Sulphonation of Polystyrene-Butadiene Rubber with Chlorosulphonic Acid for Proton Exchange Membrane: Kinetic Study

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ABSTRACT: Proton exchange membrane for fuel cell application was synthesized from a hydrophobic polystyrene-butadiene rubber (PSBR) via sulphonation at different temperatures (22, 35, 55, 65, and 75°C) and varying time with chlorosulphonic acid. Infra-red spectroscopy (IR) and proton nuclear magnetic resonance (^{1}H-NMR) were used to confirm the occurrence of sulphonation. Sulphonation occurred only on the phenyl ring with a maximum degree of sulphonation of 70.96 mole percent. Consequently, 10^{-3}–10^{-2} S/cm proton conductivity was achieved. Two models for the reaction kinetics were investigated: first-order reversible and first-order irreversible, respectively. However, the reaction kinetic was found to obey the first-order reversible model. The activation energy (E_a) of the reaction was calculated to be 41.56 kJ/mol of PSBR repeat unit, which is an indication that the reaction is nonspontaneous. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3473–3479, 2010

Key words: polystyrene-butadiene rubber; degree of sulphonation; proton conductivity; kinetic and activation energy

INTRODUCTION

Energy crises have remained a huge challenge in recent time due to the inability to balance the energy supply with increasing human population and industries. This therefore, calls for renewal energy devices since fossil fuels are nonrenewable and are limited. Over use of fossil fuels with depleting fossil fuel reserves have thus resulted into energy crises in the world today. This has thus necessitated researchers to engage on alternative sources of energy that will be efficient. Fuel cells are recognized as viable alternative due to their high energy efficiency and environmental friendly nature.[1–3] Proton exchange membrane fuel cell (PEMFC) is one of the most promising alternative source due to its high power density, relatively quick start up, portability and environmental friendliness.[4,5] The heart of PEMFC is the polymer electrolyte membrane (PEM) which functions as an ionic conductor between the two electrodes, a binder for the electrocatalyst and a barrier for passage of electron and gas cross leakage between electrodes[2,6,7]

The current state-of-the art membrane is the perfluoronated ionomer Nafion® with high proton conductivity ($\sigma \geq 10^{-2}$ S cm^{-1}) and excellent durability under the fuel cell operating conditions (a life time of 50,000 hrs).[8] However, it has some major drawbacks: very high cost; loss of conductivity at high temperature (>80°C); and high methanol crossover. These negative characteristics result in dramatic loss of proton conductivity due to dehydration of the membrane and thus hinder their further application.[4,9,10] In fact in USA, Nafion® costs U.S$ 700 m^{-2} corresponding to U.S$ 135 kW^{-1} at 0.65 V, which is known to be closer to the operating potential of a stationary power plant.[8] The cost is perceived to be too high, particularly for widespread application of PEMFCs in passenger cars.[8] As a result of the disadvantages associated with this membrane, a widespread effort is conducted to develop an alternative economical polymer that can be used as PEM especially under high temperature use.[7] Homopolymers, random copolymers and block, as well as graft copolymers containing aromatic rings or double bonds, have been recognized as suitable materials for PEMs in fuel cell application.[11] The use of polystyrene-butadiene rubber (PSBR) for PEM synthesis in this study was carefully chosen because it is cost effective and versatile characteristics which enable it to be used in different applications especially in

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automobile tires and accessories. The thermal analysis of the PEM synthesized from PSBR of earlier report[12] using differential calorimetric analysis (DSC) and thermographic analysis (TGA) showed that the synthesized membrane is thermally stable for fuel cell application, as it exhibited a glass transition temperature (T_g) of above 200°C. The water uptake of the membrane which is very vital for ionic transport across the membrane was found to be moderate. This article therefore presents the ionic (proton) conductivity and much emphasis on the kinetic study of the sulphonation of PSBR in chlorosulphonic acid. At present, there is no work on the kinetic study of PSBR, especially using chlorosulphonic acid as the source of the electrophile (SO_3H) in which the electron rich aromatic ring attacks. This will help to reveal to some degree the mechanism of the process of PSBR sulphonation in chlorosulphonic medium and thus the process control.

EXPERIMENTAL

Ten gram of PSBR (having styrene/butadiene ratio of 25 : 75 (Part by weight)) (Karbochem, South Africa) was dissolved in 250 mL of 1, 2 dichloroethane (Analytical grade ≥98%: Merck South Africa). This was followed by the gradual addition of 1.6 *M* of chlorosulphonic acid (Analytical grade ≥98%: Merck South Africa) in 1,2 dichloroethane solution (Analytical grade ≥98%: Merck South Africa) that was initially chilled in an ice bath to eliminate heat released into a vigorously stirred solution of PSBR in a four-neck round bottom flask reactor under argon atmosphere at different temperatures. The sulphonation reaction was allowed to proceed for varying time (2–48 hrs) and temperature (22–75°C). The reaction was terminated by adding ethanol (Assay ≥98%: Merck South Africa) and the precipitated sulphonated polymer was recovered, washed with deionised water until the pH of wash reached values of 6–7. The product was then dried in an oven at 80°C for 2–3 hours. The Sulphonated Polystyrene-butadiene Rubber (SPSBR) was characterized using FTIR (Vector 0-model Spectrometer) and ^{1}H-NMR (Brucker 400 Spectrometer).[12] Degree of Sulphonation (DS) of SPSBR was determined by measuring the percentage of sulphur present in the dry sample of SPSBR using elemental analysis method. The degree of sulphonation was obtained from the IEC calculated using eq. (1)[13]:

$$\mathrm{IEC} = \frac{1000\mathrm{S_c}}{MW_s} \tag{1}$$

where: S_c = the sulphur content (percentage weight rate), MW_s = the molecular weight of sulphur and 1000 is the multiplying factor to obtain IEC value in mmol/g. Value of IEC calculated from eq. (1) was then used to obtain the DS of SPSBR using the relationship shown in eq. (2)[14]:

$$\mathrm{DS} = \frac{\mathrm{IEC} \times \mathrm{M_{PSBR}}}{1 - (\mathrm{IEC} \times \mathrm{MW}_{\mathrm{SO_3}H})} \tag{2}$$

where: IEC is the ion exchange capacity (mol/g), M_{PSBR} is the molecular weight of the polystyrene-butadiene (g/mol) and $\mathrm{MW_{SO_3H}}$ is the molecular weight of SO_3H (g/mol).

Membrane preparation

A known weight of SPSBR (10 g) was dissolved in 200 mL of 1,2 dichloroethane at elevated temperature forming a casting solution of about 15–30% wt, and then cast onto a clean polymer paper support using a laboratory doctor blade casting machine. But before the casting, the doctor blade was adjusted to a known thickness with the aid of feeler gauges of the appropriate thickness. The casting was performed by dragging the casting head of the blade along the length of the substrate, and cured for 4 days by exposing it to air and thereafter peeled off from the support. The cast membrane was dried further in an oven at 75°C for 4–5 hours and was finally vacuum dried for about 4 h in a bid to removing residual solvent. The prepared membrane was not crosslinked.

Measurement of proton conductivity

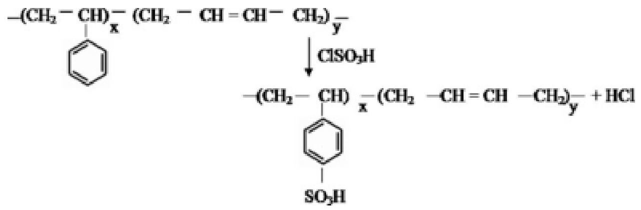
The proton conductivity of the membrane was measured using alternating current impedance over a frequency range of 1–10^6 Hz in 1 *M* H_2SO_4 as an electrolyte. The value at the intersection of the high frequency impedance curve with the real axis was taken as the membrane resistance and the proton conductivity was thus calculated using eq. (3):

$$\sigma = \frac{T}{RS} \tag{3}$$

where: σ = the proton conductivity (S/cm), T (cm), S (cm^2) and R = the thickness, surface area of the membrane samples and the resistance determined from the impedance plane, respectively.

Quantification of Hcl in aqueous solution of the copolymer

The aromatic sulphonation of PSBR with chlorosulphonic acid is expected to produce HCl acid as a by-product according to the balance chemical equation shown in Scheme 1.



Scheme 1 Sulphonation reaction of PSBR with chlorosulphonic acid.

The need to quantify the concentration of HCl produced is important as to judge its effect on the rate of PSBR sulphonation. A scenario of two acids ($ClSO_3H$ and HCl) in the aqueous solution would be a problem in determining the actual concentration of HCl. As a result, acid-salt precipitation reaction was immediately carried out to yield a precipitating product of $BaSO_3$ from the $ClSO_3H$ acid. Here, after sulphonation reaction was terminated, solution mixture was filtered and the precipitated PSBR was recovered. A required volume of $1.8 \times 10^{-3}M$ $BaCl_2$ (in excess of acid) solution was added into 150 cm^3 of the filtered solution mixture in a 500 mL beaker, containing 40 mL of 0.2 M sodium acetate buffer (pH 6.7). This was accompanied with stirring for about two minutes. A clean, dry cover slide was placed over it and properly sealed with a paraffin material. The experiment was left to stand for about 5 h to allow white precipitate of $BaSO_3$ to settle. The solution mixture was again filtered to obtain a clear supernatant. A total solution volume of 100 cm^3 was thereafter used in the acid–base reaction. This involves placing (100 cm^3) an aqueous solution of the precipitated filtered copolymer in a 500 mL beaker and titrated against 25 mL NaOH of a predetermined concentration (3.9×10^{-5} mol L^{-1}) using methyl red as an indicator. The change in color from red to yellow confirmed acid–base reaction. The end point of each neutralization reaction was determined from different volumes of the base consumed. Each experiment was repeated at least twice, starting with blank titration.

RESULTS AND DISCUSSION

The process of sulphonation on polymers is very vital in converting polymers which are hydrophobic and insulator in nature to be hydrophilic and proton conductive. The sulphonation of inexpensive and commercially available PSBR in South Africa was carried out in chlorosulphonic acid as sulphonating agent. The analysis of the synthesized membrane was found to be thermally stable (>120°C) with moderate water uptake suitable for fuel cell application. Recalling, glass transition temperature (T_g) is the temperature at which polymer becomes brittle on cooling and soft on heating. The DSC analysis of the thermal stability of the synthesized membrane showed a T_g of about 198°C. The analysis showed that the styrene group where the SO_3H attached after sulphonation becomes weak only at higher temperature (>198°C) and consequently resulted in the degradation of the group from the main chain. Thermo gravimetric analysis (TGA) is used to determine change in weight relative to temperature. Three losses in weight, in three ranges of temperature, were observed in the TGA curves for the synthesized membrane. The first weight loss was observed in the range of 23–219°C, which was attributed to the presence of moisture and some other additives used in the production of PSBR. The second loss in weight was observed around 307–412°C depending on the degree of sulphonation and was mainly associated with the loss of styrene-sulphonic group. The final loss in weight was the third transition in the range of 412–475°C which represented the decomposition of the main chain. The attached SO_3H group on the aromatic group was, in a way, reinforced the strength of the synthesized membrane.[12] On water uptake, the degree of sulphonation (resulting from the ion exchange capacity of the membrane) and water uptake contributed to the proton transport through the dense synthesized membrane. At a degree of sulphonation of 37.23% an $\sim$ 60% of water uptake per gram of dry membrane was realized as against <20% with a membrane of 5.85% degree of sulphonation. All the membranes investigated showed an initial rapid uptake of water which decreased with time until saturation was reached after 4 days. However, the percentage degree of swelling of the membrane was in the range of 2–18% depending on the membrane thickness and temperature.[12] This trend in the results is in agreement with those obtained by Sangeetha (2005), while investigating the conductivity and solvent uptake of polystyrene triblock polymer.[17] In this study, the IR, ^{1}H-NMR, the proton conductivity and the kinetic study of the synthesized membrane are thus discussed.

FTIR and ^{1}H-NMR studies

Figure 1 presents the IR of the PSBR and SPSBR where the weak broad band appearing in SPSBR spectra at 3573 cm^{-1} represents the O—H vibration from sulphonic acid group upon sulphonation which increases slightly with increase in DS. The peak identified on the spectra at 1346 cm^{-1} is as a result of the asymmetric stretching of S═O group. The symmetric vibration from this bond on the rubber causes the characteristic splint between 1309 and 1235 cm^{-1}, with the effect of the asymmetric stretching of the introduced S═O group causing a reduction in the intensity of peaks around the region

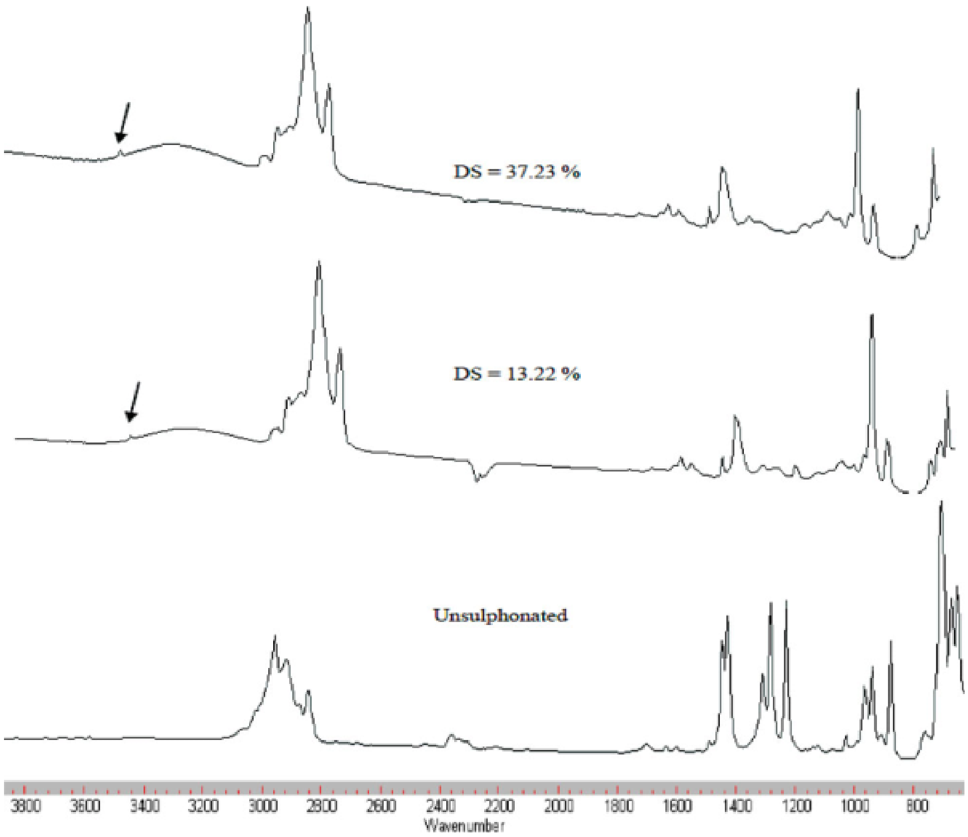


Figure 1 FTIR of SPSBR and PSBR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(1400–1000 cm^{-1}) for the sulphonated. The peaks identified at 2846, 2919, and 3027 cm^{-1} for both the PSBR and SPSBR are the bands for C—H, C—C, and C=C, respectively. While the aromatic C=C and C—C can be identified at 1649 and 1494 cm^{-1}, respectively.[15,16] The effect of sulphonation tends to reduce the sharp band (unsulphonated) at 1450 cm^{-1} to a broad peak after sulphonation. This can be associated with the interaction of the introduced sulphonic group on the polymer matrix. The ^{1}H-NMR spectra presented in Figure 2 shows only a band appearing between 3 and 4 ppm which indicates the presence of sulphonic acid linkage on the aromatic benzene ring. This shows that the sulphonation of PSBR is an electrophilic substitution reaction as shown in Scheme 1 where substitution involves the aromatic ring of each repeat unit of the PSBR. The shift in peaks at 1.9 and 5.5 ppm are due to the presence of the electrophile introduced into the PSBR ring, being the effect of sulphonation occurrence.

Proton conductivity of the synthesized membrane

A proper hydrated membrane is seen as a pre-requisite to a desirable level of conductivity especially for a membrane synthesized from styrene copolymers that rely on sulphonic acid to conduct proton.[17] Result in Table I shows that the proton conductivity of the synthesized membrane is in the order of 10^{-3}–10^{-2} S/cm which increases as degree of sulphonation and temperature increase. This is the expected proton conductivity range for fuel cell application.[17] The result shows that the membrane will conduct better when it is fully hydrated than when it is partially hydrated. For instance, the proton conductivity of the partially hydrated membrane (10 hours hydration period) and fully hydrated (>24 hrs) at room temperature and degree of sulphonation of 37.23% are 5.0×10^{-3} and 6.3×10^{-3} S/cm, respectively. The results also show that as degree of sulphonation increases, the difference between the proton conductivities of the partially and fully hydrated membranes decreases due to ionic strength, as high degree of sulphonation equals high ion exchange capacity. This will inferably lead to high possibility of the membrane to be fully hydrated as the degree of sulphonation increases and therefore better ionic mobility

Kinetic study of PSBR sulphonation

Sulphonation is an electrophilic substitution reaction[18,19] and its application depends on the substituents present on the ring.[19] Aromatic sulphonation is

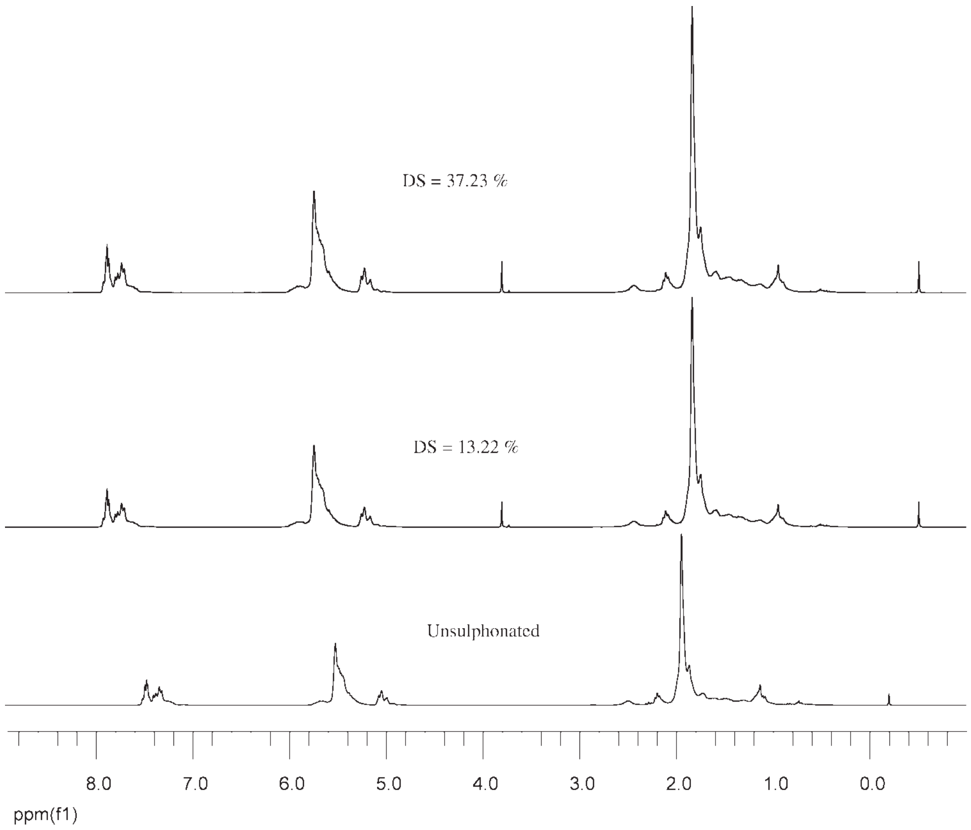


Figure 2 ^{1}H-NMR of SPSBR and PSBR.

widely used in chemical synthesis and fuel refinery.[20] The corresponding arylsulphonic acid is achieved with various aromatic structures upon sulphonation. Thus, property modification of aromatic polymers is possible as a result of the sulphuric group that is strongly acidic[19,21]

The rate of aromatic sulphonation is considered to be first-order with respect to the substrate concentration which is the phenyl ring.[21–23] In this study, the repeat unit is regarded as a small aromatic molecule for the kinetic treatment. From Scheme 1, only the vacant para-position is the farthest from the electron attracting effect of the carbonyl group compared to the meta and ortho positions. It will therefore possess higher electron density and thus be a point for aromatic substitution. It can be assumed that only one $\mathrm{-SO_3H}$ group can attached to each of the repeat units. Taking this into consideration, the assumptions below can be made in this study.

1. Only the phenyl ring of each repeat unit of PSBR is sulphonated at a time.
2. The electrophilic substitution reaction involves only the vacant para proton on the aromatic ring.
3. Degree of sulphonation equals reaction conversion (X).
4. Probable volume change in the course of reaction is ignored.
5. Reaction may not be explicitly irreversible considering the effect of HCl produced. As a result two reaction mechanisms are proposed:

For a first-order irreversible process of PSBR sulphonation with respect to PSBR repeat unit concentration (C) in a batch reactor system

$$-\frac{dC}{dt} = k_1 C \tag{4}$$

TABLE I
Proton Conductivity of the Synthesized Membranes

Degree of sulphonation (%)	Partially hydrated (20°C)	Fully hydrated (20°C)	Fully hydrated (50°C)
4.75	0.0030	0.0036	0.0042
5.85	0.0032	0.0037	0.0045
8.23	0.0034	0.0037	0.0052
11.92	0.0036	0.0038	0.0057
12.34	0.0037	0.0039	0.0062
28.07	0.0046	0.0048	0.0082
34.18	0.0047	0.0055	0.0093
37.23	0.0050	0.0063	0.0129
46.22	0.0067	0.0072	0.0273
49.04	0.0077	0.0081	0.0365
54.73	0.0079	0.0096	0.0483
68.54	0.0086	0.0120	0.0615
70.96	0.0147	0.0235	0.0868

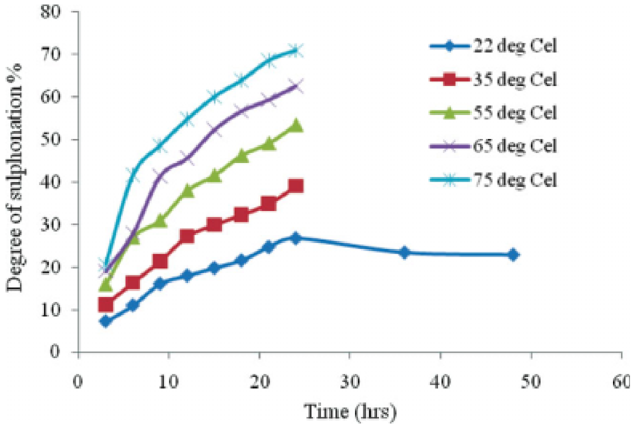


Figure 3 Kinetic of PSBR sulphonation at different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where t and k_1 represent the reaction time and the rate constant, respectively. Equation (4) is integrated to obtain:

$$-\ln\frac{c}{c_0} = k_1 t \tag{5}$$

Equation (6) describes the substrate concentration as

$$\frac{c_0 - c}{c_0} = X \tag{6}$$

where X is equal to reaction conversion

Substituting eq. (6) into eq. (5) gives:

$$-\ln(1 - X) = k_1 t \tag{7}$$

If the reaction is first-order and irreversible then a plot of $-\ln(1 - X)$ against t should give a straight line unless otherwise HCl produced has effect on the reaction, causing reversibility. Figure 3 shows the kinetic of PSBR sulphonation at different temperatures.

The above figure shows that the degree of sulphonation of PSBR increases with time, however, an optimum time of 24 hrs of sulphonation is required to achieve an optimum degree of sulphonation as the experiment carried out at 22°C shows reduction in the degree of sulphonation above 24 hrs of sulphonation. This shows that prolong time of sulphonation (>24 hrs) is unfavorable to PSBR which leads to possible breakdown of the polymer chain with reduction of available site of attachment (for $-SO_3H$ group) and hence, a reduction in the degree of sulphonation.[24] The result also shows that increase in temperature significantly increases the degree of sulphonation (over twofolds) of the resulting polymer. This indicates that elevating the temperature of the sulphonation process the thermal energy of the system is raised which therefore facilitates the rate of electrophilic substitution on the aromatic ring. Figure 4 is the first-order irreversible treatment of the sulphonation of PSBR.

It can be seen from the figure that data only simulate a linear function at the early stage of the reaction and the rate subsequently becomes slow, with the difference between the data and the straight line gradually increasing with time. This suggests that the HCl produced has an inhibiting tendency on the reaction rate and thus the probability of casing reversibility of the process. Hence the first-order reversible process is hereby considered.

For a first-order reversible process of PSBR sulphonation with respect to PSBR repeat unit concentration (C) in a batch reactor system

$$-\frac{dC}{dt} = \frac{k_2 C}{k_3(C_0 - C)} \tag{8}$$

where k_2 and k_3 are the rate constants for both the forward and backward reactions, respectively.

Integrating eq. (8) from C_0 to C gives:

$$-\int_{c_0}^{c} \frac{C_0 - C}{C} dc = \frac{k_2}{k_3} \int_0^t dt \tag{9}$$

$$-C_0 ln\frac{C}{C_0} + C - C_0 = \frac{k_2}{k_3} t \tag{10}$$

But substrate concentration is given in eq. (6) and substituting into 10 gives:

$$-C_0 ln\frac{c_0(1 - X)}{C_0} + C_0 - C_0X - C_0 = \frac{k_2}{k_3} t \tag{11}$$

But $\frac{k_2}{k_3} = K_c = K$(equilibrium constant)

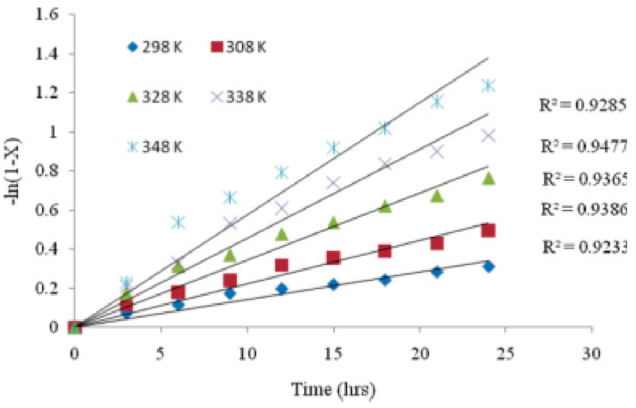


Figure 4 Kinetic treatment of PSBR in chlorosulphonic acid: the first-order irreversible rate treatment with respect to the substrate concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Then equation becomes:

$$C_0\{-X-\ln(1-X)=Kt \tag{12}$$

A plot of $C_0\{-X - \ln(1 - X)$ against t (time) gives a straight line as shown in Figure 5. The plot of Figure 5 fits a straight line for all the experiments considered. Each of the least square fits of the plot intersect (0,0), indicating that the sulphonation of PSBR in chlorosulphonic acid is a first-order reversible process. Table II shows the concentration of HCl produced alongside the sulphonation of PSBR. The result shows that the concentration of HCl produced increases gradually with time of sulphonation and temperature, having a reversible effect on the sulphonation of PSBR in chlorosulphonic acid.

The activation energy (E_a) of the process is thus obtained from the logarithm of equilibrium constant versus the reciprocal temperatures. An E_a of the reaction is calculated to be 41.56 kJ/mol of PSBR repeat unit, which is an indication that the reaction is nonspontaneous. This is the reason why increase in temperature favors the degree of sulphonation of the resulting polymer. The high value of E_a obtained is expected because of the high molecular weight of PSBR, being a copolymer of both plastic and rubber blend characteristic.

CONCLUSION

The sulphonation kinetic of PSBR for the synthesis of a proton exchange membrane for fuel cell application has been studied in chlorosulphonic acid and result showed that the sulphonation of PSBR is a firs-order reversible process due to the effect of HCl produced alongside the sulphonation process. The process was found to exhibit expected high activation energy.

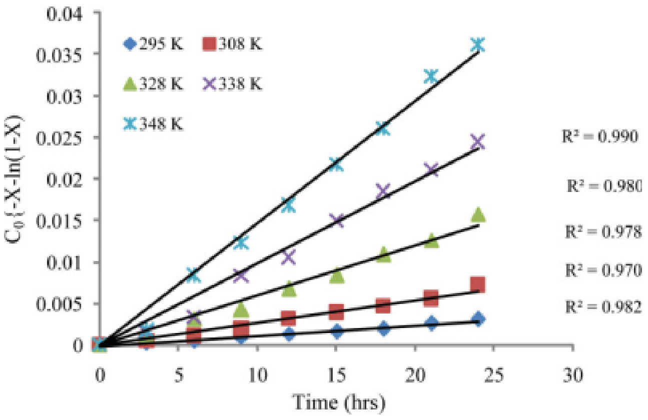


Figure 5 First-order reversible treatment of PSBR with chlorosulphonic acid with respect to the substrate concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Amount of HCl Produced Alongside Sulphonation of PSBR

	HCl Concentration Produced (mol L^{-1})		
Temperature (K)	3 hrs	12 hrs	24 hrs
295	2.68×10^{-5}	2.83×10^{-5}	2.9×10^{-5}
308	2.73×10^{-5}	2.89×10^{-5}	3.12×10^{-5}
328	2.8×10^{-5}	2.97×10^{-5}	3.19×10^{-5}
338	2.88×10^{-5}	3.02×10^{-5}	3.25×10^{-5}
348	2.97×10^{-5}	3.12×10^{-5}	3.29×10^{-5}

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