parison of Tables II and III. The titration behavior of this polymer in terms of $\Delta H$ and $T\Delta S$ is very sensitive to temperature, much more sensitive than would be indicated by potentiometric titration alone. For a given ionic strength and charge state, $\Delta G$ is not very different for the two temperatures. The differences in $\Delta H$ and $T\Delta S$, however, are quite dramatic. The available polyelectrolyte theories cannot quantitatively explain this effect. Qualitatively, the origin of the temperature effect must come from changes in polymer conformation that are dependent on charge state and temperature. Conformational changes directly influence $\Delta S$ and indirectly effect $\Delta H$ through a change in heat capacity. The latter is a reasonable explanation for the change in $\Delta H$ with temperature at constant $\alpha$.

In summary, the various thermodynamic parameters as a function of $\alpha$ for both polymers are shown in Figure 1. The electrostatic and counterion condensation models failed to accurately predict the changes in $\Delta H$ and $T\Delta S$ for both PVA and PIE, especially in the region $\alpha = 0$–0.5. The nearest-neighbor model mentioned above, which allows for the assignment of a separate $\Delta H$ for each triad and a change in triad distribution with $\alpha$, is being explored. However, a complete description must take into consideration the changes in polymer conformation and all of their ramifications. The $T\Delta S$ term is apparently most sensitive to these effects. Calorimetric and NMR data should make an important contribution to our understanding of polyelectrolyte behavior.

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# Carbon-13 and Nitrogen-15 Spin–Lattice Relaxation Studies of Poly(vinylamine) and Poly(iminoethylene)

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ABSTRACT: $^{13}C$ and $^{15}N$ dipolar relaxation rates of poly(vinylamine) and poly(iminoethylene) were measured. Relaxation in poly(vinylamine) is consistent with relatively unhindered rotation of the $NH_3^+$ group. At neutral pH, the rotation rate is slowed, consistent with hydrogen bonding between alternate $NH_3^+$ and $NH_2$ groups. Rotational jump rates and barriers are reported. The motion of the NH groups of poly(iminoethylene) is more restricted relative to the polymer backbone $CH_2$ groups. This is reflected by the $^{15}N/^{13}C$ $NT_1$ ratios.

## Introduction

In order to identify the segmental and group internal motions of poly(vinylamine) and, in particular, to determine whether $^{13}C$ and $^{15}N$ relaxation data were consistent with a proposed model where rapid $NH_3^+$ group rotation occurs up to a pH where alternate $NH_2$ and $NH_3^+$ groups interact to quench this motion, we studied the $^{13}C$ and $^{15}N$ relaxation properties of this polymer.

In general, relaxation of a given nucleus has a variety of mechanisms which all contribute to its total relaxation time, $T_1^{total}$ (eq 1). These include, in the order shown in

$$\frac{1}{T_1^{total}} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{CSA}} + \frac{1}{T_1^{SR}} + \frac{1}{T_1^{Q}} + \frac{1}{T_1^{SC}} \quad (1)$$

eq 1, dipolar, chemical shift anisotropy, spin rotation, quadrupolar, and scalar mechanisms for relaxation.

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Paramagnetic relaxation is simply the sum of contributions from dipolar and scalar interactions with unpaired electrons. Of these mechanisms, it is the dipolar interactions with protons which most readily allows the analysis of molecular motion of organic molecules. For the cases of $^{15}N$ and especially $^{13}C$, with directly bonded protons, dipolar interaction with these protons is usually the predominant mechanism for relaxation and is given by eq 2,

$$\frac{1}{NT_1^{DD}} = \frac{\gamma_H^2\gamma_X^2\hbar^2}{r_{XH}^6}\tau_{eff} \quad (2)$$

where $\gamma_H$ and $\gamma_X$ are the magnetogyric ratios of $^1H$ and $^{13}C$ or $^{15}N$, $r_{XH}$ is the internuclear distance, $N$ is the number of directly bonded protons, and $\tau_{eff}$ is the effective correlation time (assuming pseudoisotropic motion). Equation 2 assumes that the extreme spectral narrowing condition is satisfied (i.e., $\omega^2\tau_{eff}^2 \ll 1$, where $\omega$ is the observation frequency of nucleus X). Under these conditions, the nuclear Overhauser enhancement factor (NOEF) is given by

$$\text{NOEF} = \frac{\gamma_H}{2\gamma_X}\frac{T_1^{total}}{T_1^{DD}} \quad (3)$$

Therefore, even when other mechanisms contribute to the total relaxation rate, $T_1^{DD}$ can be obtained.

The comparison of $^{15}N$ and $^{13}C$ relaxation times of CH, $CH_2$, and $NH_3^+$ should allow determination of the relative motion of these substituents (e.g., whether or not rapid $NH_3^+$ rotation occurs as with $CH_3$). However, assumptions must be made in order to extract this information. First, the "extreme spectral narrowing condition" must be satisfied so that the simple relationship between $1/T_1^{DD}$ and the correlation time $\tau_{eff}$ can be used. Since the $T_1$'s are relatively long and the NOEF's are full, this assumption is justified for most of the polymer systems studied. Secondly, it is assumed that complications arising from complex motions which cause unusual field-dependent behavior[2] are not present. Again, this assumption is reasonable since the NOEF's are all close to the theoretical maxima for $^{13}C$ and $^{15}N$.

If similar motion causes relaxation of these two nuclei in a molecule, the ratio of these dipolar $T_1$'s is given by

$$\frac{NT_1^{DD,^{15}N}}{NT_1^{DD,^{13}C}} = \left(\frac{r_{NH}}{r_{CH}}\right)^6\frac{\gamma_{^{13}C}^2}{\gamma_{^{15}N}^2} = 4.4 \quad (4)$$

where the $r_{NH}$ and $r_{CH}$ bond distances used are 1.03 and 1.09 Å, respectively. Note that the ratios must be corrected for the number of directly bonded protons, $N$.

## Experimental Section

Samples of poly(vinylamine) and poly(iminoethylene) were provided by Professor T. St. Pierre, University of Alabama, Birmingham, Ala., and are described in the preceding paper.[3]

$^{13}C$ spectra were obtained at 67.9 MHz on a Bruker HX-270 spectrometer, using 10-mm tubes, and $^{15}N$ spectra were obtained at 15.2 MHz on the in-house-design SEMINOLE spectrometer (operating at 150-MHz proton frequency), using 25-mm tubes (typically, 1–4K scans were accumulated for the $^{15}N$ $T_1$ experiments). Spectra were accumulated using quadrature detection, a ±2-kHz spectral window, and 4K/4K data points. $T_1$'s were measured by using a fast inversion–recovery pulse sequence[4a] and were analyzed by a nonlinear three-parameter fitting procedure.[4b] NOEF's were determined using gated decoupling with a delay of $5T_1$ to $10T_1$ between pulses. Temperature was regulated between 30 and 35 °C for all experiments.

In many instances tacticity effects resulted in the observation of multiple $CH_2$ and CH resonances in the $^{13}C$ NMR spectra. In these instances, the $T_1$'s reported are the averaged values of the resonances (the individual $T_1$'s did not deviate from the average by more than 10%). Tacticity effects could not be resolved in any of the $^{15}N$ spectra, where a single broad line was observed at all times, particularly at high pH. (At low pH the "line" was narrower, ca. 10 Hz.)

Table I
Relaxation Data for 17% Aqueous Poly(vinylamine)

| | $T_1$,[a] s | | | NOEF[b] | | |
|---|---|---|---|---|---|---|
| pH | CH | $CH_2$ | $NH_x$ | CH | $CH_2$ | $NH_x$ |
| [c] | 0.25 | [d] | 0.94 | 1.7 | [d] | −2.0 |
| 2.8 | 0.21 | 0.10 | 1.06 | 1.6 | 1.7 | −5.0 |
| 3.8 | 0.29 | 0.18 | 1.34 | 1.6 | 1.6 | −4.7 |
| 6.7 | 0.38 | 0.17 | 0.89 | 1.7 | 1.8 | −5.0 |
| 8.6 | 0.52 | 0.26 | 0.92 | 1.9 | 1.9 | −2.7 |
| 10.1 | 0.50 | 0.27 | 1.2 | 2.0 | 1.8 | −5.0 |

[a] ±10%. [b] ±20%. [c] In methanesulfonic acid, 20% (w/v). [d] Obscured by solvent resonance.

Table II
$^{13}C$ and $^{15}N$ Dipolar Spin-Lattice Relaxation Data for 17% Aqueous Poly(vinylamine)

| | | $T_1^{DD}$, s | | | | dipolar $NT_1$ ratios ($^{15}N/^{13}C$) | |
|---|---|---|---|---|---|---|---|
| pH | $\eta$, cP | CH[a] | $CH_2$[a] | $NH_3^+$[b] | $NH_2$[b] | $NH_3^+$ | $NH_2$ |
| [c] | | 0.25 | [d] | 2.4 | | 30 | |
| 2.8 | | 0.21 | 0.10 | 1.1 | | 16 | |
| 3.8 | 27.2 | 0.29 | 0.18 | 1.4 | | 13 | |
| 6.7 | 9.2 | 0.35 | 0.17 | 0.89[e] | | 6.4[e] | |
| 8.6 | 6.5 | 0.52 | 0.26 | 1.3[e] | | 6.3[e] | |
| 10.1 | | 0.50 | 0.27 | | 1.2 | | 5.0 |

[a] ±10%; NOEF's are theoretical maximum within experimental error. [b] $T_1^{DD}$'s calculated from $T_1$'s and NOEF's, ± 20%. [c] In methanesulfonic acid, 20% (w/v). [d] Obscured by solvent resonance. [e] Near equivalence point. Assumes nitrogens only half-protonated.

## Results and Discussion

**Poly(vinylamine).** The $^{13}C$ and $^{15}N$ dipolar spin–lattice relaxation times of aqueous poly(vinylamine) at various pHs are given in Table I, along with the data for a 20% solution in methanesulfonic acid. In all cases $CH_2$ $T_1$'s are approximately half of the CH $T_1$'s, consistent with pseudoisotropic segmental motion of the polymer backbone. The shortest $T_1$'s measured (~0.2 s) are just outside the extreme narrowing region, and although use of the extreme narrowing approximation does not lead to a significant error in calculating $\tau_{eff}$, the NOEF's are predicted to be measurably lower than the theoretical maximum of 1.99. For an $NT_1$ of 0.2 s, the NOEF is predicted to be 1.7, consistent with the observed values shown in Table I.

Due to the freer motion of the nitrogen, $^{15}N$ $T_1$'s are well within the extreme narrowing region; however, some of the $^{15}N$ NOEF's are still far below the theoretical maximum value of 4.98. Presumably, this is due to the presence of paramagnetic impurities (usually metal ions) which coordinate to the basic nitrogen atoms. Since binding is directly to nitrogen, this nucleus is most sensitive to the effects of paramagnetic relaxation. Conversely, the relaxation of carbon, which is usually several bonds removed from the paramagnetic center, is not usually affected by the presence of trace paramagnetic impurities. When other mechanisms contribute to the total relaxation, the dipolar term ($T_1^{DD}$) which is of interest can readily be obtained from eq 3. It is these $T_1^{DD}$'s which are given in Table II.

Assuming pseudoisotropic motion, the effective correlation time ($\tau_{eff}$) for the polymer backbone can be obtained from the dipolar $^{13}C$ $T_1$'s and eq 2. Assuming rotation between three equivalent positions, the correlation time

Table III
Calculated Motional Properties and $NH_x$ Rotational Barriers for 17% Aqueous Poly(vinylamine)

| pH | $\tau_{eff}$, s | $R$, $s^{-1}$ | $E_a$, kcal/mol |
|---|---|---|---|
| a | $1.9 \times 10^{-10}$ | $<1.3 \times 10^{11}$ | <2.8 |
| 2.8 | $2.35 \times 10^{-10}$ | $2.1 \times 10^{10}$ | 3.9 |
| 3.8 | $1.45 \times 10^{-10}$ | $2.1 \times 10^{10}$ | 3.9 |
| 6.7 | $1.35 \times 10^{-10}$ | $4.0 \times 10^{9}$ | 5.0 |
| 8.6 | $9.1 \times 10^{-11}$ | $6.2 \times 10^{9}$ | 4.8 |
| 10.1 | $9.1 \times 10^{-11}$ | $1.0 \times 10^{9}$ | 5.3 |

[a] In methanesulfonic acid, 20% (w/v). [b] Error <±10%.

for rotation of the $NH_3^+$ group can then be calculated by eq 5 in a manner analogous to that for a $CH_3$ group. In

$$\frac{1}{NT_1^{15N}} = \frac{3\gamma_H^2\gamma_N^2\hbar^2}{(r_{NH})^6}\left[\frac{A}{6D_{eff}} + \frac{B+C}{6D_{eff}+R_{int}}\right] \quad (5)$$

eq 5 $A$, $B$, and $C$ are geometric constants (calculated assuming tetrahedral geometry at nitrogen) and $D_{eff}$ and $R_{int}$ are the molecular diffusion constant and the jump rate for $NH_3^+$ rotation, respectively ($D_{eff}$ is related to correlation time (obtained from the $^{13}C$ $T_1^{DD}$ by $\tau_{eff} = 1/(6D_{eff})^{5,6}$). Using these calculated diffusion constants for internal rotation, one can calculate the energy barriers for $NH_3^+$ group rotation by using the relationship described by eq 6. $R_0$ is the value for unrestricted rotation and is given

$$E_a = -RT \ln (R_{int}/R_0) \quad (6)$$

by eq 7, where $I$ is the moment of inertia about the axis

$$R_0 = \tfrac{1}{2}(kT/I)^{1/2} \quad (7)$$

of rotation. Values of $R_0 = 1.4 \times 10^{13}$ and $1.7 \times 10^{13}$ $s^{-1}$ were calculated for $NH_3^+$ and $NH_2$ groups, respectively.

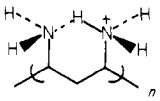
If group rotation does not occur, the $^{15}N/^{13}C$ $NT_1$ ratio should be 4.4. For unrestricted group rotation $R_0$ is substituted for $R_{int}$ in eq 5 and the $^{15}N/^{13}C$ $NT_1$ ratio is calculated to be ca. 40.

The last column in Table II gives the $^{15}N/^{13}C$ dipolar $NT_1$ ratios. Note that the $^{13}C$ $NT_1^{DD}$ values used to calculate these ratios are corrected to reflect relaxation of $^{13}C$ from a single proton. $^{13}C$ $NT_1^{DD}$ values are the average values for CH and $CH_2$ and were obtained by using

$$NT_1^{DD} = (T_1^{CH} + 2T_1^{CH_2})/2 \quad (8)$$

$^{15}N$ $NT_1^{DD}$'s were obtained by using an estimate for the number of protons attached ($NH_x$, where $x = 3$ at pH 2.8–3.8, $x \simeq 2.5$ at pH 6.7–8.6, and $x = 2$ at pH 10.1). In some cases the dipolar $T_1$ ratios are considerably higher than the expected value of 4.4.

At low pH (2.8) the $NT_1^{DD}$ ratio (~16) is significantly higher than the expected value of 4.4, indicating a large amount of group rotation. At neutral pH, as the fraction of protonated amine decreases, this ratio drops sharply (to approximately 6), close to the expected value for no rotation. This is consistent with restricted motion due to the formation of a hydrogen-bonded structure such as I, which would restrict free $NH_2$ and $NH_3^+$ group rotation. The $T_1$ ratio of 5.0 at pH 10.1 is the same (within experimental error) as that calculated for a "rigid" $NH_2$ group.



I

The first entries in Table I and II refer to the relaxation data of poly(vinylamine) in methanesulfonic acid. In methanesulfonic acid, a relatively noninteracting solvent, the $T_1$ ratio of 30 is extremely large. A freely rotating $NH_3^+$ group would be expected to have an $NT_1$ ratio near 40; the methanesulfonic acid results indicate that $NH_3^+$ in this medium undergoes rotation with a very low energy barrier. However, rotation of $NH_3^+$ in water is somewhat hindered, no doubt due to interactions with the solvent molecules and/or counterions.

The calculated correlation times and energy barriers for poly(vinylamine) are given in Table III. Although $\tau_{eff}$ for the backbone carbons varies by only a factor of 2, $\tau_{rot}$ for $NH_x$ varies by almost 2 orders of magnitude. Group rotation is almost unrestricted in the nonnucleophilic methanesulfonic acid, and it decreases in aqueous solution from rapid rotation at low pH to essentially no rotation at pH ≳6 (on this $T_1$ time scale), and at higher pH the rotation rate increases again.

The energy barriers for $NH_x$ group rotation also reflect this trend. The rotation barrier is very low in methanesulfonic acid. In the aqueous media the low barrier to rotation increases to a maximum near the point of half-protonation. This is consistent with a strong interaction between $NH_3^+$ and neighboring $NH_2$ groups (as in I). There is evidence of a different nature in the preceding paper in support of this theory.[3]

Blunt and Stothers[7] have shown that under certain conditions calculated rotation barriers can be sensitive to the geometry assumed for the rotating group. However, this is only significant for barriers less than ca. 2 kcal/mol. Thus, only the barrier of the freely rotating $NH_3^+$ group of PVA in methanesulfonic is subject to large inaccuracies from this source.

**Poly(iminoethylene).** Since the NH (or $NH_2^+$) groups are incorporated into the backbone of this polymer, their motion should more closely resemble the $CH_2$ groups. Note again that at low pH (all $NH_2^+$) the $^{15}N/^{13}C$ $NT_1$ ratio should be 4.4 for similar motion, assuming isotropic motion. This is similar to observed ratios in Table IV. The $T_1$ ratios are consistently low compared with the expected value.[8] This is probably due to some motional restriction of the NH group resulting from intramolecular interactions and hydrogen bonding to the solvent. Note that at all pHs where $^{15}N$ $T_1$ data were obtained, a significant portion of the amine is probably still protonated. Note that at pH 2.1, the $^{13}C$ and $^{15}N$ NOEF's are significantly lower than the theoretical maximum values. This

Table IV
$^{13}C$ and $^{15}N$ Dipolar Spin-Lattice Relaxation Data for 17% Aqueous Poly(ethylenimine)

| pH | $\eta$, cP | $T_1$,[a] s | | NOEF[b] | | $T_1^{DD}$, s | | dipolar $NT_1$ ratios ($^{15}N/^{13}C$) |
|---|---|---|---|---|---|---|---|---|
| | | $CH_2$ | $NH_2^+$ | $CH_2$ | $NH_2^+$ | $CH_2$ | $NH_2^+$ | |
| 2.1 | 8.5 | 0.87 | 1.6 | 1.5 | −3.5 | 0.87 | 2.3 | 2.6 |
| 3.3 | 4.0 | 0.68 | 2.0 | 1.8 | −4.7 | 0.68 | 2.1 | 3.1 |
| 5.6 | 2.2 | 0.54 | 2.6 | 1.9 | −5.0 | 0.54 | 2.6[c] | 3.6[c] |
| 7.7 | | 1.1 | 2.6 | 1.9 | −3.5 | 1.1 | 3.9[c] | 2.7[c] |

[a] ±10%. [b] ±20%. [c] Near equivalence point. Assumes nitrogens only half-protonated ($N = 1.5$).

is probably due to the presence of complex molecular motions which cause deviations from the predictions of simplified theories.[2] $^{15}N$ $T_1$ measurements could not be performed at higher pH due to low sensitivity resulting from broad lines (in turn due to polymer precipitation).

## Conclusion

$^{15}N/^{13}C$ $T_1$ ratios are similar to those predicted theoretically for polymers such as poly(iminoethylene), where the motional characteristics of $CH_2$ and $NH_2^+$ are similar. In poly(vinylamine) the motional characteristics of backbone CH and $CH_2$ carbons are not similar to those of the $NH_3^+$ group. The $^{15}N/^{13}C$ $NT_1$ ratios at low pH indicate free rotation of the $NH_3^+$ group analogous to the $CH_3$ group rotation.

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(8) Assumption of pseudoisotropic motion for poly(iminoethylene) is not necessarily appropriate. Only one carbon type is available, unlike the situation for poly(vinylamine).

# Carbon-13 Nuclear Magnetic Resonance Studies on Soluble Poly(diacetylenes)

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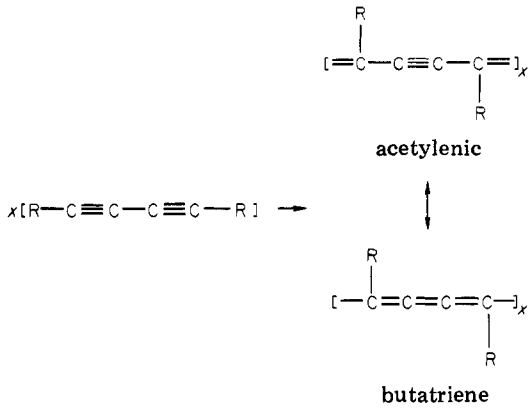
ABSTRACT: $^{13}C$ NMR studies on two poly(diacetylenes), $(=CR-C\equiv C-CR=)_x$, where R is $-(CH_2)_{3,4}OCONHCH_2COO(CH_2)_3CH_3$, in different solvents and at different temperatures are reported. The peaks for —C= and —C≡ indicate that the backbone has the enyne structure, commonly known as the acetylenic structure, in solution. The solutions form solid gels at lower temperatures. Polymer molecules acquire a rigid planar conformation in the gels. As a result, the peaks for the backbone carbons and methylene carbons adjacent to the backbone disappear and those of carbonyl and methylene groups are broadened in the gels.

## Introduction

Diacetylenes, R—C≡C—C≡C—R, where R is a substituent group, polymerize in the solid state either upon thermal annealing or upon exposure to high-energy radiation.[1-3] The polymerization occurs via 1,4 trans addition of the triple bonds:




The structure of the backbone is a resonance hybrid of the acetylenic and the butatriene structures. Raman spectra of a number of poly(diacetylenes) show bands for —C≡C— and —C=C— symmetrical stretching vibrations.[4] The polymers are colored because the electron density is delocalized extensively along the conjugated backbone.[4]

Since most poly(diacetylenes) are insoluble in common organic solvents, no $^{13}C$ NMR studies of poly(diacetylenes) have been reported. However, we recently synthesized a new class of poly(diacetylenes) which show high solubility in a number of common organic solvents, e.g., chloroform, dimethylformamide, nitromethane, dichlorobenzene, and methyl ethyl ketone.[5] The substituent groups of the soluble poly(diacetylenes) are $(CH_2)_lOCONHCH_2COO(CH_2)_mCH_3$, where $l$ = 3 or 4 and $m$ = 1 or 3. We used samples from this class of poly(diacetylenes) for the present $^{13}C$ NMR studies. We shall refer to the poly(diacetylenes) as poly*l*ACMU, where ACMU stands for [(alkoxycarbonyl)methylene]urethane and $l$ represents the number of methylene groups adjacent to the backbone.

Solutions of the soluble poly(diacetylenes) undergo sharp, reversible color changes, yellow ↔ blue (or red), when the solvent/nonsolvent ratio[5] or the temperature[6] is varied. In the case of poly3BCMU the lowest energy optical transition shifts by more than 5000 $cm^{-1}$ (21 300 to 15 900 $cm^{-1}$). The color changes are due to a nonplanar ↔ planar conformational transition of the backbone. On the basis of spectroscopic studies,[5,6] it is shown that the poly(diacetylenes) acquire a planar conformation in blue (or red) solution or gel while the conformation is nonplanar

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