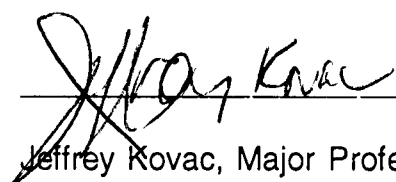
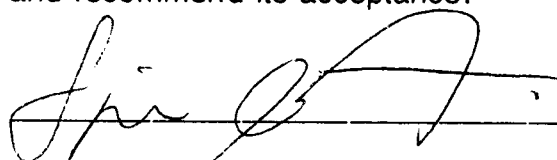


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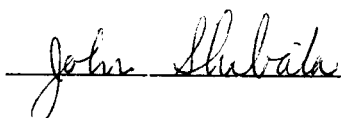
I am submitting herewith a thesis written by Kathryn Elaine Dowlen entitled "Spin-Lattice Relaxation Measurements of Poly(ethylene oxide) in Aqueous Salt Solutions." I have examined the final copy of this fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.


Jeffrey Kovac, Major Professor

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Associate Vice Chancellor
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SPIN-LATTICE RELAXATION MEASUREMENTS OF
POLY(ETHYLENE OXIDE) IN AQUEOUS SALT SOLUTIONS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee-Knoxville

Kathryn Elaine Dowlen

December 1994

DEDICATION

This thesis is dedicated to my parents

Betty Green Dowlen

and

John Roe Dowlen

for their continued support and love.

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ABSTRACT

The effect of salt on the internal motions of poly(ethylene oxide) (PEO) in aqueous solution was investigated using ^{13}C spin-lattice (T_1) relaxation nuclear magnetic resonance experiments. Comparative studies with short chain PEO and diethylene glycol monoethyl ether aided in the interpretation of the polymer data. Isotropic and internal libration models were used to interpret the interactions of ions with the molecular motion. It was concluded that the internal motions of PEO are affected by salt in solution, but a larger effect is found in the small molecule analogue cases.

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CHAPTER I

INTRODUCTION

A. The Problem

Current Theory

Dynamic bond percolation theory¹⁻⁷ is currently the leading theoretical model of ion transport along a polymer chain in the solid state. This theory suggests that as polymer segmental motion occurs, ions form transitory coordination bonds with sites on the polymer chain. Transport is then achieved and enhanced through the internal motion of the polymer.⁸ Although this is the leading theoretical model for ion transport in polymeric solids, it has not been thoroughly investigated experimentally. Most studies have focused on the effect of polymers on ion motion⁹ instead of the effect of ions on polymer motion.

Some studies on ion-polymer interaction in solids and liquids have employed dynamic mechanical and dielectric relaxation experiments,^{10,11} while more recently, nuclear magnetic resonance (NMR) spin lattice relaxation experiments and NMR spin diffusion experiments^{12,13} have been utilized to detect interactions between polymers and diluents (small molecules or ions) at distinct sites within the polymer repeat unit. However, NMR spin lattice relaxation measurements have not been fully implemented to uncover the affect of ion interactions on segmental motions with respect to ions in solution.

B. The Need

Experimental Support

There is a need to experimentally investigate the influence of ions on the internal motion of polymers. Uncovering the details of the polymer motion could support or modify the dynamic bond percolation theory and the theoretical conclusions put forth by those researchers who have concentrated on ion transport mechanisms in neat polymer systems.⁹ NMR spin lattice relaxation experiments would support the theory that if ions are transported primarily through an independent hopping mechanism in which the interaction between polymer and ion is small; then the resultant effect of ionic motion on the polymer motion would also be quite small. On the other hand, if ions form temporary coordination bonds with the polymer at one (or possibly more) sites within the polymer or between polymers, then the resultant effect of the presence of ions on the polymer motion would produce a large dependence of polymer motion on salt concentration. In either case, NMR spin lattice experiments would give additional information that may aid in the theoretical description of polymer-ionic interaction or to further experimental avenues through which investigation could be continued.

C. Proposed Solution

Experimental Model

The objective of this research is to investigate proposed mechanisms of ionic interaction in polymer electrolyte systems by studying a simplified model.

The study is based on ^{13}C NMR spin lattice relaxation experiments of solutions with varying ion and polymer concentrations. A comparative study with small molecule analogues enhances the theoretical interpretation of polymeric data.

CHAPTER II

HISTORICAL REVIEW

A. Molecular Dynamics

1. Small Molecule Analogue

For small molecules in solution there are several intermolecular forces that play a role in the dynamics of the system. Dispersion forces are found in all molecular substances and are described as attractions between temporary dipoles in adjacent molecules. Dipole forces exist between polar molecules such as the common solvent H_2O . These forces describe the attraction of the partially positive end of a molecule to the partially negative end of an adjacent molecule. An added attractive force that is found between molecules of H_2O is the hydrogen bond. This occurs when an H atom bonded to an N, O, or F atom in one molecule is attracted to the unshared electron pair of an N, O, or F atom in a neighboring molecule. As small molecules move about in solution, each intermolecular force can affect the dynamics of the system.

The theory of diffusion kinetics¹⁴ is also essential in describing an electrolytic solution. This theory proposes the idea of solvent cages surrounding and stabilizing free ions to prevent the recombination of salt molecules and thereby freely associating the ions throughout the solution in a random fashion. The solvent molecules or groups of solvent-ion molecules collide following a basic equation of kinetic diffusion:

$$F = -D\partial C/\partial x. \quad (\text{Eq. 2.1})$$

Where F is the rate of transfer per cross-sectional area, C is the concentration of the diffusing substance, x is the space coordinate measured normal to the section, and D is the diffusion coefficient. Although the solutions are in constant flux, an overall equilibrium will be established and maintained with respect to the intermolecular forces. Continual Brownian motions¹⁵ randomize ions throughout the solution with an equal probability distribution. These dynamic theories and motions are used to describe what is occurring in the liquid state. It is necessary to characterize the solution dynamics since this aids in the interpretation of the results.

The small molecules that will be studied for comparative NMR spin relaxation experiments are diethylene glycol monoethyl ether (DGME) ($\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-H}$) and poly (ethylene oxide) ($\text{H-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-H}$) of molecular weight 200 g/mol (PEO 200).

The salts that will be used in this study are NaCl and NaI. In each case Na^+ ions are expected to interact with the two lone pairs of electrons on the oxygen atoms of PEO and DGME. By studying NaCl and NaI one can interpret differences in the molecular motion due to the size or stability of the anion in solution.

D_2O is used as the solvent in these studies for an NMR deuterium lock. There are some minor differences in properties of D_2O versus distilled H_2O . The hydrogen bonding effect is not as strong in D_2O as it is in H_2O , so this will slightly affect the strength of the stability cage that is formed around ions in

solution. This will affect all aspects of the strength of solvent-solvent interactions and solvent-solute interactions. Although these differences exist, the magnitude of the effects is not significant enough to hinder the interpretation of the NMR data obtained. This is a common assumption in NMR studies since a deuterium lock is required for many NMR experiments. In this study, we were not concerned with isotope effects. Consequently, this assumption does not interfere with the results we obtained.

2. Polymer

For polymers in solution there are two types of interactions that aid in defining the system: polymer-solvent (P-S) and polymer-polymer (P-P) interactions. If P-S interactions are more favorable than P-P interactions then the solvent is termed a good solvent and the polymer will dissolve. Solvent molecules surround the polymer chains and increase the excluded volume effect which describes the amount of space taken up by solvent molecules within and around a single polymer chain. If P-P interactions are more favorable than P-S interactions, the polymer will fold up into compact conformations and may clump with other polymer chains thereby precipitating out of solution. This is representative of a poor solvent. When the P-S interactions are equal in strength to the P-P interactions the condition of the theta point is achieved. At the theta point, the polymer chain becomes ideal with respect to the probability of conformations and solution statistics. Furthermore, the excluded volume effect does not exist.

In the system isolated for this study, the solvent chosen is D_2O and the polymer is poly (ethylene oxide) $(HO(-CH_2CH_2O)_n-H)$ (PEO). In this system, D_2O is a good solvent which indicates that the intramolecular motions of the polymer are not hindered by chain tangling or interference. This also causes the solvent to be essential in the mechanism of ion transport on the polymer backbone, since there is a higher probability of P-S interactions than P-P interactions.

For the experiments in this study, there are several important dynamic motions in polymers. One important motion is the translational motion of the entire polymer molecule through the solution. This motion is described by a diffusion coefficient, measured using viscosity or light scattering experiments. Another important motion of a polymer is segmental motion. This refers to the continual conformational changes along the polymer chain. These internal motions have been thoroughly studied and described through the aid of time resolved fluorescence depolarization spectroscopy,¹⁵⁻¹⁸ picosecond holographic relaxation spectroscopy,¹⁹ and NMR relaxation experiments.²⁰ Other "internal motions" are found through molecular dynamic interpretations of polymer motion. One motion described by Howarth^{21,22} is a librational motion. This motion is characterized by a "rocking" of the backbone in a polymer. Another internal polymer motion mentioned by Howarth is a chain tumbling effect where small areas of the chain move about as if they were a single unit. All of these motions are important in the interpretation of NMR data.

The three conformational states (see Figure 2.1) along the poly(ethylene oxide) chain which each repeat unit can assume are trans, gauche (+), and gauche (-). The rotational energy barriers between the conformational positions are sketched in Figure 2.2. The difference in the energy levels between the trans, gauche (+), and gauche (-) is great enough to distinguish a relative "lowest" energy position. Yet the energy barrier between the three energy states is small enough to allow transitions from one state to another freely. For a polymer, both isolated bond rotations and cooperative bond rotations exist. A random probability of energy states (random coil) along with the excluded volume effect from solvent D₂O characterizes the flexibility and probable configuration of PEO in solution.

In this study, a series of ¹³C NMR spin lattice relaxation (T₁) experiments are performed using solutions of poly(ethylene oxide) (PEO), diethylene monoethylether (DGME), NaI, NaCl, and D₂O. From this data, information concerning diluent (solvent or ionic) effects on polymer motion are obtained.

B. Nuclear Magnetic Resonance

1. NMR Theory

A nucleus with a nonzero spin I has a magnetic moment μ given by:

$$|\vec{\mu}| = \frac{\gamma h [I(I+1)]^{1/2}}{2\pi}. \quad (\text{Eq. 2.2})$$

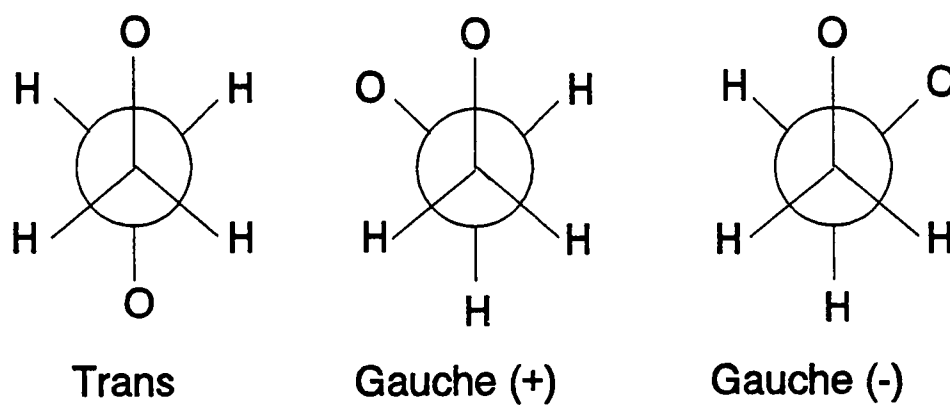


Figure 2.1. Conformational states along PEO chain.

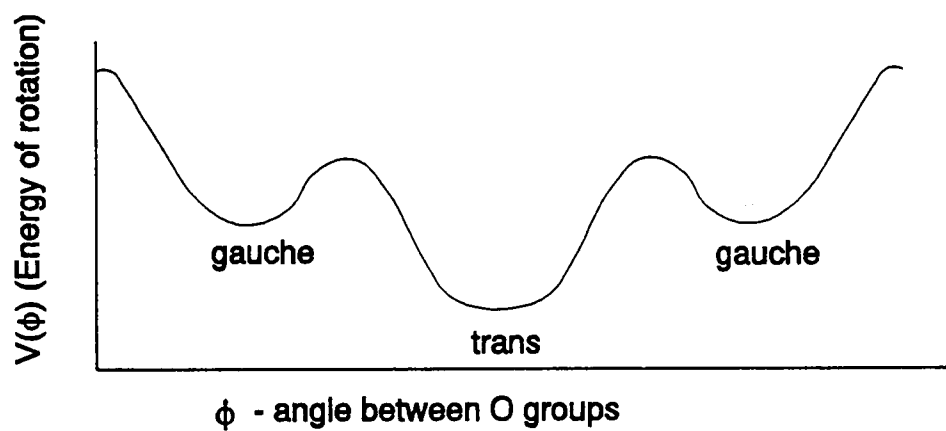


Figure 2.2. Energy states graphically depicted with respect to comparative energy levels.

Where $\hbar$ is Planck's constant and γ is the magnetogyric ratio. The z component of μ (μ_z) is given by:

$$\mu_z = m_l \gamma \hbar / 2\pi. \quad (\text{Eq. 2.3})$$

Where m_l represents the magnetic quantum number $(-l, -l+1, \dots, 0, \dots, l-1, l)$. There are $2l+1$ possible states (m_l) for the nucleus. The energy of the nucleus is independent of m_l in the absence of a magnetic field. However, the degeneracy is removed when an external field is applied. In an external magnetic field H_o , whose direction defines the z axis, the energies are given by:

$$E = -\mu_z H_o = -m_l \gamma \hbar H_o / 2\pi. \quad (\text{Eq. 2.4})$$

Consider spin $\frac{1}{2}$ nuclei (^1H , ^{13}C , ..). There are two states corresponding to $m_l = +\frac{1}{2}$ and $-\frac{1}{2}$. The energy spacing between the two states (see Figure 2.3) is:

$$\Delta E = [-(-1/2) \gamma \hbar H_o] - [(-1/2) \gamma \hbar H_o] = \gamma \hbar H_o$$

$$\Delta E \propto H_o \quad (\text{Eq. 2.5})$$

Since $\Delta E = h\nu_o$ and $\hbar = h/2\pi$, we have $\nu_o = \gamma H_o / 2\pi$. For ^{13}C $\gamma = 6,728 \text{ rad s}^{-1} \cdot \text{gauss}^{-1}$ and $\nu_o = 50.290 \text{ MHz}$ where H_o is 46.974 gauss. The classical picture is as follows. In an external magnetic field, μ lies at a fixed angle with respect to H_o . Also, $\theta = \cos^{-1}(\mu_z/\mu)$ (see Figure 2.4).

The interaction of the nucleus with H_o causes μ to precess about H_o . The frequency of this motion is called the Larmor frequency. The two energy

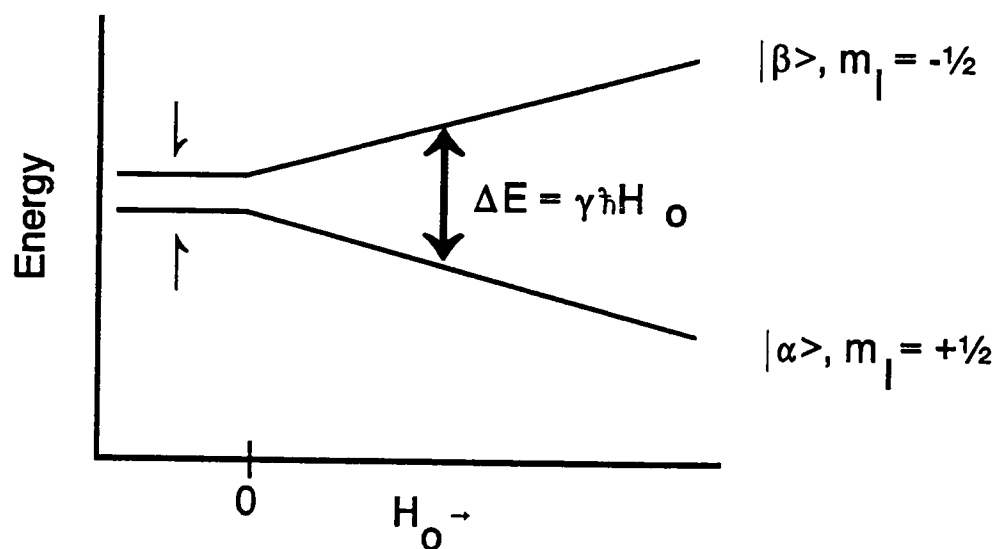


Figure 2.3. Energy spacing between the states of $m_I = +1/2$ and $-1/2$.

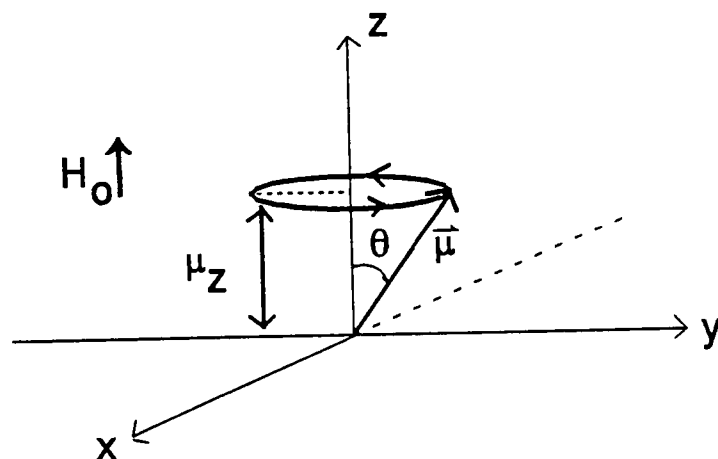


Figure 2.4. Classical picture of a precessing nuclear vector.

states of a spin $\frac{1}{2}$ nucleus correspond to precession of μ about the axis aligned with or opposed to the applied field. Consider ^1H . At $300 \text{ MHz} = \nu_0$, $\Delta E \approx 2 \times 10^{-25} \text{ J}$. In comparison, kT at $295 \text{ K} \approx 4 \times 10^{-21} \text{ J}$. Thus $\Delta E < kT$. Hence, a sample containing a collection of spin $\frac{1}{2}$ nuclei at equilibrium in the presence of H_0 will have a small excess population in the lower energy state according to the Boltzmann distribution:

$$\frac{N_\alpha}{N_\beta} = e^{\Delta E/kT} = e^{\gamma \hbar H_0/kT}. \quad (\text{Eq. 2.6})$$

Hence, there is a net magnetization in the $+z$ direction and no net magnetization in the xy plane (see Figure 2.5).

In an NMR experiment, an oscillating magnetic field, H_1 , is applied perpendicular to the static field, H_0 . This is achieved by passage of a radiofrequency current through a coil whose axis is along the x -direction (see figure 2.6).

H_1 is equivalent to the vector sum of two magnetic vectors of equal amplitude, counter rotating in the xy plane (see Figure 2.7). One component vector rotates precisely in step with the precessing nuclei at ν_0 . The other component does not interact (rotating in the opposite sense). The field exerts a torque $\tau = \mathbf{M}_z \times \mathbf{H}_1$ on $\mathbf{M}$ so as to tip $\mathbf{M}$ away from the z -axis. This gives rise to a component $\mathbf{M}_{xy}$ of $\mathbf{M}$ in the xy plane.

Once the component $\mathbf{M}_{xy}$ is generated, another torque (τ) $\tau = \mathbf{M}_{xy} \times \mathbf{H}_1$

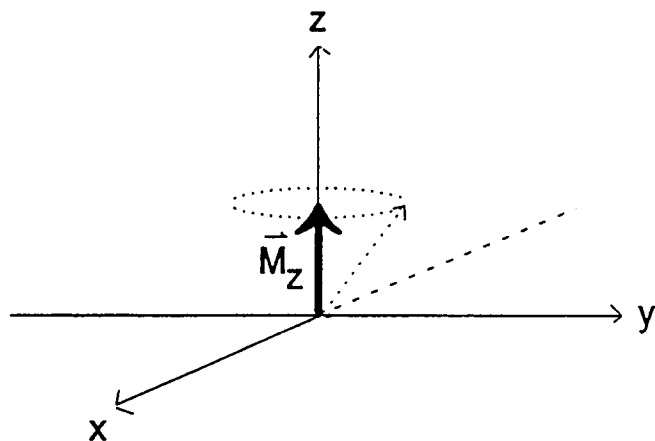


Figure 2.5. Net magnetization (M_z) in the +z direction.

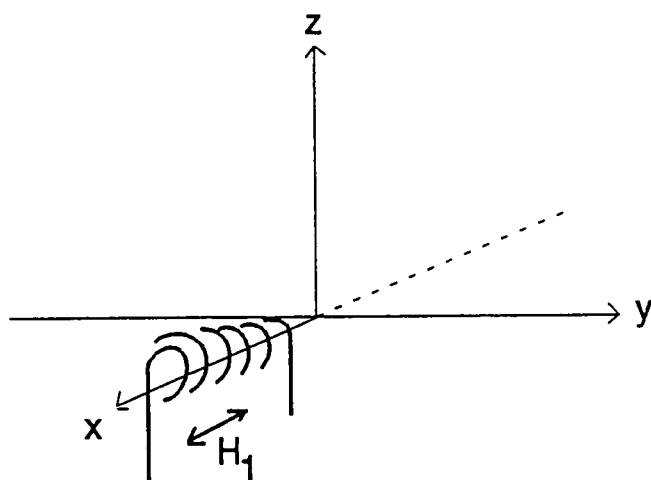


Figure 2.6. Coil along x axis through which a radiofrequency is passed.

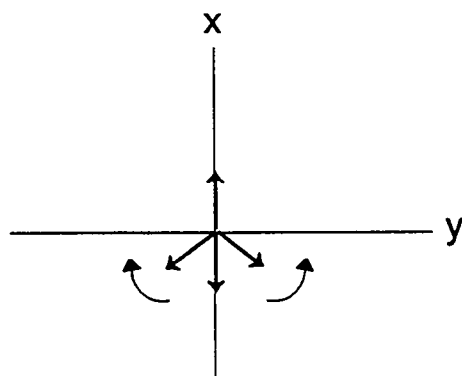


Figure 2.7. (H_1) Two magnetic vectors of equal amplitude counter rotating in the xy plane.

appears, driving $\mathbf{M}$ into an anti-parallel configuration with respect to $\mathbf{H}_0$ (absorption of energy). This is analogous to absorption of UV/VIS photons by a chromophore. However the modes of relaxation (excited $\rightarrow$ ground state) differ. $\mathbf{H}_1$ oscillating at the Larmor frequency induces both upward and downward spin transitions of a nucleus with equal probability. As long as there is a greater number of nuclei in the lower energy state, the rate of energy absorption exceeds the rate of emission, and a signal is observed. Unless there is an additional relaxation mechanism for the nuclei to return to the lower energy state, continued $\mathbf{H}_1$ irradiation causes the spin population to become equal (saturation). If saturation occurs, no net absorption of energy occurs. Thus, there is no signal. For a signal to occur, there must exist additional relaxation mechanisms in order to have a greater number of nuclei in the lower energy state, since spontaneous emission occurs only to a negligible extent. The relaxation mechanisms that allow for a greater number of nuclei to be in the lower energy state are the focus of this research. These relaxation mechanisms allow for the transference of energy to the environment which flips μ to the lower energy state.

For spins, energy can be transferred to their environment by interaction with a local magnetic field that is oscillating at the Larmor frequency ν_0 (stimulated emission). The origins of a local fluctuating field can be rationalized by considering the microscopic environment. On the microscopic level, a molecule in a nonviscous liquid perpetually tumbles at random. We can

represent this motion by the time variant angle of an internuclear vector (between nuclei of the molecule) with the H_0 axis. This creates randomly varying magnetic fields at the site of the nucleus, and the component of this fluctuation at the Larmor frequency will be effective in stimulating transitions.

The time dependence of molecular motion is related by the Fourier Transform to a distribution of motional frequencies. For many cases, a correlation time τ_c can be obtained which characterizes the motion. For a small molecule in a nonviscous liquid, $\tau_c \sim 10^{-12}$ - 10^{-10} s. A 10^{-11} s correlation time corresponds to a frequency range from 0 to over 10^5 MHz. With this broad range there will be a frequency component of molecular motion at the Larmor frequency. It is this molecular motion, creating fluctuating magnetic fields at the Larmor frequency, that allows the nuclei to exchange energy with their surroundings and return toward the equilibrium population. This process of "spin-lattice relaxation" is nominally first order. The rate constant is $1/T_1$, where T_1 is the spin-lattice relaxation time. If the source of the randomly fluctuating magnetic field is another nuclear magnetic moment, then the relaxation process is called nuclear dipole-dipole relaxation. There are other sources of fluctuating magnetic fields leading to other relaxation processes such as paramagnetic relaxation, and chemical shift anisotropy relaxation. An example of nuclear dipole-dipole relaxation is the interaction between a ^{13}C nucleus and a proton that is near, but not necessarily bonded to the carbon. The strength of this interaction depends on the distance between nuclei ($1/r^6$), and on the angle Ψ

between μ and the internuclear vector (see Figure 2.8). The direction of μ is fixed with respect to H_0 . But as the molecule tumbles, the internuclear vector reorients with respect to H_0 , and Ψ changes. The average value of the induced field is zero, so it has no effect on chemical shifts. But it does provide the fluctuating field for relaxation.

The order of magnitude of T_1 depends on $1/r^6$ and on the inverse correlation time ($1/\tau_c$). In liquids, dipolar relaxation produces typical proton or carbon T_1 values of about 10^{-2} to 10^2 s. A small molecule in a nonviscous medium will have a short correlation time and a long T_1 value. For a viscous polymer, T_1 values will be very short.

The NMR experiment is capable of detecting the loss in the xy magnetization as a result of dephasing of the magnetization, in addition to the nuclei returning to their equilibrium orientations about the z axis. The loss of detectable magnetization is characterized by T_2^* , the effective spin-spin relaxation time. T_2^* includes lack of H_0 homogeneity, T_1 processes, low frequency motions ($\ll \nu_0$), spin exchange to nearby nuclei, and chemical exchange effects.

$1/\pi T_2^*$ is the FWHM of an NMR absorption band. True spin-spin relaxation excludes H_0 inhomogeneity. For liquids $T_1 \sim T_2$ (T_2 is always $\leq T_1$). In pulse NMR experiments, the nuclei in the entire frequency region of interest is excited by a single burst of RF power (pulse). The resulting signal is measured after the RF is turned off. FT is required to convert the resulting

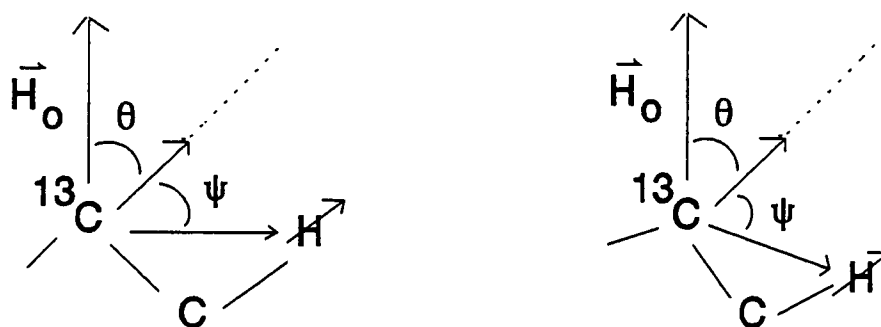


Figure 2.8. Changes in Ψ due to the motion of the molecule.

signal into a usable form. Pulse NMR is often called FT-NMR. A pulse of monochromatic RF with a rectangular envelope can be described in the frequency domain as a band of frequencies centered at the RF frequency. The Fourier Transform of a rectangular RF pulse t_p in duration with frequency ν_s and amplitude A (see Figure 2.9) is:

$$\frac{A t_p}{2} \frac{\sin[\pi t_p (\nu - \nu_s)]}{\pi t_p (\nu - \nu_s)}. \quad (\text{Eq. 2.7})$$

ν_s is the monochromatic frequency produced by the pulse generator which is termed the spectrometer frequency. As the pulse length decreases, the width of the frequency band increases. For a typical pulse length of 10 μs , the flat portion of the frequency band (<1% difference with respect to peak value) is about 16,000 Hz wide. For a 300 MHz ^1H , 75 MHz ^{13}C instrument, this easily spans the range of chemical shifts (15 ppm or 4500 Hz for protons, 200 ppm or 15,000 Hz for ^{13}C). Note: a short pulse results in lower power at the center frequency. The RF generator must deliver high power pulses with a precisely defined envelope.

In discussing how the nuclei respond in a pulse experiment, we go to the rotating frame. Consider the spins in the laboratory frame. There is an excess of spins aligned with $\mathbf{H}_0$ (+z- direction) and precessing about +z at the Larmor frequency ν_0 (see Figure 2.10). An alternate representation of the same situation is to allow the axes to rotate at the Larmor frequency ν_0 . The spins

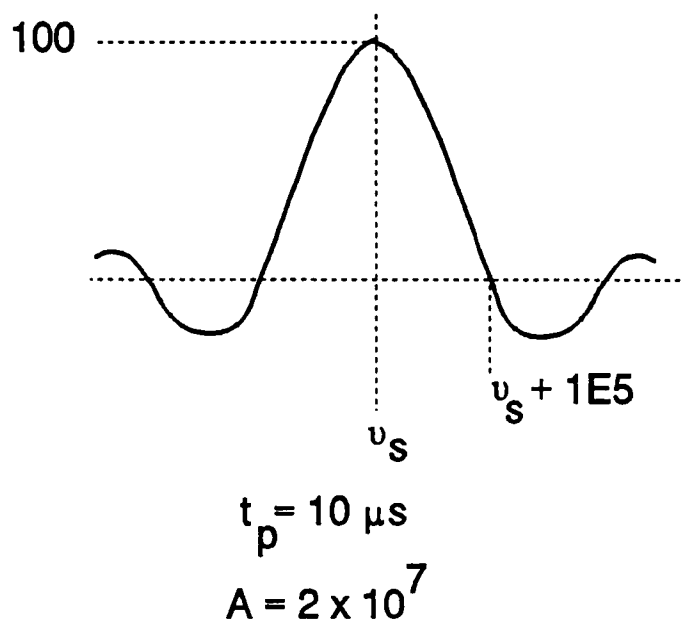
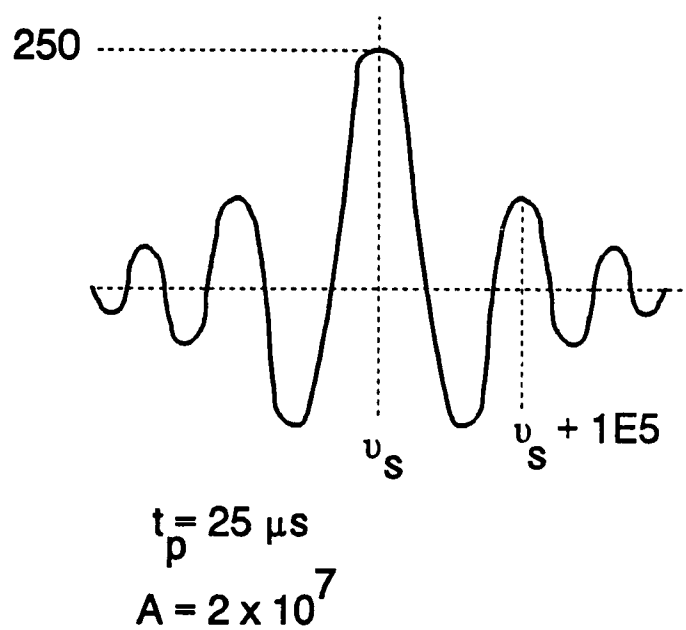


Figure 2.9. Comparative ν_s , t_p , and A for spectrometer frequencies 250 and 100 MHz.

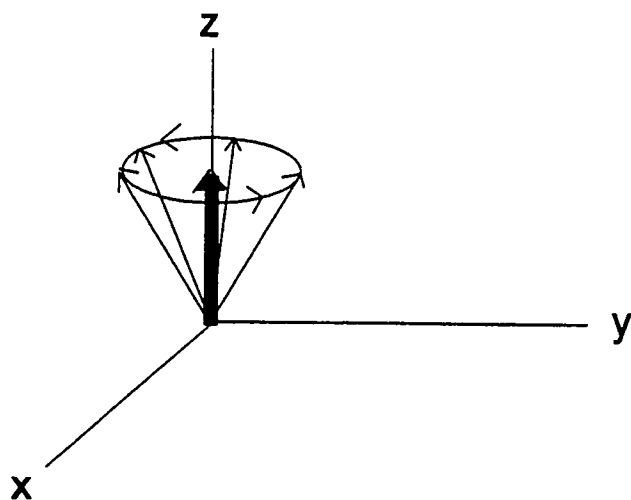


Figure 2.10. Excess of spins aligned with H_0 and precessing about the $+z$ axis at the Larmor frequency.

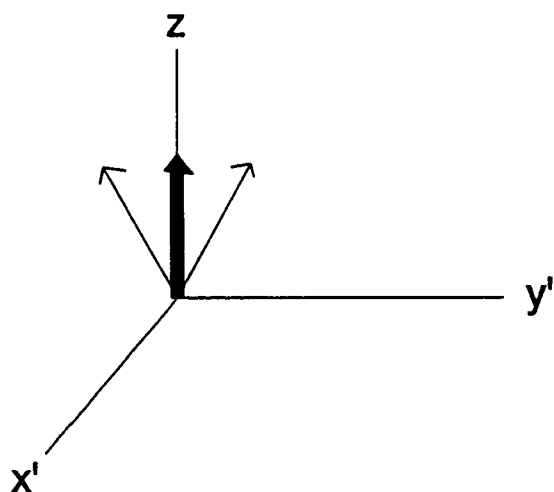


Figure 2.11. Rotating frame from the view of the $x'y'$ plane.

now appear to be fixed in orientation with respect to the x' and y' axes (see Figure 2.11). In both cases, the equilibrium magnetization ($\mathbf{M}$) points along the $+z$ direction. The rotating frame will now be utilized.

Consider the application of an RF field whose frequency (ν_s) is the same as the rotation frequency of the frame. The applied RF consists of two counterrotating vectors. One vector rotates in the same direction as the frame, while the other vector appears to rotate at twice ν_s and can be ignored (outside the range of chemical shifts). In the rotating frame, the stationary vector behaves as a nonoscillating magnetic field ($\mathbf{H}_1$) perpendicular to $\mathbf{H}_0$. If $\nu_s = \nu_0$ (Larmor frequency), the nuclei tend to precess about $\mathbf{H}_1$. If the RF field is applied as a pulse for a duration t_p , where $\mathbf{H}_1$ is along the $+x'$ direction, the effect is a partial rotation of $\mathbf{M}$. $\mathbf{M}$ is said to be tipped toward the $-y'$ axis (see Figure 2.12). The tip angle (α) is given by $\alpha = \gamma H_1 t_p$. The RF pulse is usually designated by the value of α that it produces (and the axis to which it is applied). The term $(\pi/2)_x$ or 90_x° refers to a pulse that tips the magnetization vector 90° along the $-y'$ axis. $\mathbf{H}_1$ is directed along the $-y'$ axis. The typical length of a 90_x° pulse is $\approx 10 \mu\text{s}$. Because the pulse produces a wide band of frequencies of almost equal amplitude, the nuclei throughout the entire chemical shift range are all effectively tipped by the same angle. The rotating frame is assigned to a single frequency ν_s , the value at the center of the band (see Figure 2.13). In the absence of relaxation effects, $\mathbf{M}$ would remain along the $-y'$ axis for nuclei whose Larmor frequency corresponds to the frequency of the

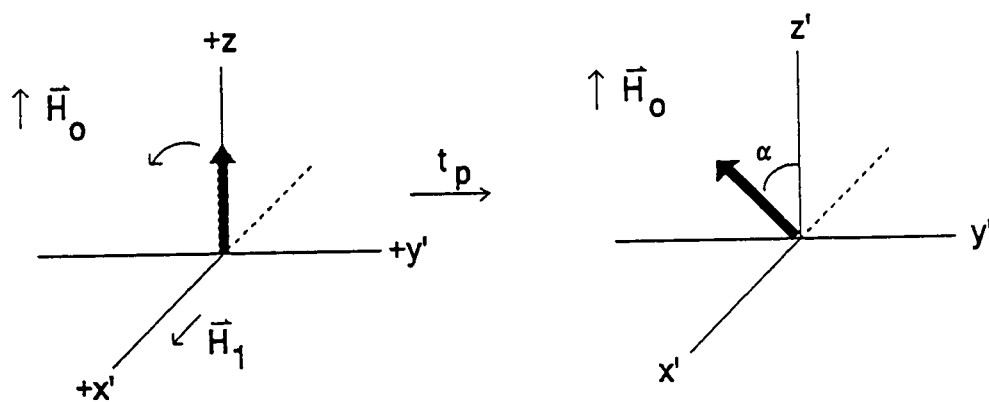


Figure 2.12. **M** tipping by the RF pulse.

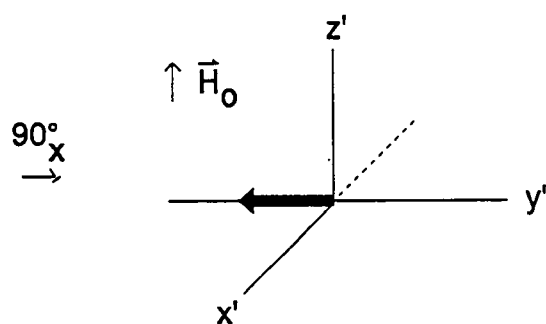


Figure 2.13. 90_x° pulse.

rotating frame. However, T_1 and T_2^* processes act to reduce the $-y'$ component of the magnetization. T_1 effects cause a gradual return of the magnetization towards the z -axis, further decreasing the component along $-y'$. Because field inhomogeneities usually result in $T_2^* < T_1$, one often gets the situation in which the $-y'$ component of $\mathbf{M}$ decays to zero before the spin population can achieve the Boltzmann distribution and reach the equilibrium value of $\mathbf{M}$ (see Figure 2.14). At some later time, $\mathbf{M}$ returns to its equilibrium value. For the detection of magnetization we return to the laboratory frame where the $-y'$ component corresponds to a magnetization vector rotating in the xy plane. A receiver coil (usually the same coil used to excite the nuclei) is situated in the xy plane where it senses the rotating magnetization. As the $-y'$ component decreases, the oscillating voltage from the coil decays, and reaches zero when the spins return to their equilibrium positions. The record of the receiver voltage in the time domain is called the free induction decay (FID) because the nuclei are allowed to precess freely in the absence of $\mathbf{H}_1$. The FID is the Fourier partner of the NMR frequency spectrum (see Figure 2.15). The mathematical expression for the Fourier transform is:

$$f(\omega) = \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt \quad (\text{Eq. 2.8})$$

Here $f(t)$ represents the time domain data, and $f(\omega)$ the required frequency spectrum.

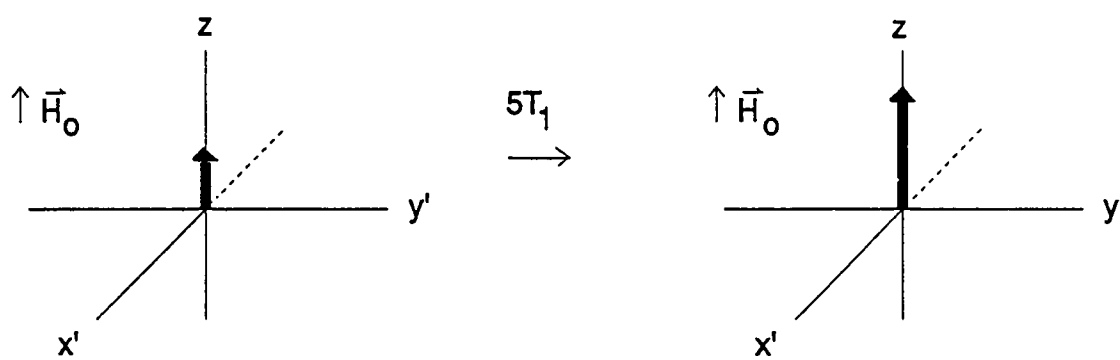


Figure 2.14. T_1 relaxation.

2. NMR T_1 Experiment

The inversion recovery method was used for the T_1 experiments performed in this research. The +z magnetization is inverted using a 180° pulse and then a specific time interval τ elapses during which the signal has time to relax. A final 90° pulse is applied so that the signal can be measured along the y' axis. The τ values vary in length from approximately zero (complete inversion) to at least $5 \times T_1$ so that the sample is given enough time to fully relax back to equilibrium. This list of τ values is termed a variable delay list and the value sets may differ between samples (see Figure 2.16). To calculate the T_1 value a plot of intensity versus τ values is evaluated (see Figure 2.17).

3. Internal Polymer Motion

Along the polymer chain, continual internal motions are occurring. This cooperative motion allows a particular nucleus to sample various surroundings. There will be a frequency component of each different type of internal molecular motion at the Larmor frequency and this allows for spin lattice relaxation to occur. Relaxation causes the nuclear vector to achieve the equilibrium state. The rate of this relaxation is dependent on viscosity. Viscosity affects the internal motions of the polymer and therefore the different types of surroundings the nuclei sample in solution. How strong an influence this is will be dependent on the frequency range of the internal motion and on the Larmor frequency of the nuclei in question. Cooperative bond rotations and isolated bond rotations

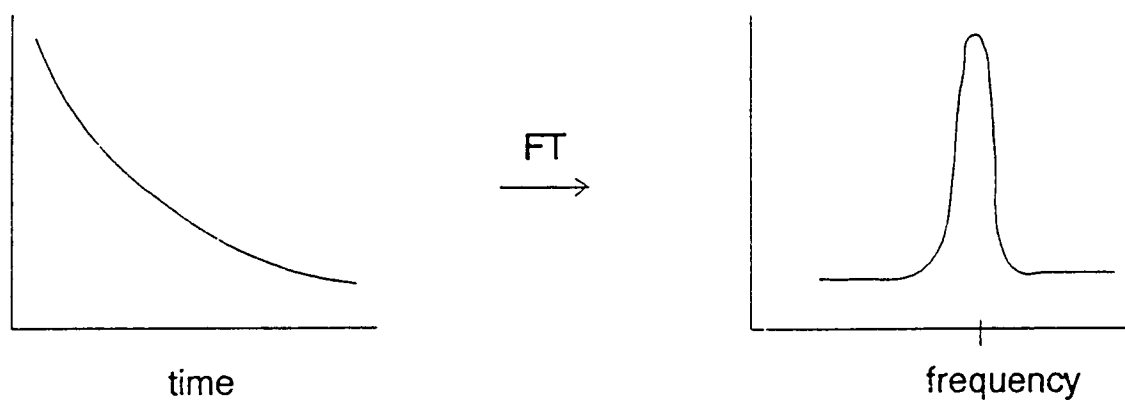


Figure 2.15. Free Induction Decay (time domain) versus the NMR spectrum (frequency domain).

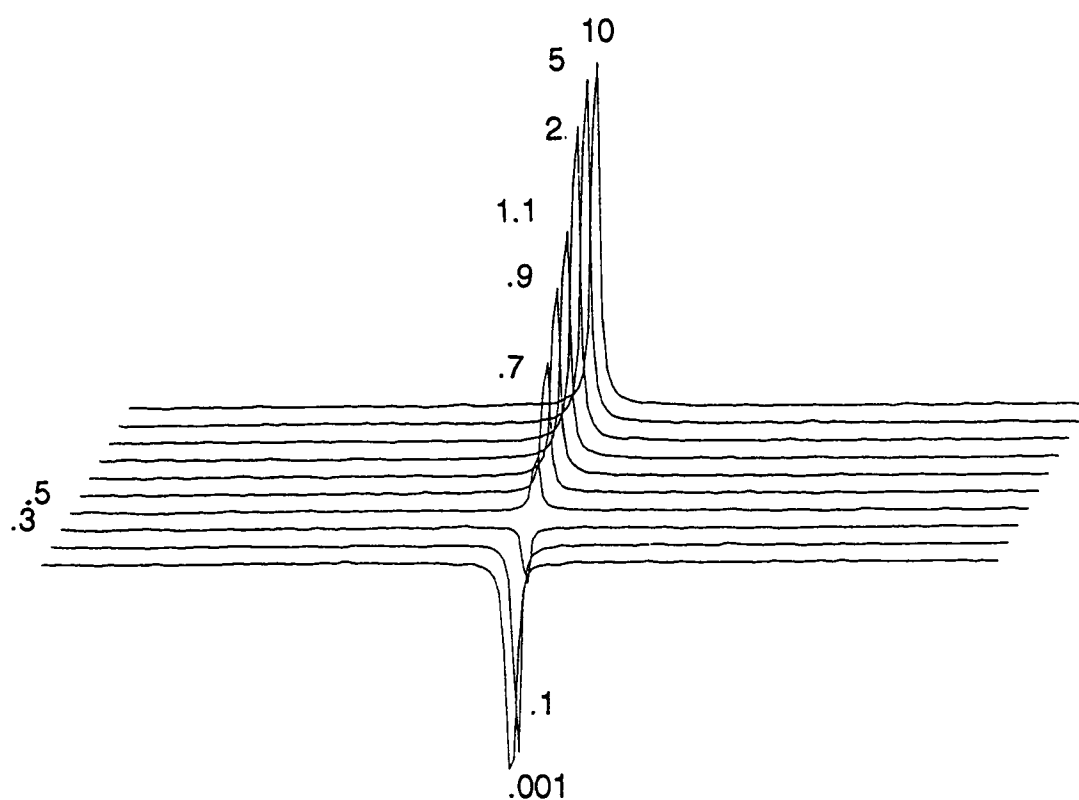


Figure 2.16. Example T_1 experiment with indicated tau values (s).

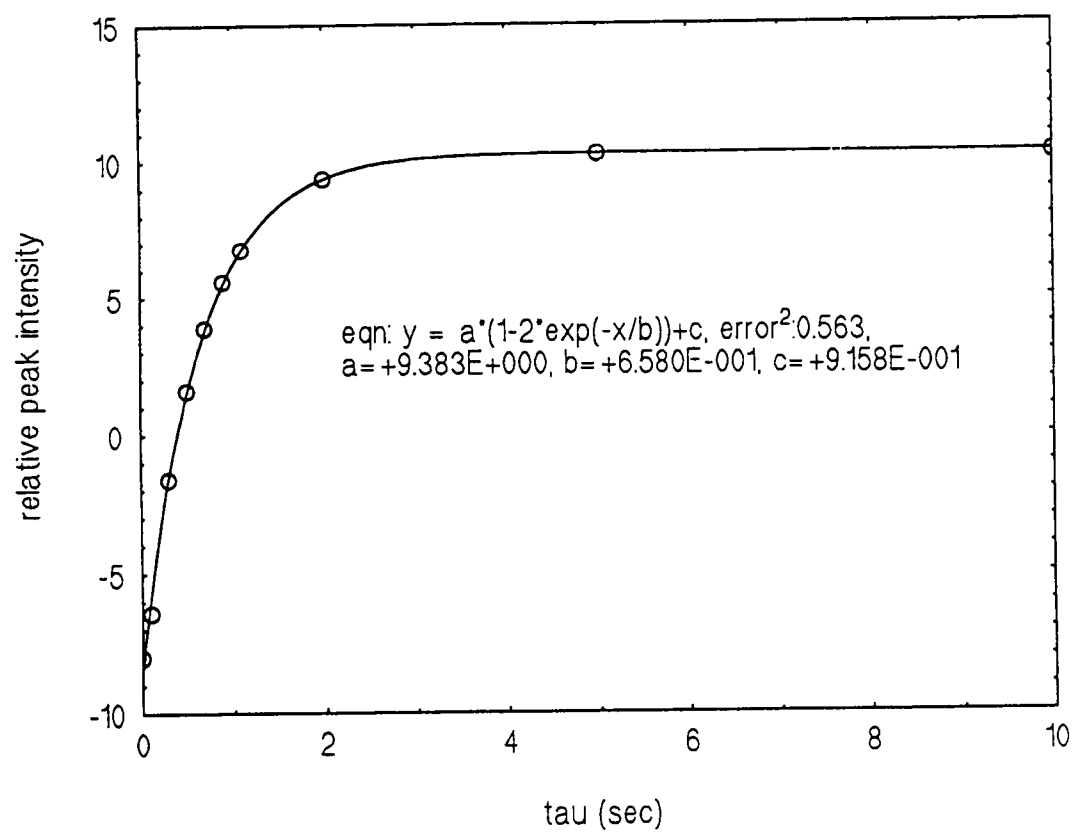


Figure 2.17. Example T_1 calculation using Easyplot.

both have particular correlation times associated with their molecular motion. To be able to distinguish the exact motion taking place in solution requires a highly detailed model. As viscosity slows the internal motions of the carbon bonds, the ^{13}C nucleus is able to feel the effect of a neighboring fluctuating magnetic field (e.g. the H attached to the adjacent carbon) differently and for a different amount of time since the motions are hindered. Thus the probability of energy exchange is higher for a more slowly moving polymer backbone. If ions are added to the polymer solution and coordination bonds form between polymer molecules and different chain sections of the same polymer this would also hinder the motions of the polymer backbone and thus allow for the ^{13}C nuclear vectors to also exchange energy with its surroundings. If the ions are not directly involved in slowing the polymer motion then there would be no effect shown on relaxation data with added salt.

C. Dynamic Bond Percolation Theory

1. Description

Dynamic bond percolation (DBP) theory¹⁻⁷ is a detailed microscopic theory that describes the transport mechanism in solid polymer electrolytes. This theory is an extension of static percolation theory which describes the particles as "hopping" from site to site on a fixed lattice of available unfilled sites. A brief outline of the essential aspects of DBP theory follows. The fundamental equation of motion for the hopping ions is:

$$\frac{dP_i(t)}{dt} = \sum_{ij} (W_{ij}P_j(t) - W_{ji}P_i(t)) \quad (Eq. 2.9)$$

where $P_i(t)$ is the probability that an ion is at lattice site i at time t , W_{ij} is the rate at which the ion hops from site i to site j , and the summation is taken over all nearest neighbor sites j . W_{ij} takes on a value w if the hop can take place, which occurs with probability f , and 0 if the hopping from i to j is blocked, which occurs with probability $1-f$. In dynamic bond percolation theory, W_{ij} is time dependent, with a rate λ , in which W_{ij} is either 0 or w . Above the glass transition temperature, this is believed to be a reasonable model for polymer electrolytes since the polymer host is in motion. The sites in which the ions can reside move with respect to one another, thus altering the open or closed condition of particular jumps. Hopping probabilities readjust, or renew their values on a timescale τ_{REN} determined by the polymer motion. This theory expresses transport as the result of a combination of polymer segmental motions with independent hopping movements of the ions. The rate determining step in the transport process depends on the local segmental mobility of the polymer host. This has been supported by studies using the ability of free volume theories to account for the ionic conductivity over a broad range of temperatures.⁷ Although ionic hopping is considered to occur on a time scale much shorter than that corresponding to motional dynamics of the polymer, the conditions under which hopping can occur are viewed as a

comparatively rare occurrence. There are three characteristic parameters in DBP theory that can be probed experimentally: f , $\tau_{\text{HOP}} (= w^{-1})$, and τ_{REN} . The most pertinent parameter in reference to this research is τ_{REN} , which is characteristic of the segmental motions of the polymer. Although the segmental and local motions are characterized in general by a distribution of relaxation times, the renewal time should be related to an average relaxation time for polymer motion. Consequently, τ_{REN} should increase with molecular weight for short polymer chains.^{23,24} In addition, increasing salt concentration should decrease τ_{REN} since salt acts as a crosslink between polymers. In terms of free volume theory, the segmental relaxation time of a polymer/solvent system is given by:

$$\tau = A e^{\left[\frac{B(1-v)}{v} \right]}$$

$$v = v_1 - c \phi_2. \quad (\text{Eq. 2.10})$$

where v is the fractional free volume, v_1 is the fractional free volume of diluent and ϕ_2 is the weight fraction of polymer.²⁵ A and c are constants at a given temperature. By associating τ_{REN} with the segmental relaxation times, the relaxation time for a polymer/salt/solvent system should obey the above equation as a function of concentration of polymer. DBP theory can be further developed by experiments which produce data on relaxation processes at the microscopic level; by the extension of the lattice formalism to describe more fully an amorphous system; and by the more direct correlation of the W , f , and

τ_{REN} parameters to the statistical mechanics of the segmental and ion motions.

2. Importance

DBP theory interprets ionic motion along polymers in the solid state, therefore it is not strictly applicable to the solution studies in this thesis. Yet, since DBP theory is the leading theoretical model of ion transport, a basic understanding of this theory is required to facilitate interpretation and comparison of the solution studies done. The correlation times of the internal polymer solution motions may be compared to the τ_{REN} of the dynamic bond percolation theory. τ_{REN} should behave similarly to the correlation times obtained in this study if the ideas of DBP theory are supported in the solution studies. Therefore if the same relationships exist we should see an increase in the correlation time as molecular weight or polymer concentration increases and there should be a decrease in correlation time with added salt if salt acts as a crosslink between PEO sections thereby slowing the internal polymer motion. From our results we will be able to compare these theories and judge whether or not the solution behaves similar to the solid state predictions.

CHAPTER III

MATERIALS AND APPARATUS

A. Chemicals

1. Purchasing Information

PEO purchased from Tosoh Corporation was used to prepare 0.183 m PEO solution (nominal molecular weight 26000), $M_w/M_n = 1.20$, and 0.382 m PEO (nominal molecular weight 45000), $M_w/M_n = 1.07$. All other large polymer samples were made using PEG 12600 Mw with M_w/M_n of 1.04 from Polymer Laboratories (PL). The PEO (200 M_w) was purchased from Polysciences, Inc. and the diethylene glycol monoethyl ether (DGME) was purchased from SIGMA. The NaCl, NaI, and D_2O were purchased from Aldrich at greater than 99.9% purity. The samples were measured by the w/w% method and stored under $N_2(g)$.

B. Sample Preparation and Apparatus

1. Chemical Handling

Samples from TOSOH were refrigerated until use. The PEO from PL was stored under N_2 in a Labconco controlled atmosphere glove box. Each solution was prepared to approximately 1 ml total volume in NMR sample tubes. The PEO needed was transferred using a clean spatula into a tared glass vial on an American Scientific Products electronic balance and the weight was recorded to 0.0001 g. The theoretical amount of D_2O was then calculated for the % solution desired. The D_2O was sealed under N_2 and refrigerated

between uses or stored in the glove box. The actual amount of D₂O was transferred using disposable pipets into the PEO vial and the weight was recorded.

$$\frac{g\text{ PEO}}{g\text{ D}_2\text{O}} \times 100\% = w/w\% \text{ PEO.} \quad (\text{Eq. 3.1})$$

NaI and NaCl were stored under N₂ in the glove box between uses. The theoretical amount of salt was calculated for the desired Na:O ratio from the PEO in the sample vial. This approximate amount was added to the sample vial using a clean spatula and the weight was recorded. The solution was then allowed to sit until equilibrium was reached (usually overnight). The solution was then transferred using a disposable pipet into a clean and dry Ultraprecision 5 mm NMR tube (No. 508 from Norell, Inc./235). The NMR tube was sealed under N₂ and used in this manner for experimentation.

2. Instrumentation

The nuclear magnetic resonance instruments used were the Bruker AC250 MHz, and Bruker AMX400 MHz.

CHAPTER IV

EXPERIMENTAL APPROACH

A. NMR T_1 Experiments

1. 250 MHz T_1 Programs

For the experiments using the Bruker AC250 MHz spectrometer a standard C^{13} T_1 inversion recovery program (see Figure 4.1) was used to obtain the FIDs of the PEO solutions with a chosen variable delay list. The variable delay lists were selected depending on the sample and the experiment time allotted for the instrument. The 90 degree pulse was checked for each sample, and other routine parameters were constant. The FIDs were processed using a T1PROC.AU program (see Figure 4.2).

2. 250 MHz T_1 Calculation

From the resulting spectra, peak intensity values were recorded for each variable delay tau. Using EASYPLOT, the peak intensities were plotted vs. tau and Eq. 4.1 was used to fit the resulting curve, thus giving the T_1 value for the sample.

$$y = a(1 - 2e^{-x/b}) + c ; \text{where } b = T_1. \quad (\text{Eq. 4.1})$$

The experiment on a particular sample would be redone depending on the lineshape of the given spectrum, the signal to noise ratio, and the validity of intensity values. Values for repeated experiments were averaged for a final T_1 value with experimental error averaging ± 0.02 s.

```

;INVREC.AUR
;INVERSION-RECOVERY T1 WITH DELAY LIST CYCLING
;D1-180-VD-90-FID
1 ZE
2 WR #1          ;PREPARE A SET OF ZEROED DISK FILES
3 IF #1
4 LO TO 2 TIMES C    ;FIRST C=NO. OF FILES=NE
    VC            ;SELECT SECOND 'C'
5 RF #1.001        ;RESET FILE EXTENSION, BEGIN CYCLE
6 RE #1            ;READ CURRENT FID
7 D1               ;RELAXATION DELAY FOR EQUILIBRIUM
8 P2               ;180 DEG PULSE
9 VD               ;VARIABLE DELAY (TAKEN FROM CURRENT 'VD' LIST)
10 GO #7           ;ACQUIRE DATA AFTER 90 DEG PULSE, LOOP TO 7
11 WR #1           ;STORE CURRENT FID
12 IF #1           ;INCREMENT FILE EXTENSION
13 IN=6            ;LOOP TO 6 AND INCREMENT VD LIST POINTER
14 LO TO 5 TIMES C ;REPEAT CYCLE THROUGH DELAY LIST
    ;C IS SECOND IN VC LIST
15 EXIT

;PROGRAM REQUESTS FILENAME FOR FIDS
;NE DEFINES THE NUMBER OF TAU VALUES IN THE VD LIST, THE ;NUMBER
OF FIDS STORED.
;THE CURRENT VD LIST MUST CONTAIN THE SET OF RECOVERY ;DELAYS
TO BE USED (IN ANY ORDER).
;D1=5*T1
;P2=180 PULSE (CONSTANT PHASE)
;RD=0, PW=90 PULSE
;NS=MULTIPLE OF 8, DS=0
;CURRENT VC LIST MUST CONTAIN AN ENTRY WHICH DEFINES THE
;NUMBER OF FILES (=NE) AND A SECOND ENTRY WHICH DEFINES THE
;NUMBER OF CYCLES TO BE MADE THROUGH THE VD LIST FOR LONG-
;TERM AVERAGING.
;TOTAL TRANSIENTS PER FILE=C*NS.

```

Figure 4.1. Inversion Recovery T_1 program for the Bruker AC250 MHz NMR.

1 RE #1	;READ CURRENT FID
2 IF #1	;INCREMENT FILE EXTENSION
3 EM	;WINDOW MULTIPLICATION
4 FT	;FOURIER TRANSFORMATION
5 PK	;PHASE CORRECTION
6 WR #2	;WRITE SPECTRUM ONTO DISK
7 IF #2	;INCREMENT FILE EXTENSION
8 IN=1	;LOOP TO 1, NE TIMES
9 EXIT	

Figure 4.2. FID processing program for T_1 experiments.

3. 400 MHz T_1 Program

The experiments done on the Bruker AMX400 MHz NMR were achieved using a program written by Jay Gregory which follows the standard C^{13} T_1 inversion recovery format (see Figure 4.3). The 90 degree pulse was obtained for each sample, while the other parameters were kept constant. The variable delay list was chosen depending on the sample and the experiment time allotted. Each experiment was repeated at least twice, depending on agreement between T_1 values.

4. 400 MHz T_1 Calculation

The T_1 values are calculated using intensity values from the processed spectra by software furnished by Bruker. The experimental error in the T_1 values obtained from the AMX400 MHz averaged ± 0.007 s.

B. Molecular Dynamics Modelling Programs

1. Introduction

"Molecular Dynamics Modelling for Nuclear Magnetic Resonance Spin-Relaxation" (MOLDYN Version 3.01) produced by Syracuse University²⁶ is a combined package containing several possible models for the interpretation of NMR data. The program is written in Fortran 77 for VAX computers running under VMS. For the models in this program experimental T_1 values were entered and limits on other parameters were fixed. The program would then calculate the optimized correlation times. The package was used to find appropriate models to interpret the NMR data obtained in this study. The

;t1rdc.jmg
;T1 measurement using Inversion recovery

```
1 ze
  d11 s2 cpd
2 d1
3 p2 ph1
  vd
  p1 ph2
  go=2 ph31
  d1 iv wr #0 if #0 zd
  lo to 3 times 14
do
exit
```

```
ph1=0 2
ph2=0 0 2 2 1 1 3 3
ph31=0 0 2 2 1 1 3 3
```

```
;hl1: ecoupler high power level
;p1: 90 degree transmitter high power pulse
;p2: 180 degree transmitter high power pulse
;d1: relaxation delay; 1-5*T1
;d11: delay for disk I/O [30 msec]
;vd: variable delay, taken from vd-list
;define VDLIST
;this pulse program produces a ser-file (PARMODE = 2D)
```

Figure 4.3. Inversion Recovery T_1 program for the Bruker AMX400 MHz NMR.

models that best fit the data were: an isotropic model with two correlation times and an internal libration model^{21,22} developed by O. W. Howarth. Other models were tried to interpret the NMR data. One such model was the popular VJGM (Valeur, Jarry, Geny, and Monnerie) model²⁷⁻²⁹ which distinguishes the relative importance of backbone three-bond jumps and four-bond jumps to describe the internal motion of the polymer. This model was unable to interpret the NMR data for various possible reasons. One reason is that the model may require further experimental data including T_2 values or NOE information to generate interpretable correlation times. Another possible reason this model failed could be due to the lack of information on reasonable constraints for parameters and correlation times within the program.

2. Isotropic Model

The isotropic model was initially used to describe the motion of each of the three systems under study: the diethylene glycol monoethyl ether (DGME), PEO (200), and PEO (12600). The model was found effective for the diethylene glycol monoethyl ether, but ineffective for describing the motion of PEO (200 and 12600). The isotropic model describes the motion of an I-S nuclear spin vector (I=observed nucleus, S=dipolar nucleus) attached to a molecule undergoing isotropic overall motion described by correlation time τ_1 . A second motion is also present (this may be regarded as an internal isotropic motion) having correlation time τ_2 . The relative importance of the two motions are weighted by coefficients C1 and C2 which sum to one in order

to meet normalization conditions. For all cases the C1 and C2 values did not vary far from 0.5, giving each tau equal importance.

3. Internal Libration Model

The internal libration model was found to fit the data of the PEO (200 and 12600) data. This model isolates correlation times for the motions of internal "rocking" along the axis (libration τ_G) restricted by a maximum angle X and an internal tumbling motion (τ_R). This model was also able to fit the NMR data from DGME. The autocorrelation function that defines the relationship of the correlation times is as follows:

$$\langle F_1^*(t+\tau)F_1(t) \rangle = \frac{2}{15} (A \exp(-|\tau|/\tau_R) + (1-A) \exp[-|\tau|/(1/\tau_R + 1/\tau_G)]) \quad (Eq. 4.2)$$

Where A is related to X by the equation:

$$[(\cos X - \cos^3 X) / 2(1 - \cos X)]^2 = A \quad (Eq. 4.3)$$

CHAPTER V

EXPERIMENTAL RESULTS

A. NMR T_1 Data

1. Bruker 250 MHz NMR T_1 Data

The T_1 values for PEO (12600) in D_2O measured on the Bruker AC250 MHz NMR with varying ratios of NaI and molalities of PEO are summarized in Table 5.1. A plot of these values is provided in Figure 5.1. In this data set, the T_1 values decrease fairly uniformly with increasing ion I^- molality and with increasing polymer concentration.

The T_1 values for PEO (26000*), PEO (42000**), and PEO (12600) measured on the Bruker AC250 MHz NMR with varying ratios of NaCl and PEO molalities are summarized in Table 5.2. A plot of these values is provided in Figure 5.2. This data set also has T_1 values that decrease with increasing Cl^- ion and polymer concentration, but there is an irregularity to the pattern, more than was seen in the I^- ion data.

2. Bruker AMX400 MHz NMR T_1 Data

The T_1 values for varying molality PEO 12600 with differing NaI and NaCl molalities for the Bruker AMX400 MHz NMR are summarized in Tables 5.3 and 5.4 respectively. Plots of these data are provided in Figures 5.3 and 5.4 respectively. For the data in Tables 5.3 and 5.4 the same general trends are again found as T_1 values decrease for increasing ion and polymer concentration. Yet the differences in the samples without salt as polymer

Table 5.1. 250 NMR T_1 values with Na:O ratios for NaI

mPEOx10 ²	0:1	1:4	1:2.57	1:2.11	1:1.33	1:1	1:1.646	1:3.22
.397	.6646	.7462			.6622	.6764		.3315
.794	.6282	.6166			.5334	.4581	.3329	
1.11	.6057	.5958			.4120	.3283		
2.38	.5008	.4609		.3873	.2353			
3.18	.4470	.3347	.2920					
5.95	.3321	.1725						

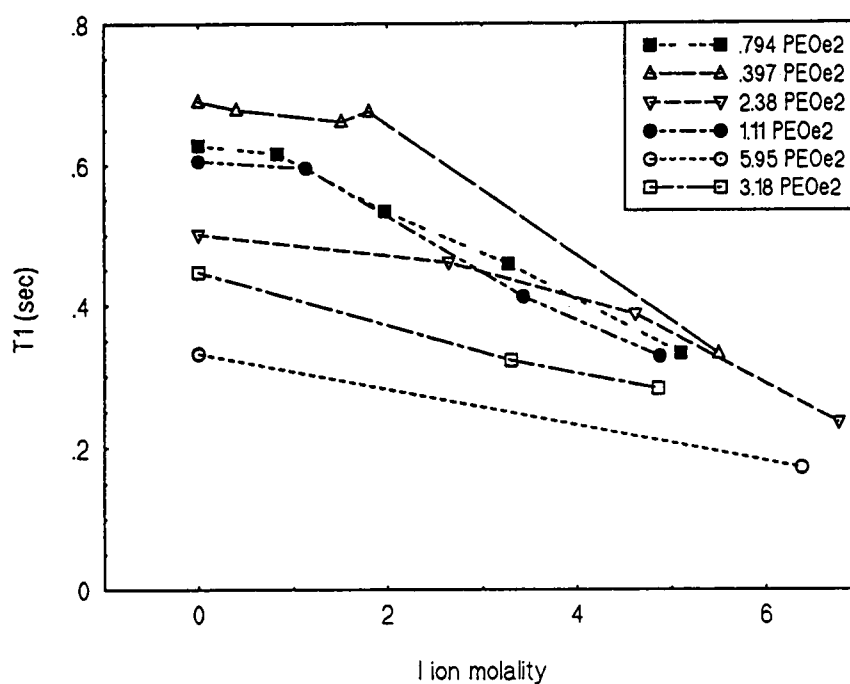
Figure 5.1. 250 MHz NMR T_1 values for PEO 12600 with respect to increasing I⁻ ion molality.

Table 5.2. 250 NMR T_1 values with Na:O ratios for NaCl

mPEOx10 ²	0:1	1:5.9	1:4	1:3	1:2.38	1:1.33	1:1	1:1.73	1:1.67	1:1.44
.183*	.6518	.7158		.7530			.6512		.5235	
.382**	.5790		.5735			.4130	.3805		.3395	
.397	.6646		.6769			.6406	.6685			.4127
.794	.6282		.6138			.5515	.4587	.4039		
1.11	.6057		.5802			.4867	.3870			
2.38	.5008		.4425		.3380					
3.18	.4470		.3952							
5.95	.3321									

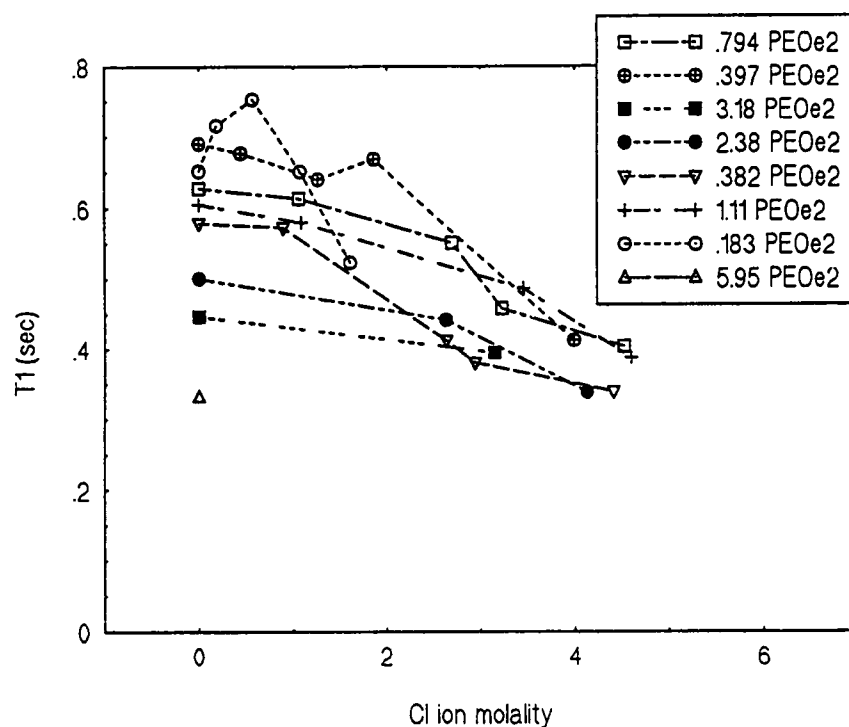
Figure 5.2. 250 MHz NMR T_1 values for PEO 12600 with respect to increasing Cl⁻ ion molality.

Table 5.3. 400 NMR T_1 values with Na:O ratios for NaI

mPEO $\times 10^2$	0:1	1:4	1:1.33	1:1	1:1.646	1:1.322
.397	.6220	.6389	.5711	.5616		.3215
.794	.6083	.5557	.4597	.4016	.3435	
1.11	.6033		.4024	.3729		

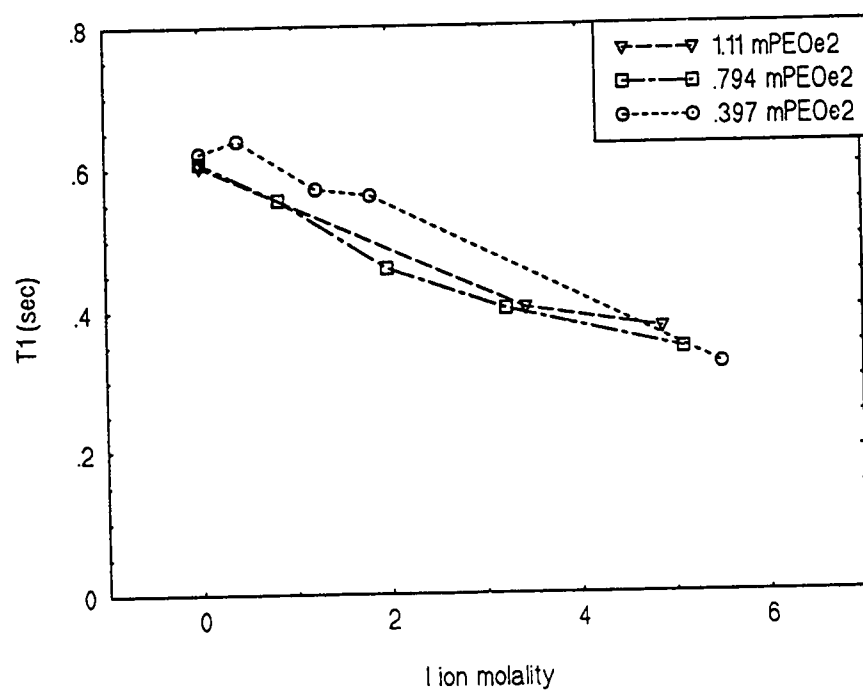
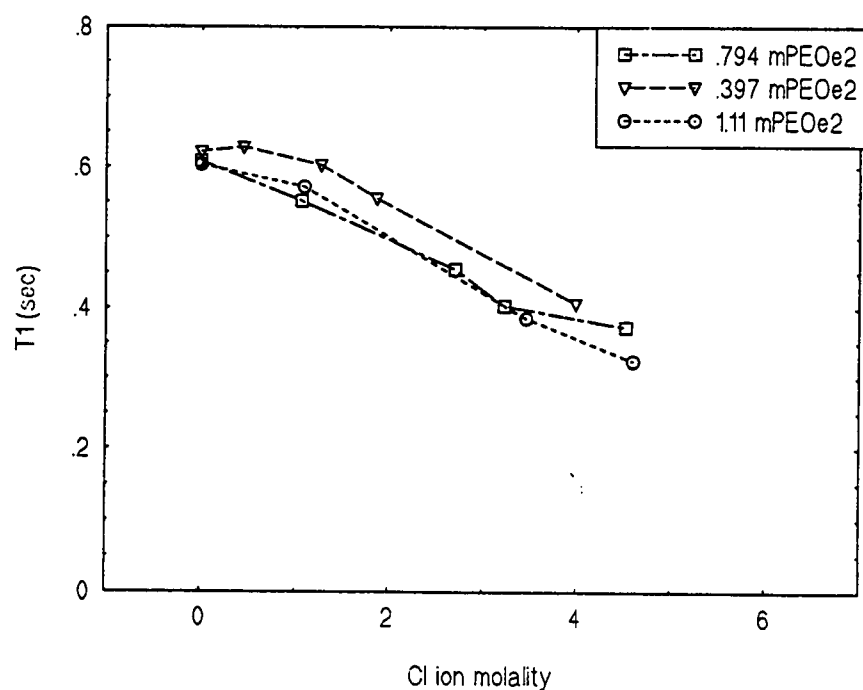
Figure 5.3. 400 MHz NMR T_1 values for PEO 12600 with respect to increasing I⁻ ion molality.

Table 5.4. 400 NMR T_1 values with Na:O ratios for NaCl

mPEO $\times 10^2$	0:1	1:4	1:1.33	1:1	1:1.730	1:1.436
.397	.6220	.6283	.6028	.5556		.4067
.794	.6083	.5512	.4550	.4034	.3731	
1.11	.6033	.5717	.3855	.3245		

Figure 5.4. 400 MHz NMR T_1 values for PEO 12600 with respect to increasing Cl^- ion molality.

concentration increases are much smaller than the differences found in the 250 NMR data (0.6646-0.6057 s in comparison to 0.6220-0.6033 s).

3. Bruker 250 MHz T_1 Data/2nd samples

There was a question of whether exposure to air would effect the T_1 value of the sample. Therefore, NMR spectra of samples prepared under N_2 were obtained and then these samples were exposed to air for over one week and reanalyzed. The results are summarized in Table 5.5. The data indicates that there is no significant difference in T_1 values due to exposure to air. Although there may be an effect at higher concentrations, in this case, there is insufficient evidence that an effect exists.

4. Small Molecule Analogues

The T_1 values for DGME at varying molalities and NaI concentrations are summarized in Table 5.6. The carbon numbers correspond to the labeling shown in Figure 5.5. The overall trend is still adhered to in this small molecule whereas T_1 values decrease with increasing ion and DGME concentration. The T_1 values for DGME are larger (as high as 3.9 s) with a broader range (3.9 to 0.4 s) than the PEO values (0.7 to 0.1 s) obtained.

The T_1 values for different molalities of PEO 200 at varying concentrations of NaI are summarized in Table 5.7. The carbon numbers correspond to the labeling shown in Figure 5.6. The cause of the multiple peaks (each labeled with prime numbers) is attributed to the different conformations found in PEO 200. The T_1 values for this small molecule

Table 5.5. 250 NMR T_1 values, Na:O ratios for NaI, N_2 samples (PEO 12,600)

mPEOx10 ²	0:1	1:1.33	1:1
.794 1.11	.6270 ± .01 .5981 ± .03	.6193 ± .02	.5364 ± .02
Air .794 1.11	.6288 ± .004 .4741 ± .03	.6014 ± .01	.5548 ± .0008

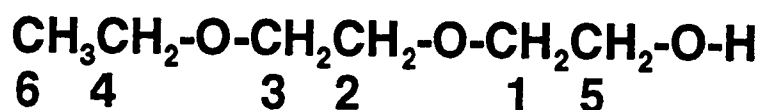


Figure 5.5 Carbon numbers for DGME.

Table 5.6. 250 NMR T_1 values, Na:O ratios for NaI, under N_2 , (DGME)

m eth	Na:O	C# 1	2	3	4	5	6
.378	0:1	2.68 ± .2	1.87 ± .02	2.14 ± .15	3.70 ± .47	2.21 ± .004	3.91 ± .87
7.5	0:1	1.21 ± .02	1.23 ± .08	.890 ± .17	2.67 ± .18	1.18 ± .04	3.70 ± .36
7.5	1:11	1.15 ± .02	.843 ± .16	.993 ± .03	2.24 ± .2	1.06 ± .13	3.16 ± .17
7.5	1:3.8	.956 ± .05	.627 ± .03	.852 ± .02	2.28 ± .06	.866 ± .04	2.39 ± .16
7.5	1:2	.511 ± .02	.462 ± .02	.401 ± .001	1.21 ± .01	.46 ± .001	2.19 ± .04

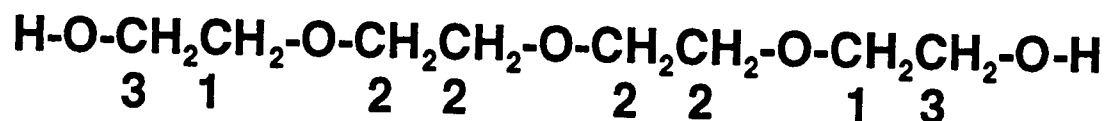


Figure 5.6. Carbon numbers for PEO 200.

Table 5.7. 250 NMR T_1 values, Na:O ratios for NaI, N_2 samples (PEO 200)

m PEO	Na:O	C# 1	1'	2	2'	2''	3
1.34	0:1	1.67 ± .016		1.02 ± .07	.72 ± .002	.89 ± .01	1.11 ± .06
4.7	0:1	.965 ± .07		.50 ± .05	.49 ± .02	.52 ± .08	.811 ± .02
4.7	1:9.5	.761 ± .04	.91 ± .08	.45 ± .05	.28 ± .01	.4 ± .01	.72 ± .03
4.7	1:6	.577 ± .1	.77 ± .13	.46 ± .06	.33 ± .02	.43 ± .04	.65 ± .05
4.7	1:5	.684 ± .05	.75 ± .05	.46 ± .02	.38 ± .07	.45 ± .08	.70 ± .02
4.7	1:2	.251 ± .017	.33 ± .02	.20 ± .007	.21 ± .01	.195 ± .02	.3 ± .004
20	0:1	.506 ± .006		.28 ± .004	.29 ± .01	.31 ± .002	.51 ± .003
20	1:40	.369 ± .001		.25 ± .001	.21 ± .001	.26 ± .03	.37 ± .002

analogue also decrease with increasing ion and PEO 200 concentration. The no salt T_1 values are also higher (1.7 s) than the large molecular weight PEO data obtained (0.6 s).

B. Molecular Analysis Data

1. Isotropic Model

The isotropic model results for DGME are summarized in Figures 5.7 and 5.8. In these figures one can distinguish the carbon pairs (4-6, 1-5, and 2-3) for the DGME samples. These carbon pairs have similar calculated tau values for this model, thus the carbon pairs indicate those carbons which react similarly to added salt. The attempted use of the isotropic model for PEO 200 is shown in Figures 5.9 and 5.10. These figures show the discontinuity of the model with the data set. Thus the motion in PEO 200 cannot be adequately described by the isotropic model. The isotropic model was also used to fit the PEO 12600 data, but it was found to be inadequate for interpretation of PEO motion.

2. Internal Libration Model

The internal libration model of Howarth was used to fit the DGME, PEO 200, and PEO 12600 T_1 data. This model has the following important parameters (relationships described in IV.B.3): X (maximum angle for libration), τ_G (librational motion), and τ_R (internal tumbling motion). The restrictions defined by the model were $X = 0.35$ rad (20°) and $\tau_G = 10$ ps.²² The internal libration model results are shown in figures 5.11, 5.12, and 5.13, respectively.

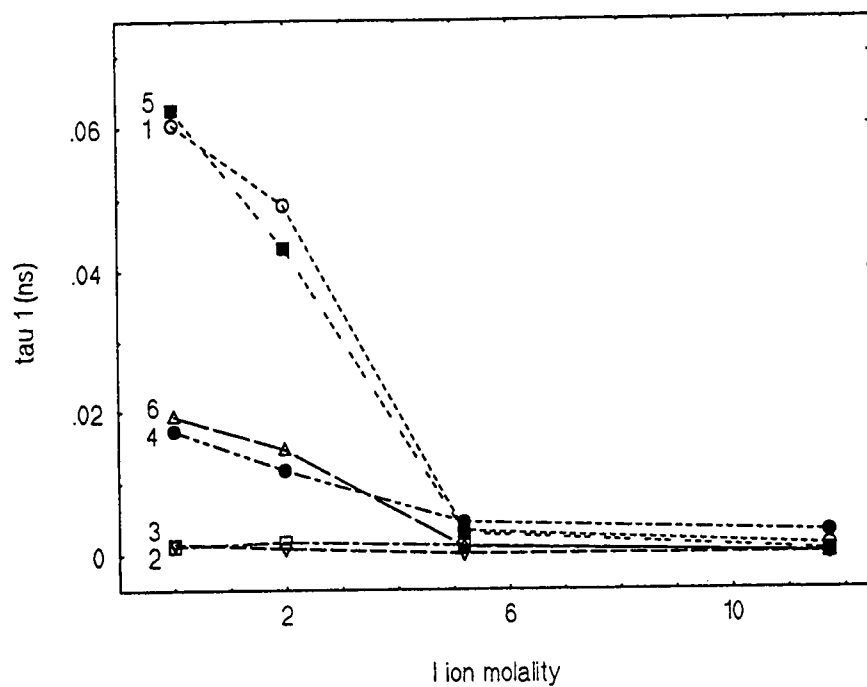


Figure 5.7. Isotropic Model DGME data for tau 1.

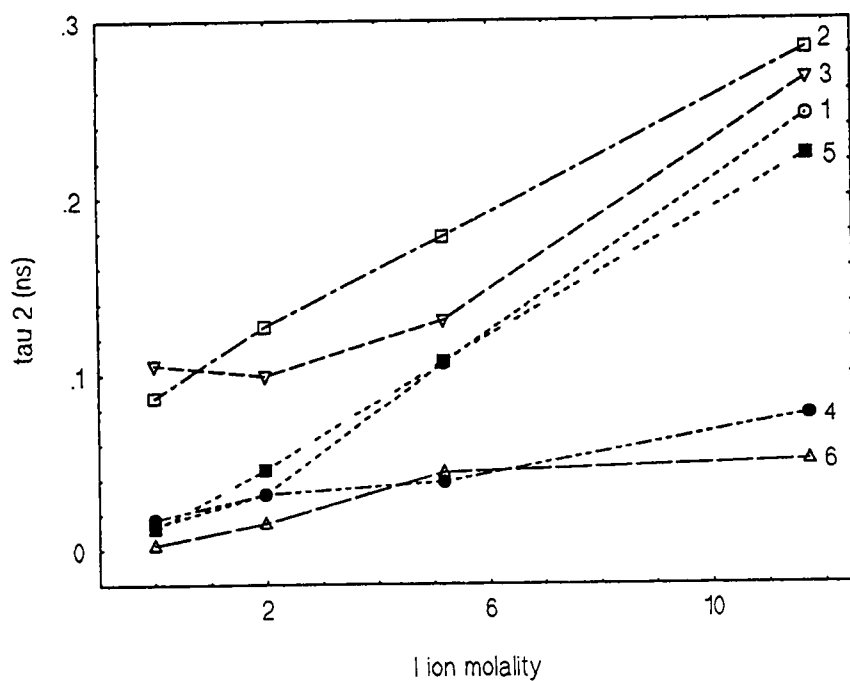


Figure 5.8. Isotropic Model DGME data for tau 2.

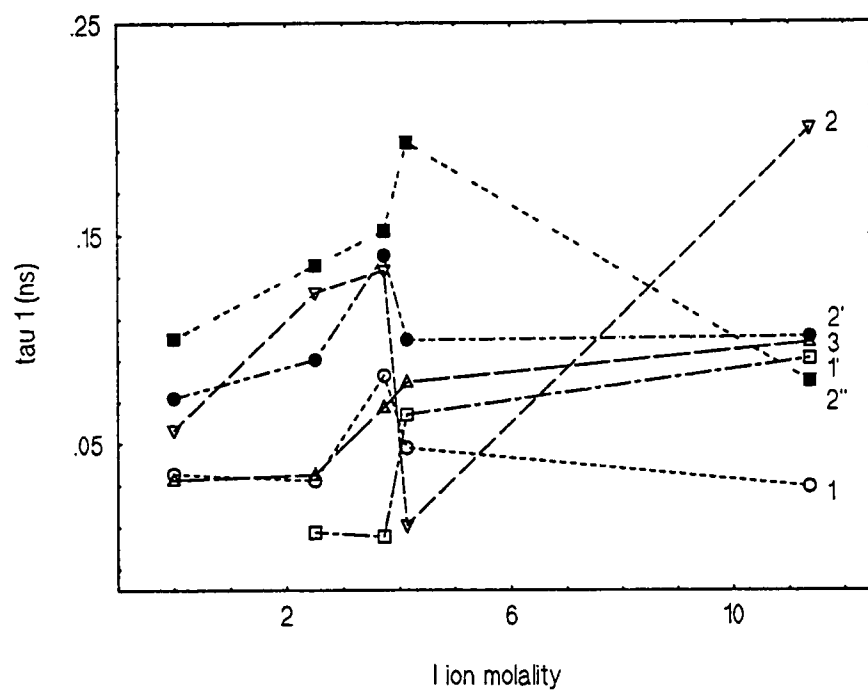


Figure 5.9. Isotropic Model PEO 200 data for tau 1.

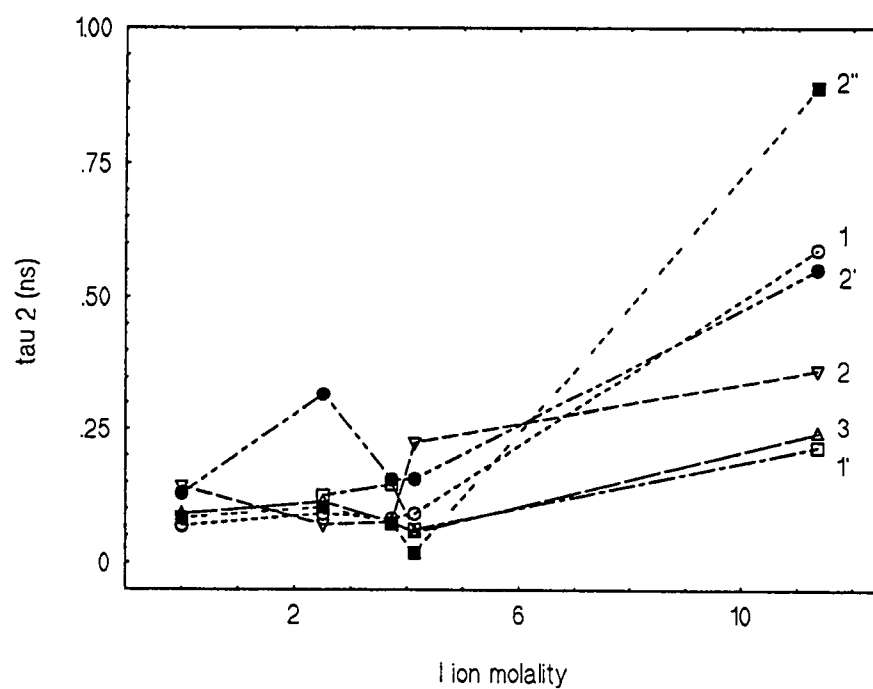


Figure 5.10. Isotropic Model PEO 200 data for tau 2.

The Howarth model shows a decrease in τ_R with an increase in ion concentration for the small molecule analogues. For PEO there is a decrease in τ_R with an increase in ion and polymer concentration.

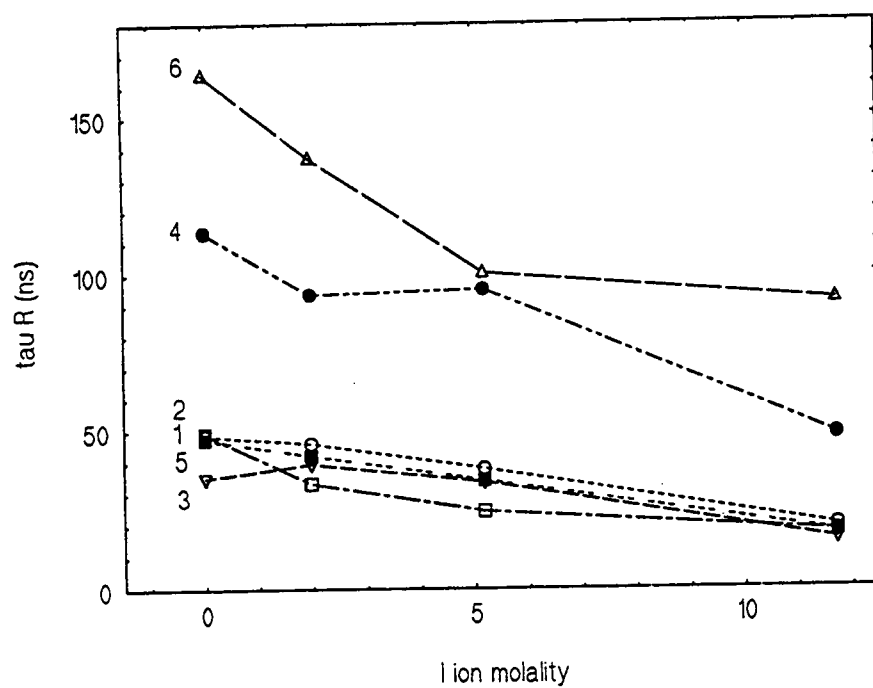


Figure 5.11. Libration Model DGME for τ_R .

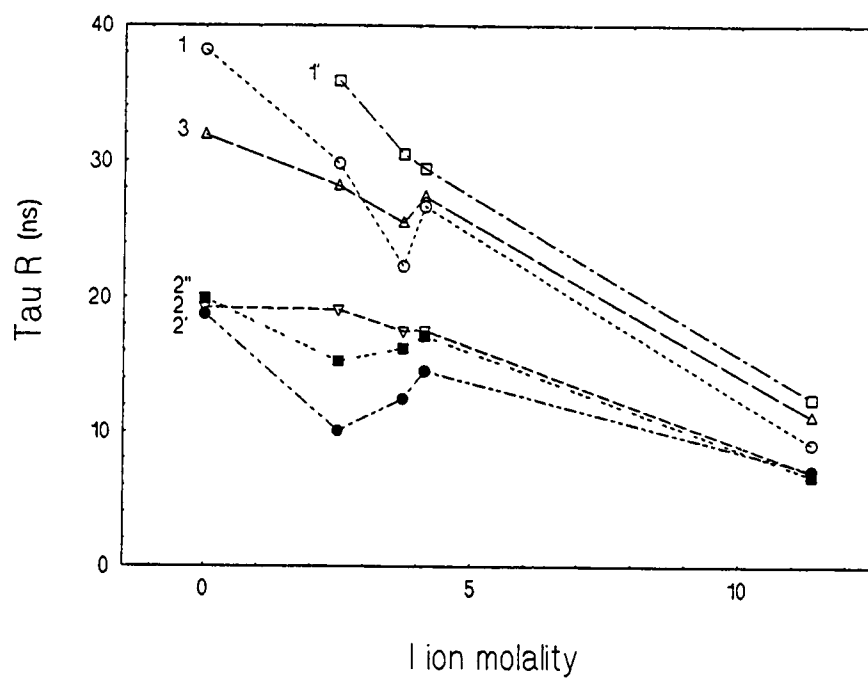


Figure 5.12. Libration Model PEO 200 for τ_R .

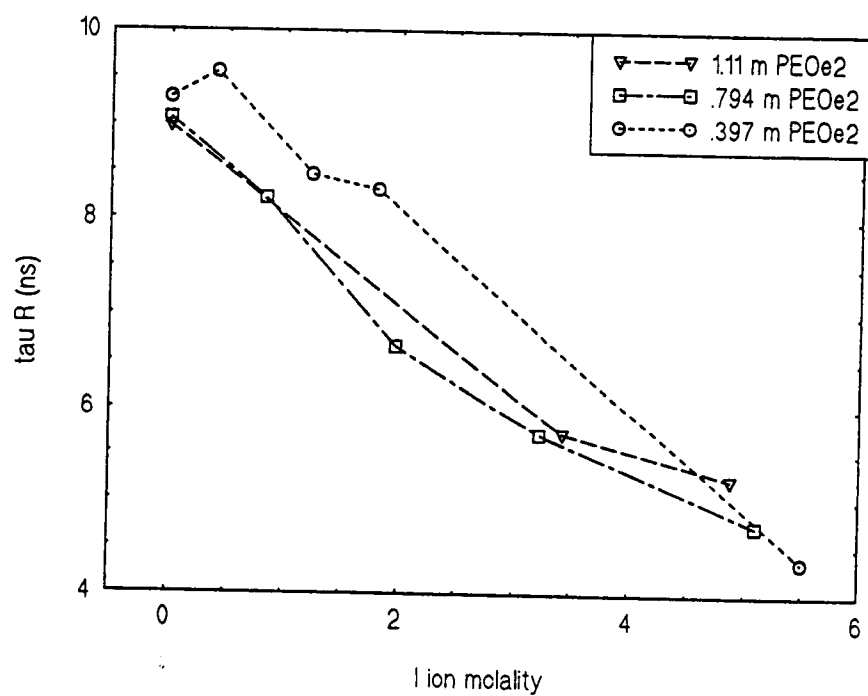


Figure 5.13. Libration Model PEO 12600 for τ_R using data from the 400 MHz NMR with NaI samples.

CHAPTER VI

DISCUSSION AND CONCLUSIONS

A. T_1 Data

1. NaI vs. NaCl

From Figures 5.1 and 5.2 the general tendency for T_1 values to decrease both with increasing polymer and ion concentration is evident. Yet there are distinct differences in the uniformity and extent of the decrease with respect to NaI versus NaCl. For NaI samples the salt has a more uniform and more significant effect on the T_1 values. In addition, the solubility of NaI is greater than NaCl so the data for NaI is extended to higher molalities. The difference in NaI and NaCl data is more evident from the data on the 250 MHz NMR than the 400 MHz NMR. This is because the effects are greater at higher concentrations of polymer and high polymer concentration experiments were not done on the 400 MHz NMR. Therefore there are insufficient results for concluding that the difference between I^- and Cl^- T_1 data would not be seen on the higher frequency spectrometer at higher polymer concentrations. The data obtained on the 250 MHz NMR suggest that the I^- ion in solution allows the Na^+ ion to interact to a greater extent with the polymer or small molecule analogue than the Cl^- ion. This could be explained by the enhanced stability of the I^- ion in solution because of its size. The I^- ion can stabilize the negative charge more easily than the Cl^- ion because the charge density of I^- is smaller. Therefore, the Cl^- makes more demands of its Na^+ partner for stability purposes

and inhibits the Na^+ from interacting with the PEO in solution. Although this is not a large effect, it is detectable.

2. 250 MHz NMR vs. 400 MHz NMR

From Figures 5.3 and 5.4, the effects of polymer and ion concentration are similar to each other. The values match very closely with the data obtained from the 250 MHz NMR so that having a different magnetic field did not show a significant difference in the T_1 values when taking into consideration the error associated with these values. Since high polymer concentrations were not done on the 400 MHz NMR we cannot establish whether there may be a difference in regions uninvestigated.

3. Small molecule analogues vs. PEO 12600

The T_1 value range of PEO 200 (1.7 - 0.2 s) and DGME (3.9 - 0.4 s) is greater in comparison to PEO 12600 (0.6 - 0.1 s). This indicates that the effect of ions in solution is larger for smaller molecules than PEO 12600. This is supported by the fact that the smaller molecules will have an enhanced dynamic interaction with the salt because of the shorter chain lengths and smaller solution viscosity.

B. Isotropic Model

1. DGME

From Figures 5.7 and 5.8, the relationship between carbon pairs is evident as was stated earlier. In Figure 5.7, τ_1 represents the correlation time of an overall isotropic motion. It is evident that the end carbon pairs (6-4

and 5-1) are effected by their overall motion significantly with increasing salt concentration. And in this case 5-1 is effected to a greater extent than 6-4. There is a definite interaction between salt and the end groups of DGME to alter the overall isotropic motion. In Figure 5.8, tau 2 represents an internal motion of the molecule that is not specifically defined. Yet from this figure it is noteworthy that carbon pair 2-3, which would most resemble the backbone carbons of PEO, is affected by salt in a more pronounced way than the other carbon pairs. Also the 1-5 carbon pair is more affected than the 6-4 carbon pair. This could be explained by the $\text{CH}_3\text{CH}_2\text{-O-}$ character of 6-4. This group will not coordinate with salt as much as the $\text{-O-CH}_2\text{-CH}_2\text{-O-H}$ character of 5-1.

2. PEO (200)

From Figure 5.9 it is difficult to extract any useful information. We therefore conclude that the isotropic model does not describe the overall motion well. Consequently, the overall motion of PEO 200 must be at a level of complexity greater than this model can interpret. From Figure 5.10 the tau 2 value increases with increasing salt concentration, yet this increase is not uniform and again does not fully describe the internal motions that are occurring. Therefore the internal motions that are occurring are more complex than this model can interpret.

C. Internal Libration Model

1. Restrictions

The restrictions defined by the model were that the maximum X value (angle of libration) is set at 0.35 rad (20°) and $\tau_G = 10$ ps (librational motion).²² τ_R was optimized using the experimental T_1 values.

2. DGME

From Figure 5.11 we again see a separation of carbon pairs. The 4-6 group has larger correlation times than the 2-3 or 5-1 pairs, and as a whole DGME has higher τ_R values than PEO 200 and PEO 12600. This would lead one to believe that the internal tumbling motion of the group 6-4 is more affected by salt concentration than the other groups in DGME. It also supports the trend that the effect of salt is greater in DGME than PEO 200 and PEO 12600.

3. PEO 200

From Figure 5.12 there is an influence of salt on the internal tumbling motion of the molecule. A more marked influence than is found in PEO 12600. One can picture that the short chain length in PEO 200 allows it to interact more freely with the ions in solution.

4. PEO 12600

Figure 5.13 indicates that there is an influence of salt on the internal tumbling motion of PEO segments, yet this influence is very slight in comparison to the small molecule analogue. One can envision the ions

interacting with the polymer, but only to a slight extent. For example, the ions may be interacting nonspecifically near a single polymer, or only between two polymers since the interaction does increase with polymer concentration.

D. Conclusions

1. From the Results

In this study we set out to experimentally investigate the influence of ions on the internal motion of polyethylene oxide and the proposed mechanism that occurs in solution between ions and the polymer chain. The results indicate that there is a definite influence of salt concentration on the motion of molecules in solution. This effect is stronger in solutions of DGME and PEO 200 when the chain lengths are smaller and the solution less viscous. For polyethylene oxide (12600) the effect of salt is notable, but less extravagant. The salt affects the internal tumbling motion (τ_R) of the polymer backbone as the internal librational motion is held constant with respect to a maximum angle X . This would suggest that there are temporary coordination bonds between Na^+ and PEO, but with a long chain in solution this interaction is possibly limited to the outer surfaces of a polymer sphere in solution, or between polymer spheres in solution. The internal polarity of the polymer molecule may be such that Na^+ ions are not drawn in freely about every part of the chain. Thus, the existence of ions in solution affects the internal polymer motion, therefore the mechanism of ion transport must include details of this motion.

2. Future Studies

The internal libration model by Howarth does not give us enough information to accurately define all the interactions of ions and polymers in solution. Therefore it would be advantageous to utilize a different model with or without further experimental data. Some further experiments might include looking at different types of salts, since there was a noticeable difference when using another anion. Other experimental data such as T_2 and NOE values could allow one to utilize a more definitive model. All of these avenues would further define the effects of ions on the internal motions of a polymers in solution.

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VITA

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