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4-Methylbenzenesulfonic Acid as an Alternative Proton Conducting Functional Group for Elevated Temperature Polymer Electrolyte Membranes Fuel Cell

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Abstract
Polysulfones carrying (4-Methylbenzenesulfonic Acid) side chains were prepared and investigated for use as proton-conducting fuel-cell membranes.The resulting ionomers were cast into membranes and properties such as mechanical and thermal stability, ion-exchange capacity, proton conductivity and water sorption were evaluated. Sulfonations of membrane were achieved by varying the degree of sulfonation (DS) in reaction time.The presence of sulfonic group after sulfonation process in the modified polymers was characterized by nuclear magnetic resonance (NMR), elementary analysis and infrared spectroscopy (FT-IR). Fourier Transform Infared (FTIR) were used to verify and it was clearly confirmed the presence of SO_3 stretching bond at frequency 1030 cm^{-1} Thermo gravimetric analysis (TGA) show that these membranes are thermally stable up to 390°C in dry air, which implying that they have a good potential to be used as the membranes for high-temperature PEM fuel cells. Under anhydrous situation, ionic conductivity of the membrane reach the highest point value of 5.02×10^{-4} at 150 °C associated with the activation energy of (22.04 kJ mol^{-1}) for proton transport. Scanning electron microscopy was used to examine the surface morphology of the formed membrane. Characterizations of different degree of sufonated membranes were conducted through elemental analysistal, Fourier Transform Infared (FTIR) and swelling test.

Keywords: fuel cell, polymer electrolyte membrane, Polysulfone (PSF), 4-Methylbenzenesulfonic Acid (MBSA), benzyl chloride.

1. INTRODUCTION

There is no objection that the global demand for energy in the future will dramatically increase due to technical innovation and invention of machine. In addition energy consumption in the residential sector in the world is steadily increasing because both the consumption per household and the number of households are increasing.

Most useful fuel in the worlds, Petroleum, is becoming inadequate and is confined to a few regions of the world and the continuity of supply is governed by political, economical, and ecological factors. Its burning produces emissions which shoulder much of the blame for air pollution. Contributions also come from deforestation, carbon dioxide from the burning of coal, and methane release. This has prompted research for clean and efficient alternatives for power generation In order to reverse the trend of destroying the environment. Several method of producing energy such as hydrodynamic, wind, geothermal, solar and tidal is desirable as alternative of petroleum. These methods are presently employed in a somewhat small scale, but require specific environments in order to work effectively. One of the most attractive alternatives is electrochemical fuel cell technology which needs no particular environment to work well. [1]

Proton exchange membrane fuel cells (PEMFCs) are the latest promising energy producers designed for the future century. At the present capable of providing power for a wide variety of applications including portable electronics, automotive transportation and military devices. Proton exchange membrane fuel cells in general have a high power density; the membrane provides an ionic path for protons to travel from the anode to the cathode, moderately efficient in their conversion of chemical energy to electrical energy, low operating temperatures and low greenhouse gas emissions. [1-5] Electrolyte membrane is one of the most important parts of the fuel cell components and consists of porous material which is often made from polymeric molecule. The majority of common polymer electrolyte membranes used in fuel cells applications are perfluorinated polymer membranes, e.g. DuPont's Nafion membranes. These membranes consist of a hydrophobic fluorocarbon backbone and hydrophilic sulfonic pendant side chains. The structure of Nafion makes a micro phase-separated morphology of membranes and thus they exhibit excellent thermal, mechanical, and electrochemical properties. [6]

In spite of those good qualities, Nafion has several deficiencies such as high cost, high methanol crossover through membranes and low proton conductivity at high temperatures (low humidity circumstances). Nafion is unstable at high temperatures because proton conduction is more effective only in the presence of water which limits the fuel cell operating temperature to less than 80 ºC [7] The development of innovative membrane for use in fuel cells which can function at a temperature range >100 ºC has become a highly attractive objective for researchers. [8]

Consecutively, to get the most efficient system of PEMFC, the membrane needs to have a good and stable under operating at desired temperature and pressure. The need of developing membrane that satisfies this condition with the minimum cost of production and maintenance are recommended. The development of novel electrolyte membranes with dense structure, good mechanical flexibility, and high proton conductivity, but with little or no dependence on humidity at temperatures above 100°C remains an important challenge to the realization of practical PEM fuel cells.

Lately, there have been extensive researches efforts on how to find another fuel cell membrane that are stable at relatively high temperatures, low cost, and possess similar performance as the standard Nafion membrane. [9, 10] For several years, a number of polymers have been investigated intensively for their possible as membrane materials in polymer electrolyte membrane fuel cells. Research groups have bought to improve the existing materials and to find substitute polymer that possess similar performance as the standard Nafion membrane. [12]

Aromatic polymers like polysulfones are future replacement of perfluorinated materials. These materials meet most of the specifications of the fuel cell membranes, especially high protonic conductivity, stability in oxidant and reducing environment, good mechanical, thermal, and chemical stability. [11-12] From a chemical point of view, the good oxidation resistance of aromatic hydrocarbons is due to the fact that the C-H bonds of the benzene ring have typical bond strength of around 435 kJ mol^{-1}, compared with aliphatic C-H bond strengths, around 350 kJ mol^{-1}

Because of their low cost, processability, and high-quality of mechanical, thermal and oxidative stability, aromatic hydrocarbon based membranes are a promising alternative to Nafion [12-17]. Among them, sulfonated aromatic polymers exhibits high conductivity and are therefore of interest for PEMFCs. Due to the aromatic rings, these hydrocarbon polymers as backbones allow the introduction of sulfonic acid moieties to make the desired level of conductivity for fuel cell application and also possess good chemical resistance and mechanical properties. [18,19].

Aromatic hydrocarbon such as polysulfones (udel) has been reported in literature. This is because udel polymers are soluble in many organic solvents compared to other polysulfones like radel, which enables it to use in different reactions for chemical modification such as Electrophilic substitution and nucleophilic reactions. [12] Chemical modification of the polysulfones by introducing new reactive functional groups to the main chain proved to be a useful way to change their properties, such as thermal behavior, conductivity, flexibility and mobility and increase the reactivity of the main chain that permit further chemical reactions.[12-17].

Many reviews have been reported on the chemical modification of polysulfone by different mechanisms for the introduction of functional groups onto the polysulfone backbone. The modification of polysulfone is mostly based on adding various functional groups, such as carboxylic, fluorine, and methyl chloride to the aromatic ring, and by sulfonation, nitration, and lithiation [18, 19].

In this work, we focusing the development of polymer membranes capable at high temperature PEMFCs application based on 4-Methylbenzenesulfonic Acid- polysulfones functionalize.

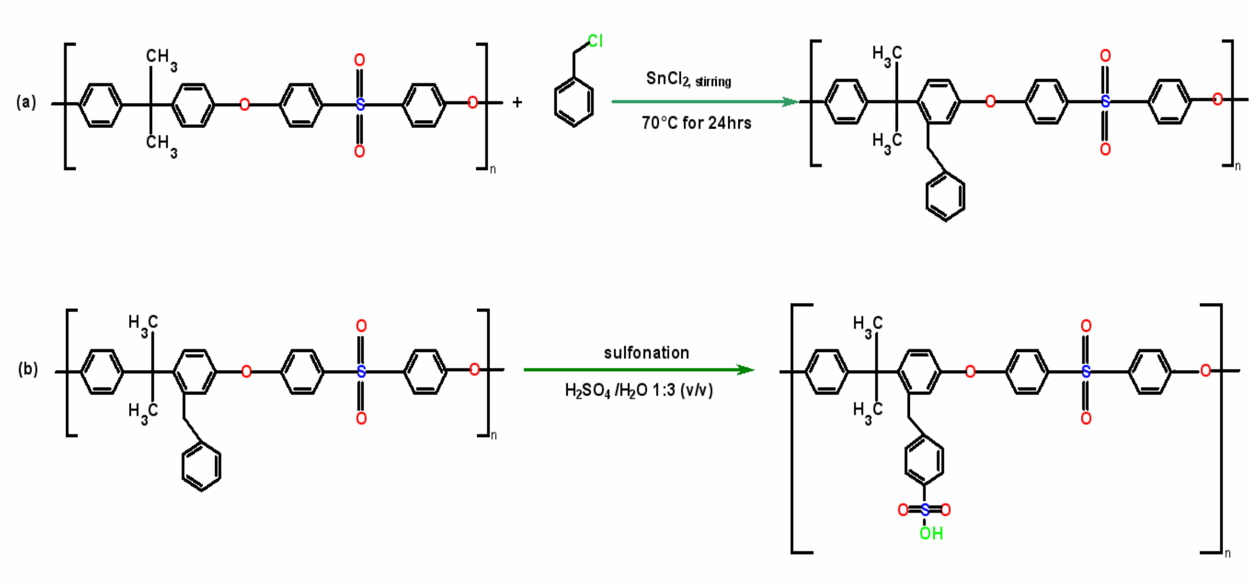
2. EXPERIMENTAL SECTION

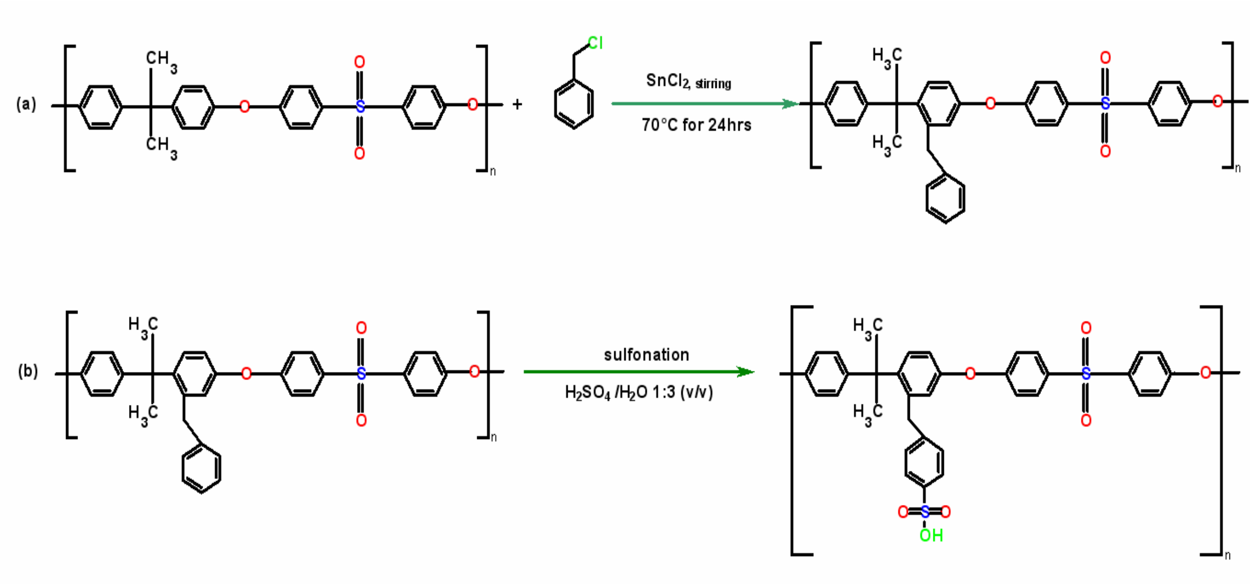
2.1 Materials

Polysulfone (Udel) polymers were purchased from Solvay Advanced Polymers and dried at 100 ºC under vacuum before use. Benzyl chloride and fuming sulfuric acid was purchased from Sinopharm Chemical Reagent Co. Ltd., China and used as received. Stannic tetrachloride ($SnCl_4$) as a catalyst, N, N-dimethyl acetamide (DMAc), Hydrochloric acid and methanol were purchased from commercial source and used in the synthesis. Each reagent were purchased from commercial vendors and used without further purification unless specified.

2.2 Modification of polysulfones (PSF)

The modification of PSF was carried out according to Scheme 1a. In the first step, PSF was functionalized with methylbenzene side chains through the following procedures. In a 250 mL three necked bottle flask equipped with a magnetic stirrer and reflux condenser, 80 mL of dimethyl acetamide (DMAC) was added followed by 2 g of polysulfones (PSF). After complete dissolution, 10g of Benzyl chloride and 0.18g of Tin (IV) chloride were added and stirred constantly at 70 ºC for 24 h, to maintain Friedal-Crafts between benzyl chloride and PSF. The resulting solution was precipitated in ethanol under stirring. The polymer precipitate was filtered and rinsed in dilute hydrochloric acid to remove Tin (IV) chloride. Next washed with ethanol and then DI water and finally dried in vacuum oven to constant weight of methylbenzene -Polysulfone (MB-PSF).





Scheme 1.Chemical modification of polysulfone

2.3 Membrane preparation

1.0 g of Methylbenzene Polysulfone (MB-PSF) copolymer was dissolved in N, N-dimethyl acetamide (DMAc) as solvent to prepare a 10 % (w/v) solution of MB-PSF. and the solution was stirred at room temperature for 30 min. The resulting solution was cast on a pre-cleaned glass substrate and heated in the open air at 80 °C for 24 h and 100 °C for another 24 h to remove the solvent. The freshly prepared membranes were immersed in water for at least 20 h to get rid of any solvent residues and other impurities followed were then dried in vacuum at 50 °C for 24 h. The membrane was ion-exchanged in a 0.5M HCl solution for at least 24 h, and then washed repeatedly in distilled water until constant pH was reached. The thickness of the prepared membranes was between 100 and 120 µm.

2.4 Sulfonation of methyl benzene –PSF

Sulfonation of methyl benzene –polysulfone (MB-PSF) was carried out as shown in scheme 1b. The cast membrane was soaked in the solution of H_2SO_4/H_2O 1:3 (v/v) for 48 h. Then the membrane was thoroughly washed with de-ionized water to maintain constant pH. Finally the resulting sulfonated membrane was dried in vacuum at 60 ^{0}C for 24 h.

2.5 Determination of degree of substitution (DS) of polysulfone

The number of side chains per repeat unit of the PSF is the most important step in preparing Methylbenzene sulfonic acid Polysulfone (MBSA-PSF) copolymer. It was difficult to obtain more than one side chain per repeating unit of the polysulfone due to problems of reactivity connected with steric hindrance and side reactions. It determines the degree of sulfonation, which in turn determines the ionic conductivity and mechanical strength of the membrane fabricated. The degree of substitution occurs via Friedel–Crafts alkylation between benzyl chloride and the phenyl ring of polysulfone. DS was determined on basis of the change in molecular weight of PSF before and after attaching methylbenzene. DS is calculated using the equation,

DS $=[\mathrm{Mm}-441]/91$.

where 441 is the molecular weight of PSF repeat unit subtracting hydrogen atoms on the phenyl ring, which are assumed to be replaced by methylbenzene, and 91 is the molecular weight of methylbenzene group (–CH2-C6H5) and Mm =442 m/m_0, where 442 is the molecular weight of PSF repeat unit, m and m_0 are the mass of MBPSF and PSF, respectively. To avoid loss of mass particular care has been taken during MBPSF synthesis and handling.

2.6 Determination of the degree of sulfonation

Three different methods has been used to determine the degree of sulfonation (DS), which is defined as the percentage of repeating units of 4-Methylbenzenesulfonic polysulfones that has been sulfonated, these methods are;

[1] The amount of sulfur present in the MBSA-PSF by elemental analysis
[2] ^{1}H NMR spectra.

3. MEMBRANE CHARACTERIZATION

Fourier transform infrared spectroscopy (FTIR) study of the membranes was performed using (FT-IR, Bio-Rad FTS 300) with a resolution of 4cm^{-1} from 400 cm^{-1} to 4000 cm^{-1} as a means of investigating the chemical phase of the various structures.

The structural characterization ^{1}H NMR was performed using BRUKER DRX400MHz spectrometer with dueturated dimethylsulfoxide (DMSO-d_6) as the solvent of all modified polysulfones and deuterated chloroform for the unmodified polysulfones.

The water uptake was calculated by weighing the membrane under both hydrated and dry situations. First the membrane is immersed in water for 24 h, and then rapidly drying the surfaces with tissue paper and weighing to get the mass of the wet membrane (Wwet). After that, the membranes were dried in vacuum at 50 ºC for 15 h before determining the mass of the dry membrane (Wdry). The water uptake was then calculated as:

$$\textbf{Water uptake}(\%) = \mathbf{100}\left[\frac{\mathbf{W(wet)}}{\boldsymbol{W}(\mathbf{dry})} - \mathbf{1}\right]$$

The tensile strength of the composite membranes was carried out by using Instron mechanical testing machine (Hounsfield H50KS) at temperature 25 ºC and 80 % humidity. Membrane samples having thicknesses ranging from 80-150 µm were cut into strips of 70 mm long and 15 mm wide. Tensile strength, yield strength, Young's modulus, elongation at break, elongation at yield, and film toughness were all calculated from the tensile data,

The proton conductivity of membranes can be measured by AC impedance spectroscopy. Two platinum electrodes were placed on the same face of membranes that were sandwiched between two PTFE sheets. It is generally easier to determine membrane conductivities by measuring the resistance in the plane of the membrane. This method allows for higher and more easily measurable resistances and a simplified set-up. The distance between the two electrodes was 1.5 cm. Impedance data were collected in the frequency range 10^{-1} – 10^{7} Hz at amplitude of 100 mV. The membrane conductivity (σ, S cm-1) is calculated from the impedance data by using the following equation:

$$\sigma = \frac{\mathrm{S}}{Rtw}$$

Where S is the distance (cm) between the two electrodes, t is the thickness of membrane (cm), w is the width of the membrane and R is the membrane resistance obtained from the AC impedance data. Thermogravimetric Analysis (TGA) was performed using NETZSCH STA 449 F3 Jupiter® thermal analyzer. The TGA heating rate was 10 ºC min^{-1}. over a temperature range of 50–900 ºC under nitrogen atmosphere.

The surface morphology of the formed membrane was examined using scanning electron microscopy (SEM, JEOL JSM-5610LV equipped with Energy Dispersive Spectrum Analyzer) under tapping mode to determine the surface morphology and distribution of particles inside the membrane. Scanning electron microscopy of the cross-sectional direction of the membrane was performed. The sample for cross-sectional SEM images was obtained by fracturing in liquid nitrogen.

4. RESULTS AND DISCUSSION

The mechanical strength and toughness of the membranes is essential for successful membrane-electrode assembly

(MEA) fabrication and for cell lifetime improvements. Membranes undergo a fair amount of stress during MEA fabrication and even more hygrothermal stresses during fuel cell operation. Figure 1 below shows the stress vs. strain curves obtained for the MBSA-PSF membranes, with difference time interval of sulfonation (a) 48h and (b) 72h. Membrane with 72h of sulfonation showed the best mechanical performance, with the highest yield strength and longest elongation before tearing. This is due to high water uptake of this membrane.

Also mechanical properties and membrane conductivity has a considerate effect on the water uptake of PEMs; [27-28] High degree of water absorption is needed in order to ensure high proton conductivity. The behavior of proton conducting ionomers containing water provides much information on how the material will behave under fuel cell conditions. Membranes with small water uptake typically have low proton conductivity, while the mechanical strength is compromised in membranes with too high water sorption and if the water absorption is too high, the dimensional stability will suffer and the membrane may disintegrate due to the swelling pressure.

The result of swelling shows that the water uptake of these composite membrane is increased with the increase of the concentration of HSO_3 group by increase the time of sulfonation of membrane, this is due to higher affinity of the sulfonic acid groups towards hydration. The Water up take experiment shows that the amount of water absorbed by the membrane at 46 ^{o}C is 57 %.

The ^{1}H NMR spectra of PSF, MB-PSF and 4-MBSA-PSF are shown in Figure 2(a), 2(b), and 2(c) respectively, confirmed the successful introduction of the 4-MBSA-PSF side chains onto polysulfones.

1H NMR signals arising from the methyl protons at δ=1.6 ppm and from the aromatic protons at δ= 7. 43–8.3 ppm for all modified and unmodified polysulfones. New peaks are present in the spectrum of MBSA-PSF in figure 2(c) at δ=8.4 ppm, the peaks corresponding to Hydrogen atoms from the sulfonic acid.

FTIR spectroscopy was used to characterize the polymers synthesized. The FTIR spectra of the unmodified and modified polymer are shown in Figure3. Typical FTIR spectra of PSF, MB-PSF and 4-MBSA-PSF are shown in Figure 3(a), (b) and (c) respectively.

Characteristic bands at 2910 cm^{-1} in Figure 3 (b) and (c) were assigned to C-H stretching of methyl group from methylbenzene.These observations indicated the successful grafting of methyl benzene units onto PSF. These peaks are missing in figure 3(a). Characteristic bands at 1024 cm^{-1} Figure 3 (c) were assigned to (S=O) stretching. These observations indicated the successful grafting HSO_3 group onto methyl benzene-PSF., these additional peaks are absents in fig. 3a and 3b.

The linear regression of log (conductivity) vs.1000T^{-1} as shown in Fig. 4, assuming an Arrhenius performance was used to estimate the activation energy for ion-migration (Ea) of 4-MBSA-PSF membrane. The ion transport activation energy (Ea) for the 4-Methylbenzenesulfonic Acid polysulfone functionalizes membrane was calculated using the following equation;

$$\mathbf{Ea = -b \times R}$$

Where b is the slope of the line regression of log (Scm^{-1}) vs. 1000T^{-1} (K^{-1}) plots, and R is the gas constant (8.31JK^{-1} mol^{-1}). The Ea of the 4-Methylbenzenesulfonic Acid polysulfone membranes is 22.04kJ mol−1. These values are higher than the (Ea) of imidazole-1-yl- 4 - methyl benzoate –PSF (10.6 kJmol^{-1}).[31] This shows that HSO_3 ion mobility in these membranes is more sensitive to temperature than proton migration in imidazole-1-yl-4 - methyl benzoate –PSF. The proton conductivity of membranes was well correlated with the temperature. As increasing the temperature, the proton conductivity of membrane was better.

Thermal stability of the membranes is a significant property that indicates the durability under fuel cell operation. The analysis was investigated by thermo gravimetrical analysis (TGA) by heating the membranes at heating rate of 10 °C/min under N_2 and the results are shown in Figure 5(c). The membrane showed a total weight loss of~05.01%, over the temperature range of 110 −220°C. This weight loss is due to removal of the residual water that is bound with the membrane associated with the sulfonic acid groups , attributed to thermal desorption of physisorbed water and traces of residual organic solvents, respectively, from the hydrophilic character of the membrane and the solvents used in the synthesis. Beyond this temperature, the large weight loss occurred around 230 – 390°C where by the material experiences a rapid weight loss due to thermal decomposition of sulfonic acid group. The membrane shows a total weight loss about 20% at this stage. The material further degrades gradually over the temperature range above 500 °C, 4.21% weight losscorresponds to the main polymer chain decomposition.

From these results, it is concluded that, the membranes are thermally stable within the temperature range for PEMFC applications

The morphology of the MBSA-PSF membrane was studied and SEM images are presented in Fig. 6. (a-d). The membrane was sulfonated with different time interval of 12h, 30h, 48h and 72h (a, b, c and d respectively). The surface view of the membrane clearly shows a smooth and homogeneous membrane surface which indicates the infiltration of HSO_3 in polymer back bone is successfully. The homogeneity of the surface of these membranes confirms that the polymer are dispersed well and there is no incompatibility among the materials used .

5. CONCLUSION

We have prepared an anhydrous polymer electrolyte membranes material based on polysulfone ionomers 4-Methylbenzenesulfonic Acid units placed on pendent aromatic side chains by using an effectual two-step grafting procedure. In most cases, it was difficult to obtain more than one side chain per repeating unit of the polysulfone due to the problems of reactivity connected with sterical hindrance and side reactions.

Benzyl chloride was bonded to the side chains of polysulfones (PSF) giving aryl methyl-functionalized polysulfones via Friedal-Crafts reactions .

For controlling of the fabricated membrane properties, the number of side chains per repeat unit of PSF and sulfonation process was achieved by adjusting of the experimental parameters. The sulfonation of MB-PSF was confirmed by NMR and FTIR to determine the degree of sulfonation. Such reaction imparted the membrane water uptake, swelling ratio, Ion Exchange Capacity and conductivity that strongly depended on the degree of sulfonation of methylbenzene polysulfone.

The sulfonic acid group can be immobilized in the proton conducting membrane and can act as proton transporting media under elevated temperature with anhydrous conditions and increase the water uptake, as well as the conductivity. At high temperature the long-range proton transfer is induced by the structural reorganization of incorporated sulfonic acid and the proton conductivity increases with the temperature. The anhydrous proton conductivity of 5.02 10^{-4} s/cm at 150 °C related with the activation energy of 22.04 kJ mol^{-1} for proton transport was observed.

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LIST OF FIGGURES

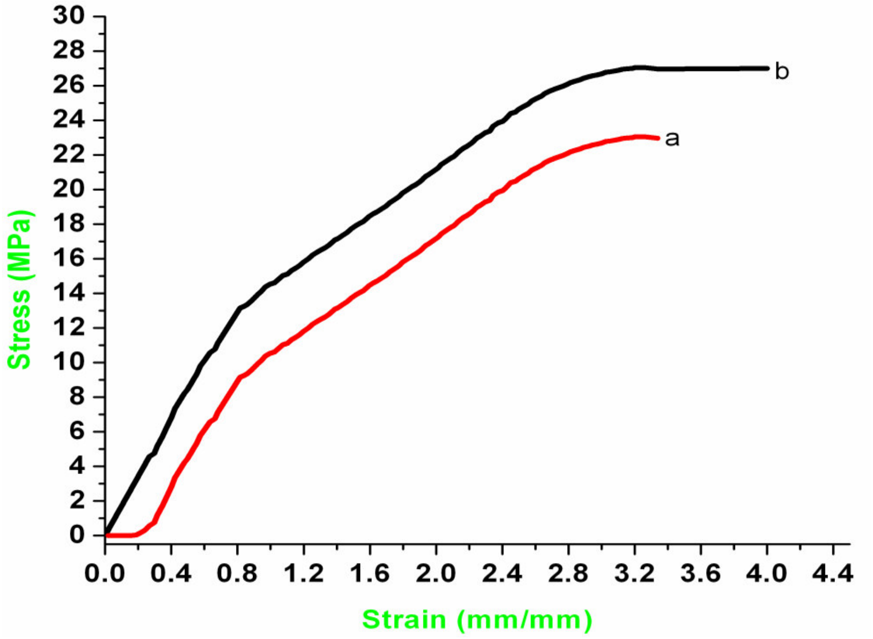
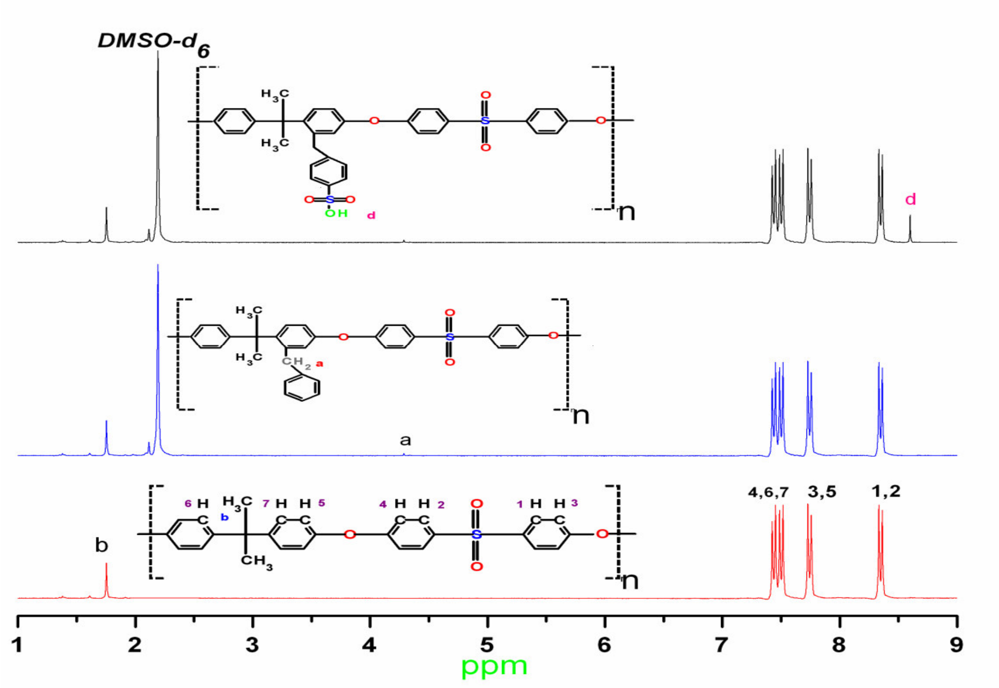


Figure 3



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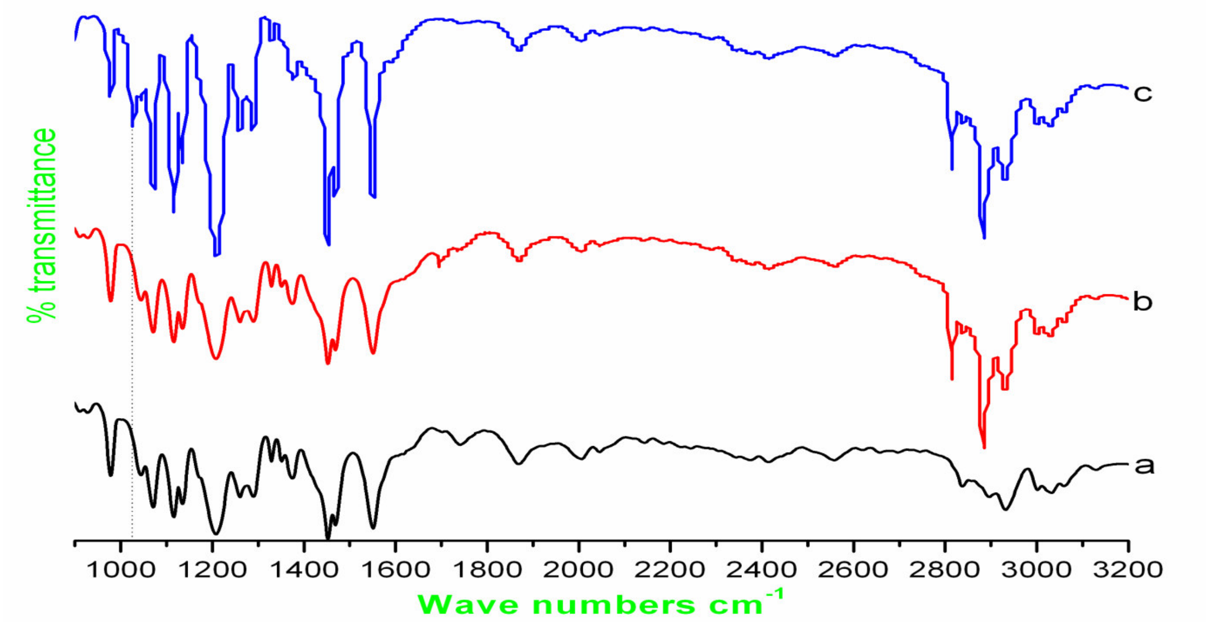
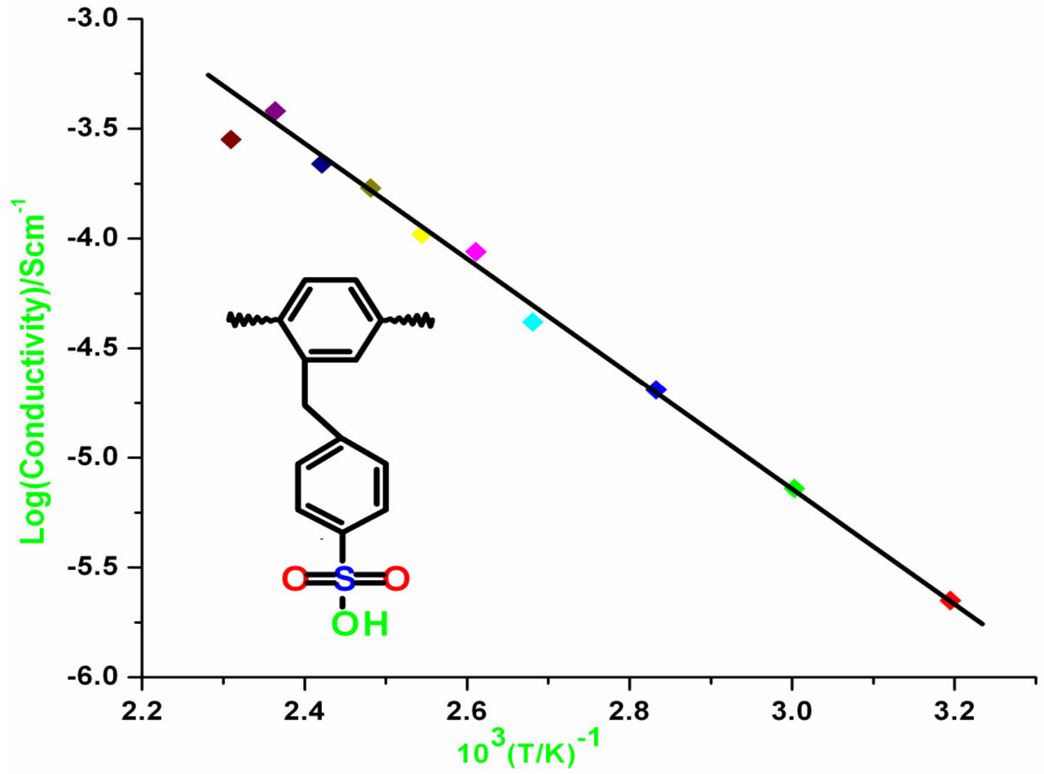


Figure 5



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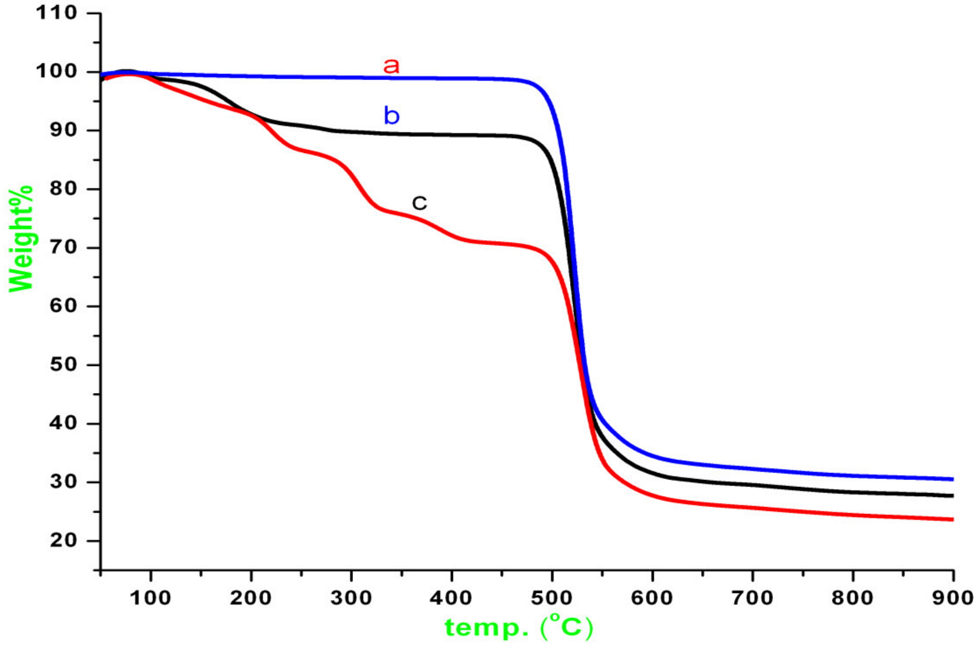

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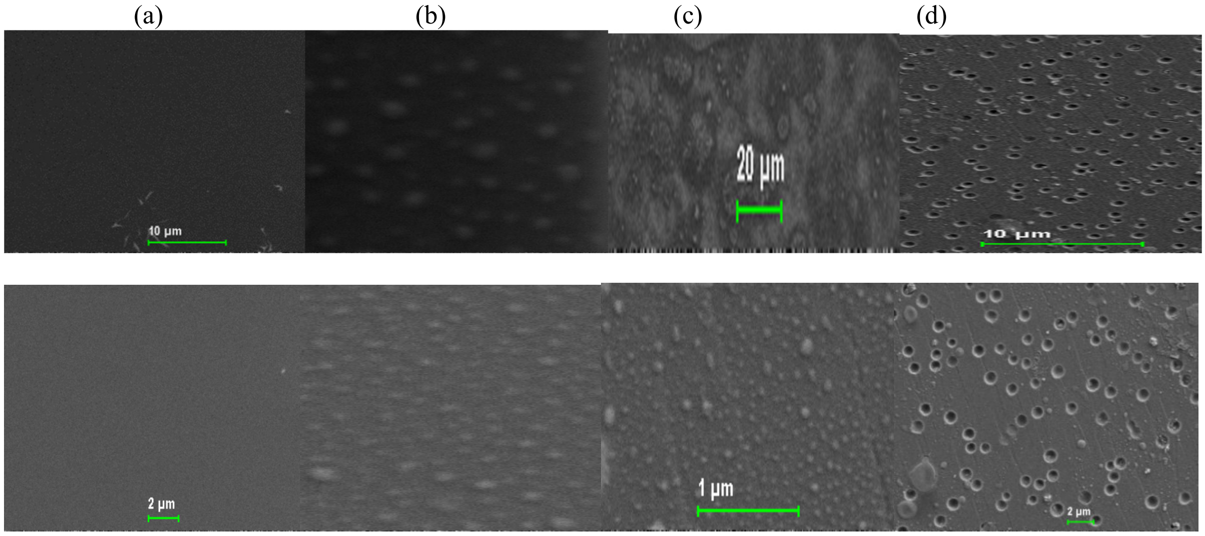

Figure 8

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