Morphology Studies of High Temperature Proton Conducting Membranes Containing Hydrophilic/Hydrophobic Ionic Liquids

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ABSTRACT: The morphology of proton conducting membranes based on sulfonated poly(aryl ether ketone) (SPAEK-6F) and recast Nafion membranes containing hydrophilic/hydrophobic ionic liquids has been investigated by small-angle X-ray scattering (SAXS) and tapping mode atomic force microscopy (TM-AFM). The hydrophilic/hydrophobic nature of the ionic liquid has been found to affect the morphology, conductivity and thermal stability of the membranes. The small angle upturn in scattering intensity at very low angles observed in SAXS for different membranes suggests the presence of large scale fluctuations, whereas the absence of ionomer peak for membranes based on SPAEK-6F is possibly due to the higher rigidity of hydrophobic part of the polymer despite the presence of ionic domains. The correlation between morphology and properties of different membranes containing ionic liquids will be helpful in improving the design of proton conducting membranes containing ionic liquids for applications in polymer electrolyte fuel cells (PEFCs) at medium (100−200 °C) temperatures and under anhydrous conditions.

Introduction

Nafion membranes are commonly used in polymer electrolyte fuel cells (PEFCs) due to some of their special properties like high ionic conductivity, good mechanical stability, durability, etc.[1] However, the CO poisoning of the Pt catalyst and poor thermal properties of Nafion membranes lead to the deterioration of the performance of PEFCs.[2] Some of these drawbacks can be removed if the fuel cell could be operated at relatively higher temperatures, generally above 100 °C.[3] However the conductivity of Nafion membranes, presently being used in PEFCs, is strongly humidity dependent and if the temperature of operation is increased above 80 °C, then the conductivity of membrane decreases drastically due to the loss/evaporation of water.[4] So there is a growing need to develop alternative suitable membranes, which could work at higher temperatures and under low humidity conditions. Different research groups are actively involved in the development of such membranes mainly by the following approaches:[5−8]

- The development of alternative proton conducting membranes based on different sulfonated polymers, which could work at higher temperatures (>100 °C) but still need humidity.
- The development of proton conducting membranes that use, instead of water, a less volatile solvent having higher boiling point, so that it could be used at higher temperatures under anhydrous conditions for long periods.

The main aim of both the approaches is to develop suitable proton conducting membranes having high conductivity and other suitable properties so that the PEFC could operate at higher temperatures (100−200 °C) and under low humidity or by using some other suitable solvent instead of water, which is presently being used in Nafion membranes. A lot of research efforts are being devoted to develop different types of alternative membranes which have been reviewed recently[9] and will not be discussed here. However most of the alternative membranes still require humidity for high conductivity and hence need a pressurized humidity system, but can be operated at temperatures higher than 100 °C. Similarly membranes in which water has been replaced by other solvents have also been reported, but the performance of such membranes in fuel cells, as compared with Nafion under fully hydrated conditions, is not satisfactory[10,11] and needs further improvement.

The high proton conductivity and other suitable properties of water swollen Nafion membranes are generally explained to be due to their unique morphology, which consists of the presence of hydrophilic regions which swell under hydrated conditions and result in high proton conductivity, and hydrophobic regions which provide high mechanical strength to the backbone of these membranes.[12] Some of the alternative membranes being developed for high temperature fuel cells also consist of block copolymers, out of which one part is hydrophobic and the other is hydrophilic and these blocks play the same role as in Nafion membranes. The composition of such membranes can be adjusted in such a way that it is thermally stable up to higher temperatures (100−200 °C), and show high conductivity even under low humidity levels. Sulfonated poly(aryl ether ketone) (SPAEK-6F) is one such random sulfonated polymer proposed recently[13] for the development of high temperature proton conducting membranes for PEFCs. Its structure along with that of Nafion is given in Scheme 1.

In the second approach, as the proton conductivity of Nafion membrane is strongly dependent on humidity level and it shows high conductivity under fully hydrated conditions only, so there have been studies on alternative membranes in which water has been replaced with other solvents. Initially, phosphoric acid (H_3PO_4) was used in polybenzimidazole (PBI)-based mem-

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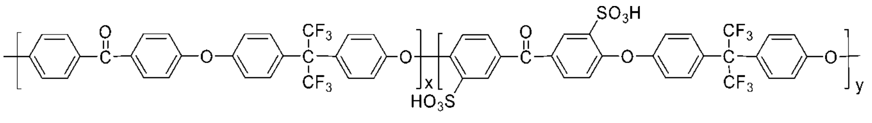
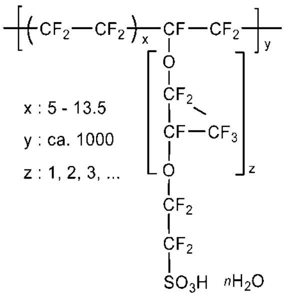
Scheme 1



(SPAEK-6F)



(Nafion)

branes, which showed higher conductivity, comparable with Nafion membranes under hydrated conditions.[10] However the prolonged use of such membranes at higher temperatures under actual fuel cell conditions led to the release of H_3PO_4 from the membranes, resulting in a loss in ionic conductivity of the membranes, which led to lower fuel cell performance. Similarly proton conducting membranes containing imidazole and other heterocycles were also proposed but poisoning of the catalyst by imidazole resulted in poor fuel cell performance.[11] As the solvent used in fuel cell membranes should be less volatile and thermally stable up to higher temperatures, so ionic liquids (ILs) having these properties could be a good choice. The ionic liquids (also known as room temperature molten salts) are generally salts with melting point below 100 °C.[14] They are important due to some of their special properties like high ionic conductivity, negligible vapor pressure and hence low volatility, high thermal and wide electrochemical stability, wide temperature liquid range, etc. These properties are also desirable for their use in proton conducting membranes for PEFCs. After the report of air and water stable ILs based on nonchloroaluminate anions, ILs have been proposed for use as electrolytes in various electrochemical devices.[15,16] Initially ILs were proposed as electrolytes for alkaline fuel cells,[17] but the performance of the fuel cell deteriorated as temperature was increased and second IL being liquid in nature there were problems of leakage, portability etc. The leakage of ILs is generally avoided by using free-standing films, obtained by incorporating ILs in suitable polymers. Nafion membranes impregnated with different ILs have been also studied and the resulting membranes were reported to have high ionic conductivity due to the protons in the Nafion membranes or ILs, on the order of 10^{-1} S cm^{-1} at 180 °C, but no fuel cell results are available for these membranes.[18] The use of protic ionic liquid-based membranes in PEFCs has also been proposed and it has been reported that these membranes were electroactive, but the current density obtained was quite low.[19−22] However in principle these IL-based membranes can be used in PEFCs under anhydrous conditions. Polymer electrolyte membranes having different ILs incorporated in commercial polymers have been also reported, but the current density reported was quite low and needed improvement by 1−2 orders of magnitude, along with better mechanical and thermal properties.[23,24] Keeping this point in view, sulfonated polymers having hydrophilic and hydrophobic regions were synthesized for use in proton conducting membranes containing ILs. Membranes based on sulfonated poly(aryl ether ketone) (SPAEK, SPAEK-6F) and containing different ILs have been developed by our group for use in PEFCs at higher temperatures under anhydrous conditions.[25] The sulfonated polymers are similar in nature to Nafion and have a hydrophilic part and a hydrophobic part. The results obtained have been compared with recast Nafion membranes containing the same ILs, as incorporated in SPEAK-6F-based membranes. Although the properties of ILs depend upon the nature of cation and anion and a large number of possibilities exist on their choice, yet in the present case, ILs containing the widely studied dialkylimidazolium (EMI) cation and triflate (Tf or $CF_3SO_3^-$) and imide (Im or $N(CF_3SO_2)_2^-$) anions have been used. The choice of these anions is due to the hydrophilic and hydrophobic nature of the resulting ILs (EMITf, EMIIm) respectively and its effect on the ionic conductivity, morphology and other properties of membranes can be studied.

The development of new high temperature proton conducting membranes for PEFCs requires a better understanding of the working of the membrane. The transport properties of widely studied water swollen Nafion membrane has been generally explained to be due to the phase separated morphology. However the morphology of random sulfonated polymers (SPAEK-6F) proposed for high temperature PEFCs under anhydrous conditions has not been studied.[25] An understanding of the morphology and its correlation with transport properties will be quite helpful in optimizing the performance of such membranes in PEFCs.

The present work deals with the study of morphology of membranes based on sulfonated poly(aryl ether ketone) (SPAEK-6F) and recast Nafion containing hydrophilic (EMITf) and hydrophobic (EMIIm) ionic liquids. The conductivity of membranes has been measured at higher temperatures under anhydrous conditions. The morphology of the membranes has been studied by tapping mode atomic force microscopy (TM-AFM) and small-angle X-ray scattering (SAXS), and the presence of ionic clusters, ion channels, pathways etc has been discussed. The effect of the hydrophobic/hydrophilic nature of ILs on the properties and morphology of the membranes has been also investigated. The thermal stability of these membranes has been studied by TGA measurements.

Materials and Methods

Polymer. Sulfonated poly(aryl ether ketone) (SPAEK-6F) random copolymers with degree of sulfonation (DS), 40, were synthesized via nucleophilic aromatic substitution as described in our previous work.[13] The Nafion solution (perfluorosulfonic acid/TFE copolymer resin (5−6%), 1-propanol (42−54%), water (40−50%), ethyl alcohol (<8%), mixed ethers, and other VOCs (<2%)) was purchased from Dupont.

Ionic Liquid. All ILs used in this study, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf), and 1-ethyl-3-meth-

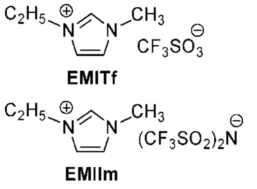


Figure 1. Chemical structure of EMITf and EMIIm.

ylimidazolium bis(trifluoromethanesulfonyl imide) (EMIIm) were purchased from TCI.

Composite Membranes. Polymer electrolytes containing 50 wt % IL and 50 wt % polymer were prepared by the solution casting method described elsewhere.[25,26] The requisite amount of each IL was added into 10 wt % polymer solutions in *N*,*N*-dimethylacetamide (DMAc) and the solutions were stirred overnight. All the samples were cast in Petri dishes and were finally dried in a vacuum oven at 60 °C to evaporate the solvent slowly.

Characterization. The electrochemical properties of the ionic liquids and composite membranes were investigated at elevated temperatures and under anhydrous conditions. Ionic conductivity of the composite membrane samples was measured by the four-point-probe conductivity cell described elsewhere.[27] The conductivity cell was placed in the headspace of a temperature controlled sealed vessel, which maintained an anhydrous atmosphere. The size of membrane samples was 2 cm long and 1 cm wide. The impedance data for ionic conductivity of the membranes were obtained by impedance spectroscopy using a Solartron 1260 gain phase analyzer, interfaced to a Solartron 1480 multistat. The measurements were carried out in potentiostatic mode in the frequency range of 0.1 Hz to 10 MHz with 5 mV oscillating voltage. Ionic conductivity of the samples was calculated from the impedance data using the equation:

$$\sigma = \frac{L}{RWd}$$

where σ is the ionic conductivity (S cm^{-1}), L the distance between two potential sensing platinum wires, R the membrane resistance derived from the impedance value at zero phase angle, W the width of the potential sensing platinum wire and d the membrane thickness. The electrochemical data were averaged using three measurements, and the standard deviation of all data was below 1%.

The thermal stability of the ILs and composite membranes was examined by thermogravimetric analysis (TGA) using a TGA 2050 instrument (TA instruments). Heat scans were carried out under nitrogen and a heating rate of 10 °C/min was used over the temperature range of 50 to 600 °C.

Morphology characterization of the membranes was studied by the small-angle X-ray scattering (SAXS) and tapping mode atomic force microscopy (TM-AFM). SAXS experiments were performed at a Rigaku D/max-2500 (5 kW) with an image plate system equipped using X-rays with a wavelength of 1.5406 Å. AFM images were obtained by a Bio-AFM D3100 (Veeco) in the tapping mode with the standard etched silicon probe tips. All the images shown in this study are phase images scanned at 1.0 Hz frequency and 256 scan rates and have been filtered through the "planefit" procedure. The crystalline/amorphous nature of composite membranes was studied by X-ray diffraction (XRD) analysis using Rigaku D/MAX-RB X-ray diffractometer.

Results and Discussion

The chemical structures of the ionic liquids used in the present study are given in Figure 1. The ILs (EMITf, EMIIm) have been reported to have dynamic viscosity at 20 °C of 45 and 34 cP and conductivity at 20 °C of 8.6 and 8.8 mS cm^{-1} respectively.[28] The miscibility of the ILs with water has been also reported by measuring water content (mass % at 20 °C) at saturation. EMITf has been reported to be water soluble (hydrophilic), whereas the solubility of EMIIm in water is 1.4% (hydrophobic).[28] The ionic conductivity of recast Nafion membranes containing these ILs was measured at different temperatures and Figure 2a shows the variation of conductivity with temperature. The ionic conductivity of Nafion membranes containing hydrophilic IL (EMITf) is higher than containing hydrophobic IL (EMIIm) at all temperatures. This trend is similar to that reported earlier for Nafion membranes swollen with the same ILs.[29] The nearly equal value of absolute slope for Nafion/EMITf (0.90) and for Nafion/EMIIm (0.96) membranes suggests that the same type of conduction mechanism takes place in both the membranes. The ionic conductivity of membranes based on sulfonated random copolymers, i.e., sulfonated poly(aryl ether ketone) (SPAEK-6F), and containing the same ILs (EMITf and EMIIm) was also measured at different temperatures and Figure 2b shows the variation of ionic conductivity with temperature. The curved nature of the plot between log conductivity and reciprocal temperature is due to the highly amorphous nature of these membranes. Both the membranes based on SPAEK-6F show ionic conductivity of the same order over the 30−200 °C temperature range and the SPAEK-6F/EMIIm membrane shows slightly higher conductivity than SPAEK-6F/EMITf membrane. The absolute slope for

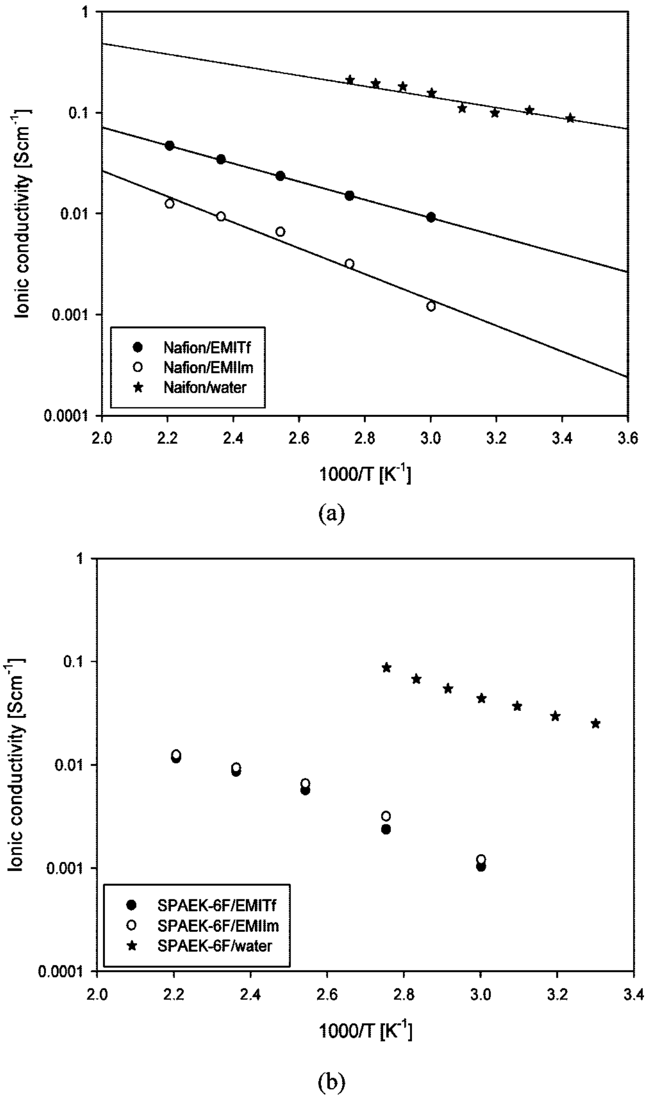


Figure 2. Ionic conductivity of composite membranes: Nafion/EMITf, Nafion/EMIIm, and Nation/water (a) and SPAEK-6F/EMITf, SPAEK-6F/EMIIm, and SPAEK-6F/water (b) at different temperatures under ambient humidity conditions.

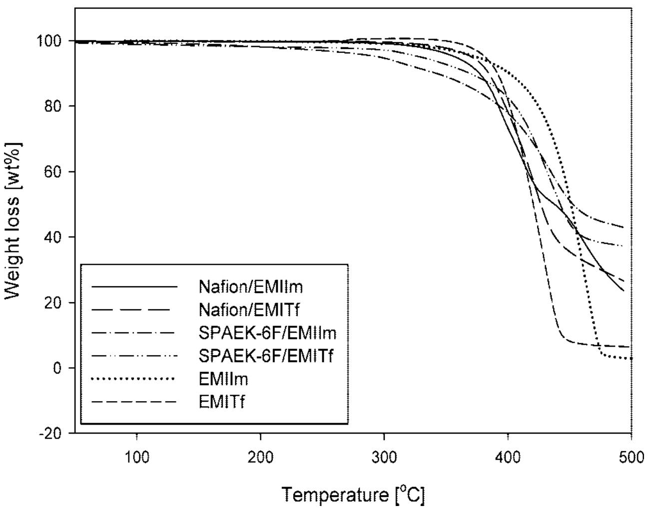


Figure 3. Thermogravimetric analysis (TGA) weight loss curves for EMITf, EMIIm, Nafion/EMITf, Nafion/EMIIm, SPAEK-6F/EMITf and SPAEK-6F/EMIIm.

SPAEK-6F/EMIIm membrane is 1.16, whereas for SPAEK-6F/EMITf membranes 1.36. A comparison of the ionic conductivity of the membranes based on recast Nafion and SPAEK-6F and containing the same ILs (EMITf and EMIIm), as given in Figure 2, shows that the membranes based on recast Nafion have slightly higher ionic conductivity than those based on SPAEK-6F. σ(Nafion/EMITf) > σ(SPAEK-6F/EMITf) and σ(Nafion/EMIIm) > σ(SPAEK-6F/EMIIm) have been observed at all temperatures in the 30−200 °C range. The proton conductivity of Nafion/EMITf and Nafion/EMIIm membranes is slightly lower than for the fully hydrated Nafion, but it is much higher than for the conductivity of Nafion under anhydrous conditions. Similar trend has been also observed for SPAEK-6F-based membranes. The conductivity of membranes based on Nafion and SPAEK-6F and containing EMITf and EMIIm is due to the protons contributed by -SO_3H groups present in sulfonated polymers. The EMI^+ cation of the IL interacts with the polymer and displaces the counterion (H^+) away from the exchange site ($-SO_3H$). The replacement of counterion (H^+) with EMI^+ (studied by ATR-FTIR) results in shifting of the peak due to the symmetric sulfonate stretching vibration of the sulfonate exchange sites to lower wavenumber. The counterions (H^+) can associate with the free anions (Tf^- or Im^-) of the IL, which are loosely associated with EMI^+ cations and can transport by hopping among anion sites present in membranes containing ILs.[25,29]

As the present membranes are being developed as high temperature proton conducting membranes to be used in PEFCs at 100−200 °C, so they should be thermally stable up to higher temperatures. The thermal stability of these membranes was measured and the TGA scans for the ILs (EMITf, EMIIm) and for membranes based on recast Nafion (Nafion/EMITf, Nafion/EMIIm) and SPAEK-6F (SPAEK-6F/EMITf, SPAEK-6F/EMIIm) are given in Figure 3. The onset temperature of weight loss by 5% and 10% for different samples of ILs and membranes has been determined from TGA curves and is listed in Table 1. Both the ILs shows a one-step degradation process whereas the recast Nafion- and SPAEK-6F-based membranes exhibit a two-step degradation process. ILs have been observed to be thermally stable up to temperatures above 300 °C and EMITf has been found to be thermally more stable than EMIIm. The membranes based on recast Nafion and SPAEK-6F, are thermally stable up to ~300 °C. The dissociation temperature corresponding to 5 and 10% weight loss is above 300 °C for all the membranes, which indicates that these membranes can be used in the higher temperature (100−200 °C) range for PEFC applications.

Table 1. TGA Data for the ILs and Composite Membranes

	temperature at 5 and 10 wt % loss	
sample	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)
EMITf	382	392
EMIIm	375	401
Nafion/EMITf	371	383
Nafion/EMIIm	358	377
SPAEK-6F/EMITf	330	369
SPAEK-6F/EMIIm	296	342

In order to understand and explain the ionic conductivity results obtained from the recast Nafion and SPAEK-6F containing hydrophilic (EMITf) and hydrophobic (EMIIm) ILs, the morphology of membranes was studied by small-angle X-ray scattering (SAXS) and SAXS spectra have been recorded. The Nafion membranes generally consist of a hydrophobic part which is the fluorocarbon part of the polymer and a hydrophilic part which has the sulfonate ion-exchange sites at the ends of the pendant side chains. The unique morphology of water swollen Nafion membranes consists of two phases separated from each other, out of which one is rich in ionic groups and contributes to the high ionic conductivity of the Nafion and the second phase, which is rich in the fluorocarbon polymer, provides mechanical strength to the membrane and being hydrophobic in nature does not allow the polymer to dissolve in water. The models used to explain the SAXS results are generally classified into intraparticle[30,31] and interparticle[32−34] models. The intraparticle models explain the ionomer peak due to the interference within the ionic cluster which indicates that the scattering maximum is related to the internal structure of the cluster. The interparticle models explain the ionomer peak due to the interference between different ionic clusters which indicate that the Bragg spacing is the center to center distance between two clusters. However the origin of ionomer peak is still not fully resolved. The cluster network model[12,32] and the core shell model[30,31] are the two main models widely used to explain the morphology and ionic conductivity of water swollen Nafion membranes based on SAXS results. In the cluster network model, the ionic clusters are proposed to be distributed within an inert fluorocarbon matrix and these ionic clusters are connected to each other by narrow channels. These interconnected channels lead to the unique transport properties of Nafion. In the core shell model, the ionic clusters surrounded by a fluorocarbon phase are embedded in an intermediate ionic phase, which consists of both fluorocarbon polymer and non clustered ionic sites. A third model[35] has been based on nonspherical ionic clusters and a third phase, which is intermediate between the ionic clusters and the fluorocarbon phase, is also present.

Recently, on the basis of quantitative analysis of published SAXS data, it has been shown that none of the models match the experimental SAXS data.[36] The proposed model consists of parallel cylindrical water channels which are lined with hydrophilic groups and stabilized by hydrophobic backbone. Scattered intensity, $I(q)$, calculated from this model can be reproduced as a function of the ionomer peak and the q^{-1} or q^{-4} dependence at low and high q values respectively. However, the validity of this model for Nafion at low hydration levels is not known.

The morphology of ionic clusters formed in water swollen Nafion membranes has been studied by SAXS. Although the exact morphology is still not clearly understood, the overall SAXS profile for water swollen Nafion membranes has been reported[37−39] to show the following general features:

- The first is an upturn of the intensity $I(q)$ at small angles, which is strongly related to the ionic aggregates. This is generally associated with the long-range inhomogeneities in the spatial distribution of the ionic clusters.[40]

- The second is the presence of a peak, centered at $q \sim 0.07$ Å^{-1}, called the matrix peak. This peak generally appears as a shoulder and the intensity of this maximum strongly depends on the crystallinity of the Nafion films or the presence of crystallites in the fluorocarbon hydrophobic phase.[41]
- Third is the well-known "ionomer peak" centered at $q \sim 0.2$ Å^{-1}. The ionomer peak originates from either the shape of the ionic clusters or their spatial distribution. The angular position of the ionomer peak has been proposed to correspond to the mean center to center spacing between the ionic clusters. However the intensity and position of the signal and the structure responsible for this maximum are still not clearly understood.
- Finally, the tail region of the SAXS profile shows an asymptotic scattering behavior in the high q-region and follows Porod's law $I(q) \alpha q^{-4}$, which is an indication that the polymer−solvent interface is sharp and also confirms the phase separation.[42]

However, the high temperature membranes being proposed for use in PEFCs under anhydrous conditions are not studied in detail by SAXS and only few reports are available. For such membranes most of the SAXS studies are for water swollen membranes, which require humidity for high conductivity at higher temperatures. Membranes containing nonaqueous solvents have not been widely studied by SAXS. In this study, membranes containing ILs have been analyzed by SAXS and the results obtained have been compared with the SAXS results for water swollen Nafion membranes. In Figure 4 we show the SAXS intensity, for the recast Nafion membranes containing EMITf and EMIIm ionic liquids and pure Nafion, at room temperature and ambient humidity as a function of the scattering vector q ($q = 2\pi/d$, $d = \lambda/(2 \sin \theta)$, where 2θ is the scattering angle). The SAXS results for both the membranes are quite different and have been found to be strongly dependent on the hydrophilic/hydrophobic nature of the IL. From the SAXS results given in Figure 4, the following points have been observed.

- The upturn (increase) in intensity at small values of q (at small scattering angles) is present in Nafion and recast Nafion membranes containing EMITf and EMIIm. In an earlier study[29] on Nafion membranes swollen with the same ILs, it has been reported that an upturn in intensity at small values of q was not present in membranes doped with EMIIm, which was explained to be due to the hydrophobic nature of the IL. However the different behavior in the present case may arise from the different method of synthesis of membranes.
- A shoulder appearing at low values of q has been assigned to be due to the matrix peak at $q = 0.0219$ in Nafion/EMITf membrane and at $q = 0.0282$ for the Nafion/EMIIm membrane. The slope of the intensity line in this q region is near −1 for the Nafion/EMITf membrane, whereas for the Nafion/EMIIm membrane the slope is higher than −1.
- The "ionomer peak" is present in Nafion/EMITf membrane at $q = 0.0681$ ($d = 92.2$ Å), whereas in the Nafion/EMIIm membrane, the ionomer peak has been observed at $q = 0.047$ ($d = 134$ Å). The ionomer peak is weak in the membrane containing EMIIm, and some smaller peaks are also observed at higher q values.
- After the ionomer peak, the scattered intensity has been observed to fall sharply and the slope of the tail region is close to −4 and follows Porod's law.

The intensity of the matrix peak has been reported to be strongly dependent on the crystallinity of the Nafion membranes. The crystallinity of the Nafion/EMITf and Nafion/EMIIm membranes has been studied by X-ray diffraction and XRD pattern for Nafion and Nafion membranes are shown in Figure 5. The two broad peaks observed at d-values of 2.3 and 5.1 Å are generally attributed to the crystalline stacking in the hydrophobic microphase. However in the present case, as given in Figure 4, the intensity of the matrix peak, which has been

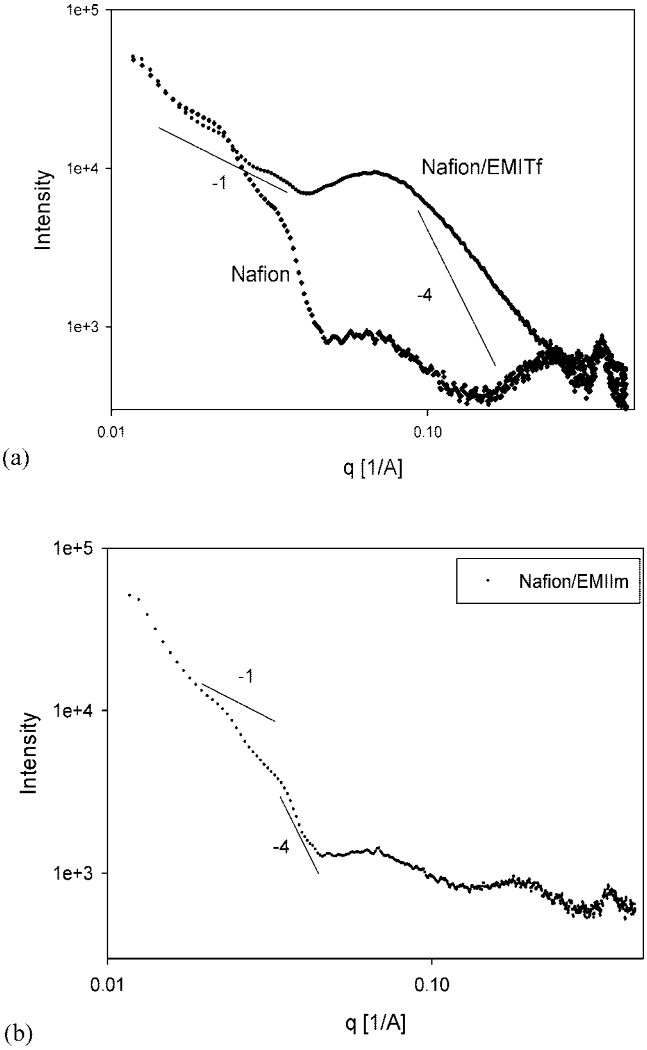


Figure 4. SAXS spectra of recast Nafion membranes: (a) Nafion and Nafion/EMITf and (b) Nafion/EMIIm, prepared by solvent casting method.

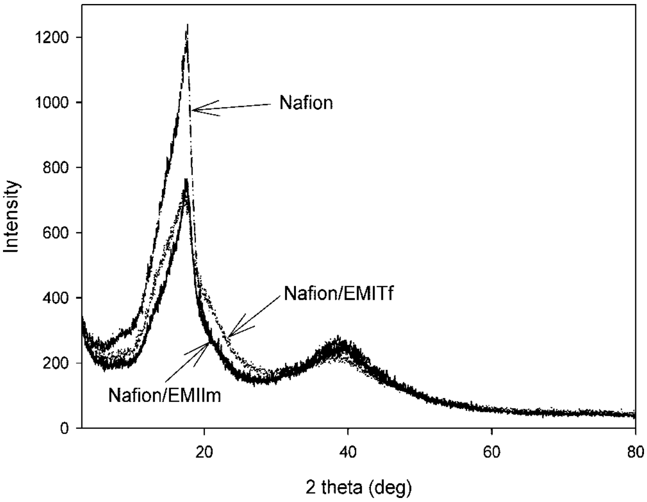


Figure 5. X-ray diffraction pattern for Nafion, Nafion/EMITf and Nafion/EMIIm membranes.

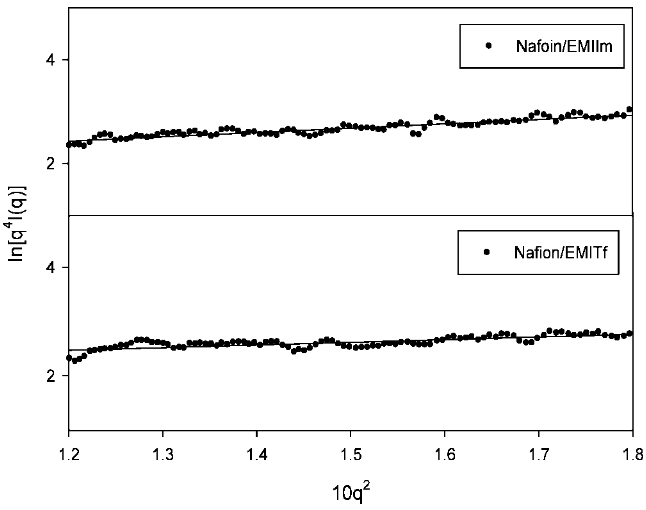
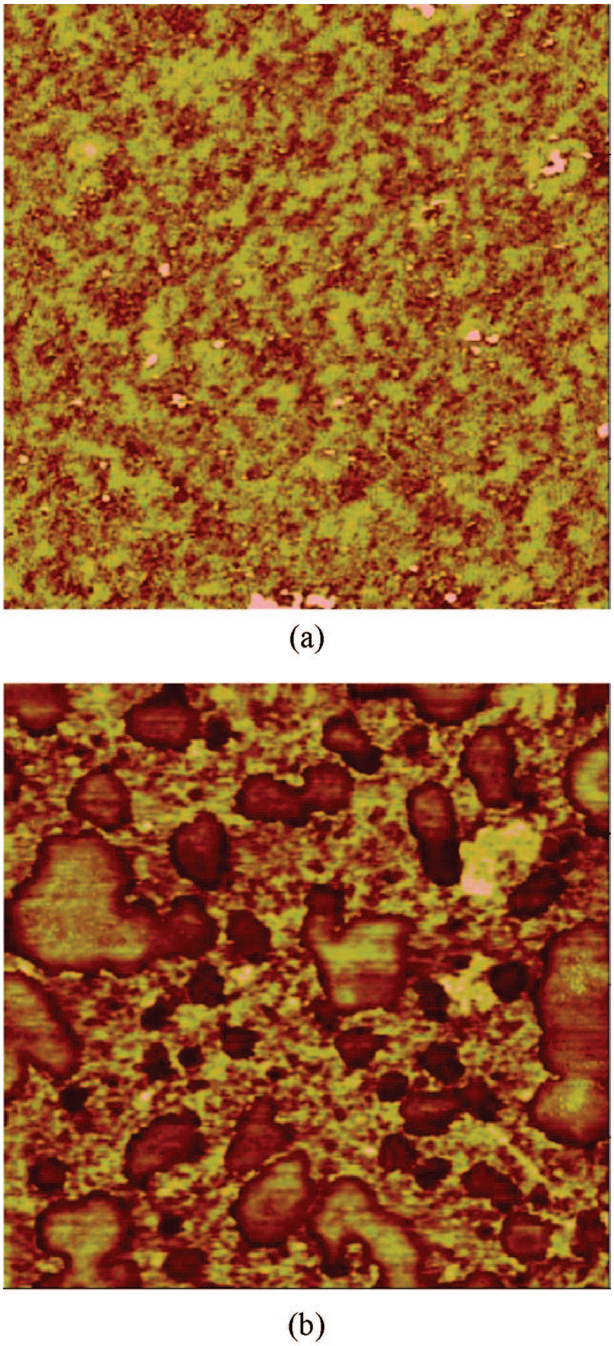


Figure 6. The $\ln[q^4 I(q)]$ versus $10q^2$ curves for Nafion/EMITf and Nafion/EMIIm membranes.


(a)

(b)

Figure 7. Tapping mode atomic force microscopy (TM-AFM) phase images (size 1 μm) of Nafion/EMITf (a) and Nafion/EMIIm (b) membranes.

observed as a shoulder superimposing on an increase in intensity in the SAXS spectra for the membranes, indicates that both the membranes have large amorphous content. This may be due to the large size of the anions ($CF_3SO_3^-$, $N(CF_3SO_2)_2^-$) of the ILs used in the present case, due to which the IL acts as a plasticizer and increases amorphicity of the membranes. A sharp fall in intensity after the ionomer peak has been observed and Figure 4 shows dotted lines with slope −4 in this region for comparison only. It has been observed that in case of the Nafion/EMITf membrane, the slope of a $I(q)$ vs q curve is less than −4, which suggests that polymer/IL interface may not be very sharp, but it confirms the phase separation in the membrane. However in case of Nafion/EMIIm membrane $I(q)$ α q^{-4} behavior has been also observed and the slope is very close to −4 as shown in Figure 4 by a dotted line. This indicates a relatively sharp interface between the polymer and IL and also the presence of phase separation. The different slope (from −4) of the scattered line in this region, observed for the recast Nafion membranes, may be due to the use of IL instead of water.

The asymptotic behavior of the scattering curve at large values of q generally reflects the nature of the interface between the hydrophilic and hydrophobic domains in the water swollen membranes. According to the Porod analysis of SAXS data at higher q values, the slope of the $ln[q^4 I(q)]$ versus $10q^2$ plot can give information about the thickness of the interface between the hydrophilic and hydrophobic phase. The plot between $ln[q^4 I(q)]$ versus $10q^2$ for the recast Nafion membranes containing ILs is shown in Figure 6. The slope for the Nafion/EMITf and Nafion/EMIIm membranes has been found to be 0.494 and 0.837 Å^2 respectively. The distance between the two phases has been found to be lower in membranes containing hydrophilic EMITf than hydrophobic EMIIm ionic liquid. These results appear to be consistent with the TM-AFM results for these membranes as discussed below.

An upturn in intensity at very small values of q has been observed for both the membranes, which indicates the presence of long-range inhomogeneities in the spatial distribution of ionic clusters. However, recent results reported the absence of an upturn at small values of q as well as the matrix and ionomer peak for the Nafion membranes swollen with EMIIm, whereas it was present in the membranes swollen with EMITf.[29] This was explained to be due to the hydrophobic nature of the IL (EMIIm) used in the membrane. The ionic clusters are homogeneously distributed in the polymer matrix and no phase separation takes place. The different behavior in the present case may arise from the different method of synthesis of membranes, which is reported to affect the SAXS behavior, along with the hydrophobic nature of the IL. It has been reported in literature and also observed in Figure 4a that Nafion membranes, even in the dry state, show the presence of an ionomer peak[43] which suggests that the ionomer peak should be also present in Nafion membranes containing ILs.

The morphology of recast Nafion membranes containing ILs was also studied by TM-AFM and the micrographs (phase images) for the Nafion/EMITf and Nafion/EMIIm membranes are shown in Figure 7. The light regions are generally due to the softer domains, which represent the hydrophilic sulfonated groups, whereas the dark regions are due to the hydrophobic regions. The size and connectivity of the hydrophilic groups control the conductivity and other transport properties of membranes. The micrographs for the membrane containing hydrophilic IL (EMITf) show better connectivity between the hydrophilic domains than for the membrane containing hydrophobic IL (EMIIm). The observation of channels, formed due to the phase separation in the membrane containing EMITf, is also consistent with the SAXS results (Figure 4), in which a well defined ionomer peak has been observed with $d = 92.2$ Å. However, in case of the membrane containing EMIIm, the connectivity between ionic domains is not very good, which is related to the presence of the weak ionomer peak in the SAXS spectra (Figure 4b) and the formation of domains with $d = 142$ Å. The TM-AFM images for this membrane also show the presence of relatively larger domains as compared with the membrane containing EMITf. The relatively smaller size of domains in Nafion/EMITf membranes can also be due to the similar structure of triflate anion and Nafion. The lower connectivity between ionic domains for this membrane results in lower conductivity as has been observed in the ionic conductivity results for these membranes in Figure 2. The ionic domains have been also observed to be randomly distributed in the AFM images which have been found to result in an increase in intensity at small scattering angles, in the SAXS spectra of these membranes (Figure 4).

The alternative membranes being developed for use at high temperatures and under low humidity have slightly lower ionic conductivity as compared with water swollen Nafion membranes. The lower performance of such membranes is generally attributed to be due to the different morphology. In order to improve the performance of membranes based on SPAEK-6F, the morphology of membranes based on SPAEK-6F and containing the same ILs (EMITf and EMIIm) has been also studied by SAXS spectroscopy. These membranes were studied by SAXS at room temperature and under ambient humidity conditions and the SAXS spectra for SPAEK-6F, SPAEK-6F/EMITf and SPAEK-6F/EMIIm membranes are given in Figure 8. The degree of sulfonation (DS) of the polymer (SPAEK-6F) used in the synthesis of membranes has been kept constant at 40 for both the membranes.

The SAXS spectra for SPAEK-6F and both the membranes show an increase in intensity at very small values of q, and this upturn has been also observed for recast Nafion membranes containing EMITf and EMIIm. It is generally ascribed to be due to the presence of long-term inhomogeneities in the spatial distribution of the ionic clusters. Small shoulders observed at low value of $q = 0.025$ for SPAEK-6F/EMITf and at $q = 0.0219$ for SPAEK-6F/EMIIm membrane are due to the matrix peak and the low intensity of the shoulders is due to the low crystallinity of the membranes containing ionic liquids. The crystallinity of SPAEK-6F, SPAEK-6F/EMITf and SPAEK-6F/EMIIm membranes was also checked by X-ray diffraction and the XRD plots for the membranes are shown in Figure 9. The presence of a very broad peak at d-value of ~5 Å indicates the highly amorphous nature of SPAEK-6F membranes containing ILs. The ionomer peak also appears as shoulder superimposed on an increase in intensity at the same value of $q = 0.036$ ($d = 174$ Å) for both SPAEK-6F/EMITf and SPAEK-6F/EMIIm membranes. The low intensity of the ionomer peak may be either because the electron density contrast between the clusters and hydrophobic polymer phase is small or the $-SO_3H$ groups are randomly dispersed in the polymer matrix. The protonated polymers have been reported to show a lower phase separation as compared with perfluorinated membranes,[44] which result in a peak at low angles as compared with Nafion. The pronounced ionomer maximum has also not been observed in SPEEK-based membranes.[44,46] In such membranes, either the ionic groups are homogeneously distributed in the membrane due to the statistical distribution of the ionic groups along the polymer chains or the ionic domains are not large enough to give rise to a visible peak. The method of synthesis of statistical polymers using only one-step condensation is also different from that of block polymers, which can also result in different structure.[45] The polymer (SPAEK-6F) used in the present study is random polymer and such polymers generally do not form great phase separate unless both the components (hydrophilic and hydrophobic) are very dissimilar in nature. The absence of ionomer

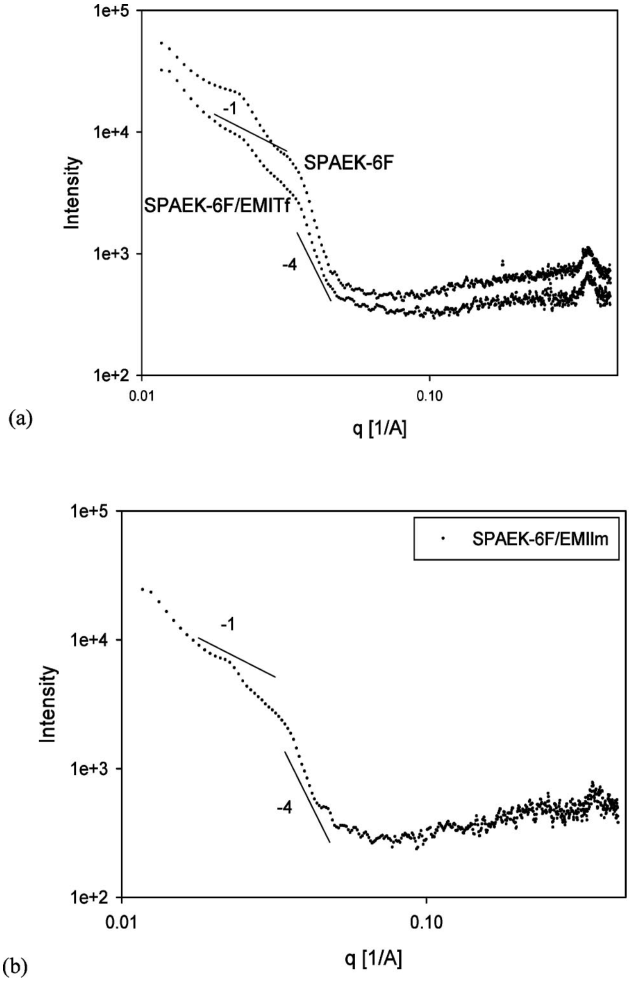


Figure 8. SAXS spectra of composite membranes: SPEAK-6F, SPAEK-6F/EMITf (a) and SPAEK-6F/EMIIm (b), prepared by solvent casting method.

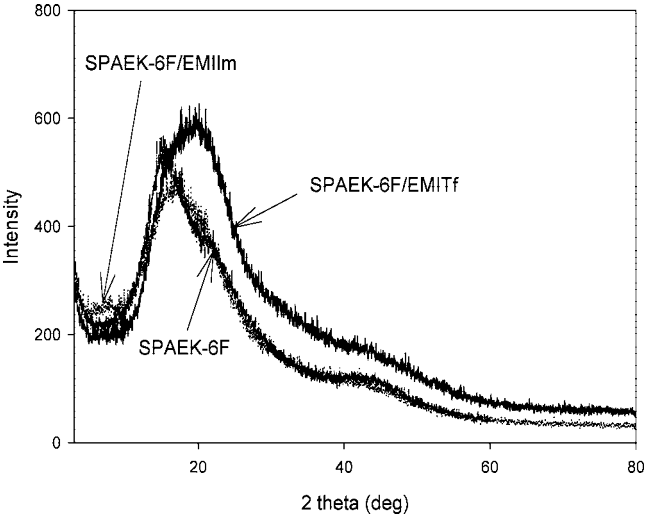


Figure 9. X-ray diffraction pattern for SPEAK-6F, SPAEK-6F/EMITf, and SPAEK-6F/EMIIm membranes.

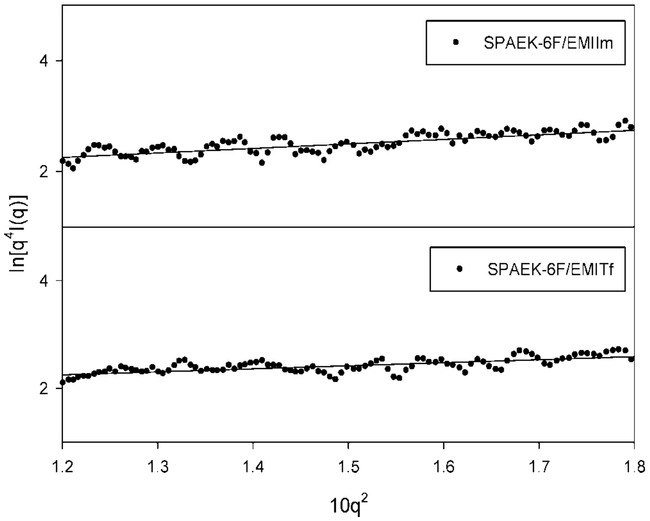


Figure 10. The $\ln[q^4I(q)]$ versus $10q^2$ curves for SPAEK-6F/EMITf and SPAEK-6F/EMIIm membranes.

peak in SAXS spectra is also related to the higher polymer chain rigidity, due to the presence of fluorine atoms in the hydrophobic part of the polymer. On the other hand, the presence of ionomer peak is related to the flexibility of the hydrophobic part much more than that of the hydrophilic part and the flexibility of the hydrophobic part controls the reorganization of the structure and the formation of ionic domains. The scattered intensity does not vary as q^{-1} in the low q region, as is evident from the dotted line drawn with a slope −1 in Figure 8. After the position of ionomer peak, the scattered intensity changes very sharply and in this region a dotted line having slope −4 has been drawn for comparison, which indicates that Porod's law is followed at high q values. However some small multiple peaks with low intensity are also observed at higher q values, which may be due to the higher order scattering maxima. The asymptotic behavior at large angles of the scattering curve, which reflects the nature of the interface between the hydrophilic and hydrophobic domains, was also studied and Figure 10 shows the plot of $\ln[q^4I(q)]$ versus $10q^2$ for the membranes based on sulfonated polymers. The slope of the $\ln[q^4I(q)]$ versus $10q^2$ line for the SPAEK-6F/EMITf and SPAEK-6F/EMIIm membranes has been found to be 0.564 and 0.815 Å^2, respectively. The distance between the hydrophilic and hydrophobic phases has been observed to be higher in the SPAEK-6F/EMIIm membrane containing hydrophobic IL than the SPAEK-6F/EMITf membrane containing hydrophilic IL. These results have been found to be consistent with the TM-AFM results for these membranes as discussed below. The general shape of the SAXS spectrum for these membranes is similar to that observed for some other water swollen high temperature membranes based on sulfonated polymers like sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(ether ether ketone ketone) (SPEEKK) and sulfonated polyimides (SPIs).[44−46] However the direct comparison of data from different experimental studies is not possible, as the morphology and transport properties have been reported to depend upon the membrane processing, thermal history and thickness.

The morphology of SPAEK-6F membranes containing ILs was also studied by TM-AFM and the micrographs (phase images) are shown in Figure 11 for SPAEK-6F/EMITf and SPAEK-6F/EMIIm membranes. The connectivity between ionic domains (which appear lighter) seems to be poor for membranes containing EMITf and EMIIm. There appears to be a large distribution in the size of domains, which are randomly distributed in the membranes. The absence of ionomer peak in the SAXS spectra of these membranes is thus due to the homogeneous dispersion of ionic groups in the polymer matrix or the size of domains is not sufficient to get a visible peak. The random distribution of ionic domains is also responsible for an increase in scattered intensity at low q values, as observed for both the membranes. The similar SAXS spectra observed for SPAEK-6F/EMITf and SPAEK-6F/EMIIm membranes along with the results of TM-AFM studies support the nearly equal value of ionic conductivity observed for these membranes, as shown in Figure 2.

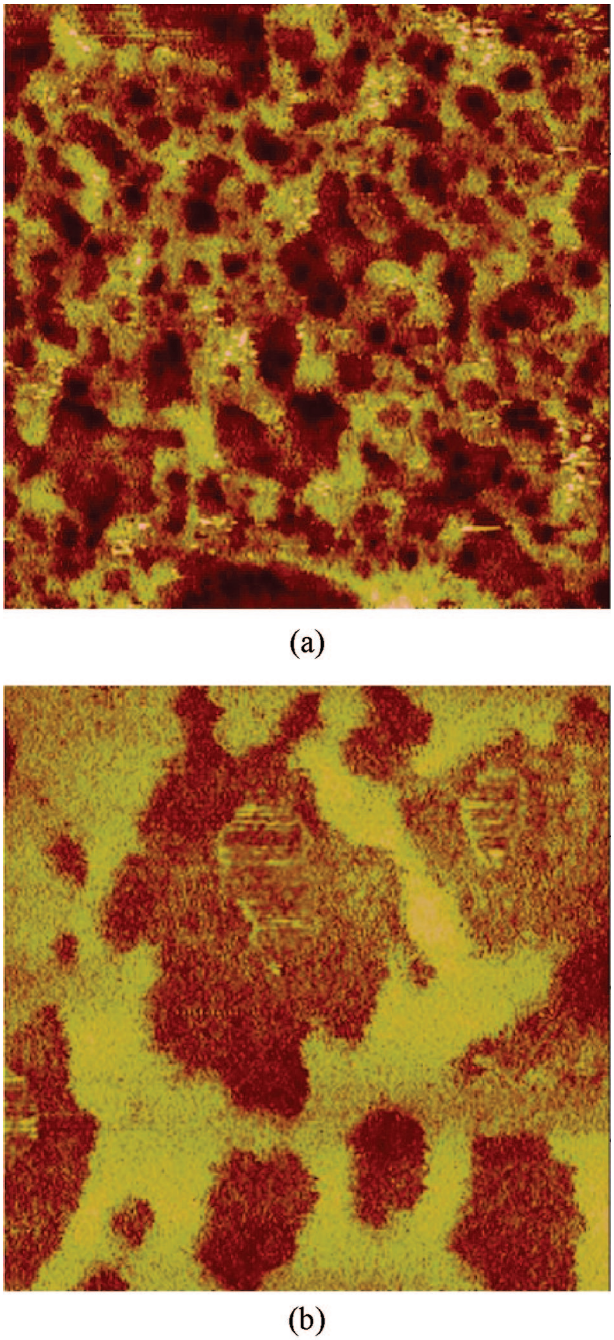


Figure 11. Tapping mode atomic force microscopy (TM-AFM) phase images (size 1 μm) of SPAEK-6F/EMITf (a) and SPAEK-6F/EMIIm (b) membranes.

The mechanical strength of some membranes was also measured at room temperature. The stress at break for the SPAEK-6F/EMITf membrane has been found to be 11.07 MPa, which is comparable with that of dry Nafion 117 (10 MPa), whereas other membranes show lower mechanical strength. SPAEK-6F-based membranes have been observed to show better mechanical strength than recast Nafion membranes containing ILs.

The different morphology observed from SAXS studies for recast Nafion and sulfonated polymer (SPAEK-6F) -based membranes containing the same ionic liquids is due to the different nature of the polymer used. In case of the recast Nafion-based membranes, the ionic groups ($-SO_3H$) are attached to the pendant chains, whereas the side chains are absent in SPAEK-6F, and as a result the hydrophobic and hydrophilic groups are very dissimilar to each other in Nafion so that it results in good phase separation when doped with hydrophilic IL (EMITf). The backbone rigidity is also different in both the polymers and it also affects the formation of ionic domains. On the other hand, the sulfonated polymer used in the present study (SPAEK-6F) is random copolymer, in which both the hydrophilic and hydrophobic parts are similar to each other and as a result the phase separation is not very prominent when doped with IL and hence no sharp ionomer peak has been observed for membranes based on SPAEK-6F. Such a morphology difference brings about the slightly lower ionic conductivity of SPAEK-6F-based membranes as compared with recast Nafion-based membranes, with both containing the same ILs. Thus, the morphology plays an important role in the performance of proton conducting membranes being developed for use in PEFCs at higher temperature and under anhydrous conditions.

Conclusions

The morphology of proton conducting membranes based on recast Nafion and random sulfonated polymer (SPAEK-6F) containing hydrophilic (EMITf) and hydrophobic (EMIIm) ionic liquids has been studied by TM-AFM and SAXS. The absence of ionomer peak in membranes based on SPAEK-6F, despite the presence of ionic clusters, has been explained to be due to the rigidity of neutral hydrophobic part of the polymer. However the upturn in scattered intensity at low q values and Porod's behavior at high q values have been observed for recast Nafion- and SPAEK-6F-based membranes. The previous study[25] revealed that SPAEK-6F showed higher entrapment ability of ILs than recast Nafion. In order to develop better IL-based composite membranes, the hydrocarbon-based sulfonated copolymer which has very dissimilar structures of hydrophobic and hydrophilic part should be used. The correlation of morphology of these membranes with the ionic conductivity, thermal stability and other properties will be quite helpful in improving the design of high temperature proton conducting membranes based on SPAEK-6F and containing ionic liquids for applications in PEFCs at high temperatures (100−200 °C) and under anhydrous conditions.

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