National Aeronautics and Space Administration

Synthesis and properties of cross-linked polyamide aerogels

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Overview

- Aerogel Basics/Applications
- Relevant prior work involving polyamides and polyimides
- Hurdles
  - The first step growth polyamide aerogel
- Optimization of completely aromatic systems
- Results
  - Density
  - Porosity
  - Surface area
  - Compressive strength
  - Dielectric measurements
- Conclusions/Acknowledgements

# What are aerogels?

Sol → Gel → Aerogel
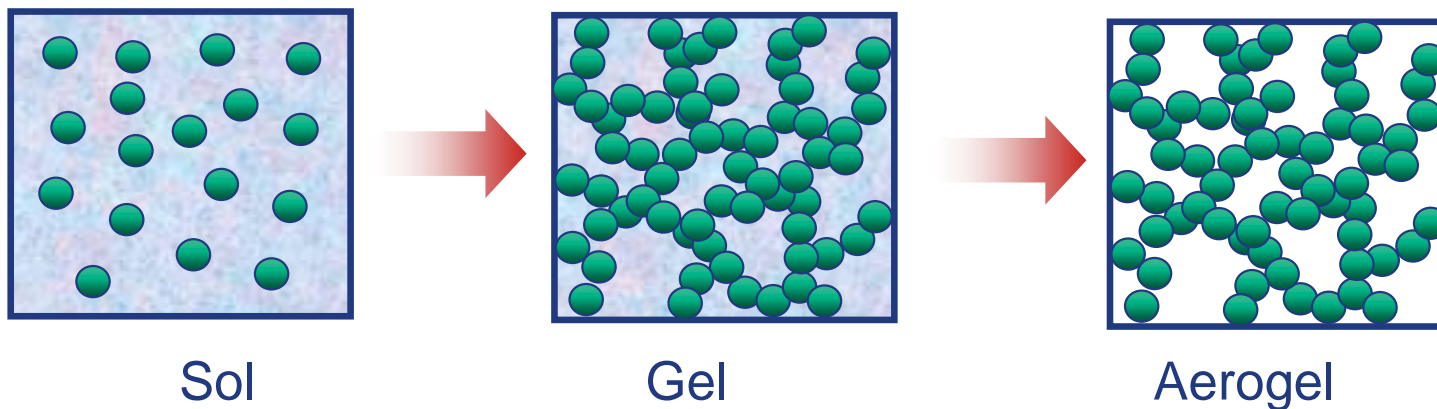
- Highly porous solids made by drying a wet gel without shrinking

- Pore sizes extremely small (typically 10-40 nm)—makes for very good insulation

- 2-4 times better insulator than fiberglass under ambient pressure, 10-15 times better in light vacuum

- Invented in 1930's by Prof. Samuel Kistler of the College of the Pacific
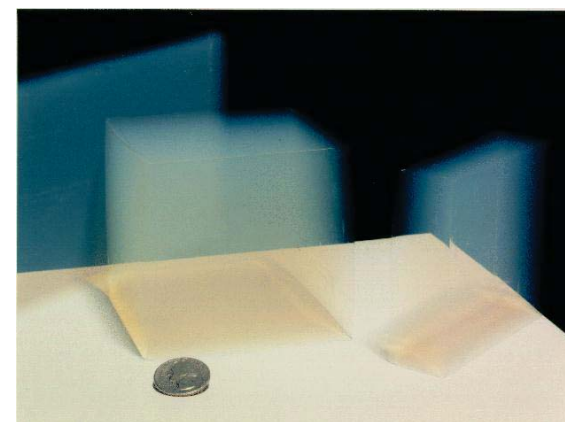
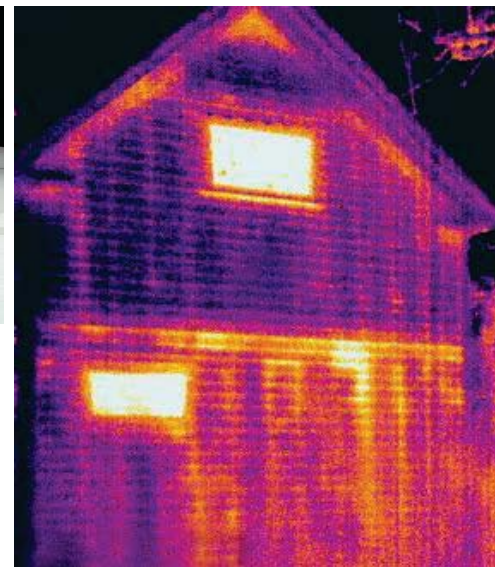*Typical monolithic silica aerogels*
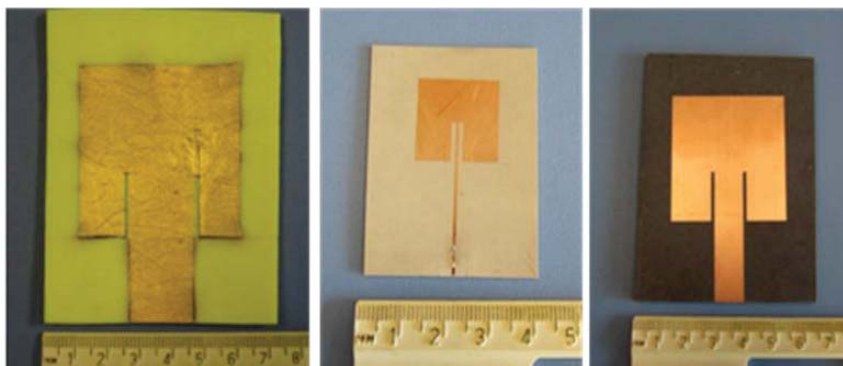
Potential applications
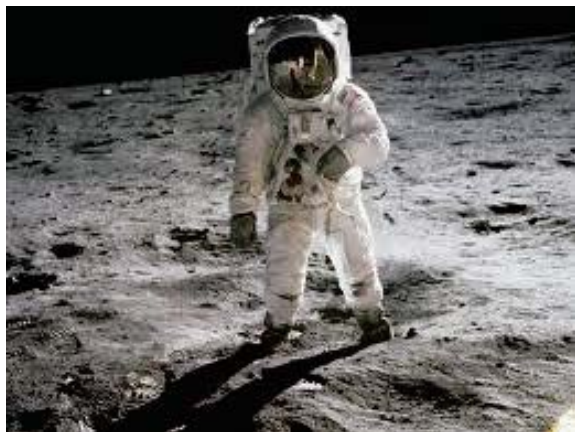
Flexible Insulation
for spacesuits

Insulation for crucial
mechanical components
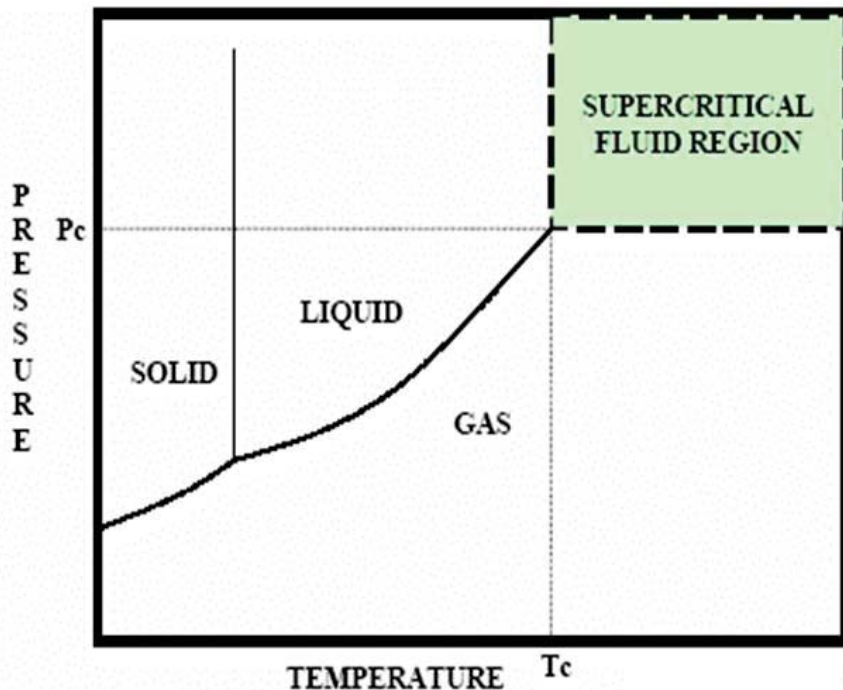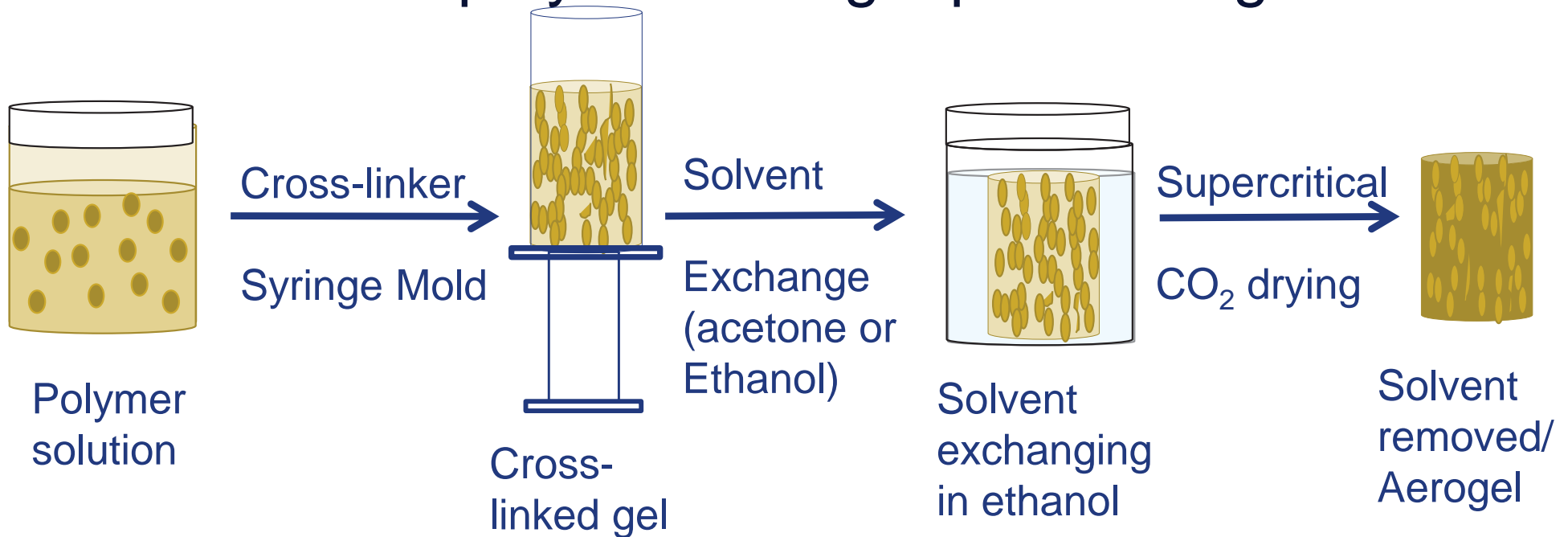

Durable/Fire
resistant
structural
insulation

Low dielectric antenna substrates

Optically transparent antennae for use
with solar components

Basic polymer aerogel processing

Cross-linker

Syringe Mold

Polymer solution

Cross-linked gel

Solvent

Exchange (acetone or Ethanol)

Supercritical

CO_2 drying

Solvent exchanging in ethanol

Solvent removed/ Aerogel

PRESSURE

Pc

SOLID

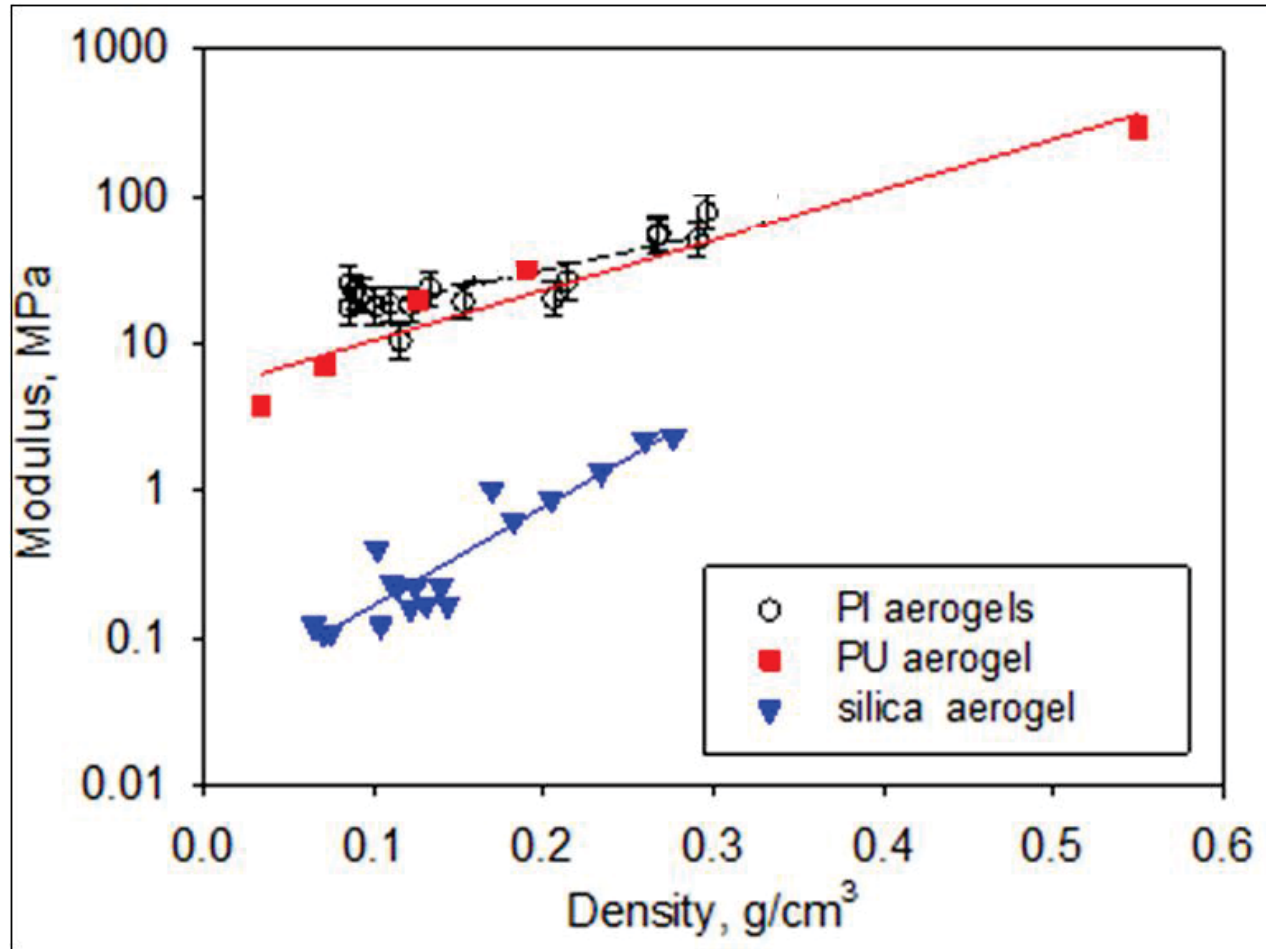LIQUID

GAS

SUPERCRITICAL FLUID REGION

TEMPERATURE   Tc

4 STEPS

1. Polymer solution prepared
2. Cross-linking agent is added and the mixture is poured into a mold
3. The resulting gel is solvent exchanged with a SCF compatible solvent such as ethanol
4. The solvent is then removed using an SCF such as carbon dioxide

Polymer Aerogels vs. Silica Aerogels

Recently developed polyurea and polyimide aerogels have Young's moduli that are orders of magnitude larger than traditional silica aerogel.

The motivation behind investigating stepgrowth polyamide aerogels is to see if we can obtain species that are even stronger.

Early literature involving polyamide aerogels

Desmodur RE (TIPM) + **Trimesic acid (TMA)** → (90°C, anh. DMF, -CO₂)

X,Y=Aromatic

90°C, anh. DMF

(-CO₂)
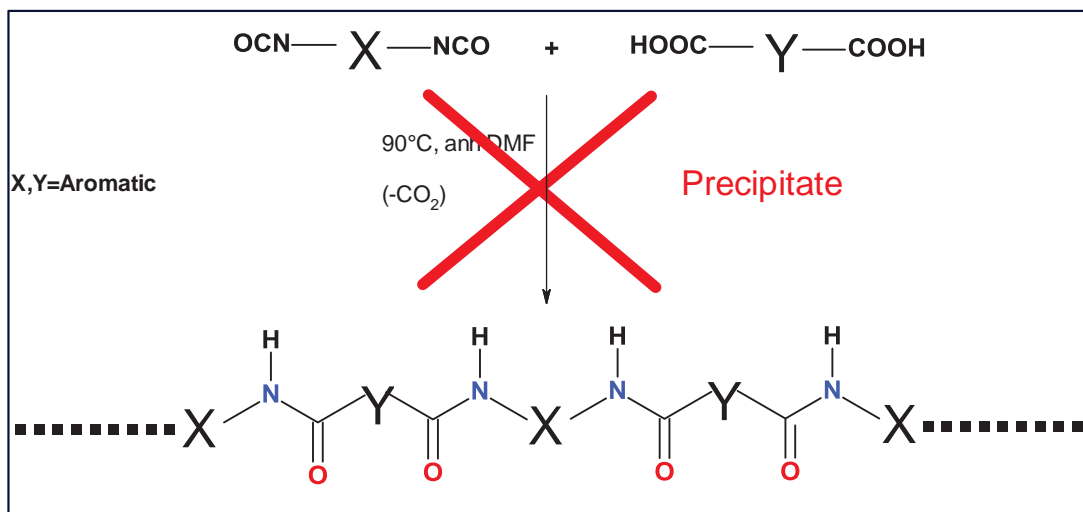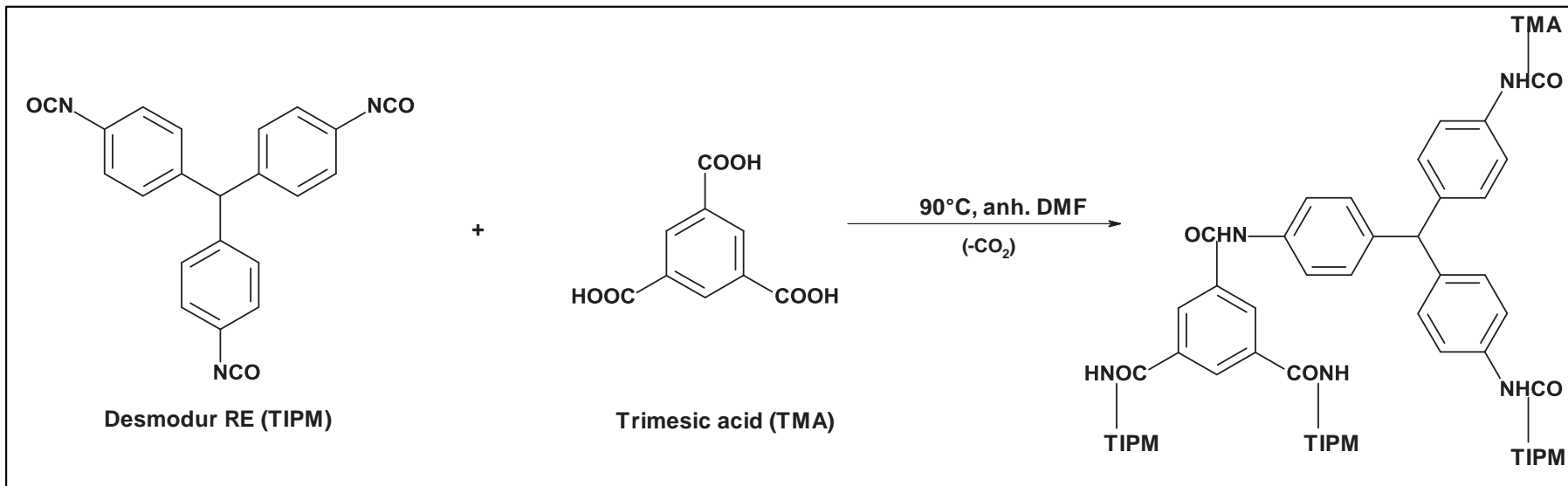
Precipitate

- Made via non-conventional amide forming methodology
- No control over chain length
- Glove box conditions
- Long reaction times
- High temperature
- Attempts at polymer chain formation lead to precipitation

Leventis et. al. J. Mater. Chem., 2011, 21, 11981

Polyimides as a Model for Polyamide Aerogels
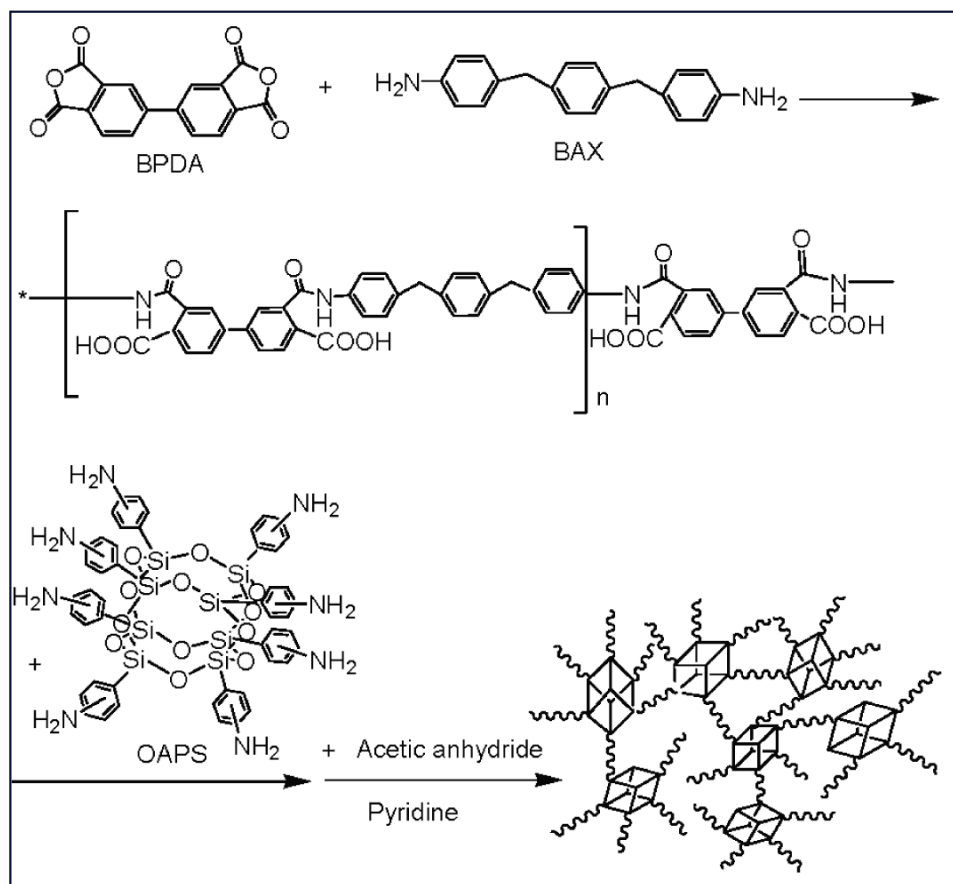
Comparable to polyimide aerogel processes.

Similarities include:
1. Analogous polymerization between diamines and diacid chlorides
2. Crosslinking through the use of a trifunctional monomer (higher degrees of functionality are also possible)
3. Quick reaction times
4. No glove box required
5. Low temperature reaction conditions
6. Polymer chains that stay in solution

Cross-linked Polyamides (general)

X=Aromatic
Y=Aromatic or
Aliphatic

0°C, NMP

n=20-30

0°C, NMP
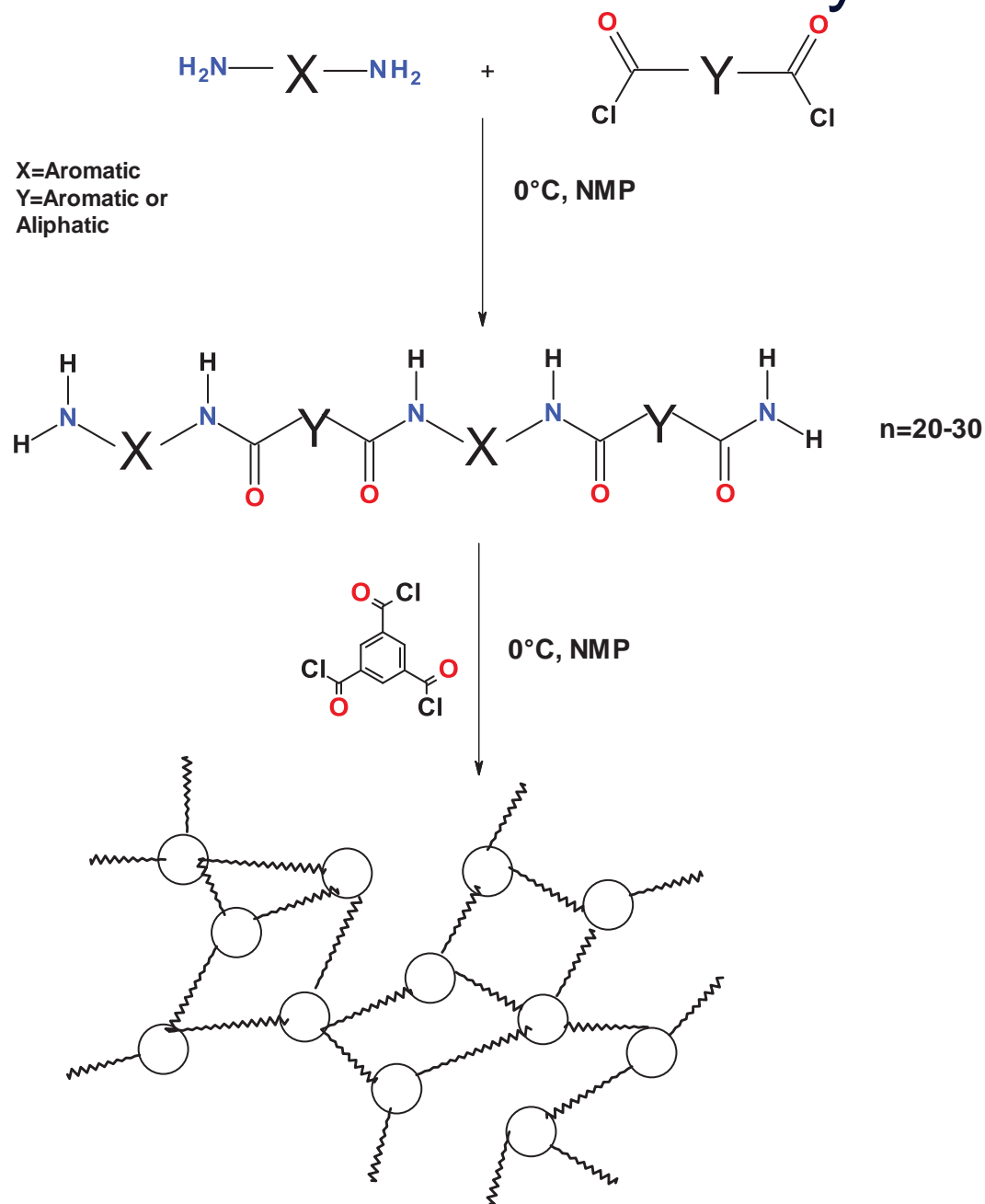
Aromatic amines do not require a catalyst

Aliphatic amines do require a catalyst (Et_3N)

Polymer 41 (2000) 8487-8500
Niesten et. al.

Potential features of polyamide aerogels

- Wide range of properties
  - From flexible/soft to rigid/strong
  - Hydrophobic/Hydrophilic
  - Colorless (maybe translucent/clear)
  - Low cost (monomers, cross-linker)
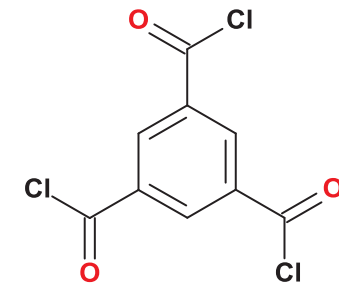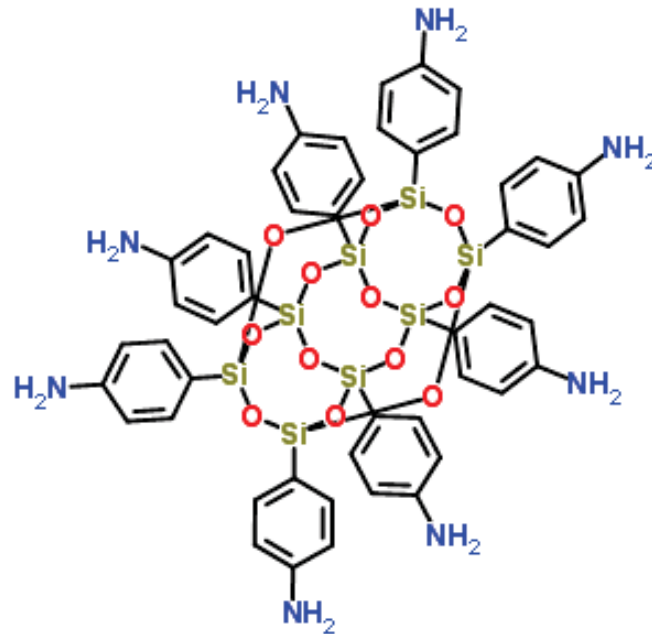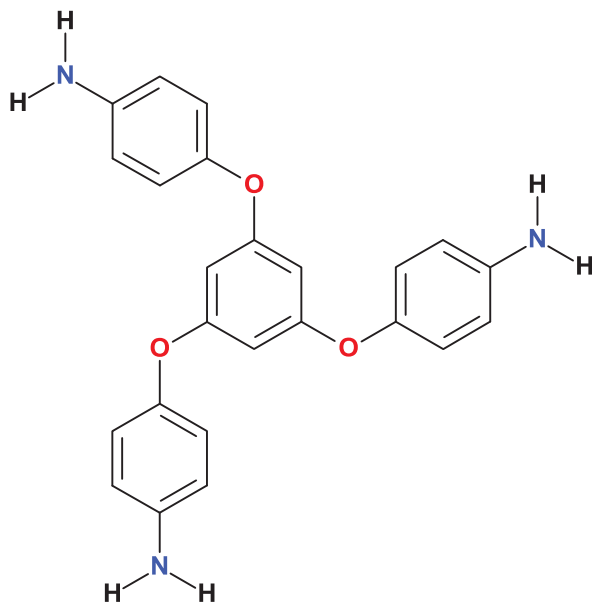
First attempt at polyamide aerogels

NMP, Et$_3$N, Glove Box

First stepgrowth polyamide aerogel

Jarrod-1 6.0kV 6.0mm x100k SE(M)   300nm
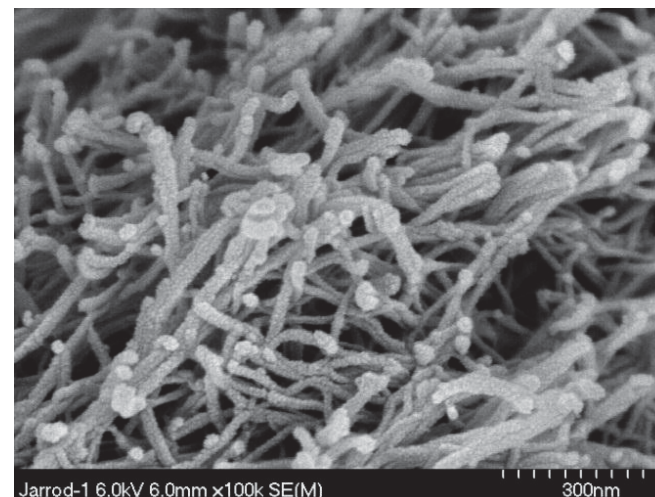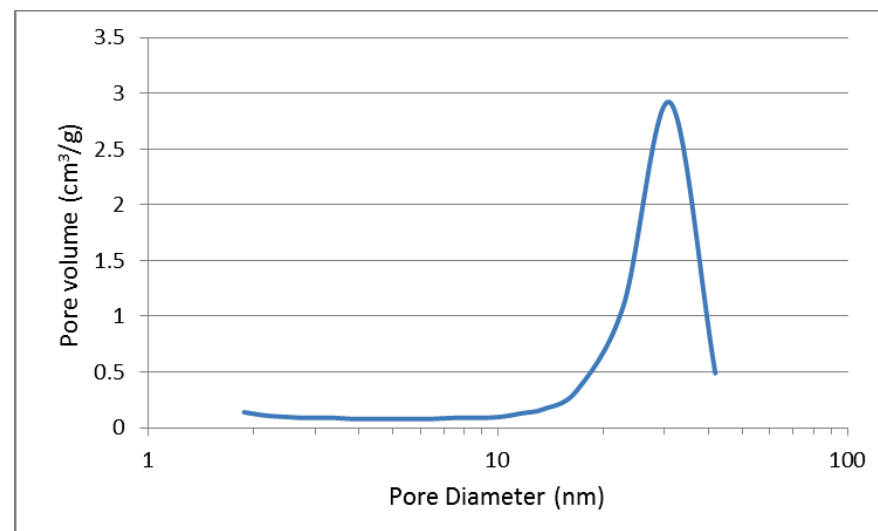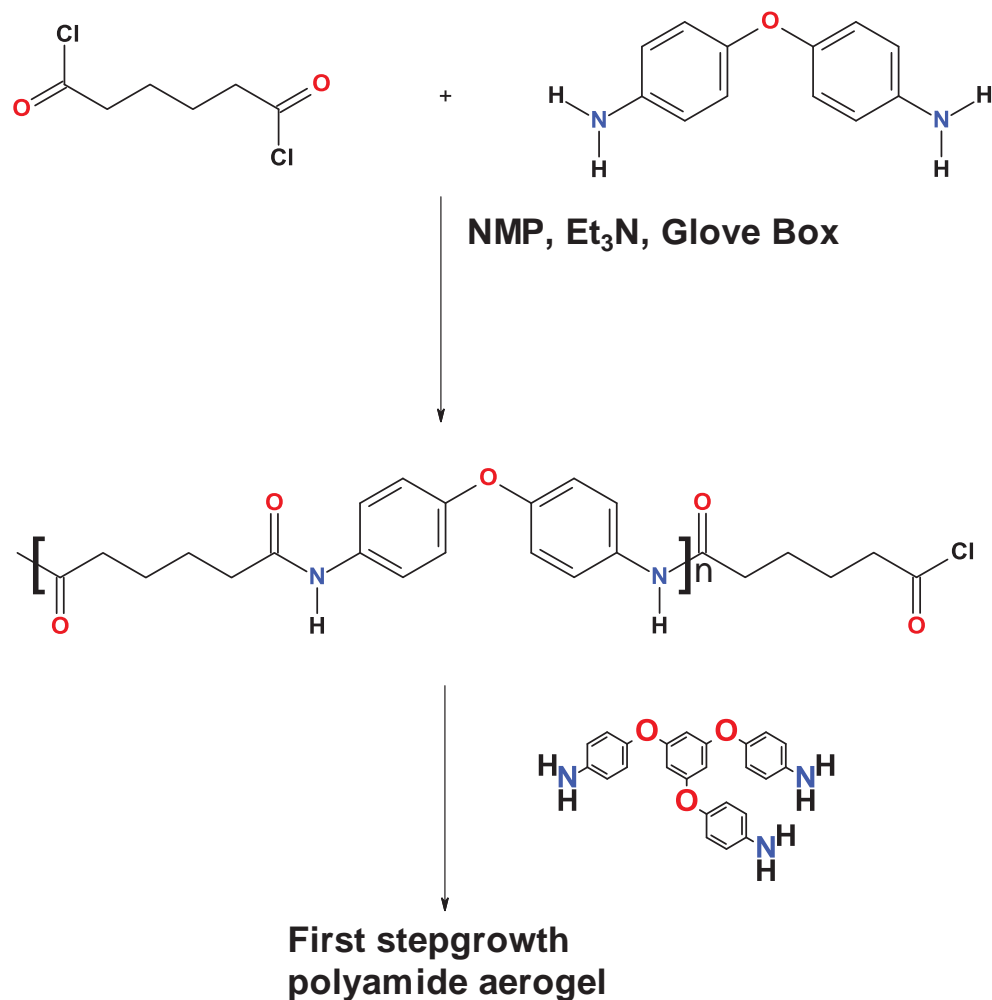
Aerogels with high surface areas (259m^2/g) and mesoporosity (~29nm) were produced; gelled from emulsion

Completely aromatic systems

Advantages:

1. No catalyst required (NMP complexes with HCl)
2. Amine end caps make mixture stable to moisture indefinitely.
3. Reaction mixtures remain homogenous
4. Reactions undergo reliable gelation (more user friendly than acid chloride endcaps)
5. Control over rigidity
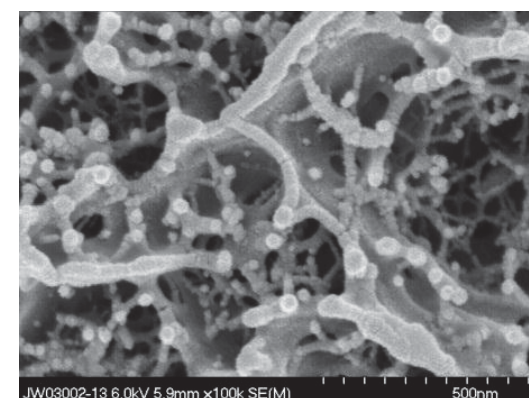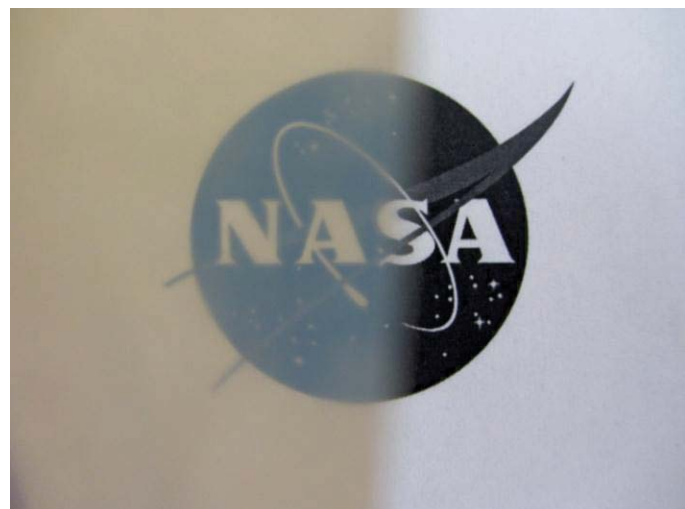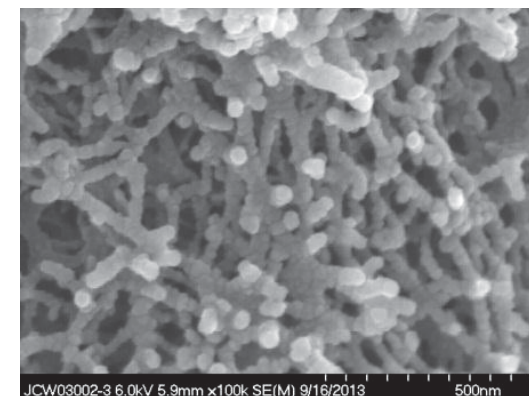
One problem remained..........

DMBZ

Isophthaloyl chloride

NMP, Room temperature

NMP, 0°C

Cross-linked Polyamide Network
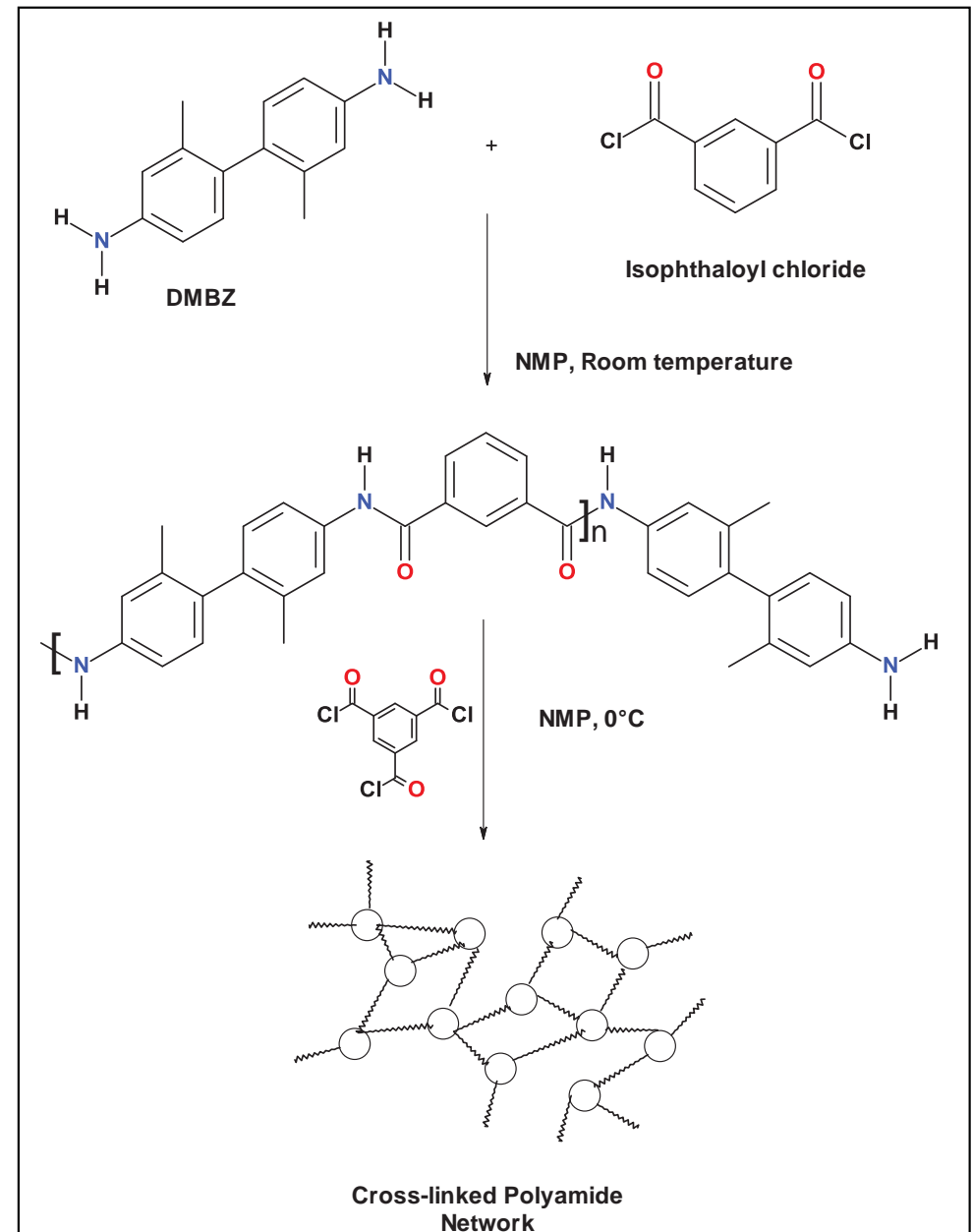
Optimized vs. Non-optimized Systems

Left two figures: Polyamide aerogels before procedure optimization.
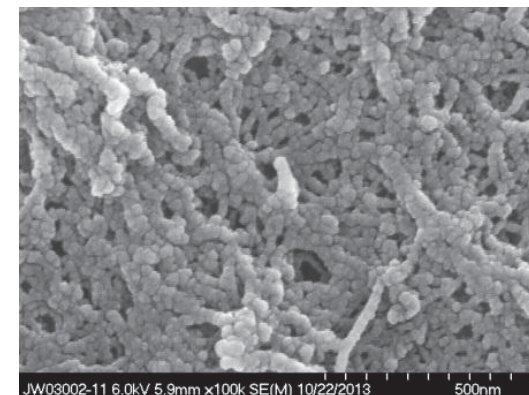
Right two figures: Three different polyamide aerogels (and SEMs) made via and optimized procedure.
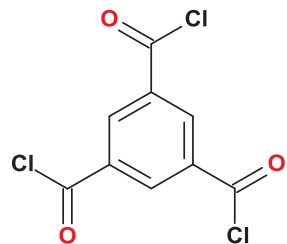
Optimization of Polyamide Aerogels

- To minimize distortion, the following reaction parameters were examined and optimized
    - Reaction and Cross-linking temperature
    - Stirring time/Stirring speed
    - Concentration of solutions
    - Cross-link density
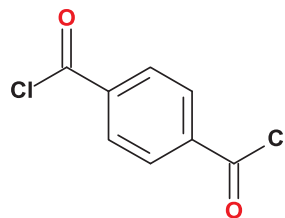   - Order and manner of addition of the reactants
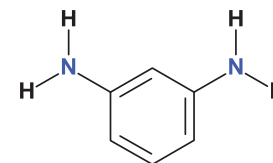   - Monomer species

Monomers

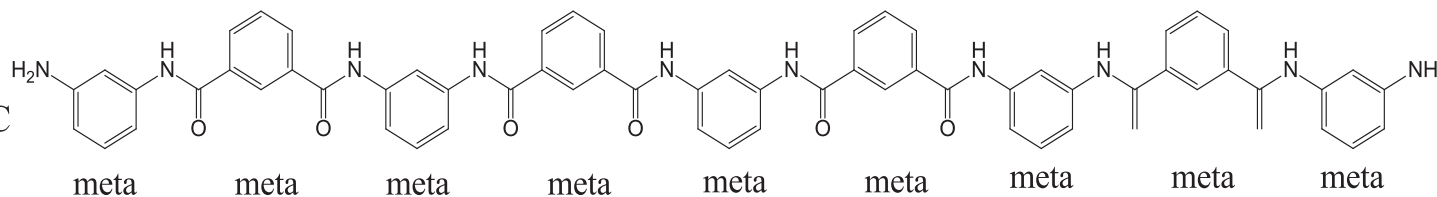**1,3,5-Benzenetricarbonyl trichloride (1,3,5-BTC)**
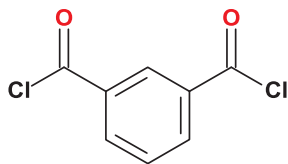
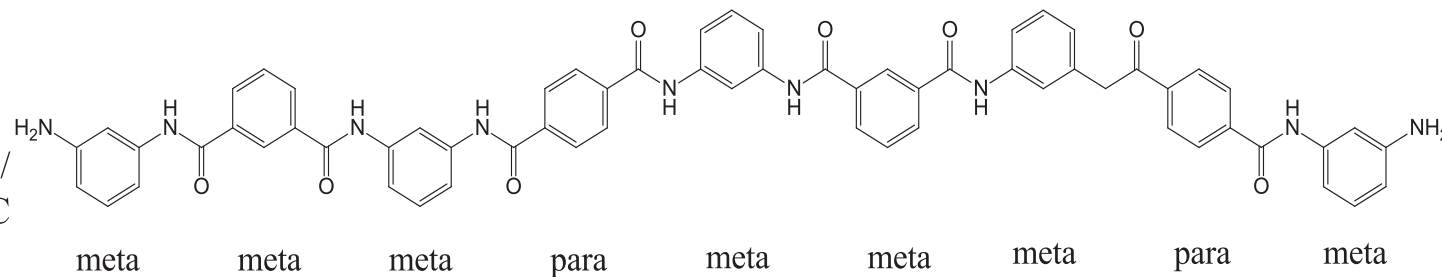**Isophthaloyl chloride (IPC)**

Terephthaloyl chloride (TPC)
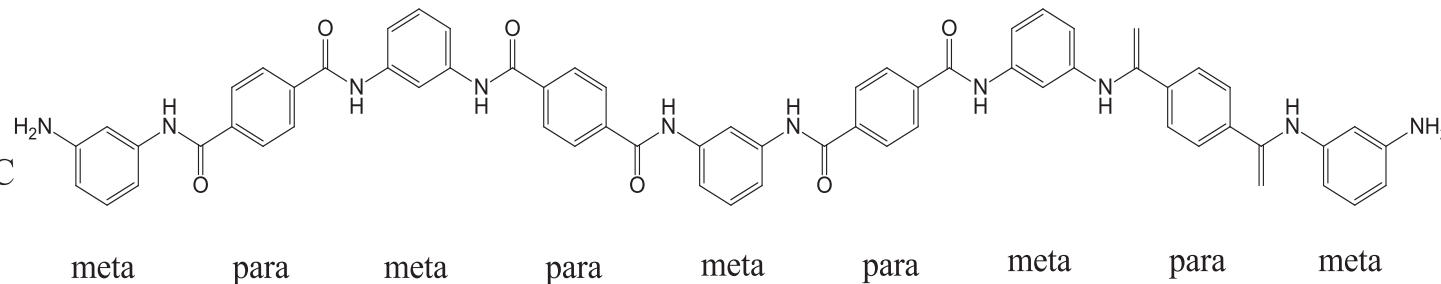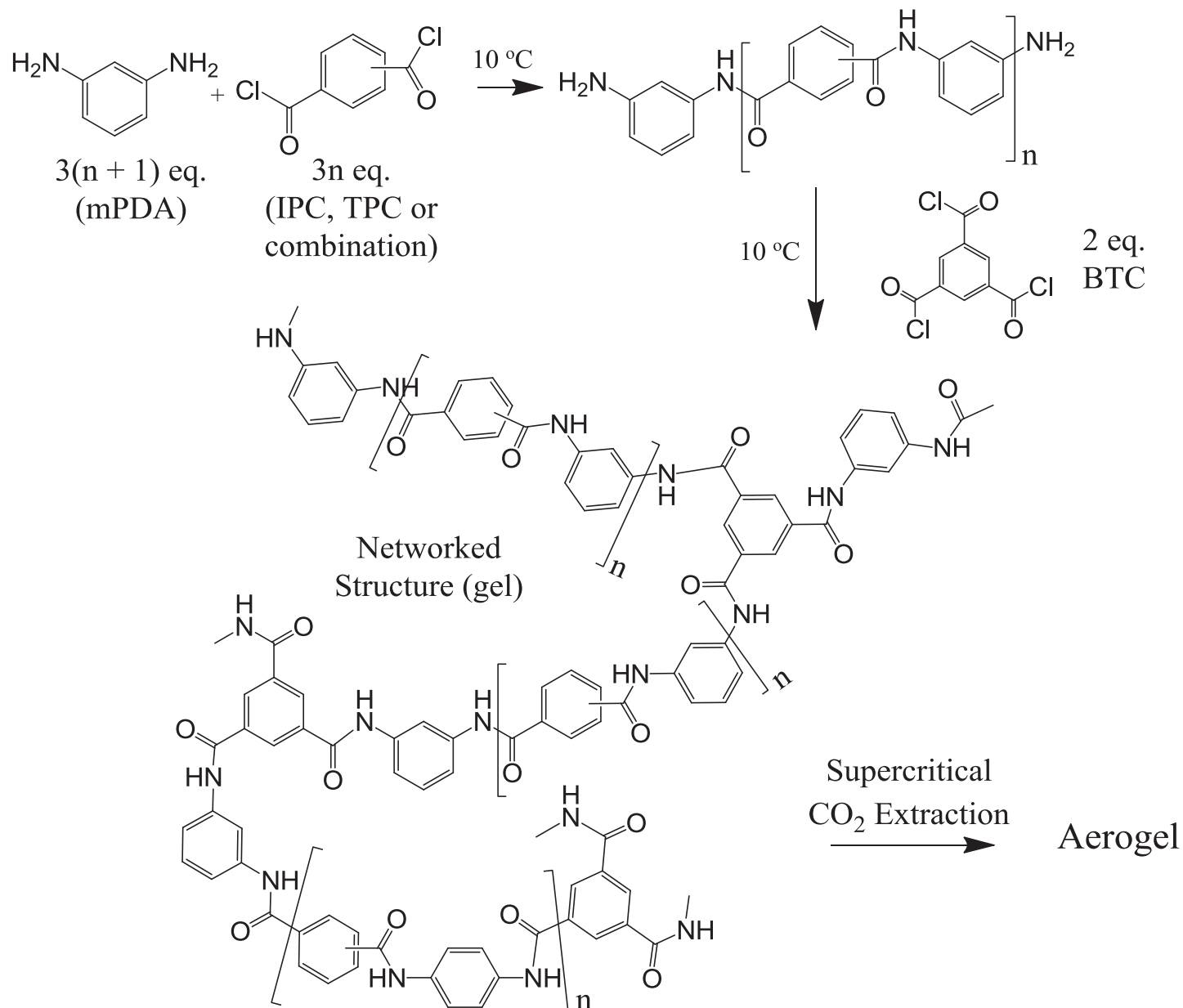
***m*-phenylenediamine (mPDA)**

100 % IPC

meta   meta   meta   meta   meta   meta   meta   meta   meta

50 % IPC/ 50 % TPC

meta   meta   meta   para   meta   meta   meta   para   meta

100 % TPC

meta   para   meta   para   meta   para   meta   para   meta

Aerogel Synthesis

Networked
Structure (gel)

Supercritical
CO_2 Extraction

Aerogel

3(n + 1) eq.
(mPDA)

3n eq.
(IPC, TPC or
combination)

10 ºC

10 ºC

2 eq.
BTC

Samples From Optimized Procedure
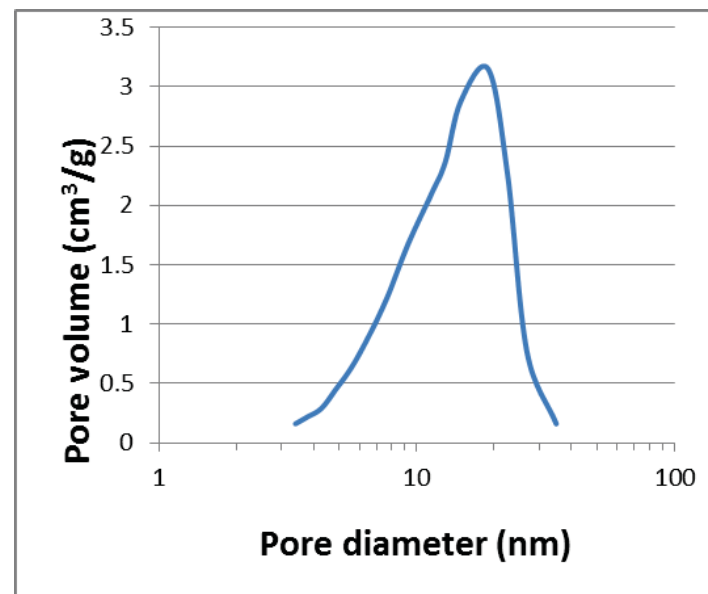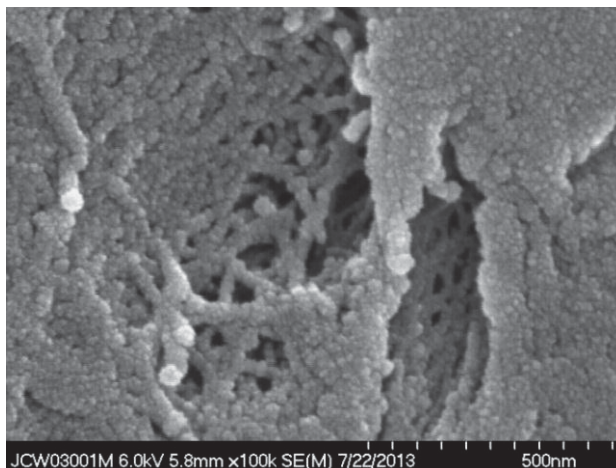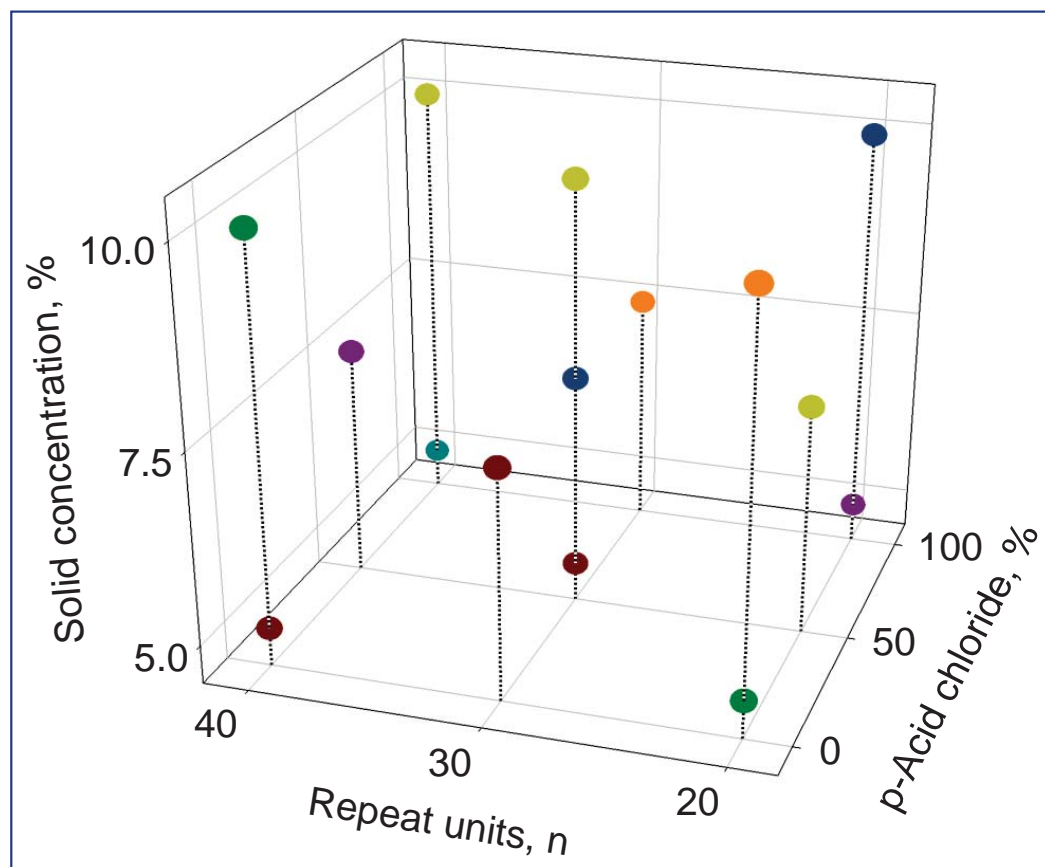

Terephthaloyl chloride, 0.33g/cm^3, 77% porous, 384 m^2/g.
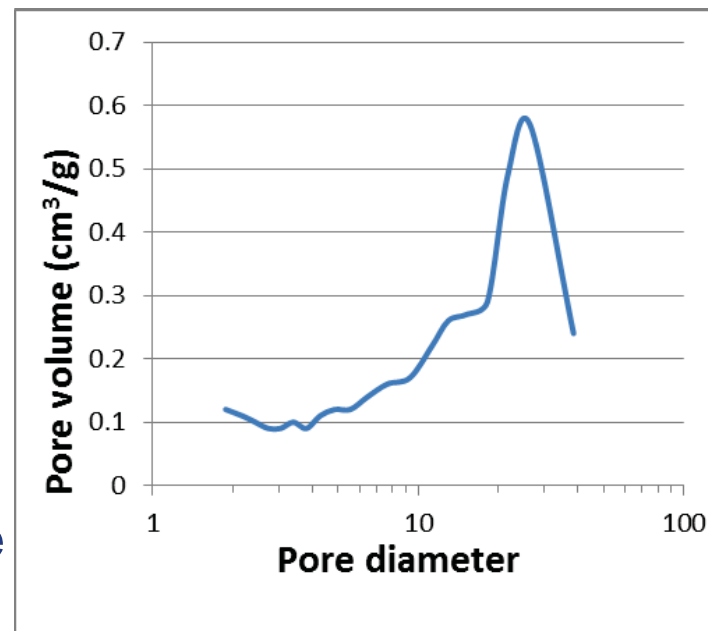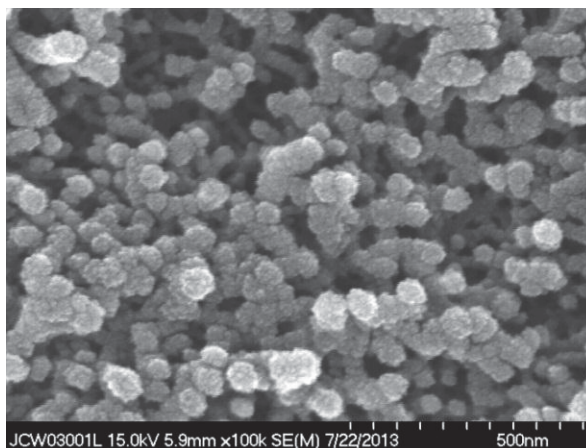
Isophthaloyl chloride, terephthaloyl chloride, m-phenylene diamine, 0.10g/cm^3, 93% porous, 192 m^2/g.
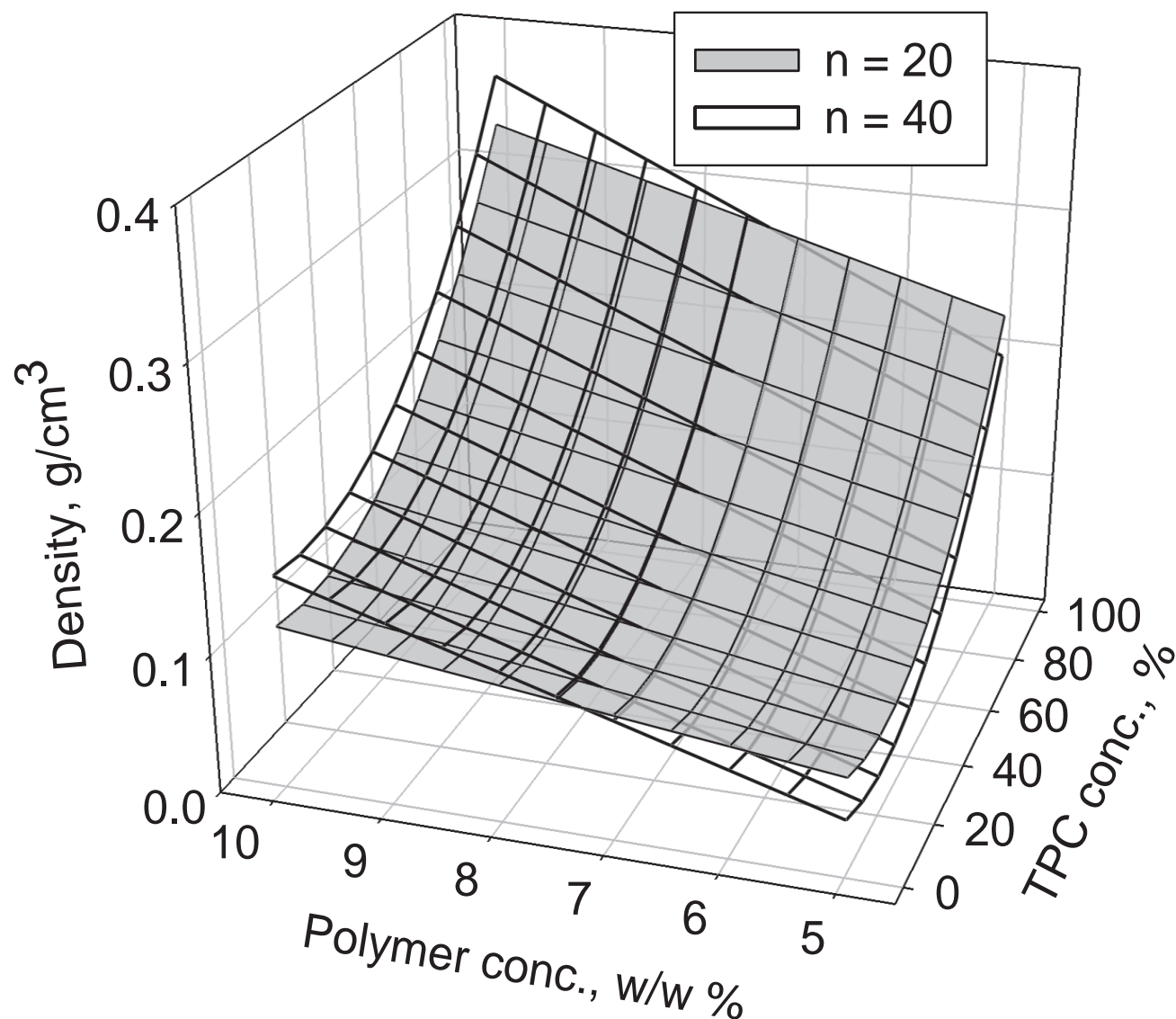
Experimental design study

- **Face-centered central composite design**

- **15 different data points to model full quadratic equation**

- **4 repeats of the center point to assess error**
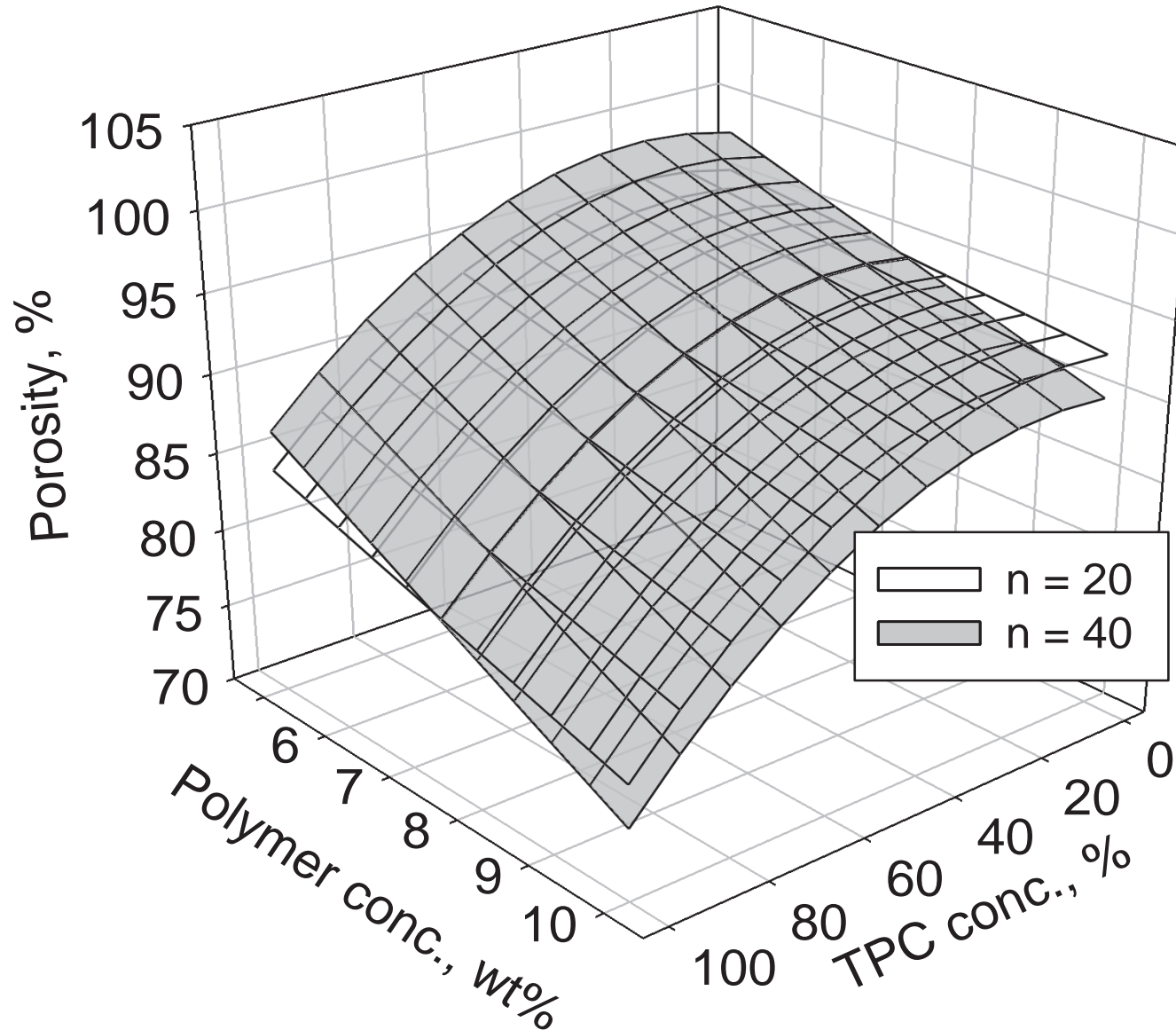
Results: Density

- Density increases as the fraction of the para substituted acid chloride increases.

- Density increases as the concentration of solids in the gel increases.

- n-value or length of the polymer chains, is not a significant factor for density
- Standard deviation=0.016
- R^2=0.98

Results: Porosity

- Porosity decreases as the fraction of the para substituted acid chloride increases.

- Porosity decreases as the concentration of solids in the gel increases.

- n-value of the polymer chains is not a significant factor for porosity.
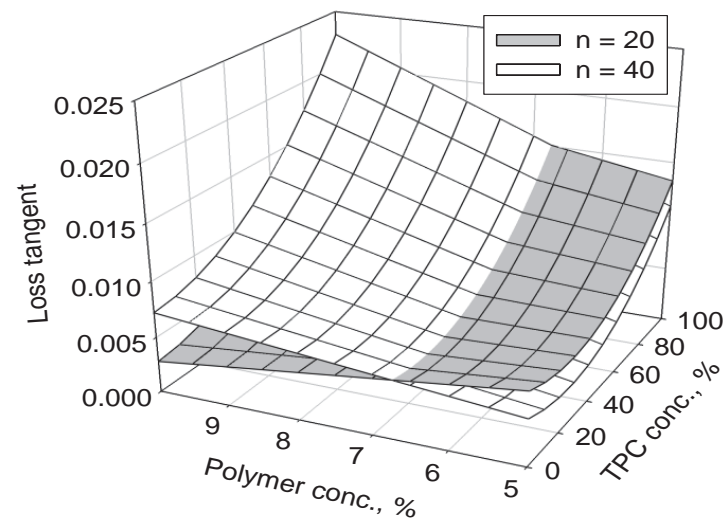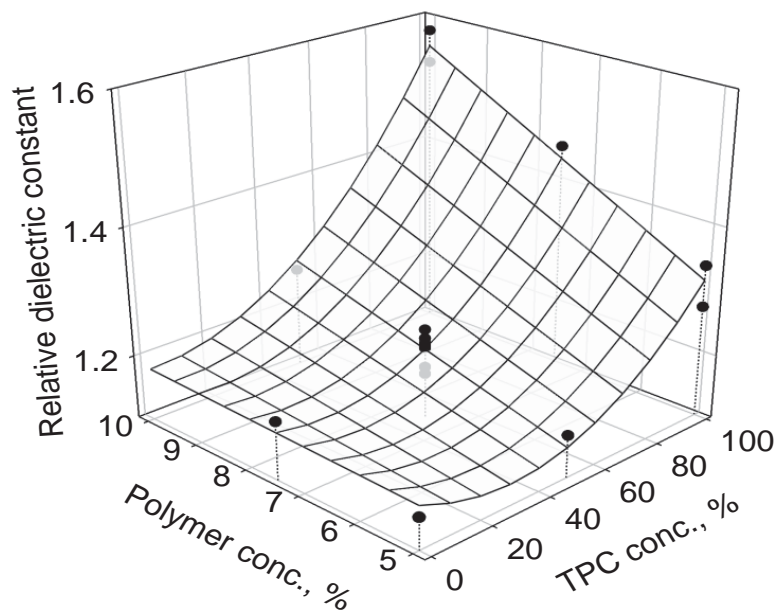
- SD=1.26

- R^2=0.98

Surface area

- All three variables significant
- Data was log transformed before fitting to normalize data
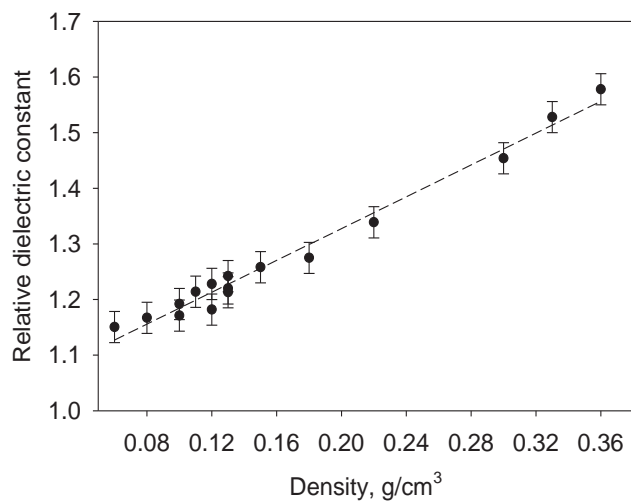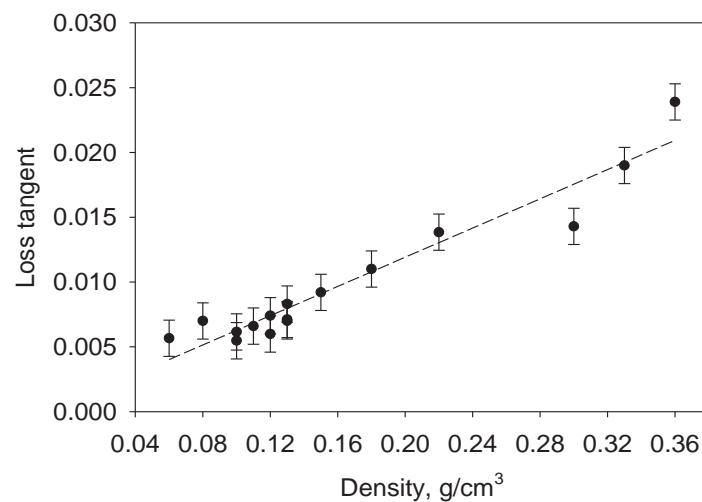- S.D. = 36.64
- R^2=0.88
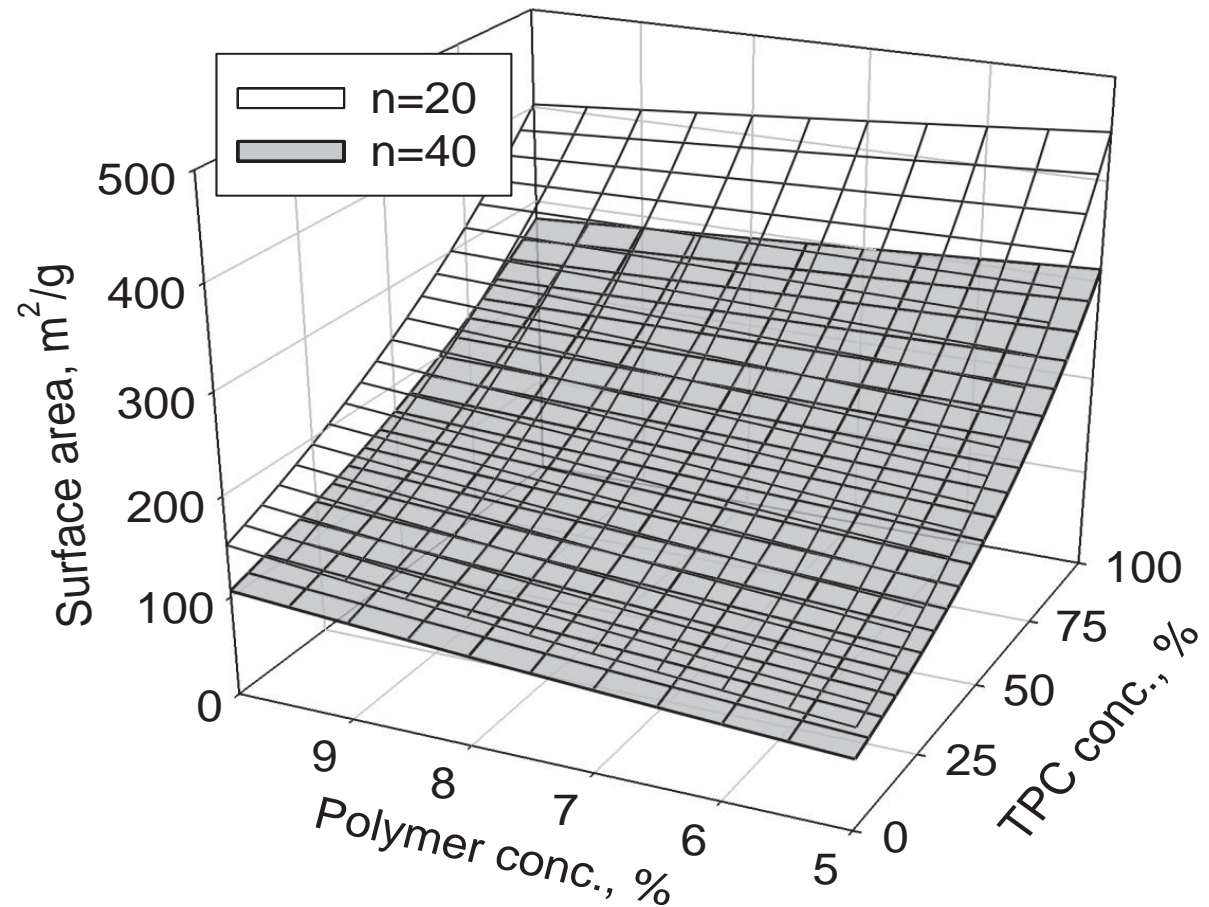
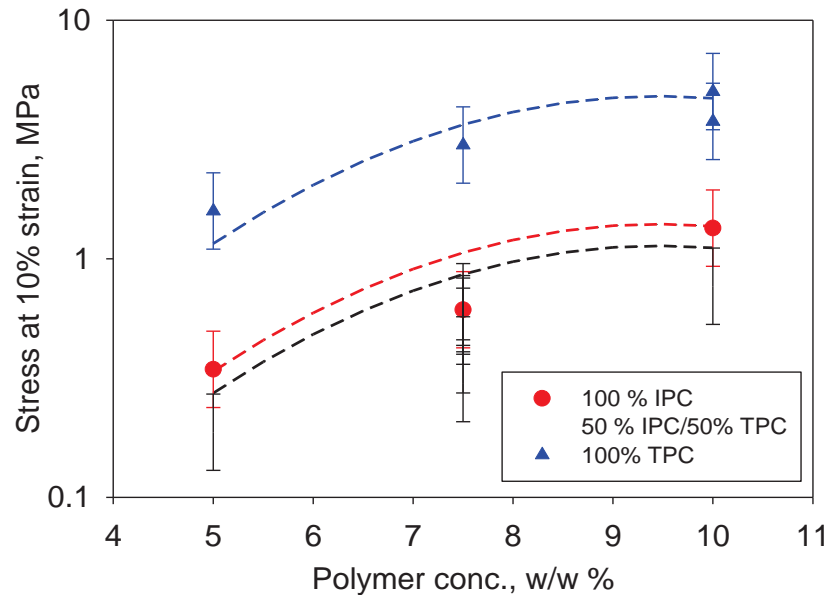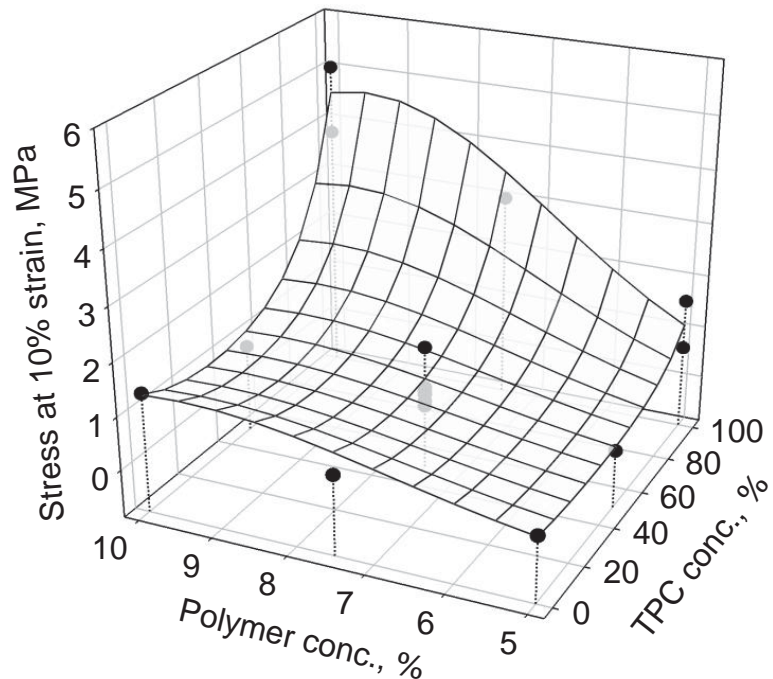# Dielectric and Loss Tangent
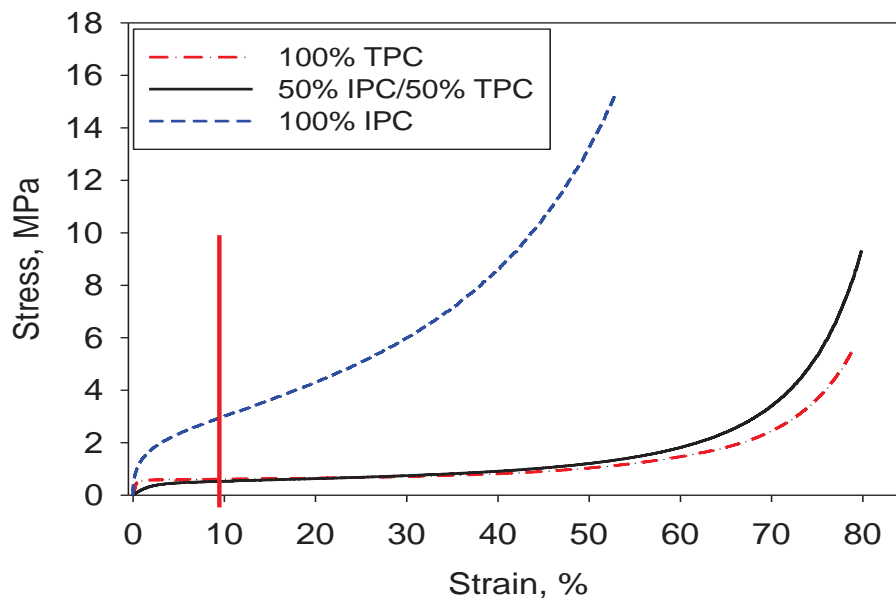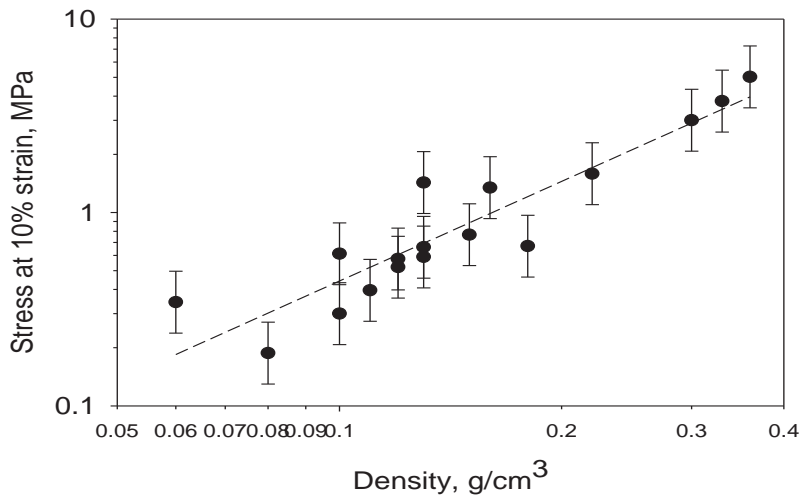

SD=0.042, R^2=0.92
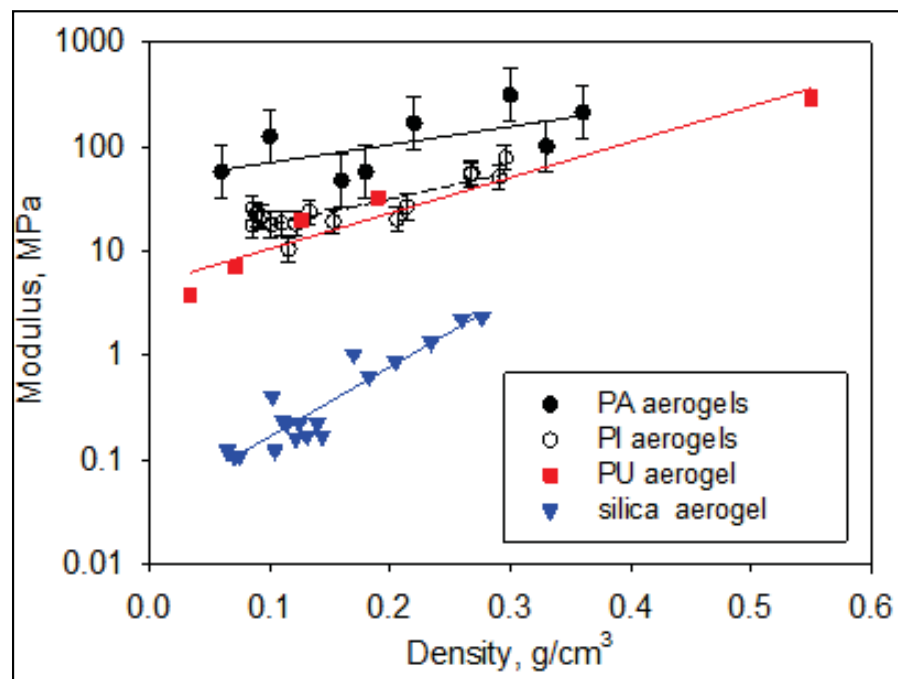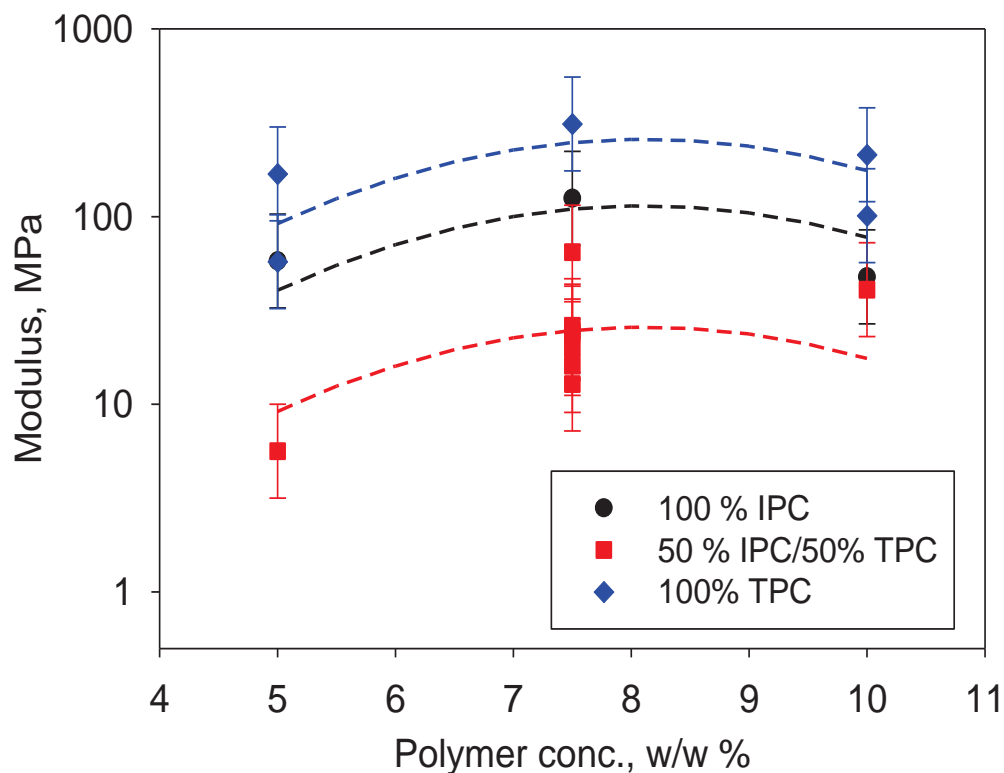
SD=0.0017, R2=0.93

Compressive Strength

SD=0.16, R^2=0.90

Young's Modulus

(log standard deviation=0.25, R^2=0.79)

1. Guo et. al. ACS. Appl. Mater. Interfaces, **2011**, 3, 546-552.
2. Leventis et. al. *J. Mater. Chem.* **2011**, *21*, 11981-11986.
3. Fricke et. al. *J. Non-Cryst. Solids*, **1988**, *100* 169-173.

Conclusions/Summary

- A simple procedure for the fabrication of polyamide aerogels has been developed and optimized

- A series of polyamide aerogels were produced that having densities ranging from 0.06g/cm^3 to 0.3g/cm^3, high porosities (77-93% porous), and surface areas as high as 426m^2/g

- Diverse properties arise through controlling monomer types, stoichiometry and weight percent solids

- Remaining work
  - Examine new monomer species
  - Experiment with different crosslinking methodologies
  - N-alkylate for hydrophobicity

Acknowledgements

NASA Glenn

1. Dr. Mary Ann Meador
2. Stephanie Vivod
3. Baochau Nguyen
4. Heidi Guo
5. Linda McCorkle
6. Dan Haas
7. Dan Scheiman

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