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**NEW POLYSILOXANE BASED
SALT-IN-POLYMER ELECTROLYTES**

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**NEW POLYSILOXANE BASED
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Abstract

In this study, novel organo-substituted polysiloxane based “salt-in-polymer” electrolytes were investigated with improved stability and conductivity. Furthermore, fundamental studies have been carried out with regard to some organo-substituted polyphosphazenes which together with the polysiloxanes form the most interesting classes of polymers apart from polyethylene oxides with very good prospect for a use as polymer electrolytes in batteries.

The main part of this study concerns the synthesis and characterisation of a number of poly(organosiloxane) polymers and some poly(organophosphazene)s with different organic substituents, as well as the preparation of polymer electrolyte membranes and extensive conductivity measurements. Both, polysiloxanes and polyphosphazenes have the advantage that their chemical and physical properties can easily be varied over a very broad range by a huge number of different substituents at the silicon and phosphorous atoms, respectively.

The polysiloxanes were functionalised with different side groups via hydrosilylation of commercially available poly(methylhydrosiloxane) (PMHS). “Salt-in-polymer” polymer electrolytes were prepared from these by dissolving lithium triflate and lithium bis(trifluoromethanesulfone)imide. Both, pure polymers and electrolyte membranes prepared by solvent casting techniques were characterized. Extensive conductivity studies were done by impedance spectroscopy.

Polymer electrolytes prepared by dissolving lithium triflate in oligoether functionalized polysiloxane (OPS) showed maximum conductivities as high as $10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which already approaches a range for a possible practical application in batteries. In order to achieve higher mechanical stabilities, cross linking techniques were developed based on mixed substitution of the polysiloxanes with 90 % oligoether side chains as mentioned above and an additional 10 % oligoether side chains with terminal trimethoxysilyl groups ($T_{0.1}\text{OPS}$). The latter could be used for cross linking to form Si-O-Si bridges which gave mechanically stable membranes. Cross linking was carried out with both hydrochloric acid (HCl) and dibutyltin dilaurate (DBTL) as catalysts. DBTL enhanced the efficiency of cross linking by far.

In all these experiments, however, crosslinking lead to a considerable decrease of the conductivity. The conductivity decrease observed for T_{0.1}OPS based membranes with DBTL cross linking even amounted to one order of magnitude.

The electrical properties of polysiloxanes with increased length of the oligoether side chains (L-OPS) were almost identical to those of T_{0.1}OPS based polymer electrolytes. However, taking polypropylene oxide as side chains on the polysiloxanes (PPO-PS) lowered the conductivities down to values of 10⁻⁶ S·cm⁻¹ at ambient temperatures.

Subsequently, two routes have been explored in order to enhance the conductivity of the above mentioned polysiloxanes. On the one hand, T_{0.1}OPS based polymer electrolytes were prepared by blending with finely dispersed nanoparticles (Al₂O₃ and SiO₂). However, neither Al₂O₃ nor SiO₂ particle dispersions in the matrix showed a noticeable effect on the conductivity. This is contrary to the experience with particle dispersed polyethylene oxide based electrolytes. It seems that the surface charge effects observed with some polymer electrolytes are only noticeable for very low initial conductivities. Ionic mobilities and charge carrier concentrations in polymer electrolytes that already exhibit a relatively high conductivity are not influenced by surface interactions of dispersed particles.

On the other hand, the influence of two boric acid esters (B(OR)₃ (R = oligoether) was tested as low molecular weight ingredients. Positive effects of such additives are well known for polyethylene oxide base electrolytes. Possible explanations in the literature are a plasticizer effect and/or an enhancement of the salt dissociation by a Lewis acid-base interaction of anions with the boric acid esters. For T_{0.1}OPS, a considerable increase of the conductivity by a factor of 10 was observed for both borate esters applied in this work. Hence, this second approach is by far the most promising route for further enhancement of the salt-in-polymer conductivities.

As already mentioned above, polyphosphazenes with various substituents were also synthesized. For the first time, a polyphosphazene has been characterized by a SANS experiment, in this case poly(bismethoxyphosphazene) (PBMP) was used. For the pure PBMP melt as well as for a solution in deuterated dimethylformamide, the SANS experiment gave an almost ideal polymer behaviour as expected for a random coil configuration.

The interaction of dissolved lithium triflate with the PBMP matrix was investigated, too. The solutions showed a considerable conductivity of the order of $10^{-5} \text{ S}\cdot\text{cm}^{-1}$, which is as high as found for classical oligoether substituted polyphosphazenes (MEEP). The experiments revealed no distinguishable effect of the dissolved salt on the conformation of PBMP in spite of a large salt concentration up to 15 wt-%.

Finally, some polyphosphazene based polyelectrolytes, both polycation as well as polyanion forms were synthesized and applied for the first time for polyelectrolyte multilayers. The multilayer preparation was promising and comparable conductivity values were obtained as compared to other commonly employed polyelectrolytes used for the formation of multilayers.

Zusammenfassung

In der vorliegenden Arbeit wurden neue "Salz-in-Polymer"-Elektrolyte aus organo-substituierten Polysiloxanen mit verbesserter Stabilität und Leitfähigkeit hergestellt. Darüber hinaus wurden weitere Untersuchungen an einigen organo-substituierten Polyphosphazenen durchgeführt, die zusammen mit den Polysiloxanen neben den Polyethylenoxiden die interessantesten Polymerklassen für Polymerelektrolytanwendungen sind.

Der größte Teil dieser Arbeit behandelt die Synthese und Charakterisierung einer ganzen Reihe von Poly(organosiloxanen) und von einigen Poly(organophosphazenen) mit verschiedenen Substituenten wie auch die Herstellung entsprechender Polymerelektrolytmembranen und ausgedehnte Leitfähigkeitsuntersuchungen daran. Sowohl Polysiloxane als auch Polyphosphazene haben besondere Vorteile, da die chemischen und physikalischen Eigenschaften in einem besonders weiten Bereich durch die flexible Substituentenwahl veränderbar und gezielt einstellbar sind.

Die Polysiloxane wurden in dieser Arbeit über die Hydrosilylierung aus kommerziellem Poly(methylhydrosiloxan) (PHMS) mit verschiedenen Seitengruppen funktionalisiert. "Salz-in-Polymer"-Elektrolyte wurden daraus mit Lithiumtriflat und Lithium-bis(trifluormethansulfon)imid hergestellt. Sowohl die reinen Polymerelektrolytmembranen als auch die salzhaltigen Membranen wurden ausgiebig charakterisiert. Leitfähigkeiten wurden mit der Impedanzspektroskopie untersucht.

Maximale Leitfähigkeiten von etwa $10^{-4} \text{ S} \cdot \text{cm}^{-1}$ wurden an Lösungen von Lithiumtriflat in Polysiloxan mit kurzen Oligoether-Seitenketten gefunden (im Folgenden: OPS). Diese Werte sind schon recht nah an praktisch relevanten Leitfähigkeiten für Batterien. Um höhere mechanische Stabilität zu erreichen, wurden Techniken zur Quervernetzung eingesetzt. Dazu wurde eine gemischte Substitution der Polysiloxane mit etwa 90% Oligoether-Seitengruppen und 10% der restlichen Substituenten mit endständigen Trimethoxysilylgruppen genutzt ($T_{0.1}\text{OPS}$). Letztere diente zur Quervernetzung durch Bildung von Si-O-Si-Brücken, was sehr stabile Membranen lieferte. Die Vernetzungsreaktion wurde sowohl mit Salzsäure (HCl) als auch mit Dibutylzinndilaurat (DBTL) als Katalysatoren durchgeführt. Mit DBTL wurde eine erheblich verstärkte Vernetzung erzielt.

Leider führte ein zunehmender Quervernetzungsgrad zu einer deutlichen Reduzierung der Leitfähigkeiten, für mit DBTL vernetzte T_{0.1}OPS-Membranen beispielsweise sank die Leitfähigkeit um eine Größenordnung.

Die elektrischen Eigenschaften von Polysiloxanen mit erhöhter Länge der Oligoetherseitenketten (L-OPS) war fast identisch mit denen, die an T_{0.1}OPS erzielt wurden. Bei Verwendung von Polypropylenoxidseitenketten (PPO-OPS) allerdings fielen die Leitfähigkeiten stark ab auf etwa $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ bei Raumtemperatur.

Im weiteren Verlauf der Arbeit wurden zwei weitere Ansätze zur Erhöhung der Leitfähigkeit erprobt. Zunächst wurden T_{0.1}OPS-basierte Polymerelektrolyte mit fein verteilten Nanopartikeln aus Al₂O₃ und SiO₂ hergestellt. Die eingelagerten Partikel führten jedoch zu keiner merklichen Leitfähigkeitserhöhung. Dies steht im Gegensatz zur Erfahrung mit Partikeldispersionen in vom Polyethylenoxid abgeleiteten Elektrolyten. Offensichtlich führen Adsorptions- und Oberflächenladungseffekte an solchen Partikeln nur bei niedrigen Leitfähigkeiten zu nennenswerten Effekten. Ionenbeweglichkeit und Konzentration freier Ionen in Polymerelektrolyten mit bereits hoher Eigenleitfähigkeit können durch eingelagerte Nanopartikel nicht mehr verbessert werden.

In einem zweiten Ansatz wurden niedermolekulare Ester der Borsäure (B(OR)₃ (R = Oligoether) in den Polymeren gelöst. Positive Auswirkungen auf die Leitfähigkeit sind bekannt von Polyethylenoxid. Erklärungsmöglichkeiten aus der Literatur konzentrieren sich auf einen Weichmachereffekt oder auf eine erhöhte Salzdissoziation durch Lewis-Säure/Base-Wechselwirkung mit den Anionen. Für T_{0.1}OPS wurde ein beträchtlicher Leitfähigkeitsanstieg um den Faktor 10 gefunden. Der hier erprobte Ansatz ist also sehr vielversprechend.

Neben den Polysiloxanen wurden einige verschieden substituierte Polyphosphazene synthetisiert. In einer Kooperation mit Prof. Richter in Jülich wurden erstmals SANS-Untersuchungen an einem Polyphosphazen mit kurzen Substituenten durchgeführt. Hier wurde das Poly(bismethoxyphosphazen) (PBMP) benutzt. Reine PBMP-Schmelze wie auch Lösungen in deuteriertem Dimethylformamid zeigten, dass PBMP sich in diesen Fällen praktisch wie ein ideales statistisches Knäuel verhält.

Die SANS-Messungen wurden auch auf Lösungen von Lithiumtriflat in PBMP ausgedehnt. Überraschend hoch Leitfähigkeiten von $10^{-5} \text{ S}\cdot\text{cm}^{-1}$ wurden gefunden, die ähnlich hoch wie in klassischen oligoether-substituierten Polyphosphazen sind. Die

Neutronenstreudaten zeigten, dass die gelösten Salze trotz der hohen Konzentrationen von bis zu 15 Gew.-% keinen merklichen Einfluss auf die statistische Konformation der Polymermoleküle hatten.

Ergänzend wurden noch einige Polyelektrolyte auf der Basis von Polyphosphazenen mit kationisch und anionisch geladenen Substituenten hergestellt und in der Arbeitsgruppe Prof. Schönhoff in Form von Polyelektrolyt-Multischichten getestet. Die erreichten Leitfähigkeiten entsprachen den an klassischen Polyelektrolytmultischichten beobachteten Werten.

To my wife and my family

“Hayatta en hakiki mürşit ilimdir – Our true mentor in life is science”

Mustafa Kemal ATATÜRK

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1 INTRODUCTION

1.1 Introduction

Consumption of energy resources is apparently harmless. However, producing that energy requires resources and contributes to air and water pollution. Energy production that relies on the combustion of fossil fuels is forecast to have a severe future impact on world economics and ecology. While burning they generates air pollutants including carbon dioxide (CO₂), sulfur dioxide and trioxide (SO_x), nitrogen oxides (NO_x) and some other trace pollutants. Carbon dioxide is an important greenhouse gas which is thought to be responsible for some fraction of the rapid increase in global warming seen especially temperature records in the 19th century, as compared with tens of thousands of years worth of temperature records which can be read from ice cores taken in arctic regions. Therefore the need for clean and efficient energy generation and storage devices is contingent upon the development of modern society. Efficient energy storage devices are therefore very essential that can also be coupled with the fuel cells as one of the promising energy generating devices. The hybrid-electrical-vehicles incorporating both conventional combustion engines along with high energy density rechargeable batteries are not only more efficient in terms of fuel but also less polluting than the conventional internal combustion engines. In addition, the need of more efficient both in terms of capacity and size is crucial as a component in portable electronic appliances like laptops, cellular phones etc.

1.2 Lithium Ion Batteries

Portable power applications continue to drive research and development of advanced battery systems. In recent years, the need for portable power has accelerated due to the miniaturization of electronic appliances where in some cases the battery system is as much as half the weight and volume of the powered device. Certainly, when compared, energy storage cannot keep pace with the rate of progress in the electronic industry, yet the past decade has produced spectacular advances in chemistry and engineering within the emerging technologies of Ni–MeH and Li-ion batteries. These cells are now supplanting the well known Ni–Cd batteries. **Fig. 1.1** gives an overview about the common battery systems, where the growth in x and y axis contributes to smaller size and lighter weight.

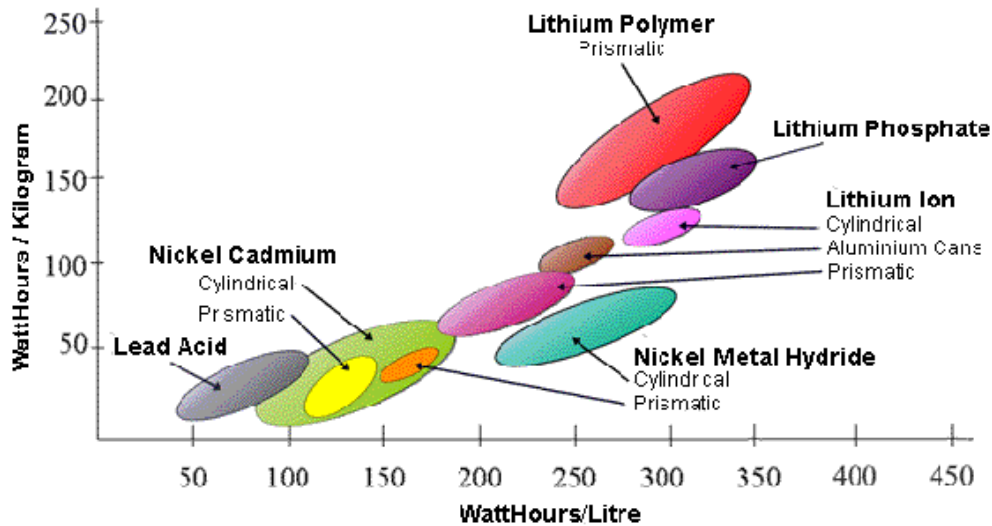


Fig. 1.1 Comparison of the energy densities of the various batteries.

Li-based batteries, because of their high energy density and design flexibility, currently outperform other systems, account for 63% of worldwide sales in portable batteries [1].

A battery is composed of several electrochemical cells that are connected in series and/or in parallel to provide the required voltage and capacity, respectively. Each cell consists of a positive (cathode) and a negative (anode) electrode (both sources of chemical reactions) separated by an electrolyte solution containing dissociated salts, which enable ion transfer between the two electrodes.

Lithium has long received much attention as a promising anode material, as it is the most electronegative (-3.04 V versus standard hydrogen electrode), and the lightest metal (0.534 g cm^{-3} , and specific gravity $\rho = 0.53 \text{ g cm}^{-3}$). The former confers upon it a negative potential that translates into high cell voltage when matched with certain cathodes, and the latter makes it an anode of high specific capacity (3.86 A h g^{-1}). Intensive research activities resulted in the commercialization of a series of non non-rechargeable lithium batteries in early 1970s [2]. Soon it was realized that needlelike lithium crystals (called “dendrite”) grew on the anode upon charge and discharge that could grow piercing the separator and result in an internal short and explosion ensue (Fig. 1.2 (a)). The dendrite formation prompted the search for a way to circumvent the drastic change of the anode during cell cycling. As a result host-guest chemistry, also known as intercalation, was considered, as earlier applied to cathode materials for lithium batteries represented by Whittingham [3] and significantly improved by Goodenough [4-6]. Most of these materials are transition metal oxides or chalcogenides with stable lattices, and their layer

or tunnel structures provide the pathways for guest ions such as the lithium ion to diffuse. The concept was confirmed experimentally by using lithiated oxides as anodes and other oxides as cathodes in nonaqueous electrolytes [7, 8] as seen in **Fig. 1.2** (b).

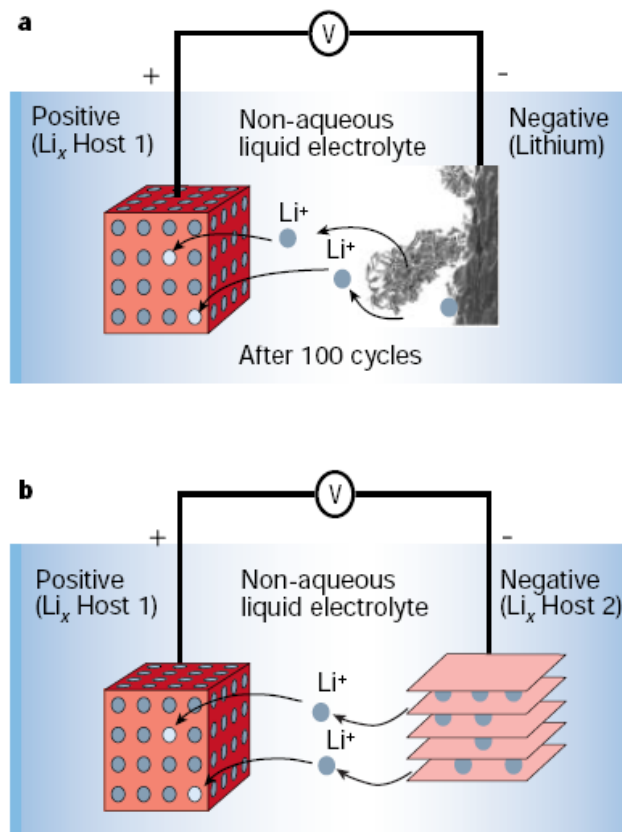
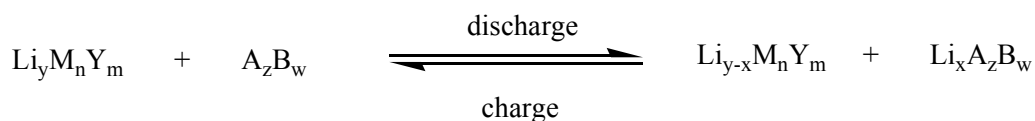


Fig. 1.2 Schematic representation and operation principle of Li batteries. (a) Rechargeable Li-metal battery (dendritic growth at Li surface), (b) Rechargeable Li-ion battery [1].

The breakthrough was made when Japanese researchers exploited an old concept of using carbonaceous materials as anode intercalation host [9-11]. In the charged state of these carbonaceous anodes, lithium exists in its ionic rather than metallic state, thus eliminating any possibility of dendrite growth. The charge and discharge of lithium battery is represented in **Scheme 1.1**.



Scheme 1.1 Charge and discharge of a lithium battery.

where, $\text{Li}_y\text{M}_n\text{Y}_m$ is Li_xC_6 , LiWO_2 or LiFe_2O_3 and A_zB_w is TiS_2 , V_2O_5 , WO_3 or NbS_2 .

2 THEORY

2.1 Ion Conducting Polymers

The present development trend in lithium ion batteries is focused on the replacement of the common liquid electrolyte with a lithium ion conducting polymer electrolyte membrane to finally achieve the fabrication of batteries having a full plastic structure. Such plastic lithium ion batteries are expected to be less expensive and more easily scaled up than their liquid counterparts. In addition, the absence of free liquid allows packaging in light-weight plastic containers unlike conventional batteries which require metallic casing. Finally, since the electrolyte membrane and the associated plasticized electrodes can be formed as laminates, the plastic battery can be fabricated in any desired shape or size, a target difficult to be achieved with liquid electrolyte cells.

The key component of the plastic battery is the polymer electrolyte that has to fulfill a series of stringent requirements, including among others: (1) good mechanical properties (to assure easy battery fabrication), (2) high ionic conductivity (to assure low internal resistance), (3) high lithium ion transport (to avoid concentration polarization), (4) wide electrochemical stability (to be compatible with high voltage electrodes), (5) low cost (in order to fill a large market) and (6) benign chemical composition (to be environmentally compatible).

The identification of membranes capable of combining all the above stressed features is not an easy task. And indeed, intensive research and development work has been devoted in recent years to achieve this goal.

Historically, the first type of ion conducting polymer to be considered for battery applications were those formed by blending high molecular weight poly(ethylene oxide) (PEO) with a lithium salt as reported by Wright *et al.* in 1973 [12]. PEO however suffers from the crystallinity, therefore the low value conductivity at room temperature ($\sim 10^{-8} \text{ S}\cdot\text{cm}^{-1}$), since the ionic conduction mainly takes place through the amorphous region of polymer host. Therefore many attempts have been tried in order to enhance the conductivity. The incorporation of nano sized particles such as SiO_2 , Al_2O_3 , TiO_2 etc. to form composite polymer electrolytes attracts many interest, whereby the crystallization can be prevented [13, 14]. The addition of small molecular weight aprotic solvents as

plasticizer to result in so called “gel-electrolyte” is another commonly employed method not only for PEO but also many other polymer electrolyte systems to attain higher conductivities [15-18].

On the other hand, much better enhancement for polymer with highly flexible backbones, bearing oligoether as side chains, where the short ether groups guarantee fast segment motion, thus rapid ionic diffusion. Many new types of polymeric systems based on inorganic polymers like polyphosphazenes [19-23] and polysiloxanes [24-58] have been extensively synthesized and investigated for their application as polymer electrolytes in the past few decades.

2.2 Solvation in Macromolecules

Beside the electrodes, electrolyte, which commonly refers to a solution comprising the salts and solvents squeezed in between two electrodes, constitutes the third key component of a battery. Although the role of electrolyte is often considered trivial, its choice is actually crucial as it rules out the main properties of a battery.

Solvents. A salt dissolves only if the associated energy and entropy changes produce an overall reduction in free energy of the system as a result of the ionic species and the coordinating sites. The effect of the solvent can be predicted using the concept of donor-acceptor approach, where donor number (DN) measures the ability of the solvents to donate electrons for the solvation of cations and acceptor number (AN) quantifies the capability for anion solvation [59]. Ethers have donor number of around 22 and relatively low acceptor number 10 due to lack of hydrogen bonding for anion solvation. PEOs with two carbons per each repeat unit are the most suitable solvent compared to the other ethers. Neither poly(methylene oxide), $(\text{CH}_2)_n$, nor poly(propylene oxide), $(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n$, tend to form polymer electrolytes [60]. Both the rigidity of the chains in the former and the inability of the ether polymer to adopt low-energy conformations to maximize the polymer-cation coordinations can account for this. Nitrogen heteroatom polyethers, on the other hand, are likely to form stronger bonds with cations because of the higher donor number (DN = 60) of the amine group. There are too few reports of the use of sulfur analogs of the polyethers as solvent because many preparations result in insoluble crosslinked materials.

Salts. The interaction of solute with salt can be explained by hard-soft acid-base (HSAB) principle suggested by Pearson [61-63]. Those acids and basis that are small and tend to hold their electrons tightly are termed hard, and those that are large and hold their valance electrons loosely are called soft. The ethers that have highly electronegative donor atoms are hard bases, thus PEO may be regarded as also hard. In addition, it is sufficient to know since the main focus is lithium in lithium ion batteries that Li^+ is also hard.

Aprotic liquids and polymers have negligible anion stabilization energies as the dielectric constant of the solvents is in general low. Therefore the most proper choices of anion is weak and bulky bases with relatively low lattice energy, which could be either soft (I^-) or hard (ClO_4^-). The following order would be expected for the anions as polyether-type polymers as solvent:



2.3 Ion Conduction Mechanism

The ability to conduct ions is the basic function of electrolytes, which would determine how fast the energy stored in electrodes could be delivered. In liquid electrolytes, the transport of ions is realized via two step process: (1) the solvation and dissociation of ionic compounds by solvent molecules, (2) the migration of these solvated ions through the solvent media. During the solvation, the lattice energy is compensated by the coordination of solvent dipoles with the naked ions (usually cations); therefore these ions should always migrate with solvation sheath around them, which consists of a certain number of oriented solvent molecules. The theoretical and some experimental results revealed that the small ionic radius of lithium usually allows no more than four solvent molecules in its solvation sheath [2]. The segmental motion of polymers are believed to promote ion mobility in this sense by making and breaking the loosely formed coordinations between cations and polymer chain, and hand-to-hand transfer of cations by fast segmental motion of the polymer chains. **Fig. 2.1** represents a simple schematic representation of this type of motion.

Fig. 2.1 (a) shows how a cation could be transferred from one solvation sheath to another one either within the same or neighboring polymer chain, promoted by the segmental motion of the chains themselves. The model is very much an oversimplification of the real situation since it does not consider effects such as ion-ion interactions, for example.

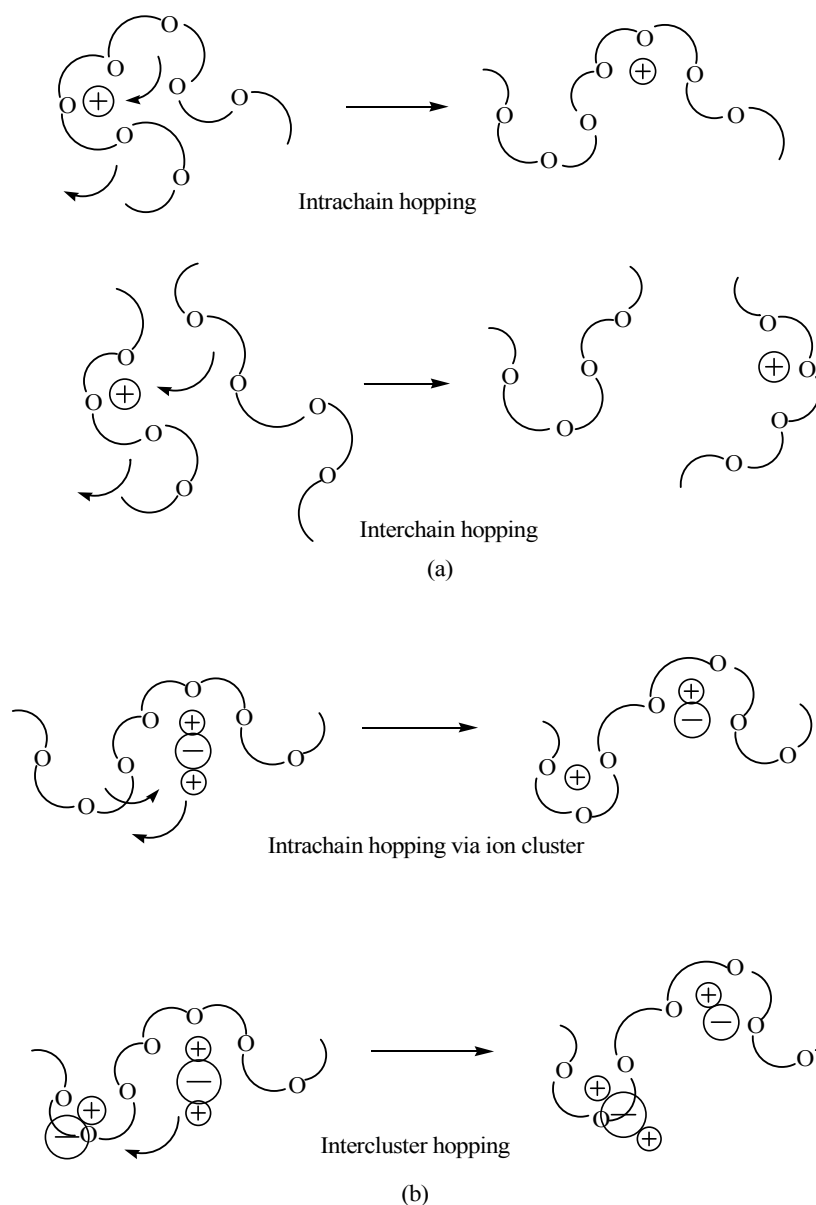


Fig. 2.1 Representation of (a) cation and (b) ionic cluster motion assisted by segmental motion of the polymer in an electrolyte.

The first scheme of **Fig. 2.1** (b) exhibit one example of how ion-associates may assist in conduction mechanism. The extreme example seen as the second scheme shows the polymer chains acting solely as anchor points with conduction in this case resulting from ions (cations or anions) moving from ionic cluster to ion cluster. All these mechanisms are feasible and may depend to a large extent on the concentration of salt in the matrix.

2.4 Polysiloxanes as Polymer Electrolytes

2.4.1 Properties and Chemistry of Polysiloxanes.

Inorganic polymers, i.e. polymers that have a backbone containing other elements than carbon, nitrogen and oxygen, to which organic or organometallic substituents can be attached have a multitude of actual and potential uses. Among them, polysiloxanes are unique and by far the most important with regard to commercial applications. Polyphosphazenes are moreover another class of inorganic polymer studied extensively due to its ease of functionalization by substituting highly reactive chlorine atoms of poly(dichlorophosphazene). Since the main scope of the current study comprises the polysiloxanes as polymer electrolytes, polyphosphazenes will not be mentioned in detail but the detailed explanation concerning the history and potential applications can be found elsewhere [64].

Polysiloxanes have been used technologically for almost 50 years because of their utility over a wide temperature range (-100 to 300 °C) and very low T_g values (for instance -123 °C for poly(dimethylsiloxane)). The polysiloxanes owe their high flexibility to its significantly larger Si-O bond length (1.64 Å) and also more open Si-O-Si bond angle ($\sim 143^\circ$) that can invert through the axis with little cost in energy [65].

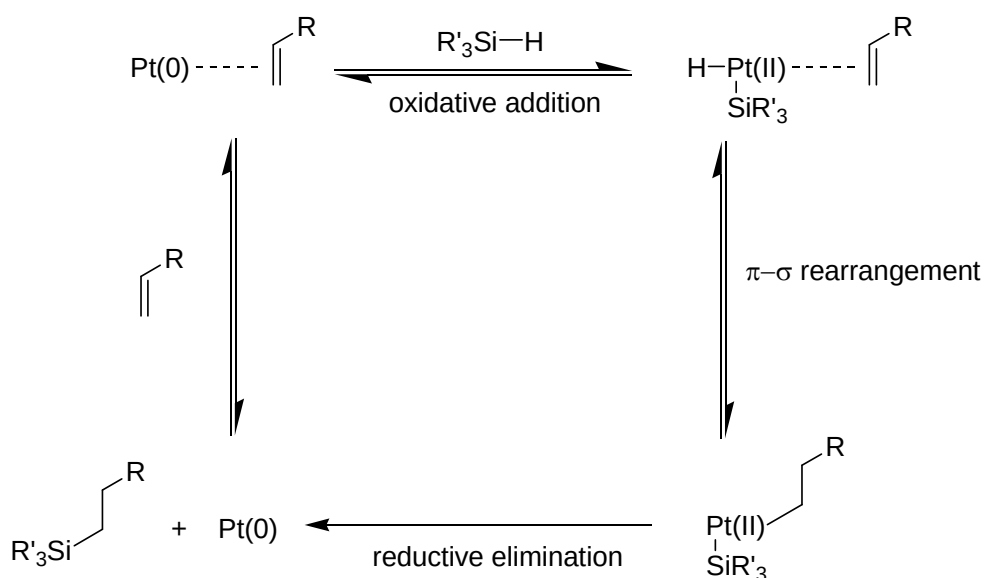
There are two methods commonly employed to prepare polysiloxanes. Polycondensation reaction of R_2SiCl_2 under kinetically controlled conditions are one way of polymerization where monomers are extremely important because they provide access to the preparation of a wide variety of substances having both organic and inorganic character [66, 67]. Polycondensation approach has been however largely replaced by ring-opening polymerization catalyzed by acid or base as catalyst [67, 68].

2.4.2 Macromolecular Functionalization of Polysiloxanes.

The macromolecular substitution of polysiloxane is very rare, since polymers with displaceable substituents are not readily prepared and handled. Poly(methylhydrosiloxane)s (PMHSs), where each repeating unit contains one Si-H bond, are the only polymer in this class which has been extensively investigated. The macromolecular substitution can be achieved by (1) dehydrocoupling or (2) hydrosilylation reaction of the Si-H functional groups. The former reaction involves the

reaction of alcohols in the presence of a catalyst to form Si-O-C bond and hydrogen gas. A wide variety of catalyst was employed by Kohoma to promote the dehydrocoupling reaction of poly(methylhydrosiloxane) [69], the idea was then applied in the field of polymer electrolyte [27, 33]. Recently there is renewed interest in the exploration of transition metal complexes as catalyst for the dehydrocoupling of PMHS [32].

The susceptibility of Si-O-C bonds to hydrolysis and subsequent structural degradation is a severe problem unless moisture can be completely eliminated. Si-C bonds, on the other hand, are very stable and polymers containing this type of linkage are therefore desirable [70]. Hydrosilylation reactions are the other alternative and among the most important reactions in silicone and siloxane chemistry [71, 72], which involves the addition of a Si-H unit on the polysiloxane to a carbon-carbon double bond under relatively mild conditions. One important application of these reactions in industry is to crosslink hydrosiloxanes with vinyl terminated dimethylsiloxane to give elastomers [72]. Platinum catalysts are the most frequently applied catalysts for this purpose due to their high efficiency and tolerance to a variety of functional groups and also low danger for side reactions [73-78] and Karstedt's catalyst [73, 74] among the others have found widespread use in the preparation of polysiloxane based polymer electrolytes. In 1964, Chalk and Harrod [79-81] proposed a mechanism for platinum catalyzed hydrosilylation reactions based on simple elementary steps commonly observed in organometallic chemistry, such as oxidative addition and reductive elimination as illustrated in **Scheme 2.1** and has been widely accepted for alkene hydrosilylation.



Scheme 2.1 Chalk-Harrod Mechanism of platinum catalyzed hydrosilylation.

2.4.3 Polysiloxane based Polymer Electrolytes.

Inorganic polymers such as polysiloxanes and polyphosphazene have attracted a great interest in the polymer electrolyte area over few decades as they possess superior properties to PEOs in terms of low glass transition temperature and complete amorphous structure. A number of studies of siloxane based polymer electrolytes have been reported in the literature. Some polysiloxane structures synthesized and investigated as polymer electrolytes are given in **Fig. 2.2**.

Nagaoka [24] reported the synthesis of linear polymer, poly(dimethylsiloxane-co-ethylene oxide) by polycondensation reaction of dimethyldichlorosilane with short chain poly(ethylene glycol)s. The highest conductivity at 25 °C was found to be $1.5 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ for LiClO_4 complexed with DMS-4EO.

Although comb like polysiloxanes by dehydrocoupling reaction of PMHS with different alcohols was explained by Kohama in 1977 [69], their ionic conductivity after substituting with poly(ethylene glycol) monomethyl ether with wide variety of repeating units was only investigated almost after a decade [25-31]. Zinc octanoate [25-27] and triethylamine [28, 30] were commonly used as catalyst. The length of the side chain did not appear to greatly affect the conductivity, which was in the order of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ for LiClO_4 electrolytes at room temperature. The effect of salt type and side chain length on the electrical properties of polysiloxanes were investigated by Acosta [30]. A similar preparation technique was used. The room temperature conductivity value over $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ was recorded for bis(trifluoromethylsulfonyl)imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$) salt complexed with polysiloxane with long oligoether ($n = 12$). The polymers were crosslinked by incorporating bifunctional poly(ethylene glycol) in the reaction sequence, which reduced the conductivities at least by an order of magnitude [26, 27]. The current study on polysiloxanes upon the interest to explore new transition metal complexes as catalysts for dehydrocoupling revealed that there is a significant difference in the structure of the polymers substituted by different catalysts, which can not be detected by gel permeation chromatography (GPC) and $\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$ and $\text{Pd}_2(\text{dibenzylideneacetone})_3$ catalysts function better than commonly used zinc octanoate and other catalysts as determined by ^{29}Si NMR [32].

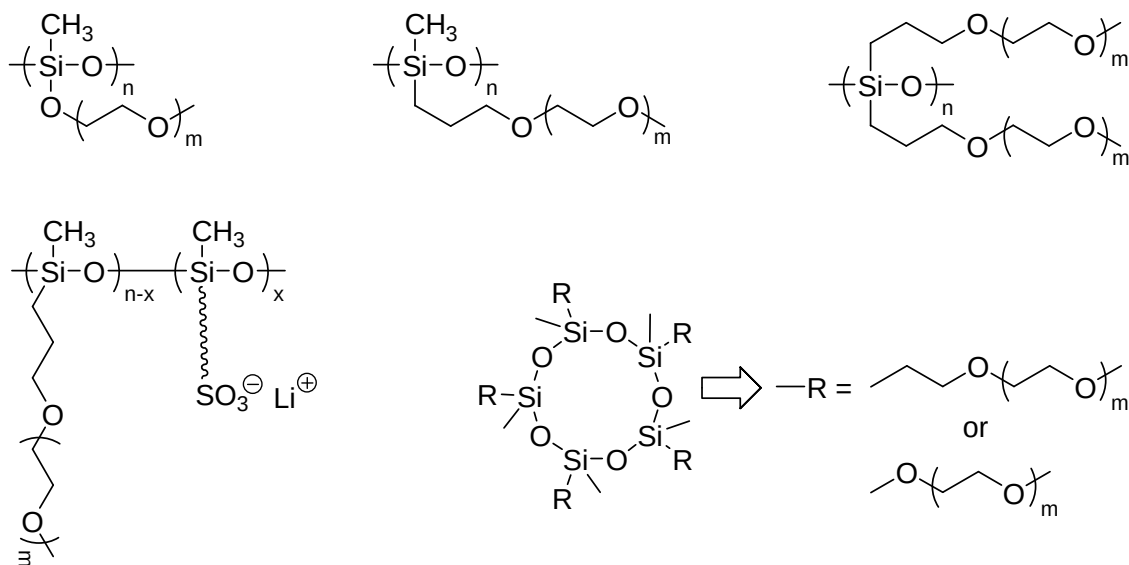


Fig. 2.2 Some polysiloxane structures investigated as polymer electrolytes [24-58].

Nevertheless, the susceptibility of Si-O-C bond as mentioned above revealed the necessity of new functionalization techniques. The hydrosilylation in the presence of platinum catalyst, which was used long time back for the preparation of polysiloxane elastomers [71, 72], the synthesis of a comb polysiloxane with well defined structure was not synthesized until 1988 [29]. Comb like polysiloxanes, poly{[ω -methoxyoligo(oxyethylene)propyl]siloxane}s, were prepared by reacting PMHS with different allyl ethers $\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{CH}_3$, where $n = 2, 7, 9$, and 12 [29, 33, 34]. Ionic conductivities of LiClO_4 complexes appeared to be similar to that of polysiloxanes prepared by dehydrocoupling reactions.

West and co-workers on the other hand synthesized and characterized a series of double comb polysiloxanes, two oligoether side chains per silicon, by hydrosilylation of dichlorosilane with allyl ethers, followed by rapid polycondensation in the presence of triethylamine [35-37]. The effect of oligoether ($n = 1$ to 7) length [35, 36], as well as branching and crown ether [37] on the electronic properties were extensively studied. The optimum reported conductivity of $3 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ implies that consequential change in the conductivity from mono comb to double comb is negligible.

A similar strategy was applied by Zhou [38, 39] to synthesize polysiloxane polyelectrolyte, i.e. the anion is incorporated to the polymer and immobilized. A percentage of allyl ether was replaced by epoxy containing side chain. The epoxy ring

then reacted with $\text{Na}_2\text{S}_2\text{O}_5$ to give sulfonate end group, and the other counterions were synthesized by ion exchange. Increasing the sulfonate content from 0 to 70 % produced materials with properties ranging from liquid to waxes to solid and the conductivity increase in the order of $\text{Li} < \text{Na} < \text{K} < \text{Cs}$. Shriver reported the synthesis of single Li^+ ion conducting trifluoromethylsulfonamide [40] and fluorinated sulfonate [41, 42] derivatives of comparable structures. The ionic conductivity values in the order of $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ were reported for each.

Many of these systems explained up to here, however, suffers from the poor dimensional stability. Such materials, which flow even under very mild pressure at room temperature, cannot be used as separator membranes for electrochemical applications. Recently, synthesis and conductivity studies were published for mono mono-comb polysiloxane cross-linked by α,ω -diallyl poly(ethylene glycol) with $n = 13$. The conductivity value of $1.3 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ for optimum doping level of $(\text{LiN}(\text{SO}_2\text{CF}_3)_2)$ were reported [43, 44]. Moreover, Kang [45] reported the radical crosslinking of the acrylate end-capped mono comb polysiloxanes, where the highest conductivity were measured to be $5.8 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$.

Recent efforts, moreover, focus on the synthesis of linear [46-51] or cyclic [46, 52-56] liquid i.e. very low molecular weight polymer electrolytes due to the fact that the ionic conductivity will increase as the glass transition temperature (T_g) and the viscosity of the polymer decreases. Both dehydrocoupling [46-50, 56] and platinum catalyst hydrosilylation [46-49, 54-56] reactions were employed for the synthesis. The linear liquid electrolytes provided higher conductivity than its cyclic counterparts [56]. Among all, {[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]methyl} trimethylsilane imparted a very high conductivity value of $1.3 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 25°C as reported for lithium bis(oxalate)borate as salt.

2.4.4 Gel Electrolytes.

In spite of large efforts devoted to increase the ionic conductivity of polymer electrolytes, the optimum conductivity value usually lies in the order of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which is still smaller than the minimum conductivity value ($10^{-3} \text{ S}\cdot\text{cm}^{-1}$) expected for the practical applications. Therefore a compromise is chosen for engineering purposes to entrap organic solvents, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) or their mixture, in polar polymer matrix. The strategy here is different from

solvent free polymer electrolytes. The direct crosslinking of the polymers maintain the mechanical stability with at least one order of magnitude sacrifice in the conductivity values due to decreased segmental mobility and free volume of the polymer. In gel electrolytes, however, the polymer host principally ensures the mechanical strength, in which the solvents have more freedom to maintain the ionic conductivity. Thus high conductivity values in this case are not surprising. The most commonly used polymers for this purpose are poly(vinylidene fluoride) [82, 83], poly(vinylidene fluoride-co-hexafluoropropylene) [84, 85], poly(acrylonitrile) [86, 87], and poly(methyl methacrylate) [88]. Owing to its weak structure, the application of polysiloxanes in this area is scarce. The crosslinked, acrylate end-capped comb polysiloxane was an example for the application as gel-electrolyte, where the maximum conductivity of $3.9 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 30°C was reported for 70 % EC/PC (1:1) containing electrolyte [57]. Using the same concept, the concept of polymer electrolyte alloy was introduced by Noda [58]. In place of the common solvents here low molecular weight comb polysiloxanes that was kept in a low conducting but high mechanical strength network were used. Comparable conductivity values to solvent free polymer electrolytes ($10^{-4} \text{ S}\cdot\text{cm}^{-1}$) were reported.

2.4.5 Research Motivation

Lithium ion conducting polymer electrolytes have attracted widespread attention owing to their enormous potential electrochemical devices. PEO is undoubtedly the best solvating medium for a variety of salts, however the degree of crystallinity that melts first above 60°C yielding reasonable conductivities limits their ambient temperature applications. Obviously this constraint for the application of PEOs directed the research interest for the design of new polymer architectures having enough local relaxations and segmental motion.

Recognizing the fact that ionic transport extensively takes place in the amorphous region of matrix, numerous polymer structure have been designed incorporating poly(ethylene oxide) oligomers into a high molecular weight polymer structure either as copolymer units or side chains, where they can act as solvent for the salt in an amorphous medium. Comb like polysiloxanes are one of the best polymers satisfying the structural requirements as polymer electrolytes owing to their extremely low glass transition temperatures and high flexibility.

The presently available solvent free polymer electrolytes have lots of drawbacks and are far from ideal, which leaves much room for research activities, thus is a source of aspirations as well as numerous exciting challenges for the design and development of new polymer systems. One of the motivations for the present work was the quest for developing an ideal polymer electrolyte based on polysiloxane backbone. For this purpose, new ion conducting salt-in-polymer electrolytes were synthesized and characterized. The primary aim was to design and fine tune the conductivity and physical properties of the materials obtained by substituting different side chains. The efforts made to establish structure-property relationship for the polysiloxane based polymer electrolytes here could certainly provide some hints and perspective for the future researchers in this area.

The thesis continues with **Chapter 3** outlining a concise summary of the basis of experimental techniques used for the investigation of the polymers as well as the synthetic procedures for the preparation of all polysiloxanes and polyphosphazenes investigated throughout this study. **Chapter 4** onwards concentrates on the results and discussion of the synthesized polymers and their characterization as salt-in-polymer electrolytes. The comb polysiloxane with oligoether side chains is investigated in **Chapter 4.1**. The study focuses in **Chapter 4.2** on the optimization of crosslinker ratio for the sol-gel crosslinking of the polymer, which is accompanied by the comparison of different catalysts used for this purpose. **Chapter 4.3** and **4.4** focus entirely on the effect of long oligoether and oligopropyleneoxide respectively on the physical and electrical properties of the electrolytes. Composite polymer electrolytes doped with nano sized SiO_2 and Al_2O_3 are explained in **Chapter 4.5** as well as the effect of low molecular weight borate esters (B2 and B3). **Chapter 4.6** deals with the Small Angle Neutron Scattering (SANS) experiment of model polyphosphazene polymer. In **Chapter 4.7**, the synthesis and implementation of polyphosphazene as polyelectrolyte multilayer is explained. Finally, **Chapter 5** includes summary and general conclusions from the research carried out on the polymer electrolyte systems and hints for the future developments that can be done.

3 EXPERIMENTAL

3.1 Solvents and Reagents

The reagent quality solvents and reagents, purchased from the chemical companies were, unless otherwise noted, used directly without further purifications. Poly(methylhydrosiloxane), poly(ethylene glycol) 350 monomethyl ether and other alcohols were kept under an atmosphere of dry nitrogen over molecular sieves.

The common solvents were purified using standard procedure. All reactions and manipulations were carried out under an atmosphere of dry nitrogen gas and using standard vacuum-line Schlenk techniques. The chemicals used throughout this study were listed in Appendix 1.

The chemical, thermal and electrical properties of the synthesized materials and the polymer electrolytes are fully investigated using the instrumental techniques, which are explained in detail in the following section.

3.2 Instrumental Techniques

3.2.1 Electrochemical Impedance Spectroscopy (EIS)

Practically each liquid and solid is able to conduct current when a voltage is applied to it. When an ac voltage in a sinusoidal form of:

$$U(t) = U_0 \cos(\omega t) \quad [3.2.1]$$

where U_0 is the amplitude at time t , ω is the radial frequency (related to the frequency ν (in Hz) by $\omega = 2\pi\nu$), the resulting current response will be again measured as:

$$I(t) = I_0 \cos(\omega t + \varphi) \quad [3.2.2]$$

where, $I(t)$ is the current at time t , $I_0(t)$ is the current amplitude at time t and φ is the phase shift in radians as seen in **Fig. 3.1**. The waves are not only different in amplitude but also shifted in time. An expression analogous to Ohm's Law can be used to express the impedance of the system as:

$$Z(t) = \frac{U(t)}{I(t)} = \frac{U_0 \cos(\omega t)}{I_0 \cos(\omega t + \varphi)} = |Z| \frac{\cos(\omega t)}{\cos(\omega t + \varphi)} \quad [3.2.3]$$

where Z_0 is the absolute impedance.

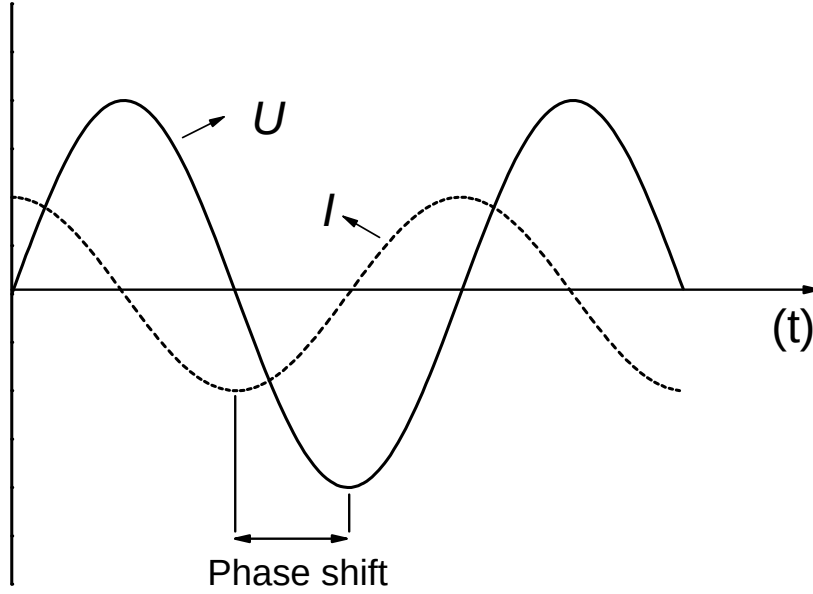


Fig. 3.1 AC waveforms for an Applied Voltage (U) and a Resulting Current (I).

However, impedance is usually expressed as a complex function, $Z = Z' + jZ''$. Using Eulers relationship, the applied voltage and current response can be written as:

$$U(t) = \exp(j\omega t) \quad \text{and} \quad I(t) = \exp(j\omega t + \varphi) \quad [3.2.4]$$

The impedance is then represented as a complex number:

$$Z = \frac{U(t)}{I(t)} = |Z| (\cos \varphi + j \sin \varphi) = |Z| \exp(-j\varphi) \quad [3.2.5]$$

where $Z_0 \cos \varphi$ represents the real part ($\text{Re}(Z) = Z'$) of the impedance and $Z_0 \sin \varphi$ is the imaginary part ($\text{Im}(Z) = Z''$). Note that, this complex quantity is only real when phase angle is zero, that is, pure resistive behavior which is independent from frequency. In the equation, $|Z|$ is the magnitude or modulus of total impedance, which can be calculated as:

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad [3.2.6]$$

with the phase angle:

$$\varphi = \tan^{-1}(Z''/Z') \quad [3.2.7]$$

At the end of a typical impedance measurement, the raw data at each measured frequency consists of real and imaginary part of both applied voltage and the current response. **Nyquist Plot** is one of the most commonly used formats to represent these data, where it was produced by plotting the imaginary impedance component (Z'') against the real one (Z') at each excitation frequency (**Fig. 3.2**). Although, this format makes it easy to monitor the effects of ohmic resistance in addition to the comfortable comparison of the results between two different experiments, it has some disadvantages. The major shortcoming is that the frequency does not appear explicitly; therefore the electrode capacitance cannot be calculated directly.

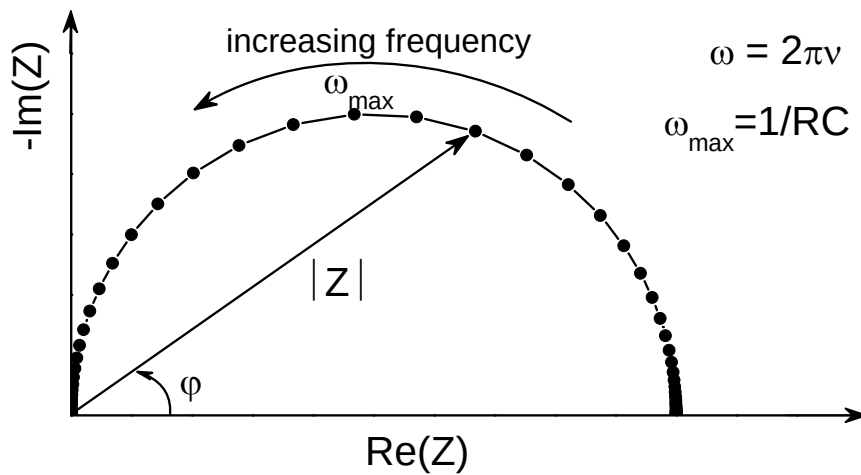


Fig. 3.2 Nyquist Plot of a resistor in parallel to a capacitor.

Another popular data presentation method is the **Bode Plot**. The impedance is plotted against the logarithm of the frequency on the x-axis, and both the absolute impedance and phase shift on both sides of the y-axis (**Fig. 3.3**). The superiority of Bode Plot comes from that the frequency appears as one of the axes; therefore, it is easy to follow the impedance changes as a function of frequency over a wide range on logarithmic scale. Moreover, the phase angle, φ , which appears on the right hand side of the figure, indicates the ohmic

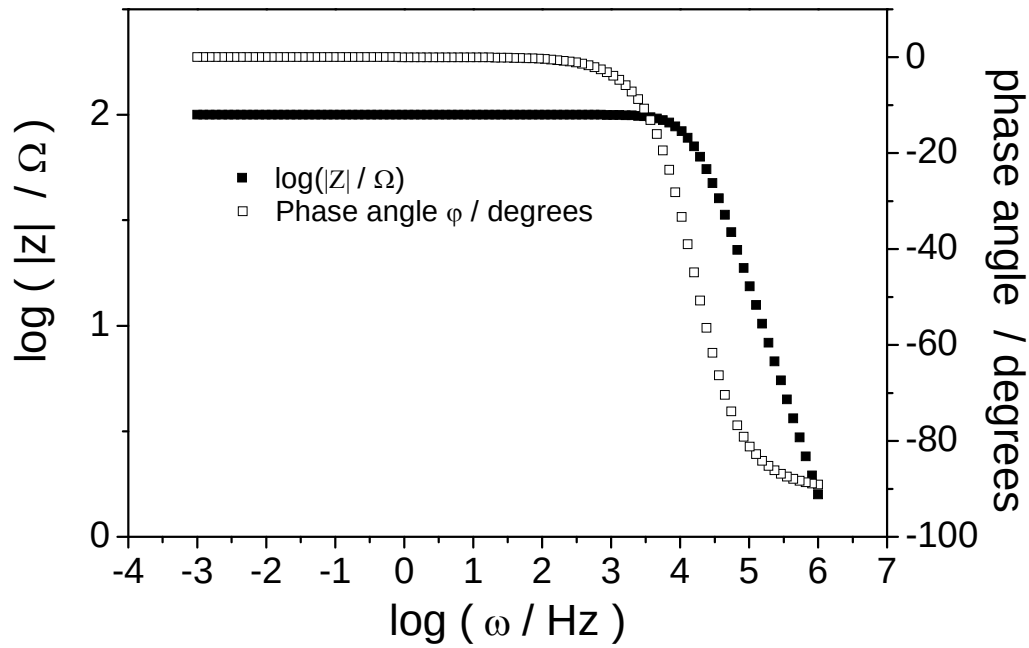
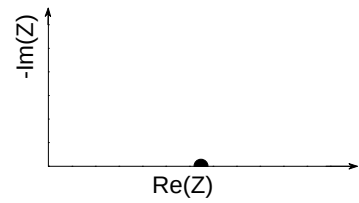
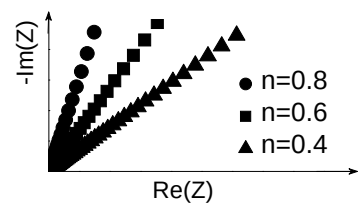
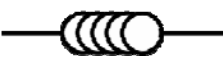
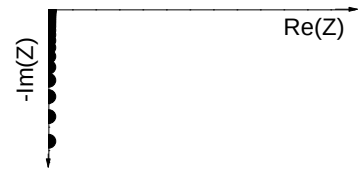
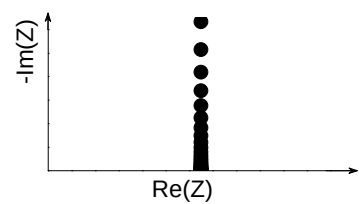
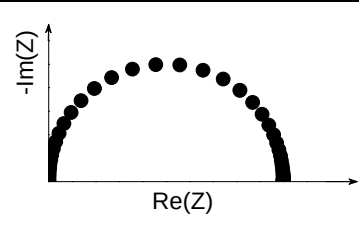
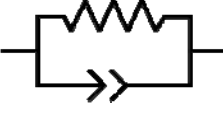
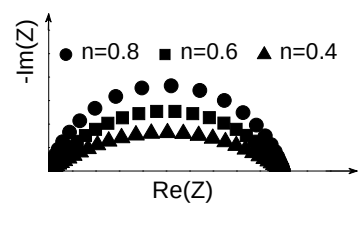


Fig. 3.3 Bode Plot of a resistor in parallel to a capacitor.

behavior if its value approaches to zero or imaginary component can be determined as well if the phase angle increases, which corresponds to a pure capacitive behavior if the slope is -1.

The equivalent circuits are important in the sense that they are mimicking the behavior of a system. These circuits are formulated by a series or parallel combinations of individual circuit elements which are shown with their impedance equations and representative Nyquist Plots in **Table 3.1**. The impedance of a **resistor** has no imaginary component at all. Since there is no imaginary component, the current through a resistor is always in phase with the voltage and the impedance is independent from the frequency (see the Nyquist Plot in the Table). Conversely, the impedance of a **capacitor** and an **inductor** has no real component, and therefore, completely imaginary. The current in a capacitor is always -90 degrees shifted with respect to the voltage. Moreover, inverse relationship between the impedance of a capacitor and the frequency makes it to act as a short circuit at high frequencies. At low frequencies (approaching dc), accordingly, a capacitor act as an open circuit and impedance tends toward infinity. The impedance versus frequency behavior of an **inductor** is opposite to that of a capacitor. The current is always 90 degrees out of phase with the voltage applied. It acts as short circuit at low frequencies and

Table 3.1 Common electrical elements with their impedance equations and representative Nyquist Plots.

Circuit Element	Impedance Equation	Nyquist Plot
Resistor (R) 	$Z = R + 0j$	
Capacitor (C) 	$Z = 0 - \frac{1}{\omega C} j$	
Constant Phase Element (CPE) 	$Z = 0 + \frac{1}{T(j\omega)^n}$ $0 \leq n \leq 1$	
Inductor (L) 	$Z = 0 + j\omega L$	
R and C in series 	$Z = R - \frac{1}{\omega C} j$	
R and C in parallel 	$Z = \frac{R}{1 + \omega^2 C^2 R^2} - \frac{j\omega C R^2}{1 + \omega^2 C^2 R^2}$	
R and CPE in parallel 	$Z = \frac{R}{1 - (-1)^n \omega^{2n} T^2 R^2} - \frac{(j\omega)^n T R^2}{1 - (-1)^n \omega^{2n} T^2 R^2}$	

impedance increases with increasing frequency.

Capacitors, on the other hand, do not behave ideally in real systems and usually represented with the empirical **Constant Phase Element (CPE)**. Its mathematical expression and typical Nyquist Plots for different n values are given in the Table below. The parameter n can take any value between 0 and 1. When $n=1$, the equation becomes same as for an ideal capacitor with $C=T$. And for $n=0$, it gives an expression for a resistor with $R=1/T$.

The real systems however can not be usually represented by a simple electrical element. Therefore, a combination of the simple elements is required to represent the real systems, which are done by simple rules. For the circuit elements in series, the equivalent impedance is simply calculated by vector sum of the individual impedance values:

$$Z_{eq} = Z_1 + Z_2 + Z_3 + \dots + Z_n \quad [3.2.8]$$

In a complex representation, the real parts must be added together to form the real component and the imaginary parts must be added together to make up the imaginary component:

$$Z_{eq} = (Z'_1 + Z'_2 + Z'_3 + \dots + Z'_n) + j(Z''_1 + Z''_2 + Z''_3 + \dots + Z''_n) \quad [3.2.9]$$

The total impedance of a simple system comprised of a resistor and a capacitor and its Nyquist Plot is shown in **Table 3.1**.

For circuit elements in parallel, the equivalent impedance can be calculated as follows:

$$\frac{1}{Z_{eq}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3} + \dots + \frac{1}{Z_n} \quad [3.2.10]$$

The impedance data once collected were fitted with equivalent circuit models consisting of the electrical components explained above connected in series and parallel to each other. To obtain the mathematical values of the circuit elements a Complex Non-Linear Least Square (CNLS) fitting technique was utilized. This is usually a non-linear fit of real and imaginary part or the magnitude and the phase angle of the experimental impedance data.

The impedance spectra were recorded using a Solarton SI 1260 frequency analyzer and a Solarton SI 1287 electrochemical interface in a frequency range from 10^6 to 10^{-1} Hz or PAR 283 potentiostat in a frequency range from 6.5×10^{-5} to 10^{-1} Hz, which was connected with a ThermoHaake Phoenix II heating circulator water bath. Some of the measurements

were performed using Novocontrol Alpha High Resolution Dielectric Analyzer integrated with Quatro Cryosystem in a frequency range from 3×10^6 to 10^{-2} Hz.

The membranes were sandwiched between two stainless steel or platinum electrodes (1 cm^2 each) under an inert atmosphere of nitrogen and the conductivity measurement was done. The noncrosslinked polymer electrolytes were measured in between stainless steel electrodes separated by Teflon ring with a diameter of 16.8 mm and thickness of 1 mm.

The plateau on the Bode diagram, where the phase angle approaches to zero, was taken as the bulk resistance of a system. This plateau was usually observed in the mid frequency region (10 - 10^3 Hz). The ionic conductivity (σ) was then calculated as follows:

$$\sigma = \frac{1}{R} \cdot \frac{l}{A} \quad [3.2.11]$$

where, R is the ohmic resistance, l is the thickness of the sample and A is the area of the sample. The quantity l/A is called cell constant. The conductivity values for the samples are given as tables in Appendix 4.

3.2.2 Nuclear Magnetic Resonance (NMR)

^1H , ^{13}C and ^{31}P spectrum were recorded on a Bruker AC 200, Bruker ARX300 and a Varian Mercury 400 Plus spectrometer. For measuring the proton and carbon spectra, Tetramethylsilane ($\text{TMS}-(\text{CH}_3)_4\text{Si}$) was used as a reference. For the ^{31}P spectra 85 % H_3PO_4 was used as reference. All the spectra were measured in suitable deuterated solvents (CDCl_3 , D_2O). The spectra were processed and evaluated using MestRec[®] software.

3.2.3 Fourier Transform – Infrared Spectroscopy (FT-IR)

All the polymers and polymer electrolytes were characterized by FT-IR by pressing between KBr pellets in the range 4000 and 400 cm^{-1} . A Bruker IFS 113v IR-Spectrometer and a Shimadzu IRPrestige-21 were used.

3.2.4 Differential Scanning Calorimetry (DSC)

The thermal characterization of the polymer and polymer electrolytes was done using Differential Scanning Calorimetry (DSC). The Glass Transition Temperature (T_g) and Crystalline Melting Temperature (T_m) were determined using a Netzsch DSC 204

instrument at a heating rate of 10 K min^{-1} . All the samples were subjected to three cycles of heating and cooling $[-150^{\circ}\text{C}$ to $+150^{\circ}\text{C}]$ to certify the absence of a thermal hysteresis effect.

3.2.5 CHN – Elemental Analysis

A VARIO EL III CHN analyzer was used to determine the elemental C, H and N in the synthesized polyphosphazenes.

3.2.6 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC), also known as Size Exclusion Chromatography (SEC), is a technique used to determine the average molecular weight distribution of a polymer sample. Using the appropriate detectors and analysis procedure it is also possible to obtain qualitative information on long chain branching or determine the composition distribution of copolymers.

As the name implies, GPC or SEC separates the polymer according to size or hydrodynamic radius. This is accomplished by injecting a small amount of polymer solution (0.01-0.6 %) into a set of columns that are packed with porous beads (typically silica or crosslinked polystyrene) having pore size in μm range and the mobile phase as common organic solvent (e.g. THF), which also dissolves the polymer to be analyzed. The mobile phase along with the sample polymer solution is forced through the column at typical rates of 1 ml/min and under pressure of 50-200 bars by an isocratic pump. Smaller molecules can penetrate the pores and are therefore retained to a greater extent than the larger molecules which continue down the columns and elute faster.

One or more detectors can be attached to the output of the columns. For routine analysis of linear homopolymers, this is most often a Differential Refractive Index (DRI) or a UV detector. For branched or copolymers, however, it is necessary to have at least two sequential detectors to determine molecular weight accurately. Branched polymers can be analyzed using a DRI detector coupled with a “molecular weight sensitive” detector such as an on-line viscometer (VIS) or a low-angle laser light scattering (LALLS) detector

The Agilent 110 isocratic pump and RI detector(η -1001 Viscosimeter WGE Dr Bures) were equipped with two PSS-SDV linear XL columns ($8 \times 300\text{ mm}$, 5μ) from Polymer Standards Service (PSS, Mainz) and calibrated with polystyrene standards (ReadyCal,

PSS, Mainz). The measurements were recorded using PSS WINGPC 6 (PSS; Mainz) software.

The actual experimental conditions employed for the GPC analysis done for this thesis are given below

Flow rate : 0.8 ml / min

Pressure : 80 bar

Mobile phase : THF with 0.1 wt-% tetra-n-butyl ammonium bromide [89]

Concentration of the polymer in solvent : 4 mg / ml

3.3 Synthesis of Functionalized Polysiloxanes

The main aim of this part is to synthesize and develop new polymer electrolytes, which are capable of dissolving (especially lithium) salts, and therefore can be used as separator and ion conductors in between the electrodes. Having a very flexible backbone and completely amorphous structure, polysiloxanes, as well polyphosphazenes, match the main requirement to serve as solvent free salt-in-polymer electrolytes, once they are properly substituted with heteroatom containing (i.e. O, N, S) side chains in order to maintain the solvation of the cation (hard acid in case of Li^+) via acid-base type interaction with the basic sites (heteroatoms).

This part of the thesis involves largely the synthesis of the series of polysiloxanes as polymer electrolytes. The most extensively investigated poly(ethylene oxide) and poly(propylene oxide) in polymer electrolyte studies are used to prepare the substituted polysiloxanes. The first two polymer systems (OPS and TOPS) reported here consist of short oligo-ethyleneoxy side chain functionalized polysiloxanes, which is followed by long oligo-ethyleneoxy substituted polysiloxane (L-TOPS). Subsequently the synthesis of the polysiloxane with oligo-propyleneoxy as side chain is reported. The rationale behind the synthesis of these materials is discussed in the results and discussions chapter.

One of the most commonly used method for the preparation of comb polysiloxanes is to functionalize the commercially available poly(methylhydrosiloxane) (PMHS) with allyl or vinyl functionalized side groups via transition metal catalyzed hydrosilylation reaction [71, 72], which involves the addition of a Si-H unit on the polysiloxane to a carbon-carbon double bond under relatively mild conditions (**Scheme 3.1**). Since the platinum catalysts

are the most frequently applied catalysts for this purpose due to their high efficiency and tolerance to a variety of functional groups and also low danger for side reactions [73-77], Karstedt's catalyst [73, 74] will be employed as a tool for the functionalization of PMHS via hydrosilylation.

3.3.1 Oligoether Substituted Polysiloxane (OPS) (3)

Allyl functionalized oligoether (**2**) was prepared from the reaction of sodium salt of 2-(allyloxy)ethanol with the synthesized 2-(2-(2-methoxyethoxy)ethoxy)ethoxy p-toluenesulfonate (**1**) at room temperature as shown in **Scheme A.3.1** and isolated by vacuum distillation. The detailed description for the synthesis of compound (**1**) and (**2**) can be found in Appendix 3.

Platinum catalyzed functionalization of PMHS via hydrosilylation to synthesize OPS (**3**) was achieved at 75 °C in toluene (**Scheme 3.1**). Since the hydrosilylation by Karstedt's catalyst suffers from the reduction of compound (**2**) in addition to the formation of *cis* and *trans* isomers in the course of the synthesis, an excess of oligoether was used in order to guarantee the complete reaction of Si-H groups on the polysiloxane main chain. The reaction was monitored by ^1H NMR until no more Si-H signal can be detected (**Fig. 3.4**). After the reaction was complete, OPS (**3**) was isolated by precipitation into pentane. The details of the synthesis are given in Appendix 3.

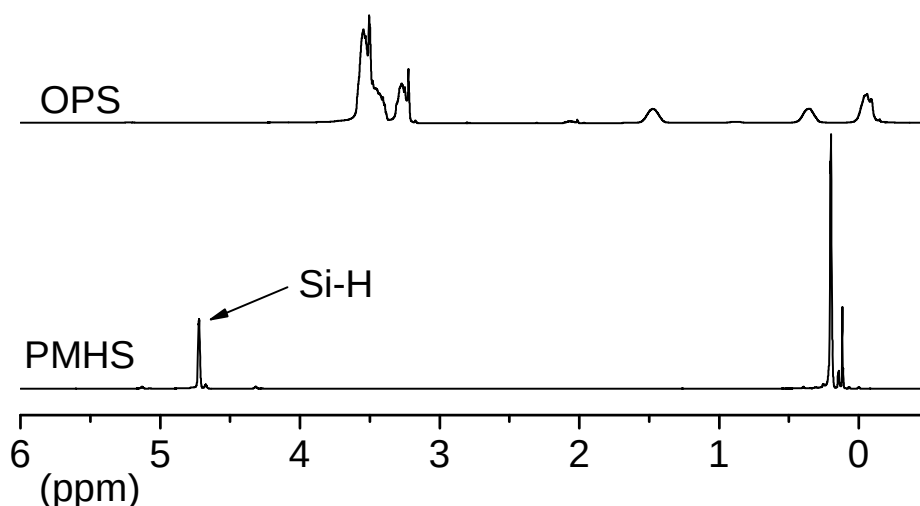


Fig. 3.4 ^1H NMR spectra of PMHS and OPS.

3.3.2 Allyltrimethoxysilane and Oligoether co-Substituted Polysiloxane (T_x OPS) (4)

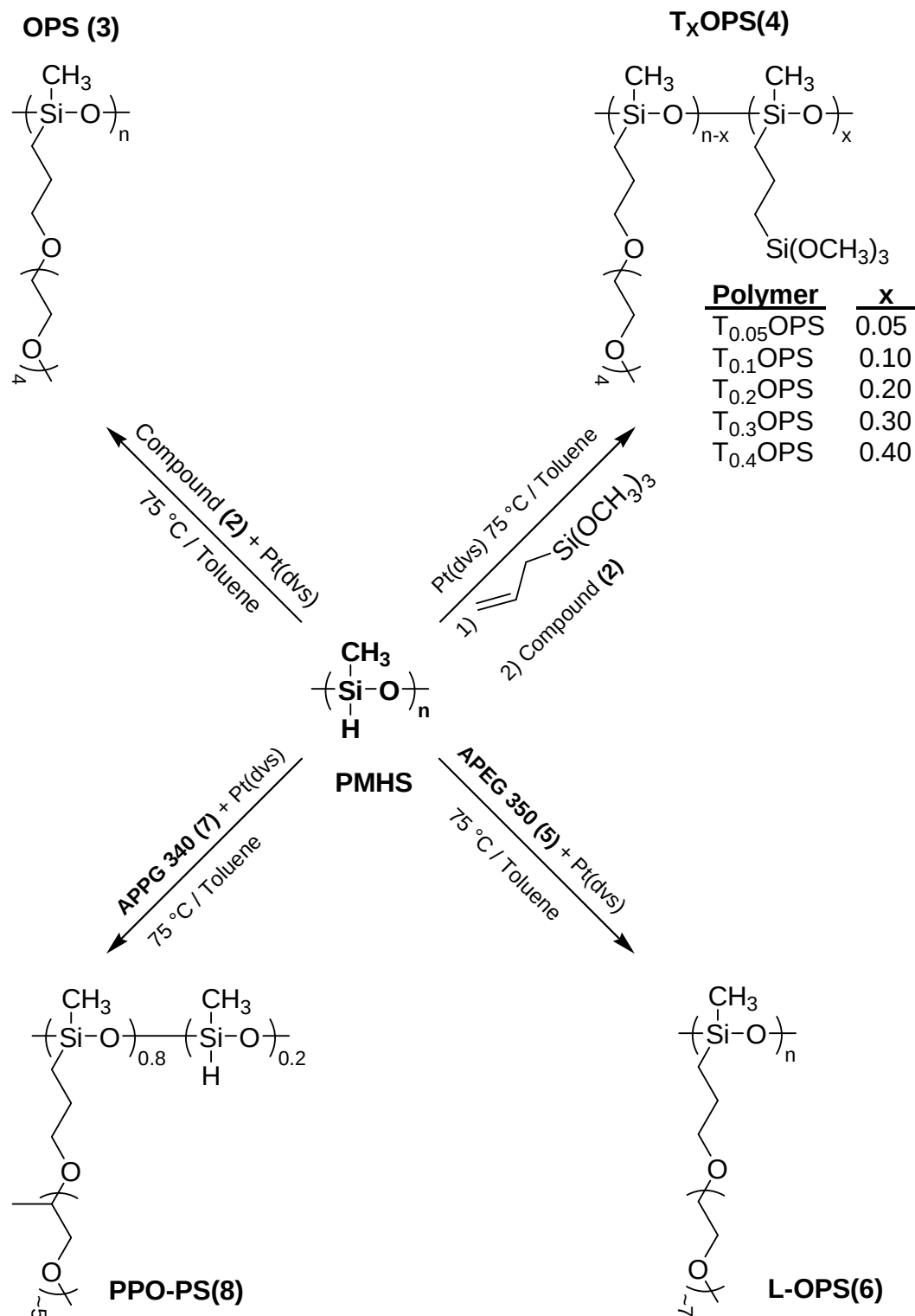
The same oligoether (**2**) was used together with allyltrimethoxysilane (ATMS) for the synthesis of T_x OPS precursor polymers from random substitution of PMHS. A series of polysiloxanes, where x/n ratio varies from 0.05 to 0.40 as shown in **Scheme 3.1**, have been synthesized in order to find the optimum polymer, which can later serve as the best host for the ion transfer with optimum cross-linking density to have mechanically stable membranes.

Hydrosilylation of the polymers were achieved in a similar manner to OPS (**3**) polymer, PMHS was first randomly substituted with the required amount of ATMS in toluene at 75 °C. The disappearance of allylic protons was monitored by ^1H NMR, which usually took 2 to 6 hours depending on the ATMS concentration. The substitution was forced to completion by the addition of excess oligoether (**2**) and reaction continued until all Si–H groups were substituted. The detailed procedures and characterization of each polymer are given in Appendix 3.

3.3.3 Longer Oligoether Substituted Polysiloxane(L-OPS) (6)

In order to investigate the effect of long chain oligoether on the electrical properties as polymer electrolytes, PMHS was also substituted with allyl functionalized poly(ethylene glycol) 350 monomethyl ether (APEG 350) (**5**), which was readily synthesized from commercially available poly(ethylene glycol) 350 monomethyl ether and allyl bromide (Appendix 3).

The similar procedure (Pt catalyst at 75 °C in toluene) for the full functionalization of Si–H groups was also considered for the synthesis of L-OPS (**6**) polymer (**Scheme 3.1**). Due to the relative bulkiness of the APEG 350, however, more excess of this material together with catalyst were required to bring the reaction to the end. After the hydrosilylation was complete (determined by ^1H NMR), L-OPS polymer was purified and isolated as explained in Appendix 3.



Scheme 3.1 Synthesis of oligo-ethyleneoxy and oligo-propyleneoxy substituted polysiloxane based polymer electrolytes.

3.3.4 Poly(propylene oxide) Substituted Polysiloxane (PPO-PS) (8)

Since the poly(propylene oxide)s are one of the most extensively studied polymers in polymer electrolyte area after poly(ethylene oxide)s, it was also integrated as an example of polymer electrolyte system into the topic in order to have more complete overview among the whole synthesized polysiloxanes.

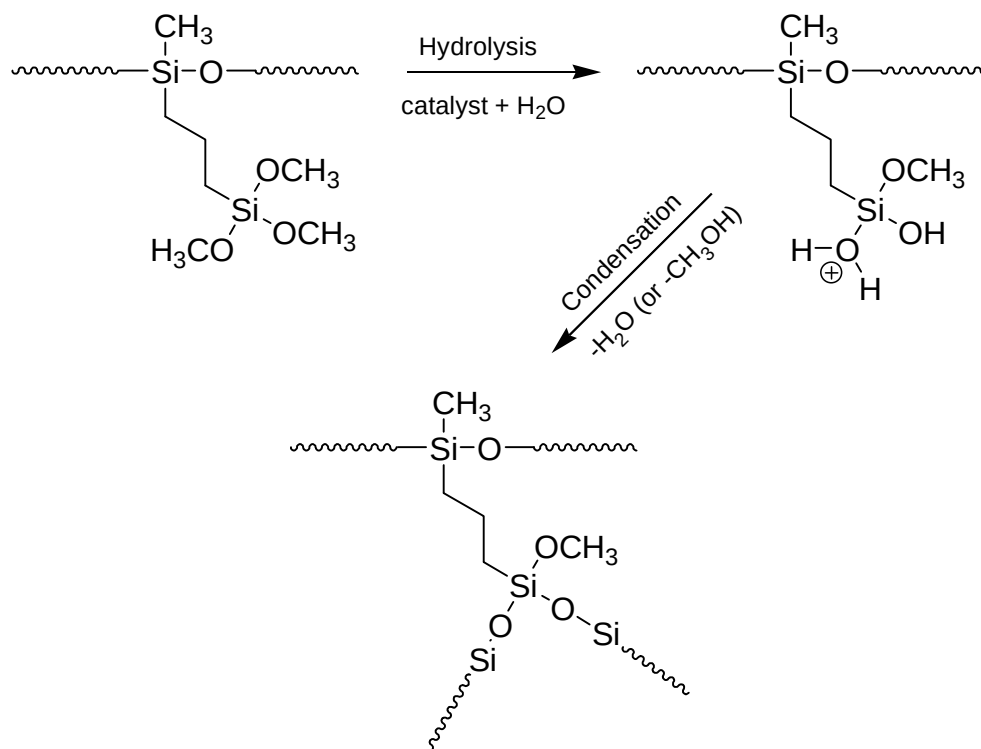
The synthesis of PPO-PS was achieved in an analogous manner to the other polysiloxanes explained above by substitution of PMHS using allyl functionalized poly(propylene glycol) monobutyl ether (APPG 340) (**7**) with a number average molecular weight of 340 (see Appendix 3 for the synthesis of side chain).

The substitution of PMHS in this case, however, was not as easy as the others. The substitution could not be brought to the completion even in the presence of excess of (**7**) and catalyst. The longer reaction time did not also change the substitution pattern. Therefore the reaction was performed in 1:1 ratio of PMHS:(**7**) at 75 in toluene, which resulted in 80 % functionalization, and then the polymer was isolated (Appendix 3).

3.3.5 Preparation of Polysiloxane Based Polymer Electrolytes

The synthesized polysiloxane based precursor polymers were used to prepare salt-in-polymer electrolytes in order to investigate the electrical properties. For this purpose the polymers were doped with lithium salt in varying concentrations (the salt concentrations will be expressed in terms of weight-%, unless otherwise is stated).

The trimethoxysilane moiety, which was randomly substituted to the polysiloxane backbone, was used to cross-link the polymers. The acid catalyzed sol-gel process was the well known tool used for this purpose, where the alkoxide groups are first protonated as a rapid step, then followed by the nucleophilic attack by water to form silanols. Then, the siloxane bridges were formed between the chains by either alcohol producing or water producing condensation resulting in dimensionally stable polymer electrolyte membranes (**Scheme 3.2**).



Scheme 3.2 Schematic representation of acid catalyzed sol-gel cross-linking.

PTFE or polypropylene molds were used to prepare the membranes since they are not sticky and inert to the polymers. The solvent has also crucial importance on the preparation of good quality of membranes. First of all it should dissolve all the components involved at the beginning or produced during the cross-linking process to maintain the homogeneity of the system. Moreover the boiling point of the solvent used for solution-casting should be neither too low nor too high leading to the formation of bubbles, difficulty for complete removal or semicrystalline precipitates at the end. The good solvents having the boiling points between 60 °C to 100°C are the most convenient ones.

Noncross-linked polymer electrolytes based on OPS or T_xOPS were prepared simply mixing polymer with desired amount of salt in THF and drying this homogeneous mixture under vacuum to dryness.

Polymer electrolytes from both T_xOPS and L-OPS polymers were prepared using solution-casting technique. In the general procedure, the precursor polymer was dissolved in THF and catalytic amount of acid was added to initiate the sol-gel process. Appropriate amount of salt in THF was added and homogeneous mixture was further stirred. The

mixture then poured onto the platinum electrodes, placed into a Teflon mould. The solvent was allowed to evaporate slowly over night, followed by drying in an oven at 75 °C for 3 days and at 100 °C for one hour. Homogeneous and transparent films with average thickness around 150-200 μm were obtained in this way. These films were insoluble in all solvents; only swollen in THF.

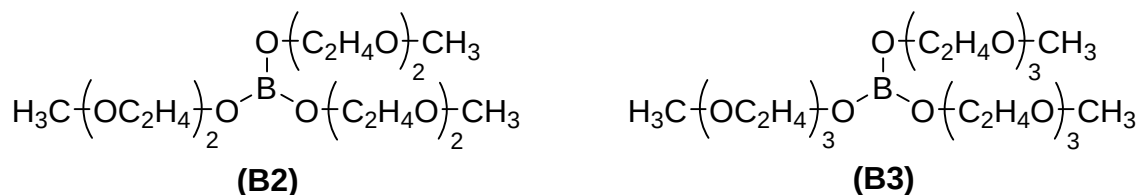
L-OPS based polymer electrolytes were cross-linked using one of the T_xOPS polymers as a matrix since the cross-linking of the very short trimethoxysilane moiety near the very long oligoether side chains was not successful.

The cross-linking of PPO-PS, on the other hand, was performed making use of the unreacted Si-H groups on the main chain. In a typical preparation, PPO-PS solution in THF was mixed with an excess of α , ω -diallyl poly(ethylene glycol) (**9**) with 13 repeating ethylene oxide units [43]. The required amount of lithium salt was added and hydrosilylation was initiated by means of platinum catalyst. The reaction was continued at 60 °C overnight and then polymer was casted directly on the electrodes in Teflon mold. Transparent films were obtained after drying in oven at 75 °C for two days and at 100 °C for one hour.

Cross-linking of the T_xOPS polymers were also tried using another more efficient catalyst, namely Dibutyltin dilaurate (DBTL), in order to further increase the cross-linking efficiency and dimensional stability of the prepared membranes [90, 91]. The curing of the polymer electrolytes was carried out in bulk using the atmospheric moisture as co-catalyst. In this new method, the polymer and the required amount of salt were dissolved in THF. DBTL was then added to the mixture, where the ratio of catalyst to the number of trimethoxysilane moiety was kept as 0.25 for all cases, followed by pouring the homogeneous mixture into polypropylene mould. THF was subsequently removed to dryness and then the polymer electrolytes were cured at 40°C over 2 days. The membranes obtained in this way were 100-150 μm .

In addition to the electrolytes prepared up to now, some more systems were prepared in order to investigate the effect of nano particles and plasticizers on the properties of polymer electrolytes. Commercially available Al₂O₃ and SiO₂ were used as nano particles. Tris(oxaalkyl)borates (as shown in **Scheme 3.3**) were synthesized [92] and used as low molecular weight solvents for lithium salt in the polymer electrolytes. DBTL cross-linked polymer electrolytes were used as model systems to investigate these effects. Polymer

electrolytes were prepared similarly as explained above, but only the particles and borates were mixed before the addition of DBTL.



Scheme 3.3 Chemical structures of tris(oxaalkyl)borates (B2 and B3).

Thermal, chemical and electrical properties of the prepared polymer electrolytes were then investigated. The membranes were stored in a dessicator over Sicapent® to avoid moisture.

The detailed descriptions for the synthesis of the compounds and the preparation of the polymer electrolytes are given in Appendix 3.

3.4 Synthesis of Polyphosphazenes

In this part of the study, polyphosphazene based polymers were synthesized and substituted. Trichloro(trimethyl)phosphoranimine (**12**) was used to synthesize poly(dichlorophosphazene) (**13**), as shown in **Fig. 3.5**, as a precursor polymer and used for further substitution by a proper side chain.

Although only a few backbone architecture are possible for the polyphosphazenes, they comprise the largest class of the inorganic polymers due their ease of substitution by a wide variety of nucleophiles. Therefore the synthesis of this polymer has attracted a great interest of numerous investigators over last decades. The most common synthetic routes are summarized in **Table 3.2**.

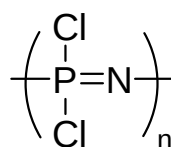


Fig. 3.5 Poly(dichlorophosphazene) (**13**)

Table 3.2 Various synthetic routes to the synthesis of poly(dichlorophosphazene);
MW =Molecular weight, PDI = Polydispersity index.

Synthetic route	Developed by	Reaction	Remarks
Thermal ring opening polymerization	Allcock [93-95]	$\text{N}_3\text{P}_3\text{Cl}_6 \xrightarrow{250\text{ }^\circ\text{C}} \textbf{(13)}$	High MW polymer, very broad PDI
Condensation polymerization	De Jaeger and co-workers [96-101]	$\text{Cl}_3\text{P}=\text{NP}(\text{O})\text{Cl}_2 \longrightarrow \textbf{(13)}$	MW of 10^5 D and PDI 1.5-3.0
Condensation polymerization	Numerous investigators[102-113]	$\text{PCl}_5 + \text{NH}_4\text{Cl} \longrightarrow \textbf{(13)}$	Medium MW, very broad PDI
Living anionic polymerization	Matyjaszewski and co-workers [114-118]	$(\text{RO})_3\text{P}=\text{NSiMe}_3 \longrightarrow \textbf{(13)}$	Medium MW, and PDI 1.3-2.4
Living cationic condensation polymerization	Manners, Allcock and co-workers [119-123]	$\text{Cl}_3\text{P}=\text{NSiMe}_3 \longrightarrow \textbf{(13)}$	Controlled MW of up to 10^6 D with narrow PDI

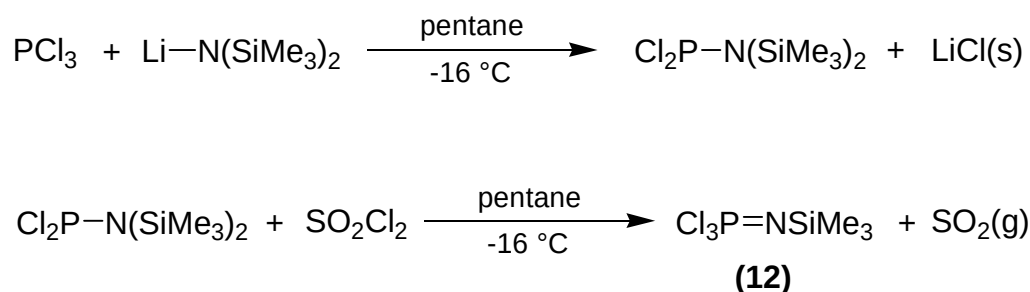
Among these synthetic routes, living cationic polymerization was used throughout this study for the synthesis of poly(dichlorophosphazene)s, since it allows better control over molecular weight of the product with a high quality product. The detailed history of these methods and their comparison will be skipped here but can be found in the literature [64].

Beside the numerous attempts to synthesize different monomer structures, many synthetic routes for the synthesis of chlorophosphoranimine monomer have been reported for the room temperature living cationic polymerization [124-128]. Among these approaches, the most successful one was the report by Wang, Rivard and Manners, where it was claimed to isolate the monomer in a two-step one pot reaction with a yield greater than 80 % [128]. This procedure was slightly modified in our group and used for the synthesis of monomer. The reasoning for the modification will not be mentioned here but can be found elsewhere [129].

3.4.1 Trichloro(trimethylsilyl)phosphoranimine, Monomer (12)

Trichloro(trimethylsilyl)phosphoranimine was synthesized using commercially available reagents in one pot. Lithium bis(trimethylsilyl)amide was weighed in a round bottomed flask and dissolved in pentane, which was subsequently immersed in an ice + salt mixture

(freezing mixture) and the temperature was kept till the end of synthesis. The freshly distilled phosphorus trichloride (PCl_3) was then added dropwise to the solution (**Scheme 3.4**). The resulting solution was stirred another half an hour before the dropwise addition



Scheme 3.4 Synthesis of trichloro(trimethylsilyl)phosphoranimine (**12**).

of freshly distilled sulfonyl chloride (SO_2Cl_2) to the slurry. The solution was mixed for another half an hour and filtered over celite to eliminate salt. The pentane was then distilled out from the filtrate and the monomer (**12**) was collected under reduced pressure. The formation of (**12**) was proved by ^{31}P NMR. The signal, $\delta = -55.84$ ppm, corresponds to the monomer (**Fig. 3.6**). Sometimes another signal at around $\delta = -18$ ppm, here that can

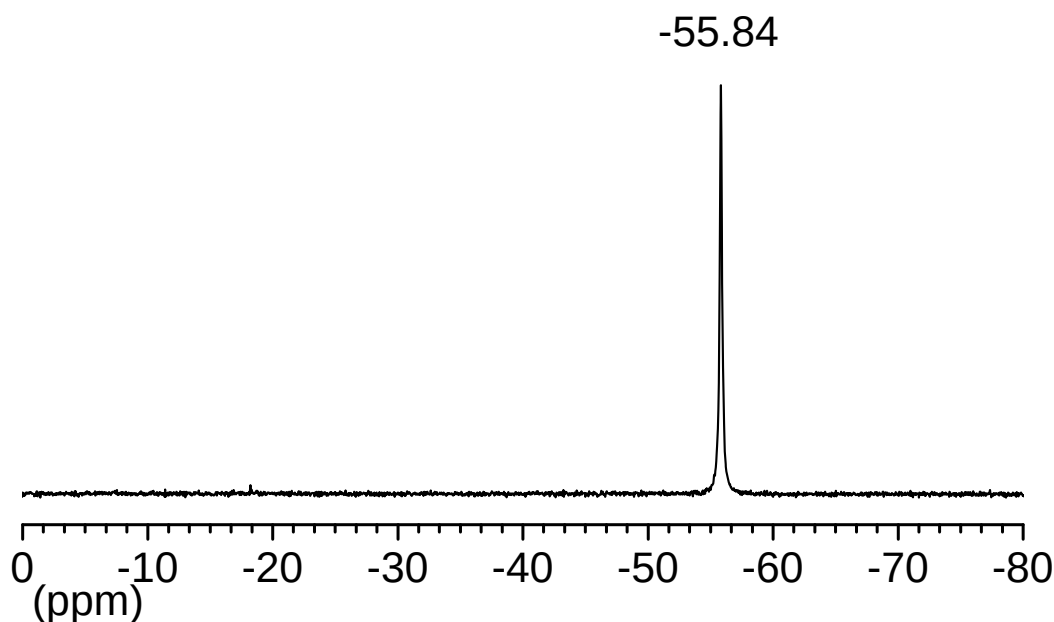


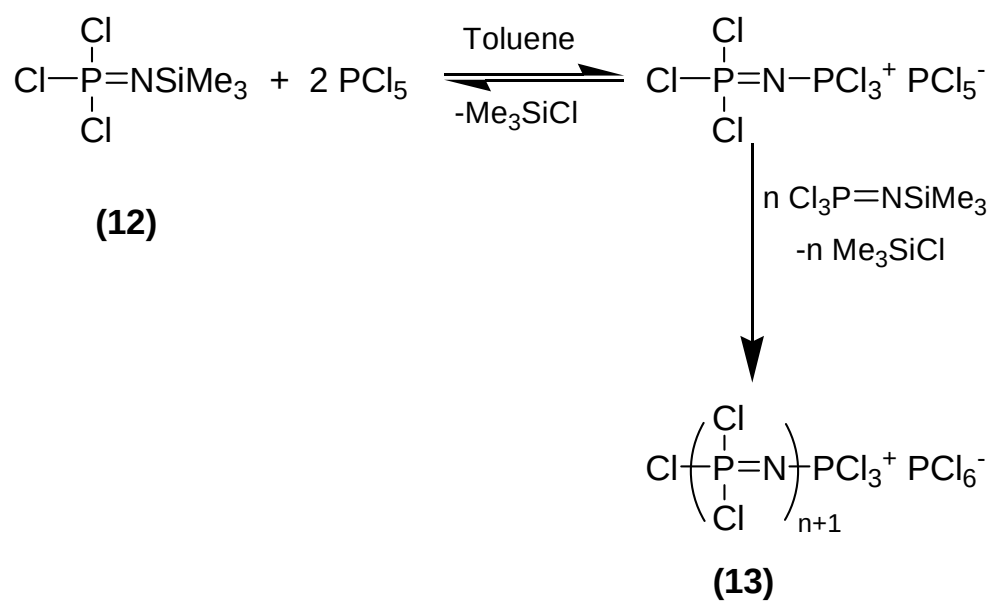
Fig. 3.6 ^{31}P NMR spectrum of $\text{Cl}_3\text{P}=\text{NSiMe}_3$ in CDCl_3 .

also be observed if carefully checked, may arise due to the polymerization of sensitive monomer in NMR tube. The details of the synthesis can be found in Appendix 3.

3.4.2 Poly(dichlorophosphazene), precursor polymer (**13**)

The polymerization of (**12**) was investigated in details by Allcock and co-workers. They studied the effect of various parameters on the polymerization, such as solvent, concentration of monomer, ratio of monomer to initiator, different initiators and temperature [130]. According to this pioneering work, PCl_5 was chosen as polymerization initiator with a ratio of monomer to initiator of 350:1 and a concentration of initiator as 0.0027 mol/L. The polymerization was carried out in toluene as a solvent whereby the quantitative yield of poly(dichlorophosphazene) was obtained (**Scheme 3.5**).

The progress of the polymerization was monitored by ^{31}P NMR by disappearance of monomer signal at around $\delta = -56$ ppm. After completion of the polymerization, the toluene was removed under vacuum to give a milky, highly viscous (**13**). As seen in **Fig. 3.7**, the single peak at $\delta = -18.25$ ppm indicates the formation of precursor polymer. Another signal at $\delta = +20$ ppm was also observed in some cases, which was attributed to the phosphazene cyclic trimer, namely hexachlorocyclotriphosphazene, with a quantity determined from peak integration usually less than 1 %. The isolated precursor polymer was then functionalized (for the experimental procedure, refer to Appendix 3).



Scheme 3.5 Room temperature living cationic condensation polymerization of (12) with PCl_5 catalyst in toluene to poly(dichlorophosphazene) (13).

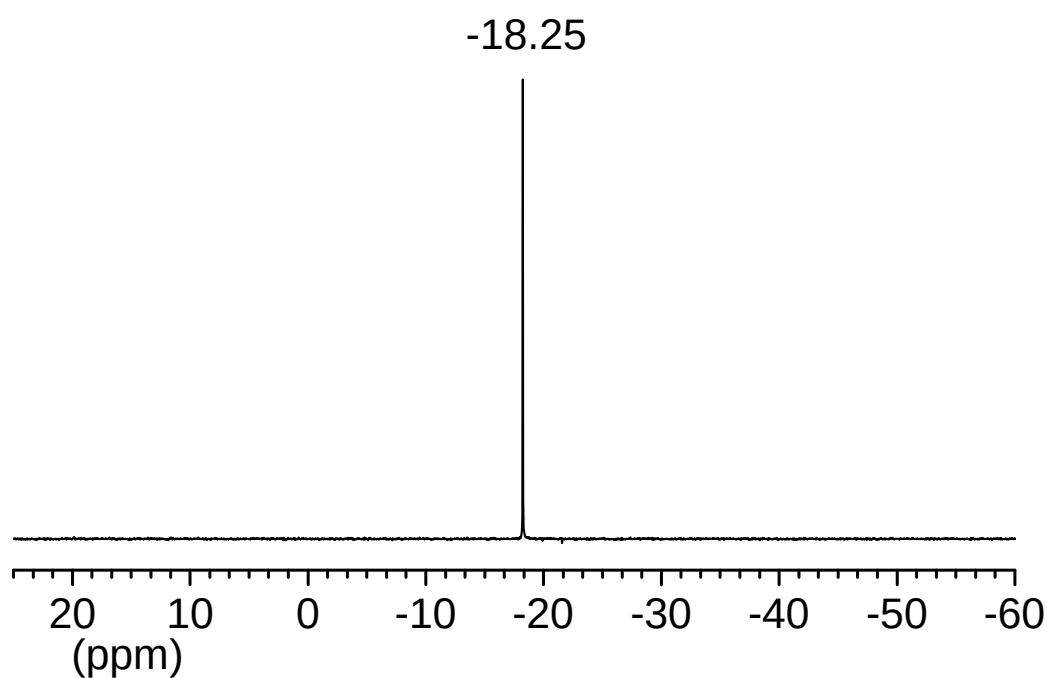
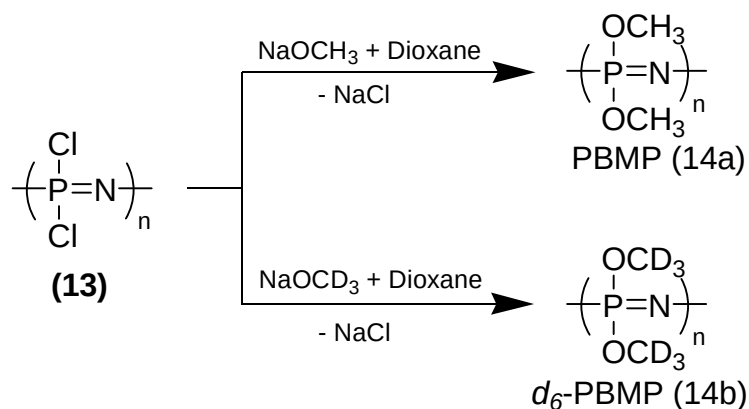


Fig. 3.7 ^{31}P NMR spectrum of poly(dichlorophosphazene) in CDCl_3 .

3.4.3 Poly(bismethoxyphosphazene)s (PBMP)s (14a and b)

Poly(dichlorophosphazene) was functionalized with both methoxy and d_3 -methoxy groups to prepare a model polyphosphazene for Small Angle neutron Scattering (SANS) experiment. The synthesized precursor polymer was dissolved in dioxane and divided into two equal portions in order to maintain the identical macromolecular properties for both polymers. Sodium salts of alcohols prepared in dioxane were added and macromolecular substitution was performed at room temperature in 2 days (**Scheme 3.6**).

The synthesized polymers were purified by dialysis in de-ionized water for 5 days and the slightly yellow colored polymers were isolated almost in quantitative yield after the removal of water. The details for the preparations are given in Appendix 3.

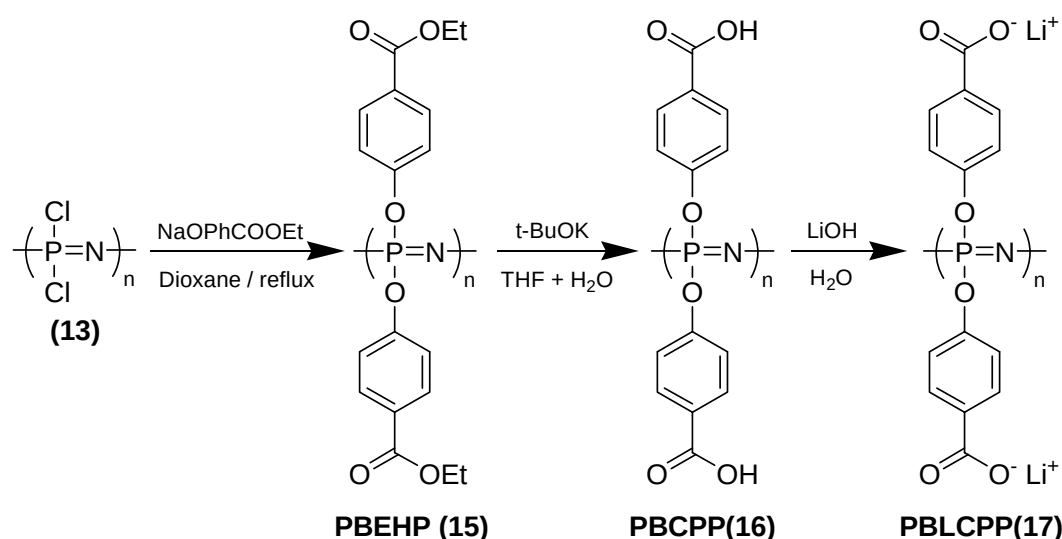


Scheme 3.6 Synthesis of poly(bismethoxyphosphazene)s; (14a) and (14b).

3.4.4 Poly[bis(lithium carboxylatophenoxy)phosphazene] (PBLCPP) (17)

Poly[bis(lithium carboxylatophenoxy)phosphazene] PBLCPP was synthesized as a model polyanion for its application as polyelectrolyte multilayers. The synthesis of the polymer was performed similar to the literature [131]. Sodium salt of ethyl 4-hydroxybenzoate was slowly given to the solution of precursor polymer (13) in dioxane and refluxed for 2 days. The full functionalization afforded poly[bis(ethyl 4-hydroxybenzoate)phosphazene] (PBEHP) (15) in a good yield (**Scheme 3.7**). The conversion of ester to carboxylic acid was achieved in the presence of potassium *tert*-butoxide and water at room temperature over 2 days. Poly[bis(carboxylatophenoxy)phosphazene] (PBCPP) (16) was isolated after acid

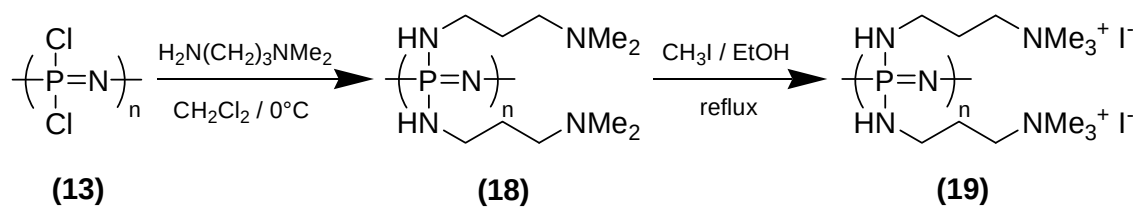
treatment as a crystalline product. This water insoluble polymer was then reacted with lithium hydroxide in water until the polymer dissolved completely. Poly[bis(lithium carboxylatophenoxy)phosphazene] (PBLCPP) (**17**) was then isolated (**Scheme 3.7**) as a white powder using freeze-drying method (the detailed chemical preparation of this polymer is given in Appendix 3).



Scheme 3.7 Synthesis of PBLCPP (**17**).

3.4.5 Poly[bis(3-amino-*N,N,N*-trimethyl-1-propanaminium iodide)phosphazene] (PBPAIP) (**19**)

Poly[bis(3-amino-*N,N,N*-trimethyl-1-propanaminium iodide)phosphazene] (**19**) was used also as a model polyelectrolyte for multilayer study. The synthesis was carried out similar to the literature with slight modifications [132]. 3-(dimethylamino)-1-propylamine was slowly given to the solution of (**13**) in dichloromethane at 0 °C and macromolecular substitution reaction was continued overnight at room temperature. The mixture was concentrated and the polymer was purified by dialysis against water for 3 days and poly[bis(3-(dimethylamino)-1-propylamino)phosphazene] (PBDPP) (**18**). The isolated polymer (**18**) was dissolved in absolute ethanol and let to react with methyl iodide under reflux. The resulting mixture was again concentrated and PBPAIP (**19**) was isolated after dialysis against water for 3 days (**Scheme 3.8**). The details for the synthesis are given in Appendix 3.



Scheme 3.8 Synthesis of PBPAIP (19).

4 RESULTS AND DISCUSSION

4.1 Oligoether Substituted Polysiloxane (OPS) (3)

It is well known the ion conduction in salt-in-polymer electrolytes takes place predominantly in the amorphous domain of the system and therefore segmental motion of the polymers have crucial effect on ion conduction. However, polymer electrolytes based on long linear polymers, such as poly(ethylene oxide)s, suffer usually from the low room temperature conductivity due mainly to the degree of crystallinity. Different architectures can be used to design new efficient polymer electrolytes but probably the best way of achieving this aim is to synthesize comb-like polymer electrolytes with high segmental mobility with low T_g values. Keeping this concept in mind, comb-like polysiloxane was synthesized by substituting poly(methylhydrosiloxane) with oligoether side groups in order to investigate as a model polymer electrolyte.

4.1.1 Characterization of OPS Polymer

NMR Spectroscopy. The degree and the completeness of substitution were elucidated by ^1H NMR. As shown in **Fig. 4.1**, poly(methylhydrosiloxane) (PMHS) shows a broad signal at around 4.7 ppm. This signal was monitored throughout the substitution process to decide the completeness of the reaction. The disappearance of this signal in the NMR spectrum of polymer (3) after the substitution was attributed to the complete functionalization of PMHS. Moreover the vanishing of the signals from the allyl group of the tetraethylene glycol allyl methyl ether (2) side chain showed that the reaction was straightforward. The appearance of only three new signals as propyl spacer in between the Si and oxygen atoms (a,b and c) signified that the macromolecular hydrosilylation did not suffer from a number of drawbacks, including the formation of *cis* and *trans* isomer together with dehydrocondensation adducts as mentioned in the literature [78]. Very slightly yellow colored or colorless product was a good indication of an efficient removal of the colloidal Pt species formed during the course of the hydrosilylation reaction.

FT-IR Spectroscopy. The substitution process was also analyzed by FT-IR measurements. The disappearance of the characteristic Si-H stretching of PMHS at 2167 cm^{-1} indicated the complete substitution reaction. The FT-IR spectrum of polymer (3) is

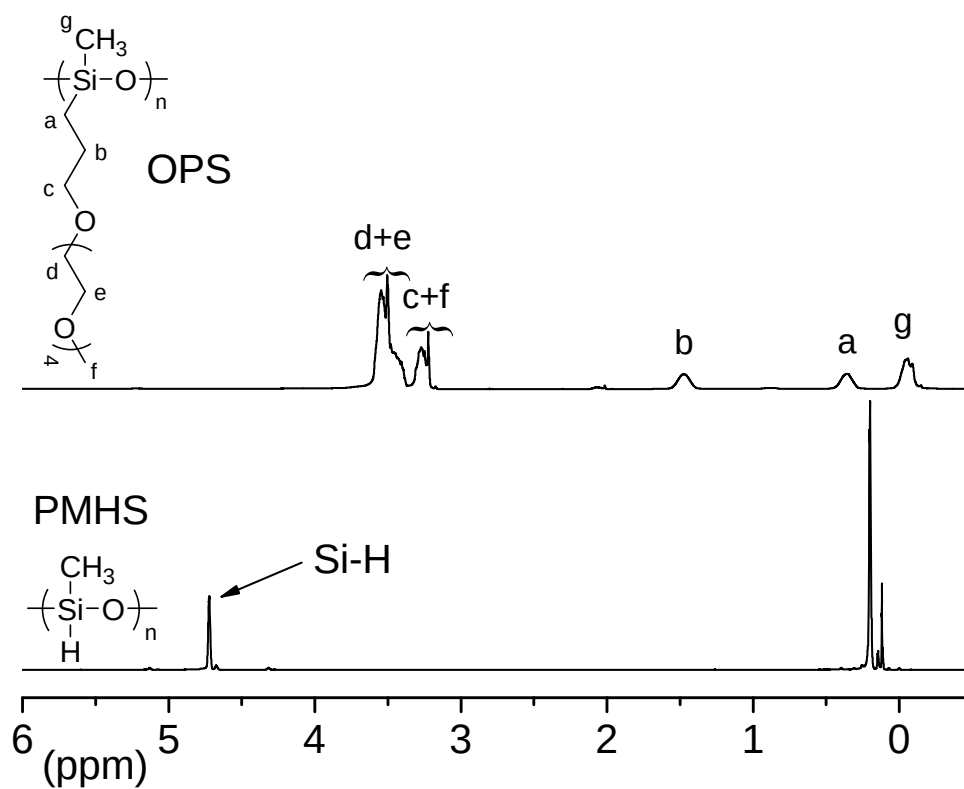


Fig. 4.1 ^1H NMR of poly(methylhydrosiloxane) (PMHS) and Oligoether Substituted Polysiloxane (OPS).

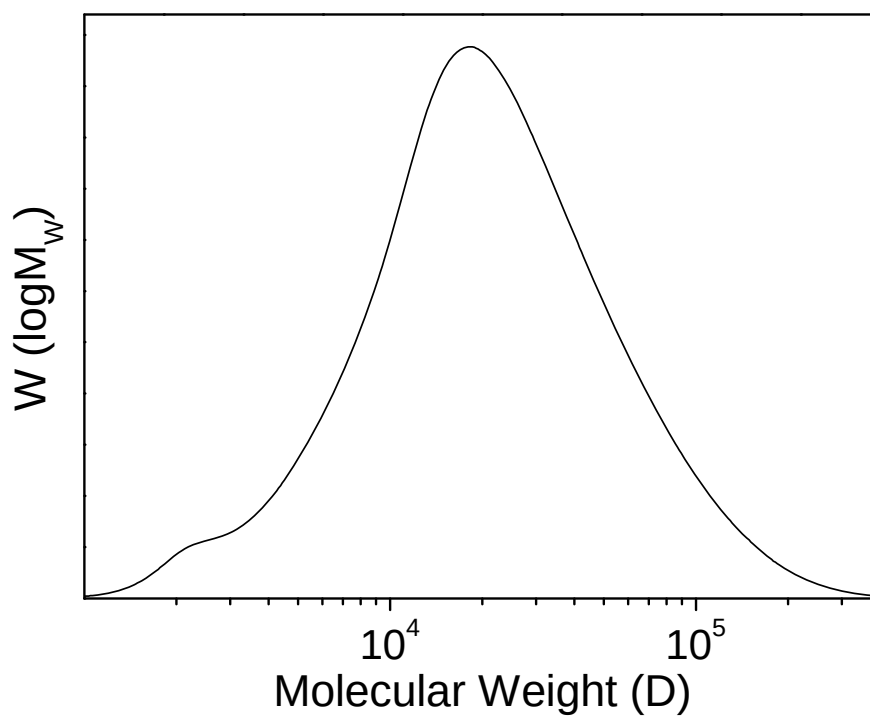


Fig. 4.2 GPC Chromatogram of OPS.

given in **Fig. 4.3** together with its characteristic absorption frequencies as listed in **Table 4.1**.

Gel Permeation Chromatography. The GPC elution curve showed a single peak for the molecular weight distribution of the polymer (**3**) with a number average molecular weight (M_n) of 1.34×10^4 D and a polydispersity index of 2.23 using the calibration curve from the polystyrene standard. The slightly higher polydispersity of (**3**) can be attributed to the commercial PMHS, which has already a certain degree of polydispersity with an average repeating units of 35. Knowing this fact, the expected M_n value can be calculated as approximately 1.1×10^4 , which seems to be at the first glance in accordance with the experimental result. However the separation by GPC is regulated by the size of the polymers in the solution and polymer solutions of similar hydrodynamic volume but different molecular weight will elute at the same retention volume as seen commonly for the comb like polymers. A correction factor of 3 was, in fact, reported for comb like polystyrene compared to the linear polystyrene [133]. If this is true, the real molecular weight turns out to be a factor of almost 4 higher than the expected one, which implies a possible macromolecular condensation of the hydrophilic PMHS before or during the substitution reactions to form Si-O-Si bridges considering the fact that 1 to 2 % water remained in the polymer matrix, according to FT-IR and NMR spectra, despite extensive attempts to dry poly(methylhydrosiloxane) backbone [134].

Differential Scanning Calorimetry. Thermal properties of the polymer were investigated using DSC in the temperature range of -150 °C to 150 °C. The polymer showed a very low T_g value of -83.5 °C as expected and was thermally stable in the measured range. However a small crystallization peak was detected at -60 °C due to the side chain crystallization of the oligoether side chains, which melted subsequently at around -30 °C (**Fig. 4.4**). This melting point may be seen as a limiting point for the use as a solid polymer electrolytes but the polymer is completely amorphous at room temperature. Moreover, the crystallinity disappeared totally (as will be seen in the following part) after complexation with lithium salts due to most probably the coordination of the etheric oxygens to the cations preventing the self packing of the side chains.

4.1.2 OPS Polymer Electrolytes

OPS (**3**) was used to investigate for its lithium ion conducting properties by forming salt-in-polymer type of polymer electrolytes. Lithium triflate (LiSO_3CF_3) was used as

electrolytic salt. The polymer (**3**) was doped with 5, 10, 15, 20, 30, and 40 wt-%, which corresponds to the following molar ratios of the O atoms to lithium: O/Li = 50 (for 5 wt-% salt) to 6.25 (for 40 wt-% salt) (see also **Table 4.2**). The as obtained polymer electrolytes were highly viscous but did not form mechanically stable membranes. The resulting salt-in-polymer systems were investigated for thermal and electrical properties.

FT-IR Spectroscopy. The interaction of lithium salt with the polymer was elucidated using FT-IR spectra of the polymer and polymer electrolytes. **Fig. 4.3** gives the FT-IR spectra of the polymer (**3**). The characteristic absorption frequencies are listed in **Table 4.1**.

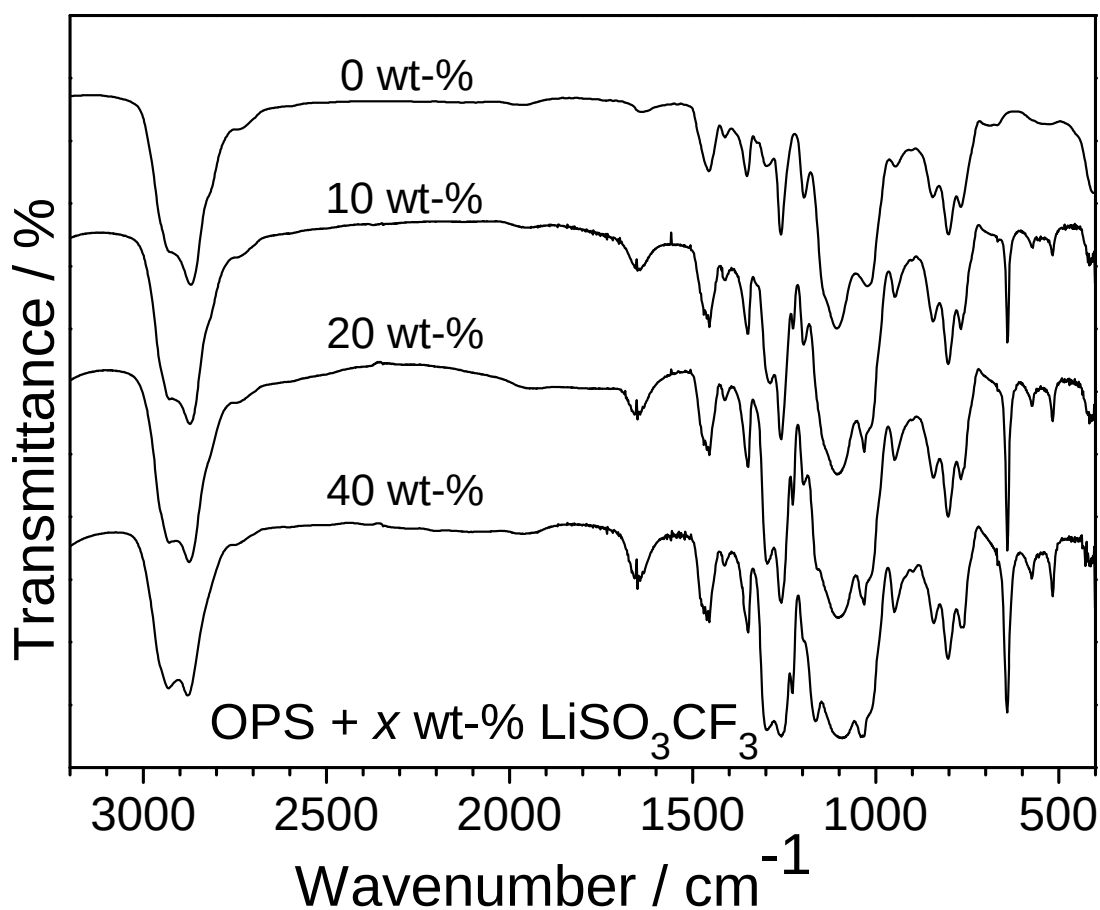


Fig. 4.3 FT-IR spectra of OPS and OPS based polymer electrolytes with 10, 20, and 40 wt-% LiSF₃CF₃.

The polymer (**3**) can be easily identified with the doublet seen close to 1100 and 1020 cm^{-1} , which is characteristic for the polysiloxanes containing more than eight silicon atoms. The strong and very characteristic symmetric deformation of Si-CH₃ appears at 1261 cm^{-1} . The only band characteristic of C-O-C groups is seen at around 1237 cm^{-1} as a shoulder due to the shielding of quite strong Si-O-Si band coming at the same region. Therefore it could not be used to monitor the coordination effect of the cations, which usually results in frequency shift of the C-O-C signal to the lower frequencies as the concentration of salt increases. Nevertheless the broadening of the signal at around 1100 cm^{-1} which shifted slightly to the lower frequencies could be linked to the cation-oligoether interaction in a coarse approach. In addition, slightly shifting and broadening of the SO₂ deformation band at 640 cm^{-1} with increasing salt content is consistent with the interpretation of free ion and higher aggregates [135]. Unfortunately, the other characteristic stretching of triflate anion used to investigate many salt-in-polymer systems, for example symmetric SO₃ vibration at around 1030 cm^{-1} , were useless for this case since partially or fully overlapped with the polymer frequencies. Some of the characteristic absorption frequencies were listed in **Table 4.1**.

Table 4.1 Characteristic absorptions (cm^{-1}) in FT-IR spectra for OPS (**3**) and its polymer electrolytes; signal intensity (s) = strong, (m) = medium; (str.) = stretching, (def.) = deformation vibrations.

Sample	Lithium salt (wt-%)	-CH ₂ - (str.)	-CH ₂ - (def.)	-Si-O-Si- (str.)	-C-O-C- (str.)	-Si-CH ₃ - (def.)
OPS (3)	0	2929 (s), 2869 (s)	1456 (m)	1107 (s), 1024 (s)	1137 (s)	1259 (s)
OPS + LiSO ₃ CF ₃	5	2929, 2872	1456	1103, 1024	-	1259
	10	2929, 2872	1455	1103, 1024	-	1257
	15	2929, 2872	1454	1103, 1024	-	1257
	20	2929, 2872	1454	1103, 1024	-	1257
	30	2929, 2872	1454	1103, 1024	-	1257
	40	2929, 2872	1454	1103, 1024	-	1257

Differential Scanning Calorimetry. Thermal properties of the polymer were investigated using DSC in the temperature range of -150 °C to 150 °C. As shown in **Fig. 4.4**, a small

crystallization peak was observed for polymer (**3**), which melted subsequently at around $-30\text{ }^{\circ}\text{C}$. This crystallization behavior, which is common for polymers having relatively long side chain, diminished substantially after the addition of 5 wt-% lithium salt and completely disappeared above 10 wt-% salt concentration. Beside the T_g values, no further transition peaks were observed for the polymer electrolytes. The T_g value of the polymer (**3**) ($-83.5\text{ }^{\circ}\text{C}$) was shifted gradually to the higher values as the amount of salt in the polymer electrolyte increased and reached to $-48.7\text{ }^{\circ}\text{C}$ for 40 wt-% salt concentration (see **Table 4.2**). This progressive rise can be attributed to the decrease in the segmental mobility of the side chain, which is usually interpreted as a result of the effects of an increase in intramolecular and intermolecular coordinations between coordinating sites on the same or different polymer chains caused by the ions acting as transient crosslinks.

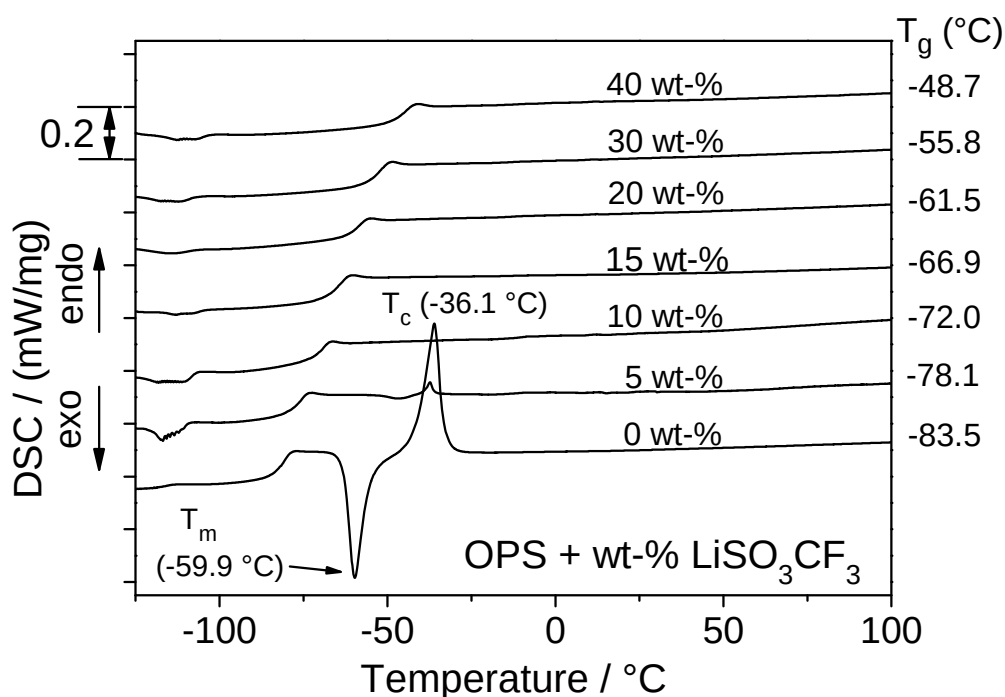


Fig. 4.4 DSC thermogram of OPS and OPS based polymer electrolytes with variable amount of lithium triflate salt.

T- and Li- Salt Dependence of Conductivity. The ionic conductivities of the OPS polymer electrolyte samples were determined by impedance spectroscopy with the temperature ranging from $-60\text{ }^{\circ}\text{C}$ to $90\text{ }^{\circ}\text{C}$ under an inert atmosphere of nitrogen. The membranes were placed between two ion blocking gold plated electrodes with a diameter

of 1.66 cm. Since the polymer electrolytes were viscous but not free standing membranes, a PTFE spacer was used in between the electrodes so that the polymer electrolyte was held without flowing. The impedance value, where the phase angle vanished nearly to zero, was taken as the bulk impedance of the polymer electrolyte and the conductivity values were evaluated by equation [3.2.11] as discussed in section 3.2.

The temperature dependent ionic conductivity of OPS polymer electrolytes with varying lithium salt content was shown in **Fig. 4.5**. A systematic increase in the concentration of the lithium salt was followed to find the optimum doping concentration for the polymer electrolyte system. The conductivities for the electrolytes varied in the range from 1.1×10^{-12} to $2.9 \times 10^{-10} \text{ S}\cdot\text{cm}^{-1}$ at -60°C and at 90°C from 4.9×10^{-4} to $7.2 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$. The ionic mobility is closely related to the relaxation modes of the polymer host, which is greatly effected by the salt content. As seen below, and for many of the other polymer electrolytes, the conductivity increased with increasing salt content to a maximum and

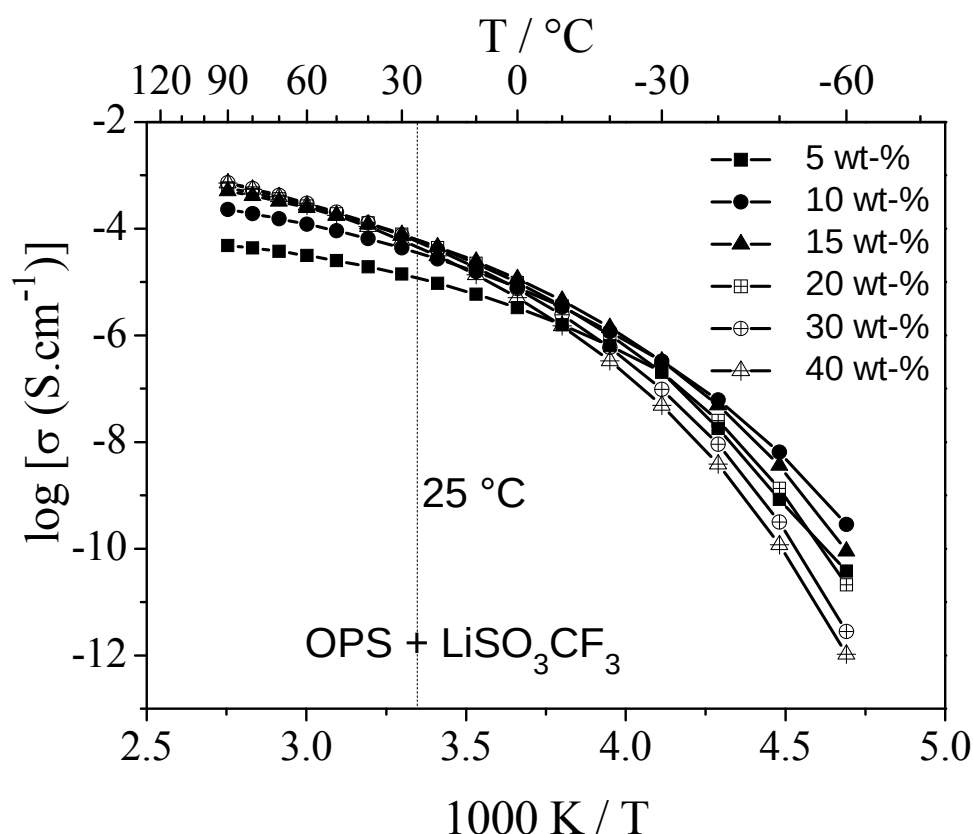


Fig. 4.5 Arrhenius plot of OPS polymer electrolytes with various amounts of lithium triflate.

gradually tailed away. The viscosity of the polymer is one of the reasons influencing the conductivity of a system in a negative manner, since there is an inverse relationship between the conductivity and the viscosity. At low salt content, the mobility of the ions is relatively unaffected by concentration. At higher concentrations, the conductivity drops due to the reduced ion mobility, which was caused by an increase in inter- and intramolecular coordinations of the polymer host to the salt creating transient (ionic) cross-links (the stiffening effect of the salt concentration on the T_g was already discussed in the previous section). In addition, above a critical concentration, ion pairs and higher aggregates, which are less mobile, are predicted to form and therefore to influence the conductivity [70].

Above 15 wt-% salt concentrations, polymer electrolytes showed similar conductivities at room temperature but the maximum conductivity value of $5.9 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ was recorded for the one with 20 wt-% salt concentration and then decreased gradually at higher concentrations. The conductivity value of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ was reached by 20 and 40 wt-% lithium doped at around 35 °C. This value is comparable to the results reported for similar mono or comb like polysiloxane based polymer electrolytes, except for that the optimum doping level for them was found usually above 20 for the ratio of O:Li [30, 36, 43].

For a single molecule, or nonpolymeric materials, a straight line for the temperature dependent ionic conductivity that can be fitted by Arrhenius equation would be expected. Instead, the plots shown in the figure above showed noticeable deviation from Arrhenius behavior, which suggests that the oligoether side chains contribute also the transport of the ions. Hence the curves were fitted by empirical Vogel-Tamman-Fulcher (VTF) equation, as for many other amorphous polymer electrolytes and ion conducting glasses:

$$\sigma = \sigma_0 \cdot \exp[-B/(T - T_0)] \quad [4.1]$$

where T_0 is the ideal glass transition temperature, B is pseudo activation energy and σ_0 is weakly temperature-dependent prefactor. **Table 4.2** summarizes the VTF parameters obtained from the fits.

The prefactor σ_0 is relates to the number of mobile charge carriers in the system [70]. As the lithium concentration increases, σ_0 should also increase. A linear correlation of σ_0 with lithium salt concentration exists for OPS + LiSO_3CF_3 system as seen in the table. The term B , which includes the pseudo activation energy ($E_a = k \cdot B$), can be thought as a critical

volume for displacement within the free volume concept or the energy barrier for the rotational motion of polymer segments. For both approaches, the value of B are predicted to increase monotonously as the concentration of the lithium salt rises as also the case for this system. This event can be attributed to the stiffening of polymer segments due to the increased amount of ionic cross-links formed in the matrix. Moreover T_0 values lie usually 20-50 °C below the T_g values and below T_0 , free volume or excess configurational entropy of a polymer assumed to vanish. The values found for T_0 are listed in the table below.

At lower temperatures, the conductivity value according to VTF equation is greatly affected by the value of T_0 , which is closely related to glass transition temperature. The inverse relation between salt concentration and conductivity at sufficiently low temperatures is therefore well described by this equation. On the other hand, the temperature increase gives rise to the number of free ions as described by the term σ_0 (refer to **Table 4.2** for the numerical values) that works against the effect of T_0 . Therefore the conductivity curves as also seen in **Fig. 4.5** converge usually at a certain temperature and then start diverging under the influence of σ_0 dominating the conductivity value at higher temperatures.

Table 4.2 Glass transition temperatures (T_g) of OPS and its polymer electrolytes, ratios of O:Li for the corresponding wt-% of lithium triflate and fitting parameters of VTF equation to the temperature dependent conductivities.

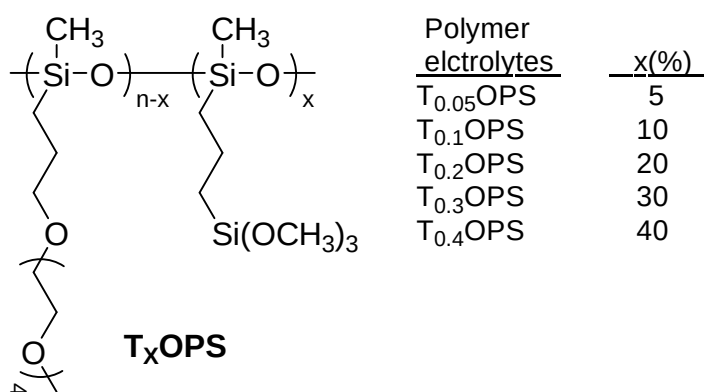
LiSO ₃ CF ₃ (wt-%)	Ratio O:Li	T_g [K]	T_0 [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
0	–	189.7	–	–	–
5	50	195.1	181	1.4	5723
10	25	201.2	168	1.6	8088
15	17	206.3	170	4.6	8724
20	13	211.7	172	17.5	9081
30	8	217.4	172	175.0	10241
40	6	224.5	170	305.9	11434

4.1.3 Final Commentary.

Synthesis of oligoether functionalized polysiloxane (OPS) (**3**) was successfully done, which can be used as a host material for salt-in-polymer electrolytes. Small side chain crystallization was observed well below room temperature, which disappeared completely after complexation with LiSO_3CF_3 . Although the synthesis of mono comb polysiloxanes with different oligoethers as side chains have been performed, the electrical properties for this particular noncrosslinked system doped with lithium triflate were reported for the first time. The polymer electrolytes showed a conductivity value of nearly $10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which is only an order of magnitude lower than the requirement for industrial applications. However the polymer electrolytes suffered from poor dimensional stability. The question now is that if the dimensional stability can be enhanced without sacrificing the conductivity.

4.2 Allyltrimethoxysilane and Oligoether co-Substituted Polysiloxane (T_x OPS) (4)

The preceding section on OPS (**3**) polymer electrolytes showed rather encouraging results for ionic conductivity measured for LiSO_3CF_3 doped systems. However the as obtained salt-in-polymer systems were quite viscous but dimensionally unstable, which limits the practical application as polymer separator for lithium ion batteries since it would flow out when pressed between two electrodes. Thus in order to overcome this shortcoming of mechanical stability, a new architecture, enabling appropriate cross-linking of this polymer with no or negligible depression of the ionic conductivity must be designed. This section explains the synthesis of a series of mono-comb polysiloxanes by random co-substitution of the hydrogen of poly(methylhydrosiloxane) with oligoether groups and partly with trimethoxysilane side groups (as cross-linking moieties ranging from 5 mol-% up to 40 mol-% respectively) (**Scheme 4.1**).



Scheme 4.1 Chemical structure of $T_x\text{OPS}$ precursor polymers.

The rationale of this study was to examine the effect of the trimethoxysilane moiety on both the ionic conductivity of as-prepared salt-in-polymer membranes and the dimensional stability of the resulting solvent free polymer electrolytes after cross linking. Moreover, hydrochloric acid (HCl) and dibutyltin dilaurate (DBTL) were used and compared as catalysts for the preparation of polymer electrolyte membranes. The use of trimethoxysilane units is attractive as the crosslink density can be fine tuned by altering the loading of trimethoxy units and as it opens up a link to sol-gel techniques and can be

applied to build up inorganic-organic hybrid systems with a high potential for further increase of ionic conductivities.

4.2.1 Characterization of T_x OPS (4) Precursor Polymers

NMR Spectroscopy. The degree and the completeness of substitution were elucidated by ^1H NMR. Representative ^1H NMR spectra for $T_{0.1}$ OPS and $T_{0.4}$ OPS precursor polymers are shown in **Fig. 4.6**. The vanishing of the Si-H at 4.7 ppm, as discussed in the previous section, was a clear indication of complete substitution pattern. The signals were assigned using 2-D NMR measurements. The difference in the peak intensities of the trimethoxysilane moiety (a', b', and c') among the precursor polymers were obvious and in good agreement with the intended composition of crosslinker concentration.

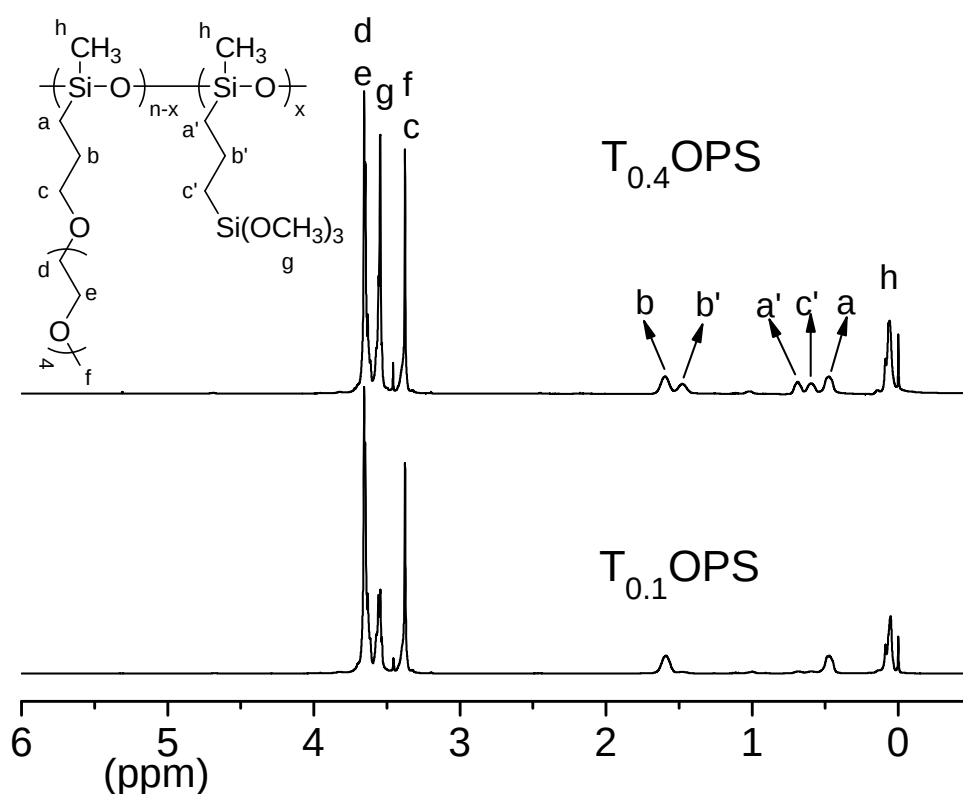


Fig. 4.6 Representative ^1H NMR spectra for $T_{0.1}$ OPS and $T_{0.4}$ OPS.

FT-IR Spectroscopy. **Fig. 4.8** includes the representative FT-IR spectra of $T_{0.1}$ OPS and $T_{0.4}$ OPS precursor polymers. In addition to NMR results, the disappearance of characteristic Si-H signal at 2167 cm^{-1} confirms the full substitution of the

poly(methylhydrosiloxane). The spectra recorded for precursor polymers were quite similar to that for OPS polymer except that the monotonically increasing signal at around 904 cm^{-1} , which was attributed to the antisymmetric stretching of $-\text{CH}_3$ groups of Si-O-CH_3 . Other characteristic signals of trimethoxysilane moiety were not distinct since they were shielded by the strong absorption signals of polymer backbone and side chains. Therefore this signal will be the focus of our interest in the following sections in order to explain the crosslinking efficiency of the polymer electrolytes crosslinked by HCl and DBTL as catalysts.

Gel Permeation Chromatography. The average molecular weight of the precursor polymers was found to be in the order of 10^4 D with polydispersity values of below 2 as seen in the following Table. These results were in parallel to the one found for OPS polymer as discussed in Section 4.1.1. Upon the theoretical calculations, the molecular weight of the polymers would follow gradually decreasing pattern as the “x” value increases, since relatively bulk oligoether side chains were replaced by small trimethoxysilane functional groups, but experimental values were essentially constant. Moreover, an attempt to determine the exact molecular weight of the polymers by MALDI-TOF failed giving only low molecular weight fragments.

Table 4.3 Molecular weight and T_g values for $T_x\text{OPS}$ polymers.

Sample	M_n [D]	M_w [D]	Polydispersity index PDI	T_g (°C)
$T_{0.05}\text{OPS}$	1.32×10^4	2.53×10^4	1.91	-84.1
$T_{0.1}\text{OPS}$	1.17×10^4	2.35×10^4	2.01	-83.6
$T_{0.2}\text{OPS}$	1.35×10^4	2.40×10^4	1.77	-84.8
$T_{0.3}\text{OPS}$	1.37×10^4	2.45×10^4	1.79	-85.2
$T_{0.4}\text{OPS}$	1.34×10^4	2.41×10^4	1.80	-86.5

Differential Scanning Calorimetry. The thermal properties of the polymers were investigated by DSC and no evidence of thermal decomposition or primary transition of the polymer precursors were observed up to $300\text{ }^\circ\text{C}$. **Fig. 4.7** shows the DSC thermograms of the $T_x\text{OPS}$ polymers up to $50\text{ }^\circ\text{C}$. The polymers showed T_g between $-82\text{ }^\circ\text{C}$ and -87

°C, which decreases slightly as trimethoxy moiety on the polymer chain increased (**Table 4.3**). This may be due to the free volume created by decreasing concentration of relatively bulk oligoether side chains via the replacement of relatively small trimethoxysilylpropyl groups. However, crystallization temperature was detected for each at around -60 °C due to the side chain crystallization of oligoether, which melted subsequently at around -40 °C. The presence of melting point for the base polymers marks the lower temperature limit for the use of these polymers as a solid polymer electrolyte in energy storage devices but room temperature applications are still possible since all the polymers are completely amorphous at room temperature. Moreover, the complexation with salt hinders the crystallization as will be discussed in the following sections.

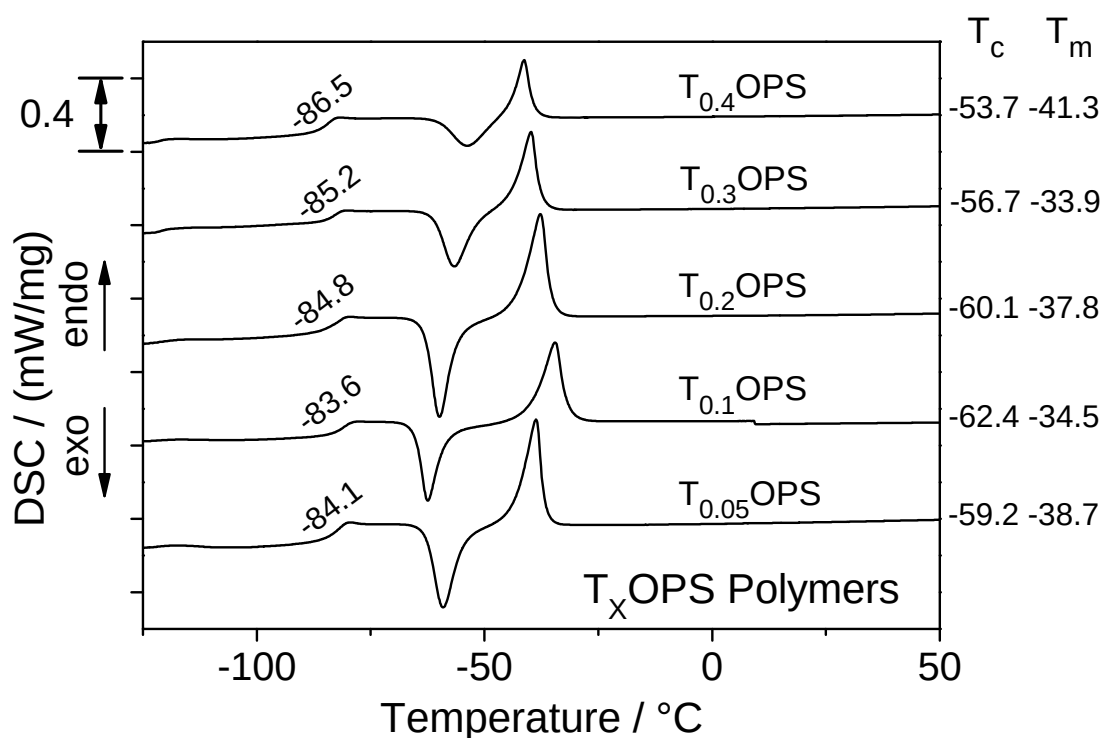


Fig. 4.7 DSC thermogram of T_xOPS polymers.

4.2.2 T_xOPS + 10 wt-% $LiSO_3CF_3$ Polymer Electrolytes

T_xOPS (**4**) was used to investigate for its lithium ion conducting properties by forming salt-in-polymer type of polymer electrolytes. The essence of this section was to optimize the amount of trimethoxysilane moiety, thus the crosslinking density, of the precursors to

yield highly conducting but mechanically stable polymer electrolytes. For this purpose, salt-in-polymer membranes at a constant concentration of 10 wt.-% lithium triflate were prepared by HCl crosslinking and investigated for thermal and electrical properties.

FT-IR Spectroscopy. The representative FT-IR spectra of $T_{0.1}$ OPS and $T_{0.4}$ OPS polymer electrolytes with 10 wt.-% LiSO_3CF_3 were given in **Fig. 4.8** together with $T_{0.1}$ OPS and $T_{0.4}$ OPS precursor polymers for the sake of comparison. LSCF_{10} in the graph corresponds to 10 wt.-% lithium triflate. As explained before, the signal at 904 cm^{-1} was attributed to the $-\text{Si-O-CH}_3$ groups, which increases gradually as the concentration of crosslinking groups increases. After complexation with salt and crosslinking with HCl, sinking in the intensity of this signal was observed, but not completely vanished. In other words, not all of these groups were involved throughout the crosslinking process.

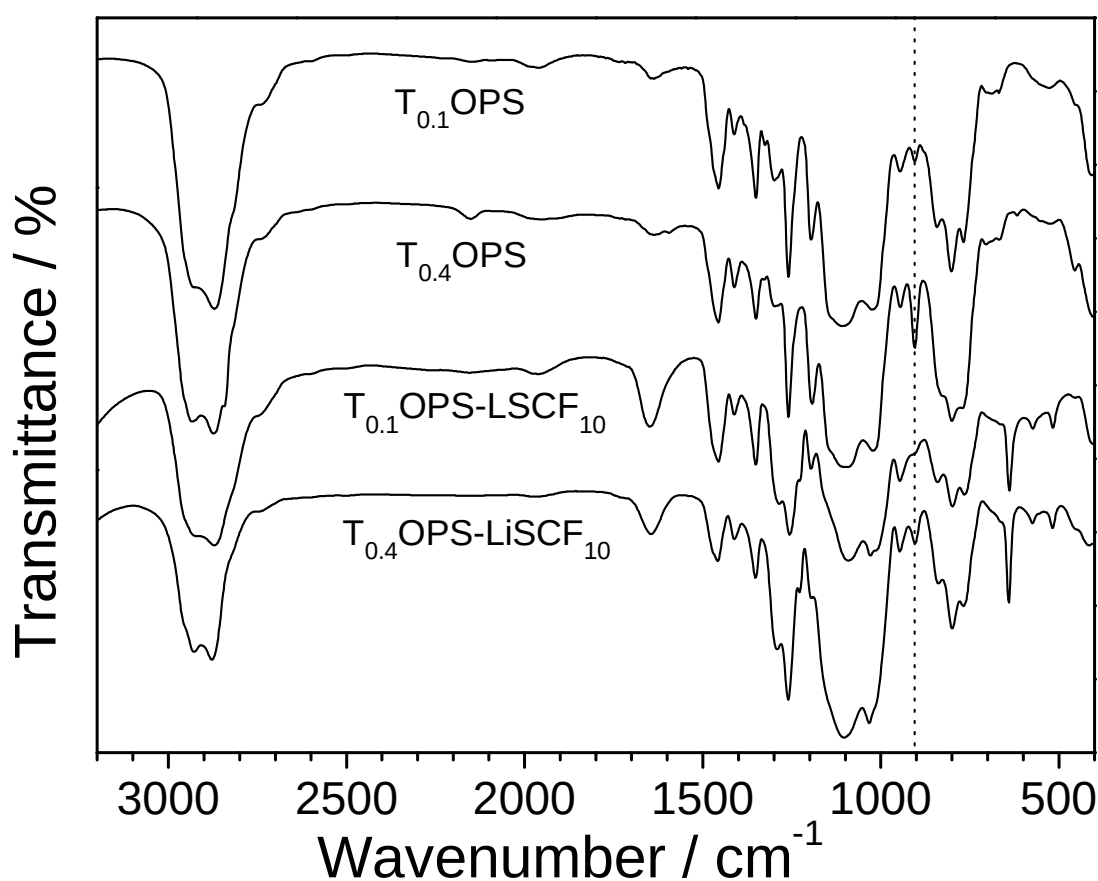


Fig. 4.8 Representative FT-IR spectra of $T_x\text{OPS}$ polymers and $T_x\text{OPS-LiSCF}_{10}$ polymer electrolytes for $x=0.1$ and 0.4 . $T_x\text{OPS-LiSCF}_{10}$ in the graph indicates $T_x\text{OPS} + 10\text{ wt.-% LiSO}_3\text{CF}_3$. Dotted line corresponds to 904 cm^{-1} .

Differential Scanning Calorimetry. The DSC thermogram of T_X OPS polymers each complexed with 10 wt-% LiSO_3CF_3 salt was given in **Fig. 4.9**. The T_g values of the membranes shifted from around -85°C to the higher temperatures (between -70°C and -55°C) as listed in **Table 4.4**. The lowest T_g value in this case was observed for the membrane prepared by 5 mol-% trimethoxysilylpropyl substituted base polymer. Moreover, the crystallinity observed for the precursor polymers surprisingly disappeared after complexation with salt and crosslinking. This was most probably due to the coordination of etheric oxygens to the lithium cations in the matrix so that the oligoether side chains could not find the chance to form crystallites.

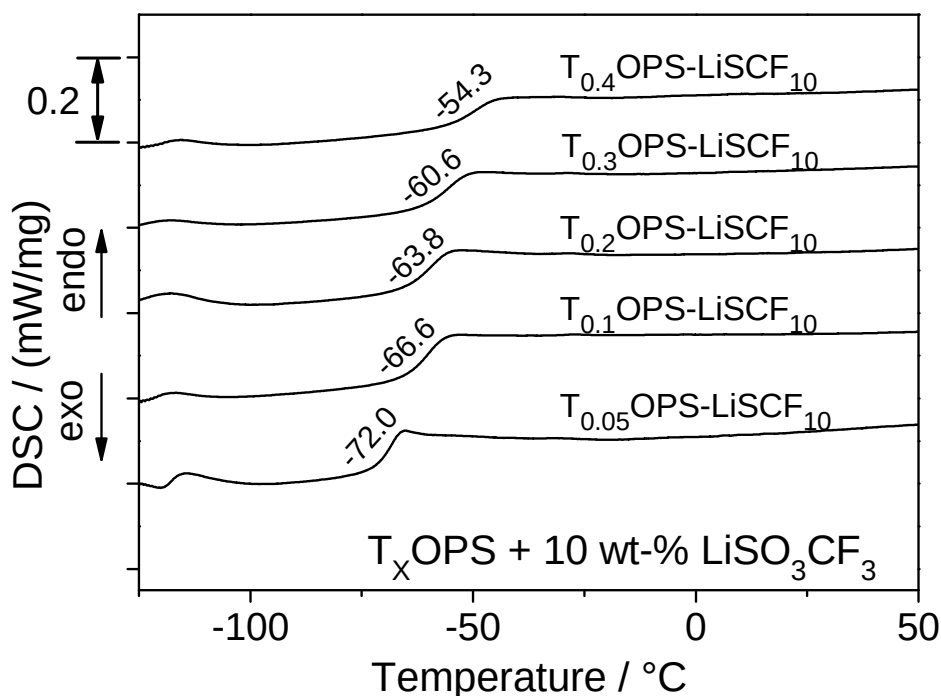


Fig. 4.9 DSC thermogram of T_X OPS polymers with fixed amount of 10 wt-% Li triflate. LiSCF_{10} in the graph indicates 10 wt-% LiSO_3CF_3 .

Temperature Dependence of Conductivity. The conductivity measurement was carried out on crosslinked salt-in-polymer membranes at a constant concentration of 10 wt-% lithium triflate with variation of the content of cross linking groups. A clear dependence of the conductivity was found on the molar ratio between cross linking and solvating groups. The conductivities varied in the range from 4.6×10^{-5} to $6.9 \times 10^{-7} \text{ S cm}^{-1}$ at 30°C and at 90°C from 2.5×10^{-4} to $8.6 \times 10^{-6} \text{ S cm}^{-1}$ (for the detailed conductivity values refer to

Table A.4.2 in Appendix 4). $T_{0.05}$ OPS and $T_{0.1}$ OPS polymer electrolytes showed very similar conductivities but the maximum conductivity was observed for PE 4 with 10 mol-% crosslinking side groups. An Arrhenius plot of the ionic conductivities is shown in **Fig. 4.10**, where the general trend was that the conductivity decreased with decreasing concentration of the oligoether side chains and increasing trimethoxysilylpropyl moiety. The largest step in the conductivity is found from $T_{0.1}$ OPS to $T_{0.2}$ OPS salt-in-polymer systems as seen below, which can be attributed to the strong loss of the free volume and the segmental mobility with cross-linking in the polymer electrolyte network. Shortly, the optimum for having both good mechanical properties and high conductivity at the same time lies between 5 mol-% ($T_{0.05}$ OPS) and 10 mol-% ($T_{0.1}$ OPS) crosslinking groups. The minimum number of linkages per macromolecule to achieve a 3D network with good mechanical properties is 2. That is really near to the average crosslinking units calculated for $T_{0.1}$ OPS, which is slightly bigger than 3. This number goes to around 4.5 for $T_{0.2}$ OPS which corresponds to a crosslinking point for every sixth segment on the chain on the average. The large jump on the conductivity from $T_{0.1}$ OPS to $T_{0.2}$ OPS showed that the number of increasing crosslinking sites per macromolecule had a threshold value near 4 where the chain mobility is dramatically lowered due to the crosslinking. Therefore, the optimum conditions to have both good conductivity and reasonable mechanical properties lie in a narrow range around 10 mol-% cross-linking units ($T_{0.1}$ OPS).

The temperature dependence of ionic conductivity in T_X OPS with 10 wt-% salt can be fitted using empirical VTF equation. The fit parameters are summarized in **Table 4.4**. The values found for σ_0 were pretty small and no general trend was observed. However the value of B increased in general with increasing crosslinking ratio, indicating that more compact structure of the matrix increased the energy required for ion transport.

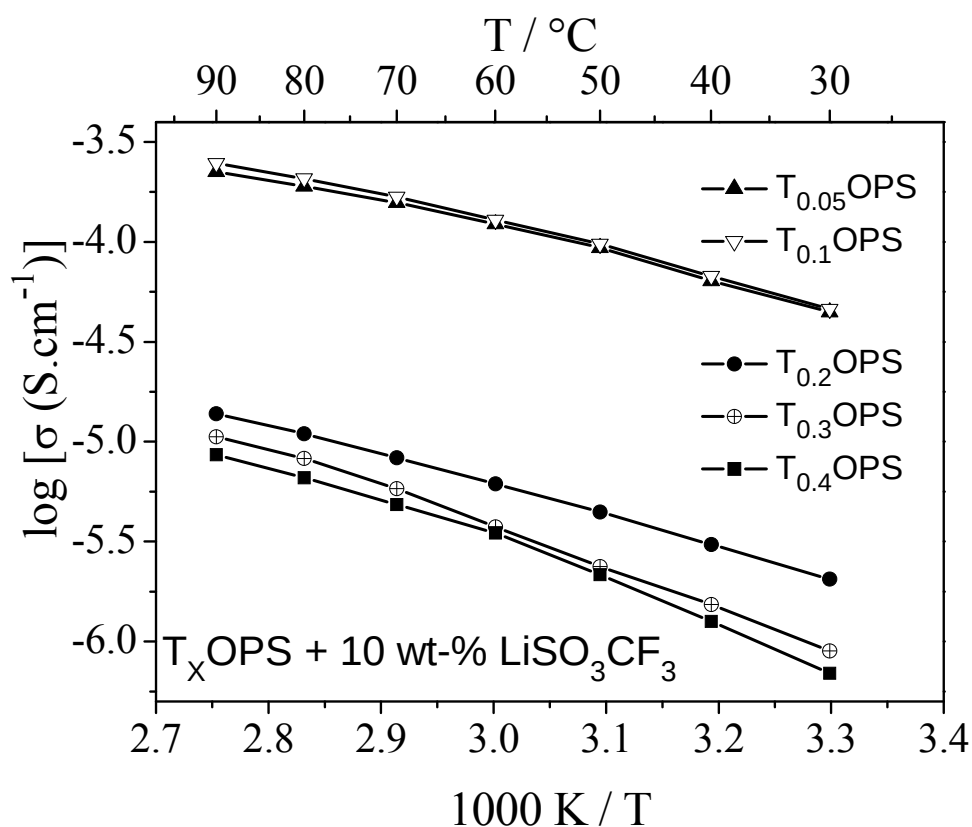


Fig. 4.10 Arrhenius plot of $T_x\text{OPS} + 10 \text{ wt-\% Li triflate}$.

Table 4.4 Glass transition temperatures (T_g) of $T_x\text{OPS} + 10 \text{ wt-\% Li triflate}$ and fitting parameters of VTF equation to the temperature dependent conductivities.

Polymers	LiSO_3CF_3 (wt-%)	T_g [K]	T_0 [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
$T_{0.05}\text{OPS}$	10	201.2	213	2.7	371
$T_{0.1}\text{OPS}$	10	206.6	200	4.6	476
$T_{0.2}\text{OPS}$	10	209.4	136	2.9	1213
$T_{0.3}\text{OPS}$	10	212.6	139	10.7	1543
$T_{0.4}\text{OPS}$	10	218.9	215	0.36	553

4.2.3 T_{0.1}OPS Polymer Electrolytes Crosslinked by HCl

The T_xOPS polymer electrolytes each complexed with 10 wt-% LiSO₃CF₃ were optimized for the optimum mechanical properties as well as the highest conductivity as explained in the previous section. Among all, the polymer containing 10 mol-% crosslinker (T_{0.1}OPS) showed superior conductivity values with acceptable dimensional stability. This section mainly focuses on further optimization of the electrical properties by varying the salt concentration in the matrix. Two different lithium salts will be employed for this purpose namely, lithium triflate (LiSO₃CF₃) and lithium bis(trifluoromethanesulfone)imide (LiN(SO₂CF₃)₂) in order to study the effect of anion on the conductivity. To obtain the optimum doping concentration, salt-in-polymer electrolytes from 5 wt-% to 20 wt-% of the lithium salts were prepared and crosslinked by hydrochloric acid (HCl) as catalyst. The resultant polymer electrolytes were investigated by FT-IR (to determine the polymer salt interaction), DSC (effect of salt and crosslinking on the thermal properties) and impedance spectroscopy (ionic conductivity)

FT-IR Spectroscopy. The chemical structures of T_{0.1}OPS polymer electrolytes complexed with varying amounts of LiSO₃CF₃ and LiN(SO₂CF₃)₂ were investigated by FT-IR. **Fig. 4.11** gives the spectra of lithium triflate series, where the characteristic stretching signal of –Si-O-CH₃, which shows up at 904 cm⁻¹, was again the focus of interest to elucidate the crosslinking efficiency of the precursor polymer. The signal intensity decreased as expected but did not disappear totally, which indicated that there were still some functional groups not involved in the crosslinking process. Observing the same behavior for LiN(SO₂CF₃)₂, it can also be concluded that neither the type of salt nor the concentration had any effect on the course of sol-gel crosslinking, where the anion parts of the salts can in principle catalyze the sol gel crosslinking.

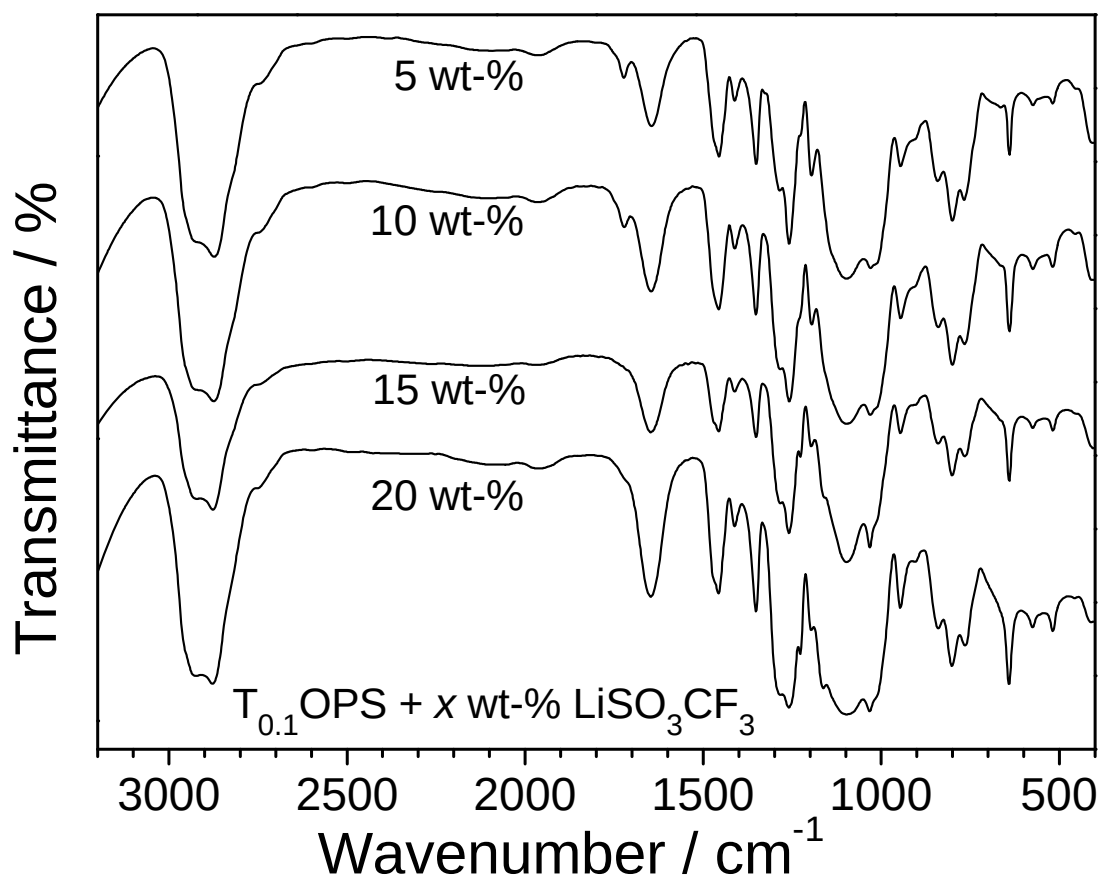


Fig. 4.11 FT-IR spectra of HCl crosslinked $T_{0.1}$ OPS polymer electrolytes with varying lithium triflate concentration.

The signal screened but seen as a shoulder at around 1136 cm^{-1} was again attributed to the ether signal. The interaction of lithium salt with the polymer using ether band could not be used due to the reasons as explained earlier for OPS polymer electrolytes.

Differential Scanning Calorimetry. Thermal properties of the polymer electrolytes were investigated using DSC up to $150\text{ }^{\circ}\text{C}$. The thermograms shown in **Fig. 4.12** clearly indicate that even a small amount of impurity was enough to hamper the crystallization of oligoether side chains seen for undoped precursor polymer as explained in the previous section. The as obtained polymer electrolytes were completely amorphous. For both type of salts, a gradual increase, as expected, in the T_g values was observed. The numerical values were listed in **Table 4.5** and **Table 4.6**. This increase can be attributed to both the formation of inter- or intermolecular transient crosslinks due to the coordination of

polymer segments to cations and the decrease in the free volume of the polymer matrix due to chemical crosslinking. Comparing the trends in the T_g changes for both noncrosslinked (**Table 4.2**) and HCl crosslinked (**Table 4.5**) polymer electrolytes, it can be concluded that the salt content has superior effect on these values than chemical crosslinking.

Moreover, the rise in T_g values of polymer electrolytes doped with lithium bis(trifluoromethanesulfone)imide was much smoother than that of lithium triflate. That means the former system shows relatively higher segmental mobility, thus should in principle facilitate the ion conduction more in a coarse approach.

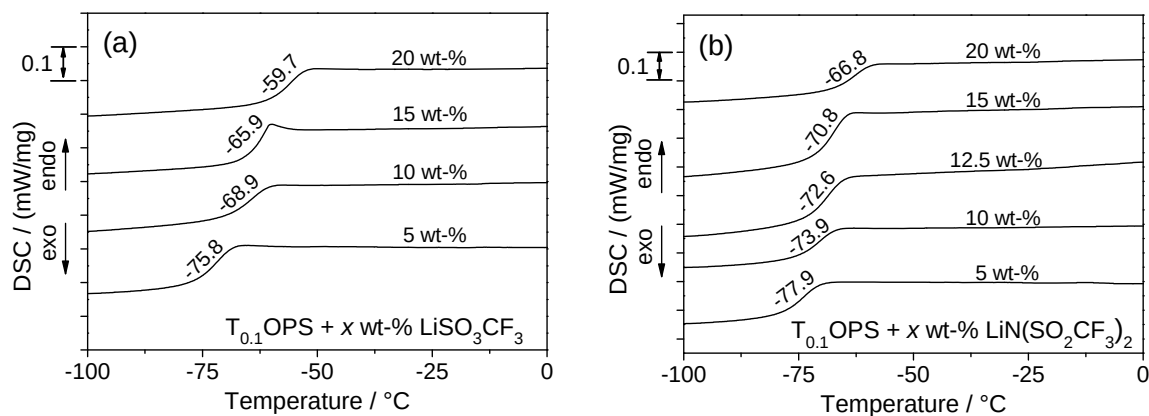


Fig. 4.12 DSC thermogram of $T_{0.1}OPS$ with varying amount of, (a) lithium triflate and (b) lithium bis(trifluoromethanesulfone)imide.

T- and Li- Salt Dependence of Conductivity. The ionic conductivities of the $T_{0.1}OPS$ based polymer electrolytes complexed with lithium bis(trifluoromethanesulfone)imide and lithium triflate were investigated using impedance spectroscopy in the temperature range from 30 °C to 90 °C under an atmosphere of dry nitrogen.

The temperature dependent ionic conductivities of both salt systems showed deviation from Arrhenius behavior as commonly observed for the amorphous polymeric materials, which were depicted in **Fig. 4.13** for $LiSO_3CF_3$ and **Fig. 4.14** for $LiN(SO_2CF_3)_2$ salt-in-polymer systems. The conductivity values for all temperatures and concentrations of both systems were given in Appendix 4.

The conductivity of best polymer electrolyte system based on $T_{0.1}OPS$ polymer, which was optimized according to the concentration of crosslinking groups as mentioned in the

previous section, was further optimized to determine the optimum salt concentration by varying the salt content. Electrical properties of this particular system was also investigated using another salt ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$) to look for the effect of increasing anion in the conductivity.

The transport of the ions in homogeneous polymer electrolytes was realized by solvation/dissociation and then migration. Ionic conductivity reflects the influence of these two processes in terms of free ion number, n_i , and the ionic mobility, μ_i , as follows:

$$\sigma(T) = \sum n_i \mu_i q_i \quad [4.2]$$

where q_i is the charge on each charge carriers. This equation can be used to understand the behavior of the electrolyte systems.

As clearly seen in the figures, the conductivity of the polymer increases as the amount of salt increases and peaks at an optimum concentration, here the optima for our system corresponded to 15 wt-% of LiSO_3CF_3 and 12.5 wt-% of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ as seen in the figures. Expected rise of the conductivity can be explained by the increase in the number of free ions with salt concentration according to equation [4.2]. Beyond the optimum, any increase in salt content results in higher ion aggregation and higher viscosity of the solution, which reduces both the free ion number and the ionic mobility, thus hinders the conductivity. This behavior of the lithium salt dependence of the conductivity was commonly observed for the polymer electrolytes [2, 70].

One of the attempts to increase the conductivity is to use salts with relatively large anions for the preparation of polymer electrolytes to enhance the dissociation. The effect of large anion was quite clear for the systems under consideration, where the conductivity in case of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ containing polymer electrolytes was higher as compared to the LiSO_3CF_3 based electrolytes (refer to Appendix 4 for numerical values). The increase in the conductivity is usually attributed to the fact that larger and especially fluorinated ions induce better ion pair formation, in addition to generating a larger free volume [2, 136]. This result was consistent with the DSC results discussed earlier.

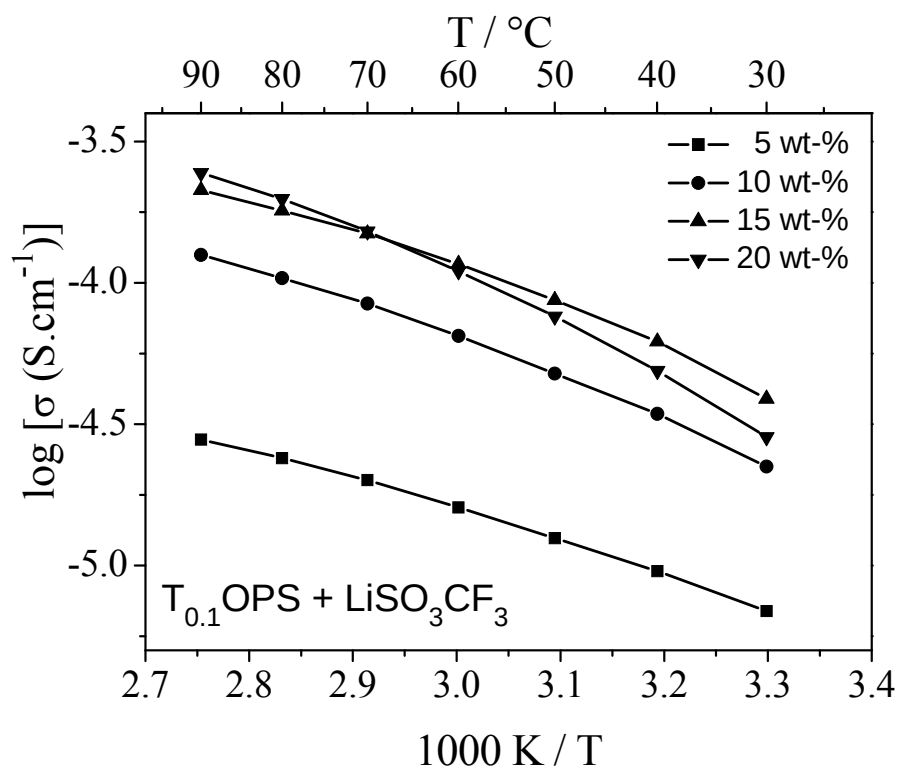


Fig. 4.13 Arrhenius plot of $T_{0.1}\text{OPS}$ with variable amount of LiSO_3CF_3 .

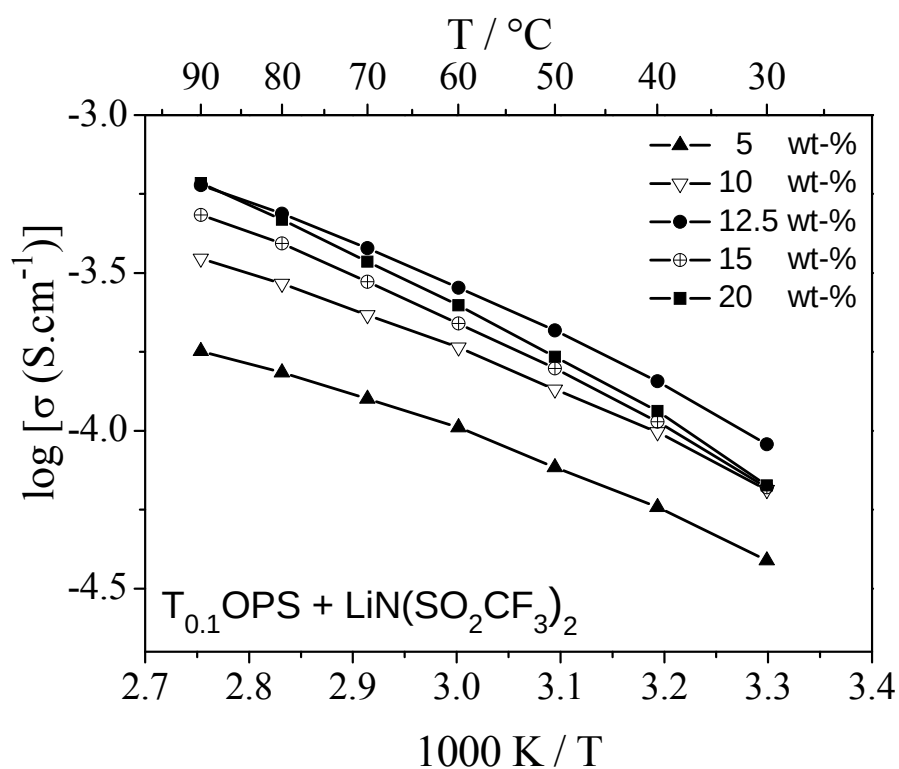


Fig. 4.14 Arrhenius plot of $T_{0.1}\text{OPS}$ with variable amount of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$.

The temperature dependence of the ionic conductivity of both polymer electrolyte systems can be fitted using the empirical VTF equation. The corresponding VTF parameters for both triflate and sulfonimide are summarized in **Table 4.5** and **Table 4.6** respectively. The T_0 values were not well below the T_g values but linear increase in pre factor σ_0 , which relates to the number of charge carriers in the system, with increasing salt concentration was observed. Although there was no regular expansion of the B value for triflate system, a regular increase of this pseudo activation energy containing term was detected for the latter case as seen in the Table below. This finding was not a surprise since an increase in salt concentration suggests an increase in the energy required to achieve ion transport.

Table 4.5 Glass transition temperatures (T_g) of $T_{0.1}$ OPS and its polymer electrolytes, ratios of O:Li for the corresponding wt-% of lithium triflate and fitting parameters of VTF equation to the temperature dependent conductivities.

LiSO ₃ CF ₃ (wt-%)	Ratio O:Li	T_g [K]	T_0 [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
0	–	189.6	–	–	–
5	52	197.4	185	0.45	493
10	26	204.3	204	2.2	454
15	17	207.3	231	1.65	270
20	13	213.5	216	5.7	462

Table 4.6 Glass transition temperatures (T_g) of $T_{0.1}$ OPS and its polymer electrolytes, ratios of O:Li for the corresponding wt-% of LiN(SO₂CF₃)₂ and fitting parameters of VTF equation to the temperature dependent conductivities.

LiN(SO ₂ CF ₃) ₂ (wt-%)	Ratio O:Li	T_g [K]	T_0 [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
0	–	189.6	–	–	–
5	96	195.3	213	1.8	345
10	48	199.3	198	6.7	487
12.5	38	200.6	195	18.1	572
15	32	202.4	190	20.7	650
20	24	206.4	180	53.3	821

4.2.4 $T_{0.1}$ OPS Polymer Electrolytes Crosslinked by DBTL

The optimum polymer electrolyte system, which was explored as $T_{0.1}$ OPS polymer after crosslinking by HCl, was further optimized for salt concentration and type in the previous section. In this section, dibutyltin dilaurate (DBTL) is the main focus of interest as an alternative catalyst to HCl for the sol-gel crosslinking to obtain polymer electrolytes using again the same precursor. The polymer electrolytes with varying amount of lithium triflate were crosslinked by DBTL to optimize the conductivity. The resultant polymer electrolytes were investigated again by FT-IR (to determine the polymer salt interaction), DSC (effect of salt and crosslinking on the thermal properties) and impedance spectroscopy (ionic conductivity).

FT-IR Spectroscopy. The chemical structures of $T_{0.1}$ OPS polymer electrolytes complexed with varying amount of LiSO_3CF_3 and crosslinked by DBTL were investigated by FT-IR. Representative FT-IR spectrum with 20 wt-% salt was given in **Fig. 4.15**.

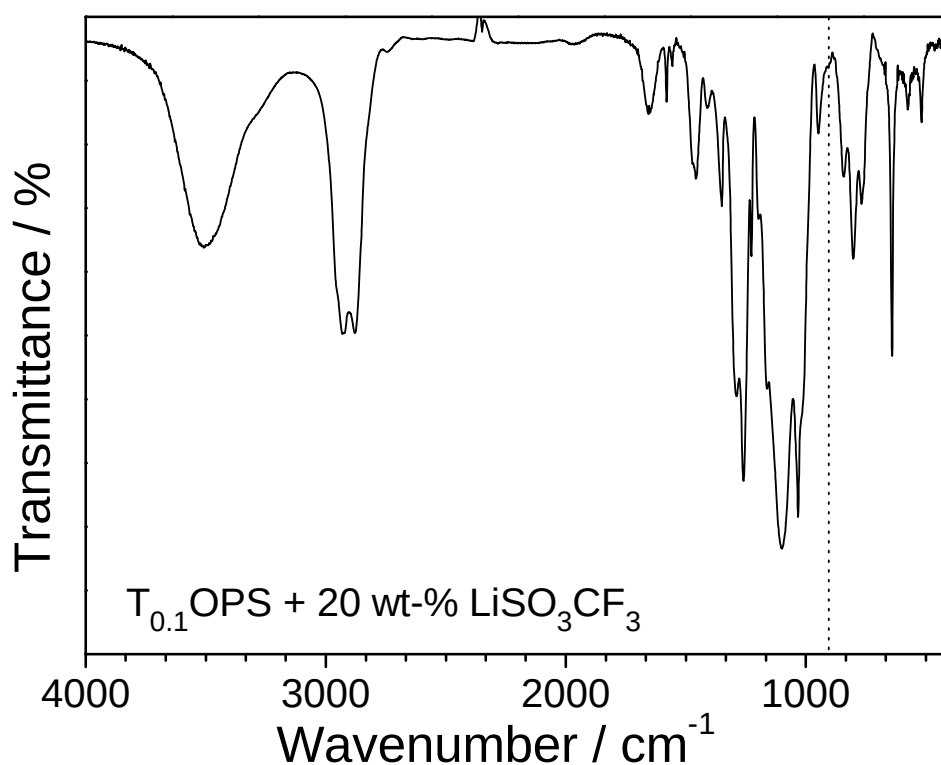


Fig. 4.15 Representative FT-IR spectra of $T_{0.1}$ OPS polymer electrolytes with 20 wt-% lithium triflate crosslinked by DBTL. Dotted line corresponds to 904 cm^{-1} .

The characteristic stretching signal of $-\text{Si-O-CH}_3$ at 904 cm^{-1} , which was signed as dotted line on the spectrum, was again monitored to judge the crosslinking efficiency of the precursor polymer.

The almost entirely vanishing of the signal indicated that these groups were extensively involved in the sol-gel crosslinking of the precursor, which was not the case for the same system crosslinked by HCl as discussed earlier.

Differential Scanning Calorimetry. Thermal properties of the polymer electrolytes were investigated. The polymers were stable up to $150\text{ }^\circ\text{C}$ with no primary transition belonging to the polymer. The very small transition detected around $0\text{ }^\circ\text{C}$, which was not observed for the other polysiloxanes studied up to now, was ascribed to the bulk catalyst (**Fig. 4.16**).

T_g values of the polymer electrolytes increased with increasing salt concentration and reached to $-57.8\text{ }^\circ\text{C}$ at $20\text{ wt-\%}$ salt. These values, as summarized in **Table 4.7**, were quite parallel to the results observed for the electrolytes crosslinked by HCl.

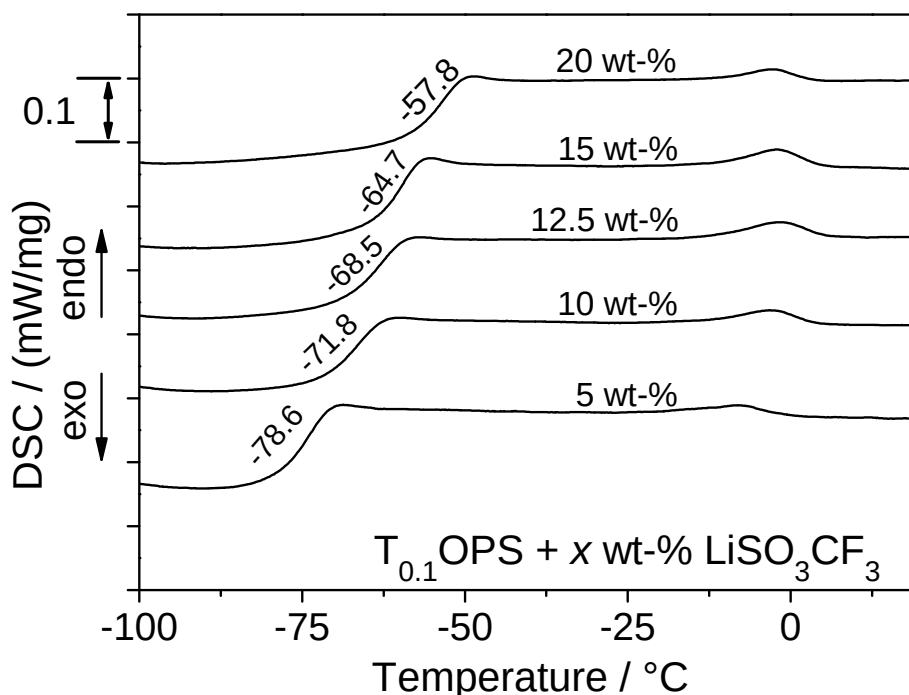


Fig. 4.16 DSC thermogram of $T_{0.1}\text{OPS}$ with varying amount of lithium triflate crosslinked by DBTL.

T- and Li- Salt Dependence of Conductivity. Impedance measurements were performed in the temperature range from -30 °C to 90 °C. The as obtained polymer electrolytes were free standing membranes and much more easy to handle as compared to the HCl crosslinked ones. The ionic conductivities were measured for lithium triflate up to 20 wt-% salt content.

The conductivity of the polymer increased as the amount of salt increased and reached to the optimum value at 15 wt-% lithium triflate salt and then decreased as depicted in **Fig. 4.17**.

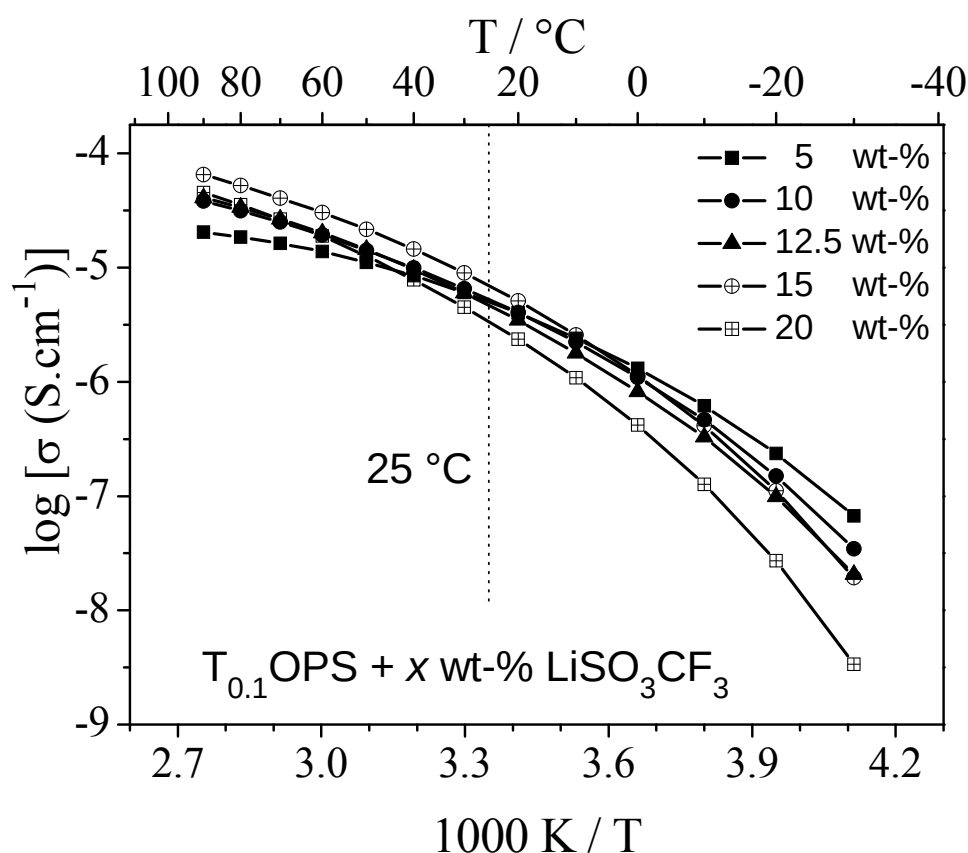


Fig. 4.17 Arrhenius plot of $T_{0.1}\text{OPS}$ with variable amount of LiSO_3CF_3 crosslinked by DBTL.

The optimum conductivity observed at 30°C was $7.3 \times 10^{-6} \text{ S/cm}$ that was almost 5 times lower than the conductivity value obtained for the same composition crosslinked by HCl. Considering the more dense structure of the DBTL crosslinked electrolytes as a result of more efficient crosslinking as clearly seen from the swelling experiment results (refer to **Table 4.8**). These conductivity results were acceptable as the contraction of the matrix due

to more efficient crosslinking probably diminished the free volume available for ion transport.

The ionic conductivity values of the electrolytes showed the maximum conductivity at -30 °C for 5 wt-% salt concentration, which shifted to the 15 wt-% as the temperature increased. The acceleration of the drop in the ionic conductivity at lower temperatures can be the result of higher viscosity of the system gained by the salt content, which relates inversely to the mobility of the ions by Stock-Einstein relation as well as the formation of ion pairs and higher aggregates [2]. The number and the mobility of the free ions, which relates to the conductivity according to equation 4.2, increased with temperature and the conductivities converged nearly at higher temperatures as expected.

The curved structure of the conductivity lines showed nonArrhenius behavior, which can be fitted by empirical VTF equation. **Table 4.7** gives the VTF parameters obtained for the polymer electrolytes, where the gradual increase of the σ_0 and B values was in good accordance with the concept of higher number of charge carriers and increase in the energy required for ion transport.

Table 4.7 T_g of $T_{0.1}OPS$ and its polymer electrolytes crosslinked by DBTL, ratios of O:Li for the corresponding wt-% of lithium triflate and fitting parameters of VTF equation to the temperature dependent conductivities.

LiSO ₃ CF ₃ (wt-%)	Ratio O:Li	T _g [K]	T ₀ [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
0	–	189.6	–	–	–
5	52	194.6	190	0.3	450
10	26	201.4	181	1.5	664
12.5	21	204.7	178	2.8	770
15	17	208.5	184	3.8	721
20	13	215.4	185	4.8	824

4.2.5 Final Commentary

A systematic study on the mono comb oligoether polysiloxanes was performed. The optimum structure for the study was determined to be $T_{0.1}OPS$ crosslinked by HCl, which

was further optimized according to salt concentration. The optimum conductivity values at 30 °C were found to be 3.9×10^{-5} S/cm for LiSO_3CF_3 and 9.1×10^{-5} S/cm for $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, which was lower than the noncrosslinked one as expected. The crosslinking by DBTL resulted in better control of crosslinking with more depressed conductivity values as shown in **Fig. 4.18**. Although the efficiency of the crosslinking by DBTL was detected by FT-IR measurements, the swelling experiment results of the polymer electrolytes were also useful for the characterization.

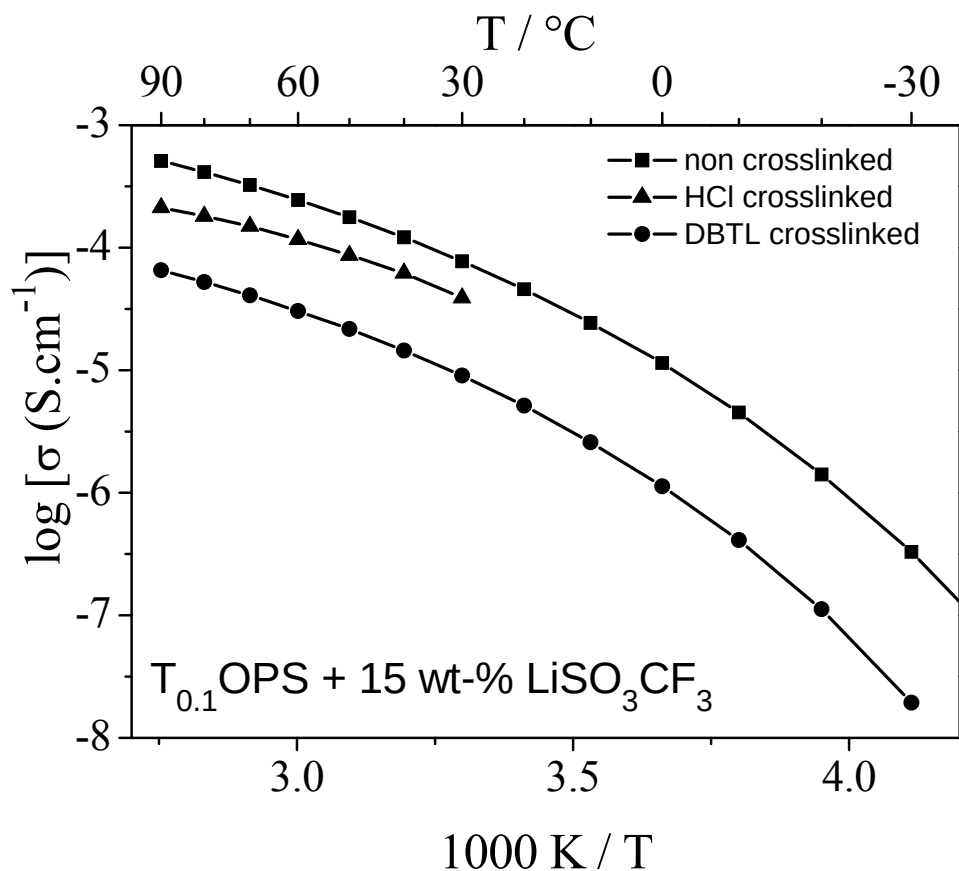


Fig. 4.18 Arrhenius plot of $T_{0.1}\text{OPS} + 15 \text{ wt-\% LiSO}_3\text{CF}_3$; noncrosslinked, crosslinked by HCl and DBTL

ASTM D2765-95 (Method-C) is used to determine the swelling ratio of the polymers. For each polymer sample three different measurements were performed and average values were recorded. The following formula was used to determine q (swelling ratio).

$$q = \frac{Wd + (Wg - Wd)K}{Wd} \quad [4.3]$$

where Wd and Wg are weight of dry and swollen samples respectively and K is the ratio of density of the solvent to the density of polymer. (Polymer densities were taken as 1 g/cm^3 for both samples). The results were summarized in **Table 4.8**. The polymer electrolyte crosslinked by HCl swollen nearly 3 times more than the one crosslinked by DBTL, which also indicated the loose structure of electrolyte obtained by HCl crosslinking.

Table 4.8 Swelling experiment results for $T_{0.1}$ OPS crosslinked by HCl and DBTL, q refers to swelling ratio.

Sample	q (in THF)
OPS (noncrosslinked)	soluble
$T_{0.1}$ OPS crosslinked by HCl	6.4
$T_{0.1}$ OPS crosslinked by DBTL	1.9

Noncrosslinked precursor polymer and the prepared polymer electrolytes by HCl and DBTL catalysts are shown in **Fig. 4.19**.

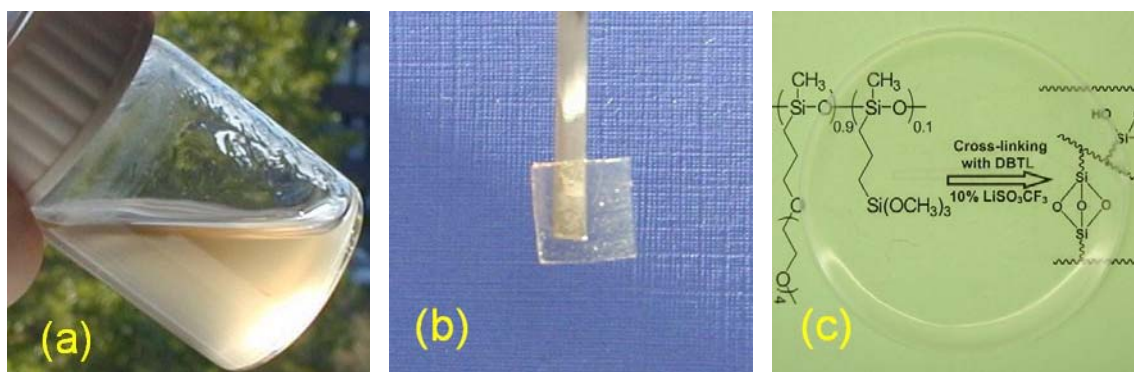


Fig. 4.19 Digital photographs of the Li^+ ion conducting polysiloxane polymer electrolytes (a) noncrosslinked $T_{0.1}$ OPS, (b) HCl crosslinked $T_{0.1}$ OPS, (c) DBTL crosslinked $T_{0.1}$ OPS.

Shortly, the crosslinking of the polymer increased the mechanical properties in both cases with the sacrifice in the conductivity values. The question now whether the conductivity of the polymer electrolytes can be further increased by heterogeneous particle dispersion or by low molecular solvents to attain the required high conductivity for the practical application. Moreover the effect of different side chains on the mechanical and electrical properties of the salt-in-polymer electrolytes will be investigated in order to have a more complete overview about the polymer electrolyte systems.

4.3 Longer Oligoether Substituted Polysiloxane (L-OPS) (6)

The earlier two sections involved the full characterization of noncrosslinked and crosslinked salt-in-polymer systems of short oligoether substituted polysiloxanes. The dimensional stability of the polysiloxanes was maintained by HCl and DBTL catalyzed sol-gel crosslinking with a little sacrifice in ionic conductivity. This section of the thesis will cover the long oligoether, namely APEG 350, substituted polysiloxane based polymer electrolyte systems to have more complete understanding of the effect of side chain on the mechanical and electrical properties of the polymer. The structure of the polymer is given in **Fig. 4.20**.

4.3.1 Characterization of L-OPS (6) Polymers

NMR Spectroscopy. The degree and the completeness of substitution were determined by ^1H NMR. The Si-H signal of the poly(methylhydrosiloxane) was again used to monitor the progress of the substitution reaction. As shown in **Fig. 4.20**, the disappearance of this distinctive signal as well as the newly formed propyl spacer (a,b and,c) in between polysiloxane backbone and oligoether side chains were clear indications of smooth substitution without any side reactions as explained in section 4.1.1 for OPS polymer.

FT-IR Spectroscopy. The completeness of substitution was also analyzed by the disappearance of the characteristic Si-H stretching of PMHS at 2167 cm^{-1} as clearly seen in **Fig. 4.22**.

Gel Permeation Chromatography. The GPC elution curve showed a single peak for the molecular weight distribution of the polymer (6) with a number average molecular weight (M_n) of 1.52×10^4 D and a polydispersity index of 2.12 using the calibration curve from the polystyrene standard (**Fig. 4.21**). The slightly high polydispersity of (6) can be attributed to the polydispersity of commercial PMHS with an average repeating unit of 35. Moreover the commercial PEG 350, which was used for the synthesis of the side chains, had the polydispersity index of 1.25 as determined from the MALDI-TOF measurement. The GPC chromatogram of the L-OPS was quite identical to that of OPS, and therefore the interpretations for OPS as explained in section 4.1.1 are also valid for L-OPS.

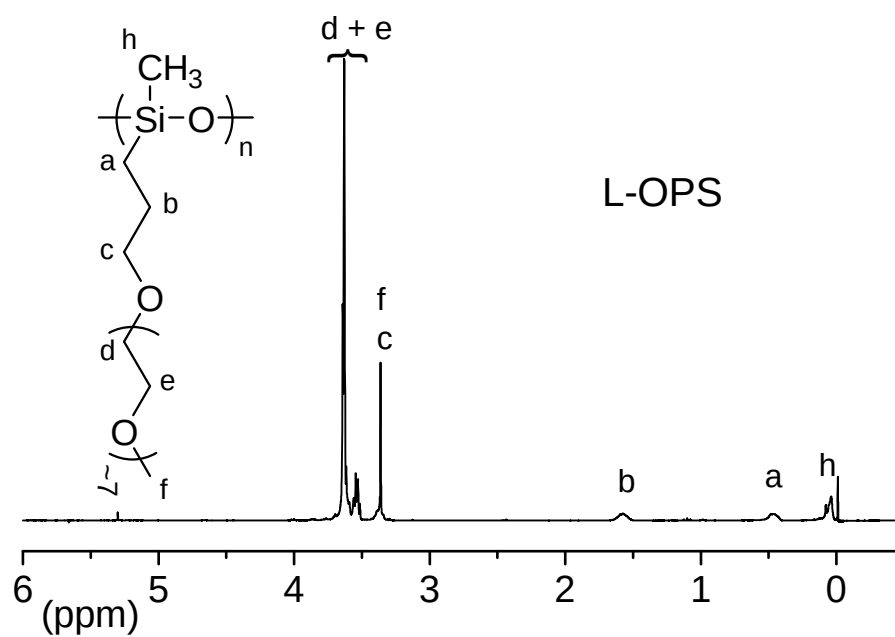


Fig. 4.20 ^1H NMR of Longer Oligoether Substituted Polysiloxane (L-OPS) (6).

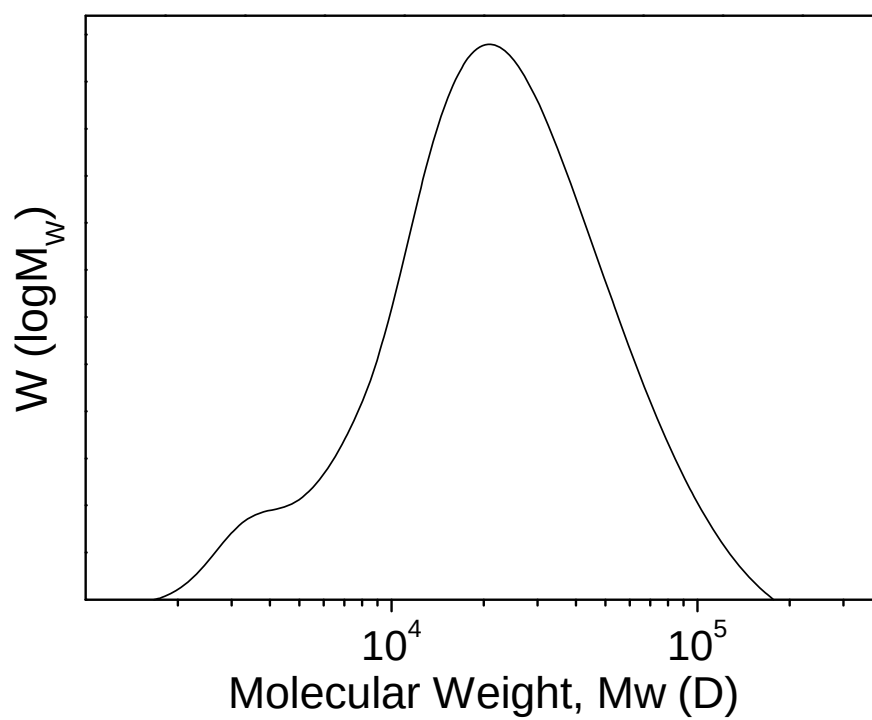


Fig. 4.21 GPC Chromatogram of L-OPS.

Differential Scanning Calorimetry. Thermal properties of the polymer were investigated using DSC in the temperature range of -150 °C to 150 °C. The polymer showed a very low T_g value of -78.1 °C as expected and was thermally stable in the measured range. A crystal melting temperature was detected at -5 °C as seen in **Fig. 4.23**. This behavior was also analogous to OPS polymer except here no extra crystallization was observed, which suggests that the crystallization was already accomplished while cooling.

4.3.2 L-OPS Polymer Electrolytes Crosslinked by HCl

L-OPS (**6**) was used to investigate for its lithium ion conducting properties by forming salt-in-polymer type of polymer electrolytes. Lithium triflate (LiSO_3CF_3) was used as electrolytic salt. The attempt to sol-gel crosslinking of the polymer trimethoxysilane co-substituted polysiloxane failed. The bulky oligoether might be preventing the relatively small crosslinking groups come together and condense. Therefore another strategy of crosslinking was utilized, in which the L-OPS polymer and salt was trapped in a 3D network of $T_{0.4}\text{OPS}$ crosslinked by HCl. The optimum conductivity and the mechanical properties of the polymer electrolytes, which was complexed with 10 wt-% lithium triflate as a preliminary experiment, was found for the one containing 20:80 weight composition of $T_{0.4}\text{OPS}$ to L-OPS and this composition was used for the preparation of the other polymer electrolytes in this section. The polymer (**6**) was doped with 5, 10, 12.5, 15, and 20 wt-%, which corresponds to the following molar ratios of the O atoms to lithium: $\text{O/Li} = 57$ (for 5 wt-% salt) to 14 (for 20 wt-% salt) (see also **Table 4.9**). The as obtained polymer electrolyte membranes were then investigated for thermal and electrical properties.

FT-IR Spectroscopy. The chemical structures of L-OPS polymer electrolytes complexed with varying amounts of LiSO_3CF_3 were investigated by FT-IR. The descent in the intensity of the characteristic stretching signal of $-\text{Si-O-CH}_3$ was in accordance with the results obtained earlier (see section 4.2.3). Moreover the broadening and shifting of the signal at 1100 cm^{-1} could be explained as the predominant interaction of the cationic part by oxygen atoms of the oligoether side groups as discussed in section 4.1.2.

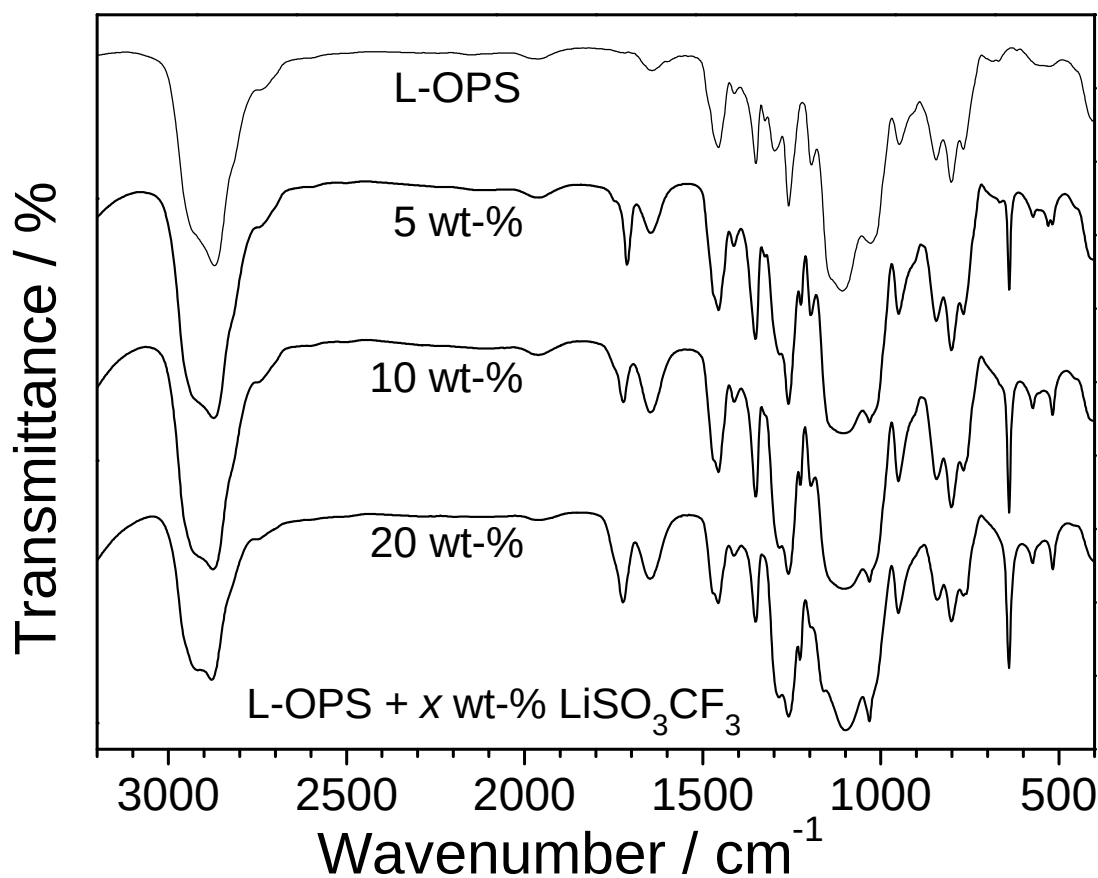


Fig. 4.22 FT-IR spectra of L-OPS and its polymer electrolytes for 5, 10 and 20 wt-% lithium triflate crosslinked by HCl.

Differential Scanning Chromatography. The DSC thermogram of L-OPS polymers polymer electrolytes were given in **Fig. 4.23**. The T_g values of the polymer electrolytes shifted incrementally from -78 °C up to -56 °C as a result of increasing transient crosslinks among the chains (also listed in **Table 4.9**). The expected melting signal due to self orientation of relatively longer side chains, which was even more extensive than the short chain derivative, became significantly smaller as the salt content increased and nearly vanished at 12.5 wt-% salt concentration since because increasing extent of coordination to the cations prevented the side chains to pack together. Beside the T_g values, no further transition peaks were observed at higher salt concentrations.

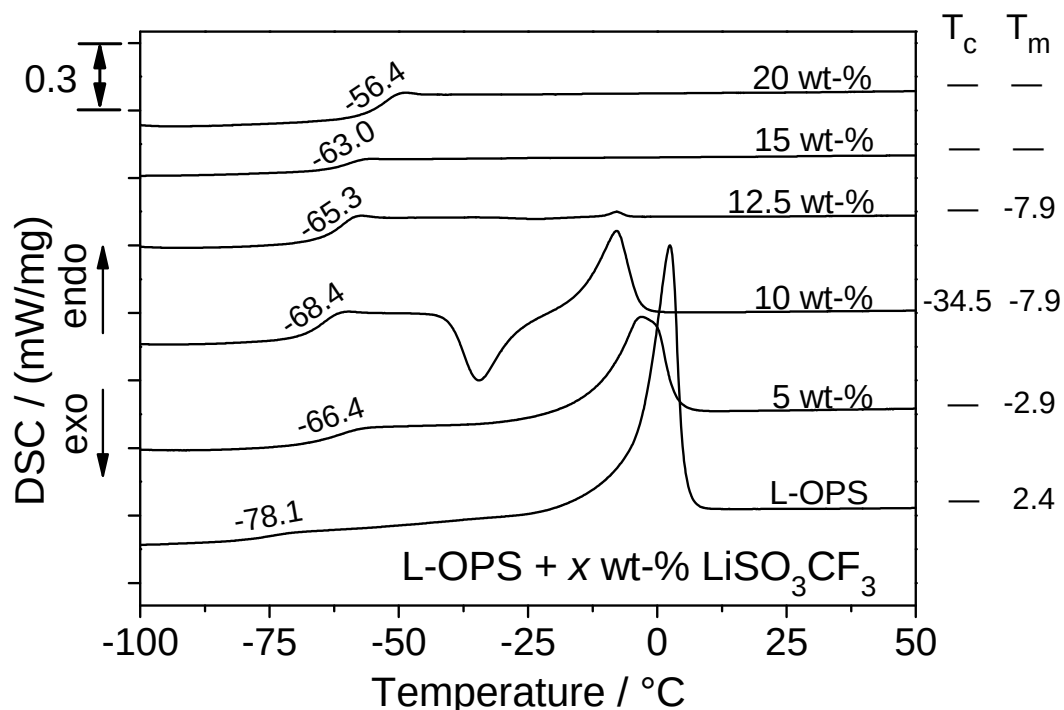


Fig. 4.23 DSC thermogram of L-OPS and its polymer electrolytes with varying amount of lithium triflate crosslinked by HCl.

T- and Li- Salt Dependence of Conductivity. The ionic conductivities of the L-OPS + lithium triflate polymer electrolytes were investigated using impedance spectroscopy in the temperature range from 30 °C to 90 °C under an atmosphere of dry nitrogen. The logarithm of the ionic conductivity is plotted versus the reciprocal temperature in an Arrhenius plot in **Fig. 4.24**. The polymer electrolytes showed a deviation from Arrhenius behavior as is found for most of the amorphous polymer electrolytes, indicating that the conductivity mechanism is coupled to the segmental motion of the polymer. The conductivity values for all temperatures and concentrations of both systems could be found in Appendix 4.

As clearly seen in the figure, the conductivity of the polymer increased with increasing salt content up to 10 wt-% salt concentration due to increase in free ions and then decreased above this concentration the conductivity tailed away as a result of ion aggregation and higher viscosity, thus decrease in the free ion number and the ionic mobility according to equation 4.2 as discussed earlier. 10 and 12.5 wt-% salt containing polymers showed similar ionic conductivity at 30 °C, implying that the optimum

conductivity lies in between these two concentrations, which corresponds to O:Li ratio of from 28 to 23 as inscribed in **Table 4.9**. This finding was in conformity with the optimum O:Li ratio of 24 reported by Hooper [35, 36].

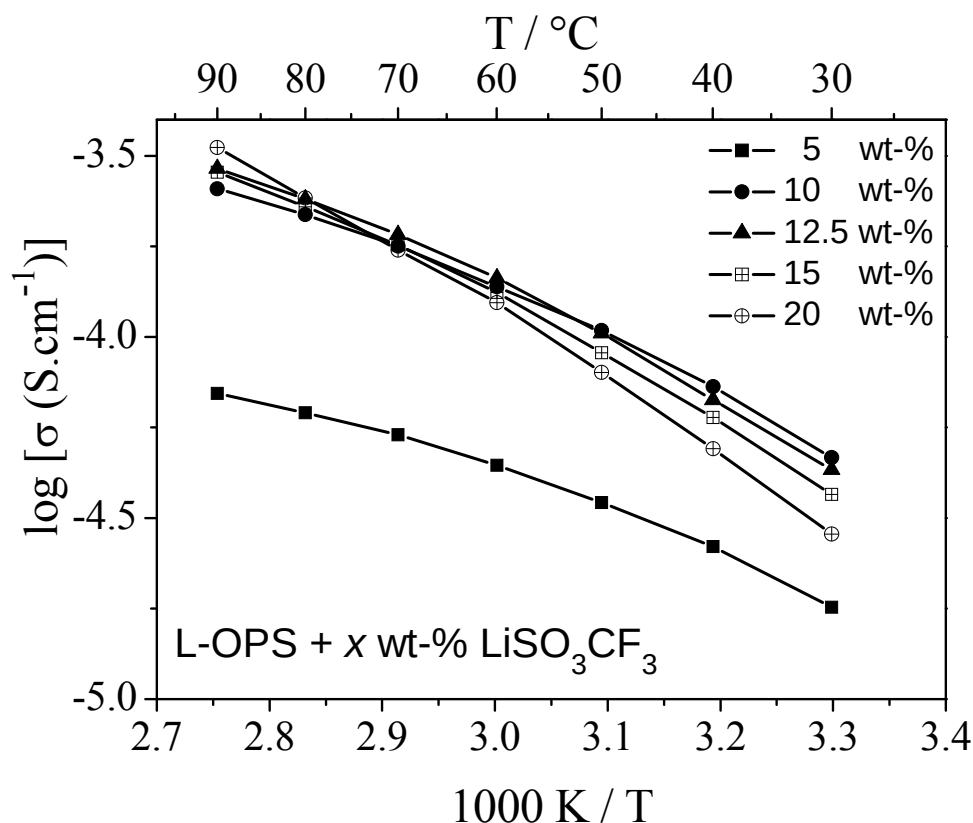


Fig. 4.24 Arrhenius plot of L-OPS with variable amount of LiSO_3CF_3 crosslinked by HCl.

The maximum conductivity value observed at 30 $^{\circ}\text{C}$ for 10 wt-% salt concentration, where viscosity and aggregates were dominant, shifted to 20 wt-% salt content at 90 $^{\circ}\text{C}$ due to additional energy acquired to dissociate higher aggregates and a decrease in the viscosity as explained in section 4.2.4.

The curved lines in the Arrhenius plot can be fitted by empirical VTF equation. The parameters obtained for the polymer electrolytes were tabulated in **Table 4.9**. The T_0 values determined by fitting were not 20-50 $^{\circ}\text{C}$ below the T_g values as usually expected for the polymer electrolytes but the gradual increase of the σ_0 and B values was in good

accordance with the presumed increase in the number of mobile charge carriers and energy barrier for the rotational motion of the polymer segments.

Table 4.9 *T_g of L-OPS and its polymer electrolytes crosslinked by HCl, ratios of O:Li for the corresponding wt-% of lithium triflate and fitting parameters of VTF equation to the temperature dependent conductivities.*

LiSO ₃ CF ₃ (wt-%)	Ratio O:Li	T _g [K]	T ₀ [K]	σ ₀ ×10 ³ [S·cm ⁻¹]	B [K]
	–	195.1	–	–	–
5	57	206.8	240	0.3	177
10	28	204.8	226	2.3	302
12.5	23	207.9	215	5.1	423
15	19	210.2	207	7.9	516
20	14	216.8	170	75.8	1050

4.3.3 Final Commentary

Long oligoether derivative of the polysiloxane was investigated in order to see the effect of longer side chains on the chemical and electrical properties of the polysiloxane polymer electrolytes. Comparable properties with respect to short chain derivative were observed accept the lack of sol-gel crosslinking ability, which was overcome by incorporating the polymer in T_{0.4}OPS polymer precursor. This long oligoether containing system imparted slightly better ionic conductivity than T_{0.1}OPS based polymer electrolytes, nevertheless the latter system can be favored in the sense of superior homogeneity and probable phase separation for the former one although there was none.

4.4 Poly(propylene oxide) Substituted Polysiloxane (PPO-PS) (8)

The preceding sections on polysiloxanes covered the properties of short ($n=4$) and longer ($n=7$) repeating unit oligoether functionalized polysiloxanes as polymer electrolytes. They showed rather encouraging results for ionic conductivity. Beside poly(ethylene oxide) systems, poly(propylene oxide) is one of the most extensively studied polymer electrolyte since it has amorphous structure. Thus, this concept is the main focus in the current section, where poly(methylhydrosiloxane) was functionalized by short chain propylene oxide with approximately 5 repeating units. The structure of the polymer is given in **Fig. 4.25**.

4.4.1 Characterization of PPO-PS Polymers

NMR Spectroscopy. The synthesized poly(propylene glycol) 340 allyl butyl ether (APPG 340) (7) was used to functionalize poly(methylhydrosiloxane). The degree of substitution was elucidated by ^1H NMR. As seen in **Fig. 4.25**, the substitution by propylene oxide was not complete as some of the Si-H groups at 4.7 ppm remained unreacted. The attempts by adding excess compound (7) at higher temperatures and longer

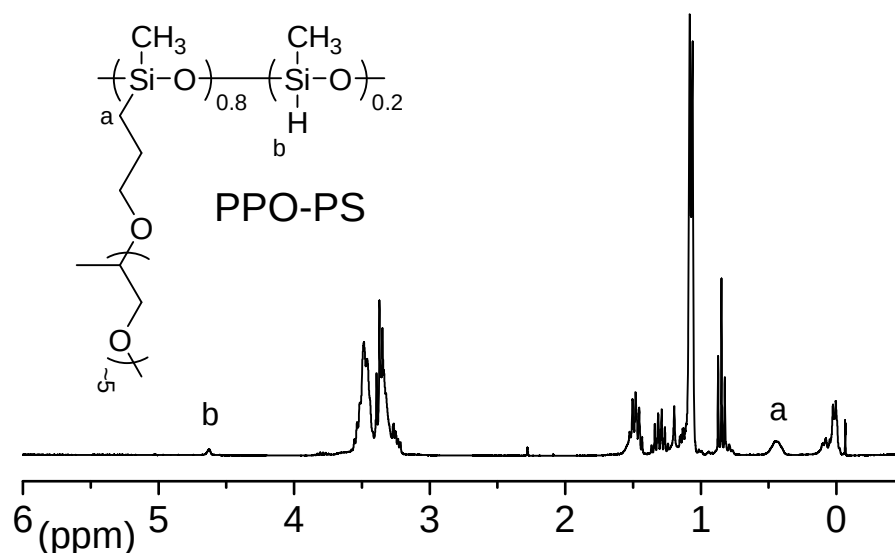


Fig. 4.25 ^1H NMR of Poly(propylene oxide) Substituted Polysiloxane (L-OPS) (8).

reaction times did not affect the course of substitution that could be on account of bulky nature of the side chains. From the relative peak integration of butyl group and Si-CH₂- (a) to Si-H (b) signal, the degree of substitution was found to be around 80 %. The chemical shifts for ¹H and ¹³C NMR were given in Appendix 3.

FT-IR Spectroscopy. The incomplete substitution pattern was also supported by the small characteristic Si-H frequency observed at 2155 cm⁻¹ as seen in **Fig. 4.26**.

Gel Permeation Chromatography. A single peak for the molecular weight distribution of the polymer (**8**) with a number average molecular weight (M_n) of 1.71×10^4 D and a polydispersity index of 1.72, which seemed to be in good agreement with the theoretical value calculated as 1.30×10^4 D but still the considerations for the comb like polymers as discussed previously should be considered as well. The GPC thermogram was quite similar to the ones obtained for the other polysiloxanes. Moreover, the attempt by MALDI-TOF measurement to define the exact molecular weight resulted in again fragmented low molecular species.

Differential Scanning Chromatography. The glass transition temperature of the polymer was decided by routine DSC measurement in the temperature range of -150 °C to 150 °C. The polymer showed a very low T_g value of -89.5 °C as expected (**Fig. 4.27**). A concomitant heating cycle up to 400 °C suggested that the polymer itself was stable up to 250 °C without decomposition and any further transitions.

4.4.2 PPO-PS Polymer Electrolytes

PPO-PS (**8**) was used to investigate for its lithium ion conducting properties by forming salt-in-polymer type of polymer electrolytes. The unreacted Si-H groups on the main skeleton was not further substituted for example by trimethoxysilane groups, since the sol-gel crosslinking could be prevented by the bulk nature of the propylene oxide side chain as it was the case for L-OPS polymer precursor but directly coupled with α , ω -diallyl poly(ethylene glycol) 600 (**9**) via hydrosilylation. The polymer (**8**) was complexed with 5, 10, 15 and 20 wt-%, which corresponds to the following molar ratios of the O atoms to lithium: O/Li = 46 (for 5 wt-% salt) to 12 (for 20 wt-% salt) (see also **Table 4.10**), where only 18 % of the oxygen was donated by ethylene oxide units (compound **9**). The obtained membranes were then investigated as polymer electrolytes using FT-IR, DSC, and impedance spectroscopy.

FT-IR Spectroscopy. Fig. 4.26 gives the FT-IR spectra of PPO-PS and its two representative polymer electrolytes doped with 10 and 20 wt-% lithium triflate. As seen in the figure, the typical signal of unreacted Si-H groups disappeared completely after complexation and crosslinking, indicating a successful preparation of the electrolytes. Moreover, the shift in the characteristic ether signal at 1136 cm^{-1} indicated a similar ion interaction with the side chains as already discussed in the previous sections.

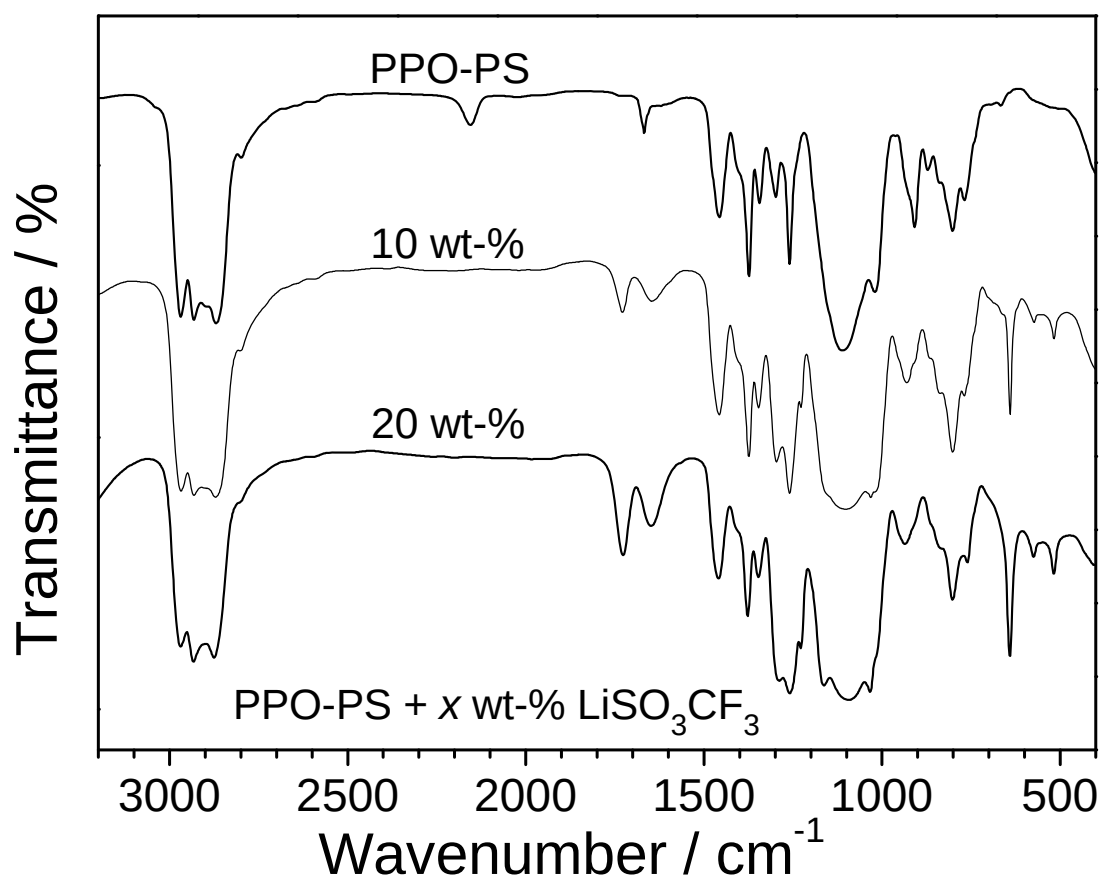


Fig. 4.26 FT-IR spectra of PPO-PS and its polymer electrolytes for 10 and 20 wt-% lithium triflate.

Differential Scanning Chromatography. The thermal properties of the polymer electrolytes were investigated by DSC in the temperature range from $-150\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ and the T_g values were listed in **Table 4.10**. The polymer electrolytes were stable within the range and exhibited only second order transition (**Fig. 4.27**). The PPO-PS showed only a clear transition at $-89\text{ }^{\circ}\text{C}$. However another phase was gradually formed with increasing

salt concentration at around $-45\text{ }^{\circ}\text{C}$. The transition at 15 wt-% salt was observed as a very broad signal over a temperature range from $-89\text{ }^{\circ}\text{C}$ to $-45\text{ }^{\circ}\text{C}$. The similar behavior for the propylene oxide (PPG 340) functionalized polyphosphazene doped with lithium triflate, where the broad transition was observed at 10 wt-% salt concentration [129]. This behavior indicates that the electrolyte is multiphase with at least two distinct amorphous phases having different LiSO_3CF_3 concentrations. The comparable result was also reported for alkyl amino substituted polyphosphazene doped with LiClO_4 with an additional melting endotherm due to possible salt ion pair crystalline region [137]. Moreover, this transition point at 15 wt-% salt content corresponds to O:Li ratio of 15 (see **Table 4.10**), which is presumably the highest concentration for small lithium in this particular system since it allows no more than four solvent molecules in its solvation sheath [2]. Hence above this concentration, the polymer host could suffer from the lack of coordination sites, which is also in conformity with the conductivity results as discussed below.

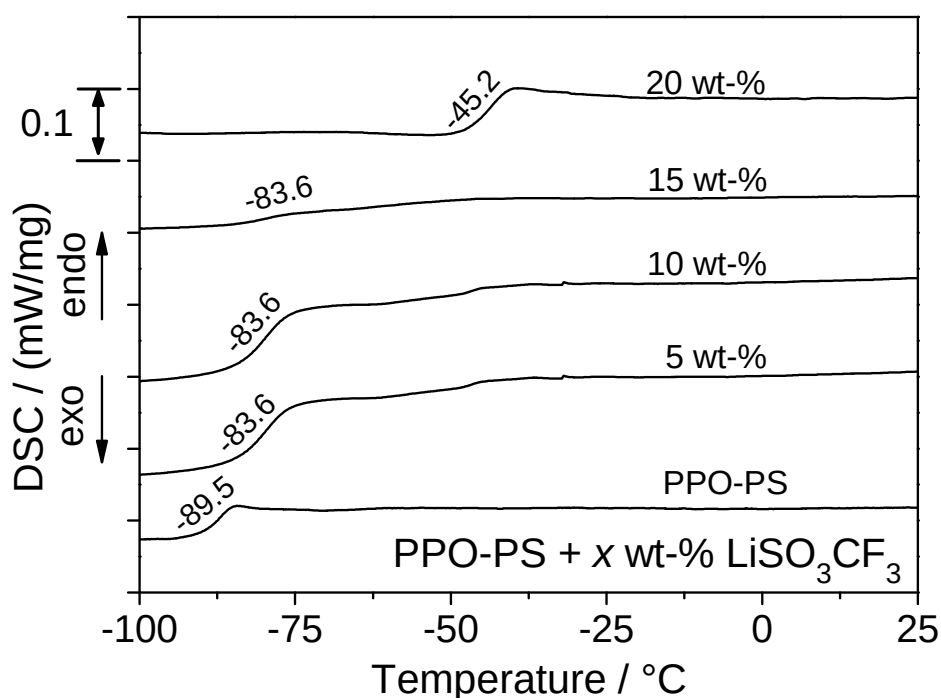


Fig. 4.27 DSC thermogram of PPO-PS and its polymer electrolytes with varying amount of lithium triflate.

T- and Li- Salt Dependence of Conductivity. The ionic conductivity of the PPO-PS + LiSO_3CF_3 polymer electrolytes were scanned from 30 °C to 90 °C under inert atmosphere of nitrogen. Temperature dependent ionic conductivity plots were rather linear with only slight curvature in the temperature range studied, which pointed out almost Arrhenius behavior, in other words polymer decoupled motion of the ions through the matrix as illustrated in the figure below. The rise in the concentration of lithium triflate resulted in increase in the number of free ions whereby the conductivity increased. This obvious trend continued up to 15 wt-% salt content and then stabilized. The saturation of

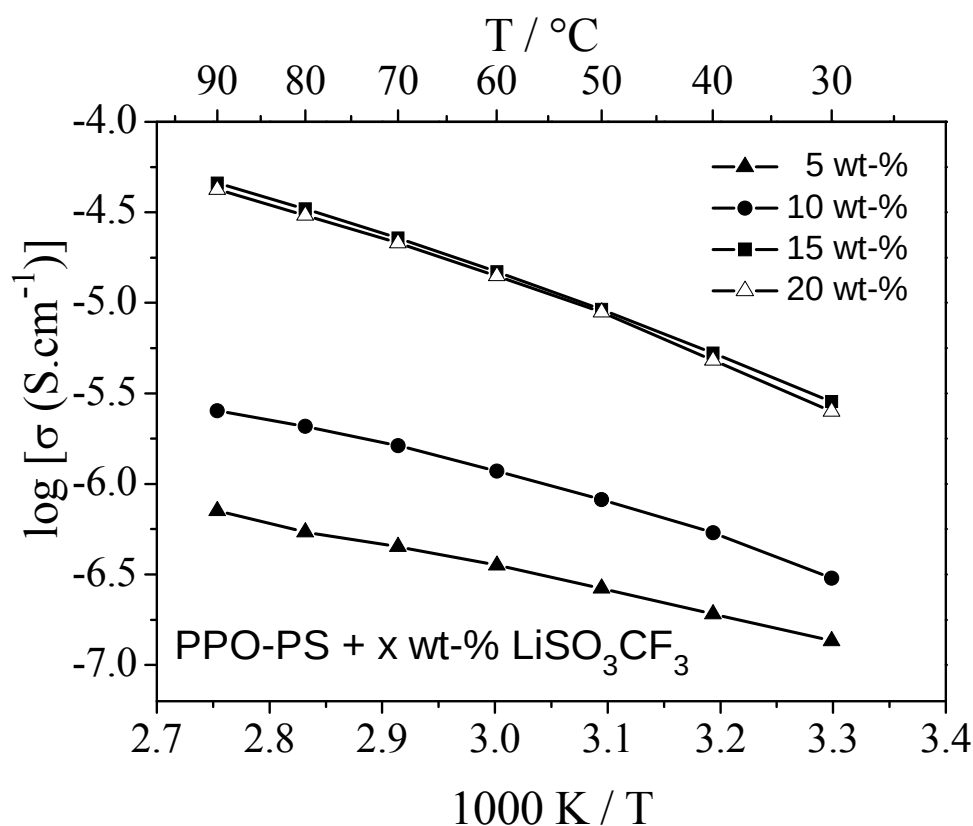


Fig. 4.28 Arrhenius plot of PPO-PS + LiSO_3CF_3 polymer electrolytes.

the coordinating sites accompanied by an increase in viscosity and larger aggregates could be the reason of slight decrease in the conductivity. The optimum conductivity value obtained at 15 wt-% salt concentration was $2.85 \times 10^{-6} \text{ S/cm}$ and in perfect agreement with the reported value of $2.0 \times 10^{-6} \text{ S/cm}$ for the similar architecture designed by polyphosphazene as the polymer backbone [129].

The VTF parameters evaluated from the linear fits for the salt-in-polymer electrolytes were listed in **Table 4.10**. There was no tendency for the calculated T_0 values as usually expected for the polymer electrolytes to be 20-50 °C lower than the T_g values. The inconsistency continued also for the σ_0 and B parameters but in general they increased up to optimum salt concentration, followed by a decrease due to probably the ion pairing leading to a decrease in number of free ion, σ_0 , and thus an increase in the energy required to achieve ion transport as expected.

Table 4.10 T_g of PPO-PS and its polymer electrolytes, ratios of O:Li for the corresponding wt-% of lithium triflate and fitting parameters of VTF equation to the temperature dependent conductivities.

LiSO ₃ CF ₃ (wt-%)	Ratio O:Li	T_g [K]	T_0 [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
0	–	183.7	–	–	–
5	46	189.6	140	0.1	940
10	23	189.9	227	0.1	369
15	15	189.8	173	19.6	1151
20	12	228.0	200	5.4	792

4.4.3 Final Commentary

APPG 340 functionalized polysiloxane was examined in order to see the effect of propylene oxide side chain on the chemical and electrical properties of the electrolytes. The conductivity values observed for PPO-PS based polymer electrolytes were in general more depressed than the ones obtained for polysiloxane systems studied up to here. The salt-in-polymer electrolytes having different structural architecture let us to have an overall view about the electrical properties of the electrolytes. Further enhancement in the mechanical and electrical properties of each system can be achieved by incorporation of oxide nano particles or low molecular weight solvents.

4.5 T_{0.1}OPS Based Blends

In the preceding sections, chemical, structural and electrical properties of polysiloxanes with different structural architectures, i.e. short and longer oligoether and propylene oxide as side chain, were studied extensively. Among these salt-in-polymer systems, T_{0.1}OPS based polymer electrolytes crosslinked by DBTL possessed superior properties in terms of stability, structural homogeneity and conductivity. The optimum conductivity was reached at 15 wt-% triflate concentration on the limit of 10^{-5} S/cm, which still lies below the required conductivity value of 10^{-3} S/cm for practical applications. One of the general approaches to enhance the conductivity value and mechanical properties further is to prepare blends with inorganic fillers or low molecular weight solvents. Therefore this chapter focuses on this aspect forming blends based on the optimum polysiloxane polymer electrolyte, which was T_{0.1}OPS + 15 wt-% LiSO₃CF₃ crosslinked by DBTL. For simplicity, T_{0.1}OPS-LiSCF₁₅ is used as acronym for T_{0.1}OPS polymer precursor complexed with 15 wt-% LiSO₃CF₃ throughout this section.

4.5.1 Al₂O₃ and SiO₂ Composites of T_{0.1}OPS

One of the effective ways to attain higher conductivities while retaining good mechanical properties is to add inorganic fillers as a third component. This approach was widely applied to poly(ethylene oxide) based polymer electrolytes [13, 14]. Although a direct relation with increasing filler content was generally mentioned, the optimum concentration of this component varied over a wide range. The conductivity enhancement was obtained, for example, at around 10 wt-% for poly(ethylene oxide) based polymer electrolyte composites by many authors [13, 14, 138, 139]. There the common agreement in the conductivity enhancement is a decrease in polyether crystallinity, although Wieczorek et al. [140] reported the change in conductivity resulted from acid-base type interactions involving polyether oxygens and filler acid or base centers. On the other hand, the addition of filler to the completely amorphous polyphosphazene resulted in a decrease or a negligible change in the conductivity results with an optimum filler content of 2.5 wt-% [141, 142]. These results open now a question whether the effect of filler is strongly dependent to the morphological properties of the studied system. Hence the present work is aimed to study the effect of nano sized SiO₂ (7 nm) and Al₂O₃ (40 nm).

Thermal Properties of Composites by DSC. The glass transition temperatures, T_g , of both Al_2O_3 and SiO_2 composite polymer electrolytes obtained from DSC measurements are listed in **Table 4.11**. The composites were stable within the temperature range studied up to $150\text{ }^\circ\text{C}$ and no first order transitions were observed except for the one around $0\text{ }^\circ\text{C}$ due to the bulky catalyst as discussed before. The DSC thermograms are given in **Fig. 4.29**. The T_g value of $\text{T}_{0.1}\text{OPS-LiSCF}_{15}$ was found as $-64.7\text{ }^\circ\text{C}$ as seen in figures and neither Al_2O_3 nor SiO_2 addition caused a perceivable change indicating that the coordination between Li^+ ion and polysiloxane was not significantly effected by the third component.

T- and Li- Salt Dependence of Conductivity. **Fig. 4.30** shows the Arrhenius plots of the temperature dependence of $\text{T}_{0.1}\text{OPS-LiSCF}_{15}$ composite polymer electrolytes for both Al_2O_3 and SiO_2 . The conductivity for particle free polymer electrolyte is also given for comparison. The numerical values of conductivities could be found in Appendix 4.

As seen in **Fig. 4.30 (a)**, the maximum enhancement in the conductivity of Al_2O_3 added composite polymer electrolytes were observed at 8 wt-% filler content, but no significant increase in the conductivity as compared to the alumina free polymer electrolytes was attained. The overall decrease in the conductivity cannot be attributed to the restricted segmental motion of the polymer host, since the glass transition temperatures of the polymer host remained almost constant as discussed above. The lengthening of conduction pathway due to the phase separation between polymer host and alumina particles seemed to be more responsible for this behavior. The increase in the concentration of alumina in the host causes the dilution of the polymer matrix as well as an increase in the pathway for the conduction, which is most probably the reason for the drop in the conductivity overall. Moreover the surface properties of the particle has crucial effect on the electrical properties, since it may form acid-base type interaction with polymer chains and salt in the matrix as explained by Wieczorek for poly(ethylene oxide) based polymer electrolytes [143-146]. The initial increase among the alumina containing composites could be therefore due to the interaction of alumina with the salt to promote ion dissociation, thus the number of free ions leading to an increase in conductivity to some extent [14]. On the other hand, the conductivity started decreasing again when 8 wt-% alumina concentration was reached. This trend could be explained by a great increase in the interaction between ions and the surface of the fillers in addition to the adsorption like process taking place at the surface as reported by Liu, which is accompanied by an increase in lithium

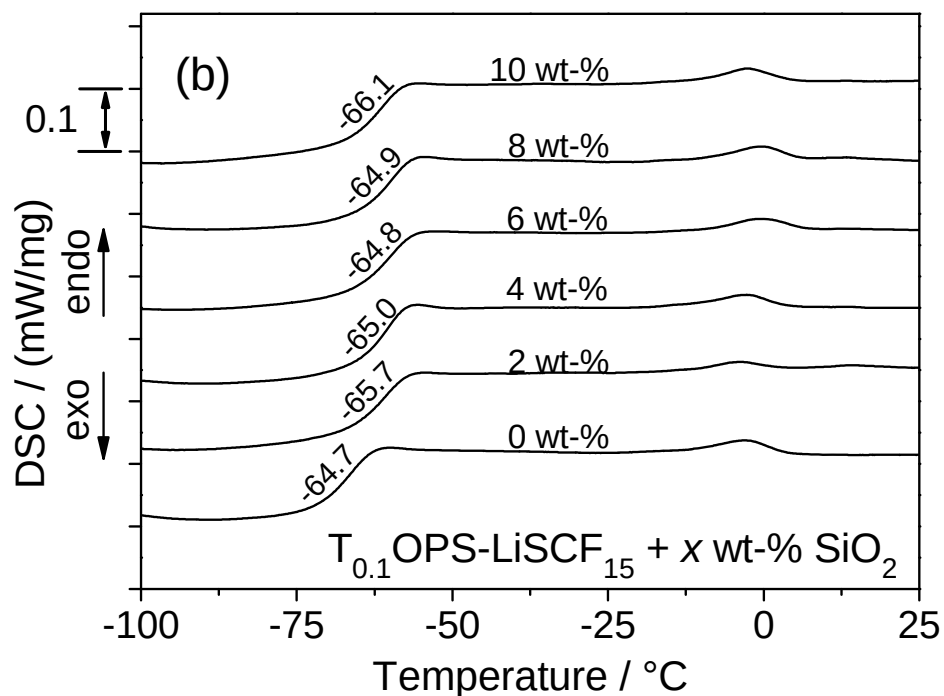
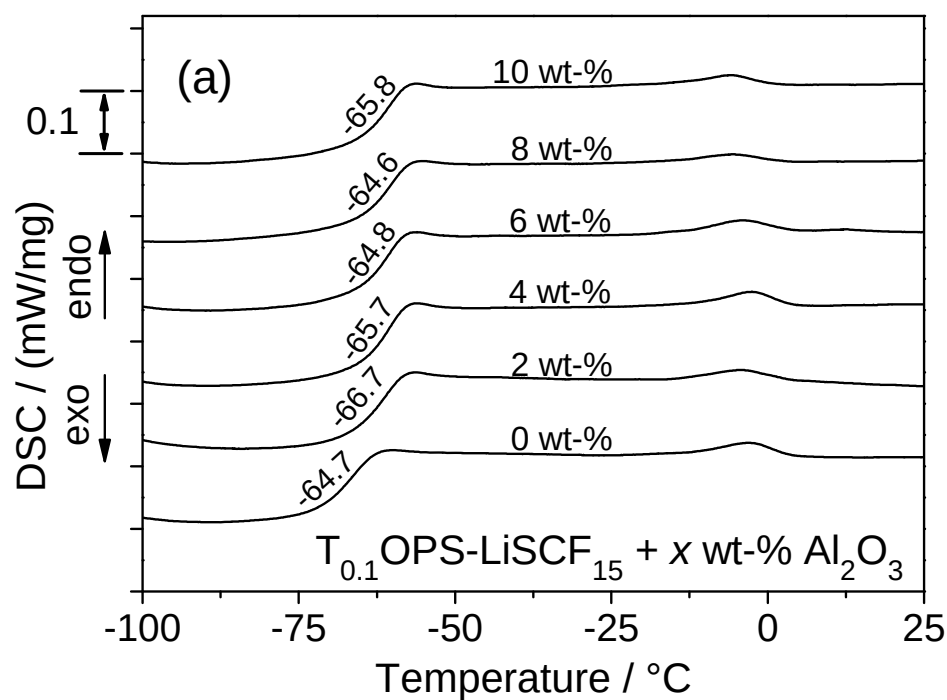


Fig. 4.29 DSC thermogram of $T_{0.1}\text{OPS-LiSCF}_{15}$ composite polymer electrolytes with (a) Al_2O_3 , (b) SiO_2 . LiSCF_{15} in the figure indicates 15 wt-% LiSO_3CF_3 .

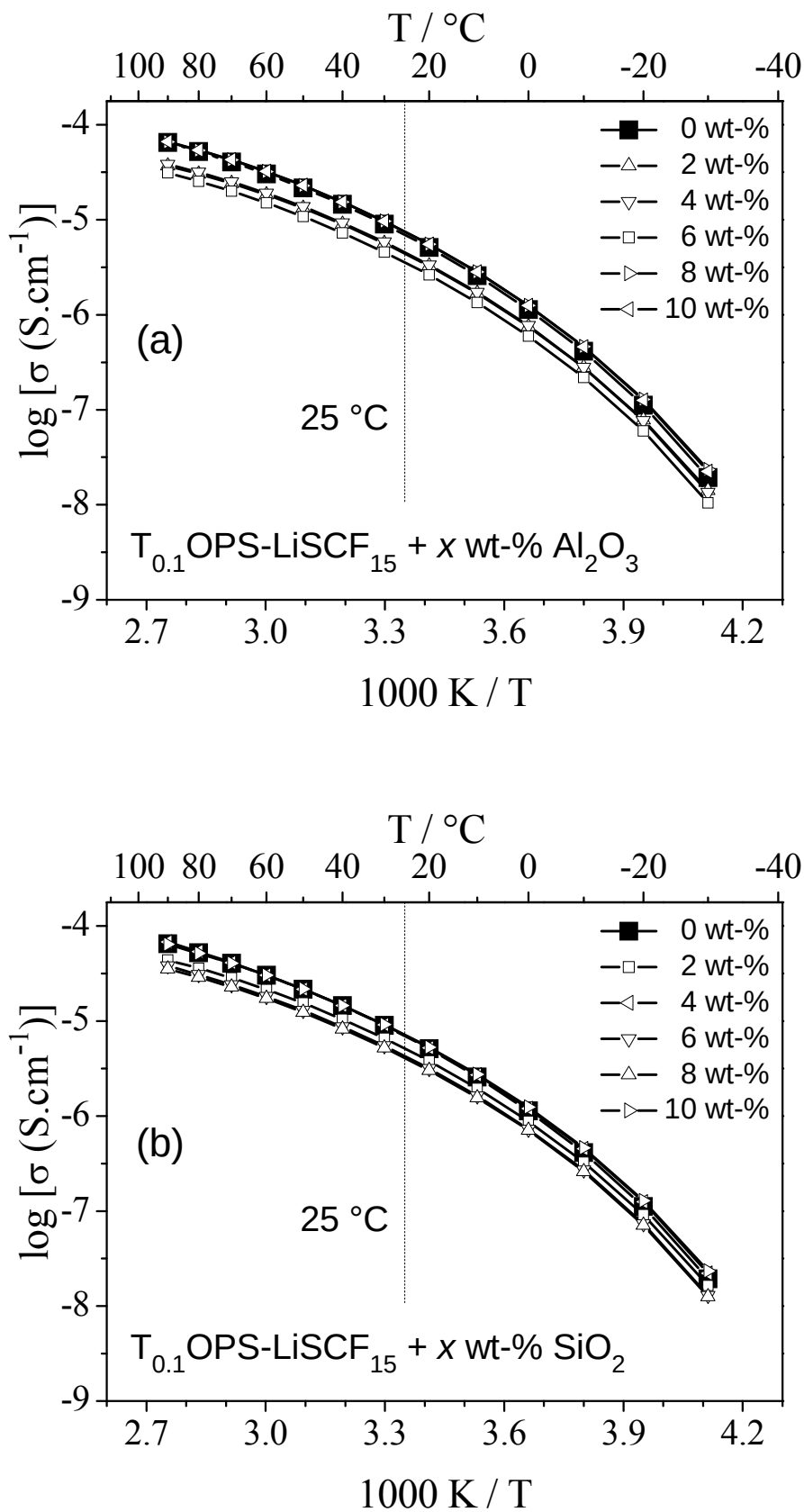


Fig. 4.30 Arrhenius plot of $T_{0.1}\text{OPS-LiSCF}_{15}$ composite polymer electrolytes with (a) Al_2O_3 , (b) SiO_2 . LiSCF_{15} in the figure corresponds to 15 wt-% LiSO_3CF_3 .

transference number [147]. The similar behavior was also reported in the sense of transference number for nano particle embedded polyphosphazenes in our group [129]. From all, it can be concluded that the initial increase in the conductivity accompanied by a decrease after an optimum was reached, which was in any case lower than the conductivity value obtained for particle free electrolyte could be a compromise among the explanations given above.

The effect of SiO_2 was also not much different from Al_2O_3 as seen in **Fig. 4.30** (b). The maximum enhancement in the conductivity was observed at 4 wt-% silica content and then tailed away similarly. This maximum can be explained by the relatively high surface area of finer silica particles as compared to alumina. The reasoning for alumina incorporated composite polymer electrolytes is also valid for the samples with silica particles.

Table 4.11 T_g of $T_{0.1}\text{OPS-LiSCF}_{15}$ and its composite polymer electrolytes with Al_2O_3 and SiO_2 , and fitting parameters of VTF equation to the temperature dependent conductivities.

Polymers	Al_2O_3 (wt-%)	T_g [K]	T_0 [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
$T_{0.1}\text{OPS-LiSCF}_{15}$	0	208.5	184	3.8	721
$T_{0.1}\text{OPS-LiSCF}_{15}$	2	206.6	185	1.8	685
$T_{0.1}\text{OPS-LiSCF}_{15}$	4	207.5	187	1.9	677
$T_{0.1}\text{OPS-LiSCF}_{15}$	6	208.4	185	1.6	695
$T_{0.1}\text{OPS-LiSCF}_{15}$	8	208.6	185	3.3	692
$T_{0.1}\text{OPS-LiSCF}_{15}$	10	207.4	185	3.4	696

Polymers	SiO_2 (wt-%)	T_g [K]	T_0 [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
$T_{0.1}\text{OPS-LiSCF}_{15}$	0	208.5	184	3.8	721
$T_{0.1}\text{OPS-LiSCF}_{15}$	2	207.5	185	2.2	686
$T_{0.1}\text{OPS-LiSCF}_{15}$	4	208.2	183	3.8	725
$T_{0.1}\text{OPS-LiSCF}_{15}$	6	208.4	185	1.9	692
$T_{0.1}\text{OPS-LiSCF}_{15}$	8	208.3	185	1.8	690
$T_{0.1}\text{OPS-LiSCF}_{15}$	10	207.1	184	3.3	702

The temperature dependence of ionic conductivity was again fitted by empirical VTF equation, and the parameters were listed in **Table 4.11**. The T_0 values were all approximately 20 °C lower than the T_g values determined by DSC and remained unchanged as also experimentally proved. The pseudo activation energy containing term B was also not effected by the addition of particles indicating that there was no considerable change in the ion conduction mechanism.

4.5.2 $T_{0.1}$ OPS-Borate Esters (B2 and B3); Gel Electrolytes.

Another way to improve the ionic conductivity of a polymer electrolyte is to add low molecular weight nonprotic organic solvents such as ethylene carbonate, propylene carbonate, dialkyl carbonate or their mixtures, which serve as plasticizer. Borate esters are also interesting compounds since they can be used as plasticizer as well as Lewis acid that can trap the anions leading to an increase in lithium transference number which is usually below 0.3 [70, 148, 149]. Therefore the effect of tris(2-(2-methoxyethoxy)ethyl) borate (B2) and tris(2-(2-(2-methoxyethoxy)ethoxy)ethyl) borate (B3) on electrical properties of the $T_{0.1}$ OPS-LiSCF₁₅ polymer electrolytes will be the main focus on this part. The polymer electrolytes were loaded to the limit (40 wt-% for both), where the membranes could be peeled out of the polypropylene moulds.

Thermal Properties by DSC. The thermal properties of the gel electrolytes were scanned in the temperature range up to 150 °C. They were completely amorphous with pretty low T_g values as listed in **Table 4.12**. The T_g value of borate ester free electrolyte, which was determined to be -64.7 °C, decreased gradually to -68.3 °C with the addition of B2 and -77.1 °C when B3 added as clearly seen in **Fig. 4.31**. These results showed that B3 was more efficient as plasticizer and therefore would in principle contribute more to the conductivity value as it reduced the viscosity of the system to a greater degree.

T- and Li- Salt Dependence of Conductivity. Arrhenius plots of the temperature dependence of $T_{0.1}$ OPS-LiSCF₁₅ based gel electrolytes doped with B2 and B3 each was given in **Fig. 4.32**. The conductivity for borate ester free polymer electrolyte is also plotted for comparison. The numerical values of conductivities could be found in Appendix 4.

The ionic transport in a gel electrolyte can be achieved by fast and slow diffusive motion of the low molecular weight component and segmental motion of polymer matrix

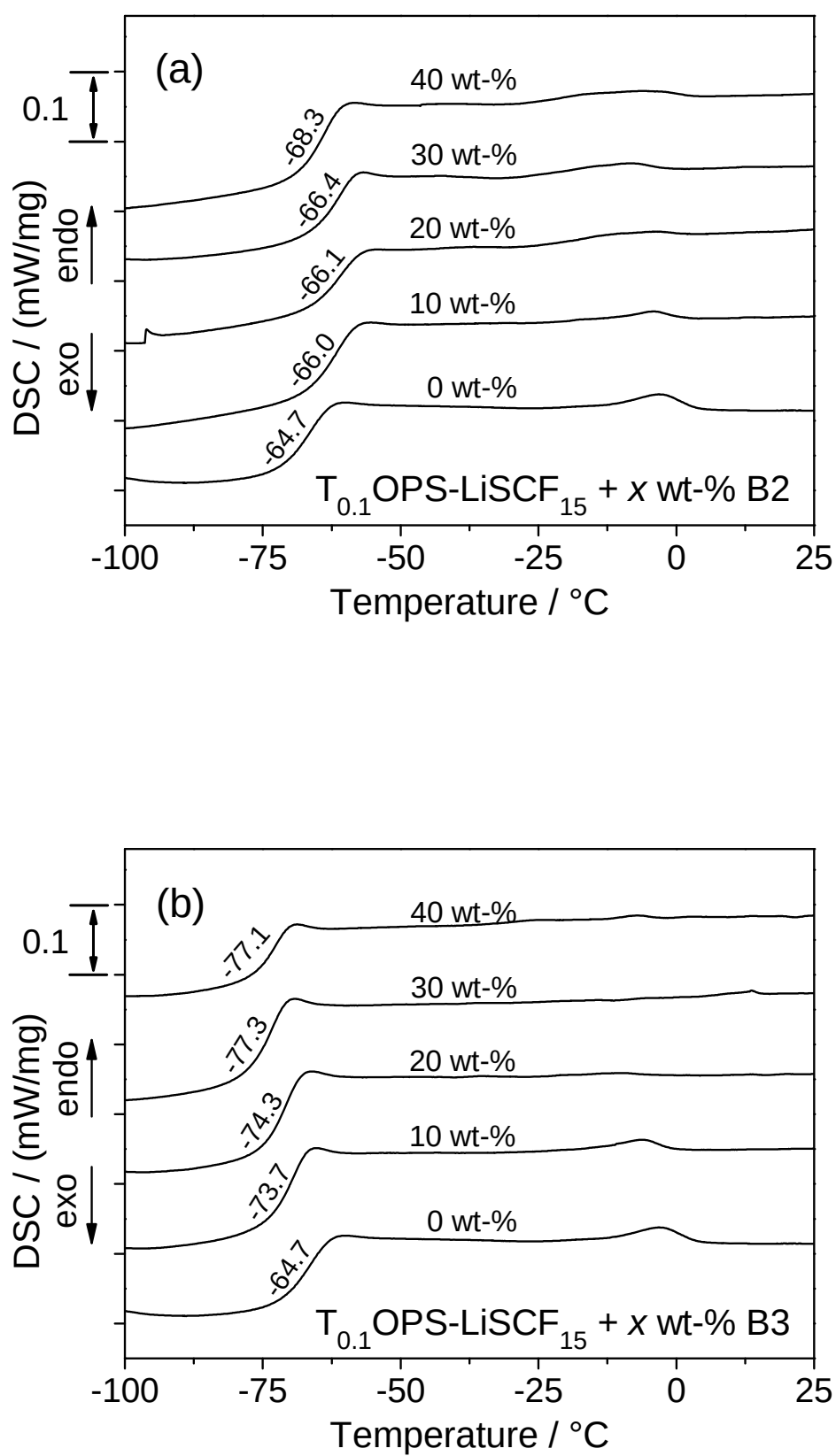


Fig. 4.31 DSC thermogram of $T_{0.1}\text{OPS-LiSCF}_{15}$ composite polymer electrolytes with (a) B2, (b) B3. LiSCF_{15} in the figure indicates 15 wt-% LiSO_3CF_3 .

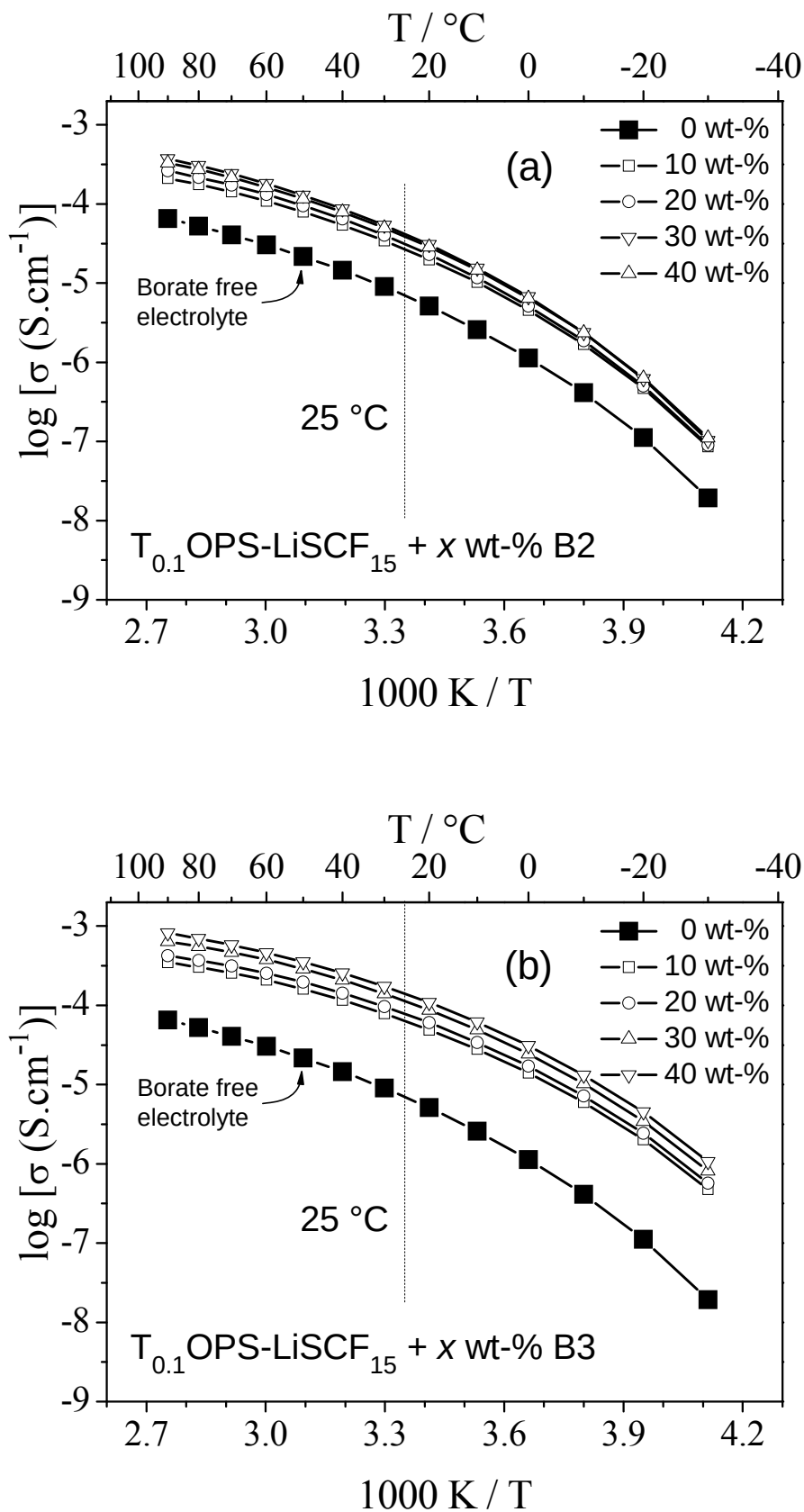


Fig. 4.32 Arrhenius plot of $T_{0.1}\text{OPS-LiSCF}_{15}$ composite polymer electrolytes with (a) B2, (b) B3. LiSCF_{15} in the figure corresponds to 15 wt-% LiSO_3CF_3 .

according to Svanberg [150, 151]. The temperature dependence of the diffusive process was Arrhenius type while the segmental motion deviated from Arrhenius behavior. As depicted in **Fig. 4.32**, the temperature dependence conductivity values of polymer electrolytes plasticized by both borate esters were higher than the borate ester free electrolyte and the conductivity plots were all nonArrhenius. It implies that the ionic conductivity was mainly dominated by transport due to segmental motion of the polymer chains, although the positive effect of borates was obvious. The decreased viscosity by the addition of borates seemed to be the one reason for the increase in ionic conductivity. The improvement with B3 was more significant than B2 reaching above 10^{-4} S/cm and in accordance with the T_g values discussed above. Moreover, *ab initio* calculations on B2 and pentaglyme, which has the same number of oxygen atoms, indicated that borate ester interacted with especially anion part of the salt much more efficiently than oligoether derivatives [152]. The interaction is not too strong to interact with lithium triflate to deplete them near the polysiloxane [153]. Because of the higher permittivity of borate esters, therefore, stronger interactions with the salt may be expected enhancing the concentration of the carrier ion, hence the conductivity.

The conductivity of B2 based gel electrolytes increased up to 30 wt-% of the borate ester and remained almost constant after that. This concentration corresponds to almost 1:1 ratio of borate to lithium triflate and can be thought as the optimum point when the interaction of electron deficient boron center with the salt taken into consideration. The increasing trend among B3 containing electrolytes was followed ceaselessly until 40 wt-% of the borate ester. The measurement was stopped at 50 wt-%, which matches the 1:1 ratio of B3 to lithium triflate, since it resulted in mechanically unstable membranes, thus no judgment could be done concerning this part.

The empirical VTF equation was used again in order to fit the temperature dependence of the ionic conductivities. The fit parameters were listed in **Table 4.12**. The general expectation for the difference $T_0 - T_g$ was nicely followed in fitting results. The pre-factor σ_0 , which relates to the number of mobile charge carriers, increased linearly up to 30 wt-% B2 and then decreased. The linear correlation in B3 was also valid. The perfect harmony between the experimental data and the fittings should not be overlooked. In addition, lower values of pseudo activation energies ($k \cdot B$) of B3 containing polymer electrolytes than that of B2 could be interpreted as easiness of corresponding ion transport thus higher conductivity as experimentally proved.

Table 4.12 T_g of $T_{0.1}OPS-LiSCF_{15}$ and its composite polymer electrolytes with B2 and B3, and fitting parameters of VTF equation to the temperature dependent conductivities.

Polymers	B2 (wt-%)	T_g [K]	T_0 [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
$T_{0.1}OPS-LiSCF_{15}$	0	208.5	184	3.8	721
$T_{0.1}OPS-LiSCF_{15}$	10	207.2	186	9.8	667
$T_{0.1}OPS-LiSCF_{15}$	20	207.1	186	13.2	682
$T_{0.1}OPS-LiSCF_{15}$	30	206.8	187	18.7	682
$T_{0.1}OPS-LiSCF_{15}$	40	204.9	187	15.1	666

Polymers	B3 (wt-%)	T_g [K]	T_0 [K]	$\sigma_0 \times 10^3$ [S·cm ⁻¹]	B [K]
$T_{0.1}OPS-LiSCF_{15}$	0	208.5	184	3.8	721
$T_{0.1}OPS-LiSCF_{15}$	10	199.5	188	8.3	540
$T_{0.1}OPS-LiSCF_{15}$	20	198.9	188	10.3	542
$T_{0.1}OPS-LiSCF_{15}$	30	195.9	187	16.8	560
$T_{0.1}OPS-LiSCF_{15}$	40	196.1	186	21.2	567

4.5.3 Final Commentary

The effect of nano sized inorganic particles and low molecular weight borate esters on the conductivity of $T_{0.1}OPS-LiSCF_{15}$ based polymer blends were fully investigated.

There is a common agreement that there is an increase in the conductivity of semi crystalline polymer electrolytes due to a decrease in crystallinity as filler is added. Usually less significant or sometimes depressive impact of fillers on the conductivity is observed when polymers are completely amorphous. The structure of the polymer host has, therefore, more decisive effect on the electrical properties of the composite polymer electrolytes comprised of inorganic fillers. In our case, neither Al_2O_3 nor SiO_2 resulted in any improvement on the conductivity value of particle free polymer electrolytes.

On the contrary, the addition of low molecular weight borate esters brought about quite promising results. The conductivity of $T_{0.1}OPS-LiSCF_{15}$ polymer electrolyte doped with B3 increased at least one order of magnitude. These borates are not only interesting that

they can be used as a plasticizer but also they have electron deficient boron groups which can strongly interact or extensively trap the anions relying on their structures, thus increasing both the ionic conductivity by creating more free ions and the lithium transference number of the polymer electrolyte system.

4.6 Poly(bismethoxyphosphazene)s (PBMP)s (14a, 14b).

Polyphosphazenes, which contain phosphor and nitrogen atoms joined by formally unsaturated bonds, comprise by far the largest class of the inorganic macromolecules, since a wide variety of side chains can be used to modify and fine tune the both chemical and physical properties of these polymers. One of the applications of these inorganic polymers is as solid polymer electrolytes, where these materials serve as ionic conductors for energy storage devices. The most famous polyphosphazene architecture is poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) which was first synthesized and extensively characterized by Allcock [19-21]. Since then, many techniques have been applied to the polyphosphazenes up to now, however through investigations of its structure in solution and molten state using small angle neutron scattering are still missing. Neutron scattering experiments have been thus performed with the model polyphosphazenes as seen in **Fig. 4.33** in order to investigate the solution and bulk properties of the polyphosphazenes. The next step of the SANS experiment was to look for the influence of dissolved salt on the melt conformation of the polymers. The electrical conductivities as polymer electrolytes were also investigated by impedance spectroscopy.

Here it is fair to mention that the SANS experiments were performed cooperatively in the research group of Prof. Dieter Richter and the help of Dr. Wim Pyckhout-Hintzen and Dr. Reiner Zorn in Jülich Research Centrum.

4.6.1 Characterization of PBMPs.

NMR Spectroscopy. The polymers were synthesized via macromolecular substitution of the precursor poly(dichlorophosphazene) using sodium methoxide. The degree of chlorine substitution was confirmed using ^{31}P NMR.

The disappearance of poly(dichlorophosphazene) signal at -18 ppm (refer to **Fig. 3.6**) was a very clear indication of complete substitution and hence high purity of products as shown in **Fig. 4.33**. The only signal at -4.1 ppm for each was attributed to the target polymers. Moreover the absence of any other signals especially in the range of 5-20 ppm clearly revealed that neither cyclic trimers nor tetramers were produced throughout the synthesis. The ^1H and ^{13}C NMR spectra supported the substitution by CH_3O - and CD_3O -groups.

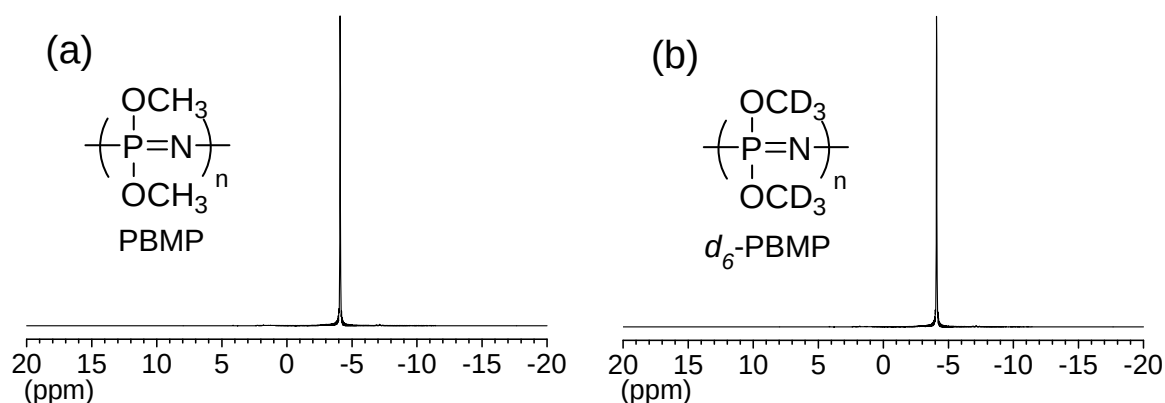


Fig. 4.33 ^{31}P NMR of (a) poly(bismethoxyphosphazene) (PBMP) and (b) poly(bis- d_3 -methoxyphosphazene) (d_6 -PBMP).

Here it is worth to say that the attempts to prepare high quality polyphosphazenes in THF due to concomitant methoxy induced anionic ring opening polymerization of the solvent to yield poly(tetrahydrofuran) as detected spectroscopically. Therefore another solvent, dioxane, which is resistant to ring opening polymerization, was employed for the synthesis. The details can be found in Appendix 3.

FT-IR Spectroscopy. The FT-IR spectrum of PBMP was given in **Fig. 4.35**. The characteristic stretching of $\text{P}=\text{N}$ at 1244 cm^{-1} , and the typical bands for $\text{P}-\text{O}-\text{C}$ at 1186 , 1032 , and 820 cm^{-1} supported the expected chemical structure of PBMP. The hydrocarbon stretching of d_6 -PBMP shifted to $2250\text{--}2050\text{ cm}^{-1}$ regions and was accompanied by a change in $\text{P}-\text{O}-\text{C}$ stretching from 1032 to 1051 cm^{-1} (not shown in the figure).

Gel Permeation Chromatography. The GPC measurements were performed using the conditions as briefly described in Section 3.2.6. The number average molecular weight of the precursor polymer $[\text{NPCl}_2]$ was found to be $6.63 \times 10^4\text{ D}$ with a low PDI of 1.27 which corresponds to approximately 570 monomer units. After the substitution, the molecular weight of both polymers turned out to be in the order of 10^5 D as seen in GPC chromatograms in **Fig. 4.34**.

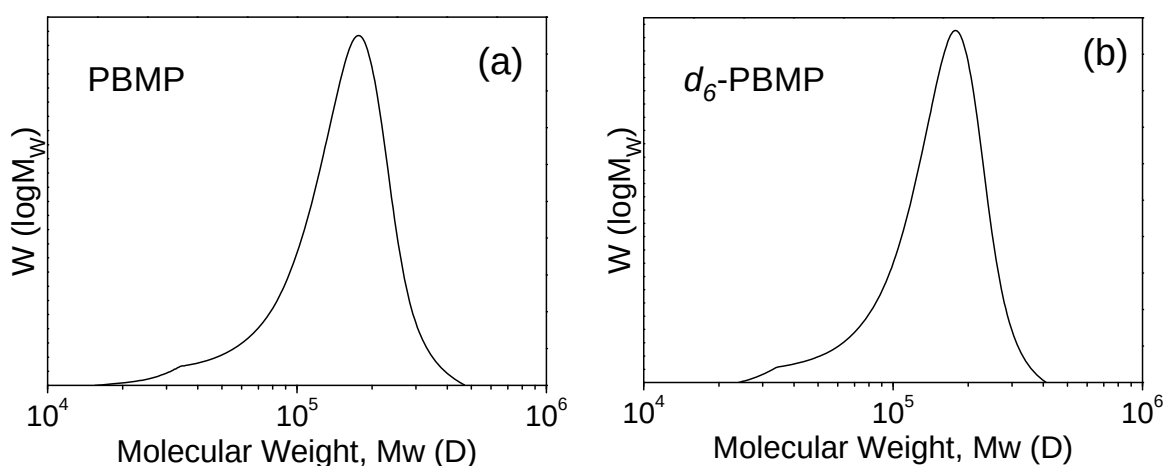


Fig. 4.34 GPC chromatogram of (a) PBMP and (b) d_6 -PBMP.

The number average molecular weight of PBMP was 1.25×10^5 D with PDI of 1.28 and 1.31×10^5 D with PDI of 1.23 for d_6 -PBMP that means an increase in M_n values by a factor of approximately 2 as compared to the precursor. Calculated repeating units by GPC measurements were 1170 and 1160 for PBMP and d_6 -PBMP respectively. These results indicated that there occurred no perceivable degradation or chain cleavage but a probable macromolecular condensation among the polymer chains.

Differential Scanning Chromatography. The DSC thermogram of the PBMP was given in **Fig. 4.36**. The polymer showed no primary transition in the range of temperature scan up to around 170 °C but rearrangement and degradation for both types of polymers were detected above this temperature (not shown in the figure), as also reported by the former studies concerning the same polyphosphazene [64, 154, 155]. This rearrangement and degradation temperature decreased considerably up to 100 °C with the addition of salt. The T_g values for PBMP and d_6 -PBMP were detected to be -79.5 °C and -81.8 °C.

4.6.2 PBMP Polymer Electrolytes

PBMP was complexed with lithium triflate and investigated with regard to its conductivity as salt-in-polymer electrolytes. Polymer electrolytes with salt contents of 5, 10, 15, 20 30, and 40 wt-% were prepared, but the conductivity measurement was only performed up to 20 wt-% salt content due to observed phase separation and precipitation of the salt from the polymer electrolytes, which indicates a maximum salt solubility around 20 wt-%..

The structure of PBMP as polymer electrolyte host could be judged before doing the experiments since it has no long oligoether or other side group which can support the

dissociation of salt by solution of lithium ions and enhance the conductivity. However the main idea in this section is to compare these results with the neutron scattering experiments as will be discussed in the forthcoming section to have an overall perspective about the polyphosphazene structure and the electrical properties of this model polymers.

FT-IR Spectroscopy. The interaction of salt with polyphosphazene was monitored by FT-IR spectroscopy. The representative spectra for 10 and 20 wt-% lithium triflate containing salt-in-polymer electrolytes were given together with salt free PBMP in **Fig. 4.35**. The cations here might be solvated either by the oxygen of side groups or the nitrogen on the main chain or both. The spectra of polymer electrolytes demonstrated that the intensities and the peak frequencies of the characteristic absorption of P=N at 1450 cm^{-1} , P-O-C at 1185 and 1032 cm^{-1} , and P-O-CH₃ at 821 cm^{-1} predominantly remained unchanged, indicating that the interaction of salt with the polymer was weak and did not revealed in the spectra. This suggests a polymer decoupled motion of the salt in the matrix.

Differential Scanning Chromatography. The polymer electrolytes, investigated by DSC in the temperature range from $-150\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$, also showed very low glass transition temperatures with no additional first order transitions as illustrated in **Fig. 4.36**.

The addition of salt depressed the decomposition temperature from $170\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$ (not shown in the figure). It also affected the T_g values first giving rise to an upwards shift to $-68.4\text{ }^{\circ}\text{C}$ for 5 wt-% salt. A second glass transition appeared at $-54.5\text{ }^{\circ}\text{C}$ for the sample with 10 wt-% salt content, which indicated the presence of microheterogeneities at this composition. After a broad glass transition range found for 15 wt-%, the 20 wt-% sample again showed a sharp single transition at $-55.8\text{ }^{\circ}\text{C}$. The appearance of a second transition in the 10 wt-% sample can again be connected to the presence of two distinct amorphous phases of different salt concentrations as discussed in detail in section 4.4.2 for PPO-PS based polymer electrolytes.

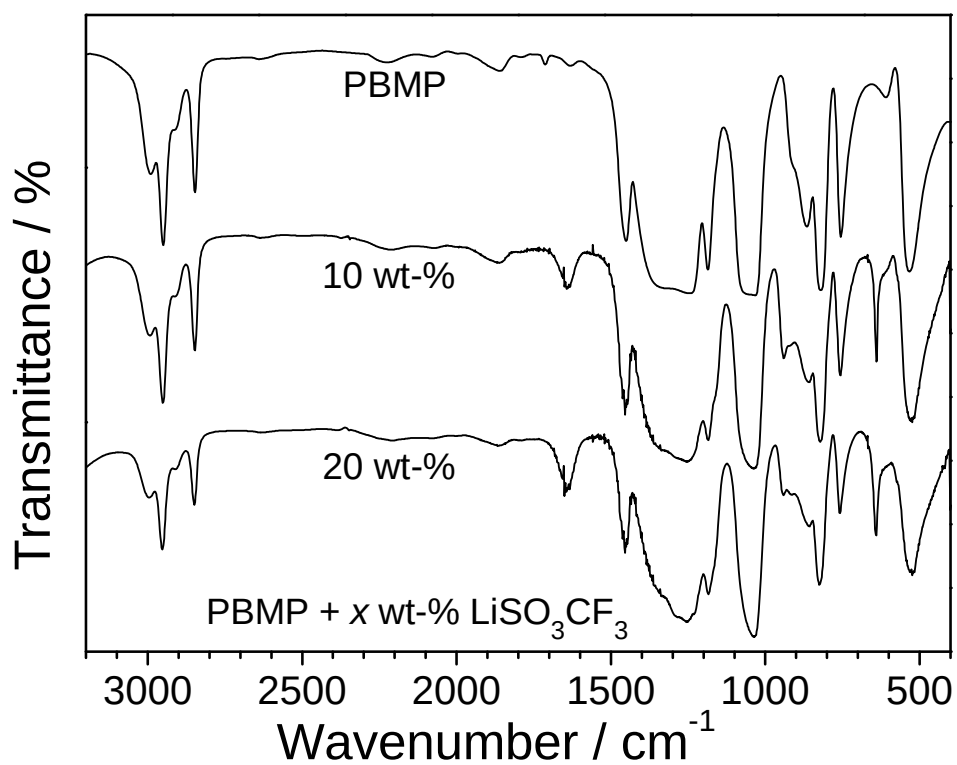


Fig. 4.35 FT-IR spectra of PBMP and its polymer electrolytes for 10 and 20 wt-% lithium triflate.

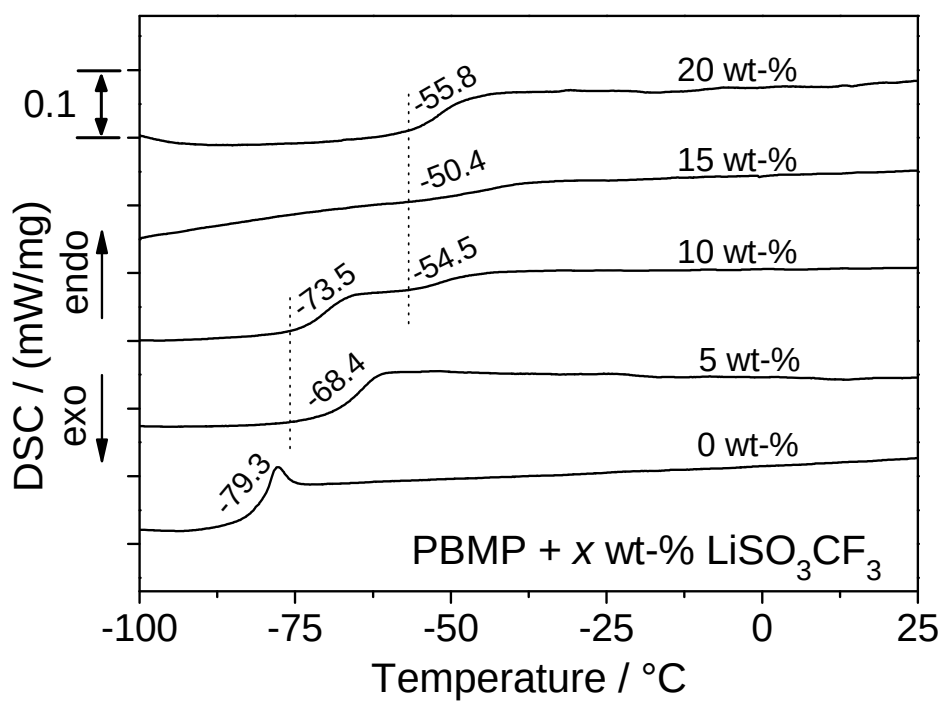


Fig. 4.36 DSC thermogram of pure PBMP and salt-in-PBMP systems with varying amount of lithium triflate.

T- and Li- Salt Dependence of Conductivity. The ionic conductivity of polymer electrolytes was determined using impedance spectroscopy. In order to avoid possible degradation as detected by DSC measurement at around 100 °C, the first heating and cooling cycle were performed up to 70 °C and then a last cycle up to 90 °C.

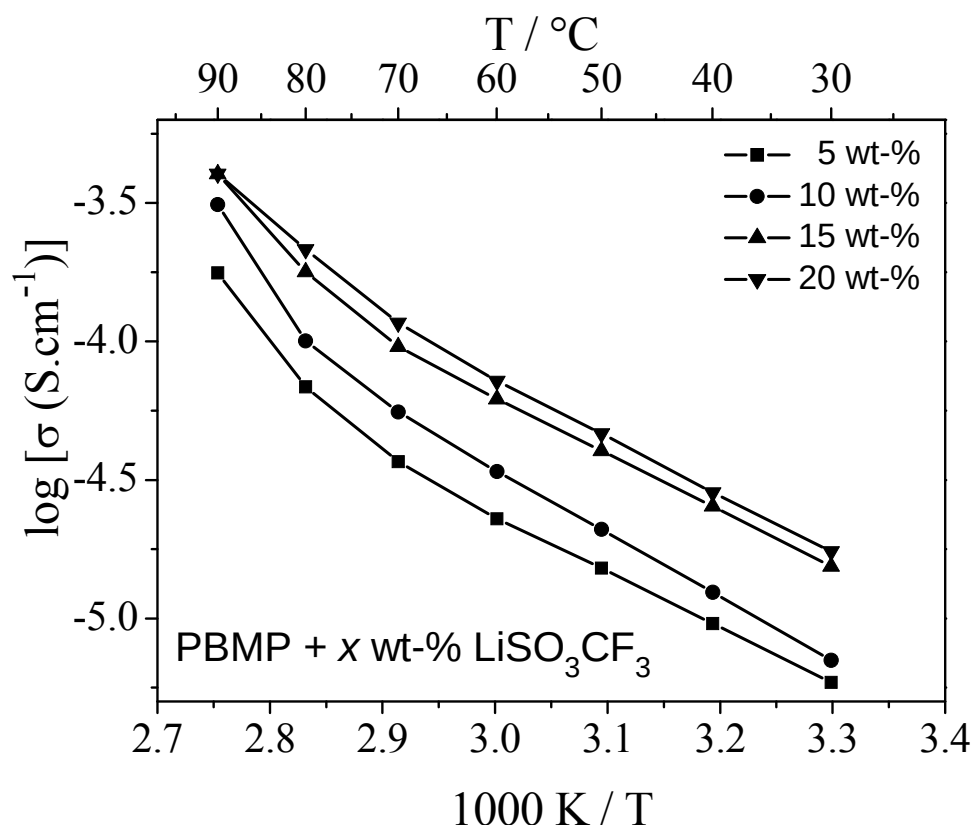


Fig. 4.37 Arrhenius plot for the conductivity of PBMP with variable amount of LiSO_3CF_3 .

The temperature dependence of the ionic conductivity is depicted in **Fig. 4.37**. It increased regularly as the salt content increased. Although a conductivity maximum is usually detected for most salt-in-polymer electrolytes, the investigated system here did not yield a conductivity peak. That could come at higher salt concentrations if the salt were soluble. The conductivity of the polymer electrolytes followed the Arrhenius type behavior up to 70 °C as commonly seen for glasses and low molecular weight solvents, indicating that the ionic conductivity is nearly decoupled from the segmental mobility of the polymer host (**Fig. 4.37**). The conductivity values unexpectedly deviated from the linearity above 70 °C for all electrolyte systems increasing much faster between 70 °C and 90 °C. The degradation leading to low molecular weight polymeric or cyclic trimeric or tetrameric

organophosphazenes [155] may cause a decrease of the viscosity acting similar to a plasticizer, thus leading to these surprising enhanced increase of the conductivities since the viscosity is inversely proportional to the conductivity.

4.6.3 SANS Experiment on PBMP

SANS experiments were performed at the KWS1 spectrometer at the FRJ-2 Dido Reactor at Jülich, Germany. The experimental and theoretical background of the experiment is shortly given below but more detailed discussion on the theory is beyond the scope of this thesis and can be found elsewhere [156, 157]. Only some basic equations will be mentioned through this section for better understanding of the experimental results

The reactor runs at 20 MW and has a D2O moderator. Data were collected at distances sample-to-detector of 2 m, 8 m and 20 m which lead to an equivalent scattering vector range q between 0.002 and 0.2 Å⁻¹ approximately using a neutron wavelength $\lambda = 7$ Å with a wavelength spread $\Delta\lambda/\lambda = 0.20$. These distances provide the full scattering angle (Θ) range and overlap nicely which avoids systematic errors due to different counting statistics. The incoming neutron beam with entrance 30 x 30 mm² was collimated with respectively 4.8 and 20 m to a sample aperture of 10 x 10 mm² to achieve maximum possible flux at the sample. The scattering vector q is the modulus of the resultant between the incident, k_i , and scattered, k_s , wavevectors and related to the scattering angle (Θ) by:

$$q = |q| = |k_s - k_i| = \frac{4\pi}{\lambda} \cdot \sin\left(\frac{\Theta}{2}\right) \quad [4.4]$$

Roughly with this scattering vector corresponds to distances of $2\pi/q$, which ranges between 25 Å and 3000 Å, the intensity values can be resolved by the detector in 128 x 128 separate channels of each 5.2 x 5.2 mm². The detector was of the photomultiplier type which has the advantage over gas detectors that the dynamical range of intensities is high and no damage due to local high counting rates can be expected. Its dead time τ is 4.5 µsec, allowing integral counting rates of approximately 20.000 counts per second. The sensitivity of the detector channels was obtained from the measurement of a flat-scattering incoherent sample, i.e. Plexiglas[®] and every cell was corrected for it pixel wise. The measured neutrons in each configuration were transformed to an absolute intensity scale (cm⁻¹) which allows comparison with theoretical calculations. This also allows comparison with different spectrometers at other neutron sources. The corrected

intensities are obtained after appropriate subtraction of empty cell scattering, background noise due to stray neutrons and γ photons and dark current noise from the electronics. Eventual dead time effects are accounted for in the calibration. Absolute cross-sections, (here further abbreviated as intensities I) were obtained after calibrating with a 1.5 mm thick secondary standard of Plexiglas[®] which was previously calibrated to vanadium and obtained as [156, 157]:

$$\frac{d\Sigma}{d\Omega}(q) = \frac{(T_p D_p \frac{d\Sigma_p}{d\Omega}) L_S^2}{T_S T_{EC} D_S L_p^2 < I_p >} [(I_S - I_{BC}) - T_S (I_{EC} - I_{BC})] \varepsilon_{ij} \quad [4.5]$$

where subscripts p, S, EC, BC stand for Plexiglas[®], sample, empty cell and boron carbide. Vanadium is the typical neutron standard since it scatters only incoherently and the incoherent scattering cross section is well known. Because of its low scattering, however, secondary standards like Plexiglas[®] have become popular. The detector sensitivity correction is contained in the ε_{ij} matrix. The thickness of each component in the beam is stored in D . T denotes the transmission of the respective component to air. The first term in the nominator concerns data of Plexiglas[®] and the product of T , D and absolute scattering intensity for Plexiglas[®] was $5.2 \cdot 10^{-2}$ for $\lambda=7 \text{ \AA}$, its accuracy is 4%. The detector distance is symbolized by L and defines the solid angle as given by $d\Omega = (\text{pixelarea})/L^2$. Measuring the standard Plexiglas[®] at identical collimation conditions as the sample i.e. at the same flux conditions but at a shorter distance, and then scaling the intensity to the correct solid angle leads to an automatic overlap of the different camera distances. Instead of dividing the intensity by the flat intensity of the calibrant, the average intensity of Plexiglas[®] is used together with a sensitivity correction per channel (ε_{ij}). This has the advantage of decoupling calibration and sensitivity corrections. All above corrections are performed in 2d (128×128) pixel wise after which a radial averaging of the data - i.e. gathering of intensities at the same scattering vector - reduces the full 2d data to I vs. q data.

The dilute polymer solutions of PBMP in DMF- d_7 were prepared to study solution characteristics up to 1 vol-%. The bulk properties of polymers were investigated for a mixture consisting of by 5 vol-% PBMP and 95 vol-% d_6 -PBMP. The same composition was also used to prepare 5 and 10 mol-% LiSO_3CF_3 containing salt-in-polymers (corresponding to 7.5 and 15 wt-% salt contents respectively). The solutions were

contained in Hellma Quartz cells of path lengths of 1 mm. The transmissions were measured in situ from a monitor at $q = 0$ inside the beamstop. The melts have been placed between 2 quartz plates of each 2 mm thickness with a spacer inside keeping the gap between the plates at a value of 1 mm ($\pm 5\%$). The sample aperture was changed for the melt samples to $8 \times 8 \text{ mm}^2$. These cells were put into a brass furnace and the temperature arranged so as to achieve 12.5, 36.6 and 60.6°C inside the sample using a calibration formula.

Polymer Solutions in DMF- d_7 . Dilute solutions were characterized using the Zimm's extrapolation method, the same method as usually applied for light scattering experiments [156, 157]. Double extrapolation: letting $c \rightarrow 0$ leads to the single chain limit without interaction and allows the radius of gyration to be extracted. Letting $q \rightarrow 0$ allows the determination of the forward scattering without effects of interaction because the second virial coefficient A_2 then approaches zero [156]. A_2 itself can be estimated as well (Fig. 4.38).

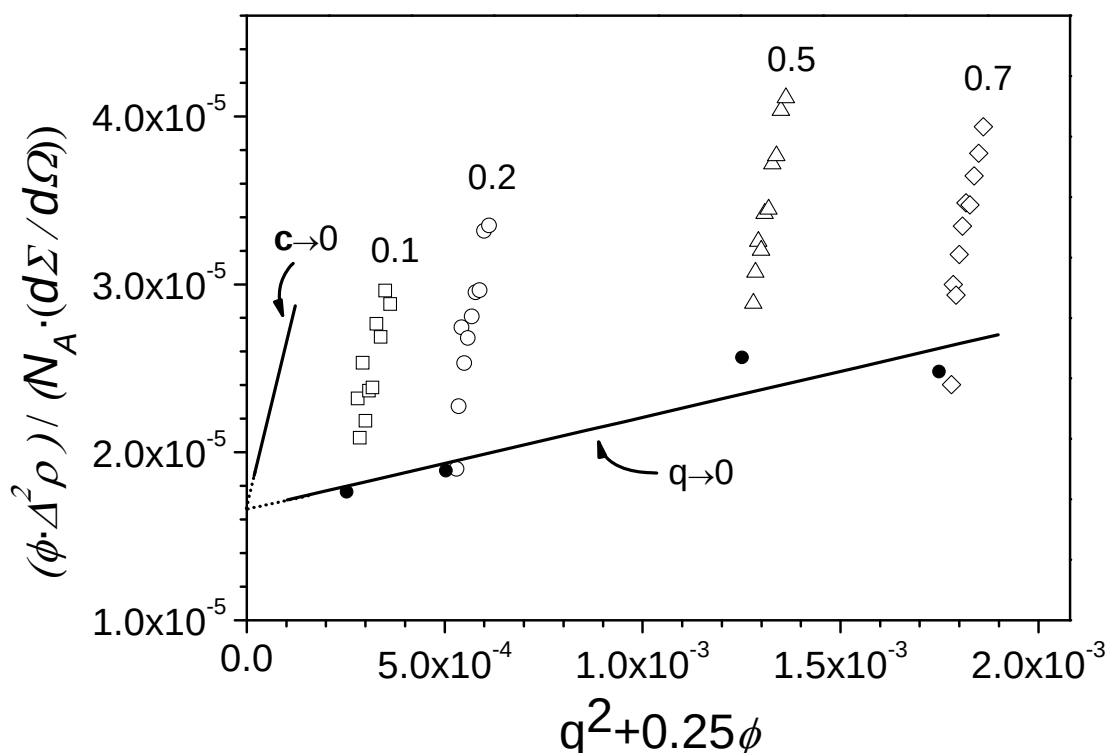


Fig. 4.38 Zimm plot of PBMP prepared in 0.1, 0.2, 0.5, and 0.7 vol-% in DMF- d_7 . Open symbols are experimental results. Lines are extrapolations as $c \rightarrow 0$ and $q \rightarrow 0$.

In the figure, the y axis is inversely proportional to the structure factor, $S(q)$. ϕ , $\Delta^2\rho/N_A$ and $d\Sigma/d\Omega$ are, respectively, volume fraction of polymer, contrast factor describing the interaction of neutrons and the atoms of the samples and macroscopic cross section. The number 0.25 was chosen arbitrarily to spread the curves horizontally.

Data (crosses) are selected only from the 8 m data as the lower q (20 m), data were of less statistical quality or showed extra scattering, being non characteristic for the polymer. Only the linear part of the 8 m data in the above representation are used ($0.005 < q < 0.011 \text{ \AA}^{-1}$). This range in q allows determining values for R_g of the chains ranging between 90 and 200 $\text{\AA}$, i.e. $1/q$ which is appropriate for us. The 1 vol-% polymer solution was skipped since it was too concentrated and no random chain behavior was observed.

Besides the R_g value extracted from the Zimm plot, the estimated value of the second virial coefficient A_2 is important as it relates to Flory-Huggins parameter χ which describes the polymer interaction according to

$$2A_2 = 1/\Omega - 2\chi \quad [4.6]$$

where Ω represents the molecular volume of a random chain. A positive, zero and negative A_2 mean, respectively, a good, a “theta*”, or bad solvent according to the general classification. The following parameters were extracted from Zimm’s approximation: z-average radius of gyration=144.7 $\text{\AA}$, the molar volume is 64000 cm^3/mol which corresponds to $M_w = 95000 \text{ D}$. This value for M_w is lower than the value as determined

* The θ temperature corresponds to the Boyle point in an imperfect gas and is the range in which the virial coefficient B in the expanded gas law becomes zero. This same concept applies to the modification of the gas law ($PV = nRT$) used to determine the osmotic pressure (π) of a polymer solution as:

$$\frac{\pi}{C} = \frac{RT}{M_n} \cdot [1 + A_2C + \dots] \quad [4.7]$$

where R is the universal gas constant, T is the temperature in Kelvin, M_n is the number average molecular weight, and C is the concentration of polymer in solution. The second virial coefficient A_2 is related to the solvent polymer interactions and usually determined by the slope of the line in Zimm plot by letting $\theta \rightarrow 0$ in light scattering or $q \rightarrow 0$ in small angle neutron scattering experiments.

from GPC by a factor of 0.6. The obtained second virial coefficient A_2 in DMF at $RT = 8.6 \times 10^{-4}$ is of the same order as known from other polymers in a good solvent.

In experimental contexts, the Zimm's approximation is preferred when the q values are low. At higher q values, polymer solutions with excluded volume interactions show a high q behavior proportional to $q^{-1/\nu}$ where ν is the excluded volume exponent, which can be determined from the slope of a plot of intensity, I vs. q at high q values ($\nu = 3/5$ for fully swollen chains, $\nu = 1/2$ for "theta" chains, and $\nu = 1/3$ for collapsed chains). **Fig. 4.39** shows the scattering intensity of polymer solutions for high q -data (after subtraction of the incoherent background of the solvent $= 0.055 \text{ cm}^{-1}$).

The slope was -1.647 and hence in almost exact agreement with the expected excluded volume exponent by Flory which is $5/3$ affirming again the good solvent property of this system.

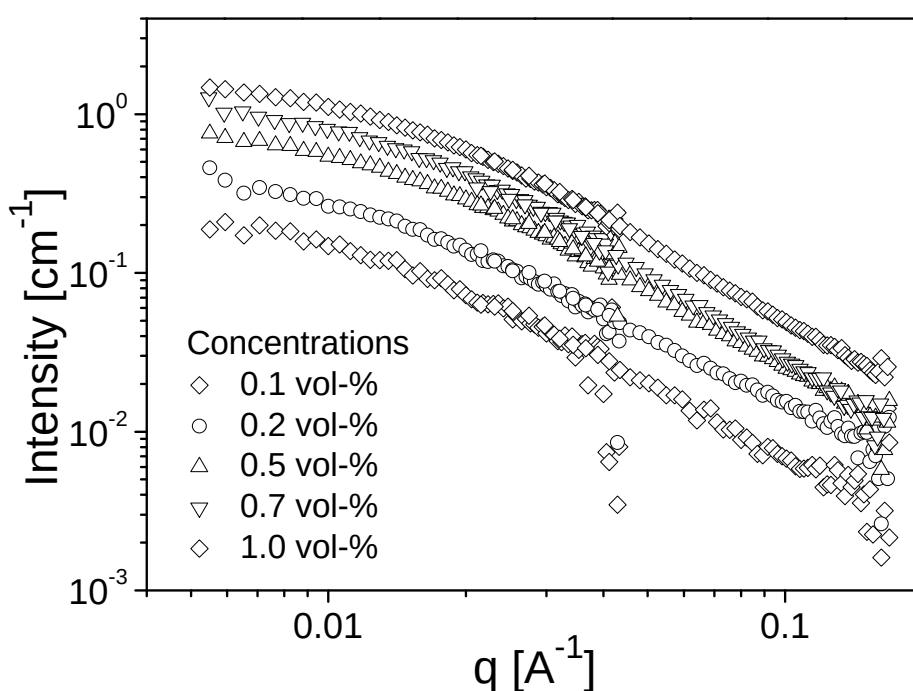


Fig. 4.39 Scattering intensity of polymer solutions as a function of wave factor. The numbers correspond to volume concentration in DMF- d_7 .

Polymer and salt-in-polymer (in molten state). Polymer melts were prepared by mixing 5 vol-% of the deuterated polyphosphazene with 95 vol-% of non-deuterated one. 5 and

10 mol-% LiSO_3CF_3 of the polymer segments (corresponding to approximately 7.5 and 15 wt-%) containing salt-in-polymer systems were investigated additionally using the same molten polymer mixture.

The blends show considerable parasitic scattering at low q . It can be excluded based on the observed q -dependence (which is close to q^{-4}) that this is due to a ‘simple’ isotope mixing effect or Flory-Huggins interaction term between PBMP and d_6 -PBMP. It was also present in the salt free samples as well. Therefore, the salt had no distinctive contribution to that. It might be due to much larger structures in the polymer in the pre-gel state (i.e. branched structures) or trapped voids in the melt sample. The data show, however, a typical leveling-off in the same way as for the solutions (usable data: $q > 0.007 \text{ \AA}^{-1}$), which can be interpreted as the Guinier plateau of the chain. Below this q , the intensity rises. The Guinier function is simple and in fact, the former used Zimm’s approximation is just an expansion of the Guinier function. **Fig. 4.40** shows a representative plot for the bulk polymer without salt.

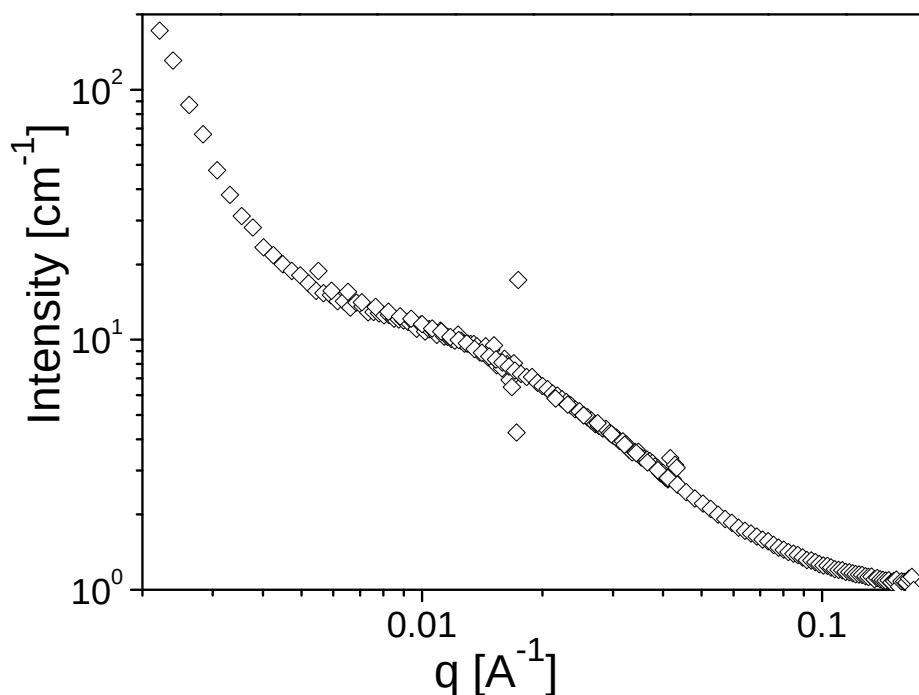


Fig. 4.40 Scattering intensity of polymer blend 5 vol-% PBMP + 95 vol-% d_6 -PBMP as a function of wave factor at 12.5 °C.

The Guinier fitting parameters of the mentioned q range using:

$$\ln(I) = \ln(I_0) - (q \cdot R_g)^2 / 3 \quad [4.8]$$

are listed in **Table 4.13**.

Table 4.13 Guinier fitting parameters at $q > 0.007 \text{ \AA}^{-1}$.

Sample	T	$\ln(I_0)$	R_g
Polymer melt	12.5	2.68	85.0
Polymer melt	36.6	2.65	83.6
Polymer melt	60.6	2.62	83.2
5 mol-% salt-in-polymer	12.5	2.55	84.5
5 mol-% salt-in-polymer	36.6	2.54	84.4
5 mol-% salt-in-polymer	60.6	2.53	85.1
10 mol-% salt-in-polymer	12.5	2.41	83.1
10 mol-% salt-in-polymer	36.6	2.41	84.2
10 mol-% salt-in-polymer	60.6	2.39	84.4

Briefly, R_g decreases only a little from 85 to 83, if the temperature is increased from 12.5 C ° to 60.6°C for the polymer melt and remains virtually constant for both salt-in-polymer systems. Although these results showed that the salt exhibited no distinguishable effect on the conformation of the polymer molecules even with increasing temperature, there must be in fact at least a weak interaction. Otherwise it would not be possible to dissolve lithium triflate up to 20 wt-% without any phase separation. As seen in the DSC thermograms of the polymer electrolytes (**Fig. 4.36**), the T_g value is only slightly increased with the addition of salt and the second transition observed (as the salt content increased further) could be attributed to the presence of heterogeneity with two distinct amorphous regions, possibly one salt free and one salt rich. Nevertheless the coordination of the oxygen and nitrogen atoms of the polymer should be weak overall. This is also realized from the temperature dependence of the ionic conductivity which suggested a decoupling from segmental motion of the polymer. This diminished cation coordination might be so localized within the polymer matrix that they did not effect the overall random coiled conformation of the free polymer chains.

The intensity in the complete q -range, however, cannot be fitted to a simple monodisperse Debye-function. This can be recognized already from the slight mismatch of the high “ q ”

slope with -2. Instead, a Schultz-Zimm-Flory (SZF) distribution was used to fit the polydispersity (**Table 4.14**).

Table 4.14 *Schulz-Zimm-Flory distribution*

Name	T	Phi	R _g	R _{gn}	B _{gr}	ε
Polymer melt	12.5	0.89	85	61.9	0.903	1.01
Polymer melt	36.6	0.84	83.6	60.1	0.931	1.02
Polymer melt	60.6	0.85	83.2	61.9	0.925	1.01
5 mol-% salt-in-polymer	12.5	0.78	84.5	62.0	0.86	1.01
5 mol-% salt-in-polymer	36.6	0.73	84.4	59.4	0.89	1.02
5 mol-% salt-in-polymer	60.6	0.73	85.1	60.6	0.90	1.02
10 mol-% salt-in-polymer	12.5	0.69	83.1	62.0	0.85	1.00
10 mol-% salt-in-polymer	36.6	0.65	84.2	60.5	0.87	1.02
10 mol-% salt-in-polymer	60.6	0.66	84.4	62.5	0.87	1.01

For monodisperse Gaussian chains, the form factor of the chain $P_{chain}(q, M)$ is expressed by the well known Debye scattering function,

$$P(q) = 2 \cdot e^{-\frac{(q \cdot R_g^2) - 1 + \frac{q \cdot R_g^2}{(q \cdot R_g)^4}}{4}} \quad [4.9]$$

In the polydisperse case, the radius of gyration, R_g implicitly depends on $W(M)$. A correction for polydispersity must be then made by e.g. including a Schultz-Zimm-Flory (SZF) distribution:

$$W(M) = b^{h+1} \cdot M^h \cdot e^{-\frac{b \cdot M}{\gamma \cdot (h+1)}} \text{ with } b = (h+1)/M_w \text{ and } h = \left(\frac{M_n}{M_w} - 1 \right)^{-1} \quad [4.10]$$

The radius we obtain from these fittings here is the number average of R_g . For a SZF distribution $M_w/M_n^\dagger$ can be taken as equal to $M_z/M_w^\dagger$ which is always $(1+\epsilon)/(1+2 \cdot \epsilon)$. This leads to:

[†] M_n , M_w and M_z are statistically described averages to represent the molecular weight and the distribution of a polymer. The number average molecular weight, M_n , is the number average value corresponding to a measure of chain length of polymer chains. That can be measured by any technique that “counts” the

$$R_{gw} = \sqrt{R_{gn} \cdot ((1 + 2 \cdot \varepsilon) / (1 + \varepsilon))} \quad [4.11]$$

The fitted polydispersity ($PDI = 1 + \varepsilon = 2.01$) was larger than the GPC result for the polydispersity, which was around 1.3. M_w value of 120000 D was calculated from Schulz-Zimm-Flory distribution, which corresponds to a M_n value of 60400 D using the obtained polydispersity. This result was in really good agreement with the value extracted from the experiment done by polymer solutions in DMF- d_7 , for which the M_n value of 64000 D was estimated. These exact molecular weight results as measured by the SANS experiment were slightly different from the relative molecular weights determined by GPC using polystyrene standards. The M_n value from GPC was 125000 D with a PDI of 1.28 indicating that a correction factor of 0.5 is required for results from GPC measurements.

4.6.4 Final Commentary

For the first time, PBMP was characterized by a Small Angle Neutron Scattering experiment (SANS). SANS is impressive since it gives quantitation insight into the macromolecular conformation of the polymers. The M_n values measured by GPC, which is an indirect method to estimate the molecular weight, was compared with the more precise M_n values acquired by SANS experiment. The molecular weight was overestimated using GPC technique and a correction factor of 0.5 is required for GPC measurements on polyphosphazenes.

On the other hand, the influence of the salt on the melt conformation of the polyphosphazene was investigated. Addition of salt to PBMP had virtually no significant

molecules. The weight average molecular weight, M_w , is similarly described except that the sizes of the polymer chains are concerned. M_w is mathematically second power average of M_n . Melt elasticity, on the other hand, is more closely dependent on the z-average molecular weight, M_z , and the third power average of M_n . These values are calculated mathematically as:

$$M_n = \frac{\sum_i n_i \cdot M_i}{\sum_i n_i}, M_w = \frac{\sum_i n_i \cdot M_i^2}{\sum_i n_i \cdot M_i}, \text{ and } M_z = \frac{\sum_i n_i \cdot M_i^3}{\sum_i n_i \cdot M_i^2} \quad [4.12]$$

where the polymer consists of n_i chains of exact molecular weight of M_i and the i^{th} component has a degree of polymerization of i . Moreover, the polydispersity (PDI) of a polymer is defined by M_w/M_n .

effect on the R_g values indicating a weak interaction between salt and polymer itself. The FT-IR and impedance measurements were also in conformity with the SANS results indicating a predominantly diffusive transport of the ions within this particular polyphosphazene system. DSC measurements in addition indicated the presence of two microphases with different glass transition temperatures at lower temperatures that might be due to local salt rich domains within the polymer. To conclude, the interaction of salt and polymer overall is small does hardly affect the conformation of the polymer.

Moreover, it is worth to mention that the room temperature conductivity of PBMPs was surprisingly high and comparable to the well known MEEP polymer electrolytes. This is contradictory to the common thought that a polymer should contain solvating groups, such as oligoethers, to establish a high ionic conductivity. These results here show that a highly flexible polymer having weak solvent interactions with salts can also result in conductivity values as classic PEO based salt-in-polymer systems. A key factor may be the enhanced molecular mobility of the polymer solvent.

4.7 PBLCPP (17) and PBPAIP (19) Polyelectrolytes

Nanostructured material formation employing the self-assembly of the polymers in the preparation of multilayered structure has taken a great interest since the first report of Hong more than two decades ago on the basic principle that the alternating exposure of a charged substrate to solutions of positive and negative polyelectrolytes [158]. The alternating adsorption on a colloidal particle or layered surface results in self-assembled polyelectrolyte multilayers (PEM)s, stabilized by strong electrostatic forces. Inorganic particles, functional polymers, proteins, orientable chromophores, charged biopolymers such as DNA, or mesogenic units including local order have been extensively employed as building blocks for the preparation of PEMs as explained in some recent reviews [159-163]. Although organic polymers have been widely investigated as polyelectrolytes for the formation of multilayers, inorganic polymers are still untouched in this area. The main focus in this section will be therefore the synthesis, characterization and application of the polyphosphazene polyelectrolytes as a building block for PEMs.

4.7.1 Characterization of PBLCPP

NMR Spectroscopy. Structural characterization of poly[bis(lithium carboxylatophenoxy)phosphazene] (PBLCPP), performed via macromolecular substitution and functionalization was determined by NMR technique. The reaction steps can be found in **Scheme 3.7** and the spectral properties for each synthesized polymer in Appendix 3.

^1H and ^{13}C spectra of PBLCPP are depicted in **Fig. 4.41** with the assigned chemical shifts indicating a single pure polymer.

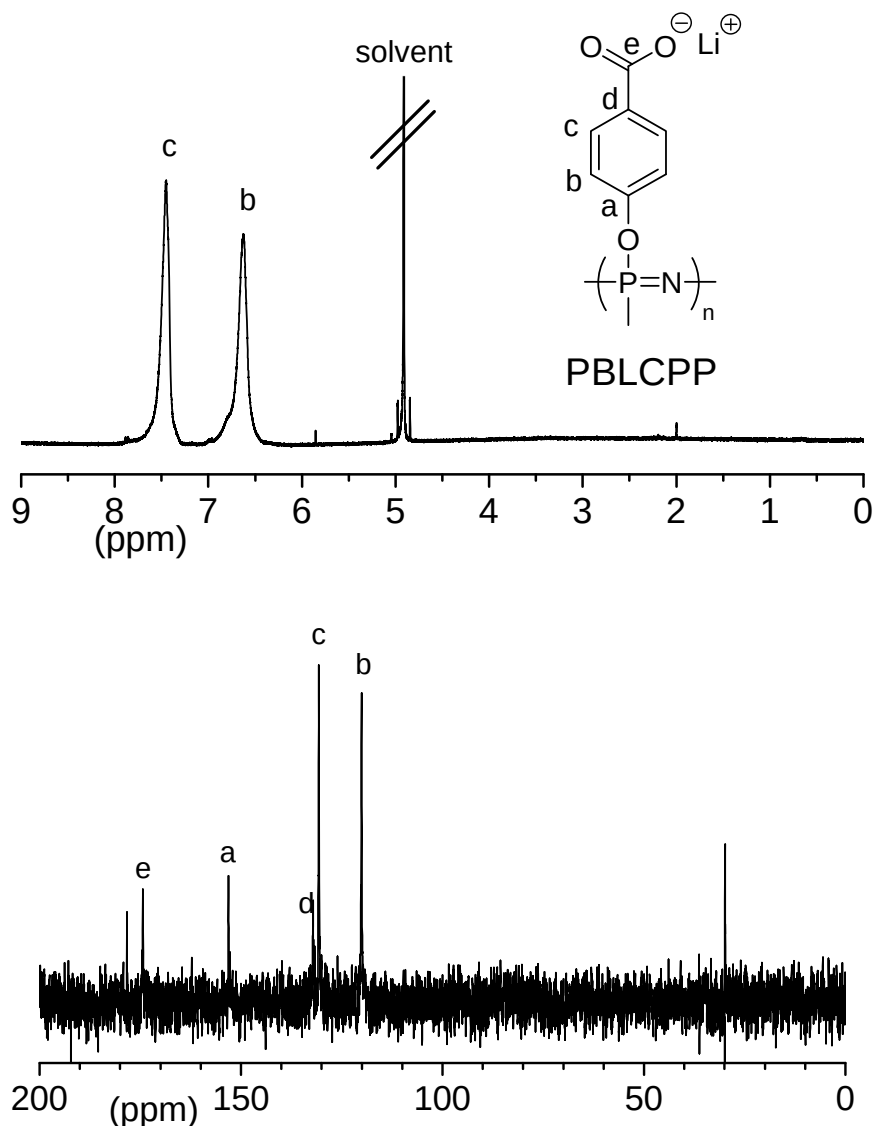


Fig. 4.41 ^1H and ^{13}C NMR of PBLCPP (**17**) in D_2O .

The ^{31}P NMR spectra of the polymers in the synthesis order are stacked in **Fig. 4.42** (for the abbreviations and chemical structures refer to **Scheme 3.7**). The completeness of substitution was elucidated using ^{31}P NMR. The substitution of poly(dichlorophosphazene)s with aryl groups usually requires forcing conditions. After substitution with phenoxy groups in THF, one fourth of the chlorines remains unsubstituted and do not hydrolyze even after dialysis in water due to bulk nature of aryl groups according to our experiences. The very sharp signal at -19.8 ppm was attributed to fully substituted units accompanied by a small one at -15.5 ppm presumably belonging to the half substituted phosphorus, which contributed no more than 2 %. The similar

chemical signals for phosphorous substituted with two phenoxy (-18.2 ppm) and the one with one chlorine and one phenoxy (-15.2 ppm) was already reported by Allcock [64]. This sharp signal shifted to -15.5 ppm after deprotection of ester group. The relative position of the half substituted repeating unit remained virtually the same but another small signal at around -8 ppm was observed. This small signal can be assigned to hydrolyzed chlorine atoms of the half substituted phosphorus under strong basic conditions during 2 days of reaction time. The converting PBCPP to PBLCPP did not change the chemical shifts considerably. The relative sharp signal implies very less or no considerable chain cleavages during the substitution and functionalization steps.

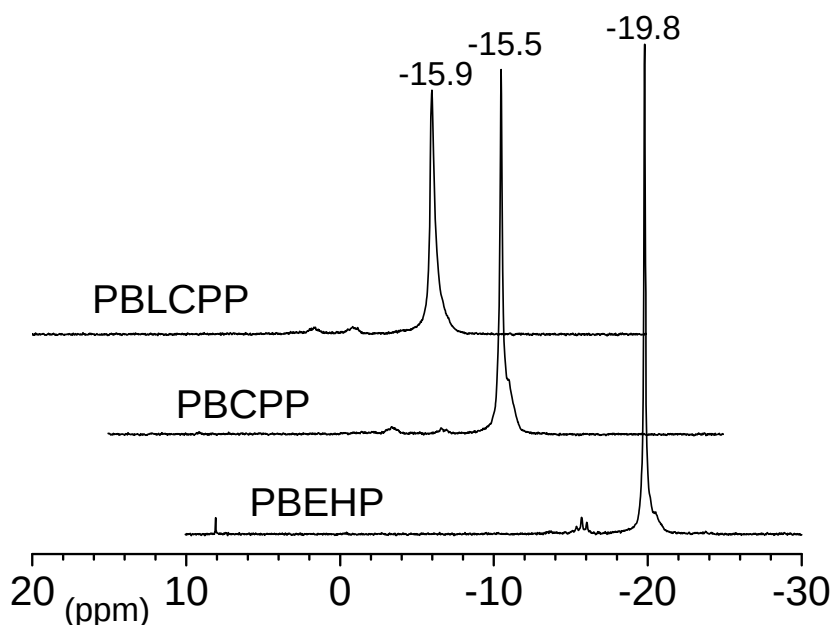


Fig. 4.42 Stacked ^{31}P NMR spectra of PBEHP (15), PBCPP (16) and PBLCPP (17).

Gel Permeation Chromatography. The number average molecular weight of poly[bis(ethyl 4-hydroxybenzoate)phosphazene] (PBEHP) was found to be 6.9×10^4 D with PDI of 1.83. A shoulder at low molecular weight region was observed as seen in **Fig. 4.43**, but the unavailability of GPC measurement for precursor poly(dichlorophosphazene) obstructs the comparison and evaluation of available data. This could be a tailing effect due to high concentration of the solute or improper solvent composition as eluent for this particular polymer in GPC column. Or it could be simply due to the degradation and chain cleavage during the course of substitution reaction.

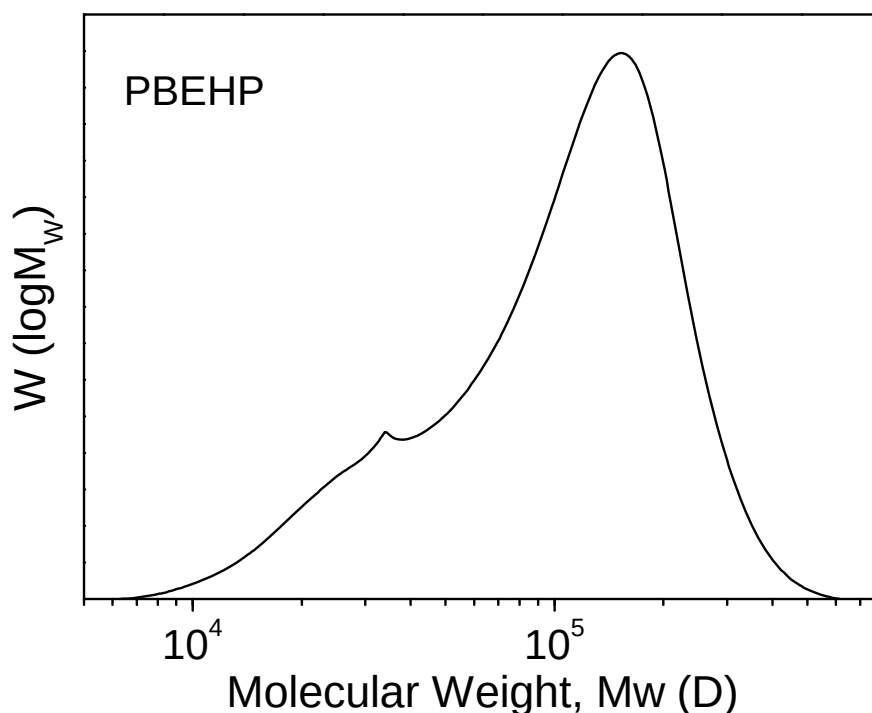


Fig. 4.43 GPC chromatogram of PBEHP (15).

Moreover the GPC measurement could not be performed for PBCPP and PBLCPP due to their insolubility in THF but owing to relatively high yields obtained for them after dialysis with 12000-14000 molecular weights cut off membrane, it might be speculated that no severe degradation or chain cleavage took place during the subsequent reactions.

Differential Scanning Chromatography. The thermal properties of the polymers were investigated in the temperature range up to 200 °C by DSC. PBEHP polymer showed a second order transition, T_g , at 5.9 °C accompanied by a crystalline melting at 114.9 °C. Deprotection of ester groups to yield acid (PBCPP) resulted in a tremendous change in the thermal properties. T_g value of the polymer increased to around 160 °C and no other transition was observed in the same temperature range. Moreover, polyanion (PBLCPP) possessed no transition temperature at all.

4.7.2 Characterization of PBPAIP

NMR Spectroscopy. Structural elucidation of poly[bis(3-amino-*N,N,N*-trimethyl-1-propanaminium iodide)phosphazene] (PPAIP) was performed again by NMR measurements. The reaction steps can be found in **Scheme 3.8** and the spectral properties for both synthesized polymers in Appendix 3.

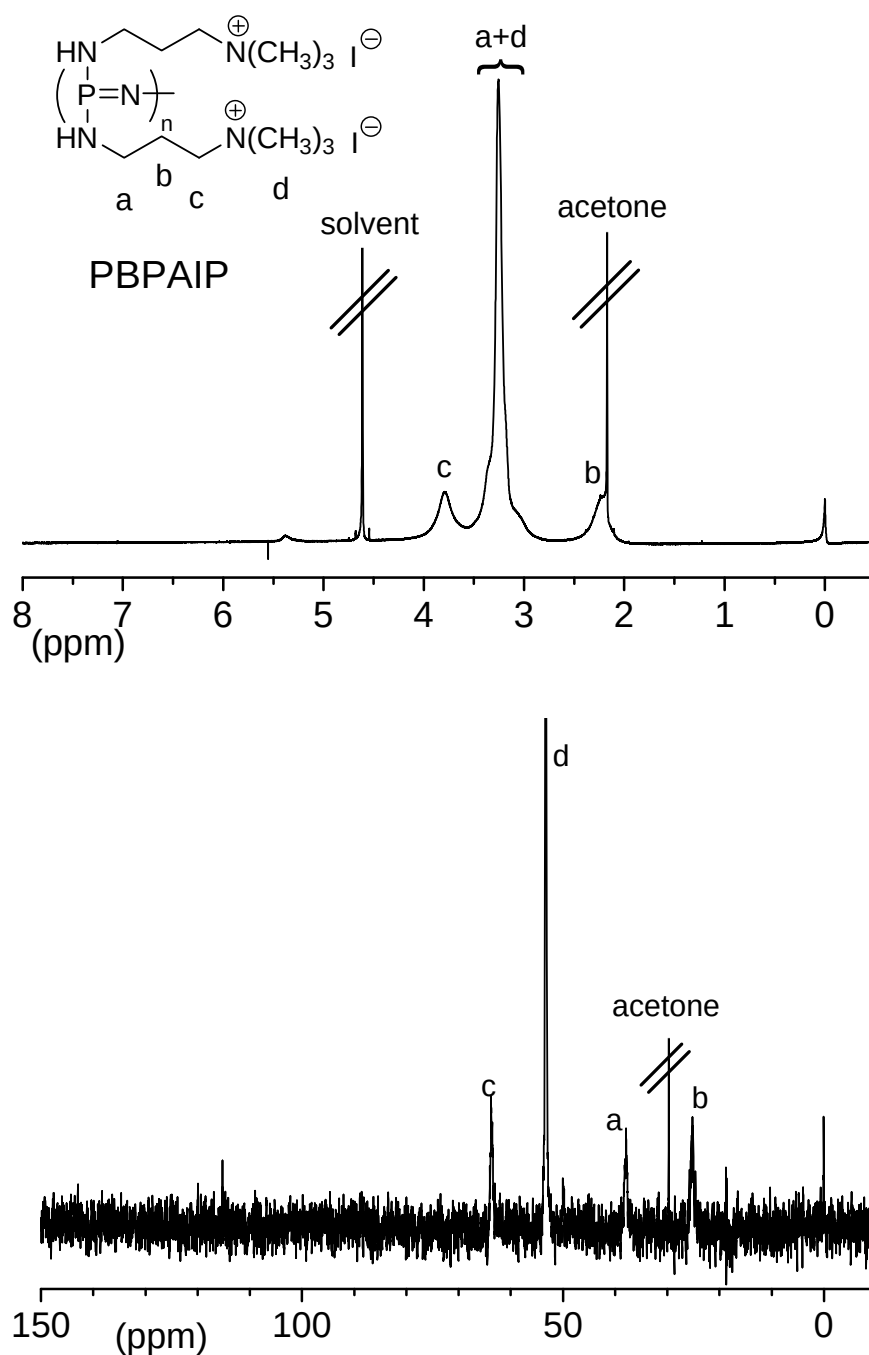


Fig. 4.44 ^1H and ^{13}C NMR spectra of PBPAIP (19) in D_2O .

^1H and ^{13}C spectra of PBLCPP are depicted in Fig. 4.44 with the assigned chemical shifts according to 2D NMR spectra indicating the pure single polycation.

Fig. 4.45 represents the ^{31}P NMR spectra of the polymers involved in the synthesis of polycation (19) (the abbreviations and chemical structures can be found in **Scheme 3.8**).

The substitution pattern was followed by ^{31}P NMR. The signal at 6.5 ppm was attributed to the fully substituted repeating units, which was accompanied by relatively small one at 14.7 ppm (**Fig. 4.45** (a)). This small signal was already present before exposing the polymer solution to air or to dialysis water thus it seems unlikely that the signal represents the presence of hydrolysis product. The reason could be originated from some competing reactions originated from tertiary amine groups [164]. The quaternization reaction yielding PBPAIP, on the other hand, resulted in great broadening of the NMR signal (**Fig. 4.45** (b)), as commonly observed for the macromolecular functionalization reactions where the nitrogen atom on the polymer backbone could also be involved in the reaction, especially when the reagent employed is considerably small (like methyl iodide in this particular case).

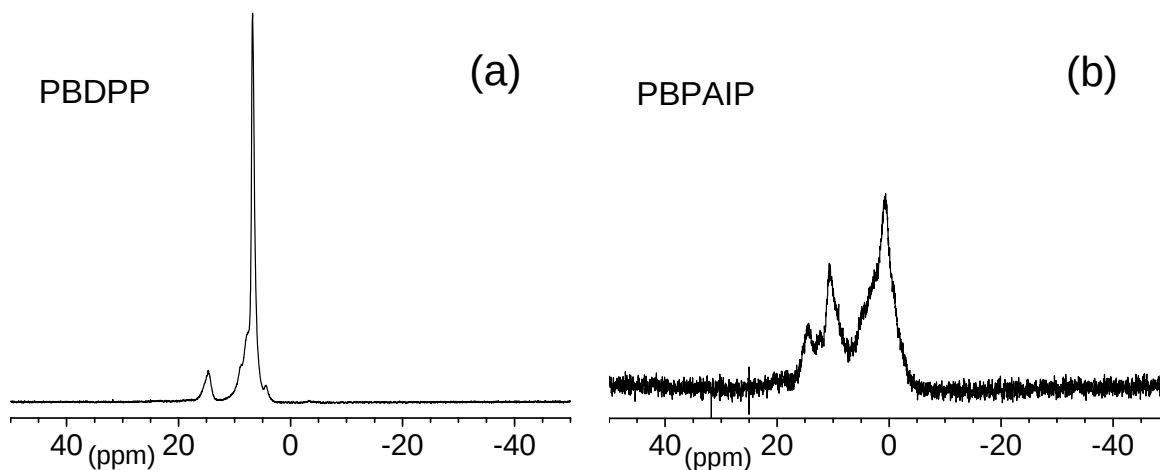


Fig. 4.45 ^{31}P NMR of (a) PBDPP (**18**) and (b) PBPAIP (**19**).

Gel Permeation Chromatography. The number average molecular weight of poly[bis(3-(dimethylamino)-1-propylamino)phosphazene] (PBDPP) was determined to be 2.6×10^4 D with PDI of 1.41. **Fig. 4.46** represents the GPC chromatogram of the polymer. No comparison could be done again since GPC measurement for poly(dichlorophosphazene) was not available. The molecular weight of the polycation (**19**) could not be determined owing to its insolubility in THF, but nevertheless the ^{31}P NMR signal and rather low yield after dialysis (33 %) reflects the presence of severe degradation and chain cleavage during quaternization.

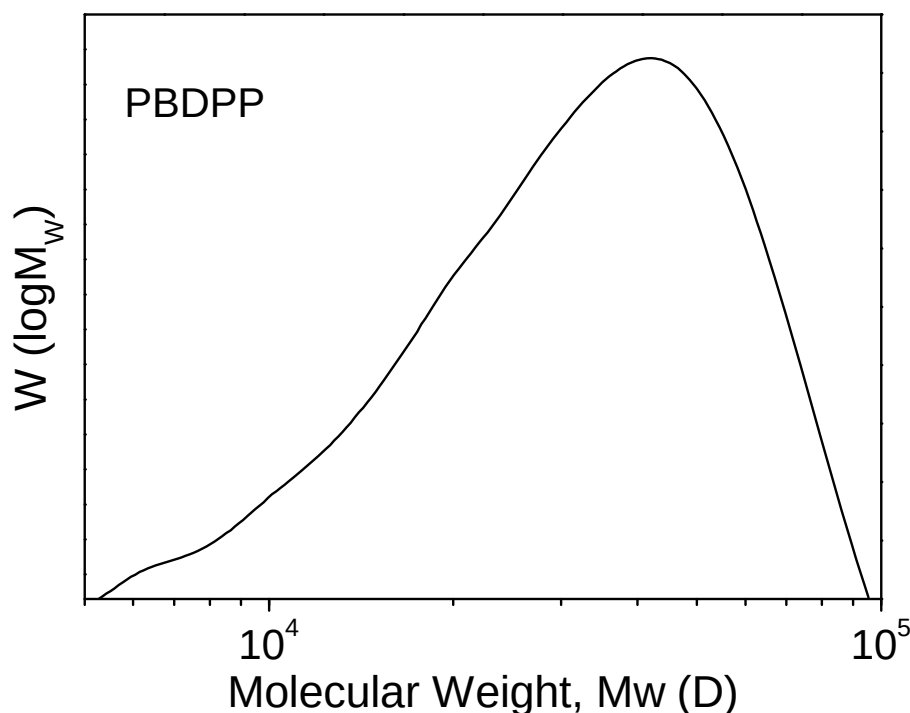


Fig. 4.46 GPC chromatogram of PBDPP (18).

4.7.3 Application as Polyelectrolyte Multilayers

The first polyelectrolyte multilayer system composed completely of polyphosphazene (PBPAIP/PBLCPP) as well as with some other organic polymer namely poly(styrene sulfonate) (PSS) and poly(acrylic acid) (PAA) for comparison have been prepared under different conditions, for instance salt concentration or pH, and investigated for their electrical properties by Hofmann [165]. Here only a small part of these results will be presented for the wholeness of current section with Hofmann's permission.

Fig. 4.47 gives the layer growth of PBPAIP/PSS with (0.5 mol/L NaCl) and without salt together with PBPAIP/PBLCPP with 0.1 mol/L LiCl, where PBPAIP was buffered to 5.1. A linear increase of 1 nm per layer was detected for PBPAIP/PSS system without salt. The increase in layer growth was considerably high (slope = 2.45) with 0.5 M NaCl, which was in accordance with the results observed for other PEMs. This was usually attributed to the increased ionic strength of the solution forming coiled structure and resulted in lower degree of interdigitation, thus accelerating layer growth [166]. Unfortunately, no regular growth for PBPAIP/PBLCPP was observed under varying pH values but still reproducible

results could be obtained when PBPAIP was buffered. More detailed results and explanations can be found elsewhere [165].

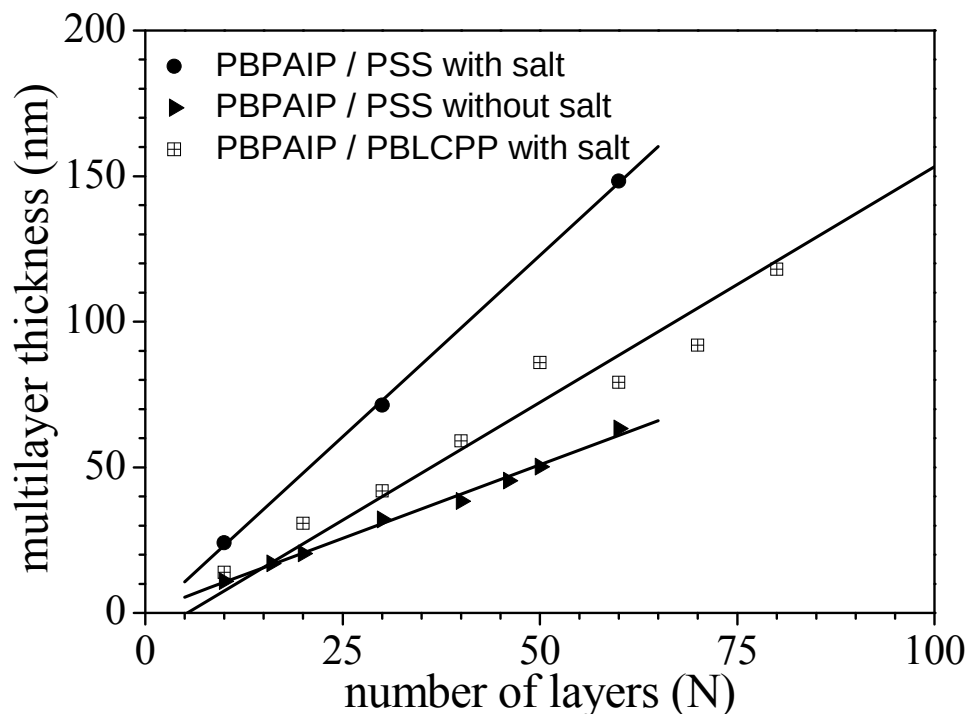


Fig. 4.47 Multilayer thickness of PBPAIP / PSS with 0.5 mol/L NaCl and without salt and PBPAIP / PBLCPP with 0.1 mol/L LiCl.

T- and Li- Salt Dependence of Conductivity. The ionic conductivities of the PEMs were scanned in the frequency range from 5 Hz to 13 MHz. The frequency dependent conductivities of some selected PEMs were given in **Fig. 4.48**. The theoretically expected DC plateau, where the conductivity is independent from frequency, was surprisingly not observed for the PEMs, which was attributed to the polarization effect at lower frequencies but relatively smooth region below 10^3 Hz could be regarded as DC conductivity. The measured conductivities at different layer thicknesses turned out to be not the same. The detailed investigation revealed that the penetration of gold electrodes coated on the surface of polymer electrolytes was dependent to varied from one technique to another and also one sample to another. The corrected conductivity plots of PBPAIP/PBLCPP with 100 and 200 layers were depicted in the following figure, where they showed quite similar conductivity curves. The conductivity measurement of the same sample from the same measuring point at a different time showed however a great

deviation in the conductivity spectrum. These differences could be a result of 10-20 wt-% moisture content of the samples [159], which can also vary with the humidity of the ambient atmosphere.

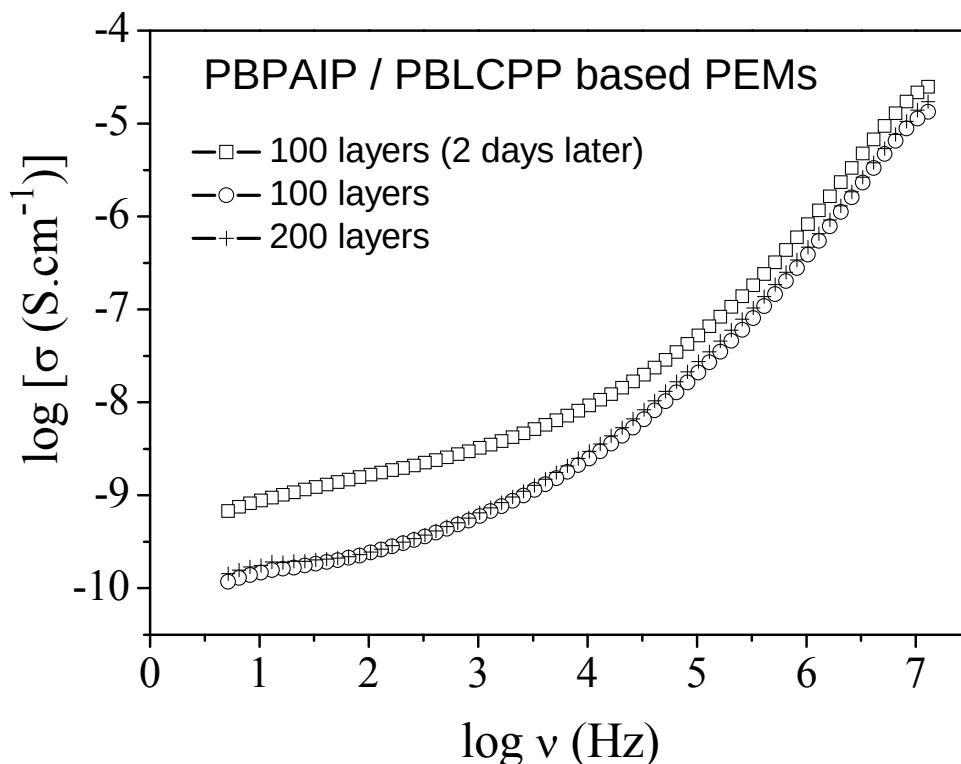


Fig. 4.48 Frequency dependent conductivity of PBPAIP / PBLCPP based PEMs.

4.7.4 Final Commentary

PEMs composed of only polyphosphazene PBPAIP/PBLCPP as well as PBPAIP/PSS and PBPAIP/PAA were successfully prepared for the first time. The PBPAIP should be buffered for PBPAIP/PBLCPP system in order to be able to obtain reproducible results.

The conductivity values in the order of 10^{-9} S/cm was obtained for the PEMs, however the variation in the moisture content of the atmosphere imparted some difficulties in terms of reproducibility of the conductivity measurements. Thus, a bit more controlled atmosphere is required to acquire reliable and reproducible results.

5 SUMMARY, CONCLUSIONS AND OUTLOOK

5.1 Summary and Conclusions

The main aim of the present study was to synthesize and demonstrate the advantages and versatility of modified inorganic based polymers as host materials for salt-in-polymer electrolytes. A larger part of this thesis concerned the preparation of new polysiloxanes for this purpose, which were chosen due to their superior thermal and chemical stability. Both lithium triflate and lithium bis(trifluoromethanesulfone)imide were used as electrolytic salts.

Chapter 4.1 starts with the synthesis of oligoether functionalized polysiloxane (OPS). The functionalization was straightforward via platinum catalyzed hydrosilylation reactions. The electrical properties of this comb polysiloxane were investigated after dissolving lithium triflate in the form of salt-in-polymer membranes. Although the synthesis of similar polymer structures has been reported already in the literature, no results on this particular salt-in-polymer electrolyte have been reported. The slight crystallization tendency observed well below room temperature for the pure polymers disappeared after salt addition. The room temperature conductivity of the polymer electrolyte at an optimum salt concentration was near to $10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which is only an order of magnitude lower than the requirement for industrial applications. This result also showed that the approach to design comb like polymers with a flexible backbone and solvating oligoether side chains was really promising to attain improved polymer electrolyte systems as compared to linear poly(ethylene oxide)s. On the other hand, in the absence of cross linking, the inadequate dimensional stability of the almost liquid polymers limits the application of such materials as battery separators.

Chapter 4.2 was devoted to overcome the low dimensional stability possessed by OPS type polymer electrolytes. Sol-gel cross linking of the trimethoxy units that was co-substituted randomly to the main chain was chosen as the tool to maintain the dimensional stability of the membranes. It was aimed to accomplish cross linking with a small sacrifice in the conductivity. A systematic study, where the concentration of trimethoxy moiety increased gradually, was performed to find a compromise between mechanical and electrical properties. The polymer precursor synthesized by 10 mol-%

cross linker ratio ($T_{0.1}$ OPS) was found to be optimum as the host material. The conductivity values obtained for the acid catalyzed salt-in-polymer electrolytes doped with both lithium triflate and lithium bis(trifluoromethanesulfone)imide were only slightly less than the one for uncrosslinked polysiloxane. The relatively high conductivity values observed in the latter case were quite in accordance with the positive influence of larger anions with increased number of fluorine bearing groups. However rapid removal of the acid during solvent casting of the membranes sometimes imparted insufficient cross linking and therefore caused reproducibility problems. The cross linking by DBTL as an alternative catalyst resulted in a much better control of the cross linking degree. The more efficient cross linking by DBTL on the other hand resulted in an order of magnitude decrease in the conductivity value as compared to the uncrosslinked polysiloxane.

In Chapter 4.3 and 4.4, the effect of increasing the side chains was tested. Longer oligoether (L-OPS) and propylene oxide (PPO-PS) as side chains were investigated in order to get a more complete overview on the role of the side chains on the polysiloxane conductivities. The L-OPS based salt-in-polymer electrolytes possessed comparable electrical properties to the short chain derivatives except the lack of sol-gel cross linking ability. This was not surprising since the relatively small cross linking units could not react with each other due to the bulky oligoether sheath. This was overcome by incorporating the polymer in $T_{0.4}$ OPS polymer precursor, where the number x in T_x OPS indicates the molar fraction of trimethoxysilane on the introduced substituents along the polysiloxane chain. Although the L-OPS showed slightly better electrical properties than $T_{0.1}$ OPS as a polymer electrolyte, the latter system is more favorable in the sense of superior homogeneity on cross linking. Moreover, there is a higher probability for phase separation between the cross linked matrix and entrapped polymer chains in the former system although it was not observed in this study. On the other hand, the conductivity values observed for PPO-PS based salt-in-polymer systems were in general more depressed than the others.

These results on the effect of different catalysts and different polymer architectures provided a deeper insight into different polysiloxanes as polymer electrolytes. It also enabled us later on to choose a model system in order to study the effect of additives for improving the conductivity further.

$T_{0.1}$ OPS crosslinked by DBTL was chosen as the polymer host due to its preeminent dimensional stability and reproducibility to study the effect of additives. Oxide nano particles and low molecular weight borate esters were employed for this purpose in Chapter 4.5.

However, neither Al_2O_3 nor SiO_2 particles resulted in any noticeable improvement of the conductivity compared to particle free polymer electrolytes. This was in line with the common opinion that the conductivity enhancement was due to the decrease in crystallinity upon filler addition. Hence, the effect of filler particles has a less significant and sometimes even a depressive impact for completely amorphous systems.

On the contrary, the addition of low molecular weight borate esters as plasticizers brought about quite promising results with more than one order of magnitude increase in conductivity, for example, for the polymer electrolyte doped with B3. On the other hand, the Non-Arrhenius behavior observed in the presence of borate esters implied that the ionic conduction was mainly dominated by the segmental motion of the polymer chains rather than the possible diffusive motion of the low molecular weight component. These borates are not only interesting as plasticizers but also as electron deficient species which can strongly interact or even trap the anions. This can increase the ionic conductivity by creating more free cations and providing higher lithium transference numbers.

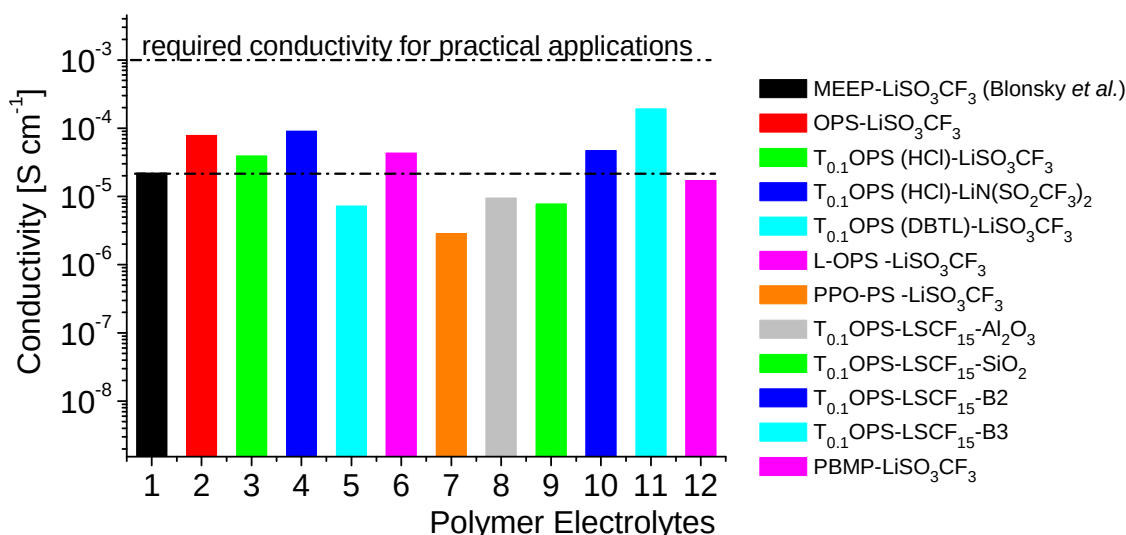


Fig. 5.1 Comparison of the conductivity of MEEP-LiSO₃CF₃ with those synthesized and characterized in this study. The maximum values of conductivities at 30 °C are depicted.

Since poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) is one of the most extensively investigated inorganic polymers for salt-in-polymer electrolytes, it is interesting to compare the conductivity of MEEP-LiSO₃CF₃ [19, 20] polymer electrolytes with the polymer electrolytes synthesized and investigated in this study. As can be seen in **Fig. 5.1**, the conductivities are in general comparable to MEEP systems. The effect of different salts (polymer electrolyte 3 and 4) on the conductivity value is clearly seen. The impact of oxide particle additives on the conductivity (8 and 9) can be monitored when compared with additive free polymer electrolyte system (5). Among them, the most promising results were obtained for dissolved molecular additives such as the borate esters, especially for B3 (10 and 11). In that case, the conductivity was almost 10 times higher as compared to the classic MEEP system. It can be expected that concepts like these are suitable to reach the desired conductivity of 10⁻³ S·cm⁻¹ for practical applications.

Up to this point, the results obtained for the polysiloxane based salt-in-polymer systems in this study are quite encouraging. The obtained insight and the observed positive factors for increasing conductivity show a considerable potential for electrolyte applications in rechargeable high-current lithium ion batteries and related electrochemical devices.

The last part of the thesis covered the synthesis and characterization of some model polyphosphazenes. This was the first time that a polyphosphazene was analyzed by Small Angle Neutron Scattering (SANS) in order to investigate molecular conformation and size and the interaction of dissolved salt with the polymer phase (Chapter 4.6). The radius of gyration and, with it, the molecular weight of the polymer were compared between the SANS experiment (direct method) and GPC results (indirect method). The data implied a correction factor of 1/2 for GPC results as compared to the exact molecular weight which lies in a range as expected from the accuracy of this technique.

The influence of the salt on the melt conformation of the polyphosphazene was also investigated. Addition of salt to PBMP had almost no effect on the R_g values indicating that there is virtually no decisive interaction between salt and polymer itself. The FT-IR and impedance measurements were also in accordance with the SANS results. The characteristic signals of the potential coordination sides predominantly remained unchanged. Moreover, the Arrhenius behavior of the temperature dependent conductivity revealed that the ionic conductivity is almost decoupled from the segmental mobility of polymer host. The data indicated a dominant diffusive transport of the ions for this

particular polyphosphazene system. Moreover and surprisingly, the conductivity value was comparable to that of the famous MEEP polymer electrolytes (**Fig. 5.1**). The result was contradictory to the general belief that a polymer electrolyte should contain an excess of solvating units such as oligoethers to attain higher solubilities and conductivities.

In Chapter 4.7 model polycations and polyanions based upon polyphosphazenes were synthesized and characterized. The synthesis of polyanions using polyphosphazenes functionalized with aryl side chains was quite straightforward. However, severe chain cleavage of polycations during the process of quaternization was observed. The alkyl spacer used for the polycation synthesis should also be exchanged in future developments with an aryl group to prevent the main chain again from aggressive conditions. PEMs composed of only polyphosphazene PBPAIP/PBLCPP[‡] as well as PBPAIP/PSS[‡] and PBPAIP/PAA[‡] were prepared for the first time. The PBPAIP should be buffered for PBPAIP/PBLCPP system in order to be able to obtain reproducible results. Conductivity values of the order of 10^{-9} S/cm were obtained for the PEMs, however the variation in the moisture content of the atmosphere imparted some difficulties in terms of the reproducibility of the conductivity measurements. Thus, carefully controlled dry atmosphere is needed to acquire reliable and reproducible results.

5.2 Outlook

The development of solvent free polymer electrolytes is highly dependent on the macromolecular structure of the polymer which is the host for all required components, such as electrolytic salts, fillers or plasticizers. The results of this study together with many other published data indicate an upper conductivity limit for solvent free, pure salt-in-polymer electrolytes near 10^{-4} S·cm⁻¹ which is still an order of magnitude lower than the technically required.

[‡] Multilayers prepared by different polyelectrolytes. PBPAIP and PBLCPP are polyphosphazene polyelectrolytes explained in Appendix 2. The other abbreviations are; PSS = poly(styrenesulfonate), PAA = poly(acrylic acid).

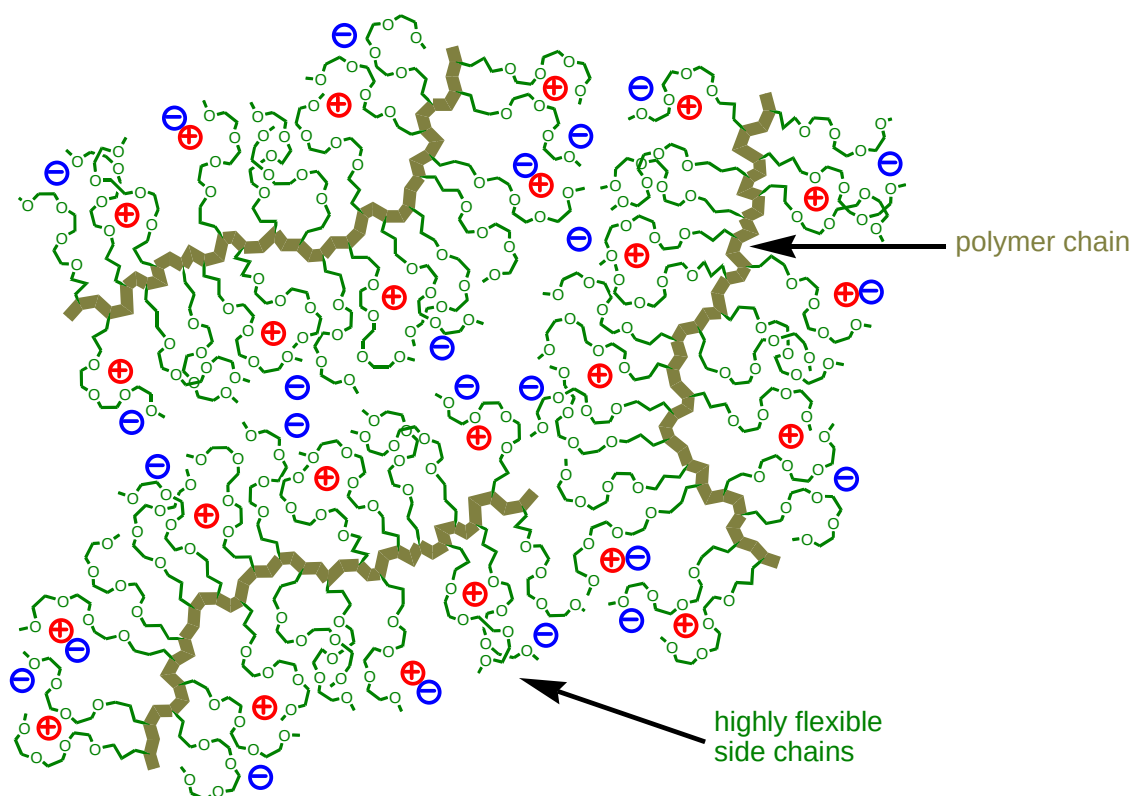


Fig. 5.2 Representative structure of salt-in-polymer electrolyte with flexible side chains.

The conduction of the ions takes place extensively in the amorphous region of the polymer via hand-to-hand transfer of cations by the segmental motion of the coordinating chains and a strong coupling to neighbouring anions. The free volume as well as a low viscosity are key factors for this mechanism in order to attain desirable conductivity values. So keeping these facts in mind, some other approaches are prerequisite to fine tune the properties and develop an ideal polymer electrolyte. **Fig. 5.2** represents a solvent free comb like salt-in-polymer electrolyte.

The results on the borate esters described in Chapter 4.5 showed that low molecular weight additives had a considerable effect on the conductivity of the polymer electrolytes. This resembles comparable experiences commonly applied for gel-electrolyte architectures where a rigid polymer structure is highly doped with aprotic solvents such as linear or cyclic carbonates to achieve a network with large channels and a large degree of free volume and high molecular mobility. The plasticizing effect of the additives, hence the decrease in glass transition temperature, is commonly regarded as the main factor for the increase in conductivity. Although the borate ester doped polymer systems in this

study showed quite promising results, the electrical properties still need further improvement.

The experiences and results of this work give rise to the definition of some promising routes towards high conductivity polymer electrolytes. One approach for the future improvement of fast ion conducting polymer electrolytes should concern an adopted way of cross linking. The cross linking via side chains as performed in this study or via longer oligoether groups as reported earlier would guarantee the dimensional stability but with a sacrifice in free volume since the cross linkages strongly depress the required mobility of polymer segments. The use of rod like rigid polymers, such as oligomeric liquid crystals, as spacer between the polymer chains could lead to much improvement. The representative structure of salt-in-polymer system separated by rigid polymer segments is given in **Fig. 5.3**. In such a network, the spacers prevent the flexible polymer chains from coming too close and entangling with each other, thereby enabling a higher degree of segmental motion and free volume, and as a result, enhancing the conductivity farther. The proper selection of low molecular weight additives, like borate esters, would also support solvation and high lithium transference number in such a loose structure.

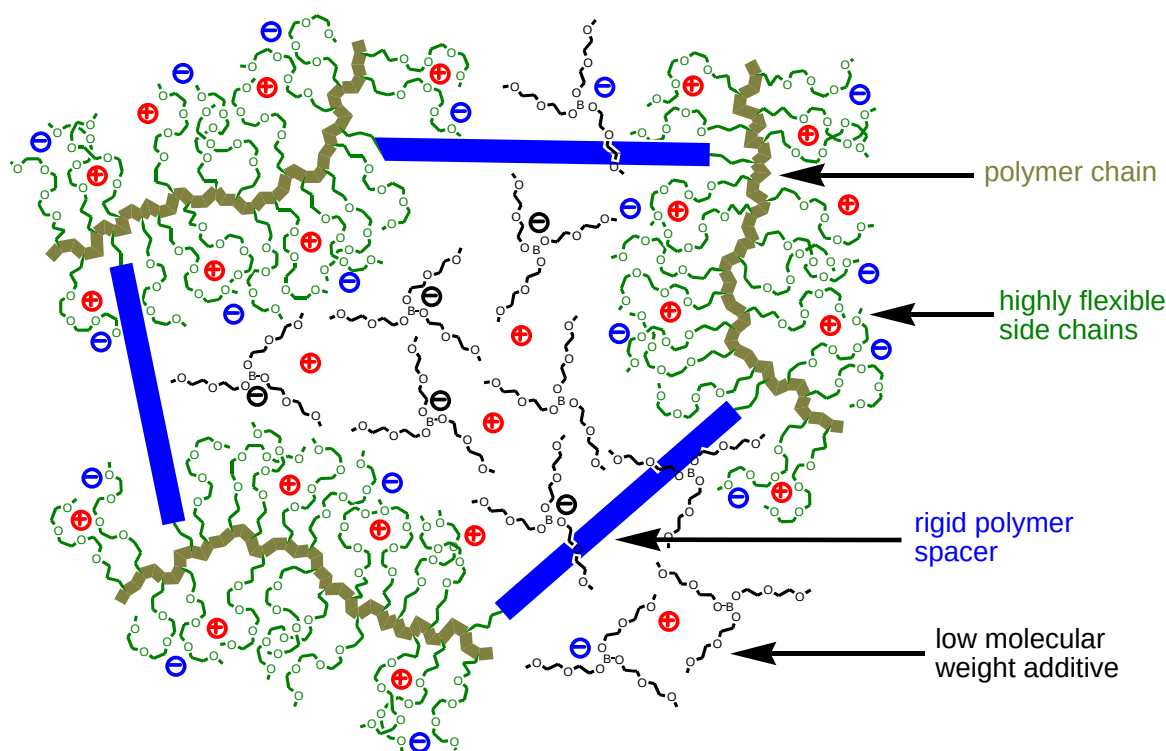


Fig. 5.3 Salt-in-polymer electrolyte with low molecular weight additives cross linked by rigid polymers.

Furthermore, this work as well as other recent publications gave strong hints that linear or low molecular weight polymers should result in better polymer electrolytes as discussed in the last part of Chapter 2.4.3. It is evident that such materials show a clearly enhanced conductivity owing to the high mobility and low viscosity. Therefore, entrapping a low molecular weight polymer solvent in a mechanically stabilized loose network, like polysiloxanes, MEEP or poly(ethylene oxide) will be another promising direction for further development.

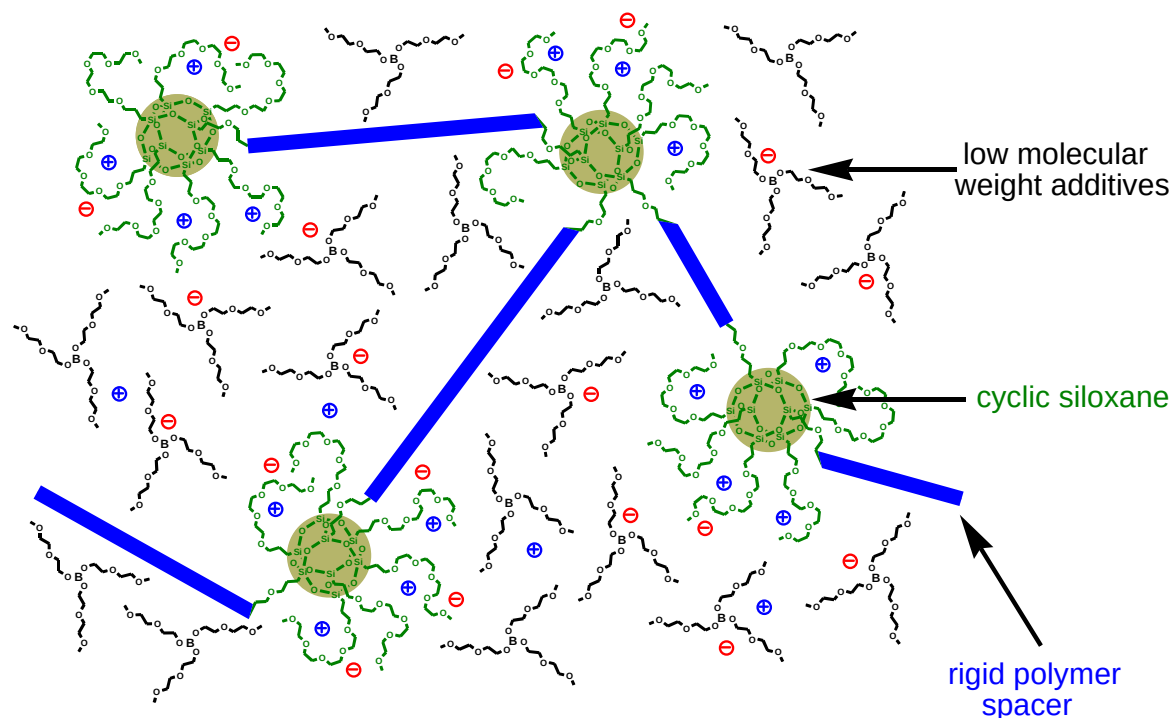


Fig. 5.4 *Cyclic siloxane based polymer electrolytes with low molecular weight additives cross linked by rigid polymers*

Lastly, the cyclic as well as cubic siloxanes, like polyhedral oligomeric silsesquioxanes known as POSS [167-170], could be investigated for the preparation of interpenetrating polymeric networks separated again by rigid rod like polymers. Silsesquioxanes are especially interesting compounds since they allow the formation of more regular structures due to their cubic nature. A representative structure of such a polymer electrolyte based on cyclic siloxane is depicted in **Fig. 5.4**. The approaches concerning low molecular weight solvents and polymers as argued above are also applicable here.

To conclude, there still exists a big challenge for further steps in the development of fast ion conduction polymer electrolytes towards industrial application in rechargeable lithium ion batteries. Polymers with inorganic backbones like polysiloxanes and polyphosphazenes seem to be among the most interesting candidates to reach the goal in this area.

5.3 List of Publications

Papers:

- 1. Synthesis of cross-linked comb polysiloxane for polymer electrolyte membranes.** Y. Karatas, N. Kaskhedikar, M. Burjanadze, H.-D. Wiemhofer, *Macromolecular Chemistry and Physics* 207 (4): 419-425 (2006).
- 2. Ionic conductivity of polymer electrolyte membranes based on polyphosphazene with oligo(propylene oxide) side chains.** N. Kaskhedikar, J. Paulsdorf, M. Burjanadze, Y. Karatas, D. Wilmer, B. Roling, H.-D. Wiemhofer, *Solid State Ionics* 177 (7-8): 703-707 (2006).
- 3. Investigation of chain dynamics in poly(bismethoxyphosphazene).** Y. Karatas, H.-D. Wiemhöfer, *Neutron Scattering at FRJ-2, Experimental Reports 2005/6*, 431-432 (2006).
- 4. Proton conducting membranes from sulfonated poly[bis(phenoxy)phosphazenes] with an interpenetrating hydrophilic network.** M. Burjanadze, J. Paulsdorf, N. Kaskhedikar, Y. Karatas, H.-D. Wiemhofer, *Solid State Ionics*, in Press (2006).
- 5. Polyphosphazene based composite polymer electrolytes.** N. Kaskhedikar, J. Paulsdorf, M. Burjanadze, Y. Karatas, B. Roling, H.-D. Wiemhöfer, *Solid State Ionics*, in Press (2006).
- 6. Polymer electrolytes based on cross-linked cyclotriphosphazenes.** N. Kaskhedikar, M. Burjanadze, Y. Karatas, H.-D. Wiemhöfer, *Solid State Ionics*, accepted (2006).
- 7. Ionic conductivity and investigation of chain dynamics in poly(bismethoxyphosphazene).** Y. Karatas, W. Pyckhout-Hintzen, R. Zorn, H.-D. Wiemhöfer, in preparation.
- 8. Mono comb polysiloxane-g-oligo(ethyleneoxide) polymer electrolytes crosslinked by different catalysts: synthesis, ionic conductivity and diffusion measurement using PFG-NMR.** Y. Karatas, M. Kunze, M. Schönhoff, H.-D. Wiemhöfer, in preparation.
- 9. Synthesis and characterization of polymer electrolytes grafted by poly(ethylene oxide).** Y. Karatas, N. Kaskhedikar, M. Burjanadze, H.-D. Wiemhöfer, in preparation.

10. Polymer electrolytes based on mono comb polysiloxane-g- poly(propylene oxide). Y. Karatas, N. Kaskhedikar, M Burjanadze, H.-D. Wiemhöfer, in preparation.

11. Ionic conductivity in oligoether functionalized mono comb polysiloxane based composite polymer electrolytes containing nano sized Al_2O_3 or SiO_2 . Y. Karatas, N. Kaskhedikar, M Burjanadze, H.-D. Wiemhöfer, in preparation.

12. The effect of low molecular weight borate esters on the conductivity of crosslinked mono comb polysiloxane-g-oligoether polymer electrolytes. Y. Karatas, N. Kaskhedikar, M Burjanadze, H.-D. Wiemhöfer, in preparation.

Oral Presentations:

1. Polyphosphazene based Composite Polymer Electrolytes. N. Kaskhedikar, J. Paulsdorf, M. Burjanadze, Y. Karatas, B. Roling, H.-D. Wiemhöfer, *International Conference on Solid State Ionics (SSI – 15)*, 17-22 July 2005, Baden-Baden (Germany).

2. Cross Linked Comb Polymers Based on Polysiloxanes as Polymer Electrolytes. Y. Karatas, N. Kaskhedikar, M. Burjanadze, H.-D. Wiemhöfer, *European Materials Research Society (E-MRS)*, Spring Meeting, 29 May – 02 June 2006, Nice (France).

Posters:

1. Conductivity and Thermal Study in UV-radiation Crosslinked MEEP Polymer Electrolytes. N. Kaskhedikar, J. Paulsdorf, M. Burjanadze, Y. Karatas, H.-D. Wiemhöfer, *84th International Bunsen Discussion Meeting*, 6-8 October 2004 Münster (Germany).

2. Mono- and mixed-substituent Poly[(aryloxy)phosphazenes with Acid Functional Groups. M. Burjanadze, N. Kaskhedikar, J. Paulsdorf, Y. Karatas, H.-D. Wiemhöfer, *Bunsen Discussion Meeting*, 6-8 October 2004 Münster (Germany).

3. Maßgeschneiderte Polyphosphazene – Biokompatible Polymermaterialien mit Anwendungsmöglichkeiten in Medizin, Pharmazie und Biosensorik. M. Burjanadze, N. Kaskhedikar, Y. Karatas, J. Paulsdorf, H.-D. Wiemhöfer, *Current Topics in Medical Technology*, 9. December 2005, Münster (Germany).

4. Synthesis of Cross-linked Comb Polysiloxane for Polymer Electrolyte Membranes.

Y. Karatas, N. Kaskhedikar, M. Burjanadze, H.-D. Wiemhöfer, *GDCh – Jahrestagung 2005*, 11-14 September, Düsseldorf (Germany).

5. Ionic Conductivity and Thermal Studies In Polyphosphazene Based Composite Polymer Electrolytes.

N. Kaskhedikar, J. Paulsdorf, M. Burjanadze, Y. Karatas, H.-D. Wiemhöfer. *GDCh – Jahrestagung 2005*, 11-14 September, Düsseldorf (Germany).

6. Sulfonated poly[(aryloxy)phosphazenes] as proton conductive membranes.

M. Burjanadze, N. Kaskhedikar, J. Paulsdorf, Y. Karatas, H.-D. Wiemhöfer, *GDCh – Jahrestagung 2005*, 11-14 September, Düsseldorf (Germany).

7. Polymere Ionenleiter auf der Basis Chemisch Modifizierter Polyphosphazene und Polysiloxane und davon Abgeleiteter Heterogener Polymersysteme.

M. Burjanadze, N. Kaskhedikar, J. Paulsdorf, Y. Karatas, H.-D. Wiemhöfer, *SFB – Referee Meeting, 30.August.2005*, Münster (Germany).

8. Poly[(Aryloxy)Phosphazenes] with Acid Functional Groups.

M. Burjanadze, N. Kaskhedikar, J. Paulsdorf, Y. Karatas, H.-D. Wiemhöfer, *International Conference on Solid State Ionics (SSI – 15)*, 17-22 July 2005, Baden-Baden (Germany).

9. Polymer Electrolytes Based on Cyclophosphazenes.

N. Kaskhedikar, J. Paulsdorf, M. Burjanadze, Y. Karatas, H.-D. Wiemhöfer, *European Materials Research Society (E-MRS), Spring Meeting*, 29 May – 02 June 2006, Nice (France).

1 Appendix

Materials

2-(Allyloxy)ethanol (98%)	Aldrich
Allyl bromide (98%)	Aldrich
Allyltrimethoxysilane (95%)	Aldrich
Celite [®] 545	Merck
Dialysis membrane (MWCO = 12000-14000 D)	Reichelt Chemietechnik
Dibutyltin dilaurate (>97%)	Merck
Dichloromethane (99.8%)	Merck
<i>N,N</i> -Dimethyltrimethylenediamine (>98%)	Merck
Ethyl 4-hydroxybenzoate (99%)	Aldrich
Iodomethane (purum)	Merck
Karstedt's catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution, 0.1 M)	Aldrich
Lithium bis(trifluoromethanesulfone)imide (purum)	Aldrich
Lithium bis(trimethylsilyl)amide (97%)	Aldrich
Lithium triflate (purum)	Aldrich
Methanol- <i>d</i> ₄ (99.8%)	Aldrich
Potassium tert-butoxide (98%)	Fluka
n-Pentane (98)	Baker
Phosphorus pentachloride (99%)	Merck
Phosphorus trichloride (99%)	Merck
Poly(ethylene glycol) 600	Fluka
Poly(ethylene glycol) 350 monomethyl ether (M _n = 350)	Fluka

Poly(methylhydrosiloxane) ($M_n = 1700-3200$)	Aldrich
Sicapent [®]	Merck
Sodium hydride (60% dispersion in oil)	Acros
Sulfuryl chloride (98%)	Merck
Tetrahydrofurane (99.9%)	Riedel-de Haën
Toluene (99.7%)	Scharlau
<i>p</i> -Toluenesulfonyl chloride (>99%)	Acros
Triethylene glycol monomethyl ether (95%)	Aldrich

2 Appendix

List of Abbreviations

ATMS	Allyltrimethoxysilane
DBTL	Dibutyltin dilaurate
DSC	Differential Scanning Calorimetry
FT-IR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
Mol-%	Mol percent
M _n	Number average molecular weight
M _w	Weight average molecular weight
NMR	Nuclear Magnetic Resonance
PEG 350	Poly(ethylene glycol) 350 monomethyl ether
PEG 600	Poly(ethylene glycol) 600
PPG 340	Poly(propylene glycol) monobutyl ether 340
Pt(dvs)	Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane
PMHS	Poly(methylhydrosiloxane)
T _g	Glass transition temperature.
THF	Tetrahydrofuran
wt-%	Weight percent

List of Abbreviations of the Synthesized Materials

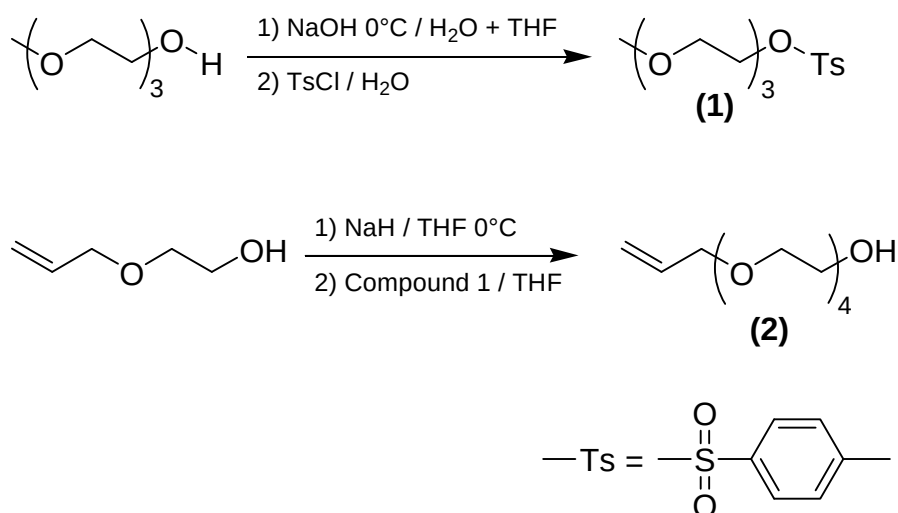
Compound	Abbreviation	Number
2-(2-(2-methoxyethoxy)ethoxy)ethoxy p-toluenesulfonate	-	(1)
Tetraethylene glycol allyl methyl ether	-	(2)
<u>O</u> ligoether Substituted <u>P</u> olysiloxane	OPS	(3)
5% Allytrimethoxysilane and 95% oligoether co-substituted poly(methylhydrosiloxane)	T _{0.05} OPS	(4)
10% Allytrimethoxysilane and 90% oligoether co-substituted poly(methylhydrosiloxane)	T _{0.1} OPS	(4)
20% Allytrimethoxysilane and 80% oligoether co-substituted poly(methylhydrosiloxane)	T _{0.2} OPS	(4)
30% Allytrimethoxysilane and 70% oligoether co-substituted poly(methylhydrosiloxane)	T _{0.3} OPS	(4)
40% Allytrimethoxysilane and 60% oligoether co-substituted poly(methylhydrosiloxane)	T _{0.4} OPS	(4)
Poly(ethylene glycol) 350 allyl methyl ether	APEG 350	(5)
Longer Oligoether Substituted Polysiloxane	L-OPS	(6)
Poly(propylene glycol) 340 allyl butyl ether	APPG 340	(7)
Poly(propylene oxide) Substituted Polysiloxane	PPO-PS	(8)
α , ω -diallyl poly(ethylene glycol) 600	DPEG 600	(9)
tris(2-(2-methoxyethoxy)ethyl) borate	B2	(10)
tris(2-(2-(2-methoxyethoxy)ethoxy)ethyl) borate	B3	(11)
Trichloro(trimethylsilyl)phosphoranimine	-	(12)
Poly(dichlorophosphazene)	-	(13)
Poly(bismethoxyphosphazene)	PBMP	(14a)
Poly(bis- <i>d</i> ₃ -methoxyphosphazene)	<i>d</i> ₆ -PBMP	(14b)
Poly[bis(ethyl 4-hydroxybenzoate)phosphazene]	PBEHP	(15)
Poly[bis(carboxylatophenoxy)phosphazene]	PBCPP	(16)
Poly[bis(lithium carboxylatophenoxy)phosphazene]	PBLCPP	(17)
Poly[bis(3-(dimethylamino)-1-propylamino)phosphazene]	PBDPP	(18)
Poly[bis(3-amino- <i>N,N,N</i> -trimethyl-1-propanaminium iodide)phosphazene]	PBPAIP	(19)

3 Appendix

A3.1 Synthetic Procedures - Polysiloxanes

2-(2-(2-methoxyethoxy)ethoxy)ethoxy p-toluenesulfonate(1).

Compound **1** is prepared according to the method described by Ouchi et al [171]. Triethylene glycol monomethyl ether and (224 mL, 1.4 mol) in 300 mL of THF was added dropwise to a solution of NaOH (80 g, 2 mol) in water and THF (400 mL and 300 mL) at 0 °C. This mixture was stirred for a further 30 min and added dropwise the solution of p-toluenesulfonyl chloride (247 g, 1.3 mol) in 500 mL THF. After being stirred at room temperature for a further 2 hours, the organic phase was separated by separatory funnel and all volatiles were removed by rotary evaporation. Residue and aqueous phase were combined and the mixture was extracted with 3 x 500 mL dichloromethane, that was subsequently dried with magnesium sulfate and all volatiles were removed by rotary evaporation, yielding a colorless oil, which was pure enough and used without further purification, 415 g (100 %). ^1H NMR (CDCl_3): δ = 7.78 (d, 2H), 7.34 (d, 2H), 4.15 (m, 2H), 3.69–3.50 (m, 10H), 3.35 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (CDCl_3), δ = 144.5, 132.8, 129.5, 127.6, 71.6, 70.4-70.1, 69.0, 68.3, 58.6, 21,2; MS (70 eV): m/z = 319 (MH^+).



Scheme A.3.1 Preparation of oligoether side chain for the preparation of OPS and $T_x\text{OPS}$ polymers.

Tetraethylene glycol allyl methyl ether (2).

A solution of 2-(allyloxy)ethanol (28.9 mL, 0.27 mol) in 200 mL of THF was added dropwise to a suspension of NaH (60 wt-% suspension in mineral oil) (12.0 g, 0.30 mol) in 100 mL THF chilled to 0 °C. This mixture was stirred for a further 1 h and a solution of compound **1** (79.5 g, 0.25 mol) in 250 mL of THF was dropwise added and stirred for another two hours before allowing to warm to the room temperature. This mixture was then stirred overnight and filtered in order to remove salt and unreacted NaH. All volatiles were removed by rotary evaporation to yield slightly yellow oil. This oil was dissolved into 200 mL water and extracted with 3 x 100 mL dichloromethane, that was subsequently dried and distilled (130 °C, 5 mmHg) to yield tetraethylene glycol allyl methyl ether, 50.5 g (80 %). ^1H NMR (CDCl_3): δ = 5.90 (m, 1H), 5.21 (dd, 2H), 4.01 (d, 2H), 3.70-3.50 (m, 16H), 3.37 (s, 3H), 2.4 (s, 3H); ^{13}C NMR (CDCl_3): δ = 134.4, 116.4, 71.7, 71.5, 70.3–70.1, 70.0, 69.0, 58.5; MS (70 eV): m/z = 249 (MH^+).

Oligoether Substituted Polysiloxane (OPS) (3)

3.89 g (60 mmol Si–H) of PMHS were transferred into a 100 mL flask under nitrogen using standard Schlenk techniques. High vacuum was applied to the flask for half an hour before the addition of tetraethylene glycol allyl methyl ether (1.3 times excess of the Si–H was used, 78 mmol, 19.3 g). The mixture was then dissolved in 50 mL of toluene and 20 μL of Pt(dvs) was syringed into the flask. The homogeneous mixture was degassed and placed into an oil bath, which was previously set to 75 °C. The reaction continued overnight and the completeness was checked by ^1H NMR, (if there were still unreacted Si–H groups another portion of tetraethylene glycol allyl methyl ether was added and reaction continued for further 3 hours and checked again by ^1H NMR). The solution was filtered in toluene through a column of activated carbon sandwiched between two layers of celite in order to remove the platinum catalyst. All the volatiles were removed by rotary evaporation and the polymer was precipitated at least three times into pentane to remove side products. Finally, all volatiles were removed under vacuum and further evacuated under high-vacuum for 24 hours to isolate the colorless viscous polymer, 16.7 g (89 %). ^1H NMR (CDCl_3): δ = 3.86–3.43 (broad, 16H), 3.33 (broad, 5H), 1.54 (broad, 2H), 0.41 (broad, 2H), 0.0 (broad, 4H); ^{13}C NMR (CDCl_3): δ = 73.8, 71.7, 71.6, 70.3, 69.8, 58.7, 22.9, 13.3, -0.6. One peak was observed in the GPC measurement with the average molecular weight $M_n = 1.32 \times 10^4$ D and a polydispersity index (PDI) of 2.34.

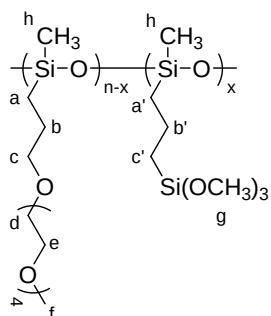
Precursor T_{0.05}OPS (4)

In a typical reaction, 3.89 g (60 mmol Si–H) of PMHS were transferred into a 100 mL flask under nitrogen using standard Schlenk techniques. High vacuum was applied to the flask for half an hour before the addition of ATMS (0.487 g, 3 mmol). The mixture was then dissolved in 40 mL of toluene and 20 μ L of Pt(dvs) was syringed into the flask. The homogeneous mixture was degassed and placed into an oil bath, which was previously set to 75 °C. The reaction continued until no residual ATMS allyl protons were detected in the ¹H NMR (the reaction was complete typically between 2 to 6 hours depending on the ATMS concentration). Tetraethylene glycol allyl methyl ether was added afterwards in order to substitute the remaining Si–H (1.2 times excess of the remaining Si–H was used, 68.4 mmol, 17.0 g) and reaction continued at 75 °C overnight. The completeness of the reaction was again monitored by ¹H NMR, (if there were still unreacted Si–H groups another portion of tetraethylene glycol allyl methyl ether was added and reaction continued for further 3 hours and checked again by ¹H NMR). The solution was filtered in toluene through a column of activated carbon sandwiched between two layers of celite in order to remove the platinum catalyst. All volatiles were removed by rotary evaporation and the polymer was precipitated at least three times into pentane to remove side products. Finally, all volatiles were removed under vacuum and further evacuated under high-vacuum for 24 hours to isolate the colorless viscous polymer, 15.6 g (84 %). ¹H and ¹³C NMR data are listed in **Table A.3.1**. Only one peak was observed in the GPC measurement with the average molecular weight $M_n = 1.32 \times 10^4$ D and a polydispersity index (PDI) of 1.91.

Precursor T_{0.1}OPS (4)

T_{0.1}OPS (4) was prepared in a manner similar to that described for T_{0.05}OPS (4). The following reagents and quantities were used: PMHS (3.89 g, 60 mmol Si–H), ATMS (0.973 g, 6 mmol), toluene (40 mL), Pt(dvs) (20 μ L), tetraethylene glycol allyl methyl ether (1.2 times excess of the remaining Si–H, 64.8 mmol, 16.1 g). The product was isolated to yield 15.0 g (83 %) polymer with the average molecular weight $M_n = 1.26 \times 10^4$ D and a PDI of 1.72. ¹H and ¹³C NMR data are listed in **Table A.3.1**.

Table A.3.1 ^1H and ^{13}C data for $T_x\text{OPS}$ polymers, (for the numbers refer to **Scheme 3.1**)

	x	$^1\text{H} / ^{13}\text{C}$ chemical shifts (ppm)									
		a	b	c ⁽⁺⁾	d+e	f	a'	b'	c'	g	h
$T_x\text{OPS(4)}$ 	0.05	0.48 13.2	1.59 22.8	3.36 73.6	3.51-3.69 69.6-71.6	3.36 58.6	0.69 —	1.47 —	0.60 —	* 50.0	0.06 -0.6
	0.1	0.47 13.4	1.59 23.0	3.38 73.9	3.52-3.69 69.9-71.9	3.38 58.9	0.68 —	1.48 —	0.60 —	* 50.3	0.06 -0.5
	0.2	0.47 13.5	1.59 23.1	3.38 74.0	3.53-3.69 69.9-71.9	3.38 58.9	0.68 —	1.48 16.5	0.60 —	3.55 50.3	0.05 -0.5
	0.3	0.48 13.4	1.60 23.0	3.38 73.9	3.52-3.69 69.8-71.8	3.38 58.8	0.69 13.3	1.48 16.3	0.60 21.5	3.54 50.2	0.06 -0.6
	0.4	0.48 13.3	1.60 23.0	3.38 73.8	3.51-3.68 69.8-71.8	3.38 58.8	0.69 13.2	1.48 16.3	0.60 21.5	3.55 50.2	0.06 -0.6
	(⁺)	proton signals are screened by “f” protons									
	*	screened by “d” and “e” protons									
	—	signals could not be detected									

Precursor $T_{0.2}\text{OPS}$ (4)

$T_{0.2}\text{OPS}$ (**4**) was prepared in a manner similar to that described for $T_{0.05}\text{OPS}$ (**4**). The following reagents and quantities were used: PMHS (3.89 g, 60 mmol Si–H), ATMS (1.99 g, 12 mmol), toluene (40 mL), Pt(dvs) (20 μL), tetraethylene glycol allyl methyl ether (1.2 times excess of the remaining Si–H, 57.6 mmol, 14.3 g). The product was isolated to yield 14.5 g (81 %) polymer with the average molecular weight $M_n = 1.35 \times 10^4$ D and a PDI of 1.77. ^1H and ^{13}C NMR data are listed in **Table A.3.1**.

Precursor $T_{0.3}\text{OPS}$ (4)

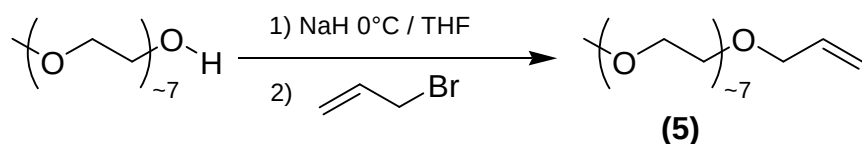
$T_{0.3}\text{OPS}$ (**4**) was prepared in a manner similar to that described for $T_{0.05}\text{OPS}$ (**4**). The following reagents and quantities were used: PMHS (3.89 g, 60 mmol Si–H), ATMS (3.1 g, 18 mmol), toluene (40 mL), Pt(dvs) (20 μL), tetraethylene glycol allyl methyl ether (1.2 times excess of the remaining Si–H, 50.4 mmol, 12.5 g). The product was isolated to yield 14.8 g (85 %) polymer with the average molecular weight $M_n = 1.37 \times 10^4$ D and a PDI of 1.79. ^1H and ^{13}C NMR data are listed in **Table A.3.1**.

Precursor T_{0.4}OPS (4)

T_{0.4}OPS (**4**) was prepared in a manner similar to that described for T_{0.05}OPS (**4**). The following reagents and quantities were used: PMHS (3.89 g, 60 mmol Si–H), ATMS (4.1 g, 24 mmol), toluene (40 mL), Pt(dvs) (20 μ L), tetraethylene glycol allyl methyl ether (1.2 times excess of the remaining Si–H, 43.2 mmol, 10.71 g). The product was isolated to yield 13.0 g (77 %) of polymer with the average molecular weight $M_n = 1.33 \times 10^4$ D and a PDI of 1.80. ¹H and ¹³C NMR data are listed in **Table A.3.1**.

Poly(ethylene glycol) 350 allyl methyl ether (APEG 350) (5)

Poly(ethylene glycol) 350 allyl methyl ether was synthesized by the method described in the literature [23, 36]. A solution of poly(ethylene glycol) monomethyl ether (35 g, 0.1 mol) in 200 mL of freshly distilled THF was added dropwise to a suspension of NaH (60 wt-% suspension in mineral oil) (4.8 g, 0.12 mol) in 50 mL of THF chilled to 0 °C in a round-bottom flask under the flow of dry nitrogen. The mixture was further stirred for 3 hours before the dropwise addition of allyl bromide (14.5 g, 0.12 mol) in 50 mL of THF. The precipitation of NaBr was observed soon after the addition of allyl bromide. The reaction was continued at room temperature another 5 hours and followed by the addition of ~5 mL of wet acetone to quench any unreacted NaH. The mixture was filtered to remove salt and all the volatiles were removed by rotary evaporation. The oil was dissolved in 200 mL of salt-water and extracted with 3 x 100 mL of dichloromethane, that was subsequently dried (Na₂SO₄) and concentrated to yield clear colorless APEG 350, 38.2 g (98 %). ¹H NMR (CDCl₃): δ = 5.89 (m, 1H), 5.23 (dd, 2H), 3.99 (m, 2H), 3.76-3.45 (m, 29H), 3.34 (s, 3H); ¹³C NMR (CDCl₃): δ = 134.4, 116.5, 71.7, 71.5, 70.5-69.9, 69.1, 58.5; MALDI-TOF $\cong$ 491 (MNa⁺)



Scheme A.3.2 Synthesis of APEG 350 (**5**)

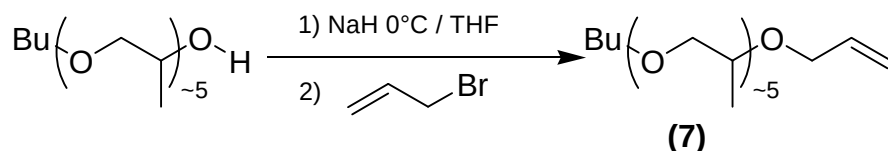
Longer Oligoether Substituted Polysiloxane (L-OPS) (6)

2.59 g (40 mmol Si–H) of PMHS were transferred into a 100 mL flask under nitrogen using standard Schlenk techniques. High vacuum was applied to the flask for half an hour before the addition of APEG 350 (**5**) (1.3 times excess of the Si–H was used, 52 mmol, 20.3 g). The mixture was then dissolved in 50 mL of toluene and 40 μ L of Pt(dvs) was syringed into the flask. The homogeneous mixture was degassed and placed into an oil bath, which was previously set to 75 °C. The reaction continued overnight and the completeness was checked by ^1H NMR, (if there were still unreacted Si–H groups another portion of tetraethylene glycol allyl methyl ether was added and reaction continued for further 3 hours and checked again by ^1H NMR). The solution was filtered in toluene through a column of activated carbon sandwiched between two layers of celite in order to remove the platinum catalyst. All the volatiles were removed by rotary evaporation and the polymer was precipitated at least three times into pentane to remove side products. Finally, all volatiles were removed under vacuum and further evacuated under high-vacuum for 24 hours to isolate the colorless viscous polymer, 16.0 g (88 %). ^1H NMR (CDCl_3): δ = 3.75–3.49 (broad, 36H), 3.36 (broad, 5H), 1.58 (broad, 2H), 0.47 (broad, 2H), -0.04 (broad, 4H); ^{13}C NMR (CDCl_3): δ = 73.8, 71.8, 70.8–70.1, 69.8, 58.8, 23.0, 13.4, -0.5. One peak was observed in the GPC measurement with the average molecular weight $M_n = 1.51 \times 10^4$ D and a polydispersity index (PDI) of 2.08.

Poly(propylene glycol) 340 allyl butyl ether (APPG 340) (7)

A solution of poly(propylene glycol) monobutyl ether (34 g, 0.1 mol) in 200 mL of freshly distilled THF was added dropwise to a suspension of NaH (60 wt-% suspension in mineral oil) (4.8 g, 0.12 mol) in 50 mL of THF chilled to 0 °C in a round-bottom flask under the flow of dry nitrogen. The mixture was further stirred for 3 hours before the dropwise addition of allyl bromide (14.5 g, 0.12 mol) in 50 mL of THF. The precipitation of NaBr was observed soon after the addition of allyl bromide. The reaction was continued at room temperature another 5 hours and followed by the addition of ~5 mL of wet acetone to quench any unreacted NaH. The mixture was filtered to remove salt and all the volatiles were removed by rotary evaporation. The oil was dissolved in 200 mL water and extracted with 3 x 100 mL of dichloromethane, that was subsequently dried (Na_2SO_4) and concentrated to yield clear slightly yellow poly(propylene glycol) 340 allyl butyl ether, 36.0 g (92 %). ^1H NMR (CDCl_3): δ = 5.90 (m, 1H), 5.19 (dd, 2H), 4.06 (m, 2H), 3.72–3.12

(m, 21H), 1.55 (m, 2H), 1.37 (m, 2H), 1.24-1.05 (m, 18H), 0.91 (t, 3H); ^{13}C NMR (CDCl_3): δ = 135.5, 116.1, 75.8-72.7, 71.1, 70.0, 31.7, 19.2, 17.6-17.1, 13,8.



Scheme A.3.3 Synthesis of APPG 340 (7)

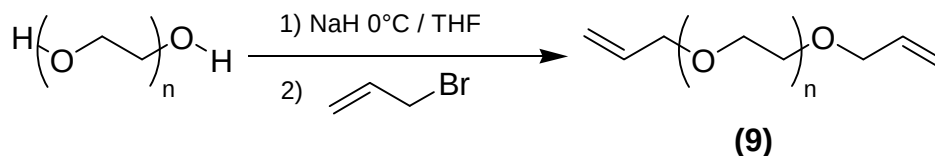
Poly(propylene oxide) Substituted Polysiloxane (PPO-PS) (8)

2.59 g (40 mmol Si-H) of PMHS were transferred into a 100 mL flask under nitrogen using standard Schlenk techniques. High vacuum was applied to the flask for half an hour before the addition of APPG 340 (7) (40 mmol, 15.2 g). The mixture was then dissolved in 50 mL of toluene and 40 μL of Pt(dvs) was syringed into the flask. The homogeneous mixture was degassed and placed into an oil bath, which was previously set to 75 $^{\circ}\text{C}$. The reaction continued overnight and the reaction progress was checked by ^1H NMR. The solution was filtered in toluene through a column of activated carbon sandwiched between two layers of celite in order to remove the platinum catalyst. All the volatiles were removed by rotary evaporation and the polymer was further evacuated to dryness under high-vacuum for 24 hours to isolate the colorless viscous polymer, 16.0 g (90 %). ^1H NMR (CDCl_3): δ = 4.69 (s), 4.09-2.88 (m), 1.55 (m), 1.37 (m), 1.24-1.09 (m, 18H), 0.91 (t), 0.50 (broad), 0.07 (broad); ^{13}C NMR (CDCl_3): δ = 76.3-74.7, 73.8, 73.4, 71.7, 32.3, 19.8, 18.4-17.6, 14,3, 0.1. One peak was observed in the GPC measurement with the average molecular weight $M_n = 1.71 \times 10^4$ D and a polydispersity index (PDI) of 1.71.

α , ω -Diallyl poly(ethylene glycol) 600 (DPEG 600) (9)

The synthesis of α , ω -diallyl poly(ethylene glycol) was carried out using the same reactions described above for APEG 350. The following reagents and quantities were used: NaH (4.8 g, 0.12 mol of 60 wt-% suspension in mineral oil), THF (50 mL), poly(ethylene glycol) 600 (30 g, 0.05 mol), THF (75 mL), allyl bromide (14.5 g, 0.12 mol), THF (50 mL). The product was isolated to yield 30 g (88 %) of colorless oil. The number of repeating unit was calculated to be around 9 from ^1H NMR peak integration. ^1H

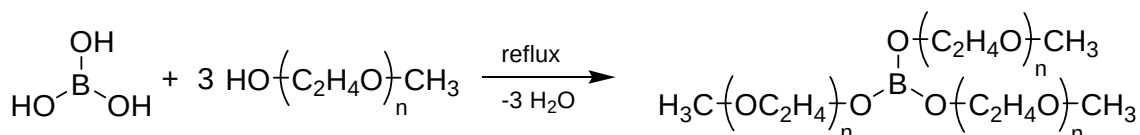
NMR (CDCl₃): δ = 5.79 (m, 2H), 5.14 (dd, 4H), 3.91 (d, 4H), 3.66-3.36 (m, 40H); ¹³C NMR (CDCl₃): δ = 134.5, 116.6, 71.8, 70.5-70.0, 69.2.



Scheme A.3.4 Synthesis of DPEG 600 (9).

Tris(2-(2-methoxyethoxy)ethyl) borate (B2) (10)

Tris(2-(2-methoxyethoxy)ethyl) borate was synthesized according to method described by Gierczyk et al [92]. 30.9 g (0.5 mol) of boric acid, 192.3 g (1.6 mol) of 2-(2-methoxyethoxy)ethanol and 100 mL of benzene were placed into a 500 mL round bottom flask attached to a Dean-Stark apparatus with a reflux condenser. The solution was refluxed until no more water isolated (24 hours). After removing the solvent, the oily product was distilled under reduced pressure (181 °C, 1.4 mmHg) to yield colorless B2, 153.5 g (83 %). ¹H NMR (CDCl₃): δ = 3.88 (dd, 6H), 3.57 (dd, 6H), 3.53 (dd, 6H), 3.47 (dd, 6H), 3.31 (s, 9H); ¹³C NMR (CDCl₃): δ = 71.8, 71.5, 70.3, 62.6, 58.9.



Scheme A.3.5 Synthesis of tris(oxaalkyl)borates B2 (10) and B3 (11).

Tris(2-(2-(2-methoxyethoxy)ethoxy)ethyl) borate (B3) (11)

Tris(2-(2-(2-methoxyethoxy)ethoxy)ethyl) borate was synthesized as B2. The following reagents and quantities are used: boric acid (15.5 g, 0.25 mol), 2-(2-(2-methoxyethoxy)ethoxy)ethanol (131.4 g, 0.8 mol), benzene (100 mL). The product was isolated under high vacuum (222 °C, 5x10⁻² mmHg) to yield B3, 112 g (90 %). ¹H NMR (CDCl₃): δ = 3.88 (dd, 6H), 3.65-3.57 (m, 18H), 3.54 (dd, 6H), 3.50 (dd, 6H), 3.33 (s, 9H); ¹³C NMR (CDCl₃): δ = 71.5, 71.2, 70.3, 70.1, 70.0, 62.3, 58.5.

Preparation of Polysiloxane Based Polymer Electrolytes

Noncrosslinked salt-in-polymer systems were prepared as follows: 0.5 g of the polymer was weighed into 5 mL of a screw-top vessel and dissolved in 1.5 mL of THF and thoroughly stirred for half an hour before the addition of required amount of lithium salt from a previously prepared stock solution in THF. The mixture was stirred for another 1 hour and the solvent was removed first by rotary evaporator and then under vacuum for at least 1 day.

In a typical cross-linking of T_xOPS polymers with HCl as catalyst, 0.75 g of precursor polymer was dissolved in 4 mL of THF and thoroughly mixed for half an hour before the addition of catalytic amount of acid (one drop of 0.1 N HCl solution) to initiate the cross-linking process. After stirring another 3 hours, required amount of lithium triflate from the previously prepared stock solution in THF (0.2 g/mL) was added to the mixture and stirring continued for further one hour. The mixture then poured onto 1 cm² platinum electrode, which was placed into a Teflon mould with a diameter of 4 cm. The mould was covered with parafilm and solvent was allowed to evaporate slowly over night. Finally, the membrane was dried in an oven at 75 °C for 3 days and at 100 °C for one hour. Homogeneous and transparent films with average thickness of 200 µm were obtained in this way. These films were insoluble in all solvents; only swollen in THF.

The preparation of L-OPS was performed similarly as explained above, except for that L-OPS was mixed with 20 % of T_{0.4}OPS in order to maintain the dimensional stability.

Since PPO-PS polymer has still non-substituted Si-H bonds and they are sensitive to the moisture, a stock solution of the precursor polymer was prepared in THF to prevent self cross-linking during storage. For the preparation of PPO-PS polymer electrolytes, 0.5 g (0.24 mmol Si-H, 2 mL) of polymer was added 60 mg (0.12 mmol) of α , ω -diallyl poly(ethylene glycol) and mixed for half an hour before the addition of proper amount the lithium salt from the previously prepared stock solution (0.2 g/mL). The resulting solution was mixed another half an hour and Pt catalyst (5 µL) was syringed into the solution, which was kept at 60 °C overnight. The mixture then poured onto 1 cm² platinum electrode placed in a Teflon mold with a diameter of 4 cm. The mould was covered with parafilm and the solvent was allowed to evaporate. Finally the membrane was dried in an oven at 75 °C for 3 days.

Beside the methods mentioned above, the cross-linking with DBTL catalyst was mainly performed in bulk. T_{0.1}OPS was used as model precursor polymer for the synthesis. In a typical preparation 0.7 g (2.34×10^{-4} mol of $-\text{Si}(\text{OMe}_3)_3$) solution of T_{0.1}OPS in 2 mL of THF was added desired amount of lithium salt from the stock solution (0.2g/mL) and stirred for 1 hour, which was followed by the addition of 35 μL (0.59×10^{-4} mol) of DBTL as catalyst. The resulting solution was mixed further for half an hour, poured into polypropylene molds with a diameter of 5.5 cm and the solvent was removed to dryness under vacuum for 3 hours. Finally the curing of the sample was completed in an oven at 40 °C in 2 days and the sample was then dried another 1 day under vacuum.

For the preparation of nano particles and borate ester containing polymer electrolytes, the similar cross-linking procedure, which was explained above for T_{0.1}OPS with DBTL as catalyst was used. These new additives were only mixed at the beginning with polymer and in nano particle case the prepared solutions were kept in ultrasonic bath for 15 minutes before continuing with the next step.

A3.2 Synthetic Procedures - Polyphosphazenes

Trichloro(trimethylsilyl)phosphoranimine (12)

20.0 g (119.5 mmol) of lithium bis(trimethylsilyl)amide was weighed in a 500 ml four neck round bottom flask fixed with a calibrated thermometer and having a magnetic stirrer in a glove box. Through one of the opening the flask was attached to Schlenk line by a rubber tube. The flask was evacuated and filled with dry N₂ gas three times. To it 300 ml freshly distilled n-pentane is added using syringe, the lithium salt was completely dissolved in the solvent by stirring on a magnetic stirrer. The solution was then cooled down to around -16°C by immersing the flask in an ice + salt mixture (freezing mixture). After the temperature was stabilized for few minutes, 12.0 ml (137.5 mmol) of freshly distilled PCl₃ was added to the lithium salt solution dropwise (care should to be taken that the temperature does not rise above 0°C). After complete addition of PCl₃, the solution is stirred for half an hour at the same temperature (-16°C). Subsequently, 11.3 ml (119.5 mmol) of SO₂Cl₂ is added to the solution dropwise and the solution is further stirred for half an hour at the same temperature (-16°C). After this stage the precipitated white salt is filtered through 1 cm thick bed of Celite[®] and the clear filtrate is collected in another 500 ml round bottomed flask. The reaction flask was subsequently washed with 3 × 20 ml

freshly distilled n-pentane. After completion of the filtration, the flask was attached to a vacuum distillation assembly consisting of a water cooled condenser and a 100 ml three neck flask (this flask was weighed before connecting to the condenser) to collect the monomer, $\text{Cl}_3\text{P}=\text{NsiMe}_3$. The monomer solution flask was immersed into a water bath and n-pentane, which was first distilled out (0°C , 20 mm Hg), was collected into solvent traps using liquid nitrogen attached before the vacuum pump. After complete removal of the solvent, the temperature in the system raised gradually to *ca.* 21°C . At this temperature the colorless monomer was collected into the 100 ml collector flask. After completion of the distillation the flask along with the monomer is weighed and the amount of monomer is calculated. The formation and purity of monomer was confirmed by ^{31}P NMR of the monomer in CDCl_3 ; $\delta = -57$ ppm. *Yield = 70-75 %*

Poly(dichlorophosphazene) (13)

PCl_5 was as initiator for polymerization in a freshly distilled toluene as solvent. The molar ratio of monomer to PCl_5 was kept around 350:1. PCl_5 was sublimated prior to the polymerization and used freshly. The concentration of PCl_5 in the polymerization solution was kept about 0.0027 mol/L.

9.9 g of $\text{Cl}_3\text{P}=\text{NSiMe}_3$ were dissolved in 50 ml of freshly distilled toluene in a 100 ml three neck round bottom flask. A solution of PCl_5 in toluene was then added dropwise to the monomer toluene solution. The resultant solution was then stirred for 48 hours at room temperature. The completion of reaction was confirmed by ^{31}P NMR whereby a single peak for poly(dichlorophosphazene) ($\delta = -18$ ppm) was observed and the peak for monomer completely disappeared ($\delta = -57$ ppm). After completion of the polymerization, toluene was removed under vacuum to afford white colored viscous linear poly(dichlorophosphazene). *Yield: 100 %*

Poly(bismethoxyphosphazene) (PBMP) (14a)

10.5 g (90.5 mmol) of poly(dichlorophosphazene) were dissolved in 200 mL of freshly distilled dioxane. This solution was given slowly to the solution of sodium methoxide, which was prepared previously from metallic sodium (4.58 g, 199.2 mmol) and excess alcohol (6.96 g, 217.3 mmol) in 500 mL three neck round bottom flask overnight under reflux. The solution was let to stir at R.T. for 2 days under an inert atmosphere of nitrogen. When the substitution was complete (checked by ^{31}P NMR), the solution was concentrated

under vacuum and dialyzed against first in 0.1 M HCl solution and then against water for 4 days (dialysis membrane; regenerated cellulose, molecular weight cut off 12000-14000). Finally the water removed by rotary evaporator and dried under high vacuum until constant weight was reached, yielding 9.34 g (96 % yield) of slightly yellow highly viscous product. ^1H NMR (CDCl_3): δ = 3.63 (broad s); ^{13}C NMR (CDCl_3): δ = 52.8; ^{31}P NMR (CDCl_3): δ = -4.1. One peak was observed in the GPC measurement with the average molecular weight $M_n = 1.32 \times 10^5$ D and a polydispersity index (PDI) of 1.22. Elemental analysis for (**14a**), calc. (found) (%); C 22.44 (22.42), H 5.65 (5.73), N 13.08 (13.15).

Poly(bis- d_3 -methoxyphosphazene) (d_6 -PBMP) (14b)

The synthesis and purification of d_6 -PBMP was performed using the same reactions described above. The following reagents and quantities were used: poly(dichlorophosphazene) (10.5 g, 90.5 mmol), sodium (4.58 g, 199.2 mmol), d_3 -methanol (7.84 g, 217.3 mmol). The product was 10.03 g (98 %) with a slight yellow color. ^1H NMR (CDCl_3): no peak; ^{13}C NMR (CDCl_3): δ = 52.0; ^{31}P NMR (CDCl_3): δ = -4.0. One peak was observed in the GPC measurement with the average molecular weight $M_n = 1.31 \times 10^5$ D and a polydispersity index (PDI) of 1.23. Elemental analysis for (**14a**), calc. (found) (%); C 21.24 (21.19), D 10.69 (10.74), N 12.39 (12.22).

Poly[bis(ethyl 4-hydroxybenzoate)phosphazene] (PBEHP) (15)

Ethyl 4-hydroxybenzoate (32.97 g, 198.4 mmol) was dissolved in 200 mL of dioxane and added to the suspension of sodium pieces (3.51 g, 152.6 mmol) in 200 mL of dioxane in a 1 liter round bottom flask, and the mixture was stirred at reflux until the sodium reacted completely. To this solution was then added slowly poly(dichlorophosphazene) (**13**) (4.42 g, 76.3 mmol) in 100 mL of dioxane and the reaction mixture was stirred at reflux for 2 days. The solution was concentrated and coagulated into 500 mL pentane. The solvent was decanted and the residue was washed with 600 mL water. The isolated solid was dissolved in THF and extracted first with basic solution of water to remove unreacted ethyl 4-hydroxybenzoate and then two times with water. THF solution was dried over Na_2SO_4 and the solvent removed, yielding 13.2 g (92 %) of white solid polymer (**15**). ^1H NMR (CDCl_3): δ = 7.45 (br, 4H), 8.62 (br, 4H), 4.23 (br, 4H), 1.28 (br, 6H); ^{13}C NMR (CDCl_3): δ = 165.1, 153.9, 130.8, 126.7, 119.9, 60.8, 14.2; ^{31}P NMR (CDCl_3): δ = -19.8. One peak

was observed in the GPC measurement with the average molecular weight $M_n = 6.9 \times 10^4$ D and a polydispersity index (PDI) of 1.83. Elemental analysis for **(15)**, calc. (found) (%); C 57.6 (53.45), H 4.83 (4.67), N 3.73 (3.45).

Poly[bis(carboxylatophenoxy)phosphazene] (PBCPP) (16)

Potassium tert-butoxide (58.0 g, 517 mmol) was dissolved in 750 mL of THF, cooled down to 0 °C with an ice bath and 3 mL of water was added slowly. A solution of PBEHP **(15)** (10 g, 26.6 mmol) in 750 mL of THF was then added slowly over 30 min. After another 15 minutes at 0 °C, the reaction mixture was allowed to warm up to room temperature and stirred for 2 days. The mixture was then concentrated and dialyzed against water for 3 days. The polymer was then precipitated by acidification with hydrochloric acid and isolated by filtration, which was dried under vacuum giving 6.5 g (77 %) of slightly yellow crystalline polymer **(16)**. ^1H NMR ($\text{DMSO-}d_6$): $\delta = 7.44$ (br, 4H), 6.65 (br, 4H), 5.11 (br, 2H); ^{13}C NMR ($\text{DMSO-}d_6$): $\delta = 166.0, 153.3, 130.5, 127.1, 119.8$; ^{31}P NMR ($\text{DMSO-}d_6$): $\delta = -15.5$. Elemental analysis for **(16)**, calc. (found) (%); C 52.68 (44.38), H 3.16 (3.20), N 4.39 (3.91).

Poly[bis(lithium carboxylatophenoxy)phosphazene] (PBLCPP) (17)

The purified PBCPP **(16)** (6.0 g, 18.8 mmol) was treated with 1 mol/L lithium hydroxide in 100 mL of water until polymer dissolved completely to give lithium salt of **(16)**. The solution itself was purified by dialysis against water for 3 days to remove excess lithium hydroxide. The solution was filtered to eliminate insoluble suspensions and then isolated using freeze-drying method, giving 4.7 g (75 %) of white powder of **(17)**. ^1H NMR (D_2O): $\delta = 7.45$ (br, 4H), 6.63 (br, 4H); ^{13}C NMR (D_2O): $\delta = 174.4, 153.1, 132.1, 130.7, 120.1$; ^{31}P NMR (D_2O): $\delta = -16.0$. Elemental analysis for **(17)**, calc. (found) (%); C 50.79 (45.15), H 2.44 (3.42), N 4.23 (3.85).

Poly[bis(3-(dimethylamino)-1-propylamino)phosphazene] (PBDPP) (18)

A solution of poly(dichlorophosphazene) **(13)** (5.3 g, 45.96 mmol) in 100 mL of dichloromethane was added dropwise to the solution of *N,N*-dimethyltrimethylenediamine (45.8 mL, 367 mmol) in 230 mL of dichloromethane, which was cooled previously to 0 °C in an ice bath. After an additional 30 minutes at 0 °C, the reaction mixture was allowed to warm up to room temperature and stirred overnight. The clear solution was concentrated

and, dialysis was done first against water for 1 day, then against 1 M K₂CO₃ for another day, and finally against water until the solution was not basic anymore. Drying the product under high vacuum afforded (**18**) as a colorless, gummy material (10.0 g, 88 % yield). ¹H NMR (D₂O): δ = 2.85 (br, 4H), 2.34 (br, 4H), 2.18 (br, 6H), 1.66 (br, 4H); ¹³C NMR (D₂O): δ = 56.5, 43.8, 39.0, 28.6; ³¹P NMR (D₂O): δ = 6.8. One peak was observed in the GPC measurement with the average molecular weight M_n = 1.9 x 10⁴ D and a polydispersity index (PDI) of 2.1.

Poly[bis(3-amino-*N,N,N*-trimethyl-1-propanaminium iodide)phosphazene] (PBPAIP) (19**)**

To a solution of PBDPP (**18**) (10 g, 40.4 mmol) in 300 mL of absolute methanol was syringed dropwise with a teflon needle 1.1 equivalent of methyl iodide (6.3 mL, 101.1 mmol) at room temperature. The reaction mixture was then heated at reflux for 7 hours. The solvent removal was followed by dialysis against water for 3 days and the solution was first filtered to remove insoluble suspensions before precipitating the polymer into acetone. The drying of the polymer under vacuum yielded 7 g (33 %) of (**19**) as a white powder. ¹H NMR (D₂O): δ = 3.79 (br, 4H), 3.47-2.90 (br, 22H), 2.23 (br, 4H); ¹³C NMR (H₂O): δ = 63.8, 53.3, 37.9, 25.3; ³¹P NMR (D₂O): δ = 1.0 (br).

4 Appendix

Conductivity Data Tables

Table A.4.1 Conductivity table for OPS + LiSO₃CF₃ polymer electrolytes.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]					
OPS + LiSO ₃ CF ₃ polymer electrolytes	-60	3.81E-11	2.86E-10	8.06E-11	2.09E-11	2.79E-12	1.05E-12
	-50	8.37E-10	6.47E-9	3.24E-9	1.35E-9	3.17E-10	1.19E-10
	-40	1.80E-8	6.15E-8	4.42E-8	2.52E-8	9.08E-9	3.87E-9
	-30	2.06E-7	3.26E-7	2.95E-7	2.05E-7	9.81E-8	4.87E-8
	-20	6.42E-7	1.18E-6	1.27E-6	1.01E-6	5.92E-7	3.34E-7
	-10	1.59E-6	3.40E-6	4.04E-6	3.55E-6	2.43E-6	1.52E-6
	0	3.29E-6	7.91E-6	1.02E-5	9.77E-6	7.51E-6	5.09E-6
	10	5.91E-6	1.56E-5	2.18E-5	2.23E-5	1.88E-5	1.37E-5
	20	9.54E-6	2.73E-5	4.10E-5	4.43E-5	3.99E-5	3.08E-5
	30	1.41E-5	4.34E-5	6.95E-5	7.84E-5	7.49E-5	6.08E-5
	40	1.94E-5	6.48E-5	1.09E-4	1.28E-4	1.29E-4	1.09E-4
	50	2.53E-5	9.09E-5	1.59E-4	1.88E-4	2.03E-4	1.79E-4
	60	3.14E-5	1.21E-4	2.20E-4	2.65E-4	3.01E-4	2.74E-4
	70	3.76E-5	1.55E-4	2.92E-4	3.60E-4	4.20E-4	3.96E-4
	80	4.34E-5	1.90E-4	3.71E-4	4.66E-4	5.62E-4	5.45E-4
	90	4.85E-5	2.28E-4	4.56E-4	5.85E-4	7.25E-4	7.19E-4
		5	10	15	20	30	40
		Amount of LiSO ₃ CF ₃ (wt-%)					

Table A.4.2 Conductivity table for $T_x\text{OPS-LiSCF}_{10}$ polymer electrolytes crosslinked with HCl . $T_x\text{OPS-LiSCF}_{10}$ indicates $T_x\text{OPS} + 10 \text{ wt-\% LiSO}_3\text{CF}_3$.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]				
$T_x\text{OPS-LiSCF}_{10}$ polymer electrolytes	30	4.45E-5	4.62E-5	2.05E-6	8.97E-7	6.92E-7
	40	6.39E-5	6.74E-5	3.05E-6	1.53E-6	1.26E-6
	50	9.34E-5	9.77E-5	4.45E-6	2.37E-6	2.16E-6
	60	1.23E-4	1.29E-4	6.16E-6	3.75E-6	3.48E-6
	70	1.57E-4	1.68E-4	8.29E-6	5.82E-6	4.84E-6
	80	1.90E-4	2.07E-4	1.10E-5	8.25E-6	6.61E-6
	90	2.24E-4	2.48E-4	1.38E-5	1.06E-5	8.61E-6
		0.05	0.1	0.2	0.3	0.4
“x” values for $T_x\text{OPS}$ polymers						

Table A.4.3 Conductivity table for $T_{0.1}\text{OPS} + \text{LiSO}_3\text{CF}_3$ polymer electrolytes crosslinked with HCl .

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]			
$T_{0.1}\text{OPS} + \text{LiSO}_3\text{CF}_3$ polymer electrolytes	30	6.91E-6	2.24E-5	3.9E-5	2.8E-5
	40	9.55E-6	3.44E-5	6.2E-5	4.9E-5
	50	1.25E-5	4.77E-5	8.7E-5	7.6E-5
	60	1.60E-5	6.49E-5	1.2E-4	1.1E-4
	70	2.01E-5	8.44E-5	1.5E-4	1.5E-4
	80	2.40E-5	1.04E-4	1.8E-4	2.0E-4
	90	2.79E-5	1.25E-4	2.1E-4	2.4E-4
		5	10	15	20
Amount of LiSO_3CF_3 (wt-%)					

Table A.4.4 Conductivity table for $T_{0.1}OPS + LiN(SO_2CF_3)_2$ polymer electrolytes crosslinked with HCl.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]				
$T_xOPS - LiN(SO_2CF_3)_2$ polymer electrolytes	30	3.88E-5	6.51E-5	9.05E-5	6.62E-5	6.71E-5
	40	5.73E-5	9.91E-5	1.44E-4	1.07E-4	1.16E-4
	50	7.66E-5	1.35E-4	2.08E-4	1.58E-4	1.71E-4
	60	1.02E-4	1.84E-4	2.84E-4	2.19E-4	2.50E-4
	70	1.26E-4	2.33E-4	3.78E-4	2.97E-4	3.44E-4
	80	1.53E-4	2.93E-4	4.87E-4	3.92E-4	4.66E-4
	90	1.79E-4	3.52E-4	6.00E-4	4.83E-4	6.09E-4
		5	10	12.5	15	20
		Amount of $LiN(SO_2CF_3)_2$ (wt-%)				

Table A.4.5 Conductivity table for $T_{0.1}OPS + LiSO_3CF_3$ polymer electrolytes crosslinked with DBTL.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]				
$T_{0.1}OPS + LiSO_3CF_3$ polymer electrolytes	-30	6.73E-8	3.45E-8	1.84E-8	1.55E-8	3.37E-9
	-20	2.37E-7	1.51E-7	8.90E-8	8.98E-8	2.72E-8
	-10	6.16E-7	4.65E-7	2.96E-7	3.30E-7	1.27E-7
	0	1.31E-6	1.10E-6	7.37E-7	9.09E-7	4.17E-7
	10	2.40E-6	2.23E-6	1.59E-6	2.07E-6	1.09E-6
	20	4.02E-6	4.04E-6	3.10E-6	4.11E-6	2.36E-6
	30	6.06E-6	6.57E-6	5.40E-6	7.24E-6	4.50E-6
	40	8.51E-6	9.92E-6	8.67E-6	1.17E-5	7.82E-6
	50	1.12E-5	1.41E-5	1.29E-5	1.74E-5	1.26E-5
	60	1.38E-5	1.93E-5	1.80E-5	2.44E-5	1.89E-5
	70	1.64E-5	2.52E-5	2.39E-5	3.27E-5	2.65E-5
	80	1.86E-5	3.15E-5	3.02E-5	4.21E-5	3.55E-5
	90	2.04E-5	3.85E-5	3.67E-5	5.24E-5	4.56E-5
		5	10	12.5	15	20
		Amount of $LiSO_3CF_3$ (wt-%)				

Table A.4.6 Conductivity table for L-OPS + LiSO₃CF₃ polymer electrolytes crosslinked with HCl.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]				
L-OPS + LiSO ₃ CF ₃ polymer electrolytes	30	1.79E-5	4.65E-5	4.30E-5	3.68E-5	2.85E-5
	40	2.64E-5	7.29E-5	6.70E-5	5.99E-5	4.92E-5
	50	3.49E-5	1.04E-4	1.02E-4	9.03E-5	7.98E-5
	60	4.43E-5	1.38E-4	1.45E-4	1.33E-4	1.24E-4
	70	5.36E-5	1.78E-4	1.92E-4	1.80E-4	1.74E-4
	80	6.17E-5	2.18E-4	2.40E-4	2.29E-4	2.42E-4
	90	6.98E-5	2.56E-4	2.92E-4	2.85E-4	3.34E-4
		5	10	12.5	15	20
		Amount of LiSO ₃ CF ₃ (wt-%)				

Table A.4.7 Conductivity table for PPO-PS + LiSO₃CF₃ polymer electrolytes.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]			
PPO-PS + LiSO ₃ CF ₃ polymer electrolytes	30	1.36E-7	3.01E-7	2.85E-6	2.51E-6
	40	1.91E-7	5.36E-7	5.27E-6	4.80E-6
	50	2.65E-7	8.18E-7	9.20E-6	8.87E-6
	60	3.55E-7	1.18E-6	1.48E-5	1.41E-5
	70	4.50E-7	1.62E-6	2.28E-5	2.13E-5
	80	5.41E-7	2.08E-6	3.31E-5	3.05E-5
	90	7.12E-7	2.53E-6	4.58E-5	4.22E-5
		5	10	15	20
		Amount of LiSO ₃ CF ₃ (wt-%)			

Table A.4.8 Conductivity table for $T_{0.1}\text{OPS-LiSCF}_{15} + \text{Al}_2\text{O}_3$ polymer electrolytes crosslinked with DBTL. $T_{0.1}\text{OPS-LiSCF}_{15}$ indicates the fixed composition of $T_{0.1}\text{OPS} + 15 \text{ wt-\% LiSO}_3\text{CF}_3$.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]				
$T_{0.1}\text{OPS-LiSCF}_{15} + \text{Al}_2\text{O}_3$ polymer electrolytes	-30	1.13E-8	1.29E-8	9.46E-9	2.28E-8	2.11E-8
	-20	6.23E-8	7.35E-8	5.40E-8	1.25E-7	1.19E-7
	-10	2.23E-7	2.68E-7	1.98E-7	4.50E-7	4.33E-7
	0	6.01E-7	7.35E-7	5.40E-7	1.22E-6	1.18E-6
	10	1.34E-6	1.65E-6	1.22E-6	2.74E-6	2.65E-6
	20	2.60E-6	3.21E-6	2.37E-6	5.38E-6	5.21E-6
	30	4.51E-6	5.59E-6	4.12E-6	9.40E-6	9.09E-6
	40	7.16E-6	8.89E-6	6.56E-6	1.50E-5	1.46E-5
	50	1.06E-5	1.31E-5	9.75E-6	2.23E-5	2.17E-5
	60	1.46E-5	1.83E-5	1.36E-5	3.12E-5	3.04E-5
	70	1.93E-5	2.41E-5	1.81E-5	4.13E-5	4.04E-5
	80	2.43E-5	3.03E-5	2.30E-5	5.24E-5	5.12E-5
	90	2.96E-5	3.68E-5	2.82E-5	6.40E-5	6.25E-5
		2	4	6	8	10
		Amount of Al_2O_3 (wt-%)				

Table A.4.9 Conductivity table for $T_{0.1}OPS-LiSCF_{15} + SiO_2$ polymer electrolytes crosslinked with DBTL. $T_{0.1}OPS-LiSCF_{15}$ indicates the fixed composition of $T_{0.1}OPS + 15 \text{ wt-\% } LiSO_3CF_3$.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]				
$T_{0.1}OPS-LiSCF_{15} + SiO_2$ polymer electrolytes	-30	1.41E-8	1.88E-8	1.03E-8	1.03E-8	2.05E-8
	-20	7.86E-8	1.06E-7	5.85E-8	5.84E-8	1.14E-7
	-10	2.82E-7	3.82E-7	2.13E-7	2.15E-7	4.07E-7
	0	7.58E-7	1.02E-6	5.78E-7	5.82E-7	1.09E-6
	10	1.69E-6	2.28E-6	1.29E-6	1.28E-6	2.41E-6
	20	3.27E-6	4.43E-6	2.51E-6	2.49E-6	4.66E-6
	30	5.66E-6	7.73E-6	4.34E-6	4.29E-6	8.08E-6
	40	9.00E-6	1.23E-5	6.91E-6	6.81E-6	1.28E-5
	50	1.33E-5	1.83E-5	1.03E-5	1.01E-5	1.91E-5
	60	1.85E-5	2.57E-5	1.43E-5	1.42E-5	2.67E-5
	70	2.45E-5	3.47E-5	1.91E-5	1.88E-5	3.55E-5
	80	3.09E-5	4.54E-5	2.43E-5	2.38E-5	4.54E-5
	90	3.77E-5	5.76E-5	3.01E-5	2.91E-5	5.64E-5
		2	4	6	8	10
		Amount of SiO_2 (wt-%)				

Table A.4.10 Conductivity table for $T_{0.1}OPS-LiSCF_{15}$ + B2 polymer electrolytes crosslinked with DBTL. $T_{0.1}OPS-LiSCF_{15}$ indicates the fixed composition of $T_{0.1}OPS$ + 15 wt-% $LiSO_3CF_3$.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]				
$T_{0.1}OPS-LiSCF_{15}$ + B2 polymer electrolytes	-30	1.55E-8	8.60E-8	7.68E-8	8.85E-8	7.24E-8
	-20	8.98E-8	4.68E-7	4.33E-7	5.35E-7	4.12E-7
	-10	3.30E-7	1.68E-6	1.60E-6	2.05E-6	1.55E-6
	0	9.09E-7	4.54E-6	4.41E-6	5.81E-6	4.23E-6
	10	2.07E-6	1.02E-5	1.01E-5	1.33E-5	9.63E-6
	20	4.11E-6	1.98E-5	1.98E-5	2.65E-5	1.87E-5
	30	7.24E-6	3.42E-5	3.47E-5	4.67E-5	3.25E-5
	40	1.17E-5	5.43E-5	5.56E-5	7.49E-5	5.18E-5
	50	1.74E-5	7.95E-5	8.20E-5	1.11E-4	7.62E-5
	60	2.44E-5	1.09E-4	1.14E-4	1.56E-4	1.06E-4
	70	3.27E-5	1.42E-4	1.49E-4	2.08E-4	1.41E-4
	80	4.21E-5	1.76E-4	1.87E-4	2.64E-4	1.78E-4
	90	5.24E-5	2.11E-4	2.25E-4	3.22E-4	2.16E-4
		0	10	20	30	40
		Amount of B2 (wt-%)				

Table A.4.11 Conductivity table for $T_{0.1}OPS-LiSCF_{15}$ + B3 polymer electrolytes crosslinked with DBTL. $T_{0.1}OPS-LiSCF_{15}$ indicates the fixed composition of $T_{0.1}OPS$ + 15 wt-% $LiSO_3CF_3$.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]				
$T_{0.1}OPS-LiSCF_{15}$ + B3 polymer electrolytes	-30	1.55E-8	5.43E-7	4.20E-7	1.10E-6	9.33E-7
	-20	8.98E-8	2.28E-6	1.79E-6	4.67E-6	3.95E-6
	-10	3.30E-7	6.79E-6	5.32E-6	1.40E-5	1.15E-5
	0	9.09E-7	1.59E-5	1.26E-5	3.32E-5	2.71E-5
	10	2.07E-6	3.17E-5	2.50E-5	6.70E-5	5.39E-5
	20	4.11E-6	5.57E-5	4.46E-5	1.19E-4	9.48E-5
	30	7.24E-6	8.91E-5	7.13E-5	1.91E-4	1.51E-4
	40	1.17E-5	1.31E-4	1.05E-4	2.84E-4	2.23E-4
	50	1.74E-5	1.82E-4	1.45E-4	3.92E-4	3.07E-4
	60	2.44E-5	2.36E-4	1.87E-4	5.12E-4	4.01E-4
	70	3.27E-5	2.91E-4	2.31E-4	6.34E-4	5.03E-4
	80	4.21E-5	3.44E-4	2.73E-4	7.55E-4	6.05E-4
	90	5.24E-5	3.93E-4	3.12E-4	8.69E-4	7.14E-4
		0	10	20	30	40
		Amount of B3 (wt-%)				

Table A.4.12 Conductivity table for PBMP + $LiSO_3CF_3$ polymer electrolytes.

Polymer sample	Temp. [°C]	Conductivity [S·cm ⁻¹]			
PBMP + $LiSO_3CF_3$ polymer electrolytes	30	5.87E-6	7.05E-6	1.5E-5	1.7E-5
	40	9.59E-6	1.24E-5	2.5E-5	2.8E-5
	50	1.52E-5	2.10E-5	4.0E-5	4.6E-5
	60	2.29E-5	3.39E-5	6.2E-5	7.2E-5
	70	3.68E-5	5.55E-5	9.6E-5	1.2E-4
		5	10	15	20
		Amount of $LiSO_3CF_3$ (wt-%)			

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