SYNTHESIS OF IONIC POLYMERS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS AND VISCOSITY MODIFICATIONS

BY

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(الحمد لله اللذي بنعمته تتم الصالحات)

All praise and glory be to Allah for his limitless help and guidance. Peace and blessings of Allah be upon his prophet Mohammed.

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DISSERTATION ABSTRACT

Name: Nedal Y. M. Abu-Thabit

Title: Synthesis of Ionic Polymers for Proton Exchange Membrane Fuel Cells and Viscosity Modifications

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The cycloterpolymerizations of hydrophilic monomer (1,1-Diallyl-4-formylpiperizinium chloride) with hydrophobic monomer (diallyloctadecylammonium chloride) and sulfur dioxide in dimethyl sulfoxide using azobisisobutyronitrile (AIBN) as the initiator afforded a series of water-soluble monocationic polyelectrolytes (MCPEs) in well over 90% yields. The solution properties of the resultant series of interconverting polyelectrolytes (MCPE→DCPE↔BCPE) were investigated. The DCPEs exhibited sharp increase in viscosity in salt (NaCl)-added solution as compared to salt-free water. The pH-responsive BCPE is shown to demonstrate better associative properties in the absence of HCl. In addition, a tremendous increase in the viscosity values of the DCPE was observed in the presence of cationic surfactant.

The zwitterionic monomer, ethyl 3-(*N*,*N*-diallylammonio)propanephosphonate, was cyclopolymerized in aqueous solution using azobisisobutyronitrile or ammonium persulfate as initiators to afford a polyphosphonobetaine (PPB), a zwitterionic polymer. The polymers, on treatment with HCl and NaOH, gave the aqueous solutions of the corresponding cationic polyphosphononic acid (CPP) and anionic polyphosphonate (APP). The solution properties of the PPB having two pH-responsive functionalities were investigated in detail by potentiometric and viscometric techniques. Basicity constants of the amine groups in APP were found to be "apparent" and as such follow the modified Henderson-Hasselbalch equation. The PPB showed 'antipolyelectrolyte'solution behavior.

The synthesis of phosphonated polysulfone was performed by a post phosphonation method utilizing the Michaels-Arbuzov reaction. High degree of phosphonation up to150 % was achieved. The obtained membranes/polymers in the ester form were hydrolyzed by refluxing in aqueous hydrochloric acid. The high level of phosphonic acid content 150% led to high water uptake level 52 wt % which is necessary to reach high proton conductivity values. The synthesized membranes with highest phosphonic acid content 150% reached 12 mS/cm at 100 ºC under fully hydrated conditions and showed low methanol crossover (9.12×10^{-8} cm^2/s) compared to Nafion 117 membranes.

Also, the synthesized phosphonated polysulfones in their ester and acid forms with degree of phosphonation up to 1.0 were utilized for the preparation of polymer blend with sulfonated poly(etheretherketone). Ionic networks were formed through hydrogen bonding bridges between the strong sulfonic acid groups and the amphoteric phosphonic acid groups. This ionically crosslinked polyelectrolyte membranes showed enhanced properties in terms of water swelling, methanol uptake, methanol permeability and thermal stability without loss of proton conductivity.

Doctor of Philosophy in Chemistry
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ملخص الرسالة

الاســـــــــــم: نضـــال يوســف محـــمد أبو ثابـــت.

عنوان الرسالة: تصنيع مبلمرات أيونية لتطبيقات الأغشية الأيونية لخلايا الطاقة والتعديل والتحكم باللزوجة.

التخصـــــــص: الكيـــميـــاء

تاريخ التخرج : مـــايـــو 2010

وcycloterpolymerizations من ماء مونومر كلوريد 1،1 - Diallyl - 4 - formylpiperizinium) مع مونومر فعال جدا (كلوريد diallyloctadecylammonium) وثاني أكسيد الكبريت في sulfoxide ثنائي ميثيل باستخدام azobisisobutyronitrile (AIBN) باعتباره المبادر المعطاة في سلسلة من محلول كهربائي ذو وزن جزيئي مرتفع monocationic للذوبان في الماء (MCPEs) في ما يزيد عن 90 ٪. وقد تم التحقيق في خصائص حل البوليمر الناتج من interconverting محلول كهربائي ذو وزن جزيئي مرتفع (DCPE → MCPE ↔ BCPE). وعرضت DCPEs الزيادة الحادة في اللزوجة في الملح (كلوريد الصوديوم) المضافة حل بالمقارنة مع المياه المالحة خالية. ويرد BCPE الرقم الهيدروجيني التي تستجيب لشرح خصائص النقابي على نحو أفضل في حالة عدم وجود حمض الهيدروكلوريك. وبالإضافة إلى ذلك ، زيادة هائلة في القيم اللزوجة من DCPE في حضور السطحي الكاتيوني.

وكان cyclopolymerized مونومر zwitterionic ، إيثيل 3 -- (ن ، ن ، diallylammonio) propanephosphonate ، في محلول مائي باستخدام فوق كبريتات الأمونيوم azobisisobutyronitrile أو كما بادرت إلى تحمل polyphosphonobetaine (جزء في البليون) ، والبوليمر zwitterionic. والبوليمرات ، في المعاملة مع حمض الهيدروكلوريك وهيدروكسيد الصوديوم ، أعطى المحاليل المائية للحمض المقابلة polyphosphononic الكاتيوني (CPP) وpolyphosphonate الأنيونية (APP). خصائص حل جزء في البليون وجود اثنين من جرى التحقيق في وظائف الرقم الهيدروجيني التي تستجيب للتفصيل تقنيات فرق الجهد وتحليل اللزوجة. تم العثور على الثوابت قاعدية المجموعات أمين الوكالة في أن تكون "واضحة" ، وعلى النحو التالي هذه المعادلة هندرسون وHasselbalch تعديل. وأظهر PPB antipolyelectrolyte'solution' السلوك.

وقد أجريت توليف سلفون phosphonated من قبل وظيفة طريقة phosphonation الاستفادة من رد فعل مايكلز - Arbuzov. ارتفاع درجة phosphonation تم تحقيقه حتى to150 ٪. الأغشية التي تم الحصول عليها / البوليمرات في شكل استر وتحلل من قبل refluxing في حمض الهيدروكلوريك المائية. على مستوى عال من محتوى حمض الفوسفونيك 150 ٪ أدى إلى ارتفاع منسوب المياه امتصاص 52 ٪ بالوزن وهو أمر ضروري للوصول إلى ارتفاع قيم التوصيل البروتوني. الأغشية توليفها مع أعلى محتوى حمض الفوسفونيك بلغت 150 ٪ 12 ملي / سم عند 100 درجة مئوية تحت ظروف رطبة تماما وأظهرت انخفاض نفادية الميثانول (9.12 × 10 $^{-8}$ cm^2 / ث) بالمقارنة مع أغشية Nafion 117.

أيضا ، واستخدمت في تصنيعه polysulfones phosphonated في شكل حمض مع درجة تصل إلى 1.0 phosphonation لإعداد البوليمر مع مزيج (SPEEK). وتم تشكيل شبكات أيونية عبر الجسور من خلال الرابطة الهيدروجينية بين المجموعات حامض السلفونيك القوي والمجموعات المترددة من amphoteric حامض الفوسفونيك. وأظهرت هذه الأغشية polyelectrolyte crosslinked ionically تعزيز الخصائص من حيث امتصاص المياه ، وامتصاص الميثانول ، ونفادية الميثانول والاستقرار النفاذية الحرارية من دون خسارة كبيرة في الموصلية البروتونية.

دكتوراه في العلوم الكيميائية
جامعة الملك فهد للبترول والمعادن
الظهران – السعودية
مايو 2010

CHAPTER 1

1. INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Ionic polymers are those polymers bearing ionic groups in the polymer backbone. The ionic groups can be can be sulfonic acid ($-SO_3H$) or phosphonic acid ($-PO_3H_2$) groups. Ionic polymers have a variety of applications. Forexample, the acidic groups in the ionic polymers can serve as cationic exchanger to replace sodium, calcium and magnesium ions during the water softening process. An interesting applications of ionic polymers are in the area of Enhanced Oil Recovery (EOR) and Polyelectrolyte Membrane Fuel Cells (PEMFCs) **Fig. 1.1**

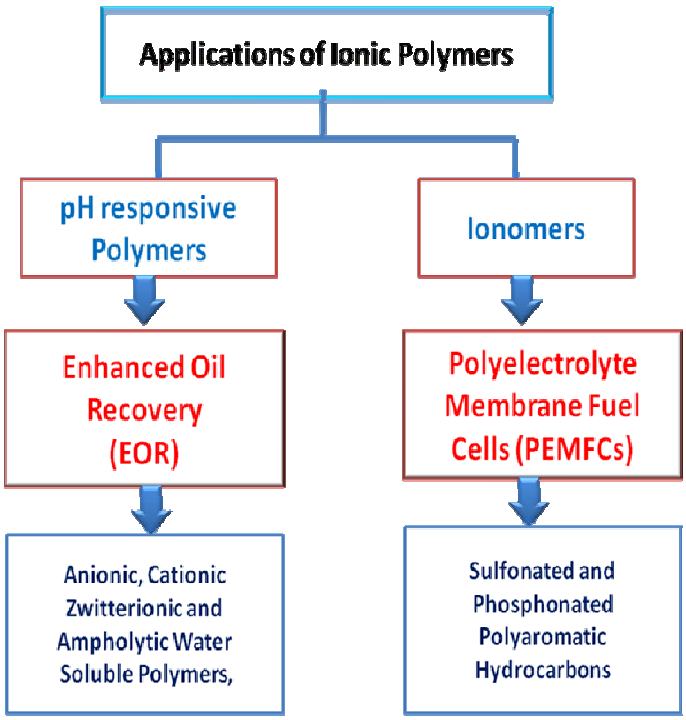


Fig. 1.1 Potentail Applications of Ionic Polymers.

1.1.1 pH Responsive Polymers :

pH responsive polymers are ionic polyelectrolytes which have different properties at different pH values. A special class of the pH responsive polymers which known as "Associative Polyelectrolytes" can be utilized for the enhanced oil recovery (EOR) applications **Fig. 1.2**. These associative polyelectrolytes have hydrophobic pendant groups in their backbone. These hydrophobes can associate in the presence of specific brine to give high viscosity. During the primary and secondary oil recovery, only about one third of the oil can be recoverd from thr oil well. However, one can reach above 50% oil recovery if the tertiary oil recovery is applied. In the tertiary recovery process, polymer-flooding is utilized to enhance the oil recovery by injecting associative water-soluble polymers with high viscosity which lead to an efficient displacement of the moderately viscous oil**.**

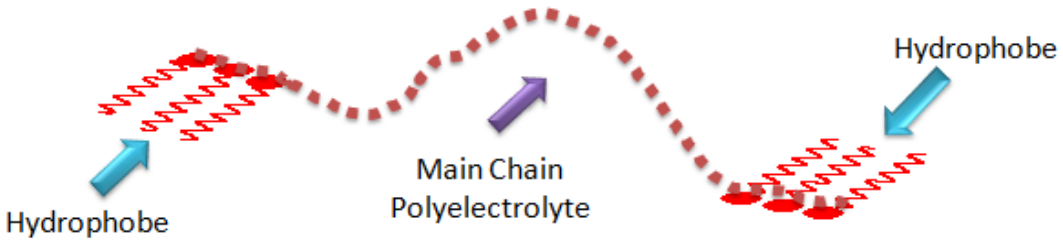


Fig. 1.2 Associative Polyelectrolytes with Hydrophobic Groups

1.1.2 Ionomers :

Ionomers are special kind of ionic polyelectrolyte. First of all, they are copolymers. They contain both nonionic repeat units, and a small amount of ion containing repeat units (< 15% of the ionomer) as shown in **Fig. 1.3.**

Ionomers can be used as solid electrolytes or proton exchange membranes for Polyelectrolyte Membrane Fuel Cells applications (PEMFCs). A well known ionomer for PEMFCs is Nafion® with structure shown in **Fig. 1.4.** A major breakthrough in PEMFC technology came with the advent of perfluorosulfonic acid Nafion® membranes. These membranes provided improved chemical stability and an increase in conductivity compared to the sulfonated polystyrene membranes. The performance

and lifetime of PEMFCs have significantly improved since the introduction of Nafion® in 1966 by DuPont. Nafion® is the most widely studied PEM because it possesses high proton conductivity, good mechanical strength, excellent stability, and is commercially available.

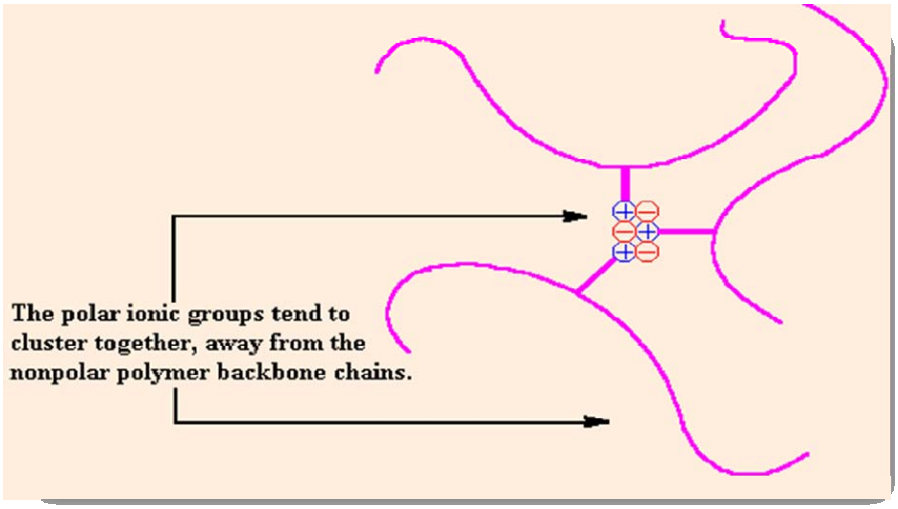


Fig. 1.3 Representation Ionomers as Polyelectrolytes

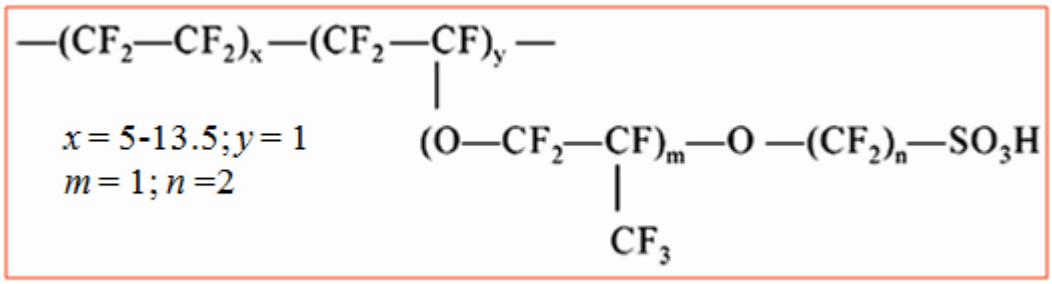
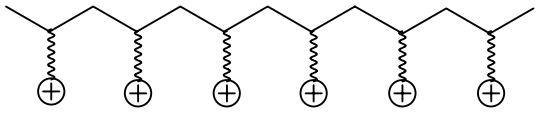


Fig. 1.4 Chemical Structure of Nafion®

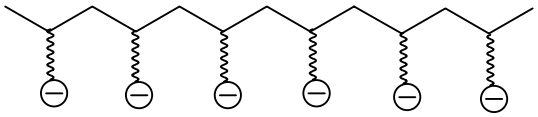
1.2 LITERATURE REVIEW

1.2.1 Synthesis of Ionic Polymers for Viscosity Modifications:

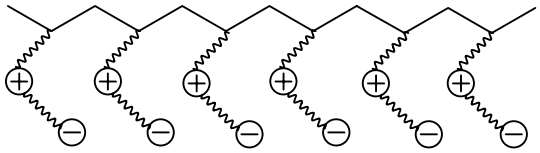
There has been considerable academic as well as industrial interest in the preparation and properties of water-soluble ionic polymers (Scheme 1).



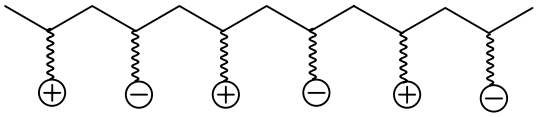
Cationic polyeletrolytes



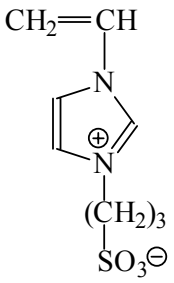
Anionic polyeletrolytes



Zwitterionic polyeletrolytes



Polyampholytes



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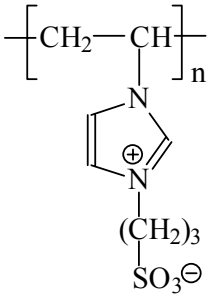
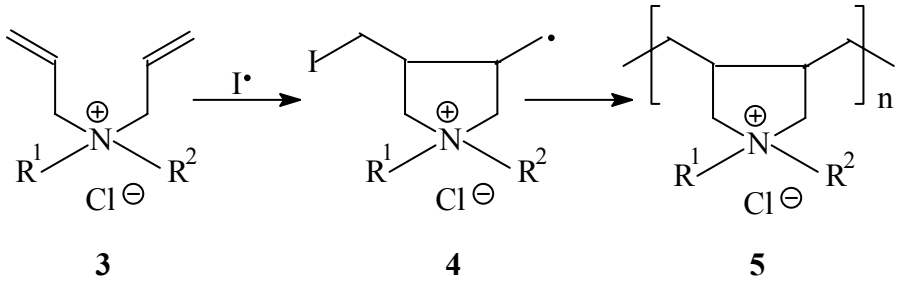


2

Scheme 1.

Among a plethora of water-soluble polymers, cationic quaternary ammonium polyelectrolytes have etched a place of distinction due to their diverse commercial applications. Pioneering work by Butler and co-workers [1] led to the polymerization of a variety of diallyl quaternary ammonium salts **3** via an intra- and inter-molecular chain

propagation (termed cyclopolymerization) through the five-membered cyclic structure **4** to yield linear water-soluble polymers **5** (Scheme 2).

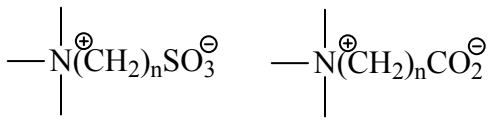


3 **4** **5**

Scheme 2.

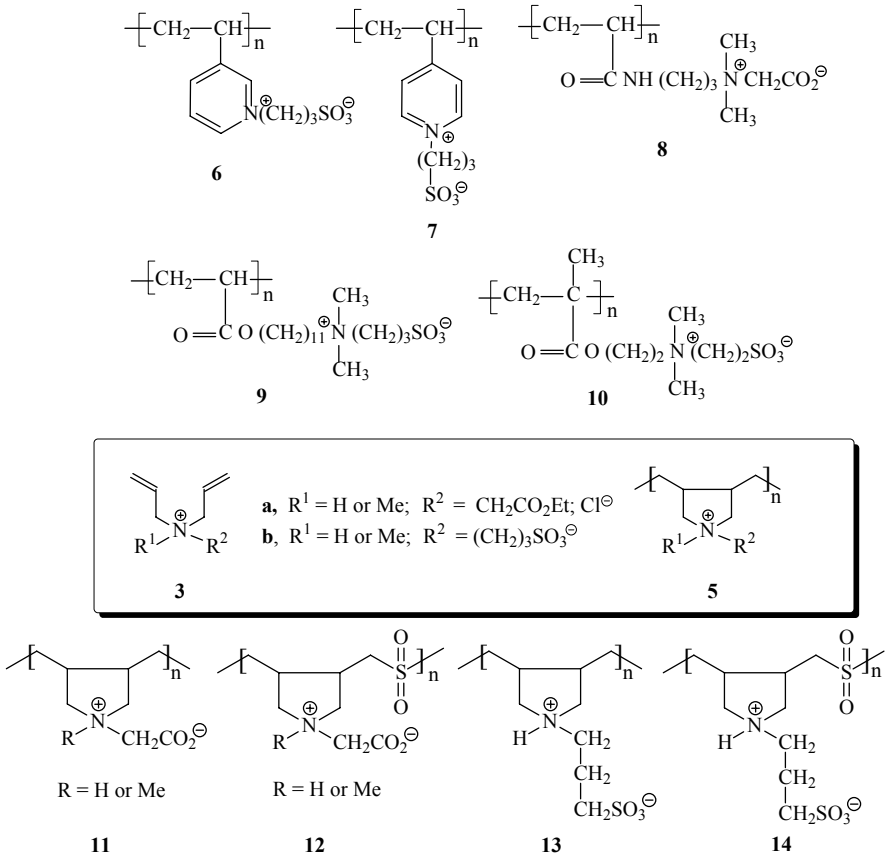
Homo- and co-polymers of diallyl-dialkylammonium salts have found extensive industrial and commercial applications. Polydiallyldimethylammonium chloride alone accounts for over 1000 patents and publications. [2,3] Quaternary ammonium salts (**3**)-sulfur dioxide copolymers are also manufactured commercially and are useful as textile furnishes, polymer additives, coagulants and thickeners. Further inroad into the water-soluble polymers has been reported [4-6] which describes the synthesis of a novel class of piperazine-based homo- and co-polymers containing quaternary as well as trivalent nitrogen in the same polymer.

Some of the representative examples of polyzwitterions **(6-14)** [7-20] are given in Scheme 3. The cyclopolymerization [13-16,17,18,20] of the monomers **3** gave zwitterionic/or cationic homocyclopolymers **5** or cyclocopolymers [16,19]with SO_2. The polymers **5** or **5**/SO_2 which were then hydrolyzed to their corresponding anionic or zwitterionic polyelectrolytes **11-14.** Polyvinylbetaines of the types



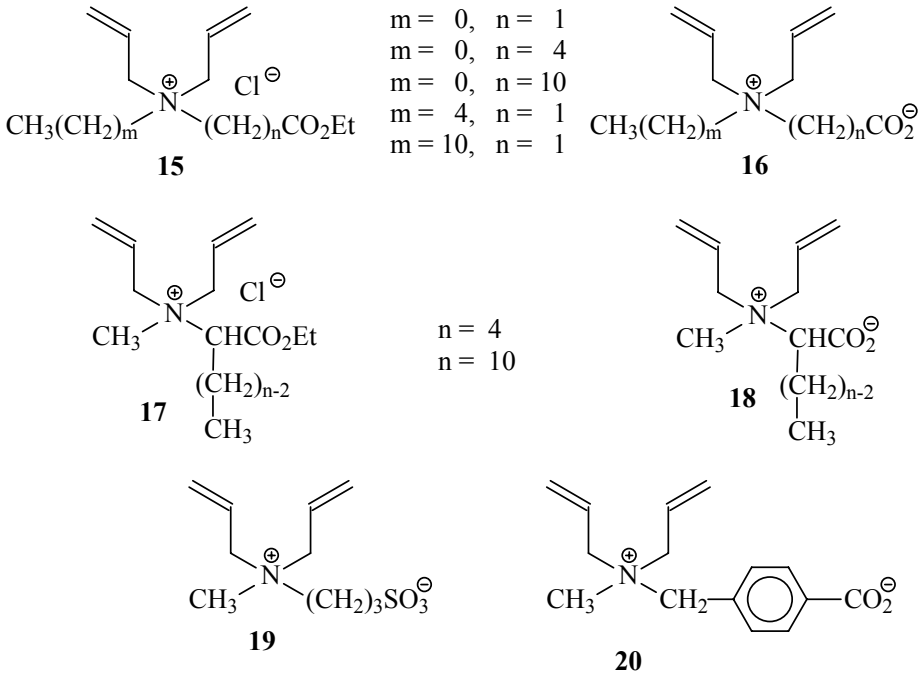
show "antipolyelectrolyte behavior". In contrast to the normal polyelectrolytes, viscosity of the ampholytic (zwitterionic) polymers is known to increase with increasing

concentration of added salt (like NaCl). Water solubility is promoted by electrolytes, which disrupt the intra- and inter-molecular ionic or dipolar network [21,22]. The increase in viscosity, which is observed in the presence of brine (anti-polyelectrolyte behavior), make the polyampholytes ideal candidates for high salinity media and attractive in view of possible applications in enhanced oil recovery . It is to be noted that the viscosity of polyelectrolytes decreases drastically in presence of salt like NaCl.



Scheme 3

A series of new polycarbobetaines from monomers **15-20** is synthesized varying the length and the position of the hydrophobic side chains; together with the cationic analogs [23]. The polycarbobetaines form homogeneous blends with selected inorganic salts, to provide organic-inorganic hybrid materials (Scheme 4).



Scheme 4.

1.2.1.1 Ionic polymers: hydrophobically associating ionic polymers

Hydrophobically associating polymers derived from copolymerization of hydrophilic monomer **3** having small R groups (Scheme 2) and a few mole percent of hydrophobic monomer **3** having long R groups, may have potential application in enhanced oil recovery (EOR) and other applications where viscosification of water is of interest . Interchain hydrophobic association of pendant long chain alkyl group leads to dynamic structure in aqueous solution and pseudo high molecular weight polymer **(Fig. 1.5).**

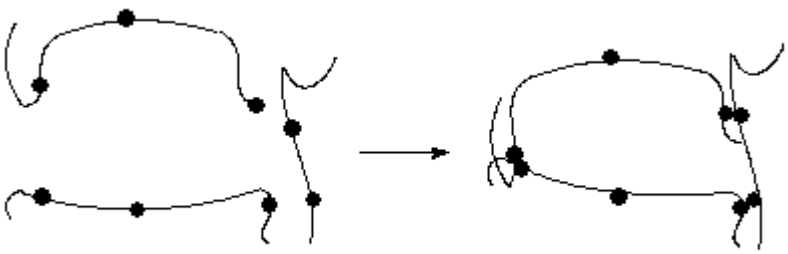
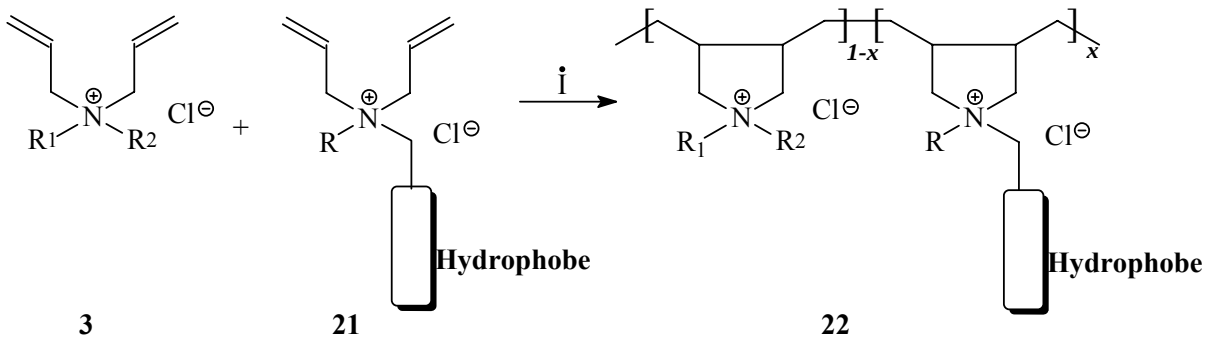


Fig. 1.5 Hydrophobic association of pendant (●) groups leading to increased hydrodynamic volume and viscosity.

In recent years, an increasing number of studies have focused on the hydrophobic association of water-soluble polymers [24,25]. The copolymerization of a water-soluble monomer with a few mole percent of a hydrophobic comonomer in a miceller system [26-29] results in a random distribution of the hydrophobic monomer as small blocks in the hydrophilic polymer chain. Although acrylamide is mostly used as the main water-soluble monomer, the miceller polymerization process has also been used in the synthesis of hydrophobically modified polyelectrolytes and polyampholytes using suitable ionic comonomer [29-32]. Above a certain polymer concentration (called association concentration) in aqueous solution, intermolecular associations of the hydrophobic groups lead to a reversible formation of three-dimensional physical network of polymer chains [33-36].

There are a few reports, which described the synthesis of associating ionic copolymers prepared by Butler's cyclopolymerization technique (Scheme 5). Cyclopolymerization of hydrophilic and hydrophobic diallyl monomers in such a high concentration has been reported to yield a random copolymer rather than a microblocky copolymer even though the hydrophobic monomer possesses surfactant properties.



3 **21** **22**

Scheme 5.

1.2.2 Synthesis of Ionic Polymers for Proton Exchange Membrane Fuel Cells.

1.2.2.1 Commercially Available Proton Exchange Membranes (PEMs):

NASA employed a PEMFC on the Gemini program as an auxiliary power source, which initially used crosslinked sulfonated polystyrene as the membrane. This copolymer possessed insufficient oxidative stability under operating conditions. A major breakthrough in PEMFC technology came with the advent of perfluorosulfonic acid Nafion® membranes. These membranes provided improved chemical stability and an increase in conductivity compared to the sulfonated polystyrene membranes. The performance and lifetime of PEMFCs have significantly improved since the introduction of Nafion® in 1966 by DuPont. Nafion® is the most widely studied PEM because it possesses high proton conductivity, good mechanical strength, excellent stability, and is commercially available. The high electronegativity of the fluorine atoms bonded to the same carbon atom as the sulfonic acid group makes the $-SO_3H$ a superacid. The Teflon-like backbone (~87% in Nafion 1100) provides Nafion with excellent oxidative stability at the cathode and also at the anode, which may generate small amounts of hydrogen peroxide. The most dramatic result obtained using Nafion® was that the lifetime of the PEMFCs increased by at least four orders of magnitude over

previous membranes. It has been reported that a lifetime of over 50,000 hours has been achieved at 80 ^{o}C. One of the major drawbacks of perfluorosulfonic acid membranes has been and still is their high cost (~\$700/m^{2} for films). This high cost is due to the expensive fluorinated comonomer. Further more, Nafion still suffer from high methanol cross over which limits the efficiency of the fuel cell.

1.2.2.2 Importance of the Proposed research and Justification

Proton exchange membrane (PEM) fuel cells are becoming increasingly important as alternative energy sources for stationary, automobile and portable power. This is evident by the recent presidential Hydrogen Fuel Initiative to reverse the United States' growing dependence on foreign oil by developing commercially viable clean, hydrogen-power fuel cell technology. In 2003, the United States consumed an average of 20 million barrels of oil and natural gas per day, or 7.3 billion barrels per year. U.S. oil reserves total 22.7 billion barrels, which would last less than eight years at today's rates of consumption and imports, and gasoline for cars and light trucks accounts for about 45% of U.S. oil consumption. The need for viable alternative energy conversion technology is obvious. Proton exchange membrane fuel cells generate more power for a given volume or weight of a hydrogen-air fuel cell than any other type of fuel cell. This high-power density characteristic has the potential to be compact and lightweight. In addition, the operating temperature is less than 120 ºC, which allows rapid start-up. These traits and the ability to quickly

change power output are some of the characteristics that make the proton exchange membrane fuel cell the top candidate for several power applications. In addition, proton exchange membrane fuel cells have drawn a lot of attention because of their high efficiencies, quiet operation, use of fuel from totally renewable resources, and environmentally friendly processes. Ideally, the only byproduct of a hydrogen-powered PEM fuel cell is water. However, there are many challenges that face materials scientists to prepare catalysts layers and polymeric materials that can operate under the aggressive in-cell environment for long times. It is recognized in the fuel cell industry that cost is still the major issue. Reduction of cost and improved performance are two major goals of almost all companies working on this technology. Most of these organizations are working to adapt current technology, which is typically accomplished in small steps, but bold improvements are needed. One such approach is to completely replace the costly perfluorinated sulfonic acid membranes such as Nafion® with *novel polymeric systems*. Heterocyclic polymers are used in many areas such as microelectronics, automotive, structural adhesives and aerospace industries due to their excellent thermal and chemical resistance and superior mechanical integrity. These properties suggested that appropriate heterocyclic aromatic polymer systems should be good candidates for proton exchange membranes.

1.2.2.3 Sulfonated Polymers:

1.2.2.3.1 PEM's based on Sulfonated Poly(arylene ethers):

In general, post-sulfonated poly(arylene ether sulfone) copolymers, have one randomly placed sulfonic acid per repeat unit on the activated phenyl ring of the polymer. Also, materials derived from bisphenol A are susceptible to acid catalyzed hydrolysis. Two methods have been reported to place the sulfonic acid groups on the deactivated sites of the repeat unit. By having the sulfonic acid groups on deactivated rings, the final polymer may have improved stability and possibly higher acidity due to the electron-withdrawing sulfone group. The first method is a metalation-sulfination-oxidation process used by Kerres *et al.* [37], and is discussed in the Post-Sulfonation section below. However, post-functionalization of polymers is difficult to control and may lead to side reactions. An improved method was described by Ueda *et al.* [38], where disulfonated poly(arylene ether sulfone) copolymers were synthesized from a sulfonated monomer, 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS).

The preparation of SDCDPS was previously reported as a flame retardant additive for poly(arylate)s [39]. Ueda *et al.* [38] reported the general conditions for the sulfonation of 4,4'-dichlorodiphenylsulfone (DCDPS) to SDCDPS; however, the potential applications were not discussed. More recently, Wang et al. modified this procedure to synthesize high molecular weight wholly aromatic disulfonated

poly(arylene ether sulfone) copolymers.The preparation of SDCDPS was previously reported as a flame retardant additive for poly(arylate)s [39,40]. Two other sulfonated monomers for poly(arylene ether) synthesis have been reported, and are shown in **(Fig. 1.6, 1.7)**. The first, SDFDPS, was prepared by Wang et al. Fluorine is a better leaving group for the nucleophilic displacement reaction used for poly(arylene ether) synthesis, and allowed higher molecular weight materials to be synthesized at lower temperatures. The second monomer, sodium 5,5'-carbonylbis(2-fluorobenzenesulfonate) (SDFK) was synthesized for poly(aryl ether ketone)s [41]. Several disulfonated poly(arylene ether ketone) copolymers were prepared from SDFK, and the solubility and thermal properties of the resulting polymers are discussed [42].

Direct copolymerization offers several advantages over the post-sulfonation reactions, including ease of control over the degree of sulfonation by varying the ratio of sulfonated to nonsulfonated monomers, degradation-free preparation, and the lack of cross-linking reactions. Wang *et al.* [43] recently made significant progress by preparing wholly aromatic sulfonated poly(arylene ether sulfone)s by direct copolymerization**.** These copolymers are synthesized via a high temperature nucleophilic substitution reaction of SDCDPS, DCDPS, and 4,4'-biphenol **(Fig. 1.8)**. The random wholly aromatic disulfonated copolymers were prepared with up

Figure 1.6 Sulfonated activated aromatic di-halide monomers for poly(arylene ether) Synthesis

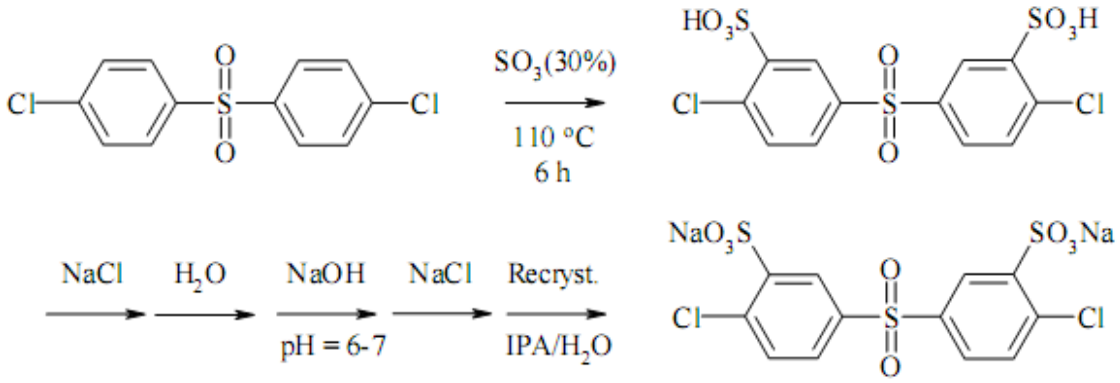


Figure 1.7 Disulfonation of 4,4'-dichlorodiphenylsulfone (DCDPS) to 3,3'-disulfonate-4,4'- dichlorodiphenylsulfone (SDCDPS) [43].

to 1.2 sulfonic acid groups per repeat unit [44]. The copolymers are polymerized in the sulfonate salt form, cast into films and were subsequently acidified. Either a room temperature acidification method (Method 1) or a boiling acidification method (Method 2) was used to convert the sodium sulfonate groups to sulfonic acid moieties [45]. The initial degree of disulfonation was unchanged by the different acidification treatment methods. It was shown that the sulfonic acid

groups were successfully introduced into the copolymers without any side reactions, and the acidification treatment did not induce any further sulfonation.

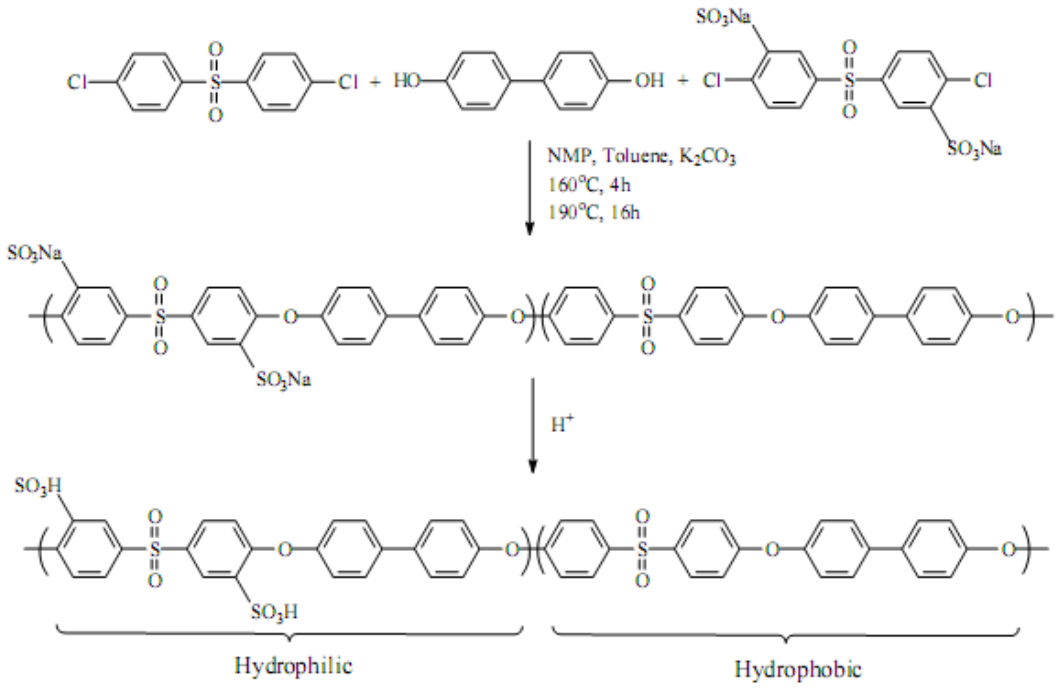


Figure 1.8 Direct copolymerization of wholly aromatic BPSH copolymers [44].

The successful introduction of sulfonic acid groups was confirmed by IEC, FT-IR, and TGA. The experimental IEC values agreed with the calculated IEC values, which were based on the molecular structure of the copolymer. The copolymers from 10-50% disulfonation have essentially no weight loss until 300 ^{o}C, a feature that compares favorably to the weight loss behavior of Nafion 1135®. DSC data showed that the sulfonic acid groups had two large effects on the glass transition temperature. An ionomer effect and an increase in molecular bulkiness of the

sulfonate group caused an increase in T_g as the degree of disulfonation increased. Additionally, above 50% disulfonation for membranes prepared by Method 1, two T_gs were noticed. The water uptake, atomic force microscopy (AFM), and DSC data show that there is a percolation threshold at 50% disulfonation. By Method 1 acidification, the water uptake data increased almost linearly and then increased abruptly to 180% for 60% disulfonation. A major increase in water uptake was noted for membranes acidified by Method 2 and subsequently the percolation threshold decreased. In addition, conductivity values near or above those of Nafion® have been shown. An increase in conductivity in membranes prepared by Method 2 compared to those prepared by Method 1 was noticed. This effect may be attributed to the higher water uptake values or the more open morphology observed by AFM.

Another series of wholly aromatic copolymers from SDCDPS has been synthesized using commercially available hydroquinone in place of biphenol. These polymers exhibited higher IECs at the same degree of disulfonation, and thus higher conductivity. Although the conductivity of these polymers was enhanced, the water uptake values also increased and the percolation threshold decreased [46].

Additional work has focused on alternate sulfonated poly(arylene ether sulfone) copolymers. Udel-type (commercial name of Solvay Advanced Polymers)

sulfonated copolymers were synthesized from Bisphenol-A, SCDCDS, and DCDPS. Although these polymers were more economical due to the inexpensive Bisphenol-A monomer, the aliphatic groups may not withstand acidic and or oxidative fuel cell conditions. Utilizing Bisphenol-AF, partially fluorinated copolymers were synthesized. The introduction of fluorine into the random copolymer backbone enhanced the surface characteristics of these polymers. The fluorine groups in these copolymers self-assemble to create a highly fluorinated surface, which may make them interesting candidates for bonding to the cathode catalyst layer. Water is produced at the cathode during fuel cell operation and at the same time oxygen needs to permeate through the cathode to catalyst sites. The hydrophobicity of the fluorine-containing copolymer may help reduce water swelling in the cell [46].

Block copolymers of BPSH and either poly(arylene ether phosphine oxide) or polyimides were prepared [47,48]. The BPSH copolymers have high water uptake values at high degrees of sulfonation that lead to a reduction in the mechanical properties. This swelling may be reduced by adding a hydrophobic block to a highly sulfonated BPSH block, while maintaining high ionic conductivity. A hydrophobic poly(arylene ether phosphine oxide) (PEPO) with a molecular weight of 5,000 g/mol and hydroxyl end-groups was synthesized and characterized. Then a 100% sulfonated chlorine-terminated BPSH (BPS-100) copolymer, which also

has a molecular weight 5,000 g/mol, was prepared. The PEPO was added directly to the BPS-100 polymerization to obtain a high molecular weight sulfonated block copolymer shown **(Fig. 1.9)**. Each carbon in the block copolymer showed a strong single ^{13}C NMR peak with a weak shoulder, indicating the block structure with the shoulder peak corresponding to the connecting point of the two segments.

Several sulfonated poly(arylene ether sulfone)-block-polyimide copolymers were prepared with various block lengths [49]. In the nucleophilic substitution reaction of SDCDPS and biphenol, calculated amounts of *m*-aminophenol were added to end-cap the polymers at desired molecular weights. The molecular weight of the amine end-capped oligomers was verified by ^{1}H NMR and end-group titration. The diaminotelechelic sulfonated segment was then reacted with several dianhydrides and diamines to produce multiblock, hydrophobic polyimide-hydrophilic sulfonated polyarylene ether copolymers. A series of tough, film-forming segmented copolymers was prepared and characterized. It was concluded that the segmented or block systems have the potential to enhance certain desirable PEM characteristics in fuel cells, particularly those related to swelling, retention of mechanical strength at elevated temperatures, and critical adhesion issues in membrane electrode assemblies.

Besides sulfonated poly(arylene ether sulfone)s, sulfonated poly(arylene thioether sulfones)s and poly(phthalazinone ether sulfone)s were also synthesized [50,51].

Sulfonated poly(arylene thioether sulfone)s were prepared from SDFDPS, DFDPS, and 4,4'-thiobenzenethiol.40 High molecular weight copolymers were obtained and tough films of the acid form were produced. Future work includes utilizing SDCDPS as the sulfonated dihalide, studying the methanol permeability and morphological features of these polymers for comparison to the BPSH series. Sulfonated poly(phthalazinone ether sulfone) copolymers were prepared by direct copolymerization from SDFDPS, difluorodiphenylsulfone (DFDPS), and 4-(4-hydroxyphenyl)phthalazinone (HPPT) [51]. The swelling of these polymers was in the range of 14.0-22.9% for 20-40% disulfonation. This low degree of swelling originates from the hydrogen bonding between hydrogen atoms of the sulfonic acid groups and the carbonyl groups of HPPT. However, the hydrolytic stability of these materials was not reported.

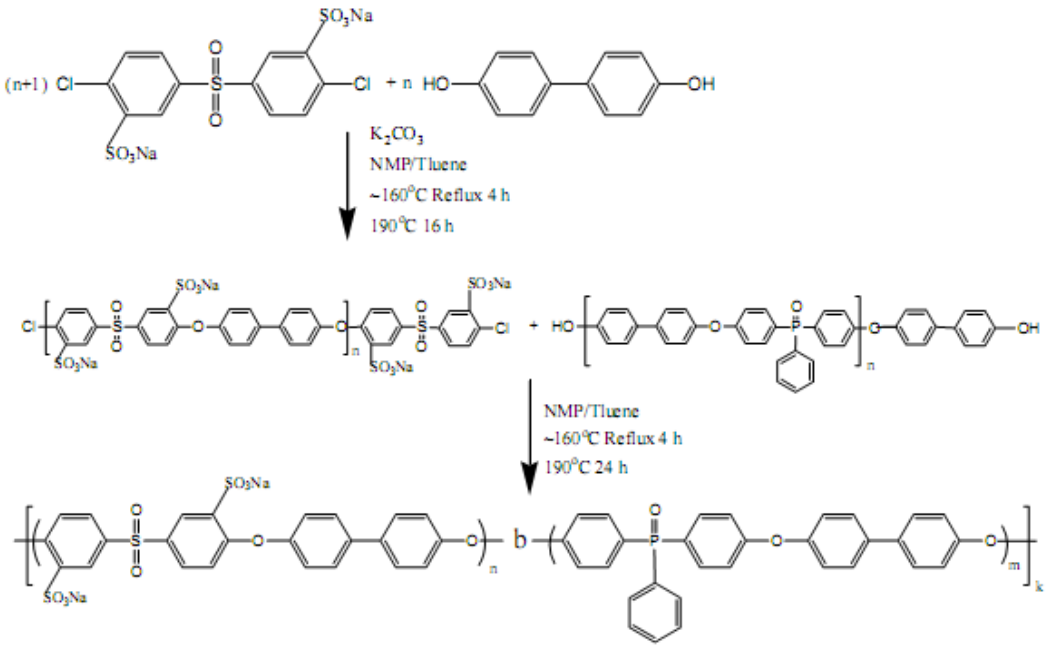


Figure 1.9 Synthesis of sulfonated poly(arylene ether sulfone)-b-poly(arylene ether phosphine oxide) (5k/5k) [47].

1.2.2.3.2 PEM's based on Sulfonated Poly(imides):

Five-membered ring polyimides are high performance thermally stable materials that have been investigated for many years [52]. However, when sulfonated five membered ring (phthalic) polyimides are used for proton exchange membranes in fuel cells, they quickly degrade and become brittle, whereas six-membered ring (naphthalenic) polyimides do not. It is likely that hydrolysis of the phthalimide structure under strong acid conditions quickly leads to chain scission and causes the membrane to become brittle [53]. Since the six-membered ring of the naphthalenic polyimide is much more stable to hydrolysis, this membrane is better suited for fuel cell applications [54]. It was reported that a sulfonated six-membered ring polyimide was stable for over 3000 hours at 60 ^{o}C and that it performed as well as Nafion 117® under fuel cell conditions [55].

To date, the synthesis of sulfonated six-membered ring polyimide copolymers has been by a direct copolymerization procedure. This approach requires that a sulfonated monomer is used in the copolymerization, as opposed to sulfonation of the parent polymer. Stoichiometric amounts of sulfonated diamine relative to nonsulfonated diamine, and NDA as the dianhydride, have been used for sulfonated copolyimide synthesis. A 1:1 stiochiometric ratio of total diamine to dianhydride was used to obtain high molecular weight polymer. The degree of sulfonation could be varied by changing the ratio of sulfonated to nonsulfonated

diamine. The copolymerizations were always a one-step high temperature polycondensation in *m*-cresol; however, the catalysts employed have been varied. In all cases, the triethylammonium salt form of the sulfonated diamine is used to synthesize high molecular weight polyimides. The acid and sodium sulfonate forms of most diamines are insoluble in *m*-cresol. By adding triethylamine to a sulfonated diamine in *m*-cresol at room temperature for about 4 hours, the triethylammonium salt form of the sulfonated diamine was formed which was soluble in the reaction media. Also, the free uncomplexed aromatic amine will be more reactive. Usually, benzoic acid is used as catalysts for imide formation.

1.2.2.4 PEM's Based on Phosphonated Polymers

1.2.2.4.1 Preparation of Phosphonated Ionomers by Chemical Modification

One attractive way to achieve such ionomers is by chemical modification of commercially available polymers. Chemical modification offers a versatile route to introduce acidic units either directly on the polymer main chain, or on side chains to the polymer main chain, and has recently been reviewed [56]. In general, polymers undergo the same reactions as their low-molecular-weight analogs, and it is generally assumed that the reactivity of a functional group is in the same range regardless if it is placed on a small molecule or a polymer, as long as the reaction is carried out under homogeneous conditions under the appropriate

conditions. Several considerations have to be taken into account in the choice of an efficient chemical reaction to modify a polymer: (1) high yields are required in order to achieve high levels of modification, (2) the concentration of the reagent within the polymer coils in solution is important for the overall rate of reaction, (3) the polymer may precipitate from the reaction media as the reaction proceeds, thereby limiting the extent of modification, (4) side reactions may result in crosslinked polymers, (5) sterical hindrance will affect the polymer reactivity, especially if the functional group is close to the polymer main chain, (6) neighboring-group effects of already reacted segments on the remaining reactive sites might be detrimental . The phosphonation of a number of common polymers

has been studied so far, usually with the aim to enhance solubility in different solvents or to improve polymer–polymer miscibility [58].

The use of chloro- or bromomethylated polymers as precursors for the preparation of phosphonated polymers has attracted a lot of attention.

Indeed, such groups may readily be converted to alkyl phosphonates by using the well-established Michaelis–Arbuzov and Michaelis–Becker. In an early work by Cabasso and co-workers, the Michaelis–Arbuzov reaction was employed to prepare phosphonated Polystyrene (PS) and poly(phenylene oxide) (PPO) to be used in desalination processes **Fig. 1.10** [58]. The two polymers are of particular interest since aromatic polymers have the basic stability to serve as backbone polymers for alternative ionomers to the commonly used Nafion® ionomer. First, Cabasso et al. investigated the bromination of PPO and the chloromethylation of PS in order to introduce the halogenated sites needed for the subsequent modification via reaction with triethyl- or trimethylphosphite. In the case of PS, the desired modification was difficult to achieve due to gelation and formation of insoluble products.

However, by choosing a polydentate etheral solvent (such as diethyl carbitol) the gelation was avoided. Concerning the phosphonation of PPO the authors reported no problems with crosslinked products and the introduction of up to two phosphonate ester groups per repeating unit of the PPO was achieved. Xu and

Cabasso [58] also investigated the use of phosphonated PPO as a proton conducting material for fuel cells.

Lafitte and Jannasch have attempted the phosphonation of PSUs via lithiation and reaction with chlorophosphonic acid esters **Fig. 1.11** [59].

In a recent study, Lafitte and Jannasch have also prepared PSUs carrying benzoyl(difluoromethylenephosphonic acid) side chains **Fig. 1.12** [60]. In the first step, PSUs were lithiated and reacted with methyl iodobenzoates to prepare p- and o-iodobenzoyl PSUs. Next, the Phosphonated PSUs were prepared via CuBr-mediated cross-coupling reactions between the iodinated polymer and the [(diethoxyphosphinyl)difluoromethyl] zinc bromide. Finally, dealkylation using bromotrimethylsilane afforded the highly acidic -CF_2-P(O)(OH)2 derivatives. The replacement of the iodine atoms by -CF_2-P(O)(OEt)2 units was found to be almost quantitative in the case of o-iodobenzoyl PSU. Polymers having degrees of phosphonation up to 0.5 were synthesized and studied.

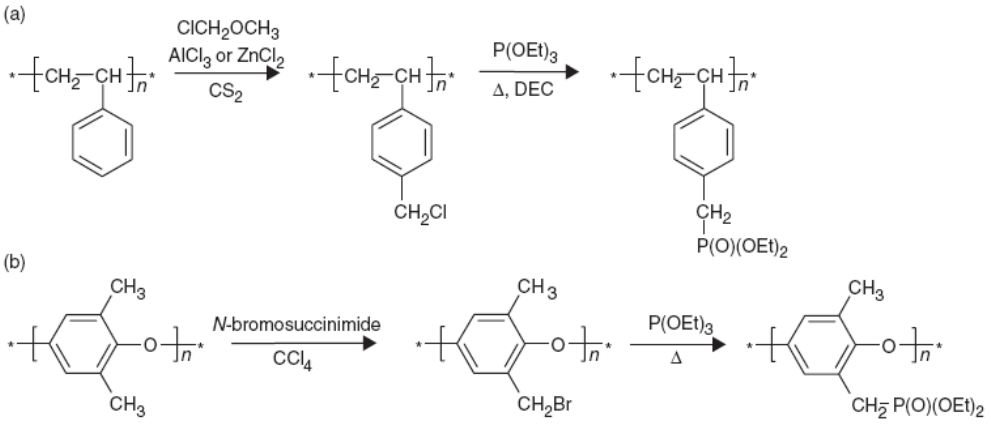


Figure 1.10 Phosphonation of (a) poly(p-chloromethylstyrene) and (b) poly(2,6-dimethyl-1,4-phenylene oxide) [58].

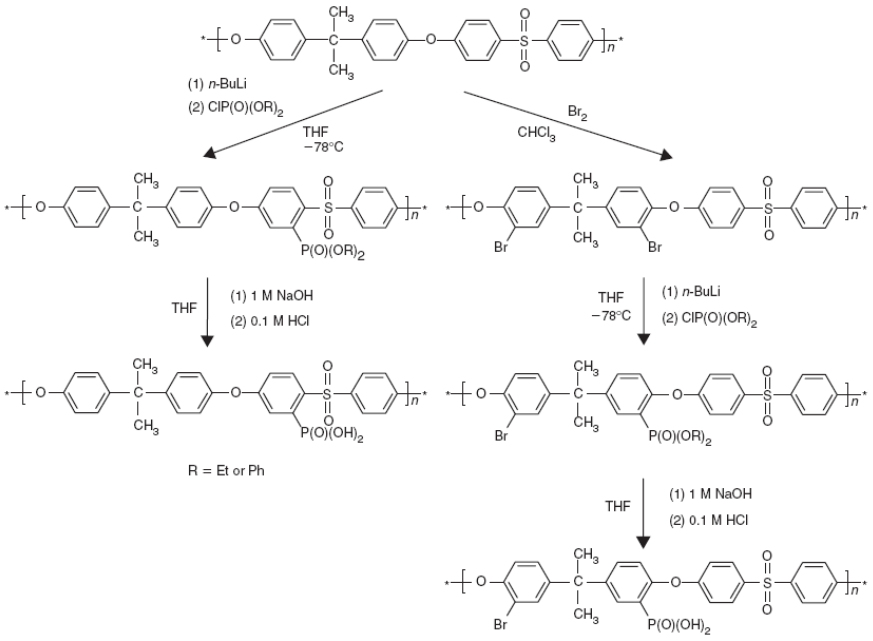


Figure 1.11 Phosphonation of PSU via lithiation and reaction with chlorophosphonic acid esters [59].

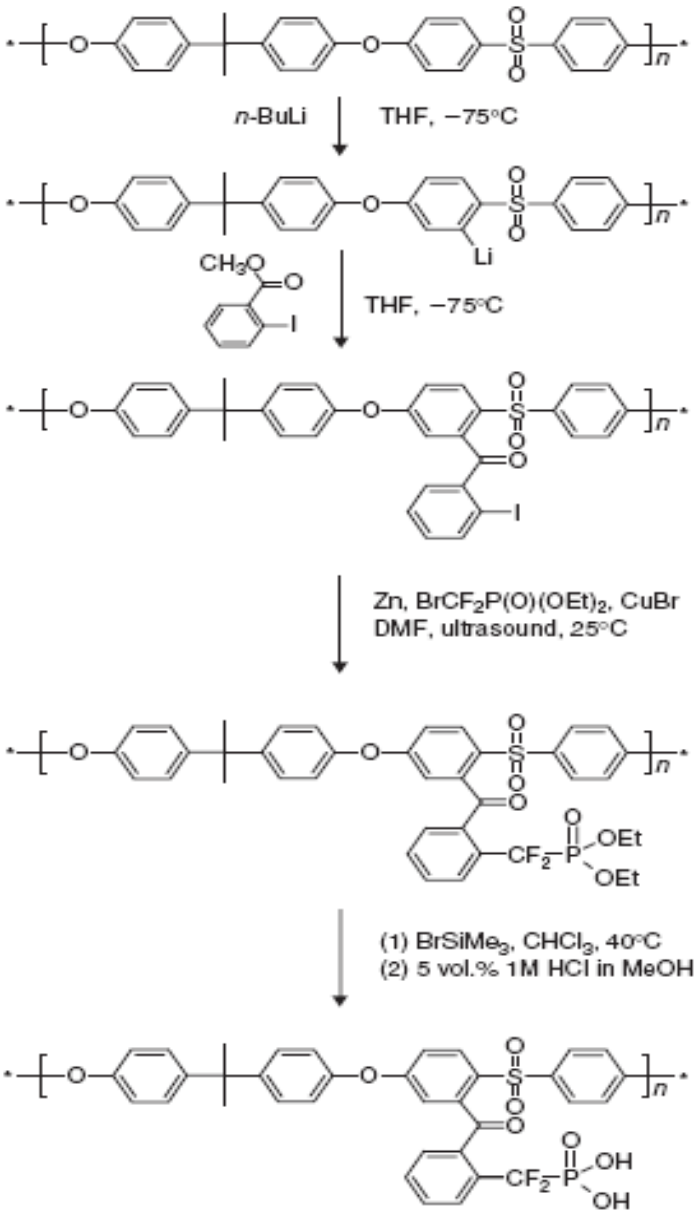


Figure 1.12 Synthetic pathway to o-benzoyl(difluoromethylenephosphonic acid) PSU [60].

CHAPTER 2

2. OBJECTIVES AND METHODOLOGY

2.1 Objectives and Methodology for Part I: Synthesis of Ionic Polymers for Viscosity Modifications

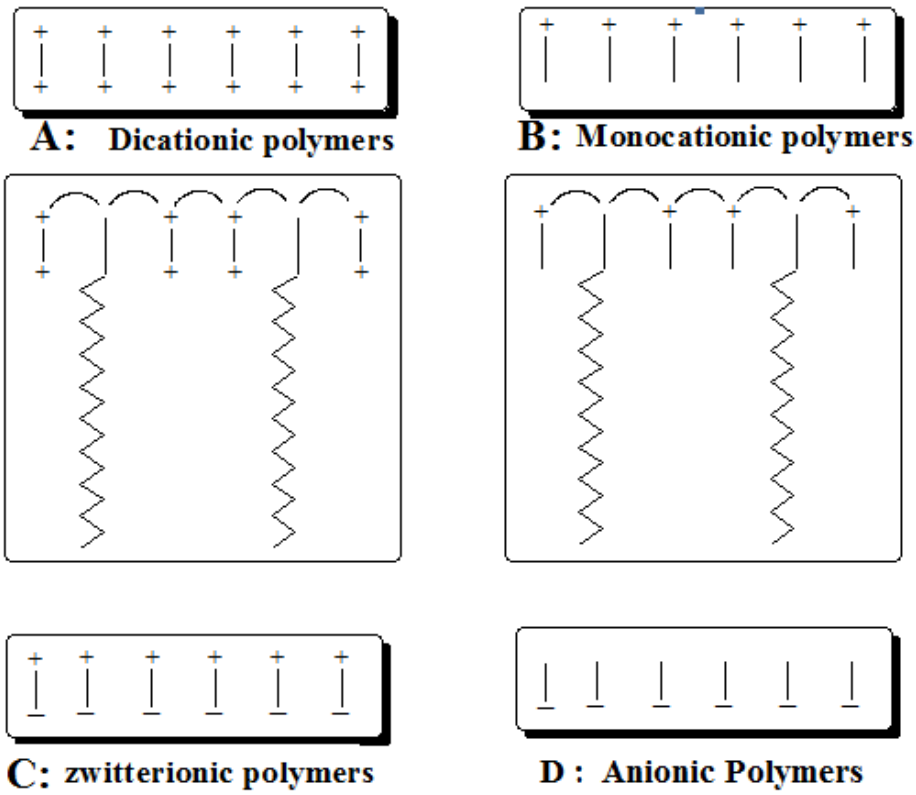
2.1.1 General Objectives

The general objectives of the proposed research for viscosity modification are to design and synthesize following new ionic polymers :

(a) Dicationic and monocationic polymers as depicted by **A** and **B** in Scheme 6. **A** and **B** will be interconvertible and as such the charge densities in the polymer backbone can be varied.

(b) All these polymers with varying degrees of charges and amount of hydrophobes will enable us to study their effects on the solution properties of the ionic polymers.

(c) To synthesize novel phosphonated monomers for free radical polymerization and to utilize them for preparation of homopolymers and copolymers with sulfur dioxide and to study their behavior as pH-responsive polymers. The Zwitterionic polymer C and anionic polymer D are expected to be interconvertible under the influence of pH.


A: Dicationic polymers
B: Monocationic polymers
C: zwitterionic polymers
D : Anionic Polymers

Scheme 6.

2.1.2 Specific Objectives

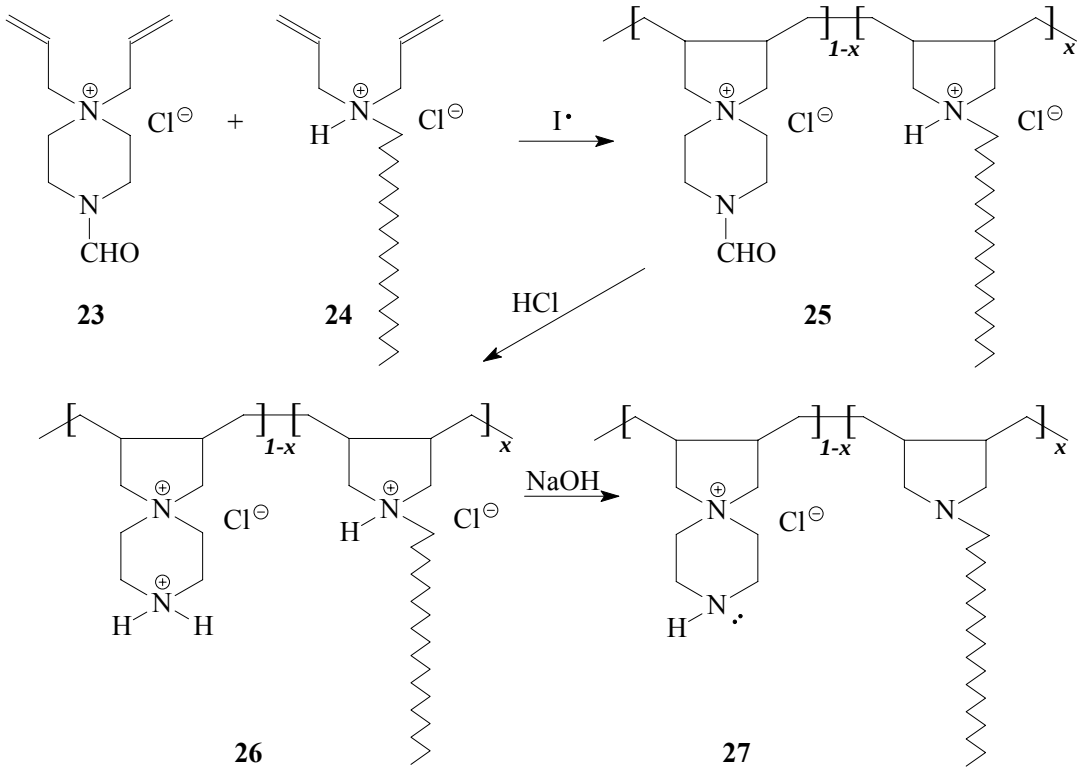
Preparation of the monomer **23** from piperazine and hydrophobic monomer **24** (probably a C_{18} alkyl chain) from diallylamine and their copolymerizations (**Scheme 7**). This will lead to polymers of the type represented by **A** and **B** in (**Scheme 6).**

1. Preparation of the monomer **28** and preparation of interconvertible homopolymers **(29→30→31** and (**29→32)** as shown in **(Scheme 8)** and study their pH responsive behavior .

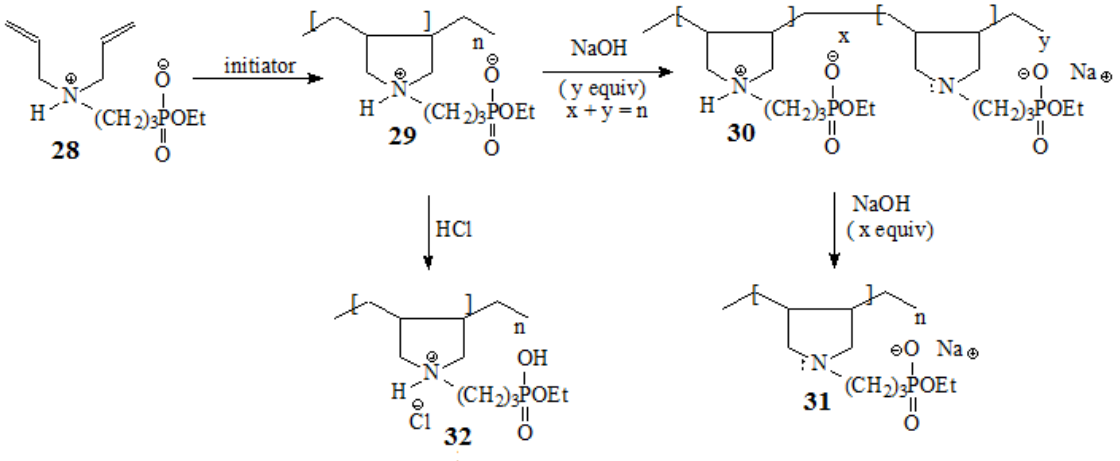
2. The new phosphonated monomers and polymers shown in (**Scheme 8)** will be characterized using spectroscopic techniques such as ^{1}H, ^{13}C and ^{31}P NMR spectroscopy to determine the chemical microstructure i.e. the detailed sequence and stereochemical relationship of structural units in the polymer chain.

3. Viscosity behavior of the several types of the new ionic associating polymers **(Schemes 7 and 8)** as mentioned above will be studied in detail with a special attention given to salt tolerance and pH values.

4. The new polymers (**Schemes 7 and 8)** will be characterized using spectroscopic techniques, specially the use of proton and ^{13}C NMR spectroscopy to determine the chemical microstructure i.e. the detailed sequence and stereochemical relationship of structural units in the polymer chain.



Scheme 7.

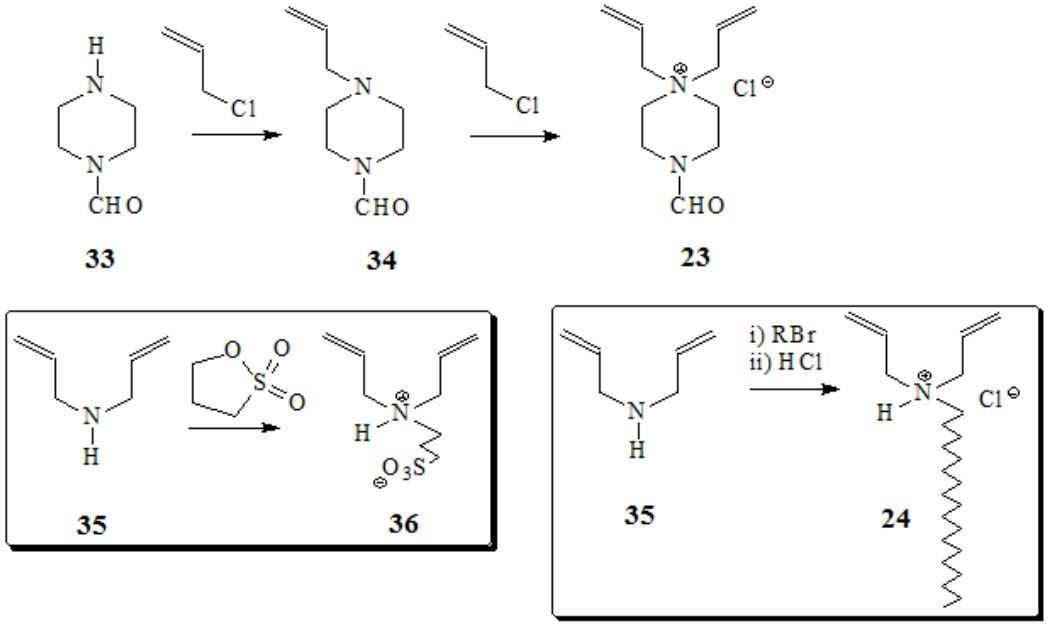


Scheme 8

2.1.3 Methodology

2.1.3.1 Synthesis of the monomers 23, 24 and cyclopolymerizations

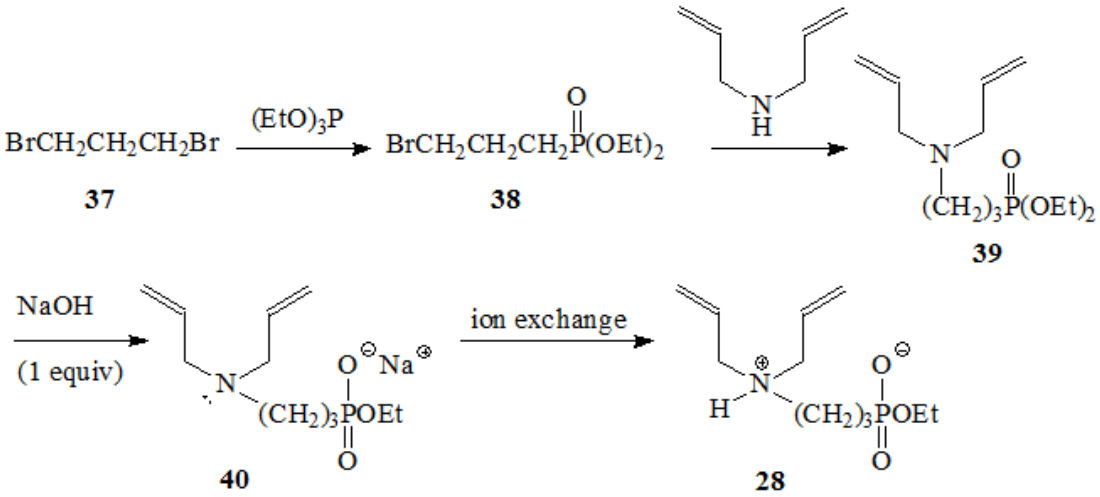
Scheme 9 shows the synthetic pathway for preparation of monomers **23** and **24.** The monomers **23** and **24** would be subjected to free radical copolymerization. The homopolymerization of the monomer has been studied in detail [15-17]. In our study the incorporation of the hydrophobic monomers will be limited in the range 5-10 mol%. The monocationic polymers **25** thus obtained can be transformed by acidic hydrolysis to dicationic polymers **26**, which may then be transformed to the monocatioinic polymers **27** by changing the pH of the polymer solution **(Scheme 7)**. The polymers **26/27** can also demonstrate the pH-responsive viscosity behavior as a result of the presence of trivalent nitrogen whose valence has not been quenched.



Scheme 9

2.1.3.2 Synthesis of the monomers 32 and homopolymerizion

Scheme 10 shows the synthetic pathway of monomer **28**. Reaction of 1,3 dibromopropane with triethylphosphite will yield the precursor **38** which will be reacted with dialylamine to yield the diester monomer **39**. This monomer will be hydrolyzed to the basic monoester derivative **40.** Ion-exchange of monomer **40** will yield the zwitterionic monomer **28**. This monomer will be subjected to free radical polymerization with objective to produce homopolymer **29 (Scheme 8).** The zwitterionic homopolymer **29** is pH responsive and can be treated with acid to yield monocationic polymer **32.** Treatment of zwitterionic homopolymer **29** with equivalent amount of base will yield the zwitterionic/anionic polymer **30**; and treatment of zwitterionic homopolymer **29** with two equivalents base will yield the anionic polymer **31**. The viscosity behavior of the pH responsive polymers **29,30,31** and **32** will be studied in detail.



Scheme 10

2.2 Objectives and Methodology for Part II: Synthesis of Ionic Polymers for Proton Exchange Membrane Fuel Cells.

2.2.1 General Objectives

The overall objective of this part of the proposed study is to synthesize and characterize a new polyelectrolyte membranes for fuel cells applications based on modification of the commercially available polymers such as polysulfone PSU.

2.2.2 Specific Objectives

1. Modification of polysulfone backbone by phosphonation and introduction of the phosphonic acid -PO_3H_2 functionality as proton conducting sites as shown in Fig. 2.1.

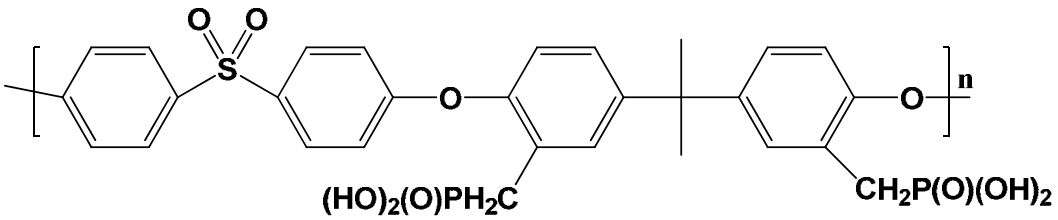


Fig. 2.1 Chemical Structure of Target Phosphonated Polysulfone PPSU

2. Preparation of new polyelectrolyte membrane by blending phosphonated polysulfone in both ester and acid forms with the commercially available sulfonated poly(etheretherketone) as illustrated in Fig. 2.2

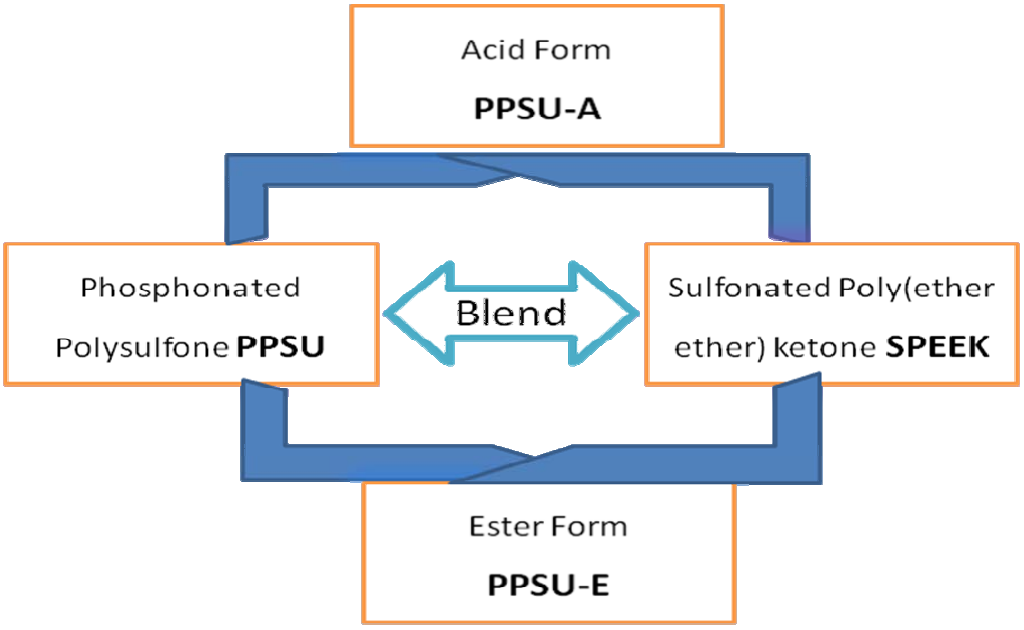


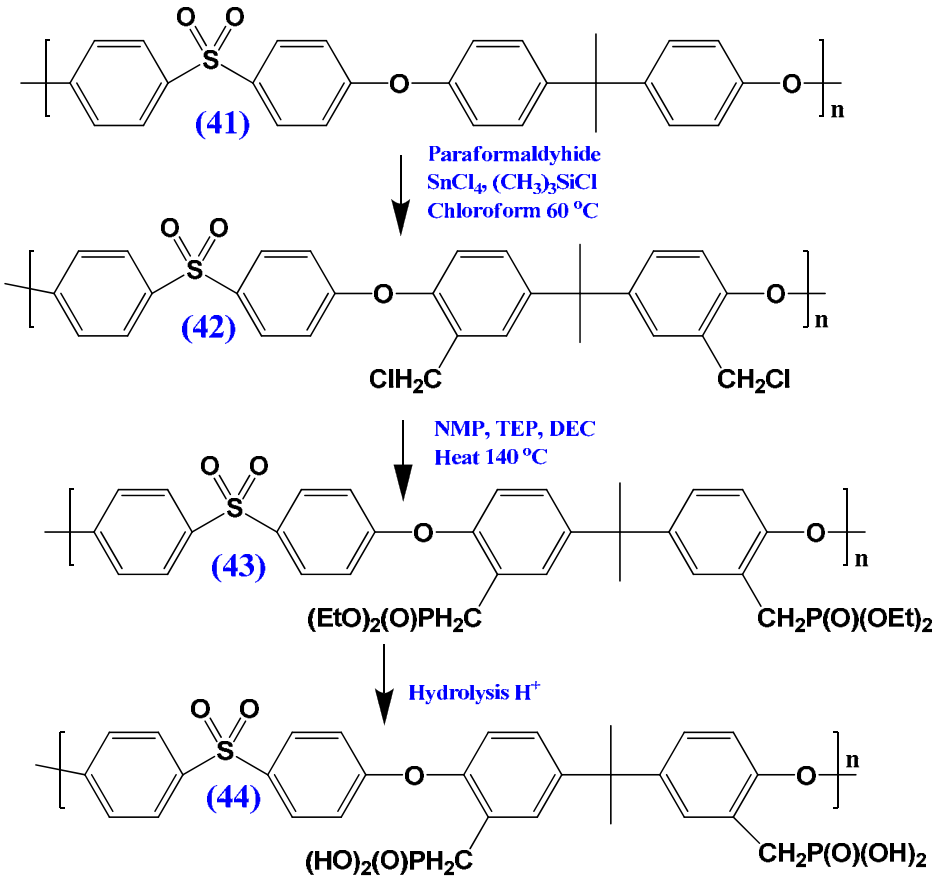
Fig. 2.2 Target Polyelectrolyte Membranes based on PPSU-A/SPEEK and PPSU-E/ SPEEK Polymer Blends.

3. To characterize the synthesized polymers by NMR, FTIR, IEC, DSC and TGA; and to study the properties of the polyelectrolyte membranes such as proton conductivity and methanol permeability for potential applications as PEMFCs.

2.2.3 Methodology:

2.2.3.1 Modification of Polysulfone by Phosphonation :

Commercially available polysulfone **(41)** will be chloromethylated to yield chloromathylated polymer **(42)** which will be converted to the diphosphonate form **(43)**. The last step will be the hydrolysis to produce the corresponding diacid form **(44)**. **(see scheme 11).**

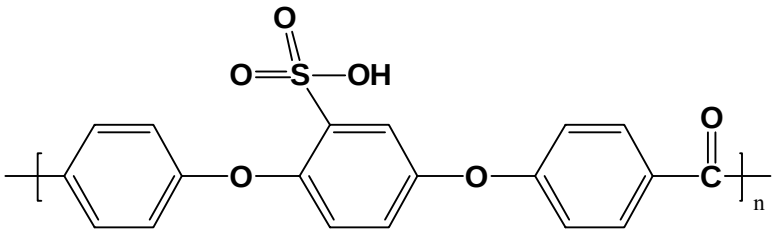


Scheme 11 - Phosphonation of polysulfone PSU

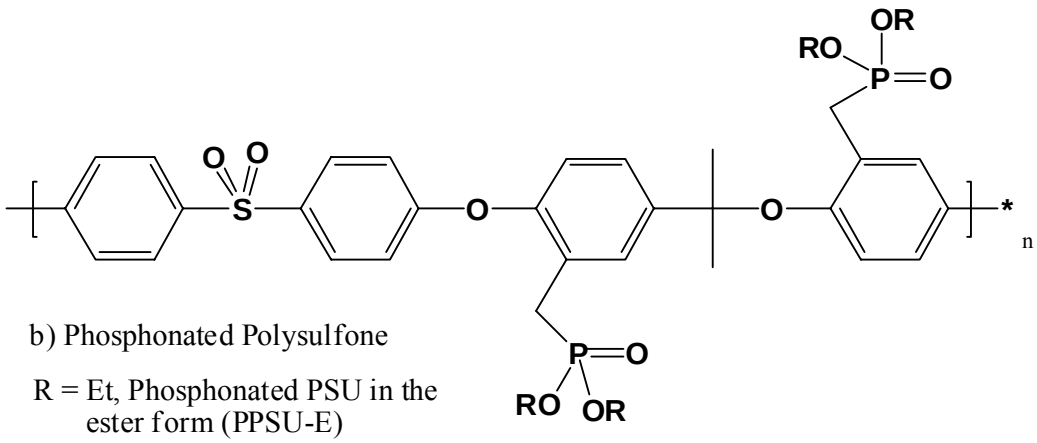
2.2.3.2 Synthesis Novel Ionically Crosslinked Polyelectrolyte membranes

In this context , the synthesized phosphonic acid functionalized polysulfones will be utilized to prepare polymer blends with highly sulfonated poly(etheretherketone) SPEEK DS=75% **(see scheme 12).**

This polymer blend is expected to have ionic networks between the strong acid functionality of SPEEK and PPSU. The properties of the polymeric blend membranes such as proton conductivity, methanol permeability, thermal stability, water swelling and methanol uptake will be studied in this context.



a) Sulfonated Poly(etheretherketone) (SPEEK)



b) Phosphonated Polysulfone

R = Et, Phosphonated PSU in the ester form (PPSU-E)

R = H, Phosphonated PSU in the acid form (PPSU-A)

Scheme 12. Structures of a) SPEEK b) Phosphonated Polysulfone (PPSU)

CHAPTER 3

3. SYNTHESIS AND SOLUTION PROPERTIES OF AMPHIPHILIC CYCLOTERPOLYMERS OF 1,1-DIALLYL-4-FORMYLPIPERIZINIUM CHLORIDE, DIALLYLOCTADECYLAMMONIUM CHLORIDE AND SULFUR DIOXIDE

Taken from

Shaikh A. Ali, Hasan A. Al-Muallem, Nedal Y. Abu-Thabit, Synthesis and solution properties of amphiphilic cycloterpolymers of 1,1-diallyl-4-formylpiperizinium chloride, Ziallyloctadecylammonium chloride and sulfur dioxide, *European Polymer Journal*, 45, (2009) 131.

SUMMARY:

The cycloterpolymerizations of hydrophilic monomer (1,1-Diallyl-4-formylpiperizinium chloride) with hydrophobic monomer (diallyloctadecylammonium chloride) and sulfur dioxide in dimethyl sulfoxide using azobisisobutyronitrile (AIBN) as the initiator afforded a series of water-soluble monocationic polyelectrolytes (MCPEs) in well over 90% yields. Acidic (HCl) hydrolysis of the *N*-formyl groups in MCPEs to $NH_2^+Cl^-$ groups gave the dicationic polyelectrolytes (DCPEs), which on treatment with 1 equivalent of NaOH furnished the basic cationic polyelectrolytes (BCPEs) containing basic as well as quaternary nitrogens. The solution properties of the resultant series of interconverting polyelectrolytes (MCPE→DCPE↔BCPE) were investigated by viscometric techniques. The polymer concentration C^*_{HA} of 0.2 g/dL was required for the manifestation of hydrophobic associations in a MCPE containing 4.5 mol% octadecyl pendents. The DCPEs exhibited sharp increase in viscosity in salt (NaCl)-added solution as compared to salt-free water. The pH-responsive BCPE is shown to demonstrate better

associative properties in the absence of HCl; upon addition of HCl, the charge density increases in the polymer chains thereby resulting in increased electrostatic repulsions and decreased associations. Polymer surfactant interactions were investigated using cationic surfactant cetyltrimethylammonium chloride (CTAC); tremendous increase in the viscosity values of the DCPE was observed in the presence of the surfactant.

Keywords: Associating ionic polymers; cyclopolymerization; diallylammonium monomers; dicationic polymer; viscosity.

3.1 Introduction

Hyrophobically associating water-soluble polymers, by virtue of their having interesting solution properties, are becoming increasingly important to the industries [61,62]. The copolymerization of a water-soluble monomer with a few mole percent of a hydrophobic comonomer in a homogeneous solution affords amphiphilic polymers with random distribution of the hydrophobes as isolated units. However, the micellar copolymerization systems [62] involving hydrophilic monomer (~3 wt%) in a continuous water phase and hydrophobic monomer inside the micelles favor a random distribution of the hydrophobes as small blocks in the hydrophilic polymer chains [63-70]. Above a hydrophobic association concentration (C^*_{HA}), these polymers form a reversible three-dimensional physical cross-links of polymer chains which are responsible for the superior viscosity behavior of the microblocky polymers derived from micellar process in

comparison to the random polymers that exhibit largely intramolecular associative behavior [71].

The discovery of the cyclopolymerization of *N,N*-diallyl quaternary ammonium salts by Butler [72,73] and subsequently, their copolymerization with sulfur dioxide [74] led to the synthesis of an array of water-soluble cationic polyelectrolytes (CPE) [75] of tremendous scientific and technological interest. There are some reports [76-82], which describe the synthesis of associating ionic copolymers prepared by Butler's cyclopolymerization technique. Previous kinetic studies [83] have indicated that a monomer concentration of 50-65 wt % is required to obtain polymers with high conversion, high molecular weight, and low residual double bonds. The micellar technique is not available in the Butler's copolymerization process; cyclopolymerization of hydrophilic and hydrophobic diallyl monomers in such high concentrations has been reported to yield random rather than microblock copolymers even though the hydrophobic monomer possesses surfactant properties [77]. The copolymers obtained via Butler's process with a hydrophobic content of 8.22 mol% and pendent lengths of the equivalent of 10 or 11 CC bonds were found to have an undesirable fairly high C^*_{HA} (in the range 15-17 wt%) compared to the hydrophobically associating non-ionic copolymers of acrylamide (C^*_{HA} less than 1 wt%) [77,78]. However, increasing the hydrophobic pendent length to C_{18}[79-82] as well as the use of twin- and triple-tailed hydrophobes [24] led to copolymers with superior viscosity behavior and C^*_{HA} less than 1 wt%.

In our continuing studies of associating ionic polymers, we intend to synthesize interconvertible pH-responsive polymers of variable charge densities as depicted in **Fig.**

3.1. The two nitrogens in a piperazine-based monomer are intended to be utilized to vary the charge densities on the polymer chains. It is worth mentioning that piperazine is inexpensive and itself used as a drug; piperzaine moiety occurs in various pharmaceuticals with interesting biological activities [85]. We report herein the synthesis and solution properties of the monocationic polyelectrolytes (MCPEs) **3** and dicationic polyelectrolytes (DCPEs) **4** and its corresponding pH-responsive basic cationic polyelectrolytes (BCPEs) **5** (containing quaternary as well as trivalent nitrogens) by cycloterpolymerization of a piperazine-based hydrophilic monomer **1** (M_1) with SO_2 in the presence of various amounts of hydrophobes **2** (M_2) (Scheme 1). The interconvertibility of the polymers (**3→4↔5**) will indeed provide an ideal situation to compare their solution properties since the polymers will have identical degree of polymerization.

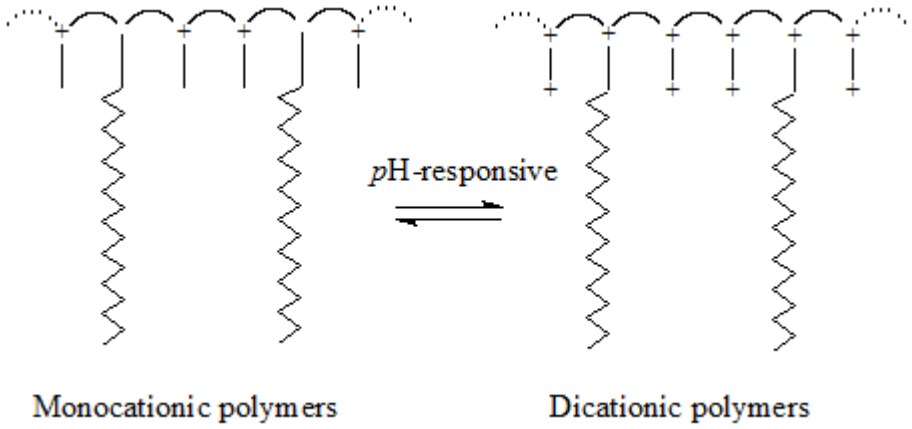
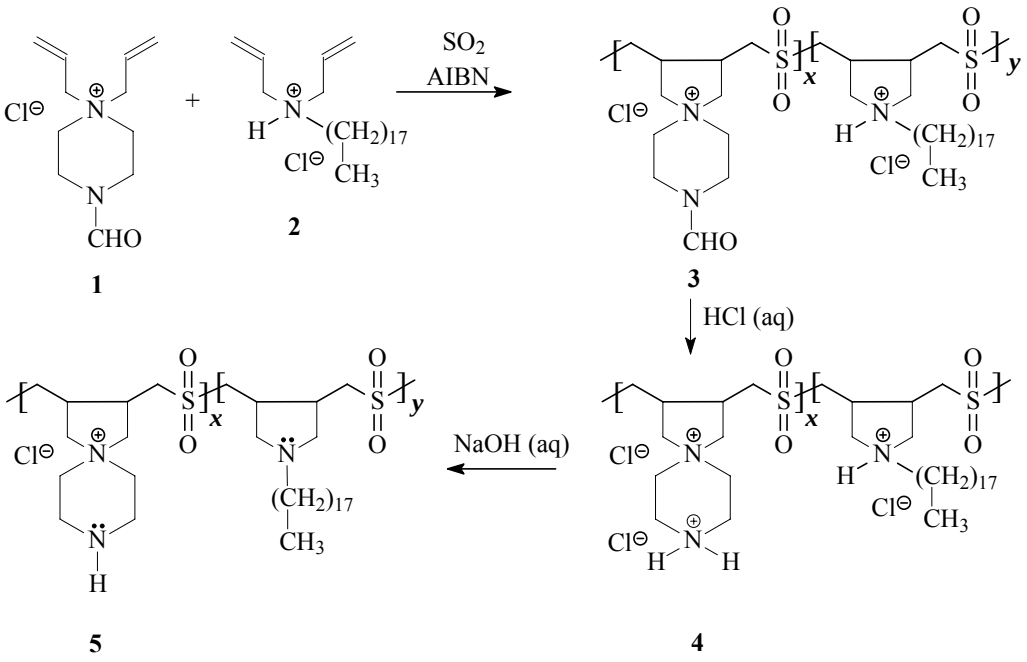


Figure 3.1 Hydrophobically modified mono- and di-cationic polymers.

3.2 Experimental

3.2.1 Materials

2,2'-Azobisisobutyronitrile (AIBN) from Fluka Chemie AG (Buchs, Switzerland) was purified by crystallization from a chloroform-ethanol mixture. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a boiling point of 64-65°C (4 mmHg). Cetyltrimethylammonium chloride (CTAC), 25 wt.% solution in water from Aldrich was used as received. All glassware were cleaned using deionized water. 1,1-Diallyl-4-formylpiperizinium chloride **(1)** was prepared as described in a previous report [86]. *N,N*-Diallyl-N-octadecylammonium chloride **(2)** was prepared as before [79].



Scheme 1. Synthesis of amphiphilic polyelectrolytes by free-radical cycloterpolymerization.

3.2.2 Physical Methods

Elemental analysis was carried out on a *EuroVector* Elemental Analyzer Model EA3000. IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer. ^{1}H NMR spectra of the polymers were measured in D_2O on a JEOL LA 500 MHz spectrometer. Viscosity measurements were made by Ubbelohde viscometer using CO_2-free water under N_2 in order to avoid CO_2 absorption that may affect the viscosity data. A gentle stream of N_2 was passed through distilled deionized water at 90 ^oC for 15 min in order to remove the dissolved gases. Digital Brookfield rotational viscometer with UL adaptor or SC4-18 spindle accessories was used to measure apparent viscosities at various shear rates.

3.2.3 General procedure for the terpolymerization of 1/2/SO_2

All the polymerizations were carried out using conditions as described in the **Table 3.1.** In a typical experiment, SO_2 was absorbed in a solution of the monomers **1/2** (i.e., M_1/M_2) in DMSO in a 25 cm^3 round-bottom flask. The required amount of the initiator (AIBN) (as listed in **Table 3.1**) was then added under N_2 and the closed flask was stirred using a magnetic stir at 60 ^oC for 24 h. Magnetic stir bar stopped moving within minutes after addition of the initiator. At the end of the elapsed time, the hard polymeric mass was crushed to powder, soaked in methanol, filtered and washed with liberal excess of hot (50 ^oC) methanol to ensure the complete removal of the unreacted monomer (as indicated by ^{1}H NMR). The copolymer was then dried to a constant weight at 60 ^oC under vacuum. The white polymers, MCPE **3,** were stored in a desiccator.

3.2.4 Thermal Decomposition, Elemental Analyses of the polyelectrolytes

The onset of thermal decomposition (Closed capillary): **3**-M_2-*0*: 255-260 ^oC (turned brown) 290-300 ^oC (decomposed, turned blackish)**;** **4**-M_2-*0*: 240-250 ^oC (turned brown) 290-300 ^oC (decomposed, turned blackish)**;** **3**-M_2-*4.5*: 240-250 ^oC (turned brown) 280-290 ^oC (decomposed, turned blackish)**;** **4**-M_2-*4.5*: 240-250 ^oC (turned brown) 280-290 ^oC (decomposed, turned blackish)**.**

The elemental analyses ascertained the mole ratio of $(M_1+M_2):M_3(SO_2)$ as 1 : 1 as reported [74] for the copolymer **3**-M_2-0. The NMR and IR spectra and elemental analyses of the terpolymers closely resembled those of the copolymer **3**-M_2-0 as reported [74]. The ^1H NMR spectra for **3**-M_2-0, **3**-M_2-3.5, and **4**-M_2-3.5 are shown in **Fig. 3.2**

Elemental Analyses for **3** $(\mathbf{M_1}.SO_2)_x$ $(\mathbf{M_2}.SO_2)_{1-x}$ were as follows (the numbers in parentheses represent the calculated values where $x \leq 1$):

- **3**-M_2-*0*: C, 44.6% (44.82%); H, 6.6% (6.50%); N, 9.4% (9.50%); S, 10.6% (10.88%)**.**
- **3**-M_2-*2*: C, 45.0% (45.20%); H, 6.7% (6.59%); N, 9.2% (9.37%); S, 10.6 % (10.80%)**.**
- **3**-M_2-*3.5*: C, 45.2% (45.49%); H, 6.8% (6.65%); N, 9.1% (9.28%); S, 10.5% (10.75%)**.**

- **3**-M_2-*4.5*: C, 45.4% (45.68%); H, 6.8% (6.69%); N, 9.1% (9.21%); S, 10.5% (10.71%)**.**

- **3**-M_2-*5.5*: C, 45.5% (45.88%); H, 6.9% (6.73%); N, 9.0% (9.15%); S, 10.4% (10.67%)**.**

- **3**-M_2-*7.0*: C, 45.9% (46.17%); H, 6.9% (6.80%); N, 8.9% (9.05%); S, 10.3% (10.62%)**.**

3.2.5 General procedure for the acidic hydrolysis of the MCPEs 3

A mixture of the MCPE **3**-M_2-*0* (entry 1, **Table 3.1**) (3.5 g) in 15% aqueous HCl (80 cm^3) was stirred in a closed flask at 20 ^oC for 48 h (or until the hydrolysis of the amide group was complete as indicated by the absence of the HCO signal in the ^1H NMR spectrum). The solution was then precipitated in methanol. After filtration and washing with methanol, the white polymer was dried under a high vacuum at 50 ^oC for 6 h (or until constant weight of the polymer was achieved) to give the dicationic polymer DCPE **4** in well over 90% yield. The DCPEs **4** also gave satisfactory elemental analysis.

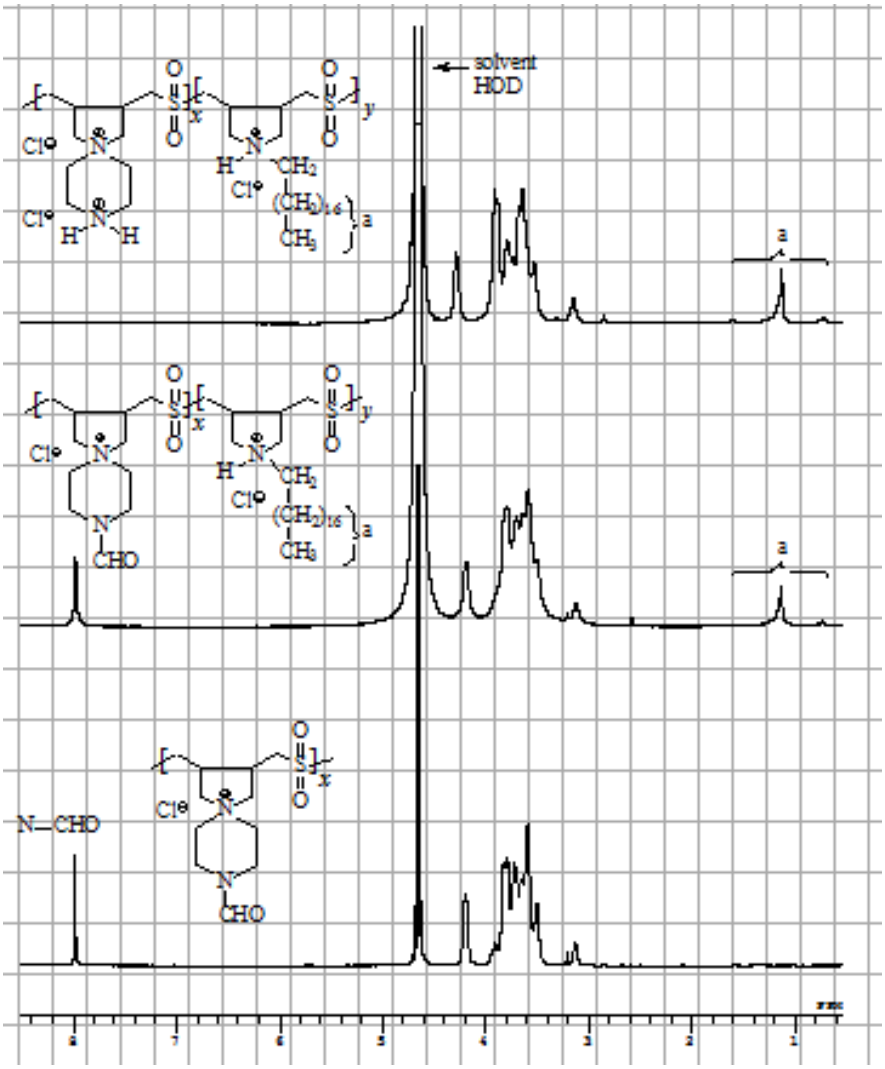


Fig. 3.2 ^{1}H NMR spectrum of **3**-M_2-0, **3**-M_2-3.5, and **4**-M_2-3.5 in D_2O.

3.3 Results and discussion

3.3.1. Synthesis and Physical Characterization of the Terpolymers

The hydrophilic monomer **1** (M_1), hydrophobic comonomers **2** (M_2) and SO_2 underwent cycloterpolymerization in solvent DMSO using AIBN as the initiator to give the terpolymers monocationic polyelectrolytes (MCPEs) **3** in over 90% yields. Terpolymer **3**-M_2-3.5 (entry 3, **Table 3.1**), for instance, indicates the use of 3.5 mol% of the hydrophobe (M_2) **2** in the feed, while the incorporation was found to be 3.3 mol% as determined by ^{1}H NMR spectroscopy (*vide infra*). Cyclocopolymerization of the hydrophilic monomer **1** with SO_2 (in the absence of hydrophobic monomer) under the same conditions was carried out to obtain the MCPE **3**-M_2-0 (entry 1, **Table 3.1**). Hydrophobe incorporations were found to match closely with the feed ratio (**Table 3.1**). This is expected since the polymers were obtained at high conversions (~90%). The sulfur analyses ascertained the mole ratio of (M_1+M_2):SO_2 as 1:1. The MCPEs **3** were hydrolyzed in 15% aqueous HCl to produce dicationic polyelectrolytes (DCPEs) **4** (in well over 90% yields), which on treatment with 1 equivalent of NaOH afforded the basic cationic polyelectrolytes (BCPEs) **5** containing basic as well as quaternary nitrogens. The polymers **3** and **4** were found to be stable up to ~250 ^{o}C.

Fig. 3.2 displays the ^{1}H NMR spectrum of the MCPEs **3**-M_2-0, **3**-M_2-3.5, and DCPE **4**-M_2-3.5. It is evident after comparing the proton spectra of the polymers **3**-M_2-3.5

Table 3.1 Terpolymerization of the monomer **1** (M_1), **2**(M_2) and SO_2[a]

Entry No.	Sample	M_1 mmol	M_2 mmol	Polymer[b] M_1:M_2	Yield %	Intrinsic Viscosity[c] (dl g^{-1}) **3**-MCPE	**4**-DCPE[d]	**5**-BCPE[e]
1	**3**-M_2-0	20.0	0	100:0	95	0.809	1.61	0.878
2	**3**-M_2-2	19.6	0.40	98.1:1.9	94	1.01	1.93	1.10
3	**3**-M_2-3.5	19.3	0.70	96.7:3.3	95	— [f]	2.25	— [f]
4	**3**-M_2-4.5	19.1	0.90	95.4:4.6	96	— [f]	2.06	— [f]
5	**3**-M_2-5.5	18.9	1.10	94.7:5.3	93	— [f]	— [f]	— [f]
6	**3**-M_2-7	18.6	1.40	93.3:6.77	91	— [f]	— [f]	— [f]

[a]Polymerization reactions were carried out in DMSO (6.7 g) containing 20 mmol of SO_2 in the presence of AIBN (100 mg) at 60 ºC for 24h.

[b]mol% polymer (as determined by ^{1}H NMR)
[c]Obtained by extrapolation of the linear parts of the curves usually in the range 0.2-0.025 g/dL polymer solution in 0.1 N NaCl at 30°C measured with an Ubbelohde viscometer.

[d]Prepared by acid hydrolysis of the corresponding MCPEs **3**.

[e]Prepared by treating DCPEs **4** with 1 equivalent of NaOH.
[f]Not determined (insoluble).

that the NCHO proton, which appeared at δ 7.98 ppm (s), is absent in the spectrum of the **4**-M_2-3.5**,** thus indicating the complete removal of the formyl groups after hydrolysis.

the incorporation of the hydrophobic monomers was calculated using ^{1}H NMR integration of the signals in the range around δ0.6-1.65 ppm (for $(CH_2)_{16}CH_3$ methyl protons of the hydrophobic pendents).

3.3.2 Solubility, Viscosity Measurements and Solution Properties

To allow meaningful assessment of the associative behaviors of the synthesized polymers, the polymerization conditions were kept similar as rigorously as possible in order to obtain polymers having similar degree of polymerizations. In fact, all the polymerizations were carried out simultaneously using a single oil bath.

While the MCPE **3** and BCPE **5** containing hydrophobe higher than 2 mol% were found to be insoluble in 0.1N NaCl, the DCPEs **4**-M_2-3.5 and -4.5 were soluble in 0.1N NaCl (**Table 3.1**) but **4**-M_2-5.5 and -7 gave cloudy solution. The incorporation of higher proportion of hydrophobes led to their insolubility especially in the salt-added water (0.1N NaCl). This behavior at higher salt concentration could be caused by the salting-out effect of NaCl: the solubility of the hydrophobic parts of the molecule decreases, the polymer chains are unable to manifest effective intermolecular associations and tend to precipitate.

Extrapolation of linear part of the viscosity plots in the concentration range 0.20-0.025 g/dL permitted us to determine the intrinsic viscosities [η] for the polymers in 0.1N

NaCl (**Table 3.1**). The polymers **3**, **4** and **5** are expected to have similar degree of polymerizations since **4** and **5** are directly derived from **3**. While **3** and **5** have similar viscosity values, the polymers **4** were found to have higher viscosity values. This is expected since the former polymers are monocationic while **5** is dicationic thereby leading to the extension of polymer chains as a result of higher charge density hence higher degree of repulsion among the like charges.

Fig. 3.3 displays the variations of viscosity with concentration of MCPE **3**-M_2-4.5 at various shear rates in salt-free water. Hydrophobic associations, as indicated by exponential increase in the viscosity values, began to manifest around C_{HA}* value of 0.2 g/dL of the polymers. The strong interchain associations contribute significantly to the thickening [68,82, 87-89].

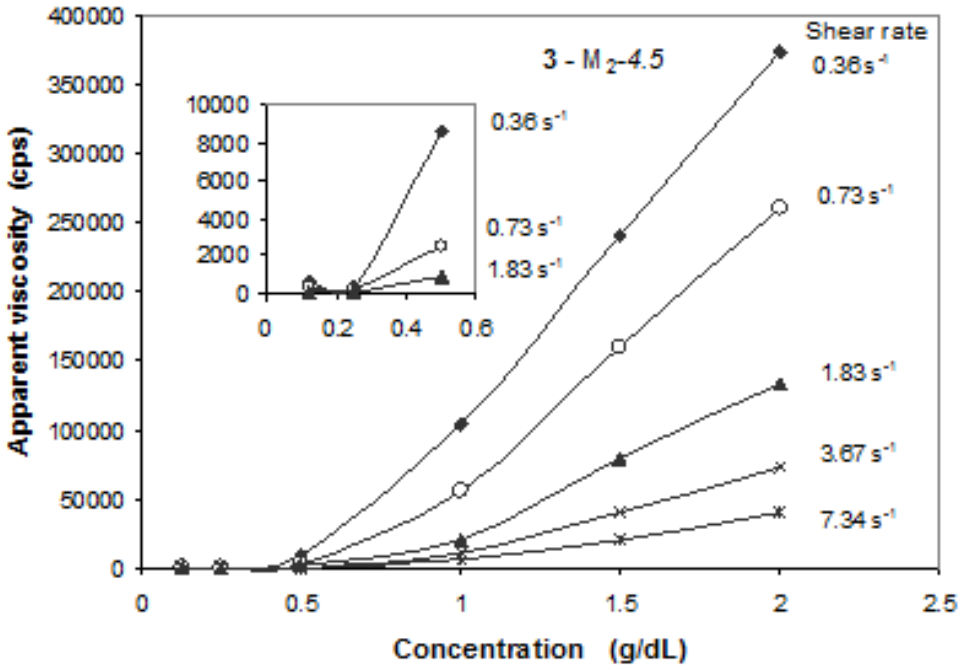


Fig. 3.3 Variation of viscosity with concentration of **3-**M_2-*4.5* at various shear rates in salt-free water at 30 °C. (Inset showing the variation in the lower concentration range).

Fig. 3.4 displays the variation of viscosity with shear rates of a 2 g/dL solution **3-**M_2-*0, -2.0, -3.5, -4.5, -5.5* and -*7.0* samples in salt-free water at 30 °C; at a shear rate of 0.36 s^{-1}, the polymers were found to have apparent viscosity values 1940, 3099, 338000, 374000, 340000, and 128000 cps, respectively. The polymer **3-**M_2-*4.5* was thus found to have the highest viscosity values. As evident from the **Fig. 3.3**, a modest decrease in the apparent viscosities with increasing hydrophobe incorporation in **3-**M_2-*5.5* and -*7.0* reflects the increasing participation of intramolecular micellization. Polymers with higher hydrophobe-content are known to demonstrate higher degree of intramolecular association

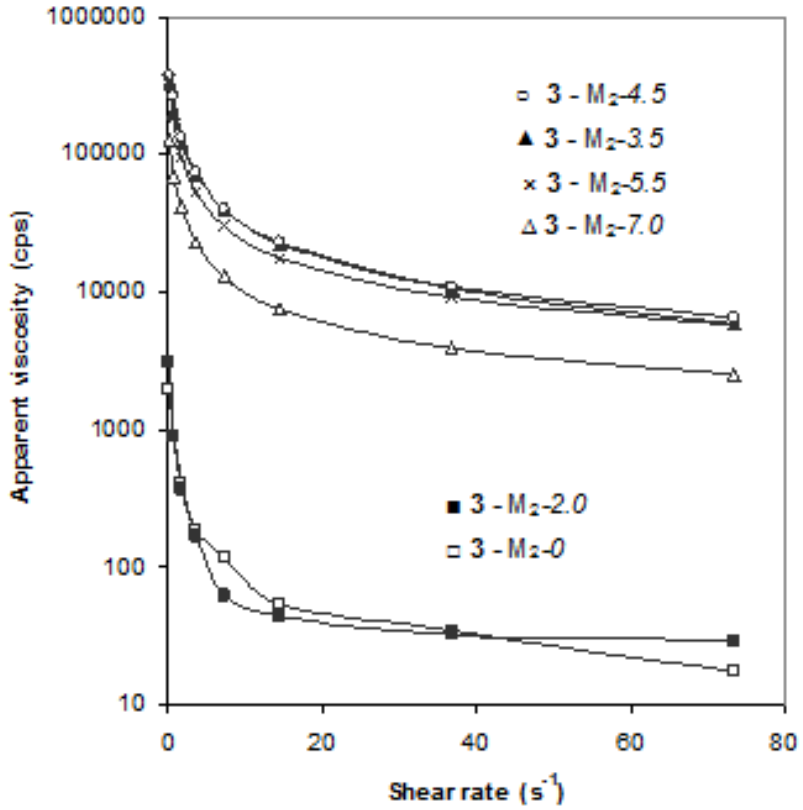


Fig. 3.4 Variation of viscosity of a 2 g/dL solution of **3**-M_2-*0, -2.0, -3.5, -4.5, -5.5* and -*7.0* at various shear rates in salt-free water at 30 °C.

[76]. At lower hydrophobe incorporation as in **3-**M_2-*2* the polymer failed to demonstrate associations in the semidilute concentration of 2 g/dL.

The ineffective associations of hydrophobic groups in this case could be discussed in terms of critical micelle concentration similar to that for small-molecule surfactants. At low hydrophobe incorporation (2 mol%) and polymer concentration (2 g/dL), an insufficient number of hydrophobic groups are present on any individual polymer chain to form a stable ensemble.

Figs. 3.5 and **Fig. 3.6** display the variation of viscosity with shear rates of a 2 g/dL solution of **4-**M_2-*0, -2.0, -3.5, -4.5, -5.5* and -*7.0* samples in salt-free water and 0.1N NaCl, respectively, at 30 °C. At a shear rate of 0.36 s^{-1}, the polymers were found to have apparent viscosity values 130, 1240, 2000, 83582, 97979, and 67985 cps, respectively in salt-free water, while the corresponding values in 0.1N NaCl were found to be 85, 1710, 490000, 654000, 354000, and 27995 cps. As evident from the **Figs. 3.4** and **Fig. 3.5**, MCPEs **3** are found to demonstrate better associative properties compared to the DCPEs **4** in salt-free water. The greater repulsive forces associated with the excessive positive charges on the polymer chains of the dicationic polymers DCPEs **4** do not permit the chains to approach close enough for effective associations. However, there is a tremendous enhancement in the viscosity values of the DCPEs **4** in the presence of NaCl (**Fig. 3.6**). Lower values of the viscosity for the **4-**M_2-*7.0* could be attributed to the solubility problem in 0.1N NaCl. In the presence of added salt, the increase in viscosity correlates well with the known effects of NaCl on hydrophobic association [90]. The positive charges in the polymer chains are shielded by chloride ions. The decreased

repulsion between the charges in the polymer chains leads to compaction of the polymer coil, and as a result the viscosity is expected to decrease in the presence of the added salt. However,.

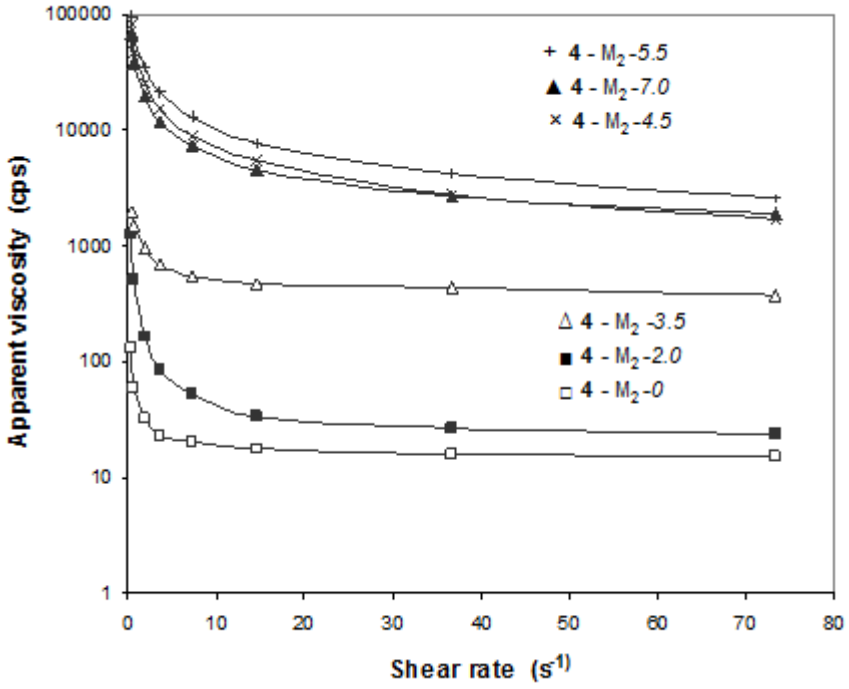


Fig. 3.5 Variation of viscosity of a 2 g/dL solution of **4**-M_2-*0*, -*2.0*, -*3.5*, -*4.5*, -*5.5* and -*7.0* at various shear rates in salt-free water at 30 °C.

the presence of NaCl allows the polymer chains to approach closer, makes the aqueous system more hostile to the hydrophobes thus forces them to associate intermolecularly as a result of reduced electrostatic repulsions

Variation of viscosity of a 2 g/dL solution of **4-**M_2-2.0 with shear rates at various concentration of NaCl at 30 °C is displayed in **Fig. 3.7** The viscosity values were found to increase with the increase in NaCl concentration up to 0.2 N. Further increase in NaCl concentration to 0.3 N leads to a decrease in viscosity values, which however remained higher than that in salt-free water. In the presence of chloride ions, the relative significance of the opposing effects of polymer compaction by shielding and increased hydrophobic associations on the viscosity determines the viscosity values. The remarkable effect of added salt on the viscosity of a 2 g/dL solution of **4-**M_2-3.5 is displayed in **Fig. 3.8**; at a shear rate of 0.36 s^{-1}, the polymers in 0, 0.03, 0.07, 0.1 and 0.2N NaCl were found to have the apparent viscosity values of 2000, 168000, 220000, 490000, and 380000 cps, respectively.

The differences in the associative properties of MCPE **3-**M_2-3.5 in salt-free water and its corresponding DCPE **4-**M_2-3.5 in salt-free water and 0.1N NaCl are clearly demonstrated in **Fig. 3.9**; at a shear rate of 0.36 s^{-1}, the polymers were found to have apparent viscosity values 338000, 2000, and 490000, cps, respectively. Even though the MCPE **3-**M_2-3.5 is insoluble in 0.1N NaCl, the **4-**M_2-3.5 was soluble in salt-free water as

well as 0.1N NaCl; solubility in salt-added solution is attributed to the highly exposed cationic charges in the DCPE **4**. In the absence of shielding, the repulsion among the

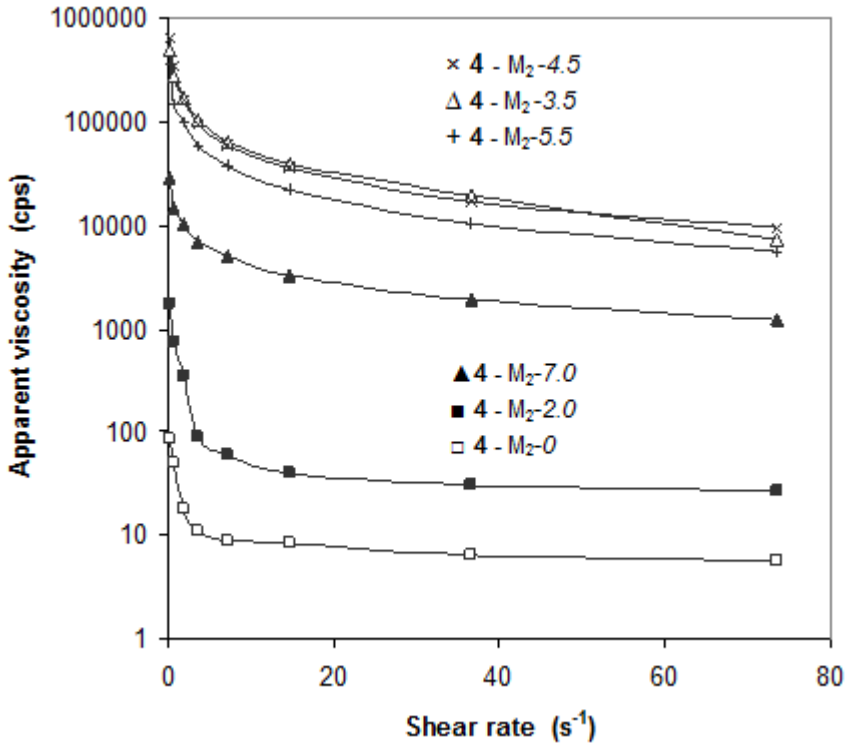


Fig. 3.6 Variation of viscosity of a 2 g/dL solution of **4**-M_2-0, -2.0, -3.5, -4.5, -5.5 and -7.0 at various shear rates 0.1 N NaCl at 30 °C.

cationic charges in **4** does not permit the polymer chains to approach close enough to demonstrate effective association of the hydrophobes. However in the presence of 0.1N NaCl, the cationic charges are shielded, and as a result, the viscosity increases by an astonishing factor of 245.

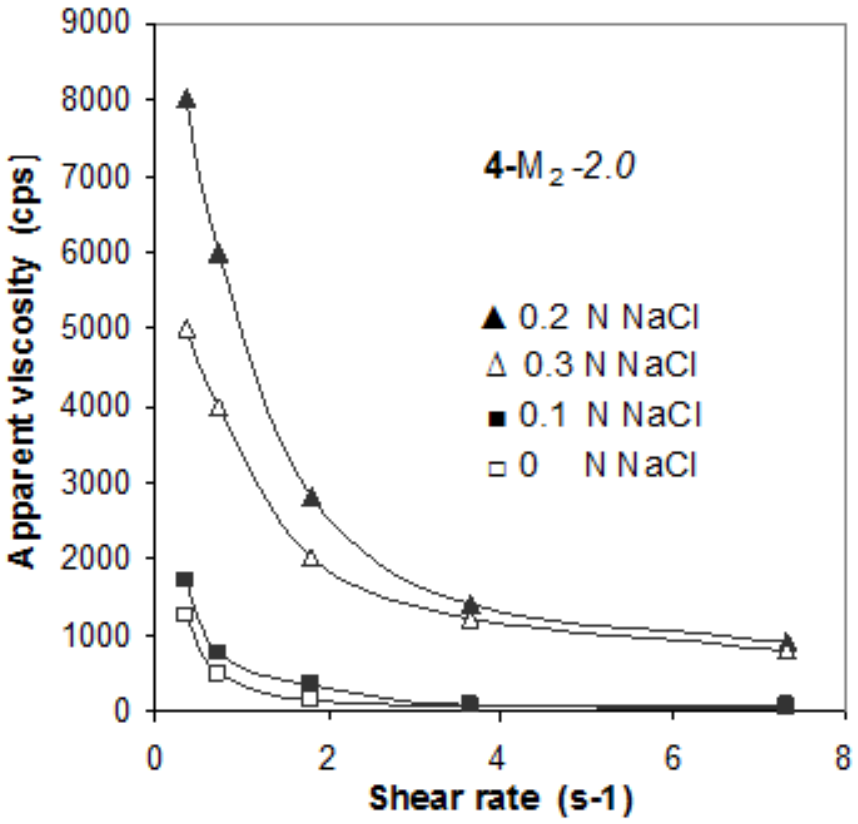


Fig. 3.7 Variation of viscosity of a 2 g/dL solution of **4**-M_2-2.0 with shear rates at various concentration of NaCl at 30 °C.

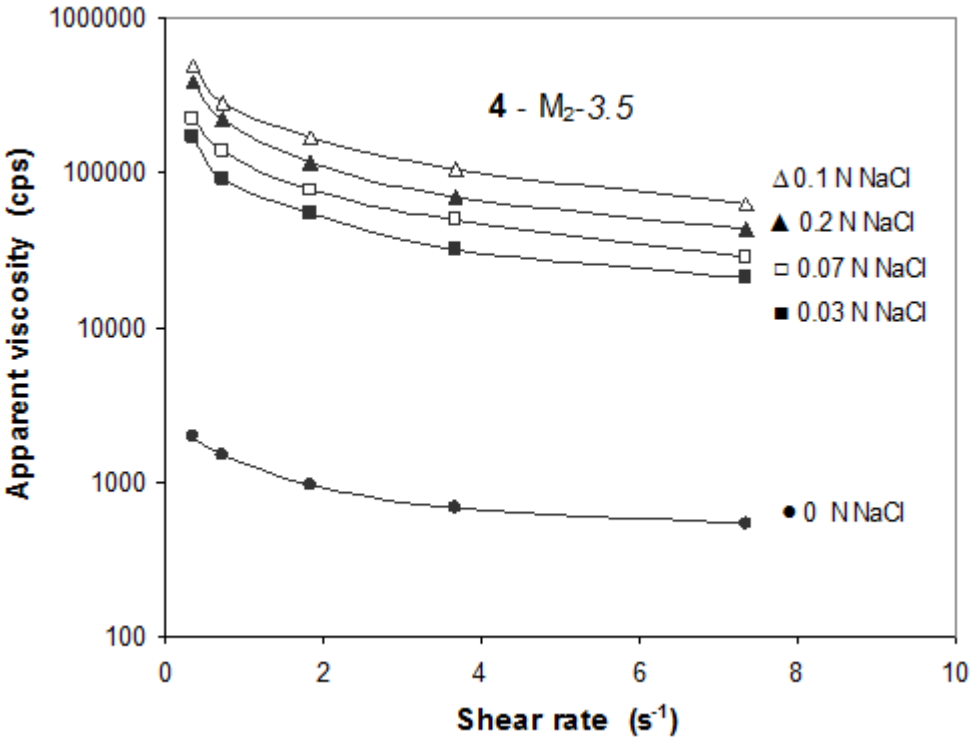


Fig. 3.8 Variation of viscosity of a 2 g/dL solution of **4**-M_2-3.5 with shear rates at various concentration of NaCl at 30 °C.

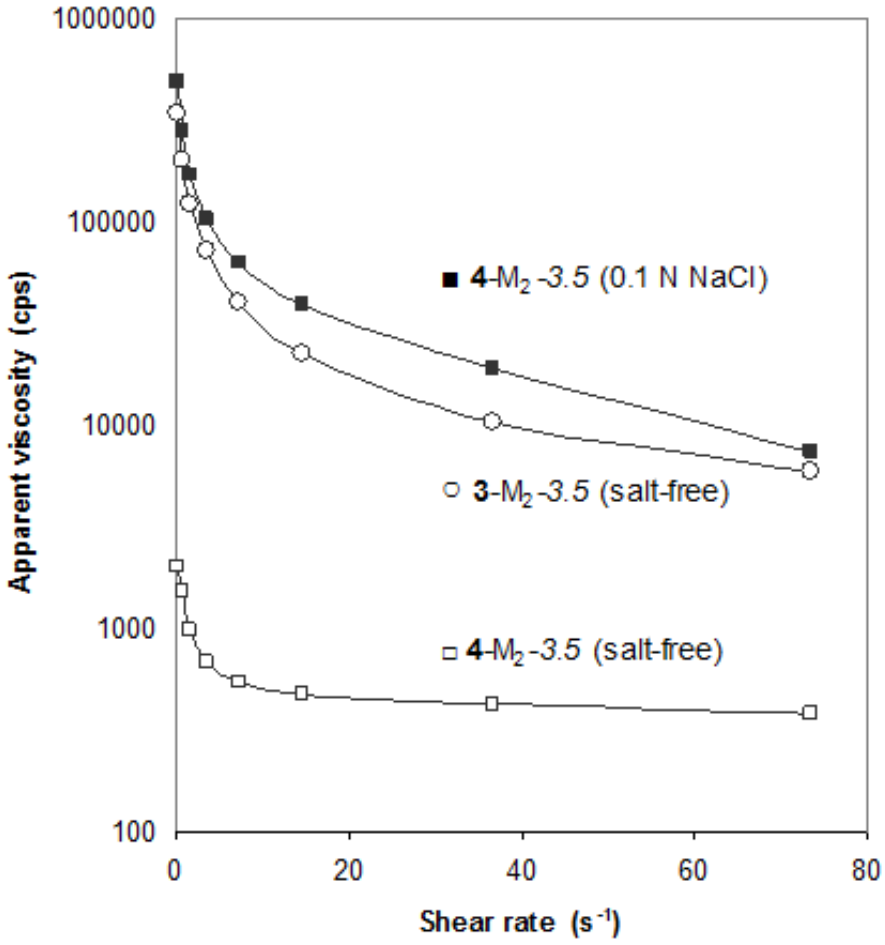


Fig. 3.9 Variation of viscosity of a 2 g/dL solution of **3**-M_2-3.5, **4**-M_2-*3.5* in salt-free water and **4**-M_2-*3.5* in 0.1N NaCl at various shear rates at 30 °C.

Variation of viscosity with shear rates profile of a 1 g/dL solution of BCPE **5**-M_2-*4.5* in the presence of various equivalents of HCl in 0.032 N NaCl at 30°C is shown in **Fig. 3.10**. Addition of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 equivalent of HCl led to the apparent viscosity values of 180000, 56000, 42000, 34000, 24000, and 16000 cps, respectively, at a shear rate of 0.36 s^{-1}. The viscosity thus attains its maximum value in the absence of HCl, and decreases upon additions of HCl, attaining its minimum value in the presence of 1.0 equivalent of HCl, which converts the BCPE **5**-M_2-*4.5* to DCPE **4**-M_2-*4.5*. Increasing cationic charges on the polymer chains, hence increasing interchain electrostatic repulsions, thus, diminishes the degree of intermolecular association.

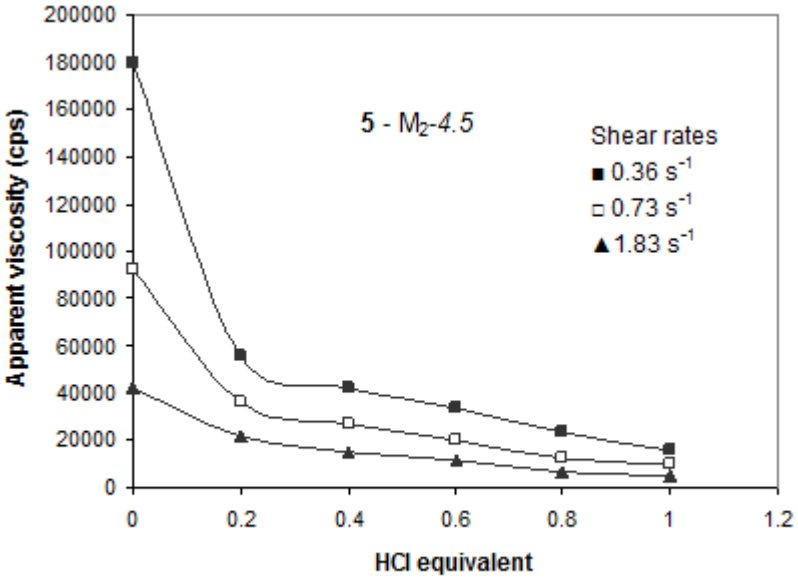


Fig. 3.10 Variation of viscosity with the shear rates of a 1 g/dL solution of **5**- M_2-*4.5* in the presence of various equivalents of HCl in 0.032 N NaCl at 30 °C.

3.3.3 Polymer Surfactant Interactions

An interesting feature of amphiphilic polyelectrolytes with poor water solubility is that redissolution is greatly facilitated by addition of surfactants, which indicates the existence of surfactant/copolymer interactions such that surfactant micelles provide the solublization of the hydrophobic moieties of the amphiphilic polyelectrolyte. The interactions are driven by electrostatic attraction and/or association of the hydrophobic groups on the polymers and those of the surfactant molecules. The polymer surfactant interaction was examined using viscometric measurements on DCPE **4**-M_2-*5.5* in the presence of cationic cetyltrimethylammonium chloride (CTAC) surfactant. **Fig. 3.11** illustrates the viscosity behavior of a 1 g/dL solution of **4**-M_2-*5.5* in the presence of cationic surfactant CTAC at various shear rates. A concentration of 1 g/dL of **4**-M_2-*5.5* corresponds to a concentration of 1.8 mM octadecyl pendents. Upon the addition of CTAC above its critical micelle concentration (CMC) 0.92 mM, the solution of **4**-M_2-*5.5* became more viscous which indicates the existence of surfactant/terpolymer interactions. Above a critical complexation concentration of ~0.7 mM CTAC, the viscosity increases sharply as a result of the formation of mixed micelles of CTAC and octadecyl pendents of the polymer. At a shear rate of 0.36 s^{-1}, the polymer **4**-M_2-*5.5* was found to have apparent viscosity values of 8,000 and 900,000 cps in the absence and presence of 5 mM CTAC, respectively. This interaction of cationic polyelectrolyte with surfactant of like charge (CTAC) is rather unusual, but it is not unique. An interaction in aqueous solutions of hydrophobically modified polyelectrolytes with surfactants of the same charges has been recently reported [91]. Upon further increase in the CTAC concentration, the viscosity

continues to increase, suggesting gradual polymer restructuring and formation of mixed micelle domains which contain hydrophobic groups belonging to two or more distinct polymer chains. The viscosity attains its maximum value at a CTAC concentration of 5 mM, which corresponds to approximately 3 CTAC molecules per octadecyl pendent of the polymer. Comicellization between the polymer and surfactant provides bridging between the polymer chains [92]. Further increase in concentration of CTAC leads to the formation of more micelles and the number of micelles per polymer bound hydrophobe increases and this eventfully disfavors comicellar bridge.

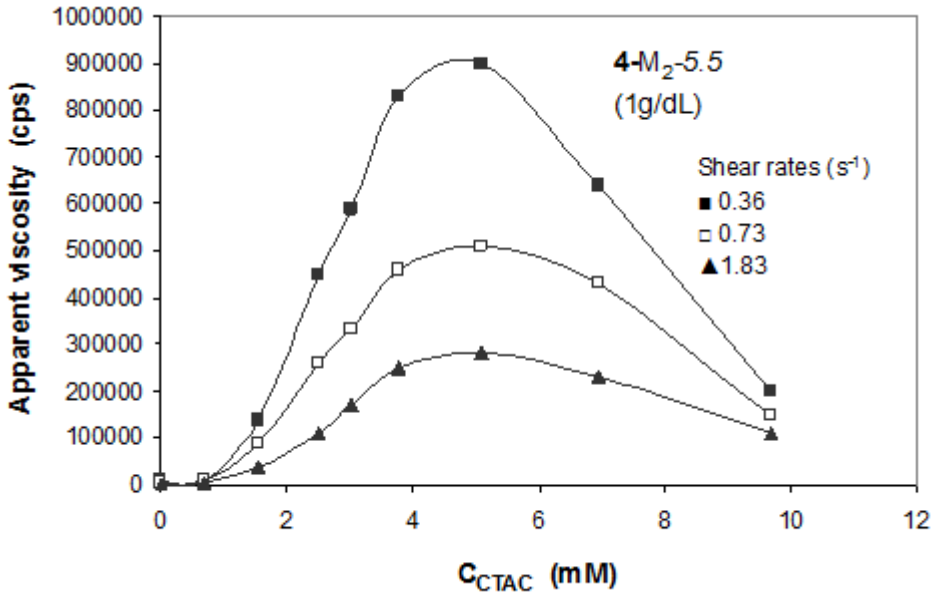


Fig. 3.11 Variation of viscosity with CTAC concentrations of a 1 g/dL solution of **4**-M_2-*5.5* at different shear rates at 30 ^{o}C in salt-free water.

3.4 Conclusion

The interconvertible polymers (**3**→**4**→**5**) have been synthesized in excellent yields and there solution properties have been compared. The work involves an interesting class of interconvertible polymers having identical degree of polymerization thus allowing a meaningful assessment of their solution properties. The hydrophobe incorporation has considerably enhanced the viscosity values in the terpolymers. While the increasing charge density in the polymer chains of DCPEs leads to decreased hydrophobic associations in salt-free water, the tremendous enhancement in the viscosity values is observed in the presence of added salt. The addition of small amounts of CTAC to a solution (1 g/dL) of **4**-M_2-*5.5* makes the solution very viscous indicating polymer-surfactant interactions. The shear thinning or thixotropy behavior associated with the reversible nature of these physical cross-links may lead to their applications in water-borne coatings, paints, cosmetics, and enhanced oil recovery. The pH-induced change in the conformation of the DCPEs can be manipulated judiciously in the effective use of these hydrophobically modified polymers in protein partitioning in aqueous two-phase polymer systems [93].

Acknowledgements:

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CHAPTER 4

4. SYNTHESIS AND SOLUTION PROPERTIES OF A pH-RESPONSIVE CYCLOPOLYMER OF ZWITTERIONIC ETHYL 3-(*N,N*-DIALLYLAMMONIO)PROPANEPHOSPHONATE

SUMMARY: The zwitterionic monomer, ethyl 3-(*N,N*-diallylammonio)propanephosphonate, was cyclopolymerized in aqueous solution using azobisisobutyronitrile or ammonium persulfate as initiators to afford a polyphosphonobetaine (PPB), a zwitterionic polymer. The polymers, on treatment with HCl and NaOH, gave the aqueous solutions of the corresponding cationic polyphosphononic acid (CPP) and anionic polyphosphonate (APP). The solution properties of the PPB having two pH-responsive functionalities were investigated in detail by potentiometric and viscometric techniques. Basicity constants of the amine groups in APP were found to be "apparent" and as such follow the modified Henderson-Hasselbalch equation. In contrast to many polycarbo- and –sulfobetaines, the PPB, as well as CPP and APP were all found to be soluble in salt-free water as well as in salt (including calcium and lithium)-added solutions. The PPB showed 'antipolyelectrolyte'solution behaviour. Interestingly the PPB showed higher intrinsic viscosity value in 1.0 N NaF or LiCl than in NaCl.

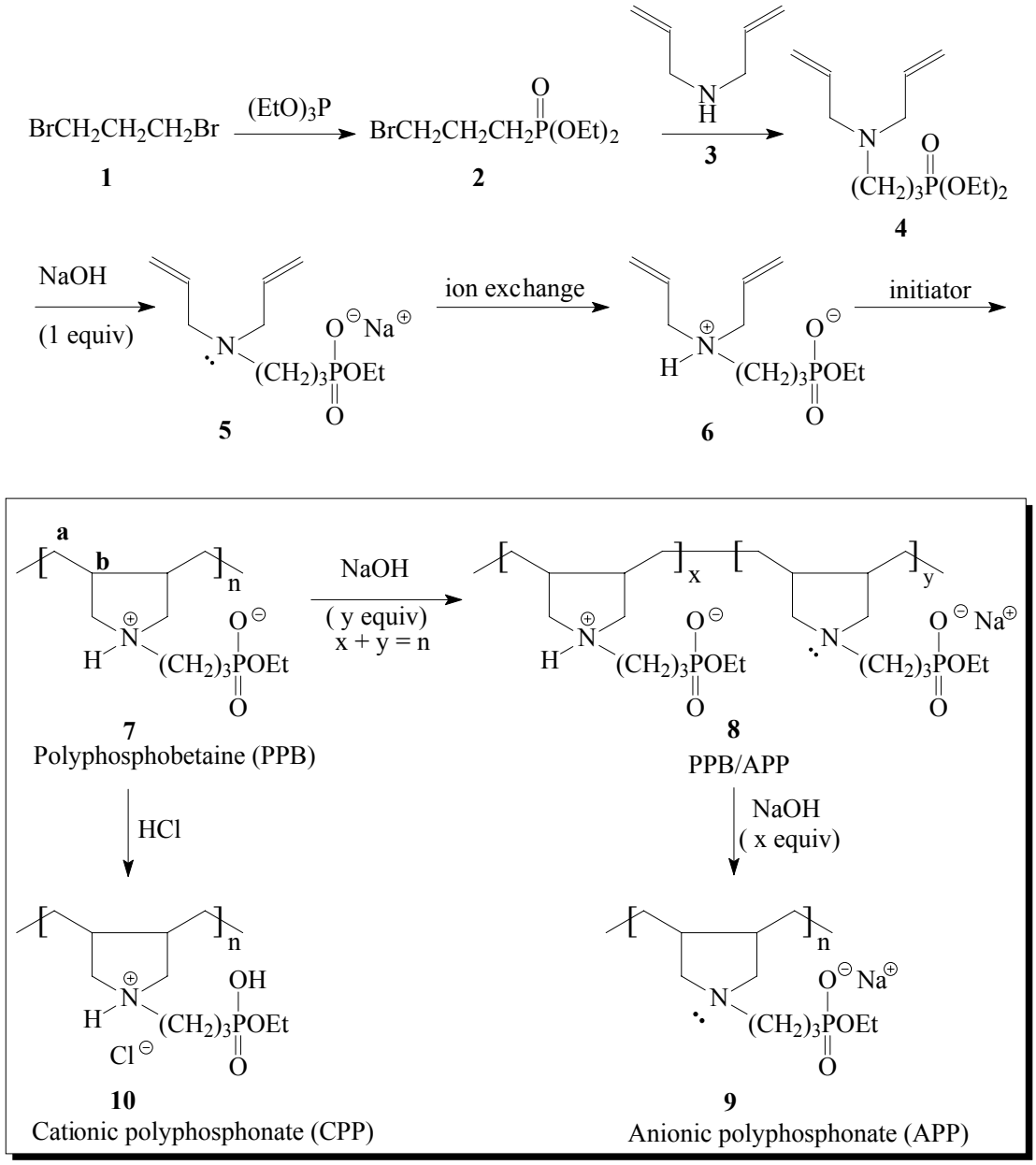
KEYWORDS: Polyelectrolyte; polybetaine; polyphosphonobetaine.

4.1 Introduction

While the polymerization of monomer betaines (zwitterions) ($M^{\pm}$) having charges of both algebraic signs in the same molecular framework lead to polybetaines (polyzwitterions),[1-3] the presence of both M^+ and M^- in the same polymer chain constitutes a polyampholyte with or without charge symmetry. Polybetaines may be grouped into several subclasses like polycarbobetaines, polysulfobetaines, and polyphosphobetaines. While biopolymers like proteins or DNA mediate life processes, commercial polyampholytes and polyzwitterions, whose structure and behavior seem to mimic biopolymers, have offered many new applications in medicine, biotechnology, hydrometallurgy and oil industry. The polyzwitterions are usually derived from acrylamide and acrylate-based zwitterionic monomers[4], while Butler's cyclopolymerization reaction of zwitterionic diallylammonium monomers or their copolymerizations with sulfur dioxide has been an attractive method for the synthesis of polyzwitterions.[5-8] Polyampholytes and polyzwitterions, unlike polyelectrolytes, exhibit 'anti-polyelectrolyte behavior'[6,9-11] i.e. enhancement in viscosity and solubility in the presence of added electrolytes (e.g. NaCl) due to the neutralization of the ionically cross-linked network in a collapsed coil conformation of the polymers. Polyphosphobetaines, which seem to mimic phospholipid biomembranes, have offered many new applications.[1,12] Most of the known polyphosphobetaines are polymeric phospholipid analogues, as these are obtained from monomers containing polymerizable groups incorporated at various positions of phosphorylcholine moiety.[13] While all these polyphosphobetaines contained dialkylphosphate motif (a derivative of phosphoric acid,

H_3PO_4), to our knowledge, there are only two reports[14,15] that describe the cyclopolymerization of phosphorous acid (H_3PO_3) derivatives like diallylaminomethylphosphonic acid to polyphosponobetaines (PPB). A novel phosphonic acid monomer containing methacrylate and methylacrylamide motives has been prepared for use in dental composites.[16] Proton conducting ionomers containing phosphonic acid motif has been used for possible application in polymer electrolyte fuel cells.[17,18]

Extraordinary chelating properties of compounds containing aminomethylphophonic acid groups in the molecule have attracted considerable attention to synthesize low molecular-weight chelating agents containing these functional groups that should be able to form polymer-heavy metal ion complexes from waste water.[19-21] In pursuit of tailoring pH-responsive polymers, we continue to synthesize the cyclopolymers of zwitterionic monomer, ethyl 3-(*N,N*-diallylammonio)propanephosphonate (**6**) (Scheme 1). The conversion of the zwitterionic motif to phosphonate ($-PO_3^-$) in the polymer backbone would allow us to study polyzwitterion - to – anionic polyelectrolyte transition involving polymers having identical degree of polymerization. To the best of our knowledge zwitterionic polyphosphonobetaine (PPB) with three carbon spacer between its charge centers would represent the first example of this class of ionic polymers.


BrCH2CH2CH2Br
(EtO)3P
BrCH2CH2CH2P(OEt)2
1
2
3
4
NaOH
(1 equiv)
5
ion exchange
6
initiator
a
b
n
7
Polyphosphobetaine (PPB)
NaOH
(y equiv)
x + y = n
x
y
8
PPB/APP
HCl
NaOH
(x equiv)
10
Cationic polyphosphonate (CPP)
9
Anionic polyphosphonate (APP)

SCHEME 1.

4.2. EXERIMENTAL

4.2.1 Materials

Triethyl phosphite, 1,3-dibromopropane, *t*-Butylhydroperoxide (70% in water), diallyl amine, ammonium persulfate and Dowex 50 W X 8 resin (ionic form: H^+) from Fluka Chemie AG (Buchs, Switzerland) were used as received. All glassware was cleaned with deionized water. For dialysis, a Spectra/Por membrane with a molecular weight cut-off (MWCO) value of 6000-8000 was purchased from Spectrum Laboratories, Inc.

4.2.2 Physical methods

Melting points were recorded in a calibrated Electrothermal-IA9100- Digital Melting Point Apparatus. Elemental analysis was carried out on a Perkin Elmer Elemental Analyzer Series 11 Model 2400. IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured in $CDCl_3$ (using TMS as internal standard) or D_2O at +25 °C (using HOD peak at δ 4.65 and the ^{13}C peak of dioxane at δ67.4 ppm as internal standard) on a JEOL LA 500 MHz spectrometer. ^{31}P was referenced with 85% H_3PO_4 in DMSO.

A gentle stream of N_2 was passed through distilled deionized water at 90 ^{o}C for 15 min in order to remove dissolved gases. This water was used for viscosity measurements in salt-free and salt (NaCl, 99.9% purity) solutions. Viscosity measurements were made by Ubbelohde viscometer (having Viscometer Constant of 0.005718 cSt/s at all temperatures) using CO_2-free water under N_2 in order to avoid CO_2 absorption that may affect the viscosity data. Thermogravimetric analysis (TGA) experiments were carried out using

Shimadzu DTG-60H equipment. The samples were heated from 25 ºC to 600 ºC at 10 ºC /min under air. Molecular weights of some synthesized polymers were determined by GPC analysis using Viscotek GPCmax VE 2001. The system was calibrated with nine polyethylene oxide monodispersed standards at 30°C using two Viscotek columns G5000 and G6000 in series.

4.2.3 1-Bromo-3-(diethylphosphonato)propane (2)

A mixture of triethyl phosphate (68 cm^3, 397 mmol) and 1,3-dibromopropane (**1**) (207 cm^3, 2.03 mol) was heated from 25 °C to 155 °C (20 min). At around 155 °C, the ethyl bromide was generated and was allowed to be distilled off without using a condenser. After the cease of formation of ethyl bromide (15 min), the reaction mixture was then heated at 160 °C for a further 15 min. Thereafter, the excess 1,3-dibromopropane was immediately distilled off at 60-80 °C (30-40 mm Hg), followed by the desired product **2** as a colorless liquid (75 g, 73%), bp $_{0.6\ mbarHg}$ 107-108°C. δ_H ($CDCl_3$) 1.34 (6H, t, *J* 7.0 Hz), 1.90 (2H, m), 2.16 (2H, m), 3.48 (2H, t, *J* 6.4 Hz), 4.11 (4H, m). It should be noted that heating for 1 h or 4 h at 160 °C as reported[22] yielded the product in very low yields; a complicated mixture of side products were formed. In another trial, adding triethyl phosphate dropwise (1 h) to 1,3-dibromopropane at 160 °C then heating at 160 °C for 6 h did not give the desired compound; instead an intractable mixture of compounds were obtained.

4.2.4 N,N-Diallyl-3-(diethylphosphonato)propylamine (4)

A solution of diallylamine **3** (58.3 g, 0.600 mol) and 1-Bromo-3-(diethylphosphonato)propane **2** (52 g, 0.200 mol) in toluene (80 cm^3) was heated at 85 °C for 12 h. The mixture was treated with aqueous NaOH (0.2 mol NaOH in 100 cm^3 H_2O). The mixture was then extracted with ether (3×100 cm^3) and the combined organic layers was dried (Na_2SO_4) and concentrated. The residual liquid was then purified by distillation to obtain 1-diallylamino-3-(diethylphosphonato)propane **4** as a colorless liquid, bp 0.1 mbarHg, 112 °C (48 g, 87%). (Found: C, 56.6; H, 9.4; N, 5.0. $C_{13}H_{26}NOP$ requires C, 56.71; H, 9.52; N, 5.09%.); $\nu_{max.}$ (neat) 3074, 2978, 2930, 2804, 1642, 1445, 1417, 1391, 1367, 1244, 1162, 1097, 1027, 960, 824, 782, and 701 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.32 (6H, t, *J* 7.0 Hz), 1.74 (4H, m), 2.47 (2H, t, *J* 6.4 Hz), 3.07 (4H, d, *J* 6.4 Hz), 4.08 (4H, m), 5.14 (4H, m), 5.82 (2H, m); δ_C (125 MHz, $CDCl_3$): 16.48 (d, 2C, Me, ^3J (PC) 6.2 Hz), 20.15 (d, $PCH_2\underline{C}H_2$, ^2J (PC) 4.1 Hz), 23.38 (d, $P\underline{C}H_2$, ^1J (PC) 142 Hz), 53.35 (d, $PCH_2CH_2\underline{C}H_2$, ^3J (PC) 18.5 Hz), 56.72 (2C, =CH-$\underline{C}H_2$, s), 61.40 (d, 2C, $O\underline{C}H_2CH_3$, ^2J (PC) 6.2 Hz), 117.35 (2C, s, $\underline{C}H_2$=CH), 135.71 (2C, s, CH_2=$\underline{C}$H); δ_P (202 MHz, $CDCl_3$): 32.85 (1P, t, J 7.3 Hz).

4.2.5 Ethyl 3-(*N,N*-diallylammonio)propanephosphonate (6)

A mixture of diethyl 3-(*N,N*-diallylammonio)propanephosphonate (**4**) (40.0 g, 0.145 mol) in 1.0 N NaOH (150 cm^3) under N_2 was heated in a closed flask at 105°C for 24 h. After cooling to 20 °C, the reaction mixture was washed with ether (3×40 cm^3). The aqueous solution containing the sodium salt **5** in water was stirred with Dowex 50 W X 8 (60 g) at

20 °C for 1 h. The aqueous solution becomes acidic as indicated by litmus test. The solution was filtered through a cotton bed in a column, and the resin was thoroughly washed by passing deionized water (100 cm^3) through it. The zwitterionic monomer was recovered by freeze drying. The thick liquid was then dried to a constant weight *in vacuo* at 65 ^oC to obtain 34.5 g (96 %) of the phosphonobetaine (PB) monomer **6** as a light yellow thick liquid. (Found: C, 53.1; H, 9.3; N, 5.5. $C_{11}H_{22}NO_3P$ requires C, 53.43; H, 8.97; N, 5.66%.); $\nu_{max.}$ (neat) 3365, 3077, 2976, 2933, 2901, 2799, 1638, 1446, 1413, 1393, 1166, 1037, 936, and 780 cm^{-1}; δ_H (500 MHz, D_2O) 1.10 (3 H, t, *J* 7.0 Hz), 1.49 (2H, td, *J* 7.3, 17.3 Hz), 1.80 (2H, m), 3.07 (2H, apparent t, *J* 7.6 Hz), 3.64 (4H, d, *J* 7.3 Hz), 3.75 (2H, qunit, *J* 7.0 Hz), 5.46 (4H, m), 5.78 (2H, m); δ_C (125 MHz, D_2O): 16.47 (d, 2C, Me, ^3J (PC) 6.1 Hz), 18.65 (s, $PCH_2\underline{C}H_2$), 23.80 (d, $P\underline{C}H_2$, ^1J (PC) 137 Hz), 53.36 (d, $PCH_2CH_2\underline{C}H_2$, ^3J (PC) 15.3 Hz), 55.42 (2C, =CH-$\underline{C}H_2$, s), 61.38 (d, 2C, $O\underline{C}H_2CH_3$, ^2J (PC) 4.6 Hz), 126.56 (2C, s, $\underline{C}H_2$=CH), 127.66 (2C, s, CH_2=$\underline{C}$H); δ_P (202 MHz, D_2O): 26.50.

4.2.6 Sodium ethyl 3-(*N,N*-diallylamino)propanephosphonate (5)

In a separate experiment, sodium salt **5** was isolated as a white solid by freeze-drying its aqueous solution. Mp 182-184 °C; (Found: C, 48.9; H, 7.7; N, 5.1. $C_{11}H_{21}NNaO_3P$ requires C, 49.07; H, 7.86; N, 5.20%.); $\nu_{max.}$ (neat) 3081, 2979, 2949, 2904, 2788, 1638, 1442, 1270, 1195, 1075, 1042, 941, 918, 829, 788 and 743 cm^{-1}; δ_H (500 MHz, D_2O) 1.10 (3 H, t, *J* 7.0 Hz), 1.37 (2H, td, *J* 7.1, 16.5 Hz), 1.51 (2H, m), 2.37 (2H, apparent t, *J* 7.7 Hz), 2.99 (4H, d, *J* 7.0 Hz), 3.74 (2H, qunit, J 7.0 Hz), 5.10 (4H, m), 5.74 (2H, m); δ_C

(125 MHz, D_2O): 16.50 (d, 2C, Me, ^3J (PC) 6.1 Hz), 20.02 (d, $PCH_2\underline{C}H_2$, ^2J (PC) 4.6 Hz), 24.64 (d, $P\underline{C}H_2$, ^1J (PC) 136 Hz), 54.00 (d, $PCH_2CH_2\underline{C}H_2$, ^3J (PC) 19.8 Hz), 56.46 (2C, =CH-$\underline{C}H_2$, s), 61.22 (d, 2C, $O\underline{C}H_2CH_3$, ^2J (PC) 6.1 Hz), 120.30 (2C, s, $\underline{C}H_2$=CH), 134.87 (2C, s, CH_2=$\underline{C}$H); δ_P (202 MHz, D_2O): 28.89.

4.2.7 General Procedure for the Polymerization of 6

A solution of the monomer **6** in 0.5 N NaCl solution in a 10 cm^3 round bottomed flask was purged with N_2, and after adding the required amount of the initiator (as listed in **Table 4.1**), the mixture was stirred in the closed flask at the specified temperature and time. The reaction mixture remained transparent throughout the process. The reaction mixture was cooled, transferred to a dialysis bag and dialyzed against deionized water for 48 h in order to remove the unreacted monomer and NaCl (checked with $AgNO_3$ test). The polymer solution of PPB **7** was then freeze-dried and subsequently dried to a constant weight at 60 ^oC under vacuum.

4.2.8 Infrared spectra, thermal decomposition, elemental analyses, molecular weights ($\overline{M}_W$) and polydispesity index (PDI) of the polymers PPB 7

The polymer samples gave satisfactory elemental analyses. Analysis of a sample of PPB **7** is as follows: (Found: C, 53.2; H, 9.2; N, 5.5. $C_{11}H_{22}NO_3P$ requires C, 53.43; H, 8.97; N, 5.66%.); $\nu_{max.}$ (neat) 3326, 2987, 2929, 1446, 1385, 1158, 1029, 936, 776, 739, and 694 cm^{-1}; δ_P (202 MHz, D_2O): 26.67 and a minor (5%) signal at 24.30 ppm.

Table 4.1 Cyclocopolymerization of the monomer **6**[a]

Entry	Monomer[a] (%w/w)	Temp (°C)	NaCl (M)	TBHP[b] (mg)	Yield (%)	Intrinsic Viscosity[c] ($dl\ g^{-1}$)		$\overline{M}_W$	(PDI)[d]
						Salt-free	0.1 N NaCl		
1	70	90	0	50	7	□	□	□	□
2	70	90	0.5	50	14	□	□	□	□
3	70	80	0.5	85	49	0.112	0.132	□	□
4	70	85	0.5	100	53	0.110	0.128	□	□
5	70	85	0.5	125	55	0.115	0.135	□	□
6	75	85	0.5	150	65	0.124	0.142	61,500	2.3
7[b]	75	95	0.5	360[b]	47	0.107	0.118	33,300	2.4

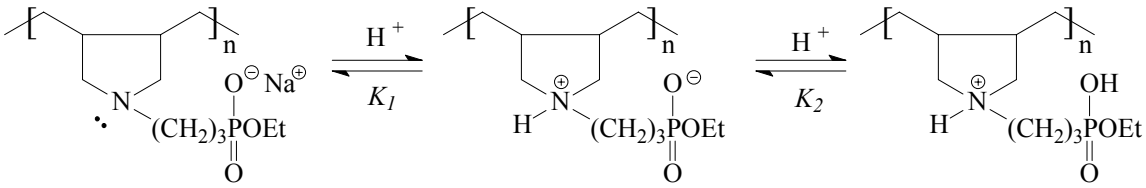
[a]polymerization reactions were carried out using 20 mmol of the monomer in salt-free/salt (NaCl)-added aqueous media at for 48 h.
[b] polymerization reaction in entry 7 was carried out using ammonium persulfate as the initiator for 3 h.
[c]Viscosity of 1-0.125 % polymer solution in salt-free and 0.1 N NaCl at 30°C was measured with a Ubbelohde Viscometer (K=0.005718).
[d]Polydispersity Index.

For the determination of molecular weights, the polymer PPB **7** was treated with one equivalent NaOH to obtain a solution of anionic polyphosphonate (APP) **9**. These samples were analyzed using an aqueous solution of 0.1 N $NaNO_3$ as the eluant. Refractive Index and viscometer detectors were used to detect polymers. The molecular weight ($\overline{M}_W$) and PDI of some of the polymers are given in **Table 4.1**.

4.2.9 Potentiometric titrations

The potentiometric titrations were carried out at 23 ^oC as described elsewhere.[23] A gentle stream of N_2 was passed through distilled deionized water at 90 ^oC for 15 min in order to remove dissolved gases. This water was used in the titration in salt-free and salt (NaCl, 99.9% purity) solutions and for viscosity measurements. For each titration, 200 cm^3 of salt-free or 0.1 N NaCl solution containing a weighed amount (usually around 0.25-0.47 mmol of the monomer or repeating unit) of PPB **6** or its sodium salt **5** or PPB **7** was used. The solution was titrated at 23 ^oC with ~0.1 M HCl (or ~0.1 M NaOH) delivered by a buret under N_2. After each addition of the titrant (in the range 0.10 – 0.25 cm^3) the solution was stirred briefly, using a magnetic stir bar, under N_2. The pH of the solution was recorded using a Corning pH Meter 220.

The protonation constant of the amine nitrogen, Log K_1, is calculated at each pH value by the well-known Henderson-Hasselbalch Equation 1 (Scheme 2) where degree of protonation (α) is the ratio $[ZH^{\pm}]_{eq}/[Z]_o$. For the titration with NaOH, the $[Z]_o$ is the initial analytical concentration of PB **6** or the monomeric units in the PPB **7** and $[ZH^{\pm}]_{eq}$ is the



9 (Z^-) **7** ($ZH^{\pm}$) **10** (ZH_2^+)

$$Z^- + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} ZH^{\pm} \qquad ZH^{\pm} + H^+ \overset{K_2}{\rightleftharpoons} ZH_2^+$$

9 **7** **7** **10**

$$\log K_i = \text{pH} - \log [(1 - \alpha)/\alpha] \quad (1)$$

$$\text{pH} = \log K_i^o + n \log [(1 - \alpha)/\alpha] \quad (2)$$

$$\log K_i = \log K_i^o + (n - 1) \log [(1 - \alpha)/\alpha] \quad (3)$$

SCHEME 2.

Table 4.2 Experimental Details for the Protonation of Monomer **6** ($ZH^{\pm}$), monomer precursor **5** (Z^-), and Polymer PPB **7** ($ZH^{\pm}$) at 23 °C in Salt-Free Water

run	$ZH^{\pm}$ or Z^- (mmol)	C_T [a] (mol dm^{-3})	α–range	pH–range	Points [b]	Log K_1° [c]	n_1 [c]	R^2, [d]
Polymers PPB 7 ($ZH^{\pm}$) in salt-free water								
1	0.4133 ($ZH^{\pm}$)	− 0.0947	0.81–0.43	8.87-10.83	21	10.49	2.49	0.9927
2	0.3142 ($ZH^{\pm}$)	− 0.0947	0.81–0.41	8.83–10.90	19	10.50	2.48	0.9931
3	0.2507 ($ZH^{\pm}$)	− 0.1001	0.84–0.43	8.63-10.72	18	10.56	2.56	0.9874
Average						10.52 (4)	2.51 (4)	
Log K_1° = 10.52 + 1.51 log [(1-α)/α]; For the reaction: $Z^- + H^+ \rightleftharpoons ZH^{\pm}$								
Monomer precursor 5 (Z^-) and monomer 6 ($ZH^{\pm}$) in salt-free water								
1	0.4651 ($ZH^{\pm}$)	− 0.1230	0.79-0.47	8.40-9.02	16	8.99	1.06	0.9936
2	0.3478($ZH^{\pm}$)	− 0.0947	0.85-0.51	8.12-8.92	17	8.96	1.04	0.9891
3	0.2752 (Z^-)	+0.1083	0.21-0.79	9.66-8.46	18	9.03	1.07	0.9961
Average						8.99 (4)	1.06 (2)	
Log K_1° = 8.99; For the reaction: $Z^- + H^+ \rightleftharpoons ZH^{\pm}$								
Polymers PPB 7 ($ZH^{\pm}$) in salt-free water								
1	0.4044 ($ZH^{\pm}$)	+0.09930	0.088–0.40	3.25–2.55	15	2.42	0.83	0.9968
2	0.3235 ($ZH^{\pm}$)	+0.09930	0.090–0.35	3.32-2.67	15	2.44	0.86	0.9961
3	0.2507 ($ZH^{\pm}$)	+0.09930	0.091–0.32	3.30–2.67	14	2.39	0.88	0.9897
Average						2.42 (3)	0.86 (3)	
Log K_2° = 2.42 - 0.14 log [(1-α)/α] For the reaction: $ZH^{\pm} + H^+ \rightleftharpoons ZH_2^+$								
Monomer precursor 5 (Z^-) and monomer 6 ($ZH^{\pm}$) in salt-free water								
1	0.3842 ($ZH^{\pm}$)	+0.1083	0.14-0.50	3.29-2.47	15	2.38	0.98	0.9942
2	0.3033 ($ZH^{\pm}$)	0.1083	0.10-0.42	3.43-2.53	17	2.42	1.07	0.9874
3	0.3438 (Z^-)	+0.1083	0.09-0.56	3.33-2.29	16	2.38	0.99	0.9933
Average						2.39 (2)	1.01 (5)	
Log K_2° = 2.39; For the reaction: $ZH^{\pm} + H^+ \rightleftharpoons ZH_2^+$								

[a] Titrant concentration (negative and positive values indicate titrations with NaOH and HCl, respectively).
[b] Number of data points from titration curve. [c] Values in the parentheses are standard deviations in the last digit.
[d] R = Correlation coefficient. [e] $\log K_1 = \log K_1^{\circ} + (n-1) \log [(1-\alpha)/\alpha]$.

Table 4.3 Experimental Details for the Protonation of Monomer Precursor **5** (Z^-), Monomer **6** ($ZH^\pm$), and Polymer PPB 7 ($ZH^\pm$) at 23 °C in 0.1 M NaCl

run	$ZH^\pm$ or Z^- (mmol)	C_T [a] (mol dm^{-3})	α–range	pH–range	Points[b]	Log K_i° [c]	n_i [c]	R^2 [d]
Polymers PPB 7 ($ZH^\pm$) in 0.1 N NaCl								
1	0.4085 ($ZH^\pm$)	− 0.1001	0.81–0.32	8.75–10.78	22	10.01	2.12	0.9932
2	0.3276 ($ZH^\pm$)	− 0.1001	0.78–0.34	8.90–10.62	20	10.09	2.09	0.9946
3	0.2669 ($ZH^\pm$)	− 0.1001	0.82–0.33	8.61–10.77	18	10.07	2.10	0.9918
Average						10.06 (04)	2.10 (2)	
Log K_1° = 10.06 + 1.10 log [(1-α)/α] For the reaction: $Z^- + H^+ \rightleftharpoons ZH^\pm$								
Monomer precursor 5 (Z^-) and monomer 6 ($ZH^\pm$) in 0.1 N NaCl								
1	0.3114 ($ZH^\pm$)	− 0.0947	0.80-0.28	8.09-9.07	17	8.70	1.03	0.9949
2	0.4226 ($ZH^\pm$)	− 0.0947	0.87-33	7.95-9.02	23	8.73	0.961	0.9974
3	0.3045 (Z^-)	+0.1083	0.10-0.80	9.67-8.12	18	8.80	1.03	0.9883
Average						8.74 (5)	1.01 (4)	
Log K_1° = 8.74 ; For the reaction: $Z^- + H^+ \rightleftharpoons ZH^\pm$								
Polymers PPB 7 ($ZH^\pm$) in 0.1 N NaCl								
1	0.2750 ($ZH^\pm$)	+ 0.0993	0.12-0.51	3.33-2.59	16	2.61	0.85	0.9960
2	0.2912 ($ZH^\pm$)	+ 0.0993	0.09-0.50	3.45-2.59	16	2.56	0.88	0.9843
3	0.3276 ($ZH^\pm$)	+ 0.0993	0.12-0.48	3.41-2.69	17	2.62	0.90	0.9876
Average						2.60 (3)	0.88 (3)	
Log K_2° = 2.60 - 0.12 log [(1-α)/α] For the reaction: $ZH^\pm + H^+ \rightleftharpoons ZH_2^+$								
Monomer precursor 5 (Z^-) and monomer 6 ($ZH^\pm$) in 0.1 N NaCl								
1	0.3045 (Z^-)	+0.1083	0.18-0.50	3.24-2.52	16	2.50	1.11	0.9930
2	0.3761 ($ZH^\pm$)	+0.1083	0.13-0.44	3.22-2.59	18	2.50	0.93	0.9879
3	0.2752 ($ZH^\pm$)	+0.1083	0.08-0.48	3.59-2.58	17	2.55	0.98	0.9944
Average						2.52 (3)	1.01(11)	
Log K_2° = 2.52 For the reaction: $ZH^\pm + H^+ \rightleftharpoons ZH_2^+$								

[a] Titrant concentration (negative and positive values indicate titrations with NaOH and HCl, respectively).
[b] Number of data points from titration curve. [c] Values in the parentheses are standard deviations in the last digit.
[d] R = Correlation coefficient. [e] $\log K_i = \log K_i^\circ + (n-1) \log [(1-\alpha)/\alpha]$.

concentration of the protonated species at the equilibrium given by $[ZH^{\pm}]_{eq} = [Z]_o - C_{OH}^- - [H^+] + [OH^-]$, where C_{OH}^- is the concentration of the added NaOH; $[H^+]$ and $[OH^-]$ at equilibrium were calculated from the pH value.[24]

The typical electrolytes having apparent basicity constants could be described by the Equation 2 (Scheme 2) where log K^o = pH at $\alpha = 0.5$ and $n = 1$ in the case of sharp basicity constants. The linear regression fit of pH *vs*. log $[(1-\alpha)/\alpha)]$ gave log K^o and '*n*' as the intercept and slope, respectively. Simultaneous protonation of the two basic sites is least likely since the basicity constant for the $PO(OEt)O^-$ group is less than that of the amine group by at least 7 orders of magnitude. The second step protonation constant (log K_2) involving the $PO(OEt)O^-$ is calculated by titration of the PB **6** or the monomeric units in the PPB **7** with HCl. In this case, α represents the ratio $[ZH_2^+]_{eq}/[Z]_o$ whereby $[ZH_2^+]_{eq}$ equals $C_H^+ - [H^+] + [OH^-]$ and C_H^+ is the concentration of the added HCl. For titration of the monomeric sodium salt **5** with HCl, Log K_1, is calculated using $[ZH^{\pm}]_{eq} = C_H^+ - [H^+] + [OH^-]$, while the second step protonation constant (log K_2) involving the $P(=O)(OEt)O^-$ is calculated by subtracting the equivalent volume from the total volume of the titrant, and using $[ZH_2^+]_{eq} = C_H^+ - [H^+] + [OH^-]$.

The experimental details of the potentiometric titrations are summarized in **Tables 4.2** and **4.3**. Inserting the value of pH from Equation 2 into Equation 1 leads to modified Henderson-Hasselbalch equation (Eq. 3)[25,26] (Scheme 2) where $(n - 1)$ gives a measure of the deviation of the studied polymers from the behavior of small molecules showing sharp basicity constants (for molecules having sharp basicity constants, *n* becomes 1).

4. 3 RESULTS AND DISCUSSION

4.3.1 Synthesis and Physical Characterization of the Polymers

The new zwitterionic phosphonobetaine (PB) monomer **6** was prepared in excellent yield as outlined in Scheme 1. Using reported procedure we were unable to obtain 1-bromo-3-(diethylphosphonato)propane **2** in yield anywhere near to that reported.[22] However, a modified reaction conditions led to the desired compound in good yield (Experimental).

Diallylamine (**3**) upon alkylation with **2** afforded 1-diallylamino-3-(diethylphosphonato)propane **4** in 87% yield. One of the ester groups in the diallylamine diester derivative **4** was selectively hydrolyzed with 1 equivalent of sodium hydroxide to give the sodium salt of monoester **5** which upon cation exchange with Dowex 50 W X 8 (in H^+ form) led to PB **6** (96% yield). Attempt to cyclopolymerize monomer **6** in salt-free water failed to give the corresponding zwitterionic polyphosphobetaine (PPB) **7** in reasonable yield (7%, entry 1, **Table 4.1**). However, monomer **6** did undergo cyclopolymerization in aqueous solution containing 70-75 wt% monomer and 30-25 wt% 0.5 N NaCl. (Scheme 1). The results of the polymerization under various conditions are given in **Table 4.1**. As evident from **Table 4.1**, changing the initiator from *t*-butylhydroperoxide (TBHP) to ammonium persulfate (entry 7) did not improve the polymer yield. A reasonable yield (65%) of polymer PPB **7** was obtained with a 75 wt% monomer (entry 6) using TBHP as the initiator. The low yield and molecular weight as indicated by lower intrinsic viscosity values (**Table 4.1**) could be a result of chain

transfer between polymer and monomer through the alkoxy groups attached to the P atoms.

PPB **7** was found to be very stable and did not show any appreciable decomposition or color change up to 400 °C. However, upon exposure at 400 °C for a longer duration (ca. 20 min), the polymer charred to brown color. The TGA curve for PPB **7** is given in **Figure 4.1.** Three main regions can be identified. The initial weight loss (~10%) at 100 – 200 ºC was attributed to the reversible desorption of moisture. The second weigh loss occurred from 200-350 ºC (12%) is probably due to the loss of ethylene unit from the mono-ester. A remarkable weight loss is observed in the range of 350-410 ºC (10%) which is probably due to defragmentation of the pendant propyl moiety from the main chain polymer.

The PPB **7** was found to be readily soluble in water as well as in most of the protic solvents having higher dielectric constants (**Table 4.4**). Hydrogen bonding with the protic solvents is expected to be the major driving force for the solubility behavior. The polymer was found to be insoluble in nonprotic solvents like DMF and DMSO even though they have very high dielectric constants. The solubility of polyzwitterions in water is not that unusual. A considerable number of polycarbo- and sulfobetaine are reported to be soluble in salt-free as well as salt (NaCl) added solutions.[28] Carbobetaines having carboxyl pK_a values of $\leq$ 2.0 are found to be insoluble in salt-free water and soluble in salt added solutions. The negative charges on the carbobetaines, having apparent carboxyl pK_a values $\geq$ 2.0 as a result of increasing distance between the charges, are expected to be less dispersed, hence more hydrated.[23,29,30] In such a scenario, carboxylate groups tend to

exhibit weaker Coulombic interactions with the cationic charges.[31] Sterically crowded cationic charges are also reported to be unable to manifest effective intra- or intermolecular Coulombic interactions, thereby leading to its solubility in salt-free

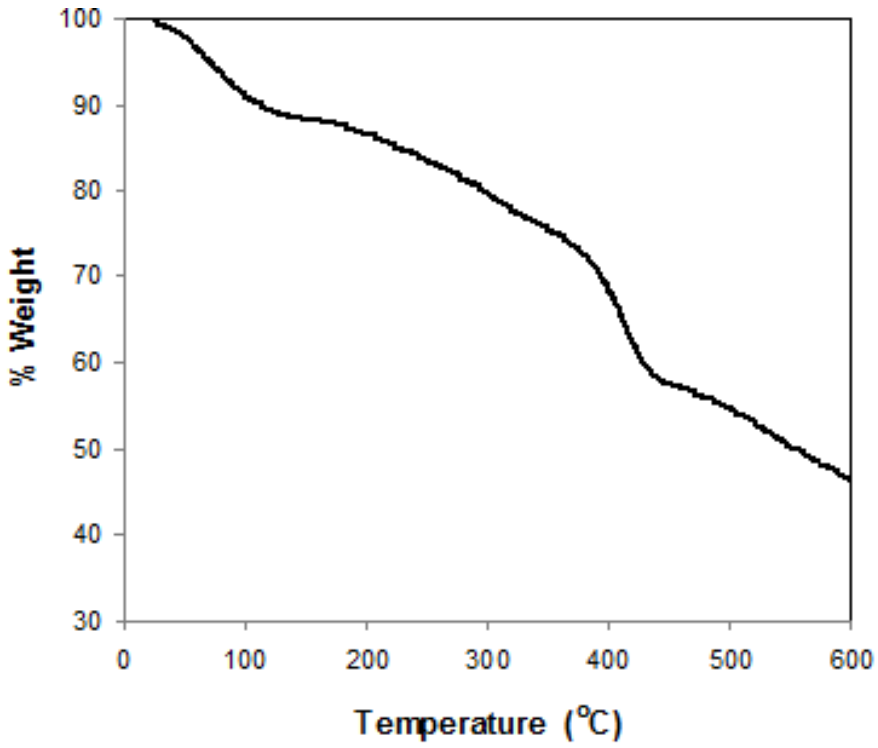


Figure 4.1 TGA curve of PPB **7**.

water.[6,32] It is worth mentioning that the temperature and molecular weight also have a say in the solubility behavior of pylbetaines.[33] Since the phosphonate pK_a (i.e. log K_2) in PPB **7** was determined to be > 2, the phosphobetaine is expected to be soluble in salt-free as well as salt-added water.

Table 4.4 Solubility[a,b] of PPB 7

Solvent	Dielectric constant, ε	solubility
Formamide	111.0	+
Water	78.4	+
Formic acid	58.5	+
DMSO	47	□
Ehylene glycol	37.3	+
DMF	37	□
Methanol	32.7	+
Diethyleneglycol	31.7	+
Ethanol	24.5	±
Acetone	21	□
Acetic acid	6.1	□

[a]2%(w/w) of polymer solution was made after heating the mixture at 70°C for 1 h and then cooling to 23°C.

[b]'+' indicates soluble; '-' indicates insoluble; '±' indicates partially soluble.

4.3.2 Infrared and NMR spectra

The strong absorptions at 1158 and 1029 cm^{-1} in the IR spectrum of PPB **7** were attributed to the stretching frequency of P=O and P-O-C, respectively. ^{1}H and ^{13}C NMR spectra of the PPB **7** and its monomer PB **6** are displayed in **Figures 4.2 and 4.3**, respectively. The absence of any residual alkene proton or carbon signal in the homopolymer spectra also suggested the degradative chain transfer process[34] for the termination reaction.

The assignments of the ^{13}C peaks are based on earlier works[30,35-38] on quaternary ammonium salt monomers which undergo cyclopolymerization to afford kinetically favorable five-membered ring structure. The substituents at the C-b of the PPB **7** can either be in the symmetrical *cis* (major) or unsymmetrical *trans* (minor) dispositions (Scheme 1). Integration of the relevant peaks in the ^{13}C spectrum yields the *cis/trans* ratio of the ring substituents to be 75/25 which is similar to that observed for the related homopolymers derived from the corresponding quaternary ammonium salts.[7,30]

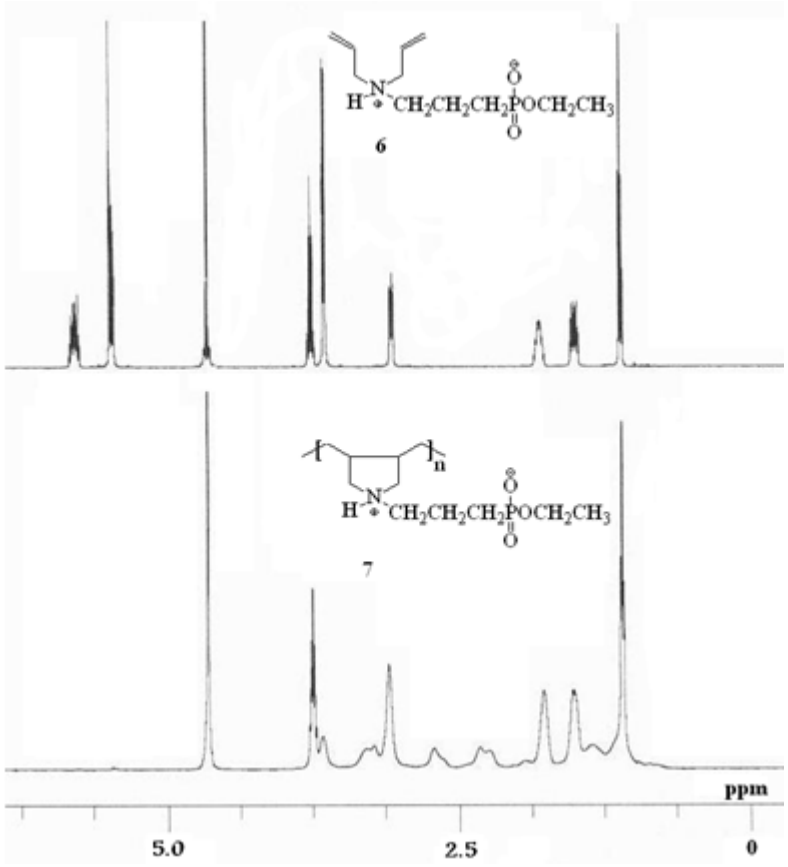


Figure 4.2 ^{1}H NMR spectrum of (a) PBB **7**, (b) monomer **6** in D_2O.

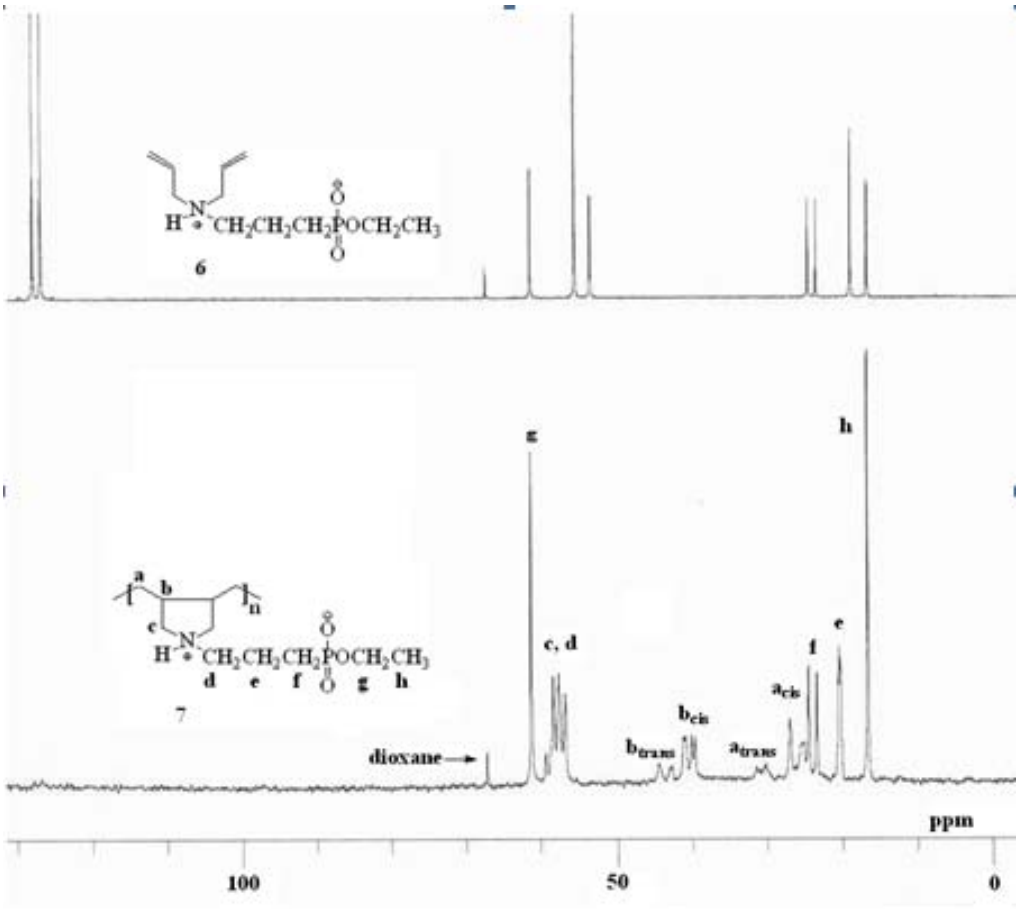


Figure 4.3 ^{13}C NMR spectrum of (a) PBB **7**, (b) monomer **6** in D_2O.

4.3.3 Viscosity measurements

Viscosity data were evaluated by the Huggins equation: $\eta_{sp}/C = [\eta] + k[\eta]^2 C$. Unlike in the case of a polyelectrolyte, the Huggins viscosity plot for PPB **7** in the absence or presence of added salt (NaCl) remains linear. The intrinsic viscosity, slope and Huggins constant are included in **Tables 4.1** and **4.5**. An increase in the intrinsic viscosity in the presence of an added salt is a demonstration of the "anti-polyelectrolyte" behavior of the PPB **7**. Note that for a common Na^+ cation, the intrinsic viscosity increases as the anion is changed from Cl^- to I^- (**Figure 4.4, Table 4.5**). This is expected as the iodide anion is more polarizable (soft), hence it is particularly effective in neutralizing the cationic charges on the polymer backbone. The more exposed phosphonate anions in the presence of NaI are not shielded (neutralized) to a similar extent by the cation Na^+. Cationic sodium's hydration shell in water is generally fairly large, hence the distance of closest approach is not sufficient to effectively neutralize the charge on the pendent phosphonate anions; the increased repulsion between the negative charges thereby increases the hydrodynamic volume hence the viscosity values. A decrease in the value for the Huggins constant k in the presence of NaI in comparison to NaCl may be associated with an increased polymer-solvent interaction. One important feature of this investigation is that divalent cation Ca^{2+}, which is usually known to precipitate anionic polyelectrolytes from aqueous solution even at low concentrations, did not precipitate the PPB **7**. Contrary to earlier reports on polycarbo- and sulfobetaines,[6,7,9] it is interesting to note that the viscosity values were found to be higher in the presence of LiCl than NaCl (**Figure 4.4**).

To the best of our knowledge, we do not have any report that documented such an observation on ionic

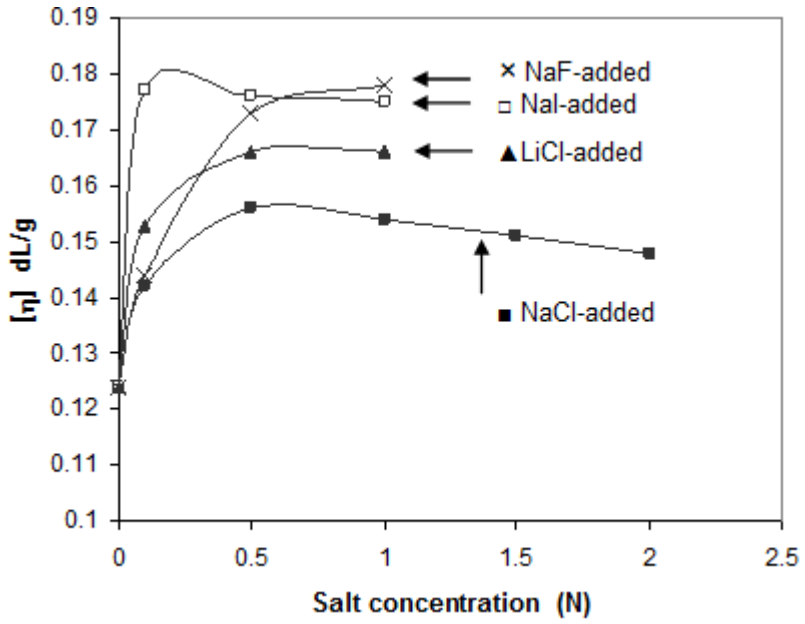


Figure 4.4 The intrinsic viscosity [η] behavior of PPB **7** in the presence of varying concentrations of added salts at 30 ^{o}C using an Ubbelohde Viscometer.

Table 4.5 Effect of added salts on the intrinsic viscosity ([η])[a] and Huggins constant (k') of PPB **7**

Solvent	slope	[η]	k
Salt-free H_2O	0.0426	0.124	2.77
0.1 N NaF	0.0239	0.144	1.15
0.5 N NaF[b]	0.0081	0.173[b]	0.271
1.0 N NaF	0.0086	0.178	0.271
0.1 N NaCl	0.0317	0.142	1.58
0.5 N NaCl	0.0173	0.156	0.711
1.0 N NaCl	0.0230	0.154	0.970
1.5 N NaCl	0.0224	0.151	0.982
2.0 N NaCl	0.0198	0.148	0.904
0.1 N NaI	0.0132	0.177	0.421
0.5 N NaI	0.0197	0.176	0.634
1.0 N NaI	0.0222	0.175	0.725
0.1 N LiCl	0.0283	0.153	1.21
0.5 N LiCl	0.0192	0.166	0.697
1.0 N LiCl	0.0218	0.166	0.791
0.1 N $CaCl_2$	0.0220	0.157	0.892
0.1 N HCl	0.0162	0.131	0.944

[a]Viscosity of 1-0.125 % salt-added polymer solution at 30°C was measured with a Ubbelohde Viscometer (K=0.005718).
[b][η] of PPB **7** in 0.5 N NaF in the presence of 1.0 equiv NaOH was determined to be 0.161 dL/g.

polymers. For a common Cl^- anion, a rationale for such an observation can be made with respect to the increase in the intrinsic viscosity as the cation is changed from Na^+ to Li^+. The larger charge/radius ratio for Li^+ makes its hydration shell larger than that of Na^+, and as such makes it less effective than Na^+ in shielding the phophonate anions. As a result the repulsions among the more exposed anionic pendants lead to a higher viscosity value in the presence of LiCl. 'Antipolyelectrolyte' solution behavior of PPB **7** is demonstrated in **Figure 4.4.** In the presence of added salts (LiCl, NaF, NaCl and NaI), the viscosity increased with the increase in the concentration of the added salts from 0-0.5 N. At higher salt concentrations, the increase in [η] levels off, and in fact in the case of NaCl it tends to decrease a little in the concentration range 1-2 N. Upon completion of the site and atmospheric binding[9] of the cationic charges on the nitrogens by Cl^-, the exposed anionic pendents in a sea of Na^+ ions are also expected to be shielded to a certain degree. Thus, subsequent to a leveling off, the [η] values may decrease as observed in our study. Fluoride anion is known to be the least able to neutralize the cationic charges in polysulfobetaines; in fact the polymers remain insoluble in the presence of any amount of added NaF.[9] It is interesting to note the viscosity behavior of PPB **7** in 1.0 N NaF; the intrinsic viscosity was found to be higher than in 1.0 N LiCl, NaCl or even NaI. The viscosity data indicate that the binding ability of Na^+ to the anionic sites is much higher than that of the binding ability of F^- to the cationic charges in the polymer backbone. As a result the polymer backbone has a net positive charge whose repulsive interactions lead to a higher hydrodynamic volume, hence higher viscosity value.

The pH-responsiveness of PPB **7** was measured by viscometry. The reduced viscosities of a 1.0 g/dL solution of the polymer (entry 6, **Table 4.1**) in salt-free water at 30°C in the presence various amounts of HCl and NaOH are displayed in **Figure 4.5.** Reduced viscosity increases slightly with the addition of HCl; the presence of increasing proportion of the protonated cationic polyphosphonate (CPP) **10** is expected to increase the viscosity as a result of increased repulsions among the unshielded cationic charges on the nitrogens. A steep increase in the viscosity values is observed on the addition of NaOH which changes the polymer PPB **7** to the zwitterionic/anionic polymer (PPB/APP) **8**, thereby provoking a continuous extension of the polymer backbone as a result of increased repulsion among negative charges. The proportion of the anionic motifs in **8** is expected to increase with the increase in the amount of the added NaOH; the viscosity value reaches the maximum after addition of 1 equivalent of NaOH. A decrease in the viscosity upon further addition of NaOH could be attributed to the effect of increasing ionic strength that can shield the anionic pendants. On the acidic side of the titration, the chain extension, hence increment in the reduced viscosity values, are not so significant indicating that the polymer conformation remain compact in the acidic media.

Viscosity data for PPB **7** in neutral medium and in the presence of 1 equivalent of HCl and NaOH are presented in **Figure 4.6**. In the absence of added salt (NaCl), the plot for (PPB **7** + 1 equiv NaOH) i.e APP **9** system is marginally typical for a polyelectrolyte i.e. concave upwards as the reduced viscosity increases slightly with decreasing concentration of the polymer. APP **9** in aqueous solution will be in dynamic equilibrium with the PPB/APP **8** via protontion of the basic nitrogens in **9**. In the higher concentration range,

there is a balancing act happening between the polyelectrolytic effects of the anionic portion of **8** and its zwitterionic portion, which tend to increase and decrease viscosity values, respectively, with increasing dilution. However, at higher dilution, the reduced viscosity tends to fall off owing to an increase in the proportion of the zwitterionic species ($ZH^{\pm}$) in **8** by increased protonation of the anionic portion (Z^-) (i.e. $Z^- + H_2O \leftrightharpoons ZH^{\pm} + OH^-$).

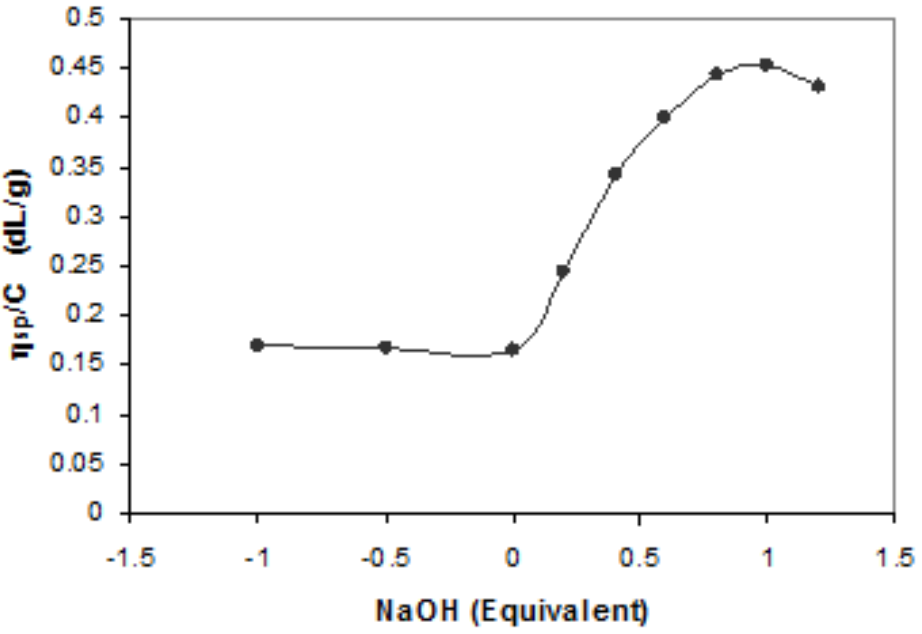


Figure 4.5 Reduced viscosity (η_{sp}/C) of a 1.0 g/dL solution of polymer PPB **7** in salt-free water versus equivalent of added NaOH at 23°C. Negative (-) values indicate the equivalent of added HCl.

4.3.4 Basicity constants

In order to gain further information on the conformational transitions, we have determined the basicity constants, K_i^o, and the corresponding n_i values relative to the protonation of the tertiary amine and carboxylate in polymer PPB **7**, monomer **6** and its precursor anion **5** in salt-free water and 0.1 N NaCl solution. Basicity constants and the corresponding n_i values as well as the experimental details of the potentiometric titrations are given in **Tables 4.2** and **4.3**.

The basicity constants log K_1 for the protonation of the trivalent nitrogen of this polymer are found to be "apparent"[25,26,39,40] in salt-free as well as 0.1 N NaCl solution since the n values are not equal to 1; n values were found to be 2.52 and 2.12, respectively. The log K_1 thus varies with the degree of protonation (α). This behavior i.e. the variation of K with α, is known as polyelectrolyte effect; polymer exhibiting a strong polyelectrolyte effect shows a large change in log K in going from one end to the other end of the titration. The magnitude of the n reflects the polyelectrolye effect, and can be regarded as an index of accessibility of the proton to the amine nitrogen during the protonation reaction. The basicity constant (log K_1^o) of the amine group was found to be 10.52 and 10.06 salt-free water and 0.1 N NaCl, respectively (**Figure 4.7 and Tables 4.2 and 4. 3**). The n_1 values for the protonation of the amine nitrogen of APE **9** in salt-free water and 0.1 N NaCl were found to be 2.51 and 2.10, respectively. Since the n_1 values are greater than 1, the approach of the incoming protons to the amine nitrogens becomes more and more difficult as the degree of protonation (α) of the whole macromolecule increases. The

decrease in the overall negative charge density in the macromolecule decreases the electrostatic field force that attract the proton thereby decreases basicity constant (log K) with the increase in degree of protonation (α).

Several studies[41] indicated that the protonation of polymers is dictated by entropy effects involving release of water molecules from the hydration shell of the repeating unit that is being protonated. The APP **9** (i.e. PPB **7** + 1 equiv NaOH) in salt-free water is more extended as indicated by higher viscosity values (**Figure 4.6a vs. 4.6b**) and as such more hydrated (more water molecules in each hydration shell) than in salt solution (0.1 N NaCl) where the polymer chain adopts a compact conformation due to screening of the negative charges by the sodium ions. Upon each repeating unit in APP **9** being protonated, contraction of the macromolecule chain in salt-free water (**Figure 4.6a** transforming into **4.6d**) is larger than in 0.1 N NaCl (**Figure 4.6b** transforming into **4.6c**). This would lead to the loss of greater number of water molecules from the hydration shell of the repeating unit being protonated in salt-free water. This is reflected by the higher n_1 value (2.52), greater basicity constant (log K_1^o: 10.52), and greater changes in the basicity constant in salt-free water (**Figure 4.7**) than in 0.1 N NaCl.

The basicity constants and the n_2 values for the protonation of the P(=O)OEtO$^-$ group are found to be similar in the salt-free and 0.1 N NaCl solution (log K_2^o = 2.42, n_2 = 0.86 in salt-free water; log K_2^o = 2.60, n_2 = 0.88 in 0.1 N NaCl). As a result of the increased distance between the anionic pendants, one anionic centre does not have any considerable influence on the protonation process of its neighbor. The slightly higher log K_2^o in 0.1 N

NaCl could be attributed to the higher viscosity value in the saline media (**Figure 4.5c** vs**. 4.5d**) in which the macromolecule is more hydrated. As a result of each protonation, greater number of water molecules is released in 0.1 N NaCl thereby leading to the higher basicity constant.

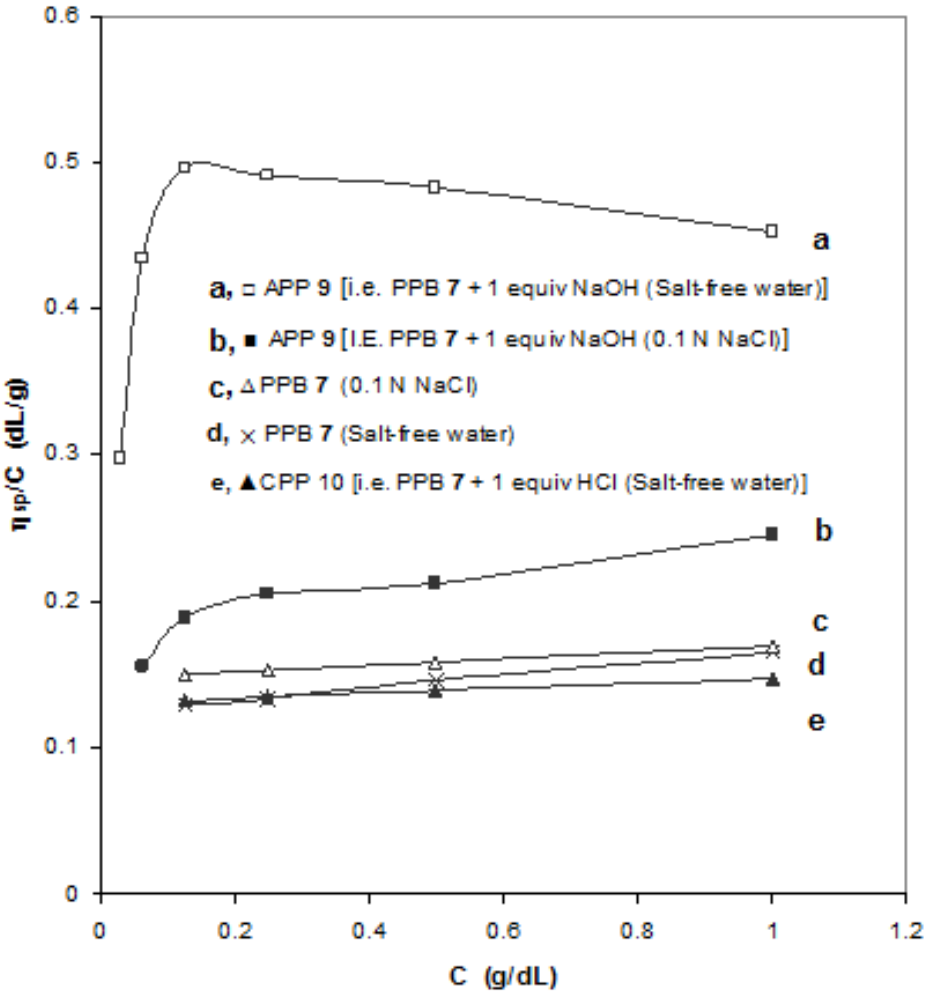


Figure 4.6 The viscosity behavior of the PPB **7**, APP **9** and CPP **10** (obtained *via* PPB **7** from entry 6, **Table 4.1**) in salt-free water and 0.1 N NaCl at 30 ^{o}C using Ubbelohde Viscometer.

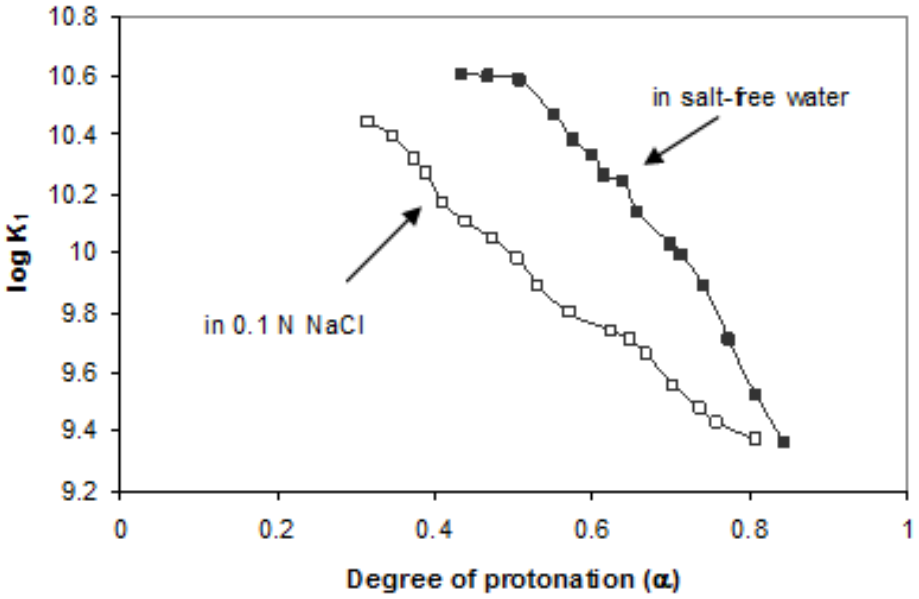


Figure 4.7 Plot for the apparent log K_1 versus a for PPB **7** in salt-free water and 0.1 N NaCl.

4.4 CONCLUSIONS

We have, for the first time, synthesized a pH-responsive polyphosphobetaine (PPB) **7** (containing a three carbon spacer between the charges) using Butler's cyclopolymerization process. The pH-triggerable amine and carboxylate functionalities permitted us to determine their basicity constants in salt-free as well as 0.1 N NaCl. The PPB showed 'antipolyelectrolyte' behavior in salt-added media. The study demonstrated a correlation between the basicity constants and viscosity values. Conformational behavior of the polymers is strongly influenced by the nature and the net charge on the macromolecular chain; overall higher negative charge density led to higher viscosity values, while excess positive charge density were found to have a limited influence on the viscosity values. The PPB was found to soluble in protic but insoluble in aprotic solvents. The polymer was found to be soluble in the presence of Ca^{2+} ions thereby it may find potential application, for instance, in desalination plants in inhibiting $CaCO_3$ scaling by making soluble polymer-Ca^{2+} metal complex. Phosphonate pK_a being > 2 made the PPB soluble in salt-free as well as salt-added water. The PPB showed 'antipolyelectrolyte' behaviour. In contrast to polycarbo- and sulfobetaines, the current polyphosphobetaine showed higher intrinsic viscosity values in 1.0 N NaF or LiCl than in NaCl.

Acknowledgements

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CHAPTER 5

5. New Highly Phosphonated Polysulfone Membranes for PEM Fuel Cells

Taken from

Nedal Y. Abu-Thabit , Shaikh A. Ali and S. M. Javaid Zaidi, New Highly Phosphonated Polysulfone Membranes for PEM Fuel Cells, *Journal of Membrane Science*, 360, (2010) 26-33.

SUMMARY :

This paper reports the development and characterization of phosphonated poly(arylene ether sulfone) polymer electrolytes for direct methanol fuel cells. The synthesis of phosphonated polysulfone was performed by a post phosphonation method *via* chloromethylation of the polysulfone backbone followed by phosphonation utilizing the Michaels-Arbuzov reaction. High degree of phosphonation up to150 % was achieved without crosslinking side reactions. The obtained membranes/polymers in the ester form were hydrolyzed to the corresponding phosphonic acid by refluxing in aqueous hydrochloric acid. The modified polymers were characterized by nuclear magnetic resonance, infrared spectroscopy, ion exchange capacity, differential scanning calorimetry and thermal gravity analysis. The high level of phosphonic acid content 150% led to high water uptake level 52 wt % which is necessary to reach high proton conductivity values. The synthesized membranes with highest phosphonic acid content 150% reached 12 mS/cm at 100 ºC under fully hydrated conditions and showed low methanol crossover (9.12×10^{-8} cm^2/s) compared to Nafion 117 membranes. Also, membranes with 150% phosphonic acid content exhibit high thermal stability up to 252 ºC under air which entitle them as future candidates for proton exchange membrane fuel cells PEMFCs.

***Keywords*:** Phosphonated polysulfone; Ion exchange membrane; Water uptake; Proton conducting electrolyte; Methanol permeability.

5.1 Introduction

Phosphonic acid functionalized polymers, owing to their high thermal stability and lower methanol permeability, have recently attracted attention as an alternative to sulfonic acid polymers for proton exchange membrane fuel cells (PEMFCs) [135]. Only few studies have been reported on the polymerization of phosphonic acid functionalized monomers because of limited available synthetic pathways and possible side-reactions which resulted in oligomeric products and poor yields [136-139]. An alternative technique is the chemical modification of the polymer backbone where the phosphonic acid units may be appended, thus giving access to ionomers. Thermally and chemically stable polyaromatic hydrocarbons such as polystyrene, polyphenylene oxide, polyphosphazane, polyimide and polysulfone (PSU) have been functionalized with phosphonic acid groups by this method for various applications [140-143]. Among these polymers, PSUs were functionalized with phosphonic acid groups via different approaches in order to obtain high phosphonic acid functionality.

Jannasch and coworkers suggested the use of phosphonic acid-based grafted polysulfones as proton exchange membranes (PEMs) in fuel cell application instead of sulfonic acid-based counterparts [135]. In one of their studies, they have used bromination-lithiation-phosphonation to prepare up to 50% phosphonic acid functionalized PSUs in both bisphenol A and biphenyl sulfone segments [143]. Higher degree of phosphonation was not achieved due to the competing crosslinking side reactions. These polymers showed high thermal stability up to 350 ºC under nitrogen and insignificant water uptake (<2%) which limited their potential application as PEMs.

In a later study, Jannasch and Lafite have prepared PSU with pendant acidic $CF_2PO_3H_2$ units located in the aromatic side chains with 0.5 degree of phosphonation [144]. The prepared membranes took up 6 wt% and reached a proton conductivity of 5 mS/cm at 100 °C.

In order to overcome the limitation of crosslinking side reactions and to obtain higher phosphonic acid content, the same group grafted PSUs with bisphosphonated alkyl side chains which possess both high acidity and high phosphonic acid content as an approach to achieve higher proton conductivities [145]. Degree of phosphonation up to 1.4 was achieved by incorporation of bis(phosphonic acid) moiety and the prepared membranes reached a conductivity of 25 mS/cm at 120 °C under immersed conditions.

Recently, PSUs were successfully grafted with poly(vinylphosphonic acid) using an anionic grafting methodology [146]. The poly(vinylphosphonic acid) grafted chains formed separate phases in the membranes with high local concentrations of interacting phosphonic acid units, giving rise to large hydrogen-bonded aggregates. These aggregates are essential for efficient proton conductivity in the nominally dry state. At 120 °C, the membrane with the poly(vinylphosphonic acid) content (57 wt%) reached a conductivity of 4.6 mS/cm under nominally dry conditions and 93 mS/cm under 100% relative humidity (RH).

Nuñes et al. have utilized palladium catalyzed phosphonation reaction to introduce the phosphonic acid groups directly attached to the polysulfone aromatic backbone [147]. This approach resulted in maximum degree of phosphonation of 0.9 which was attributed to the sterical hindrance. An attempt to increase the degree of phosphonation by using temperatures above 120 °C resulted in polymer degradation.

In addition, chloromethylation-phosphonation route was utilized to prepare a variety of phosphonic acid functionalized polymers as PEMs for fuel cells applications [148,149]. These polymers were hydrolyzed in concentrated hydrochloric acid which revealed their high chemical and oxidative stability under strong acidic conditions. Furthermore, ion exchange capacity (IEC) up to 6.51 meq/g was achieved in case of phosphonic acid functionalized polystyrene with 70-80% phosphohonic acid content [150]. This high IEC is necessary for obtaining high proton conductivity values when using low acidity phosphonic acid groups compared to the sulfonic acid functionalized polymers.

Chloromethylated PSUs were utilized as precursors for different applications [151-153], including the preparation of PEMs for alkaline fuel cells [154,155]. However, to our knowledge, no reports were available for the utilization of chloromethylated PSUs for the preparation of PEMFCs. The objective of this study is to utilize the chloromethylation-phosphonation reaction to prepare phosphonic acid functionalized PSUs with high degree of phosphonation and evaluate their potential use as PEMs for the fuel cells applications.

5.2 Experimental

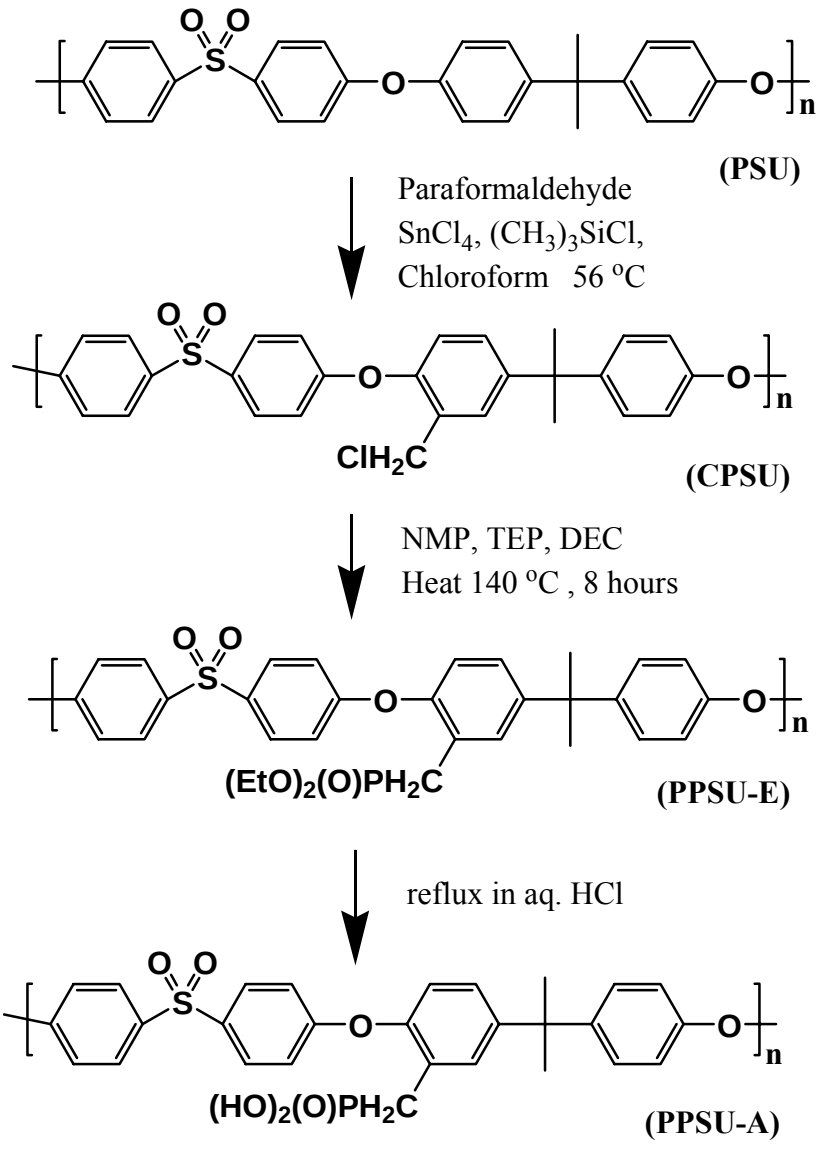
5.2.1 Materials

Polysulfone (Aldrich; 35 Kg/mol) was dried overnight at 60 °C under vacuum. Triethyl phosphite (TEP) (Fluka; >97%), paraformaldehyde (Fluka), chlorotrimethylsilane (Aldrich; 99+%), stannic chloride fuming (Fluka; >98%), diethyl carbitol (DEP) (Fluka; >98%), methanol (Aldrich; 99.8%), chloroform (Aldrich; >99%) and N-methyl-2-pyrrolidinone (NMP) (Aldrich; 98%) were used as received.

For the sake of clarity, the following polymers will be referred to by their acronyms: Polysulfone as PSU; chloromethylated PSU as CPSU; phosphonated PSU in the ester form as PPSU-E; phosphonated PSU in the acid form as PPSU-A (Scheme 1).

5.2.2 Chloromethylation of polysulfone

Chloromethylation of PSU was performed following the procedure of Avram and coworkers [156]. In a typical reaction, PSU (5 g) was dissolved in chloroform (220 mL). Next, paraformaldehyde (3.4 g), $SnCl_4$ (0.2 mL), and $(CH_3)_3SiCl$ (15 ml) were added to the PSU solution. The reaction mixture was heated and the temperature was maintained at 56 ºC. The progress of the reaction was followed by ^1H NMR to reach a certain degree of chloromethylation according to equation 1 (vide infra). After the desired reaction time, the reaction mixture was precipitated in excess methanol and the polymers CPSUs were isolated by filtration. The polymer was purified by dissolution in chloroform and



Scheme 1 - Phosphonation of polysulfone PSU

precipitation with methanol, and then dried to a constant weight at 60 ºC under vacuum (usually for 6 h).

5.2.3 Phosphonation of chloromethylated polysulfone

The Phosphonation reaction was carried out using 5% polymer solution to avoid crosslinking. In a typical reaction, chloromethylated PSU (i.e. CPSU) (5 g) was dissolved in NMP (70 mL). Next, diethyl carbitol (30 mL) and triethyl phosphite (15mL) were added to the polymer solution. The reaction mixture was heated at 140 ºC for 8 hours and cooled to room temperature. The polymer solution was precipitated in excess deionized water with vigorous stirring. The resulting polymer was purified by dissolution in chloroform and precipitation with methanol, then filtered and dried to a constant weight at 60 ºC under vacuum.

5.2.4 Hydrolysis

The phosphonic acid functionalized polymers PPSU-A were obtained by hydrolyzing the phosphonic acid ester polymers PPSU-E by refluxing in aqueous hydrochloric acid. In typical reaction, the dried polymer/membrane in the ester form PPSU-E (0.5 g) was placed in concentrated hydrochloric acid (30 mL) and refluxed for 8 h. The resulting polymer/membrane in the acid form PPSU-A was filtered off and washed with water. Then the obtained phosphonic acid functionalized polymers/membranes were dried to a constant weight at 60 ºC under vacuum.

5.2.5 Characterization

^{1}H, ^{13}C, ^{31}P and DEPT 135º NMR spectra of the modified polymers were recorded for structural characterization. Data were collected on a JEOL LA 500 MHz spectrometer using DMSO-d_6 or $CDCl_3$ according to the solubility of the synthesized polymers. IR spectra were recorded for the dried polymers using NICOLET 6700 FTIR equipped with Smart Orbit; 32 scans were collected for each sample in the range of 400-4000 cm^{-1}.

5.2.6 Functionalization degree

The degree of functionalization is equal to the number of units of certain functionality per repeating unit of PSU. In all the spectra, the integral (A) of the signal at δ1.6 ppm represents 6 protons of the two methyl groups in each repeating unit of the PSU. The area per proton would then be equal to A/6. The area (B) for two protons at δ 4.56 ppm represents the signal for CH_2Cl; the area would then be B/2 for the single proton. The degree of chloromethylation (DC) was then obtained by the following equation (1):

$$DC = \frac{(B/2)}{(A/6)} \qquad Eq.1$$

Likewise, degree of phosphonation (DP) was calculated from the area B for two protons of $\underline{CH_2}P$- at δ3.0-3.1 ppm, C for six protons of $(\underline{CH_3}CH_2O)_2$- at 1.25 ppm and D for four protons of $(CH_3\underline{CH_2}O)_2$- at 4.0 ppm. The areas for one proton of the phosphonate pendent would then equate to B/2 or C/3 or D/2. The average area i.e. (1/3){(B/2) + (C/6) + (D/4)} would then equal to a single phosphonate pendent. Since the area for a single proton of $C(CH_3)_2$ at δ1.60 ppm is A/6, the degree of phosphonation (DP) was then obtained by the following equation (2):

$$DP = \frac{(1/3)\{(B/2)+(C/6)+(D/4)\}}{(A/6)} \qquad Eq.2$$

5.2.7 Membranes Preparation

Membranes of phosphonated PSUs in their protonated form were prepared by two methods according to their solubility. In method (A), phosphonated polymers in the acid form PPSU-A with DP =0.4 and DP=0.75 were cast into Petri dishes from 10 wt % solutions in DMAc at 60 ºC which resulted in tough and flexible transparent membranes, whereas in method (B), phosphonated polymers in the ester form PPSU-E with various DP were cast from DMAc at 60 ºC, dried for 6 h at 120 ºC under vacuum to remove the excess solvent and finally membranes were hydrolyzed to the acid form by refluxing in

aqueous HCl for 8 h. Tough and flexible white opaque membranes without any observed defects were obtained by using method (B). The obtained membranes were stored in deionozed water for subsequent use. It should be mentioned that all membranes in this study were prepared by using method (B), unless otherwise stated, for the sake of comparison of the obtained data.

5.2.8 Ion exchange capacity (IEC)

The hydrolyzed membranes in the acid form were dried under vacuum at 60 ºC overnight in order to get their dry weight. The IEC was determined using a method described by Allcock et al. [157]. In a typical experiment, a known weight of dried membrane (about 0.4 g) was placed in a solution of H_2O (25 mL) and 0.10 M NaOH (10 mL) and swirled for 24 h. Three 10 mL aliquots were then removed and titrated with 0.020 M HCl to a methyl red endpoint. The IEC was then taken as the average IEC of the three samples calculated using the following equation:

$$IEC\,(meq/g) = \frac{(10\text{ mL NaOH})\,(0.1\text{ M NaOH}) - 3.5\,(\text{x mL HCl})\,(0.020\text{ M HCl})}{\text{g}_{\text{dry weight}}} \qquad Eq.3$$

5.2.9 Thermal stability

Thermogravimetric analysis (TGA) experiments were carried out using Shimadzu DTG-60H equipment. All the samples were vacuum dried at 120 ºC for at least one hour before the analysis. The samples were heated from 25 ºC to 800 ºC at 10 ºC /min under air. The temperature at 5 wt% loss was denoted as $T_{d,5\%}$.

Differential scanning calorimetry (DSC) was performed using dried polymer samples in the ester form using a TA NETZSCH DSC 204 F1 instrument. The samples were heated from 25 ºC to 250 ºC at 10 ºC /min under nitrogen, and this was followed by cooling to 25 ºC and finally a second heating scan to 250 ºC at 10 ºC /min. The T_g values

of the polymers were taken as the inflexion points of the thermograms recorded during the second heating scan.

5.2.10 Water uptake

In order to study the water uptake (W_{water}) , the membranes were first dried under vacuum at 80 °C overnight to obtain their dry weights (W_{dry}) and then immersed in deionized water for 24 h at the desired temperatures. Excess water was removed from both surfaces before the weights of the water swollen membranes (W_{wet}) were obtained. The water uptake was then calculated as:

$$W_{water} = [(W_{wet} - W_{dry})/ W_{dry}] \times 100\%$$

5.2.11 Proton conductivity measurements

The proton conductivity of the polymeric membranes was measured by electrochemical impedance spectroscopy (EIS) technique. It was performed over the frequency range 0.1–1.2 × 10^6 Hz with 10 mV amplitude. A potentiostat (Model 283) and lock in amplifier (Model 5210) connected to a PC through GPIB card, were used to measure the impedance data. The detailed procedure for conductivity measurements used in this work is described elsewhere [158]. Membrane samples of around 1.5 cm×1.5 cm were neatly cut and put between the stainless steel electrodes of the conductivity cells. Before the test, the membranes were soaked in water until sufficiently wet and compressed tightly between the blocking electrodes. The conductivity (σ) of the membrane sample was calculated from the impedance data, using the relation $\sigma = t/RA$, where t is the thickness of the membrane, A the face area and R is derived from the impedance data. The measurements have been repeated three times to get reproducible results and the percentage of the error in the conductivity readings was found to be in the range of 1-5%.

5.2.12 Methanol permeability measurements

Methanol permeability experiment was carried out using a test cell, which included two compartments separated by the tested membrane. The volume of each compartment was 100 ml and the effective membrane area was 5.10 cm^2. The feeding compartment (A) was filled with 1M methanol solution and the permeate compartment (B) was filled with ultra pure water. Both compartments were continuously stirred by magnetic stir bars during permeability measurements. The methanol concentration in compartment (B) was determined at different time intervals by HPLC (Waters 2695) using a μBondapak C_{18} 125 A^o column (3.9x300mm).

Methanol permeability (*P*) through the PEM was then calculated from the slope of the time–concentration curve of methanol in compartment (B) as expressed in the following equation:

$$P = (m \times V_B \times L) / (S \times C_A) \qquad \text{Eq. 4}$$

where *m* is the slope of the linear plot of C_B versus t (dC_B/dt); V_B is the volume of compartment B; C_A is the concentration of methanol in compartment A; L is the thickness of the membrane; S is the effective area of the membrane.

5.3 Results and discussion:

5.3.1 Synthesis of phosphonic acid functionalized polysulfones (PPSUs)

Scheme 1 represents the chemical pathway used for the synthesis of the phosphonic acid functionalized polysulfones PPSU-A **1-5**. Chloromethylation of PSU was the first step in the synthesis. The degree of chloromethylation per repeat unit (DC) was controlled by varying the reaction time as shown in (Table 5.1). The variation of the DC from 0.4 to 2.0 was successfully achieved without crosslinking side reactions. The incorporation of chloromethyl group was confirmed by the appearance of a new singlet peak at δ4.56 ppm in the ^{1}H NMR spectrum (Fig. 5.1-a) and the DC was calculated according to equation 1 (vide supra). Obtaining PSUs with high DC was one of the objectives of this work in order to obtain polymers containing high phosphonic acid content which can compensate for the lower acidity of the phosphonic acid moiety in comparison with the sulfonic acid functionalized polymers.

Phosphonation of chloromethylated PSU (CPSU) was carried out using classical Michaels-Arbuzov reaction. In order to avoid gelation, it was necessary to use the polydentate etheral solvent such as diethyl carbitol (DEC) along with low polymer concentrations (5%) as described by Cabasso et al. in the case of phosphonation of chloromethylated polystyrenes at 160 ºC [140]. Slightly lower reaction temperature (140 ºC) and shorter reaction time (8 h) were enough to achieve 100% phosphonation in comparison to ETFE-*graft*-VBC and FEP-*graft*-VBC which gave 80% phosphonation after 24 h at 140 ºC [148]. The success of the phosphonation reaction was confirmed by ^{1}H, ^{31}P and ^{13}C NMR as well as FTIR analysis of the resulting polymers. The disappearance of the (-CH_2Cl) singlet peak at δ 4.56 ppm and appearance of the new distinct (-CH_2P=O) doublet peak at δ 3.0-3.1 ppm with coupling constant ($^{2}J_{H-P}$ = 21 Hz) in the ^{1}H NMR indicated the completeness of the phosphonation reaction (Fig. 5.1-b). The presence of a signal at δ 26.00 ppm in the ^{31}P NMR provided a strong evidence of the absence of any side reactions or crosslinked products (Fig. 5.2-a). ^{13}C NMR provided further confirmation by the appearance of the doublet peak (-CH_2P=O) at δ 26.6-27.7

Table 5.1 Characterization data for the chloromethylated and phosphonated PSUs in the ester form.

Sample	Chloromethylation Reaction Time (Days)	DC[1] CPSU	DP[2] PPSU-E	Tg[4] (°C) PPSU-E
PPSU-E-0.4	1	0.4	0.4	176
PPSU-E-0.75	2	0.75	0.75	138
PPSU-E-1.0	4	1	0.93	122
PPSU-E-1.5	6	1.5	1.46	108
PPSU-E-2.0	8	2.0	N.D[3]	N.D[3]

1) Degree of chloromethylation was determined by ^{1}H NMR (see eq. 1).

2) Degree of phosphonation was determined by ^{1}H NMR (see eq. 2).

3) N.D = Not determined due to insolubility of the polymer.

4) Tg of neat polysulfone = 185 °C.

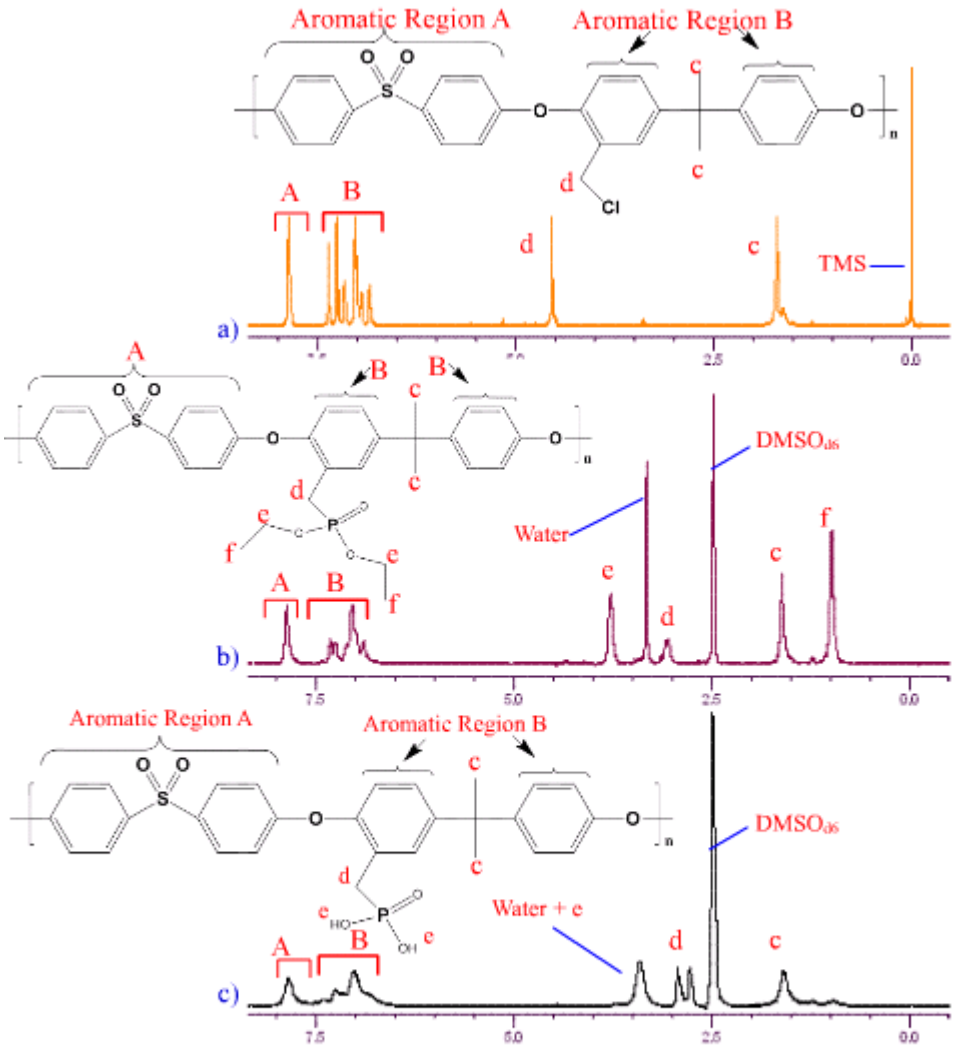


Fig. 5.1 H NMR of a) chloromethylated PSU (CPSU-0.75) in $CDCl_3$
b) Phosphonated PSU in the diester form (PPSU-E-0.75) in $DMSO_{d6}$
c) Phosphonated PSU in their diacid form (PPSU-A-0.75) in $DMSO_{d6}$

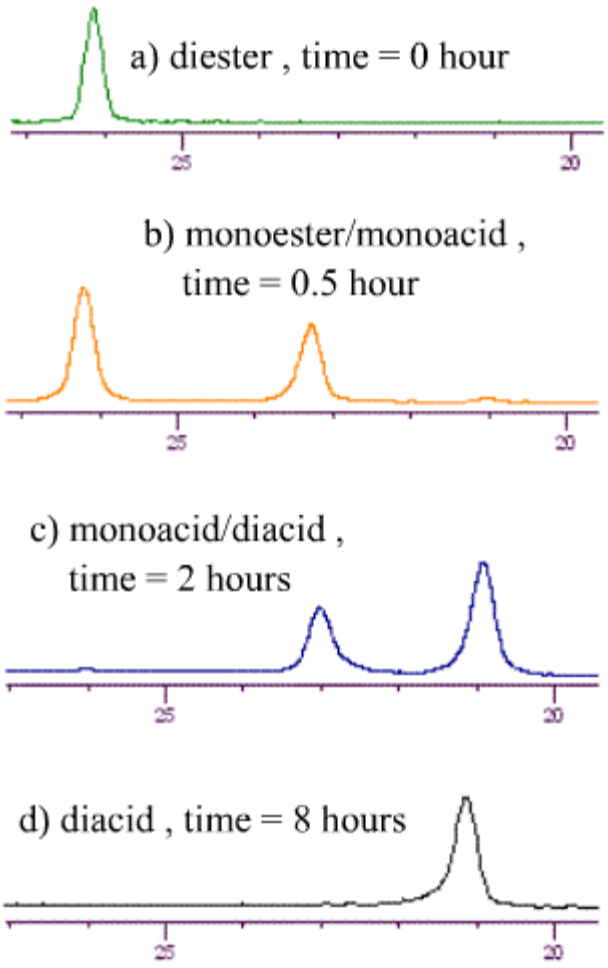


Fig. 5.2 ^{31}P NMR Progress of the hydrolysi reaction for PPSU-E-0.75, a ⟶ d

ppm with coupling constant ($^{1}J_{C-P}$ = 141 Hz) as shown in (Fig. 5.3-a). DEPT 135º analysis was used to verify the presence of CH_2 carbons in the phosphonated polysulfone PPSU-E-0.75 (i.e. DP=0.75) (Fig. 5.3-b).

FTIR spectra of the phosphonated polymers shown in (Fig. 5.4) further confirmed the presence of phosphonic groups. By comparing the FTIR spectra of the phosphonated polymers with the FTIR spectrum of neat PSU, three new peaks were identified in spectra b-d in (Fig 5.4). The bands at 1018 and 746 cm^{-1} were assigned to (P)-O-C absorptions of the ester group, and the band at 956 cm^{-1} was ascribed to P-O-(C) vibrations. As expected, the intensities of the former peaks increased with increasing the DP of the corresponding polymers.

The complete hydrolysis of the diester derivatives to the diacid derivatives is considered to be essential to achieve high proton conductivities in case of phosphonic acid functionalized polymers [145]. Hydrolysis of the phosphonic acid esters can be achieved by refluxing polymers/membranes in concentrated HCl or HBr solutions which is advantageous when the chemical resistance for strong acids is required as in the case of fuel cell applications.

In this study, phoshonic acid derivatives were obtained by refluxing the phosphonic acid esters PPSU-Es in concentrated hydrochloric acid for 8 h. Shorter hydrolysis times were insufficient to reach high degree of hydrolysis and resulted in mixture of diester/monoacid/diacid as depicted by ^{31}P (Fig. 5.2). The quantitative hydrolysis was confirmed by the disappearance of the signals attributed to the diester ethyl protons appeared at δ1.25 ppm and 4.00 ppm. The residual ethyl protons of the monoacid-monoester derivative were observed at slightly higher chemical shifts of δ 0.96 ppm and 3.7 ppm. The distinct ($-CH_2P=O$) doublet peak was slightly shifted to δ 2.8-2.9 ppm with coupling constant ($^{2}J_{H-P}$ = 23 Hz) in the $^{1}HNMR$ spectra. In addition, the disappearance of the ^{31}P signal at δ26 ppm of the diester and appearance of new signal at 21 ppm (diacid) further confirmed the successful of hydrolysis reaction. DEPT 135º NMR spectra also was

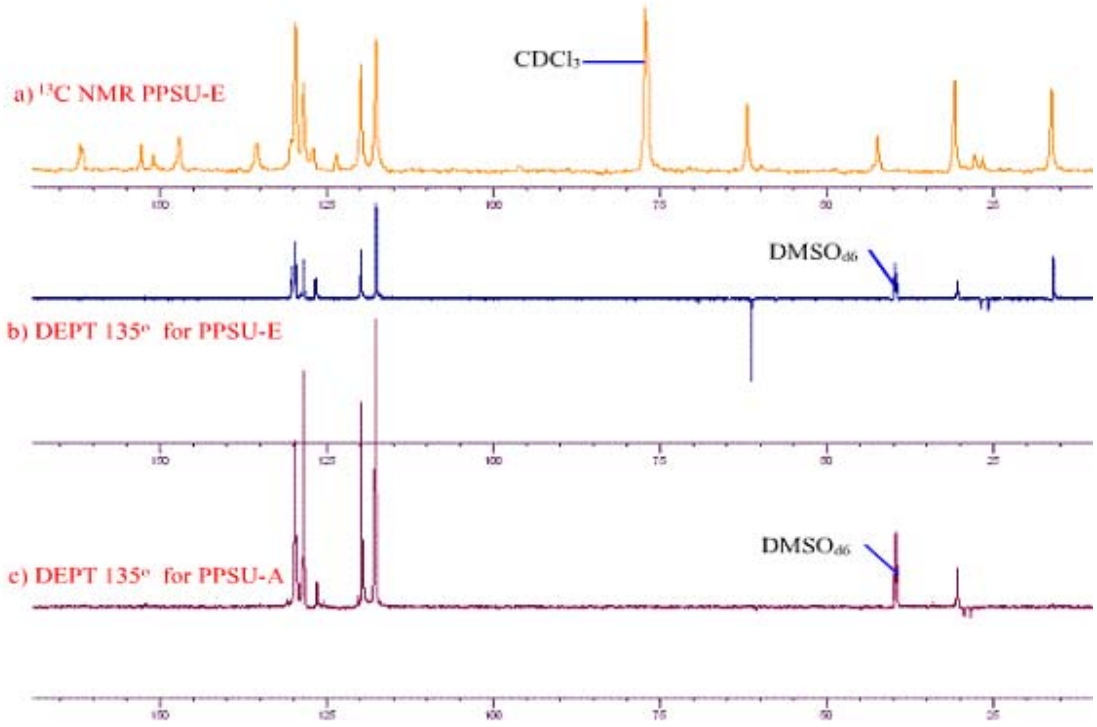


Fig. 5.3 (a) ^{13}C NMR spectra for PPSU-E(0.75), (b) DEPT 135 ° analysis for PPSU-E(0.75) and (c) DEPT 135 ° analysis for PPSU-A (0.75)

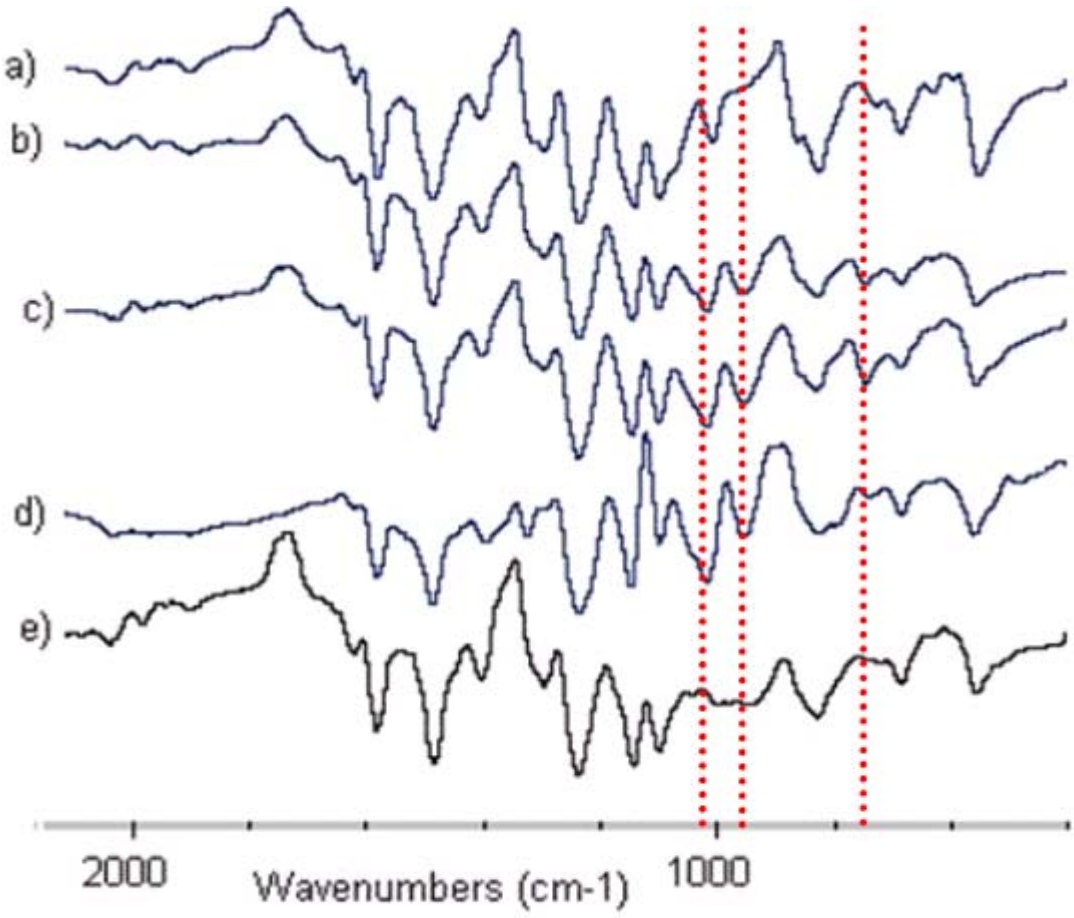


Fig. 5.4 FTIR spectra of the neat PSU and phosphonated PSUs in the ester and acid forms a) PSU b) PPSU-E-0.4 c) PPSU-E-0.75 c) PPSU-E-1.5 e) PPSU-A-1.5

recorded for the PPSU-A-0.75 (i.e DP=0.75) in $DMSO_{d6}$ and clearly showed the complete disappearance of the ethoxy carbons (-P(O)$\underline{C}H_2\underline{C}H_3$) at δ 16.3 ppm and δ 61.9 ppm.

FTIR analysis of the hydrolyzed polymers showed the disappearance of the phosphonic acid ester bands at 746 cm^{-1}, 956 cm^{-1} and 1018 cm^{-1} (Fig. 5.4 - e) which provided further evidence for the quantitative hydrolysis of the obtained copolymers.

In order to cast membranes from synthesized phosphonated polysulfones , the polymers should be soluble in appropriate organic solvents such as DMAc, DMF, DMSO and NMP. Rikukawa and Sanui have reported that the synthesized ethylphosphorylated PBI was insoluble in organic solvents which was attributed to the aggregation of phosphonic acid moieties during the substitution reaction [136]. Nuñes et al. have reported that phosphonated PSUs having IEC = 1.6 mmole/g were soluble in dimethylacetamide (DMAc) only after the addition of 5% concentrated hydrochloric acid [159]. In addition, Miyatake and Hay have reported that phosphonated poly(arylene ether) having DP = 2 were found to swell in DMSO even though the temperature was raised to 100°C [160]. One way to solve this problem is to cast the membranes in their phosphonate ester form followed by acid hydrolysis. However, this was not successful in case of perfluorinated ionomers prepared by Kotov et al. due to the poor quality of the obtained membranes [161].

The solubility of phosphonated polysulfones in the ester form PPSU-E **1-5** was determined in a number of common organic solvents as shown in (Table 5.2). The polymers were readily soluble in chloroform only when the DP was less than 1. This behavior was expected because of the introduction of polar phosphonic acid ester groups to the non-polar bis-phenol A moiety in the PSU backbone which resulted in increasing the polarity of the PSU backbone. However, all phosphonated polymers in their ester form with DP < 2 were found to be soluble in DMF, DMAc and DMSO at room temperature. On the other hand, the hydrolyzed polymers in their acid form with DP < 1 were found to be soluble in DMSO and DMAc at room temperature, where as polymers with DP = 1 and

DP = 1.5, were only swollen in DMSO and DMAc even at 100 ºC. This was probably due to the formation of physical crosslinks (H-bonding) which restricted the mobility of the

Table 5.2 Solubility of the phosphonic acid esters (PPSU-E) in common organic solvents at room temperature[1]

Polymer Sample	$CHCl_3$	THF	DMF	DMAc	DMSO	NMP
PPSU-E-0.4	+ve	+ve	+ve	+ve	+ve	+ve
PPSU-E-0.75	+ve	+ve	+ve	+ve	+ve	+ve
PPSU-E-1.0	±ve	+ve	+ve	+ve	+ve	+ve
PPSU-E-1.5	-ve	-ve	+ve	+ve	+ve	+ve
PPSU-E-2.0	-ve	-ve	-ve	-ve	-ve	-ve

1) +ve = soluble; -ve = insoluble; ±ve = partially soluble.

phosphonated PSU backbone [162]. Similar finding was reported by Nuñes et al. in the case of palladium-catalyzed phosphonated polysulfones with DP = 0.88 due to the strong ionic clusters in the highly phosphonated materials. These clusters were destroyed by addition of 2 vol.-% HBr[147]. In similar way, addition of 5-10 vol.-% concentrated hydrochloric acid to the polymeric solutions at 60 ºC led to complete dissolution of the highly phosphonic acid functionalized polymers with DP=1 and DP=1.5. However, by adopting this procedure, the resulted membranes were observed to have phase separation which probably can be explained by reforming the ionic clusters during the solvent evaporation which resulted in re-aggregations of phosphonic acid units and consequently phase separation. Unfortunately, the copolymers with the highest phosphonate content DP=2, in both ester and acid forms, were found to be insoluble in any of the above solvents even when heated to 100 ºC or when the concentrated hydrochloric acid was added to the polymeric solution.

5.3.2 Thermal Properties

The thermal behavior of the phosphonated polysulfone in the ester form (PPSU-E-1.5) is shown in (Fig. 5.5). The initial weight loss of the polymer between 250-350 ºC was attributed to the loss of ethylene fragments of the phosphonic esters, and this was clearly indicated by the presence of the endothermic peak in the same range in the DTA thermogram[140,145]. The second major weight loss occurred around 400 ºC which was attributed to the main chain polymer degradation. This high thermal stability reflects the strength of the aryl-carbon-P bond of the functionalized polysulfones with comparison to the phosphonated polysulfones having direct aryl-P bond.

Fig. 5.6 shows the thermal behavior of the phosphonated polysulfones in the acid form with different degree of phosphonation. The initial weight loss (5-10 %) at 100 – 300 ºC was attributed to the reversible desorption of water produced by the condensation of phosphonic acid[143]. As degree of phosphonation increases, the condensation of the phosphonic acid increases and hence the water desorption increases which causes the

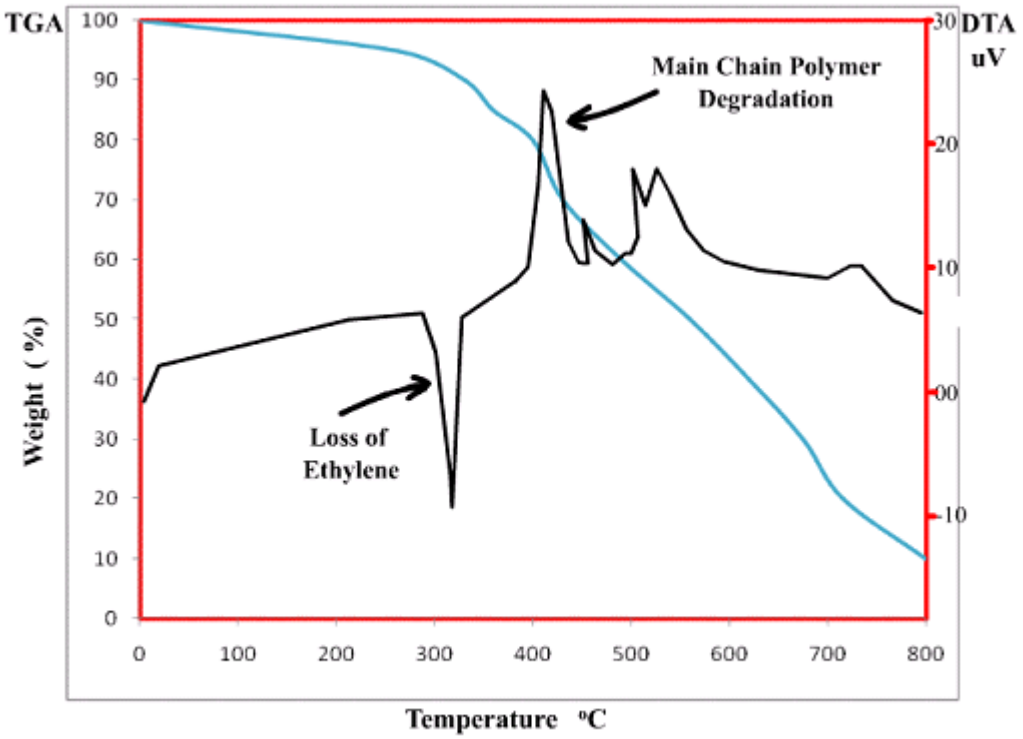


Fig. 5.5 TGA-DTA analysis for the sample PPSU-E-1.5

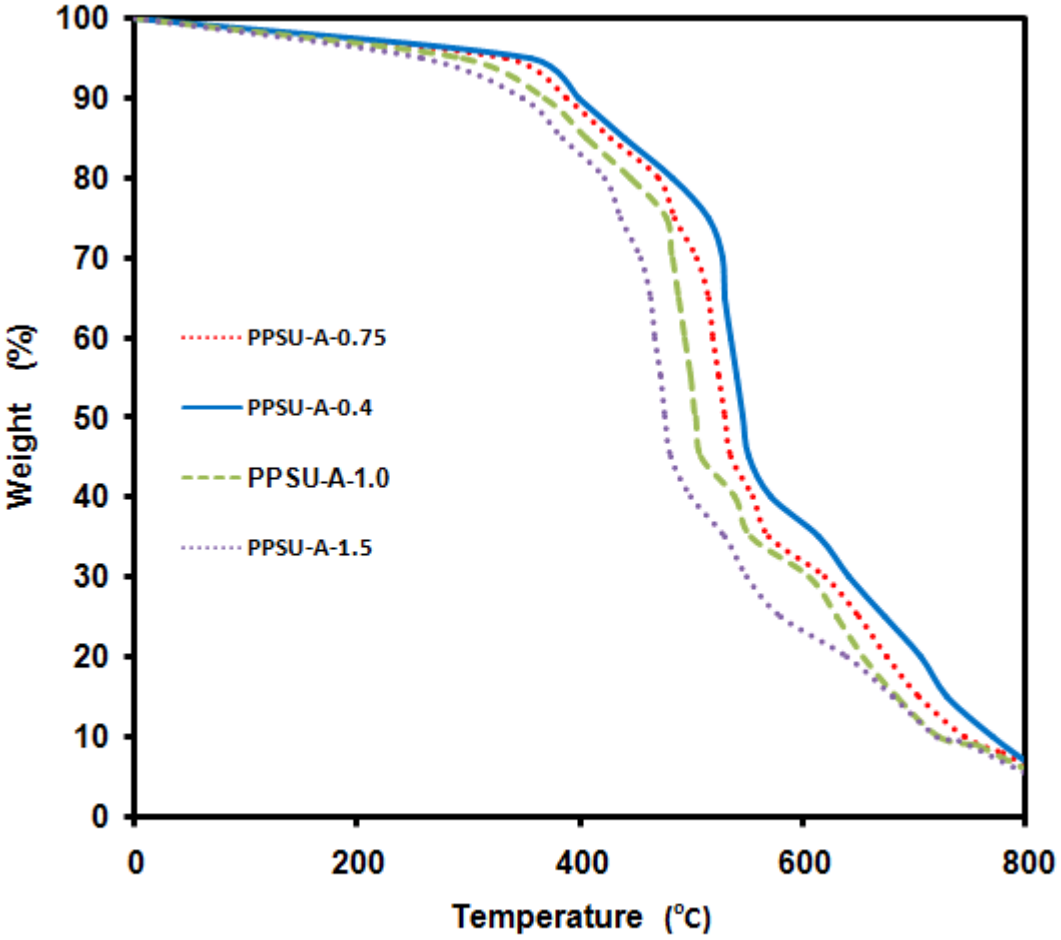


Fig. 5.6 TGA analysis of phosphonated polysulfones in the acid form.

Table 5.3 Characterization data for the phosphonated PSUs in the acid form

Membrane	DP[1]	Experimental IEC (meq/g)	$T_{d,5\%}$ °C	Water Uptake (wt%), 23 °C		Water Uptake (wt%), 80 °C
				A[2]	**B**[3]	**B**[3]
PPSU-A-0.4	0.4	0.9	356	6	18	18
PPSU-A-0.75	0.75	1.7	334	10	27	28
PPSU-A-1.0	0.93	2.2	295	N/A[4]	32	33
PPSU-A-1.5	1.46	3.8	252	N/A[4]	52	55

1) Degree of phosphonation was determined by ^{1}H NMR (see eq. 2).

2) Membranes were prepared using method A, see section 2.7

3) Membranes were prepared using method B, see section 2.7

4) Not Applicable.

decrease in the measured $T_{d5\%}$ values as shown in (Table 5.3). However, the main polymer chain degradation of the phosphonic acid polymers was observed around 400 ºC in a similar trend to the ester form polymers.

The DSC measurements showed that the Tg values of the phosphonic esters functionalized copolymers decrease as the degree of phosphonation increase, which indicates that the phosphonic acid ester side chains had a strong internal plasticizing effect on the PSU (Table 5.1). For example, the T_g of the PPSU-E-1.5 was lowered by 72 ºC which is similar to the PSU functionalized with bis(phosphonic acid) alkyl side chain (DP = 1.4) prepared by Jannasch et al[145].

5.3.3 Membrane Properties

It is well known that the water uptake of the phosphonated ionomers is very low in comparison with the sulfonated ionomers having the same IEC[135]. For this reason, it is important to obtain ionomers with high degree of phosphonation to overcome the low levels of water uptake. In the current study, the obtained water uptake levels were considerably high in comparison to the previously obtained results in the literature (Table 5.3). For example, the membrane with a DP of 0.4 took up 18 wt %, whereas the phosphonated membranes with phosphonic acid placed directly on the aryl rings (i.e. having phosphorous directly bonded to the aryl carbon) in the PSU with a DP of 0.5 took up less than 2 wt% under immersed conditions[143]. The highly phosphonated membrane with a DP of 1.5 and (IEC=3.8) took up 52 wt% compared to 28 wt% for the PSUs grafted with bis(phosphonic acid) having a similar DP [145]. It is worth noting that membranes prepared from phosphonated ETFE-*graft*-VBC by using method (B), with IEC of 3.2 took up 24 wt % at 30 ºC and 30 wt% at 90 ºC [148].

Since membranes with DP= 0.4 and DP=0.75 are soluble in both acid and ester forms, they were prepared by methods (A) and (B) for the comparison of the water uptake values of the resulting membranes as shown in (Table 5.3). Membranes prepared from the

ester form using DMAc as solvent and then hydrolyzed (method B) were found to have 3-4 folds higher water uptake values in comparison with membranes prepared directly from the hydrolyzed polymers in their acid form by using DMAc as solvent (method A). This probably could be ascribed to the voids that are created in the membrane during the acid hydrolysis which may be indicated by the opaque nature of the resulted membranes. Another possibility is the achievement of higher degree of hydrolysis - when using thin films - which has significant effect on the water uptake values as reported by Jannasch et al. [145].

Furthermore, the water uptake of the synthesized membranes was slightly affected by increasing the temperature as shown in (Table 5.3). This can be considered as an advantage for operation of DMFC above 80 ºC in comparison to the sulfonated ionomers which swell excessively after reaching a critical temperature or a critical degree of sulfonation.

In case of direct methanol fuel cells (DMFCs), methanol barrier properties are of prime importance. Methanol crossover is a severe drawback of the Nafion membrane and is critical at temperatures above 100 ºC. The synthesized phosphonated membranes in their acid form showed lower methanol permeability in comparison with commercial Nafion 117 membrane (Table 5.4). The methanol permeability increased with increasing the degree of phosphonation and the highly phosphonated membrane PPSU-A-1.5 showed 75 times lower permeability compared to Nation 117 membrane.

Fig. 5.7 presents the proton conductivity of the phosphonated membranes measured by EIS under fully hydrated conditions. As expected, the proton conductivity increased with increasing the DP and water uptake of the phosphonated membranes. However the measured proton conductivities at ambient temperature reached a maximum of (1.2 mS/cm) for the membrane with DP of 1.5. This result clearly indicates the dependence of the proton conductivity on two factors, the first, is the local concentration of the acidic sites (IEC) available in the hydrophilic domain and the second factor is the strength of those acidic sites which reflects their ability to be solvated by the neighboring

water molecules and their ability to be transported by proton-hopping mechanism. In case of phosphonic acid functionalized membranes, the presence of self-hydrogen bonding (i.e. physical crosslinking) can decrease the available phosphonic acid sites for hydrogen bonding with water molecules, which explains the obtained low proton conductivities at ambient temperature. However, proton conductivity increased with increasing temperature and reached 12 mS/cm at 100 ºC for membranes with DP of 1.5 which is about 8 times less than the commercial Nafion membrane. Theses results reflect the possibility of using these membranes for fuel cell applications at temperatures around 80 ºC.

Table 5.4 Methanol permeability data for selected phosphonated membranes[1].

Membrane	DP[2]	Methanol permeability (cm^2/s)
PPSU-A-0.75	0.75	3.98×10^{-8}
PPSU-A-1.5	1.46	9.12×10^{-8}
Nafion 117	-	6.80×10^{-6}

1) Membranes were prepared using method B, see section 2.7

2) Degree of phosphonation was determined by ^1H NMR (see eq. 2).

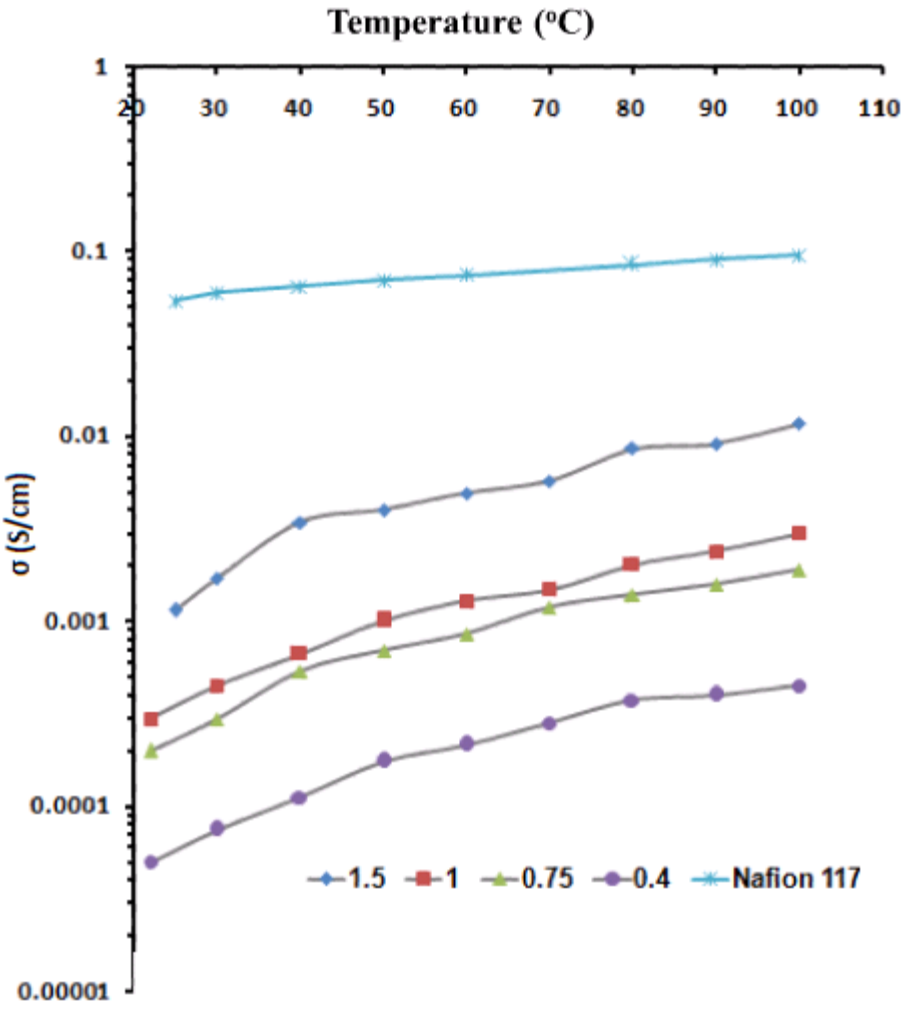


FIg. 5.7 Proton conductivities data for phosphonic acid functionalized membranes and Nafion 117 membrane as measured by EIS under 100% humidity conditions.

5.4 Conclusions:

PSUs were successfully grafted with phosphonic acid groups in two steps, chloromethylation-phosphonation utilizing Michaels-Arbuzov reaction. The synthesized polymers were grafted with different phosphonic acid content (40-150 %) per repeating unit. The obtained polymers/membranes in their ester form were hydrolyzed in concentrated hydrochloric acid which revealed their high stability in acidic environment. The membranes with DP of 1.5 showed high levels of water uptake (52 wt %) in comparison to phosphonated polymers reported in the literature. This high level of water uptake is attributed to the high concentration of phosphonic acid moieties. Directly acid hydrolyzed membranes showed higher amounts of water uptake compared to the membranes casted from hydrolyzed polymers in their acid form. The highest phosphonic acid content membrane with DP of 1.5 reached a conductivity of 12 mS/cm at 100 ºC under fully hydrated conditions. Furthermore, the synthesized membranes possess high thermal stability up to 252 ºC and low methanol permeability compared to the sulfonic acid based ionomers such as Nafion which is advantageous in case of operation of direct methanol fuel cell.

Acknowledgements

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CHAPTER 6

6. NOVEL IONICALLY CROSSLINKED SPEEK AND PHOSPHONATED POLYSULFONES AS POLYELECTROLYTE MEMBRANES FOR FUEL CELLS APPLICATIONS

SUMMARY :

Phosphonated polysulfones in both ester (PPSU-E) and acid (PPSU-A) forms with degree of phosphonation DP = 0.4, 0.75 and 0.96; were successfully synthesized and utilized for the preparation of polymer blend with sulfonated poly(etheretherketone) SPEEK having a degree of sulfonation DS=0.75 . The resulted blend membranes were characterized by infrared spectroscopy, ion exchange capacity, methanol permeability and thermal gravity analysis. In case of SPEEK/PPSU-A blend membranes, ionic networks were formed through hydrogen bonding bridges between the strong sulfonic acid groups and the amphoteric phosphonic acid groups; which showed enhanced properties in terms of water swelling, methanol uptake, methanol permeability and thermal stability without loss of proton conductivity. Furthermore, SPEEK/PPSU-A blend membranes with DP = 0.75 and 0.96, were transparent to visible light, which means that blend microphases, if existent, have dimensions smaller than visible light. When compared to parent SPEEK membranes, the new ionically crosslinked membranes SPEEK/PPSU-A showed slightly lower methanol permeability and increased proton conductivities in the temperature range of 30–120 ^{o}C.

6.1 Introduction :

Direct methanol fuel cell (DMFC) is one of the promising power sources for portable devices where methanol is fed directly to the fuel cell without any fuel processing beforehand. The liquid-feed system does not require any fuel processing equipment and can even be operated at room temperature. These advantages lead to simplicity of operation in DMFC compared to systems using a reformer to produce hydrogen from liquid fuel (i.e. indirect methanol fuel cells) [163].

However, despite these practical system benefits, operation of DMFCs at temperatures below 100°C leads to significantly lower power density and lower efficiency than a PEMFC operating with hydrogen because of the slow oxidation kinetics of methanol and methanol crossover from the anode to the cathode[164-166]. Typical perfluorinated ionomer membranes, such as Nafion® (DuPont), Aciplex® (Asahi Chemical), Flemion® (Asahi Glass), are permeable to methanol transport, thereby significantly reducing fuel utilization efficiency of the fuel cell [167]. Improving power density can be achieved by increasing the fuel cell operating temperature to increase the kinetics of methanol oxidation and reduce adsorption of its oxidation intermediates at the anode catalyst, but typical membranes experience significant membrane dehydration at higher temperatures, leading to high ohmic drop and poor cell performance [168].

A number of studies have been done in order to overcome the limitations of PFI membranes. Among several types of polymer membranes, it is evident that sulfonated poly(ether ether ketone) (SPEEK) membrane has the potential to be used as the electrolyte in DMFC [168-175], which due to its high mechanical strength, high thermal stability, cheap, easily to handle, low methanol crossover and also moderate proton conductivity.

The presence of sulfonic acid group make the SPEEK becomes highly hydrophilic, since this functional group increases the acidity of polymer. Apart from that,

sulfonation also modifies the chemical character of PEEK, by reducing the crystallinity and consequently affects the polymer solubility as shown in (Table 1).

The proton conductivity of the SPEEK membranes can be increased by increasing the degree of sulfonation; or by increasing the operating temperature of DMFC. However, SPEEK membranes exhibit high swelling in water when reaching critical degree of sulfonation (>70%); or when reaching critical temperature (>60-80 C) which leads to poor mechanical properties and low ion permeaselectivity, which can be considered as sever shortcoming for the application in DMFC, especially at elevated temperatures >60–80°C.

Thus there is a crucial need for the swelling reduction and improvement of mechanical properties of SPEEK ionomer membranes. Different approaches were utilized for the swelling reduction of the ionomer membranes such as blending with hydrophobic polymers, incorporation of inorganic additives, covalent crosslinking and ionic crosslinking.

Among these approaches, ionically crosslinked acid-base polymers represents an effective approach to development of proton conducting membranes, as recently reviewed by Kerres [176]. The acidic polymer donates protons to the electron-rich basic sites of the basic polymer like in a normal acid-base reaction as illustrated below :

A-Polymer-$\mathbf{SO_3H}$ + B-Polymer-**X:** → {[A-Polymer-$\mathbf{SO_3}$]$^-$ $^+$ [B-Polymers-**X**-H]}

Where, A-polymer represents an acidic polymer such as SPEEK, SPSU; **X:** represents the basic moiety in the basic polymer (B-Polymer) such as ether, alcohol, imine, amide, imide or amine, including range of basic polymers such as poly(4-vinylpyridine) (P4VP) [177], aminated PSF [178,179], aminated PEEK [180] and pyridine containing polymers [181,182] .

Kerres and coworkers have prepared blend membranes composed of SPEEK (IEC = 1.8) as acidic polymer and aminated polysulfone (H_2N-PSU), polyetheramide (PEI) and polyamide(PA) as basic polymers [183]. For the polyetherimide and polyamide blend membranes, the ionic networks were formed through hydrogen bonding interaction. In case of aminated polysulfone blend membranes, the swelling reduction was attributed to acid-base interaction which led to formation of polysalt and caused a decrease in ionic conductivity due to partial blocking of SO3- groups for cationic transport in comparison with proton conductivity of the hydrogen bond blends.

The utilization of acid-base blend membranes was limited to the commercially available basic polymers. In order to prepare a wide range of acid-base blends with different properties and to understand the effect of basicity on the blend membranes, Kerres and coworkers have utilized different nitrogen-containing aromatic esters, aldehydes and ketones to modify the backbone of polysulfone and prepare a variety of polysulfone-based basic copolymers with different PK values [184]. The prepared basic membranes were blended with water soluble SPEEK (IEC = 2.53) and water insoluble SPEEK (IEC = 1.64). The blend membranes showed a good proton conductivities at ion-exhange capacities >= 1, good thermal stabilities and nearly complete molecular miscibility.

In a later study, the same group prepared two types of aminated polysulfone [180]. In the first type, amination was introduced to the aromatic rings of PSU in the electron-rich bisphenol-A moiety; and in the second type, amination was introduced to the electron-poor arylene- sulfone moiety which provided low basicity polymers compared to the first type. The prepared aminated PSUs along with aminated PEEK as basic polymers were blended with SPSU (IEC=3.02) and SPEEK (IEC=2.68) as acidic polymers. The blend membranes showed properties being dependent onto basic group-basicity and alkylation degree of the basic group. It was found that the combination of the sulfonated polymers with alkylated polymeric bases led to phase-separated membranes with bad mechanical properties, which was attributed to incompatibility between the two polymers because of steric hindrance of the alkylated base. Thus, an important aspect for designing

acid-base blend membranes is the absence of microphase separation and complete miscibility of the blend membranes.

In a recent patent [185], Kerres and coworkers prepared a variety of low-molecular hydroxymethylene-oligo-phosphonic acids $R\text{-}C(PO_3H_2)_xOH_y$ which can be utilized to prepare polymer blends with wide range of commercially available acidic and basic polymers through covalent crosslinking, ionic crosslinking or covalent-ionic crosslinking.

From proton conducting mechanism points of view, phosphoric and phosphonic acids are interesting because they are more amphoteric, having both proton donor (acidic) and proton acceptor (basic) groups to form dynamic hydrogen bond networks, in which protons can readily transfer by hydrogen bond breaking and forming processes, as recently rationalized by Kreuer and co-workers [186–188].

In this study, we report the first example of ionically crossliked polymer blend membranes based on SPEEK as the acid polymer, and the phosphonic acid or phosphonic acid ester functionalized polysulfones as the reinforcing polymer which can form ionic crosslinking with SPEEK through hydrogen bonding interaction Fig 1. The objective of this study is to explore the effect of such ionic interactions between strong acid polymer (SPEEK) and weak or ampheotoric phosphonic acid functionalized polymer (PPSU-A and PPSU-E) on the properties of the resulted blend membranes such as swelling, proton conductivity, methanol permeability and thermal stability.

6.2 Experimental

6.2.1 Materials

Sulphonated poly(etheretherketone) (IEC = 2.16) was supplied by Fumatech company, Polysulfone (Aldrich; 35 Kg/mol) was dried overnight at 60 °C under vacuum. Triethyl phosphite (TEP) (Fluka; >97%), paraformaldehyde (Fluka), chlorotrimethylsilane (Aldrich; 99+%), stannic chloride fuming (Fluka; >98%), diethyl carbitol (DEP) (Fluka; >98%), methanol (Aldrich; 99.8%), chloroform (Aldrich; >99%) and N-methyl-2-pyrrolidinone (NMP) (Aldrich; 98%) were used as received.

For the sake of clarity, the following polymers will be referred to by their acronyms: Sulphonated poly(etheretherketone) as SPEEK; Polysulfone as PSU; chloromethylated PSU as CPSU; phosphonated PSU in the ester form as PPSU-E; phosphonated PSU in the acid form as PPSU-A (Fig. 6.1).

6.2.2 Chloromethylation of polysulfone

Chloromethylation of PSU was performed as following. In a typical reaction, PSU (5 g) was dissolved in chloroform (220 mL). Next, paraformaldehyde (3.4 g), $SnCl_4$ (0.2 mL), and $(CH_3)_3SiCl$ (15 ml) were added to the PSU solution. The reaction mixture was heated and the temperature was maintained at 50-52 ºC. The progress of the reaction was followed by ^1H NMR to reach a certain degree of chloromethylation according to equation 1 (vide infra). After the desired reaction time, the reaction mixture was precipitated in excess methanol and the polymers CPSUs were isolated by filtration. The polymer was purified by dissolution in chloroform and precipitation with methanol, and then dried to a constant weight at 60 ºC under vacuum (usually for 6 h).

6.2.3 Phosphonation of chloromethylated polysulfone

The Phosphonation reaction was carried out using 5% polymer solution to avoid crosslinking. In a typical reaction, chloromethylated PSU (i.e. CPSU) (5 g) was dissolved in NMP (70 mL). Next, diethyl carbitol (30 mL) and triethyl phosphite (15mL)

were added to the polymer solution. The reaction mixture was heated at 160 ºC for 8 hours and cooled to room temperature. The polymer solution was precipitated in excess deionized water with vigorous stirring. The resulting polymer was purified by dissolution in chloroform and precipitation with methanol, then filtered and dried to a constant weight at 60 ºC under vacuum.

6.2.4 Hydrolysis

The phosphonic acid functionalized polymers PPSU-A were obtained by hydrolyzing the phosphonic acid ester polymers PPSU-E by refluxing in aqueous hydrochloric acid. In typical reaction, the dried polymer/membrane in the ester form PPSU-E (0.5 g) was placed in concentrated hydrochloric acid (30 mL) and refluxed for 8 h. The resulting polymer in the acid form PPSU-A was filtered off and washed with water. Then the obtained phosphonic acid functionalized polymers were dried to a constant weight at 60 ºC under vacuum.

6.2.5 Characterization

^{1}H, ^{13}C, ^{31}P and DEPT 135º NMR spectra of the modified polymers were recorded for structural characterization. Data were collected on a JEOL LA 500 MHz spectrometer using DMSO-d_6 or $CDCl_3$ according to the solubility of the synthesized polymers. IR spectra of the all dried membranes using NICOLET 6700 FTIR equipped with Smart Orbit; 32 scans were collected for each sample in the range of 400-4000 cm^{-1}.

6.2.6 Functionalization degree

The degree of functionalization is equal to the number of units of certain functionality per repeating unit of PSU. In all the spectra, the integral (A) of the signal at δ1.6 ppm represents 6 protons of the two methyl groups in each repeating unit of the PSU. The area per proton would then be equal to A/6. The area (B) for two protons at δ 4.56 ppm represents the signal for CH_2Cl; the area would then be B/2 for the single proton. The degree of chloromethylation (DC) was then obtained by the following equation (1):

$$DC = \frac{(B/2)}{(A/6)} \qquad Eq.1$$

Likewise, degree of phosphonation (DP) was calculated from the area B for two protons of $\underline{CH_2}P$- at δ3.0-3.1 ppm, C for six protons of $(\underline{CH_3}CH_2O)_2$- at 1.25 ppm and D for four protons of $(CH_3\underline{CH_2}O)_2$- at 4.0 ppm. The areas for one proton of the phosphonate pendent would then equate to B/2 or C/3 or D/2. The average area i.e. (1/3){(B/2) + (C/6) + (D/4)} would then equal to a single phosphonate pendent. Since the area for a single proton of $C(CH_3)_2$ at δ1.60 ppm is A/6, the degree of phosphonation (DP) was then obtained by the following equation (2):

$$DP = \frac{(1/3)\{(B/2)+(C/6)+(D/4)\}}{(A/6)} \qquad Eq.2$$

6.2.7 Preparation of blend membranes:

Since SPEEK, PPSU-Es and PPSU-As polymers used in this study are all soluble in DMAc at room temperature, DMAc was selected as the casting solvent. A desired weighed amounts of the used polymers SPEEK/PPSU-E or SPEEK/PPSU-A, were dissolved together in DMAc to form 10-15 wt% solutions. The solutions were stirred overnight and then kept for 24 hours in order to release air bubbles. The solutions were poured into Petri dishes and the solvent was evaporated at 60C. The formed membranes were dipped in distilled water for few hours in order to be released out. Then the membranes were dried under vacuum at 90C for 3 hours and t stored in ultra pure deionized water for subsequent use.

6.2.8 Solvent uptake

In order to study the water and methanol uptake ($W_{solvent}$), the prepared membranes were first dried under vacuum at 80 °C overnight to obtain their dry weights (W_{dry}) and then immersed in deionized water/pure methanol for 3 hours at the desired temperatures. Excess water/methanol was quickly removed from both surfaces before the

weights of the swollen membranes (W_{wet}) were obtained. The solvent uptake was then calculated as:

$$W_{solvent} = [(W_{wet} - W_{dry})/ W_{dry}] \times 100\% \qquad \text{Eq. 3}$$

6.2.9 Thermal stability

Thermogravimetric analysis (TGA) experiments were carried out using Shimadzu DTG-60H equipment. All the prepared membraness were vacuum dried at 120 ºC for at least one hour before the analysis. The samples were heated from 25 ºC to 800 ºC at 10 ºC /min under air. The temperature at 5 wt% loss was denoted as $T_{d,5\%}$.

6.2.10 Proton conductivity measurements

The proton conductivity of the blend membranes was measured by electrochemical impedance spectroscopy (EIS) technique. It was performed over the frequency range 0.1–1.2 × 10^6 Hz with 10 mV amplitude. A potentiostat (Model 283) and lock in amplifier (Model 5210) connected to a PC through GPIB card, were used to measure the impedance data. The detailed procedure for conductivity measurements used in this work is described elsewhere [158]. Membrane samples of around 1.5 cm×1.5 cm were neatly cut and put between the stainless steel electrodes of the conductivity cells. Before the test, all the blend membranes were soaked in deionized water at 60 C for 30 minutes and the final thickness of the resulted membranes were used in calculations. The conductivity (σ) of the blend membranes was calculated from the impedance data, using the relation $\sigma = t/RA$, where t is the thickness of the membrane, A the face area and R is derived from the impedance data.

6.2.11 Methanol permeability measurements

Methanol permeability experiment was carried out using a test cell, which included two compartments separated by the tested membrane. The volume of each

compartment was 100 ml and the effective membrane area was 5.10 cm^2. The feeding compartment (A) was filled with 1M methanol solution and the permeate compartment (B) was filled with ultra pure water. Both compartments were continuously stirred by magnetic stir bars during permeability measurements. The methanol concentration in compartment (B) was determined at different time intervals by HPLC (Waters 2695) using a μBondapak C_{18} 125 A^o column (3.9x300mm).

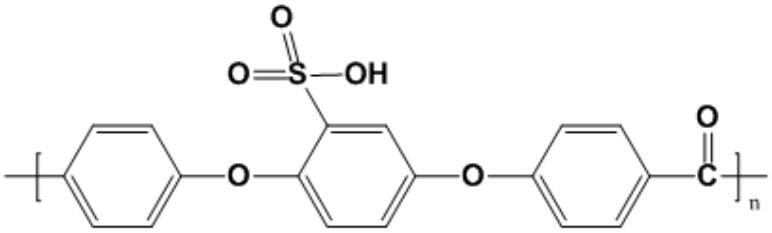
Methanol permeability (*P*) through the PEM was then calculated from the slope of the time–concentration curve of methanol in compartment (B) as expressed in the following equation:

$$P = (m \times V_B \times L) / (S \times C_A) \qquad \text{Eq. 4}$$

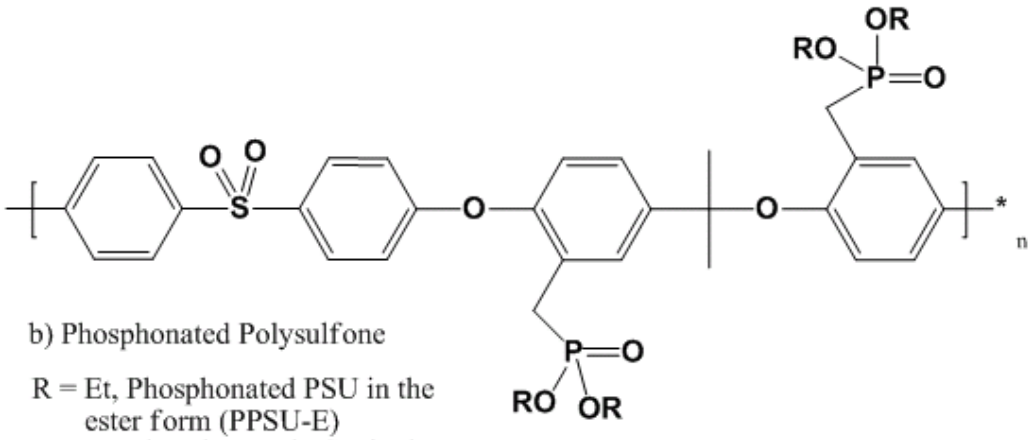
where *m* is the slope of the linear plot of C_B versus t (dC_B/dt); V_B is the volume of compartment B; C_A is the concentration of methanol in compartment A; L is the thickness of the membrane; S is the effective area of the membrane.

6.2.12 Scanning Electrom Microscopy

Cross section images of the blend membranes were obtained using JSM-5800LV scanning electon microscope.



a) Sulfonated Poly(etheretherketone) (SPEEK)



b) Phosphonated Polysulfone

R = Et, Phosphonated PSU in the ester form (PPSU-E)

R = H, Phosphonated PSU in the acid form (PPSU-A)

Fig. 6.1 Structures of a) SPEEK b) Phosphonated Polysulfone (PPSU)

6.3 Results and discussion :

6.3.1 Synthesis of phosphonated of polysulfones:

In our recent paper [189], we have successfully synthesized phosphonated polysulfones by two steps procedure, chloromethylation of polysulfone backbone followed by phosphantion utilizing Michaels-Arbuzov reaction. The degree of chloromethylation and phosphonation was controlled from 0.4 up to 2 without crosslinking side reactions. Then the phosphonated polysulfones in the ester form were quantitatively hydrolyzed to the corresponding acid form by refluxing in aqueous hydrochloric acid. Fig. 6.1 shows the NMR spectra of the synthesized chloromethylated polysulfones (a), phosphonated polysulfones in the ester form (b) and phosphonated polysulfones in the acid form (c). It was found hat the acid functionalized phosphonated polysulfones with degree of phosphonation up to 1 were soluble in DMAc, NMP and DMSO solvents. For this reason acid functionalized phosphonated polysulfones with degree of phosphonation greater than one were not considered for this study. Furthermore, the variation of phosphonic acid functionality can allow for possible fabrication of membranes with customized fin-tuned properties.

Table 6.1 shows the solubility data of SPEEK, phosphonated polysulfones in the ester form (PPSU-Es) and phoshonated polysulfones in the acid form PPSU-As. The polymer hydrophilicity increased with increasing the degree of sulfonation or phosphonation. However, when reaching degree of sulfonation above 70% , excessive swelling for SPEEK membranes is observed and the membranes became soluble in methanol. By comparison, the phosphonated polysulfone membranes in both ester and acid forms are totally insoluble in methanol and water even at 150% phosphonation. Furthermore, these polymers have similar hydrophilicity compared to SPEEK; which is an advantage over the parent neat hydrophobic polysulfone polymer. Our preliminary investigations showed that the neat polysulfone polymer can not be blended with SPEEK having high degree of sulfonation above 70% due to immiscibility and large phase

separation between the two polymers. One of the objectives of the current study is to utilize phosphonated polysulfones as suitable hydrophilic materials for blending with SPEEK with high degree of sulfonation. In addition, the acid fictionalized phosphonated polysulfones having low acidity but high local concentration of amphoteric phoshonic acid moieties make them suitable candidates for forming ionic networks with highly acidic SPEEK through hydrogen bonding interaction.

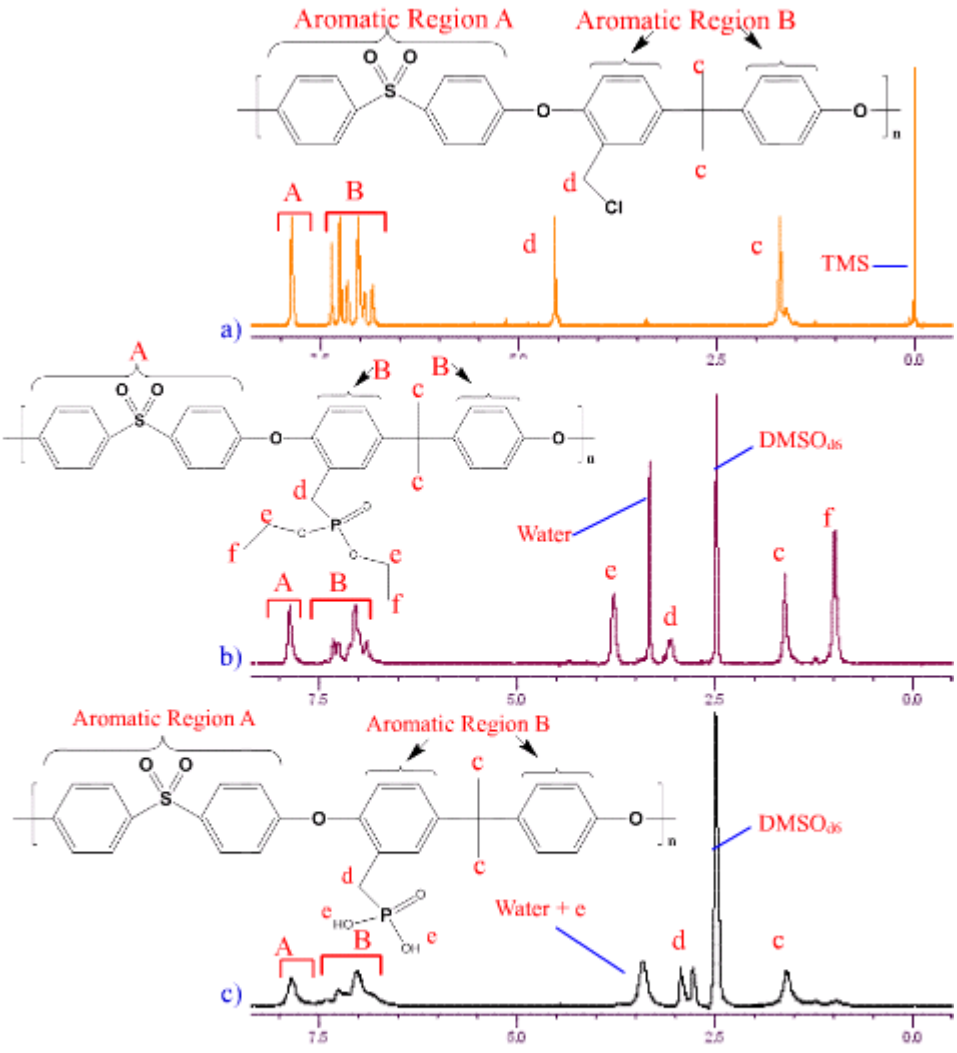


Fig. 6.2 1H NMR of a) chloromethylated PSU (CPSU-0.75) in $CDCl_3$
b) Phosphonated PSU in the diester form (PPSU-E-0.75) in $DMSO_{d6}$
c) Phosphonated PSU in their diacid form (PPSU-A-0.75) in $DMSO_{d6}$

Table 6.1 Solubility data for 1) SPEEK with various degree of sulfonationk; 2) PPSU-E and 3) PPSU-A with various degree of phosphpnation[1)].

	1) Sulfonated Poly(ether ether ketone) SPEEK					
DS = 0	<30	30-40	40-70	>70-100	>100	
PEEK Hydrophobic	Soluble only in conc. H_2SO4	Hot-1, Hot-2, Hot-3	1,2,3	1,2,3,4, Hot 5	1,2,3,4, 5	
	2) Phosphonated Polysulfone in the ester form (PPSU-E)					
DP = 0	<30	30-40	40-70	>70	>=100-150	200
PSU Hydrophobic	1,2,3,6,7	1,2,3,6,7	1,2,3,6,7	1,2,3,6,7	1,2,3	-
	3) Phosphonated Polysulfone in the acid form (PPSU-A)					
DP = 0	<30	30-40	40-70	>70	>=100	200
PSU Hydrophobic	1,2,3	1,2,3	1,2,3	1,2,3	(1,2 &3) in presence of 5-10 wt% conc. HCl at 60 C.	-

1) **Solvent type**, DMAc =1, DMSO =2, DMF =3, Methanol =4, Water =5, $CHCl_3$ =6, CH_2Cl_2 =7.

6.3.2 FTIR analysis of blend membranes :

FTIR spectra of the utilized polymers in this study is shown in Fig. 6.3 There is a clear overlap between the FTIR bands of pure SPEEK and pure PSU membranes in most of the characteristic peaks which can be attributed to structure similarity of both polymers, (a and b in Fig. 6.3).

By comparing the FTIR spectra of the phosphonated polysulfone in the ester form PPSU-E with the FTIR spectrum of neat PSU, three new absorption bands at 1018, 746 and 956 cm^{-1} can be identified in spectra c in (Fig 6.3). These bands are overlapped with SPEEK peaks in the same range. In the same time, the former three bands are disappeared after quantitative hydrolysis to the corresponding acid form PPSU-A d in (Fig 6.3). However, the characteristic absorption bands at 2871, 2942 and 2965 cm-1; which is attributed to CH-stretching of the bisphenol-A $-(CH_3)_2$ moiety of PSU, PPSU-E and PPSU-A polymers can be utilized to confirm the presence of the phosphonated polymers in the blend membranes.

Fig. 6.4 shows the FTIR spectra of the pure SPEEK membrane (a), SPEEK/50PPSU-E-0.75 (b) and SPEEK/PPSU-As (c-e) blend membranes. Compared to pure SPEEK membrane, all phosphonated membranes in both ester and acid forms clearly display the characteristic FTIR bands in the range of 2870-2970 cm-1. In addition, new FTIR absorption bands of the polymer blends can be identified at 1103, 830, 688 and 555 cm-1. It can be seen also that the intensity of SPEEK absorption bands in the polymer blends at 1011, 902, 764 and 609 cm-1 is decreased. An interesting observation in the FTIR spectrum of the polymer blends is the absence of OH-of SO3H band around 3400 cm-1 when the percentage of SPEEK polymer is above 40% which indicates clearly the high level of ionic crosslinking in this blend and low concentration of free SO3H groups Fig 6.4.

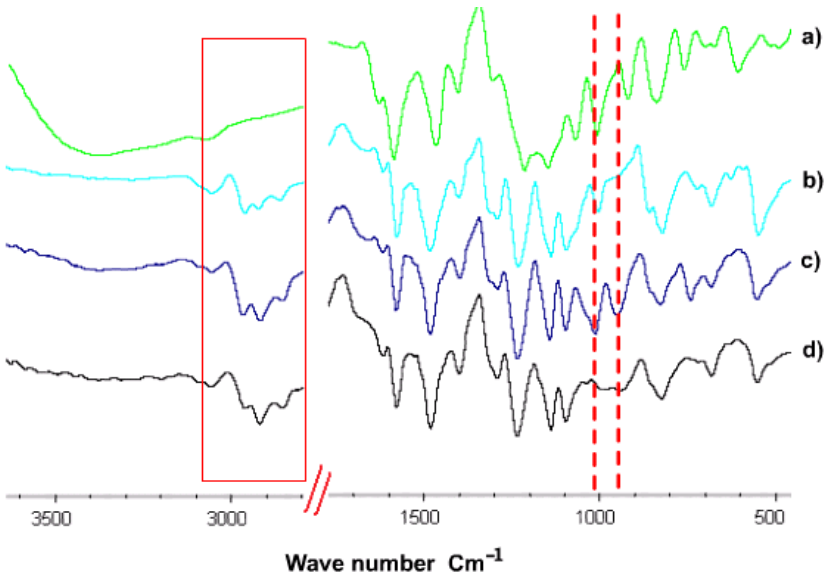


Fig. 6.3 FTIR spectrum of a) neat SPEEK DS=75%, b) neat PSU, c) PPSU-E-0.75 and d) PPSU-A-0.75

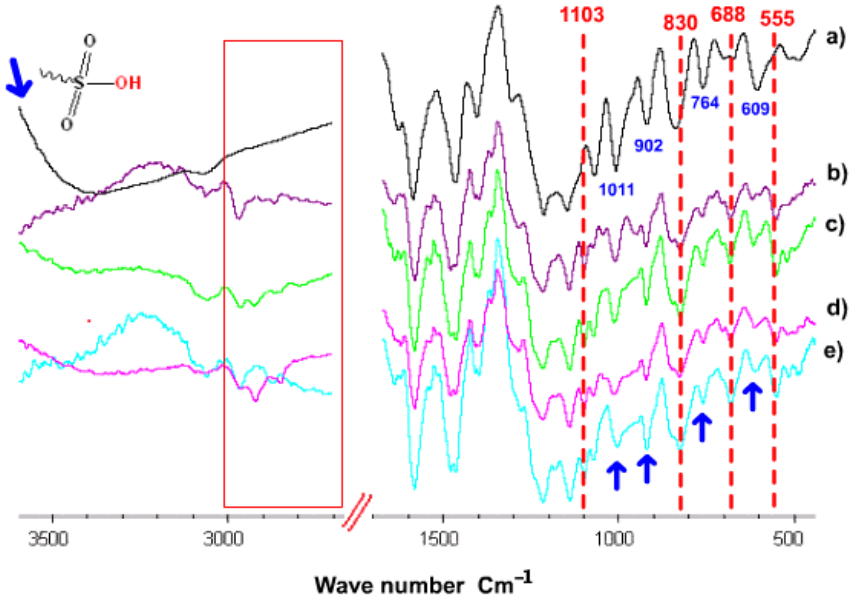


Fig. 6.4 FTIR spectrum of a) neat SPEEK DS=75%, b) 50PPSU-E-0.75, c) 50PPSU-A-0.4, d) 50PPSU-A-0.75 and e) 50PPSU-A-0.98

6.3.3 Fabrication of SPEEK/PPSU-Es polymer blend membranes:

The SPEEK with DS = 75% was selected for this study for several reasons. First, the proton conductivity of this polymer is comparable to Nafion 117 and the water uptake at room temperature is good enough (60%) so it can be blended with low water uptake polymers such as phosphonated polysulfones in order to obtain reasonable net proton conductivity.

In addition, SPEEK with DS= 75% is soluble in methanol at room temperature and soluble in water at 60C. This solubility behavior is not suitable for operation of at temperatures above 50 C especially for DMFC; so one can investigate the improvement in the side of solvent uptake and permeability of the blend membranes compared to the parent SPEEK membrane.

Blending of the hydrophobic PSU with highly sulfonated SPEEK resulted in large phase separation and poor quality membranes (Table 6.2, entry 1 and 2). This blend (i.e SPEEK/PSU) is partially soluble in methanol and turbid in water at 60 C which confirms the immiscibility between the two polymers. By comparing SPEEK/PSU blend with the whole series of SPEEK/PPSU-Es (Table 6.2, entries 3-10), it is clear that the improved hydrophilicity of the phosphonated polysulfones in the ester form leads to improved membrane quality shown by small phase separation and flexibility of resulted membranes. This can be attained through dipole-dipole interactions as well weak hydrogen bridges formed between the sulfonic acid groups and the phosphonic acid ester functionality -P=O of the phosphonated polysulfones PPSU-Es as illustrated in Fig. 6.5 a and b respectively. As a result, SPEEK/PPSU-E membranes shows higher water uptake compared to SPEEK/PSU with the same percentage of SPEEK polymer. When the percent of SPEEK is the same in the SPEEK/PPSU-E blend, the water uptake was slightly decreased with increasing the degree of phosphonation from 0.4 to 0.96 due to the higher interaction between the sulfonic acid groups and the –P=O of the ester linkage.

So, to prepare membranes with low water swelling at temperatures up to 60 C, one should use at least 50% or above of the PPSU-E in the polymer blend; which in turn will

affect the proton conductivity of the resulted blend membranes. The proton conductivity data for selected SPEEK/PPSU-E blend membranes is shown in Table 6.3. It is clear that the proton conductivities of the 50% blend are very low regardless of the moderate water uptake of these membranes. A possible explanation for this result is due to the block of proton transporting channels at high concentration of the phosphonic ester moieties in the blend membranes (≥50%) . Hence, the sulfonic acid groups remain inactive as the proton hopping mechanism became invisible. These results show that the blending of hydrophilic PPSU-Es with SPEEK is an inefficient way to attain both reasonable proton conductivities and water swelling reduction simultaneously. In this context, one can recall the observed behavior for non-fluorinated hydrocarbon based ionomers due to the less developed and dead-ended hydrophilic domains as proton transporting channels.

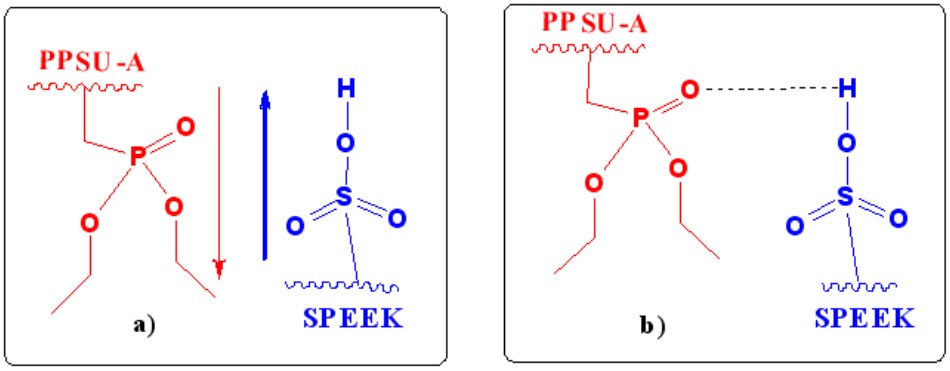


Fig. 6.5 a) Dipole-Dipole Interaction between SPEEK/PPSU-E blend membranes b) weak hydrogen bonding interaction between SPEEK/PPSU-E blend membranes.

Table 6.2 Water and methanol uptake values and solubility data for SPEEK blend membranes with neat PSU and phosphonated PSU in the ester form PPSU-E.

Entry No.	Membrane Code	Water Uptake		Methanol Uptake at r.t	Solubility Data In water	Appearance At r.t
		rt	60 C			
1	30PSU	32	Partially Soluble	Partially Soluble	Turbid at 60 C	White opaque with Large P.S and Poor quality(brittle)
2	50PSU	20	Partially Soluble	Partially Soluble	Turbid at 60 C	White opaque with Large P.S and Poor quality
3	40PPSU-E-0.4	45	Partially Soluble	Partially Soluble	Turbid at 60 C	White opaque with small P.S/ Flexible
4	50PPSU-E-0.4	40	46		Stable up to 60C	White opaque with small P.S/ Flexible
5	30PPSU-E-0.75	50	Partially soluble	Partially Soluble	Turbid at 60 C	White opaque with small P.S/ Flexible
6	40PPSU-E-0.75	39	Partially Soluble	Turbid	Stable up to 60C	White opaque with small P.S/ Flexible
7	50PPSU-E-0.75	38	45	Turbid	Stable up to 60C	White opaque with small P.S/ Flexible
8	30PPSU-E-0.96	41	Turbid	Turbid	Turbid > 80C	White opaque with small P.S/ Flexible
9	40PPSU-E-0.96	37	Turbid	Turbid	Stable up to 60C	White opaque with small P.S/ Flexible
10	50PPSU-E-0.96	34	42	Turbid	Stable up to 80C	White opaque with small P.S/ Flexible

Table 6.3 Proton conductivity for selected SPEEK/PPSU-E membranes.

Membrane Code	Proton conductivity (mS/Cm)	
	Room Temp.	80 C
SPEEK (DS=75%)	6	15
PPSU-A-0.96	0.3	1.8
30PPSU-E-0.96	3.4	6.2
40PPSU-E-0.96	1.7	4.8
50PPSU-E-0.96	1.0	1.1
50PPSU-E-0.4	1.8	4.7
50PPSU-E-0.75	1.2	1.9

6.3.4 Fabrication of SPEEK/PPSU-As ionically crosslinked polymer blend membranes:

Table 6.4 shows the data for methanol uptake, water solubility and physical appearance of the SPEEK/PPSU-As blend membranes. SPEEK/PPSU-A-0.4 blend membranes are white opaque in nature which is probably due to low degree of phosphonation of these membranes. However, there is no clear phase separation in these membranes compared to SPEEK/PSU membranes which are characterized by large phase separation. In addition, by comparison with SPEEK/PPSU-E-0.4 blend membranes which are partially soluble in methanol at room temperature and showed clear turbidity in water at 60C, SPEEK/PPSU-A-0.4 blend membranes have about 400% swelling in methanol without any evident turbidity and are stable in water up to 80 C. These results clearly shows the successful formation of hydrogen bonding bridges between the phosphonic acid functionalized polysulfones and the sulfonated poly(etheretherketone) even at low degree of phosphonation i.e 40% and displays potential use as polyelectrolyte membranes for fuel cells applications.

By comparison, SPEEK/PPSU-A-0.75 and SPEEK/PPSU-A-0.96 blend membranes are transparent to visible light which confirms the miscibility between the two polymers by means of formation of hydrogen bridges as shown in Fig. 6.6 .In addition, the former two membranes are stable in water up to 150 C due to high number of formed hydrogen bridges compared to PPSU-A-0.4 blend membrane. As shown in table 6.4, methanol uptake values decrease as the degree of phosphonation increases or when the percent of the phosphonic acid functionalized polysulfone increases with respect to SPEEK in the blend membranes.

Water uptake is considered a key property for the membranes intended to be used as polyelectrolyte membranes for fuel cells applications. Water uptake values of SPEEK/PPSU-As with different degree of phosphonation (0.4, 0.75 and 0.96); and different percentage in the polymer blend (PPSU-A =20%,30%, 40% and 50%) are displayed in Table 6.5. The water uptake of pure SPEEK membrane at room temperature

is 60% and this membrane is soluble in water at 60 C. By incorporation of 20% of PPSU-As polymers in the blend membranes, the blend membranes became water-insoluble and

Table 6.4 Water and methanol uptake values and solubility data for SPEEK blend membranes with neat PSU and phosphonated PSU in the acid form PPSU-A.

Membrane Code	Methanol Uptake at room temp.	Solubility Data in water	Appearance
SPEEK-75	Soluble .	Soluble at 60C	Transparent and flexible
30PPSU-A-0.4	380	Stable up to 80 °C Turbid at 100 °C	White opaque, Flexible, No phase separation
40PPSU-A-0.4	270		
50PPSU-A-0.4	190		
30PPSU-A-0.75	390	Insoluble up to 150 C	Transparent, Flexible, No phase separation
40PPSU-A-0.75	140		
50PPSU-A-0.75	50		
30PPSU-A-0.96	315		
40PPSU-A-0.96	100		
50PPSU-A-0.96	32		

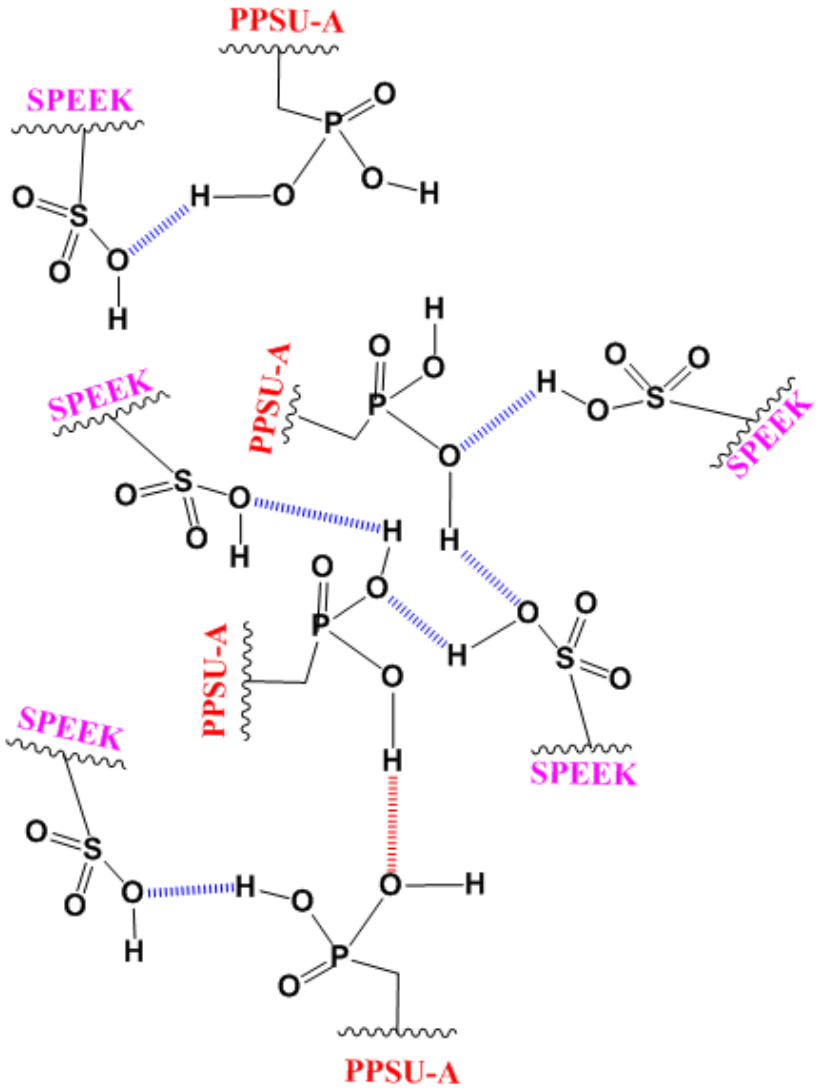


Fig. 6.6 Formation of ionic networks between SPEEK and PPSU-A polymer blends through the formation of hydrogen bridges.

Table 6.5 Water uptake values of SPEEK/PPSUAs blend membranes at room temperature and 80 C.

	Percent of PPSU-A in the SPEEK/PPSU-A blend membrane							
	20% PPSU-A		30% PPSU-A		40% PPSU-A		50% PPSU-A	
	Water Uptake		Water Uptake		Water Uptake		Water Uptake	
	r.t	80 C	r.t	80 C	r.t	80 C	r.t	80 C
PPSU-A-0.4	31	170	25	103	20	50	15	14
PPSU-A-0.75	37	195	30	170	26	70	18	25
PPSU-A-0.96	40	240	36	202	29	98	17	32

display relatively high water swelling at 80 C. In creasing the percentage of PPSU-As in the polymer blend to 50% results in low water uptake values at 80C which is not practical for proton transport through the membranes. This probably as a result of high percentage of the low water uptake phosphonated polysulfones. It seems that incorporation of 30% and 40% of the PPSU-As in the polymer blend provided a reasonable water uptake values in the range of 60%-200%; and avoids excessive swelling at 80 C.

Proton conductivities of the ionically crosslinked blend membranes SPEEK/PPSU-A-0.96 are shown if Fig. 6.7. The conductivity of SPEEK membranes increases with increasing tempeartre and reaches about 0.017 S/cm at 100 C and then decreases afterwards. This is probably due to membrane dehydration at temperatures above 100 C. 30PPSU-A-0.96 blend membranes show higher proton conductivities at temperatures above 40 C compared to the pure SPEEK membrane. This behavior continues up to 120 C to reach a conductivity of 0.134 S/Cm which is comparable to Nafion 117 membrane. This improved proton conductivity can be attributed to the enhancement of water retention through the formed ionic networks between the two polymers which allow for proton transportation. As the percent of PPSU-A-0.96 increases in the polymer blend, the proton conductivities decreases as a result of increasing the hydrophobic domains of the phosphonated polysulfone which has low water uptake compared to SPEEK; which in turn help to partially block the water channels for proton transportation; in the same time, the percentage of available free sulfonic acid groups decreases as the percent of PPSU-A-0.96 increases in the blend membrane.

Proton conductivities of the SPEEK/PPSU-A-0.75 blend membranes display similar behavior to the SPEEK/PPSU-A-0.96 blend membranes as shown in Fig. 6.8. However these membranes has slightly lower proton conductivities compared to SPEEK/PPSU-A-0.96 blend membranes which can be attributed to their lower water uptake values compared to SPEEK/PPSU-A-0.96 blend membranes.

The same comparison can be made for the SPEEK/PPSU-A-0.4 blend membranes which have a remarkable lower proton conductivities compared to SPEEK, SPEEK/PPSU-A-0.96 and SPEEK/PPSU-A-0.75 membranes as shown in Fig. 6.9. The

proton conductivities of 30SPEEK/PPSU-A-0.4 blend membrane is lower than pure SPEEK except when reaching above 90 C and 40SPEEK/PPSU-A-0.4 blend membrane shows lower proton conductivities compared to pure SPEEK membrane except at temperatures above 100 C. The 50SPEEK/PPSU-A-0.4 blend membrane shows a lower proton conductivities about ten times lower than the pure SPEEK membrane. The obtained lower proton conductivities of the SPEEK/PPSU-A-0.4 blend membranes can be attributed to lower number of hydrogen bonding bridges formed in the polymer blend which results in dead end channels for water transportation through the blend membranes.

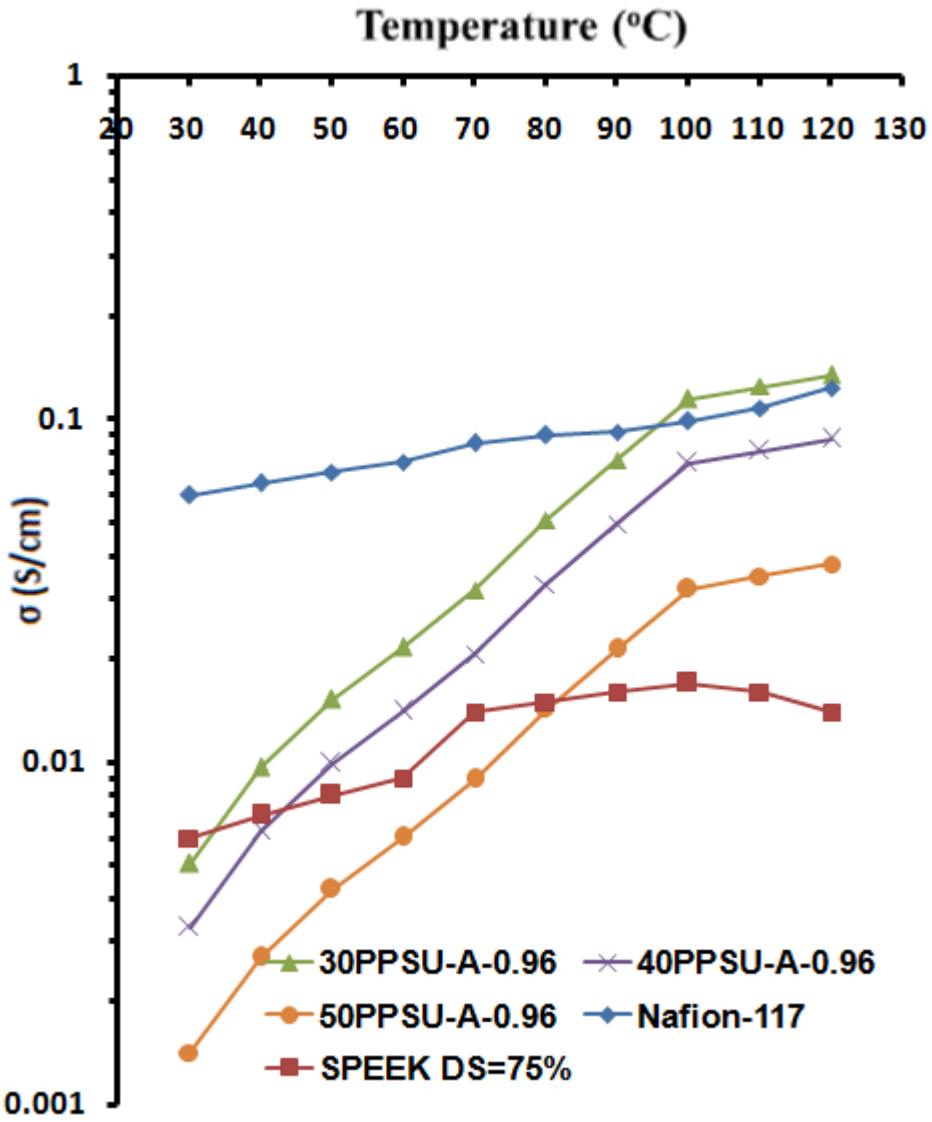


Fig. 6.7 Proton conductivity data for SPEEK/PPSU-A-0.96 blend membranes under fully humidified conditions.

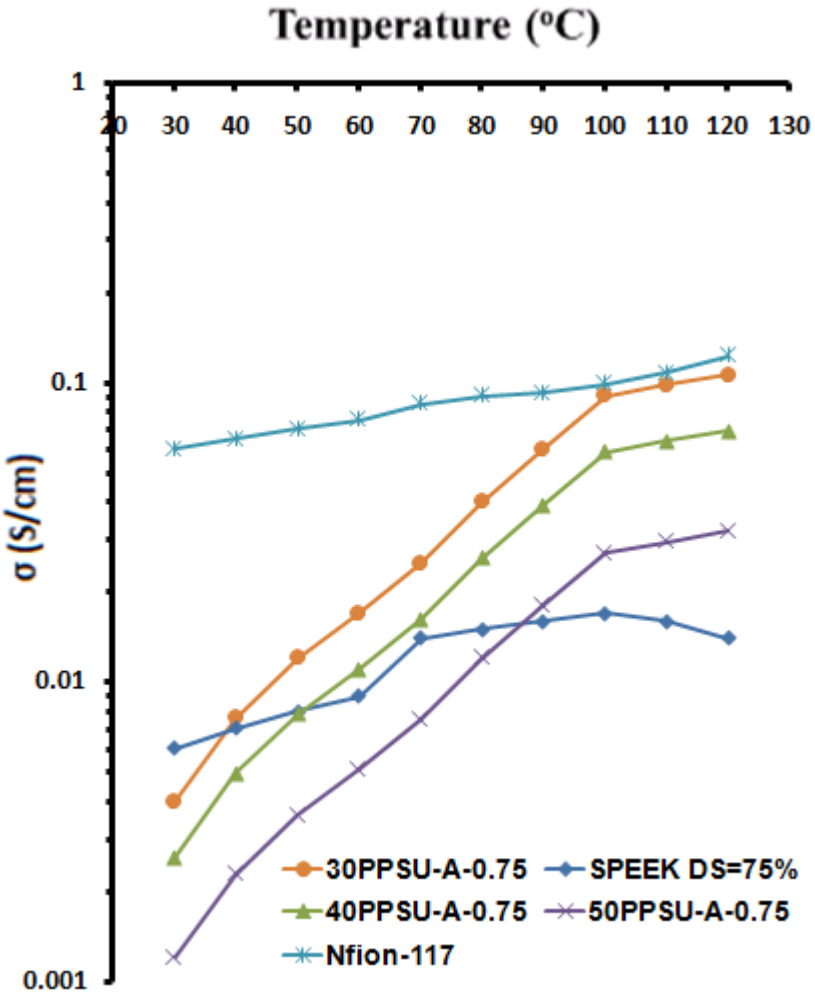


Fig. 6.8 Proton conductivity data for SPEEK/PPSU-A-0.75 blend membranes under fully humidified conditions

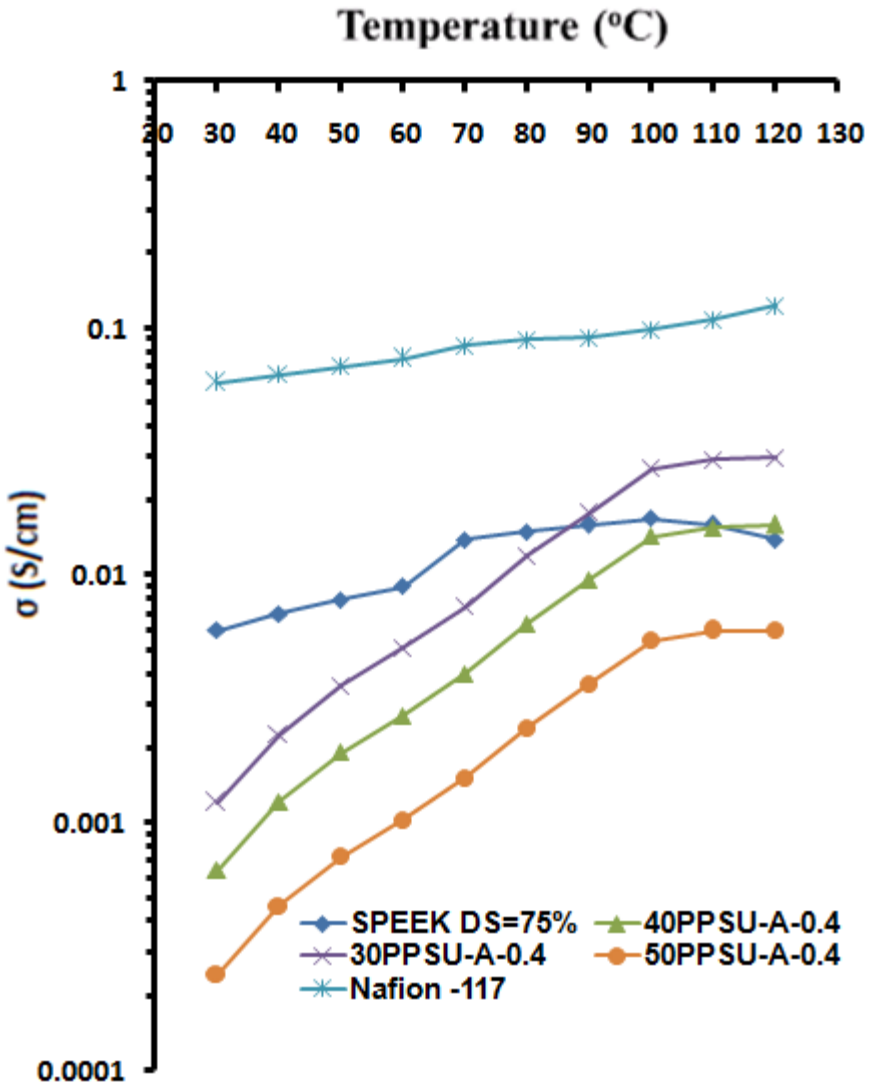


Fig. 6.9 Proton conductivity data for SPEEK/PPSU-A-0.4 blend membranes under fully humidified conditions

6.3.5 Methanol permeability of the SPEEK/PPSU-As blend membranes

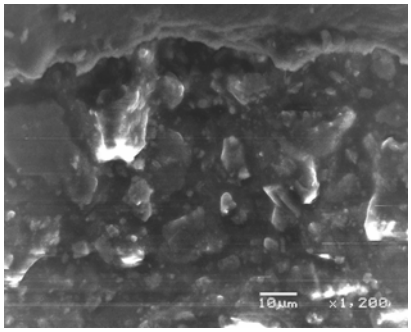
The blend membrane with highest proton conductivity SPEEK/PPSU-A-0.98 was selected for methanol permeability measurements as shown in Table 6.6. Although pure SPEEK-75 membranes are soluble in methanol, the methanol permeability of pure SPEEK membrane with DS=75% is about 4 times lower than Nafion 117; this considerably high permeability is attributed the high degree of sulfonation. However, SPEEK/PPSU-A-0.98 blend membranes show slightly lower methanol permeability with comparison to pure SPEEK membrane. This behaviors was expected since the blend membranes are insoluble in methanol at room temperature due to the formation of ionic networks which facilitate the solvent retention capability of the membrane for the water molecules as well as methanol. Methanol permeability of the blend membranes was found to have slight increase as the percent of PPSU-A in the blend membrane decreases in a similar trend to the obtained water and methanol uptake values displayed in Table 6.4. This result shows the possibility of the use of these blend membranes for direct methanol fuel cells applications.

Table 6.6. Methanol permeability data for Nafion-117, SPEEK DS=75% and SPEEK/PPSU-A-0.98 blend membranes.

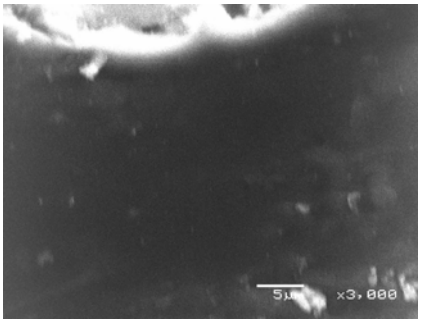
Membrane Code	Methanol Permeability (cm^2/s)
Nafion-117	6.80×10^{-6}
SPEEK DS=75%	1.62×10^{-6}
30PPSU-A-0.98	1.30×10^{-6}
40PPSU-A-0.98	1.22×10^{-6}
50PPSU-A-0.98	1.18×10^{-6}

6.3.6 SEM morphological study of the blend membranes :

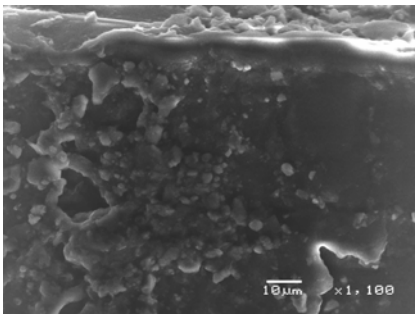
Fig. 6.10 shows the SEM images of selected SPEEK blend membranes prepared in this study. It is clear that SPEEK/PSU blend membrane has large phase separation as shown in Fig. 6.10 (a) which resulted in poor quality and brittle membranes. The blend membranes of SPEEK/PPSU-Es (b-d) show less phase separation compared to SPEEK/PSU blend membrane. This is as a result of improved hydrophilicity of the functionalized polysulfone which led to less phase separation between the two polymers through the dipole-dipole interactions as well as the formation of weak hydrogen bonding as illustrated in Fig 6.5. It can be seen that as the degree of phosphonation increases from 0.4 to 0.98 in SPEEK/PPSU-Es blend membranes, the miscibility between the two polymers is enhanced and the phase separation became less predominant to provide white opaque flexible and tough membranes. All the SPEEK/PPSU-As blend membranes were found to be completely transparent to visible light which means that blend microphases, if existent, have dimensions smaller than visible light. SEM micrographs of 30PPSU-A-0.98 shown in Fig. 6.10 (e and f) has no clear phase separation compared to SPEEK/PSU or SPEEK/PPSU-Es blend membranes which demonstrates the successful formation of ionic networks through hydrogen bonding bridges between the highly acidic sulfonic acid groups SO_3H and the weak phosphonic acid groups PO_3H_2. Also, 50PPSU-A-0.75 blend membrane has no clear phase separation even though it has large amount of functionalized polysulfone (i.e 50%) as shown in Fig. 6.10 (g and h).



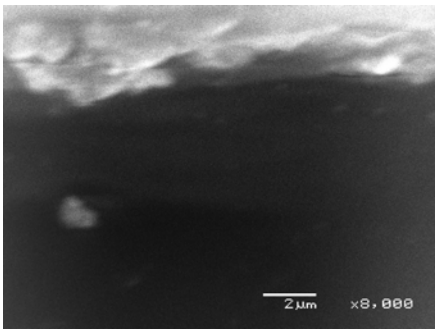
a) 30PSU



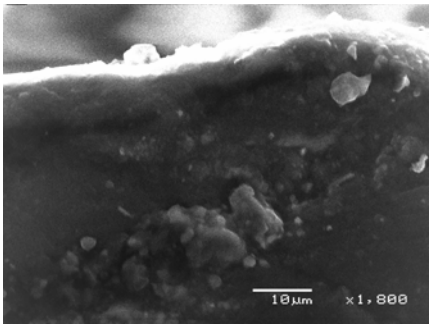
e) 30PPSU-A-0.98



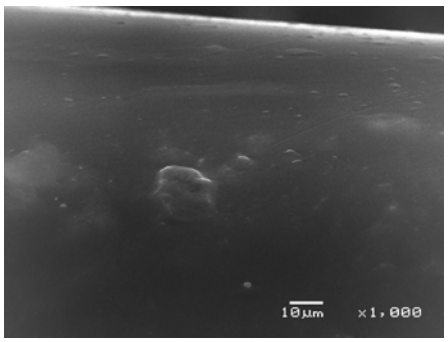
b) 40PPSU-E-0.4



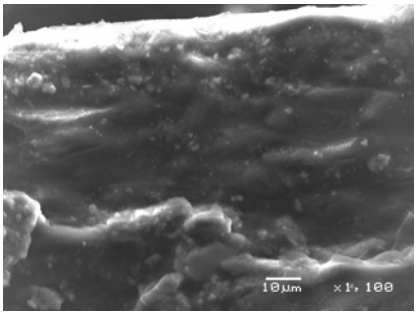
f) 30PPSU-A-0.98



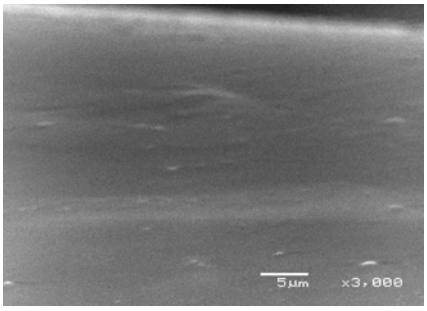
c) 40PPSU-E-0.75



h) 50PPSU-A-0.75



d) 40PPSU-E-0.98



i) 50PPSU-A-0.75

Fig. 6.10 SEM micrographs of selected SPEEK blend membranes.

6.3.7 Thermal Stability of the Blend Membranes :

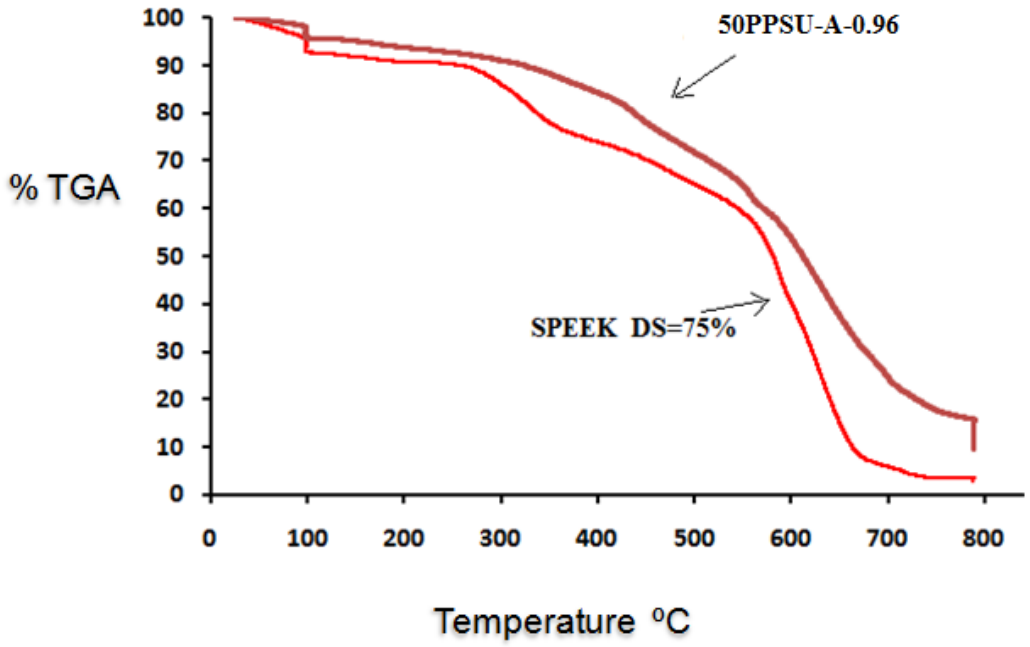


Fig. 6.11 TGA analysis for pure SPEEK and 50PPSU-A-0.96 blend membrane.

One advantage of the ionically crosslinked membranes is their higher themal stability compared to the covalently crosslinked membranes [176]. Fig. 6.11 displays the thermal gravity analysis of pure SPEEK and 50PPSU-A-0.96 membranes. SPEEK membrane showed a remarkable degradation in the temperature range of 250-350 ºC due to the loss of sulfonic acid groups. However, this step of degredation was not observed in the case of 50PPSU-A-0.98 which confirmed the successful formation of ionic networks in the blend membrane which provided higher thermal stability. By comparing the tow thermograms, pure SPEEK membrane showed a 10 wt% loss at 250 ºC and 20 wt% loss at 350 ºC;

where as the 50PPSU-A-0.96 blend membrane showed a 10 wt% loss at 350 ºC and 20 wt% loss at 450 ºC repectively.

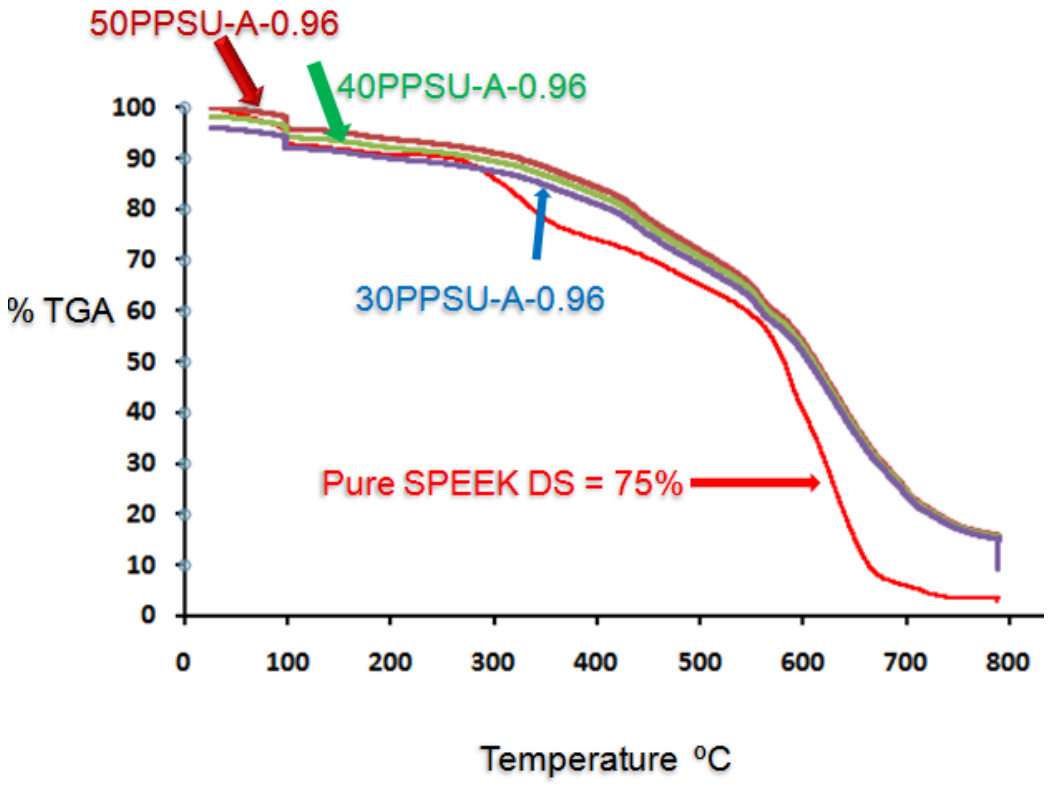


Fig. 6.12 TGA analysis comparison between the whole PPSU-A-0.96 series blend membranes.

Fig. 6.12 showed the comparison of the thermal stability behavior of the pure SPEEK membrane and the whole series of the highst proton conductivity blend membranes PPSU-A-0.96 (i.e containing 30%, 40% and 50% of PPSU-A-0.96 polymer). All the three blend membranes showed enhanced thermal stability and less weight loss in the range of 250- 350 ºC due to the formation of ionic networks. However, the 50%PPSU-

A-0.96 blend membrane showed the highst thermal stability which can be attributed to the formation of highst number of hydrogen bridges between the PPSU-A-0.96 and SPEEK. Hence, thermal stability increases as the percent of PPSU-A-0.96 increases in the blend membrane. By comparison to SPEEK membrane, 30PPSU-A-0.96 with lowest phosphonic acid content, has higher thermal stability than the neat SPEEK.

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