Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications

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Project ID # FC13

Overview

Timeline

- Start: April 2006
- End: April 2011
- 20% complete

Budget

- Total project funding
  - DOE share $1.5M
  - Contractor share $500K
- Funding received in FY06 $150K
- Funding for FY07: $300K

Barriers

- Barriers addressed
  - Thermal stability of PEMs
  - High temperature, low RH proton conductivity
  - Cost

Partners

- Univ. of Southern Mississippi
- ORNL

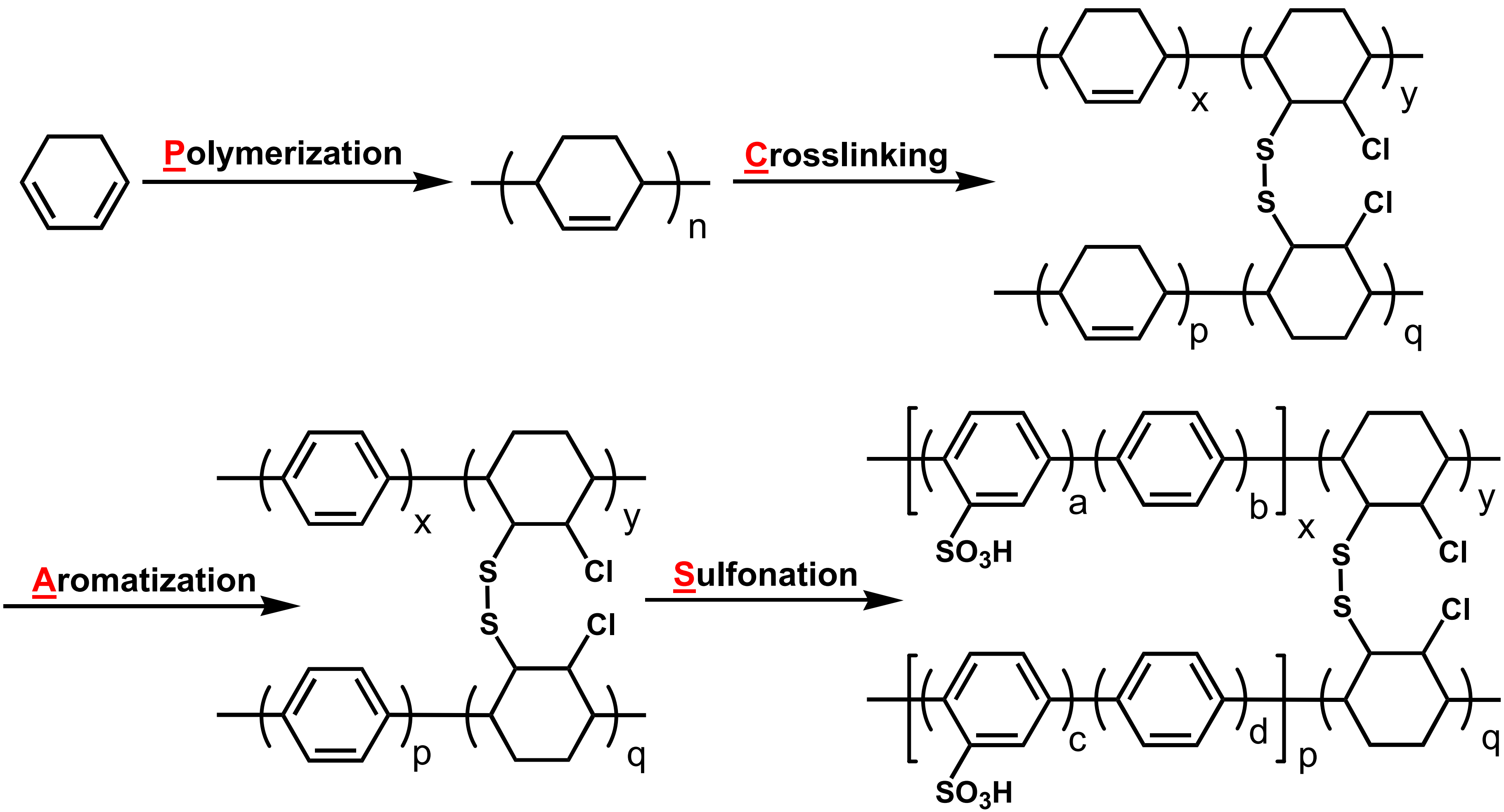
Objectives

- The objective of the work proposed herein is to synthesize and characterize novel neat and inorganically modified fuel cell membranes based on poly(1,3-cyclohexadiene) (PCHD) .
- To achieve these objectives, a range of homopolymer and copolymer materials incorporating poly(cyclohexadiene) will be synthesized, derivatized, and characterized.
- Successful completion of this project will result in the development of novel PEM membranes engineered to have high conductivity at elevated temperatures and low relative humidity.

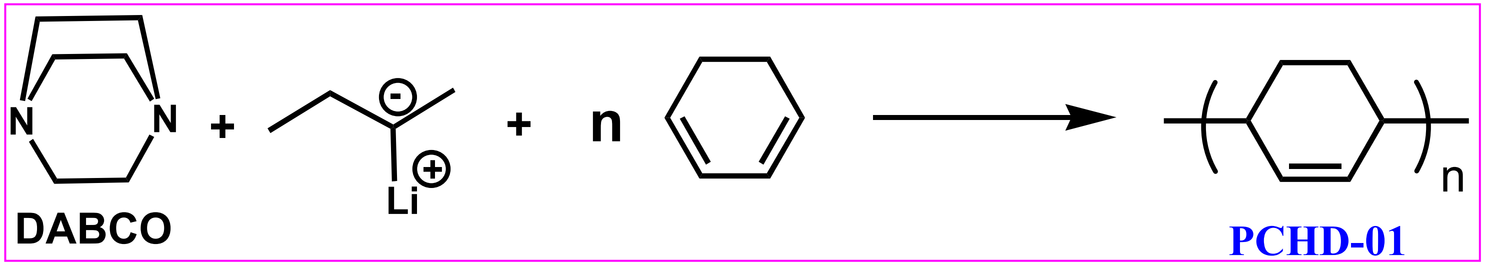
Approach

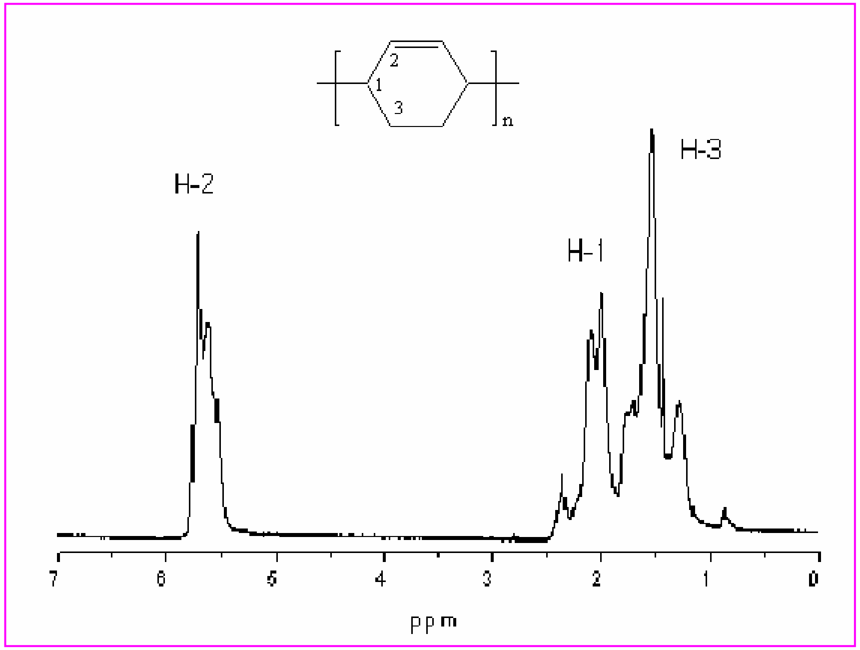
- Anionic polymerization and post-polymerization chemistry are utilized to synthesize novel thermally stable proton conducting membranes based on a potentially inexpensive hydrocarbon monomer, 1,3-cyclohexadiene.
- Inorganic modification of these novel membranes via a sol/gel process is used to enhance proton conductivity and thermal stability.
- Thorough characterization of the membranes is carried out to develop structure/property relationships.

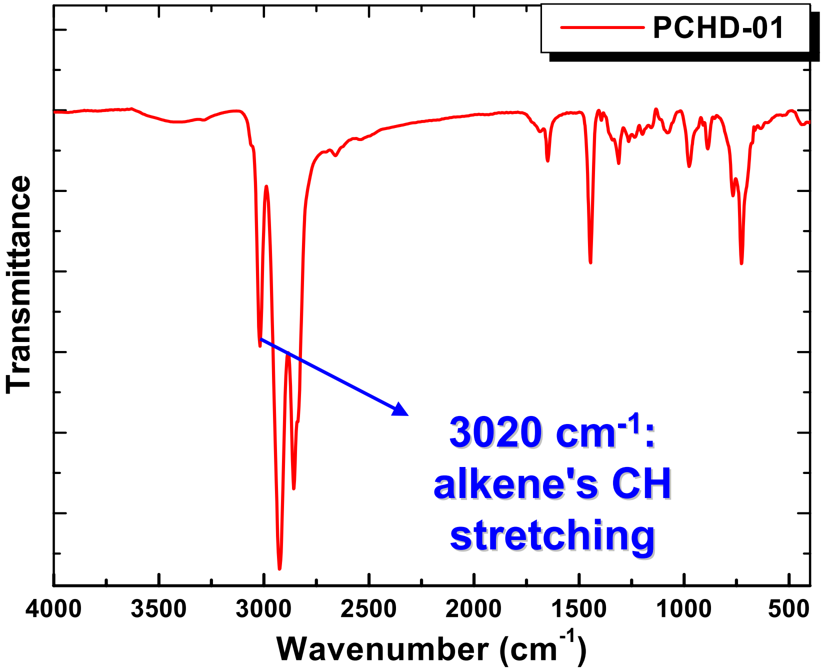
PCAS Approach to Fuel Cell Membranes



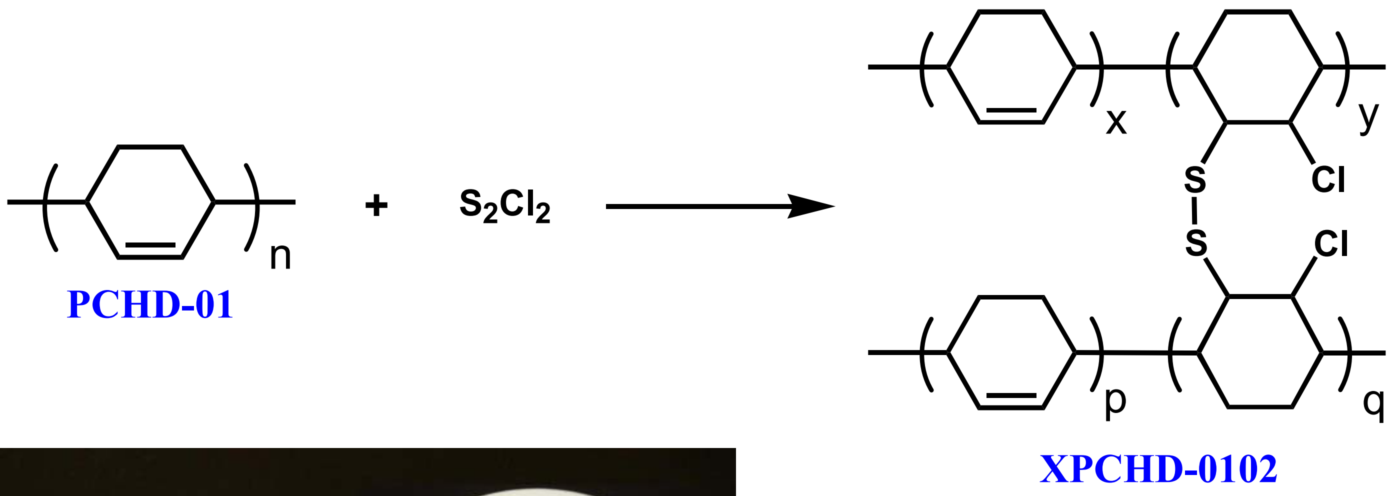
I: Synthesis of PCHD-01

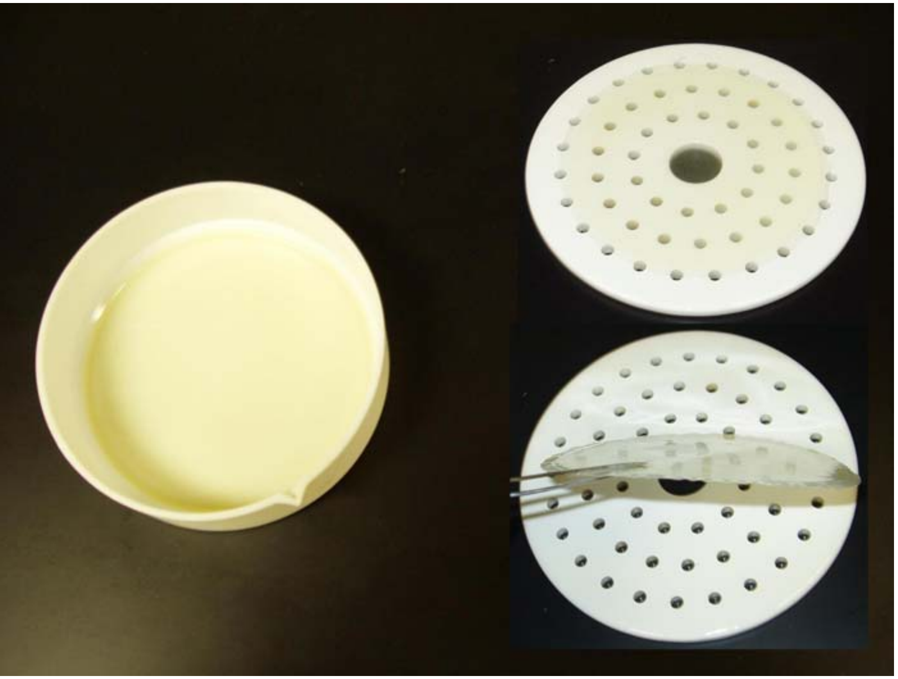






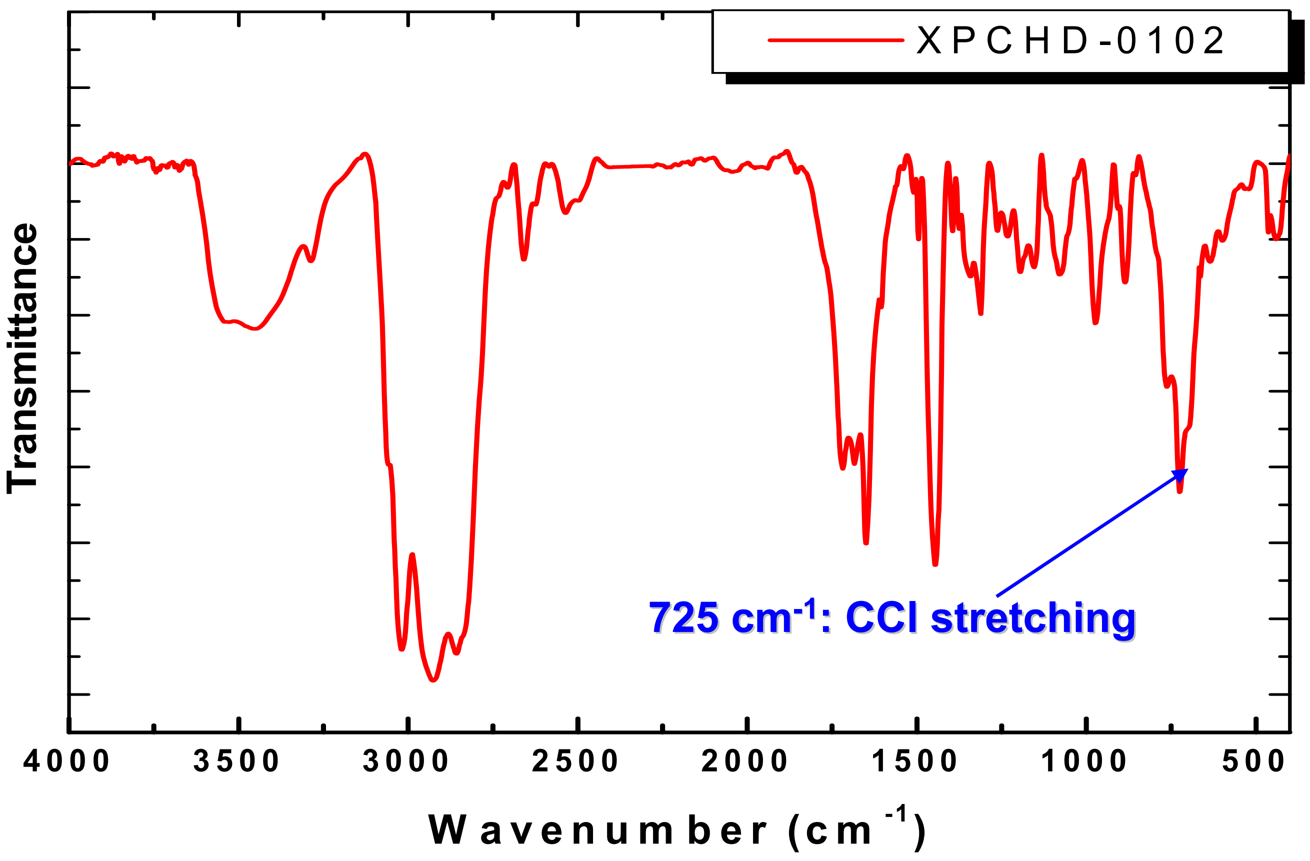
II: Cross-linking of PCHD-01



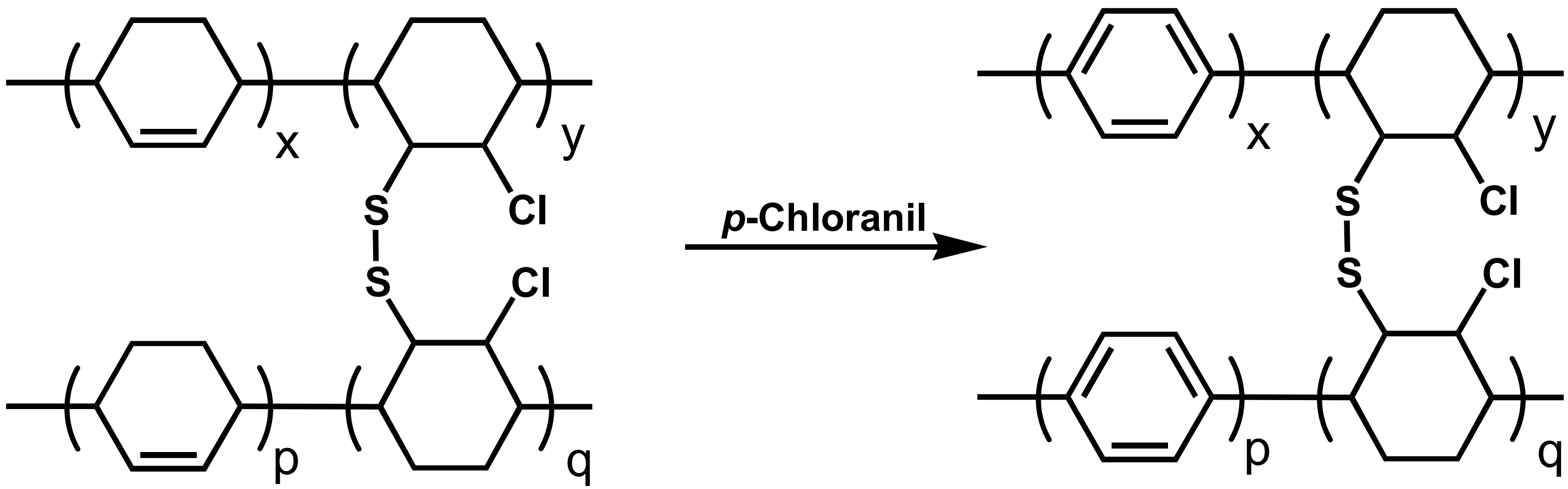


- ~ 10% cross-linked
- Very flat and thin (thickness less than 1.0 mm)
- Not a single crack
- The quality of this membrane is crucial for the subsequent reactions

FT-IR Spectrum of XPCHD-0102

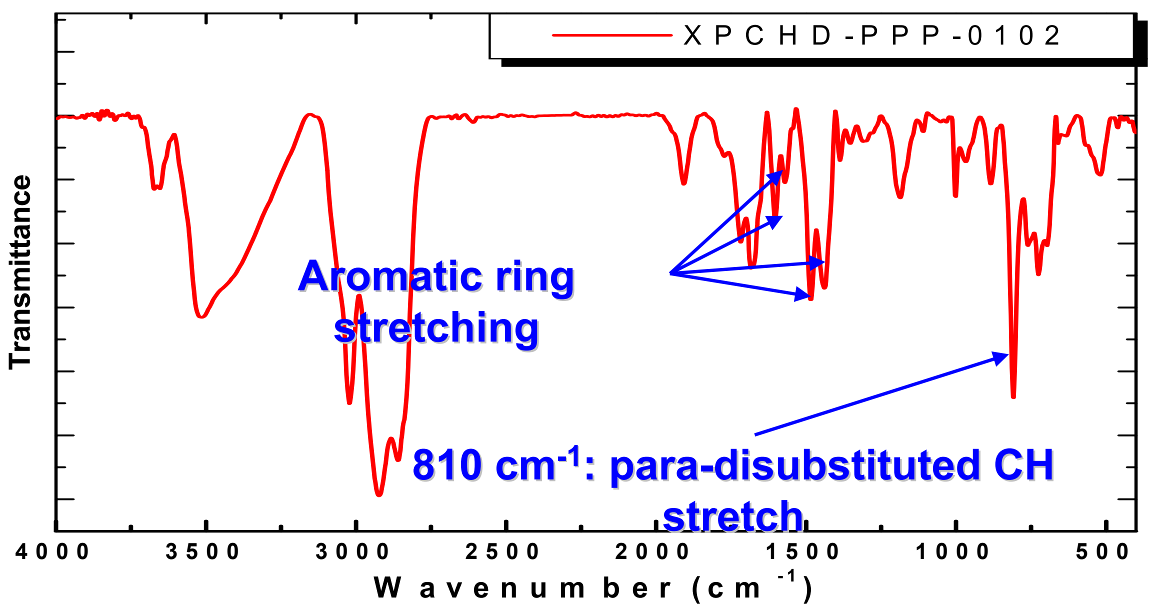


III: Aromatization of XPCHD-0102

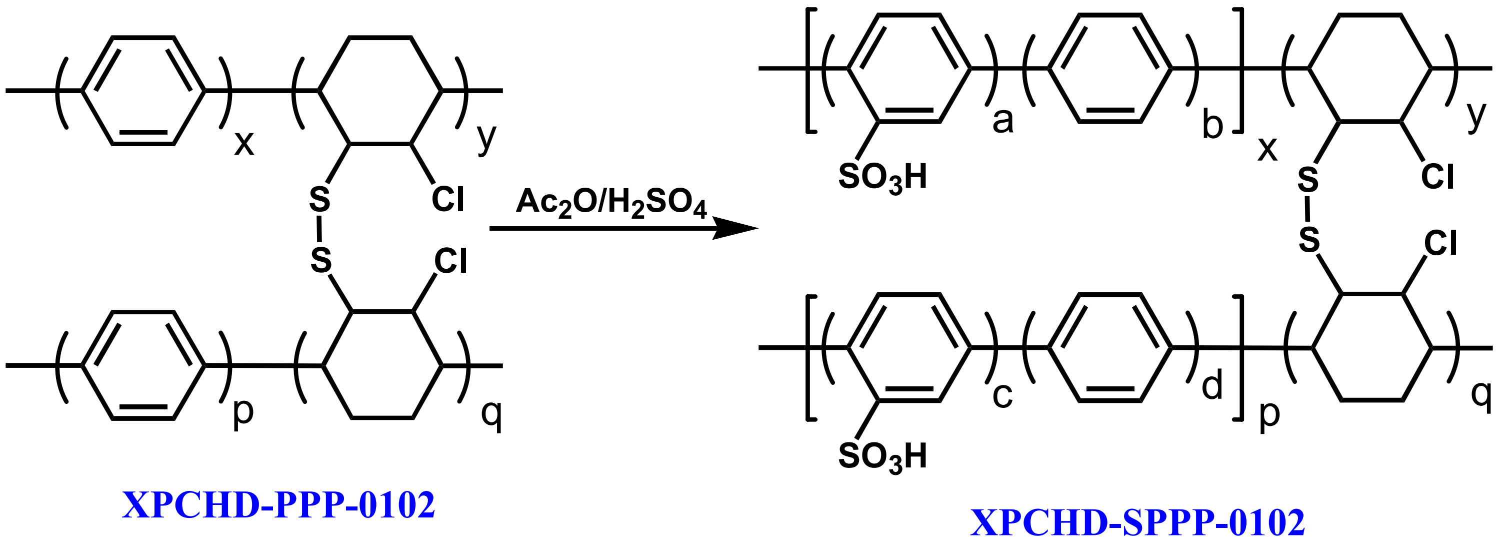


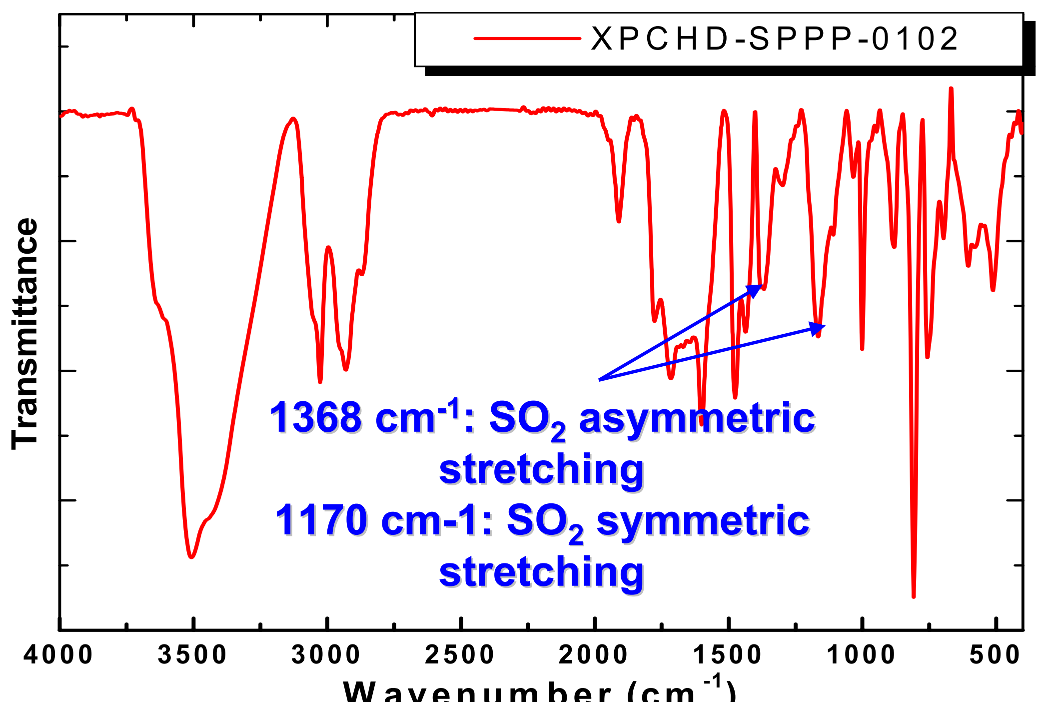
XPCHD-0102

XPCHD-PPP-0102



IV: Sulfonation of XPCHD-PPP-0102

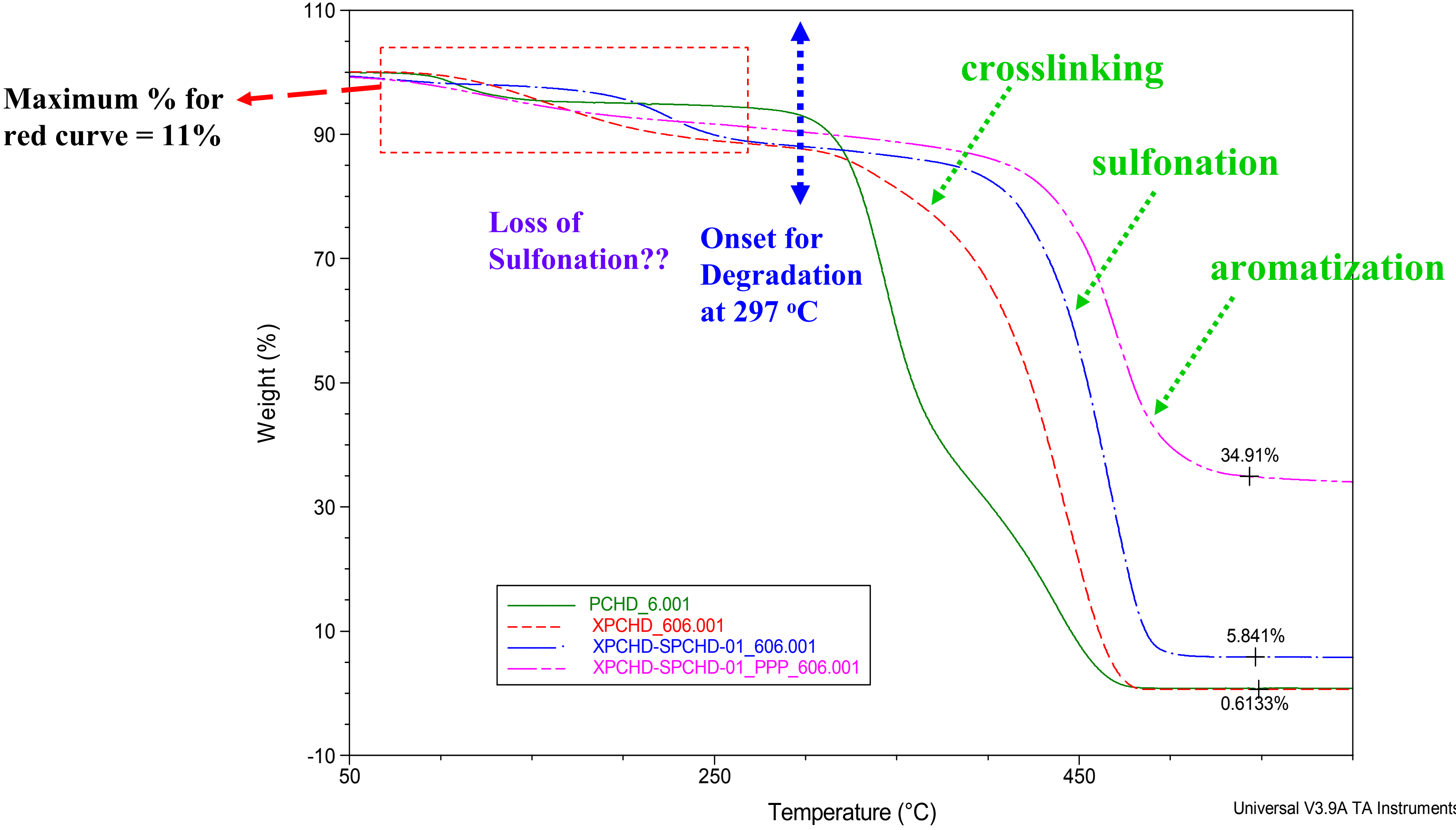




Elemental Analysis of XPCHD-SPPP-0102

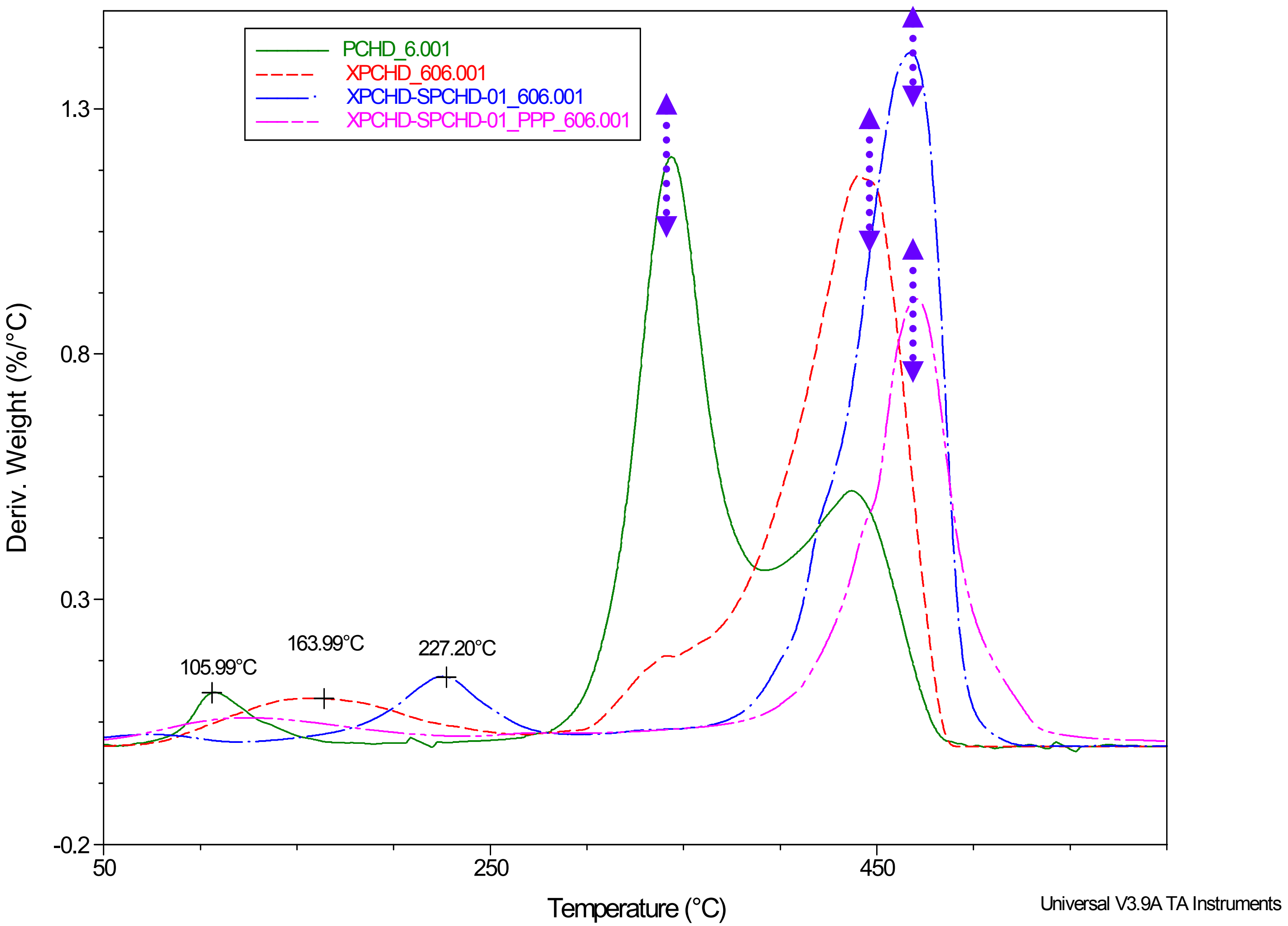
Sample Name	Experimental Data	Calculated Formula	Degree of Reaction
PCHD-01	C: 83.52 %; H: 9.40 % N: < 0.5%; O: 9.65%	$C_6H_{8.05}N_{0.03}O_{0.52}$	NA
XPCHD-0102	C: 79.94 %; H: 9.38 % N: < 0.5%; O: 2.47% S: 3.93 %; Cl: 4.30 %	$C_6H_{8.39}N_{0.03}O_{0.15}(SCl)_{0.11}$	~ 11 % crosslinking
XPCHD-PPP-0102	C: 75.91 %; H: 4.96 % N: < 0.5%; O: 6.92% S: 2.31 %; Cl: 10.71 %	$C_6H_{4.67}N_{0.03}O_{0.41}S_{0.07}Cl_{0.29}$	~ 100% Aromatization
XPCHD-SPPP-0102	C: 73.44 %; H: 4.00 % O: 9.71%; S: 4.24 % Cl: 8.24 %	$C_6H_{3.90}O_{0.60}S_{0.13}Cl_{0.23}$	6 % sulfonation

TGA Curves for XPCHD-SPPP_606 Sample



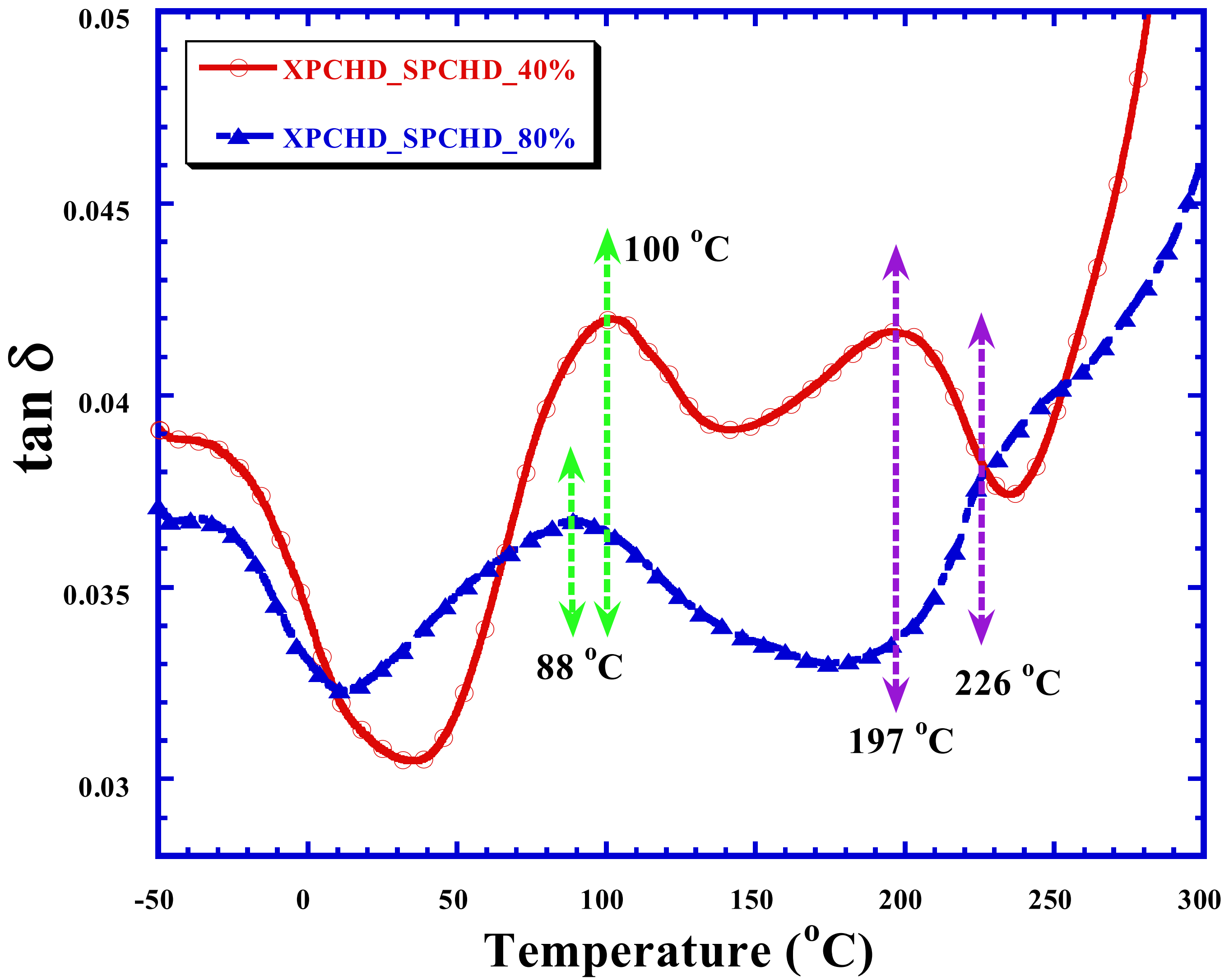
Temperature Derivative of Remaining Weight % of the TGA Curves for XPCHD-SPPP_606 Sample

Improved thermal stability by crosslinking, sulfonation and aromatization



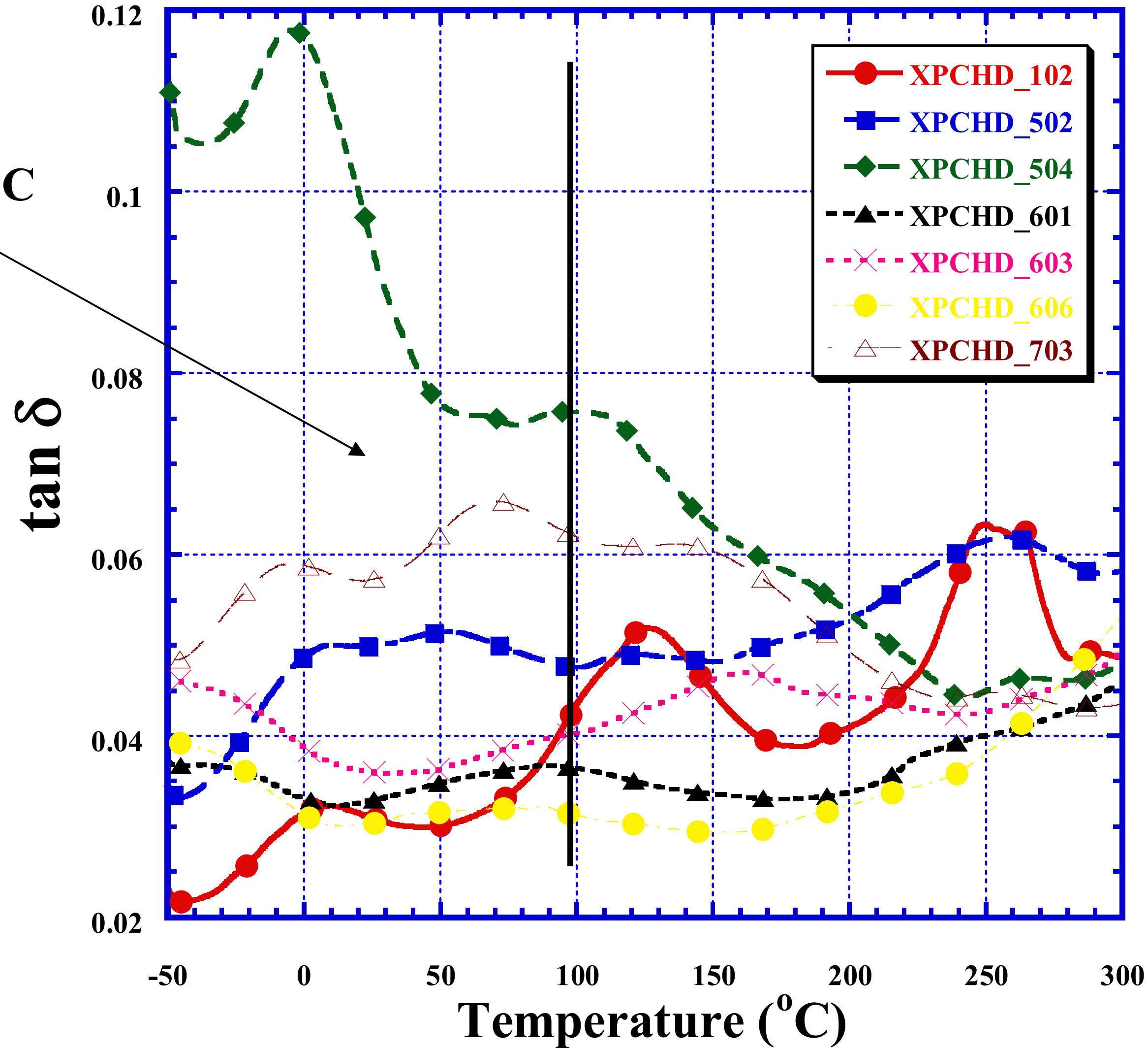
DMA Curves for XPCHD-SPPP_606 Sample

Effect of % Sulfonation



DMA Comparison of XPCHD-SPPP_Different Batches

Note: polymer relaxations operative < 100° C



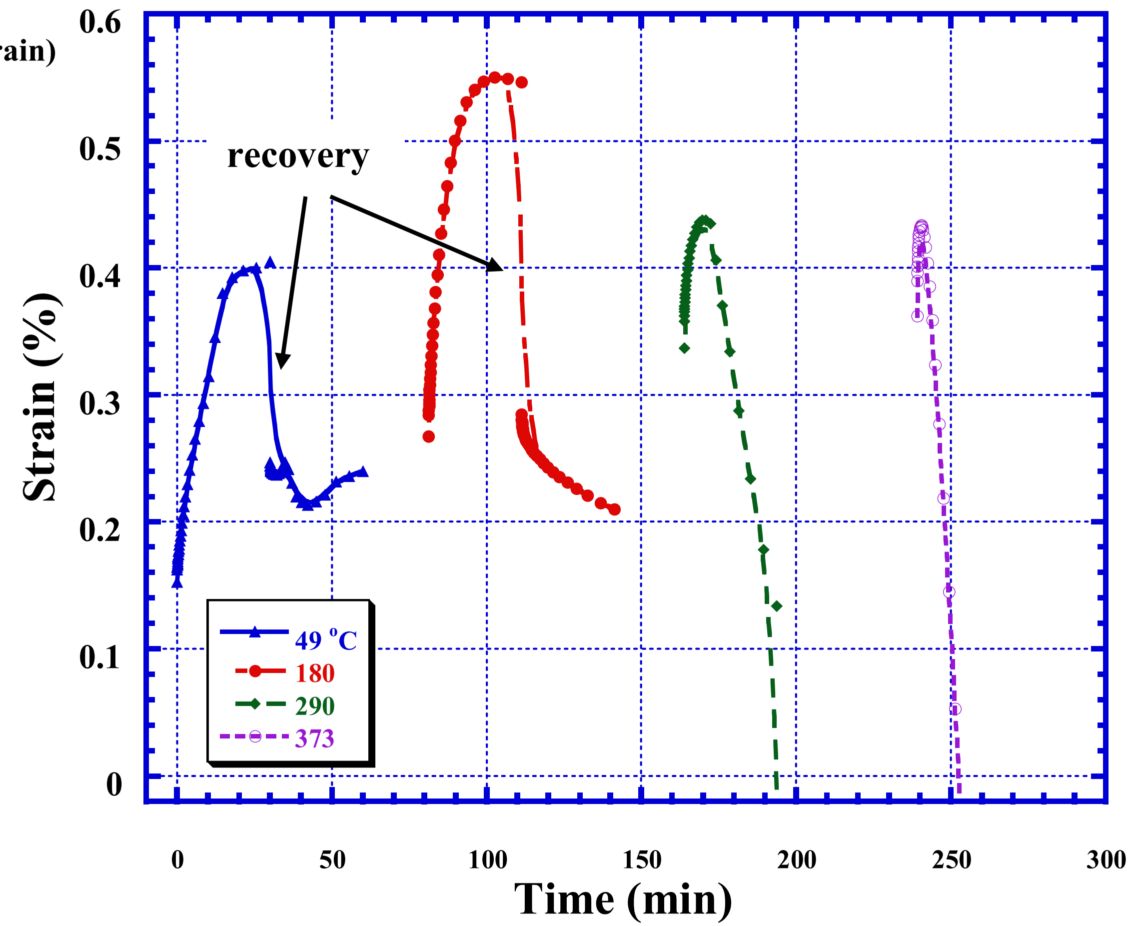
DMA Creep Curves for XPCHD-SPPP_102

- Creep increases until the stress is removed and this is followed by recovery (decrease in percent strain)

-In post-2 curve, at the higher temperature, shows greater percent strain at a given stress.

-This can be rationalized in the general view of increased chain mobility, especially due to the activation of the relaxation 2 process, but permanent set established at the end of the prior recovery period must also be considered.

Sample displaced under constant stress of 1MPa vs. time



Sol-gel reaction

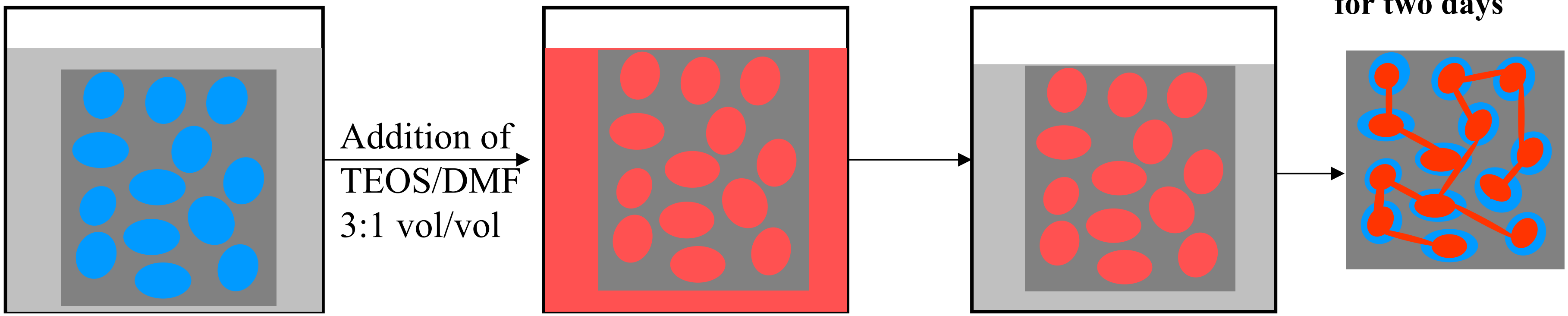
TEOS = Tetraethoxy Silane
H_2O:TEOS = 4:1 mol/mol

DMF/water (3:1 vol/vol) Swelling for one day

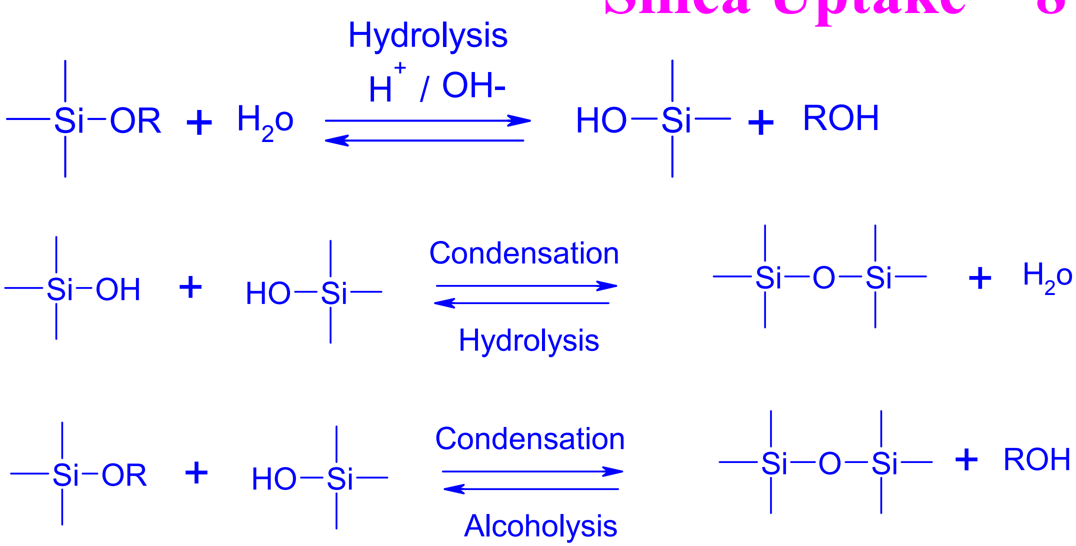
TEOS diffusion and reaction/stirring at R.T. for one day

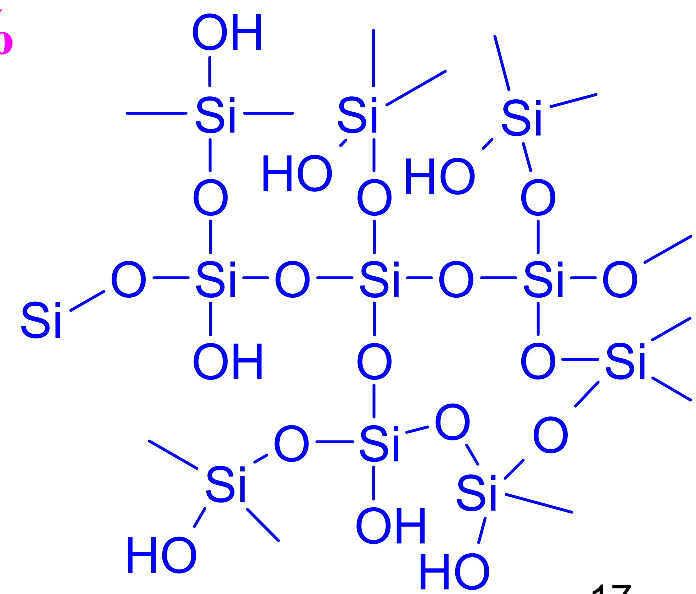
DMF wash to remove surface silicate

Oven Drying under vacuum at 100 °C for two days



Silica Uptake = 8%





Task Schedule

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Synthesis of 6 different crosslink type membranes	03/31/07			100%	On-Track
2	Synthesis of multiblock copolymers	03/31/08			5%	
3	Synthesis of initial statistical copolymers of fluorinated PCHD and sulfonated PaMS	03/31/07			100%	On-track
4	Molecular and thermal characterization of polymers	ongoing			30%	On-Track
5	Determine properties of non-sol-gel modified membranes				10%	initiated

Future Work

- Continue sol/gel experiments with crosslinked sulfonated PCHD materials.
- Carry out proton conductivity measurements using impedance spectroscopy (4 point probe) on membranes with and without inorganic modification.
- Select best crosslinked PCHD membrane to go forward.
- A key issue thus far with this class of membranes is brittleness. Improve via optimization of chemistry.

- Begin to characterize poly(α-methylstyrene)/PCHD copolymers (“Type B” membranes).

- Begin work on PCHD-fluorocarbon block copolymers (“Type C” membranes).

Summary

- The chemistry for creation of a new class of inexpensive poly(cyclohexadiene)-based fuel cell membranes has been developed.
- The materials show promising thermal properties and good mechanical properties, although issues with brittleness need to be addressed.
- Work on inorganic modification of these membranes and proton conductivity measurements is being initiated, and other polymer structures based on PCHD are being synthesized.