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Spin–Lattice Carbon-13 and Proton Relaxation of Poly(vinylidene chloride) in Hexamethylphosphoramide-d_{18}

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ABSTRACT: Spin–lattice relaxation times and nuclear Overhauser enhancements at 15 MHz are reported for the ^{13}C nuclei of poly(vinylidene chloride) (PVDC) in hexamethylphosphoramide-d_{18} solution over the temperature range 11–89 °C and at concentrations of 15 and 25% (w/w). The derived correlation times are quite similar to those of poly(vinylidene fluoride) and polyisobutylene when the influence of solvent viscosity is taken into account. The apparent activation energy for these motions in PVDC is of the order of 25 kJ mol^{-1}, corresponding in the Kramers diffusion-limit theory to a barrier height of about 11 ± 3 kJ mol^{-1}. Proton longitudinal relaxation times are also reported.

The dynamical behavior of poly(vinylidene chloride), PVDC, in solution is of interest because of its simple chain structure and the general scarcity of dynamic information about dissolved vinylidene-type polymers. As not many solvents are known[1] for PVDC at ordinary temperatures, the experimental possibilities are quite limited. Following an earlier study[2] of the equilibrium conformational properties of the polymer, we now report some ^{13}C and ^{1}H nuclear magnetic relaxation measurements on solutions in deuterated tris(dimethylamino)phosphine oxide (hexamethylphosphoramide, HMPA) at concentrations of 15.0 and 24.8% (w/w) over the temperature range 11–89 °C. Allowing for the relatively high viscosity[3] of this solvent, we find that the rates of local conformational change in PVDC as deduced from the ^{13}C data are quite similar to those of polyisobutylene and poly(vinylidene fluoride), indicating similar barriers to backbone internal rotation. In addition, by applying the free-volume treatment of Mashimo,[4] we find that our results are consistent with published dielectric relaxation measurements on bulk PVDC.

Experimental Section

The polymer was prepared by free-radical polymerization and characterized as described previously.[2] The sample used for the NMR measurements was unfractionated, with a viscosity-average molecular weight of 30 × 10^3 and an intrinsic viscosity in HMPA of 0.21 dL g^{-1} at 25 °C. The solvent, HMPA-d_{18} (Aldrich, 99 atom % D), was used as received.

Polymer solutions were sealed in 10-mm NMR tubes after five cycles of freezing, pumping, and flushing with dry nitrogen to remove dissolved oxygen. The standard inversion–recovery pulse sequence π–t–$\pi/2$–τ, with τ = 0.6 s, at a frequency of 15.04 MHz was used to measure T_1 for the methylene ^{13}C in a JEOL 60Q spectrometer, with complete noise decoupling of the protons. The NOE was evaluated from the ratio of the peak areas under conditions of complete noise decoupling of the protons and under gated decoupling only during data acquisition following each pulse. The magnetic field was locked on the deuterium resonance. Relaxation times for the CCl_2 carbon are not reported here. However, proton spin–lattice relaxation times were measured at 59.75 MHz. The reproducibility of T_1 is considered to be of the order of 5% and that of NOE perhaps 15%.

Because solutions of PVDC in HMPA invariably turn brown at higher temperatures,[2] presumably because of degradation through loss of HCl, measurements were made in order from low to high temperature and completed as rapidly as feasible. Temperature control during measurement was to within 1 °C.

Results and Discussion

The results of the measurements described above are given in Table I. At the lower temperatures the NOE values (given in parentheses) are significantly below the extreme-narrowing limit of 2.99. The possibility that these low figures may be due to insufficient delay time τ for application of the gated decoupling technique appears to be ruled out,[5] since we have $\tau \geq 10T_1$ at all temperatures where the NOE was observed. These results cannot be reproduced by a model employing a simple exponential time correlation function for the ^{13}C–^{1}H magnetic dipole–dipole interaction. At least two parameters are needed to describe the observed behavior.

Table I
^{13}C and Proton Spin–Lattice Relaxation Times and Nuclear Overhauser Enhancements of Poly(vinylidene chloride) in HMPA-d_{18}

	T_1/ms (NOE in parentheses)			
	^{13}C		^{1}H	
temp, °C	15.0% (w/w)	24.8% (w/w)	15.0% (w/w)	24.8% (w/w)
89	124	81	139	125
75	78	67	113	98
65	68 (2.6)	56 (2.6)	93	85
53	59 (2.7)	44 (2.7)	75	67
40	39 (2.3)	32 (2.1)	66	62
26	32 (2.1)	27 (2.0)	59	60
11	20 (2.0)	16 (1.6)	57	69

Several related two-parameter models are available[6-8] for treating data of this kind. They are all based on more or less the same local process, typified by (though not required to match in detail) a three-bond distorted crankshaft rearrangement in a chain confined to a tetrahedral lattice. They differ, however, in the precise way in which the cooperativity of the motions is reduced below that of a strict lattice chain. It has been shown[9] that all three models are about equally successful in fitting typical experimental results, and the interpretation of the model parameters is also quite similar. Recent excimer fluorescence experiments,[10] computer simulations,[11] and theoretical considerations[12] all suggest strongly that the crankshaft picture is generally incorrect for dilute polymer solutions. Nevertheless, the model parameters, if not taken too literally, can serve as useful indicators of mean correlation time and degree of departure from simple exponential behavior, much as the two parameters of a Cole–Davidson dielectric response function.

It is convenient for us to apply the treatment of Jones and Stockmayer,[7] which corresponds to superposition of a finite number s of exponential processes in the time correlation function

$$\phi(t) = \sum_{k=1}^{s} G_k \exp(-t/\tau_k) \qquad \sum G_k = 1 \tag{1}$$

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Table II
Harmonic Mean Correlation Times (τ_h/ns) and Calculated NOE (in Parentheses) from ^{13}C Relaxation Times

temp, °C	$s = 1$	$s = 3$	$s = 4$
		15.0% (w/w)	
89	0.19	0.055	0.041
75	0.30 (2.97)	0.091	0.069
65	0.35 (2.96)	0.106 (2.88)	0.082 (2.81)
53	0.40 (2.96)	0.124 (2.85)	0.098 (2.75)
40	0.64 (2.91)	0.22 (2.62)	0.20 (2.37)
26	0.80 (2.86)	0.31 (2.42)	0.30 (2.14)
11	1.50 (2.61)	0.86 (1.83)	1.05 (2.00)
		24.8% (w/w)	
89	0.29	0.087	0.066
75	0.36 (2.99)	0.108	0.084
65	0.42 (2.95)	0.132 (2.83)	0.106 (2.71)
53	0.55 (2.93)	0.18 (2.72)	0.15 (2.52)
40	0.79 (2.87)	0.31 (2.43)	0.29 (2.15)
26	1.10 (2.76)	0.56 (2.07)	0.56 (1.97)
11	2.40 (2.26)		

Thus, the harmonic and arithmetic mean correlation times are given by

$$\phi'(0) = \sum \tau_k^{-1} G_k \equiv \tau_h^{-1} \qquad \int_0^\infty \phi(t)\, dt = \sum \tau_k G_k \equiv \tau_a \quad (2)$$

The values of the G_k and the individual correlation times τ_k are dictated by the model, and a relation

$$\tau_a = s\tau_h$$

is always obeyed. Thus the parameter s is a direct measure of the breadth of the correlation-time distribution, i.e., of the nonexponential character of the correlation function.

Table II gives the harmonic mean correlation time τ_h calculated with the above model from each observed ^{13}C T_1 value at several different values of the breadth parameter s. As in Table I, the corresponding NOE is appended in parentheses. Comparison of the calculated NOE's with the observed figures from Table I shows the degree to which a chosen value of s can represent the measurements with the model described. It is seen that the simple exponential model ($s = 1$) is inadequate but that reasonably satisfactory fits can be achieved with $s = 3$ or 4.

A reliable analysis of the observed proton relaxation times is not feasible, as significant dipole–dipole contributions come from protons on second-neighbor CH$_2$ groups, and the effects of Cl nuclear quadrupoles may not be negligible. However, if we ignore cross correlations and take H–H distances characteristic of a planar all-trans backbone conformation, we calculate values of τ_h some 30–70% larger than those based on the ^{13}C data at the same s. In view of the ambiguities mentioned, this is considered to be satisfactory agreement.

Returning to the ^{13}C results, we observe that the calculated correlation times of Table II are several orders of magnitude shorter than that to be expected for overall molecular tumbling. As in earlier work,[13,14] the latter can be estimated from the relation

$$\tau_{rot} = 1/6D_{rot} \simeq 2M[\eta]\eta_0/3RT \quad (3)$$

For example, at 40 °C we obtain $\tau_{rot} = 4 \times 10^2$ ns. Thus the present measurements unequivocally reflect local chain motions.

There is some concentration dependence of the mean correlation time, and this is considered in detail below. First we discuss the temperature dependence and the related intramolecular barrier height. The τ_h values of Table II give good Arrhenius plots with apparent activation energies of 24 ± 2 kJ mol^{-1} for $s = 3$ or 28 ± 2 kJ mol^{-1} for $s = 4$. We may presume that, as for local motions in other polymers of the duration of 0.1 ns or longer, the present system corresponds to the diffusion limit of a generalized Kramers expression[15-17] of the type

$$\tau = A\eta_0 \exp(U^*/RT) \quad (4)$$

where η_0 is the local viscosity (equal to that of the solvent in sufficiently dilute solution) and U^* is the height of the intramolecular potential energy barrier that is crossed in the rate-controlling process, whether of the crankshaft or single-barrier type. The here unspecified constant A involves curvatures of the potential in initial and transition states and, more importantly, the effective friction coefficient of the system that diffuses across the barrier. Subtracting a viscous-flow activation energy of 15 kJ mol^{-1} for HMPA,[3] as dictated by eq 4, we find a barrier height $U^* = 11 \pm 3$ kJ mol^{-1} for PVDC. This figure lies below that observed for polystyrenes[13,17,18] but above those for alkanes[19] or aliphatic polyethers.[20] Its small magnitude tends to favor the single-barrier model for the local relaxation process.

Table III
Comparison of Three Vinylidene Polymers

	-CH$_2$CCl$_2$-		-CH$_2$C(CH$_3$)$_2$-		-CH$_2$-CF$_2$-
frequency, MHz	15	15	25	15	25
solvent	HMPA	HMPA	CCl$_4$	CCl$_4$	DMF
concentration	15% (w/w)	25% (w/w)	25% (w/v)	25% (w/v)	30% (w/v)
temperature, °C	40	40	40	45	41
T_1, ms	32	39	165	132	310
s	3	3	2	2	1
τ_h, ps	220	310	65	82	75
solvent viscosity η_0 (cgsu)	2.52	2.52	0.74	0.69	0.74
$10^8\tau_h/\eta_0$ (cgsu)	0.9	1.2	0.9	1.2	1.0
reference	this work		21	22	23

Our results for PVDC at 40 °C are compared in Table III to literature values[21-23] for two other vinylidene-type polymers at or near the same temperature. The quotients τ/η_0 are of similar magnitudes, as would be expected from eq 4 if the barrier heights and sizes of substituents were not greatly different. Indeed, for polyisobutylene a barrier height of $U^* = 8.4$ kJ mol^{-1} has been reported,[22] not far from our result for PVDC.

To consider the concentration dependence of the relaxation process, we now rely on an elaboration due to Mashimo[4] of the Fujita free-volume treatment.[16,24] Mashimo writes the correlation time as a function of concentration in terms of the fractional free volumes $\alpha(T)$ and $\beta(T)$ of the pure polymer and solvent, respectively, in the following way:

$$\tau = B(T) \exp[\alpha(T) + \sigma(T)\phi]^{-1} \quad (5)$$

The temperature function $B(T)$ depends only on the polymer and need not concern us further here; the volume fraction of solvent in the system is denoted by ϕ, and

$$\sigma(T) = \beta(T)[1 + \alpha(T)]/[1 + \beta(T)] \quad (6)$$

Mashimo examined dielectric relaxation data for six different polymers in toluene and found that the value of α at the glass temperature T_g is 0.034 for all the polymers;

for poly(vinyl acetate) it increases linearly with temperature according to the relation

$$\alpha(T) = \alpha(T_g) + (7.7 \times 10^{-4})(T - T_g) \qquad (7)$$

We now apply this method to the PVDC–HMPA system at 40 °C. Retaining eq 7 for PVDC, which has a recorded glass temperature of 255 K, we obtain $\alpha = 0.078$. For the solvent, $\beta(T)$ should be proportional to the reduced temperature, and from Mashimo's figure of 0.308 for toluene at 40 °C and the normal boiling temperatures of 382 and 504 K for toluene and HMPA, respectively, we obtain $\beta = 0.233$ for HMPA, leading to $\sigma(T) = 0.204$. Now for the 24.8% (w/w) solution the solvent volume fraction is 0.816, and at 40 °C the harmonic mean correlation time τ_h is close to 0.3 ns and thus τ_a is about 1 ns. Taking a time intermediate to these, from eq 5 we find $B(T) \simeq 10^{-11}$ μs at this temperature, and then from the same equation we obtain $\tau \simeq 10$ μs for 100% PVDC. Of course, this refers to the amorphous material.

Dielectric relaxation measurements on pure PVDC were made long ago by Saito and Nakajima,[25] from whose curves we find $f_{max} \simeq 7$ kHz at 40 °C. This corresponds to a dielectric relaxation time of about 20 μs. Since this should be about 2–3 times that for the magnetic relaxation, the agreement between the dielectric and NMR results is highly gratifying and attests to the usefulness of the Mashimo treatment.

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Calorimetric Titration of Poly(vinylamine) and Poly(iminoethylene)[1]

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ABSTRACT: The thermodynamic parameters ΔG, ΔH, and ΔS for proton ionization of the hydrochloride salts of poly(vinylamine) at 298 K and of poly(iminoethylene) at 298 and 323 K have been measured by calorimetric and potentiometric titrations. These data are reported for both polymeric amines as a function of charge state and for three ionic strengths. The dependence of the hydrodynamic volume of poly(vinylamine) on charge state was determined by analytical ultracentrifugation measurements and is also reported. The titration data appear anomalous in comparison to most polymeric acids and bases studied previously in that the changes in ΔG with charge state are not predictable on the basis of electrostatic arguments alone. Simple theory also fails to predict the changes in ΔH and ΔS, for which there is little basis for comparison. An explanation of these results based on nearest-neighbor effects and on structural features of the polymers at intermediate degrees of protonation is presented. The data obtained in calorimetric experiments, like those reported here, will be important in the development or refinement of polyelectrolyte theories.

The acid–base properties of polyelectrolytes have been studied extensively by potentiometric titration.[2] The general theory of polyelectrolyte behavior is based on this body of knowledge: i.e., K_a or ΔG as a function of charge state, counterions, and ionic strength. However, until very recently,[3] there have been few reports of calorimetric titration of synthetic polyelectrolytes. As part of a comprehensive thermodynamic study of proton ionization from polymeric amines and amino acids we report now the calorimetric and potentiometric titrations of the hydrochloride salts of poly(vinylamine) (PVA) and linear poly(iminoethylene) (PIE).[1] The ΔG, ΔH, and $T\Delta S$ values

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