

Dynamics and Lithium Binding Energies of Polyelectrolytes Based on Functionalized Poly(*para*-phenylene terephthalamide)

F. C. Grozema,^{*,†,‡} A. S. Best,[§] L. van Eijck,^{||} J. Stride,[⊥] G. J. Kearley,^{||} S. W. de Leeuw,[†] and S. J. Picken[§]

Department of Physical Chemistry and Molecular Thermodynamics, Delft University of Technology, Julianalaan 136, 2628BL, Delft, The Netherlands, Laboratory for Applied Inorganic Chemistry, Delft University of Technology, Julianalaan 136, 2628BL, Delft, The Netherlands, Polymer Materials and Engineering, Dutch Polymer Institute, Delft University of Technology, Julianalaan 136, 2628BL, Delft, The Netherlands, Interfaculty Reactor Institute, Department of Neutron Scattering and Mossbauer Spectroscopy, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands, and Institut Laue Langevin, Grenoble, France

Received: December 7, 2004; In Final Form: February 14, 2005

Polyelectrolyte materials are an interesting class of electrolytes for use in fuel cell and battery applications. Poly(*para*-phenylene terephthalamide) (PPTA, Kevlar) is a liquid crystalline polymer that, when sulfonated, is a polyelectrolyte that exhibits moderate ion conductivity at elevated temperatures. In this work, quasi-elastic neutron scattering (QENS) experiments were performed to gain insight into the effect of the presence of lithium counterions on the chain dynamics in the material. It was found that the addition of lithium ions decreases the dynamics of the chains. Additionally, the binding of lithium ions to the sulfonic acids groups was investigated by density functional theory (DFT) calculations. It was found that the local surroundings of the sulfonic acid group have very little effect on the lithium-ion binding energy. Binding energies for a variety of different systems were all calculated to be around 150 kcal/mol. The DFT calculations also show the existence of a structure in which a single lithium ion interacts with two sulfonic acid moieties on different chains. The formation of such “electrostatic cross-links” is believed to be the source of the increased tendency to aggregate and the reduced dynamics in the presence of lithium ions.

1. Introduction

The use of polymers as ion conducting membranes in electrochemical devices such as lithium-ion batteries and fuel cells has distinct advantages over the use of liquid electrolytes or ion transporting ceramics.¹ Problems related to the escape of flammable or toxic liquids are overcome by the use of polymer-based electrolyte materials. Moreover, the use of polymers also offers the opportunity to use alternative processing techniques. The performance of polymer electrolytes and polyelectrolytes in lithium-ion batteries is critically dependent on their ability to solvate and transport lithium ions. In neutral polymer electrolytes, for example, polyethyleneoxide (PEO), both the lithium cation and a counteranion are dissolved in the polymer matrix, and, in principle, both can contribute to the ion conductivity.² In polyelectrolytes, the anion is covalently incorporated in the polymer, leaving only the lithium cation as a mobile ion.³ The use of ionizable groups as substituents on polymers offers the possibility of using a well-known polymer with favorable mechanical properties as an ion-transporting medium; however, the introduction of such side chains will also influence the mechanical properties of the material.

Poly(*para*-phenylene terephthalamide) (PPTA, Kevlar) forms a nematic liquid crystalline (LC) solution in sulfuric acid. The fibers that can be processed from these solutions exhibit extreme mechanical strength. The high strength and stiffness of the materials arise due to the alignment of the polymer chains in the axial direction. The high degree of hydrogen bonding between the aramid-units along the chains and the strong van der Waals interactions perpendicular to the plane of the molecule govern the mechanical properties of PPTA.⁴ The strong interactions between the PPTA chains render the polymer virtually insoluble. Introduction of a sulfonic acid group on the main chain, giving so-called sulfo-PPTA,^{5,6} is believed to reduce the extent of hydrogen bonding between the chains due to steric interactions, hence leading to a more soluble polymer. The sulfonic acid groups also have a high affinity for water and other protic solvents, which is another factor that influences the solubility in such solvents. It was shown recently by Viale et al.⁵ that sulfo-PPTA is soluble in water giving lyotropic alignment in solution. Substitution with ionizable sulfonic acid groups also introduces binding sites for ionic species such as lithium ions. Together with the LC nature of the polymer, this opens the possibility of two-dimensional fast single-ion conduction that is of considerable interest for application in lithium-ion batteries.

Viale et al.⁵ and VandenBergh et al.⁷ have described the preparation and LC properties of sulfo-PPTA, shown in Figure 1 (model 1). Sulfo-PPTA is known to form molecular aggregates in solution, which are the building blocks of the nematic phase; however, this phase is obscured by the formation of a gel at

* Corresponding author. E-mail: grozema@tnw.tudelft.nl.

[†] Department of Physical Chemistry and Molecular Thermodynamics, Delft University of Technology.

[‡] Laboratory for Applied Inorganic Chemistry, Delft University of Technology.

[§] Dutch Polymer Institute, Delft University of Technology.

^{||} Department of Neutron Scattering and Mossbauer Spectroscopy, Delft University of Technology.

[⊥] Institut Laue Langevin.

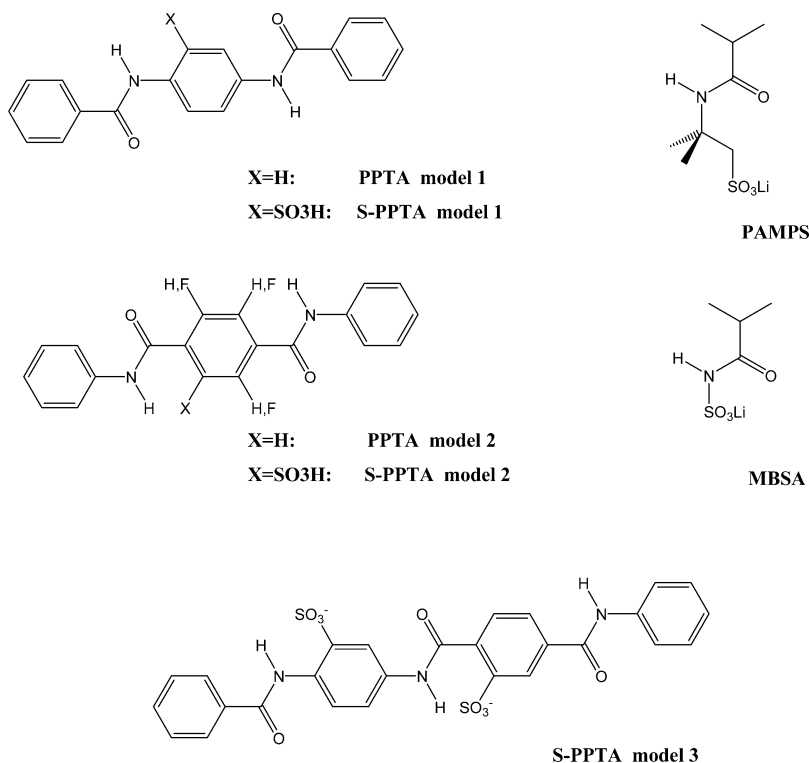


Figure 1. Structures and acronyms of the compounds studied in this work.

low polymer concentrations in water. Interestingly, the work of Mendes et al. suggests that these aggregates are enhanced in the presence of LiCl,⁸ whereas Okamoto et al. argues that the opposite occurs.⁶ Enhanced aggregation in the presence of lithium suggests that lithium binding plays a specific role in the interactions between polymer chains.

More recently, some of us have described so-called “sulfo-invert-PPTA”,^{9,10} Figure 1 (model 2), where we have displaced the sulfonic acid group on the main chain from the diamine ring to the terephthalic acid ring and observed significant differences in the solubility and the liquid crystalline properties of the polymer chains in solution.

Okamoto et al.¹¹ showed that sulfonated-PPTA exhibits a high-temperature ionic conductivity of the order of 10^{-8} S cm⁻¹ at 150 °C. Interestingly, the shape of the conductivity plots suggested that the ion conductivity is temperature activated, following a simple Arrhenius behavior, much like traditional fast-ion conductors such as ceramic electrolytes. In contrast, traditional polymer electrolytes based on PEO generally exhibit dominantly VTF-type thermally activated behavior, indicating a correlation between motion of ions and segmental motion of the polymer.¹² The work of Okamoto et al.¹¹ mentioned above raises an interesting question with respect to the binding energies of ions to the sulfonic acid group of the polymer. By reducing the strength of the interaction of ions with this moiety, it may be possible to enhance the ionic conductivity of the polyelectrolyte as a whole.

By performing quasi-elastic neutron scattering (QENS) experiments on poly(sulfonated *para*-phenylene terephthalamide), we have investigated to what degree polymer mobility assists ionic conductivity in a main chain liquid crystalline polymer. Moreover, we have investigated how ion-complexation affects the dynamics of the polymer chains. Ab initio calculations have been used to study the geometry of sulfo-PPTA model systems to establish to what extent the geometry of the PPTA parent compound is changed by introduction of sulfonic acid groups. Ab initio methods were also used to determine the

binding energies of lithium-ions to the sulfonic acid group of sulfo-PPTA and examine the extent to which the molecular structure surrounding the sulfonic acid moiety influences this binding energy. Moreover, we have computationally explored the possibility of the formation of a lithium-ion bridge between separate chains. In this way, we aim to gain more insight into physical properties and the conduction mechanism in this polyelectrolyte. Additional calculations using a classical force were performed to establish whether the interactions can be described in a fully classical way. This is of special interest for future work where the interactions between polymer chains and lithium ion will be studied on a larger scale using molecular dynamics simulations.

2. Experimental Section

2.1. Synthetic and QENS Methodologies. The synthesis method used to prepare both the model compounds and the polymers examined in this work have been previously described.^{5,9,10} Mass spectrometry analysis (ICP-MS) has been used to ensure that the lithium-ion concentration is such that all of the sulfonic acid groups are lithiated in the final materials. Prior to QENS measurements, the samples have been dried under vacuum at 60 °C for several days before being sealed for transport to ILL, where they were again under vacuum prior to being sealed in aluminum cans to prevent contamination of the sample with moisture.

The quasi-elastic neutron scattering (QENS) experiments were performed on the IN5¹³ spectrometer at the Institute Laue Langevin (ILL) in Grenoble, France. This time-of-flight spectrometer is highly adjustable in momentum transfer range and energy resolution by changing the wavelength profile of the incoming neutron beam. The instrument was set for these measurements to give a moment transfer, Q , range of $0.3 \leq Q < 1$ Å⁻¹ and a fwhm energy resolution of 30 μeV. The raw data were corrected using the software package INX provided by the ILL.¹⁴ The raw data were corrected for background and

sample can contamination, and we performed a measurement on a vanadium slab to correct for detector efficiencies. This vanadium measurement was also used to obtain the purely incoherent instrumental resolution function that is needed in the data analysis. Temperatures (up to 225 °C) were controlled using a standard ILL cryo-furnace, and standard ILL aluminum sample cans with Viton O-ring sealing were used.

The quasi-elastic broadening of the corrected QENS data was analyzed with the software package PROFIT¹⁵ by using the observed instrumental resolution function and one or two Lorentz functions. The quasi-elastic broadening of the incoherent elastic peak observed in these measurements is the Fourier transform of the Van Hove self-correlation function.¹⁶ When this broadening has a Lorentzian dependence on the neutron energy transfer, as was observed in our measurements, we are probing a self-correlation function that has an exponential time dependence on the observed picosecond-time scale. Furthermore, the broadening is a function of momentum transfer where a quadratic dependence is indicative of a diffusive motion.

2.2. Computational Methods. The geometries of the S-PPTA model systems were fully optimized by density functional theory calculations using the Becke–Lee–Yang–Parr gradient corrected functional. All calculations were performed using Dunning's correlation corrected polarized double- ζ basis set (cc-pVDZ).¹⁷ The vertical lithium-ion binding energies were calculated for the fully optimized structures. These vertical interaction energies were corrected for the basis set superposition error (BSSE) using the counterpoise method.¹⁸ This correction was found to be important because BSSE errors of the order of 0.5 eV were calculated for all model systems. The relaxation energy is defined as the difference between the energy of the S-PPTA model system in the optimized complex (Li⁺-S-PPTA-model) geometry and the energy of the S-PPTA model in its relaxed "monomer" geometry. The relaxed Li⁺ binding energies were obtained by adding the BSSE-corrected binding energy and the relaxation energy. Atomic charges were obtained by fitting them to the electrostatic potential obtained from a DFT calculation in points selected according to the CHelpG scheme.¹⁹ All ab initio calculations were performed using the Gaussian 98 software package.²⁰

Calculations of classical interactions were performed using a polarizable force field implemented in the DRF90 package.^{21,22} In this force field, molecules and ions are represented by sets of physically relevant atomic properties: atomic charges, atomic polarizabilities, and repulsion radii. The individual interactions are expressed in terms of these three parameters. Electrostatic interactions are calculated as the interaction between atomic point charges obtained from DFT calculations. Induction interactions are calculated by the interaction between point charges and polarizabilities. The presence of explicitly polarizable atoms also takes many-body terms (three-body etc.) in the interactions into account. Such many-body terms can be expected to play a role in systems involving highly polar and ionic species due to the large dipole moments induced in such systems. The DRF90 force field has been shown to describe such many-body interactions accurately, as compared to ab initio methods.²³

3. Results and Discussion

3.1. QENS Data. QENS experiments were performed for the S-PPTA trimer model 1 (see Figure 1) at different temperatures. The experiments were also conducted for the same model system but with all acid protons exchanged by Li⁺ (Li-S-PPTA model 1). For the protonated model 1, the broadening is fitted using

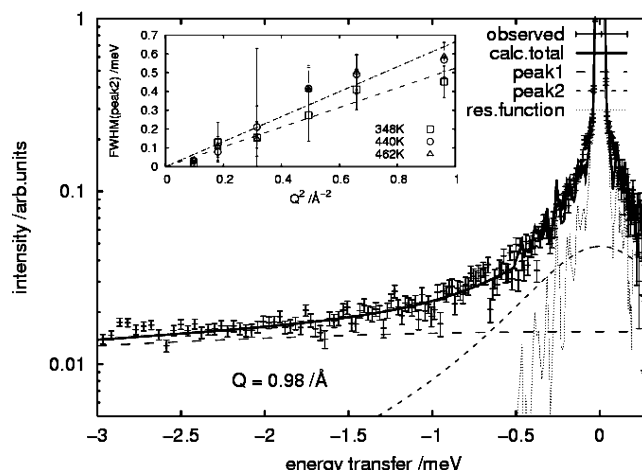


Figure 2. Fit of the QENS signal for protonated S-PPTA model 1 using two Lorentzian curves and the response function of the apparatus. Inset: dependence of the fwhm of the narrow QENS component on Q^2 for different temperatures.

two Lorentzian lines (see Figure 2): a narrow component with an average width of $\sim 300 \mu\text{eV}$ and a very broad component with a width of $\sim 10 \text{ meV}$. In the data for the lithiated model 1, the narrow component is completely absent, suggesting that the narrow component in the protonated oligomer is due to the motion of the acid protons in the sample.

The inset in Figure 2 shows that the width of this narrow component depends quadratically on Q , which is indicative of diffusive motion of the protons through the material. The slope of fitted lines in the inset is proportional to the proton diffusion coefficient D_H , which was found to be close to $5 \times 10^{-5} \text{ cm}^2/\text{s}$. This value is somewhat larger than that found for Nafion 117 ($\sim 1.6 \times 10^{-5} \text{ cm}^2/\text{s}$ at room temperature) on the basis of diffusion experiments using radiotracers.²⁴ The proton diffusion coefficient is of the same order of magnitude as values found from molecular dynamics calculations.^{25,26}

The broad component is more difficult to assign because its width decreases with Q in the range of $Q = 0.3\text{--}1.0 \text{ \AA}^{-1}$. We observe a decrease with temperature, whereas the intensity of the function increases with Q and T , as expected. We do not know of a model describing the dependence of this width as we have fitted. The intensity of the broad component is approximately 7 times higher than that of the narrow component. This is most likely due to the dynamics of the S-PPTA molecule as a whole. We note that the temperature dependence could be a result of the liquid crystalline properties of S-PPTA; however, we do not have supporting observations for this hypothesis at the time of writing this manuscript.

The width of the broad component was found to decrease upon replacement of the acid protons by lithium ions for all temperatures by roughly 1 meV averaged over Q . This indicates that the presence of lithium ions slows down the dynamics of PPTA chains. We suggest that a structure is formed in which a single lithium ion interacts with two sulfonic acid groups on different oligomers. Such ionic cross-linking leads to a more rigid structure, analogous to PEO-based polymer electrolytes. These results are in agreement with SANS measurements by Mendes et al. who observed that on addition of Li⁺ the S-PPTA (in solution) shows a stronger tendency to form needlelike aggregates.⁸ The possibility of the formation of such a structure is confirmed by ab initio calculations as discussed below.

3.2. Geometry of Sulfonated PPTA Model Systems. The PPTA and sulfonated PPTA model systems studied in this work are shown in Figure 1. The geometry of PPTA model systems

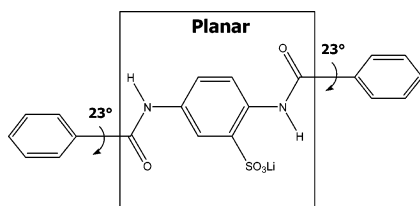


Figure 3. Geometry of S-PPTA model 1.

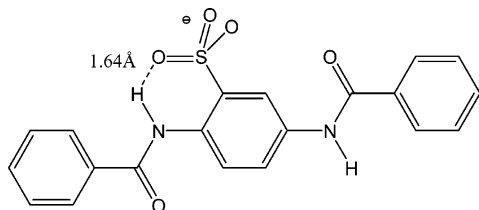


Figure 4. Internal cyclization in S-PPTA model 1.

was fully optimized by DFT calculations as discussed in section 2. For the unsulfonated PPTA model systems, the geometry was found to be relatively planar and rigid. The plane of the amide linkage is found to be in the same plane as the phenyl belonging to the phenylenediamine monomer for all PPTA models, as indicated in Figure 3. The angle between the terephthalic acid phenyl ring and the amide-plane was found to be close to 23° . These angles are similar for all PPTA model systems. The geometry obtained here is more planar than that previously described by Irwin and Vorpapel who optimized the geometry using the semiempirical AM1 method.²⁷ In these AM1 studies, the authors reported an angle of around 45° for the amide-carbon phenyl bond.

The energy difference between the syn (with both amide-oxygen atoms pointing in the same direction) and anti conformers of PPTA model 1 is rather small; the anti conformer is 0.82 kcal/mol more stable. In the case of PPTA model 2, the difference is even smaller; the anti conformer is more stable by 0.44 kcal/mol. This indicates that deviations from a linear rigid structure are energetically possible by syn-orientation in the chain. As discussed by Irwin and Vorpapel,²⁷ a single syn-defect in the chain causes a chain-bend of around 20° .

The introduction of sulfonic acid groups on the central phenyl rings of the model compounds (S-PPTA models 1 and 2) does not lead to large distortions of the rigid-rod polymer backbone. The sulfonic acid moiety is oriented toward the amide hydrogen atom in all model systems, as they are drawn in Figure 1. Geometries where the sulfonic acid groups point toward the amide oxygen are not stable because of steric and electrostatic repulsions (see also below for the charge distribution).

In the sulfo-PPTA model 1, where the sulfonic acid is on the phenyl ring belonging to the di-amine, one of the sulfonic acid oxygen atoms interacts strongly with the amide hydrogen atom, which has a considerable positive charge; see below. This leads to an internal cyclization in which a six-ring is formed in which there is a hydrogen-bond-like interaction between the oxygen and the amide hydrogen; see Figure 4. The distance between the amide hydrogen atom and the sulfonic acid oxygen was found to be 1.64 Å for the singly charged (i.e., no lithium counterion is present) model 1. Interestingly, coordination of a lithium ion to the sulfonic acid group leads to a considerable increase of this O—H distance to 1.89 Å, because of the electrostatic repulsion between the lithium and the amide hydrogen.

Viale et al. have postulated an internal cyclization between the proton on the amide bond and the sulfonic acid group on

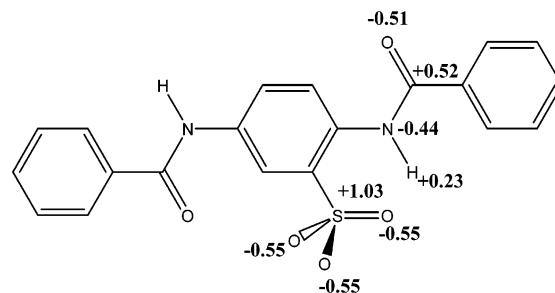


Figure 5. Charge distribution in S-PPTA model 1 obtained from DFT calculations.

the basis of the appearance of a shifted infrared absorption band.¹⁰ The authors assert that this interaction does not allow the true nematic phase to be revealed and reduces the water solubility of the polymer chain leading to the formation of a birefringent gel. From the calculations performed here, a cyclization was also found in geometry optimizations for the model 2 compound. However, in this case, a seven-ring is formed, which is likely to be less stable.

The reduced interaction between the amide hydrogen and the sulfonic acid oxygen in S-PPTA model 2 is also evident from the calculated infrared (IR) absorption spectra, particularly the N—H stretch vibration. In the unsulfonated PPTA model compounds, the energy of this stretch vibration is close to 3490 cm^{-1} . In S-PPTA model 1 with a six-ring cyclization, the energy of this vibration is considerably reduced to 3348 cm^{-1} , indicating a marked effect of the interaction with the sulfonic acid oxygen. In S-PPTA model 2 where a seven-ring cyclization is found, the N—H stretch vibration energy is 3403 cm^{-1} , intermediate between that for S-PPTA model 1 and the “free” N—H stretch vibration energy. The reduced interaction in the case of S-PPTA model 2 may explain the absence of the specific IR features that were attributed to the cyclization for sulfo-PPTA by Viale et al.¹⁰

3.3. Charge Distribution and Lithium-Ion Binding. The charge distribution for the model systems that are considered here can be analyzed in terms of atomic point charges. These point charges were obtained from DFT calculations on model systems without the lithium ion by fitting to the electrostatic potential. The charges obtained in this way are shown in Figure 5 for selected atoms for S-PPTA model 1.

Charge distributions in other model systems containing the sulfonic acid group were found to be virtually the same. As expected, there is considerable negative charge ($\sim -0.55e$) on the three oxygen atoms of the sulfonic acid group, while the sulfur atom carries a large positive charge ($\sim +1e$). Interestingly, the negative charge on the oxygen atom in the amide linkage is almost the same as that on the sulfonic acid oxygen atoms. Comparison with the charge distribution in, for example, ethyl-aldehyde and diethyl-ether shows that in those small molecules the charge on the oxygen atom is only slightly lower ($\sim -0.4e$). The charge distribution on the sulfonic acid-substituted PPTA model systems suggests two favorable binding positions for the lithium ion, the sulfonic acid group and the amide-oxygen.

Geometry optimizations have been performed, including the lithium ion close to the positions suggested by the charge distribution. If the lithium ion is placed close to the sulfonic acid moiety, a minimum energy conformation is obtained where the ion interacts with two oxygen atoms in the sulfonic acid group and is in the O—S—O-plane; see Figure 6. The distance from the lithium ion to both of the oxygen atoms is ca. 1.9 Å. If the lithium ion is placed close to the amide-oxygen, the ion tends to migrate toward the sulfonic acid group. In one case, a

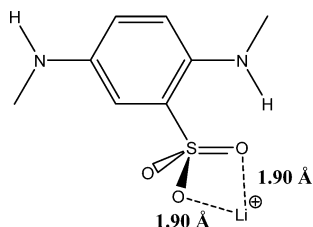


Figure 6. Position of Li^+ with respect to the sulfonic acid group.

TABLE 1: Vertical and Relaxed Lithium Binding Energy for Various Coordinating Groups Calculated by DFT and by Classical DRF90 Calculations

structure	binding energy (vertical, kcal/mol)		binding energy (relaxed, kcal/mol)
	DFT	classical	
model 1	-154.97	-160.55	-145.51
model 2	-149.66	-155.18	-140.67
<i>ortho</i> -fluoro model 2	-154.51		-142.51
<i>meta</i> -fluoro model 2	-149.43		-139.98
<i>para</i> -fluoro model 2	-148.05		-139.05
PAMPS	-162.81		-146.20
MBSA	-158.20		-146.90
ether	-46.35	-45.95	-44.51
aldehyde	-44.74	-54.57	-43.58
ketone	-49.58	-60.18	-48.20

local minimum was found where the lithium ion binds to the oxygen atom in the peptide linkage. The distance between the lithium atom and the oxygen was found to be ca. 1.8 Å, a slightly smaller distance than at the sulfonic acid position.

The interaction energy between lithium ions and the model systems was calculated for the lowest energy conformations obtained from the geometry optimizations using the full counterpoise theory to correct for basis set superposition errors.¹⁸ The binding energies, both vertical and relaxed, are listed in Table 1.

When comparing the binding energies for the two model systems studied here (S-PPTA models 1 and 2, see Figure 1), we note that the lithium-ion binding energy depends only to a small extent on the position of the sulfonic acid group. The lithium-ion binding energy for a sulfonic acid group on a phenyl ring between two secondary amines (S-PPTA model 1) is larger by ca. 5 kcal/mol than for a sulfonic acid group positioned between two carbonyl moieties.

In the case of the model system containing multiple sulfonic acid groups, the binding energies of lithium to the individual sites are not independent. This is evident from calculations for S-PPTA model 3, which contains two sulfonic acid groups. The interaction of the lithium ion with the distant sulfonic acid group is significantly influenced by the presence of a second lithium ion at that site. The energy required to remove the first lithium ion from S-PPTA model 3 is approximately 150 kcal/mol, similar to binding energies for S-PPTA models 1 and 2. Removing the second lithium ion requires 190 kcal/mol, which is considerably more than for removal of the first ion. This increased binding energy is due to the long-range electrostatic interaction with the distant (negatively charged) sulfonic acid group. The distance between the lithium ion and the distant sulfonic acid group is ca. 8.5 Å, depending on the exact position of the ion (i.e., to which two oxygen atoms it is bound). The interaction between two point charges ($1e$) of opposite charge at this distance is 39 kcal/mol, almost the same as the difference between the energies for removal of the first and second lithium ion. If a lithium ion is present on the distant sulfonic acid group, the attractive interaction with this sulfonic acid group is

counteracted by repulsive interactions with the second lithium ion, which is at approximately the same distance.

To put the binding energies described here in perspective with those for other commonly used polyelectrolyte systems, calculations have been performed on poly(2-acrylamido-2-methyl-1-sulfonic acid) (PAMPS). This polymer has been used by a number of researchers as both a fuel cell membrane and a lithium-conducting electrolyte; in both cases, the polymer is swollen with a solution, water or aprotic solvents, respectively.^{3,28} We also examined another analogue polyelectrolyte to PAMPS, MBSA that does not contain an alkyl chain between the tertiary amine and the sulfonic acid group. In both cases, the binding energies of lithium are approximately equal to those calculated for the sulfonated derivatives of PPTA. Interestingly, we note that the structure to which the sulfonic acid group is attached has very little effect on the binding energy of the lithium ion to the sulfonic acid group. In light of these results, the significant increase in ionic conductivity observed in PAMPS-based polyelectrolytes doped with ionic liquid-based zwitterions can in part be attributed to the reduced binding energies of the lithium-ion to the sulfonic acid group due to enhanced charge dissociation.²⁹

Johansson, in a number of papers,^{30,31} has described the salt solvating ability of these host systems as a function of the coordinating number of the host polymer. In the case of PEO, it is the number of oxygen atoms interacting with lithium ion, and it is the number of nitrogen atoms in the case of PAN. In all cases, it has been noted that the binding energy of lithium per coordinating unit is inversely proportional to the number of coordinating atoms surrounding it.³¹ In this case, the binding energy should be compared to a situation where two coordinating atoms interact with the lithium-ion because two oxygens in the sulfonic acid are coordinated to the ion. For such cases, the binding energy is generally close to 100 kcal/mol,³¹ significantly lower than for the sulfonic acid–lithium-ion binding. We attribute this difference to the total charge of the system. In the case of polymer electrolytes such as PEO, the polymer has no net charge, whereas in our system there is a full negative charge that is strongly localized around the sulfonic acid group. If the lithium-ion binding energies found in our calculations are compared to dissociation energies for a series of lithium salts with relatively small anions that were calculated by Kim et al.,³² the values are indeed of similar magnitude. Comparison with the recent work of Markusson et al. shows that the lithium-ion binding energies found here are also comparable to binding energies found for extended PPI anion model systems where the lithium ion binds to a sulfonyl moiety that is present in the main chain of the molecule.³³

The preference for lithium-ion binding at the sulfonic acid group rather than at the carbonyl group on the aramid bond can be rationalized by the smaller binding energy at this position. This is illustrated by the binding energies calculated for the aldehyde and ketone model systems in Table 1; these binding energies are close to 50 kcal/mol, which is ca. 3 times lower than the binding energy for a sulfonic acid group.

To gain more insight into the nature of the bonding between the lithium ion and the polyelectrolyte model systems, we have performed “classical” calculations using the polarizable DRF90 force field. This enables us to analyze the interaction energy in terms of physically meaningful contributions, such as electrostatic interactions, induction interactions, dispersion, and short-range repulsion interactions. The electrostatic interactions are calculated as the interaction between point charges, while the induction part is obtained from the interaction between the point

TABLE 2: Different Contributions to the Classical Interaction Energy Calculated Using the DRF90 Force Field

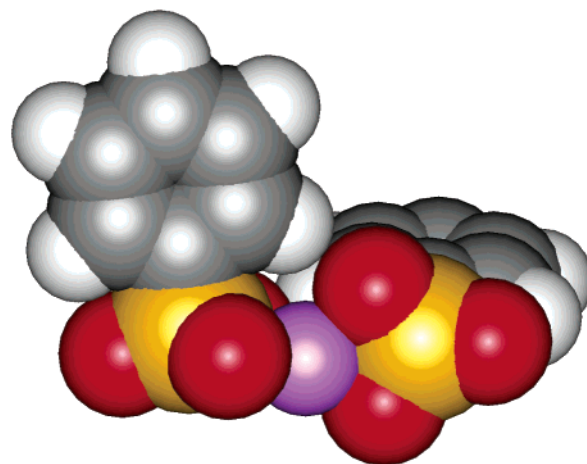
	S-PPTA model 1	S-PPTA model 2	ether
electrostatic	-125.99	-120.54	-20.89
induction	-34.58	-34.65	-25.08
dispersion	-0.30	-0.30	-0.20
repulsion	+0.31	+0.31	+0.20
total	-160.55	-155.18	-45.95

charges and the atomic polarizabilities that are explicitly present in the calculations. The interaction energies calculated using the DRF90 force field are given in Table 1. The interaction energies are in reasonable agreement with the values from DFT calculations. In Table 2, it can be seen that for the interaction between a lithium ion and the sulfonic acid group the electrostatic interaction dominates the total binding energy. It should be noted, however, that induction interactions are also contributing considerably; they are close to 30% of the electrostatic interaction for all sulfonic acid-substituted model systems. In the ether model, the contribution of induction interactions are even somewhat larger than the electrostatic part; see Table 2. For the keton and aldehyde models, the induction interaction was also found to be of size similar to that of the electrostatic part. This shows that, as can be expected in the case of ionic interactions, the inclusion of an explicit description of induction interactions in the force field is desirable for a good description of the total interaction energy. This does not necessarily mean that force fields without explicit induction terms are not suitable for describing the dynamics of lithium ions in “solid” polyelectrolyte systems. If the induction interaction of the lithium ion with the polymer matrix is similar everywhere in the material, induction only gives a uniform lowering of the energy and does not influence the mobility of the ion very much.

3.4. Effect of Fluorination. We have investigated the influence of fluorination on different positions on the main chain, neighboring that of the sulfonic acid group for S-PPTA model 2. Calculations were performed in which a single fluorine atom was introduced at the *ortho*, *meta*, or *para* position, with respect to the sulfonic acid group (see Figure 1). The addition of such electron-withdrawing moieties is commonly used in the design and preparation of new anions for lithium salts, the most successful of these materials being the lithium bis(trifluoromethanesulfonyl)amide salt.³⁴ In the case of this work, we have been careful to ensure that we do not add moieties that may disturb the liquid crystalline nature of the polyelectrolyte, and, as such, fluorination of the ring is one way to achieve this.

By putting fluorine atoms on three separate positions of S-PPTA model 2, we do not observe any significant decrease in the binding energy of the lithium-ion to the sulfonic acid group, as is evident from the interaction energies for the fluorinated S-PPTA compounds in Table 1.

Fluorination of sulfonic acid-based polyelectrolytes has been shown to lead to a high ion conductivity in commercially used Nafion membranes where the sulfonic acid group is attached (by a *n*-CF₂ linker) to a perfluorinated polymer backbone.³⁵ We have examined the effect of fluorination on the lithium binding ability of the sulfonic acid group for such systems by calculating the binding energy for a sulfonic acid group attached to an ethyl group and comparing it to the binding energy for a perfluorinated ethyl group. The calculated vertical binding energies were -168.3 and -157.7 kcal/mol for the hydrogenated and fluorinated ethyl groups, respectively. The lowering of the lithium binding energy by ~10 kcal/mol achieved by fluorination is mostly due to a lowering of the charge on the sulfonic acid oxygen atoms, from -0.6e to -0.55e induced by the electro-

**Figure 7.** Optimized geometry for a system in which a lithium ion interacts with two sulfonic acid groups on different polymer chains.

negative fluorine atoms. It was found that there is considerable negative charge on the fluorine atoms, ~0.16e, whereas in the hydrogenated case the charge on the hydrogen atoms is negligible. The considerable negative charge of the fluorine atoms in the polymer backbone and linkers suggests an additional reason for the increased ion conductivity in the perfluorinated Nafion, as compared to the fully hydrogenated case. The attractive interaction between lithium and the fluorine atoms reduces the energy to move the ion from a sulfonic acid group to a fluorine-rich region in the Nafion membrane.³⁶

3.5. Coordination Number. Most electrolytes for lithium-ion batteries are based on the polymer electrolyte concept, in which a salt is dissolved into a polymer matrix sometimes with the assistance of an intermediate solvent. Dissociation of the ions occurs due to the strong electrostatic interactions between the ions and coordinating groups in the polymer. A commonly used polymer for this purpose is poly(ethylene oxide) (PEO). In PEO, the ether oxygen atoms in the main chain act as the coordinating groups. Other polymers used as polymer electrolytes are poly(propylene oxide) (PPO, the amorphous version of PEO) and poly(acrylonitrile) (PAN). As mentioned above, the interaction energy per coordinating group generally decreases with increasing number of coordinating groups.

To investigate this further, we have considered the possibility of a lithium ion interacting with two sulfonic acid groups on different polymer chains by optimizing the geometry of a trimeric system consisting of a lithium ion and two sulfonic acid-substituted benzene groups. The simplification of attaching just a phenyl ring to the sulfonic acid group and not using the entire model system is not expected to influence the results to a large extent because we have shown above that the lithium binding energy is independent of the backbone or side chain to which the sulfonic acid group is connected. For this complex, a minimum energy conformation was found in which the lithium ion interacts with four oxygen atoms, two on each sulfonic acid group; see Figure 7. The four oxygen atoms surround the lithium ion in a distorted tetrahedral geometry to maximize the distance between the negatively charged oxygens on different molecules. From Figure 7, it is clear that binding of the lithium ion to three or more sulfonic acid group is rather unlikely due to steric effects.

The distance between the lithium ion and the oxygen atoms is somewhat larger than in the case where only one sulfonic acid group interacts with the lithium-ion. In addition, the interaction of the lithium is not symmetric for both of the oxygens in the same sulfonic acid group. The O-Li distances

TABLE 3: Analysis of Interaction Energies for a Lithium Ion Coordinated between Two Sulfonic Acid Groups

interaction	DFT (kcal/mol)	DRF90 force field (kcal/mol)
Li–Sulf1	–156.42	–158.05
Li–Sulf2	–156.41	–157.98
Sulf1–Sulf2	+66.18	+58.79
three-body int.	+36.91	+31.97
total	–209.74	–225.27

are 2.08 and 2.00 Å for the two oxygen atoms in a single sulfonic acid group; these two distances are the same for both of the sulfonic acids. The increase in the distance is caused by the electrostatic repulsion between the two negatively charged sulfonic acid groups. This is also evident from the vertical interaction energies for the trimer system in Table 3. All of the interaction energies are fully corrected for BSSE; that is, all calculations were performed in the full trimer basis set. The interaction energy for a lithium ion with a single sulfonic acid group was found to be similar to that for the model systems considered above, ca. –155 kcal/mol. However, the total interaction energy for the trimer system is considerably smaller than twice the interaction energy for a single sulfonic acid group because of the repulsion between the two sulfonic acid groups, which is ca. +66 kcal/mol. Additionally, the highly polar nature of the lithium ion and the sulfonic acid groups leads to the occurrence of a three-body interaction. The lithium ion induces large dipole moments in both of the sulfonic acid groups; these dipoles are repulsive, and therefore the three-body term also leads to a lowering of the total interaction energy. Table 3 also shows the interaction energies obtained using the DRF90 force field. The correspondence between the “classical” and quantum chemical interaction energies is rather good; even the three-body term is nicely reproduced. The occurrence of a considerable three-body interaction also confirms the desirability of a polarizable force field to describe the interactions in these systems.

4. Summary and Conclusions

In this work, we have investigated the chain dynamics and lithium-ion binding properties of sulfonic acid-substituted poly(*para*-phenylene terephthalamide) (S-PPTA). Quasi elastic neutron scattering (QENS) experiments on short model systems of sulfonic acid-substituted PPTA were performed to examine the chain dynamics and the dynamics of protons in this material. A narrow component in the quasi-elastic broadening of the QENS signal was found in the protonated sample. This component was completely absent for a sample in which all protons were replaced by lithium ions; consequently, this narrow component was attributed to diffusion of acid protons. The proton diffusion coefficient was found to be 5×10^{-5} cm²/s. The width of a broad QENS component was found to decrease upon lithiation, indicating that the presence of lithium ions slows down the chain dynamics.

Ab initio calculations have been used to determine the optimum geometry of several model systems based on sulfonated PPTA and derivatives. Using density functional theory (DFT), we find that the addition of sulfonic acid groups to different positions on the main chain does not disturb the structure; in fact, the twist in the amide bond is found to be less than previously calculated.²⁷

The calculated lithium-ion binding energies show there is no dependence of the binding energy on the position of the sulfonic acid group, approximately 150 kcal/mol in all cases. Introduction of fluorine atoms close to the sulfonic acid group was found to

have little influence on the binding energy of lithium ion. The binding energy was found to be 3 times higher than those for ether, aldehyde, and ketone-based systems, which were used as model systems for the lithium-ion binding groups in polymer electrolyte such as PEO. The much larger binding energy is due to the negative charge on the sulfonic acid group. Additional calculations of the lithium-ion binding energy were performed using a polarizable classical force field. The binding energies were found to be close to the DFT results. From these force-field calculations, it was found that the lithium-ion binding is dominated by electrostatic interaction; however, it was also shown that the contribution of induction (monopole-induced dipole) interactions can contribute significantly, up to 30% of the electrostatic interaction. This illustrates the desirability of using a polarizable force field for molecular dynamics simulations on lithium dynamics in the systems considered here.

On the basis of DFT calculations, we conclude that a stable configuration can be formed where one lithium ion is sandwiched between two sulfonic acid groups on different chains. In this structure, the lithium ion interacts with two oxygen atoms on each sulfonic acid group, which surround the lithium ion in a distorted tetrahedral conformation. The formation of such a structure can be an explanation for the reduced chain dynamics upon lithiation, as was observed in QENS measurements in this work. It also explains the increased tendency of sulfonated PPTA to aggregate if lithium ions are present.⁸

The structural data and lithium-ion binding energies presented in this work will be used as a basis for molecular dynamics simulations in which the chain and lithium-ion dynamics will be studied on a larger scale and compared to the data from QENS experiments.

Acknowledgment. Mr. S. Viale, M.Sc., is acknowledged for preparing the model system and polymers investigated in this work. Dr. M. Swart is acknowledged for making available the DRF90 software. This work forms part of the research program of the Dutch Polymer Institute (DPI).

References and Notes

- (1) Gray, F. M. *Solid Polymer Electrolytes*; John Wiley & Sons: New York, 1991.
- (2) Mao, G.; Fernandez Perea, R.; Howells, W. S.; Price, D. L.; Saboungi, M.-L. *Nature* **2000**, *405*, 163–165.
- (3) Travas-Sejdic, J.; Steiner, R.; Desilvestro, J.; Pickering, P. *Electrochim. Acta* **2001**, *46*, 1461–1466.
- (4) Rao, Y.; Waddon, A. J.; Farris, R. J. *Polymer* **2001**, *42*, 5925–5935.
- (5) Viale, S.; Jager, W. F.; Picken, S. J. *Polymer* **2003**, *44*, 7843–7850.
- (6) Yun, H. C.; Chu, E. Y.; Han, Y. K.; Lee, J. L.; Kwei, T. K.; Okamoto, Y. *Macromolecules* **1997**, *30*, 2185–2186.
- (7) VandenBerg, E. J.; Diveley, W. R.; Filar, L. J.; Patel, S. R.; Barth, H. G. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3745–3757.
- (8) Mendes, E.; Viale, S.; Santin, O.; Heinrich, M.; Picken, S. J. *J. Appl. Crystallogr.* **2003**, *36*, 1000.
- (9) Viale, S.; Best, A. S.; Mendes, E.; Jager, W. F.; Picken, S. J. *Chem. Commun.* **2004**, *14*, 1596–1597.
- (10) Viale, S.; Li, N.; Schotman, A. H. M.; Best, A. S.; Jager, W. F.; Picken, S. J., submitted for publication.
- (11) Okamoto, Y.; Xu, Z. S.; McLin, M. G.; Fontanella, J. J.; Pak, Y. S.; Greenbaum, S. G. *Solid State Ionics* **1993**, *60*, 131–134.
- (12) Forsyth, M.; Meakin, P.; Macfarlane, D. R.; Hill, A. J. *J. Phys.: Condens. Matter* **1995**, *7*, 7601–7617.
- (13) <http://whisky.ill.fr/YellowBook/IN5>.
- (14) <ftp://ftp.ill.fr/pub/cs/inx>.
- (15) <ftp://ftp.ill.fr/pub/cs/profit>.
- (16) Bée, M. *Quasielastic neutron scattering*; IOP publishing Ltd.: Bristol, 1988.
- (17) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (18) van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873.

- (19) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.
- (20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (21) van Duijnen, P. T.; Rullmann, J. A. C. *Int. J. Quantum Chem.* **1990**, *38*, 181.
- (22) van Duijnen, P. T.; Swart, M. *J. Phys. Chem. A* **1998**, *102*, 2399.
- (23) Grozema, F. C.; Zijlstra, R. W. J.; van Duijnen, P. T. *Chem. Phys.* **1999**, *246*, 217–227.
- (24) Verbrugge, M. W.; Schneider, E. W.; Conell, R. S.; Hill, R. F. *J. Electrochem. Soc.* **1992**, *139*, 3421–3428.
- (25) Spohr, E.; Commer, P.; Kornyshev, A. A. *J. Phys. Chem. B* **2002**, *106*, 10560–10569.
- (26) Din, X.-D.; Michaelides, E. E. *AIChE J.* **1998**, *44*, 35–47.
- (27) Irwin, R. S.; Vorpapel, E. R. *Macromolecules* **1993**, *26*, 3391–3402.
- (28) Karlsson, L. E.; Wesslen, B.; Jannasch, P. *Electrochim. Acta* **2002**, *47*, 3269–3275.
- (29) Tiyyapiboonchaiya, C.; Pringle, J. M.; Sun, J.; Byrne, N.; Howlett, P. C.; Macfarlane, D. R.; Forsyth, M. *Nat. Mater.* **2004**, *3*, 29–32.
- (30) Johansson, P. *Polymer* **2001**, *42*, 4367–4373.
- (31) Johansson, P.; Edvardsson, M.; Adebahr, J.; Jacobsson, P. *J. Phys. Chem. B* **2003**, *107*, 12622–12627.
- (32) Kim, C. K.; Won, J.; Kim, H. S.; Kang, Y. S.; Li, H. G.; Kim, C. K. *Int. J. Quantum Chem.* **2001**, *22*, 827–834.
- (33) Markuss, H.; Tokuda, H.; Watanabe, M.; Johansson, P.; Jacobsson, P. *Polymer* **2004**, *45*, 9057–9065.
- (34) Armand, M.; Gorecki, W.; Andreani, R. In *Second International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier: New York, 1990.
- (35) Doyle, M.; Lewittes, M. E.; Roelofs, M. G.; Perusich, S. A.; Lowery, R. E. *J. Membr. Sci.* **2001**, *184*, 257–273.
- (36) Paddison, S. J.; Pratt, L. R.; Zawodzinski, T.; Reagor, D. W. *Liquid-Phase Equilibria* **1998**, *150–151*, 235–243.