Original Article

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Ionic conductivity investigation of [bmim]Cl/polystyrene film as polymer electrolyte prepared by a versatile ionic liquid based microemulsion method

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Abstract

Due to their surprising properties, ionic liquids (ILs) are attracting considerable attention in many areas of chemistry and industry. Among these properties, ILs can play an important role in polymer electrolytes due to their excellent ionic conductivity up to their decomposition temperature. In this study, IL/poly(methyl methacrylate) composites were prepared as a polymer electrolyte with excellent ionic conductivity in IL-based microemulsion. Hydrophilic ionic liquid, [bmim]Cl), was used to prepare the IL/polymer composite. The [bmim]Cl/polystyrene membrane composite was characterized by AFM technique. After the addition of 2.5 wt.% [bmim]Cl in the microemulsion formulation, at 150 °C produced [bmim]Cl/polystyrene with the highest ionic conductivity, 5.7×10^{-3} S/cm. It was concluded that the addition of hydrophylic [bmim]Cl ionic liquid increased ionic conductivity and interface stability at the solid [bmim]Cl/polystyrene film. The resulting IL/polymer composites shouldhave potential as polymer electrolytes and can be used in fuel cell.

Keyword: Polymer electrolyte; Fuel cell; Polystyrene, [bmim]Cl ionic liquid**,** Ionic conductivity

1. Introduction

ILs (designer solvent or green solvent) have attracted considerable interest in many areas of chemistry because of their remarkable properties, such as nonvolatility, non-flammability, excellent thermal stability, high ionic conductivity and wide electrochemical window [1-4]. Among these properties, the excellent ionic conductivity up to their decomposition temperature enables ILs to play an important role in polymer electrolytes. There is an excellent principle via in situ polymerization of vinyl monomers in an IL solvent that the successful preparation of IL-based polymer electrolytes is critically dependent on the compatibility between the IL and the polymer matrix [5-8]. Polymer electrolytes combine polymers and ionic salts, and are a type of electrolyte used in Lithium-ion batteries. Incorporating them into Lithium-ion batteries has led to significant advances in battery technology, including improved safety, increased capacity and longer cycle life. The history of polymer electrolytes in Lithium-ion batteries dates back to the late 1990s [9]. The first commercial application of polymer electrolytes in Lithium-ion batteries took place in the early 2000's. Sony Corporation marked a significant milestone in the battery industry by introducing these batteries in its consumer electronics products. Sony represented a departure from traditional liquid electrolyte-based batteries with the introduction of the first polymer electrolyte- based Lithium-ion batteries [10]. As an alternative approach to prepare ionic conductive polymer electrolytes, polymerization of the IL-based microemulsions, therefore, is investigated in this work. Microemulsions are isotropic, macroscopically homogeneous and thermodynamically stable solutions including at least three components, namely a polar phase (usually water), a non-polar phase (usually oil) and a surfactant and sometime co-surfactant [11-13]. Of particular recent interest is the combination of surfactant and ionic liquids (ILs), as a substitute for water, to create novel microemulsion systems [14-16]. It is believed that IL microemulsions, in comparison to traditional microemulsions, can provide hydrophilic or hydrophobic nanodomains and thereby expanding the potential uses of ILs as reaction media, and consequently synthesize the special nanocomposites [16-19].

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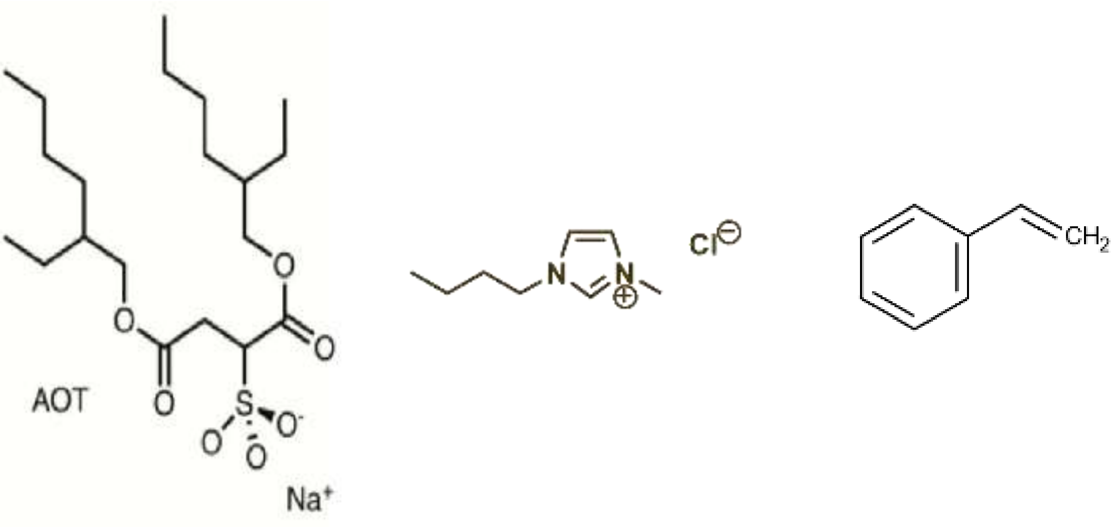
Here, we report the preparation and polymerization of microemulsions containing IL polar cores dispersed in polymerizable styrene monomer oil. Our expectation is that the IL nanostructures formed in these microemulsions could be preserved in the resultant polymeric matrix by polymerization of an oil-continuous phase.

2. Experimental section

2.1. Materials

Hydrophilic ionic liquid 1-Butyl-3-methylimidazolium chloride, 99%, [bmim]Cl) as the model of IL, and the sodium bis(2-ethylhexyl) sulfosuccinate as anionic surfactant AOT were purchased from Sigma-Aldrich. Styrene monomer as polymerizable oil (AR grade), benzoyl peroxide (BPO) and 1-butanol were received from Merck.



Sodium bis(2-ethylhexyl) sulfosuccinate (AOT)

1-Butyl-3-methyl imidazolium chloride, ([bmim]Cl)

Styrene monomer

Scheme. 1. The Molecular structure of sodium bis(2-ethylhexyl) sulfosuccinate (AOT), 1-Butyl-3-methylimidazolium chloride, ([bmim]Cl) ionic liquid, and styrene monomer

2.2. Preparation of the [bmim]Cl/polystyrene

A stable microemulsion formulation composed of [bmim]Cl (2.50 Wt. %) polar phase, styrene oil phase (89.94 Wt. %), AOT surfactant (7.56 Wt. %) was prepared at 60 °C [20]. AOT is a double-ended anionic surfactant with a sulfosuccinate head group. It is stabilized as a salt by a sodium cation. The AOT molecule has an inverted conical structure and has been shown to be an effective emulsifier, resulting in a wide range of applications and numerous intensive studies. Next, BPO as an initiator (0.7 wt %) and divinyl benzene as a cross-linker (2-4 wt %) based on the weight of styrene monomer in the formulation were added for starting polymerization process. Finally, transparent film was prepared. No apparent visible phase separation was observed during polymerization process for all samples [21]. The free-standing membrane with the thickness of 100 µm is transparent and flexible. Fig. 1 shows a photograph of the resulting the [bmim]Cl/polystyrene film preparation based on the ionic liquid-in-styrene oil microemulsion.

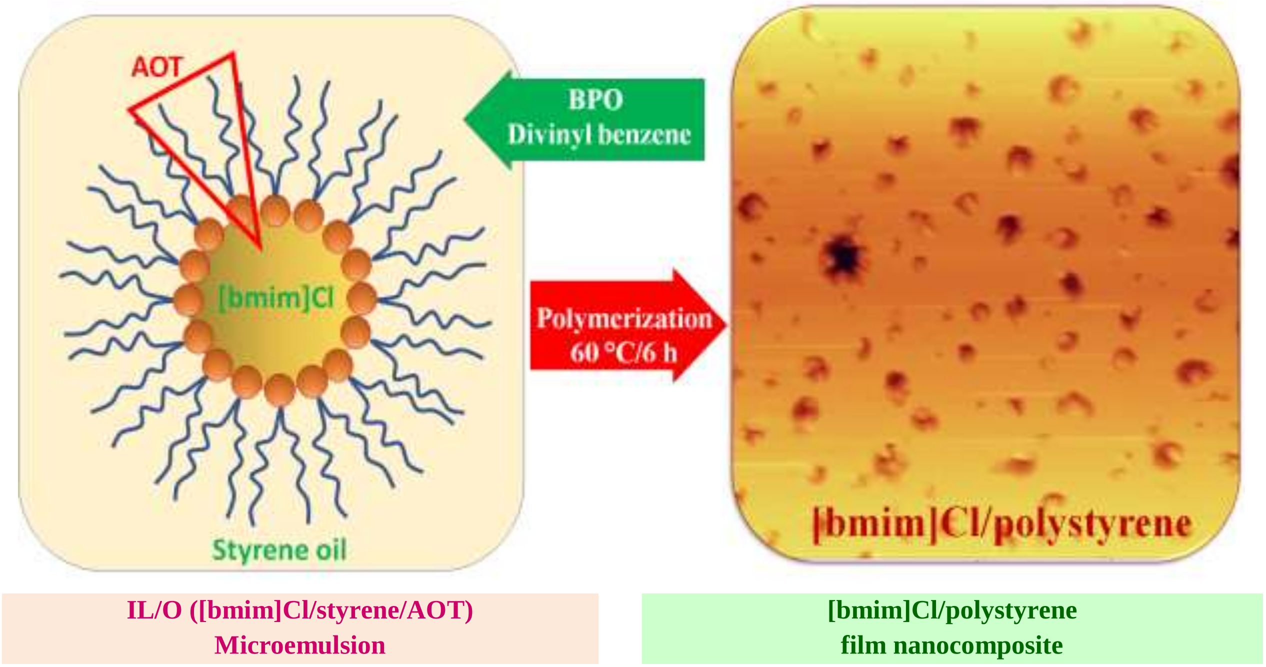


Fig. 1. Photograph of [bmim]Cl/polystyrene thin film nanocomposite produced by IL/O microemulsion polymerization of [bmim]Cl/styrene/AOT (2.50/89.94/7.56 wt. %) system, initiated by BPO at 60 °C.

2.3. Characterization of the [bmim]Cl/polystyrene

The microstructures of the resultant [bmim]Cl/polystyrene film nanocomposite was characterized by phase-lag atomic force microscopy (AFM) images on a Vico Scientific Sales Pvt Ltd AFM in none contact mode. The oscillation frequency was set to ~255 kHz with a Si cantilever which had a spring constant of about 11.5 N/m and speed of 2 Lin/S.

2.4. The ionic conductivity of the polymer electrolyte film study

The ionic conductivity of the polymer electrolyte film was measured by means of electrochemical impedance spectroscopy (EIS), in which a solid electrolyte was placed between two pieces of stainless steel. The EIS analysis was performed using the Metrohm Nova Auto Lab B.V. instrument. The frequency range was 1 MHz^{-1} Hz and the voltage was 12 mV. The following equation is used to calculate the ionic conductivity of the sample [22]:

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where σ is ionic conductivity, t is film thickness, R_b is resistance and A is effective film-electrode contact area. The temperature dependence of the ionic conductivity has been recorded in the range 30-150 °C.

3. Result and discussion

3.1. AFM study

Fig. 2 shows the AFM phase image of the fracture cross section of the [bmim]Cl/polystyrene composites containing 2.26 Wt.% of [bmim]Cl ionic liquid. As can be seen, the brighter regions correspond to hard polymer domains, while the dark regions correspond to the soft IL domains. In AFM image Fig. 3, one can observe that [bmim]Cl droplets with the diameter of ~22 nm (dark areas) with spherical morphology are dispersed in a "continuous" polymeric matrix (bright areas). It is noteworthy that at the bottom of some IL domains one can observe smaller inner openings with the diameter of ~22 nm. These pores might be derived from the interconnected IL-filled domains or channels. The formation of IL-based nanostructures preserved in the resulting polymers can explain why the obtained [bmim]Cl/polystyrene membrane are transparent even though they are incompatible with each other [23,24].

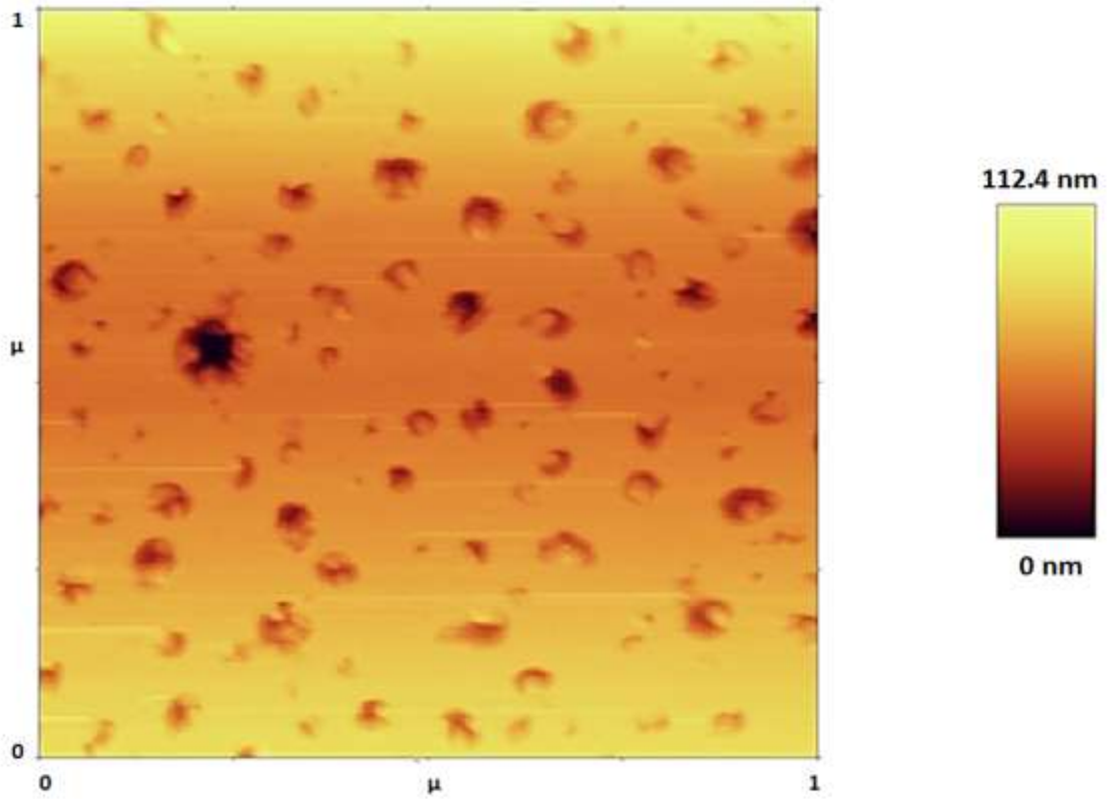


Fig. 2. AFM phase of the [bmim]Cl/polystyrene membrane, brighter regions correspond to hard polymer domains. Dark regions correspond to soft ionic liquid domains. Each image frame is 1 μm × 1 μm× 100 μm.

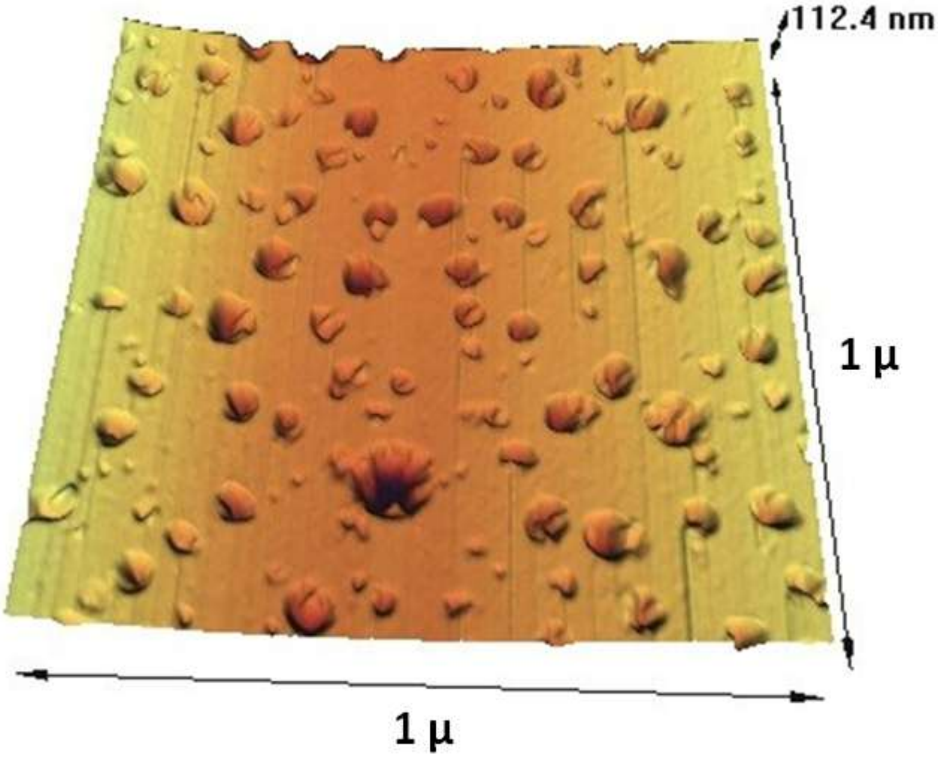


Fig. 3. 3D-AFM image of the [bmim]Cl/polystyrene film, image frame is 1 μm × 1 μm× 100 μm.

3.2. The ionic conductivity measurement

3.2.1. [bmim]Cl weight fraction effect in ionic conductivity

As can be seen from Fig. 4. the conductivity of the [bmim]Cl/polystyrene membranes increases with an increase in the weight fraction of ILs. As calculated from Eq. (1), the ionic conductivity of the prepared polymer electrolyte increased after the addition of a high amount of ionic liquid in the microemulsion formulation. The conductivity is about 4.5 $\times 10^{-3}$ S/cm in dry air for a polymer film containing 2.26 Wt.% of [bmim]Cl. For comparison, under the same experimental conditions, [bmim]Cl alone has a conductivity of 1.15 $\times$ 10^{-4} S/cm. This is similar to the value (1.16 $\times$ 10^{-4} S/cm) reported in previous reports [25]. Therefore, it is believed that the [bmim]Cl is the only active group that promotes the ionic conduction through the polymeric membrane.

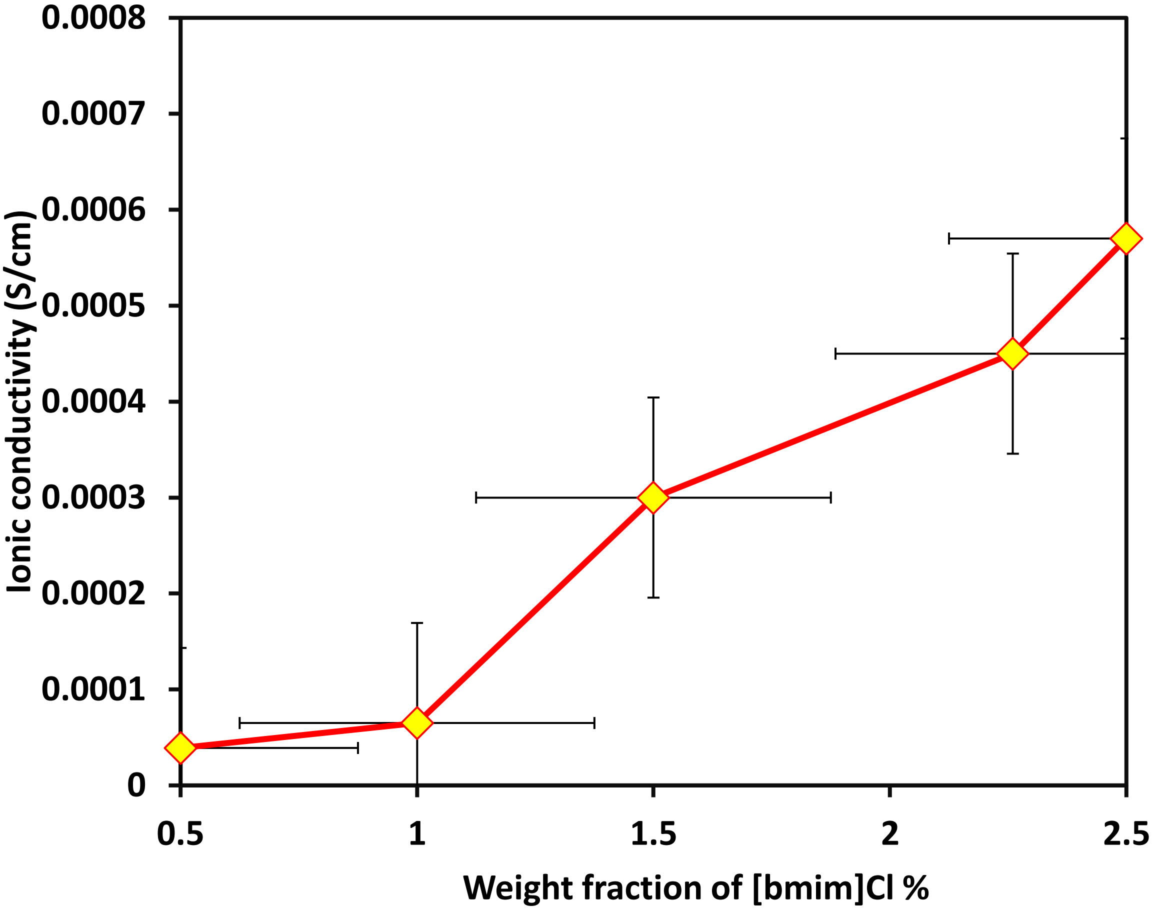


Fig. 4. Ionic conductivity as a function of the weight fraction of [bmim]Cl in the microemulsion formulation to prepare polymer film at 28°C

3.2.2. Temperature effect in ionic conductivity

Fig. 5, presents the effect of temperature dependence of the ionic conductivity of a polystyrene membrane. The highest temperature dependent ionic conductivity of solid polymer electrolyte. As shown, the ionic conductivity of the resulting composite membranes also increases with increasing temperature [26]. The temperature dependence of the ionic conductivity of a polystyrene membrane is shown in Fig. 3. We believe that the interconnected IL nanochannels formed in the [bmim]Cl/polystyrene membrane are mainly responsible for this relatively higher ionic conductivity. As an excellent result, we propose that the resulting [bmim]Cl/polystyrene membrane is the most effective candidate that can be employed in fabricating fuel cells as a polymer electrolyte. As mentioned above, the ionic conductivity of the obtained sample film was 4.5 $\times$ 10^{-3} S/cm in dry air and increased to 5.7×10^{-3} S/cm after the addition of 2.5 wt.% [bmim]Cl. The highest ionic conductivity of solid

[bmim]Cl/polystyrene is due to the decrease in the degree of crystallinity and the generation of more amorphous regions. In general, the ionic conductivity of solid polymer electrolytes increases with increasing temperature. This is due to the charge movement in the polymer chain in the amorphous phase which increases with increasing temperature.

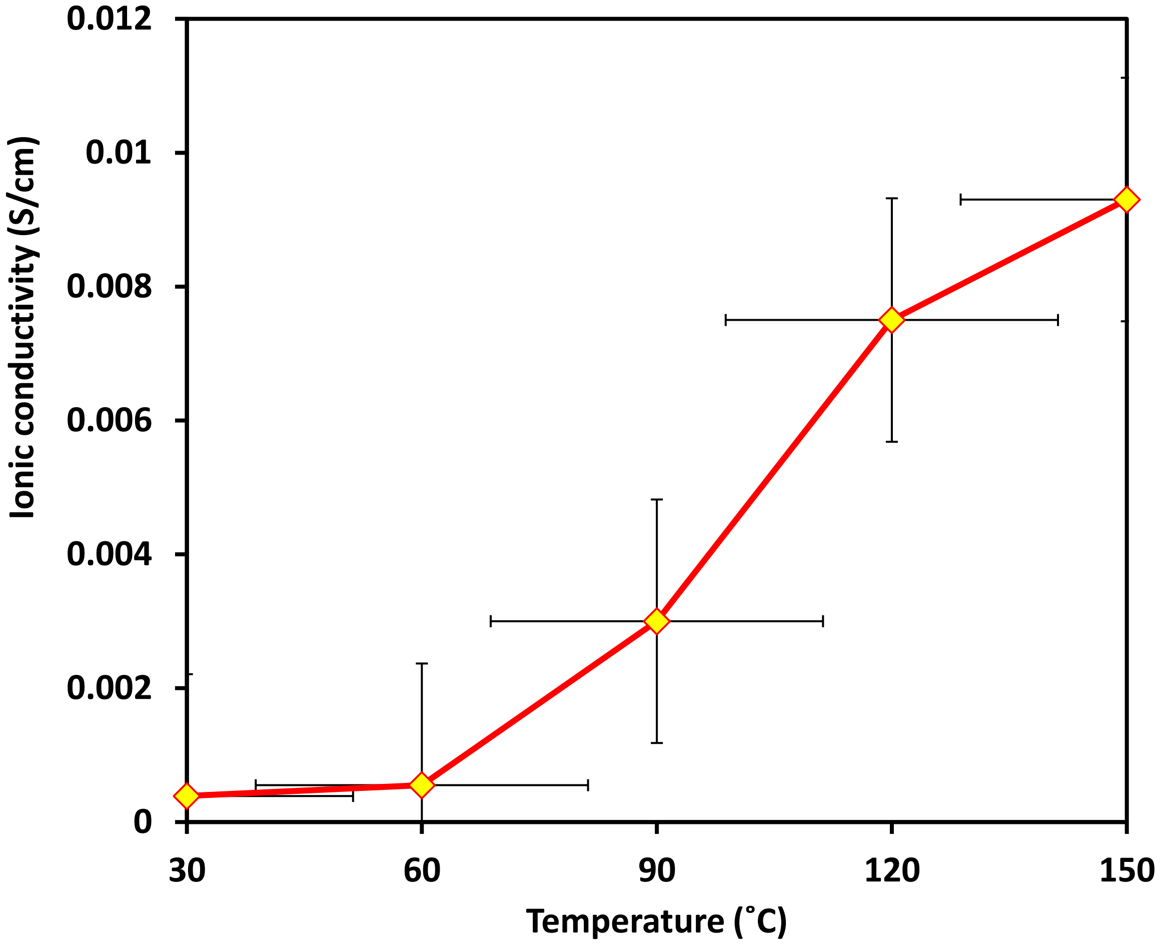


Fig. 5. Ionic conductivity as a function of temperature for the polymer membrane which containing 2.26 Wt. % of [bmim]Cl.

4. Conclusion

Polymerization of these IL-based microemulsions yielded transparent polymer membranes with high conductivity as wellas a rubbery property and provides a versatile platform for the preparation of solid polymer electrolyte including IL cores. The [bmim]Cl/polystyrene membrane composite was characterized by AFM technique. After the addition of 2.5 wt.% [bmim]Cl in the microemulsion formulation, at 150 °C produced [bmim]Cl/polystyrene with the highest ionic conductivity, 5.7×10^{-3} S/cm. It was concluded that the addition of hydrophylic [bmim]Cl ionic liquid increased ionic conductivity and interface stability at the solid [bmim]Cl/polystyrene film. The resulting IL/polymer composites shouldhave potential as polymer electrolytes and can be used in fuel cell. The obtained [bmim]Cl/polystyrene membrane show high conductivity at both room temperature and elevated temperature. We hope to offer an excellent procedure for fabrication of IL/polymer electrolyte membrane that can use in fuel cell technology.

Conflicts of Interest

The author declares no conflict of interest.

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