>
<tr>
<td>1.00</td>
<td>6.81</td>
<td>14.9</td>
</tr>
<tr>
<td>1.00</td>
<td>7.55</td>
<td>22.5</td>
</tr>
<tr>
<td>1.00</td>
<td>7.96</td>
<td>21.0</td>
</tr>
<tr>
<td>1.00</td>
<td>8.52</td>
<td>14.1</td>
</tr>
<tr>
<td>1.00</td>
<td>8.56</td>
<td>14.9</td>
</tr>
<tr>
<td>1.00a</td>
<td>8.50</td>
<td>23.6</td>
</tr>
</tbody>
</table>

*a*Added 0.200 N Dabco.
Figure 11. First-order rate constants for the dedeuteration of 0.054 M isobutyraldehyde-2-d at 35° and pH 8.51 ± 0.09 vs. normality of polyethylenimine: □ PEI-1800; ◇ PEI-50,000.
estimated from a plot of the percentages of the three types of amino groups in PEI-600, 1200, and 1800 (Table 10) versus molecular weight. In Figure 12 it can be seen that as the molecular weight increases the percent tertiary increases while the percent primary decreases. Since the molecular weight of PEI-50,000 is much greater than that of the smaller polymers, the percentages of primary and tertiary should be approximately equal. Thus from Figure 12 a value of about 29% for primary and tertiary nitrogens can be estimated. This value can be compared with the value obtained experimentally. PEI-50,000 was acetylated with acetic anhydride in the same manner as the smaller polymers (taking into account the 67% water in the polymer sample) and titrated with p-toluenesulfonic acid. After correcting for the presence of 0.88% hydrochloric acid in the sample initially (3.1%), a value of 26.5% tertiary was obtained. However as in the case of the smaller polymers this value reflects only the tertiary nitrogens that can be titrated. To account for the untitratable nitrogens the experimental values for PEI-600, 1200, and 1800 were increased by 0.4, 1.0, and 1.5, i.e., correction of 1.9, 4.0, and

31. For example, if PEI-50,000 is acyclic and contains primary end groups, the percentages should differ by only 2/1160 or 0.2%.
Figure 12. Percentages of the three types of amino groups in polyethylenimines vs. molecular weight: ○ primary nitrogens; △ secondary nitrogens; □ tertiary nitrogens.
5.9%, respectively. A maximum value of about 14% unti-
trated nitrogens can be estimated for PEI-50,000 by
assuming that all tertiary nitrogens are grouped together.
If a value halfway between the value for PEI-1800 and
that of 14% is taken (about 10%), the experimental value
for PEI-50,000 can be corrected to 29.1%, in agreement
with the value estimated from Figure 12. Thus PEI-50,000
is estimated to contain about 29% primary, 42% secondary,
and 29% tertiary amino groups.

The rate constants for the attack of Dabco on the
iminium ions formed from isobutyraldehyde-2-d and each
of the PEI's can be compared with the fraction of all the
nitrogens protonated ($F_{N+}$) at pH 8.5 to determine if Dabco
experiences any steric effect with the larger polymer.
Since it was previously estimated (Table 20) that it is
mainly the primary nitrogens that are protonated, $F_{N+}$
should be related to the extent of iminium ion formation.
In Table 28 the Dabco rate constants are listed along
with $F_{N+}$ for each polymer, determined from the amount of
hydrochloric acid required to reach a pH value of 8.5 in
the reactions solutions (and corrected for the amount of
hydrochloric acid present initially in the polymer sample).
Division of the rate constant by the respective value of
$F_{N+}$ leads to consistent values; the value for PEI-50,000
is only 6% from the average value which is well within
### TABLE 28
COMPARISON OF DABCO RATE CONSTANTS WITH THE EXTENT OF PROTONATION IN POLYETHYLENIMINES AT pH 8.5

<table>
<thead>
<tr>
<th>PEI (sec⁻¹)</th>
<th>10⁵k_p</th>
<th>FN⁺</th>
<th>10⁵k_p/FN⁺</th>
<th>FP</th>
<th>%P⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>13.9ᵇ</td>
<td>0.344</td>
<td>40.4</td>
<td>0.355ᶜ</td>
<td>97.0</td>
</tr>
<tr>
<td>1200</td>
<td>12.5ᵇ</td>
<td>0.321</td>
<td>38.9</td>
<td>0.329ᶜ</td>
<td>97.6</td>
</tr>
<tr>
<td>1800</td>
<td>10.9ᵇ</td>
<td>0.279</td>
<td>39.1</td>
<td>0.316ᶜ</td>
<td>88.4</td>
</tr>
<tr>
<td>50,000</td>
<td>9.5ᵈ</td>
<td>0.223</td>
<td>42.6</td>
<td>0.29ᵉ</td>
<td>77</td>
</tr>
</tbody>
</table>

Ave 40.25

ᵃCalculated from the amount of hydrochloric acid added to the kinetic solution to bring the pH to 8.5 (after the addition of aldehyde), corrected for 0.2, 0.3, 0.6, and 3.1% protonation by hydrochloric acid in the original sample determined by Volhard analysis.

ᵇFrom Table 25.

ᶜFrom Table 10.

ᵈFrom comparison of the fifth and seventh entries in Table 27.

ᵉEstimated from Figure 12.
the experimental uncertainty. Therefore it is evident that Dabco can attack the iminium ions formed from PEI-50,000 with the same ease as it attacks the iminium ions formed from the smaller polymers.

Also listed in Table 28 are the fractions of primary nitrogens in each of the polymers. If we assume for the moment that only primary nitrogens are protonated, the percent of the primaries that are protonated (\(\% P^+\)) can be calculated. The resulting values show that the extent of protonation decreases with the larger polymers. However the magnitude of this effect is not very large and can be explained in terms of the increasing build up of positive charge on the larger polymers.
EXPERIMENTAL

Chemicals

Acetic Acid, glacial, reagent grade, was obtained from J. T. Baker Chemical Co.

Acetic Anhydride, reagent grade, was obtained from J. T. Baker Chemical Co.

Chloroform, reagent grade, was obtained from J. T. Baker Chemical Co.

1,4-Diazabicyclo[2.2.2]octane (Dabco) was obtained from Aldrich Chemical Co.

Diethylamine, reagent grade, was obtained from J. T. Baker Chemical Co.

Diethyl Ether, anhydrous, reagent grade, was obtained from J. T. Baker Chemical Co.

Ethyl Alcohol, 95%, USP grade, was obtained from J. T. Baker Chemical Co.

Ferric Ammonium Sulfate, reagent grade, was obtained from Mallinckrodt Chemical Works.
Formaldehyde, 37\%, certified A.C.S. grade, was obtained from Fisher Scientific Co.

Formic Acid, 97-100\%, was obtained from Matheson Coleman and Bell.

Hexamethyltriethylenetetramine, was obtained from Ames Laboratories.

Hydrochloric Acid, concentrated, reagent grade, was obtained from J. T. Baker Chemical Co.

Hydrochloric Acid solutions of standard normality were obtained from the Reagent Laboratory of The Ohio State University.

Hydrogen Chloride, anhydrous, technical grade, was obtained from Matheson Co.

Isobutyraldehyde was obtained from Aldrich Chemical Co.

Isobutyraldehyde-2-d was supplied by Dr. Edward F. Glod of The Ohio State University. It was synthesized by the \( \text{D}_2\text{SO}_4 \) catalyzed hydrolysis of isobutenyl acetate in \( \text{D}_2\text{O} \) and stored at \(-10^\circ\) over molecular sieves.

Nitric Acid, reagent grade, was obtained from J. T. Baker Chemical Company.

Nitrogen for general use was obtained from Burdett Oxygen Co. and labelled "High Purity Dry Nitrogen."

Pentamethyldiethylenetriamine was obtained from Ames Laboratories.

Polyethyleneimines with average molecular weights of 600 (trade name Montrek-6, lot #534-1-47), 1200 (trade name Montrek-12, lot #534-2-2), 1800 (trade name PEI-18, S. I. #278454, lot #TA09028BON), and 50,000 (trade name Montrek-600, S. I. #595743, lot #01047B0I) were obtained from Dow Chemical Co.

Potassium Thiocyanate, reagent grade, was obtained from J. T. Baker Chemical Co.

Silver Nitrate, reagent grade, was obtained from Allied Chemical Co.

Sodium Chloride, reagent grade, was obtained from Matheson Coleman and Bell.

Sodium Hydroxide, reagent grade, was obtained from J. T. Baker Chemical Co.
Sodium Hydroxide solutions of standard normality were obtained from the Reagent Laboratory of The Ohio State University.

Sodium Sulfate, reagent grade, was obtained from J. T. Baker Chemical Co.

p-Toluenesulfonic Acid, monohydrate, was obtained from Matheson Coleman and Bell.

Tris(2-aminoethyl)amine was obtained from Ames Laboratories.

Water, double-distilled, was obtained from The Ohio State University Reagent Store and degassed before making aqueous solutions.

Elemental Analyses were preformed in duplicate by the Clark Microanalytical Laboratory, Urbana, Illinois, and the Scandanavian Microanalytical Laboratory, Herlev, Denmark.

Standard Buffer Solutions for calibration of the pH meters at 35° were prepared by using NBS standard buffers obtained from Beckman as #14059 (pH 9.102) and #14054 (pH 4.02).
**Instrumentation**

**Boiling Point Determinations**

Boiling points were taken as the distillation temperature of the fraction collected. All boiling points are uncorrected.

**Constant Temperature Baths**

For pH and kinetic studies an E. H. Sargent and Co. Heater-Circulator and Model SW Thermonitor or a Brownwell Thermoregulator were used to control the temperature within $35.00 \pm 0.05^\circ$.

The temperature of the UV cells was controlled by circulating and heating a 50:50 ethylene glycol:water mixture at $35^\circ$ with a Haake Constant Temperature Circulator Model FE.

A Precision Scientific Co. Lo-Temptrol 154, set to circulate a water:ethylene glycol mixture at $35^\circ$, was used for temperature control with the Radiometer pH meter.

**NMR Measurements**

NMR spectra were determined on a Varian A60 Nuclear Magnetic Resonance Spectrometer.

**pH Measurements**

pH measurements for kinetic runs were obtained
using either a Beckman 101900 Research pH Meter with a Corning combination electrode #576050 or a Radiometer Model 26 pH Meter with a Radiometer GK2301C combination electrode.

**pH Titrations**

Automatic titrations were carried out using a combination of a Radiometer Model 26 pH Meter, Model 11 Titrator, Model ABU16 Auto-Burette equipped with a 2.5 ml syringe, Model SBR2c Titrigraph recorder, TTA3 Titration Assembly with a thermostated cell holder, and G202B (0-14 pH) glass and K401 reference electrodes.

The pH meter was standardized at 35° with a pH 9.102 and a pH 4.02 buffer.

**UV Measurements**

Ultraviolet absorbances were measured on a Cary Model 1605 Recording Spectrophotometer. Beckman 1 cm quartz cells were used.

**Vapor Phase Chromotography**

An F and M Model 720 or an Aerograph Model A-700 gas chromatographs were used.

**Weight Determinations**

All accurate measurements were made on a Mettler Model 35H26 balance with a 1 mg sensitivity.
Kinetic Measurements

Kinetics of the Dedeuteration of Isobutyraldehyde-2-d

A) General Procedure

The kinetics of the dedeuteration of isobutyraldehyde-2-d in the presence of various amine catalysts were carried out in a similar manner. Amine solutions of a higher concentration than desired for the actual kinetic runs were prepared. In order to give the solutions a certain pH, hydrochloric acid was added and the solution diluted to the desired concentration. Since the pH of some of the amine solutions changed considerably when aldehyde was added, the amount of acid needed was determined beforehand usually on a trial and error basis. Ten milliliters of the amine solutions were pipetted into 15 ml, greased glass-stoppered centrifuge tubes and equilibrated in a constant temperature bath at 35°. To initiate the reaction 50 µl of isobutyraldehyde-2-d (purified by vpc on a ten-foot DEGS column at 55°) was added by syringe, the tube was immediately stoppered, shaken, and replaced in the bath. To quench the reaction excess acetic acid was added by syringe. The aldehyde was extracted with 0.8 ml of chloroform and the extract transferred to a nitrogen-purged nmr tube. The isobutyraldehyde-isobutyralde-
hyde-2-d chloroform extract was conveniently analyzed by nmr. The triplet of isobutyraldehyde-2-d (centered at $\tau 8.90, J = 1.05$ c.p.s.) is caused by coupling of the methyl groups with the deuterium in the 2 position; the doublet of isobutyraldehyde ($J = 6.88$ c.p.s.) closely surrounds the triplet of the deuterated compound. The height of the downfield component of the isobutyraldehyde doublet ($h$) was compared to the height of the center peak of the triplet ($d$) to give the concentration of deuterated aldehyde, $[AD]$. 

\[
[AD] = \frac{d}{d + h}
\]

The pseudo first-order rate constant ($k_p$) was calculated from the equation

\[
- \frac{d[AD]}{dt} = k_p[AD]
\]

or

\[
\ln \left( \frac{d}{(d + h)_t} \right) = -k_pt + \ln \left( \frac{d}{(d + h)_o} \right)
\]

A least squares treatment of the slope of a plot of $\ln \left( \frac{d}{d + h}_t \right)$ versus time gave $k_p$. The linear least squares computer program is given in Appendix B.
B) Kinetics in the Presence of PEI-600, 1200, and 1800 and in the Presence of PEI-600, 1200, and 1800 plus Dabco

Dabco was purified by recrystallization from 95% ethyl alcohol of the hydrochloride, which was prepared by bubbling hydrogen chloride gas into a diethyl ether solution of the amine. Aqueous titration of the hydrochloride with standard sodium hydroxide showed it to be 99% pure. The appropriate amount of hydrochloride was added in preparing the polymer solutions for runs in which Dabco was present. The high viscosity of the PEI's presented some problems during weighing and precautions were taken to avoid contact with air owing to their hygroscopic nature. Data for a typical run are given in Table 29 and the results are summarized in Table 25.

C) Kinetics in the Presence of PEI-50,000

PEI-50,000 (Montrek 600) was assumed to be 33% polymer as reported.² The same procedure used in the previous section was employed. Data for a typical run are given in Table 30 and the results are summarized in Table 27.

TABLE 29

KINETICS OF THE DEDEUTERATION OF 0.054 M ISOBUTYRALDEHYDE-2-d IN THE PRESENCE OF 1.00 N PEI-1200 AND 0.200 N DABCO AT 35° AND pH 8.48

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Time, h, min</th>
<th>d, cm</th>
<th>( \frac{d}{d + h} ) (_t)</th>
<th>-ln ( \frac{d}{d + h} ) (_t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>6.75</td>
<td>0.737</td>
<td>0.3054</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>13.05</td>
<td>0.624</td>
<td>0.4709</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>19.6</td>
<td>0.532</td>
<td>0.6317</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>19.1</td>
<td>0.477</td>
<td>0.7408</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>21.25</td>
<td>0.401</td>
<td>0.9128</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>18.6</td>
<td>0.350</td>
<td>1.051</td>
</tr>
</tbody>
</table>

slope = -0.01475 ± 0.00037\(^a\)

y-intercept = -0.1692 ± 0.0144\(^a\)

linear correlation = 0.9987

standard deviation = 0.01548

\( k_p \) = 0.01475 min\(^{-1}\) = 24.6 x 10\(^{-5}\) sec\(^{-1}\)

\( t_{1/2} \) = 47.0 min

\(^a\)Standard deviation.
TABLE 30
KINETICS OF THE DEDEUTERATION OF 0.054 M ISOBUTYRALDEHYDE-2-d IN THE PRESENCE OF 1.00 N PEI-50,000 AT 35° AND pH 7.55

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Time, min</th>
<th>h, cm</th>
<th>d, cm</th>
<th>$(\frac{d}{d+h})_t$</th>
<th>$-\ln(\frac{d}{d+h})_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>7.9</td>
<td>18.3</td>
<td>0.698</td>
<td>0.3589</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>14.45</td>
<td>17.9</td>
<td>0.553</td>
<td>0.5918</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>18.8</td>
<td>15.8</td>
<td>0.457</td>
<td>0.7838</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>17.3</td>
<td>10.35</td>
<td>0.374</td>
<td>0.9826</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>20.0</td>
<td>8.8</td>
<td>0.306</td>
<td>1.186</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>21.05</td>
<td>7.1</td>
<td>0.252</td>
<td>1.378</td>
</tr>
</tbody>
</table>

slope = -0.01348 ± 0.00019

y-intercept = -0.1725 ± 0.0110

linear correlation = 0.9996

standard deviation = 0.01184

$k_p = 0.01348 \text{ min}^{-1} = 22.5 \times 10^{-5} \text{ sec}^{-1}$

$t_{1/2} = 51.4 \text{ min}$

aStandard deviation.
D) Kinetics in the Presence of Diethylamine Buffers

The concentration of the diethylamine-diethylamine hydrochloride solutions were determined titrimetrically. The pseudo first-order rate constants, $k_p$, were determined in the same manner as in the previous cases. The second-order rate constant for attack of diethylamine on isobutyraldehyde-$2$-$d$, $k_B$, was determined from the following equation.

$$k_p = k_h[OH^-] + k_w[H_2O] + k_B[Et_2NH]$$  \hspace{1cm} (1)

Since it has been shown that the protonated forms of secondary amines are not involved in the kinetics\(^3\) additional terms containing diethylammonium ions were neglected. The attack of the carbinolamine formed from diethylamine and isobutyraldehyde-$2$-$d$ was also neglected (see following section). Since the values of $k_h$ and $k_w$ were known,\(^1\) it was convienient to define $k_{cor}$ as

$$k_{cor} = k_p - k_h[OH^-] - k_w[H_2O]$$  \hspace{1cm} (2)

The hydroxide ion concentration was calculated in the following manner. The $pK_a$ values of diethylamine at $35^\circ$ and ionic strengths ($I$) of 0, 0.05, 0.10, and 0.20 were linearly extrapolated from the corresponding values at

20° and 40° reported by Evans and Hamann. The pKw values at 35° and the same ionic strengths were obtained from a plot of $-\log K_w$ vs. $\sqrt{I}$. The pKb value was then calculated from the equation

$$pK_b = pK_w - pK_a$$

A plot was made of pKb vs. I and the pKb at the particular I of the reaction solution was read from the curve. The concentration of hydroxide ion was then calculated. The concentration of water in eq 2 was taken as 55 M. From eqs 1 and 2 the second-order rate constant was calculated from the equation

$$k_B = \frac{k_{cor}}{[Et_2NH]}$$

Data for a typical run are given in Table 31 and the results are summarized in Table 32.


### TABLE 31

**KINETICS OF THE DEDEUTERATION OF 0.054 M ISOBUTYRALDEHYDE-2-d IN THE PRESENCE OF 0.0247 M Et₂NH - 0.164 M Et₂NH₂⁺ AT 35°**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Time, hr</th>
<th>d, cm</th>
<th>( \frac{d}{d + h} )ₜ</th>
<th>-ln ( \frac{d}{d + h} )ₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>3.7</td>
<td>0.837</td>
<td>0.1779</td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>7.4</td>
<td>0.704</td>
<td>0.3510</td>
</tr>
<tr>
<td>3</td>
<td>1.50</td>
<td>11.6</td>
<td>0.615</td>
<td>0.4868</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>15.4</td>
<td>0.523</td>
<td>0.6478</td>
</tr>
<tr>
<td>5</td>
<td>2.50</td>
<td>16.8</td>
<td>0.455</td>
<td>0.7885</td>
</tr>
<tr>
<td>6</td>
<td>3.00</td>
<td>18.4</td>
<td>0.389</td>
<td>0.9449</td>
</tr>
</tbody>
</table>

slope = -0.3033 ± 0.0042<sup>a</sup>

y-intercept = -0.03530 ± 0.00817<sup>a</sup>

linear correlation = 0.9996

standard deviation = 0.008774

\[ k_p = 0.3033 \text{ hr}^{-1} = 8.42 \times 10^{-5} \text{ sec}^{-1} \]

\[ t_{1/2} = 2.28 \text{ hr} \]

<sup>a</sup>Standard deviation.
**Ultraviolet Measurements**

**Equilibrium Constant for Carbinolamine Formation between Diethylamine and Isobutyraldehyde**

In order to find out if the dedeuteration of isobutyraldehyde-2-d in diethylamine buffers was complicated by the formation of carbinolamines, the addition of the amine to isobutyraldehyde was studied by uv at 35° and 284 nm.

\[
\text{Me}_2\text{CHCHO} + \text{Et}_2\text{NH} \rightleftharpoons \text{Me}_2\text{CHCHNET}_2
\]

The Cary 1605 was zeroed with water in both cells (1 cm). The water in the sample cell was replaced with 3.00 ml of

**Table 32**

**Kinetics of the Dedeuteration of 0.054 M Isobutyraldehyde-2-d in the Presence of Diethylamine Buffers at 35°**

<table>
<thead>
<tr>
<th>[Et$_2$NH], M</th>
<th>[Et$_2$NH$_2^+$], M</th>
<th>$10^4$[OH$^-$], M</th>
<th>$10^5$k$_p$, sec$^{-1}$</th>
<th>$10^5$k$_{cor}$, sec$^{-1}$</th>
<th>$10^3$k$_B$, sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0241</td>
<td>0.0774</td>
<td>4.52</td>
<td>8.77</td>
<td>7.37</td>
<td>3.06</td>
</tr>
<tr>
<td>0.0247</td>
<td>0.164</td>
<td>2.45</td>
<td>8.42</td>
<td>7.66</td>
<td>3.10</td>
</tr>
<tr>
<td>0.0498</td>
<td>0.136</td>
<td>5.82</td>
<td>17.9</td>
<td>16.1</td>
<td>3.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average 3.13</td>
</tr>
</tbody>
</table>
0.1016 M hydrochloric acid; no absorbance was observed. In order to determine if Et$_2$NH absorbed at 284 nm, 100 µl of the amine (purified by vpc on a ten-foot 10% Carbowax-2% KOH column at 55°) was injected into the sample cell; an absorbance of 0.0125 was observed. The solution in the sample cell was then replaced with 3.00 ml of standard acid and 20 µl of isobutyraldehyde (purified on a ten-foot DEGS column at 55°) was injected. From the resulting absorbance, 1.103, and the concentration of aldehyde, 0.0728 M, an extinction coefficient, ε, of 15.15 cm$^{-1}$M$^{-1}$ was calculated according to Beer's law. Next 100 µl of Et$_2$NH was injected into the sample cell and the absorbance decreased to 1.082. Subtracting the absorbance due to the amine, the absorbance due to the aldehyde was 1.070. Using the value of ε determined above, the final concentration of aldehyde, [Me$_2$CHCHO]$_f$, was calculated to be 0.0706 M. Correcting the initial concentration, [Me$_2$CHCHO]$_i$, from 3.02 to 3.12 ml gave a value of 0.0705 M. An additional run using the same concentrations gave a value of 0.0712 M for [Me$_2$CHCHO]$_f$. Values for [Et$_2$NH]$_o$ and [Et$_2$NH$_2^+$]$_o$ were calculated to be 0.206 M and 0.0107 M, respectively, when the dilution of the solution and the ionization of Et$_2$NH were taken into account. Thus with a three fold excess of amine over aldehyde, no decrease in the aldehyde concentration
was observed, i.e., no formation of carbinolamine was observed.

An upper limit for the magnitude of $K_{CA}$ can still be estimated. Since an increase of 0.0007 M was observed in the concentration of aldehyde, this can be taken as the range of the experimental uncertainty. Thus the concentration of carbinolamine must have been less than 0.0007 M.

$$K_{CA} = \frac{[\text{Me}_2\text{CHCHNMe}_2]_f}{[\text{Me}_2\text{CHCHO}]_f [\text{Et}_2\text{NH}]_f} < \frac{0.0007 \text{ M}}{(0.0698 \text{ M})(0.205 \text{ M})} < 0.05 \text{ M}^{-1}$$

**Synthesis**

**Tris(2-dimethylaminoethyl)amine**

Tris(2-aminoethyl)amine was methylated according to the Eschweiler-Clark procedure. 6-8


Tris(2-aminooctyl)amine (0.05 mol, 7.3 g) was added to 90% formic acid (0.75 mol, 38.3 g, 32.0 ml) with stirring at 0°. 35% Formaldehyde (0.33 mol, 28.2 g, 30.4 ml) was added and the red mixture was heated under reflux for 16 hr. (The reflux period in the literature varies from 6-12 hr.) Concentrated hydrochloric acid (15 ml) was added. The formic acid and any excess formaldehyde were evaporated on a steam bath; the remaining volatile fractions were removed under reduced pressure. The tan residue was dissolved in water and made basic with 25% sodium hydroxide. The amine was extracted several times with diethyl ether and dried over potassium hydroxide and then sodium sulfate. The ether was removed under reduced pressure and the amine vacuum distilled: bp 71-75° (0.1 mm) [lit. 8 bp 70-71° (0.5 mm)]; total yield 3.5 g (31%). However, vpc showed the presence of an impurity which proved to be hexamethylenetriethylenetetramine. Continuous extraction of the water layer with diethyl ether for 24 hr yielded additional amine.
Determinations

Percent Tertiary Amines Nitrogen in Polyethyleneimines

A) Preparation of Solutions

Standard p-toluenesulfonic acid (p-TsOH) was prepared by dissolving p-TsOH monohydrate (0.09 mol, 17.24 g) in 400 ml of glacial acetic acid. Acetic anhydride (0.09 mol, 9.17 g, 8.46 ml) was then added in order to remove the water. The solution was diluted to 500 ml with glacial acetic acid and allowed to stand for 24 hr at room temperature. The volume had decreased slightly and was again diluted to 500 ml.  

\[
\text{Normality} = \frac{17.24 \text{ g}}{(190.2 \text{ g/mol})(500 \text{ ml})} = 0.181 \text{ N}
\]

B) Procedure

A typical determination consisted of weighing 0.932 g of PEI-1800 into a 100 ml round-bottomed flask. Forty milliliters of glacial acetic acid was added and the sample was dissolved by swirling. After the addition of 40 ml of acetic anhydride, the solution was heated under reflux for two hours. (Varying the reflux period from two to four to six hours had no effect on the final

result.) The solution was allowed to cool, transferred quantitatively (using 25 ml of acetic acid) to a 250 ml beaker, and titrated potentiometrically (standard calomel and glass electrodes) with 0.181 M p-TsOH. A plot of \(-mv\) vs. ml acid added was made (see Figure 1); however, since the end point was not very sharp a plot was made of \(\Delta(-mv)\) vs. ml acid added. The end point was then determined from the maximum of the second graph. The percent tertiary amine nitrogen was then calculated from the formula

\[
\% \text{Tertiary Amine Nitrogen} = \frac{A \times N \times 1.4}{S}
\]

where

- \(A = \text{ml titrant}\)
- \(N = \text{normality titrant}\)
- \(S = \text{sample wt, g}\)

For the present determination

\[
\% \text{Tertiary Amine Nitrogen} = \frac{(30.1)(0.181)(1.4)}{0.932}
\]

\[= 8.17\%
\]

10. Reference 2, p. 16.
A) Purity

The purity of the amines was determined by vapor phase chromatography (10% Carbowax-2% KOH) and by aqueous titration with hydrochloric acid.

Pentamethyldiethylenetriamine (1) was found to be >99.8% pure by vpc and 99.6% pure by titration.

Hexamethyltriethylenetetramine (2) and tris(2-dimethylaminoethyl)amine (3) were purified via their hydrochlorides. The hydrochlorides were prepared by the addition of excess hydrochloric acid to an aqueous solution of the amine at 0°. After evaporation on a hot plate, the solid residue was washed with acetone to remove a yellow impurity and recrystallized from ethanol-water. The free amines were regenerated by dissolving the salts in the minimum amount of water and adding 25% sodium hydroxide until the solutions were strongly basic. The amines were extracted with diethyl ether and vacuum distilled. 2 was found to be >99.8% pure by vpc and 99.5% pure by titration. 3 was found to be 96.3% pure by vpc (with the 3.7% impurity shown to be 2) and 99.6% pure by titration.

Tris(2-aminoethyl)amine (4) was shown to be 86.8% pure by vpc (with the 13.2% impurity shown to be triethyl-
enetetramine) and 97.0% pure by titration.

B) Titration with p-Toluenesulfonic Acid.

Solutions of 1, 2, and 3 in acetic acid-acetic anhydride were titrated with standard p-TsOH in glacial acetic acid in the same manner as described in the titrations of acetylated polymers. Compound 4 was acetylated in the same manner as the polymers prior to titration. The results are summarized in Table 5.

Amount of Chloride Ions in PEI-50,000

The amount of Cl⁻ in PEI-50,000 (Montrek 600) was determined by the Volhard method.¹¹

A) Preparation of Solutions

Solutions of AgNO₃ and KSCN (0.100 M) were prepared by addition of the appropriate weights of the solids to volumetric flasks and addition of water to the mark. One milliliter of KSCN was found to be equivalent to 1.004 ml of AgNO₃. A saturated solution of ferric ammonium sulfate in 1 N nitric acid was prepared for use as an indicator. Nitric acid-water (1:1) was boiled to remove any nitrous acid.

B) Cl\(^-\) Titer of the AgNO\(_3\) Solution

To reagent grade sodium chloride (0.2 g) in 50 ml of water was added 5 ml of 1:1 HNO\(_3\)_H\(_2\)O and then excess AgNO\(_3\). After the addition of 3 ml of nitrobenzene (to coat the AgCl precipitate so that it would not interfere with the KSCN titration) and 1 ml of indicator solution, the solution was titrated with KSCN solution until the appearance of a red-brown color. From the volume of KSCN solution used, the volume of excess AgNO\(_3\) solution was calculated and deducted from the total volume to obtain the net volume of AgNO\(_3\) required for precipitation of the chloride. From the net volume and the meq of NaCl used, the concentration of AgNO\(_3\) and the Cl\(^-\) titer were calculated. The AgNO\(_3\) solution was found to be 0.1007 M and the Cl\(^-\) titer was 3.57 mg Cl\(^-\)/ml AgNO\(_3\).

C) % Cl\(^-\) in PEI-50,000

The same general procedure was followed as in the determination of the Cl\(^-\) titer. Samples of PEI-50,000 (2-3 g) in 50 ml of water were first acidified with 4-6 ml of 8 M HNO\(_3\) (1.3-2.0 equivalents), which made the solution cloudy. Excess AgNO\(_3\) was added and the solution turned milky-white. After the addition of 2-3 ml of nitrobenzene and 1 ml of indicator solution, KSCN was slowly added until the solution became red-brown in
color. The results of five determinations was that PEI-50,000 was $0.86\% \text{Cl}^-$ with an average deviation of 0.06.

### $pK_a$ Values of Polyamines

**Pentamethyldiethylenetriamine (1)**

Aqueous samples of 1 (0.03 M) were titrated with 1 M hydrochloric acid at $25 \pm 2^\circ$. The titration curve gave one end point at two equivalents of acid. As a first approximation, $pK_{a1}$ and $pK_{a2}$ were taken as the values of the pH at 0.5 and 1.5 equivalents of acid (9.47 and 8.38). More accurate values were obtained in the following manner. In general for a dibasic amine

\[
\text{BH}^+ \rightleftharpoons H^+ + B
\]

\[
\text{BH}_2^{++} \rightleftharpoons H^+ + \text{BH}^+
\]

Therefore

\[
K_{a1} = \frac{[H^+][B]}{[\text{BH}^+]} \tag{3}
\]

\[
K_{a2} = \frac{[H^+][\text{BH}^+]}{[\text{BH}_2^{++}]} \tag{4}
\]

12. Literature values determined in the same manner are 9.4 and 8.4, respectively.

The concentration of total base is given in eq 5.

\[
[B]_{\text{total}} = [B] + [BH^+] + [BH_2^{2+}] \quad (5)
\]

The concentration of total acid added is given in eq 6, neglecting \([H^+]\).

\[
[H^+]_{\text{added}} = [BH^+] + 2[BH_2^{2+}] \quad (6)
\]

Substituting for \([BH^+]\) and \([BH_2^{2+}]\) from eqs 3 and 4 into eqs 5 and 6, solving for \([B]\) in each of the resulting equations, and setting them equal, gives eq 7.

\[
\left( \frac{2[B]_{\text{total}} - [H^+]_{\text{added}}}{K_{a1} K_{a2}} \right) [H^+]^2 + \\
\left( \frac{[B]_{\text{total}} - [H^+]_{\text{added}}}{K_{a1}} \right) [H^+] - \\
[H^+]_{\text{added}} = 0 \quad (7)
\]

The only unknown in eq 7 is \([H^+]\), which can be solved for using the quadratic formula. Thus the pH was calculated at several points along the titration curve (pH_{calcd}) and compared to the observed values (pH_{obsd}). The quantity (pH_{obsd} - pH_{calcd}), or \(\delta\), at each point was squared and the sum of all the \(\delta\)'s \((\Sigma \delta^2)\) was calculated. An iterative procedure was then performed in which pK_{a1} was decreased by some factor, such as 0.01, and \(\Sigma \delta^2\) recalculated. If \(\Sigma \delta^2\) decreased, the pK_{a} was decreased again; however if
$\Sigma \delta^2$ increased, the $pK_a$ was increased. $pK_{a1}$ was changed until $\Sigma \delta^2$ did not decrease any further. $pK_{a2}$ was then changed in the same manner as $pK_{a1}$. After changes in $pK_{a2}$ no longer decreased $\Sigma \delta^2$, $pK_{a1}$ was again changed. This process was continued until changes in both $pK_a$'s no longer decreased $\Sigma \delta^2$. Values of $pK_{a1}$ and $pK_{a2}$ obtained were 9.33 and 8.52, respectively.

Hexamethyltriethylenetetramine(2)

Aqueous samples of 2 (0.02 M) were titrated with 1 M hydrochloric acid at $25 \pm 2^\circ$. The titration curve gave two end points, at two and three equivalents of acid. As a first approximation, $pK_{a1}$, $pK_{a2}$, and $pK_{a3}$ were taken as the value of the pH at 0.5, 1.5, and 2.5 equivalents of acid (9.34, 8.28, and 5.16, respectively). More accurate values were obtained in the following manner. In general for a tribasic amine

\[
\begin{align*}
BH^+ &\rightleftharpoons H^+ + B \\
BH_2^{++} &\rightleftharpoons H^+ + BH^+ \\
BH_3^{++} &\rightleftharpoons H^+ + BH_2^{++}
\end{align*}
\]

Therefore

14. Literature values determined in the same manner are 9.2, 8.2, and 4.8, respectively.
The concentration of total base is given in eq 11.

\[[B]_{\text{total}} = [B] + [BH^+] + [BH_2^{2+}] + [BH_3^{3+}] \] (11)

The concentration of total acid added is given in eq 12, neglecting \([H^+].\)

\[[H^+]_{\text{added}} = [BH^+] + 2[BH_2^{2+}] + 3[BH_3^{3+}] \] (12)

Substituting for \([BH^+], [BH_2^{2+}],\) and \([BH_3^{3+}]\) from eqs 8, 9, and 10 into eqs 11 and 12, solving for \([B]\) in each of the resulting equations, and setting them equal, gives eq 13.
\[
\left( \frac{3[B]_{\text{total}} - [H^+]_{\text{added}}}{K_{a1} K_{a2} K_{a3}} \right) [H^+]^3 + \\
\left( \frac{2[B]_{\text{total}} - [H^+]_{\text{added}}}{K_{a1} K_{a2}} \right) [H^+]^2 + \\
\left( \frac{[B]_{\text{total}} - [H^+]_{\text{added}}}{K_{a1}} \right) [H^+] - \\
[H^+]_{\text{added}} = 0 \quad (13)
\]

The only unknown in eq 13 is \([H^+]\). Dividing through by the coefficient of the third-degree term transforms eq 13 into the general cubic equation

\[
y^3 + py^2 + qy + r = 0
\]

where \(y = [H^+]\). Values of \([H^+]\) at several points along the titration curve were obtained using the general solution to a cubic equation.\(^{15}\) \(pH_{\text{calcd}}, \delta, \) and \(\Sigma \delta^2\) were calculated as described in the previous section.

An iterative procedure was then performed on \(pK_{a1}, pK_{a2}, \) and \(pK_{a3}\) in which each was changed until \(\Sigma \delta^2\) no longer decreased. The values of \(pK_{a1}, pK_{a2}, \) and \(pK_{a3}\) obtained

were 9.18, 8.43, and 5.15, respectively.

**Tris(2-dimethylaminoethyl)amine (3)**

The sample of 3 used contained a 3.7% impurity of compound 2 (vpc analysis). Aqueous samples of 3 (0.02 M) were titrated with 1 M hydrochloric acid at 25 ± 2°. The titration curve showed one end point at three equivalents of acid. The values of $pK_{a1}$, $pK_{a2}$, $pK_{a3}$ read directly from the curve were 9.58, 8.52, and 7.18, respectively. More accurate values of 9.43, 8.58, and 7.21 were calculated using the same procedure as in the previous section.
APPENDIX A

PROGRAM PEI

Computer Program for Generating Polyethylenimines
The following is a list of the main symbols used in the program. They are listed in their order of appearance.

NRUNS - number of runs.
PQ, SQ, TQ - values of I in P(I,J), S(I,J), and T(I,J); maximum number of primary, secondary, and tertiary nitrogens, respectively, possible.
K - value of J in P(I,J), S(I,J), and T(I,J).
MW - molecular weight.
N - number of nitrogens in a polymer of a given molecular weight.
KK - KK = 1, 2, and 3 for polymers of molecular weight 576, 1178, and 1780, respectively.
RATIO - k_p/k_s.
IX - initial odd integer between ILOW and IHIGH that starts the random number generator (IRANU).
ILOW - smallest random number for attack by primaries.
IMAXP - largest random number for attack by primaries.
IMINS - smallest random number for attack by secondaries.
IHIGH - largest random number for attack by secondaries.
M - maximum distance possible from any nitrogen to a primary.
TN - total number of tertiaries.
NP, NS, NT - total number of primaries, secondaries, and tertiaries, respectively, at a given distance from
all primaries in a given polymer.

**KKK** - KKK = 1, 2 --- 25 for each of the 25 polymers generated of a given molecular weight.

**P, S, T** - two dimensional arrays for storing primary, secondary, and tertiary nitrogens, respectively.

**MP, MS, MT** - total number of primaries, secondaries, and secondaries, and secondaries, respectively, at a given distance from all primaries in 25 polymers.

**MMMNs** - primary nitrogen on the main chain with the smallest number.

** MMMMs** - primary nitrogen on the main chain with the largest number.

** MMMM** - number of nitrogens in the polymer at a given time.

**IX** - random number produced by the random number generator (IRANU).

**PERT** - percent tertiary nitrogen.

**PN** - total number of primaries.

**AP, AS, AT** - number of primaries, secondaries, and secondaries, respectively, at a given distance from the average primary.
PROGRAM PEI - FLOWCHART

MAIN PROGRAM

NRUNS
PQ, SQ, TQ, K
MW(KK), N(KK), KK = 1, 3

300
NR = 1, NRUNS
RATIO, IX

ILow = INT(10.0 * RATIO)
IMAXP = ILOW + (ILOW * PQ) - 1
IMINS = IMAXP + 1
IHIGH = IMAXP + (10 * SQ)
IXX = IX

RATIO, IXX, ILOW, IMAXP, IMINS, IHIGH

200
KK = 1, 3
M = N(KK) - 1
TN = 0

80
I = 1, M
NP(I) = 0
NS(I) = 0
NT(I) = 0

100
KKK = 1, 25
$\text{NP}(I) = \text{MP}(I) + \text{NP}(I)$
$\text{NS}(I) = \text{MS}(I) + \text{NS}(I)$
$\text{NT}(I) = \text{MT}(I) + \text{NT}(I)$

$\text{PERT} = \frac{\text{TN} \times 100}{(25 \times \text{FLOAT}(N(KK)))}$
$\text{PN} = \text{TN} + (2 \times 25)$

$\text{AP}(I) = \frac{\text{NP}(I)}{\text{PN}}$
$\text{AS}(I) = \frac{\text{NS}(I)}{\text{PN}}$
$\text{AT}(I) = \frac{\text{NT}(I)}{\text{PN}}$

$\text{RATIO}, \text{IXX}, \text{ILOW}, \text{IMAXP}, \text{IMINS}, \text{IHIHG}, \text{MW}(KK), \text{TN}, \text{PERT}$
$I, \text{AP}(I), \text{AS}(I), \text{AT}(I), I=1,M$

200
300
END
SUBROUTINE PRI

PRI

MMS=0

I=1, SQ

S(I,1)=0 T MMS=I

MMS=0 F

I=IG

J=1,K

S(MMS,J)=P(I,J)

12

13

11

14

J=1,K

P(I,J)=0 AND P(I,J-1)=0

P(I,J)=Q - -

RETURN
SUBROUTINE SEC

SUBROUTINE SEC

MM=0
NN=0

21
I=1,PQ

P(I,1)=0 T
F

T(I,1)=0 T
F

MM=0 AND NN=0 T
F

21

22
I=IG

23
J=1,K

T(MM,J)=S(I,J)

RETURN
SUBROUTINE C1

C1
SUM=0

30  J=2,K

TEMP=P(I,J)+S(II,J)
SUM=TEMP+SUM

30

TEMP=|P(I,1)-S(II,1)|
SUMT=TEMP+SUM
MS(SUMT)=MS(SUMT)+1.

RETURN

SUBROUTINE C2

C2
SUM=0

31  J=1,K

P(I,J)=S(II,J)^T
F

32  ITEMP=J+1

33  J=ITEMP,K

TEMP=P(I,J)+S(II,J)
SUM=TEMP+SUM

33

TEMP=|P(I,ITEMP-1)-S(II,ITEMP-1)|
SUMT=TEMP+SUM
MS(SUMT)=MS(SUMT)+1.

RETURN
SUBROUTINE C3

SUM = 0

J = 2, K

TEMP = P(I, J) + T(II, J)

SUM = TEMP + SUM

40

TEMP = |P(I, 1) - T(II, 1)|
SUMT = TEMP + SUM
MT(SUMT) = MT(SUMT) + 1.

RETURN

SUBROUTINE C4

SUM = 0

J = 1, K

P(I, J) ≠ T(II, J)

T

F

ITEMP = J + 1

41

J = ITEMP, K

TEMP = P(I, J) + T(II, J)
SUM = TEMP + SUM

42

43

TEMP = |P(I, ITEMP - 1) - T(II, ITEMP - 1)|
SUMT = TEMP + SUM
MT(SUMT) = MT(SUMT) + 1.

RETURN
SUBROUTINE C5

\[ \text{SUM} = 0 \]

\[ J = 2, K \]

\[ \text{TEMP} = P(I, J) + P(II, J) \]
\[ \text{SUM} = \text{TEMP} + \text{SUM} \]

\[ J = 50 \]

\[ \text{TEMP} = |P(I, 1) - P(II, 1)| \]
\[ \text{SUMT} = \text{TEMP} + \text{SUM} \]
\[ \text{MP(SUMT)} = \text{MP(SUMT)} + 1 \]

RETURN

SUBROUTINE C6

\[ \text{SUM} = 0 \]

\[ J = 1, K \]

\[ \text{TEMP} = P(I, J) + P(II, J) \]
\[ \text{SUM} = \text{TEMP} + \text{SUM} \]

\[ J = 51 \]

\[ \text{TEMP} = |P(I, J) - P(II, J)| \]
\[ \text{SUMT} = \text{TEMP} + \text{SUM} \]
\[ \text{MP(SUMT)} = \text{MP(SUMT)} + 1 \]

\[ J = \text{ITEMP}, K \]

\[ \text{TEMP} = P(I, J) + P(II, J) \]
\[ \text{SUM} = \text{TEMP} + \text{SUM} \]

\[ J = 53 \]

\[ \text{TEMP} = |P(I, \text{ITEMP} - 1) - P(II, \text{ITEMP} - 1)| \]
\[ \text{SUMT} = \text{TEMP} + \text{SUM} \]
\[ \text{MP(SUMT)} = \text{MP(SUMT)} + 1 \]

RETURN
PROGRAM PEI

POLYETHYLENIMINES OF MOLECULAR WEIGHTS 576, 1178, 1780 GENERATED

INTEGER, PC, SQ, TQ, P, S, T
REAL NP, NS, NT, MP, MS, MT
DIMENSION P(22, 20), S(40, 20), T(22, 20), MP(41), MS(41), MT(41),
       CP(41), NS(41), NT(41), AP(41), AS(41), AT(41), IYY(42), MW(3), N(3)

645 FORMAT(F5.1, I5)
646 FORMAT(1H1, 5X, 'KP/KS', 7X, 'IX', 7X, 'ILCH', 5X, 'IMAXP', 5X, 'IMINS', 5X)
C IHIGH'//F10.1, 5101
647 FORMAT(16I5)
648 FORMAT(13I5)
649 FORMAT(23X, 11HPRIMARIES)
650 FORMAT(23X, 11HSECONDARIES)
651 FORMAT(23X, 11HTERTIARIES)
652 FORMAT(20I5)

685 FORMAT(1H5/PEI, 1S//'; TOTAL TERTIARY NITROGENS = ', F5.0//' % TERTIAPEI
       CRY NITROGEN = ', F5.1, 1H%)
686 FORMAT(1H5//TOTAL NUMBER CF PRIMARIES, SECONDARIES, AND TERTIARIESPEI
       C AT (CH2CH2N) UNITS FROM THE AVERAGE PRIMARY://'
       C (CH2CH2N) #P/P #S/P #T/P'/(16, 4X, 3F10.3))

READ(5, 647) NRUNS
READ(5, 647) PC, SQ, TQ, K
READ(5, 647) (M(J, KK), N(KK), KK = 1, 3)
DO 300; IX = 1, NRUNS
THE FOLLOWING STATEMENTS CALCULATE THE RANGE OF RANDOM NUMBERS
FOR ATTACK AT PRIMARY AND SECONDARY NITROGENS
READ(5, 645) RATIO, IX
ILX = INT(10.0 * RATIO)
IMAXP = IMIN + (ILX * RATIO) - 1
IMINS = IMAXP + 1

THE FOLLOWING STATEMENTS FILL THE ARRAYS P, S, AND T.
P(1,1)=80
P(2,1)=92
S(1,1)=31

1 CONTINUE
CALL IRANU(IX,ILLOW,IHIGH,IY)
IF(MMM.GE.N(KK)) GO TO 8
IF(IY.GE.IMINS.AND.IY.LE.IHIGH) GO TO 10
IG=IY/ILCH
IF(P(IG,1).EQ.0) GO TO 1
MM=M+1
IVY(MMN)=IY
CALL PRI(P,S,SO,IG,K,MMM,MNN)
GO TO 1

10 IG=(IY-(IMINS-10))/10
IF(S(I,1).EQ.0) GO TO 1
MM=M+1
IVY(MMN)=IY
CALL SEC(P,S,T,PQ,IG,K)
TN=TN+1
GO TO 1

8 CONTINUE
WRITE(6,665) W(KK), KKK
WRITE(6,666) (IVY(MMN),MMMM,N(KK))
WRITE(6,675)
DO 20 I=1,PQ
IF(P(I,1).EQ.0) GO TO 20
WRITE(6,676) (P(I,J),J=1,K)
20 CONTINUE
WRITE(6,676)
DO 30 I=1,SO
IF(S(I,1).EQ.0) GO TO 30
WRITE(6,678) (S(I,J),J=1,K)
30 CONTINUE
WRITE(6,677)
DO 40 I=1,TQ
IF (T(I,1).EQ.0) GO TO 40
WRITE(6,672) (T(I,J),J=1,K).
40 CONTINUE

THE FOLLOWING STATEMENTS COUNT THE NUMBER OF PRIMARIES,SECONDARIES AND TERTIARIES AT (CH2CH2N) UNITS FROM THE PRIMARIES

DO 2 I=1,PQ
DC 2 J=1,TQ
IF(P(I,1).EQ.0 .OR.S(I1,1).EQ.0 )GO TO 2
IF(P(I,1).NE.S(I1,1)) CALL C1 (P,MS,I,II,K)
IF(P(I,1).EQ.S(I1,1)) CALL C2 (P,MS,I,II,K)
2 CONTINUE

DO 3 I=1,PQ
DC 3 J=1,TQ
IF(P(I,1).EQ.0 .OR.T(I1,1).EQ.0 )GO TO 3
IF(P(I,1).NE.T(I1,1)) CALL C3 (P,MT,I,II,K)
IF(P(I,1).EQ.T(I1,1)) CALL C4 (P,MT,I,II,K)
3 CONTINUE

DO 4 I=1,PQ
DC 4 J=1,TQ
IF(P(I,1).EQ.0 .OR.P(I1,1).EQ.0 )GO TO 4
IF(P(I,1).NE.P(I1,1).AND.1.NE.II) CALL C5 (P,MP,I,II,K)
IF(P(I,1).EQ.P(I1,1).AND.1.NE.II) CALL C6 (P,MP,I,II,K)
4 CONTINUE

THE FOLLOWING STATEMENTS TABULATE THE RESULTS

DO 5 I=1,M
NP(I)=NP(I)+NP(I)
NS(I)=NS(I)+NS(I)
NT(I)=NT(I)+NT(I)
5 CONTINUE

PERF=TN*100./(25.*FLOAT(N(KK)))
PN=TN+2.*25.
SUBROUTINE PRI (P, S, SQ, IG, K, MMMM, MMMN)

INTEGER P, S, SQ
DIMENSION P(22, 20), S(40, 20)
MMS = 0
DO 11 I = 1, SQ
   IF (S(I, 1) .EQ. 0) MMS = I
   IF (MMS .NE. 0) GO TO 12
11 CONTINUE
12 IG = I
DO 13 J = 1, K
   S(MMS, J) = P(I, J)
13 CONTINUE
IF (P(I, 2) .EQ. 0 .AND. P(I, 1) .LE. 80) MMMN = MMMN - 1
IF (P(I, 2) .EQ. 0 .AND. P(I, 1) .LE. 80) P(I, 1) = MMMN
IF (P(I, 2) .EQ. 0 .AND. P(I, 1) .GE. 82) MMMN = MMMN + 1
IF (P(I, 2) .EQ. 0 .AND. P(I, 1) .GE. 82) P(I, 1) = MMMN
SEC 2
SEC 24 END
SEC 2
SEC 22 RETURN
SEC 2
SEC 20 DO 25 J=1,K
SEC 19 RETURN
SEC 18 IF (J/I)=1.NE.0 601077
SEC 17 IF (I/J)=0 DO 27 S(I/J)=2
SEC 16 CONTINUE
SEC 15 IF (S(I/J)=1.NE.0) DO 24 CONTINUE
SEC 14 IF (S(I/J)=1) RETURN
SEC 13 DO 23 J=1,K
SEC 12 RETURN
SEC 11 I=16
SEC 10 IF (NN*NE.0) 90 0 IF (NN*0.0 NE.0) 160 TO 22
SEC 9 IF (I*1)=1.1*160 TO 22
SEC 8 IF (I*1)=1.*1 DO 21 I=1,14
SEC 7 IF (1*1)=1. DO 20 I=1,1
SEC 6 IF (1*1)=2. DO 19 I=1,14
SEC 5 IF (1*1)=1. DO 18 I=1,1
SEC 4 IF (1*1)=1. DO 17 I=1,1
SEC 3 IF (I*1)=1.9 DO 16 I=1,1
SEC 2 IF (I*1)=1.4 DO 15 I=1,1

PRINT 21
PRINT 20 RETURN
PRINT 19 DO 15 J=1,K
PRINT 18 IF (I*1)=1.9 AND. P(I,J)=1.9 IF (I*1)=P(I,J)+1
PRINT 17 DO 15 J=1,K
PRINT 22 END
SUBROUTINE C1 (P, S, MS, I, II, K)
INTEGER SUMT, P, S, SUM, TEMP
REAL MS
DIMENSION P(22, 20), S(40, 20), MS(41)
SUM = 0
DO 30 J = 2, K
TEMP = P(I, J) + S(II, J)
SUM = TEMP + SUM
30 CONTINUE
TEMP = IABS(P(I, J) - S(II, J))
SUMT = TEMP + SUM
MS(SUMT) = (MS(SUMT) + 1.)
RETURN
END

SUBROUTINE C2 (P, S, MS, I, II, K)
INTEGER SUMT, P, S, SUM, TEMP
REAL MS
DIMENSION P(22, 20), S(40, 20), MS(41)
SUM = 0
DO 31 J = 1, K
IF (P(I, J) .NE. S(II, J)) GO TO 32
31 CONTINUE
32 ITEMP = J + 1
DO 33 J = ITEMP, K
TEMP = P(I, J) + S(II, J)
SUM = TEMP + SUM
33 CONTINUE
TEMP = IABS(P(I, ITEMP - 1) - S(II, ITEMP - 1))
SUBROUTINE C3 (P, T, MT, I, II, K)

INTEGER SUMT, P, T, SUM, TEMP
REAL HT

DIMENSION P(22,20), T(22,20), MT(41)

SUM = 0
DO 40 J = 2, K
   TEMP = P(I, J) + T(II, J)
   SUM = TEMP + SUM
40 CONTINUE

TEMP = IABS(P(I, 1) - T(II, 1))
SUM = TEMP + SUM
MT(SUMT) = (MT(SUMT) + 1.)
RETURN
END

SUBROUTINE C4 (P, T, MT, I, II, K)

INTEGER SUMT, P, T, SUM, TEMP
REAL MT

DIMENSION P(22,20), T(22,20), MT(41)
SUM = 0
DO 41 J = 1, K
    IF (P(I, J) .NE. T(I1, J)) GO TO 42
41 CONTINUE
ITEM = J + 1
DO 42 J = ITEM, K
    TEMP = P(I, J) + T(I1, J)
    SUM = TEMP + SUM
CONTINUE
43 TEMP = IABS(P(I, ITEM-1) - T(I1, ITEM-1))
    SUMT = TEMP + SUM
MT(SUMT) = (MT(SUMT) + 1.)
RETURN
END

SUBROUTINE C5 (P, MP, I, II, K)
INTEGER SUMT, P, SUM, TEMP
REAL MP
DIMENSION P(22, 20), MP(4)
SUM = 0
DO 50 J = 2, K
    TEMP = P(I, J) + P(I1, J)
    SUM = TEMP + SUM
50 CONTINUE
TEMP = IABS(P(I, 1) - P(I1, 1))
SUMT = TEMP + SUM
MP(SUMT) = (MP(SUMT) + 1.)
RETURN
END
```
SUBROUTINE C6 (P, MP, I, II, K)
  INTEGER SUMT, P, SUM, TEMP
  REAL MP
  DIMENSION P(22,20), MP(41)
  SUM = 0
  DO 51 J=1, K
    IF (P(I, J) .NE. P(II, J)) GO TO 52
  CONTINUE
  51 CONTINUE
  52 ITEM = J + 1
  DO 53 J = ITEM, K
    TEMP = P(I, J) + P(II, J)
    SUM = TEMP + SUM
  CONTINUE
  53 CONTINUE
  TEMP = IABS(P(I, ITEM - 1) - P(II, ITEM - 1))
  SUM = TEMP + SUM
  MP(SUMT) = (MP(SUMT) + 1.0)
  RETURN
END
```
APPENDIX B

Linear Least Squares Computer Program
C  Y=MX+B LEAST SQUARES CALCULATION OF M AND B.
C  'K' SETS OF DATA
C  'N' NUMBER OF POINTS WITHIN EACH SET
C
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 M

DIMENSION X(50), Y(50)

500 FORMAT (I4).
510 FORMAT (9F10.7)
610 FORMAT (/A(1PE13.3))
620 FORMAT (/' M =',1PE12.3,'/',R =',1PE12.3,'/' LINEAR CORRELATION =
C!',0PF8.4,'/' STANDARD DEVIATION IN M =',1PE12.3,'/' STANDARD DEVIATION IN R =',1PE12.3)
700 FORMAT (/H1 //'LEAST SQUARES CALCULATION OF M AND B IN...Y=MX+B!/'
C //12X,'X',12X,'Y',8X,'CALCY', 6X,'Y-CALCY')

READ (5,500) K
DO 1 J=1,K
READ (5,500) N
READ (5,510) X(I),Y(I),I=1,N
READ (5,510) X(I),Y(I),I=1,N
SUMX=0.
SUMY=0.
SUMXY=0.
SUMXX=0.
SUMYY=0.
DO 10 I=1,N
SUMX=SUMX+X(I)
SUMY=SUMY+Y(I)
SUMXY=SUMXY+X(I)*Y(I)
SUMXX=SUMXX+X(I)**2
SUMYY=SUMYY+Y(I)**2
10 SUMYY=SUMYY+Y(I)**2
G=N
DENOM1=SUMXX**2-G*SUMXX

DENOM2 =DSORT((G*SUMXX -(SUMX)**2) * (G*SUMYY -(SUMY)**2))

N = (SUMXX*SUMY-G*SUMXY)/DENOM1

F = (SUMXX*SUMXY-SUMYY*SUMXX)/DENOM1

C = (G*SUMXY-SUMXX*SUMYY)/DENOM2

S =DSORT((SUMYY-(SUMX**2/G)+G*SUMXY-SUMX*SUMYY)**2/(G*DENOM1))

C / (G-2.)

SM=S*(DSORT(-G/DENOM1)_)

SB =S*(DSORT(-SUMXX/DENOM1)_)

WRITE(6,700)

DO 20 I=1,N
CALCY=M*X(I)+P.
DIF =Y(I)-CALCY
20 WRITE(6,610) X(I), Y(I), CALCY, DIF
WRITE(6,620) M, R, C, S, SM, SB
1 CONTINUE
END
BIBLIOGRAPHY

Books


Journal Articles


Hine, J., M. S. Cholod, and J. H. Jensen. Ibid., 93, 2321 (1971).


_____ E. F. Glod, R. E. Notari, F. E. Rogers, and F. C. Schmalstieg. Ibid., in press.


