1.0. Introduction

The increasing concern about the environmental pollution produced by the conventional fuels during the generation of electricity and the propulsion of several types of vehicles forces scientists to think about alternative source of energy. Fuel cell is one such source of energy. The discovery of the fuel cell as an energy conversion system has started long back since around middle of 19th century. The main contribution in this technology was from Sir William Grove, but the principle of fuel cell was developed by Christian Friedrich Schönbein1, a Professor at the University of Basle who was having regular contact with professor Grove during the development of fuel cell technology. In the starting, conventional energy conversion was used as prototype and at a small scale, but later large scale power plants have been constructed. In the case of fuel cells also, it would become important that it will give power of all types and would fulfil the demanding need of the modern human life.

1.1. Fuel cell basics

Fuel cell is composed of various components and is a fabricated system, which converts fuel energy in to electricity for use. A fuel cell does not undergo a material change or run down2. On the other hand, it does not need recharging like batteries and other power storage devices and operates as long as fuel is last. The concept behind hydrogen/oxygen fuel cell was first introduced by Sir William Grove in 1893. Though, fuel cells did not gain much attention until in 1960s when it was first employed in Gemini space programme by NASA, USA. On operation, fuel cell generates electric power in direct current (DC) and produce water as a by-product and heat from fuel and oxygen. As far as fuel is concerned, it is hydrogen or methanol or other hydrogen donor fuels. As it generates water as a by-product and produces heat
as a side reaction, fuel cell is an eco-friendly device. But, conventional conversion of fuel energy into electric energy is carried out by some heat engine (steam or internal combustion). The maximum theoretical value of heat engine is 40-50% only, but on the other hand, fuel cell is not a heat engine, it converts energy isothermally. Fuel cell is not anyhow subjected to Carnot’s cycle theory and almost all the fuel energy may be converted into electric energy. Moreover, fuel pumps and if necessary, electrolyte pumps are the only mechanical parts that can move in this device. These ensure silent operation, high reliability of the device with almost no maintenance. As far as main components are concerned, it is composed of two electrodes and a separator or the electrolyte which prevent short-circuit of the cell as well as allow the flow of fuel ions but prevents the chemical species of the fuel to transfer in other side.

1.2. Types of fuel cells

Fuel cells are of many types according to the fuels and electrolytes used, the major types of the fuel cells are shown in Table 1.1.

<table>
<thead>
<tr>
<th>Type of Fuel Cell</th>
<th>Electrolyte</th>
<th>Operating Temperature (°C)</th>
<th>Efficiency (%)</th>
<th>Electric Power</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline (AFC)</td>
<td>Potassium Hydroxide</td>
<td>60-90</td>
<td>45-60</td>
<td>Up to 20 kW</td>
<td>Submarine, spacecraft</td>
</tr>
<tr>
<td>Molten Carbonate</td>
<td>Immobilized Liquid Molten Carbonate</td>
<td>650</td>
<td>45-60</td>
<td>&gt; 1 MW</td>
<td>Power stations</td>
</tr>
<tr>
<td>(MCFC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>Ceramic</td>
<td>1000</td>
<td>50-65</td>
<td>&gt;200 kW</td>
<td>Power stations</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>Immobilized Liquid Phosphoric Acid</td>
<td>200</td>
<td>35-40</td>
<td>&gt;50kW</td>
<td>Power stations</td>
</tr>
<tr>
<td>Proton Exchange Membrane (PEMFC)</td>
<td>Ion Exchange Membrane</td>
<td>60-130</td>
<td>40-60</td>
<td>Up to 250kW</td>
<td>Vehicles, stationary</td>
</tr>
<tr>
<td>Direct Methanol (DMFC)</td>
<td>Ion Exchange Membrane</td>
<td>60-130</td>
<td>40</td>
<td>&lt;10kw</td>
<td>Portable Applications</td>
</tr>
</tbody>
</table>

Table 1.1. Types of fuel cells
1.3. Polymer electrolyte membrane fuel cells (PEMFCs)

Polymer electrolyte membrane or solid electrolyte membrane fuel cell is the most capable and encouraging candidate among the various types of the fuel cell systems in terms of its mode of applications and working conditions. PEMFCs, generally, operate at low temperature range (30-150°C) and produce a specific electric power and their power density is higher than any other types of fuel cell available. The operation of the hydrogen/oxygen PEMFCs is relatively easy and straightforward and membrane electrode assembly (MEA) or catalyst coated membrane is the core of this technology. MEA has two electrodes (anode and cathode) separated by the ion exchange polymer membrane. When hydrogen fuel is fed in the anode side and air is fed at the cathode side, and then following two half-cell reactions take place.

**Anode half – cell reaction:** \( H_2 \rightarrow 2H^+ + 2e^- \)  \hspace{1cm} (Eq. 1.1)

**Cathode half – cell reaction:** \( \frac{1}{2}O_2 + 2H^+ \rightarrow H_2O \) \hspace{1cm} (Eq. 1.2)

Hydrogen is oxidized into hydrogen positive ion (H\(^+\)) and electrons in the presence of a catalyst. The resulted H\(^+\) ions are transported across the polymer electrolyte membrane in an aqueous environment to the cathode. Here, the protons move through the membrane by proton hopping mechanism. The electrons move from anode through outer circuit to cathode and useful electrical energy is produced. At the cathode, oxygen is reduced and combined with hydrogen ions and electrons. Overall, one mole of water is produced by one mole of hydrogen and half mole of oxygen.

**Overall reaction:** \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \) \hspace{1cm} (Eq.1.3)
"Polymer Electrolyte Membranes for Fuel Cell Applications"

Figure 1.1. Schematic diagram of a polymer electrolyte membrane fuel cell.

The PEMFC is schematically shown in Figure 1.1. PEMFCs use polymeric ionomers in the form of a thin membrane, as an electrolyte, which is a bad proton conductor in the dry state, but, highly conductive in the presence of certain amount of moisture. Hence, the hydration of the electrolyte membrane is the core of PEMFC performance. The absorption of water by sulfonated polymers has a considerable effect on the proton conductivity and mechanical strength of the membrane. Polymer membranes which have low water uptake (WU) capacity, generally have low proton conductivity, but physical strength of the membranes have to compromised in membrane where water uptake or water sorption is high. The absorbed water percentage in polymer electrolyte is generally represented by WU capacity and the
number of molecules of water per one sulfonic acid group, -SO$_3$H. The water absorption percentage or WU capacity of the membrane can be estimated by weighing the membrane under hydrated and dry states and the water uptake ‘S’ can be calculated by using the following equation.

\[
S \, (\%) = W_s - \frac{W_d}{W_d} \times 100
\]  

*(Eq. 1.4)*

Where \( W_s \) and \( W_d \) are the weights of the membrane in swollen and in dry states respectively.

The ion exchange capacity (IEC) of polymer membrane is defined as the number of fixed moles of ionic groups such as sulfonic acid groups per gram of the polymer. The IEC can be calculated by a well-known acid-base volumetric titration method. IEC can be determined by the following equation.

\[
IEC \left( \text{mequiv/g} \right) = X \times \frac{N_{NaOH}}{\text{weight (polymer)}}
\]  

*(Eq. 1.5)*

Where X is the amount of NaOH used and \( N_{NaOH} \) is the normality of NaOH solution.

In polymer electrolyte membrane fuel cell systems, conductivity of polyelectrolyte membrane is very important and it plays a crucial role. High degree of proton conductivity gives the advantage of delivering higher power density. The proton conductivity of electrolyte membrane in hydrated state generally increases considerably with the increase in temperature and water content. Hence, it is very important to describe the exact desired conditions of the proton conductivity experiment in PEMFCs.

The proton conductivity of fuel cell membrane can be measured by impedance analyser. Under real fuel cell operation, the protons released passed through the plane
of the membrane, but, this experiment is difficult to perform, because interfacial resistance in the measurement of proton conductivity. To overcome this problem, an easy approach was developed by Los Alamos National Laboratories to determine proton conductivity by in-plane\textsuperscript{7} resistance\textsuperscript{8}. In this technique, more measurable resistance and simple experimental set-up is needed to determine proton conductivity, '\( \sigma \)' which is calculated by impedance resistance data using the following equation.

\[
\sigma \left( \frac{S}{cm} \right) = \frac{1}{\Omega} \times \frac{d}{A}
\]

\((Eq. 1.6)\)

Where, \(d\) is the distance between electrodes, \(A\) and \(\Omega\) are the area and resistance of the membrane respectively.

The properties of PEMs such as thermal stability, electro-osmotic drag and fuel crossover are important properties which decide performance of fuel cell. IEC, WU, and proton conductivity are other important properties which decide the performance of PEMFCs. Proton exchange membranes should possess the following characteristics to be a good candidate under true fuel cell conditions:

- Low cost of the membrane
- Good film forming properties
- High conductivity (at low relative humidity)
- Low electron conductivity
- Water retention should be above 100 °C
- Thermal stability, oxidative and hydrolytic stability should be high
- Effective separator for reactants
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• Ability to form good MEAs fabrication

• Mechanically stable at relatively high temperature (80 – 140°C) for long uses for example, 2,000 hours for portable power, 5,000 – 10,000 hours for automobiles, 40,000 hours for stationary applications.

To meet the above requirements, there are many hurdles and challenges in the proton exchange membranes preparation and one of the important factors is to produce low cost material that could fulfil the above requirements to some extent. On the other hand, Nafion®, a perfluorinated and commercially available membrane (DuPont) is costly and shows low proton conductivity at comparatively lower water content as well as low physical mechanical strength at higher temperature and average glass transition temperature. To overcome these shortcomings some alternative materials are being proposed. Some of the alternatives and most promising materials for PEMs are polyimides, poly (arylene ether sulfoines), polybenzimidazoles, poly (ether ketones), etc. The various advantages of these polymers as proton exchange membranes are: low cost than Nafion® and their ability to control of polar groups to increase the water sorption over a wide temperature range.

1.4. Commercial availability of PEMs

Gemini space programme launched by NASA, USA had used polyelectrolyte membrane fuel cell as a power source and cross-linked sulfonated polystyrene was used as a proton conductive membrane. But, the copolymer showed lower oxidative stability under fuel cell conditions. After this, perfluorosulfonic acid containing membrane, Nafion® has been discovered as a perm selective membrane and it was a major success in polymer electrolyte membrane fuel cell technology, as this showed better chemical stability as well as higher conductivity and improved oxidative
stability than sulfonated polystyrene membranes. Due to the improved properties of Nafion®, it was most studied and explained PEM as it has higher conductivity, better mechanical strength, and good chemical inertness as well as it is commercially available⁹. In addition, sulfonic acid group in Nafion® becomes more and more acidic in nature due to the presence of the most electronegative atom, fluorine, which is bonded to the same carbon atom where -SO₃H group is attached. The backbone of Nation® membrane is like Teflon (about 87 % in Nation® 1100) which provides better oxidative stability at both the electrodes and generation of hydrogen peroxide (H₂O₂) amount is generally small. The most successful result obtained by using Nation® as a polyelectrolyte membrane in fuel cells, is its lifetime, which is four times higher than the cross-linked polystyrene membranes. It is reported that the lifetime of Nation® is about 50,000 hours at 80 °C¹⁰. Despite Nafion® has various improved properties over polystyrene membranes, the major drawback of Nafion® is its high cost and this is because of the expensive perfluorination. Nafion® is synthesized in total four steps: (1) first the reaction of tetrafluoroethylene with SO₃ to form cyclic sulfone (2) condensation reaction with Na₂CO₃ followed by the copolymerization of perfluoro vinyl ether sulfonyl fluoride with tetrafluoroethylene to afford an insoluble thermoplastic resin (3) the basic hydrolysis of sulfonyl fluoride extruded film to form a perfluorosulfonic polymer and (4) exchange of sodium counter ion with a proton in a suitable electrolyte. The molecular structure of Nafion® membrane is shown in Figure 1.2.
The chemical composition of the Nafion® membranes could be changed to achieve good properties, like improved membrane chemical structure and proton conductivity by producing composite structure membranes\textsuperscript{11}. Asahi Chemicals and W.L. Gore have successfully reinforced perfluorosulfonic acid membranes with the Teflon fabric. Improved proton conductivity and mechanical strength could be achieved by preparing thin films. Moreover, composite membranes were synthesized by swelling the perfluorinated membrane using ionic liquid to get increased its high thermal stability\textsuperscript{12}. The problem of carbon monoxide (CO) poisoning is also improved.

**1.5. Alternative polymer systems as proton exchange membrane**

Nafion\textsuperscript{®} is a contemporary proton exchange membrane (PEM) system available commercially as ion-selective separator in chloro-alkali electrolyzers\textsuperscript{13}. Nafion’s poly (perfluorosulfonic acid) moiety gives exceptional oxidative and chemical stability which are very important in fuel cell applications. Nafion is the most studied polymer membrane for fuel cells because of its commercial availability. Composite membranes of Nafion have also become important in academic research and in industries. In composite membranes, it is impregnated in inert Teflon like polymer matrix or some inorganic additives to support Nafion matrix to get improved electrochemical and physical properties. Despite, Nafion and some of its derivatives show better and
improved properties as a proton exchange membrane. But these membranes are very expensive in synthetic point of view. In addition, Nafion membrane shows lower proton conductivity at lower water content and poor mechanical strength at higher temperature with moderate glass transition temperatures.

A polymer electrolyte membrane with high proton conductivity at low relative temperature as well as low water content and better membrane stability etc., are the important properties in high-performance PEMFCs. Though Nafion and Nafion-type membranes are promising candidates, they have some serious disadvantages, like high cost, low operating temperature (< 80 °C), and high fuel crossover. To overcome these drawbacks, various research groups have focused to develop some alternative polymer materials other than the perfluorinated polymer materials with low cost of synthesis and better performance under fuel cell operating conditions. These materials include sulfonated poly(phenylene oxide)s, polysulfones, sulfonated poly(ether ether ketone)s, sulfonated poly(benzimidazole)s, phosphoric acid doped polybenzimidazoles, and sulfonated polyimides.

1.6. Poly (arylene ether) as proton exchange membranes

The backbone of the polymer exchange membrane composed of the entirely aromatic systems are considered as more promising ways to achieve better performance materials. These membranes show good processability and available in wide varieties of chemical composition and structures. Especially, poly (arylene ether) materials like poly (arylene ether ether ketone) (PEEK), poly (arylene ether sulfone) have attracted much attention. Synthesis of these materials for polymer electrolyte membranes has been widely reported in literature. In this class of high performance material, the copolymer is considered to be more attractive for their use in fuel cell systems as a suitable candidate because they have better oxidative stability as well as water
stability under harsh conditions and the availability of various types of chemical structures, which include partly or fully fluorinated materials. Sites of proton exchange in ploy (arylene ether)s can be achieved by a post-sulfonation as well as by direct copolymerization of already sulfonated monomers.

1.6 (a). Post-sulfonation of already synthesized polymers

The common strategy to sulfonate aromatic polymer is by electrophilic aromatic substitution reaction. Aromatic polymers can be easily sulfonated by using concentrated sulphuric acid (H₂SO₄), fuming sulphuric acid (H₂SO₄·SO₃), chlorosulfonic acid (ClSO₃H) or sulphur trioxide (SO₃). But, in this route of achieving sulfonation of existing aromatic polymer is not very precise. The degree and position of functionalization cannot be predetermined and it has the drawback of the side reactions such as degradation of polymer main backbone. Despite all of these drawbacks, this route of synthesizing PEMs has gained much consideration and many have become the important source of the evolving alternative materials as PEMs in FCs such as sulfonated poly(ether ether ketone).²¹ On the other hand, sulfonated poly(arylene ether sulfone)s have been synthesized by attaching the ionic group or the proton conducting moiety by modification reactions of polymer and this has been investigated in detail by the innovative work of Nosay and Rebeson. They have established a mild procedure for sulfonation of the polymers which are available commercially like bisphenol-A based poly(ether sulfone).²² Various types of sulfonating reagents have been utilised for polymer modifications reactions, like chlorosulfonic acid²³,²⁴, SO₃-triethyl phosphate complex. Sulfonation of aromatic ring is an electrophilic substitution reaction and it depends on the substituents pattern on the ring. This reaction is favoured by the groups which are electron-donating (ED) and
hindered by electron-withdrawing (EW) groups. Furthermore, -SO$_3$H group is customarily limited to activated position on the benzene ring. In bis-phenol A-based schemes, only one –SO$_3$H group could be introduced per repeating unit $^{25}$, as shown in Figure 1.3. Genova and Dimitrova have analysed various sulfonating agents and their aim was to consider the characteristic properties of chlorosulfonic acid and its derivative, trimethylsilylchlorosulfonate, on the sulfonation of bisphenol A-based polysulfone. They concluded that strong sulfonating agent like chlorosulfonic acid does not give a homogeneous reaction and that could be solubilized in dimethylformamide (DMF) as co-solvent. On the other hand, reaction with trimethylsilylchlorosulfonate as a sulfonating agent was found to be homogeneous. Chlorosulfonic acid result in some chain cleavage during sulfonation and it could be determined by viscometric technique, but in milder reagent like trimethylsilylchlorosulfonate, no chain scission and cross-linking found. But, in case of milder reagents, some of the drawbacks still present such as low sulfonation efficiency as well as short reaction time around 4 hours maximum could give 0.85 degree of sulfonation. Even if we use more and more reagent (3-times), low sulfonation degree is resulted.
Polymers Electrolyte Membranes for Fuel Cell Applications

![Chemical structures of non-sulfonated and sulfonated PEEK.](image)

**Figure 1.3.** Position of $-\text{SO}_3\text{H}$ group in poly(arylene ether sulfone).

PEEK is a better high performance material with better chemical stability, thermal stability and oxidative stability. As it has some crystallinity, PEEK show less solubility in some common organic solvents. As far as solubility is concerned, by the addition of the sulfonic acid groups to the main polymer backbone, solubility is increased$^{26, 27}$ and crystallinity decreased.

![Chemical structures of non-sulfonated and sulfonated PEEK.](image)

**Figure 1.4.** Chemical structures of non-sulfonated and sulfonated PEEK.

One of the most used poly(arylene ether)s for post-modification is commercially available Victrex® and so many procedures are reported for sulfonation of PEEK,$^{28, 29}$ the general structure of PEEK is given in Figure 1.4.
The process of sulfonation of poly (ether ether ketone) is second-order reaction kinetics and takes place at benzene ring flanked by two ether linkage. This is because of the high electron density of aromatic ring. But, the electron density of other two rings in the repeating unit is lower due to the electron withdrawing nature of the adjoining carbonyl group. As a result, one –SO$_3$H group is added per repeating unit. The sulfonation rate in PEEK in the presence of sulphuric acid could be controlled by changing the concentration of sulphuric acid, reaction temperature and reaction time to afford polymers with a sulfonation range of about 30-100 % without polymer degradation in the main chain as well as some cross-linking side reactions. Moreover, sulfonation of PEEK by concentrated sulphuric acid does not give true random copolymer and sulfonation degree is also found to be low around less than 30 %. This is because both of the dissolution as well as sulfonation result in the heterogeneous environment.

Some authors have tried to control the position of sulfonic acid group and degree of sulfonation of poly (arylene ether) polymer backbone. Al-Omran and Rose copolymerized some sulfones like, 4,4’-dichlorodiphenyl sulfone, durohydroquinone, and hydroquinone to get statistical copolymers. But, only the hydroquinone part was sulfonated by sulfuric acid. Placing of sulfonic acid group in the polymer backbone remains the attractive field in the field of sulfonation of polymers for fuel cell. A different route, but little costly has been used to get sulfonated polysulfone by Kerres group and it was based on many steps like metallation, sulfination in the presence of SO$_2$ gas followed by oxidation as given in Figure 1.5.
In this route, the most important step is oxidation and the selection of the oxidant for the conversion of lithium sulfinate to free sulfonic acid. On the other hand, ion exchange capacity (IEC) of the polymer materials may reduce during oxidation step due to the unwanted cross-linking side reactions and the polymer degradation during sulfonation, may give lower mechanical strength of the membranes. It was observed that H$_2$O$_2$ is good oxidizing agent for the materials of low IEC, as this has the capacity to reach to all the ionic groups present in the polymeric solution. On the other hand, materials with high IEC were obtained by KMnO$_4$ oxidation and without some undesirable side reactions such as polymer degradation and cross-linking. Also, this route allow some controlled cross-linking of polymer and which in turn is correlated to swelling behaviour as well as gas permeability$^{35,36}$ across the membrane under fuel cell operating conditions. Hence, authors who have studied this method argue that this method can be applied to any polymer material under consideration which could be
lithiated, and hence this is an attractive strategy to get the desired sulfonation degree if the polymer backbone degradation is to be avoided.

![Chemical structure of sulfophenylated polysulfone.](image)

**Figure 1.6.** Chemical structure of sulfophenylated polysulfone.

Similar procedure can be applied for introducing sulfophenyl group by lithiation and an ionic reaction with 2-sulfobenzoic acid cyclic anhydride. Here, while converting polysulfone to sulfonated polysulfone, pendant sulfonated phenyl group is attached through ketone linkage as shown in **Figure 1.6**.

1.6 (b). **Direct co-polymerization of sulfonated monomers**

Although post-sulfonation modification of already existing polymers give the materials which can be used in fuel cell as a PEM, still they have several major drawbacks such as lack of control over sulfonation degree and position of the sulfonic acid groups in the polymer. So it has gain much interest to study the effect of the sulfonation on deactivated repeating units, as we can expect enhanced stability as well
Higher acidity of the two –SO$_3$H groups generally attached to electron deficient ring compared to the sulfonic acid group attached to electron-rich benzene ring.\textsuperscript{38} In addition to the control over the molecular weight of polymers, enhancing the durability is possible if we avoid post-modification strategy to sulfonate the commercially available polymer materials. The difference between post-sulfonation and direct copolymerization of the sulfonated monomers is shown in Figure 1.7.

![Figure 1.7. Position of sulfonic acid group in post-sulfonation and direct copolymerization.](image)

Robeson and Matzner\textsuperscript{39} have reported the first required sulfonated monomer and they obtained a composition which was initially used as a flame retarding material. Recently, sulfonation reaction of 4,4'-dichlorodiphenyl sulfone has been reported by Ueda group.\textsuperscript{40} McGrath et al. has introduced a modified procedure for the introduction of the -SO$_3$H groups, particularly introduction of two sulfonic acid groups in the desired monomer as shown in Figure 1.8.

Sulfonated copolymers can be synthesised by direct copolymerization in any desired composition e.g., poly(arylene ether sulfone).\textsuperscript{41, 42} The procedure to get the sulfonated
copolymer materials is the same as it was used for the non-sulfonated poly (arylene ether) s in presence of weak base. But, some little higher temperature and longer reaction time is needed to get high molecular weight copolymer because of the sterically hindered sulfonated dihalide monomer.

![Figure 1.8. Synthesis of 3,3’-disulfonated 4,4’-dichlorodiphenyl sulfone.](image)

If more reactivity is required, more expensive disulfonated difluoro dihalide could be used and copolymerization to get the potassium salt of 3,3’-disulfonated 4,4’-dichlorodiphenyl sulfone which has the advantage of the increased stability of sulfonic acid salt. These statistical copolymers show a hydrophilic and hydrophobic domain and phase separated morphology which in turn depends on the degree of the disulfonation as shown in Figure 1.9.

![Figure 1.9. Synthesis of directly copolymerized sulfonated poly(arylene ether sulfone).](image)
Water uptake capacity and proton conductivity of this series of polymer materials have been increased with disulfonation. But, if the degree of disulfonation of the polymer reached above 50 mol % then a semicontinuous hydrophilic phase has been observed and its effect resulted in drastic membrane swelling and eventually it become hydrogel, which is not useful for PEMs preparation. Hence, it is indicated that proton conductivity must be fine-tuned with water absorption and swelling as well as mechanical strength of the membranes in these statistical (random) copolymers. Many variations in the chemical properties and structure are possible for direct copolymerization of sulfonated monomers, as many varieties of structures of monomers.

![Figure 1.10. Structures of poly(arylene ether)s.](image)

To determine the effect of the structures on the synthesis of sulfonated poly(arylene ether)s has been studied and four different types of bis-phenol structures have been used to synthesize poly(arylene ether)s containing ionic groups such as bis-phenol-A, hexafluoroisopropylidene bis-phenol (6F), 4,4’-bisphenol and hydroquinone. Sulfonated poly(arylene ether sulfone) copolymer has been synthesized directly by using sulfonated 4,4’-difluorodiphenyl sulfone, non-sulfonated 4,4’-difluorodiphenyl sulfone, and 4,4’-thiobisbenzenethiol. As a result their properties
were also found comparable with non-sulfonated poly(ether sulfone)s membranes. However, the copolymer from hexafluoroisopropylidene and bisphenol (6F) has been found to be interesting in the fuel cell application tests.\textsuperscript{46} It has been thought that fluorine content improves adhesion and compatibility in electrochemical properties with Nafion based electrodes as well as it reduces the swelling and mechanical strength of the membrane because of their hydrophobic nature.

Sulfonated poly(arylene ether ketone) polymer electrolyte membrane is also possible by using a sulfonated dihalide ketone as a monomer sodium 5,5’-carbonylbis(2-fluorobenzenesulfonate). Wang\textsuperscript{47, 48} has reported it first time and structure of the monomer is shown in Figure 1.11. The selection of bis-phenols for polymerization to obtain poly(arylene ether ketone) is very important.\textsuperscript{49, 50}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{monomer_structure.png}
\caption{Structure of sodium 5,5’-carbonylbis-(2-fluorobenzenesulfonate) monomer.}
\end{figure}

Various types of sulfonated monomers are available for the synthesis of poly(arylene ether)s and these monomers provide flexibility in the resulting polymer and due to this flexibility sulfonated poly(arylene ether)s can be considered as an ideal host for inorganic compounds to give nanocomposite PEMs.\textsuperscript{51} To increase the additional functionality in inorganic, organic composite can be incorporated to poly(arylene ether)s, PAE by polymerization of 2,6-dichlorobenzonitrile, hexafluoroisopropylidene bis-phenol (6F),and 3,3’-disulfonate-4,4’-dichlorodiphenyl sulfone.\textsuperscript{52}
In addition to the various advantages of nanocomposite membranes as PEM, these display little lower water uptake capacity (WU) in comparison to the analogue sulfonated poly(arylene ether sulfone) and this suggests that there are some interactions between aromatic nitrile and -SO₃H group.

1.7. Polyphosphazenes as PEMs

Polymer electrolyte membranes which are based on the polyphosphazene backbone are also of interest for fuel cell application for hydrogen/air as well as direct methanol fuel cell because of their better thermal and chemical stability as well as various attached side chains for ion exchange sites and -P=N- polymer main chain. As far as polyphosphazenes are concerned this was used initially as elastomers and later used in lithium ion batteries as solvent free solid polymer electrolytes and eventually as polymer electrolyte membranes for fuel cell. This class of material is of immense importance for their technological and synthetic advantages, as various functional groups can be attached over a wide range of molecular structures, which give the advantage of having unique properties. The surface chemistry of some specific polyphosphazenes were studied by Allcock and group with respect to the sulfonation process of the material. To do careful characterization, small and simple cyclic trimeric phosphazenes were used and small molecules analysis techniques have been used initially for the target sulfonation reactions. Once it was developed, same conditions of reactions were used for the sulfonation of corresponding polymers. Later, same reaction was used for the surface modification of the polyphosphazene films and the resulted modifications were determined by various surface analysis techniques. In 1993 Allcock reported the sulfonation of aminophosphazenes in the presence of 1,3-propanesultone. But, these materials are not ideal as a suitable candidate, but this type of study shows a novel route for the synthesis of sulfonated
polyphosphazene materials that could provide more control over sulfonated polymer as PEMs than general sulfonation of a basic polymer by a strong sulfonating agent. Pintauro et al. have sulfonated the poly[(3-methylphenoxy)(phenoxy)phosphazene] and poly[bis(3-methylphenoxy)phosphazene] by adding SO₃ solution in dichloromethane (DCM) into polymer solution in dichloromethane. Non-sulfonated and sulfonated polyphosphazenes have been shown in Figures 1.12 and 1.13 respectively.

![Figure 1.12. Phosphazine PEM](image)

Polymer degradation is also a very important concern of sulfonated polyelectrolyte membranes but in case of polyphosphazenes materials with high ion exchange capacity, IEC (2 meq g⁻¹) show no measurable degradation of the polymer.

![Figure 1.13. Potential sulfonation sites on poly[(3-methylphenoxy)(phenoxy)phosphazene].](image)

Sulfonation reaction of polyphosphazenes can be controlled but some report show that reaction at backbone nitrogen takes place before actual sulfonation on the pendent
ring in case of poly[(3-methylphenoxy)(phenoxy)phosphazene] as shown in Figure 1.13.

As far as mechanical properties are concerned, sulfonated polymers with IEC around 1.4 meq g\(^{-1}\), display good mechanical strength at room temperature and in dry as well as in hydrated states. The glass transition temperature exhibited in the range -20 to -10°C for non-sulfonated poly[bis(3-methylphenoxy)phosphazene] and corresponding sulfonated polymer with an IEC of 2.1 meq g\(^{-1}\). This range of low glass transition temperature generally causes failure of the polymer membranes under real fuel cell operation conditions.

1.8. Polyimide based PEMs

Polyimide materials are the polymers in which a heterocyclic imide functional group is present in the repeating unit as given in Figure 1.14 and their general synthetic method is the reaction of diamines and dianhydrides. Because of their wide applications in different fields, their synthetic routes have been investigated for easy and cheap preparations. However, the discussion of polyimide is not complete without the consideration of five-membered and six-membered ring polyimides. If the five-membered ring polyimides are very common, on the other hand six-membered ring is potential candidate as PEMs.

![General chemical structure of polyimides, R= Cycloaliphatic or aromatic, R’= Aliphatic or aromatic](image)

**Figure 1.14.** General chemical structure of polyimides, R= Cycloaliphatic or aromatic, R’= Aliphatic or aromatic

1.8 (a). Five-membered ring polyimides
Polyimides are high performance materials and have been investigated for their various applications in different fields. Hence, polyimides with five membered ring structures also known for many applications. But sulfonated phthalic polyimides are used for fuel cell application as proton conductive membrane but this readily degrades in fuel cell operating conditions.

1.8 (b). Synthetic methods of five-membered ring polyimides

(I) Two steps route synthesis

In this method, an intermediate, the poly(amic acid) is involved and this route was developed initially by the DuPont Company USA. This route is used to get high molecular weight insoluble polyimides, e.g., Kapton®. In initial stage a dianhydride and aromatic diamine were dissolved in a dipolar aprotic solvent, like dimethylsulfoxide (DMSO), N-methylpyrrolidinone (NMP), dimethylacetamide (DMAc). Here strong hydrogen bonding interaction between solvent and intermediate, poly (amic acid), helps to form stable poly (amic acid). Moreover, strong basic solvents favour the reaction due to the interaction between the acid intermediate and solvent. The reaction temperature generally keep low as the formation of the poly(amic acid) is an exothermic reaction. In actual practice, high molecular weight poly(amic acid) can be obtained at lower temperatures and at this stage, soluble polymer solution is cast onto the glass plate to get the film. After this the resulted film is cured thermally or by chemical process to get the final polyimide. Though, the formation of the poly (amic acid) is a major reaction, some side reactions are also possible.

In this method of polyimides synthesis, hydrolysis shifts the equilibrium balance of the main reactants, the dianhydrides and diamines end groups and as a result α-
dicarboxylic acid which is formed in the reaction is unreactive with the aromatic diamines under poly (amic acid) reaction conditions. As a result, molecular weight of the resulted polyimide is not high enough. Therefore, because of this reason, the solvents and monomers should be free from moisture to get high molecular weight polymers. In addition, careful drying and distilling of monomers and solvents are must before actual copolymerization.

Poly(amic acid) reaction is considered to be takes place via formation of the charge-transfer complex between anhydride and diamine. Here, amine’s nitrogen attacks the carbonyl carbon and displacement of the adjoining carboxyl group and stabilized by hydrogen bonding with the polar aprotic solvents favouring the reaction towards the completion of the polymerization. Hence, by this strategy of synthesis of high molecular weight poly(amic acid) can be used for a wide range of different structures of dianhydrides and diamines and by running the reaction for long time, even less reactive monomers give high molecular weight polyimides. Subsequently, the poly(amic acid) reaction propagation takes place by nucleophilic substitution reaction at the carbonyl carbon of anhydride also anhydrides react faster due to their more electrophilic nature. As far as reactivity of dianhydrides are concerned, it can be correlated with the electron affinity of the dianhydrides. Hence, more the electrophilic nature of the dianhydrides more it will be reactive with the given nucleophile. Moreover, more basic diamines tend to have faster reaction rates, such as \( p \)-phenylene diamine and \( 4, 4' \)-oxydianiline.
(II) Bulk imidization route

In this route, poly(amic acid) precipitates on cyclization due to the rigidity of polymer chain. This is known as bulk imidization. Polyamic acid is cured in a vacuum oven in different stages or in an inert atmosphere to start cyclization and to remove additional solvent and water. The most accepted procedure to get bubble free films from polyamic acid is heating the film in vacuum oven initially for one hour at 30°C, another one hour at 100 °C followed by one hour at 200 °C, and 300 °C. To remove trapped water and air from the films, which are produced in the cyclodehydration reaction and need time to diffuse out, therefore, heating process is very crucial. The degree of imidization immensely depends on the chains mobility during thermal treatment, which depends on the concentration of the residual solvent, diamine and dianhydride. On the other hand, viscosity of polyamic acid solution increases with the decrease in polar solvent as the residual solvent is needed for the plasticization that favours good film formation and provides required chain mobility to get high degree of imidization.

(III) Chemical imidization route

In thermal imidization, the main disadvantage is the decreased molecular weight of the resulting polyimides. This eventually affects the mechanical properties of polyimide films. To overcome this problem milder reaction conditions are used for the cyclodehydration reaction. Chemical imidization is a significant method in which chemical agents are used as catalyst for ring closure at lower temperature than thermal imidization. Common dehydrating reagents used in chemical imidization are acetic, propionic, n-butyric, benzoic anhydrides in aprotic polar solvents or in tertiary amines like trialkylamines, pyridine, lutidine, and N-methylmorpholine. In chemical
imidization, most frequently used reagents to get high molecular weight polyimides are the equi molar mixture of pyridine and acetic anhydride. The most accepted mechanism is the formation of mixed anhydride intermediate followed by an iminolactone and then the imide linkage, which is the thermodynamically favoured product. Polyamic acid could be converted to polyisoimide with many chemical combinations of reagents. Mostly, pyridine and trifluoroacetic anhydride facilitate isoimide formation. But, isoimide linkage is unstable because of its less thermal and mechanical properties than the imide linkage. Although polyisoimide has wide range of applications as it has improved processability and good solubility. Furthermore, isoimides could be thermally converted to corresponding imides in the presence of a tertiary amine.

(IV) Solution imidization route

In this route of solution polymerization, one ideal example which is available commercially and prepared by one-pot method is Ultem™. It was prepared from diamine and dianhydride in the presence of o-dichlorobenzene (o-DCB) which is shown in the Figure 1.15.

Figure 1.15. Synthesis of Ultem™ by one-pot solution imidization.
Polyimides are not soluble in common organic solvents due to their rigid and less cyclized backbone structure. To synthesize fully cyclized and soluble polyimides, the rigid structure of the polyimides should be modified to reduce stiffness and inter-chain order. To get improved solubility and amorphous nature of the polyimides many strategies\textsuperscript{65, 66} have been developed without compromising the excellent physical properties. Some of the most common strategies are given below.

1. By the introduction of some flexible bridging groups such as -O-, -S-, -CO-, -SO\textsubscript{2}-, -C(CH\textsubscript{3})\textsubscript{2}- and -C(CF\textsubscript{3})\textsubscript{2}-.

2. Bulky groups also have good effect on the solubility. Hence, by the introduction of monomers with bulky groups in the side chains increase solubility.

3. Incorporation of the monomers with the \textit{meta}-linkages

4. Introduction of the unsymmetrical structure in the main chain

5. Some end-capping by monofunctional groups

The benefits of using one of these strategies to yield soluble amorphous polyimides are as follows:

1. One-step Reaction: homogeneous solution imidization

2. Less than 1\% of the amic-acid groups remain unimidized

3. Long shelf life due to the increased hydrolytic stability of the polyimide

4. The resulting polyimide is soluble in polar solvents for spin casting or solution casting films

5. No issue of water release during film drying process

6. Isotropic physical properties of the material

Soluble polyimides in fully cyclized form can be imidized thermally from the polyamic acid in solution at higher temperature. Cyclodehydration process requires high boiling solvents (160 °C-200 °C) but in the presence of azeotropic solvents\textsuperscript{67}, these bring the removal of the water formed during the reaction and favour the
reaction towards the completion. Some common azeotropic solvents such as toluene, xylene and \textit{o}-dichlorobenzene are generally used for this purpose. Moreover, this method can be performed at lower temperature than bulk polymerization method. As a result, other side reactions, such as polymer degradation can be prevented, as this reaction can takes place at lower temperature.

It was observed during the reaction that polyamic acid chains cleaved to form \textit{o}-dicarboxylic acid and amine end-groups due to the presence of water which is liberated during the reaction and initiate partially hydrolysed poly(amic acid).\textsuperscript{68} As the reaction proceeds, the end-groups recombined and intrinsic viscosity increased to form high molecular weight polyimides. This process can be monitored by \textsuperscript{1}H NMR using peak for free amine in solution. Kim has found that the rate determining step in the imidization is acid catalysed and second-order reaction.\textsuperscript{69, 70} Synthesis of high molecular weight poly(amic acid)s is not indispensable in solution imidization process. Though imidization still proceeds via an amic acid intermediate, the concentration of amic acid is very low during the polymerization as the lifetime of polyamic acid at high temperature is short. Hence, the poly(amic acid)s can be directly imidized in solvent at high temperature.

1.9. Properties of polyimides

High performance aromatic polyimides have found various applications in different fields particularly in aerospace industries and micro-electronics due to their excellent mechanical properties, low dielectric constant, thermal stability, chemical resistance, and high glass transition temperatures. High performance polyimides materials are the products of diamines and dianhydrides, and the final properties like tensile strength, toughness, modulus, and upper-use temperature depend on the choice of the starting
materials used for polymerization. Aromatic polyimides ideally show high glass transition temperature in the range of 200-400 °C or little higher and this depends on the rigidness of the polymer backbone. Moreover, highly imidized polyimides with highly conjugated and rigid rod like chemical structure are generally insoluble and due to this insolubility, their direct processing is very difficult or impossible. To overcome these problems of processability and solubility of polyimides, some general rules have been adopted universally like introduction of aliphatic moiety or some flexible linkages to reduce the stiffness. Introduction of bulky side groups have the same effect on the main chain. This supports in the separation of polyimides chains and hinder molecular packing and crystallization. Usage of enlarged monomers containing angular bonds, which suppress coplanar structures. Use of 1, 3-substituted instead of 1, 4-substituted monomers, and asymmetric monomers lower regularity and molecular ordering. Conversely, these factors leading to better solubility or lower glass temperature, $T_g$ or melting temperature, $T_m$, in a polymer like polyimide. Therefore, a fine-tuned degree of variation must be applied for optimization in properties.

1.10. Six-membered ring polynaphthalimides based polyimides

Polyimides synthesized by the use of aromatic diamines and phthalic dianhydrides show usually low chemical as well as hydrolytic stability. This is due to the presence of strained five-membered imide ring, and more positive charge on the carbonylic carbon. On the other hand, in six-membered ring polyimide there is less ring strain and low positive charge on the carbonylic carbon. Hence, chemical and thermal stabilities of polyimides are increased when bis-(naphthalenic) dianhydrides is
introduced in place of bis-(phthalic) anhydrides. Also these show superior fire resistance properties compared to the corresponding five membered ring polyimides.76

1.11. Dianhydrides for polyimides

Naphthalene-1, 4, 5, 8-tetracarboxylic dianhydride (NTDA) and perylene-3, 4, 9, 10-tetracarboxylic dianhydride (PDA) are the two most important six-membered ring dianhydrides which are being used very frequently to synthesize polynaphthalimides because of their commercial availability. Polyimides synthesized from either from NTDA or PDA and commercially available diamines like p-phenylene diamine, m-phenylene diamine and 4, 4’-oxydianiline are not soluble in common organic solvents. Therefore, to get soluble and easily processable polyimides more flexible diamines or two or more different types of diamines are used.

1.11 (a). Naphthalene-1, 4, 5, 8-tetracarboxylic dianhydride (NTDA)

Polyimides synthesized from NTDA and commercially available aromatic diamines have been studied77-79 in detail. So far, NTDA is the only six-membered ring dianhydride which is being used for the preparation of proton exchange membranes, possibly due to its relatively low cost, high reactivity, and commercial availability. Rusanov group have shown by electronic calculations that NTDA is most reactive among the naphthalenic dianhydrides, even though a more recent paper shows otherwise.80 Hodgkin has tested the reactivity of NTDA with a number of aromatic diamines.81 When an amine reacts with NTDA, the dianhydride becomes more reactive
towards other amine molecules. Consequently, when NTDA reacts with aniline, the main product is the di-substituted molecule as shown in Figure 1.16.

![Figure 1.16. Reaction of NTDA with aniline.](image)

Furthermore, when NTDA is dissolved in solution with aromatic diamine at 80 °C or at higher temperature, the diimide is the major product once again and one example is given in Figure 1.17.

![Figure 1.17. Reaction product from NTDA and 4, 4'-oxydianiline.](image)

In the above example, it is observed that after the attachment of the first amine group to the dianhydride, the reactivity of the second amine group is hugely decreased.

1.11 (b). Perylene-3, 4, 9, 10-tetracarboxylic dianhydride (PDA)

Perylene is a conjugated system and generally used in the dye industries as a chromophore. Due to their better and high thermal and photochemical stability, perylene and its derivatives are core components in the solar cells, fluorescent solar collectors as well as in novel lasers. By the use of PDA and some of its derivatives,
various polyimides series have been synthesized including 1, 6, 7, 12-tetrachloro-3,4,9,10-perylene dianhydride (Cl-PDA). Mullen et al. have synthesized six-membered ring containing sulfonated polyimides with the use of four chlorine groups on Cl-PDA. Chloro-PDA and phenol were reacted by nucleophilic aromatic substitution reaction and the resulted monomer was then copolymerized with diamine. Eventually it was sulfonated by concentrated sulphuric acid at room temperature. No side reactions like cleavage of phenoxy substituents and excess sulfonation were detected by $^1$H NMR spectroscopy. These sulfonated polyimides give good film forming property on solution casting. But it is water soluble and hence, it does not have any application except the improved solubility.

1.12. Novel dianhydrides for polyimide

As far as solubility of five-membered ring polyimides are concerned, this can be improved by the introduction of the bulky groups/substituents or by flexible linkages in phthalic dianhydride structure. Hence, in the same way solubility of the six-membered ring can be improved by the introduction of the single bonds or flexible/hinge groups between the two naphthalenic anhydrides. Based on these facts, several dianhydrides have been synthesized by the introduction of the flexible linkages in the moiety like ether, sulfone, sulfide, ketone, and methyl groups as shown in Figure 1.18.

![Figure 1.18](image)

**Figure 1.18.** Novel dianhydrides, where $X = O, S, SO_2, CO,$ or $CH_2.$
Therefore, dianhydride with flexible linkage was reacted with oxy-dianiline (ODA) in m-cresol as a solvent. The resulting polyimides were soluble fully in m-cresol at 10% concentration. But, on the other hand, polyimides synthesized by using the NTDA and the diamine, oxydianiline (ODA) precipitated during the polymerization in m-cresol. It is true that by the introduction of the flexible groups in the dianhydrides, solubility was increased but, these flexible groups are electron donating. As a result, electrophilic reactivity of the anhydride decreases and eventually low molecular weight polymer resulted. Polyimides synthesis have also been reported by using the dianhydrides with amide or ester linkages. Though, this improves solubility of polyimides, it simultaneously reduces chemical stability as ester and amide groups are capable of cleaving easily.

Carbonyl group, on the other hand, increases the reactivity of dianhydrides, as shown in Figure 1.19 and polyimides synthesized from these dianhydrides have found to have good solubility as well as high molecular weight.

![Figure 1.19. Dianhydride with carbonyl group.](image)

Monomers synthesized from acenaphthene and aromatic dicarboxylic acid dichlorides by Friedel-Craft reaction have been reported by many authors. Rusnov has studied the detailed conditions of the reaction and found that purity of the reaction product and yield are depend on the quantity and nature of the catalyst used, nature of the solvent used, order of adding the reagents, temperature and time duration of reaction. But, the
ideal conditions of the condensation reactions are four hours and 0-60°C temperature and tetrachloroethane as solvent, aluminium chloride as a catalyst.

Polyimides have been synthesized by using bis-(naphthalenic anhydride), which in turn prepared by oxidation of bis-acenaphthyls followed by dehydration of tetracarboxylic acids. The outcome of polyimide structure on the reduced viscosity has been studied.\textsuperscript{50} The authors have used a number of different aromatic diamines and two naphthalic dianhydrides, 1,3- and 1,4-bis(1,8-dicarboxylic anhydride-4-naphthaloyl)benzene. It was found that structure of dianhydrides and diamines have significant role in the reduced viscosity of the resulted polyimides. The polyimide which has been derived from 1,4-bis(1,8-dicarboxylic anhydride-4-naphthaloyl)benzene show more reduced viscosity compared to those derived from 1,3-bis(1,8-dicarboxylic anhydride-4-naphthaloyl)benzene. Hence, it was concluded that para-linkage in dianhydride and diamine compared to meta-linkages produces high molecular weight polyimides. For example, polyimides prepared from 1, 4-phenylenediamine display higher reduced viscosities compared to those prepared from 1, 3-phenylenediamine with the same dianhydride.

1.13. Mechanism of six-membered ring polyimides and their reaction conditions

Six-membered ring polyimides display higher chemical and thermal stability in comparison to their five-membered ring counterparts. But, chemical reactivity of the naphthalenic anhydride is less than phthalic anhydride. Although several groups have tried to get high molecular weight polyimides but they were not successful, only few groups could synthesize high molecular weight six-membered ring polyimides. Anhydrides with six-membered ring structures are far more stable than their five-membered ring counterparts and it was found that the reactivity of these anhydrides
towards amine is less. Hence, to improve the reactivity of the six-membered ring anhydrides towards amine it is indeed necessary to use some catalyst during the reaction to get higher molecular weight polyimides. As far as catalysts are concerned, so many different types of catalyst could be used for this purpose. Major catalysts include benzoic acid, quinoline, isoquinoline, pyridine, imidazole, triphenylphosphine, and triphenyl oxide and their effects have been studied on the reaction of high molecular weight polyimides synthesis. Acidic and basic catalyst have found tremendous effect on the reduced viscosity but phosphorus catalyst have either very low or no effect on the viscosity of the polyimides. The far more and reliable catalyst used for high molecular weight polyimides is benzoic acid, which is generally used in 2:1 molar ratio with respect to dianhydride. It is added at the starting of the reaction and isoquinoline is added to the reaction after nine hours with the same moles as of the benzoic acid used. Moreover, high molecular weight polyimides can also be obtained by using only single catalyst benzoic acid, and based on these observation, many groups of researchers have tried benzoic acid or its combination with isoquinoline as catalyst in the polymerization of six-membered ring polyimides. 

To determine the detailed mechanism of single-step high temperature polycondensation of six-membered ring polyimides, many model compounds have been synthesized from 4-benzyol-1,8-naphthalene anhydride including amines and aromatic diamines and many techniques such as $^1$H NMR, $^{13}$C NMR and $^{15}$N NMR spectroscopy have been used for this purpose. Similar mechanism is also operated in polycondensation of phthalic imides in which poly(amic acid) is the intermediate. On the other hand, poly(amic acid) is formed first in one-step high temperature polycondensation of five-membered ring diamines and dianhydrides. It readily dehydrates to give polyimides, as polyamic acid is considered to be a short-lived
species, even though it not detected. On the other hand, to figure out the role of the acidic catalyst, the benzoic acid in the polycondensation reactions, 4-benzoyl-1, 8-naphthalene anhydride and different amines including oxy-dianiline (ODA), and 4-phenyloxyaniline were reacted by using several mole ratio of the catalyst (benzoic acid) with respect to the dianhydride. By these model reactions, it is observed that benzoic acid should catalyse the formation of amic acid with the high yield of the product, but as acidity of the reaction solvent increased by the benzoic acid, the product yield decreased. By considering all these observations, it is concluded that poly(amic acid) was not the intermediate species in the reaction concerned and it is confirmed by the NMR spectroscopic technique.\(^{89}\) \(^{13}\)C NMR spectra display that structures of the products were independent of the reaction conditions.

To confirm that the compounds under investigation are imides or isoimides, carbon peaks for isomide (isocyanate) and a tertiary amine (imide) have been used. \(^{13}\)C NMR result matches with isomide chemical shifts. In spite of NMR spectroscopy, other characterizations also carried out to confirm the intermediate structure involved in the reaction. Ultraviolet-visible spectroscopy (UV-VIS) and differential scanning calorimetry (DSC) have been utilized for this aim and eventually confirmed that intermediate in single-step high temperature condensation is isoimide. Moreover, when the acidity increases, colours of the naphthalimide model compounds becomes more and more deep and based on this observation it is suggested that two isomers of the isoimide have formed in the acidic reaction medium and this was confirmed by the UV-VIS spectroscopic technique. As far as imides are concerned, they do not show absorption in the UV-VIS region above 300 nm and the compounds synthesized without using acid catalyst display absorption at 344 nm and 352 nm which correspond to the lactone carbonyl group and C=N bond respectively. When acid is
Polymers Electrolyte Membranes for Fuel Cell Applications

present, one additional absorption band seen at 480 nm in UV-VIS region. Therefore, two isomers of the isoimides, one cis and another trans has been confirmed by UV-VIS and DSC analysis techniques in the high temperature polycondensation reactions of polyimides synthesis. And it is suggested that in the presence of the acid like benzoic acid, only trans-isoimide has formed and this is only converted to the corresponding imide structure. The reaction mechanism for the reaction of aromatic diamines with 1, 8-naphthalene anhydrides is shown in the Figure 1.20.

Figure 1.20. Reaction of 1, 8-naphthalene type anhydride with an aromatic amine.
Trans-isoimide can also be formed without catalyst and by using hydrochloride salt form of diamine in the presence of HMPT (hexamethylphosphorus triamide).\textsuperscript{90} It is important to note that compounds prepared by the use of benzoic acid and \textit{m}-cresol as the solvent and in HMPT with amine hydrochloride give the same results. As HMPT is costly, polyimides synthesis through this route is not cheap. After the detailed studies of

\textbf{Figure1.21 }\textit{cis}-isoimide mechanism.
six-membered ring polyimides, mechanism has been established and the proposed mechanism for cis and trans isoimides formation is shown in the Figure 1.21 and Figure 1.22 respectively.

1.14. Conversion of trans-isoimides to imide

The conversion of the trans-isoimides to the corresponding polyimide is difficult to achieve spontaneously but to do this; some catalysts are required to facilitate this process to occur. Efficient catalysts for this purpose are high boiling heterocyclic compounds particularly the bases like quinoline, isoquinoline. Isoquinoline is more important due to mechanism point of view. Here nitrogen atom on isoquinoline attacks the carbonyl carbon and accordingly breaks the carbon-ether oxygen bond.
followed by nucleophilic attack by nitrogen atom to carbonyl carbon and isoquinoline leaves forming the naphthalimide as shown in Figure 1.23.

![Figure 1.23. Conversion of trans-isoimide to imide.](image)

### 1.15. Polyimides by nucleophilic substitution reaction

Synthesis of the polyimides by the usual methods is not the only way to get them; rather they can be synthesized through some novel methods. In these methods, imide containing monomers have been synthesized initially followed by the use of another polymerization technique to get polyimides. The important reaction by which aromatic bis-phenolates and dihalides combines, is nucleophilic substitution reaction, which is commonly used for the synthesis of poly(arylene ether)s. Here, there is no need to use acidic solvents like m-cresol, m-chlorophenol etc., as they are not easy to handle during the reaction, also high molecular weight polymers could be synthesized in basic conditions in dimethylacetamide (DMAc) or N-methylpyrrolidinone (NMP) as solvent. Aromatic dichloride monomers containing naphthalimide has been reported first time by Sonpatki group\(^9\) and the structure of the monomer is shown in Figure 1.24.
Figure 1.24. Dichloro imide monomer.

As shown in the Figure 1.24 chlorine atoms are situated on para-position with respect to six-membered ring, hence, they are more prone to nucleophilic substitution displacement by oxygen or sulphur atom containing reagents. In polyimide synthesis one should be sure that whether the final product is an imide or isoimide. To confirm this $^{13}$CNMR can be used as a tool. In imide signals are less than the corresponding isoimide. The reason for less number of signals is the symmetrical structure of imide. Moreover, as the chlorine atoms withdraw electron density, their reactivity towards nucleophiles increases. In NMR spectrum, chlorine attached carbons are more deshielded. Hence, more reactive carbons were found to display the peak in $^{13}$C NMR at 132.5 ppm.  

Nucleophilic polycondensation reactions by using naphthalimide and bisphenols in NMP at 200 °C were carried out by Sonpatki, but, later it was observed that molecular weight of the resulted compounds were low.  

Zheng and Wang obtained high molecular weight polymer from naphthalimide monomer bis-phenol by nucleophilic substitution reaction. Many scientists have prepared naphthalimide based bisphenols by reacting commercially available naphthalenic dianhydride like NTDA, PDA and aminophenol. After that bis-phenols have been used to polymerize naphthalimide containing poly(arylene ether)s or
polyesters. Wang and Mackinnon have used NTDA, PDA and reacted 2-(4-aminophenyl)-2-(4-hydroxyphenyl) propane to synthesize novel bisphenols as given in Figure 1.25. These bis-phenols were reacted with any aromatic difluorides to get the polymers. The inherent viscosities of six-membered ring polyimides were found to have low values (0.11 - 0.44 dL/g), but, monomer preparation is mainly interesting. As an alternative of using m-cresol as a solvent and benzoic acid and isoquinoline as the catalysts, they have synthesized the naphthalimide-containing bis-phenols in DMAc or NMP with zinc acetate as a catalyst. Moreover, zinc acetate has been considered a lewis acid and it could acts in a similar way that benzoic acid does in the trans-naphthalisoimide formation.

The main advantages of synthesizing six-membered ring polyimides through nucleophilic substitution reactions are:

**Figure 1.25.** Bis-phenol monomer with imide-containing moiety.
Polymers availability with low cost.

Polymerization reaction conditions are easy to handle.

Polar aprotic solvents under basic conditions are only required. Furthermore, they have not used m-cresol in the monomer or polymer synthesis. So this approach was found to be encouraging route to synthesize six-membered ring polyimides. But their polyimides have found to be low molecular weight, probably due to the choice of monomers. Somatic revealed that high molecular weight polyimides can be prepared from dichloro-naphthalenic monomers by nucleophilic substitution, because of the increased electrophilic of the chlorine atom which is due to imide moiety. The most promising method to prepare high molecular weight polynaphthalimides without using m-cresol may be a combination of these techniques. The dichloro-naphthalenic monomers can be prepared in DMAc/zinc acetate and then used in poly (arylene ether) synthesis with suitable bis-phenols.

1.16. Diamines in polyimides synthesis

Diamines in the synthesis of the polyimides also play very crucial role to get a desired polyimide with different properties. Several sulfonated as well as non-sulfonated diamines are being discovered by various research groups. Although, many sulfonated diamines are commercially available, many diamines are being synthesized to get novelty in the resulted polyimides and to fine-tune some structure property relationship. On the other hand non-sulfonated diamines are synthesized much more as compare to the sulfonated diamines and this is because of the difficulties in the synthesis of the sulfonated diamines.
1.17. Proton conducting moieties

In polymer electrolyte membranes, the ion conducting moiety is generally being used as sulfonic acid group. But researchers who are engaged in developing the new polymeric materials for PEM also now focusing to develop or introducing some other proton conducting ionic groups in PEM materials. In this direction, phosphonic acid based proton conductors in polymer as well as in monomer have reported by some groups. Phosphonic and phosphinic acid containing polymers have very limited synthetic routes and due to this they have not studied in detail as compared to the sulfonic acid based PEMs. Miyatake and Hay have prepared polymers containing phosphonic acid as ion conducting (proton conducting) moiety using aromatic difluorides as shown in Figure 1.26.

![Figure 1.26. Phosphonic acid containing poly (arylene ether).](image)

In this polymer, the acid group is present in the main chain of the polymer and apart from this, other reports of phosphonic acid group as proton conducting moiety was also found in the literature. But, this group has lower acidity as compared to the sulfonic acid group, but its good thermal as well as chemical stability provides advantage as compared to the sulfonic acid containing PEMs. Meng have synthesized polymer containing phosphonic acid group as proton conducting moiety for fuel cell application as PEMs and it was based on phenolphthalein. Starting from
phenolphthalein and \( m \)-aminophenylphosphonic acid bis-phenol monomer have synthesized. Poly(arylene ether)s with phosphonic acid group has synthesized starting from bis-phenol as shown in Figure 1.27. These materials were found to display high glass transition temperature as well as high molecular weight, but their proton conductivities were found to be low values. This restricts them to be good candidate for proton exchange membranes.

**Figure 1.27.** Phosphonic acid containing poly (arylene ether) from a phenolphthalein-based bis-phenol.

Proton conductive moieties with high acid strength play a crucial role in the proton conductivity of the membranes. Hence, various research groups have developed some highly acidic moieties for proton conduction like sulfonimide.\(^{102-106}\) Nafion and similar bis[(perfluoroalkyl)sulfonyl]imide\(^{107}\) have been compared by DesMarteau and found that proton conductivities of both the ionomers are similar and no change in the proton conductivity while introducing sulfonimide as proton conductor in the
copolymers. The structure of Nafion and bis[(perfluoroalkyl) sulfonyl]imide are shown in Figure 1.28.

![Figure 1.28](image-url)

**Figure 1.28.** Comparison of Nafion and bis [(perfluoroalkyl) sulfonyl] imide.

The conductivities of all the ion conducting membranes described here depend on the amount of water absorbed as mobile phase. However, aim of hydrogen/air fuel cells is 50% relative humidity at 120 °C. But, under these operating conditions, proton conductivity of ionomers decrease due to less water uptake at 50% relative humidity and this results in large resistive loss in the fuel cell. To fulfil these requirements composites of organic-inorganic materials\textsuperscript{108} can be used. On the other hand, water replacement solvents\textsuperscript{109, 110} have been developed. These solvents have imidazole moiety as proton conductor to replace the water/acid complex in the modern PEMs. These moieties have been attached to polymer main chain\textsuperscript{111} as shown in the Figure 1.29.
Figure 1.29. Imidazole moiety as proton conductor attached to a polymer main chain.

1.18. Strategies in designing of new PEMs

Different classes of materials for proton conducting membranes for fuel cell application have been discussed so far. Apart from above information, there are some fundamental aspects of polymers that are not studied so far in the field of PEMs fuel cell systems. One such aspect is the molecular weight determination of ion conducting polymers. For quantitative purpose molecular weight of polymers can be determined by various techniques like gel permeation chromatography (GPC) and MALDI-TOF. Molecular weight determination of polymers containing ions in the backbone is very complicated as ion-ion interactions considerably affect the characterization of macromolecules in the presence of the solvent and this effect on polymer chains is called polyelectrolyte effect. Moreover, ions can stick to the chromatographic column, which provides random results and this effect could be reduced to some extent by the addition of lithium halides to the mobile phase in the chromatographic column. This suppresses the polyelectrolyte effect in GPC and intrinsic viscosity determination of the ionomers.
On the other hand, nuclear magnetic resonance (NMR) spectroscopy can be used to detect the end groups of the polymers and this is helpful in determine the effect of molecular weight on the properties of PEMs in fuel cell. It is concluded by many studies that molecular weight of the polymer in the range of 20-40 thousand has almost no effect on the proton conductivity, but on the other hand other properties like mechanical properties and water uptake depend on the molecular weight of the polymer under investigation due to the chains entanglement. Hence, mechanical properties of the membrane generally depend on the molecular weight of the polymers. This is also another point which is often ignored in this field.

Membrane electrode assembly (MEA) and long term durability of the polymer electrolyte membranes are very crucial and which in turn depend on the mechanical properties of the membranes in hydrated as well as in the dry states. Moreover, the membranes under fuel cell device must be mechanically robust so that they can tolerate both the electrode processing and attachment as well as it should withstand many start up and shutdown of the device and repeated heating, cooling, swelling and drying during the operation of the fuel cell device.

Nafion® shows good mechanical strength up to 80 °C and transform into a rubbery material with low value of modulus and high elongation to break the membrane and these properties of Nafion is good for MEA fabrication. But its rubbery behaviour restricts to gives good performance at higher temperature operation. Nafion when used at around 100 °C or above develops pinholes in the membrane and which is due to the viscoelastic relaxation and low hydrated glass transition temperature. A polymer electrolyte membrane with high glass transition temperature shows higher hydrated glass transition temperature and good mechanical properties at elevated
temperature and it restricts the membranes from mechanical degradation. Hence, mechanical properties and molecular weight of the polymer are two important characteristics but they are being neglected in the characterization of PEMs.

1.19. Conclusion

Polymer electrolyte membrane is main part of PEM fuel cell technology development and it is important to have clear synthetic and detailed characterization. Ion conducting moieties for proton conduction in particular, must be designed to provide better proton conductivity. There are two current problems in polymer electrolyte membranes; one is the higher proton conductivity at relatively low water uptake capacity at 120 °C and 50 % relative humidity and second is the long life of the membranes under the fuel cell conditions.

Sulfonic acid as the proton conducting moiety is the classical method for ion conduction in PEMs but they show low proton conductivity in low water content at high temperature. Moreover, novel proton conductors in PEMs are being introduced. Nafion and other similar polyperfluorosulfonic acid membranes have been studied well in detail as they are commercially available. But, synthetic strategy, chemical compositions and molecular weight of Nafion is still unclear.

Polymeric materials such as sulfonated PEEK and polysulfones (PS)s show good chemical and thermal stabilities under the real fuel cell conditions. But they have the disadvantage of lower proton conductivities due to the weak acidity of the aryl sulfonic acid group than Nafion. Lower acidity of the aryl sulfonic acid group in poly(arylene ether)s can be increased by the introduction of more sulfonic acid groups in the polymer; but more acid groups in the polymer lead to the more swelling of the membranes. On the other hand, weaker acid moieties in the polymer like poly(arylene
Polymers also provide good performance of the membranes at low relative humidity in fuel cell conditions and these could fulfil the alternatives membranes to the Nafion at or above 80% relative humidity and their applicability for relative low humidity applications are more challenging in fuel cell applications.

Sulfonation is also an important step in the synthesis of new polymer electrolyte membranes and two methods have been used for the introduction of the sulfonic acid groups into the polymer. Post-sulfonation results in some undesirable sides reactions and cannot be controlled the number and locations of the sulfonic acid groups in the polymer. On the other hand, direct using of the sulfonated monomers to afford the sulfonated polymers have attracted much attention as in this method, sulfonation degree as well as molecular weight can be controlled. Sulfonated poly(styrene), sulfonated polyimides and poly(arylene ether)s have been synthesized by the direct copolymerization of the sulfonated monomers. Moreover, by using direct synthetic method one can get block copolymers with the sulfonated and non-sulfonated blocks and this has been achieved in poly(styrene) or poly(acrylonitrile) based polymer materials by using styrene sulfonic acid and using sulfonated diamines in polyimides. It is interesting to note that by using the block copolymers as PEMs, proton conductivity of the membrane can be increased without the considerable water swelling of the PEMs. So in this field, new materials are required for high temperature applications. Hence, sulfonated poly(arylene ether)s have found as good candidate for durability in the real fuel cell operating conditions.

Polyimides and poly(styrene) materials are good PEM candidate but, hydrolytic and oxidative stabilities are not up to the mark and these properties limit their potential to be a good PEM in fuel cell device. Sulfonated high-performance polymers based on
poly (phenyl quinoxaline)s, poly (phthalazinone ether ketone)s, poly (benzimidazole)s, and some aromatic or heteroaromatic materials systems, polyimides and poly(arylene ether sulfone)s are good alternative membranes in PEMs. These backbones would increase the hydration without being hydrolytically sensitive membranes. Inorganic poly(phosphazene) as PEMs have gained huge attention as it can be easily synthesized and modified. But these membranes generally display low value of glass transition temperature and low mechanical properties which are most important in the fuel cell technology. Fuel cell technology can be further advanced by using advanced materials as PEMs and these include composites materials. Further developments are being carried out by emphasizing the fabrication and designing of stacks by using current or new materials and new materials must fulfil the present day demand of this technology.