POLYPHENYLENE SULFONIC ACIDS AS PROTON EXCHANGE MEMBRANES
FOR FUEL CELLS

by

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A heartfelt appreciation and the most sincere gratitude are delivered by the author to all of those who participated in this research effort and contributed in any way. Thankfulness is conveyed to advisors, Dr. Morton H. Litt and Dr. Stuart J. Rowan, for their direction, dedication, time and invaluable support during the past five years. Without their passion and guidance, I would not have completed this dissertation. The author is indebted to the Chemistry Department of Case Western Reserve University and DOE grant DE-FC36-06GO16039 for generous support.

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,7-(DBBS)-SP</td>
<td>2,7-bis(4-bromo-3,3’-biphenyl disulfonic acid)-9,9’-spirobifluorene</td>
</tr>
<tr>
<td>6FBP</td>
<td>hexafluoroisopropylidene bisphenol</td>
</tr>
<tr>
<td>ACPs</td>
<td>aromatic condensation polymers</td>
</tr>
<tr>
<td>AFC</td>
<td>alkaline fuel cell</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BDA</td>
<td>4,4’-diamino-2,2'-biphenyl disulfonic acid</td>
</tr>
<tr>
<td>BINAP</td>
<td>1,1’-binaphthalene</td>
</tr>
<tr>
<td>BP</td>
<td>bisphenol</td>
</tr>
<tr>
<td>BPy</td>
<td>bipyridyl</td>
</tr>
<tr>
<td>BTMA-OH</td>
<td>benzyl trimethyl ammonium hydroxide</td>
</tr>
<tr>
<td>CuTC</td>
<td>copper(I)-thiophene-2-carboxylate</td>
</tr>
<tr>
<td>DAFC</td>
<td>direct alcohol fuel cells</td>
</tr>
<tr>
<td>DBBPDSA</td>
<td>4,4’-dibromobiphenyl-3,3’-disulfonic acid</td>
</tr>
<tr>
<td>DBBPDSA-Li</td>
<td>4,4’-dibromobiphenyl-3,3’-disulfonic acid dilithium salt</td>
</tr>
<tr>
<td>DBFDSA</td>
<td>2,7-dibromofluorene-3,5-disulfonic acid</td>
</tr>
<tr>
<td>DBFDSA-Li</td>
<td>2,7-dibromofluorene-3,5-disulfonic acid dilithium salt</td>
</tr>
<tr>
<td>DBFDSCI</td>
<td>2,7-dibromofluorene-3,5-disulfonyl chloride</td>
</tr>
<tr>
<td>DBPDSA</td>
<td>1,4-dibromobenzene-2,5-disulfonic acid</td>
</tr>
<tr>
<td>DBPDSA-Li</td>
<td>1,4-dibromobenzene-2,5-disulfonic acid dilithium salt</td>
</tr>
<tr>
<td>DCDPS</td>
<td>4,4’-dichlorodiphenylsulfone</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>DCFC</td>
<td>direct carbon fuel cells</td>
</tr>
<tr>
<td>DEGDE</td>
<td>diethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>DTBP</td>
<td>2,6-di-t-butylphenol</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron-Spin Resonance</td>
</tr>
<tr>
<td>EW</td>
<td>equivalent weight</td>
</tr>
<tr>
<td>FRA</td>
<td>Frequency Response Analyzer</td>
</tr>
<tr>
<td>FV</td>
<td>“Frozen-in” free volume per SO$_3$H group</td>
</tr>
<tr>
<td>FWHH</td>
<td>full width at half height</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>IEC</td>
<td>ion exchange capacity</td>
</tr>
<tr>
<td>K</td>
<td>macro to molecular volume conversion coefficient</td>
</tr>
<tr>
<td>KCGP</td>
<td>Kumada chain growth polycondensation</td>
</tr>
<tr>
<td>MCFC</td>
<td>molten carbonate fuel cell</td>
</tr>
<tr>
<td>MV</td>
<td>molar volume, per SO$_3$H group</td>
</tr>
<tr>
<td>NDA</td>
<td>1,4,5,8-tetracarboxylic dianhydride</td>
</tr>
<tr>
<td>NMP</td>
<td>1-methyl-2-pyrrolidinone</td>
</tr>
<tr>
<td>NPB</td>
<td>neopentylbenzene</td>
</tr>
<tr>
<td>ODA</td>
<td>4,4’-oxidianiline</td>
</tr>
<tr>
<td>PAFC</td>
<td>phosphoric acid fuel cell</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PBPDSA</td>
<td>poly(biphenylene-3,3’-disulfonic acid)</td>
</tr>
<tr>
<td>PEEK</td>
<td>poly(ether ether ketone)</td>
</tr>
<tr>
<td>PEFC</td>
<td>polymer electrolyte fuel cell</td>
</tr>
<tr>
<td>PEM</td>
<td>proton exchange membranes</td>
</tr>
<tr>
<td>PES</td>
<td>poly(ether sulfone)</td>
</tr>
<tr>
<td>PFSI</td>
<td>perfluorosulfonated ionomer</td>
</tr>
<tr>
<td>POM</td>
<td>Polarizing Optical Microscopy</td>
</tr>
<tr>
<td>PPBP</td>
<td>poly(4-phenoxybenzoyl-1,4-phenylene)</td>
</tr>
<tr>
<td>PPDSA</td>
<td>poly($p$-phenylene-2,5-disulfonic acid)</td>
</tr>
<tr>
<td>PPP</td>
<td>poly($p$-phenylene)</td>
</tr>
<tr>
<td>PPS</td>
<td>polyphenylene sulfide</td>
</tr>
<tr>
<td>PSPPI</td>
<td>sulfonated phenoxy polyperylenemide</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>PxF1</td>
<td>poly(phenylene disulfonic acid_co-fluorene disulfonic acid)</td>
</tr>
<tr>
<td>S</td>
<td>Siemens, the SI derived unit of electric conductance and electric admittance</td>
</tr>
<tr>
<td>SANS</td>
<td>Small-Angle Neutron Scattering</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small-Angle X-ray Scattering</td>
</tr>
<tr>
<td>SDCDPS</td>
<td>disodium 3, 3-disulfonate-4, 4-dichlorodiphenylsulfone</td>
</tr>
<tr>
<td>SOFC</td>
<td>solid oxide fuel cell</td>
</tr>
<tr>
<td>SPAEs</td>
<td>sulfonated poly(aryl ether sulfones)</td>
</tr>
<tr>
<td>S-PBI</td>
<td>arylsulfonated poly(benzyimidazole)</td>
</tr>
<tr>
<td>SPC</td>
<td>Suzuki polycondensation</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>S-PEEK</td>
<td>sulfonated poly(ether ether ketone)</td>
</tr>
<tr>
<td>S-PEES</td>
<td>sulfonated poly(ether ether sulfone)</td>
</tr>
<tr>
<td>SPIs</td>
<td>sulfonated polyimides</td>
</tr>
<tr>
<td>S-PPBP</td>
<td>sulfonated poly(4-phenoxybenzoyl-1,4-phenylene)</td>
</tr>
<tr>
<td>S-PPO</td>
<td>sulfonated poly(phenylene oxide)</td>
</tr>
<tr>
<td>S-PPQ</td>
<td>sulfonated poly(phenylquinoxaline)</td>
</tr>
<tr>
<td>S-PPS</td>
<td>sulfonated poly(phenylene sulfide)</td>
</tr>
<tr>
<td>S-PPX</td>
<td>sulfonated poly(p-xylene)</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TBAF</td>
<td>tetra(n-butyl)ammonium fluoride</td>
</tr>
<tr>
<td>TEGDME</td>
<td>triethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TFE</td>
<td>tetrafluoroethylene</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>VdMV</td>
<td>polymer Van der Waals molar volume</td>
</tr>
<tr>
<td>WAXD</td>
<td>Wide Angle X-ray Diffraction</td>
</tr>
<tr>
<td>WU</td>
<td>water uptake</td>
</tr>
</tbody>
</table>
Polyphenylene Sulfonic Acids As Proton Exchange Membranes For Fuel Cells

Abstract

by

DAXUAN DONG

High molecular weight poly(biphenyl-3,3’-disulfonic acid) (PBPDSA) homopolymer was synthesized using the Ullmann coupling reaction. The molecular weight of PBPDSA was improved by changing the solvent, counter ion and drying method. A water insoluble copolymer PBPDSA-g-NPB was obtained by grafting PBPDSA with neopentylbenzene (NPB). The proton conductivity of this film was 0.114 S/cm at 50%RH and 80°C, which is higher than the initial DOE target 0.1 S/cm.

In order to further improve the conductivity, a novel copolymer poly(phenylene disulfonic acid_co-fluorene disulfonic acid) (PxF1) was designed and synthesized. PxF1 was synthesized by reacting 1,4-dibromobenzene-2,5-disulfonic acid (DBPDSA) and 2,7-dibromofluorene-3,5-disulfonic acid (DBFDSA) using the Ullmann coupling. This copolymerization was optimized by screening temperature, solvent, coordination reagent and drying method. The best conditions are DBPDSA-Li, DBFDSA-Li and copper dried separately under vacuum and then together under an argon steam at 200°C and copolymerized in NMP at 200°C using 2,2’-bipyridine (BPy) as a coordination reagent. In order to obtain water insoluble membranes, PxF1 was further grafted with benzyl groups and crosslinked.
PxF1 and its grafted copolymers exhibited an abnormal increase in reduced viscosity at low concentrations. The Polarizing Optical Microscopy (POM) studies, the film dimensional changes as a function of relative humidities and WAXD measurements are consistent with a nematic liquid crystalline structure.

A copolymer hexagonal packing model was proposed and verified by studying the relationship between the calculated molar volume and the measured molar volume using a curve fitting program. The use of WAXD combined with measurements of volume and weight increase for copolymer as a function of relative humidity enabled us to make a direct estimate of frozen-in free volume. The frozen-in free volume from this analysis is 32.0 cc/SO_3H (λ = 1.8) for P10F1 and 32.1 cc/SO_3H (λ = 1.8) for P10F1-g-Bn27% (4-46).

The in plane proton conductivity of these materials, measured as a function of relative humidity and temperature, was 10 times higher than that of Nafion212®. TGA study indicates that the copolymers are stable up to 304°C. The mechanical properties of those copolymers are affected by the grafting degree and relative humidity. The grafted copolymer has reasonable mechanical properties (breaking stress 13.3 MPa at 6.6% strain) at 23%RH.
Chapter 1

General Introduction

1.1. Fuel cell fundamentals

Improvements in living standards and technology around the world have been accompanied by increases in energy consumption. As such, the energy problem is a huge challenge for society. As the most popular energy converting devices, internal combustion engines were an impetus to the development of society for the past century. But internal combustion engines generate environmentally unfriendly chemicals and their conversion efficiency is limited by the Carnot cycle. Therefore, a new alternative energy conversion device is in high demand.¹

![Figure 1.1. Schematic of an individual hydrogen/oxygen fuel cell](image)

Fuel cells are non-polluting and highly efficient energy conversion devices, and have become one area of research focus. The principle of the fuel cell was discovered by
the German scientist Christian Friedrich Schönbein in 1838 and further developed by the Welsh scientist Sir William Robert Grove in 1845².

Fuel cells are electrochemical devices that directly convert chemical energy from fuels into electrical energy. The core of a fuel cell is composed of unit cells. The basic physical structure of a fuel cell unit cell consists of three parts: an electrolyte sandwiched between an anode and a cathode. A schematic representation of a hydrogen/oxygen fuel cell with the hydrogen/oxygen and the ion conduction flow directions through the cell is shown in Figure 1.1.

The electrochemical reactions in the electrodes are complex, as shown in Figure 1.2. By diffusion, the fuel gas hydrogen reaches the surface of the anode electrode, normally platinum (Pt). Catalyzed by Pt, the hydrogen molecule is dissociated into two hydrogen atoms that are bonded to the surface of Pt. The electron is released from the hydrogen atom and the resulting proton is transferred through a proton exchange membrane (PEM) to the cathode. In the cathode, the proton reacts with oxygen and electrons to produce water.

\[
\text{Oxidation half reaction: } 2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^- \\
\text{Reduction half reaction: } \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \\
\text{Cell reaction: } 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}
\]

**Figure 1.2.** General electrochemical reactions for the H₂/O₂ fuel cell

The electrolytes and fuels used in a fuel cell determine the electrode reactions and type of ions carried in the electrolytes. Therefore, fuel cells can be classified by the choice of electrolytes and fuels. The most common classification of fuel cells is by the
choice of electrolytes used and includes 1) the polymer electrolyte fuel cell (PEMFC), 2) the alkaline fuel cell (AFC), 3) the phosphoric acid fuel cell (PAFC), 4) the molten carbonate fuel cell (MCFC), and 5) the solid oxide fuel cell (SOFC). Another classification method is based on the type of fuels used and includes 1) direct alcohol fuel cells (DAFC) and 2) direct hydrogen fuel cells (DHFC). Each fuel cell has its own operating temperature and is best suited to a particular application. The main features of the five types of fuel cells are summarized in Table 1.1.

Table 1.1. Operating temperatures and common applications for hydrogen fuel cells as a function of electrolyte used.

<table>
<thead>
<tr>
<th>Fuel Cell types</th>
<th>Electrolyte</th>
<th>Operating temperature (°C)</th>
<th>Application</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Electrolyte Fuel Cell (PEMFC)</td>
<td>Solid organic polymer</td>
<td>60-100</td>
<td>Electric utility, Portable Power, Transportation</td>
<td>Solid electrolyte reduces corrosion and management problems. Low temp. Quick start-up.</td>
<td>Low temperature requires expensive catalysts</td>
</tr>
<tr>
<td>Alkaline Fuel Cell (AFC)</td>
<td>Aqueous solution of potassium hydroxide soaked in a matrix</td>
<td>90-100</td>
<td>Military, Space</td>
<td>Cathode reaction faster in alkaline electrolyte-so high performance</td>
<td>Expensive removal of CO₂ from fuel and air streams required</td>
</tr>
<tr>
<td>Phosphoric Acid Fuel Cell (PAFC)</td>
<td>Liquid phosphoric acid</td>
<td>175-200</td>
<td>Electric utility, Transportation</td>
<td>Up to 85% efficiency in co-generation of electricity and heat. Impure H₂ as fuel</td>
<td>Pt catalyst. Low current and power. Large size/weight</td>
</tr>
<tr>
<td>Molten Carbonate Fuel Cell (MCFC)</td>
<td>Liquid solution of lithium, sodium and/or potassium carbonates soaked in a matrix</td>
<td>600-1000</td>
<td>Electric utility</td>
<td>High temperature promotes higher efficiency and flexibility to use more types of fuels and catalysts.</td>
<td>High temperatures enhances corrosion and breakdown of cell components</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>Solid zirconium oxide</td>
<td>600-1000</td>
<td>Electric utility</td>
<td>Similar high temperature advantage to MCFC and similar electrolyte advantages to PEMFC</td>
<td>High temperature enhances breakdown of cell components</td>
</tr>
</tbody>
</table>
PEMFCs were invented by Willard Thomas Grubb and Lee Niedrach of General Electric and were first used as a substitute for solid-oxide fuel cells in the Gemini space missions of the early 1960s. However, their high price, short lifetime, and fuel gas purity requirements limited their commercial application⁴. By the late 1980s/early 1990s, several pivotal innovations (e.g. low platinum catalyst loading and thin film electrodes) drove the cost of PEMFC down and made their applications more feasible.

The difference between PEMFCs and other fuel cells is that PEMFCs use a solid phase polymer membrane as the cell separator/electrolyte. Because the cell separator is a polymer film and the cell operates at relatively low temperatures, issues such as sealing, assembly, and handling are less complex than with most other fuel cells. The requirement to handle corrosive acids or bases is eliminated in this system. PEMFCs typically operate at low temperatures (60°C to 80°C), allowing for potentially faster startup compared to higher temperature fuel cells. While PEMFCs are particularly suitable for operation with pure hydrogen, fuel processors have been developed that will allow for the use of conventional fuels such as natural gas or gasoline. The merits mentioned above make PEMFCs prime candidates for applications in vehicles and portable electricity supply systems⁵-⁴.

The core of a PEMFC is the ion exchange membrane, which dissociates into positively charged and negatively charged ions in the presence of water, thereby making the water solution electrically conductive. The ion exchange membrane must possess some specific properties⁴c, such as:

- Low permeability with respect to oxygen and hydrogen (to prevent membrane breakdown);
- High swelling (to provide efficient dissociation of acids and to form a hydrated ionic phase within the thickness of the membrane);
- Good water uptake at temperatures above 100°C;
- High ion-exchange capacity, sufficient to provide a conductivity of the order of $10^{-1} \text{ S cm}^{-1}$ (S is Siemen) at temperatures near 50°C;
- High proton conductivity at temperatures above 100°C and below 0°C;
- High chemical and mechanical stability for long-term operation under severe conditions (over 2000 h for electric vehicle applications).

Initially, the ion exchange membrane used in PEMFC’s was made of sulfonated polystyrene, which is expensive and suffers easily from oxidative degradation. A major breakthrough has been the use of Nafion® membranes (DuPont), which potentially enables terrestrial applications of PEMFCs.

1.2. Nafion® and other perfluorosulfonated polymers

Nafion® has excellent thermal and mechanical stability and is the first of a class of synthetic polymers with ionic properties called ionomers. Nafion® was synthesized by copolymerizing tetrafluoroethylene (TFE) and an alkyl vinyl ether derivative with a sulfonyl fluoride group. The resulting thermoplastic $-\text{SO}_2\text{F}$ precursor must be extruded into sheets of required thickness, since it does not possess cluster morphology. By reacting the precursor with different reagents, the precursor can be converted into, for example, K⁺ form by reacting the precursor with KOH in water and DMSO. The $-\text{SO}_3\text{H}$ form is achieved by soaking the film in a sufficiently concentrated aqueous acid solution. The molecular weight of Nafion® is uncertain because of difficulty in processing solution morphology. Conventional methods of determining molecular weight such as light
scattering and gel permeation chromatography are not applicable because Nafion® is insoluble. The molecular weight of Nafion® has been estimated at $10^5$ - $10^6$ Da. Because of this uncertainty in the molecular weight, the equivalent weight (EW) and material thickness are used to describe most commercially available membranes. EW is the number of grams of dry Nafion® per mole of sulfonic acid. The meaning of commercial Nafion117® is that it has 1100 g EW and is 0.007 inch thick.

The combination of the stable Teflon® backbone with the sulfonic acid groups gives Nafion® its special characteristics. Nafion® can resist chemical attack. Only alkali metals (particularly sodium) can degrade Nafion® at normal temperatures and pressures. The Teflon® backbone with dangling sulfonate ions gives Nafion® a high operating temperature, e. g. up to 100°C. Perhaps the most desirable property of Nafion® is its high protonic conduction due to its dangling strong perfluorosulfonic acid groups; Nafion® has a proton conductivity of $10^{-2}$ - $10^{-1}$ S/cm.

Nafion®'s unique properties allow for broad applications. Nafion® has been used in fuel-cells, electrochemical devices, chlor-alkali production, metal-ion recovery, water electrolysis, plating, surface treatment of metals, batteries, sensors etc. The success of Nafion® has stimulated the development of other perfluorosulfonated polymers, which are shown in Figure 1.3 4b. Perfluorinated membranes (Dow membrane) were developed at Dow Chemical Co. (USA). They have equivalent masses of 800-850 and a dry state thickness of ~ 5 μm. Flemion® membranes with equivalent masses ~ 1000 were developed at Asahi Glass Co. (Japan). Aciplex-S® membranes, developed at Asahi Chemical Industry (Japan), are characterized by equivalent masses of 1000-12004c. Recently, 3M developed a new ionomer (Figure 1.4) with a slightly shorter side chain
than standard PFSA (Figure 1.3) without the pendant –CF₃ group, which gives the new ionomer a high degree of crystallinity, high modulus and higher Tₒ (α relaxation glass transition temperature) at a given EW and improves membrane mechanical properties.

![Chemical structure of perfluorinated polymer electrolyte membranes](image)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>m</th>
<th>n</th>
<th>y</th>
<th>x</th>
<th>EW (g/[SO₃H])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 117®</td>
<td>≥1</td>
<td>2</td>
<td>1</td>
<td>7-20</td>
<td>1000-1200</td>
</tr>
<tr>
<td>Flemion</td>
<td>0</td>
<td>1-5</td>
<td>1</td>
<td>5-10</td>
<td>1000</td>
</tr>
<tr>
<td>Aciplex</td>
<td>0, 3</td>
<td>2-5</td>
<td>1</td>
<td>1.5-14</td>
<td>1000-1200</td>
</tr>
<tr>
<td>Dow membrane</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>3.6-10</td>
<td>800-850</td>
</tr>
</tbody>
</table>

**Figure 1.3.** Chemical structures of perfluorinated polymer electrolyte membranes

![3M polymer](image)

**Figure 1.4.** 3M polymer (EW = 850)

In order to optimize the chemical structure, microstructure, and morphology of Nafion® for applications such as PEMFCs, it is crucial to understand the relationship between structure, morphology and physicochemical properties. As an ionomer, Nafion® has a phase separated structure due to aggregation of the sulfonic acid functionality to form hydrophilic domains. The morphology of Nafion® has chiefly been investigated...
through Small-Angle X-ray Scattering (SAXS), Small-Angle Neutron Scattering (SANS)\textsuperscript{8}, Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM).

SAXS and SANS spectra of Nafion\textsuperscript{®} membranes show a broad maximum in the medium angular range (the so-called ionomer peak) and an upturn of scattering intensity at very low angles. Many models\textsuperscript{9} have been proposed to explain the obtained information by fitting observed scattering profiles, and recognize that a network of clusters is formed by ionic groups in the perfluorinated polymer matrix that allows for significant swelling by water and efficient ionic transport through nanometer-scale domains. Study of the evolution of perfluorosulfonated ionomer (PFSI) structure from the dry state through the water-swollen state to solution and with respect to recent studies suggest that a PFSI solution contains rod-like structures\textsuperscript{10}. Gebel proposed a conceptual description for the swelling and dissolution process, shown schematically in Figure 1.5\textsuperscript{9g}. In this qualitative model, the dry membrane is considered to contain isolated, spherical ionic clusters. With the absorption of water, the clusters swell to hold pools of water surrounded by ionic groups at the polymer-water interface. For a water volume fraction $X_v$ between 0.3 and 0.5, a structure of spherical ionic domains connected by cylinders of water dispersed in the polymer matrix forms. As the water content increases ($X_v$ larger than 0.5), an inversion of the morphology occurs and the membranes correspond to a connected network of rod-like polymer aggregates surrounded by water. A spherical domain cannot be obtained at $X_v$ values larger than 0.5 because the polymer volume associated with each ionic group is too large compared to the average distance between ionic groups along the polymer chain. The best compromise between the minimization of
the interfacial energy and the packing constraints is to form connected cylindrical particles.

**Figure 1.5.** Structural evolution of Nafion117® depending on water content. (Reprinted with permission from Elsevier)
TEM and AFM provide direct visualization of phase separation and the presence of ionic clusters in Nafion® membranes. A TEM study carried out by Porat and coworkers\textsuperscript{11a} on very thin, recast Nafion® films show the Nafion® fluorocarbon back bone is in the form of a linear zigzag chain as in PE and not a twisted chain in the structure similar PTFE; the sulfonic acids were randomly distributed in clusters of 5 nm size. McLean \textit{et al.} demonstrated that TM-AFM in phase contrast mode can be used to characterize the positions in space of both ionic domains and crystalline lamellae or lamellar stacks in Nafion® membranes. Ion clusters were imaged by low oscillation amplitude tapping of Nafion® membranes and were affected by various conditions such as humidity\textsuperscript{11b}.

\textbf{Figure 1.6}. TM-AFM phase images of Nafion117® (K+) ionomer membrane after exposure to: a) room temperature humidity; b) deionized water. Scan boxes are 300×300 nm with a scale of 0–80 nm. (Reprinted with permission from American Chemical Society)

Figure 1.6 shows the low-energy phase images of Nafion117®,K⁺ after exposure to a) room temperature humidity and b) liquid water. Membranes at low humidity have...
smaller regions of uniformly spaced ionic clusters of around 4-10 nm in size; membranes at high humidity have bigger regions of ionic clusters around 7-15 nm in the narrowest dimension, coalesced into channel-like shapes. This technique provides direct images of ion clusters in their aggregated form and the water can be absorbed into the channel-like morphology.

Although Nafion® membranes are the most widely used and still considered the benchmark of proton conducting polymer membranes, they have some intrinsic drawbacks caused by the microstructure and morphology along with the perfluorosulfonic acid’s high cost. Furthermore, when the temperature is higher than 80°C and relative humidity is lower than 100%, Nafion® becomes dehydrated, which causes the proton conductivity of Nafion® to drop quickly (Figure 1.7)\textsuperscript{12}.

![Figure 1.7. Nafion212®: Conductivity versus relative humidity at 80 and 120°C](image)

These drawbacks have compelled scientists to develop new alternative electrolytes for Nafion®. Similar to the morphology of Nafion®, most of the new
electrolytes have the microphase separated system, which is believed to be the best way to balance conductivity and mechanical properties.

1.3. Sulfonated aromatic hydrocarbon polymers

Although Nafion® and other perfluorosulfonated membranes are the most popular polymers used as PEMs, high cost and low conductivity at low humidity prevent them from being ideal membranes for H2/ air fuel cells. Therefore, the development of new solid polymer electrolytes, which combines sufficient electrochemical characteristics and low cost, is of current interest. One promising way of resolving these problems is to prepare membranes based on aromatic condensation polymers (ACPs). ACPs have some advantages that make them particularly attractive:

1. ACPs are cheaper than perfluorinated polymers.
2. ACPs containing polar groups have higher water uptake than Nafion® over a wide temperature range.
3. Decomposition of ACPs can to a great extent be suppressed by proper molecular design.
4. ACPs are easily recycled by conventional methods.

Sulfonated aromatic condensation polymers can be synthesized by two methods: sulfonation of high molecular mass ACPs or by condensation of monomers containing sulfonic acid groups.

1.3.1. Postsulfonation of existing aromatic hydrocarbon polymers.

The most common way of modifying aromatic polymers for application as PEM is to employ electrophilic aromatic sulfonation. Different classes of high molecular mass polymers have been used to synthesize sulfonated ACPs, such as substituted poly(1,4-phenylenes), poly(p-xyylene), poly(1,4-oxyphenylenes), poly(ether ether ketones)
(PEEK)\textsuperscript{16}, polyarylene (ether sulfones)\textsuperscript{17}, poly(phenylene sulfides)\textsuperscript{18}, polyperyleneimides\textsuperscript{19} and some other ACPs. The structures of sulfonated poly(4-phenoxylbenzoyl-1,4-phenylene) (S-PPBP), poly(p-xylylene) (S-PPX), poly(phenylene sulfide) (S-PPS), poly(phenylene oxide) (S-PPO), poly(ether ether ketone) (S-PEEK), poly(ether ether sulfone) (S-PEES) arylsulfonated poly(benzyimidazole) (S-PBI) sulfonated poly (phenylquinoxaline) (S-PPQ) and sulfonated phenoxy polyperyleneimide (PSPPI) are shown in Figure 1.8.

Sulfonated ACPs are synthesized through sulfonation by sulfonation agents, such as concentrated sulfuric acid\textsuperscript{16e}, chlorosulfonic acid\textsuperscript{20}, \(\text{SO}_3\) (either pure or in a mixture)\textsuperscript{16g}, \textsuperscript{20-21}, a mixture of methanesulfonic acid with concentrated sulfuric acid\textsuperscript{22} and acetyl sulfate\textsuperscript{23}. Sulfonation with chlorosulfonic acid or fuming sulfuric acid sometimes causes chemical degradation in these polymers. According to Bishop \textit{et al.}\textsuperscript{16j}, the sulfonation rate of ACPs in sulfuric acid can be controlled by varying the reaction time and the acid concentration. Using this method, sulfonated ACPs with a sulfonation range of 30-100\% can be prepared without chemical degradation or crosslinking reaction\textsuperscript{24}. However, this direct sulfonation reaction cannot be used for preparation of randomly sulfonated copolymers at a sulfonation level of less than 30\%, because the heterogeneous conditions under which sulfonation in sulfuric acid occurs causes high viscosity of the reaction solutions\textsuperscript{16d, e}. For this reason, the dissolution process was kept short, less than 1h, in order to produce a more random copolymer. Sulfonation levels in PEEK and poly(4-phenoxylbenzoyl-1,4-phenylene) (PPBP)\textsuperscript{25} as a function of reaction time at room temperature are presented in Figure 1.9. When the degree of sulfonation increases, the solubility of polymers changes. For example, S-PEEK can be dissolved in DMF, DMSO
and 1-methyl-2-pyrrolidinone (NMP) when it contains 30% sulfonic acid groups; at 70% sulfonation the polymer is soluble in methanol and at 100%, in water.

Figure 1.8. Chemical structures of sulfonated aromatic condensation polymers

16d
Figure 1.9. Levels of sulfonation of PEEK and PPBP as a function of reaction time in sulfuric acid at room temperature. (Reprinted with permission from Elsevier)

The biggest problem of the postsulfonation method for existing aromatic hydrocarbon polymers is that, due to the electrophilic nature of the sulfonation reaction, a phenyl group in the polymer cannot incorporate more than one sulfonic acid group. As a type of electrophilic substitution reaction, the sulfonation reaction depends strongly on the nature of substituents in the rings. Electron-donor substituents in the aromatic ring favor the reaction, while electron-acceptor substituents do not. Thus, when the phenyl ring is substituted by one sulfonic acid group, it decreases the reactivity for addition of the next sulfonic acid group. Typical sulfonation extents that result in an acceptable compromise between mechanical properties and proton conductivity range between 60% and 85% of the repeat units containing one sulfonic acid group. The proton conductivity reported for most of these materials is comparable to or somewhat inferior to that found for Nafton® membranes.
The thermal stability of polymer membranes based on S-PPBP was studied by heating the samples (thermogravimetric analysis (TGA) at a heating rate of 10°C/min in nitrogen atmosphere), followed by elemental analysis. Degradation of sulfonated polymer was observed between 250 and 350°C, much lower than the decomposition temperatures of non-sulfonated PPBP. As the degree of sulfonation increased, the degradation temperature decreased. However, no thermal decomposition temperature below 200°C was observed for any of the sulfonated polymers, which means that the thermal stabilities of the polymer are sufficient for fuel cells application even at high sulfonation levels.\textsuperscript{4b}

Experiments determining absorption of water vapor by polymer films prepared from S-PEEK show similar results to those reported in an analogous study of Nafion® membranes.\textsuperscript{26} The equilibrium water content of S-PEEK increases as the sulfonation level increases. In the first region (relative humidities in the range from 0% to 50%), due to solvation of proton and sulfonate ions, a relatively small increase in the water uptake was observed. In the second region (relative humidities in the range from 50% to 100%), a much greater increase in the water uptake was observed. This is attributed to interaction with ionic components of the polymer during solvation.

Up to the present most of the sulfonated ACPs showed no advantage in mechanical properties compared with Nafion® and the major drawbacks of postmodification method still exist, research on ACPs is still active because of the significant advantage in price, and in some cases ease of synthesis.
1.3.2. **Direct polymerization of sulfonated aromatic hydrocarbon monomer units**

As is usual when dealing with macromolecules, the lack of control over the degree and location of functionalization is still one of the major drawbacks of postmodification methods. Stability and acidity are expected to be enhanced by attaching two sulfonic acid groups to an electron-deficient aromatic ring, compared with one sulfonic acid group attached to an electron-rich aromatic ring. Moreover, it is unlikely that durability is enhanced by controlling and/or increasing molecular weight through a postreaction on an existing commercial product. Alternative methods involve synthesizing the copolymer by directly copolymerizing sulfonated monomers, such as sulfonated poly(p-phenylene)\(^{27}\), sulfonated PEEKs\(^{28}\), sulfonated poly(phthalazinone ether ketones)\(^{29}\), sulfonated poly(arylene ether sulfones) (S-PAESs)\(^{30}\), sulfonated poly(thiophenylene sulfones)\(^{31}\), sulfonated poly(phthalazinone ether sulfones)\(^{32}\) and sulfonated polyimides\(^{33}\). Among these, sulfonated polyarylene ethers, sulfonated polyimides and their derivatives are the focus of many investigations.

**1.3.2.1. Polyarylene ether sulfone copolymers**

Compared to post-sulfonated aromatic copolymers, copolymers synthesized by direct copolymerization have several advantages. Directly copolymerized copolymers have better proton conductivity and enhanced chemical/mechanical stability because the synthetic procedure allows two sulfonic acid groups to be precisely attached at the meta position of the deactivating sulfone group instead of one sulfonic acid group randomly bonded at the ortho position of the electron-rich aromatic ether bond\(^{34}\).

The first sulfonated monomer was prepared by Robeson and Matzner\(^{35}\) and further developed by Ueda el al\(^{36}\) by the sulfonation of 4,4’-dichlorodiphenyl sulfone.
McGrath’s group modified the procedure for disulfonation of the monomer, and sulfonated poly(arylene ether sulfone) copolymers\textsuperscript{37} were synthesized via direct copolymerization in any composition, as in Figure 1.10.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure110.png}
\caption{Synthesis of directly copolymerized wholly aromatic sulfonated poly(arylene ether sulfone)\textsuperscript{37}, BPSH-xx, where xx is the ratio of sulfonated/unsulfonated activated halide. (Reprinted with permission from Elsevier)}
\end{figure}

In order to take advantage of the stability of the sulfonic acid salt, the potassium salt form of the 3,3’-disulfonated-4,4’-dichlorodiphenylsulfone was used in the copolymerization reaction\textsuperscript{37a}. The resulting random copolymers displayed a hydrophilic/hydrophobic phase separated morphology that varied depending on the degree of disulfonation. The conductivity and water uptake of this series of copolymer increased with the degree of disulfonation. However, 60 mol% disulfonation in the copolymer resulted in a semicontinuous hydrophilic phase and dramatically swelled gel-like
membranes, which implies that protonic conductivity must be balanced with the water swelling and mechanical properties of the membrane in these copolymers.

In order to study the influence of the bisphenol (BP) structure on the properties of sulfonated poly(aryl ether sulfones) (SPAEs) polymers, a series of SPAEs (Figure 1.11) were synthesized by McGrath et al. using the technique of direct copolymerization of sulfonated monomers, in which the ratio of a fluorine-bearing component (hexafluoroisopropylidene bisphenol, 6FBP) was varied against a hydrocarbon component bisphenol (BP) while maintaining the ratio of sulfonated to unsulfonated sulfone at 45 mol%\(^\text{38}\). Polymer water uptake decreased from 95\% to 40\% over the range of 6FBP:BP = 0.00 to 0.30 and remained constant over the range 0.30 to 1.00, which was partially due to a decreasing ionic content and the hydrophobicity imparted by the 6FBP. The decreasing ionic content resulting from the large molar weight increase of the 6FBP repeat unit also caused the proton conductivity to decrease linearly.

![Figure 1.11. Chemical structures of SPAEs copolymers synthesized by McGrath etc. (Reprinted with permission from Elsevier)](image)

Watanabe et al. have synthesized SPAEs homopolymer with fluorenyl pendant groups (Figure 1.12 A) and their copolymers (Figure 1.12 B)\(^\text{39}\).
As expected, these polymers show the trend of increasing water uptake as a function of IEC. But, the results show little variation among different membrane types. However, the swelling of B ($R_1 = R_2 = R_3 = CH_3$) is less than A ($R_1 = R_2 = H$); even though B has a high IEC (3.26 meq g$^{-1}$ versus 2.76 meq g$^{-1}$) and exhibits a higher water uptake. The presence of the methyl group in B increased dimensional stability as well as oxidative and mechanical stability. The increased dimensional stability promotes chain

Figure 1.12. Chemical structures of SPAEs copolymers synthesized by Watanabe et. al.
entanglement, which restricts the extent of swelling, and/or B adopts a morphology more resistant to swelling. The conductivity of B was also higher than A (R₁ = H, R₂ = H or CH₃) especially at low RH (20%) and high temperatures (80-120°C), and even comparable to or higher than Nafion212®. Scanning Transmission Electron Microscopy (STEM) measurement show that the ionic domains of B appeared more connected than A, which may be the cause of higher proton conductivity.

Recently, Watanabe et al. reported the effect of the size of hydrophobic moieties upon the properties of SPAEs (Figure 1.11 C1-4)⁴⁰. Semiempirical molecular orbital calculations estimated that the approximate volume dimensions of these components are of the order: C₁>C₂>C₃>C₄. STEM showed that as the hydrophobic component decreases in size, the ionic domains increase in size. For the smallest molecule C₄, the hydrophilic component aggregated, in contrast to the bulkier hydrophobic components that hinder aggregation of both hydrophobic and ionic domains. The resulting microphase separation behavior has implications on water uptake and proton conductivity. For C₁, the bulkiest hydrophobic group induced the highest water uptake, due to the less well-developed hydrophilic clusters, while C₃ and C₄ exhibit lower water uptakes over a range of temperature and RH for their better-developed ionic domains. C₃ and C₄ show higher proton conductivity over the same range of temperature and RH, compared to C₁. Proton diffusion coefficients for these polymers, estimated by the authors using the Nernst-Einstein equation, are found to decrease in the order C₃, 4 >C₁, 2. This is due to the better connectivity between hydrophilic clusters in the case of C₃, 4.

BPSH copolymers are potentially a promising alternative to perfluorinated Nafion®-like materials, since they have lower cost, sufficient stability, lower water uptake
and comparable proton conductivity to Nafion®. For example, the copolymer synthesized by polycondensation of disodium 3,3’-disulfonate-4,4’-dichlorodiphenylsulfone (SDCDPS), 4,4’-dichlorodiphenylsulfone (DCDPS) and 4,4’-biphenol has 0.17 S/cm at 80°C and 100%RH (SDCDPS/DCDPS = 0.6) which is higher than fluorinated copolymer Nafion1135® control (0.12 S/cm) at the same temperature and RH. However, BPSH copolymers still suffer the same drawback observed in perfluorinated polymers. The conductivity of BPSH copolymers was affected greatly by temperature and relative humidity. Due to the phase separated morphology similar to that observed for perfluorosulfonated polymers, the conductivity of BPSH decreases quickly as the relative humidity drops and temperature rises.

In order to obtain new PEMs with reasonable conductivity and dimensional stability for fuel cells at low relative humidities and high temperature, extensive work related to BPSH copolymers has been conducted that showed research efforts may need to focus on exploring not only new materials, but also new polymer morphologies.

1.3.2.2. Sulfonated polyimides

Sulfonated polyimides (SPIs) are a class of rigid-rod polyaromatics with a number of attractive characteristics including excellent chemical, thermal, and mechanical stability, resistance to swelling, commercial availability and relative ease of synthesis. However, as PEMs, the five-membered ring sulfonated poly(phthalimides) degrade quickly in fuel cells. It is likely that hydrolysis of the phthalimide structure leads to chain scission and causes the membrane to become brittle. Currently, the more hydrolytically stable six-membered ring of the naphthalenic polyimide has been applied as PEM in fuel cells, even though its stability is still questionable.
In order to underline the possible imide cycle hydrolysis associated with -SO_3H presence, Genies et al.\textsuperscript{34} used NMR and IR analysis to obtain clear information about structural modification using model compounds. Model compounds of the sulfonic acid containing phthalic imide (model A) and the sulfonic acid containing naphthalenic imide (model B) were prepared by a one-step high temperature condensation in \textit{m}-cresol, shown in Figure 1.13.

**Figure 1.13.** Synthesis of model imide compounds A and B. (Reprinted with permission from Elsevier)

In distilled water at 80°C, model A compound had a structure modified in 1 h and was totally decomposed in 10 h, shown by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy; Model B compound was stable for 120 h and decomposed after 120 h. IR and NMR spectroscopy indicated the hydrolysis products to be an amide/carboxylic acid and an amide/anhydride. Quantitative determination of the amount of hydrolysis products as a function of time showed that the relative amount of carboxylic acid becomes constant after some time. The authors suggest that equilibrium occurs between model B and products formed during hydrolysis.
Genies et al.\textsuperscript{45} developed a synthetic method to produce random and block (segmented) sulfonated copolyimides (SPIs). The synthetic procedure for their most studied copolymer is shown in Figure 1.14. A high degree of sulfonation generally leads to high swelling or even dissolution of the polyimide membrane; a block length of three sulfonated repeat units yields the highest proton conductivity\textsuperscript{46}.

![Synthesis of SPI](image)

**Figure 1.14.** Synthesis of SPI, a sulfonated six-membered ring polyimide from 4,4'-diamino-2,2'-biphenyl disulfonic acid (BDA), the unsulfonated diamine 4,4'-oxidianiline (ODA), and 1,4,5,8-tetracarboxylic dianhydride (NDA). (Reprinted with permission from Elsevier)

The poor solubility of six-membered ring polyimides limits membranes and their subsequent use in the fuel cells, but can be improved by introducing a small fraction of
unsulfonated diamine, as shown in Figure 1.13\textsuperscript{47}. The preparation of sulfonated polyimides with different ion exchange capacities and sulfonated block lengths show that the solubility of the polyimides was greatly improved by introducing phenyl-ether bonds and bulky groups into the polymer backbones; randomly sulfonated copolyimides exhibit better solubility in organic solvents than the sequenced ones. Therefore, improved solubility is a result of the unsulfonated diamine and microstructure of the polymer chain. The absorbed water is mainly located in the hydrophilic domains, and the number of water molecules per ionic group and polymer conductivity is systematically lower for random microstructures than for sequenced copolymers.

In order to compare the hydrolytic stability of several sulfonated six-membered ring polyimides, an aging experiment was carried out where membranes were placed in distilled water at 80°C until a loss of mechanical properties was observed\textsuperscript{48}. The stability of membranes was improved for polymers with lower degrees of sulfonation and for random copolymers, as opposed to block or sequenced copolymers. Moreover, the membrane stability was greatly affected by the flexibility of the sulfonated diamine in the polymer structure. Considering that the reactivity of the diamines is due to the basicity of diamines, aromatic diamines with higher basicity are generally more reactive with dianhydrides than those with lower basicity. Since hydrolysis is the reverse reaction of polymerization, polyimides derived from more basic diamines should have higher hydrolytic stability.

Litt and co-workers proposed a fundamentally different approach to the use of sulfonated polyimides as PEM’s\textsuperscript{49}. Based on their design, nanoscale non-collapsible pores lined with sulfonic acid groups can be generated using rigid-rod nematic liquid
crystalline polyimides with a small amount of bulky or angled comonomers. These nanopores can increase water absorption and strongly hold water, and thus increase the proton conductivity at low relative humidities and high temperature. Figure 1.15 illustrates the structural approach and some of the bulky and angled co-monomers used in the copolymer synthesis.

![Figure 1.15](image)

**Figure 1.15.** Structural approach for the synthesis of rigid rod liquid crystalline polyimides

Encouraging proton conductivity and mechanical properties of this type of polyimide copolymers confirmed their design. Using membranes containing 5% of the hexaphenylbenzene units (red in Figure 1.15) for example, showed a very high proton conductivity (0.8 S/cm) at room temperature and 100% relative humidity while maintaining a conductivity >0.001 S/cm at room temperature and 15% relative humidity. The high proton conductivity observed at low relative humidity were was attributed to the “frozen-in” free volume present in the membrane generating from the rigid rod structure of the polymer molecules, which is shown in Figure 1.16. Incorporating the larger
comonomer, which prevents regular close parallel packing of the backbones, can further increase this volume. The authors demonstrated that they had achieved a solid state structure inherently different from that commonly found in other polymers being studied as candidates for use as PEM’s. The materials produced by the Litt group seem to organize in such a way that the membranes exhibit non-collapsible continuous hydrophilic domains that gives them high proton conductivity at low relative humidity.

![Graph showing proton conductivity vs relative humidity](image)

**Figure 1.16.** Room temperature proton conductivity for sulfonated polyimide copolymers as a function of relative humidity

Although much effort has been put into the research of polyimides copolymers and many characterizations of the material obtained showed very promising results, these membranes suffer from the drawback that they hydrolyze slowly. Attempts to increase the hydrolytic stability by using thermally and physically cross-linked membranes showed only modest improvements.
1.4. Motivation and justification in structural design of polyphenylene sulfonic acids

Based on the concept proposed previously by the Litt group that rigid rod, liquid crystal polyimides with sulfonic acid group and a small mole fraction of bulky groups can produce separation between two polymer chains and create a channel to hold the water\textsuperscript{49}, a similar but stable liquid crystal polymer polyphenylene with sulfonic acid was designed.

The polyimides developed by the Litt group showed high conductivity at low relative humidities, but they hydrolyzed slowly. However, the results showed the idea can improve the proton conductivity at low relative humidities. In order to overcome the drawback of polyimides where they are easy to hydrolyze, a new type of stable polymer poly(biphenylene-3,3'-disulfonic acid) (PBPDSA) was designed. PBPDSA synthesized by Ullmann coupling showed high proton conductivity and thermal stability\textsuperscript{50a}. Even after grafted with bulky or crosslinkable hydrophobic groups, it still had a higher or comparable conductivity to that of Nafion\textsuperscript{®}. But this PBPDSA homopolymer had poor mechanical properties. Mechanical properties can be improved by increasing the molecular weight of PBPDSA, which can be realized by optimizing the reaction conditions. Grafting and crosslinking the homopolymer or copolymerizing with bulky water insoluble co-monomer can generate water insoluble polymer with bulky groups. However, grafting decreases the number of sulfonic acid groups and lowers conductivity, but the copolymerization could not only make water insoluble copolymer but also increase the “frozen-in” free volume by introducing bulky groups into the backbone. Dr. Kang synthesized the homopolymer poly(p-phenylene-2,5-disulfonic acid) (PPDSA) from 1,4-dibromobenzene-2,5-disulfonic acid (DBPDSA) using the Ullmann reaction\textsuperscript{50b}. The obtained PPDSA had very high conductivity at low relative humidity due to its high
IEC and high “frozen-in free volume”\textsuperscript{51}. The general approach for this thesis stems from the application of the previous developed structural concept: the use of rigid rod liquid crystalline sulfonated fully aromatic copolymers to generate highly conductive, water insoluble PEM’s.

1.5. Overview of the dissertation

We propose that high molecular weight poly(phenylene sulfonic acid) can afford good mechanical properties and can copolymerize to generate water insoluble copolymer. Specifically, we have synthesized a new type of bulky, bending comonomer, 2,7-dibromofluorene-3,5-disulfonic acid (DBFDSA). We have made high molecular weight poly(biphenylene-3,3’-disulfonic acid) (PBPDSA), and copolymers of poly(phenylene disulfonic acid\_co-fluorene disulfonic acid) (PxF1). The resulting copolymers exhibit exceptional properties: high IEC (ion exchange capacity), high proton conductivity at high temperature and low humidity, high water uptake, high water retention and a unique solid state with “frozen-in” free volume.

The dissertation continues with Chapter 2, describing the optimization of the polymerization approach for the synthesis of high molecular weight PBPDSA. Chapter 3 focuses on the design and optimization of the copolymerization, grafting by addition of benzyl (Bn) groups and crosslinking reactions for the new copolymers: (PxF1), PxF1-g-Bn and crosslinked PxF1-g-Bn. Chapter 4 describes the basic chemical, thermal and mechanical properties of these new copolymers and discusses some aspects of their solid state structure, solution behavior and calculation of “frozen-in” free volume. Chapter 5 deals with general conclusions about the advantages and disadvantages of copolymers and future work proposing possible ways to reduce or eliminate their shortcomings.
1.6. References


Chapter 1


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Chapter 2

Synthesis of high molecular weight

poly(biphenylene-3,3’-disulfonic acid) (PBPDSA)

2.1. Introduction

2.1.1. Existing synthetic methods for poly(p-phenylene) (PPP)

As one of the most structurally simple of all the linear, rigid-rod polymers, poly(p-phenylene) is exclusively composed of benzene rings\(^1\). The stable sp\(^2\) hybrid carbon atoms in the benzene rings offer PPP exceptional mechanical strength\(^2\), remarkable thermal stability\(^2a\) and excellent chemical resistance, while maintaining a relatively low density\(^2a\). In the early stage, PPP was studied as a high-performance engineering material in extreme environments. But now PPP is one of the most promising photoelectronic polymers, with the discovery of electrical conductivity in the conjugated polymer system in the late 1970s. When PPP’s \(\pi\) conjugated system is doped with an electron donor or acceptor, PPP can be converted from an electrical insulator in its pristine state (\(\sigma \leq 10^{-10} \text{ S cm}^{-1}\)) to a highly electrically conductive doped polymer charge-transfer complex (\(\sigma \geq 500 \text{ S cm}^{-1}\))\(^3\).

However, the stable, rigid sp\(^2\) hybrid carbon atoms in the PPP backbone generate problems when processing PPP into forms suitable for device construction. Unsubstituted PPP is such an inert material that it is hard to process and fabricate. The only way to process PPP is by high-temperature sintering under vacuum. In order to circumvent this
limitation, two divergent synthetic strategies have been developed. One is to synthesize a highly soluble, controllable molecular weight precursor polymer that can be quantitatively converted to pristine PPP. One example of the precursor route to PPP is Grubbs and coworkers’ improvement on the ICI process by employing an organonickel catalyst to synthesize the first high molecular weight, structurally regular PPP (Figure 2.1). The success of this route depends on two factors: the nickel catalyst controls not only the high regioselectivity and stereoselectivity of the polymerization reaction but also the molecular weight to some degree; the acid catalyst lowers the conversion temperature in the elimination step.

![Figure 2.1](image)

**Figure 2.1.** The Grubbs Precursor route to structurally well-defined PPP using a stereospecific organotransition-metal polymerization catalyst. (Py, pyridine; TBAF, tetra(n-butyl)ammonium fluoride).

Another strategy to synthesize processible PPP involves adding functionalized side-chains to the PPP aromatic backbone. The functionalized side-chain increases the
solubility of the PPP analog during polymerization and processing. Thus, high molecular weight polymers can be obtained and processing is no longer a stumbling block. Compared to the parent PPP, PPP analogs with a functional group on the aromatic backbone have significantly different physical and chemical properties. These two advantages make the synthesis of side-chain-functionalized PPP analogs a hotspot in PPP research. However, the introduction of side-chains can diminish many of the desirable properties of parent PPP, such as chemical and solvent resistance, and high electrical conductivity.

Four methods have been used to synthesize PPP and substituted PPP analogs: 1. Step-growth coupling of 1,4-dihalobenzenes using metals\(^6\); 2. Chemical oxidation of benzene (Kovacic method\(^2\)); 3. Electrochemical oxidation of benzene\(^7\); 4. Diels-Alder polycondensation of aromatic bis(pyrone)s with 1,4-diethynylbenzenes\(^6\).

1. Step-growth coupling of 1,4-dihalobenzenes using metals

a) Coupling by the Wurtz-Fittig Reaction

The Wurtz-Fittig reaction is the chemical reaction of aryl halides and sodium metal to give substituted aromatic compounds\(^8\). Goldschmiedt obtained poly(\(p\)-phenylene) consisting of 13 phenylene units with terminal bromine atoms\(^9\) (Figure 2.2) using the Wurtz-Fitting reaction. Metallic sodium and potassium were heated in refluxing xylene for 5 h to form KNa\(_2\). The KNa\(_2\) was added to a mixture of 1,4-dichlorobenzene and dioxane at 95\(^\circ\)C and the mixture was heated for 24-28 h. The polymerization product was collected, dried overnight and extracted with benzene. The yield of PPP was 10%; it was practically insoluble in organic solvents.
Figure 2.2. PPP synthesized using the Wurtz-Fittig Reaction

b) Coupling by the “classic” Ullmann Reaction

The “classic” Ullmann reaction is the synthesis of biaryls via copper-catalyzed coupling. Kern et al. first reported the synthesis of poly(phenylene) by the Ullmann reaction\textsuperscript{10}. 4,4’-Diiodo-3,3’-dimethylbiphenyl was heated with copper powder in high boiling solvents such as 1-methylnaphthalene for 16 h. Although the highest molecular weight fraction of the resulting soluble polyphenylenes reached up to 300,000, side reactions possibly gave meta-linked or branched product and changed the molecular shape of those polymers to be neither rigid nor rod-like.

Hellman et al. gradually heated a mixture of activated copper and 1,4-diiodo-2,3,5,6-tetrafluorobenzene to 200°C\textsuperscript{11} (Figure 2.3). The resulting polymer was benzene soluble and stable at 500°C in a sealed tube. The structure was confirmed by mass spectrometry and the degree of polymerization was determined by elemental analysis (n = 10).

Figure 2.3. PPP synthesized using the Ullmann reaction
c) Coupling by the Kumada Reaction

The advantages of the Kumada reaction are that it can be carried out at low temperature without side reactions, resulting in linear polymers with a high degree of polymerization and narrow molecular weight distribution. The mechanism of this catalytic reaction is illustrated in Figure 2.4. Ni(II) compound was reduced by 2 equiv of Grignard reagent. The resulting Ni(0) compound undergoes oxidative addition to the aromatic halide. This addition product was transmetalated with another molecule of Grignard reagent. In the final step, two aromatic groups are coupled together by reductiveartzpires in another catalytic cycle.

Figure 2.4. Catalytic cycle of the Kumada reaction

In 2004, a new polymerization method, named Kumada chain growth polycondensation (KCGP) polymerization was found by Yokozawa et al. in a reaction
using Ni(dppp)Cl$_2$ (dppp = 1,3-bis(diphenylphosphino)propane) to catalyze the Kumada polymerization of (2-bromo-5-chloromagesio-3-hexyl)thiophene$^{12}$. In 2006, Yokozawa et al. applied KCGP method to the synthesis of poly(p-phenylene) with controlled molecular weight and low polydispersity$^{13}$. Treatment of 1,4-dibromo-2,5-dihexyloxybenzene with 1 equiv of $i$-PrMgCl in THF at room temperature for 24 h gave the corresponding Grignard compound. Without separation, 1.8 mol % of Ni catalyst was added to the reaction mixture and polymerization was carried out. In order to get high molecular weight and a narrow distribution PPP, several Ni catalysts such as Ni(dppp)Cl$_2$, Ni(dppe)Cl$_2$ (dppe = 1,2-bis-(diphenylphosphino)ethane)) and Ni(dppf)Cl$_2$ (dppf = 1,1’-bis-(diphenylphosphino)ferrocene) were screened. Ni(dppe)Cl$_2$ gave the best result, with LiCl as an additive. The role of LiCl is to break the aggregation of Gignard type monomer and inhibit the side reaction in the initial stage. The living polymerization chain-growth mechanism was demonstrated by three facts: 1) the $M_n$ values increased in proportion to the conversion, and the $M_w/M_n$ ratios were less than 1.18 over the whole conversion range; 2) the molecular weight of PPP is controlled by the feed ratio of the monomer to the Ni catalyst; and 3) higher molecular weight PPP ($M_n = 20400, M_w/M_n = 1.25$) was prepared by adding a fresh feed of corresponding Grignard reagent to the prepolymer ($M_n = 8000, M_w/M_n = 1.22$).

d) Coupling by the Suzuki Reaction

Although the Kumada reaction is a successful method in PPP synthesis, its low tolerance to functional groups limits its further application. In order to increase PPP solubility, side chains need be attached to the benzene ring, which decreases its reactivity in the Kumada reaction.
The Suzuki reaction using palladium catalyst to couple organic boronic acids or their esters with organic bromides has high tolerance toward a wide variety of functional groups on either coupling partner and does not involve migration of reaction sites. The reaction mechanism is shown in Figure 2.5. Pd(0) I first adds oxidatively to Ar’X. The halogen anion in the resulting intermediate, II, is exchanged with base (NaOH) to form intermediate III. Via transmetalation with Ar’B(OH)₃, intermediate III is converted to intermediate IV. Reductive elimination of the coupling product Ar’-Ar restores the original palladium catalyst Pd(0) I.

![Figure 2.5. The Suzuki reaction mechanism: illustration](image)

The Suzuki coupling polymerization reactions normally are carried out in two-phase systems: one phase is an organic phase containing the palladium complex, monomer and produced polymer; the second phase is aqueous with inorganic base and boric acid byproduct generated from the reaction. The optimized reaction conditions
require vigorous stirring, reflux temperature and an inert atmosphere. One of the outstanding examples of the Suzuki reaction application in PPP synthesis is the synthesis of sulfonatoalkoxy-substituted PPP from 2,5-bis(3-sulfonatopropoxy)-1,4-dibromobenzene copolymerized with benzene-1,4-bis(boronic acid) (Figure 2.6)\textsuperscript{14}. The Suzuki reaction shows two advantages in this reaction, tolerance to the sulfonatoalkoxy substituent group, and homogeneous reaction using a DMF/water solvent and a water-soluble palladium complex.

\textbf{Figure 2.6.} PPP copolymer synthesized using the Suzuki reaction

e) Coupling by zero-valent nickel

This coupling reaction is carried out in polar solvents such as DMF and DMAC in the presence of ligand and Ni(0) generated in situ by the reduction of nickel(II) with zinc. The mechanism of this coupling reaction is illustrated in Figure 2.7. Similar to the Suzuki and Kumada reactions, zero-valent nickel catalyzed coupling reaction also requires 3 steps: oxidative addition, transmetalation and reductive elimination. The zero-valent nickel coupling reaction can be applied to synthesize PPP with special functional groups such as ketones and esters which react with Grignard reagents and cannot be prepared using the corresponding boronic acids or esters. Thus, methyl 2,5-dichlorobenzoate was polymerized by this method\textsuperscript{15} (Figure 2.8).
Figure 2.7. The mechanism of the zero-valent nickel coupling reaction

Figure 2.8. Poly(3-dodecyl-\(p\)-phenylene) synthesized using zero-valent nickel
2. Chemical Oxidation of Benzene (Kovacic method\textsuperscript{2a})

Kovacic’s method consists of oxidatively coupling benzene using aluminum(III) chloride, a Lewis acid catalyst, and copper(II) chloride as the oxidant under a nitrogen flow\textsuperscript{16}. The oxidative cationic mechanism of Kovacic polymerization method is illustrated in Figure 2.9. The poly(phenylene) prepared by Kovacic method was assumed to be a linear polymer. However, the more intense Electron-Spin Resonance (ESR) signals of the Kovacic PPP than found for polymer prepared by other methods means it contains polycyclic defects\textsuperscript{17}.

\[
\begin{align*}
\text{H}_2\text{O} + \text{AlCl}_3 & \quad \leftrightarrow \quad \text{H}_2\text{O} - \text{AlCl}_3 \quad \leftrightarrow \quad \text{H}^+\text{AlCl}_3(\text{OH}) \\
\text{C}_6\text{H}_6 & \xrightarrow{\text{H}^+ \text{Initiation}} \quad \text{H}^+ \text{C}_6\text{H}_6 \quad \xrightarrow{\text{C}_6\text{H}_6 \text{Propagation}} \quad \text{H}^+ \text{C}_6\text{H}_6 \quad \xrightarrow{\text{CuCl}_2 -2\text{H}} \quad \text{H}^+ \text{C}_6\text{H}_6
\end{align*}
\]

\textbf{Figure 2.9.} Mechanism of the Kovacic method of synthesizing PPP

3. Electrochemical Oxidation of Benzene

Electrochemical synthesis of PPP is the anodic oxidation of benzene in an electrolytic cell\textsuperscript{7}. In this process, benzene is first oxidized at the anode of the cell to generate a resonance-stabilized radical cation. Two radicals combine together to form a dication, which loses two protons to generate biphenyl. Biphenyl has a lower oxidation potential and is more easily oxidized than benzene itself. Thus, the polymer chains prefer to extend once the reaction is initiated. However, the polymers obtained from this method
have low molecular weight because PPP becomes insoluble after six or seven phenyl rings are connected. As a radical polymerization reaction, there are many side reactions, which can disrupt the linearity of the polymer. The molecular weight of PPP can be improved by a solid-state polymerization of the polymer chains with radical cations still in solution. Electrochemical polymerization of benzene can be carried out under scrupulously anhydrous conditions in media of low nucleophilicity and high acidity. The latter factor can reduce the oxidation potential of benzene and facilitate initiation of the polymerization by formation of $\sigma$- or $\pi$-complexes of benzene with a strong Lewis acid. For example, electrochemical polymerization of benzene in the presence of a boron trifluoride-ethyl ether complex afforded a flexible film of PPP. Alkoxyl substituents also can decrease the oxidation potential of benzene. 2-Methoxy-bromobenzene can be electrochemically polymerized in 0.1 M tetrabutylammonium tetrafluoroborate solution in acetonitrile.

4. Diels-Alder Polycondensation of Aromatic Bis(pyrone)s with 1,4-Diethynylbenzenes

Poly($p$-phenylene) can be prepared by a Diels-Alder reaction between 5,5'-$p$-phenylene bis-2-pyrone with $p$-diethynylbenzene in solution at 200-300°C, followed by the elimination of carbon dioxide. Beside $para$- position coupling, $meta$- position coupling side reactions were also found, based on the model reaction of 2-phenylpyrone with phenylacetylene and the corresponding IR spectra. The polymers had number-average molecular weights of 40,000-100,000. The yellow, amorphous PPP is completely soluble in common organic solvents (benzene, chloroform, etc.). Measurement of the
intrinsic viscosities of the sulfonated PPP in acetone-water revealed a slight polyelectrolyte effect, which can be eliminated by addition of salt.

2.1.2. Synthesis of high molecular weight PBPDSA

The conductivity of a proton exchange membrane depends on the number of sulfonic acid groups in the phenyl rings. One of the advantages of direct polymerization of sulfonated aromatic hydrocarbon monomers is that more sulfonic acid groups can be embedded into the polyphenylene backbone. However, as a special functional group, the sulfonic acid or its ester limits the useful synthetic methods. Since chemical oxidation methods give low molecular weight and irregularly coupled PPP, electrochemical anodic polymerization synthesizes doped conducting polymer by directly grafting onto the electrode surface while Diels-Alder methods require specially designed monomers. Only the organometallic coupling method, which generates more regioregular head-to-tail polymers with high molecular weights and conductivities, can be considered. As the earliest method for preparing PPP, the Wurtz-Fittig reaction generates low molecular weight PPP with low yield. The Suzuki reaction has a wide variety functional group tolerance and provides an example of the synthesis of sulfonate PPP via coupling and subsequent hydrolysis of its corresponding sulfonate esters. However, there are no reports on the synthesis of a sulfonated aryl diboronic acid or ester; which limits the maximum mole fraction of sulfonic acids that can be put on the PPP backbone to 66%. Sulfonic acid or ester groups also cause side reactions in the metal coupling reaction; they react with the Grignard reagent in the Kumada reaction and are attacked by the nickel complex in the Ni(0) catalyzed aryl-aryl coupling reaction; the tetrakis triphenyl phosphine ligand used in the Suzuki polycondensation (SPC) could produce undesired
metal-ligand reaction which changes the expected rigid rod structure of the resulting PPP\textsuperscript{19}.

Based on the considerations outlined above, the possibility of applying the Ullmann reaction for coupling of a sulfonated aromatic hydrocarbon monomers was explored. As a copper-mediated coupling reaction, the Ullmann reaction has two advantages in the synthesis of PPP: it is compatible with the sulfonic acid, and the sulfonated monomer can be easily made. The cost of this polymerization reaction is low due to the inexpensive metal copper and easily made sulfonated aryl halide monomer. Previous work in Litt’s group\textsuperscript{20} demonstrated that the Ullmann reaction is a very efficient method to prepare sulfonated PPP from sulfonated aromatic hydrocarbon monomers.

The Ullmann Reaction was first reported in 1901 by Fritz Ullmann\textsuperscript{21}. It is a reaction to form a C-C bond between two aryl groups. (Figure 2.10)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{The Ullmann coupling of two aryl halides}
\end{figure}

Typically this reaction is run at high temperature (above 200°C) with two molecular equivalents of aryl halide and two equivalents of finely divided copper\textsuperscript{21}. In the past 100 years, considerable improvements in the Ullmann coupling reaction have been made. Dimethylformamide used as a solvent can lower the reaction temperature and the proportion of copper. The reaction temperature can be lowered (85°C) and yields can be improved by using an activated form of Cu powder made by the reduction of copper (I)
iodide with potassium. Heterogeneous Ullmann reactions can be accelerated by ultrasound\textsuperscript{22}. Liebeskind \textit{et al.}\textsuperscript{23} developed an innovative copper(I) reagent copper(I)-thiophene-2-carboxylate (CuTC) which can promote Ullmann-reductive coupling of substituted aromatic iodides, bromides and 2-iodoheteroaromatics at room temperature. The reactivity of the Ullmann reaction is greatly affected by the substituent group, especially \textit{ortho}-substituted groups. Regarding the relationship between the structure of an aryl halide and its reactivity, electron-withdrawing groups such as nitro and carboxymethyl, especially in the position \textit{ortho} to the halogen atom, provide an activating effect. On the other hand, the presence of substituents which provide alternative reaction sites, such as amino, hydroxyl, and free carboxyl groups, greatly limits or prevents the reaction. Furthermore, bulky groups in the \textit{ortho}-position show sterics hindrance.

Dr. Granados-Focil in Dr. Litt’s group successfully synthesized poly(biphenylene-3,3’-disulfonic acid) (PBPDSA) by the Ullmann coupling reaction\textsuperscript{20a}. The proton conductivity of the resulting PBPDSA is higher than that of Nafion\textsuperscript{117} over the whole tested range of relative humidity and temperature. TGA and FTIR studies indicate that the polymers are stable up to 175\textdegree C\textsuperscript{20a}. However, PBPDSA film prepared by Dr. Granados-Focil had relatively poor mechanical properties due to its low molecular weight. Dr. Kang in Dr. Litt’s group successfully synthesized high molecular weight poly(p-phenylene-2,5-disulfonic acid) (PPDSA) using a more soluble monomer, 1,4-dibromobenzene-2,5-disulfonic acid dilithium salt (DBPDSA-Li)\textsuperscript{20b}. In this chapter, several factors affecting PBPDSA molecular weight are explored: the reaction conditions were optimized by screening the temperature, solvent, sulfonic acid counterion and drying conditions. A high molecular weight PBPDSA was obtained from polymerizing
thoroughly dried 4,4’-dibromobiphenyl-3,3’-disulfonic acid dilithium salt (DBBPDSA-Li) in 1-methyl-2-pyrrolidinone (NMP). The high molecular weight PBPDSA was grafted with neopentyl benzene and films cast from isopropanol-water mixture were ductile. The proton conductivity of the grafted polymer, PBPDSA-g-NPB, membrane was more than thrice that of Nafion212® and higher than the initial DOE target at 80°C. A detailed study of the synthesis and properties of PBPDSA and the grafted polymer is reported and discussed in this chapter.

2.2. Experimental section

2.2.1. Materials

Except for 15% oleum (the concentration of SO₃ gas = 13~17%, purchased from Alfa Aesar), all other reagents were purchased from Aldrich Chemical Co. 1-Methyl-2-pyrrolidinone (NMP) and dimethylformamide (DMF) were stirred with calcium hydride overnight under N₂ at 80°C, vacuum distilled and degassed with N₂ prior to use. The remaining solvents and reagents were used without further purification. Copper bronze powder (organic synthesis grade) was activated according to a previously reported procedure²⁴ and used immediately after preparation.

2.2.2. Characterization techniques

¹H- and ¹³C- NMR spectra of the polymers and monomers in D₂O, CD₃OD or DMSO-d₆ were obtained using a Varian Oxford 400 MHz or Gemini 300 MHz spectrometer. Polymer solution viscosities in H₂O were measured using a Cannon Ubbelohde viscometer in a constant temperature bath at 35°C. Gel Permeation Chromatography (GPC) was run using a Waters 510 pump, two main columns (Waters HR-5E DMF and HR-4E DMF) and two detectors: a UV detector (Waters 996
Photodiode Array Detector) and a refractive index detector (Waters 2414 Refractive Index Detector). The GPC sample (0.1 g/dL) was eluted with DMF at 0.7 mL/min and 35°C.

2.2.3. Monomer and polymer synthesis

2.2.3.1. Monomer synthesis

2.2.3.1.1. Synthesis of 4,4’-dibromobiphenyl-3,3’-disulfonic acid (DBBPDSA)

4,4’-Dibromobiphenyl (30 g, 96.2 mmol) was placed in a 250 mL 3-necked flask equipped with a mechanical stirrer and 75 mL fuming sulfuric acid (15%) was added. The flask was heated to 110°C in an oil bath with stirring for 30 to 40 min. After the mixture was cooled, it was poured into 900 g crushed ice. The resulting white precipitate was filtered and 100 g NaCl was added to the filtrate. A white solid salted out; it was filtered and recrystallized from acidified methanol (HCl) solution. 25 g DBBPDSA was obtained. Yield is 55%. 

$$\delta$$ 8.12 (d, 2H, J = 2.1 Hz), 7.70 (d, 2H, J = 8.1 Hz), 7.47 (dd, 2H, J = 2.1, 8.4 Hz).

2.2.3.1.2. Preparation of 4,4’-dibromobiphenyl-3,3’-disulfonic acid dilithium salt (DBBPDSA-Li) and di(benzyltrimethylammonium) salt (DBBPDSA-BTMA)

Crude DBBPDSA disodium salt (DBBPDSA-Na) (42g, 81 mmol) was dissolved in 1375 mL water and BTMA-Cl (33 g, 178 mmol) was added. The solution volume was reduced to 500 mL by rotary evaporation, filtered hot and cooled to 0°C. The resulting precipitate was filtered and recrystallized from water. 17 g DBBPDSA-BTMA was obtained.

$$\delta$$ 8.05 (d, 2H, J = 2.4 Hz), 7.73 (d, 2H, J = 8.4 Hz), 7.46 (dd, 2H, J = 2.1, 8.1 Hz), 7.44–7.36 (m, 10H), 4.3 (s, 4H), 2.97 (s, 18H).
The pure DBBPDSA-BTMA was converted into DBBPDSA using a proton exchange column. Pure DBBPDSA-Li was made by titrating DBBPDSA with LiOH and recrystallizing from methanol and isopropanol. $^1$H NMR (300 MHz, D$_2$O) $\delta$ 8.19 (d, 2H, $J = 2.1$ Hz), 7.77 (d, 2H, $J = 8.4$ Hz), 7.52 (dd, 2H, $J = 2.1$, 8.1 Hz).

2.2.3.2. Experiments towards the synthesis of high molecular weight homopolymer, PBPDSA

2.2.3.2.1. Polymerization of DBBPDSA-Li in NMP

A 500 mL 3-necked flask was charged with DBBPDSA-Li (4.0 g, 8.3 mmol) and activated Cu (4.8 g, 75 mmol) and dried at 90°C for 30 min under vacuum (8 torr). Freshly distilled NMP (250 mL) was added using a double needle. The flask was placed into an oil bath and heated for 62 h at 140°C with mechanical stirring. After cooling, the solids were filtered and the filtrate was stripped by distillation to remove NMP. The resulting solid was dissolved in water and passed through a proton exchange column to generate an impure acid form of the polymer, PBPDSA-H. The polymer was purified as follows: the solid was dissolved in methanol and acetone was added to precipitate the polymer. The precipitate was collected, dissolved in i-PrOH and insoluble material was filtered. Subsequently, the PBPDSA-H i-PrOH solution was converted to PBPDSA-Na by titrating with NaOH methanol solution. i-PrOH was removed by evaporation, the solid was washed with acetone and converted to PBPDSA-H using a proton exchange column. 750 mg PBPDSA-H was obtained (Yield = 29%). $^1$H NMR (300 MHz, D$_2$O) $\delta$ 8.29 (b, 2H), 8.01 (s, 0.3 H$_2$), 7.88 (b, 2H), 7.50 (b, 2H).
2.2.3.2.2. Polymerization of DBBPDSA-Li in DMF

DBBPDSA-Li (4 g, 8.3 mmol) and activated copper (4.8 g, 75 mmol) were placed in a 500 ml 3-necked flask and dried at 90°C for 30 min under vacuum (8 torr). Freshly distilled DMF (250 mL) was added by double needle. This reaction was monitored by GPC: at certain times, 0.1 mL reaction solution was extracted in an airbag and diluted with DMF and a few drops of water to 2.0 mL. Insoluble particles were removed by filtering through a 0.45 μm PTFE membrane filter. After 125 h, the solution viscosity had not changed and a white precipitate was seen on the top of the copper powder. The insoluble material was filtered and extracted with water. The resulting polymer PBPDSA-Li was converted into PBPDSA-H using a proton exchange column. 1.3 g PBPDSA-H was obtained (yield = 50%). \(^1\)H NMR (400 MHz, D₂O) \(\delta\) 8.30 (b, 2H), 8.21 (s, 0.4 H,), 8.15 (b, 0.3 H,), 8.10 (s, 0.4 H,), 7.88 (b, 2H), 7.79 (t, 0.7 H, J = 7.2), 7.61 (t, 0.4 H, J = 8.0), 7.49 (b, 2H).

2.2.3.2.3. Polymerization of high-vacuum dried DBBPDSA-Li and DBBPDSA-BTMA in DMF

The procedures and reagent weights or volumes were identical for both experiments. The reaction of the Li salt is described below. DBBPDSA-Li (0.10 g, 0.2 mmol) and activated copper powder (0.12 g, 1.9 mmol) were put into a 50 mL ACE glass pressure tube and dried at 90°C for 6 h under high vacuum (30 mTorr). DMF was dried with CaH₂ at 90°C overnight under N₂ and distilled under vacuum (24°C/ 800 mtorr). Dried DMF (5 mL) was syringed into the reaction tube and the system was degassed using 3 freeze/thaw cycles. The tube was purged with N₂ and placed in a preheated oil bath at 140°C with magnetic stirring. The reaction was monitored by GPC: at certain
times, 0.1 mL reaction solution was extracted in an airbag and diluted with DMF and a few drops of water to 2.0 mL. Insoluble particles were removed by filtering through a 0.45 μm PTFE membrane filter. During the reaction, the reaction mixture became dark brown. After 48 h, if the stirring was stopped, a layer of white powder was visible above the copper powder. After 10 days the reaction was terminated. The solid was filtered and extracted overnight with 50 mL of deionized water. The mixture was filtered to remove unreacted copper and the water solution was evaporated to dryness. The product was dried in the vacuum oven at 80°C and weighed. The polymer, the PBPDSA-Li yield was 0.050 g (75%), and PBPDSA-BTMA yield was 0.060 g (76%).

2.2.3.2.4. Polymerization of high-vacuum dried DBBPDSA-Li and DBBPDSA-BTMA in NMP

The procedures and reagent weights or volumes were identical for both experiments. The reaction of the Li salt is described below. DBBPDSA-Li (0.10 g, 0.2 mmol) and activated copper powder (0.12 g, 1.9 mmol) were put into a 50 mL reaction tube and were dried at 90°C for 6 h under high vacuum (pump vacuum was 15 mTorr.). NMP was stirred with CaH₂ at 90°C overnight under N₂ and distilled under vacuum (58°C/420 mTorr). Dried, distilled NMP, 5 mL, was syringed into the reaction tube and the system was degassed using 3 freeze/thaw cycles. The reaction tube was purged with N₂ and placed in a preheated oil bath at 140°C. Those two reactions (DBBPDSA-Li and DBBPDS-BTMA) were monitored by GPC: at certain times, 0.1 mL reaction solution was extracted in an airbag and diluted with DMF and few drops of water to 2.0 mL. Insoluble particles were removed by filtering through a 0.45 μm PTFE membrane filter. Those two reactions were run at 140°C for 13 days and at 170°C for 1 day. By this time,
the reaction mixture had become dark brown. The DBBPDS-BTMA reaction solution was viscous at 140\(^\circ\)C with a white solid above the copper powder. At room temperature, the DBBPDS-Li reaction looked like a gel. The solid was filtered and extracted overnight with 50 mL of deionized water. The suspension was filtered and the water solution was evaporated to dryness. The product was dried in the oven and weighed. The yield of PBPDSA-Li was 0.060 g (90\%), and the yield of PBPDSA-BTMA was 0.050 g (69\%).

2.2.3.2.5. Polymerization of high-vacuum dried DBBPDSA-Li in NMP at high concentration

DBBPDSA-Li (2.5 g, 4.8 mmol) and freshly activated copper powder (3.0 g, 47 mmol) were put into a 100 mL reaction tube. The reaction tube was dried at 90\(^\circ\)C for 6 h under high vacuum (30 mtorr) with stirring. NMP was stirred with CaH\(_2\) at 90\(^\circ\)C overnight under N\(_2\) and distilled under vacuum (58\(^\circ\)C/ 420 mTorr). 25 mL NMP was added to the reaction tube by syringe and the reaction system was degassed using 3 freeze/thaw cycles. The reaction tube was purged with N\(_2\) and placed in an oil bath preheated to 140\(^\circ\)C. The reaction was run at 140\(^\circ\)C for 8 days. The reaction mixture became viscous by the 8\(^{th}\) day. The reaction temperature was then raised to 170\(^\circ\)C for 1.5 days. The solution was dark brown. The solvent was removed by filtering and a grey gel-like solid was obtained. The solid was stirred with 50 mL of water overnight. Insoluble material was filtered and the solution was passed through a proton ion exchange column to acidify the polymer. The water was evaporated and the obtained polymer was dissolved in methanol and titrated with a NaOH methanol solution to neutrality. The polymer sodium salt precipitated during titration. The precipitate was filtered, dissolved
in water and passed through a proton ion exchange column. 462 mg material was obtained (yield = 29%).

2.2.3.2.6. Polymerization of thoroughly dried DBBPDSA-Li in NMP at low concentration.

A 100 mL reaction tube was charged with DBBPDSA-Li (1.14 g, 2.4 mmol) and activated copper powder (1.34 g, 20.9 mmol) and dried at 90°C for 24 h under high vacuum (30 mTorr.). NMP was stirred with CaH$_2$ at 90°C overnight under N$_2$ and distilled under vacuum (27°C). 25 mL freshly distilled NMP were syringed into the reaction tube and the system was degassed using 3 freeze/thaw cycles. The reaction tube was purged with N$_2$ and placed in a preheated oil bath. This reaction was run at 140°C for 8 days, 160°C for 1 day and 170°C for 2 days and monitored by GPC: at certain times, 0.1 mL reaction solution was extracted in an airbag and diluted with DMF and few drops of water to 2.0 mL. Insoluble particles were removed by filtering through a 0.45 μm PTFE membrane filter. The solution was dark brown and became a gel at room temperature. Insoluble solid was filtered and the NMP insoluble solid and the NMP solution were studied. The NMP insoluble solid was extracted using 80 mL deionized water and insoluble particles were filtered. The filtrate was passed through an ion exchange column. The obtained polymer acid form, PBPDSA-H, was titrated with NaOH methanol solution and the generated PBPDSA-Na precipitated from the methanol solution. The grey precipitate was collected, dissolved in water and passed through the ion exchange column again. A yellow solid (550 mg) was obtained after vacuum oven drying at 80°C. Yield is 76%. Low molecular weight PBPDSA-Na (0.2 g) from methanol filtrate was also collected.
2.2.3.2.7. Polymerization of thoroughly dried DBBPDSA-Li (dried separately with activated copper powder) in NMP

Activated copper powder (2.35 g, 36.7 mmol) was placed in a 100 mL pressure tube and dried at 100°C under 30 mtorr for 24 h. DBBPDSA-Li (1.51 g, 3.1 mmol) predried at 120°C under 30 mtorr for 2 days was added to the reaction tube and the mixture was dried at 130°C at 26 mtorr for another 24 h. NMP was stirred with CaH₂ at 90°C overnight under N₂ and distilled under vacuum (36°C). Freshly distilled NMP (35 mL) was syringed into the reaction tube and the system was degassed using 3 freeze/thaw cycles. The reaction tube was purged with N₂ and placed in a preheated oil bath. It was run at 140°C for 39 h, 170°C for 39 h. Reactions were monitored by GPC: at certain times, 0.1 mL reaction solution was extracted in an airbag and diluted with DMF and few drops of water to 2.0 mL. Insoluble particles were removed by filtering through a 0.45 μm PTFE membrane filter. After 11 h, the solution color had changed to yellow brown and solid had precipitated from the solution. By the time the reaction was stopped and cooled to room temperature, the solution color had turned dark brown. The NMP solution was removed by centrifugation and the residue was extracted with 100 mL methanol containing 0.5 mL concentrated HCl. The methanol solution was evaporated and a green solid was obtained. The green solid was re-dissolved in 100 mL MeOH and titrated with NaOH methanol solution. A blue precipitate (2 g) was collected and passed through a proton ion exchange column. 730 mg PBPDSA-H was obtained. Yield is 72%.
2.2.3.2.8. Scaled up polymerization of thoroughly dried DBBPDSA-Li (dried separately with activated copper powder) in NMP

A 500 mL 3-necked flask was charged with activated copper (6.5 g, 102 mmol) and dried at 100°C at 50 mtorr for 24 h. DBBPDSA-Li (5.0 g, 10.3 mmol) was placed in the flask and was dried at 120°C for another 24 h at 45 mTorr. A glass mechanical stirring rod with a Teflon paddle in a lubricated Trubore glass joint was fitted to the flask under Ar atmosphere. Subsequently, the Ar stream (100 mL/min) purged the flask for 3 h at 140°C. Freshly distilled NMP (150 mL) was injected into the flask by syringe. The reaction was run at 140°C at a stirring speed of 100 rpm for 22 h. The NMP solution was brown with a white solid above the copper powder. The solid was filtered and stirred overnight with 50 mL of deionized water. The suspension of unreacted copper was filtered and the filtrate was passed through a proton exchange column. In order to remove any remaining NMP, the polymer acid was dissolved in MeOH and titrated with NaOH solution. The precipitated polymer sodium salt was filtered and collected. A yellow solid (2.4 g) was obtained (yield = 72%).

2.2.3.3. Grafting high molecular weight PBPDSA polymer with neopentyl benzene

PBPDSA-H (2g, 12.8 mEq.), and H₃PO₄ (10 mL, 147 mmol acid plus 141 mmol H₂O) were placed in a 50 mL 3-necked round bottom flask under nitrogen flow and stirred at 300 rpm and 80°C. After 20 to 30 minutes, a homogeneous solution formed. P₂O₅ (25g, 176 mmol) was then added in batches of 500 mg in order to keep the reaction mixture temperature below 100°C. After the P₂O₅ addition was complete, a condenser was fitted to the flask and the temperature was raised to 140°C. Freshly distilled
neopentylbenzene (1.87g, 12.8 mEq.) was added and the reaction mixture was stirred rapidly at 140°C for 6 h. It was then poured into ice and left overnight. The following day the precipitate was filtered and dried at 90°C. The resulting powder was insoluble in water but formed a colloidal dispersion. The ¹H NMR spectrum of a sample dissolved in D₂O-DMSO-d₆ mixture was recorded. High quality, flexible film was cast from isopropanol-water mixture and its proton conductivity was measured by Bekktech.

2.3. Results and Discussion

2.3.1. Synthesis of high molecular weight PBPDSA

Two monomer salts, DBBPDSA-BTMA and DBBPDSA-Li were prepared according to the procedure in Section 2.3.3.1.2. Pure DBBPDSA-BTMA was made from the ion exchange between DBBPDSA-Na and BTMA-Cl and further purified by the recrystallization from water. The obtained DBBPDSA-BTMA was converted to DBBPDSA using a proton exchange column. Monitored by pH paper, the titration of DBBPDSA with LiOH gave DBBPDSA-Li, which was purified by recrystallization from methanol and isopropanol.

2.3.1.1. Synthesis of PBPDSA in different solvents (DMF, NMP)

The aim of these two experiments was to screen the proper solvent for the Ullmann coupling reaction. Compared with Dr. Granados-Focil’s reaction conditions where 100 mg/mL PBPDSA-BTMA was polymerized in NMP for 12 h at 140°C, a low concentration of monomer (16 mg/mL) PBPDSA-Li was reacted for longer times. It was hoped that the low monomer concentration would prevent the generated polymer from precipitating at low molecular weight; the long reaction time can let polymer chain
continue growing and generate higher molecular weight PBPDSA. The resulting polymers were analyzed by viscosity measurement and $^1$H NMR (Figures 2.11 & 2.12).

The viscosity measurements in Figure 2.11 showed that the viscosity of those two polymers was low. The two spectra in Figure 2.12 cannot be compared since they look so different. The spectrum in Figure 2.12a is very noisy which probably explains why the peaks are so broad. The triplets at 7.6 and 7.79 ppm showed that some Br was replaced by H. It implies that both samples were not dried properly. Water reacts with the cuprous complex to replace Br with H, stopping the polymerization. The viscosity measurements of those two polymers shows the degree of polymerization in NMP is higher than in DMF, which means the PBPDSA polymerization in NMP has higher molecular weight than in DMF. However, since both viscosities were low and both monomers were wet, it cannot be concluded that NMP is better polymerization solvent than DMF.

![Figure 2.11. Viscosity measurements (in D. I. water at 35°C) of PBPDSA from the polymerization reactions in DMF and NMP](image-url)
2.3.1.2. Synthesis of PBPDSA from DBBPDSA with different counter ions

Monomers with two different counterions, DBBPDSA-Li and DBBPDSA-BTMA, were polymerized in two different solvents, DMF and NMP. When the reactions were stopped, only DBBPDSA-Li in NMP gave a gel-like solution. It looks like high molecular weight PBPDSA was generated in this reaction system. All four reactions were monitored by GPC, shown in Figure 2.13.
Figure 2.13. GPC curve of a) DBBPDSA-BTMA polymerized in DMF for 132 h. b) DBBPDSA-Li polymerized in DMF for 132 h. c) DBBPDSA-BTMA polymerized in NMP for 180 h. d) DBBPDSA-Li polymerized in NMP for 180 h.

Although the absolute molecular weight of PBPDSA cannot be measured by GPC, the relative molecular weights of the corresponding polymers can be compared, based on the peaks in the GPC curves. For the polymerization reaction in DMF, polymerization of
DBBPDSA-BTMA gave relatively lower molecular weight polymer (polymer peak 12.5 min) than that from the polymerization of DBBPDSA-Li (polymer peak 12.0 min). There is a big difference between the polymers from two monomers polymerized in NMP. High molecular weight PBPDSA was obtained from the polymerization of DBBPDSA-Li in NMP (polymer peak 10.0 min). DBBPDSA-Li shows higher polymerization reactivity than DBBPDSA-BTMA both in DMF and NMP. Although the molecular weight of the polymer from DBBPDSA-BTMA polymerized in NMP is relatively low compared to that of the polymer from DBBPDSA-Li in NMP, it is still higher than those of the two polymers obtained from reaction in DMF, based on two small high molecular weight peaks (10.5, 11.0 min) in Figure 2.13 c.

The polymer resulting from the polymerization of DBBPDSA-Li in NMP was characterized by NMR and viscosity measurements, Figures 2.14 & 2.15. After deconvolution, we found that the small peaks were much sharper than the large peaks; they are probably from the ends of the polymer molecule. Using this assumption, the degree of polymerization was calculated based on the ratio of the integration of peaks at 8.29 and 8.09 ppm (end group). It was found to be about 32 (64 phenylene units). The viscosity is higher than any PBPDSA made before (C = 0.5 g/dL, \( \eta_{sp}/C = 0.97 \) dL/g). However, the polymerization reaction was cooked too long (> 10 days) and could be shortened.
2.3.1.3. Polymerization of high concentration DDBPDSA-Li in NMP

The polymerization of DDBPDSA-Li at a 10% concentration was run in NMP. Although the solution viscosity increased after 8 days, no gel-like material formed. Only 29% water soluble polymer was obtained. The water insoluble fraction is probably the polymer cuprous salt, since it dissolved in dilute acid or ammonia. The $^1$H NMR
spectrum of the water soluble fraction is shown below, Figure 2.16. The degree of polymerization is about 15, which is lower than that of the polymer (the degree of polymerization is 32) from the low concentration (2%) polymerization of DBBPDSA-Li. Besides concentration (10% versus 2%), the difference between high concentration and low concentration monomer polymerizations was the scale of the reaction (2.5 g versus 0.1 g). Because the reaction vessel used is narrow, and the monomers in the larger scale reaction filled its bottom 3 cm, it is difficult to dry the monomers, even under high vacuum (pump vacuum was 15 mtorr) at elevated temperature. The triplets at 7.7 and 7.6 ppm in Figure 2.16 show that the monomer was still not dry. The existing water reacted with the cuprous complex and a Br atom was eliminated, which caused low molecular weight fragments. (See Section 2.3.1.5 for a discussion of this.).

Figure 2.16. 400 MHz $^1$H NMR (D$_2$O) spectrum of PBPDSA from the high concentration polymerization of DBBPDSA-Li in NMP
2.3.1.4. Polymerization of thoroughly dried DBBPDSA-Li (dried separately with activated copper powder) in NMP

Although high molecular weight PBPDSA was obtained in Section 2.3.1.2, two week’s reaction time is too long to be acceptable. By changing of the drying procedure, the reaction can be shortened dramatically to 80 h. The activated copper and DBBPDSA-Li were dried separately before being mixed. The NMR spectrum and viscosity plot of the obtained PBPDSA are shown below, Figures 2.17 and 2.18.

![NMR Spectrum](image)

Figure 2.17. 400 MHz $^1$H NMR (D$_2$O) spectrum of PBPDSA from polymerization of DBBPDSA-Li (dried separately with activated copper powder) in NMP

The small peaks at 8.31 and 8.19 ppm are assigned to isolated hydrogens in the phenylene units at the polymer chain ends. Based on this, deconvolution of the spectrum gives us a degree of polymerization of ~35, or 70 benzene rings. The other small sharp
peaks are attributed to the two ortho hydrogens in the terminal repeat units of the polymer. The spectrum approaches the base line at 8.25, 8.15, 7.5 and below 7.3 ppm, showing that there were no side reactions that generated other structures.

The reduced viscosity plot, Figure 2.18, shows the highest viscosity we have obtained for any run. The better reaction conditions produced polymers that clustered around a limiting viscosity of 0.95 to 1.05 dL/g at 0.5% g/dL.

Figure 2.18. Viscosity measurement (D. I. water, 35°C) of PBPDSA from polymerization of DDBPDSA-Li (dried separately with activated copper powder) in NMP.

Using the optimized reaction conditions developed above, a 5 g scaled-up polymerization reaction was carried out successfully in a flask with argon stream drying and mechanical stirring. The reaction time was further shortened to 22 h. The obtained polymer was characterized by $^1$H NMR and viscosity measurement, shown in Figures 2.19 and 2.20.
Figure 2.19. 400 MHz $^1$H NMR (D$_2$O) spectrum of PBPDSA from scaled up polymerization of DBBPDSA-Li in NMP

Figure 2.20. Viscosity measurement (D. I. water, 35°C) of PBPDSA from scaled up polymerization of DBBPDSA-Li in NMP
The degree of polymerization could be calculated from the deconvoluted proton NMR of PBPDSA-H. The small peaks at 8.32 and 8.20 ppm are assigned as the hydrogens between the sulfonic acid and the two benzene rings at the polymer ends. The terminal benzene still has a bromo group attached (1H, s, 8.20 ppm). The peak at 8.32 ppm is assigned to the analogous hydrogen in the penultimate benzene ring. When the end group areas were compared to the total proton integration, the degree of polymerization was found to be ~34 (68 phenylene rings). However, based on the viscosity plot, the molecular weight of the material obtained from the larger scale reaction is higher than that of polymer prepared in the small scale reaction. (Reduced viscosity $\eta_{sp}/C = 1.35$ versus $1.05 \text{ dL/g}$ for earlier runs, at $C = 0.5 \text{ g/dL}$.)

Rigid rods consisting of ~70 benzene rings have a length of about 30 nm. Normally, rigid rod polymers of this chain length should have intrinsic viscosities greater than 100 dL/g. The relatively low reduced viscosity could imply that the polymers are highly aggregated. However, the sharp NMR peaks for the acid form imply rapid diffusional relaxation which could not occur if the molecules aggregated strongly. The low viscosity is probably mainly due to shear orientation of the molecules in the viscometer flow field.

2.3.1.5. The key factors for the synthesis of high molecular weight PBPDSA

In order to synthesize high molecular weight polymers, several factors have been screened. Based on the data and analyses in the previous section, three factors are thought to have major effects on the synthesis of high molecular weight polymer. They are the solubility of the monomer and polymer, which is related to their concentration, monomer counterion and reaction solvent. In Section 2.3.1.2, the results show that reaction in NMP
can afford higher molecular weight polymer compared to reaction in DMF; DBBPDSA-Li can generate higher molecular weight polymer than DBBPDSA-BTMA. Those results are consistent with the solubility data for DBBPDSA and PBPDSA, shown in Table 2.1.

### Table 2.1. DBBPDSA and PBPDSA salt solubility* at 25°C in DMF and NMP

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>10 wt.%</th>
<th>5.0 wt.%</th>
<th>2.5 wt.%</th>
<th>1.25 wt.%</th>
<th>0.62 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-BTMA</td>
<td>NMP</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>P-BTMA</td>
<td>NMP</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>M-Li</td>
<td>NMP</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4+</td>
</tr>
<tr>
<td>P-Li</td>
<td>NMP</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>M-Cs</td>
<td>NMP</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>P-Cs</td>
<td>NMP</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>M-BTMA</td>
<td>DMF</td>
<td>-</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5-</td>
</tr>
<tr>
<td>P-BTMA</td>
<td>DMF</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>M-Li</td>
<td>DMF</td>
<td>-</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4+</td>
</tr>
<tr>
<td>P-Li</td>
<td>DMF</td>
<td>-</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4+</td>
</tr>
<tr>
<td>M-Cs</td>
<td>DMF</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>P-Cs</td>
<td>DMF</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

* A five-point solubility scale was used where 1 = insoluble and 5 = perfectly soluble (no turbidity or sediment). M = DBBPDSA and P = PBPDSA

Although M-BTMA has the best solubility both in DMF and NMP due to the organic BTMA group, P-BTMA has the poorest solubility both in DMF and NMP. Thus, the polymerization of M-BTMA shows worse results both in DMF and NMP. 1.6–4.5 wt%
M-Li was used in the polymerization reaction. At this concentration range, the M-Li and P-Li have slightly higher solubility in NMP than that in DMF, which is consistent with the reaction result that the polymerization of M-Li in NMP is better than that in DMF. When the concentration was increased to 10 wt%, most of M-Li and P-Li were insoluble in reaction solvent. This provides a possible explanation for the low molecular weight and yield of the PBPDSA that was obtained in Section 2.3.1.3. In conclusion, the solubility of monomer and polymer has great effect on the molecular weight of the obtained polymer and low concentration is helpful to increase the polymer molecular weight.

The second factor is monomer reactivity. The low molecular weight polymer obtained from the polymerization reaction of DBBPDSA-BTMA in NMP and DMF is not only attributed to the solubility of the monomer and polymer salt but also the reactivity of the corresponding monomer. Dr. Granados-Focil\textsuperscript{19a} found the long chain cetyl trimethylammonium, CTMA, used as the cation of DBBPDSA, gave lower molecular weight PBPDSA than that of the DBBPDSA-BTMA. He thought the long alkyl chain interfered with the coupling process. The alkyl chain might obstruct the carbon-halogen bond, making it less accessible for complexation with the copper and less prone to attack by the organometallic copper complex. Compared to Li ion, the BTMA cation is bulky and might shield the carbon-halogen bond and organometallic copper complex. Therefore, the reactivity of DBBPDSA-BTMA could be lower than that of the DBBPDSA-Li in the Ullmann coupling reaction.

Third is the dryness of the reaction system including the monomer and activated copper. Recently, work in our group found that some Br end groups in PBPDSA had
been replaced by -H, which was caused by the water attacking the copper-aryl halide complex during the polymerization. Fanta and coworkers \(^{25}\) proposed a mechanism. They thought the \textit{ortho} electronegative group had a particular role in promoting the reaction by acting as a chelating agent as well as withdrawing electrons from the aromatic nucleus, which facilitates nucleophilic attack of copper, shown in the Figure 2.21.

![Proposed mechanism for the Ullmann coupling reaction](image.png)

**Figure 2.21.** Proposed mechanism for the Ullmann coupling reaction

In the first stage, the copper reacts with the aryl halogen to form copper-aryl halogen complex. In the second stage, a second molecule of aryl halide couples with the copper-aryl halogen complex. In the final step, the covalent biaryl bond is formed and the halogen is released. When water is present in the reaction system, the water hydrogen can replace the halogen in the copper-aryl halogen complex in the first stage and the polymer chain growth will be stopped. This mechanism also explains why drying activated copper...
and monomer separately can increase the molecular weight of PBPDSA and shorten the reaction. During the copper activation process, concentrated HCl was introduced and the obtained activated copper powder could still have trace amounts of HCl. This HCl can turn DBBPDSA-Li to DBBPDSA-H, which can react with copper-aryl complex.

2.3.2. Grafting on high molecular weight PBPDSA polymer and conductivity measurements

In order to make water insoluble membranes, we attempted to graft high molecular weight PBPDSA with 3,5-bis-trifluoromethyl biphenyl. The NMR spectrum showed no reaction between these materials. But PBPDSA was grafted with neopentylbenzene to yield copolymers with low degree of grafting (several percent). While the copolymers containing neopentylbenzene (NPB) groups did not give molecular solutions in water (formally, the copolymers were insoluble in water) they formed colloidal suspensions indicative of some hydrophobic nature due to the grafts.

![Figure 2.22.](image)

Figure 2.22. $^1$H NMR (D$_2$O/DMSO-d$_6$) spectrum of PBPDSA-g-NPB copolymer

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The PBPDSA-g-NPB copolymer (1:1 molar ratio of NPB to PBPDSA-H during grafting) gave very interesting results. The $^1$H NMR spectrum of the polymer, Figure 2.22, had a grafting degree of 3.8%, based on integrations of aromatic hydrogens versus aliphatic hydrogens. This polymer was water insoluble but soluble in an isopropanol-water mixture and gave a good, flexible film upon solvent casting at room temperature (Figure 2.23). The dry film appeared to be quite ductile. It is transparent, showing that crystal growth is inhibited.

The film was sent to Florida Solar Energy Center (FSEC) and conductivity was measured by Bekktech. The result is graphically presented and compared to Nafion212© in Figure 2.24 and 2.25. The Nafion© data shown in the figure was taken from www.bekktech.com. A value of 0.114 S/cm was obtained at 50%RH and 80°C which is more than thrice that of Nafion212© measured under the same conditions and higher than the initial DOE target, 100 mS/cm at 50%RH and 80°C.

![Figure 2.23. Photograph of a cast PBPDSA-g-NPB copolymer proton conducting membrane](image)
Figure 2.24. Proton conductivity of PBPDSA-g-NPB membrane at 30°C, 80°C and 120°C, measured by Bekktech

Figure 2.25. Proton conductivity of PBPDSA-g-NPB membrane compared with Nafion212® at 80°C
2.4. Conclusions

Several reaction conditions for the Ullmann reaction were screened in order to obtain high molecular weight homopolymer, poly(biphenylene-3,3’-disulfonic acid) (PBPDSA). The best conditions found were when 3 wt% 4,4’-dibromobiphenyl-3,3’-disulfonic acid dilithium salt (DBBPDSA-Li) and activated copper were dried separately at high vacuum and polymerized in NMP at 140°C for 22 h.

The polymerization of DBBPDSA-Li in NMP can offer higher molecular weight PBPDSA than that in DMF. During reaction, the generated polymer precipitated from the reaction solvent and chain growth was stopped. Thus, higher solubility for the monomer and polymer can increase the chance of generating high molecular weight polymer.

The difference in reactivity between DBBPDSA-BTMA and DBBPDSA-Li is partly due to the solubility and stereochemistry. DBBPDSA-Li and its corresponding polymer have better solubility over the whole testing range. BTMA cation is a bulky ion which causes steric hindrance, preventing the formation of the copper-aryl halide.

The polymerization is sensitive to active hydrogens, which can be due to residual water and trace HCl in the activated copper. The key step of the Ullmann reaction is the formation of the copper-aryl halide intermediate, which can react with the water or the HCl proton. By drying DBBPDSA-Li and copper separately under high vacuum, this problem was avoided and highest molecular weight PBPDSA was obtained.

The optimized reaction conditions were applied in the copolymer synthesis, which will be described in the following chapters.
2.5. References


3. Elsenbaumer, R. I.; Shacklette, L.W. *In Handbook of Conducting Polymers* 1986, 1, 213.


20. (a) Granados-Focil, S. Ph.D. Thesis, Case Western Reserve University 2006. (b)
26. Grafting was done by Dr. Ryszard Wycisk, now at the Department of Chemical and Biomolecular Engineering, Vanderbilt University.
Chapter 3

Synthesis and grafting of polyphenylene copolymers

3.1. Introduction

In Chapter 2, the synthesis and grafting of high molecular weight poly(biphenylene-3,3’-disulfonic acid) (PBPDSA) and its grafted copolymer were described. The resulting grafted copolymer PBPDSA-g-NPB exhibited a high conductivity, 114 mS/cm at 80°C and 50%RH. However, the conductivity of grafted PBPDSA depends on the specific direction. Dr. Granados-Focil found the through conductivity of PBPDSA-g-di-tert-butylphenol8.4% was only one quarter that of the parallel conductivity. In order to further improve the conductivity, extra sulfonic acid groups were put on the phenyl ring. This type of polyelectrolyte, poly(p-phenylene-2,5-disulfonic acid) (PPDSA), was synthesized from 1,4-dibromobenzene-2,5-disulfonic acid (DBPDSA) by Dr. Kang. It has a high ion exchange capacity (IEC), 8.46 meq/g, and the position of the sulfonic acids on its backbone is well controlled. The optimized reaction conditions for the synthesis of high molecular weight PBPDSA were used in the synthesis of high molecular weight PPDSA, performed by Dr. Kun Si (Figure 3.1). Since PPDSA has such a high IEC, in this chapter the copolymerization between DBPDSA and a designed comonomer is explored.
However, both homopolymers (PBPDSA and PPDSA) are water soluble, which prevents the application of those two materials in MEA fabrication. Two methods can be used to overcome this structural shortcoming. One is to graft bulky or crosslinkable hydrophobic groups on the sulfonic acid groups in the backbone. This reaction uses a Friedel-Crafts catalyst, initially proposed by Graybill. The polymer grafted with biphenyl has been synthesized by Dr. Kun Si using polyphosphoric acid. However, the degree of the grafting is obtained at the cost of proton conductivity. The grafting reaction consumes the sulfonic acid and decreases the polymer conductivity.

Another way to synthesize water insoluble copolymer is to copolymerize sulfonated phenyl monomers with comonomers that contain the desired bulky or crosslinkable motif. This approach opens the possibility of making not only random, but also block copolymers. However, hetero-coupling of two aromatic halides with different chemical structures in the Ullmann reaction has special requirements for the substrate structure, in order to avoid producing a large fraction of homo-coupled product. In order to obtain the hetero-coupled copolymer by the Ullmann reaction, reactivities of the monomer and comonomer must be as close as possible. The ideal comonomer structure has an end group similar to that of DBPDSA, 4-bromophenyl-3-sulfonic acid. Previous work in Dr. Litt’s group showed that comonomers with modified sulfonic acid groups...
like sulfonic esters or sulfones have low copolymerization reactivity with monomer DBPDSA, see Figure 3.2. This is due to the steric hindrance caused by the modified sulfonic acid group.

![Figure 3.2. Comonomers with modified sulfonic acid groups used for the Ullmann coupling copolymerizations](image)

In order to develop an efficient copolymerization reaction using the Ullmann coupling, Dr. Granados-Focil\textsuperscript{1a} designed several comonomers that have a bulky or crosslinkable structure in the middle and two reactive ends identical to those of DBBPDSA, Figure 3.3.
Figure 3.3. New comonomers for the Ullmann coupling copolymerization designed by Dr. Granados-Focil

However, the same problem still existed; the steric hindrance caused by the bulky hydrophobic or crosslinkable groups reduced the comonomer reactivity, even when those groups were far from the end group. The best copolymer obtained by Dr. Granados-Focil was from copolymerization of 4,4’-dibromobiphenyl-3,3’-disulfonic acid, DBBPDSA,
and 2,7-bis(4-bromo-biphenyl-3,3’-disulfonic acid)-9,9’-spirobifluorene, 2,7-(DBBS)-SP
with $\eta_{sp}/C = 0.38$ dL/g, $C = 0.2$ g/dL.

Thus, a group without steric hindrance but easily further modified by the addition
of bulky hydrophobic or crosslinkable groups is desired in this type of copolymerization
reaction. The fluorenyl group, which has an active methylene group and is easily
alkylated by long alkyl chains or reacted with crosslinkable groups, was considered as a
central core in a designed comonomer, Figure 3.4. However, the synthesis of this
molecule was not finished in the lab. As a molecule with two of the same functional
groups, this commoner was supposed to be synthesized from one 2,7-dibromofluorene
and two DBPDSA by a coupling reaction. However, in this type of bifunctional coupling
reaction, it is hard to control the reaction product. The obtained product is a mixture of
once reacted compound (DBPDSA: fluorene = 1:1), twice reacted compound (DBPDSA:
fluorene = 2:1) and further reacted oligomers, even when a large amount of DBPDSA
was used. The generated twice reacted compound was difficult to isolate from the
mixture. An alternative synthetic route is to use a compound with two different functional
groups instead of DBPDSA. One functional group can react with the fluorene compound;
the other one helps to introduce an ortho sulfonic group and can be converted to bromo
group. But as a special functional group, the sulfonic acid group is not tolerated in
bromination reactions and the corresponding product is difficult to obtain.
A much more convenient and economical method for comonomer synthesis was considered. 2,7-Dibromofluorene might be directly sulfonated to 2,7-dibromofluorene-3,6-disulfonic acid, which has the same end structures as DBPDSA. However, the major product of the two sulfonation reactions, shown in Figure 3.5, was the 2,7-diboromofluorene-3,5-disulfonic acid (DBFDSA). This was used as the comonomer in the copolymerization studies. The details of those two sulfonation reactions and the copolymer syntheses and grafting will be discussed in this chapter.

The copolymer PxF1 was synthesized by reacting DBPDSA-Li and DBFDSA-Li using Ullmann coupling. Coordination reagents for copper and lithium ion were studied. The results will be discussed in several sections of this chapter. A high molecular weight PxF1 was obtained using 2,2'-bipyridyl as a coordination reagent. A scale-up copolymerization reaction was carried out using mechanical stirring and argon/nitrogen stream drying.
Model alkylation reactions of 2,7-dibromofluorene were studied. Both bulky base potassium tert-butoxide and lithium hydroxide saturated solutions give 100% yield of dialkylated product. The copolymer grafting reaction was also studied and the results will be discussed in other sections of this chapter. We eventually confirmed that water in the system dramatically affects the reaction. The grafted copolymer was cross-linked at high temperature under vacuum. A detailed study of the properties of these polyphenylene sulfonic acid copolymers will be reported in Chapter 4.

3.2. Experimental section

3.2.1. Materials

Except for 15% oleum (the concentration of SO₃ gas = 13~17%, purchased from Alfa Aesar) and 2,7-dibromofluorene from TCI, all other reagents were purchased from Aldrich Chemical Co. 1-Methyl-2-pyrrolidinone (NMP) and dimethylsulfoxide (DMSO) were stirred with calcium hydride overnight under N₂ at 80°C, vacuum distilled and degassed with N₂ prior to use. The remaining solvents and reagents were used without further purification. Copper bronze powder (organic synthesis grade) was activated according to a previously reported procedure⁵ and used immediately after preparation.

3.2.2. Characterization techniques

¹H- and ¹³C- NMR spectra of the polymers and monomers in D₂O (dioxane as a standard), CD₃OD or DMSO-d₆ were obtained using a Varian Oxford 400 MHz or Inova 600 MHz spectrometer. Polymer viscosities in H₂O were measuring using a Cannon Ubbelohde viscometer in a constant temperature bath at 35°C. FTIR spectra were recorded on a Midal Corporation M series FTIR spectrometer. ESI mass spectra were obtained from Finnigan Lcq Deca XP Max.
3.2.3. Monomer and comonomer synthesis

3.2.3.1. Synthesis of 1,4-dibromobenzene-2,5-disulfonic acid dilithium salt (DBPDSA-Li)

A 500 mL flask was charged with 1,4-dibromobenzene (64 g, 266 mmol) and 200 mL fuming sulfuric acid (15% SO₃) and heated at 220~230°C for 24 h under argon. When the flask was cooled to room temperature, a solid precipitated from the fuming sulfuric acid solution. This precipitate was filtered and neutralized with NaOH. The obtained solid was recrystallized from water several times until its NMR spectrum showed that the pure 2,5-benzenedisulfonic acid disodium salt (DBPDSA-Na) was obtained. Subsequently, DBPDSA-Na was converted to DBPDSA using a proton exchange column. DBPDSA-Li was obtained by titrating the DBPDSA with LiOH and recrystallizing from methanol and isopropanol. 25 g DBPDSA-Li was obtained (yield of pure material = 23%). ¹H NMR (400 MHz, D₂O) δ 8.28 (s).

3.2.3.2. Synthesis of 2,7-dibromofluorene-3,5-disulfonic acid dilithium salt (DBFDSA-Li)

3.2.3.2.1. Sulfonation of 2,7-dibromofluorene with fuming sulfuric acid

A 50 mL 3-necked flask equipped with a mechanical stirrer and condenser was charged with 2,7-dibromofluorene (2 g, 6.2 mmol) and fuming sulfuric acid (15% SO₃, 6 mL, 21 mmol). The flask was placed in a preheated 110°C oil bath. The solution turned green immediately and white in 15 min. This reaction was run for 2 h. After cooling, the precipitate was filtered and washed with a small amount of THF. (The precipitate was soluble in THF) The precipitate was put into 100 mL water and the insoluble solid was filtered (starting material, 200 mg). The filtrate was concentrated to 20 mL and 1 mL
con. HCl was added; a white precipitate (mixture of once and twice sulfonated compounds) was obtained. Another 2 mL of conc. HCl was added to the filtrate, a second precipitate was obtained (mixture of once and twice sulfonated compounds, 50 mg). A third precipitate was obtained when 10 mL conc. HCl was added to the filtrate (twice sulfonated compound). The remaining solution was stripped and the resulting oil was treated using the procedure described above. 1.35 g of twice sulfonated compound, DBFDSA (55%), 530 mg of a mixture of twice and once sulfonated (dibromofluorene-4-sulfonic acid) compounds, and 200 mg of starting material were obtained (10%). $^1$H NMR of DBFDSA (400 MHz, CD$_3$OD) $\delta$ 9.68 (s, 1H), $\delta$ 8.12 (d, 1H, $J = 2.0$ Hz), 7.88 (s, 1H), 7.83 (d, 1H, $J = 1.6$ Hz), 3.98 (s, 2H)

3.2.3.2.2. Sulfonation of 2,7-dibromofluorene with chlorosulfonic acid

3.2.3.2.2.1. Synthesis of 2,7-dibromofluorene-3,5-disulfonyl chloride (DBFDSCl)

A 3-necked flask was charged with 2,7-dibromofluorene and the desired amount of chlorosulfonic acid (see Table 3.1) was syringed in. The fluorene dissolved and the solution turned green. Initially, reactions were run at specified temperatures for specified times. Later runs were stopped when the green color disappeared; a white precipitate was found in the flask. Two work-up procedures were used. For runs 1&7, the reaction mixture was poured onto ice; the precipitate was filtered and dissolved in chloroform to remove the water. Evaporation of the chloroform solution gave pure mixed 3,5- and 3,6-disulfonyl chlorides. For the other runs, the precipitate from fuming sulfuric acid, assumed to be pure dibromofluorene-3,5-disulfonyl chloride, was filtered, washed with
water, dried and weighed. The filtrate was poured on ice and the precipitate was collected, washed with water, dried and weighed. The results are listed in Table 3.1.

**Table 3.1.** Effect of chlorosulfonation mole ratio and reaction temperature on the mole ratios of 3,5- and 3,6-disulfonyl chloride dibromofluorene

<table>
<thead>
<tr>
<th>Run</th>
<th>Fluorene: g, mmol</th>
<th>CISO₂H: mL, mmol</th>
<th>Temperature/Time</th>
<th>Product Ratio: 3,5- to 3,6-disulfonyl chloride&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conversion to di-sulfonyl chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.296, 4.0</td>
<td>5.0, 75</td>
<td>25°C/1 h</td>
<td>1/0.11</td>
<td>1.93 gm, 93%</td>
</tr>
<tr>
<td>2</td>
<td>1.296, 4.0</td>
<td>7.0, 105</td>
<td>25°C/43 h</td>
<td>1/0.15</td>
<td>2.02 gm, 97%</td>
</tr>
<tr>
<td>3</td>
<td>1.296, 4.0</td>
<td>7.0, 105</td>
<td>70°C/5 h</td>
<td>1/0.18</td>
<td>1.89 gm, 91%</td>
</tr>
<tr>
<td>4</td>
<td>1.296, 4.0</td>
<td>8.0, 120</td>
<td>70°C/15 min.</td>
<td>1/0.11</td>
<td>1.83 gm, 88%</td>
</tr>
<tr>
<td>5</td>
<td>1.296, 4.0</td>
<td>8.0, 120</td>
<td>25°C/2.5 h</td>
<td>1/0.15</td>
<td>1.80 gm, 86%</td>
</tr>
<tr>
<td>6</td>
<td>0.648, 2.0</td>
<td>5.0, 75, in 5 mL CHCl₃</td>
<td>25°C/3.5 h; 50°C/6.5 h</td>
<td>1/0.03</td>
<td>1.40 gm, &gt;100%</td>
</tr>
<tr>
<td>7</td>
<td>1.296, 4.0</td>
<td>8, 120</td>
<td>0°C/ 5 h</td>
<td>1/0.12</td>
<td>1.97 gm, 95%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Based on total yield.

![Figure 3.6. 400 MHz <sup>1</sup>H NMR (CDCl₃) spectrum of soluble fraction of disulfonyl chloride, Table 3.1, Run 2](image-url)
Figure 3.6 shows the $^1$H NMR spectrum of mixed disulfonyl chlorides from the soluble fraction of Run 2. There are four peaks (1 H each) from the unsymmetric material (3,5-disulfonly chloride), at 8.10, 8.12, 8.34 and 9.49 ppm. There are two peaks (2 H each) from the symmetric desired material, at 8.10 and 8.65 ppm. This solution was filtered at room temperature. The soluble fraction was 23% of the total; the symmetric fraction was 53%, based on Figure 3.6 (yield = 12%).

### 3.2.3.2.2. Synthesis of 2,7-dibromofluorene-3,5-disulfonic acid dilithium salt (DBFDSA-Li)

A 50 mL flask charged with 2,7-dibromofluorene-disulfonyl chloride (0.121 g, 0.23 mmol; mixture of dibromofluorene-3,5- and 3,6-disulfonyl) and ethanol (10 mL) was refluxed overnight. The clear solution was stripped and 110 mg of white solid (the disulfonic acid) was obtained (100%). It was titrated with LiOH and the resulting dilithium salt was recrystallized from isopropanol and methanol. 60 mg pure 2,7-dibromofluorene-3,5-disulfonic acid dilithium salt (DBFDSA-Li) was obtained (Yield = 50%). $^1$H NMR of DBFDSA-Li (400 MHz, CD$_3$OD) $\delta$ 9.65 (s, 1H), 8.13 (d, 1H, J = 2.0 Hz), 7.86 (s, 1H), 7.82 (d, 1H, J = 2.0 Hz), 3.97 (s, 2H). $^{13}$C NMR (150 MHz, CD$_3$OD) $\delta$ 149.01, 148.57, 144.08, 142.07, 139.59, 137.59, 131.31, 130.97, 130.40, 129.59, 121.12, 120.48, 37.44. ESI-MS m/z 489.07 (M – Li$^+$), 483.07 (M + H$^+$ - 2Li$^+$).

### 3.2.3.2.3. Rearrangement of DBFDSCI

In order to obtain a high yield of 2,7-dibromofluorene-3,6-disulfonic acid, the conversion of the obtained 2,7-dibromofluorene-3,5-disulfonyl chloride to 2,7-dibromofluorene-3,6-disulfonic acid by a rearrangement reaction was attempted.
3.2.3.2.3.1. Rearrangement of DBFDS\textsubscript{Cl} using 85\% H\textsubscript{2}SO\textsubscript{4}

A 50 mL flask was charged with 2,7-dibromo fluorene 4,6-disulfonyl chloride (0.261 g, 0.5 mmol) and 85\% H\textsubscript{2}SO\textsubscript{4} (10 mL). The solution was heated to 165\°C for half an hour and a black precipitate appeared. Conc. HCl was added to the cooled sulfuric acid solution, and 90 mg of a white precipitate was obtained. \textsuperscript{1}H NMR shows no rearrangement happened; starting material was recovered.

3.2.3.2.3.2. Rearrangement of DBFDS\textsubscript{Cl} using conc. H\textsubscript{2}SO\textsubscript{4}

A 25 mL flask was charged with 2,7-dibromofluorene-3,5-disulfonyl chloride (0.261 g, 0.5 mmol) and conc. H\textsubscript{2}SO\textsubscript{4} (8.5 mL). The flask was heated to 210\°C for 12 h. The color of the solution turned brown, then dark brown, finally black. After the solution was cooled, the precipitate was filtered. The filtrate was poured onto 70 g ice and the solution turned black. After the solution stood overnight, black solid precipitated and settled to the bottom. The solid was filtered and dried in a vacuum oven (0.78 g). The obtained solid was dissolved in water and titrated with barium hydroxide to pH = 1 tested by a pH paper. The generated BaSO\textsubscript{4} was filtered and the filtrate was stripped to afford of an oil (0.213 g). \textsuperscript{1}H NMR shows no rearrangement happened; a mixture of starting material and decomposed compounds was seen.

3.2.3.3. Synthesis of 9,9’-dibenzyl-2,7-dibromofluorene-3,5-disulfonic acid dilithium salt (DBnDBFDSA-Li)

A 50 mL 3-necked flask was charged with 20 mL DMSO, DBFDSA-K (mixture of symmetric and asymmetric compounds, 1.0 g, 2.1 mmol), benzyl chloride (0.76 mL, 6.5 mmol) and 18-crown-6 (13.2 mg, 0.05 mmol) under argon atmosphere and degassed for 0.5 h. The flask was transferred to a glove box and Potassium \textit{tert}-butoxide (0.729 g,
6.5 mmol) was added. The solution was stirred at 45°C overnight, cooled, and dropped into 400 mL acetone. The precipitate was collected and purified by recrystallization from water. 850 mg of slightly yellow doubly substituted fluorene, DBnDBFDSA-K, was obtained (yield = 54%). The lithium salt of DBnDBFDSA was obtained by converting DBnDBFDSA-K to the acid form using a proton exchange column, followed by titration with LiOH. Pure DBnDBFDSA-Li was obtained by recrystallization from methanol and isopropanol. \(^1\)H NMR of DBnDBFDSA-Li (400 MHz, CD\(_3\)OD) \(\delta\) 9.32 (s, 1H), 8.00 (d, 1H, J = 2.0 Hz), \(\delta = 7.78\) (s, 1H), 7.78 (s, 1H), 6.96 (m, 6H), 6.69 (dd, 4H, J = 2.0, 7.6 Hz), 3.41 (d, 4H, J = 1.6 Hz). ESI-MS \(m/z\) 669.07 (M –Li\(^+\)), 662.93 (M + H\(^+\) - 2Li\(^+\)).

### 3.2.4. Homopolymerization and copolymerization

#### 3.2.4.1. Homopolymerization of DBFDSA-Li

Copper and DBFDSA-Li in flasks were dried separately at 140°C under vacuum for 48 h. Subsequently, the 2,7-dibromofluorene-3,5-disulfonic acid dilithium salt (0.415 g, 0.8 mmol) and copper (0.7 g, 11 mmol) were put into a pressure tube and dried at 140°C under vacuum for another 48 h. NMP was stirred with CaH\(_2\) at 90°C overnight under N\(_2\) and distilled under vacuum. Freshly distilled NMP (15 mL) was syringed into the pressure tube and the reaction system was degassed using two freeze/thaw cycles to remove oxygen. The pressure tube was filled with N\(_2\) and submerged in a preheated oil bath at 140°C. This homopolymerization reaction was run for 13 h. NMP insoluble material was filtered and extracted with acidified water; an oil was obtained from this part. Solid was precipitated from the NMP solution by dropping it into a large amount of acetone. A brown yellow solid was obtained (200 mg, 66%). \(^1\)H NMR (400 MHz,
CD$_3$OD) $\delta$ 9.63 (s, 1H), 8.10 (d, 1H, $J = 2.0$ Hz), 7.73 (d, 1H, $J = 2.0$ Hz), 7.48 (s, 1H), 3.88 (d, 1H, $J = 23.2$ Hz), 3.64 (d, 1H, $J = 22.8$ Hz).

3.2.4.2. Synthesis of copolymer: poly(phenylene disulfonic acid_co-fluorene disulfonic acid) (PxF1)

3.2.4.2.1. Syntheses of copolymer in NMP and DMSO (no coordination reagent)

The copolymerization reaction parameters were studied by changing the temperature, solvent, time and the monomer/comonomer ratios. The results are given in Tables 3.2 & 3.3.

**General copolymerization procedure:** Monomer DBPDSA-Li (816 mg, 2.0 mmol) and comonomer DBFDSA-Li (99.2 mg, 0.20 mmol) were dried in a pressure tube at 140°C and 35 mtorr for 24 h. Activated copper powder was dried separately at 140°C and 35 mtorr for 24 h. The dried copper powder was put into the pressure tube and the mixture was dried at 140°C and 35 mtorr for 48 h. 1-Methyl-2-pyrrolidinone (NMP) was stirred with CaH$_2$ at 90°C overnight under N$_2$ and distilled under vacuum at 25°C. Freshly distilled NMP was syringed into the pressure tube and the solution was degassed using 3 freeze/thaw cycles. The tube was filled with N$_2$, sealed and submerged in a preheated oil bath for a specified temperature and time. NMP insoluble material was filtered and extracted with dilute HCl. The HCl solution was stripped and the redissolved solid was passed through a proton exchange column. tert-Butanol was added to the acidified solution which was stripped again. (tert-Butanol reacts with HCl and HBr to give tert-butyl halides that evaporate during stripping. This removes any excess acid.) The obtained yellow solid was further purified by ultrafiltration. A second crop was obtained by dropping the filtered NMP solution into a large amount of acetone. The precipitate
was purified using the procedures described above. The copolymers were characterized by NMR and viscosity. The NMR spectra of the polymers will be shown in the Results and Discussion section. Polymer films were made by casting from aqueous solution in a Teflon dish and evaporating the water.

**Table 3.2. Summary of copolymerization reaction conditions**

<table>
<thead>
<tr>
<th>Run</th>
<th>Comonomer/Monomer&lt;sup&gt;a&lt;/sup&gt; Wt., mg; Mole Ratio</th>
<th>Time h</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.2/816; 1.0/10</td>
<td>38</td>
<td>NMP insoluble, 332 mg, ( \eta_{sp}/C = 0.38 \text{ dL/g} ); NMP soluble, 51 mg. Yield&lt;sup&gt;c&lt;/sup&gt; = 62%.</td>
</tr>
<tr>
<td>2</td>
<td>198.4/816; 2.0/10</td>
<td>37</td>
<td>NMP insoluble, 280 mg, ( \eta_{sp}/C = 0.26 \text{ dL/g} ); NMP soluble, 340 mg. Yield&lt;sup&gt;c&lt;/sup&gt; = 85%.</td>
</tr>
<tr>
<td>3</td>
<td>Comonomer 415 mg; 1.0/0</td>
<td>37</td>
<td>All NMP soluble (dimer), Yield&lt;sup&gt;c&lt;/sup&gt; = 200 mg, 66%.</td>
</tr>
<tr>
<td>4</td>
<td>49.6/816; 1.0/20</td>
<td>84</td>
<td>NMP insoluble, 71.8 mg, ( \eta_{sp}/C = 0.47 \text{ dL/g} ); NMP soluble, 500 mg. Yield&lt;sup&gt;c&lt;/sup&gt; ~100%.</td>
</tr>
<tr>
<td>5</td>
<td>99.2/816; 1.0/10</td>
<td>84</td>
<td>NMP insoluble, 300 mg, ( \eta_{sp}/C = 0.37 \text{ dL/g} ); NMP soluble, 150 mg, ( \eta_{sp}/C = 0.11 \text{ dL/g} ). Yield&lt;sup&gt;c&lt;/sup&gt; = 73%.</td>
</tr>
<tr>
<td>6</td>
<td>99.2/816; 1.0/10</td>
<td>37</td>
<td>NMP insoluble, 280 mg, ( \eta_{sp}/C = 0.42 \text{ dL/g} ); NMP soluble, 100 mg. Yield&lt;sup&gt;c&lt;/sup&gt; = 62%.</td>
</tr>
<tr>
<td>7</td>
<td>99.2/816; 1.0/10</td>
<td>46.5</td>
<td>215 mg NMP insoluble material, ( \eta_{sp}/C = 0.24 \text{ dL/g} ), yield&lt;sup&gt;d&lt;/sup&gt; = 38%.</td>
</tr>
<tr>
<td>8</td>
<td>198.4/816; 2.0/10</td>
<td>18</td>
<td>130 mg NMP insoluble material, ( \eta_{sp}/C = 0.21 \text{ dL/g} ), yield&lt;sup&gt;d&lt;/sup&gt; = 20%.</td>
</tr>
<tr>
<td>9</td>
<td>99.2/816; 1.0/10</td>
<td>18</td>
<td>250 mg NMP insoluble material, ( \eta_{sp}/C = 0.36 \text{ dL/g} ), yield&lt;sup&gt;d&lt;/sup&gt; = 43%.</td>
</tr>
<tr>
<td>10</td>
<td>99.2/816; 1.0/10</td>
<td>16.5</td>
<td>44 mg NMP insoluble material.; ( \eta_{sp}/C = 0.41 \text{ dL/g} )</td>
</tr>
</tbody>
</table>

<sup>a.</sup> Comonomer, DBFDSA-Li; monomer, DBPDSA-Li.
<sup>b.</sup> All reactions run using 30mL NMP and 1.4 g Cu, except for Run 3 (15 mL, 0.7 gm Cu). Reaction temperature was 140°C except for Run 6 (170°C) and Run 10 (170°C, Monomer, comonomer and copper were dried at 200°C).
<sup>c.</sup> Yields calculated assuming dried copolymer has one water per -SO₃H.
<sup>d.</sup> Most of the product was lost during ultrafiltration because of a solution spill.
<sup>e.</sup> Reduced viscosity was measured at 0.5 g/dL.
Table 3.3. Copolymerizations in DMSO, conditions\textsuperscript{b} and results.

<table>
<thead>
<tr>
<th>Run</th>
<th>Comonomer/Monomera Wt., mg; Mole Ratio</th>
<th>Cu, g</th>
<th>Results\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>99.2/816; 1.0/10</td>
<td>1.4</td>
<td>500 mg (81% yield), $\eta_{sp}/C = 0.12$ dL/g</td>
</tr>
<tr>
<td>8</td>
<td>198.4/816; 2.0/10</td>
<td>1.4</td>
<td>548 mg (80% yield), $\eta_{sp}/C = 0.12$ dL/g</td>
</tr>
</tbody>
</table>

\textsuperscript{a.} Comonomer: DBFDSA-Li; Monomer: DBPDSA-Li.  
\textsuperscript{b.} Both reactions run using 30 mL DMSO at 140°C for 38 h. Yield assumes 1 H\textsubscript{2}O/acid.  
\textsuperscript{c.} All polymer DMSO soluble. Reduced viscosity was measured at 0.5 g/dL.

3.2.4.2.2. Synthesis of copolymer using coordination reagent 2,2’-bipyridyl (BPy)

In order to increase the solubility of the resulting copolymer PxF1 cuprous salt, the coordination reagent, 2,2’-bipyridyl, which is supposed to coordinate with the cuprous ion, was added. The copolymerization reaction results as a function of temperature and time were studied. The results are given in Table 3.4.

**General copolymerization procedure:** Monomer DBPDSA-Li (816 mg, 2.0 mmol) and comonomer DBFDSA-Li (99.2 mg, 0.20 mmol) were dried in a pressure tube at 140°C or 200°C at 35 mtorr for 24 h. Activated copper powder was dried separately at 140°C or 200°C at 35 mtorr for 24 h. The dried copper powder was put into the pressure tube and the mixture was dried at 140°C or 200°C at 35 mtorr for 48 h. 1-Methyl-2-pyrrolidinone (NMP) was stirred with CaH\textsubscript{2} at 90°C overnight under N\textsubscript{2} and distilled under vacuum at 25°C. 2,2’-Bipyridyl (BPy) (343 mg, 2.2 mg) was placed in a 50 mL 3-necked flask and dried under vacuum for 48 h at room temperature. Freshly distilled NMP (10 mL) was added to that flask and the solution was degassed for 0.5 h by bubbling with argon. Freshly distilled NMP (20 mL) and the BPy/NMP solution (10 mL) were syringed into the pressure tube and the solution was degassed using three freeze/thaw cycles. The tube was filled with N\textsubscript{2}, sealed and submerged in a preheated oil
bath for a specified temperature and time. NMP insoluble material was filtered and the precipitate was extracted with dilute HCl to dissolve the copolymer. The solution was stripped and purified by ultrafiltration using 0.01 N HCl and water. The solution was evaporated to dryness; the solid was redissolved and further purified by proton exchange to remove remaining cuprous ions. A second crop was obtained by dropping the filtered NMP solution into a large amount of acetone. The precipitate was purified using the procedures described above. The copolymers were characterized by NMR and viscosity, shown in the Results and Discussion section.

Table 3.4. Copolymerizations using 2,2’-bipyridyl (BPy) as Cu complexing agent.

<table>
<thead>
<tr>
<th>Run</th>
<th>Comonomer/Monomer&lt;sup&gt;a&lt;/sup&gt; Wt, mg; Mole Ratio</th>
<th>BPY, mg, mmol</th>
<th>Temp., °C</th>
<th>Time, h</th>
<th>Results&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.2/816; 1.0/10</td>
<td>343, 2.2</td>
<td>140</td>
<td>46.5</td>
<td>482 mg NMP insoluble material, yield&lt;sup&gt;c&lt;/sup&gt; = 84%; η&lt;sub&gt;v/C&lt;/sub&gt; = 0.46 dL/g.</td>
</tr>
<tr>
<td>2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>99.2/816; 1.0/10</td>
<td>343, 2.2</td>
<td>140</td>
<td>46.5</td>
<td>313 mg NMP insoluble material, yield&lt;sup&gt;c&lt;/sup&gt; = 55%; η&lt;sub&gt;v/C&lt;/sub&gt; = 0.24 dL/g.</td>
</tr>
<tr>
<td>3</td>
<td>99.2/816; 1.0/10</td>
<td>343, 2.2</td>
<td>140</td>
<td>18</td>
<td>446 mg NMP insoluble material, yield&lt;sup&gt;c&lt;/sup&gt; = 78%; η&lt;sub&gt;v/C&lt;/sub&gt; = 0.29 dL/g.</td>
</tr>
<tr>
<td>4</td>
<td>99.2/816; 1.0/10</td>
<td>343, 2.2</td>
<td>170 (200)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>16.5</td>
<td>459 mg NMP insoluble material, yield&lt;sup&gt;c&lt;/sup&gt; = 80%; η&lt;sub&gt;v/C&lt;/sub&gt; = 0.17 dL/g.</td>
</tr>
<tr>
<td>5</td>
<td>See e</td>
<td>343, 2.2</td>
<td>170 (200)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>16.5</td>
<td>484 mg NMP insoluble material, yield&lt;sup&gt;c&lt;/sup&gt; = 77%; η&lt;sub&gt;v/C&lt;/sub&gt; = 0.60 dL/g.</td>
</tr>
</tbody>
</table>

<sup>a</sup> Comonomer: DBFDSA-Li; monomer: DBPDSA-Li. NMP volume = 30 mL, Cu weight = 1.4 g.
<sup>b</sup> Bipyridyl was added after the reaction had run for 2 h.
<sup>c</sup> Yield calculated assuming dried copolymer has one H₂O/SO₃H
<sup>d</sup> Monomer, comonomer and copper were dried at 200°C.
<sup>e</sup> This was a three component copolymerization: DBPDSA-Li (0.490 mg, 1.2 mmol), DBBPDSA-Li (0.387 mg, 0.8 mmol) and DBFDSA-Li (99.2 mg, 0.2 mmol). (Copolymer ratios P6B4F1)
<sup>f</sup> Reduced viscosity measured at C = 0.5 g/dL.
3.2.4.2.3. Synthesis of copolymer with coordination reagent, triethylene glycol dimethyl ether (TEGDME), added:

DBPDSA-Li (816 mg, 2.0 mmol) and DBFDSA-Li (135.3 mg, 0.2 mmol) were dried in a 100 mL 3-necked flask at 200°C and 40 mtorr for 24 h. Activated copper powder (1.4 g, 21.9 mmol) was dried separately in a flask at 200°C and 40 mtorr for 24 h. The dried copper powder was added to the 3-necked flask and the solids were dried at 200°C and 35 mtorr for 24 h. Subsequently, the flask was equipped with a mechanical stirrer and purged with ultrapure argon. The flask was dried at 200°C for 3 h with argon flow (0.1 L/min). Separately, 1-methyl-2-pyrrolidinone (NMP) and TEGDME (11 mL in 270 mL NMP, 0.22 mmol/mL) were stirred with CaH₂ at 90°C overnight under argon and distilled under vacuum at 35°C. The freshly distilled NMP/TEGDME solution (30 mL, 0.105 mmol/mL, measured using ¹H NMR) was syringed into the 100 mL flask. The reaction was run at 170°C for 34.5 h and the solution became dark brown; it was not possible to tell if polymer had precipitated during the reaction. After cooling, a precipitate was found. The NMP insoluble material was filtered and the solids were extracted with 1% HCl. The solution was stripped; the solid was dissolved in deionized water and passed through a proton exchange column. The copolymer was further purified as follows. It was dissolved in methanol and neutralized using a sodium hydroxide/methanol solution. The copolymer sodium form precipitated from methanol. It was filtered and reconverted to the acid form by passage through a proton exchange column. This procedure was repeated. The copolymer acid form was further purified by ultrafiltration to afford a dark brown solid (250 mg, yield = 42%). More copolymer was obtained by pouring the NMP solution into acetone; polymer and cuprous bromide
precipitated. It was filtered; the precipitate was dissolved in deionized water and passed through a proton exchange column to afford 125 mg of material after drying (Yield = 21%). This material was characterized by NMR and viscosity measurements, which will be shown in the Results and Discussion section.

3.2.4.2.4. Synthesis of copolymer using argon/nitrogen drying

Two 5 g scale copolymerization reactions (DBPDSA-Li/DBFDSA-Li = 10:1, 20:1) were carried out. The polymerization procedure is described below.

Monomer, DBPDSA-Li (4.08 g, 20 mmol), and comonomer, DBFDSA-Li (496 mg, 2.0 mmol), were dried in a 500 mL 3-necked flask at 200°C and 35 mtorr for 24 h. Activated copper powder (7.0 g, 0.11 mol) was dried separately in a flask at 200°C at 35 mtorr for 24 h. The dried copper powder was placed in the 3-necked flask and the solids were dried at 200°C at 35 mtorr for 48 h. Subsequently, the flask was purged with ultra pure argon and equipped with a mechanical stirrer. The flask was argon dried (0.1 L/min) at 200°C for 4 h. 1-Methyl-2-pyrrolidinone (NMP) was stirred with CaH₂ at 90°C overnight under N₂ and distilled under vacuum at 25°C. BPy (1.72 g, 11 mmol) was placed in a 50 mL 3-necked flask and dried under vacuum for 48 h at room temperature, after which freshly distilled NMP (20 mL) was added to that flask and the solution was degassed for 0.5 h by bubbling with argon. Freshly distilled NMP (130 mL), after degassing for 0.5 h was transferred to the 3-necked flask by double needle and the BPy NMP solution (20 mL) was added to the 3-necked flask by syringe. The reaction was run at 200°C for 19 h. NMP insoluble material was filtered and washed with dilute HCl to dissolve any copolymer. The solution was stripped and purified by ultrafiltration with 0.01 N HCl and water. The obtained solution was stripped again and the obtained solid
further purified by proton exchange to remove remaining cuprous ions. A dark brown solid was obtained (2.52 g, 88.3%). A second crop was obtained by dropping the filtered NMP solution into a large amount of acetone. The precipitate was purified using the procedures described above to afford a dark brown solid (0.29 g, 10.2%). The copolymers were characterized by NMR and viscosity, shown in the Results and Discussion section.

3.2.4.3. Direct synthesis of grafted copolymer using alkylated comonomer

Monomer DBPDSA-Li (816 g, 2.0 mmol) and comonomer DBnDBFDSA-Li (135.3 mg, 0.2 mmol) were dried in a 100 mL pressure tube at 170°C and 42 mtorr for 24 h. Activated copper powder (1.4 g, 22 mmol) was dried separately in a 100 mL flask at 120°C and 42 mtorr for 24 h. The dried copper powder was put into the pressure tube and the mixture was dried at 170°C at 42 mtorr for 48 h. 1-Methyl-2-pyrrolidinone (NMP) was stirred with CaH₂ at 90°C overnight under N₂ and distilled under vacuum at 35°C. 2,2’-bipyridyl (BPy) (343.6 mg, 2.2 mmol) was placed into a 100 mL 3-necked flask, dried for 48 h under vacuum at room temperature, and 10 mL freshly distilled NMP was added to the flask. Freshly distilled NMP (20 mL) and the Bpy/NMP (343.6 mg in 10 mL) solution were added to the pressure tube by syringe. The solution was degassed using 3 freeze/thaw cycles. The reaction was run at 170°C for 20 h. The NMP insoluble material was filtered and stirred with dilute HCl. Insoluble Cu was filtered and the clear solution was evaporated. The residue was dissolved in water and passed through a proton exchange column; acidified material was further purified by ultrafiltration to afford 0.42 g of P10F1-Bn200%; yield = 71%.
3.2.4.4. Direct synthesis of grafted copolymer using alkylated comonomer, with argon/nitrogen drying

DBPDSA-Li (816 g, 2.0 mmol) and DBnBFDSA-Li (135.3 mg, 0.2 mmol) were dried in a 100 mL 3-necked flask at 200°C and 35 mtorr for 24 h. Activated copper powder (1.4 g, 21.9 mmol) was dried separately in a flask at 200°C and 35 mtorr for 24 h. The dried copper powder was added to the 3-necked flask and the solids were dried at 200°C and 35 μtorr for 24 h. Subsequently, the flask was purged with ultrapure argon and equipped with a mechanical stirrer. The flask was argon dried (0.1 L/min) at 200°C for 4 h. 1-Methyl-2-pyrrolidinone (NMP) was stirred with CaH₂ at 90°C overnight under N₂ and distilled under vacuum at 35°C. 2,2’-bipyridyl (BPy 687.2 mg, 4.4 mmol) was placed into a 50 mL 3-necked flask and dried for 48 hours at room temperature. Then 5 mL freshly distilled NMP was added into the flask. Freshly distilled NMP (25 mL) and BPy/NMP solution (687.2 mg in 5 mL) were syringed into the 3-necked flask. This reaction was run at 170°C for 18 h. NMP insoluble material was filtered and extracted with HCl acidified water. The solution was stripped and the resulting solid was dissolved and purified by ultrafiltration with 0.01 N HCl and D. I. water to neutrality. The final solution was stripped and the obtained solid further purified by passing through a proton exchange column to remove remaining cuprous ions. A dark brown solid was obtained (0.55 g, Yield = 92%). The copolymers were characterized by NMR and viscosity, shown in the Results and Discussion section.
3.2.5. Copolymer grafting reactions

3.2.5.1. Titration of 2,7-dibromofluorene-3,5-disulfonic acid dilithium salt (DBFDSA-Li)

To a 2,7-dibromofluorene-3,5-disulfonic acid dilithium salt (496 mg, 1.0 mmol) solution in 10 mL water was added LiOH (42 mg, 1.0 mmol) and stirred for 1 h. The solution was titrated by 0.093 N HCl. The pH value was monitored by pH meter. PKa was calculated from the following equation:

\[ pK_a = pH + \log\frac{[HA]}{[A^-]} \]  

(Equation 3.1)

[HA] is the concentration of DBFDSA, g/mL; [A\(^-\)] is the concentration of deprotonated DBFDSA, g/mL.

3.2.5.2. Model monomer alkylation reaction (Description of Run 7a, Table 3.5)

A 50 mL 3-necked flask was charged with 10 mL DMSO, DBFDSA-Li (496 mg, 1.0 mmol), 1-bromododecane (0.74 mL, 3.0 mmol) and 18-crown-6 (6 mg, 0.02 mmol). It was purged with argon and placed in an air bag. Potassium tert-butoxide (344 mg, 3.0 mmol) was added to the flask and the solution was stirred at 42°C for 24 h. KOAc (300 mg, 3.0 mmol) was then added. The precipitate was filtered and washed with isopropanol. The insoluble solid was filtered and dried; 0.341 g solid was obtained. The DMSO solution was stripped using a rotary evaporator and the residue was washed with isopropanol. The solid was filtered and dried; 0.706 g was obtained. The reagents and reaction conditions are given in Table 3.5. \(^1\)H NMR of 9,9’-di-dodecyl-2,7-dibromofluorene-3,5-disulfonic acid (400 MHz, CD\(_3\)OD) δ 9.31 (s, 1H), 7.90 (d, 1H, J =
2.0 Hz), 7.67 (d, 1H, J = 2.0 Hz), 7.57 (s, 1H), 1.97 (t, 4H, J = 8.0 Hz), 1.21 (m, 28H), 1.01 (m, 12H), 0.84 (t, 6H, J = 6.4 Hz).

### Table 3.5. Model monomer alkylation reactions: conditions and yields.

<table>
<thead>
<tr>
<th>Run</th>
<th>C_{12}H_{25}-Br conc. (mL, mmol)</th>
<th>Base &amp; additives</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.32 mL, 1.3 mmol</td>
<td>BTMAOH, 1.3 mmol</td>
<td>DMF 10 mL</td>
<td>25</td>
<td>2</td>
<td>BTMA salt of comonomer</td>
</tr>
<tr>
<td>2a</td>
<td>0.32 mL, 1.3 mmol</td>
<td>LiOH, 1.2 mmol</td>
<td>DMF/H_2O 10/0.5 mL</td>
<td>25</td>
<td>12</td>
<td>Mixture of once, twice and unreacted material</td>
</tr>
<tr>
<td>3a</td>
<td>0.54 mL, 2.2 mmol</td>
<td>LiOH, 2.2 mmol</td>
<td>DMF/H_2O 10/0.5 mL</td>
<td>80</td>
<td>12</td>
<td>Mixture of once, twice and unreacted material</td>
</tr>
<tr>
<td>4a</td>
<td>0.37 mL, 1.5 mmol</td>
<td>KOH, 1.5 mmol</td>
<td>DMF 8 mL</td>
<td>90</td>
<td>8</td>
<td>Mixture of once, twice and unreacted material</td>
</tr>
<tr>
<td>5a</td>
<td>0.74 mL, 3.0 mmol</td>
<td>potassium tert-butoxide, 3.0 mmol</td>
<td>DMF 10 mL</td>
<td>40</td>
<td>12</td>
<td>Mixture of once, twice and unreacted material</td>
</tr>
<tr>
<td>6a</td>
<td>0.74 mL, 3.0 mmol</td>
<td>potassium tert-butoxide, 3.0 mmol</td>
<td>DMSO 10 mL</td>
<td>42</td>
<td>24</td>
<td>Most is twice reacted material</td>
</tr>
<tr>
<td>7a</td>
<td>0.74 mL, 3.0 mmol</td>
<td>potassium tert-butoxide, 3.0 mmol</td>
<td>DMSO 10 mL</td>
<td>42</td>
<td>24</td>
<td>Twice reacted material</td>
</tr>
<tr>
<td>8a</td>
<td>0.13 mL, 1.1 mmol</td>
<td>50 wt% NaOH sol’n, 1.2 mL</td>
<td>DMSO 9 mL</td>
<td>25</td>
<td>12</td>
<td>Twice reacted material</td>
</tr>
</tbody>
</table>

- **a.** 0.496 g, 1.0 mmol DBFDSA-Li used except for Run 4 (0.248 g, 0.50 mmol)
- **b.** All additives shown in footnotes
- **c.** KI (49.8 mg, 0.3 mmol); 18-crown-6 (3 mg, 0.01 mmol)
- **d.** 18-crown-6 (6 mg, 0.02 mmol)
- **e.** Alkylation with benzyl chloride

### 3.2.5.3. Grafting on copolymers PxF1

#### 3.2.5.3.1. Grafting copolymer (PxF1) with 1-bromododocosane

A 50 mL 3-necked flask containing a magnetic stirring bar was charged with dried (90°C, 10 mm, 24 h) copolymer Li salt P10F1-Li (259 mg, 1/10 mole ratio), (Run 5, Table 3.2) and 20 mL DMSO purged with argon. The solution was heated to 90°C and stirred overnight. After the polymer dissolved, 18-crown-6 (6 mg, 0.02 mmol) and 1-
bromodocosane (1.4 g, 3.6 mmol) were added. The flask was transferred to a glove box and potassium tert-butoxide (397.2 mg, 3.5 mmol) was added. The flask was put into an oil bath at 60°C and heated overnight with stirring. After cooling, the solution was poured into 300 mL of acetone. The precipitate was filtered and washed with methanol to afford 130 mg of yellow insoluble material. This material was soluble in 6M HCl but insoluble in 12M HCl, which was used to wash the material. After drying, the polymer swelled when water was added and finally dispersed. This grafted material was characterized by 1H NMR, shown in the Results and Discussion section.

3.2.5.3.2. Grafting copolymer (PxF1) with benzyl chloride using potassium tert-butoxide as a base

The alkylation reaction parameters were studied by varying the temperature and the method for adding the reagents. The results are given in Table 3.6.

**General alkylation procedure:** 4Å molecular sieves were dried at 280°C under 60 mtorr for 8 h. P10F1-Li was dissolved in DMSO at 100°C in a 100 mL 3-necked flask. After all the copolymer had dissolved, the DMSO solution was dried with activated 4Å molecular sieves overnight. The dried reaction solution was transferred to another 50 mL 3-necked flask using a double needle; benzyl chloride and 18-crown-ether were added. The flask was transferred to a glove box and potassium tert-butoxide was added under a nitrogen atmosphere. For most runs, after the reaction had run for 8 h at 45°C another batch of benzyl chloride, 18-crown-ether and potassium tert-butoxide was added and the reaction was run for another 8 h. The DMSO solution was poured into 300 mL acetone and the resulting precipitate was filtered. It was dissolved in water and purified by
ultrafiltration. The obtained material was characterized by $^1$H NMR and viscosity measurements, shown in the Results and Discussion section.

**Table 3.6.** Summary of copolymer alkylation reaction conditions and yields.

<table>
<thead>
<tr>
<th>Run</th>
<th>P10F1-Li, g, mmol F</th>
<th>Molecular sieves, g</th>
<th>Benzyl chloride, mL, mmol</th>
<th>Potassium tert-butoxide, mg, mmol</th>
<th>18-Crown-ether, g, mmol</th>
<th>DMSO mL</th>
<th>Polymer weight and % alkylation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>0.25, 0.088</td>
<td>4</td>
<td>0.14, 1.2</td>
<td>112, 1.0</td>
<td>0.264, 1.0</td>
<td>35</td>
<td>0.20 g, 34% mono-benzylated.</td>
</tr>
<tr>
<td>2$^b$</td>
<td>0.30, 0.107</td>
<td>6</td>
<td>0.28, 2.4</td>
<td>224, 2.0</td>
<td>0.528, 2.0</td>
<td>40</td>
<td>0.25 g, 37% mono-benzylated.</td>
</tr>
<tr>
<td>3$^b$</td>
<td>1.5, 0.535</td>
<td>15</td>
<td>0.70, 6.0</td>
<td>561, 5.0</td>
<td>1.32, 5.0</td>
<td>100</td>
<td>1.24 g, 22% mono-benzylated.</td>
</tr>
<tr>
<td>4$^c$</td>
<td>0.79, 0.220</td>
<td>10</td>
<td>0.35, 3.0</td>
<td>561, 5.0</td>
<td>0.66, 3.0</td>
<td>40</td>
<td>0.66 g, 27% mono-benzylated.</td>
</tr>
</tbody>
</table>

a. 0.2 mL water was added to the DMSO to help dissolve P10/F1. Benzyl chloride, potassium tert-butoxide and 18-crown-ether were added in one batch.
b. Benzyl chloride, potassium tert-butoxide and 18-crown-ether were added in two batches.
c. The starting polymer in this reaction was the product from Run 3. Benzyl chloride, potassium tert-butoxide and 18-crown-ether were added in two batches.

**3.2.5.3.3. Grafting copolymer (PxF1) using LiOH saturated solution as a base**

A 50 mL 3-necked flask was charged with 0.5 mL water, DMSO 18 mL and copolymer P20F1(4-75-2) (100 mg, 0.022 mmol). After all the copolymer was dissolved, the yellow DMSO solution and a saturated LiOH solution were degassed with argon for 30 min. Saturated aqueous LiOH solution (2.4 mL) and benzyl chloride (0.21 mL, 1.8 mmol) were added to the 50 mL 3-necked flask. This reaction was run overnight. The yellow DMSO solution was neutralized with conc. HCl and stripped. The remaining solid was dissolved in water and purified by ultrafiltration. The obtained water solution was
stripped and a yellow film (105 mg) was obtained. The obtained material was characterized by NMR, shown in the Results and Discussion section.

3.2.5.3.4. Other grafting reactions.

A 50 mL 3-necked flask containing a magnetic stirring bar was charged with dried (90°C, 10 mm, 24 h) copolymer. P10F1-Li (0.239 mg, 0.084 mmol), 20 mL DMSO and 10 mL toluene; a small vacuum jacked fractionating column filled with glass beads was attached and the solution was heated to 180°C. The toluene/water azeotrope initially distilled at 106°C. The stopcock was opened carefully, and distillate was removed at a rate of about 1 drop per 10 sec. When the distillation temperature rose to 110°C and the distilled liquid was clear, the system was cooled to room temperature under an argon flow. 18-Crown-6 (50.2 mg, 0.19 mmol) and 1-bromododecane (62 mg, 0.25 mmol) were added. The flask was transferred to a glove box and potassium tert-butoxide (21 mg, 0.19 mmol) was added. The flask was put in an oil bath and heated overnight at 40°C with stirring. After cooling, the solution was poured into 300 mL of acetone. The precipitate, 220 mg, was filtered and analyzed by 1H NMR.

3.2.6. Crosslinking of grafted polymer films

The grafted polymer was cast from water or water/methanol solution in a Teflon dish. Strips (0.3 x 3 cm), cut from the cast film, were heated in ACE-8648 tubes inside a Buchi TO-51 glass oven at 210°C for 3 h under high vacuum (80 mtorr).
3.3. Results and Discussion

3.3.1. Synthesis of comonomer and homopolymer

The lithium salts of monomer and comonomer used in the polymerization were converted from their corresponding acid forms (purity was characterized by $^1$H NMR) by titrating with LiOH; the Li salt was further purified by recrystallization from methanol and isopropanol.

3.3.1.1. Syntheses of comonomer 3,5-DBFDSA-Li

With end groups similar to those of DBPDSA, 2,7-dibromofluorene-3,6-disulfonic acid (3,6-DBFDSA) should react well with DBPDSA in the Ullmann coupling reaction. 3,6-DBFDSA-Li can directly copolymerize with DBPDSA-Li; the resulting copolymer could be further reacted with alkyl halides to make the final water insoluble copolymers. We expected that 3,6-DBFDSA could be synthesized by direct sulfonation of 2,7-dibromofluorene. Two approaches were used to make the target molecule: sulfonation with fuming sulfuric acid or reaction with chlorosulfonic acid and hydrolysis with a protonic solvent. 2,7-Dibromofluorene was reacted with fuming sulfuric acid (15% SO$_3$) at 110°C for 2 h. Dibromo fluorene 3,5-disulfonic acid (60%) and dibromofluorene-4-sulfonic acid (40%) were isolated. The NMR spectrum of the mixture is shown in Figure 3.7. The initial attack seems to be at the 4-position at this temperature; the disulfonated material was almost 100% 3,5-disulfonic acid. The hydrogens of dibromo fluorene-4-sulfonic acid are labeled by letters and assigned in Figure 3.7. The large peaks at 9.64, 8.10, 7.80 and 7.76 ppm are from the aromatic hydrogens of dibromofluorene-3,5-disulfonic acid. The peak at 3.88 ppm is from the methylene hydrogen group.
Figure 3.7. 400 MHz $^1$H NMR (CD$_3$OD) spectrum of the mixture of dibromofluorene-3,5-disulfonic acid and dibromofluorene-4-sulfonic acid (A is aromatic region and B is aliphatic region)
The sulfonation reaction of 2,7-dibromofluorene with chlorosulfonic acid can be completed at low temperature. The obtained materials were a mixture of 3,5- and 3,6-disulfonyl chlorides, shown in Figure 3.8.

The sulfonation using fuming sulfuric acid shows that the first sulfonation is in the 4-position for two reasons. First, steric hindrance dominates over the Br directing influence. Second, because the other benzene ring is strongly o, p-directing, the 4-position is favored. Sulfonation is controlled by kinetic and thermodynamic factors. High temperature can increase random attack since entropy starts to dominate. But based on the results shown in Table 3.1, high temperature and long reaction time may increase ratio of 3,6-disufonyl chloride from 0.11 to 0.18. This little improvement implies that it is difficult to rearrange the sulfonic acid group. The following rearrangement experiment further proved this conclusion. Because the yield of 2,7-dibromofluorene-3,6-disulfonyl chloride, shown in Table 3.1, is still low, we hoped to rearrange 2,7-dibromofluorene-3,5-disulfonyl chloride to 2,7-dibromofluorene-3,6-disulfonic acid by heating with 85% or concentrated sulfuric acid at high temperatures. No rearrangement was found using these reaction conditions. The harsh reaction conditions caused the material to decompose or polymerize.

2,7-Dibromofluorene-3,5-disulfonic acid dilithium salt was obtained by hydrolyzing the corresponding disulfonyl chloride, titrating with lithium hydroxide and recrystallizing from i-PrOH and methanol. It was characterized by $^1$H NMR (Figure 3.8), FT-IR (Figure 3.9) and $^{13}$C NMR (Figure 3.10).
Figure 3.8. 400 MHz $^1$H NMR (CD$_3$OD) spectrum of DBFDSA-Li

Figure 3.9. FT-IR spectrum of DBFDSA-Li in a KBr pellet.
3.3.1.2. Homopolymerization of DBFDSA-Li

The polymer synthesized from DBFDSA-Li using Ullmann coupling was characterized by $^1$H and $^{13}$C NMR (Figure 3.11A&B). There is a set of four large
aromatic peaks accompanied by a series of small peaks in Figure 3.11A, which might be a small amount of trimer and perhaps tetramer. In order to generate such a simple spectrum, almost every fluorene residue must be in the same chemical environment. The $^{13}$C NMR, Figure 3.11B, shows that the number of C peaks is equal to that in the comonomer.

The structure of the homopolymerization product must be a symmetrical dimer. The comonomer, DBFDSA-Li, has different reacting sides, labeled A and B. (Figure 3.12) There are 2 possible reactions (Figure 3.13) that will form symmetrical structures. When the NMR spectrum, Figure 3.11A, is compared to that of monomer, DBFDSA-Li, (Figure 3.8.), a shielding effect was found. The highest chemical shift peak (the 4 position hydrogen) meta to the A side bromine atom was slightly changed (9.63 ppm versus 9.66 ppm) when the 2-bromo was replaced by a phenyl group. The other H peaks shifted; the 1-hydrogen peak shifted dramatically from 7.86 ppm in the monomer to 7.48 ppm in the polymer; a slight upfield shift is seen for the 6- and 8- hydrogens, from 8.09 to 8.11 and 7.73 to 7.80 ppm. For the two possible structures shown in Figure 3.13, the BAAB is more asymmetric, with the two fluorene units twisted strongly because the two sulfonic acids on the A side are both ortho to the linking bond. The B-B link should be almost coplanar. Earlier work in our group showed that the A position was more reactive than the B position in the Ullmann reaction of 2,5-dibromobenzene sulfonic acid. This should also be true for this dimer, generating the structure shown in Figure 3.14, which could explain the strong shielding of that proton by aromatic electrons.
Figure 3.11. A 400 MHz $^1$H NMR (CD$_3$OD) spectrum of poly(fluorenyl disulfonic acid); B 150 MHz $^{13}$C NMR (CD$_3$OD) spectrum of poly(fluorenyl disulfonic acid)
Axial chirality is a special case of chirality in which the molecule possesses an asymmetric axis rather than chiral center. Axial chirality is commonly manifested in biaryl and binaphthyl derivatives in which rotation around the C-C bond between two aryl rings is restricted. Classical cases are systems based on 1,1’-binaphthalene (BINAP). In biaryls, axial chirality is usually seen in systems in which two non-equivalent bulky groups are adjacent to a biaryl C-C bond. The CH$_2$ (9-position) fluorenyl hydrogens in Figure 3.14, are split into 4 peaks with chemical shifts from 3.61 to 3.90 ppm. In the monomer, the methylene hydrogens give a single peak at 3.97 ppm. Steric hindrance in the homopolymer could change the chemical shift and cause splitting if the dihedral angle is not random and rotation is slow. The ring orientations at the A-A link should favor a
dihedral angle with the least steric hindrance and would preferentially shield one aliphatic hydrogen more than the other; while B-B or A-B attached fluorene groups are close enough to cause the –CH₂ hydrogen split. A second NMR scan was run at 50°C to test this. The 4 ppm regions are compared in Figure 3.15. At the higher temperature, the four peaks moved to higher ppm and splitting decreased (3.61 to 3.90 at 30°C versus 3.77 to 3.97 ppm at 50°C); the geminal coupling remained at 23 Hz. The high temperature expedites the rotation of the aromatic groups and each hydrogen spends some of its time during each scan in the opposite orientation. That brings the peaks closer together. The same trend is found for the aromatic peaks; the peak positions for the 1, 6 and 8 hydrogens rise slightly, about 0.05 ppm, from 30 to 50°C. The 4-hydrogen peak position rises only 0.02 ppm.

**Figure 3.15.** 600 MHz ¹H NMR (CD₃OD) spectra; comparison of DBFDSA dimer CH₂ peaks at 30 and 50°C.
3.3.2. Copolymer syntheses

3.3.2.1. Copolymerization of DBPDSA-Li and DBFDSA-Li without coordination reagent

Copolymers, PxF1, were synthesized using DBBPDCA-Li homopolymerization reaction conditions, developed in Chapter 2. The reaction conditions were varied to try to increase molecular weight, see Table 3.2.

The NMP insoluble fractions of the 1/10 runs were compared. Copolymers obtained from polymerization at 170°C (Runs 6 & 10) had slightly higher viscosity. Run 5 had almost the same viscosity as Run 1. Reaction time did not affect the viscosity; all copolymers precipitated after about 10 h. When the comonomer fraction was increased, the reduced viscosity of the NMP insoluble fraction decreased (Runs 2 & 8). The NMP soluble fraction of Run 1 had a very low viscosity; we expect this to be true for all the copolymers. The relatively low viscosity of the obtained copolymer was probably caused by the reaction system not being completely dry. We have found that the comonomer Li salt holds water more tenaciously than the major monomers. This will be further discussed in Section 3.3.2.6. The ¹H NMR spectra will be discussed in the next section.

In order to increase the copolymer molecular weight, a different solvent was tested. Testing showed that DMSO was a very good solvent for the copolymer. One of the factors limiting copolymer molecular weight is the solubility of its lithium salt in the reaction solvent. When NMP was used, the copolymer precipitated when it reached a certain molecular weight. It was hoped that DMSO would be a better solvent for the copolymer, allowing it to reach a higher molecular weight. The copolymers made in
DMSO (Table 3.3) were soluble but had very low viscosities, 0.12 dL/g (C = 0.5 g/dL), compared with 0.4 dL/g for polymer made in NMP, Table 3.2. It is possible that the polymerization rate in DMSO is slower than in NMP. DMSO might work well if reaction times are extended or if the temperature is raised.

3.3.2.2. Structure of copolymer PxF1 based on NMR and elemental analysis

All the obtained copolymers were analyzed by $^1$H NMR and some of them were analyzed by elemental analysis. Combined with the homopolymer structure analysis using NMR spectra, a possible copolymer structure is proposed.

Figure 3.16. 400 MHz $^1$H NMR (CD$_3$OD) spectrum of the NMP insoluble fraction of copolymer P10F1 Run 5, Table 3.2.

A typical spectrum, the 400 MHz $^1$H NMR spectrum of the NMP insoluble copolymer fraction, Table 3.2 Run 5, acid form is used as an example for all the copolymers, Figure 3.16. The peaks at ~4 ppm are from the CH$_2$ and those between 9-10 ppm are from the isolated 4-H on the fluorene moiety. The areas are very small but agree
reasonably well, giving \(~3\%\) comonomer rather than 9.1%, the comonomer mole %
starting composition. It is possible that a large fraction of the fluorene peaks are very
broad. The 4-hydrogen (See Figure 3.12) on the fluorene moiety, at 9.6 ppm in the
monomer, is split into at least 7 peaks, too many to be from sequence distribution
chemical shifts. Like what we found in the DBFDSA dimer, the fluorene CH\(_2\) group at \(~4\)
ppm is split into 4 peaks. The coupling constant of this split is 24 Hz, which is close to
that of DBFDSA dimer. The aliphatic hydrogen splitting in the copolymer implies that
these hydrogens are in different environments and have different chemical shifts. As
mentioned before, this may be caused by axial chirality. The fluorene unit is attached to a
sulfonic acid containing aromatic moiety that rotates very slowly due to steric hindrance.

Another method, elemental analysis (Galbraith Laboratories), was used to
determine the copolymer composition of Run 5, Table 3.2. This is absolute, affected only
by impurities in the material. The data are given in Table 3.7. The comonomer fraction
was calculated based on the mole ratios of carbon and sulfur in the monomer,
comonomer and copolymer, as shown in Equation 3.2.

\[
3x + 6.5(1 - x) = \frac{C}{S}
\]  

(Equation 3.1)

The C/S ratio in the monomer is 3.0, 6.5 in the comonomer and 3.34 in the
copolymer, based on the data in Table 3.7; \(x\) is the mole fraction of monomer in the
copolymer. The copolymer composition is calculated as 9.4% FDSA, agreeing with its
starting mole ratio (\(1/11 = 9.1\%\)) within experimental error.
The copolymer structure was expected to be random; however, it is impossible to determine the detailed structure of a copolymer from a single NMR spectrum. In Section 3.3.1.2., the structure of DBFDSA dimer was analyzed by NMR. The two –Br groups with different reactivity in DBFDSA-Li, assigned A and B respectively, were shown in Figure 3.12. According to the NMR study of the DBFDSA dimer at different temperatures (Figure 3.15), and previous work in our group that showed that the A side has higher reactivity than the B side, the proposed structure of the DBFDSA dimer is given in Figure 3.14. The monomer DBPDSA-Li has two identical –Br groups which are hypothesized to have lower reactivity than the A side -Br group in DBFDSA-Li, but higher reactivity than B side –Br group in DBFDSA-Li. During the polymerization reaction, the A side of comonomer DBFDSA prefers to react with itself or with DBPDSA. That is why there are so many peaks at ~9.5 ppm. The B side of the comonomer cannot react with A side slowly because of the big reactivity difference, and the B side even more slowly reacts with itself due its low reactivity. But the monomer can react with B side, though slowly, since there is a smaller reactivity difference between them. During polymerization, the A side will react rapidly with other A sides.
and with the main monomer until it is used up. The relative amounts of A-A and A-
monomer sequences will depend on the monomer ratios and polymerization rate
constants. B side is the least reactive side and has the most possibility to stop the
polymerization reaction. Thus, the structure of this random copolymer consists of many
PDSA units with embedded FDSA and terminated with FDSA with an unreacted B side,
shown in Figure 3.17.

![Figure 3.17. Proposed structure for PxF1 copolymer](image)

### 3.3.2.3. Copolymerization of DBPDSA-Li and DBFDSA-Li using 2,2’-bipyridyl (BPy)
as a coordination reagent

The copolymerization reactions shown in Table 3.2 gave low molecular weight
copolymer. One possible reason is that the copolymer cuprous salt that was generated
precipitated. Another possible way to increase copolymer solubility might be to add a
coordination reagent that could complex the cuprous ions. The Ullmann coupling
generates Cu(I) which could exchange with the Li to form an insoluble cuprous polymer
salt. 2,2’-Bipyridyl (BPy) complexes strongly with Cu(I); hopefully this would increase
copolymer solubility. Firstly, the addition order of BPy was screened. Three reactions
were run side by side: 1. Control: No BPy was used, 2. NMP was added to the dried BPy
and the solution was added to the reaction flask, and 3. Pure NMP was placed in the
reaction flask and the reaction was run for 2 h. Then a solution of BPy in NMP was
added. Since each monomer has two Br groups, it uses two copper atoms. Half an
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equivalent of BPy was added. The products were characterized by NMR and viscosity.

The conditions and results are given in Table 3.8.

**Table 3.8.** Copolymerizations using 2,2'-bipyridyl (BPy) as Cu complexing agent with different addition orders of BPy

<table>
<thead>
<tr>
<th>Run</th>
<th>Comonomer/Monomer&lt;sup&gt;a&lt;/sup&gt; Wt., mg; mole ratio</th>
<th>BPy, mg, mmol</th>
<th>Time, h</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.2/816; 1.0/10</td>
<td>0</td>
<td>40</td>
<td>81.6 mg NMP insoluble material, yield&lt;sup&gt;c&lt;/sup&gt; = 13%; η&lt;sub&gt;sp/C&lt;/sub&gt; = 0.24 dL/g</td>
</tr>
<tr>
<td>2</td>
<td>99.2/816; 1.0/10</td>
<td>343, 2.2</td>
<td>40</td>
<td>267 mg NMP insoluble material, yield&lt;sup&gt;c&lt;/sup&gt; = 43%; η&lt;sub&gt;sp/C&lt;/sub&gt; = 0.46 dL/g</td>
</tr>
<tr>
<td>3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>99.2/816; 1.0/10</td>
<td>343, 2.2</td>
<td>38</td>
<td>397 mg NMP insoluble material, yield&lt;sup&gt;c&lt;/sup&gt; = 64%; η&lt;sub&gt;sp/C&lt;/sub&gt; = 0.24 dL/g</td>
</tr>
</tbody>
</table>

<sup>a</sup> Comonomer: DBFDSA-Li; monomer: DBPDSA-Li. Reaction temperature, 140°C, NMP volume = 30 mL, Cu weight = 1.4 g.

<sup>b</sup> Bipyridyl was added after the reaction had run for 2 h.

<sup>c</sup> Yield calculated assuming dried copolymer has one H<sub>2</sub>O/-SO<sub>3</sub>H

Although the low yield in the control reaction (Table 3.8, Run 1, 13%) meant the reaction did not proceed properly, the relatively high yields in Runs 2 and 3 (43% and 64%) implies that BPy improved the copolymerization kinetics. The best copolymerization (Run 2) using BPy had a reduced viscosity (C = 0.5% g/dL) of 0.46 dL/g, higher than the best run without BPy in Table 3.2, Run 6 (0.42 dL/g).

The copolymerization reaction using BPy was further studied by changing the temperature and time (Table 3.4). All the copolymerization reactions run with BPy gave high yields of copolymer. Even when BPy was added after two hours (Table 3.4, Run 2), a relatively high yield of copolymer was obtained. BPy really increases the amount of
copolymers obtained; probably because it allows the formation of higher molecular weight polymer. Low molecular weight polymer might go through the 5000 Dalton cut-off ultrafilter. However, the copolymer viscosities obtained from these reactions were inconsistent. The highest copolymer reduced viscosity obtained was 0.46 dL/g (Table 3.4, Run 1); the others were very low.

**Figure 3.18.** DSC plot of comonomer DBFDSA-Li. First scan was heated to 207°C at 10°C/min and cooled to 100°C; second scan was heated to 200°C at 10°C/min and from 200°C to 300°C at 1°C/min.

The low copolymer viscosities may be attributed to water remaining in the reaction system. Both the monomer DBPDSA-Li and comonomer DBFDSA-Li have
water of hydration. Previous work in our group showed the water in DBPDSA-Li was lost at about 100°C. In order to know the temperature at which the DBFDSA-Li lost absorbed water, a Differential Scanning Calorimetry (DSC) scan was run (Figure 3.18). In the first heating cycle (up to 207°C) there was an endotherm of 1.4 W/g at ~ 200°C; in the second heating cycle the endotherm was reduced to 0.04 W/g, at ~217°C. This implies that the endotherm is due to water evaporation. Therefore, in order to obtain thoroughly dried comonomer, the drying temperature should be about 200°C. Higher viscosity copolymers were obtained for Run 10, Table 3.2 and Run 5, Table 3.4, dried at 200°C. For Run 4 polymer made in Table 3.4, due to moisture accidentally introduced during NMP addition the viscosity was low. These reactions generated information that was applied in designing the procedures used in the scale-up reaction.

3.3.2.4. Copolymerization of DBPDSA-Li and DBFDSA-Li with triethylene glycol dimethyl ether (TEGDME) as a coordination reagent

In Section 3.3.2.3., the coordination reagent BPy was found to increase the yield and viscosity of the copolymer PxF1. It was attributed to strong coordination between BPy and cuprous cation, which could increase the solubility of the generated PxF1 in NMP solution. Considering that most of the PxF1 exists as lithium salt in the reaction solution, the solubility of the PxF1 could possibly be dramatically increased by adding a lithium cation coordination compound, triethylene glycol dimethyl ether (TEGDME).

This hypothesis was tested by determining if the coordinated polymer was soluble in NMP. Two vials were charged separately with 10 mg P20F1 (the ratio of DBPDSA and DBFDSA-Li is 20:1), 2 mL NMP, 0.1 mL methanol and 1 drop of water. After the polymer dissolved, 0.1 mL diethylene glycol dimethyl ether (DEGDE) was placed in one
vial. These two vials were heated to 120°C with argon purging. After one hour, the vial without the DEGDE had a white precipitate, while the vial with DEGDE remained a clear solution. At high temperature with argon purging almost all the methanol and water in the NMP would be removed; P20F1-Li precipitated from pure NMP solvent. The clear solution in the vial with DEGDE meant that the coordinated polymer was soluble in NMP. The complexed lithium ion occupies a large volume and probably keeps the polymer chains separated, preventing their aggregation.

This copolymerization reaction to make P10F1 was run at 170°C. Triethylene glycol dimethyl ether, TEGDME, was used instead of DEGDE since TEGDME has 4 oxygens, which should coordinate a lithium ion more strongly than DEGDE. However, viscosity measurements of the copolymer, P10F1(4-85) (4 is the notebook number and 85 is the page number), showed that the copolymer molecular weight was low ($\eta_{sp}/C = 0.36$ dL/g when C = 0.5 g/dL). Its viscosity is much lower than that of P10F1 prepared in Section 3.2.4.4. ($\eta_{sp}/C = 0.9$ dL/g at C = 0.5 g/dL), prepared at 200°C.

3.3.2.5. The effect of coordination reagents on the molecular weight of the resulting copolymer PxF1

The assumption is that these coordination reagents function to coordinate the sulfonic acid counterion and increase the copolymer PxF1 solubility. The results in Section 3.3.2.3 show that BPy addition can increase both yield and viscosity of copolymer. However, when TEGDME was used as a coordination reagent, low yield and low viscosity copolymer was obtained. One possible reason for the copolymer low molecular weight was the amount of the TEGDME in the reaction. The concentration of TEGDME added (Section 3.2.4.2.3) was 0.105 mmol/mL, less than the initial concentration 0.22 mmol/mL because TEGDME has a higher boiling point than NMP; the Li ion content
was 4.4 mmol/mL and there may not have been enough to keep the polymer from precipitating. However, this is not likely, since the polymer’s viscosity is lower than that found for earlier preparations of P10F1, even at 140°C. Another possibility is that TEGDME adsorbs on the copper surface, deactivating it. If this happens, a smaller ratio may still keep the polymer soluble while not deactivating the copper.

Another possible explanation is that BPy not only increases the copolymer cuprous solubility in NMP, but also can coordinate cuprous ion as a catalyst for the Ullmann coupling reaction. BPy is a very good complexing agent for cuprous ion. Lange’s Handbook of Chemistry reports an equilibrium constant of $10^{14.2}$.

Liebeskind et al. developed an innovative copper(I) reagent, copper(I)-thiophene-2-carboxylate (CuTC), which can promote Ullmann-reductive coupling of substituted aromatic iodides, bromides and 2-iodoheteroaromatics, at room temperature. This reductive coupling requires a polar, coordinating solvent such as NMP. The mechanism of this ambient temperature Ullmann-like reductive coupling is through an oxidation addition pathway. The authors consider the role of CuTC is not internal coordination as depicted in Figure 3.19, but may be due to an inherent ability of carboxylate as a ligand to stabilize the oxidative addition product, as shown in Figure 3.20. Compared with Liebeskind’s Ullmann coupling reaction, the copolymerization reaction of DBPDSA and DBFDSA used the same reaction solvent (NMP) and had a similar oxidation pathway (Section 2.3.1.5.). Therefore, the generated CuBPyBr from the coordination between Cu(I)Br and BPy during polymerization reaction may have the same function in the polymerization reaction as the CuTC in Liebeskind’s the Ullmann coupling reaction.
Figure 3.19. Internal coordination model of CuTC oxidation addition intermediate. (Reprinted with permission from American Chemical Society)

Figure 3.20. Proposed two oxidation pathways. (Reprinted with permission from American Chemical Society)

3.3.2.6. The effect of drying conditions on the molecular weight of the resulting copolymer PxF1

Previous studies show the Ullmann coupling copolymerization is sensitive to moisture in the system. In order to obtain high molecular weight material, an efficient drying method should be applied. In Section 2.2.2.8., a high molecular weight material was obtained by drying the reaction system with an Ar/N₂ stream. The DSC spectrum of DBFDSA-Li, Figure 3.18, showed that the absorbed water is lost at about 200°C. Based on the above analysis, a scaled-up copolymerization reaction (5 g) was run with a new
drying procedure. The comonomer, monomer and copper were pre-dried at 200°C under vacuum and further dried at 200°C by purging with ultra-pure argon while using mechanical stirring. The obtained copolymer P10F1 was characterized by $^1$H NMR (Figure 3.21), viscosity (Figure 3.22) and FT-IR (Figure 3.23).

Figure 3.21. 400 MHz $^1$H NMR (D$_2$O) spectra of the NMP insoluble P10F1 (4-28-4-1) from the scaled up reaction. A shows the aromatic region, B the aliphatic region.
Figure 3.22. Viscosity plot (D. I. water, 35°C) of P10F1 (4-28-4-1) from the scaled up reaction.

Figure 3.23. FT-IR of copolymer P10F1 (4-28-4-1) in a KBr pellet.

The three peaks above 9.0 ppm in Figure 3.21A are from the isolated 4-H on the fluorene moiety. Based on the area of these peaks compared to the remaining aromatic
area, the fluorene content of the copolymer was calculated as 3.6% instead of the expected 9.1%.

Instead of a single peak at ~4 ppm for the fluorene CH\textsubscript{2} group, there are two major sets of peaks: one shows four broad peaks suggesting an AB splitting pattern, while the other consists of three or four sharp peaks. (The large singlet at 3.75 ppm is from added dioxane.) The quartet peaks are similar to those found for earlier copolymers, except that the chemical shift is at higher field, 4.15 ppm, and the splitting is greatly reduced; it is probably due to the different NMR solvent used. The other peaks have a very small area, which may come from the end parts of the polymer chain. If we add the areas they sum to 0.22, less than that of the aromatic 4-H fluorenyl peaks above 9 ppm, 0.24. From this measure, the comonomer content would be 1.8%. Obviously, \textsuperscript{1}H NMR is not a good method to determine the copolymer structure. Due to the polymer chain steric configuration, some hydrogens are buried in the polymer chain and cannot completely relax. Corresponding integrations of those hydrogens are less than their actual value. Probably, elemental analysis may give us some useful information. The viscosity of this copolymer (Figure 3.24) shows it has a reasonably high molecular weight. At C = 0.5 g/dL, $\eta_{sp}/C = 0.90$ dL/g, twice as high as the highest viscosity found for the previously obtained copolymer (Table 3.4, Run 1, $\eta_{sp}/C = 0.46$ dL/g).

This new drying method, described in Section 3.2.4.4., generates thoroughly dry reaction conditions which can produce high molecular weight copolymer in high yield.
3.3.3. Grafted copolymer

3.3.3.1. Model grafting reactions

In order to produce water insoluble material, PxF1 copolymers must be alkylated at the fluorenyl methylene position. A series of model alkylation reactions on monomer were run to determine the best alkylation procedure, Table 3.5.

The copolymer is water soluble, so a DMF/water mixture was initially used as solvent. The pKa of DBFDSA-Li was estimated by titration (Figure 3.24) to be about 11. Benzyltrimethylammonium hydroxide (BTMA-OH) solution should be basic enough to deprotonate the fluorenyl CH₂. However, DBFDSA-BTMA precipitated and starting material was recovered (Table 3.5, Run 1a).

![DBFDSA-Li titration curve](image)

**Figure 3.24.** DBFDSA-Li titration curve (see Section 3.2.5.1).

LiOH or KOH was then used; their salts are soluble in DMF/water. However, a mixture of unreacted plus once and twice reacted material was obtained (Table 3.5, Runs 2a, 3a and 4a). Solvent and base changes were made because OH⁻ could hydrolyze or dehydrohalogenate the alkyl bromide. The hindered base, potassium tert-butoxide, (less
reactive towards bromoalkanes) and dried DMSO (better solubility for copolymer) were used in Runs 5a, 6a and 7a. When potassium tert-butoxide in THF solution was used, the reaction was not complete (Table 3.5, Run 5a), possibly because the THF/DMF solvent partly precipitated the starting salt. When solid potassium tert-butoxide was used, twice reacted compound was obtained in moderate yield (Table 3.5, Run 6a). In order to increase the reaction rate, a catalytic amount of 18-crown-6 was added. This coordinates the K ion and frees the anion to react (Table 3.5, Run 7a). As expected, a high yield of twice reacted compound was obtained, Figure 3.25.

**Figure 3.25.** 400 MHz $^1$H NMR (DMSO-d$_6$) spectrum of twice dodecane alkylated comonomer.

In order to avoid introducing water and OH$^-$ into the organic phase with DBFDSA, which can hydrolyze or dehydrohalogenate the alkyl bromide, a saturated NaOH aqueous solution was tried in an alkylation reaction with benzyl chloride. As we expected, the
saturated NaOH aqueous solution and DMSO solutions were not mutually soluble and phase separation occurred. This two phase system prevents base from coming into the DMSO phase, but the DBFDSA can dissolve and be deprotonated in aqueous phase, and then alkylated in the organic phase. A high yield of twice reacted compound was obtained, Figure 3.26.

![Figure 3.26. 400 MHz $^1$H NMR (CD$_3$OD) spectrum of twice benzylated comonomer](image)

The key for this model alkylation reaction is to avoid the reaction between base and alkylation reagent. The steric hindrance of bulky base can prevent it from reacting with the alkylation reagent and just deprotonate the fluorenyl group. The optimized alkylation reaction was applied into the synthesis of grafted copolymer.

### 3.3.3.2. Synthesis of grafted copolymer

The reaction conditions for alkylation of the copolymer were adapted from the successful one used in the model alkylation reaction, Table 3.5. The hindered base, potassium tert-butoxide, in DMSO was used, with a catalytic amount of 18-crown-6 to
increase the potassium salt solubility. A long chain alkyl bromide, 1-bromodocosane, was used to ensure that the reacted copolymer was water insoluble. However, the acidified material obtained from this alkylation reaction was still water soluble. For the copolymer with 1/10 comonomer/monomer ratio, if each fluorene residue had added two docosane chains, the ratio of the aromatic to aliphatic hydrogens should be 24:90. Its NMR spectrum (Figure 3.27) shows an aromatic to aliphatic hydrogen ratio of 24:42. Only one fluorenyl methylene hydrogen reacted. There are several possible causes. The Li salts hold water so strongly that the reacting system had at least 2 mmol of water that could form hydroxide ions. These could transform the alkyl bromide to the alcohol which might then react with more alkyl bromide to form the ether. While the first fluorenyl substitution should occur rapidly, the second takes place at a highly hindered position and would go slowly. Competing reactions are dehydrohalogenation of the alkyl bromide by the tert-butoxide anion as well as alcohol and ether formation. Enough water was initially present to consume all the base in side reactions.

Considering that water is the initiator of the side reaction, a proper method should be used to remove the water. Azeotropic distillation is normally used to remove water in a reaction system. We used the water/toluene azeotrope as a method for removing the water in the solvent and copolymer. However, with the procedure described in Section 3.2.5.3.4, the equilibrium boiling point of the toluene-water azeotrope, 84.1°C, was never reached. The initial distillation temperature was 106°C; it rose slowly to 110°C.
Figure 3.27. 400 MHz ¹H NMR (CD₃OD plus D₂O) spectrum of docosyl alkylated P10F1.

Figure 3.28. 400 MHz ¹H NMR (CD₃OD) spectrum of dodecyl alkylated P10F1-Li.
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The NMR spectrum of the obtained material, Figure 3.28, shows that the fluorene CH₂ conversion was low. Based on the integration of the fluorene CH₂ group at ~4 ppm and the dodecyl group at 0.7 to 1.5 ppm in Figure 3.28, the extent of reaction on the fluorene CH₂ group was calculated as 23% rather than the expected 200%. Since the moles of base and alkyl bromide that were used were exactly equivalent to the fluorene CH₂ in the reaction, a very small quantity of water (0.08 mmol, 1.5 mg) could react to destroy the reagents by forming dodecyl ether and generate the low yield. More water could produce dodecanol. The low conversion shows that azeotropic distillation did not completely remove all the water; the water content was very low and a relatively poor fractionating column was used.

Molecular sieves 4Å can absorb approximately 22 percent of their weight in water. It is a good dehydrator for DMSO used in alkylation reactions. Molecular sieves 4Å in an ACE-8648 pressure tube were activated by heating in a Buchi TO-51 glass oven at 280°C under high vacuum for 8h and transferred to the reaction system under argon atmosphere. The copolymer alkylation reaction conditions are summarized in Table 3.6. Figures 3.29, Runs 1 to 4, show the NMR spectra of the corresponding alkylated copolymers. The alkylation ratio was calculated based on separate integrations of the aromatic peaks above and below 7.0 ppm. We assume that the backbone ratio of phenyl to fluorene groups in the copolymer P10F1 is 10:1. The data show that when the reagents were added in two batches, alkylation increased (Table 3.6, Runs 2 and 4). When the weight of copolymer P10/F1 was increased, the alkylation ratio decreased (Table 3.6, Run 3). A possible reason is that more water from the hydrated copolymer was retained in the system. potassium tert-butoxide can exchange with the water and the generated OH⁻ group can
react rapidly with benzyl chloride to produce benzyl alcohol. This can react further to generate dibenzyl ether. One mole of water may thus remove two moles of benzyl chloride plus two moles of base. While the CH<sub>2</sub> hydrogens in fluorene are relatively acidic, in the polymer they are surrounded by anions which can reduce their acidity. Also, the polymer increases steric hindrance. When the reaction was scaled up, the retained water increased, decreasing the degree of alkylation. The 4Å molecular sieves that were used to dry the solvent were put into the flask and allowed to stand overnight. The stirring generated small particles that could not be separated from copolymer. If it is not stirred, it will take a very long time for all the water to diffuse to the sieves, since some will be far from the sieves. Also, if the sieves are left in the reaction vessel during reaction, some water can diffuse out and react if all the free water has reacted. Thus, the key to this alkylation reaction is to remove water completely; this needs further study.

**Figure 3.29.** 400 MHz <sup>1</sup>H NMR (CD<sub>3</sub>OD) spectrum of P10F1-g-Bn34%. (Table 3.6 Run 1)
**Figure 3.29.** 400 MHz $^1$H NMR (D$_2$O) spectrum of P10F1-g-Bn37%. (Table 3.6 Run 2)

**Figure 3.29.** 400 MHz $^1$H NMR (D$_2$O) spectrum of P10F1-g-Bn22%. (Table 3.6 Run 3)

**Figure 3.29.** 400 MHz $^1$H NMR (D$_2$O) spectrum of P10F1-g-Bn27%. (Table 3.6 Run 4)
Another method that might give high yields of twice alkylated fluorene compound is using NaOH aqueous solution as base; the results are given in Table 3.5. Because solubility of the copolymer sodium salt in DMSO is low, LiOH saturated solution was used in the alkylation reaction. The reaction procedure was given in Section 3.2.5.3.3; the obtained copolymer was analyzed by $^1$H NMR (Figure 3.30). The grafting degree was calculated as 55%, higher than any other runs in Table 3.6. Although saturated LiOH solution gave the best grafting result, it still cannot give fully alkylated copolymer. The problem is attributed to the water in the DMSO phase since a LiOH solution was used. A new dehydration method needs be developed in order to obtain fully alkylated copolymer.

Figure 3.30. 400 MHz $^1$H NMR (CD$_3$OD) spectrum of P20F1-g-Bn55%
3.3.3.3. Direct synthesis of grafted copolymer from alkylated comonomer

Since we were having difficulty in achieving complete benzyl group substitution, we decided to prepare the dibenzylated comonomer and try to copolymerize that. Two copolymerization methods were applied, First, reaction in a pressure tube after drying under vacuum, and second, reaction in a flask after drying with argon at 200°C for 4 h. Both reaction conditions gave low molecular weight material. Here, the copolymer P10F1-g-Bn200% (4-75-1) obtained from the reaction in a flask is analyzed. It was characterized by NMR (Figure 3.31) and viscosity.

Figure 3.31 shows the fluorenyl 4-H peaks at 9.26 ppm. The CH$_2$ peaks at 3.50 ppm are from the benzyl groups. The bulky benzyl groups seemed to have huge steric hindrance since the copolymer had a very low viscosity ($\eta_{sp}/C = 0.23$ dL/g at $C = 0.5$ g/dL). The P/F ratio is not 10. The ratio of the benzyl hydrogen areas to the rest of the aromatic area gives a copolymer composition of P14F1. Since the copolymer was ultrafiltered, very short molecules could have been lost. A calculation of P/F ratio as a function of low molecular weight material lost (with a lower P/F ratio) gives a value of 14 at an 83% yield and 13 for an 89% yield. The yield is reported as 92%. The weights given in Section 3.2.4.6 are for dried monomers and polymer but the materials contained water of hydration. This was calculated and subtracted from the measured weights. Within the broad limits on accuracy imposed by starting with hydrated monomers and producing a hydrated copolymer, the fit is reasonable. This copolymer should have a degree of polymerization of about 30.
3.3.4. Crosslinking the grafted copolymer

The grafted copolymer was crosslinked by heating in a glass oven under vacuum. The copolymer was heated at different temperatures for different times. The results are shown in the Table 3.9.

From Table 3.9., it is certain that crosslinking occurred under these reaction conditions. However, although the obtained material crosslinked at temperature higher than 215°C is water insoluble, its properties deteriorate at 100%RH or in pure water. Based on the copolymer TGA data, discussed in the next chapter, the copolymer decomposes or crosslinks on the benzyl groups above 215°C. When copolymer was crosslinked at 210°C, the generated crosslinked copolymer retained its properties; this will be discussed in the next chapter.
Table 3.9. Summary of crosslinking conditions for P10F1-g-Bn27% (4-46) and results.

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Condition</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250°C for 1 h at 60 mtorr</td>
<td>The material is brittle when dry, but had good physical properties at high RH. The film broke in pure water.</td>
</tr>
<tr>
<td>2</td>
<td>250°C for 2 h at 84 mtorr</td>
<td>The material is brittle when dry, but had good physical properties at high RH. The film broke in pure water.</td>
</tr>
<tr>
<td>3</td>
<td>225°C for 1 h at 60 mtorr</td>
<td>The film had good physical properties below 97%RH. At 100%RH, the film became so soft it could not be peeled from the vial.</td>
</tr>
<tr>
<td>4</td>
<td>210°C for 3 h at 80 mtorr</td>
<td>The film had good physical properties at 100%RH. It could be peeled from the glass slide without tearing.</td>
</tr>
</tbody>
</table>

3.4. Conclusions

A designed possible comonomer using the fluorenyl group as a core and two bromobenzene-2,5-sulfonic acid units as end groups could not be made. The directly sulfonated fluorene compound 2,7-dibromofluorene-3,5-disulfonic acid dilithium salt (DBFDSA-Li) was synthesized and used in copolymerization reactions. High molecular weight copolymer, PxF1, was obtained and grafted with benzyl chloride, which was crosslinked to make water insoluble material.

The direct chlorosulfonation of 2,7-dibromofluorene compound gave a mixture of 2,7-dibromofluorene 3,5 and 3,6 disulfonic acid. In order to increase the yield of the 2,7-dibromofluorene-2,6-disulfonic acid, the reaction yields as a function of temperature and time were screened. This sulfonation reaction is thermodynamically controlled: high temperature and long time increase the yield of 2,7-dibromofluorene-3,6-disulfonic acid compound. But the yield of 2,7-dibromofluorene-3,6-disulfonic acid is still low. 2,7-
dibromofluorene-3,5-disulfonic acid was isolated and used in the copolymerization reaction.

The copolymerization reaction was optimized by screening temperature, solvent, coordination reagent and drying method. The best conditions are DBPDSA-Li, DBFDSA-Li and copper dried separately under vacuum and then together under an argon stream at 200°C and copolymerized in NMP at 200°C using 2,2'-bipyridine (BPy) as a coordination reagent. The function of BPy is not only as a coordination reagent to increase the copolymer solubility but also probably to complex with cuprous ion as a catalyst, which needs further study. The copolymer composition was analyzed by NMR and elemental analysis. The active end 2-position Br in DBFDSA-Li prefers to react with DBPDSA-Li or itself, but not with the 7-position Br.

In order to deprotonate the methylene in DBFDSA, the pKa of DBFDSA was measured by titration. Several bases were screened in the model alkylation reaction. It turned out the bulky base potassium tert-butoxide or saturated NaOH aqueous solution can give the twice alkylated fluorene monomer in high yield. Potassium tert-butoxide can deprotonate the fluorene compound without attacking alkyl halogen; saturated NaOH aqueous solution is not mutually soluble with DMSO. However, copolymer with a low degree of grafting was obtained when our best grafting reaction conditions were used. The reason is that water exists in the DMSO solution. A new drying method needs to be developed in order to obtain fully alkylated copolymer.

The properties of these copolymers and their corresponding grafted and crosslinked copolymers are described in detail in Chapter 4.
3.5. References


Chapter 4

Characterization and properties of copolymers and grafted copolymers

4.1. Introduction

Chapter 3 focused on the design and optimization of the synthesis of high molecular weight copolymer, poly(phenylene disulfonic acid_co-fluorene disulfonic acid) (PxF1) using the Ullmann coupling reaction. In order to make water insoluble material, alkylation and crosslinking of the PxF1 copolymer also were studied. In order to be a candidate for a proton exchange membrane, the structure and thermal, mechanical and electrochemical properties of this polymer need to be further studied.

As a rigid rod polyelectrolyte, the copolymer exhibits abnormal viscosity behavior: reduced viscosity showed an upturn as concentration decreased. A linear relationship between $C^{0.5}$ and reduced viscosity was found and a possible explanation is given.

This type of rigid rod, liquid crystal copolymer can form nano-channels due to steric hindrance between bulky substituents, called “frozen-in free volume”. The “frozen-in” free volume was studied using Wide Angle X-ray Diffraction (WAXD) combined with measurements of volume and weight increase of the copolymers as a function of relative humidity.
Other properties relating to the application of this material as proton exchange membranes, such as proton conductivity, mechanical properties and thermal properties have also been measured and are discussed in this chapter.

4.2. Experimental section

4.2.1. Materials

Copolymer PxF1, grafted copolymer PxF1-g-Bn and crosslinked copolymer PxF1-g-Bn xlinked were prepared (Chapter 3). PxF1-Li was converted to the acid form using a proton exchange column. The copolymer and grafted copolymers were cast from water or water/methanol solutions in a Teflon® dish. The copolymer was crosslinked by heating grafted copolymer PxF1-g-Bn strips (0.3 X 3 cm) at 210°C under high vacuum for 3 h.

All other reagents were purchased from the Aldrich Chemical Co. and used without further purification.

4.2.2. Characterization techniques

4.2.2.1. Viscosity measurements

The intrinsic viscosity was determined using the Ubbelohde capillary viscometer, shown in Figure 4.1.

![Illustration of the Ubbelohde capillary viscometer](image)

**Figure 4.1.** Illustration of the Ubbelohde capillary viscometer
Chapter 4

The liquid initially drawn into the small upper bulb is not connected to the reservoir as it flows down the capillary during measurement. Connected with the pressure-equalization tube, this ensures that the only pressure difference between the top of the bulb and the bottom of the capillary is that due to the hydrostatic pressure.

According to Poiseulle’s law, viscosity is expressed by Equation 4.1:

\[ \eta = \frac{\pi R^4 P}{8Ql} \]  

(Equation 4.1)

\( Q \) is the volumetric flow rate through the capillary in cm\(^3\)/sec., \( P \) is the pressure head forcing the liquid through the capillary, \( R \) is the radius of the capillary; \( l \) is the length of the capillary; \( \eta \) is the viscosity. Because the bulb volume in the Ubbelohde viscometer is fixed, the flow rate, \( Q \), is inversely proportional to the time between marks. \( P \), the hydrostatic pressure is proportional to the density of the fluid. Thus, the above equation can be simplified to the following relationship:

\[ \eta \propto t \rho \]

\( \rho \) is the density of the fluid and \( t \) is the flowtime. For the capillary viscometer, what needs to be measured is the time it takes a volume of polymer solution or pure solvent to flow through a thin capillary. According to the Poiseulle’s law, the following relationships are obtained.

\[ t_{solvent} = \frac{\eta_{solvent}}{\rho_{solvent}} \]

\[ t_{sol'n} = \frac{\eta_{sol'n}}{\rho_{sol'n}} \]
The relative viscosity is defined as the ratio, $\eta_{soln}/\eta_{solvent}$. Because the concentration of polymer solution measured is very dilute, the approximate value of $\rho_{soln}/\rho_{solvent}$ is 1. Thus, the relative viscosity is written as a simple ratio (Equation 4.2).

$$\eta_r = t_{soln}/t_{solvent}$$  
(Equation 4.2)

A “specific viscosity” also is defined as the fractional change in viscosity upon addition of polymer (Equation 4.3):

$$\eta_{sp} = \frac{\eta_{soln} - \eta_{solvent}}{\eta_{solvent}}$$  
(Unitless)  
(Equation 4.3)

The Huggins (Equation 4.4) and the Kramer equation$^1$ (Equation 4.5) are used, shown below:

$$\eta_{sp}/C = [\eta] + K'[\eta]^2 C$$  
(Equation 4.4)

$$\ln(\eta_r)/C = [\eta] + \beta[\eta] C$$  
(Equation 4.5)

When $\eta_{sp}/C$ and $\ln(\eta_r)/C$ are plotted versus concentration, the two lines have the same intercept, which means these two lines have the same $[\eta]$ at zero concentration. This $[\eta]$ is called the intrinsic viscosity (Equation 4.6).

$$[\eta] = \lim_{c\to0} \frac{\eta_{sp}}{C} = \lim_{c\to0} \frac{\ln\eta_r}{C}$$  
(Equation 4.6)

**General viscosity measurement procedure:** 50 mg copolymer (weight after subtracting absorbed water) was dissolved in 10 mL D. I. water. After the copolymer dissolved, the solution was filtered using a 0.45 μm syringe filter. Flow times were measured at six different concentrations (0, 0.5, 0.4, 0.3, 0.2, 0.1 g/dL) at least three times (accuracy of ± 0.5 s) for each concentration. The specific viscosity $\eta_{sp}$ then could be calculated using the Equations 4.2 and 4.3. $\eta_{sp}/C$ versus concentration, C, was plotted.
4.2.2.2. Polarizing Optical Microscopy (POM)

Two types of sample were prepared for the POM. One was a dry film and the other was a copolymer solution. The solution sample was prepared by dissolving copolymers in water to give a viscous solution (20~30 g/dL). This viscous solution was dropped on a glass slide and covered with a cover glass. The dry sample was made from the solution sample by putting a drop on a glass slide and drying at room temperature overnight. All the images were recorded using a Leica DM 2500m polarized light microscopy equipped with a CCD camera.

4.2.2.3. One dimensional Wide Angle X-ray Diffraction (WAXD)

The WAXD measurement linear $\theta/2\theta$ X-ray intensity scans were recorded using a Rigaku diffractometer with CuK$\alpha$ Radiation (1.542 Å) with a long fine focus mode. Setting values of each WAXD parameter are listed in Table 4.1.

Table 4.1. Setting parameters for WAXD measurements. Div. slit and Div. H. L. slit are the height and width of the slit, respectively. Rec. slit and Sct. slit are the recording slit and scattering slit, respectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Setting values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start angle (°)</td>
<td>2.0</td>
</tr>
<tr>
<td>Stop angle (°)</td>
<td>35.0</td>
</tr>
<tr>
<td>Power</td>
<td>30kV/30mA</td>
</tr>
<tr>
<td>Sampling Width (°)</td>
<td>0.1</td>
</tr>
<tr>
<td>Scanning speed (%/min)</td>
<td>0.1</td>
</tr>
<tr>
<td>Div. slit (mm)</td>
<td>2.0</td>
</tr>
<tr>
<td>Div. H. L. slit (mm)</td>
<td>5.0</td>
</tr>
<tr>
<td>Rec. slit (mm)</td>
<td>Open</td>
</tr>
<tr>
<td>Sct. Slit (mm or °)</td>
<td>Open</td>
</tr>
</tbody>
</table>
PxF1 copolymer films were cast from water solutions in a Teflon® dish. In order to measure the orientation of the copolymer chains, the PxF1 films were equilibrated at 0%, 11.3%, 32.8%, 54.4%, 66.0%, 75.3% relative humidity. The 0% relative humidity was controlled by drying the film in a vacuum oven at 110°C for 24 h. Other relative humidities were generated by using different saturated inorganic salt solutions (Table 4.2):

**Table 4.2.** Saturated solutions used to generate listed relative humidity at 25°C

<table>
<thead>
<tr>
<th>Salt</th>
<th>LiCl</th>
<th>KOAc</th>
<th>MgCl₂</th>
<th>Mg(NO₃)₂</th>
<th>NaNO₂</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity (% at 25°C)</td>
<td>11.3</td>
<td>22.5</td>
<td>32.8</td>
<td>54.4</td>
<td>66.0</td>
<td>75.3</td>
</tr>
</tbody>
</table>

In order to lock the water in the films, after equilibration in the relative humidity chamber, films were sealed immediately between two pieces of food wrap films (polyvinyl film, ~16 μm). WAXD data were collected in transmission and reflection modes.

Copolymer WAXD data were loaded into ACD Labs curve processing software. Peaks were labeled and peak heights and areas were calculated by curve deconvolution. d spacings were calculated using Bragg’s law (Equation 4.7).

\[
d = \frac{\lambda}{2\sin(\theta)}
\]  

(Equation 4.7)

\(2\theta\) was obtained from the peak positions of the deconvoluted curves; \(\lambda\) is 1.542 Å for CuKα radiation. The standard deviation of the d spacing changes with relative humidity, ±deviations in \(2\theta\) for all deconvoluted peaks was defined as half of FWHH (full width at half height), and the values in Å were calculated from the ±deviations of \(\theta\) for each peak, using Bragg’s law.
4.2.2.4. Water uptake

4.2.2.4.1. Water content evaluation

Weighing bottles with a ground glass joint and cap were placed in an oven at 110°C for 24 h. Bottles were taken out of the oven quickly and cooled in desiccators containing dried molecular sieves (4Å). The weight of the weighing bottle and cap was measured before putting dried film in it. After the film and pre-weighed bottle were vacuum dried at 110°C for 24 h and cooled in desiccators with molecular sieves, the dried film was weighed in the pre-weighed capped weighing bottle and the weight of the dried film was calculated. The weight of films at different relative humidities was obtained using the following procedure: weighing bottles were equilibrated for 24 h at a given relative humidity, weighed, re-equilibrated containing a dried, weighed film for another 24 h and then reweighed. The different saturated salt solutions used for humidity control are shown in Table 4.2. The weight fraction of water uptake (WU) at each humidity was calculated using Equation 4.8. \( W_1 \) is the weight of the dried polymer film and \( W_2 \) is the weight of the humidified polymer film after equilibration.

\[
WU = \frac{(W_2 - W_1)}{W_1} \quad \text{(Equation 4.8)}
\]

4.2.2.4.2. Lambda (\( \lambda \)) measurement

Lambda (\( \lambda \)), the number of water molecules per acid group in the membrane was calculated using \(^1\)H NMR and sulfonic acid titration.

Polymer films in vials were dried in a vacuum oven at 110°C for 24 h. The vials were taken out, capped quickly and cooled in a desiccator containing dried molecular sieves (4Å) to room temperature. After cooling, the vials were opened; the NMR solvent was added quickly and the vials were recapped. Two standard NMR solvents: D\(_2\)O with
dioxane as an inner standard reference and CD$_3$OD with few drops of D$_2$O were used in these NMR experiments. After films were dissolved, the solution was transferred quickly to an NMR tube. The water content was calculated by integration of the OH peak and subtracting the OH area of the standard solvent $^1$H NMR spectrum; the ratio of sulfonic acid residues was calculated from the integration of the aromatic hydrogen peaks. $\lambda_0$ ($\lambda$ at 0%RH) was obtained as the quotient of the area of water molecules in the polymer film and the area of sulfonic acid residues.

The polymer equivalent weight was measured by titration with NaOH standard solution. Sodium hydroxide solution was standardized as follows: 2.0 mL of potassium hydrogen phthalate aqueous solution (0.103M) and bromothymol blue alcohol solution (2 to 3 drops) as an endpoint indicator were put into a beaker. Sodium hydroxide aqueous solution (about 0.01M) was placed in a 50mL burette and the potassium hydrogen phthalate solution was titrated drop by drop with stirring until a permanent blue was shown. The molar concentration of the sodium hydroxide solution was calculated from the volume of sodium hydroxide solution used.

Films were dried and their weights were recorded as described in the water uptake section. Weighed, dried films were put into conical flasks and 5 mL of 2M aqueous sodium chloride was added to each bottle. The resulting solution was titrated with the standardized sodium hydroxide solution using bromothymol blue alcohol solution as the end-point indicator. The equivalent weight of the polymer was calculated from the titration volume. Combining the water uptake and NMR data, $\lambda$ was calculated using Equation 4.9.

$$\Lambda = \frac{WU}{18[SO_3^-]} + \lambda_0$$  
(Equation 4.9)
Where WU is the water uptake (unitless), calculated from Equation 4.8, 18 is the molecular weight of the water, \([\text{SO}_3^-]\) is the moles of sulfonic acid per gram of polymer or copolymer at 0%RH, determined from the titration with the standardized sodium hydroxide solution. \(\lambda_0\) is lambda at 0%RH, determined by \(^1\)H NMR.

### 4.2.2.5. Dimensional change

The length, width and thickness of the polymer films were measured as a function of relative humidity. The polymer film was dried in a vacuum oven at 110°C and the length (L\(_{\text{dry}}\)), width (W\(_{\text{dry}}\)) and thickness (T\(_{\text{dry}}\)) were measured. Subsequently, the dried film was put in different relative humidity chambers with the humidity controlled by the saturated salt solutions shown in Table 4.2, and equilibrated for 24 h. Corresponding three dimensions (L\(_{\text{wet}}\), W\(_{\text{wet}}\) and T\(_{\text{wet}}\)) were measured immediately.

The method for the three dimensional measurements is described as follows. Films were put between two glass slides. The thickness of these two glass slides with and without the film was measured by micrometer. The thickness of the film is the difference between these two thicknesses (slides with a film and slides without a film). Photos of the film between two glass slides were taken with a scale behind it. Obtained pictures were enlarged in the computer and length and width were measured with calipers. Using these data, L\(_{\text{re}}\), W\(_{\text{re}}\), T\(_{\text{re}}\) and \(\Delta V\), defined below, were calculated.

\[
L_{\text{re}} = \frac{L_{\text{wet}}}{L_{\text{dry}}} \times 100\% \quad \text{(Equation 4.10)}
\]

\[
W_{\text{re}} = \frac{W_{\text{wet}}}{W_{\text{dry}}} \times 100\% \quad \text{(Equation 4.11)}
\]
\[ T_{\text{re}} = \frac{T_{\text{wet}}}{T_{\text{dry}}} \times 100\% \]  
(Equation 4.12)

\[ \Delta V = \frac{(L \cdot W \cdot T)_{\text{wet}}}{(L \cdot W \cdot T)_{\text{dry}}} - 1 \] \times 100\%  
(Equation 4.13)

### 4.2.2.6. Proton conductivity measurements

#### 4.2.2.6.1. Theoretical base

**Scheme 4.1.** Equivalent circuit for an AC impedance conductivity measurement

The proton conductivity of a thin polymer membrane is evaluated using AC measurements not only in order to avoid electrochemical reactions but also to avoid introducing the extra impedance from the electrode\(^2\). When the membrane is in contact with the metal electrodes, interfacial impedance is generated at the metal/ionomer interface. The extra impedance can affect the accuracy of membrane resistance measurement. This phenomenon is usually modeled using the equivalent circuit shown in...
Scheme 4.1, where the resistors and capacitors in parallel represent the interfacial impedance between the electrode and membrane.

The electrode interfaces can be modeled as a resistor with high impedance (R₁ and R₃, where R₁ ≈ R₃) in parallel with a capacitor (C₁ and C₃, where C₁ ≈ C₃). The membrane is modeled as a simple resistor (R₂). The electrodes and membrane are modeled as impedances in series.

The resistor in series with the two interfacial resistor/capacitor impedances represents the resistance to the proton motion through the membrane. The impedance of a resistor is simply its resistance while the impedance of a capacitor can be calculated from the following equations:

\[ V = V_0 e^{j\omega t} \]
\[ j^2 = -1 \]

\[ Z'' = \frac{V}{I} \]

\[ I = \frac{dQ}{dt} = \frac{dCV}{dt} = \frac{CdV}{dt} = \frac{CdV_0 e^{j\omega t}}{dt} = j\omega CV \]

\[ Z'' = \frac{1}{j\omega C} \]

\[ (Equation 4.14) \]

Q is the electric charge in coulombs, \( \omega \) is the frequency at which the voltage is cycled in Hz and C is the capacitance in Farads. The resulting circuit can then be simplified to three impedances in series.

\[ Z = Z_1 + Z_2 + Z_3 \]

\[ Z_1 = Z_3 \]

The resulting impedance can be found from the following equations:
From the above equations, it is known that the impedance measured consists of two parts, \( \frac{R_2}{1 + (\omega C_1 R_1)^2} \), and \( R_2 \) which is the resistance of membrane. One method to eliminate the effect of \( \frac{R_2}{1 + (\omega C_1 R_1)^2} \), is to use high frequency. At the high frequency limit, the imaginary part of the equation becomes \( 1/\omega CR \), which tends towards zero. Thus, at high frequency the effect of the electrode/membrane contact impedance can be eliminated leaving only the membrane resistance, \( R_2 \). Normally, a four point probe is used to measure the membrane resistance. The corresponding proton conductivity can be calculated using Equation 4.16.

\[
\sigma = \frac{1}{K \ WT} \frac{L}{R_2} \\
\]  
(Equation 4.16)

\( \sigma \) refers to proton conductivity, S/cm; \( K \) is the resistance, \( R_2 \), obtained from the impedance measurement, \( L \) is the distance between the center two electrodes in cm; \( W \) is the width of the sample in cm and \( T \) is the thickness of the polymer film in cm. The value calculated from the dimensions of the film, \( (L/W*T) \) is typically known as the cell constant.

4.2.2.6.2. Conductivity measurement: experiment and instrument

In order to eliminate the interfacial impedance from the metal/ionomer interaction, a four–pole method was applied in the copolymer conductivity measurement.
Measurements were performed in a setup consisting of: (1) a custom made PTFE cell with four graphite electrodes enclosed in a stainless steel humidification chamber, (2) a heating oven with built-in temperature controller, and (3) a Solartron 1260 Frequency Response Analyzer (FRA) and a Solartron 1287 potentiostat. The AC impedance scans were performed over a frequency range of 1Hz to 20 KHz. The results were collected by Z-view and analyzed by Z-plot software.

Copolymer films were cut into approximately 3 cm by 0.2~0.3 cm strips. The width and thickness were measured before the strips were assembled into the configuration shown in Scheme 4.2.

![Scheme 4.2. Assembly of copolymer film/electrodes for conductivity measurements](image)

Graphite paper (Tonnen company, Japan) was chosen as the electrode material and stainless steel alligator clips were used to fix the film and act as electrical contact points. The two inner electrodes were spaced approximately 10 mm apart, the exact distance was measured 3 times and averaged before the conductivity measurement.
The cell temperature was set to 80°C and RH was controlled by placing a small container with a saturated salt solution inside the humidification chamber. The following salts were employed for humidity control (Table 4.3).

**Table 4.3. Saturated salt solutions used to control relative humidity at 80°C**

<table>
<thead>
<tr>
<th>Salt</th>
<th>LiCl</th>
<th>MgCl₂</th>
<th>K₂CO₃</th>
<th>NaBr</th>
<th>NaNO₃</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity, %</td>
<td>10.5</td>
<td>27.1</td>
<td>41.1</td>
<td>51.4</td>
<td>65.2</td>
<td>76.3</td>
</tr>
</tbody>
</table>

Prior to the impedance measurement, the strips assembly was equilibrated over 8 h at 80°C. The impedance of each copolymer film was measured using the AC impedance spectroscopic techniques: four-probe method in the frequency range from 1 Hz to 20 kHz at a constant voltage of 20 mV. The impedance of the film sample at controlled humidity and temperature can be measured by the way of a Nyquist plot. Both the real ($Z'$) and imaginary parts ($Z''$) of the components of impedance in the membrane sample were simultaneously measured over the frequency range. When the imaginary component containing both the inductive reactance and the capacitive reactance approaches zero at higher frequency, the real $Z'$-axis intercept is close to the ohmic resistance and can be considered as the ohmic resistance of a film sample, eliminating any effect of the resistance caused by the lead inductance and the stray capacitance.

At every relative humidity, the conductivity was measured several times to make sure the sample was fully equilibrated. The results were collected by Z-view and analyzed by Z-plot software. A typical impedance plot is shown in Figure 4.2. The polyelectrolyte resistance was usually determined from the high frequency intersection with the real axis in the impedance plot.
Figure 4.2. Impedance plot of P10F1-g-Bn37% film obtained from 4-probe impedance measurement at 27.1%RH and 80°C

Figure 4.3. Impedance plot of P10F1-g-Bn34% film obtained from 4-probe impedance measurement at 41.1%RH and 80°C
In cases when the impedance did not intersect the real axis, the curve was fitted by the Z-view program, which gave the low and high intercepts shown in the box in Figure 4.3. The high frequency intercept, which was close the real curve, was used as the resistance of the film.

The obtained resistance $K$, length, width and thickness of the film were put into Equation 4.16 and the conductivity of the sample was calculated.

4.2.2.7. Thermogravimetric analysis (TGA)

A TGA Q500 thermogravimetric analyzer were employed to assess thermal stability of the copolymer and the alkylated copolymer. All samples were run under N$_2$ atmosphere (60 mL/min) at 10$^\circ$C/min heating rates.

A sample was pre-dried under vacuum at 110$^\circ$C for 24 h and sealed in a vial. When the pan was tared and ready to load the sample, the vial was opened quickly and the sample was loaded on the TGA pan and heated from room temperature to 800$^\circ$C.

4.2.2.8. Mechanical testing

The samples used for Dynamic Mechanical Analysis (DMA) was approximately 26 mm long, 3 mm wide and 50~200 $\mu$m thick. Stress-strain experiments were performed using a TA Instruments Q800 under a N$_2$ atmosphere. The method used in this stress-strain test is a linear ramp at 0.05%/min to 25% with a 0.01 N pre-load.
4.3. Results and Discussion

4.3.1. Viscosity measurement

4.3.1.1. A general survey of normal polymer behavior in solution

Here is a general survey of the normal polymer behavior in solution, which is different from the copolymer PxF1 and its derivatives. Viscosity is an important parameter for polymer characterization which provides a way to obtain information about the relative molecular weight of the polymer and its solution properties. Several instruments can be used to measure viscosity. They are a) Capillary, b) Couette and c) Cone and Plate. The capillary is the most convenient and most used instrument. As mentioned in Section 4.2.1., in dilute solution, the relative viscosity can be obtained from a simple flow time ratio:

$$\eta_r = \frac{t_{\text{soln}}}{t_{\text{solvent}}}$$  \hspace{1cm} (Equation 4.2)

where \( t_{\text{soln}} \) and \( t_{\text{solvent}} \) are the flow times of solution and solvent, respectively. \( \eta_{sp} \) can be further obtained which is equal to \( \eta_r - 1 \). Using the Huggins’ (Equation 4.4) and the Kramer equation (Equation 4.5), two curves \( \eta_{sp}/C \) versus \( C \) and \( \ln(\eta_r)/C \) versus \( C \) are plotted. Intrinsic viscosity, property of the polymer chain itself, can be obtained by extrapolating the concentration to zero (Equation 4.6). A typical plot of the curves \( \eta_{sp}/C \) versus \( C \) and \( \ln(\eta_r)/C \) versus \( C \) is shown in Figure 4.4.

$$\eta_{sp}/C = [\eta] + K'[\eta]^2 C$$  \hspace{1cm} (Equation 4.4)

$$\ln(\eta_r)/C = [\eta] + \beta[\eta]^2 C$$  \hspace{1cm} (Equation 4.5)

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C} = \lim_{C \to 0} \frac{\ln\eta_r}{C}$$  \hspace{1cm} (Equation 4.6)
The intrinsic viscosity, $[\eta]$, can be further related to the polymer molecular weight using the Mark-Houwink equation (Equation 4.17).

$$[\eta] = KM^\alpha$$  \hspace{1cm} (Equation 4.17)

Thus, log-log plots of $[\eta]$ against molecular weight have an intercept $\log(K)$ and slope $\alpha$. The slope contains information about the shape of the molecules:

- $\alpha = 1/2 \Rightarrow$ flexible polymer chain in a theta solvent
- $0.5 < \alpha < 0.8 \Rightarrow$ flexible polymer chain in "good" solvent (excluded volume limit)
- $\alpha > 0.8 \Rightarrow$ "stiff" chain

$[\eta]$ is an intrinsic property of the polymer chain and is affected by the polymer conformation. The intrinsic viscosity of a given chain will be the same in all its theta solvents (a solvent in which polymer coils act like ideal chains). However, the value $[\eta]$
of a chain in a theta solvent will differ from that in a good solvent, because the chain is more expanded in a good solvent. Two different solvents induce very different polymer chain conformations.

4.3.1.2. Copolymers PxF1 and grafted copolymer PxF1-g-Bn behavior in solution

As rigid rod, liquid crystal polyelectrolytes, copolymer PxF1 and its derivatives exhibit abnormal solution behaviors: an upturn of the reduced viscosity with decreasing concentration (Figure 4.5).

**Figure 4.5.** Viscosity measurements of copolymers PxF1 and grafted copolymers PxF1-g-Bn in D. I. water at 35°C

Copolymers PxF1 and their corresponding grafted copolymers PxF1-g-Bn (Figure 4.5) exhibit an abnormal viscosity behavior in the measurement range (C = 0.5~0.1 g/dL), compared with the typical Huggins’ equation plot in Figure 4.4. This behavior is normally attributed to a polyelectrolyte effect caused by the repulsion from the like charges on the polymer chain. Normally, this effect can be eliminated by adding salt. The
counterions added can diffuse into the polymer matrix or domain, bond to the charges on the polymer chain and decrease the electrostatic repulsion. A linear plot of $\eta_{sp}/C$ versus $C$ is obtained. However, the solution viscosities of polyphenylene sulfonic acids (PBPDSA and PPDSA) synthesized in our group deceased when salts were added, but still kept the similar upturn trend, which cannot be explained by the polyelectrolyte effect.

In Figure 4.5, when the polymer concentration is reduced, the reduced viscosity increases. As the concentration drops, the reduced viscosity increases slowly at first; and then rises rapidly below a certain concentration. Copolymer P10F1, polymerized at 200°C has a higher viscosity than copolymer P20F1, polymerized at 170°C (see Sections 3.2.4.2.4. and 3.2.5.3.2.). After P10F1 was grafted with benzyl chloride, the obtained copolymers had higher viscosities than the starting polymer. The attached benzyl groups might interact by weak hydrophobic association, which would raise the viscosity of the grafted copolymer. (This could be tested by running viscosity measurements in methanol or ethanol.) The viscosity rise does not parallel the calculated grafting %. This is probably due to the difficulty in determining the exact degree of grafting by NMR. The spectrum shows broad peaks in addition to the well resolved ones, because the NMR solutions measured were too concentrated. Integration is not accurate since it is difficult to fit the base line exactly.

This abnormal behavior is true for all the polyphenylene sulfonic acids (PBPDSA and PPDSA) prepared in our group and other rigid rod poly(p-phenylene)s. For those rigid rod poly(p-phenylene)s containing carboxylic or sulfonic acid, the abnormal solution behavior was attributed to polymer aggregation. Rulkens et al. studied the solution behavior of a series of polyphenylene sulfonic acids, shown in Figure 4.6.
“Rulkens 2” and “Rulkens 3” in Figure 4.6. had solution behavior similar to that of the polyphenylene sulfonic acids synthesized in our group. Rulkens et al. proposed two aggregate structures to explain this abnormal solution behavior: double layered planar micelles and cylindrical micelles. They considered that the ionic concentration controlled polymer aggregation. Low ionic strength caused the dissociation of the polymer aggregates at low concentration which increased the solution viscosity. The salt content could decrease the electrostatic repulsion between the neighboring sulfonic acids, stabilize the cylindrical micelle and favor the formation of larger polymer aggregates.

Dr. Granados-Focil used the proposed planar micellar structure to explain the solution behavior of PBPDSA. The major difference between the solution viscosity behavior of PBPDSA and “Rulkens” is that PBPDSA still keeps the viscosity upturn trend after salt was added. Dr. Granados-Focil thought it was due to the chemical structure difference between those two types of polymers. Without alkyl chains in the polymer backbone, PBPDSA has no hydrophobic interactions between the polymer
chains and favors the planar lamellar structure over the cylindrical lamellae. A cartoon of the dissociation is shown in Scheme 4.3.

![Viscosity of PBPDsA-Na in water](image.png)

**Scheme 4.3.** Model of dissociation behavior of PBPDsA

The PBPDsA aggregates form anisotropic planar micelles with their longest axis being of similar length to that of single chain and a width that depends on the polymer concentration. As the polymer concentration decreases, these aggregates dissociate and the reduced viscosity increases.

However, the NMR spectrum of high molecular weight PBPDsA, Figure 2.17, showed narrow peaks which implied the polymer is dissociated in NMR solution with concentration around 2.0 g/dL. Thus, Dr. Granados-Focil’s aggregation model for the abnormal solution behavior is not correct. Further study is needed in the future.

In 1951 Fuoss et al.\(^6\) proposed a phenomenological equation (Equation 4.18) for a polyelectrolyte polymer in semi-dilute and moderately dilute “salt-free” solutions. Although this equation cannot be used to explain the solution behavior of the
polyphenylene synthesized in our group, it gives a relationship between $\eta_{sp}$ and $C^{0.5}$.

$$\frac{\eta_{sp}}{C} = \frac{A}{1 + B\sqrt{C}} = \frac{[\eta]}{1 + B\sqrt{C}}$$  \hspace{1cm} (Equation 4.18)

Figure 4.7 is a plot of $\eta_{sp}/C^{0.5}$ versus $C^{0.5}$ aqueous PPDSA solutions$^{3b}$.

![Figure 4.7](image)

*Figure 4.7. Plot of $\eta_{sp}/C^{0.5}$ versus $C^{0.5}$ of aqueous PPDSA solutions in D. I. water at 35°C$^{3b}$*

Similar straight lines were obtained when $\eta_{sp}/C^{0.5}$ or $\ln(\eta_{sp})/C^{0.5}$ for PxF1 and PxF1-g-Bn versus $C^{0.5}$ were plotted (Figures 4.8 & 4.9). When the lines in Figures 4.8 & 4.9 are compared, their slopes are related to the copolymer viscosity: the high viscosity copolymer has a higher slope. Dr. Kang$^{3b}$ proposed a modified Huggins equation (Equation 4.19) to rationalize the abnormal solution behavior of the PPDSA. However, the meanings of the slope and intercept in Equation 4.19 are still unclear.

$$\frac{\eta_{sp}}{\sqrt{C}} = \frac{[\eta]}{\sqrt{K}} + \frac{k[\eta]^2}{K}\sqrt{C}$$  \hspace{1cm} (Equation 4.19)
Figure 4.8. Plot of $\eta_{sp}/C^{0.5}$ versus $C^{0.5}$ for PxF1 and PxF1-g-Bn solutions in D. I. water at 35°C

Figure 4.9. Plot of $\ln(\eta)/C^{0.5}$ versus $C^{0.5}$ of PxF1 and PxF1-g-Bn solutions in D. I. water at 35°C
4.3.2. Polarizing Optical Microscopy (POM)

As polymers with rigid rod structures, PxF1 and PxF1-g-Bn are expected to form lyotropic liquid crystalline phases. The mesophase identification of the copolymer can give us macroscopic information about the liquid crystal structure. There are four classes of liquid crystalline structures: a) Cholesteric, b) Smectic, c) Discotic, d) Nematic. The most widely used method is optical microscopy between crossed polarizers to identify the texture of each type of liquid crystal phase. Many liquid crystalline polymers exhibit Schlieren texture. According to the number of brushes meeting at a point (disclinations) displayed in Schlieren texture, nematic and smectic phases can be distinguished. The declination strength is calculated from Equation 4.20.

\[ |s| = \frac{\text{number of brushes meeting}}{4} \]  \hspace{1cm} (Equation 4.20)

The sign of \( s \) is determined by its motion versus that of the direction of the rotated polarizers: the same is positive and the opposite is negative. Mesophase identification by this procedure requires that

\[ s = \pm \frac{1}{2}; \pm 1 \text{ Nematic;} \]
\[ s = \pm 1 \text{ Smectic} \]

Nematic and smectic phases also can be distinguished by DSC on the basis of the magnitude of the enthalpy changes accompanying the transition to the isotropic phase. Typical Schlieren texture of a nematic structure and its corresponding disclinations are shown in Figure 4.10.
Figure 4.10. Typical Schlieren texture in a nematic liquid crystal\textsuperscript{7}. (Reprinted with permission from author)

Figure 4.11. POM photos of films and solutions: a) Film cast from P10F1 (4-28-4-1) aqueous solution. The image is seen under polarized light (X 500).
b) Figure 4.11. POM photos of films and solutions: b) 30 g/dL P10F1 (4-28-4-1) aqueous solution. The image is seen under polarized light (X 500).

c) Figure 4.11. POM photos of films and solutions: c) Film cast from P10F1-g-Bn27% (4-46). The image is seen under polarized light (X 500).
Figure 4.11. POM photos of films and solutions: d) 30 g/dL P10F1-g-Bn27% (4-46) aqueous solution. The image is seen under polarized light (X 500).

Optical microscopy images of P10F1 (4-28-4-1) and its grafted copolymer P10F1-g-Bn27% (4-46) films and aqueous solutions were recorded under polarized light, (Figure 4.11). Disclinations where two brushes meet are identified by an arrow; the strength of these disclinations equals ±½.

In Figure 4.11, images of copolymer P10F1 and grafted copolymer P10F1-g-Bn27% show typical nematic Schlieren textures. However, this texture was only visible in sheared solutions with a polymer concentration above 20 g/dL. It disappeared when the shearing stopped. When the polymer concentration was below 20 g/dL, a biphasic structure was seen, partly liquid crystal and partly true solution (Figure 4.12.).
Figure 4.12. 20 g/dL P10F1 (4-28-4-1) aqueous solution, seen under cross polarized light (X 200)

A typical nematic liquid crystal local mesophase topology is shown in Figure 4.13. The nematic phase has no positional order, but has orientational order; polymer chains lie parallel to each other in one dimension at equilibrium. The copolymer orientation will be further discussed in the dimensional change and X-ray diffractogram sections.

Figure 4.13. Nematic liquid crystal structure
4.3.3. Evaluation of water uptake and lambda (λ)

For ionomers used as proton exchange membranes, the water held by the hydrophilic functional group by hydrogen bonding and hydronium ion formation is important for proton transfer and conductivity. Lambda (λ), the number of water molecules per acid group in the membrane, was calculated from the water content. According to Equation 4.9, several parameters: water uptake, $\lambda_0$ and [$\text{SO}_3^-]$ (the moles of sulfonic acid per gram copolymer at 0%RH) need to be measured in order to calculate $\lambda$.

![Figure 4.14. Water uptake of PxF1 and PxF1-g-Bn as a function of relative humidity, at room temperature](image)

The water uptake was measured following the procedure in Section 4.2.2.4.1. Copolymer films were dried in a vacuum oven at 110°C for 24 h and weighed. Films were equilibrated for 24 h in humidity chambers with the humidity controlled by a saturated salt solution, see Table 4.2, and weighed again. The difference in weight was
attributed to absorbed water. Results of the water content evaluation are expressed as a plot of water uptake versus relative humidity, presented in Figure 4.14.

λ₀ was calculated from the NMR spectra of PxF1 and PxF1-g-Bn in D₂O (dioxane as inner reference) and CD₃OD (few drops D₂O). λ₀, the water molecules per sulfonic acid group in the copolymer at 0%RH, was obtained based on the integration of hydrogen areas from water and from the aromatic hydrogens (see Section 4.2.2.4.2). The calculated λₖᵋs are presented in Table 4.4.

Table 4.4. λ₀ of vacuum dried copolymers measured by NMR

<table>
<thead>
<tr>
<th>Solvent/Polymer</th>
<th>P10F1</th>
<th>P10F1-g-Bn34%</th>
<th>P10F1-g-Bn37%</th>
<th>P10F1-g-Bn27%</th>
<th>P20F1</th>
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</thead>
<tbody>
<tr>
<td>λ₀ (Methanol-d₆ )</td>
<td>1.14</td>
<td>1.47</td>
<td>1.22</td>
<td>1.15</td>
<td>0.92</td>
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<tr>
<td>λ₀ (D₂O )</td>
<td>1.13</td>
<td>1.26</td>
<td>1.24</td>
<td>1.20</td>
<td>0.70</td>
</tr>
<tr>
<td>λ₀ (Average)</td>
<td>1.14</td>
<td>1.37</td>
<td>1.23</td>
<td>1.18</td>
<td>0.81</td>
</tr>
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</table>

Table 4.5. [SO₃⁻] and equivalent weight of dried copolymers measured by titration

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>NaOH Concentration (mol/L)</th>
<th>NaOH mL</th>
<th>Copolymer Wt., mg</th>
<th>[SO₃⁻] (meq/g)</th>
<th>Equivalent Weight</th>
<th>λ₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>P10F1 (4-28-4-1)</td>
<td>0.01004</td>
<td>18.18</td>
<td>25.3</td>
<td>7.21</td>
<td>139</td>
<td>1.14</td>
</tr>
<tr>
<td>P10F1-g-Bn37% (4-41)</td>
<td>0.01004</td>
<td>17.22</td>
<td>26.1</td>
<td>6.62</td>
<td>151</td>
<td>1.47</td>
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<tr>
<td>P10F1-g-Bn34% (4-39)</td>
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<td>6.5</td>
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<td>P10F1-g-Bn27% (4-46)</td>
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<td>1.15</td>
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<td>P20F1 (4-75-2)</td>
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<td>39.5</td>
<td>7.26</td>
<td>138</td>
<td>0.92</td>
</tr>
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</table>
Figure 4.15. Lambda as a function of relative humidity for PxF1 and PxF1-g-Bn at 25°C and Nafion117® at 30°C

\[ [\text{SO}_3^-] \] is the moles of sulfonic acid per gram of dry polymer film (0%RH), which was measured by titration. \([\text{SO}_3^-]\) values for the copolymers are shown in Table 4.5. Combining all the parameters listed above, lambdas of each copolymer at different relative humidities were calculated using Equation 4.9 and are plotted in Figure 4.15.

Calculated \(\lambda\)s are higher than those of Nafion117® over the whole relative humidity range, shown in Figure 4.15, which can result in higher proton mobility and higher proton conductivity. The grafting seems to inject more free volume into the polymers, possibly by decreasing crystallinity. \(\lambda\) increases with increase of copolymer grafting degree.
4.3.4. Dimensional changes with water uptake

Dimensions, divided by their dry values as a function of relative humidity, are given in Table 4.6 as percentages. P10F1, P10F1-g-Bn and crosslinked P10F1-g-Bn dimensional changes are anisotropic (Figure 4.16). If the polymer chain is parallel to the XY plane and there are no swelling restrictions from oppositely oriented domains, the X or Y dimensional change should be the square root of the Z change. If the average chain orientation is not horizontal, the film should swell less in the Z direction and more in the X and Y directions. Different copolymers give different relationships between Z change and those in the X and Y directions (Table 4.6). For P10F1, Z change is larger than that in Y direction, less than that in X direction. For P10F1-g-Bn27%, Z change is larger than that in X and Y direction. For crosslinked P10F1-g-Bn27%, the Z change is smaller than those in the X and Y directions. Within experimental error, the changes of the X, Y and Z directions in the uncrosslinked films are almost the same except at 75%RH.
Table 4.6. Dimensional changes of copolymer as % of dried film dimensions a) P10F1 (4-28-4-1) b)P10F1-g-Bn27% (4-46) c) crosslinked P10F1-g-Bn27% (4-46)

a)

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<tr>
<th>Relative humidity</th>
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<th>22.5%RH</th>
<th>32.8%RH</th>
<th>54.5%RH</th>
<th>75.3%RH</th>
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<tr>
<td>X</td>
<td>100%</td>
<td>108%</td>
<td>109%</td>
<td>110%</td>
<td>115%</td>
<td>123%</td>
</tr>
<tr>
<td>Y</td>
<td>100%</td>
<td>106%</td>
<td>107%</td>
<td>108%</td>
<td>114%</td>
<td>125%</td>
</tr>
<tr>
<td>Z</td>
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<td>106%</td>
<td>108%</td>
<td>109%</td>
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b)

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<td>108%</td>
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<tr>
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<td>110%</td>
<td>112%</td>
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<tr>
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<td>111%</td>
<td>114%</td>
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<tr>
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<td>142%</td>
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<td>4.58</td>
<td>5.91</td>
<td>8.16</td>
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c)

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<th>32.8%RH</th>
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<th>85.0%RH</th>
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<td>Y</td>
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<td>108%</td>
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<td>105%</td>
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<td>108%</td>
<td>109%</td>
<td>138%</td>
<td>181%</td>
<td>185%</td>
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<tr>
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<td>161%</td>
<td>251%</td>
<td>538%</td>
<td>567%</td>
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Figure 4.16. Dimensional changes of copolymer films versus relative humidity. a) P10F1 (4-28-4-1).

Figure 4.16. Dimensional changes of copolymer films versus relative humidity. b) P10F1-g-Bn27% (4-46).
4.3.5. Wide Angle X-ray Diffraction (WAXD)

Copolymer P10F1 (4-28-4-1) and grafted copolymer P10F1-g-Bn27% (4-46) films conditioned at different relative humidities were sealed in food wrap film (polyvinyl chloride film, 16μm) and WAXD scans were run. WAXD scans for the food wrap in transmission and reflection modes are shown in Figure 4.17. Three very weak peaks were found at around 20 degrees in the transmission mode; five diffraction peaks (A, D1, D2, E, G) were found in the reflection mode. Figures 4.18 and 4.19 a) and b) show the WAXD scans of the copolymer P10F1 (4-28-4-1) and graft copolymer P10F1-g-Bn27% (4-46) in reflection and transmission modes, respectively. The d spacings and their “standard deviation” are given in Tables 4.7 & 4.8. Seven peaks (A, B, D1, D2, E, F, G) were assigned in the reflection mode and five peaks (B, C, D, E, F) were assigned in the transmission mode.
Figure 4.17. WAXD diffractograms of food wrap in transmission mode and in reflection mode (uneven surface, one flat layer and two flat layers)

Peak A is seen in the copolymer and food wrap reflection mode. At some humidity, peak A disappeared. When one or two layers of food wrap films were stretched carefully and flattened, the intensity of Peak A decreased dramatically in the reflection mode, Figure 4.17. It means Peak A was generated by the uneven surface of food wrap film.

Compared with other peaks, peak B is very sharp both in copolymer reflection and transmission modes. Only peak B depends on relative humidity; the other peaks do not change. As the relative humidity increases, the 2 theta angle of the B peak decreases. Peak B intensity is much higher in the transmission mode than in the reflection mode.

Other peaks (D1, D2, E, G) are found both in the food wrap reflection mode and copolymer WAXD profiles: Peaks D1, D2 and G are seen in the food wrap reflection mode spectrum and Figure 4.18 & 4.19 a) and b); peaks C and D are seen only in Figure 4.18 & 4.19 b). When the peak positions and intensities in Figures 4.17, 4.18 and 4.19 are compared, peaks D1, D2 and G are probably from the food wrap film.
Figure 4.18. WAXD diffractograms of copolymer P10F1 (4-28-4-1): a) in reflection mode b) in transmission mode
As shown in Tables 4.7 & 4.8, the B peak d spacings increase with increasing relative humidity. The film absorbs water and the distance between the polymer chains
increases. The different relative peak intensities between the reflection and transmission mode are related to the average molecular orientation. If the molecules were oriented perpendicular to the film surface, the B peaks would be very small to non-existent in the reflection mode. If the molecular domains are parallel to the film surface but randomly oriented in the X, Y directions, the interchain spacing reflection would be visible in both WAXD scans. There can be no reflection from domains oriented at angles other than 0 or 90° to the Z direction. The strong Peak B intensity in transmission mode and weak low angle reflections imply that the polymer molecules were oriented mainly perpendicular to the film surface.
Table 4.7. WAXD peak data for copolymer P10F1 (4-28-4-1) in a) reflection mode and b) transmission mode. ±deviation in degrees was estimated using 0.5*FWHH for each deconvoluted peak, d(Å) was calculated using Bragg’s law.

a)

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<th>Peak</th>
<th>RH%</th>
<th>2 theta (º)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0</td>
<td>10.5±2.9</td>
<td>8.4±2.3</td>
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<tr>
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<td>8.8±0.8</td>
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<tr>
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<td>F</td>
<td>0</td>
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b)

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<th>d-space Å</th>
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<td>3.2±0.3</td>
</tr>
<tr>
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<td>28.4±3.0</td>
<td>3.1±0.3</td>
</tr>
<tr>
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<td>32.8</td>
<td>27.8±3.0</td>
<td>3.2±0.3</td>
</tr>
<tr>
<td></td>
<td>54.4</td>
<td>28.1±3.0</td>
<td>3.2±0.3</td>
</tr>
<tr>
<td></td>
<td>75.3</td>
<td>27.7±3.0</td>
<td>3.2±0.3</td>
</tr>
</tbody>
</table>
Table 4.8. WAXD peak data for copolymer P10F1-g-Bn27% (4-46) in a) reflection mode and b) transmission mode. ±deviation in degrees was estimated using 0.5*FWHH for each deconvoluted peak, d(Å) was calculated using Bragg’s law.

<table>
<thead>
<tr>
<th>Peak</th>
<th>RH%</th>
<th>2 theta (º)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
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<td>9.2±1.0</td>
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<td>3.4±0.3</td>
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<td>27.4±2.7</td>
<td>3.3±0.3</td>
</tr>
<tr>
<td></td>
<td>54.4</td>
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<td>3.3±0.4</td>
</tr>
<tr>
<td></td>
<td>75.3</td>
<td>27.2±2.7</td>
<td>3.3±0.3</td>
</tr>
</tbody>
</table>

b)

<table>
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<th>2 theta (º)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
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<td>75.3</td>
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<td>6.5±1.4</td>
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<td>11.3</td>
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<td>54.4</td>
<td>28.3±3.0</td>
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<td>75.3</td>
<td>28.6±3.0</td>
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</tr>
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4.3.6. Density of the absorbed water in PxF1 and PxF1-g-Bn at different humidity

The copolymer density as function of relative humidity for PxF1 and PxF1-g-Bn can be obtained from the weights and volumes of the films. According to the weight of copolymer, Figure 4.14, the volume of copolymer, Table 4.6, and [SO₃⁻], Table 4.7,
combined with the density, \( d \), of the copolymer measured at 0\%RH, the equivalent weights (EW) and molar volumes of the films were calculated, Tables 4.9 a) and b).

**Table 4.9. Density, molar volume and weight change of a) P10F1 (4-28-4-1) b) P10F1-g-Bn27\% (4-46)**

a)

<table>
<thead>
<tr>
<th>%RH</th>
<th>( \lambda )</th>
<th>WU</th>
<th>V</th>
<th>d (g/mL)</th>
<th>[SO(_3^\text{−})] (meq/g)</th>
<th>EW (g per mol of SO(_3^\text{H}))</th>
<th>Molar volume (cc/ SO(_3^\text{H}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.14</td>
<td>0</td>
<td>100</td>
<td>1.18</td>
<td>7.21</td>
<td>139</td>
<td>118</td>
</tr>
<tr>
<td>11.3</td>
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<td>0.23</td>
<td>121</td>
<td>1.20</td>
<td>5.86</td>
<td>171</td>
<td>143</td>
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<tr>
<td>22.5</td>
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<td>1.21</td>
<td>5.59</td>
<td>179</td>
<td>148</td>
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<tr>
<td>32.8</td>
<td>3.96</td>
<td>0.36</td>
<td>129</td>
<td>1.24</td>
<td>5.30</td>
<td>189</td>
<td>152</td>
</tr>
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<td>54.4</td>
<td>4.98</td>
<td>0.50</td>
<td>151</td>
<td>1.17</td>
<td>4.81</td>
<td>208</td>
<td>178</td>
</tr>
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<td>75.3</td>
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<td>1.17</td>
<td>3.96</td>
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</table>

b)

<table>
<thead>
<tr>
<th>%RH</th>
<th>( \lambda )</th>
<th>WU</th>
<th>V</th>
<th>d (g/mL)</th>
<th>[SO(_3^\text{−})] (meq/g)</th>
<th>EW (g per mol of SO(_3^\text{H}))</th>
<th>Molar volume (cc/ SO(_3^\text{H}))</th>
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<tbody>
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<td>5.35</td>
<td>188</td>
<td>140</td>
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<td>22.5</td>
<td>3.84</td>
<td>0.32</td>
<td>132</td>
<td>1.32</td>
<td>5.11</td>
<td>197</td>
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<tr>
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<td>4.79</td>
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<td>156</td>
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<td>4.30</td>
<td>234</td>
<td>176</td>
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<tr>
<td>75.3</td>
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<td>0.84</td>
<td>207</td>
<td>1.17</td>
<td>3.67</td>
<td>274</td>
<td>234</td>
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</tbody>
</table>

The densities of the absorbed water at different humidity were calculated from changes of equivalent weight and molar volume, shown in Table 4.10. Because of the existence of the frozen-in free volume, the absorbed water has a smaller volume and higher density than free water. Normally the water is first absorbed into the “frozen-in” free volume at low relative humidity and has a high density. As the “frozen-in” free volume is filled, further water is absorbed at its normal volume and the average density of the absorbed water decreases. The higher density of the absorbed water at intermediate relative humidities in Table 4.10, was probably caused by experimental error.
Table 4.10. Measured and calculated molar volume changes of a) P10F1 (4-28-4-1) b) P10F1-g-Bn27% (4-46) at different humidity. The calculated water densities are obtained from the change in equivalent weights and volumes.

a)

<table>
<thead>
<tr>
<th>%RH</th>
<th>λ</th>
<th>Measured molar volume (cc)</th>
<th>Δ [Measured molar volume] (cc)</th>
<th>EW (g per mol of SO₃⁻)</th>
<th>Δ EW (g per mol of SO₃⁻)</th>
<th>Density of absorbed water (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>118</td>
<td>0</td>
<td>139</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>11.3</td>
<td>2.94</td>
<td>143</td>
<td>25</td>
<td>171</td>
<td>32</td>
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<td>152</td>
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<td>189</td>
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<td>1.47</td>
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<td>114</td>
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</table>

b)

<table>
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<th>Measured molar volume (cc)</th>
<th>Δ [Measured molar volume] (cc)</th>
<th>EW (g per mol of SO₃⁻)</th>
<th>Δ EW (g per mol of SO₃⁻)</th>
<th>Density of absorbed water (g/cc)</th>
</tr>
</thead>
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<td>1.44</td>
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<td>3.84</td>
<td>149</td>
<td>36</td>
<td>197</td>
<td>48</td>
<td>1.33</td>
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<tr>
<td>32.8</td>
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<td>47</td>
<td>210</td>
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<td>1.30</td>
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<td>234</td>
<td>85</td>
<td>1.35</td>
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<tr>
<td>75.3</td>
<td>8.16</td>
<td>234</td>
<td>121</td>
<td>274</td>
<td>125</td>
<td>1.03</td>
</tr>
</tbody>
</table>

4.3.7. Bending angle of the fluorenyl group in the molecular chain

Copolymers PxF1 and PxF1-g-Bn are rigid rod but not linear compounds due to the bending angle existing in the fluorenyl group. It is important to obtain the value of bending angle in order to understand the relationship of the copolymer structure and properties. This calculation was carried out using Chemdraw 3D program. Optimized structures of small compounds shown in Figure 4.20 were obtained by energy minimization using MM2 method.
Figure 4.20. The optimized structure of a) 2,7-dibromofluorene-3,5-disulfonic acid (DBFDSA)

Figure 4.20. The optimized structure of b) DBFDSA reacted with two DBBDSA.
c)  

**Figure 4.20.** The optimized structure of c) DBFDSA reacted with four DBBDSA.

Angles of C3-C2-C1 (Figure 4.20 a)110°, b)110°, c) 110°) and C2-C1-C5 (Figure 4.20 a)107°, b)108°, c) 107°) in the five membered ring are almost the same in these compounds. When fluorene reacts with two DBPDSAs, the C8-C7-C6 angle (Figure 4.20 a)120°, b)114°) and the C13-C12-C11 angle (Figure 4.20 a)120°, b)116°) decreased; the C8-C7-C6 angle is smaller than the C13-C12-C1 angle. When two more DBPDSAs were added, the C8-C7-C6 angle (Figure 4.20 c) 116°) increased and angles C8-C7-C6 and C13-C12-C11 (Figure 4.20 c) 116°) were equal.

Because the compound structure shown in Figure 4.20 c) is the closest one to copolymer structure, the angle parameters in Figure 4.20 c) were used to calculate the bending angle of fluorenyl group in the copolymer molecular chain. Using the model in Figure 4.21, the bending angle a-b-c could be calculated: the angle c-a-b is half of the angle C8-C7-C6; the angle b-c-a is equal to the angle C2-C1-C5 and the angle a-b-c = 180° - angle c-a-b - angle b-c-a = 180° - 107° - 116°/2 = 15°. The angle a'-b'-c' = 12° was calculated using the same method. Thus, the bending angle of fluorenyl group equals to the sum of angles of a-b-c and a'-b'-c', 27°.
The existing bending angle in PxF1 copolymer structure greatly affects copolymer properties. It is expected to add flexibility to the copolymer chain and increase the mechanical properties. The bending angle can help pack the copolymer PxF1 chain; the existence of bending angle can help bulky groups to separate the grafted copolymer PxF1-g-Bn chain more efficiently, which is assumed to increase the copolymer frozen-in free volume.

4.3.8. Model study

The typical nematic liquid crystalline structure of the copolymer PxF1 and PxF1-g-Bn shown in the POM images, Figure 4.11 a and c, indicates a hexagonal packing solid state of these copolymers. With a structure similar to copolymer PxF1 and PxF1-g-Bn, “Rulkens 3” (Figure 4.6) reported a hexagonal structure of columns of three associated polymer backbones\(^4,10\).

In order to study the copolymer chain packing, the following model was proposed (Figure 4.22). The volume of the copolymer PxF1 or PxF1-g-Bn can be calculated following Equation 4.21.
Figure 4.22. Schematic of the proposed packing model for PxF1 and PxF1-g-Bn. Filled circles represent a bundle of polymer chains or one polymer chain. d is the d spacing found using WAXD. The distance between two filled circles was calculated as \( d / \sin(\gamma) \).

\[
V = \frac{d}{\sin(\gamma)} \times d \times l = K \times l \times d^2 \quad \text{K} = \frac{1}{\sin(\gamma)} \quad \text{(Equation 4.21)}
\]

\( d \) is the distance between two planes of chain centers, obtained from WAXD; \( l \) is the length of the repeat unit per sulfonic acid group. The length of phenyl ring is 4.2 Å. Without consideration of the fluorenyl group, \( l \) equals to 2.1 Å (2 sulfonic acid groups per ring) in the copolymer. When the fluorenyl group was considered, assuming the ratio of phenyl rings and fluorenyl groups is 10:1, then an average \( l \) can be calculated using Equation 4.22.

\[
l = \frac{5 \times 4.2 + 4.2}{11} = 2.29 \text{ Å} \quad \text{(Equation 4.22)}
\]

In order to determine the K value, the molar volume of copolymer needs to be calculated and compared with the measured one, which can be obtained from Equation 4.23.

\[
\text{Molar volume} = V \times SO_3H = K \times l \times d^2 \times N_A = K \times l \times d^2 \times 10^{-24} \times 6 \times 10^{23} \quad \text{(Equation 4.23)}
\]

Without considering the fluorenyl group, the molar volume = \( K \times 1.26d^2 \text{ cc/}SO_3H \)

Considering the fluorenyl group, the molar volume = \( K \times 1.37d^2 \text{ cc/}SO_3H \)
Table 4.11 lists the measured molar volumes and the calculated values, $1.26d^2$ cc/\(\text{SO}_2\text{H}\) and $1.37d^2$ cc/\(\text{SO}_2\text{H}\) of PxF1 and PxF1-g-Bn respectively. By plotting the measured molar volume and molar volume with square packing (Figure 4.23) and linear fitting, a K value was obtained.

**Table 4.11.** Measured molar volume and molar volume with square packing a) P10F1 (4-28-4-1) and b) P10F1-g-Bn27% (4-46)

<table>
<thead>
<tr>
<th>%RH</th>
<th>(\lambda)</th>
<th>Measured molar volume (cc)</th>
<th>(d) (Å) spacing from WAXD (transmission model)</th>
<th>1.26 * (d^2) (Å³)</th>
<th>1.37 * (d^2) (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.14</td>
<td>118</td>
<td>7.9</td>
<td>79</td>
<td>86</td>
</tr>
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<td>8.7</td>
<td>95</td>
<td>104</td>
</tr>
<tr>
<td>32.8</td>
<td>3.96</td>
<td>152</td>
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<td>104</td>
<td>113</td>
</tr>
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<td>4.98</td>
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<td>9.9</td>
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<td>134</td>
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</table>

<table>
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<tr>
<th>%RH</th>
<th>(\lambda)</th>
<th>Measured molar volume (cc)</th>
<th>(d) (Å) spacing from WAXD (transmission model)</th>
<th>1.26 * (d^2) (Å³)</th>
<th>1.37 * (d^2) (Å³)</th>
</tr>
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<tbody>
<tr>
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<tr>
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<td>8.16</td>
<td>234</td>
<td>10.5</td>
<td>139</td>
<td>151</td>
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</tbody>
</table>

After linear fitting, the two plots in Figure 4.23 a) and b) give \(\sin(\gamma)\) values for the copolymer P10F1 (4-28-4-1) of 0.78 and 0.85, respectively. The corresponding \(\gamma\) angles are 51° and 58°. It implies that the fluorenyl should be considered in molar volume calculation, which gives a \(\gamma\) angle close to the hexagonal model (60°). Using the same method, the \(\gamma\) angles for copolymer P10F1-g-Bn27% (4-46) are, 33.2° and 36.7° in Figure 4.23 a) and b), respectively. Both of them are very close to 30°. Packing models for these two copolymers are proposed, shown in Figure 4.24.
Figure 4.23. Correlation of molar volume, measured and from averaged $d^2$, as a function of measured molar volume, cc/$SO_3H$. a) molar volume = $K*1.26d^2$ cc/$SO_3H$, b) molar volume = $K*1.37d^2$ cc/$SO_3H$.

These two models show that both P10F1 (4-28-4-1) and P10F1-g-Bn27% (4-46) packed hexagonally. The linear fit implies that both the a and b axes of the unit cell
expand proportionally with the water content, so the data can be analyzed to estimate “frozen-in” free volume. In Figure 4.24 model b, the distance increases from $2/\sqrt{3} \ d$ (model a) to $2d$. This contradicts the estimate of free volume, calculated in Section 4.3.9, P10F1 (4-28-4-1) and P10F1-g-Bn27% (4-46) have the same free volume. The result is probably due to the complexity of the polymer chain packing, and is not understood at present.

![Figure 4.24](image)

**Figure 4.24.** Two packing models for copolymer a) P10F1 (4-28-4-1) b) P10F1-g-Bn27% (4-46). Filled circles represent a bundle of polymer chains or one polymer chain.

### 4.3.9. Estimation of “Frozen-In” Free Volume

For polyphenylene sulfonic acids type materials which have rigid-rod chains, their molecules tend to form nematic liquid crystals with all backbones parallel. The polymer chain can be separated by introducing groups with large cross-sectional areas, which can form an array of nano-pores lined with sulfonic acid groups. At high humidity, water is absorbed by sulfonic acids and held by both H-bonding and capillary attraction. These special structures generate an energy barrier for water removal because the structure becomes distorted. The equilibrium excess volume over the polyphenylene sulfonic acid Van der Waals volume is called “frozen-in free volume”.

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For a polymer with “frozen-in” free volume, water is held very strongly at dry condition to relieve the compressive strain. Absorbed water fills the “frozen-in free volume” first, which shows as the high density of the absorbed water >1.0 g/cc. After all the “frozen-in” free volume is filled; further volume increase reflects water absorption with a density of 1 g/cc.

Two curve fitting equations are proposed for “frozen-in” free volume calculation (Equation 4.24 and 4.25). The hyperbolic tangent function fits the conceptual approach of the model. Equation 4.24 assumes no volume increase for the dry polymer water absorbing, but as water fills all the free volume the polymer volume/λ slope increases to a final value of 18 cc/λ. Equation 4.25 includes a macro-to-micro conversion factor that correlates the d spacings with the measured molar volumes.

\[
MV = V_dMV + 18 \lambda + FV \times (1 - \tanh(18 \lambda / FV)) \tag{Equation 4.24}
\]

\[
1.37 d^2 = K \times MV \tag{Equation 4.25}
\]

- MV = Molar Volume, per SO3H group
- \(V_dMV\) = Polymer Van der Waals Molar Volume
- FV = “Frozen-in” free Volume per SO3H group
- K = Macro to molecular volume conversion coefficient

Parameters (\(V_dMV\) and FV) were calculated using MicroMath Scientist (version 2.01) software. The obtained calculated molar volume from Equation 4.24 with other types of molar volume are listed in Table 4.12. The corresponding curves of molar volume and lambda are plotted in Figure 4.25.
Table 4.12. Lambda and measured and calculated molar volumes a) P10F (4-28-4-1) b) P10F1-g-Bn27% (4-46)

<table>
<thead>
<tr>
<th>Lambda(λ)</th>
<th>Measured molar volume (cc/SO₃H)</th>
<th>Molar volume from Eq. 4.25</th>
<th>Calculated molar volume from Eq. 4.24</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.14</td>
<td>118</td>
<td>101</td>
<td>118.75</td>
</tr>
<tr>
<td>2.94</td>
<td>143</td>
<td>122</td>
<td>139.53</td>
</tr>
<tr>
<td>3.96</td>
<td>152</td>
<td>133</td>
<td>156.37</td>
</tr>
<tr>
<td>4.98</td>
<td>178</td>
<td>157</td>
<td>174.23</td>
</tr>
<tr>
<td>7.43</td>
<td>216</td>
<td>198</td>
<td>218.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lambda(λ)</th>
<th>Measured molar volume (cc/SO₃H)</th>
<th>Molar volume from Eq. 4.25</th>
<th>Calculated molar volume from Eq. 4.24</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18</td>
<td>113</td>
<td>79</td>
<td>112.85</td>
</tr>
<tr>
<td>3.33</td>
<td>140</td>
<td>101</td>
<td>139.57</td>
</tr>
<tr>
<td>4.58</td>
<td>160</td>
<td>109</td>
<td>160.95</td>
</tr>
<tr>
<td>5.91</td>
<td>176</td>
<td>132</td>
<td>184.60</td>
</tr>
<tr>
<td>8.16</td>
<td>234</td>
<td>151</td>
<td>225.03</td>
</tr>
</tbody>
</table>

Equation 4.25 was used to fit the measured molar volumes; both equations were needed in order to correlate the d spacings. Parameters were calculated by least squares fit: the polymer Van der Waals volume for P10F1 was 84.4(±2.4) cc/SO₃H and free volume was 32.0(±5.8) cc/SO₃H (λ = 1.8). For P10F1-g-Bn27% (4-46), the Van der Waals volume was 78.1(±4.0) cc/SO₃H and free volume was 32.1(±10.0) cc/SO₃H (λ = 1.8). The relatively large standard errors for free volume are due to the inclusion of the 0%RH points. The 0%RH WAXD scan in Figure 4.19 differs from other scans; it is low intensity and broad. It implies the chains cannot pack uniformly: The sulfonic acid/benzene bond angles and phenyl/phenyl dihedral angles are distorted if too much water is removed. The calculated free volume of P10F1 (4-28-4-1) and P10F1-g-Bn27% (4-46) is almost the same, which can be explained by the low degree of benzyl chloride grafting in the copolymer. Further improvement need be carried out in copolymer grafting research.
Figure 4.25. Determination of “frozen-in” free volume using Eq. 4.24. WAXD scans taken through films.
4.3.10. Proton conductivity measurements

The in-plane proton conductivity of P10F1 and P10F1-g-Bn was measured at 80ºC at different relative humidities using a four-electrode AC impedance method, Figure 4.26.

![Figure 4.26. In-plane proton conductivity at 80ºC as a function of relative humidity for P10F1, P10F1-g-Bn and Nafion212®](image)

The polymer is water soluble and the films lose their mechanical integrity due to excessive swelling at RHs higher than 80%. The proton conductivity of Nafion212® was measured under the same conditions for comparison. The copolymer conductivity is 10 times higher than that of Nafion212® over whole test range. It drops with increasing graft %. P10/F1 (4-28-4-1) before grafting has a very high conductivity; it drops about 30% when grafted with 2 to 3% of benzyl groups per sulfonic acid. The grafted groups probably create obstacles to the proton movement and decrease proton mobility. PxF1
and PxF1-g-Bn have higher conductivity than PPDSA and its biphenyl grafted copolymer (PPDSA-g-BP) (Figure 4.27). It is probably due to the bending angle in the fluorenyl group, which can increase the frozen-in free volume; and the sulfonic acid groups lost during the PPDSA crosslinking reaction.

![Figure 4.27. In-plane proton conductivity at 80°C as a function of relative humidity for PPDSA, PPDSA-g-BP, crosslinked PPDSA-g-BP and Nafion212](image)

4.3.11. Thermogravimetric analysis (TGA)

As candidates for proton exchange membranes used at high temperature (120°C) and low relative humidity, copolymers PxF1 and PxF1-g-Bn should be stable in the ranges between 120°C and 150°C over extended periods of time. TGA is an analytical technique used to determine a material’s thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. Copolymer films were dried in a vacuum oven at 110°C for 24 h; relative humidity in this condition was considered as 0%. The TGA measurement was run following the
procedure in Section 4.2.2.7. The weights of the copolymer films were recorded as a function of increasing temperature. (Figure 4.28)

![TGA thermograms of PxF1 and PxF1-g-Bn films dried at 110°C for 1 day. Heating rate is 10°C/min under N2 (60mL/min).](image)

Figure 4.28. TGA thermograms of PxF1 and PxF1-g-Bn films dried at 110°C for 1 day. Heating rate is 10°C/min under N2 (60mL/min).

In Figure 4.28, data are shown for PxF1 copolymer and grafted copolymers, PxF1-g-Bn. There are two weight loss points. The first one (dehydration temperature) corresponds to the water loss and the second one (decomposition temperature) is due to the loss of sulfonic acid groups. Increasing fluorenyl and benzyl group content decreases the dehydration and decomposition temperatures and increases the water content. It shows that inclusion of fluorenyl and benzyl groups can increase the material water holding capability. However, $\lambda$ calculated from the water loss at the dehydration temperature is larger than $\lambda_0$. The films probably absorbed water before the TGA scan started.
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The decomposition temperature relates to the degree of sulfonation. Polyphenylene sulfide (PPS) with high degree of sulfonation \((m = 2)\) has a higher decomposition temperature than that of PPS with \(m = 0.6\)\(^{12}\). The strongly electron-withdrawing sulfonic acid groups increased the compound stability. Table 4.13 shows that increase of sulfonation of the phenyl group can stabilize the polymer at high temperature. The decomposition temperatures of the PxF1 and PxF1-g-Bn are above 304°C, which is similar to that of PPDSA (304°C) and higher than that of PBPDSA (245°C) and Nafion® (190°C).

Table 4.13. Dehydration and decomposition temperatures and corresponding weight of copolymer films

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>P20F1 (4-75-2)</th>
<th>P10F1 (4-28-4-1)</th>
<th>P10F1-g-Bn27% (4-46)</th>
<th>P10F1-g-Bn34% (4-39)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydration temp. &amp; weight</td>
<td>316°C, 80.7%</td>
<td>311°C, 78.4%</td>
<td>306°C, 69.4%</td>
<td>304°C, 65.5%</td>
</tr>
<tr>
<td>Decomposition temp. &amp; weight</td>
<td>379°C, 57.5%</td>
<td>378°C, 48.0%</td>
<td>363°C, 40.9%</td>
<td>362°C, 43.6%</td>
</tr>
<tr>
<td>(\lambda_0^a)</td>
<td>0.81</td>
<td>1.14</td>
<td>1.18</td>
<td>1.23</td>
</tr>
<tr>
<td>Water loss(^b)</td>
<td>1.60</td>
<td>1.87</td>
<td>3.02</td>
<td>3.61</td>
</tr>
</tbody>
</table>

\(a.\) See Table 4.4  
\(b.\) Copolymer water loss per SO₃H from 100% weight at dehydration temperature

4.3.12. Mechanical testing

Proton exchange membranes should meet certain mechanical property requirements in order to be used in fuel cells. As a rigid rod aromatic polymer, PxF1 and grafted PxF1 have different mechanical properties from those of Nafion®. They exhibited very high Young’s moduli and low elongation at break (Figure 4.29).
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Figure 4.29. Stress-strain curves for P10F1 and grafted and crosslinked P10F1-g-Bn27% at ~22%RH

As expected, P10F1 has high Young’s modulus (734 MPa) and low break strain (1%). When this copolymer was grafted with benzyl groups, Young’s modulus was reduced to 495 MPa but the strain increased dramatically to 6.6%. After crosslinking, the modulus of P10F1-g-Bn increased to 666 MPa and the strain dropped to 1.8%. The introduction of benzyl groups increased “frozen-in” free volume and improved the lambda of the copolymer, which resulted in lower modulus. After the P10F1-g-Bn was crosslinked, the generated network restricted the movement of the polymer molecules, which increased the modulus.
The mechanical properties of PxF1 and PxF1-g-Bn are dramatically affected by the relative humidity. The stress-strain curves of P10F1-g-Bn27% at different humidities are shown in the Figure 4.30. When the relative humidity increased, both the modulus and strain dropped. The typical modulus of rigid rod materials should be around 5~20 GPa. The low modulus of P10F1 and its corresponding grafted and crosslinked copolymers can be explained by the plasticizing effect of the absorbed water. Water molecules absorbed in the polymer can increase the inter-chain distance, and the polymer chains can slide at low stress.

Figure 4.30. Stress-strain curves for P10F1-g-Bn27% at 23 and 42%RH.
4.4. Conclusions

This chapter focused on characterization of the structure and properties of novel polyphenylene sulfonic acids, PxF1, PxF1-g-Bn and crosslinked PxF1-g-Bn.

Copolymers exhibit abnormal solution properties due to their rigid rod backbone with attached sulfonic acids. Reduced viscosity showed an upturn as concentration decreased. Copolymer reduced viscosities have a linear relationship with $C^{0.5}$. The reason for this phenomenon is still unknown and more study is needed to understand the system fully.

OPM images show the copolymer has nematic liquid crystalline structure based on the declination strength. This result is consistent with that from the WAXD data: the polymer chains were oriented mainly perpendicular to the film surface. The measured dimensional changes show that at low humidity the swelling is the same in X, Y and Z directions with more Z direction swelling at high relative humidity. Crosslinked copolymer swelled less in the Z direction than in the X, Y directions over the whole relative humidity range except at 75%RH, where the swelling in the Z direction is more than that in X, Y directions.

Based on d spacings from WAXD, an equation about the molar volume calculation was proposed. To study the relationship between the calculated molar volume and the measured molar volume, a hexagonal packing model was proposed.

The “frozen-in” free volume could be directly estimated using WAXD combined with measurement of volume and weight increase for the copolymer as a function of relative humidity. While an equation based on the copolymer water absorption is considered curving fitting, it has the correct shape for such an analysis. The measured
molar volume correlated exactly with the calculated molar volume from d spacings. It implies the absorbed water comes into the volume between two chains and expands two chain distances isotropically. The frozen in free volume from this analysis is 32.0 cc/SO$_3$H ($\lambda = 1.8$) for P10F1 (4-28-4-1) and 32.1 cc/SO$_3$H ($\lambda = 1.8$) for P10F1-g-Bn27% (4-46). The small free volume difference between P10F1 and its grafted copolymer was due to the low grafting degree.

Like other polyphenylene sulfonic acids prepared in our group, P10F1 and its grafted copolymers have high conductivity. Conductivity rises as humidity increases and drops with increasing graft%. The conductivity of P10F1 and its grafted copolymer is higher than that of PPDSA and PPDSA-g-BP, due to the bending angle in the fluorenyl group and the loss of sulfonic acid groups during the PPDSA grafting reaction. TGA showed that P10F1 and its grafts decomposed at 304°C, higher than Nafion® (190°C), which exceeds the fuel cell operating temperature (120-150°C). As expected, rigid rod P10F1 has low stress (5.8 MPa) and low strain (1%) to break. However, after grafting, the copolymer mechanical properties improved dramatically; the stress and strain at break were 13.3 MPa and 6.6%. After the grafted copolymer was crosslinked, it had a still higher breaking stress, 7.8 MPa, and strain, 1.8%, than P10F1. However, the mechanical properties are greatly affected by absorbed water. High relative humidity lowers the modulus, and strain and stress at break dramatically.

The crosslinked copolymer is insoluble in water and remains intact at 100% relative humidity. But at high humidity, the film became too soft to handle. Future work needs to focus on increasing the copolymer grafting degree.
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Chapter 5

General conclusions and future directions

5.1. General conclusions

High molecular weight poly(phenylene sulfonic acid) homopolymers and copolymers were synthesized using the Ullmann coupling reaction. The copolymers were grafted and crosslinked to generate water insoluble films. The basic chemical, thermal and mechanical properties of these copolymers were described.

The molecular weight of homopolymer poly(biphenylene-3,3’-disulfonic acid) (PBPDSA) can be improved by optimizing the reaction conditions. Three factors, solubility, reactivity and dryness of the reaction system, are thought to have major effects on polymer molecular weight. The polymer molecular weights are limited by their solubility because the polymerization stops when the generated polymer precipitates. The 4,4’-dibromobiphenyl-3,3’-disulfonic acid (DBBPDSA) monomer counter ion affects the monomer and polymer solubility but also the monomer reactivity due to steric hindrance. Water in the reaction reacts with a bromo group in cuprous complex and stops the polymerization. The best conditions found were: 3 wt% DBBPDSA-Li and activated copper were dried separately at high vacuum and polymerized in NMP at 140°C for 22 h.

The obtained high molecular weight PBPDSA was further grafted with neopentylbenzene (NPB). The resulting PBPDSA-g-NPB polymer could be cast as a transparent, water insoluble film. The proton conductivity of this film was 0.114 S/cm at
50%RH and 80°C, which is higher than DOE initial target 0.1 S/cm at the same temperature and RH.

Although the grafted copolymer PBPDSA-g-NPB exhibited high conductivity, there is still some room for the conductivity of poly(phenylene sulfonic acid) to improve. One method is to use a higher IEC monomer 1,4-dibromobenzene-2,5-disulfonic acid (DBPDSA). The water insoluble film generated by grafting and crosslinking is made at the cost of consuming the sulfonic acid groups, which decreases the conductivity of film. An alternative method is to synthesize water insoluble copolymer by copolymerizing with comonomers that contain the desired bulky or crosslinkable motif.

A new comonomer 2,7-dibromofluorene-3,5-disulfonic acid (DBFDSA) was synthesized by the direct sulfonation of 2,7-dibromofluorene and copolymerized with DBPDSA using Ullmann coupling. A novel copolymer, poly(phenylene disulfonic acid co-fluorene disulfonic acid), (PxF1), was synthesized. This copolymerization reaction was optimized by screening temperature, solvent, coordination reagent and drying method. The best conditions are: DBPDSA-Li, DBFDSA-Li and copper dried separately under vacuum and then together under an argon steam at 200°C and copolymerized in NMP at 200°C using 2,2’-bipyridine (BPy) as a coordination reagent. The function of BPy is not only as a coordination reagent to increase the copolymer solubility but also probably to complex with cuprous ion as a catalyst, which needs further study. The copolymer composition was analyzed by NMR and elemental analysis. The active end 2-position Br in DBFDSA-Li prefers to react with DBPDSA-Li or itself.
A model alkylation reaction of 2,7-dibromofluorene was used to screen the reaction conditions for grafting. The bulky base potassium tert-butoxide and saturated NaOH aqueous solution can give the twice alkylated fluorene compound in high yield. However, when used with the copolymer, the best model reaction conditions gave only a low grafting degree, probably due to reaction with the water existing in the system. A new drying method needs be developed in order to get high grafting degree copolymers.

PxF1 and its grafted copolymer exhibited a complex behavior in solution. An abnormal increase of reduced viscosity in the low concentration region was observed under all conditions. The optical polarizing microscopy (OPM) studies and the film dimensional changes as a function of relative humidity showed that PxF1 and its grafts had nematic liquid crystalline structures. This result was confirmed by the WAXD data: the polymers were oriented mainly perpendicular to the film surface.

PxF1 and grafted PxF1 have a hexagonally packed nematic liquid crystal polydomain structure with “frozen-in” free volume. The proposed hexagonal packing structure in the domains was supported by the WAXD and model study. Based on d spacings from WAXD, an equation to estimate the molar volume was proposed. The inter-chain distance increased with relative humidity; the calculated molar volume was a first order function of the measured molar volume and fit well with the hexagonal packing model.

The “frozen-in” free volume can be directly estimated using WAXD data combined with measurement of volume and weight increase of copolymer as a function
of relative humidity. The estimate of “frozen-in” free volume is 32.0 cc/SO$_3$H ($\lambda = 1.8$) for P10F1 and 32.1 cc/SO$_3$H ($\lambda = 1.8$) for P10F1-g-Bn27%.

P10F1 and its grafted copolymer have tenfold higher conductivity than Nafion212® between 11 and 75%RH due to their high IEC. Conductivity rises as humidity increases and drops with increasing graft%. The decomposition temperature of P10F1 and its grafted copolymers is around 304°C, higher than Nafion117® (190°C); it exceeds the fuel cell operating temperature (120-150°C). The copolymer mechanical properties are affected by the grafting degree, crosslinking and relative humidity. The copolymer mechanical properties are increased by grafting and decreased by crosslinking and relative humidity. The material with best mechanical properties is P10F1-g-Bn27% (breaking stress 13.3 MPa and strain 6.6%) at 23%RH.

So far, our random copolymers, PxF1, with the highly conductive poly($p$-phenylene-2,5-disulfonic acid) (PPDSA) backbone with fluorenyl embedded groups shows special properties, but also brings questions. In order to be a PEM candidate for use in fuel cells, the copolymerization and grafting reactions must be optimized. The full characterization of this material should be carried out.

5.2. Future work

The top priority for the next stage of research is to increase the grafting degree of copolymer. Low grafting degree makes the grafted copolymer water soluble. Although, the crosslinking reaction could give water insoluble films, the corresponding mechanical properties worsened. For the high molecular weight copolymers, the solubility in the organic solvents is poor. Normally, water is needed to help solubilize them. However, it
is known from our grafting experiments that the water existing in the system killed the reaction. Thus, a method is required to dissolve the copolymers without water. As mentioned in Chapter 3, triethylene glycol dimethyl ether (TEGDME) is a very good complexing reagent for the lithium ion. It can be used to help dissolve the copolymer lithium salts. The procedure is described as following: copolymer PxF1-Li can be dissolved in NMP with the help of water or methanol. Subsequently, TEGDME is added. It should complex with the lithium ion nicely. The water or methanol can be removed by heating under vacuum. The generated mixture can be alkylated under argon using potassium tert-butoxide as a base.

In the copolymerization reaction, the adding of the coordination agent 2,2′-bipyridyl could increase the molecular weight. It is assumed to increase the solubility of copolymer cuprous salt and complex with the cuprous ion to catalyze the Ullman reaction. Based on this hypothesis, we hope to improve the molecular weight by screening different cuprous coordination agents. Liebeskind et al. developed an innovative copper(I) reagent copper(I)-thiophene-2-carboxylate (CuTC) which promoted Ullmann coupling of substituted aromatic iodides, bromides and 2-iodoheteroaromatics at room temperature. Probably, CuTC could be a catalyst candidate for our copolymerization reaction.

This new variety of polymeric materials needs full characterization of their properties and their correlation to their chemical structures. Only after a well-designed study and such correlations have been found, can a new material be optimized and developed. Many studies of the new copolymer properties have been carried out in this work to find the structure-property correlations. Although a qualitative confirmation of
structure hypothesis was produced, still a lot of work is needed in order to fully understand this new variety of material.

This rigid rod material exhibited an abnormal solution behavior in that the reduced viscosity increased in the low concentration region and showed a linear relationship between $\eta_{sp}/C^{0.5}$ and $C^{0.5}$. The reason for this is still unknown.

Although crosslinked copolymer was obtained, it was not fully characterized. Studies of its solid state structure, “frozen-in” free volume, conductivity and thermal stability need be carried out in the future. Ultimately, the right MEA fabrication methods for these films needs to be found. A new formulation for the catalyst suspensions will have to be developed because these materials are not compatible with the perfluorosulfonated polymers.

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