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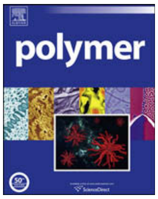

Spectroscopic investigation of proton-conducting, cross-linked linear poly(ethylenimine) hydrochloride membranes

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ABSTRACT

The degree of cross-linking for linear poly(ethylenimine) hydrochloride, cross-linked using malonaldehyde generated in situ, was determined from the ratio of the cross-link to backbone hydrogens obtained using ^{1}H NMR spectroscopy. The a.c. conductivity is highest at intermediate degrees of cross-linking (ca. 0.45), approximately 1×10^{-3} S/cm at room temperature and 75% relative humidity. IR and Raman spectroscopy were used to characterize the cross-linked network. The presence of the β-aminoethenyliminium cross-linker units can be identified through a series of bands between 1570 and 1640 cm^{-1}. Other changes in the spectra identified as a function of degree of cross-linking are discussed.

1. Introduction

Recent interest in fuel cell technologies has prompted research in the area of solid polymer electrolytes for use as proton-conducting membranes. Membrane development has focused on finding systems that have good mechanical properties, electrochemical stability at operating conditions, cost effectiveness and high proton conductivity [1,2]. Several different types of membranes are currently being investigated, including poly(perfluorosulfonic acids) [3,4], sulfonated poly(arylenes) [5–10], and acid-doped polymer complexes [11–16]. A cross-linked linear poly(ethylenimine) hydrochloride/phosphoric acid system, using 1,1,3,3-tetramethoxypropane as the cross-linker, has been presented as a potential membrane alternative that has good conductivity, mechanical integrity and thermal stability up to 150 °C [17]. Cross-linking has a significant effect on the physical properties of the resulting material in addition to its spectroscopic signatures and proton conductivity. However, determination of the degree of cross-linking and a thorough investigation of the cross-linked network with NMR, IR, Raman, and impedance spectroscopy has not been reported. Such studies are the focus of this paper.

Cross-linked poly(ethylenimine) hydrochloride/phosphoric acid membranes are multi-component systems, and the presence of phosphoric acid further complicates an already intricate network. Thus, two steps were taken to simplify the analysis of these materials in this report: (1) the cross-linked network is examined without phosphoric acid (Scheme 1) and (2) small molecules are used to model portions of the polymer network. This allows the spectroscopic signature of various parts of the network to be identified. For example, 3-(dimethylamino)acrolein is used to model β-aminoacrolein branching groups, one possible reaction product of the cross-linker with the base polymer.

2. Experimental section

2.1. Synthesis of membranes

Linear poly(ethylenimine)-hydrochloride (PEI-HCl) was prepared by acidic hydrolysis of poly(2-ethyl-2-oxazoline) (Aldrich, average M_w ca. 500,000) [18,19]. Cross-linked membranes were made as previously described [17]; the procedure is briefly summarized as follows. PEI-HCl was dissolved in water (~1.2 M in repeat units) and varying amounts of 1,1,3,3-tetramethoxypropane (Aldrich) were added while stirring, generating malonaldehyde in situ. The solutions were capped and allowed to stir for approximately 15 min. The solutions were cast onto a silicone rubber substrate and covered. After two days the samples were uncovered and placed in an oven at ~40 °C to facilitate evaporation of residual water and form a freestanding membrane. The resulting membranes ranged in thickness from 0.3 to 0.9 mm.

2.2. Sample characterization

Samples were characterized using infrared, Raman, NMR, and impedance spectroscopy. Samples for IR spectroscopic

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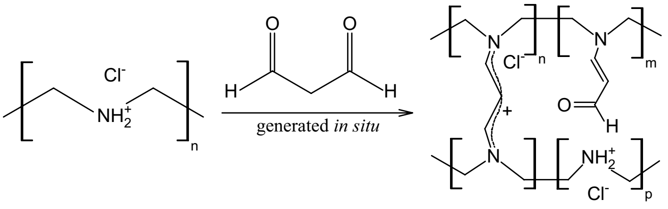

Scheme 1.

measurements were cast from solution (PEI-HCl, ~0.6 M) on ZnSe windows ~1.5 h after mixing to form thin films. Approximately 12–24 h after preparation, the cast films were dried under vacuum. Infrared spectra were collected using a Bruker IFS 66v spectrometer with a KBr beam splitter; 64 scans at a spectral resolution of 1 cm^{-1} were averaged for each spectrum. Spectra of cast membranes were measured under vacuum (pressure = 11 mbar), while those of the liquid model compound, 3-(dimethylamino)acrolein (DMAA) (Aldrich, 90%), were measured under a dry air purge. Samples for Raman and solution-state NMR experiments were made from the same solutions (PEI-HCl, ~0.6 M) used for the IR experiments. These solutions were placed in glass tubes 15 min after mixing to form a gel. Raman spectra were collected on a Bruker Equinox 55 FRA 106/S with a Nd:YAG laser (1064 nm) and a CCD detector. Solution-state NMR experiments on the gels were carried out using a Varian Mercury-300 spectrometer (300.1 MHz ^{1}H). Water was suppressed from the spectra by pre-saturation using a PRESAT pulse sequence as supplied by Varian, Inc. The spectra were collected after 48 scans and were referenced to d_4-Methanol (3.32 ppm). High-resolution magic-angle-spinning (HRMAS) NMR spectra were collected with a Varian ^{13}C{^{1}H} HRMAS Nanoprobe® and a Mercury VX 300 MHz NMR Spectrometer. VnmrJ 1.1D software (Varian, Inc) was used for data collection, while iNMR 2.6.1 software (Mestrelab Research, 2008) was used for data processing. The ^{1}H chemical shift values were referenced to the residual water signal (HOD) at 4.79 ppm. A deuterium lock was maintained throughout data acquisition to control the field frequency ratio over the sample. Cross-linked PEI-HCl membranes were soaked in D_2O for at least 1 h prior to data collection and then loaded into a ceramic rotor. Subsequently, the rotor was filled with D_2O and spun at a rate of 2000 Hz. Sample spinning was achieved with a Torlon drive ring and dry air. The sample temperature was controlled at 25 °C. Due to the changes in chemical shift and broadening of signals as cross-linking occurs, care was taken to integrate peaks for the PEI backbone protons at ca. 3.2–4.5 ppm (Fig. 1), for the cross-link protons at ca. 7.7 ppm, and the branch aldehyde protons at ca. 9.4 ppm over 1.100, 0.750, and 0.065 ppm ranges, respectively. A baseline correction was applied to each integration. These integrations were used to calculate the degree of cross-linking (vide infra). A.C. conductivity measurements were made using an in-plane four probe technique that has been previously described [17]. The samples were allowed to equilibrate at room temperature and 75% relative humidity for 24 h prior to measuring the conductivity. The relative humidity was maintained using a saturated sodium chloride solution as a constant activity source [20,21].

3. Results and discussion

Glatzhofer and coworkers previously described the general process by which cross-linking occurs in this system [17]. 1,1,3,3-Tetramethoxypropane can be used to generate malonaldehyde in situ, which can react with amine sites to form β-aminoacrolein moieties [22]. The β-aminoacrolein moieties can further react with amine sites to form β-aminoethenyliminium salts [23]. Thus there are three possible species that may be found in the cross-linked membranes as represented in Scheme 1. There may be some protonated amine sites remaining, designated by *p*, in addition to the new β-aminoethenyliminium cross-linked moieties, designated by *n*. At high cross-linker concentrations non-reacted β-aminoacrolein branching units may remain, designated by *m*, due to inaccessibility of the remaining amine sites.

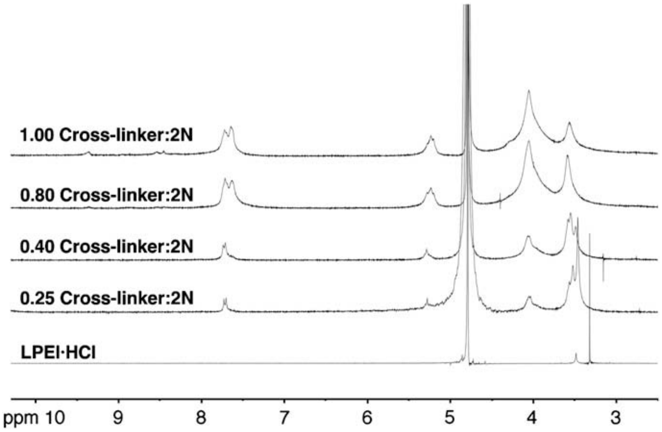

Fig. 1. HR-MAS Solid State ^{1}H NMR spectra of cross-linked poly(ethylenimine) hydrochloride (PEI-HCl) in water and solution ^{1}H NMR of linear poly(ethylenimine) hydrochloride in water-d_2. The notation xlinker: 2 N designates the number of cross-linker molecules added to the solution for every two PEI-HCl nitrogen atoms.

3.1. ^{1}H NMR spectroscopy and degree of cross-linking

^{1}H NMR spectra of aminoethenyliminium salts have been reported in the literature previously, making it possible to assign the chemical shifts observed for this polymer system. The ^{1}H NMR spectrum of *N*,*N*,*N*′,*N*′-tetraethyl-1,5-diazapentadienium chloride ($[(CH_3CH_2)_2NCH{=}CHCH{=}N(CH_2CH_3)_2]^+$ Cl^-, TEDCl) in CD_3OD shows resonances at δ1.27 (6H, t), 1.32 (6H, t), 3.56 (8H, q), 5.51 (1H, t), and 7.72 (2H, d) [24]. A ^{1}H NMR spectrum of non-cross-linked LPEI·HCl in D_2O and HRMAS ^{1}H NMR spectra of several cross-linked films are presented in Fig. 1. Similar spectra are obtained using solution-state NMR techniques for gelled samples. As shown in Fig. 1, the sharp singlet at 3.32 ppm that is characteristic of the methylene protons in the backbone of LPEI·HCl is affected by the cross-linking reaction. The resonance shifts downfield as the number of neighboring iminium cross-link moieties increases and appears as a collection of overlapping peaks of decreasing relative intensity. There is a concomitant appearance of a new, broad backbone hydrogen peak at 4.02 ppm, which corresponds to the ethyl methylenes in TEDCl at 3.56 ppm shifted further downfield by neighboring ammonium or iminium moieties. As expected, the intensity of this peak increases when the amount of cross-linker added in the reaction is increased. A resonance at 5.23 ppm, corresponding to the β-methine hydrogen of TEDCl, appears when the polymer has been cross-linked. This peak appears to be a broad singlet at lower cross-linker concentrations but at higher concentrations a broad triplet becomes apparent. A doublet also appears around 7.65 ppm, corresponding to the α-methine hydrogens of TEDCl, that increases in intensity as cross-linking increases. At high cross-linker concentrations other features are visible. A broad peak above 9 ppm is consistent with the presence of β-acrolein branching moieties. It has been reported that the aldehyde proton in 3-(*N*,*N*-dimethylamino)acrolein has a resonance at 9.06 ppm, while the hydrogens at the 2 and 3 positions appear at 5.04 ppm and 7.41 ppm [25]. The presence of these branches increases the integrated area of the peaks in the region corresponding to the

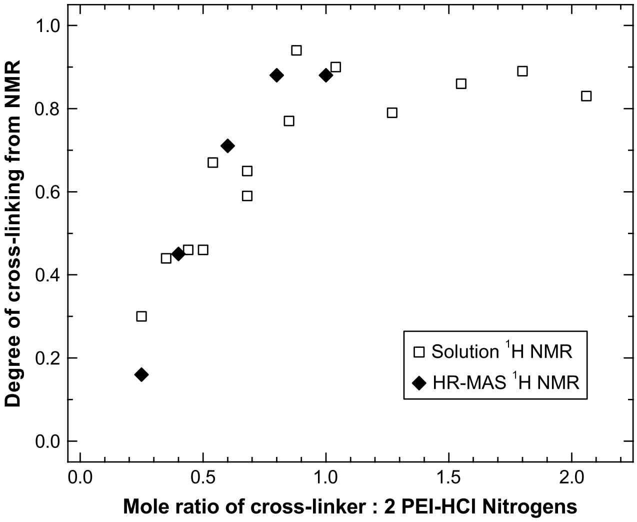

Fig. 2. Calibration curve for degree of cross-linking determined from NMR data: (□) Solution ^{1}H NMR, (◆) HR-MAS ^{1}H NMR.

hydrogen atoms from the cross-linking substituents (7.05–7.8 ppm). Fortunately, this can be corrected by subtracting branching unit hydrogen atoms from the integrated values as indicated by the number of aldehyde end groups. Other peaks around 8.37–8.62 ppm are also consistent with the formation of the *O*-protonated 3-(*N*,*N*-dialkylamino)acrolein branch, but this moiety does not have hydrogens with resonances in the region of interest in the spectra [25].

The integrated ^{1}H NMR spectra described above allow estimation of the degree of cross-linking for different samples from the ratio of backbone hydrogen atoms to hydrogen atoms from the cross-linking moieties. The degree of cross-linking is defined here as the percentage of nitrogen sites that effectively participate in the cross-linking of the polymer. A ratio of eight backbone hydrogens to three cross-link hydrogens would indicate a 100% degree of cross-linking. Thus, the degree of cross-linking within a particular sample may be estimated by comparing the measured ratio to this theoretical maximum. However, it was noted that the peak for the β-methine proton at 5.23 ppm in D_2O decreased in intensity relative to the other peaks over time, indicating exchange. The integration for this peak was consequently considered unreliable. Therefore a ratio of eight backbone hydrogens to the two α-methine cross-link hydrogens was taken to indicate 100% degree of cross-linking and the degree of cross-linking was estimated by comparing the measured ratio to the theoretical maximum.

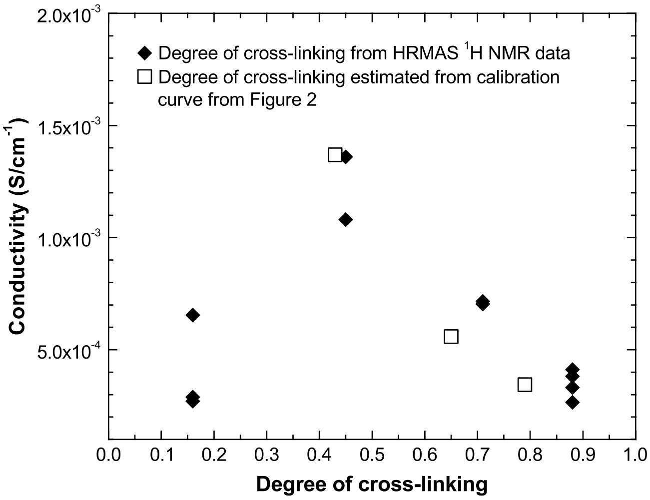

Fig. 3. Log of conductivity as a function of degree of cross-linking. Degree of cross-linking as determined by: (◆) HR-MAS ^{1}H NMR, (□) estimation from the average calibration curve in Fig. 2.

A plot of the estimated degree of cross-linking as determined from these NMR values versus the nominal values for the number of moles of cross-linker per two moles of PEI-HCl nitrogen atoms is shown in Fig. 2. At most cross-linker concentrations, the degree of cross-linking increases roughly linearly as the number of moles of cross-linker is increased. However, at high cross-linker molar ratios, the degree of cross-linking plateaus at ca. 0.85–0.90 and even decreases slightly as fresh malonaldehyde molecules compete with acrolein units to react with the remaining nitrogen atoms on the backbone. Higher cross-linker concentrations promote substantial branching. Data points from the solution NMR experiments are also shown in Fig. 2 and agree well with the HRMAS NMR results. Therefore, the plot shown in Fig. 2 can be used as a calibration curve to estimate the degree of cross-linking for samples simply from the nominal amount of cross-linker used in sample preparation.

3.2. Ionic conductivity

The conductivity of cross-linked PEI-HCl was investigated as a function of the degree of cross-linking within the polymer films as determined by NMR spectroscopy. The logarithm of the conductivity as a function of the degree of cross-linking is shown in Fig. 3. The conductivity is highest, approximately 1×10^{-3} S/cm, at

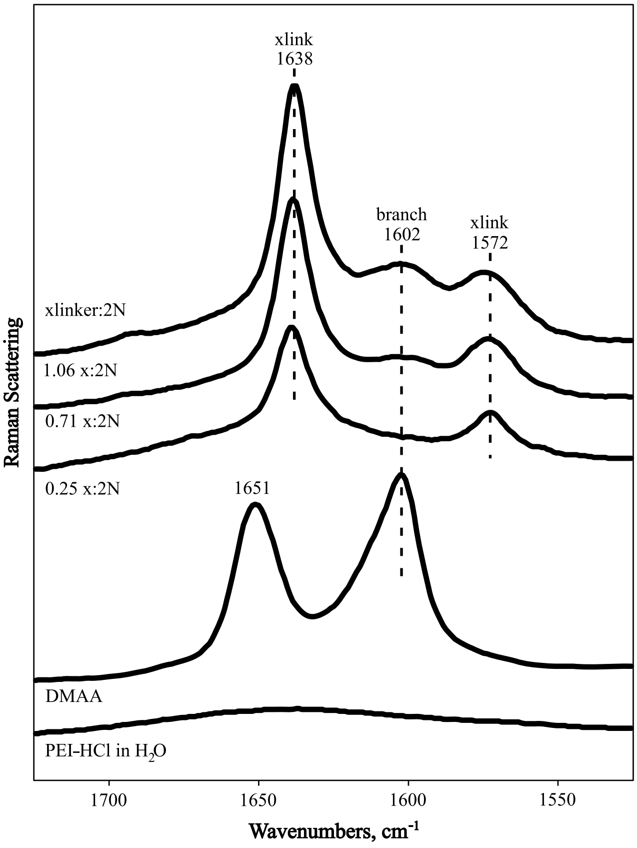

Fig. 4. Raman spectra of cross-linker stretching region. Cross-linked polyethylenimine-hydrochloride, 3-(dimethylamino)-acrolein (DMAA) and polyethylenimine-hydrochloride (PEI-HCl) in water. The notation xlinker: 2 N designates the number of cross-linker molecules added to the solution for every two PEI-HCl nitrogen atoms.

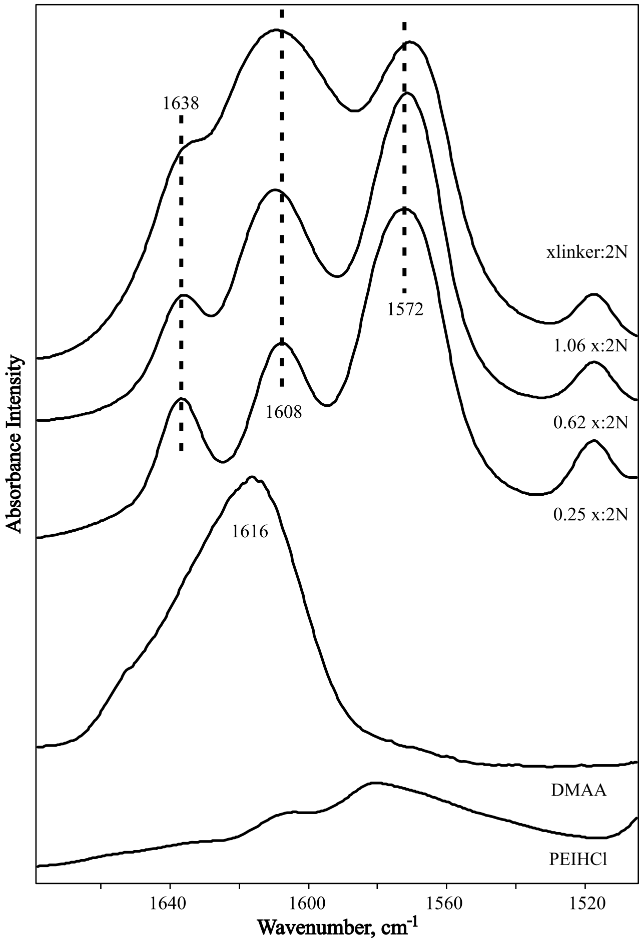

Fig. 5. Infrared spectra of cross-linker stretching region. Cross-linked polyethylenimine-hydrochloride, 3-(dimethylamino)-acrolein (DMAA) and polyethylenimine-hydrochloride (PEI-HCl). The notation xlinker: 2 N designates the number of cross-linker molecules added to the solution for every two PEI-HCl nitrogen atoms.

intermediate degrees of cross-linking (ca. 0.45) and decreases at both smaller and larger degrees of cross-linking. Similar conductivity behavior has been seen in both non-cross-linked linear and branched PEI$\cdot$H$_3$PO$_4$ systems at low acid concentrations ($<$0.4 mole ratio) [26–29]. In the case of cross-linked PEI-HCl there are several factors that may influence the conductivity behavior. The initial increase in conductivity may be the result of reduced crystallinity on cross-linking and changes in the pK_a of the ammonium groups (p, in Scheme 1) neighboring the positively charged cross-linking moieties (n, in Scheme 1). Eventually, stiffening of the network and a decreasing number of labile ion sites lead to decreasing the conductivity at high degrees of cross-linking. At high degrees of cross-linking, the presence of the branching units (m, in Scheme 1) may also have an undetermined effect. It should also be noted that the conductivity measurements were made at 75% relative humidity, and the absorbed water at equilibrium, which undoubtedly changes as a function of cross-linking, certainly plays a significant role in the conduction mechanism. Further studies of conductivity as a function of cross-linking, temperature, and relative humidity to elucidate the role of absorbed water on the conductivity behavior of these systems are currently underway.

3.3. Vibrational spectroscopy

IR and Raman spectroscopy were used to investigate the cross-linked network. The presence of the cross-linker unit can be identified through a series of bands between 1570 and 1640 cm^{-1}. In the Raman spectra shown in Fig. 4, two bands at 1572 and 1638 cm^{-1} can be seen at lower cross-linker concentrations, with a third band appearing at 1602 cm^{-1} at higher concentrations. The 1602 cm^{-1} band is attributed to the presence of acrolein branching units that are only found at the higher cross-linker concentrations. This conclusion is supported by comparing the Raman spectrum of a highly cross-linked membrane with DMAA – a small molecule model compound for the branching units. The model compound has two bands at 1651 and 1602 cm^{-1}. The bands at 1602 cm^{-1} in both the DMAA model compound and the cross-linked membrane are assigned to the CO stretch from the aldehyde group. The 1638 and 1572 cm^{-1} bands in the cross-linked membrane are primarily the result of the CC stretching motions from the cross-linker [30]. Fig. 5 shows the IR spectra of this region; the bands in the IR spectra are more complex than in the Raman spectra. Three bands at 1638, 1608, and 1572 cm^{-1} are seen at all cross-linker concentrations. The 1608 cm^{-1} band is significantly broadened as the cross-linker concentration increases; this broadening is accompanied by a slight frequency shift from 1608 to 1610 cm^{-1}. The IR spectrum of the model compound consists of one broad asymmetric band located at 1616 cm^{-1} that contains coupled CO stretching modes [31]. The mixing of these modes would lead to the broadening and slight frequency shift seen in the membrane at high cross-linker concentrations.

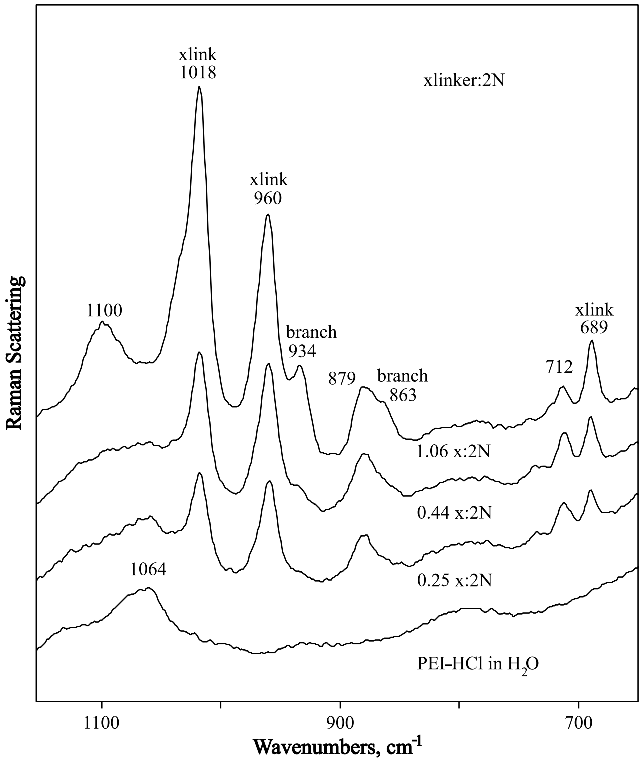

Fig. 6. Raman spectra of lower frequency region. Cross-linked polyethylenimine-hydrochloride, and polyethylenimine-hydrochloride (PEI-HCl) in water. The notation xlinker: 2 N designates the number of cross-linker molecules added to the solution for every two PEI-HCl nitrogen atoms.

The stretching bands directly associated with the cross-link unit can be clearly identified in the region between 1570 and 1640 cm^{-1}. However, the lower frequency regions are more complicated because they contain bands that are associated with both the polymer backbone and the cross-link unit. Fig. 6 shows the Raman spectra between approximately 1100 and 600 cm^{-1}. Bands in this region contain mixed modes that are sensitive to the conformation of the polymer backbone [32,33]. There are three bands at 1018, 960 and 689 cm^{-1} that appear even at low cross-linker concentrations. These bands are probably associated with the cross-link unit itself. Most

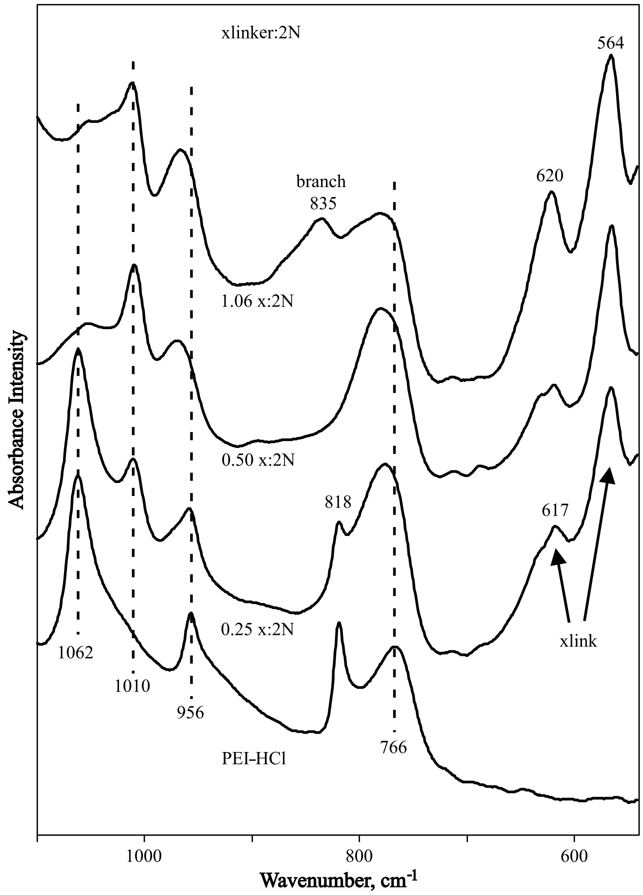

Fig. 7. Infrared spectra of lower frequency region. Cross-linked polyethylenimine-hydrochloride, and polyethylenimine-hydrochloride (PEI-HCl) in water. The notation xlinker: 2 N designates the number of cross-linker molecules added to the solution for every two PEI-HCl nitrogen atoms.

likely the vibrational modes resulting in these bands are a mixture of CCC bending and CH in-plane bending motions [34]. In contrast, the band at 1064 cm^{-1} in the PEI-HCl spectrum shifts to 1100 cm^{-1} as the cross-linker concentration increases. The bands at 863 and 934 cm^{-1} appear only at high cross-linker concentrations and therefore may be attributed to the acrolein branching units. Similar trends can be seen in the IR spectra of Fig. 7, which covers essentially the same range. Bands at 1010, 620 and 564 cm^{-1} are most likely associated directly with the cross-link unit, whereas the bands at 1064 and 1010 cm^{-1} are attributed to the polymer backbone. Bands in this range of the spectrum contain CN and CC stretching motions.

As the cross-linking reaction occurs, the nitrogen atoms of the polymer backbone become covalently bonded to the cross-linker molecule. This will necessarily result in a redistribution of electron density around the nitrogen and adjacent carbon atoms on the polymer backbone, changing both the effective force constants of the backbone CN and CC bonds and dipole moment and polarizability derivatives for these modes. Those changes will appear as frequency shifts and intensity changes in the corresponding IR and Raman bands. Therefore, as the amount of cross-linker increases, the intensity of the 1062 cm^{-1} band decreases and the related band at 1010 cm^{-1} increases. The band at 835 cm^{-1} may be attributed to the acrolein branching units, consistent with the assignment of the 863 cm^{-1} band in the Raman spectrum. Finally, it is interesting to note that spectrum labeled 0.25:2 N (cross-linker: 2 N) resembles a superposition of pure PEI-HCl and the 0.50:2 N spectra. This would indicate that membranes with mole ratios of ca. 0.25:2 N or less contain domains of pure PEI-HCl in addition to the cross-linked moieties.

4. Summary and conclusions

Membranes made of cross-linked PEI-HCl have been investigated as a function of the degree of cross-linking with a number of different spectroscopic techniques and measurements of the conductivity. The degree of cross-linking was determined using NMR spectroscopy. The maximum degree of cross-linking attained is approximately 90%. Above this cross-linking level, some of the remaining sites react with one end of a malonaldehyde molecule. However, there are no available amine sites sufficiently close to allow the malonaldehyde to react with a second nitrogen atom. This results in an acrolein branching unit whose presence is inferred from spectroscopic data. Vibrational modes associated with the cross-link unit can be identified in both the IR and Raman spectra from bands that are present even at low cross-linker concentrations, but are not present in the pure polymer. In comparison, bands that are present in pure PEI-HCl but exhibit shifts in frequency and intensity as the amount of cross-linker increases are attributed to the polymer backbone. These shifts are associated with a redistribution of electron density along the backbone due to the reaction of the cross-linker molecule with the polymer. The bands associated with the acrolein branching units can be distinguished from those associated with both the cross-linker and the polymer backbone as they are present only at high cross-linker concentrations.

The conductivity of cross-linked PEI-HCl was highest, $\sim 1 \times 10^{-3}$ S/cm, at a intermediate degrees of cross-linking and may be attributed to the movement of protons or chloride ions or both. The shape of the ionic conductivity curve observed in this study resembles curves characteristic of almost all polymer-salt electrolyte systems. In those systems, the ionic conductivity decreases at high salt concentrations because of a reduction in the segmental motion and the number of available coordination sites of the polymer. This decrease in segmental motion is usually considered to result from an increase in the coordination of ions between sites on the polymer chains, where the ions act as transitory cross-links [35]. In the present case, the peak in the conductivity data may reflect a balance between the stiffening of the polymer network and the number of labile ion sites available but having water present during the measurements at 75% relative humidity complicates these interpretations. Studies to elucidate the effects of absorbed water on conductivity in these systems are ongoing.

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