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# $^{15}N$ NMR Spectroscopy
# 29. Oligo- and Polyethylene Imine

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***In honour of Prof. Dr. Drs. h. c. mult. G. V. Schulz on the occasion of his 75th birthday***

## SUMMARY

The 9.12 MHz $^{15}N$ NMR spectrum of an industrially produced polyethylene imine displays six signals indicating a high degree of branching. Various mono- and oligo-amines as well as their hydrochlorides were measured in water, and structure/shift relationships are discussed. The relatively low sensitivity of the nuclear Overhauser effect of oligo- and polyethylene imine to paramagnetic cations is demonstrated and explained by strong complexation of the cations.

## INTRODUCTION

It is known that the cationic polymerization of ethylene imine leads to branched polyethylene imine. Because $^{15}N$ NMR signals were found to be sensitive to structure and sequence of various monomer units [1-4], it was our intention to investigate in this work whether $^{15}N$ NMR spectra are also useful for the characterization of polyethylene imine.

## RESULTS and DISCUSSION

Polyethylene imine: Natural abundance 9.12 $^{15}N$ NMR spectra of an industrially produced sample of polyethylene imine (Sigma Chemicals) were measured in water at pH 11.0 (original pH without additives) and at pH 1.0 in HCl. The spectrum taken from the acidic solution exhibited only three broad signals without fine structure. The spectrum run with the alkaline solution is more informative and displays 6 peaks (Fig.1B). These

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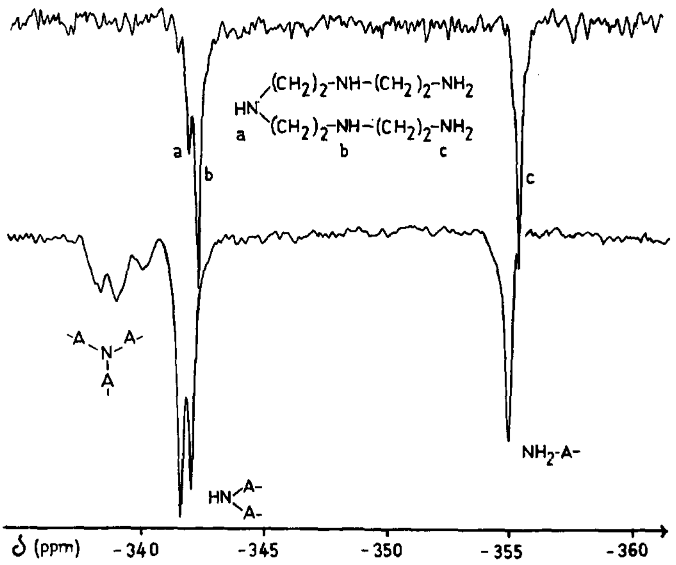
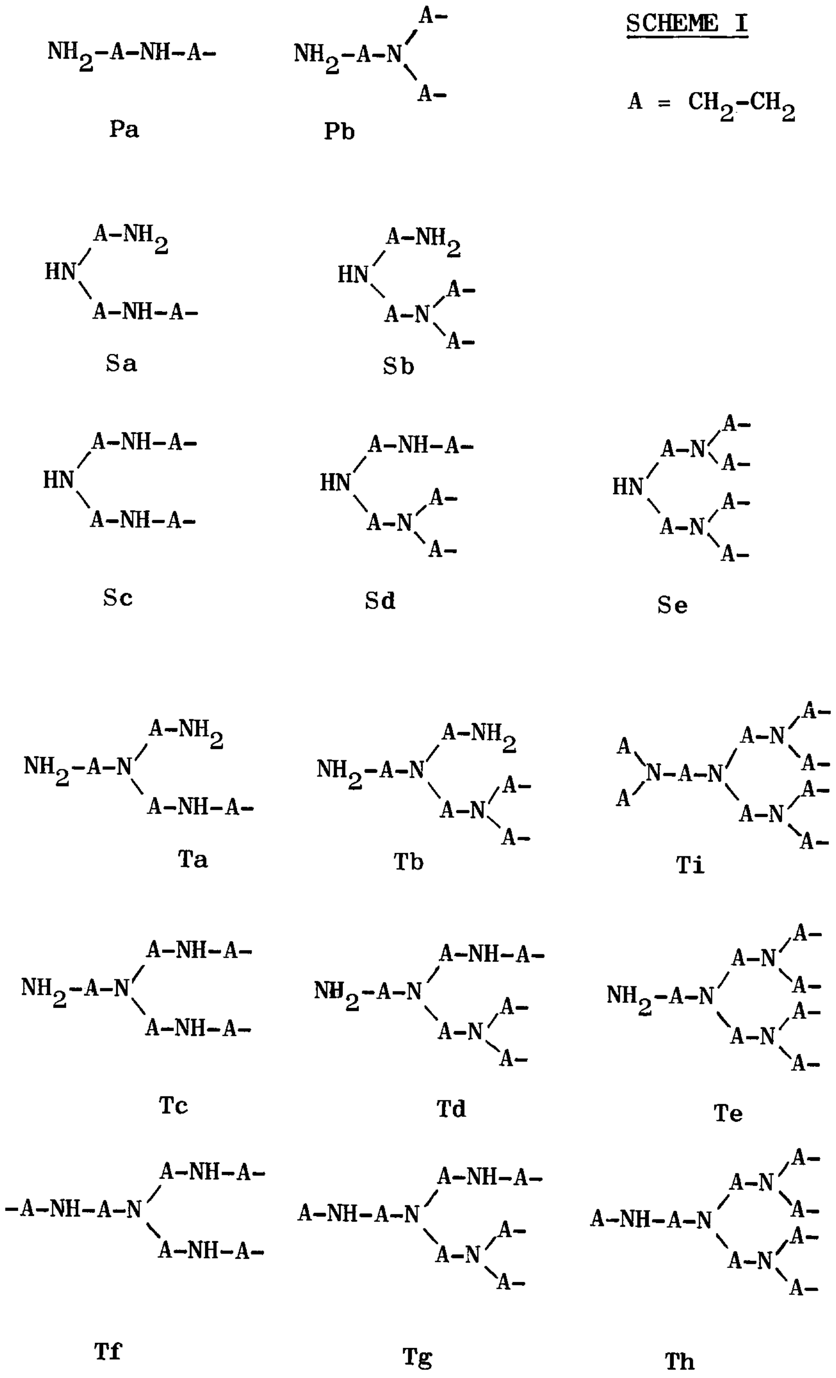


Fig.1 Natural abundance 9.12 MHz $^{15}N$ NMR spectra of tetraethylene-pentamine (A, ca. 4000 transients) and of polyethyleneimine (B, ca. 60 000 transients) in $H_2O$.

peaks can be subdivided into three groups which, by comparison with model compounds (Tab.1), can be attributed to primary, secondary and tertiary nitrogens. From the signal intensities it may be concluded that our polyethylene imine is highly branched, so that on the average every third nitrogen in the polymere backbone is a tertiary amine group. An exact calculation of the degree of branching was not possible because the signal intensities are influenced by nuclear Overhauser effects (NOEs) which are certainly different for primary, secondary and tertiary nitrogens because of different segmental mobilities. However, an inverse-gated $^1H$ decoupled measurement which allows one to eliminate the NOE was not feasible on our 2.1 Tesla NMR spectrometer. In this connection it is noteworthy that St.Pierre has published 5) a detailed $^{13}C$ NMR study of another industrial-

SCHEME I

$A = CH_2\text{-}CH_2$



ly produced polyethylene imine which also demonstrates that the polyamine obtained by cationic polymerization of ethylene imine is highly branched.

To understand the fine structure of the polyethylene imine signals the various sequence units listed in Scheme I have to be considered. That only six of the potential nineteen sequence units give well resolved signals in the 9.12 MHz spectrum of Fig. 1B may have two reasons:a) insufficient resolution and b) low concentration of individual structure elements. For example a low concentration is expected for the sequence unit Sc,because of the high degree of branching, and for the sequence unit Ti because of steric hindrance. Such considerations along with a comparison of the chemical shifts with those of the model compounds (Tab.1) lead us to the following conclusions. The $NH_2$ signal of polyethylene imine represents mainly sequence unit Pb. The downfield peak of the NH signal originates certainly from unit Se, while the highfield peak represents mainly Sd (eventually together with Sb). In the case of the tertiary nitrogen even tentative assignments of the three peaks are difficult to make. However, it is obvious that mainly the sequence units Ta, Tc, Td and Tf are responsible for the observed resonances. Finally it is noteworthy that the signal of the central NH group of tetraethylene pentamine ("a" in Fig. 1A) also represents the signal of an entirely linear polyethylene imine.

Oligoamines: To understand the structure/shift relationships of polyethylene imine we have investigated the chemical shifts of series of simple mono- and oligoamines. Measurements of these amines in water (or methanol) were necessary, because only few data of water solutions of amines are known$^{6)}$. These data stem mostly from $^{14}N$ NMR measurements$^{7)}$ and disagree largely

Tab. 1 $^{15}$N NMR chemical shifts $\delta$ (ppm,relative to external $NO_3^{\ominus}$) of amines and amine hydrochlorides

| Amine | of Amine | of Hydrochloride |
|---|---|---|
| Ethylamine | -347.0; | -339.9 |
| Diethylamine | -326.8;(-329.3)$^{a)}$ | -325.2 |
| Triethylamine | n.sol.;(-327.7)$^{a)}$ | -317.9 |
| n-Propylamine | -351.4;(-355.3)$^{a)}$ | -342.5 |
| Di-n-propylamine | n.sol.;(-335.8)$^{a)}$ | -329.7 |
| Ethanolamine | -358.1;(-361.9)$^{a)}$ | -347.1 |
| Diethanolamine | -346.9;(-348.7)$^{a)}$ | -339.3 |
| Ethylenediamine | -356.3;(-360.5)$^{a)}$ | -344.5 |
| N-Ethyl ethylenediamine | -333.1;-355.5 | -318.0;-339.9 |
| N,N-Diethyl ethylene diamine | -330.7;-355.1 | -321.0;-344.7 |
| N,N,N'-Triethyl ethylene diamine | -331.0;-334.4 | -321.0;-330.1 |
| Diethylenetriamine$^{b)}$ | -343.2;-355.6 | -334.1;-343.9 |
| Triethylenetetramine | -342.8;-355.6 | -333.8;-344.0 |
| Tetraethylenepentamine | -342.6;-355.7<br>-342.9; | -333.7;-344.1 |
| Polyethyleneimine | -339.1;-339.8<br>-340.9;<br>-342.4;-342.8<br>-355.5; | -333.6<br>-344.5<br>-350.3 |

a) in methanol b) in methanol: -346.8; -359.8

with our $^{15}$N NMR data (Tab.1). Our measurements lead to the following conclusions:

1) Ethyl groups cause strong, non additive downfield shifts relative to ammonia as shown by ethylamine, diethylamine and triethylamine or their hydrochlorides [6,8]. This downfield shift is mainly due to the carbons in ß-position (ß-effect) and, hence, ethylene groups behave analogously as shown by the chemical shifts of polyethyleneimine (Fig.1B).

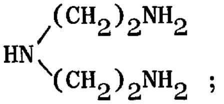
2) Substituents in γ-position relative to the nitrogen under investigation cause upfield shifts, and owing to this γ-effect the signals of polyethylene imine absorb upfield of ethylamine, diethylamine and triethylamine. γ-Effects of carbons were first reported by Sogn et al. for α-amino acids [9]; and it was later shown by us that these substituent effects are solvent dependent[10]. A comparison of n-propylamine, ethanolamine and 1,2-diaminoethane or of di-n-propylamine, diethanolamine and di-(2-aminoethyl) amine demonstrates (Tab.1) that the γ-effects also depend on the nature of the γ-substituent: $OH > NH_2 > CH_3$.

3) Alkyl substituents at a γ-nitrogen cause weak downfield shifts (δ-effect) which increase with the number of substutuents. These δ-effects found for various oligoamines are also responsible for the sequence effects in the case of polyethyleneimine.

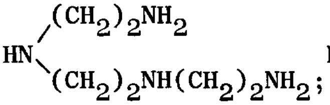
$NH_2\text{-}(CH_2)_2\text{-}NH_2$; -356.2 ppm

$NH_2\text{-}(CH_2)_2\text{-}NH\text{-}Et$; -355.5 ppm

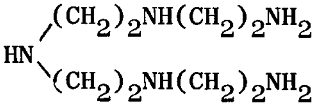
$NH_2\text{-}(CH_2)_2\text{-}NEt_2$ -355.1 ppm



-343.2 ppm



-342.8 ppm



-342.6 ppm

Influence of paramagnetic cations: Because the NOE, and thus the signal intensity, of free amino groups is highly sensitive to the influence of the paramagnetic impurities present in water ($Cu^{2+}$, $Fe^{3+}$), signal nulling is frequently observed when amines are measured in tapwater[4,11]. We did not have any difficulties to measure ca. 2 M solutions of various amines (Tab. 1) in tapwater; however, the signals of oligoamines, such as

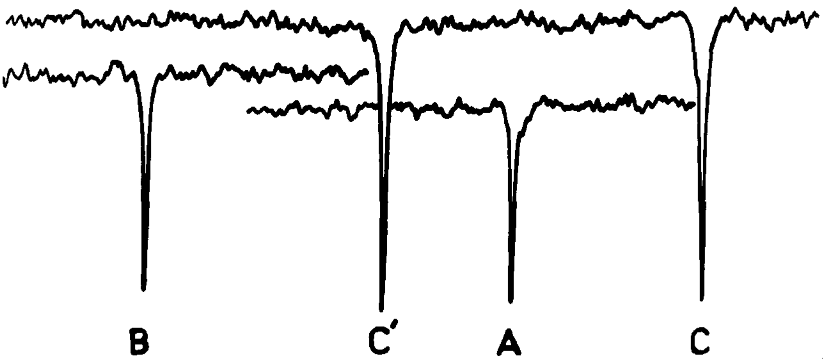


Fig.2 Natural abundance 9.12 MHz $^{15}N$ NMR spectra: A) n-propylamine, 2.5 M in tap-water; B) same solution after addition of polyethylene imine (10% by weight relative to propylamine; C)triethylene tetramine, 1.25 M in tap-water.

triethylene tetramine, showed a 30-50% higher intensity when compared with monoamines under identical conditions (Fig.2A/C). Furthermore, the signal intensities of ethylamine or propylamine were ca. 20% increased when polyethylene imine (10% by weight) was added to their solution (Fig.2A/B). Since oligo- and polyethylene imines are polydentate ligands, they can form stable complexes with various cations. If the lifetime of these complexes is long relative to the NMR time scale,most amine molecules are not affected by the cations during the accumulation of an FID. Thus, high complex constants may result in a lower sensitivity of the NOE to paramagnetic impurities. Finally, it is noteworthy that when $CuSO_4$ was added to various amine solutions (nitrogen/Cu ratio = $10^4$) signal nulling was observed for all free amines, but not for their hydrochlorides. This means a plot of NOE sensitivity versus complex constants must have a maximum for momoamines and two minima. The absolute minimum is caused by the poorest ligands, namely by ammonium ions, while the second, less pronounced minimum results from polydentate ligands, such as polyethylene imine.

## MEASUREMENTS

All 9.12 MHz $^{15}N$ NMR spectra were run on a Bruker WH-90 PFT-spectrometer at 28-29°C. Ca. 1.5-2.0 g amine or amine hydrochloride dissolved in 8-9 ml water (ca.2 M solutions) were measured in 20 mm diameter sample tubes with 5 mm diameter coaxial tubes containing a ca. 25% (by weight) solution of $^{15}NH_4{}^{15}NO_3$ in $D_2O$ (shift difference of $NH_4^{\oplus}$ and $NO_3^{\ominus}$ = 356.5 ppm). The following acquisition parameters were used:

A) Primary and secondary amines and all hydrochlorides: 1 K data points/400 Hz spectral width, zero-filled to 2K for Fourier-transform; expon. line-broadening 1.5 Hz; 2000-4000 transients. In the case of Fig.2 a delay time of 2 s was used to account for different relaxation times; pulse width 30 µs (ca. 35°).

B) Tertiary amines: pulse width 25 µs (ca.25°); delay time 2.8 s; 8000-10000 transients.

C) Polyethylene imine: pulse width 40 µs (ca.45°); 2 K data points/500 Hz spectral width, zero-filled to 4 K; expon. line-broadening 1.0 Hz; 60 000 transients.

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