Proton and Electron Conducting Polymer Composite Films Based on SBS Triblock Copolymer

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Summary: Conducting polymer films were prepared by introducing ionic groups *via* chemical modification of one of the blocks of the polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymer and by adding different amount of metal salts into the modified block copolymer. The butadiene part of the copolymer was partially sulphonated to prepare the proton conducting film while the epoxidized form was used to fabricate electron conducting films with different inorganic salts. The products were characterized by Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM) and potential as well as conductivity measurements.

Keywords: block copolymer; conducting polymer; electron microscopy; epoxidation; FTIR spectroscopy; sulphonation

Introduction

Several sulfonic acid group functionalized polymers, such as that of polystyrene, polyarylether sulfone, polysulphazene, polyphenyloxide, and polyether-ether-ketone, and different kinds of nanostructured block copolymers, have been investigated with the aim of exploring their potential in polymer electrolyte membrane (PEM) fuel cells.[1–7]

Styrenic copolymers such as polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymers constitute an important class of thermoplastic elastomers.[8] SBS and SIS are non-polar and non-electron conducting polymers. However, sometimes it is useful to increase their molecular polarity by inserting some functional groups for some specific applications. Also the functionalization of the copolymer matrix with epoxy group and fabricating the blends with metal compounds leads to the formation of a novel conducting materials.[9] Further, the unique properties arise in such nanostructured polymers by incorporating functional groups into polymers *via* sulfonation. These features have led to an exploration of different applications for sulfonated block copolymers, such as in ion exchange resins, batteries, sensors etc.[6,7,10]

In a series of studies Dalas and coworkers epoxidized star shaped styrene-butadiene block copolymers and measured several functional properties.[11,12] In an effort to prepare electron conducting blends from insulating materials, styrene-butadiene copolymer was used as the host matrix of solid polymer electrolyte and its functionalization with epoxide groups and mixing with cupric oxide was found to lead to the formation of a flexible rubber-like 'metallic' conductor.[11,12] In star block copolymer/cupric oxide blend at certain compositions, the material was found to be conductive at room temperature. A model of solid electrolyte batteries was proposed using the composite powder as cathode.[9]

In the present work, electron conducting membranes are synthesized by modifying one of the blocks of linear SBS triblock copolymer by epoxidation reaction followed by preparation of composite with various metal salts. The objective of this

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Table 1.
List of metal salts used to fabricate the composites with the eBCP and their electrical properties.

Sample code	Metal salts	Wt.- %. of metal salt	Observation
A_1	CuO	30	Non-conducting
A_2	CuO	80	Conducting
A_3	Fe_2O_3	30	Conducting
A_4	$(CH_3COO)_2Mg.4H_2O$	30	Conducting
A_5	$FeCl_3$	30	Conducting
A_6	$SnCl_2.H_2O$	30	Conducting
A_7	Pb_3O_4	30	Non-conducting

work is to further develop flexible conducting ionomer membrane that may be useful in sustainable fuel cell applications.

Experimental Part

Materials

The polymer used in this work was polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymer (commercial name: Kraton D1184 CS) with 70 wt. % polybutadiene and having weight average molecular weight (M_w) of 310,000 g/mol. Toluene (99%), formic acid (85%), polyethylene glycol (PEG-400) and hydrogen peroxide (30%-w/v), methanol (99.5%), sodium bisulphite ($NaHSO_3$), sodium bicarbonate ($NaHCO_3$), tetraethylammonium bromide (TEAB), N-N dimethyl aniline (DMA) and different inorganic compounds (see Table 1) were purchased from local market and used as received.

Synthesis of Epoxidized (eBCP) and Sulfonated Block Copolymer (sBCP)

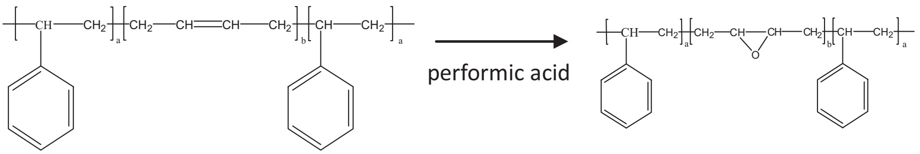
The SBS block copolymer was epoxidized to different degrees following the standard procedures discussed in literature.[13–15] The synthetic procedure is schematically illustrated in Scheme 1.

The eBCP sample having approximately 25% epoxidation level was dissolved in toluene to prepare 10% (mass by volume) solution. Two drops of 5% tetraethyl ammonium bromide (TEAB) solution was added as phase transfer catalyst. In the resultant solution, 2 ml of 5 wt.-% dimethyl aniline (DMA) was added as a ring-opening catalyst. An aqueous solutions of $NaHSO_3$ and Na_2SO_3 (molar ratio $= NaHSO_3/eBCP = 1.8$) were then added with vigorous stirring at 60 °C for 7 hours.[16] The reaction was terminated by adding a small amount of acetone solution containing antioxidant 2, 6-di-tert-butyl-4-methyl phenol. The synthetic procedure is illustrated in Scheme 2. The samples were sulphonated to an extent of 25, 50 and 100%.

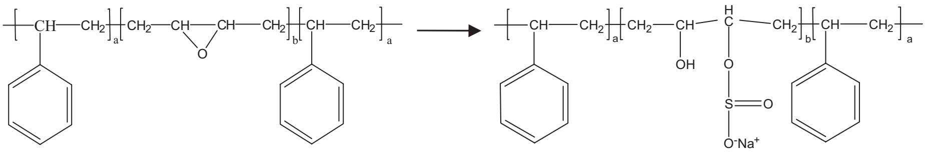
The specimens were prepared *via* solution casting using toluene as solvent and allowing the solvent to evaporate slowly over several days at room temperature to form uniformly thick films. The resulting film was dried to constant weight.

Preparation of Electron Conducting Membrane

Polymer/metal salt composite membranes were also prepared by solution casting using toluene as solvent and using various inorganic compounds. Calculated amount



Scheme 1.
Scheme showing epoxidation reaction of the SBS block copolymer; the butadiene block undergoes chemical modification resulting in epoxide groups.



Scheme 2.

Scheme showing the formation of ionomer from eBCP through ring opening reaction.

of polymer and inorganic compound was mixed thoroughly in a conical flask and poured into a Petri dish. In this case, the solvent was evaporated rapidly so as to avoid undesired condensation of the salts at the bottom of the dish. The films had a thickness of 100 μm.

Characterization Techniques

The samples were characterized by a Bruker (Germany) Fourier Transform Infrared (FTIR) spectrometer. The fracture surfaces of each sample were studied by Scanning Electron Microscopy (SEM; Jeol, JSM 6300, Japan) after coating with a thin layer of carbon film. The detailed morphology of the samples was inspected by Atomic Force Microscopy (AFM) in tapping mode (Multimode AFM, Digital Instruments, Santa Barbara, CA).

In order to confirm the laboratory test for ion conductivity through the ionomer film, a simple cell having two compartments was designed, those being separated by the ionomer membrane. The ion conductivity was measured by recording the change in potential of the cell resulting from change in concentration of H^+ ions in one of the compartments.

Results and Discussion

Characterization of Block Copolymers

Figure 1 presents the AFM phase image of thin film of the block copolymer used in this study. The film was prepared by dip coating technique following by vacuum annealing at 120 °C for 24 hours.

The morphology comprises ordered cylindrical domains of polystyrene (bright appearing in the phase image) dispersed in the matrix of polybutadiene (dark appearing in Figure 1), the latter being the majority component of the block copolymer. The chemical modification intended in the present work will take place in this matrix. Hence, it may be expected that, in particular, the matrix property of the copolymer may be modified.

The FTIR spectra of BCP, eBCP and sBCP (ionomer) are compared in Figure 2. The peaks centered at 910 cm^{-1} and 966 cm^{-1} are characteristic of the C=C linkages present in the butadiene units of the block copolymer which represent the vibrations associated with *trans*- and *cis*-C=C double bonds of 1,4-polybutadiene, respectively.[17]

In the FTIR spectrum of epoxidized version, i.e., in eBCP, different additional peaks appear that are not present in the virgin copolymer. Among various peaks observed in the spectra, it is interesting to carefully look at the peaks centered at 734 cm^{-1}, 1072 cm^{-1} and 1158 cm^{-1} which

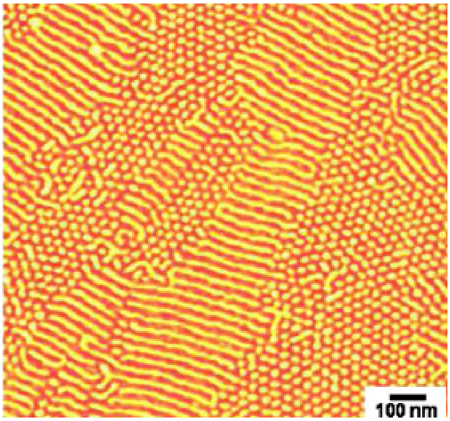


Figure 1.

Tapping mode AFM phase image of SBS triblock copolymer used in this work.

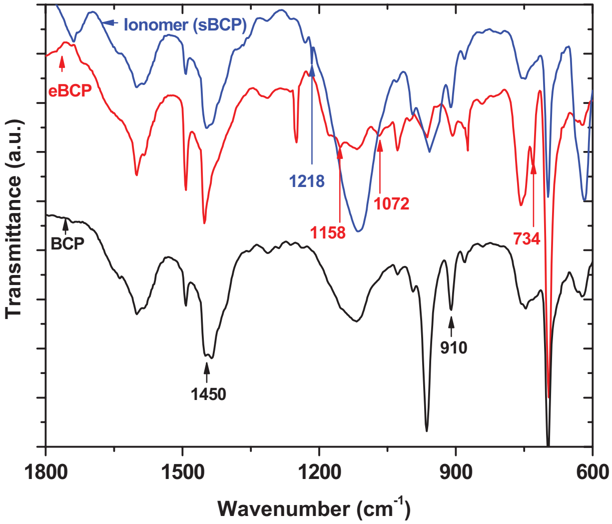


Figure 2.
FTIR spectra of different specimens (BCP, eBCP and sBCP) investigated in present work.

have been assigned to the epoxy ring stretching.[17,18] The appearance of those peaks, thus, indicates the insertion of epoxy groups in the BCP and formation of epoxidized BCP (eBCP). In case of ionomer film, the disappearance of peaks at 734 cm^{-1}, 1072 cm^{-1}, and 1158 cm^{-1}, which were present in eBCP samples, and appearance of a distinct peak at 1218 cm^{-1} indicate the complete sulfonation of the eBCP into its sulphonated version (i.e., sBCP). Similarly, the peak observed around 1027 cm^{-1} manifests further the presence of sulphonic group (SO_3H) in the polymer backbone as also observed by Johnson *et al.*[18]

Laboratory Test of Ionomer Films as Proton Conducting Membrane

One of the objectives of the present work has been to test the ionomer film (i.e., sBCP) thus prepared for fuel cell application. Thus, a simple laboratory device was designed to demonstrate the ion conductivity through the film. The device consists of two half cells comprising platinum (Pt) wires as electrodes immersed in the solution of sulphuric acid, both of them being separated by the ionomer membrane (see Figure 3). The electrical circuit is completed by connecting them properly with a high impedance digital multimeter.

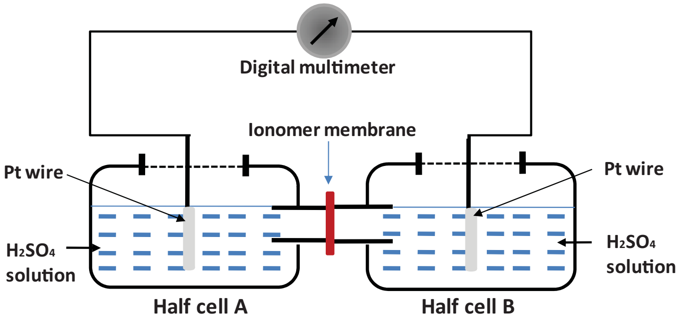


Figure 3.
Schematic representation of a concentration cell used to demonstrate the flow of ions through the polymer membrane.

The assembly of the components of the cell is schematically represented in Figure 3. The cell was constructed using two identical polyethylene bottles having internal diameter of 4 cm towards the belly and of 1.5 cm towards the neck each. The two bottles were joined in such a way that the bottle mouths were separated by the ionomer membrane under investigation. The whole apparatus was tightened in order to avoid the undesired leakage of the solution.

During the experiment, the ionomer membrane having 25% sulphonation of available epoxy groups was taken to separate the two half cells. The potential was measured keeping the concentration of H_2SO_4 in half cell A (0.33 ml of about 2M solution in 20 ml of distilled water) constant and changing the concentration of acid in the half cell B by the progressive addition of concentrated sulphuric acid into it. The solution was thoroughly mixed and the overall cell potential was measured. The same experiment was repeated also using Agar-Agar gel salt bridge instead of the polymer membrane. The device thus constructed represents a concentration cell whose total electromotive force (EMF) changes with the variation in electrolyte concentration of the half cells. The cell under consideration can be represented as follows:

$$\mathrm{Pt/H_2SO_4(a = x)\|H_2SO_4(a = y)/Pt} \qquad (1)$$

or

$$\mathrm{Pt/H^+(a = x)\|H^+(a = y)/Pt} \qquad (2)$$

The corresponding reaction will be:

$$\mathrm{H^+ + e \Leftrightarrow 1/2H_2} \qquad (3)$$

The cell EMF, which depends upon the acid concentration difference in the half cells, will be given by the corresponding Nernst equation:

$$E_{\mathrm{Cell}} = -\frac{RT}{F}\ln\frac{[H^+]_A}{[H^+]_B} \qquad (4)$$

where the symbols have usual meanings.

In order to evaluate the reproducibility of the results, similar sets of experiments were performed using the polymer membrane with 50 and 100% sulphonation. The results are presented in Figure 4. The block copolymer (BCP) films with sulphonation degree of 25, 50 and 100% have been designated as sBCP-25, sBCP-50 and sBCP-100, respectively.

It is interesting to note that the total cell potential, measured potentiometrically

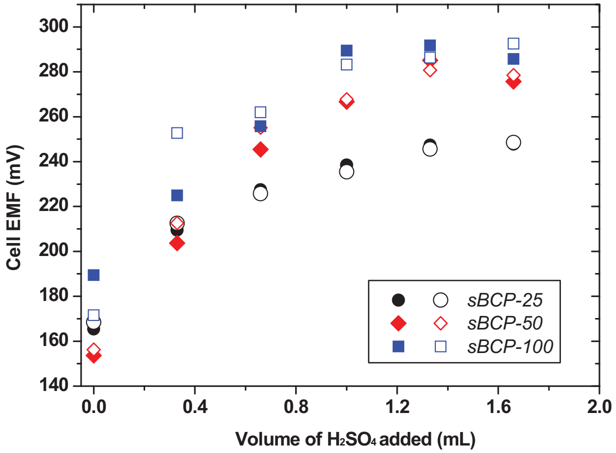


Figure 4.

Variation in total cell potential due to change in the concentration of H^+ ions in cell B presented in Fig. 3; the full symbols stand for the potential measured with ionomer membrane while open symbols represent the values measured with salt bridge.

(shown by filled symbols in Figure 4) using the ionomer membrane, between the half cells increases progressively on increasing the concentration of H^+ ions by adding concentrated sulfuric acid into the half cell B. For all the experiments, nearly identical results were observed on using Agar-Agar gel based salt bridge (see the data shown by open symbols in Figure 4) instead of the membrane. These observations clearly imply that there is an unhindered flow of the H^+ ions from one compartment of the cell to another through the sBCP ionomer membrane and therefore confirming its proton conducting ability.

Electrical Properties of Polymer/Metal Salts Composites

So far, the electrical property of sBCP based ionomers has been discussed. The study was extended to the formation of composite materials by adding different inorganic salts in different proportions with the epoxidized copolymer (eBCP), see Table 1.

It is well known that the solid metal salts are insulator due to the absence of free electrons. SBS block copolymer and its epoxidized versions (i.e., sBCP) are also insulators. However, the composites fabricated with suitable proportion of eBCP and metal salt may conduct electricity as there is a possibility of overlapping of the energy levels of the electronegative atoms involved in the composites.

Keeping the stated idea in mind, several metal salts were mixed with the epoxidized block copolymer (eBCP) having degree of epoxidation of 25%.

The conductivity of the sample films were measured by means of a high internal impedance digital multimeter (40 MΩ). The results are summarized in Table 1. The electrical conductance of the composite films was measured by setting these films in between two silver discs and connecting the two terminals. In the case of conducting film a fixed value of resistance was observed while in the case of non-conducting film, the multimeter did not show any value. This was a qualitative test but yet powerful enough to know if a film was conducting or not. It was assumed that a film having resistance of 40 MΩ or less can be regarded as being conducting. As shown in Table 1, not all the composites having any proportion of metal salt and eBCP can conduct electricity. Among various composites, only A_2, A_3, A_4, A_5 and A_6 were found to be electron conductor.

The detailed study was performed on the eBCP/CuO composites. The composites showed conducting behavior only when the filler content reached as high as 80 wt.-%. In contrast, for several other composites, the filler content of up to 30 wt.-% was sufficient to make them conducting.

The observations indexed in Table 1 leads to the assumption that the interaction between oxygen atom of the epoxidized groups of the eSBS and the CuO filler molecules are responsible for the observed electron conductivity and the semi-metal properties of the composite films. Thus, these materials have a small negative thermal energy gap (e.g., in the range of −.03 eV) which means the energy band overlap.[11] The conduction of electrons leading to the ‘insulator to semi-metal transition’ is probably due to the polymer chains which introduce coupling between electrons at the eBCP and CuO interface and the thermal motion of the epoxide group, resulting in an attraction between two electrons by emission and absorption of virtual phonons which can exceed their screened Coulombic repulsion.[2]

In some literatures it has been mentioned that only star shaped block copolymers show such electron conducting properties, which is not always true, as illustrated by the present study. Indeed, the aspect of how far the properties variation due to molecular architecture of the polymers can be reflected in their electrical properties should be further investigated.

In the previous section it was shown that some of the metal salts/polymer composites behaved in similar manner as other kinds of electron conducting solids while the others did not do in that way. Hence, it was interesting to look into the microstructural origin of the observed behavior. The results obtained on selected samples investigated by scanning electron microscopy in normal secondary electron (SE) mode as well as in back scattered electrons (BSE) mode are presented in Figure 5 and 6.

The SE and BSE mode SEM micrographs recorded in the same area of the composite comprising 80 wt.-% of CuO are presented in Figure 5. It can be observed that the inorganic particles are interconnected by the threads of stretched flexible organic film. The inorganic portion appears as tiny Cauliflowers homogeneously and compactly distributed in minority organic polymer matrix.

In case of BSE imaging, the contrast originates basically from the local difference in back scattered electrons productions (BSEs). The inorganic portions appear brighter than the organic portions. Thus, organic and inorganic areas can be conveniently distinguished in BSE mode imaging in scanning electron microscopy (SEM). Such an imaging (such as Figure 5b) shows the co-continuous network of brighter and darker regions representing

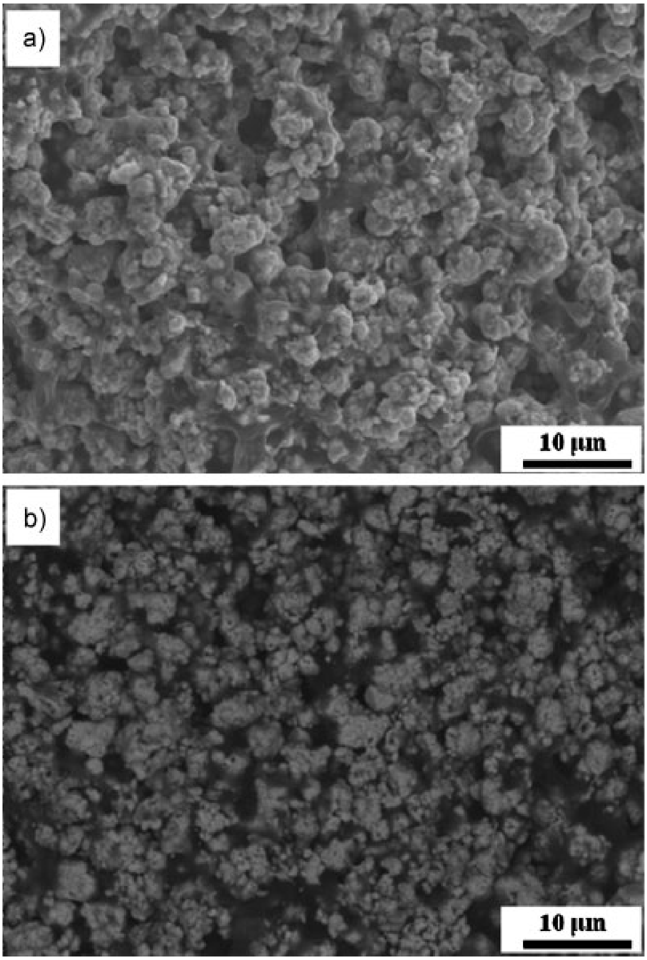


Figure 5.
SE mode (top) and BSE mode (bottom) SEM images of different magnifications of the composite having polymer/CuO weight ratio of 20/80.

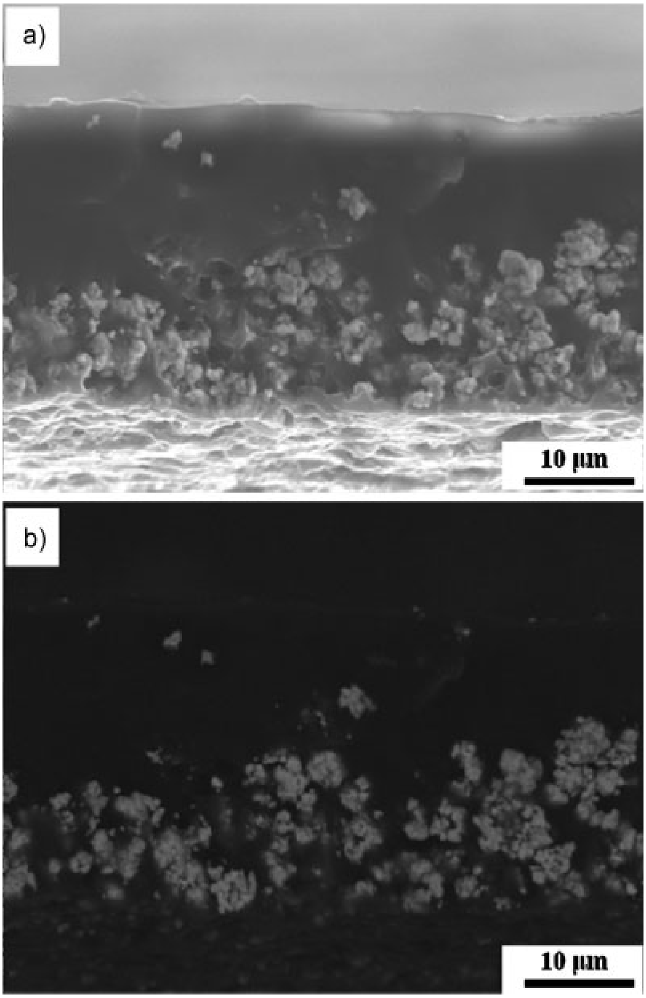


Figure 6.
SE mode (top) and BSE mode (bottom) SEM images of polymer/CuO (70/30 weight ratio) composite.

the inorganic (more BSEs producing areas) and organic (less BSEs producing areas), respectively. Figure 5 confirms the assumptions of structural construction of the composite so far discussed. Indeed, the compound can be regarded as highly filled co-continuous network of flexible organic polymer and inorganic filler. The continuous arrangement of the polymer throughout the composite structures enables the easy overlapping of the energy bands of epoxidized polymer and the electronegative atoms of metal salts endowing them then electrical conductivity.

Finally, let us throw a quick glance at the structure of the polymer/CuO (70/30 by weight) composite having much lesser amount of CuO, which was found to be non-conducting (see Table 1). SEM micrographs of the sample are presented in Figure 6 in which the images have the identical magnifications and interpretation as that of images presented in Figure 5. It becomes immediately obvious that the dispersion of the filler in the polymer matrix is not uniform. There is no co-continuous organic/inorganic network in this sample which hinders the overlapping of the energy bands; and hence the composite exhibits no electron conductivity.

Conclusion

The commercially available polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymer was subjected to the epoxidation reaction using performic acid generated *in situ* as a result of reaction between formic acid and hydrogen peroxide. The products were characterized by different techniques such as FTIR spectroscopy, electron microscopy, conductivity measurement. The eBCP was further successfully modified into different ionomers. The formation of ionomer membrane was confirmed by proton conductivity measurement, the electron conductivity and SEM analysis.

Some eBCP/metal salts composite were electron conducting which may be attributed to the overlap of their respective energy bands, the latter being facilitated by co-continuous network of the composites components. The ionic conductivity was found to increase with the increase in degree of sulfonation in the ionomer.

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