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^{13}-NMR Analysis of Branched Polyethyleneimine

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^{13}C-NMR Analysis of Branched Polyethyleneimine

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ABSTRACT

A commercial, branched polyethyleneimine was analyzed by ^{13}C-NMR. The chemical shift assignments for the eight principal peaks were compared to the calculated chemical shifts using an additivity relationship developed for low molecular weight acyclic aliphatic amines. The change in carbon chemical shift induced by H/D exchange at nearby nitrogens was examined for this polymer and low molecular weight model compounds. The direction and magnitude of the shift are determined by the number and proximity of exchangeable NH's and are described by a simple formula. The spin lattice relaxation times for the various methylenes indicate the usual decreasing mobility for units at chain ends, internal units, and units close to branch points in that order. The integrated spectrum, under equilibrium conditions, is not consistent with the reported amine distribution, 1°:2°:3° = 1:2:1. Our results indicate 38% 1°, 36% 2°, and 26% 3°.

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INTRODUCTION

It has been known for many years that the ring-opening polymerization of ethyleneimine leads to branched polyethyleneimine (PEI) This is understandable in terms of the reaction scheme where ethylenimine and polymeric nitrogens compete as nucleophiles in the ring-opening process. This leads to a multiplicity of amine functions with a reported distribution of 1°:2°:3° = 1:2:1 [1].

There is considerable interest in this polymer as a polybase, a polynucleophile, and a polydentate ligand for transition and other metal ions. However, the interpretation of these results is at best difficult due to the lack of simple order such as would be found in the linear polyiminoethylene (PIE). The first step in the solution of this problem is to define explicitly the branch types and branch frequency for PEI.

As in the case of low density polyethylene, ^{13}C-NMR is well suited as a structural probe because the proton decoupled spectrum is relatively simple and well resolved. Furthermore, the assignment of peaks is less ambiguous because of the additivity relationships established by Grant and Paul [2] and refined by Lindeman and Adams [3]. This fact was recognized by Lukovkin and co-workers [4] in their initial ^{13}C-NMR study of PEI and the subsequent study by Okahata and Kunitake [5]. Recent NMR studies of PEI include the ^{13}C work of Smets and co-workers [6] and the ^{15}N work of Kricheldorf [7].

In this work we confirm the chemical shift assignments of Lukovkin, explore the additivity relationships for aliphatic amines, study differences in chemical shift produced by NH/ND exchange, measure spin-lattice relaxation times, and measure the quantitative relationship of various structural units. We also report some NMR results for reference compounds [8].

RESULTS AND DISCUSSION

Chemical Shift and Additivity Principle

The noise decoupled ^{13}C-NMR of branched PEI (PEI-18, Dow Chemical) is shown in Fig. 1. There are eight principal peaks, which is reasonable, based on the various placements shown in the insert. The number in the structural formula refers to the CH_2 which gives rise to the peak of the corresponding number. There is evidence of additional structural information in Peaks 1, 4, and 5. In this and the next section these are treated as single peaks. The fine structure will be discussed in the last two sections. The peak assignments for PEI, listed in Table 1, were based on Lukovkin's work and on the principle of additivity which was developed for acyclic amines and diamines by Reilly and co-workers [9] in the form of

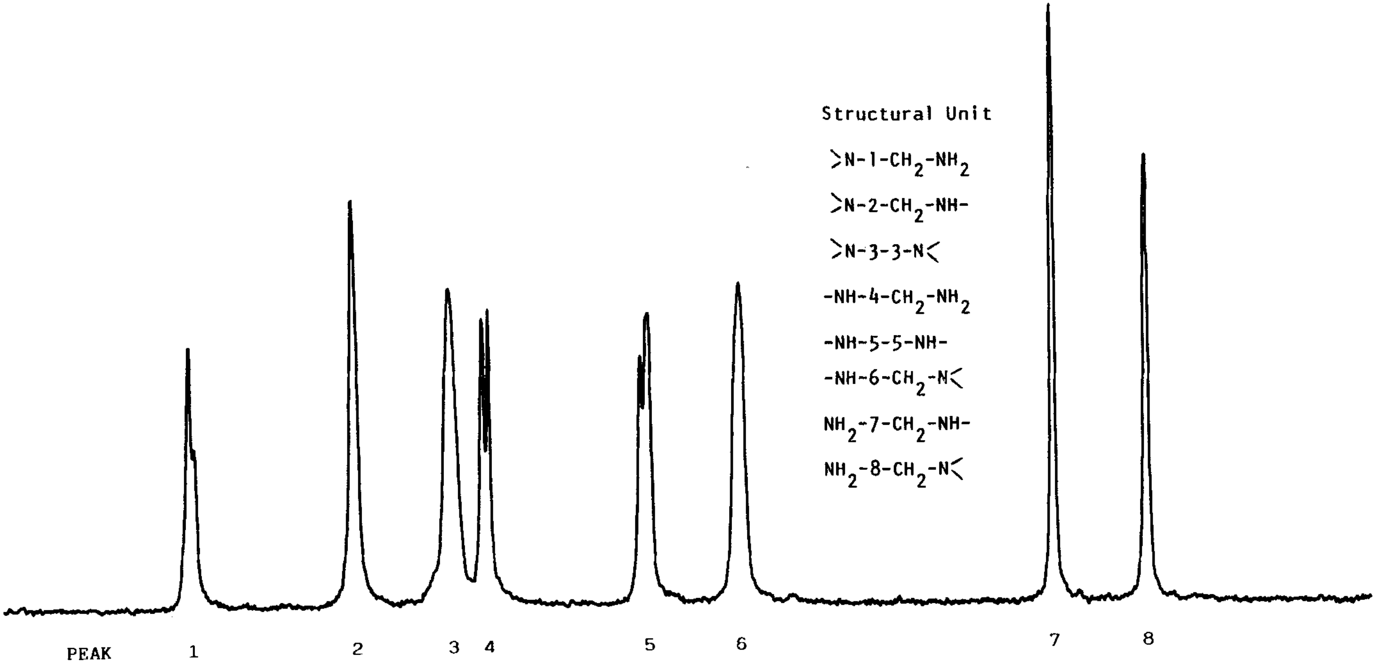


FIG. 1. ^{13}C-NMR of PEI. The peak number corresponds to the methylene substituted by the same number of the appropriate structural unit. The experimental conditions and chemical shifts indicated in Table 1 apply to this spectrum.

TABLE 1. Carbon-13 Chemical Shift of PEI-18 at 100.62 MHz[a]

Structural unit	This work[b]	Lukovkin[c]	Calculated[d]	Difference[e]
$>N\text{–}1\text{–}CH_2\text{–}NH_2$	57.41	57.2	55.70	-1.71
$>N\text{–}2\text{–}CH_2\text{–}NH\text{–}$	54.43	54.4	53.86	-0.57
$>N\text{–}3\text{–}3\text{–}N<$	52.54	52.9	52.03	-0.51
$\text{–}NH\text{–}4\text{–}CH_2\text{–}NH_2$	51.68	51.8	52.46	0.78
$\text{–}NH\text{–}5\text{–}5\text{–}NH\text{–}$	48.71	48.8	50.48	1.77
$\text{–}NH\text{–}6\text{–}CH_2\text{–}N<$	46.90	47.3	48.51	1.60
$NH_2\text{–}7\text{–}CH_2\text{–}N\text{–}$	40.94	41.7	44.27	3.33
$NH_2\text{–}8\text{–}CH_2\text{–}N$	39.15	39.5	42.15	3.00

[a] In ppm from TMS using dioxane as in internal reference (67.4 ppm).

[b] As a 10% (w/v) solution in D_2O at 333 K.

[c] These results were reported in ppm from internal benzene and were corrected to ppm from TMS by subtracting the given shift from 128.7.

[d] Calculated according to Ref. 9 and illustrated in the text.

[e] Calculated minus observed.

$$\delta^{c} = \delta_{alk}H^{n} + \sum_{j=2}^{n} (Ni)_j \qquad (1)$$

In this relationship δ_{alk} is the chemical shift of the carbon of the corresponding hydrocarbon fragment, H = 0.932, n is the number of amino N's within five bonds of the carbon in question, and Ni is the chemical shift parameter for the variously placed amino N's, specifically $N_\alpha = 22.58$ $N_\beta = 2.02$, $N_\gamma = 0.20$, and $N_\delta = 1.63$. The assignment of δ_{alk} was based on branched polyethylene [10] or the practically identical calculated values using the Lindeman-Adams constants. The calculated shift for $CH_2 = 8$ is $(15.34 + 9.75 - 2 \times 0.25)(0.932)^2 + 22.58 + 2.02 = 42.15$. This shift, and the others calculated in a like manner, appear in Table 1. These calculated values do not agree exactly with the observed values, but they do predict the relative order of peak assignments except for the closely spaced pair. It is interesting to note that the discrepancy between the calculated and observed values is systematic rather than random, which implies that the additivity formula can be refined to give better agreement.

NH/ND Exchange

The chemical shifts for the various PEI carbons show a small but significant dependence on the solvent, H_2O or D_2O, an effect which has been observed by others. Our results, shown in Table 2, indicate that the difference is a function of the number and proximity of exchangeable NH's. Ladner et al. [11] reported a similar effect for amino acids and dipeptides and ascribed shift factors of 93 ppb for $\underline{C}ND$ and 33 ppb for $\underline{C}CND$ for each H/D exchange, but these were not adequate to describe our results, especially the fact that the shift for 3° amines was opposite to that of 2° and 1° amines. A study of simple model compounds, listed in Table 3 with their chemical shifts in each solvent, leads to a simple regression equation in terms of α and β, the number of exchangeable NH's at those respective positions:

$$\delta(H_2O) - \delta(D_2O) = -72.6 + 113.7\alpha + 90.7\beta \qquad (2)$$

This equation reflects a positive difference for carbons experiencing a nearby NH/ND covalent exchange and a negative difference for carbons experiencing a nearby N–H/N–D hydrogen bonding exchange. The latter is masked by the former except in those cases where α and β are equal to zero, as is the case for $CH_2 = 3$. This equation

TABLE 2. The Effect of NH/ND Exchange on the Chemical Shift of PIE[a]

Structural unit	In H_2O, ppm	In D_2O, ppm	Difference, ppb
$>N-1-CH_2-NH_2$	57.552 ± 0.019	57.414 ± 0.021	138 ± 40
$>N-2-CH_2-NH-$	54.438 ± 0.007	54.434 ± 0.014	4 ± 21
$>N-3-3-N<$	52.452 ± 0.010	52.540 ± 0.023	-88 ± 33
$-NH-4-CH_2-NH_2$	51.876 ± 0.008	51.683 ± 0.013	193 ± 21
$-NH-5-5-NH-$	48.855 ± 0.003	48.705 ± 0.009	160 ± 12
$-NH-6-CH_2-NH-$	46.956 ± 0.002	46.903 ± 0.014	53 ± 16
NH_2-7-CH_2-NH-	41.180 ± 0.007	40.983 ± 0.012	242 ± 17
$NH_2-8-CH_2-N<$	39.312 ± 0.016	39.154 ± 0.012	158 ± 28

[a] The conditions are the same as given in Table 1. The results are the average of three or four determinations.

predicts the proper chemical shift differences for PEI within the limits of its precision. (Correlation coefficient = 0.984, and standard error = 23.04.)

Spin Lattice Relaxation Time (T_1)

The T_1's for PEI were measured by the inversion recovery method using an exponential regression equation to fit the peak intensities. It is assumed that, under the experimental conditions employed here, the extreme narrowing limit prevails and T_1 is a reflection of carbon mobility. This is supported by the apparent direct correlation between T_1 and the half-line width. The T_1's for the two components of Peak 4 are approximately equal. The major and minor components of Peaks 1 and 5 relax at different rates, T_1 for the up-field component being larger than the T_1 for the down-field component. The T_1 data for single and the major components of multiple peaks are summarized in Table 4.

The T_1 pattern is reasonable, reflecting high mobility of CH_2's at the chain ends and progressively lower mobility for CH_2's approaching the branch points. A comparison of PEI and branched polyethylene indicates that the mobility of the hydrocarbon chain units is much

TABLE 3. The Effect of NH/ND Exchange on the Chemical Shift of Low Molecular Weight Complex Amines[a]

Compound	Structural unit	Chemical shift, ppm		Shift difference, ppb	
		In H_2O	In D_2O	Observed	Calculated
Ethylenediamine	$NH_2\underline{C}H_2\underline{C}H_2NH_2$	44.069	43.828	241	238
Diethylenetriamine	$NH_2\underline{C}H_2CH_2NH-$	40.990	40.785	205	206
"	$NH_2CH_2\underline{C}H_2NH-$	51.613	51.508	105	109
Triethylenetetramine	$NH_2\underline{C}H_2CH_2NH-$	40.988	40.783	205	206
"	$NH_2CH_2\underline{C}H_2NH-$	51.709	51.599	110	109
"	$-NH\underline{C}H_2\underline{C}H_2NH-$	48.566	48.486	80	77
Tetramethylethylene-diamine	$>N-CH_2CH_2N<$	56.069	55.984	-85	-84
1,4,7,10-Tetraza-cyclododecane	$-NH\underline{C}H_2\underline{C}H_2NH-$	45.830	45.780	50	77
Piperazine	$-NH\underline{C}H_2\underline{C}H_2NH-$	45.928	45.826	102	77
Diazabicyclooctane	$>N-\underline{C}H_2\underline{C}H_2N<$	46.060	46.111	-51	-84

[a] The same conditions apply here as for Table 1. The data below the dashed line was not used in the regression formula which does not strictly apply to these cyclic compounds.

TABLE 4. Carbon-13 T_1 and Peak Areas for PEI[a]

Structural unit	T_1, ms[b]	Peak area, %[c]	T_1, s[d]
$>N-1-CH_2-NH_2$	212	8.6	-
$>N-2-CH_2-NH-$	152	14.4	1.0
$>N-3-3-N<$	145	18.5	-
$-NH-4-CH_2-NH_2$	384	10.4	3.7
$-NH-5-5-NH-$	223	12.6	2.0
$-NH-6-CH_2-N<$	177	15.4	1.3
NH_2-7-CH_2-NH-	665	10.3	7.1
NH_2-8-CH_2-N	335	9.7	-

[a] Same general conditions as in Table 1.

[b] Inversion recovery method, average of seven determinations.

[c] Data collect at pulse intervals of ten times the longest T_1.

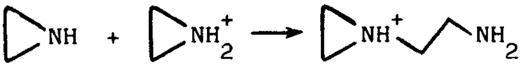
[d] For the corresponding CH_2's of branched polyethylene, Ref. 10.

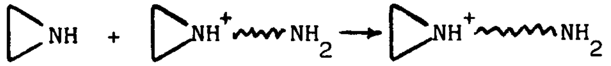
greater than the PEI units. Replacing a CH_2 of polyethylene with a heteroatom normally results in greater segmental mobility [14], which is the case for polyethyleneoxide. However, the mobility of PEI in water is no doubt restricted by a strong hydrogen bonding network. It would be interesting to compare these results with the T_1's of PEI in a solvent not capable of hydrogen bonding, in which case the only hydrogen bonding would be N–H–––N of the polymer.

Peak Area and Structural Analysis

The areas under conditions where the pulse interval was 10 × $t_{1/2}$ for the slowest relaxing peak are reported in Table 4. These results were unexpected because the contribution of closely spaced 3° amines, CH_2 = 3, is surprisingly high, but more important, these results do not support the commonly accepted distribution of amines, i.e., 1°:2°:3° = 1:2:1. In the analysis of these peaks we should first look for a 1:1 correspondence between Peaks 1-8, 2-6, and 4-7. The discrepancy ranges from 10% for the first pair to 1% for the last pair. The ratio of amine types is given by 1°:2°:3° = $(A_7 + A_8):(A_4 + A_5 + A_6)/2:(A_1 + A_2 + A_3)/3$. Our results give 1°:2°:3° = 1.45:1.39:1:1 or 38% 1°, 36% 2°, and

26% 3° amine. If one considers the usual mechanism of polymerization of ethyleneimine catalyzed by acids, Eqs. (3) - (6), the ratio of 1° to 3° amines of unity must be preserved.


(3)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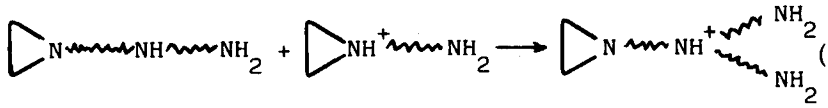
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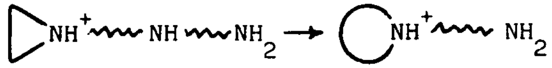
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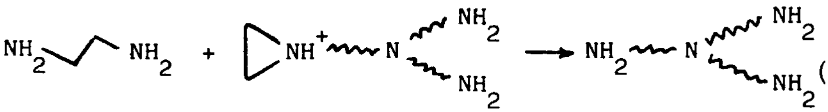
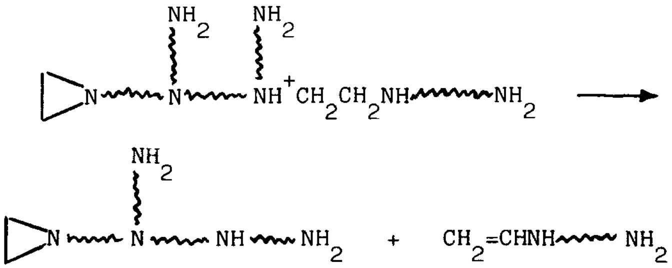

(7)

There are two possible explanations for this apparent discrepancy. The nuclear Overhauser effect (NOE) is not the same for all carbons, or chain stoppers such as ethylene diamine were used, Eq. (7), to control the molecular weight [1]. The fact that the carbons of PIE are all of the same type, CH_2's, would support the assumption that the NOE's are the same. The side reaction involving the elimination of a protonated 3° amine, Eq. (8), and the subsequent hydrolysis of the enamine product, Eq. (9), would have the same effect as Eq. (7). In the fragmentation process a 3° amine is converted to 1° amine. In reality, in one fragment a 3° amine is converted to a 2° and in the other a 2° to a 1°. Reactions (7) or (8) + (9) lead to a polymer with n 3° amines, xn 2° amines, and (n + 2) 1° amines.


(8)

$$CH_2{=}CHNH\sim\sim\sim NH_2 + H_2O \longrightarrow CH_3{-}CHO + NH_2\sim\sim\sim NH_2 \quad (9)$$

Applying our NMR results to this polymer, x = 1, and solving 3°/1° = n/(n + 2) = 0.68 for n gives n = 4.3. It is also true that $\overline{DP}_n = \Sigma N's$ which, according to our results, gives $\overline{DP}_n$ = 15 (4.3 3° + 4.3 2° + 6.3 1°) as opposed $\overline{DP}_n$ = 42 based on $\overline{M}_n$ for this polymer (see Experimental). This is a very critical test of these results. An experimental value for 3°/1° 10% bigger would give $\overline{DP}_n$ = 33. This analysis would also be strongly influenced by the presence of linear polymer where 3°/1° = 0. It is clear from these results that ^{13}C-NMR is revealing in terms of the structural units present and their relative contribution to the total structure; however, it is clear this technique is not without its quantitative limitations. It is safe to say that for this particular sample of PIE the amine distribution is 1° > 2° ≃ 3°.

The fine structure in Peaks 1, 4, and 5, the minor components of 1 and 5 being designated 1' and 5', may yield additional structural information. The relative peak areas, left to right, are approximately 2.2:1 in 1, 1.2:1 in 4, and 1:1.6 in 5. The unspecified bonds of nitrogen adjacent to CH_2 = 1 may lead to the following combination of nitrogens, 1° 2°, 1° 3°, 2° 2°, 2° 3°, and 3° 3° with normalized probabilities of 0.27, 0.27, 0.13, 0.19, and 0.07, respectively.

Peak 1' relaxes at a faster rate than Peak 1. If the first combination is ascribed to 1' and the others to 1, the ratio of peak areas would be 2.4:1. In the ^{15}N-NMR which yields long-range sequence distribution, Kricheldorf identifies three of the five combinations listed above: the first, third, and fourth. The analysis of Peak 4 is simplified by the fact that there is only one unspecified nitrogen bond and it must lead to a 3° or 2° nitrogen with probabilities of 0.58 and 0.42, respectively, or relative peak areas of 1.4:1. Kricheldorf identifies only one of these two peaks as making a significant contribution to the 28 component of the ^{15}N-NMR. For Peak 5 the two unspecified bonds are not equivalent with respect to the carbon in question, in contrast to Peak 4, which leads to eight combinations. There is no particular rational for analyzing this peak.

EXPERIMENTAL

The polymer used in this study is commercial PEI-18 (Dow Chemical) with a reported $\overline{M}_n$ = 1800. The low molecular amines used in this project were bought and used as received. Solutions of each amine, in the free base form, were prepared in H_2O or D_2O at 10% (w/v) to which was added dioxane as the internal reference. Since PEI-18 is supplied as a 33% solution in water, the polymer was lyophilized before it was used in the D_2O runs. The amount of H introduced with the sample was less than 5%. The NMR spectra were recorded using a Bruker WH-400 at 100.62 MHz at a probe temperature of 333 K. The chemical shifts were calculated against dioxane at 67.40 ppm from TMS. The inversion recovery method was used to generate the data which were fitted by an exponential regression routine to calculate T_1's. For the integrated spectra collected under equilibrium conditions, the pulse interval was at least 10 times the $t_{1/2}$ of the slowest relaxing peak.

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