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Inductive Effect and Hydrogen Bonding in Complexes of Branched Poly(ethylenimine) with Sodium Tetraphenylborate and Sodium Triflate

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ABSTRACT: Systems of branched polyethylenimine (BPEI) complexed with sodium triflate (NaTf) and sodium tetraphenylborate ($NaBPh_4$) are examined using FT-IR spectroscopy, differential scanning calorimetry, and impedance spectroscopy. Cation−polymer, cation−anion, and hydrogen-bonding interactions are investigated by evaluating the frequency shifts of the host BPEI upon complexation with the salts. The inductive effect of sodium is highly dependent on its interaction with the anion, with the effect stronger in BPEI:$NaBPh_4$ complexes than in BPEI:NaTf complexes. DSC data show that the glass transition temperatures for the BPEI:$NaBPh_4$ system are significantly higher than the T_g values for the BPEI:NaTf system at the same salt compositions. The ionic conductivities of the BPEI:NaTf complexes are significantly higher than the conductivities of the BPEI:$NaBPh_4$ complexes at all comparable compositions and temperatures. This result is consistent with the DSC data and the greater sodium ion inductive effect in the BPEI:$NaBPh_4$ complexes. The highest conductivity values occur in the 20:1 BPEI:NaTf complex and are on the order of 10^{-6} S cm^{-1} at 25 °C.

Introduction

It is well-known that metal salts can be dissolved in a polymer matrix containing heteroatoms such as oxygen in poly(ethylene oxide) (PEO) or nitrogen in poly(ethylenimine) (PEI) to form ionically conducting systems that can be used as electrolytes. The ionic conduction of such materials results from dissociation of the salt; the cation is solvated by the lone pair electrons of the polymer heteroatoms, and in certain cases the anion is solvated by the polymer via hydrogen bonding.[1] So far, the majority of studies have focused on PEO-based electrolytes due to their relatively high ionic conductivities above 80 °C (10^{-5} Ω^{-1} cm^{-1}). However, the conductivity in PEO-based electrolytes is limited by the formation of crystalline complexes upon addition of salts.[2−6] Amorphous polymers and polymers that do not tend to crystallize with addition of salts are the focus of research, as the ionic conductivity is generally higher in an amorphous phase.[7−9]

Branched poly(ethylenimine) (BPEI) is fully amorphous and has a T_g of −55 °C, unlike the linear form which is crystalline at room temperature. BPEI has a high concentration of polar groups, with a molar ratio of primary to secondary to tertiary amine reported as 25:50:25.[10,11] However, Pierre et al. have found a different result by ^{13}C NMR. Their reported ratio is 38:36:26.[12] In early studies, the ionic conduction and T_g of BPEI complexed with $LiCF_3SO_3$ and $NaCF_3SO_3$ have been reported by Paul et al.[13] and Harris et al.,[14] respectively.

The complexity of BPEI−salt complexes makes it difficult to develop even a qualitative, molecular-level understanding of the nature of the ionic conductivity. Cation−polymer and cation−anion interactions as well as hydrogen-bonding interactions are expected to play a major role in the mechanism of ion transport. Unfortunately, all these factors are interdependent in the BPEI−salt system. However, a comparative spectroscopic study of BPEI complexed with sodium trifluoromethanesulfonate, $NaCF_3SO_3$ (NaTf), and with sodium tetraphenylborate ($NaBPh_4$) offers an excellent opportunity to sort these competing effects, to a significant degree. The sodium ion of both salts is expected to coordinatively interact with the nitrogen atom of BPEI, although to a different extent because of the presence of relatively strong cation−anion interactions in the NaTf complexes. However, the lack of heteroatoms in the tetraphenylborate anion precludes the formation of hydrogen bonds with the N−H groups upon complexation, in contrast to the N−H···O hydrogen bonds expected in the NaTf complexes.

In this study, infrared spectroscopy is used to characterize polymer−salt interactions by analyzing the frequency shifts of the host BPEI modes upon complexation with a salt; additional insight into these interactions is obtained from differential scanning calorimetry measurements. Both hydrogen-bonding and inductive effects shift the vibrational frequencies of the BPEI primary amine functional group. The comparative infrared spectroscopic data of the BPEI:$NaBPh_4$ and BPEI:NaTf complexes are augmented by DSC data. Finally, these data are used to explain the significant differences in the conductivities of the two complexes.

Experimental Section

Preparation of Polymer Electrolytes. BPEI (number-average molecular weight = 10,000), $NaCF_3SO_3$ (NaTf), and sodium tetraphenylborate ($NaBPh_4$) were obtained from Aldrich and used as received. The NaTf was dried under vacuum at 120 °C for 48 h before use. Methanol used as a cosolvent was distilled over sodium metal. All the chemicals were stored and used in a dry argon atmosphere glovebox (VAC, ≤1 ppm of H_2O) at room temperature. All polymer−salt solutions were prepared by dissolving weighed amounts of BPEI and the salt in dry methanol and stirring for ~24 h to ensure a homogeneous solution before casting as films. The compositions of the samples are reported as a nitrogen to cation molar ratio (N:M$^+$).

FT-IR Spectroscopy. The FT-IR samples were made by casting the solutions directly onto zinc selenide windows and

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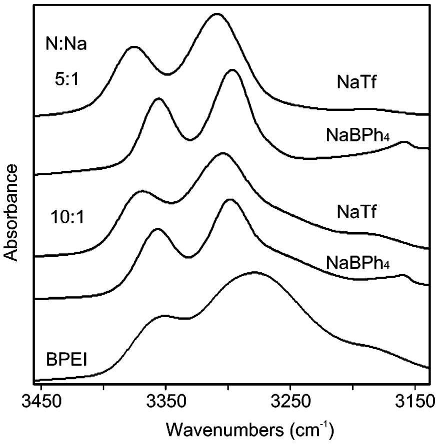

Figure 1. IR spectra of the N−H stretching vibrations of BPEI and its NaTf and $NaBPh_4$ complexes ($N:Na^+ = 10:1, 5:1$).

drying under argon for 24 h. The samples were then placed under vacuum at room temperature for an additional 24 h to ensure solvent removal. Infrared data were collected using a Bruker IFS66V FT-IR spectrometer (KBr beam splitter) under vacuum (11 mbar). The data were recorded over a range of 500−4000 cm^{-1} with a spectral resolution of 1 cm^{-1}.

Differential Scanning Calorimetry. Solutions were cast on Teflon, dried under argon for 24 h, and placed under vacuum at room temperature for at least 48 h. Samples with compositions ≤10:1 were translucent with a light yellow tint. For higher salt compositions, both BPEI:$NaBPh_4$ and BPEI:NaTf samples appeared lighter in color and more brittle. After drying, 20−30 mg samples were sealed in 40 μL aluminum pans under an argon atmosphere. Thermal data were collected using a Mettler DSC 820 calorimeter under a dry nitrogen purge at heating and cooling rates of 5 °C/min. The thermograms were then analyzed using a star^e v.6.10 software from Mettler Toledo. Each sample was cycled three times, with the first cycle from room temperature to 150° and then to −100 °C. The next two cycles were from −100 to 100 °C and back to −100 °C. The reported data correspond to an average of the second heating cycle of at least three different samples.

Complex Impedance. The samples were cast directly onto a 12.5 mm diameter stainless steel electrode in an argon atmosphere. The samples were allowed to dry 24 h in the glovebox and 48 h under vacuum at room temperature before testing. The film thickness was measured using a micrometer built into the conductivity cell. Conductivity measurements were made over the frequency range 0.005−10 000 kHz using a Hewlett-Packard 4192A LF impedance analyzer with Labview 5.1 software (National Instruments). All the conductivity data were measured using a heating cycle ranging from room temperature to 80 °C in 10 °C increments. After the first heating cycle, the sample was allowed to cool to room temperature overnight, and a second heating cycle was performed. For both BPEI:NaTf and $NaBPh_4$ systems, the conductivities were not measured for compositions of 5:1 and above due to interfacial contact problems between the electrodes and the electrolyte. The impedance plots were curve fitted using commercially available software Solartron Instruments LTD, Levm 7.1v.

Results and Discussion

NH Stretch and NH Bend. The NH stretching vibrations of the BPEI amine groups are shown in Figure 1 for BPEI and complexes of BPEI with NaTf and with $NaBPh_4$.

The primary amine group in BPEI gives rise to two N−H stretching modes: the symmetric NH_2 stretching mode, $\nu_s(NH_2)$, at 3279 cm^{-1} and the asymmetric NH_2 stretching mode, $\nu_{as}(NH_2)$, at 3352 cm^{-1}. The vibrational frequency of the secondary amino group in BPEI, ν(NH), overlaps with $\nu_s(NH_2)$.[15] The shoulder at 3185 cm^{-1} is an overtone of the NH_2 deformation band at 1594 cm^{-1}. These frequency data are summarized in the first row of Table 1. The breadth of the bands in the BPEI spectrum is characteristic of the heterogeneous hydrogen-bonding environment in the amorphous host that leads to a distribution of intermolecular and intramolecular interactions. In dilute solutions of primary amines, $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ occur around 3500 and 3400 cm^{-1}, respectively, and the N−H stretch of secondary amines occurs in the region 3350−3310 cm^{-1}.[15] The decrease in the $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ frequencies compared to those of dilute solutions or gaseous phases of primary amines results from hydrogen-bonding interactions.

Table 1. N−H Stretching Frequencies (cm^{-1}) of BPEI and Its Complexes with NaTf and $NaBPh_4$

	$\nu_{as}(NH_2)$		$\nu_s(NH_2)$	
composition	NaTf	$NaBPh_4$	NaTf	$NaBPh_4$
pure	3352	3352	3279	3279
10:1	3369	3356	3304	3298
5:1	3376	3356	3309	3297

When NaTf or $NaBPh_4$ is dissolved in BPEI, both the ν_{as} and the ν_s bands shift to higher frequencies and the bandwidths decrease, as shown in Figure 1. These frequency data are also summarized in Table 1. In general, a decrease in bandwidth signifies a decrease in heterogeneous broadening, i.e., a more homogeneous distribution of potential energy environments of the vibrating species. In the case of hydrogen-bonded species, a decrease of N−H stretching mode bandwidths also indicates a decrease in the strength of hydrogen-bonding interactions.[16,17] It is probable that both of these effects occur upon complexation of BPEI with a salt. However, more detailed information about hydrogen-bonding interactions can be gained from a closer examination of the frequency shifts.

Paul et al. have pointed out that with the addition of lithium triflate there is a progressive replacement of hydrogen-bonded N−H···N groups by the entity Li^+···N−H···$^-O_3S-CF_3$.[13] There are two effects in the salt complexes that shift the frequencies relative to the pure BPEI system. The replacement of the N−H···N hydrogen bonds by weaker N−H···O hydrogen bonds to the triflate oxygen atoms shifts the N−H stretching modes to higher frequencies.[14,18] In addition, NH_2 frequency shifts can occur through the inductive effect, which results from the solvation of a cation by the lone pair of a nitrogen atom. This interaction weakens the N−H bond by decreasing its electron density and thereby decreases the mode frequency.[19] However, the interaction of the cation with the nitrogen atom also breaks N−H···N bonds, which would tend to increase the NH_2 stretching frequencies. The simultaneous occurrence of these effects makes it difficult to understand their relative importance in determining the NH_2 frequency shifts observed in the NaTf complexes.

The tetraphenylborate anion does not contain heteroatoms that participate in hydrogen-bonding interactions. Therefore, a comparative study of the frequency shifts in BPEI−$NaBPh_4$ complexes with analogous shifts in BPEI−NaTf complexes provides an excellent opportunity to understand the relative contributions of the various effects present. The frequency data in Figure 1 and Table 1 are graphically illustrated in Figure 2 as an aid to the following discussion.

In both NaTf and $NaBPh_4$ complexes, the coordination of the sodium ion with the nitrogen atoms of BPEI

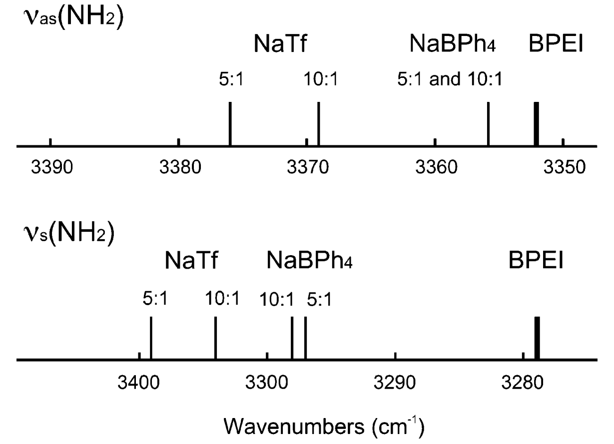

Figure 2. Schematic representation of the $\nu_s(NH_2)$ and the $\nu_{as}(NH_2)$ frequency shifts in BPEI:NaTf and BPEI:NaBPh$_4$ complexes (N:Na$^+$ = 10:1, 5:1) using the BPEI modes as a reference.

Table 2. Band Center Frequencies (cm^{-1}) in the $\delta_s(CF_3)$ and $\nu_s(SO_3)$ Regions for BPEI:NaTf

composition	$\delta_s(CF_3)$		$\nu_s(SO_3)$			assignt
20:1		755		1033	1031	"free" ions
10:1		755		1034	1031	
5:1	757		1037			ion pairs

should break N−H···N hydrogen bonds, increasing its N−H stretching frequency. However, the sodium inductive effect simulteneously causes a decrease in the N−H stretching frequency. In general, the frequency shifts observed in the NaTf complexes are higher than in the NaBPh$_4$ complexes, although there are weak hydrogen-bonding interactions of the NH$_2$ group with the triflate oxygen atoms, which would tend to slightly lower those frequencies. Therefore, the inductive effect appears to be stronger in BPEI−NaBPh$_4$ than in BPEI−NaTf, suggesting that the Na$^+$−N interaction is slightly stronger in the former system. This difference may be due to significant cation−anion interactions in the NaTf complex that hinder the coordinative interaction of the sodium ions with the nitrogen of the NH$_2$ group, whereas tetraphenylborate is a charge-protected anion that is unable to significantly interact with the sodium cation.

The presence of strong cation−anion interactions in BPEI−NaTf is confirmed by an examination of triflate ion intramolecular modes whose frequencies are sensitive to cation−anion interactions, e.g., the CF$_3$ symmetric deformation band, $\delta_s(CF_3)$,[20−22] and the SO$_3$ symmetric stretching band, $\nu_s(SO_3)$.[20,23,24] These data are summarized in Table 2 (spectra not shown).

The assignments of these bands to various triflate ion species have been developed in the ethylene oxide systems and extended to ethylenimine systems.[25,26] The addition of salt increases the degree of ionic association as seen by the increase of the $\delta_s(CF_3)$ and $\nu_s(SO_3)$ frequencies. Another measure of ionic association is the splitting of the SO$_3$ antisymmetric stretching mode, $\Delta\nu_{as}(SO_3)$, which originates in the breaking of the 2-fold degeneracy of the $\nu_{as}(SO_3)$ mode through the sodium ion−triflate ion interactions. The value of $\Delta\nu_{as}(SO_3)$ increases from 11 cm^{-1} in the 20:1 composition to 15 cm^{-1} in the 5:1 composition. This increase in $\Delta\nu_{as}(SO_3)$ reflects the growing importance of ion pair interactions with increasing salt concentration and the accompanying decrease in the strength of the sodium ion−nitrogen atom interactions.

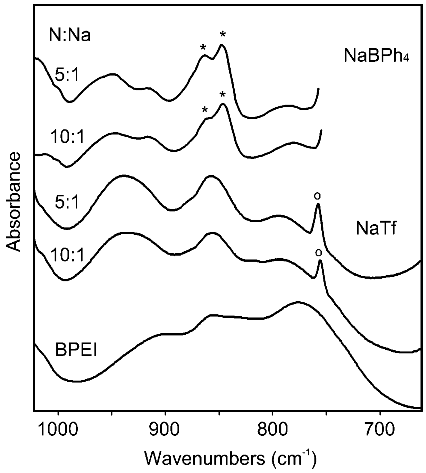

Figure 3. IR spectra of BPEI and its NaTf and NaBPh$_4$ complexes (N:Na$^+$ = 10:1, 5:1) from 670 to 1020 cm^{-1}. Asterisks indicate tetraphenylborate bands, and circles indicate triflate bands.

Polymer−Salt Interactions. The addition of NaBPh$_4$ or NaTf results in striking changes in the BPEI spectra in the 700−1000 cm^{-1} region, as illustrated in Figure 3.

This figure shows a comparison of the IR spectra of pure BPEI, BPEI:NaBPh$_4$, and BPEI:NaTf, both at 10:1 and 5:1 compositions. BPEI modes in this region are comprised mainly of a mixture of N−H bending, CH$_2$ rocking, CH$_2$ wagging, CH$_2$ twisting, and N−H wagging motions.[27] The $\delta_s(CF_3)$ mode of the triflate anion also occurs in this region at 755 and 757 cm^{-1} for the BPEI:NaTf 10:1 and 5:1 compositions, respectively. In both BPEI:NaBPh$_4$ and BPEI:NaTf complexes, the polymer band at 775 cm^{-1} shifts to a higher frequency with increasing salt concentration. The polymer band at 855 cm^{-1} cannot be observed in the BPEI:NaBPh$_4$ complexes due to multiple tetraphenylborate bands. Upon addition of the sodium salts, the polymer band at 901 cm^{-1} shifts to 932 cm^{-1} in BPEI:NaTf 5:1 and to 947 cm^{-1} with a second band at 916 cm^{-1} in BPEI:NaBPh$_4$ 5:1. The larger frequency shift in the sodium tetraphenylborate complex is consistent with the stronger sodium ion−BPEI nitrogen atom interaction suggested earlier.

Spectral changes accompanying the addition of NaTf have been previously reported in the BPEI primary amine asymmetric C−C−N stretching mode, $\nu_{as}(CCN)$, and the secondary amine asymmetric C−N−C stretching mode, $\nu_{as}(CNC)$.[14] A comparison of BPEI:NaBPh$_4$ and BPEI:NaTf in this region (Figure 4) provides additional information despite the presence of a number of tetraphenylborate and triflate bands.

The figure shows the IR spectra of the 5:1 and 20:1 compositions of BPEI:NaBPh$_4$ and BPEI:NaTf complexes in this region. The weak polymer band corresponding to the $\nu_{as}(CCN)$ mode of the primary amine at roughly 1073 cm^{-1} (seen as an asymmetric wing on the high-frequency side of the 1050 cm^{-1} band and marked by an arrow) shifts to 1085 cm^{-1} in 5:1 BPEI:NaBPh$_4$ (also marked by an arrow) and 1076 cm^{-1} in 5:1 BPEI:NaTf. However, the $\nu_{as}(CNC)$ vibrations of the secondary amine at 1128 and 1107 cm^{-1} shift to 1123 and 1101 cm^{-1} in the 5:1 BPEI:NaBPh$_4$ complex but do not seem to shift in the BPEI:NaTf complex. In summary, the polymer bands in this spectral region seem

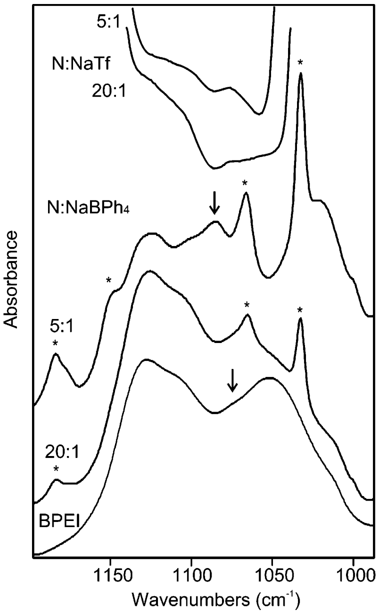

Figure 4. IR spectra of the asymmetric C−N stretching vibrations of BPEI and its complexes with NaTf and $NaBPh_4$ (N:Na^+ = 20:1, 5:1). Asterisks indicate tetraphenylborate bands.

Table 3. Glass Transition Temperatures T_g (°C) of BPEI, BPEI:NaTf, and BPEI:$NaBPh_4$ Complexes at Various Nitrogen:Cation Ratios

composition N:Na	BPEI:NaTf	BPEI:$NaBPh_4$
pure BPEI	−55	−55
30:1	−49	−38
20:1	−46	−26
10:1	−21	13
5:1	5	57

to be more affected in the BPEI:$NaBPh_4$ complexes than in the BPEI:NaTf complexes. Additionally, in both salt complexes, the ν_{as}(CCN) band of the primary amines shifts further than the ν_{as}(CNC) band of the secondary amines of BPEI. This observation suggests that the primary amines are more involved in the solvation of the salt than the secondary amines. This result is consistent with an early study of the binding of metal ions by BPEI, which showed that the primary amine groups are more involved than the secondary amine groups in the formation of BPEI−metal ion complexes.[28]

Thermal Analysis. The glass transition temperatures (T_g) of BPEI and BPEI with various compositions of NaTf and $NaBPh_4$ are summarized in Table 2. BPEI is a fully amorphous polymer at room temperature and has a glass transition temperature of −55 °C. Upon addition of NaTf or $NaBPh_4$, the T_g increases as the coordination of the alkali metal ions to the nitrogen atoms increasingly inhibits polymer segmental motion. However, the T_g values for the BPEI:NaTf system are significantly lower than the T_g values for the BPEI:$NaBPh_4$ system at all salt compositions. Again, this trend is consistent with stronger sodium ion−BPEI nitrogen interactions in the BPEI:$NaBPh_4$ complexes. The dramatic increase of the glass transition temperatures in the BPEI:$NaBPh_4$ system with increasing salt concentration was further investigated with vibrational spectroscopic techniques. Infrared measurements in the mid-IR and far-IR regions as well as Raman scattering experiments were performed on the BPEI:$NaBPh_4$ 5:1 sample, as it has the highest glass transition temperature. In the mid-IR and far-IR, the measurements were performed from 20 to 100 °C in 10 °C increments; in the Raman experiments, data were collected from 0 to 100 °C, in 10 °C increments, in a region from 1000 to 50 cm^{-1}. However, none of the spectra revealed any changes in the polymer backbone vibrations and the NH stretching vibrations upon crossing the glass transition temperature. Segmental motion of a polymer starts to occur in the vicinity of the glass transition temperature and increases with increasing temperature. In BPEI, segmental motion consists of torsional bending motions around the C−C and C−N bonds, presumably in both the backbone and side chains. Below the glass transition temperature, the polymer chains exist in a variety of energetically favorable conformations, but they are "frozen" in place in the sense that there is no thermally driven change of local conformation. A spectroscopic measurement sees the distribution of "frozen" conformations. Above T_g, the polymer segments have sufficient thermal energy to visit a variety of energetically favorable conformations. In a typical polymer electrolyte, segmental motion occurs at about 1 GHz at room temperature, which is approximately 10^3−10^5 slower than the vibrations that are measured using infrared and Raman spectroscopy.[29,30] Therefore, a vibrational measurement provides a static snapshot of the distribution now available to the polymer segments. The failure to observe any spectral changes as the sample passes through T_g argues that the "frozen" population distribution below T_g is essentially the ensemble average of the populations in dynamic equilibrium above T_g.

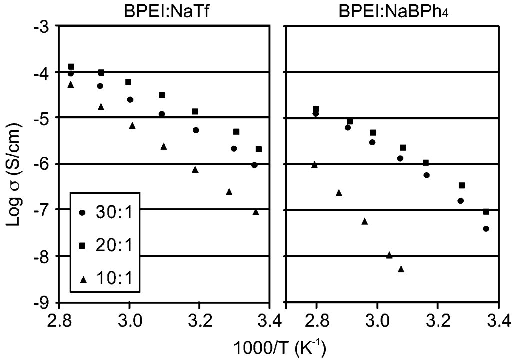

Figure 5. Temperature-dependent conductivity data of BPEI at various compositions of NaTf and $NaBPh_4$ (30:1, 20:1, 10:1).

Ionic Conductivity. Conductivities of BPEI:NaTf and BPEI:$NaBPh_4$ were measured from room temperature to 80 °C in increments of 10 °C. A second set of measurements was performed after allowing the samples to cool overnight. No hysteresis was observed in the conductivity behavior. The samples were examined for water using IR spectroscopy. Those samples that were found to be contaminated with water during the measurement process exhibited higher conductivity values, and these measurements were discarded.

The resulting conductivity values for BPEI:NaTf and BPEI:$NaBPh_4$ complexes are plotted in Figure 5.

The 20:1 composition for both polymer−salt complexes shows the highest conductivity, which result from the expected conductivity maximum in a plot of conductivity as a function of salt concentration.[29,31,32] It is noteworthy that the conductivities of the BPEI:NaTf complexes are significantly higher than the conductivities of the BPEI:$NaBPh_4$ complexes at all comparable compositions and temperatures, consistent with the observation that at comparable salt concentrations the

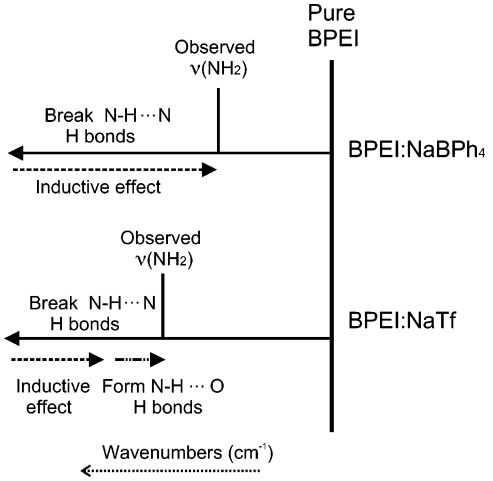

Figure 6. Schematic representation of hydrogen-bonding and inductive effects on the $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ frequencies in BPEI:NaTf and BPEI:NaBPh$_4$ complexes.

glass transition temperature of BPEI:NaTf is markedly lower than that of BPEI:NaBPh$_4$.

Conclusions

The comparison of the spectroscopic and calorimetric data of the BPEI:NaTf and BPEI:NaBPh$_4$ complexes indicates an important difference in the nature of the cation−polymer interactions in the two complexes. The consistently higher values of the glass transition temperatures in the BPEI:NaBPh$_4$ complexes along with the greater frequency shifts of the BPEI backbone modes clearly indicates that the sodium ions interact more strongly with the amine nitrogen atoms in the BPEI:NaBPh$_4$ complexes.

The conductivity data for the NaTf complexes are consistently higher than those of the NaBPh$_4$ complexes, although the BPh_4^- anion does not undergo significant cation−anion interactions as occurs in the NaTf system. It is important to note that in almost all polymer−salt systems studied to date the transference number of the anion is markedly larger than that of the cation; i.e., these systems are primarily anionic conductors.[33] Therefore, the relatively lower conductivity in BPEI:NaBPh$_4$ may result from a lower mobility of the bulky BPh_4^- ion as compared with the Tf^- ion. In this study the highest conductivity values occur in the 20:1 BPEI:NaTf complex and are on the order of 10^{-6} S cm^{-1} at 25 °C. These data are similar to those previously published by Harris et al.[14]

The spectroscopic comparison of BPEI:NaBPh$_4$ with BPEI:NaTf in the NH stretching region provides an opportunity to examine the relative importance of hydrogen bonding and the inductive effect. The following discussion is schematically illustrated in Figure 6.

The breaking of N−H···N hydrogen bonds by coordination with the cation occurs to the same extent in both complexes at a given composition as indicated by the left arrow for each complex which represents the accompanying frequency increase. The inductive effect of the sodium ion is larger in the BPEI:NaBPh$_4$ complex, which leads to a larger decrease in the NH stretching frequency. In the BPEI:NaTf complex, the replacement of N−H···N hydrogen bonds by weaker N−H···O hydrogen bonds leads to an additional small decrease in the N−H stretching frequency. However, this additional decrease is not sufficient to compensate for the significantly larger inductive decrease occurring in the BPEI:NaBPh$_4$ complex.

Finally, the addition of sodium tetraphenylborate shows that the CN stretch of the primary amines is more affected by coordination with the cation than the CN stretch of the secondary amines. This observation along with previous studies suggests that the cation preferentially coordinates to the primary amine nitrogen rather than the secondary amine nitrogen.

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