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UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

LOCAL STRUCTURES AND CONDUCTIVITY IN FOLYETHYLENIMINE AND POLYPHOSPHAZENE POLYMER ELECTROLYTES

A Dissertation

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

Doctor of Philosophy

By

Shawna Raye Starkey York

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LOCAL STRUCTURES AND CONDUCTIVITY IN POLYETHYLENIMINE AND POLYPHOSPHAZENE POLYMER ELECTROLYTES

A Dissertation APPROVED FOR THE DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

BY



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TABLE OF CONTENTS

Acknowledgements		iv
Abstract	••••	vii
Preface	••••••	ix
1. Introduction	••••	1
1.0 Research Objectivtes		1
1.1 Polymer Electrolytes	••••	2
1.2 PEO	••••••	3
1.3 LPEI	••••	5
1.4 Polyphosphazenes		9
1.5 Theories of Ionic Conductivity		11
1.6 Measurements of Ionic Conductivity	••••	14
1.7 Ionic Association	••••	14
2. Experimental	••••	16
2.1 Materials	••••	18
2.2 Sample Preparation	••••	19
2.3 Instrumental	••••	21
3. Results	••••	24
3.1 DMEDA and LPEI	••••••	24
3.2 Polyphosphazenes	••••	42
4. Concluding Remarks	•••••	53
References	••••	55
Appendix A: Included Papers		
Paper I	••••	60
Paper II	•••••••••	66
Paper III	••••	72
Paper IV	••••	83
Paper V		112
Appendix B: Papers not included	•••••	124

ABSTRACT

Polymer electrolytes are ionic conductors which consist of a salt dissolved in a polymer host. The potential importance of polymer electrolytes in applications such as rechargeable lithium batteries has stimulated intense interest in these systems. Extensive fundamental investigations into the nature of ionic conductivity in these systems have previously been done on poly(ethylene oxide) with dissolved lithium triflate, LiCF₃SO₃. These investigations are now complemented by considering related polymer-salt systems. This dissertation investigates two such systems.

Linear polyethylenimine (LPEI) is structurally analogous to poly(ethylene oxide), with an N-H group in place of the ether oxygen. LPEI systems with dissolved lithium and sodium triflate were prepared and characterized via Raman and FT-IR vibrational spectroscopy, differential scanning calorimetry, and complex impedance. The understanding of local interactions in the LPEI-salt systems is enhanced by consideration of a small-molecule model of LPEI, N-N' – dimethylethlenediamine (DMEDA). Vibrational spectroscopy of DMEDAlithium salt systems was used to elucidate ion-ion interactions and the interaction of the solvent with the salt. Mode assignments were made in the DMEDA system. It was shown that the vibrational modes from 700 to 900 cm⁻¹, which are a mixture of CH₂ rock and NH bend, are sensitive to interaction with the lithium cation. It was found from the frequency shifts in the NH stretching region that LPEI is more extensively hydrogen bonded than DMEDA and that in both systems hydrogen bonding is decreased when LiTf is added. It was also found that the vibrational modes of the triflate anion are influenced by solvent interactions in the LPEI and DMEDA systems, probably via a hydrogen bonding interaction.

Poly(bis-methoxyethoxyethoxyphosphazene), MEEP, has the same coordinative moiety (CH₂CH₂O) as is found in the poly(ethyleneoxide) system, but attached to a flexible phosphazene backbone. A spectroscopic comparison of MEEP and three other phosphazenes with ethoxy sidechains of different lengths shows that the dissolved lithium cation coordinates primarily to the ether oxygens in these systems. A comparison of ionic speciation to the concentration-dependant condicutivity in the MEEP-lithium triflate system has led to the proposal of a mechanism of ionic conductivity involving associated ionic species via dissociation and rapid reassociation.

PREFACE

This thesis consists of this summary and work from the following publications which are included in Appendix I. These publications are referred to in the text by their Roman numerals.

- I. A Comparative Vibrational Spectroscopic Study of Lithium Triflate and Sodium Triflate in Linear Poly(ethylenimine), S. York, R. Frech, A. Snow, and D.T. Glatzhofer, *Electrochimica*. Acta 46, (10-11), 1533-1537 (2001).
- II. A Vibrational Spectroscopic Study of Lithium Triflate in Polyphosphazenes with Linear Oligoethyleneoxy Side Chains of Different Lengths, S. York, E.C. Kellam III, H.R. Allcock, and R. Frech, *Electrochimica Acta* 46, 1553-1557 (2001).
- III. An Experimental and Computational Investigation of the Structure and Vibrations of Dimethylethylenediamine, a Model for Poly(ethylenimine), S. E. Boesch, S.S. York, R. Frech, and R.A. Wheeler, *PhysChemComm*(1), (2001).
- IV. The Effect of Lithium Triflate and Lithium Bromide on the Vibrational Frequencies of DMEDA, Shawna S. York, Scott E. Boesch, Ralph A. Wheeler*, and Roger Frech*, to be submitted
- V. Ionic Transport in Polymer Electrolytes: The Essential Role of Associated Ionic Species, R. Frech, S. York, E.C. Kellam III, and HR Allcock, to be submitted.

CH 1. INTRODUCTION

1.0 RESEARCH OBJECTIVE

Extensive studies have been done to develop a molecular level understanding of the factors controlling ionic conductivity in poly(ethylene oxide)-salt systems [1-11]. My research objective is to gain further insight into the nature of cation-anion and ion-polymer interactions in polymer electrolyte systems by considering two systems that are related to PEO. The first system, linear poly(ethylenimine), or PEI, {CH₂CH₂NH₁, is structurally analogous to PEO, with an N-H group in place of the oxygen. The second system, polyphosphazenes with linear oligoethyleneoxy side chains, have the same coordinative moiety (CH_2CH_2O) as is found in PEO, but attached to a polyphosphazene backbone. This study characterizes systems of these polymers with dissolved salts using vibrational spectroscopy, differential scanning calorimetry, and complex impedance measurements. The understanding of LPEI and polyphosphazene systems has also been aided by comparison to model systems of dimethylethylenediamine and diglyme.

I

1.1 POLYMER ELECTROLYTES

Polymer electrolytes are ionic conductors consisting of a salt dissolved in a polymer host. Interest in polymer electrolytes started with the investigations of alkali metal salts dissolved in polyethylene oxide, PEO, by Fenton, Parker, and Wright [12] in 1973 and was expanded by Wright [13] and Armand [14, 15] in the late 1970's.

The most common method of producing solid polymer electrolytes is to dissolve the polymer and salt in a common solvent, such as acetonitrile or methanol, followed by removal of the solvent. The dissolution of the salt into the polymer is thermodynamically favorable only if the change in Gibbs free energy upon solvation of the salt by the polymer is negative. The Gibbs free energy, ΔG , is given by

$$\Delta G = \Delta H - T \Delta S \qquad \qquad Eq. 1.1$$

where ΔH is the change in enthalpy and ΔS is the change in entropy. The change in the entropy has a positive contribution from the disordering of the ions from the crystalline lattice and a negative contribution from stiffening of the polymer chain due to the formation of cation-polymer bonds. The change in enthalpy is primarily affected by the lattice energy of the salt and the solvation of the salt by the polymer chains [16]. Therefore, salts with low lattice energies must be used in order for the salt to dissolve in the polymer host. Most salts used in polymer electrolytes have alkali-metal cations. The most thoroughly investigated cation is Li⁺ due to its potential use in batteries with intercalation cathodes, although Na⁺, NH₄⁺ and several divalent cations, such as Ca⁺², Mg⁺², and Zn⁺², have been studied [2, 4, 17-20]. Anions which are favorable for the formation of polymer electrolytes have large ionic radii, such as I^- , CF₃SO₃⁻, [(CF₃SO₃)₂N]⁻, and ClO₄⁻ [11, 21-25]. In order to coordinate the cation, the polymer host must have a high concentration of polar (Lewis base) groups. The polymer host should also have a low glass transition temperature Tg, and therefore a high chain flexibility, to enable the local polymer segments to rearrange to accommodate the cation. [15, 26-29]

Most polymer electrolytes hosts are based on oxygen-containing monomers, although nitrogen and sulfur-based systems have also been used. The polymer host which has been most extensively studied is poly(ethylene oxide), PEO.

1.2 PEO

Poly(ethylene oxide), PEO, readily dissolves a variety of metal salts to form ionically-conducting systems that can be used as electrolytes. PEO-based electrolytes have attracted much widespread fundamental and technological interest. Attempts to increase the ionic conductivity of such systems have led to numerous studies focused on developing a molecular level understanding of the factors controlling the ionic conductivity.

PEO is semi-crystalline, with about 60% crystallinity in the bulk at room temperature. PEO-salt complexes may consist of a heterogeneous mixture of phases at a given salt composition and temperature. There may be pure crystalline PEO, crystalline PEO-salt complex, and salt dissolved in amorphous PEO [8, 30, 31]. Ion transport has been shown to occur primarily in the amorphous phase of PEO-salt systems [17, 18]. Numerous studies have been done to investigate ion-polymer and ion-ion interactions in PEO-salt systems, in particular PEO with dissolved triflate salts [2, 3, 8-11, 21, 30-37]. The vibrational modes of the triflate ion, Tf, (CF₃SO₃.) are very sensitive to the local environment, and "free" ions, ion pairs, and more associated ionic species have been shown to have distinguishable spectroscopic signatures [4, 5, 8-11, 23, 31, 38-48].

Small molecule oligomers of PEO have been used to model PEO systems. These oligomers are called glymes, short for glycol dimethyl ethers [49-55]. Several theoretical and experimental studies have been done on glyme-salt systems in order to understand the interactions in these materials. *Ab initio* calculations and vibrational spectroscopic studies have yielded information on spectra-structure correlations, local coordination geometries, changes in conformation upon salt complexation, and ionic association in glyme-salt systems [5, 7, 10, 19, 25, 31, 35, 56-63].

1.3 LPEI

Fundamental investigations into the nature of polymer electrolytes are complemented by considering polymers other than PEO. A polymer analogous to PEO is linear poly(ethylenimine) or LPEI, $-[CH_2CH_2NH]_n$ -, which has an NH group in place of the oxygen atom.

The commercially available form of poly(ethylenimine) is highly branched and completely amorphous. Linear poly(ethylenimine), LPEI, was first prepared from 2-oxazoline by Saegusa et al.[64] in 1972 and was shown to be highly crystalline. That synthesis produced LPEI of approximately 2000 molecular weight, and a later synthesis by Tanaka, et al.[65] produced a higher molecular weight LPEI (~10⁵ MW). The melting temperature of LPEI is ~60 °C [64, 66].

The crystal structure of anhydrous LPEI is shown in Figure 1.1 [67]. The anhydrous LPEI crystal contains double-stranded helices, with each chain forming a 5/1 helix. There is extensive interchain hydrogen bonding between the two helices, as indicated in Figure 1.1, with each nitrogen atom hydrogen-bonded to an N-H group on the other strand.

Chatani, et al. attribute the formation of the double-stranded helices to the N-H...N hydrogen bonds [67].



Figure 1.1. Double-stranded helical chains of LPEI viewed in three directions. Dashed lines indicate N-H^{...}N hydrogen bonds (ref 67)

Crystal structures for several hydrates of LPEI [68, 69] have been reported by Chatani, et al. In the dihydrate, hemihydrate, and sesquihydrate, the LPEI strands are no longer double -stranded helices, but extended planar zigzags. Also, there are no N-H...N hydrogen bonds in these hydrates, but instead each nitrogen atom is coordinated by two water molecules [69]. The melting temperature of each of these three hydrates is approximately 80 °C. Chatani et al. have also found crystal structures for an LPEI-hydrogen chloride 1:1 complex[66] and an LPEIacetic acid 1:1 complex [70]. As in the hydrates, the LPEI chains in these two complexes are in a planar zigzag conformation. In the LPEI-HCl complex, there is N-H.-Cl hydrogen bonding[66] and in the LPEI-CH₃COOH complex there is both N-H...O and O-H...N hydrogen bonding. The melting temperature of the LPEI-HCl complex is 265 °C [66] and the melting temperature of the LPEI-acetic acid complex is ~135 °C [70]. The lower melting temperature of the anhydrous LPEI compared to the LPEI hydrates and the two complexes is ascribed to the relative weakness of N-H --- N hydrogen bonds [66].

Several studies have been made of low MW LPEI with dissolved salts to form polymer electrolytes. Ab initio calculations have been performed on low molecular weight LPEI oligomers to find the bonding energies in LPEI [61, 71] and to model LPEI-lithium ion interactions [61].

Chiang et al. have made complexes of low molecular weight (2000 MW) LPEI with NaI,[72] LiBr, LiI, LiSCN, LiClO₄, and LiBF₄ [73]. The LPEI-NaI system forms a 3:1 crystalline complex which melts at 150 °C[72]. The LPEI-NaI system exhibits a conductivity of 1.5 x 10⁻⁶ S/cm at 60 °C with 0.1 mole percent NaI.

There have also been studies on high molecular weight (~100,000 MW) LPEI-based polymer electrolytes. Harris, Shriver, and Ratner studied LPEI-sodium triflate complexes [22]. They reported the formation of a crystalline complex of 4:1 LPEI:NaTf stoichiometry, which has a melting temperature of ~160 °C. The LPEI-NaTf system exhibits conductivities of 5.6×10^{-8} for the 4:1 complex at 41 °C and 3.1×10^{-7} for a 5:1 composition at 41 °C. [22] Tanaka, et al. have measured the conductivity of LPEI complexed with LiClO₄ and LiTf [74]. The highest conductivity value reported was 2×10^{-6} S cm⁻¹ at 60 °C for LPEI-LiTf at a 15:1 N:Li composition [74].

Attempts have been made to reduce the crystallinity of PEI systems by using branched PEI [75, 76] or by modifying the linear PEI by alkylating the imine groups. [65, 74, 77, 78] Branched PEI is completely amorphous and has primary, secondary, and tertiary amines [76]. Complexes of branched PEI with LiTf and NaTf are reported to have a

maximum conductivity at 60°C on the order of 10⁻⁶ S/cm at an N:M composition of 20:1 for either cation [75, 76]. Tanaka et al. report a conductivity maximum for poly(methyl ethylenimine):LiTf at a 6:1 N:Li composition[74].

1.4 POLYPHOSPHAZENES

The conductivities of PEO-salt systems are limited by their high degree of crystallinity. In polymer-salt systems the amorphous phase appears to be the primary conductivity pathway [17, 18]. Therefore, the conductivity is greatest in polymer electrolytes that are highly disordered or amorphous in nature. Synthetic strategies to enhance conductivity emphasize the preparation of single-phase polymers that are intrinsically amorphous. Polyphosphazenes have been extensively studied as polymer electrolyte hosts due to their amorphous nature and the ability to substitute a wide variety of sidegroups onto the phosphazene backbone [79]. Polyphosphazenes have the general formula {NPR₂}_n.

Poly(bis-methoxyethoxyethoxysyphosphazene) (MEEP) was synthesized in 1965 by Allcock and Kugel [80] and first studied as a polymer electrolyte by Blonsky, Shriver, Austin, and Allcock [83]. MEEP forms completely amorphous complexes with many salts, including triflate salts of lithium, sodium, silver, and zinc [81]. There have been numerous

studies of the conductivity and thermal characteristics of polymer electrolytes based on MEEP [79, 81-86]. MEEP with dissolved LiTf is amorphous over a temperature range of -100 to 100 °C [87]. The maximum room-temperature conductivity of the MEEP-LiTf system is 2.7 x 10⁻⁵ S/cm at a monomer:Li ratio of 4:1 [81]. The chief disadvantage of MEEP as a polymer electrolyte host is its tendency to flow under pressure [85, 88].

Other polymers based on the phosphazene backbone have been studied to determine the effect of different sidechains on ionic conductivity and physical properties of polyphosphazenes and polyphosphazene-salt systems [79, 82, 87-94]. These different sidechains include alkyl groups. aromatic rings, ethyleneoxy groups, sulfur-containing groups, and mixed of polyphosphazenes substituents. In studv with а mixed methoxyethoxyethoxy and alkyl side groups with dissolved lithium triflate, it was found that as the length of the alkyl side group increased, the conductivity decreased and that the mixed-substituent polyphosphazenes had lower conductivities than polyphosphazenes with only ethyleneoxy sidegroups [89, 90]. In a system of lithium triflate dissolved in polyphosphazenes bearing only ethyleneoxy sidechains, the optimum conductivity increased as the side chain length increased up to seven ethoxy units for linear ethoxy sidechains [87, 91]. Additionally,

polyphosphazene systems with branched ethoxy sidechains showed comparable ionic conductivities and higher stability at room temperature [87].

1.5 THEORIES OF IONIC CONDUCTIVITY

Ionic conductivity in a dilute system can be expressed as

$$\sigma = \sum n_i q_i \mu_i$$
 Eq. 1.2

where n_i is the concentration of charge carriers, q_i is their charge, and μ_i is their mobility, summed over *i* species. All charged species contribute, including single cations, single anions, and charged aggregates.

Ionic conductivity in polymer electrolytes is complex and for a thorough description the reader is referred to the treatments of Bruce and Ratner [16, 29]. Polymer segmental motions, polymer-ion interactions, and ion-ion interactions are all important in understanding the mechanism of ionic conductivity in polymer electrolytes. Therefore, at low salt concentrations, carrier numbers increase as salt is added, and σ increases. At the high ion concentration found in most polymer electrolytes, ionic association will strongly influence conductivity, as Coulombic attraction between ions acts to reduce the effective number of charge carriers [29]. At high salt concentrations, σ will therefore decrease with increasing salt concentration [83]. Segmental motions of the polymer

host contribute to the mobility of the ions. [29] Therefore, below Tg ionic conductivity drops to very small values. Above Tg a polymer is rubbery rather than glassy, and the local environment around a given polymer chain becomes liquid-like.

The temperature dependence of ionic conductivity is of interest. If a plot of log σ vs. 1/T yields a straight line, the behavior can be fit to the Arrhenius equation

$$\sigma(T) = \sigma_0 e^{-Ea/kT}$$
 Eq. 1.3

where σ is the conductivity at temperature T, σ_0 is a constant, and E_a is the activation energy. On an Arrhenius plot, an abrupt change in slope can generally be traced to a phase change [15, 29]. In the 4:1 LPEI-NaTf system, the conductivity data can be fit to an Arrhenius equation in two regions, above and below 65 °C [22], and in LPEI-LiClO₄ and LPEI-LiBF₄, the conductivity as a function of temperature was reported to exhibit an abrupt change in slope around 50 °C [73].

Frequently in polymer electrolyte systems, plots of log σ vs. 1/T yield curved lines instead of straight lines. These may be described by the VTF equation [15, 16, 95]

$$\sigma(T) = \sigma_0 e^{-B/(T \cdot T_0)} \qquad \qquad \text{Eq } 1.4$$

In the VTF equation, the preexponential factor σ_0 may contain a T or T^{1/2} factor, T₀ is the reference temperature, frequently taken to be Tg – 50K,

and B is a constant whose dimensions are energy but which is not to be interpreted as an activation energy term. Many polymer electrolytes have temperature-dependent behavior that can be fit to the VTF equation, including branched and linear PEI-based systems[73, 76]. The VTF equation is consistent with the idea that thermal motion contributes to transport processes and that faster segmental motion occurs for low Tg. The VTF description has no direct relationship to the mobility of the charged species, except insofar as the ion transport is coordinated to polymer segmental motion.

The VTF equation is an empirical generalization rather than the result of a theoretical approach. However, several theoretical approaches have been developed and applied to describe conductivity in polymer electrolytes. Free volume theory is consistent with VTF behavior. The free volume model[96] is the simplest way to understand polymer segmental mobility. As temperature increases, the segmental motion of the polymer backbone produces local empty space, or free volume, into which ions, solvated molecules, or polymer segments can move. The overall mobility of the material is therefore determined by the amount of free volume present in the material.

The VTF and free volume models do not give a microscopic description of ionic transport. The dynamic bond percolation model, DBP,

is a microscopic model that characterizes ionic motions in terms of jumps between neighboring positions. A detailed treatment of this theory, developed by Druger, Nitzan, and Ratner, is presented elsewhere [28, 29, 97, 98]. In DBP model, ions hop from site to site. The ion may only hop to a nearest-neighbor site. The tranport of ions in this picture occurs via the breaking and making of cation-ether oxygen bonds. For polymer electrolytes above Tg, segmental motions change the local coordination environment of the ion with a characteristic renewal timescale t_{ren} . Specifically, a jump to a site which is unavailable because the chains are improperly arranged at a time t can become available, due to chain reorientation, at a time t + t_{ren} . The DBP model has been successfully applied to a few polymer electrolyte systems[28, 29, 97]

1.6 MEASUREMENTS OF IONIC CONDUCTIVITY

The specific conductivity σ of a sample measured in a conductivity cell can be found using the bulk resistance of the sample, R_b and the geometric factor

$$\sigma = d/R_bA$$
 Eq 1.5

where d is the separation of the electrodes and A is their area. Alternating current methods are the most commonly used for determining bulk ionic conductivity in polymer electrolytes[99]. Measurements are made with

the electrolyte sandwiched between a pair of electrochemically inert electrodes, typically stainless steel. A sinusoidal potential is applied and the magnitude and the phase shift of the current I is measured. This measurement is repeated at a series of frequencies that range from 10⁻⁴ Hz to as high as 10 MHz. From these data, it is possible to extract the resistance of the bulk electrolyte sample.

The following analysis of complex impedance data to obtain bulk conductivity Cole[100] was proposed by and developed bv MacDonald[101]. The ac impedance, $Z^*=E^*/I^*$, where I^* is the current and E* is the ac potential, can be expressed as a real and imaginary part, $Z^*=Z' + iZ''$. In an impedance spectrum, the imaginary part (-Z'') of the impedance is plotted against the real part (Z') for data collected at a series of frequencies. The bulk resistance of the electrolyte can be derived from such a plot, as shown in Figure 1.2. The conductivity can then be calculated using equation 1.5.



The combination of a resistor and capacitor in parallel produces a semicircle in the complex plane. In an ideal system with perfectly blocking electrodes, the impedance spectrum would consist of a perfect semicircle with a vertical spike. The actual data obtained from ac impedance measurements typically consists of a flattened semicircle and a spike at an angle.

1.7 IONIC ASSOCIATION

The nature of the ionic species present in a polymer electrolyte is an important aspect of the microscopic structure of the system. Ionic species have generally been classified as "free" ions, contact ion pairs, and aggregates. The "free" ions are solvent-separated ion pairs. The aggregates are species more highly associated than ion pairs and may be charged, e.g. M_2X^+ or MX_2^- . The existence of these different species can be inferred spectroscopically by observing shifts or splittings in the vibrational bands of a polyatomic ion. Observed vibrational bands have been assigned to specific ionic species by comparison of spectra of triflate salts in different solvents[48] and by quantum-mechanical calculations[38, 39].

CH 2. EXPERIMENTAL

2.1 MATERIALS

Linear poly(ethylenimine), LPEI, was synthesized by Albert Snow at the University of Oklahoma. LPEI is structurally analogous to PEO, having the formula $\{CH_2CH_2NH\}_{n.}$ The LPEI was synthesized by acid hydrolysis of ~200,000 MW poly(oxazoline), yielding approximately 80,000 MW LPEI. The LPEI was dried under vacuum for 2 days at ~50°C (below the melting point of ~60°C), then dried an additional day under vacuum at 70°C (above the melt). The absence of water in the dried LPEI was confirmed by DSC. The anhydrous LPEI is a very hard, slightly yellow solid.

Phosphazene polymers with linear ethoxy side chains were synthesized by E. Clay Kellam, III at Penn State University. Four polymers were utilized, of the form

$$(OCH_2CH_2)_{x}OCH_3$$

 $\{N=P\}_n$
 $(OCH_2CH_2)_{x}OCH_3$

where x = 0,1,2, or 5. The x= 1,2, and 5 polymers were dried under vacuum at ~45 °C for 24 hours. The x=0 polymer was dried under vacuum at 35 °C for 24 hours. The absence of water in the dried polyphosphazenes

was confirmed by IR. The x=1,2, and 5 polyphosphazenes are dark brown, very sticky solids that flow easily. The x=0 polyphosphazene is a viscous, sticky white solid.

N,N'-dimethylethlenediamine, DMEDA, 99%, was used as received from Aldrich. DMEDA is a small-molecule analogue of LPEI, having the formula $CH_3NHCH_2CH_2NHCH_3$. DMEDA is a liquid at room temperature.

Lithium triflate (LiTf), lithium bromide (LiBr), and tetra-nbutylammonium triflate (TbaTf) were obtained from Aldrich. Sodium triflate (NaTf) was obtained from Fluka. All salts were dried under vacuum at ~120 °C for 24 hours.

Methanol (99.9%, anhydrous) from Aldrich was triple-distilled and stored over molecular sieves. Tetrahydrofuran (THF) from Aldrich was stored over molecular sieves.

All polymers, salts and solvents were stored in a dry nitrogenatmosphere glovebox with <1ppm water to ensure no water contamination. The absence of water in all materials except methanol was confirmed by the absence of O-H stretching peaks in the FT-IR spectra.

2.2 SAMPLE PREPARATION

All polymer-salt films were prepared by a solvent-casting method. The thickness of the films was controlled by adjusting the composition of the polymer-salt-solvent solutions, with the weight percent of (polymer + salt) in the solvent varying from $\sim 10 - 20\%$.

Stoichiometric amounts of LPEI and LiTf or NaTf were dissolved in methanol and allowed to stir overnight. Thin films were then cast onto Teflon® sheets, glass microscope slides, or salt plates and the methanol was allowed to evaporate at room temperature inside the glovebox for 24-48 hours. The resultant films were dried under vacuum for 24 hours at ~70°C. The composition of the LPEI-salt samples is expressed as a nitrogen:cation (N:M) ratio.

The polyphosphazene:LiTf films were prepared by dissolving stoichiometric amounts of the polyphosphazene and LiTf in THF. These solutions were allowed to stir overnight, then cast onto Teflon sheets, glass microscope slides, or salt plates and the THF allowed to evaporate at room temperature inside the glovebox for 48 hours. The resultant films were dried under vacuum for 48 hours at 35°C. The composition of the polyphosphazene-LiTf samples is expressed either as an ether oxygen:lithium ratio, or as a P:Li (i.e., monomer to cation) ratio.

To prepare the DMEDA:LiTf, DMEDA:LiBr and DMEDA:TbaTf samples, stoichiometric amounts of DMEDA and salt were mixed and allowed to stir at least overnight in the glovebox at room temperature. The concentration of the DMEDA:salt samples is expressed in a

DMEDA:cation ratio, e.g., a 10:1 sample would have 10 moles of DMEDA to 1 mole of salt, or a 20:1 N:M ratio.

2.3 INSTRUMENTAL

2.3.1 Vibrational spectroscopy

Raman spectra of all samples were recorded on an ISA Jobin-Yvon T64000 Ultimate Raman Spectrometer with CCD detector. All spectra were taken in the triple subtractive mode using an 8-16 s acquisition time and 5-20 accumulations. The 514 nm line of an argon laser was used as the exciting line. The laser power was 300 mW at the laser head and approximately 50mW at the sample. Spectra of polymer films were collected under a microscope with an 80x objective lens in a backscattering geometry. Polymer films for Raman spectroscopy were cast directly onto glass microscope slides. Spectra of liquids (DMEDA and DMEDA-salt samples) were collected in a 90° scattering geometry. Liquid Raman samples were placed in quartz cuvettes.

IR spectra were recorded using a Bruker IFS66V FT-IR in the range 500-4000 cm⁻¹ at a resolution of 1.0 cm⁻¹. Spectra of polymer films were obtained using AgBr, ZnSe, or NaCl salt plates, or as freestanding films in an evacuated sample chamber. Spectra of liquid samples were taken using ZnSe or NaCl salt plates under dry-air purge. Curve fitting analysis of IR and Raman spectra was accomplished using a commercial program (Galactic Grams ® version 5.05). Spectra were curve-fit to a straight base line and either a Gaussian or Gaussian-Lorenzian product function for each band using a non-linear least squares method.

Hybrid Hartree-Fock/density functional calculations to obtain geometry optimizations and vibrational frequencies for DMEDA and DMEDA-LiTf and DMEDA-LiBr were performed by Scott Boesch using the program Gaussian 94[102].

2.3.2 Thermal characterization

Differential scanning calorimetry (DSC) thermograms were collected on a Mettler DSC 820 calorimeter under nitrogen with a flow rate of 87 ml/min in sealed aluminum crucibles. Data were collected with a heating/cooling rate of 5°C/min.

2.3.3 Conductivity measurements

Complex impedance measurements were made over the frequency range 5 Hz to 10,000 kHz using a Hewett-Packard 4192A LF impedance analyzer. Samples were sandwiched between 12.5 mm stainless steel electrodes in an airtight cell which was maintained at the desired
temperature using a circulating bath. The thickness of the sample was determined by a micrometer built into the conductivity cell. Impedance plots were fitted using the program, LEVM 7.1[103].

CH 3. RESULTS

3.1 DMEDA AND LPEI SYSTEMS

Papers III and IV deal with the vibrational spectroscopy of DMEDA and DMEDA-LiTf, DMEDA-LiBr and DMEDA-TbaTf systems.

Paper I deals with the vibrational spectroscopy, thermal characterization, and conductivity of LPEI-LiTf and LPEI-NaTf systems.

Fundamental investigations into the nature of interactions in polymer electrolyte systems based on a poly(ethylene oxide) host can be complemented by considering a polymer having a backbone structure similar to that of poly(ethylene oxide), but with a non-oxygen heteroatom. Linear poly(ethylenimine), or LPEI, $-\{CH_2CH_2NH\}_n$, is structurally analogous to PEO, with an N-H group in place of the oxygen. Just as studies of glymes have been used to further understanding in ethyleneoxide based systems, [7, 10, 49, 56, 58] it is useful to consider a smallmolecule model compound for ethylenimine systems. The simplest model compound for PEI is N,N'-dimethylethylenediamine (DMEDA, Figure 3.1)

The vibrational analysis of DMEDA was undertaken in order to gain a better understanding of the vibrations of poly(ethylenimine) and polymer electrolytes based on a poly(ethylenimine) host. FT-IR and Raman spectra were recorded and analyzed in pure DMEDA, DMEDA-



LPEI

DMEDA

Figure 3.1 LPEI and DMEDA

LiTf complexes from 20:1 to 1.5:1 compositions, DMEDA-tetra-nbutylammonium triflate(TbaTf) complexes from 7:1 to 40:1 compositions, and DMEDA-LiBr at a 5:1 composition. The mode assignments for DMEDA and DMEDA-salt complexes were made by comparing experimental Raman and IR spectra to vibrational frequencies and intensities obtained using hybrid Hartree-Fock/density functional calculations. Because complete assignments for the vibrational modes of PEI are not available in the literature, I have assigned some of the modes in the subsequent discussion based on comparison to corresponding modes in DMEDA. Figure 3.2 shows the IR spectra of DMEDA and LPEI from 675 to 1525 cm⁻¹.



Figure 3.2. IR spectra of LPEI and DMEDA. Modes that have been tentatively assigned by comparison with DMEDA are marked with a vertical line.

Frequencies in several possible low-energy conformations of DMEDA and DMEDA-lithium salt complexes were calculated. The different conformations may be distinguished by the dihedral angles along the C-N-C-C-N-C backbone. For example, a TGT conformation signifies that the first dihedral angle (C-N-C-C) is trans, T, corresponding to an angle of 180°±60°, the second dihedral angle (N-C-C-N) is gauche, G, corresponding to a dihedral angle 60°±60°, and the third dihedral angle (C-C-N-C) is trans. Since DMEDA is a liquid, several different conformations contribute to the experimentally measured vibrational spectrum. For pure DMEDA, the three lowest energy geometries are in a TGT conformation with 0, 1, or 2 intramolecular hydrogen bonds, referred to respectively as DMEDA(0), DMEDA(1), and DMEDA(2). Comparison of calculated and experimental frequencies and intensities indicates that the pure DMEDA liquid is primarily a mixture of DMEDA(1) and DMEDA(0), with smaller contributions from other conformations. For the DMEDA-salt complexes, the most probable conformations are TGT or TGG with no intramolecular hydrogen bonds. For the DMEDA-LiTf complexes, it was found that the lithium was coordinated to the two nitrogen atoms of the DMEDA and two oxygen atoms of the triflate anion. Table 3.1 shows the experimental IR and Raman frequencies of DMEDA and DMEDA-LiTf 1.5:1 with mode assignments.

Several regions of the spectra are of particular interest in the DMEDA-salt and LPEI-salt systems: the region from ~700-1000 cm⁻¹ consisting of modes which are primarily a mixture of N-H perpendicular bend and CH₂ rock, the N-H stretching region from 3000-3400 cm⁻¹, and the triflate CF₃ symmetric deformation and SO₃ symmetric stretching regions. In paper III it is shown that the calculated frequencies and intensities of the modes from 700 to 1000 cm⁻¹ shift significantly when the conformation is changed. There are notable changes in the experimentally observed band intensities and frequencies in this region upon addition of LiTf.

Mode Assignments	DMEDA	DMEDA-LITF	DMEDA	DMEDA-LiTf	
	IR	1.5:1 IR	Raman	1.5:1 Raman	
$\delta_{as}SO_3$		518			
$\delta_{as}CF_3$		573		576	
$\delta_{s}SO_{3}$		639			
$\delta_{s}CF_{3}$		757		763	
N-H ⊥ bend	736				
	789	808	805(b)		
$\rho \operatorname{CH}_2 + \operatorname{N-H} \perp \operatorname{bend}$		839		840	
$\rho \text{ CH}_2$	879	898	881		
ω CH ₃	985		990	990	
ρ CH ₂ + ω CH ₃		1006		1012	
v C-C	1022		1021		
	1042		1039		
$v_{s} SO_{3}$		1033		1043	
[
1. C-N	1106	1092	1113	1112	
	1122	1104	1124		
	1151	1122	1152		
$v_{as}CF_3$		1160			
τCH ₂	1251		1255		
$v_{as}SO_3$		1259		1277	
ω CH ₂	1346	1352	1347	1356	
	1361		1363	1363	
$\delta_{s} CH_{3}$	1418		1420		
N-H bend + $\delta_{as}CH_3$	1444	1458	1450	1461	
$\delta CH_2 + \delta_{as} CH_3$	1473	1475	1473	1476	
<i>v</i> C-H	2681	2689	2679	2693	
	2788	2794	2790	2741	
	2840	2847	2843	2813	
	2887	2888	2891	2867	
	2934	2937	2939	2890	
	2967		2970	2956	
υ Ν-Η	3280	3295	3290	3300	
	3323	3323	3327	3337	

Table 3.1. Mode assignments for DMEDA and DMEDA-LiTf

* δ =bend, v=stretch, ω =wag, ρ =rock, τ =torsion, s/as=symmetric/antisymmetric

In the Raman spectrum of pure DMEDA, there is a broad band present at 805 cm⁻¹ which consists of underlying bands at frequencies ranging from \sim 760 to 805 cm⁻¹. There is a band in the infrared spectrum around 770 cm⁻¹ ¹ which can be deconvoluted into bands at 789 and 736 cm⁻¹. These bands are assigned to primarily N-H bending. When LiTf is added to DMEDA, the broad band around 770 cm^{-1} in the IR decreases drastically in intensity as the LiTf concentration increases, disappearing in the 1.5:1 sample except for a shoulder at 808 cm⁻¹. A band assigned to a mixture of N-H bend and CH₂ rock appears in the Raman spectrum at 836 cm⁻¹ and steadily increases in intensity. This band appears in the IR spectrum at 836 cm⁻¹ in the 20:1 sample, shifting to 839 cm⁻¹ in the 1.5:1 composition. In the Raman spectra in this region one can see the DMEDA band at 881 cm⁻¹ broaden and disappear as the concentration of lithium triflate increases. The Raman band at 881 cm⁻¹ and the infrared band at 879 cm⁻¹ in the pure DMEDA are assigned to the CH_2 rock. As the LiTf concentration increases, the band at 879 cm⁻¹ in the IR spectrum of DMEDA moves from 881 cm⁻¹ in the 20:1 composition to 898 cm⁻¹ in the 1.5:1 composition. Very similar frequency and intensity changes are seen with the addition of LiBr as with LiTf, as is shown in paper IV. The comparison of the experimental spectra with the calculated frequencies indicates that these spectral changes reflect the structural changes

calculated in the geometry optimization upon addition of LiTf or LiBr to DMEDA, i.e., that the N-C-C-N dihedral angle of DMEDA is changed and an intramolecular hydrogen bond is broken. The N-H bending contribution to the modes in this region is probably most influenced by the change in hydrogen bonding. The dramatic changes observed in the CH₂ rocking and N-H bending modes upon complexation of DMEDA with LiTf were not unexpected. In the related diglyme-LiTf system, changes in the frequency and intensity of the modes assigned to mixed CH₂ rocking [50, 51] have been shown to indicate changes in the O-C-C-O dihedral angle upon interaction with the lithium ion. [10, 31]

Dramatic changes occur in the region from 1400 to 1050 cm⁻¹ in the Raman spectra of the LPEI-LiTf (shown in figure 3.3) and LPEI-NaTf systems with increasing salt concentration. This region consists of LPEI modes that are mixtures of CH₂ rocking, N-H bending, CH₂ wagging, C-C stretching and C-N stretching motions. The spectra of the 20:1 LPEI-LiTf and LPEI-NaTf samples closely resemble the spectrum of pure LPEI, with most of the LPEI bands slightly broadened and a loss of intensity in some of the weaker bands. However, in the spectra of the 10:1 samples the bands have considerably broadened with a general collapse of vibrational band structure, so that there are only three very broad features originating in LPEI vibrations visible in this region in the LiTf system. The NaTf system retains only slightly more of the LPEI band structure than the LiTf system. In the 5:1 samples the trend of band broadening and loss of structure continues. This phenomenon is observed throughout the entire vibrational spectrum: significant band broadening and a dramatic collapse of band structure in the LPEI modes so that only the triflate anion modes can be easily distinguished.



Figure 3.3. Raman spectra of LPEI and LPEI-LiTf from 1400-1000 cm⁻¹.

These data strongly suggest that the LPEI-LiTf and LPEI-NaTf systems are very disordered at the 10:1 and 5:1 compositions. X-ray diffraction measurements of LPEI-LiTf and LPEI-NaTf films at the 5:1 composition show that these samples are highly amorphous. Differential scanning calorimetry also confirms the decrease in crystallinity of the LPEI as LiTf is added. There is a large endothermic peak at ~60°C in the thermogram of pure LPEI attributed to the melting of crystalline LPEI. Upon addition of LiTf, the peak decreases dramatically at a 10:1 composition, and at a 5:1 composition the crystalline LPEI melting peak has completely vanished. These observations are consistent with the collapse of vibrational band structure seen in the Raman spectra.

The N-H stretching frequencies are very sensitive to hydrogen bonding interactions; hydrogen bonding causes the frequencies to be lowered[104]. In pure DMEDA, the N-H stretching frequencies in the IR spectrum are 3323 and 3280 cm⁻¹, and in the Raman spectrum are 3327 and 3290 cm⁻¹. These relatively low N-H stretching frequencies indicate that hydrogen bonding is present in liquid DMEDA. In DMEDA-LiBr there are bands at 3210 and 3270 cm⁻¹ in the IR spectrum and at 3220, 3280 and 3320 cm⁻¹ in the Raman spectrum. In DMEDA-LiTf there are distinct IR bands at 3295 and 3323 cm⁻¹ and Raman bands at 3301 and 3327 cm⁻¹. As the LiTf concentration is increased from 20:1 to 1.5:1, the frequencies of the N-H stretches in the Raman spectra of the DMEDA-LiTf increase.

The interpretation of the N-H stretching region in the DMEDA systems is complicated by the variety of possible hydrogen bonding interactions. In the pure DMEDA, the presence of intermolecular as well as intramolecular hydrogen bonding is indicated. In the DMEDA-salt systems, there may still be hydrogen bonding between DMEDA molecules, as well as between the amine hydrogens and the anions. The increase in the experimentally observed frequencies of the N-H stretches upon the addition of LiTf to DMEDA implies that hydrogen-bonding interactions are decreased. The presence of more than one N-H stretching band in these systems probably indicates that the N-H mojeties exist in several different environments, with different types of hydrogen bonding interactions present. Our calculations, coupled with observations from other regions of the experimental vibrational spectra, lead us to conclude that intramolecular hydrogen bonds are broken when salt is added to DMEDA. However, at low salt concentrations some intramolecular hydrogen bonds may remain.

The IR spectrum of pure LPEI in the N-H stretching region consists of a relatively sharp, strong band centered at 3218 cm⁻¹, and a less intense, very broad feature centered at roughly 3270 cm⁻¹ and extending

beneath the sharp, lower frequency band. The sharp band may originate in domains of crystalline LPEI where the extensive hydrogen bonding shifts the frequency of the N-H stretch to a lower frequency compared with a free N-H stretching mode. The relatively narrow bandwidth in LPEI is due to the high degree of crystallinity in those domains. The broad feature may be due to more disordered regions of LPEI where hydrogen bonding is still present to a significant extent. The much lower frequencies of the N-H stretches in LPEI than in DMEDA indicate a higher degree of hydrogen bonding in the former. This is unsurprising, considering that pure crystalline LPEI exists as an extensively hydrogenbonded double helix [67]. The spectra of the 5:1 LPEI-LiTf and LPEI-NaTf compositions are similar in this region. In the LiTf system there are two bands, at 3294 and 3325 cm⁻¹, while the NaTf system exhibits a band at 3301 cm⁻¹ and a clearly resolved shoulder at 3325 cm⁻¹. In both salt systems the bands are shifted to higher frequency compared with pure LPEI. These shifts originate in the disruption of the hydrogen bonds that occurs with the addition of salt. The N-H stretching bands in the DMEDA-LiTf system are also shifted to higher frequencies with the addition of LiTf, due to changes in the hydrogen-bonding environment in DMEDA.

The $\delta_s(CF_3)$ and $v_s(SO_3)$ modes of the triflate anion are very sensitive to ionic speciation, i.e., as the triflate anion becomes more associated, the frequencies of these modes increase [39]. These bands are non-degenerate, and the presence of multiple bands arises from the triflate anion vibrating in different local environments. Figure 3.4 shows the results of the curvefitting analysis for the Raman and IR data in these two regions.



Figure 3.4. Curvefitting results for the DMEDA-LiTf system

The symmetric CF_3 deformation can be deconvoluted into three bands centered around 755, 758-760 and 763 cm⁻¹. In ethylene-oxide based systems, [38] bands at 752-753 cm⁻¹ are attributed to "free" ions, bands at 756-757 cm^{-1} are attributed to contact ion pairs, and bands at 763 cm⁻¹ are attributed to the Li₂Tf⁺ aggregate. The symmetric SO₃ stretching region can be deconvoluted into bands centered around 1032-1036, 1038-1044, and 1050-1054cm⁻¹. According to the literature, [5] "free" ions are at 1032-1033 cm⁻¹, ion pairs are at 1042 cm⁻¹, and Li₂Tf⁺ at 1050-1052 cm⁻¹. Based on a comparison of the $\delta_s(CF_3)$ and $v_s(SO_3)$ regions, it appears that in the DMEDA-LiTf system the "free" ion and ion pair components of the $\delta_{s}(CF_{3})$ band are at slightly higher wavenumbers than in ethylene oxide systems [5, 10, 11, 31, 47]. The curve fitting of the $\delta_s(CF_3)$ bands in the IR spectrum and the $v_s(SO_3)$ bands in the Raman spectrum is complicated by the presence of DMEDA bands in these regions, therefore the relative intensities obtained by curvefitting may have a larger error than in other regions of these spectra. There are qualitative similarities between the ionic speciation as determined from these spectral regions. As the concentration of LiTf in the DMEDA system increases, the degree of ionic association of the triflate anion appears to increase, changing from a mixture of "free" ions and ion pairs to a mixture that includes a more associated aggregate. There are, however, notable differences in the

quantitative comparison of the species as determined from the CF₃ symmetric deformation or the SO₃ symmetric stretch. The amount of aggregate in the 1.5:1 sample is almost 100% as determined from the Raman spectrum in the $\delta_{s}(CF_{3})$ region, while in the same spectrum the amount of aggregate appears to be only 16% as determined from the relative integrated intensities in the $v_{s}(SO_{3})$ region. In the 20:1, 10:1 and 5:1 samples, the pair seems to dominate, with the "free" ion band making up less than 15% of the total area in the curvefitting of the Raman $\delta_{s}(CF_{3})$ region, while in the $v_{s}(SO_{3})$ region the intensities of the "free" ion and ion pair components for these three concentrations are nearly equal. Discrepancies in the ionic speciation as determined from the $\delta_{s}(CF_{3})$ and $v_{s}(SO_{3})$ regions have been observed by Ferry, et al. in a PEO oligomer[105]and in poly(propylene glycol) [42].

Tetra-n-butylammonium triflate (TbaTf) has been used to study cation-anion interactions[48]; since TbaTf is a bulky cation with a wellprotected charge, interactions with the anion are minimal. IR spectra in the $\delta_s(CF_3)$ and $v_s(SO_3)$ regions of DMEDA-TbaTf over a concentration range of 44:1 to 7:1 show neither a complex band structure nor a shift in frequency in these two modes with increasing salt concentration, indicating no change in ionic association, as expected. The $v_s(SO_3)$ region exhibits a single band at 1031 cm⁻¹, consistent with a "free" ion, although

at a slightly lower frequency than is usual in ethylene-oxide-based systems. In the $\delta_{s}(CF_{3})$ region, a single band is seen at 755 cm⁻¹, which is higher than the "free" triflate frequency in LiTf-ethylene oxide systems. [11, 47]. It has been noted that the frequency of the $\delta_s(CF_3)$ mode of TbaTf is solvent-dependent, while the $v_s(SO_3)$ mode appears to be solventindependent [48]. However, significant hydrogen-bonding interactions between the triflate anion and a protic solvent may slightly lower the $v_s(SO_3)$ frequency from the usual values expected for a "free" ion in an aprotic environment. The "free" ion should therefore be regarded as a solvent-separated ion pair, free of cation-anion interactions, but not necessarily free of solvent-ion interactions. The frequency of 755 cm⁻¹ for the $\delta_{s}(CF_{3})$ mode observed in the DMEDA system with both LiTf and TbaTf, may therefore arise from a "free" ion, with the unusually high frequency being due to anion-solvent interactions rather than cation-ion interactions. Furthermore, the possibility that the frequency of the CF_3 symmetric stretching mode is affected by solvent interactions suggests that the SO_3 symmetric stretch may be a better indicator of ionic association in the DMEDA system. However, there are clearly significant interactions of the triflate ion with the solvent, presumably a hydrogenbonding interaction between the triflate oxygen atoms and the amine hydrogen atom of the DMEDA. Therefore, any quantitative conclusions

about the relative concentration of ion species based on comparisons of relative integrated intensities from either the $\delta_s(CF_3)$ or the $v_s(SO_3)$ spectral region must be regarded as uncertain.

The nature of the triflate aggregate should be considered. One triflate aggregate is the triple cation, Li₂Tf⁺, in which each triflate ion is coordinated to two lithium cations. The triple cation may exist as an independent species, charge-balanced by "free" triflate anions, or as part of a more complex structure such as is seen in the diglyme-LiTf system. In that system, a combination of vibrational spectroscopy and x-ray diffraction of a diglyme-LiTf crystal shows that this spectroscopic signature (763 cm⁻¹ for the $\delta_s(CF_3)$ mode) arises from a dimer structure, diglyme₂Li₂Tf₂ ,wherein each lithium is coordinated to three oxygen atoms of a diglyme molecule and one oxygen from each triflate [31]. Each triflate then vibrates as a Li₂Tf⁺ entity, although it is part of a Li₂Tf₂ dimer. It is reasonable to hypothesize that a similar bonding geometry could exist in the DMEDA-LiTf system.

The results of the curvefitting analysis of the Raman data in the $\delta_{s}(CF_{3})$ region for LPEI-LiTf and LPEI-NaTf are presented in Table 3.2.

Table 3.2. Curvefitting results for the $\delta_s(CF_3)$ mode in LPEI-LiTf and LPEI-NaTf. Frequency and percentage of integrated band intensity (in parenthesis)

LPEI-LiTf							
Composition	Band center frequency, cm ⁻¹ (Intensity)						
20:1			755 (74%)	752 (26%)			
10:1		759 (18%)	756 (69%)	753 (13%)			
5:1	763 (10%)	760 (83%)	757 (7%)				
LPEI-NaTf				<u>.</u>			
Composition	Band center frequency, cm ⁻¹ (Intensity)						
20:1			756 (100%)				
10:1			757 (100%)				
5:1	762 (9%)		757 (80%)	754 (11%)			

Unfortunately, the sharp LPEI band at 1045 cm⁻¹ in both the Raman and the IR prevents a reliable curvefitting analysis of the SO₃ symmetric stretch in the LPEI-triflate salt systems. However, it is clear that in the LPEI-LiTf system, the ionic association increases with increasing salt concentration. This behavior is also seen in the PEO-LiTf system. Based on the conclusions from the DMEDA-LiTf curvefitting analysis, it seems that the speciation in the LPEI-LiTf system changes from a mixture of "free" ions and ion pairs at the 20:1 composition to a mixture of ion pairs and Li₂Tf⁺ at the 5:1 composition. The triple cation must be chargebalanced; therefore absence of spectroscopically detectable "free" triflate anion suggests that the Li₂Tf⁺ exists as part of a larger aggregate, perhaps in a line compound as is seen for high-molecular weight PEO₃LiTf complex [8]. Surprisingly, the LPEI-NaTf system appears to be to have almost no change in ionic association over the concentration range studied. This observation is in sharp contrast to PEO-NaTf system, which exhibits two very distinct, more highly associated ionic species at compositions of 40:1 to 10:1 (O:Na), in addition to "free" ions and contact ion pairs [40].

Complex impedance measurements were made of the LPEI-LiTf 5:1, 10:1 and 20:1 samples at 10°C increments from 30 to 70°C. Figure 3.5 shows the results of these measurements. These samples have conductivities on the order of 10^{-7} S cm⁻¹ at 30°C and 10^{-5} S cm⁻¹ at 70°C. The conductivity at 30°C is higher for the 5:1 salt composition, while the conductivity at 70°C is higher for 20:1 salt composition. The 20:1 data fall almost on a straight (Arrhenius) line, with a slight curvature, whereas the 5:1 data cannot fit a single straight line. The much smaller conductivity of the 20:1 composition compared to the 10:1 and 5:1 compositions at 30 and 40°C may be attributable to the much higher degree of crystallinity still present at the 20:1 composition as evidenced in the Raman spectra and the DSC thermograms.



Figure 3.5. log σ vs. 1/T for LPEI-LiTf

3.2 POLYPHOSPHAZENES

Paper II deals with the vibrational spectra of several polyoligoethyleneoxyphosphazenes. Paper V deals with the vibrational spectra and conductivity of MEEP.

Because the amorphous phase in polymer-salt systems is the primary conductivity pathway, [18]the value of the conductivity is generally largest in polymer electrolytes that are highly disordered or amorphous in nature. An important class of amorphous polymer hosts is based on a polyphosphazene backbone with various sidechains. Poly(bismethoxyethoxyphosphazene), or MEEP, was first synthesized and studied as a polymer electrolyte by Shriver, Allcock, and their coworkers. [83] MEEP with dissolved LiCF₃SO₃ is amorphous over a temperature range of at least -100 to 100° C and has room temperature conductivities much higher than analogous PEO-LiCF₃SO₃ systems, on the order of 10^{-5} S cm⁻¹ [81].

Raman vibrational spectroscopy has been used to examine a series of polymer electrolytes based on poly(oligoethyleneoxy phosphazenes). Ionic association and local structural changes of the polymers were studied as a function of salt concentration and the length of the ethylene oxide sidechains. The details of this investigation are in paper II. The polymers, of the form $\{NP((OCH_2CH_2)_xOCH_3)_2\}_n$, with x=0, 1, 2, or 5, have been mixed with LiCF₃SO₃ in oxygen:lithium composition ratios ranging from 10:1 to 40:1. The polymers will be referred to collectively as ME_xP.

In the Raman spectra of the ME_xP x=1,2,5 there is a large peak at 630 cm⁻¹ which appears, from comparison with model chlorophosphazene and phenylphosphazene compounds[106-108], to originate in phosphazene backbone vibrations involving P-O stretching and N-P-O bending and motions. When LiTf is added to these three polymers at a composition of 10:1, this band exhibits only a small shift to 634 cm⁻¹. This indicates that the backbone vibrations are only slightly affected by the addition of LiTf to the ME_xP polymers containing ether oxygen atoms in the sidechains. In contrast, in the x=0 polymer, this mode shows a significant frequency shift, which suggests that the degree of interaction between the nitrogen atom and the lithium cation is much greater in the x=0 system than in the ME_xP systems bearing longer sidechains. This is not surprising, since each x=0 sidechain has only a single methoxy oxygen to coordinate the lithium ion.

The ionic association of the lithium triflate in the ME_xP polymers can be obtained from curvefitting the spectral region containing the CF₃ symmetric deformation mode, $\delta_s(CF_3)$, of the triflate anion. The trend seen for the triflate anion is that a higher frequency of the $\delta_s(CF_3)$ mode occurs for a higher degree of association of the triflate anion with the cation. Curve-fitting analysis of the $\delta_s(CF_3)$ mode in the ME_xP-LiTf systems identified frequencies of 751-752 cm⁻¹ for the "free" ion, 755-757 cm⁻¹ for the ion pair, and 760-761 cm⁻¹ for the triple ion Li₂Tf⁺. These assignments are in accordance with *ab initio* calculations of LiTf species [39] and spectroscopic studies of PEO [8, 9] and glyme [10, 31]systems with dissolved LiTf.

At the 40:1 composition in all four ME_xP systems the triflate anion occurs primarily as a contact ion pair, with some "free" ion present. At a

composition of 10:1 in all four systems, the triflate anion is found mostly as the triple ion species Li₂Tf⁺, with some contact ion pairs and no "free" In all four ME_xP -LiTf systems the degree of ionic association ions. increases with increasing LiTf concentration. In the $ME_{x}P$ -LiTf 10:1 systems with x=1,2,5 the triflate ion exists almost entirely as the Li₂Tf⁺ triple ion, with a very minor contribution from contact ion pairs. Further, there is little dependence of the triflate speciation on sidechain length in these three 10:1 systems. In contrast, at the 10:1 composition in the x=0system there is a significant contribution from ion pairs, although the triple ion is still the dominant species. In none of the systems at the 10:1 composition are there measurable amounts of "free" ion. In the ME_xP-LiTf 40:1 systems there are no triple ions observed for any sidechain length. For the x=1,2,5 ME_xP-LiTf systems at the 40:1 compositions, the percentage of free ion increases as sidechain length increases. However, this trend is not followed in the x=0 system. These data show that LiTf interacts with the x=0 polyphosphazene in a somewhat different manner than with the polymers containing ether oxygen atoms in the sidechains.

The evidence both from the P-O stretching mode and the ionic association suggests that some factor other than the sidechain length affects cation-anion interactions in the x=0 system. These differences between x=0 and the other three polyphosphazenes with longer sidechains

are probably due to the oxygen atoms attached to the P being involved extensively in coordinating the Li ion in the x=0 but not in the x=1,2, or 5 complexes.

A more detailed IR and Raman study was done on the MEEP-LiTf system, presented in paper V. A MEEP monomer unit consists of a P=N backbone with two ethylene oxide sidechains, which are the sites that coordinate the lithium ions. Therefore the ethylene oxide interactions of these sidechains can be modeled by diglyme, CH₃(OCH₂CH₂)₂OCH₃. The salt concentrations in paper V are given as ether oxygen: lithium ratios for ease of comparison with the diglyme system. Figure 3.6 shows a comparison of the IR spectra of MEEP, MEEP-LiTf 2:1, diglyme, and diglyme-LiTf 5:1 in the spectral region from 700 to 1000 cm⁻¹. (A 2:1 solution of diglyme-LiTf cannot be prepared because a compound forms at a 3:1 ratio.) This region has bands that are a mixture of CH₂ rock, CO stretch, and COC bend [31, 50, 51]. In several glymes and in high molecular weight PEO, this region has been shown to be sensitive to changes in the conformation of the ethoxy chain when salt is added. [31, 35]

There are several striking features in the comparison of the MEEP system to the diglyme system. As can be seen in Figure 3.6, the bands in the MEEP spectrum in this region are much broader than in the diglyme



Figure 3.6. FT-IR spectra of MEEP, MEEP:LiTf 3:1, diglyme, and digylme:LiTf 5:1.

spectrum. In particular, the breadth of the features at 804 and 851 cm⁻¹ and the collapse of the four bands in diglyme between 900 and 1000 cm⁻¹ into a broad, slightly structured feature in MEEP indicate that the conformation of the ethoxy sidechains is distributed over a wider range of dihedral angles in MEEP than in diglyme, despite the fact that diglyme is

a liquid. There are even more significant differences between the spectra when LiTf is added. In the diglyme system, there are obvious shifts in the frequency of the CH₂ rock and other bands. These frequency shifts have been associated with conformational changes [31, 35, 49-51]. As has been previously reported, these changes occur gradually as salt concentration is increased, and at the 5:1 composition, the diglyme spectrum appears to be a superposition of the pure diglyme spectrum with the spectrum of a diglyme-LiTf compound [31]. In the MEEP-LiTf spectra, even at very high salt concentration, there are no major frequency shifts in this region. This indicates that there is not a distinctive change in the conformation of the side-chains upon addition of LiTf. The interaction between the Li and MEEP occurs primarily at the ether oxygens, therefore one might have expected a greater change in those bands arising form vibrations of the side-chains. However, consideration of the steric hindrance and chainentanglement of the MEEP makes that lack of a distinctive band structure change in this region less surprising. At very high salt concentrations (greater than 10:1), there is a small band growing in at 830 cm^{-1} . This band arises from the interaction of the ether oxygen with the lithium ion, and may be indicative of a change in local ordering of the ethoxy sidechains at high salt concentrations.

The frequency and intensity of the $\delta_s(CF_3)$ mode are highly dependent on interactions of cations with triflate oxygen atoms. There are several ionic species whose presence can be detected: "free" Tf ions (or solvent-separated ion pairs), LiTf contact ion pairs, and the triple cation Li₂Tf⁺. [10, 31, 39]. The relative concentration of these ionic species as obtained from the deconvolution of the $\delta_s(CF_3)$ Raman spectral region is shown in Table 3.3.

P·li	0·Li	EO:Li	conductivity*	% speciation			
	0.2		S cm ⁻¹	"free"	pair	triple	error
1.7:1	10:1	6.6:1	1.2 x 10 ⁻⁵	0	4	96	16%
4:1	24:1	16:1	2.7 x 10 ⁻⁵	0	100	0	4%
6.7:1	40:1	26.6:1	2.2 x 10 ⁻⁵	12	88	0	4%
8:1	48:1	32:1	2.2 x 10 ⁻⁵	21	79	0	10%

Table 3.3. Conductivity and ionic species in the MEEP-LiTf system

*conductivity from Blonsky, 1986 (ref 81)

To investigate the error in this analysis, multiple samples were made at each composition and Raman spectra of each sample were measured. The various spectra thereby obtained were then subject to the same curvefitting technique. The errors estimated in this manner are also listed in the table.

From the curvefitting results, as the concentration of LiTf in MEEP is increased from 32:1 to 6.6:1, the speciation progressively changes from a mixture of "free" ions and ion pairs, to mostly ion pairs at the 26:1 and 16:1 compositions. to almost entirely triple cations at salt compositions greater than 10:1. The predominance of the triple cations with no detectable "free" triflate ions for charge balance has implications for the local structure of MEEP-LiTf. It is not possible to spectroscopically distinguish an isolated triple cation from a Li₂Tf⁺ entity vibrating as part of a more extensively associated species. In high molecular weight PEO-LiTf, the triple cation exists as part of a line compound[8], whereas in the diglyme-LiTf crystal, it is known that the Li_2Tf^+ species exists in a dimer structure, Li_2Tf_2 [31]. The triple cation Li_2Tf^+ must be present as part of a more highly associated aggregate in the MEEP-LiTf system at high salt concentrations. I postulate a dimer structure consisting of Li₂Tf₂ dimers linking two adjacent ethoxy side chains. The existence of the Li₂Tf₂ dimeric species is made plausible by the fact that the crystalline phase of diglyme-LiTf consists exclusively of isolated diglyme₂Li₂Tf₂ dimers [31]. In these dimers each triflate ion vibrates as an Li_2Tf^+ entity. Therefore I suggest that the triple cation species that dominate the MEEP-LiTf spectrum at high salt concentrations and which have the same spectroscopic signature (763 cm⁻¹) as the triple cation in the diglyme-LiTf

solution are really present as Li_2Tf_2 dimers. In these dimers each lithium ion is coordinated by oxygen atoms from two different triflate anions and also by two sidechain oxygen atoms, not necessarily from the same sidechain. The entangled nature of the side chains leads to a conformationally disordered system in spite of the presence of reasonably ordered ionic dimers.

A comparison of the ionic speciation with the conductivity yields an extremely surprising result. The conductivity is at a maximum at a composition (16:1) consisting almost entirely of ion pairs, rather than at the composition with the greatest percentage of free ion, as one might have expected. Also strikingly, over such a wide concentration range that the speciation changes from free ions and ion pairs to entirely the Li₂Tf⁺ species, the conductivity only varies within half an order of magnitude.

The spectroscopically inferred local structures have important implications for the mechanism of ionic conductivity in MEEP, as is discussed in detail in paper V. The observation of 100 percent ion pairs at the conductivity maximum leads to the hypotheses of a mechanism of ionic conductivity with associated species playing a major role. While it has been suggested that coordinated motions of charged aggregates could contribute to ionic conductivity[109], these species are very bulky and hence have low mobility. Therefore, as charge carriers they are not

expected to make a major contribution to the overall conductivity. A more likely mechanism probably involves ion-hoppping of lithium ions or triflate ions between adjacent pairs or aggregated species. The free triflate ion, although one of the two principal charge carriers in this picture, is a transient species and is present as a free ion at a concentration too small to be spectroscopically detected. In this scheme, highly mobile, individual Tf and Li⁺ ions move from a dissociation site (e.g. the Li₂Tf₂ dimer) to a reassociation site (e.g. a proximate, newly created Li₂Tf⁺ or LiTf₂⁻ site) . The more highly associated species serve as relatively "immobile" sites for ionic association/dissociation reactions. The short timescale of these hops means that the "free" ions are not spectroscopically detected. The high mobility of the lithium ions in the MEEP system arises in part through the thermal motions of entangled ethylene oxide side chains producing a locally disordered potential energy environment for the ions.

CH 4. CONCLUDING REMARKS

The most important results of this study are the following:

- 1. Identification and assignment of vibrational modes in DMEDA and DMEDA-salt systems which are affected by polymer-salt interaction, especially the N-H stretching and the mixed CH₂ rocking and N-H bending modes,
- 2. Elucidation of the effect of hydrogen-bonding on vibrational modes of triflate, i.e., that the characteristic frequencies of the $\delta_s(CF_3)$ and $v_s(SO_3)$ modes association with "free" triflate anion, ion pair, and triple cation are not the same in DMEDA as in PEO or glymes,
- 3. Demonstration of the disruption of hydrogen bonding in LPEI and DMEDA when salt is added,
- Presentation of evidence of cation interaction with ether oxygens

 (as opposed to the backbone nitrogen) in MEEP and other
 ethoxy phosphazenes,
- 5. Hypothesis of dimer structures in DMEDA- and MEEP-LiTf involving two lithium ions and two triflate ions linking two DMEDA molecules or two MEEP ethoxysidechains, based on

comparison of spectroscopic evidence between these systems and the diglyme-LiTf system,

- 6. Proof of the involvement of associated ionic species in ionic conductivity from a comparison of the speciation versus conductivity in MEEP-LiTf, and
- 7. Proposal of mechanism of ionic conductivity involving dissociation and rapid reassociation of ionic species.

This study has advanced the understanding of ionic conductivity and local interactions in polymer electrolytes based on poly(ethylenimine) and polyphosphazenes. Several new research directions are suggested by the results of this current study:

- 1. Investigation of DMEDA with other salts to further examine the effects of hydrogen bonding.
- 2. Synthesize possible crystalline structures in LPEI-salt systems
- 3. Extend the proposed associated ionic conductivity mechanism to other polymer electrolyte systems.

Research efforts toward a more thorough understanding of local structures in polymer electrolytes and the development of a <u>general</u> microscopic mechanism of ionic transport are essential to guide the development of polymer electrolytes with improved mechanical properties and conductivity.

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A comparative vibrational spectroscopic study of lithium triflate and sodium triflate in linear poly(ethylenimine)

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Abstract

Systems of linear poly(ethylenimine), LPEI, with dissolved LiCF 3SO3 and NaCF3SO3 have been studied using Raman and infrared spectroscopy. As the salt concentration is increased in the LPEI-LiCF 3SO3 system, in turn "free" ions, contact ion pairs and the triple cation [Li 3CF3SO3]* each become the dominant species present, whereas contact ion pairs appear to be the dominant ionic species over the same composition range in the LPEI-NaCF 3SO3 system. One of the major effects of adding salts to LPEI is the breaking of hydrogen boads in the host polymer. As the salt concentration is increased in both systems, a somewhat abrupt onset of band broadening and widespread loss of band structure is observed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Linear poly(ethylenimine); Vibrational spectroscopy; Ionic association; Hydrogen boading

1. Introduction

It is well recognized that poly(ethylene oxide), PEO, readily dissolves a variety of metal salts [1] to form ionically conducting systems that can be used as electrolytes [2]. Although numerous other polymers can function as hosts to form electrolytes, none have attracted such widespread fundamental and technological interest. The latter originates in the use of PEO-based electrolytes containing lithium salts in rechargeable batteries [3]. Attempts to increase the ionic conductivity of such systems have led to a rich variety of studies focused on developing a molecular level understanding of the factors controlling the ionic conductivity [4-8].

Fundamental studies of this nature can be complemented by considering a polymer having a backbone structure similar to that of PEO, but with the oxygen heteroatom replaced with another cation-coordinating

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heteroatom. A polymer analogous to PEO is linear poly(ethylenimine) or LPEI, $-[CH_2CH_2NH]_-$, which has an NH group in piece of the oxygen atom. There has been some work previously reported on PEI-polymer electrolytes. In an early study, Harris et al. described complex formation and ionic conductivity of NaCF₃SO₃ in linear PEI [9] and branched PEI [10]. Polymer electrolytes based on PEI and sodium iodide were reported by Chiang et al. [11]; this work was subsequently extended to lithium salts [12]. Linear PEI has been chemically modified to reduce the crystallinity of salt complexes formed upon the dissolution of salt [13,14]. Subsequently, Tanaka et al. studied ionic conduction in PEI and methyl-substituted PEI complexed with LiClO₄ and LiCF₃SO₃ [15].

2. Experimental

Linear poly(ethylenimine) (avg. MW ca. 86,000) was synthesized by the acidic (HCl) hydrolysis of poly(2ethyl-2-oxazoline) (Aldrich, avg. MW 200,000), fol-

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Fig. 1. Raman spectra of LPEI-LiTf at 5:1, 10:1 and 20:1 compositions in the $\delta_4(CF_3)$ region.

lowed by neutralization with aqueous NaOH. The NMR spectrum was in agreement with the literature data [16].

To prepare the electrolyte materials, LPEI was dried under vacuum at ~75°C for 48 h. Lithium triffate, LiCF₃SO₃ (LiTf), obtained from Aldrich was dried under vacuum at ~120°C for 24 h. Sodium triffate, NaCF₃SO₃ (NaTf), obtained from Aldrich was dried under vacuum at ~120°C for 24 h. Anhydrous methanol (99.8%, water, 0.002%) from Aldrich was redistilled and stored over molecular sieves. All materials were stored in a nitrogen-atmosphere glovebox with moisture less than 1 ppm. Desired ratios of LPEI and the LiTf or NaTf were dissolved in anhydrous methanol in the glovebox and stirred for 24 h. The composition of an LPEI-salt system is described by the N/M ratio, which is the ratio of nitrogen atoms to cations. To obtain thin films of the samples, the poly-

Table 1

Curve-fitting results showing the percentage of integrated band intensity (in parenthesis) for LPEI-LTTf and LPEI-NaTf in the $\delta_1(CF_3)$ spectral region

Composition	Band center frequency, cm ⁻¹ (intensity)				
LPEI-LITT					
20:1			755 (74%)	752 (26%)	
10:1		759 (18%)	756 (69%)	753 (13%)	
5:1	763 (10%)	760 (83%)	757 (7%)		
LPEI-NaTf					
20:1			756		
			(100%)		
10:1			757		
			(100%)		
5:1	762 (9%)		757 (80%)	754 (11%)	

mer solutions were cast onto glass slides and the methanol was allowed to evaporate at room temperature in the glovebox. The resulting films were dried under vacuum for 48 h at $\sim 45^{\circ}$ C.

Raman spectra were taken using an ISA Jobin-Yvon T64000 Raman spectrometer. The 514-nm line of an argon laser was used as the exciting line at a power of 300 mW at the laser head. The Raman spectra of the films were taken in a backscattering geometry under a microscope. Infrared spectra were recorded with a Bruker IFS66V FT-IR spectrometer over a range of 4000-400 cm⁻¹ at a resolution of 1 cm⁻¹. The IR spectra of the films were taken between AgBr plates in an evacuated sample chamber at room temperature. Curve-fitting analysis of the spectral data was done using a commercial program (Galactic Grams version 5.05). The spectra were curve-fit to a straight base line and one Gaussian-Lorenzian product function for each band using a non-linear least-squares method.

Complex impedance measurements were made over the range of 5 Hz to 10,000 kHz using an HP 4192A LF impedance analyzer. Samples were sandwiched between 12.5 mm stainless steel electrodes in an airtight cell, which was maintained at a desired temperature using a circulating bath. Impedance plots were fitted using LEVM version 7.1.

3. Remits and discussion

3.1. Ionic association as a function of salt concentration

Fig. 1 shows the Raman spectra in the triflate ion CF₁ symmetric deformation region, δ_1 (CF₁), for several LPEI-LiTf samples. The 20:1 composition has a broad band at 753 cm⁻¹, which is a "free" triflate ion frequency [17]. This band has shifted to 757 cm $^{-1}$ in the 10:1 sample and in the 5:1 sample it appears at 760 cm⁻¹. In ethylene oxide systems containing dissolved LITF, the frequency of 757 cm⁻¹ has been attributed to a contact ion pair and the 760 cm -1 frequency has been assigned to an (Li2Tf)+ species [18]. It is noteworthy that these band assignments also seem appropriate for the PEI-LiTf system. This seems a little surprising because the hydrogen atom of the N-H group might be expected to hydrogen bond with the oxygen of the triflate anion, thus altering the frequencies of associated ionic species. The results of curve-fitting these data are presented in Table 1. The general trend is towards an increasing degree of ionic association with increasing salt concentration, as seen in PEO-LiTf systems.

The Raman spectra for LPEI-NaTf samples in the $\delta_1(CF_3)$ spectral region are shown in Fig. 2. Here the band maxima are at 756, 757 and 758 cm⁻¹ for the compositions of 20:1, 10:1, and 5:1, respectively. These



Fig. 2. Raman spectra of LPEI-NaTf at 5:1, 10:1 and 20:1 compositions in the $\delta_4(CP_3)$ region.

frequencies are indicative of Na-Tf contact ion pairs [19], and a curve-fitting analysis of these data (also presented in Table 1) confirms that ion pairs are the dominant ionic species present at these compositions. This observation is in sharp contrast with PEO-NaTf systems, which in addition to "free" ions and contact ion pairs, exhibit two very distinct, more highly associated ionic species at compositions of 40:1 to 10:1 (O /Li) [19].

3.2. Hydrogen bonding

Fig. 3 shows the infrared absorbance spectra of pure LPEI and the 5:1 compositions of LPEI-NaTf and LPEI-LiTf in the region from 3400 to 3100 cm⁻¹. The spectrum of pure LPEI consists of a relatively sharp, strong band centered at 3218 cm⁻¹, and a less intense, very broad feature centered at roughly 3270 cm⁻¹ and



Fig. 3. Raman spectra of LPEI-LiTT at 5:1, 10:1 and 20:1 compositions and pure LPEI in the polymer CH and NH bending and stretching regions.

extending beneath the sharp, lower frequency band. The sharp band appears to originate in domains of crystalline LPEI where the extensive hydrogen bonding shifts the frequency of the N-H stretch to a lower frequency compared with a free N-H stretching mode. The relatively narrow bandwidth is due to the high degree of crystallinity in those domains. The broad feature may be due to more disordered regions of LPEI where hydrogen bonding is still present to a significant extent. The spectra of the two 5:1 salt compositions are similar in this region. In the LiTf system there are two bands, at 3294 and 3325 cm⁻¹. The analogous data for the NaTf material show a band at 3301 cm -1 and a clearly resolved shoulder at 3325 cm $^{-1}$. In both sait systems the bands are shifted to higher frequency compared with pure LPEI. These shifts originate in the disruption of the hydrogen bonds that occurs with the addition of salt.

3.3. Spectral changes in the LPEI bands at high salt concentrations

The changes in the spectra of LPEI-LiTT that occur with increasing salt concentration are especially interesting. Fig. 4 shows the Raman spectra of various LPEI-LITT compositions from 1400 to 1050 cm -1, a region which contains LPEI modes that are a complex mixture of C-H bending, N-H bending, C-C stretching and C-N stretching motions. Several triflate anion vibrations occur in this region as well. The spectrum of the 20:1 material closely resembles that of pure LPEI. with most of the LEPI bands slightly broadened and a loss of intensity in some of the weaker bands. However, in the 10:1 sample the bands have considerably broadened with a general collapse of vibrational band structure, so that there are only three very broad features originating in LPEI vibrations visible in this region. In the 5:1 sample the trend of band broadening and loss of



Fig. 4. IR absorption spectra of LPEI, LPEI-LiTf 5:1 and LPEI-NaTf 5:1 in the N-H stretching region.

63



Fig. 5. Raman spectra of LPEI-NaTf at 5:1, 10:1 and 20:1 compositions and pure LPEI in the polymer CH and NH bending and stretching regions.

structure continues. The band that first appears at 1223 cm⁻¹ in the 20:1 sample and continues to grow in intensity in the 10:1 and 5:1 samples is due to the triflate antisymmetric CF₃ stretching mode. In LPEI the strong band at 1290 cm⁻¹ and the weak band at 1264 cm⁻¹ become masked by the broad, triflate ion SO₃ antisymmetric stretching mode that grows in intensity with increasing salt concentration. We note that this phenomenon is observed throughout the entire vibrational spectrum: significant band broadening and a dramatic collapse of band structure in the LPEI modes so that only the triflate anion modes can be easily distinguished. These data strongly suggest that the LPEI-LiTf system is highly disordered at the 10:1 and 5:1 compositions.

Impedance measurements made of the LPEI-LITF 5:1 and 20:1 samples at 20 and 40°C show that these samples have a conductivity of $\sim 10^{-7}$ S cm⁻¹ at these temperatures. The conductivity of the 5:1 sample



Fig. 6. DSC traces of LPEI-LiTf 5:1, LPEI-LiTf 10:1, and LPEI from room temperature to 140°C.

was slightly lower than that of the 20:1 sample at both temperatures, but the differences may not be significant compared to the experimental error.

The effects of adding NaTf to LEPI are shown in Fig. 5 for the same spectral region as in Fig. 4. The same general trends of band broadening and collapse of band structure are observed in the NaTf system as in the LiTf system, although the 10:1 sample retains a little more band structure than the analogous LiTfsample. Therefore we conclude that the LPEI-NaTf system also becomes highly disordered at high salt concentrations. X-ray diffraction measurements of LPEI-LITT and LPEI-NaTT films at the 5:1 composition show that these samples are highly amorphous. Fig. 6 shows the DSC results for the LPEI-LiTf system. The large endothermic peak in the pure LPEI is attributed to the melting of crystalline LPEI. Upon addition of LiTT at a concentration of 10:1, the peak decreases dramatically, and at a concentration of 5:1, the crystalline LPEI melting peak has completely vanished. These observations are consistent with the collapse of vibrational band structure as seen in Figs. 4 and 5. These results are a little surprising, because Harris et al. reported the existence of a crystalline complex of LPEI-NaTI with a probable 4:1 stoichiometry [9]. The inconsistency between their results and ours possibly originates in slight differences in the synthesis of the parent LPEI or the preparation of the LPEI-salt system.

4. Conclusions

Polymer electrolytes based on poly(ethylenimine) provide an interesting and useful comparison to the more widely studied electrolytes based on poly-(ethylene oxide). In particular, studies of the ionic association present in the LiTf-PEI system clearly establish that the same ionic species are formed in the LiTf-PEI system as in the analogous PEO system, whereas the formation of species more highly associated than contact ion pairs seems to be suppressed in the NaTf-PEI system.

One significant difference between the PEI and PEO hosts is the extensive hydrogen bonding present in the former. The addition of salts to PEI disrupts the hydrogen bonding network and can be followed by the spectral changes in the N-H stretching region. At relatively high salt concentrations (between 20:1 and 10:1 compositions) in both LiTf- and NaTf-PEI the infrared transmission spectra undergo a change, with major band broadening and loss of structure attributed to a high degree of disorder in these systems.

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A vibrational spectroscopic study of lithium triflate in polyphosphazenes with linear oligoethyleneoxy side-chains of different lengths

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Abstract

A comparative vibrational spectroscopy study is reported for a series of polymer electrolytes composed of poly(oligoethyleneoxy phosphazenes) containing dissolved lithium triflate. These polymers, of the form $[NP((OCH_2CH_2)_xOCH_2)_x]$, with x = 0, 1, 2, or S, have been mixed with LiCF₃SO₃ in oxygen: lithium concentration ratios ranging from 10:1 to 40:1. Raman vibrational spectroscopy has been used to examine ionic association and local changes of the polymer as the salt concentration and the length of the ethylene oxide side-chains vary. The degree of ionic association of the triflate ion increases with increasing salt concentration. At a given salt concentration, the degree of ionic association and the nature of the ion-polymer interaction are dependent on the length of the side-chains. O 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyphosphazane; Lithium triflate; Raman spectroscopy; Ionic association; MEEP

1. Introduction

The potential importance of ionically conducting polymers as electrolytes in a variety of applications has stimulated intense interest in these systems. Extensive fundamental studies have been made into the mechanism of ionic conductivity is poly(ethylene oxide) (PEO) systems with dissolved salts such as LiCF ,SO₃ [1-3]. The dissolution of the salt into the PEO occurs through the coordination of the lithium ion by the ether oxygens. However, the conductivities of PEO systems are limited by their high degree of crystallinity. In polymer-salt systems the amorphous phase appears to be the primary conductivity pathway [4,5]. Consequently, the conductivity appears to be greatest in polymer electrolytes that are highly disordered or amorphous in nature. Synthetic strategies to enhance conductivity emphasize the preparation of single-phase polymers that are intrinsically amorphous.

Poly(bis - methoxyethoxyethoxysyphosphazeae) (MEEP) was first synthesized and studied as a polymer electrolyte by Shriver et al. [6] MEEP with dissolved LiCF_3SO_3 is amorphous over a temperature range of at least - 100 to 100°C and has room temperature conductivities much higher than analogous PEO- LiCF_3SO_3 systems. Other polymers based on the phosphazene backbone have been studied to determine the effect of different side-chains on ionic conductivity and physical properties [7-12].

To further our understanding of the fundamental interactions in phosphazene-based systems, we have undertaken a vibrational spectroscopic study of a series

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of poly(oligoethyleneoxy phosphazenes) containing dissolved lithium triflate. These polymers are of the form



where x = 0, 1, 2, or 5. We shall refer to these as x = 0, methoxyphosphazene, MP; x = 1, methoxyethoxyphosphazene, MEP; x = 2, methoxyethoxypthoxyphosphazene, MEEP; and x = 5, methoxy(ethoxy)₃phosphazene, ME₂P, and collectively as ME_xP.

2. Experimental

The materials used in the polymer synthesis were purchased from Aldrich and used as received unless otherwise noted. The precursor alcohols methanol, methoxyethoxyethanol and methoxyethoxethoxyethanol were distilled from CaH₂ prior to use. The longer chain alcohol (ME₃OH) was purified by fractional distillation from poly(ethylene glycol) monomethyl ether (350 average MW). The purity of the product was verified by 'H NMR and gas chromatography, and the compound was distilled from CaH₂ prior to use. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled prior to use. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical Co.) was recrystallized from beptane and sublimed at 40°C (0.05 mmHg).

The synthesis of these polymers follows literature procedure with only slight modifications [9]. The general synthesis is described here. Poly(dichlorophosphazene) was prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene at 250°C [13]. The appropriate alcohol was added slowly to a suspension of sodium hydride in THF and the mixture was stirred overnight until a clear solution resulted. Then a solution of poly(dichlorophosphazene) in THF was added dropwise to the resultant sodium alkoxide and the reaction was monitored by ³¹P NMR. After ~24 h of stirring at 25°C the reaction was complete and the reaction mixture was placed in dialysis against water for purification. Two weeks of dialysis in water was followed by I week of dialysis in methanol. Precipitation of the polymer into hexanes yielded the final product. The MP polymer was not precipitated into hexanes due to its slight solubility in that solvent. The resultant polymers were characterized by multinuciear NMR and GPC.

ME_xP polymers x = 1, 2, and 5 were dried under vacuum at ~45°C for 24 h. MP was dried under

vacuum at 35°C for 24 h. Lithium triflate, LiCF, SO, (LiTf) obtained from Aldrich, was dried under vacuum at ~120°C for 24 h. Tetrahydrofuran (THF) was stored over molecular sieves. All materials were stored in a nitrogen-atmosphere glovebox with moisture less than 1 ppm. Desired ratios of ME_P and LiTf were dissolved in THF in the glovebox and stirred for 48 h. The composition of the ME, P-LiTf systems is described by the O:Li ratio, which is the ratio of oxygen atoms from the side-chains to lithium atoms. We have employed this system rather than a monomer:lithium ratio to more easily compare the coordination between the ME, P polymers having different lengths of sidechains. To obtain thin films of the samples, the polymer solutions were cast onto glass slides and the THF was allowed to evaporate at room temperature in the glovebox. The resulting films were dried under vacuum for 48 h at ~ 35°C.

Raman spectra were taken using the ISA Jobin-Yvon T64000 Raman spectrometer. The 514 nm line of an argon laser was used as the exciting line at a power of 300 mW. The Raman spectra of the films were taken in a backscattering geometry under a microscope.

Curve fitting analysis was accomplished using a commercial program (Galactic Grams version 5.05). Spectra were curve-fit to a straight base line and one Gaussian-Lorenzian product function for each band using a non-linear least squares method.

3. Remits and discussion

3.1. Ionic speciation

The existence of 'free' ions, ion pairs, and more highly associated ionic species can be inferred from the vibrational spectrum in the triflate anion CF₃ symmetric deformation, $\delta_0(CF_3)$, region [14]. The trend seen for the triflate anion is that a higher frequency in the $\delta_0(CF_3)$ mode occurs for a higher degree of association of the anion with the cation [15]. Curve-fitting analysis of the $\delta_0(CF_3)$ mode in the ME₂P-LiTf systems identified frequencies of 751-752 cm⁻¹ for the 'free' ion, 755-757 cm⁻¹ for the ion pair, and 760-761 cm⁻¹ for the triple ion [Li₂Tf]⁺. These assignments are in accordance with ab initio calculations of LiTf species [16] and spectroscopic studies of PEO [3,17] and glyme [15] systems with dissolved LiTf.

Fig. 1 shows the Raman spectra in the triffate ion $\delta_i(CF_3)$ region for the four ME_xP polymers at a LiTf concentration of 40:1. In all four ME_xP systems the triffate anion occurs primarily as a contact ion pair, with some 'free' ion present. Fig. 2 shows the $\delta_i(CF_3)$ region for the four polymers at a concentration of 10:1. At this concentration in all four systems the triffate anion is found mostly as the triple ion species, [Li₂Tf]⁺,



Fig. 1. Raman spectra of ME_x P:LiTf at the 40:1 concentration in the $\delta_x(CF_1)$ region.

with some contact ion pairs, and no 'free' ions. In all four ME_P-LiTf systems the degree of ionic association increases with increasing LiTf concentration.

The concentration dependence of the triflate species can be estimated from the spectral data in Figs. 1 and 2. The contribution of each species to the total integrated intensity of the $\delta_{i}(CF_{i})$ spectral region is calcu-



Fig. 2. Raman spectra of ME_x P:LiTf at the 10:1 concentration in the $\delta_x(CF_3)$ region.

Table 1

Percent of each triflate ionic species in ME₂P:LiTf systems from curvefitting the $\delta_{q}(CF_{3})$ band.

10:1	MP (%)	MEP (%)	MEEP (%)	ME,P (%)
Free	÷	_	-	-
Pair	36	6	4	7
Triple	64	94	96	93
40:1				
Free	26	2	12	24
Pair	74	98	88	76
Triple	-	-	-	-

lated by the curve-fitting procedure described earlier. With the assumption that the relative concentrations are reflected in the fractional integrated intensities, the data in Table 1 allow a reasonable estimate to be made of the relative amounts of each species present.

Table 1 shows that in the ME₄P:LiTf 10:1 systems the triflate ion exists almost entirely as the $[Li_2Tf]^+$ triple ion for x = 1, 2, 5, with a very minor contribution from contact ion pairs. Further, there is little dependence of the triflate speciation on side-chain length in these three 10:1 systems. In contrast, in the x = 0 (MP) system the triple ion is still the dominant species, but there is a significant contribution from ion pairs. In none of the systems at the 10:1 concentration are there measurable amounts of 'free' ion.

In the ME_xP:LiTf 40:1 systems there are no triple ions observed for any side-chain length. In the MP system (x = 0), there are 74% ion pairs and 26% 'free' ions. The contribution of free ions abruptly drops in the MEP system and then begins to increase with increasing side-chain length, reaching 24% 'free' ion in the ME_yP:LiTf 40:1 system. These data, taken together with the 10:1 data, show that LiTf interacts with MP in a somewhat different manner than with the polymers containing ether oxygen atoms in the side-chains.

The ionic conductivity has been shown by Allcock et al. [9] to achieve a highest room temperature value of 2.7×10^{-3} S cm⁻¹ in the MEEP-LiTf system at a concentration of 24:1 (O:Li). Interpolation of the data in Table 1 shows that 'free' ions are present to a very small extent, a concentrations supported by additional data (not shown) at concentrations between 10:1 and 40:1. The relatively small presence of 'free' ions over this concentration range in the highly conducting MEEP system is surprising in view of previous reports [14,18] that 'free' ions are the primary charge carriers in polymer electrolytes.

3.2. Ion-polymer interaction

Fig. 3 compares MEEP, MEP and ME₃P with and without LiTf in the spectral region from 680 to 600 cm⁻¹. Earlier work by Allcock et al. [11] of a MEEP-LiTf-DMSO system via NMR and MD reported minimal interaction between the nitrogen and the lithium, with the interaction occurring primarily between the Li and the two oxygen atoms that are not directly attached to the P of the backbone. The large peak at 630 cm⁻¹ in these three polymers appears, from comparison to model compounds [19,20], to originate in phosphazene backbone vibrations involving P-O and P-N bending and stretching motions. When LiTf is added to these three polymers at a concentration of 10:1, this band exhibits only a small shift to 634 cm⁻¹ (as shown by the dashed lines in Fig. 3). This indicates that the backbone vibrations are only slightly affected by the



Fig. 3. Raman spectra of $ME_{z}P$ and $ME_{z}P$:LiTf 10:1 in the P-O and P-N bending and stretching region.

addition of LiTf to the ME_P polymers containing ether oxygen atoms in the side-chains.

The behavior of the MP (x=0) system in this spectral region differs markedly from that of the x = 1, 2, 5systems. Fig. 4 shows a band around 596 cm $^{-1}$ with a shoulder, which curve-fitting reveals to be two bands, a large band centered at 596 cm $^{-1}$ and a smaller band at 615 cm⁻¹. These bands appear to arise from the same vibrations as the band at 630 cm⁻¹ in the ME_zP systems with x = 1, 2, 5. Upon addition of LiTf at a concentration of 10:1, a complex band structure appears. Curve-fitting of the band in the MP:LiTf spectrum reveals three distinct peaks at 642, 602, and 580 cm⁻¹. The band at 580 is the triffate $\delta_{m}(CF_1)$ mode. The MP band at 596 cm⁻¹ shifts to 602 cm⁻¹, and the band at 615 cm⁻¹ shifts to 642 cm⁻¹ and increases in intensity. The large shifts of these bands suggest that the degree of interaction of between the nitrogen and the lithium cation is significantly greater in the MP-LiTf system than in the ME, Ps bearing longer sidechains. This is not surprising, since each MP side-chain



Fig. 4. Raman spectra of MP and MP:LiTf 10:1 in the P-O and P-N bending and stretching region.

has only a single methoxy oxygen to coordinate the lithium ion.

4. Conclusions

For the x = 1, 2, 5 ME_xP-LiTf systems at the 40:1 concentrations, the percentage of free ion increases as side-chain length increases, whereas at the 10:1 concentrations, the triple ion predominates regardless of sidechain length. In contrast, in the MP-LiTT system (x = 0) these trends are not followed. There is a high percentage of free ions at the 40:1 concentration, and a substantial amount of ion pair present in the 10:1 concentration. Taken together these data suggest that some factor other than the side-chain length affects cation-anion interactions in the MP system. The vibrational mode identified as originating in the phosphazene backbone appears almost unaffected by the addition of LiTT for the x = 1, 2, 5 ME, Pr; but when LiTf is added to MP, substantial changes occur in this spectral region. This observation combined with the ionic association data suggests that these differences might be due to the oxygen atoms attached to the phosphazene backbone being involved more extensively in coordinating the Li ion in MP as compared to the MEP, MEEP, and ME₁P systems. Alternatively, the nitrogen atom may play a role in coordinating the Li ion in the MP system, in contrast to the x = 1, 2, and 5systems.

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An experimental and computational investigation of the structure and vibrations of dimethylethylenediamine, a model for poly(ethylenimine)

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A combination of hybrid Hartree-Fock/density functional calculations and Raman and IR spectroscopy has been used to perform a vibrational analysis of N/M-dimethylethylenediamine (DMEDA) and provide band assignments for the experimental spectroscopic data. The structures and vibrational frequencies of asveral low energy conformations of DMEDA were calculated. The lowest energy structure was found to be TGT with a single instanolocular hydrogen bond. The effect of intramolecular hydrogen bonding on the structures and vibrational frequencies was investigated. Liquid DMEDA is found to be predominantly a mixture of two conformations: TGT with one intramolecular hydrogen bond and TGT with no intramolecular hydrogen bonds.

Introduction

The potential importance of ionically conducting polymers as electrolytes in a variety of applications, including rechergeable batteries, has simulated intense interact in these systems? A wide variety of studies have focused on driveloping a molecular level understanding of the flactors controlling insic conductivity in poly(ethylene oxide) -east systems? Several theoretical and experimental studies have been done on small molecule oligomers of poly(ethylene oxide) (PBO) (glymet) is order to better understand the interactions within these systems?¹⁶ Fundamental investigations into the nature of interactions in polymer electrolyie systems can be complemented by considering a polycer having a backbone structure similar to that of PEO, but with a non-oxygen hearo-atom. Linear poly(ethylenimine), or PEI, [CH{CH}NH], is structurally analogous to PEO, with an N-H group in place of the oxygen, PEI-based electrolytes have been statisfied by several group!.²¹

In order to understand the polymar-ank interactions in FEI systems, it is first necessary to have knowledge of the vibrational modes of PEI. The simplest model compound for PEI is NN-dimethylethylenedisemine (DMEDA, <u>First</u>.)). By conducting a complete vibrational analysis of DMEDA, one should be able to bener understand the vibrations of poly(ethyletimine) and golymar electrolyses based on a poly(ethyletimine) host. In addition to obtaining the experimental Ramas and IR spectra of DMEDA, it is useful to employ computational methods in order to calculate the structures and vibrational frequencies of DMEDA. With the use of hybrid Hatrue-Fock/density functional methods, we have stadied the vibrations of several different conformations of DMEDA and assigned frequencies is the experimental vibrational spectrum.



FIG. 1 DMEDA.

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Methodology Experimental

N,*N*-dimethylethylenediamine (DMEDA) 99% was obtained from Aldrich and stored in a dry sitrogenatmosphere glovebox. Infrared spectra were recorded with a Brukar IFS66V FT-IR over a range of 4000 to 500 cm²¹ at a ranolution of 1 cm⁻¹. The DMEDA liquid was put between ZaSe plates in a sealed sample holder in the glovebox. The IR spectra were taken under dry air parge. Raman spectra were collected using a Jobis-Yvon T64000 Raman spectroweter with a CCD detector. The S14.5 am line of an argon ion laser at a power of 300 mW at the laser head was used for excitation. Spectra were collected is a 90° scattering geomstry. Raman samples were sealed in cuvettes inside the glovebox. Curve fitting analysis was accompliabed using a commercial program (Galactic Grams version 5.05). Spectra were curve-fitted to a straight baseline and one Genessian-Lorenzian product fraction for each band using a non-linear lenst squares mshod.

Computational

The B3LYP hybrid Hartree-Fock/density functional method²²¹ was used to perform complete geometry optimizations and vibrational frequency calculations on dimethylesediamins. The three-parameter HP/DF method employs a weighted sum of Hartree-Fock $E_{\rm X}$ ⁽¹⁰⁾, local DF, and gradient corrected DF expressions for the exchange and correlation energies as in the following equation:

$$E = aE_{\pi}^{\text{flow}} + (1 - a)E_{\pi}^{\text{flow}} + bE_{\pi}^{\text{flow}} + cE_{\pi}^{\text{flow}} + (1 - c)E_{\pi}^{\text{VWH}}$$

where $\mathcal{E}_{\rm X}^{\rm Basis}$ is Shater's local spin density functional for exchange $^{\rm M}$ $\mathcal{E}_{\rm X}^{\rm Basis}$ is Becks's gradient corrected exchange functional 23 $\mathcal{E}_{\rm X}^{\rm VWH}$ is the local density correlation functional of Vosko, Wilk and Nussis.⁶ and $\mathcal{E}_{\rm X}^{\rm VT}$ is the gradient corrected correlation functional of Lee, Yang, and Parr.⁷⁷ Coefficients giving the relative weights of verients approximations for the exchange and correlation energies in this method were optimized to reproduce thermochemical data for a variety of small molecules using a slightly different correlation functional.²⁸ Unlaws

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Paper

otherwise noted, all calculations reported here were performed using the 6-31G(d) split-valence plus polarization basis set²⁹ This basis set was chosen because it accurately reproduces the structures and vibrational spectra of modium-sized organic molecules and is small enough for rapid calculations.

The quantum chemistry program GAUSSIAN947 was used for all calculations. Berny's optimization algorithm was used to perform full geometry optimizations in C_1 symmetry. It was discovered that DMEDA(0) and DMEDA(2) have a 2-fold rotation axis and they were therefore reoptimized in C2 symmetry. Harmonic frequency calculations were performed at the optimized geometries without correcting for anharmonicity. It has become customary to scale calculated frequencies to facilitate comparisons with experiment and we chose to use the multiplicative scaling factors of Scott and Radond¹ All frequencies less than 1000 cm¹ are multiplied by 1.0013 and all frequencies greater than 1000 cm² are multiplied by 0.9614.

Vibrational mode assignments were performed by animating each mode using the program XMOC² and nd bw comparing the modes of one geometry to another using the ViPA, an acronym for Vibrational Projection 0000000 program VIPA, an acconym for violational Projection Analysis.³³⁻³³ The VIPA program exploits the vector properties of vibrational modes to assess the similarity between modes of an object molecule and a structurally similar basis molecule. The program first aligns the two molecules and calculates each molecule's no modes and vibrational frequencies. For each molecule, each of the normal vibrational modes is a column vector, which is orthonormal to all other normal modes of the same molecule. The vector projection operation is done by

sequentially projecting each normal mode of the object molecule on the modes of the basis molecule. The similarity of any mode of the object molecule to any mode similarity of any mode of the object molecule to any mode of the basis molecule can then be expressed as a percentage by calculating the sum of the squares of the matrix elements and multiplying by 100. Vibrational projection analysis has been used to compare normal modes modified by isotopic or chemical substitution, oxidation-reduction and non-covalent contacts.¹³⁻¹⁶

Computational resu

Geometry optimizations were performed on DMEDA and the lowest energy structure was determined to have a TGT conformation, signifying that the first torsional angle (C-N-C-C) has a trans conformation corresponding to an angle of $180 \pm 60^\circ$, T, the second torsional angle (N-C-C-N) has again to conformation corresponding to a torsional angle $60 \pm 60^{\circ}$, G, and the third torsional angle (C-C-N-C) also adopts a trans conformation.

There are three possible structures of DMEDA having TGT conformations, These will be henceforth referred to as DMEDA(0), DMEDA(1), and DMEDA(2), (see Fig. 2a-c) with their main differences being in the central N-C-C-N torsional angle and the presence of intramolecular hydrogen bonding. DMEDA(0) has so hydrogen bonding, DMEDA(1) has DMEDA(0) and no hydrogen bonding, DMEDA(1) has one hydrogen bonding interaction and DMEDA(2) has two hydrogen bonding interactions. Fig. 3e-c show Newman projections along the central C-C bond with the methyl groups deleted. DMEDA(1) and DMEDA(2) are the lowest energy structures of eight possible conformations of DMEDA,



Fig. 2 The TGT conformations of DMEDA. (a) DMEDA(0), (b) DMEDA(1), (c) DMEDA(2). Click on the images or have to view 3D structures.



Fig. 3 Newman projections of DMEDA with mathyl groups deloted. (a) DMEDA(0), (b) DMEDA(1), (c) DMEDA(2). Click on the images or least to view 3D structures.

while the aext highest in energy are TTT, GGG, TTG, DMEDA(0), TTG and GTG. The energy difference between the lowest energy, DMEDA(1) structure and the highest energy DMEDA(0) structure is 3.13 local mol⁻¹. DMEDA(2) is only 1.53 local mol⁻¹ higher in energy than DMEDA(1), DMEDA(2), and DMEDA(2), here G DMEDA(2) is only 1.53 kcal mol⁻¹ higher in energy than DMEDA(1). DMEDA(0) and DMEDA(2) have C_2 symmetry and are more symmetrical than DMEDA(1). Table 1 shows the relative energies and dipole moments for low energy conformations of DMEDA. Calculated bond distances, bond angles, and torsional angles for the three TGT conformations of DMEDA are presented in Table 2. The C-N bond distances in these three conformations range from 1.455-1.464 Å, slightly smaller than the experimentally determined C-N

smaller than the experimentally determined C-N bond distance for methylamine, 1.47 λ^{17} The C-C

bond distance for DMEDA(0) and DMEDA(2) is calculated to be 1.530 Å, while the C-C bond distance for DMEDA(1) is 1.527 Å. These are very comparable to the C-C single bond distance of 1.54 Å in ethane. All calculated C-H distances in the three conformations are quite similar and they range from 1.095 to 1.112 Å, close to the C-H distance in methane, 1.11 Å. The calculated N-H distances for these conformations range from 1.017 to 1.020 Å.

The calculated bond angles of the two conformations are unremarkable. The calculated ∠C-N-C range from 113.4° to 113.1°, greater than the $\angle C-N-C$ value in trimethylamine of 108.7°.

Table 1 Comparison of relative energies and dipole moments for eight conformations of DMEDA

	Energy/kcal mol ⁻¹	Dipole moment/D	
DMEDA(1)	0°	0.941	
DMEDA(2)	1.54	0.043	
TTT TT	2.06	0.000	
GGG	2.10	2.042	
TTG	2.93	1.379	
DMEDA(0)	3.13	0.941	
TGG	4.00	1.256	
GTG	4.27	1.910	

"The actual total energy for DMEDA(1) is calculated to be -269.1307EL

Table 2 Comparison of the bond distances (.), selected bond angles ("), and torsional angles (") for the three TGT conformations
of DMEDA	

	DMEDA(0)	DMEDA(1)	DMEDA(2)
C2-NS	1.455	1.459	1.460
C2-H1	1.095	1.095	1.095
C2-H3	1.097	1.096	1.096
C2-H4	1.105	1.106	1.106
NSC6	1.456	1.464	1.463
C6-H7	1.102	1.097	1.106
C6-H8	1.109	1.107	1.098
C6C9	1.530	1.527	1.530
C9-H10	1.109	1.099	1.098
C9-H11	1.102	1.112	1.106
C9-N12	1.456	1.455	1.463
N12-C13	1.455	1.454	1.460
C13-H14	1.095	1.095	1.095
C13-H15	1.097	1.108	1.096
C13-H16	1.108	1.097	1.106
NSH17	1.017	1.020	1.019
N12-H18	1.017	1.019	1.019
C2-N5-C6	113.3	113.4	113.1
NS-C6-C9	112.6	110.4	111.1
C6-C9-N12	112.6	110.4	111.1
C9-N12-C13	113.3	113.4	113.1
C9-N12-H17	109.7	108.5	107.4
C6-N5-H18	109.7	107.3	107.4
C2-N5-C6-C9	166.0	185.8	169.9
NS-C6-C9-N12	46.7	62.9	53.2
C6-C9-N12-C13	166.0	189.3	169.9

For DMEDA(0), the C-C-N-C angles have a value of 166.0° and the N-C-C-N angle is 46.7°. For DMEDA(2) the C-C-N-C angles are 169.9° and the N-C-C-N angle is 52.3°. The H-N-C-C angles both have values of 42.0° for DMEDA(0) and -70.9° for DMEDA(2). For DMEDA(1), one side of the molecule has a C-N-C-C angle of 185.8° and the other side of the molecule has a C-N-C-C angle of 189.3°. The central N-C-C-N angle is 62.9°. The H-N-C-C angles are 64.5 and -48.2°.

A possible reason for the structural differences between DMEDA(0), DMEDA(1) and DMEDA(2) is intramolecular hydrogen bonding (N-H- \cdot N). In the structure of DMEDA(0), the distance from each nitrogen to the opposite amins hydrogen is 2.854 Å. In DMEDA(1), the distances from a nitrogen to the opposite amine hydrogen are 2.444 and 3.306 Å. In DMEDA(2), the distance from each nitrogen to the opposite amine hydrogen bonds, So DMEDA(0) has no intramolecular hydrogen bonds, DMEDA(1) has one intramolecular hydrogen bonds. Typically hydrogen bonds are linear and display shorter N-H--N distances; however, this is not always the case, especially in cases of intramolecular hydrogen bonding where the geometry of the molecule forbids if a the case of DMEDA(1) the N-H--N angle is 107.5°, while for DMEDA(2) the angle is 95.0°. Although the hydrogen

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Table 3 Scaled ¹¹	calculated vibrational fre	numeracies (cut ⁱ) mode sesie	mments and IR intensities	
Lable 2 Scaled	CITCRINER AIDLERNING TO	Magnetics (cut 1 minute quar	CHICKENS, AND LIV. ICHERNICHE	

Mode assignment	Mode	Sym.	Frequency	IR intensity
				6
Mathyl war: N-H band	t	R	59	3
NCCN torsion: methyl wag	ż	Ā	16	ō
Methyi wag	3	Ă	125	ō
Mathyl twist	4	Ä	221	2
Mathyl twist	5	B -	257	ī
Methyl twist: CH rock	6	Ā	284	ī
C-N-C bend: (out-of-phase)	7	B	313	3
C-N-C bend (in-obase)	1	Ā	340	3
C-N-C bend (out-of-phase); CH twist	9	B	564	57
N-H per bend (out-of-phase)	10	B	727	153
N-H per bend (in-phase)	11	A	752	6
CHe rock: CHe twist	12	B	892	0
N-H per bend (in-phase); CH twist; methyl wag	13	A	902	0
Methyl wag: CH wag	14	B	990	12
C-C stretch	15	Α	1010	0
CH ₂ rock; N-H perallel bend	16	A	1022	0
Methyl wag; N-H parallel bend	17	B	1092	2
Methyl wag: CH twist	18	Α	1112	76
CN stretch (out-of-phase)	19	В	1115	23
CN stretch (in-phase) C-C stretch	20	A	1144	2
Methyl wag; CH rock	21	B	1153	0
CH ₂ rock; methyl symmetric deformation	22	A	1195	0
CH ₂ twist	23	A	1251	7
CH ₂ twist; methyl symmetric deformation	24	B	1255	33
CH ₂ wag	25	B	1353	1
CH ₂ wag	26	Α	1359	0
Methyl symmetric deformation (in-phase)	27	A	1428	5
Methyl symmetric deformation (out-of-phase)	28	B	1429	10
N-H parallel bend; methyl antisymmetric deformation	29	A	1448	38
N-H parallel bend; methyl antisymmetric deformation	30	B	1450	3
Methyl antisymmetric deformation	31	A	1459	7
N-H parallel; mothyl antisymmetric deformation	32	B	1462	22
CH ₂ scissors; methyl antisymmetric deformation	33	B	1482	t
Methyl antisymmetric deformation	34	A.	1485	l
CH ₂ scissors; methyl antisymmetric deformation	35	B	1493	1
CH ₂ scissors	36	Α	1497	7
CH ₂ stretch	37	B	2799	116
CH ₂ stretch; CH ₃ stretch	38	A	2809	193
CH ₃ stretch	39	B	2824	96
CH ₃ stretch; CH ₂ stretch	40	A	2826	7
CH ₂ stretch	41	A	2887	94
CH ₂ stretch	42	B	2905	80
CH ₁ stretch; CH ₂ stretch	43	B	2945	15
CH ₃ stretch	44	Α	2946	30
CH ₃ stretch; CH ₄ stretch	45	B	2995	41
CH ₃ stretch; CH ₃ stretch	46	A	2996	0
N-H stretch (out-of-phase)	47	B	3373	0
N-H stretch (in-phase)	48	Α	3373	

bonds in DMEDA are probably weaker than conventional hydrogen bonds, it is not unreasonable to conclude that the hydrogen bond in DMEDA(1) is stronger than the hydrogen bonds in DMEDA(2), since the total energy for DMEDA(1) is lower and the hydrogen bonding distance is shorter than DMEDA(2). The energy difference between the non-hydrogen-bonded structure, DMEDA(0) and the singly hydrogen bondes structure, DMEDA(1), is 3.13 kcal mol⁻¹. N-H--N bonds typically have energies of 2-6 kcal mol^{-1,3,40} This also implies that the energy difference between DMEDA(0) and DMEDA(1) may be due to the presence of hydrogen bonding.

Calculated vibrational modes

Each of the conformations of DMEDA has 48 vibrational modes. We will examine in detail the vibrations of the three TGT conformations. Emphasis will be placed on the modes that have the highest infrared intensities, especially those that differ significantly for different conformations, since we can qualitatively compare these with experiment.

Table 3 presents the scaled calculated vibrational sencies, IR intensities, and mode assignments for DMEDA(0). DMEDA(0), possessing no hydrogen bonding, has a 2-fold rotation axis through the central C-C bond. The lowest vibrational frequency of DMEDA(0) is at 59 cm⁻¹ and is assigned to a mixture of methyl wagging and N-H bending. The next highest frequency at 86 cm also has some methyl wagging as well as torsional motion about the N-C-C-N angle. The next four modes, calculated at 125, 221, 257 and 284 cm¹, have the preponderance of the motion concentrated on of the methyl groups. We then have calculated frequencies involve bending of the C-N-C angles. These modes can be divided into in-phase (340 cml) and out-of-phase (313 and 564 cmi⁴) groups. Calculations show that there are three modes with significant contribution from N-H bending perpendicular to the long axis of the molecule occurring at 727, 752 and 902 cm⁴. The modes involving CH₂ rocking are calculated to occur at 892, 1022 and 1195 cm⁻¹. The C-C stretch is calculated at 1009 cm¹ and the calculated C-N stretches are at 1115 cml (out-ofphase) and 1144 cm¹ (in-phase). In the region from 1150-1500 cm⁻¹, calculations show a plethora of different types of modes involving the hydrogens. We calculate modes that have primarily methyl wagging at 1153 cm². CH₂ twisting at 1251 and 1255 cm², and CH₂ wagging at 1353 and 1359 cm⁻¹. The symmetric methyl deformations are at 1428 and 1429 cm⁻¹ and there are two modes assigned to methyl antisymmetric deformations at 1459 and 1485 cm¹. Three mod es involving N-H bending parallel to the axis of the moiscule are at 1448, 1450 and 1462 cml. The modes primarily assigned to acissoring of the CR groups are at 1482, 1493 and 1497 cm⁴. There are ten calculated frequencies that are C-H stretches and the two highest vibrational frequencies are, of course, N-H stretches. The modes for the N-H stretches are also separated into in-phase (3373 cm^{-1}) and out-of-phase (3373 cm^{-1}) motions.

Table 4 shows the scaled, calculated vibrational frequencies, mode assignments, and infrared intensities of DMEDA(1). The mode assignments for the vibrational frequencies of DMEDA(1) are, in general, quite similar to the assignments of DMEDA(0). However, due to the lowering of the symmetry, we see instances in which a particular motion that was previously associated with both ends of the molecules in DMEDA(0) is now concentrated only on one particular end of the molecule. Instances of this will be pointed out in the following discussion of the vibrational modes of DMEDA(1).

The two lowest calculated vibrational frequencies of

DMEDA(1) are at 91 and 101 cm¹ and have been as to methyl wagging. The next four modes, 165, 244, 251 and 277 cm⁻¹ involve mostly methyl twisting. We have one mode (359 cm⁴) containing large contributions from in-phase C-N-C bending and two modes (316 and 564 cfl) containing significant amounts of out-of-phase C-N-C bending. The major contributions for the next five mo occurring at 788, \$25, 904, 912 and 984 cml are N-H bending perpendicular to the axis of the molecule. The ed C-C strutch for this conformation is at 999 cati, wer by 10 cm⁻¹ than the C-C stretch for DMEDA(0). There are three calculated modes in which the C-N strutching motion has the greatest contribution. At 1098 cm⁻¹ the C-N strutching is concentrated on one end of the molecule, at 1115 cm⁻¹ the C-N stretching is conc on the opposite and of the molecule, and at 1134 crif the C-N structing motion is approximately equally distributed on each and of the molecule. The calculated frequencies between 1150-1500 cmf are again a mixture of many different types of motions involving the hydrogens. The modes at 1342 and 1362 call are mostly methyl wagging The symmetric methyl deformations are calculated at 1425 and 1428 cm⁻¹ . This is noteworthy because each of the modes is mostly concentrated on one perticular methyl group. There is primarily V-H bending parallel to the axis of the molecule in the modes at 1444 and 1451 cm² and e axis soring very definitely predominates in the mode CH₂ sci at 1476 and 1491 cm⁴. The antisymmetric methyl deformations are at 1459, 1461, 1482 and 1486 ctfl. The n calculated C-H stretches are similar to the DMEDA(0) and they occur between 2771 and 3000 cff. Unlike is DMEDA(0), the N-H stretches are each concentrated on one end of the molecule and occur at different frequencies (3338 and 3363 cm¹).

Table 5 shows the scaled harmonic vibrational frequencies, mode assignments, and infrared intensities calculated for the TGT conformation of DMEDA that has two hydrogen bonds, DMEDA(2). The vibrational modes are most similar to those of DMEDA(0), since DMEDA(2) also has C_1 symmetry. The lowest calculated vibrational frequency for DMEDA(2) is assigned to methyl wagging and is calculated at 66 cml⁴. The next highest frequency, at 101 cm², has been assigned to an N-C-C-N torsion. There is methyl wagging at 151 cm and then methyl twisting at 214, 250, and 299 cm². The out-of-phase C-N-C bend is at 320 cml and the in-phase C-N-C bending is at 342 cml1. The mode at 559 cm1 is comprised of CH₂ twisting and C-N-C bending. There are out-of-phase and in-phase perpendicular bending modes of the N-H groups at \$18 and \$35 cm², respectively. A ig modes is a combination of CH rocking and Nmode at \$53 cm⁻¹ H perpendicular bending and modes at 945 and 976 cfl are a mixture of N-H perpendicular bending and mathy wagging. The C-C stretch is calculated at 1006 cm². The davi lculated at 1036 cml¹ is assigned to CH₂ rocking and N-H parallel bending. The out-of-phase and in-ph thes are calculated at 1089 and 1138 cdf. C-N stret respectively. There is a calculated mode at 1104 cm² that is assigned to a combination of methyl wagging and CH₂ twisting. The mode at 1111 cm¹ has CH₂ rocking, methyl wagging, and CH2 twisting character. The modes calculated at 1162, 1183 and 1256 cml are assigned to methyl wagging and CH twisting. A mode at 1287 cm is primarily CH2 twisting, while the modes at 1347 and 1370 cm⁻¹ are mostly CH2 wagging. The two modes calculated at 1425 and 1426 cm⁻¹ are both assigned to symmetric methyl deformations. Modes assigned to Nparallel bending mixed with

Methyi wag 1 91 2	
Methyl was 2 101 3	
Mashal main (L. sack	
Methyl mitr CH met 6 277 1	
(min)	
C-N-C bend (in chase) 2 3 59 1	
C-N-Chend (out-of-phase) 9 564 0	
N-H ner band: CH, met: CH, mist	
N-H or band CE mck 11 #25 77	
N-H or bend; CFL regist 12 904 15	
N-H par bend (12) CH, was methy was 13 912 23	
N-H parallel head (12): methyl deformation (antisymmetric) 14 984	
N-H neraliei bd (S): ("Ik mek: methyl deformation (antisymmetric) 16 1022 II	
C-N stratch (2.5) 17 1098 30	
Methyl deformation (antisymmetric) (13): CH twist 18 1102 4	
C-N stretch: methyl deformation (
C-N stratch 20 1134 23	
CHe rock: methyl deformation (antisymmetric) 21 1163 8	
CH rock methyl was	
CH. twist: CH. mck 23 1248 3	
CH. med: CH. twist 24 1268 9	
CH, was 25 1342 20	
CH, was 26 1362 3	
Methyl deformation (symmetric) (2) 27 1425 7	
Methyl deformation (symmetric) (13) 28 1428 4	
N-H per bend (5): CH scissors 29 1444 15	
N-H par bend: methyl def (a): CH wag 30 1451 34	
Methyl deformation (antisymmetric) 31 1459 9	
Methyl deformation (antisymmetric); N-H parallel band 32 1461 5	
CH_sciences 33 1476 17	
Methyl deformation (antisymmetric); CH scissors 34 1482 14	
Methyl deformation (antisymmetric) 35 1486 8	
CH ₂ scissors 36 1491 4	
CH ₂ stretch 37 2771 86	
CH ₃ stretch 38 2822 129)
CH ₂ stretch; CH ₃ stretch 39 2831 61	
CH ₂ stretch; CH ₃ stretch 40 2842 13	3
CH ₂ stretch 41 2930 44	
CH ₃ stretch 42 2944 57	
CH2 stretch 43 2957 19	
CH2 stretch; CH5 stretch 44 2958 48	
CH3 stretch 45 2993 37	
CH ₃ stretch 46 3000 33	
N-H stretch 47 3338 1	
N-H stretch 48 3363 7	

Table 4 Scaled¹¹ calculated vibrational frequencies (cnl¹), mode assignments, and IR intensities for DMEDA(1)

antisymmetric deformation appear at 1437, 1454 and 1488 cm⁻¹ and there are modes assigned exclusively to methyl antisymmetric deformation at 1460, 1461 and 1484 cm⁻¹. The CH₂ scissoring modes occur at 1471 and 1475 cm⁻¹. The next ten highest modes are C-H stretches and the two highest modes are N-H stretches, occurring at 3347 (in-phase) and 3353 cm⁻¹ (out-of-phase).

A comparison of Tables 3, 4 and 5 shows several interesting trends. Modes involving N-H bending perpendicular to the axis of the molecule, CH₃cocking. C-N stretching or C-N-C bending change significantly in frequency between the three conformations. In contrast, modes involving the N-H bend parallel to the axis of the molecule, methyl deformations. C-C stretch or CH₂ scissors show little or no frequency change between the different conformations. The N-H stretches are lower in frequency in the hydrogen-bonded conformations than in DMEDA(0), as is expected; however, the frequency of the hydrogen-bonded N-H stretch of DMEDA(1) is higher (3363 cm⁴) than one would expect from comparison with DMEDA(2).

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Mode assignment	Mode	Sym.	Frequency	IR intensity
Methyl wag	I	В	66	7
NCCN torsion	2	Α	101	1
Methyl wag	3	Α	151	1
Methyl twist	4	Α	214	0
Methyl twist	5	B	250	1
Methyi twist; CHe rock	6	Α	299	5
CNC bend (out-of-phase)	7	B	320	4
CNC bend (in-phase)	8	A	342	1
CH ₂ twist; CNC bend	9	B	559	0
N-H per bend (out-of-phase)	10	A	\$18	58
N-H par bend (in-phase)	u	B	835	119
CH ₂ rock; N-H par bend	12	B	853	5
N-H par bend; methyl wag	13	A	945	10
N-H par bend; methyl wag	14	B	976	9
C-C stretch	15	Α	1006	2
CH ₂ rock; N-H par bend	16	Α	1036	1
C-N stretch (out-of-phase)	17	B	1089	44
Methyl wag; CH ₄ twist	18	A	1104	2
CH2 rock; methyl wag; CH2 twist	19	B	1111	58
C-N stretch (in-phase)	20	A	1138	4
Methyl wag; CHe twist	21	A	1162	12
Methyl wag; CHe twist	22	В	1183	5
CH2 twist; methyl wag	23	B	1256	17
CH ₂ twist	24	A	1287	2
CH ₂ wag	25	B	1347	23
CHi ₂ wag	26	Α	1370	5
Methyl symmetric deformation (out-of-phase)	27	В	1425	12
Methyl symmetric deformation (in-phase)	28	A	1426	0
N-H par bend; methyl antisymmetric deformation	29	B	1437	28
N-H per bend; methyl antisymmetric deformation	30	A	1454	3
Methyl antisymmetric deformation	31	В	1460	22
Methyl antisymmetric deformation	32	A	1461	0
CH2 scissors; methyl antisymmetric deformation	33	В	1471	17
CH ₂ acisaors	34	A	1475	4
Methyl antisymmetric deformation	35	B	1484	6
N-H per bend; methyl antisymmetric deformation	36	•	1488	7
CH ₂ stretch	37	<u>A</u>	2834	17
CH ₃ and CH ₂ stretch	38	B	2838	131
CH ₃ and CH ₂ stretch	39	<u>A</u> .	2841	12
CH ₃ and CH ₂ stretch	40	B	2545	198
CH ₂ stretch	41	B	2946	36
CH ₂ stretch	42	A	2947	41
CH ₃ stretch	43	B	2953	95
CH ₃ stretch	44	A	Z954	1
CH ₃ stretch	45	B	2997	3
CH ₃ stretch	46	A	2997	67
N-H stretch	47	B	3347	0
N-H stretch	48	<u>A</u>	3353	U

Table 5 Scaled¹¹ calculated vibrational frequencies (cnl¹), mode assignments, and IR intensities for DMEDA(2)

Comparison to experimental bands

The assignment of the calculated modes to the experimental The assignment of the calculated modes to the experimental bands was done by comparing calculated frequencies and intensities to experimental IR and Raman frequencies and IR intensities. The IR and Raman spectra of DMEDA are shown in Fig. 4. Since the experimental frequencies obtained are in the liquid state, it is highly probable that we are not simply dealing with a single conformation, but several different conformations. Table 6 shows the proposed mode assignments, calculated frequencies of all three TOT conformations, and experimental Raman and infrared frequencies for DMEDA. infrared requescies for DMEDA. The lowest frequencies present in the Raman spectrum

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occur at 243 and 268 cm². Calculations give us frequencies of 221 and 257 cm² for DMEDA(0), 244 and 251 cm² for DMEDA(1), and 214 and 250 cm² for DMEDA(2). These DMEDA(1), and 214 and 250 cm² for DMEDA(2). These calculated frequencies have all been assigned to a methyl twist. There are bands measured at 345, 360, 395, 425, 542 and 559 cm⁻¹ in the Raman spectrum. The calculations for the three conformations of DMEDA(0), 316, 359 and 564 cm⁻¹ for DMEDA(1), and 320, 342 and 559 cm² for DMEDA(2). They are mostly C-N-C bending and correspond most closely to the Raman frequencies at 345, 360, and 559 cm².

Mode assignments	DMEDA(0)	DMEDA(2)	DMEDA(1)	IR.	Ramar
Methyl twist	221	214	244		243
-	257	250	251		268
C-N-C bend	313	320	316		345
	340	342	359		360
					395
					425
	564	559	564		542
					559
N-H 1 bend	727			736	
	752		788	789	805(b)
		818	825		
		835			
CH ₂ rock	892	853	904	879	881
Methyl wag	990	976	984	985	990
C-C stretch	1010	1006	9 99	1022	1021
CH ₂ rock	1022	1036	1022	1042	1039
C-N stretch	1115	1089	1115	1106	1113
	1144	1138	1134	1122	1124
				1151	1152
CH ₂ twist	1255	1256	1248	1251	1255
CH ₂ wag	1353	1347	1342	1346	1347
•	1359	1370	1362	1361	1363
Methyl sym. def.	1428	1425	1425	1418	1420
	1429	1426	1428		
N-H bend, methyl as sym. def.	1448	1437	1444	1444	1450
	1450	1454	1451		
CH ₂ scissors, methyl as sym. def.	1462	1460	1459	1473	1473
	1482	1471	1476		
	1485	1488	1482		
C-H stretch	2809	2838	2771	2681	2679
	2824	2848	2822	2788	2790
	2826	2946	2831	2840	2843
	2905	2947	2842	2887	2891
	2946	2953	2944	2934	2939
	2996	2997	2958	2967	2970
N-ff stretch	3373	3347	3338	3280	3290
	3373	3353	3363	3323	3327

Table 6 Comparison of the scaled¹¹ calculated and experimental frequencies (cnl¹) of DMEDA



Fig. 4 Infrared and Raman spectra of DMEDA. Click on particular peaks of the spectra to view either a blowup of that region or an animated vibrational mode.

Fig. 5a shows the IR and Raman spectra from 950 to 650 cm^{-1} . There is a broad band present at 805 cm³ in the Raman spectrum and bands at 789 and 736 cm³ in the inflared spectrum. These are analogous to the calculated frequencies for DMEDA(0) at 727 and 752 cm³, DMEDA(1) at 788 cm³, and DMEDA(2) at 818 cm⁴ which have been assigned to N-H bending. The Raman

frequency at 881 cm⁻¹ and the infrared frequency at 879 cm⁻¹ have been assigned to a CH₂ rock since the calculated frequency for DMEDA(0) is at 892 cm⁻¹, for DMEDA(1) it appears at 904 cm⁻¹, and for DMEDA(2) it appears at 853 cm⁻¹.

The C-C stretch, which calculations show at 1010 cdf for DMEDA(0), 999 cm⁴ for DMEDA(1), and 1006 cm⁴ for DMEDA(2) occurs in the inflared spectrum at 1022 cdf ¹ and in the Raman spectrum at 1021 cdf¹. A mode calculated to occur at 1022 cm¹ for both DMEDA(0) and DMEDA(1) and at 1036 cm⁴ for DMEDA(2) has been assigned to a mixture of CF₁ rock and N-H bend; this mode appears to correspond to the band measured in the Raman spectrum at 1039 cm⁴ and in the inflared spectrum at 1039 cm⁴ and in the inflared spectrum at 1042 cm³. The calculated and experimental inflared intensities of this mode are both quies low. The C-N stretch calculated 1115 and 1144 cm⁴ for DMEDA(1), 098, 1115 and 1134 cm³ for DMEDA(1), and 1089 and 1138 cm⁴ for DMEDA(2) all have moderately high inflared intensity. These correspond to the inflared frequencies observed at 1105, 1124 and 1152 cm⁴.

The infrared frequency at [25] cml and the Raman frequency at [255 cml have been assigned to mostly CH



Fig. 5 (a) infrared and Raman spectra of DMEDA in the CH₂ rocking and NH bending region. (b) infrared and Raman spectra of DMEDA in the N-H strutching region. Click on particular peaks of the spectra to view either a blowup of that region or an animated vibrational mode.

twisting. The calculated frequencies occur at 1255 cm² for DMEDA(0), 1248 cm²¹ for DMEDA(1), and 1256 cm²¹ for DMEDA(2). The IR frequencies at 1346 and 1361 cm²¹ and the Raman frequencies at 1347 and 1363 cm²¹ have all been assigned to CH₆ wagging. These are most similar to the calculated modes at 1353 and 1359 cm²¹ for DMEDA(0), 1342 and 1362 cm²¹ for DMEDA(1), and 1347 and 1370 cm⁻²¹ for DMEDA(2). We assign the IR frequency at 1418 cm⁻¹ and the Raman frequency at 1420 cm¹¹ to a symmetric deformation of the methyl group. The calculated frequency is at 1428 cm⁻¹ for both DMEDA(0) and DMEDA(1) and 1426 cm⁻¹ for DMEDA(2). The IR frequency at 1444 cm²¹.

a mixture of N-H bending and an antisymmetric deformation of the methyl group, with a calculated frequency of 1450 cm⁴ for DMEDA(0). The bends present at 1473 cm⁻⁴ in both the Ramaa and the infrared are a mixture of CH₂ scissoring and antisymmetric deformation of the methyl group and correspond most closely to a calculated frequency of 1482 cm⁴ for DMEDA(0). The bands present in the 2600-3000 cm⁴ range are C-H structures.

The highest frequency modes are N-H stretches. The IR and Raman spectra for the N-H stretching region are shown in Fig. 5b. The calculated frequencies for the N-H stretches are important because they apport our statement that DMEDA(1) possesses some intramolecular hydrogen bonding, as hydrogen bonding causes the frequencies to be lowered.³⁶ It has been shown in the literature that DMEDA without hydrogen bonding has an N-H stretch of 3371 cm² and DMEDA with hydrogen bonding has an N-H stretch has a calculated frequency of 3374 cm², while in DMEDA(2) the N-H streaches lower to 3347 and 3353 cm⁻¹ and for DMEDA(1) the N-H streaches are 3338 and 3363 cm². Preliminary calculations with two DMEDA molecules having as insermolecular hydrogen bond predict the intermolecular hydrogen bonded N-H streaching frequencies to be 3251 cm². The N-H streaching frequencies to be 3251 cm². The N-H streaching frequencies in the IR spectrum are 3323 and 3280 cm², which indicates hydrogen bonding is present in liquid DMEDA.

indicates hydrogen bonding is present in liquid DMEDA. Since DMEDA is a liquid, it is highly probable that several different conformations contribute to the experimental spectra. The modes most sensitive to conformational change are the N-H perpendicular bend and CH₂ rock (shown in Fig. 4), and the C-N stretch. As seen in Table 5, the IR and Raman frequencies in these regions are closest to those calculated for DM(EDA(0) and are closest to unloss canonical and children of the process of 736 and 789 cm⁻¹, in good agreement with the 727 cm⁻¹ of DMEDA(0) and the 788 cm⁻¹ of DMEDA(1). The Raman spectrum in this region has a very broad band around \$05 cm⁴, which may contain underlying bands at frequencies ranging from ~760 to 805 cm⁻¹. In the CH₂ rocking region DMEDA(0) has a calculated frequency of 892 cm⁻¹ and DMEDA(1) has a frequency of 904 cm⁻¹, both of which are closer to the experimental UR and Raman frequencies of 879 and 881 cm⁻¹ than are those calculated for other conformations. The fraguencies in DMEDA(2) of \$18 and \$35 cml¹ for the N-It bend are too high and the frequency of \$3 cm² for the CH₂ rock is too low compared to the IR and Raman spectra. Also notable are the C-N stretching frequencies, for which again the DMEDA(0) and DMEDA(1) frequencies are quite close to the experimental fivequencies but the DMEDA(2) frequency of 1089 cm² is not comparable with any experimental band. Comparison was also made to the five other conformations of DMEDA (not discussed in detail in this paper), none of which showed as good an agreement b tween calculated and experi frequencies and intensities as DMEDA(1) and DMEDA(0) in these regions. For example, the TIT conformation has frequencies of 837 cm² for CH₂ rocking and 975 cm² for C-N stretching, none of which are close to any band in the experimental IR or Raman spectra. We therefore conclude that liquid DMEDA appears to consist of primerily a mixture of DMEDA(1) and DMEDA(0). n to consist with smaller contributions from other conformations. It is important to note that in the liquid DMEDA, intermolecular as well as intramolecular hydrogen bonding is possible, which may contribute to the stabilization of higher-energy conformations. Indeed our analysis of experimental vibrational mode frequencies strongly argues that such stabilization occurs in this system.

Cenclusions

Hybrid Hartree-Fock density functional calculations were performed on *N/N*-dimethylethylenediamine, DMEDA, and it was found that the lowest energy conformation is TGT with ose intramolecular hydrogen boad. The major differences between these three conformations are in the N-C-C-N torsional angle and the extent of hydrogen bonding. The conformations DMEDA(0) and DMEDA(2) both have C_2 symmetry but the presence of the single hydrogen bond in DMEDA(1) reduces it to C_1 symmetry. The non-covalent N-H···N distance in DMEDA(1) is 2.444 A and the non-covalent N-H···N distances in DMEDA(2) are both 2.853 Å.

Notable mode frequency differences between DMEDA(0) and DMEDA(2) occur in those modes whose

frequencies are most affected by hydrogen bonding. The C-N stretches and the N-H stretches are lower in frequency in DMEDA(2) than DMEDA(0), probably due to hydrogen bonding. For similar reasons, the N-H bends are higher in frequency in DMEDA(2) than DMEDA(0). The differences in the mode assignments between DMEDA(0) and DMEDA(1) due primarily to the single intramolecular hydrogen bond in DMEDA(1) causing the lose of symmetry. Compared to DMEDA(0), one of the C-N stretches remains the same and the other decreases in frequency and the N-H bends increase in frequency. The N-If stretches decrease in frequency compared to DMEDA(0), again due to hydrogen bond 82.

The assignment of the experimental infrared and Raman frequencies of DMEDA to specific vibrational modes was done using the calculated assignments. The calculated and experimental frequencies are generally in quite good agreement and IR in sensities are similar. In order to determine the conformations present in liquid DMEDA, we have compared the modes sensitive conformational change to the experimental spectra. We conclude that DMEDA appears to be primarily a mixture of DMEDA(1) and DMEDA(0). In the N-H stretching region, the presence of two bands with a large frequency aparation is also consistent with a mixture of conformations. The unusually low frequencies of one of the N-H stretches in the experimental data (3280 and 3290 cm¹ for the UR and Raman), compared with preliminary calculations on two DMEDA molecules with an intermolecular hydrogen bond, indicate the presence of intermolecular as well as intramolecular hydrogen bonding in DMEDA liquid. Further work is necessary to probe the structures and quantify the extent of intermolecular vs. intramolecular hydrogen bonding in liquid DMEDA.

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IV

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The Effect of Lithium Triflate and Lithium Bromide on the Vibrational Frequencies of DMEDA

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An experimental and computational investigation of the structures and vibrational frequencies of N,N'-dimethylethylenediamine-lithium triflate (DMEDA-LiTf) has been done using a combination of hybrid Hartree-Fock/density functional calculations and Raman and IR spectroscopy. Band assignments for DMEDA:LiBr were made by comparing the experimental Raman and IR spectra of a 5:1 DMEDA:LiBr sample with the calculated vibrational frequencies of the DMEDA-Li⁺ and DMEDA-LiBr complexes. Band assignments for DMEDA:LiTf were made by comparing the experimental spectra of samples over a concentration range of 20:1 to 1.5:1 with calculations done on the DMEDA-LiTf complexes. The effect of the lithium cation and lithium triflate on the geometries and vibrational frequencies of the DMEDA will be examined. The combined experimental data and computational results clearly show that the intramolecular hydrogen bond in pure DMEDA is broken upon addition of lithium bromide or lithium triflate.

Introduction

The potential importance of polymer electrolytes in a variety of applications, including rechargeable batteries, has stimulated intense interest in these systems. A wide variety of studies have focused on developing а molecular level understanding of the factors controlling ionic conductivity in poly(ethylene oxide)-salt systems.¹⁻⁹ Fundamental investigations into the nature of interactions in polymer electrolyte systems can be complemented by considering a polymer having a backbone structure similar to that of poly(ethylene oxide), but with a non-oxygen hetero atom. Linear poly(ethylenimine), or LPEI, $\{CH_2CH_2NH_{1n}\}$, is structurally analogous to PEO, with an N-H group in place of the oxygen.¹⁰ Several groups have studied LPEI-LiX polymer electrolytes.¹¹⁻¹⁶

In order to better understand interactions within LPEI-salt the systems, it is useful to do theoretical and experimental studies on smallmolecule model compounds. The simplest model compound for LPEI is N,N'-dimethylethylenediamine. We have previously conducted a complete analysis of DMEDA, vibrational comparing the experimental Raman and IR spectra of DMEDA to the calculated vibrational frequencies.¹⁷ We now present calculations done on the DMEDA-Li⁺, DMEDA-LiBr, and DMEDA-LiCF₃SO₃ complexes using hybrid Hartree-Fock/density functional methods and compare these to the experimental IR and Raman spectra of DMEDA-LiBr and DMEDA-LiTf systems. The DMEDA-LiTf complex is shown in Figure 1.



Lithium triflate is used because the vibrations for the triflate anion are well studied and ionic association of the triflate anion i.e. the presence of discrete, ionically associated species, may be determined spectroscopically.¹⁸⁻²³ In DMEDA several triflate anion vibrational modes are coincident with DMEDA modes, complicating the interpretation of the spectra; therefore we have also studied the DMEDA-LiBr system.

Methodology Experimental

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dimethylethylenediamine (DMEDA) 99% was used as received from Aldrich. Lithium triflate, LiCF₃SO₃, (LiTf) and lithium bromide obtained from Aldrich were dried under vacuum at ~120 ° C for 24 hours. All materials were stored in a nitrogen-atmosphere glovebox with moisture less than 1ppm. Desired ratios of DMEDA and LiTf or LiBr were mixed in the glovebox and stirred for 24 hours. The DMEDA-LiTf samples were made in concentrations ranging from a 1.5:1 to a 20:1 DMEDA to LiTf ratio. The DMEDA:LiBr sample was made at a 5:1 concentration.

Infrared spectra were recorded with a Bruker IFS66V FT-IR over a range of 4000 cm⁻¹ to 500 cm⁻¹ at a resolution of 1 cm⁻¹. The DMEDAsalt samples were placed between ZnSe plates in a sealed sample holder in the glovebox. The IR spectra were taken under dry air purge. Raman spectra were collected using a Jobin-Yvon T64000 Raman spectrometer

with a CCD detector. The 514.5 nm line of an argon ion laser at a power of 300 mW at the laser head was used for excitation. Spectra were collected in a 90° scattering geometry. Raman samples were sealed in cuvettes inside the glovebox. Curve fitting analysis was accomplished using a commercial program (Galactic Grams version Spectra were curve-fit to a 5.05). straight base line and one Gaussian-Lorenzian product function for each band using a non-linear least squares method.

Computational

The B3LYP hybrid Hartree-Fock/density functional method²⁴, 25 used to perform complete was geometry optimizations and vibrational frequency calculations on the DMEDA-Li⁺. DMEDA-LiBr. and DMEDA-LiTf complexes. The threeparameter HF/DF method employs a weighted sum of Hartree-Fock (E_x^{HF}) , local DF, and gradient corrected DF expressions for the exchange and correlation energies as in the following equation:

 $E = aE_{\chi}^{\text{Show}} + (1-a)E_{\chi}^{\text{NF}} + bE_{\chi}^{\text{Body}} + cE_{\chi}^{\text{LF}} + (1-c)E_{\chi}^{\text{IW}}$

where (E_x^{Slater}) is Slater's local spin density functional for exchange,²⁶ E_x^{Heckc} is Becke's gradient corrected exchange functional,²⁷ E_c^{VWN} is the local density correlation functional of Vosko, Wilk, and Nusair,²⁸ and E_c^{LYP} is the gradient-corrected correlation functional of Lee, Yang, and Parr.²⁹ Coefficients giving the relative

weights of various approximations for the exchange and correlation energies in this method were optimized to reproduce thermochemical data for a variety of small molecules using a slightly different correlation functional.³⁰ Unless otherwise noted. all calculations reported here were performed using the 6-31G(d) splitvalence plus polarization basis set.³¹ This basis set was chosen because it accurately reproduces the structures and vibrational spectra of mediumsized organic molecules and is small enough for rapid calculations.

quantum The chemistry GAUSSIAN94²⁴ programs and GAUSSIAN98³² were used for all Berny's optimization calculations. algorithm³³ was used to perform full geometry optimizations in Cı Harmonic symmetry. frequency calculations were performed at the optimized geometries without correcting for anharmonicity. It has become customary to scale calculated frequencies to facilitate comparisons with experiment and we chose to use the multiplicative scaling factors of Scott and Radom³⁴ All frequencies less than 1000 cm⁻¹ are multiplied by 1.0013 and all frequencies greater than 1000 cm^{-1} are multiplied by 0.9614.

Vibrational mode assignments were performed by animating each mode using the program XMOL³⁵ and comparing the modes of one geometry to another using the program ViPA, an acronym for Vibrational Projection Analysis.³⁶⁻³⁸ The ViPA program exploits the vector properties of vibrational normal modes to assess the

similarity between modes of an object molecule and a structurally similar basis molecule. The program first aligns the two molecules and calculates each molecule's normal modes and vibrational frequencies. For each molecule, each of the normal vibrational modes is a column vector. which is orthonormal to all other normal modes of the same molecule. The vector projection operation is done by sequentially projecting each normal mode of the object molecule on the modes of the basis molecule. The similarity of any mode of the object molecule to any mode of the basis molecule can then be expressed as a percentage by calculating the sum of squares of the matrix elements and multiplying by 100. Vibrational projection analysis has been used to compare normal modes modified by isotopic or chemical substitution, oxidation/reduction. non-covalent contacts, and conformation.17, 36-38

The conformations of DMEDA:Li. DMEDA:LiBr. and DMEDA:LiTf can be identified by the dihedral angles of the DMEDA. For example. а TGT conformation signifies that the first dihedral angle (C-N-C-C) is trans, T, corresponding to an angle of 180°±60°, the second dihedral angle (N-C-C-N) is gauche. G, corresponding to an angle $60^{\circ}\pm60^{\circ}$, and the third dihedral angle (C-C-N-C) is trans.

Results

Calculated Geometries

Geometry optimizations were done on a complex with DMEDA and a lithium cation. The lowest energy

structure has the DMEDA in a TGT conformation, TGT-Li⁺. Henceforth in this paper we will refer to the calculated DMEDA-Li⁺, DMEDA-LiBr, and DMEDA-LiTf complexes by the three-letter conformation of the DMEDA followed by Li⁺, LiBr, or LiTf. In TGT-Li⁺ the lithium cation is coordinated to both nitrogens of the DMEDA. Several other calculations were done to determine if other low energy structures of the DMEDA-Li⁺ complex exist. In addition to the TGT-Li⁺, geometry optimizations were done on five other possible conformations. In order of increasing energy, they are TGG-Li⁺, GGG-Li⁺, TTT-Li⁺, TTG-Li⁺, and GTG-Li⁺. Table 1 shows the relative energies of the different conformations. As in the TGT-Li⁺ conformation, the TGG-Li⁺ and GGG-Li⁺ systems have the lithium cation coordinated to both nitrogens and these conformations are only slightly higher in energy than the TGT-Li⁺ complex. In contrast, the TTT-Li⁺, TTG-Li⁺, and GTG-Li⁺ conformations have the lithium cation coordinated to single nitrogen and are significantly higher in energy than the TGT-Li⁺, TGG-Li⁺, and GGG-Li⁺ conformations.

In order to investigate the effect of the bromine or triflate anion on the structure and vibrational frequencies of DMEDA, we did calculations on complexes of DMEDA and lithium bromide (DMEDA-LiBr) and DMEDA and lithium triflate (DMEDA-LiTf). For both of these complexes, the calculations were done with the DMEDA in three different conformations (TGT, TGG, and GGG). We chose these conformations because of results found for the TGT- Li^{\dagger} complexes. In each of the calculations with lithium triflate, it was found that the lithium was coordinated to the two nitrogens of the DMEDA and two oxygens of the triflate anion.

Previous calculations have been done on DMEDA and it was found that DMEDA has three lowenergy TGT conformations with zero. one, and two intramolecular bonds (referred DMEDA(0). to as DMEDA(1). and DMEDA(2) respectively), with DMEDA(1) and DMEDA(0) providing the closest frequency correlations to the experimental spectrum of DMEDA.17

Table 2 compares the calculated bond distances, angles, and dihedral angles of the low-energy structures of DMEDA and the DMEDA-Li⁺. DMEDA-LiBr. and DMEDA-LiTf complexes. The most striking effect of Li⁺ coordination by DMEDA is the elimination of intramolecular hydrogen bonds and enforcement of a conformation similar to that of DMEDA(0). The addition of the lithium cation also slightly increases the C-N bond distances, followed by a small decrease when the triflate anion is added. The C-C distance remains essentially unchanged when the lithium or lithium triflate is added and there is little change in the bond angles. However, a significant geometrical change occurs in the dihedral angles. In DMEDA(0), the central N-C-C-N dihedral angle is 46.7°. This is increased to 60.4° in the TGT-Li⁺ complex and to 58.8° in the TGT-LiTf complex. Notice that the DMEDA-Li⁺ and DMEDA-LiTf complexes have no intramolecular hvdrogen bond, unlike the lowest

energy TGT conformation in pure DMEDA.

Vibrational Spectra Calculated Frequencies

Tables 3, 4, 5, and 6 list the calculated harmonic vibrational frequencies, IR intensities, Raman activities, and mode assignments for the TGT-Li⁺, TGT-LiBr, TGT-LiTf, and **TGG-LiTf** complexes, We will concentrate on respectively. а detailed comparison of the calculated frequencies and those bands of significant intensities observed in the IR and Raman spectra.

The lowest frequency modes calculated for the TGT-Li⁺ complex involve methyl wag or twist(78-257 cm⁻¹). There is C-N-Li/C-N-C bending at 275 cm⁻¹, and at 284 cm⁻¹ there is methyl twist mixed with C-N-Li/N-Li-N bend. The out-of-phase C-N-C bends are at 347 and 568 cm⁻¹, while the in-phase C-N-C bend is at 349 cm⁻ ¹. The Li-N stretches are at 499 cm⁻¹ cm⁻¹ (symmetric) and 500 (antisymmetric).

The vibrational modes of the $TGT-Li^{\dagger}$ and the TGT-LiBr complexes are very similar. The lowest frequency modes for the TGT-LiBr complex are torsions, methyl twists, and methyl wags. The mode calculated at 290 cm⁻ ¹ has been assigned to C-N-Li bend, while the mode at 297 is a mixture of methyl twist and wag. The out-ofphase C-N-C bends are at 353 and 568 cm⁻¹, while the in-phase C-N-C bend is at 365 cm⁻¹. The Li-N symmetric stretch is highly mixed with Li-Br stretch and is calculated at 641 cm⁻¹. The Li-N antisymmetric stretch is calculated at 401 cm⁻¹.

The DMEDA-LiTf complexes have low frequency modes that involve a movement of the entire triflate anion with respect to the DMEDA. The five lowest frequency modes for the TGT-LiTf involve these motions of the entire DMEDA-LiTf complex. The next ten modes involve methyl wag or twist. At 320 cm⁻¹, there is a C-N-C bend. There is a triflate twist at 327 cm^{-1} , and the mode at 342 cm^{-1} has contributions from triflate wag (a mixture of SO₃ and CF₃ wag), C-N-C bend, and methyl wag. The modes at 356 and 567 cm^{-1} are C-N-C bend. The Li-N stretches occur at 370 and 421 cm⁻¹. The seven lowest modes of the TGG-LiTf have been assigned to torsions of the DMEDA-lithium triflate complex. Methyl wags and twists occur in eight modes (153-290 cm^{-1}). The C-S stretch of the triflate ion is computed to be at 302 cm^{-1} . Two modes assigned to triflate ion wag are at 327 and 340 cm^{-1} . The C-N-C bends are calculated at 361 and 432 cm^{-1} . The Li-N stretch is calculated to occur at 600 cm^{-1} .

It is interesting to compare the Li-N stretches in the DMEDA-Li⁺ and -LiTf complexes to the corresponding calculated Li-O stretches in the related PEO oligomer, monoglyme. In DMEDA-Li⁺, the Li-N stretches are at 499 and 500 cm⁻¹, and in monoglyme-Li⁺, the Li-O stretches are at 505 and 541 cm⁻¹. In the TGT conformation of DMEDA-LiTf, the Li-N stretches are at 370 and 421 cm⁻¹, while in monoglyme-LiTf the Li-O stretches are at 294 and 311 cm⁻¹.

Comparison of Calculated and Experimental Frequencies

The IR and Raman spectra of DMEDA:LiBr 5:1 were compared to calculated frequencies for DMEDA and the TGT-Li⁺, TGG-Li⁺, GGG-Li⁺, and TGT-LiBr complexes. It was found that the frequencies and intensities calculated for the TGG and GGG complexes were not as consistent with the experimental spectra as those calculated for the TGT conformation. For example, in the IR spectrum of DMEDA:LiBr, we assign the observed band at 840 cm⁻¹ to a mixture of CH₂ rock and CH₂ twist. This assignment is comparable to the calculated frequency of 831 cm^{-1} in the TGT-Li⁺ conformation and 832 cm⁻¹ in the TGT-LiBr conformation. However, the calculated frequency for this mode in the TGG-Li⁺ conformation is 813 cm⁻¹ and for GGG-Li⁺ conformation is 808 cm⁻¹, which are both significantly lower than the experimental frequency.

Assignments for the modes in experimental spectra of the DMEDA:LiBr are given in Table 7. We have compared the calculated frequencies and intensities of DMEDA and the DMEDA-LiTf complexes to the IR and Raman spectra of DMEDA:LiTf over a concentration range of 1.5:1 to 20:1 and list the assignments for the experimentally observed modes in Table 8. It was found that the TGT and TGG conformations of the DMEDA-LiTf complex consistently provided the best with the experimental agreement frequencies. Some of the modes in Table 7 involving the triflate anion vibrations have been previously assigned.20, 21, 39 In the 1.5:1

composition the majority of the bands arise from the DMEDA:LiTf complex: however. in the dilute more concentrations, there are also bands that arise from uncomplexed DMEDA. Specific features in the experimental IR and Raman spectra of DMEDA:LiTf and DMEDA:LiBr are discussed below.

The spectral region from 1075 to 500 cm⁻¹

Figure 2a shows the DMEDA:LiTf concentrationdependent IR spectra in the region from 500 to 1075 cm⁻¹. There are several interesting spectral features in this region. Sharp bands at 519 and 639 cm⁻¹ arise from the $\delta_{as}(CF_3)$ and $\delta_s(SO_3)$ modes, respectively, which are calculated at 523 and 634 cm⁻¹ in DMEDA(TGT)-LiTf and at 524 and 636 cm⁻¹ in DMEDA(TGG)-LiTf.

There are notable changes in the DMEDA IR bands in the region from 700 to 900 cm⁻¹ as lithium triflate concentration changes. The bands in this region are assigned to a mixture of CH₂ rock and N-H bend. The broad band around 770 cm⁻¹ decreases drastically in intensity as the LiTf concentration increases, disappearing in the 1.5:1 sample except for a shoulder at 808 cm⁻¹. This corresponds to the calculated N-H bends at 788 and 825 cm^{-1} in DMEDA(1). A band appears at 836 cm^{-1} in the 20:1 sample. shifting to 839 cm^{-1} in the 1.5:1 concentration. This is closest to calculated bands at 834 and 858 cm⁻¹ in TGT-LiTf and bands at 817 and 859 cm⁻¹ in TGG-LiTf, which are assigned to a mixture of CH₂ rock and N-H bend. As the LiTf concentration

increases, the DMEDA band at 880 cm^{-1} shifts from 881 cm^{-1} in the 20:1 composition to 898 cm⁻¹ in the 1.5:1 composition. The mode calculated at 904 cm⁻¹ for DMEDA(1) and assigned primarily to CH₂ rock moves to calculated frequencies of 917 and 903 cm⁻¹ in the TGT-LiTf and TGG-LiTf complexes. respectively. It is important to note that these modes are assigned to a mixture of CH₂ rock and NH bend. These calculated changes very nicely underscore the point that the interaction of the cation with the DMEDA molecule host can significantly affect mode mixing and hence the nature of the normal modes. In the Raman spectra in this region (figure 2b) one can see the DMEDA band at 880 cm⁻¹, assigned to primarily N-H bend, broaden and disappear as the concentration of lithium triflate increases. A band assigned to a mixture of N-H bend and CH₂ rock grows in at 836 cm⁻¹ and steadily increases in intensity, just as in the IR spectra in this region. The comparison of the experimental spectra with the calculated frequencies indicates that these spectral changes reflect the structural changes seen in the geometry optimization upon addition of LiTf, i.e., that the central dihedral angle of the DMEDA is changed (as indicated in table1) and that an intramolecular hydrogen bond is broken. The N-H bending contribution to the modes in this region is probably most influenced by the change in bonding. The dramatic hvdrogen changes are observed in the CH₂ rocking and N-H bending modes upon complexation of DMEDA with LiTf are not unexpected. In a related



Figure 2a. IR spectra of DMEDA and DMEDA:LiTf from 1075 to 575 cm⁻¹



Figure 2b. Raman spectra of DMEDA and DMEDA:LiTf from 1075 to 575 cm⁻¹

system, diglyme-LiTf, changes in the frequency and intensity of the modes assigned to mixed CH_2 rocking have been shown to indicate changes in the central dihedral angle-upon interaction with the lithium ion.², 9, 40

The CF₃ symmetric deformation can be seen in the IR spectra as a small peak around 757 cm⁻¹ growing in on top of the CH₂ rocking band at 770 cm⁻¹. In the Raman spectra the $\delta_s(CF_3)$ peak is unobscured by DMEDA bands and the peak center is seen to shift from 757 cm^{-1} in the 20:1 sample to 760 cm^{-1} in the 5:1 sample, and then to 763 cm^{-1} in the 1.5:1 sample. The calculated CF₃ symmetric deformation is at 759 cm⁻¹ in TGT-LiTf and 758 cm⁻¹ in TGG-LiTf. The symmetric SO₃ stretches appear at 1039 and 1032 cm⁻¹ in the IR spectra, with the intensity of the 1039 cm⁻¹ band increasing as LiTf concentration increases. The bands are calculated in the TGT-LiTf and the TGG-LiTf conformations at 1092 and 1094 cm^{-1} , respectively. The SO₃ symmetric stretches appear at 1034 and 1040 cm^{-1} in the 20:1 Raman spectrum, shifting slightly to 1036 cm⁻ and 1044 cm^{-1} in the 1.5:1 sample, with the relative intensity of the higher-frequency band increasing with increasing LiTf concentration. Curvefitting analysis has been done on the IR and Raman data in the $\delta_s(CF_3)$ and $v_s(SO_3)$ regions. These modes are very sensitive to ionic speciation, i.e., as the triflate anion becomes more associated, the frequencies of these modes increase ²¹ These bands are non-degenerate, and the presence of

multiple bands arises from the triflate anion vibrating in different local environments. Figure 3 shows the results of the curvefitting. The symmetric CF₃ deformation can be deconvoluted into three bands centered around 755, 758-760 and 763 cm^{-1} . According to the literature, ²¹ bands at 752-753 cm⁻¹ are attributed to "free" ions, bands at 756-757 cm⁻¹ are attributed to contact ion pairs, and bands at 763 cm⁻¹ are attributed to the $Li_2CF_3SO_3^+$ aggregate. The symmetric SO₂ region stretching can be deconvoluted into bands centered around 1032-1036, 1038-1044, and 1050-1054 cm⁻¹. According to the literature, ⁸ "free" ions are at 1032-1033 cm⁻¹, ion pairs are at 1042 cm⁻¹, and aggregate at 1050-1052 cm⁻¹. Based on a comparison of the $\delta_s(CF_3)$ and $v_s(SO_3)$ regions, it appears that in the DMEDA-LiTf system the "free" ion and ion pair components of the $\delta_{s}(CF_{3})$ band are at slightly higher frequencies in the DMEDA:LiTf system than in ethylene oxide systems.8, 9, 19, 20, 22 The curvefitting of the $\delta_s(CF_3)$ in the IR and the $v_s(SO_3)$ in the Raman is complicated by the presence of DMEDA bands in these spectral regions, therefore the relative intensities obtained by curvefitting may have a larger error than in other regions of these spectra. There are qualitative similarities between the ionic speciation as determined from these spectral regions: in all cases, for the 20:1, 10:1 and 5:1 concentration, the LiTf appears to exist as a mixture of "free" ions and/or ion pairs, while in



Figure 3. Curvefitting results for the DMEDA-LiTf system

the 1.5:1 sample a significant amount of aggregate is present. There are, however, notable differences in the quantitative comparison of the species as determined from the CF₃ symmetric deformation or the SO₃ symmetric stretch. The amount of aggregate in the 1.5:1 sample is 100% as determined from the Raman spectra in the $\delta_s(CF_3)$ region, while in the same spectrum the amount of aggregate appears to be only 16% as determined from the relative integrated intensities in the $v_s(SO_3)$ region. In the 20:1, 10:1 and 5:1 samples, the pair seems to dominate, with the "free" ion band making up less than 15% of the total area in the curvefitting of the Raman $\delta_s(CF_3)$ region, while in the $v_s(SO_3)$ region the intensities of the "free" ion and ion pair components for these three concentrations are nearly equal. Discrepancies in the ionic speciation as determined from the $\delta_s(CF_3)$ and $v_s(SO_3)$ regions have been observed by Ferry, et al. in a PEO oligomer⁴¹ and in poly(propylene glycol).⁴²

Tetrabutylammonium triflate (TbaTf) has been used to study cationanion interactions⁴³; since TbaTf is a bulky cation with a well-protected charge, interactions with the anion are minimal. We have examined the IR spectra of DMEDA:TbaTf in the $\delta_s(CF_3)$ and $v_s(SO_3)$ regions over a concentration range of 44:1 to 7:1. We found neither a complex band structure or a shift in frequency in these two modes with increasing salt concentration, indicating no change in ionic association, as expected. The $v_s(SO_3)$ mode exhibits a single band at 1031 cm⁻¹, consistent with a "free" ion,

although at a slightly lower frequency than is usual in ethylene-oxide-based systems. In the $\delta_s(CF_3)$ region, a single band is seen at 755 cm⁻¹, which is higher that the "free" triflate frequency in LiTf-ethylene oxide systems. 19, 21, 22 In a previous study, 43 it was noted that the frequency of the $\delta_s(CF_3)$ mode of TbaTf is solvent-dependent, while the $v_s(SO_3)$ mode appears to be solventindependent.

However. recent work suggests that significant hydrogenbonding interaction between the triflate anion and a protic solvent may slightly lower the $v_s(SO_3)$ frequency from the usual values expected for a "free" ion in an aprotic environment. The frequency of 755 cm⁻¹ for the $\delta_{s}(CF_{3})$ mode observed in the DMEDA system with both LiTf and TbaTf, may therefore arise from a "free" ion, with the unusually high frequency being due to anion-solvent interactions rather than cation-ion interactions. Furthermore, the probability of the frequency of the CF₃ symmetric stretching mode being affected by solvent interactions suggests that the SO₃ symmetric stretch may be a better indicator of ionic association in the However DMEDA system. this conclusion must be very carefully qualified. There are clearly significant interactions of the triflate ion with the solvent. presumably a hydrogenbonding interaction between the triflate oxygen atoms and the amine hydrogen atom of the DMEDA. Therefore, any conclusions about the relative concentration of ion species based on comparisons of relative
integrated intensities from either the $\delta_s(CF_3)$ or the $v_s(SO_3)$ spectral region should be regarded as highly problematic in systems that have hydrogen bonding.

The IR and Raman spectra of DMEDA, DMEDA:LiBr(5:1) and DMEDA:LiTf(5:1) in this region are shown in Figures 4a and 4b. The bands centered around 780 and 880 cm⁻¹ in the IR spectrum of DMEDA (4a) broaden and shift higher to wavenumbers when LiBr or LiTf is added. A comparison of the IR spectra of DMEDA:LiBr with DMEDA in the region around 1000 cm⁻¹ shows that the bands at 983 and 1006 cm⁻¹ in the DMEDA are unchanged by LiBr addition. These bands are consistent with the C-C stretch at 999 cm⁻¹ and the CH₂ rock at 1022 cm⁻¹ in the DMEDA(1) calculation, with the C-C stretch at 983 cm^{-1} and CH_2 rock mixed with N-H bend and methyl wag at 1000 cm⁻¹ in the DMEDA-Li⁺ calculation and with the methyl wag at 1005 cm⁻¹ in the DMEDA-LiBr calculation. The very weak, broad band appearing around 800 cm⁻¹ in the pure DMEDA Raman spectrum (4b) is suppressed with the addition of either LiBr or LiTf. This band has been attributed to N-H bend from the DMEDA(1) calculation 17. A large band at 836 cm⁻¹ appears in the Raman spectra with the addition of LiBr or LiTf. This band is closest to the mode calculated at 831 cm⁻¹ in the DMEDA-Li⁺ complex and 832 cm⁻¹ in the DMEDA-LiBr complex, which we assign to a mixture of CH₂ rock and N-H perpendicular bend. The band at 880 cm⁻¹ in the Raman spectrum of pure DMEDA decreases in intensity when

LiBr or LiTf is added. These changes in the CH₂ rocking and N-H bending regions are consistent with what is seen in the IR spectra. The same type of change in the dihedral angle of DMEDA and the breaking of intramolecular hydrogen bonds that is indicated in the LiTf system also appears to occur in the LiBr system. This is expected, given that those changes were seen in the geometry optimization when a lithium cation was added to DMEDA.

The spectral region from 1600 to 1075 cm⁻¹

Figure 5 shows the IR spectra of pure DMEDA and DMEDA:LiTf from the 20:1 the 1.5:1 to compositions in the 1600 to 1075 cm⁻¹ region. There are several significant changes in this region of the IR spectra of DMEDA when salt is added. The band at 1106 cm⁻¹ gradually shifts to 1100 cm⁻¹ as LiTf concentration increases, and a band grows in at 1092 cm⁻¹. These bands are closest to calculated frequencies of 1094 or 1083 cm⁻¹ in the LiTf complexes, which are assigned to a mixture of C-N stretch and methyl wag. The analogous mode in DMEDA(1) is calculated at 1134 cm⁻¹ and assigned to C-N stretch. The band at 1123 cm⁻¹ decreases in intensity as LiTf concentration increases and appears to vanish in the 1.5:1 composition. This band is assigned to a methyl wag, which is calculated at 1115 cm⁻¹ in DMEDA(1) and at 1133 or 1128 cm⁻¹ for the TGTor TGG- LiTf complexes. The DMEDA band at 1150 cm⁻¹, assigned to C-N stretching, is replaced by new bands at 1146 and 1165 cm⁻¹ in DMEDA:LiTf, with the intensity of



Figure 4a. IR spectra of DMEDA, DMEDA:LiTf 5:1 and DMEDA LiBr 5:1 in the region 1075 cm^{-1} to 575 cm^{-1}



Figure 4b. Raman spectra of DMEDA, DMEDA:LiTf 5:1 and DMEDA LiBr 5:1 in the region 1075 cm^{-1} to 575 cm^{-1}

the 1165 band increasing relative to the 1146 cm⁻¹ as LiTf concentration increases. These bands are closest in frequency to calculated bands at 1153 and 1144 cm⁻¹ in the TGT-LiTf and TGG-LiTf and are assigned to the CF₃ antisymmetric stretch, with some contribution from the C-S stretch. The CF₃ antisymmetric stretch appears at 1226 cm^{-1} in the IR and 1227 cm^{-1} in the Raman, but is calculated at 1202 cm^{-1} in both conformations. There is a band calculated at 1251 cm⁻¹ in DMEDA(1), which appears in the pure DMEDA spectrum but which is experimentally indistinguishable under the broad, intense bands due to the SO3 stretches at 1296, 1277, and 1257 cm⁻¹ in the DMEDA-LiTf spectra. The SO₃ antisymmetric stretch is doubly degenerate in an isolated triflate ion. Upon interaction with a cation, the degeneracy is broken. We assign the band at 1277 cm⁻¹ to an unperturbed or "free" triflate ion, based on previous studies.22, 39, 44 The two bands at 1296 and 1257 cm⁻¹ are then attributed to the two components of the SO_3 symmetric stretch resulting from the breaking of the two-fold degeneracy in some fraction of the triflate ions The SO₃ antisymmetric present. stretch is calculated at 1255 or 1257 cm^{-1} . The bands from 1500 to 1400 cm⁻¹ broaden as the LiTf concentration increases. Modes involving N-H parallel bend, methyl deformation and CH₂ scissors are calculated from 1425 to 1487 cm⁻¹ in the TGT-LiTf complex and from 1421 to 1484 cm^{-1} in the TGG-LiTf complex.

The IR spectrum of DMEDA:LiBr 5:1 has similar features

to the DMEDA:LiTf spectra in the region from 1575 to 1075 cm^{-1} . In the DMEDA:LiBr spectrum, a shoulder grows in at 1094 cm^{-1} on the 1105 cm^{-1} band and the band at 1121 cm⁻¹ decreases in intensity. The modes calculated at 1042 cm⁻¹ in the DMEDA-Li⁺ complex and 1079 in the DMEDA-LiBr complex are assigned to a mixture of C-N stretch and methyl wag... The band at 1151 cm⁻¹ shifts to slightly lower wavenumbers. In the Raman spectra, the C-N stretch at 1114 cm⁻¹ (calculated at 1115 cm⁻¹ in DMEDA(1)) and the methyl wags at 1126 and 1151 cm⁻¹ (calculated at 1134 cm⁻¹ in DMEDA(1),1129 and 1157 cm^{-1} in DMEDA-Li⁺, and 1132 and 1154 cm⁻¹ in DMEDA-LiBr) are relatively unchanged upon the addition of LiBr. The Raman band at 1257 cm⁻¹ in DMEDA, attributed to CH₂ twist, decreases in intensity with addition of LiBr. Bands between 1400 and 1500 cm⁻¹ are slightly broadened with addition of either LiBr or LiTf in both the IR and Raman spectra. These modes, involving N-H bend, methyl deformation, or CH₂ scissors, are calculated to occur from 1415 to 1484 cm⁻¹ in the DMEDA-Li⁺ complex and 1425 to 1485 in the DMEDA-LiBr complex.

The spectral region from 4000 to 1600 cm⁻¹

There are C-H stretching vibrations in the IR spectra of both DMEDA-LiTf 5:1 and DMEDA-LiBr 5:1 from 2685 to 2965 cm⁻¹. These bands are calculated between 2881 and 3037 cm⁻¹ in the TGT-LiTf complex, between 2884 and 3047 cm⁻¹



Figure 5. IR spectra of DMEDA and DMEDA:LiTf in the region 1600 to 1075 cm⁻¹



in the TGG-LiTf complex, between 2885 and 3032 in the TGT-LiBr complex, and between 2930 and 3034 cm⁻¹ in the TGT-Li⁺ complex. It is well-known that density-functional methods give X-H stretching modes by ~100-200 cm⁻¹ too high and this appears to be the case here.

Figure 6 shows the IR spectra for DMEDA, DMEDA:LiBr 5:1 and DMEDA:LiTf 1.5:1 to 20:1 in the N-H stretching region. The calculated N-H stretches are at 3338 and 3363 cm⁻¹ for DMEDA(1), at 3335 and 3373 cm⁻¹ for TGG-LiTf, at 3331 and 3333 cm⁻¹ for TGT-LiTf, at 3330 and 3331 cm⁻¹ for TGT-LiBr. and two modes both calculated at 3312 cm⁻¹ for TGT-Li⁺. In pure DMEDA there are two bands. at 3280 and 3320 cm^{-1} , in both the IR and Raman spectra. In DMEDA:LiBr there are bands at 3210 and 3270 cm⁻¹ in the IR spectrum and at 3220, 3280 and 3320 cm^{-1} in the Raman spectrum. In DMEDA:LiTf there are distinct bands at 3295 and 3323 cm⁻¹ in the IR spectrum and at 3301 and 3327 cm⁻¹ in the Raman spectrum. In the concentration-dependent IR spectra of the DMEDA-LiTf, the frequencies of the N-H stretches increase as the LiTf concentration increases.

An interpretation of the N-H stretching region is complicated by the variety of possible hydrogen bonding interactions. In the pure DMEDA. there is a possibility of both intramolecular hydrogen bonds and hydrogen bonds between neighboring DMEDA molecules 17. In the DMEDA-salt systems, there may still bonding hydrogen between be DMEDA molecules. well as as between the amine hydrogens and the anions. Our calculations coupled with observations from other regions of the vibrational spectra indicate that intramolecular hydrogen bonds are broken when salt is added to DMEDA; however at low salt concentrations some intramolecular hydrogen bonds may remain.

Conclusions

In order to determine the effects of adding LiBr and LiTf to DMEDA, hybrid Hartree-Fock/density functional calculations have been performed on DMEDA-Li⁺, DMEDA-LiBr, and DMEDA-LiTf complexes. We found that changes occur in the central dihedral angle and in the intramolecular hydrogen bonding when DMEDA complexes lithium. In a previous study 17, we found that pure DMEDA exists in a mixture of low energy conformations, predominantly TGT with intramolecular hydrogen bonding. The calculated geometries for both the DMEDA-Li⁺, DMEDA-LiBr, and DMEDA-LiTf show that this intramolecular hydrogen bond in the TGT conformation is broken when lithium is added.

The differences in the experimentally observed band structure of DMEDA:LiTf or DMEDA:LiBr compared to that of pure DMEDA are also indicative of changes conformational the in DMEDA. The N-H bending and CH_2 rocking regions of the spectra are particularly sensitive to conformational changes of the DMEDA, and the N-H stretching region is strongly affected by changes in the hydrogen bonding. comparison From the of the

experimentally observed frequency shifts and changes in intensity in the $700 - 900 \text{ cm}^{-1}$ region to the calculated frequencies for the CH₂ rocking and NH bending modes for the different conformations in the pure and complexed DMEDA, a change in the dihedral angle of the DMEDA-LiBr and DMEDA-LiTf complexes compared with pure DMEDA is inferred. Comparison of the experimental IR and Raman spectra of DMEDA:LiBr to the calculated DMEDA-Li⁺ and DMEDA-LiBr frequencies for the three low energy conformations leads us to conclude that the TGT conformation is favored in the DMEDA-LiBr complex. The calculated frequencies of the DMEDA-LiTf complex in both the TGT and TGG conformations are very similar and are in good agreement with the frequencies observed in the DMEDA-LiTf spectra. However, the frequencies and intensities of the TGT conformation provide a closer match with the IR and Raman spectra in the important N-H bending, CH₂ rocking and N-H stretching regions.

As the concentration of LiTf in the DMEDA system increases, the degree of ionic association of the triflate anion appears to increase. changing from a mixture of "free" ions and ion pairs to a mixture that includes a more highly associated aggregate. One triflate aggregate is the triple cation, $[Li_2Tf]^+$, in which each triflate ion is coordinated to two lithium cations. The $[Li_2Tf]^+$ aggregate may exist as an independent species, charge-balanced by "free" triflate anions, or as part of a more complex structure such as is seen in the

diglyme-LiTf system. In that system, a combination of vibrational spectroscopy and x-ray diffraction of a diglyme-LiTf crystal shows that this spectroscopic signature (763 cm⁻¹ for the $\delta_s(CF_3)$ mode) arises from a dimer structure, diglyme₂Li₂Tf₂, in which each lithium is coordinated to three oxygen atoms of a digylme molecule and one oxygen from each triflate..⁹ Each triflate then vibrates as and Li₂Tf⁺ although it is part of an Li₂Tf₂ dimer. It is not unreasonable to hypothesize similar а bonding geometry could exist in the DMEDA-LiTf system. Differences in the frequency shifts of the $\delta_s(CF_3)$ and $v_s(SO_3)$ modes show that the $\delta_s(CF_3)$ mode and perhaps the $v_s(SO_3)$ mode as well is sensitive to anion-solvent interactions. probably through hydrogen-bonding interactions.

The addition of lithium salt has a profound effect on the hydrogen bonding in the DMEDA system. It is well known that the N-H stretch is sensitive to hydrogen bonding and that lower frequencies indicate a greater degree of hydrogen bonding.⁴⁵ There may be both intramolecular and intermolecular hydrogen bonding in DMEDA.17, 45 The increase in the experimentally observed frequencies of the N-H stretches upon the addition of LiTf to DMEDA would seem to indicate that hydrogen bonding interactions are decreased. This is consistent with the breaking of the intramolecular hydrogen bond seen in the geometry optimization. The frequencies shift to lower wavenumbers in the DMEDA-LiBr system, suggesting that there are

hydrogen-bonding stronger interactions in this system than in the DMEDA. One possible pure explanation for the stronger hydrogen bonding in the LiBr system is that there are intermolecular hydrogen bonds between the DMEDA and the Br anion. Because the triflate anion is coordinated to two lithium cations in the DMEDA-LiTf systems at high salt there are fewer concentrations. triflate oxygen atoms to available hydrogen-bond to the DMEDA. The presence of more than one N-H stretching band in these systems may indicate that the N-H moieties exist in

several different environments, with different types of hydrogen bonding interactions present.

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Table 1. Comparison of the Relative Energies(kcal/mol) of the various DMEDA-Li^{*}. DMEDA-LiBr, and DMEDA-LiTf conformations.

Conformation	Relative energy
TGT-Li*	0*
TGG-Li	0.5
GGG-Li*	1.0
TTT-Li*	27.3
TTG-Li*	29.1
GTG-Li [*]	30.2
TGT-LiBr	0*
TGG-LiBr	0.3
GGG-LiBr	0.7
	<u> </u>
TGT-LiTf	0*
TGG-LiTf	0.3
GGG-LiTf	0.9

* The actual calculated energy for TGT-Li* is –276.534596 Hartrees, TGT-LiBr is -2848.5129096 Hartrees, and TGT-LiTf is –1238.2244363 Hartrees.

Table 2:	A Comparison	of the Bond Distances,	, Bond Angles,	and Torsional	Angles of DMEDA	(0), DMEDA(1),
DMEDA-	TGT-LI', DMED	A-TGT-LiBr, and DMED	A-TGT-LiTf- cal	culated using t	the B3LYP hybrid I	Hartree-
Fock/de	nsity functional	method with a 6-31G(d) Basis.	-	-	

	DMEDA(0)	DMEDA(1)	TGT-Li	TGT-LiBr	TGT-LITF
C2-N5	1.455	1.459	1.4854	1.472	1.4692
N5-C6	1.456	1.464	1.4903	1.473	1.4709
C6-C9	1.530	1.527	1.5289	1.530	1.5296
C9-N12	1.456	1.455	1.4905	1.473	1.4756
C12-C13	1.455	1.454	1.4854	1.472	1.4737
N5-H17	1.017	1.020	1.0232	1.021	1.0218
N12-H18	1.017	1.019	1.0233	1.021	1.0209
N5-Li			2.010	2.093	2.0915
N12-Li			2.010	2.093	2.0866
C2-N5-C6	113.3	113.4	112.4	114.1	113.8
N5-C6-C9	112.6	110.4	110.8	110.0	110.4
C6-C9-N12	112.6	110.4	110.8	110.0	110.6
N9-C12-C13	113.3	113.4	112.4	114.1	112.9
C2-N5-C6-C9	166.0	189.4	188.8	190.9	189.1
N5-C6-C9-N12	46.7	62.9	60.4	58.1	58.8
C6-C9-N12-C13	166.0	185.8	189.0	190.9	187.6
H17-N5-C6-C9	41.8	64.5	71.8	70.1	67.6
H18-N12-C9-C6	41.8	-48.2	71.8	70.1	67.4
Li-Br				2.227	
Li-O(Triflate)					1.9549
Li-O(Triflate)					2.0186
0-S					1.5046
0-S					1.5036
0-S					1.4595
S-C					1.8630
C-F					1.3350
C-F					1.3364
C-F					1.3486

Mode Assignment	Frequency	IR	Raman
		Intensity	Activity
Methyl Wag: N-H perpendicular Bend	78		<u> </u>
Methyl Wag: N-C-C-N Torsion	140		<u> </u>
Methyl Twist	198	2	
Methyl Twist	223	6	<u> </u>
Methyl Wag	257		<u>+</u>
C-N-Li/C-N-C Bend: Methyl Wag	275	31	<u> </u>
Methyl Twist: C-N-Li/ N-Li-N Bend	284	15	1-1-
C-N-C Bend (out-of-phase)	347	11	i o
C-N-C Bend (in-phase) N-Li-N Bend	349	1 1	1
Li-N Symmetric Stretch	499	70	6
Li-N Antisymmetric Stretch	500	47	2
C-N-C Bend (out-of-phase): CH ₂ Twist	568	9	1
CH ₂ Rock: N-H perpendicular Bend	831	13	4
CH ₂ Wag, Methyl Wag	853	19	1 11
N-H perpendicular Bend: CH ₂ Rock	969	84	
N-H perpendicular Bend: Methyl Wag	964	10	3
C-C Stretch	983	0	2
N-H perpendicular Bend; Methyl Wag	991	48	1 2
CH ₂ Rock: N-H parallel Bend: Methyl Deformation	1000	0	1
C-N Stretch (out-of-phase)	1042	98	1
C-N Stretch (in-phase) C-C Stretch	1065	7	10
CH ₂ Twist: N-H perpendicular bend: Methyl Wag	1075	10	1
Methyl Wag	1129	19	2
Methyl Wag	1157	2	2
CH ₂ Twist: N-H perpendicular Bend: Methyl Wag	1215	4	7
CH ₂ Twist	1272	9	6
CH ₂ Twist	1273	14	4
CH ₂ Wag	1343	11	2
CH ₂ Wag	1367	0	4
N-H parallel Bend; Methyl Antisymmetric Deformation	1415	8	5
Methyl Symmetric Deformation; N-H parallel Bend	1426	7	9
Methyl Symmetric Deformation	1427	0	8
N-H parallel Bend; Methyl Antisymmetric Deformation	1428	22	1
Methyl Antisymmetric Deformation	1463	8	11
Methyl Symmetric Deformation	1464	18	19
CH ₂ Scissors, Methyl Antisymmetric Deformation	1470	17	5
CH ₂ Scissors	1474	0	15
Methyl Antisymmetric Deformation	1481	6	1
CH ₂ Scissors; Methyl Antisymmetric Deformation	1484	26	28
C-H Stretch	2930	6	21
C-H Stretch	2932	12	77
C-H Stretch	2938	45	11
C-H Stretch	2938	4	279
C-H Stretch	2967	15	91
C-H Stretch	2979	20	20
C-H Stretch	3008	13	55
C-H Stretch	3008	14	54
C-H Stretch	3034	12	67
C-H Stretch	3034	10	64
N-H Stretch	3312	1	97
N-H Stretch	3312	10	9

 Table 3: Scaled Calculated Vibrational Frequencies(cm⁻¹), Mode Assignments, IR Intensities, and Raman

 Activities for the TGT-Li^{*} complex.

Mode Description	Frequency	IR Intensity	Raman Activity
Torrigo	35		
		4	0
Torsion			
NCCN torsion and Methyl Wag	105		
NCCN torsion and Methyl Wag	155	+	
Mothyl Twiet	190		
Methyl Twist	238		
Methyl Wag	250		
Methyl Wag: C-N-Li Bend	201	11	1
Methyl Twist/Wag	297	2	1
C-N-C Bend (out of phase)	353	7	1
C-N-C Bend (in phase)	365	<u>.</u>	3
Li-N Antisymmetric Stretch	401	26	1
C-N-C Bend (out of phase)	568	1	1
Li-N Symmetric Stretch: Li-Br Stretch	641	99	3
CH ₂ Rock: N-H perpendicular Bend	832	26	4
CH ₂ Wag: N-H perpendicular Bend: Methyl Wag	857	64	7
N-H perpendicular Bend: CH ₂ Rock	913	75	3
N-H perpendicular Bend: Methyl Wag	958	41	1
CH ₂ Rock: Methyl Wag	985	20	5
C-C Stretch	986	6	1
CH ₂ Rock; Methyl Wag; N-H parallel Bend	1005	1	1
CH ₂ Twist; Methyl Wag; N-H Bend	1073	4	1
C-N Stretch; Methyl Wag	1079	74	0
Methyl Wag; C-N Stretch; C-C Stretch	1093	4	12
Methyl Wag	1132	23	4
Methyl Wag	1154	0	2
Methyl Wag; N-H perpendicular Bend	1213	2	4
CH ₂ Twist	1260	2	12
CH ₂ Twist	1267	10	3
CH ₂ Wag	1344	14	2
CH ₂ Wag	1364	2	5
Methyl Symmetric Deformation; N-H parallel Bend	1425	4	7
Methyl Symmetric Deformation	1426	1	7
N-H parallel Bend; Methyl Antisymmetric Deformation	1428	2	5
N-H parallel Bend	1441	16	5
Methyl Antisymmetric Deformation	1463	7	7
Methyl Antisymmetric Deformation	1464	21	22
CH ₂ Scissors; Methyl Antisymmetric Deformation	1472	16	3
Methyl Antisymmetric Deformation	1480	5	28
CH ₂ Scissors	1482	0	3
CH ₂ Scissors; Methyl Antisymmetric Deformation	1485	15	15
C-H Stretch	2885	6	35
C-H Stretch	2896	38	47
C-H Stretch	2899	116	57
C-H Stretch	2901	84	364
C-H Stretch	2938	7	89
C-H Stretch	2956	40	8
C-H Stretch	2989	21	50
C-H Stretch	2989	22	65
C-H Stretch	3032	13	59
C-H Stretch	3032	7	56
N-H Stretch	3330	1	99
N-H Stretch	3331	4 1	2

 Table 4: Scaled Calculated Vibrational Frequencies(cm⁻¹), Mode Assignments, IR Intensities, and Raman

 Activities for the TGT-LiBr complex.

Mode Assignment	Frequency	IR Intensity	Raman Activity
	18	1	0
		<u> </u>	<u> </u>
	42	<u> </u>	
Terrien	<u>40</u> 64		
Methyl Wag	80		
Methyl Wag	122	1	0
Methyl Wag	155	0	0
Methyl Twist	180	1	0
Methyl Twist	200	0	0
Methyl Twist: Triflate Wag	205	4	0
Methyl Twist	208	1	0
Methyl Twist	252	1	0
Methyl Wag	260	0	0
Methyl Twist	298	2	2
Methyl Twist; CH ₂ Rock; C-S Stretch	299	1	3
C-N-C Bend	320	6	1
Triflate Twist	327	1	2
Triflate Wag; C-N-C Bend; Methyl Wag	342	0	3
C-N-C Bend	356	9	1
Li-N Stretch	370	9	2
Li-N Stretch	421	23	1
SO ₃ Antisymmetric Deformation CF ₃ Antisymmetric Deformation	491	21	1
CF ₃ Antisymmetric Deformation	523	8	0
CF ₃ Antisymmetric Deformation	555	13	4
C-N-C Bend	567	0	1
CF1 Antisymmetric Deformation:	577	23	3
SO ₃ Antisymmetric Deformation			
Li-O Stretch; Li-N Stretch	595	224	1
SO ₃ Symmetric Deformation	634	99	1
CF ₃ Symmetric Deformation	759	2	10
N-H perpendicular Bend; CH ₂ Rock	834	26	5
CH ₂ Wag; CH ₂ Twist	858	69	6
N-H perpendicular Bend	917	121	6
N-H perpendicular Bend	959	83	4
SO ₃ Symmetric Stretch; N-H perpendicular Bend	979	129	17
Methyl Wag: C-N Stretch	986	13	A
C-C/C-N Stretch: CH ₂ Wag	989		3
CH ₂ Rock: Methyl Wag: N-H parallel Bend	1007	1	<u>i i i i i i i i i i i i i i i i i i i </u>
N-H parallel Bend: C-N Stretch: CH- Twist	1071	23	2
CH ₂ Twist: Methyl Wag	1080	54	1
SO ₃ Antisymmetric Stretch;	1092	177	5
C-N Stratch: Mathyl M/2c	1004	22	
Methyl Wag	1122		3
C-S Stratch: CF. Anticymmetric Stratch	1153	2J	
Methyl Wan	1157	<u></u> <u></u>	
CF. Antisymmetric Stretch: C-S Stretch	1180	118	
CF, Antisymmetric Stretch	1202	270	<u> </u>
N-H perpendicular bend; Methyl Wag;	1212	1	4
SO ₃ Antisymmetric Stretch	1255	343	4

Table 5: Scaled Calculated Vibrational Frequencies(cm⁻¹), Mode Assignments, IR Intensities, and Raman Activities for the TGT-LITf complex.

CH ₂ Twist	1261	4	10
CH ₂ Twist; N-H perpendicular Bend	1267	22	6
CH ₂ Wag	1345	17	3
CH ₂ Wag	1366	1	5
Methyl Deformation; N-H parallel Bend	1425	5	8
Methyl Deformation	1426	0	5
N-H parallel Bend; Methyl Deformation	1430	5	7
N-H parallel Bend	1449	16	5
Methyl Deformation	1465	15	25
Methyl Deformation	1465	11	12
Methyl Deformation; CH ₂ Scissors	1471	10	4
CH ₂ Scissors	1480	11	3
Methyl Deformation	1481	9	27
Methyl Deformation; CH ₂ Scissors	1487	11	17
C-H Stretch	2881	7	36
C-H Stretch	2893	55	69
C-H Stretch	2897	108	153
C-H Stretch	2900	77	226
C-H Stretch	2938	16	81
C-H Stretch	2966	27	19
C-H Stretch	2980	25	64
C-H Stretch	3000	19	60
C-H Stretch	3025	15	59
C-H Stretch	3037	10	50
N-H Stretch	3331	5	51
N-H Stretch	3333	1	58

Table 6: Scaled Calculated Vibrational Frequencies(cm⁻¹), Mode Assignments, IR Intensities, and Raman Activities for the TGG-LiTf complex.

i requericy	Intensity	Activity
		+
		<u> </u>
		+
		<u> </u>
130		
152		
100		+
190		+
204		+
204	<u> </u>	
207	······	
240	<u> </u>	
200	<u> </u>	<u> </u>
290		+
302		
327	<u> </u>	2
340		
361		
365	8	0
412	17	1
432	8	0
494	19	1
		+
524	9	
557	5	4
	27 31 41 60 66 86 130 153 171 189 204 207 240 260 290 302 327 340 361 365 412 432 494 524 557	$\begin{tabular}{ c c c c c } \hline & & & & & & & & & & & & & & & & & & $

CH ₂ Twist; N-H perpendicular Bend	561	3	1
CF ₃ Antisymmetric Deformation	578	30	3
SO ₃ Antisymmetric Deformation			L
Li-N Stretch	600	259	1
SO ₃ Symmetric Deformation; Li-N Stretch	636	79	1
CF ₃ Symmetric Deformation	758	3	10
CH ₂ Rock; N-H perpendicular Bend	817	8	3
CH ₂ Wag; CH ₂ Twist	859	49	8
N-H perpendicular Bend	903	98	2
N-H perpendicular Bend	928	31	3
SO ₃ Symmetric Stretch	978	177	19
CH ₂ Twist	1001	14	3
CH ₂ Rock	982	7	3
CH ₂ Rock; Methyl Wag; N-H parallel Bend	1008	19	1
N-H per. Bend; CH ₂ Twist; Methyl Wag	1060	16	5
C-N Stretch	1083	31	4
SO ₃ Antisymmetric Stretch	1094	190	4
CH ₂ Wag; N-H perpendicular Bend;	1114	17	5
Methyl Wag			1
Methyl Wag	1128	18	2
CF ₃ Antisymmetric Stretch; C-S Stretch	1144	179	3
Methyl Wag	1149	3	2
CF ₃ Antisymmetric Stretch	1181	118	2
Methyl Wag; CH ₂ Rock	1199	9	1
CF ₃ Antisymmetric Stretch	1202	264	ō
SO3 Antisymmetric Stretch	1257	345	3
CH ₂ Twist	1259	18	9
CH ₂ Twist	1271	7	8
CH ₂ Wag	1346	14	3
CH ₂ Wag	1363	10	4
Methyl Deformation: N-H parallel Bend	1421	4	8
Methyl Deformation	1427	0	9
N-H parallel Bend	1435	10	2
N-H parallel Bend: Methyl Deformation	1440	3	6
CH ₂ Scissors: Methyl Deformation	1459	0	19
Methyl Deformation	1466	13	17
Methyl Deformation: CH ₂ Scissors	1470	18	8
CH ₂ Scissors: Methyl Deformation	1476	8	2
CH ₂ Scissors: Methyl Deformation	1478	11	5
Methyl Deformation: CH ₂ Scissors	1484	11	32
C-H Stretch	2884	10	40
C-H Stretch	2895	47	53
C-H Stretch	2898	86	57
C-H Stretch	2900	96	336
C-H Stretch	2949	12	89
C-H Stretch	2973	29	11
C-H Stretch	2995	18	58
C-H Stretch	3006	20	47
C-H Stretch	3031	11	52
C-H Stretch	3047	7	56
N-H Stretch	3335	1	60
N-H Stretch	3373	4	72

nequencies (ci	1 / TOT DIALEDAN		and Diacon(1) with	
DMEDA:LiBr	DMEDA-LIBr	DMEDA-Li*	DMEDA(1)	Assignment
			Ļ	
534			<u> </u>	
566	568	568		C-N-C Bend
747				
775			788	N-H Bend
811				CH ₂ Rock
840	832	831		CH ₂ Rock; CH ₂ Twist
880			904	CH ₂ Rock
909				
983	986	983		C-C Stretch
1006	1005	1000		CH ₂ , N-H bend, Methyl Deformation
1034	1079	1042	1	C-N Stretch
1105			1115	
			1	
1121	1132	1129		Methyl Wag
1146	1154	1157	1	Methyl Wag
1226	1213	1215	f	CH ₂ Twist: N-H Bend
1251	1260		1248	CH ₂ Twist
1281	1267	1272		
1311				
1349	1344	1343	1342	CH ₂ Wag
1410	1425	1415	1425	N-H Bend: Methyl Deformation
1449			1451	
· -	i i			
1472	1472	1470	1476	Methyl Deformation; CH ₂ Scissors
2686	2938	2938	2771	C-H Stretch
2790	2956	2967	2822	
2844	2989	2979	2831	1
2889	2989	3008	2842	
2934	3032	3034	2944	
-				
		1		
3210	3330	3312	3338	N-H Stratch
3270	3331	3312	3363	
			1 2000	1

Table 7: Comparison of experimental IR frequencies(cm⁻¹) of DMEDA:LiBr 5:1 with the calculated frequencies (cm⁻¹) for DMEDA-LiBr, DMEDA-Li^{*} and DMEDA(1) with mode assignments

		11000 0351	5-11-10-1-10				
1.5:1	5:1	10:1	20:1	DMEDA-TGT-	DMEDA-TGG-	DMEDA(1)	Assignment
518	519	619	510	401	404	<u> </u>	SO antiques Deformation
516	516	516	513	523	524		CF ₃ antisym Deformation
558				555	557		CF ₃ antisym Deformation
574	573	573	573	577	578		CF ₃ /SO ₃ antisym
640	620	620	620	624	626		SO aver Defermation
750	- 039	- 009	750	750	030		SO3 Synt Deformation
128	/5/	/5/	738	/59	+	700 141 54	CF3 sym Derormation
	<u> </u>		110	+		788 NH DO	
823						825 NH DO	
839	838	839	836	834 or 858	817 or 859		CH ₂ Rock; N-H Bend
898	896	897	881	917	903	904(rock)	N-H Bend
910							
		982	980	979			
1006	1006	1006]	1007	1008	999 vC-C	CH ₂ Rock; Methyl Wag; N-
						1022 rock	H Bend
1038	1033	1033	1033				SO ₃ Stretch
1092	1			1094	1083		C-N Stretch, Methyl wag
1100	1104	1104	1106			1115	Methyl Wag
			4424			┣	
1	1122	1122	1121	1133	1128		Metnyi wag
					L	1134	C-N stretch
1166	1160	1159	1154	1153	1144		CF ₃ Stretch
				1180	1181		
1228	1226	1226	1226	1202	1202		CF ₃ Stretch
1257	1259	1259	1257	1255	1257		SO ₃ Stretch
						1251 twist	
1297							CF ₃ Stretch
1353	1352	1352	1347	1345	1346	1342	CH ₂ Wag
1370				1366	1363	1362	CH ₂ Wag
1458	1450	1450	1447	1449	1435	1444	N-H Bend; Methyl
		1		1465	1466	1451	Deformation
1475	1474	1474	1473	1471	1478	1476	CH ₂ Scissors; Methyl
	ļ			1487	1484	1482	Deformation
2692	2689	2689	2679	2893	2884	2770	C-H Stretch
2811	2794	2795	2789	2897	2895	2822	
2864	2847	2847	2843	2900	2898	2831	
2902	2888	2887	2887	2938	2900	2842	ł
2954	2937	2937	2935	2966	2949	2944	
3301	3295	3295	3287	3331	3335	3338	N-H Stretch
3332	3323	3323		3333	3373	3363	N-H Stretch

Table 8: Comparison of experimental IR frequencies(cm⁻¹) of DMEDA:LiTf of varying concentrations with the calculated frequencies (cm⁻¹) for DMEDA:LiTf, DMEDA-TGG-LiTF, and DMEDA(1) with mode assignments

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V

Ionic Transport in Polymer Electrolytes: The Essential Role of Associated Ionic Species

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The mechanism of ionic transport in ion-conducting polymers is currently a subject of intense interest, primarily driven by a suite of potential applications, including utilization as electrolytes in rechargeable lithium batteries. Consequently, there is a pressing need to develop a lithium ion-conducting polymer electrolyte with high ionic conductivity and desirable mechanical properties. This development has been frustrated by relatively low room temperature ionic conductivities available (10^{-7} to 10^{-8} S cm⁻¹) with single phase or "dry" polymer

electrolytes. Because the mechanism of ionic transport is poorly understood in these materials, especially at the molecular level, there are only very general outlines to guide the rational synthesis of new polymer electrolytes. A critically important fundamental issue is the nature of the dominant charge carriers.

One of the most widely studied polymer electrolyte systems is poly(ethylene oxide), PEO, containing various dissolved lithium salts[1, 2, 3]. The dissolution of the salt occurs through the coordination of the lithium ion by the ether oxygens, resulting in a heterogeneous system consisting of a pure PEO phase, an amorphous PEO phase containing dissolved salt, and often a crystalline PEO-salt compound. In these systems, the amorphous phase is the primary conduction pathway. [4, 5] Therefore, much of the effort to develop appropriate polymer electrolytes has focused on amorphous polymer hosts.

An important amorphous polymer host is poly(bismethoxyethoxyethoxyphosphazene)

(MEEP), which was first synthesized and studied as a polymer electrolyte by Shriver, Allcock, and their coworkers. [6, 7] Polymer electrolytes based on MEEP exhibit some of the highest room-temperature ionic conductivities reported to date.[8] In this paper we describe a vibrational spectroscopic study of MEEP containing dissolved LiCF₃SO₃ (LiTf), and compare these data with conductivity measurements. This system is amorphous over a temperature range of at least -100 to 100 °C with room temperature conductivities that are at least two orders of magnitude higher than PEO-LiCF₃SO₃ at comparable compositions.[6, 8]

The synthesis of MEEP and the experimental procedure are reported elsewhere.[9] Thin films of MEEP:LiTf over a concentration range of 2:1 to 32:1 (ether oxygen:Li) were prepared and Raman and IR spectra were taken.

A MEEP monomer unit consists of a P=N backbone with two ethylene oxide sidechains, which are the sites that coordinate the lithium ions. Therefore the ethylene oxide interactions of these sidechains can be modeled by diglyme, CH₃(OCH₂CH₂)₂OCH₃. Figure 1 shows a comparison of the IR spectra of MEEP, MEEP:LiTf 2:1, diglyme, and diglyme:LiTf 5:1. (A 2:1 solution of diglyme:LiTf cannot be prepared because a compound forms at a 3:1 ratio.)



Diglyme, and Diglyme LTT 5:1 (EO:Li) in the conformation region

This spectral region from 800-1000 cm⁻¹ contains modes that are a mixture of CH₂ rocking and CO stretching motions.[10, 11, 12] The frequencies and intensities of these bands are sensitive to the conformation of the EO chain.[13, 14, 15] The collapse of the four bands in diglyme

between 900 and 1000 cm⁻¹ into a broad, slightly structured feature in MEEP, coupled with a comparison of the bands primarily due to CH₂ rocking motion (particularly the breadth of the features at 804 and 851 cm⁻¹ and the absorption due to unresolved bands between these two features) indicate that the sidechain conformations are distributed over a much wider range of dihedral angles in MEEP than in diglyme despite the fact that diglyme is a liquid. Even more interesting is the observation that the addition of LiTf to MEEP produces almost no change in these and other regions of the spectrum sensitive to changes in ethylene oxide conformation, even at very high salt concentrations. These data suggest that there is no distinctive change in the conformation of the side-chains upon interaction with the lithium ions. This is in sharp contrast to the diglyme-LiTf system, where there are striking shifts in the frequencies and changes in band intensities upon addition of salt, not only in the CH₂

rocking modes but a number of other spectral regions as well. These spectral changes with increasing salt concentration lead to a spectrum which increasingly resembles that of the diglyme:LiTf crystal. In fact, at a 5:1 composition the infrared and Raman spectra appear to be mostly a superposition of the pure diglyme spectrum and the spectrum of the diglyme-LiTf compound. This leads to the conclusion that the local structures (such as ionic coordination and conformation of the ethylene oxide units) present in concentrated solutions of diglyme-LiTf are quite similar to those in the crystal structure.[13]

We infer that the formation of a MEEP-LiTf polymer electrolyte must occur with the dissolution of salt in the highly disordered ethylene oxide side chains as if those side chains constituted a liquid-like microphase interpenetrated by the polyphosphazene backbone. The degree of chain entanglement prevents a local ordering of ethylene oxide chain conformations such as occurs in solutions of diglyme-LiTf.

We now consider the ionic conductivity in parallel with the nature of the ionic species present in the MEEP-LiTf system. The triflate ion CF₃ symmetric deformation mode, $\delta_{s}(CF_{3})$, has been used to study the nature and number of ionic species present in ethylene oxide-lithium triflate systems.[3, 13, 14, 15, 16, 17, 18. 19. 20, 21] The mode frequency and intensity are highly dependent on interactions of cations with triflate oxygen atoms[17, 19]. There are several ionic species whose presence can be detected: "free" Tf ions (or solvent-separated ion pairs), LiTf contact ion pairs, and the triple cation Li_2Tf^{\dagger} . It is not possible to distinguish an isolated triple cation from an Li_2Tf^{\dagger} entity vibrating as part of a more extensively associated species. In general it is desirable to compare the speciation determined from the analysis of the $\delta_s(CF_3)$ mode with the speciation similarly obtained from the

 $v_{s}(SO_{3})$ mode. These two estimates are often in good agreement with each other, although discrepancies between the two regions have been noted.[21] Unfortunately, the $\nu_s(SO_3)$ is overlapped by an intense polymer band in the MEEP system, making deconvolution of the triflate band impossible. Table 1 compares the conductivities of several MEEP:LiTf compositions with an estimate of the relative concentration of the various ionic species present obtained from deconvolution of the $\delta_s(CF_3)$ band as measured in the Raman spectrum. This estimate is the ratio of the integrated band intensity for each species to the total integrated $\delta_{s}(CF_{3})$ band intensity. To investigate the error in this analysis, the procedure was repeated several times for each composition, beginning with the preparation of a fresh sample. This error is also listed in the table.

D·I i		EOIL	conductivity*		% speciation		
	U.LI	EO.LI	S cm ⁻¹	"free"	pair	agg	error
1.7:1	10:1	6.6:1	1.2 x 10 ⁻⁵	0	4	96	16%
4:1	24:1	16:1	2.7 x 10 ⁻⁵	0	100	0	4%
6.7:1	40:1	26.6:1	2.2 x 10 ⁻⁵	12	88	0	4%
8.1	48.1	32.1	22×10^{-5}	21	79	0	10%

 Table 1. Conductivity and ionic species in the MEEP:LiTf system as a function of composition.

*conductivity from reference 6

As expected, the relative amount of more highly associated species increases with increasing salt concentration, behavior that has been noted in many other polymer-salt and glyme-salt systems. [1, 2, 3, 13, 15, 22] At very high salt concentrations, i.e. EO:Li \leq 10:1, the dominant species is triple cation Li_2Tf^+ . On charge balance considerations, we would expect an equal concentration of "free" Tf ions, although very little is observed within experimental error. Therefore the triple cation Li_2Tf^{\dagger} must be present as part of a more highly associated aggregate. We note that the concentration dependence of the ionic species present in MEEP-LiTf is similar to the behavior observed in

solutions of diglyme-LiTf, where a dynamic equilibrium was postulated between contact ion pairs and Li₂Tf₂ dimeric species at high salt concentrations.[13] The existence of the Li₂Tf₂ dimeric species in solution is made plausible by the fact that the crystalline phase of diglyme:LiTf consists exclusively of isolated diglyme₂Li₂Tf₂ dimers. Each lithium ion is coordinated to the three oxygen atoms of a diglyme molecule and two triflate oxygen atoms, one from each of the two triflate ions in the dimer. The two triflate anions then link the two lithium ions together to form the dimeric structural unit. Consequently each triflate ion vibrates as an Li_2Tf^+ entity although the anions are part of a dimer whose ionic portion will be

written here as Li_2Tf_2 . We are aware that in the P(EO)₃LiTf compound all triflate ions also vibrate as if they were Li₂Tf⁺ triple cations.[3] However we believe that a one-dimensional extended structure of alternating lithium ions and triflate ions with ether oxygen atoms coordinating the lithium ions, such as is seen in the $P(EO)_3LiTf$ compound, is highly unlikely in MEEP-LiTf. Consequently we suggest that the triple cation species that dominate the spectrum at high salt concentrations are really present as Li_2Tf_2 dimers with each lithium ion coordinated by two or three sidechain oxygen atoms, not necessarily from the same sidechain. The highly entangled and disordered nature of the polyphosphazene backbone and the resulting close proximity of the ethylene oxide side chains leads to a conformationally disordered system in spite of the presence of isolated. ordered ionic dimers.

The most surprising result of this work is found in the comparison of ionic conductivity with the ionic

species present at various system compositions. Over a concentration range where the ionic speciation ranges from mostly contact ion pairs with a significant amount of "free" ion to mostly Li_2Tf^{\dagger} aggregate with a small amount of ion pairs, the conductivity only changes by approximately a factor of two. This is a remarkable result, considering that MEEP-LiTf exhibits one of the highest room temperature ionic conductivities known. It is particularly interesting that the conductivity is a maximum at a composition consisting almost exclusively of contact ion pairs! These data lead immediately to the question of the nature of ion transport in MEEP at higher salt concentrations.

The surprising observation of high ionic conductivity changing little over a composition range in which the ions exhibit a wide range of association behavior, requires a mechanism of ionic transport that can explain these data. This apparent indifference of the ionic conductivity (within a half order of magnitude) to the nature of the ionic species present at various concentrations, combined with extraordinary observation of the conductivity maximum at a composition almost completely dominated by neutral contact ion pairs, argues for a mechanism that generates reasonable concentrations of highly mobile charge carriers in the presence of high relative concentrations of ionically associated species. The critical question is: what is the nature of these charge carriers?

We suggest that dynamic equilibrium is established between the various ionically associated species by exchange of individual Li⁺ and Tf ions, with the net effect that the individual Li⁺ and Tf⁻ ions migrate through the liquid-like domains defined by the entangled ethylene oxide side chains. It has been previously suggested that associated ionic species play a role in the mechanism of ionic transport, with the species themselves actually transporting charge. [23] A early mechanism involving intercluster hopping was suggested by Teeters and Frech, [24] and expanded by other

workers. [25] Ferry et al. proposed that the earlier dynamic bond percolation model [26] based on the movement of ions between ether oxygen sites be augmented by considering hopping between ions in pairs and dissolved ions [27].

The work presented here clearly demonstrates that in the MEEP-LiTf system the associated species contribute charge carriers through a dissociation process. At the conductivity maximum where only neutral contact ion pairs are present to any extent, this is the only mechanism that can significantly contribute to the conductivity. Necessarily, the cations and anions in these pairs contribute to the ionic conductivity. The spectroscopic data allow us to identify the associated species, strongly supporting the postulate that the ionic transport mechanism involves the detailed dissociation/reassociation steps.

In the composition regime where contact ion pairs dominate, a mechanism describing the conductivity might begin with a step in which a LiTf contact ion pair dissociates according to

 $LiTf \leftrightarrow Li^{+} + T\bar{f} \qquad (1)$

In the contact ion pair the lithium ion is four-fold coordinated by a single triflate oxygen atom and three sidechain oxygen atoms, not necessarily from the same sidechain. After dissociation the triflate ion is relatively free although the lithium ion retains some degree of coordination with its sidechain oxygen atom. However, the potential energy environment of the cation is now considerably less deep than in its higher coordination state, and that environment is dynamically disordered through the thermal motion of the sidechains. Hence the cation is also mobile. The transference number of lithium has been measured as 0.32 at a 24:1 EO:Li composition,[6] where the contact ion pair is the dominant species present. The triflate ion can encounter another contact ion pair in its immediate vicinity, forming the triple anion species.

 $Tf + LiTf \leftrightarrow LiTf_2$ (2)

We note that the contact ion pair and the triple anion species are spectroscopically indistinguishable in that both are observed as a contact ion pair in the vibrational spectrum. However, the $LiTf_2$ species is very bulky and has a low mobility, therefore a small contribution to the overall ionic conductivity, and must dissociate to produce effective charge carriers. In this picture, the free triflate ion is present both as a transient species in its role as the principal charge carrier and as a longer-lived species that is spectroscopically detected at about a 10 % relative concentration. Of course, the longer-lived species can also contribute to the conductivity.

At compositions where the triple cation is the majority species (although present as the Li_2Tf_2 dimer as previously discussed), a simple dissociation process leads to free triflate ion

$$Li_2Tf_2 \Leftrightarrow Li_2Tf^+ + Tf^-$$
 (3)
or an Li^+ ion

$$Li_2Tf_2 \Leftrightarrow LiTf_2 + Li'$$
 (4)

In the very short timescale defined by the movement of highly mobile, individual Tf and Li^+ ions from a dissociation site (e.g. the Li_2Tf_2 dimer in Eq. 1) to a reassociation site (e.g. a nearby, newly-created Li_2Tf^+ or

LiTf₂ site), the more highly associated species serve as relatively "immobile" sites for ionic association/dissociation reactions such as those described in equations 1-4. Of course it is possible to devise other schemes involving more elaborate association/dissociation steps. However the overall concept remains the same: ionic transport consisting of highly mobile Tf and Li⁺ ions moving over short distances between proximate, ionically associated species. The high mobility in part arises through the thermal motions of entangled ethylene oxide side chains producing a locally disordered potential energy environment for the ions.

This study unambiguously demonstrates that the mechanism of ionic transport in an amorphous

polymer electrolyte necessarily involves ionic dissociation and reassociation steps. Further, we have clearly identified those ionically associated species playing a major role in this mechanism. We recognize that in a number of polymer-salt systems there are relatively large amounts of "free" ion at salt concentrations where the conductivity is significant; therefore, alternative conductivity mechanisms involving the transport of "free" ions may play an important role in those systems. Although this study has focused on the MEEP-LiTf system, the relatively high concentration of ion pairs and more highly associated species in other polymer-salt systems (such as PEO-LiTf) at compositions with large values of ionic conductivity strongly argues that an association mechanism such as we propose here is essential in a wide variety of polymer electrolytes.

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APPENDIX B: PAPERS NOT INCLUDED

- I. Effect of Temperature on Local Structure in Poly(ethylene oxide)-Zinc Bromide Salt Complexes. B. P. Grady, C. P. Rhodes, S. York, and R. Frech. Macromolecules, 34, 8523 (2001).
- II. A Comparative Study of Ionic Association in Poly(ethylene oxide) MCF₃SO₃ Systems (M=Lithium and Sodium). R. Frech, C. P. Rhodes
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- III. Plasticizer Interactions with Polymer and Salt in Propylene Carbonate
 Poly(acrylonitrile)- Lithium Triflate. Shawna Raye Starkey and
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