

Chain Flexibility and ^{31}P NMR Spin–Lattice Relaxation Measurements on Melts of Halogenated Poly(thionylphosphazenes)

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ABSTRACT: The chain flexibility of halogenated poly(thionylphosphazenes) (PTPs) [(NSOX)(NPCl₂)₂]_n (X = F, Cl) was investigated by measuring the ^{31}P spin–lattice relaxation times of PTP melts. T_1 times were obtained at two different magnetic fields and at various temperatures above the glass transition of the polymers. The minimal T_1 time occurred at lower temperatures for the fluorinated polymer than for the chlorinated polymer. This result is in agreement with trends in glass transition temperatures of these polymers and with ab initio molecular orbital calculations on the chain flexibility of model compounds of these polymers. The Hall–Helfand model for the dynamics of polymer chains was used to fit the experimental $T_1(T)$ curves. This model describes the motions of the polymer chains that lead to the longitudinal relaxation as correlated conformational jumps. T_1 measurements at two different field strengths indicated that chemical shift anisotropy contributes significantly to the spin–lattice relaxation.

Introduction

Compared to organic polymers, inorganic macromolecules can have interesting and unusual chemical, mechanical, electronic, and/or thermal properties.^{1,2} The unique properties of polymeric materials (such as the large reversible deformability of elastomers or the high impact strength of thermoplastics) are due to the many different conformations that the polymer chains can adopt.³ Knowledge of the stable conformation and the flexibility of the polymer main chain (i.e., the energy barriers between different conformations) is therefore essential to understanding the physical properties of polymers. A molecular geometry that differs from the geometry of a carbon-based backbone (e.g., larger bond lengths and bond angles) and a highly flexible main chain cause the exceptional properties of some inorganic polymers.⁴

Poly(thionylphosphazenes) [(NSOX)(NPCl₂)₂]_n (PTPs) are a new class of inorganic polymers that possess a backbone of sulfur(VI), nitrogen, and phosphorus atoms (see Figure 1). These materials can be regarded as hybrids of poly(oxothiazenes) [RS(O)=N]_n and poly(phosphazenes) [R₂P=N]_n.^{5,6} Synthesis and the thermal analysis of PTPs were first reported by Manners and co-workers.^{7,8} In previous papers we reported on the molecular geometry and torsional mobility of PTP backbones with different substituents bonded to phosphorus and sulfur.^{2,9} We used molecular orbital ab initio calculations on model compounds for these studies. The calculations on the halogenated molecules (chlorine bonded to phosphorus, and fluorine or chlorine bonded to sulfur) showed that the main chain of the fluorinated molecule (X = F) is more flexible than the backbone of the chlorinated molecule (X = Cl). This

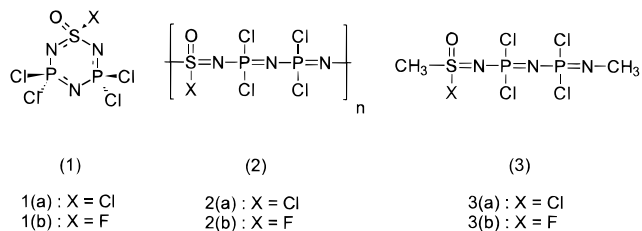


Figure 1. Chemical structure of the 6-membered thionylphosphazene rings and the repeat unit of the PTP polymer. The cyclic thionylphosphazenes **1a** and **1b** undergo thermally induced ring-opening polymerization to yield the polymers **2a** and **2b**. Short chain analogues **3a** and **3b** were used to carry out the ab initio calculations of molecular geometries and chemical shift tensors.

trend in chain flexibility can also be seen in the glass transition temperatures of the polymers: **2b** has a lower glass transition temperature ($T_g(\text{X} = \text{F}) = -56\text{ }^\circ\text{C}$) than **2a** ($T_g(\text{X} = \text{Cl}) = -46\text{ }^\circ\text{C}$). Measurements of the glass transition temperature with differential scanning calorimetry or dynamic mechanical analysis usually investigate the dynamics of a polymer on a time scale of approximately 1 s. The motions probed at this time scale around T_g are cooperative re-arrangements of many chain segments.¹⁰

If we wish to study localized motions of the chains that are more directly related to the torsional mobility of the backbone than the glass transition phenomenon, we must investigate the dynamics of the chains on a shorter time scale. Nuclear magnetic resonance measurements can be used to study the dynamics of polymer chains on a wide range of time scales. The spin–lattice relaxation time (the T_1 time) is influenced by fast reorientations of chain segments on the nanosecond scale and can therefore be used to study chain flexibility.¹¹

Lauprêtre and co-workers carried out a ^{13}C NMR study of local motions and their activation energies in various bulk polymers.¹² At temperatures well above

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T_g , the motions of the polymer chains are fast enough to average out the main tensorial interactions (chemical shift anisotropy, homonuclear and heteronuclear dipolar couplings). Therefore, we can use conventional spectrometers for solution investigation in order to obtain high-resolution ^{31}P NMR spectra.

Experimental Section

The ^{31}P NMR spectra were recorded at the University of Toronto on a Varian XL-300 spectrometer operating at 121.1 MHz and at the University of Twente on a Varian Unity 400 WB spectrometer operating at 161.9 MHz. The chemical shifts are reported relative to H_3PO_4 . We used deuterated chloroform (CDCl_3) and deuterium oxide (D_2O) for the deuterium lock. The polymer melts were in sealed 5 mm NMR tubes. We placed these tubes inside 10 mm NMR tubes that contained the deuterated solvent. The T_1 relaxation times were determined by the inversion recovery method with a standard $\pi-\tau-\pi/2$ -observe- d pulse sequence. The delay time d between the pulse sequences was greater than 5 times the spin-lattice relaxation time. We used at least eight sequences with different delay times τ between the π pulse and the $\pi/2$ read-pulse in order to observe the recovery of the z -magnetization. The T_1 times were determined with nonlinear least-squares fits. The exponential return to the equilibrium magnetization could be described with a single relaxation time T_1 .

The cyclic thionylphosphazenes **1a** and **1b** were prepared as described in the literature¹³ and purified by high-vacuum sublimation (40 °C, 0.05 mmHg). In order to obtain specimens for the NMR experiments, we sealed the cyclic thionylphosphazenes under vacuum in 5 mm NMR tubes and carried out the thermal ring-opening polymerization in the NMR tubes. The polymerization reaction has been reported previously.⁷ The progress of the reaction (i.e., the formation of the higher membered rings and the polymer) was monitored by observing the integrated intensity of the corresponding peaks in the ^{31}P NMR spectra. The polymerization reaction was carried out until the ratio of the area under the reactant peak (6-membered rings) and the area under the product peaks (12-membered rings and polymer) was approximately 0.4. The appearance of the specimen changed from a white, crystalline powder (6-membered rings) over a pale yellow liquid to a highly viscous brown gum (mixture of 6-membered rings, higher membered rings, and polymer). At low conversions, the low molar mass molecules acted as plasticizers. For these samples, the minima of the $T_1(T)$ curves were shifted toward lower temperatures. At high enough conversions (ratios of reactant and product peak intensities of less than 0.57), T_1 times became independent of the reaction extent. This observation was repeated for both polymer systems and several batches. Polymerization in the NMR tubes is thus a convenient and fast method to obtain specimens for studying polymer melts with NMR measurements.

The theoretical calculation of the NMR shielding tensors was performed with the Gaussian 94 program package on a Silicon Graphics O2 R10000 workstation.¹⁴ Since ab initio molecular orbital calculations on a long-chain polymer are currently not feasible, we used model compounds **3a** and **3b** (one monomer repeat unit terminated on both ends with a methyl group; see Figure 1). Geometry optimizations were carried out at the restricted Hartree-Fock (RHF) level of theory with the 6-31G* polarized split-valence basis set.² The chemical shift tensors were calculated with the gauge-including atomic orbital (GIAO) method at the RHF level of theory with the 6-31G* basis set.¹⁵

Results and Discussion

^{31}P NMR spectra of the "chlorinated" sample at -30, 0, and 80 °C are shown in Figure 2. Chemical shifts of 6- and 12-membered rings and the polymer are summarized in Table 1. There are two isomers of the 12-membered rings, which result in separate resonances in the NMR spectrum.⁸ In addition, there is a group of

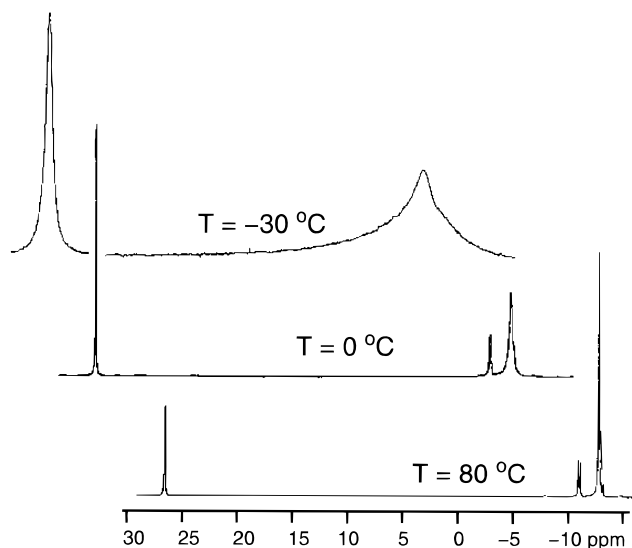


Figure 2. ^{31}P NMR spectra of the chlorinated ($X = \text{Cl}$) sample at $T = -30, 0,$ and $+80$ °C.

Table 1. Chemical Shifts (ppm) of the 6-Membered and 12-Membered Ring and the Polymer

	X = F	X = Cl
(NSOX)(NPCl ₂) ₂	26.4	26.7
[(NSOX)(NPCl ₂) ₂] ₂ , cis	-6.73	-8.08
[(NSOX)(NPCl ₂) ₂] ₂ , trans	-6.85	-8.25
[(NSOX)(NPCl ₂) ₂] _n	-8.83	-9.94

poorly resolved peaks clustered around the polymer resonance that arise from higher-membered rings (18-, 24-, 30-, and 36-membered rings). The peaks of the polymer and the twelve-membered rings cannot be resolved for temperatures lower than 0 °C due to insufficient motional narrowing of the resonances.

The temperature dependence of the T_1 relaxation times of **2a** and **2b** at two different fields is shown in Figure 3. The minimal T_1 times and the temperatures where they occurred are shown in Table 2. The minimal T_1 times were reached at lower temperatures for the fluorinated polymer than for the chlorinated polymer. In the higher field the minimal relaxation times occurred at higher temperatures and were shorter. The shape of all the $T_1(T)$ curves is asymmetrical: T_1 increases at a slower rate toward higher temperatures than it does toward lower temperatures.

The minimum of T_1 occurs when the correlation time of the chain motions, which cause the longitudinal relaxation, reaches the inverse of the spectrometer frequency.¹⁶ We controlled the correlation times of the polymer samples in our experiments by changing the temperature, since the motions of the polymer chains are thermally activated. At both field strengths, the T_1 experiments showed that the correlation time of the fluorinated polymer **2b** reaches the inverse of the ^{31}P Larmor frequency at a lower temperature than the correlation time of the chlorinated polymer **2a**. Therefore, the correlation time of the fluorinated sample is, at a given temperature, shorter than the correlation time of the chlorinated sample, and the motions of the polymer chains with fluorine bonded to sulfur are, at a given temperature, faster than the motions of the polymer chains with chlorine bonded to sulfur.

The $T_1(T)$ curves move toward shorter T_1 times if the strength of the magnetic field is increased. This is an indication that chemical shift anisotropy (CSA) contributes significantly to the spin-lattice relaxation. Many

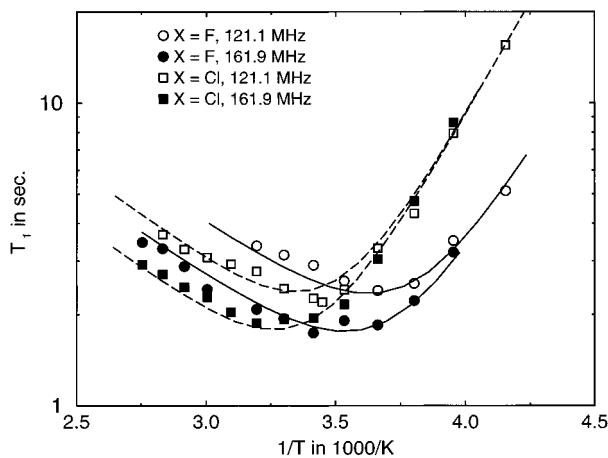


Figure 3. T_1 times of **2a** (squares) and **2b** (circles). The hollow symbols refer to measurements at 121.1 MHz, and the filled symbols denote measurements at 161.9 MHz. The lines show the results of the nonlinear least squares fits with the Hall-Helfand model.

Table 2. Minimal T_1 Relaxation Times (s) and the Temperatures Where They Occur

	$\omega(^{31}\text{P}) = 121.1 \text{ MHz}$	$\omega(^{31}\text{P}) = 161.9 \text{ MHz}$
T_1^{min} (2a) (X = Cl)	2.2 ± 0.2 at 20°C	1.9 ± 0.2 at 40°C
T_1^{min} (2b) (X = F)	2.0 ± 0.2 at 0°C	1.7 ± 0.2 at 20°C

previous studies on the T_1 relaxation of polymers focussed on the spin-lattice relaxation of ^{13}C nuclei. Dipole-dipole interaction with bonded ^1H nuclei is a highly efficient—and thus often dominating—relaxation mechanism for ^{13}C nuclei. The T_1 relaxation rates for unlike nuclei are proportional to $\gamma_1^2\gamma_2^2r^{-6}$, where γ denotes the gyromagnetic ratios of the nuclei and r denotes the internuclear distance.¹⁶ The high gyromagnetic ratio of protons and the short hydrogen-carbon bond length lead to fast relaxation rates. For the inorganic poly(thionylphosphazenes), the dipole-dipole interaction is not as dominant, since the neighboring nuclei of ^{31}P (^{14}N , ^{35}Cl , and ^{37}Cl) have lower gyromagnetic ratios, and the P-Cl and P-N bond lengths are considerably longer than the H-C bond length. Therefore, other relaxation mechanisms (e.g., CSA) can contribute significantly to the overall relaxation rate.

The following formula describes the T_1 times if chemical shift anisotropy is the relaxation mechanism:¹⁶

$$T_1^{-1} = \frac{6}{20} \gamma^2 H_0^2 \delta_z^2 \left(1 + \frac{\eta^2}{3}\right) J(\omega(^{31}\text{P})) \quad (1)$$

γ is the gyromagnetic ratio of the ^{31}P nuclei, and H_0 is the magnetic field strength. δ_z denotes the principal value, and η is the anisotropy parameter of the diagonalized symmetric component of the chemical shift tensor.¹⁷ Values for δ_z and η for polymers **2a** and **2b** were estimated from GIAO method calculations at the RHF/6-31G* level of theory on the model compounds **3a** and **3b**. We obtained $\delta_z = 72.0$ ppm and $\eta = 0.11$ for the central phosphorus nucleus of **3a**, and $\delta_z = 73.9$ ppm and $\eta = 0.09$ for the central phosphorus nucleus of **3b**.

$J(\omega)$ is the spectral density, which is proportional to the Fourier transform of the reduced orientation autocorrelation function $g(t)/g(0)$. The autocorrelation function $g(t)$ describes the molecular dynamics causing the spin-lattice relaxation.

Hall and Helfand developed an autocorrelation function that describes the reorientation of a polymer

backbone through correlated conformational jumps,¹⁸

$$g(t) = e^{-t/\tau_2} e^{-t/\tau_1} I_0(t/\tau_1) \quad (2)$$

where $I_0(t)$ is a modified Bessel function of order 0. τ_1 is the correlation time that describes the diffusional motion of conformational jumps along the chain, and τ_2 corresponds to the lifetime of the conformational states that result from the conformational jumps and have a higher energy compared to the conformational ground state. The spectral density that results from the Hall-Helfand autocorrelation function is

$$J(\omega) = \mathcal{R}\left(\frac{1}{\sqrt{\alpha + i\beta}}\right) \quad (3)$$

where

$$\alpha = \tau_2^{-2} + 2\tau_1^{-1}\tau_2^{-1} - \omega^2 \quad (4)$$

$$\beta = -2\omega(\tau_1^{-1} + \tau_2^{-1}) \quad (5)$$

and \mathcal{R} denotes the real part of a complex function.

Lauprêtre and co-workers successfully used an autocorrelation function which based on the Hall-Helfand model to describe the results of their spin-lattice relaxation measurements.¹² We used eq 1 with the spectral density of the Hall-Helfand autocorrelation function in order to describe our experimental $T_1(T)$ curves.

Correlation times of the T_1 relaxation of polymers can be associated with motions related to the glass transition phenomenon,¹² or with motions corresponding to a secondary relaxation.¹⁹ The temperature dependence of correlation times associated with the glass transition phenomenon follows a Williams-Landel-Ferry (WLF) law; the temperature dependence of the correlation times associated with secondary relaxations follows an Arrhenius law. Since we measured T_1 times at only two fields, we are not able to distinguish between a WLF-type temperature dependence and an Arrhenius-type temperature dependence of the correlation times. We assumed correlation times for the Hall-Helfand model that followed an Arrhenius law:

$$\tau(T) = \tau^\infty e^{E_a/RT} \quad (6)$$

In the case of a WLF-type temperature dependence of $\tau(T)$, eq 6 corresponds to a linear approximation of a small segment of the $\log \tau(1/T)$ curves, and E_a corresponds to an apparent activation energy.

As in the previous work of Lauprêtre and co-workers, we assumed a fixed ratio $\epsilon = \tau_2/\tau_1$ for the two correlation times. The nonlinear regressions were carried out simultaneously for all four $T_1(T)$ curves (polymers **2a** and **2b** at two different field strengths). Adjustable parameters were τ^∞ , the apparent activation energy E_a , and the ratio $\epsilon = \tau_2/\tau_1$. In addition, we included an adjustable parameter ξ , which controls the vertical position of the $T_1(T)$ curves. We assumed an identical τ^∞ and an identical factor ξ for all four curves. The nonlinear regressions were carried out with a Marquardt-Levenberg algorithm.

Results of the nonlinear regressions are shown in Figure 3 and in Table 3. The theoretical model approximates well the asymmetric shape of the experimental $T_1(T)$ curves.

Table 3. Results of the Nonlinear Regressions with the Hall–Helfand Model

	τ^∞ (s)	E_a (kcal·mol ⁻¹)	ξ	ϵ
2a (X = Cl)	9.6×10^{-14}	6.8	0.08	37.0
2b (X = F)	9.6×10^{-14}	6.3	0.07	21.0

The longitudinal relaxation can be influenced by additional mechanisms or molecular motions that are accounted for by the adjustable parameter ξ . It is reasonable to assume that dipole–dipole interaction between neighboring nuclei will also contribute to the longitudinal relaxation. Therefore, the parameter ξ includes information on the extent to which dipole–dipole interaction contributes to the T_1 relaxation. Since the dipole–dipole relaxation does not accelerate when the magnetic field is increased, the value of ξ will be less than 1. Lauprêtre and co-workers introduced a fast librational motion into their model of the polymer dynamics. This additional mode of the dynamics leads to longer T_1 times.¹² The fast librations can be included in the spectral density with a factor

$$1 - a = \left(\frac{\cos \theta - \cos^3 \theta}{2(1 - \cos \theta)} \right)^2 < 1 \quad (7)$$

where θ is the half-angle of the cone in which the fast librations of the main chain occur. The factor $(1 - a)$ is included in the adjustable parameter ξ if the fast librations are present in the dynamics of PTP melts. In addition, an ab initio calculation of the anisotropy of the chemical shift tensor on the RHF/6-31G* level of theory with short chain model compounds should be regarded as a rough estimate of the actual chemical shift anisotropy of the polymer.²⁰ The value of ξ is therefore also influenced by inaccuracies of the calculations.

The apparent activation energies of the dynamic processes that lead to the T_1 relaxation are 6.3 kcal/mol (X = F) and 6.8 kcal/mol (X = Cl). The value for $\tau^\infty = 9.6 \times 10^{-14}$ s is in the range of the values found by Heijboer for secondary relaxations of several polymers ($\log \tau^\infty = -13 \pm 1$).²¹ The diffusive motions of conformational jumps along the chains are more strongly damped for the fluorinated polymer than for the chlorinated polymer. The higher flexibility of the fluorinated chain could explain the faster damping of the diffusive motion.

Summary

³¹P spin–lattice relaxation time measurements were carried out on two halogenated PTPs (**2a** and **2b**). The measurements were done at two different field strengths and at different temperatures. At temperatures well above the glass transition temperatures of the polymers, we obtained solution-like spectra, since the main tensorial interactions were averaged out by the motions of the polymer chains. The minimal T_1 time of **2b** (X = F) occurred at both fields at lower temperatures than the minimal T_1 time of **2a** (X = Cl). Since the motions of the polymer chains are thermally activated, we concluded that polymer **2b** has, at a given temperature, a shorter correlation time than polymer **2a**. This result agrees with ab initio molecular orbital calculations of the torsional barriers and the glass transition temperatures of these polymers. The minimal T_1 times of both polymers become shorter if the field strength is increased. This is an indication that relaxation through chemical shift anisotropy contributes significantly to the overall relaxation rate. We used a theoretical model for

the dynamics of the polymer chains that was developed by Hall and Helfand in order to carry out nonlinear regressions of the experimental $T_1(T)$ curves. The Hall–Helfand model of correlated conformational jumps along the backbone of the polymer describes well the asymmetric shape of the $T_1(T)$ curves. We assumed thermally activated correlation times that follow an Arrhenius law. The nonlinear regressions resulted in an apparent activation energy of 6.3 kcal/mol for polymer **2b**, and 6.8 kcal/mol for polymer **2a**.

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