Final Report to the DOE on grant DE-FC36-06GO16039
Poly(phenylene sulfonic acids): PEMs with frozen-in free volume

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Introduction: Most of the research conducted under this grant has been published. The papers are listed below. The first three cover all the published research. Paper 4 is a preliminary version of paper 3. Paper 5 is a review summarizing much of the earlier work including the failed approaches and adding the results for the last membrane tested.

There was a large body of work on two dimensional polyelectrolytes that might be very important, but was not carried to the point where it could be published. It is the main section of the Report.

Papers published with DOE support.

1. Rigid Rod Polyelectrolytes with Frozen-In Free Volume: High Conductivity at Low RH

Morton Litt, Sergio Granados-Focil, and Junwon Kang

Fuel Cell Chemistry and Operation; Herring, A., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2010.

2. Synthesis and characterization of poly(para-phenylene disulfonic acid), its copolymers and their n-alkylbenzene grafts as proton exchange membranes: high conductivity at low relative humidity

Kun Si, Daxuan Dong, Ryszard Wycisk and Morton Litt. *Mater. Chem*., 2012, **22**, 20907

3. Rigid-Rod Poly(phenylenesulfonic acid) Proton Exchange Membranes with Cross-Linkable Biphenyl Groups for Fuel Cell Applications

Kun Si, Ryszard Wycisk, Daxuan Dong, Kevin Cooper, Marianne Rodgers, Paul Brooker, Darlene Slattery, and Morton Litt: *Macromolecules* 2013, **46**, 422−433 ma301875n

Supplemental Information: ma301875n_si_001

4. Rigid Rod Poly(phenylene sulfonic acid) PEMs and MEAs with Grafted and Crosslinked Biphenyl Groups: Mechanical and Electrical Properties

Kun Si and Morton Litt: *ECS Transactions*, **41 (1)** 1645-1656 (2011)

5. Poly(arylenesulfonic acids) with Frozen-In Free Volume as Hydrogen Fuel Cell Membrane Materials

   Morton Litt & Ryszard Wycisk, *Polymer Reviews*, **55:2**, 307-329, (2015)

Poly(phenylene sulfonic acids) PEMs with frozen-in free volume:
Final Report on 2-D polymers.

Recipient: Case Western Reserve University
Award Number: DE-FC36-06GO16039

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Project Objective:

The synthesis and characterization of rigid rod, liquid crystalline poly((phenylene sulfonic acid) and (disulfonic acid)) and its copolymers as PEMs and MEAs. These materials should have frozen-in free volume which holds water very tightly so that the membranes retain conductivity at low relative humidities. The objective is to make copolymers with good dimensional stability and mechanical properties without losing the high water retention and corresponding conductivity. This report concerns the synthesis and characterization of completely rigid 2-D hexagonal lattice polymers that agglomerate to form 3-D structures containing nano-pores. Properly cast films should have constant volume, independent of relative humidity, and retain conductivity down to very low humidities.

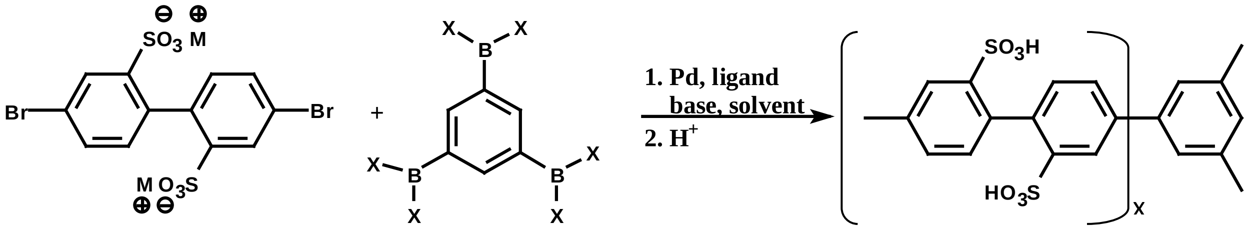
Background:

Morton Litt's group has worked over the past eight years with several systems of rigid rod, nematic liquid crystalline poly(aromatic sulfonic acid) polymers and copolymers. Incorporation of bulky comonomers forces the parallel chains apart and generates long nanopores lined with sulfonic acids that hold water very tightly. This increases conductivity at low relative humidity compared to Nafion and poly(phenylene ether sulfonic acid) structures. The initial work used poly(naphthalene bis-imides), which hydrolyzed slowly when in the acid form. Work shifted to poly(phenylene sulfonic acids), which cannot hydrolyze. Most of the research has been on poly(p-phenylenes) with one and two sulfonic acid groups on each ring.

A third area in this program was the development of 2-D polyelectrolytes containing voids that could not be compressed (true frozen-in free volume). Five years were spent developing the synthetic approach and the chemistry needed to synthesize such materials. **This is a special report covering the results obtained during the last year on the synthesis and properties of these materials**.

Status:

The project started officially on April 1, 2006. Mr. Check had been working on approaches to 2-D polymers for two years before the project started. The initial routes were not feasible synthetically; it was too difficult to get high yields of the needed intermediate materials. Mr Check suggested the present approach; the polymer could be made in one step from simple starting materials that could be synthesized in one or two steps from cheap commercial compounds. The synthetic approach used Pd(0) plus a stabilizing ligand as the coupling catalyst, the Suzuki reaction, for the polymer synthesis. Since the starting materials were water soluble, a water soluble ligand for the Pd(0) was needed. A recently reported ligand, SPhos-SO_3Na, (*Angew. Chem. Int. Ed.* **2005,** *44*, 6173-7), was tested and proved to be excellent for our purposes. It was used for all the syntheses. The synthetic approach is shown in Scheme 1.



Scheme 1. Approach to the synthesis of 2-D polymers

The proposed final structure is shown in more detail in Figure 1. The reaction should generate a two dimensional hexagonal array of aromatic rings. Each hexagon contains six sulfonic acid groups. We expect that the molecules should stack to generate nano-pores through the final structure. If the molecule is completely planar, the side-to-side diameter of a nano-pore is 22 Å with a void diameter of about 15 Å. Depending on the intermolecular distance, modeling predicts that saturated pores should hold 4 to 6 waters per sulfonic acid. Such pores should hold water very strongly both by H-bonding and capillary interaction. A cast film must be oriented so that the pores are perpendicular to the film surface in order to get high through conductivity. We expect that such structures should hold significant amounts of water down to very low humidity; a properly cast film could have high through conductivity under all working conditions.

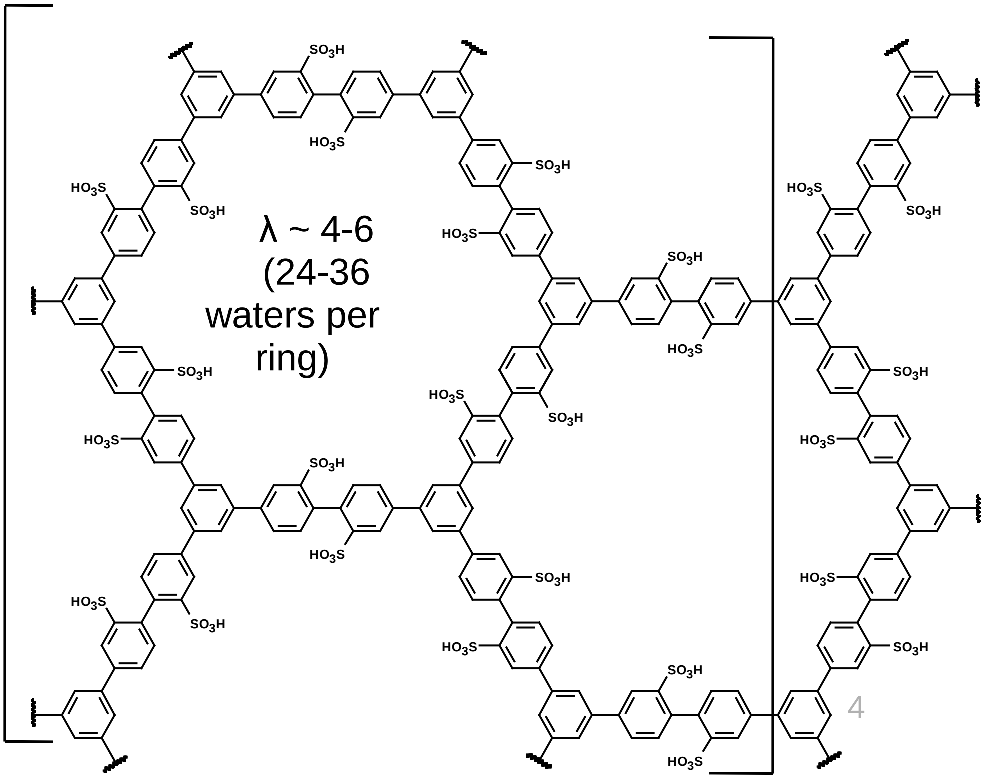


Figure 1. Proposed structure of 2-D polymer.

One further question was addressed. We realized that when palladium acetate plus ligand was added to the reaction mixture, reduction to Pd(0) was relatively slow. In order to avoid cross-linking reactions, the reaction rate needed to be very high. Monomer concentration in solution should be kept as low as possible so that cyclization would be greatly favored over any other reaction, monomer starvation conditions. Experiments were run to determine the best conditions for this. Pd(2) was reduced to Pd(0) with oxalic acid before it was added to the reaction solution. The question was: What reduction conditions generate the most active catalyst and most rapid reaction rates?

2. Experimental.

2.1.1 Suzuki coupling kinetics with pre-reduction of Pd: Synthesis of quaterphenyl-2',2"-disulfonic acid using 0.15mol% Pd/0.3mol% SPhos-SO_3Na with Na_2CO_3 in water (4% solution). Sodium 4, 4'-dibromobiphenyl-2, 2'-disulfonate (1.0006g, 1.939mmol), potassium phenyl trifluoroborate (0.7145g, 3.883mmol) and sodium carbonate (2.0607g, 19.442mmol) were placed in a 50mL 3-neck flask and dissolved in 23mL water. The solution was deoxygenated by argon for 1 hour and then equilibrated for 15 min in oil bath preheated to 80°C Activated catalyst prepared by adding SPhos-SO_3Na (0.0038g, 0.0074mmol) to a solution of $Pd(OAc)_2$ (0.00064g, 0.0029mmol) (1mL of $Pd(OAc)_2$ solution: 0.0064g in 10 mL water) in a 3mL vial, followed by addition of oxalic acid dihydrate (0.00042g, 0.0033mmol) (1mL of oxalic acid solution: 0.0042g in 10mL water). The pale yellow catalyst solution was added to the preheated reaction solution and a timer was started. Samples (1mL) were extracted at 5, 10, 15, 20, 30, 40, 50, 55, 60, 65, 70, 80, 90 and 100 min, and quenched in 0.5mL of 0.1M NaCN in water. The sample solutions were rotary evaporated to dryness, washed with methanol and filtered. The methanol solution was rotary evaporated to dryness. The resulting solid was extracted with 1mL of CD_3OD and the solution was pipetted into an NMR tube for analysis.

2.1.2 Suzuki coupling kinetics: Pre-reduction of Pd; synthesis of quaterphenyl-2',2"-disulfonic acid using 0.15mol% Pd/0.3mol% SPhos-SO_3Na with Na_2CO_3 in water (2% solution). The reaction was set up similarly to reaction 2.1.1 using twice the volume of solvent (50mL water) and identical quantities of reagents: Samples (1mL) were extracted at 5, 10, 15, 20, 30, 40, 50, 55, 60, 70, 80, 90, 100, 120 and 140 min, quenched in 0.5mL of 0.1M NaCN in water, dried and extracted with methanol for analysis..

2.1.3 Suzuki coupling kinetics with pre-reduction of Pd: Synthesis of quaterphenyl-2',2"-disulfonic acid using 0.15mol% Pd/0.3mol% SPhos-SO_3Na with Na_2CO_3 in water (4% solution) using purified potassium phenyl trifluoroboronate. The potassium phenyl trifluoroboronate was recrystallized before use. The reaction followed the procedure given for Run 2.1.1. It was complete in 100 minutes. The results are shown in Figure 2 in the Discussion section..

2.1.4 Suzuki coupling kinetics: Pre-reduction of Pd in DMF; synthesis of quaterphenyl-2',2"-disulfonic acid using 0.15mol% Pd/0.3mol% SPhos-SO_3Na with Na_2CO_3 in water (4% solution). The reaction was set up similarly to reaction 2.1.1 except the catalyst was activated by diluting the stock solutions with DMF rather than with water before mixing them in the 3mL vial. Identical quantities of reagents were used. Samples (1mL) were extracted at 5, 10, 15, 20, 30, 40, 50, 55, 60, 65, 70, 80, 90 and 100 min, quenched in 0.5mL of 0.1M NaCN in water, dried and extracted with methanol for analysis. The reaction was over within 5 minutes, when the first sample was taken. The results are shown in Figure 3 in the Discussion section.

2.2.1 Suzuki cyclopolymerization 1; Synthesis of poly(1, 3, 5-phenylene-4, 4'-biphenylene-2, 2'-disulfonic acid): 4, 4'-Dibromo biphenyl 2, 2'-disulfonic acid lithium salt (1.0003 g, 2.067 mMol) and benzene 1, 3, 5-tris(trifluoroboronate potassium salt) (0.5456 g, 1.378 mMol) were placed in a 25 mL pear shaped flask, dissolved in 20 mL water and deoxygenated for 1 hour. Na_2CO_3 (1.7553 g, 16.561 mMol) was placed in a 3-neck 250 mL round bottom flask, dissolved in water (100 mL) and deoxygenated for 1 hour. The solution of dibromobiphenyl and triboronate was taken into a syringe which was placed in a syringe pump set to deliver 0.20 mL/min. S-Phos-SO_3Na (0.0213 g, 0.042 mMol, 2 mol%) and oxalic acid dihydrate (0.0027 g, 0.021 mMol) were placed in a 3 mL screw-top vial and dissolved in DMF (1 mL); $Pd(OAc)_2$ (0.0046 g, 0.021 mMol, 1 mol%) was added to the solution. Upon shaking, the rusty-orange color of the dissolving $Pd(OAc)_2$ immediately changed to bright yellow. The activated catalyst solution was syringed into the reaction vessel and the flask was submerged in an oil bath preheated to 60°C. The syringe pump was started and the addition of the monomer solution was closely monitored. Initially, the rate of addition was very slow because the syringe had jammed. After correcting this, the monomer solution was pumped into the reaction vessel, a total of 120 minutes (20 minutes to resolve pumping issues). Near the end of monomer addition, the yellow solution became colorless and slightly cloudy. Heating was continued for 3 hours after monomer addition was complete; at this time the solution had gelled and lumps of white translucent gel were observed. The flask was cooled to RT and neutralized to pH 7. The gelled polymer was collected by centrifugation, washed in 4 M HCl (150 mL) and recentrifuged. The insoluble product was washed with water to remove excess HCl and vacuum dried.

2.2.2 Suzuki cyclopolymerization 2: Synthesis of poly(1, 3, 5-phenylene-4, 4'-biphenylene-2, 2'-disulfonic acid). The reagent quantities and reaction conditions were identical to those for Run **2.2.1**. S-Phos-SO_3Na (0.0217 g, 0.042 mmol, 2 mol%) and oxalic acid dihydrate (0.0035 g, 0.028 mmol) were placed in a 3 mL screw-top vial, dissolved in DMF (1 mL) and $Pd(OAc)_2$ (0.0045 g, 0.020 mmol, 1 mol%) was added to the solution. Upon shaking, the rusty-orange color of the $Pd(OAc)_2$ changed to bright yellow. The activated catalyst solution was injected into the reaction vessel by syringe and the flask was put into an oil bath preheated to 60ºC. The syringe pump was started and the addition of the monomer solution over the next 100 minutes was closely monitored. Immediately after monomer addition ended, a solution of 4-bromobenzenesulfonic acid sodium salt (0.2004 g, 0.774 mmol) in deoxygenated water (3 mL) was injected in order to terminate the reaction and prevent gelation. Heating was continued for an additional 30 minutes after termination to consume the remaining boronate groups. The resulting clear, yellow solution was cooled to room temperature, neutralized to pH 7 and rotary evaporated to dryness to yield a white solid. This was washed with methanol to remove catalyst residue and collected by centrifugation. The resulting solid was stirred with 4 M HCl(aq) (100 mL), collected by centrifugation, washed with water to remove excess HCl and dried. The solid was not water soluble.

2.2.3 Synthesis of cyclic poly(1, 3, 5-phenylene-4, 4'-biphenylene-2, 2'-disulfonic acid) batch 3 (CPPSA-3). Sodium carbonate (1.6977g, 16.018mmol) was placed in a 250mL 3-neck flask, dissolved in 180mL water and deoxygenated by argon for 3 hours. Sodium 4, 4'-dibromo biphenyl 2, 2'-disulfonate (1.0320g, 2.000mmol) and benzene 1, 3, 5-tris(trifluoroboronate potassium salt) (0.5280g, 1.333mmol) were placed in 25mL pear shaped flask, dissolved in 20mL water and deoxygenated by argon for 3 hours. The monomer solution was taken up in a 20mL syringe with a 12 inch needle and the syringe was placed in a syringe pump. The flask containing the sodium carbonate solution was lowered into an oil bath preheated to 80°C and allowed to equilibrate while the catalyst was activated. In a 3mL vial, SPhos-SO_3Na (0.0218g, 0.043mmol) and oxalic acid dihydrate (0.0038g, 0.030mmol) were dissolved in 1mL DMF followed by addition of $Pd(OAc)_2$ (0.0046g, 0.021mmol) to the solution (immediate formation of bright yellow color was observed - Pd(0)/L complex formation). The activated catalyst solution was injected into the reaction flask and the syringe pump was started (addition of 20mL of monomer solution at a rate of 0.2mL/min). At this time, sodium 4-bromobenzenesulfonate (0.5173g, 1.997mmol) was placed in a 20mL vial, dissolved in 5mL water and deoxygenated for 1 hour. The initially clear, pale yellow reaction solution began to turn cloudy when approximately 5mL of monomer solution was left in the syringe. After complete monomer solution addition, the reaction was immediately terminated by addition of the sodium 4-bromobenzenesulfonate solution. Heating of the solution was continued for an additional 1 hour after termination. The resulting solution was cooled to room temperature and dialyzed through a cellulose membrane to remove low molecular weight impurities (membrane pores reject MWt > 10,000 Daltons). Dialysis was monitored by measuring the pH of the filtrate. When the initially basic reaction solution became neutral, the purified sodium-form polymer solution was placed in a 250mL flask and sealed. On standing, the dialyzed polymer solution became relatively viscous (polymer concentration = 0.4% (w/v)). A film was cast by placing some of the suspension in a Petri dish and allowing the water to evaporate.

2.2.4 Synthesis of cyclic poly(1, 3, 5-phenylene-4, 4'-biphenylene-2, 2'-disulfonic acid) batch 4 (CPPSA-4): Reagent quantities and reaction conditions were identical to those of Run **2.2.2**. The flask containing the sodium carbonate was lowered into an oil bath preheated to 60°C and allowed to equilibrate while the catalyst was activated. The activated catalyst solution was injected into the reaction flask and the syringe pump was started (addition of 20mL of monomer solution at a rate of 0.2mL/min). At this time, sodium 4-bromobenzenesulfonate (0.5222g, 2.016mmol) was placed in a 20mL vial, dissolved in 5mL water and deoxygenated for 1 hour. The clear, pale yellow reaction solution remained unchanged during the monomer addition. After complete monomer solution addition, the reaction was immediately terminated by addition of the sodium 4-bromobenzenesulfonate solution. The solution was heated for an additional 1 hour after termination, cooled to room temperature and dialyzed to remove low molecular weight impurities. Dialysis was monitored by measuring the pH of the eluted water. When the basic eluate became neutral, the purified sodium-form polymer "solution" was placed in a 250mL flask and sealed. A film was cast by placing some of the "solution" in a Petri dish and allowing the water to evaporate. The dialysis filtrate was evaporated and the residue was extracted with methanol. The methanol solution was dried and the solids were analyzed (NMR, CD_3OD) to find out how much of which monomer was in solution at the end of the reaction.

2.2.5 Scaled up synthesis of poly(1, 3, 5-phenylene-4, 4'-biphenylene-2, 2'-disulfonic acid) batch 5 (CPPSA-5). Sodium carbonate (8.4859g, 80.063mmol) was placed in a 2000mL 2-neck flask containing 900mL water and equilibrated at 80°C for 3 hours while being deoxygenated by argon. Lithium 4, 4'-dibromobiphenyl-2, 2'-disulfonate (4.8408g, 10.002mmol) and potassium 1, 3, 5-tris(trifluoroboronate) benzene (2.6405g, 6.668mmol) were placed in a 100mL single neck round bottom flask, dissolved in 100mL water and deoxygenated by argon for 3 hours. Half of the monomer solution (50mL) was taken up in a 50mL syringe and placed in a syringe pump set to add 100mL of monomer solution in 100 minutes (1mL/min). $Pd(OAc)_2$ (0.0229g, 0.102mmol) was dissolved in 3 mL DMF and deoxygenated for 1 hour, followed by addition of SPhos-SO_3Na (0.1028g, 0.201mmol) and oxalic acid dihydrate (0.0158g, 0.125mmol). The yellow Pd(0)/L solution was injected into the reaction flask by syringe and the syringe pump was started. The initial reaction solution color was pale yellow. Sodium 4-bromobenzenesulfonate (2.6019g, 10.046mmol) was dissolved in 15mL water in a 20mL vial and deoxygenated for 1 hour. After the initial 50mL of monomer solution was added, the syringe was filled with the remaining 50mL of solution and pumping was resumed. The reaction solution began to turn cloudy when ~15mL of the monomer solution remaining in the syringe. The reaction was allowed to continue for an additional 5 minutes after complete monomer addition, during which time the solution became cloudier and viscous. The sodium 4-bromobenzene sulfonate solution was added and the reaction solution was heated for an additional 1 hour to complete the termination reaction. The resulting solution was cooled to room temperature; the solution was titrated to pH 7 with concentrated HCl. The neutralized solution was added to an ultrafiltration cell in 300mL portions and washed with deionized water until no cloudiness was observed when the eluate was tested with $AgNO_3$ (Test for chloride ion). The eluent solution was concentrated by rotary evaporation; the solid was collected and extracted with ethanol in a Soxhlet apparatus, with a subsequent methanol extraction, to obtain the eluted low molecular weight organics. The purified reaction solution was stirred for 2 hours and separated into 2 equal portions (each 1000mL). One portion was set aside and the other portion was acidified with 0.01M HCl, stirred overnight and added in 300mL portions to the ultrafiltration cell and washed with 2000mL of 0.01M HCl followed by deionized water until the eluent solution was neutral.

2.3.1 Titration of cyclic poly(1,3,5-phenylene-4,4'-biphenylene-2,2'-disulfonic acid) batches 1 and 2 (CPPSA-1 and CPPSA-2). Sodium hydroxide (0.01M) was prepared from saturated (50% w/v) sodium hydroxide. The concentration of the solution was calibrated by titration of a 3mL aliquot of 0.1M potassium hydrogen phthalate to pH 7 using a pH meter. The calibration was performed twice before polymer titration and once after polymer titration to ensure accuracy of the measurement. Polymer samples (0.050g) were equilibrated at room temperature and room relative humidity and placed in a 30mL weighing bottle. Sodium chloride solution (3mL of a 2M solution) was added to the polymer samples and allowed to stir for 30 minutes. A measured volume of the base solution was added to the polymer solution. It was stirred until the pH value was constant; then more base was added. The polymer samples were titrated by this procedure to pH 7, stirred overnight for an additional 14 hours and titrated again to neutrality. The quantity of sodium hydroxide solution was recorded and the equivalent weight was calculated. CPPSA-1 (0.0518g) required 19.5mL 0.00952M NaOH, yielding an equivalent weight of 279.0 g/mol ($\lambda = 5.44$ using the polymer equivalent weight of 181 Daltons). CPPSA-2 (0.0543g) required 26.3mL 0.00952 M NaOH yielding an equivalent weight of 216.8 g/mol ($\lambda = 2.0$). (These calculations assume that all the H^+ ions in the polymer had been replaced with Na^+ ions.)

2.3.2 Film casting of CPPSA-1H, CPPSA-2H, CPPSA-3H and CPPSA-4H. In order to cast films from CPPSA-1H and CPPSA-2H, the insoluble polymers were dispersed in water and placed in an ultrasonic bath at 70°C until the suspensions became clear. The clear suspensions were poured into base-treated Petri dishes and evaporated at 60°C in an oven. The resulting thin films were used for further studies. CPPSA-3H was acidified in an ultrafiltration device using 0.01M HCl as the eluent. The acidified polymer suspension was concentrated to a highly swollen gel in the ultrafiltration apparatus. The resulting solid gel was further dried in a Petri dish under ambient conditions to yield a rigid, thick polymer film. CPPSA-4 was acidified with concentrated HCl and dialyzed until the pH of the outside solution was neutral. The polymer was soluble in water. A dilute solution was placed in a base-treated Petri dish and evaporated at 60°C to yield a film which fractured radially to yield narrow, brittle strips. Portions of CPPSA-1H, CPPS-2H and CPPSA-4H were used for analysis by TGA, ^{1}H NMR and wide angle x-ray diffraction.

2.3.3 Thermogravimetric analysis (TGA). Polymer films were equilibrated at ambient conditions and small portions of the each film (5-10mg) were placed in the TGA sample pan. Several procedures were followed. 1. Films were ramped immediately at 20^o/min from room temperature to 400^oC. 2. The films were purged with nitrogen at 25°C for 60 minutes followed by ramping to 600°C at 10°C (or 2^o) per minute.

2.3.4 Water content analysis by ^{1}H NMR. Polymer films were equilibrated at ambient conditions. Sections of film were cut into thin strips (approximately 2mm x 10mm) and 10mg (0.0100g) (approximately 3 strips); they were weighed and placed in NMR tubes. The tubes were sealed and taken to the NMR spectrometer for analysis. D_2O containing

1v/v% 1, 4-dioxane was added to each NMR tube immediately before acquiring the NMR spectrum. Samples were analyzed at 0 min, 45 min, 60 min, 75 min, and 42 hours. The intensity of the water peak (HDO) vs. the 1, 4-dioxane peak was measured for each sample and for the solvent.

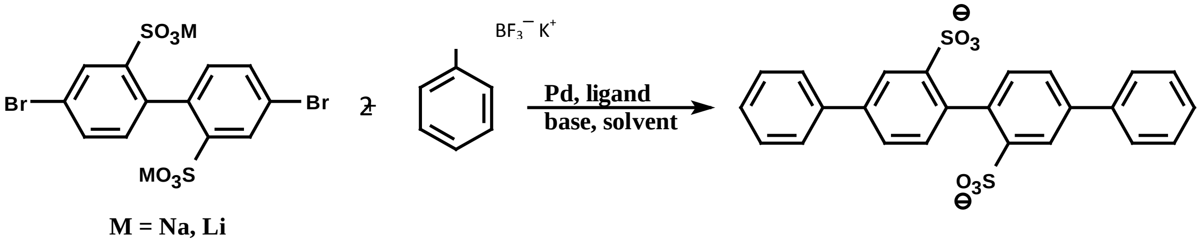
2.3.5 Wide angle x-ray diffraction (WAXD) Polymer films were mounted into the x-ray diffractometer using scotch tape to fix the film within the sample window of the sample holder. The films were run both in reflection and transmission modes. Scanning was run from 2 to 30 degrees using a 0.05 degree scanning step with a scan rate of 0.5 degrees per minute.

2.3.6 Atomic force microscopy (AFM) and scanning tunneling microscopy (STM). Atomic force microscopy (AFM) was performed on CPPSA-3 Na and CPPSA-4 Na with the help of the instrument supervisor Jack Johnson. Scanning Tunneling Microscopy (STM) was performed by Andrew Rosenberg, an undergraduate student collaborating on this project from Prof. Kash's research group in the Physics department.

3. Results and Discussion.

3.1 Evaluation of Pd(0) activation procedures: When a trifunctional monomer reacts with a difunctional co-monomer, the usual result is a cross-linked mess. Cyclization is favored if the reaction is run under starvation conditions. It is further favored if the entropy of cyclization is reduced. The reagents chosen were rigid molecules that had to connect with bond angles of 120^o. This should generate six sided rings. If the monomer concentration is kept very low, monomer must add to existing polymer molecules and the adduct can cyclize when the stereochemistry is correct.

Earlier, we had studied the kinetics of the Suzuki reaction in great detail using previously developed reaction conditions. All of the kinetic studies to this point had been run using **in situ** reduction of Pd(2) to the active Pd(0)/L complex. It was belatedly realized that the kinetic runs implied that the Pd(2) was being reduced very slowly to generate the active Pd(0) catalyst. For the cyclic polymerization reactions, a pre-reduced Pd(0)/L complex should be used in order to preserve the stochiometry of reacting groups. In order to obtain a more complete picture of the Suzuki coupling kinetics, several reactions were run with sampling using pre-reduced Pd(0)/L complexes. Scheme 2 shows the general considerations for the test reaction.



Scheme 2. General Suzuki reaction for kinetic studies.

Reactions 2.1.1 and 2.1.2 were run together to probe the effect that reagent concentration had on the rate of the reaction. Reaction 2.1.1 was run with 4% w/v of sodium 4, 4'-dibromobiphenyl-2, 2'-disulfonate concentration and reaction 2.1.2 was run at half concentration (2% w/v). In both reactions, the Pd(II) was pre-reduced by addition of a solution of $Pd(OAc)_2$ in water to a solution of SPhos-SO_3Na and oxalic acid dihydrate in water. The reduction was complicated by the poor solubility of both $Pd(OAc)_2$ and SPhos-

SO_3Na in water. The vivid yellow color that is observed in Pd(0)/phosphine-ligand complexes was not seen; only a pale yellow color formed. In both reactions the rate of generation of twice-reacted quaterphenyl-2’,2”-disulfonic acid was low and did not reach completion by the end of the sampling (100 and 140 minutes respectively). Careful analysis of the reagents used in the reaction found that the potassium phenyltrifluoroborate contained what appeared to be a phenolic impurity. This might have led to the poor results found in both reactions.

Reaction 2.1.3 was set up identically to reaction 2.1.1, but using purified potassium phenyltrifluoroborate. Figure 2 shows the conversion vs. time for this reaction. The increase in the rate of disappearance of sodium 4,4’-dibromobiphenyl-2,2’-disulfonate with time suggests that Pd(2) was being reduced very slowly. The reaction rate was slower than that found for the earlier kinetic runs that did not use oxalic acid. This implied that oxalate ion in water is not effective for the reduction of Pd(2) to the Pd(0)/L complex.

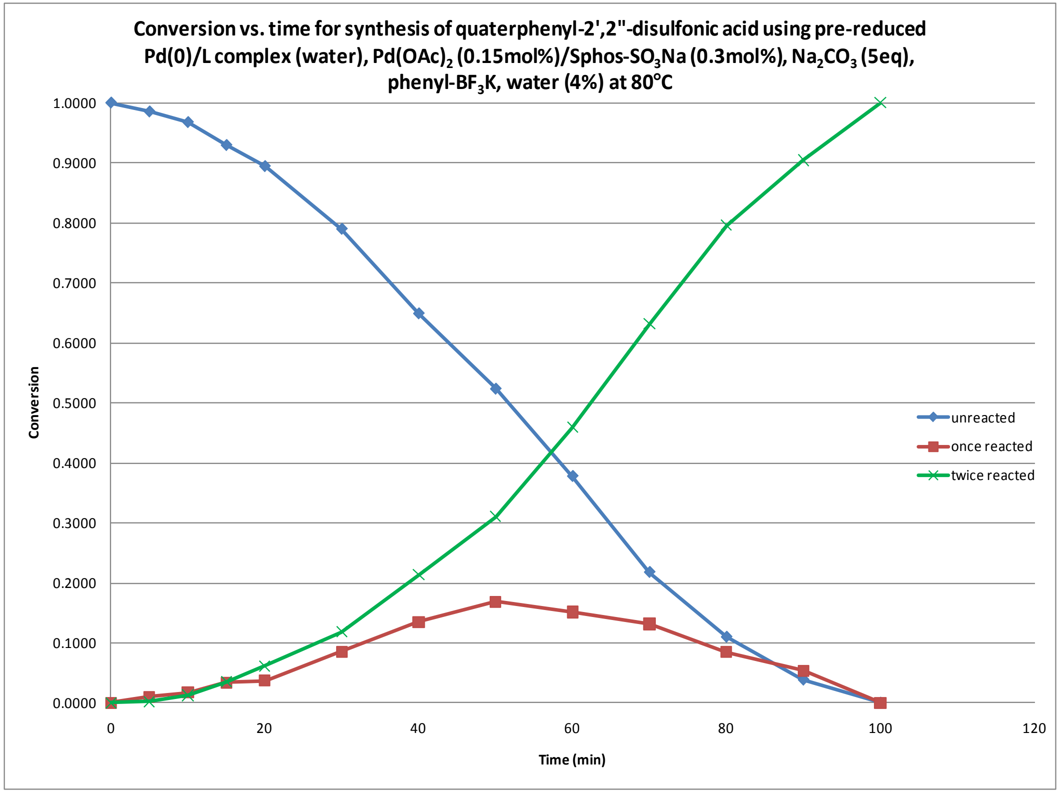


Figure 2. Conversion vs. time plot of Suzuki coupling reaction using Pd(0)/L complex prepared by reduction with oxalate ion in water, Run 2.1.3.

It was decided to pre-reduce the Pd(2) in a good solvent for all reagents; DMF was chosen. When the solution of palladium acetate in DMF was added to the solution of ligand/oxalic acid in DMF, the mixture rapidly turned brilliant yellow, showing that the palladium had been reduced and was stabilized by the ligand. Figure 3 shows the conversion vs. time plot for reaction 2.1.4. Reaction was complete in less than 5 minutes when the first sample was taken, in contrast to reaction 2.1.3 with Pd-reduction in water, which took 100 minutes. Reaction 2.1.4 showed that the cyclic polymerization reactions could be run under starvation conditions even if 0.15 mole% Pd is used. We therefore pre-reduced Pd(2) in DMF using a concentration of 1.0 mole% for all the cyclopolymerization reactions to ensure starvation polymerization conditions.

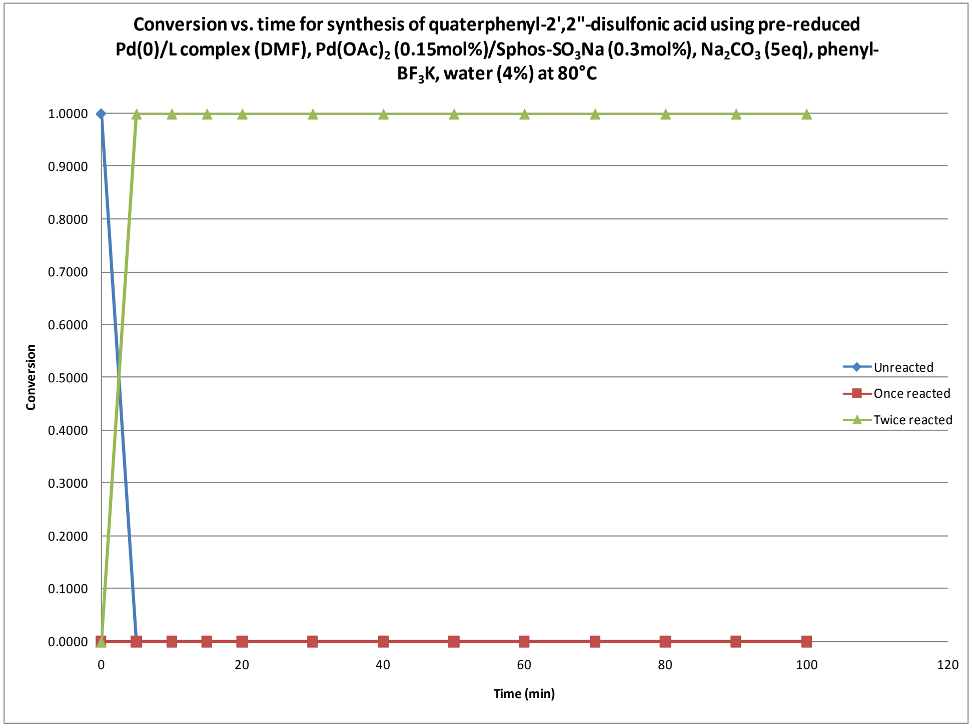


Figure 3. Conversion vs. time plot of Suzuki coupling reaction using Pd(0)/L complex prepared in DMF, Run 2.1.4.

3.2.1 First approaches to the synthesis of cyclic poly(1, 3, 5-phenylene-4, 4’-biphenylene-2, 2’-disulfonic acid); Much preliminary work had been done to find appropriate reagents and conditions for synthesis of cyclic poly(1, 3, 5-phenylene 4, 4’-biphenylene 2, 2’-disulfonic acid). Development of catalyst systems, base, reaction temperature, boronate group, and kinetics were studied in great detail in order to determine the proper method of running the polymerization to maximize cyclic structure formation. Using information from the kinetic studies along with results from the triboronate reactivity tests, the first aqueous cyclic polymerizations were run. As a first attempt (reaction 2.2.1), the polymerization was set up with pre-activated Pd(0)/L complex and base in the reaction flask. A concentrated solution of the monomers was placed in a syringe and was added slowly to the reaction flask using a syringe pump: the addition took 100 minutes. The solution remained unchanged in appearance until near the end of the monomer addition (final 10 minutes). At this point it changed from light, transparent yellow to nearly colorless and slightly milky in appearance. After complete monomer addition, the heated reaction mixture was stirred for another 3 hours. During this time the solution gelled, became translucent and contained lumps of highly swollen polymer gel. We hypothesized that the long post-addition reaction time allowed the polymer molecules to react with each other, generating an extended 3-D structure, a gel. A second polymerization was run, designed to prevent this from happening.

The reaction conditions for the second run (reaction 2.2.2) were the same as for reaction 2.2.1, except that 4-bromobenzene sulfonic acid sodium salt was injected immediately after monomer addition was completed in order to terminate the reaction.

During the monomer addition, the solution remained transparent pale yellow. Heating was continued for an additional 30 minutes after the 4-bromobenz**e**ne sulfonic acid sodium salt injection. The bromobenzene sulfonate should react rapidly with any remaining boronate groups, preventing polymer-polymer reactions. After the solution was cooled, water was stripped by rotary evaporation to yield a white powder. Low molecular weight materials, including the catalyst, were extracted by washing with methanol. Acidification with 4 M HCl (aq) yielded a swollen polymer gel that dried to a brittle, powdery film. The acidified solid was found to be insoluble in water and methanol after workup.

If the reaction works as hypothesized, the final molecules should be planar disks, one benzene ring thick and of unknown diameter. The edges, before quenching, could contain both bromo and boronate groups; these could react intramolecularly only by cyclization because they are fixed in position. However, they might react slowly with groups on other molecules, generating a gel. Crosslinking should have been prevented in the second run since the reaction was quenched with 4-bromo benzenesulfonic acid. However, after precipitation and drying the material was insoluble in water, methanol and other potential solvents. Probably, the initially soluble planar material aggregated and became insoluble. Because the idealized structure is a completely planar hexagonal lattice, it could be possible for large aggregates to form by stacking of the disks; these would be difficult to break up once formed because the molecules have many interaction sites. (See later discussion and SEM photographs.) Another possibility is that the polymerization yielded crosslinked 3-dimensional nanogels. However, this is unlikely because such material should redisperse readily in water.

Because CPPSA-1 and CPPSA-2 were completely insoluble after the workup procedure, it was difficult to cast good films for characterization. Therefore more batches of cyclic poly(1,3,5-phenylene-4,4'-biphenylene-2,2'-disulfonic acid) were synthesized to produce stock solutions of polymer for film casting. It was determined that ultrafiltration was an appropriate method to remove the reaction byproducts (excess base, salts, low molecular weight impurities) without concentrating the reaction solution, to dryness, as was done before. Following the procedure used in the initial polymerizations, CPPSA-3 (reaction 2.2.3) was synthesized. However, a hotplate without temperature control was used for the reaction; the reaction temperature stabilized at 80°C instead of the targeted 60°C. The reaction was run using monomer addition conditions identical to the previous two runs (0.2mL/min). The reaction solution began to turn cloudy with approximately 5mL of monomer solution left in the syringe, but the addition was continued without modifying the addition rate. The now translucent solution was terminated with sodium 4-bromobenzenesulfonate as soon as monomer addition was complete. Ultrafiltration was used to remove the low molecular weight impurities from the reaction solution. The sodium form of the polymer was obtained as a viscous 0.4% w/v solution and was used to cast films for further study. Because the reaction temperature was higher than desired, another batch of polymer was synthesized.

CPPSA-4 (reaction 2.2.4) was set up using a temperature controlled hotplate with thermometer set at 60°C and oil bath equilibration was reached before the reaction was started. During the monomer solution addition, the reaction solution remained clear and pale yellow. At the end of monomer addition, the reaction was terminated with a solution of sodium 4-bromobenzenesulfonate and dialyzed until the eluate reached pH 7. Half of the polymer solution was removed and stored in a flask; acid was added to the remaining amount. The acidified solution was ultrafiltered until the eluate was neutral (this process was repeated). The solutions were used for preparation of samples for further study.

3.2.2 Analysis of eluates of CPPSA-3 and CPPSA-4;. Because CPPSA-1 and CPPSA-2 polymers had been purified in a way that rendered them water-insoluble, a new method for purification was instituted. In order to prevent the agglomeration of polymer particles into an insoluble gel, ultrafiltration was used to purify the reaction solutions. This method was chosen because it could remove all low molecular weight contaminants from the solution without having to evaporate the initial reaction solution to dryness, thereby maintaining the original state of the polymer aggregates. Yet another advantage is that the low molecular weight materials can easily be collected for analysis to yield further information about the polymerization reaction. The solids obtained from evaporation of the ultrafiltration eluent solution were analyzed by ^{1}H NMR to determine if any unreacted monomer remained and if other low molecular weight compounds were formed during the reaction. Figure 4 shows the ^{1}H NMR spectrum of the methanol soluble materials obtained from CPPSA-3.

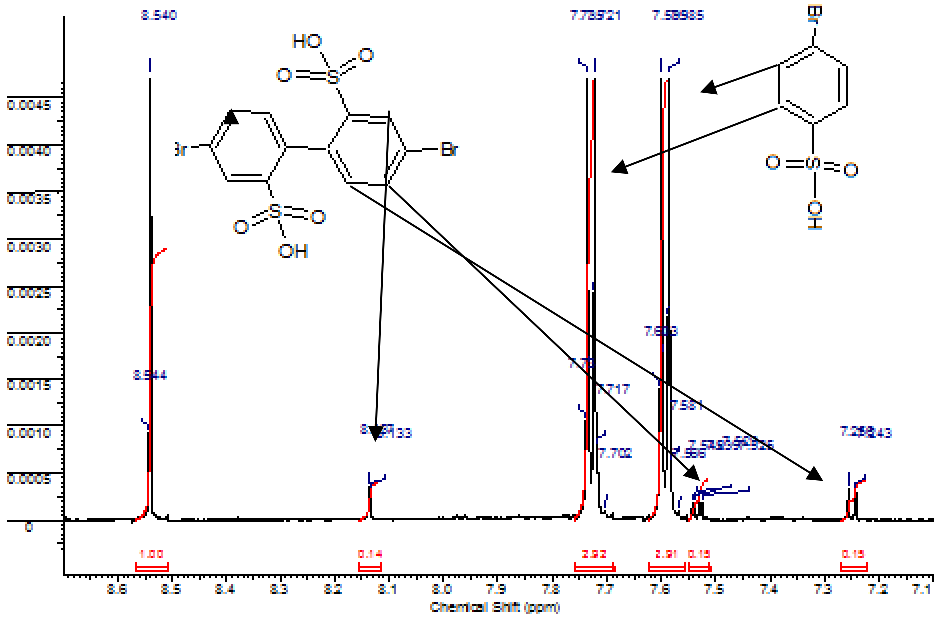


Figure 4. ^{1}H NMR (CD_3OD) of low molecular weight compounds obtained from CPPSA-3 reaction solution by ultrafiltration.

The ^{1}H NMR spectrum shows very clearly that the organic compounds found were monomer, 4, 4’-dibromobiphenyl-2, 2’-disulfonate, 4-bromobenzesulfonate and formate ion (at 8.54 ppm). Because the reaction was terminated by addition of excess monofunctional sodium 4-bromobenzenesulfonate, it was expected to be visible in the spectrum. What was unexpected was the observation of 4, 4’-dibromobiphenyl-2, 2’-disulfonate with no equivalent quantity of 1, 3, 5-phenylene tris(4-benzenesulfonate) (the reaction product of remaining monomer potassium 1, 3, 5-phenylene tris(trifluoroborate)). This observation seems to support the previous result that each of the boronate groups in the potassium 1, 3, 5- phenylene tris(trifluoroborate) react faster than the previous one ($B_1 < B_2 < B_3$). This observation implies that as the monomer solution is added, the boronate adds to the growing polymer more rapidly than the bromo-compound leaving unconsumed bromo-compound in the quenched solution.

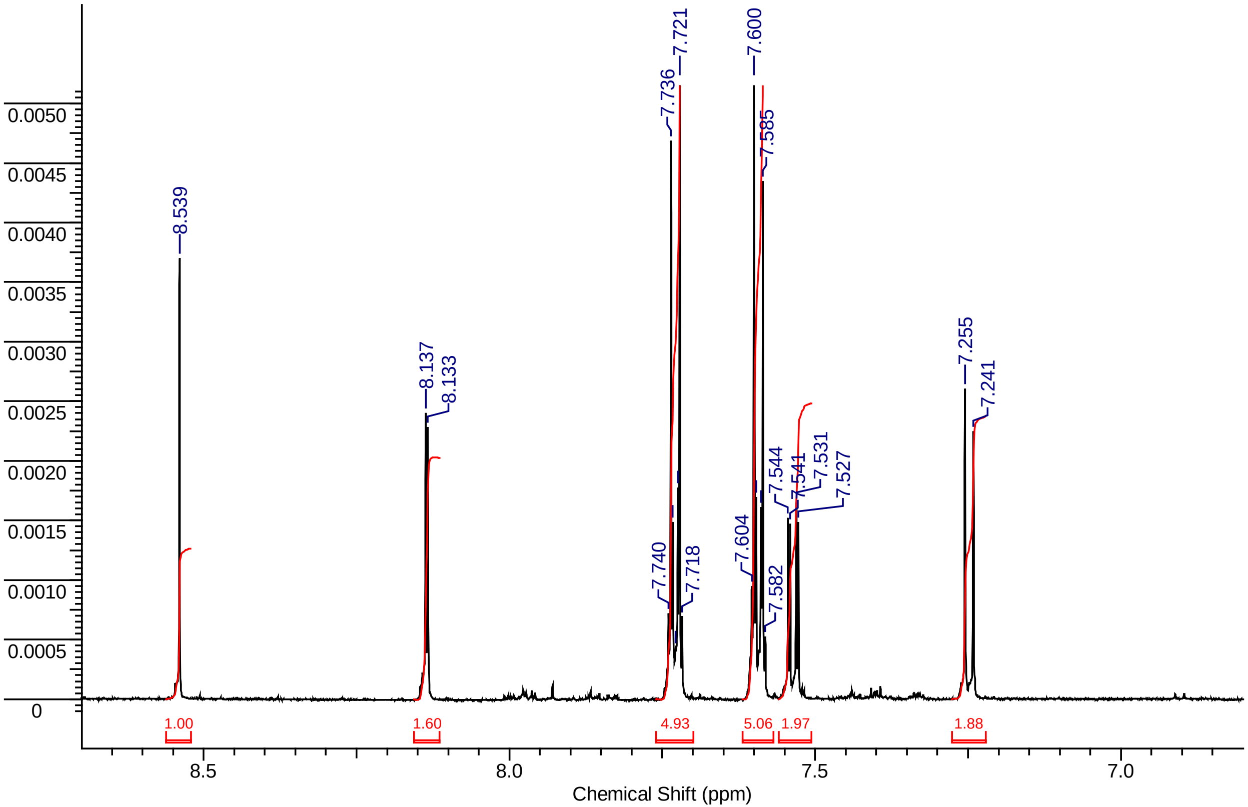


Figure 5. ^1H NMR (CD_3OD) of low molecular weight compounds obtained from CPPSA-4 reaction solution by ultrafiltration.

The same analysis for remaining monomer was applied to the eluent solution of CPPSA-4. The ^1H NMR spectrum of the compounds obtained from the CPPSA-4 polymerization solution is shown in Figure 5. The ratio of 4, 4’-dibromobiphenyl 2, 2’-disulfonate to 4-bromobenzenesulfonate is considerable higher than that found for CPPSA-3. This can be rationalized by postulating that much lower molecular weight polymer was formed. Support for this hypothesis is gained by considering the qualitative difference in mechanical properties of films cast from CPPSA-4 vs. films cast from CPPSA-3. The obtained CPPSA-4 films were extremely brittle; the polymer broke into thin strips radially in the casting dish. These thin strips were easily crumbled into smaller particles and had virtually no mechanical strength. On the other hand, while films made with CPPSA-3 cracked during drying, the individual pieces were large and easily handled without breakage; they could be flexed considerably.

Since only dibromobiphenyl monomer was found in solution, we can conclude that most or all of the partly reacted groups at the polymer edge must be boronate. If one makes the assumptions that all the edge groups are twice reacted boronate, and that the molecules are regular hexagons, the ratio of partly reacted boronates to total “boronate” residues versus the number of rings in the hexagonal structure can be easily calculated. The amount of dibromo biphenyl molecules in solution is then ½ the number of free boronate groups.

A simple model was derived based on the assumption of radial growth of the polymer molecules to form hexagonal disc-like molecules of uniform size composed of concentric rings of hexagons. The following equations describe the number of monomer units in a polymer with **n** rings of hexagons.

(Biphenyl units)	$BP(\mathbf{n}) = 3\mathbf{n}*(3\mathbf{n}-1)$
(Twice reacted boronate units)	$B(2) = 6*\mathbf{n}$
(Thrice reacted boronate units)	$B(3) = 6*\mathbf{n}*(\mathbf{n}-1)$
(Free biphenyl units)	$BP(soln) = 3*\mathbf{n}$

The fraction of free biphenyl monomer in solution divided by the total amount added is therefore $3*\mathbf{n}/(9*\mathbf{n}*\mathbf{n}) = 1/(3*\mathbf{n})$. We assume for the calculation that for every biphenyl molecule in solution, two molecules of p-bromo phenyl sulfonic acid have reacted with edge boronate groups in the polymer. If the ratio between 4, 4'-dibromobiphenyl-2, 2'disulfonate and 4-bromobenzenesulfonate is accurately reflected in the NMR integration, the molecular size can be calculated.

For both Runs 3 and 4, 2.00 mmol of biphenyl monomer were used, and 2.00 mmol of p-bromophenyl sulfonic acid were added to quench the reaction. The ratio of bromo ends from unreacted monomer to those of remaining p-bromophenyl sulfonic acid were determined from the NMR spectra, 0.15/1.46 for Run 3 and 1.9/2.5 for Run 4. From this ratio, **n** can be determined and thus the average width of the planar molecules (width = $2.2*(2*\mathbf{n}-1)$ nm.). For Run 3, $\mathbf{n} = 7.2$ and the width $\approx$ 29 nm. For Run 4, $\mathbf{n} = 1.54$ and the width $\approx$ 4.6 nm. The number average molecular weights calculate as ~163,000 and ~6,700. Obviously, something happened in Run 4 to drastically retard the polymerization.

3.2.3 XPS Analysis of CPPSA-1H and CPPSA-2H, cyclic poly(1, 3, 5-phenylene-4, 4'-biphenylene-2, 2'-disulfonic acid). The polymers obtained are not easily characterized by typical analytical techniques such as NMR due to their insolubility. In order to determine what was obtained from the reaction, x-ray photoelectron spectroscopy (XPS) was used to analyze the elemental composition of some polymer samples. Figures 6 and 7 show the XPS spectra of CPPSA-1H and CPPSA-2H. The CPPSA-1H spectrum shows the presence of carbon, sulfur, oxygen and bromine as well as some unexpected impurity elements, fluorine, nitrogen, silicon, chlorine and phosphorous. Because XPS is a surface analysis technique, element analyses can be easily skewed by the presence of surface contaminants. Fluorine could be present as fluoride or bifluoride (HF_2^-), produced by hydrolysis of the trifluoroboronate groups during the reaction. Silicon shows contamination with silicone lubricant ($SiOC_2$). Nitrogen is most likely from dimethyl ammonium ion, from hydrolysis of the DMF (C_2N) in the catalyst activation solution. (This possibility can be seen clearly by inspection of Figures 4 and 5. There are large peaks at 8.4 ppm, where formate ion is found.) The counter-ions could be fluoride, bromide, chloride and formate (CO_2) as well as the polymer sulfonate groups. Excess carbon and oxygen in the elemental analysis can be attributed to fatty acid triglycerides (body oil, $C_{19}O_2$). The XPS element analysis is rationalized as $6*(C_8SO_3) + 2.1*(NC_2) + 0.3*(SiOC_2) + 0.80*(C_{19}O_2) + 0.6*(CO_2)$, which fits exactly. The positive ion concentration exactly equals the negative ion concentration, excluding sulfonate if it is postulated that the fluorine is present as fluoride rather than bifluoride.

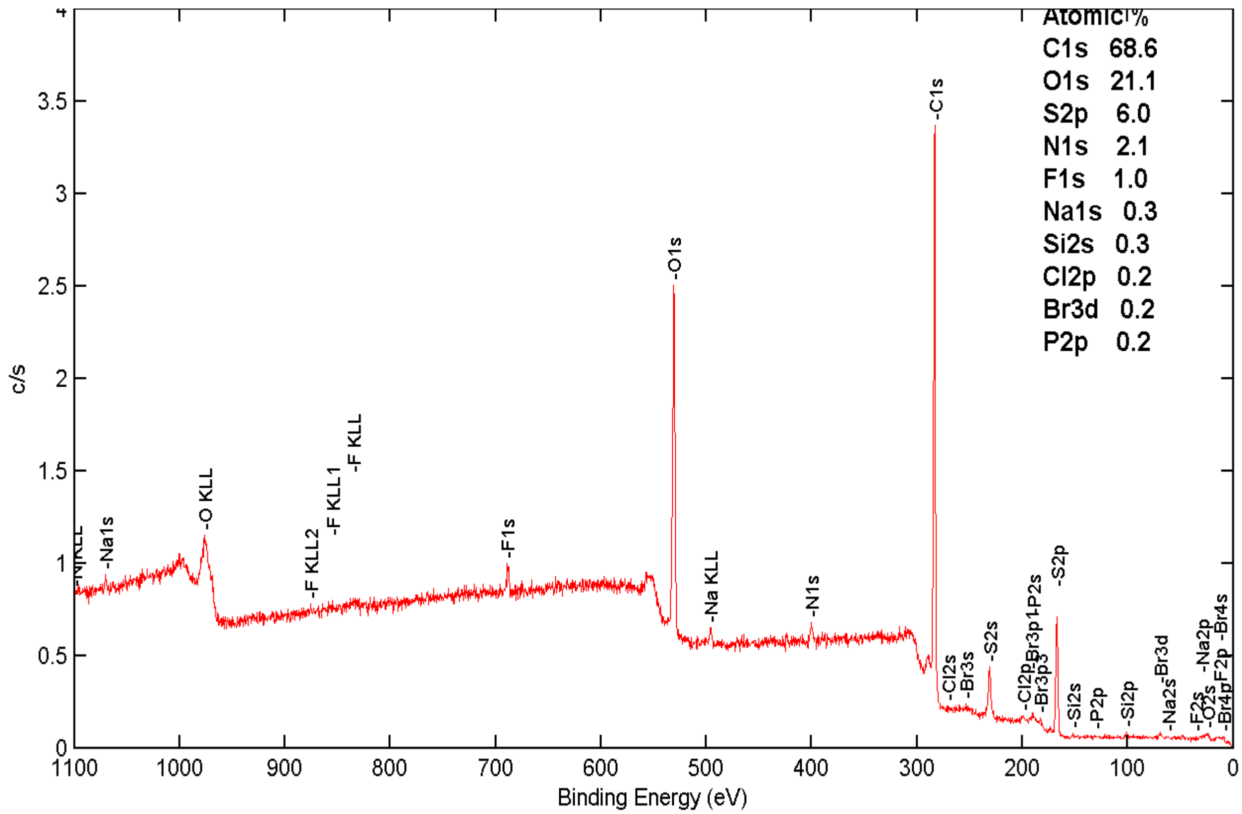


Figure 6. XPS spectrum of CPPSA-1H with element analysis.

Applying the same analysis to the elemental composition to the XPS spectrum of CPPSA-2H (Figure 7), the large amount of fluorine found can be rationalized as a partial surface layer of perfluorooctanoic acid ($C_8F_{15}O_2Na$). (Because a new Teflon stir bar was used for the reaction, it is possible that the Teflon processing agent, perfluorooctanoic acid, could be extracted from the bar and deposit as a surface contaminant.) Nitrogen is observed, probably from dimethyl ammonium ions. (Any DMF would evaporate in the ultra high vacuum used in the XPS analysis.) The molar elemental composition for such a polymer with **n**=1.54 after the boronate groups have been reacted with p-bromophenyl sulfonic acid is $C_{7.16}SO_3$. By accounting for the impurities, the XPS elemental analysis works out to $4.8*(C_{7.16}SO_3) +1.51*(C_8F_{15}O_2Na) +0.9*(NC_2) +1.1*(CO_2)$ within experimental error. Again, the positive and negative ions balance, implying that all the sulfonic acid groups had been exchanged to the acid form. A small mol fraction of bromine was observed in both analyses, which is probably from trapped bromide ions.

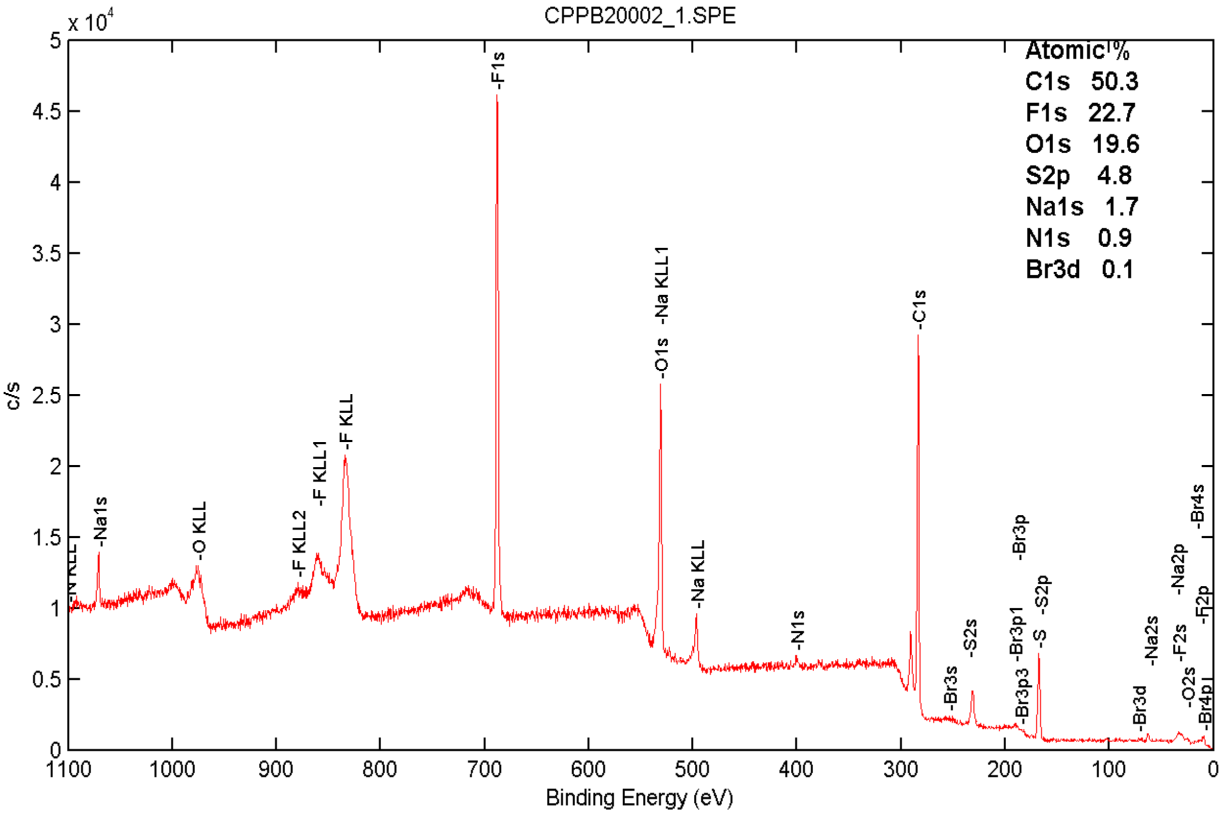


Figure 7. XPS spectrum of CPPSA-2 with element analysis.

3.2.4 Thermogravimetric analysis; water content and degradation temperature: In order to quantify the water content of the polymers, thermogravimetric analyses (TGA) and titrations were performed. Figure 8 shows the TGA of CPPSA-1H. The polymer sample was equilibrated at room temperature and room relative humidity and heated from room temperature to 400°C at 20°C/min. If all water is assumed to be lost by 270°C, each sulfonic acid group held 3 water molecules. However, titration of the polymer sample yielded an equivalent weight of 279 g/mol, $\lambda = 5.44$. Since the XPS analysis showed that all the sulfonate groups were in the acid form, this implies that there is some very strongly held water that is only lost above 270°C. If the residual weight for CPPDSA-1H at 390^{o}C is considered its dry weight, the initial weight of water per acid group is 103 gm, corresponding to $\lambda = 5.8$, close to but above the value of 5.4 obtained by titration.

The derivative curve in Figure 8 shows a maximum weight loss rate for water at ~305^{o}C, with a slope change at ~ 333^{o}C, which implies that something besides water loss is happening, probably loss of SO_2. The data fit with the titration value at a weight loss of 35%, which occurs at 367^{o}C.

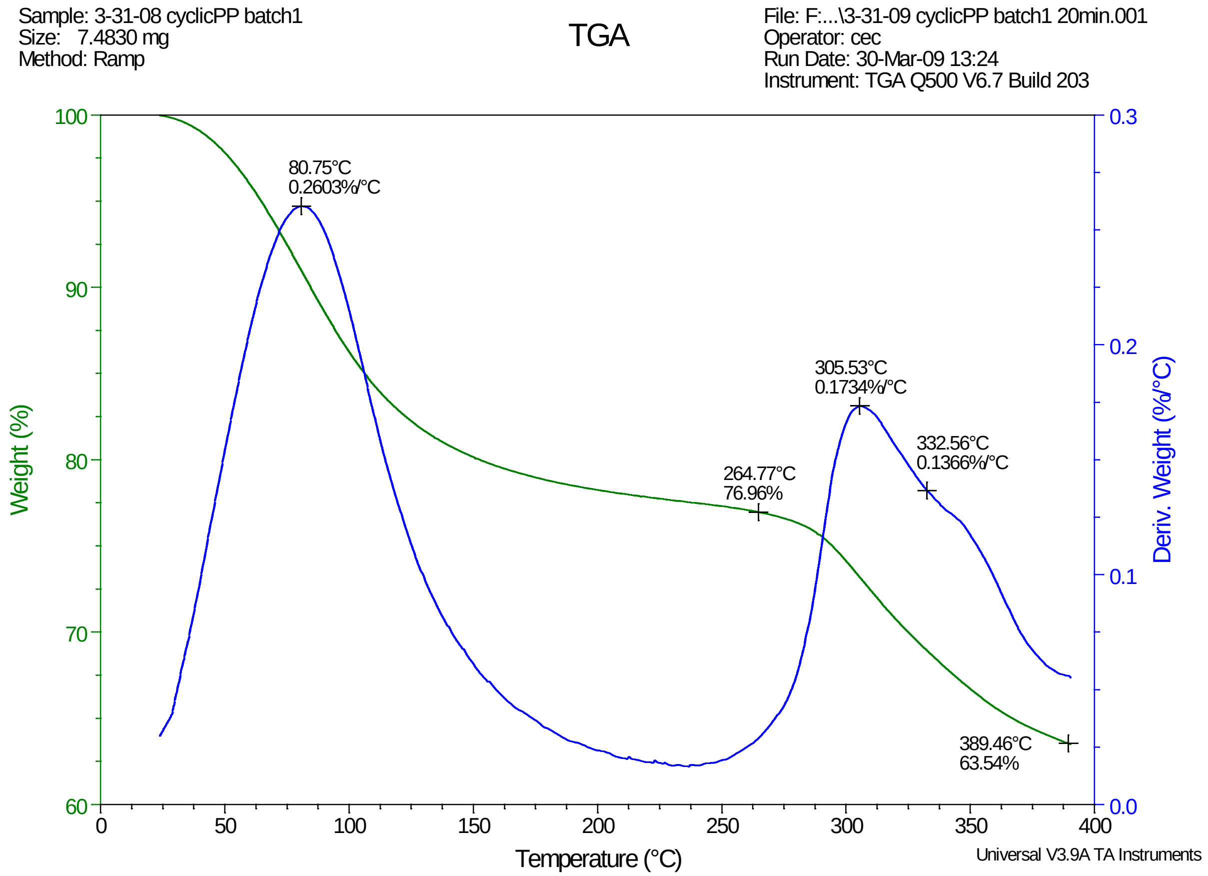


Figure 8. Thermogravimetric Analysis (TGA) scan (20^{o}/min) of CPPSA-1H, weight loss and derivative curves.

Figure 9 shows the TGA scan and its derivative for CPPSA-2H. The polymer sample was equilibrated at room temperature and room relative humidity and heated from room temperature to 400°C at 20°C/min. In contrast to CPPSA-1H, the weight loss curve does not start dropping sharply until ~290°C. If 288^{o}C is taken as the temperature where all water is lost, the water content corresponds to $\lambda = 2.5$. Titration of CPPSA-2 yielded an equivalent weight of 217 g/mol, $\lambda = 2.0$, lower than the TGA results. The maximum rate of loss of the strongly held water for CPPDSA-1H was at 305^{o}C. CPPDSA-2H loses almost no weight from 288 to 310^{o}C, implying that there was very little strongly bound water. Part of the weight loss up to 340^{o}C might be due to loss of a small amount of strongly bound water (If so, $\lambda = 3.0$.). These results imply that polymerization conditions have a very large effect on the final state of polymer aggregation. CPPDSA-1H properties fit with our postulated picture; water is held very strongly in nano-channels. The results from the TGA and titration data are encouraging, however more controlled experiments must be performed to ensure the data can be completely correlated and understood.

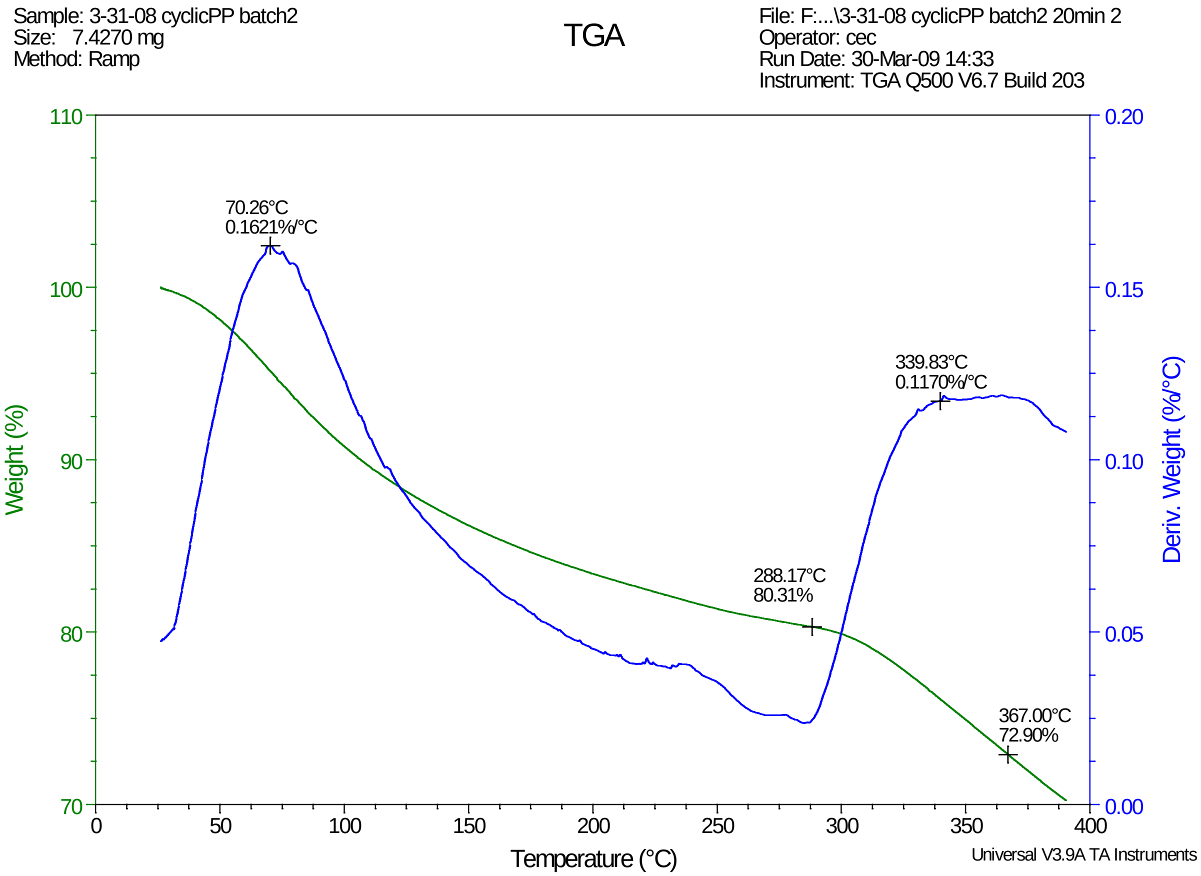


Figure 9. Thermogravimetric Analysis (TGA) scan (20^{o}/min) of CPPSA-2, weight loss and derivative curves.

The TGA analyses shown above were performed on CPPSA-1H and CPPSA-2H in the obtained powdered form. It was subsequently discovered that the insoluble polymer solids could be redispersed into transparent “solutions” by ultrasonication with heating. Polymer films with reasonable mechanical properties could be cast. These were used for a new series of analyses. Since TGA scans had been run on CPPSA-1H and CPPSA-2H powders, a comparison of water-retention and decomposition properties of the same materials with different histories can be made.

Figure 10 shows the TGA plot of CPPSA-1H film as a function of temperature. This was run by sweeping the film with dry nitrogen for one hour and then ramping at 10^{o}/min. Approximately 23% of the initial weight was lost at room temperature (25°C) during the dry nitrogen sweep. The derivative weight curve shows the rate of weight loss as a function of heating and time. Two maxima relating to water loss are seen in the derivative curve, at 75 and 294°C, with a shoulder at 324^{o}C. The high temperature composite peak implies that two processes are occurring simultaneously. Water apparently protects the sulfonic acid groups from thermal degradation. As the last water molecules are removed, the sulfonic acid groups probably start degrading, losing SO_2. The maximum that occurs above 500°C is probably due to further decomposition.

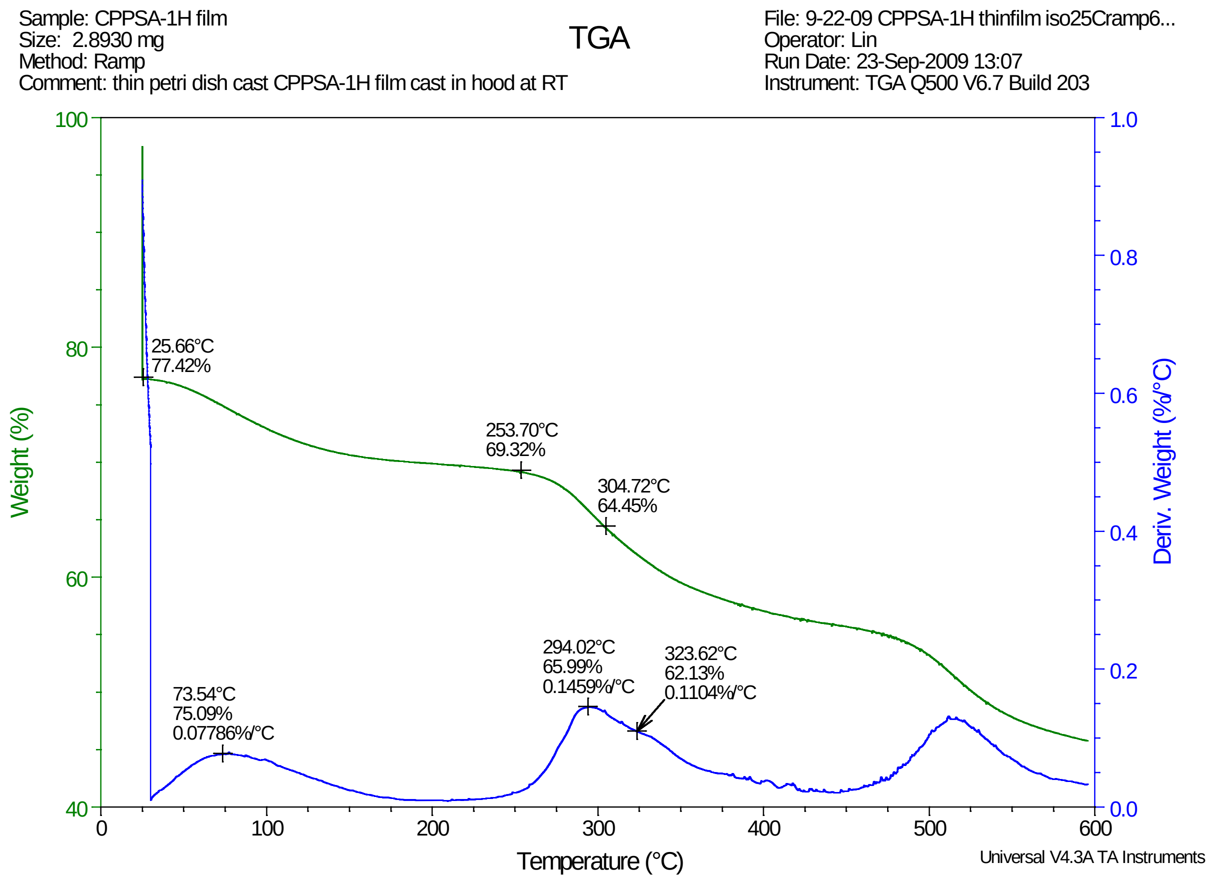


Figure 10. CPPSA-1H thin film equilibrated at ambient conditions, swept with dry nitrogen at 25°C for one hour and then ramped to 600°C at 10°C/min

Figures 8 and 10 can be compared to find out what effect sonication and film casting had on the water retention properties of CPPDSA-1H. Because the sweep rate was changed from 20 to 10^{o}/min, all maxima are at lower temperatures. CPPDSA-1 film lost 3.7 waters/SO_3H during the 60 minute room temperature sweep. An additional 1.3 waters were lost up to 253^{o}C. The final temperature taken, 324^{o}C, is arbitrary, but is lower than the temperature found for the 20^{o}/min TGA run. If all the weight loss is attributed to water loss, the starting λ was 6.1. About 1.2 waters per SO_3H were still held at 250^{o}C.

Another CPPDSA-1H film was run with a 60 minute room temperature sweep and ramped at 2^{o}/min to 600^{o}C, Figure 11. The results can be compared with the two earlier ramps, Figures 8 and 10. This sample held much less water, λ ~4-4.5, even though it was run on the same day as the 10^{o}/min ramp; perhaps the film composition was heterogeneous.

However, even with this discrepancy, we can use the temperatures at which maximum rates of weight loss occur for different ramping rates to calculate tentative activation energies. This was done using the three different ramping rates. For the ramp from room temperature to ~200^{o}C, $\Delta H_{Vap} \approx$ 66 KJ/mole. This is reasonable for a combination of normal heat of vaporization plus strong H bonding. The high temperature activation energy for water loss, from ~200 to 350^{o}C, is very large; the activation energy plot gives a value of $\Delta H_{Vap} \approx 199$ KJ/mol. This could reflect the capillary attraction in the nano-pores and compression of the rigid nano-pores with loss of water, as well as heat of transfer of protons from water to sulfonate.

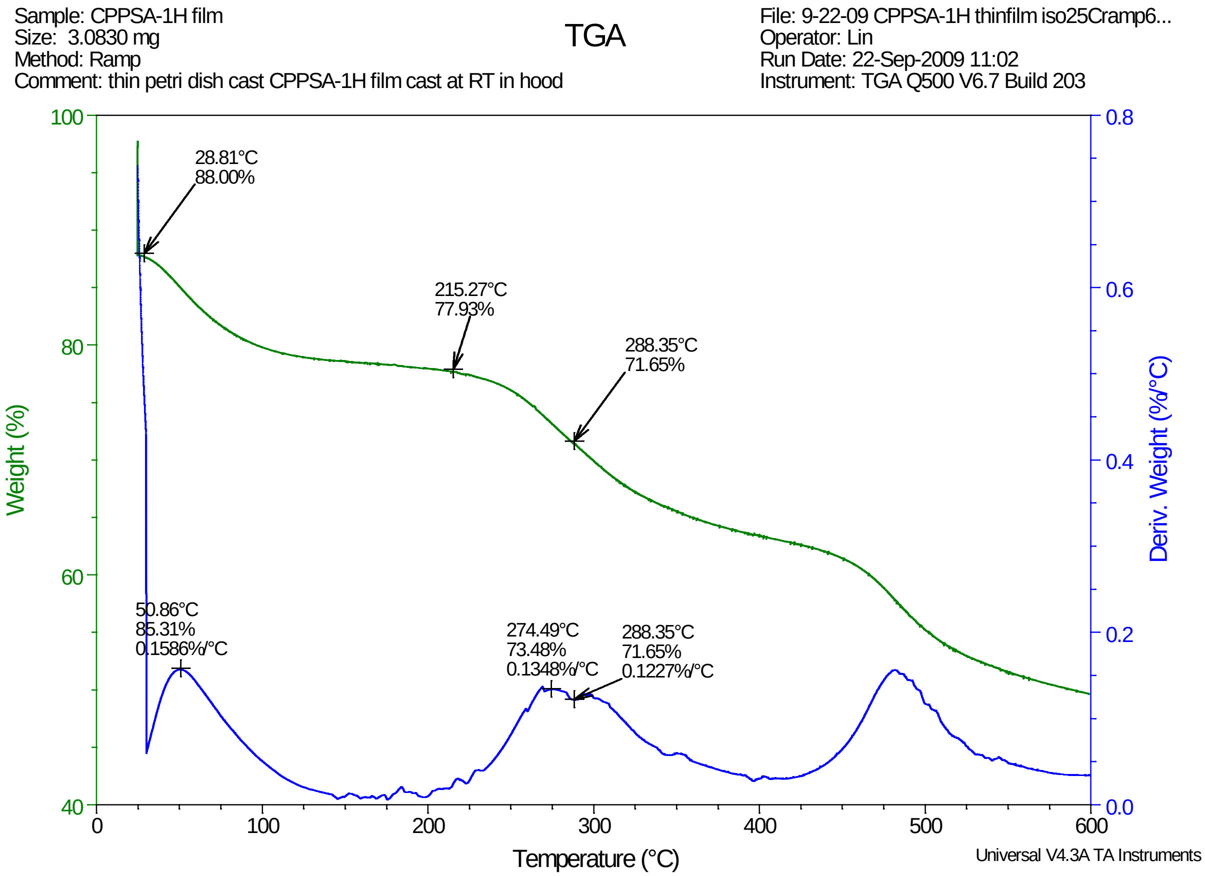


Figure 11. CPPSA-1H thin film equilibrated at ambient conditions, swept with dry nitrogen at 25°C for one hour and then ramped to 600°C at 2°C/min

Figure 12 shows the TGA plot obtained from the CPPSA-2H film sample. The shape of the curve is very different than that observed for CPPSA-1H. The initial weight loss at 25°C under dry nitrogen sweep is only 11% compared with the 23% weight loss observed for CPPSA-1H, Figure 10. The total weight loss to 320^{o}C corresponds to $\lambda = 2.7$, much less than any value for CPPDSA-1. Titration of the initial acidified precipitate found $\lambda = 2.0$.

However, the temperature picked, 320^{o}C, might be too high. In contrast to CPPSA-1H and the initial scan for CPPDSA-2H, Figure 9, the derivative curve does not have the double peak near 300^{o}C that was seen for all the earlier scans; it shows a single peak at approximately 300°C. All the water may have been lost by 260^{o}C and further weight loss may be due to polymer degradation. If all the water is lost by 260^{o}C, $\lambda = 2.2$.

The peak at 500°C is approximately in the same range as the final decomposition peak in CPPSA-1H; however, the appearance of a second decomposition peak in the neighborhood of 550°C indicates that different processes are occurring in different preparations of the polymer. Further analyses using coupled TGA-mass spectroscopy or TGA-FTIR are needed to quantify the loss mechanisms.

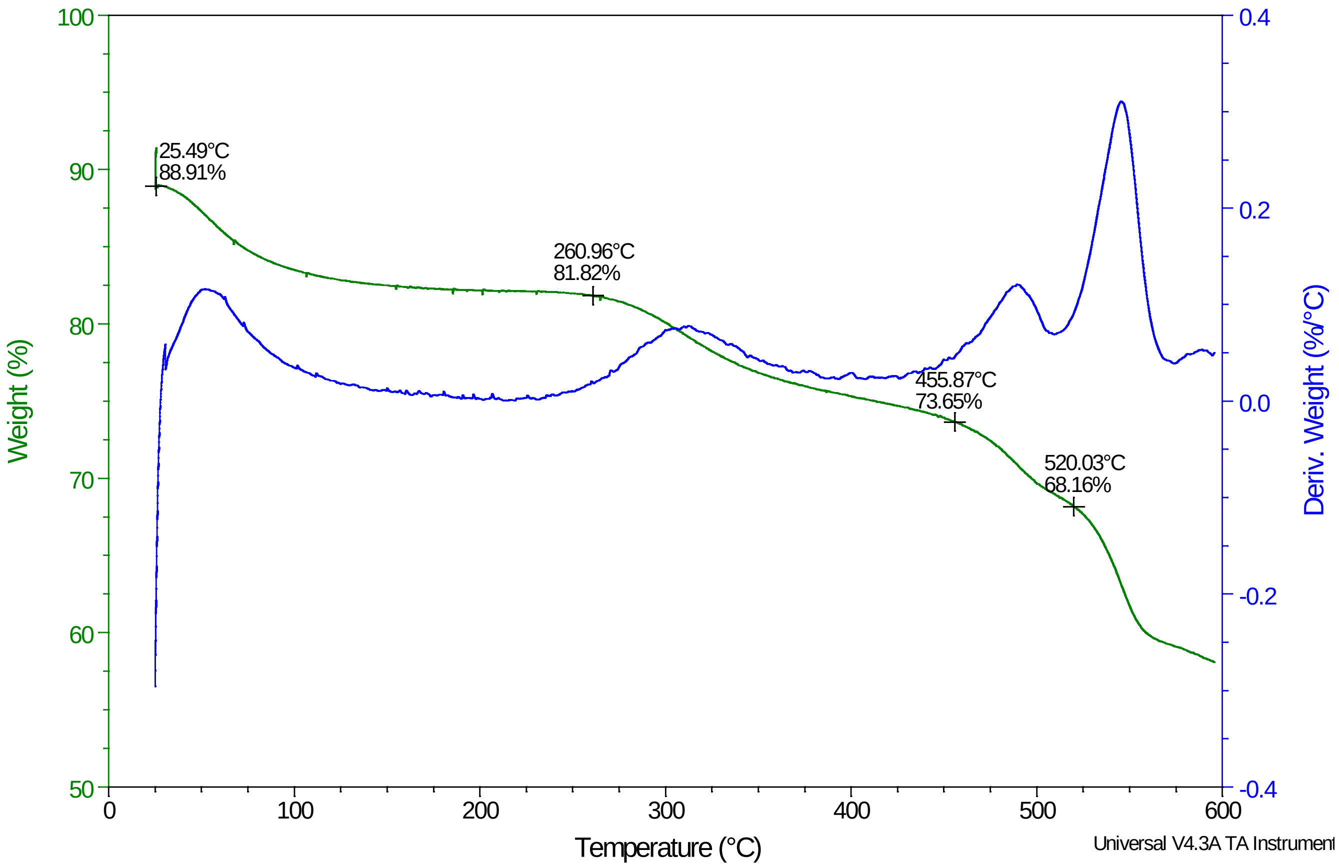


Figure 12. CPPSA-2H thin film equilibrated at ambient conditions, swept with dry nitrogen at 25°C for one hr and ramped to 600°C at 10°C/min

Figure 13 shows the TGA plot obtained from CPPSA-4H. In contrast to both CPPSA-1H and CPPSA-2H, there is almost no plateau. We know from the residual monomer analysis, section **3.2.2**, and the film physical properties that this run generated very small molecules that may not have been able to form nano-pores. The rate maximum is at 274^{o}C, lower than those of any of the earlier scans. If the temperature at the lowest weight loss rate, 241^{o}C, is considered to be where all water is lost, we find λ = 3.3. However, the higher temperature peaks correspond fairly well to those for the other samples. It is possible that the weight loss between 241 and 327^{o}C is also due to water loss. In that case, the initial λ was 4.2, with 0.7 waters/SO_3H still held at 241^{o}C.

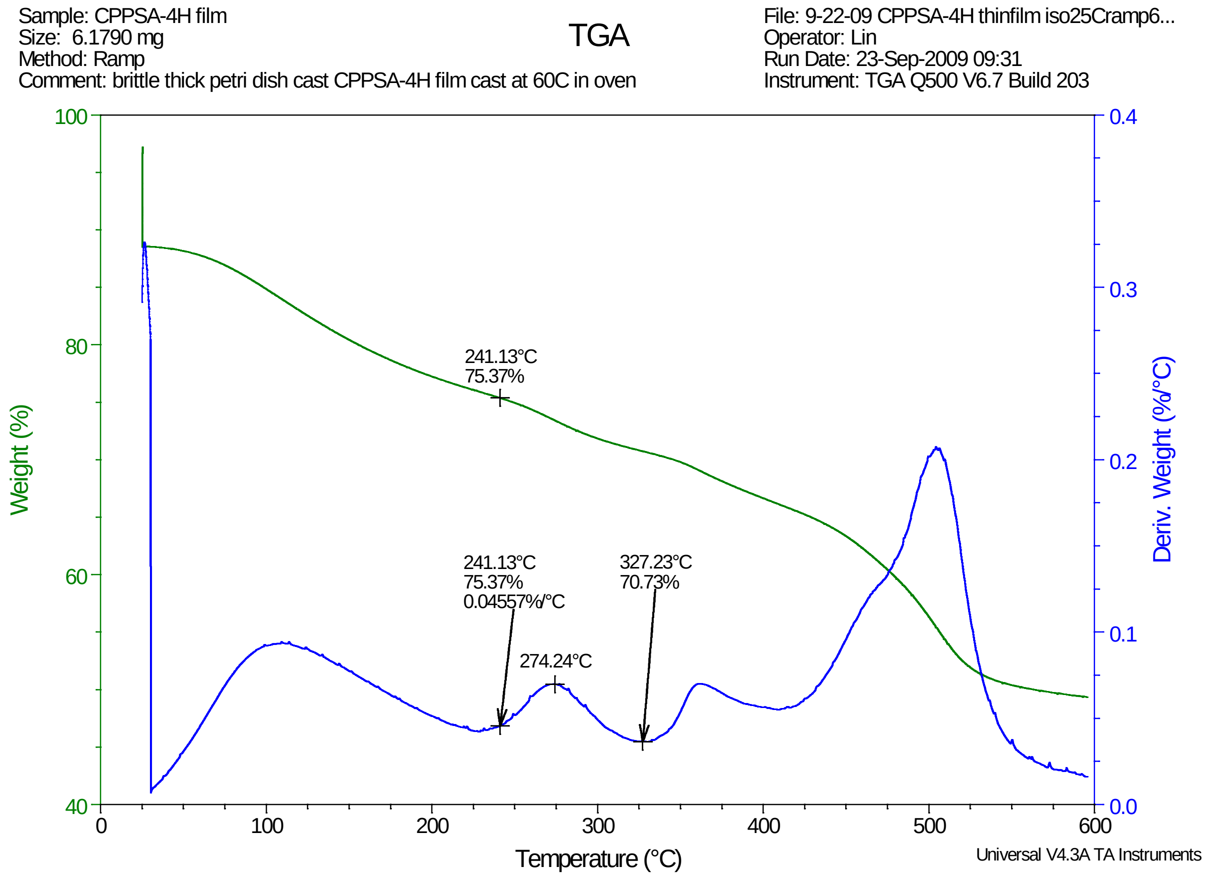


Figure 13. CPPSA-4H thin film equilibrated at ambient conditions, swept with dry nitrogen at 25°C for one hour and ramped to 600°C at 10°C/min

3.4 Water content analyses of CPPSA-1H, CPPSA-2H, and CPPSA-4H by ^{1}H NMR.

In order to determine the water-retention characteristics of these novel polymers and to help determine if the desired structures were indeed synthesized, ^{1}H NMR was used to probe the water content of the polymer films. When the acid forms of water-insoluble, powdered CPPSA-1H and CPPSA-2H were titrated,, it was found that the sulfonic acid proton diffused very slowly into the aqueous phase. The pH slowly became acidic as the polymer was stirred in the sodium chloride titration solution. It was surmised that the same type of behavior for water diffusion would be observable in the ^{1}H NMR spectrum.

The ^{1}H NMR experiments were conducted by placing several strips of polymer film (~10mg) equilibrated at ambient condition into an NMR tube and sealed with a cap. After reaching the spectrometer, a precisely measured quantity of D_2O containing a known amount of dioxane as a standardizer was added and the first spectrum was taken immediately after addition. Proton exchange before acquiring the ^{1}H NMR spectrum was minmized as much as possible by using this procedure.

Slow diffusion of water was observed for both CPPSA-1H and CPPSA-2H in the ^{1}H NMR experiment. CPPSA-4H was water soluble and therefore did not show any water-retention. The ratio of the integration of the water (HDO) peak to the 1,4-dioxane peak (known standard) was used to determine the moles of H and, by calculation the amount of water per sulfonic acid group (λ). The HDO content of the blank D_2O calibration standard was measured and this area was subtracted from the HDO peaks in the experimental spectra. This allowed the calculation of the actual quantity of water contributed by the polymer films. (If the spectra are enlarged very much, one can see small broad peaks in the aromatic region. The solid polymer does not show up in solution spectra.)

The amount of water per sulfonic acid in each of the polymer samples can be calculated using equations 1, 2 and 3.

$$Wt=(181+18*\lambda)*M \qquad 1.$$

$$H= M*(1+2*\lambda) \qquad 2.$$

By eliminating M, Eq. 1 and 2 can be rearranged to:

$$\lambda = \frac{181*H - wt}{2*wt - 18*H} \qquad 3.$$

Where:
H = moles of HDO diffused from the polymer plus bound water
M = moles of $-SO_3H$ in weighed sample
wt = the weight of polymer plus bound water
λ = water molecules per sulfonic acid group

Table 1 and Figure 14 show the results from the ^1H NMR determinations and the resulting water content values. It should be noted that the moles of H were determined by setting the integration value of the 1, 4-dioxane peak to 8.00 (8 hydrogens in 1 dioxane molecule) so that one mole of 1, 4-dioxane was equal to 1 mole of H (integration value of 1.00). The moles of H were calculated for each sample and the moles of H initially in the solvent were subtracted, giving the corrected value. The results were entered into the above equation to calculate λ. The weights of polymer used in the experiment were 0.0104g (CPPSA-1H) and 0.0093g (CPPSA-2H). The measured water content per sulfonic acid for both CPPSA-1H and CPPSA-2H increased with time. Since the NMR tubes containing the sample were sealed and the blank reference sample remained unchanged in water content during the 42 hours, it can be concluded that the increase in λ is due to the slow release of bound water. The water within the nanopores probably has a chemical shift above 15 ppm due to the high acid concentration; we did not look for it.

The HDO signal for CPPSA-1H increases at each spectral acquisition, from λ = 1.28 to 5.37. The 75 minute scan shows a λ of 2.02, only 38% of the value after 42 hours. CPPDSA-2H reached its final value of λ, 3.15, by 75 minutes. This parallels the data from the TGA scans and supports the hypothesis that some water is retained up to about 330 to 350^{o}C.

Although we have not definitely proved that the desired nano-pore lattice structure was formed during the polymerization, the results show that water is trapped within the polymer film but can diffuse out completely if given enough time. This is consistent with the hypothesis that the hexagonal lattices aggregate to generate long nano-pores. Much of the water and protons must diffuse long distances before they can find openings to the surrounding medium. The initial λ shows that portion of bound water that can interdiffuse easily. The increase from that reflects the slow diffusion from nano-pores. The longer the pores, the slower the diffusion. For CPPDSA-1H ,less than 25% of bound water is easily exchanged, while over 50% is exchanged for CPPDSA-2H. CPPDSA-2H has completely exchanged after 1.25 hours, while CPPDSA-1H has barely started.

Table 1. Water diffusion data for CPPSA-1H and CPPSA-2H determined by ^{1}H NMR

Sample	**Water peak (NMR)**	**Water peak corrected for residual water**	**Moles H**	**Moles H corrected for residual water**	**λ**
D_2O blank	0.70	-	5.751×10^{-5}	-	-
CPPSA-1H initial	2.91	2.21	2.391×10^{-4}	1.816×10^{-4}	1.28
CPPSA-1H 45 min	3.36	2.66	2.760×10^{-4}	2.185×10^{-4}	1.73
CPPSA-1H 60 min	3.54	2.84	2.908×10^{-4}	2.333×10^{-4}	1.92
CPPSA-1H 75 min	3.64	2.94	2.990×10^{-4}	2.415×10^{-4}	2.02
CPPSA-1H 42 hours	6.01	5.35	4.937×10^{-4}	4.395×10^{-4}	5.37
CPPSA-2H initial	3.05	2.35	2.506×10^{-4}	1.931×10^{-4}	1.70
CPPSA-2H 45 min	3.15	2.45	2.588×10^{-4}	2.013×10^{-4}	1.81
CPPSA-2H 60 min	3.64	2.94	2.990×10^{-4}	2.415×10^{-4}	2.41
CPPSA-2H 75 min	3.65	2.95	2.998×10^{-4}	2.423×10^{-4}	3.15
CPPSA-2H 42 hours	3.65	2.95	2.998×10^{-4}	2.423×10^{-4}	3.15

Figure 14 shows the results given in Table 1. The data are too sparse to determine diffusion rates for the materials. The standard one-dimensional diffusion equation approximation (Wolf R.Vieth Diffusion in and through Polymers, Hanser, (1991) pp 56-57, from Crank) is given below, Equation 4. It is valid to about $I_t/I_\infty = 0.8$. If λ for CPPDSA-1H is plotted versus the square root of time, we can get a feeling for the diffusion time in that material. This is shown in Figure 15. All the λ values, including that at 42 hours, fit on a line. This implies, for normal diffusion, that we are still far from complete exchange. The final λ could be well above 6 for this determination. (Titration gave a λ of 5.4 but TGA gave values as high as 6.1. Since room relative humidities were not measured when the samples were run, but probably were between 25 to 45%, depending on the season, this variation is reasonable. Literature polyelectrolytes at these relative humidities have λs in the range of 2.5 to 4.)

$$I_t/I_\infty=2*(D*t/(\pi*l^2))^{0.5} \qquad 4.$$

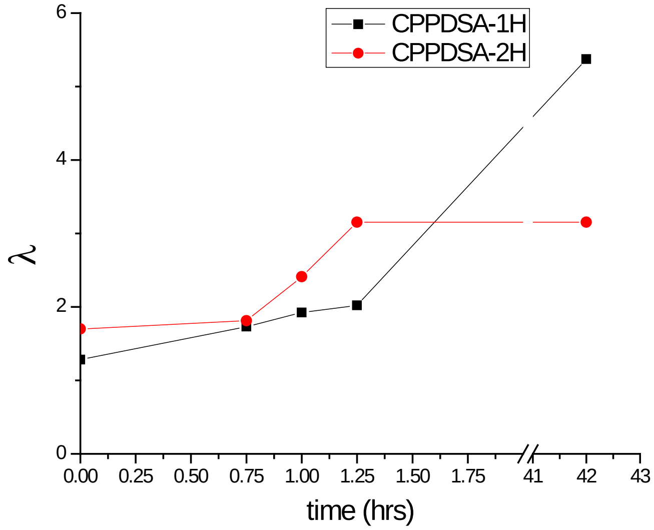
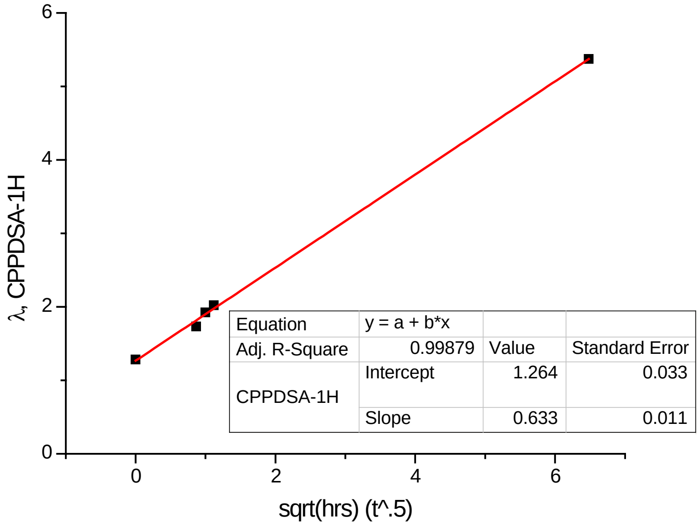


Figure 14 HDO diffusion with time from cast films of CPPDSA-1H and -2H



Equation	y = a + b*x		
Adj. R-Square	0.99879	Value	Standard Error
CPPDSA-1H	Intercept	1.264	0.033
	Slope	0.633	0.011

Figure 15 Standard plot for HDO diffusion, λ vs (time)^0.5, for CPPDSA-1H

The slope found is $0.63/hr^{0.5}$, = $0.0105/sec^{0.5}$. Eq. 4 uses I/I_∞. The λ involved in the slow diffusion is about 5; the normalized slope is about $0.002/sec^{0.5}$. If we take the lowest water diffusion constant found for Nafion117, $D = 6*10^{-7}$ cm^2/sec. at λ=2 (T. A. Zawodzinski Jr., M. Newman, Laurel O. Sillerud and Shimshon Gottesfeld, J. Phys. Chem.

1991, *95.* pp. 6040-6044), a “pore length” can be calculated. We find ~56 nm, a reasonable pore length. A larger diffusion constant, $3*10^{-6}$ cm^2/sec (λ=5) gives a pore length of ~280 nm. This will be discussed further when considering the SEM and AFM data..

The NMR and TGA studies strongly support our view that we have synthesized a polymeric structure that forms rigid, incompressible pores which hold water strongly. The difference in the results between the two polymers is probably due to differences in polymer molecular size and their treatment history.

3.5. SEM and AFM studies of the polymers. Scanning electron microscopy (SEM) was used to look at the microstructure of CPPDSA-1H and -2H, and AFM was used to for CPPDSA-3Na and -4H. Figure 16 shows the most informative SEM image of CPPSA-1 at 10K magnification. The most notable feature throughout the image is the strong suggestion of layered structures. Both structures at the lower left can be regarded as a helical assembly of flat molecules of ~0.5 and 1 µm diameter. Flat edges with 120° angles can be seen on the left helix. This is shown more clearly in Figure 17a, an enlargement of that area. Figure 17b is at the limit of resolution. It seems to show a small hexagonal stack, about 100 nm in diameter.

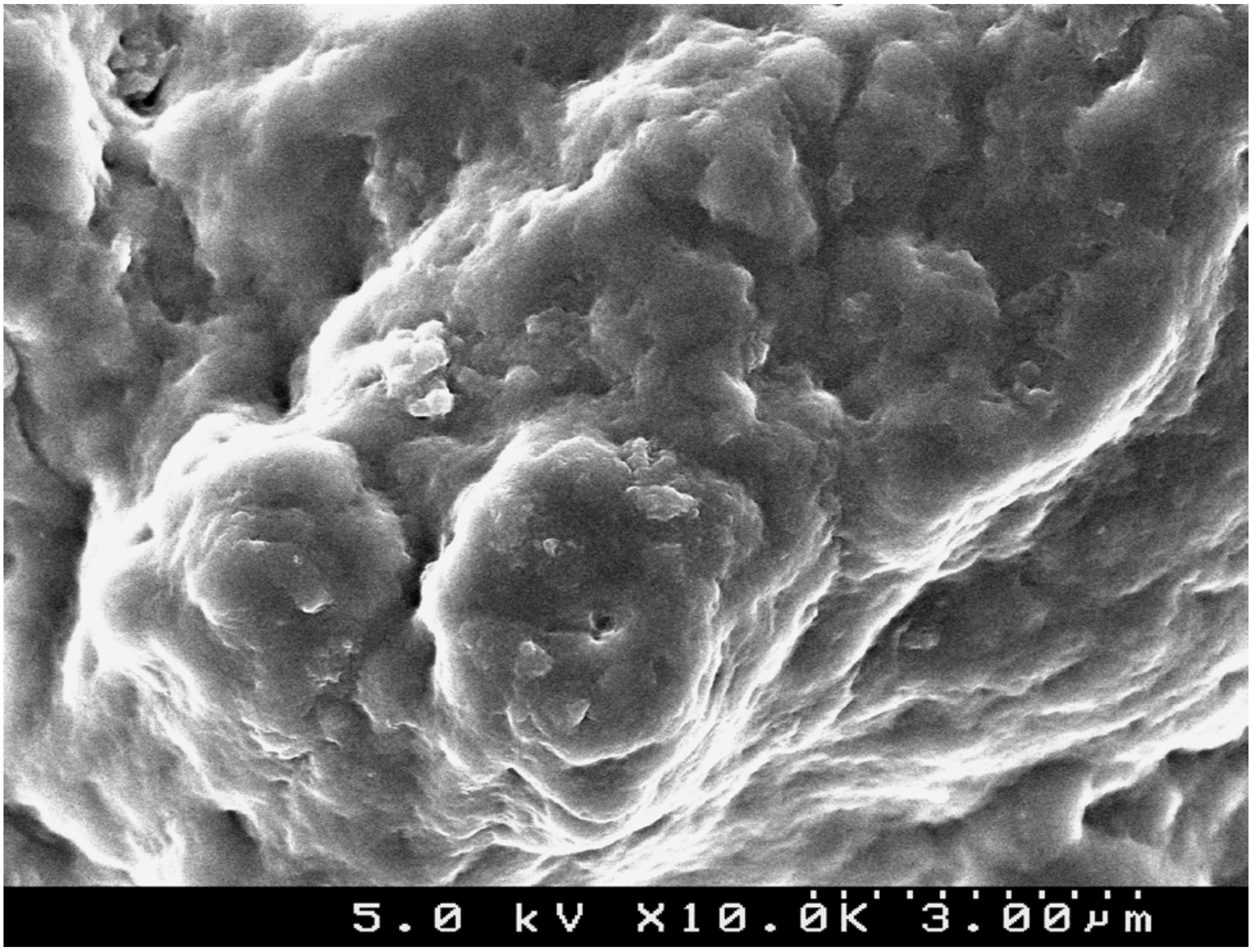


Figure 16. Scanning Electron Microscopy (SEM) image of CPPSA-1 at 3µm scale

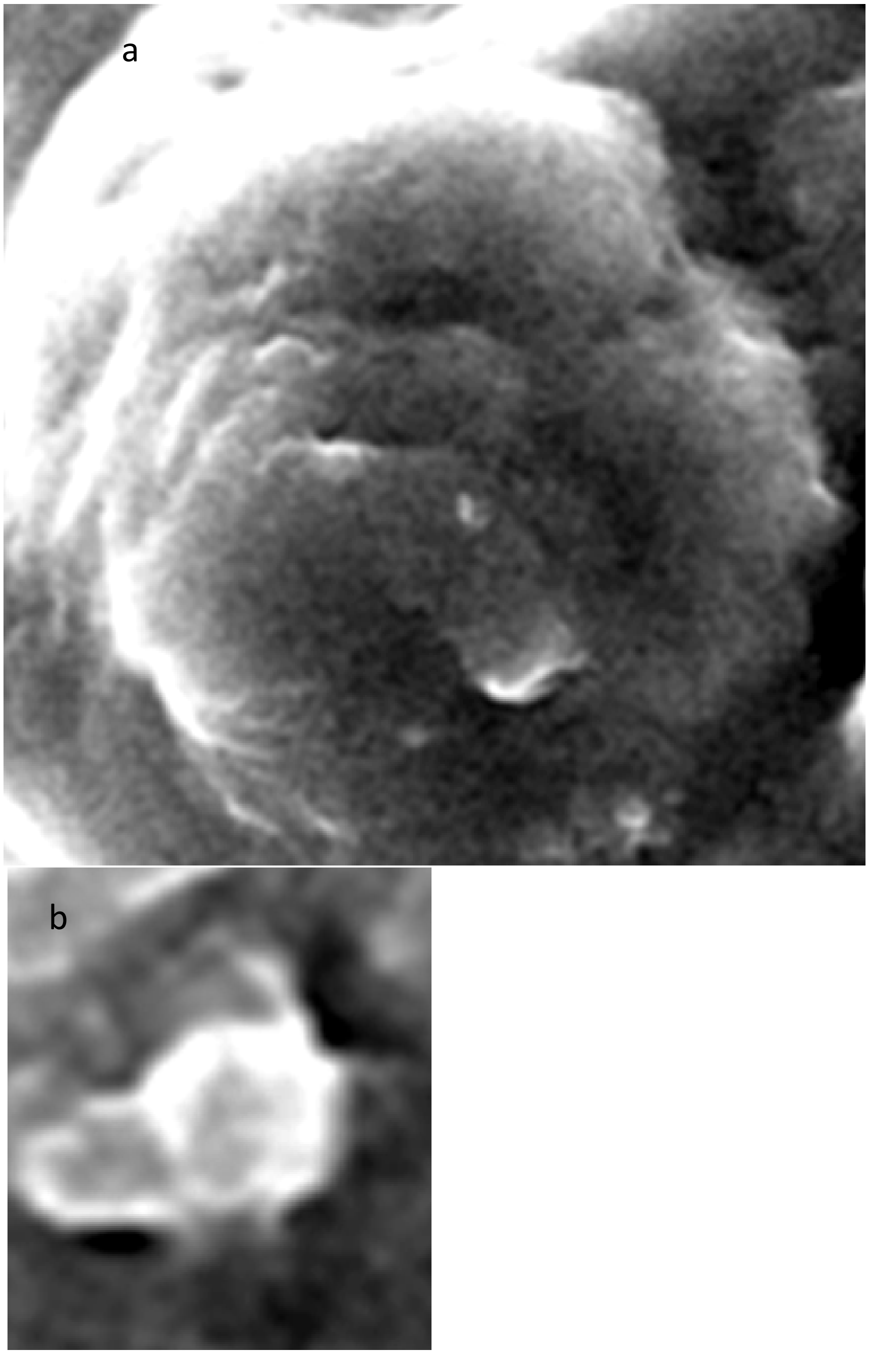


Figure 17. a) Enlargement of left column in Figure 16. b) Hexagonal structure on right column, ~ 100nm, diameter.

While height cannot be measured directly, the aggregates seem to be several µm thick. That is large enough to hold several hundred nanometer long pores. The only way such a layered material can form under the reaction conditions used is through the aggregation of large planar molecules. This supports the argument that the desired structures were created. A more systematic study is needed to determine exactly what has happened.

Figure 18 shows the most informative SEM image of CPPSA-2, at 60K magnification. Its surface is relatively planar in contrast to that of CPPDSA-1H. Since the reaction was quenched and the material did not gel spontaneously, we know that the individual molecules are smaller than those of CPPDSA-1H. This is in agreement with its NMR water diffusion data; diffusion was complete after 75 minutes. The nano-pores must be much shorter than those of the first run; there was less aggregation. It is possible that the tongue extending from the upper left corner is an aggregate stacked along the long dimension. Films cast from CPPDSA-2H had very poor mechanical properties.

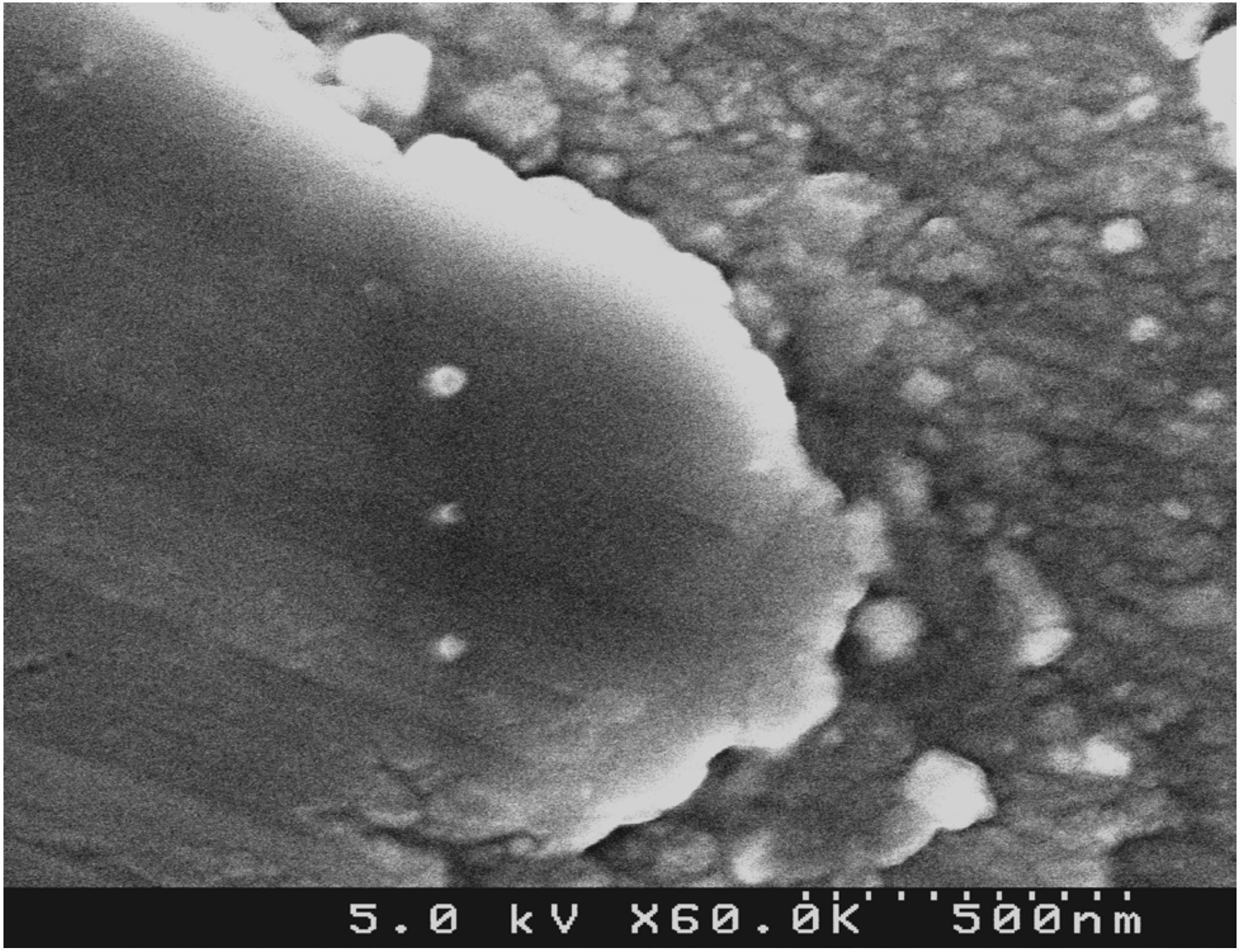


Figure 18. Scanning Electron Microscopy (SEM) image of CPPSA-2 at 500nm scale

The third and fourth runs were studied by AFM. After sonication, CPPDSA-3Na was dispersed well enough that a very dilute suspension could be cast on graphite for AFM examination. Two areas are shown in Figures 19 and 20. Figure 19 shows 2-dimensional aggregation of relatively small molecules, 50 to 100 nm diameter, into long aggregates. All the planes are aligned. There is some evidence for 3-dimensional aggregation.

Figure 20 shows aggregation into large structures, 500 to >1000 nm, with possible uniaxial orientation. There seem to be large variations in molecular size.

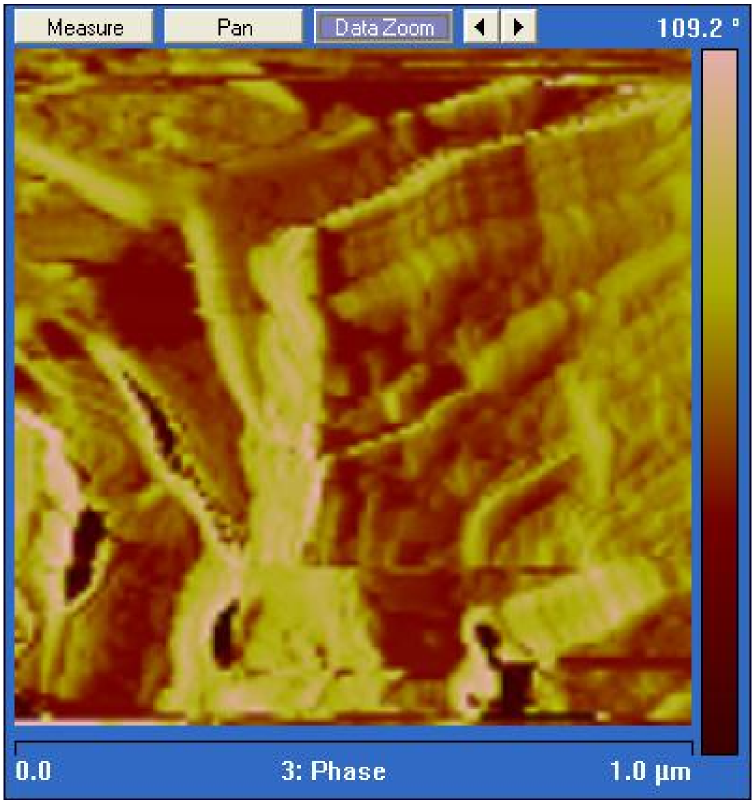


Figure 19 AFM study of area 1 of CPPDSA-3Na.

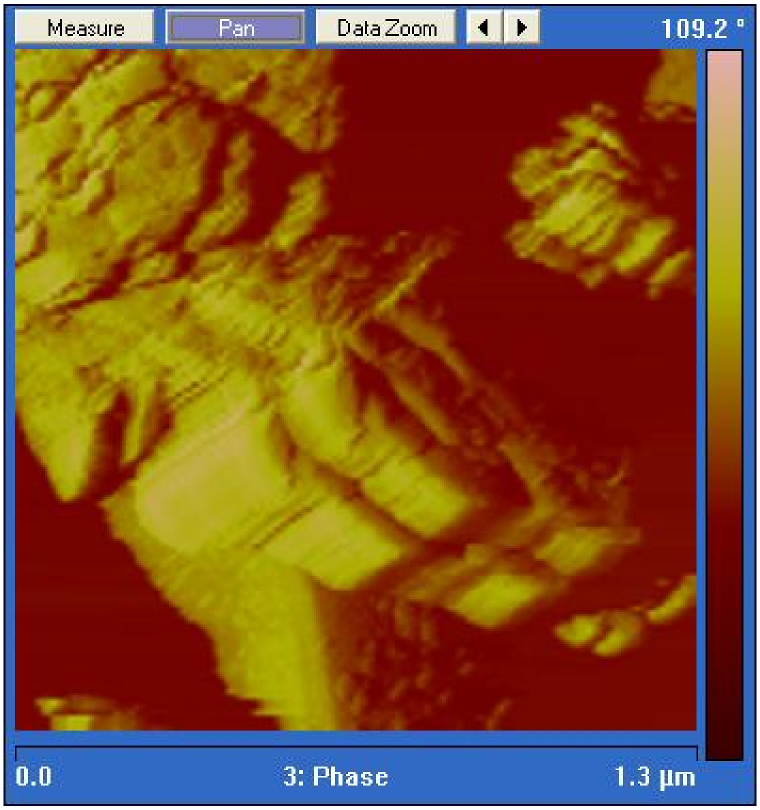


Figure 20 AFM study of area 2 of CPPDSA-3Na.

In contrast, CPPDSA-4Na, which polymerized poorly, shows aggregation into small, poorly defined structures, Figure 21. The initial calculation of average molecular diameter, ~4.6 nm, implies that individual molecules would not be visible at this scale; we are observing aggregates. Planar regions are visible which may be 3-D aggregates.

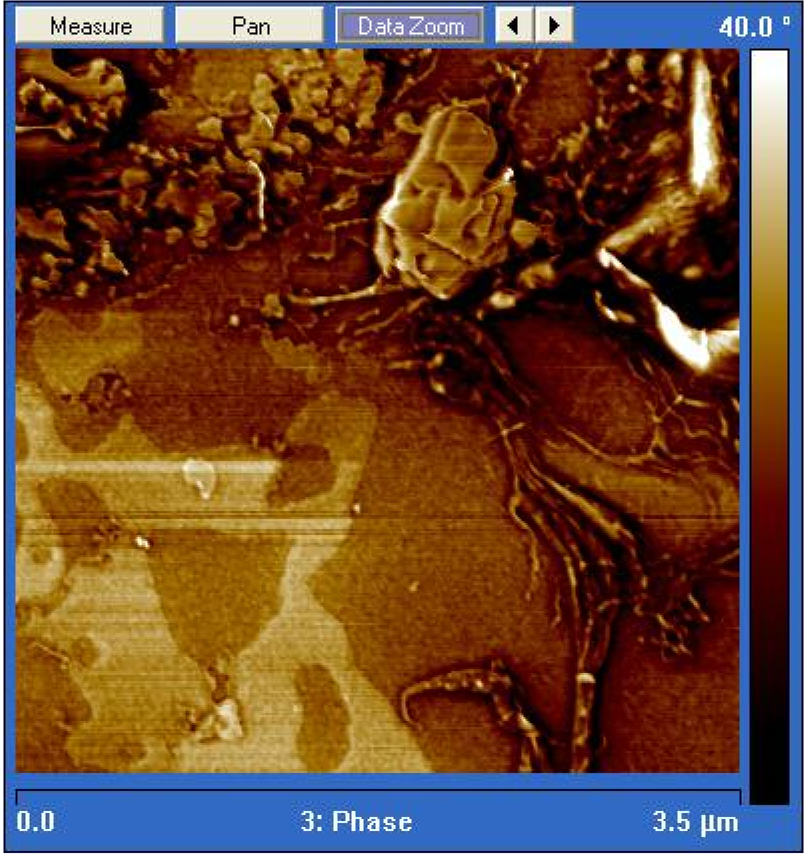


Figure 21. AFM study of CPPDSA-4Na.

3.6 WAXD Study of cast films: After mild sonication in water, all the materials were well dispersed enough that films could be cast. When casting was done in polystyrene or Teflon Petri dishes, the films shrunk dramatically and broke into very small fragments. When they were cast in base treated glass Petri dishes, CPPDSA-1H and -3Na formed transparent films with no lateral shrinkage, that lifted off the glass after they had dried. If they deposited with the molecular planes parallel to the surface, they should show no birefringence when viewed through crossed Polaroid films. If the film was tilted, we would expect to see birefringence. This is important to determine if we have the postulated structures and necessary to evaluate conductivity measurements; conductivity should be mainly within the pores and these must be perpendicular to the film surface to get the best conductivity. Most films showed some birefringence, which indicated poor aggregate orientation. CPPDSA-3Na and -1H films were relatively well oriented. Reflection and transmission WAXD scans were made on all the cast films. A scan that showed low angle peaks in the transmission but not in the reflection mode would be organized with pores perpendicular to the film surface. Scans of CPPDSA-3Na are shown below, Figure 22. Scans of a thin film of CPPDSA-1H after removal of air scattering are shown in Figure 23.

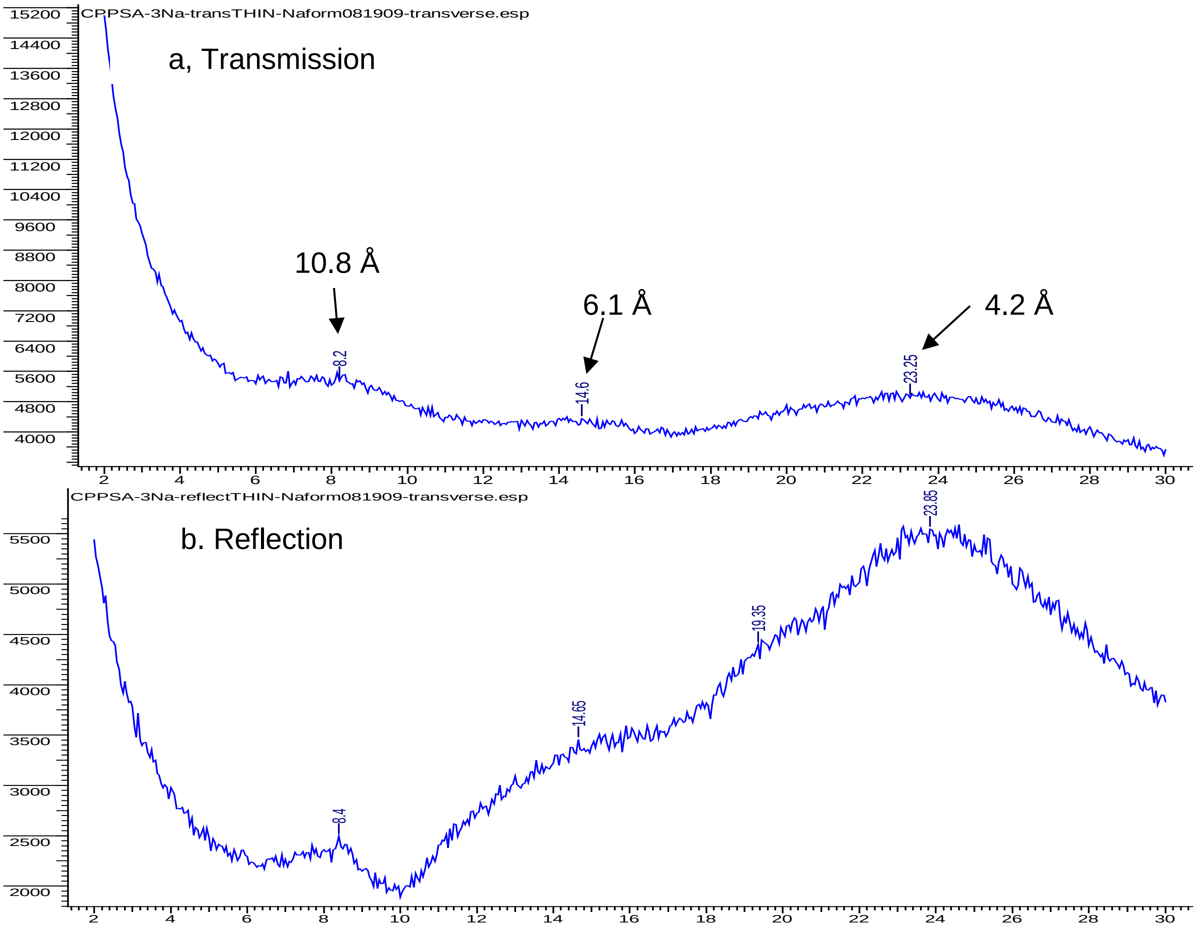


Figure 22. WAXD scans of CPPDSA-3Na film in a) Transmission and b) Reflection mode

The relative intensity of the low angle peak at 10.8 Å, half the expected hexagon diameter, versus the ~6.1 Å peak shows the orientation. Its area relative to the 6.1 Å peak is very small in the reflection mode and large in the transmission mode. This shows fairly good orientation of the aggregates with the pores perpendicular to the film surface. Molecular organization is poor; the x-ray peaks are broad, but this may be because the sulfonate groups are randomly oriented in the structure. We think that the peak at 3.8 Å reflects the average distance between polymer planes.

When air scattering is removed as in Figure 23, the orientation can be seen more clearly. The peak at ~14^{o} (6.2Å) in the reflection mode has a large area and is very broad compared to its shape the transmission mode. It may contain several reflections.

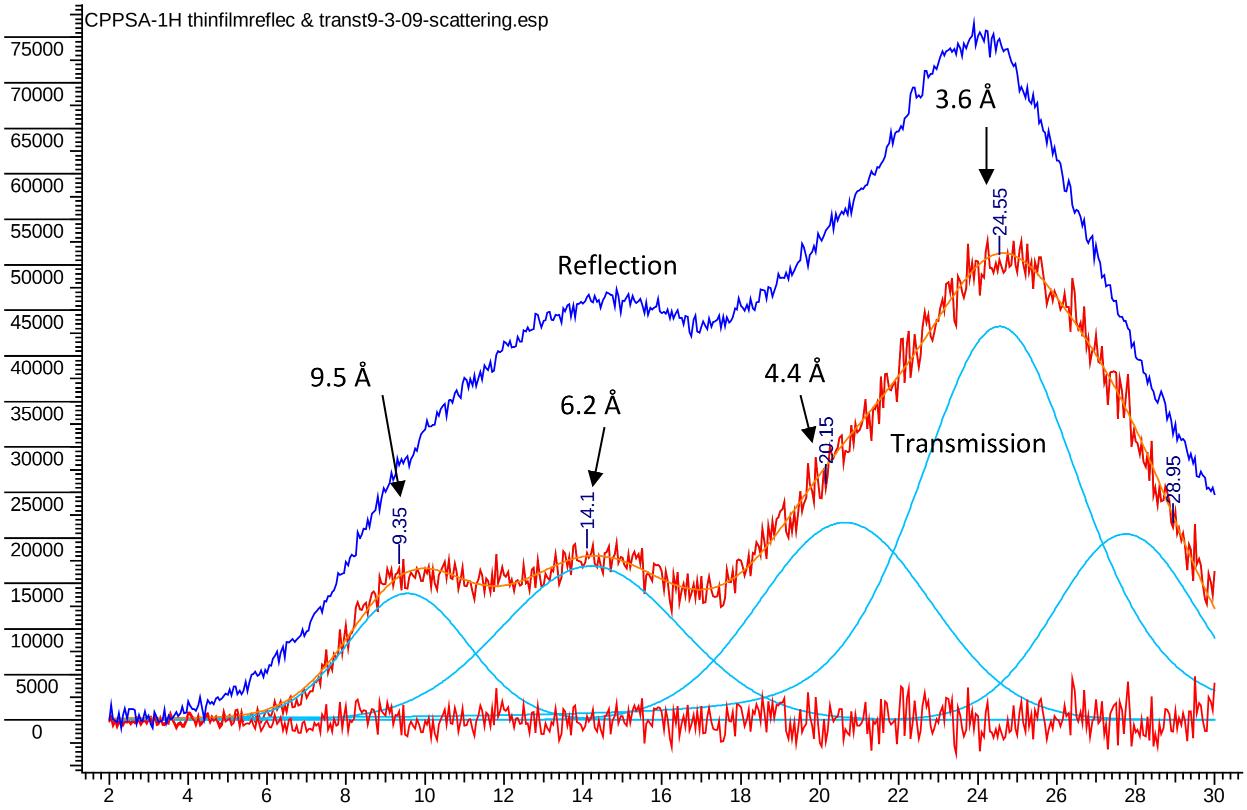


Figure 23 WAXD scans of CPPDSA-1H thin film, reflection and transmission; air scattering subtracted

Sonicated, cast films of CPPDSA-2H and -4H have spectra similar to those given above. However, the peaks in the CPPDSA-4H scans have different d-spacings, possibly because of the very small dimensions of this polymer. We have not done enough work to determine if the differences in the long spacings in Figures 22 and 23 are meaningful or are due to the broad peaks and/or possible error in the base line corrections.

3.7 Polarized light study. CPPDSA-4H cracked radially when cast in a glass Petri dish. The pieces were about 2-3 mm wide and ~1.5 cm long. The oriented cracking suggested that the molecules, or their aggregates, were oriented in the casting. Photographs of a strip oriented at 0 and 45^{o} to the polarization are shown in Figure 24. They both show birefringence; the 45^{o} oriented strip is much brighter. The parallel orientation shows nematic liquid crystalline structure, a broad dark line meandering through the piece. This, plus the cracking mode, implies that the molecular planes are oriented perpendicular to the strip long dimension and have aggregated parallel to the long direction. The WAXD scans confirm this. The reflection and transmission scans for CPPDSA-4H along the strip length are almost identical. Both show a low angle peak at ~6.2^{o} 2θ (~14Å), not seen in the other scans, which does not fit with the postulated structure.

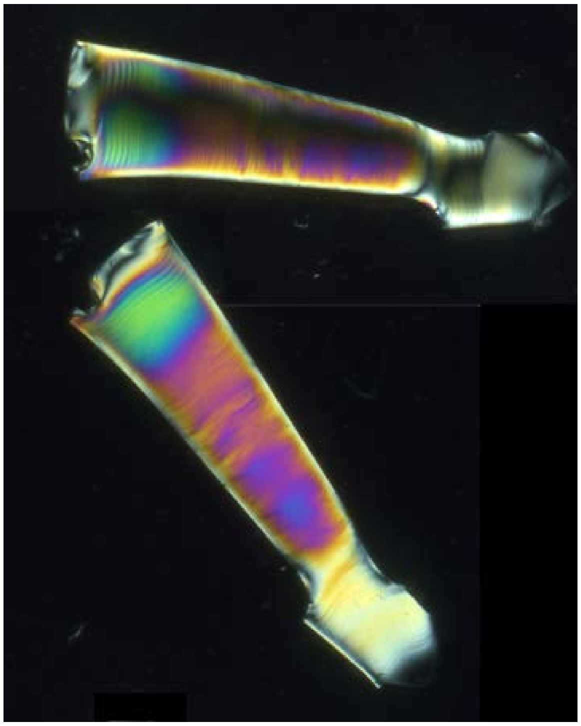


Figure 24. CPPDSA-4H cast film photographed through crossed Polaroid films parallel and at ~45° to the polarization.

3.8 Conductivity measurements. The last run, CPPDSA-5, has not been characterized. Casey Check was told to stop all experiments and write his thesis. The low molecular weight material and salts had been removed and half of the material was in the acid form when he stopped work. Dr. Wyscisc has been trying to cast films from the acidic portion that could be used for conductivity measurements. Films are stable in still water but disintegrate with prolonged stirring. The cloudy suspension turned grey with long exposure to the lab atmosphere. We think that Pd(0) aggregates are forming. He did get one film and has started measurements. We do not know the aggregate orientation in the film, nor the ligand concentration. In-plane measurements (80°C) were made at 10 and 51% RH. Conductivity was not measureable at 10% RH ($<10^{-4}$ S/cm); at 51% RH, it was 0.053 S/cm. We think that through plane values should be much higher.

4.Conclusions.

All the data confirm that we have synthesized a reasonable approximation of our desired structure. The most impressive data set is the NMR water diffusion study. CPPDSA-1H took more than two days to equilibrate, showing that the nano-pores were probably several hundred nanometers long. SEM photos showed aggregated structures that could hold such long nano-pores. Similar phenomena were observed qualitatively when the materials were titrated. The materials hold water very tightly. The last waters remain until above 300°C. However, many problems still must be solved before we can reliably prepare good polymers and films. Some problems are listed below.

1. While six sided rings should be favored, there is a possibility that the initial rings could have five or seven sides as well, causing the molecule to pucker. This

can be avoided by making new starting reagents that contain two sides of the hexagon. These can only form hexagons.

2. Monomer purity is still a problem. Supposedly identical systems have reacted at vastly different rates. We think the trifluoroboronate groups tend to decompose. Other boronate groups may be more stable; we are looking at several. They must be water soluble for the reaction to proceed properly.
3. The major problem is that the molecules aggregate during synthesis. The aggregates can form films that have mechanical strength and are not water soluble. Unfortunately, such aggregates cannot form perfect films and will probably always disintegrate under stress, if wet. It is very difficult to control the domain orientation properly. The aggregates also seem to trap Pd(0) and ligand which lowers Pd concentration in solution and reduces the reaction rate. This could be why we found so much starting monomer in the quenched solution.
   There are possible methods to keep the molecules soluble during reaction and purification. This would allow them to pack properly during casting. The question is: is there an additive that will keep the molecules isolated but can be removed easily after casting, allowing the film to consolidate with no additive remaining?