Proton and Carbon-13 Spin–Lattice Relaxation Times Investigation of the Segmental Motion of Poly(4-vinylpyridinium bromide) in Methanol Solution

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ABSTRACT: The dynamical behavior of poly(4-vinylpyridine) quaternized by HBr in methanol solution has been investigated by spin–lattice relaxation of ^1H at 100 and 250 MHz and of ^{13}C at 25 MHz between 250 and 350 K. As in the case of neutral P4VP, the relaxation data have been interpreted in terms of a quasiisotropic segmental motion of the aliphatic backbone, assuming a temperature-dependent distribution of correlation times and an oscillation of the pyridinium ring about the C4N axis. The geometrical parameters for the interpretation of the ^1H relaxation have been obtained by conformational calculations on the *rrmrr* hexad assuming that Br^- either remains in the vicinity of the pyridinium ion or it does not. The potential barriers of the different motions were calculated for a *rm* triad considering these two models of charge distribution. The best agreement between the experimental data and the T_1 vs. T^{-1} curves computed for the three spectrometer frequencies was achieved by taking $\Delta H^{\ddagger}_R = 6$ kcal mol^{-1}, $(\tau_R)_0 \simeq 10^{-13}$ s for the aliphatic backbone, $\Delta H^{\ddagger}_G \simeq 2$ kcal mol^{-1}, $(\tau_G)_0 \simeq 1.4 \times 10^{-11}$ s for the pyridinium ring. The amplitude of oscillation increases from 40 to 85° between 250 and 350 K. The increased rigidity of the P4VP upon quaternization is shown by the average ratios of correlation times relative to the protonated polymer and to neutral P4VP which are 1.7 for τ_R and 2.7 for τ_G at 300 K.

I. Introduction

The poly(vinylpyridines) which can be obtained under a neutral or a protonated cationic form are very convenient for studying the effect of electric charges on the dynamical behavior of a macromolecule in solution.

Work in progress on the molecular motions in poly(4-vinylpyridine) quaternized by *n*-alkyl bromides[1,2] prompted us to examine most particularly the influence of ionic interactions between pyridinium rings. For that purpose we have studied the simplest macromolecular model, that is the poly(4-vinylpyridine) quaternized by hydrogen bromide ($P4VPD^+$) in CD_3OD solution.

In a recent publication[3] we have proposed a theoretical model for the segmental motion of the neutral atactic poly(4-vinylpyridine) (P4VP) in methanol solution. The proton and carbon-13 spin–lattice relaxations in this polymer were interpreted by assuming a quasiisotropic reorientation of the segments of the polymer chain and an anisotropic motion of the pyridyl ring undergoing oscillations of limited amplitude about the C_4N axis.

In the present work we interpret by similar methods the temperature dependence of ^1H and ^{13}C spin–lattice relaxation times of $P4VPD^+$ in the same solvent. The interpretations of relaxation data in terms of molecular motions are supported by conformational energy calculations taking into account the charge distribution on monomer units and the dielectric constant of the solvent, the results being compared with those obtained with P4VP in similar conditions.

II. Experimental Procedure

The P4VP has been obtained by free-radical polymerization as previously reported.[3] The molecular weights determined by viscosimetry before quaternization were 130 000 and 220 000 for the polymer samples under study. The quaternization was done by dissolution of P4VP in aqueous hydrobromic acid. The quaternized polymer was recovered from aqueous solutions by addition of acetone and purified by successive precipitations by ethyl ether from methanol and dried under vacuum at 50 °C. To obtain comparable results, the ^1H and ^{13}C relaxation time measurements were carried out on solutions of equivalent concentrations, generally 0.5–0.6 M in monomer units. The relaxation times were measured in Fourier transform for magnetic fields of 23.5 kG (ν_{1H} = 100 MHz, ν_{13C} = 25.15 MHz) with a Varian XL100 spectrometer and of 58.7 kG with a Cameca TSN250 spectrometer (ν_{1H} = 250 MHz) by means of 180°,t,90° sequences for ^1H and 90°,$\tau \gg T_1$,180°,t,90° sequences for ^{13}C. The recovery time between the sequences was five to eight times the estimated value of T_1. All experiments were done on polymer solutions in CD_3OD, the magnetic field being locked on the deuteriomethyl resonance. The ^{13}C measurements were performed under noise decoupling of protons. The ^{13}C and ^1H chemical shifts given here are relative to an internal reference of Me_4Si.

III. Results

(1) ^{13}C and ^1H NMR Spectra. The ^{13}C spectrum of $P4VPD^+$ is shown in Figure 1. It is seen that the resonances of methine and methylene carbons designated hereafter by α and β are exactly superimposed at 42.5 ppm from Me_4Si, the resonances of C2 and C3 being located at 143.2 and 128.5 ppm, respectively. The resonance of the quaternary carbon is split into two peaks assigned respectively to *mm* triads (166.9 ppm, relative intensity 0.23) and to *mr* + *rr* triads (166.1 ppm, relative intensity 0.77). These relative intensities are indeed consistent with the tacticity found in the case of P4VP[3] assuming a Bernouillan statistic with P_m = 0.47. The ^1H NMR spectrum of $P4VPH^+$ (Figure 2) does not show the resonance of the proton attached to the nitrogen because of the rapid exchange with deuterons of the hydroxyl group of CD_3OD in large excess with respect to the polymer (consequently the studied polymer is $P4VPD^+$). As in the case of P4VP the resonances of Hα and Hβ of the aliphatic chain are collapsed into a single line at 2.27 ppm, whereas the weak resonance of the α protons included in *mm* triads is observed at 3.05 ppm. These results are actually in full agreement with the recent work of Matsuzaki et al.[4]

The resonances of H_2 and H_3 are located at 8.71 and 7.92 ppm, respectively. The former is a single line and the latter shows partially resolved structures with two peaks at 8.17 and 8.32 ppm, the relative intensities of which are 0.09 and 0.04. These two small peaks are tentatively assigned to *mmmr* and *mmmm* pentads, respectively, their intensities being fairly close to the corresponding values expected from Bernouillan statistic with P_m = 0.47 (0.11 and 0.05).

(2) Conformational Calculations. The local equilibrium conformations of $P4VPD^+$ and the energy required for the different kinds of segmental motions have been obtained by conformational energy calculations. For the polymer under study we have assumed that the geometry and the charge distribution in the pyridinyl ring are similar to the ones of pyridinium chloride.[5,6] We have considered two limiting cases (Table I):

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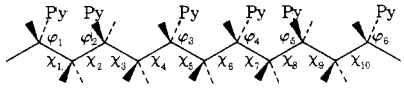
Table I
Assumed Geometry and Charge Density Distribution of the Pyridinium Ring in P4VPD$^+$ (from ref 5 and 6)

Distances, nm	Angles, deg		Charge densities × 10^3 Model II	Model I
$C_\alpha C_\beta = C_\alpha C_4 = 0.154$	$\angle C_\beta C_\alpha H_\alpha = \angle C_\beta C_\alpha C_4 = 109.5$	C_4	+139	−81
$C_4C_3 = 0.140$	$\angle C_3C_4C_{3'} = 125$	C_3	−32	−53
$C_3C_2 = 0.142$	$\angle C_4C_3C_2 = 115$	C_2	+135	+131
$C_2N = 0.132$	$\angle C_3C_2N = 118$	H_3	+140	+108
$C_\alpha H_\alpha = 0.109$	$\angle C_2NC_{2'} = 128$	H_2	+161	+137
$C_3H_3 = 0.108$	$\angle NDBr = 180$	N	−262	−275
$C_2H_2 = 0.111$		D	+313	+336
ND = 0.101		Br	(−1000)	−804
DBr = 0.220				

Table II
Stable Conformations Given by the SIMPLEX Program for the *rrmrr* Hexad Using the Following Conventions: $\chi_i = 0$ for Trans-Trans Conformation of the Aliphatic Carbon Backbone and $\Phi_i = 0$ for H_α and Pyridyl Ring in the Same Plane



	D^a	Φ_1	χ_1	χ_2	Φ_2	χ_3	χ_4	Φ_3	χ_5	χ_6	Φ_4	χ_7	χ_8	Φ_5	χ_9	χ_{10}	Φ_6
Model I	3.5	−2	−2	−5	−1	−8	−16	−3	+95	−7	+1	+17	+10	+2	+1	+1	+7
	20	−2	−6	+5	−3	−8	−1	−1	+107	+8	+1	−5	+5	+1	−3	+4	0
Model II	20	−2	−2	−1	0	−1	−1	0	+105	0	0	−2	−2	−1	0	0	3

[a] Dielectric constant.

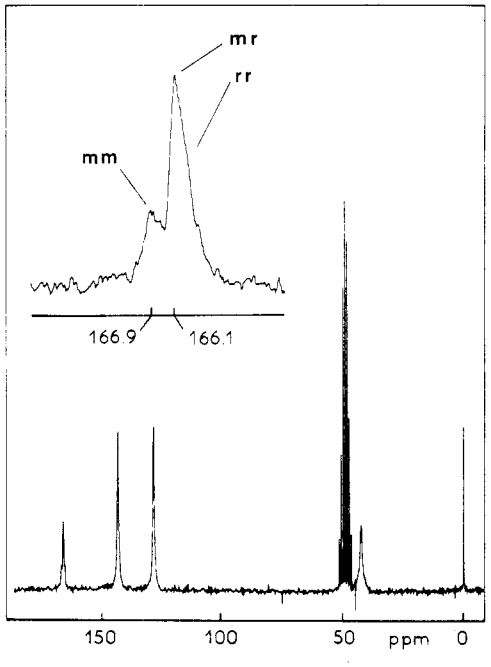


Figure 1. ^{13}C NMR spectrum of poly(4-vinylpyridinium bromide); 0.6 M in CD_3OD at 26 °C under complete noise decoupling of protons and with Me_4Si as internal reference. The expanded part of the spectrum is that of C_4.

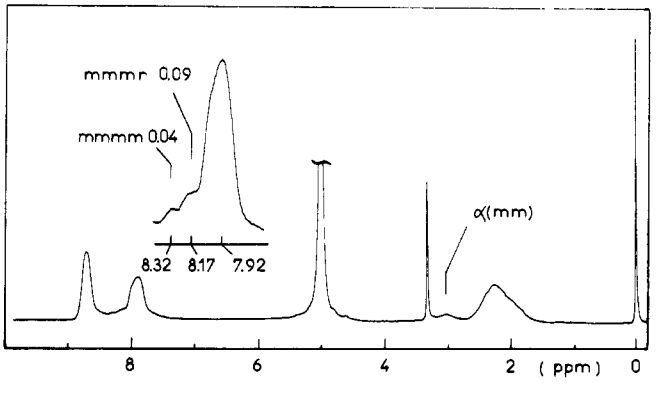


Figure 2. ^1H NMR spectrum of the P4VPD$^+$ at 250 MHz; 0.6 M solution in CD_3OD at 22 °C with Me_4Si as internal reference. Extended spectrum: resonance of H_3.

(a) The Br^- ion is located along the N^+D axis and forms a charge-transfer complex with the pyridinium ring (model I). In our calculations the D–Br distance was increased with respect to the D–Cl distance by the difference of the van der Waals radii of the two halogen atoms. The dielectric constants were taken equal to 3.5 (standard value) and to 20 as suggested by various works.[7,8]

(b) The Br^- ion is not at the vicinity of pyridinium counterions (model II) and therefore not taken into account in the calculations. This assumption implies that the polymer is fully ionized and that the dielectric constant of the solution is comparatively high so that we have taken only $D = 20$ in this case.

Using the same conventions as in our preceding work[3] we have calculated the equilibrium local conformations of the polymer by the SIMPLX[9] program of minimization taking the *rrmrr* hexad as a model for the atactic P4VPD$^+$ (Table II). The conformational energy calculations limited to *rm* triads were performed by means of the DESCARTES program by varying the different torsion angles. The minimum energy conformations found with the DESCARTES program are in agreement with those provided by the SIMPLEX program. This latter was used also for the calculation of interproton distances needed for the interpretation of proton relaxation experiments. Table II shows that the conformation of the aliphatic chain in the meso diads is very close to trans-gauche for models I and II taking $D = 3.5$ or 20 ($\chi_5 = 95$, 107, and 105°). For the racemic diads, models I and II with $D = 20$ indicate a nearly trans-trans conformation of the aliphatic backbone whereas the model I with $D = 3.5$ deviates markedly from this conformation ($\chi_4 = -16°$ and $\chi_7 = +17°$).

The interproton distances computed for models I and II with $D = 20$ are not so different and one cannot expect to

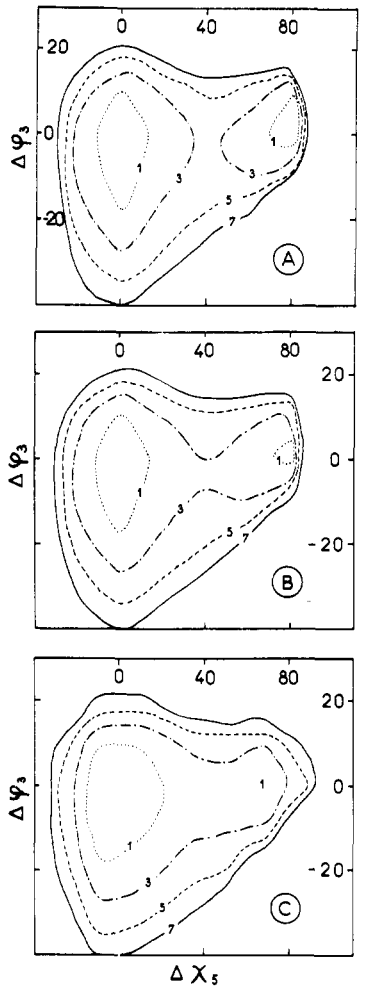


Figure 3. Conformational energy maps obtained with the DESCARTES program for the *rm* triad. The isoenergetic curves are in kcal mol^{-1}, the horizontal and vertical scales are the angular deviations in degrees from equilibrium positions, the angles ϕ_3 and χ_5 are defined in Table II: A, model I (charge transfer complex) with $D = 3.5$; B, model I with $D = 20$; C, model II (separation of ions and counterions), $D = 20$.

make a discrimination between these two models on the grounds of ^1H T_1 measurements. The theoretical values of proton relaxation times to be compared with the experimental ones have therefore been calculated for model II (separated ions) considering only the central monomer unit of the *rm* triad included in the *rrmrr* hexad. We did find out on the other hand that the model I (charge-transfer complex) with $D = 3.5$ gives interproton distances appreciably different from those of models I and II with $D = 20$. These differences do not imply fundamental changes in our interpretation of relaxation data in terms of molecular motions but only a different choice of values of the parameters involved in the calculation of proton T_1's.

The conformational energy maps derived from the DESCARTES program (Figure 3) show two minima for the aliphatic chain corresponding to the trans-gauche and trans-trans conformations, the former being the deepest one. The separation between these two minima is less marked for model II than for model I and for this latter for $D = 20$ than for $D = 3.5$. On the other hand the oscillation of the central pyridinium ring of the *rm* triad about the C4N axis seems not very dependent upon the chosen model and the dielectric constant. Its rotational freedom is larger in the *tg* than in the *tt* energy minimum and comparable to that of the neutral polymer[3] as confirmed experimentally in the present work.

(3) ^1H and ^{13}C Spin-Lattice Relaxation. (a) Aliphatic Chain. For resonances of the methine and methylene protons or carbons being superimposed, it may be shown as in the case of the P4VP[3] that the apparent relaxation rate is nearly that expected for the α proton or carbon. For the α proton of $P4VPD^+$, the relaxation rate given by the resonance of the *mm* triad at 3.05 ppm is indeed very close to that of the strong $\alpha\beta$ resonance at 2.27 ppm.

The spin–lattice relaxations of ^1H and ^{13}C in the aliphatic chain have been interpreted in terms of an isotropic segmental motion with a distribution of correlation times τ_R. For a Fuoss–Kirkwood distribution characterized by the parameter β ($\beta = 1$ for a single correlation time), the relaxation rates are given by:

$$(T_1^{-1})_{H_i} = \frac{3}{10}\gamma_H^4\hbar^2 \sum_{j\neq i} r_{ij}^{-6} \frac{\beta}{\omega_H} \times \left[\frac{(\omega_H\tau_R)^\beta}{1+(\omega_H\tau_R)^{2\beta}} + \frac{2(2\omega_H\tau_R)^\beta}{1+(2\omega_H\tau_R)^{2\beta}}\right] \quad (1)$$

$$(T_1^{-1})_C = \frac{1}{10}\gamma_C^2\gamma_H^2\hbar^2 r_{CH}^{-6}\beta\tau_R^\beta \left[\frac{(\omega_H-\omega_C)^{\beta-1}}{1+(\omega_H-\omega_C)^{2\beta}\tau_R^{2\beta}} + \frac{3\omega_C^{\beta-1}}{1+(\omega_C\tau_R)^{2\beta}} + \frac{6(\omega_H+\omega_C)^{\beta-1}}{1+(\omega_H+\omega_C)^{2\beta}\tau_R^{2\beta}}\right] \quad (2)$$

where γ_H and γ_C are the nuclear magnetogyric ratios, ω_H and ω_C are the Larmor frequencies, r_{ij} is the distance of proton i to a proton j and has been computed by the SIMPLEX program for the α protons of the *rrmrr* sequence (model II, separation of ions and counterions). We have taken $r_{CH} = 0.11$ nm for aliphatic carbons. Equation 1 is strictly valid for like protons. For unlike protons as in the present case, this equation holds only for the *initial* slope of $\log[(M_0 - (M_z)_i)/2M_0]$ vs. the time interval following the 180° pulse (see for instance ref 11 and 12).

The optimum consistency between the ^1H and ^{13}C relaxation times computed as a function of T^{-1} and compared with experimental results has been obtained for an enthalpy of activation $\Delta H^{\ddagger}_R = 6$ kcal mol^{-1} and a preexponential factor $(\tau_R)_0 = 10^{-13}$ s. The distribution parameter β was assumed to depend linearly upon T^{-1} from 0.72 at 250 K to 0.98 at 350 K (Figure 4A).

(b) Pyridinium Group. The correlation between the nuclear relaxation rates and the motion of the pyridinium ring has been established by considering the carbons 2 and 3 and the proton 3. The relaxation of H_2 of the ring appears as in the case of P4VP to be subjected to dipolar interactions with the protons of remote monomer units, due to the entanglement of the macromolecular chain. These interactions cannot be taken into account since our conformational calculations concern at most six monomer units. On the other hand H_3 may be assumed to interact predominantly with the protons of the same unit and of the vicinal ones.

As in our preceding work on P4VP[3] we have considered that the motion of the pyridinium ring is an oscillation of amplitude α, coupled with the quasiisotropic motion of the aliphatic chain. The relaxation rates of ^1H and ^{13}C are given by the following equations:[3]

$$(T_1^{-1})_{H_i} = \frac{9}{80}\gamma_H^4\hbar^2 \sum_j r_{ij}^{-6}[A(\alpha,\theta_{ij})f(\tau_R) + B(\alpha,\theta_{ij})f(\tau_t)] \quad (3)$$

$$(T_1^{-1})_C = \frac{3}{80}\gamma_H^2\gamma_C^2\hbar^2 r_{CH}^{-6}[A(\alpha,\theta)h(\tau_R) + B(\alpha,\theta)h(\tau_t)] \quad (4)$$

with $A = \frac{2}{3}(1 - 3\cos^2\theta)^2 + \sin^2 2\theta(1 + \cos\alpha) + \sin^4\theta(1 + \cos 2\alpha)$, $B = \sin^2 2\theta(1 - \cos\alpha) + \sin^4\theta(1 - \cos 2\alpha)$,

$$f(\tau) = \frac{\tau}{1+\omega_H^2\tau^2} + \frac{4\tau}{1+4\omega_H^2\tau^2}$$

Table III
Comparison between the Main Parameters Selected for the Simulation of T_1 vs. T^{-1} Curves of P4VP[3] and P4VPD$^+$

		$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta G^{\ddagger}$(300 K), kcal mol^{-1}	α,[a] deg	β[a]
Aliphatic	P4VP	4	5.5		$0.75 < \beta < 0.98$
chain	P4VPD$^+$	6	5.7		$0.72 < \beta < 0.98$
Pyridyl	P4VP	3	4.1	$60 < \alpha < 85$	
Ring	P4VPD$^+$	2	4.7	$40 < \alpha < 90$	

[a] For $250 < T < 350$ K.

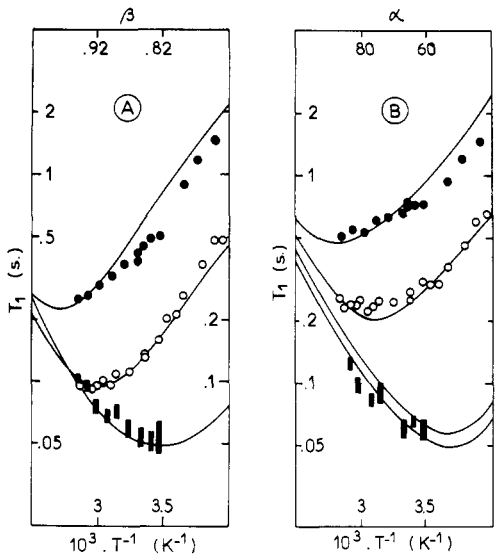


Figure 4. Fitting of $T_1 = f(T^{-1})$ curves to experimental points: ●, ^{1}H 250 MHz; ○, ^{1}H 100 MHz; and ■, ^{13}C at 25.15 MHz. For this latter the height of the heavy vertical bars gives the dispersion of experimental points. The diagram A is relative to the aliphatic chain, the parameters of the theoretical curves being $\Delta H_R^{\ddagger} = 6$ kcal mol^{-1}, $(\tau_R)_0 = 1.05 \times 10^{-13}$ s (isotropic motion assumed). The variation of the parameter of the Fuoss–Kirkwood distribution of τ_R indicated on the horizontal scale is linear with T^{-1}. The diagram B is relative to H_3, C_2, and C_3 from the pyridinium group. The fitting parameters of the theoretical curves for the oscillation motion about the N–C4 axis coupled with the isotropic segmental motion of the aliphatic backbone are $\Delta H^{\ddagger}_G = 2$ kcal mol^{-1}, $(\tau_G)_0 = 1.4 \times 10^{-11}$ s. The amplitude of oscillation α is assumed to vary linearly with T^{-1} as indicated in the horizontal scale. The upper and lower curves of ^{13}C are relative to C_2 and C_3, respectively.

and

$$h(\tau) = \frac{\tau}{1 + (\omega_H - \omega_C)^2\tau^2} + \frac{3\tau}{1 + \omega_C^2\tau^2} + \frac{6\tau}{1 + (\omega_H + \omega_C)^2\tau^2}$$

where θ is the angle between a $\vec{HH}$ or $\vec{CH}$ vector and the axis of oscillation and $\tau_t = (\tau_R^{-1} + \tau_G^{-1})^{-1}$, τ_G being the correlation time for the oscillation motion.

The theoretical curves of Figure 4B have been obtained by the following process: In a first step the angle α is kept constant and the T_1 are calculated as a function of τ_G for the protons of the central monomer unit of heterotactic triads in the conformation given by the SIMPLEX program to determine the influence of the oscillation motion on the minimum of T_1. Decreasing τ_G or increasing α brings about a raise of the T_1 minima values expected for a purely isotropic motion ($\tau_G \gg \tau_R$ or $\alpha = 0$ in eq 3). To avoid a possible overestimate of α, exceeding the oscillation amplitudes expected from conformational energy calculations, one selects the proton 3 the T_1 of which is the more dependent on α and τ_G. The $T_1 = f(T^{-1})$ computed for this proton at 100 and 250 MHz are then fitted to the experimental values by means of an APL program allowing the rapid testing of a wide range of values of the adjustable parameters, namely the enthalpy of activation $\Delta H^{\ddagger}_G$, the preexponential factor $(\tau_G)_0$, and the amplitude α of the oscillation motion. In these calculations τ_R is given by the relaxations of Hα and Cα as mentioned above, θ_{ij} and Σr_{ij}^{-6} being obtained by the SIMPLEX program. The validity of the parameters chosen to fit the experimental $T_1 = f(T^{-1})$ curves at 100 and 250 MHz needs to be confirmed by the relaxation of C_2 and C_3. For these carbons the orientations and lengths of the $\vec{CH}$ vectors are assumed to be the same as in the pyridinium cation[5] and only the dipolar interaction with the directly attached proton has to be considered. The experimental T_1's of C_2 and C_3 are equal within the limits of experimental errors, while the theoretical $T_1 = f(T^{-1})$ curves computed with C_3–$H_3 = 0.108$ nm, $\theta_{C3} = 60°$ and C_2–$H_2 = 0.111$ nm, $\theta_{C2} = 57°$ are slightly different (Figure 4B). The best agreement between the experimental T_1's and the $T_1 = f(T^{-1})$ curves computed for the three spectrometer frequencies is achieved by taking $\Delta H^{\ddagger}_G = 2$ kcal mol^{-1}, $(\tau_G)_0 = 1.4 \times 10^{-11}$ s, α varying linearly as T^{-1} from 40 to 85° between 250 and 350 K. The enthalpy of activation and the amplitude of the oscillation of the pyridinium ring are in agreement with the relevant values provided by conformational energy calculations (Figure 3).

IV. Discussion

One of the main purposes of the present study is to investigate the influence of the coulombic interactions between the positively charged pyridinium rings on the flexibility of P4VPH$^+$ compared to P4VP. This comparison is summarized in Table III. It is seen that the amplitude of oscillation of the rings and the values of the parameter of the Fuoss–Kirkwood distribution of correlation times τ_R are equal or very close for the neutral and quaternized polymers whereas the enthalpies of activation of motions of the aliphatic chain and the pyridine ring are markedly different. These differences are however partially compensated by the entropies of activation so that, on the average, the free energies of activation $\Delta G^{\ddagger}_R$ and $\Delta G^{\ddagger}_G$ are increased only by ca. 10% upon protonation of the pyridyl group. The corresponding augmentation of the rigidity of the polymer is more explicity shown by the ratios of correlation times of P4VPD$^+$ and P4VP at 300 K which are 1.7 for the segmental motion of the aliphatic chain and 2.7 for the oscillation motion of the rings. Similarly the difference between the two forms of this polymer can be pointed out by the respective ratios τ_R/τ_G. For example, at 300 K we have $\tau_R/\tau_G = 11$ for P4VP and only 6 for P4VPD$^+$.

Protonation effects have been reported in the case of poly(2-vinylpyridines)[10] and recently in a preliminary work on poly(4-vinylpyridines).[1] In this latter case the enthalpy of activation of the segmental motion of the chain was found from the ratio of proton T_1's at 100 and 250 MHz, equal to 2.4 ± 0.2 kcal mol^{-1} for the neutral and quaternized polymers. The present work indicates that this value was most likely underestimated because the distribution of correlation times was not taken into account and the temperature range of measurement was too limited.

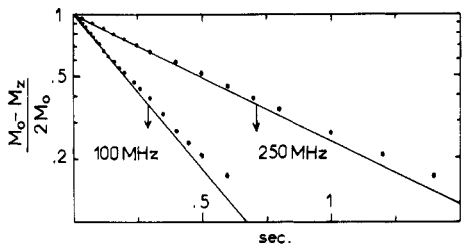


Figure 5. Semilogarithmic plots of typical longitudinal magnetization recovery curves of H_3 at 284 K for the two frequencies. The solid lines are the tangents at $t = 0$, and the vertical arrows indicate the value of T_1.

The influence of the cross relaxation on the determination of the proton relaxation times has been examined in our preceding work of P4VP[3] by simulating the recovery of the longitudinal magnetizations of Hα, Hβ, and H_3 taking account for the eight nearest neighbor protons. The conformation of the $P4VPD^+$ being not essentially different from that of P4VP, the conclusions of this previous work may be extended to the present one. As expected from other studies[11,12] it was found that the direction of the deviation of $\log[(M_0 - M_z)/2M_0]$ vs. t from the tangent at $t = 0$ changes from one branch of the $T_1 = f(T^{-1})$ curve to the other canceling out near the minimum (more exactly at $\tau_R \simeq 1.12\ \omega_H^{-1}$ for an isotropic motion). The error introduced by this deviation increases with the spectrometer frequency and may be important, exceeding 20% for correlation times longer than 5×10^{-9} s, i.e., below 250 K for the polymers under study. In the range of temperatures investigated here, this possible cause of error in the determination of T_1 was reduced as far as possible by measuring carefully the initial slope of $\log[(M_0 - M_z)/2M_0]$ vs. t in a time interval less than 30% of the estimated value of T_1 as shown in Figure 5. The problems raised by the cross relaxation make it more essential to support the interpretation of proton relaxation experiments by ^{13}C T_1 measurements where this effect is removed by noise decoupling of protons.

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Oligomeric *N*-(Phenylcarbamoyl)ethylenimine for Highly Specific Absorption of Mercury(II) and Copper(II) Ions[1]

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ABSTRACT: Poly[1-(*N*-phenylcarbamoyl)aziridine] $(CH_2CH_2N(CONHPh))_n$ ($\overline{DP}$ ca. 8) was found to show highly specific affinity for Hg^{2+} and Cu^{2+} as compared with Co^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions at pH 6–8. Absorbed ions can be removed by simply immersing in 1 N HCl solution at 32 °C. Laser Raman and IR studies showed that the Cu^{2+} ion is strongly interacting with the carbonyl oxygen atoms and weakly with nitrogen atoms. Selectivity of Hg^{2+} and Cu^{2+} ions from binary ion systems was shown to be high enough as expected from the single metal ion systems. The absorption specificity is considerably different from the ureanized polyEI, a branched higher molecular weight analogue of the poly(NPCA), and from poly[1-(*N*-methylcarbamoyl)aziridine]. Conformational requirement with regularly ordered CONHPh side group is suggested to be responsible for developing high absorption specificity, in which the phenyl group plays an important role.

We have reported a new synthetic route for oligomers of *N*-carbamoylethylenimine with a narrow molecular weight distribution (DP ca. 8) of type $(CH_2CH_2N(CONHPh))_n$ directly from 1-(*N*-phenylcarbamoyl)aziridine (NPCA).[2] The polymer showed significant specificities in the absorption of a variety of S=O or P=O compounds.[3] The specificity in absorption is probably assisted by the conformational change of the poly(NPCA) in the presence of the guest molecules, when considered the properties of related polymers of type $(CH_2CH_2N(COR))_n$ studied by several research groups.[4–7] It seems of value that the synthetic noncross-linked oligomeric compound possesses this kind of specificity in affinity for small molecules, because the host molecules must have special structural characteristics to accommodate the guest molecules in definite proportions.

Chemical property of an oligomeric compound with intermediate DP differs largely from its monomer or oligomers with smaller DP and from its high polymer. Important features of a functional oligomeric compound with intermediate DP are as follows: The oligomeric compound has enough chain atoms to keep its functional groups unseparable. The functional groups can be gathered intramolecularly to increase the functionality concentration. If the freedom in the molecule is restricted to some extent by the chemical bonds involved,

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